Supporting Information

Assembly of Functionalized *gem*-Difluoroalkenes via Photocatalytic Defluorocyanoalkylation and Defluoroacylation of α-CF_3 Styrenes with Oxime Esters

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General Information

^{1}H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 300 or 400 MHz spectrometer in $CDCl_3$ or DMSO with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-QII HRMS/MS instrument (BRUKER). PE refers to petroleum ether (bp 60-90 °C), and EA refers to ethyl acetate. Other reagents, unless otherwise noted, were purchased from commercial vendors and used without further purification. **1a** are known compounds and were prepared according to literature procedures (*Org. Chem. Front*., **2023**, *10,* 5843; *Green Chem*., **2022**, *24,* 6830; *Org. Lett*., **2024**, *26,* 100-105; *Chem. Sci*., **2023**, *14,* 14271). **2a** are known compounds and were prepared according to literature procedures (*Org. Lett*., **2020**, *22,* 863-866). **3a** are known compounds and were prepared according to literature procedures (*Chin. J. Chem.,* **2024**, *42,* 1399-1406).

Luminescence Quenching Experiment

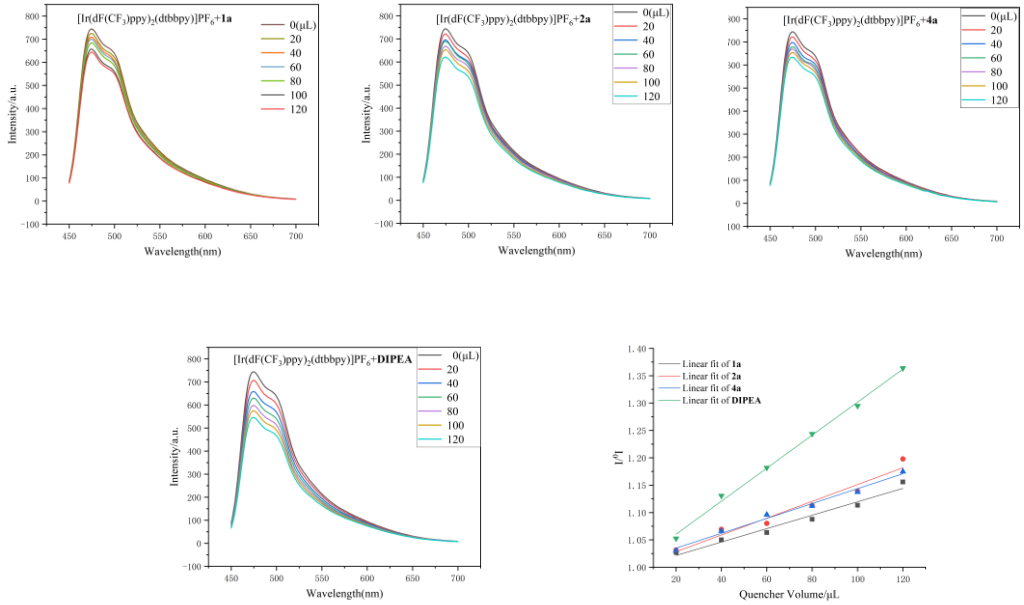
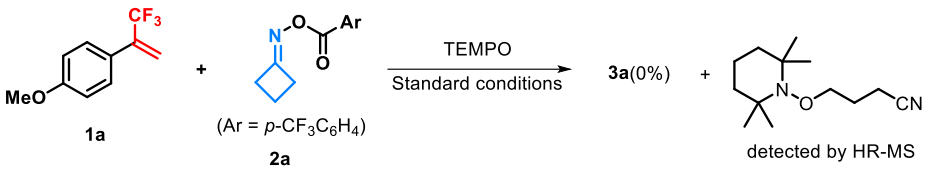


Figure S1. Stern−Volmer analysis for $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ with **1a**, **2a**, **4a**, **DIPEA**

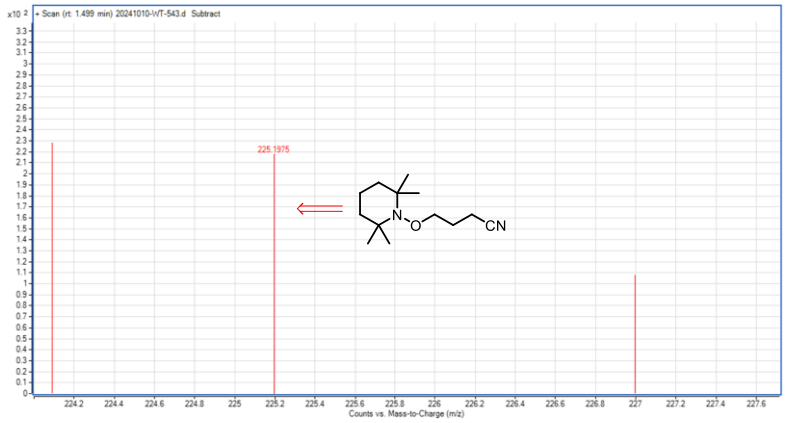
The luminescence quenching experiment was taken using a FS5 Spectrophotometer (Edinburgh FS5). The excitation wavelength was 427 nm, the emission wavelength was 475 nm, and the emission spectra were recorded between 430 and 700 nm. The samples were prepared by mixing $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1.0×10^{-4} mol/L) and different amounts of quenchers (**1a**, **2a**, **4a** and **DIPEA**) in CH_3CN (total volume = 2.0 mL) in a light path quartz fluorescence cuvette. The concentration of **1a** stock solution is 1.0×10^{-3} mol/L in CH_3CN. The concentration of **2a** stock solution is 1.0×10^{-3} mol/L in CH_3CN. The concentration of **4a** stock solution is 1.0×10^{-3} mol/L in CH_3CN. The concentration of **DIPEA** stock solution is 1.0×10^{-3} mol/L in CH_3CN.

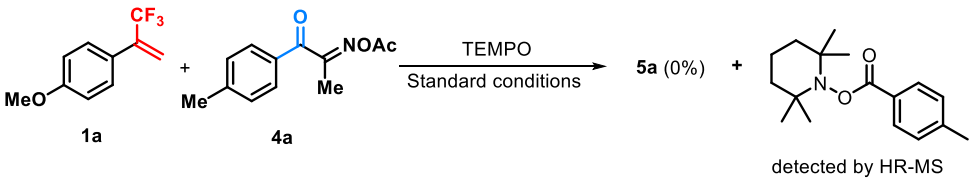
Then the emission intensity was collected and the results were presented in **Figure S1**. The observations indicate that the fluorescence intensity of $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ significantly decreases along with the increasing of concentration of **DIPEA**. The linear relationships between I_0/I and the concentrations of **1a**, **2a** and **4a** indicates that the fluorescence intensity of $[Ir(dF(CF_3)\ ppy)_2(dtbbpy)]PF_6$ slowly decreases with increasing concentrations of **1a**, **2a** and **4a**, and the $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ is believed to be quenched by **DIPEA**.

Radical-Trapping Experiment

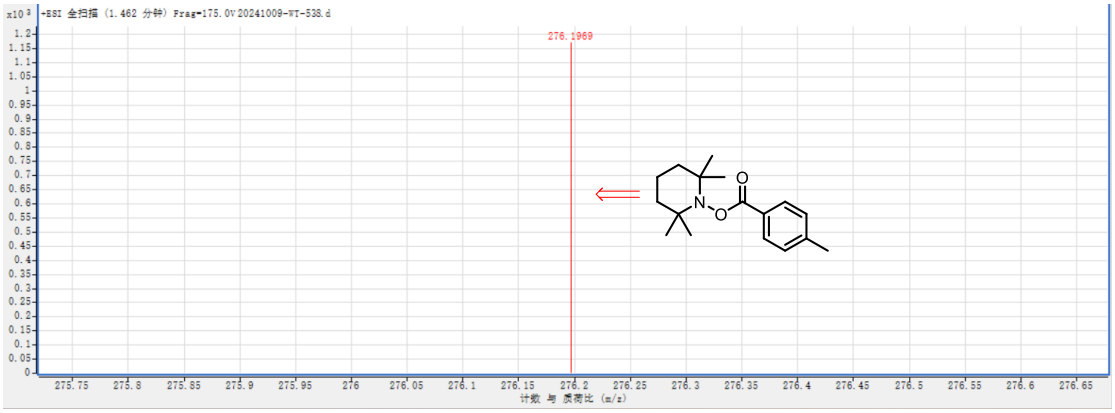


Under Ar conditions, a dried Schlenk tube was added **1a** (1.0 equiv., 0.2 mmol), **2a** (1.5 equiv., 0.3 mmol), DIPEA (2.0 equiv., 0.4 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol %), BHT/TEMPO (3.0 equiv., 0.6 mmol), CH_3CN (4.0 mL). The tube was placed exposed to 30 W blue LEDs at room temperature for 15 h. The corresponding product **3a** was not detected according to TLC analysis. The TEPMO-trapped product was detected by HR-MS. HRMS (ESI) m/z calculated for $C_{13}H_{25}N_2O$ $[M+H]^+$ 225.1967, found 225.1975.



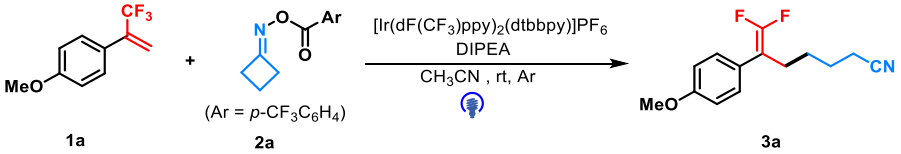


Under Ar conditions, a dried Schlenk tube was added **1a** (1.0 equiv., 0.2 mmol), **4a** (1.5 equiv., 0.3 mmol), DIPEA (2.0 equiv., 0.4 mmol), K_2CO_3 (2.0 equiv., 0.4 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol %), BHT/TEMPO (3.0 equiv., 0.6 mmol), THF (4.0 mL). The tube was placed exposed to 30 W blue LEDs at room temperature for 15 h. The corresponding product **5a** was not detected according to TLC analysis. The TEPMO-trapped product was detected by HR-MS. HRMS (ESI) m/z calculated for $C_{13}H_{25}N_2O$ $[M+H]^+$ 225.1967, found 225.1969.



General procedure for the synthesis of compounds 3 and 5

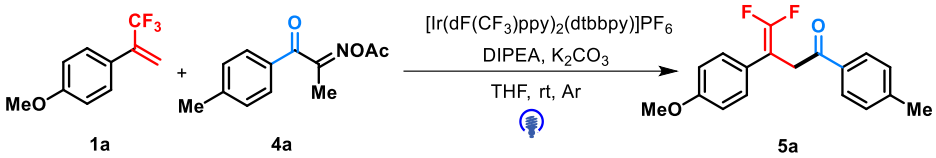
Example for the synthesis of **3a**



1a 2a 3a

Under Ar conditions, a dried Schlenk tube was added **1a** (1.0 equiv., 0.2 mmol., 40.4 mg), **2a** (1.5 equiv., 0.3 mmol., 77.2 mg), DIPEA (2.0 equiv., 0.4 mmol., 51.7 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol %), CH_3CN (4.0 mL). The tube was placed exposed to 30 W blue LEDs at room temperature for 15 h. After the reaction was complete (by TLC), the reaction mixture was washed with water and extracted with DCM. The combined organic layer was washed with brine and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purified product **3a** was obtained after column chromatography on silica gel (PE/EA= 30/1).

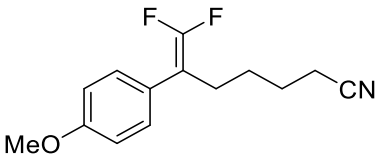
Example for the synthesis of **5a**



1a 4a 5a

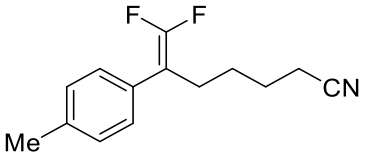
Under Ar conditions, a dried Schlenk tube was added **1a** (1.0 equiv., 0.2 mmol., 40.4 mg), **4a** (1.5 equiv., 0.3 mmol., 65.7 mg), DIPEA (2.0 equiv., 0.4 mmol., 51.7 mg), K_2CO_3 (2.0 equiv., 0.4 mmol., 55.3 mg), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol %), THF (4.0 mL). The tube was placed exposed to 30 W blue LEDs at room temperature for 15 h. After the reaction was complete (by TLC), the reaction mixture was washed with water and extracted with DCM. The combined organic layer was washed with brine and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purified product **5a** was obtained after column chromatography on silica gel (PE/EA= 30/1).

7,7-difluoro-6-(4-methoxyphenyl)hept-6-enenitrile (3a)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 35.7 mg, 71% yield; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.21 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 2.45-2.37 (m, 2H), 2.33-2.26 (m, 2H), 1.70-1.60 (m, 2H), 1.55-1.45 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm): 158.8, 157.4, 153.6 (d, *J* = 2.8 Hz), 149.7, 129.3 (t, *J* = 3.2 Hz), 125.2(8), 125.2(5), 125.1(4), 125.1(1), 119.4, 114.1, 91.00 (dd, *J* = 20.7, 14.8 Hz), 55.3, 26.9, 26.7 (t, *J* = 2.6 Hz), 24.6, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm): -92.00 (d, *J* = 45.8 Hz), -92.23 (d, *J* = 45.9 Hz). HRMS-ESI (m/z) calculated for $C_{14}H_{15}F_2NO$ $[M+Na]^+$ 274.1014, found 274.1019.

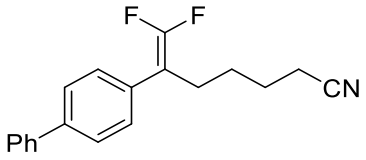
7,7-difluoro-6-(p-tolyl)hept-6-enenitrile (3b)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 26.4 mg, 56% yield; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.18 (s, 4H), 2.47-2.40 (m 2H), 2.35 (s, 3H), 2.32-2.25 (m, 2H), 1.69-1.60 (m, 2H), 1.56-1.46 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 157.4, 153.6 (d, *J* = 3.4 Hz), 149.8, 137.3, 130.1, 130.0 (dd, *J* =

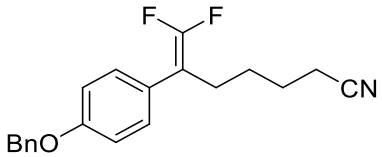
3.7, 2.5 Hz), 128.0 (t, *J* = 3.2 Hz), 119.5, 91.4 (dd, *J* = 20.8, 14.4 Hz), 26.8, 26.7(0), 26.7(6), 26.6, 24.6, 21.1, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -91.48 (d, *J* = 44.5 Hz), -91.76 (d, *J* = 44.5 Hz). HRMS-ESI (m/z) calculated for $C_{14}H_{15}F_2N$ $[M+Na]^+$ 258.1065, found 258.1065

6-([1,1'-biphenyl]-4-yl)-7,7-difluorohept-6-enenitrile (3c)



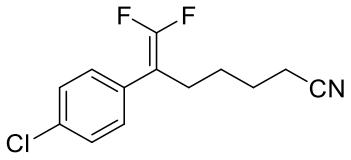
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 30.3 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.60 (d, *J* = 8.0 Hz, 4H), 7.48-7.41 (m, 2H), 7.37 (d, *J* = 8.0 Hz, 3H), 2.52-2.45 (m, 2H), 2.36-2.27 (m, 2H), 1.73-1.64 (m, 2H), 1.61-1.51 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 157.6, 153.8, 150.0, 140.4 (d, *J* = 7.8 Hz), 132.0(0), 132.0(9), 128.5 (t, *J* = 3.3 Hz), 127.5, 127.3, 127.0, 119.5, 91.3 (dd, *J* = 18.7, 16.4 Hz), 26.8 (dd, *J* = 4.5, 1.8 Hz), 24.7, 17.0. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -90.55. HRMS-ESI (m/z) calculated for $C_{19}H_{17}F_2N$ $[M+Na]^+$ 320.1222, found 320.1224

6-(4-(benzyloxy)phenyl)-7,7-difluorohept-6-enenitrile (3d)



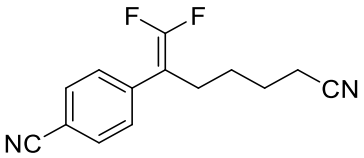
White oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 30.1 mg, 46% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.47–7.29 (m, 5H), 7.26–7.17 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 5.06 (s, 2H), 2.45-2.37 (m, 2H), 2.33-2.25 (m, 2H), 1.68–1.59 (m, 2H), 1.55-1.45 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 158.1, 157.4, 153.6 (d, *J* = 2.7 Hz), 149.8, 136.8, 129.3 (t, *J* = 3.2 Hz), 128.7, 128.1, 127.6, 127.5, 125.5, 125.4(2), 125.4(9), 119.5, 115.0, 91.0 (dd, *J* = 20.6, 14.8 Hz), 70.1, 53.5, 26.9, 26.7 (t, *J* = 2.6 Hz), 24.6, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -91.86 (d, *J* = 45.7 Hz), -92.08 (d, *J* = 45.5 Hz). HRMS-ESI (m/z) calculated for $C_{20}H_{19}F_2NO$ $[M+Na]^+$ 350.1327, found 350.1329.

6-(4-chlorophenyl)-7,7-difluorohept-6-enenitrile (3e)



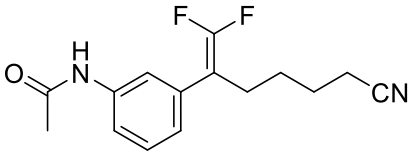
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 27.1 mg, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.49 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 2.47-2.39 (m, 2H), 2.35-2.27 (m, 2H), 1.69-1.60 (m, 2H), 1.55-1.45 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 157.5, 153.6, 149.8, 132.0, 131.8, 129.8 (t, *J* = 3.3 Hz), 121.5, 119.3, 90.9 (t, *J* = 17.9 Hz), 26.7(7), 26.7(5), 26.6, 24.6, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -90.13. HRMS-ESI (m/z) calculated for $C_{13}H_{12}ClF_2N$ $[M+Na]^+$278.0519, found 278.0516.

4-(6-cyano-1,1-difluorohex-1-en-2-yl)benzonitrile (3f)



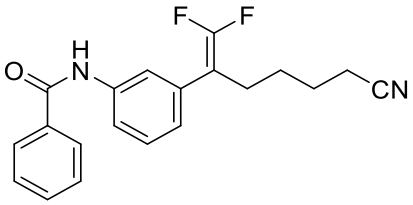
White oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 19,2 mg, 39% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.66 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.52-2.45 (m, 2H), 2.36-2.29 (m, 2H), 1.68-1.63 (m, 2H), 1.57-1.47 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 158.0, 154.1 (d, *J* = 4.5 Hz), 153.5, 132.7, 132.4, 130.9, 130.0, 128.8(4), 128.8(1), 128.8(6), 128.7, 119.2, 118.5, 111.3, 91.1 (dd, *J* = 23.0, 12.5 Hz), 65.6, 26.8, 26.7(4), 26.7(1), 26.4, 24.6, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -87.4 (d, *J* = 35.4 Hz), -87.8 (d, *J* = 35.5 Hz). HRMS-ESI (m/z) calculated for $C_{14}H_{12}F_2N_2$ $[M+Na]^+$ 269.0861, found 269.0865.

N-(3-(6-cyano-1,1-difluorohex-1-en-2-yl)phenyl)acetamide (3g)



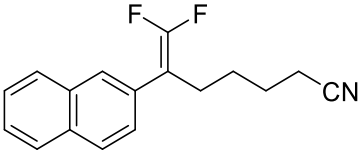
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 28.4 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.54 (s, 1H), 7.49 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.33-7.26 (m, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 2.46-2.39 (m, 2H), 2.34-2.27 (m, 2H), 2.16 (s, 3H), 1.70-1.60 (m, 2H), 1.56-1.45 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 157.6, 153.7 (d, *J* = 4.0 Hz), 149.9, 138.3, 133.9(4), 133.9(0), 133.8, 129.2, 124.1(9), 124.1(5), 124.0, 119.5 (d, *J* = 3.3 Hz), 119.0, 91.3 (dd, *J* = 21.9, 13.2 Hz), 26.7, 26.6(2), 26.6(8), 26.6(5), 24.5, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -90.2 (d, *J* = 42.1 Hz), -90.8 (d, *J* = 42.2 Hz). HRMS-ESI (m/z) calculated for $C_{15}H_{16}F_2N_2O$ $[M+Na]^+$ 301.1123, found 301.1125.

N-(3-(6-cyano-1,1-difluorohex-1-en-2-yl)phenyl)benzamide (3h)



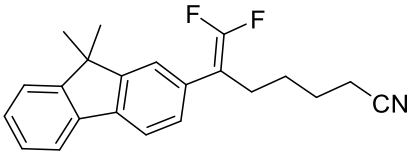
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 32.7 mg, 48% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.03 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.57 (s, 1H), 7.53-7.44 (m, 2H), 7.43-7.36 (m, 2H), 7.30-7.24 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 2.40-2.32 (m, 2H), 2.27-2.19 (m, 2H), 1.63-1.53 (m, 2H), 1.50-1.41 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 165.9, 157.6, 153.8 (d, *J* = 4.2 Hz), 149.9, 138.3, 134.7, 134.0 (dd, *J* = 4.5, 3.1 Hz), 132.0, 129.3, 128.8, 127.1, 124.4(1), 124.4(7), 124.3, 120.0, 120.0(9), 119.9, 119.6, 119.4, 91.4 (dd, *J* = 22.0, 13.5 Hz), 26.7, 26.6(0), 26.6(7), 26.5, 24.5, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -90.11 (d, *J* = 42.0 Hz), -90.71 (d, *J* = 42.0 Hz). HRMS-ESI (m/z) calculated for $C_{20}H_{19}F_2N_2O$ $[M+Na]^+$ 364.1358, found 364.1324.

7,7-difluoro-6-(naphthalen-2-yl)hept-6-enenitrile (3i)



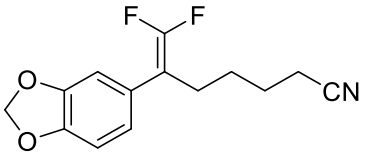
White oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 29.3 mg, 54% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.92-7.81 (m, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.58-7.45 (m, 3H), 7.34 (d, *J* = 7.2 Hz, 1H), 2.51 (s, 2H), 2.32-2.21 (m, 2H), 1.66 (d, *J* = 6.8 Hz, 2H), 1.54-1.43 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 157.2, 153.4 (d, *J* = 1.4 Hz), 149.6, 133.9, 131.6 (dd, *J* = 2.6, 1.2 Hz), 130.8 (dd, *J* = 4.7, 1.2 Hz), 128.7, 128.6, 127.4 (dd, *J* = 3.3, 1.4 Hz), 126.5, 126.1, 125.3, 124.7, 119.4, 89.6 (dd, *J* = 22.1, 17.8 Hz), 77.5, 28.7 (d, *J* = 1.6 Hz), 26.8(4), 26.8(0), 26.8(7), 24.9, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -88.10 (d, *J* = 43.0 Hz), -92.70 (d, *J* = 43.0 Hz). HRMS-ESI (m/z) calculated for $C_{17}H_{15}F_2N$ $[M+Na]^+$ 294.1064, found 294.1065.

6-(9,9-dimethyl-9H-fluoren-2-yl)-7,7-difluorohept-6-enenitrile (3j)



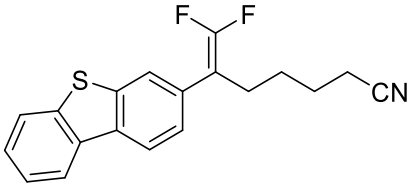
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 35.1 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.70 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37-7.30 (m, 3H), 7.26 (d, *J* = 6.8 Hz, 1H), 2.54-2.46 (m, 2H), 2.34-2.28 (m, 2H), 1.74-1.63 (m, 2H), 1.62-1,54 (m, 2H), 1.49 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 157.6, 153.9 (d, *J* = 16.3 Hz), 149.9, 138.6 (d, *J* = 6.5 Hz), 132.01, 131.95, 131.91, 127.46, 127.0 (d, *J* = 3.6 Hz), 122.6, 122.4 (t, *J* = 3.3 Hz), 120.1 (d, *J* = 3.2 Hz), 119.5, 92.0 (dd, *J* = 21.2, 13.7 Hz), 46.9, 27.2, 27.0, 26.8(1), 26.8(8), 26.7, 24.7, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -90.71 (d, *J* = 43.4 Hz), -91.09 (d, *J* = 43.4 Hz). HRMS-ESI (m/z) calculated for $C_{22}H_{21}F_2N$ $[M+Na]^+$ 360.1535, found 360.1539.

6-(benzo[d][1,3]dioxol-5-yl)-7,7-difluorohept-6-enenitrile (3k)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 26.0 mg, 49% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 6.83-6.71 (m, 3H), 5.97 (s, 2H), 2.42-2.34 (m, 2H), 2.34-2.27 (m, 2H), 1.69-1.59 (m, 2H), 1.55-1.45 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 157.4, 153.6 (d, *J* = 3.4 Hz), 149.8, 147.9, 146.9, 126.7(0), 126.7(6) 126.6(4), 126.6(0), 121.8 (t, *J* = 3.2 Hz), 119.4, 108.7 (t, *J* = 3.4 Hz), 108.4, 101.2, 91.3 (dd, *J* = 22.0, 13.8 Hz), 27.1, 26.6(4), 26.6(0), 26.6(7), 24.6, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -91.33 (d, *J* = 44.8 Hz), -91.87 (d, *J* = 44.7 Hz). HRMS-ESI (m/z) calculated for $C_{14}H_{13}F_2NO_2$ $[M+Na]^+$ 288.0807, found 288.0815.

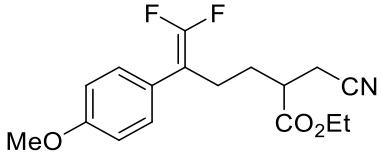
6-(dibenzo[b,d]thiophen-3-yl)-7,7-difluorohept-6-enenitrile (3l)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 36.0 mg, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.20-8.11 (m, 2H), 7.90-7.82 (m, 1H), 7.53-7.44 (m, 3H), 7.31 (d, *J* = 7.6 Hz, 1H), 2.60-2.53 (m, 2H), 2.31-2.23 (m, 2H), 1.75-1.65 (m, 2H), 1.55-1.44 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 157.2, 153.3, 149.5, 139.9, 139.8(3), 139.8(1), 139.8(9), 139.0, 136.1, 135.7, 128.2 (dd, *J* = 5.0, 1.6 Hz), 127.4 (dd, *J* = 3.0, 1.6 Hz), 127.1, 124.8, 124.6, 122.8, 121.8, 121.3, 119.4, 90.7 (dd, *J* = 23.2, 16.4 Hz), 27.2 (d, *J* = 1.3 Hz), 26.7 (t, *J* = 2.6 Hz), 24.8,

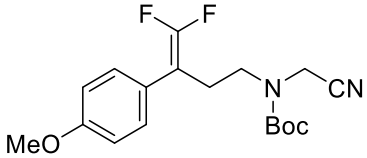
16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -86.29 (d, *J* = 38.3 Hz), -91.21 (d, *J* = 38.3 Hz). HRMS-ESI (m/z) calculated for $C_{19}H_{15}F_2NS$ $[M+Na]^+$ 350.0786, found 350.0792.

ethyl 2-(cyanomethyl)-6,6-difluoro-5-(4-methoxyphenyl)hex-5-enoate (3m)



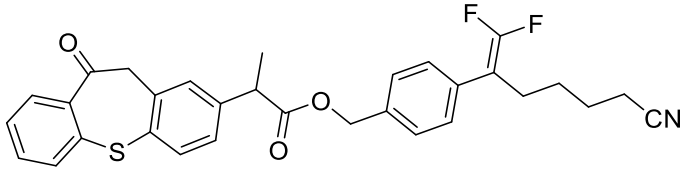
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 40.1 mg, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.21 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.24-4.16 (m 2H), 3.81 (s, 3H), 2.74-2.57 (m, 2H), 2.56-2.47 (m, 1H), 2.47-2.40 (m, 2H), 1.90-1.79 (m, 1H), 1.75-1.65 (m, 1H), 1.30-1.23 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 173.1, 165.3, 162.5, 135.4, 135.0, 134.5, 134.1, 132.1, 125.6(1), 125.6(6), 125.5(1), 125.5(6), 121.7, 61.4, 35.6 (d, *J* = 7.9 Hz), 31.0, 14.1. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -63.24, -63.24. HRMS-ESI (m/z) calculated for $C_{17}H_{19}F_2NO_3$ $[M+Na]^+$ 346.1226, found 346.1239.

tert-butyl (cyanomethyl)(4,4-difluoro-3-(4-methoxyphenyl)but-3-en-1-yl)carbamate (3n)



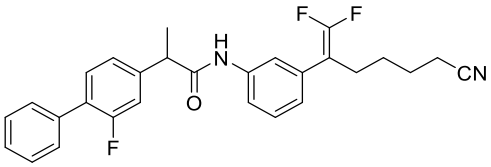
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 26.1 mg, 37% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.27 (d, *J* = 5.6 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.02 (d, *J* = 58.4 Hz, 2H), 3.82 (s, 3H), 3.34 (m, *J* = 7.1 Hz, 2H), 2.68 (m, *J* = 6.8 Hz, 2H), 1.46 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm): 159.0, 157.9, 154.1 (d, *J* = 4.8 Hz), 150.2, 129.1, 124.6, 116.0, 114.2, 81.9, 55.3, 29.7, 28.1, 26.5. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm): -89.93 (d, *J* = 41.7 Hz), -90.71 (dd, *J* = 84.8, 41.7 Hz).. HRMS-ESI (m/z) calculated for $C_{18}H_{22}F_2N_2O_3$ $[M+Na]^+$ 375.1491, found 375.1504.

4-(6-cyano-1,1-difluorohex-1-en-2-yl)benzyl 2-(10-oxo-10,11-dihydrodibenzo[b,f]thiepin-2-yl)propanoate(3o)



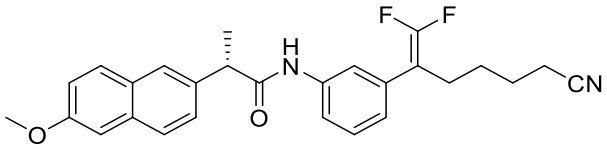
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 39.3 mg, 37% yield; ^{1}H NMR (400 MHz, CDCl3) (δ, ppm) 8.22-8.18 (m, 1H), 7.63-7.55 (m, 2H), 7.46-7.41 (m, 1H), 7.38 (s, 1H), 7.34-7.28 (m, 2H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 3H), 5.09 (d, *J* = 5.6 Hz, 2H), 4.34 (d, *J* = 2.8 Hz, 2H), 3.82-3.74 (m, 1H), 2.41-2.34 (m, 2H), 2.32-2.25 (m, 2H), 1.65-1.58 (m, 2H), 1.52-1.40 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 191.3, 173.6, 157.6, 153.7 (d, *J* = 1.9 Hz), 149.9, 142.5, 140.2, 138.0, 136.2 (d, *J* = 8.8 Hz), 133.3, 132.6, 131.5 (d, *J* = 4.9 Hz), 130.9, 130.0, 128.8 (d, *J* = 11.8 Hz), 128.0(3), 128.0(9) (t, *J* = 3.2 Hz), 127.6 (t, *J* = 3.2 Hz), 127.5, 127.0 (d, *J* = 11.5 Hz), 126.4, 119.4, 91.3 (dd, *J* = 19.7, 15.6 Hz), 76.6, 66.3, 51.0, 45.2, 26.7(0), 26.7(6), 26.6(3), 26.6(0), 24.6, 18.4, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -90.45, -90.61 (d, *J* = 5.0 Hz), -90.77. HRMS-ESI (m/z) calculated for $C_{31}H_{27}F_2NO_3S$ $[M+Na]^+$ 554.1572, found 554.1587.

N-(3-(6-cyano-1,1-difluorohex-1-en-2-yl)phenyl)-2-(2-fluoro-[1,1'-biphenyl]-4-yl)propenamide (3p)



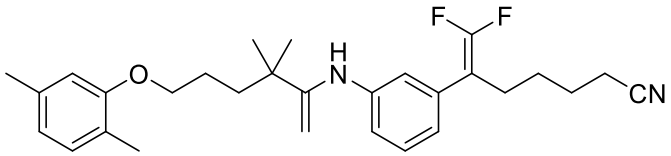
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 37.0 mg, 40% yield; (400 MHz, $CDCl_3$) (δ, ppm): 7.56 (d, *J* = 8.0 Hz, 2H), 7.48–7.43 (m, 3H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 10.8 Hz, 4H), 7.05 (d, *J* = 8.8 Hz, 2H), 4.00 (m, *J* = 7.2 Hz, 1H), 2.43 (m, *J* = 7.2 Hz, 2H), 2.29 (m, *J* = 7.2 Hz, 2H), 1.69–1.62 (m, 5H), 1.51 (m, *J* = 7.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 161.4, 158.2 153.8, 149.9, 141.1 (d, *J* = 7.7 Hz), 135.4, 131.0 (d, *J* = 4.0 Hz), 129.3 129.2(2) (t, *J* = 3.2 Hz), 129.2(8), 129.0 (d, *J* = 3.0 Hz), 128.5, 128.3, 128.1, 127.8, 123.6(1), 123.6(7), 121.5, 119.6, 115.5, 115.2, 90.9 (dd, *J* = 20.7, 15.3 Hz), 45.16 (d, *J* = 1.3 Hz), 26.9, 26.6 (t, *J* = 2.5 Hz), 24.6, 18.4, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm): -90.50, -90.67 (d, *J* = 10.3 Hz), -90.84, -117.25. HRMS-ESI (m/z) calculated for $C_{28}H_{25}F_3N_2O$ $[M+Na]^+$ 485.1812, found 485.1825.

(S)-N-(3-(6-cyano-1,1-difluorohex-1-en-2-yl)phenyl)-2-(6-methoxynaphthalen-2-yl)propenamide (3q)



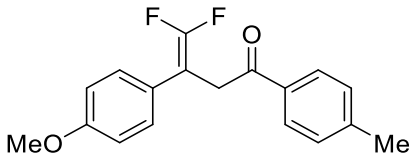
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 39.5 mg, 44% yield; ^1H NMR (300 MHz, $CDCl_3$) (δ, ppm): 7.80 – 7.71 (m, 3H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.26 – 7.13 (m, 5H), 6.98 (d, *J* = 6.0 Hz, 1H), 3.93 (s, 3H), 3.85 (m, *J* = 7.2 Hz, 1H), 2.38 (m, *J* = 7.2 Hz, 2H), 2.27 (m, *J* = 6.9 Hz, 2H), 1.63 (m, *J* = 13.6, 6H), 1.51 – 1.41 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm): 172.6, 157.9, 138.2, 135.9, 133.9 (d, *J* = 2.7 Hz), 129.3, 129.0 (d, *J* = 3.5 Hz), 127.9, 126.3 (d, *J* = 19.7 Hz), 124.1, 119.4, 118.8, 105.7, 91.4 (dd, J = 22.1, 13.6 Hz), 55.4, 48.1, 26.7, 26.6(0), 26.6(6), 26.5, 24.5, 18.6, 16.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm): -90.33 (d, *J* = 42.3 Hz), -90.98 (d, *J* = 42.3 Hz). HRMS-ESI (m/z) calculated for $C_{27}H_{26}F_2N_2O_2$ $[M+Na]^+$ 471.1855, found 471.1864.

N-(3-(6-cyano-1,1-difluorohex-1-en-2-yl)phenyl)-5-(2,5-dimethylphenoxy)-2,2-dimethylpentanamide (3r)



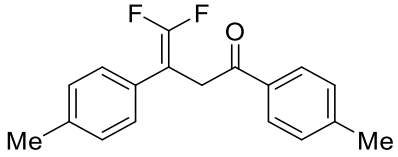
White oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 38.4 mg, 41% yield; ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.53 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.35-7.27 (m, 1H), 7.06-6.96 (m, 2H), 6.69-6.59 (m, 2H), 3.95 (s, 2H), 2.47-2.39 (m, 2H), 2.30 (d, *J* = 7.2Hz, 5H), 2.17 (s, 3H), 1.83 (s, 4H), 1.69-1.61 (m, 2H), 1.57-1.47 (m, 2H), 1.34 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 175.9 157.6 156.8, 153.8, 153.7, 149.9, 138.3, 136.6, 134.0, 133.9(3), 133.9(9), 130.3, 129.2, 124.2 (t, *J* = 3.1 Hz), 123.5, 120.9, 119.8 (t, *J* = 3.2 Hz), 119.6, 119.2, 112.2, 91.4 (dd, *J* = 22.0, 13.5 Hz), 67.9, 42.9, 37.6, 26.7 (d, *J* = 15.4 Hz), 25.6, 25.2, 24.5, 21.4, 16.9, 15.9. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -90.28 (d, *J* = 42.4 Hz), -91.00 (d, *J* = 42.1 Hz). HRMS-ESI (m/z) calculated for $C_{28}H_{34}F_2N_2O_2$ $[M+Na]^+$ 491.2481, found .491.2481.

4,4-difluoro-3-(4-methoxyphenyl)-1-(p-tolyl)but-3-en-1-one (5a)



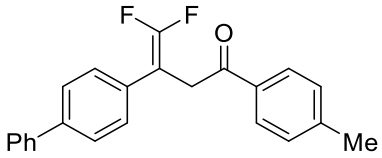
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 33.3 mg, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.87 (d, *J* = 8.0 Hz, 2H), 7.28-7.22 (m, 4H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.02-3.98 (m, 2H), 3.77 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 195.2(3), 195.2(0), 195.2(6), 195.1, 158.8, 154.5 (d, *J* = 3.7 Hz), 150.7, 144.3, 133.9, 130.5, 130.1, 129.4, 129.2(3), 129.2(8), 129.1(4), 129.1(1), 128.3, 128.2, 125.7 (t, *J* = 3.8 Hz), 114.1, 114.0, 113.9, 86.9 (dd, *J* = 21.8, 17.7 Hz), 55.2, 38.3 (d, *J* = 2.4 Hz), 21.7. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -89.43 (d, *J* = 39.7 Hz), -90.24 (d, J = 39.8 Hz). HRMS-ESI (m/z) calculated for $C_{18}H_{16}F_2O_2$ $[M+Na]^+$ 325.1011, found 325.1203.

4,4-difluoro-1,3-di-p-tolylbut-3-en-1-one(5b)



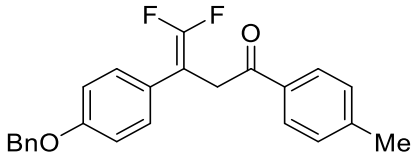
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 26.9 mg, 88% yield;^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.87 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.03-3.98 (m, 2H), 2.41 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 195.1(2), 195.1(9), 195.1(7), 195.0, 158.4, 154.6 (d, *J* = 4.2 Hz), 150.8, 144.3, 137.2, 133.9, 130.5 (t, *J* = 3.9 Hz), 129.3 (d, *J* = 14.2 Hz), 128.3, 127.8 (t, *J* = 3.4 Hz), 87.1 (dd, *J* = 21.6, 17.4 Hz), 38.2(4), 38.2(1), 21.7, 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -88.78 (d, *J* = 38.3 Hz), -89.61 (d, *J* = 38.3 Hz). HRMS-ESI (m/z) calculated for $C_{18}H_{16}F_2O$ $[M+Na]^+$ 309.1062, found 309.1062.

3-([1,1'-biphenyl]-4-yl)-4,4-difluoro-1-(p-tolyl)but-3-en-1-one (5c)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 46.6 mg, 60% yield; ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 7.90 (d, *J* = 8.1 Hz, 2H), 7.59-7.54 (m, 4H), 7.46-7.33 (m, 6H), 7.29 (s, 1H), 4.10-4.05 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 195.0(4), 195.0(1), 195.0(0), 195.0(7), 158.7, 154.8 (d, *J* = 4.6 Hz), 151.0, 144.4, 140.5, 140.2, 133.8, 132.5 (t, *J* = 4.1 Hz), 129.5, 128.8, 128.3, 127.4, 127.1 (d, *J* = 12.4 Hz), 87.3, 87.1, 87.0, 86.8, 38.1, 21.7. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -87.66 (d, *J* = 36.2 Hz), -88.61 (d, *J* = 36.2 Hz). HRMS-ESI (m/z) calculated for $C_{23}H_{18}F_2O$ $[M+Na]^+$ 371.1218, found 371.1206.

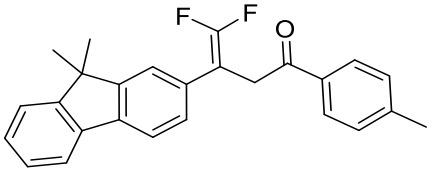
3-(4-(benzyloxy)phenyl)-4,4-difluoro-1-(p-tolyl)but-3-en-1-one(5d)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 34.8 mg, 63% yield; ^{1}H NMR (400 MHz, DMSO) (δ, ppm) 7.92 (d, *J* = 7.6 Hz, 2H), 7.44-7.33 (m, 8H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 5.09 (s, 2H), 4.19 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 195.2 (d, *J* = 3.3 Hz), 158.0, 144.3,

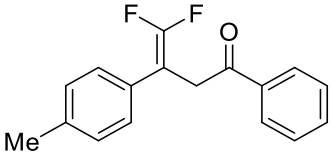
136.9, 133.9, 130.9, 129.4, 129.2 (t, *J* = 3.5 Hz), 128.6, 128.3, 128.0, 127.5, 114.9, 86.8 (dd, *J* = 21.8, 17.6 Hz), 70.0, 65.6, 38.3, 30.6, 29.7, 21.7, 19.2, 13.8. ^{19}F NMR (282 MHz, DMSO) (δ, ppm) -90.24 (d, *J* = 42.3 Hz), -91.68 (d, *J* = 42.2 Hz). HRMS-ESI (m/z) calculated for $C_{24}H_{20}F_2O_2$ $[M+Na]^+$ 401.1324, found 401.1324.

3-(9,9-dimethyl-9H-fluoren-2-yl)-4,4-difluoro-1-(p-tolyl)but-3-en-1-one (5e)



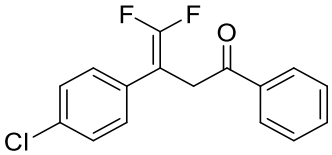
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 43.5 mg, 56% yield; ^{1}H NMR (400 MHz, DMSO) (δ, ppm) 7.95 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 6.8, 2H), 7.56-7.51 (m, 2H), 7.37-7.30 (m, 5H), 4.30-4.27 (m, 2H), 2.38 (s, 3H), 1.39 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 195.2 (dd, *J* = 3.4, 2.4 Hz), 153.8 (d, *J* = 4.2 Hz), 144.3, 138.6 (d, *J* = 7.5 Hz), 134.0, 132.4 (t, *J* = 4.0 Hz), 129.4, 128.3, 127.4, 127.0, 126.9 (t, *J* = 3.3 Hz), 122.6, 122.4(1), 122.4(5), 122.3, 120.1, 120.0, 87.8 (dd, *J* = 21.8, 17.2 Hz), 46.9, 38.5 (d, *J* = 2.3 Hz), 27.1, 21.7. ^{19}F NMR (282 MHz, DMSO) (δ, ppm) -88.86 (d, *J* = 39.2 Hz), -90.46 (d, *J* = 39.2 Hz). HRMS-ESI (m/z) calculated for $C_{26}H_{21}F_2O$ $[M+Na]^+$ 410.1453, found 410.1476.

4,4-difluoro-1-phenyl-3-(p-tolyl)but-3-en-1-one (5f)



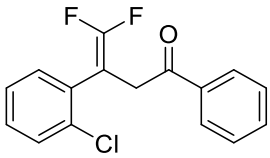
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 35.9 mg, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.90 (d, *J* = 7.6 Hz, 2H), 7.54-7.48 (m, 1H), 7.44-7.37 (m, 2H), 7.18-7.05 (m, 4H), 3.97 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 195.5, 158.5, 154.6, 150.8, 137.3, 136.3, 133.4, 130.4 (t, *J* = 3.9 Hz), 129.2, 128.7, 128.2, 127.8 (t, *J* = 3.4 Hz), 87.0 (dd, *J* = 21.6, 17.5 Hz), 38.4 (d, *J* = 2.4 Hz), 21.1. ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -88.67 (d, *J* = 38.1 Hz), -89.51 (d, *J* = 38.1 Hz). HRMS-ESI (m/z) calculated for $C_{17}H_{14}F_2O$ $[M+Na]^+$ 295.0905, found 295.0905.

3-(4-chlorophenyl)-4,4-difluoro-1-phenylbut-3-en-1-one (5g)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 31.0 mg, 51% yield;^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.97 (d, *J* = 7.2 Hz, 2H), 7.63-7.57 (m, 1H), 7.52-7.45 (m, 2H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.05 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 195.2 (dd, *J* = 3.3, 2.2 Hz), 158.6, 154.7, 150.9, 136.1, 133.5 (d, *J* = 20.4 Hz), 132.0 (t, *J* = 4.1 Hz), 130.4, 129.3 (t, *J* = 3.5 Hz), 128.8 (d, *J* = 5.4 Hz), 86.5 (dd, *J* = 22.6, 17.4 Hz), 38.2 (d, *J* = 2.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -87.42 (d, *J* = 35.3 Hz), -88.30 (d, *J* = 35.2 Hz). HRMS-ESI (m/z) calculated for $C_{16}H_{17}ClF_2O$ $[M+Na]^+$ 315.0309, found 315.0310.

3-(2-chlorophenyl)-4,4-difluoro-1-phenylbut-3-en-1-one (5h)



Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 25.8 mg, 44% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.94 (d, *J* = 7.6 Hz, 2H), 7.64-7.56 (m, 1H), 7.52-7.45 (m, 3H), 7.41-7.36 (m, 1H), 7.26-7.21 (m, 2H), 4.06 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 195.2, 158.5, 154.7, 150.8, 136.3, 133.4, 132.6, 132.5(2), 132.5(0), 129.6 (d, *J* = 4.4 Hz), 128.7, 128.2, 126.9, 85.5 (dd, *J* = 24.6, 21.4 Hz), 38.0 (d, *J* = 2.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -86.60 (d, *J* = 34.3 Hz), -90.25 (d, *J* = 34.6 Hz). HRMS-ESI (m/z) calculated for $C_{16}H_{17}ClF_2O$ $[M+Na]^+$ 315.0309, found 315.0338.

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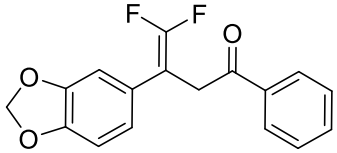
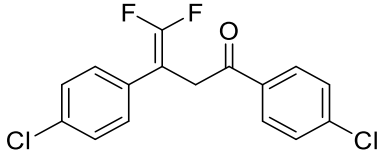
3-(benzo[d][1,3]dioxol-5-yl)-4,4-difluoro-1-phenylbut-3-en-1-one (5i)



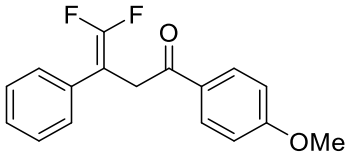
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 30.8 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.96 (d, *J* = 7.6 Hz, 2H), 7.62-7.55 (m, 1H), 7.51-7.44 (m, 2H), 6.83 (s, 1H), 6.76 (s, 2H), 5.94 (s, 2H), 4.01 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 195.41 (t, *J* = 2.9 Hz), 158.5, 154.6 (d, *J* = 3.5 Hz), 150.8, 147.7, 146.9, 136.3, 133.5, 128.7, 128.2, 127.09 (t, *J* = 3.8 Hz), 121.6 (t, *J* = 3.4 Hz), 108.8, 108.7(3), 108.7(8), 108.3, 101.2, 87.0 (dd, *J* = 22.3, 17.8 Hz), 38.6 (d, *J* = 2.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -88.90 (d, *J* = 38.3 Hz), -89.42 (d, *J* = 38.4 Hz). HRMS-ESI (m/z) calculated for $C_{17}H_{12}F_2O_3$ $[M+Na]^+$ 325.0647, found 325.0650.

