Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Iron-Catalyzed Three-Components Intermolecular Trifluoroalkyl-Esterification of Styrenes with $NaSO_2CF_3$ and Benzoic Acids

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1. General Information

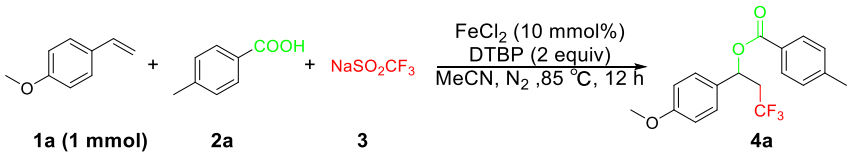
All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are characterized by ^{1}H NMR, ^{13}C NMR and ^{19}F NMR and compared with previously reported data. All experiments were conducted with a schlenk tube. Analytical thin-layer chromatography 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, 126 MHz and 470 MHz in $CDCl_3$, respectively. Chemical shifts in ppm from tetramethylsilane as an internal standard in $CDCl_3$, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet-doublet, m = multiplet, br = broad), coupling constants (Hz), and assignment. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as inter standard.

2. Experimental Procedure

(a) General procedures for the trifluoromethylation−arylesterification

To a Schlenk tube were added $FeCl_2$ (10 mol %), 4-methylbenzoic acid **2a** (2 equiv) and $NaSO_2CF_3$ (2 equiv), the tube was then evacuated and back-filled with nitrogen (N_2) for 3 times. Subsequently, acetonitrile (2 mL) was added followed by 4-methoxystyrene **1a** (0.5 mmol) and DTBP (2 equiv). The mixture was stirred at 85 ℃ until complete consumption of starting materials as monitored by TLC and/or GC-MS analysis (about 12 h). After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product **4a**.

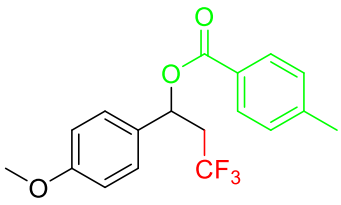
(b) General procedures for the trifluoromethylation-esterification (1 mmol)



To a Schlenk tube were added $FeCl_2$ (10 mol %), 4-methylbenzoic acid **2a** (2 equiv) and $NaSO_2CF_3$ (2 equiv), the tube was then evacuated and back-filled with nitrogen (N_2) for 3 times. Subsequently, acetonitrile (2 mL) was added followed by 4-methoxystyrene **1a** (1 mmol) and DTBP (2 equiv). The mixture was stirred at 85 ℃ (oil bath temperature) for the indicated time (about 24 h) until complete consumption of starting material as monitored by TLC and/or GC-MS analysis. After the reaction was finished, the reaction mixture was concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired product **4a** (77%, 260.5 mg).

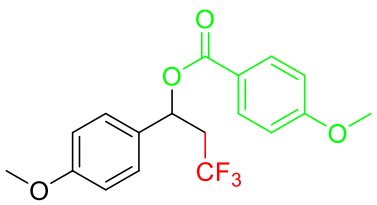
3. Characterization Data

3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 4-methylbenzoate (4a)



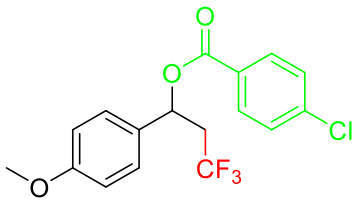
Following the general procedure, the title compound was obtained (147.0 mg, 87% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.27 (dd, J = 9.2, 4.0 Hz, 1H), 3.77 (s, 3H), 2.61 (ddd, J = 14.9, 10.3, 4.2 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.33, 159.88, 144.03, 130.92, 129.80, 129.18, 127.81, 127.16, 123.0 (q, J^{C-F} = 277.3 Hz), 114.25, 69.74 (q, J^{C-F} = 6.2 Hz), 55.29, 40.53 (q, J^{C-F} = 26.7 Hz), 21.67. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.80 (t, J = 10.2 Hz); **HRMS** (ESI, m/z) calcd for $C_{18}H_{17}F_3O_3$ $[M+H]^+$: 339.1131; found: 339.1130.

3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 4-methoxybenzoate (4b)



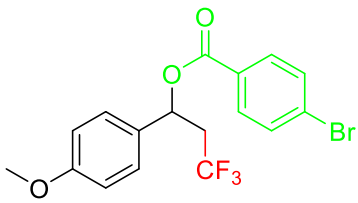
Following the general procedure, the title compound was obtained (152.2 mg, 86% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.01 (d, J = 8.9 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 6.90 (dd, J = 9.9, 8.9 Hz, 4H), 6.25 (dd, J = 9.3, 4.0 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 2.95 (dd, J = 25.0, 9.7 Hz, 1H), 2.62 (q, J = 14.6 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.99 (s), 163.63 (s), 159.81 (s), 131.80 (s), 130.97 (s), 127.78 (s), 125.15 (q, J^{C-F}= 278.5 Hz), 122.21 (s), 114.20 (s), 113.71 (s), 69.60 (q, J = 6.3 Hz), 55.46 (s), 55.29 (s), 40.50 (s) (q, J^{C-F} = 27.7Hz). **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.82 (t, J = 10.3 Hz); **HRMS** (ESI, m/z) calcd for $C_{18}H_{17}F_3O_4$ $[M+H]^+$: 355.3251; found: 355.3252.

3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 4-chlorobenzoate (4c)



Following the general procedure, the title compound was obtained (164.7 mg, 92% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.97 (d, J = 8.6 Hz, 2H), 7.38 (dd, J = 20.4, 8.6 Hz, 4H), 6.90 (d, J = 8.7 Hz, 2H), 6.26 (dd, J = 9.4, 3.8 Hz, 1H), 3.79 (s, 3H), 2.97 (dd, J = 25.1, 9.8 Hz, 1H), 2.62 (dd, J = 15.2, 6.4 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.44 (s), 159.99 (s), 139.78 (s), 131.13 (s), 130.48 (s), 128.84 (s), 128.29 (s), 127.86 (s), 125.91 (q, J^{C-F} = 288.6Hz), 114.30 (s), 70.24 (q, J^{C-F} =2.9 Hz), 55.33 (s), 40.42 (q, J^{C-F} = 27.7Hz). **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.87 (t, J = 10.0 Hz); **HRMS** (ESI, m/z) calcd for $C_{17}H_{14}ClF_3O_3$ $[M+H]^+$: 359.0582; found: 359.0584.

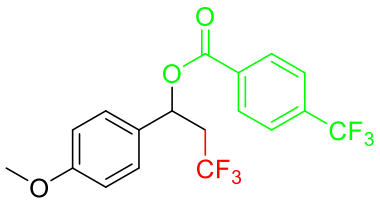
3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 4-bromobenzoate (4d)



Following the general procedure, the title compound was obtained (170.9 mg, 85% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 (d, J = 8.7 Hz, 4H), 7.28 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 6.18 (dd, J = 9.4, 3.8 Hz, 1H), 3.71 (s, 3H), 2.89 (dd, J = 25.1, 9.8 Hz, 1H), 2.54 (dd, J = 15.2, 6.4 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.24 (s), 159.79 (s), 130.93 (s), 130.28 (s), 128.65 (s), 128.10 (s), 127.66 (s), 126.41 (q, J^{C-F}= 285.92 Hz), 125.39 (s), 114.10 (s), 70.04 (q, J^{C-F} = 2.9 Hz), 55.14 (s), 40.22 (q, J^{C-F} = 28.9 Hz). **^{19}F NMR (470**

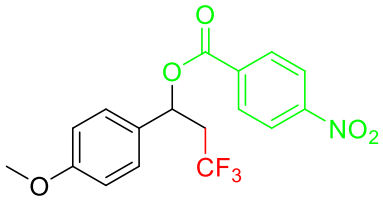
MHz, $CDCl_3$) δ -62.79 (t, J = 10.4 Hz); **HRMS** (ESI, m/z) calcd for $C_{17}H_{14}BrF_3O_3$ $[M+H]^+$: 403.0077; found: 403.0078.

3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 4-(trifluoromethyl)benzoate (4e)



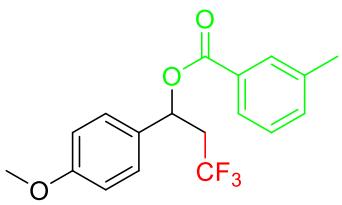
Following the general procedure, the title compound was obtained (178.4 mg, 91% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.98 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 6.27 (dd, J = 9.4, 3.8 Hz, 1H), 3.79 (s, 3H), 3.00 – 2.93 (m, 1H), 2.63 (dd, J = 25.6, 3.9 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.44 (s), 159.99 (s), 136.84 (q, J^{C-F} = 248.2 Hz), 131.13 (s), 130.48 (s), 128.95 (q, J^{C-F} = 287.8 Hz), 128.84 (s), 128.29 (s), 127.86 (s), 125.99 (q, J^{C-F} = 288.6 Hz), 125.59 (s), 114.30 (s), 70.24 (q, J = 2.9 Hz), 55.33 (s), 40.42 (q, J^{C-F} = 28.9 Hz). **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.91 (t, J = 10.1 Hz), -68.61 (d, J = 9.3 Hz); **HRMS** (ESI, m/z) calcd for $C_{18}H_{14}F_6O_3$ $[M+H]^+$: 393.0845; found: 393.0847.

3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 4-nitrobenzoate (4f)



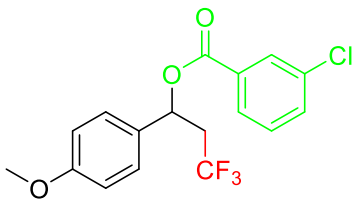
Following the general procedure, the title compound was obtained (162.4 mg, 88% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.28 (d, J = 8.9 Hz, 2H), 8.21 (d, J = 8.9 Hz, 2H), 7.39 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 6.31 (dd, J = 9.7, 3.7 Hz, 1H), 3.80 (s, 3H), 3.03 (dd, J = 25.2, 9.8 Hz, 1H), 2.67 (dd, J = 25.7, 3.8 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.45 (s), 160.17 (s), 150.69 (s), 135.20 (s), 130.85 (s), 129.91 (s), 127.98 (s), 126.49 (q, J^{C-F} = 284.1 Hz), 123.64 (s), 114.38 (s), 71.01 (q, J^{C-F} = 3.1 Hz), 55.35 (s), 40.24 (q, J^{C-F} = 27.7 Hz); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.93 (t, J = 10.1 Hz); **HRMS** (ESI, m/z) calcd for $C_{17}H_{14}F_3NO_5$ $[M+H]^+$: 370.0823; found: 370.0824.

3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 3-methylbenzoate (4g)



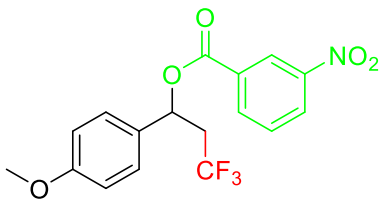
Following the general procedure, the title compound was obtained (157.2 mg, 93% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 (d, J = 5.0 Hz, 2H), 7.36 (t, J = 7.3 Hz, 3H), 7.31 (t, J = 7.8 Hz, 1H), 6.89 (d, J = 8.8 Hz, 2H), 6.28 (dd, J = 9.3, 4.0 Hz, 1H), 3.77 (s, 3H), 2.97 (dd, J = 25.0, 9.7 Hz, 1H), 2.62 (dd, J = 25.7, 4.1 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.46 (s), 159.88 (s), 138.29 (s), 134.06 (s), 130.83 (s), 130.27 (s), 129.79 (s), 128.38 (s), 127.86 (s), 126.91 (s), 125.96 (q, J^{C-F} = 288.5 Hz), 114.24 (s), 69.86 (q, J^{C-F} = 3.1 Hz), 55.32 (s), 40.49 (q, J^{C-F} = 27.7 Hz), 21.32 (s); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.81 (t, J = 10.2 Hz); **HRMS** (ESI, m/z) calcd for $C_{18}H_{17}F_3O_3$ $[M+H]^+$: 339.1131; found: 339.1130.

3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 3-chlorobenzoate (4h)



Following the general procedure, the title compound was obtained (162.9 mg, 91% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.05 - 7.98 (m, 2H), 7.92 (d, J = 7.9 Hz, 2H), 7.50 (dd, J = 8.0, 1.0 Hz, 2H), 7.35 (dd, J = 16.5, 8.4 Hz, 6H), 6.89 (d, J = 8.8 Hz, 4H), 6.29 (dd, J = 9.5, 3.8 Hz, 2H), 3.76 (s, 6H), 2.99 (dd, J = 25.1, 9.8 Hz, 2H), 2.66 (d, J = 4.0 Hz, 1H), 2.61 (d, J = 4.0 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.08 (s), 160.05 (s), 134.62 (s), 133.30 (s), 131.61 (s), 130.37 (s), 129.84 (s), 129.73 (s), 127.92 (d, J = 3.1 Hz), 125.34 (q, J^{C-F} = 278.5 Hz), 114.31 (s), 70.41 (q, J^{C-F} = 2.5 Hz), 55.28 (s), 40.32 (q, J^{C-F} = 27.7 Hz); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.85 (t, J = 10.2 Hz); **HRMS** (ESI, m/z) calcd for $C_{17}H_{14}ClF_3O_3$ $[M+H]^+$: 359.0583; found: 359.0584.

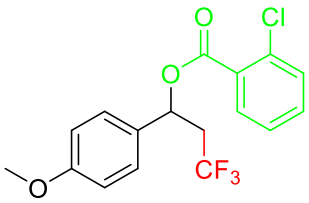
3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 3-nitrobenzoate (4i)



Following the general procedure, the title compound was obtained (151.3 mg, 82% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.85 (s, 1H), 8.42 (dd, J = 8.2, 1.2 Hz, 1H), 8.36 (d, J = 7.8 Hz, 1H), 7.66 (t, J = 8.0 Hz, 1H), 7.40 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 6.33 (dd, J = 9.6, 3.7 Hz, 1H), 3.80 (s, 3H), 3.05 (dd, J = 25.2, 9.8 Hz, 1H), 2.67 (dd, J = 25.6, 3.9 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.22 (s), 160.18 (s), 148.34 (s), 135.41 (s), 131.61 (s),

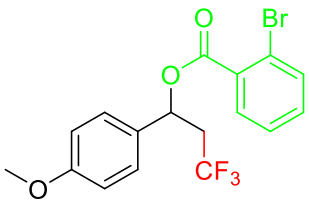
129.92 (s), 129.76 (s), 128.02 (s), 127.70 (s), 126.49 (q, J^{C-F} = 290.3 Hz), 124.62 (s), 114.38 (s), 70.98 (q, J = 3.2 Hz), 55.35 (s), 40.22 (q, J^{C-F} = 28.9 Hz); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -64.00 (t, J = 10.2 Hz); **HRMS** (ESI, m/z) calcd for $C_{17}H_{14}F_3NO_5$ $[M+H]^+$: 370.0823; found: 370.0824.

3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 2-chlorobenzoate (4j)



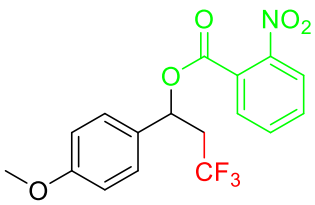
Following the general procedure, the title compound was obtained (157.5 mg, 88% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.83 (dd, J = 7.8, 1.2 Hz, 1H), 7.40 (dd, J = 16.4, 8.2 Hz, 4H), 7.29 (t, J = 7.4 Hz, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.31 (dd, J = 9.0, 4.2 Hz, 1H), 3.78 (s, 3H), 2.98 (dd, J = 24.9, 9.6 Hz, 1H), 2.64 (dd, J = 25.6, 4.4 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.12 (s), 160.00 (s), 133.99 (s), 132.85 (s), 131.52 (s), 131.20 (s), 130.30 (s), 129.51 (s), 128.09 (s), 126.66 (s), 125.30 (q, J^{C-F} = 277.2 Hz), 114.24 (s), 70.53 (q, J^{C-F} = 3.2 Hz), 55.26 (s), 40.33 (q, J^{C-F} = 27.7 Hz); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.83 (t, J = 10.2 Hz); **HRMS** (ESI, m/z) calcd for $C_{17}H_{14}ClF_3O_3$ $[M+H]^+$: 359.0582; found: 359.0584.

3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 2-bromobenzoate (4k)



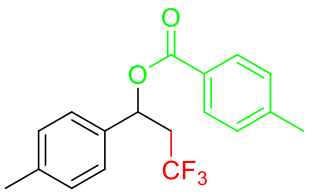
Following the general procedure, the title compound was obtained (170.9 mg, 85% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.79 (dd, J = 7.6, 1.8 Hz, 2H), 7.61 (d, J = 7.8 Hz, 2H), 7.42 – 7.19 (m, 10H), 6.90 (d, J = 8.7 Hz, 5H), 6.31 (dd, J = 8.9, 4.3 Hz, 2H), 3.77 (s, 7H), 2.98 (dd, J = 24.8, 9.6 Hz, 2H), 2.67 (d, J = 4.4 Hz, 1H), 2.62 (d, J = 4.5 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.59 (s), 160.03 (s), 134.50 (s), 132.87 (s), 131.54 (s), 131.43 (s), 130.21 (s), 128.17 (s), 127.27 (s), 125.44 (q, J^{C-F} = 278.4 Hz), 121.89 (s), 114.25 (s), 70.66 (q, J^{C-F} = 3.2 Hz), 55.28 (s), 40.27 (q, J^{C-F} = 27.7 Hz); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.74 (t, J = 10.2 Hz); **HRMS** (ESI, m/z) calcd for $C_{17}H_{14}BrF_3O_3$ $[M+H]^+$: 403.0077; found: 403.0078.

3,3,3-trifluoro-1-(4-methoxyphenyl)propyl 2-nitrobenzoate (4l)



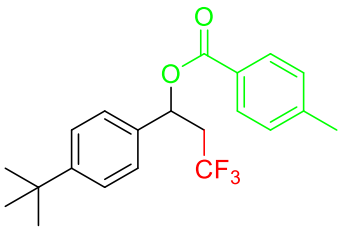
Following the general procedure, the title compound was obtained (166.1 mg, 90% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 (d, J = 7.7 Hz, 1H), 7.69 (d, J = 7.4 Hz, 1H), 7.62 (dd, J = 17.6, 7.1 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 6.28 (dd, J = 8.4, 5.0 Hz, 1H), 3.78 (s, 3H), 2.95 (dd, J = 25.0, 8.9 Hz, 1H), 2.64 (dd, J = 25.6, 4.9 Hz, 1H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 163.92 (s), 160.19 (s), 148.15 (s), 132.95 (s), 132.13 (s), 129.91 (s), 129.37 (s), 128.28 (s), 126.92 (s), 126.66 (q, J^{C-F} = 278.5 Hz), 123.90 (s), 114.26 (s), 71.60 (q, J^{C-F} = 3.2 Hz), 55.27 (s), 39.80 (q, J^{C-F} = 29.0 Hz); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.73 (t, J = 10.0 Hz); **HRMS** (ESI, m/z) calcd for $C_{17}H_{14}F_3NO_5$ $[M+H]^+$: 370.0823; found: 370.0824.

3,3,3-trifluoro-1-(p-tolyl)propyl 4-methylbenzoate (4m)



Following the general procedure, the title compound was obtained (135.2 mg, 84% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 7.9 Hz, 2H), 6.28 (dd, J = 9.4, 3.8 Hz, 1H), 2.94 (dd, J = 25.1, 9.8 Hz, 1H), 2.61 (dd, J = 25.7, 3.9 Hz, 1H), 2.38 (s, 3H), 2.31 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.32 (s), 144.05 (s), 138.62 (s), 135.94 (s), 129.83 (s), 129.58 (s), 129.20 (s), 128.95 (s), 126.27 (s), 126.24 (q, J^{C-F} = 285.1 Hz), 69.96 (q, J^{C-F} = 3.2 Hz), 40.63 (q, J^{C-F} = 29.0 Hz), 21.70 (s), 21.20 (s); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.80 (t, J = 10.2 Hz); **HRMS** (ESI, m/z) calcd for $C_{18}H_{17}F_3O_2$ $[M+H]^+$: 323.1181; found: 323.1181.

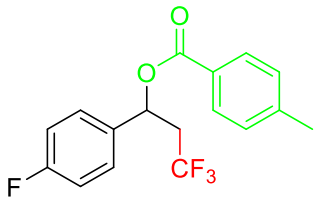
1-(4-(tert-butyl)phenyl)-3,3,3-trifluoropropyl 4-methylbenzoate (4n)



Following the general procedure, the title compound was obtained (149.2 mg, 82% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.04 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 7.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 6.30 (dd, J = 9.0, 4.3 Hz, 1H), 3.80 (s, 3H), 2.98 (dd, J = 24.8, 9.6 Hz, 1H), 2.64 (dd, J = 25.6, 4.4 Hz, 1H), 2.45 (s, 3H), 2.04 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.14 (s), 162.59 (s), 159.99 (s), 145.60 (s), 130.67 (s), 130.31 (s), 129.61 (s), 128.09 (s),124.90 (q, J^{C-F} = 274.3 Hz), 114.25 (s), 70.54 (q,

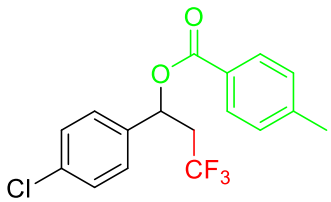
J^{C-F} = 3.0 Hz), 40.38 (q, J^{C-F} = 27.7 Hz), 31.54 (s), 21.07 (s), 14.23 (s); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.84 (t, J = 10.2 Hz); **HRMS** (ESI, m/z) calcd for $C_{21}H_{23}F_3O_2$ $[M+H]^+$: 365.1649; found: 365.1650.

3,3,3-trifluoro-1-(4-fluorophenyl)propyl 4-methylbenzoate (4o)



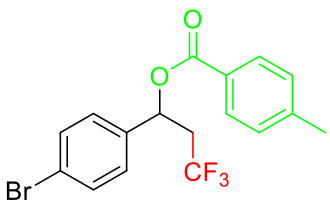
Following the general procedure, the title compound was obtained (97.8 mg, 60% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 6.18 (dd, J = 9.2, 4.0 Hz, 1H), 2.86 (dd, J = 25.0, 9.8 Hz, 1H), 2.52 (dd, J = 25.5, 4.2 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.99 (s), 157.77 (d, J^{C-F} = 27.7 Hz), 143.69 (s), 130.59 (s), 129.46 (s), 128.85 (s), 127.48 (s), 126.83 (s), 124.84 (q, J^{C-F} = 280.2 Hz), 113.91 (s), 69.41 (q, J^{C-F} =3.1 Hz), 40.20 (q, J^{C-F} = 27.7 Hz), 21.34 (s); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.69 (t, J = 10.5 Hz), -113.56 (s); **HRMS** (ESI, m/z) calcd for $C_{17}H_{14}F_4O_2$ $[M+H]^+$: 327.0930; found: 327.0930.

1-(4-chlorophenyl)-3,3,3-trifluoropropyl 4-methylbenzoate (4p)



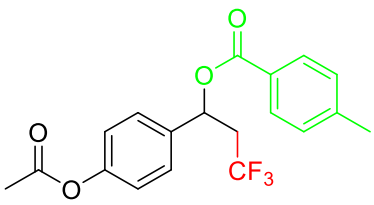
Following the general procedure, the title compound was obtained (111.2 mg, 65% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.90 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.19 (s, 2H), 7.07 (s, 2H), 5.50 (dd, J = 10.3, 3.0 Hz, 1H), 3.22 (dd, J = 11.0, 4.0 Hz, 1H), 2.80 (dd, J = 22.1, 7.0 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.32 (s), 144.05 (s), 138.62 (s), 135.94 (s), 129.83 (s), 129.58 (s), 129.20 (s), 128.95 (s), 126.27 (s), 126.24 (q, J^{C-F} = 281.4Hz) 69.96 (q, J^{C-F} = 3.2 Hz), 40.63 (q, J^{C-F} = 29.0 Hz), 21.70 (s); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.50 (t, J = 10.6 Hz); **HRMS** (ESI, m/z) calcd for $C_{17}H_{14}ClF_3O_2$ $[M+H]^+$: 343.0633; found: 343.0634.

