Supporting Information

For

Photoredox-catalyzed Fluorodifluoroacetylation of Alkenes with $FSO_2CF_2CO_2Me$ and $Et_3N{\cdot}3HF$

Song Zou[a], Xuewei Luo[a], Chao Chen[*a], and Chanjuan Xi[*a,b]

[a]MOE Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology, Department of Chemistry, Tsinghua University, Beijing 100084, China.

[b]State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

Email: cjxi@tsinghua.edu.cn.

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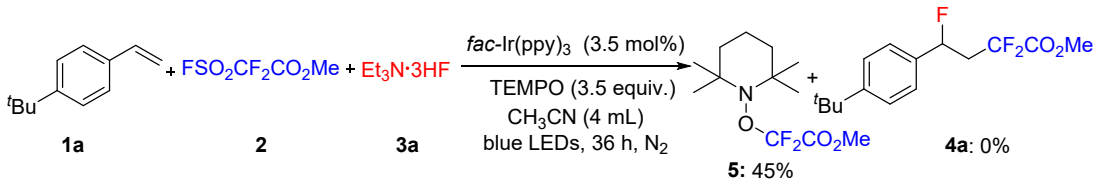
1. General Information

Unless otherwise noted, all the reactions were carried out in oven-dried sealed tube with Teflon-lined-septum under N_2 atmosphere. All materials were obtained from commercial sources and used as received. Super dry acetonitrile with molecular sieves in it was used in the reaction. ^{1}H NMR, ^{13}C{^{1}H}NMR, and ^{19}F NMR spectra were recorded on 400 MHz at ambient temperature with $CDCl_3$ as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (*J*) were given in Hertz (Hz).The term m, q, t, d, and s referred to multiplet, quartet, triplet, doublet, and singlet. The reaction was monitored by GC-MS if applicable. Column chromatography was performed with silica gel (200-300 meshes). Thin layer chromatography (TLC) was visualized using UV light. Fluorescence quenching experiments were measured on an Ahilent Technologies Cary Eclipse Fluorescence Spectrophotometer. High-resolution mass spectra were recorded on electrospray mass spectrometer (ESI-TOF).

2. General Procedures for Synthesis of Products:

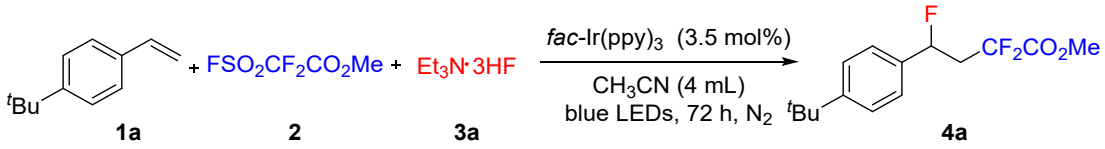
*General procedures for synthesis of products **4**:* A sealed tube equipped with a stirrer bar was charged with 6 mg *fac*-Ir(ppy)$_3$ (3.5 mol%), which was degassed and refilled with N_2 for 3 times. The alkenes **1a-1r** (0.2 mmol, 1.0 equiv.), Chen reagent ($FSO_2CF_2CO_2Me$) (46.1 mg, 0.24 mmol, 1.2 equiv.), $Et_3N{\cdot}3HF$ (193.9 mg, 1.6 mmol, 8.0 equiv.) and dry CH_3CN (4 mL) were added under N_2. The reaction mixture was irradiated for 36 h at room temperature by 3 W blue LEDs. The reaction was quenched by H_2O and the aqueous layer was extracted with ethyl acetate (EA) in twice. The combined organic layer dried by $MgSO_4$ and concentrated in vacuo. The residue was purified by chromatography on silica gel to give product **4a-4r**, which were identified by ^{1}H, ^{13}C, and ^{19}F NMR.

3. Control Experiment with TEMPO



A sealed tube equipped with a stirrer bar was charged with 6 mg *fac*-Ir(ppy)$_3$ (3.5 mol%) and TEMPO (109.2 mg, 0.7 mmol, 3.5 equiv.), which was degassed and refilled with N_2 for 3 times. 1-(*tert*-Butyl)-4-vinylbenzene **1a** (0.2 mmol, 1.0 equiv.), Chen reagent ($FSO_2CF_2CO_2Me$) (46.1 mg, 0.24 mmol, 1.2 equiv.), $Et_3N{\cdot}3HF$ (193.9 mg, 1.6 mmol, 8.0 equiv.) and dry CH_3CN (4 mL) were added under N_2. The mixture was irradiated for 36 h at room temperature by 3 W blue LEDs. The reaction was quenched by H_2O and the aqueous layer was extracted with ethyl acetate (EA) in twice. The combined organic layer dried by Na_2SO_4 and concentrated in vacuo and the residue was purified by chromatography on silica gel to afford product **5** in 45% isolated yield.

4. Control Experiment of the Turn on and off the Light



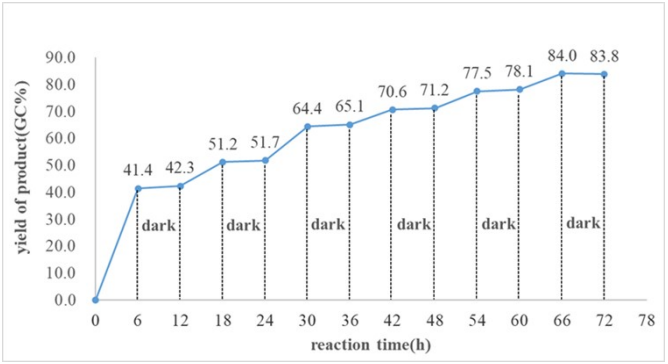


Fig S1. The experiment of turn on and off the light

To insight on reaction mechanism, an oven-dried Schleck tube charged with 6 mg *fac*-Ir(ppy)$_3$ (3.5 mol%), which was degassed and refilled with N_2 for 3 times. 1-(*tert*-butyl)-4-vinylbenzene **1a** (32.1 mg, 0.2 mmol, 1.0 equiv.), dodecane (34.0 mg 0.2 mmol, 1.0 equiv.), $FSO_2CF_2CO_2Me$ (46.1 mg, 0.24 mmol, 1.2 equiv.), $Et_3N{\cdot}3HF$ (193.9 mg, 1.6 mmol, 8.0 equiv.) and dry CH_3CN (4mL) were added under N_2. The mixture

was alternately irradiated with 3 W blue LEDs and set in dark totally for 72 h. The yield of **4a** was confirmed by GC analysis of the crude sample using dodecane as internal standard.

5. Fluorescence Quenching Experiments

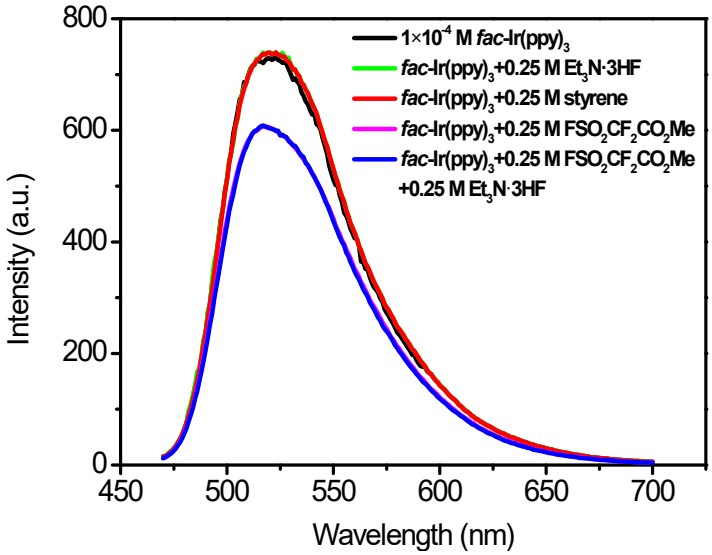
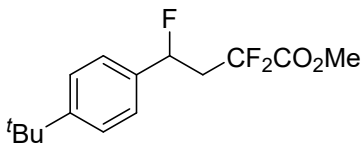


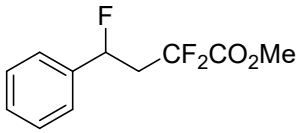
Fig S2. Fluorescence quenching experiment between photocatalyst and substrate

Fluorescence quenching experiments were measured on an Ahilent Technologies Cary Eclipse Fluoresence Spectrophotometer. The complex *fac*-Ir(ppy)$_3$ was excited at 375 nm and the emission spectrum max = 518 nm was recorded. Gradient dilution to get 1.0 x 10^{-4} M *fac*-Ir(ppy)$_3$ solution in CH_3CN, 0.25 M $FSO_2CF_2CO_2Me$ (**2**) solution in CH_3CN and 0.25 M styrene (**1b**) solution in CH_3CN, 0.25 M $Et_3N{\cdot}3HF$ (**3a**) solution in CH_3CN, 2.0 mL 1.0 x 10^{-4} M *fac*-Ir(ppy)$_3$ solution in CH_3CN and a stirrer bar were added into the 2.0 mL quartz cuvette covered with Teflon cap. 1.0 x 10^{-2} mL 0.25 M $FSO_2CF_2CO_2Me$ solution, 0.25 M styrene (**1b**) solution, 0.25 M $Et_3N{\cdot}3HF$ (**3a**) solution were added, separately. And then, the emission spectrum of the solution was collected at each addition.

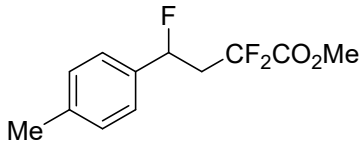
6. Spectral Data for All Products



Methyl 4-(4-(*tert*-butyl)phenyl)-2,2,4-trifluorobutanoate (4a): colorless oil liquid, 46.7 mg (81% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.27 (dd, *J* = 8.2, 1.1 Hz, 2H), 5.71 (ddd, *J* = 48.0, 9.9, 2.6 Hz, 1H), 3.84 (s, 3H), 3.19 – 2.79 (m, 1H), 2.72 – 2.37 (m, 1H), 1.32 (s, 9H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 164.3 (t, *J* = 32.3 Hz), 152.5, 135.2, 135.0, 125.8, 125.6, 125.6, 117.0 –112.0 (m), 89.5 – 87.8 (m), 53.6, 42.4 (q, *J* = 23.9 Hz), 34.8, 31.37. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.6 (dt, *J* = 23.8, 12.3 Hz), -105.0 – -110.5 (m), -167.1 – -175.3 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{15}H_{20}F_3O_2^+$ 289.1410, found 289.1412.

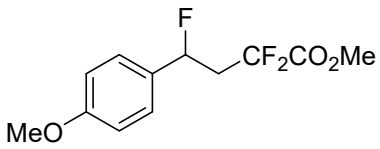


Methyl 2,2,4-trifluoro-4-phenylbutanoate (4b): colorless oil liquid, 34.3 mg (74% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.9-7.8 (m, 4H), 7.52 – 7.51 (m, 2H), 7.44 7.42 (m, 1H), 7.38-7.32 (m, 3H), 7.28 – 7.25 (m, 1H), 5.76 (ddd, *J* = 46.0, 8.0, 2.4 Hz, 1H), 3.85 (s, 3H), 3.03 – 2.92 (m, 1H), 2.68 – 2.56 (m, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 164.3 (t, *J* = 30.5 Hz), 135.5, 135.3, 133.6, 133.1, 129.0, 128.3, 127.9, 126.9, 126.8, 125.1, 122.8, 117.0-112.0 (m), 89.8 – 88.0 (m), 53.7, 42.5 (q, *J* = 22.0 Hz). ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.5 (dt, *J* = 24.5, 11.6 Hz), -106.5 – -107.3 (m), -174.2 – -174.4 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{11}H_{12}F_3O_2^+$ 233.0784, found 233.0785.

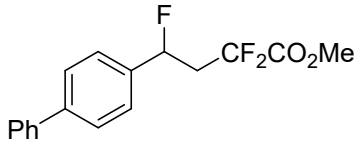


Methyl 2,2,4-trifluoro-4-(*p*-tolyl)butanoate (4c): colorless oil liquid, 41.3 mg (84% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.23 – 7.18 (m, 4H), 5.68 (ddd, *J* = 49.0, 10.5, 2.8 Hz, 1H), 3.84 (s, 3H), 2.96 – 2.83 (m, 1H), 2.59 – 2.43 (m, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 164.2 (t, *J* = 28.0 Hz), 139.2, 135.2, 135.0, 129.5, 125.8, 125.7, 117.0-112.0 (m), 89.5 – 87.8 (m), 53.6, 42.4 (q, *J* = 21.5 Hz), 21.3. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.5 (dt, *J* = 26.0,

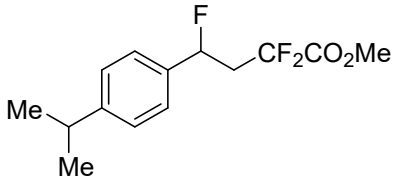
10.0 Hz), -106.7 – -107.4 (m), -172.2 – -172.4 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{12}H_{14}F_3O_2^+$ 247.0940, found 247.0939.



Methyl 2,2,4-trifluoro-4-(4-methoxyphenyl)butanoate (4d): colorless oil liquid, 36.7 mg (70% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.27 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 5.67 (ddd, *J* = 46.0, 8.0, 2.5 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.98 – 2.83 (m, 1H), 2.59 – 2.40 (m, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 164.2 (t, *J* = 30.0 Hz), 160.4, 130.1, 129.9, 127.5, 127.5, 114.2, 116.0-113.0 (m), 89.4 – 87.7 (m), 55.4, 53.6, 42.3 (q, *J* = 18.0 Hz). ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.6 (dt, *J* = 28.0, 11.5 Hz), -106.7 – -107.5 (m), -168.5 – -168.8 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{12}H_{14}F_3O_3^+$ 263.0890, found 263.0891.

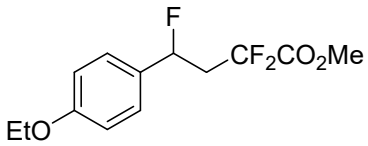


Methyl 4-([1,1'-biphenyl]-4-yl)-2,2,4-trifluorobutanoate (4e): colorless oil liquid, 56.1 mg (91% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.62 – 7.57 (m, 4H), 7.46 – 7.34 (m, 5H), 5.78 (ddd, *J* = 42.5, 11.0, 2.8 Hz, 1H), 3.86 (s, 3H), 3.03 – 2.85 (m, 1H), 2.66 – 2.47 (m, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ164.2 (t, *J* = 28.0 Hz), 142.3, 140.4, 137.1, 136.9, 129.0, 127.8, 127.6, 127.3, 126.2, 126.1, 116.9-111.9 (m), 89.4 – 87.7 (m), 53.7, 42.6 (q, *J* = 18.0 Hz). ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.5 (dt, *J* = 30.2, 10.0 Hz), -106.6 – -107.4 (m), -173.9 – -174.1 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{17}H_{16}F_3O_2^+$ 309.1097, found 309.1095.

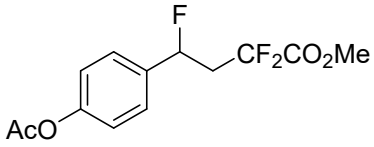


Methyl 2,2,4-trifluoro-4-(4-isopropylphenyl)butanoate (4f): colorless oil liquid, 44.9 mg (82% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.24 (d, *J* = 4.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.70 (ddd, *J* = 48.5, 10.0, 2.0 Hz, 1H), 3.86 (s, 3H), 2.94 – 2.88 (m, 1H), 2.48 (d, *J* = 4.0 Hz, 2H), 1.89 – 1.82 (m, 1H), 0.90 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ

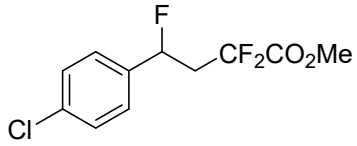
164.3 (t, J = 26.0 Hz), 143.1, 143.0, 135.5, 129.6, 125.7, 125.6, 117.0, 114.5-112.0 (m), 89.6 – 87.8 (m), 53.6, 45.2, 42.4 (q, J = 18.0 Hz), 30.3, 22.4. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.6 (dt, J = 28.5, 8.0 Hz), -106.7 – -107.5 (m), -172.2 – -172.4 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{14}H_{18}F_3O_2^+$ 275.1253, found 275.1254.



Methyl 4-(4-ethoxyphenyl)-2,2,4-trifluorobutanoate (4g): colorless oil liquid, 38.6 mg (70% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.27 – 7.24 (m, 2H), 6.89 (d, J = 8.0 Hz, 2H), 5.66 (ddd, J = 49.0, 11.5, 2.0 Hz, 1H), 4.05 – 4.00 (m, 2H), 3.84 (s, 3H), 2.95 – 2.89 (m, 1H), 2.59 – 2.43 (m, 1H), 1.42 – 1.39 (m, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 164.2 (t, J = 28.0 Hz), 159.8, 129.9, 129.7, 127.5, 127.5, 117.0 – 112.0 (m), 114.4, 89.4 – 87.7 (m), 63.6, 53.6, 42.7 (q, J = 20.5 Hz). ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.6 (dt, J = 30.5, 9.0 Hz), -106.7 – -107.6 (m), -168.3 – -168.5 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{13}H_{16}F_3O_3^+$ 277.1046, found 277.1048.

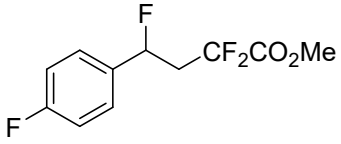


Methyl 4-(4-acetoxyphenyl)-2,2,4-trifluorobutanoate (4h): colorless oil liquid, 35.4 mg (61% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.36 (d, J = 8.0 Hz, 2H), 7.13 (d, J =8.0 Hz, 2H), 5.75 (ddd, J = 49.0, 11.5, 2.4 Hz, 1H), 3.86 (s, 3H), 3.48 (d, J = 11.0 Hz, 1H), 2.95 – 2.80 (m, 1H), 2.62 – 2.43 (m, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 169.5, 169.4, 164.1 (t, J = 28.0 Hz), 151.0 (t, J = 20.0 Hz), 137.4, 135.7, 135.5, 127.6, 127.4, 127.0, 126.9, 122.2, 122.0 – 114.3 (m), 89.0 – 87.3 (m), 53.7, 50.7, 42.9 – 42.1 (m), 41.2 – 40.7 (m), 21.2. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.6 (dt, J = 29.0, 10.0 Hz), -106.7 – -107.5 (m), -172.2 – -172.4 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{13}H_{14}F_3O_4^+$ 291.0839, found 291.0837.

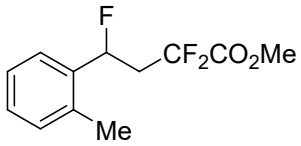


Methyl 4-(4-chlorophenyl)-2,2,4-trifluorobutanoate (4i): colorless oil liquid, 31.9 mg (60% yield). ^{1}H NMR

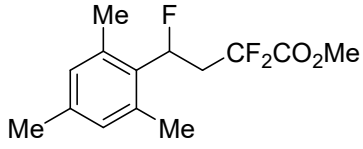
(400 MHz, CHLOROFORM-D) δ 7.38 – 7.35 (m, 2H), 7.30 – 7.25 (m, 2H), 5.70 (ddd, *J* = 49.0, 11.0, 2.5 Hz, 1H), 3.87 (s, 3H), 2.92 – 2.80 (m, 1H), 2.59 – 2.4 (m, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 164.6 (t, *J* = 28.0 Hz), 129.2, 129.0, 127.6, 127.1, 127.0, 88.9 – 87.1 (m), 53.7, 42.3 (q, *J* = 15.0 Hz). ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.5 (dt, *J* = 30.2, 9.0 Hz), -106.6 – -107.4 (m), -174.7 – -175.0 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{11}H_{11}ClF_3O_2^+$ 267.0394, found 267.0393.



Methyl 2,2,4-trifluoro-4-(4-fluorophenyl)butanoate (4j): colorless oil liquid, 29.0 mg (58% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.34 – 7.32 (m, 2H), 7.11 – 7.06 (m, 2H), 5.72 (ddd, *J* = 49.0, 11.5, 2.4 Hz, 1H), 3.87 (s, 3H), 2.92 – 2.82 (m, 1H), 2.57 – 2.41 (m, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 161.7 (t, *J* = 24.0 Hz), 128.2, 128.0, 127.8, 127.7, 127.6, 116.0 – 115.6 (m), 115.8, 89.1 – 87.3 (m), 53.8, 42.5 (q, *J* = 18.0 Hz). ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.7 (dt, *J* = 26.0, 9.0 Hz), -106.6 – -107.4 (m), -112.0 – -113.4 (m), -172.2 – -172.5 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{11}H_{11}F_4O_2^+$ 251.0690, found 251.0691.

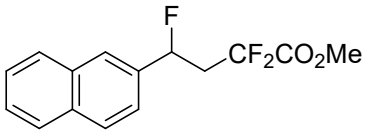


Methyl 2,2,4-trifluoro-4-(*o*-tolyl)butanoate (4k): colorless oil liquid, 41.8 mg (85% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.40 – 7.38 (m, 1H), 7.27 – 7.24 (m, 2H), 7.19 – 7.17 (m, 1H), 5.90 (ddd, *J* = 46.0, 8.0, 2.0 Hz, 1H), 3.87 (s, 3H), 2.92 – 2.80 (m, 1H), 2.57 – 2.35 (m, 1H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 164.3 (t, *J* = 20.5 Hz), 136.4, 136.2, 134.4, 134.3, 130.9, 129.0, 126.6, 125.3, 125.2, 117.0 – 112.0 (m), 87.0 – 85.3 (m), 53.6, 42.7 (q, *J* = 16.0 Hz), 18.8. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.7 (dt, *J* = 29.0, 10.0 Hz), -107.0 – -107.8 (m), -178.0 – -178.3 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{12}H_{14}F_3O_2^+$ 247.0940, found 247.0941.

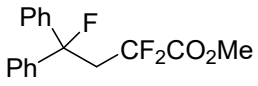


Methyl 2,2,4-trifluoro-4-mesitylbutanoate (4l): colorless oil liquid, 49.3 mg (90% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 6.83 (s, 2H), 6.11 (ddd, *J* =

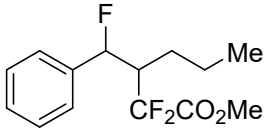
42.0, 8.0, 2.0 Hz, 1H), 3.87 (d, *J* = 4.0 Hz, 3H), 3.14 – 3.09 (m, 1H), 2.44 – 2.36 (m, 1H), 2.34 (s, 6H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 164.2 (t, *J* = 24.0 Hz), 138.5, 135.8, 135.8, 131.0, 130.8, 130.3, 116.3-113.0 (m), 87.2 – 86.0 (m), 53.6, 40.5 (q, *J* = 14.0 Hz), 20.9, 20.1 20.0. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.6 (dt, *J* = 26.0, 4.0 Hz), -106.7 – -107.5 (m), -172.2 – -172.4 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{14}H_{18}F_3O_2^+$ 275.1253, found 275.1255.



Methyl 2,2,4-trifluoro-4-(naphthalen-2-yl)butanoate (4m): colorless oil liquid, 50.2 mg (89% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.89 – 7.81 (m, 4H), 7.52 – 7.51 (m, 2H), 7.44 – 7.42 (m, 1H), 5.88 (ddd, *J* = 42.0, 8.0, 2.0 Hz, 1H), 3.85 (s, 3H), 3.03 – 2.93 (m, 1H), 2.68 – 2.56 (m, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 164.3 (t, *J* = 24.0 Hz), 135.5, 135.3, 132.6, 132.0, 129.0, 128.3, 127.9, 126.9, 126.8, 125.1, 122.8, 116.9-111.9 (m), 89.8 – 88.0 (m), 53.7, 42.6 (q, *J* = 15.0 Hz). ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.5 (dt, *J* = 24.0, 6.0 Hz), -106.5 – -107.3 (m), -174.2 – -174.4 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{15}H_{14}F_3O_2^+$ 283.0940, found 283.0937.

