Supporting Information

Copper and Zinc Co-promoted Bromo(Chloro)trifluoromethylation of Alkenes and Alkynes with Trifluoromethanesulfonic Anhydride

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1. General Information

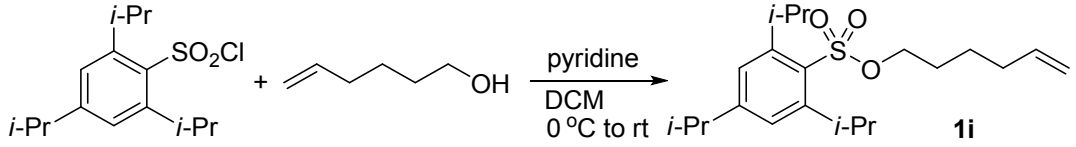
^{1}H NMR (TMS as the internal standard), ^{13}C NMR, and ^{19}F NMR spectra ($CFCl_3$ as the outside standard and low field is positive) were recorded on a 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HRMS data were obtained on a high-resolution mass spectrometer in the EI or ESI mode on a TOF mass analyzer. Unless otherwise noted, all reagents were obtained commercially and used without further purification.

2. Preparation of Substrates

Substrates **1a**-**1c**, **1g, 1h**, **1p**-**1t, 3a**, and **3b** were obtained commercially and used without further purification.

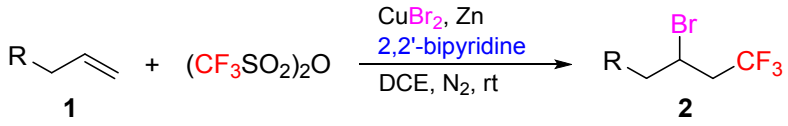
Substrates **1d**[1], **1e**[2], **1f**[3], **1j**[4], **1k**[5], **1l**[5], **1m**[6], **1n**[5], **1o**[7], **3c**[8], and **3d**[8] were prepared according to the literature.

Preparation of substrate **1i**



Hex-5-en-1-ol (0.26 mL, 2.2 mmol) and pyridine (0.18 mL, 2.2 mmol) were dissolved in dry DCM (2.0 mL). 2,4,6-Triisopropylbenzenesulfonyl chloride (605.7 mg, 2.0 mmol) was added to the solution at 0 °C. After stirring for 1 h at room temperature, the salt was filtered and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10:1) to afford **1i** (622.2 mg, 85%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.18 (s, 2H), 5.69-5.79 (m, 1H), 4.92-5.00 (m, 2H), 4.12-4.19 (m, 2H), 4.06 (t, *J* = 6.4 Hz, 2H), 2.88-2.95 (m, 1H), 2.02-2.07 (m, 2H), 1.67-1.74 (m, 2H), 1.45-1.51 (m, 2H), 1.26 (d, *J* = 6.8 Hz, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 153.5, 150.7, 137.9, 129.6, 123.7, 115.1, 69.3, 34.2, 33.0, 29.6, 28.4, 24.7, 23.6; **IR** (thin film) ν 3076, 2960, 1599, 1347, 1178, 992, 782 cm^{-1}; **MS** (ESI): *m/z* 367 $[M+H]^+$; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{21}H_{35}O_3S$: 367.2301; Found: 367.2298.

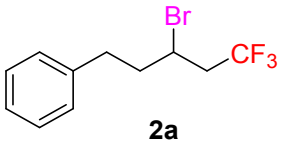
3. General Procedures for Bromotrifluoromethylation of Alkenes and Alkynes



1 2

A 10 mL schlenk tube was charged with bipyridine (249.8 mg, 1.6 mmol), $CuBr_2$ (44.6 mg, 0.2 mmol), zinc powder (26.0 mg, 0.4 mmol), and DCE (4.0 mL) under N_2 atmosphere. Alkene (0.4 mmol) or alkyne (0.4 mmol) (if the substrate was solid, it was added before DCE) and Tf_2O (0.27 mL, 1.6 mmol) was subsequently added to the reaction. The resulting mixture was stirred at room temperature overnight. After the reaction was complete, the reaction mixture was filtrated through celite, washed with DCM. The filtration was concentrated in vacuo. The resulting residue was purified by column chromatography to give the pure product.

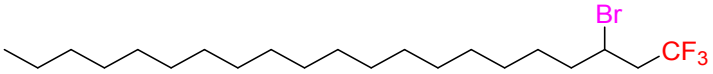
(3-Bromo-5,5,5-trifluoropentyl)benzene (2a)



2a

The product mixture was purified by silica gel column chromatography (hexane) to afford **2a** (67.2 mg, 60%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.31-7.35 (m, 2H), 7.22-7.27 (m, 3H), 4.10-4.16 (m, 1H), 2.73-2.95 (m, 4H), 2.14-2.63 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 140.1, 128.7, 128.5, 126.4, 125.3 (q, $^1J_{C-F}$ = 276.9 Hz), 44.3 (q, C−F, $^3J_{C-F}$ = 3.0 Hz), 43.2 (q, C−F, $^2J_{C-F}$ = 28.3 Hz), 40.1, 33.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.62 (t, J = 10.2 Hz, 3F); **IR** (thin film) ν 3064, 2857, 1496, 1433, 1325, 1027, 909, 665 cm^{-1}; **MS** (EI): *m/z* 280 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{11}H_{12}BrF_3$: 280.0074; Found: 280.0082. Characterization data matched with those reported in the literature.[9]

3-Bromo-1,1,1-trifluorohenicosane (2b)

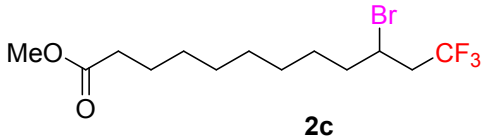


2b

The product mixture was purified by silica gel column chromatography (hexane) to afford **2b** (111.3 mg, 65%) as a white wax solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm

4.11-4.18 (m,1H), 2.61-2.85 (m, 2H), 1.84-1.87 (m, 2H), 1.26-1.31 (m, 32H), 0.88 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 125.4 (q, C−F, $^1J_{C-F}$ = 276.3 Hz), 45.1 (q, C−F, $^3J_{C-F}$ = 3.4 Hz), 43.1 (q, C−F, $^2J_{C-F}$ = 27.9 Hz), 38.5, 31.9, 29.70, 29.66, 29.64, 29.59, 29.5, 29.4, 28.7, 27.1, 22.7, 14.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.92 (t, J = 9.8 Hz, 3F); **IR** (thin film) ν 2924, 2853, 1466, 1368, 1258, 720, 596 cm^{-1}; **MS** (EI): *m/z* 428 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{21}H_{40}BrF_3$: 428.2265; Found: 428.2278.

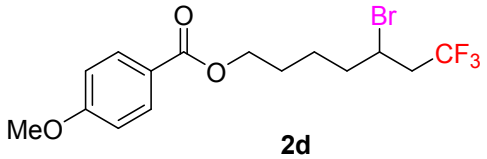
Methyl 10-bromo-12,12,12-trifluorododecanoate (2c)



2c

The product mixture was purified by silica gel column chromatography (hexane) to afford **2c** (83.5 mg, 60%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 4.11-4.17 (m, 1H), 3.66 (s, 3H), 2.63-2.82 (m, 2H), 2.30 (t, J = 7.6 Hz, 2H), 1.77-1.91 (m, 2H), 1.62 (t, J = 7.6 Hz, 2H), 1.25-1.36 (m, 10H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 174.3, 125.3 (q, C−F, $^1J_{C-F}$ = 276.5 Hz), 51.4, 45.1 (q, C−F, $^3J_{C-F}$ = 3.5 Hz), 43.1 (q, C−F, $^2J_{C-F}$ = 28.1 Hz), 38.5, 34.1, 29.13, 29.07, 29.0, 28.6, 27.1, 24.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.90 (t, J = 10.2 Hz, 3F); **IR** (thin film) ν 2931, 2857, 1739, 1459, 1259, 1150, 724, 664 cm^{-1}; **MS** (EI): *m/z* 346 M^+; **HRMS** (EI-TOF): *m/z* 346 M^+ Calculated for $C_{13}H_{22}BrF_3O_2$: 346.0755; Found: 346.0756.

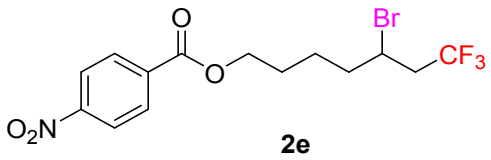
5-Bromo-7,7,7-trifluoroheptyl 4-methoxybenzoate (2d)



2d

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 30:1) to afford **2d** (106.1 mg, 69%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.97 (d, J = 8.8 Hz,2H), 6.91 (d, J = 8.8 Hz,2H), 4.31 (t, J = 6.4 Hz, 2H), 4.12-4.19 (m, 1H), 3.85 (s, 3H), 2.64-2.84 (m, 2H), 1.71-1.97 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 166.3, 163.4, 131.6, 125.3 (q, C−F, $^1J_{C-F}$ = 276.4 Hz), 122.7, 113.6, 64.1, 55.4, 44.7 (q, C−F, $^3J_{C-F}$ = 3.4 Hz), 43.1 (q, C−F, $^2J_{C-F}$ = 28.7 Hz), 38.0, 28.0, 23.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.82 (t, J = 10.2 Hz, 3F); **IR** (thin film) ν 2955, 2844, 1712， 1511, 1168, 1030, 771, 696, 595 cm^{-1}; **MS** (EI): *m/z* 382 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{15}H_{18}BrF_3O_3$: 382.0391; Found: 382.0396.

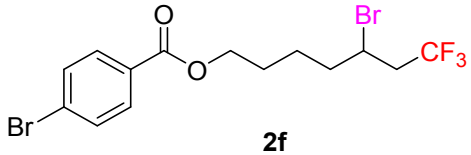
5-Bromo-7,7,7-trifluoroheptyl 4-nitrobenzoate (2e)



2e

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 30:1) to afford **2e** (111.6 mg, 70%) as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.26 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 9.2 Hz, 2H), 4.34-4.40 (m, 2H), 4.11-4.18 (m, 1H), 2.63-2.83 (m, 2H), 1.71-2.01 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 164.7, 150.6, 136.6, 130.7, 125.3 (q, C−F, $^1J_{C-F}$ = 276.4 Hz), 123.6, 65.4, 44.6, 43.1 (q, C−F, $^2J_{C-F}$ = 28.0 Hz), 37.9, 27.8, 23.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.81 (t, J = 10.2 Hz, 3F); **IR** (thin film) ν 3081, 2868, 1724, 1608, 1275, 1015, 719, 664 cm^{-1}; **MS** (EI): *m/z* 399 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{14}H_{15}BrF_3NO_4$: 397.0137; Found: 397.0140.

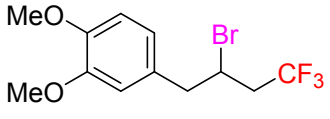
5-Bromo-7,7,7-trifluoroheptyl 4-bromobenzoate (2f)



2f

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 50:1) to afford **2f** (119.3 mg, 69%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.87 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.8 Hz, 2H), 4.31 (t, J = 6.4 Hz, 2H), 4.08-4.17 (m, 1H), 2.62-2.82 (m, 2H), 1.68-1.97 (m, 6H); **^{13}C NMR**(100 MHz, $CDCl_3$) δ ppm 164.7, 150.6, 135.7, 130.7, 125.3 (q, C−F, $^1J_{C-F}$ = 276.4 Hz), 123.6, 65.4, 44.6, 43.1 (q, C−F, $^2J_{C-F}$ = 28.0 Hz), 37.9, 27.8, 23.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -64.54 (t, J = 10.2 Hz, 3F); **IR** (thin film) ν 2958, 2876, 1716, 1590, 1397, 1266, 847, 755 cm^{-1}; **MS** (ESI): *m/z* 448 $[M+NH_4]^+$; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{14}H_{16}Br_2F_3O_2$: 430.9464; Found: 430.9456.

4-(2-Bromo-4,4,4-trifluorobutyl)-1,2-dimethoxybenzene (2g)

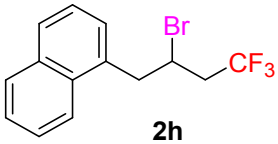


2g

The product mixture was purified by silica gel column chromatography (hexane) to afford **2g** (86.1 mg, 66%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 6.83 (d,

J = 8.0 Hz, 1H), 6.72-6.76 (m, 2H), 4.26-4.33 (m, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.16 (d, J = 7.2 Hz, 2H), 2.66-2.75 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 149.0, 148.3, 129.5, 125.4 (q, C−F, $^1J_{C-F}$ = 276.1 Hz), 121.5, 111.4, 111.3, 55.93, 55.88, 44.7, 44.4 (q, C−F, $^3J_{C-F}$ = 2.9 Hz), 41.8 (q, C−F, $^2J_{C-F}$ = 28.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.59 (t, J = 10.2 Hz, 3F); **IR** (thin film) ν 2926, 2851, 1517, 1261, 1028, 766, 594 cm^{-1}; **MS** (EI): *m/z* 232 M^+; **HRMS** (EI-TOF): *m/z* M^+ 326. Calculated for $C_{12}H_{14}BrF_3O_2$: 326.0129; Found: 326.0135.

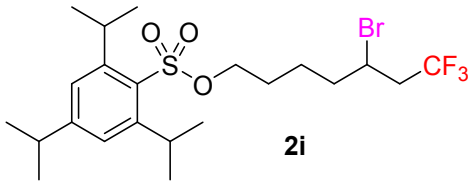
1-(2-Bromo-4,4,4-trifluorobutyl)naphthalene (2h)



2h

The product mixture was purified by silica gel column chromatography (hexane) to afford **2h** (91.8 mg, 73%) as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.90-7.95 (m, 2H), 7.83 (d, J = 8.0 Hz, 1H), 7.53-7.59 (m, 2H), 7.46 (t, J = 8.0 Hz, 1H), 7.38 (d, J = 6.8 Hz, 1H), 4.48-4.55 (m, 1H), 3.68-3.71 (m, 2H), 2.75-2.89 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 134.0, 133.1, 131.6, 129.2, 128.4, 128.1, 126.6, 125.9, 125.4 (q, C−F, $^1J_{C-F}$ = 276.2 Hz), 125.3, 122.8, 43.4 (q, C−F, $^3J_{C-F}$ = 2..9 Hz), 42.6, 42.5 (q, C−F, $^2J_{C-F}$ = 28.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.44 (t, J = 10.2 Hz, 3F); **IR** (thin film) ν 3063, 2932, 1425, 1018, 862, 734, 530 cm^{-1}; **MS** (EI): *m/z* 316 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{14}H_{12}BrF_3$: 316.0069; Found: 316.0067.

5-Bromo-7,7,7-trifluoroheptyl 2,4,6-triisopropylbenzenesulfonate (2i)

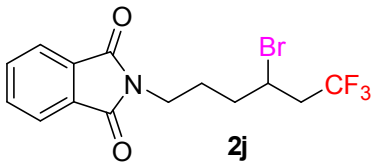


2i

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 50:1) to afford **2i** (209.4 mg, 68%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.19 (s, 2H), 4.06-4.18 (m, 5H), 2.88-2.95 (m, 1H), 2.62-2.82 (m, 2H), 1.68-1.93 (m, 6H), 1.26 (d, J = 6.8 Hz, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 153.7, 150.8, 129.4, 125.2 (q, C−F, $^1J_{C-F}$ = 276.3 Hz), 123.8, 68.9, 44.4 (q, C−F, $^3J_{C-F}$ = 3.0 Hz), 42.5 (q, C−F, $^2J_{C-F}$ = 28.1 Hz), 37.8, 34.2, 29.6, 28.2, 24.7, 23.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.86 (t, J = 10.2 Hz, 3F); **IR** (thin film) ν 2961, 2871, 1600, 1462,

1178, 940, 664, 562cm^{-1}; **MS** (EI): *m/z* 514 M^{+}; **HRMS** (EI-TOF): *m/z* 514 M^{+} Calculated for $C_{22}H_{34}BrF_3O_3S$: 514.1364; Found: 514.1368.

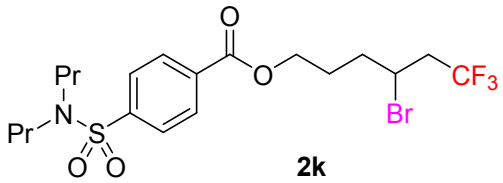
2-(4-Bromo-6,6,6-trifluorohexyl)isoindoline-1,3-dione (2j)



2j

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 10:1) to afford **2j** (101.6 mg, 70%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.84 (dd, *J* = 8.8 Hz, 5.6 Hz, 2H), 7.72 (dd, *J* = 8.8 Hz, 5.6 Hz, 2H), 4.16-4.21 (m, 1H), 3.73 (t, *J* = 6.4 Hz, 2 H), 2.62-2.81 (m, 2H), 1.82-2.03 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 168.3, 134.0, 132.0, 125.2 (q, C−F, $^{1}J_{C-F}$ = 276.4 Hz), 123.3, 43.9 (q, C−F, $^{3}J_{C-F}$ = 3.4 Hz), 43.1 (q, C−F, $^{2}J_{C-F}$ = 28.4 Hz), 36.9, 36.1, 26.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -64.07 (t, *J* = 9.8 Hz, 3F); **IR**(thin film) ν 2940, 1772, 1716, 1397, 1150, 720, 595 cm^{-1}; **MS** (EI): *m/z* 363 M^{+}; **HRMS** (EI-TOF): *m/z* M^{+} Calculated for $C_{14}H_{13}BrF_3NO_2$: 363.0082; Found: 363.0086.

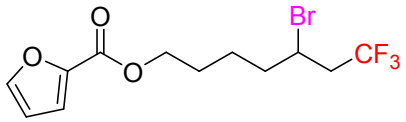
4-Bromo-6,6,6-trifluorohexyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (2k)



2k

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 7:1) to afford **2k** (160.3 mg, 80%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 8.14 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H), 4.39-4.42 (m, 2H), 4.20-4.25 (m, 1H), 3.10 (t, *J* = 7.6 Hz, 4H), 2.68-2.89 (m, 2H), 2.09-2.13 (m, 2H), 1.96-2.00 (m, 2H), 1.50-1.59 (m, 4H), 0.86 (t, *J* = 7.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 165.2, 144.4, 133.3, 130.2, 127.1, 125.2 (q, C−F, $^{1}J_{C-F}$ = 276.5Hz), 64.4, 49.9, 44.1 (q, C−F, $^{3}J_{C-F}$ = 3.2 Hz), 43.1 (q, C−F, $^{2}J_{C-F}$ = 28.4 Hz), 34.9, 26.5, 21.9, 11.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.81 (t, *J* = 10.2 Hz, 3F); **IR** (thin film) ν 2932, 2876, 1467, 1343, 1088, 1018, 799, 741 cm^{-1}; **MS** (ESI): *m/z* 502 [M+H]$^{+}$; **HRMS** (ESI-TOF): *m/z* [M+H]$^{+}$ Calculated for $C_{19}H_{28}BrF_3NO_4S$: 502.0869; Found: 502.0867.

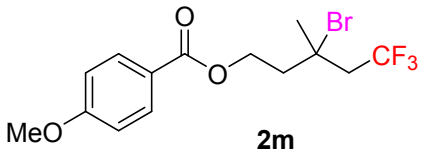
5-Bromo-7,7,7-trifluoroheptyl furan-2-carboxylate (2l)



2l

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 30:1) to afford **2l** (75.2 mg, 55%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.58-7.59 (m, 1H), 7.18-7.19 (m, 1H), 6.51-6.52 (m, 1H), 4.33 (t, J = 6.4 Hz, 2H), 4.13-4.19 (m, 1H), 2.66-2.88 (m, 2H), 1.71-2.82 (m, 4H), 1.54-1.64 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 158.7, 146.3, 144.7, 125.3 (q, C−F, $^1J_{C-F}$ = 278.4 Hz), 117.9, 111.8, 64.4, 44.6 (q, C−F, $^3J_{C-F}$ = 3.2 Hz), 43.1 (q, C−F, $^2J_{C-F}$ = 28.2 Hz), 38.0, 27.9, 23.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.83 (t, J = 10.2 Hz, 3F); **IR** (thin film) ν 2951, 1726, 1581, 1390, 1014, 885, 664 cm^{-1}; **MS** (EI): *m/z* 342 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{12}H_{14}BrF_3O_3$: 342.0078; Found: 345.0077.

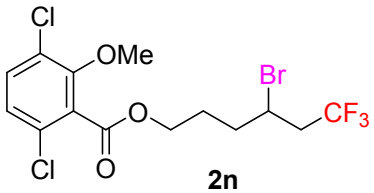
3-Bromo-5,5,5-trifluoro-3-methylpentyl 4-methoxybenzoate (2m)



2m

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 30:1) to afford **2m** (103.0 mg, 70%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.98 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 4.56-4.63 (m, 2H), 3.85 (s, 3H), 2.90-2.99 (m, 2H), 2.34-2.48 (m, 2H), 1.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 166.1, 163.5, 131.6, 125.0 (q, C−F, $^1J_{C-F}$ = 277.9 Hz), 122.3, 113.7, 62.4, 59.6 (q, C−F, $^3J_{C-F}$ = 2.8 Hz), 55.4, 48.3 (q, C−F, $^2J_{C-F}$ = 27.5 Hz), 43.2, 23.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -60.50 (t, J = 10.5 Hz, 3F); **IR** (thin film) ν 2965, 2841, 1715, 1606, 1512, 1257, 1030, 770, 634 cm^{-1}; **MS** (ESI): *m/z* 386 $[M+NH_4]^+$; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{14}H_{17}BrF_3O_3$: 369.0308; Found: 369.0304.

4-Bromo-6,6,6-trifluorohexyl 3,6-dichloro-2-methoxybenzoate (2n)

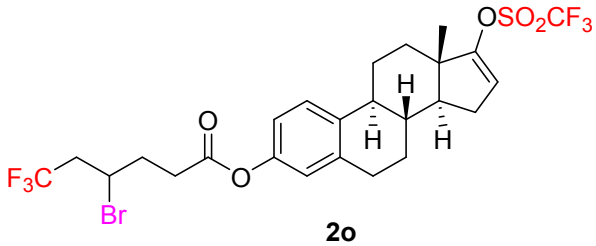


2n

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 30:1) to afford **2n** (138.9 mg, 80%) as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.36 (d, J = 8.8 Hz, 1H), 7.12 (d, J = 8.8 Hz, 1H),4.43 (t, J = 5.2 Hz, 2H), 4.15-

4.22 (m, 1H), 3.91 (s, 3H), 2.64-2.89 (m, 2H), 2.07-2.13 (m, 2H), 1.91-1.97 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 164.5, 153.8, 131.9, 130.4, 129.5, 126.8, 125.9, 124.7 (q, C−F, $^1J_{C-F}$ = 276.4 Hz), 64.9, 62.3, 44.2 (q, C−F, $^3J_{C-F}$ = 3.1 Hz), 43.2 (q, C−F, $^2J_{C-F}$ = 28.4 Hz), 34.9, 26.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.83 (t, *J* = 10.2 Hz, 3F); **IR** (thin film) ν 3080, 2854, 1881, 1404, 872, 684, 472 cm^{-1}; **MS** (ESI): *m/z* 454 $[M+NH_4]^+$; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{14}H_{15}BrCl_2F_3O_3$: 436.9528; Found: 436.9525.

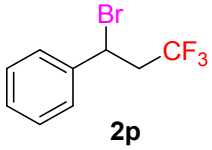
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-(trifluoromethylsulfonyloxy)-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-bromo-6,6,6-trifluorohexanoate (2o)



2o

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 20:1) to afford **2o** (145.3 mg, 58%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.27 (d, *J* = 8.8 Hz, 1H), 6.86 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 5.62-5.64 (m, 1H), 4.27-4.34 (m, 1H), 2.90-2.93 (m, 2H), 2.88-2.83 (m, 2H), 2.79-2.70 (m, 1H), 2.31-2.46 (m, 4H), 2.07-2.21 (m, 2H), 1.89-1.95 (m, 2H), 1.76-1.84 (m, 1H), 1.58-1.70 (m, 4H), 1.42-1.48 (m, 1H), 1.00 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 171.1, 159.2, 148.4, 138.0, 137.7, 126.1, 125.1 (q, C−F, $^1J_{C-F}$ = 276.4 Hz), 121.5, 118.63 (q, C−F, $^1J_{C-F}$ = 318.6 Hz), 118.59, 114.5, 53.6, 45.0, 44.4, 43.8 (q, C−F, $^3J_{C-F}$ = 3.1 Hz), 43.3 (q, C−F, $^2J_{C-F}$ = 28.3 Hz), 36.3, 33.4, 32.7, 32.1, 29.2, 28.4, 26.5, 25.7, 15.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.76 (t, *J* = 10.5 Hz, 3F), -73.60 (s, 3F); **IR** (thin film) ν 2935, 2861, 1628, 1493, 1291, 1072, 867, 836, 603 cm^{-1}; **MS** (ESI-TOF): *m/z* 650 $[M+NH_4]^+$; **HRMS** (DART POSITIVE): *m/z* $[M+H]^+$ Calculated for $C_{25}H_{28}BrF_6O_5S$: 633.0740; Found: 633.0726.

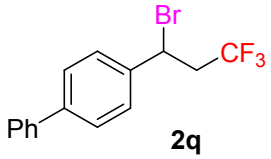
(1-Bromo-3,3,3-trifluoropropyl)benzene (2p)



2p

The product mixture was purified by silica gel column chromatography (hexane) to afford **2p** (46.0 mg, 40%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.31-7.42 (m, 5H), 5.15 (t, J = 7.2 Hz, 1H), 3.06-3.20 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 140.2, 129.05, 128.95, 127.1, 124.8 (q, C−F, $^1J_{C-F}$ = 276.7 Hz), 43.9 (q, C−F, $^2J_{C-F}$ = 28.4 Hz), 43.5 (q, C−F, $^3J_{C-F}$ = 3.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -64.21 (t, J = 9.8 Hz, 3F); **IR** (thin film) ν 2924, 2853, 1261, 800, 694, 609 cm^{-1}; **MS** (EI): *m/z* 252 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_9H_8BrF_3$: 251.9756; Found: 251.9754.

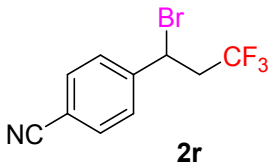
4-(1-Bromo-3,3,3-trifluoropropyl)biphenyl (2q)



2q

The product mixture was purified by silica gel column chromatography (hexane) to afford **2q** (52.4 mg, 40%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.58-7.61 (m, 4H), 7.43-7.49 (m, 4H), 7.35-7.39 (m, 1H), 5.21 (t, J = 3.8 Hz, 1H), 3.10-3.22 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 142.0, 140.2, 139.1, 128.9, 127.72, 127.65, 127.5, 127.1, 124.8 (q, C−F, $^1J_{C-F}$ = 273.6 Hz), 43.9 (q, C−F, $^2J_{C-F}$ = 28.2 Hz), 43.3 (q, C−F, $^3J_{C-F}$ = 3.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -64.13 (t, J = 9.8 Hz, 3F); **IR** (thin film) ν 3031, 2925, 1449, 1176, 1008, 768, 697, 606 cm^{-1}; **MS** (EI): *m/z* 330 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{15}H_{12}BrF_3$: 328.0069; Found: 328.0063. Characterization data matched with those reported in the literature.[10]

4-(1-Bromo-3,3,3-trifluoropropyl)benzonitrile (2r)

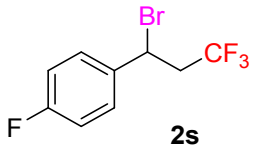


2r

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **2r** (56.3 mg, 51%) as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.65 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 5.12 (t, J = 6.8 Hz, 1H), 3.01-3.21 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 144.9, 132.8, 128.0, 124.5 (q, C−F, $^1J_{C-F}$ = 276.6 Hz), 118.1, 113.0, 43.6 (q, C−F, $^2J_{C-F}$ = 28.7 Hz), 41.5 (q, C−F, $^3J_{C-F}$ = 3.6 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -64.07 (t, J = 9.8 Hz, 3F); **IR** (thin film)

ν 2924, 2852, 2231, 1609, 1392, 1141, 746, 647 cm^{-1}; **MS** (EI): *m/z* 277 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{10}H_7NF_3Br$: 276.9714; Found: 276.9720.

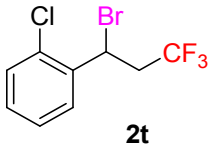
1-(1-Bromo-3,3,3-trifluoropropyl)-4-fluorobenzene (2s)



2s

The product mixture was purified by silica gel column chromatography (hexane) to afford **2s** (47.5 mg, 44%) as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.38-7.41 (m, 2H), 7.04-7.08 (m, 2H), 5.15 (t, *J* = 7.6 Hz, 1H), 3.03-3.18 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 162.7 (d, C−F, $^1J_{C-F}$ = 247.4 Hz), 136.1, 129.0, 128.9, 124.6 (q, C−F, $^1J_{C-F}$ = 276.6 Hz), 116.1, 115.9, 43.7 (q, C−F, $^2J_{C-F}$ = 28.2 Hz), 42.6 (q, C−F, $^3J_{C-F}$ = 3.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -64.13 (t, *J* = 9.4 Hz, 3F), -111.91- -111.84 (m, 1F); **IR** (thin film) ν 2960, 2851,1508, 1260, 1014, 799 cm^{-1}; **MS** (EI): *m/z* 272 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_9H_7BrF_4$: 269.9667; Found: 269.9675.

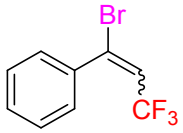
1-(1-Bromo-3,3,3-trifluoropropyl)-2-chlorobenzene (2t)



2t

The product mixture was purified by silica gel column chromatography (hexane) to afford **2t** (57.2 mg, 50%) as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.54 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.37 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H),7.31 (td, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.25 (td, *J* = 7.6 Hz, 1.6 Hz, 1H), 5.69 (t, *J* = 7.2 Hz, 1H), 3.08-3.17 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 137.4, 132.6, 130.12, 130.07, 128.8, 127.6, 124.8 (q, C−F, $^1J_{C-F}$ = 276.9 Hz), 42.9 (q, C−F, $^2J_{C-F}$ = 28.8 Hz), 38.7 (q, C−F, $^3J_{C-F}$ = 3.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -64.34 (t, *J* = 9.4 Hz, 3F); **IR** (thin film) ν 3067, 2928, 1573, 1477, 1323, 1142, 929, 615 cm^{-1}; **MS** (EI): *m/z* 288 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_9H_7BrClF_3$: 285.9372; Found: 285.9378.

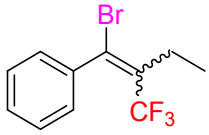
(1-Bromo-3,3,3-trifluoroprop-1-enyl)benzene (4a)



4a

The product mixture was purified by silica gel column chromatography (hexane) to afford **4a** (44.5 mg, 51%, *Z*/*E*= 15:85) as a light yellow oil. (The *Z* and *E* isomers were assigned by comparing their chemical shifts in the ^{19}F NMR spectrum. Due to the "steric deshielding", the fluorine signals of ***E*-4a** with the CF_3 group *cis* to phenyl group, are more deshielded than those of ***Z*-4a** with the CF_3 group *trans* to phenyl group. This result is consistent with previous reports[11,12] for analogous chloro/iodo- and trifluoromethyl-substituted styrene.) **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.40-7.43 (m, 5H), 6.42 (q, J = 7.2 Hz, 0.82H), 6.55 (q, J = 7.2 Hz, 0.18H); **^{13}C NMR** (100 MHz, $CDCl_3$) (major isomer) δ ppm 137.1, 135.8 (q, C−F, $^3J_{C-F}$ = 6.4Hz), 130.0, 128.2, 128.0 (q, C−F, $^4J_{C-F}$ = 1.8 Hz), 121.8 (q, C−F, $^2J_{C-F}$ = 35.0 Hz), 121.5 (q, C−F, $^1J_{C-F}$ = 270.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -57.28 (d, J = 7.1 Hz, 2.54F), -59.45 (d, J = 7.1 Hz, 0.46F); **IR** (thin film) ν 3072, 1491, 1310, 1028, 757, 619, 591 cm^{-1}; **MS** (EI): *m/z* 250 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_9H_6BrF_3$: 249.9599; Found: 249.9597.

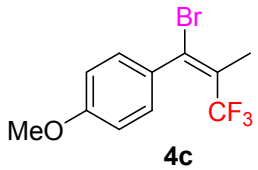
(1-Bromo-2-(trifluoromethyl)but-1-enyl)benzene (4b)



4b

The product mixture was purified by silica gel column chromatography (hexane) to afford **4b** (44.5 mg, 40%, *Z*/*E*= 8:92) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.34-7.37 (m, 3H), 7.28-7.30 (m, 2H), 2.63 (q, J = 7.6 Hz, 1.81H), 2.18 (q, J = 7.6 Hz, 0.19H), 1.25 (t, J = 7.6 Hz, 2.71H), 1.03 (t, J = 7.2 Hz, 0.29H); **^{13}C NMR** (100 MHz, $CDCl_3$) (major isomer) δ ppm 139.8, 132.7 (q, C−F, $^2J_{C-F}$ = 28.0 Hz), 132.3 (q, C−F, $^3J_{C-F}$ = 4.2 Hz), 129.0, 128.0, 127.9 (q, C−F, $^4J_{C-F}$ = 1.7 Hz), 123.0 (q, C−F, $^1J_{C-F}$ = 275.0 Hz), 27.0, 12.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -57.64 (s, 2.75F), -60.88 (s, 0.25F); **IR** (thin film) ν 3061, 2977, 2881, 1639, 1596, 868, 776, 569 cm^{-1}; **MS** (EI): *m/z* 278 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{11}H_{10}BrF_3$: 277.9912; Found: 277.9908.

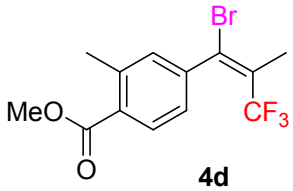
(*E*)-1-(1-bromo-3,3,3-trifluoro-2-methylprop-1-enyl)-4-methoxybenzene (4c)



4c

The product mixture was purified by silica gel column chromatography (hexane) to afford **4c** (47.0 mg, 40%) as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.24 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 160.0, 132.5 (q, C−F, $^{3}J_{C-F}$ = 4.1 Hz), 132.1, 129.5 (q, C−F, $^{4}J_{C-F}$ = 2.1 Hz), 126.7 (q, C−F, $^{2}J_{C-F}$ = 29.1 Hz), 122.7 (q, C−F, $^{1}J_{C-F}$ = 274.1 Hz), 113.4, 55.3, 19.6 (q, C−F, $^{3}J_{C-F}$ = 2.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -59.09 (s, 3F); **IR** (thin film) ν 3005, 2839, 1645, 1577, 1415, 664, 528 cm^{-1}; **MS** (EI): *m/z* 294 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{11}H_{10}BrF_3O$: 293.9862; Found: 293.9866.

