Electronic Supplementary Material (ESI) for ChemComm.

Three-Component Difluoroalkylation-Thiolation of alkenes by Iron-Facilitated Visible-light Photoredox Catalysis

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1. General Information

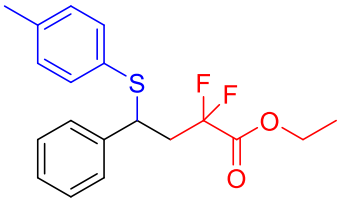
All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and compared with previously reported data. All experiments were conducted with a schlenk tube. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Waters UPLC H-class LC-MS instrument in the electrospray ionization (ESI) mode. Only molecular ions (M + 1) are given for the ESI-MS analysis. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz, 125 MHz and 470 MHz in $CDCl_3$, respectively, and chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. UV-Vis measurements were performed with an EVOLUTION 220 UV/Vis spectrophotometer.

2. Experimental Procedure

A 10 mL reaction vessel with a magnetic stirring bar was equipped with *fac*-$Ir(ppy)_3$ (1.3 mg, 0.002mmol, 0.01 equiv), $FeCl_2$ (5.1 mg, 0.04 mmol, 0.2 equiv) and thiophenol substrate **2** (0.3 mmol, 1.5 equiv for non-liquid substrates). The tube was then evacuated and back-filled with argon (Ar) for 3 times. Subsequently, CH_2Cl_2 (2 mL) was added followed by alkene **1** (0.2 mmol, 1.0 equiv), compound **3** (0.4 mmol, 2.0 equiv) and thiophenol substrate **2** (0.3 mmol, 1.5 equiv for liquid substrates) via syringe under Ar. Once added, the Schlenk tube was sealed at atmospheric pressure of Ar (1 atm). The reaction was stirred and irradiated with a 5 W blue LED lamp at r.t. for 24 h. The resulting mixture was diluted with 3 mL EtOAc. The reaction mixture was extracted by EtOAc with three times and the combined organic phases were concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc = 98/2) to give the pure desired product.

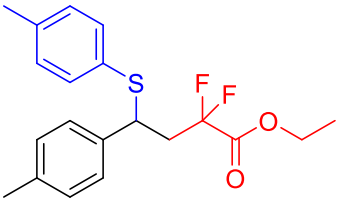
3. Characterization Data

Ethyl 2,2-difluoro-4-phenyl-4-(*p*-tolylthio)butanoate (4a)[1]



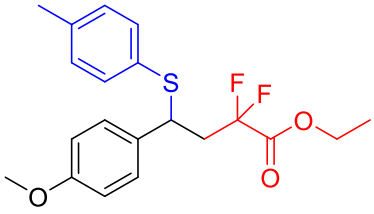
Following the general procedure, the title compound was obtained (59.5 mg, 85% yield, colorless oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 - 7.16 (m, 7H), 7.05 (d, J = 7.9 Hz, 2H), 4.29 (dd, J = 9.3, 5.1 Hz, 1H), 4.00 - 3.86 (m, 2H), 2.87 - 2.68 (m, 2H), 2.31 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.56 (t), 139.81 (s), 138.36 (s), 133.76 (s), 129.80 (s), 129.71 (s), 128.42 (s), 128.00 (s), 127.77 (s), 114.87 (t), 62.86 (s), 47.25 (s), 40.51 (s), 21.20 (s), 13.72 (s); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.21 (d, J = 11.8 Hz, 1F), -105.05 (d, J= 13.0 Hz, 1F); **ESI-MS** m/z: 351.13 $[M+1]^+$.

Ethyl 2,2-difluoro-4-(p-tolyl)-4-(p-tolylthio)butanoate (4b)



Following the general procedure, the title compound was obtained (62.6 mg, 86% yield, colorless oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.19 (d, J = 7.9 Hz, 2H), 7.14-7.01 (m, 6H), 4.28 (dd, J = 9.3, 4.9 Hz, 1H), 3.94 (tdd, J = 10.7, 7.2, 3.5 Hz, 2H), 2.86-2.63 (m, 2H), 2.30 (d, J = 2.2 Hz, 6H), 1.18 (t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.59 (t, J = 32.3 Hz), 138.20 (s), 137.48 (s), 136.73 (s), 133.56 (s), 130.03 (s), 129.81 (s), 129.12 (s), 127.87 (s), 114.94 (t, J = 252.9 Hz), 62.84 (s), 46.93 (s), 40.63 (s), 21.17 (d, J = 5.4 Hz), 13.70 (s); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.23 (d, J = 8.6 Hz, 1F), -105.21 (d, J= 5.7 Hz, 1F); **ESI-MS** m/z: 365.20 $[M+1]^+$.

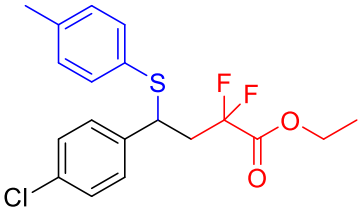
Ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-(p-tolylthio)butanoate (4c)



Following the general procedure, the title compound was obtained (67.7 mg, 89% yield, colorless oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ7.19 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 7.9 Hz, 2H), 6.79

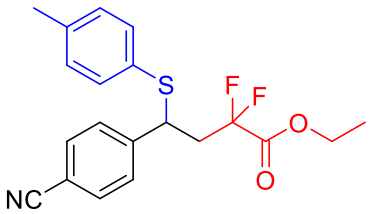
(d, J = 8.6 Hz, 2H), 4.28 (dd, J = 9.5, 4.9 Hz, 1H), 4.00-3.91 (m, 2H), 3.77 (s, 3H), 2.83-2.65 (m, 2H), 2.31 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ163.58 (t), 159.10 (s), 138.24 (s), 133.66 (s), 131.66 (s), 129.94 (s), 129.80 (s), 129.15 (s), 114.91 (t), 113.77 (s), 62.86 (s), 55.30 (s), 46.62 (s), 40.66 (t), 21.20 (s), 13.73 (s); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -102.05 (d, J = 11.5 Hz, 1F), -105.27 (d, J= 12.8 Hz, 1F); **ESI-MS** m/z: 381.19 $[M+1]^+$.

Ethyl 4-(4-chlorophenyl)-2,2-difluoro-4-(p-tolylthio)butanoate (4d)



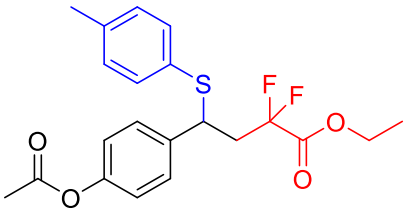
Following the general procedure, the title compound was obtained (62.2 mg, 81% yield, colorless oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.22 (d, J = 8.5 Hz, 2H), 7.14 (dd, J = 18.2, 8.3 Hz, 4H), 7.06 (d, J = 7.9 Hz, 2H), 4.26 (dd, J = 8.2, 6.1 Hz, 1H), 4.03 (qd, J = 7.1, 5.0 Hz, 2H), 2.78-2.66 (m, 2H), 2.31 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ163.52 (t), 138.67 (s), 133.97 (s), 133.42 (s), 129.89 (s), 129.31 (s), 129.17(s), 128.78 (s), 128.56 (s), 114.76 (t), 63.02 (s), 46.70 (s), 40.38 (t), 21.21 (s), 13.76 (s); **^{19}F NMR (471 MHz, $CDCl_3$)** δ-102.83 (d, J = 14.6 Hz, 1F), -104.51 (d, J= 14.9 Hz, 1F); **ESI-MS** m/z: 385.33 $[M+1]^+$.

Ethyl 4-(4-cyanophenyl)-2,2-difluoro-4-(p-tolylthio)butanoate (4e)



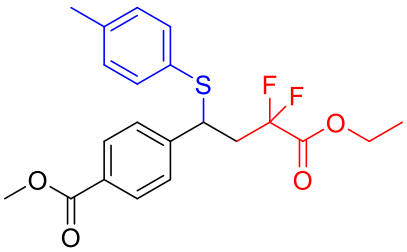
Following the general procedure, the title compound was obtained (69.1 mg, 92% yield, colorless oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.57-7.50 (m, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.08 (dd, J = 32.6, 8.0 Hz, 4H), 4.31 (dd, J = 8.6, 5.8 Hz, 1H), 4.12 (qd, J = 7.2, 2.4 Hz, 2H), 2.76 (ddd, J = 15.0, 14.4, 7.1 Hz, 2H), 2.31 (s, 3H), 1.27 (t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ163.42 (t), 145.91 (s), 139.16 (s), 134.32 (s), 132.19 (s), 130.00 (s), 128.66 (s), 128.35 (s), 118.60 (s), 114.61 (t), 111.38 (s), 63.17 (s), 47.13 (s), 39.87 (t), 21.22 (s), 13.82 (s); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -103.40 (d, J = 15.2 Hz, 1F), -104.11 (d, J= 15.5 Hz, 1F); **ESI-MS** m/z: 376.33 $[M+1]^+$.

Ethyl 4-(4-acetoxyphenyl)-2,2-difluoro-4-(p-tolylthio)butanoate (4f)



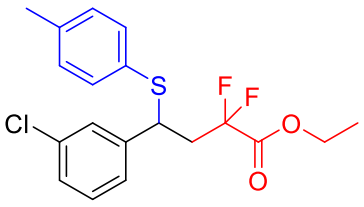
Following the general procedure, the title compound was obtained (61.2 mg, 75% yield, colorless oil).**^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.18 (dd, J = 14.2, 8.3 Hz, 4H), 7.06 (d, J = 7.9 Hz, 2H), 6.98 (d, J = 8.5 Hz, 2H), 4.28 (dd, J = 9.1, 5.2 Hz, 1H), 4.05 – 3.90 (m, 2H), 2.83 – 2.65 (m, 2H), 2.31 (s, 3H), 2.28 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ169.22 (s), 163.51 (t), 150.11 (s), 138.53 (s), 137.34 (s), 133.90 (s), 129.85 (s), 129.41 (s), 129.03 (s), 121.53 (s), 114.77 (t), 63.05 (s), 46.70 (s), 40.57 (t), 29.74 (s), 21.17 (d, J = 5.4 Hz), 13.76 (s); **^{19}F NMR (471 MHz, CDCl$_3$)** δ-102.04 (d, J = 15.8 Hz, 1F), -105.26 (d, J= 19.5 Hz, 1F); **ESI-MS** m/z: 409.35 $[M+1]^+$.

Methyl 4-(4-ethoxy-3,3-difluoro-4-oxo-1-(p-tolylthio)butyl)benzoate (4g)



Following the general procedure, the title compound was obtained (77.5 mg, 95% yield, colorless oil).**^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.92 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 4.34 – 4.29 (m, 1H), 4.04 (dd, J = 7.1, 4.6 Hz, 2H), 3.90 (s, 3H), 2.78 (ddd, J = 15.0, 8.8, 4.4 Hz, 2H), 2.30 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 166.74 (s), 163.48 (s), 145.43 (s), 138.79 (s), 134.13 (s), 130.23 (s), 129.88 (s), 129.80 – 129.19 (m), 128.88 (s), 127.96 (s), 114.73 (s), 112.72 (s), 63.02 (s), 52.17 (s), 47.13 (s), 40.13 (t), 21.20 (s), 13.77 (s); **^{19}F NMR (471 MHz, CDCl$_3$)** δ -103.20 (d, J = 14.9 Hz, 1F), -104.16 (d, J= 15.4 Hz, 1F); **ESI-MS** m/z: 309.34 $[M+1]^+$.

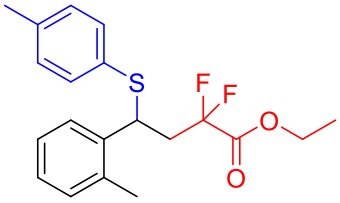
Ethyl 4-(3-chlorophenyl)-2,2-difluoro-4-(p-tolylthio)butanoate (4h)



Following the general procedure, the title compound was obtained (63.7 mg, 83% yield, colorless oil).**^{1}H NMR (500 MHz, CDCl$_3$)** δ7.23-7.13 (m, 5H), 7.10 -7.00 (m, 3H), 4.24 (dd, J = 8.6, 5.7 Hz, 1H), 4.09-3.97 (m, 2H), 2.82-2.67 (m, 2H), 2.31 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H); **^{13}C NMR**

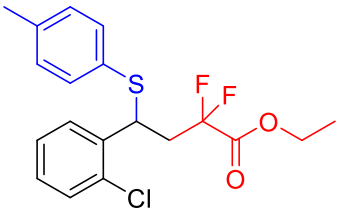
(125 MHz, $CDCl_3$) δ163.47 (t), 142.12 (s), 138.77 (s), 134.22 (s), 134.04 (s), 129.91 (s), 129.69 (s), 129.07 (s), 128.01 (s), 127.89 (s), 126.28 (s), 114.71 (t), 63.06 (s), 46.90 (t), 40.31 (t), 21.20 (s), 13.76 (s); **^{19}F NMR (471 MHz, $CDCl_3$)** δ-102.67 (d, J = 15.4 Hz, 1F), -104.60 (d, J= 17.2 Hz, 1F); **ESI-MS** m/z: 385.32 $[M+1]^+$.

Ethyl 2,2-difluoro-4-(o-tolyl)-4-(p-tolylthio)butanoate (4i)



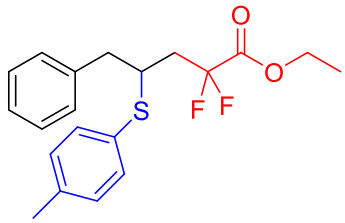
Following the general procedure, the title compound was obtained (61.9 mg, 85% yield, colorless oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ7.25-7.17 (m, 3H), 7.11 (ddd, J = 20.5, 16.3, 7.8 Hz, 5H), 4.56 (dd, J = 9.7, 4.6 Hz, 1H), 3.91-3.82 (m, 2H), 2.86 (ddt, J = 20.7, 14.8, 10.5 Hz, 1H), 2.70 (tdd, J = 15.1, 13.0, 4.6 Hz, 1H), 2.31 (d, J = 14.8 Hz, 6H), 1.17 (t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ163.59 (t, J = 32.3 Hz), 138.49 (s), 137.45 (s), 136.22 (s), 133.98 (s), 130.48 (s), 129.83 (s), 127.53 (s), 127.17 (s), 126.15 (s), 114.91 (t), 62.83 (s), 42.44 (s), 40.17 (t), 21.21 (s), 19.34 (s), 13.67 (s);**^{19}F NMR (471 MHz, $CDCl_3$)** δ-101.98 (d, J = 11.3 Hz, 1F), -105.58 (d, J= 20.5 Hz, 1F); **ESI-MS** m/z: 365.26 $[M+1]^+$.

Ethyl 4-(2-chlorophenyl)-2,2-difluoro-4-(p-tolylthio)butanoate (4j)



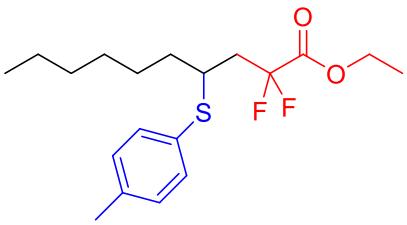
Following the general procedure, the title compound was obtained (68.4 mg, 89% yield, colorless oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.33-7.28 (m, 2H), 7.23 -7.14 (m, 4H), 7.06 (d, J = 7.9 Hz, 2H), 4.92 (s, 1H), 4.11-4.00 (m, 2H), 2.86-2.72 (m, 2H), 2.31 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ163.61 (t), 138.60 (s), 137.38 (s), 133.95 (s), 133.70 (s), 129.84 (s), 129.75(s), 129.19 (s), 128.92 (s), 128.73 (s), 126.91 (s), 114.76 (t), 63.02 (s), 42.98 (s), 39.87 (t, J = 23.4 Hz), 21.23 (s), 13.77 (s); **^{19}F NMR (471 MHz, $CDCl_3$)** δ-102.63 (d, J = 14.4 Hz, 1F), -104.6 (d, J= 17.0 Hz, 1F); **ESI-MS** m/z: 385.20 $[M+1]^+$.

Ethyl 2,2-difluoro-5-phenyl-4-(p-tolylthio)pentanoate (4k)



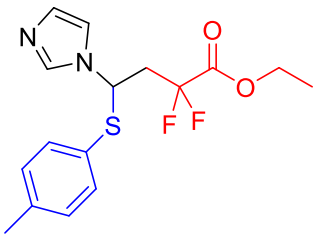
Following the general procedure, the title compound was obtained (62.6 mg, 86% yield, colorless oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ7.33 (d, J = 7.5 Hz, 1H), 7.31-7.27 (m, 3H), 7.21 (d, J = 7.1 Hz, 2H), 7.16 (d, J = 7.0 Hz, 1H), 7.11 (d, J = 7.9 Hz, 1H), 4.35-4.30 (m, 2H), 3.29-3.17 (m, 1H), 2.76-2.62 (m, 1H), 2.33 (s, 3H), 1.35 (dd, J = 9.7, 4.5 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ163.59 (t), 138.07 (s), 137.27 (s), 133.54 (s), 129.89 (s), 129.44(s), 128.67 (s), 128.48 (s), 126.77 (s), 114.94 (t), 63.04 (s), 45.63 (s), 41.70(s), 38.45 (t), 21.16 (s), 13.86 (s);**^{19}F NMR (471 MHz, $CDCl_3$)** δ-102.23 (d, J = 127 Hz, 1F), -105.03 (d, J= 140 Hz, 1F); **ESI-MS** m/z: 365.41 $[M+1]^+$.

Ethyl 2,2-difluoro-4-(p-tolylthio)decanoate (4l)



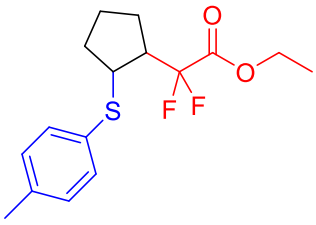
Following the general procedure, the title compound was obtained (12.2 mg, 17% yield, colorless oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ7.31 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 4.35 -4.28 (m, 2H), 3.21-3.14 (m, 1H), 2.40 (dd, J = 20.7, 6.4 Hz, 2H), 2.33 (s, 3H), 1.63 (dd, J = 10.1, 5.0 Hz, 2H), 1.40-1.35 (m, 2H), 1.32 (dd, J = 15.9, 8.7 Hz, 6H), 1.26 (s, 3H), 0.88 (d, J = 6.9 Hz, 3H); **^{19}F NMR (471 MHz, $CDCl_3$)** δ-101.23 (d, J = 16.6 Hz, 1F), -106.23 (d, J= 20.3 Hz, 1F); **ESI-MS** m/z: 359.48 $[M+1]^+$.

Ethyl 2,2-difluoro-4-(1H-imidazol-1-yl)-4-(p-tolylthio)butanoate (4m)



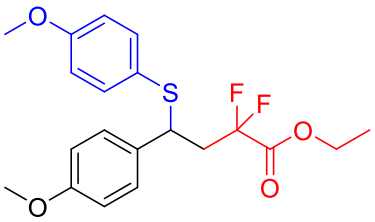
Following the general procedure, the title compound was obtained (10.9 mg, 16% yield, colorless oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.36 (d, J = 8.1 Hz, 3H), 7.14 (d, J = 7.9 Hz, 3H), 6.33 (s, 1H), 5.35 (t, J = 4.7 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.81 (q, J = 7.1 Hz, 2H), 2.34 (s, 3H), 1.33 (s, 3H); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -105.28 (d, J = 11.7 Hz, 1F), -111.27 (d, J= 15.4 Hz, 1F); **ESI-MS** m/z: 341.32 $[M+1]^+$].

Ethyl 2,2-difluoro-2-(2-(p-tolylthio)cyclopentyl)acetate (4n)



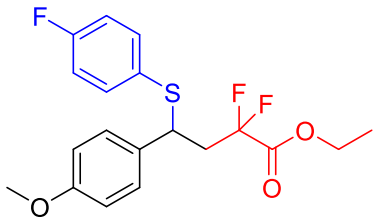
Following the general procedure, the title compound was obtained (11.3 mg, 18% yield, colorless oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ7.34 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 4.16-4.05 (m, 1H), 3.32 (dd, J = 12.0, 7.2 Hz, 1H), 2.33 (s, 3H), 2.22 (dd, J = 13.4, 5.4 Hz, 1H), 2.12-2.02 (m, 2H), 1.82-1.74 (m, 2H), 1.63-1.58 (m, 2H), 1.26 (d, J = 3.2 Hz, 3H); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -104.87 (d, J = 11.7 Hz, 1F), -110.86 (d, J= 15.4 Hz, 1F); **ESI-MS** m/z: 315.42 $[M+1]^+$.

Ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-((4-methoxyphenyl)thio)butanoate (4o)



Following the general procedure, the title compound was obtained (67.3 mg, 85% yield, yellow oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.21 (d, J = 8.7 Hz, 2H), 7.08 (d, J = 8.7 Hz, 2H), 6.81-6.75 (m, 4H), 4.18 (dd, J = 9.3, 5.1 Hz, 1H), 4.01-3.92 (m, 2H), 3.77 (d, J = 2.9 Hz, 6H), 2.84-2.62 (m, 2H), 1.20 (t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.61 (t), 160.06 (s), 159.03 (s), 136.36 (s), 131.77 (s), 129.15 (s), 123.78 (s), 114.97 (t), 114.51 (s), 113.69 (s), 62.87 (s), 55.30 (d, J = 3.9 Hz), 47.30 (s), 40.44 (t), 13.74 (s); **^{19}F NMR (471 MHz, $CDCl_3$)** δ-102.12 (d, J = 11.5 Hz, 1F), -105.06 (d, J= 12.8Hz, 1F); **ESI-MS** m/z: 397.30 $[M+1]^+$.

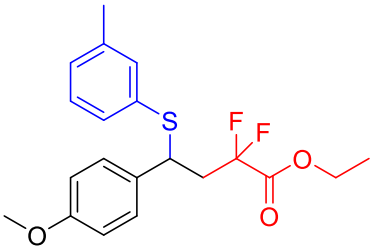
Ethyl 2,2-difluoro-4-((4-fluorophenyl)thio)-4-(4-methoxyphenyl)butanoate (4p)



Following the general procedure, the title compound was obtained (71.4 mg, 93% yield, yellow oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ7.27-7.20 (m, 2H), 7.11-7.04 (m, 2H), 6.93 (t, J = 8.7 Hz, 2H), 6.83-6.75 (m, 2H), 4.24 (dd, J = 9.1, 5.3 Hz, 1H), 4.09-3.91 (m, 2H), 3.77 (s, 3H), 2.84-2.63 (m, 2H), 1.22

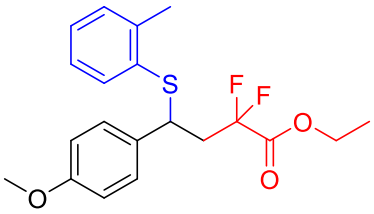
(t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ163.92 (t, J = 16.0 Hz), 161.93 (s), 159.15 (s), 136.23 (d, J = 8.3 Hz), 131.48 (s), 129.11 (s), 128.46 (s), 116.16 (s), 115.99 (s), 114.83 (t), 113.77 (s), 62.93 (s), 55.30 (s), 47.14 (s), 40.58 (d, J = 24.1 Hz), 40.30 (s), 13.74 (s). **^{19}F NMR (471 MHz, $CDCl_3$)** δ-102.33 (d, J = 13.0 Hz, 1F), -105.07 (d, J= 19.0 Hz, 1F), -112.68 (tt, J = 8.6 Hz, 1F); **ESI-MS** m/z: 385.19 $[M+1]^+$.

Ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-(m-tolylthio)butanoate (4q)



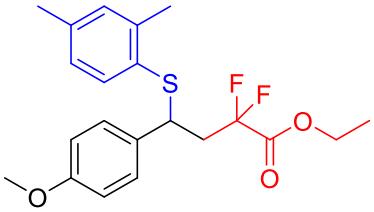
Following the general procedure, the title compound was obtained (68.4 mg, 90% yield, yellow oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ7.23- 7.13 (m, 3H), 7.13 -6.97 (m, 3H), 6.86-6.74 (m, 2H), 4.40-4.28 (m, 1H), 4.04-3.87 (m, 2H), 3.76 (d, J = 2.8 Hz, 3H), 2.90-2.61 (m, 2H), 2.29 (d, J = 12.5 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ163.56 (t), 159.15 (s), 138.81 (s), 133.57 (s), 129.88 (s), 129.18 (s), 128.84 (s), 128.73 (s), 127.99 (s), 126.53 (s), 114.89 (s), 113.79 (s), 62.88 (s), 55.31 (s), 46.12 (s), 40.72 (t), 21.28 (s), 13.74 (s).**^{19}F NMR (471 MHz, $CDCl_3$)** δ-101.98 (d, J = 15.9 Hz, 1F), -105.32 (d, J= 19.6 Hz, 1F); **ESI-MS** m/z: 381.17 $[M+1]^+$.

Ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-(o-tolylthio)butanoate (4r)



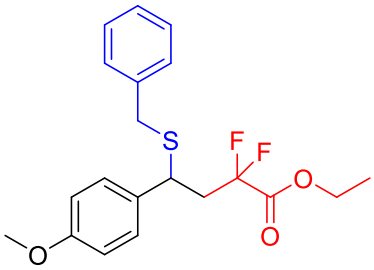
Following the general procedure, the title compound was obtained (69.9 mg, 92% yield, yellow oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ7.30 (d, J = 7.5 Hz, 1H), 7.20-7.02 (m, 5H), 6.79 (dd, J = 8.7, 7.0 Hz, 2H), 4.33 (ddd, J = 23.1, 9.4, 4.7 Hz, 1H), 4.02 – 3.89 (m, 2H), 3.76 (s, 3H), 2.89-2.65 (m, 2H), 2.30 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ163.55 (t), 159.17 (s), 140.70 (s), 133.43 (s), 133.03 (s), 130.46 (s), 129.18 (s), 129.07 (s),128.00 (s), 126.53 (s), 114.89 (s), 113.79 (s), 62.89 (s), 55.30 (s), 45.56 (s), 40.69 (t), 20.65 (s), 13.73 (s);**^{19}F NMR (471 MHz, $CDCl_3$)** δ-102.07 (d, J = 15.9 Hz, 1F), -105.23 (d, J= 19.6 Hz, 1F); **ESI-MS** m/z: 381.19 $[M+1]^+$.