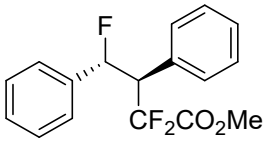


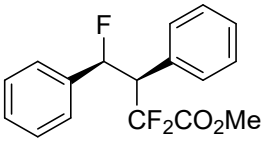
Methyl 2,2,4-trifluoro-4,4-diphenylbutanoate (4n): colorless oil liquid, 37.6 mg (61% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.38 – 7.29(m, 10H), 3.68 (s, 3H), 3.42 – 3.30 (m, 2H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 164.1 (t, *J* = 24.0 Hz), 142.1, 141.9, 128.5, 128.3, 125.2, 125.2, 116.9-111.9 (m), 89.6 – 87.8 (m), 97.0, 95.2, 53.4, 42.2 (q, *J* = 12.0 Hz). ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -99.9 – -100.0 (m), -149.5 – -149.6 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{17}H_{16}F_3O_2^+$ 309.1097, found 309.1098.



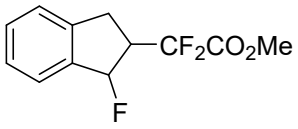
Methyl 2,2-difluoro-3-(fluoro(phenyl)methyl)hexanoate (4o): colorless oil liquid, 39.5 mg (72% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.44 – 7.25(m, 5H), 4.78 – 4.72

(m, 1H), 4.63 (d, *J* = 8.0 Hz, 1H), 3.66 (s, 3H), 1.83 – 1.68 (m, 1H), 1.54 – 1.42 (m, 1H), 1.34 – 1.25 (m, 2H), 0.88 – 0.85 (m, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 165.2 (t, *J* = 22.0 Hz), 135.2, 130.0, 129.2, 128.7, 128.5, 126.8, 118.7 – 113.6 (m), 83.0 – 82.9 (m), 53.5, 53.4, 50.1 (q, *J* = 14.0 Hz), 25.6, 19.9, 13.9. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -111.1 (dt, *J* = 24.0, 10.0 Hz), -115.3 – -116.0 (m), -180.8 – -181.1 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{14}H_{18}F_3O_2^+$ 275.1253, found 275.1252.

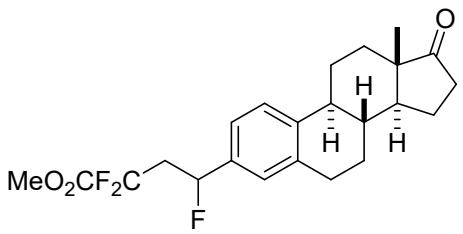




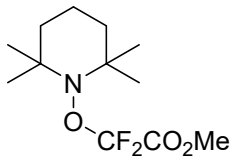
Methyl 2,2,4-trifluoro-3,4-diphenylbutanoate (4p) and methyl 2,2,4-trifluoro-3,4-diphenylbutanoate (4p′): colorless oil liquid, 41.9 mg (68% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.40 – 7.19 (m, 20H), 5.94 – 5.76 (m, 1H), 5.32 (d, *J* = 8.0 Hz, 1H), 3.80 – 3.69 (m, 2H), 3.57 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 164.6 (t, *J* = 22.0 Hz), 134.86, 130.94, 130.11, 129.89, 129.78, 129.65, 129.37, 129.23, 129.09, 128.97, 128.95, 128.88, 128.79, 128.72, 128.56, 128.39, 128.32, 128.28, 126.92, 126.86, 126.34, 126.21, 126.09, 125.96, 82.0 – 81.5 (m), 56.6 (q, *J* = 12.0 Hz), 53.58, 51.05, 49.86. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -101.3 – -105.0 (m), -169.1 – -169.3 (m), -184.6 – -184.8 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{17}H_{16}F_3O_2^+$ 309.1097, found 309.1098.



Methyl 2,2-difluoro-2-(1-fluoro-2,3-dihydro-*1*H-inden-2-yl)acetate (4q): colorless oil liquid, 33.2 mg (68% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.47 – 7.45 (m, 1H), 7.38 – 7.33 (m, 2H), 7.31 – 7.25 (m, 1H), 6.21 (ddd, *J* = 49.0, 11.0, 2.0 Hz, 1H), 3.88 (s, 3H), 3.33 – 3.25 (m, 2H), 3.09 – 3.03 (m, 1H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 164.0 (t, *J* = 22.0 Hz), 140.8, 140.7, 138.6, 138.5, 130.3, 130.2, 127.7, 127.7, 125.4, 125.1, 118.1-113.1 (m), 96.2 – 94.4 (m), 53.7, 50.9 (q, *J* = 14.0 Hz), 30.1. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -111.1 (dt, *J* = 26.0, 4.0 Hz), -115.1 – -115.9 (m), -180.7 – -180.9 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{12}H_{12}F_3O_2^+$ 245.0784, found 245.0781.



Methyl 2,2,4-trifluoro-4-((*8*R,*9*S,*13*S,*14*S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-*6H*-cyclopenta[*a*]phenanthren-3-yl)butanoate (4r): colorless oil liquid, 63.7 mg (78% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.33 (d, *J* = 8.0 Hz, 1H), 7.13 – 7.08 (m, 2H), 5.68 (ddd, *J* = 44.0, 8.0, 2.0 Hz, 1H), 3.87 (s, 3H), 2.95 – 2.93 (m, 3H), 2.52 – 2.48 (m, 3H), 2.17 (s, 1H), 2.10 – 2.06 (m, 2H), 2.04 – 1.99 (m, 1H), 1.64 – 1.49 (m, 7H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 220.8, 164.2 (t, *J* = 18.0 Hz), 141.0, 137.2, 135.6, 135.4, 126.3, 125.9, 123.3, 123.1, 123.0, 116.9-111.9 (m), 89.4 – 87.7 (m), 53.6, 50.53, 50.0, 44.4, 42.5 (q, *J* = 18.0 Hz), 38.1, 25.9, 31.6, 29.5, 29.4, 26.4, 25.8, 21.6, 13.9. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -102.4 (dt, *J* = 24.0, 6.0 Hz), -107.0 – -107.8 (m), -173.0 – -173.3 (m). HRMS (ESI) $[M+H]^+$ Calcd for $C_{23}H_{28}F_3O_3^+$ 409.1985, found 409.1986.

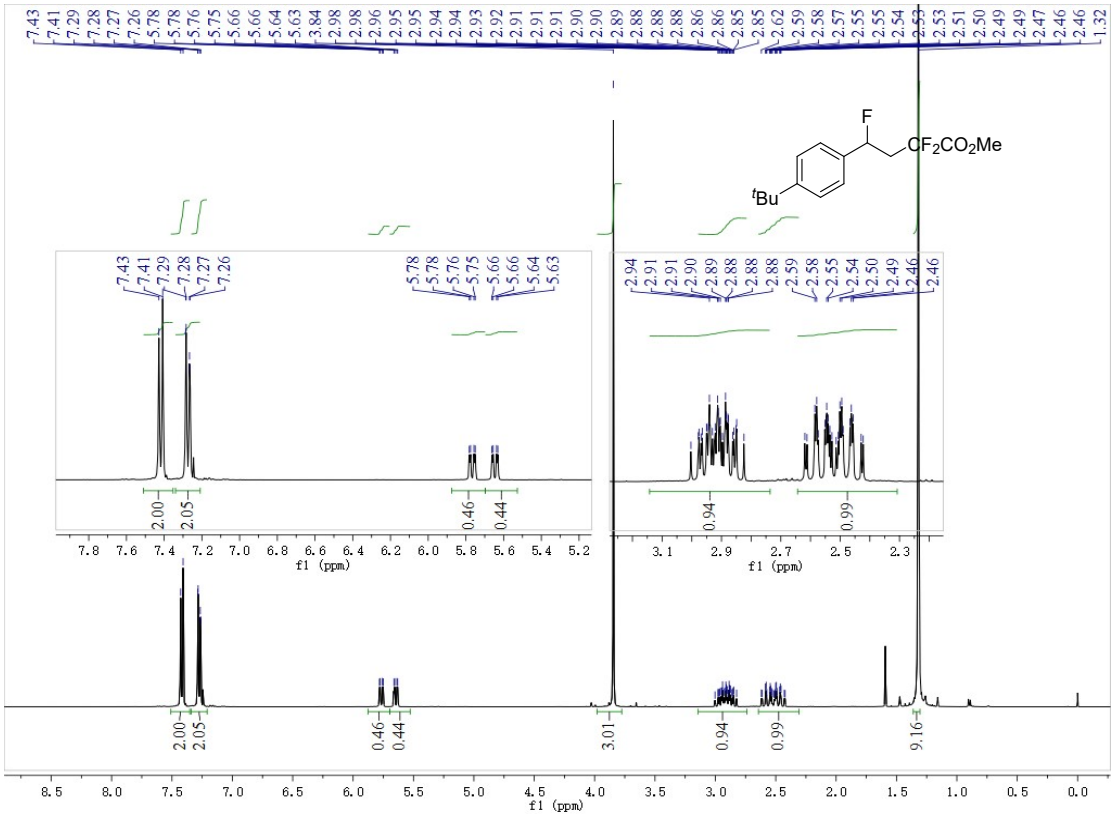


Methyl 2,2-difluoro-2-(2,2,6,6-tetramethylpiperidin-1-yl)acetate (5)[1]: colorless oil liquid, 22.4 mg (45% yield). ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 4.11 (s, 3H), 1.80 – 1.76 (m, 5H), 1.67 (s, 1H), 1.40 – 1.31 (m, 12H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 157.0 (t, *J* = 38.0 Hz), 111.35 (t, *J* = 268.0 Hz), 57.2, 49.8, 36.1, 29.3, 16.7, 12.8. ^{19}F NMR (376 MHz, CHLOROFORM-D) δ -72.6 (s).

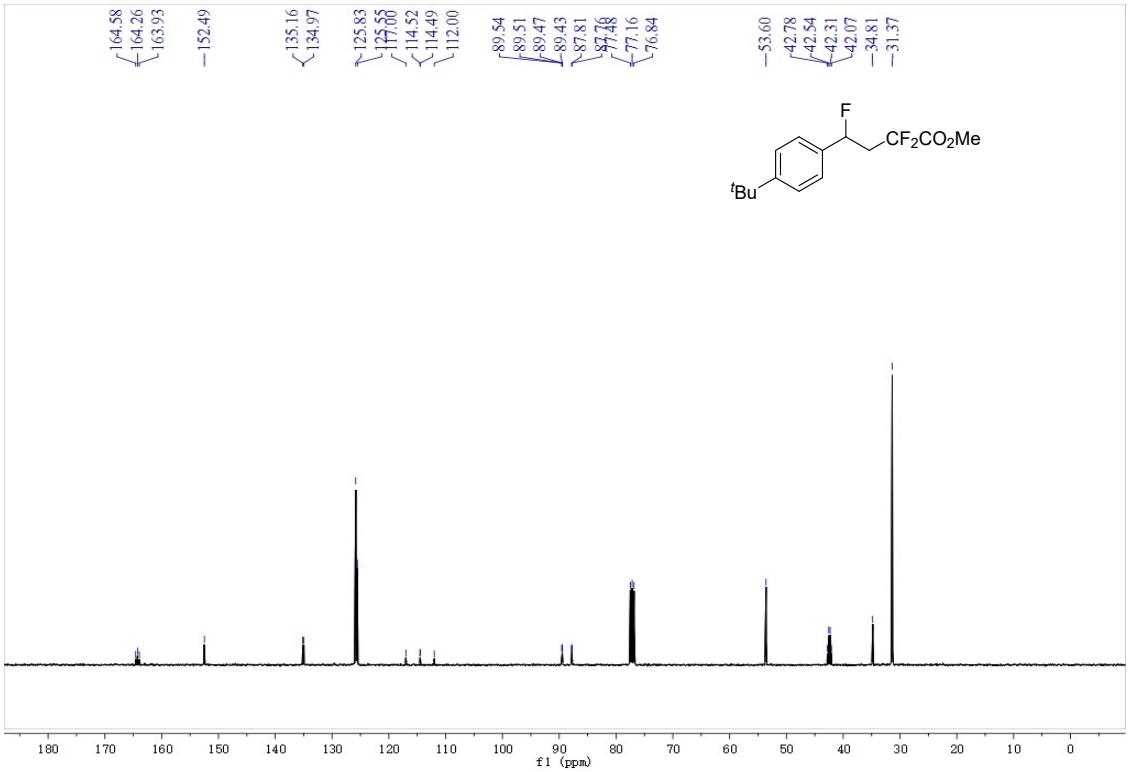
7. References:

[1] X. Luo, B. Zhang and C. Xi, *Green Chem*., 2021, **23**, 2324.

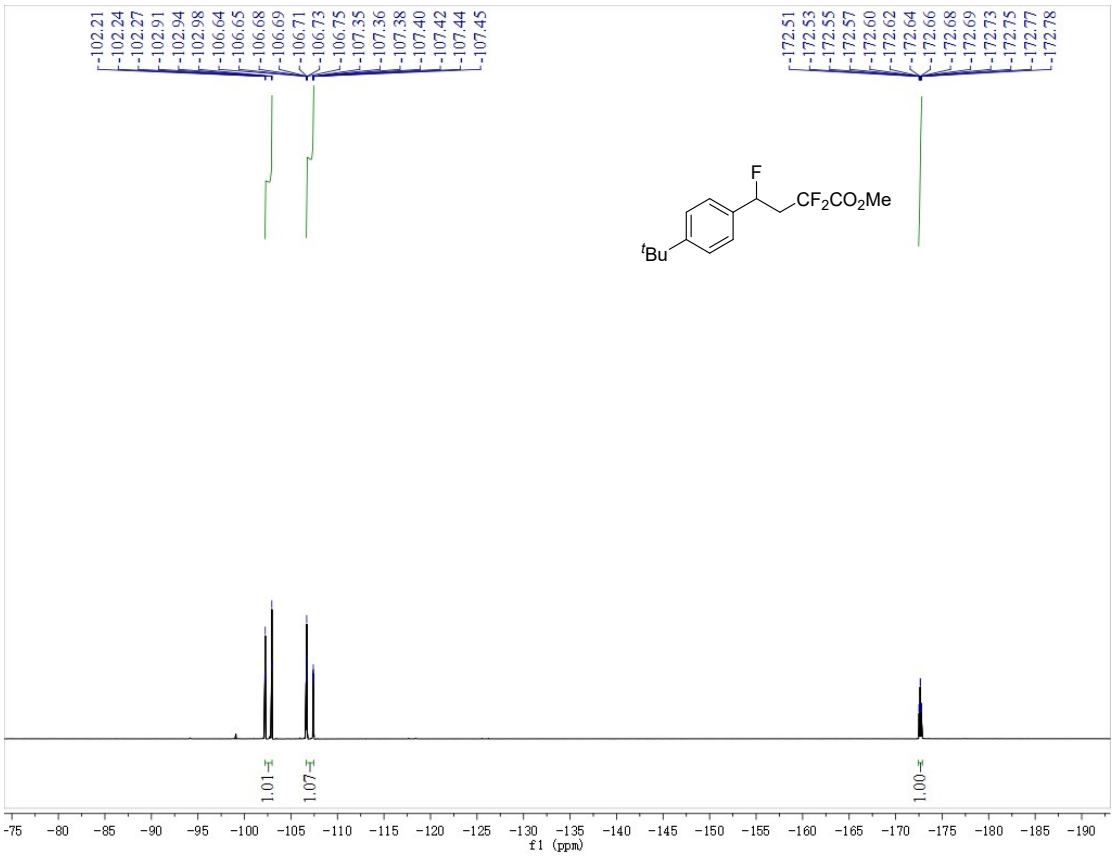
8. Copies of ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F NMR Spectra for compound 4 and 5



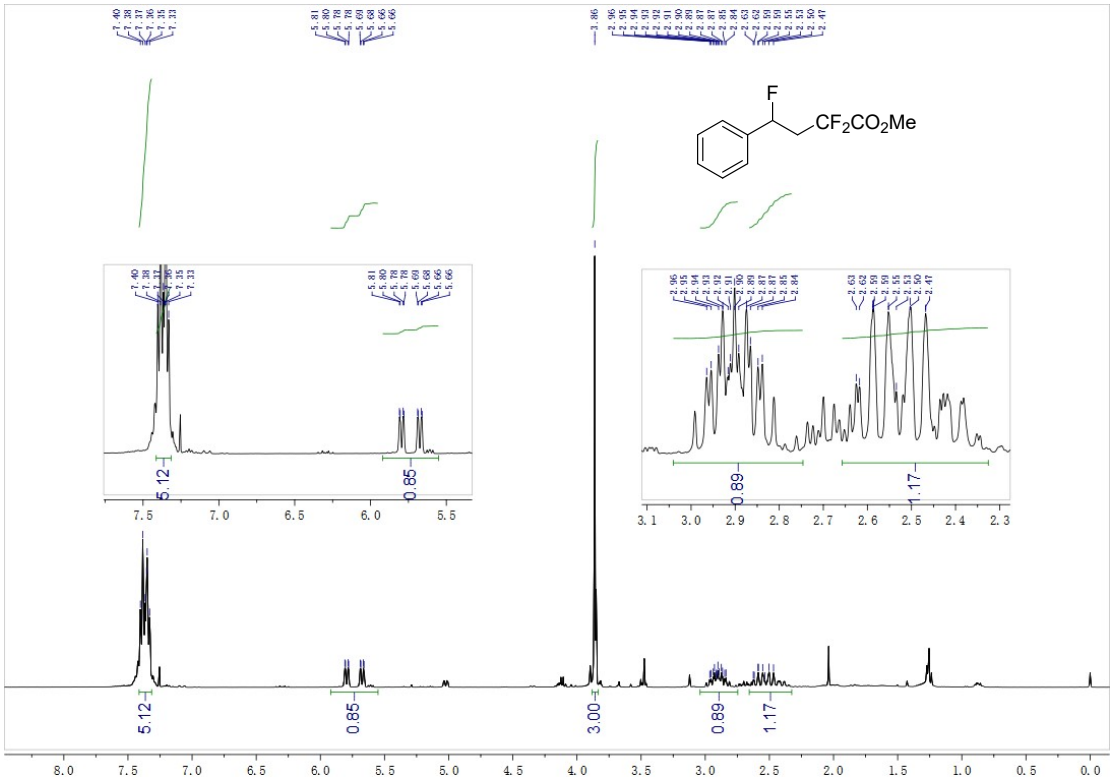
^{1}H NMR for compound **4a**



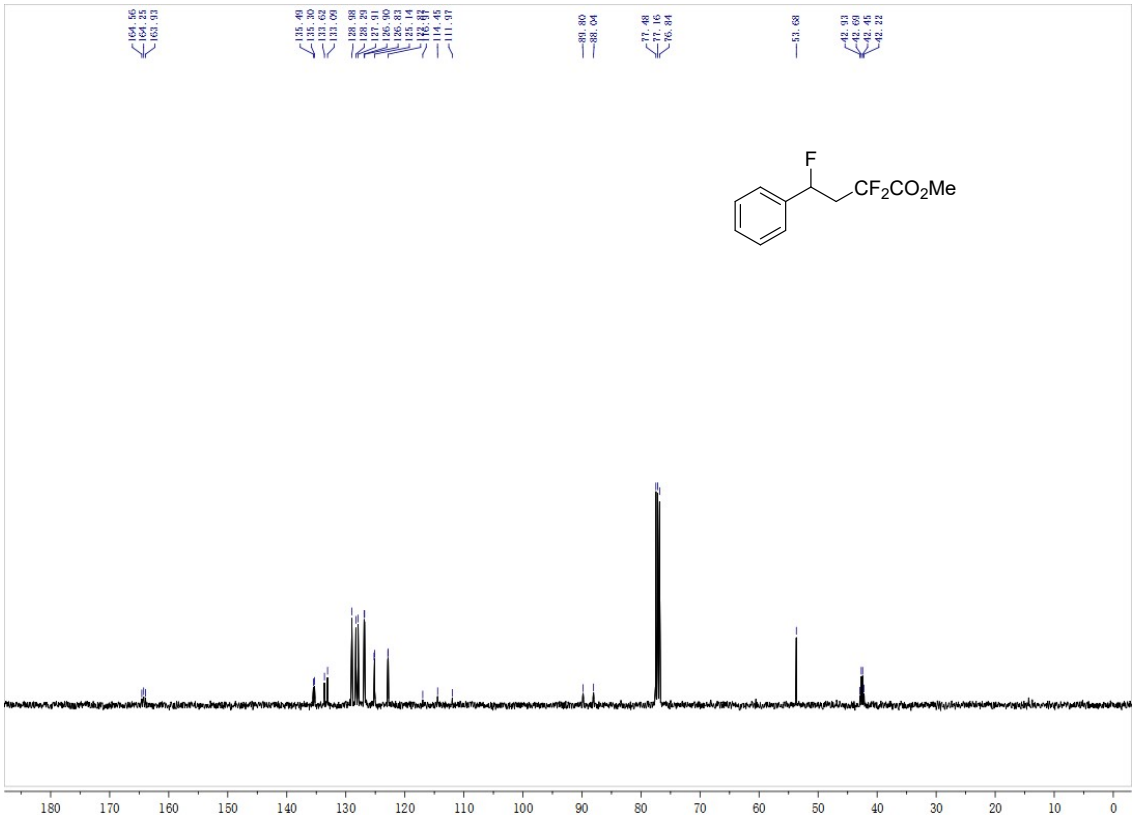
$^{13}C\{^{1}H\}$ NMR for compound **4a**