1-(4-bromophenyl)-3,3,3-trifluoropropyl 4-methylbenzoate (4q)



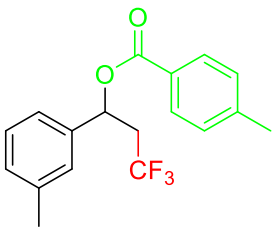
Following the general procedure, the title compound was obtained (121.6 mg, 63% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.28 (dd, J = 9.2, 4.0 Hz, 1H), 2.96 (dd, J = 25.0, 9.8 Hz, 1H), 2.62 (dd, J = 25.5, 4.2 Hz, 1H), 2.39 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.20 (s), 143.90 (s), 130.80 (s), 129.67 (s), 129.06 (s), 128.58 (s), 127.69 (s), 127.04 (s), 126.42 (s),125.05 (q, J^{C-F} = 280.2 Hz), 69.62 (q, J^{C-F} = 3.1 Hz), 40.41 (q, JC–F = 27.7 Hz), 21.55 (s); **^{19}F NMR (470 MHz, CDCl3)** δ -63.31 (t, J = 10.6 Hz); **HRMS** (ESI, m/z) calcd for $C_{17}H_{14}BrF_3O_2$ $[M+H]^+$: 387.0128; found: 387.0129.

1-(4-acetoxyphenyl)-3,3,3-trifluoropropyl 4-methylbenzoate (4r)



Following the general procedure, the title compound was obtained (106.1 mg, 58% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.46 (d, J = 8.5 Hz, 2H), 7.41 (s, 2H), 7.12-7.10 (m, 4H), 6.16 (dd, J = 16.1, 6.5 Hz, 1H), 3.00 - 2.95 (m, 1H), 2.89 - 2.83 (m, 1H), 2.30 (s, 6H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 165.53 (s), 165.22 (s), 143.95 (s), 138.52 (s), 135.84 (s), 129.73 (s), 129.48 (s), 129.10 (s), 128.85 (s), 127.21 (q, J^{C-F} = 285.2 Hz), 126.17 (s), 69.86 (q, J^{C-F} = 6.3, 3.2 Hz), 40.53 (q, J^{C-F} = 29.0 Hz), 21.60 (s), 21.10 (s); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.52 (t, J = 10.9 Hz); **HRMS** (ESI, m/z) calcd for $C_{19}H_{17}F_3O_4$ $[M+H]^+$: 367.1079; found: 367.1079.

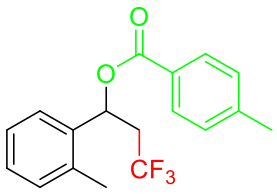
3,3,3-trifluoro-1-(m-tolyl)propyl 4-methylbenzoate (4s)



Following the general procedure, the title compound was obtained (114.3 mg, 71% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 (s, 2H), 7.82 (d, J = 8.2 Hz, 1H), 7.25 – 7.23 (m, 4H), 7.13 (d, J = 7.4 Hz, 1H), 6.27 (dd, J = 9.6, 3.6 Hz, 1H), 2.94 (d, J = 15.3 Hz, 1H), 2.59 (s, 1H), 2.41 (s, 3H), 2.35 (s, 3H); **^{13}C NMR (126 MHz $CDCl_3$)** δ 165.49 (s), 143.28 (s), 138.32 (s), 138.00 (s), 130.86 (s), 130.30 (s), 129.83 (s), 128.41 (s), 127.89 (s), 126.94 (s), 125.99 (q, J^{C-F} = 288.5 Hz), 114.27 (s), 69.89 (q, J^{C-F} = 3.1 Hz), 40.52 (q, J^{C-F} = 29.0 Hz), 22.81 (s),

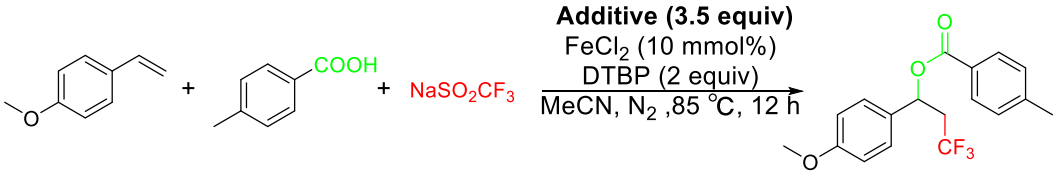
21.35 (s); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -63.91 (t, J = 10.2 Hz); **HRMS** (ESI, m/z) calcd for $C_{18}H_{17}F_3O_2$ $[M+H]^+$: 323.1180; found: 323.1181.

3,3,3-trifluoro-1-(o-tolyl)propyl 4-methylbenzoate (4t)

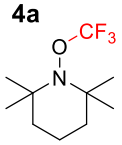


Following the general procedure, the title compound was obtained (127.2 mg, 79% yield, colorless oil). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 (s, 2H), 7.82 (d, J = 8.2 Hz, 1H), 7.25-7.23 (m, 4H), 7.13 (d, J = 7.4 Hz, 1H), 6.27 (dd, J = 9.6, 3.6 Hz, 1H), 2.94 (d, J = 15.3 Hz, 1H), 2.59 (s, 1H), 2.41 (s, 3H), 2.35 (s, 3H); **^{13}C NMR (126 MHz $CDCl_3$)** δ 165.25 (s), 144.07 (s), 137.45 (s), 134.76 (s), 130.84 (s), 129.79 (s), 129.22 (s), 128.44 (s), 128.06 (q, J^{C-F} = 273.1 Hz), 127.03 (s), 126.64 (s), 125.42 (s), 67.03 (q, J^{C-F} = 3.3 Hz), 40.09 (q, J^{C-F} = 29.0 Hz), 21.72 (s), 21.09 (s); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -64.30 (t, J = 10.3 Hz); **HRMS** (ESI, m/z) calcd for $C_{18}H_{17}F_3O_2$ $[M+H]^+$: 323.1180; found: 323.1182.

4. Control Experiments



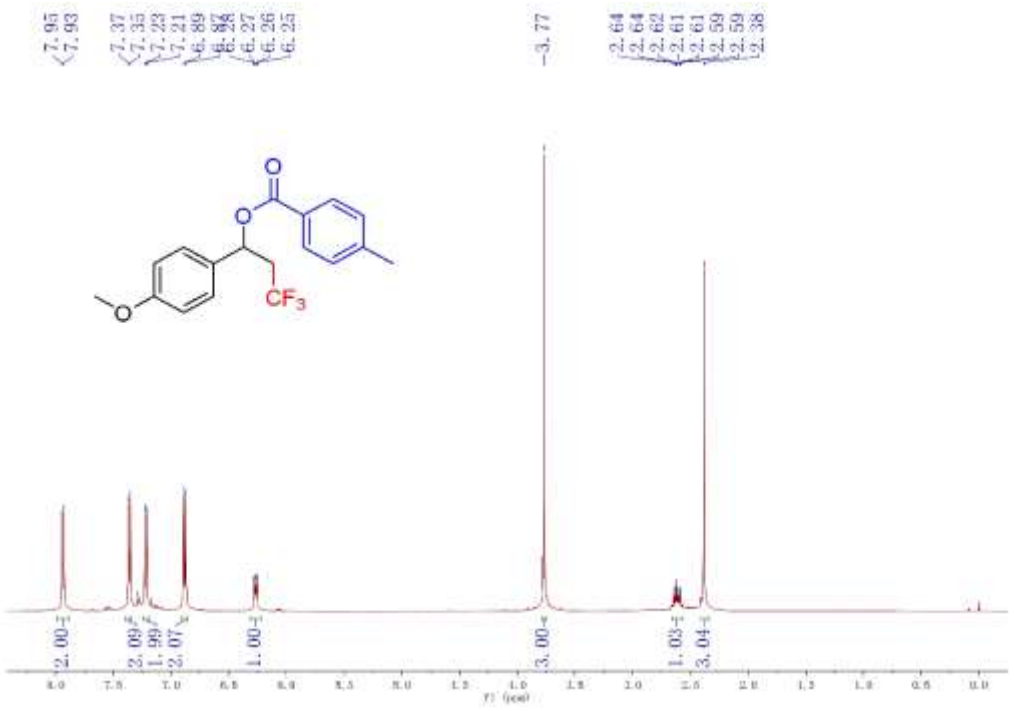
Additive	Yield of **4a**
TEMPO	trace
hydroquinone	trace
2,6-di-*tert*-butyl-4-methylphenol (BHT)	trace



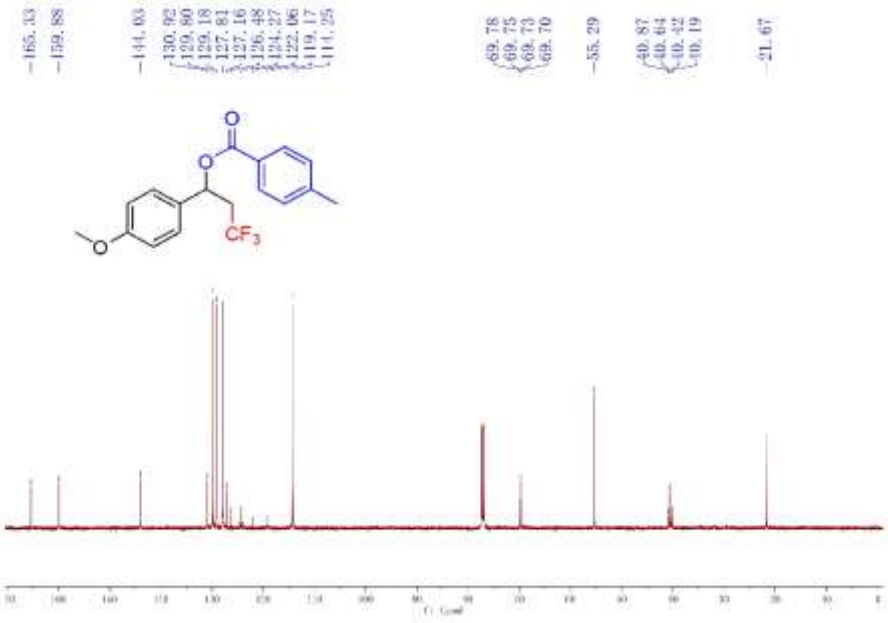
Detected by GC-MS analysis

To a Schlenk tube were added $FeCl_2$ (10 mol %), $NaSO_2CF_3$ (2 equiv) and TEMPO/BHT/hydroquinone (3.5 equiv), the tube was then evacuated and back-filled with nitrogen (N_2) for 3 times. Subsequently, acetonitrile (2 mL) was added followed by 4-methoxystyrene **1a** (0.5 mmol), 4-methylbenzoic acid **2a** (2 equiv) and DTBP (2 equiv). The mixture was stirred at 85 °C for 12h. No desired product **4a** was detected.

