Supporting Information

For

A facile method for hydroxytrifluoromethylation of alkenes with Langlois reagent and DMSO

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# These authors contributed equally to this work.

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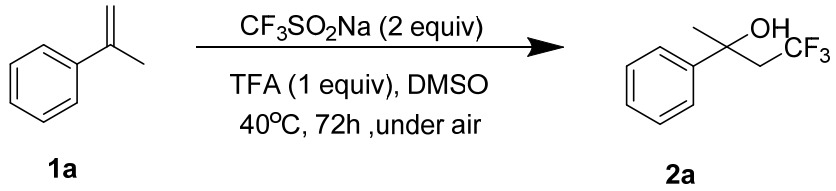
1. General remarks

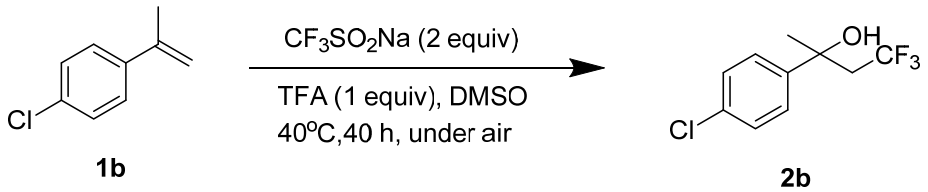
^{1}H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for ^{13}C NMR, 376 or 564 MHz for ^{19}F NMR) agilent NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) or 77.16 ppm (for ^{13}C NMR). ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ at δ 0.00 ppm. HRMS was recorded on a GCT Premier^{TM} (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, ν_{max} in cm^{-1}. Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified. The substrates we are readily prepared according to known methods (*Angew. Chem. Int. Ed.* **2007**, *46*, 4519; *Angew. Chem. Int. Ed.* **2013**, *52*, 8450.).

2. Typical experimental procedure



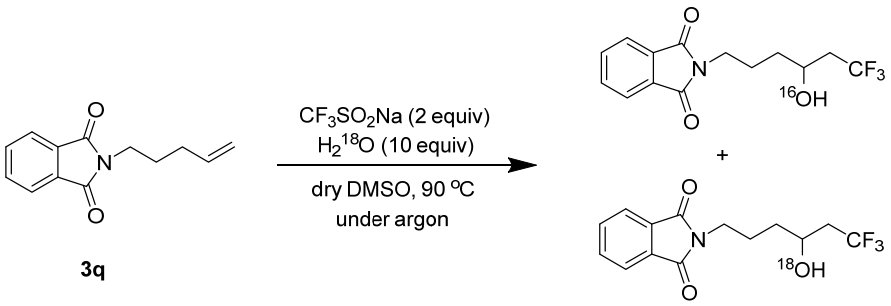
To a suspension of **1a** (94.5 mg, 0.8 mmol) and CF_3SO_2Na (249.7 mg, 1.6 mmol) in DMSO (4 mL) was added TFA (59.6 μL, 0.8 mmol) at rt. The resulting mixture was stirred under air at 40 °C. After the reaction was finished, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give **2a** as colorless oil (99.6 mg, 61% yield).