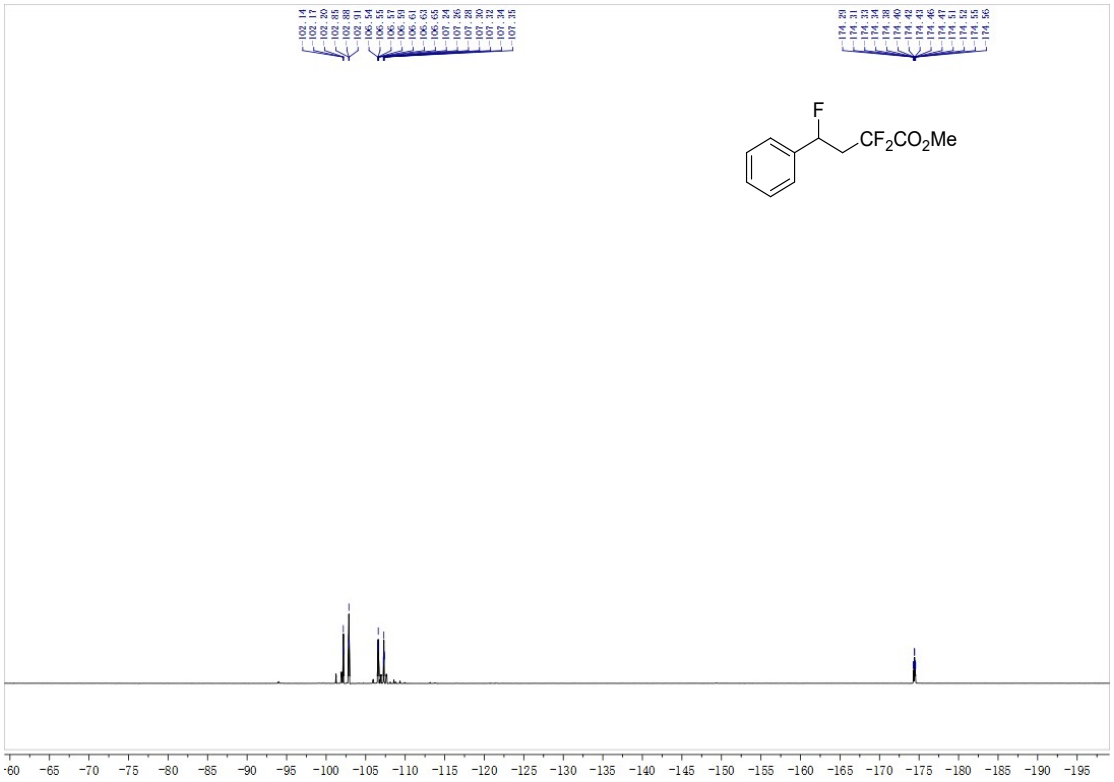
^{19}F NMR for compound **4a**



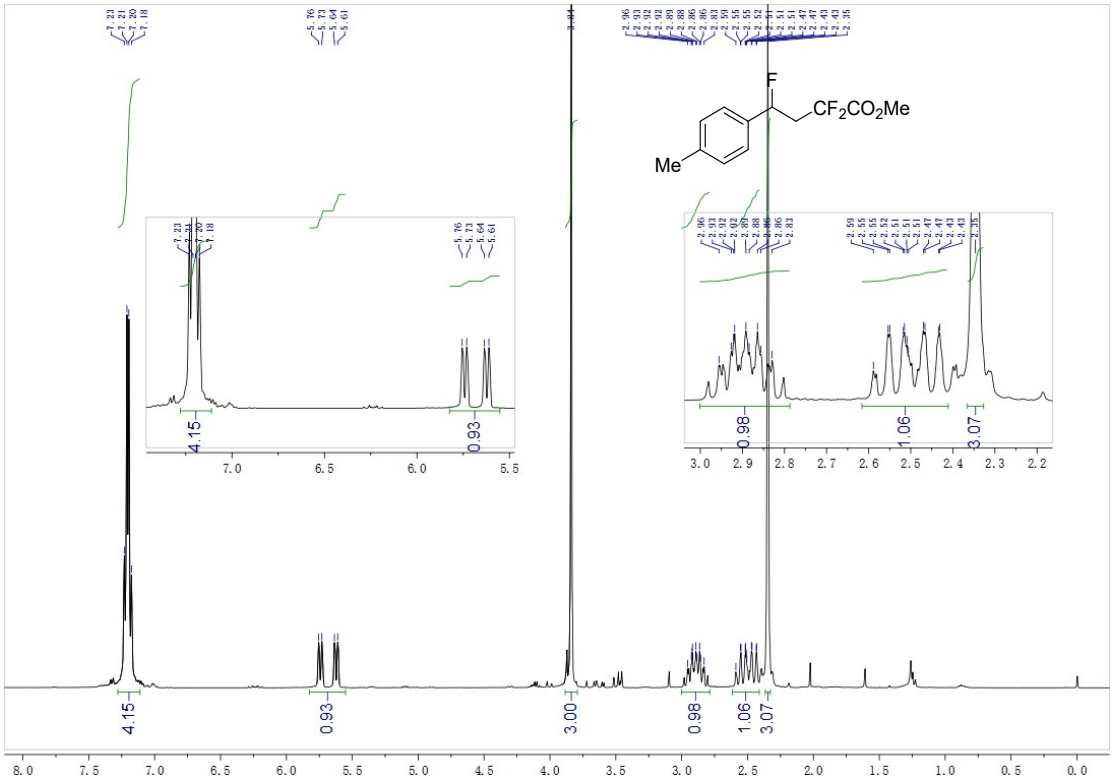
^{1}H NMR for compound **4b**



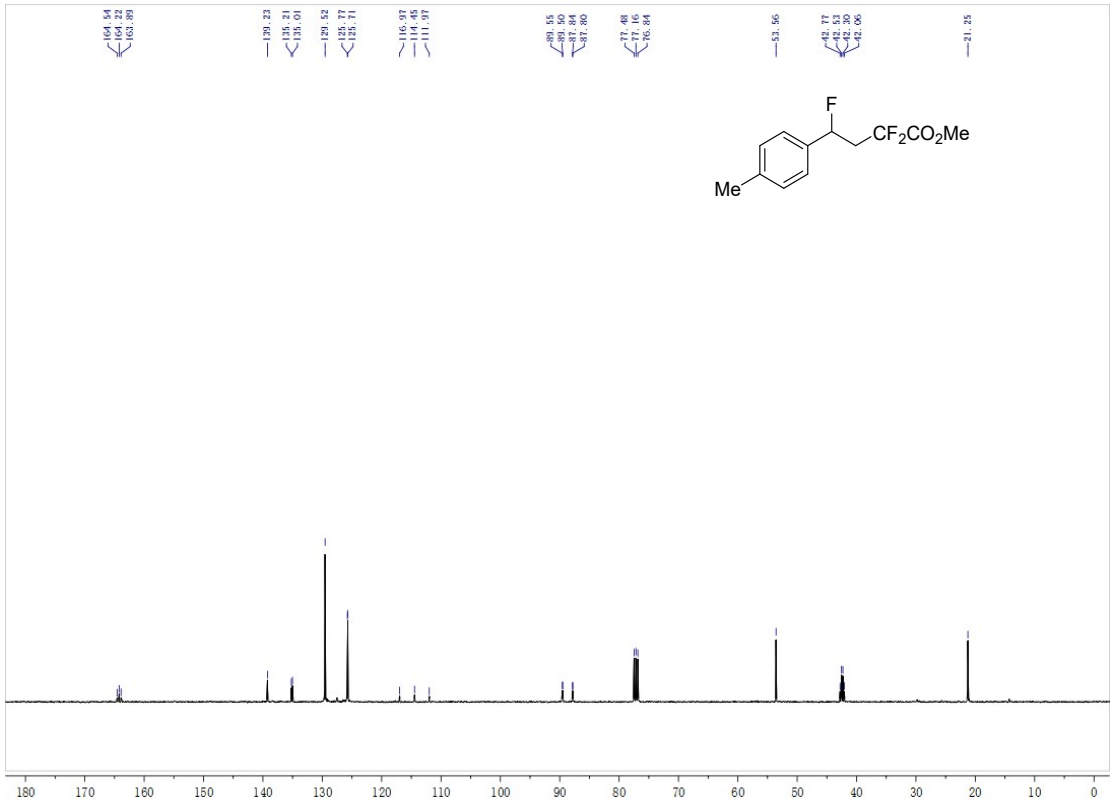
^{13}C{^{1}H} NMR for compound **4b**



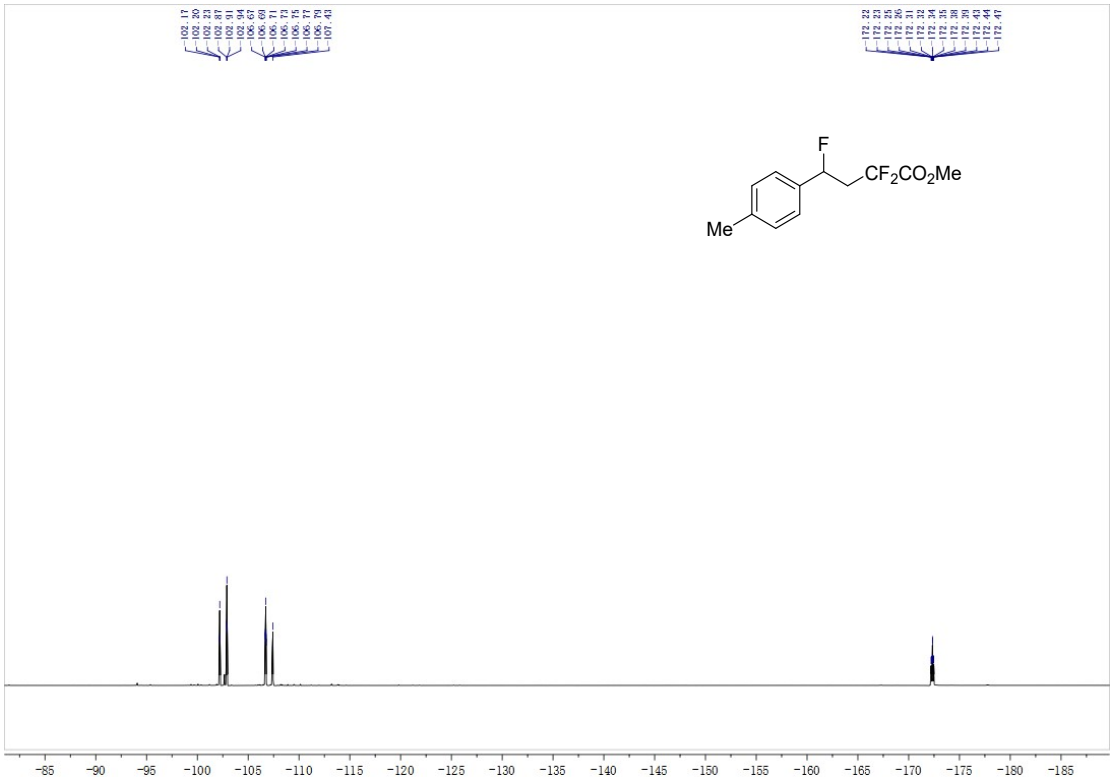
^{19}F NMR for compound **4b**



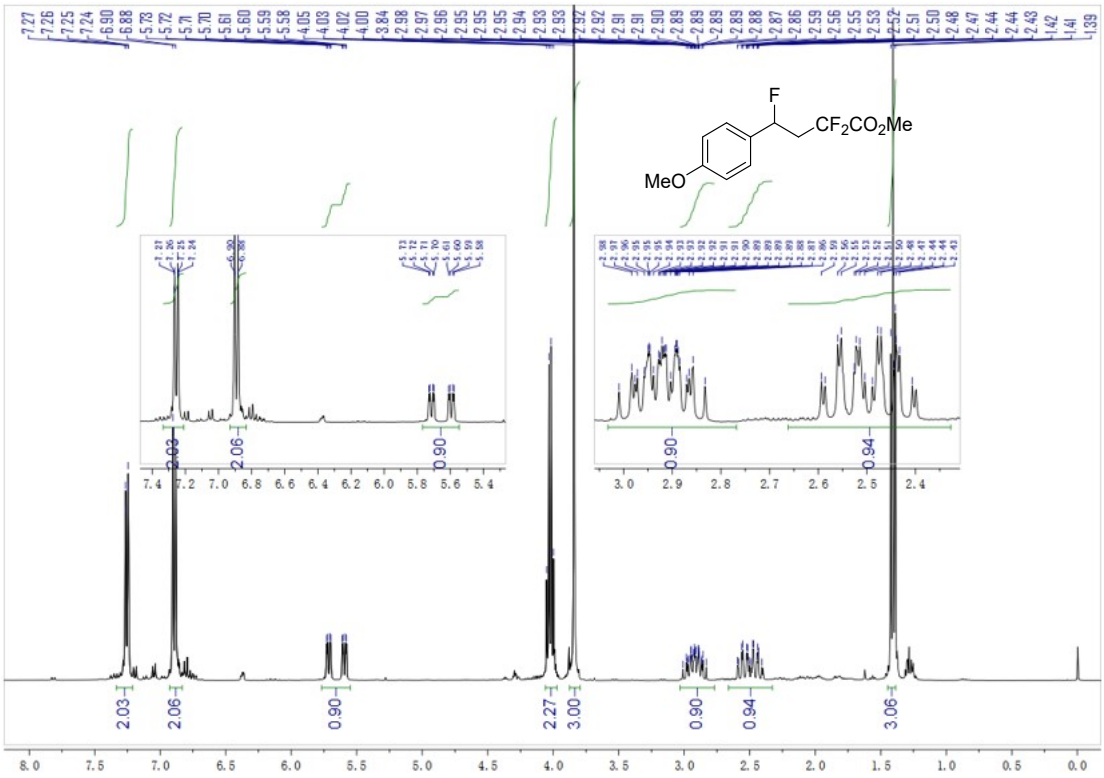
^{1}H NMR for compound **4c**



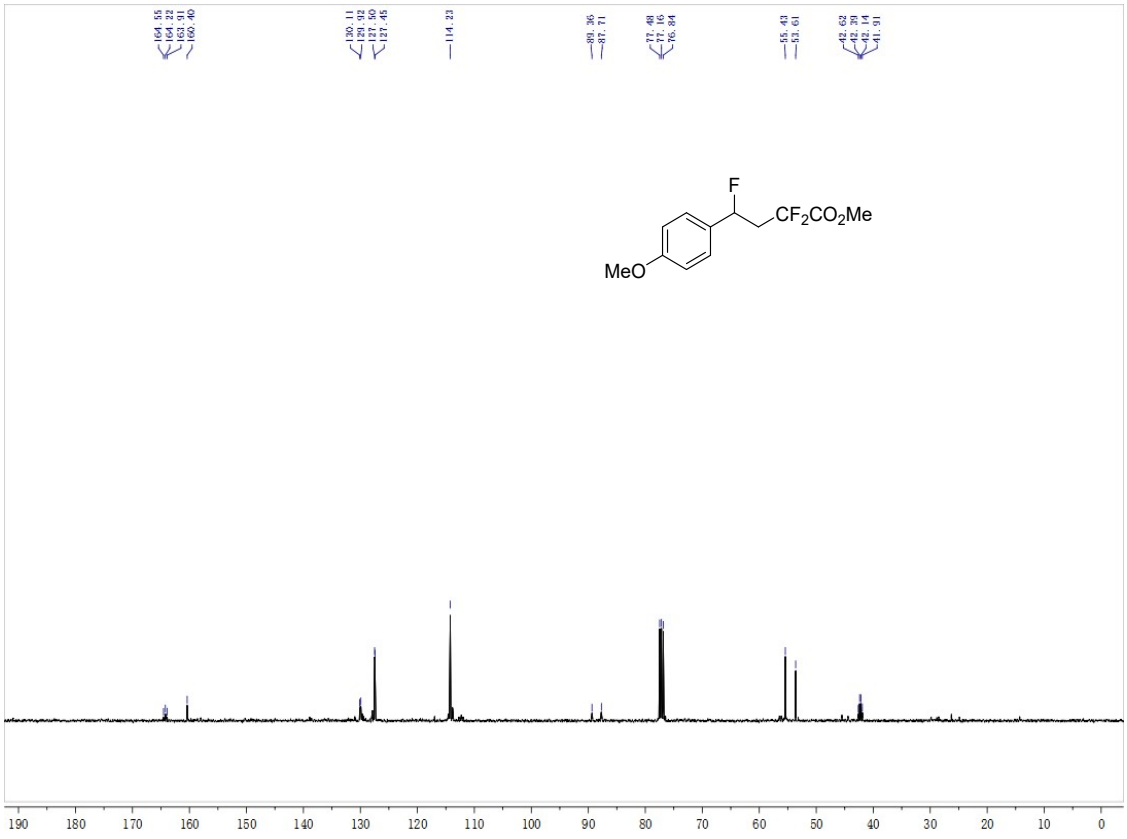
^{13}C{^{1}H} NMR for compound **4c**



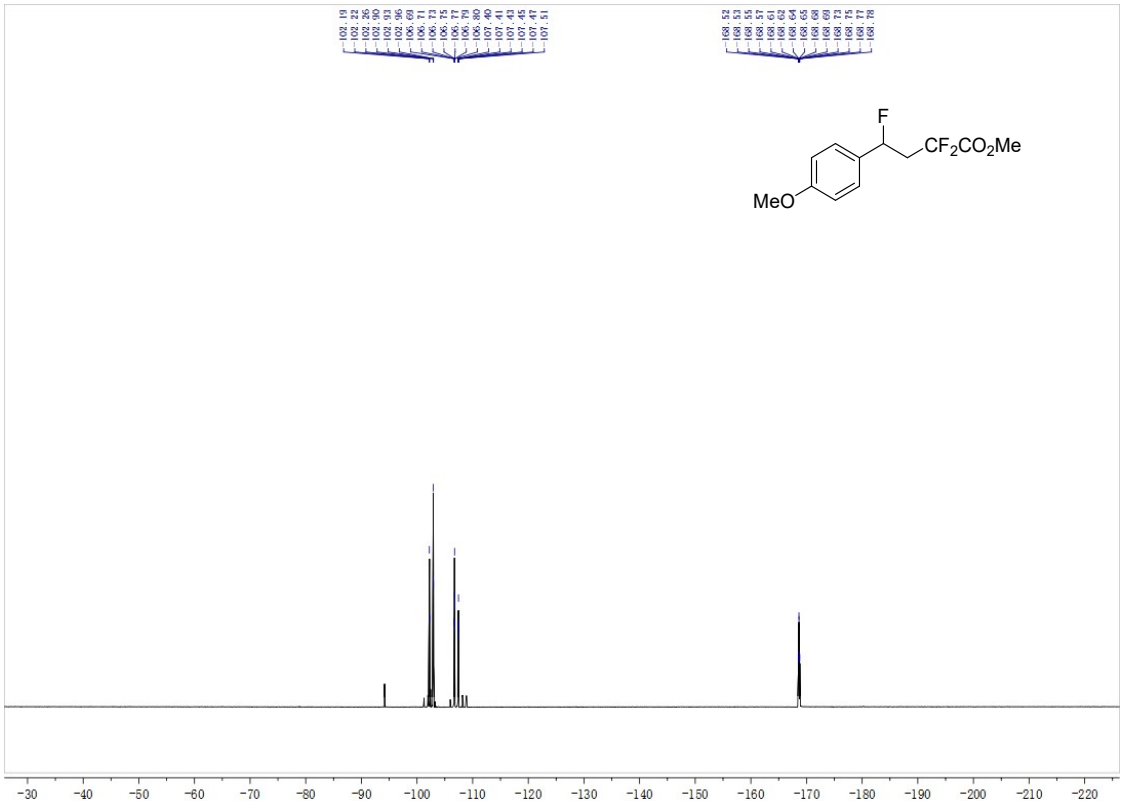
^{19}F NMR for compound **4c**



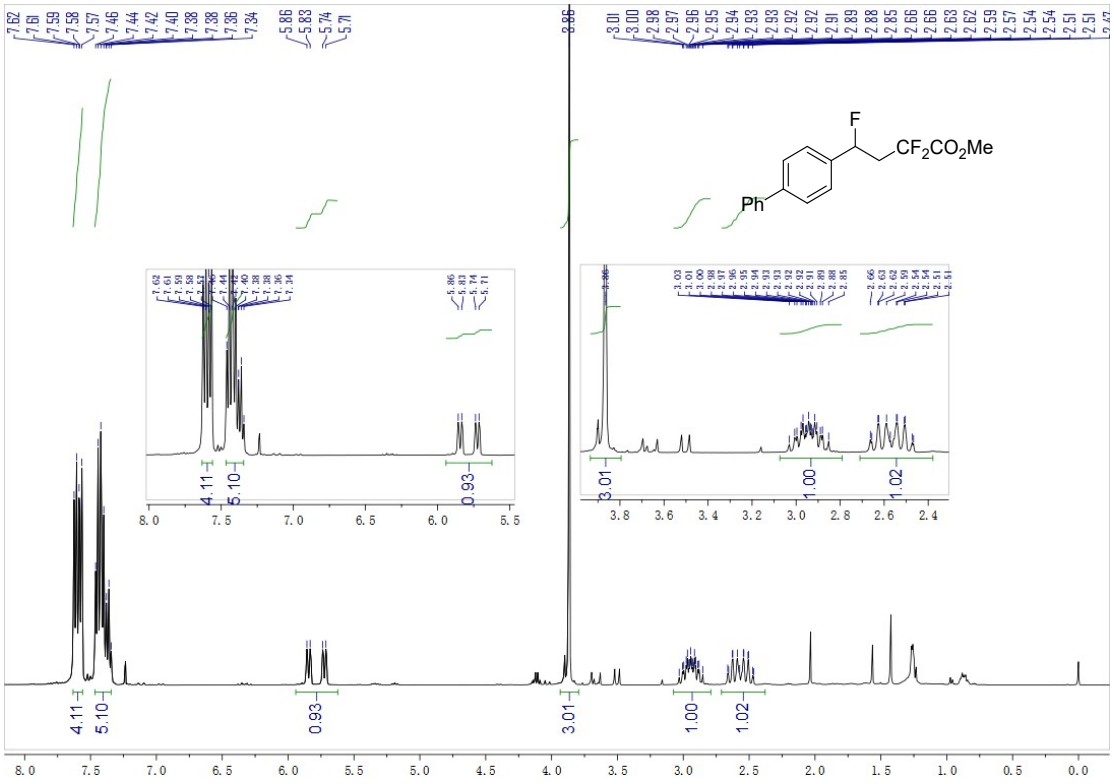