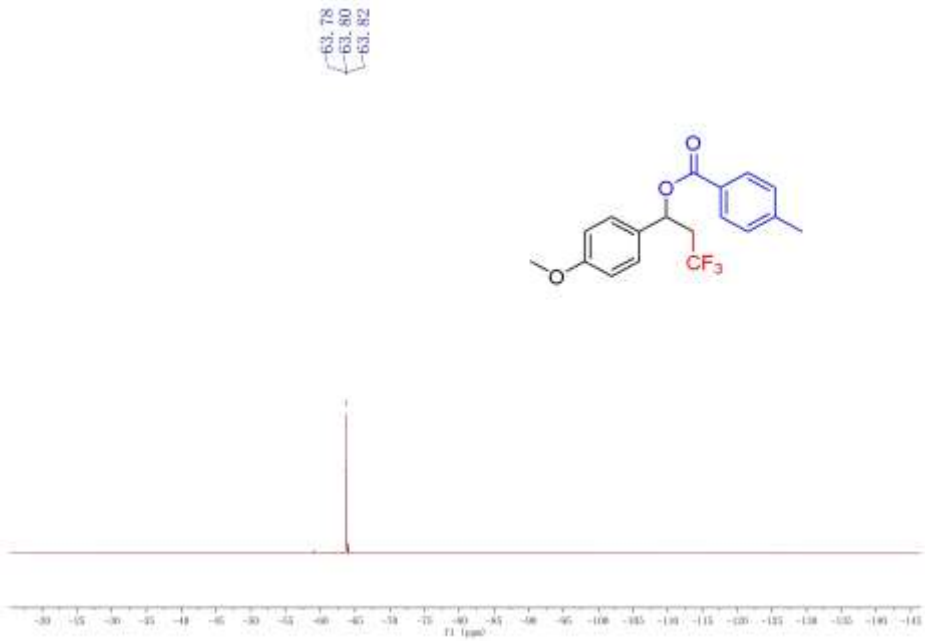
5. NMR Spectra



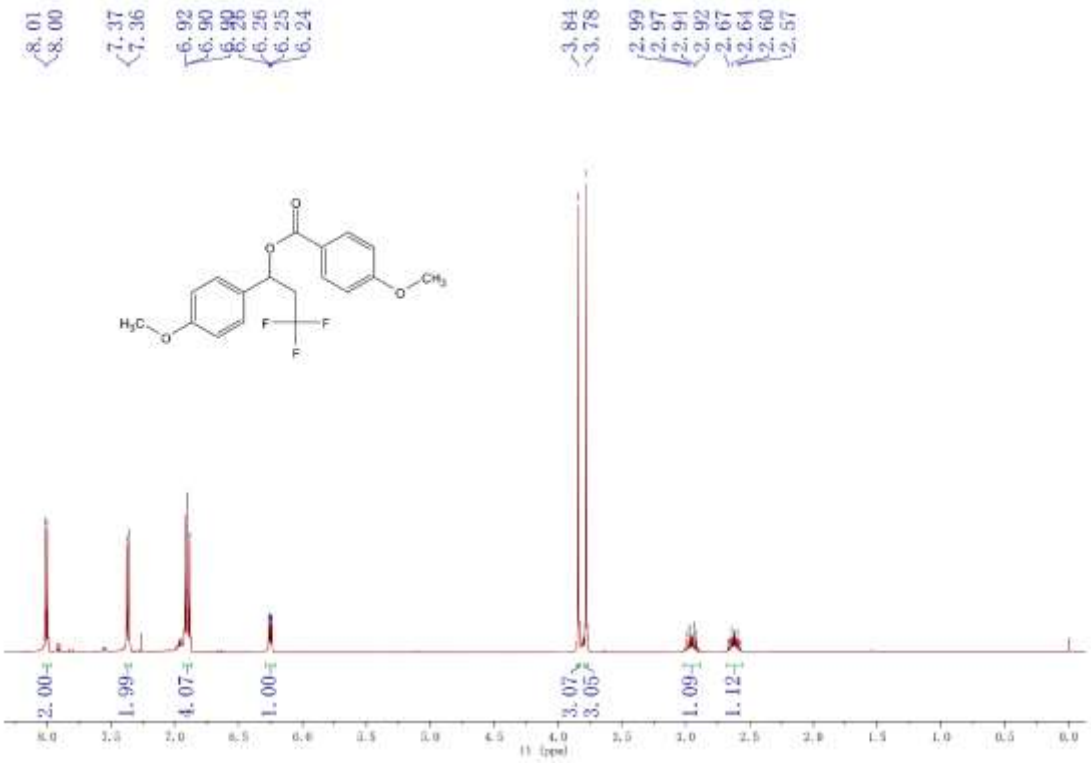
^{1}H NMR of 4a



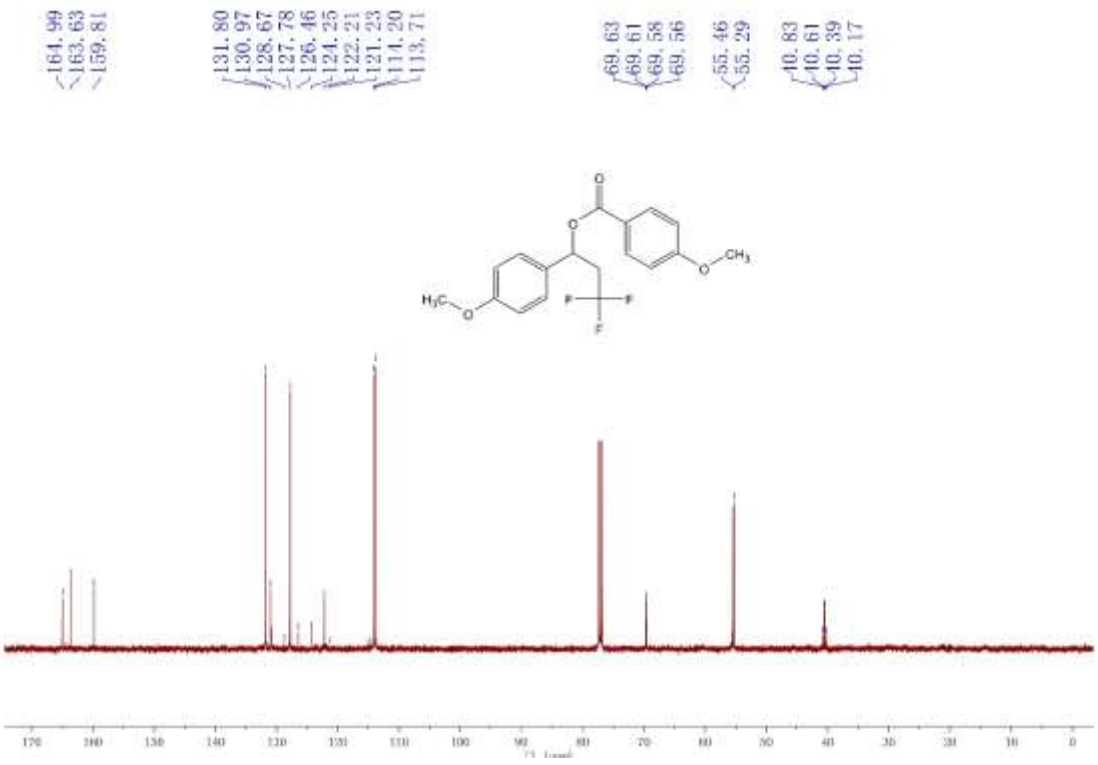
^{13}C NMR of 4a



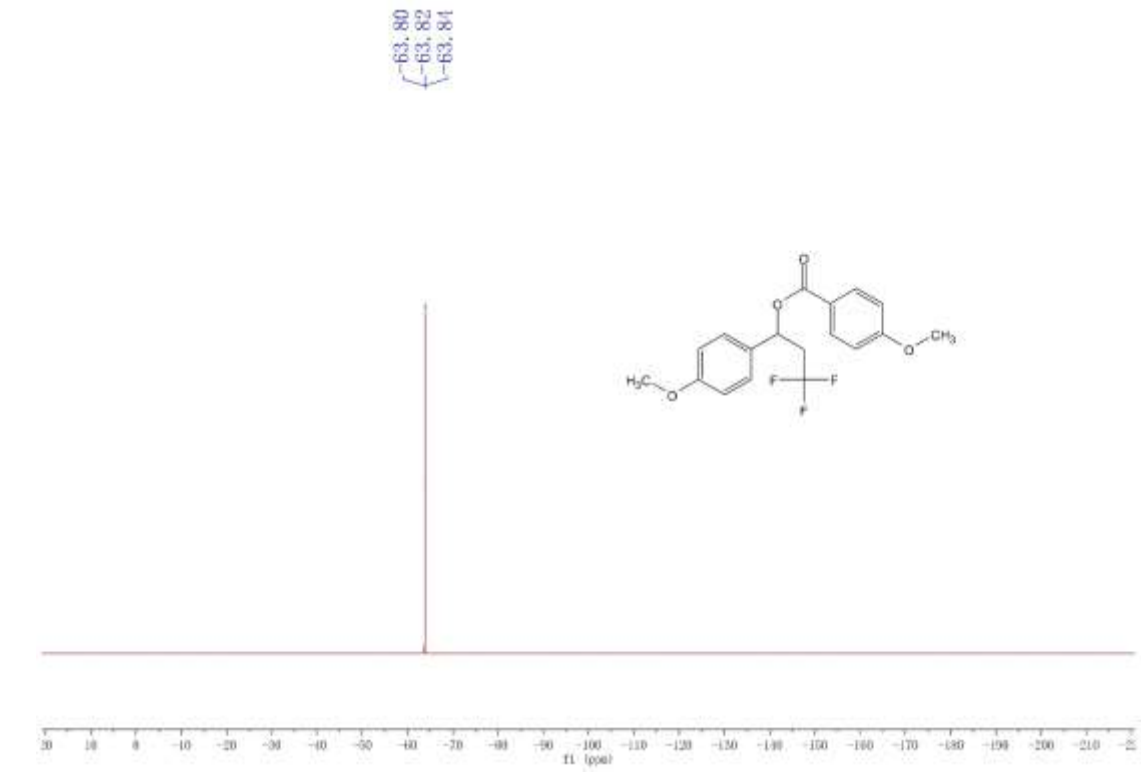
^{19}F NMR of 4a



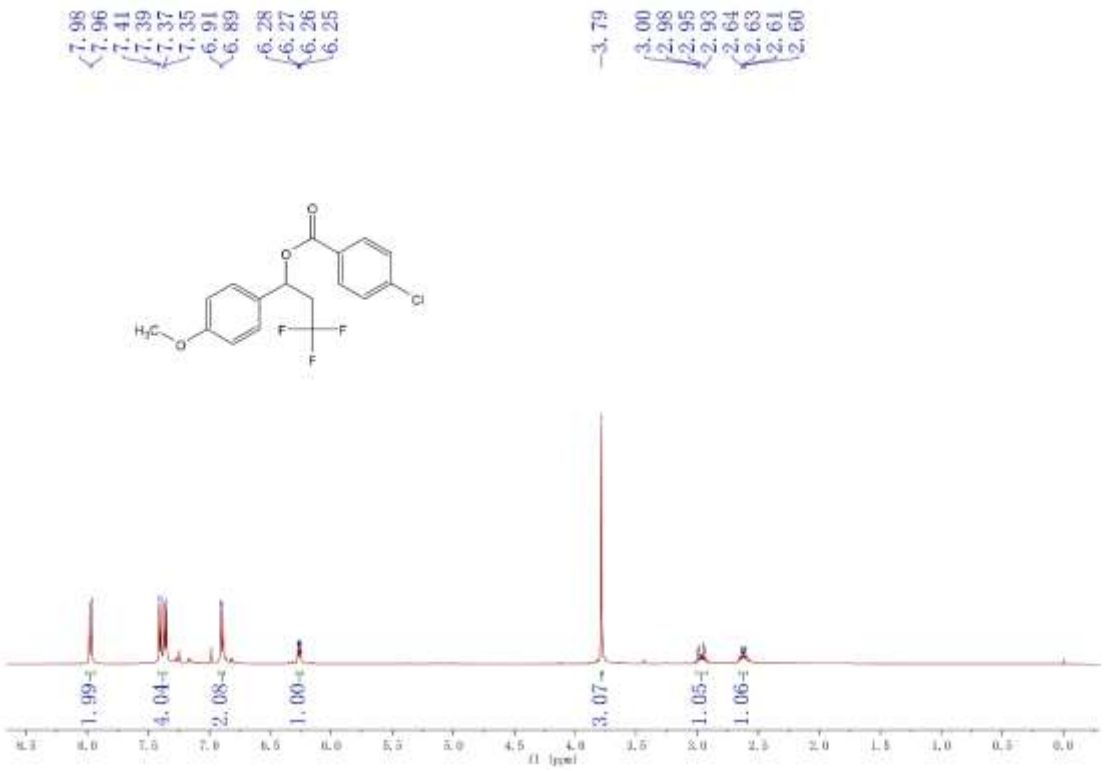
^{1}H NMR of 4b



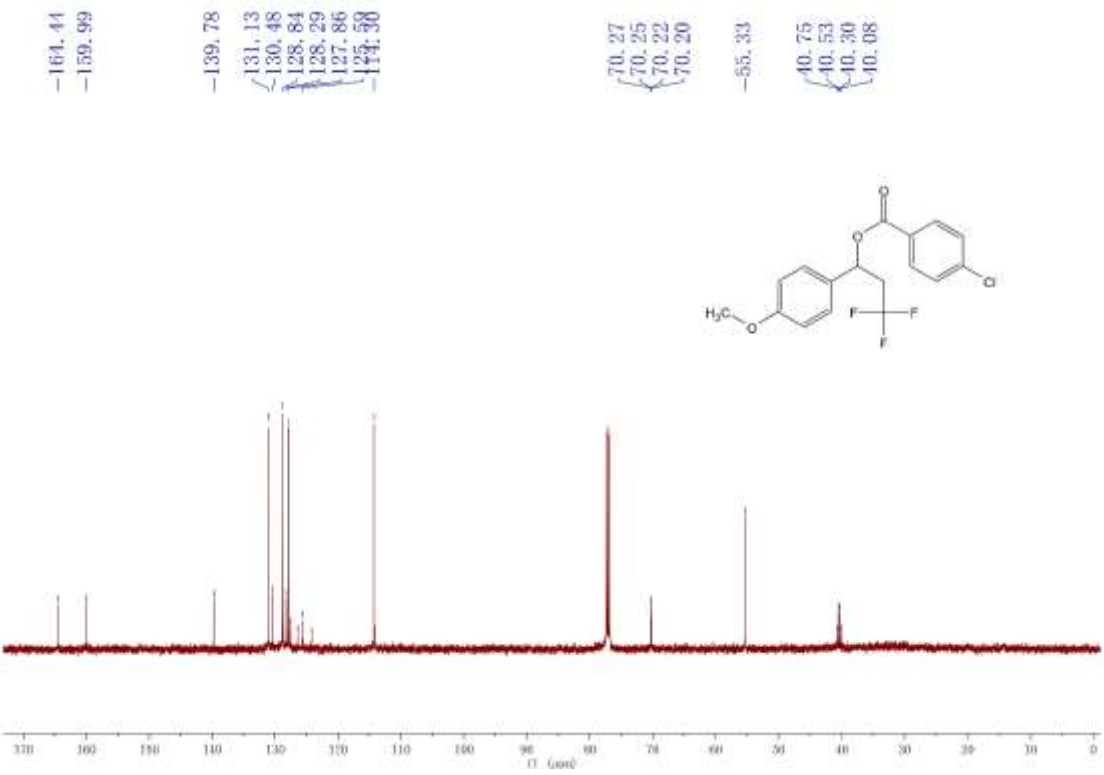
^{13}C NMR of 4b



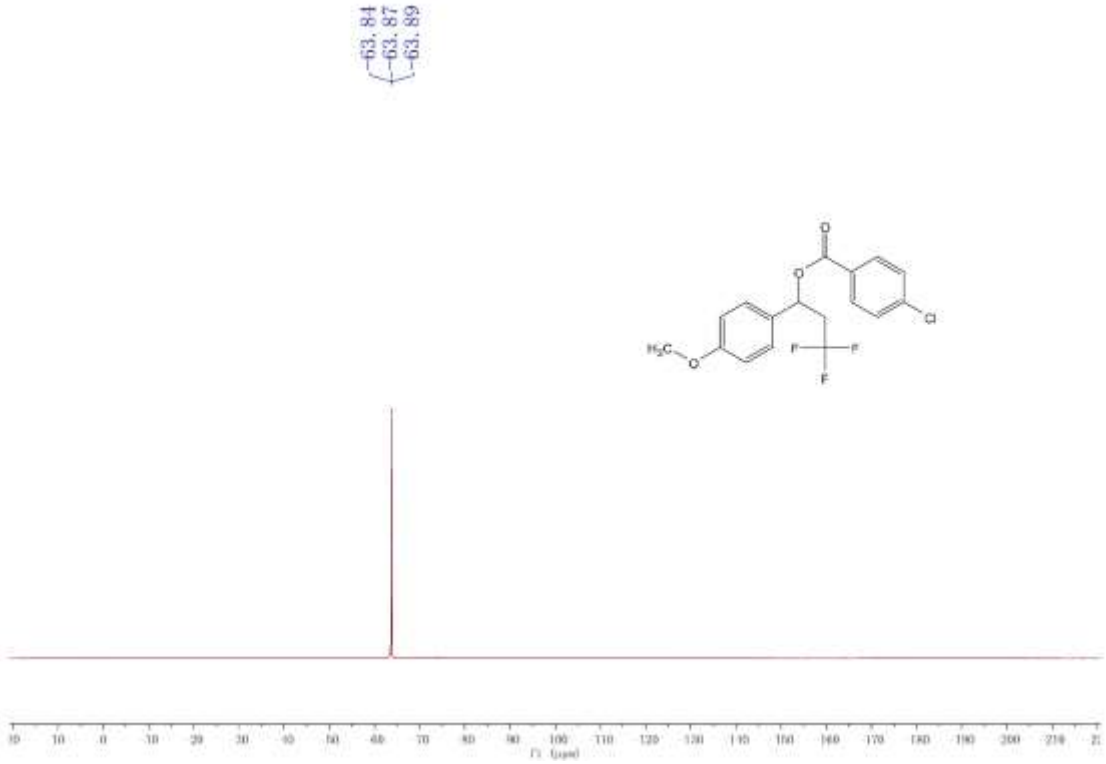
^{19}F NMR of 4b



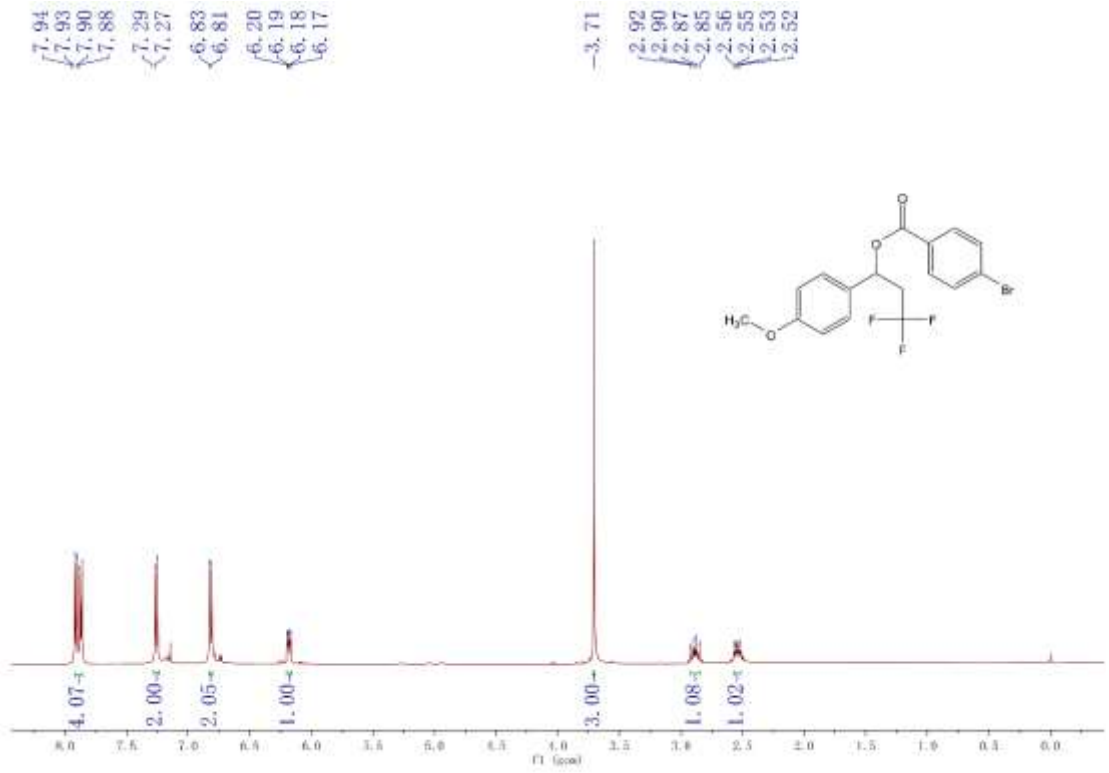
^{1}H NMR of 4c



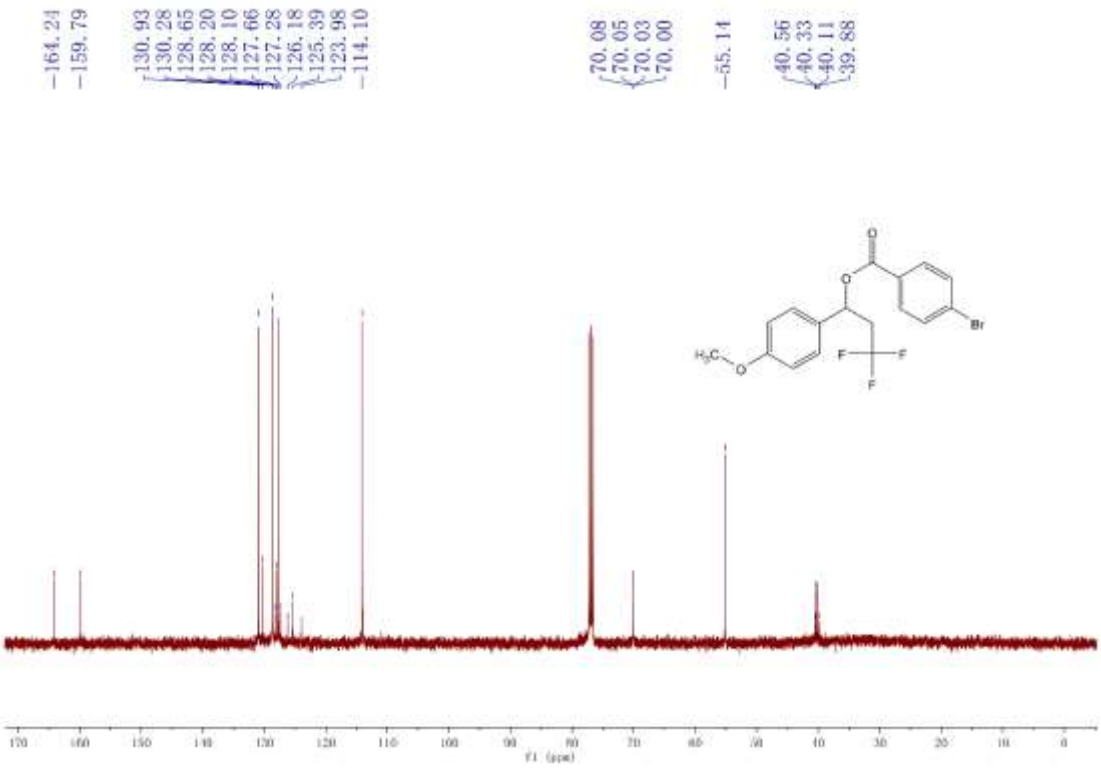
^{13}C NMR of 4c



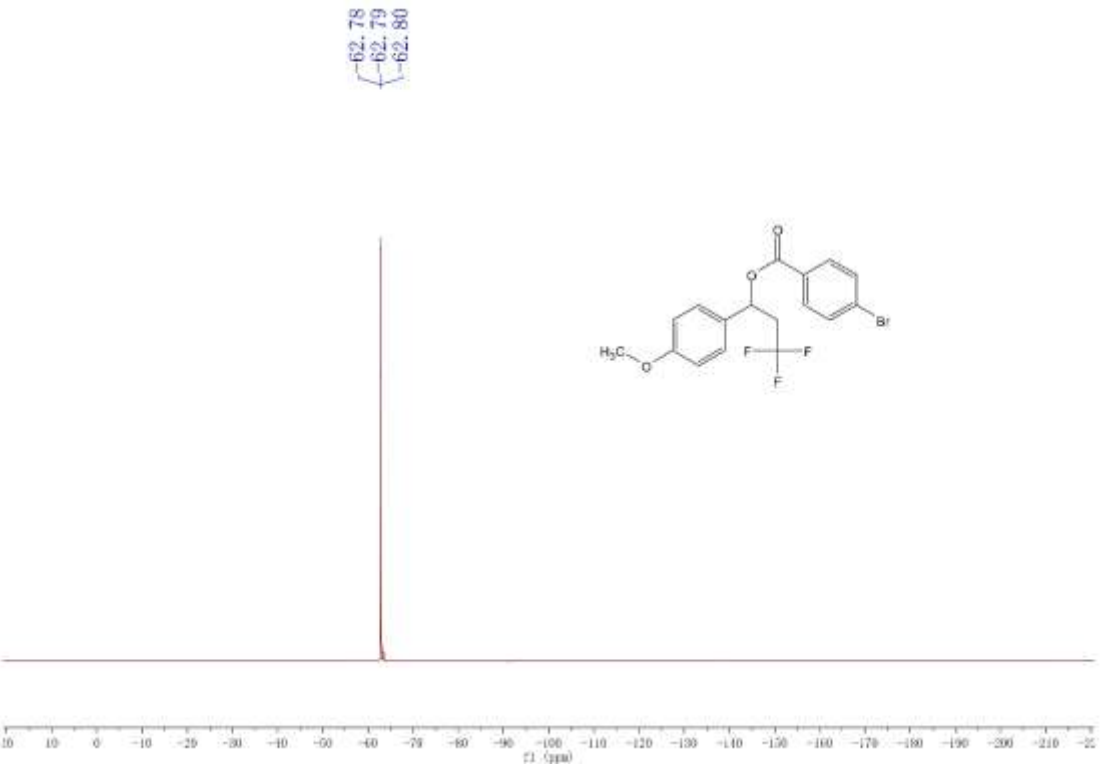
^{19}F NMR of 4c