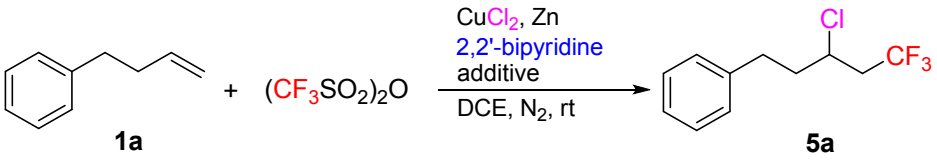
(*E*)-methyl 4-(1-bromo-3,3,3-trifluoro-2-methylprop-1-enyl)-2-methylbenzoate (4d)



4d

The product mixture was purified by silica gel column chromatography (hexane/EtOAc = 50:1) to afford **4d** (67.9 mg, 50%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.88 (s, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 2.32 (s, 3H), 2.21 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 166.6, 143.3, 135.5, 131.3, 130.6, 129.9 (q, C−F, $^{3}J_{C-F}$ = 4.1 Hz), 128.2 (q, C−F, $^{2}J_{C-F}$ = 29.6 Hz), 128.0 (q, C−F, $^{4}J_{C-F}$ = 1.7 Hz), 126.9, 122.5 (q, C−F, $^{1}J_{C-F}$ = 274.4 Hz), 52.2, 19.0, 18.7 (q, $^{3}J_{C-F}$ = 1.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -61.29 (s, 3F); **IR** (thin film) ν 2953, 2926, 2854, 1727, 1654, 1437, 1306, 1173, 1122, 764 cm^{-1}; **MS** (EI): *m/z* 336 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{13}H_{12}BrF_3O_2$: 335.9967; Found: 335.9972.

4. Optimization of Chlorotrifluoromethylation Conditions

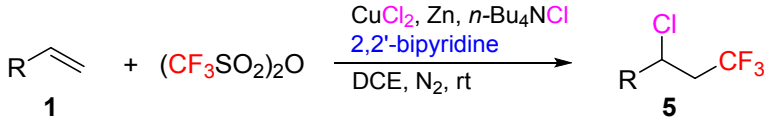


1a **5a**

entry	additive	yield (%)[b]
1	—	30
2	*n*-Bu_4NCl (2.0 equiv)	58
3	NaCl (2.0 equiv)	33
4	$CuCl_2$ (1.0 equiv)	54

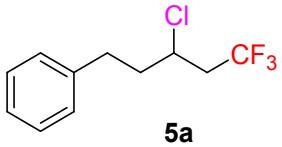
[a]Reaction conditions: **1a** (0.2 mmol), Tf_2O (0.8 mmol), 2,2′-bipyridine (0.8 mmol), $CuCl_2$ (0.1 mmol), Zn (0.2 mmol), additive, DCE (2.0 mL), N_2, rt, overnight. [b]Yields were determined by ^{19}F NMR spectroscopy using trifluoromethylbenzene as an internal standard.

5. General Procedures for Chlorotrifluoromethylation of Alkenes



A 10 mL schlenk tube was charged with bipyridine (249.8 mg, 1.6 mmol), *n*-Bu_4NCl (222.3 mg, 0.8 mmol), $CuCl_2$ (26.9 mg, 0.2 mmol), zinc powder (26.0 mg, 0.4 mmol), and DCE (4.0 mL) under N_2 atmosphere. Alkene (0.4 mmol) (if the substrate was solid, it was added before DCE) and Tf_2O (0.27 mL, 1.6 mmol) was subsequently added to the reaction. The resulting mixture was stirred at room temperature overnight. After the reaction was complete, the reaction mixture was filtrated through celite, washed with DCM. The filtration was concentrated in vacuo. The resulting residue was purified by column chromatography to give the pure product.

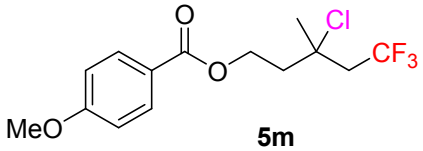
(3-Chloro-5,5,5-trifluoropentyl)benzene (5a)



5a

The product mixture was purified by silica gel column chromatography (hexane) to afford **5a** (52.9 mg, 56%) as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.30-7.33 (m, 2H), 7.20-7.25 (m, 3H), 4.05-4.12 (m, 1H), 2.89-2.96 (m, 1H), 2.75-2.82 (m, 1H), 2.49-2.69 (m, 2H), 2.01-2.20 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 140.1, 128.6, 128.5, 126.4, 125.2 (q, C−F, $^1J_{C-F}$ = 275.9 Hz), 53.4 (q, C−F, $^3J_{C-F}$ = 3.3 Hz), 42.5 (q, C−F, $^2J_{C-F}$ = 28.2 Hz), 39.6, 32.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.70 (t, J = 10.2 Hz, 3F); **IR** (thin film) ν 3064, 2863, 1434, 1028, 8327, 665 cm^{-1}; **MS** (EI): *m/z* 236 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{11}H_{12}ClF_3$: 236.0574; Found: 236.0577. Characterization data matched with those reported in the literature.[13]

3-Chloro-5,5,5-trifluoro-3-methylpentyl 4-methoxybenzoate (5m)

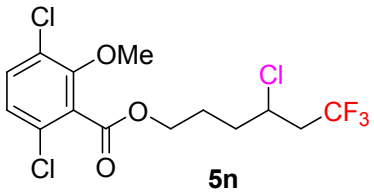


5m

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 25:1) to afford **5m** (89.7 mg, 70%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.98 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 4.55-4.60 (m, 2H), 3.86 (s, 3H),

2.72-2.84 (m, 2H), 2.31-2.41 (m, 2H), 1.79 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 166.1, 163.5, 131.6, 124.9 (q, C−F, $^1J_{C-F}$ = 277.0 Hz), 122.3, 113.7, 65.5 (q, C−F, $^3J_{C-F}$ = 2.3 Hz), 61.0, 55.4, 47.1 (q, C−F, $^2J_{C-F}$ = 27.5 Hz), 42.2, 30.4 (q, C−F, $^4J_{C-F}$ = 1.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -60.58 (t, *J* = 10.5 Hz, 3F); **IR** (thin film) ν 2964, 2842, 1715, 1606, 1512, 1258, 1030, 848, 770 cm^{-1}; **MS** (EI): *m/z* 324 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{14}H_{16}ClF_3O_3$: 324.0735; Found: 324.0729.

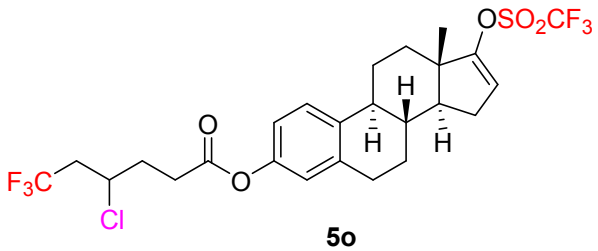
4-Chloro-6,6,6-trifluorohexyl 3,6-dichloro-2-methoxybenzoate (5n)



5n

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 8:1) to afford **5n** (108.2mg, 69%) as a light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.35 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 1H), 4.43 (t, *J* = 5.6 Hz, 2H), 4.13-4.18 (m, 1H), 3.90 (s, 3H), 2.50-2.69 (m, 2H), 2.01-2.11 (m, 2H), 1.83-1.95 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 164.5, 153.8, 131.9, 130.4, 129.5, 126.8, 125.8, 125.1 (q, C−F, $^1J_{C-F}$ = 275.9 Hz), 65.0, 62.3, 53.6 (q, C−F, $^3J_{C-F}$ = 3.2 Hz), 42.5 (q, C−F, $^2J_{C-F}$ = 28.4 Hz), 34.5, 25.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.83 (t, *J* = 10.2 Hz, 3F); **IR** (thin film) ν 3081, 2876, 1881, 1444, 1009, 872, 692, 456 cm^{-1}; **MS** (EI): *m/z* 392 M^+; **HRMS** (EI-TOF): *m/z* M^+ Calculated for $C_{14}H_{14}Cl_3F_3O_3$: 391.9955; Found: 391.9959.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-(trifluoromethylsulfonyloxy)-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 4-chloro-6,6,6-trifluorohexanoate (5o)

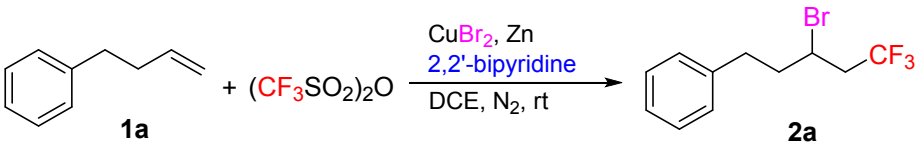


5o

The product mixture was purified by silica gel column chromatography (hexane/ EtOAc = 8:1) to afford **5o** (174.1 mg, 74%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ppm 7.26 (d, *J* = 8.4 Hz, 1H), 6.85 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 6.81 (d, *J* =2.4 Hz, 1H), 5.62-5.63 (m, 1H), 4.25-4.32 (m, 1H), 2.89-2.93 (m, 2H), 2.81-2.86 (m, 1H), 2.54-

2.76 (m, 2H), 2.30-2.42 (m, 4H), 2.03-2.14 (m, 2H), 1.88-1.96 (m, 2H), 1.76-1.83 (m, 1H), 1.55-1.70 (m, 4H), 1.39-1.50 (m, 1H), 1.00 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ppm 171.2, 159.2, 148.4, 138.0, 137.7, 126.1, 125.0 (q, C−F, $^1J_{C-F}$ = 275.9 Hz), 121.5, 118.60 (q, C−F, $^1J_{C-F}$ = 318.4 Hz), 118.57, 114.5, 53.6, 53.2 (q, C−F, $^3J_{C-F}$ = 3.3 Hz), 45.0, 44.4, 42.6 (q, C−F, $^2J_{C-F}$ = 28.6 Hz), 36.3, 32.9, 32.7, 30.8, 29.2, 28.4, 26.5, 25.6, 15.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ ppm -63.76 (t, *J* = 10.2 Hz, 3F), 73.58 (s, 3F); **IR** (thin film) ν 2935, 2862, 1757, 1628, 1493, 1072, 1022, 836, 604 cm^{-1}; **MS** (ESI): *m/z* 606 $[M+NH_4]^+$; **HRMS** (ESI-TOF): *m/z* $[M+H]^+$ Calculated for $C_{25}H_{28}ClF_6O_5S$: 589.1245; Found: 589.1243.

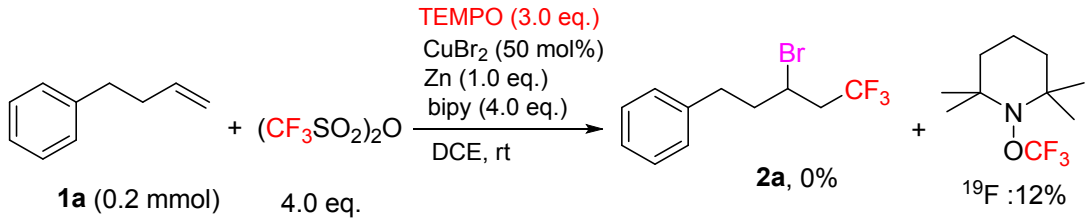
6. Scale-Up Experiment



A 25 mL schlenk tube was charged with bipyridine (624.5 mg, 4.0 mmol), $CuBr_2$ (111.5 mg, 0.5 mmol), zinc powder (65.0 mg, 1.0 mmol), and DCE (10 mL) under N_2 atmosphere. 4-Phenyl-1-butylene (0.15 mL, 1.0 mmol) and Tf_2O (0.68 mL, 4.0 mmol) was subsequently added to the reaction. The resulting mixture was stirred at room temperature overnight. After the reaction was complete, the reaction mixture was filtrated through celite, washed with DCM. The filtration was concentrated in vacuo. The resulting residue was purified by column chromatography (hexane) to afford **2a** (173.4 mg, 62%) as a yellow oil.

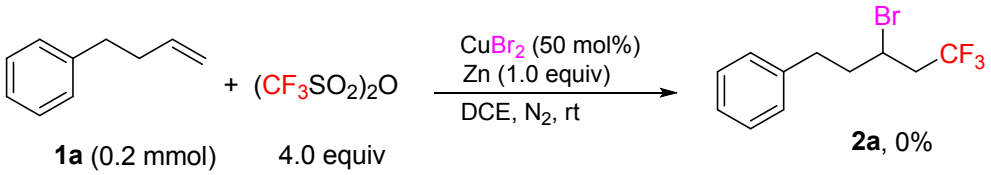
7. Mechanistic Experiments

Radical Trapping Experiment



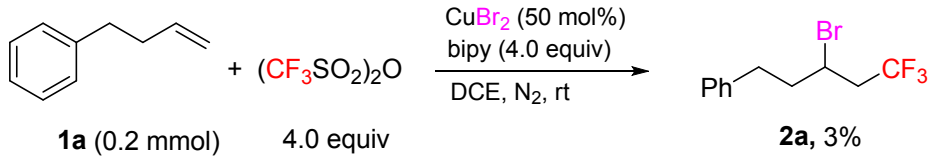
A 10 mL schlenk tube was charged with bipyridine (124.8 mg, 0.8 mmol), TEMPO (93.6 mg, 0.6 mmol), $CuBr_2$ (22.3 mg, 0.1 mmol), zinc powder (13.0 mg, 0.2 mmol), and DCE (2.0 mL) under N_2 atmosphere. But-3-en-1-ylbenzene (26.4 mg, 0.2 mmol) and Tf_2O (0.13 mL, 0.8 mmol) was subsequently added to the reaction. The resulting mixture was stirred at room temperature overnight. The reaction mixture was filtrated and analyzed by ^{19}F NMR. The ^{19}F NMR spectroscopy indicated that the desired product **2a** was completely inhibited and TEMPO−CF_3 adduct was formed in 12% yield.

Reaction without bipyridine



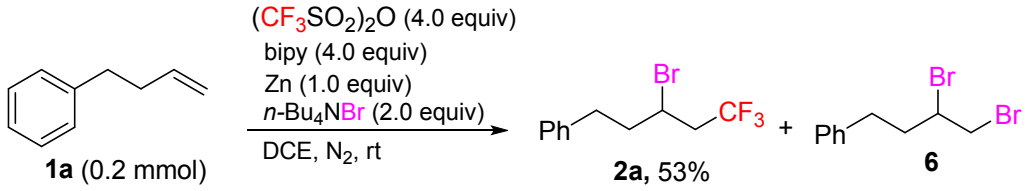
A 10 mL schlenk tube was charged with $CuBr_2$ (22.3 mg, 0.1 mmol), zinc powder (13.0 mg, 0.2 mmol), and DCE (2.0 mL) under N_2 atmosphere. But-3-en-1-ylbenzene (26.4 mg, 0.2 mmol) and Tf_2O (0.13 mL, 0.8 mmol) was subsequently added to the reaction. The resulting mixture was stirred at room temperature overnight. The reaction mixture was filtrated and analyzed by ^{19}F NMR. The ^{19}F NMR spectroscopy indicated that the desired product **2a** was not formed.

Reaction without Zn powder



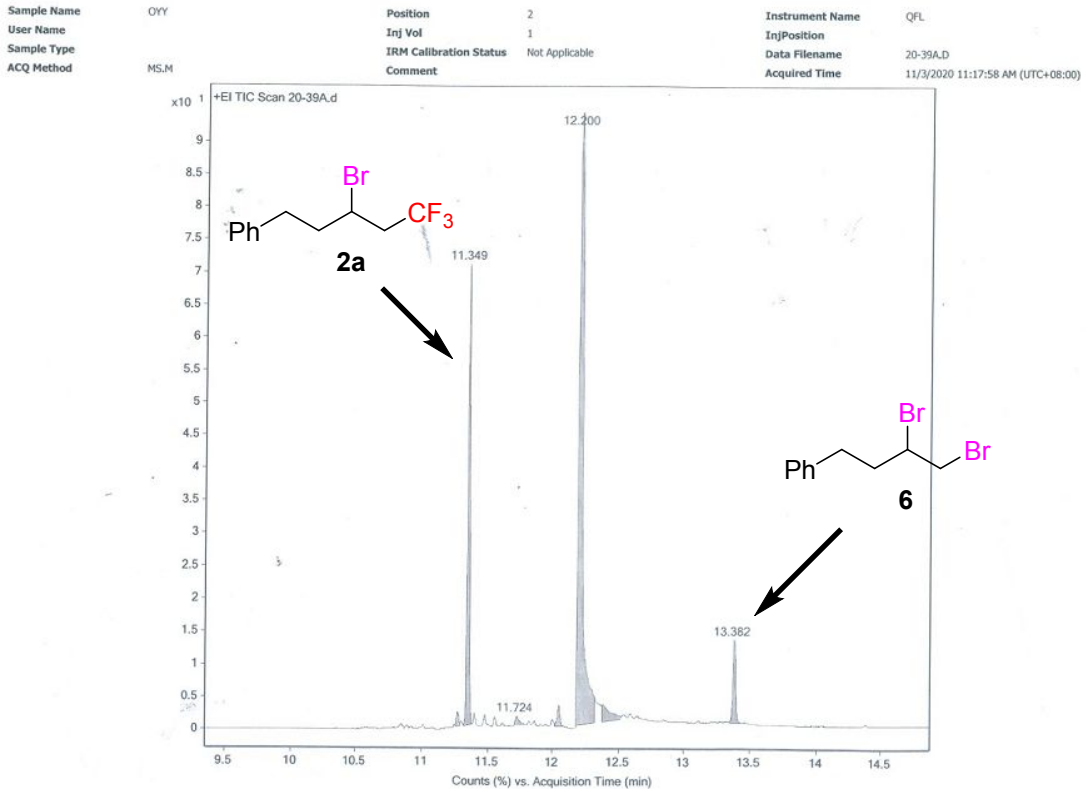
A 10 mL schlenk tube was charged with bipyridine (124.8 mg, 0.8 mmol), $CuBr_2$ (22.3 mg, 0.1 mmol), and DCE (2.0 mL) under N_2 atmosphere. But-3-en-1-ylbenzene (26.4 mg, 0.2 mmol) and Tf_2O (0.13 mL, 0.8 mmol) was subsequently added to the reaction. The resulting mixture was stirred at room temperature overnight. The reaction mixture was filtrated and analyzed by ^{19}F NMR. The ^{19}F NMR spectroscopy indicated that the desired product **2a** was formed in 3% yield.

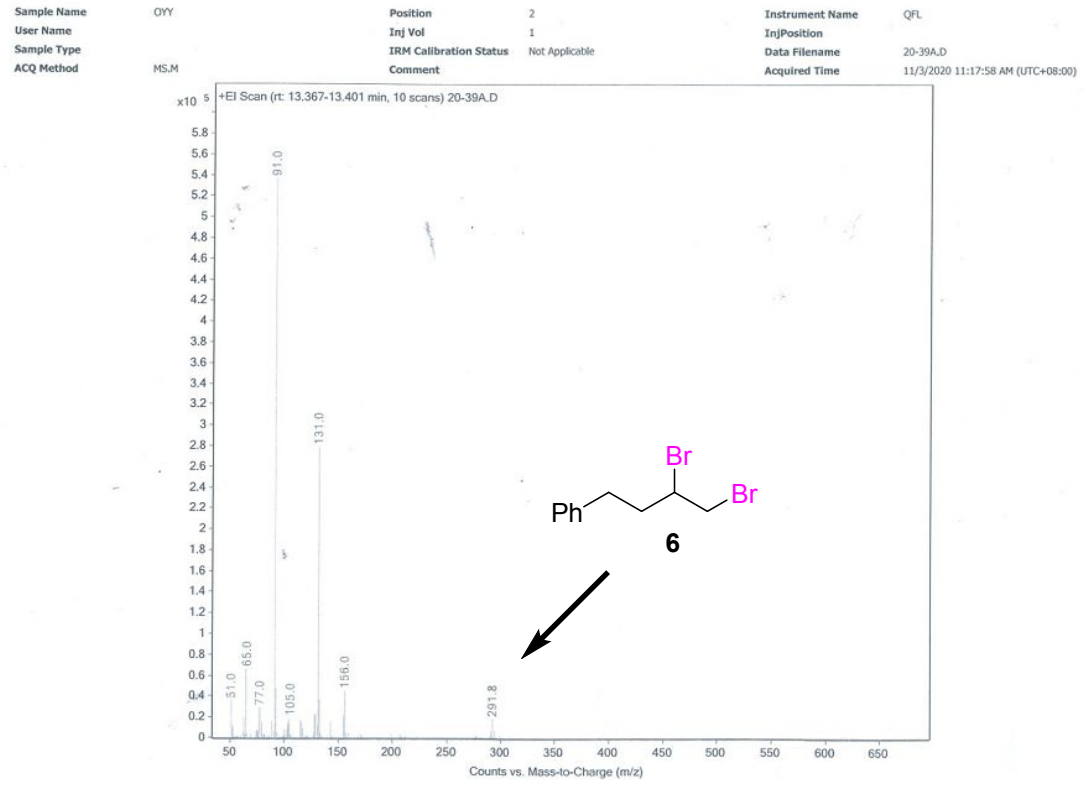
Zn-promoted reaction



A 10 mL schlenk tube was charged with bipyridine (124.8 mg, 0.8 mmol), *n*-Bu_4NBr (129.0 mg, 0.4 mmol), zinc powder (13.0 mg, 0.2 mmol), and DCE (2.0 mL) under N_2 atmosphere. But-3-en-1-ylbenzene (26.4 mg, 0.2 mmol) and Tf_2O (0.13 mL, 0.8 mmol) was subsequently added to the reaction. The resulting mixture was stirred at room temperature overnight. The reaction mixture was filtrated and analyzed by ^{19}F NMR. The ^{19}F NMR spectroscopy indicated that the desired product **2a** was formed in 53% yield. Furthermore, GC-MS analysis of the reaction showed the formation of dibrominated byproduct **6.**

GC-MS spectra of Zn-promoted reaction





8. References

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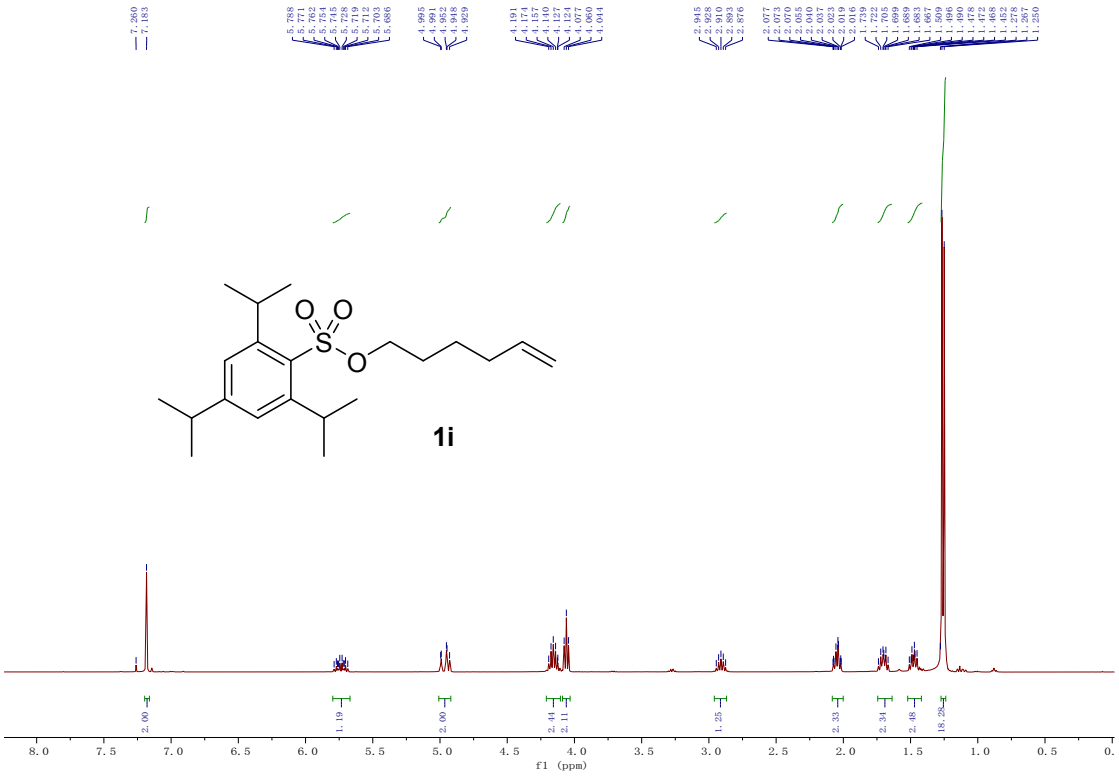
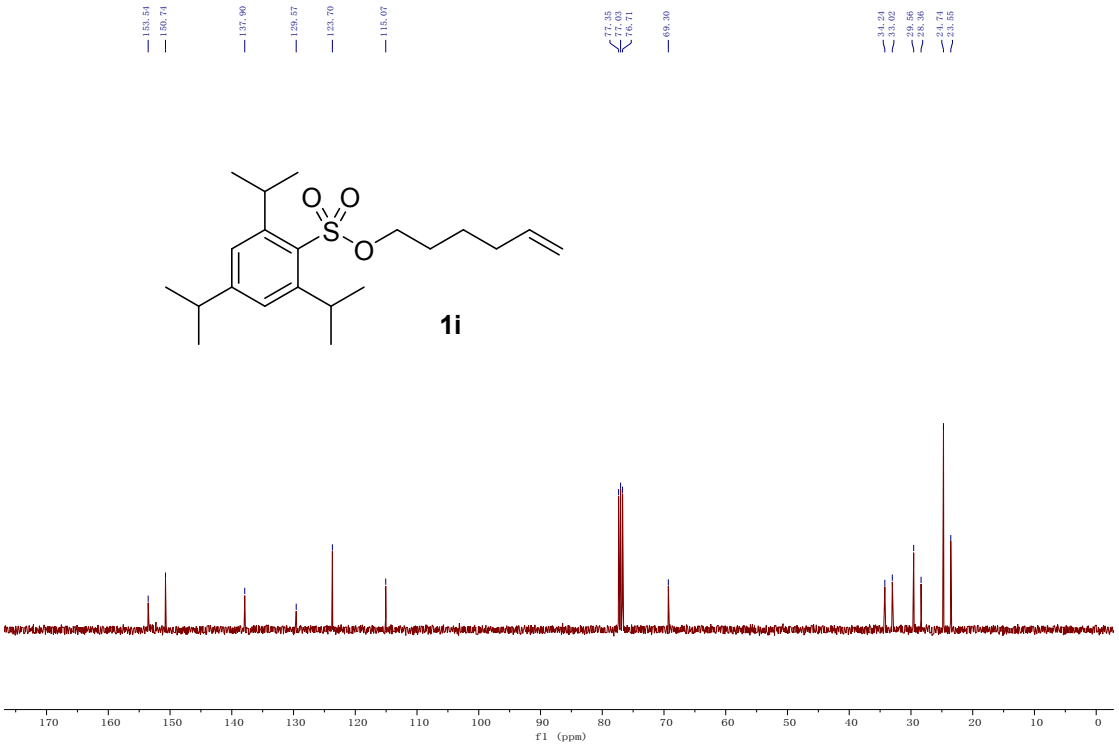
9. Copies of ^{1}H, ^{19}F, and ^{13}C NMR Spectra for the Products

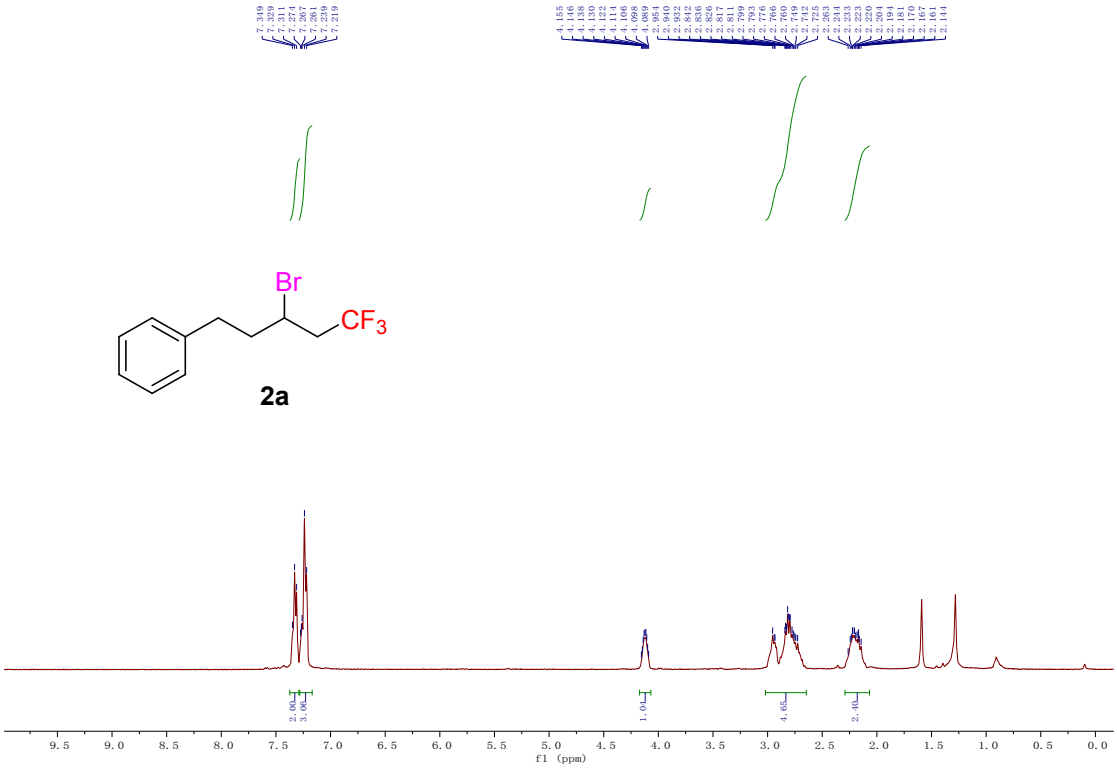
^{1}H NMR (400 MHz, $CDCl_3$)



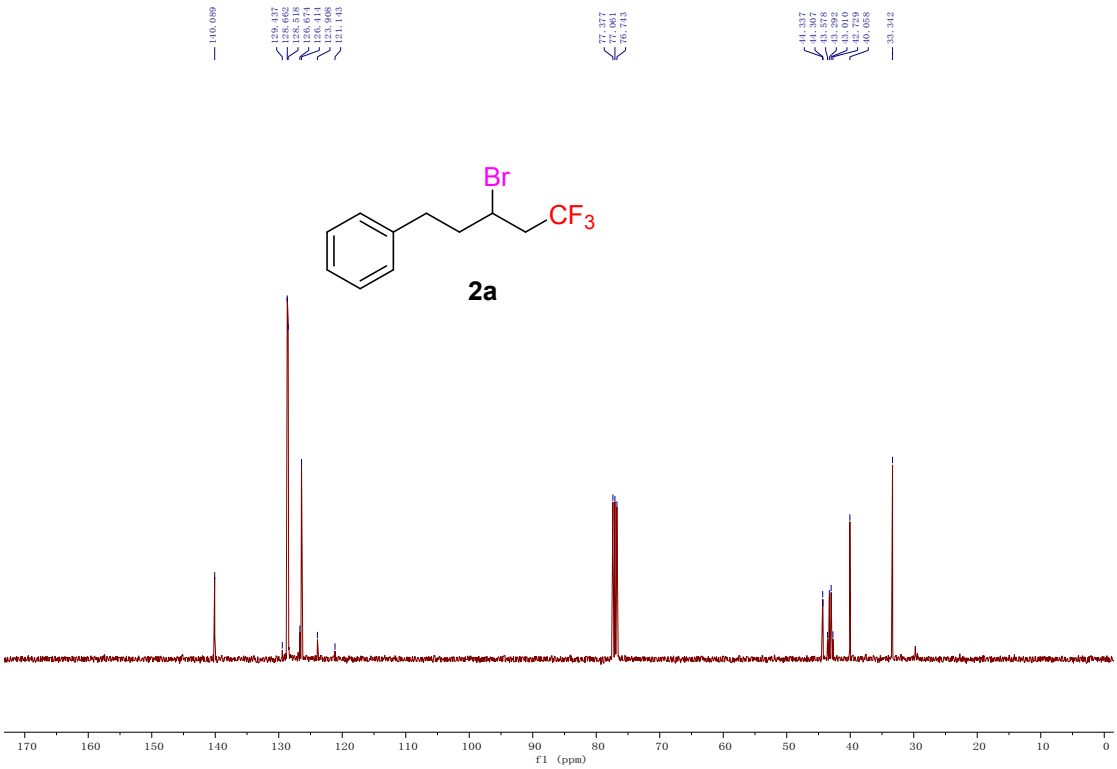
^{13}C NMR (100 MHz, $CDCl_3$)



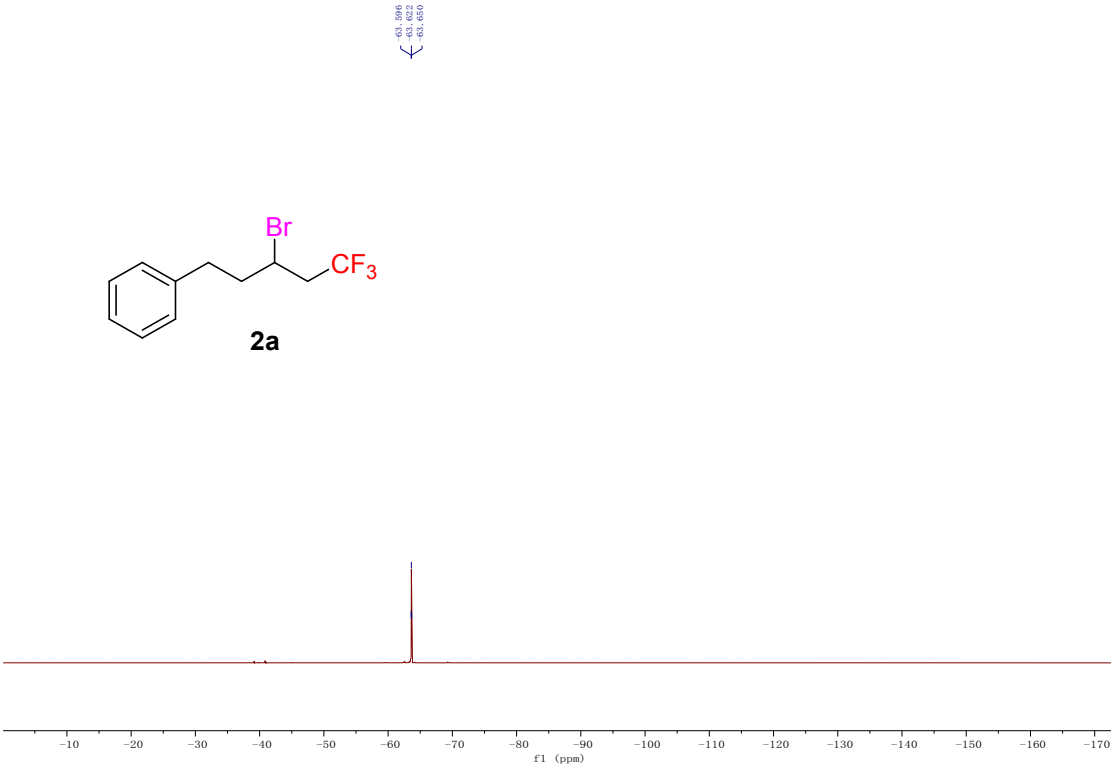
^{1}H NMR (400 MHz, $CDCl_3$)