^{1}H NMR for compound **4d**



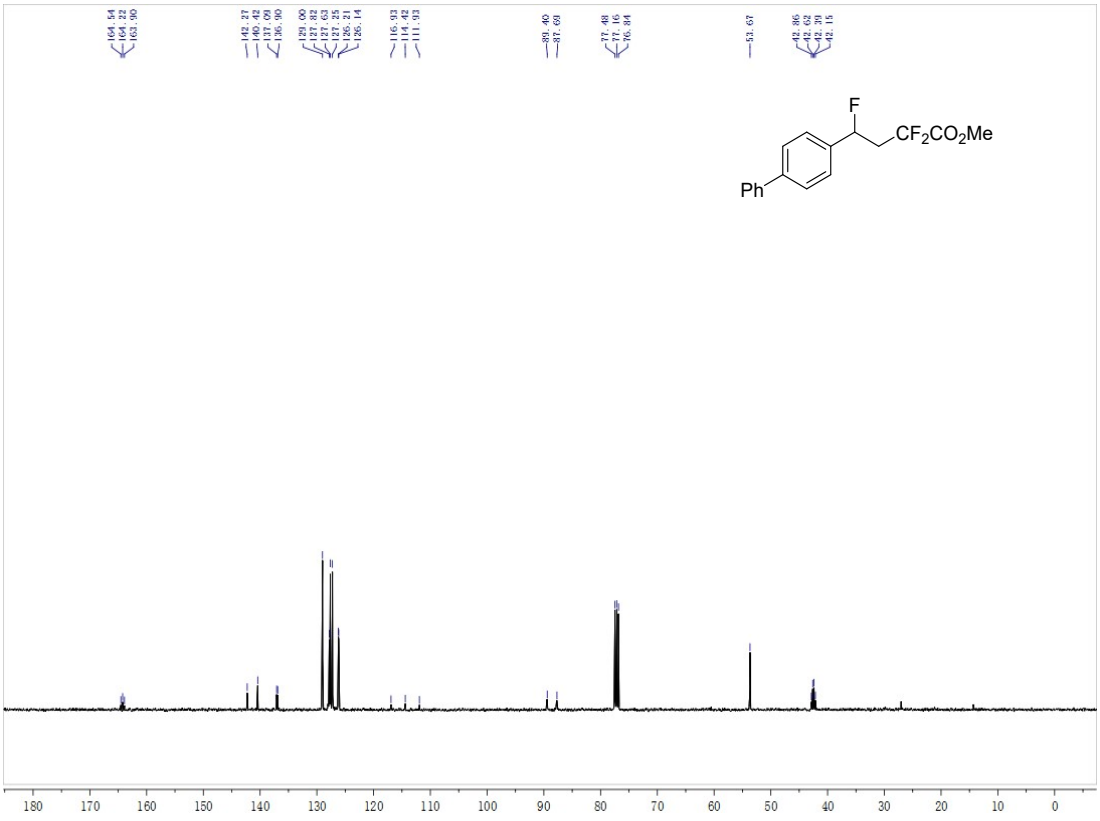
^{13}C{^{1}H} NMR for compound **4d**



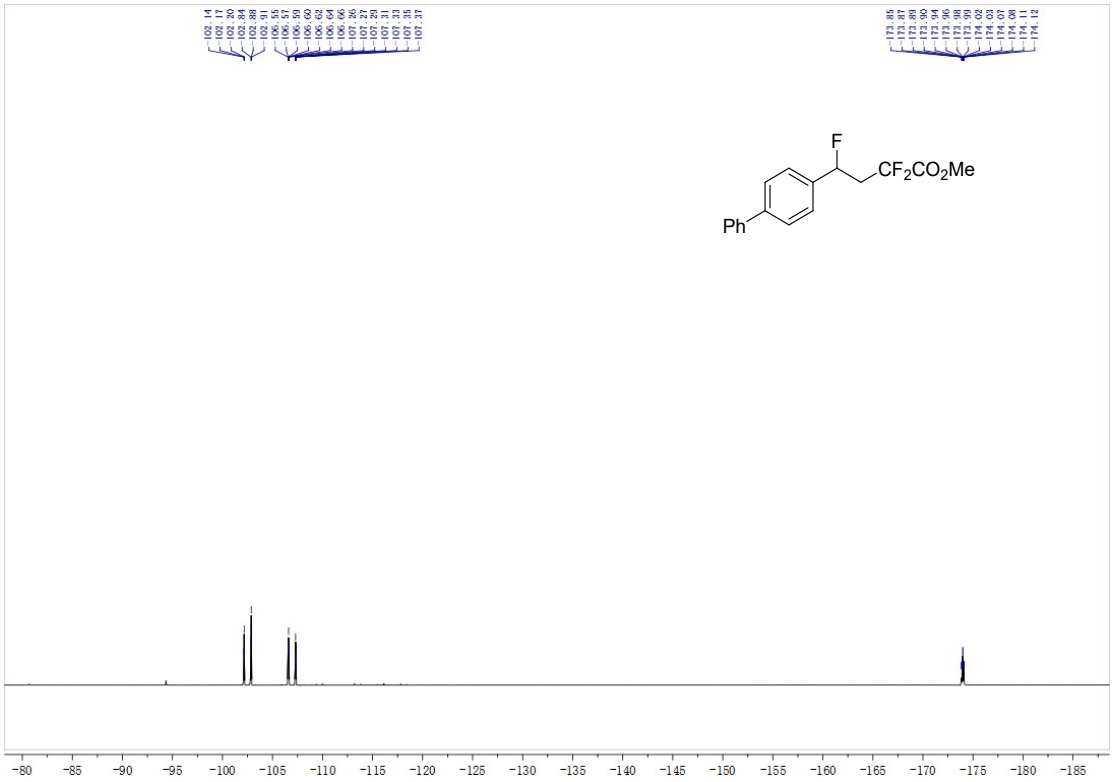
^{19}F NMR for compound **4d**



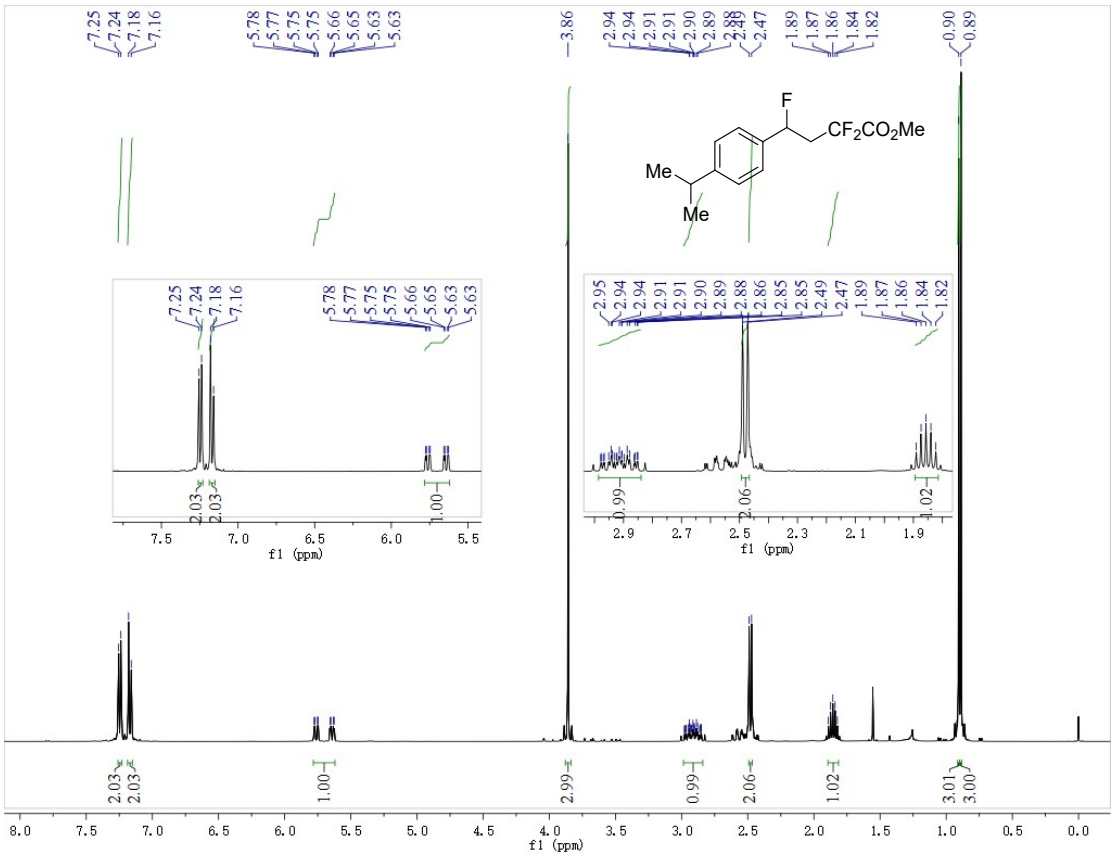
^{1}H NMR for compound **4e**



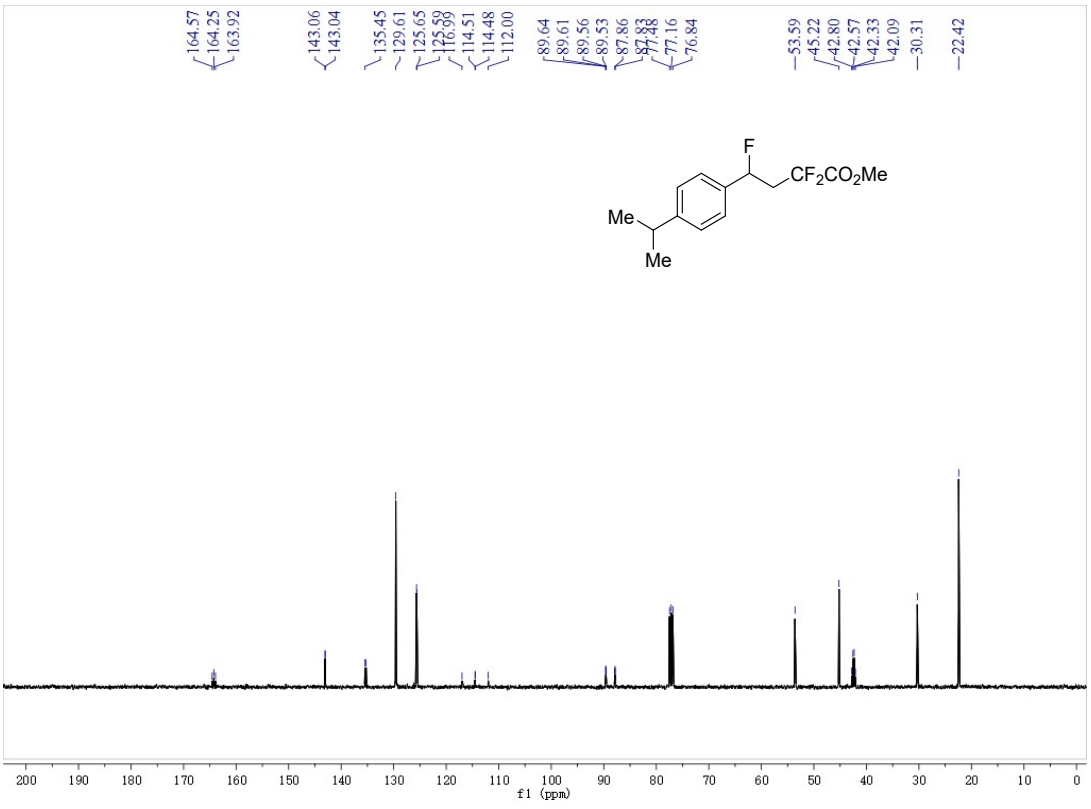
^{13}C{^{1}H} NMR for compound **4e**



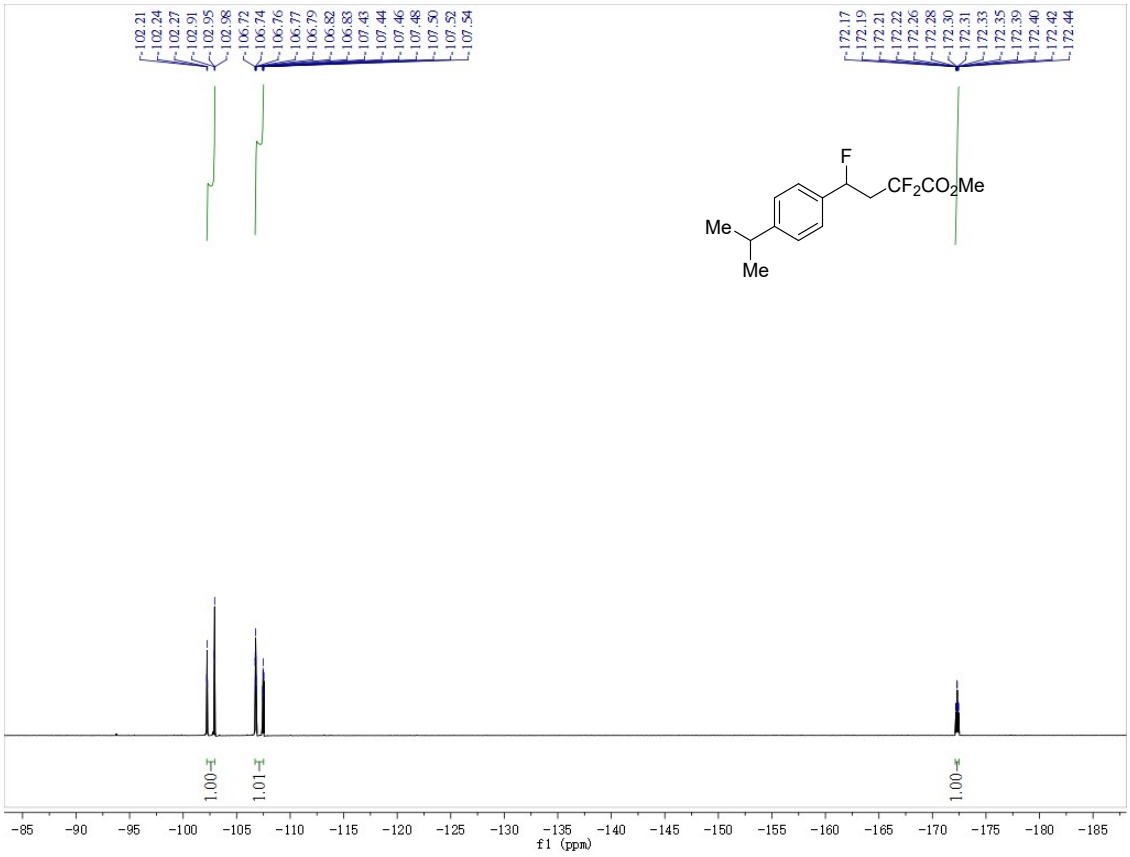
^{19}F NMR for compound **4e**



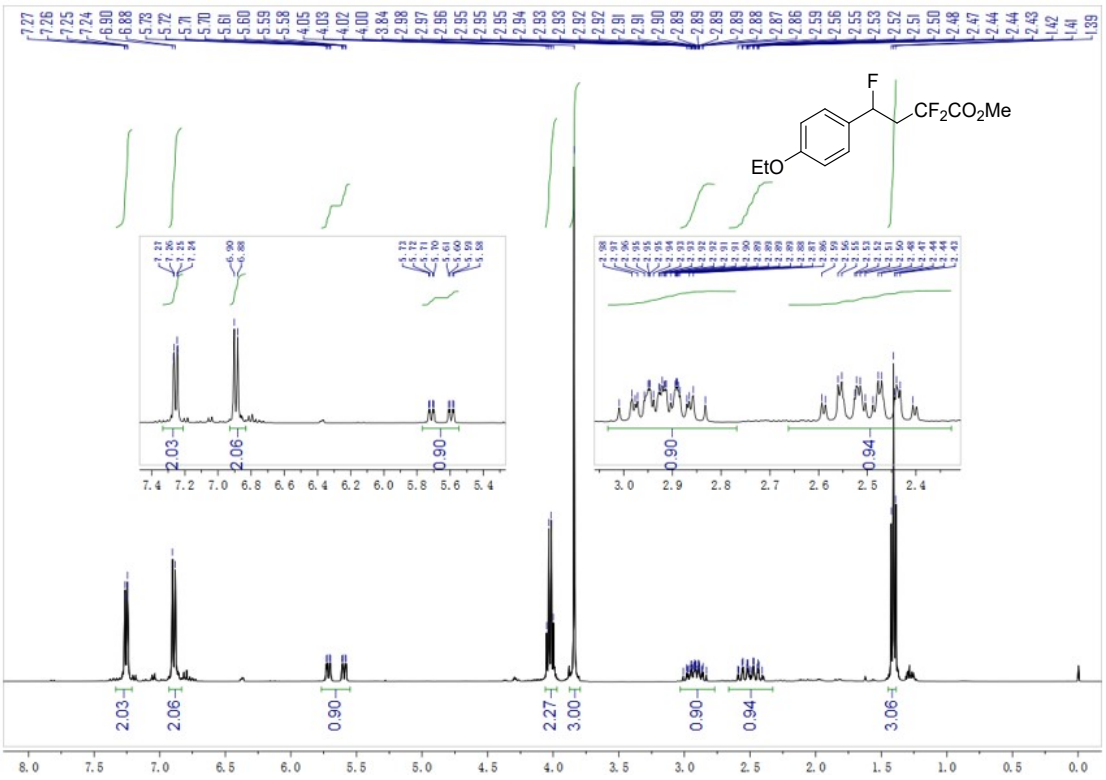
^{1}H NMR for compound **4f**



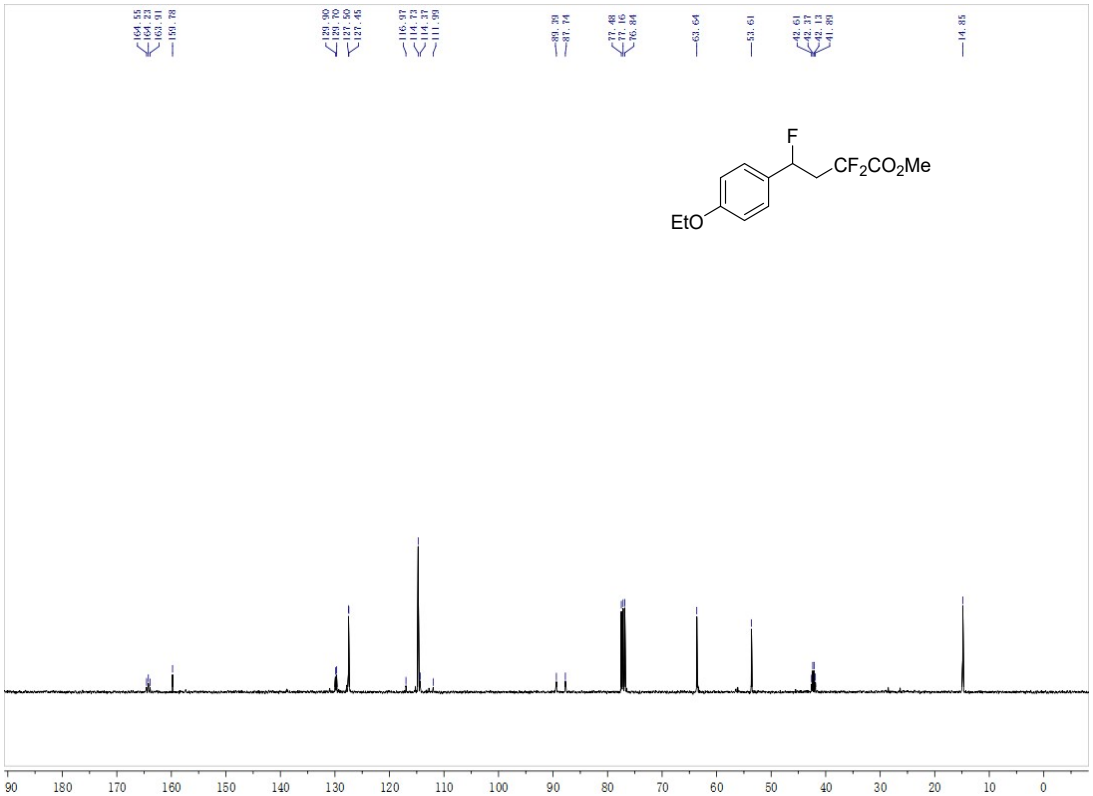
$^{13}C\{^{1}H\}$ NMR for compound **4f**