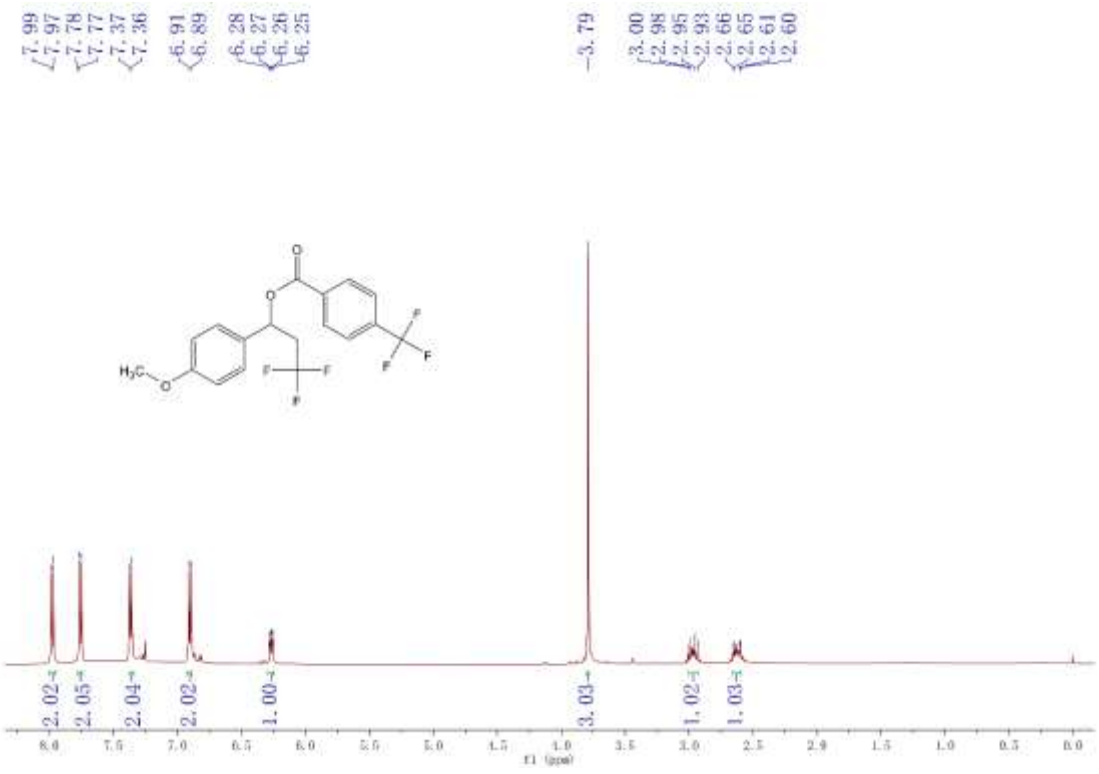
^{1}H NMR of 4d



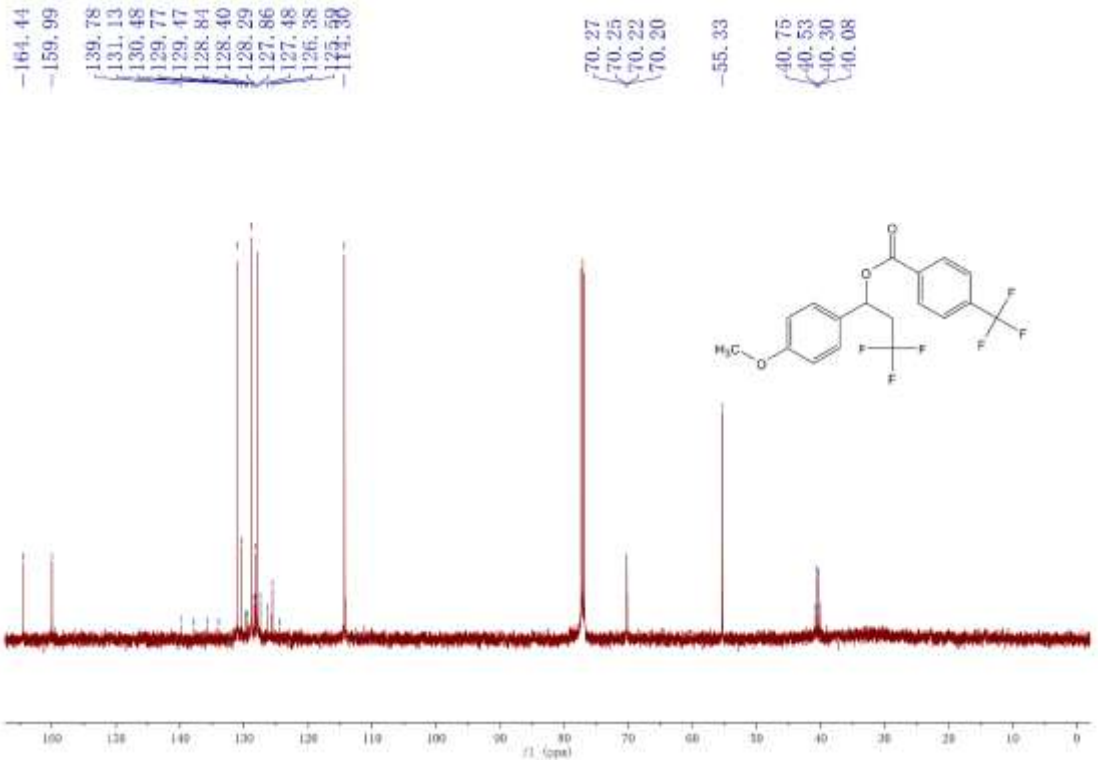
^{13}C NMR of 4d



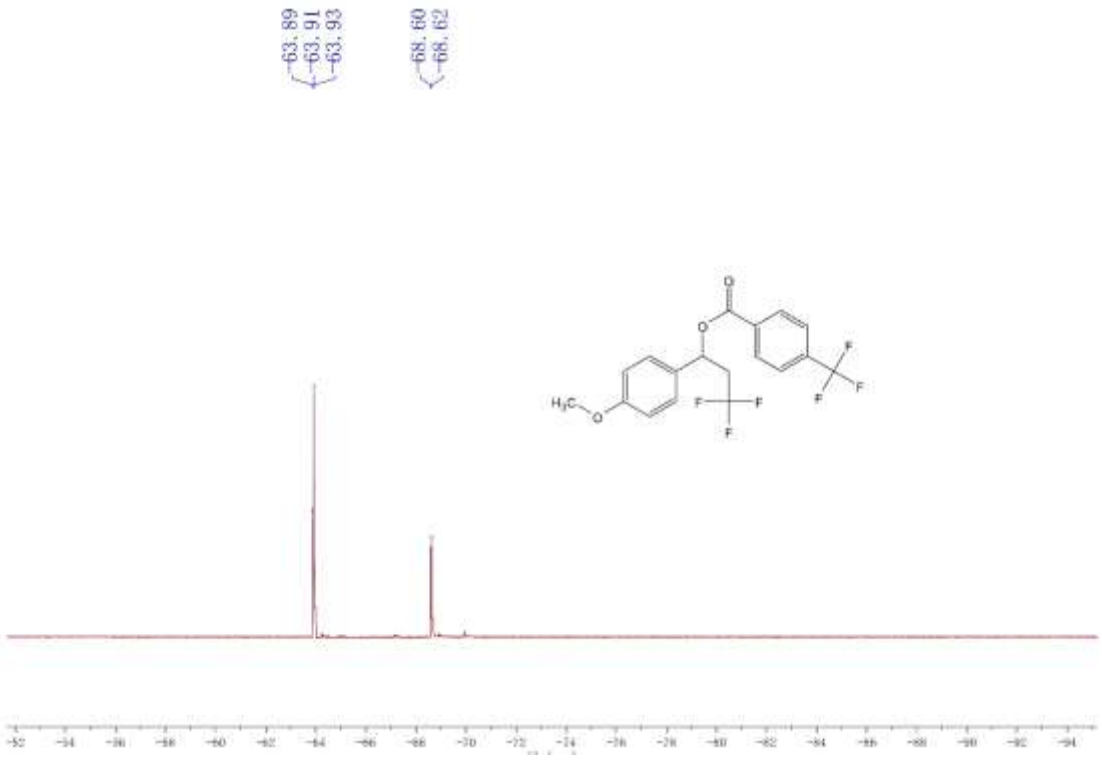
^{19}F NMR of 4d



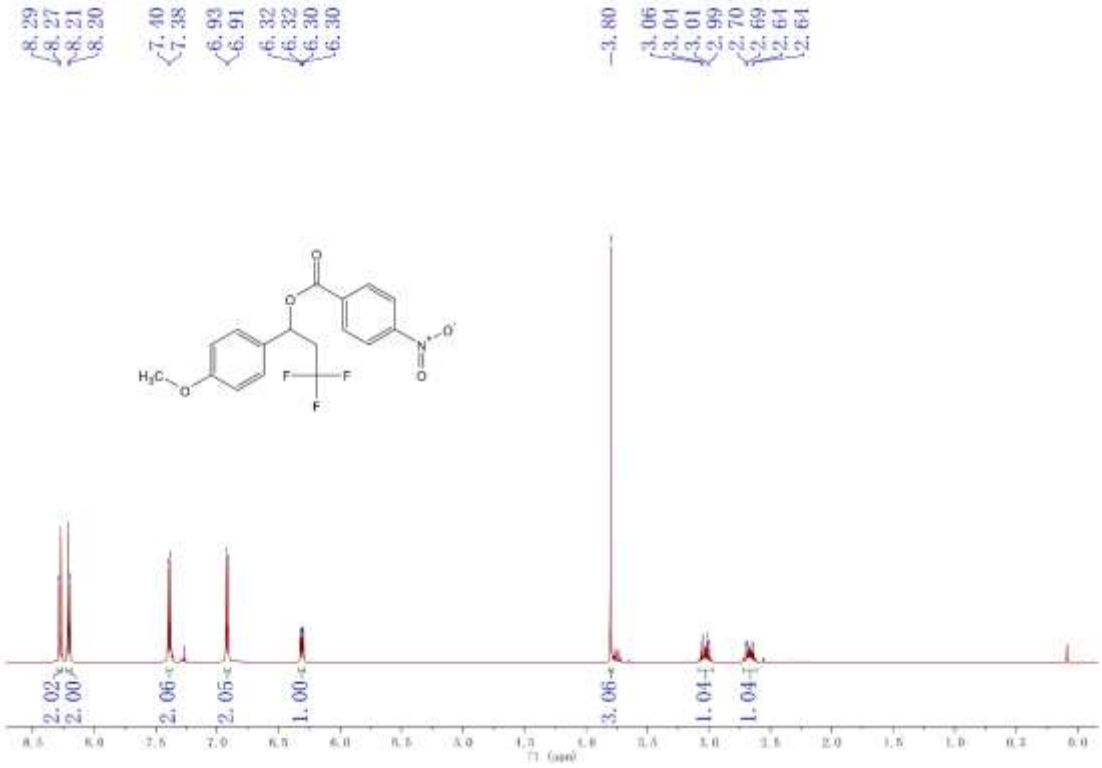
^{1}H NMR of 4e



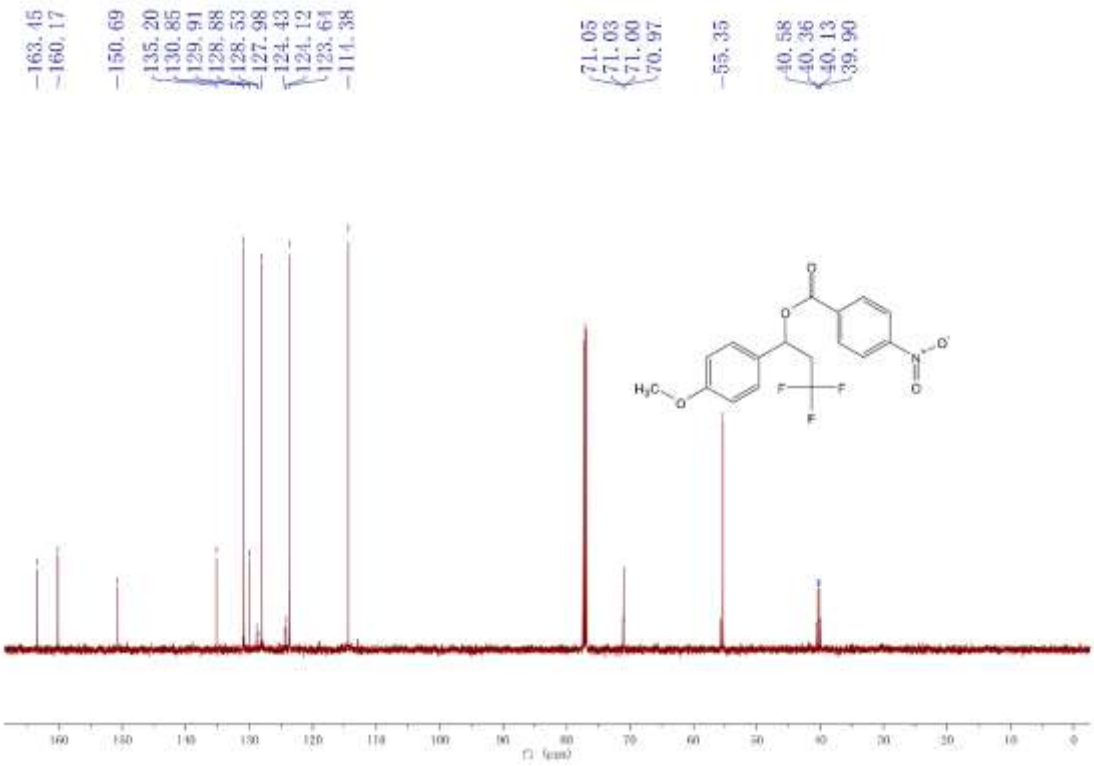
^{13}C NMR of 4e



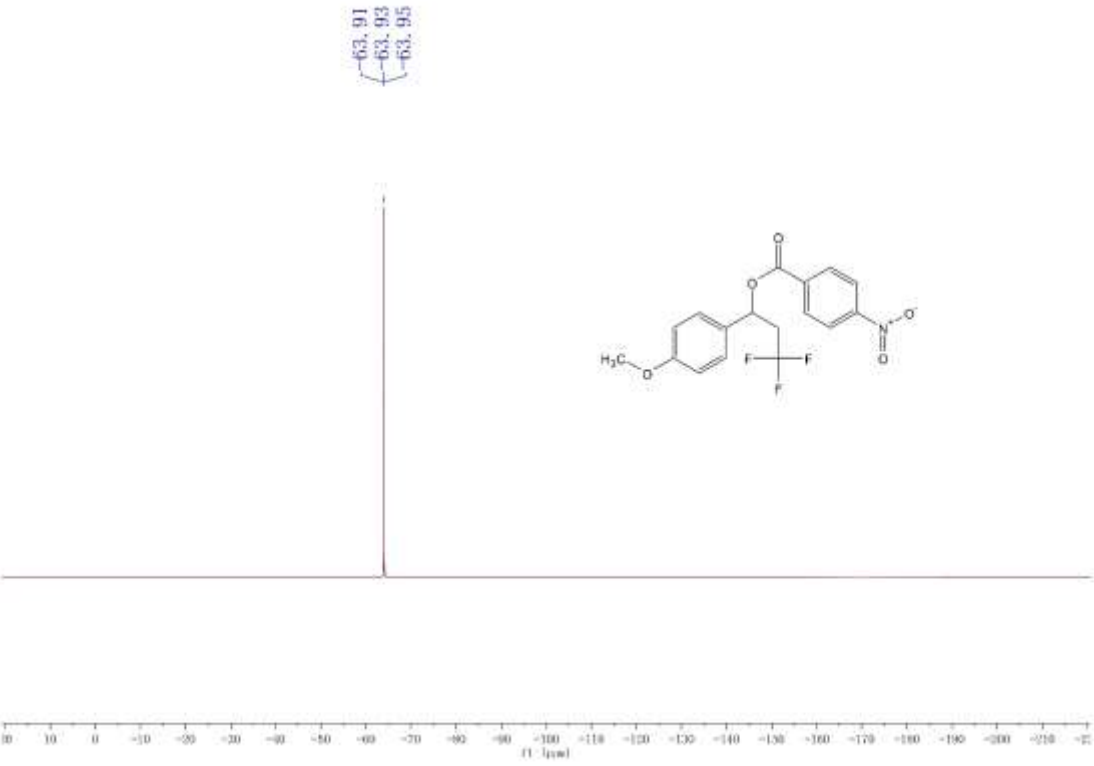
^{19}F NMR of 4e



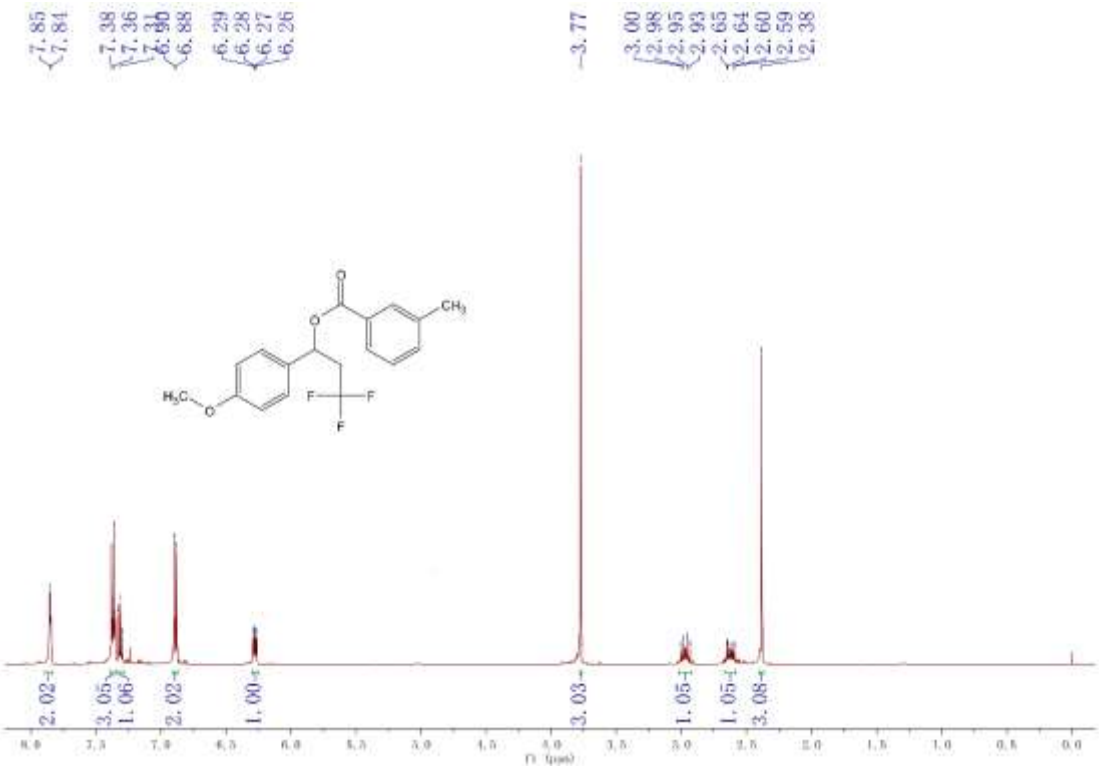
^{1}H NMR of 4f



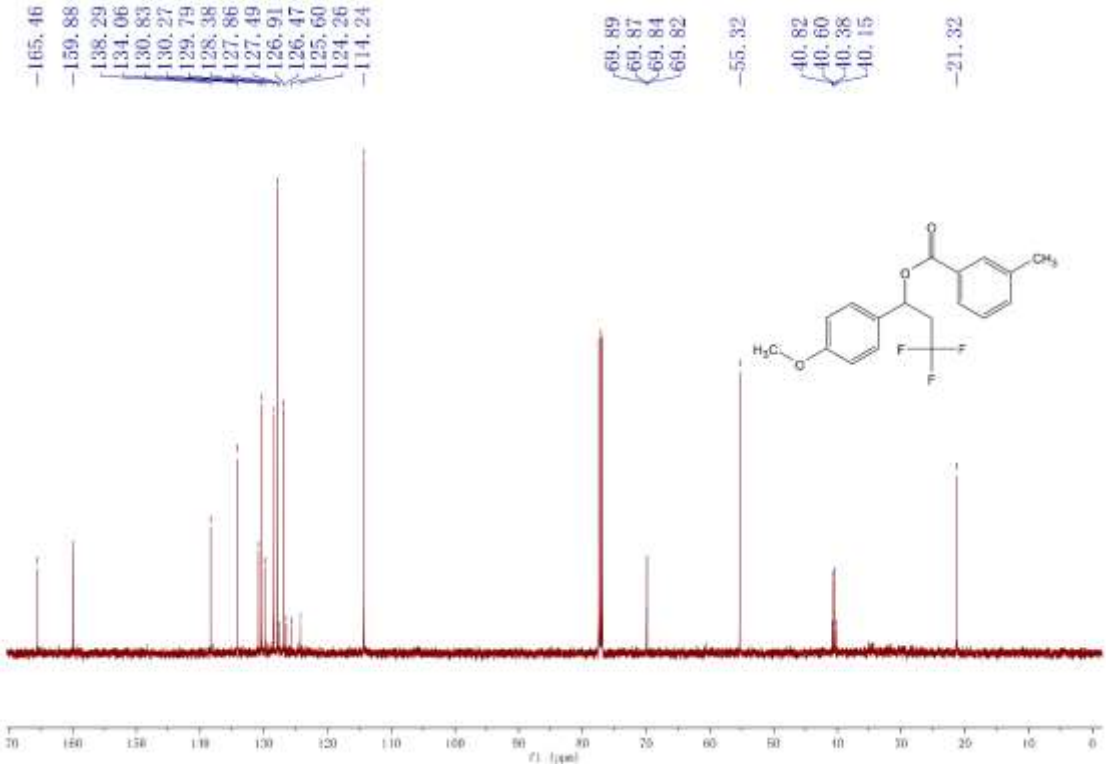
^{13}C NMR of 4f



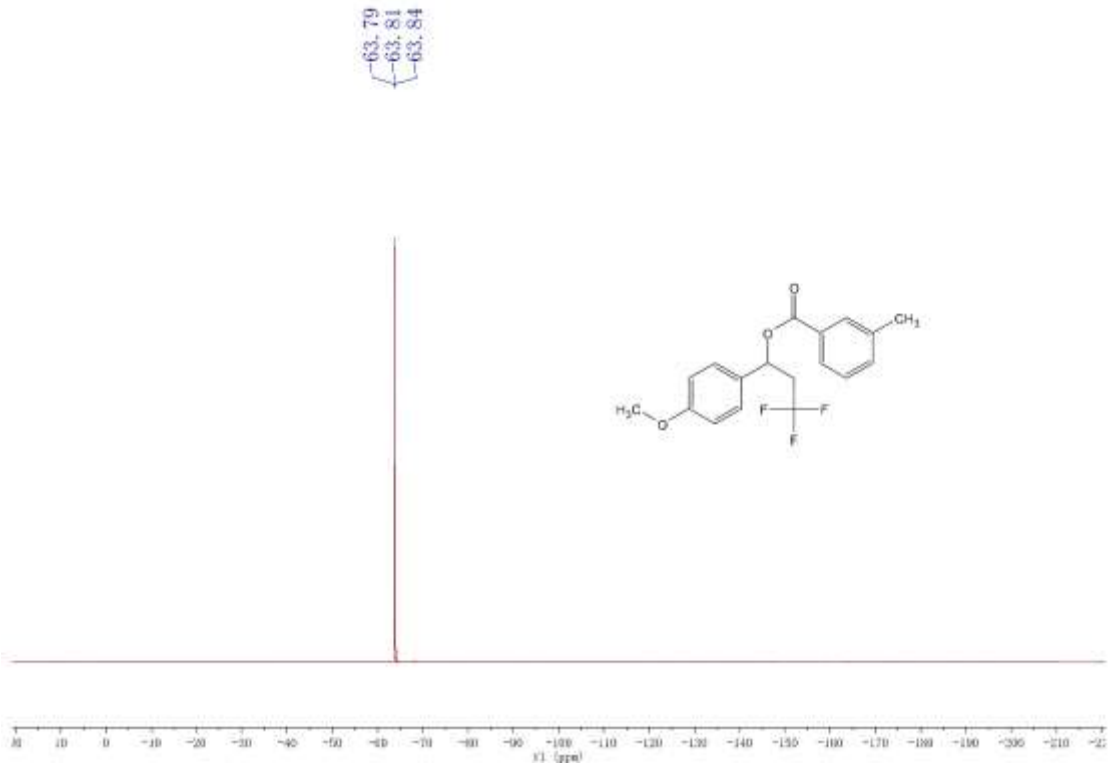
^{19}F NMR of 4f



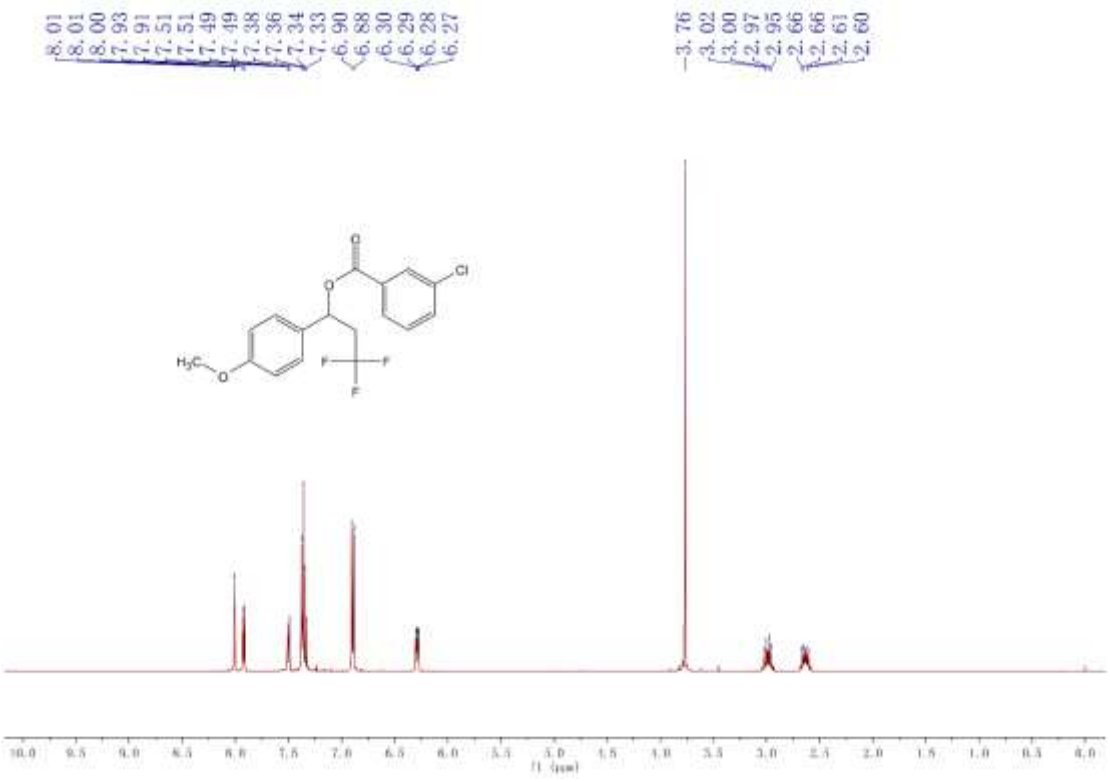