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



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



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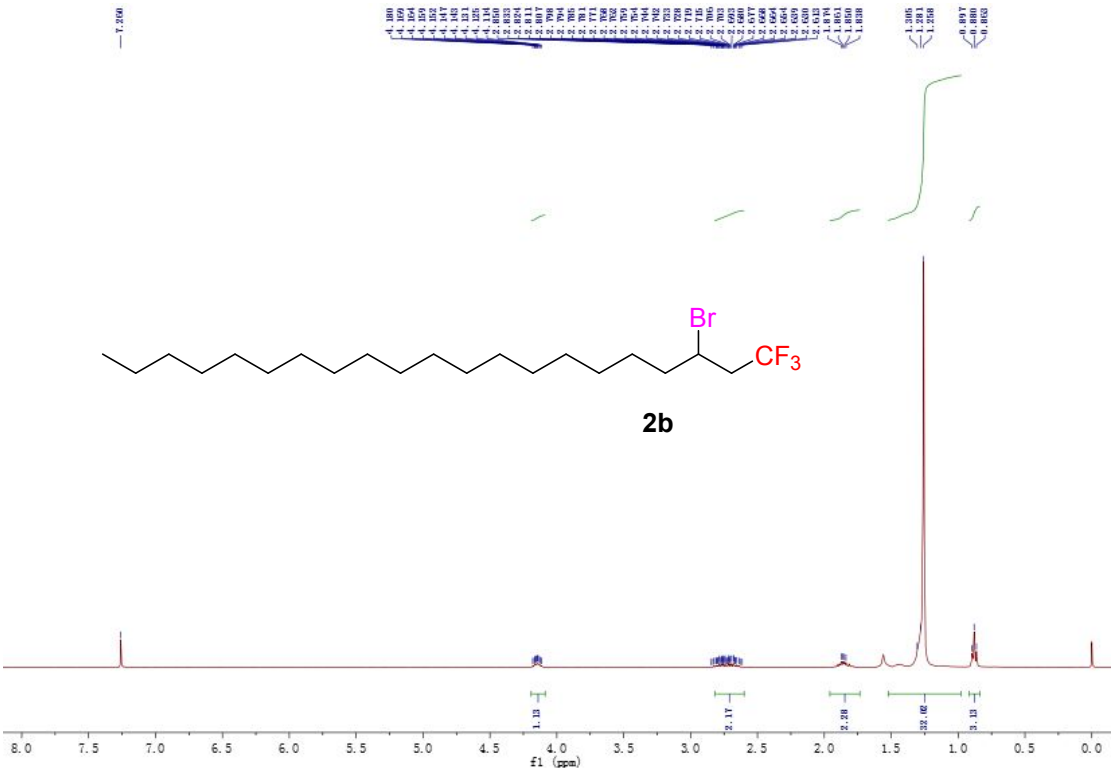
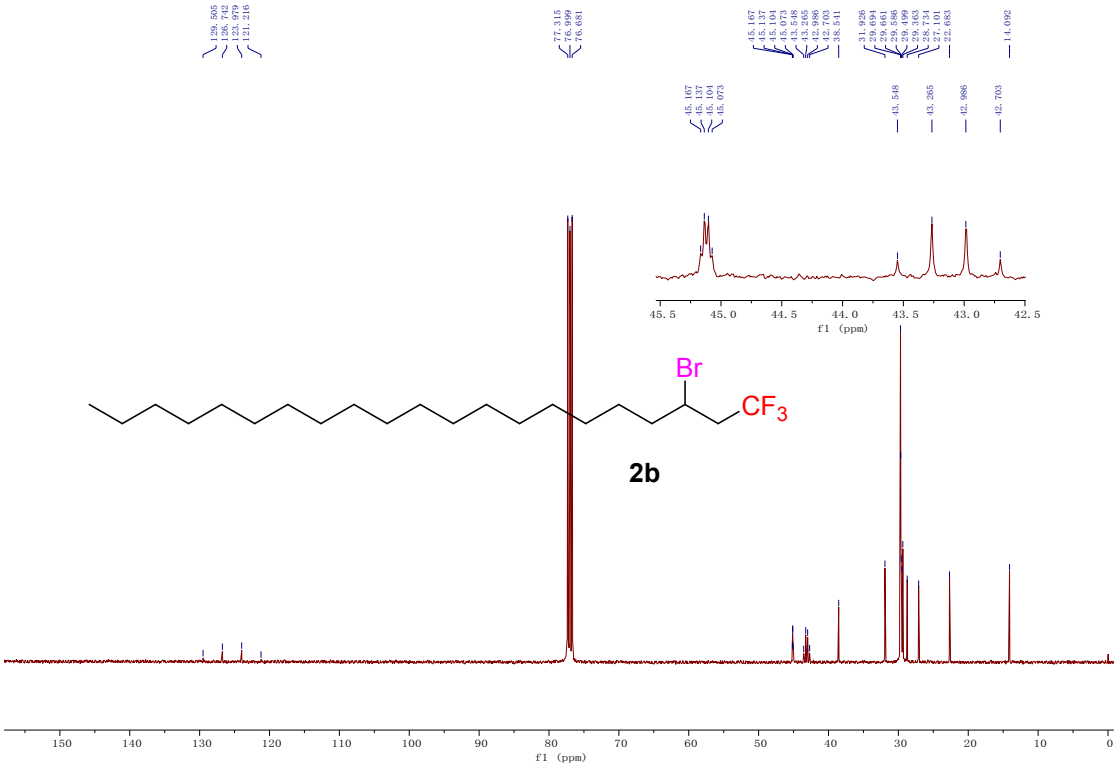
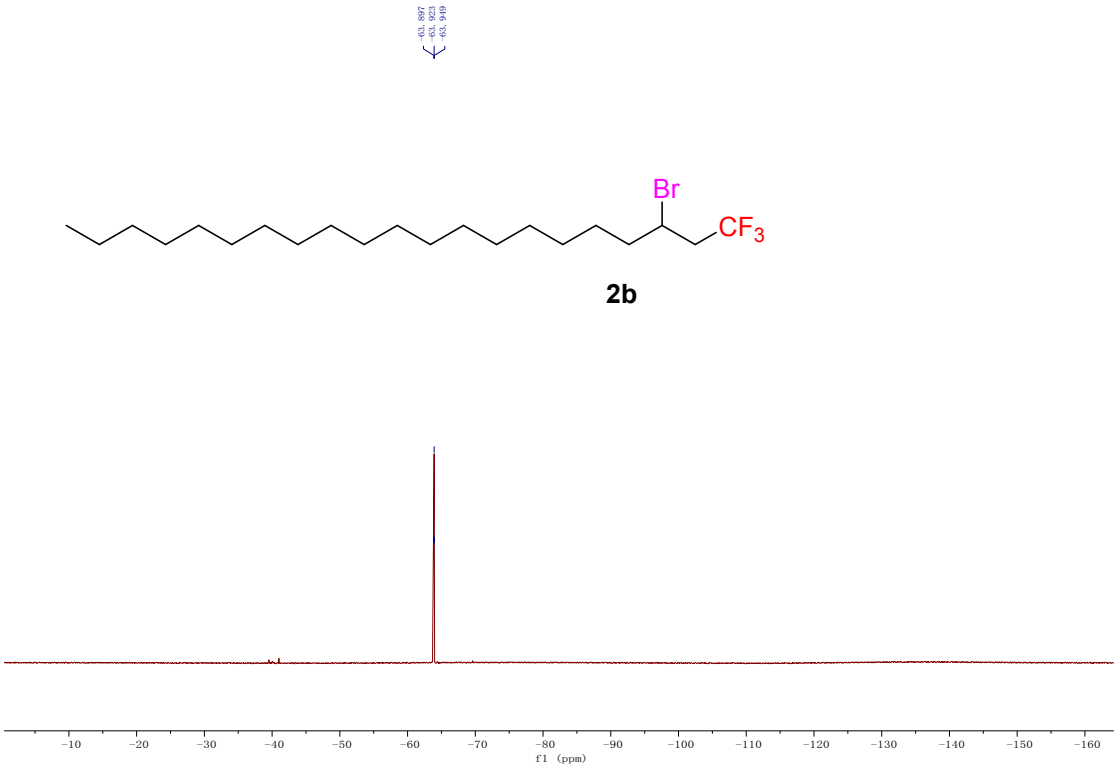


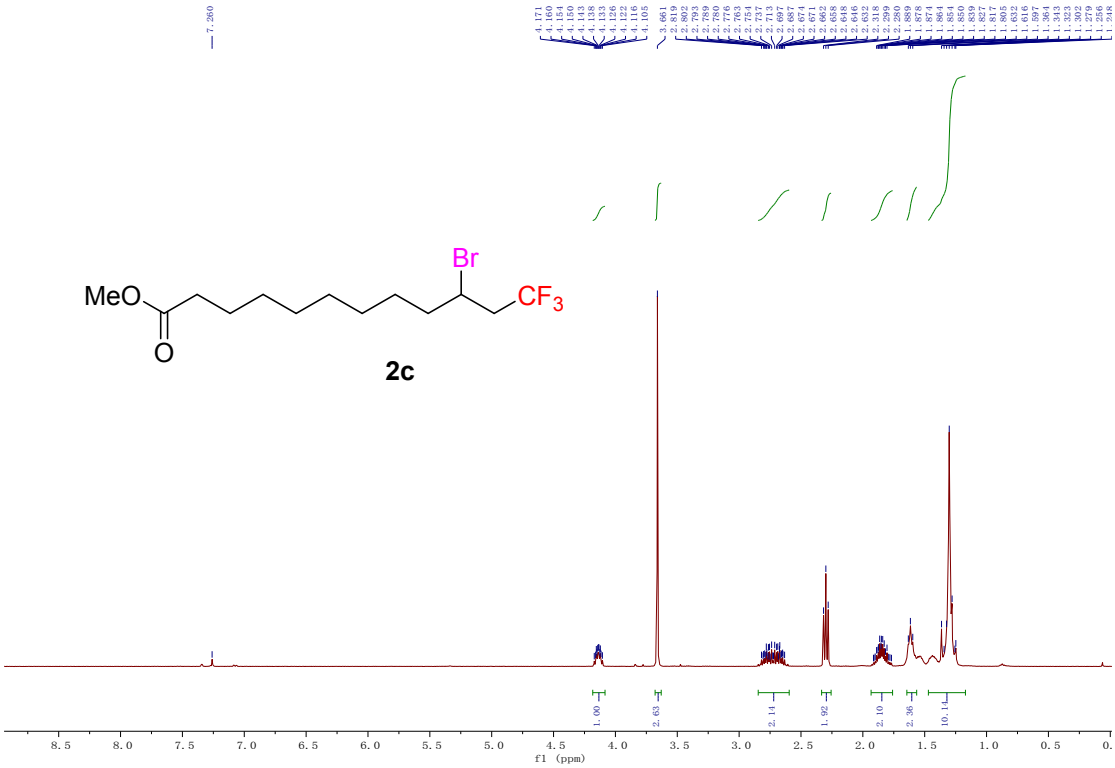
^{13}C NMR (100MHz, $CDCl_3$)



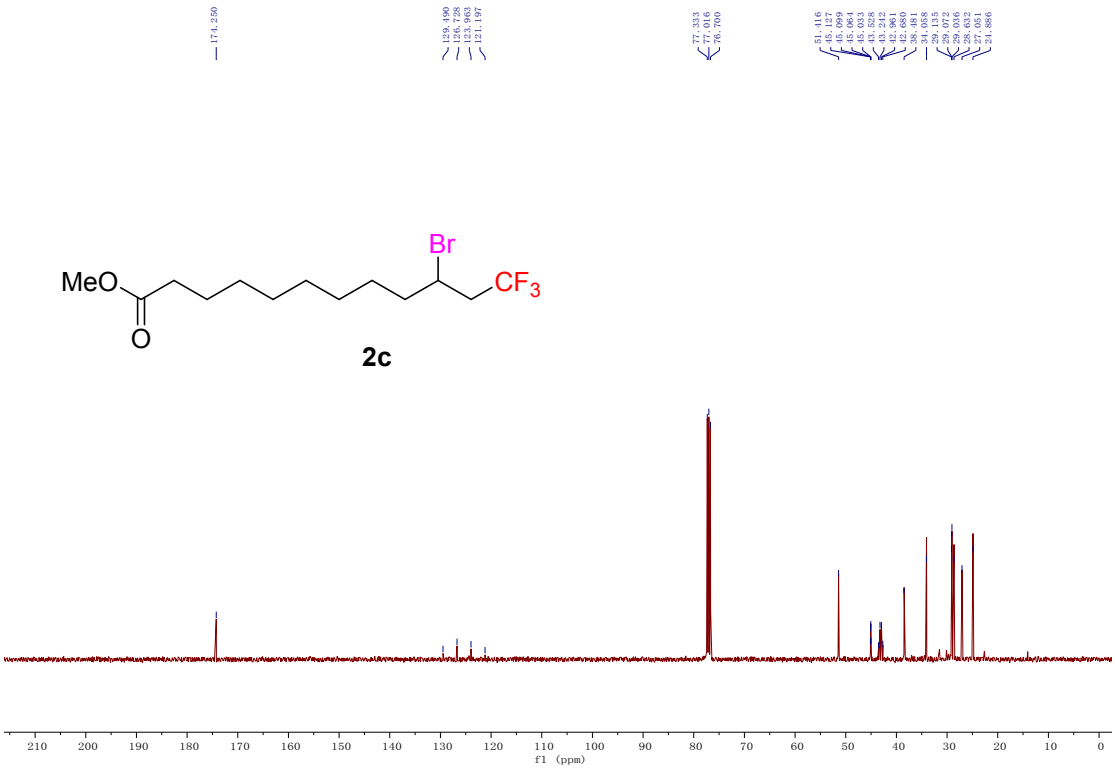
^{19}F NMR (376 MHz, $CDCl_3$)



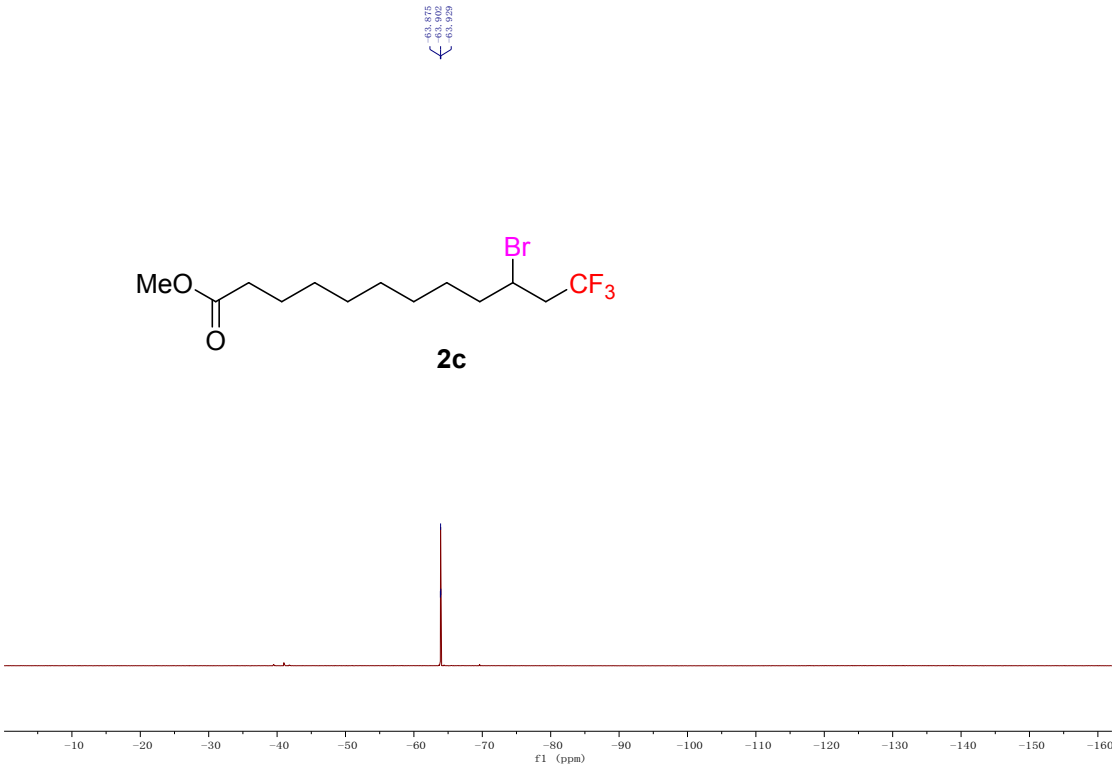
^{1}H NMR (400 MHz, $CDCl_3$)



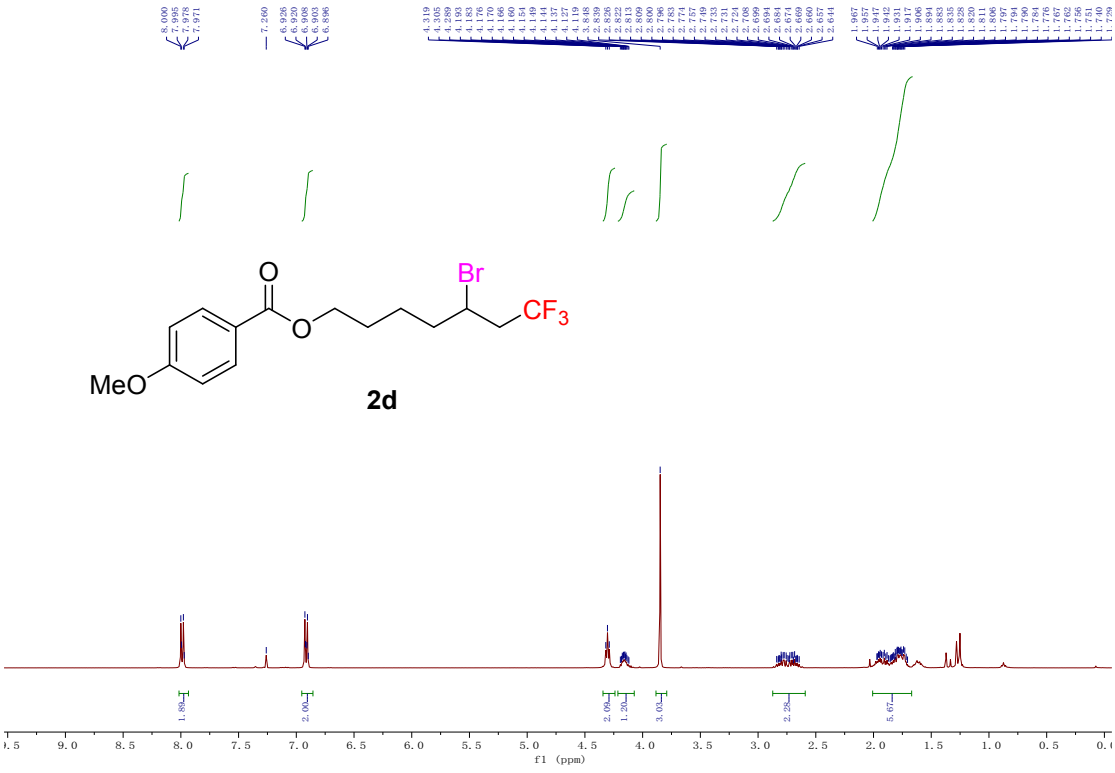
^{13}C NMR (100 MHz, $CDCl_3$)



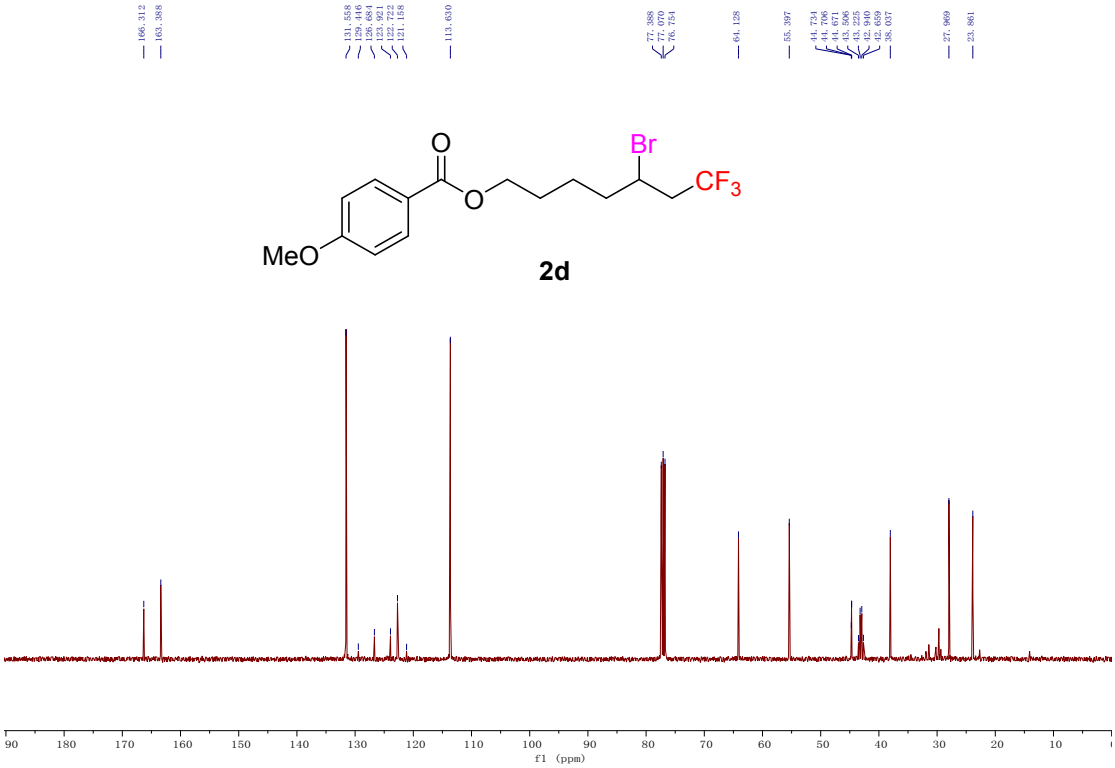
^{19}F NMR (376 MHz, $CDCl_3$)



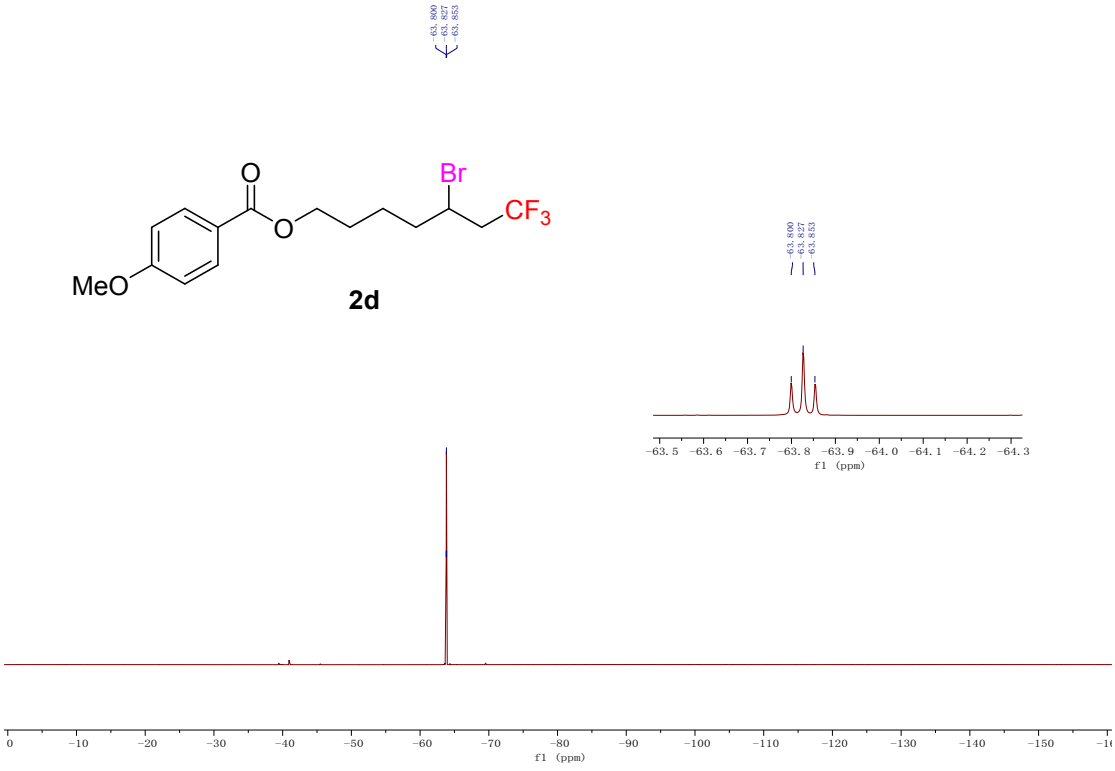
^{1}H NMR (400 MHz, $CDCl_3$)



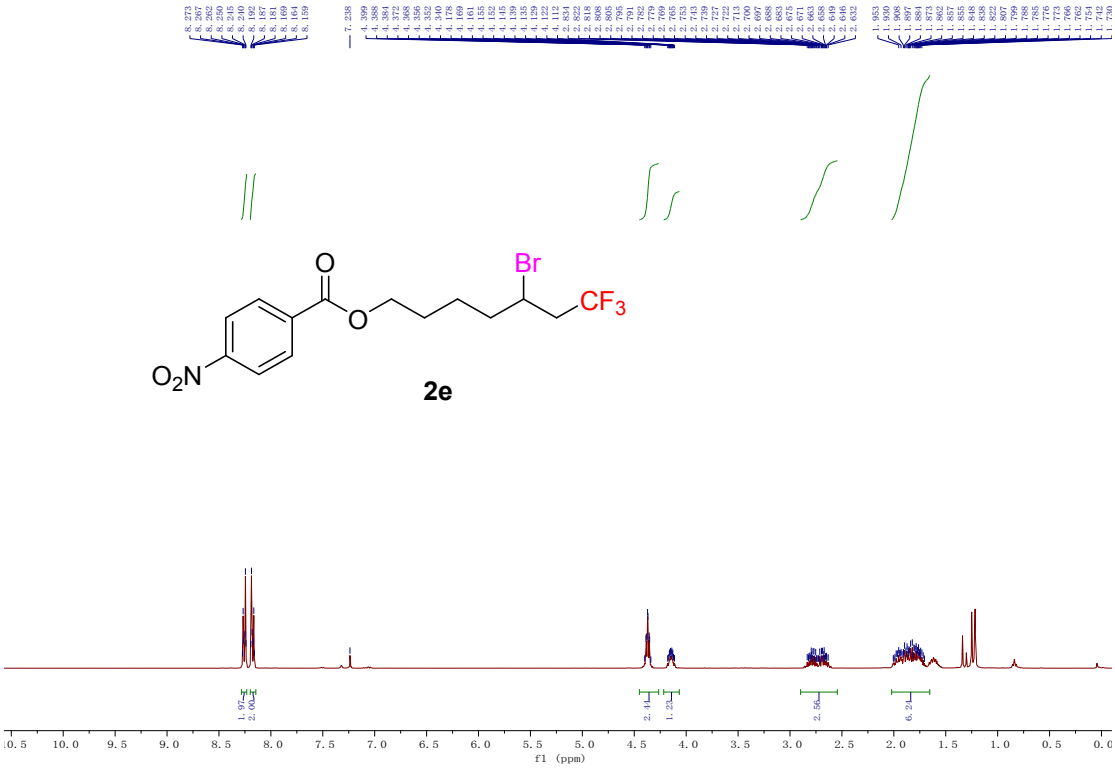
^{13}C NMR (100 MHz, $CDCl_3$)



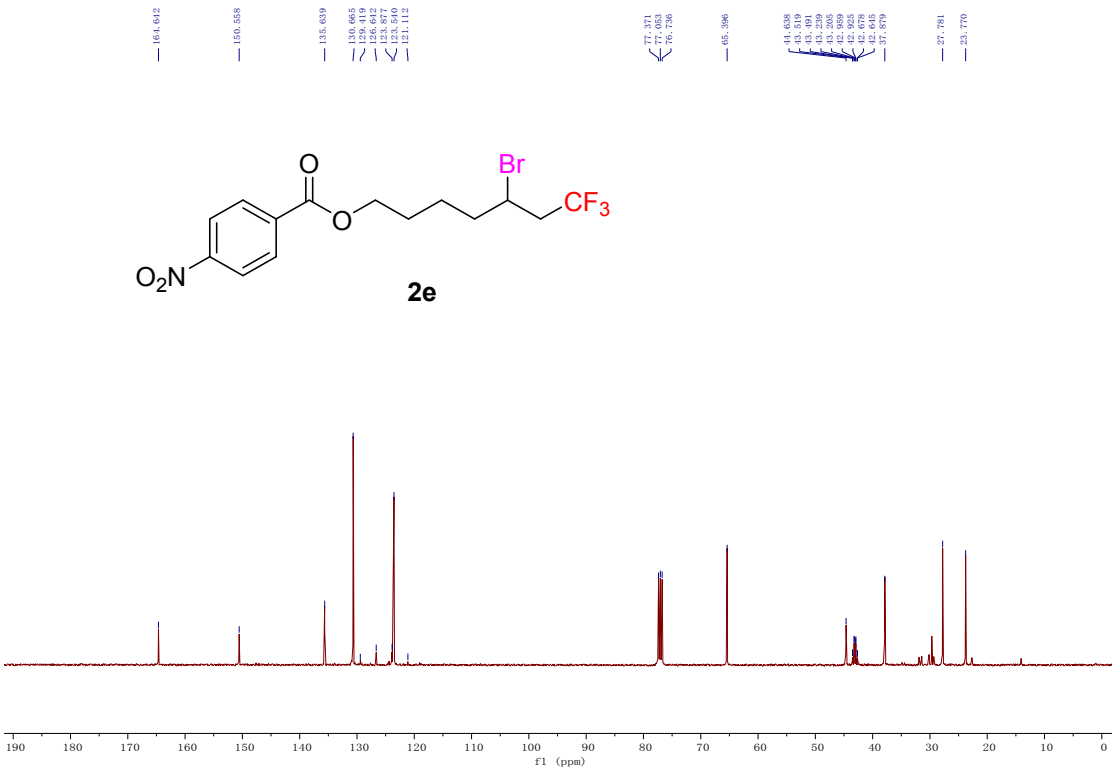
^{19}F NMR (376 MHz, $CDCl_3$)



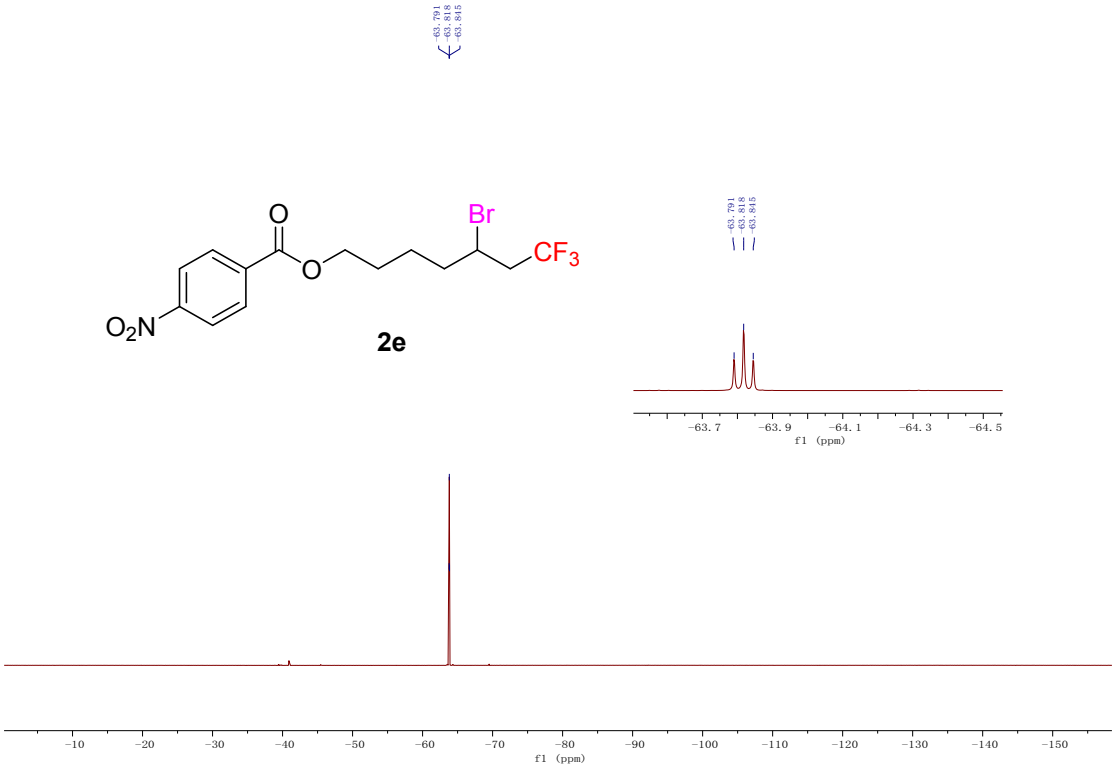
^{1}H NMR (400 MHz, $CDCl_3$)



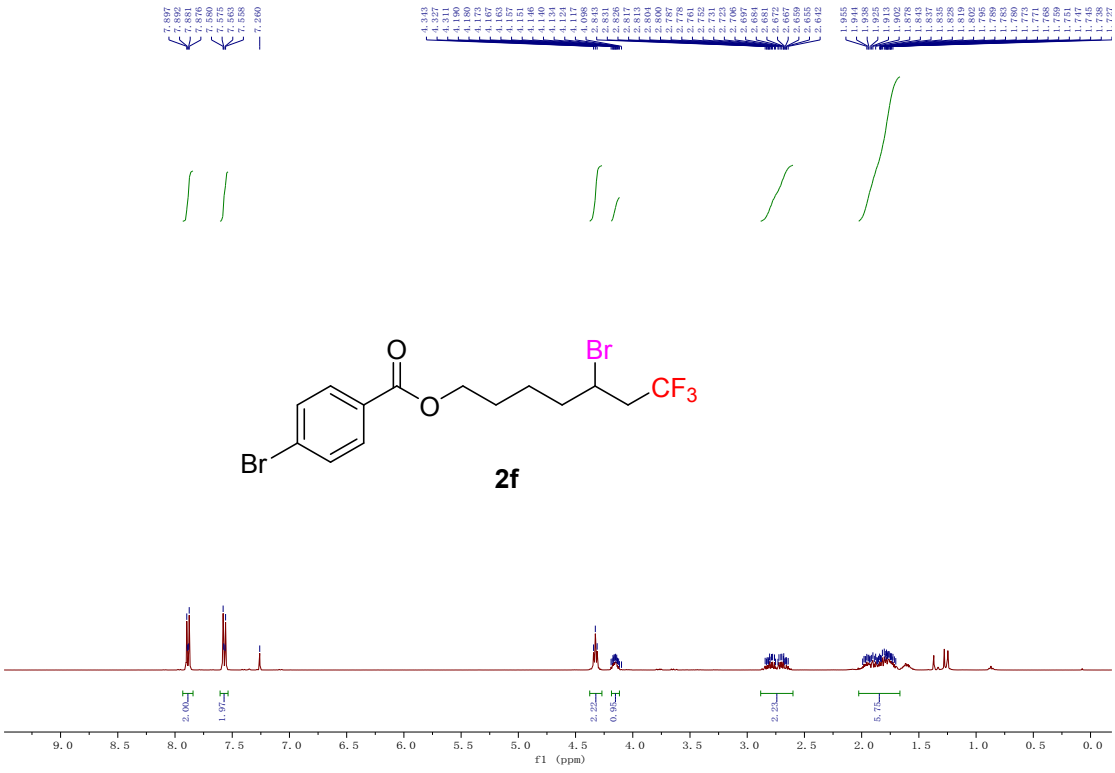
^{13}C NMR (100 MHz, $CDCl_3$)