1,3-bis(4-chlorophenyl)-4,4-difluorobut-3-en-1-one (5j)



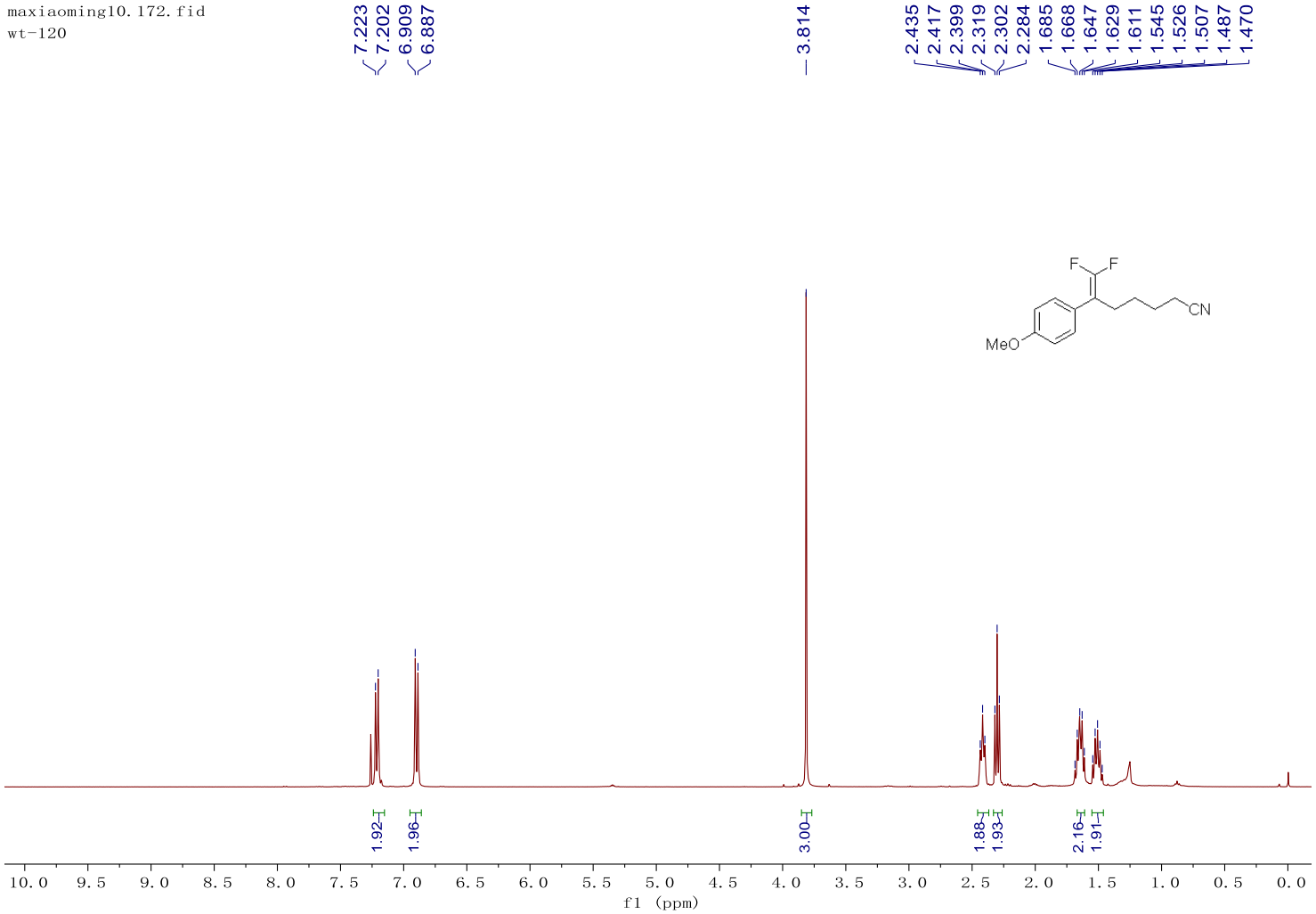
Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 29.4 mg, 45% yield; ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.90 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.01 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 194.0(4), 194.0(1), 194.0(0), 194.0(6), 158.5, 154.7 (d, *J* = 4.0 Hz), 150.8, 140.2, 134.4, 133.5, 131.7, 129.6, 129.3 (t, *J* = 3.5 Hz), 129.1, 128.8, 86.4 (dd, *J* = 22.6, 17.5 Hz), 38.2 (d, *J* = 2.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -87.23 (d, *J* = 34.8 Hz), -88.09 (d, *J* = 34.8 Hz). HRMS-ESI (m/z) calculated for $C_{16}H_{10}Cl_2F_2O$ $[M+H]^+$ 325.0077, found 325.0056.

4,4-difluoro-1-(4-methoxyphenyl)-3-phenylbut-3-en-1-one (5k)

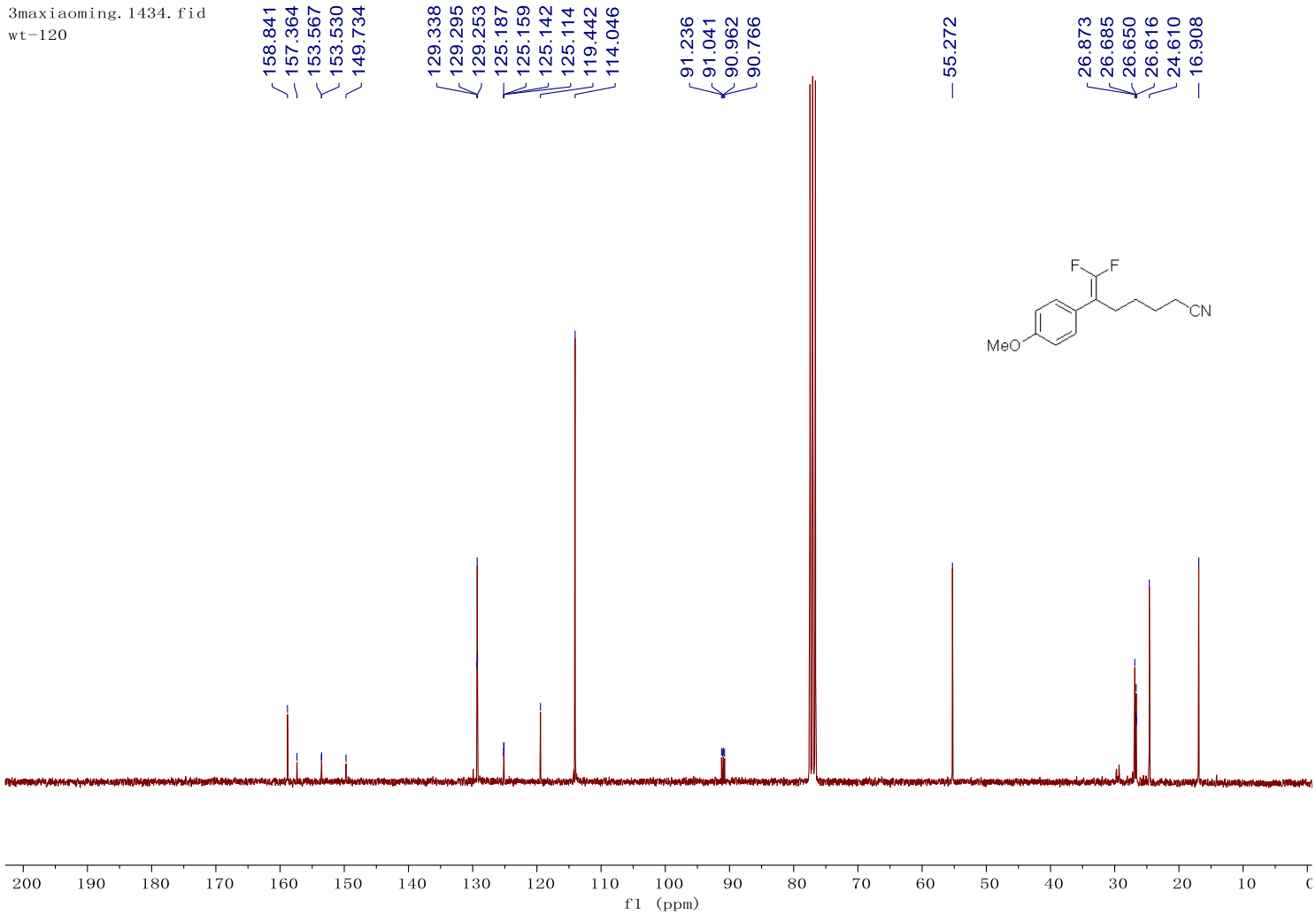


Yellow oil after purification by column chromatography (petroleum ether/ethyl acetate = 30/1); 31,7 mg, 55% yield; ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm) 7.95 (d, *J* = 9.0 Hz, 2H), 7.33-7.21 (m, 5H), 6.94 (d, *J* = 8.7 Hz, 2H), 4.01 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 193.8 (dd, *J* = 3.2, 2.3 Hz), 163.7, 158.6, 154.7 (d, *J* = 4.3 Hz), 150.9, 133.6 (t, *J* = 4.0 Hz), 130.5, 129.4, 128.5, 128.05, 128.0 (t, *J* = 3.4 Hz), 113.9, 87.4 (dd, *J* = 21.9, 17.2 Hz), 55.5, 38.0 (d, *J* = 2.4

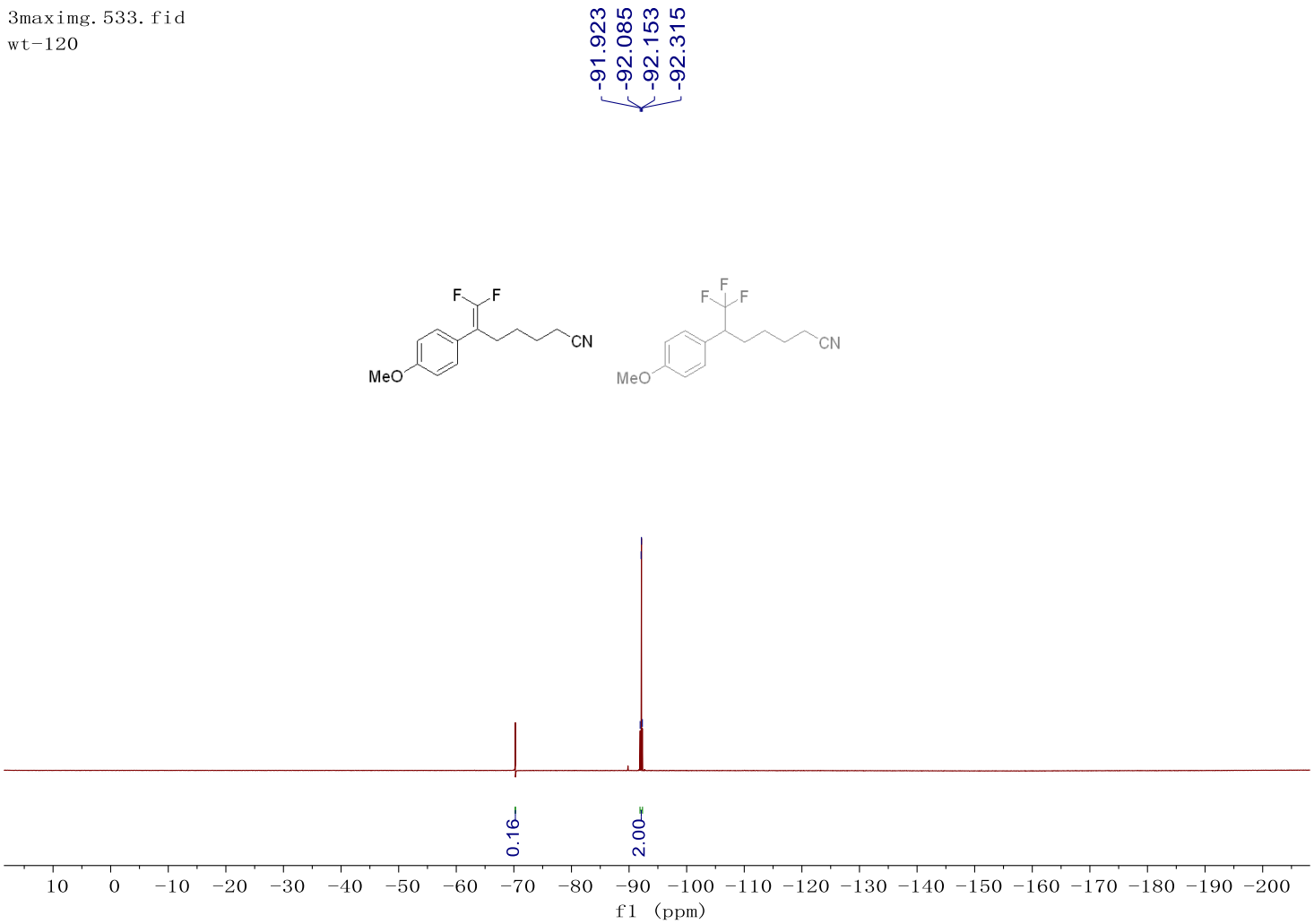
Hz). ^{19}F NMR (282 MHz, $CDCl_3$) (δ, ppm) -88.33 (d, *J* = 37.2 Hz), -89.32 (d, *J* = 37.2 Hz). HRMS-ESI (m/z) calculated for $C_{17}H_{14}ClF_2O_2$ $[M+Na]^+$ 311.0855, found 311.0857.



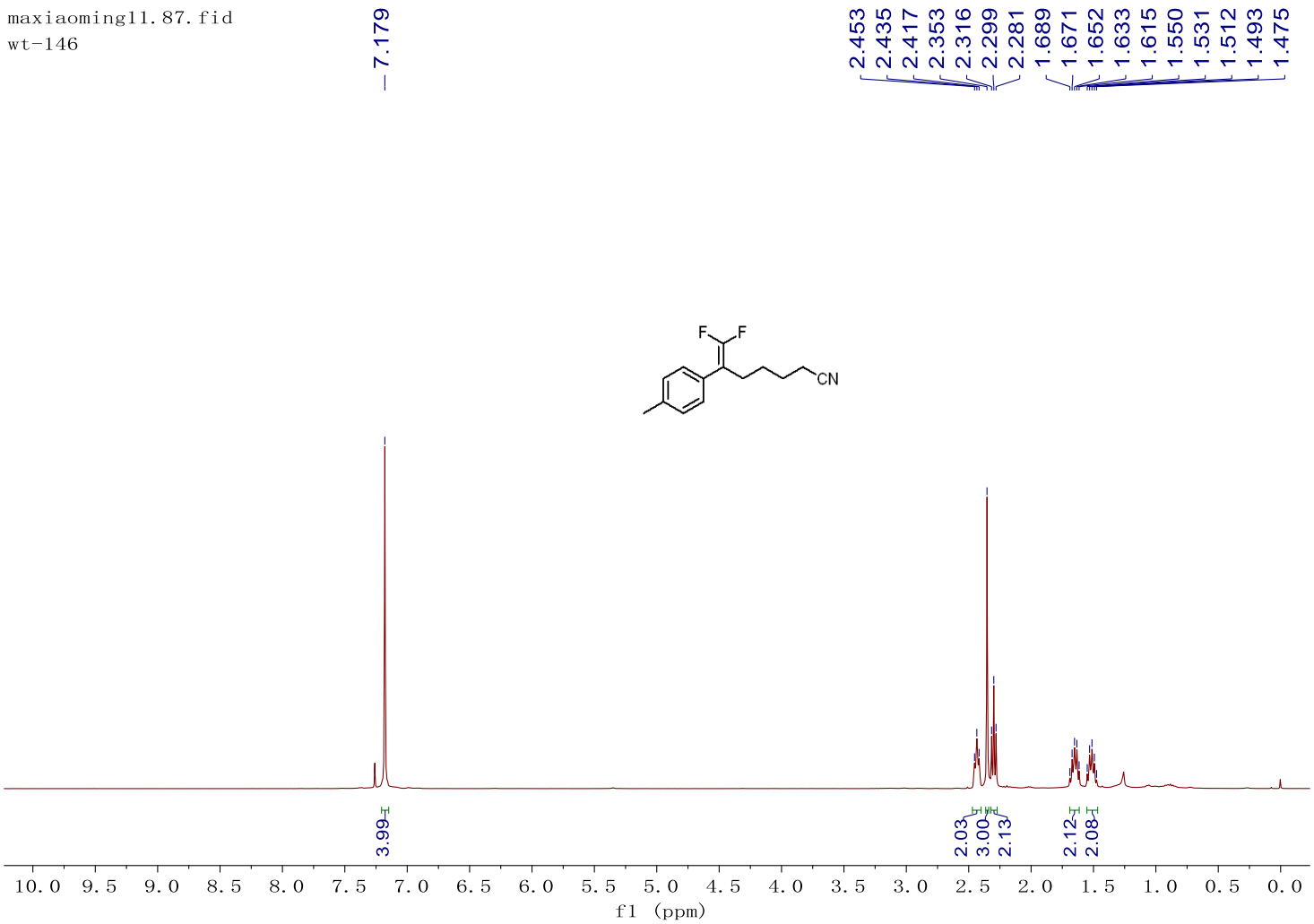
^{1}H NMR Spectrum of Compound 3a (400 MHz, $CDCl_3$)



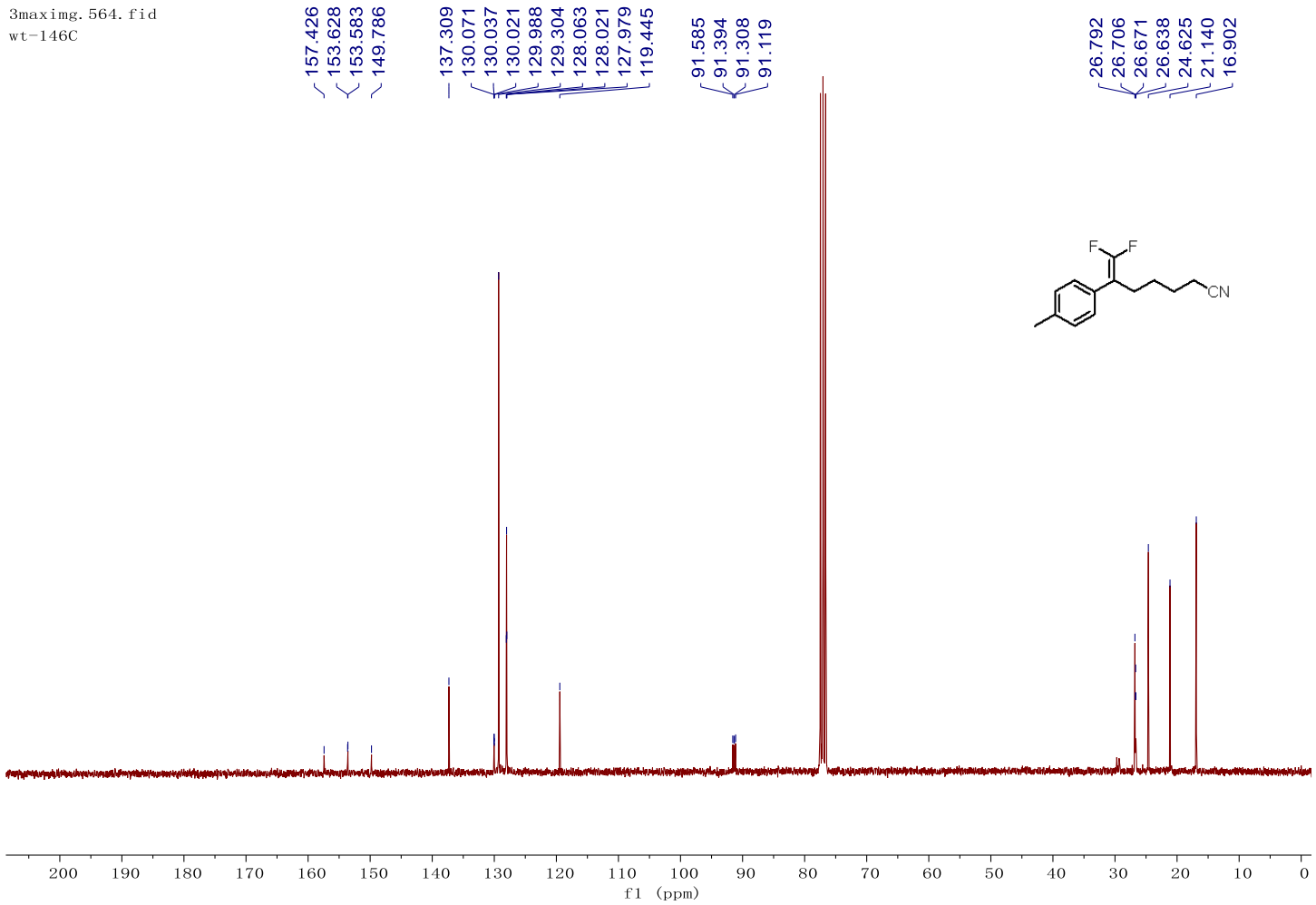
^{13}C NMR Spectrum of Compound 3a (75 MHz, $CDCl_3$)



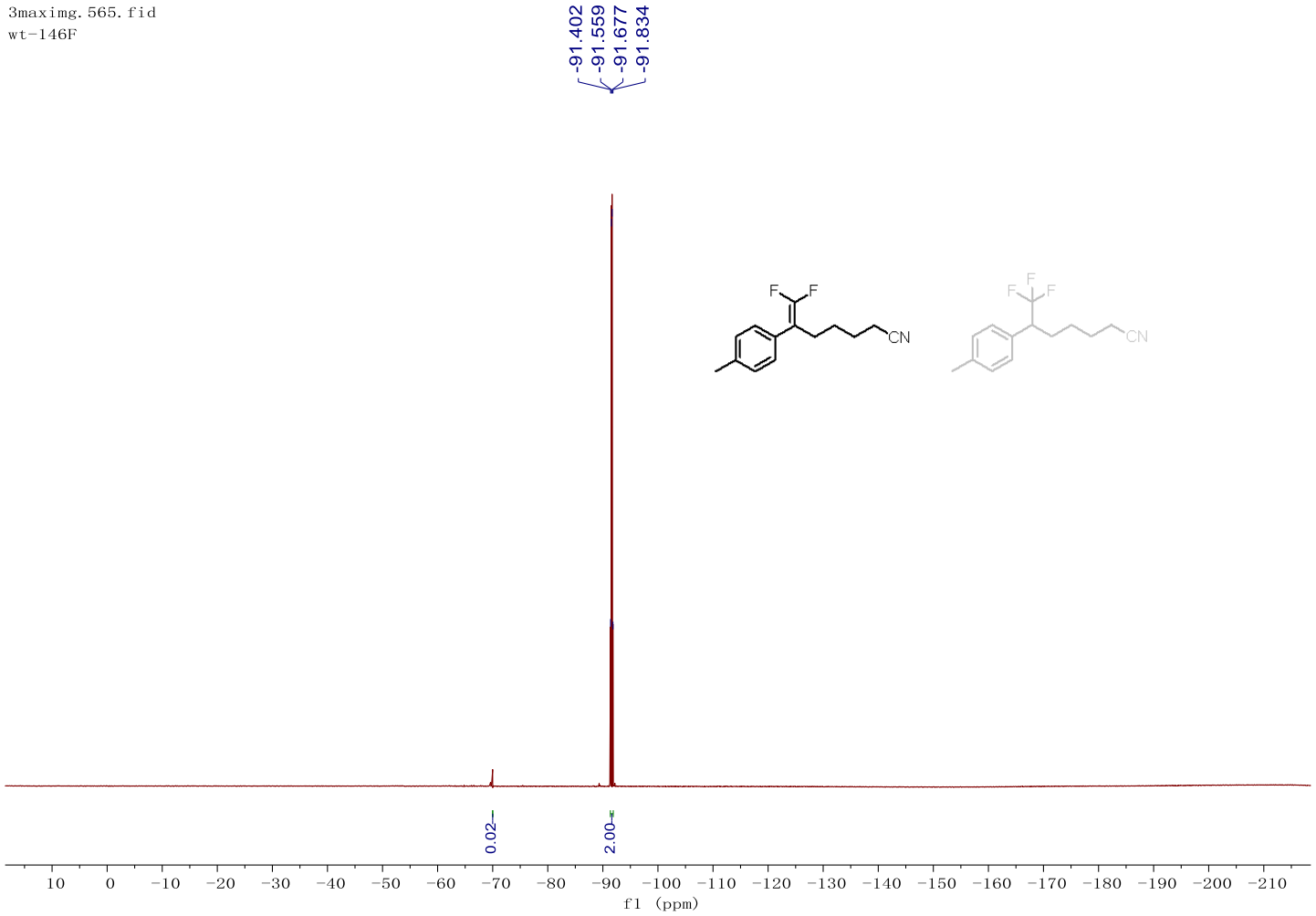
^{19}F NMR Spectrum of Compound 3a (282 MHz, $CDCl_3$)



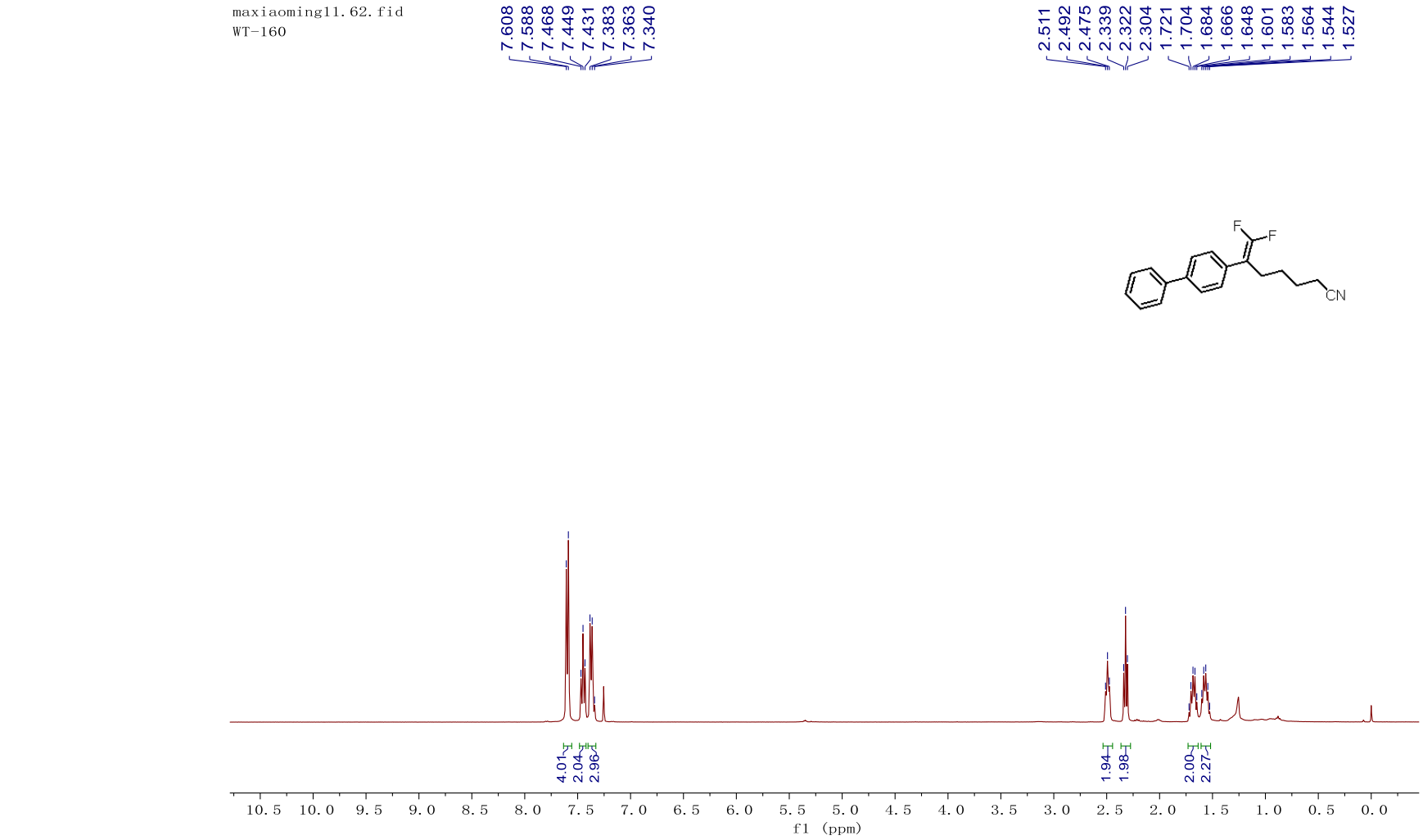
^{1}H NMR Spectrum of Compound 3b (400 MHz, $CDCl_3$)



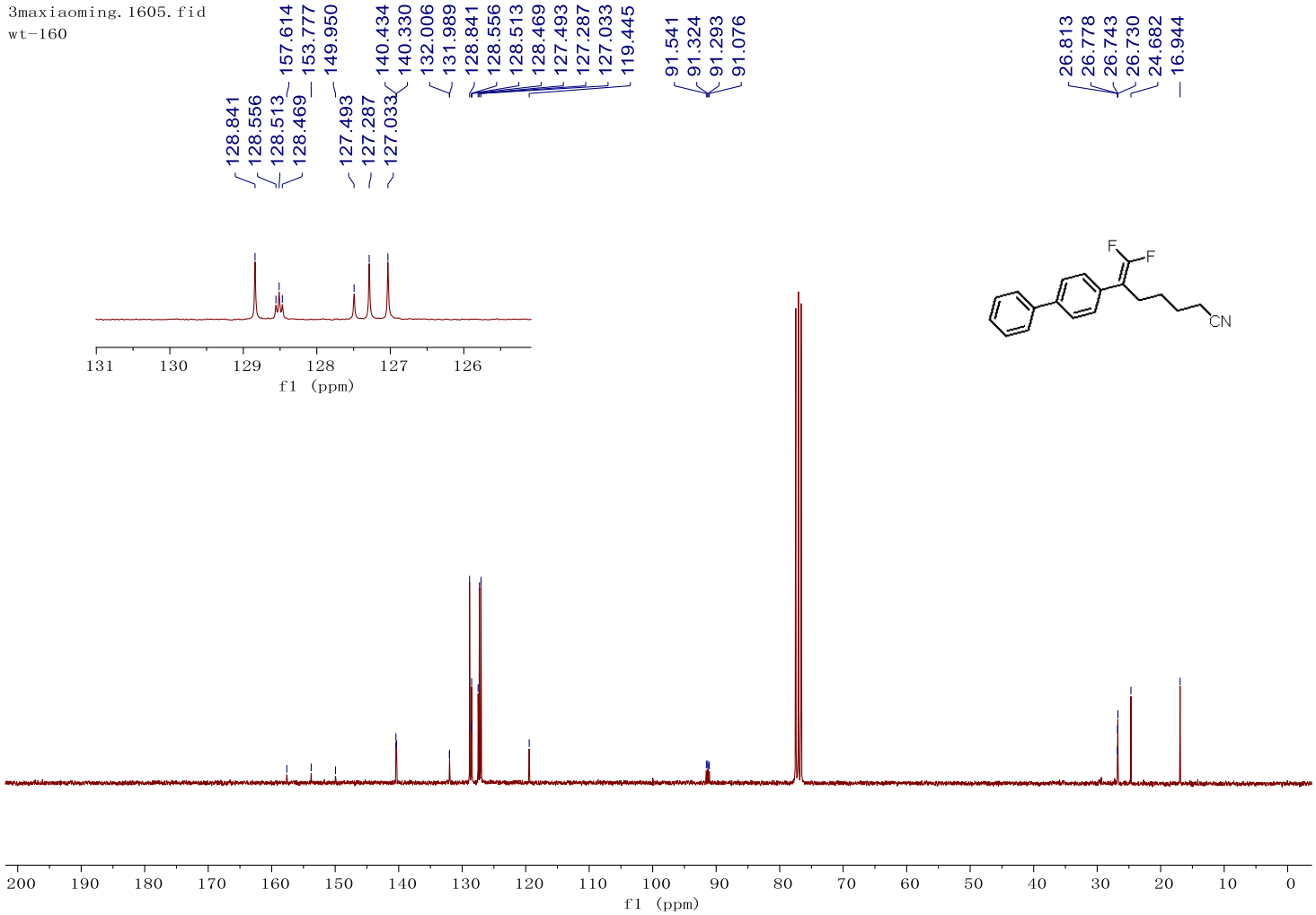
^{13}C NMR Spectrum of Compound 3b (75 MHz, $CDCl_3$)



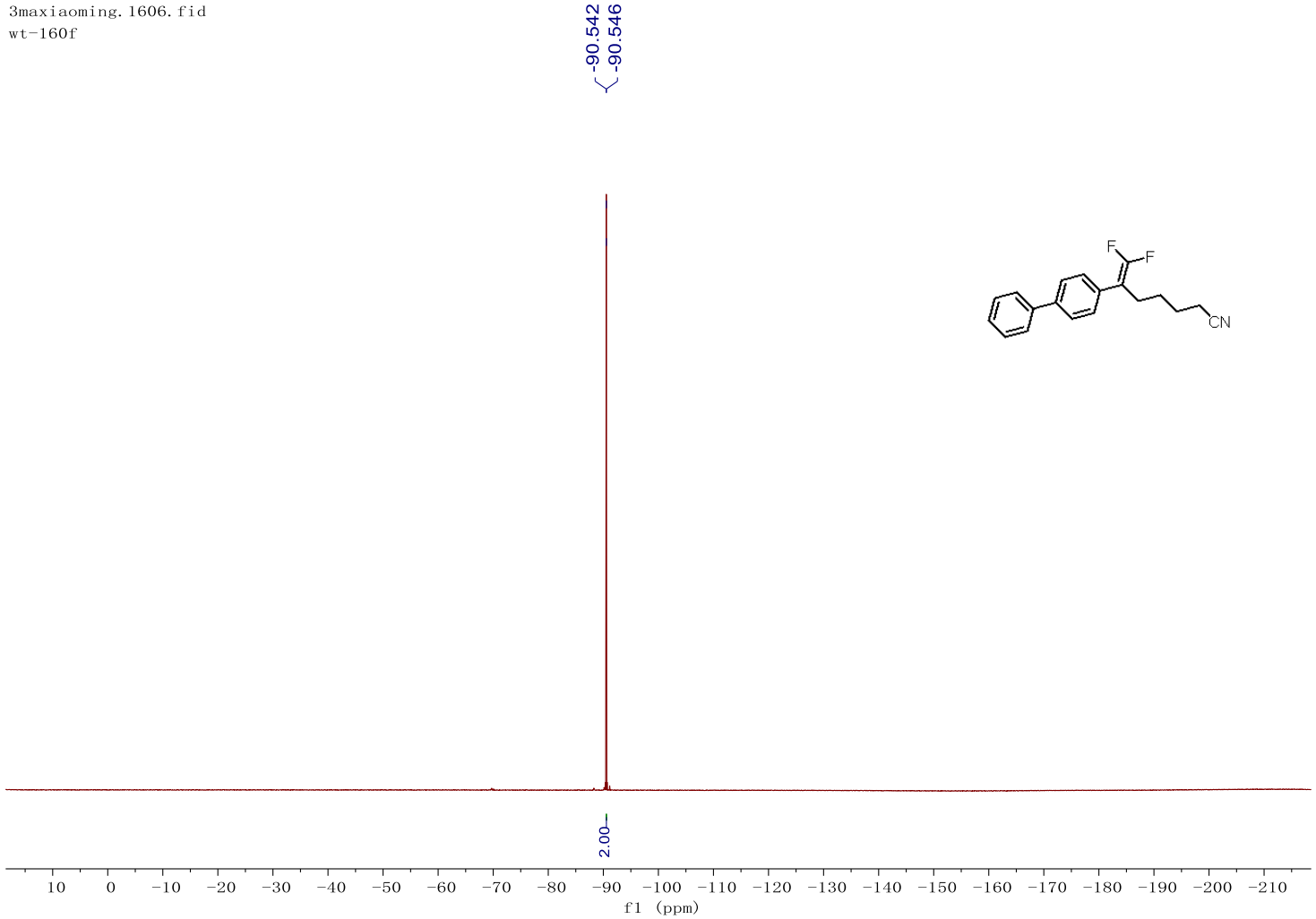
^{19}F NMR Spectrum of Compound 3b (282 MHz, $CDCl_3$)



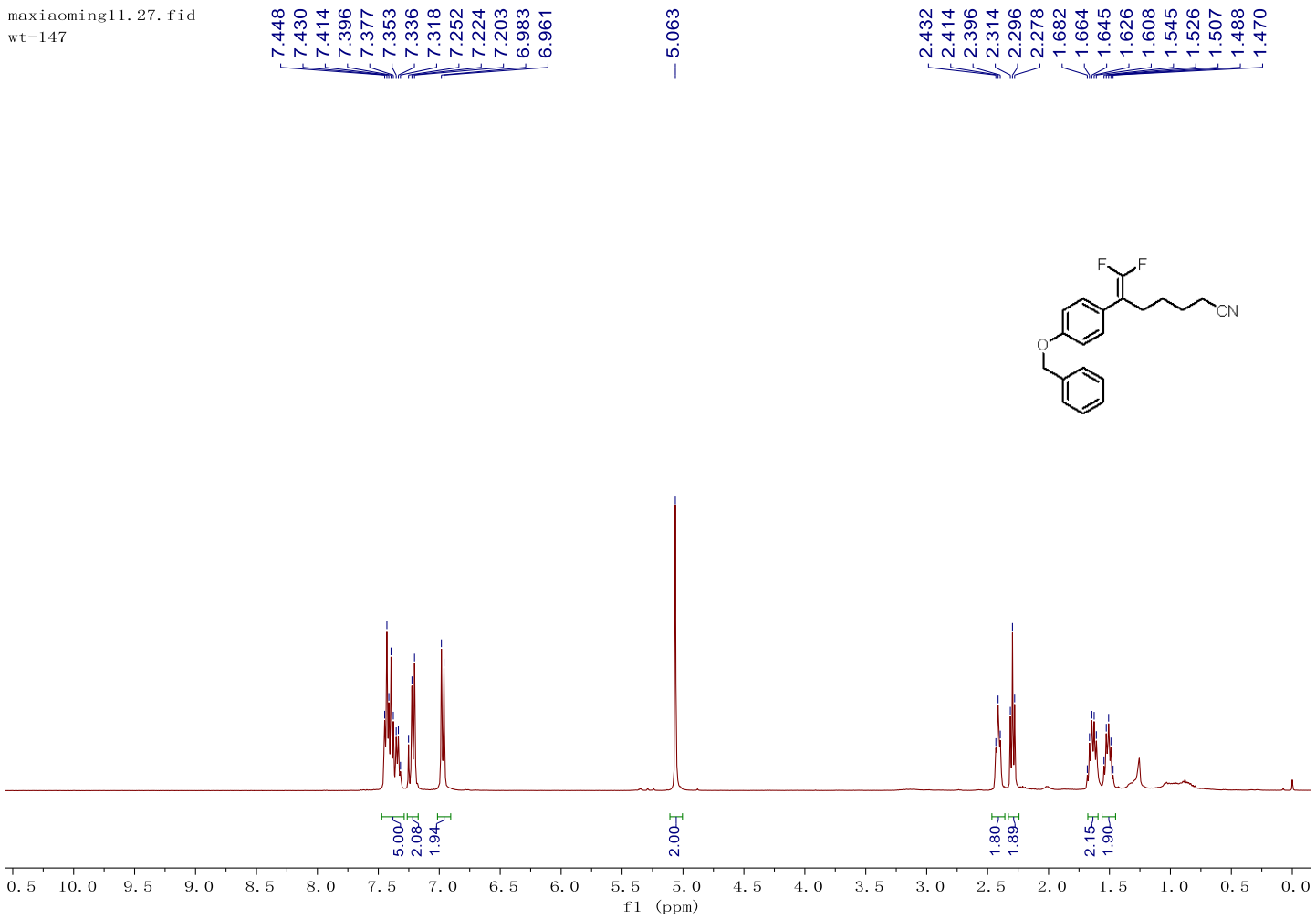
^{1}H NMR Spectrum of Compound 3c (400 MHz, $CDCl_3$)



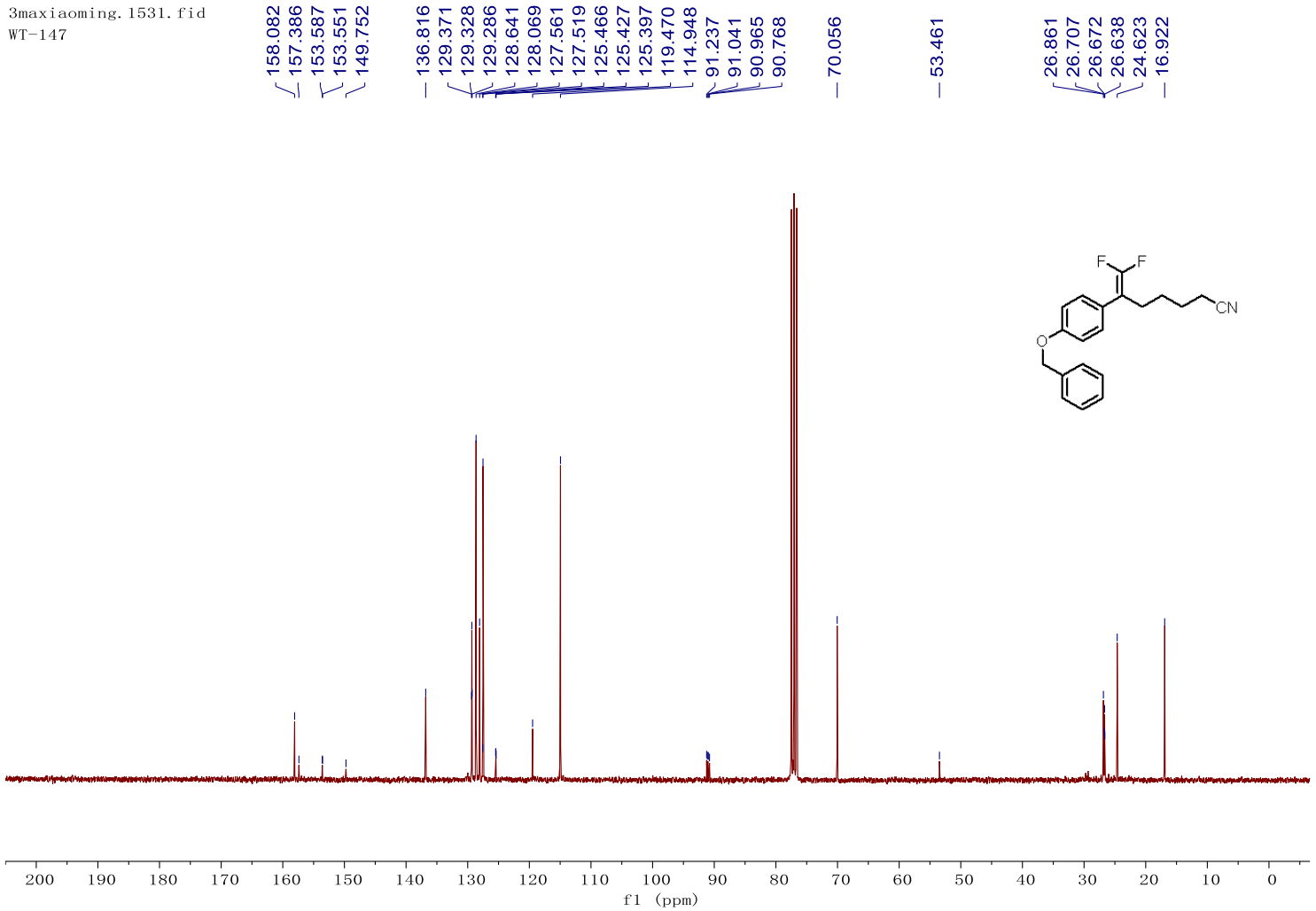
^{13}C NMR Spectrum of Compound 3c (75 MHz, $CDCl_3$)



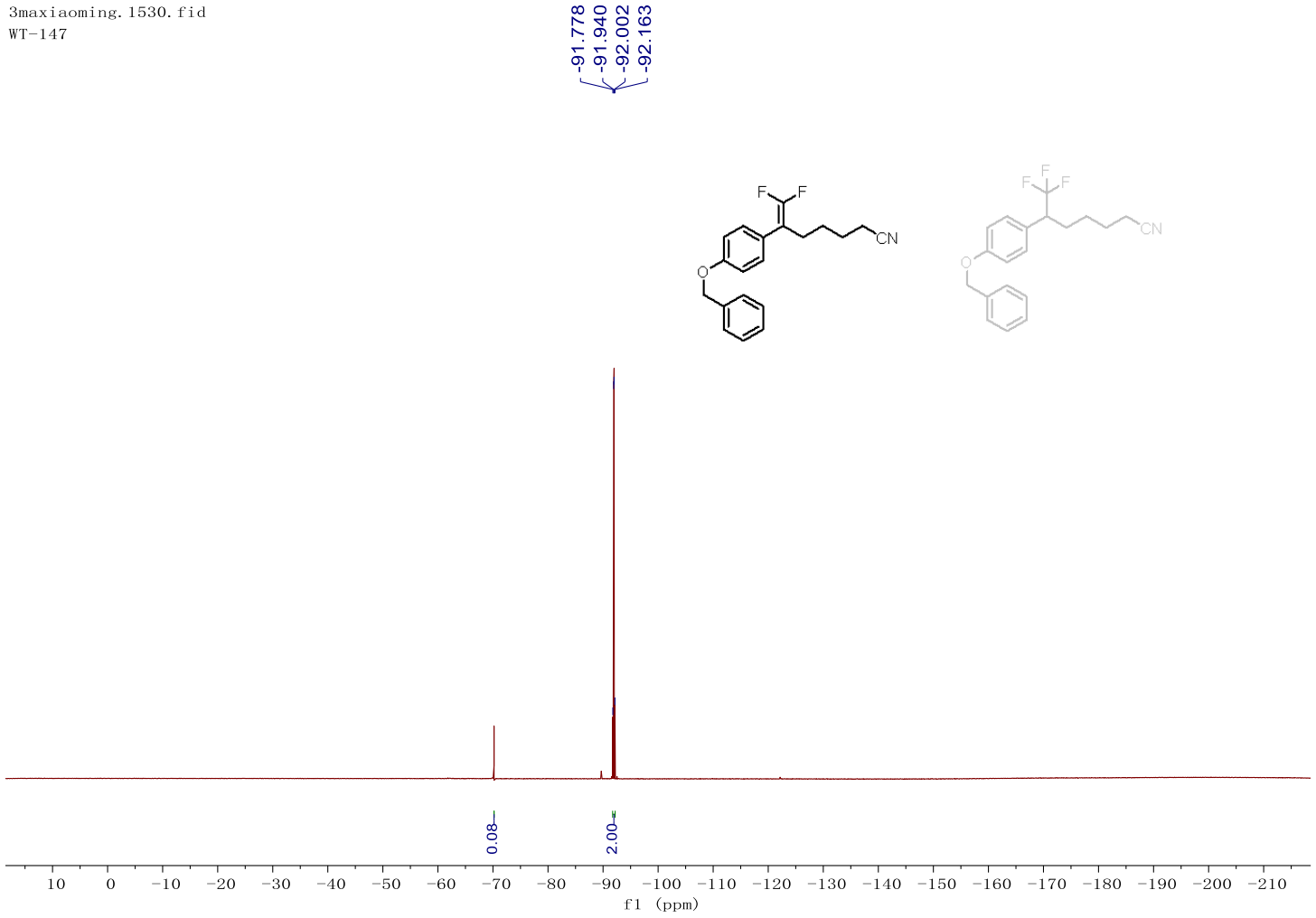
^{19}F NMR Spectrum of Compound 3c (282 MHz, $CDCl_3$)