3. Gram-scale reaction



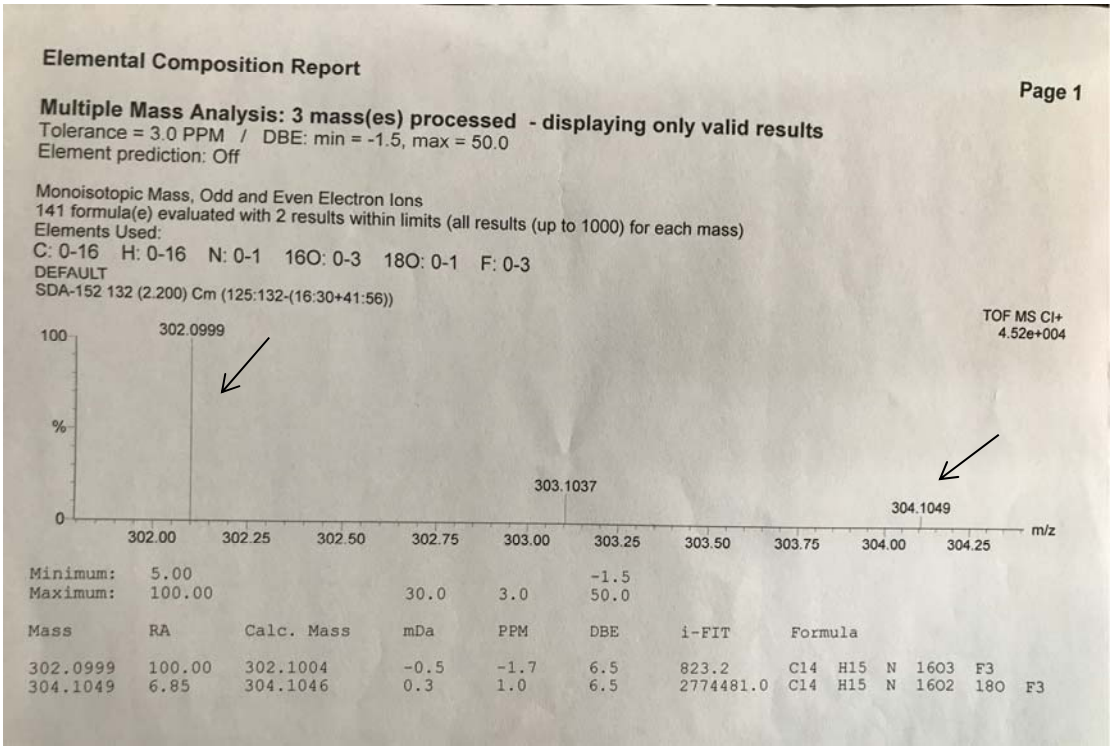
To a suspension of **1b** (1.0 g, 6.6 mmol) and CF_3SO_2Na (2.06 g, 13.2 mmol) in DMSO (33 mL) was added TFA (0.5 mL, 6.6 mmol) at rt. The resulting mixture was stirred under air at 40 °C. After the reaction was finished, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give **2b** as colorless oil (0.99 g, 63% yield).

4. Mechanistic studies



4q-^{16}O : **4q**-^{18}O = 94:6

To a suspension of **3q** (43 mg, 0.2 mmol) and CF_3SO_2Na (62.4 mg, 0.4 mmol) in dry DMSO (1 mL) was added $H_2{}^{18}O$ (40 μL, 2 mmol) at rt. The resulting mixture was stirred under argo at 90 °C. After the reaction was finished, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give **4q** as a white solid (27 mg, 45% yield).



Elemental Composition Report Page 1

Multiple Mass Analysis: 3 mass(es) processed - displaying only valid results
Tolerance = 3.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

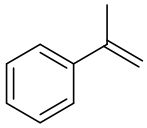
Monoisotopic Mass, Odd and Even Electron Ions
141 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-16 H: 0-16 N: 0-1 16O: 0-3 18O: 0-1 F: 0-3
DEFAULT
SDA-152 132 (2.200) Cm (125:132-(16:30+41:56))

TOF MS CI+
4.52e+004

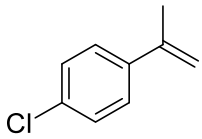
302.0999
303.1037
304.1049
m/z

Minimum:	5.00				-1.5		
Maximum:	100.00		30.0	3.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
302.0999	100.00	302.1004	-0.5	-1.7	6.5	823.2	C14 H15 N 16O3 F3
304.1049	6.85	304.1046	0.3	1.0	6.5	2774481.0	C14 H15 N 16O2 18O F3

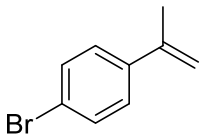
5. Characterization of the substrates and products



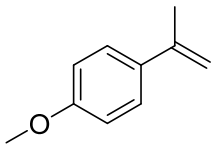
Prop-1-en-2-ylbenzene (1a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.33 (m, 1H), 5.48 (s, 1H), 5.19 (s, 1H), 2.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 141.4, 128.3, 127.5, 125.6, 112.5, 21.9.



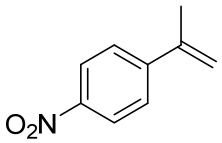
1-**Chloro-4-(prop-1-en-2-yl)benzene (1b):** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.37 (s, 1H), 5.12 (s, 1H), 2.15 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.3, 139.8, 133.3, 128.5, 126.9, 113.1, 21.9.



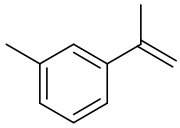
1-Bromo-4-(prop-1-en-2-yl)benzene (1c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 5.37 (s, 1H), 5.11 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.3, 140.2, 131.4, 127.3, 121.5, 113.2, 21.8.