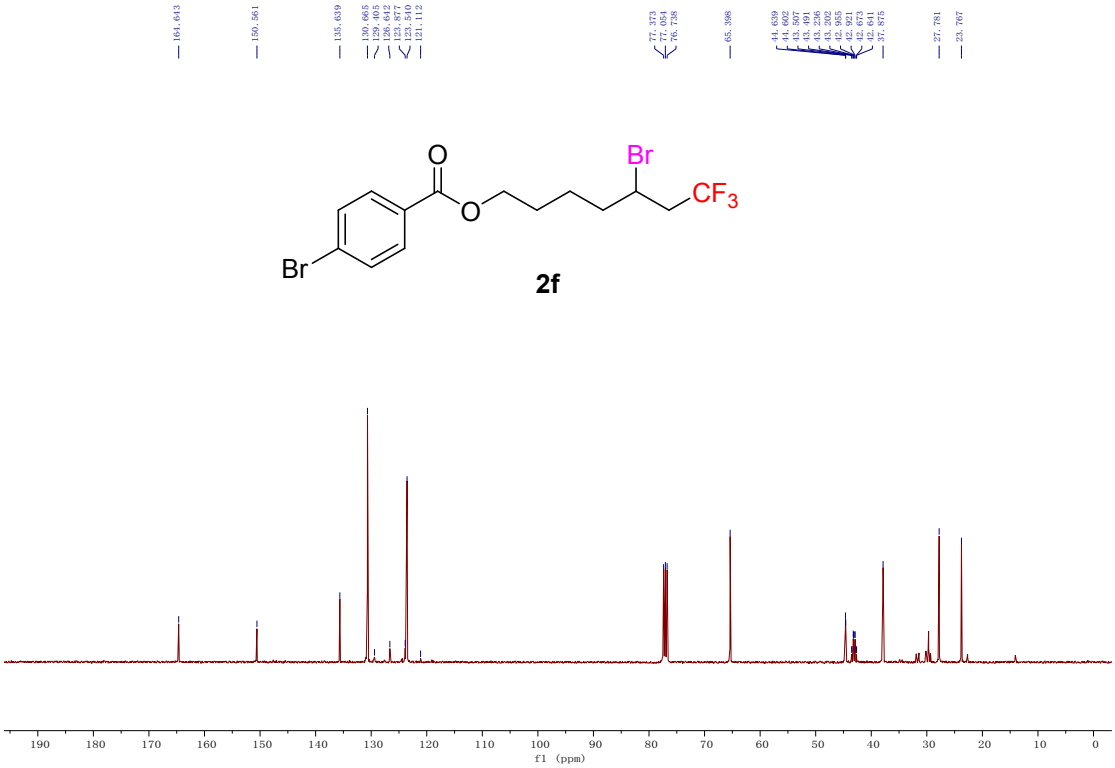
^{19}F NMR (376 MHz, $CDCl_3$)



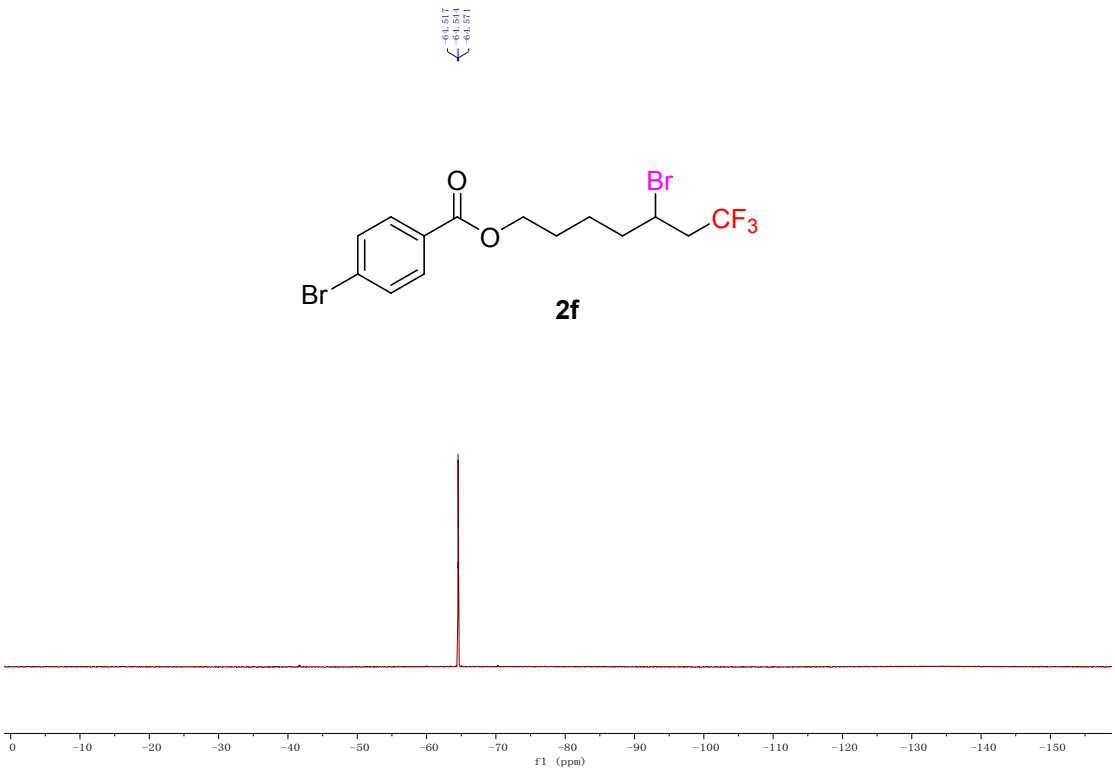
^{1}H NMR (400 MHz, $CDCl_3$)



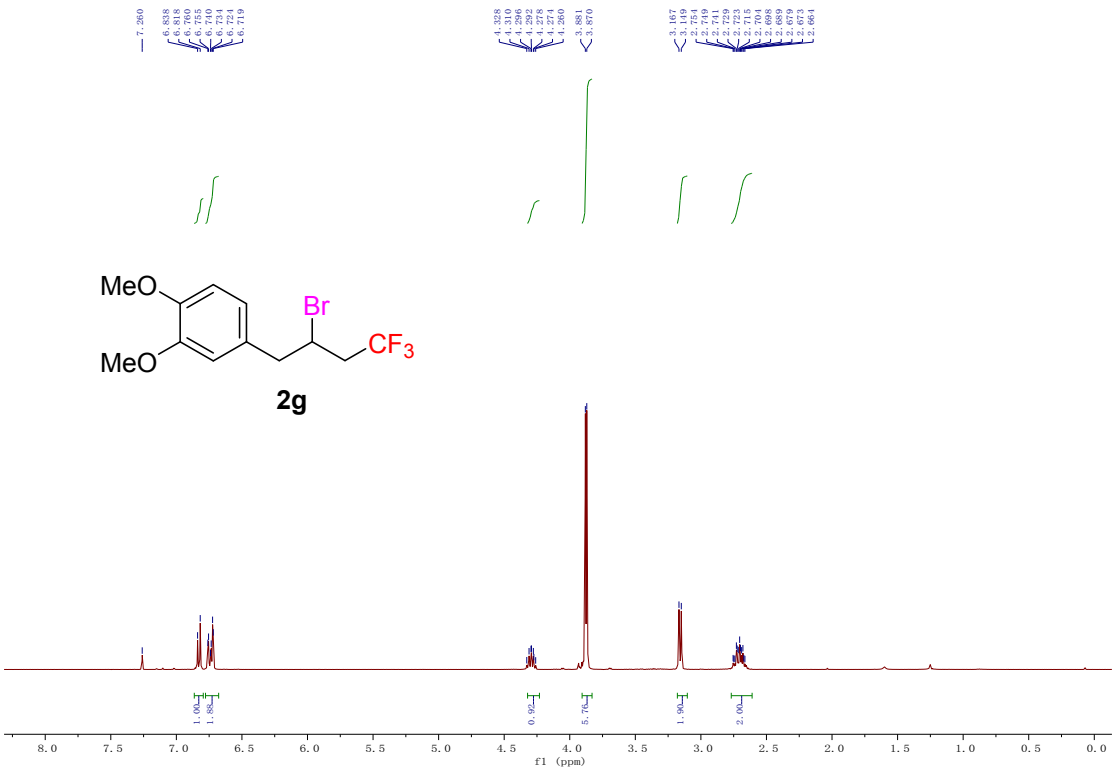
^{13}C NMR (100 MHz, $CDCl_3$)



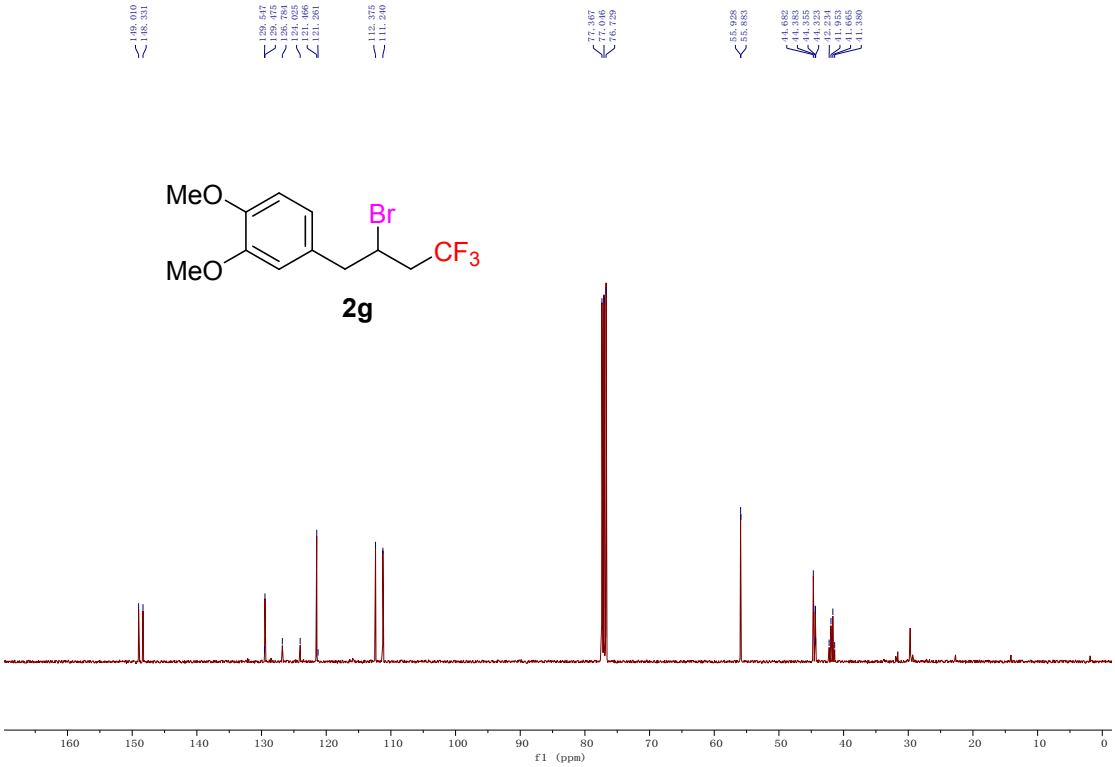
^{19}F NMR (376 MHz, $CDCl_3$)



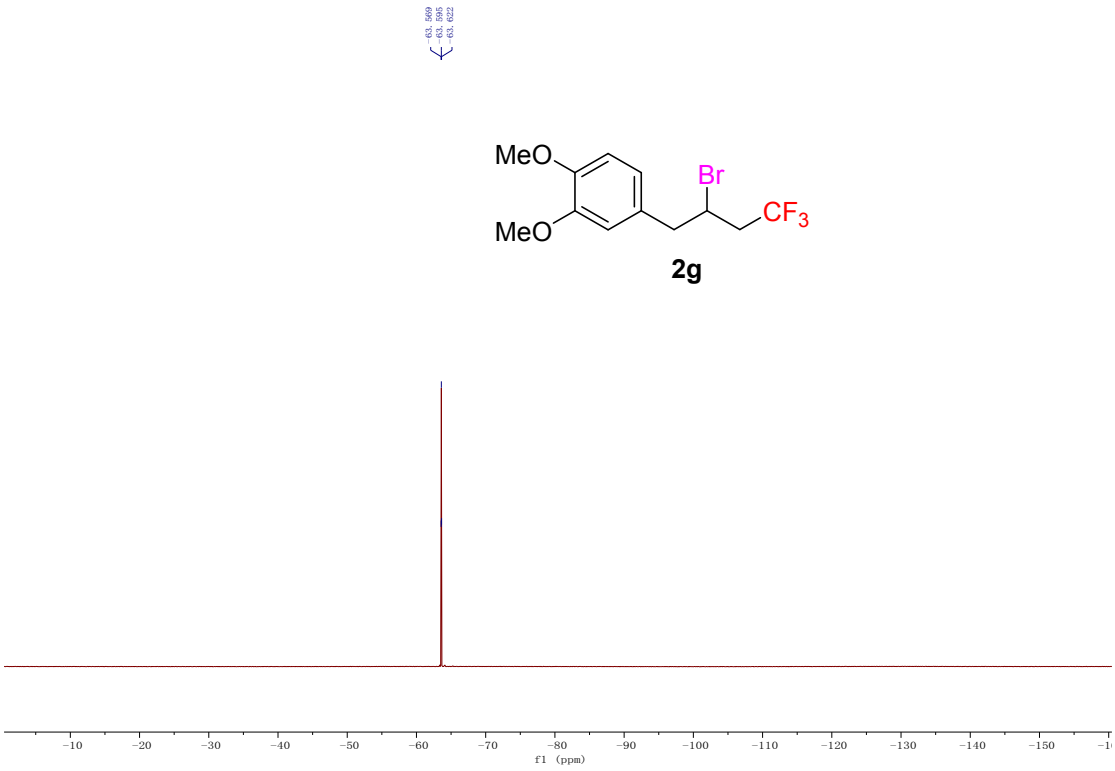
^{1}H NMR (400 MHz, $CDCl_3$)



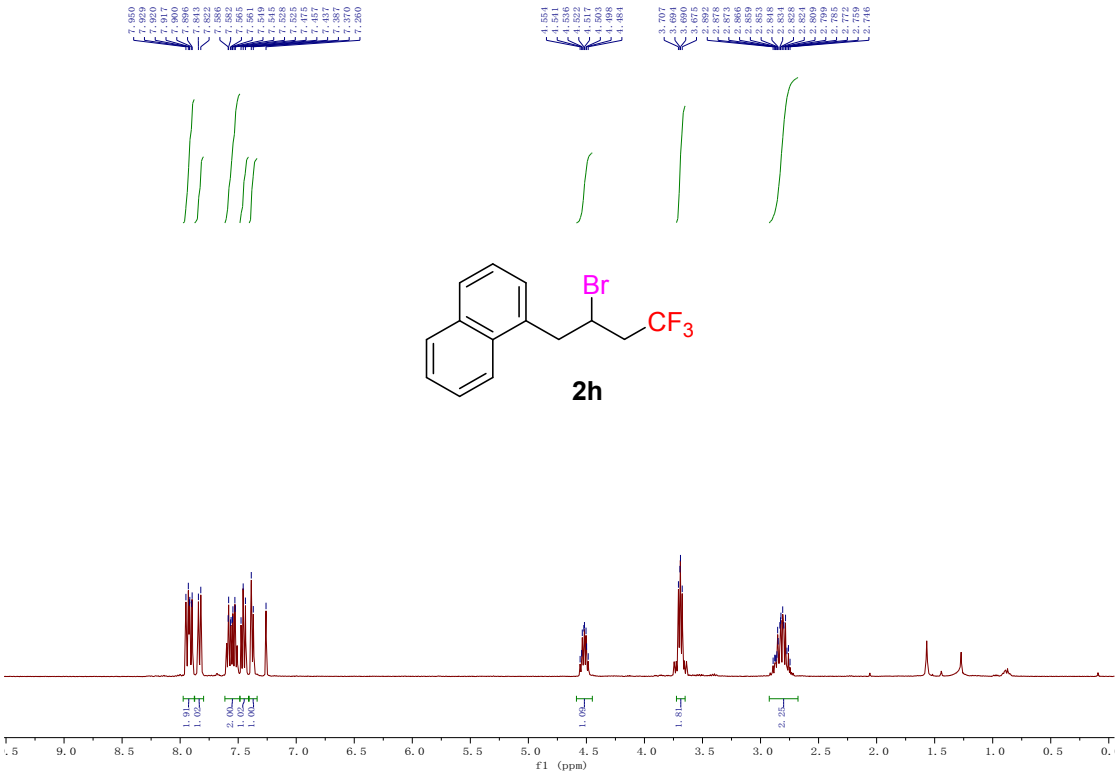
^{13}C NMR (100 MHz, $CDCl_3$)



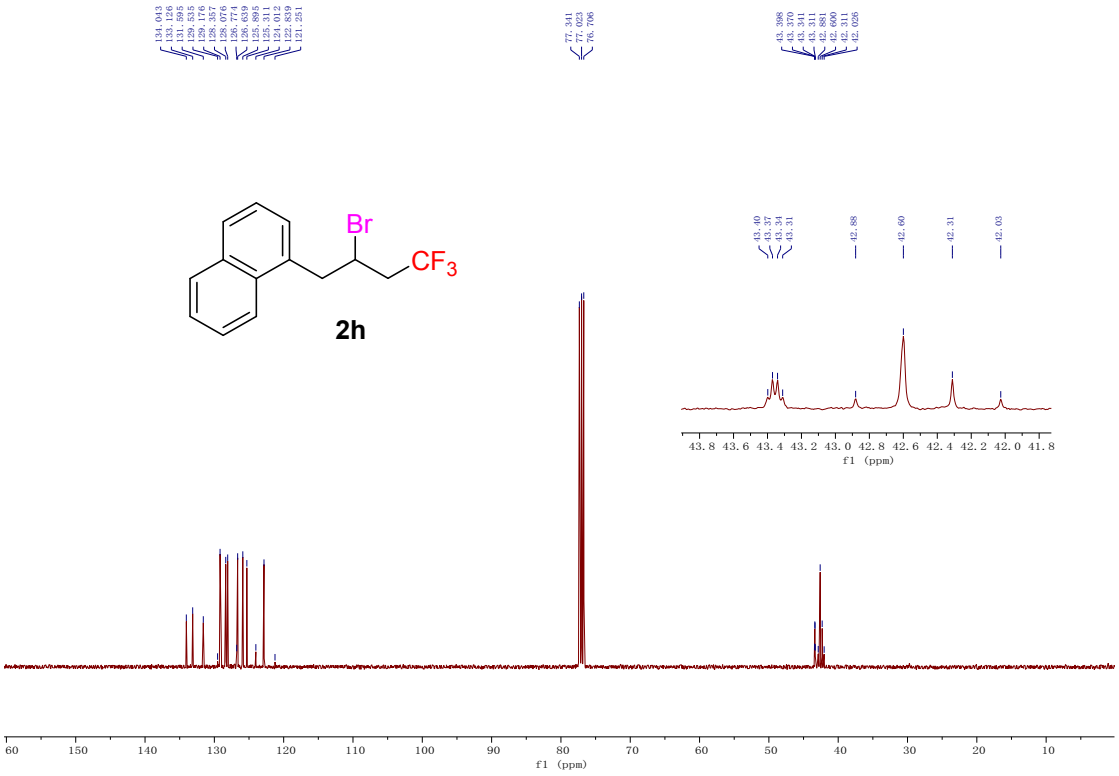
^{19}F NMR (376 MHz, $CDCl_3$)



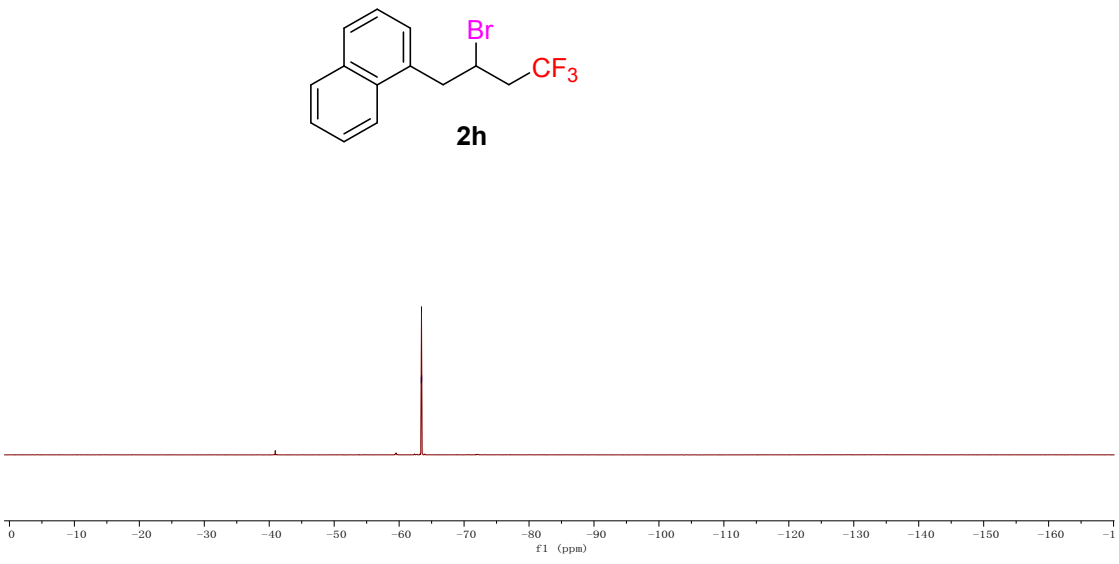
^{1}H NMR (400 MHz, $CDCl_3$)



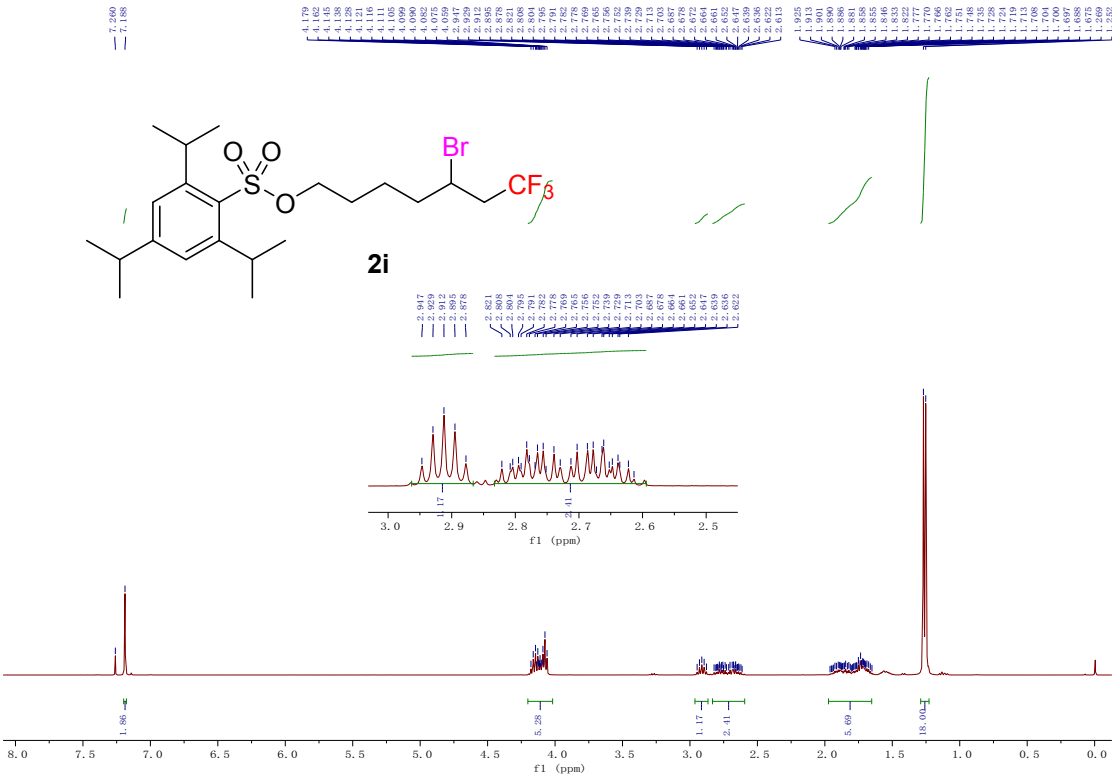
^{13}C NMR (376 MHz, $CDCl_3$)



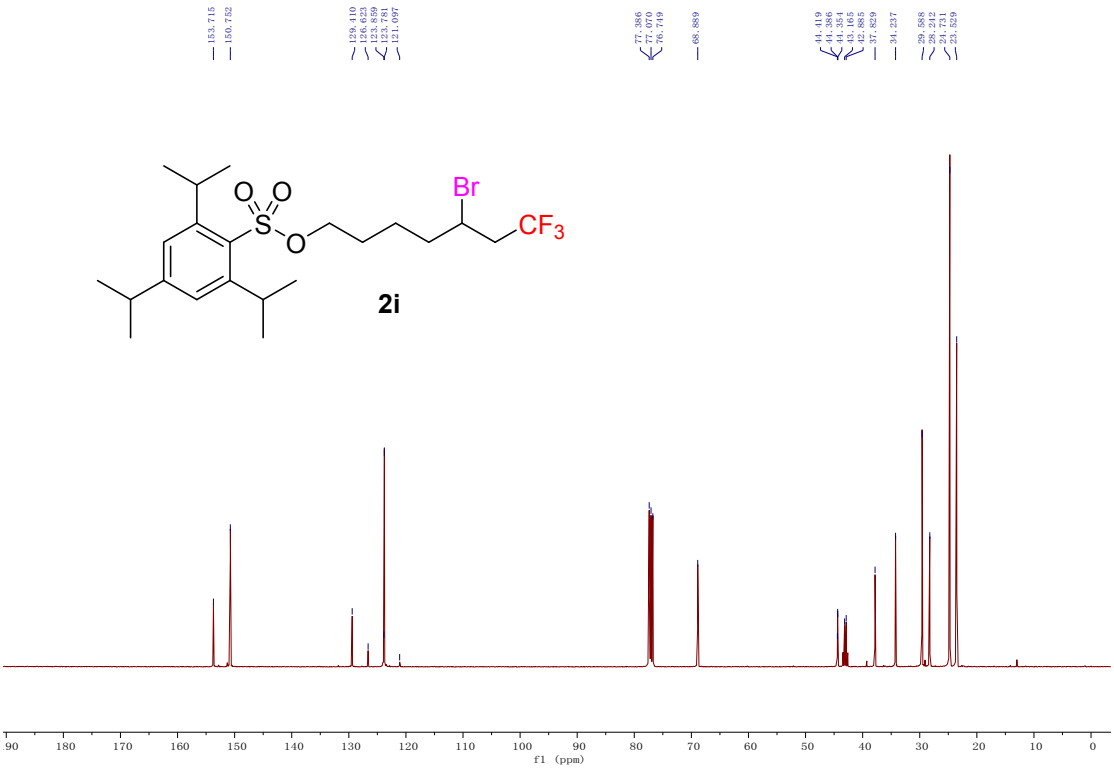
^{19}F NMR (376 MHz, $CDCl_3$)



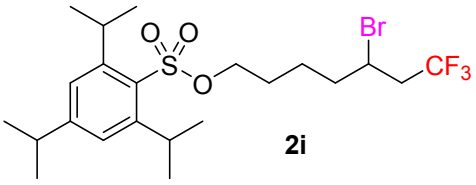
^{1}H NMR (400 MHz, $CDCl_3$)

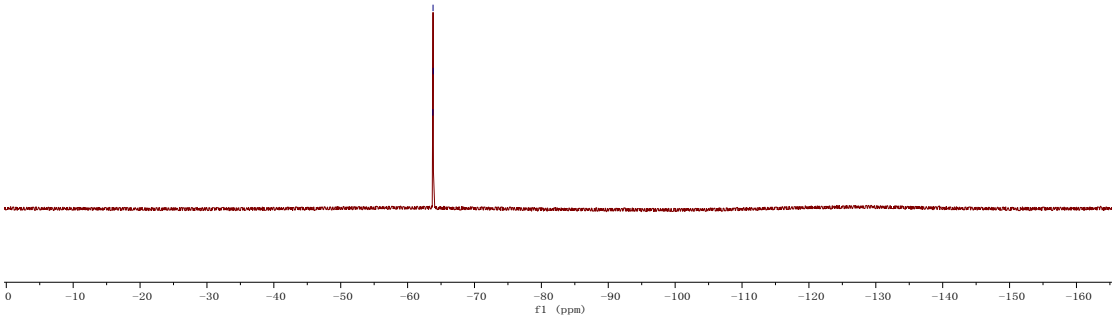


^{13}C NMR (100 MHz, $CDCl_3$)

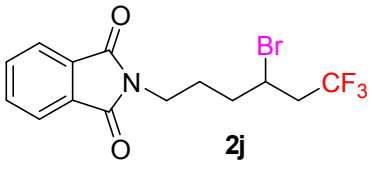


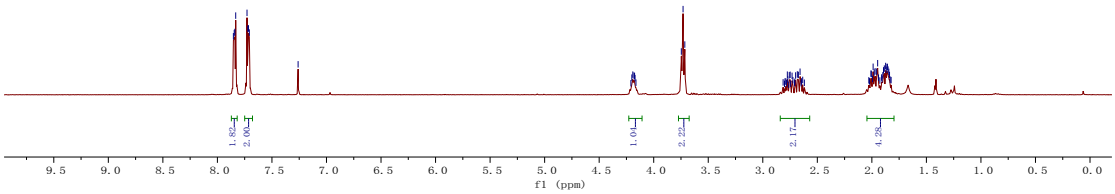
^{19}F NMR (376 MHz, $CDCl_3$)





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





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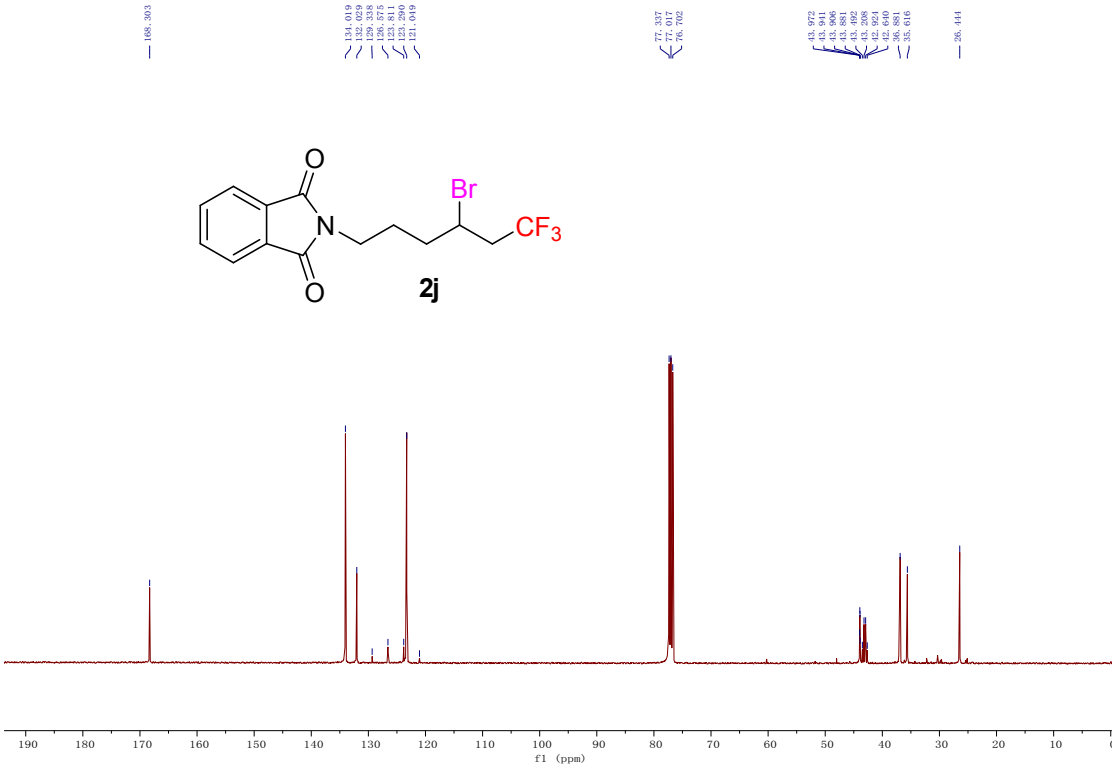
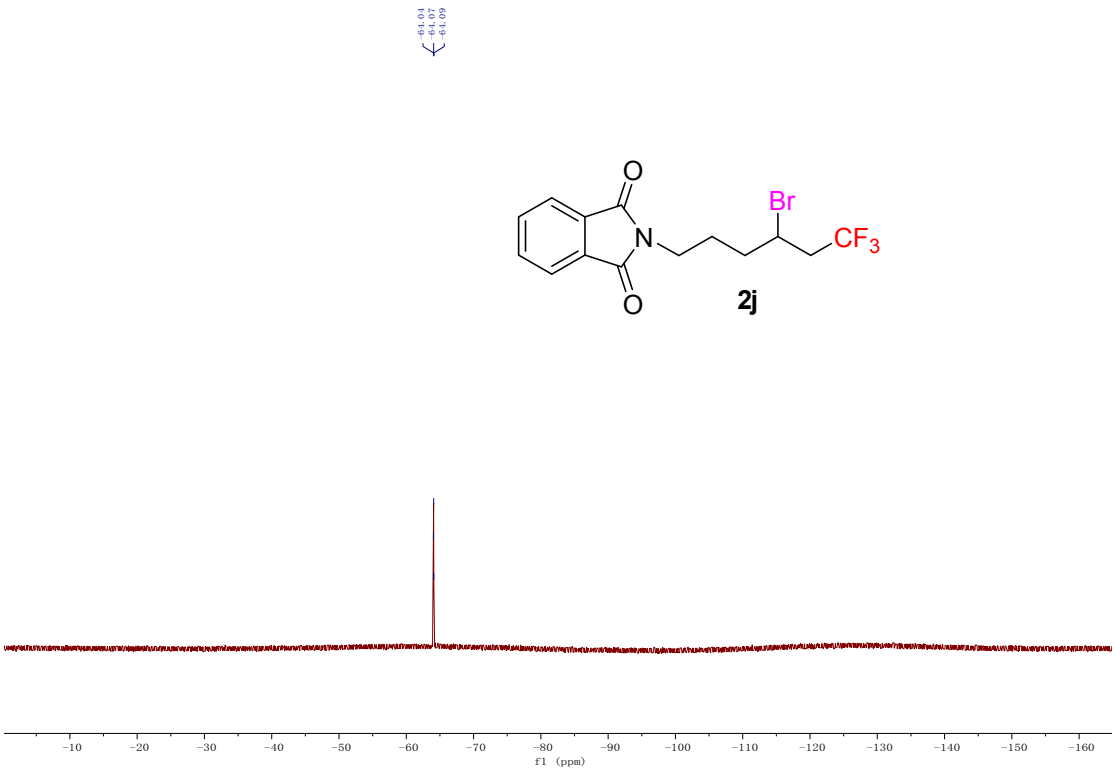
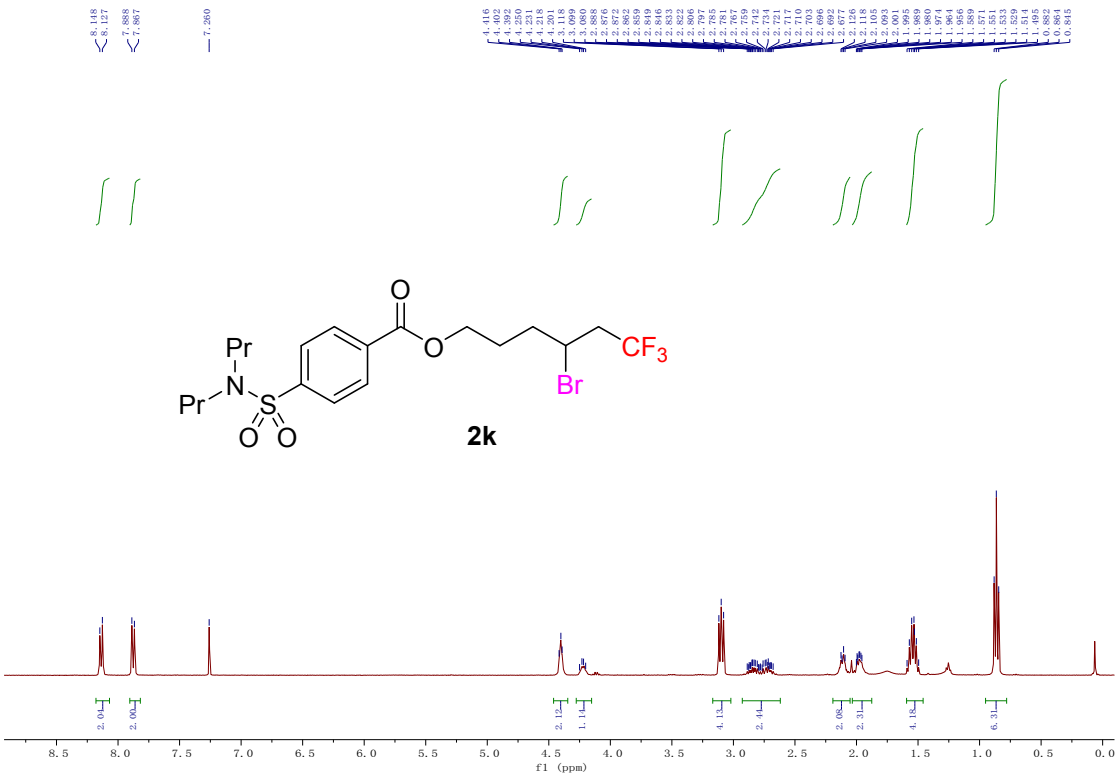