Ethyl 4-((2,4-dimethylphenyl)thio)-2,2-difluoro-4-(4-methoxyphenyl) butanoate (4s)



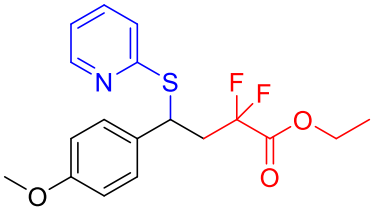
Following the general procedure, the title compound was obtained (70.1 mg, 89% yield, yellow oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.20 (d, J = 7.8 Hz, 1H), 7.13 (d, J = 8.6 Hz, 2H), 6.99 (s, 1H), 6.91 (d, J = 7.9 Hz, 1H), 6.78 (d, J = 8.6 Hz, 2H), 4.22 (dd, J = 9.8, 4.7 Hz, 1H), 4.00 – 3.88 (m, 2H), 3.77 (s, 3H), 2.85 – 2.62 (m, 2H), 2.27 (s, 6H), 1.19 (t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.57 (t), 159.11 (s), 141.08 (s), 138.35 (s), 134.43 (s), 131.70 (s), 131.35 (s), 129.28 (s), 129.06 (s), 127.32 (s), 114.02 (t), 113.75 (s), 62.84 (s), 55.30 (s), 45.91 (s), 40.60 (t), 21.08 (s), 20.62 (s), 13.72 (s); **^{19}F NMR (471 MHz, $CDCl_3$)** δ-102.02 (d, J = 15.9 Hz, 1F), -105.26 (d, J= 19.6 Hz, 1F); **ESI-MS** m/z: 395.20 $[M+1]^+$.

Ethyl 4-(benzylthio)-2,2-difluoro-4-(4-methoxyphenyl)butanoate (4t)



Following the general procedure, the title compound was obtained (66.9 mg, 88% yield, yellow oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.26 (dt, J = 21.6, 7.1 Hz, 3H), 7.19 (dd, J = 10.4, 3.8 Hz, 4H), 6.94 – 6.80 (m, 2H), 4.04 – 3.91 (m, 2H), 3.86 (dd, J = 9.0, 5.5 Hz, 1H), 3.80 (s, 3H), 3.46 (dd, J = 50.9, 13.5 Hz, 2H), 2.76 – 2.57 (m, 2H), 1.20 (t, J = 7.2 Hz, 3H).**^{13}C NMR (125 MHz, $CDCl_3$)** δ163.63 (d, J = 32.2 Hz), 163.50 (t), 159.09 (s), 137.51 (s), 132.07 (s), 129.34 (s), 128.95 (s), 128.51 (s), 127.12 (s), 116.86 (s), 114.86 (s), 113.88 (s), 62.84 (s), 55.33 (s), 41.72 (s), 41.10 (t), 35.69 (s), 13.74 (s); **^{19}F NMR (471 MHz, $CDCl_3$)** δ-102.16 (d, J = 15.9 Hz, 1F), -104.85 (d, J= 19.6 Hz, 1F); **ESI-MS** m/z: 381.24 $[M+1]^+$.

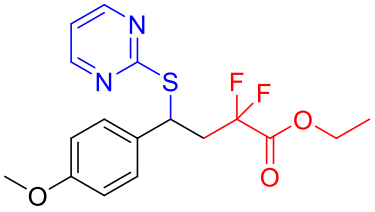
Ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-(pyridin-2-ylthio)butanoate (4u)



Following the general procedure, the title compound was obtained (66.1 mg, 90% yield, yellow oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.51 (d, J = 4.7 Hz, 1H), 7.71 (td, J = 7.8, 1.5 Hz, 1H), 7.53

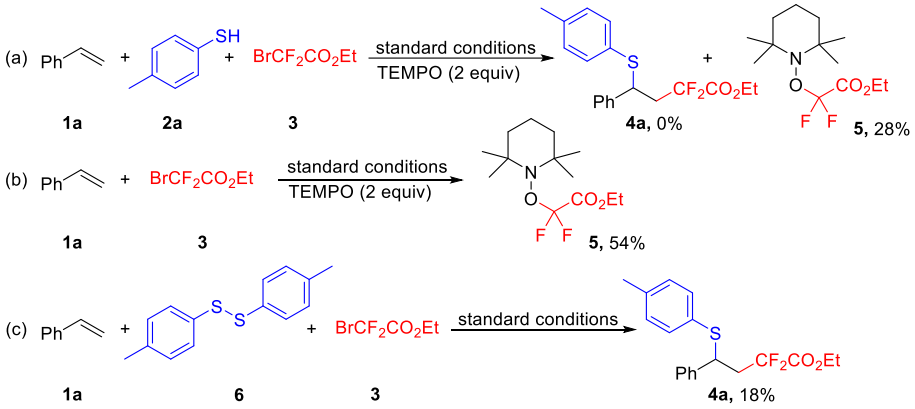
-7.48 (m, 1H), 7.38 (d, J = 8.6 Hz, 2H), 7.33-7.25 (m, 1H), 6.88 (d, J = 8.6 Hz, 2H), 4.40-4.36 (m, 1H), 4.05 (dd, J = 7.1, 3.4 Hz, 2H), 3.82 (s, 3H), 3.04-2.89 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.71 (t), 159.14 (s), 157.55 (s), 149.69 (s), 136.20 (s), 131.35 (s), 129.32 (s), 122.60 (s), 120.03 (s), 114.99 (t), 113.90 (s), 62.81 (s), 55.28 (s), 41.67 (s), 41.10 (t), 13.80 (d); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -101.83 (d, J = 16.4 Hz, 1F), -104.86 (d, J= 18.8 Hz, 1F); **ESI-MS** m/z: 368.20 $[M+1]^+$.

Ethyl 2,2-difluoro-4-(4-methoxyphenyl)-4-(pyrimidin-2-ylthio)butanoate (4v)



Following the general procedure, the title compound was obtained (65.5 mg, 89% yield, yellow oil).**^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.52 (d, J = 4.8 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 6.97 (t, J = 4.8 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 4.12 (q, J = 7.1 Hz, 1H), 4.01 (tdd, J = 10.6, 7.2, 3.6 Hz, 2H), 3.78 (s, 3H), 3.05-2.87 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ171.01 (s), 163.63 (t), 159.24 (s), 157.47 (s), 130.89 (s), 129.41 (s), 116.93 (s), 114.93 (t), 113.94 (s), 62.85 (s), 55.28 (s), 40.90 (s), 21.08 (s), 13.78 (s); **^{19}F NMR (471 MHz, $CDCl_3$)** δ -101.89 (d, J = 16.2 Hz, 1F), -105.40 (d, J= 19.0 Hz, 1F); **ESI-MS** m/z: 369.21 $[M+1]^+$.

4. Control experiments

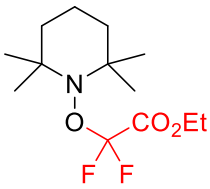


Reaction (a): A 10 mL reaction vessel with a magnetic stirring bar was equipped with *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002mmol, 0.01 equiv), $FeCl_2$ (5.1 mg, 0.04 mmol, 0.2 equiv),

4-Me phenthiol **2a** (37.2mg, 0.3 mmol, 1.5 equiv) and TEMPO (62.5mg, 0.4mmol, 2.0 equiv). The tube was then evacuated and back-filled with argon (Ar) for 3 times. Subsequently, CH_2Cl_2 (2 mL) was added followed by styrene **1a** (20.8mg, 0.2 mmol, 1.0 equiv) and $BrCF_2CO_2Et$ **3** (101.6mg, 0.4 mmol, 2.0 equiv) via syringe under Ar. Once added, the Schlenk tube was sealed at atmospheric pressure of Ar (1 atm). The reaction was stirred and irradiated with a 5 W blue LED lamp at r.t. for 24 h. Then, the solvent was removed in vacuum and the crude product was purified by silica gel flash column chromatography (silica: 200-300 mesh, petroleum ether/ethyl acetate99/1~98/2) to give the radical coupling adduct **5** (TEMPO-CF_2COOEt) as colorless oil in 28% yield. No desired product **4a** was detected.

Reaction (b): A 10 mL reaction vessel with a magnetic stirring bar was equipped with *fac*-$Ir(ppy)_3$ (1.3 mg, 0.002mmol, 0.01 equiv), $FeCl_2$ (5.1 mg, 0.04 mmol, 0.2 equiv) and TEMPO (62.5mg, 0.4mmol, 2.0 equiv). The tube was then evacuated and back-filled with argon (Ar) for 3 times. Subsequently, CH_2Cl_2 (2 mL) was added followed by styrene **1a** (20.8mg, 0.2 mmol, 1.0 equiv) and $BrCF_2CO_2Et$ **3** (101.6mg, 0.4 mmol, 2.0 equiv) via syringe under Ar. Once added, the Schlenk tube was sealed at atmospheric pressure of Ar (1 atm). The reaction was stirred and irradiated with a 5 W blue LED lamp at r.t. for 24 h. Then, the solvent was removed in vacuum and the crude product was purified by silica gel flash column chromatography (silica: 200-300 mesh, petroleum ether/ethyl acetate99/1~98/2) to give the radical coupling adduct **5** (TEMPO-CF_2COOEt) as colorless oil in 54% yield.

ethyl 2,2-difluoro-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acetate[2]



^{1}H NMR (500 MHz, $CDCl_3$) δ 4.29 (q, J = 7.1 Hz, 2H), 1.58-1.54 (m, 6H), 1.35 (t, J = 7.1 Hz, 3H), 1.21 (d, J = 2.3 Hz, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.59 (t, J = 42.6 Hz), 114.94 (t, J = 271.5 Hz), 62.84, 61.35, 40.13, 33.25, 21.19, 16.96, 13.70; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -73.46 (s). **ESI-MS** m/z: 280.33 $[M+1]^+$.

Reaction (c): A 10 mL reaction vessel with a magnetic stirring bar was equipped with *fac*-$Ir(ppy)_3$ (1.3 mg, 0.002mmol, 0.01 equiv), $FeCl_2$ (5.1 mg, 0.04 mmol, 0.2 equiv) and *p*-toluene disulfide **6** (73.8mg, 0.3mmol, 1.5 equiv). The tube was then evacuated

and back-filled with argon (Ar) for 3 times. Subsequently, CH_2Cl_2 (2 mL) was added followed by styrene **1a** (20.8mg, 0.2 mmol, 1.0 equiv) and $BrCF_2CO_2Et$ **3** (101.6mg, 0.4 mmol, 2.0 equiv) via syringe under Ar. Once added, the Schlenk tube was sealed at atmospheric pressure of Ar (1 atm). The reaction was stirred and irradiated with a 5 W blue LED lamp at r.t. for 24 h. Then only 18% yield of product **4a** was obtained, indicating that disulfide **6** may not be the active intermediate.

To gain more insight into the mechanism, we also performed UV-vis spectroscopic measurement. A blue-shift in *p*-TolSH's absorption upon NEt_3 addition was observed. This shift might be attributed to the thiolate anion's absorption. Meanwhile, we observed a more obvious visible light absorption when $FeCl_2$, *p*-TolSH and NEt_3 were combined and this change is proposed to result from the absorption of the Fe/S complex resulting from the thiolate anion and $FeCl_2$ (**Figure S1**). The spectroscopy is similar to the $[Fe(SR)_4]^{2-}$ reported in the literature[3], which supports the formation of Fe/S complex in the reaction.

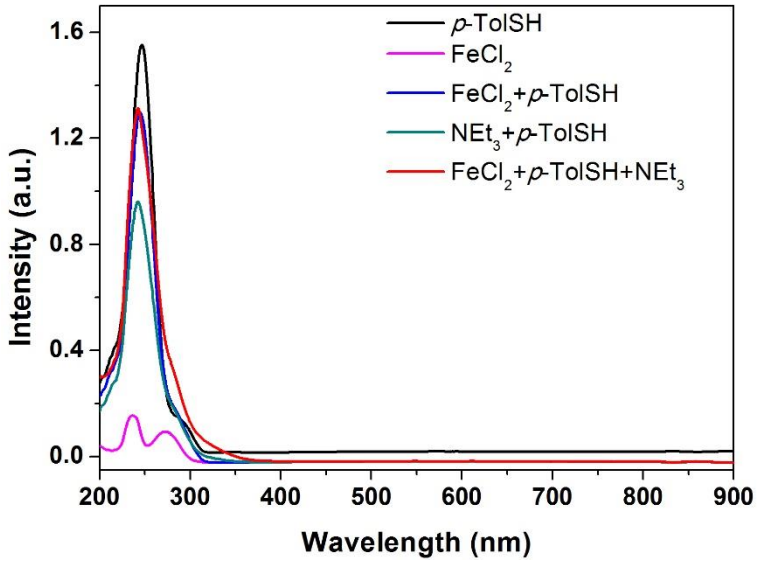


Figure S1. UV-vis spectrum of $FeCl_2$ (2.0×10^{-4} M), *p*-TolSH (1.0×10^{-3} M), mixture of *p*-TolSH (1.0×10^{-3} M) and NEt_3 (1.2×10^{-3} M), mixture of *p*-TolSH (1.0×10^{-3} M) and $FeCl_2$ (2.0×10^{-4} M), mixture of *p*-TolSH (1.0×10^{-3} M), NEt_3 (1.2×10^{-3} M) and $FeCl_2$ (2.0×10^{-4} M) in DCM under N_2.

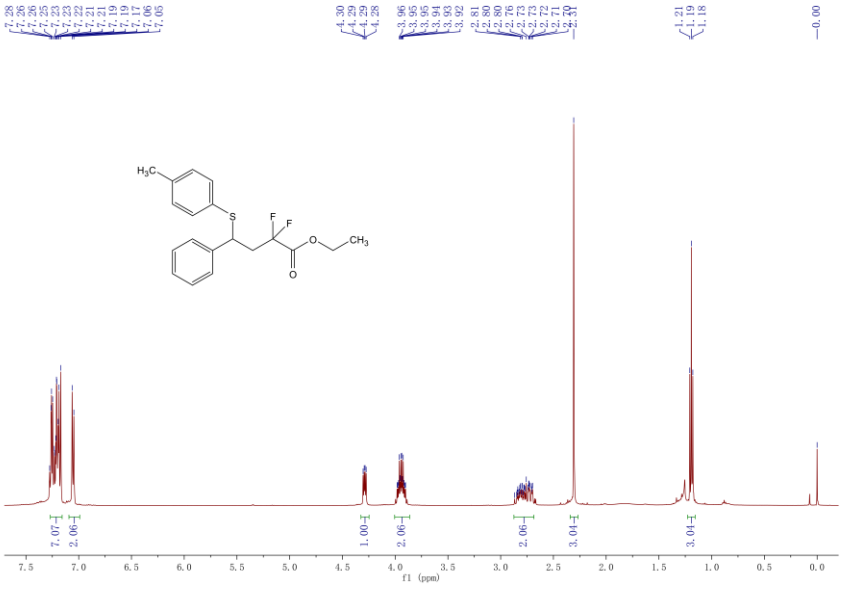
References:

[1] W.-G. Kong, C.-J. Yu and Q.-L. Song, *Org. Lett.* 2018, **20**, 4975.

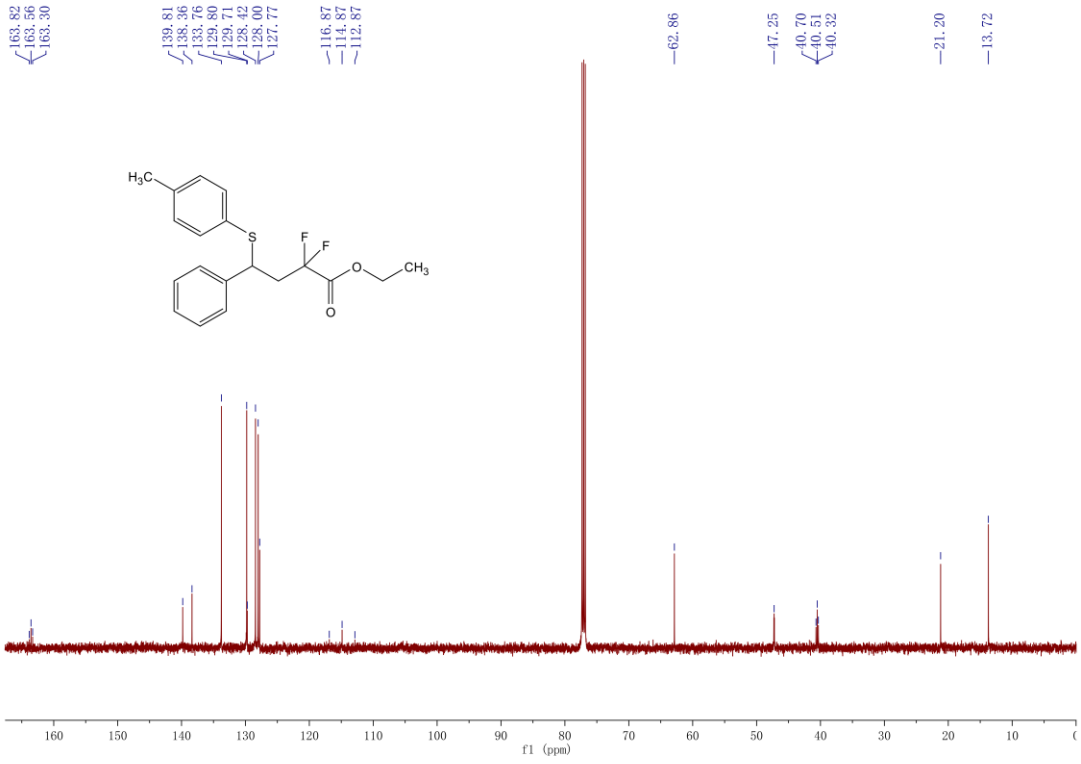
[2] Nie, X.; Cheng, C.; Zhu, G. *Angew. Chem., Int. Ed.* 2017, **56**, 1898.

[3] K. S. Hagen, J. G. Reynolds, R. H. Holm, *J. Am. Chem. Soc.* 1981, **103**, 4054.