^{1}H NMR of 4g



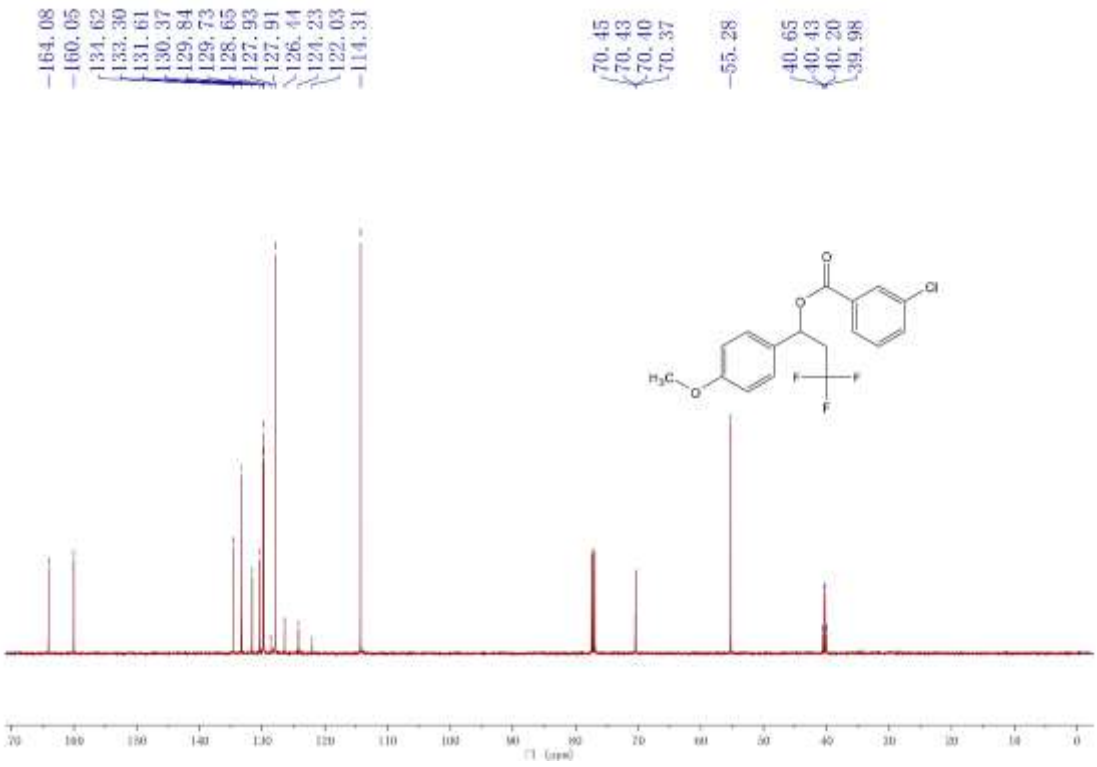
^{13}C NMR of 4g



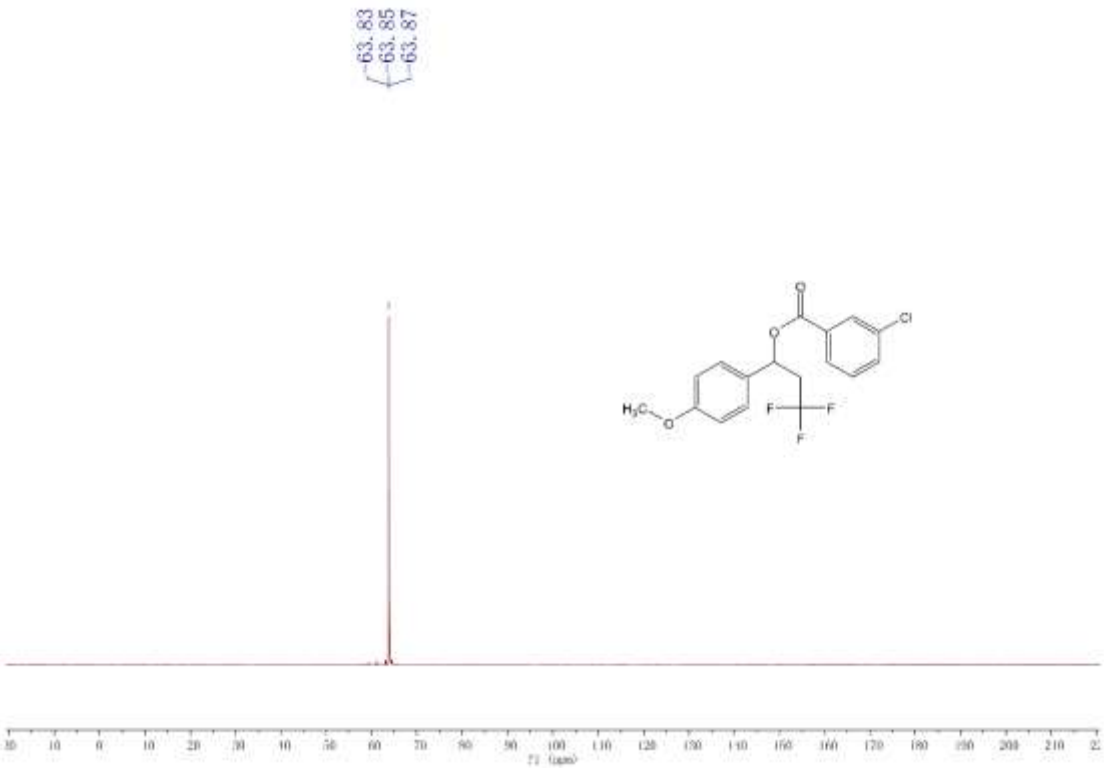
^{19}F NMR of 4g



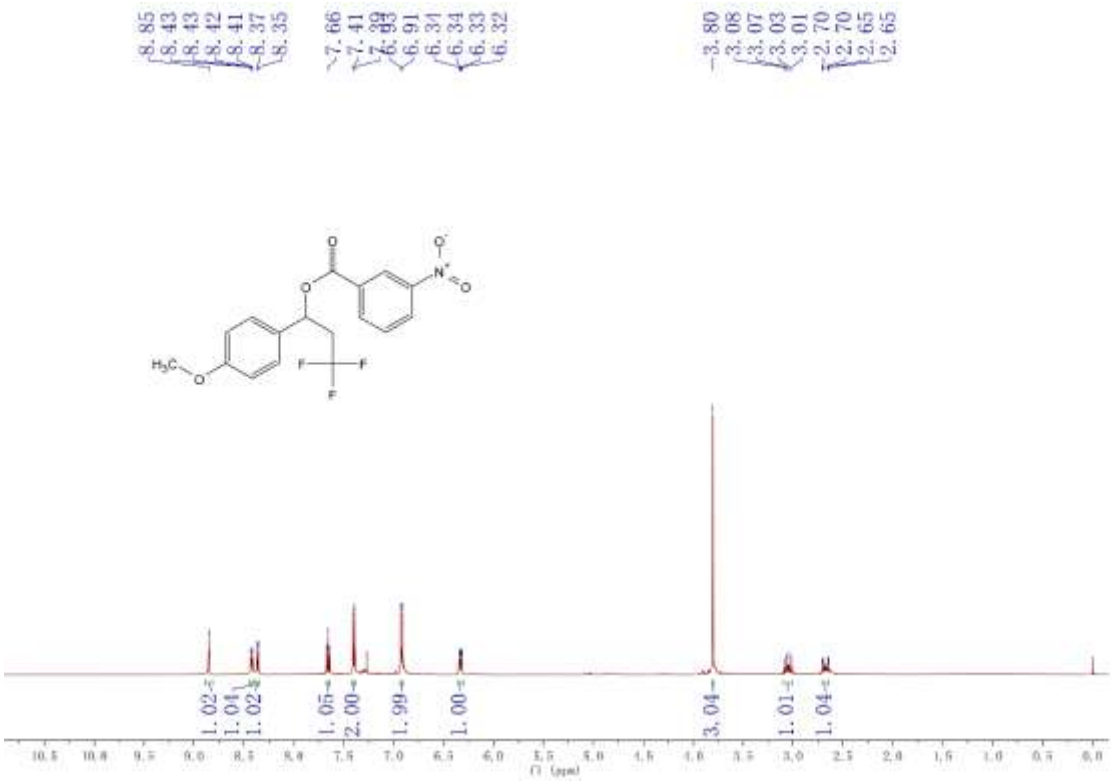
^{1}H NMR of 4h



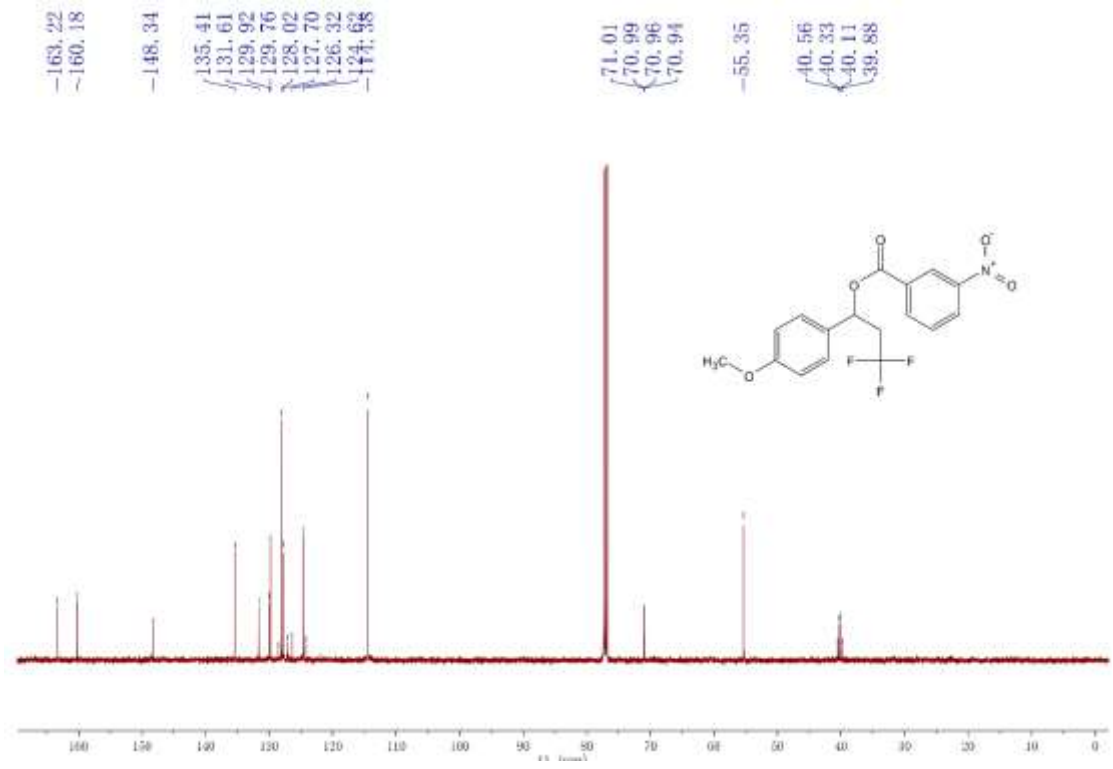
^{13}C NMR of 4h



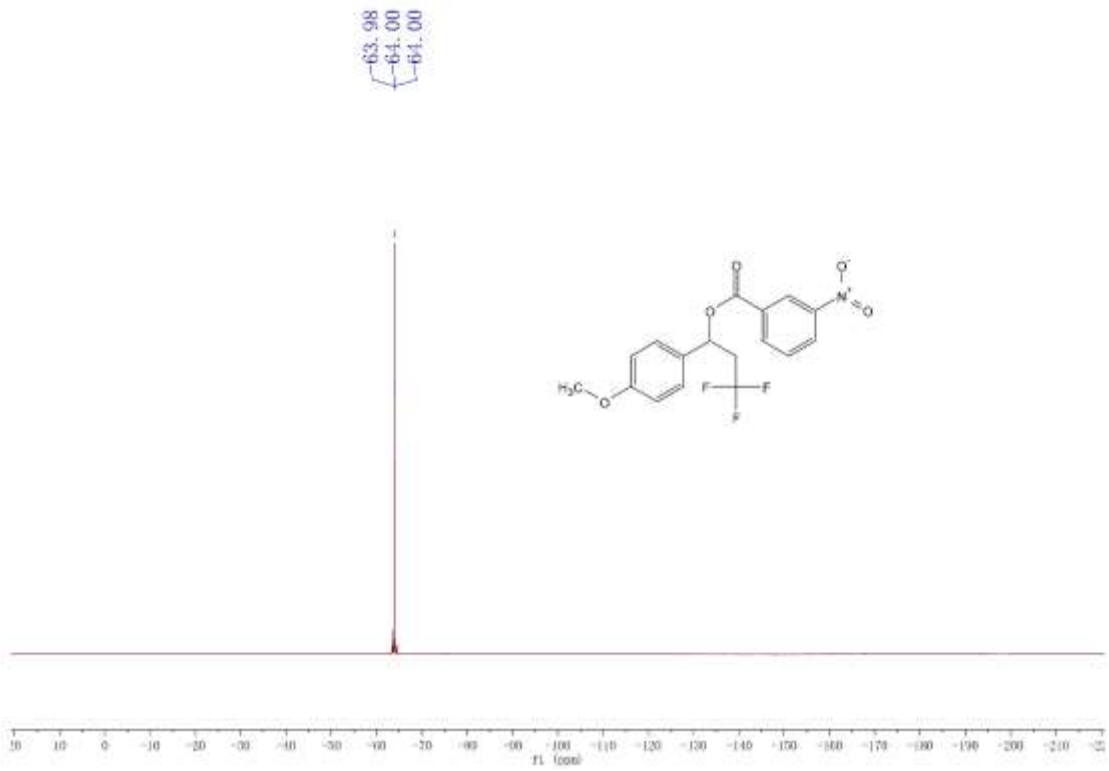
^{19}F NMR of 4h



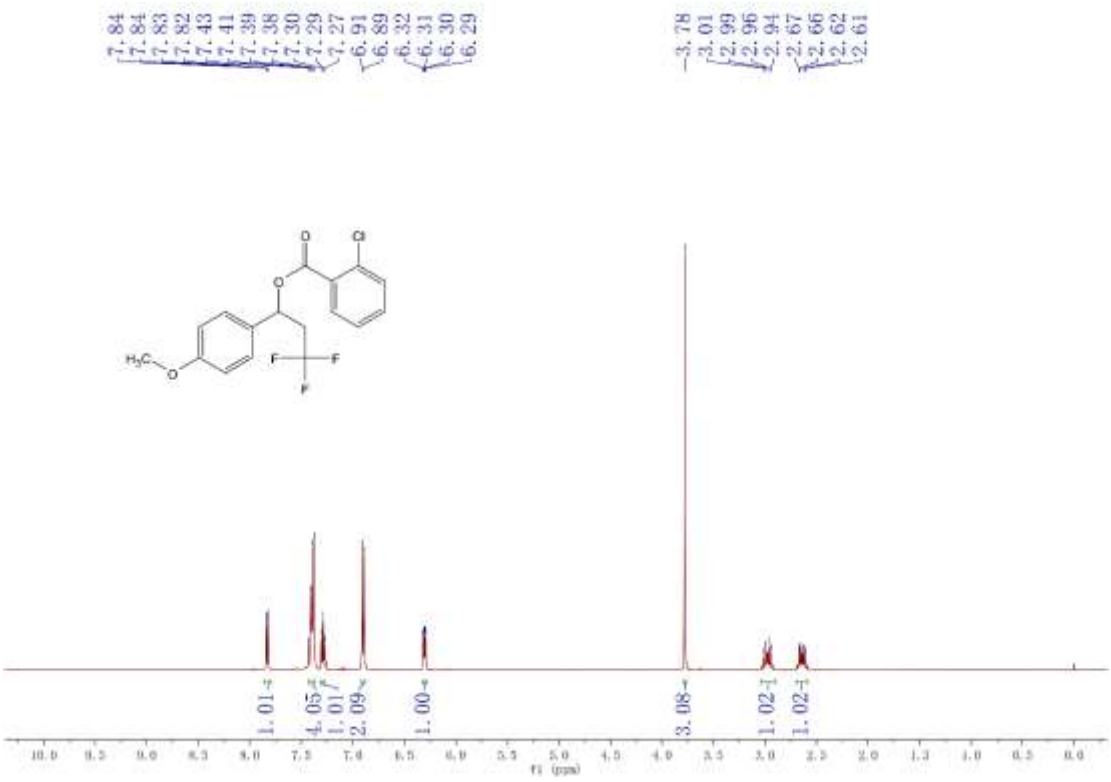
^{1}H NMR of 4i



^{13}C NMR of 4i



^{19}F NMR of 4i



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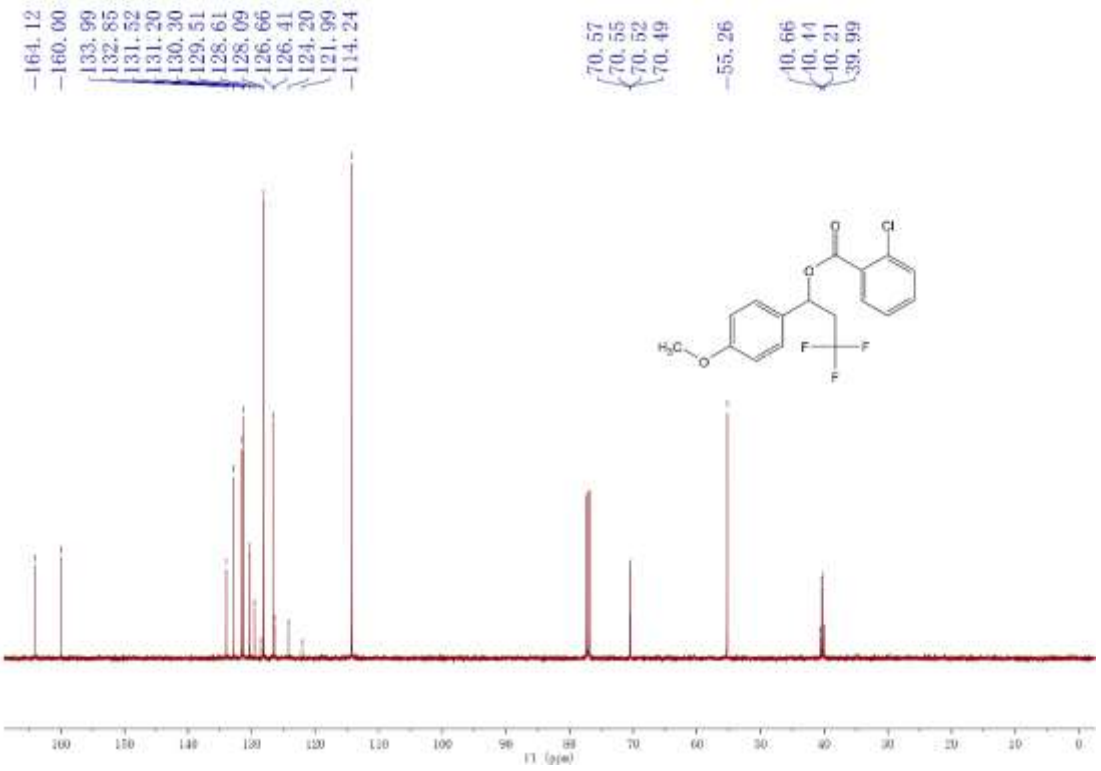
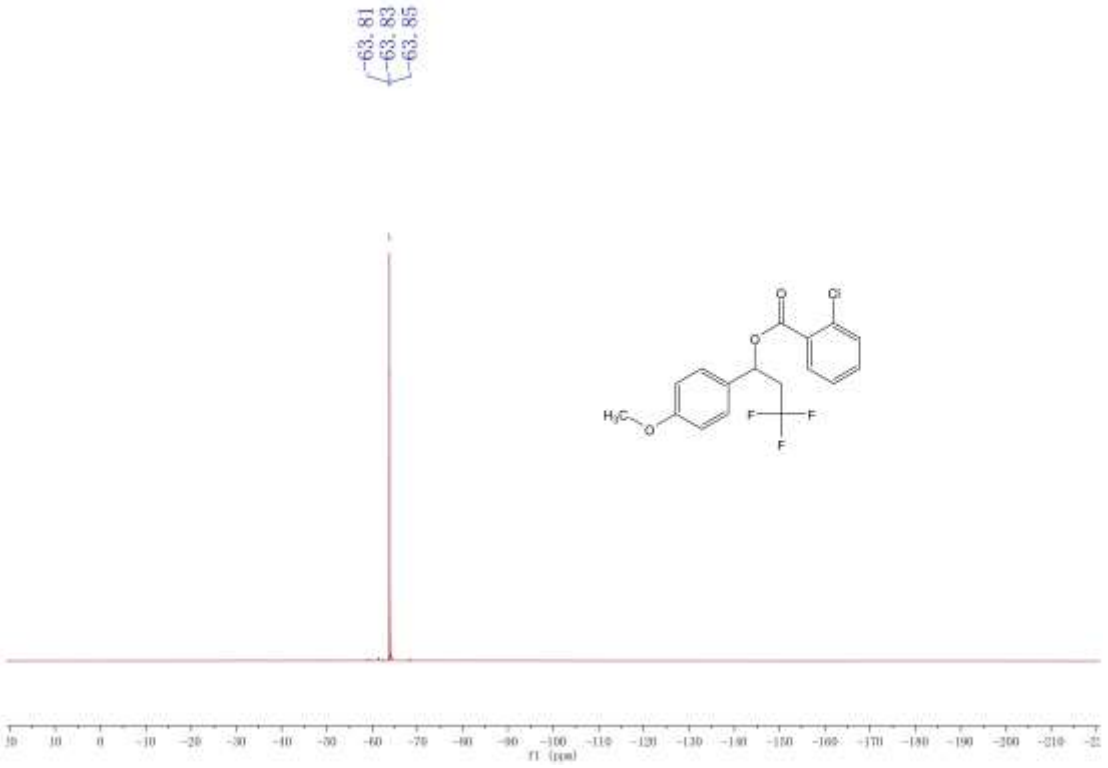
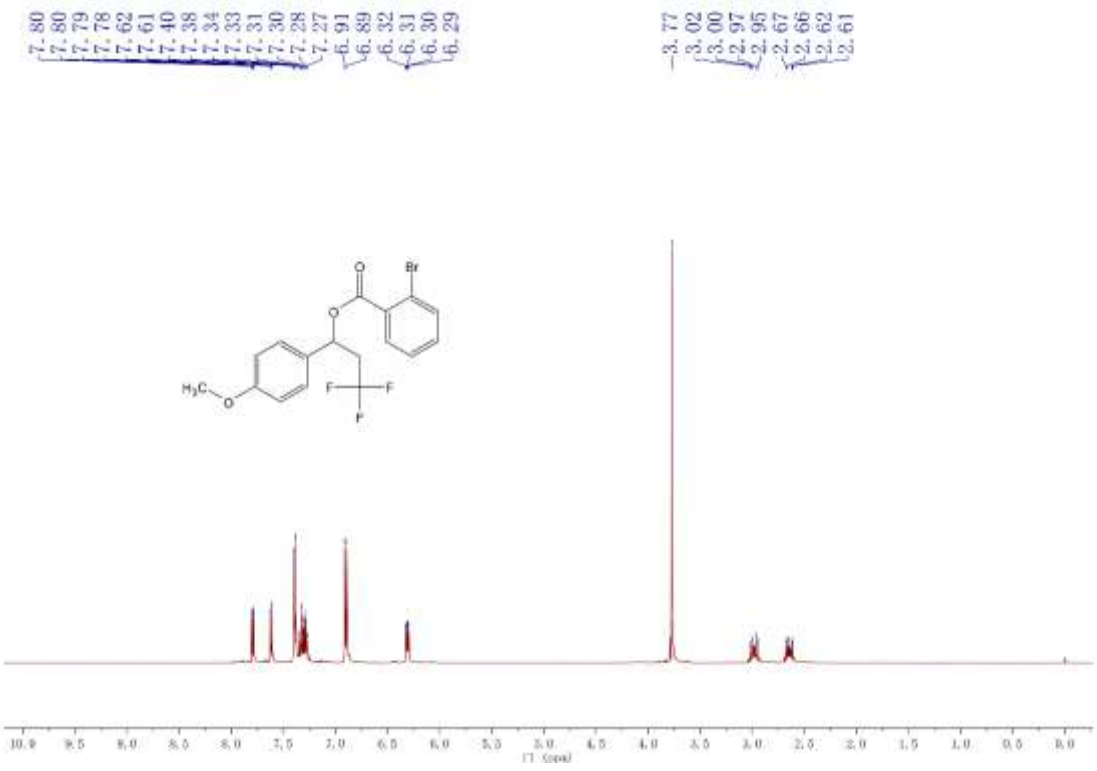