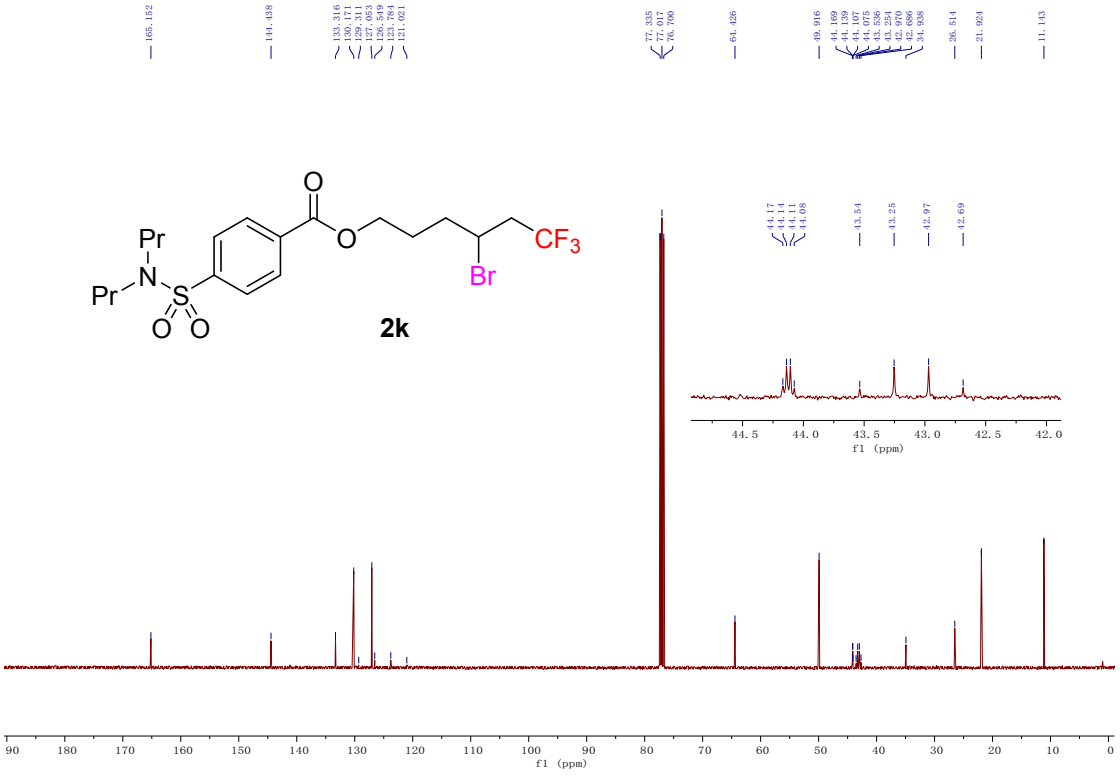
^{19}F NMR (376 MHz, $CDCl_3$)



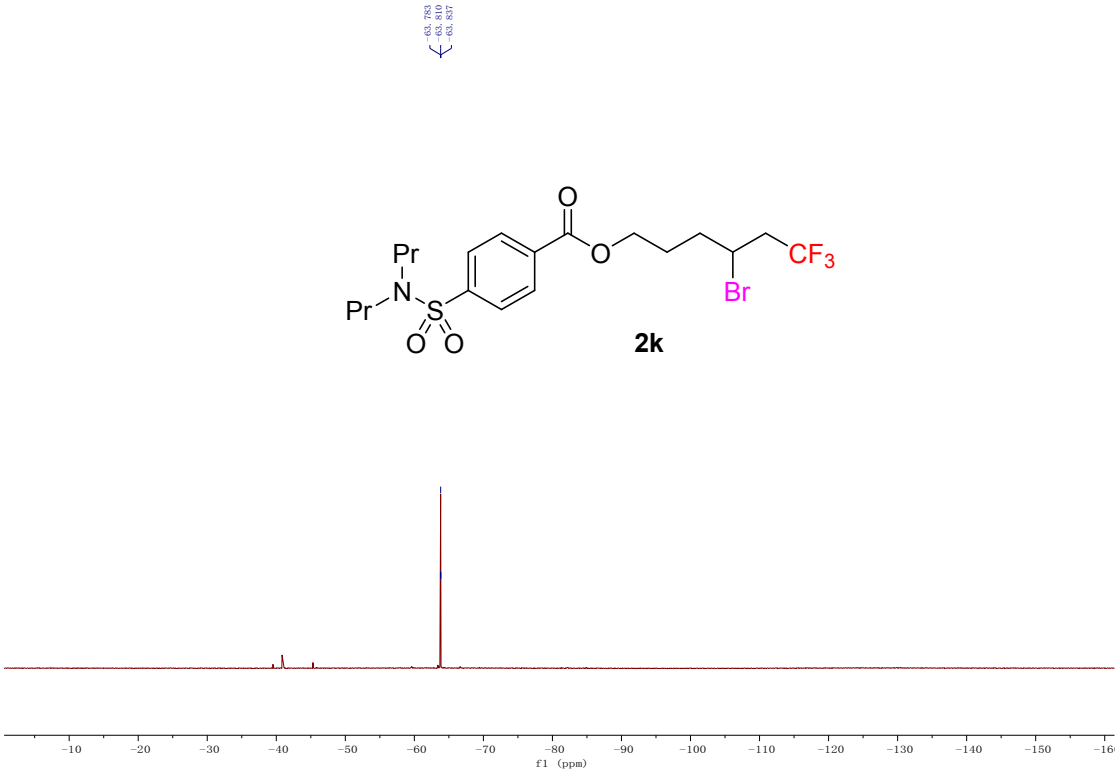
^{1}H NMR (400 MHz, $CDCl_3$)



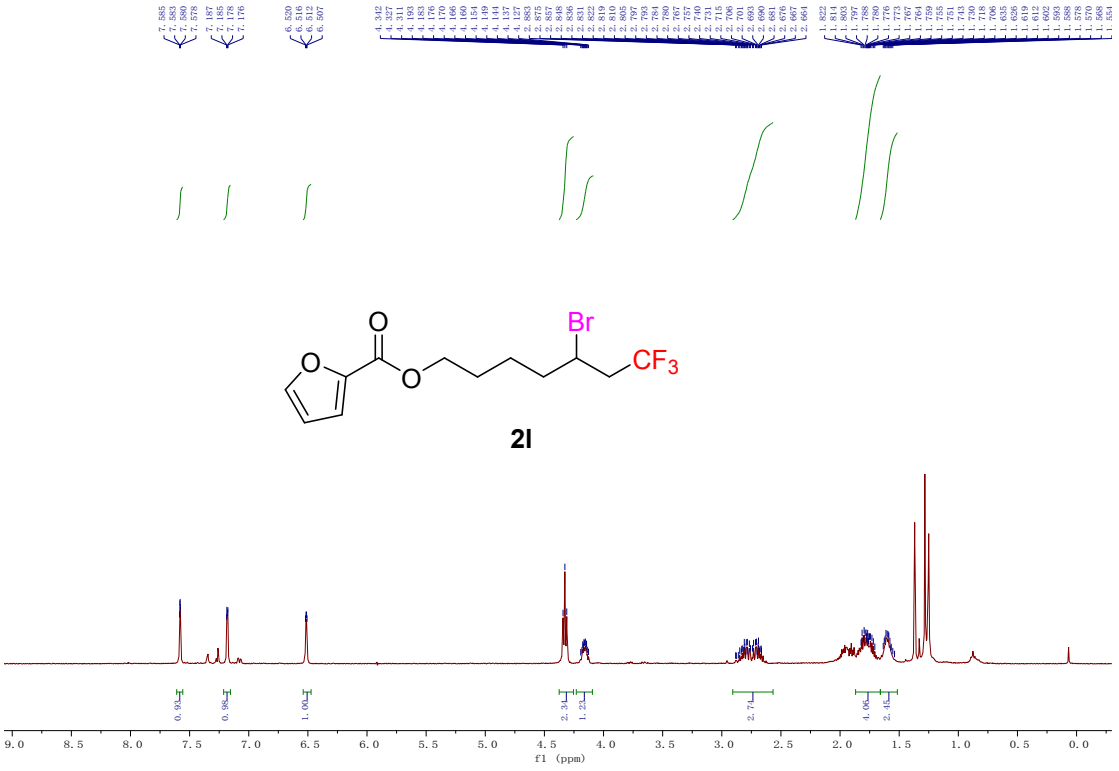
^{13}C NMR (100 MHz, $CDCl_3$)



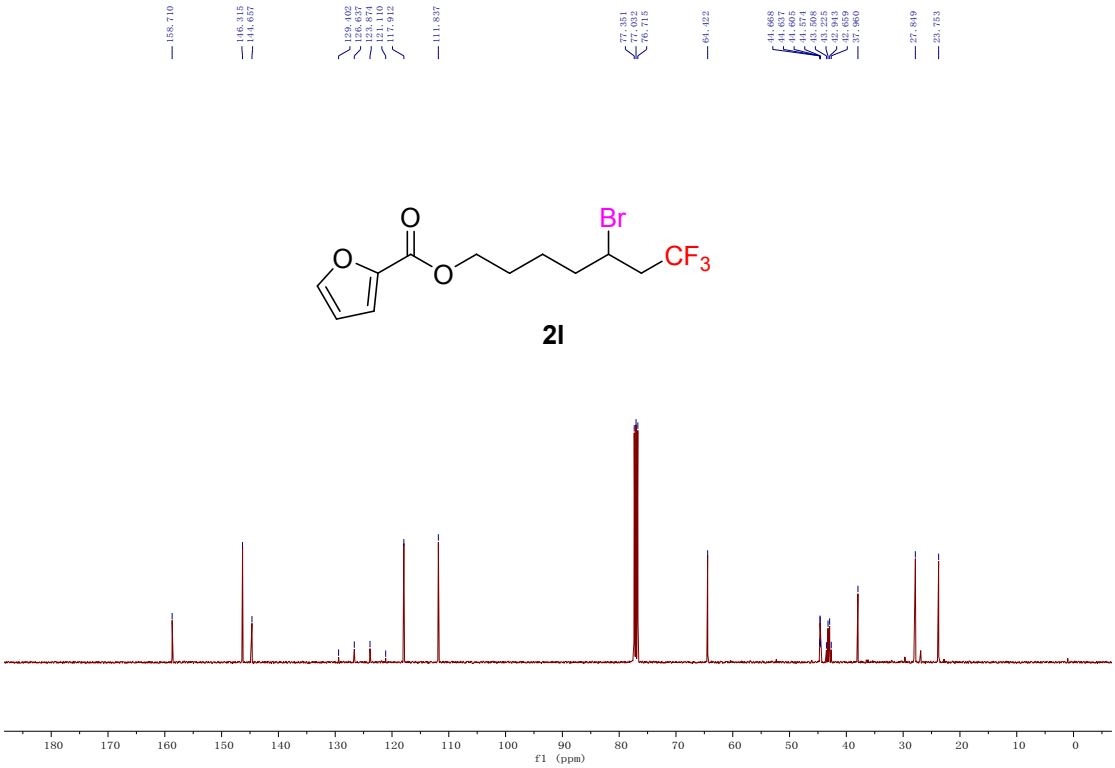
^{19}F NMR (376 MHz, $CDCl_3$)



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



^{13}CNMR (100 MHz, $CDCl_3$)



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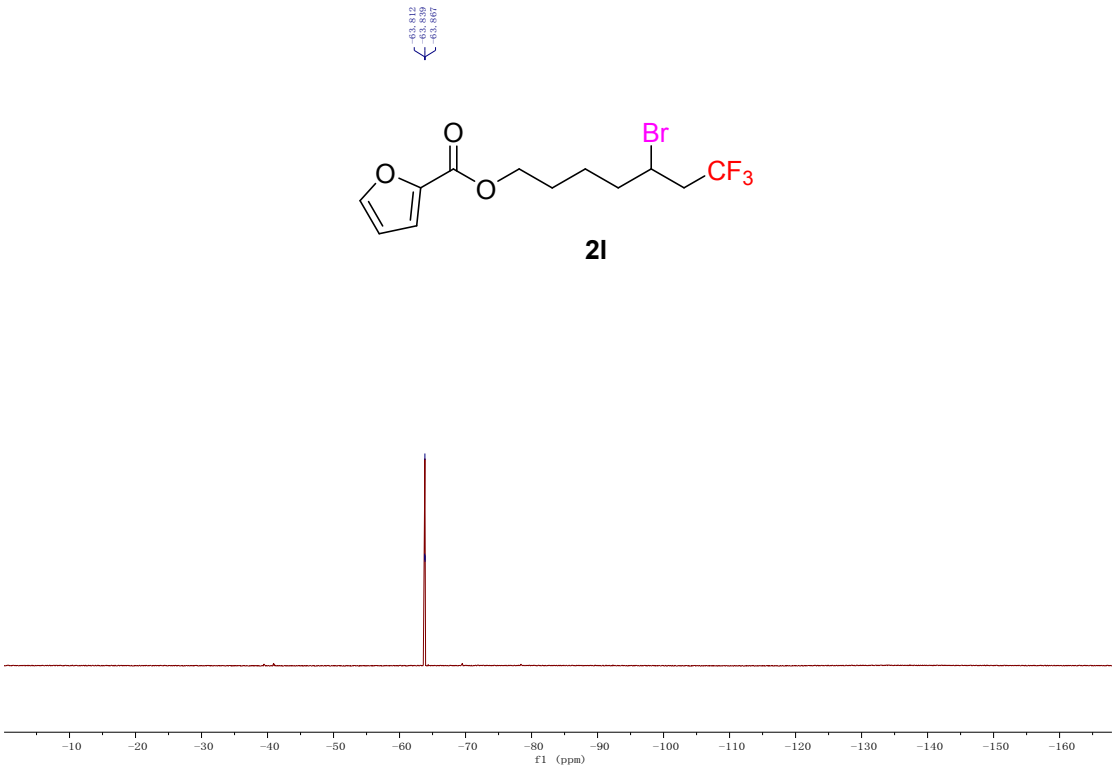

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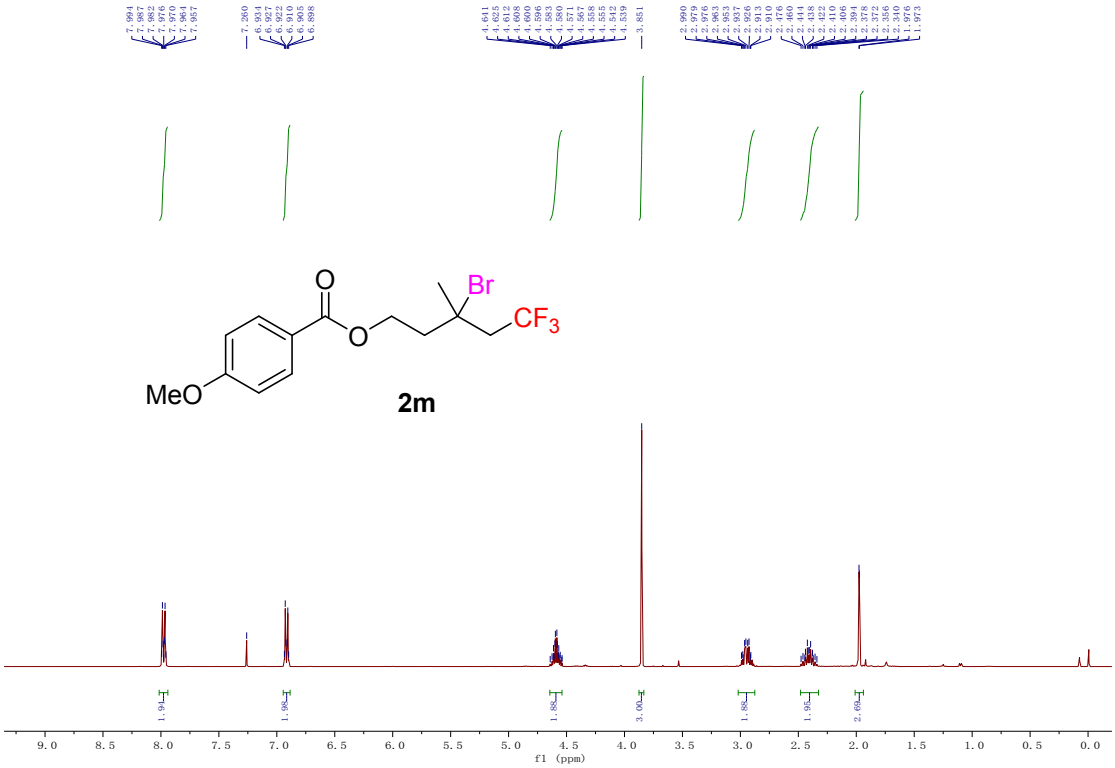
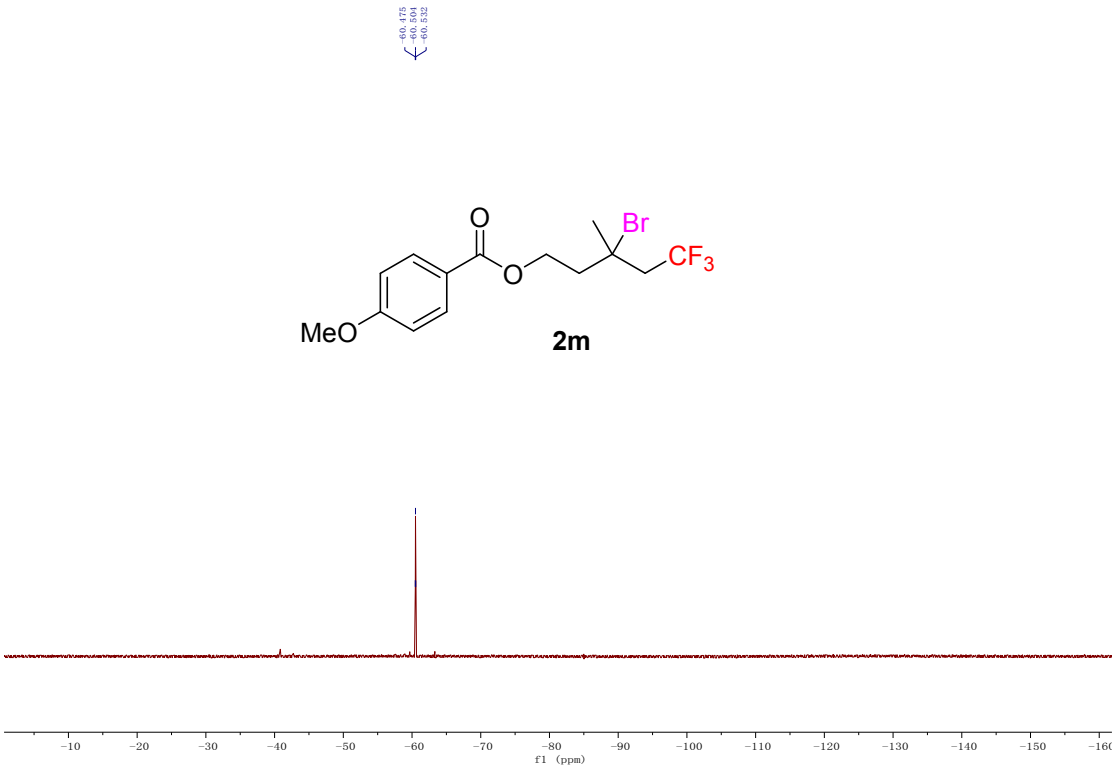


^{19}F NMR (376 MHz, $CDCl_3$)



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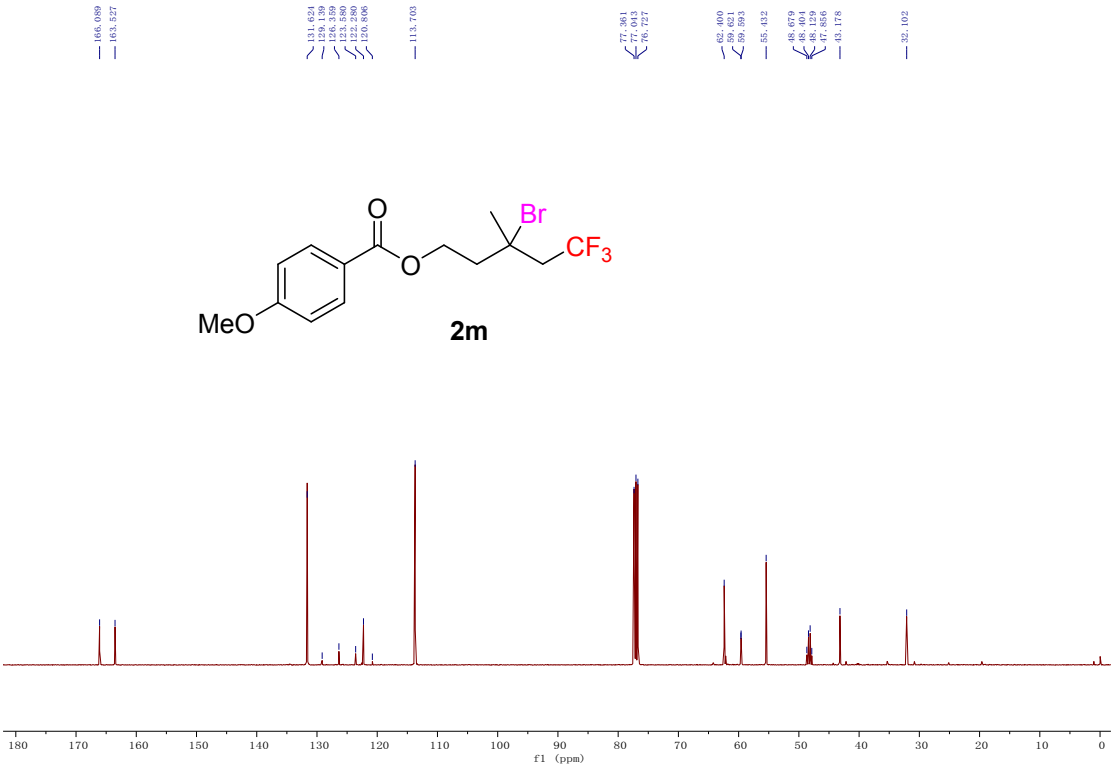

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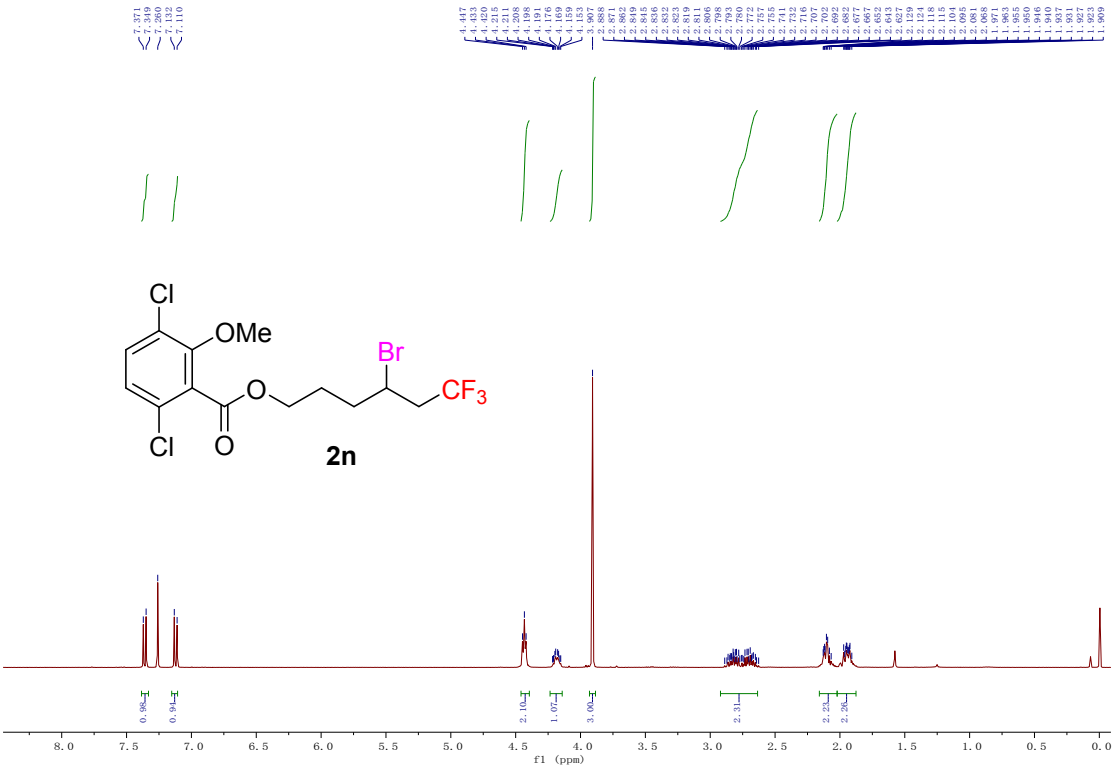

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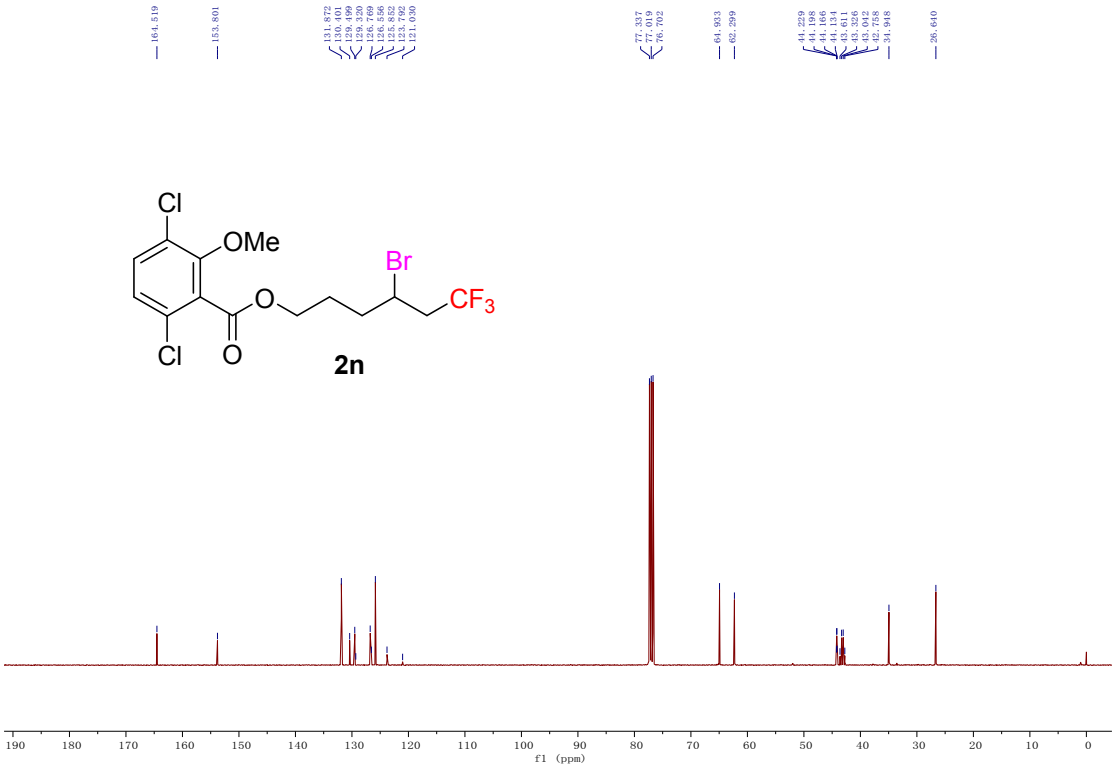

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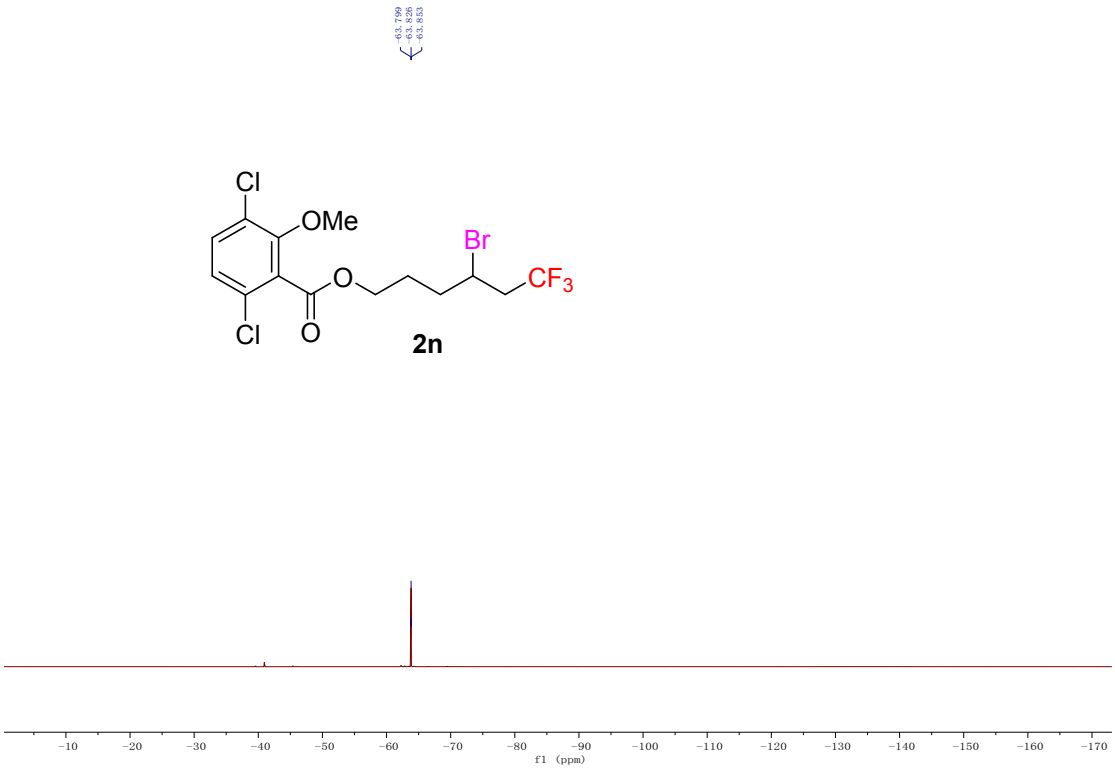