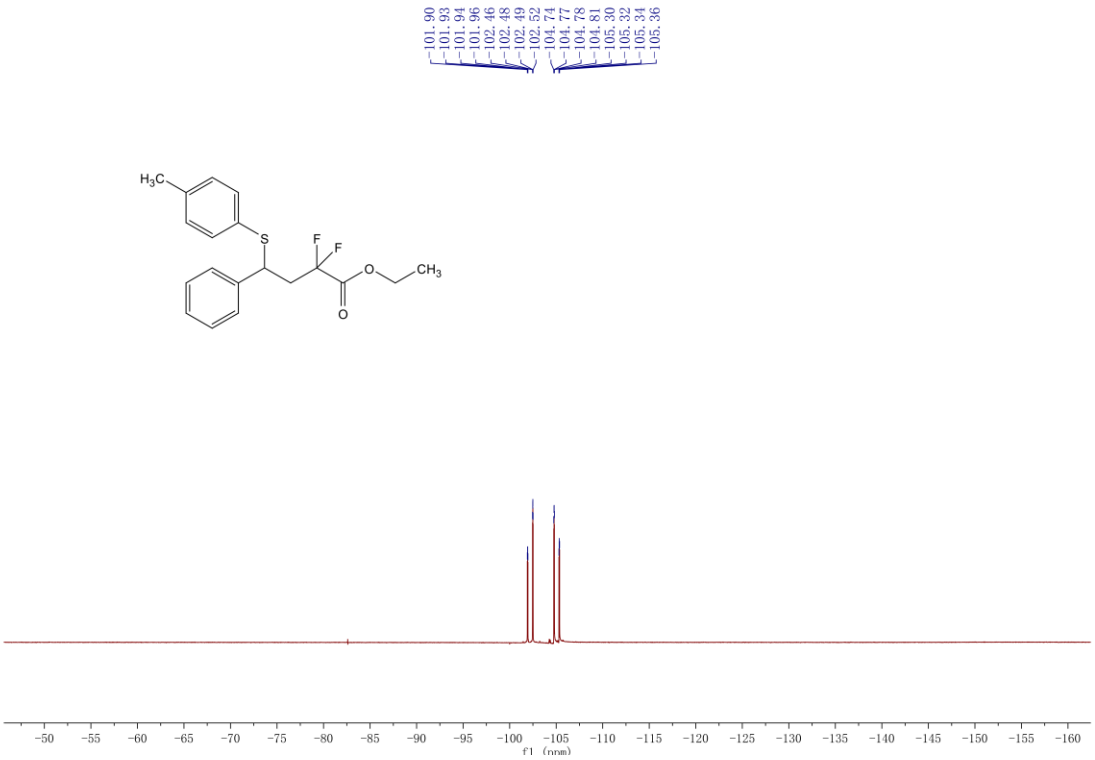
5. NMR Spectra



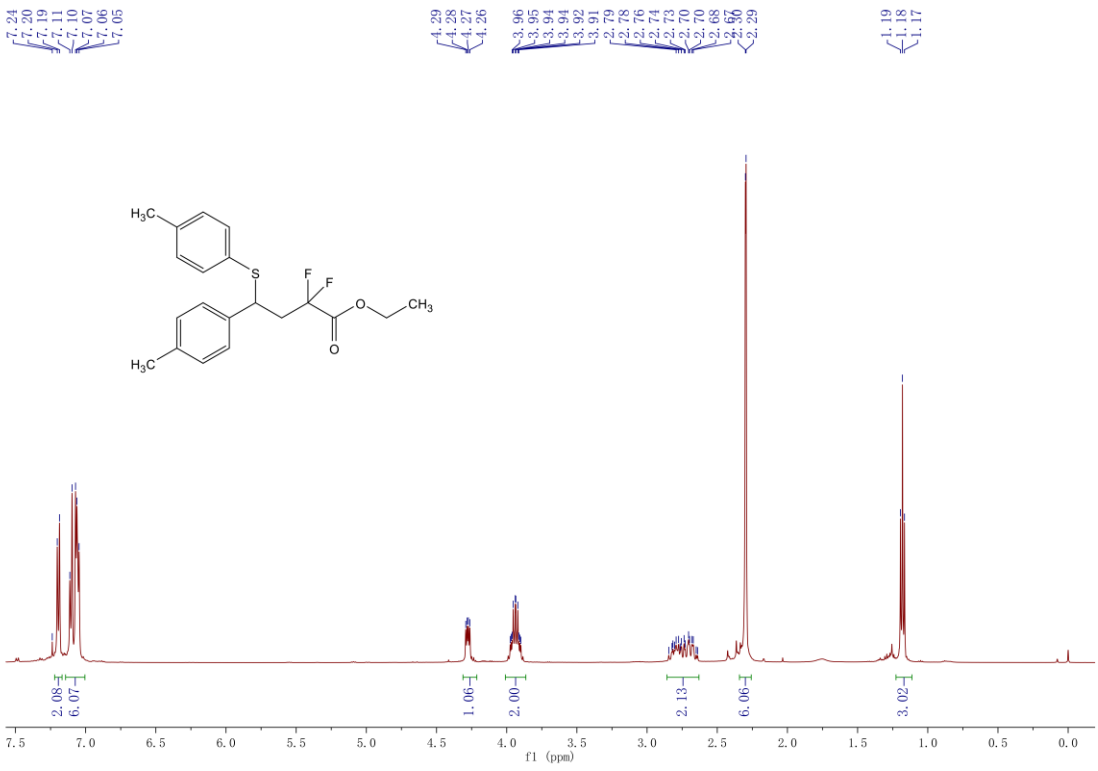
^{1}H NMR **4a**



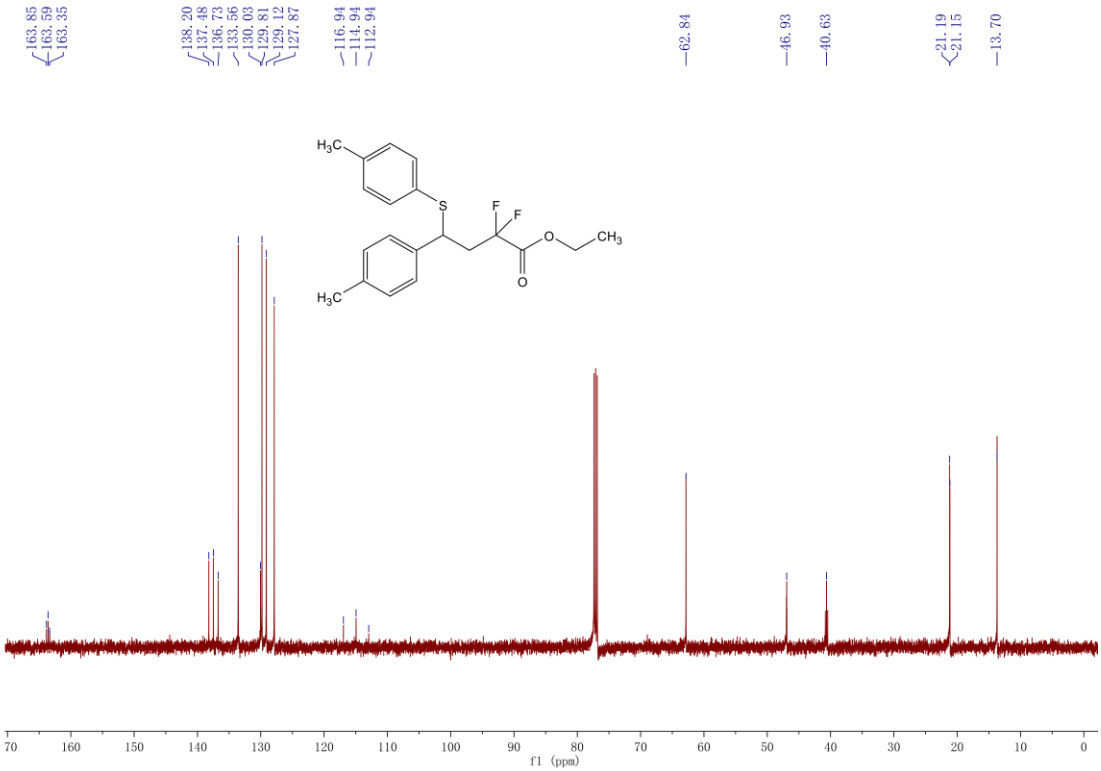
^{13}C NMR **4a**



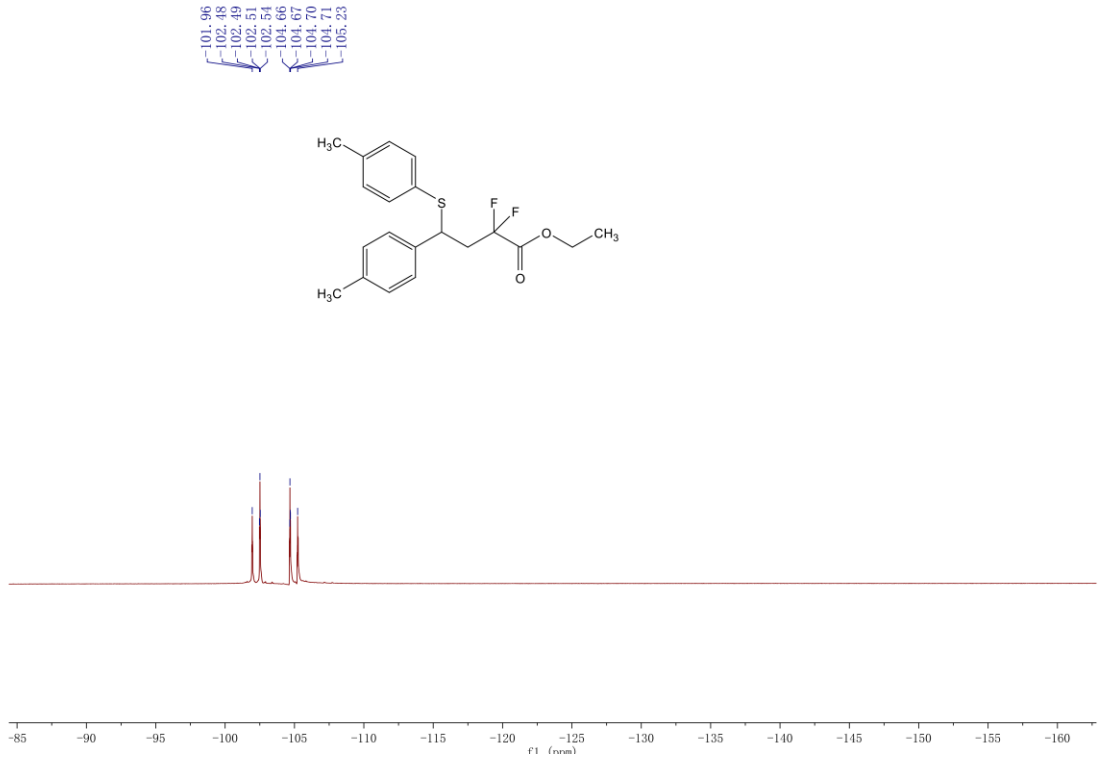
^{19}F NMR **4a**



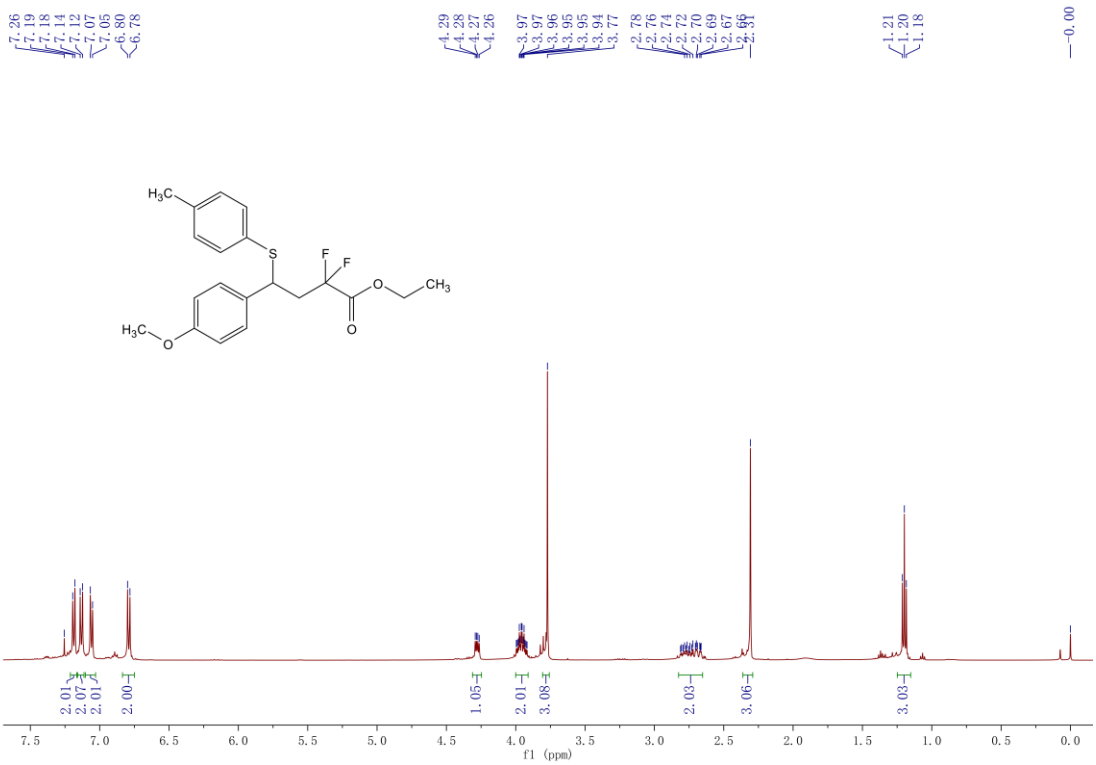
^{1}H NMR **4b**



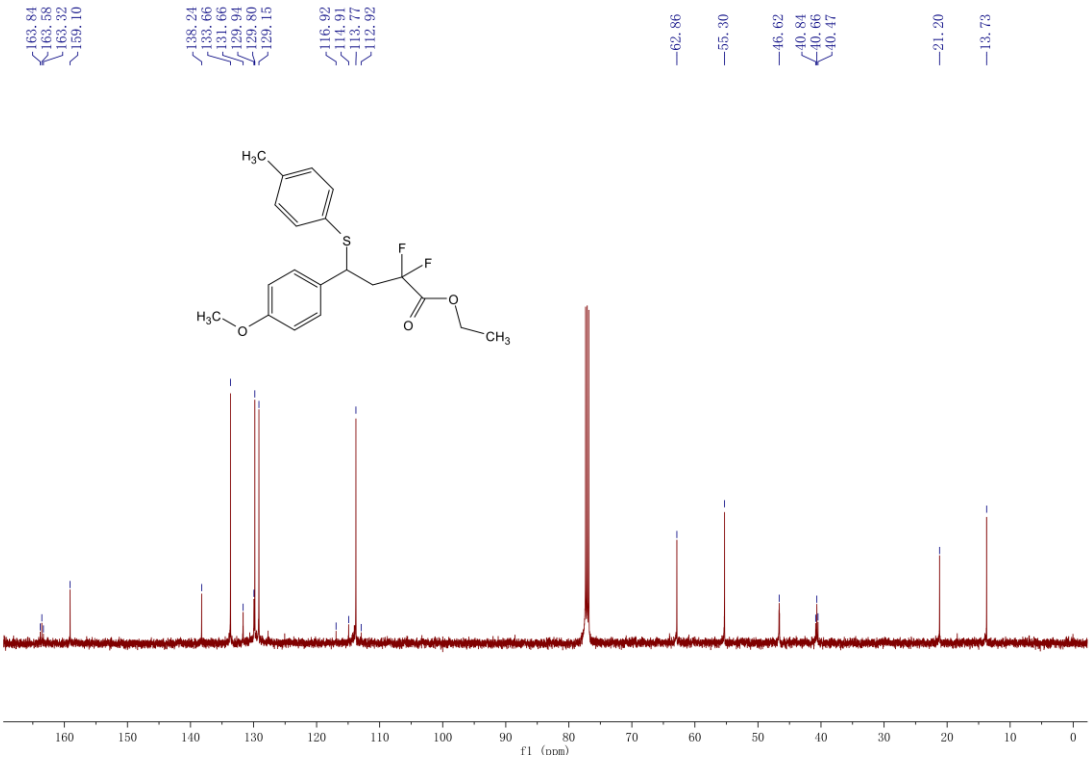
^{13}C NMR **4b**



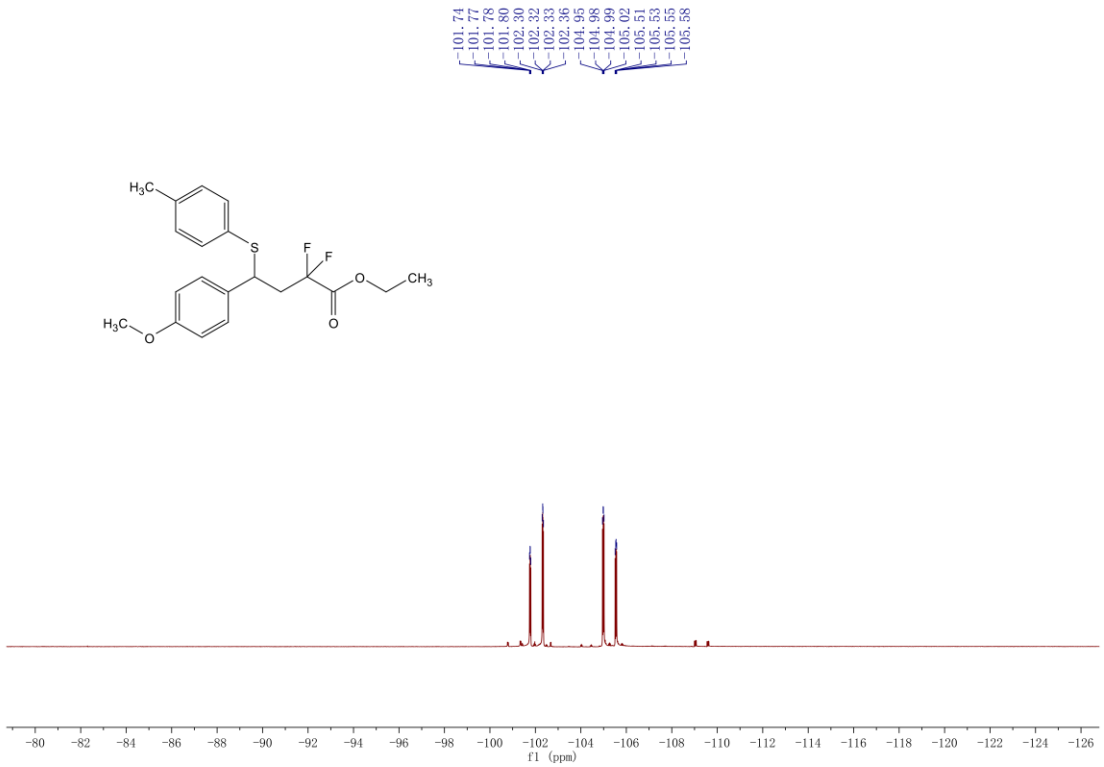
^{19}F NMR **4b**



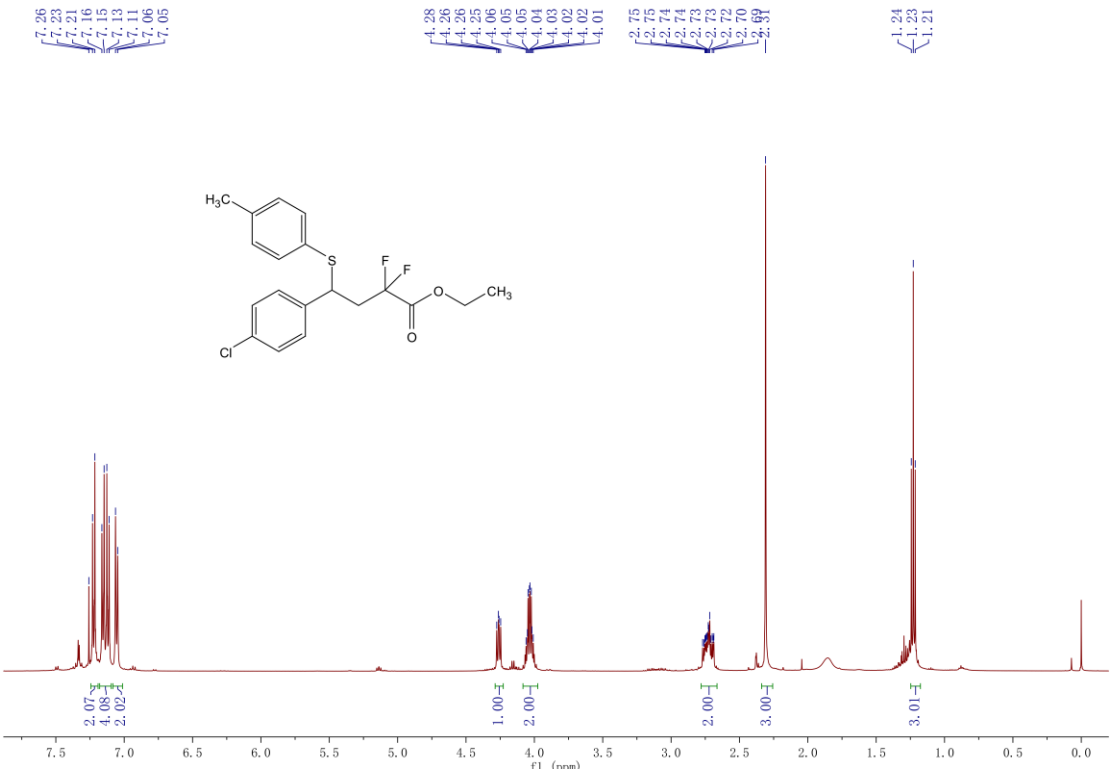
^{1}H NMR **4c**



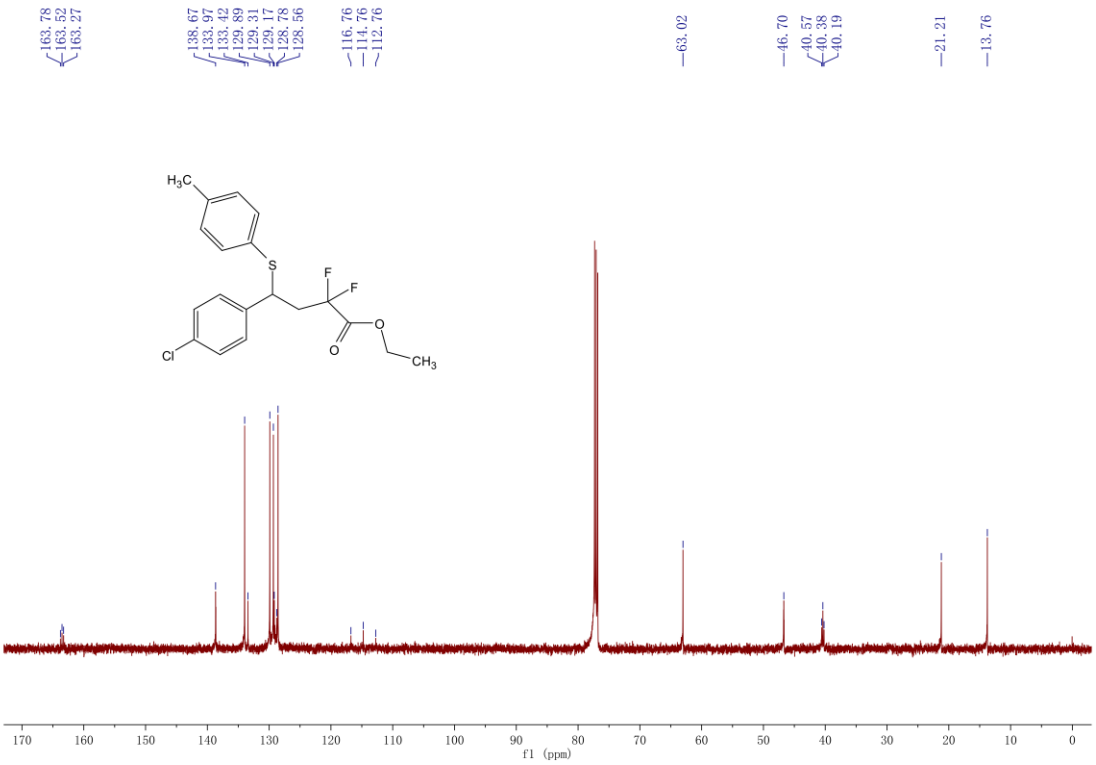
^{13}C NMR **4c**



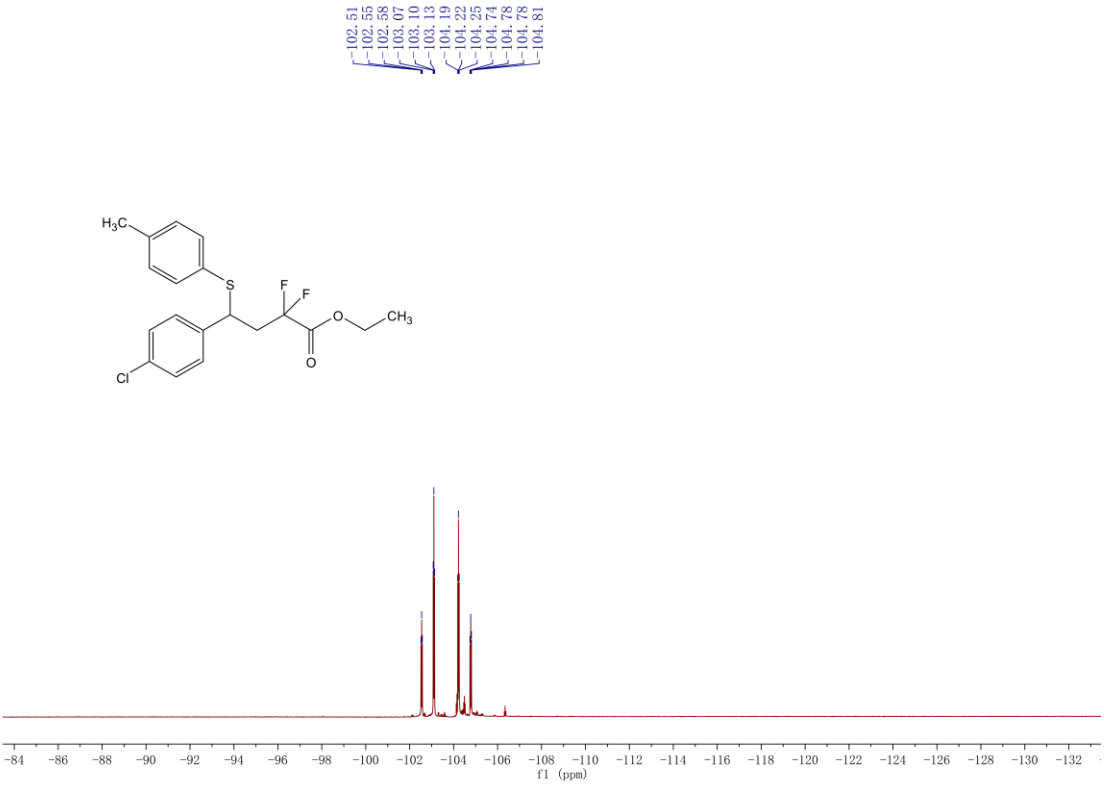
^{19}F NMR **4c**



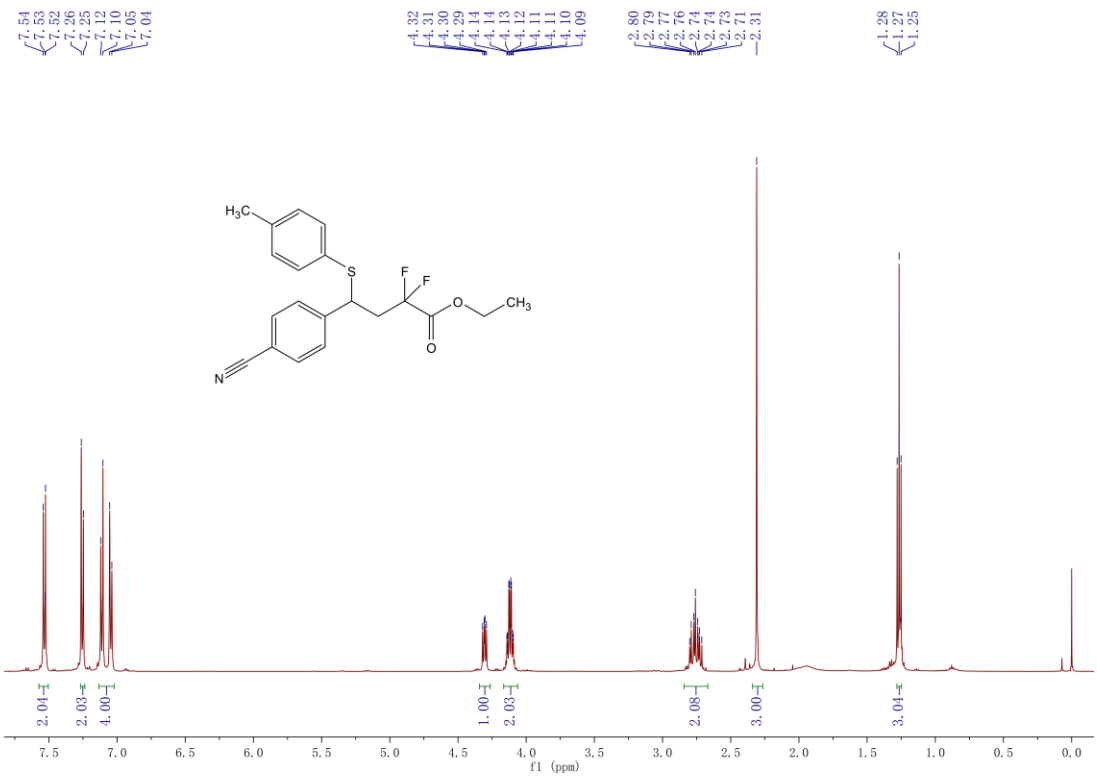
^{1}H NMR **4d**



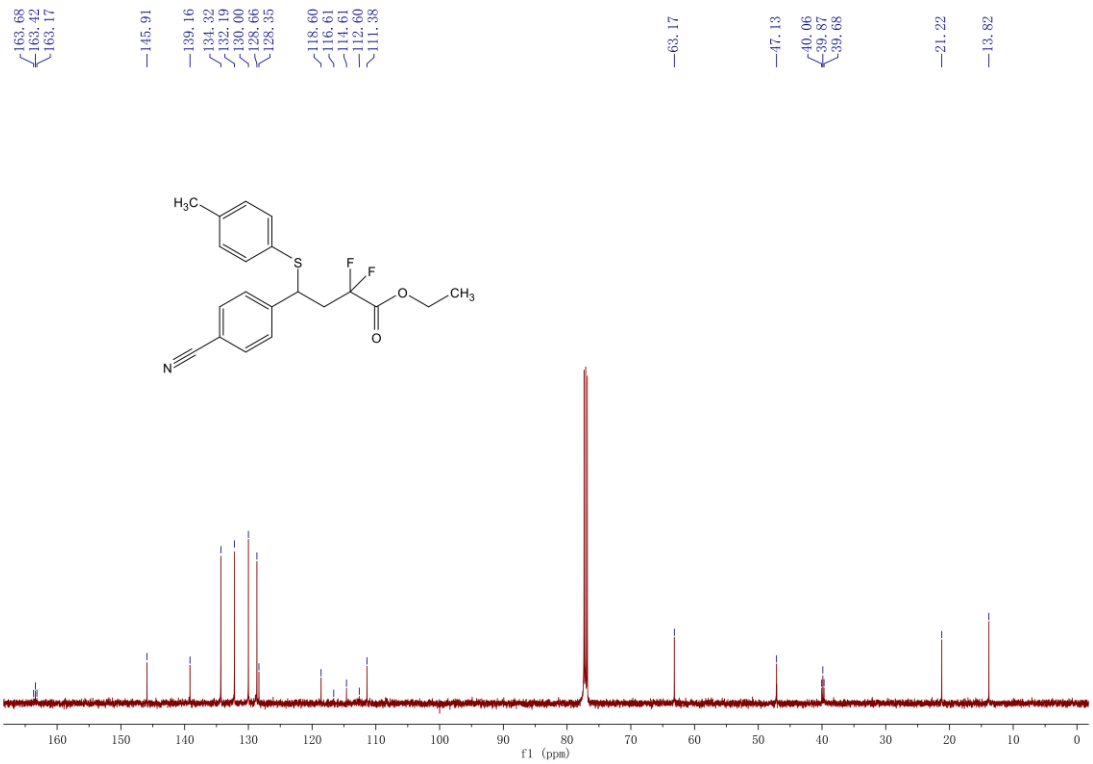
^{13}C NMR **4d**



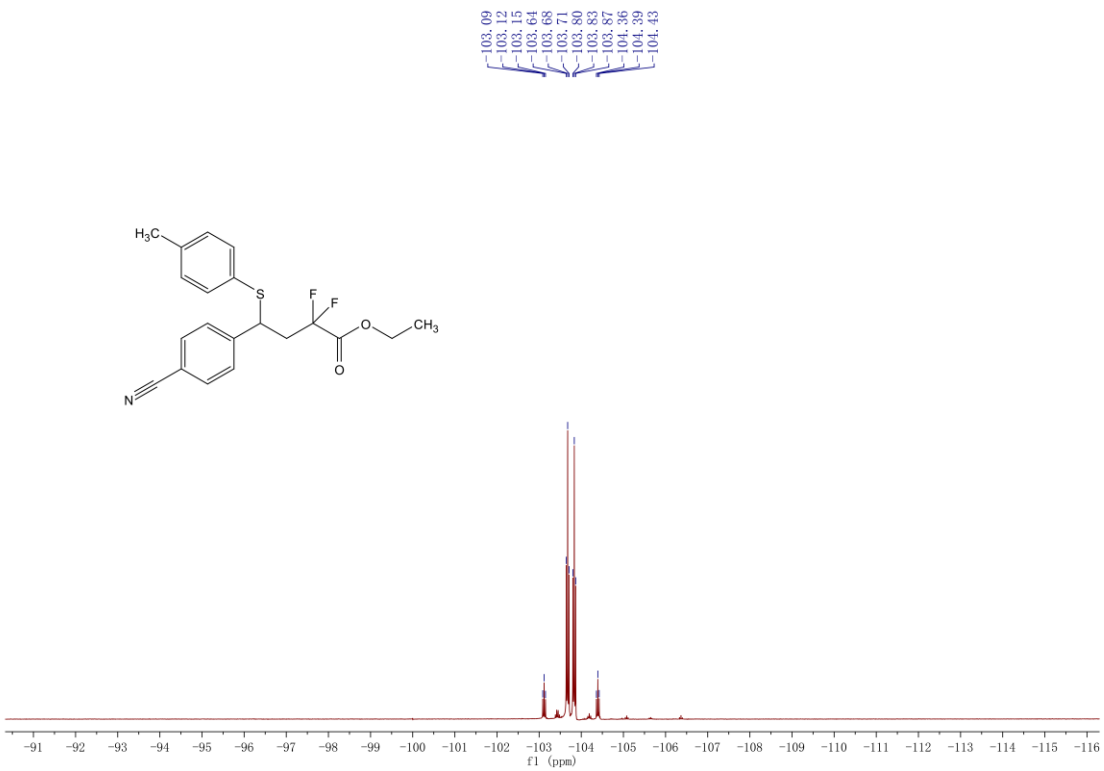