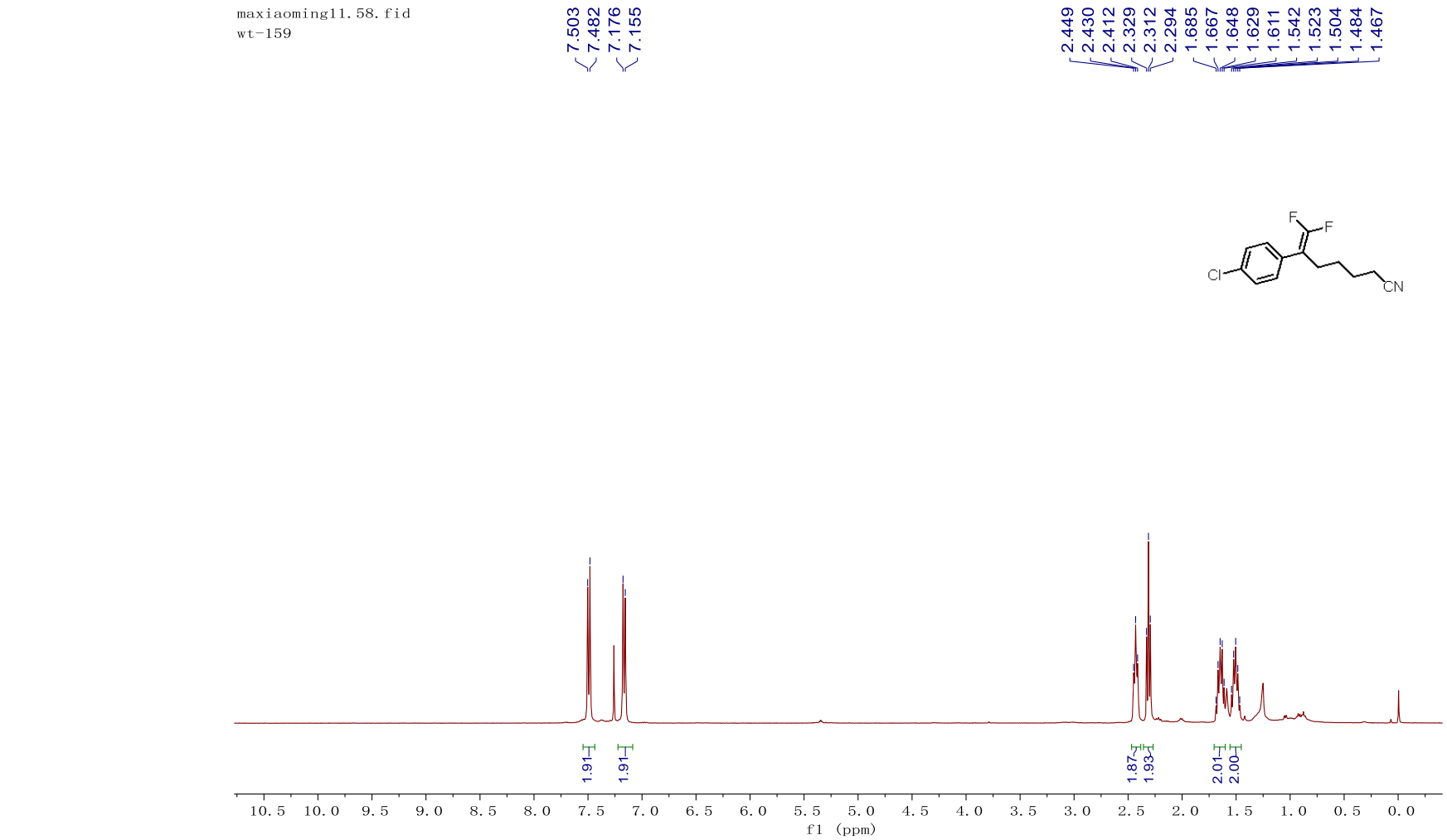
^{1}H NMR Spectrum of Compound 3d (400 MHz, $CDCl_3$)



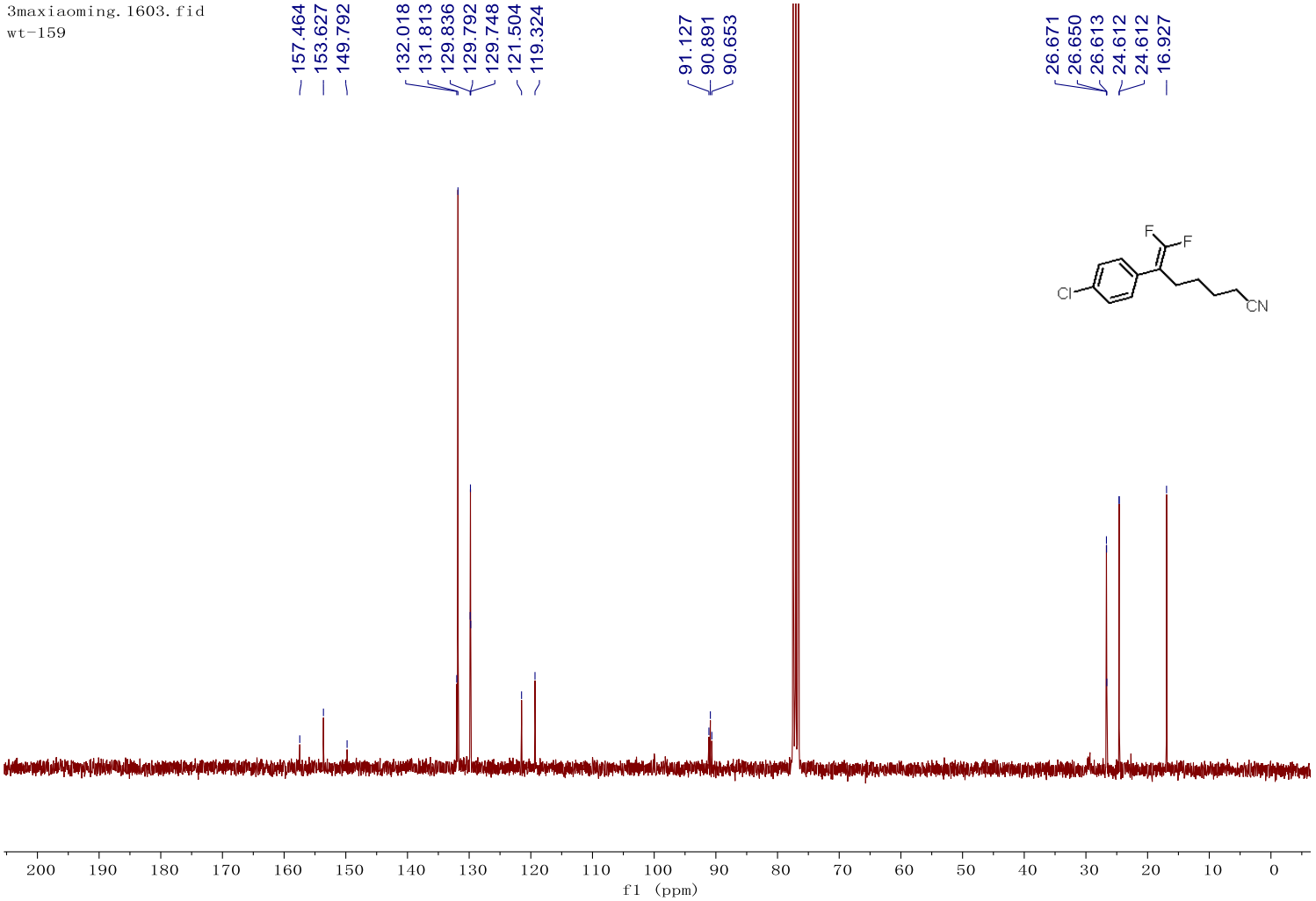
^{13}C NMR Spectrum of Compound 3d (75 MHz, $CDCl_3$)



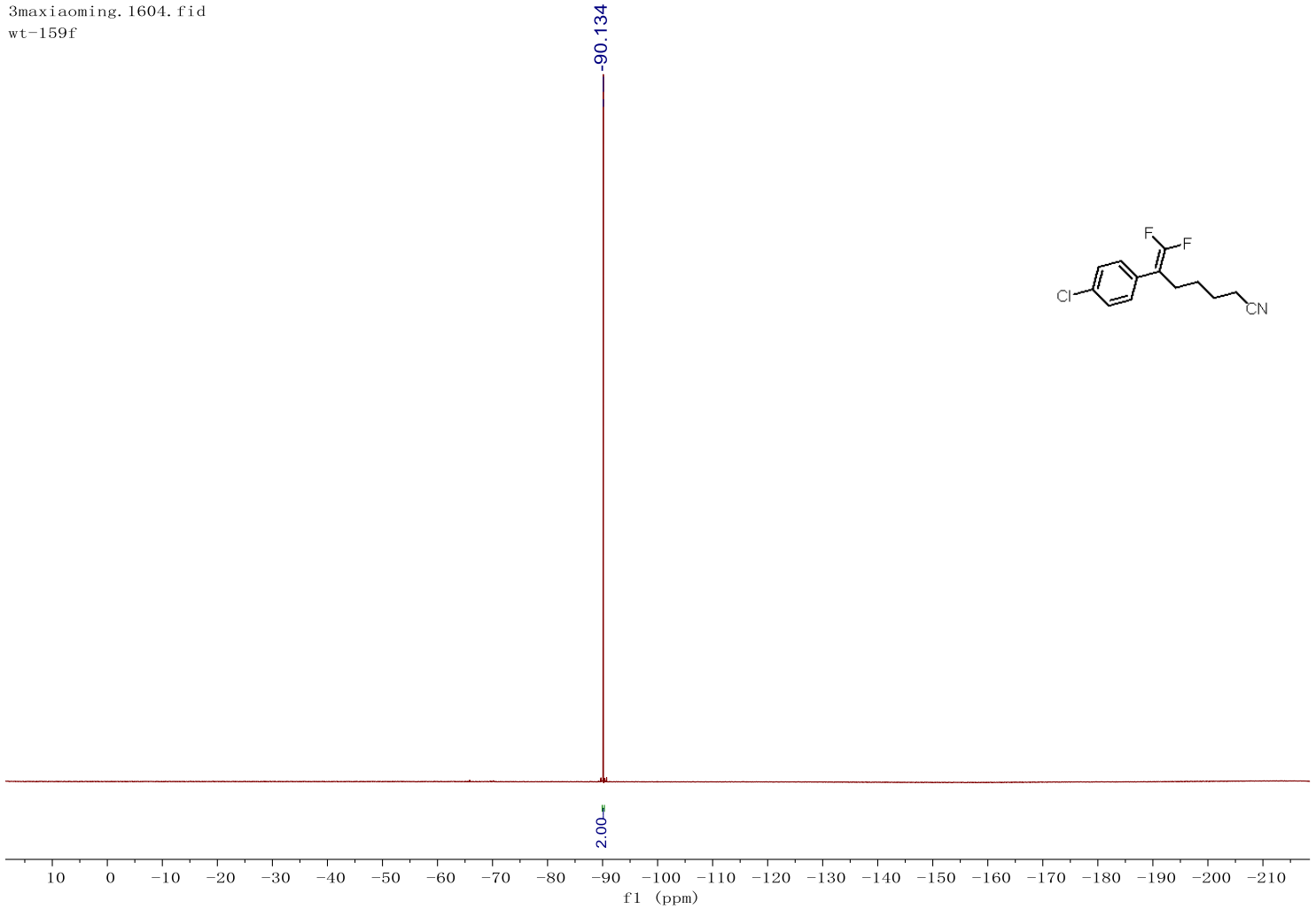
^{19}F NMR Spectrum of Compound 3d (282 MHz, $CDCl_3$)



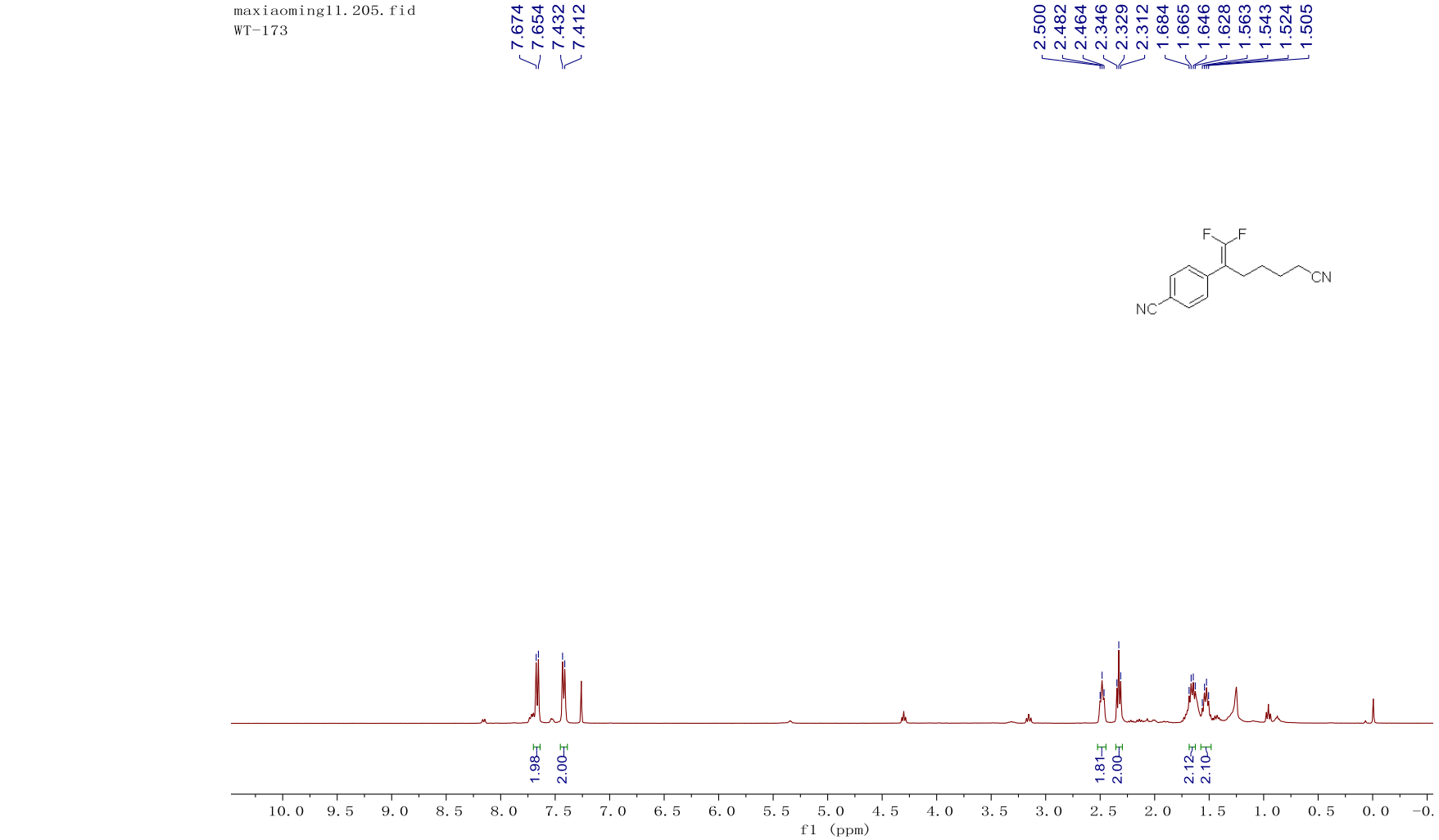
^{1}H NMR Spectrum of Compound 3e (400 MHz, $CDCl_3$)



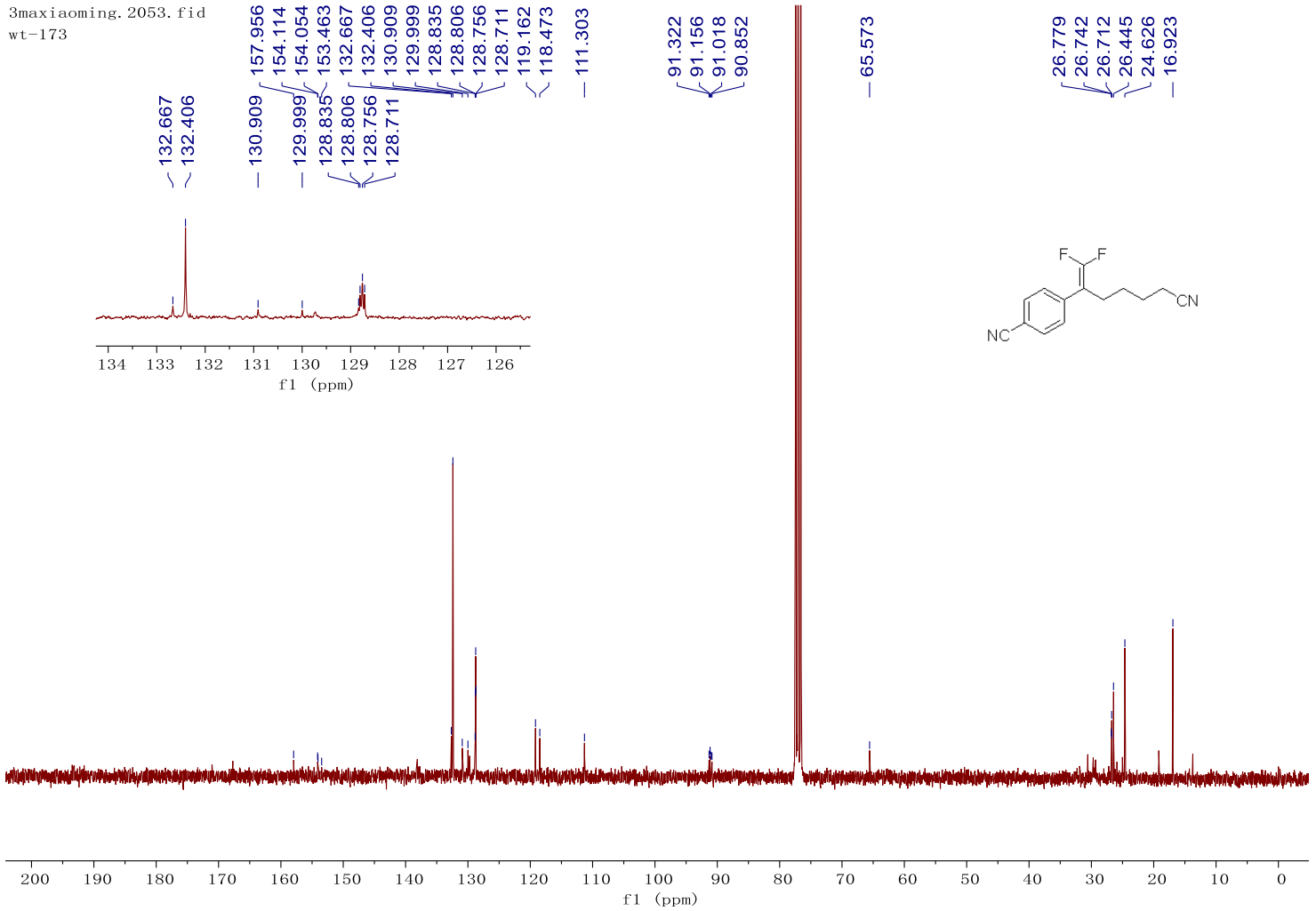
^{13}C NMR Spectrum of Compound 3e (75 MHz, $CDCl_3$)



^{19}F NMR Spectrum of Compound 3e (282 MHz, $CDCl_3$)



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



^{13}C NMR Spectrum of Compound 3f (75 MHz, $CDCl_3$)

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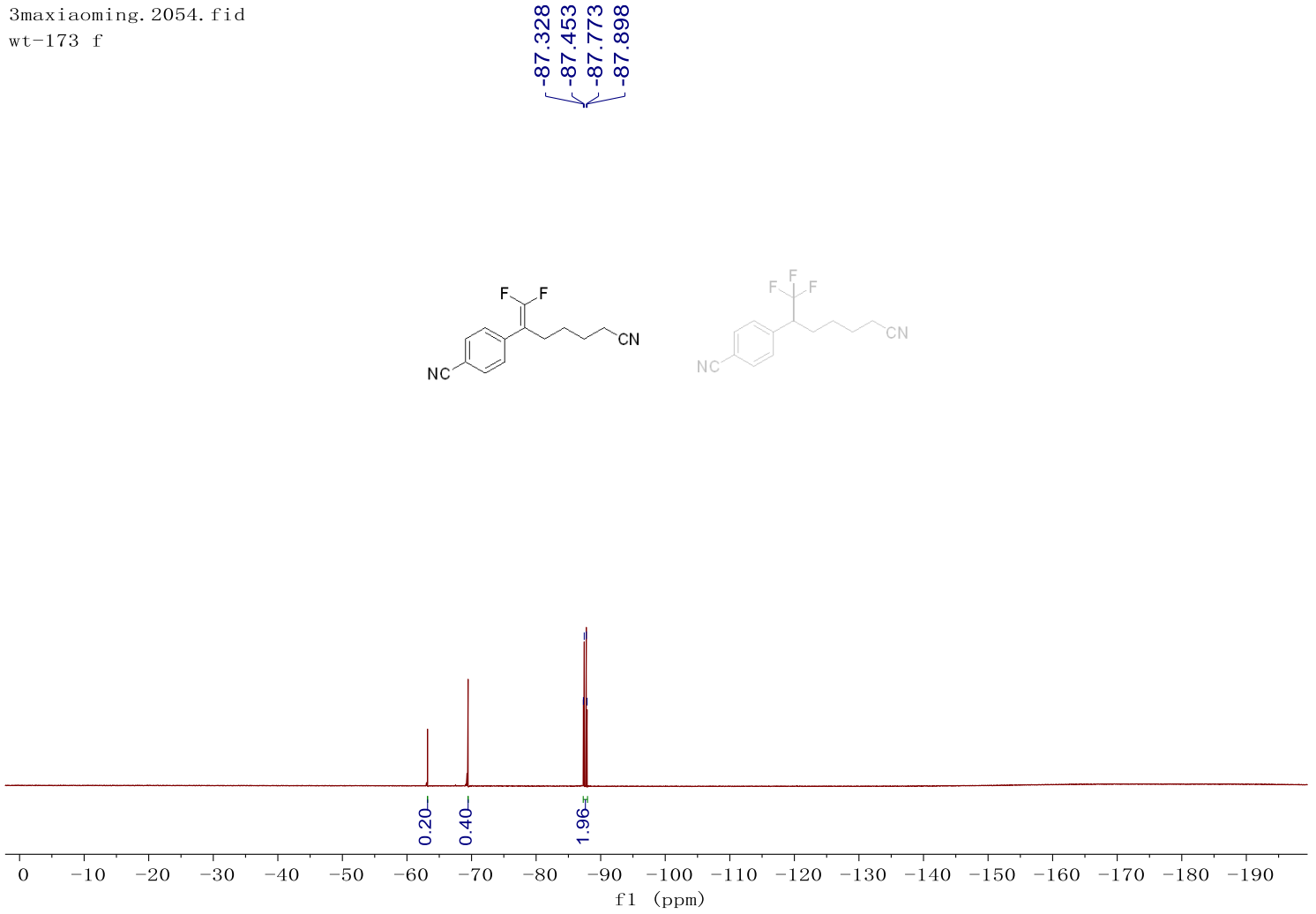
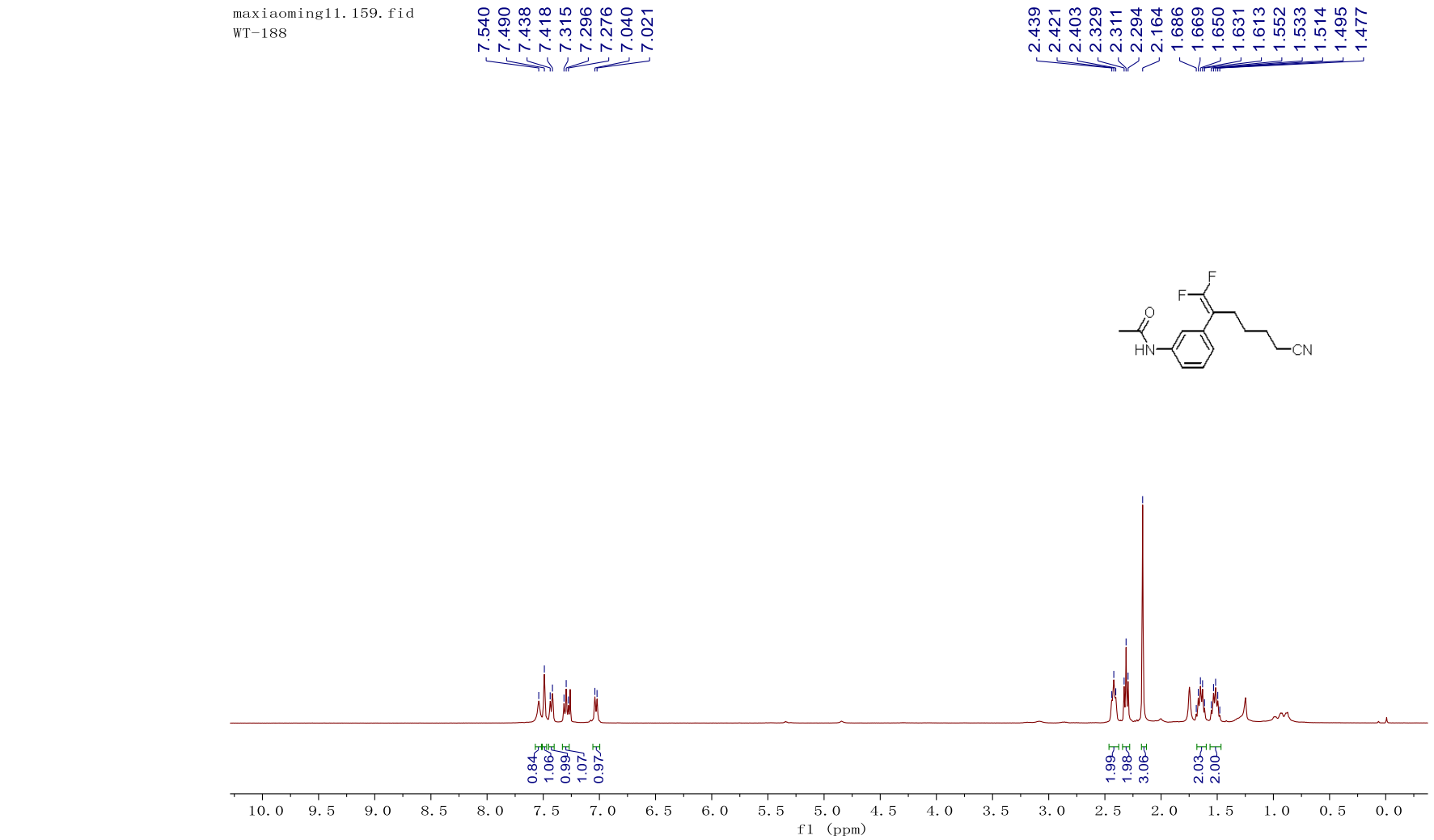
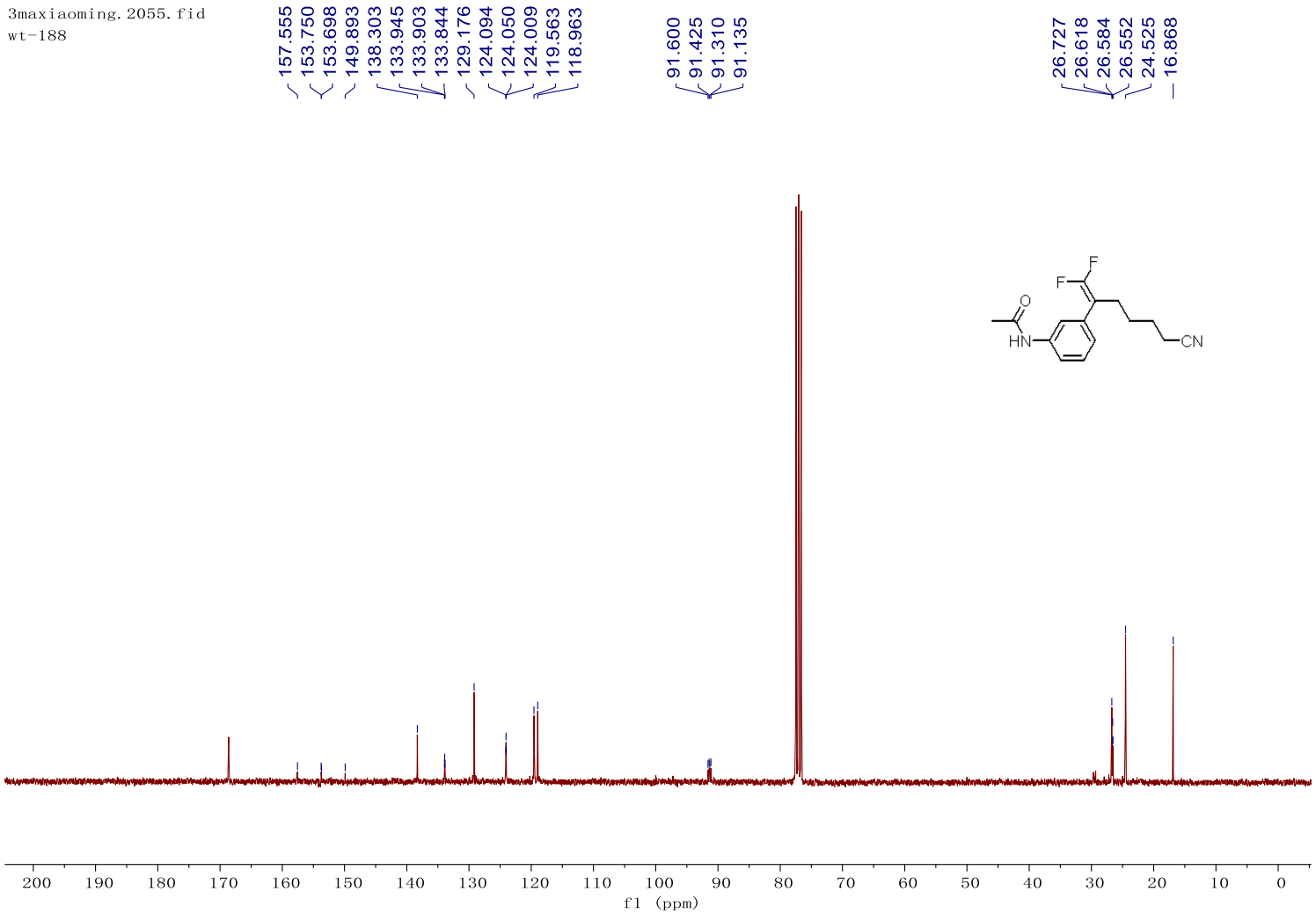
wt-173 f



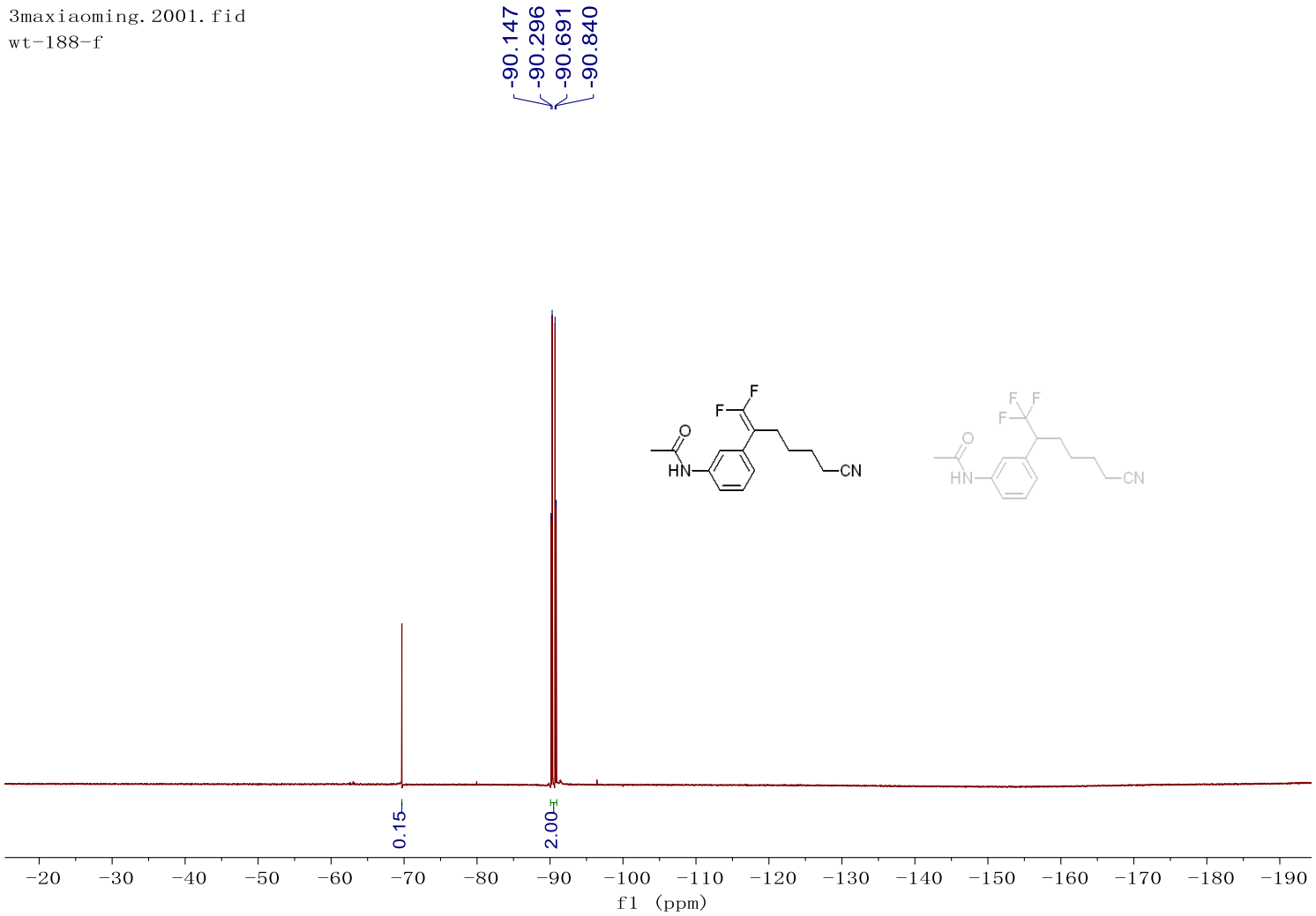
^{19}F NMR Spectrum of Compound 3f (282 MHz, $CDCl_3$)



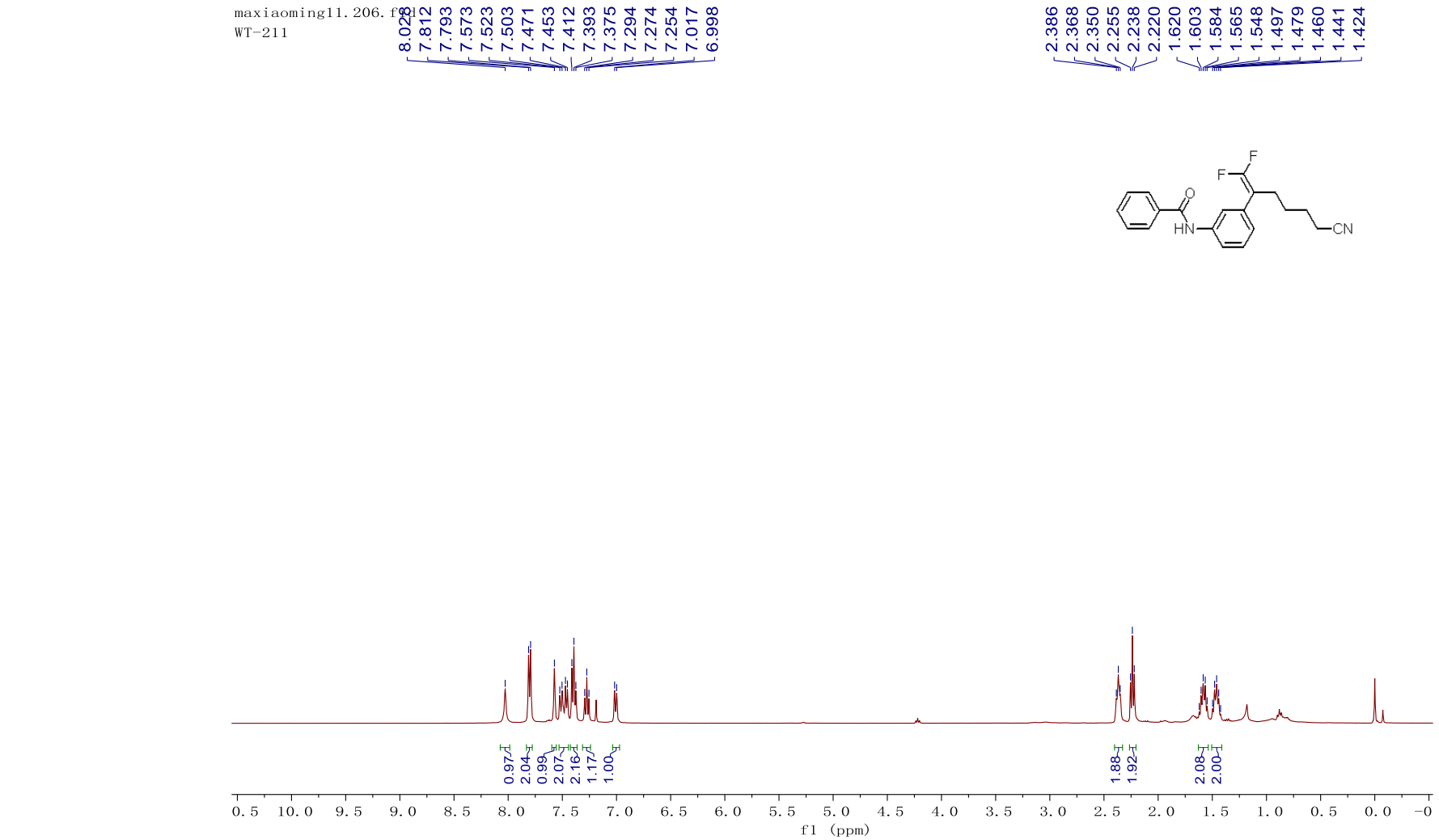
^{1}H NMR Spectrum of Compound 3g (400 MHz, $CDCl_3$)



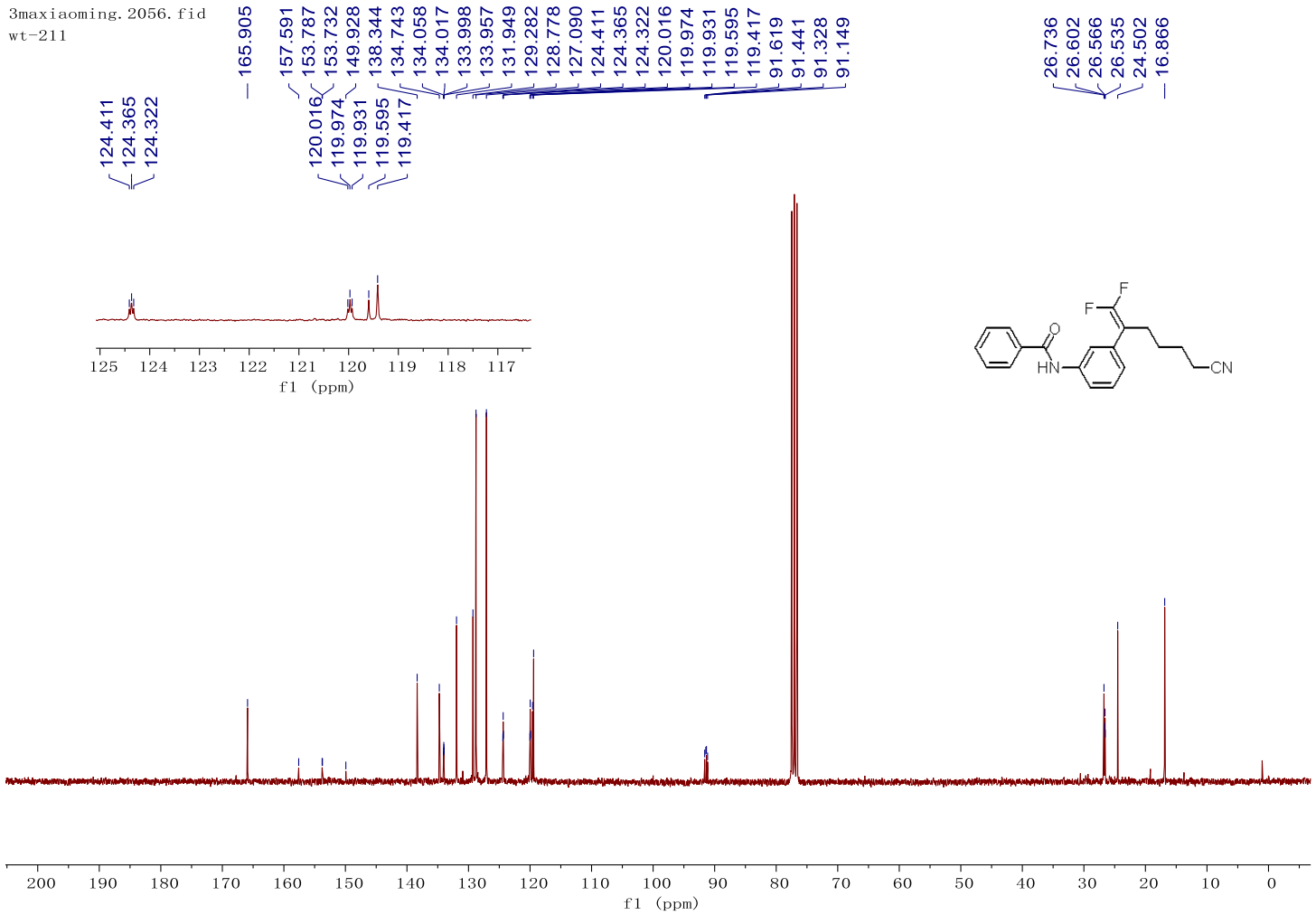
^{13}C NMR Spectrum of Compound 3g (75 MHz, $CDCl_3$)



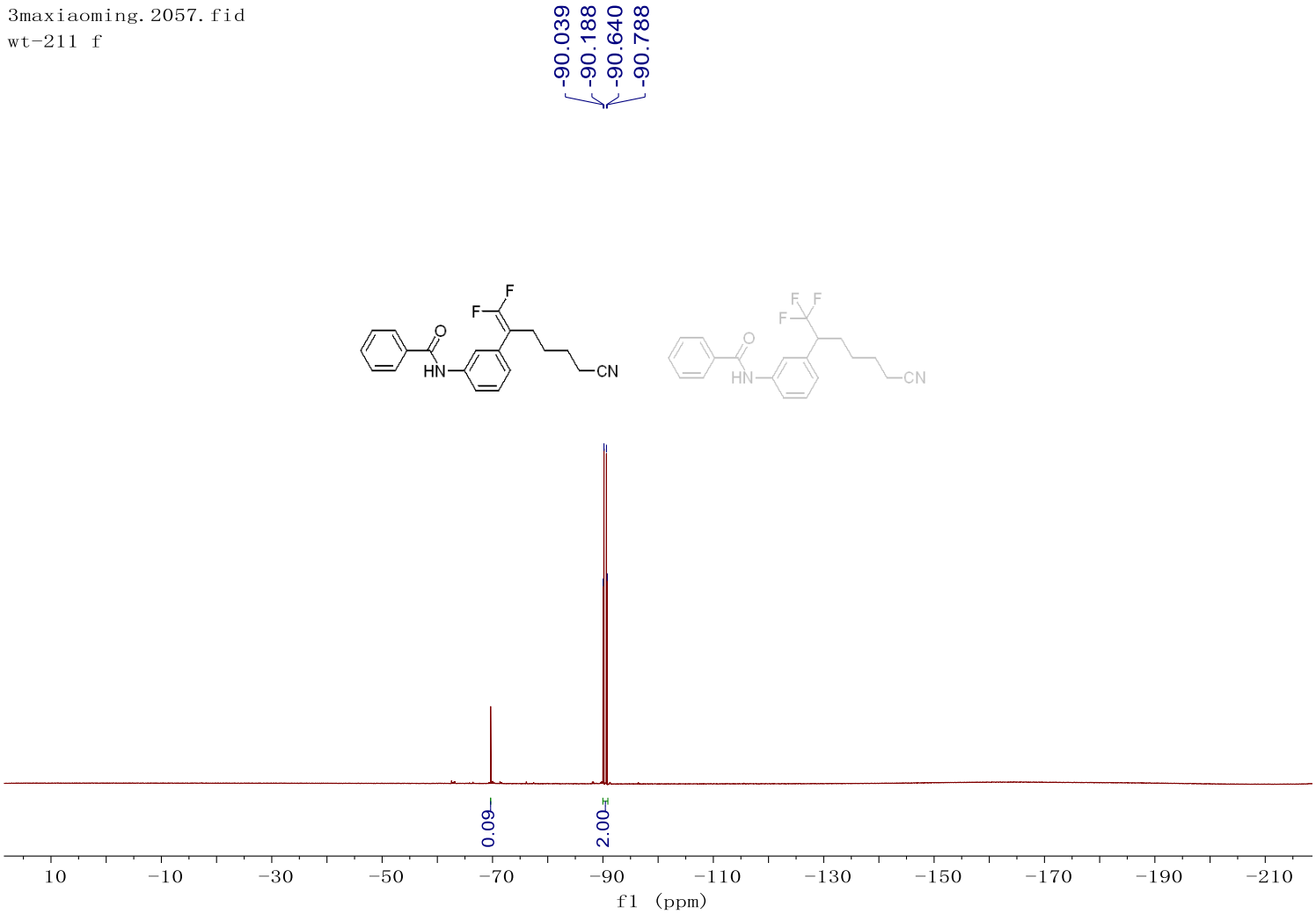
^{19}F NMR Spectrum of Compound 3g (282 MHz, $CDCl_3$)



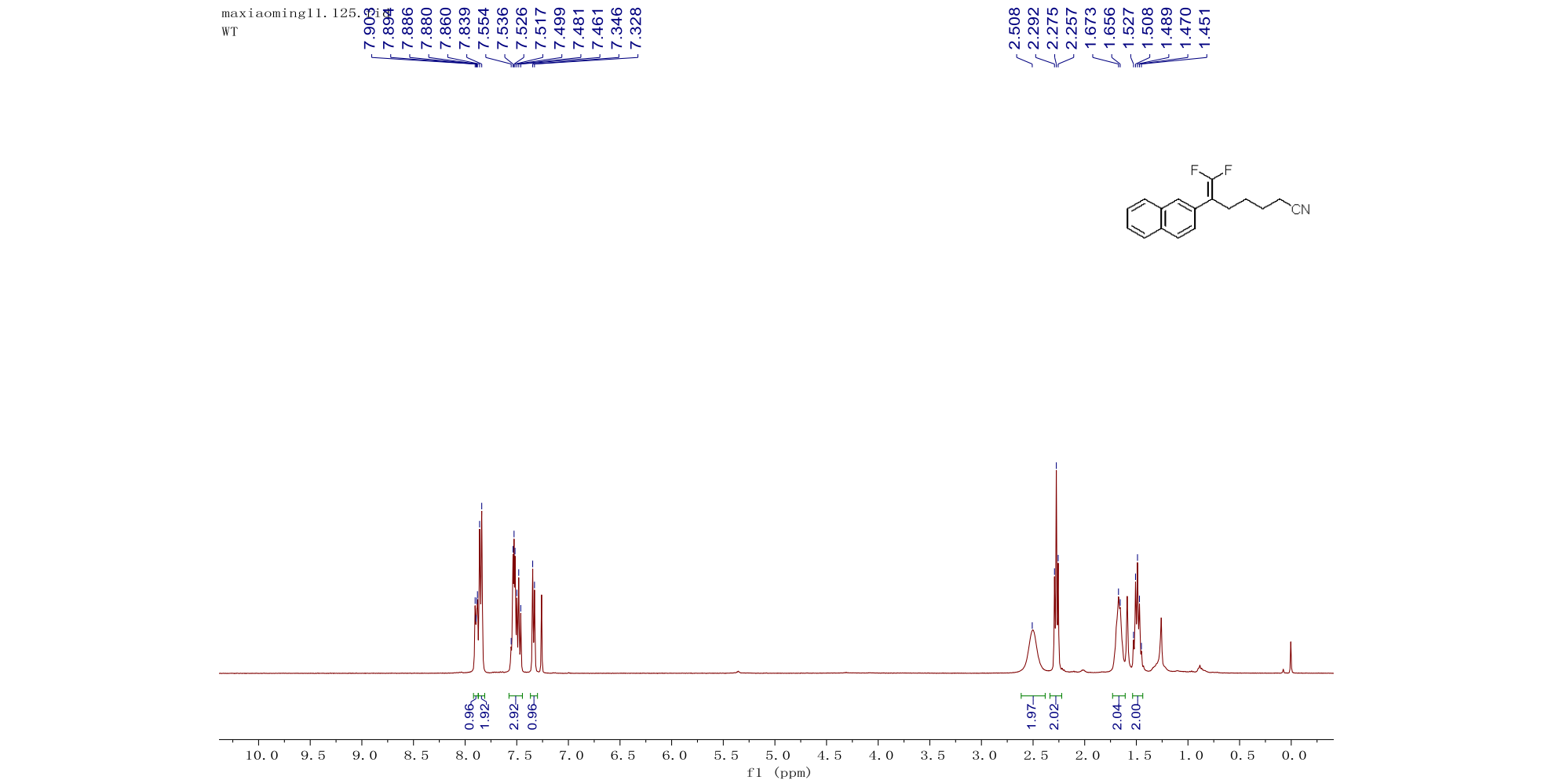
^{1}H NMR Spectrum of Compound 3h (400 MHz, $CDCl_3$)