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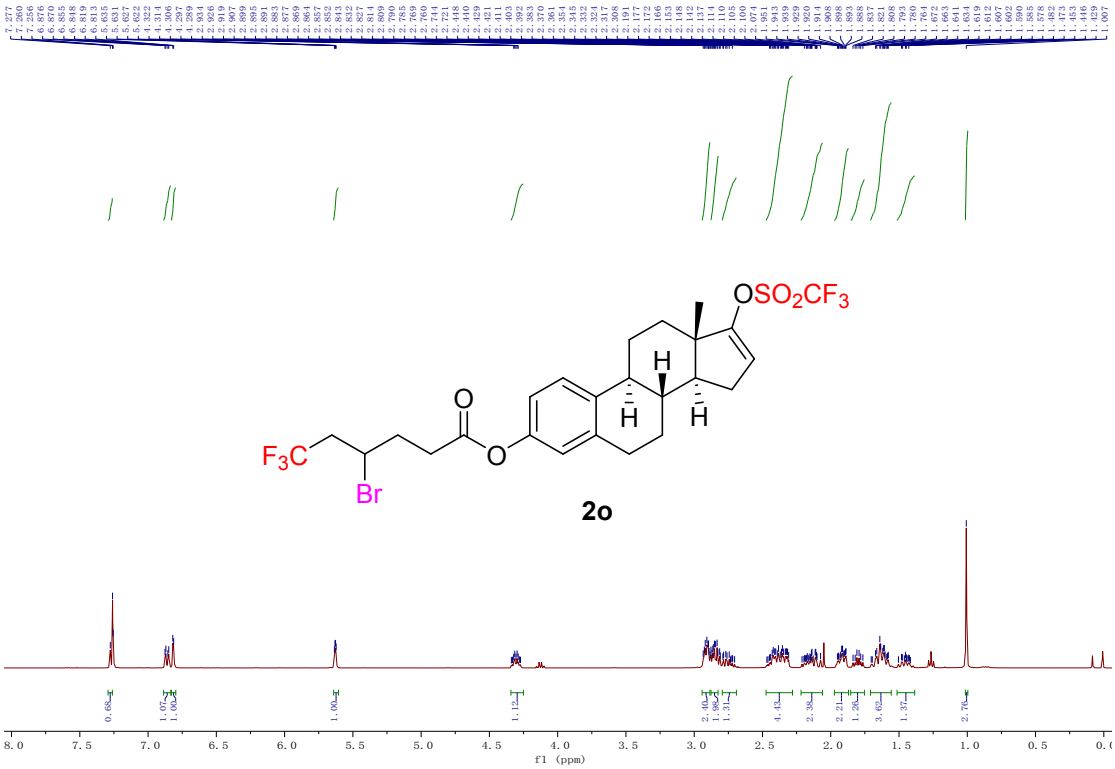

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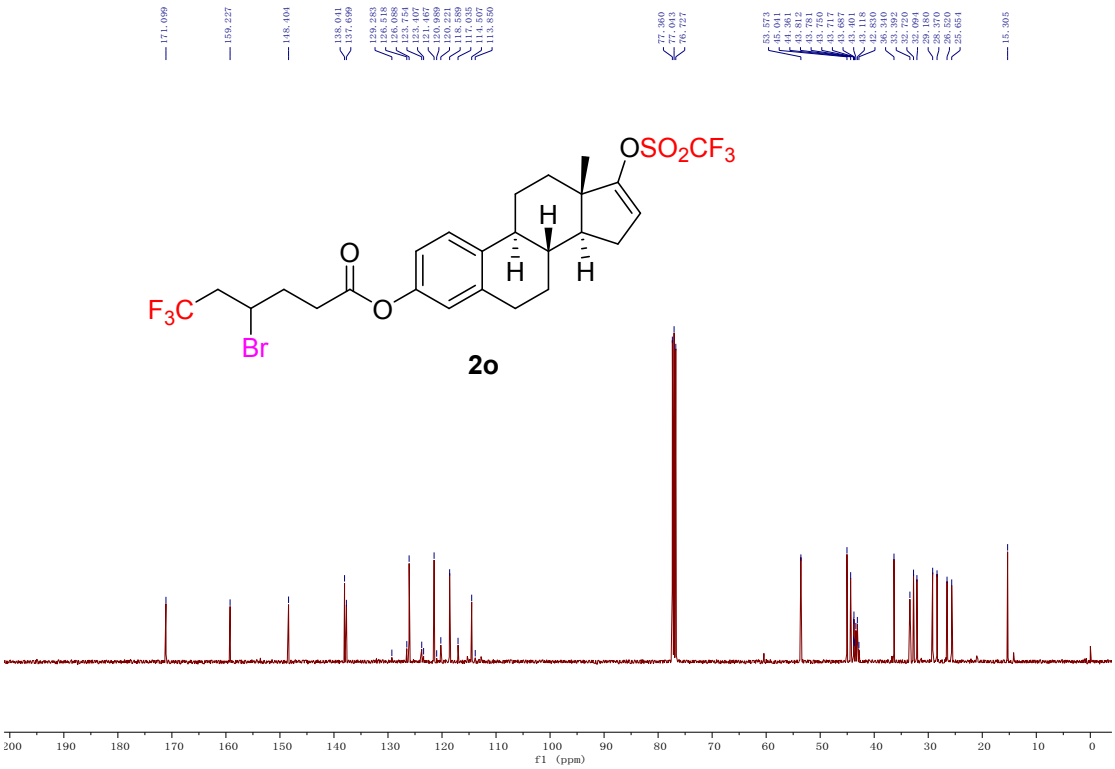

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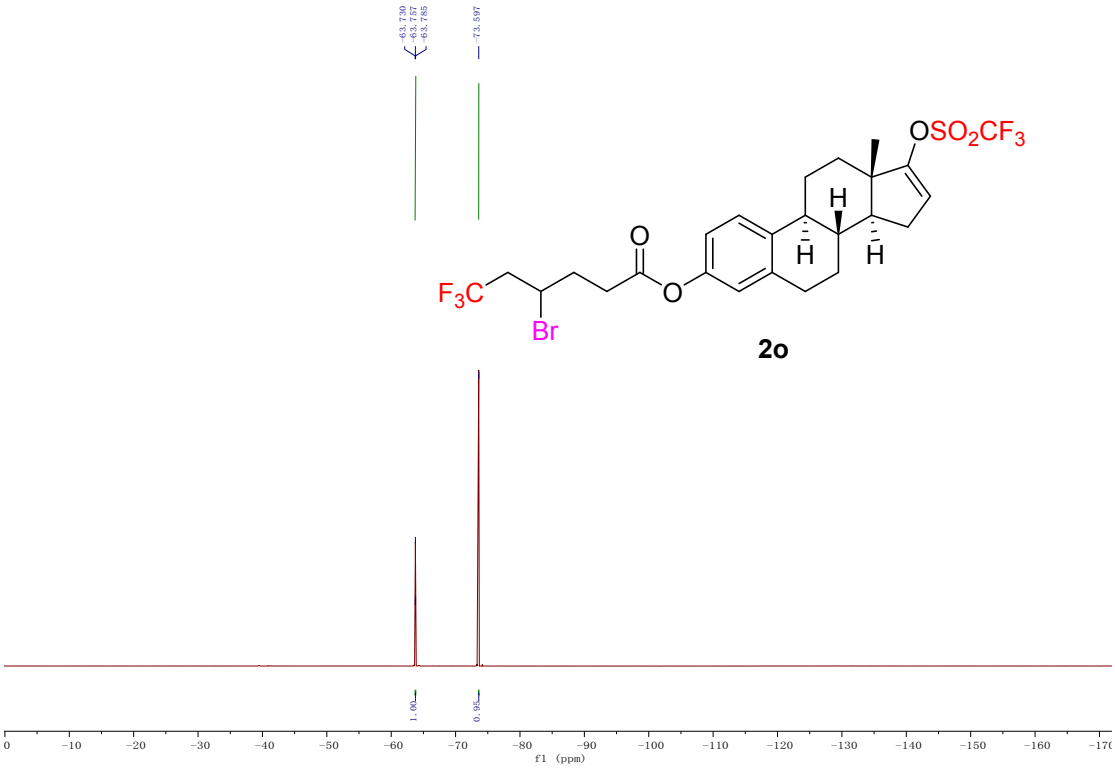

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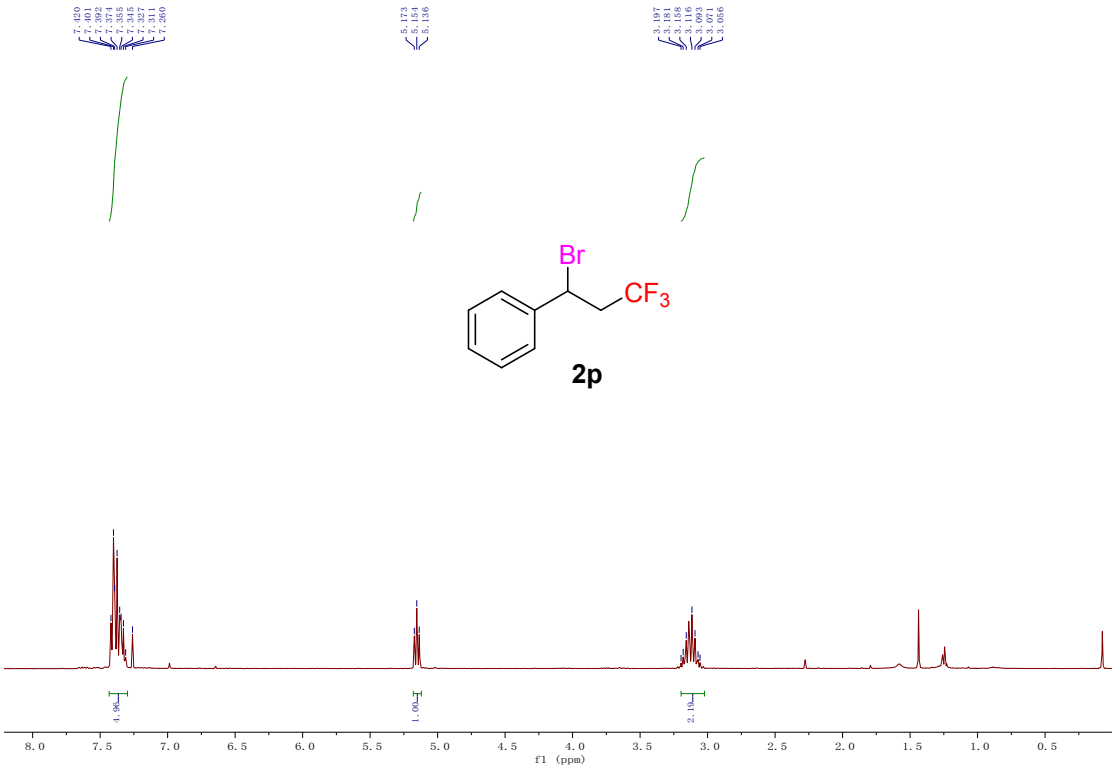

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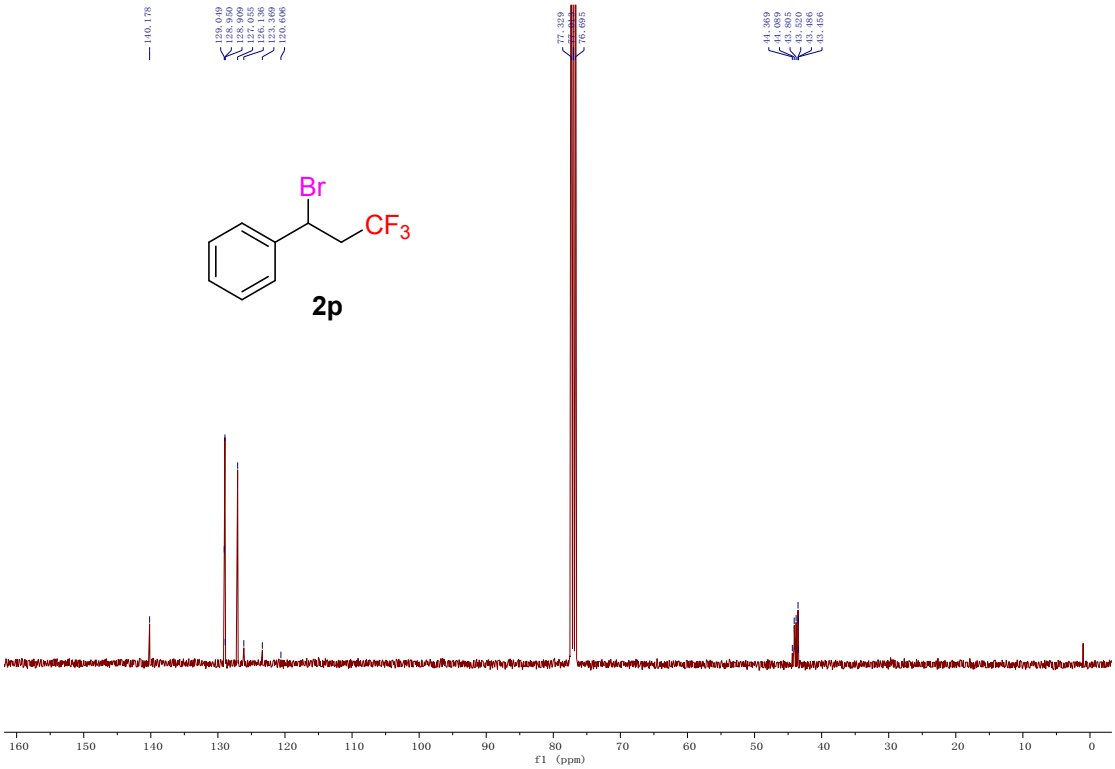
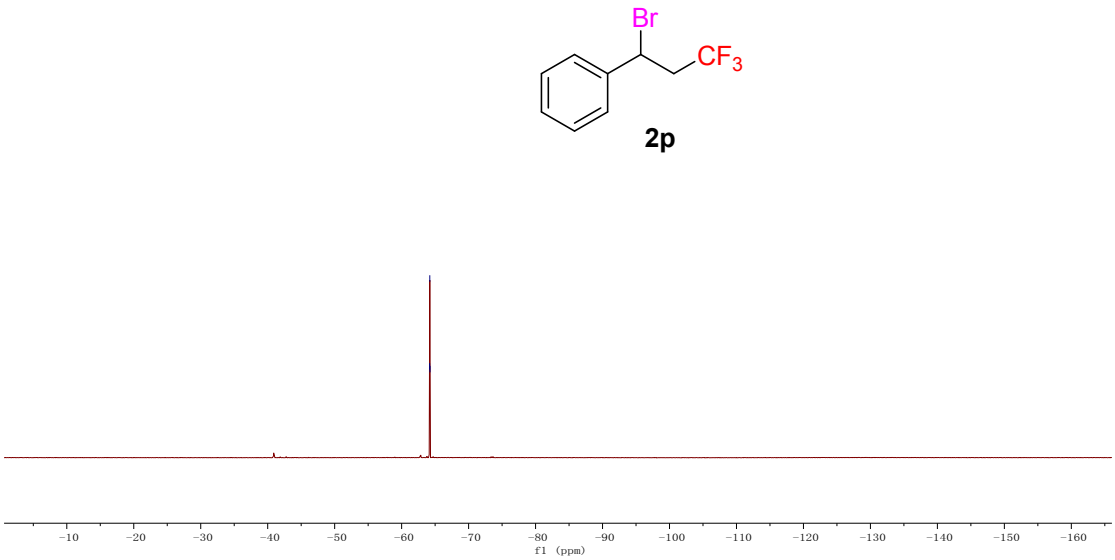
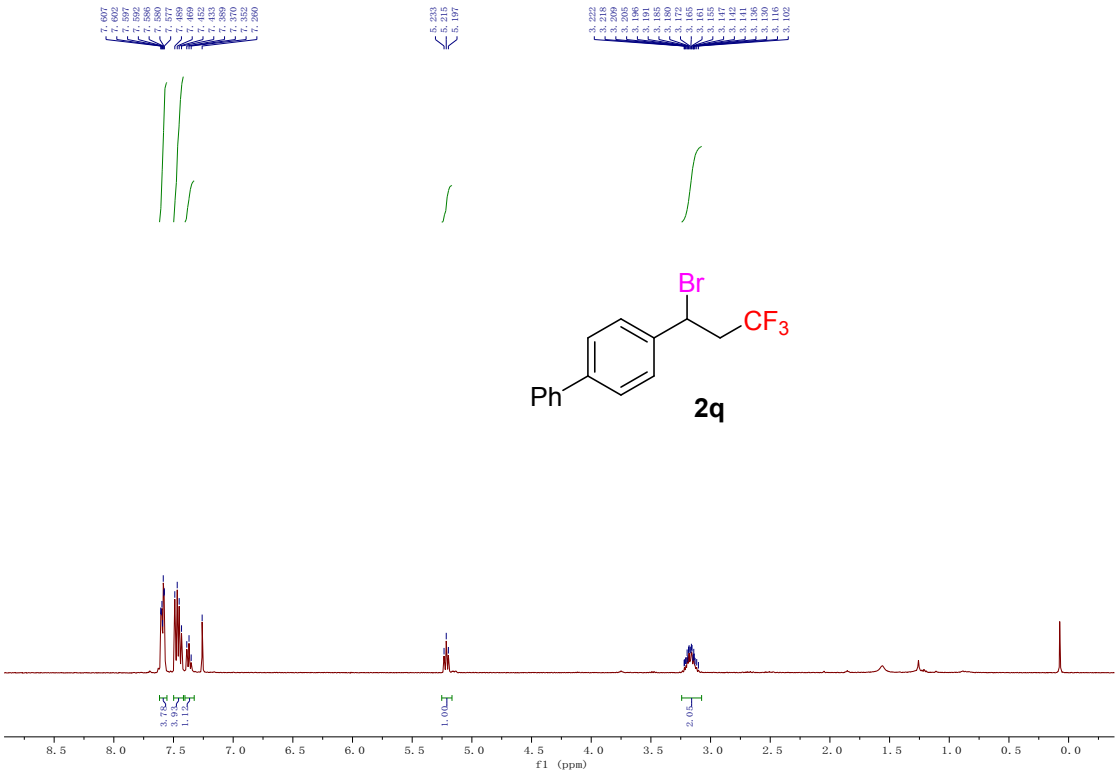


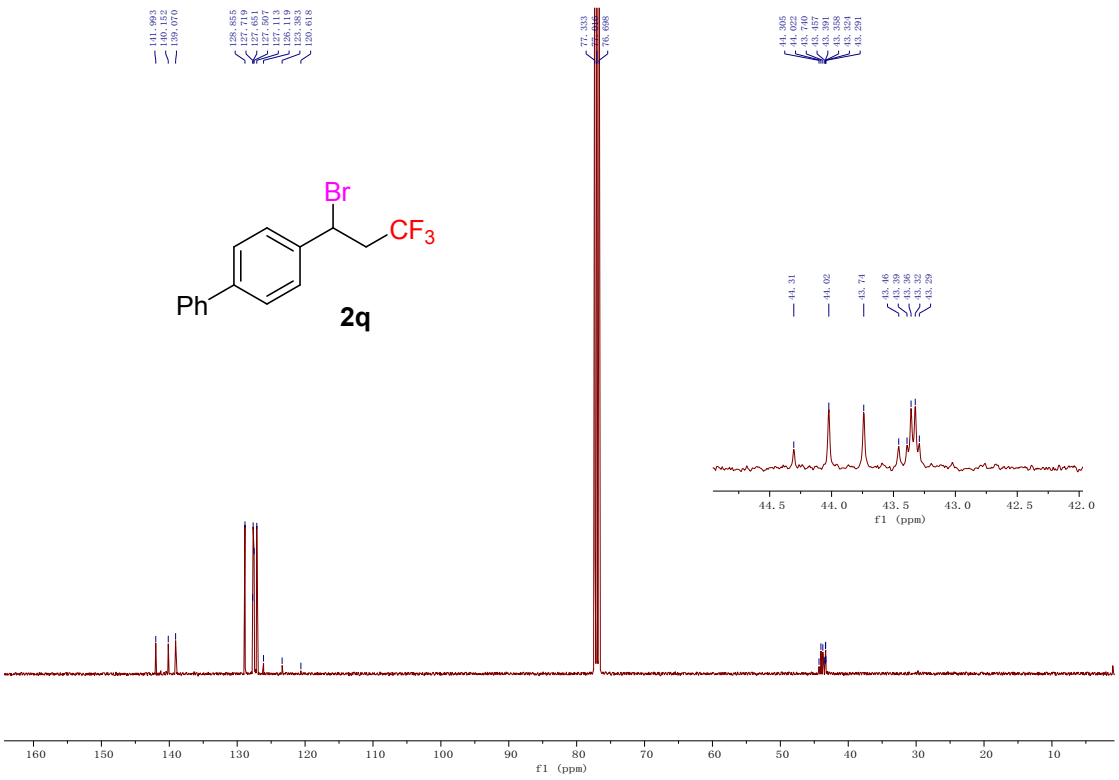
^{19}F NMR (376 MHz, $CDCl_3$)



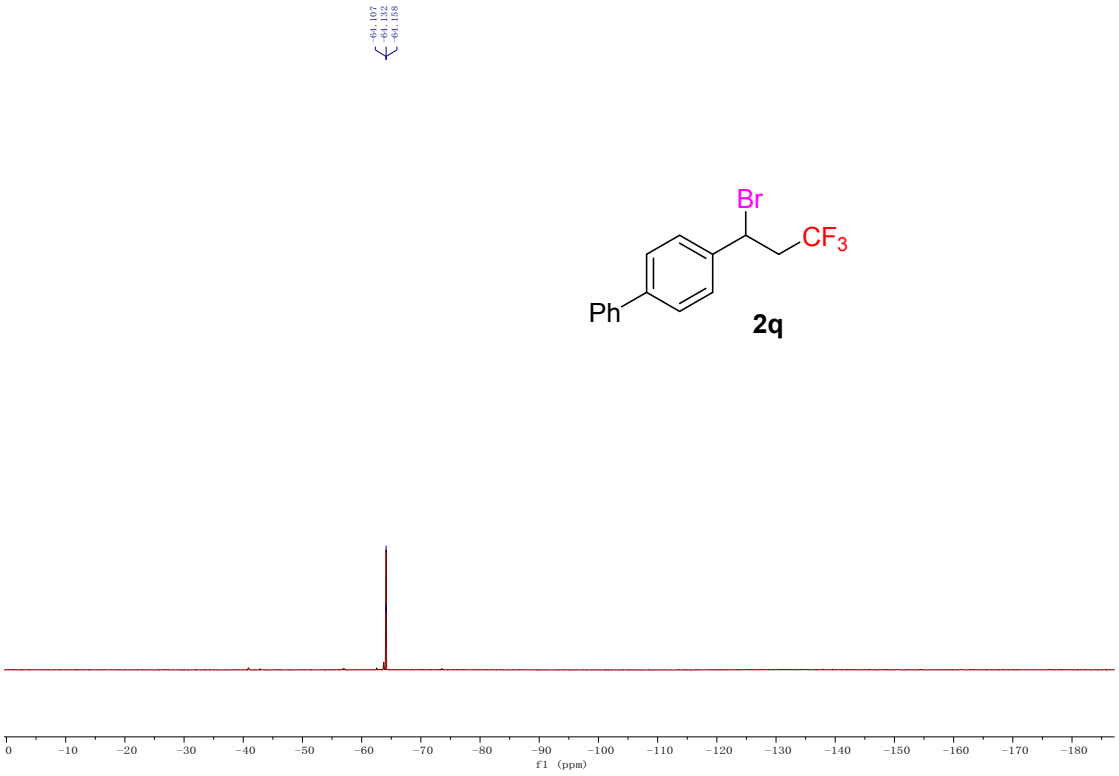
[1]HNMR (400 MHz, $CDCl_3$)



[13]C NMR (100 MHz, $CDCl_3$)



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



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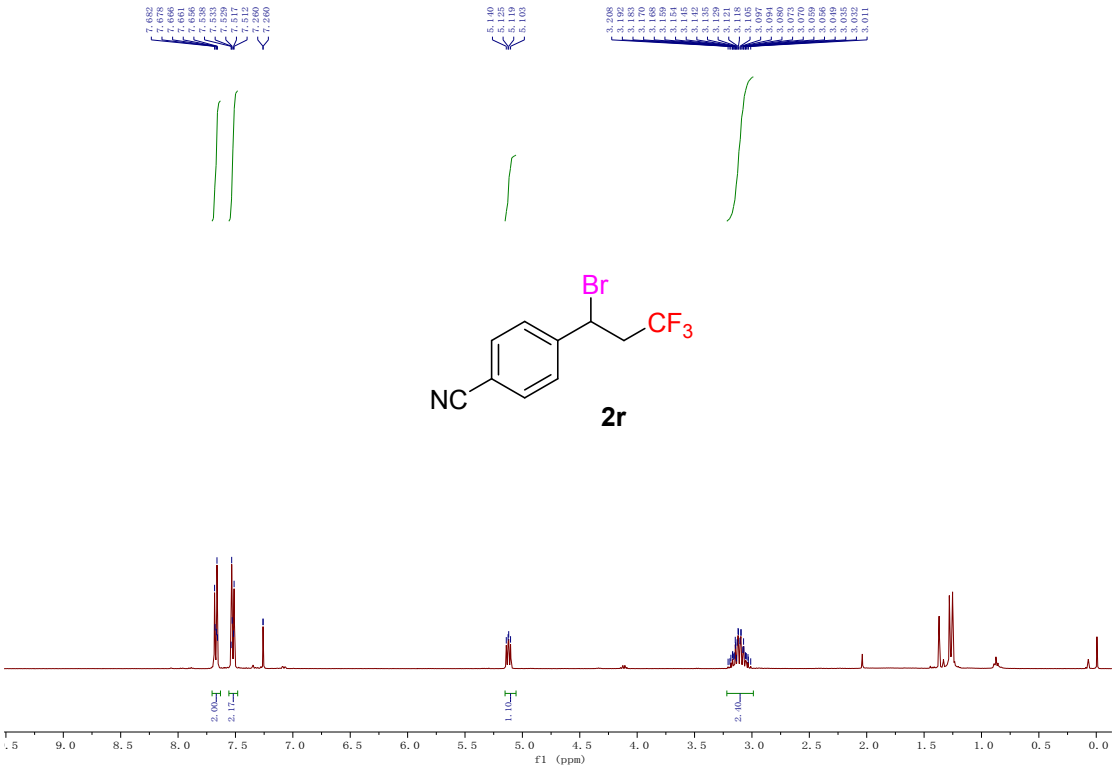

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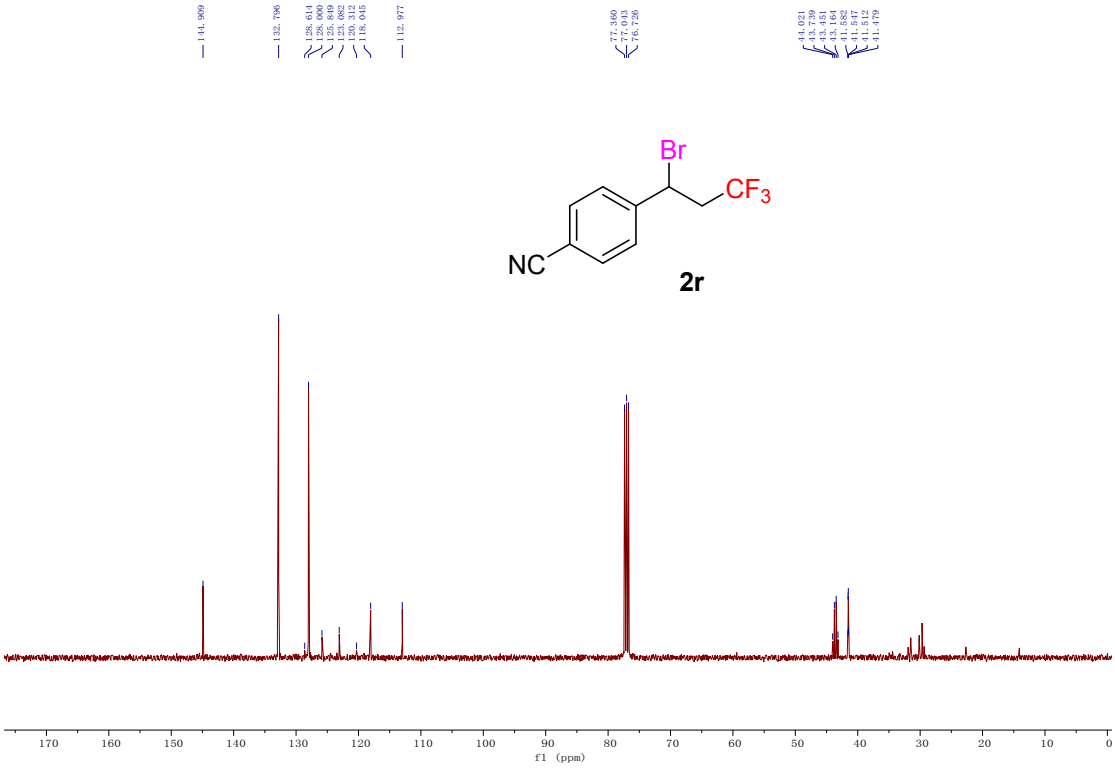
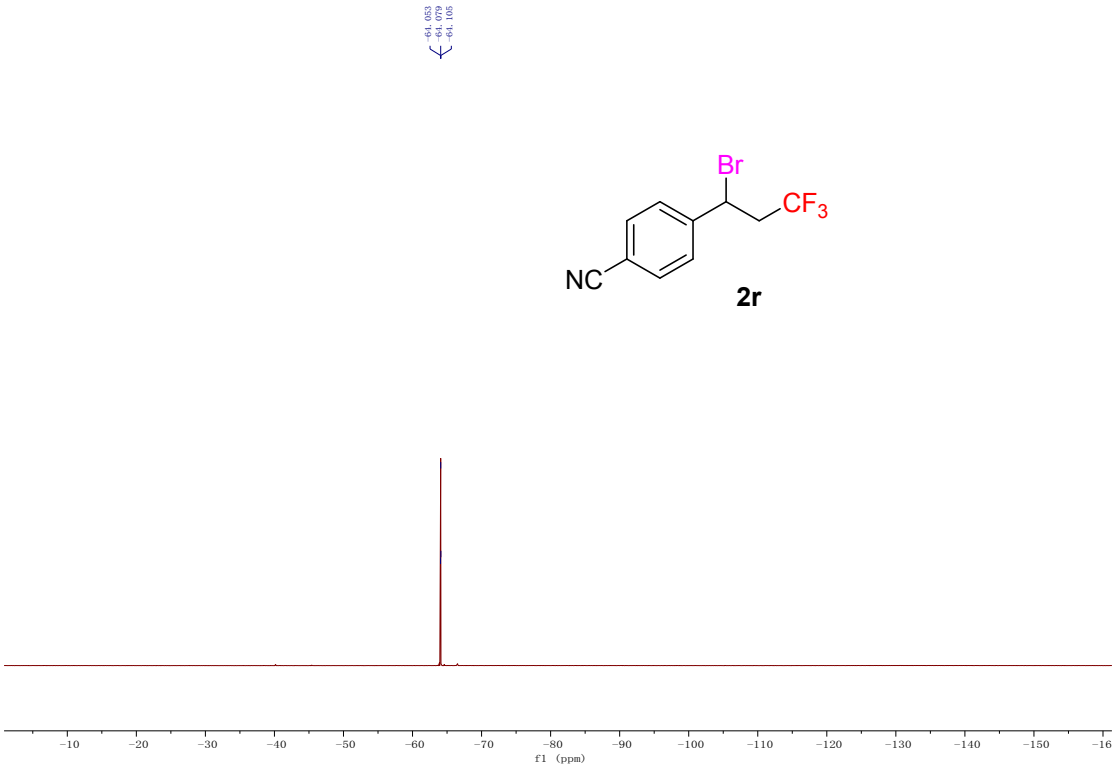
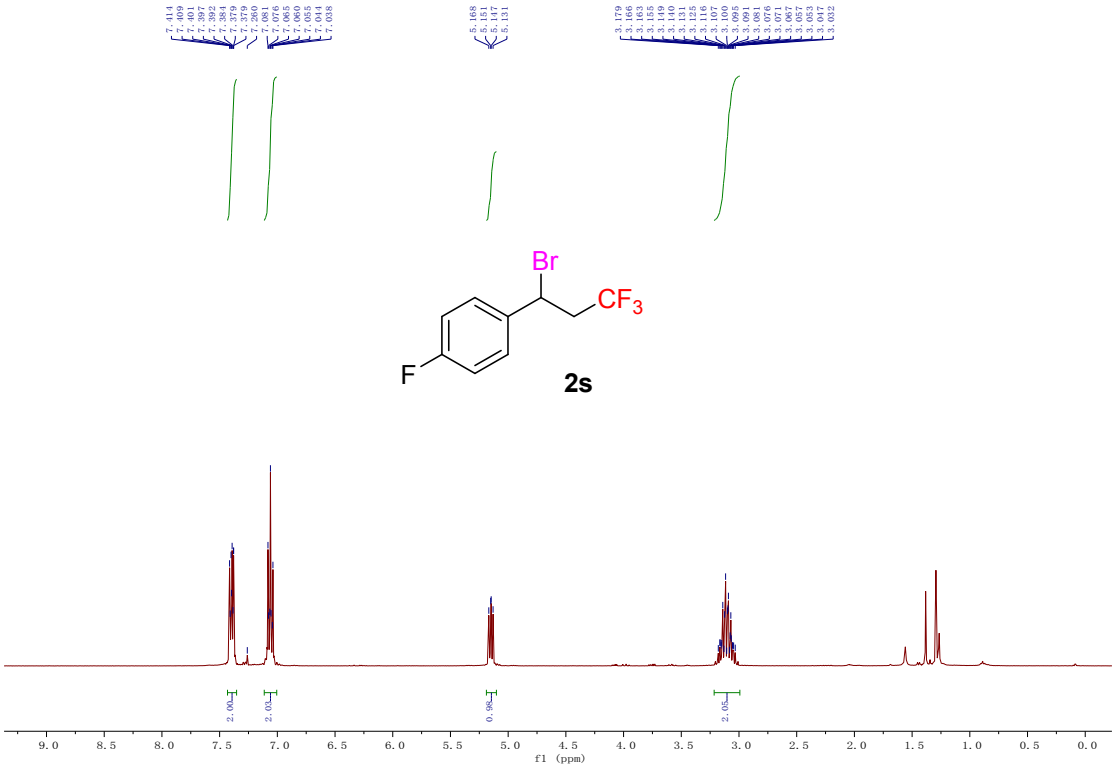


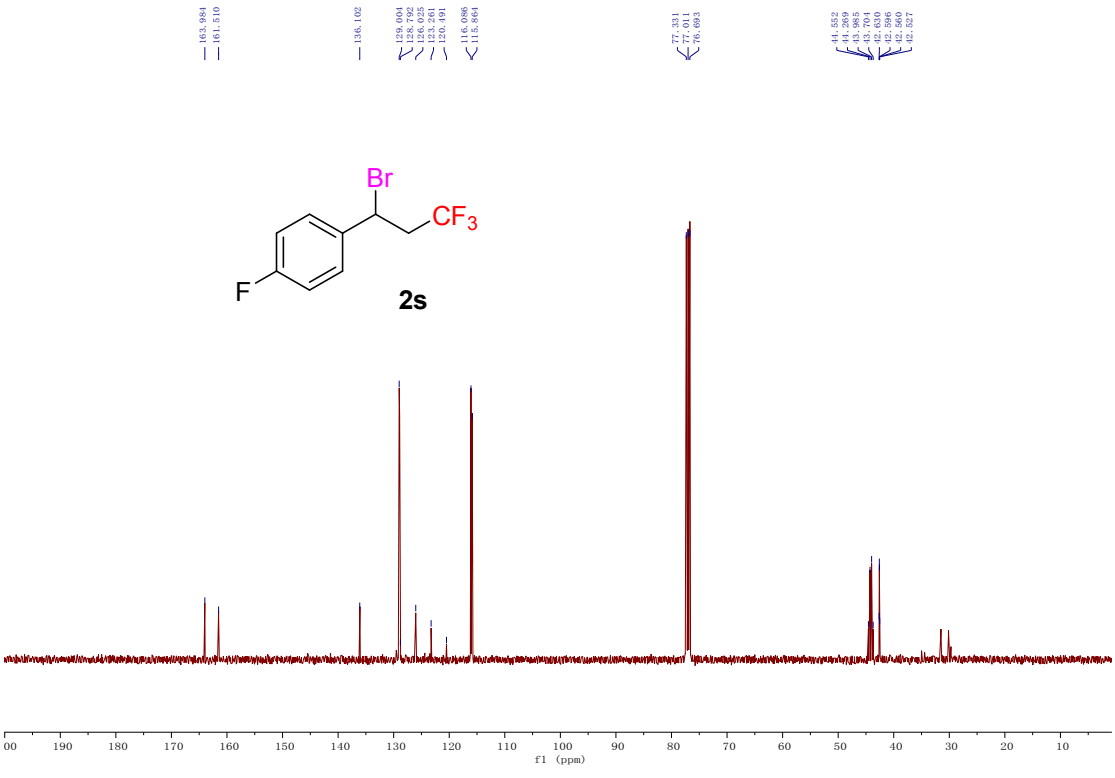
^{19}F NMR (376 MHz, $CDCl_3$)