^{19}F NMR **4d**



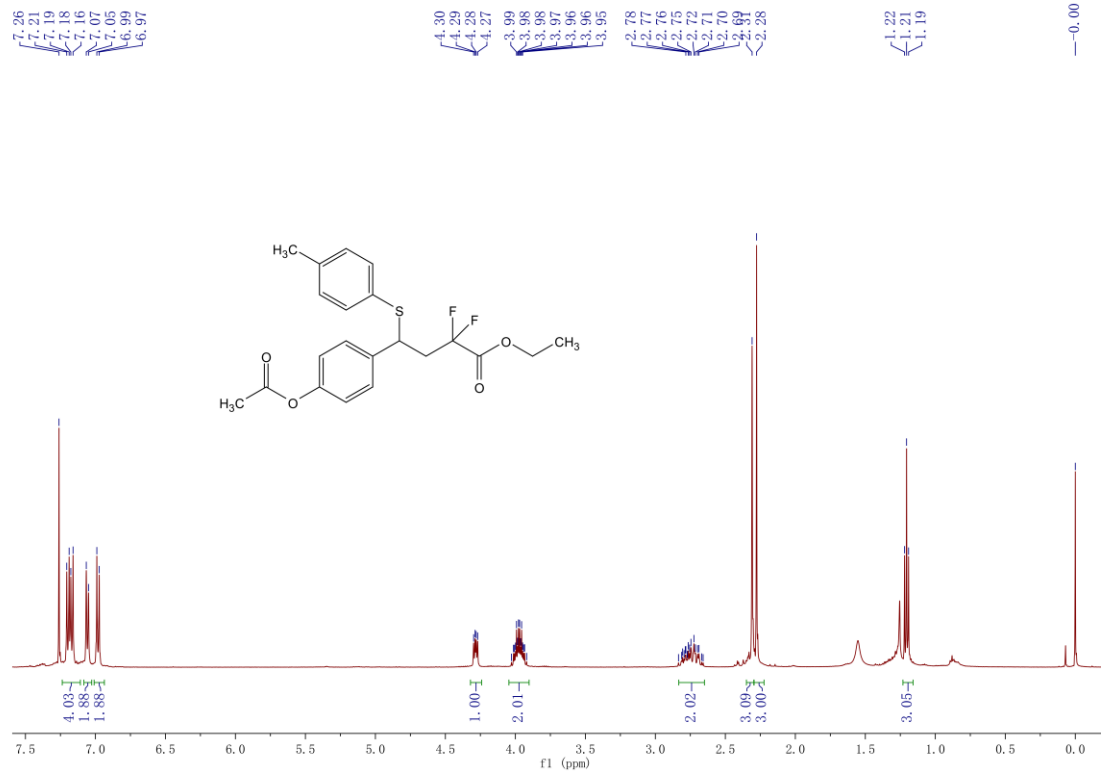
^{1}H NMR **4e**



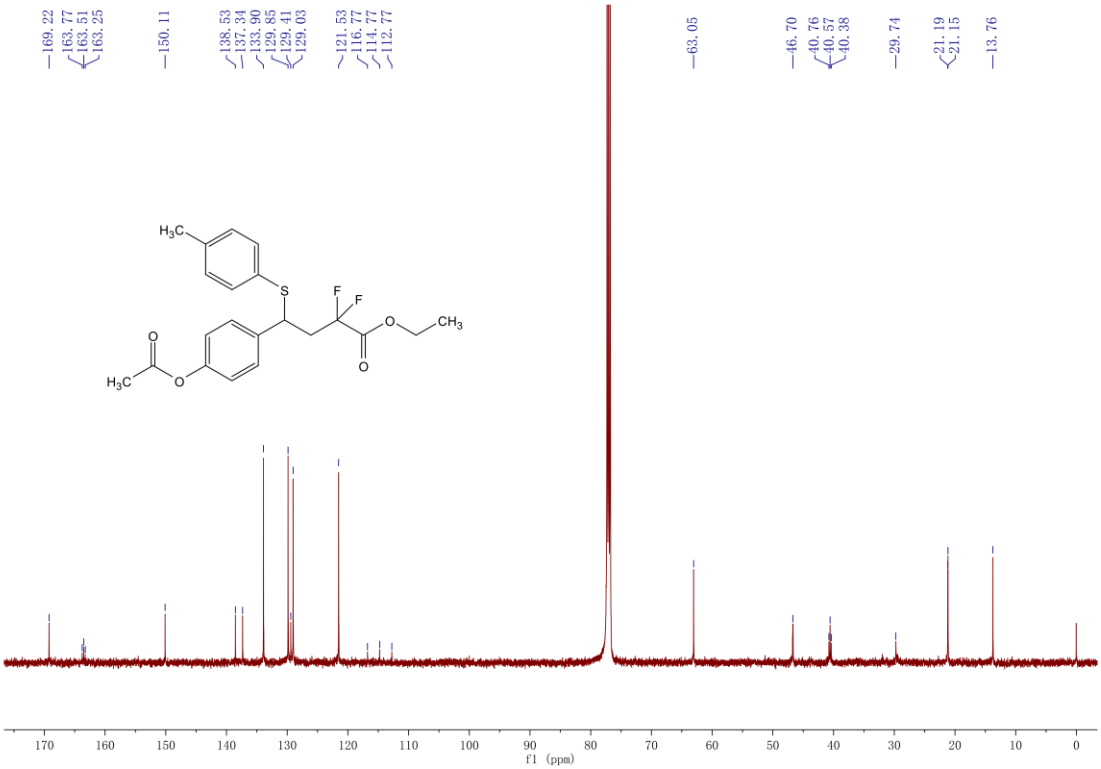
^{13}C NMR **4e**



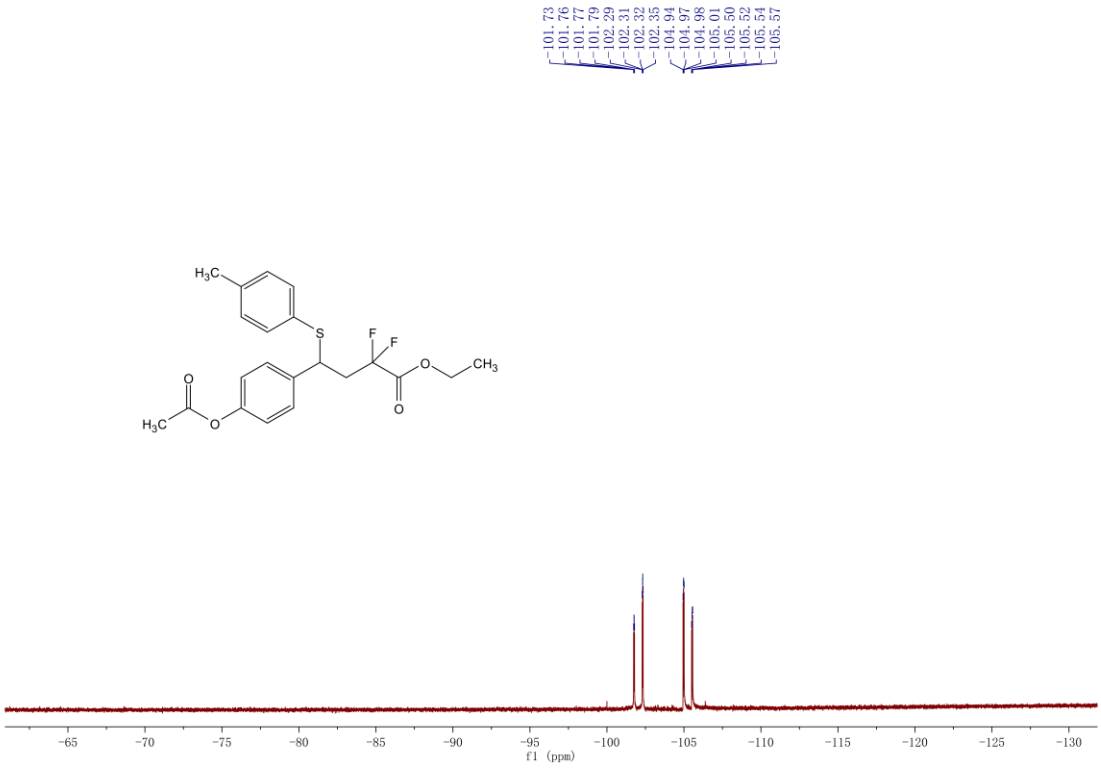
^{19}F NMR **4e**



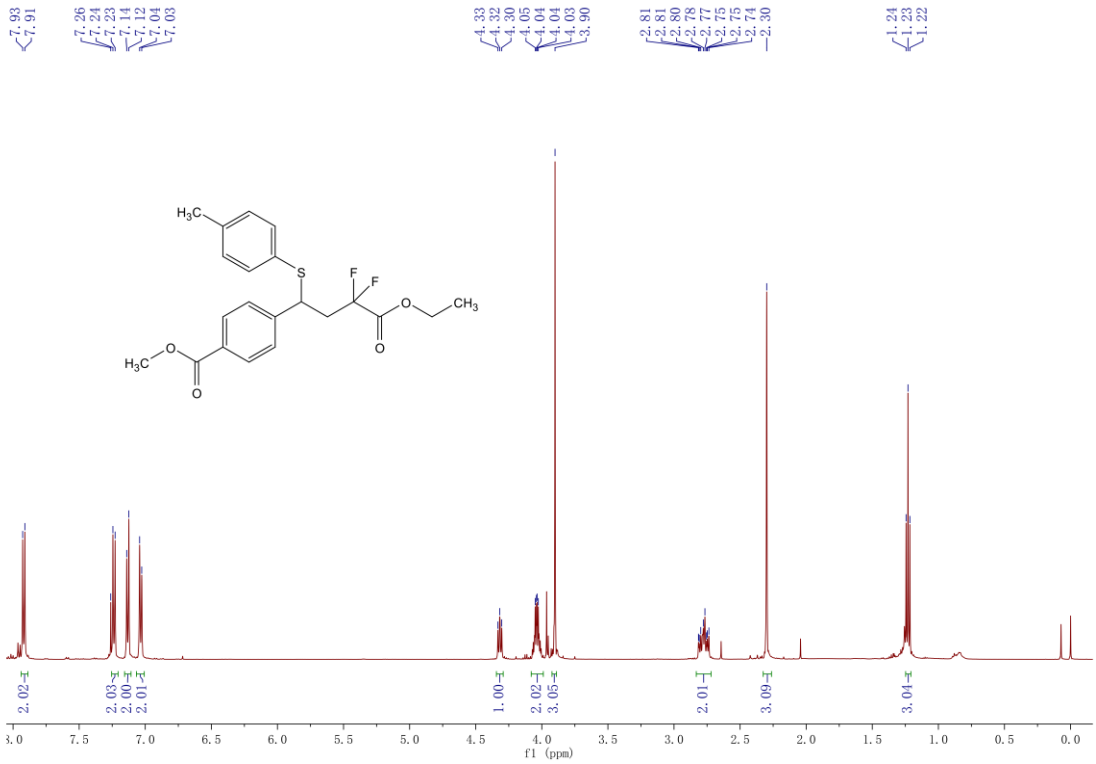
^{1}H NMR **4f**



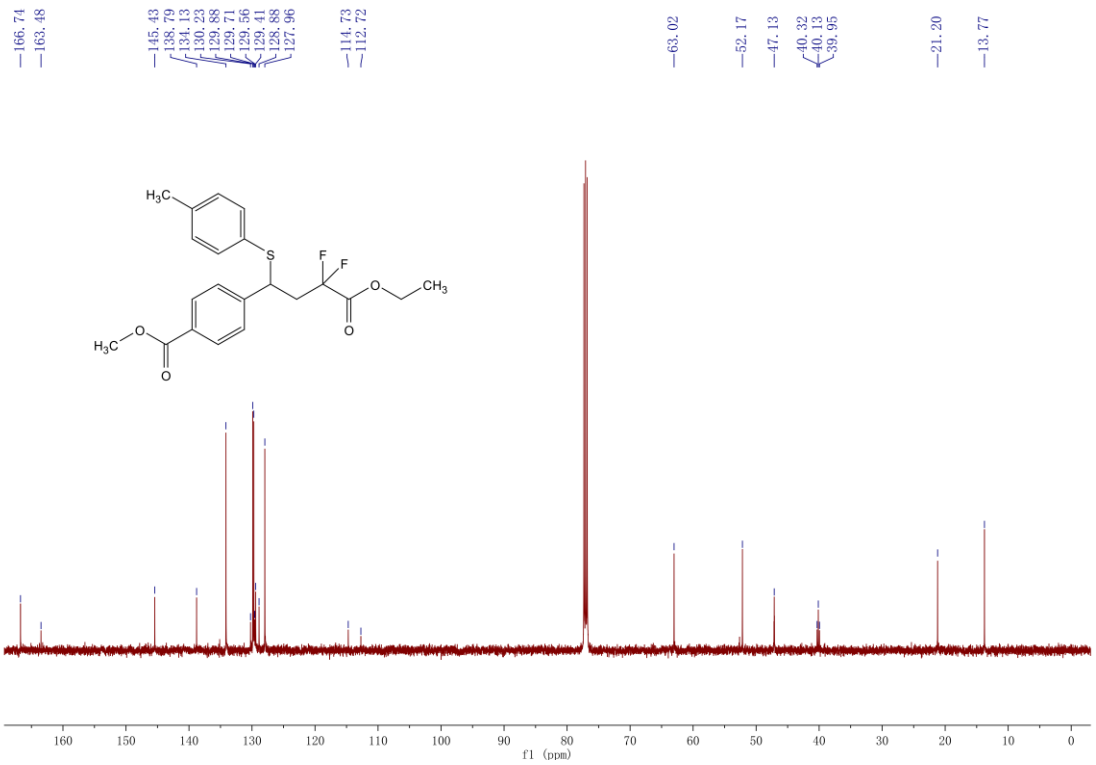
^{13}C NMR **4f**



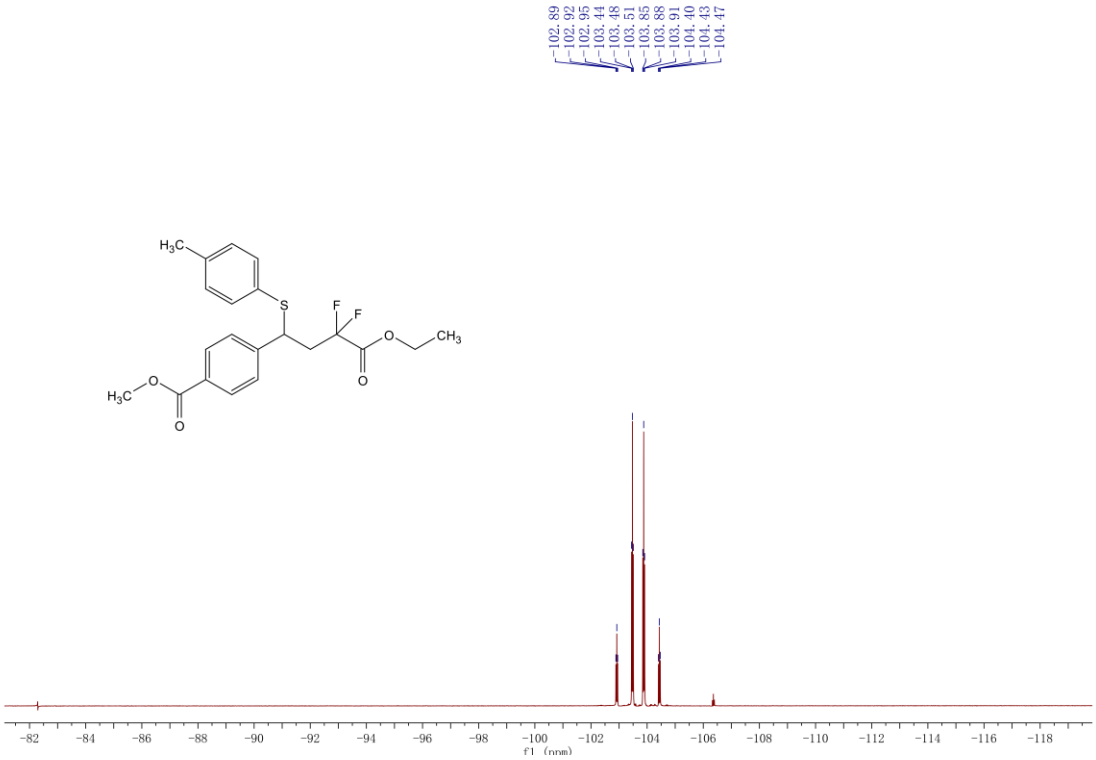
^{19}F NMR **4f**



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



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



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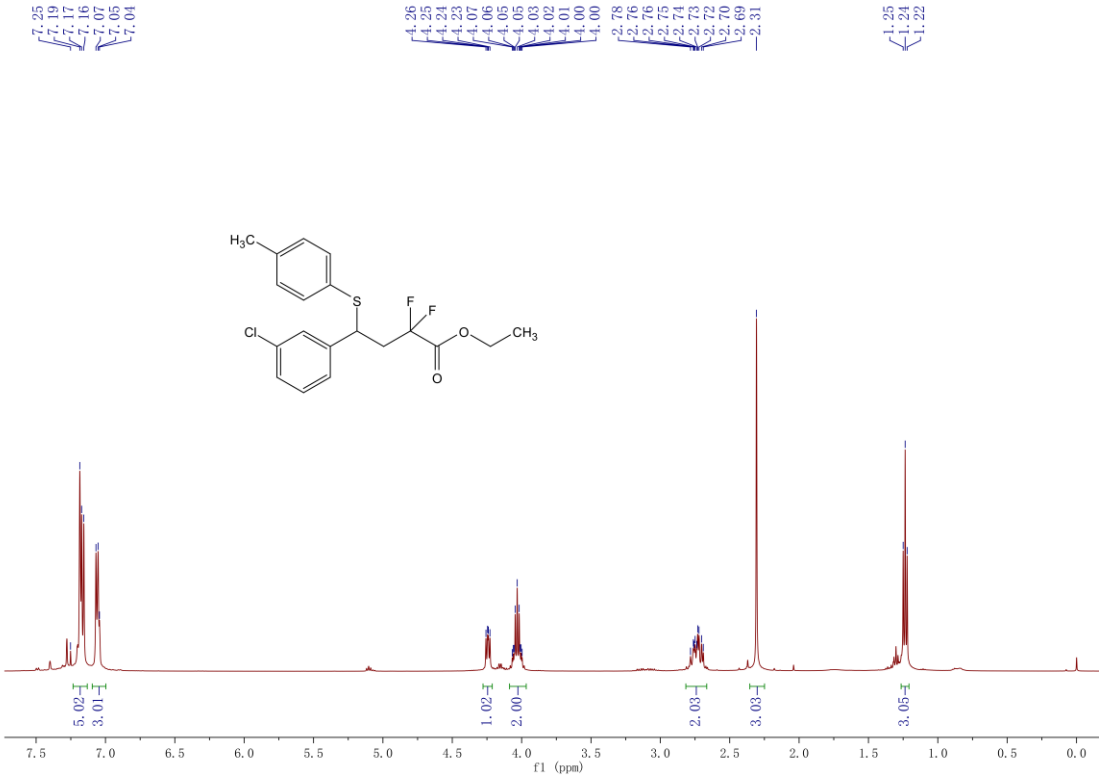

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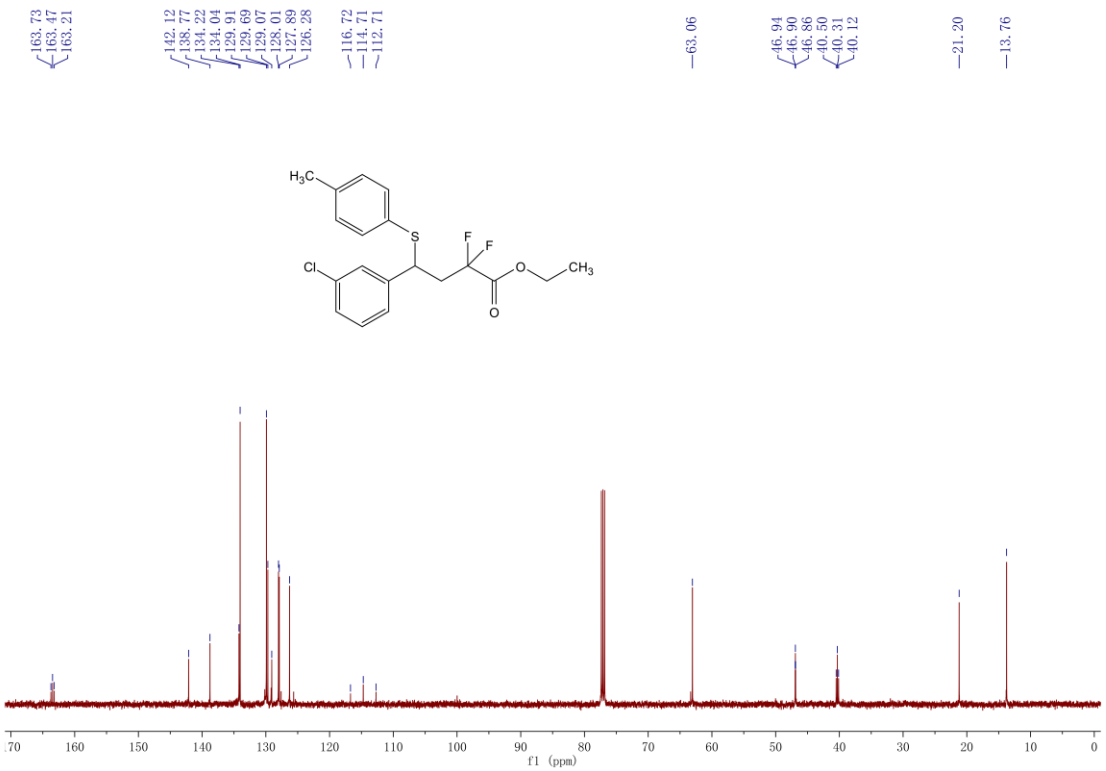
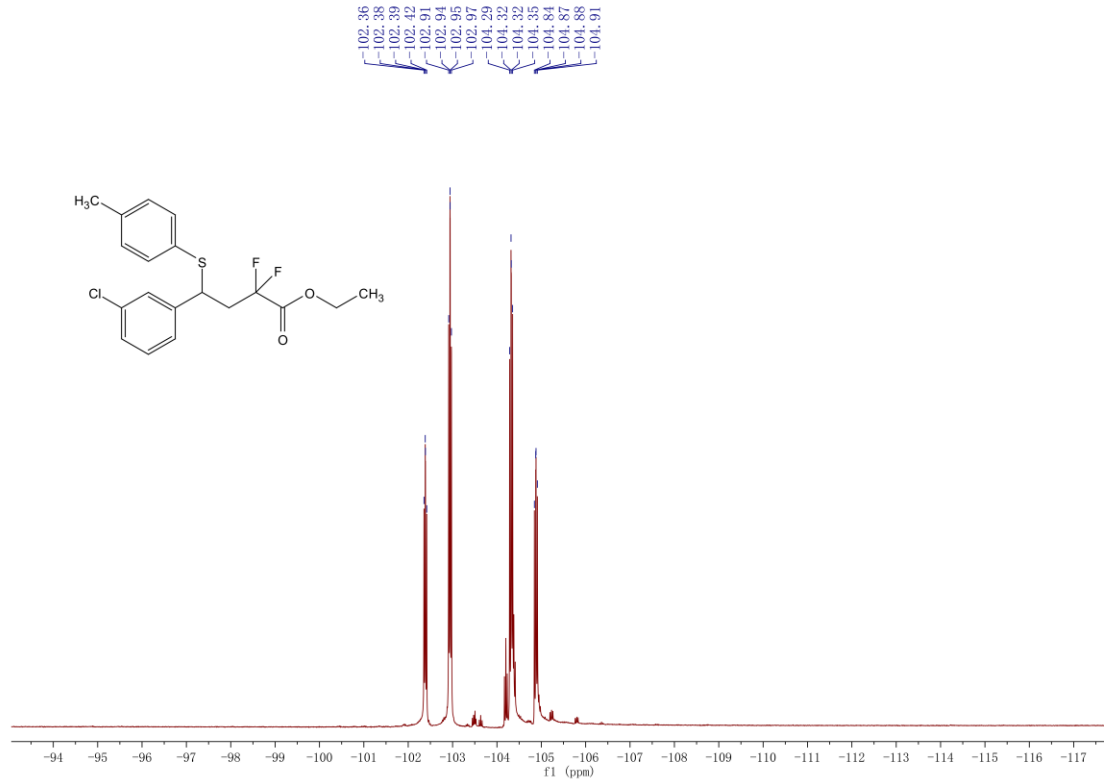
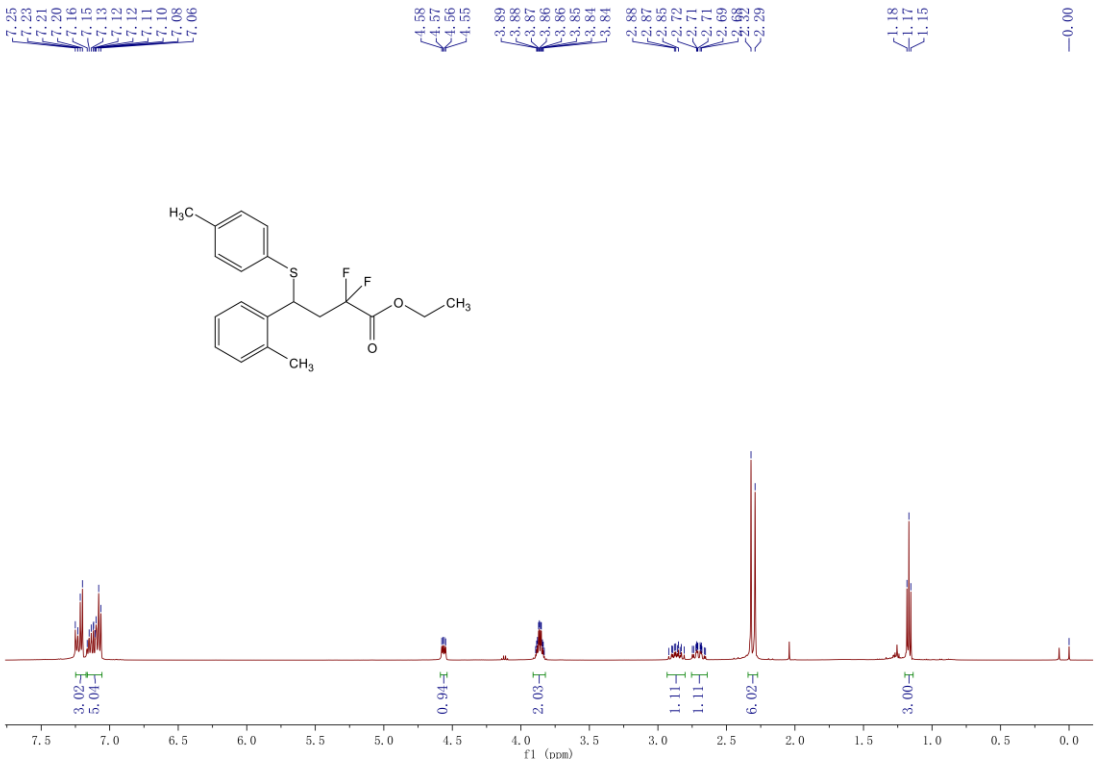