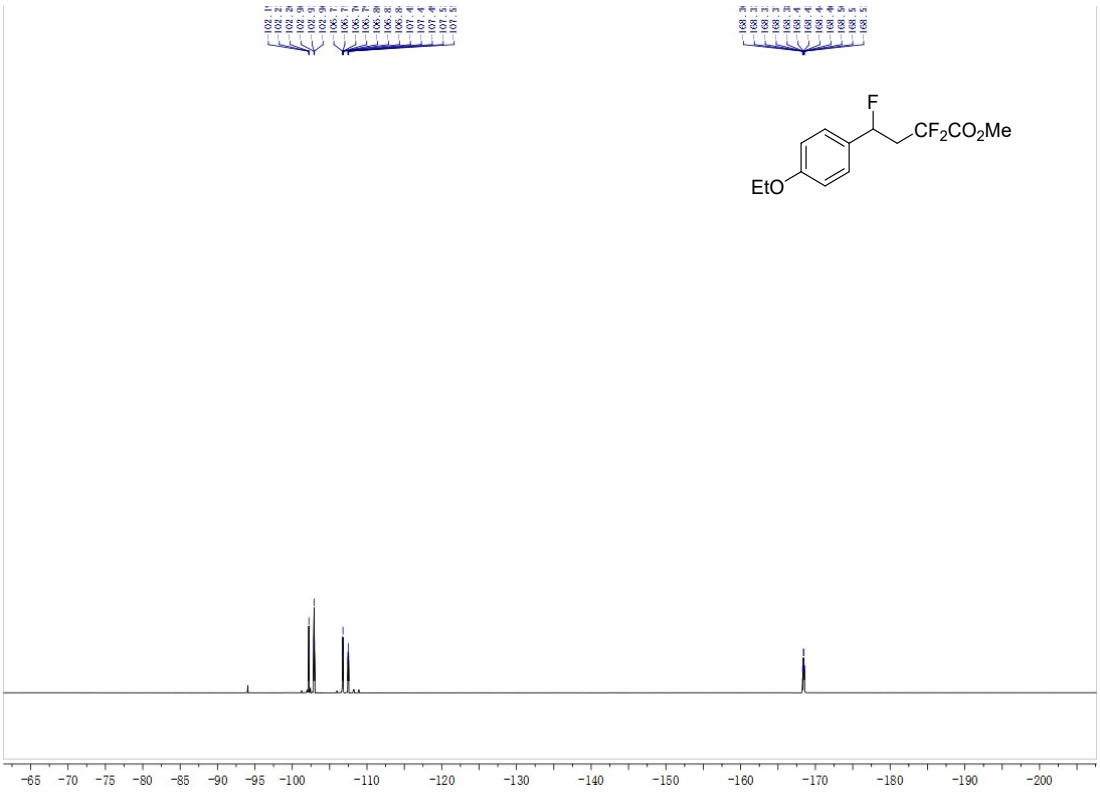
^{19}F NMR for compound **4f**



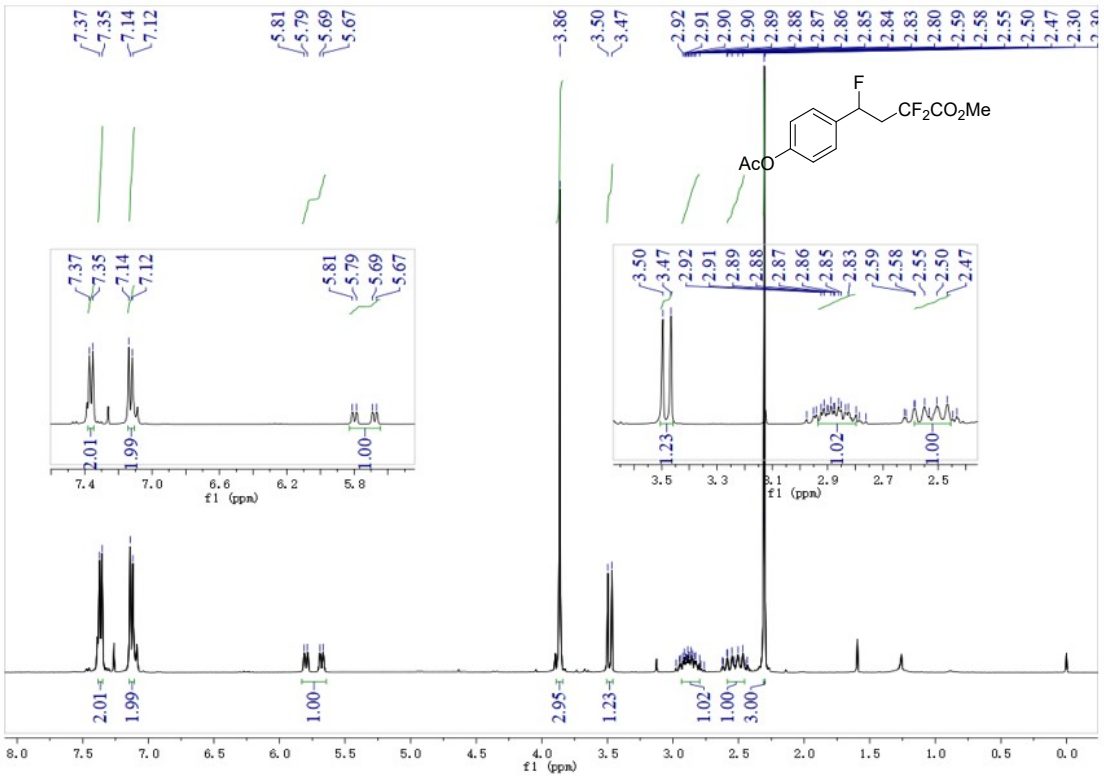
^{1}H NMR for compound **4g**



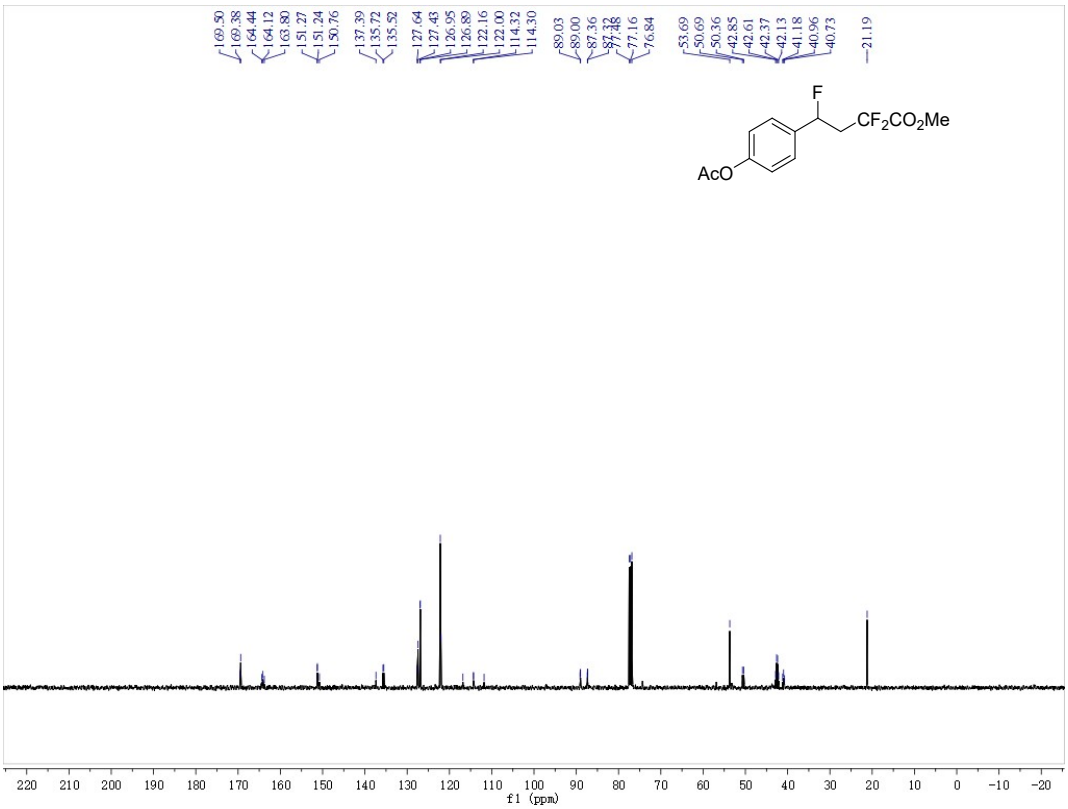
^{13}C{^{1}H} NMR for compound **4g**



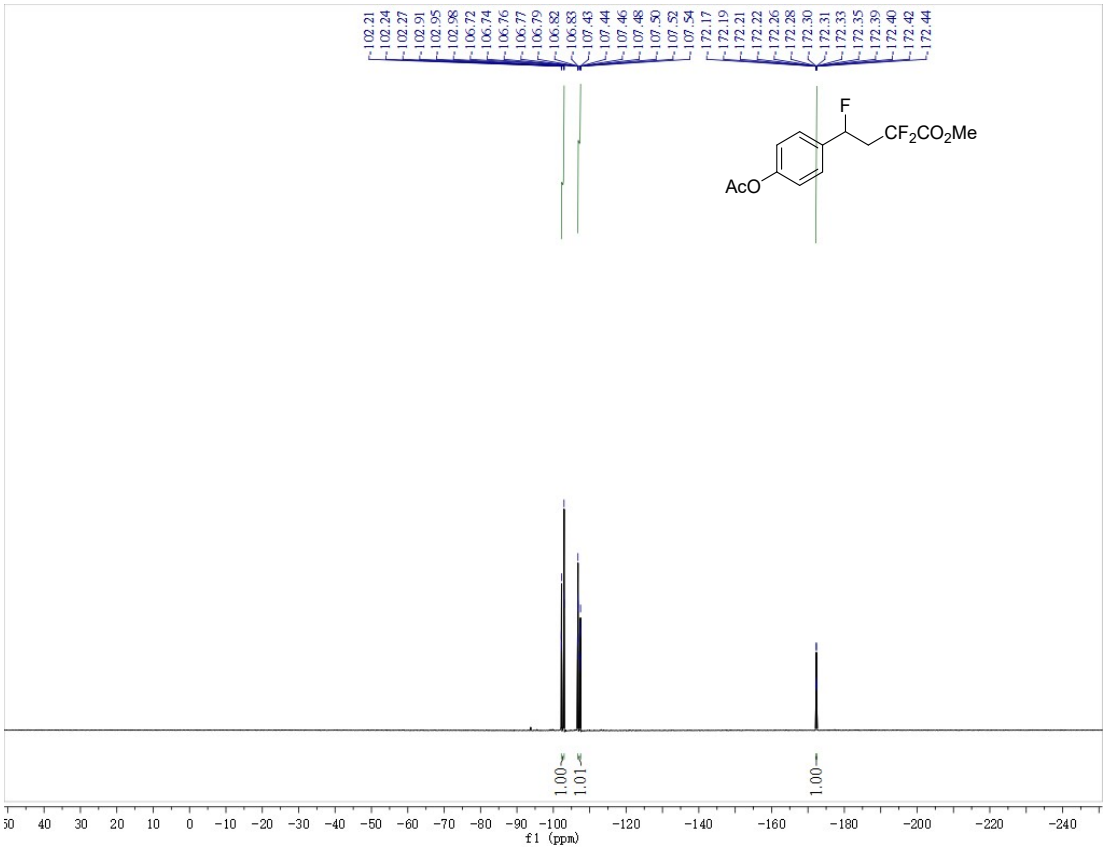
^{19}F NMR for compound **4g**



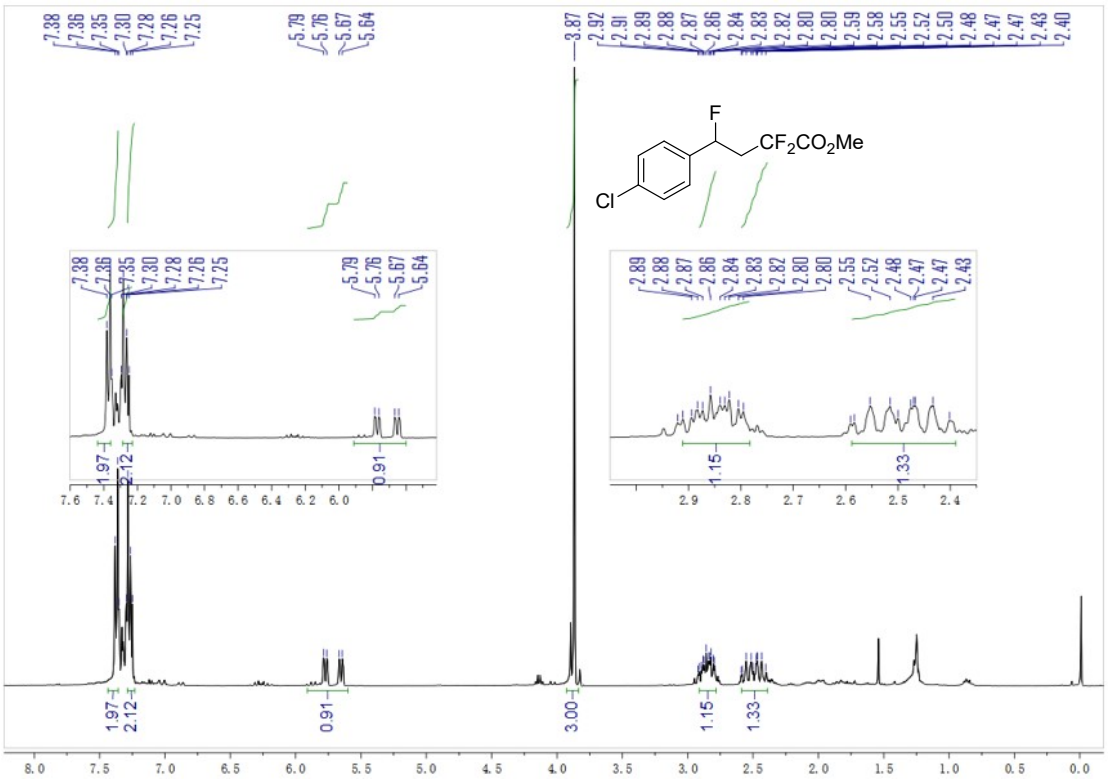
^{1}H NMR for compound **4h**



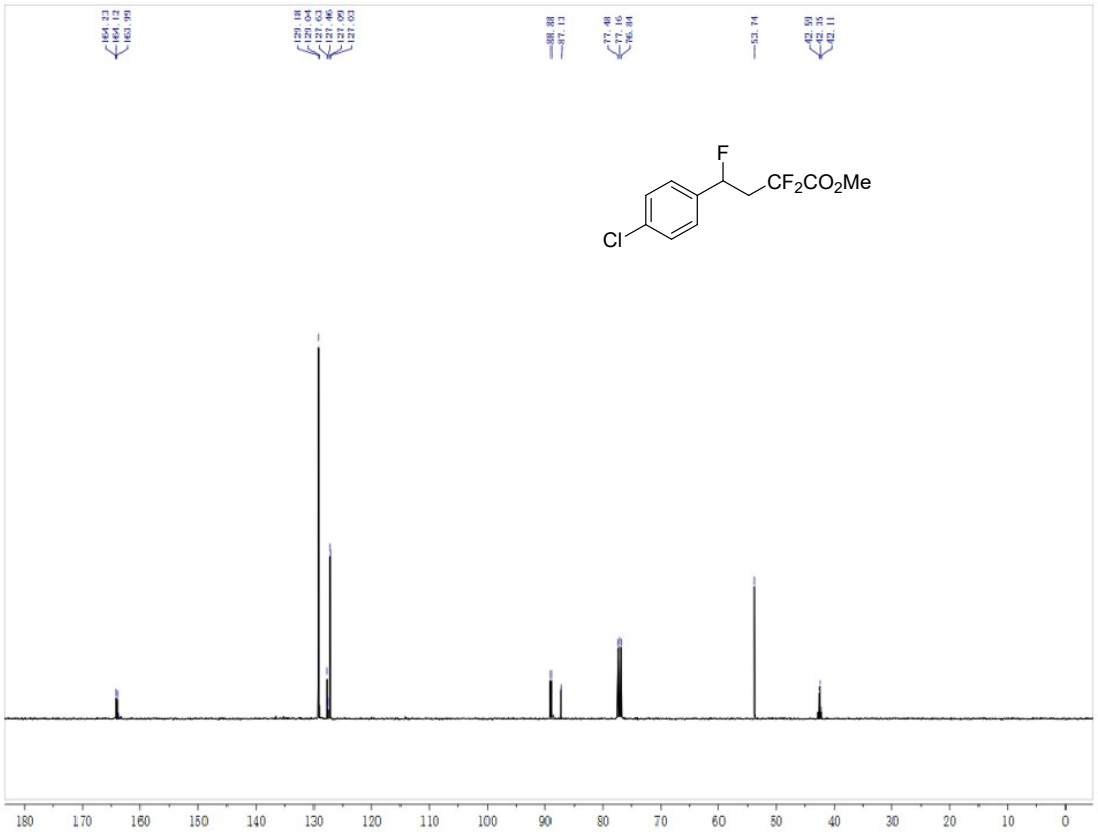
^{13}C{^{1}H} NMR for compound **4h**



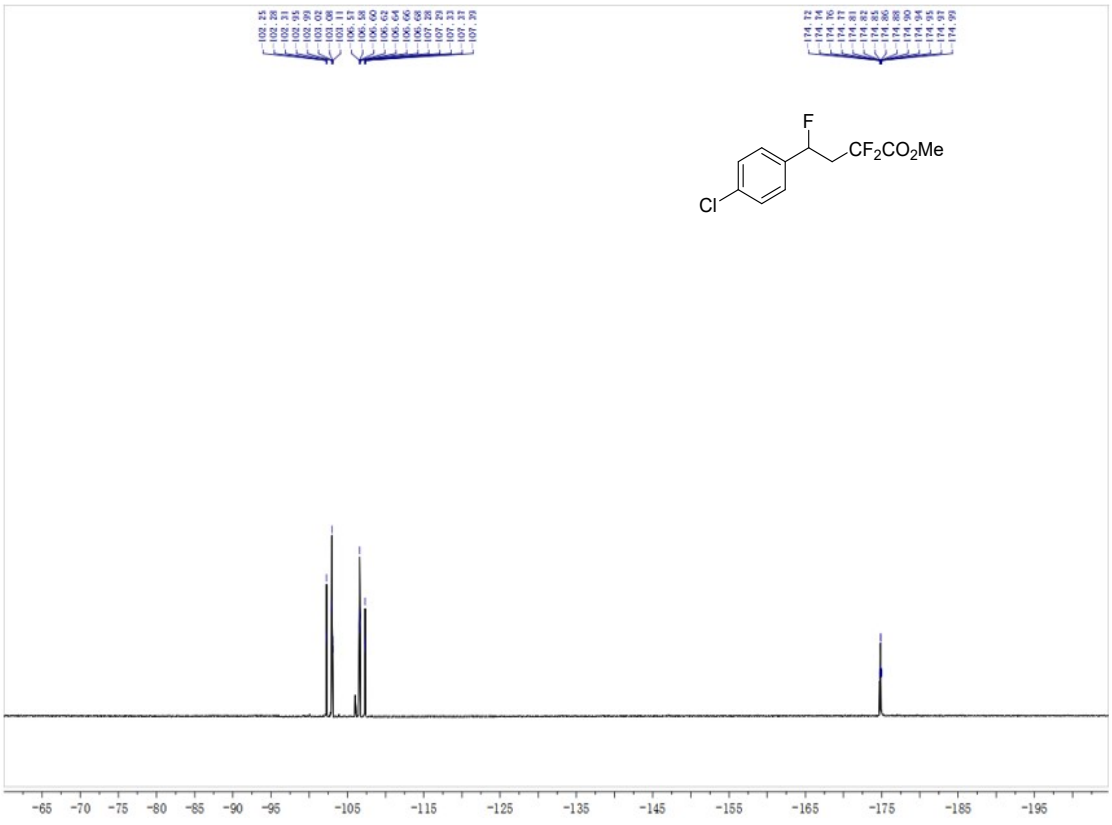
^{19}F NMR for compound **4h**



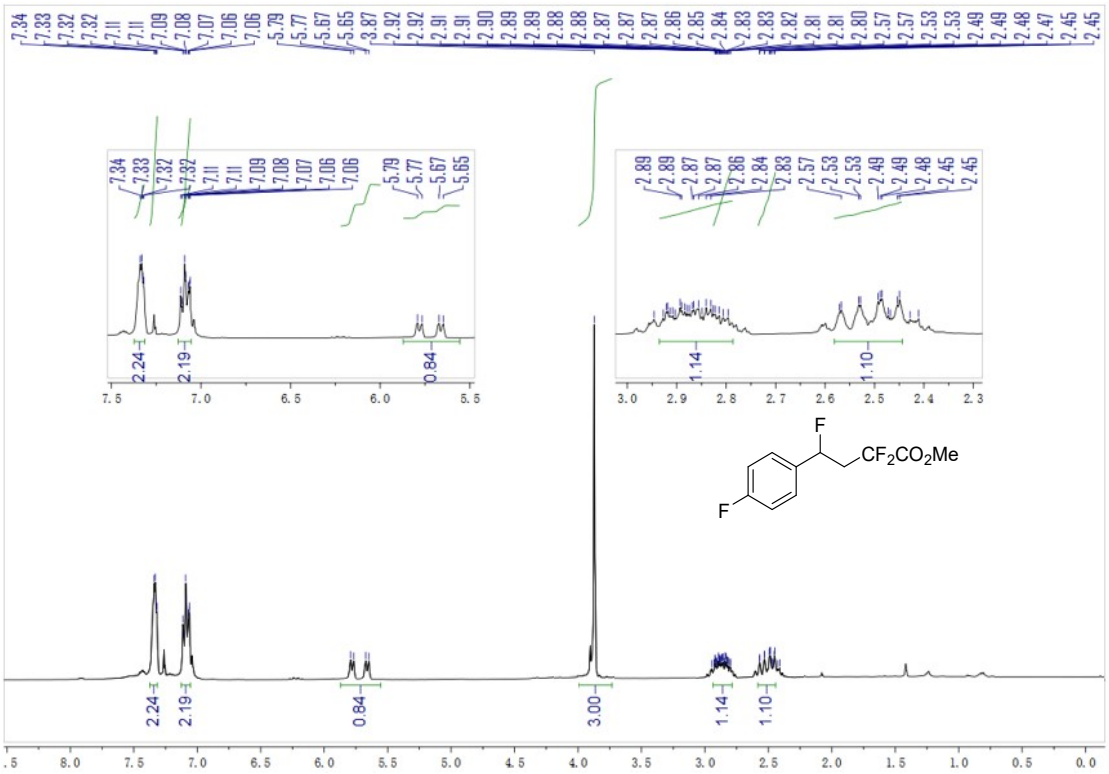
^{1}H NMR for compound **4i**



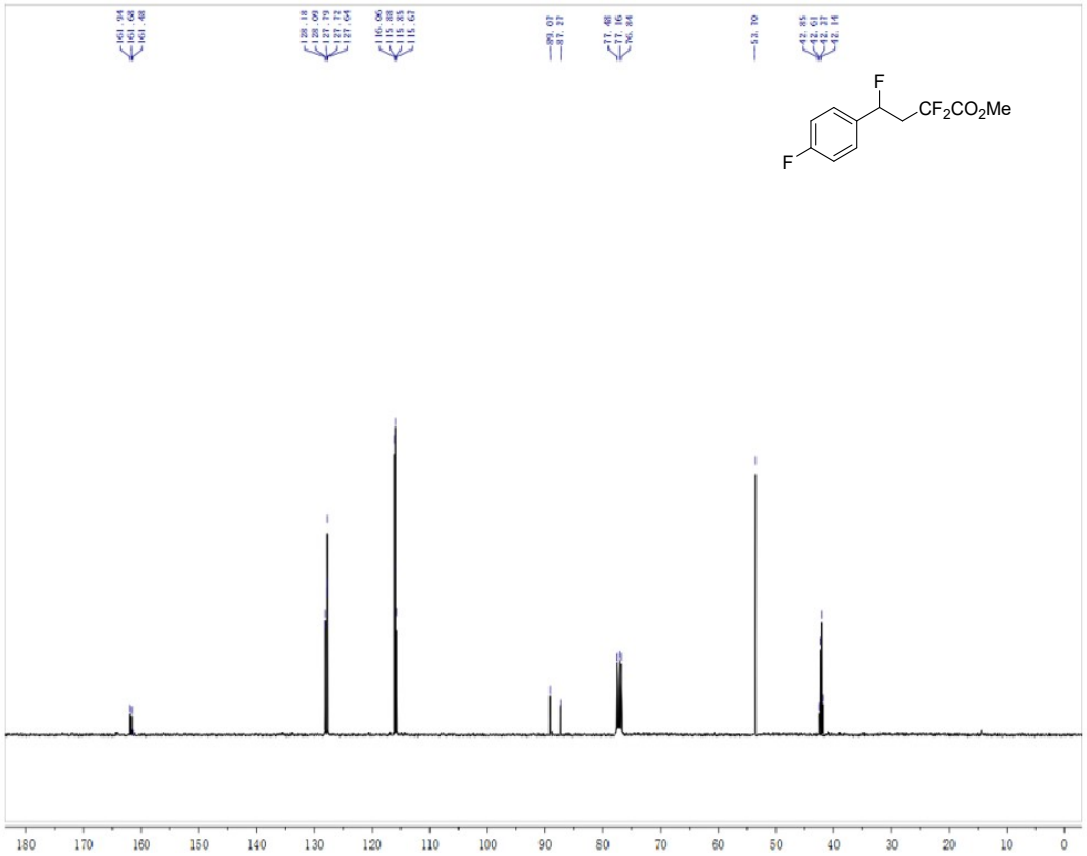
^{13}C{^{1}H} NMR for compound **4i**



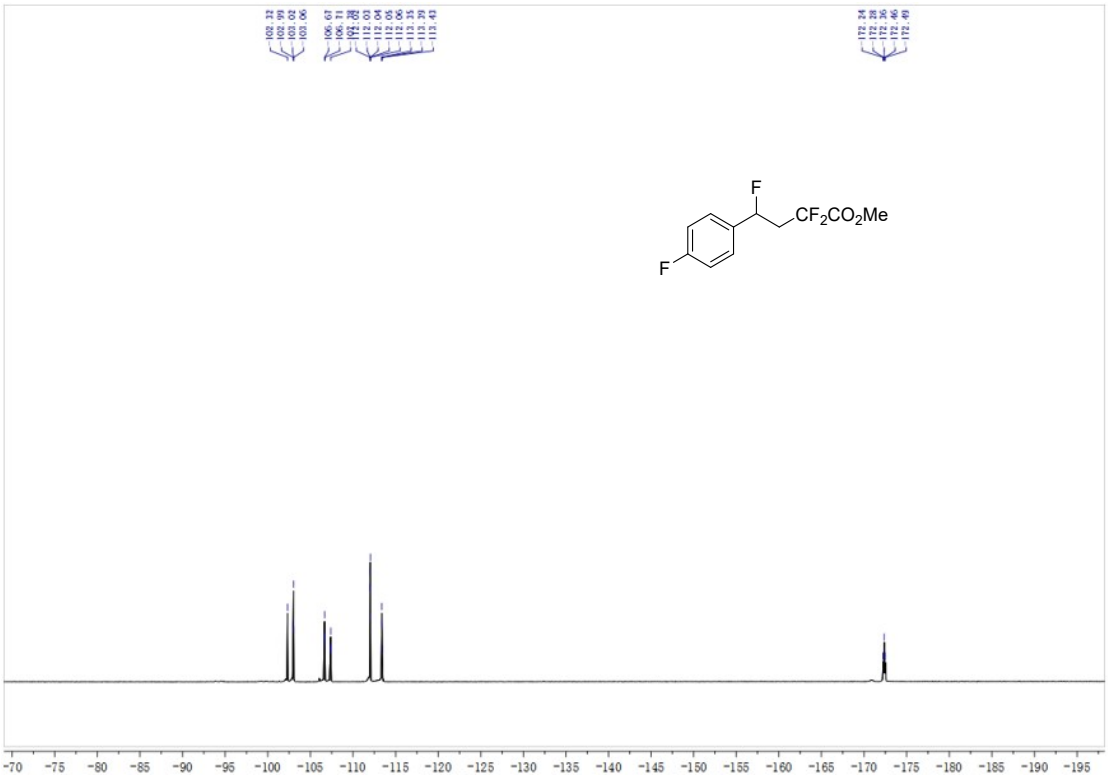
^{19}F NMR for compound **4i**