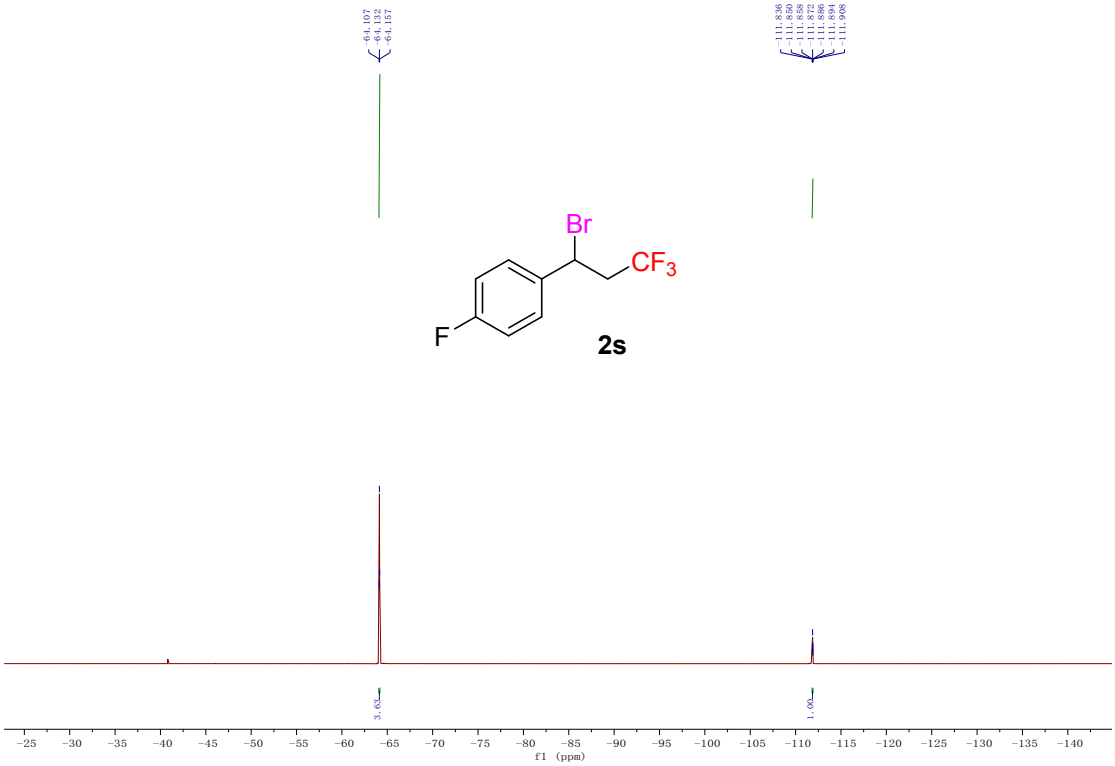
^{1}H NMR (400 MHz, $CDCl_3$)



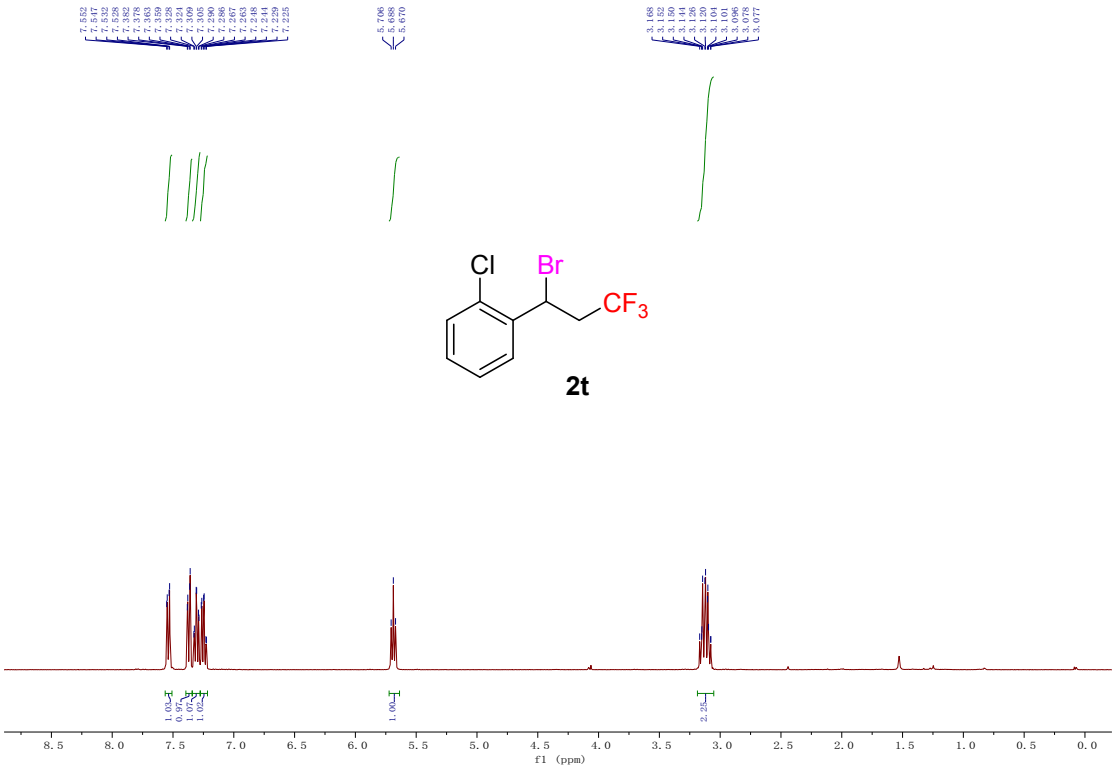
^{13}C NMR (100 MHz, $CDCl_3$)



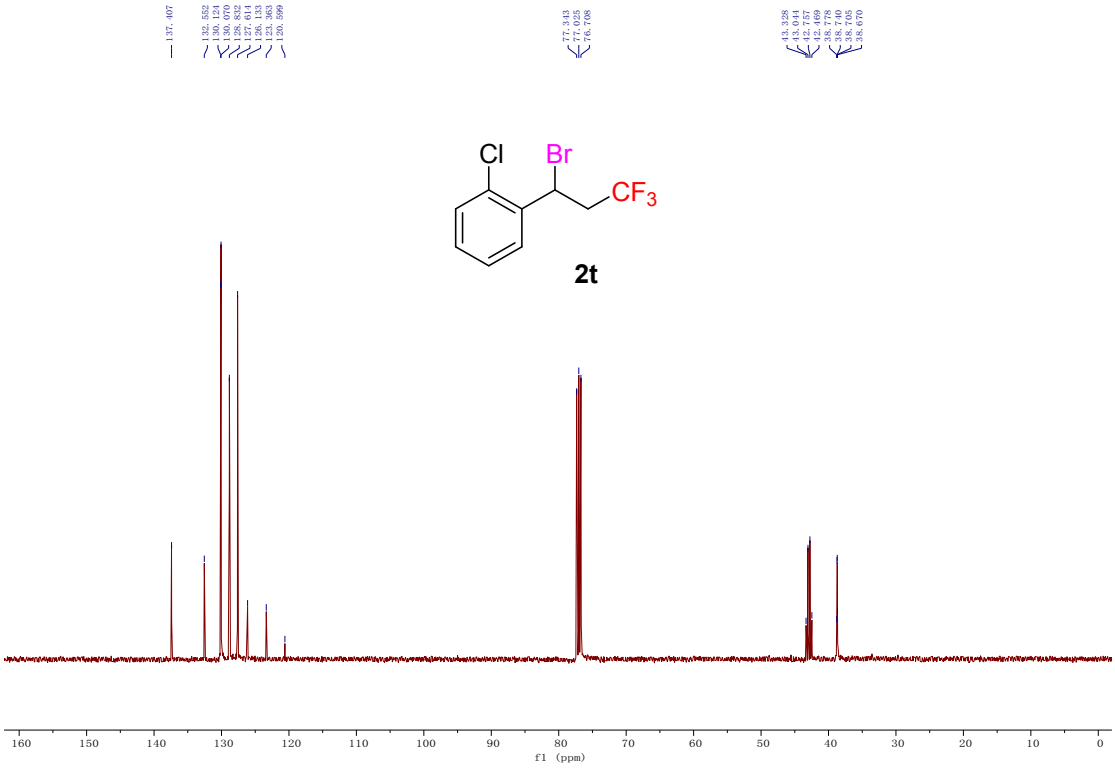
^{19}F NMR (376 MHz, $CDCl_3$)



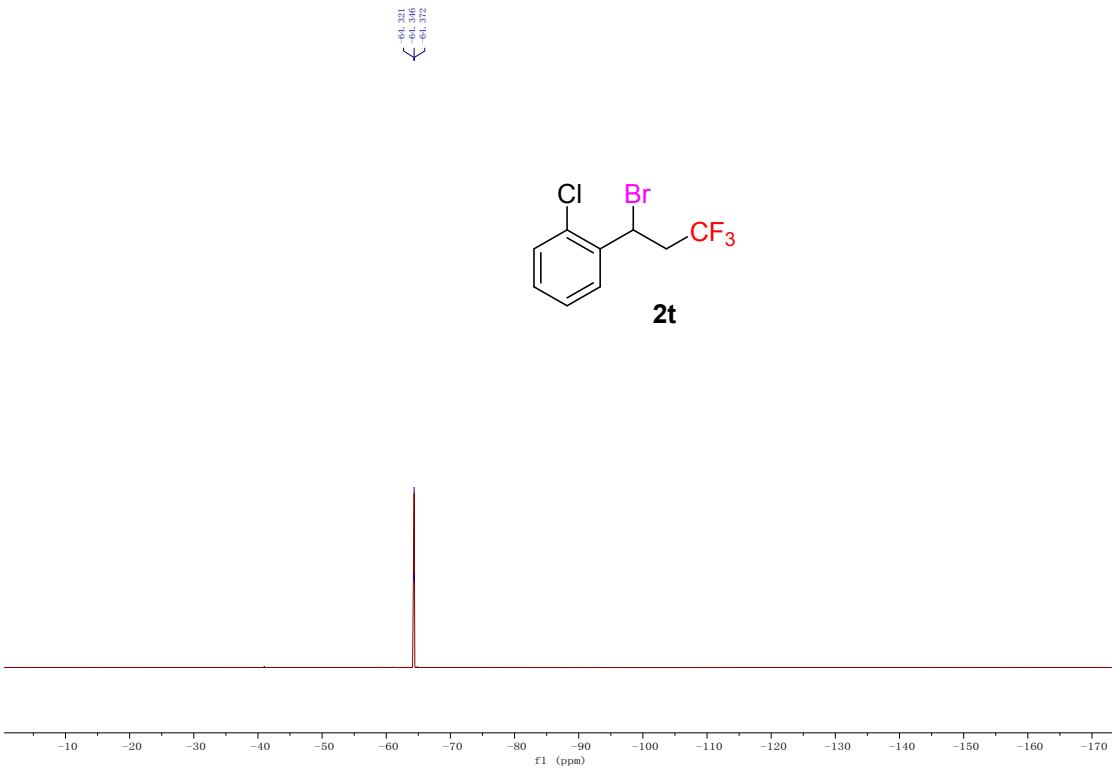
^{1}H NMR (400 MHz, $CDCl_3$)



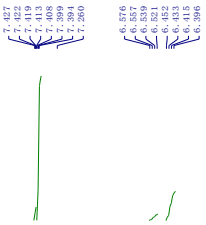
^{13}C NMR (100MHz, $CDCl_3$)

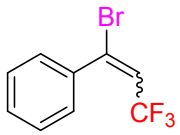


^{19}F NMR (376 MHz, $CDCl_3$)

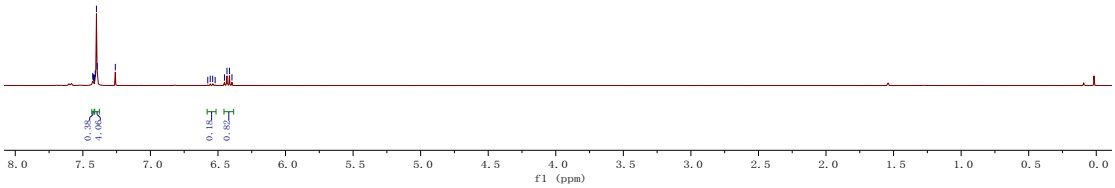


^{1}H NMR (400 MHz, $CDCl_3$)

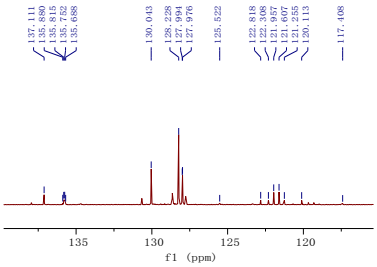


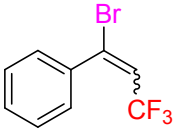


4a

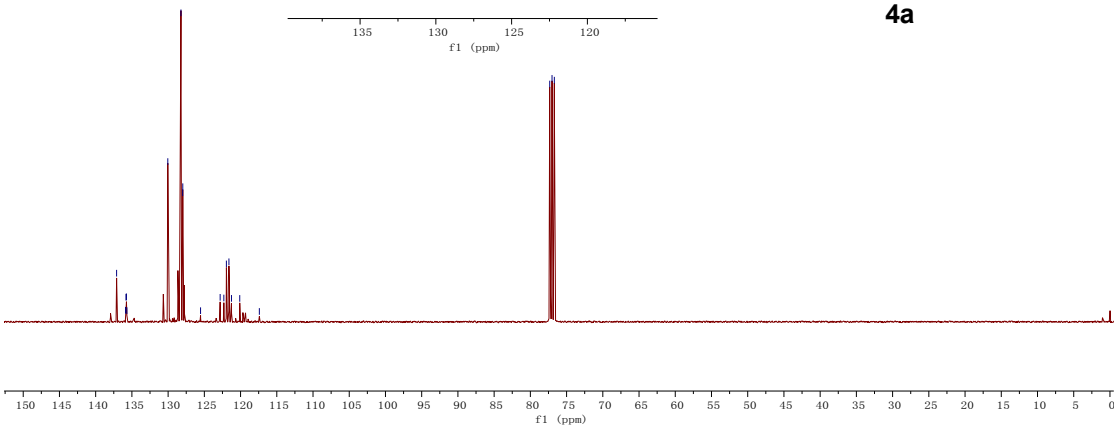


^{13}C NMR (100 MHz, $CDCl_3$)

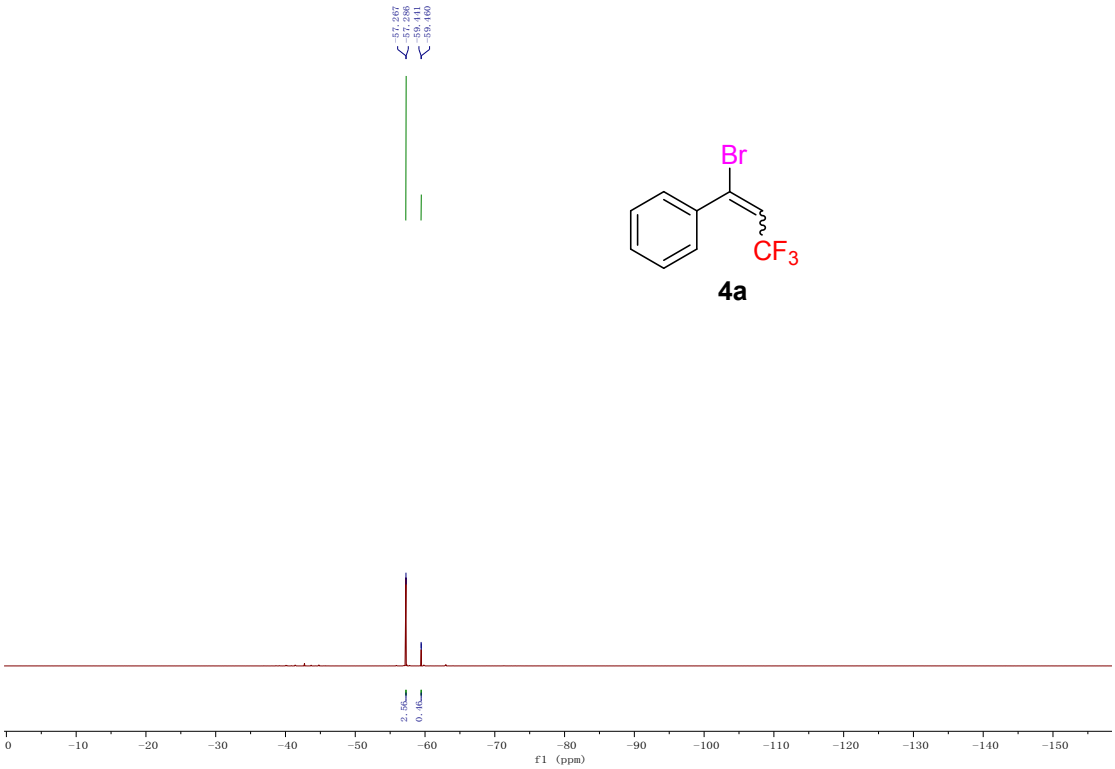




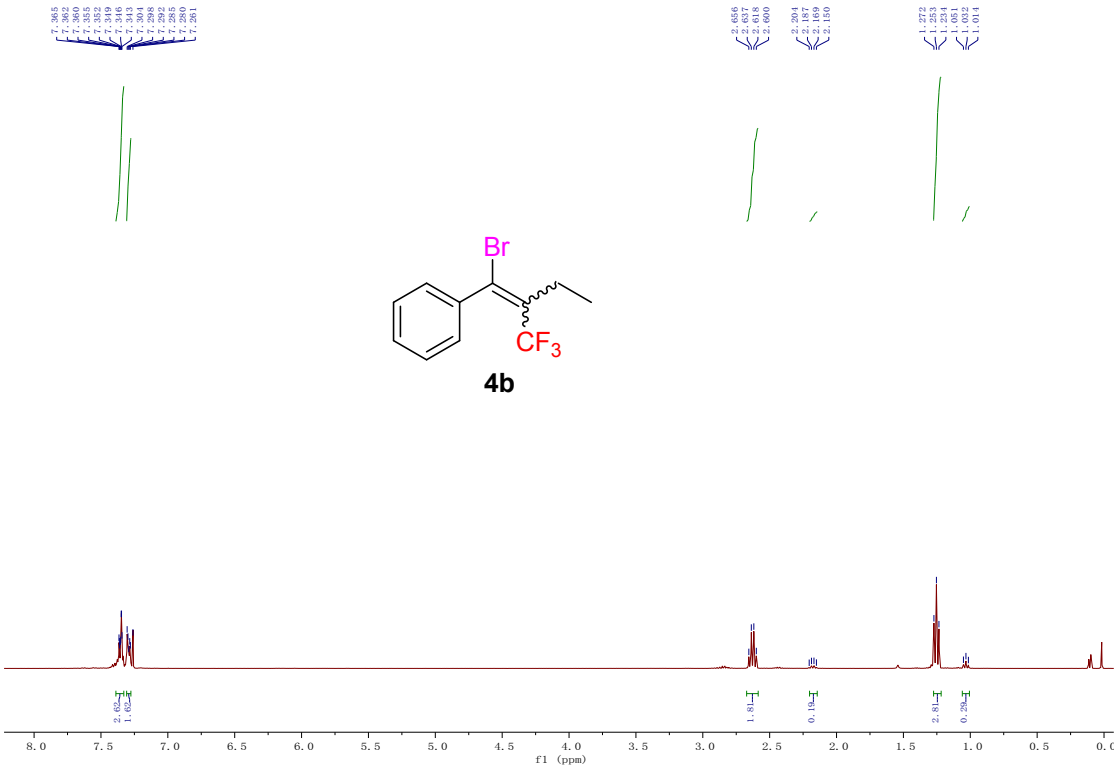
4a



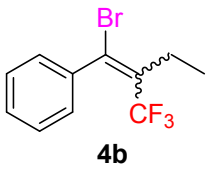
^{19}F NMR (376 MHz, $CDCl_3$)



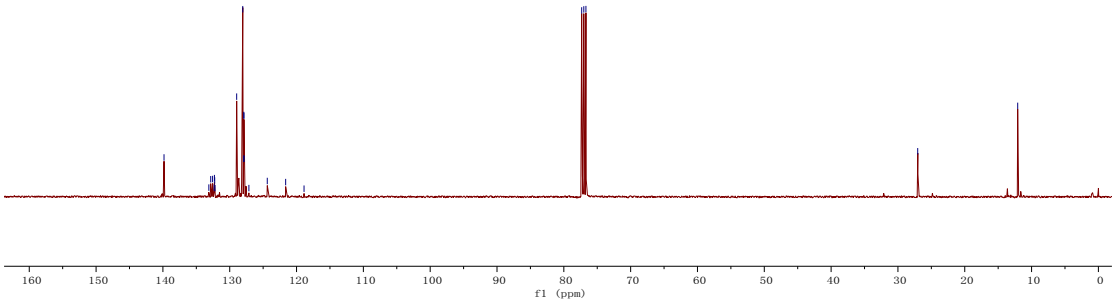
^{1}H NMR (400 MHz, $CDCl_3$)



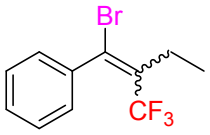
^{13}C NMR (100 MHz, $CDCl_3$)



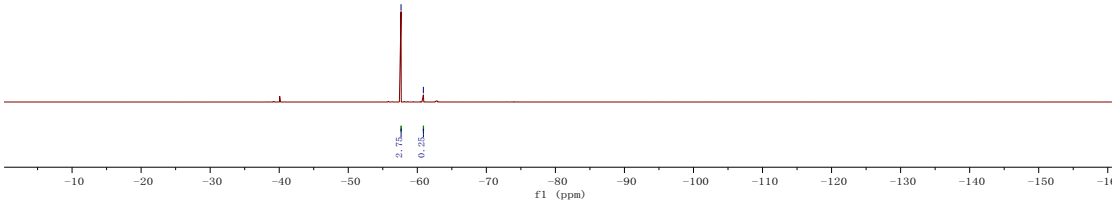
4b



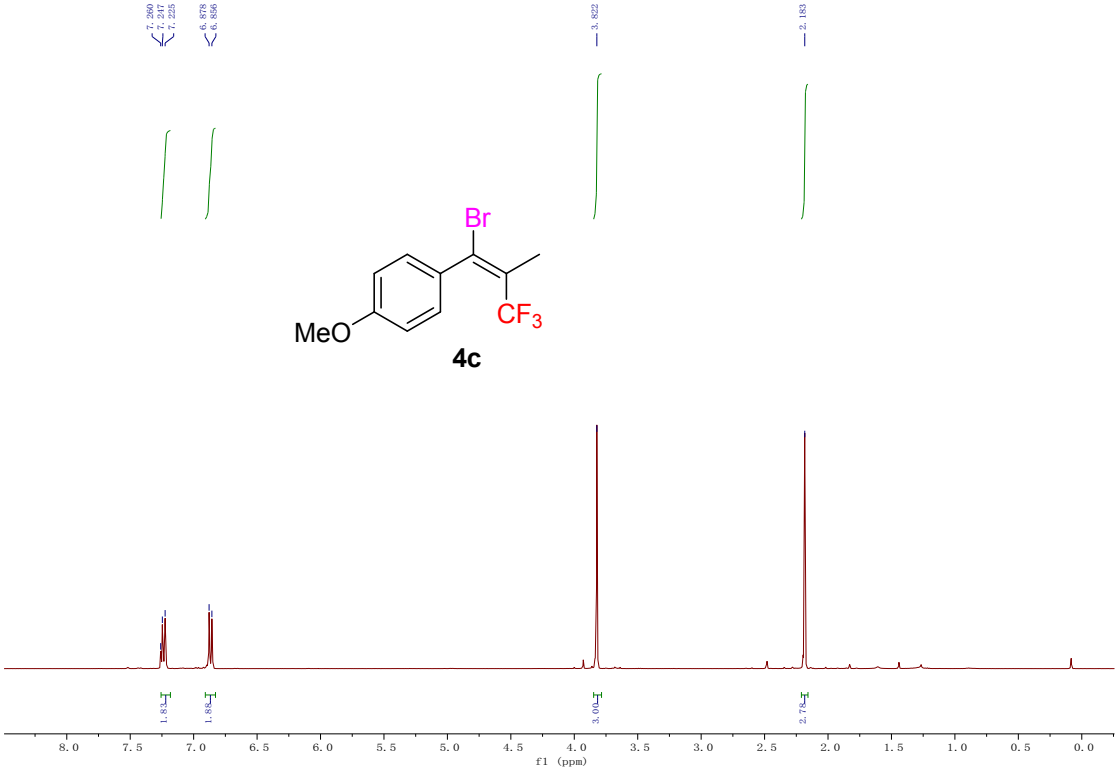
^{19}F NMR (376 MHz, $CDCl_3$)



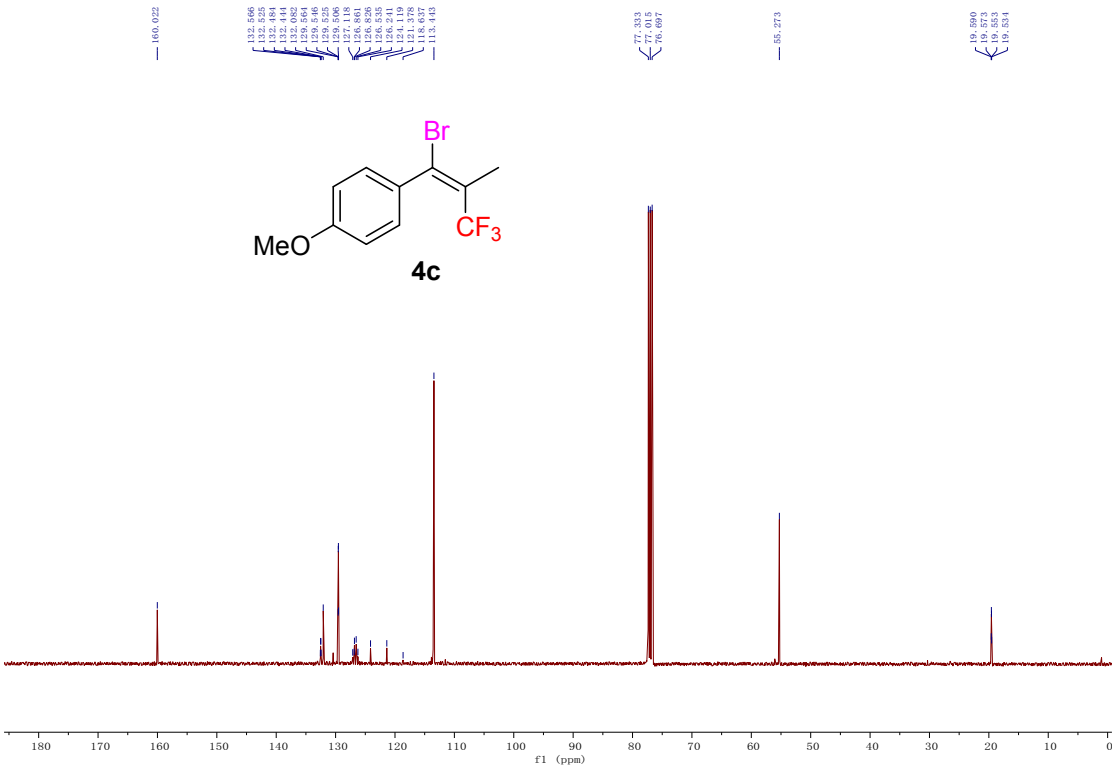
4b



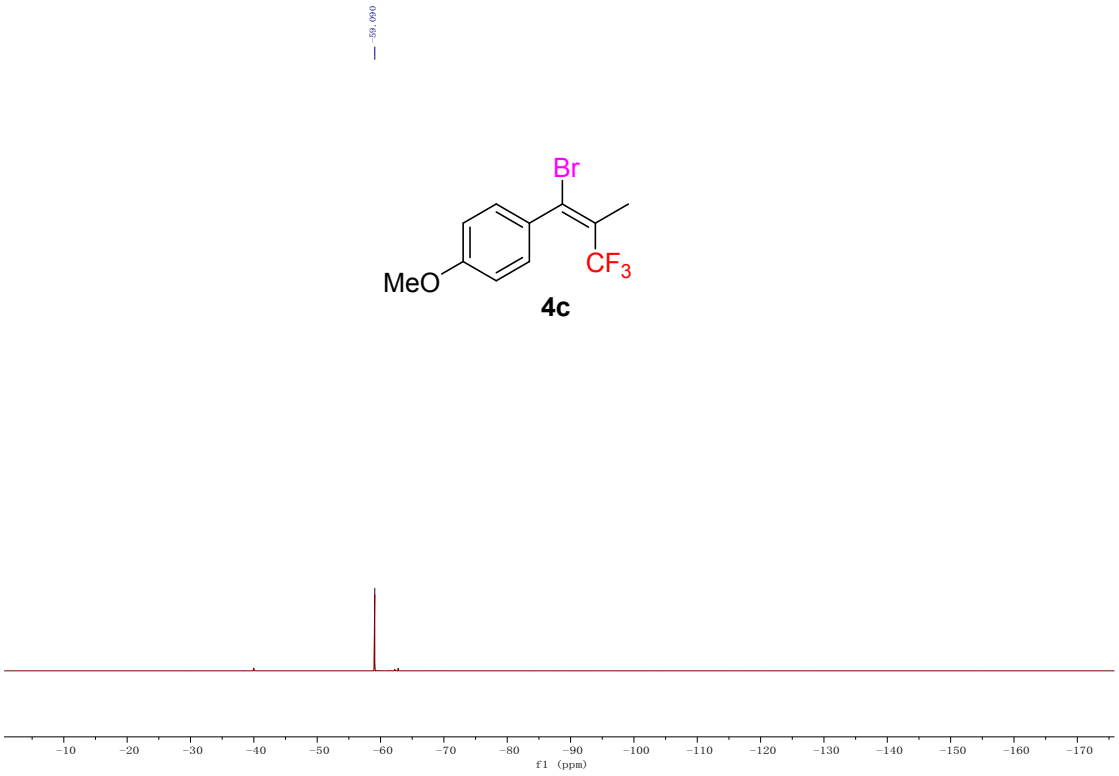
^{1}H NMR (400 MHz, $CDCl_3$)



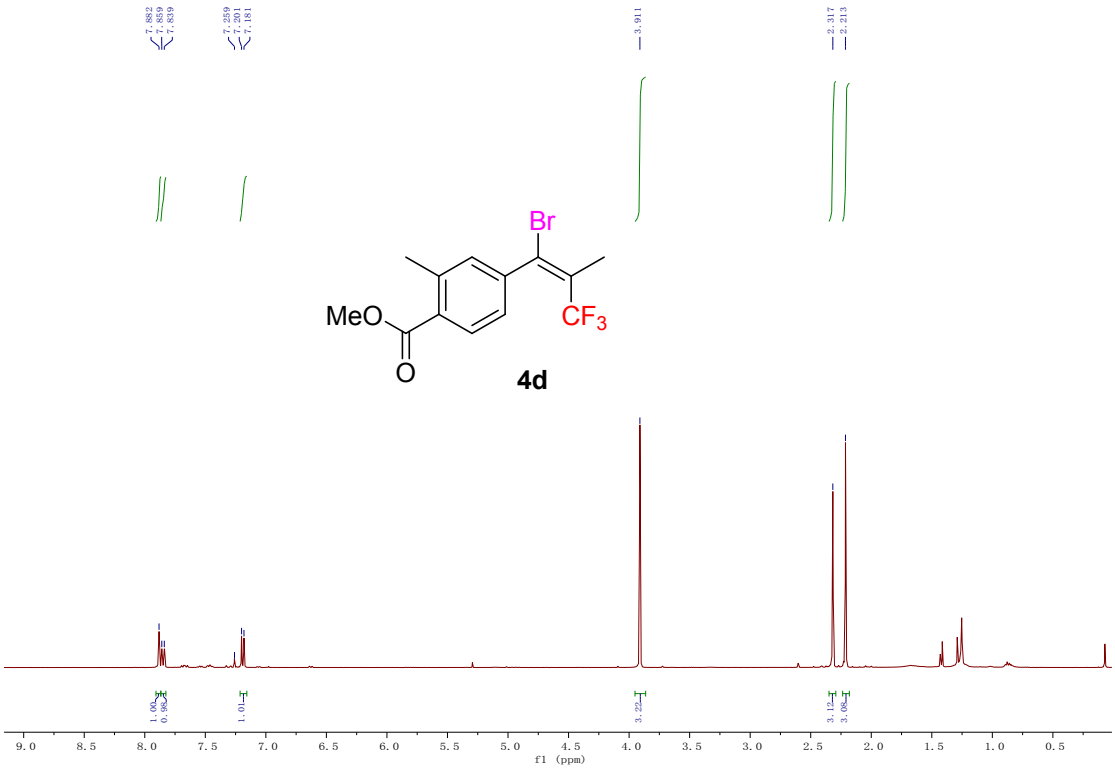
^{13}C NMR (100 MHz, $CDCl_3$)