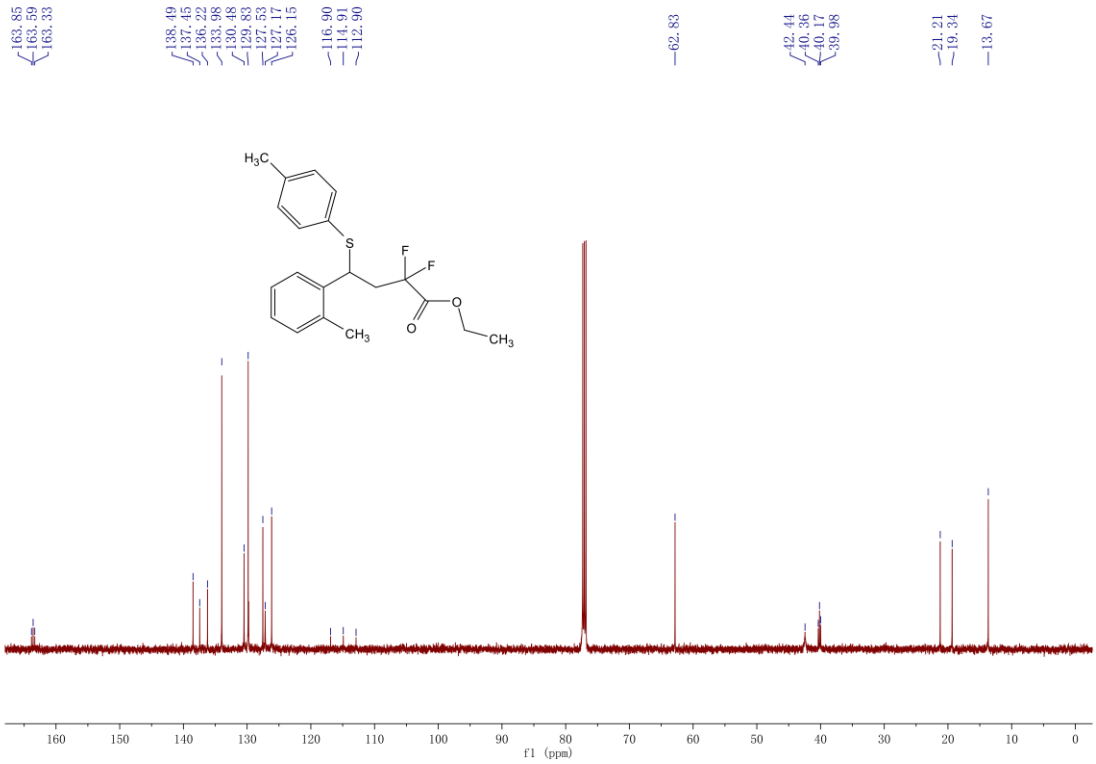
^{13}C NMR **4h**



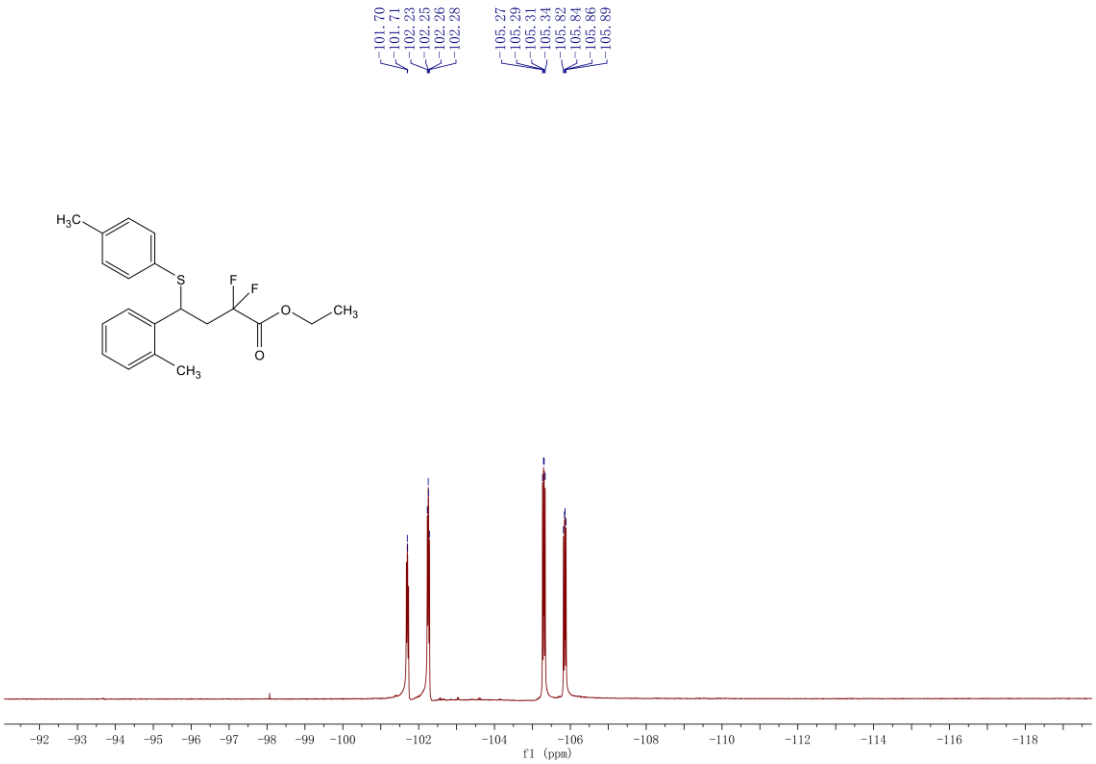
^{19}F NMR **4h**



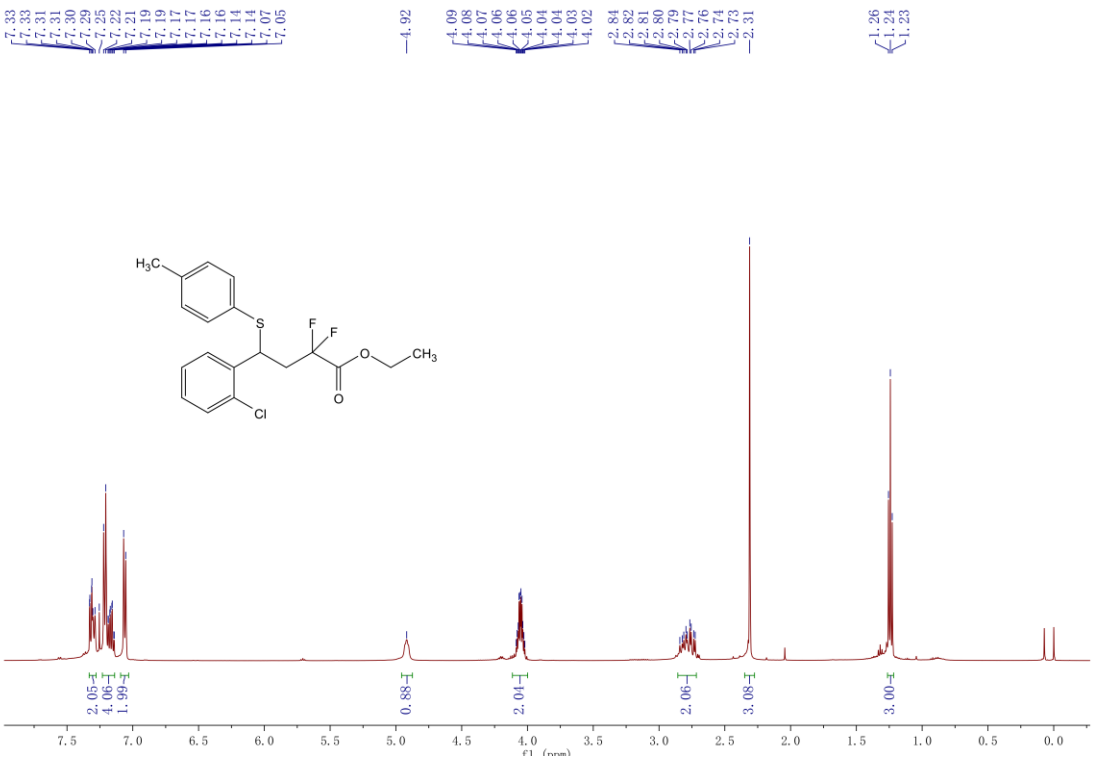
^{1}H NMR **4i**



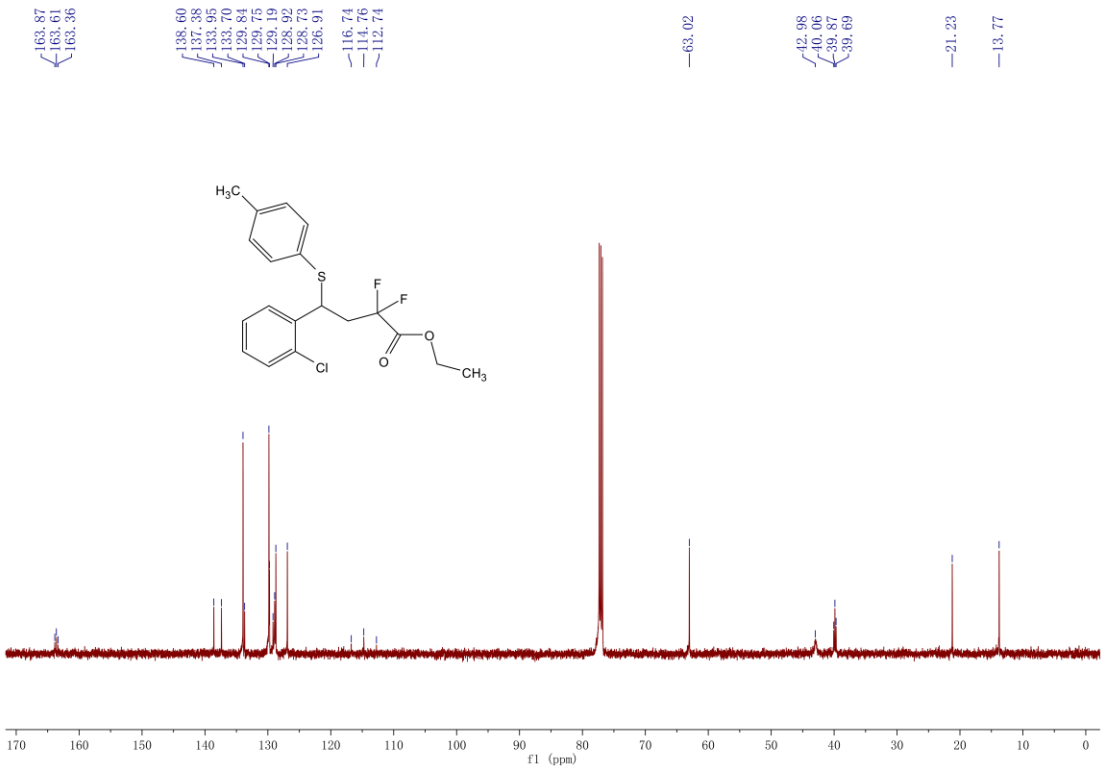
^{13}C NMR **4i**



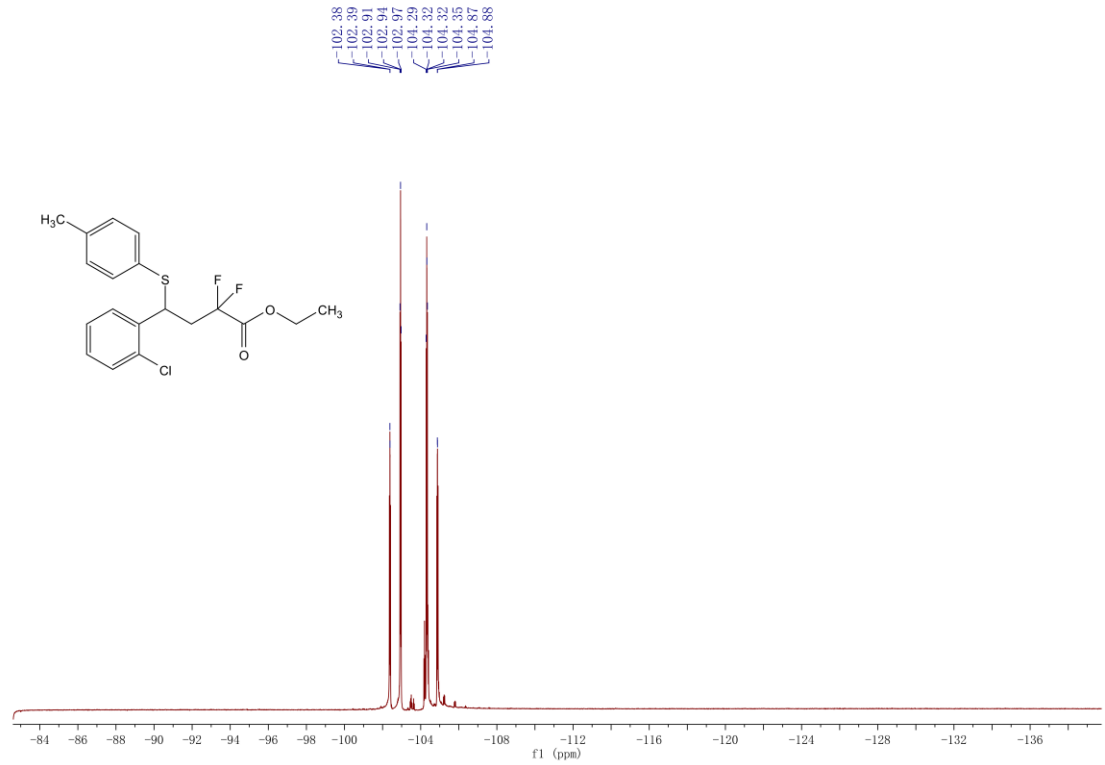
^{19}F NMR **4i**



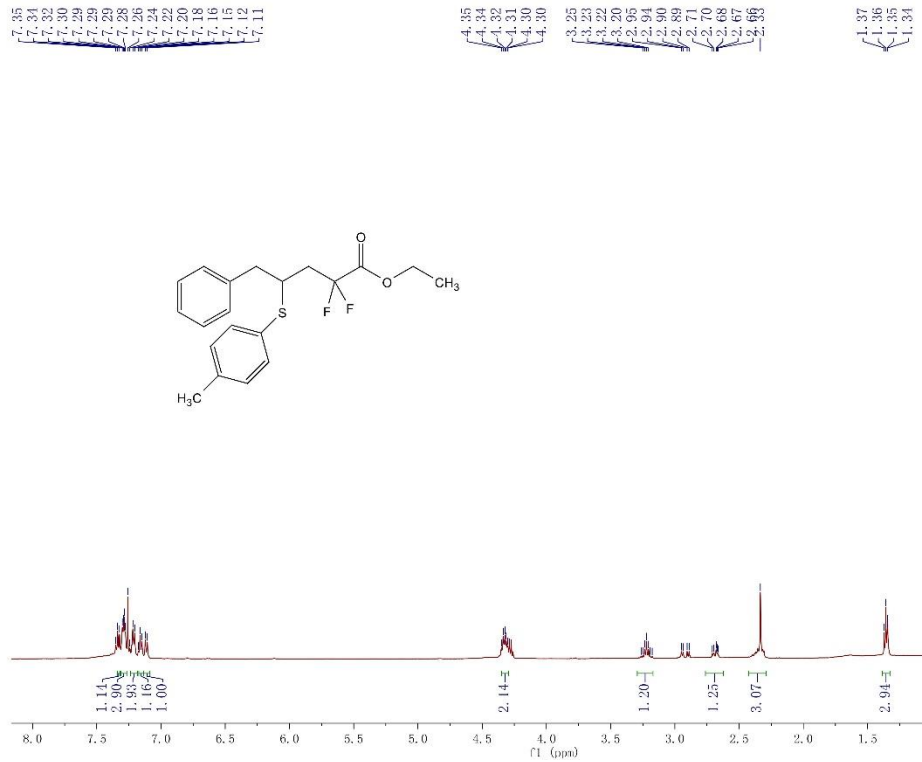
^{1}H NMR **4j**



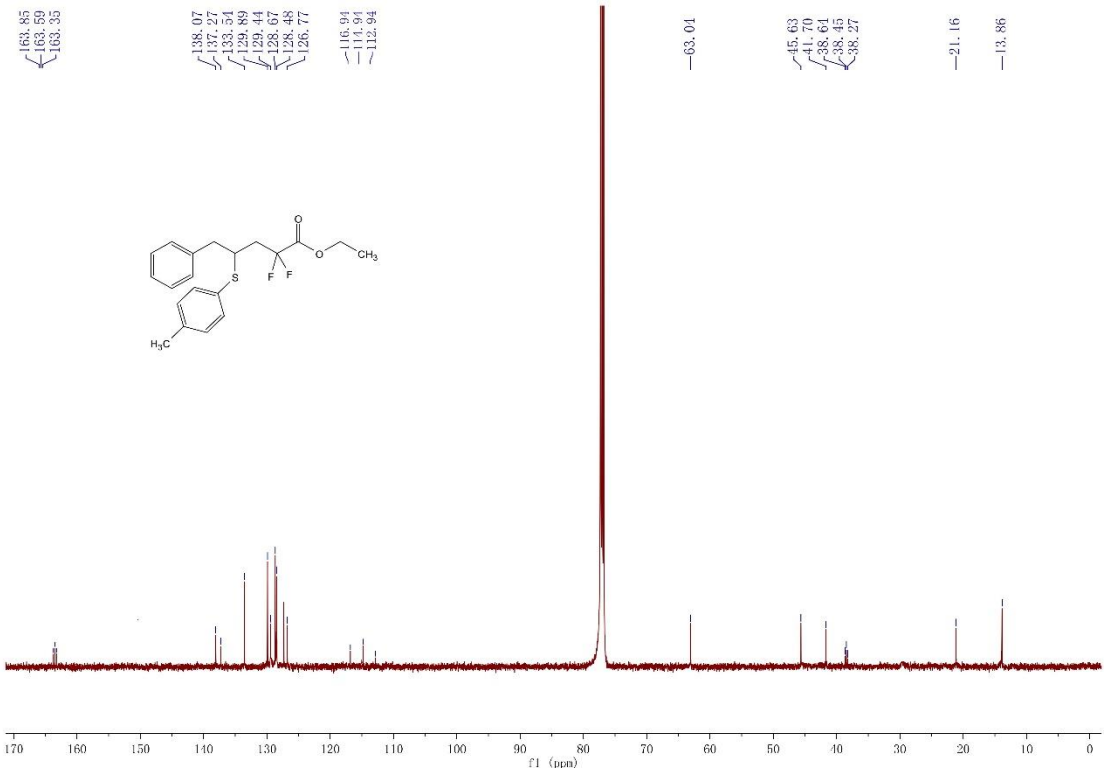
^{13}C NMR **4j**



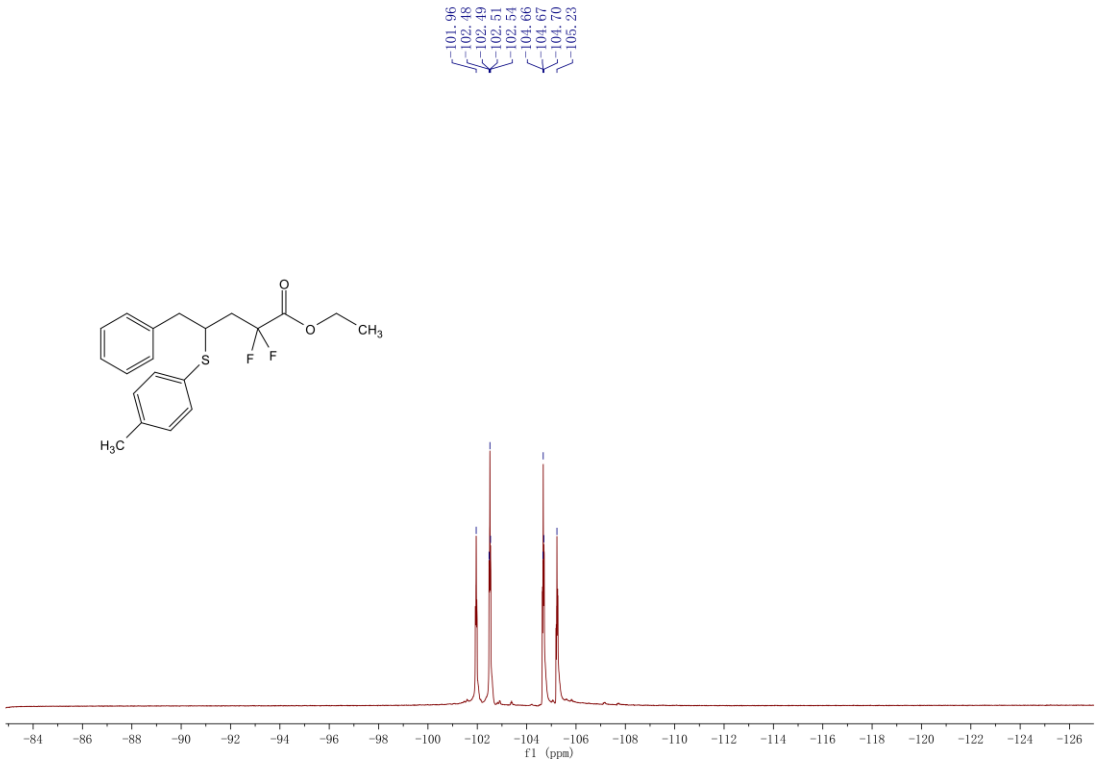
^{19}F NMR **4j**



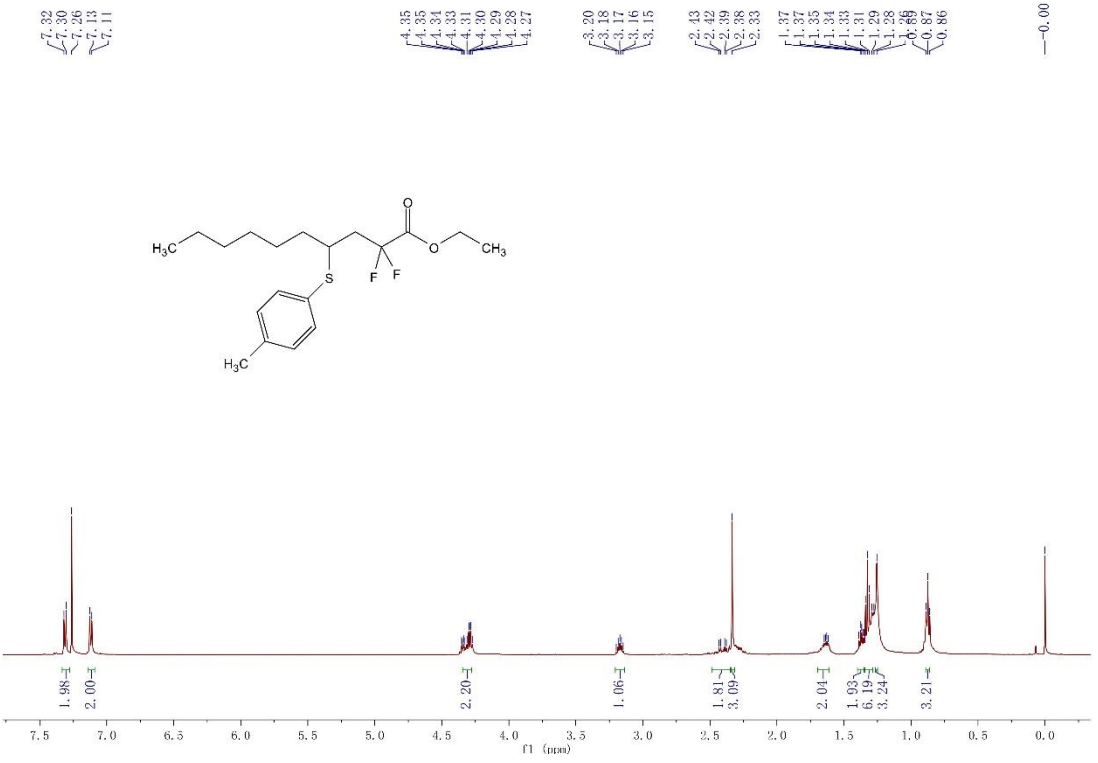
^{1}H NMR **4k**



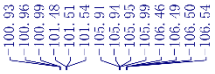
^{13}C NMR **4k**

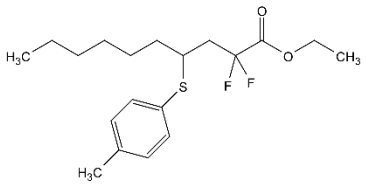