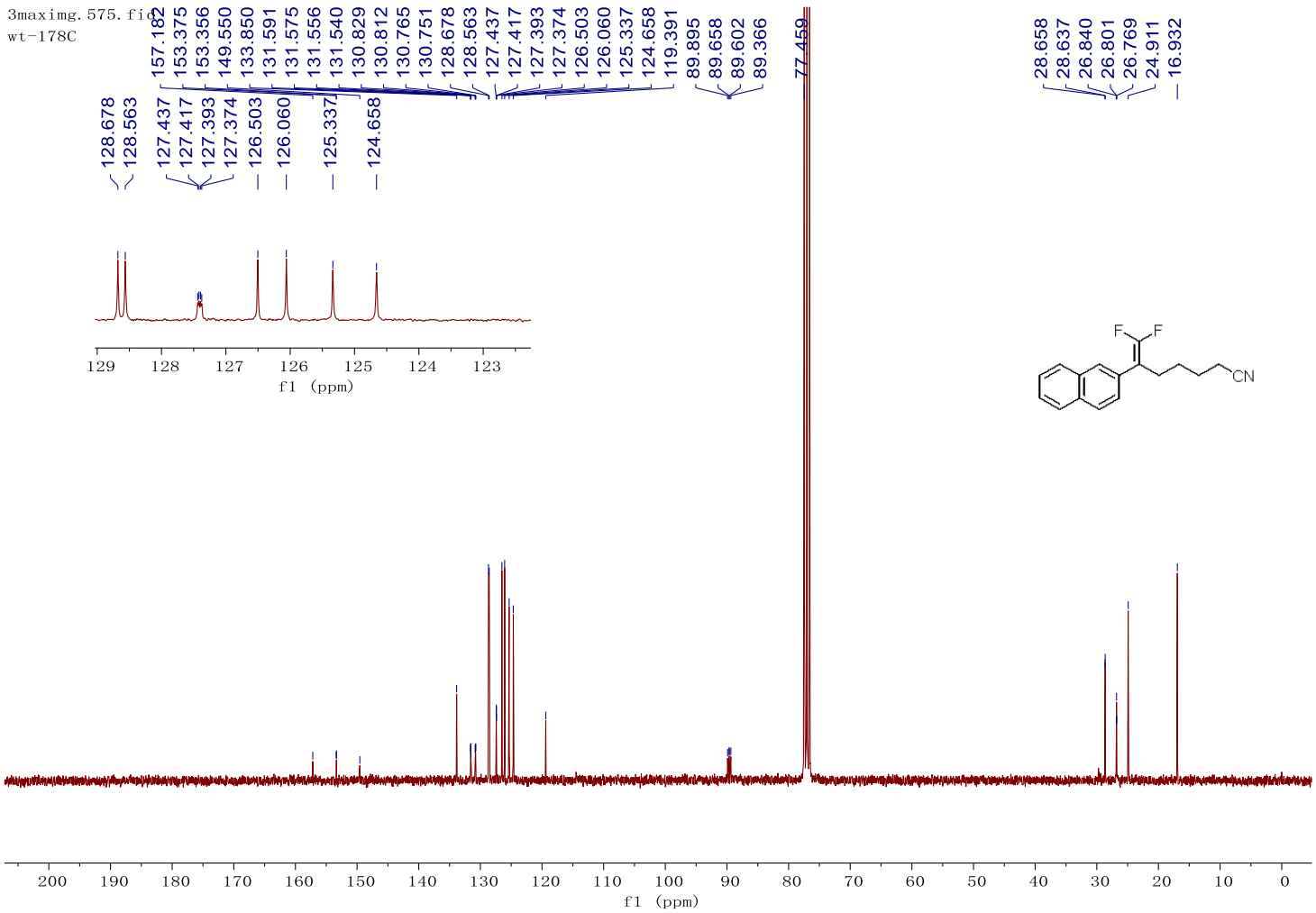
^{13}C NMR Spectrum of Compound 3h (75 MHz, $CDCl_3$)



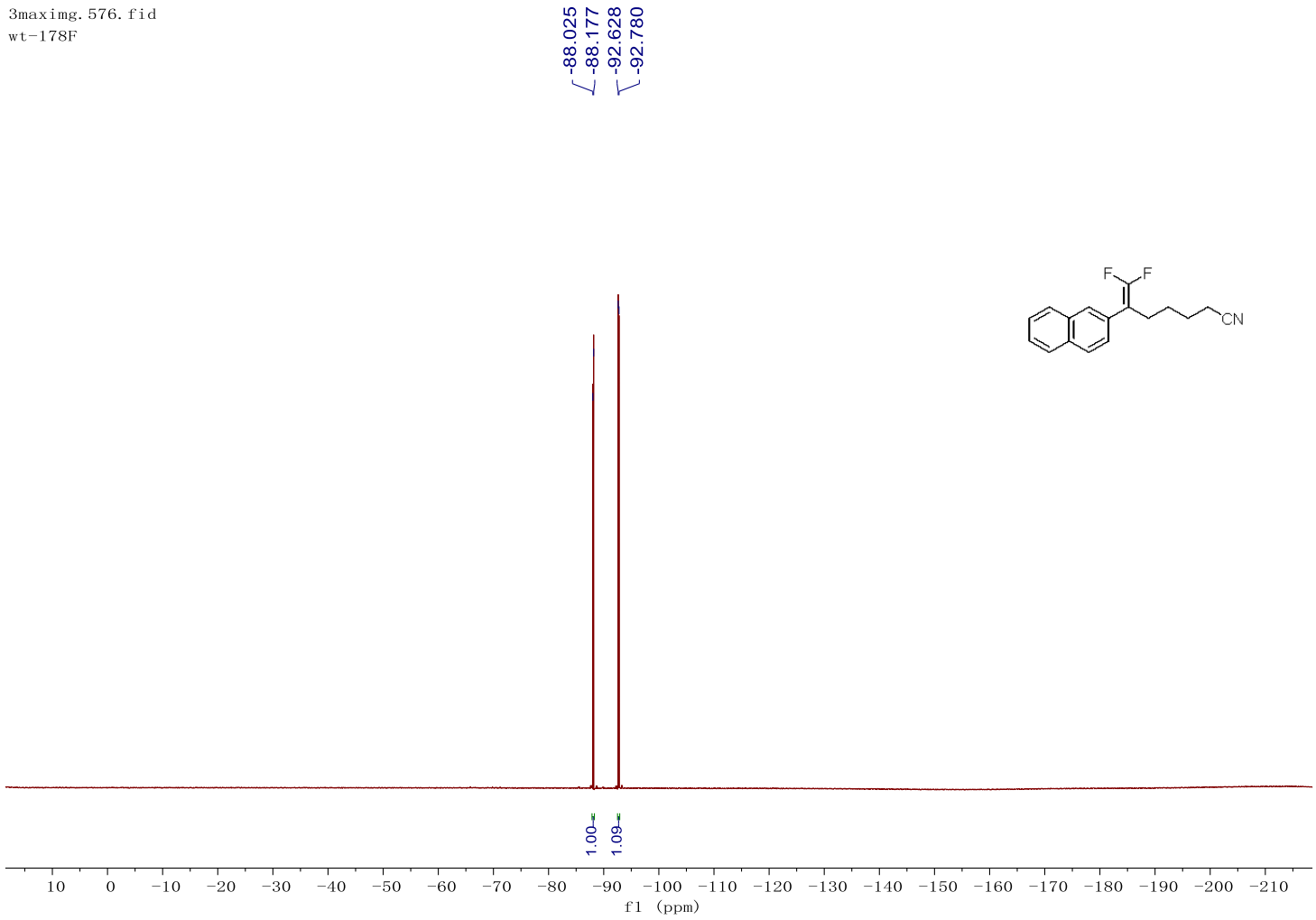
^{19}F NMR Spectrum of Compound 3h (282 MHz, $CDCl_3$)



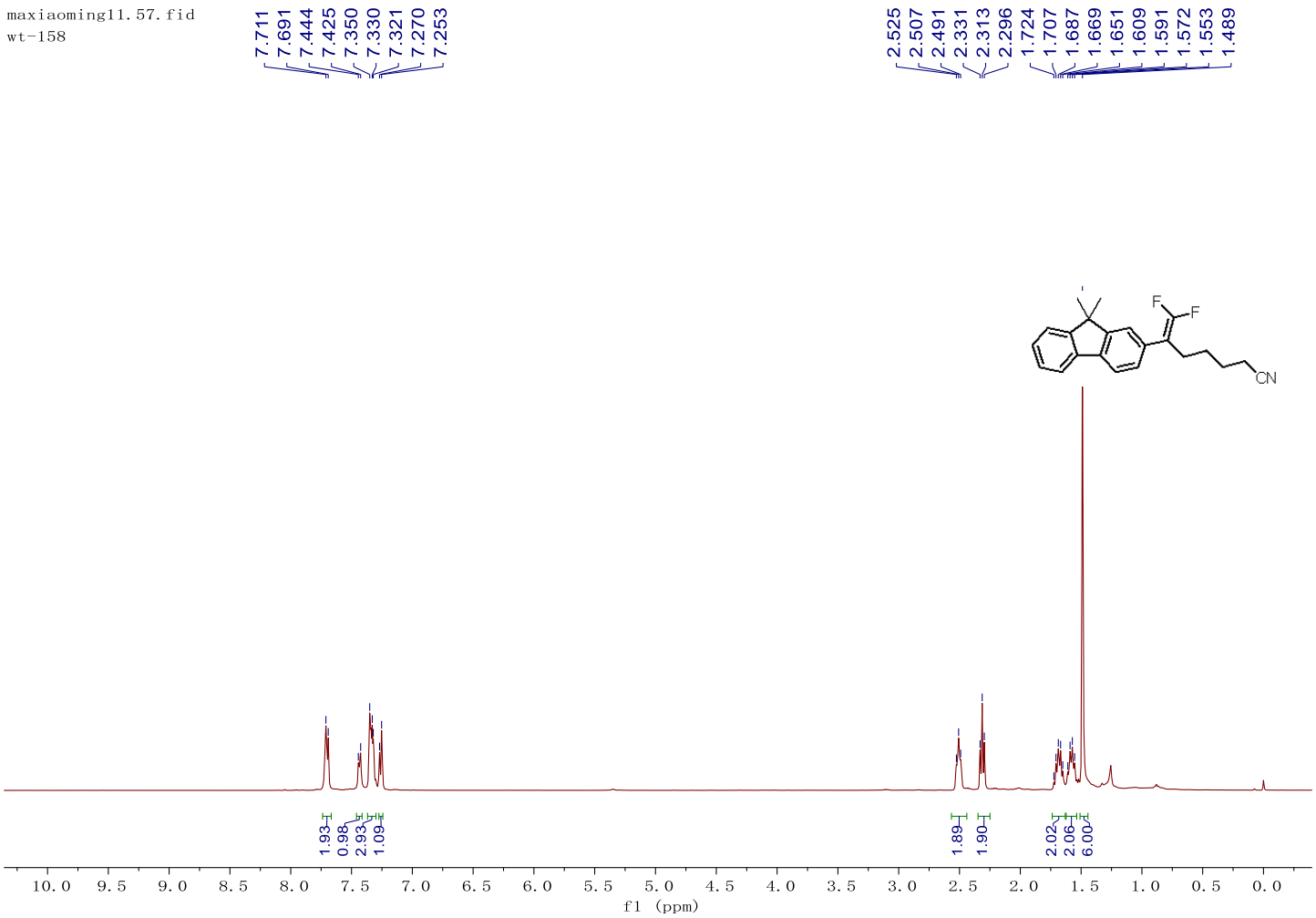
^{1}H NMR Spectrum of Compound 3i (400 MHz, $CDCl_3$)



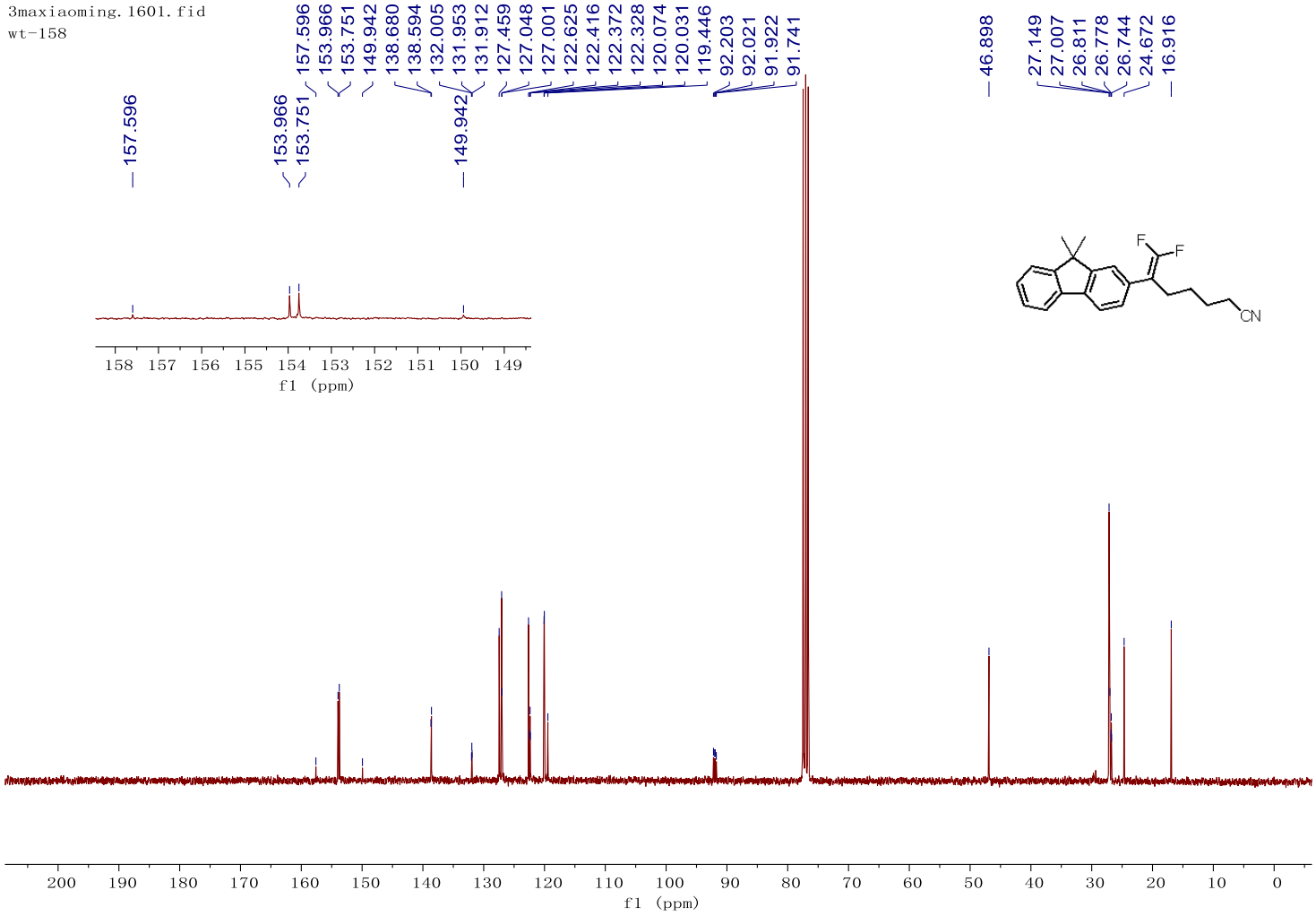
^{13}C NMR Spectrum of Compound 3i (75 MHz, $CDCl_3$)



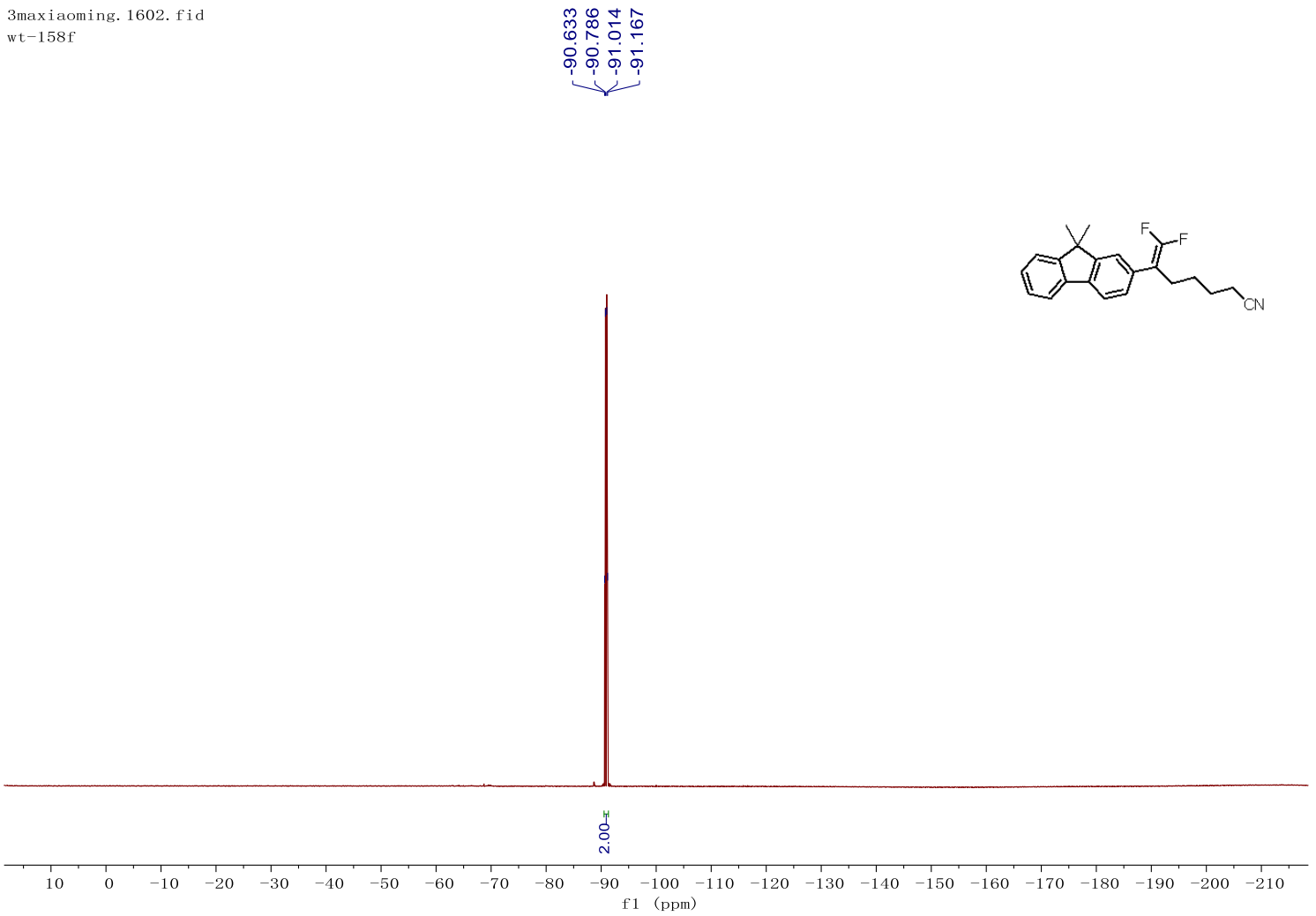
^{19}F NMR Spectrum of Compound 3i (282 MHz, $CDCl_3$)



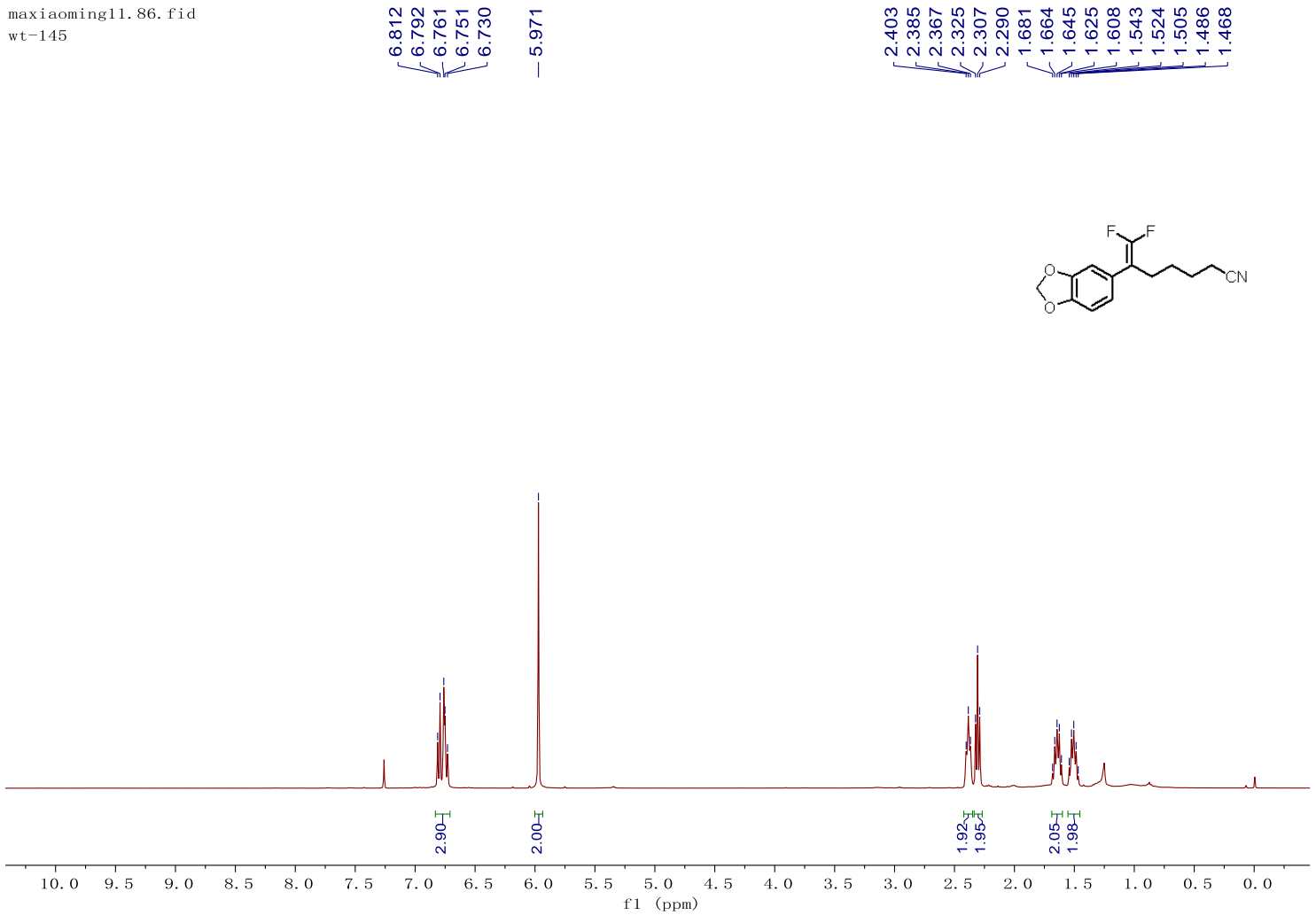
^{1}H NMR Spectrum of Compound 3j (400 MHz, $CDCl_3$)



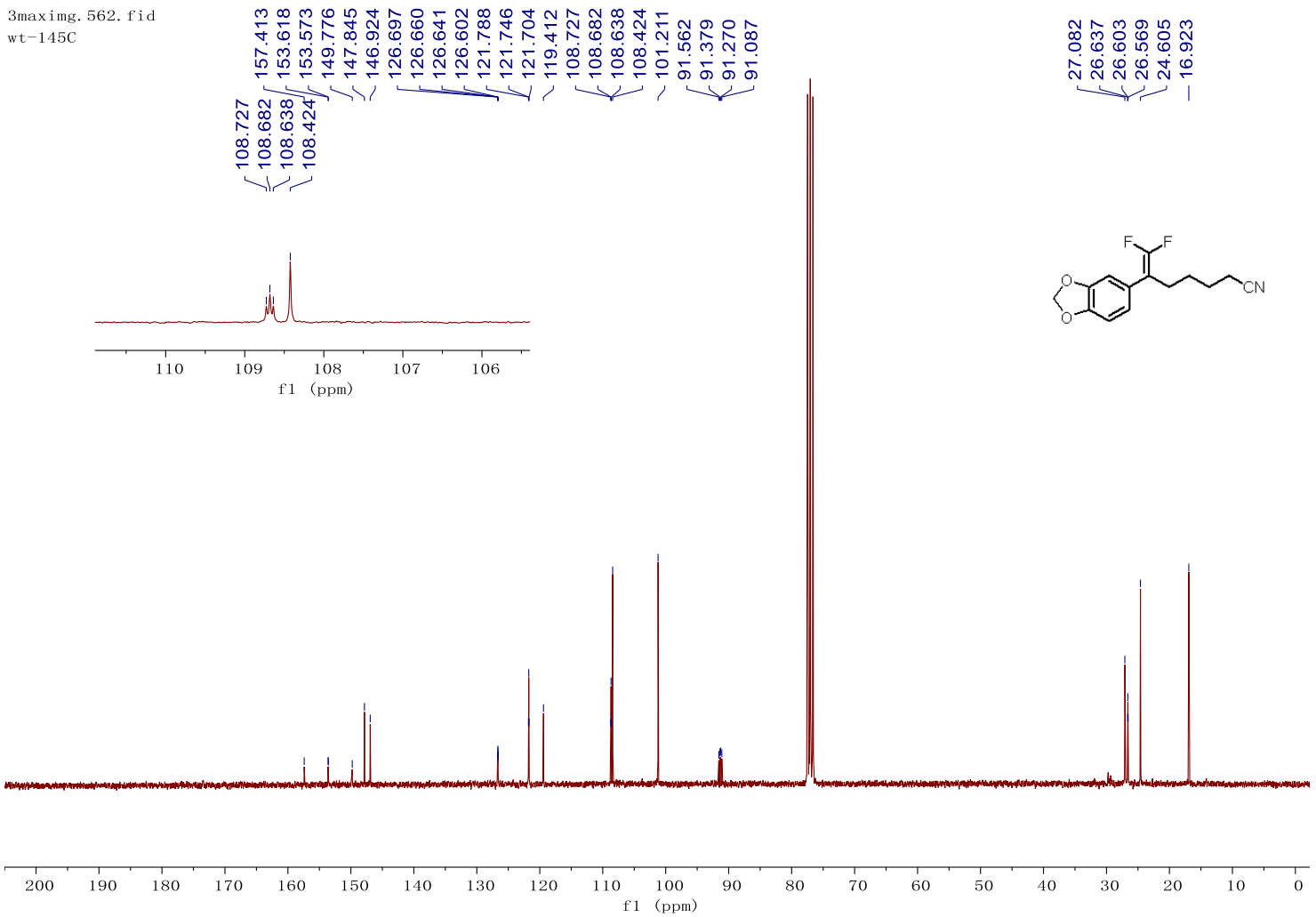
^{13}C NMR Spectrum of Compound 3j (75 MHz, $CDCl_3$)



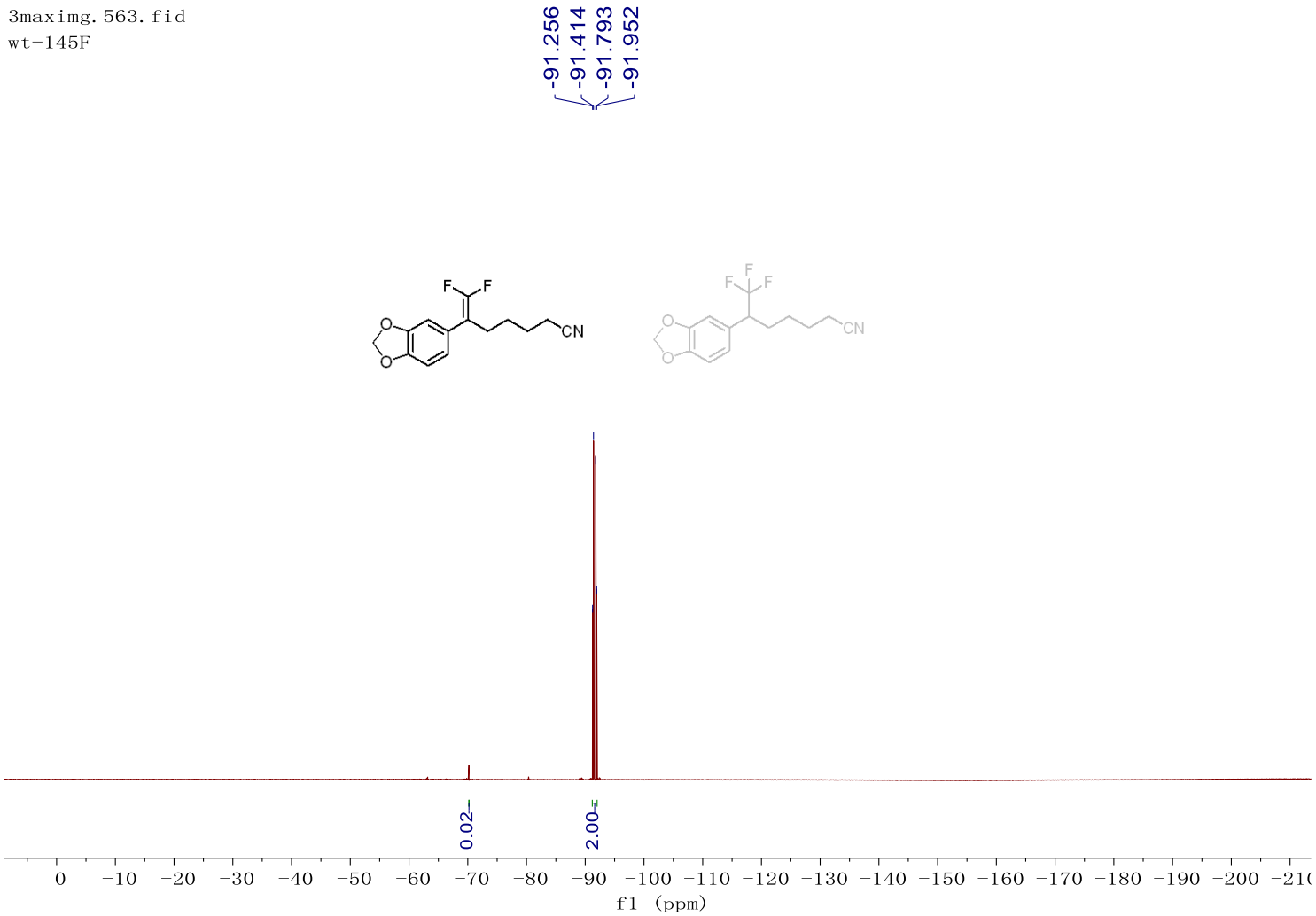
^{19}F NMR Spectrum of Compound 3j (282 MHz, $CDCl_3$)



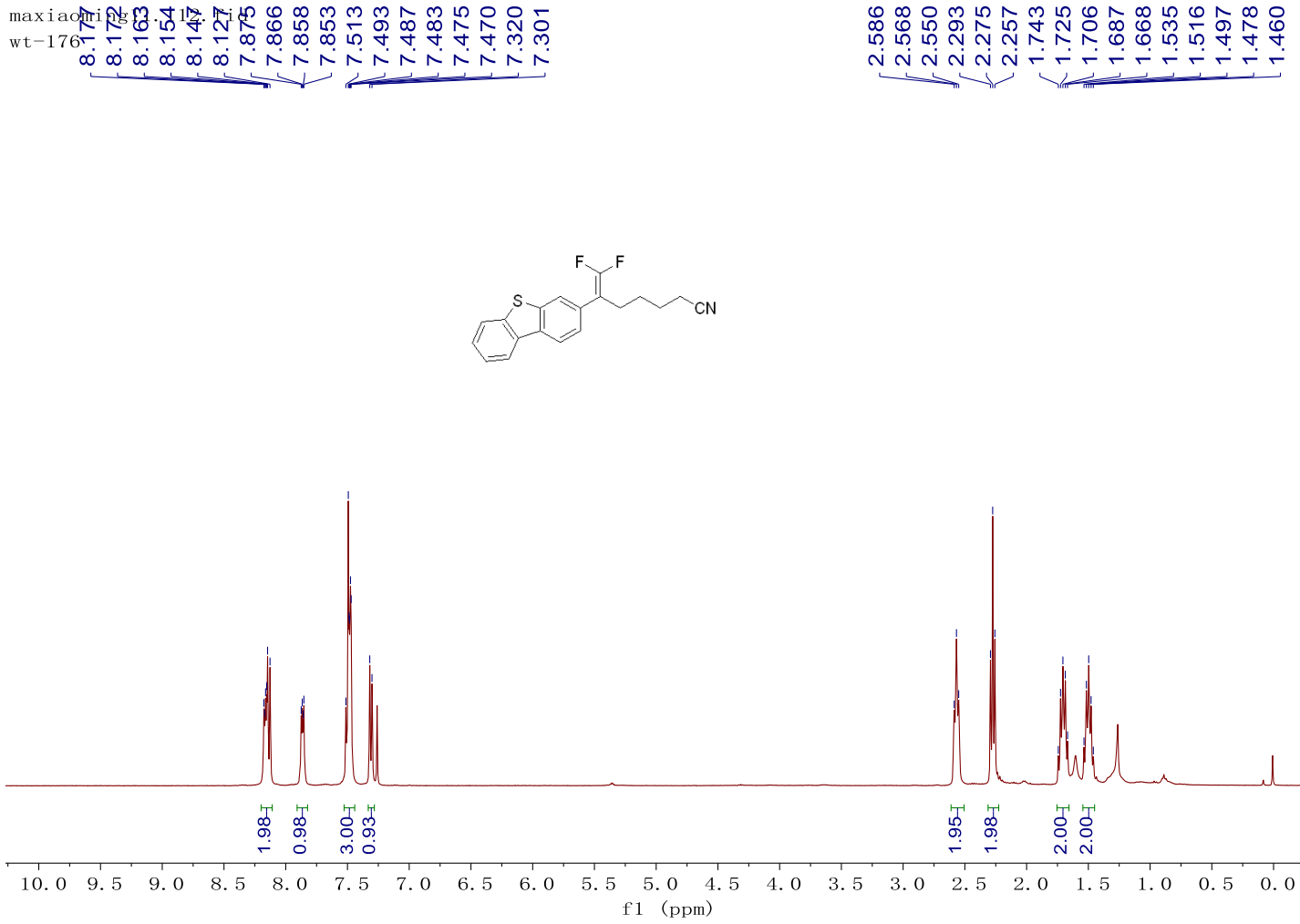
^{1}H NMR Spectrum of Compound 3k (400 MHz, $CDCl_3$)



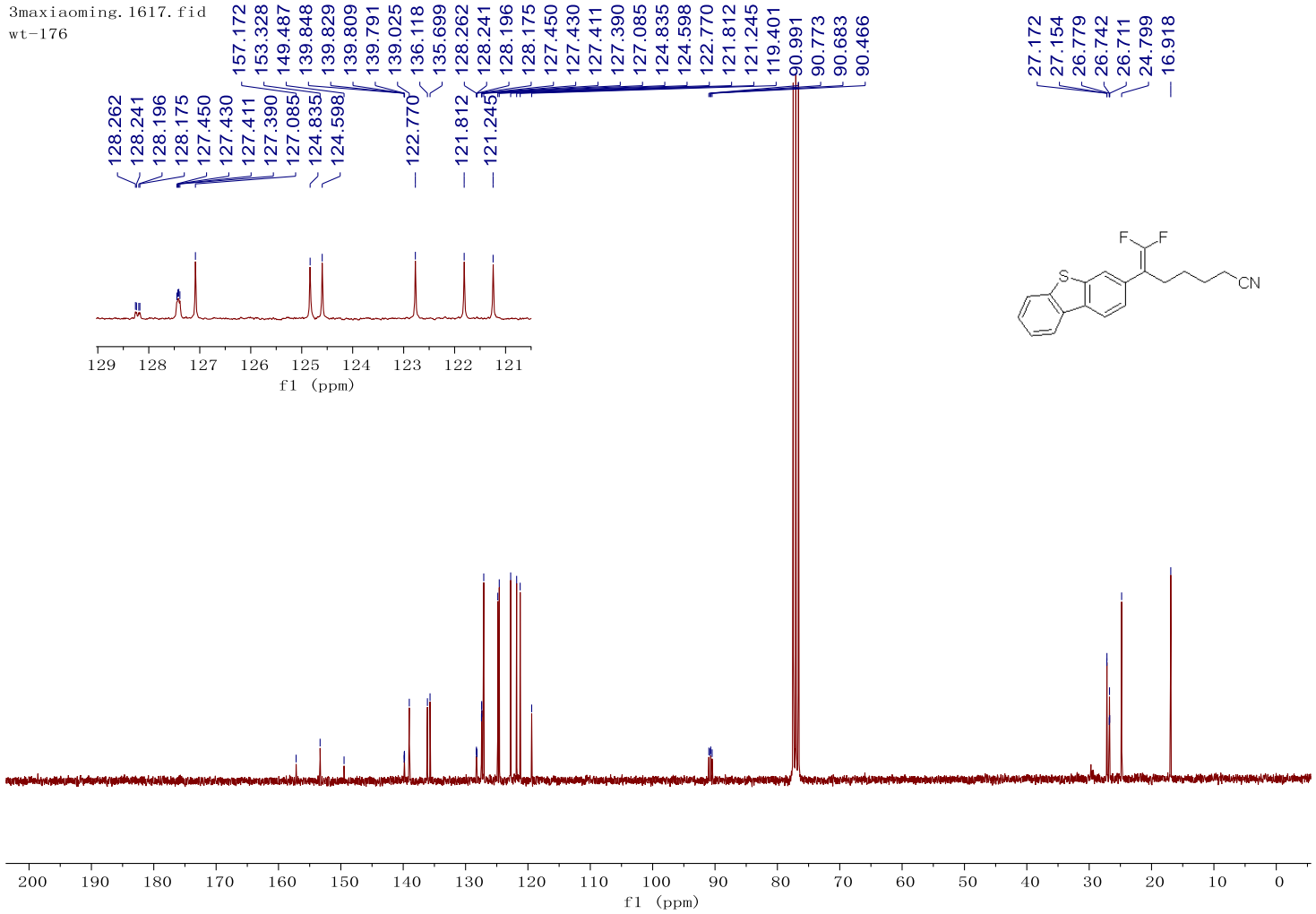
^{13}C NMR Spectrum of Compound 3k (75MHz, $CDCl_3$)



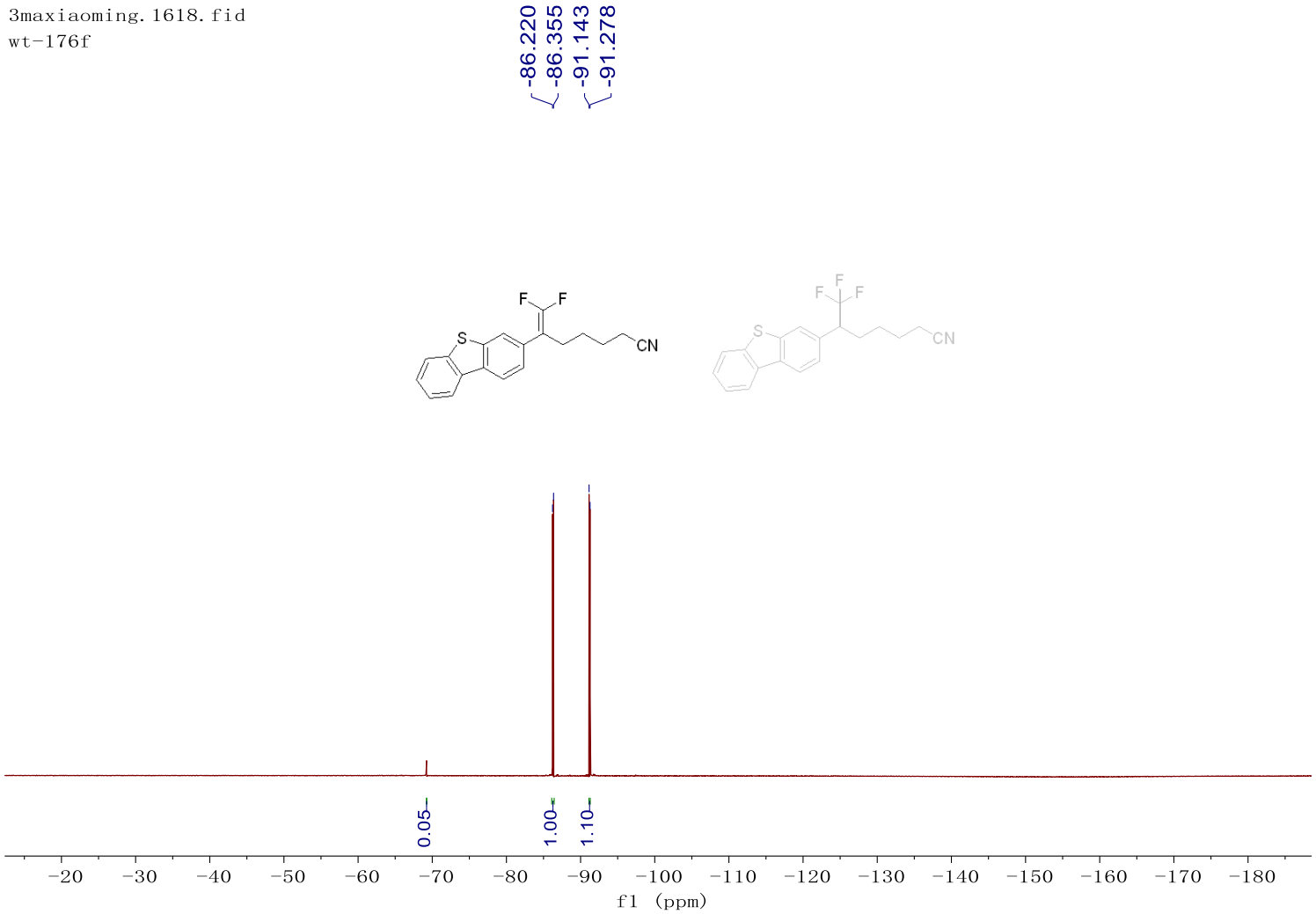
^{19}F NMR Spectrum of Compound 3k (282 MHz, $CDCl_3$)



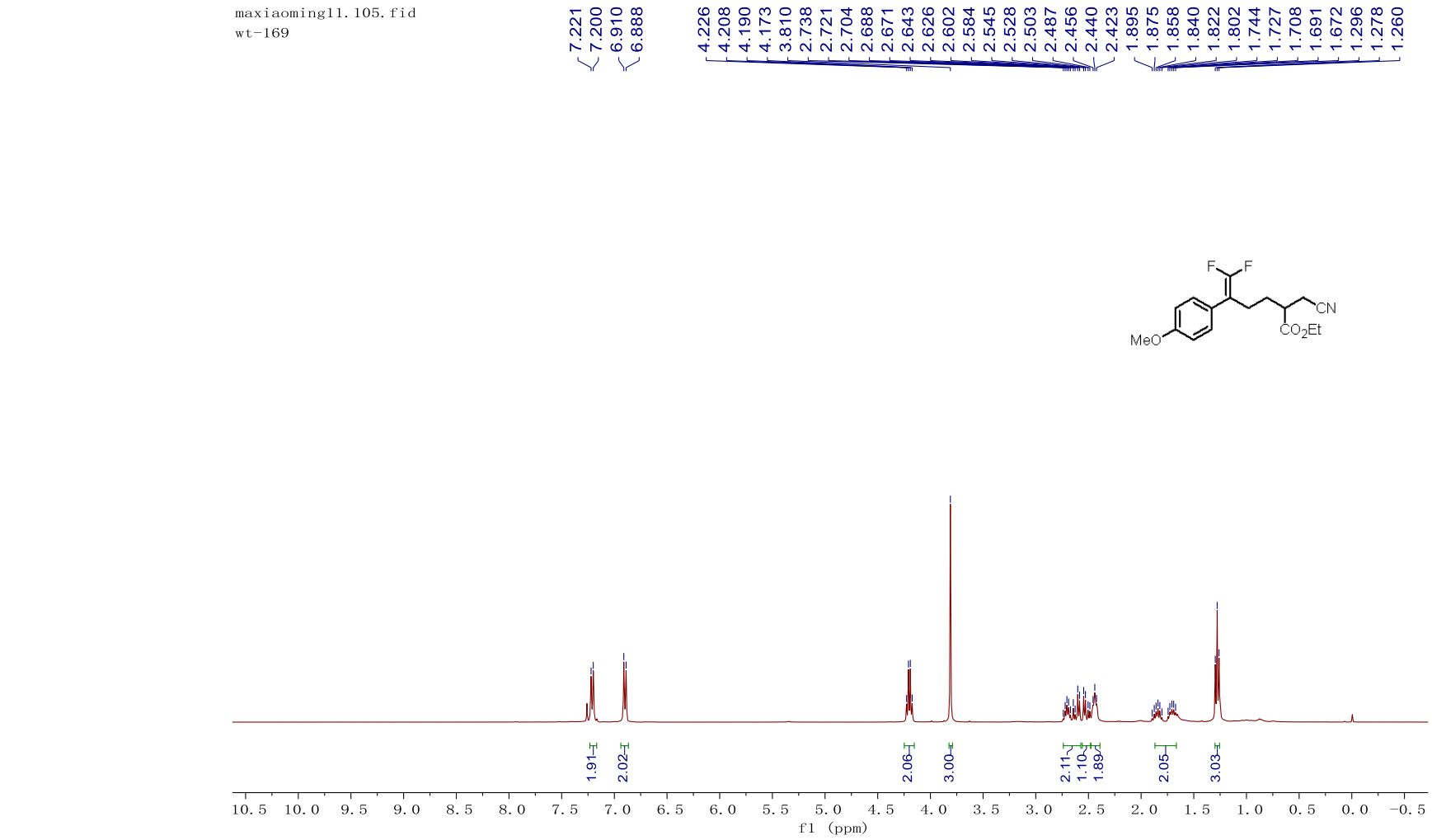
^{1}H NMR Spectrum of Compound 3l (400 MHz, $CDCl_3$)