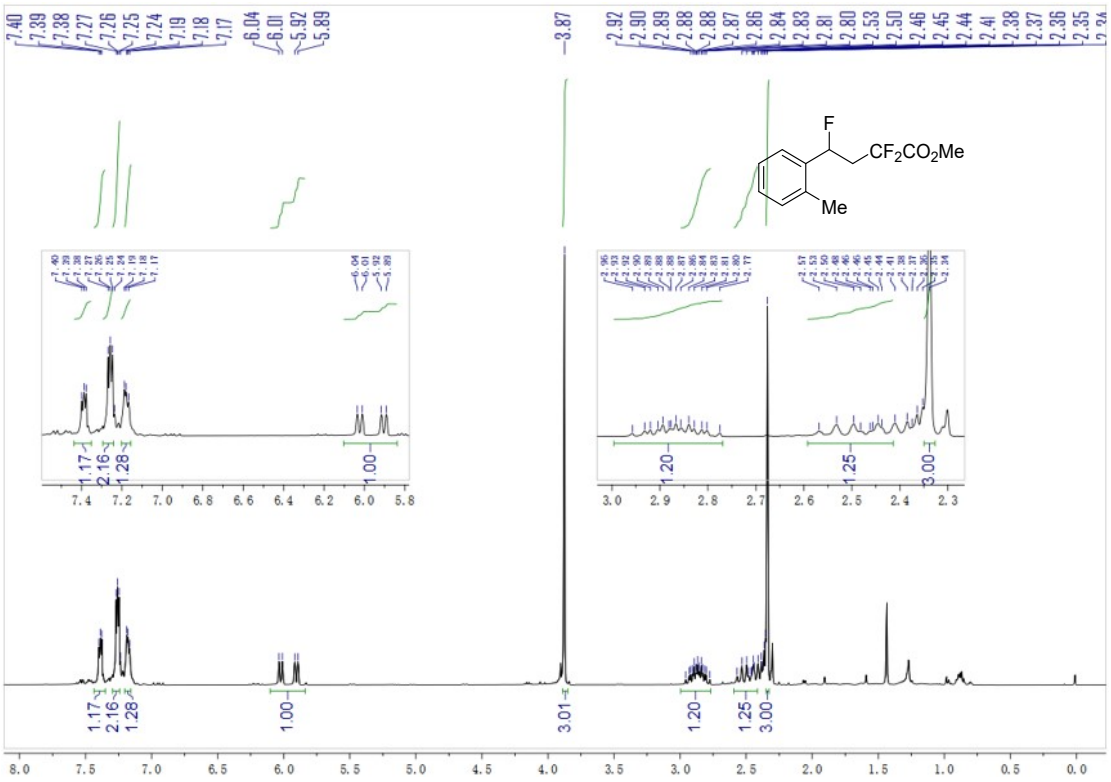
^{1}H NMR for compound **4j**



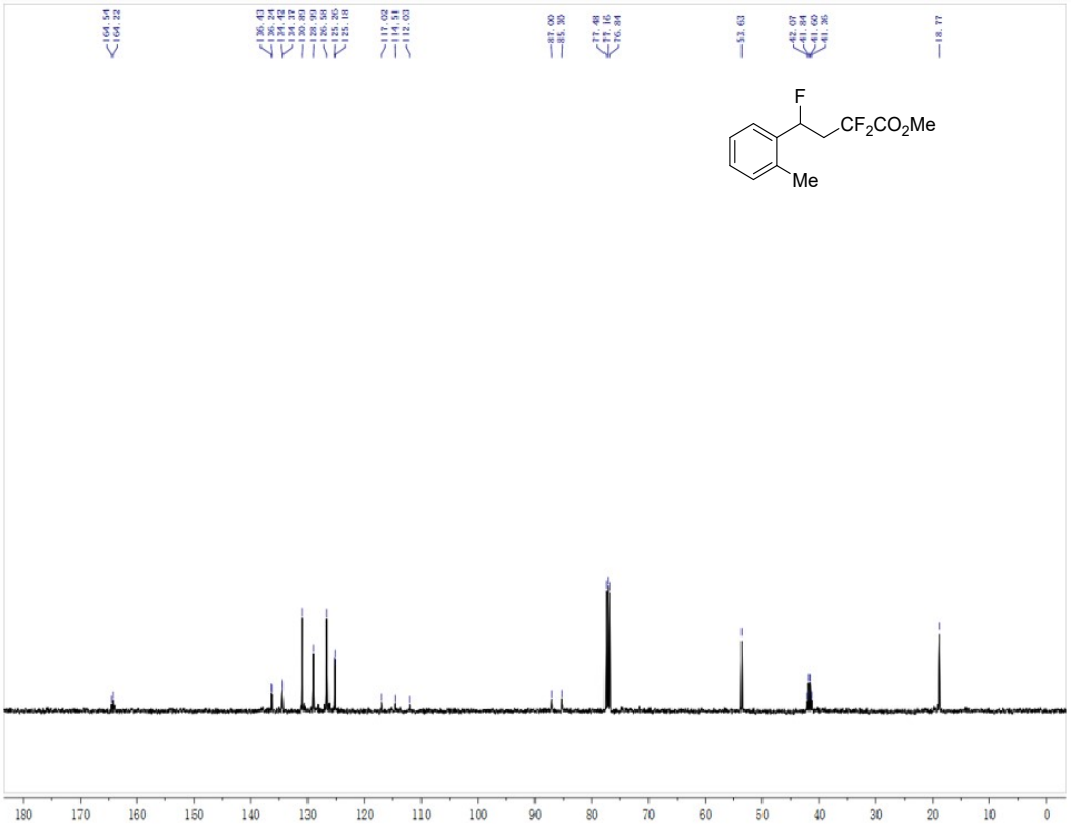
^{13}C{^{1}H} NMR for compound **4j**



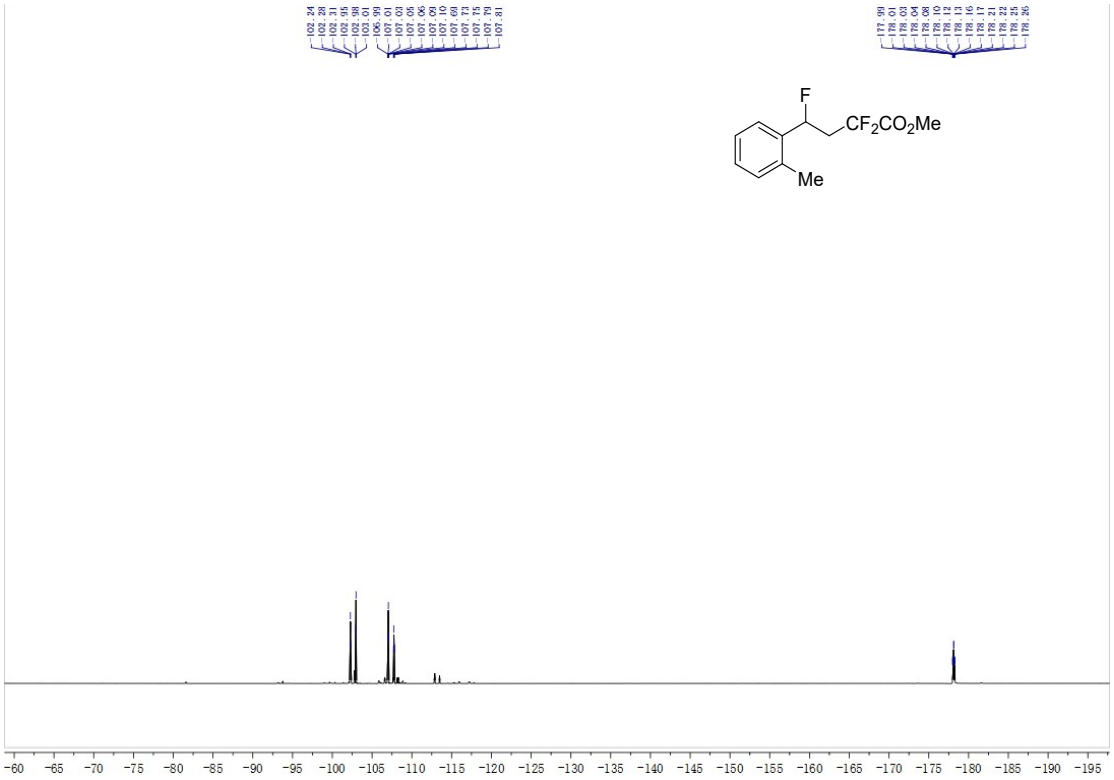
^{19}F NMR for compound **4j**



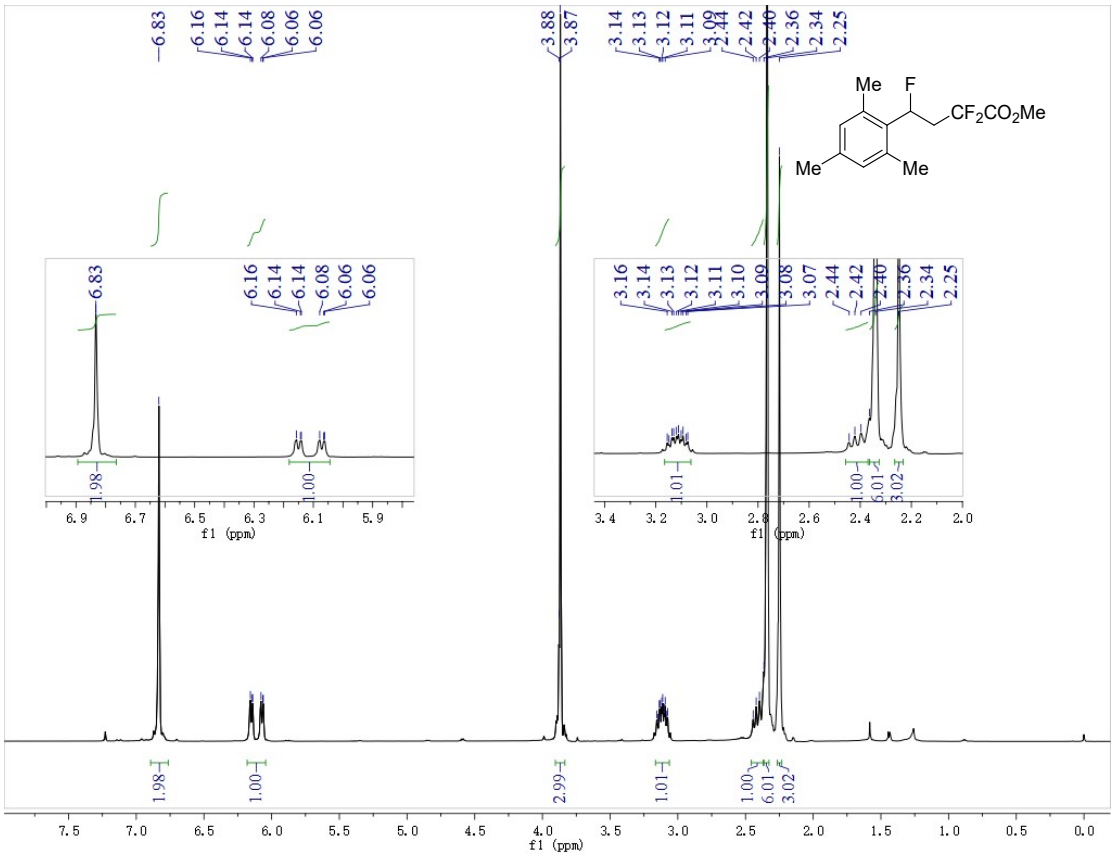
^{1}H NMR for compound **4k**



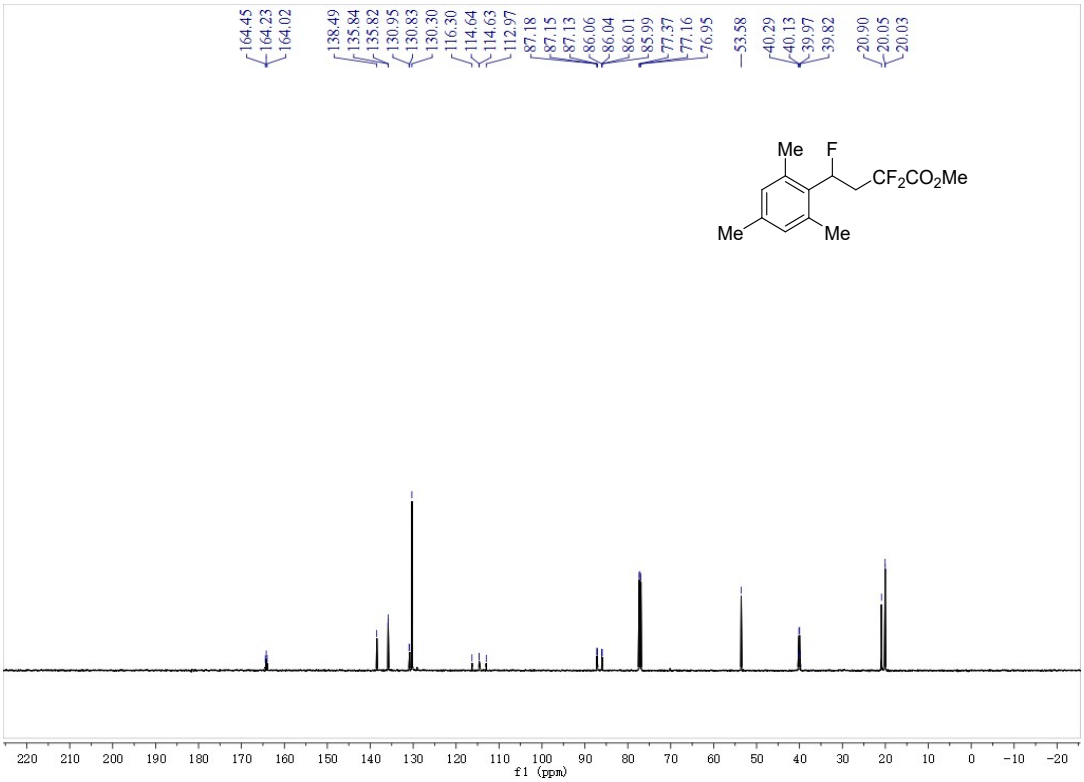
^{13}C{^{1}H} NMR for compound **4k**



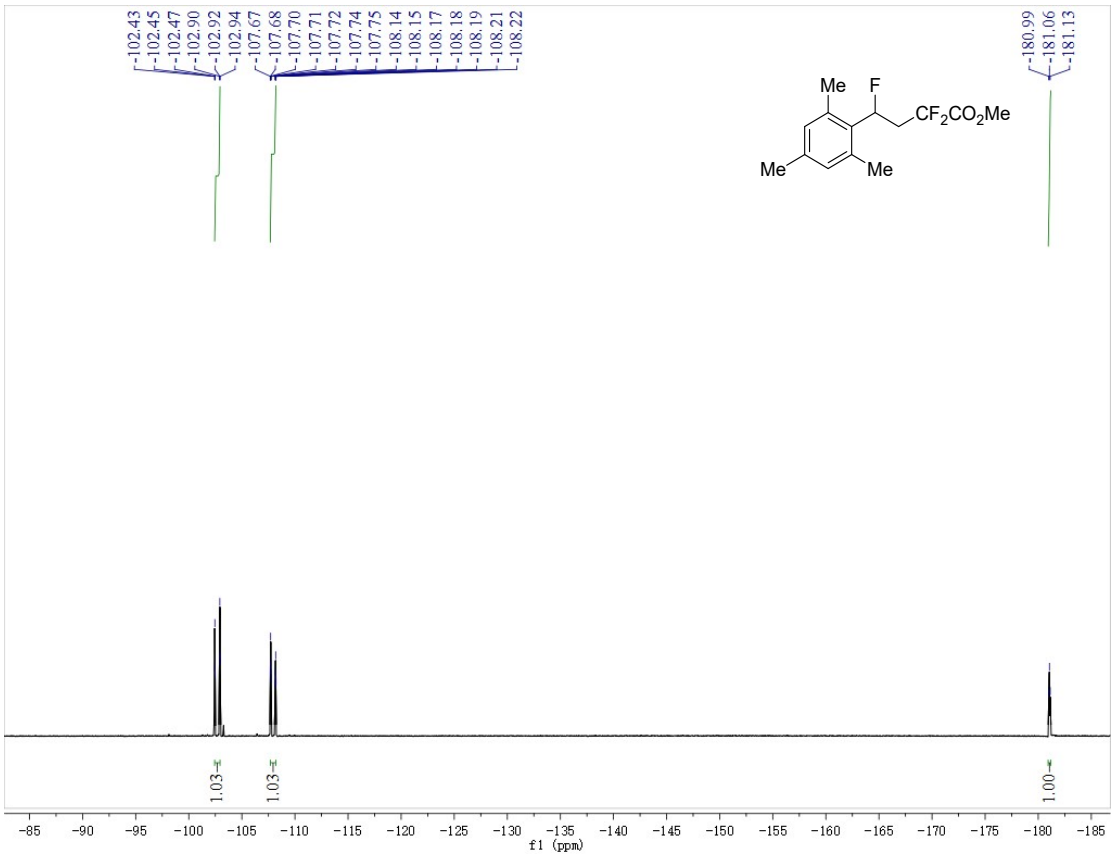
^{19}F NMR for compound **4k**



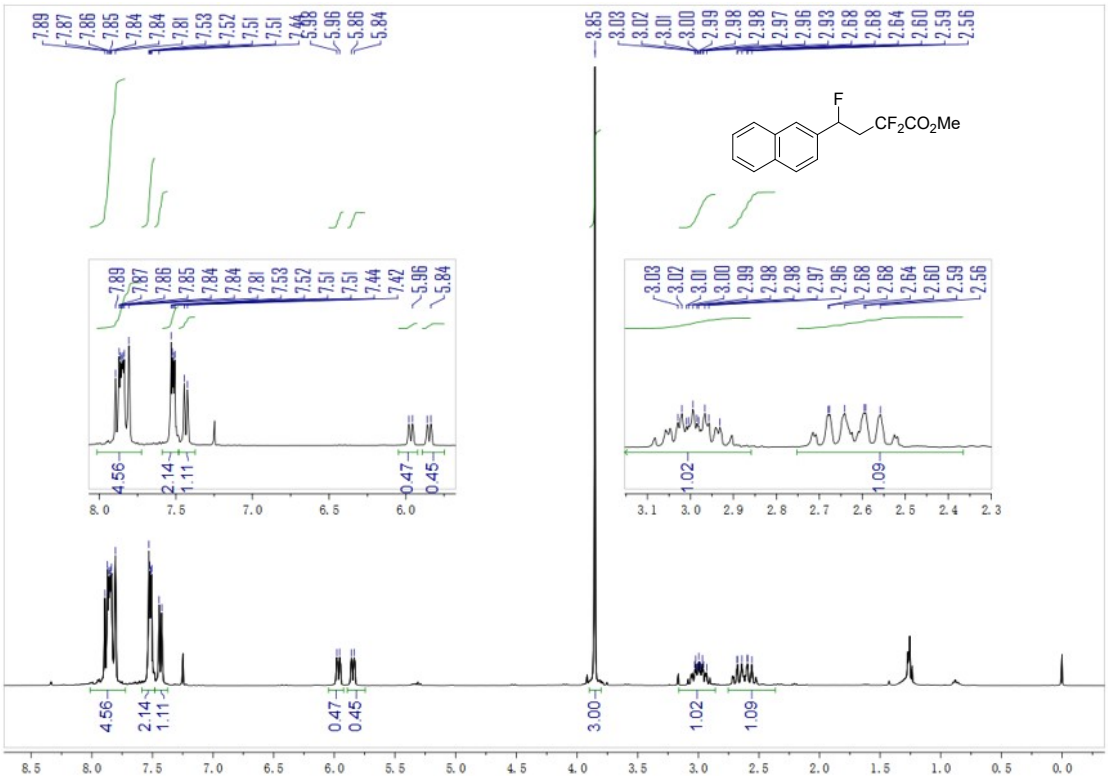
^{1}H NMR for compound **4l**



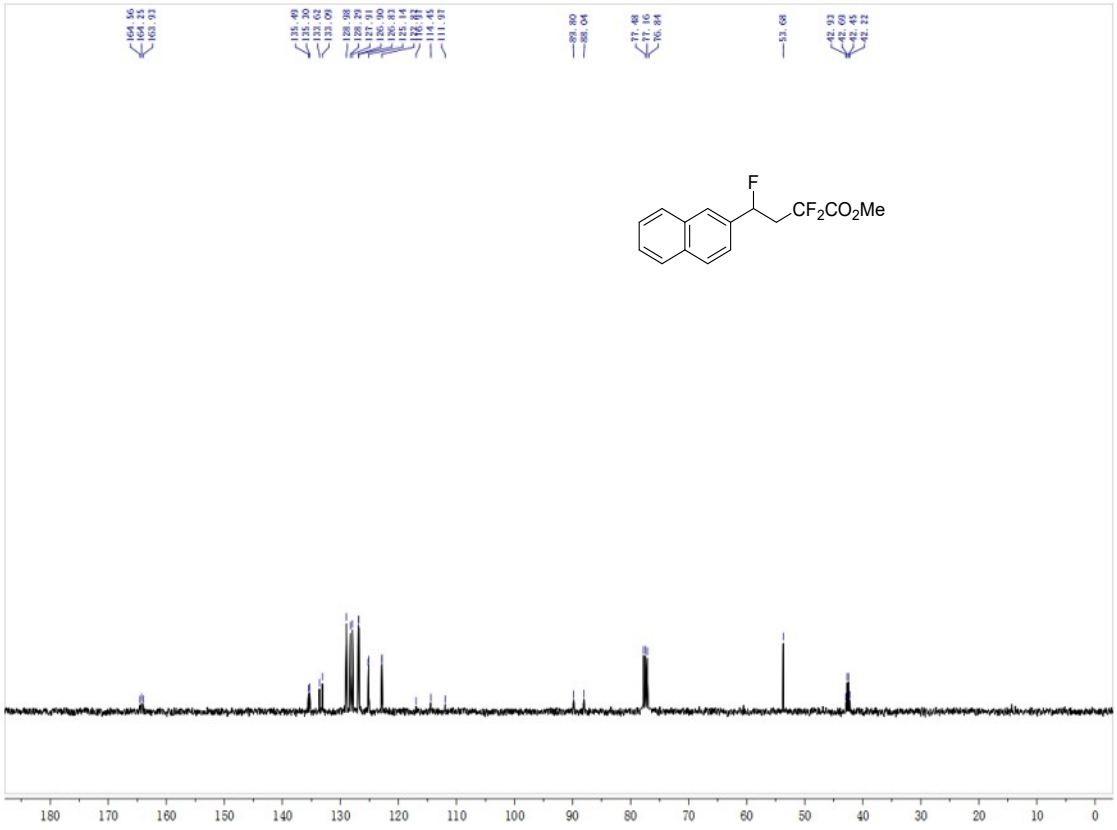
^{13}C{^{1}H} NMR for compound **4l**



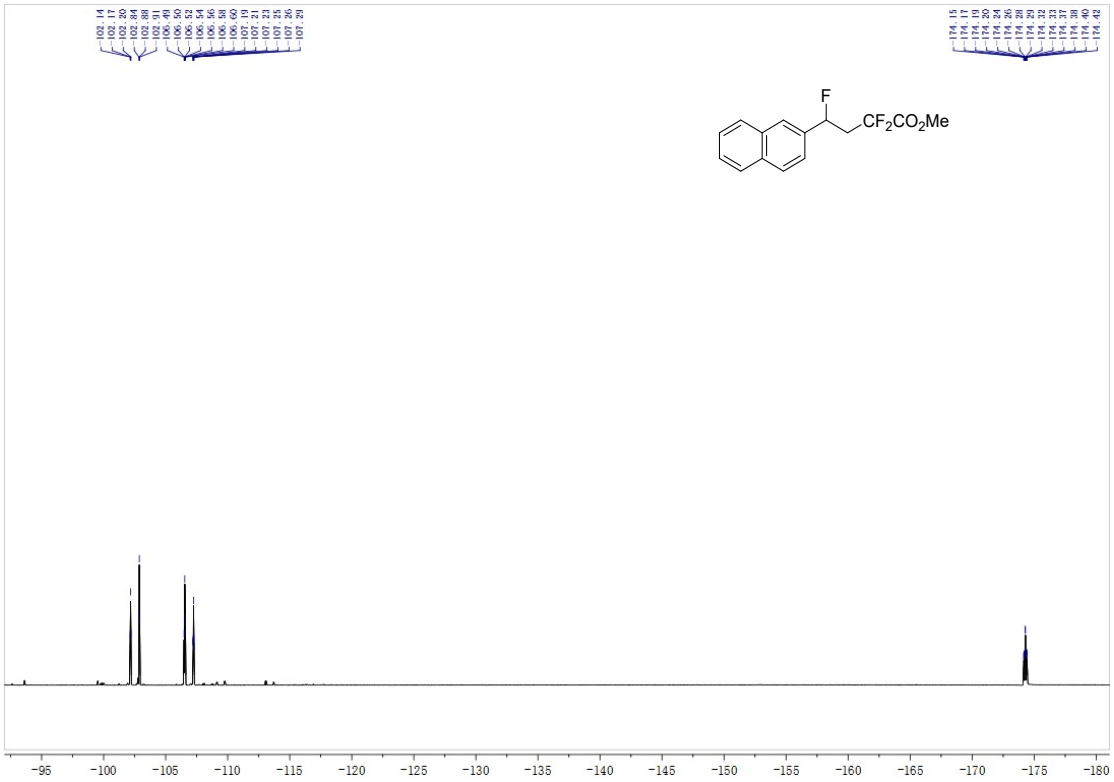
^{19}F NMR for compound **4l**



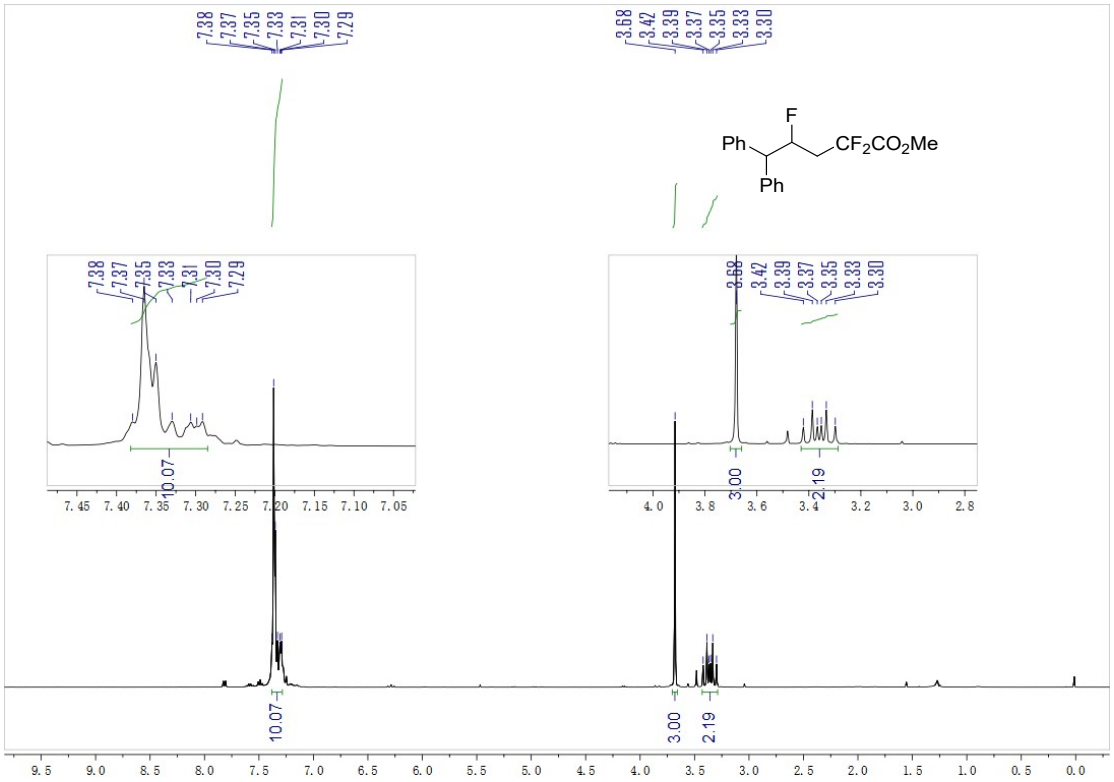