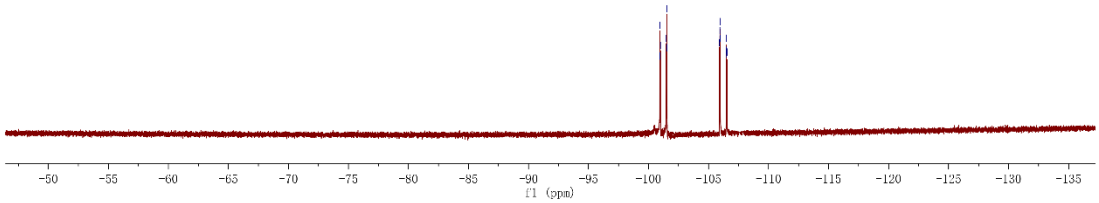
^{19}F NMR **4k**



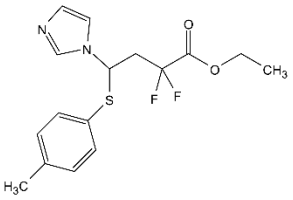
^{1}H NMR **4l**

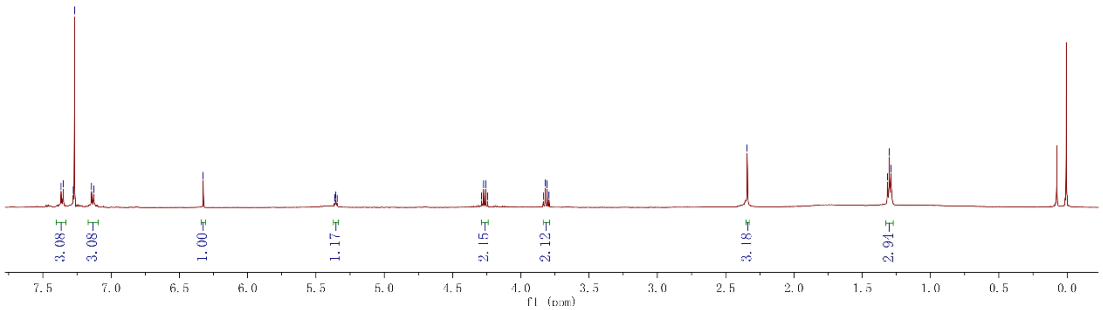




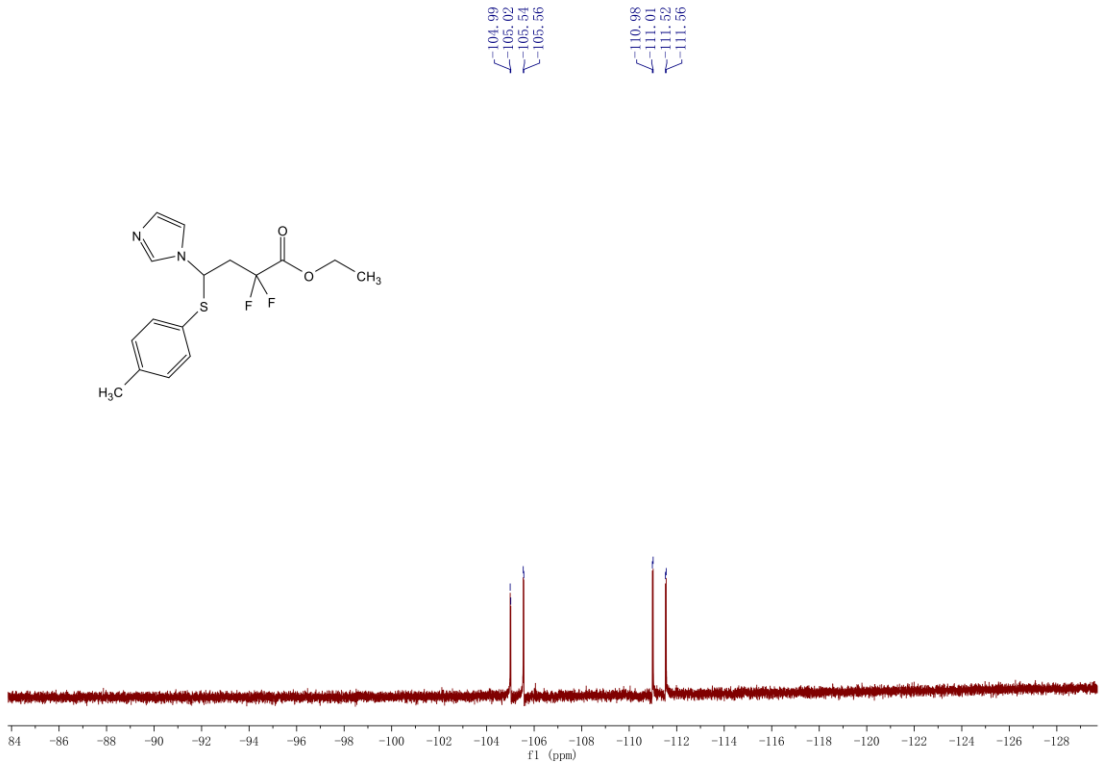


^{19}F NMR **4l**

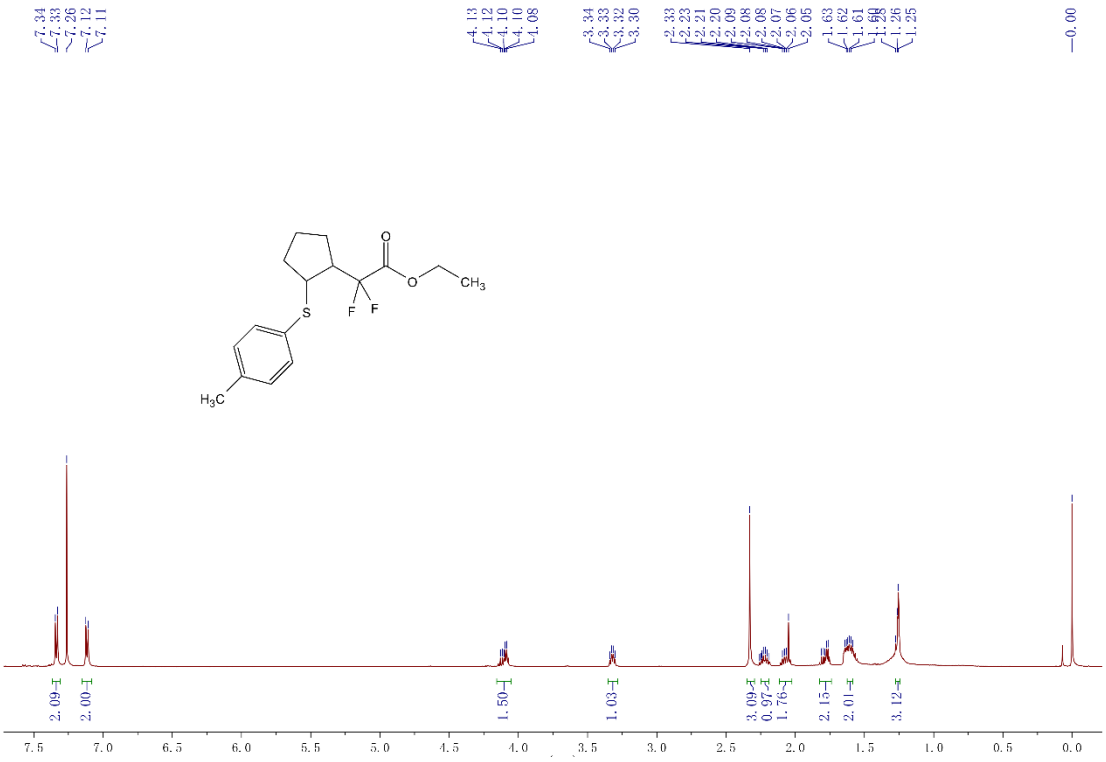




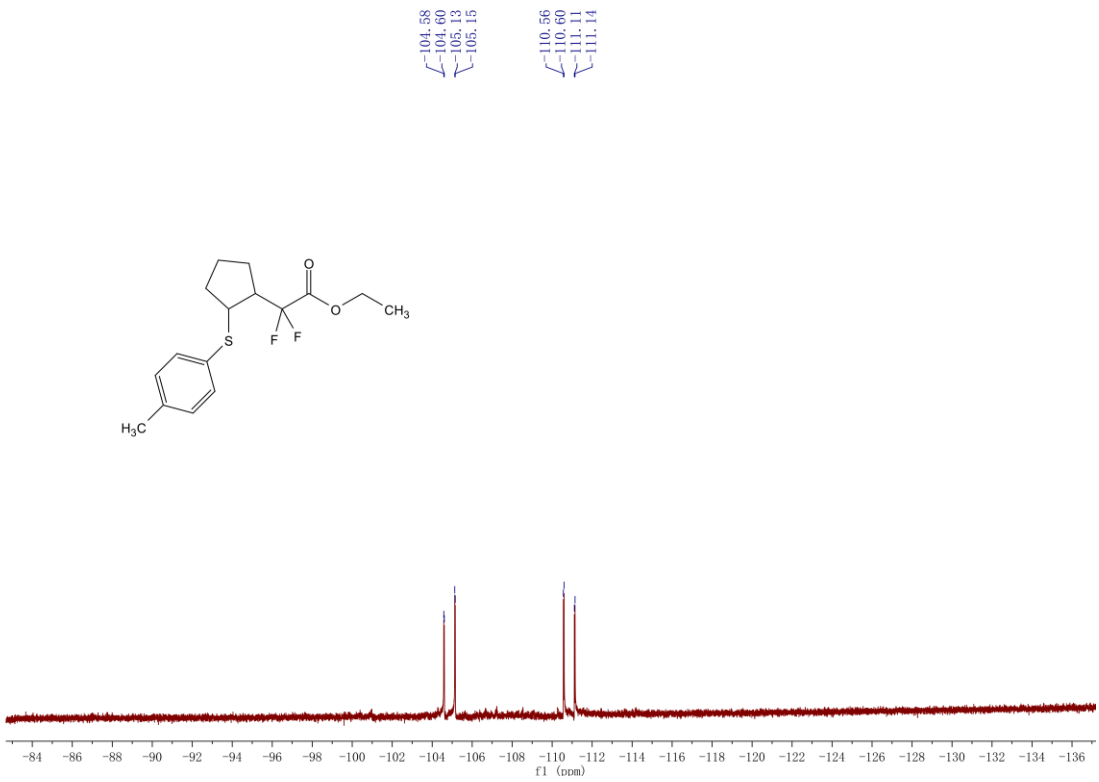
^{1}H NMR **4m**



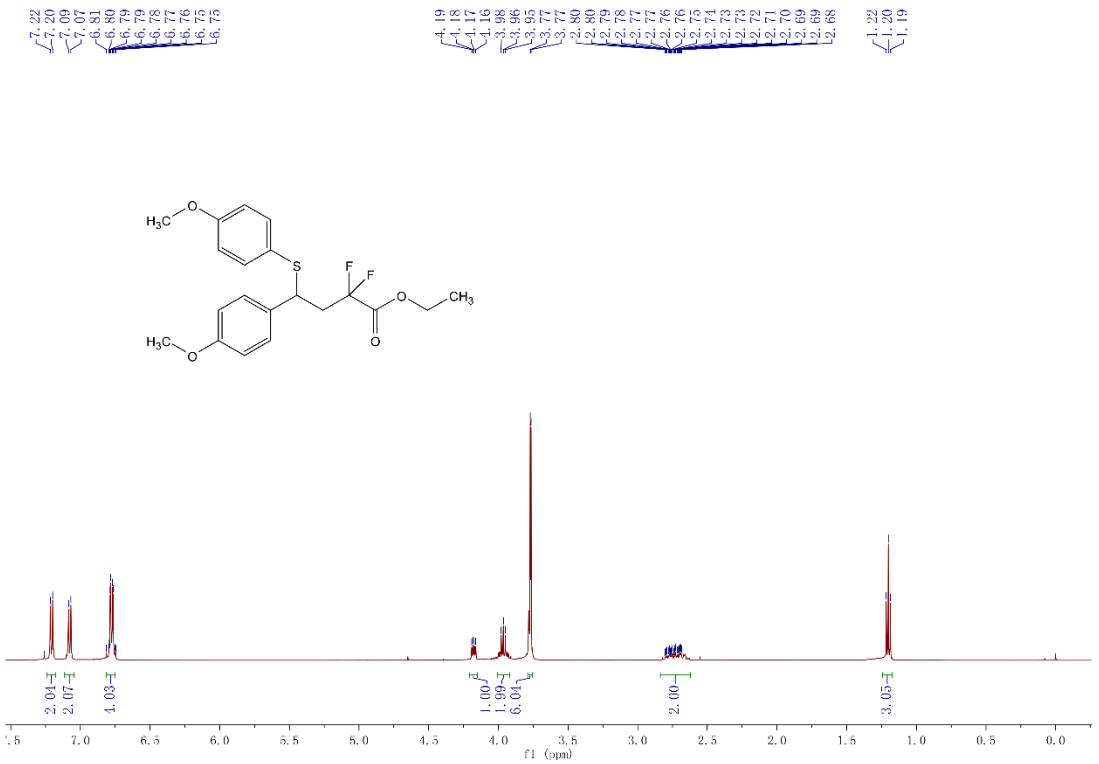
^{19}F NMR **4m**



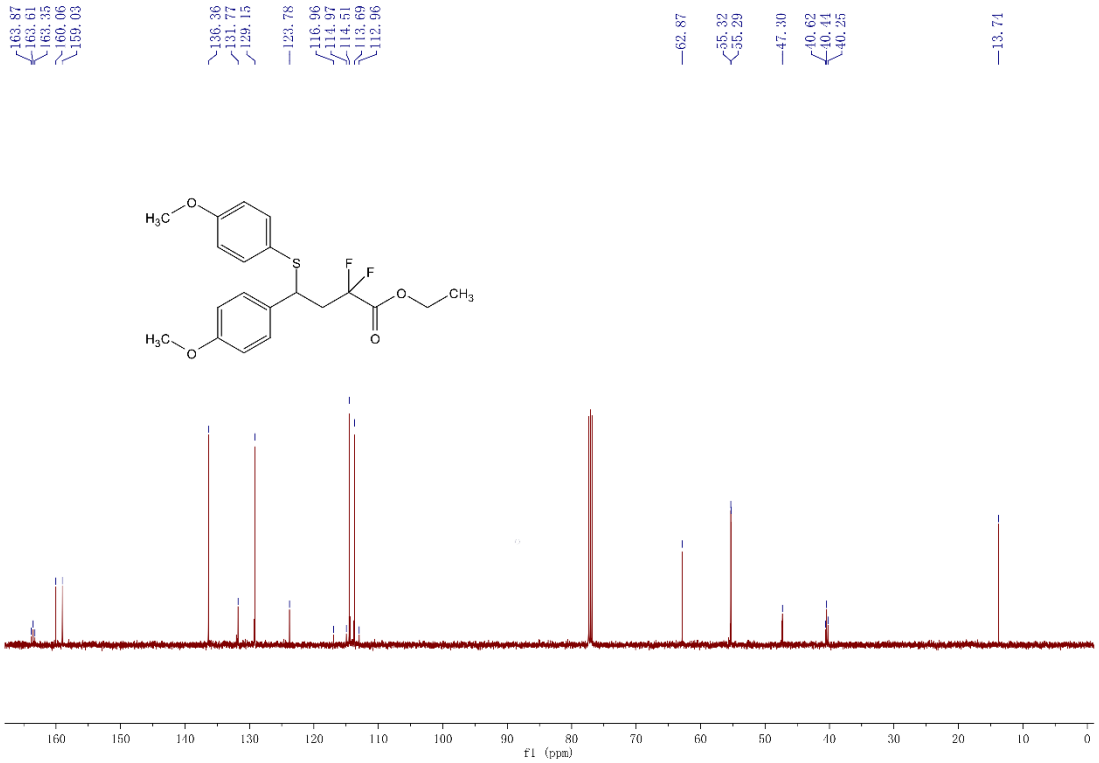
^{1}H NMR **4n**



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

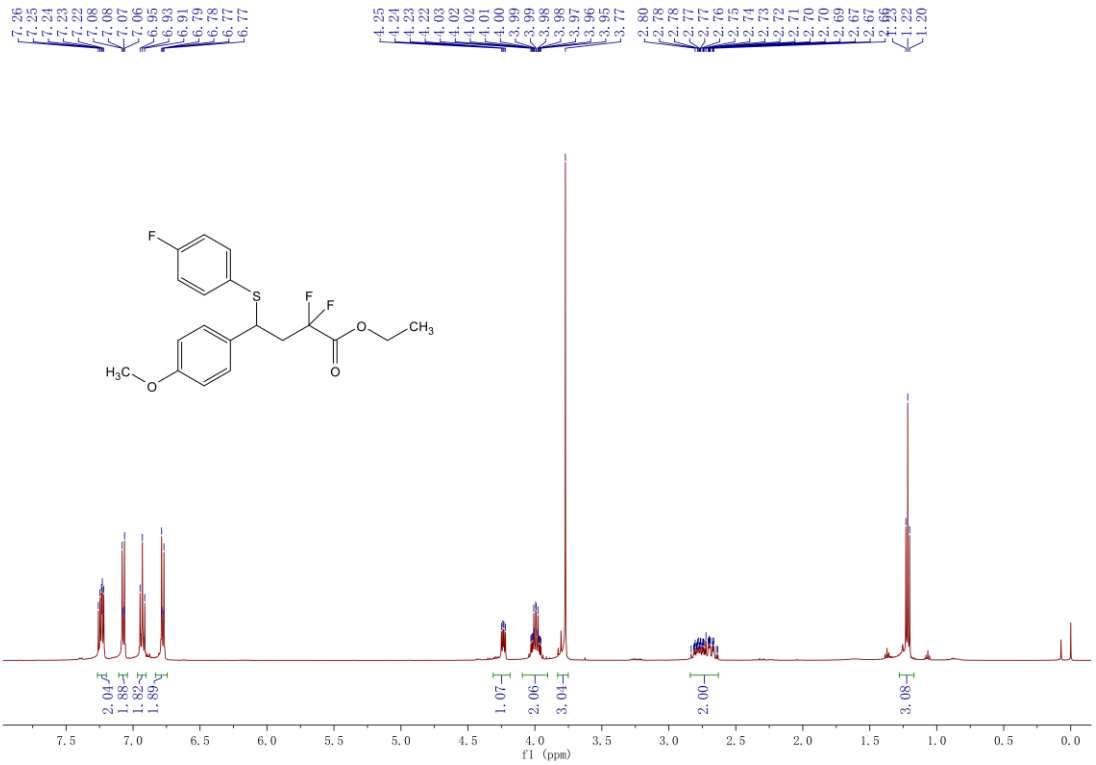


^{1}H NMR **4o**

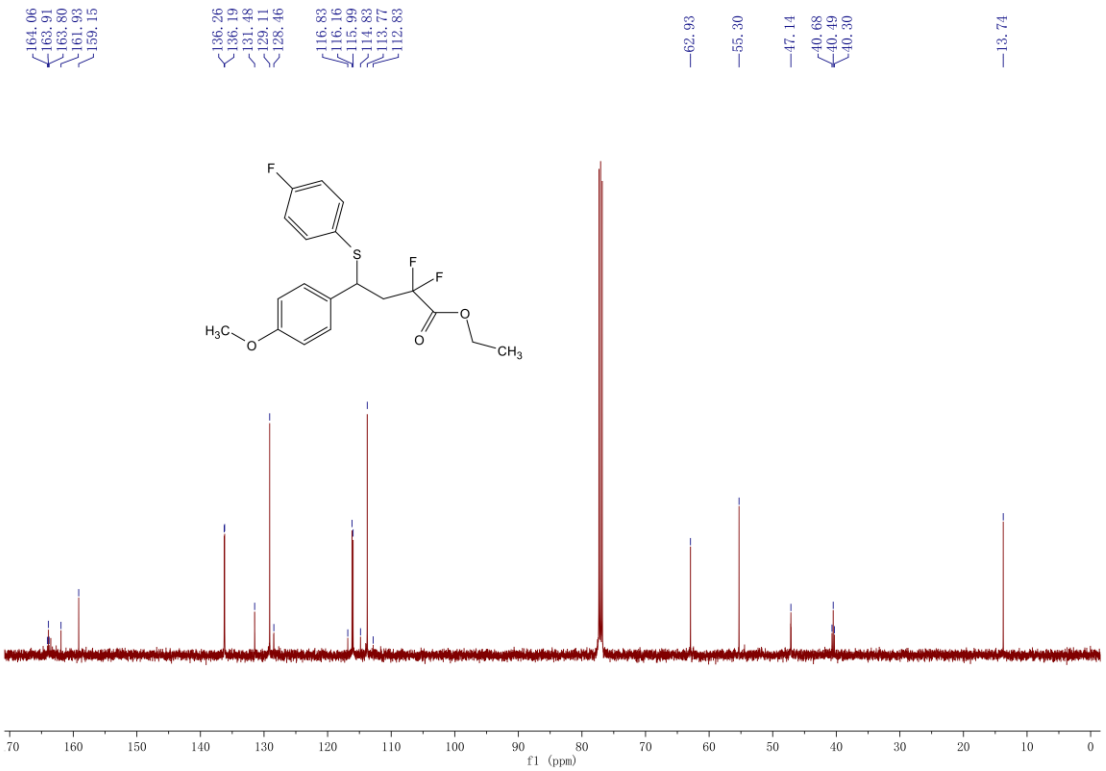


^{13}C NMR **4o**

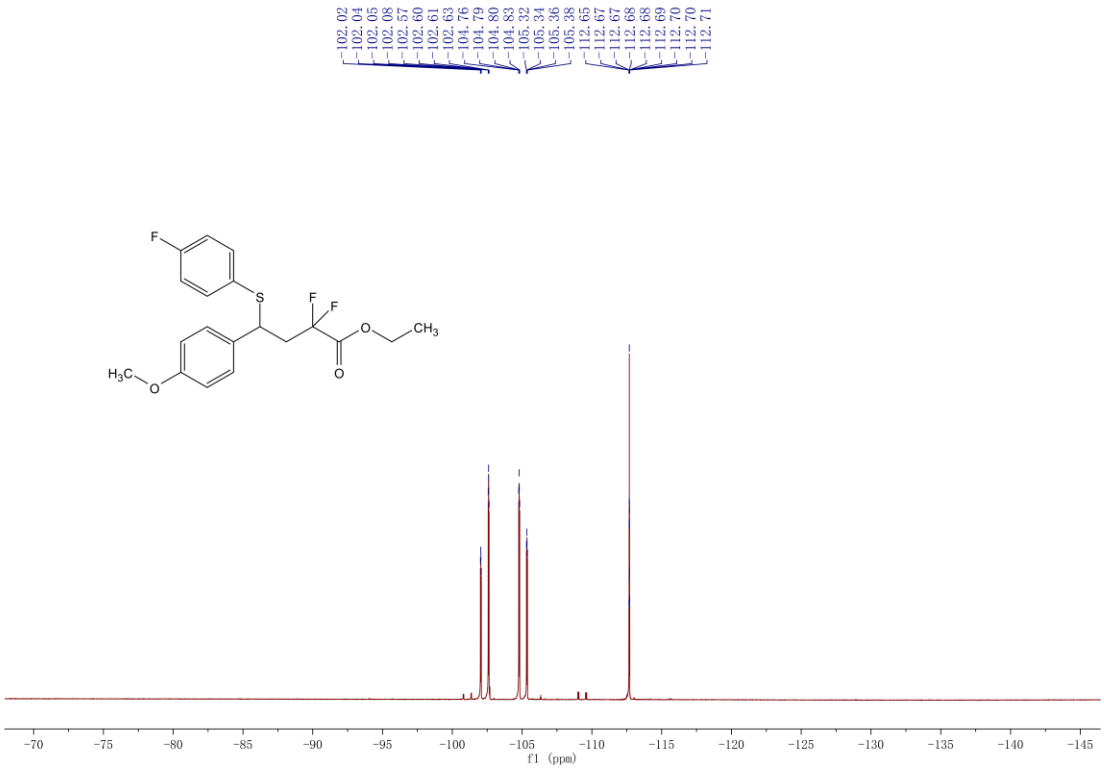
^{19}F NMR **4o**