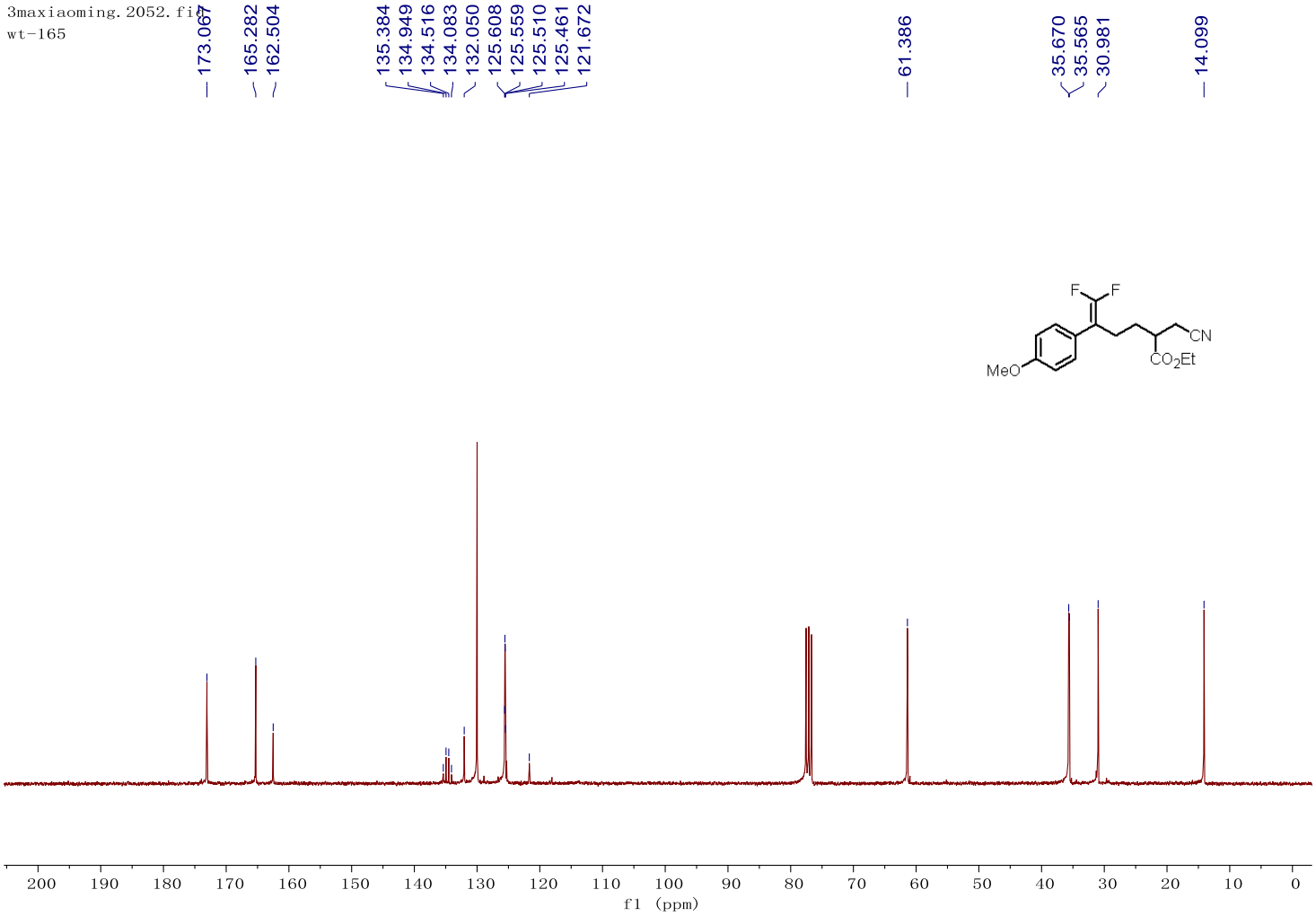
^{13}C NMR Spectrum of Compound 3l (75 MHz, $CDCl_3$)



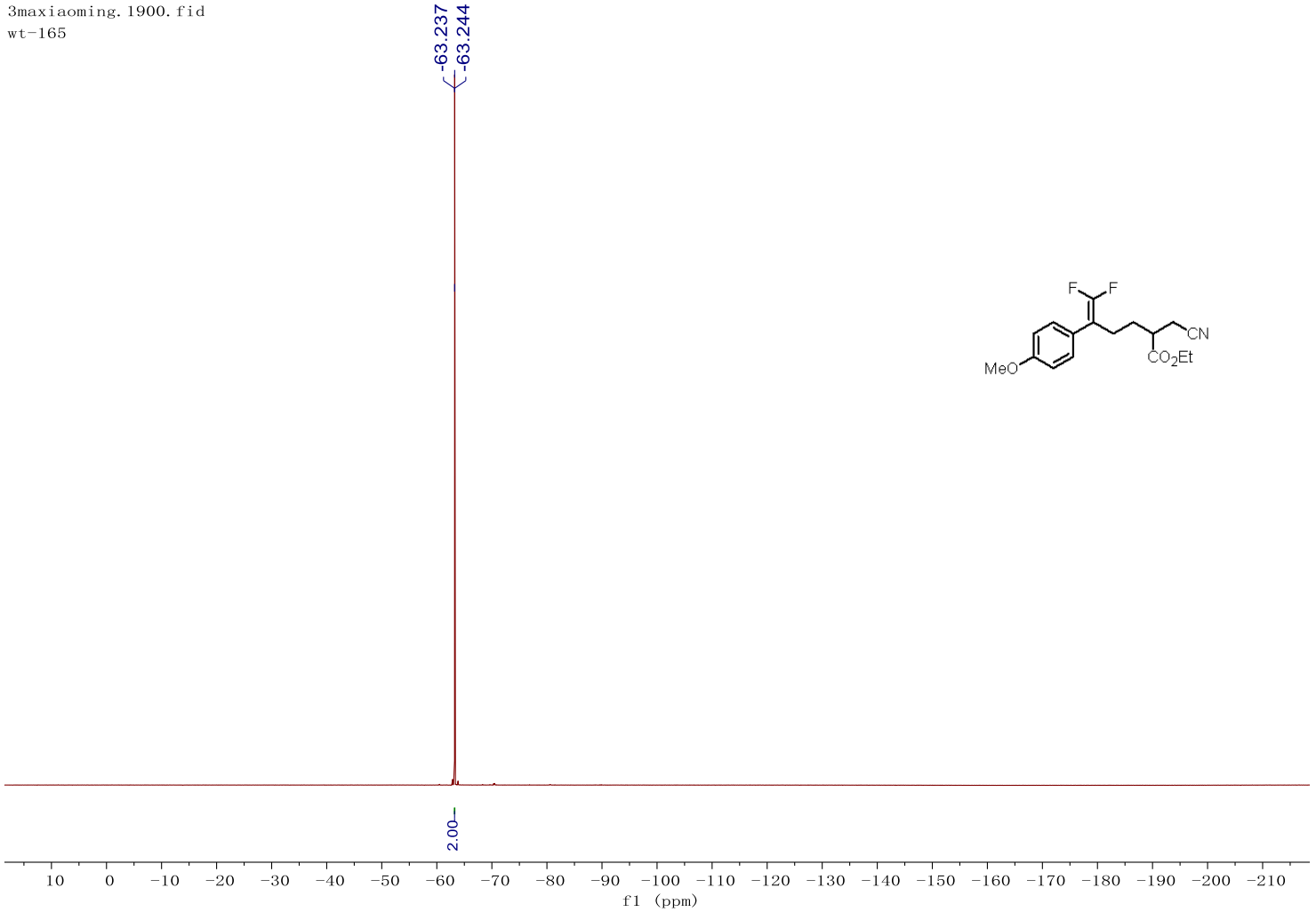
^{19}F NMR Spectrum of Compound 3l (282 MHz, $CDCl_3$)



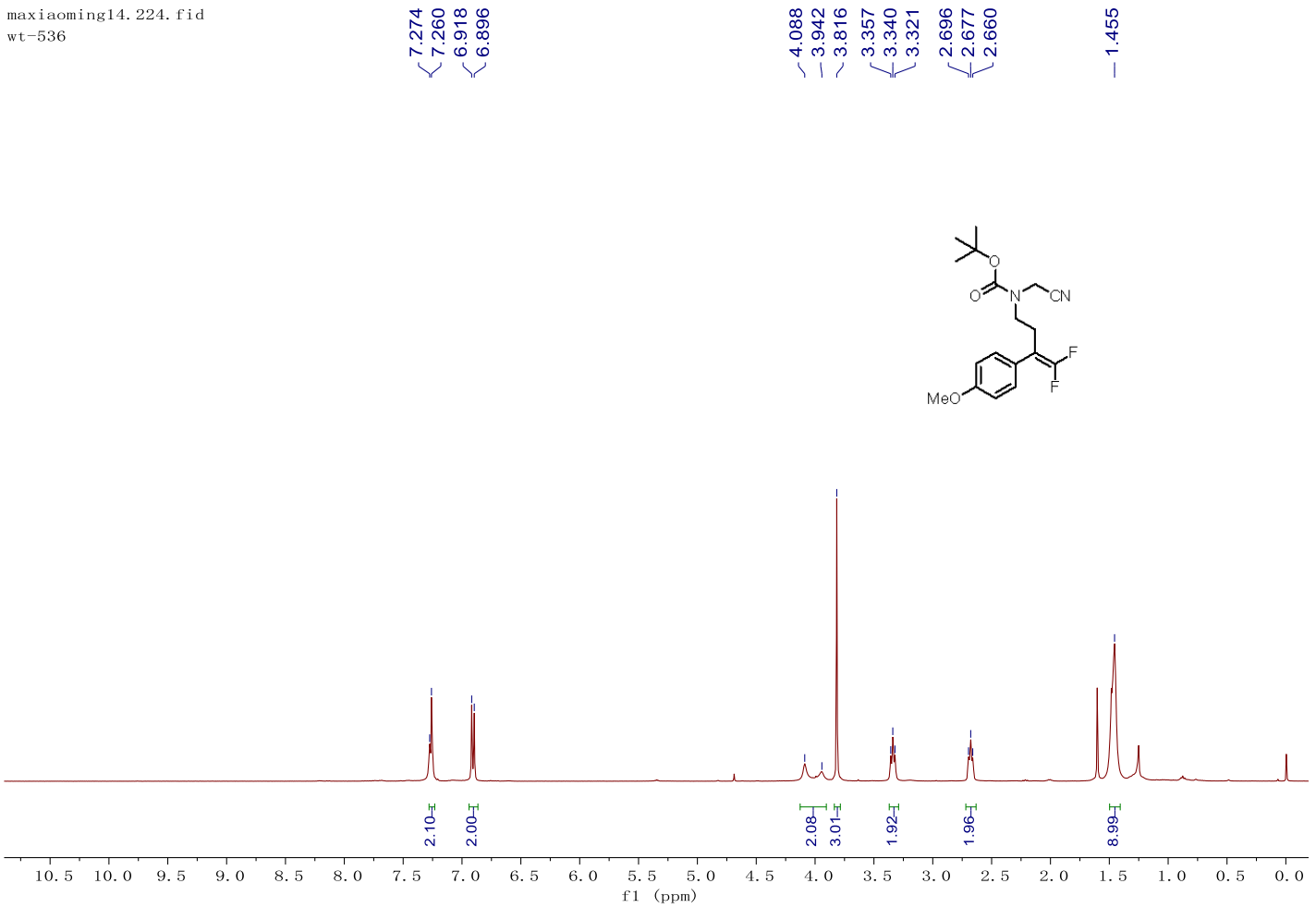
^{1}H NMR Spectrum of Compound 3m (400 MHz, $CDCl_3$)



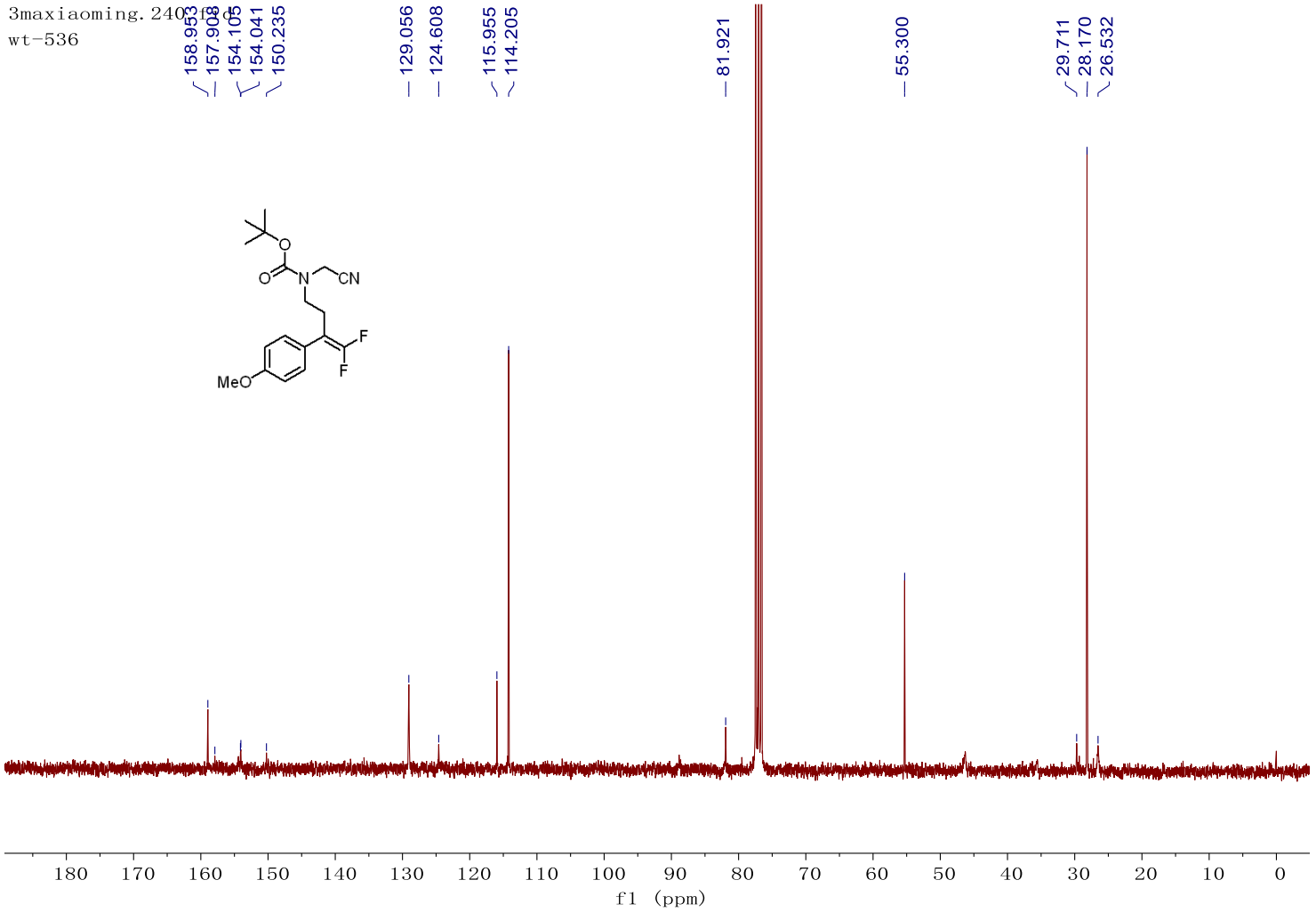
^{13}C NMR Spectrum of Compound 3m (75 MHz, $CDCl_3$)



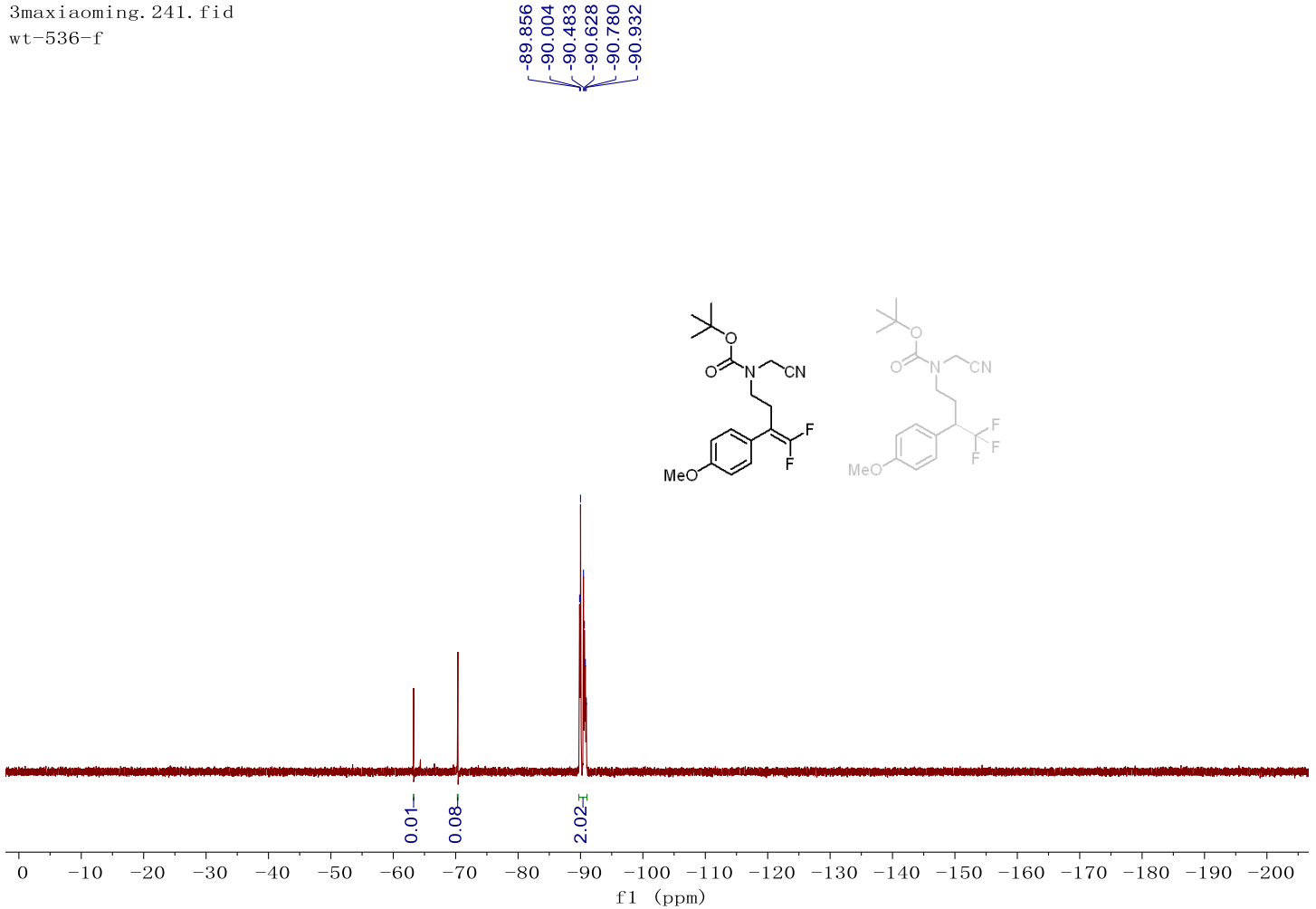
^{19}F NMR Spectrum of Compound 3m (282 MHz, $CDCl_3$)



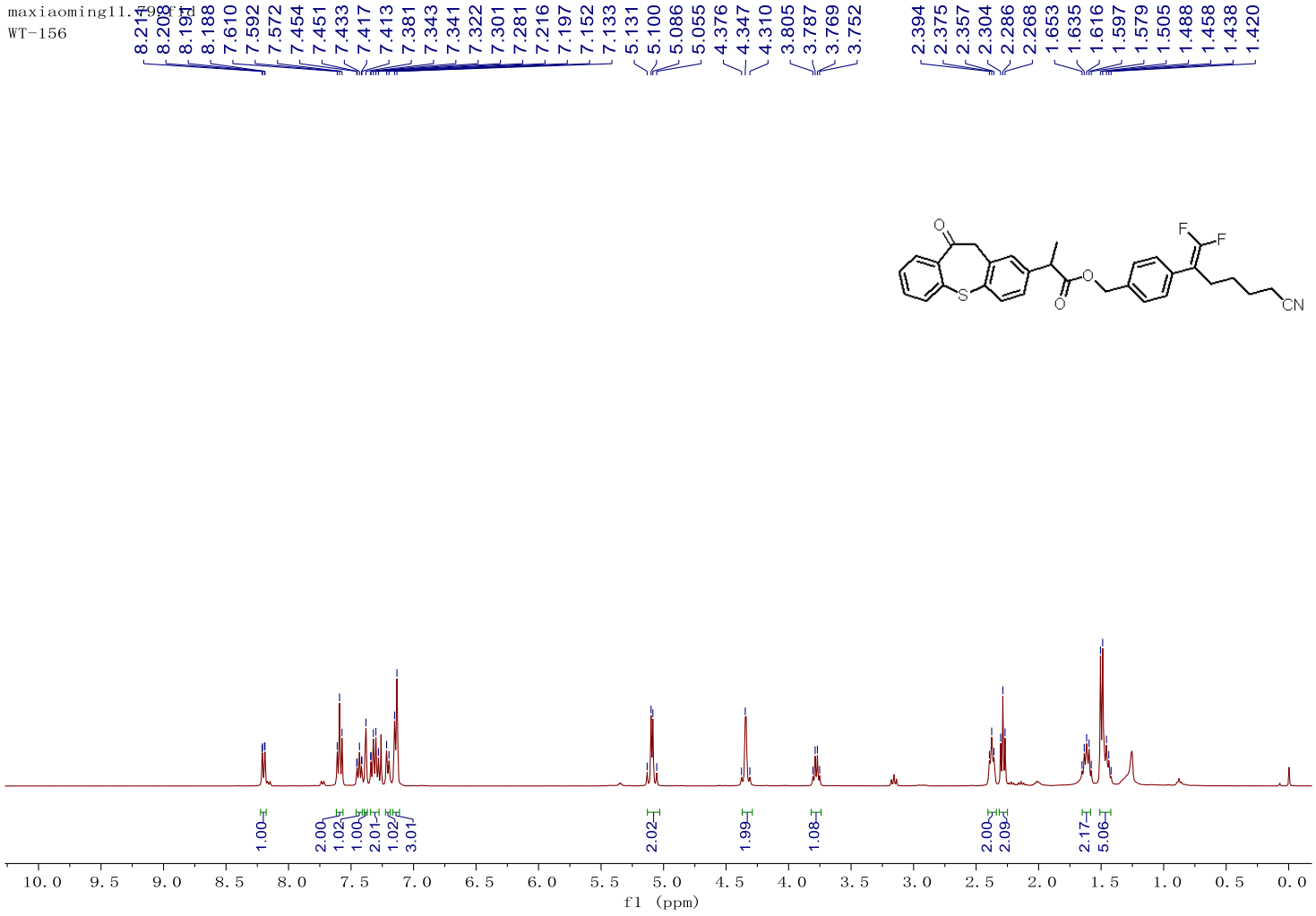
^{1}H NMR Spectrum of Compound 3n (400 MHz, $CDCl_3$)



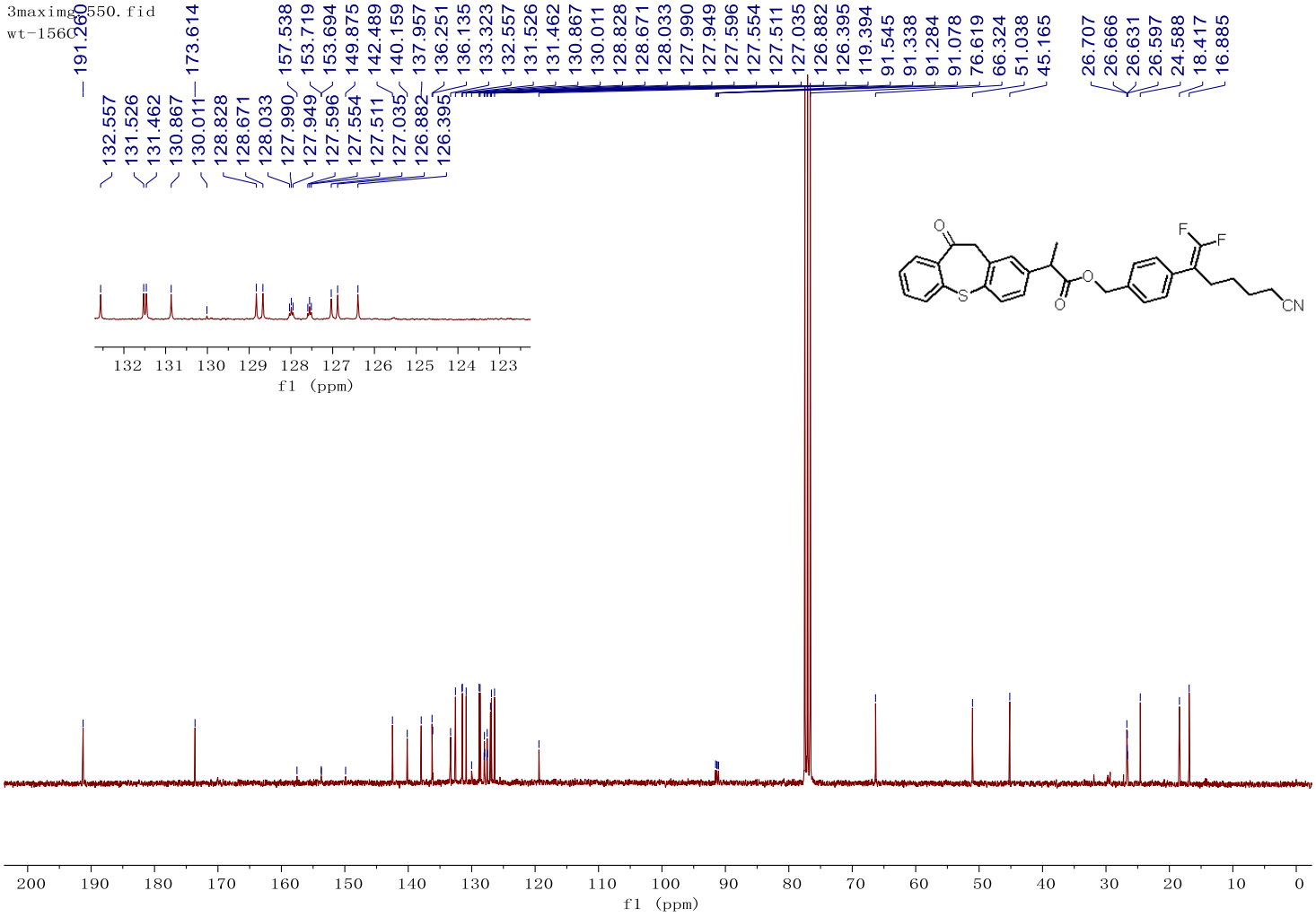
^{13}C NMR Spectrum of Compound 3n (75 MHz, $CDCl_3$)



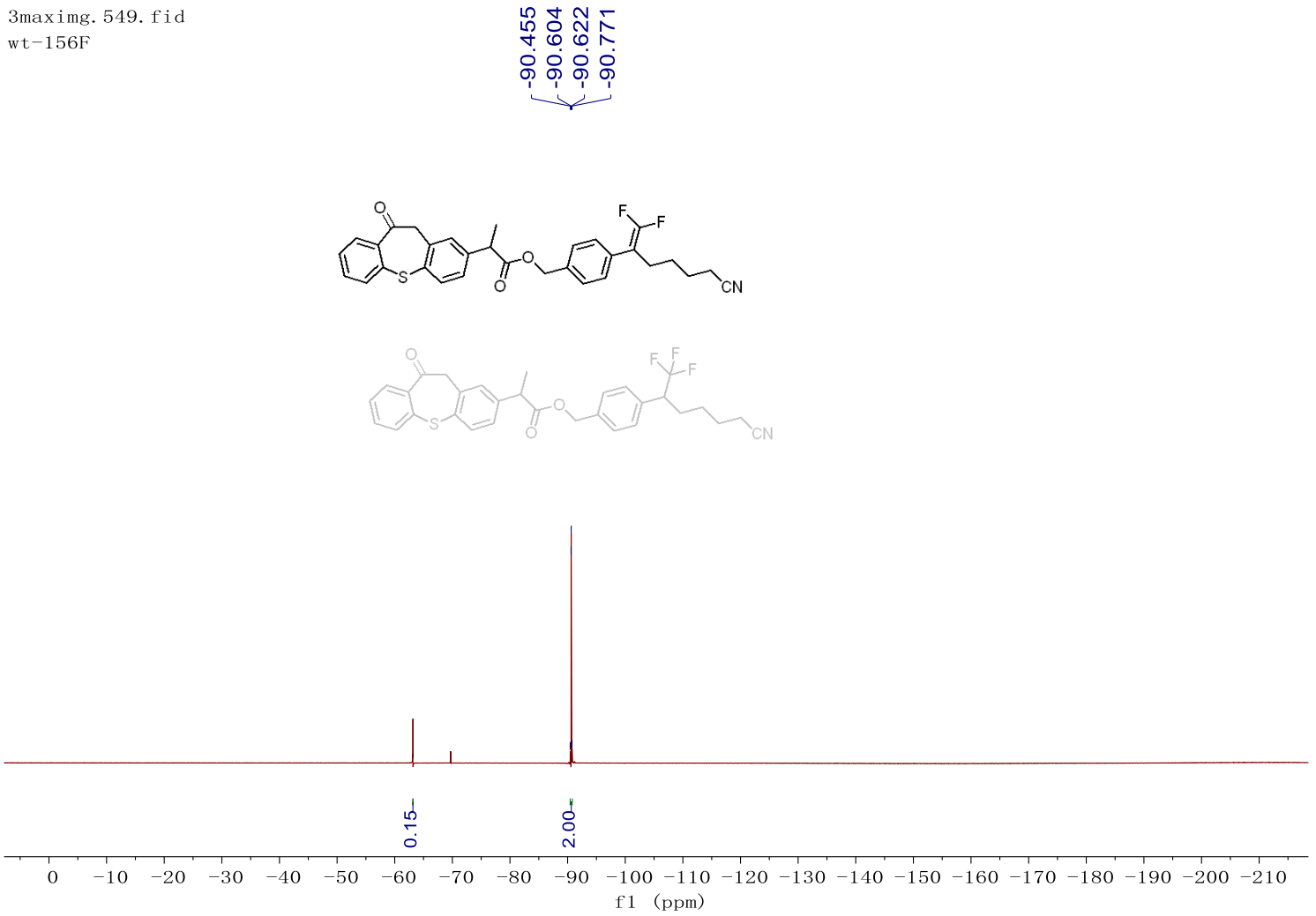
^{19}F NMR Spectrum of Compound 3n (282 MHz, $CDCl_3$)



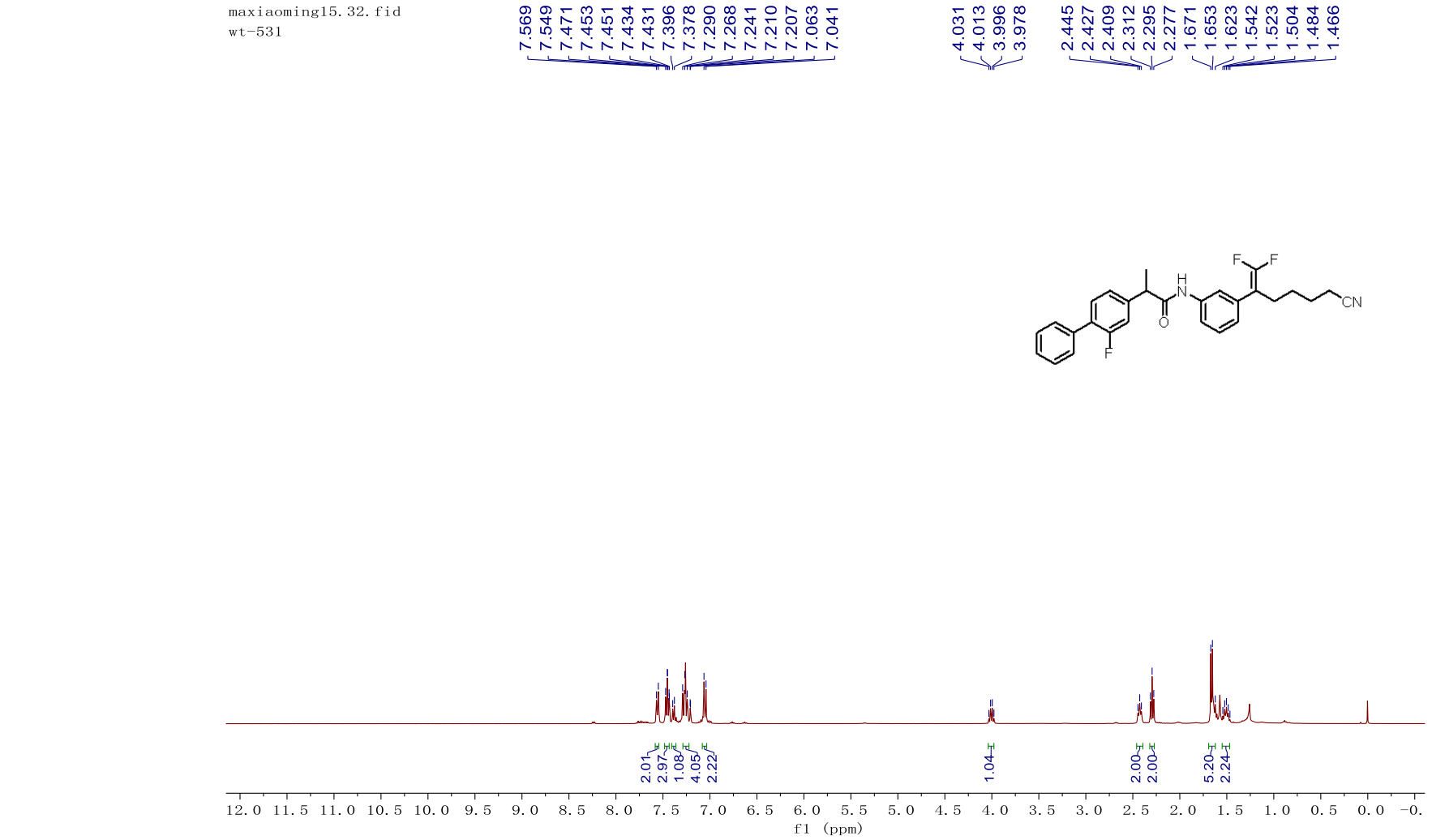
^{1}H NMR Spectrum of Compound 3o (400 MHz, $CDCl_3$)



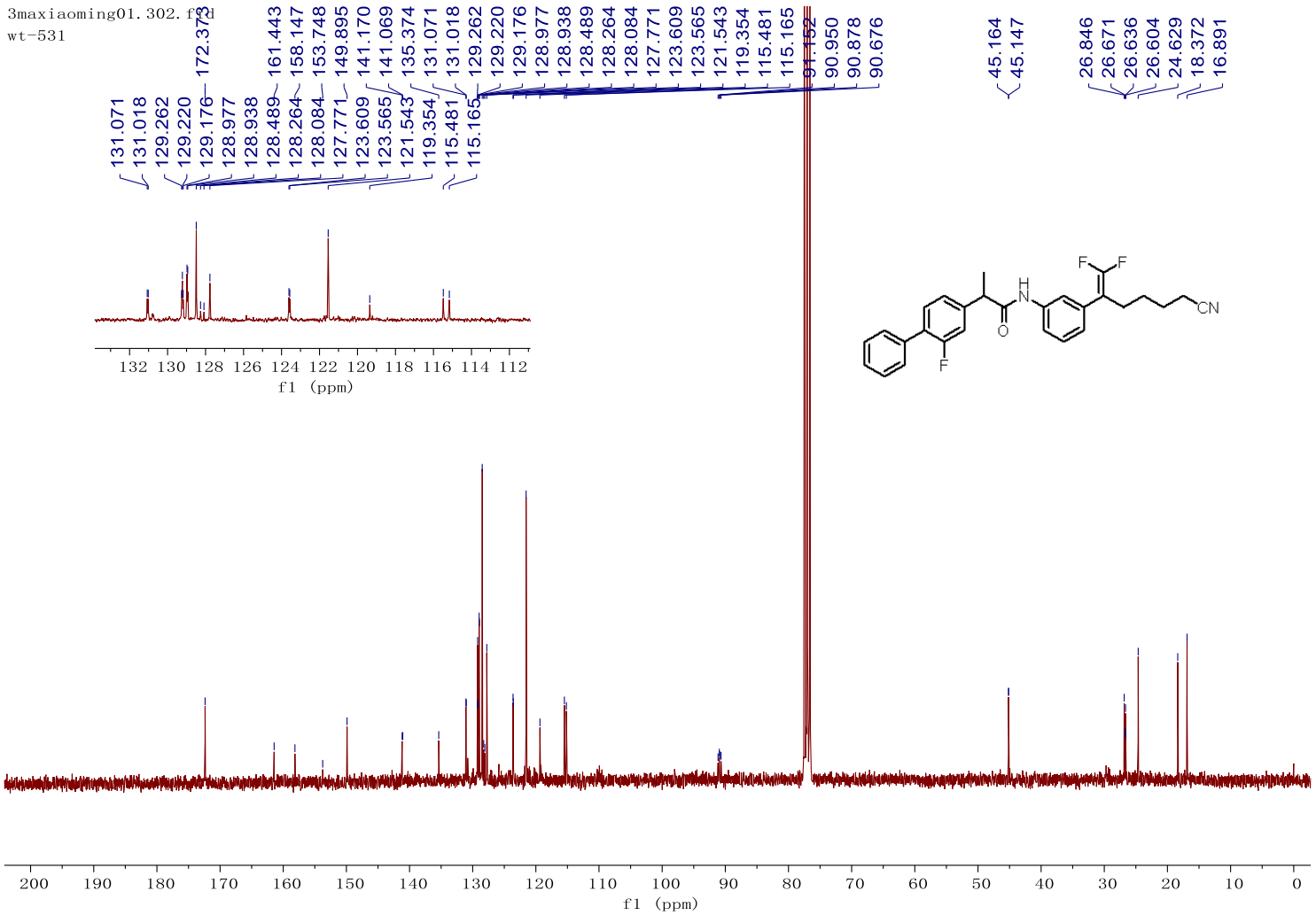
^{13}C NMR Spectrum of Compound 3o (75 MHz, $CDCl_3$)



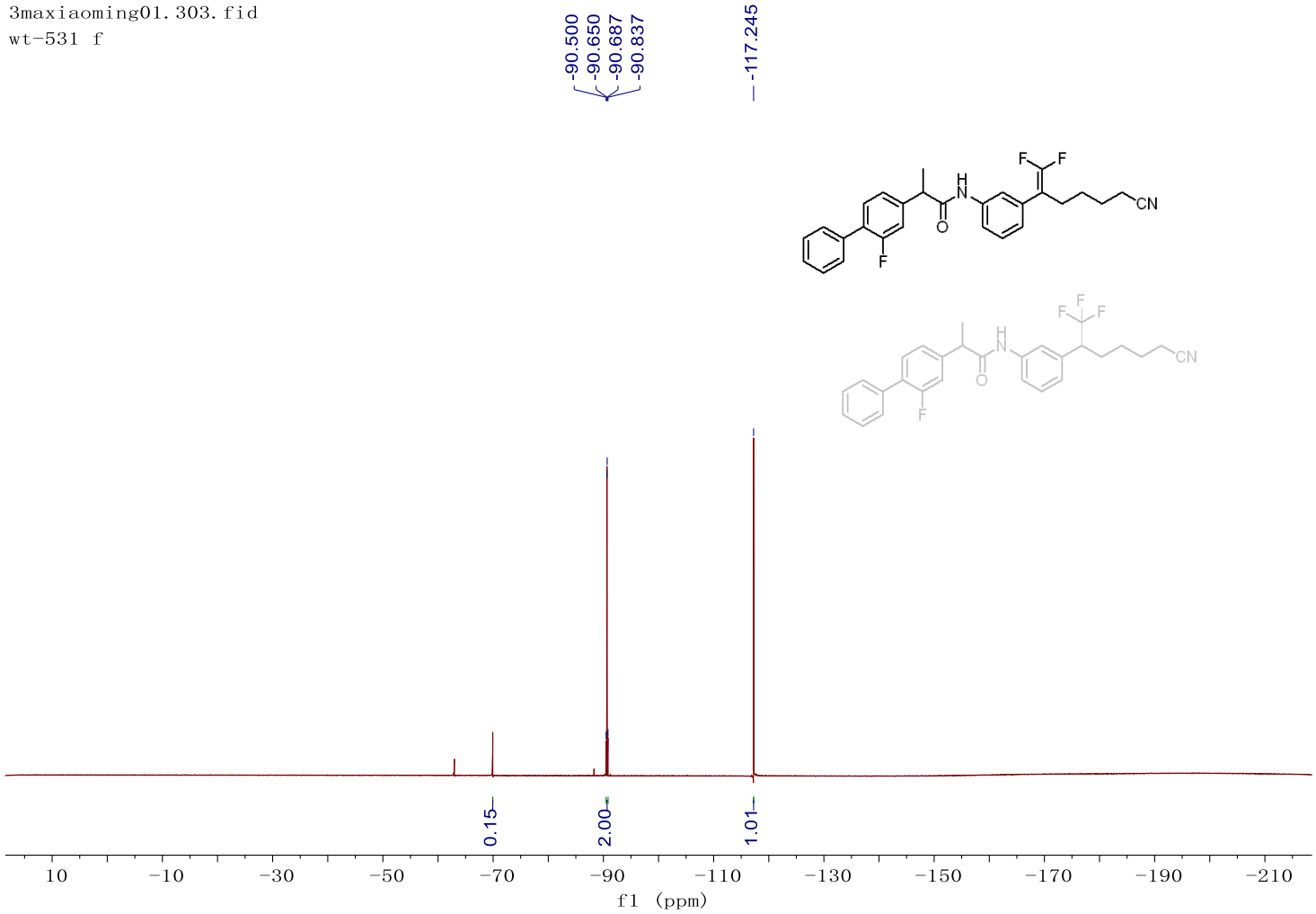
^{19}F NMR Spectrum of Compound 3o (282 MHz, $CDCl_3$)



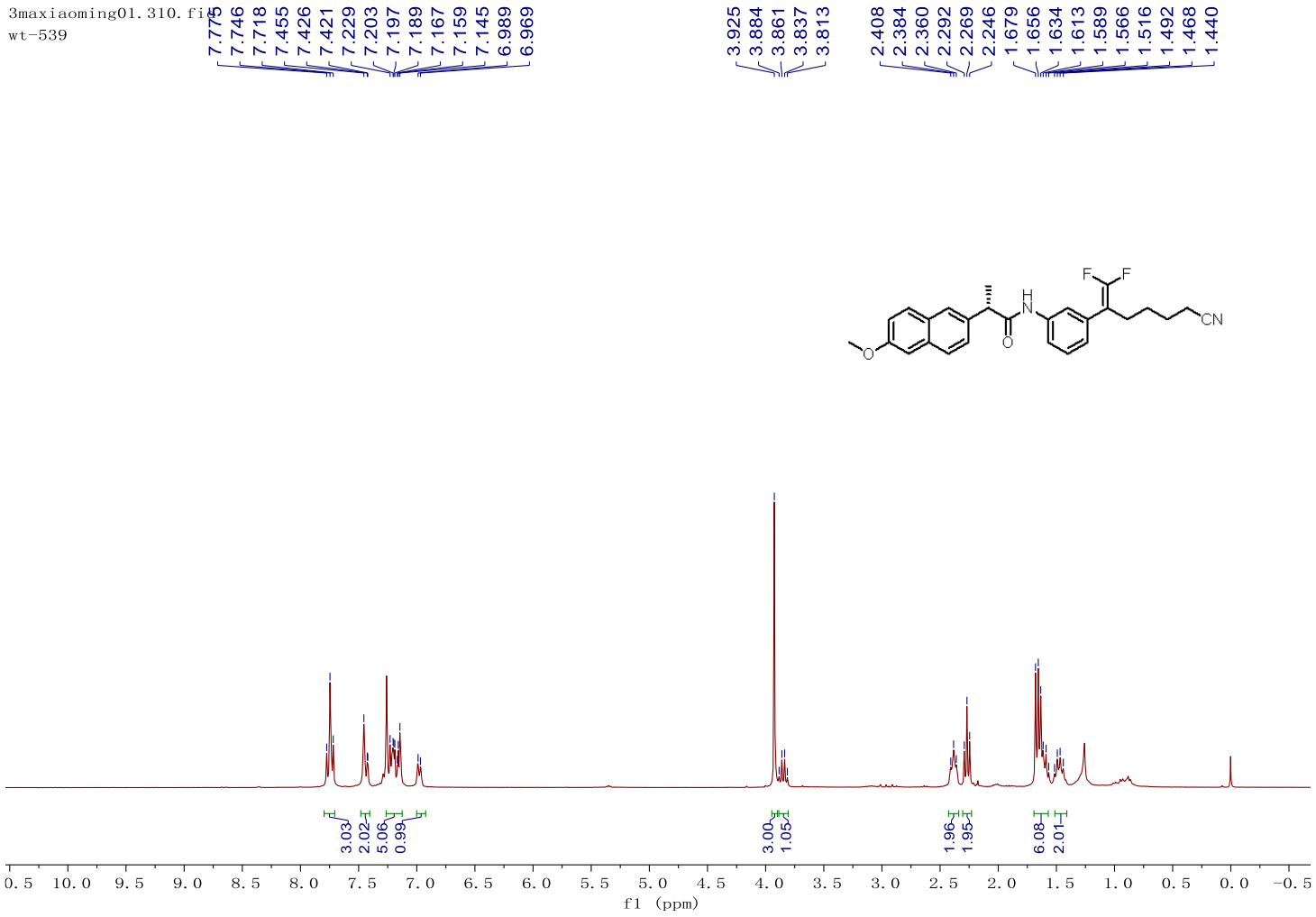
^{1}H NMR Spectrum of Compound 3p (400 MHz, $CDCl_3$)



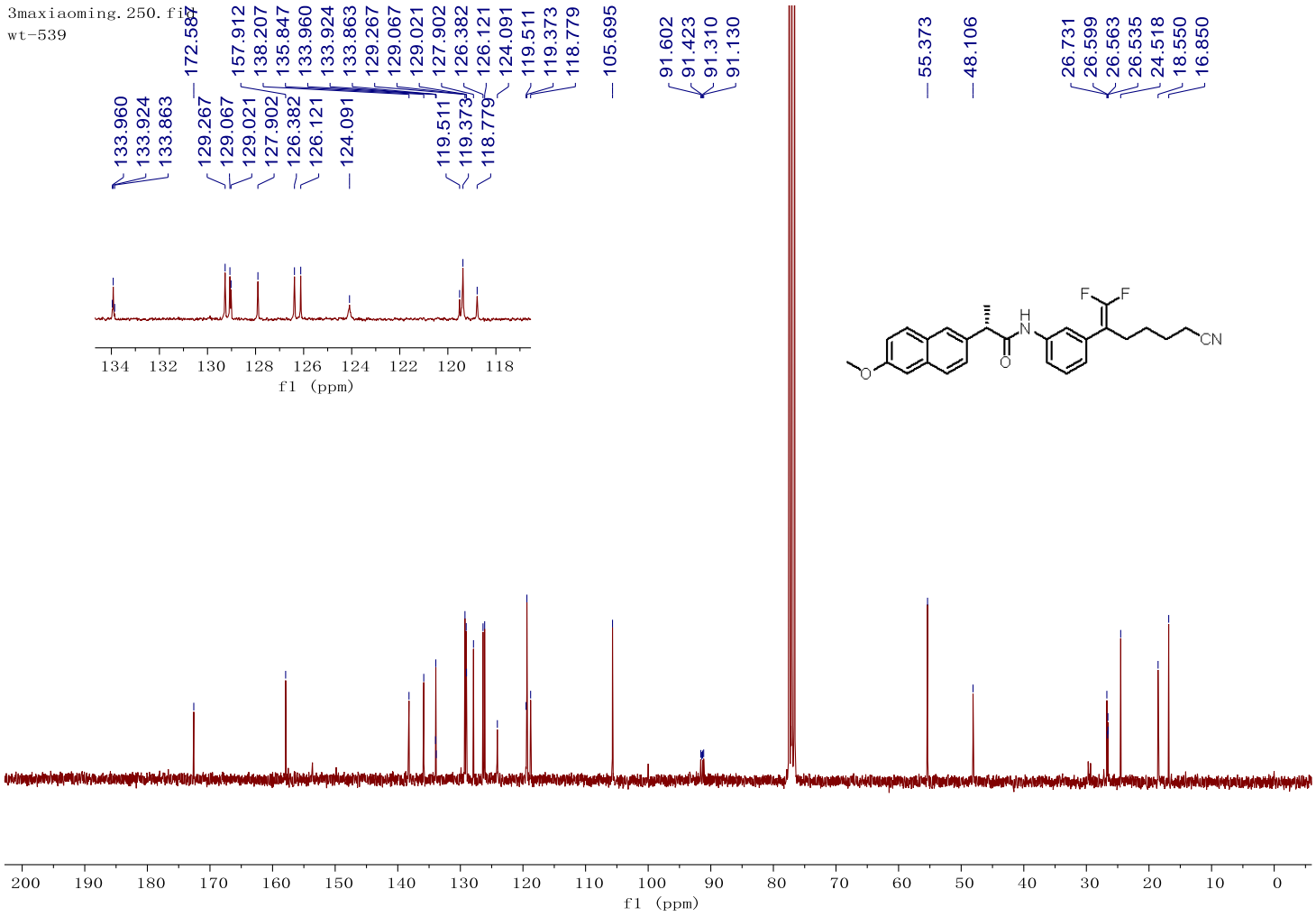
^{13}C NMR Spectrum of Compound 3p (75 MHz, $CDCl_3$)