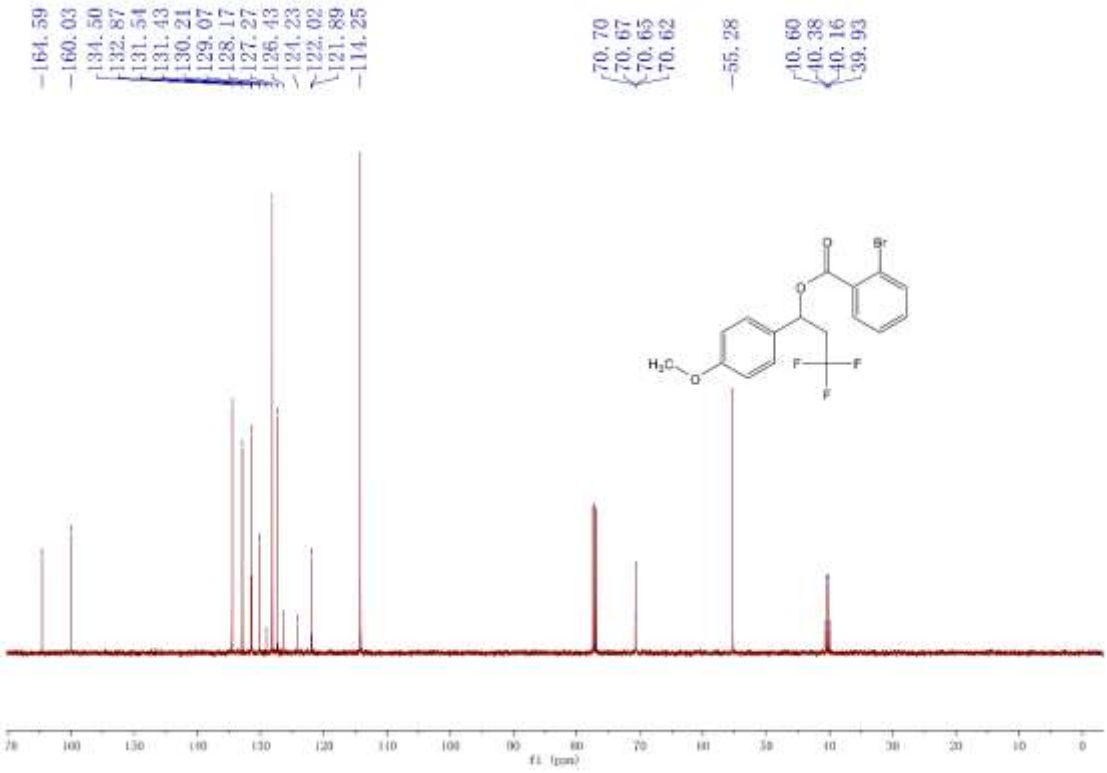
^{13}C NMR of 4j



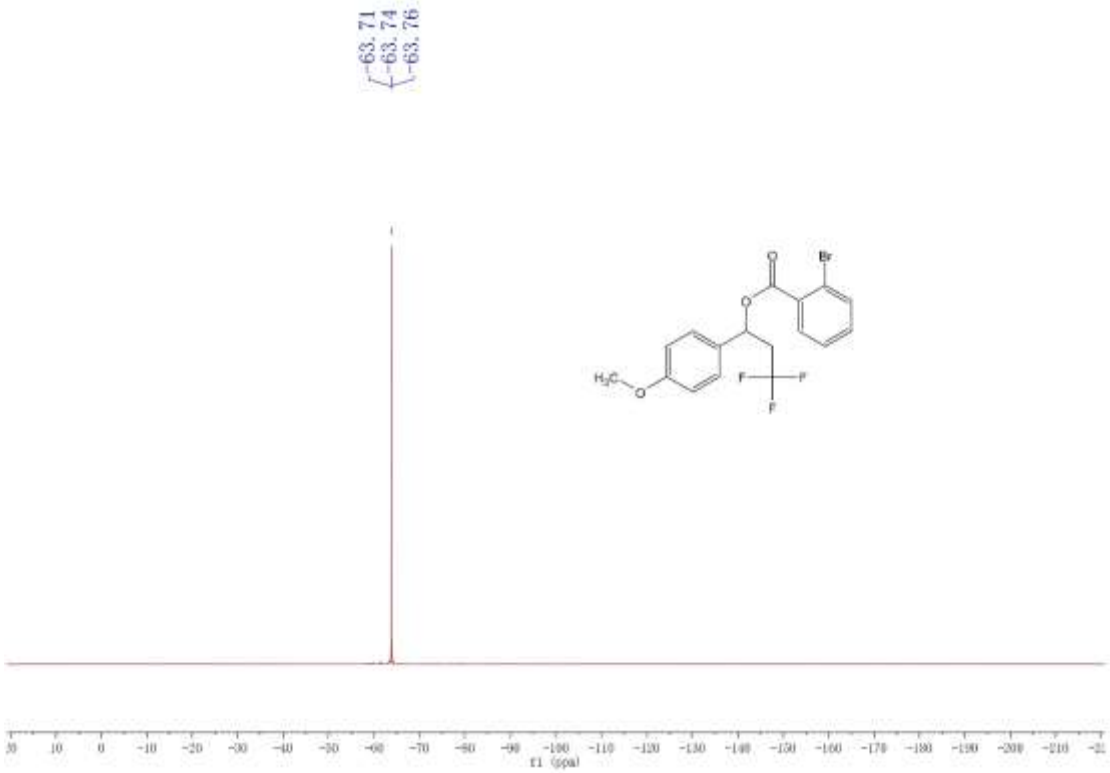
^{19}F NMR of 4j



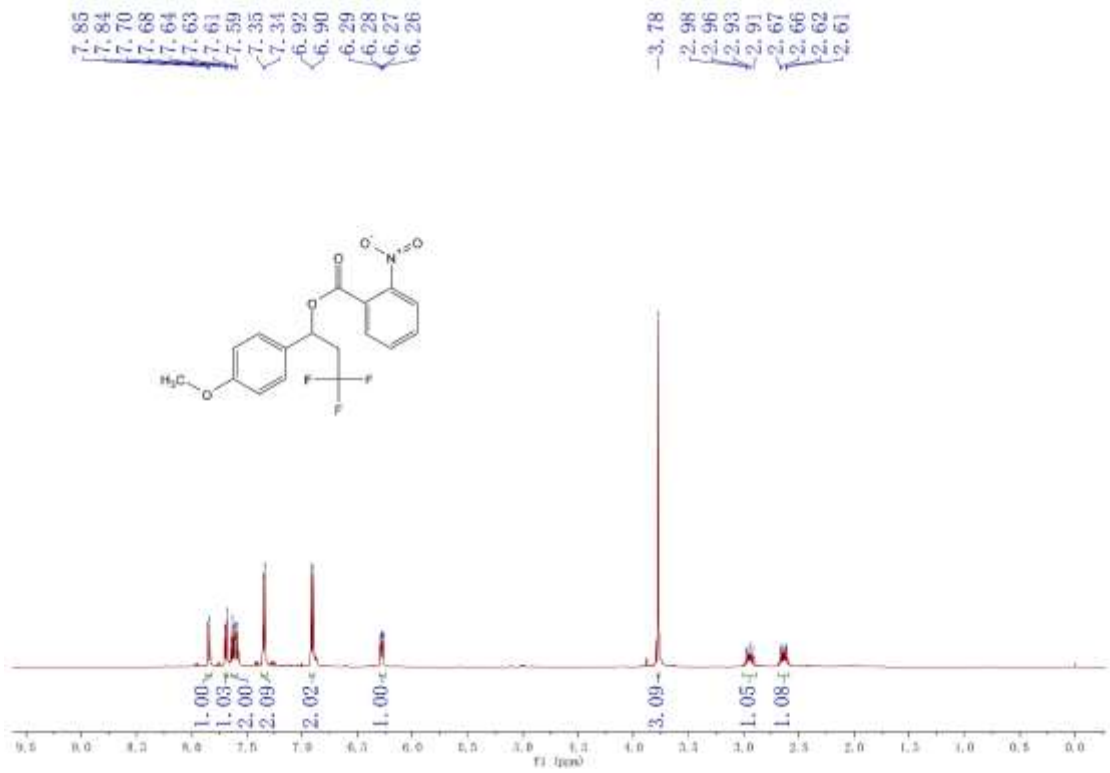
^{1}H NMR of 4k



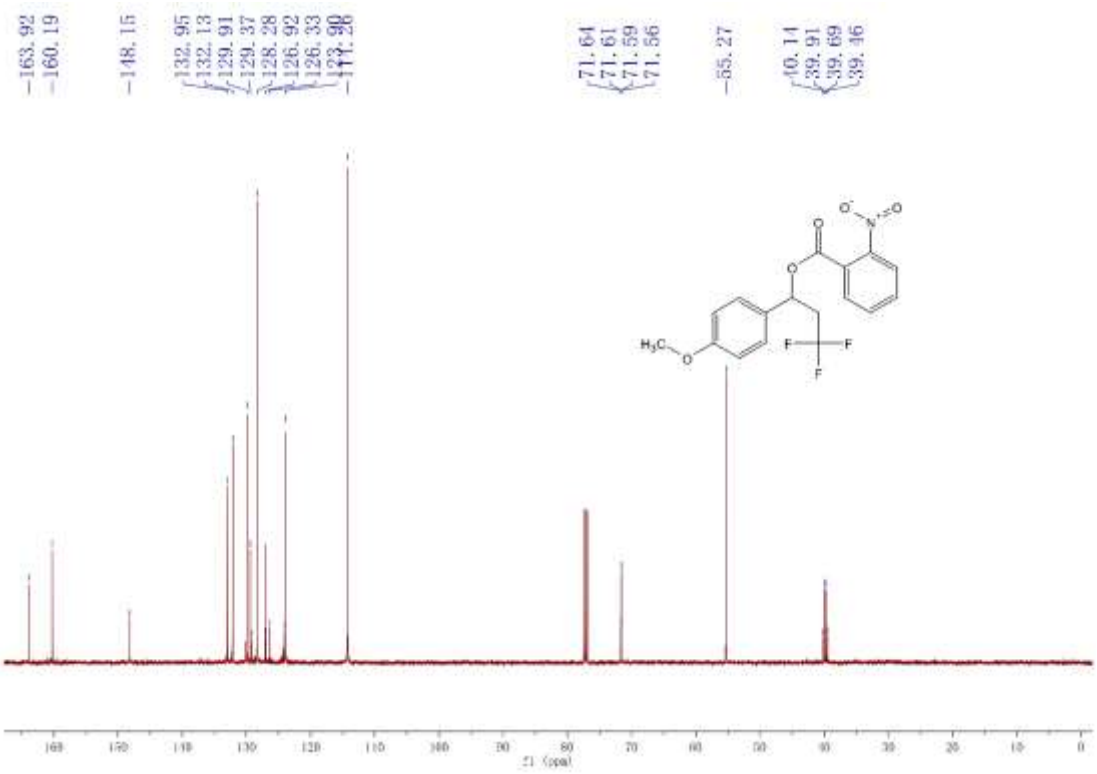
^{13}C NMR of 4k



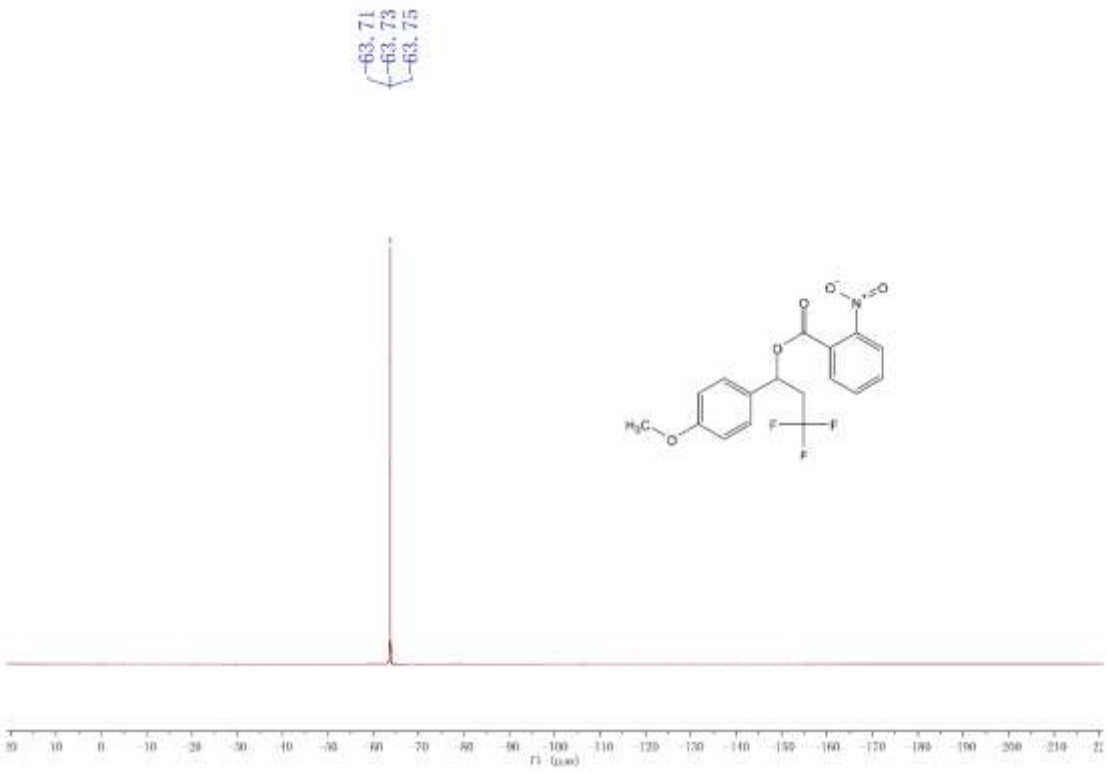
^{19}F NMR of 4k



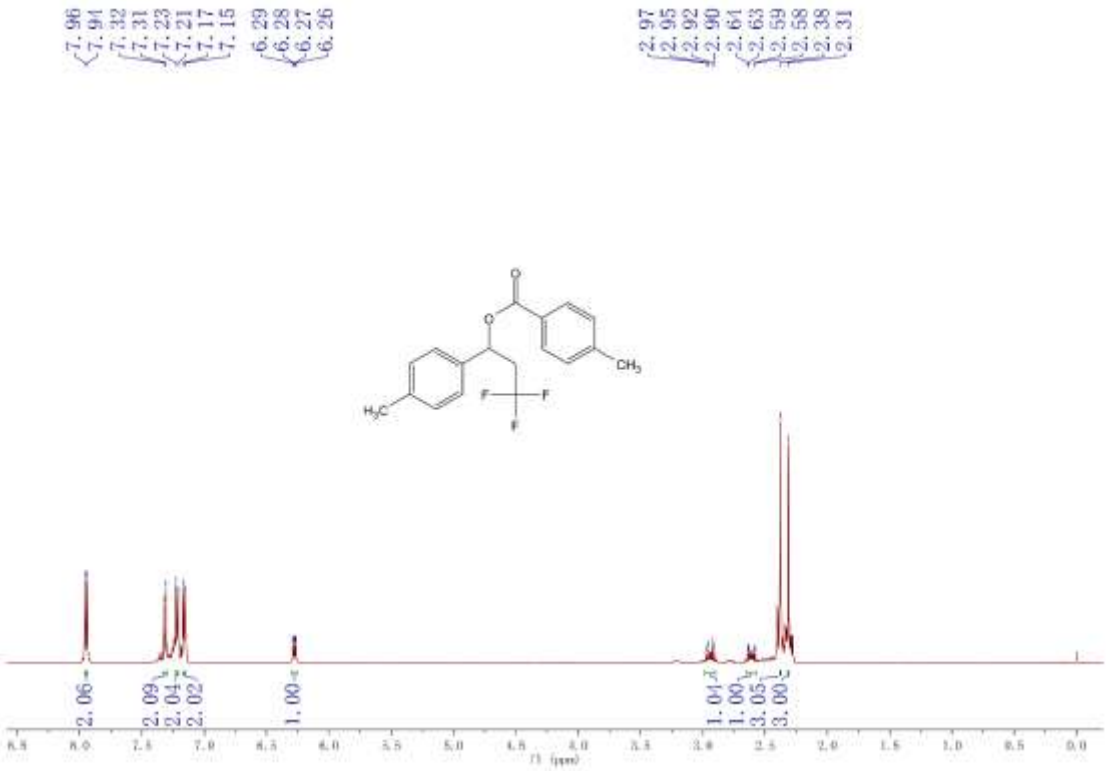
^{1}H NMR of 4l



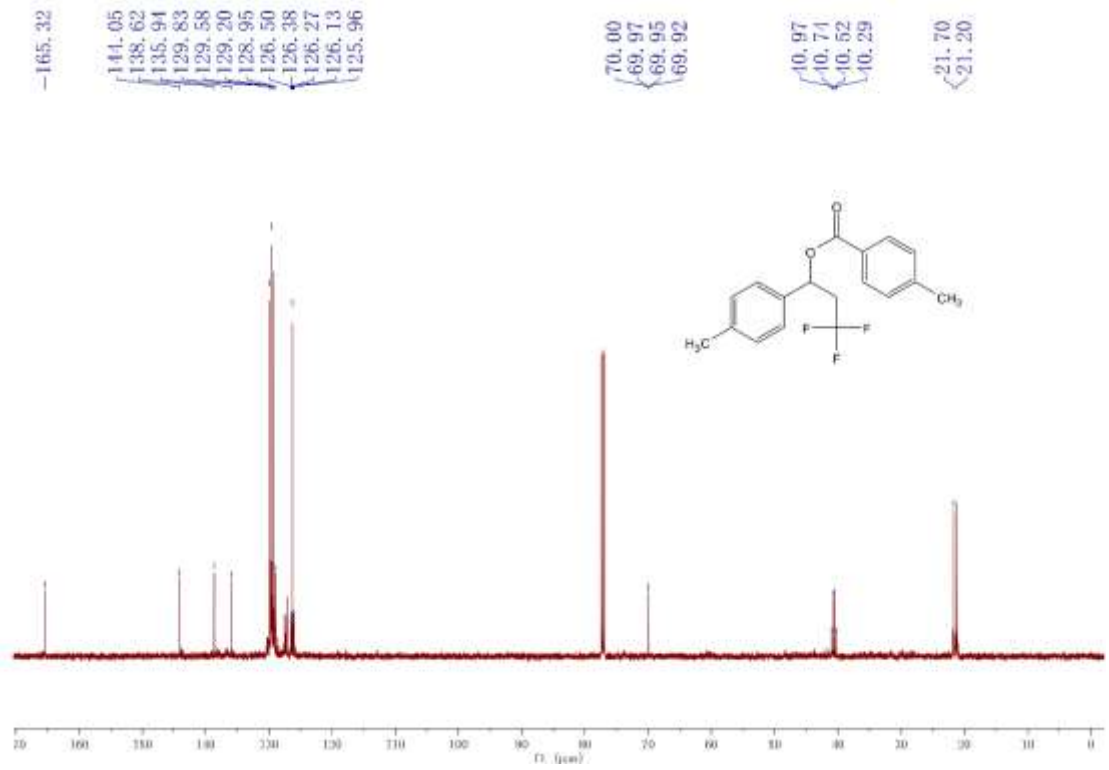
^{13}C NMR of 4l



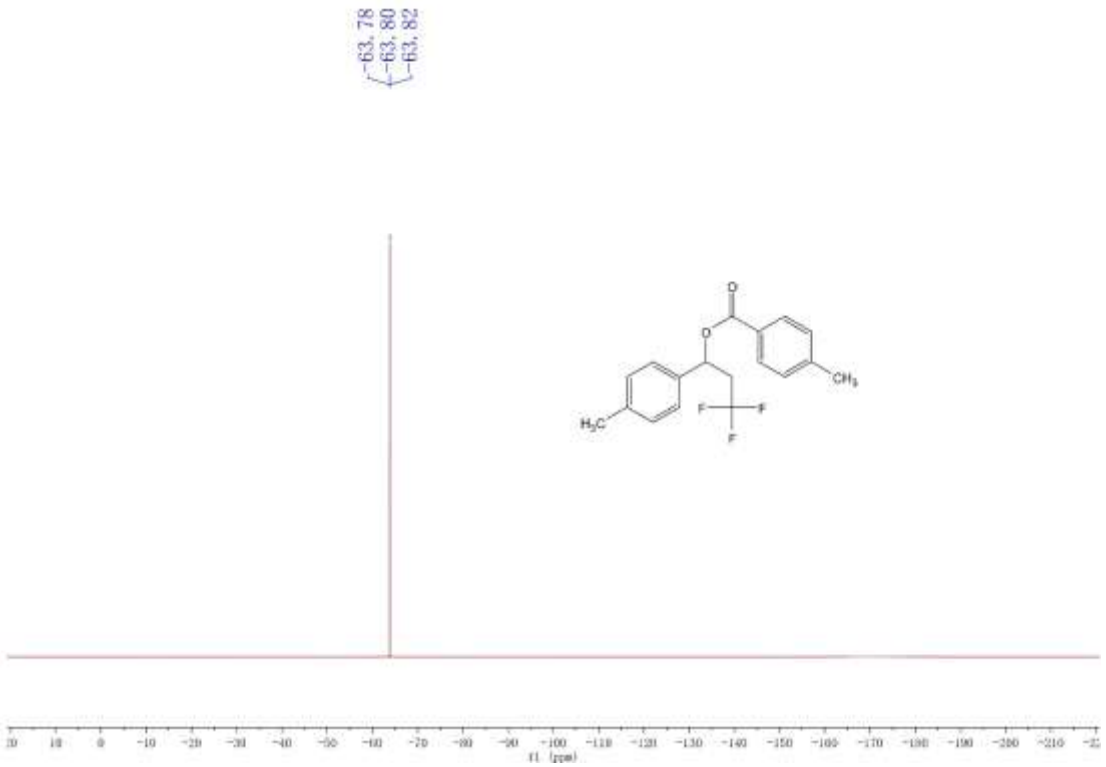
^{19}F NMR of 4l



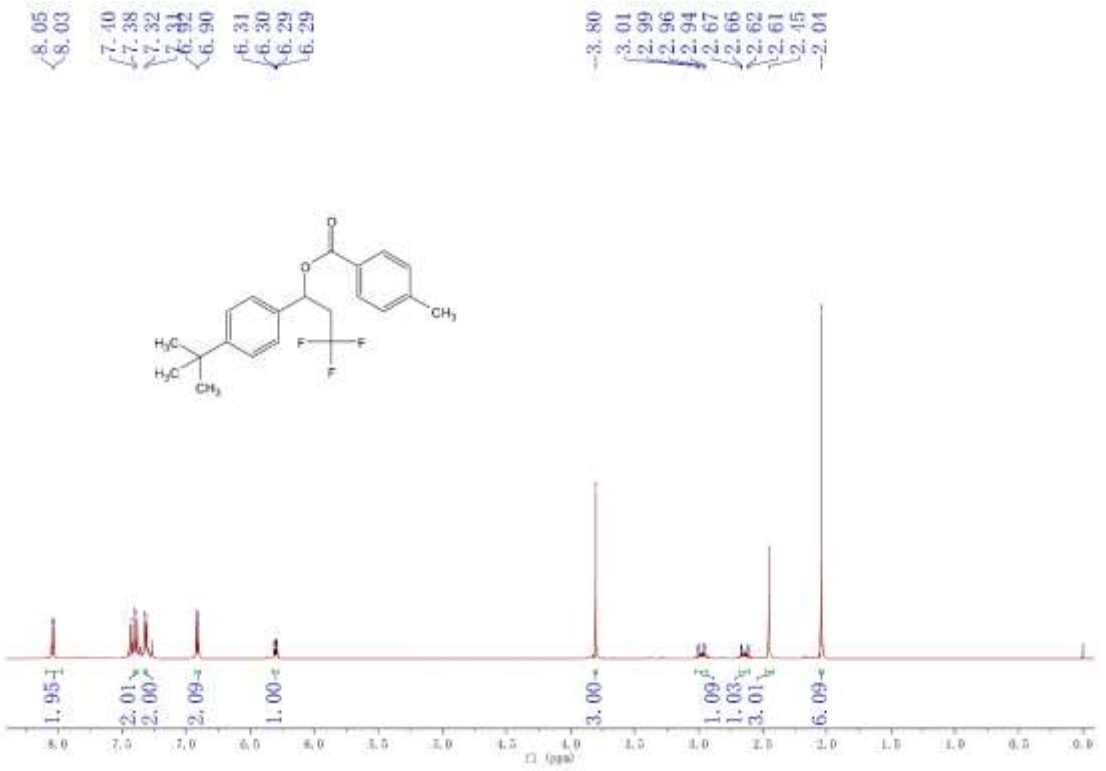
^{1}H NMR of 4m



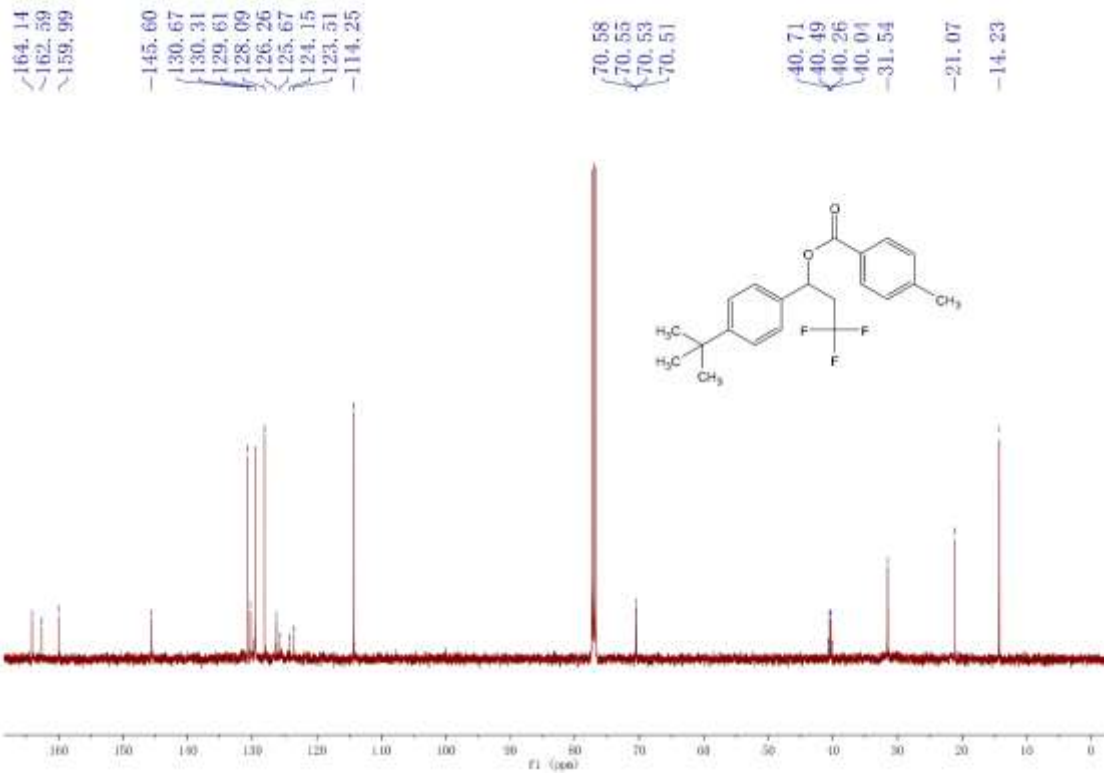
^{13}C NMR of 4m



^{19}F NMR of 4m



^{1}H NMR of 4n



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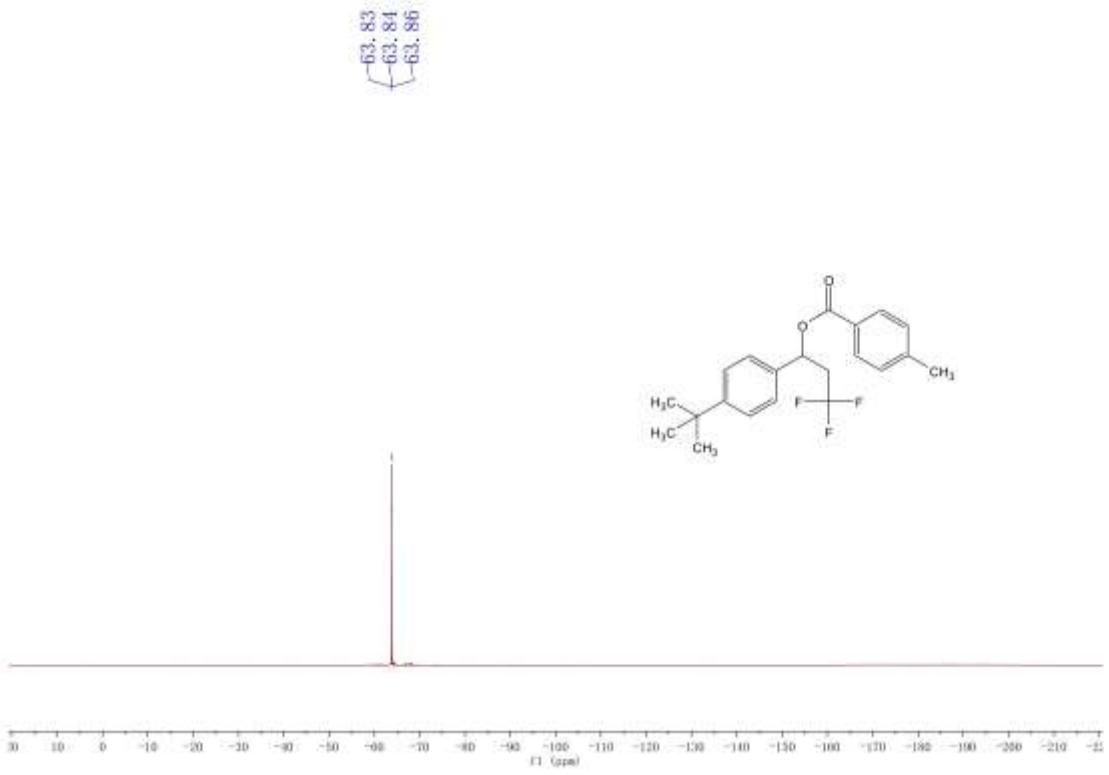
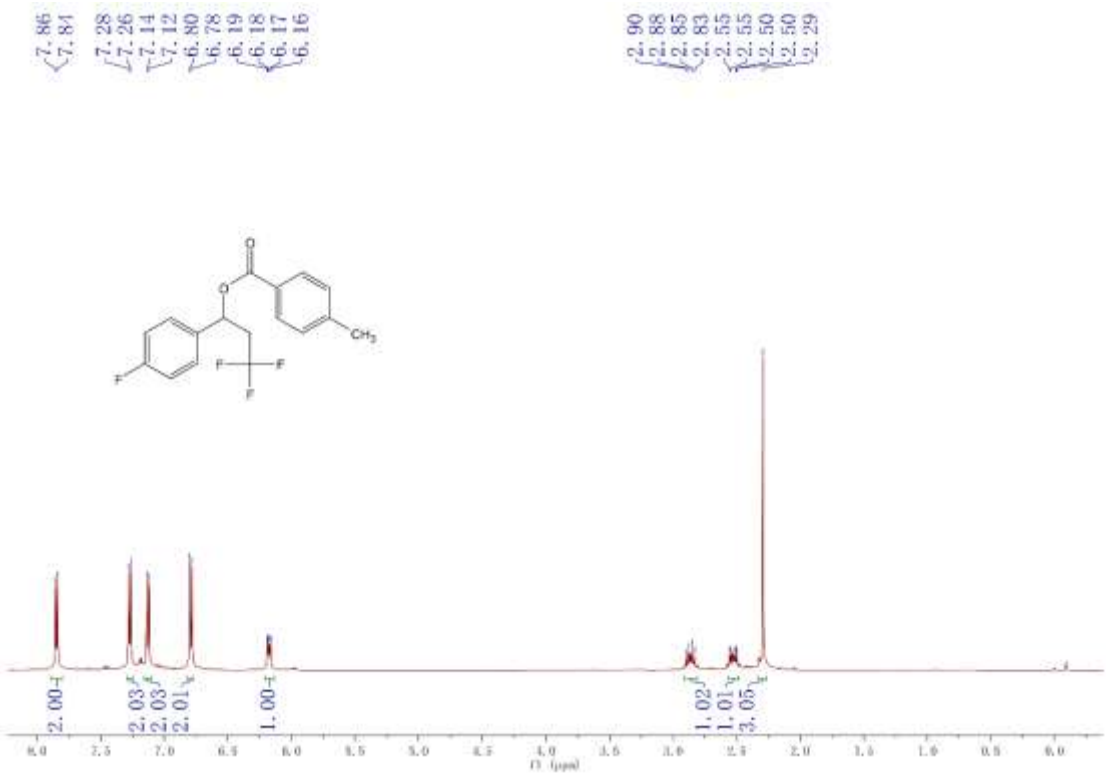
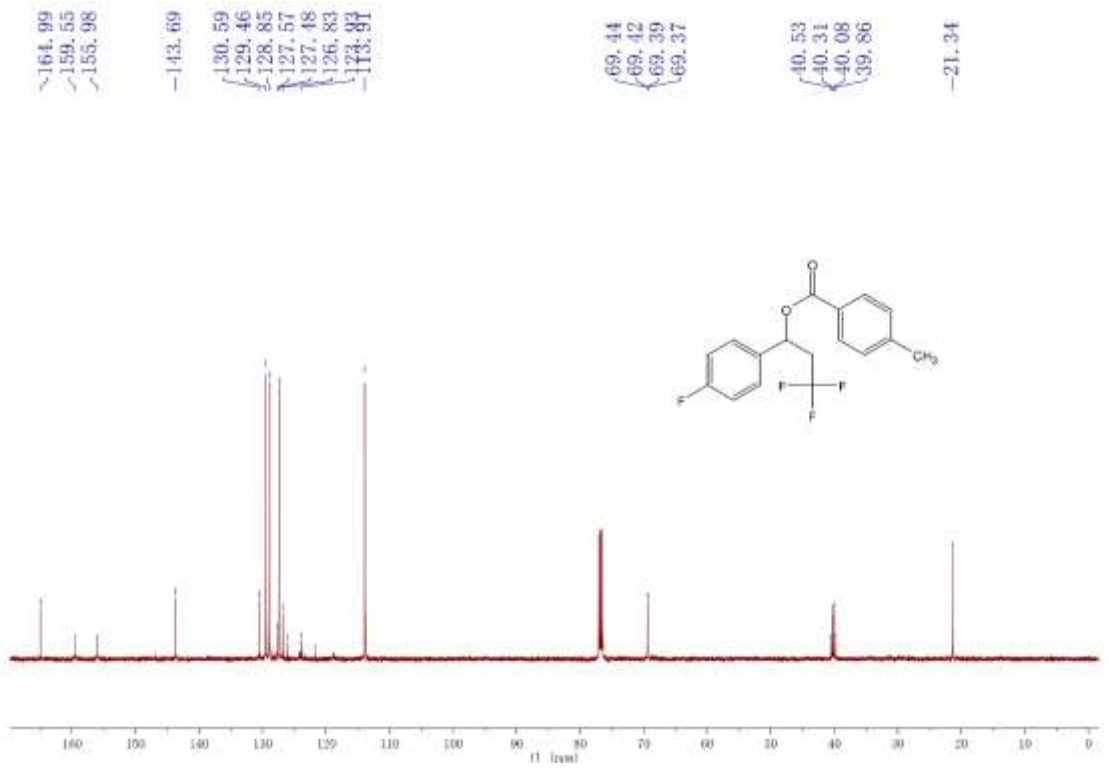