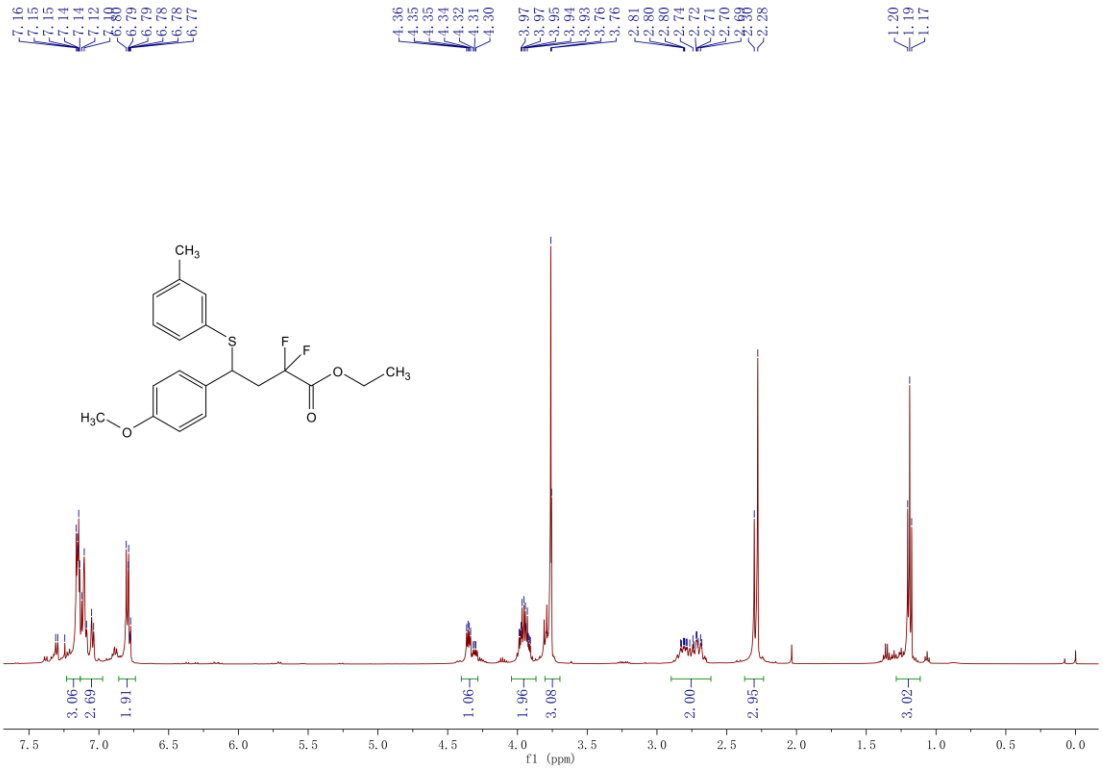
^{1}H NMR **4p**



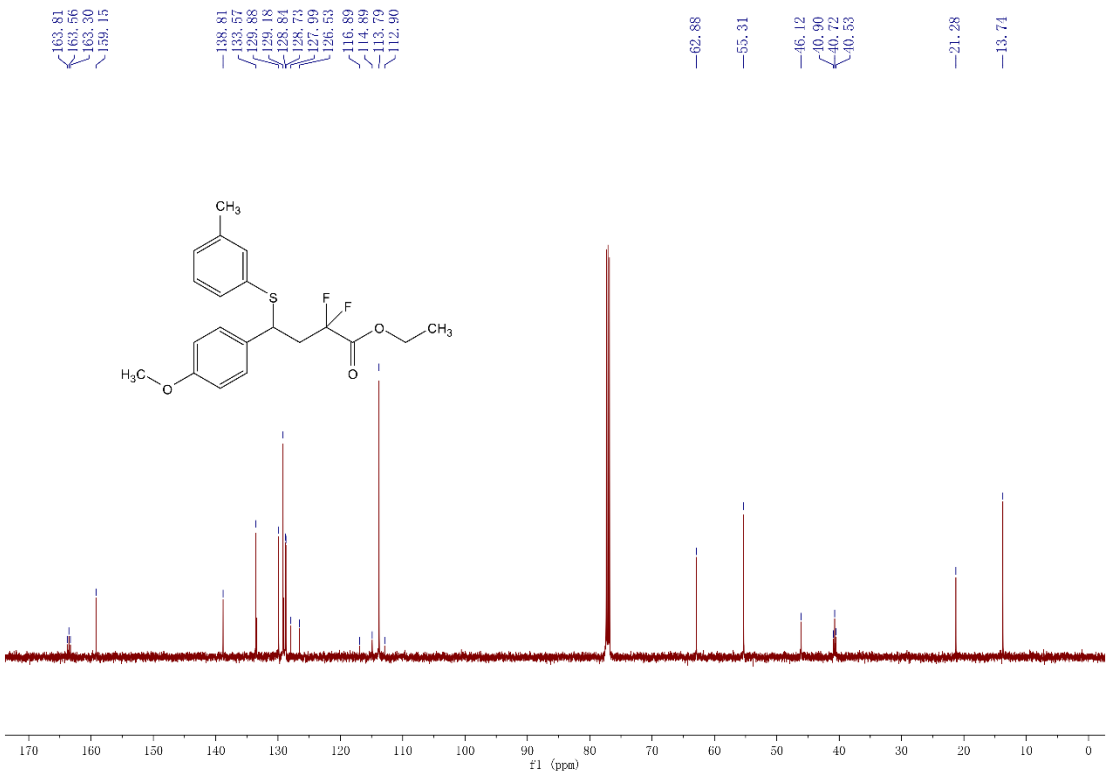
^{13}C NMR **4p**



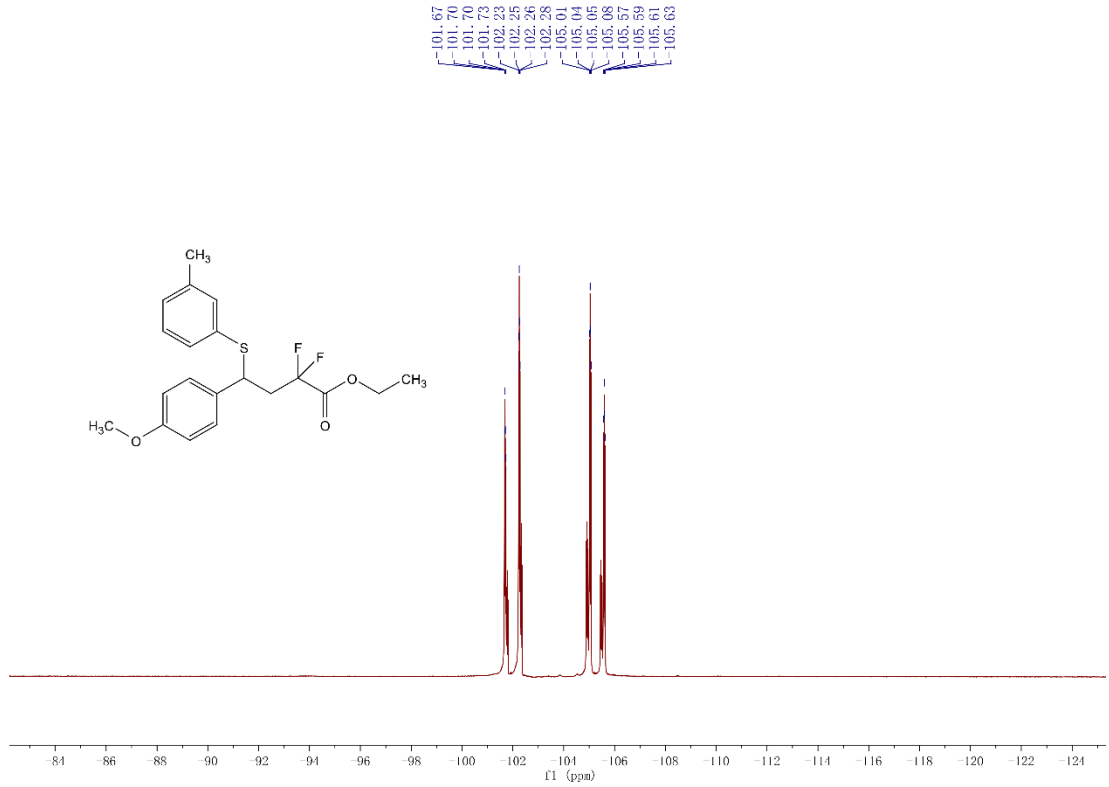
^{19}F NMR **4p**



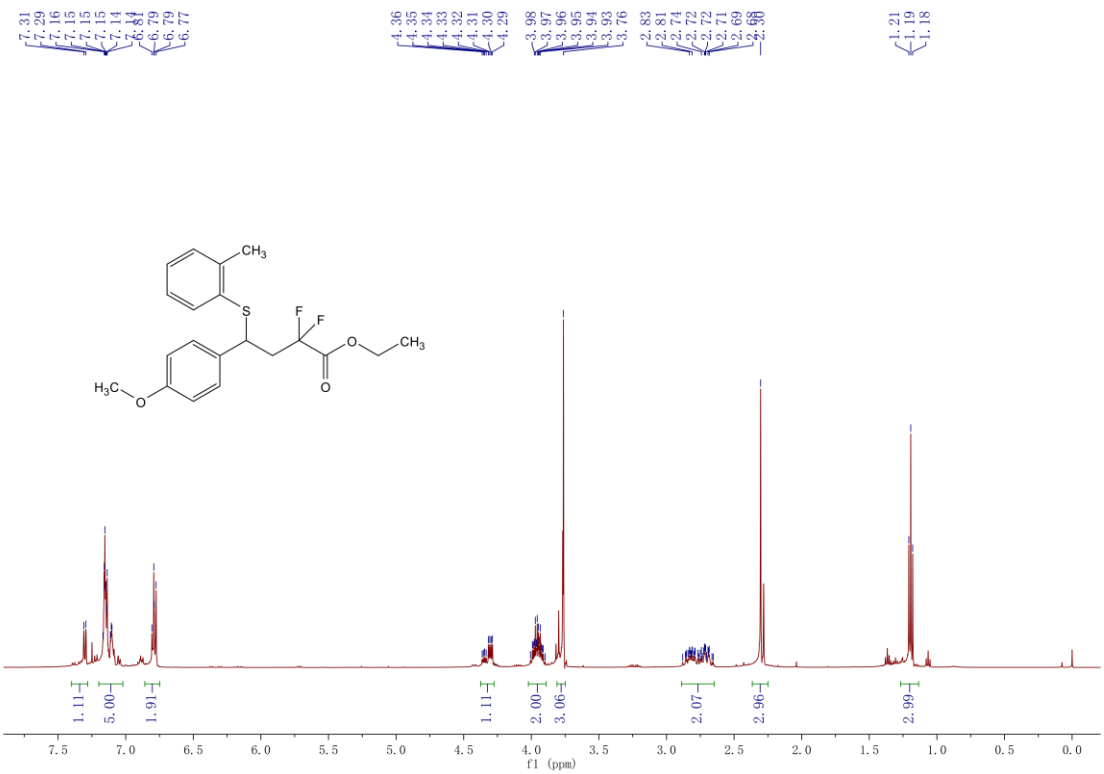
^{1}H NMR **4q**



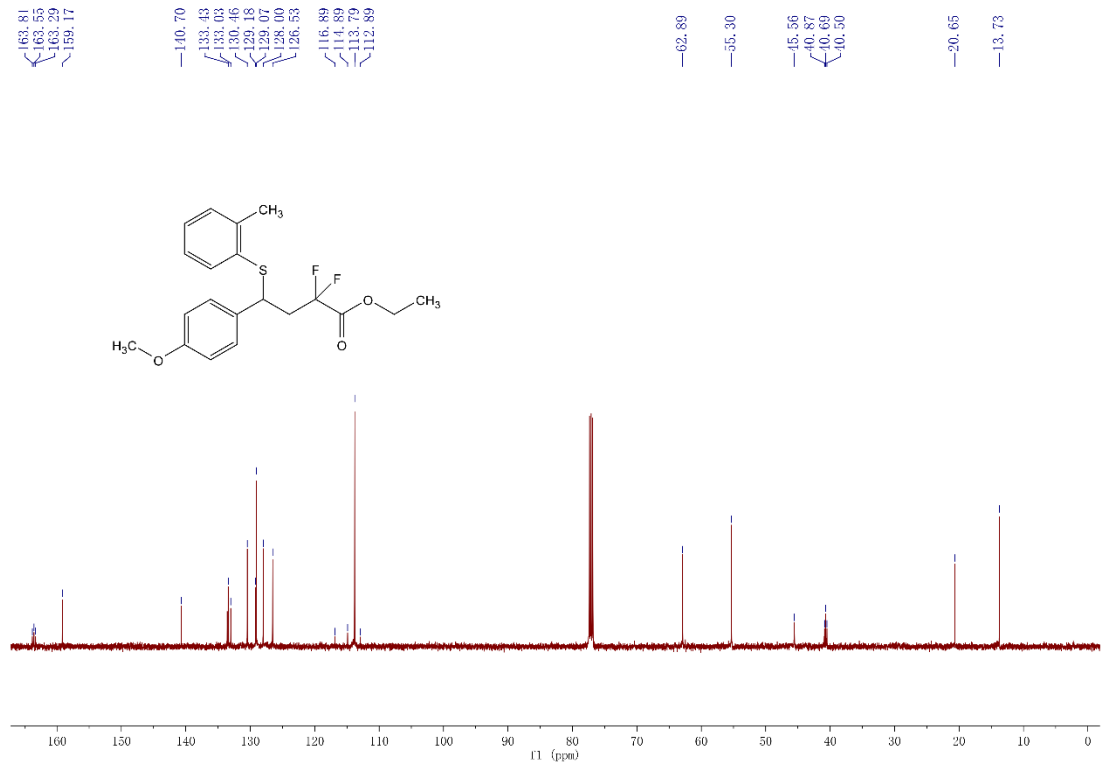
^{13}C NMR **4q**



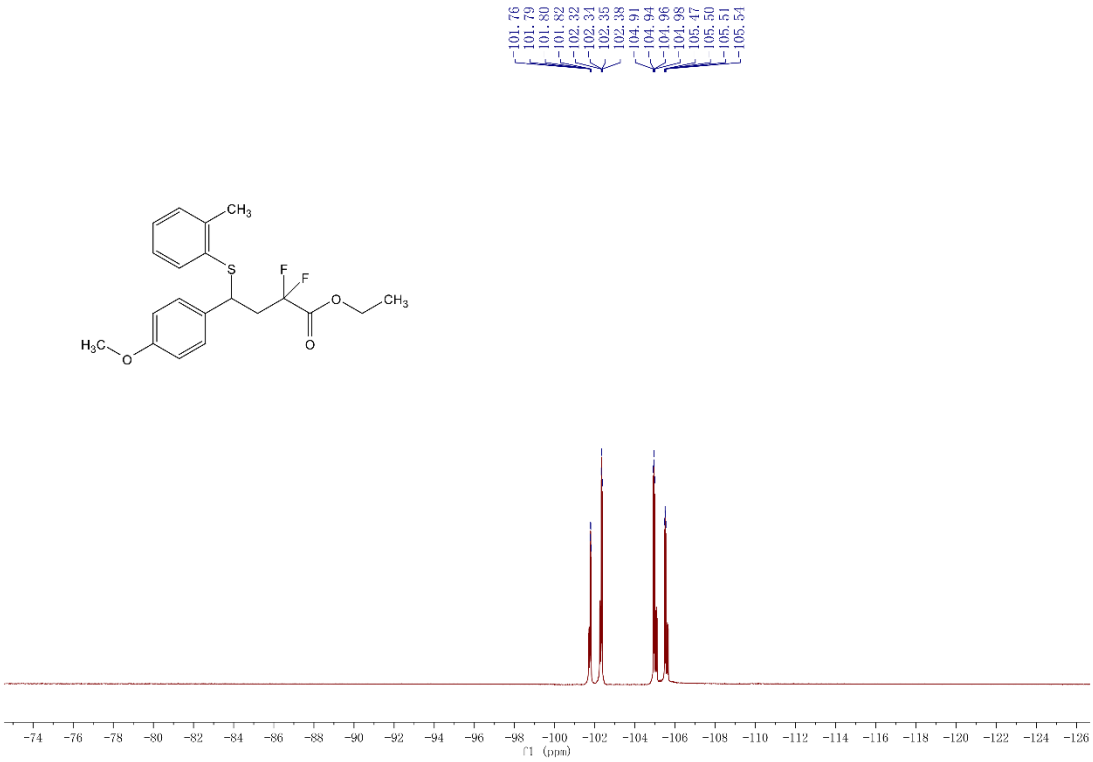
^{19}F NMR **4q**



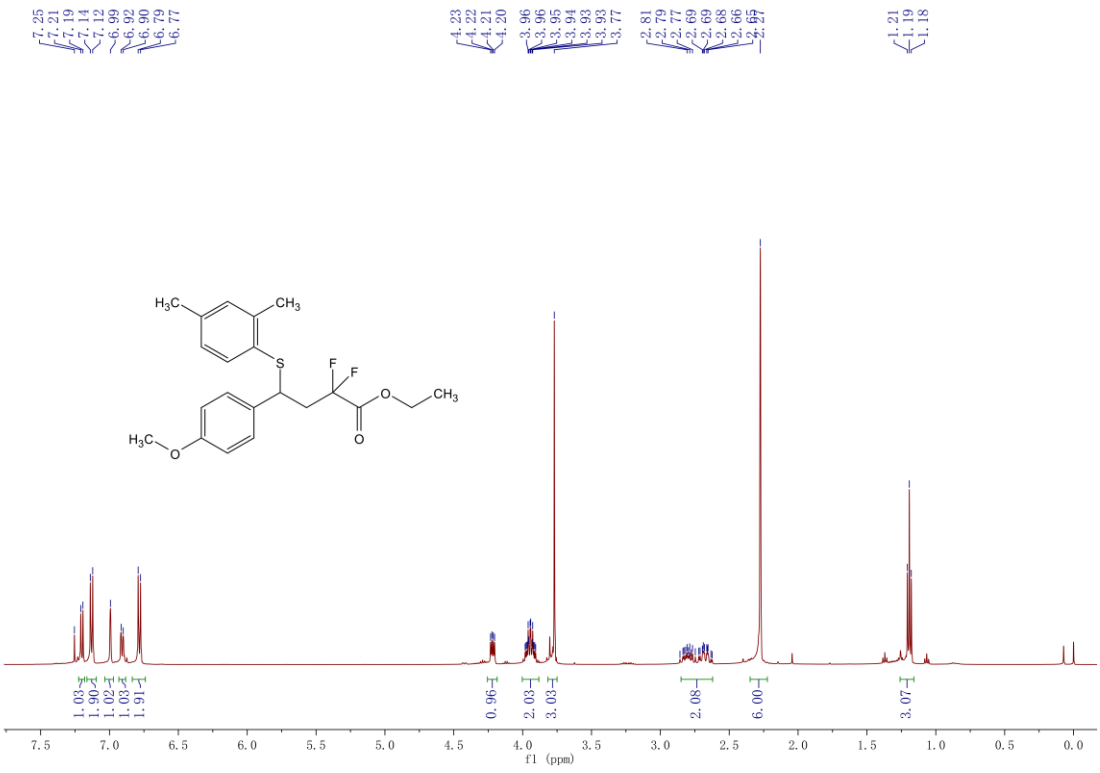
^{1}H NMR **4r**



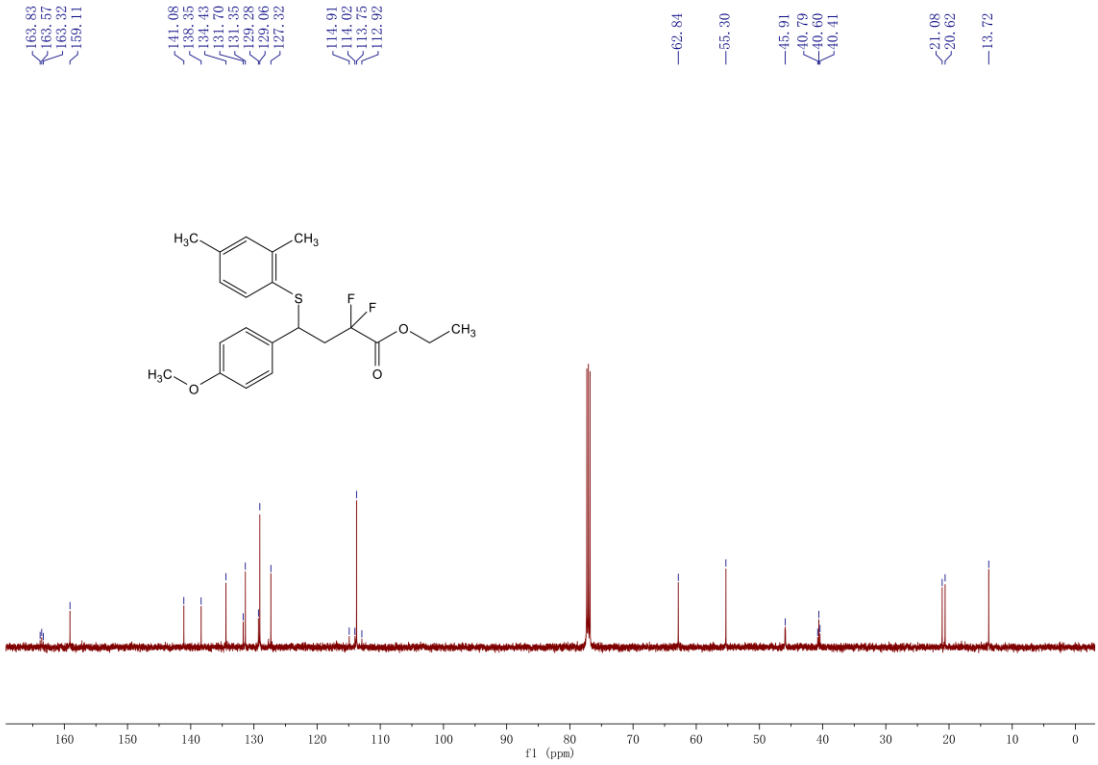
^{13}C NMR **4r**



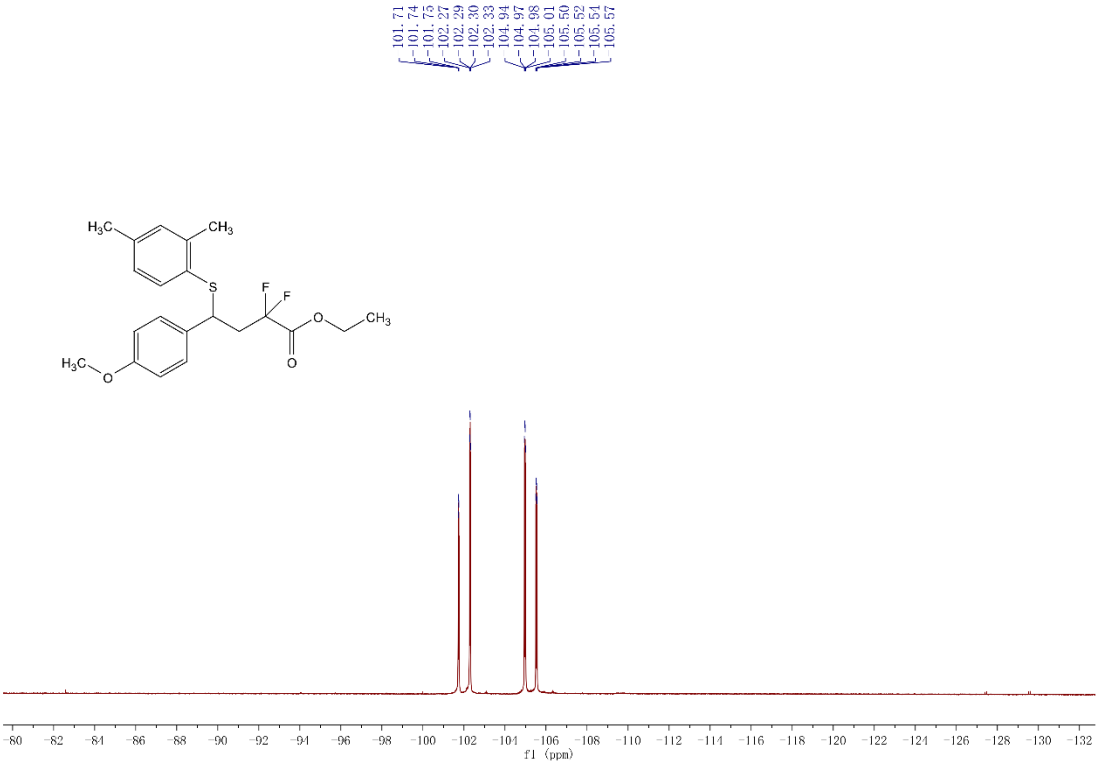
^{19}F NMR **4r**



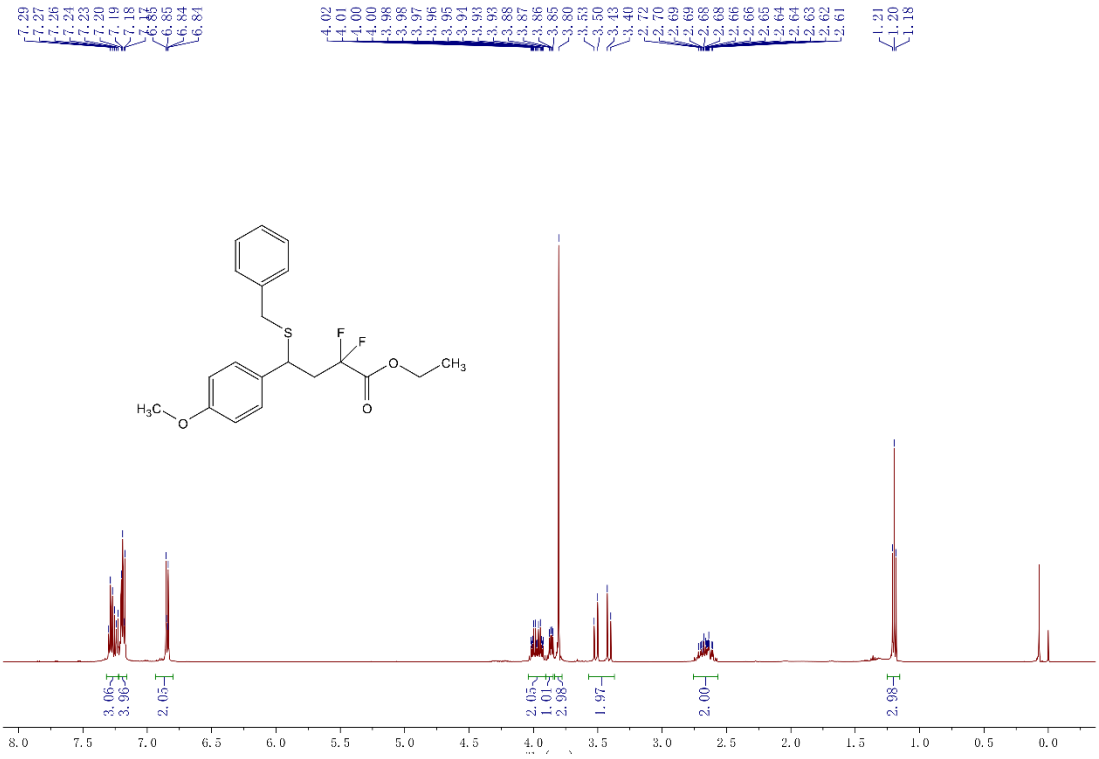
^{1}H NMR **4s**



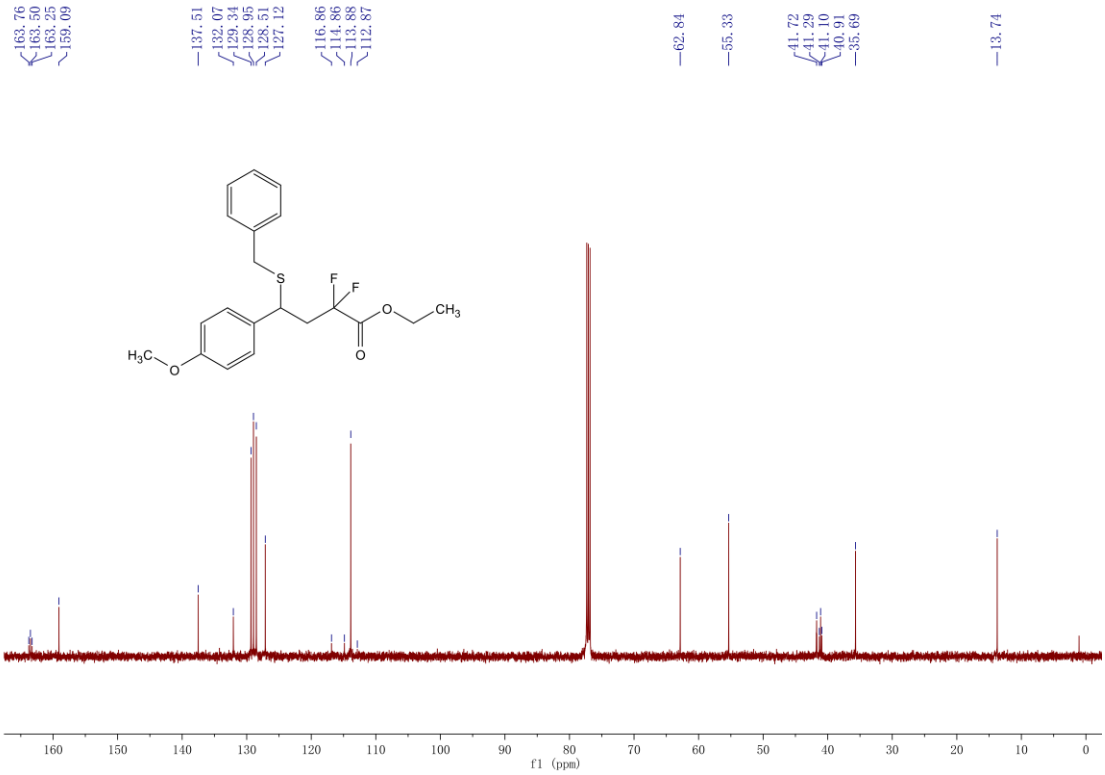
^{13}C NMR **4s**