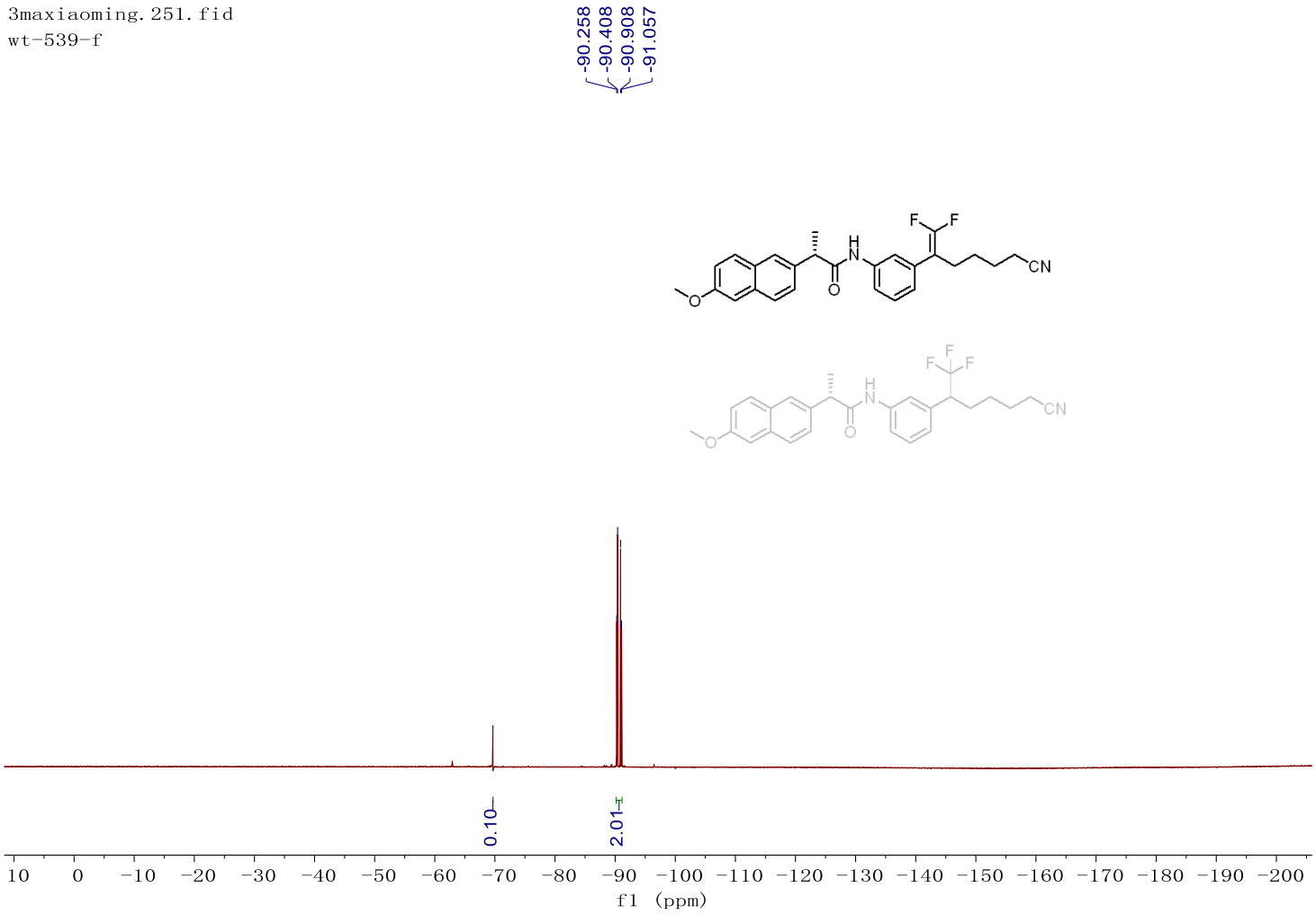
^{19}F NMR Spectrum of Compound 3p (282 MHz, $CDCl_3$)



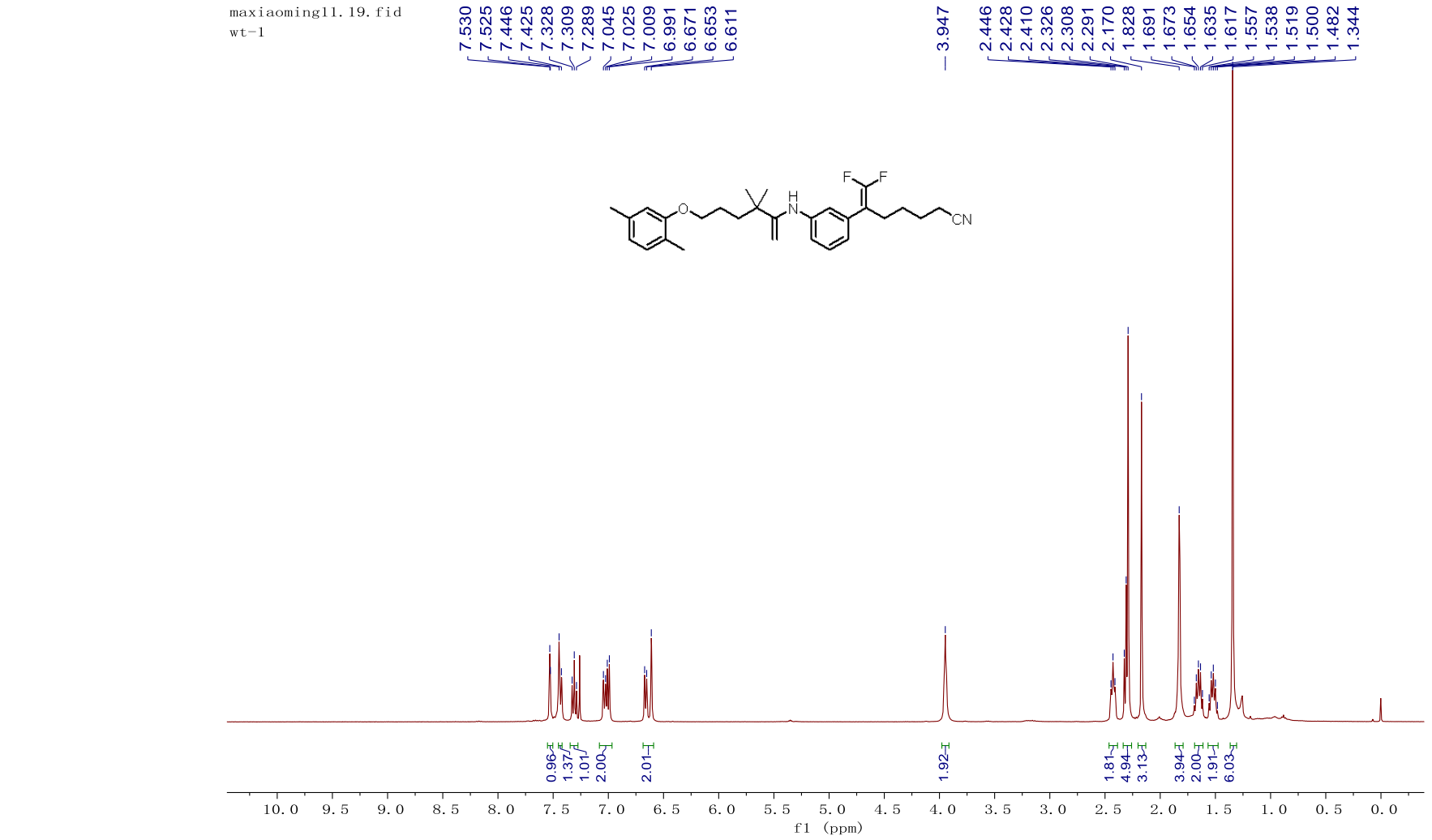
^{1}H NMR Spectrum of Compound 3q (300 MHz, $CDCl_3$)



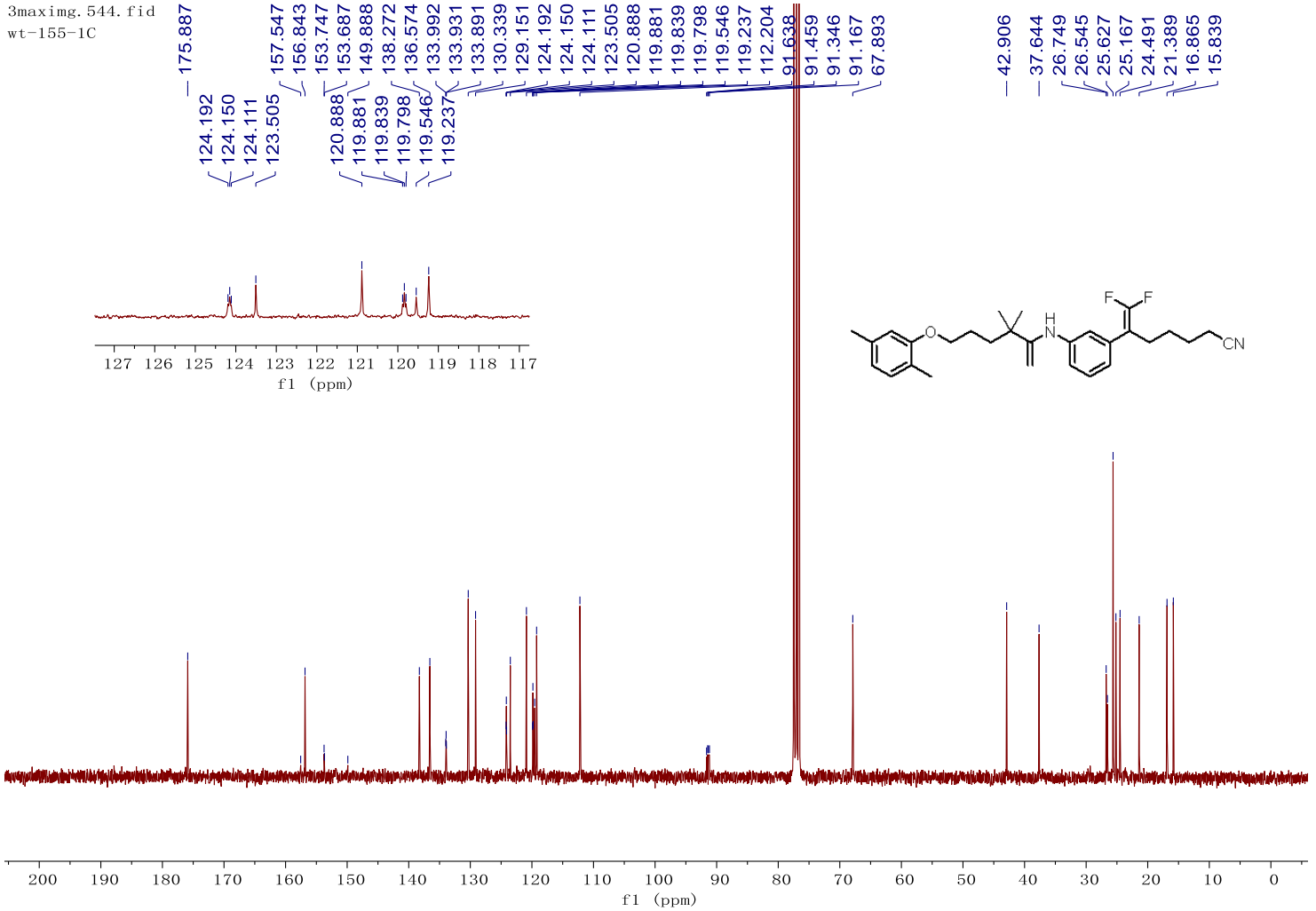
^{13}C NMR Spectrum of Compound 3q (75 MHz, $CDCl_3$)



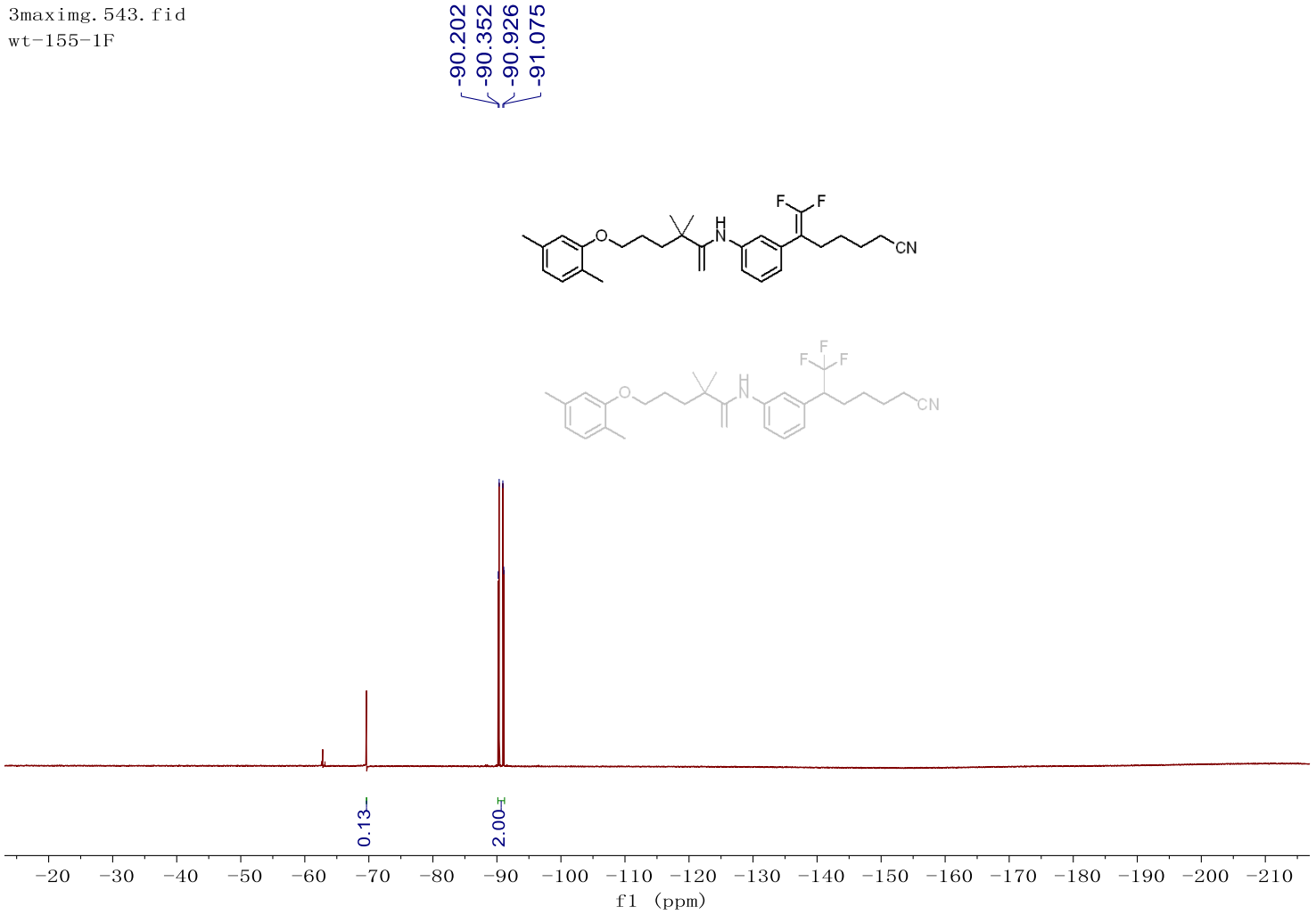
^{19}F NMR Spectrum of Compound 3q (282 MHz, $CDCl_3$)



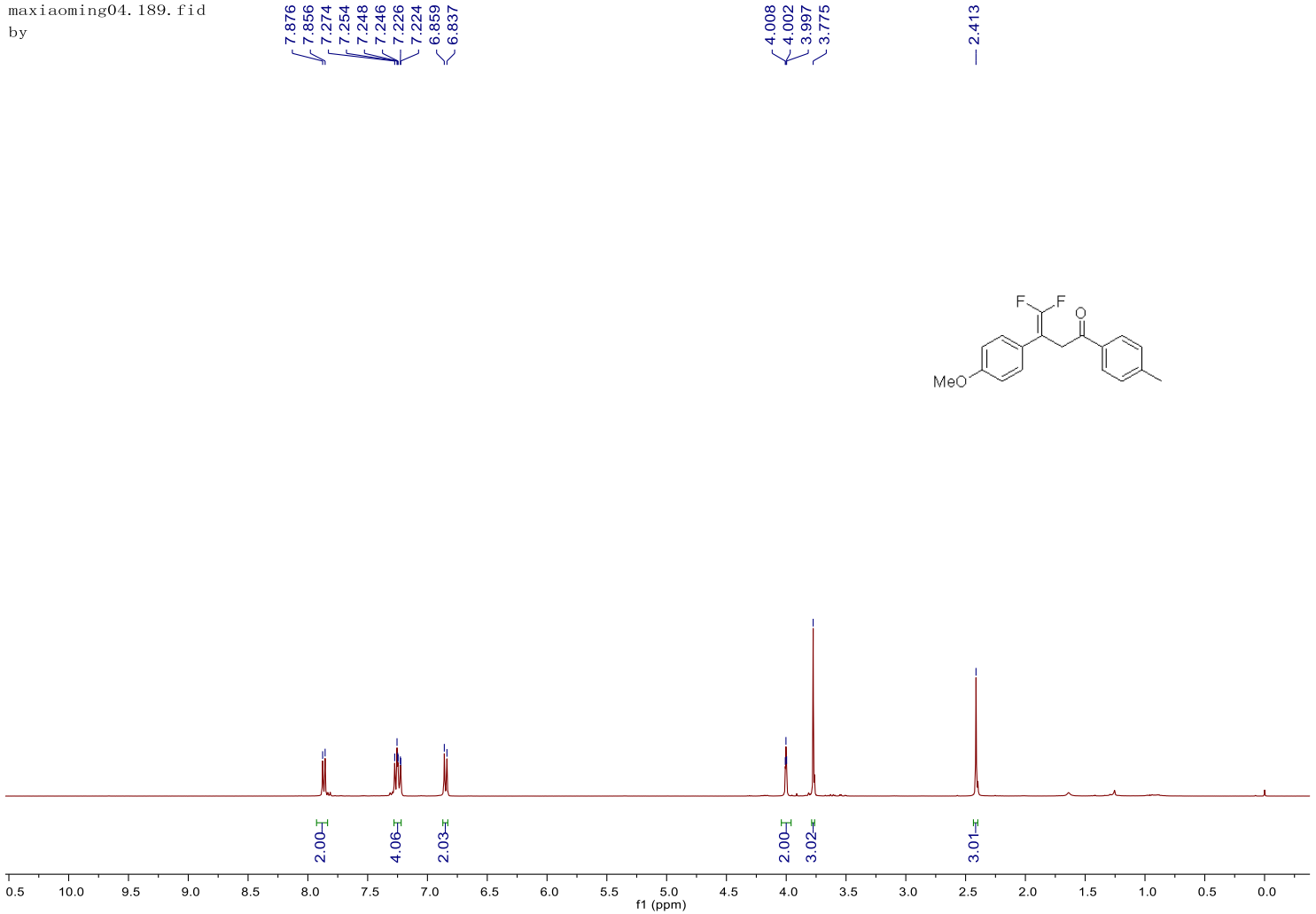
^{1}H NMR Spectrum of Compound 3r (400 MHz, $CDCl_3$)



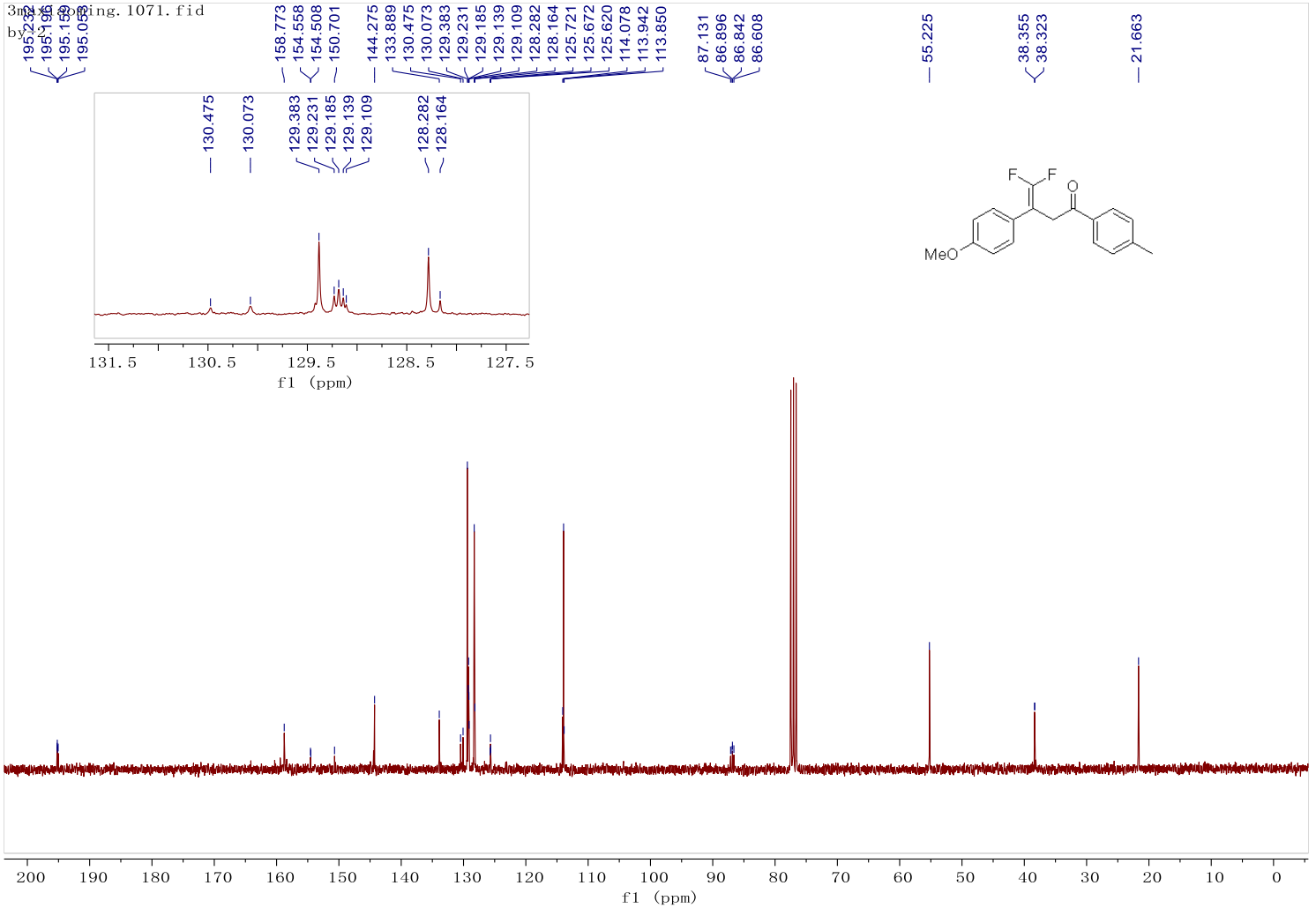
^{13}C NMR Spectrum of Compound 3r (75 MHz, $CDCl_3$)



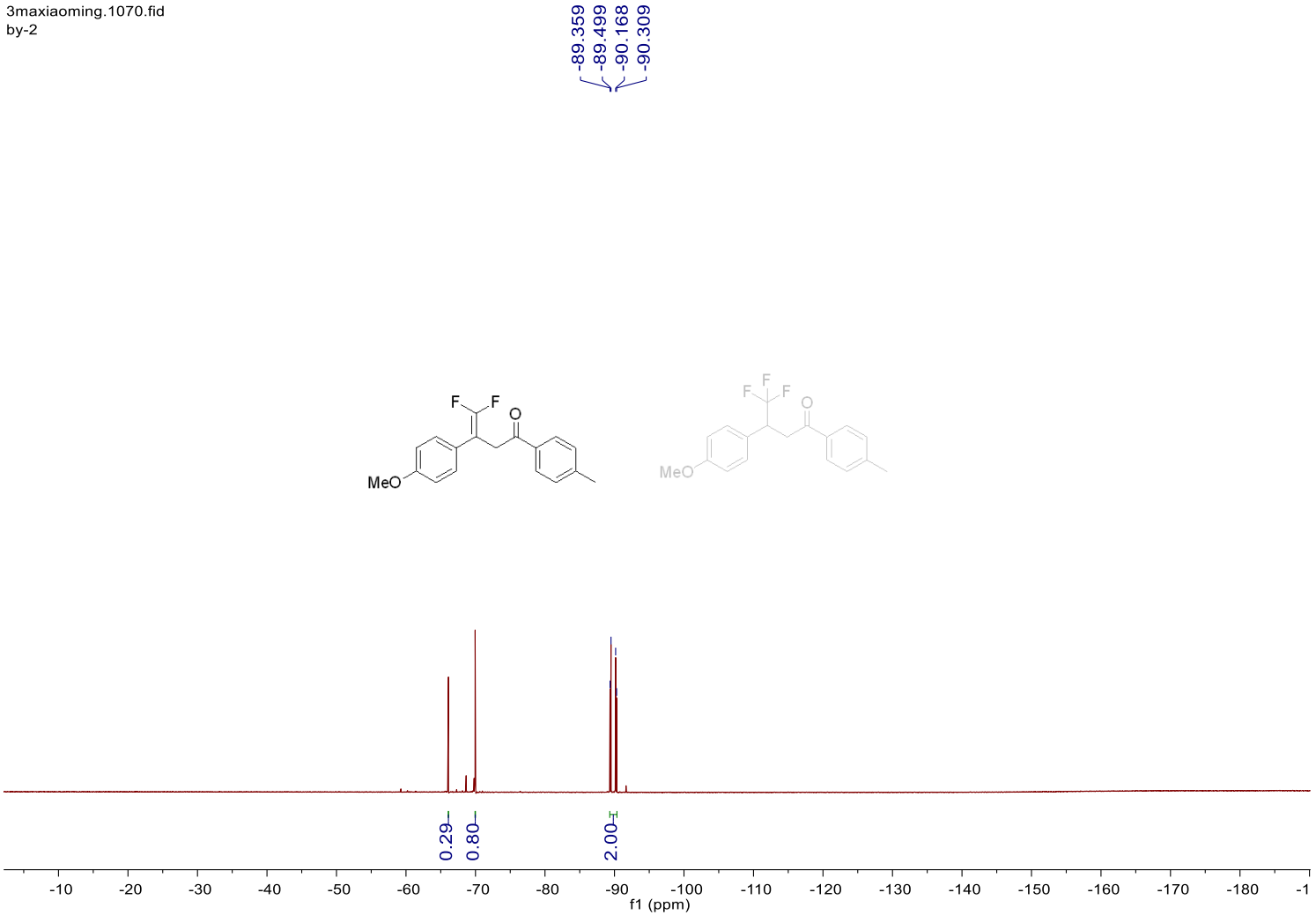
^{19}F NMR Spectrum of Compound 3r (282 MHz, $CDCl_3$)



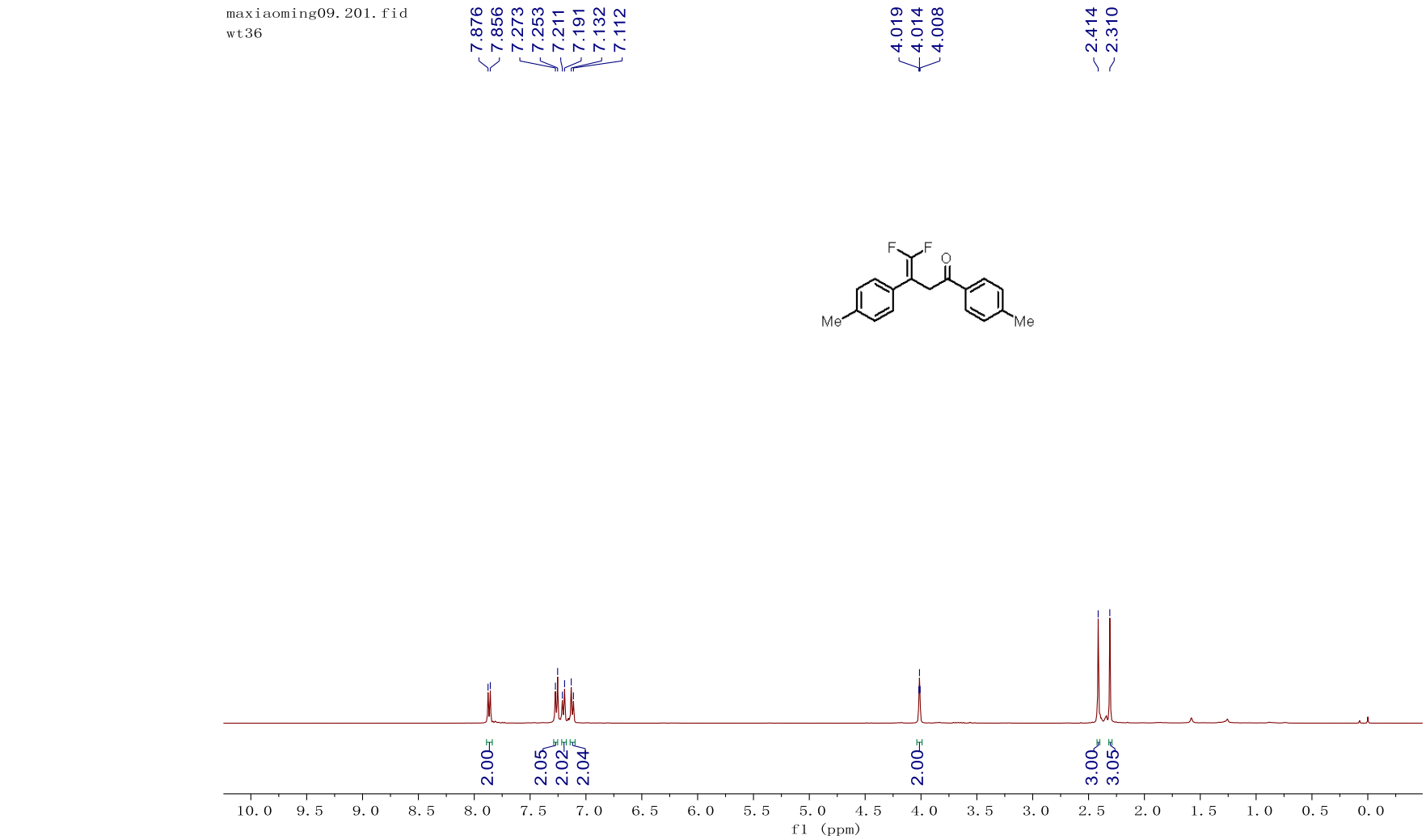
^{1}H NMR Spectrum of Compound 5a (400 MHz, $CDCl_3$)



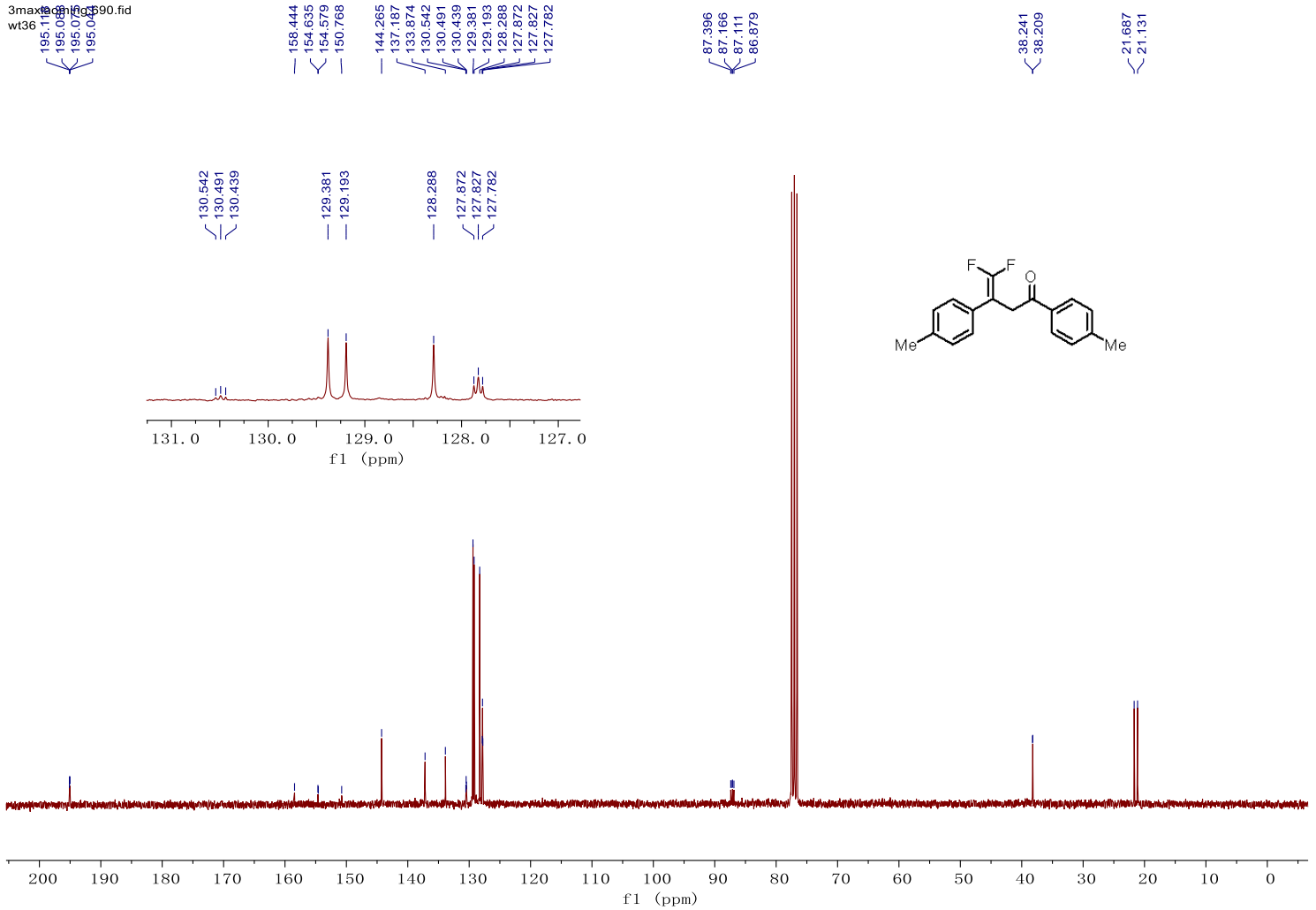
^{13}C NMR Spectrum of Compound 5a (75 MHz, $CDCl_3$)



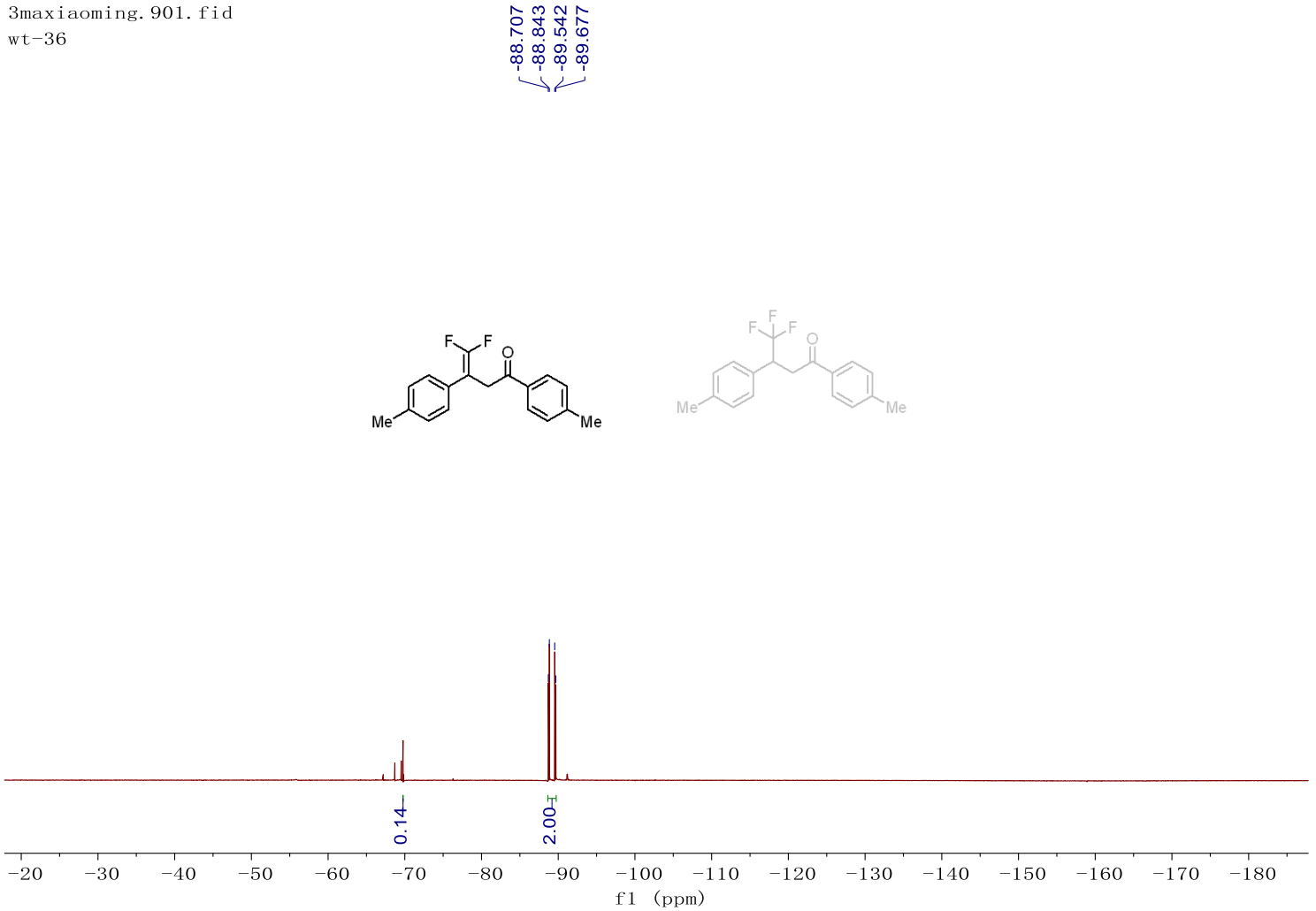
^{19}F NMR Spectrum of Compound 5a (282 MHz, $CDCl_3$)



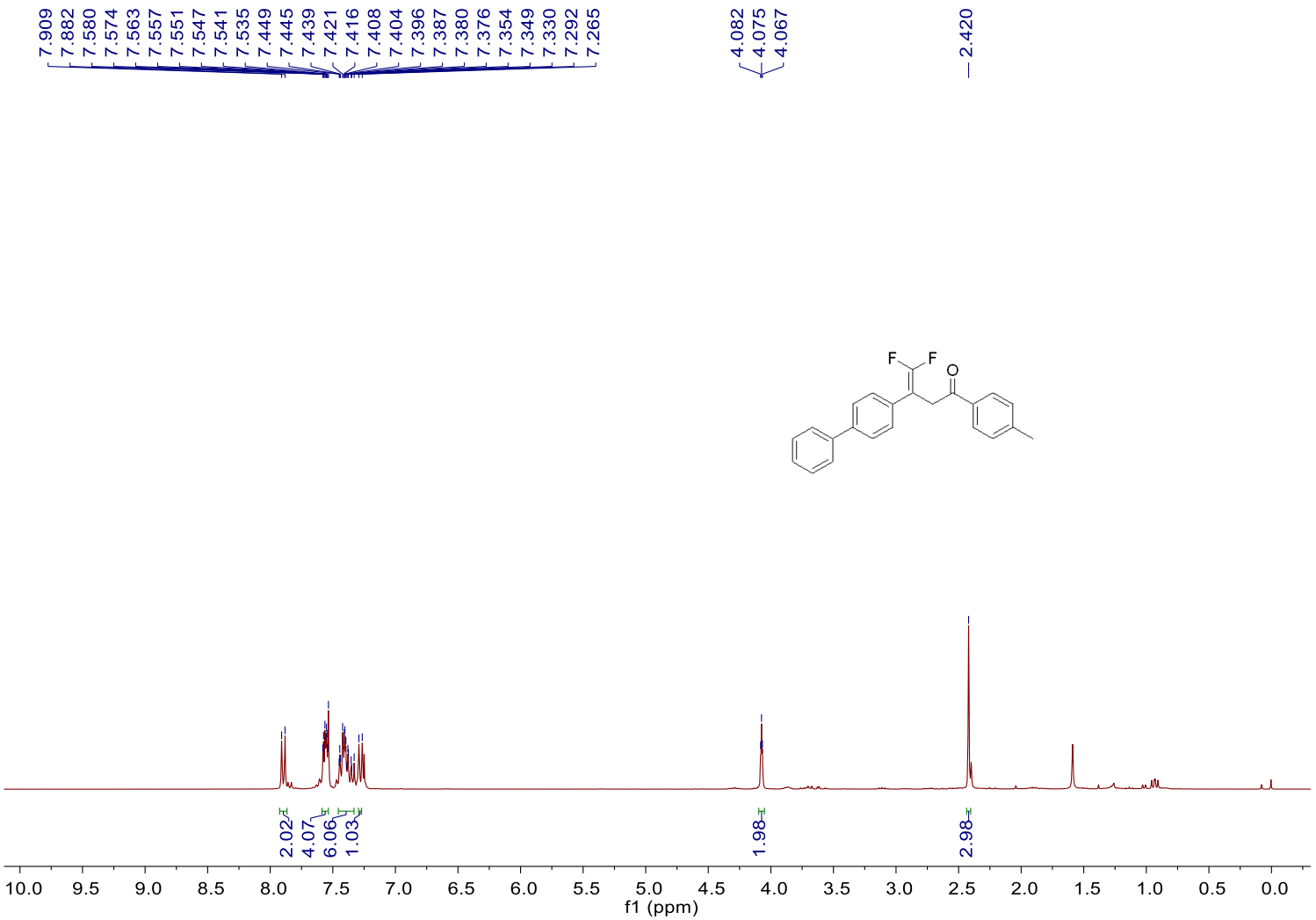
^{1}H NMR Spectrum of Compound 5b (400 MHz, $CDCl_3$)



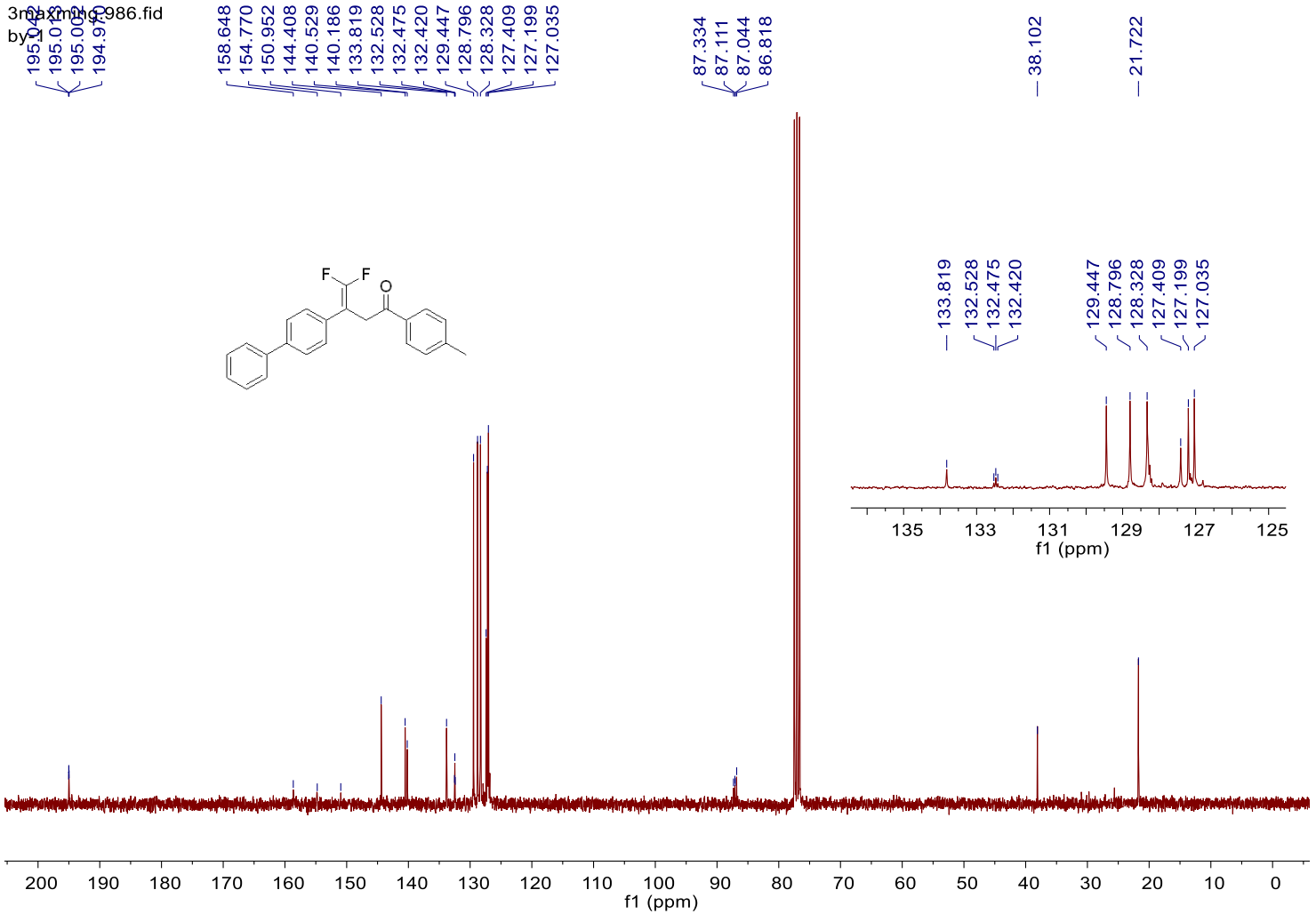
^{13}C NMR Spectrum of Compound 5b (75 MHz, $CDCl_3$)



^{19}F NMR Spectrum of Compound 5b (282 MHz, $CDCl_3$)



^{1}H NMR Spectrum of Compound 5c (300 MHz, $CDCl_3$)



^{13}C NMR Spectrum of Compound 5c (75 MHz, $CDCl_3$)