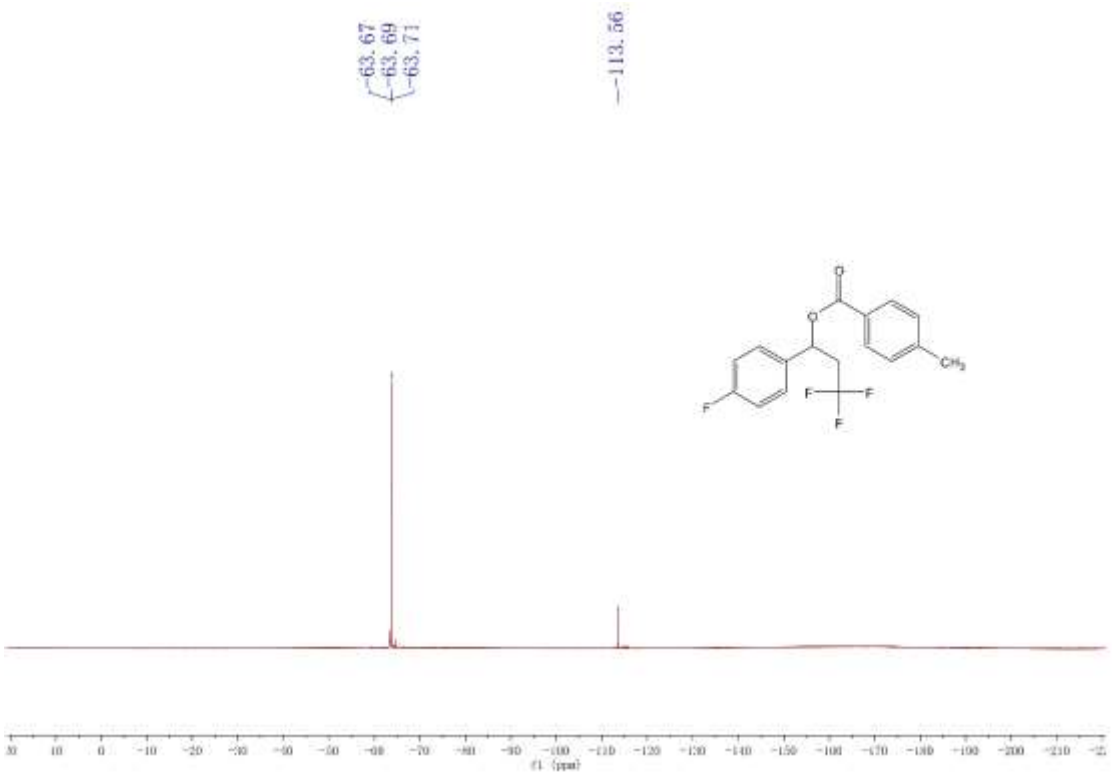
^{19}F NMR of 4n



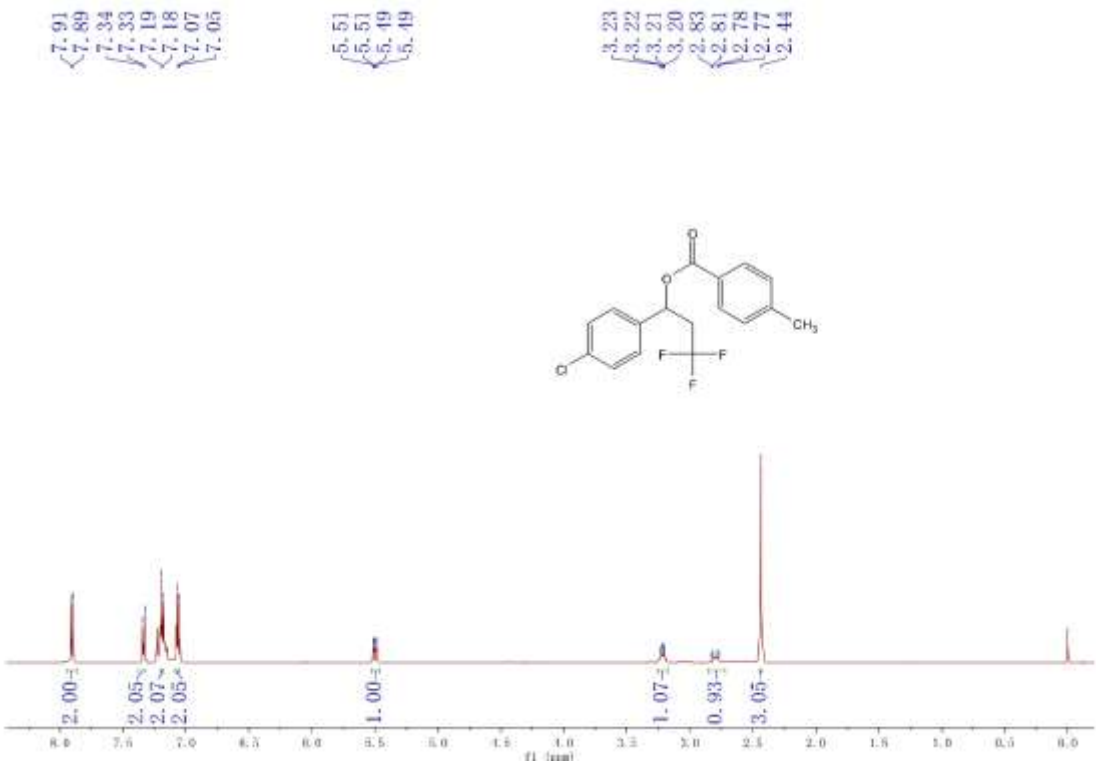
^{1}H NMR of 4o



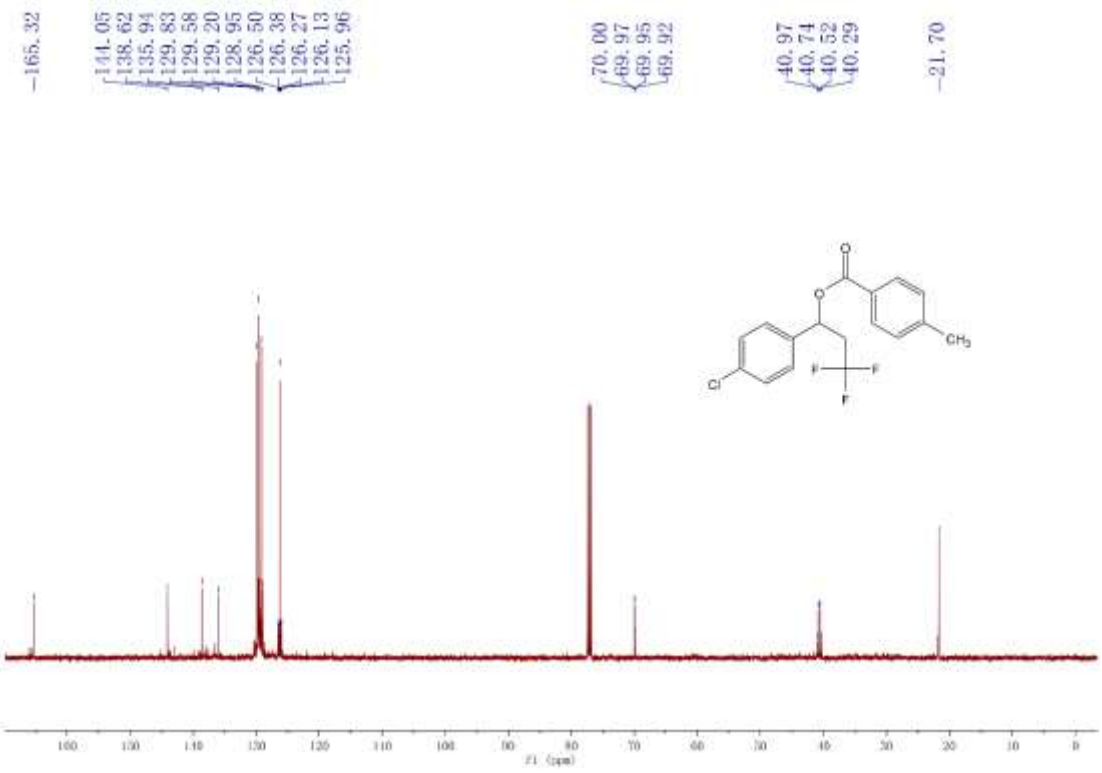
^{13}C NMR of 4o



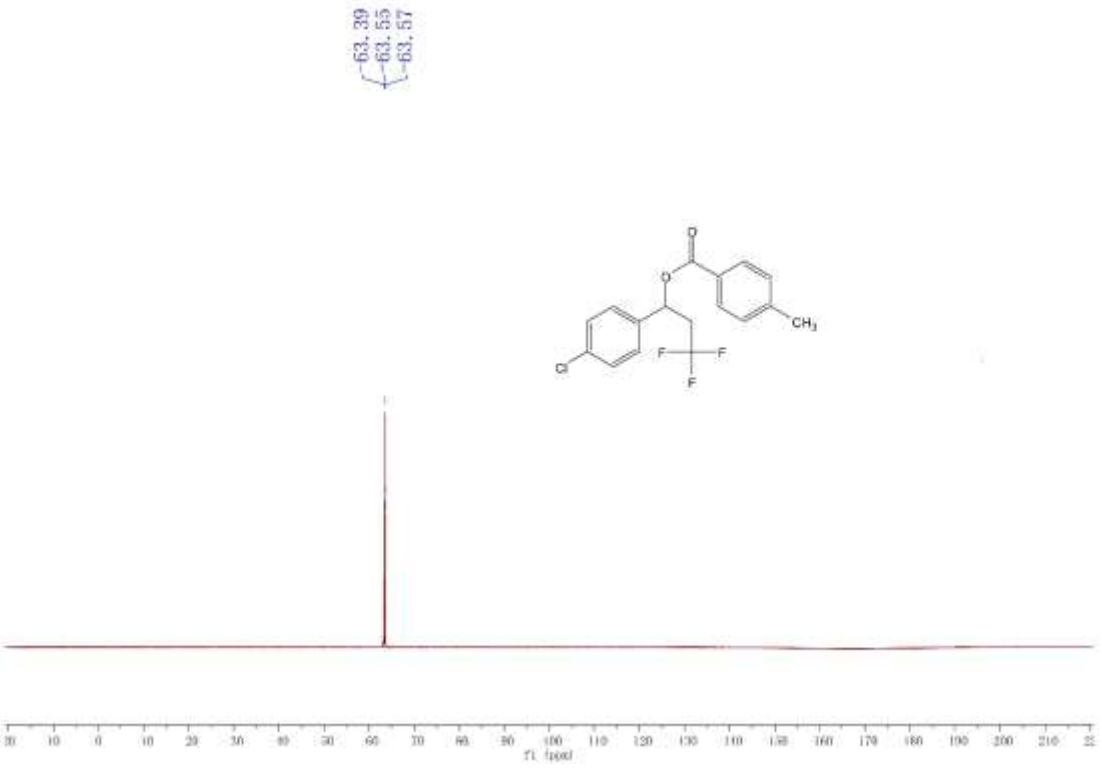
^{19}F NMR of 4o



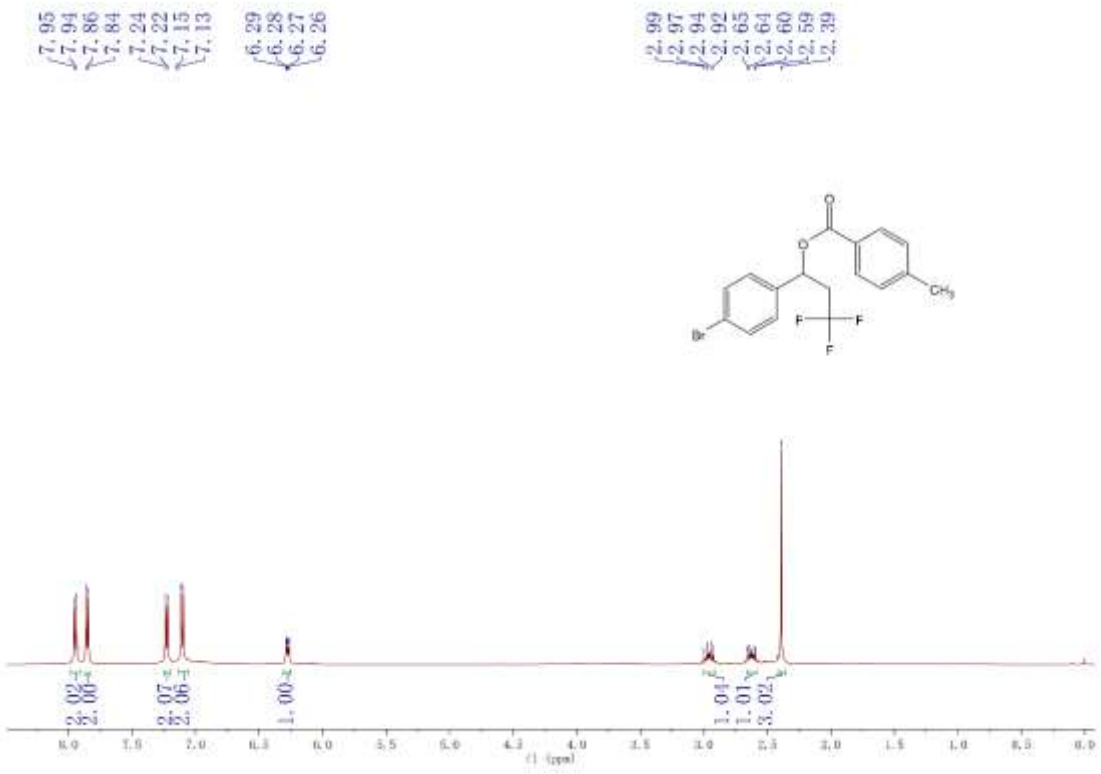
^{1}H NMR of 4p



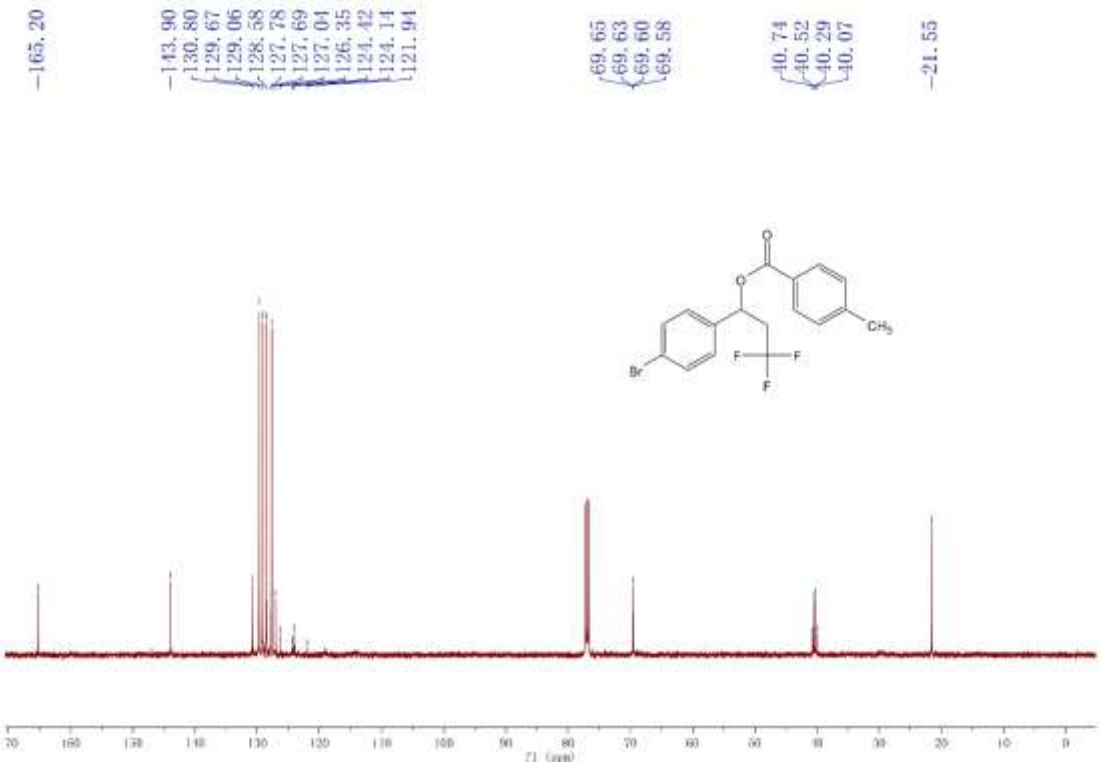
^{13}C NMR of 4p



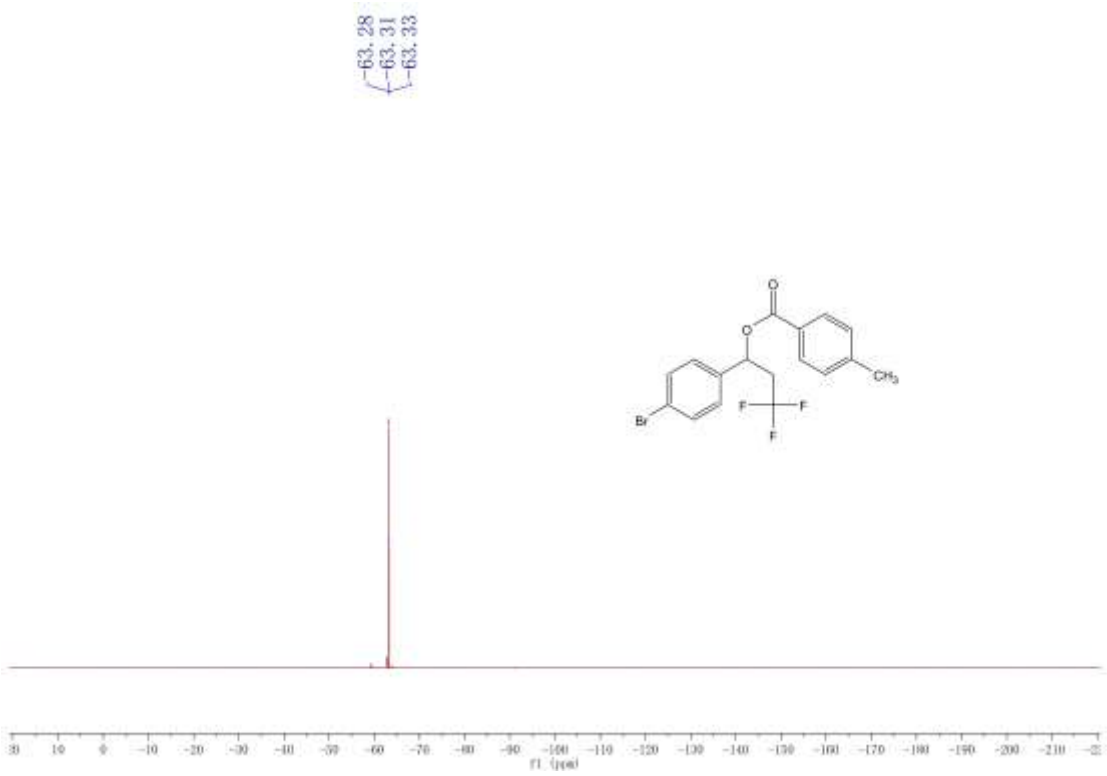
^{19}F NMR of 4p



^{1}H NMR of 4q



^{13}C NMR of 4q



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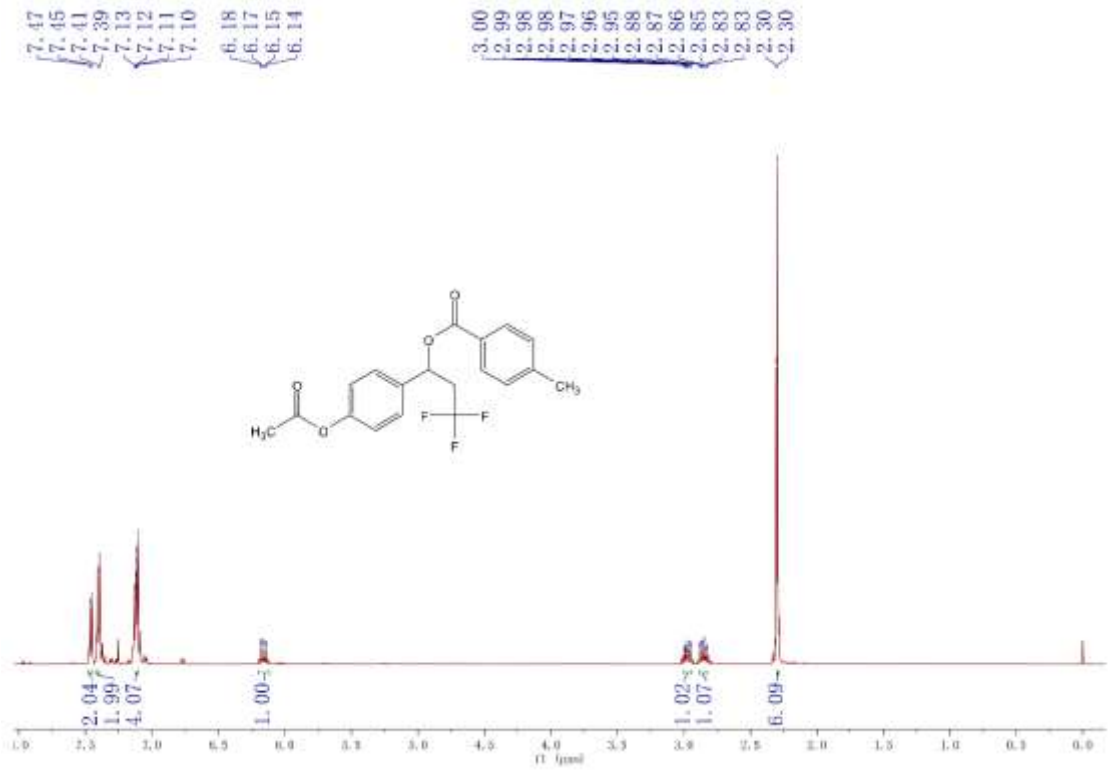
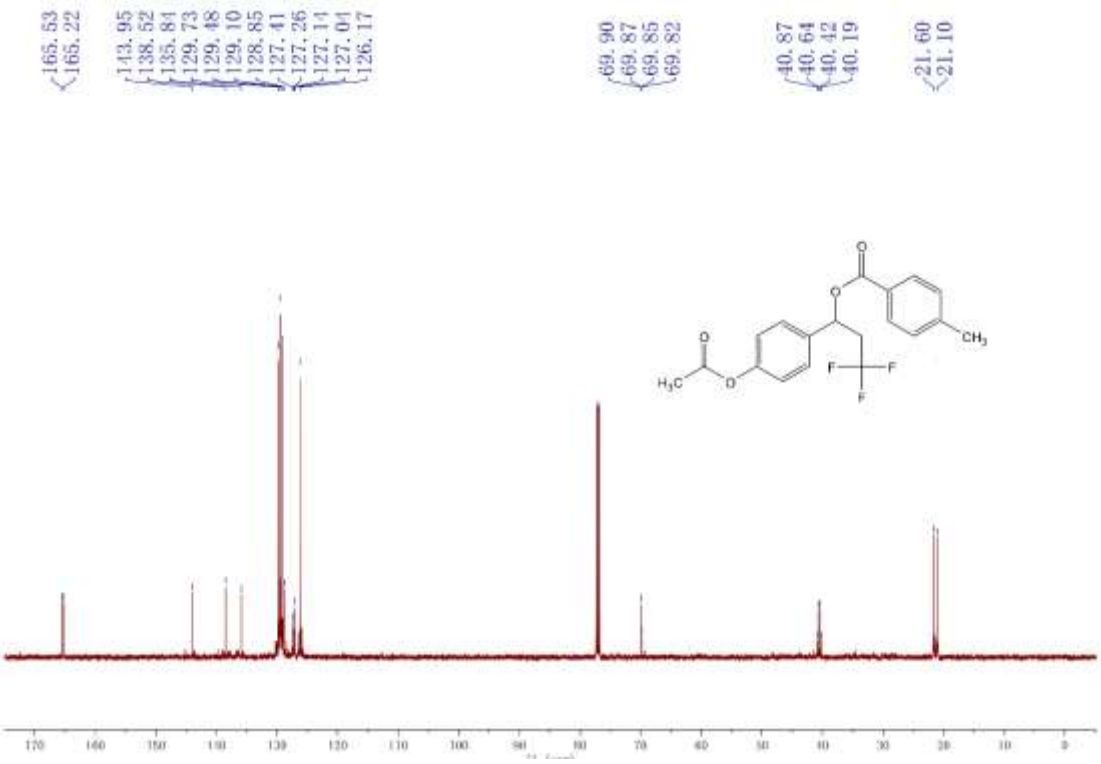