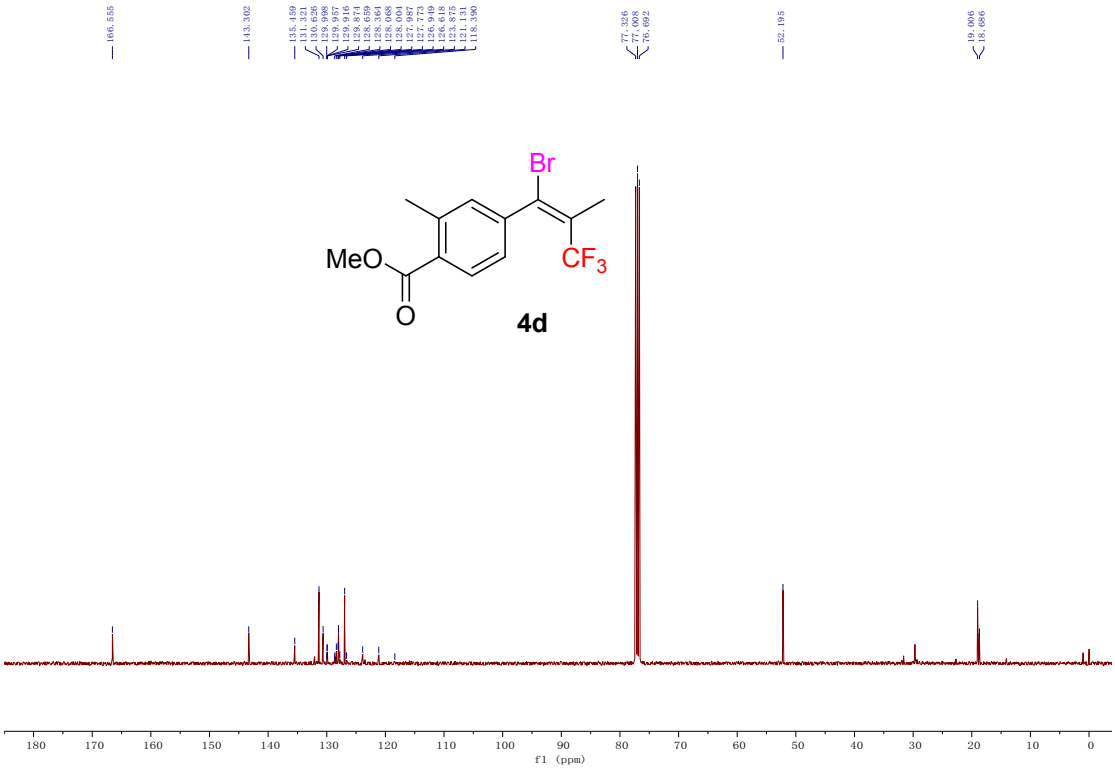
^{19}F NMR (376 MHz, $CDCl_3$)



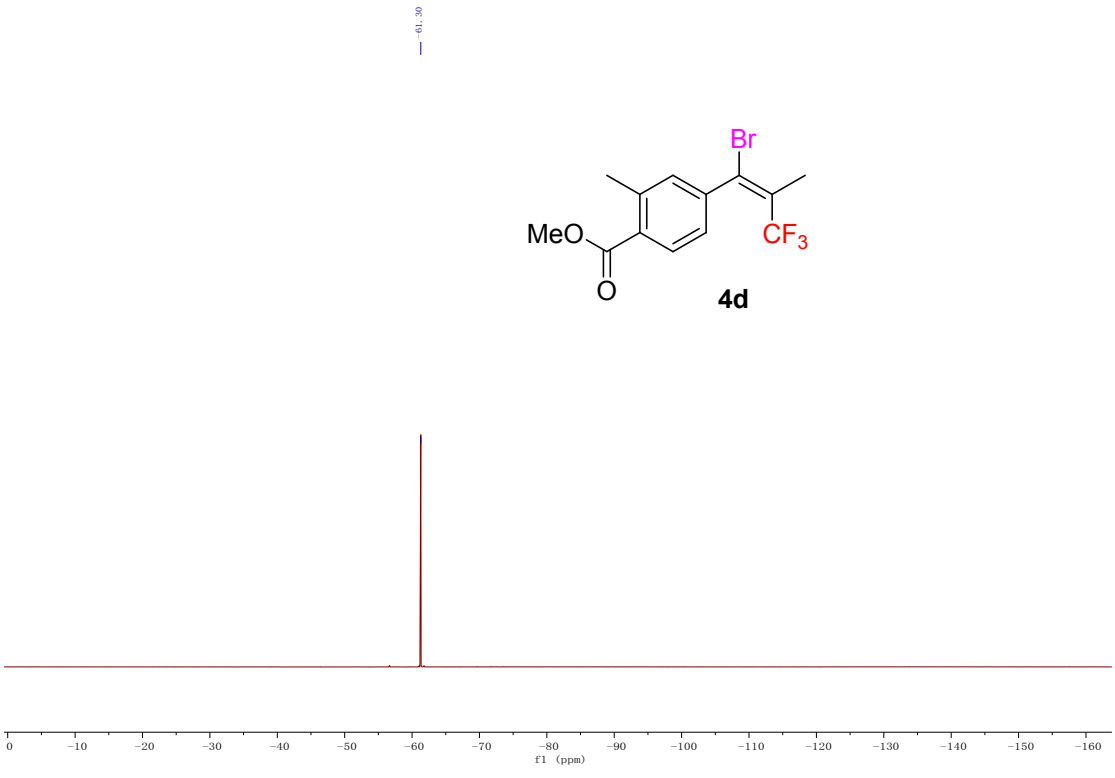
^{1}H NMR (400 MHz, $CDCl_3$)



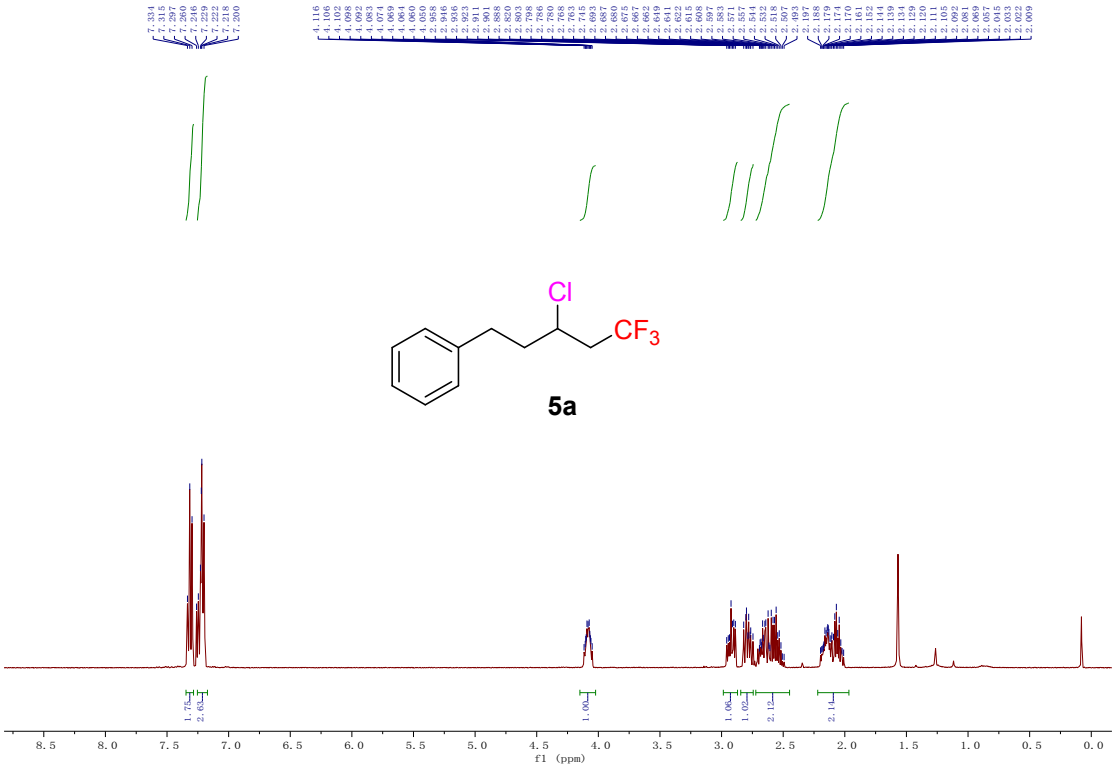
^{13}C NMR (100 MHz, $CDCl_3$)



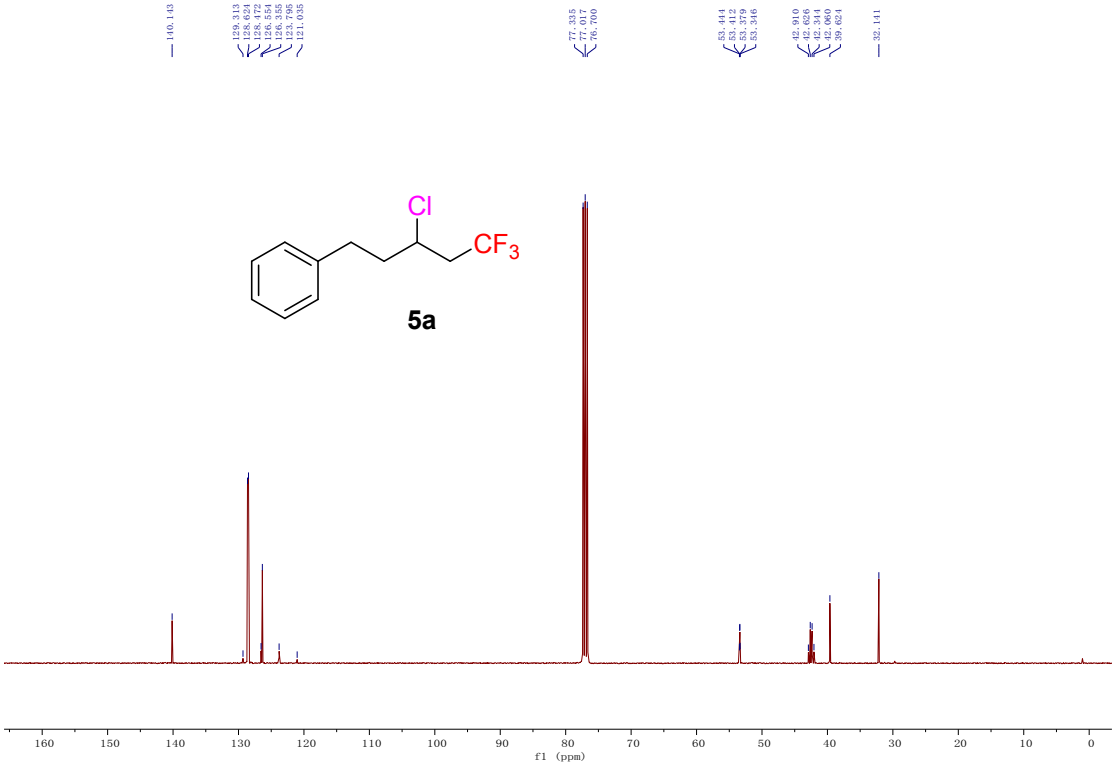
^{19}F NMR (376 MHz, $CDCl_3$)



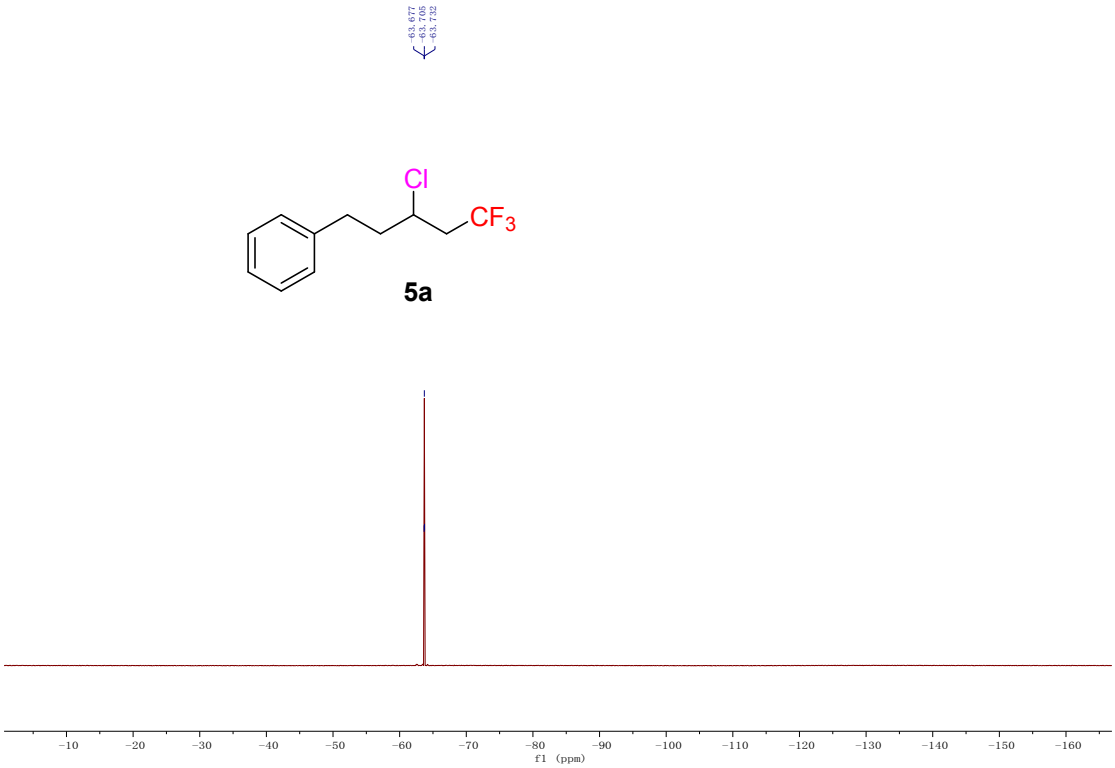
^{1}H NMR (400 MHz, $CDCl_3$)



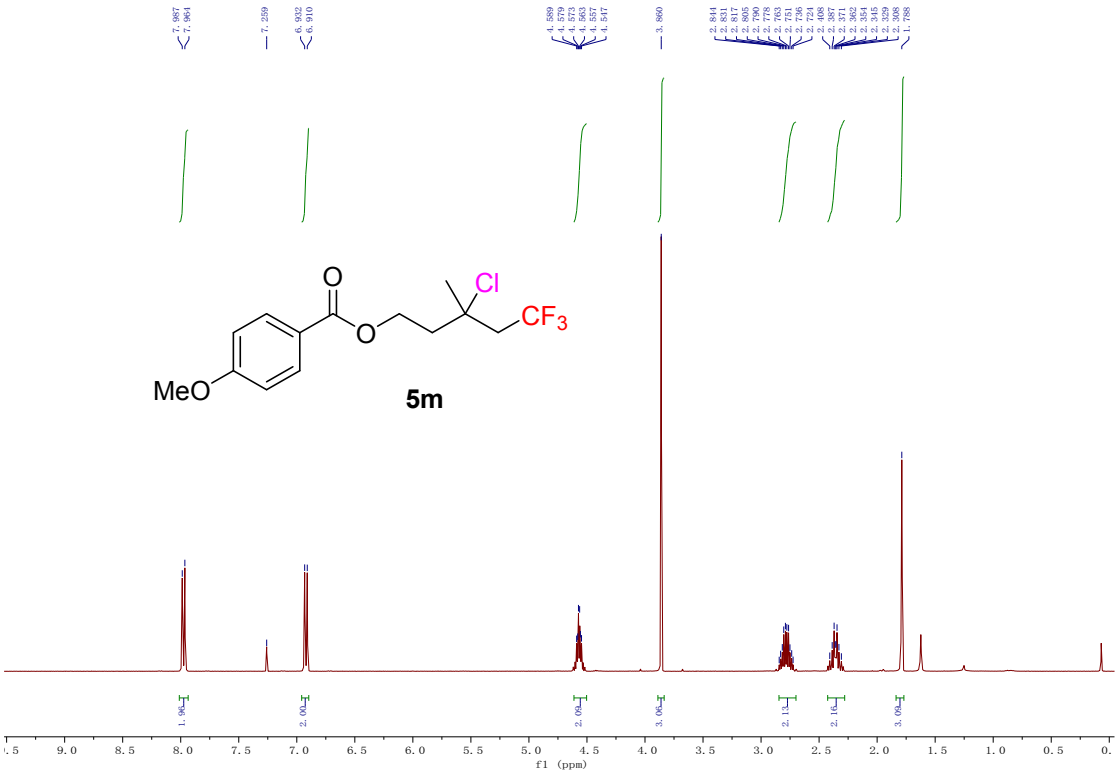
^{13}C NMR (100 MHz, $CDCl_3$)



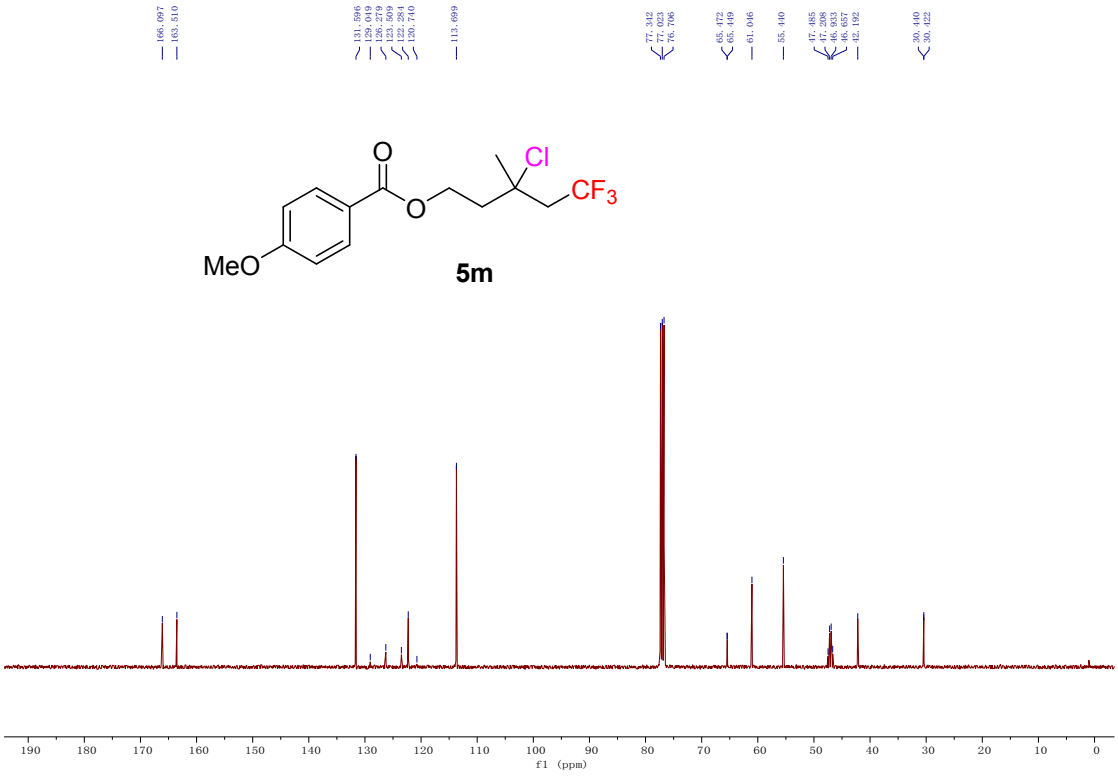
^{19}F NMR (376 MHz, $CDCl_3$)



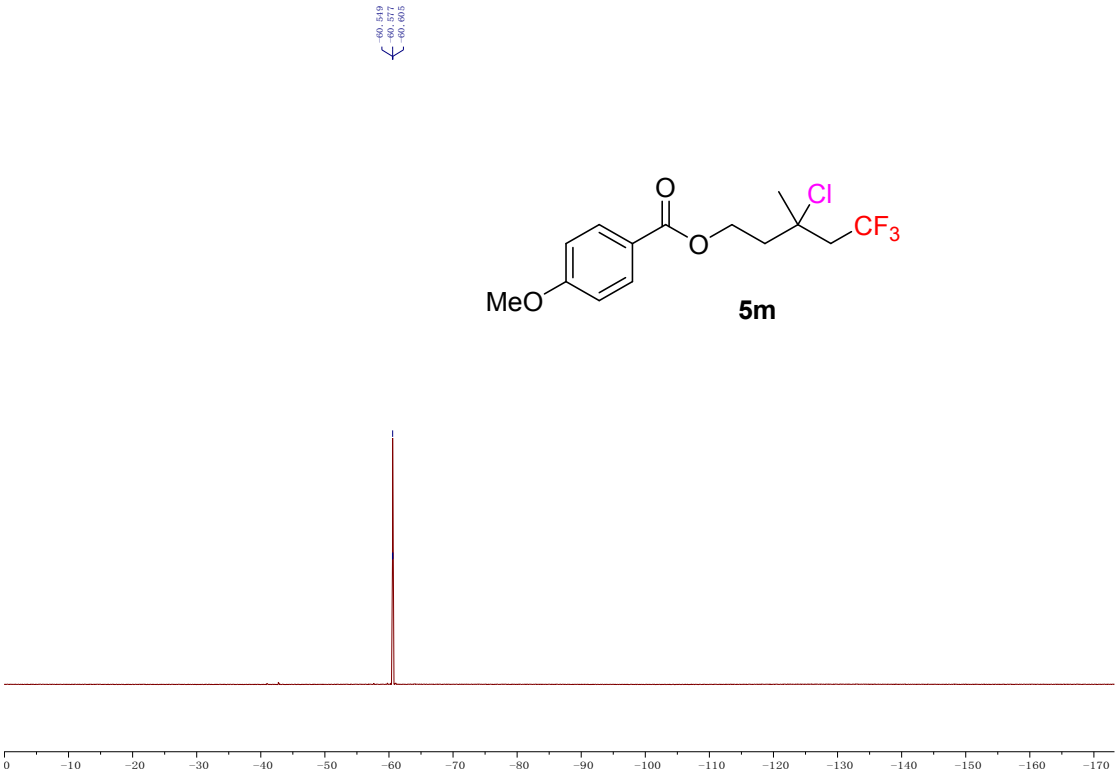
^{1}H NMR (400 MHz, $CDCl_3$)



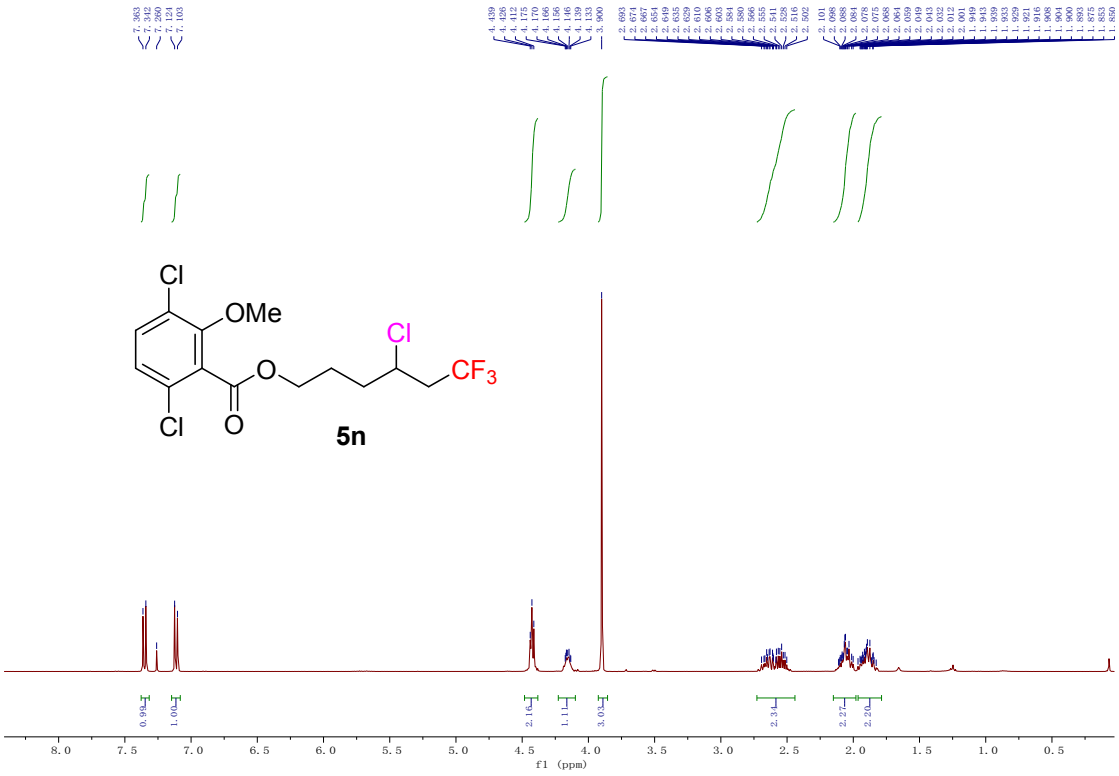
^{13}C NMR (100MHz, $CDCl_3$)



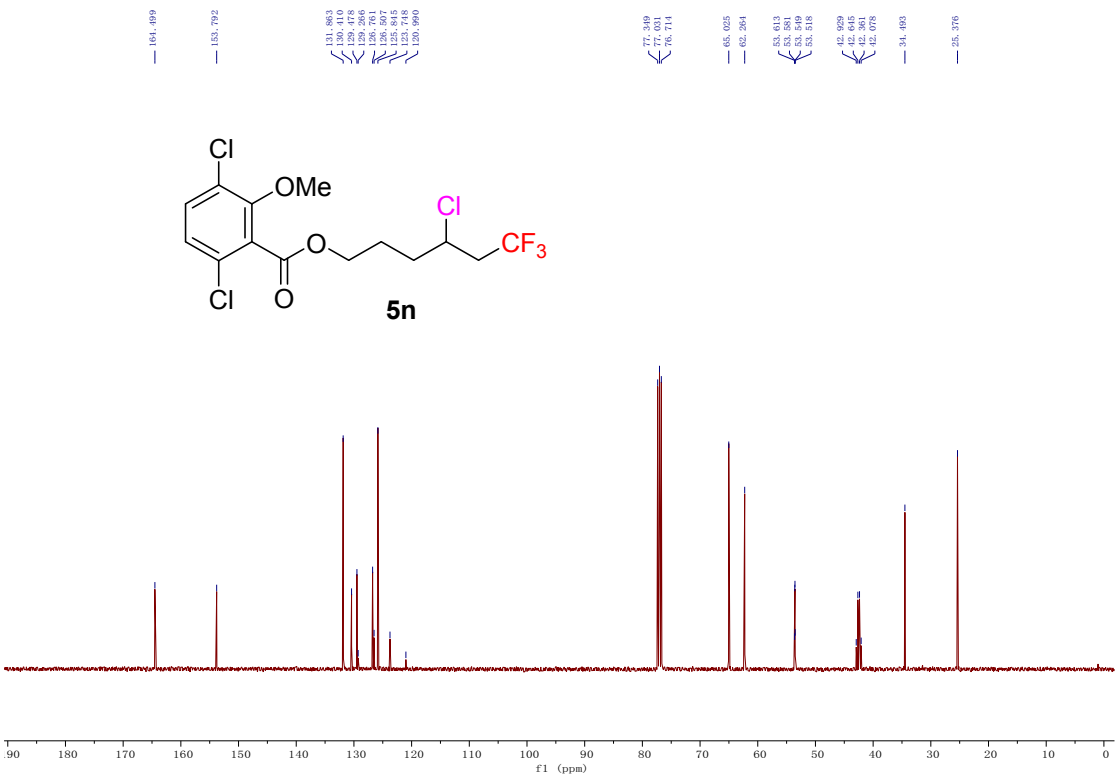
^{19}F NMR (376 MHz, $CDCl_3$)



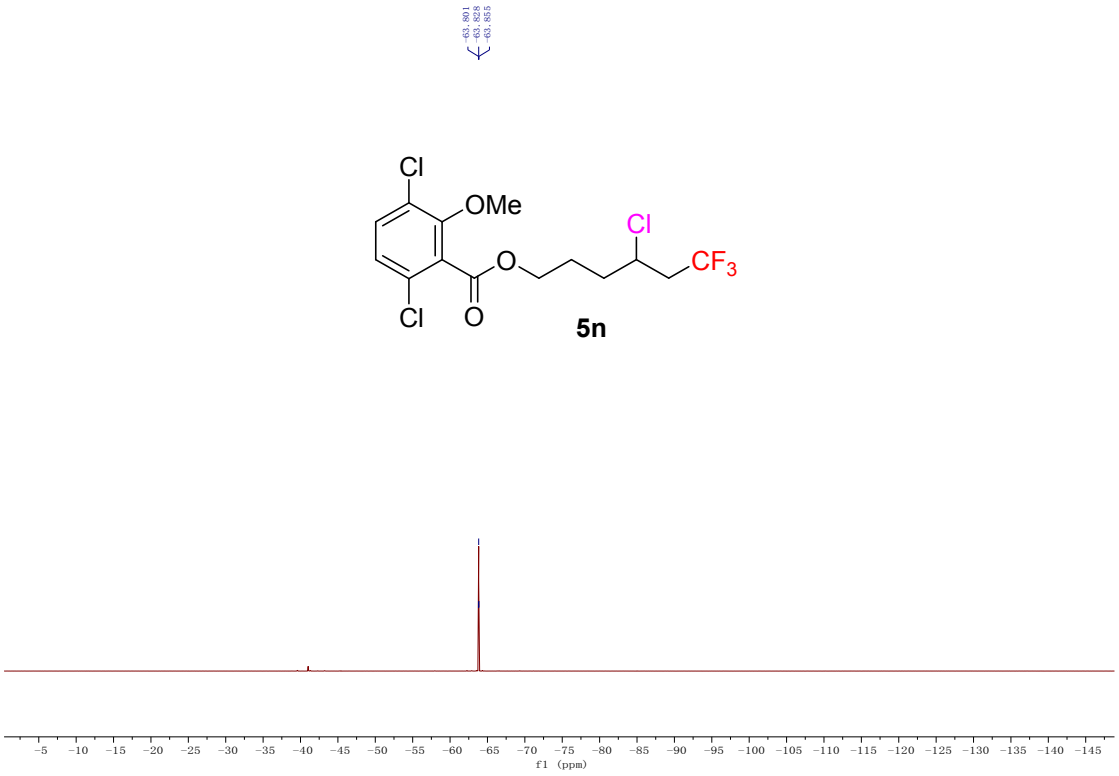
^{1}H NMR (400 MHz, $CDCl_3$)



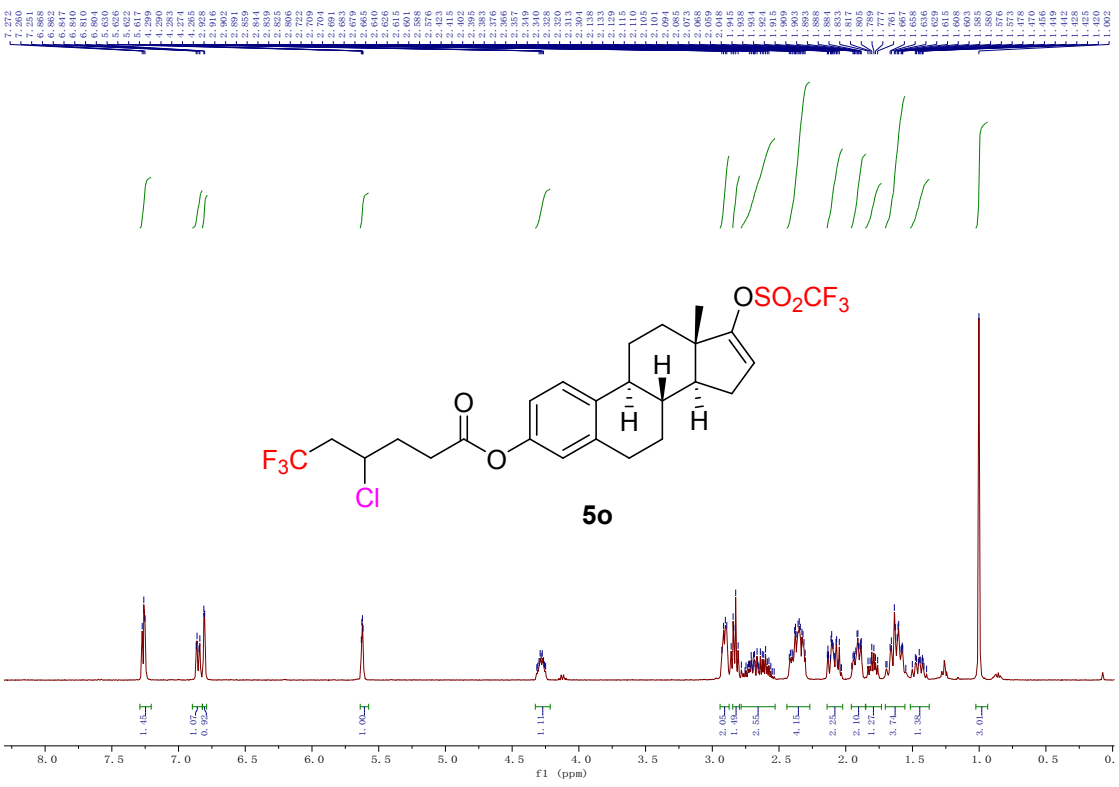
^{13}C NMR (100 MHz, $CDCl_3$)



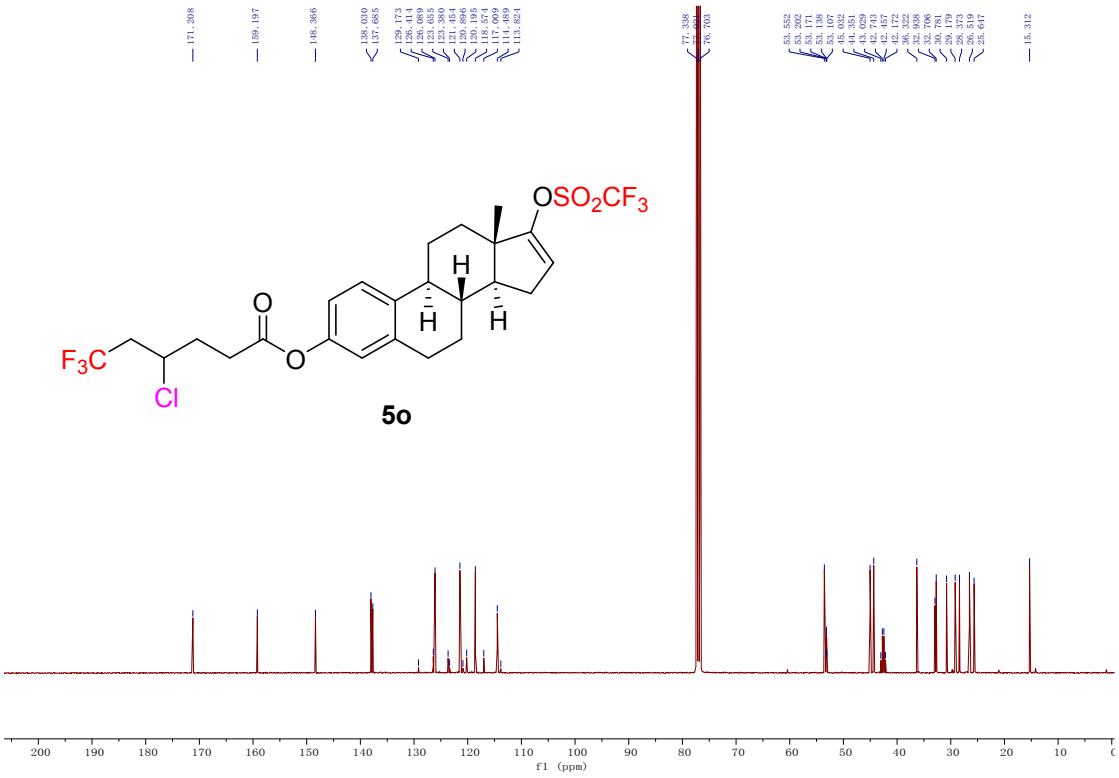
^{19}F NMR (376 MHz, $CDCl_3$)



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



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



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