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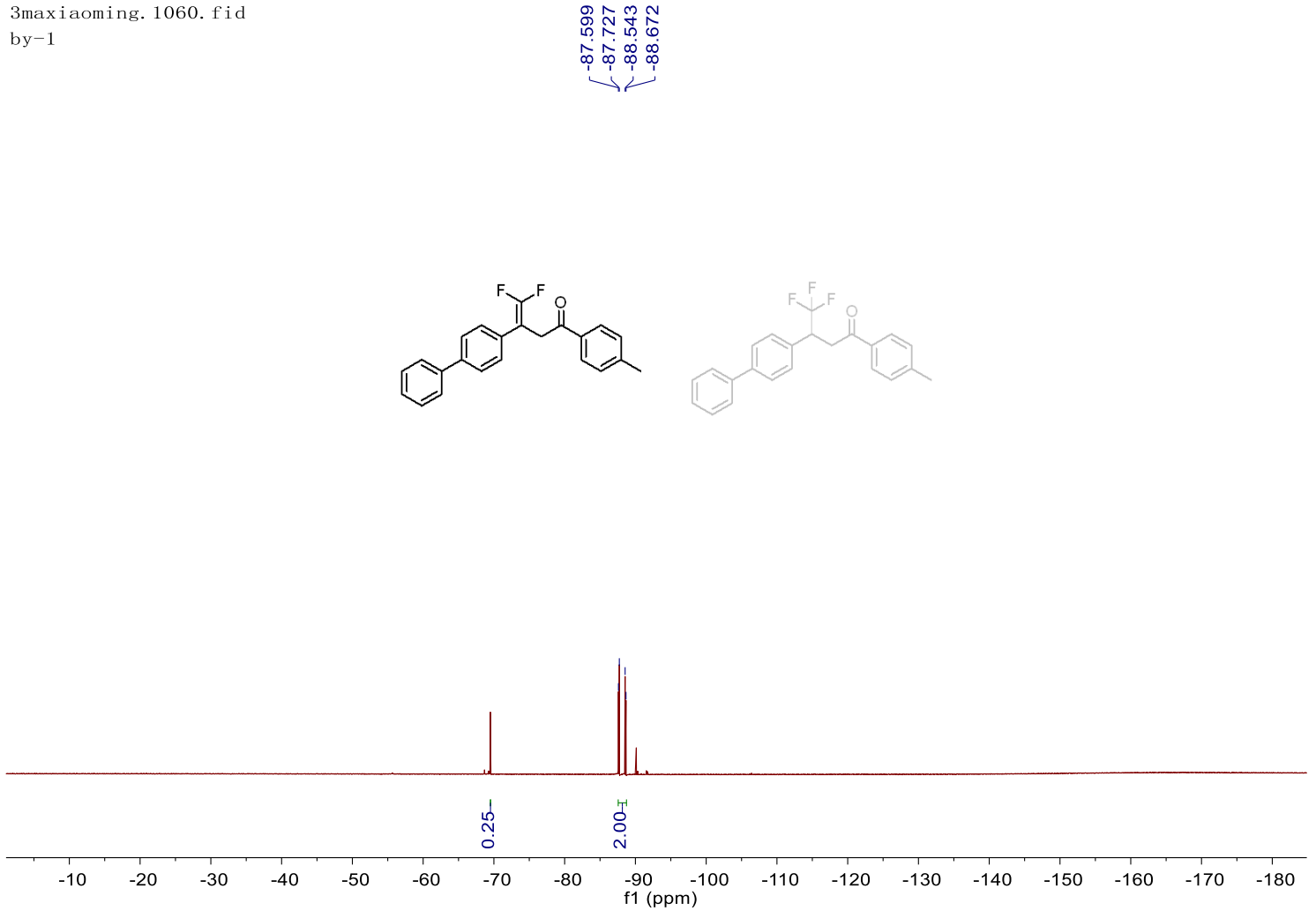
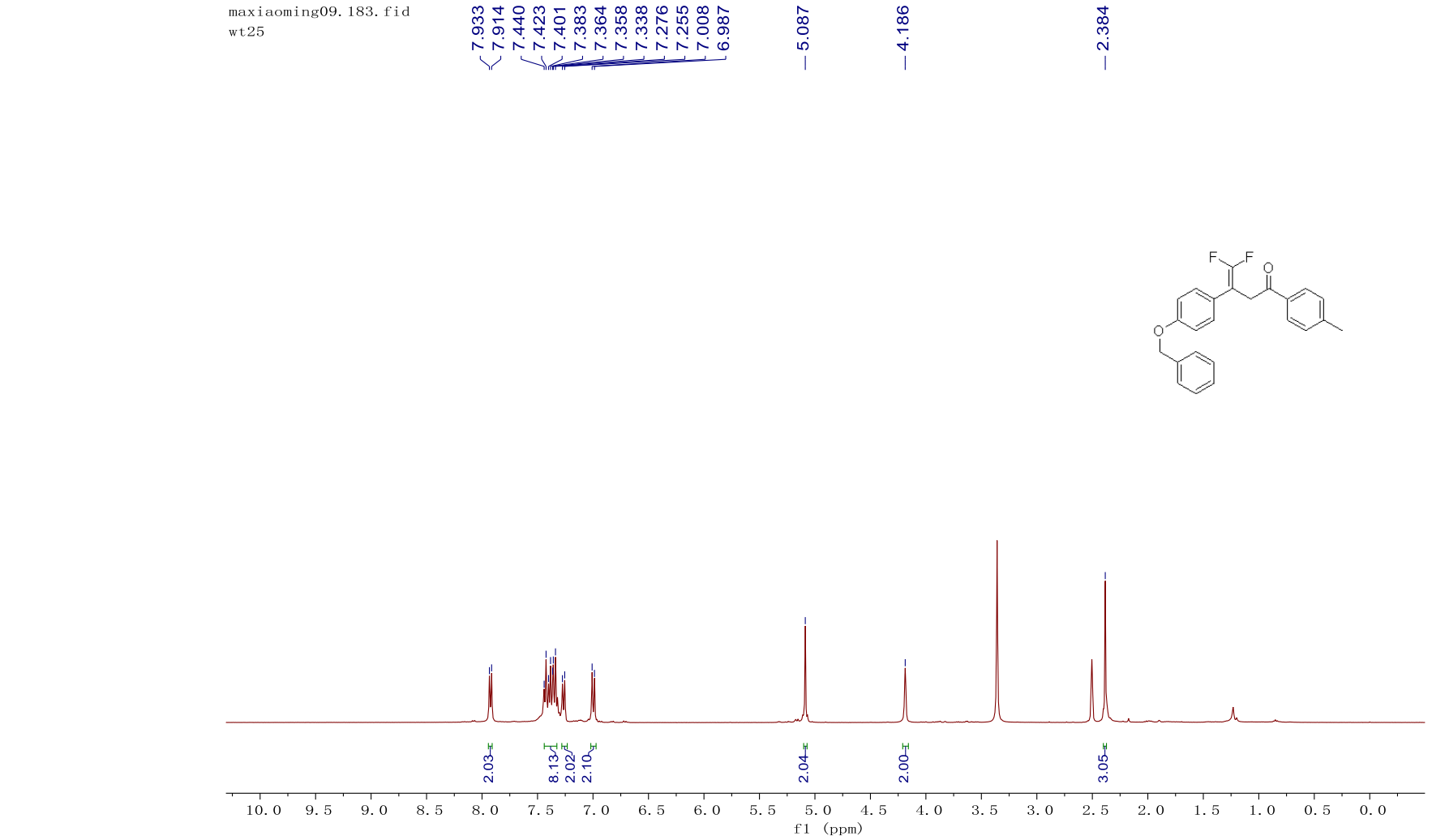
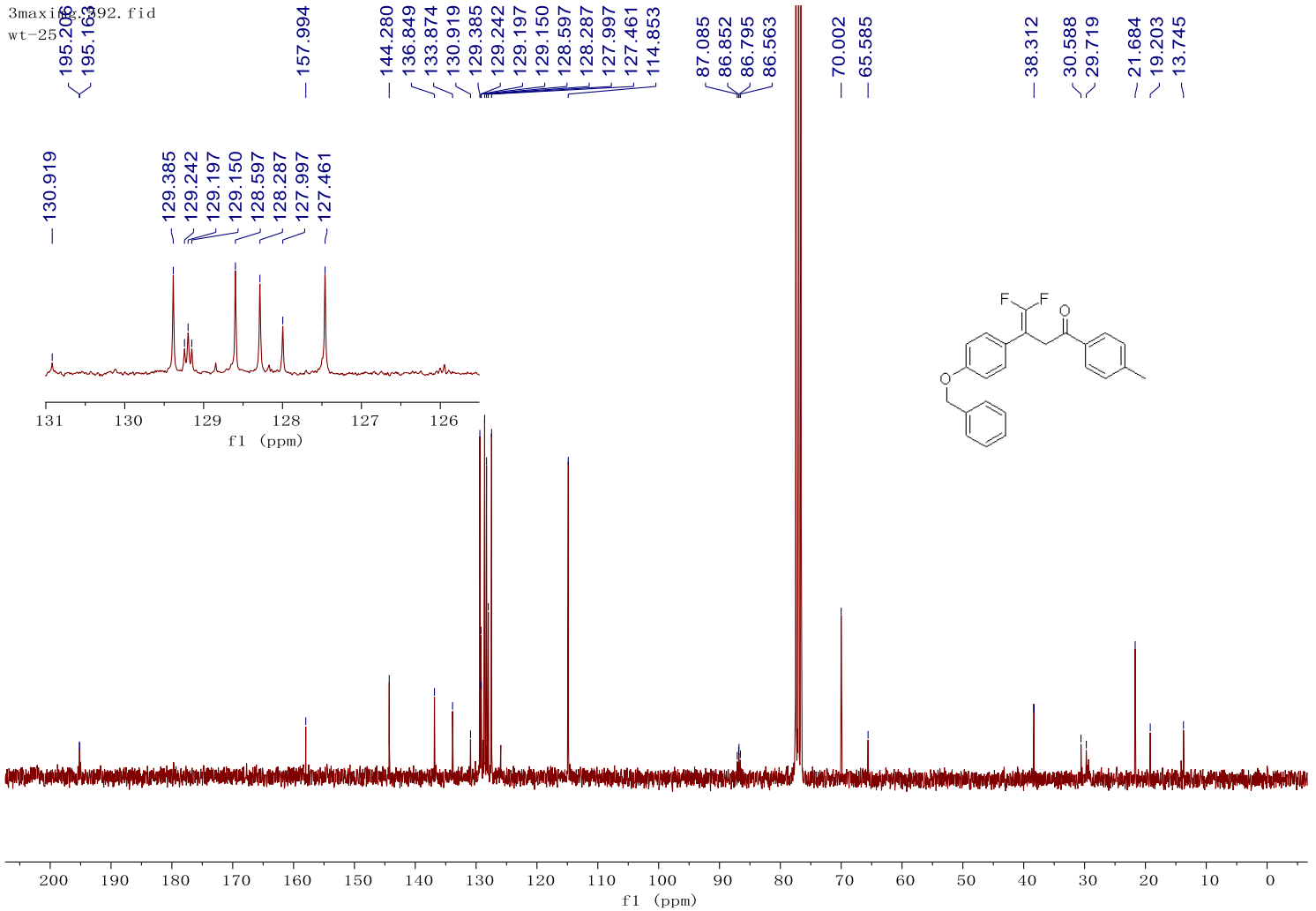


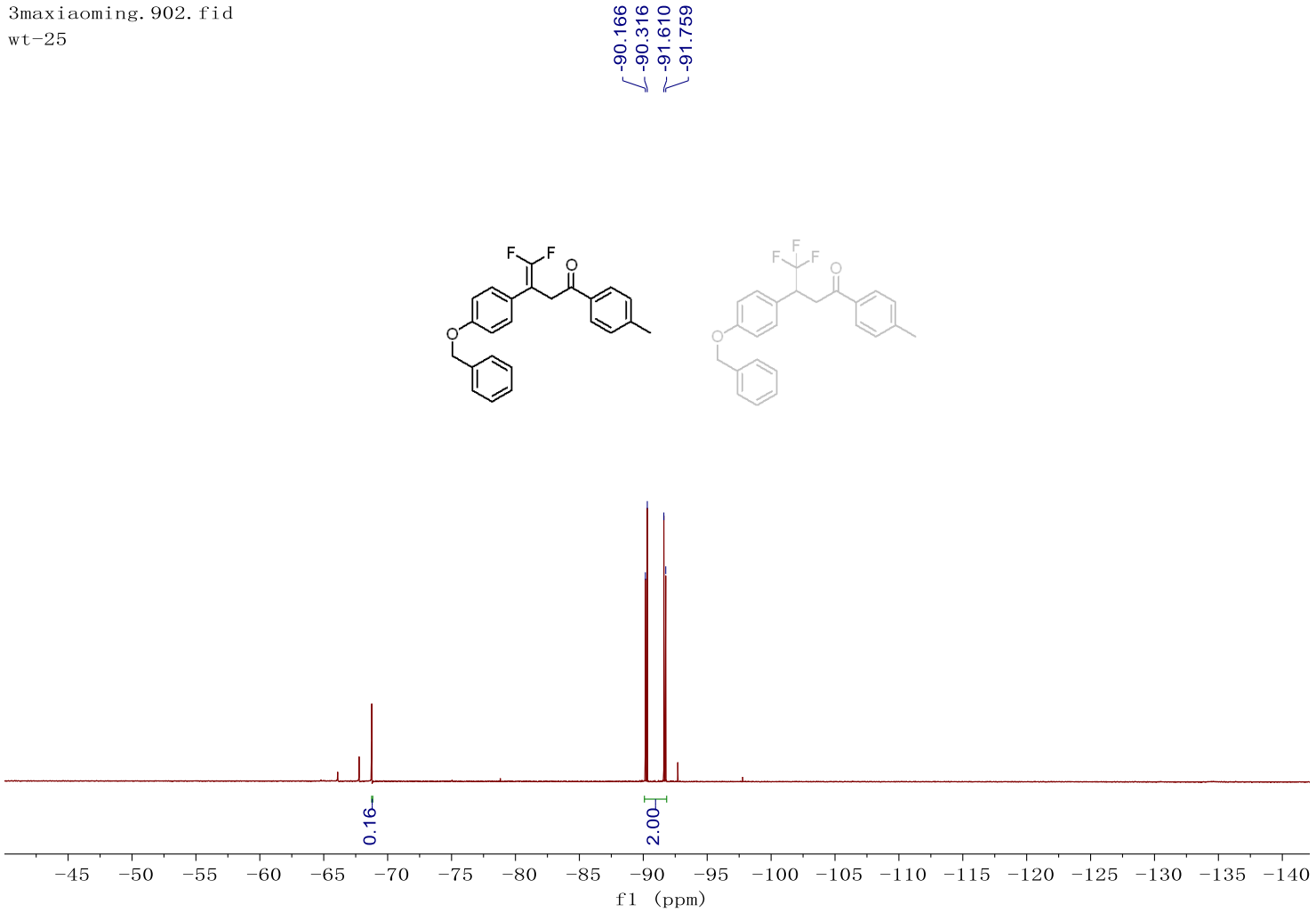
^{19}F NMR Spectrum of Compound 5c (282 MHz, $CDCl_3$)



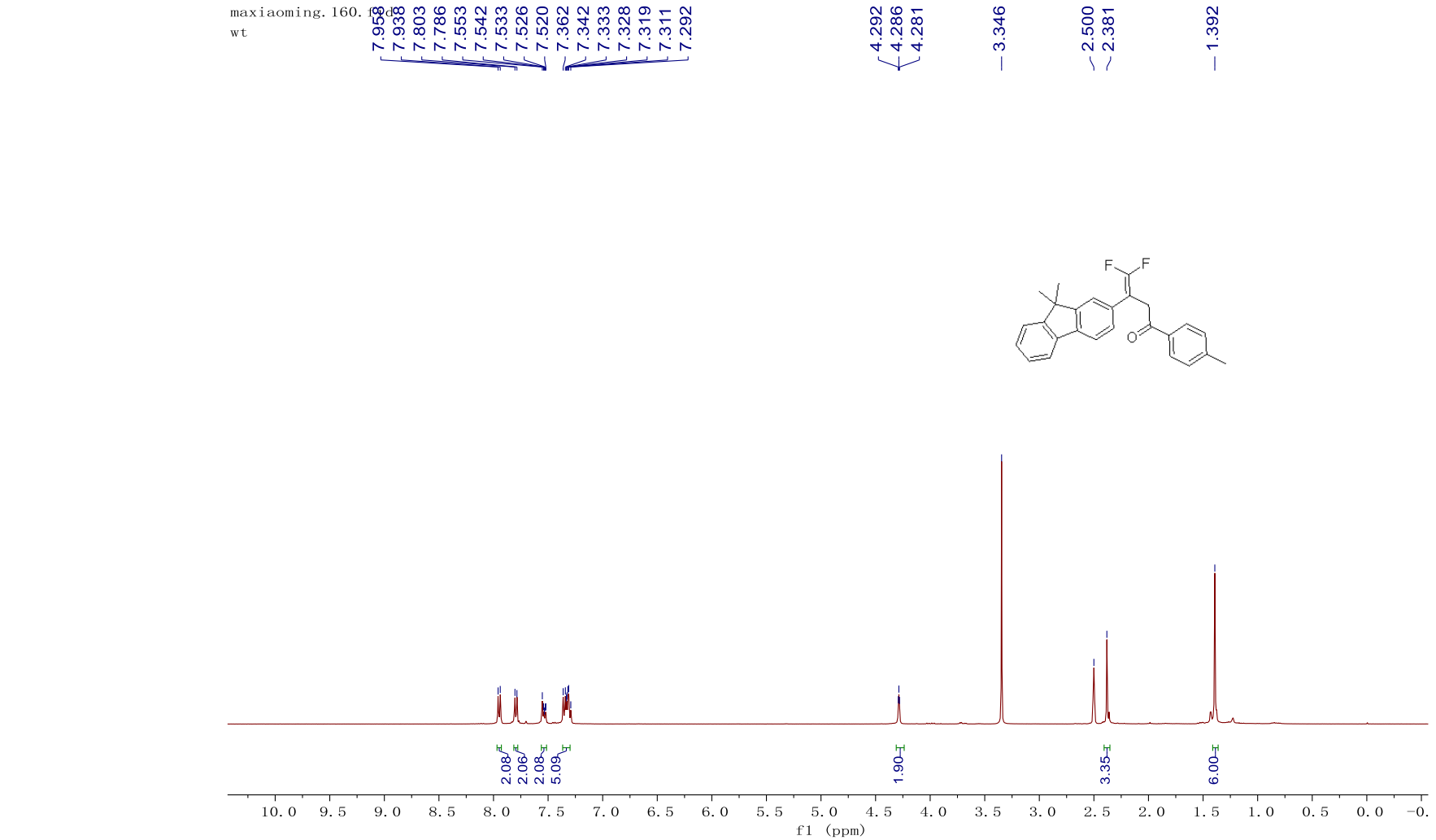
^{1}H NMR Spectrum of Compound 5d (400 MHz, DMSO)



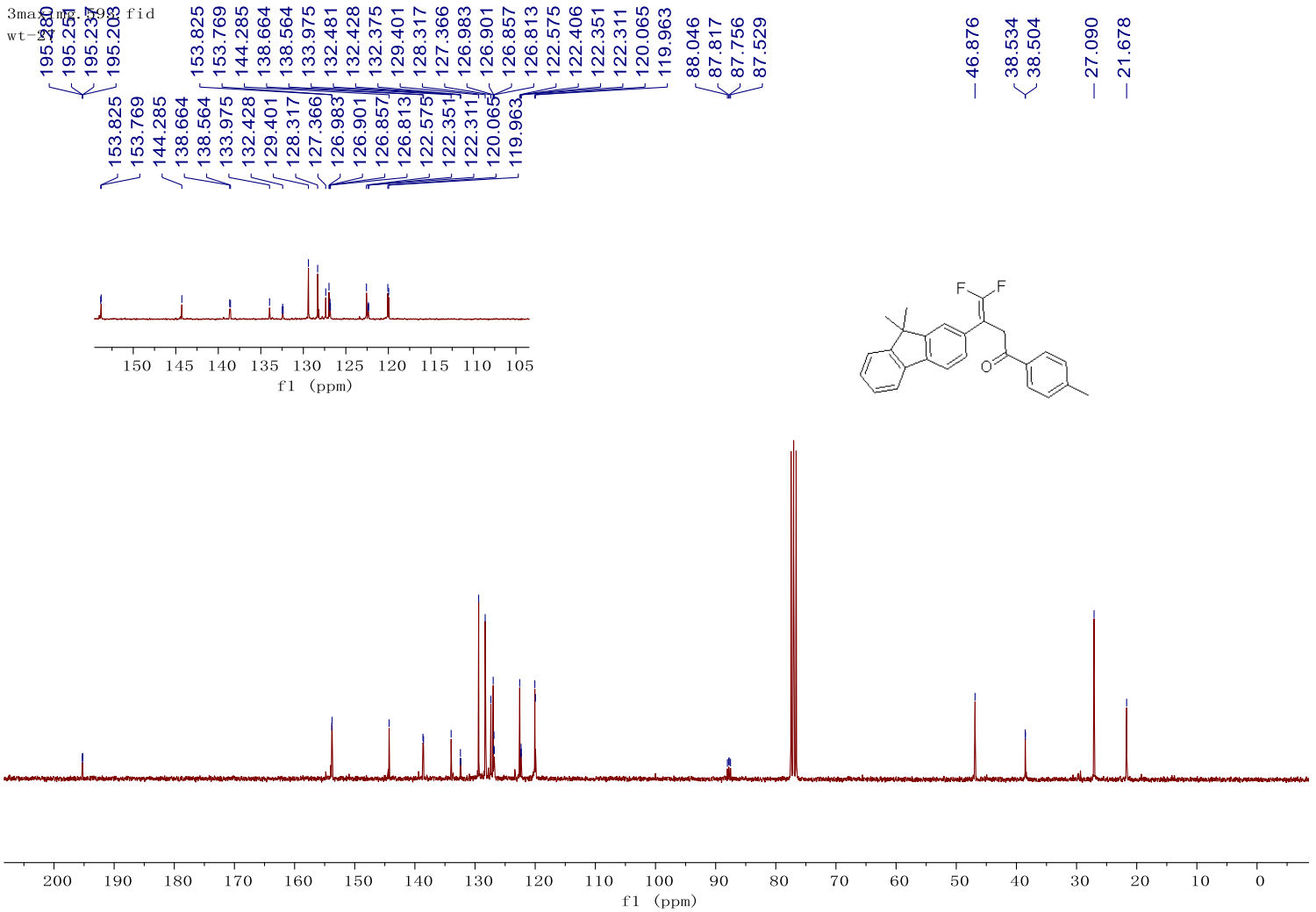
^{13}C NMR Spectrum of Compound 5d (75 MHz, $CDCl_3$)



^{19}F NMR Spectrum of Compound 5d (282 MHz, DMSO)



^{1}H NMR Spectrum of Compound 5e (400 MHz, DMSO)



^{13}C NMR Spectrum of Compound 5e (75 MHz, $CDCl_3$)

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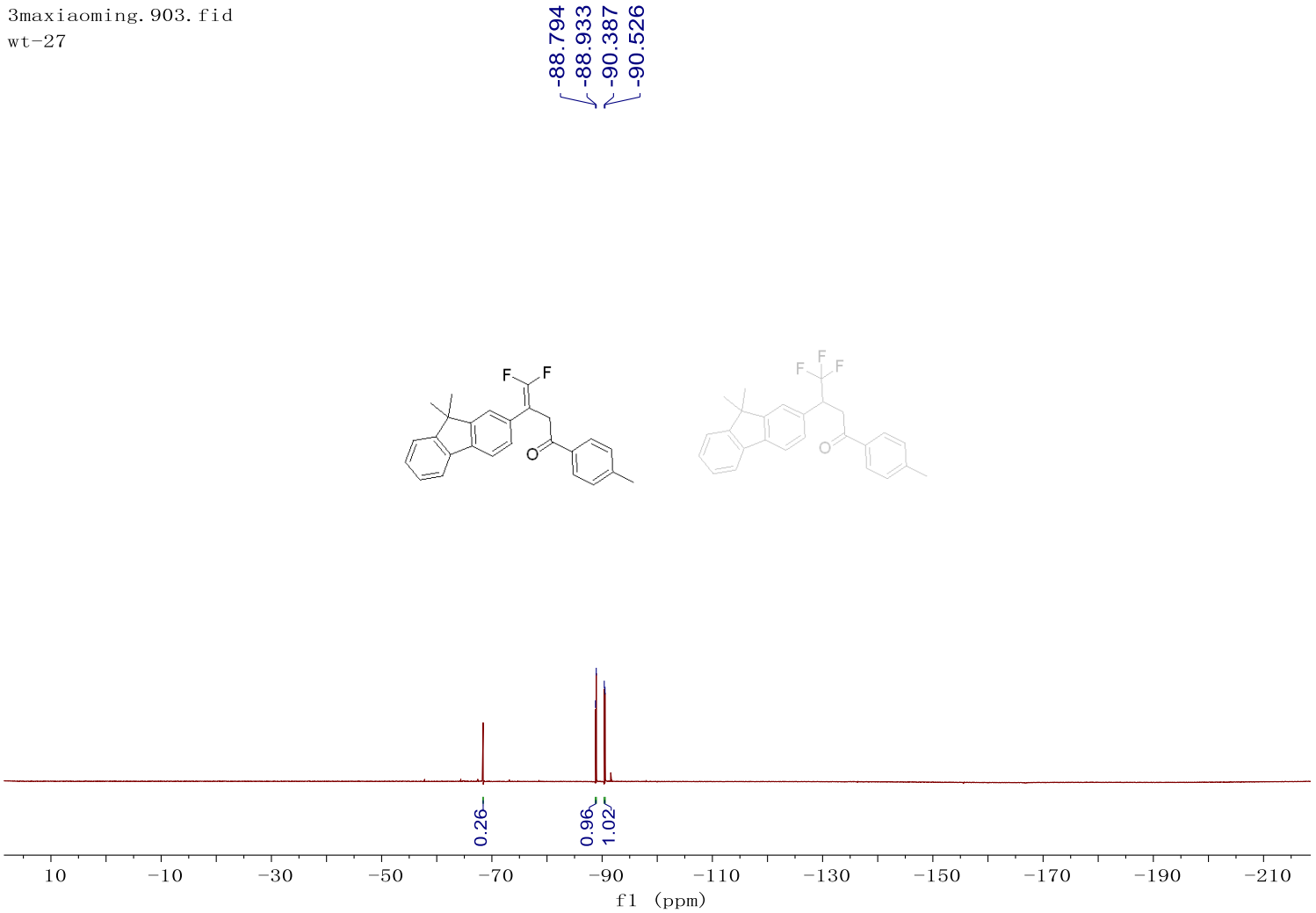
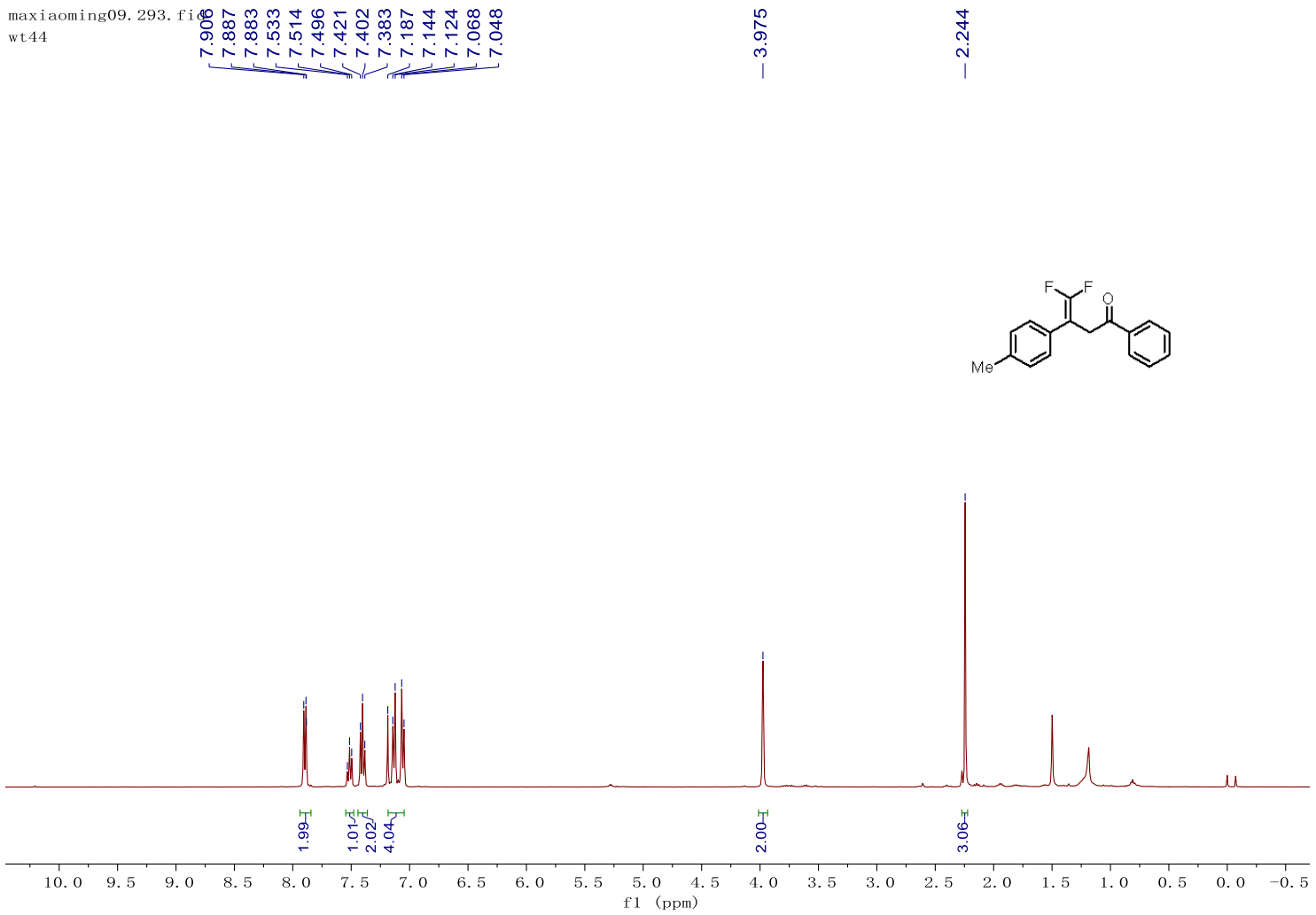
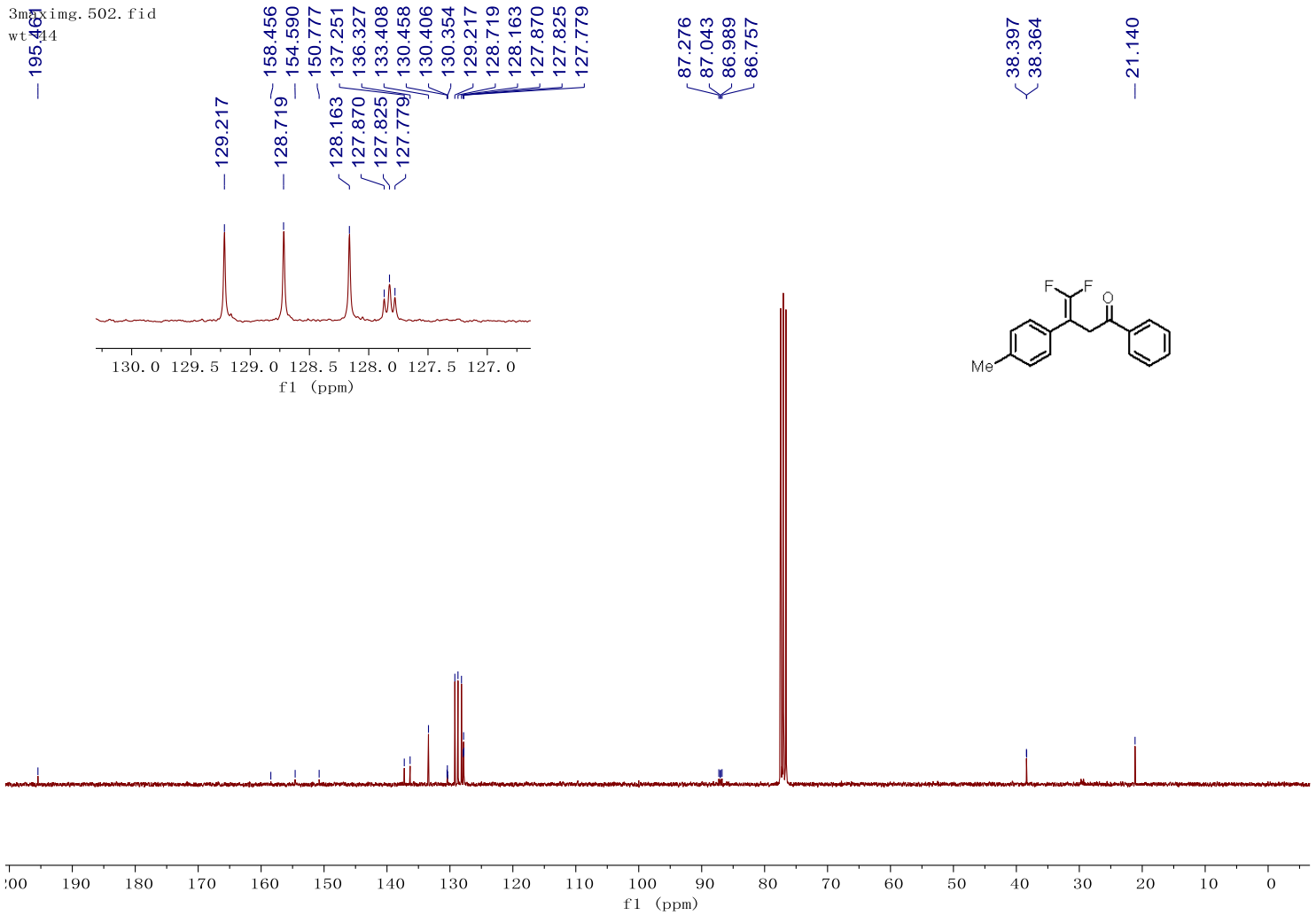


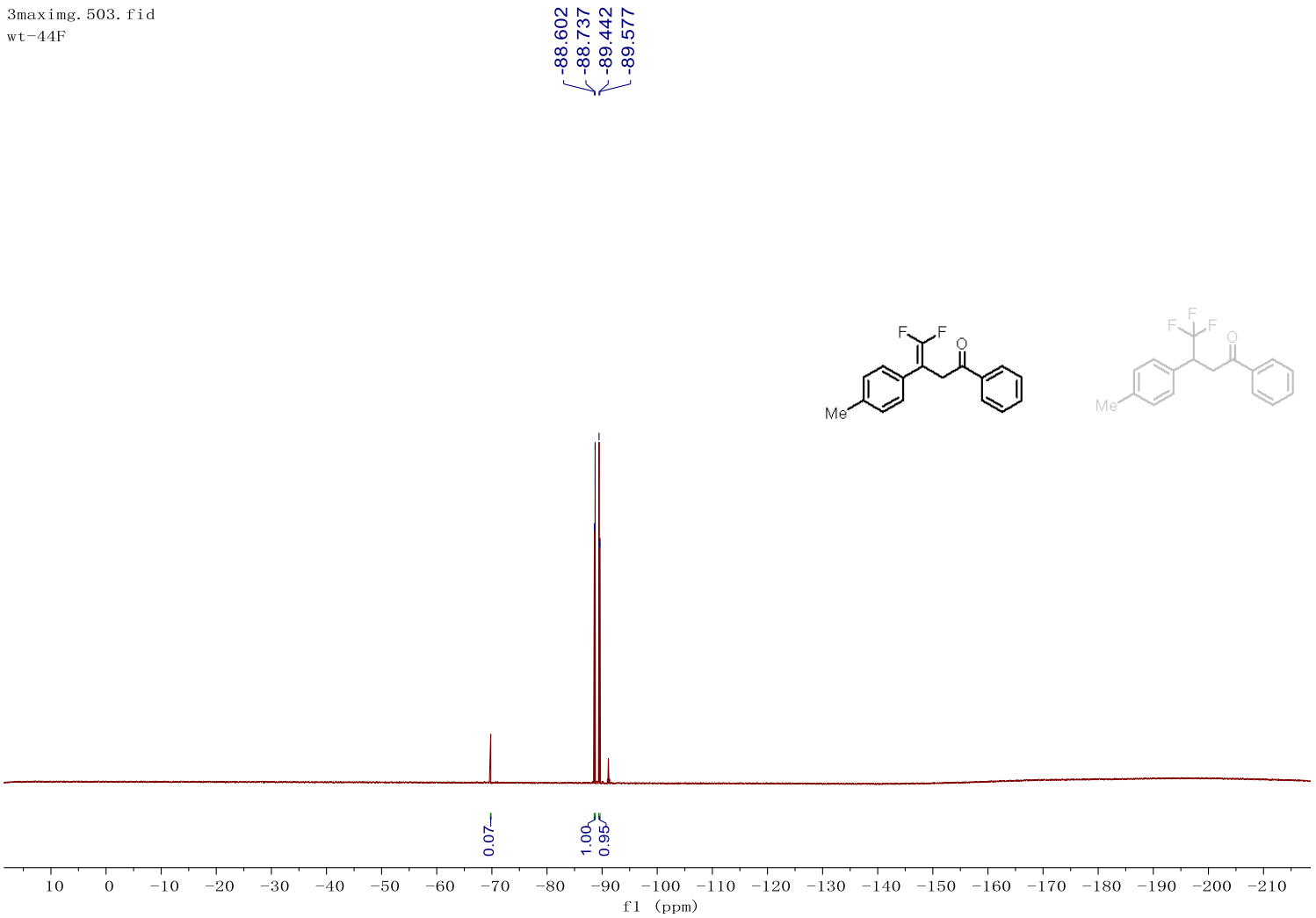
^{19}F NMR Spectrum of Compound 5e (282 MHz, DMSO)



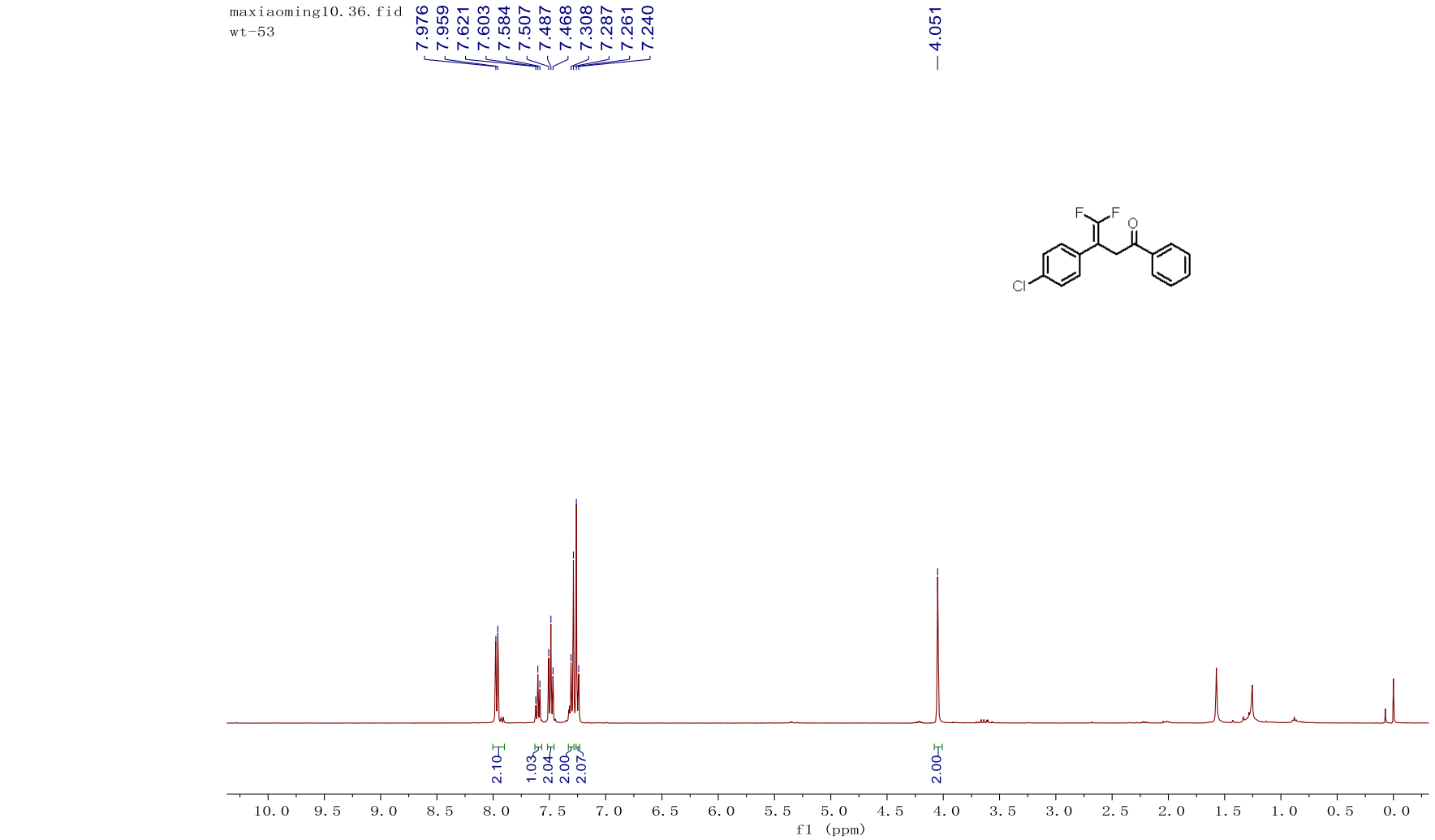
^{1}H NMR Spectrum of Compound 5f (400 MHz, $CDCl_3$)



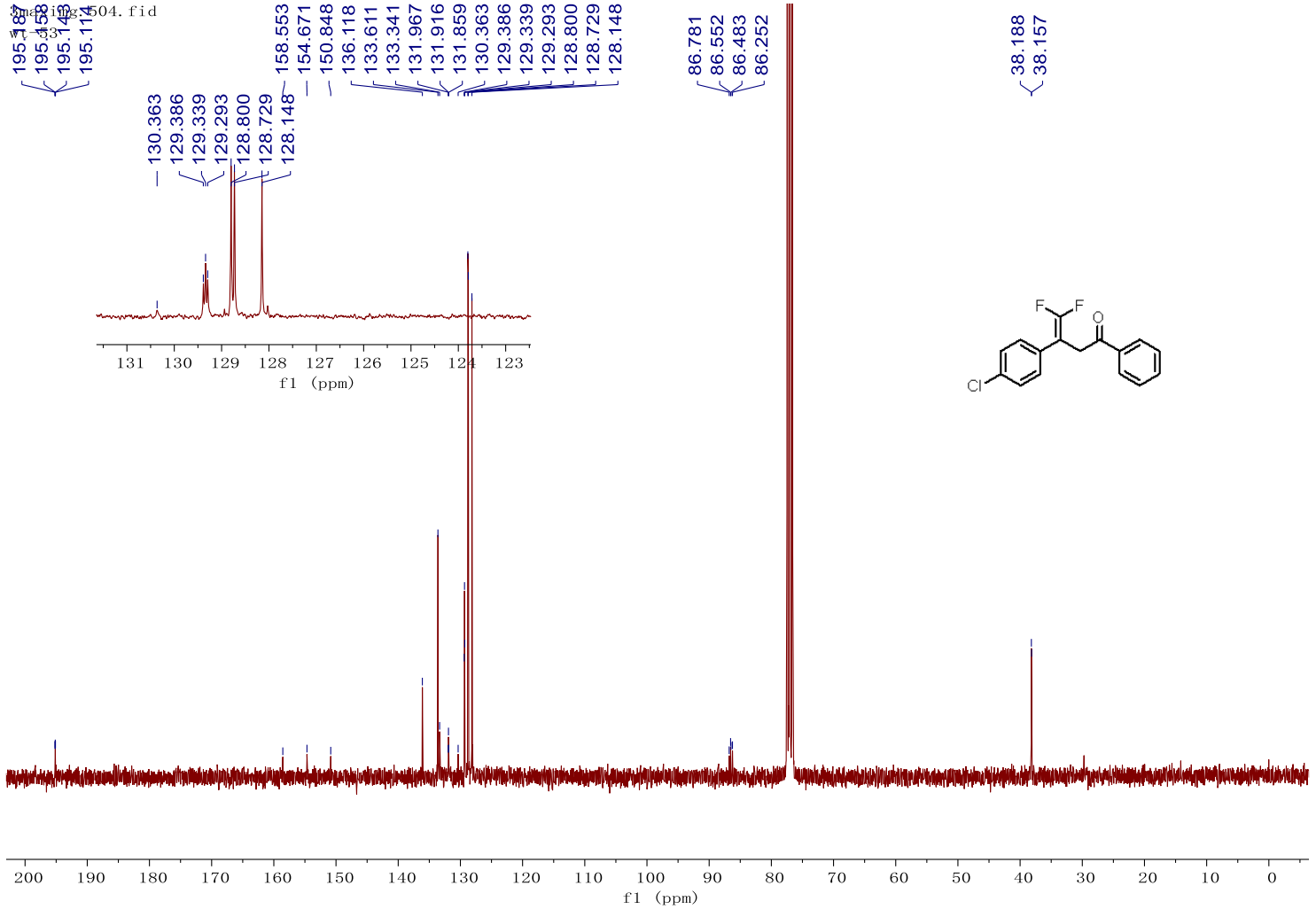
^{13}C NMR Spectrum of Compound 5f (75 MHz, $CDCl_3$)



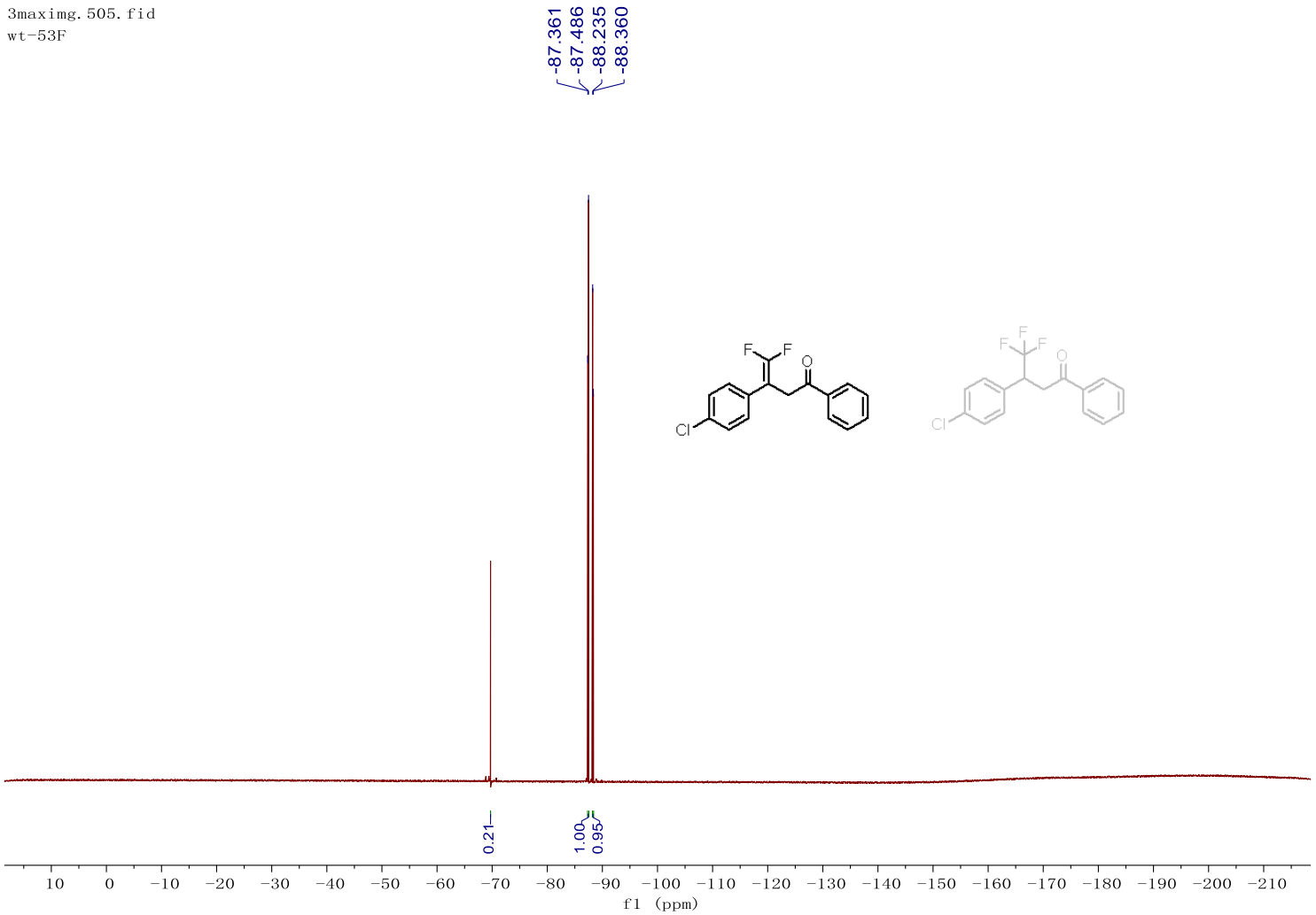
^{19}F NMR Spectrum of Compound 5f (282 MHz, $CDCl_3$)