^{1}H NMR for compound **4m**



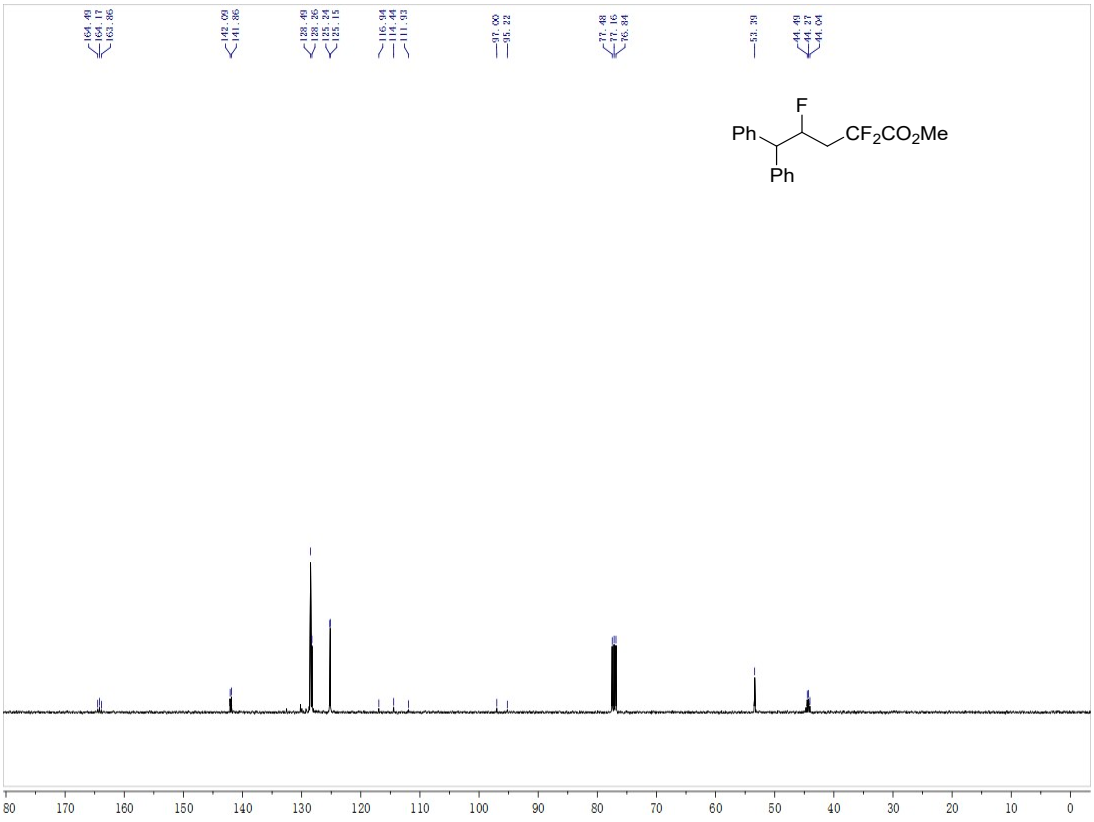
^{13}C{^{1}H} NMR for compound **4m**



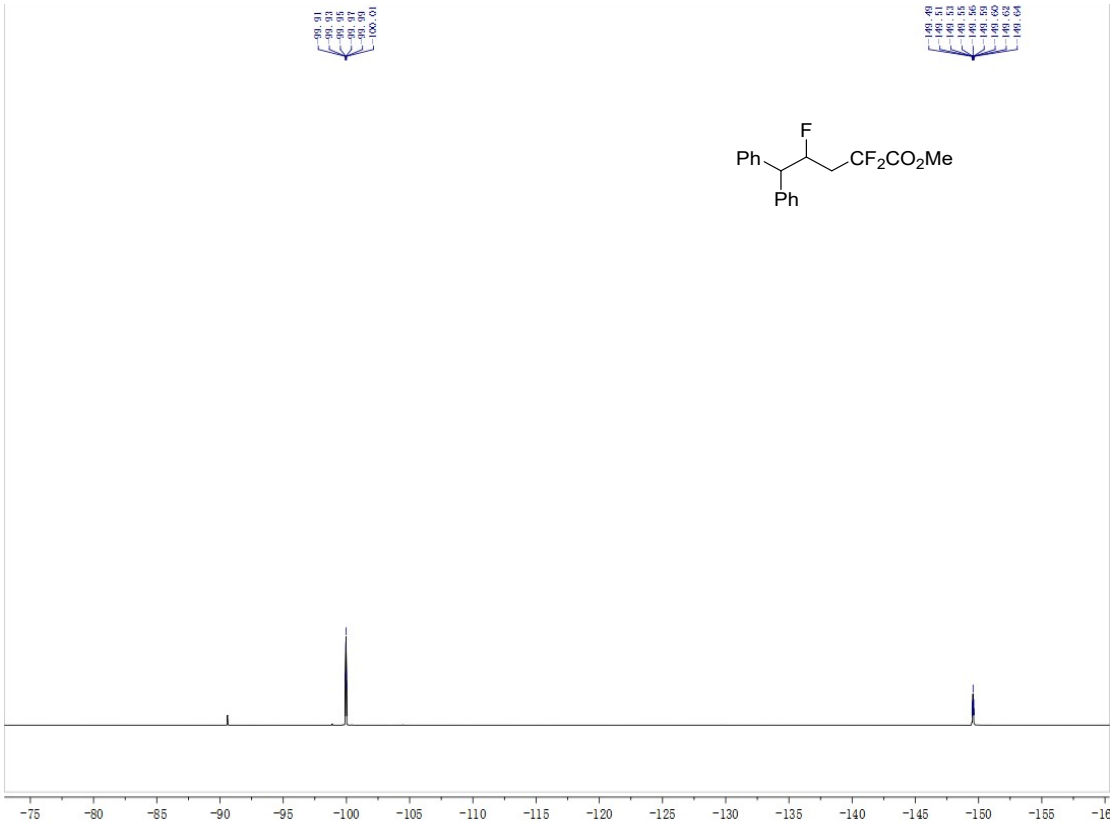
^{19}F NMR for compound **4m**



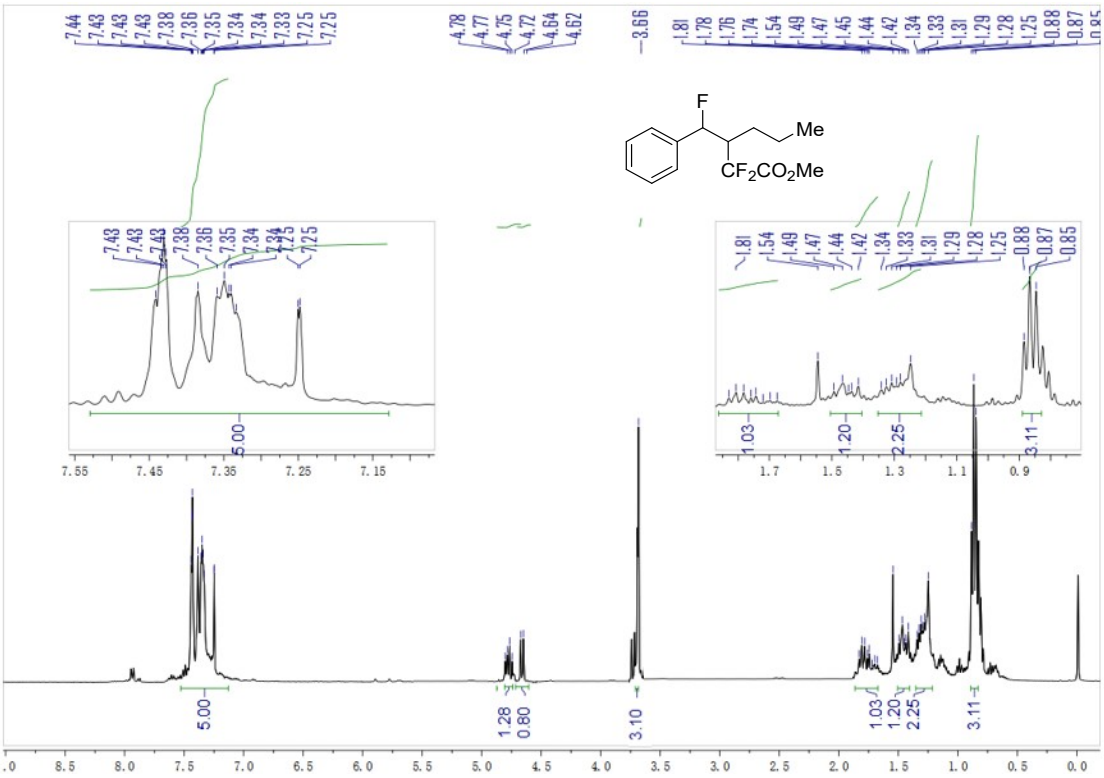
^{1}H NMR for compound **4n**



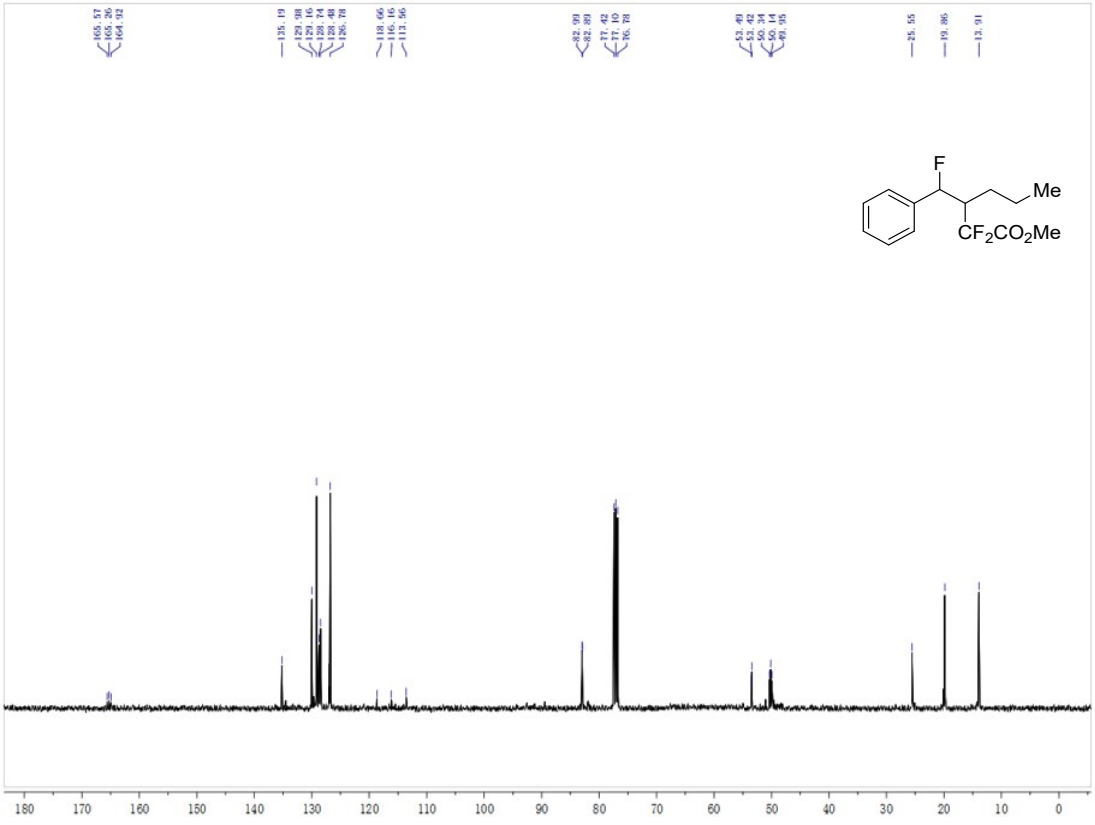
^{13}C{^{1}H} NMR for compound **4n**



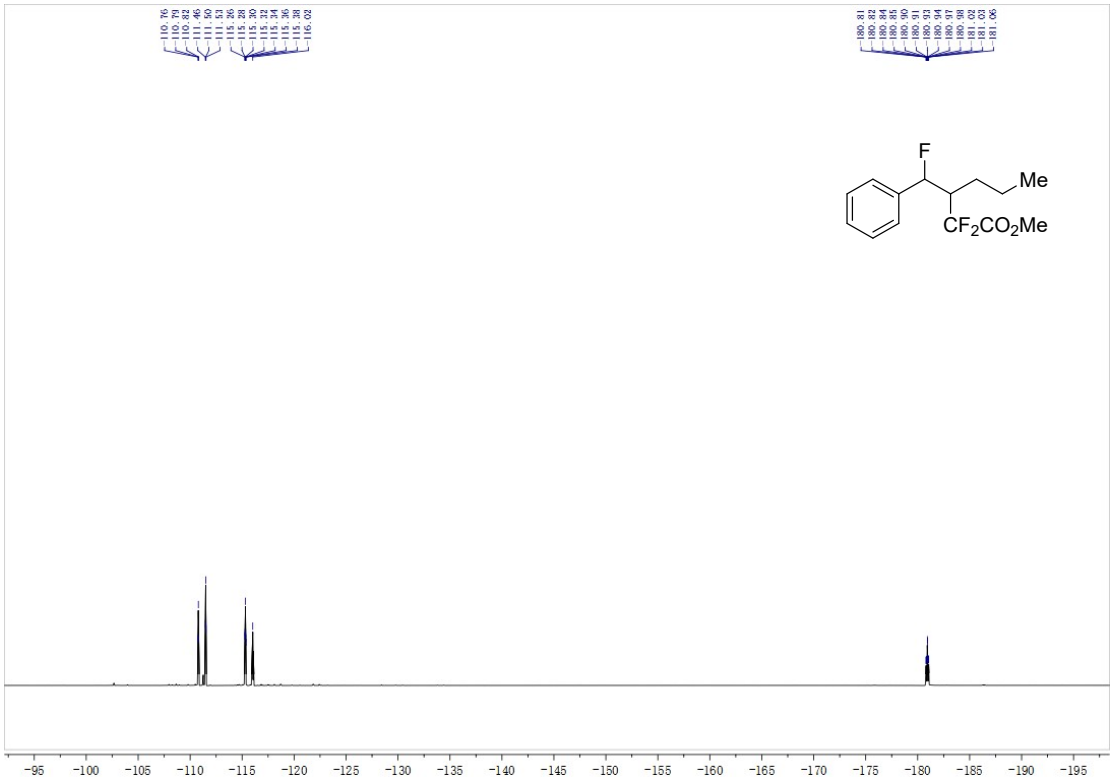
^{19}F NMR for compound **4n**



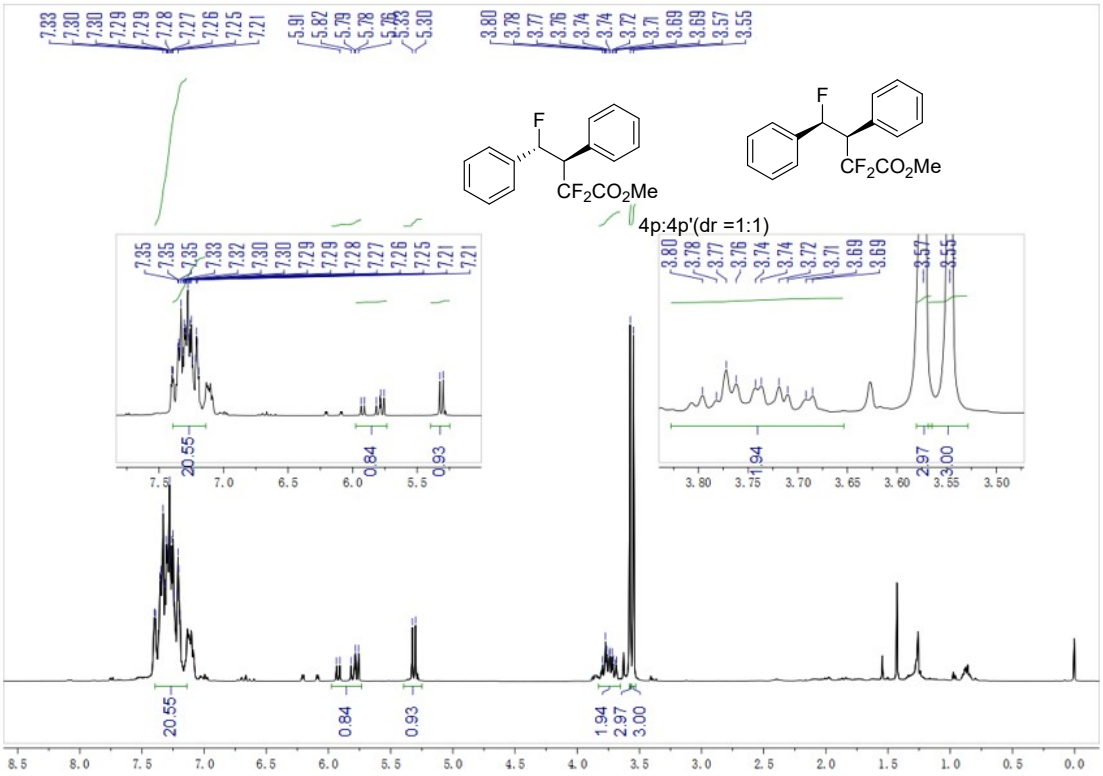
^{1}H NMR for compound **4o**



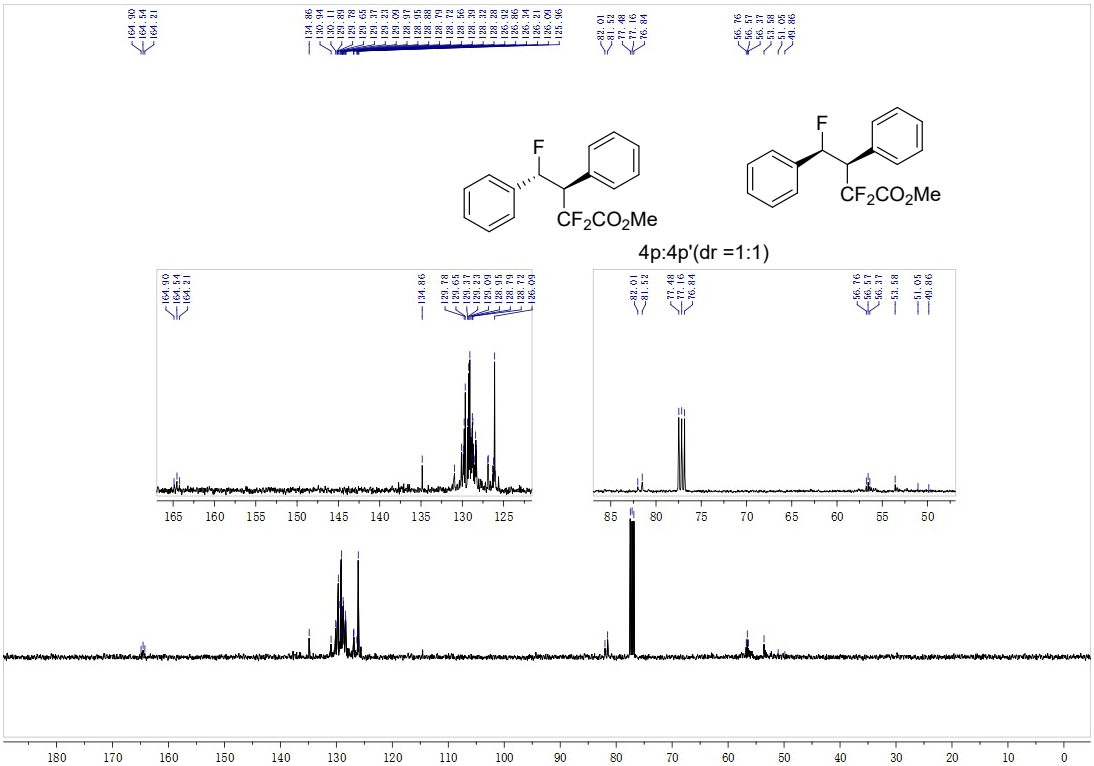
^{13}C{^{1}H} NMR for compound **4o**



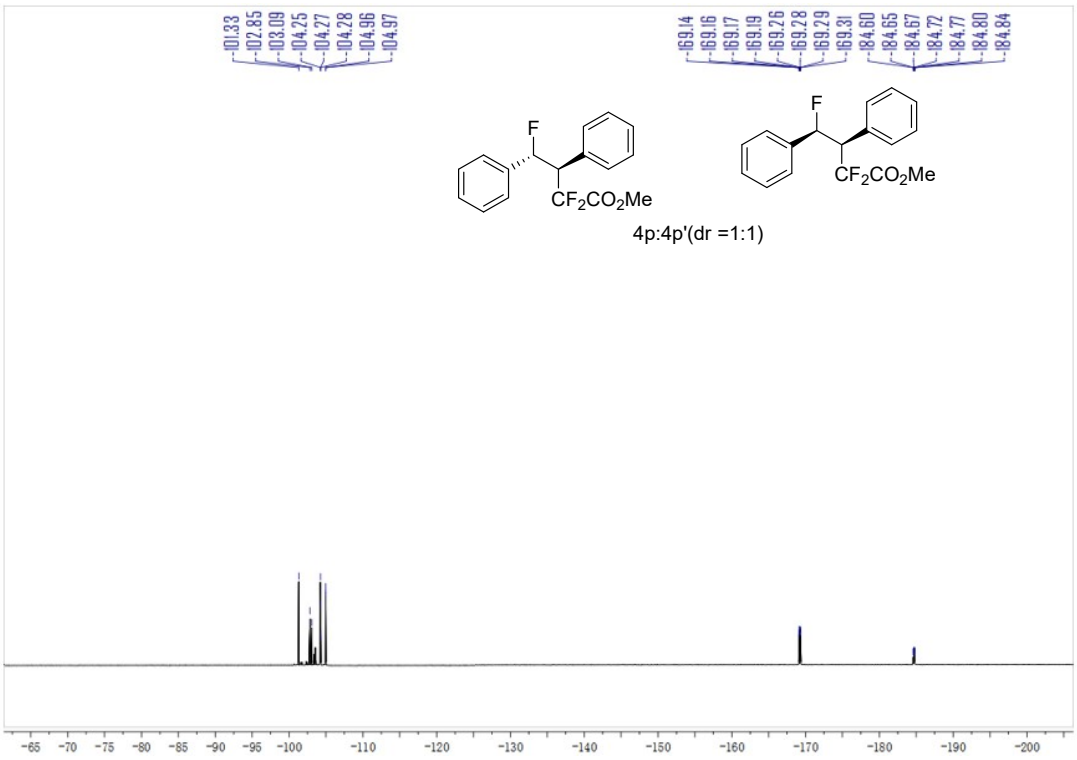
^{19}F NMR for compound **4o**



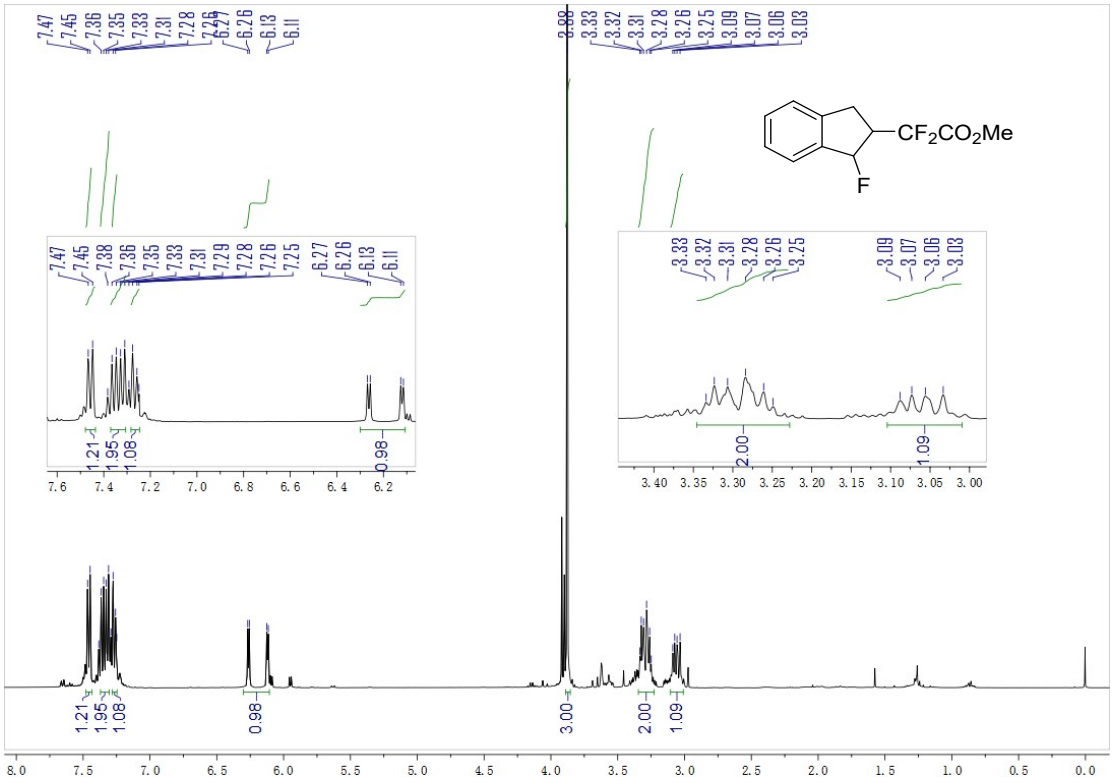
^{1}H NMR for compound of the mixture of **4p** and **4p′**