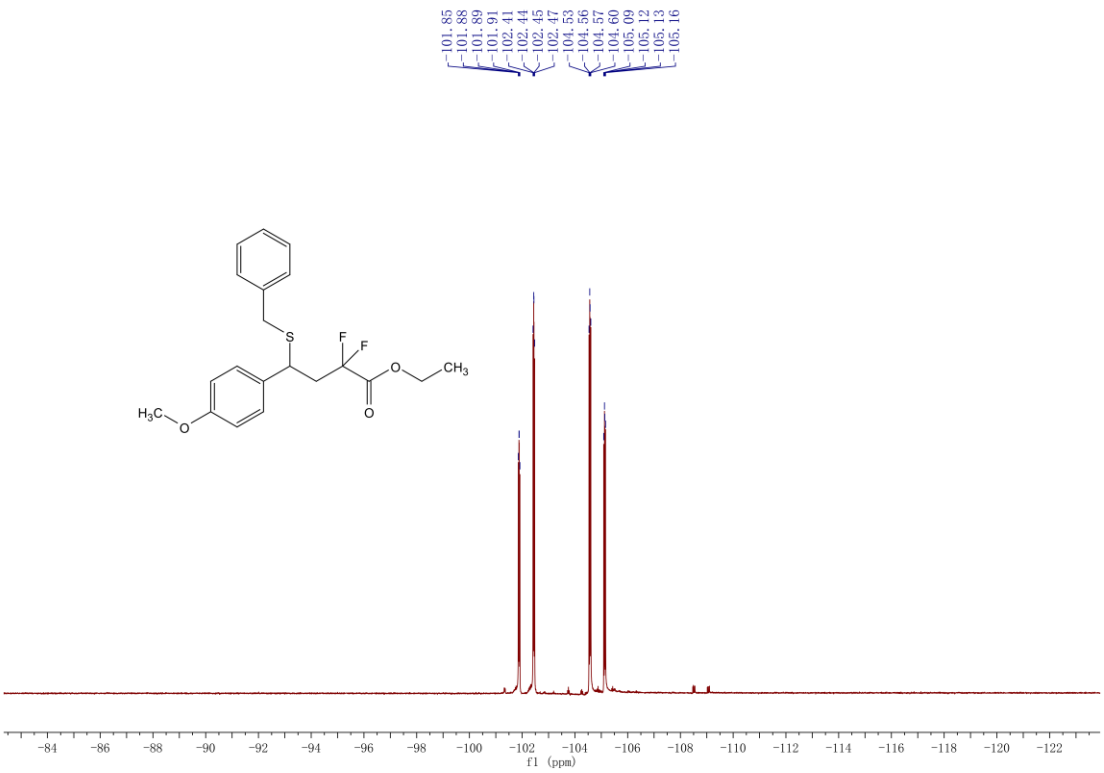
^{19}F NMR **4s**



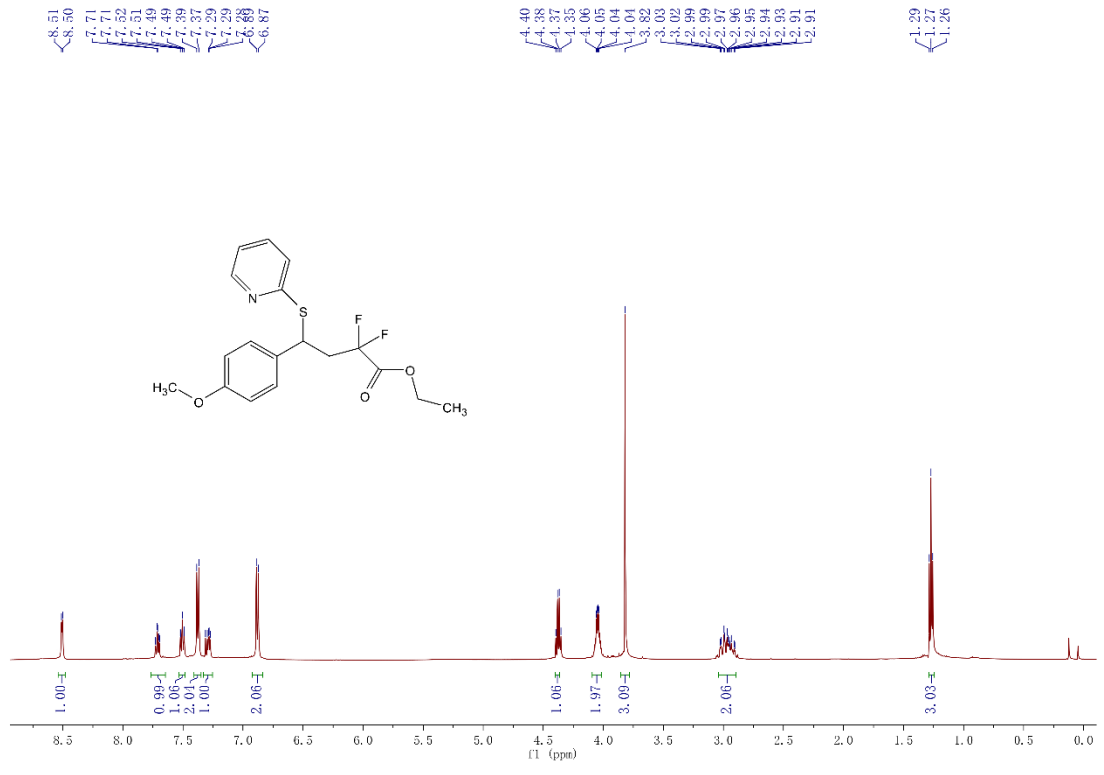
^{1}H NMR **4t**



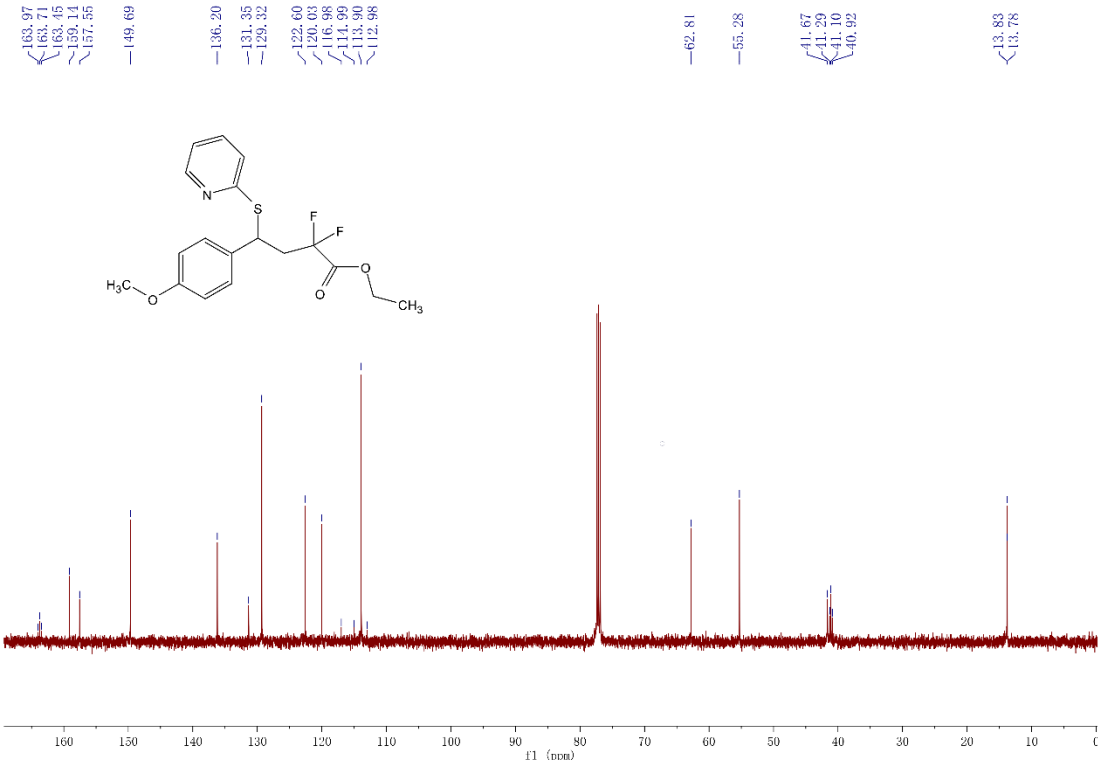
^{13}C NMR **4t**



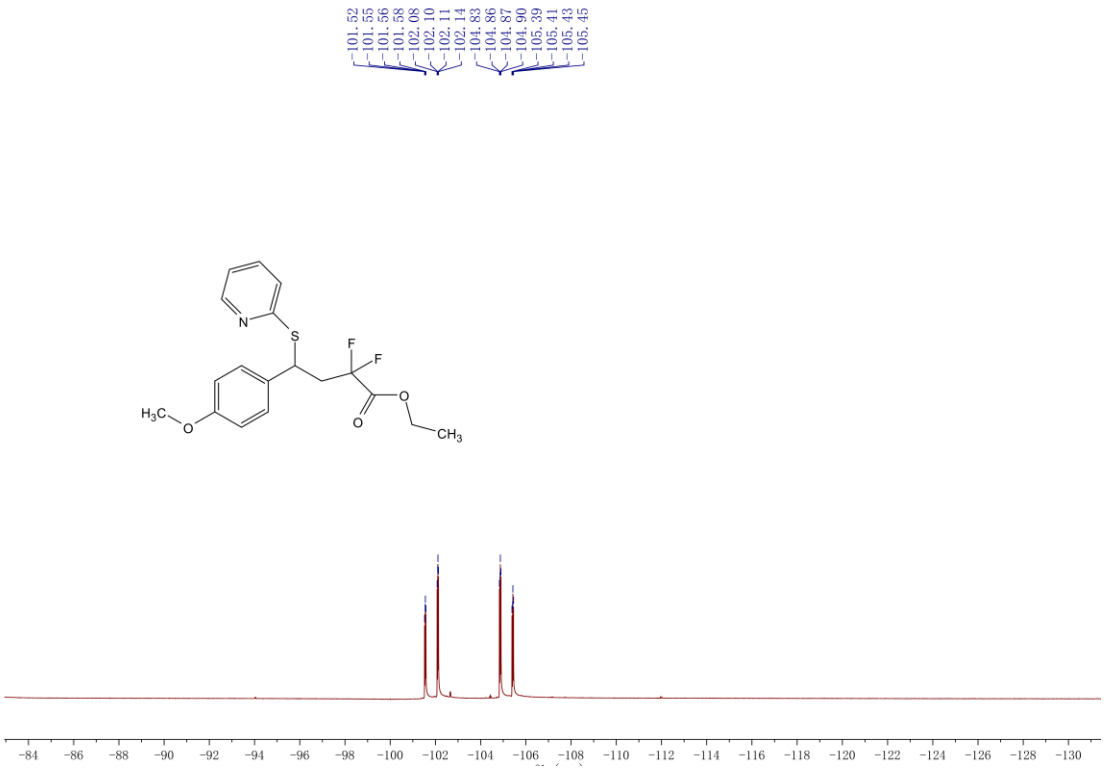
^{19}F NMR **4t**



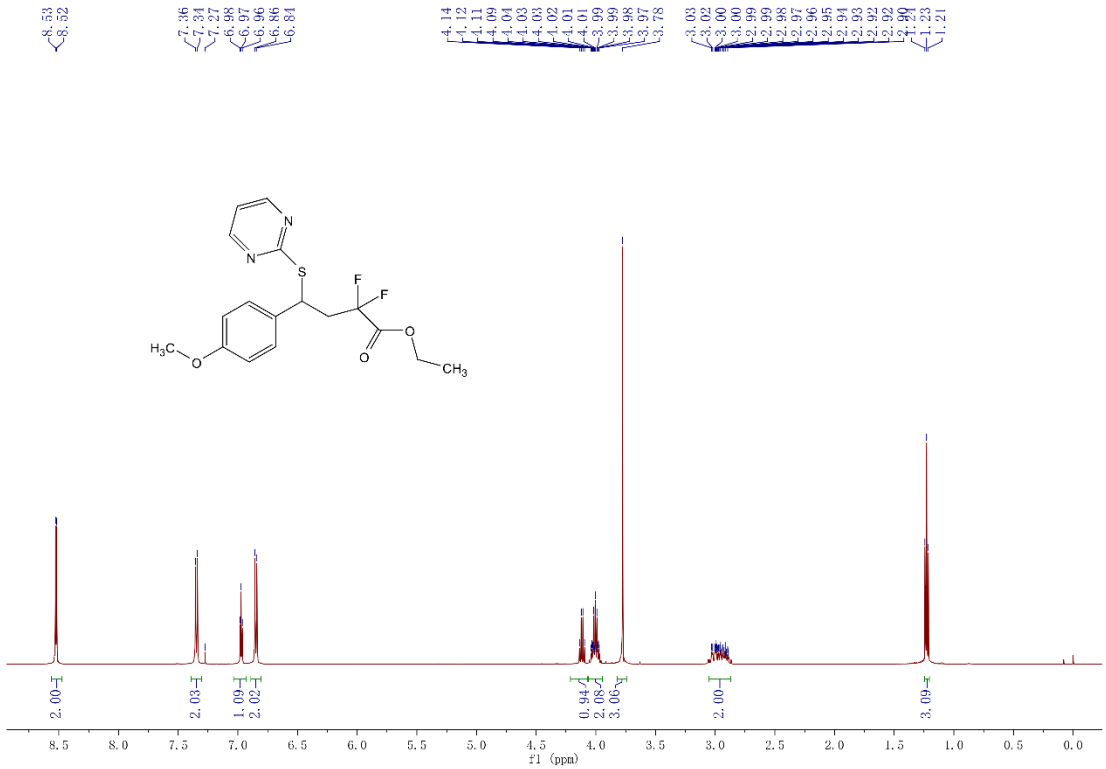
^{1}H NMR **4u**



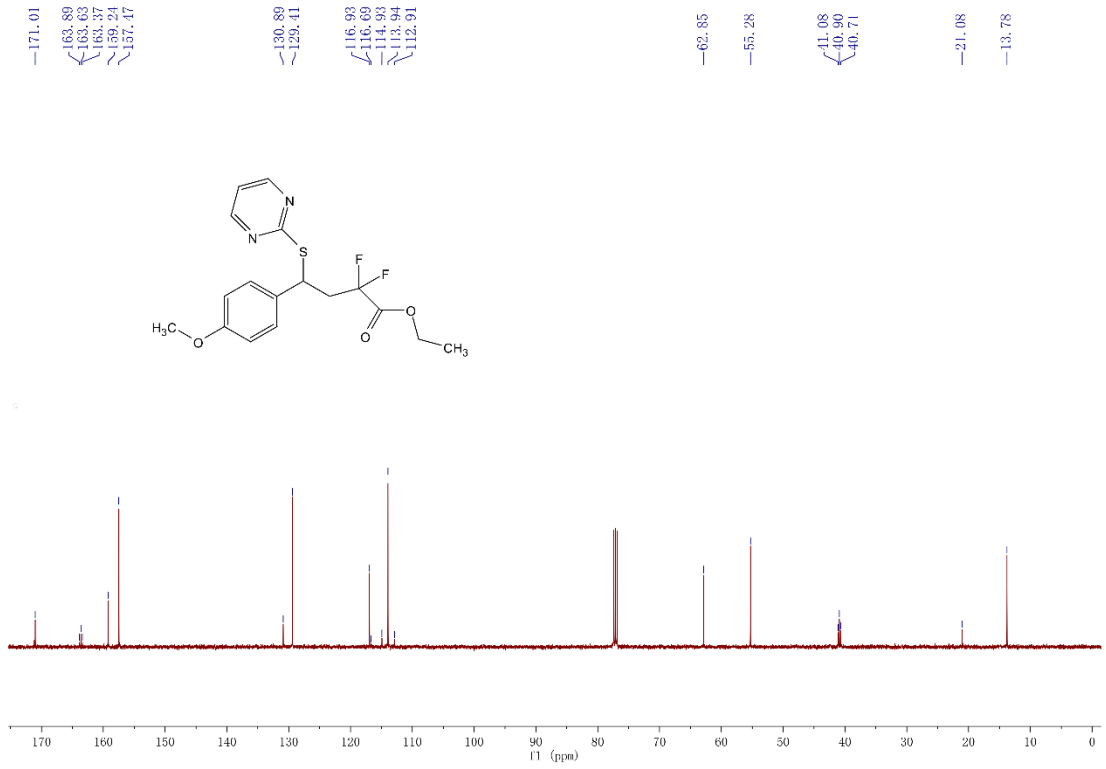
^{13}C NMR **4u**



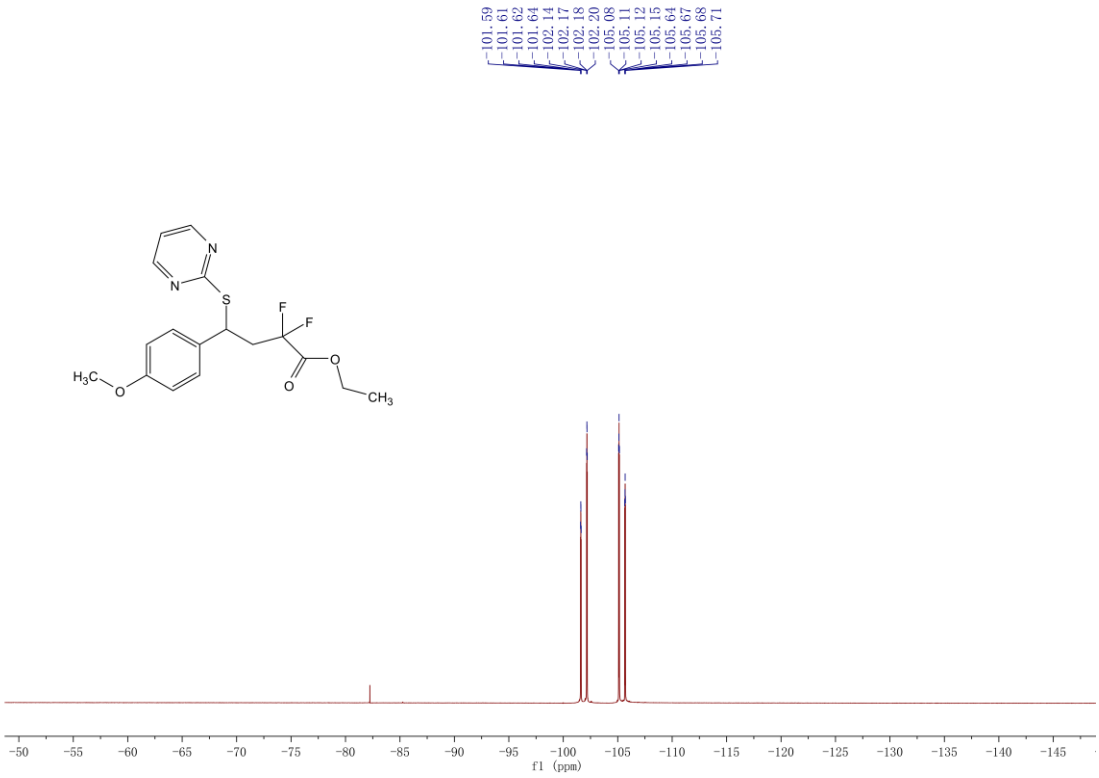
^{19}F NMR **4u**



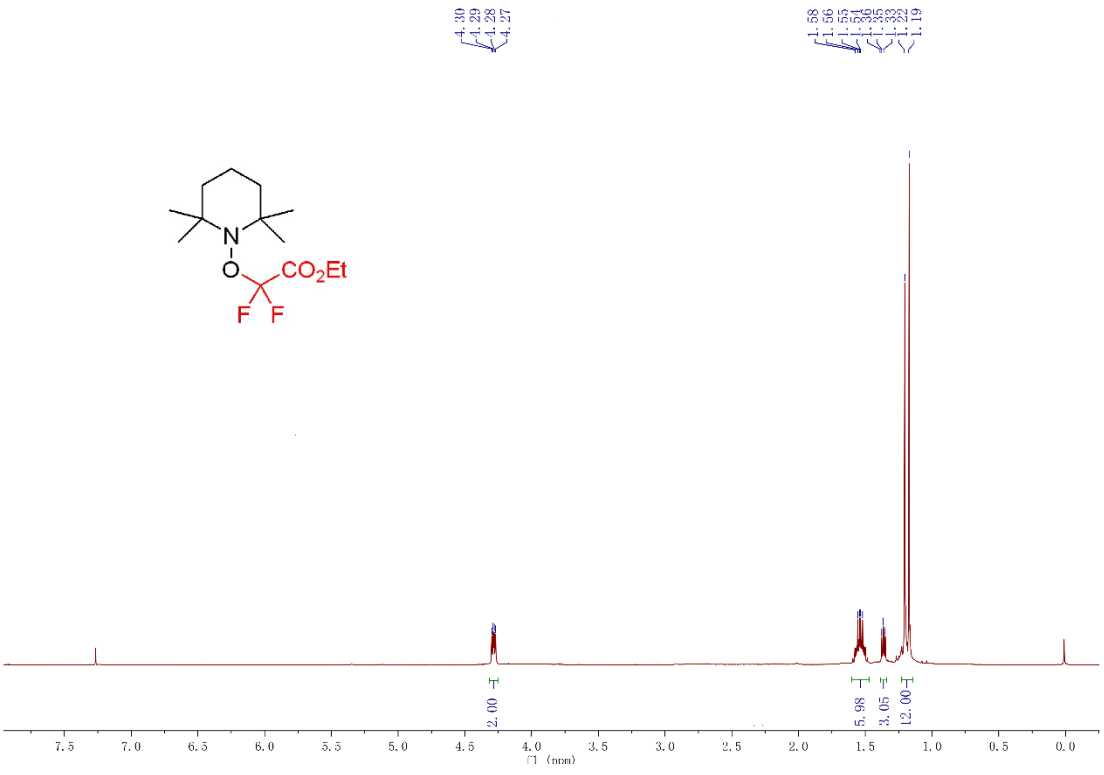
^{1}H NMR **4v**



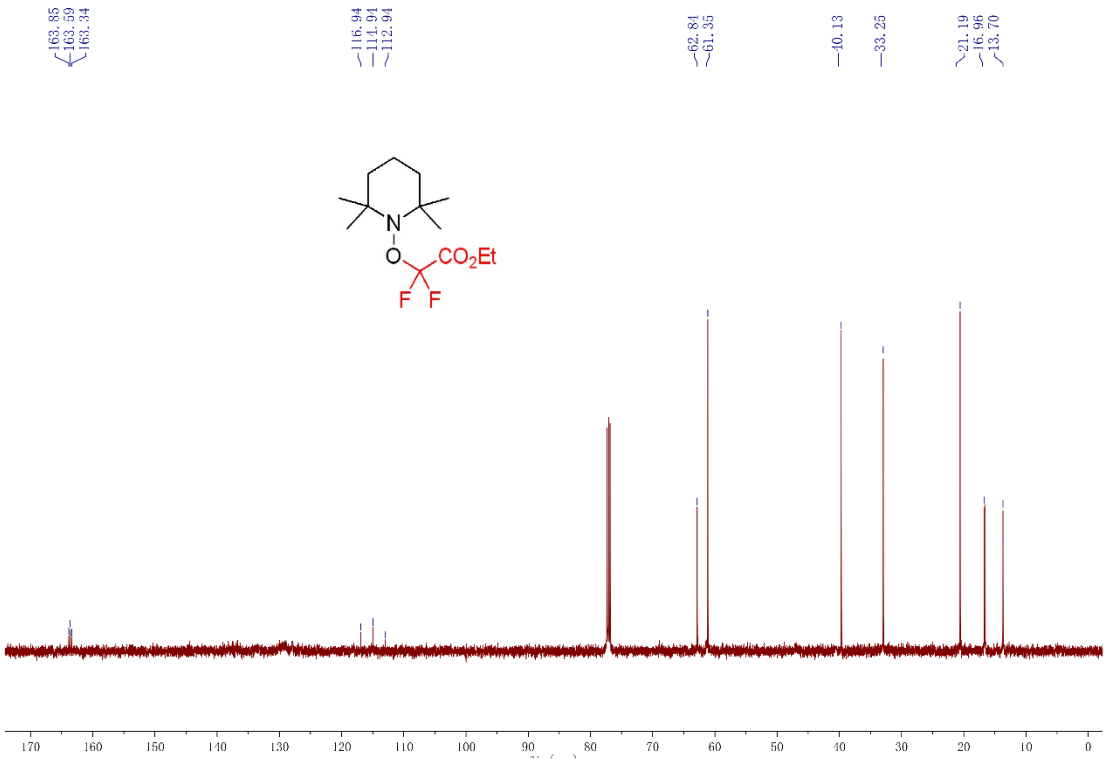
^{13}C NMR **4v**



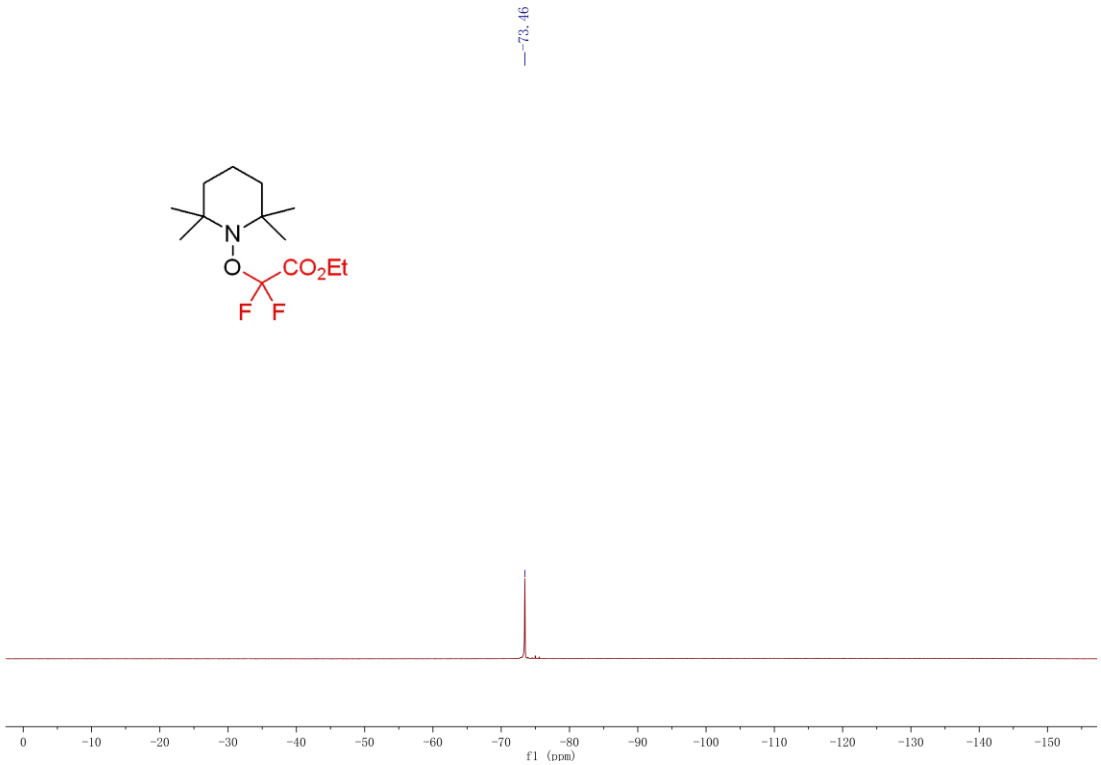
^{19}F NMR **4v**



^{1}H NMR **5**



^{13}C NMR **5**



^{19}F NMR **5**