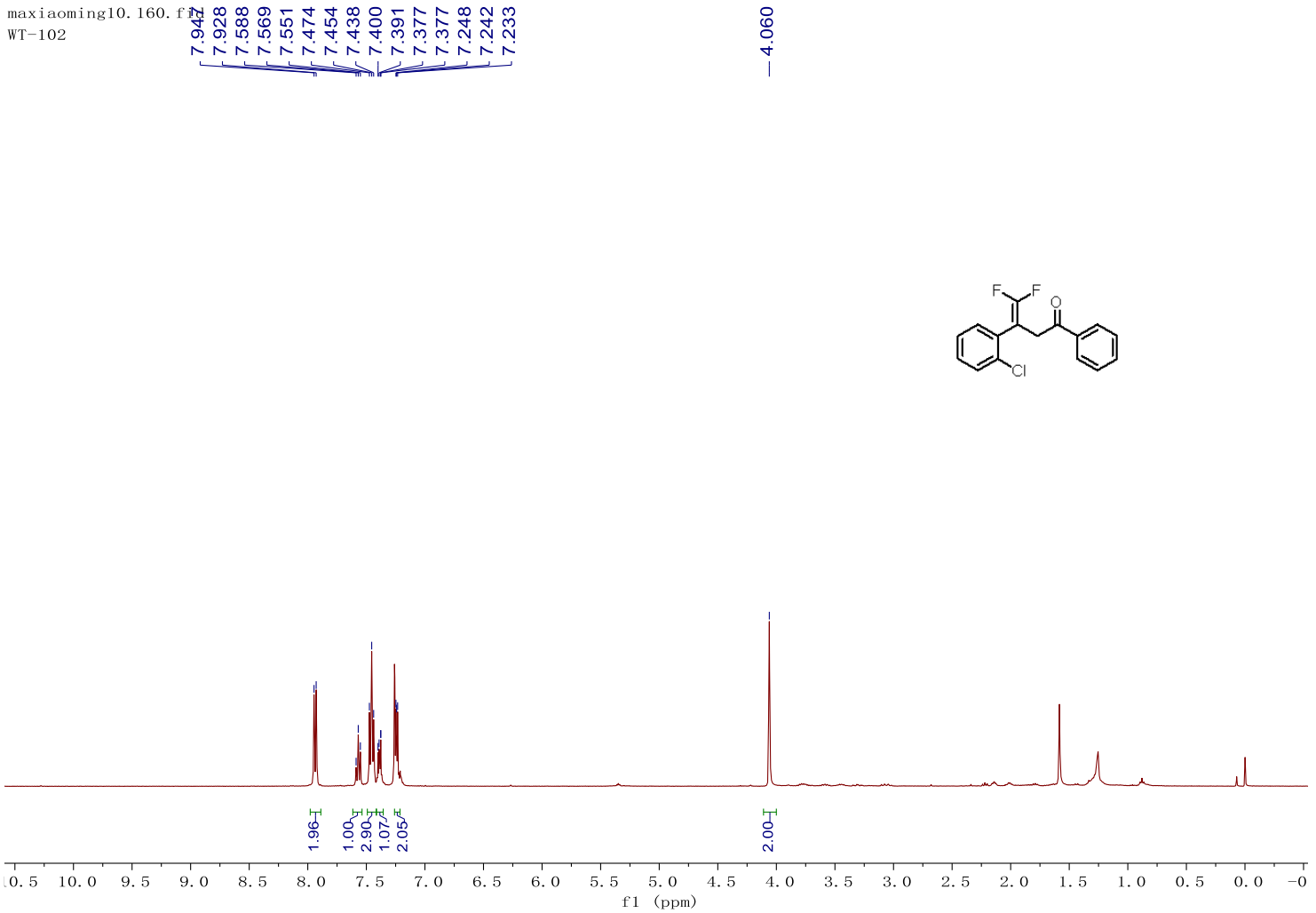
^{1}H NMR Spectrum of Compound 5g (400 MHz, $CDCl_3$)



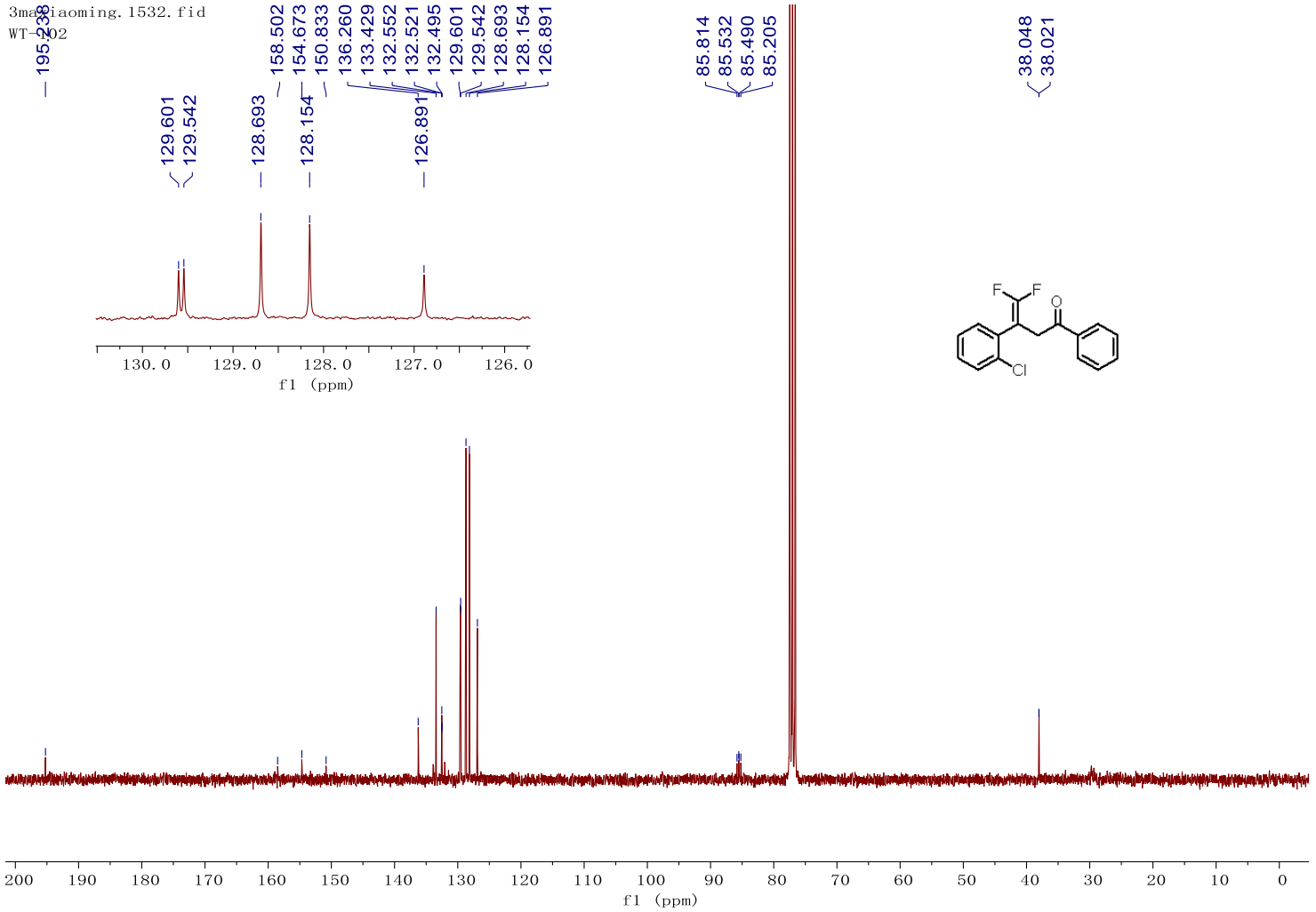
^{13}C NMR Spectrum of Compound 5g (75 MHz, $CDCl_3$)



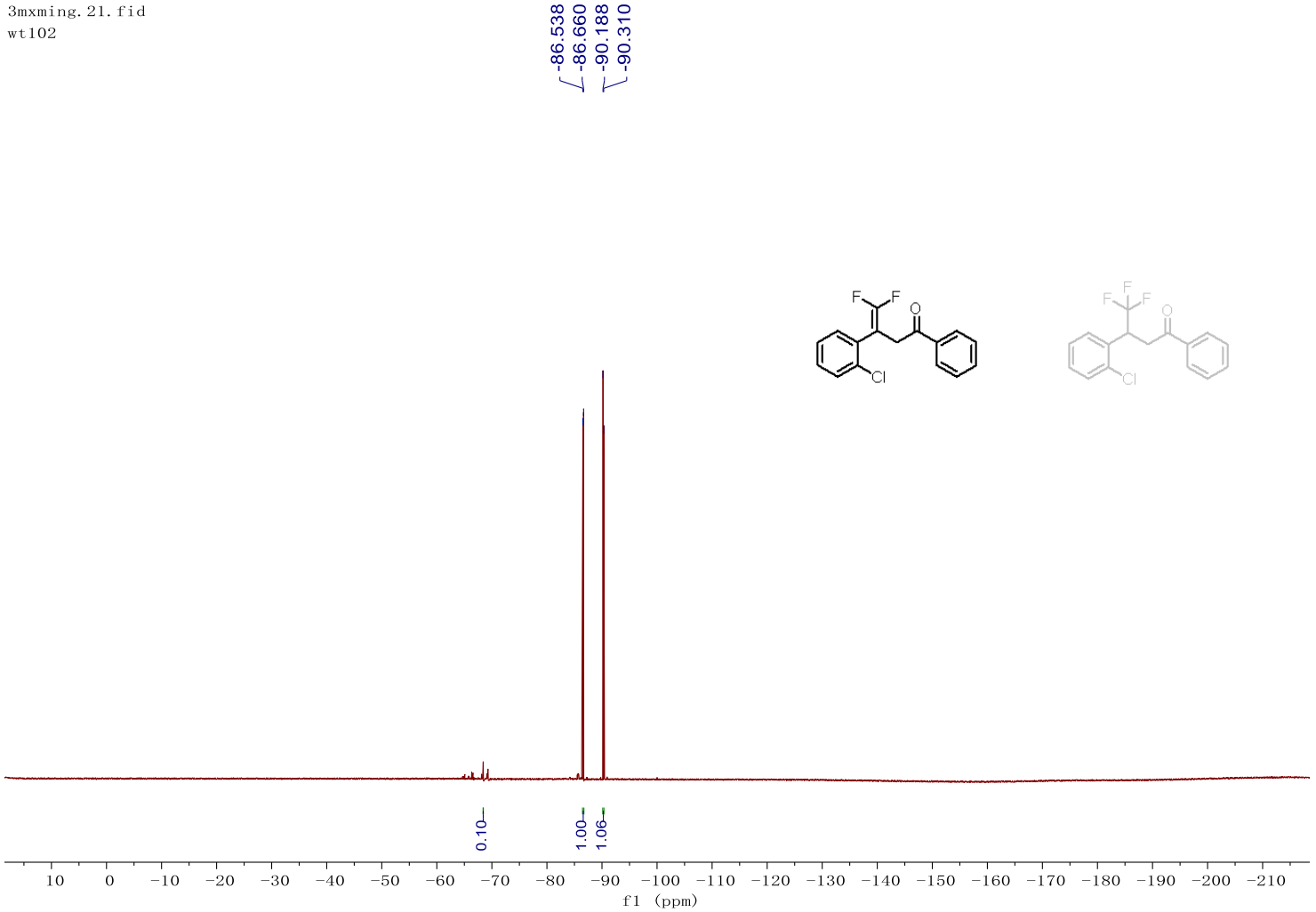
^{19}F NMR Spectrum of Compound 5g (282 MHz, $CDCl_3$)



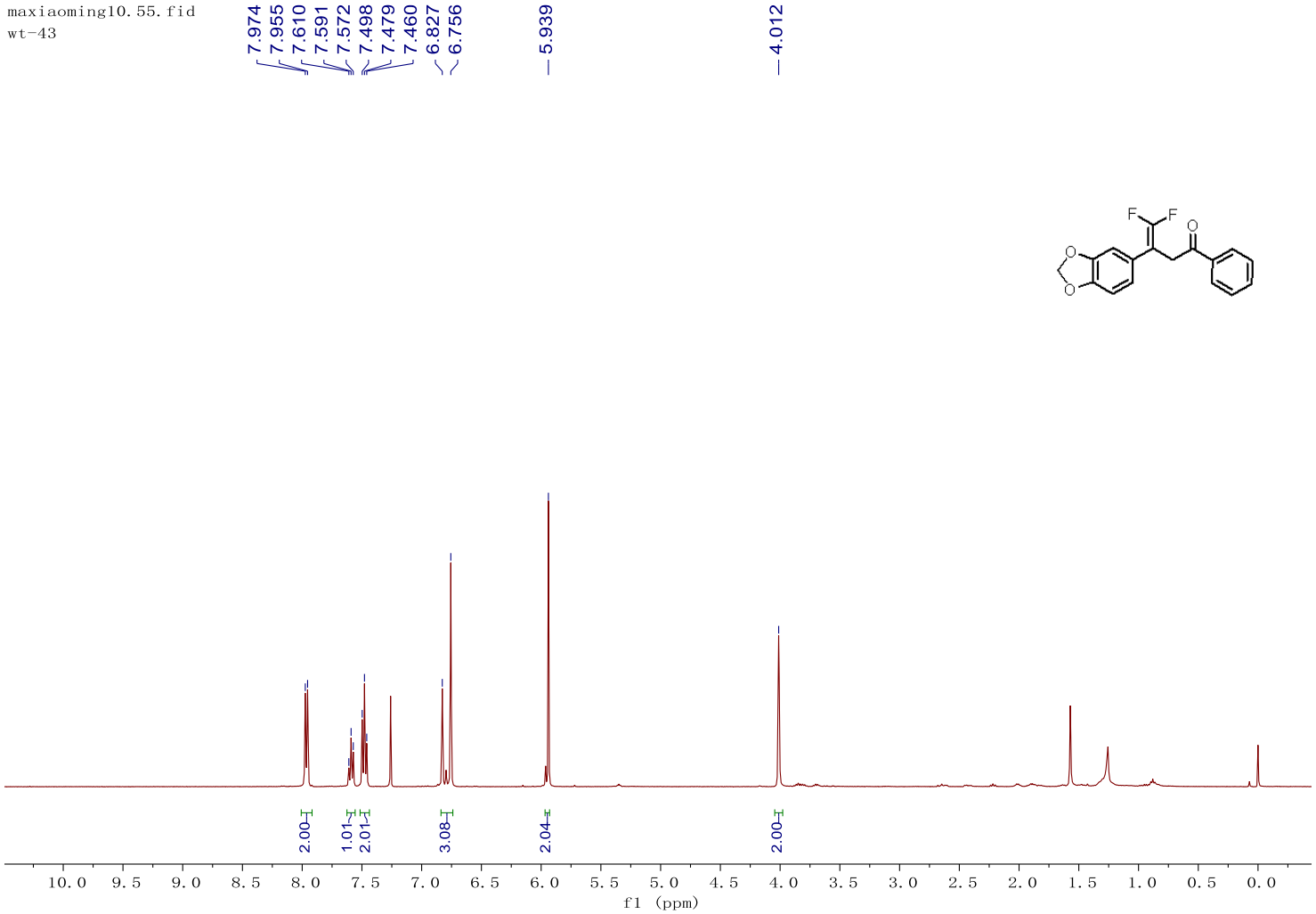
^{1}H NMR Spectrum of Compound 5h (400 MHz, $CDCl_3$)



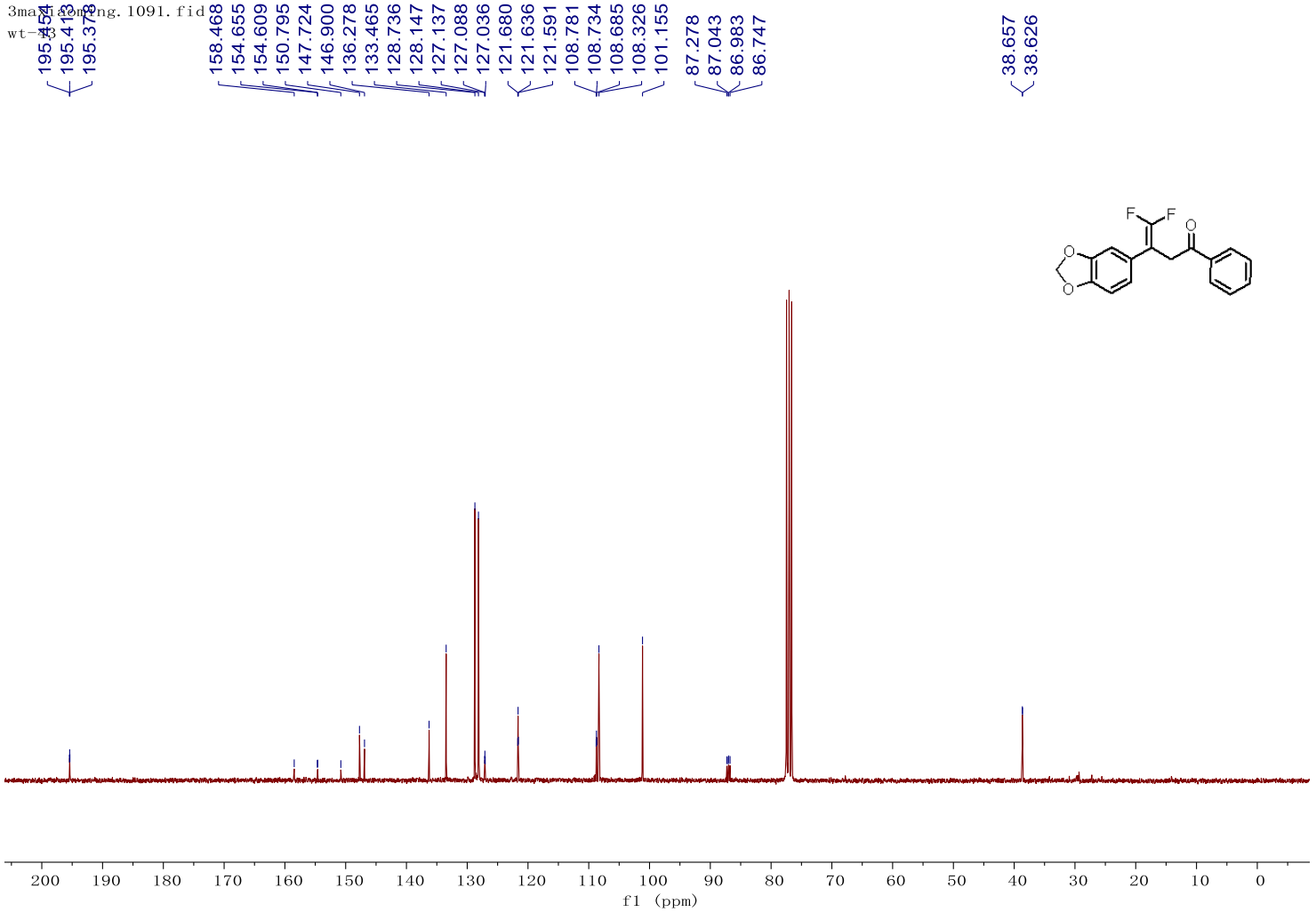
^{13}C NMR Spectrum of Compound 5h (75 MHz, $CDCl_3$)



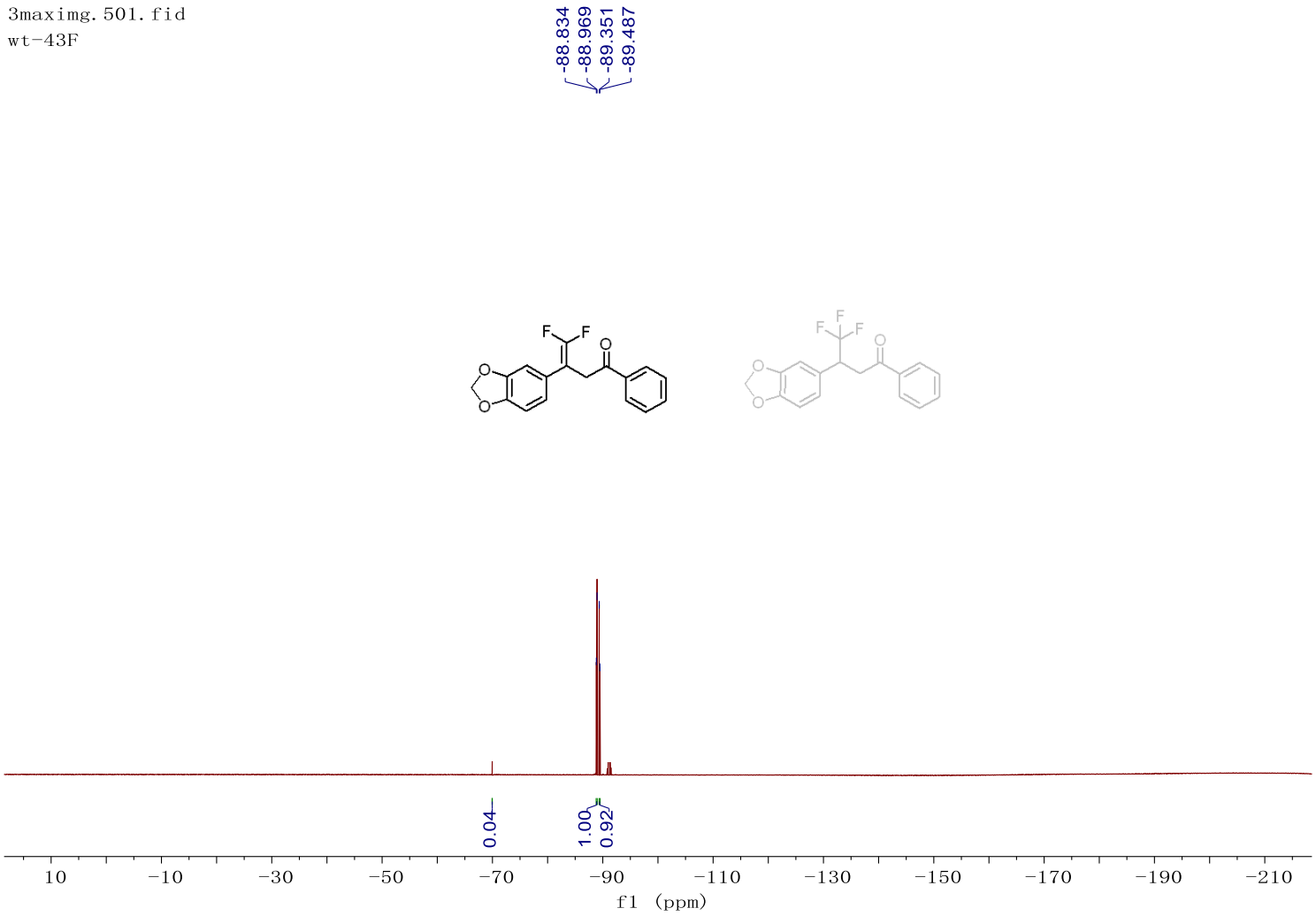
^{19}F NMR Spectrum of Compound 5h (282 MHz, $CDCl_3$)



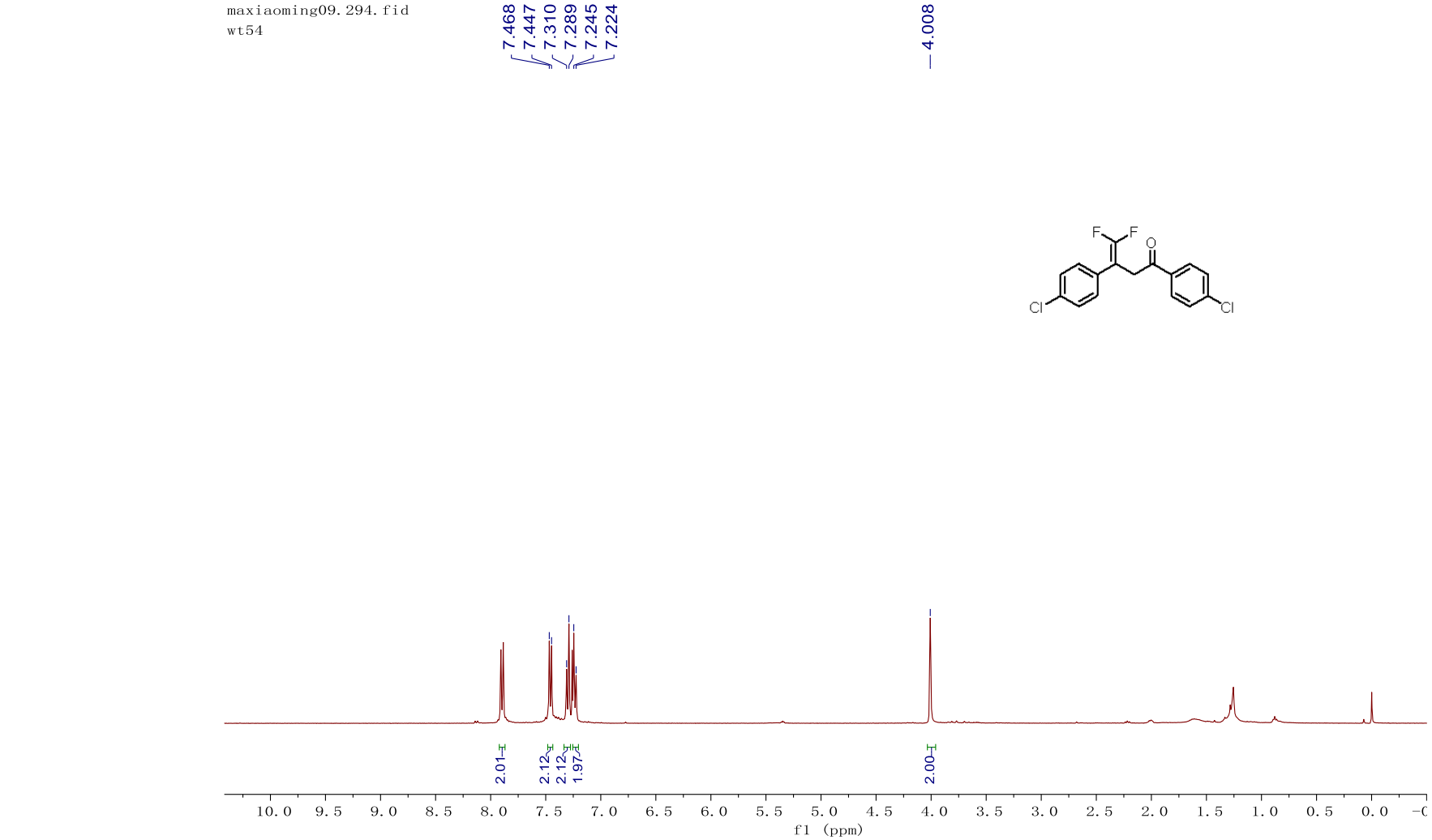
^{1}H NMR Spectrum of Compound 5i (400 MHz, $CDCl_3$)



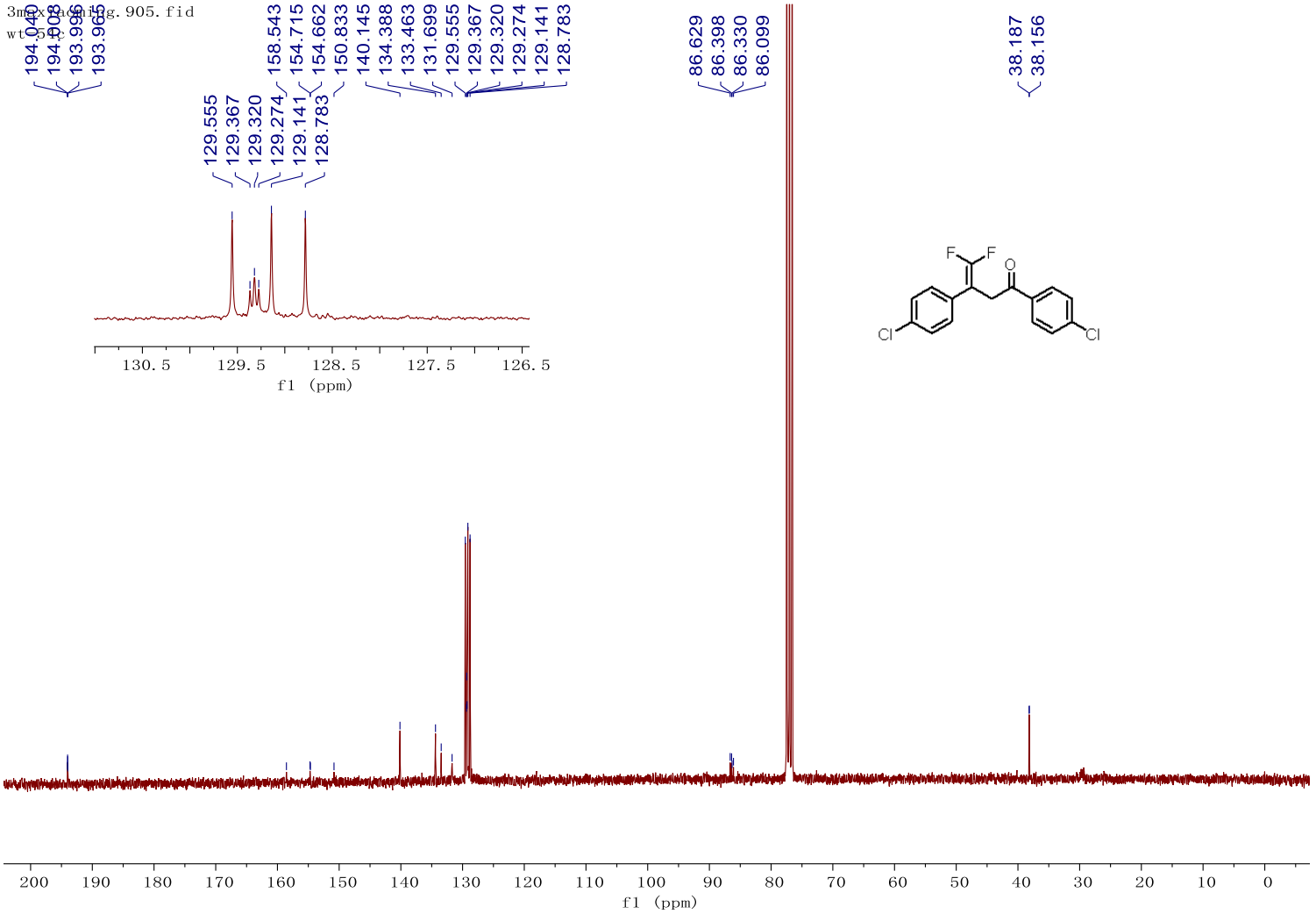
^{13}C NMR Spectrum of Compound 5i (75 MHz, $CDCl_3$)



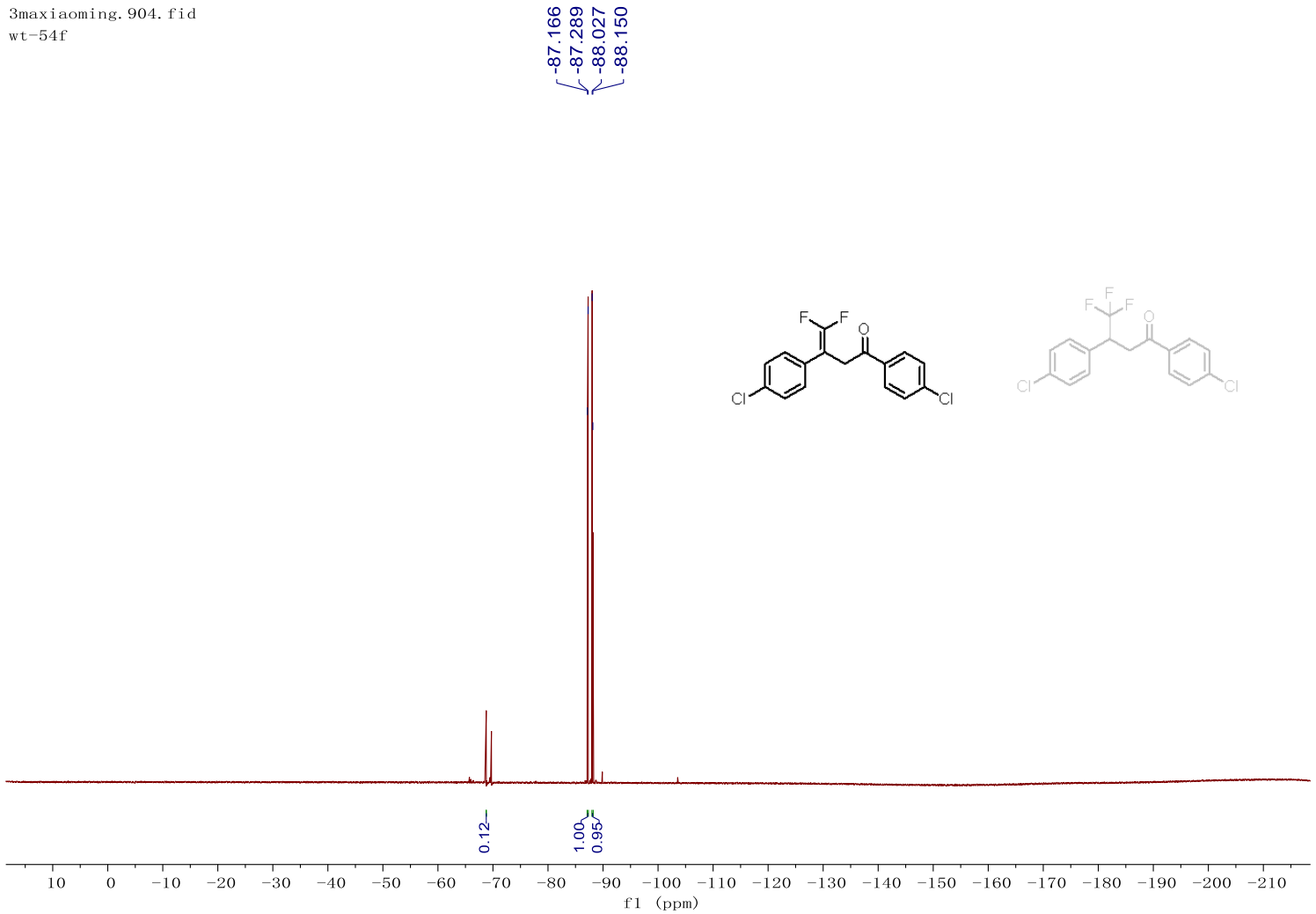
^{19}F NMR Spectrum of Compound 5i (282 MHz, $CDCl_3$)



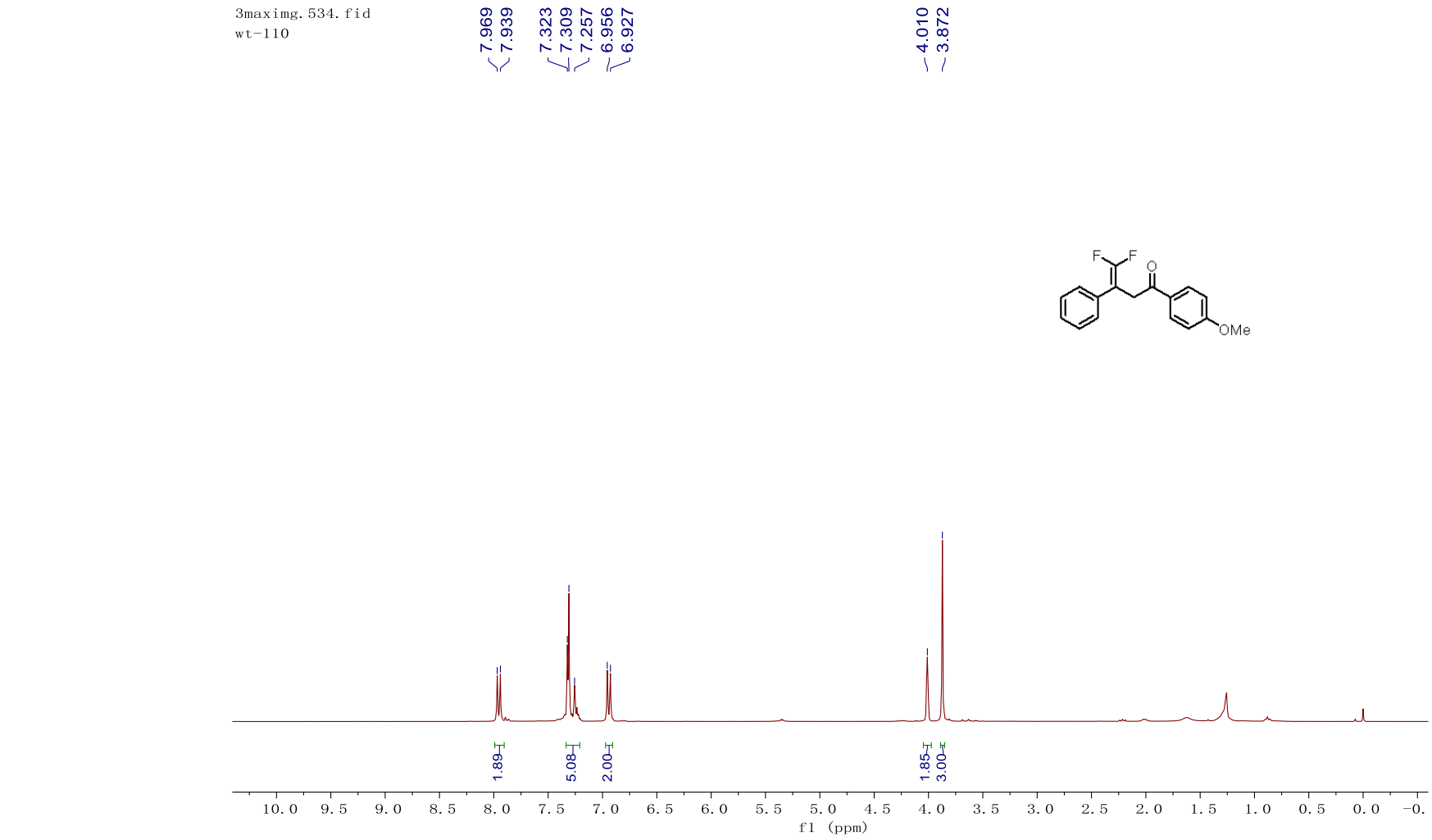
^{1}H NMR Spectrum of Compound 5j (400 MHz, $CDCl_3$)



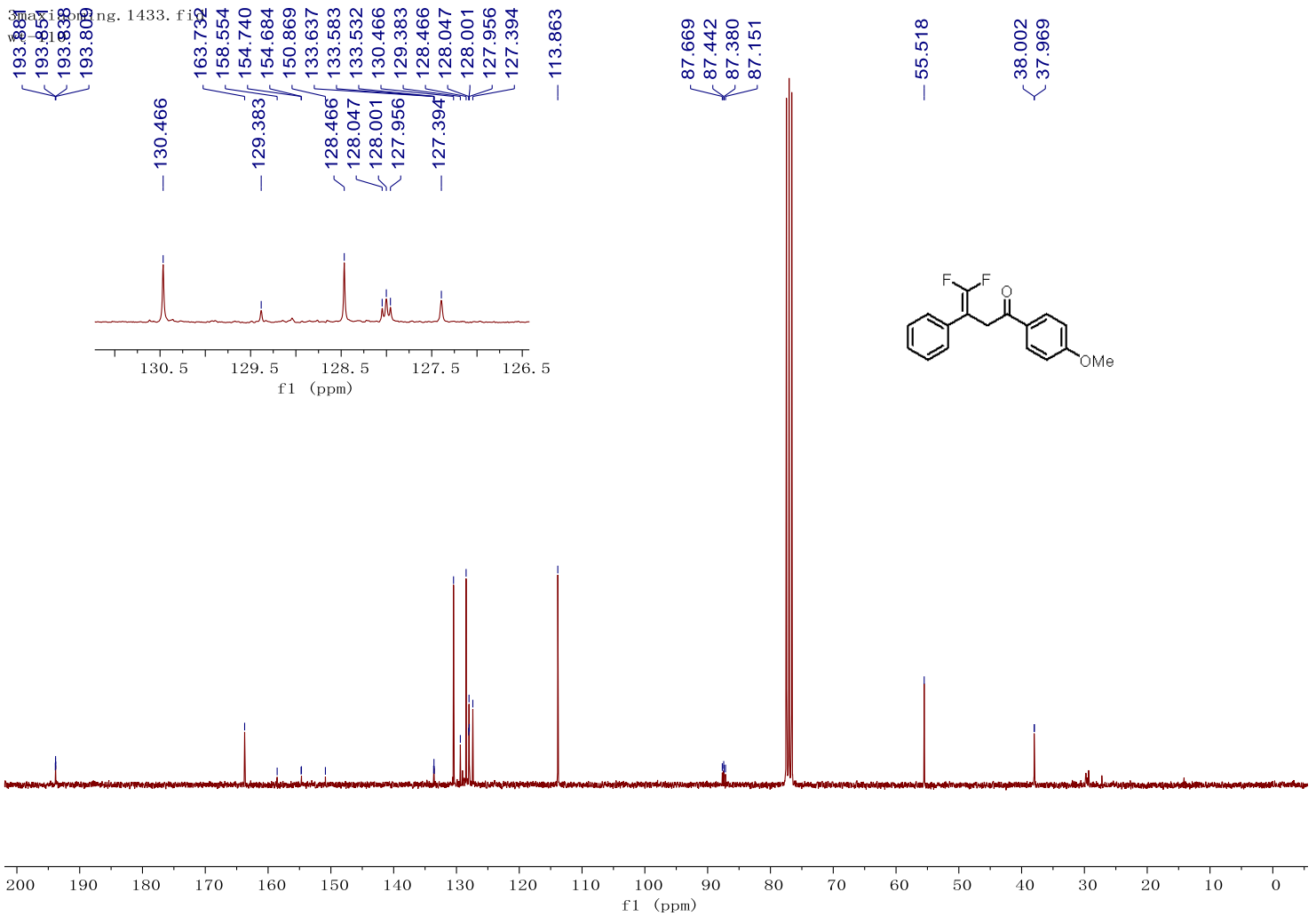
^{13}C NMR Spectrum of Compound 5j (75 MHz, $CDCl_3$)



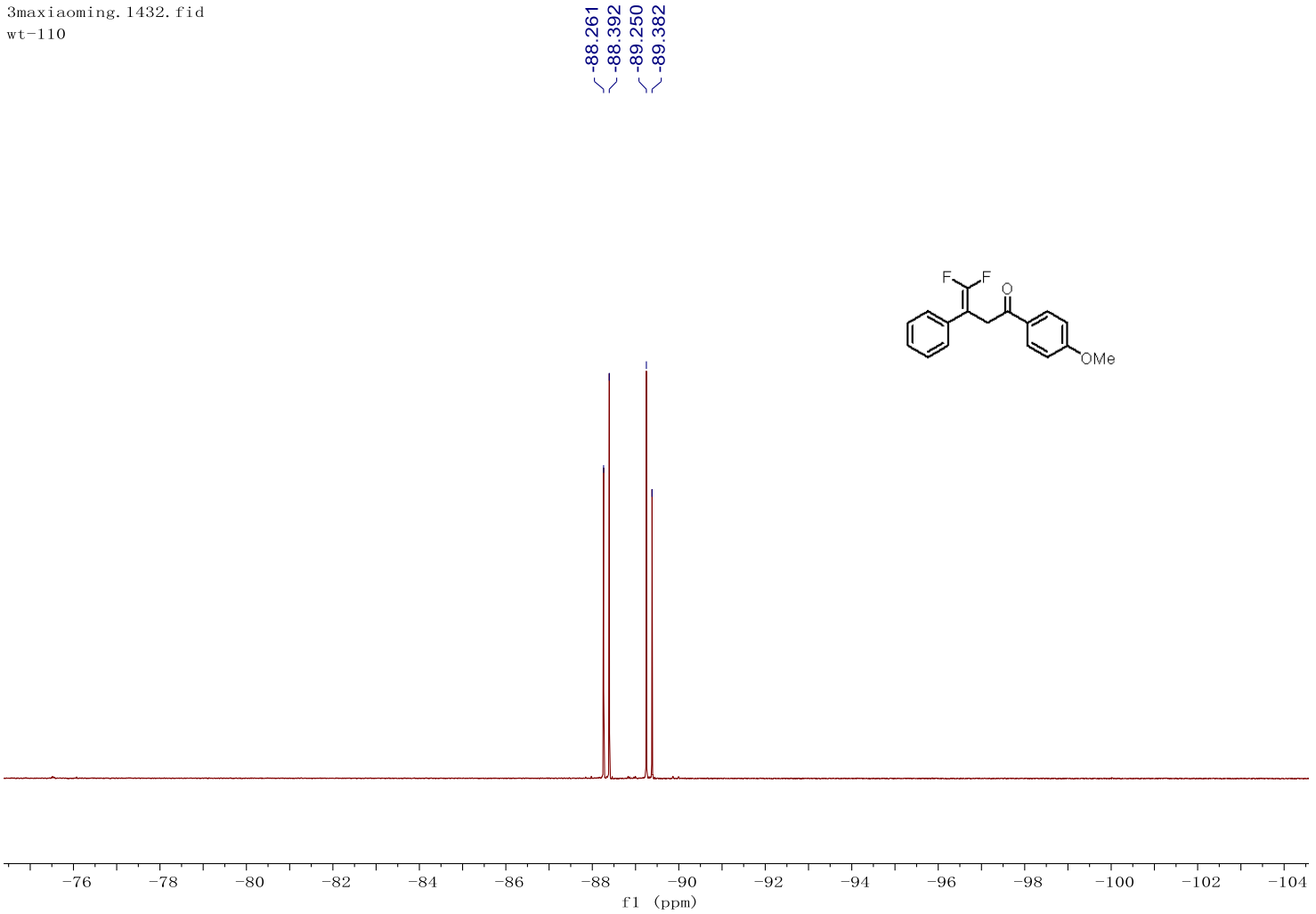
^{19}F NMR Spectrum of Compound 5j (282 MHz, $CDCl_3$)



^{1}H NMR Spectrum of Compound 5k (300 MHz, $CDCl_3$)



^{13}C NMR Spectrum of Compound 5k (75 MHz, $CDCl_3$)



^{19}F NMR Spectrum of Compound 5k (282 MHz, $CDCl_3$