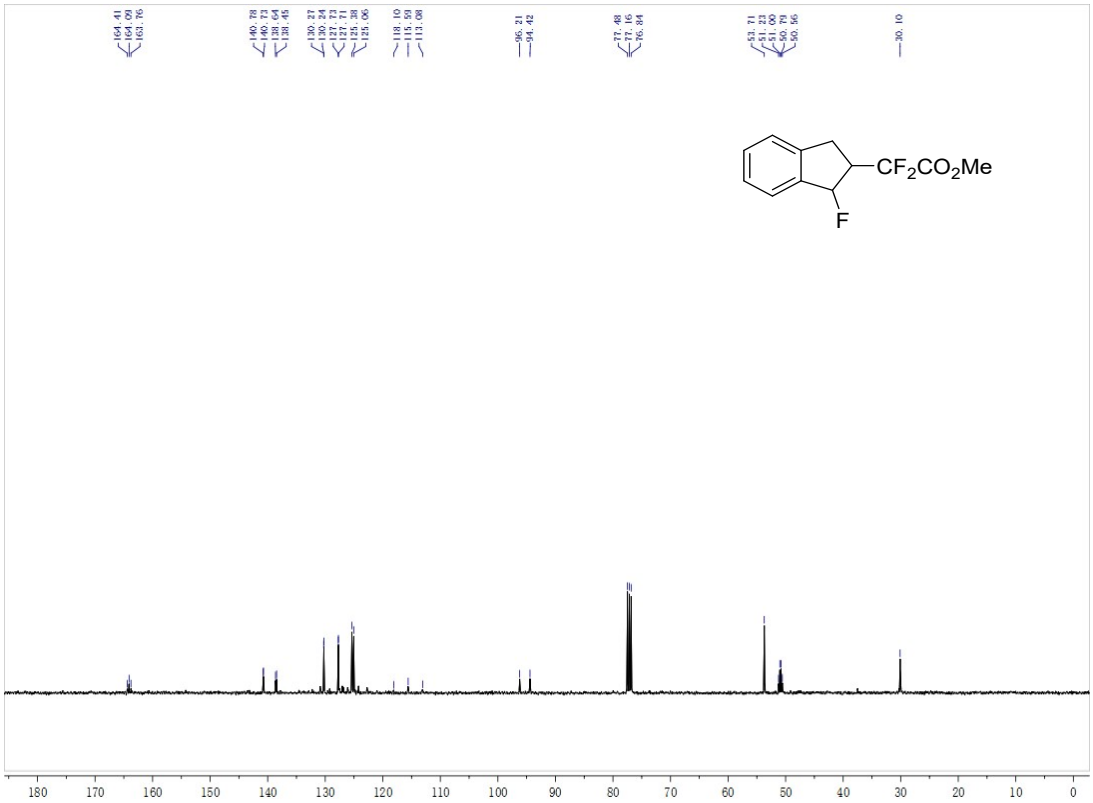
^{13}C{^{1}H} NMR for compound of the mixture of **4p** and **4p′**



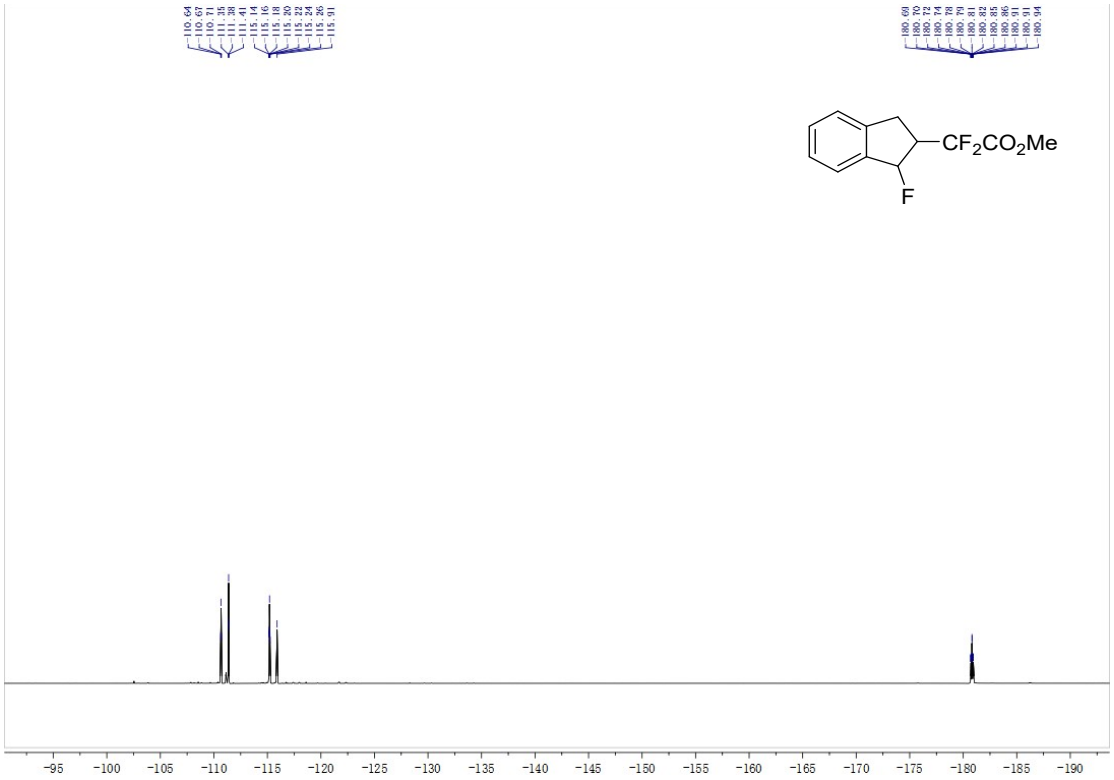
^{19}F NMR for compound of the mixture of **4p** and **4p′**



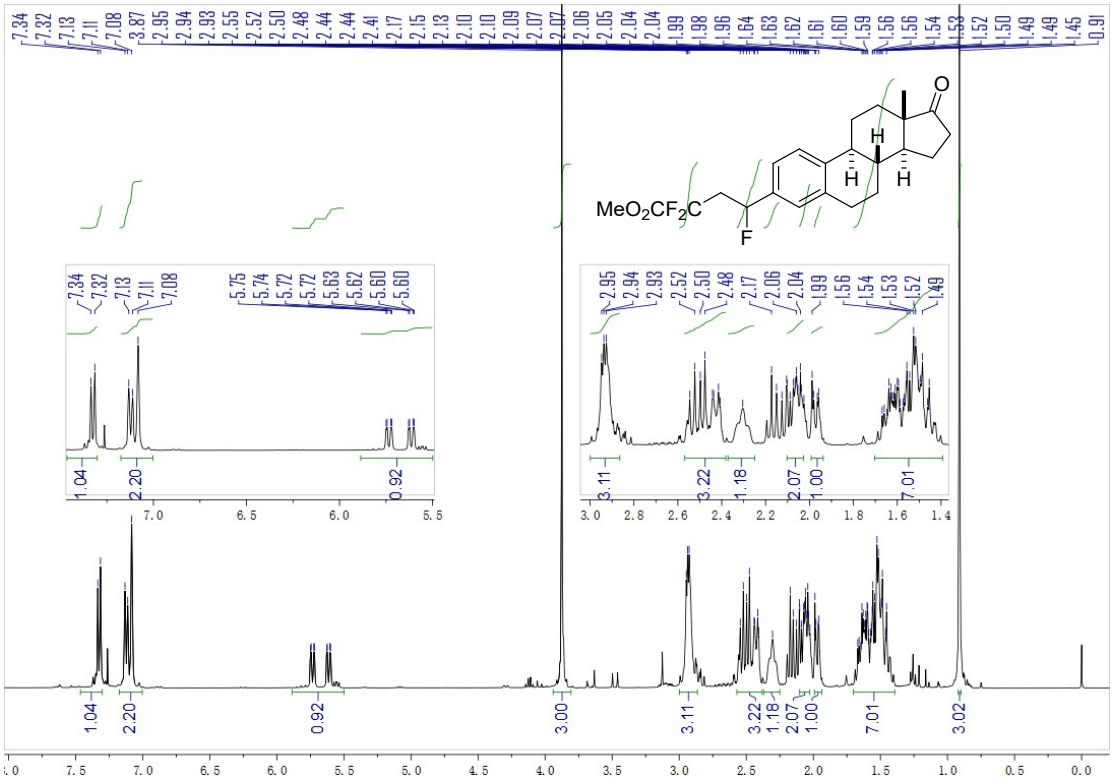
^{1}H NMR for compound **4q**



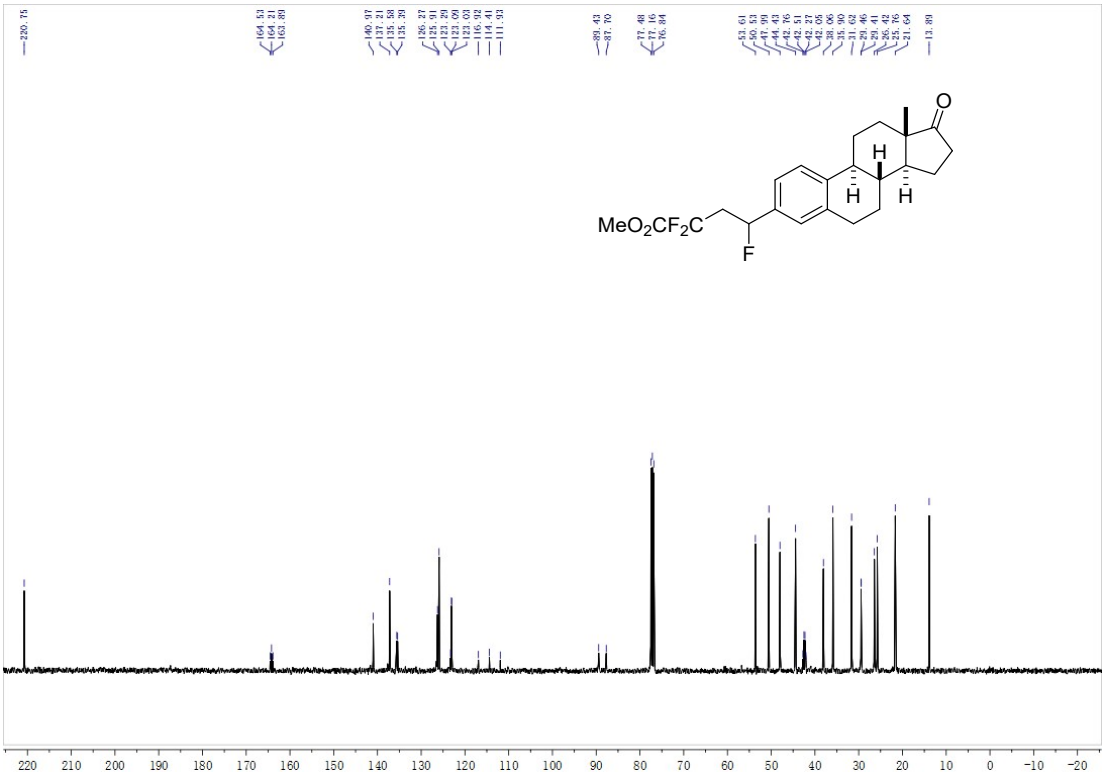
^{13}C{^{1}H} NMR for compound **4q**



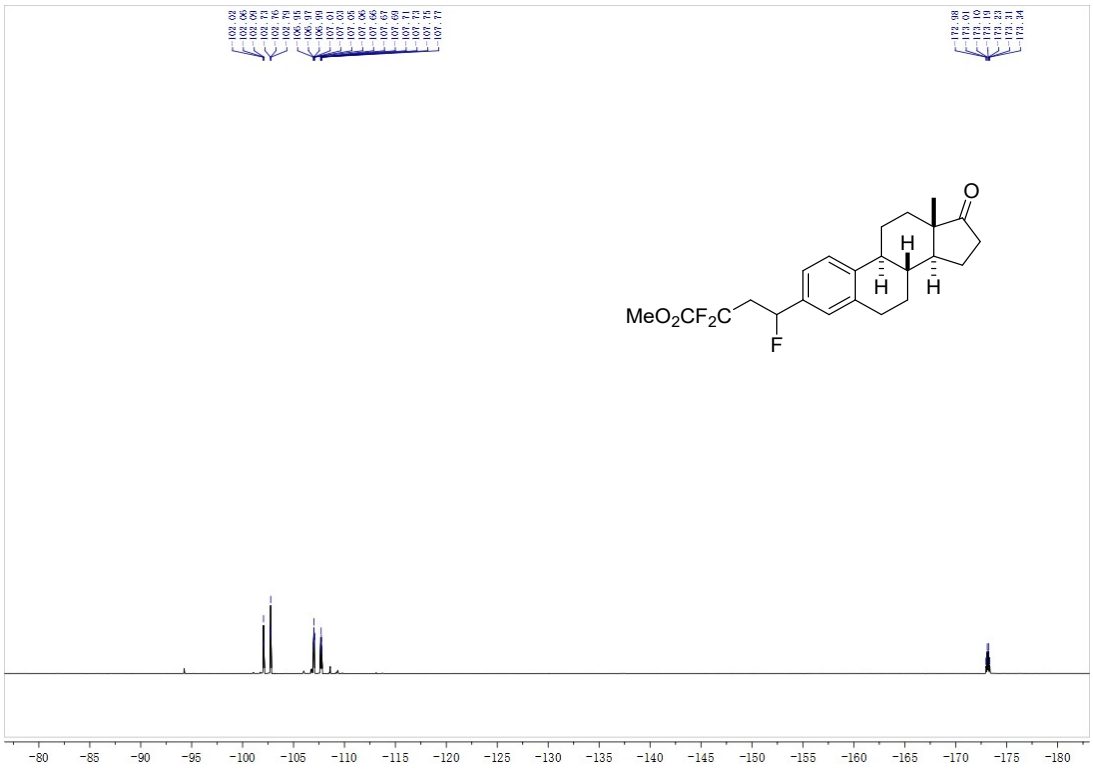
^{19}F NMR for compound **4q**



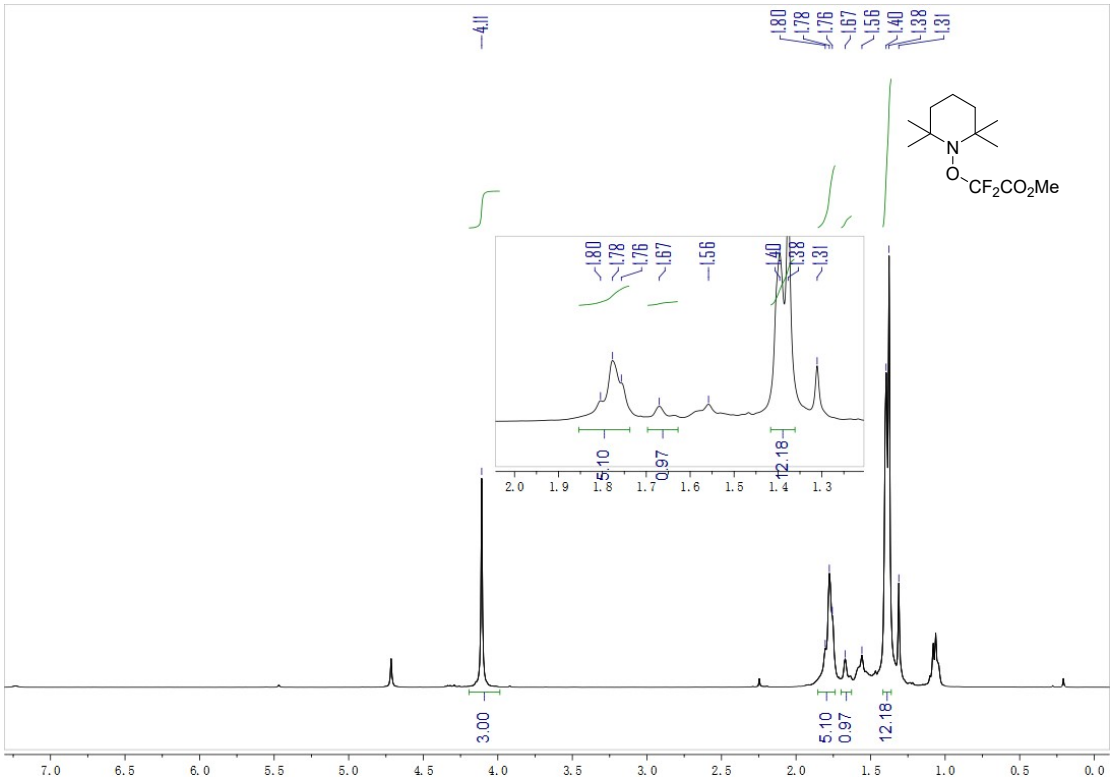
^{1}H NMR for compound **4r**



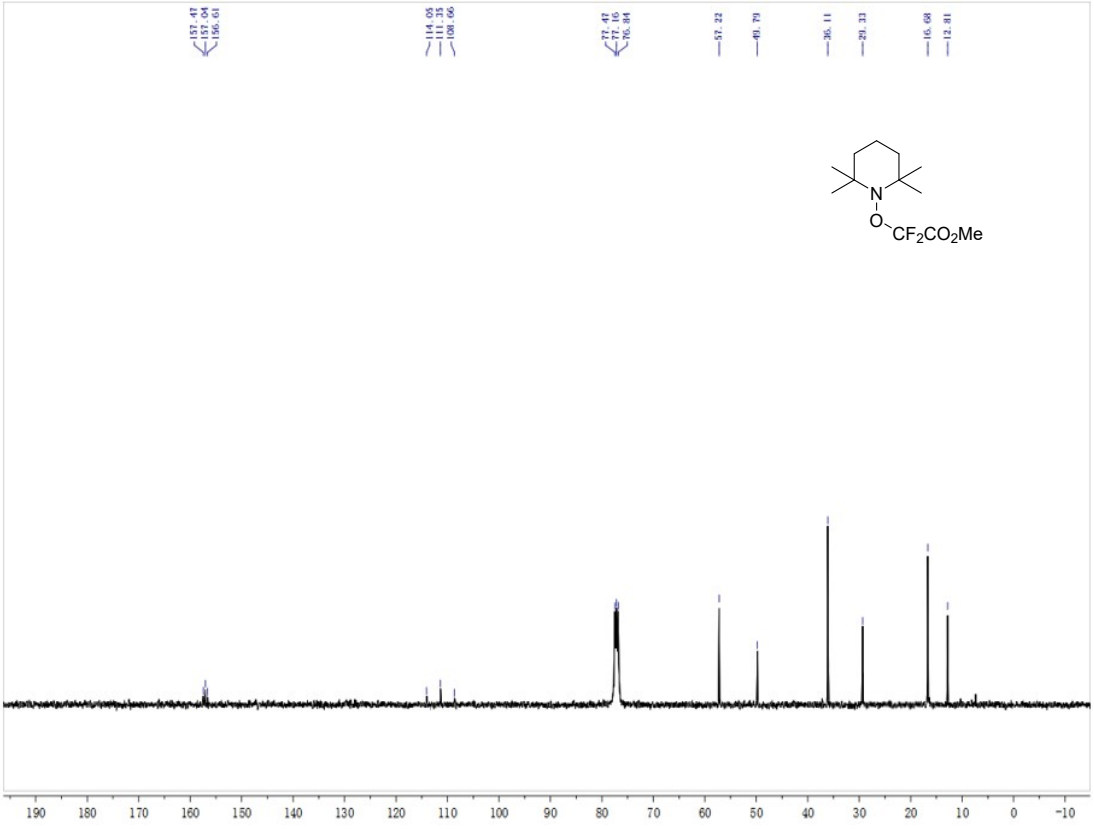
^{13}C{^{1}H} NMR for compound **4r**



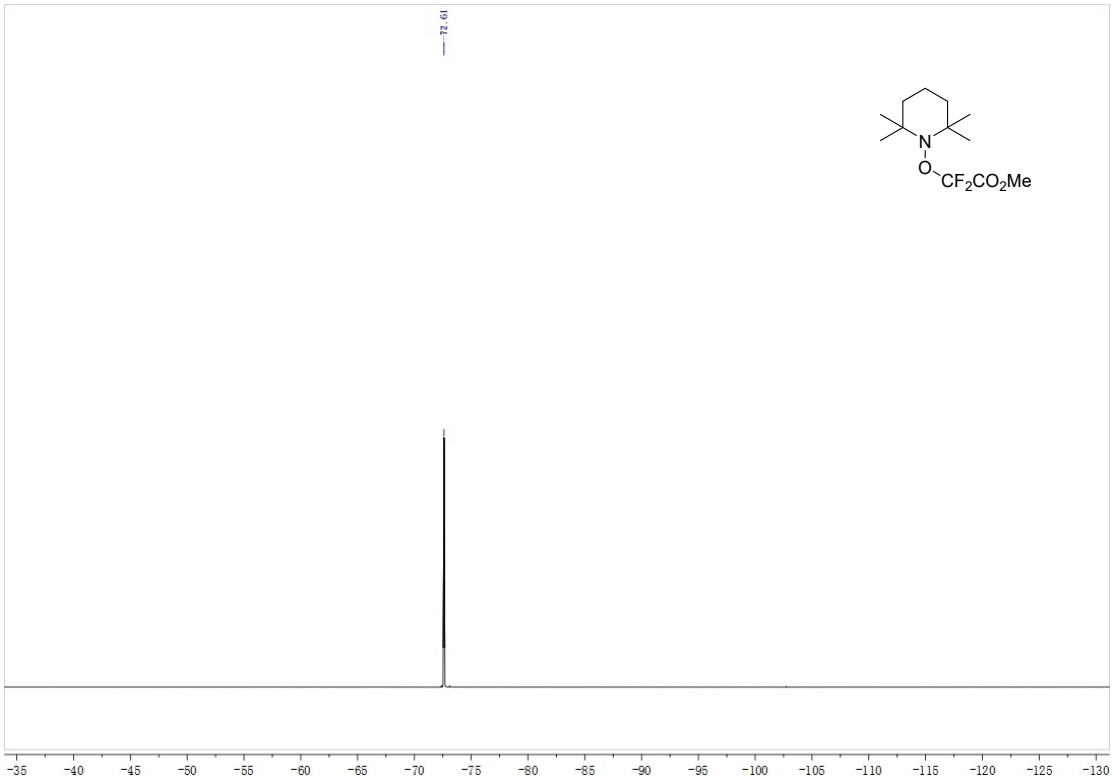
^{19}F NMR for compound **4r**



^{1}H NMR for compound **5**



^{13}C{^{1}H} NMR for compound **5**



^{19}F NMR for compound **5**