^{1}H NMR of 4r



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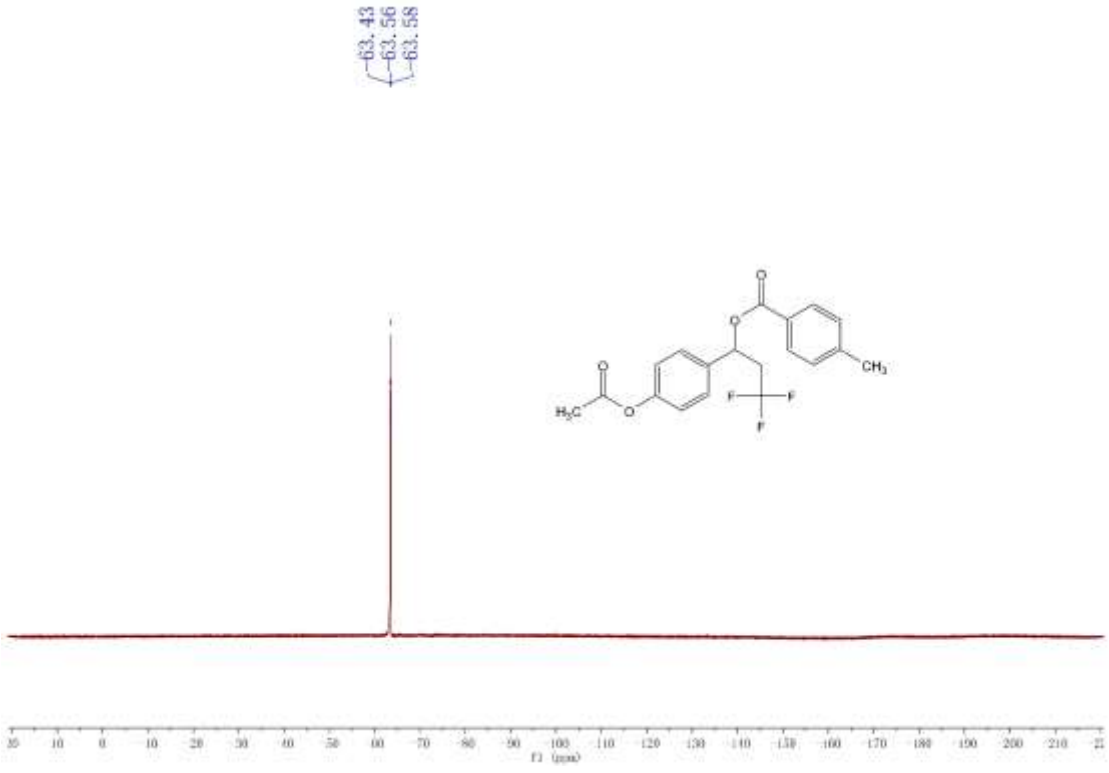
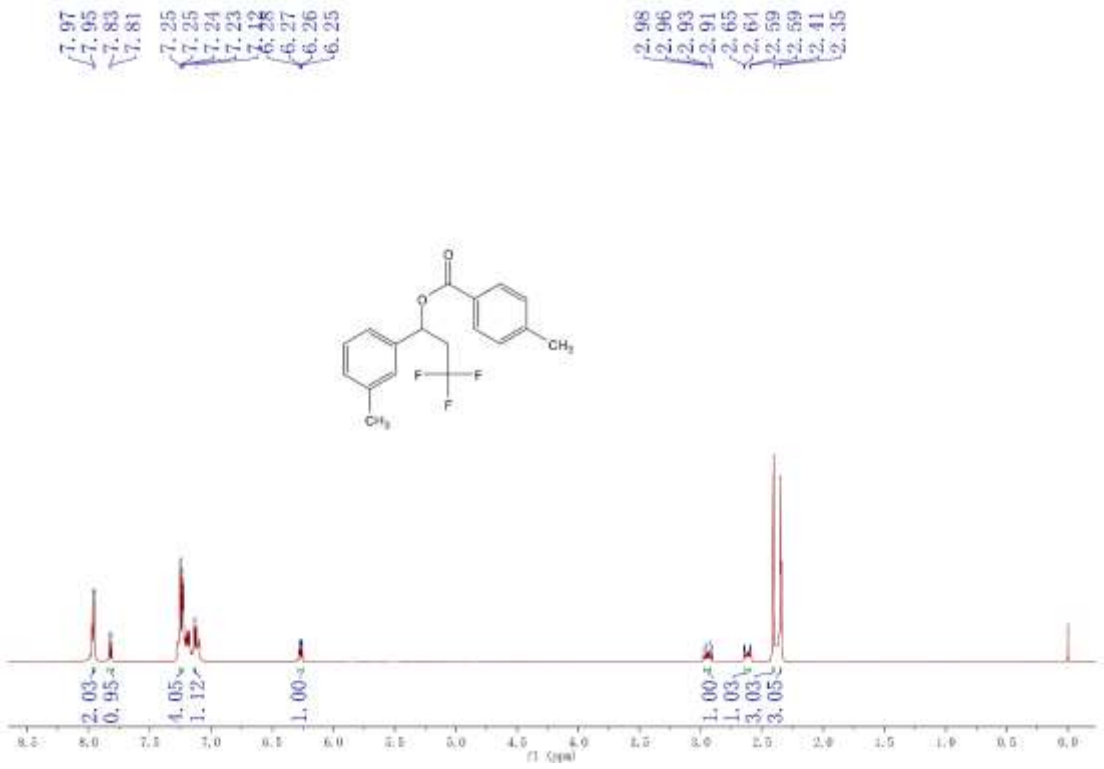
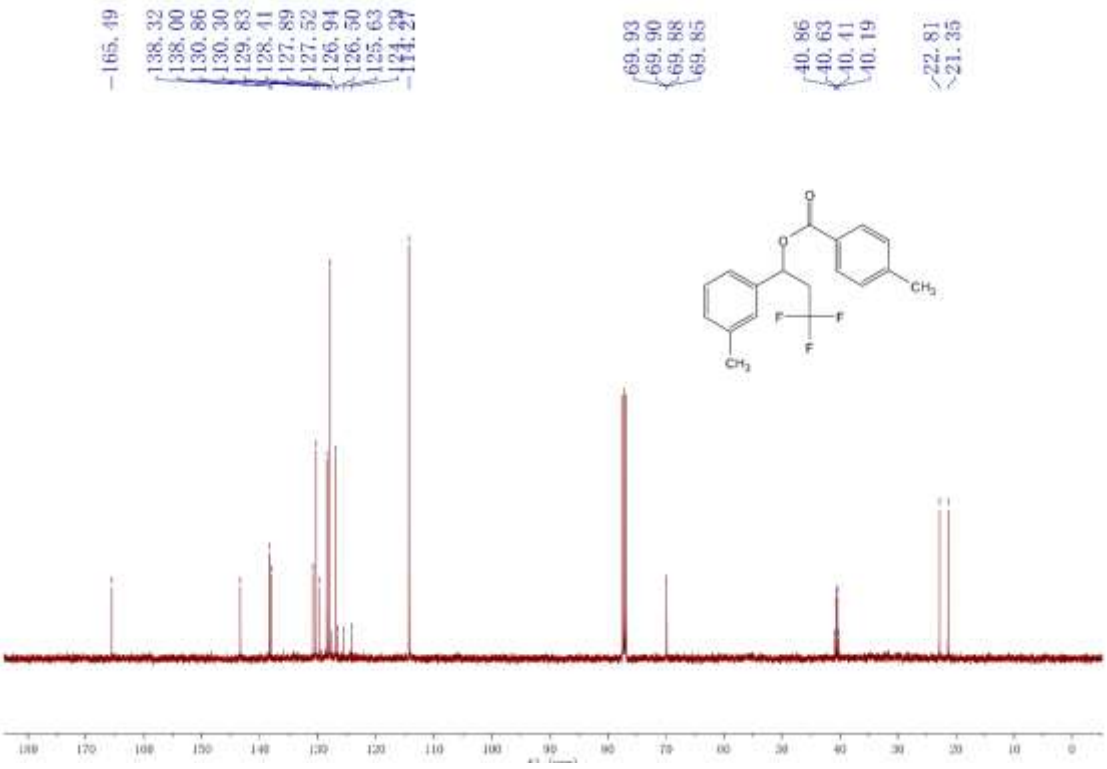


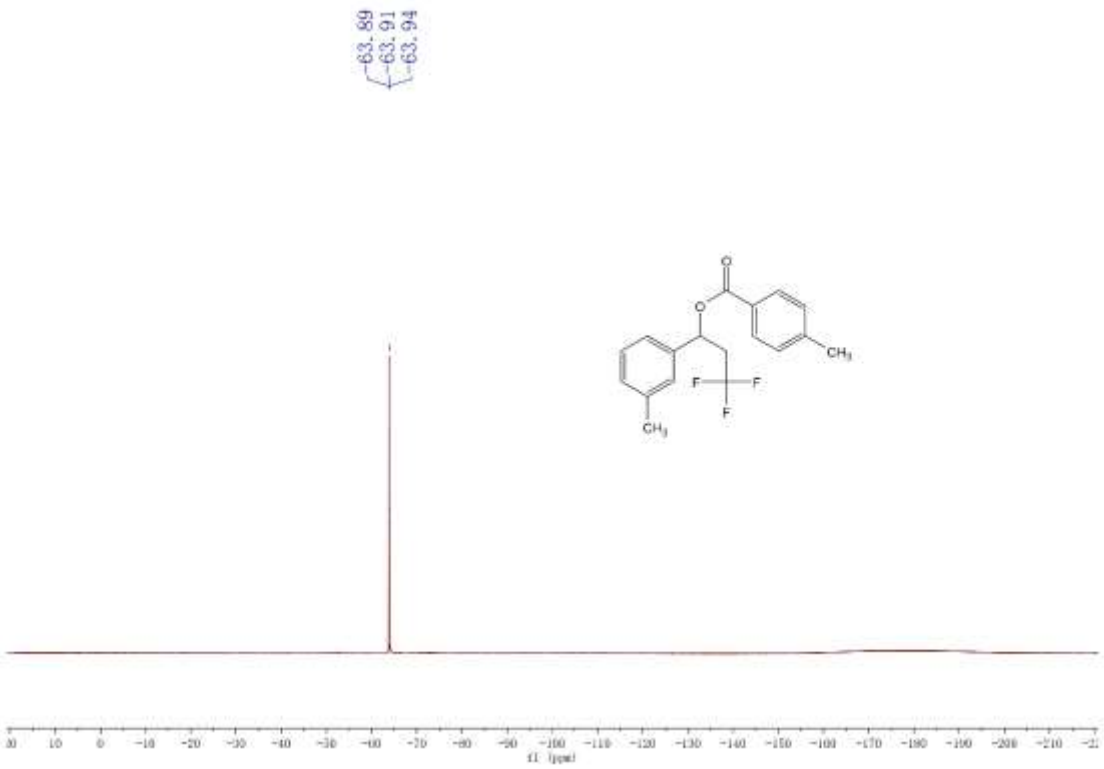
^{19}F NMR of 4r



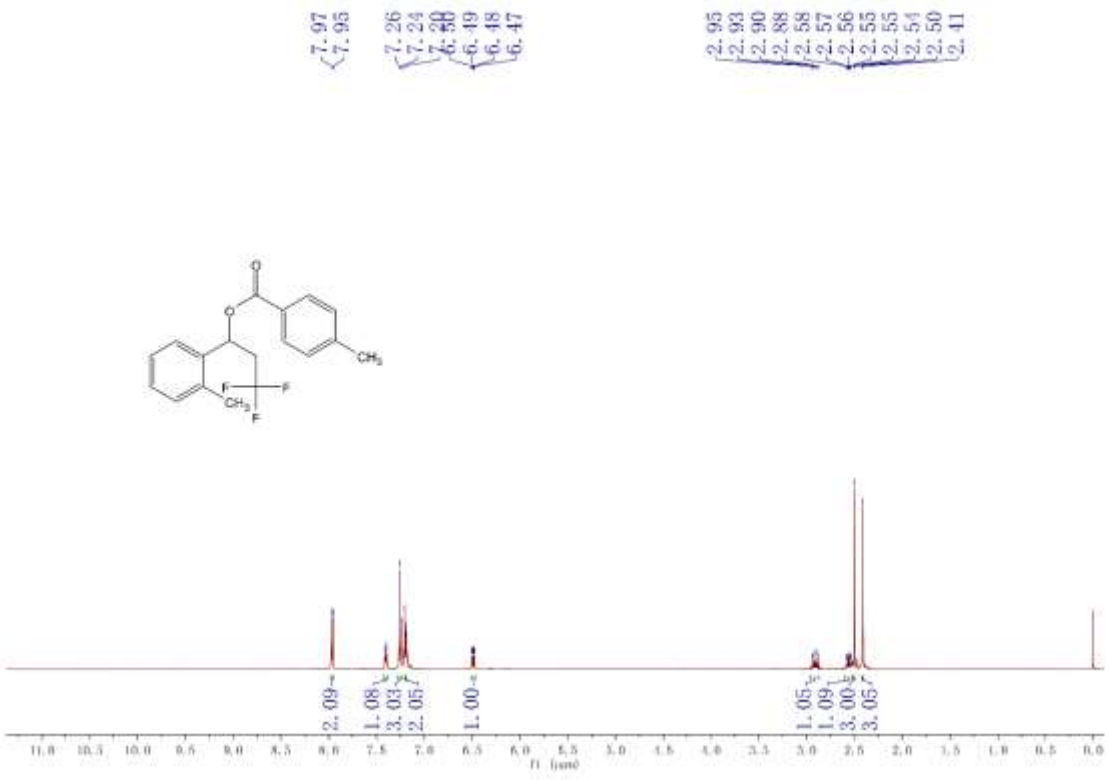
^{1}H NMR of 4s



^{13}C NMR of 4s



^{19}F NMR of 4s



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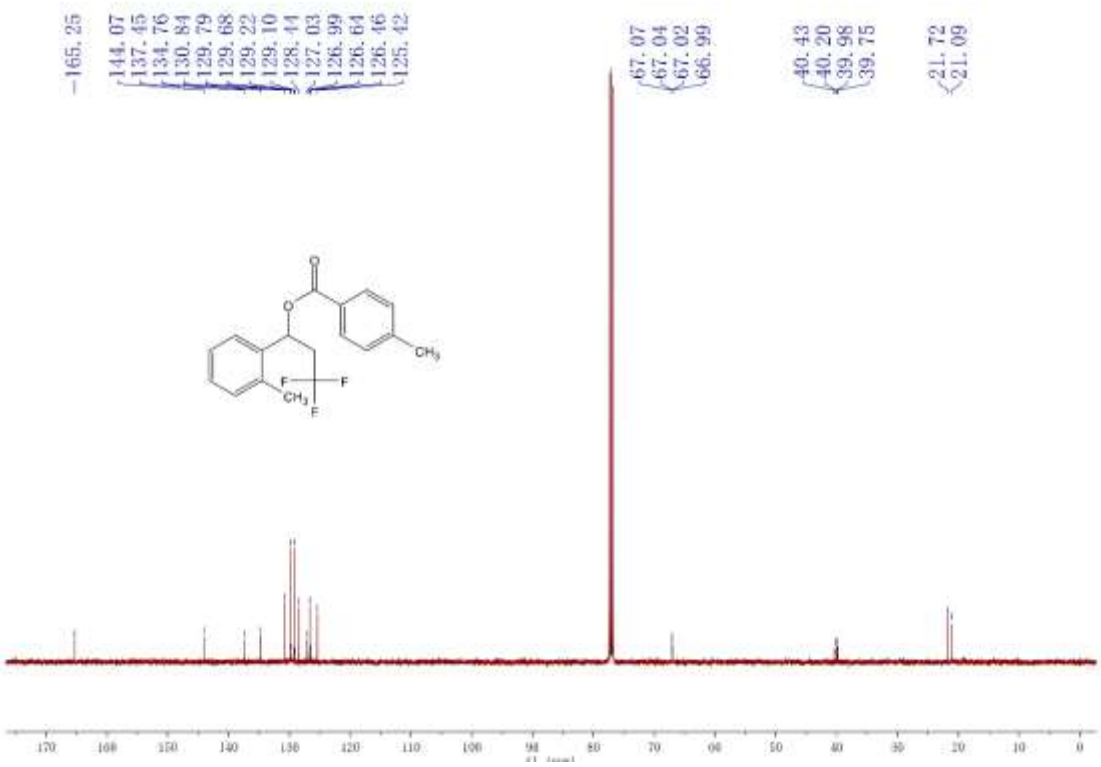
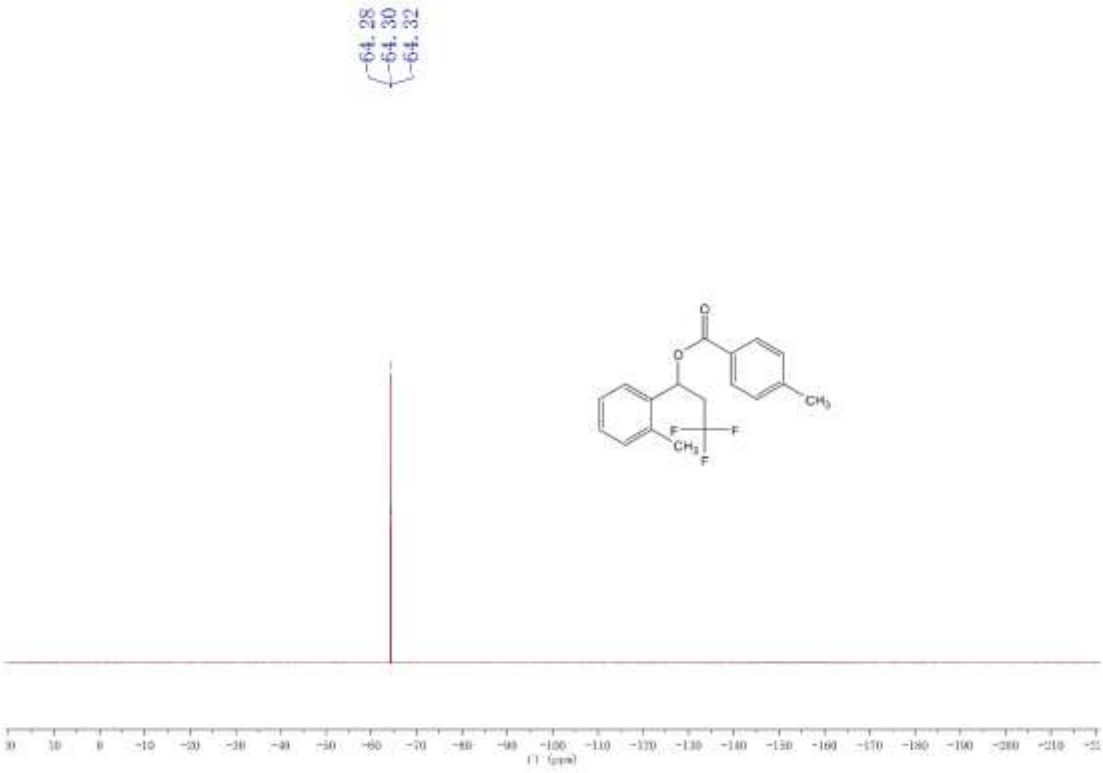


^{13}C NMR of 4t



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