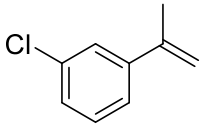
1-Methoxy-4-(prop-1-en-2-yl)benzene (1d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 5.34 (s, 1H), 5.04 (s, 1H), 3.84 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 142.6, 133.8, 126.7, 113.6, 110.7, 55.3, 22.0.



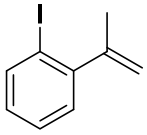
1-Nitro-4-(prop-1-en-2-yl)benzene (1e): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 5.52 (s, 1H), 5.29 (s, 1H), 2.19 (s, 3H);^{13}C NMR (150 MHz, $CDCl_3$, overlapping peaks) δ 147.8, 141.7, 126.4, 123.7, 116.5, 21.7.



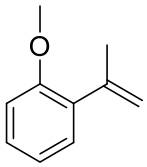
1-Methyl-3-(prop-1-en-2-yl)benzene (1f): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.24 (m, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 5.34 (s, 1H), 5.05 (s, 1H), 2.35 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.5, 141.4, 137.8, 128.3, 128.2, 126.4, 122.8, 112.4, 22.0, 21.6.



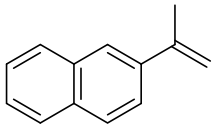
1-Chloro-3-(prop-1-en-2-yl)benzene (1g): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.33 – 7.29 (m, 1H), 7.23 – 7.21 (m, 2H), 5.36 (s, 1H), 5.11 (s, 1H), 2.11 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.2, 142.2, 134.3, 129.5, 127.5, 125.9, 123.8, 113.8, 21.8.



1-Iodo-2-(prop-1-en-2-yl)benzene (1h): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 5.24 (s, 1H), 4.91 (s, 1H), 2.08 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.9, 148.5, 139.3, 128.6, 128.5, 128.2, 116.2, 97.1, 24.0.

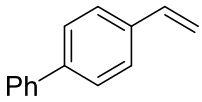


1-Methoxy-2-(prop-1-en-2-yl)benzene (1i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 6.88 – 6.77 (m, 2H), 5.08 (s, 1H), 4.99 (s, 1H), 3.76 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.7, 144.5, 132.9, 129.5, 128.4, 120.6, 115.2, 110.9, 55.5, 23.3.

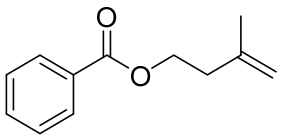


2-(Prop-1-en-2-yl)naphthalene (1j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.84 (m, 4H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.58 – 7.50 (m, 2H), 5.64 (s, 1H), 5.29 (s, 1H), 2.36 (s,

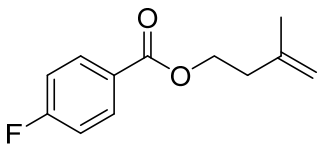
3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.1, 138.4, 133.5, 132.9, 128.4, 127.8, 127.6, 126.2, 125.9, 124.4, 124.0, 113.1, 22.0.



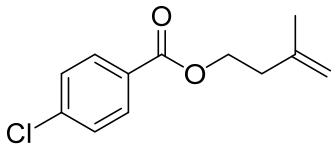
4-Vinyl-1,1'-biphenyl (1k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 4H), 7.54 – 7.43 (m, 4H), 7.37 (t, *J* = 7.2 Hz, 1H), 6.90 – 6.71 (m, 1H), 5.82 (d, *J* = 17.6 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.9, 140.7, 136.7, 136.5, 128.9, 127.5, 127.4, 127.1, 126.8, 114.0.



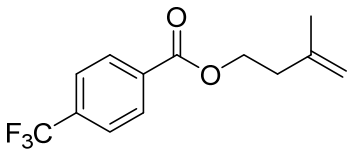
3-Methylbut-3-en-1-yl benzoate (3a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 4.83 (s, 1H), 4.81 (s, 1H), 4.42 (t, *J* = 6.7 Hz, 2H), 2.46 (t, *J* = 6.6 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.4, 141.6, 132.8, 130.4, 129.5, 128.3, 112.4, 63.1, 36.8, 22.5.



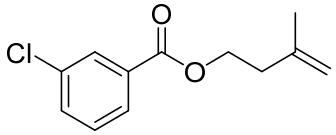
3-Methylbut-3-en-1-yl 4-fluorobenzoate (3b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.98 (m, 2H), 7.12 – 7.06 (m, 2H), 4.84 (s, 1H), 4.81 (s, 1H), 4.42 (t, *J* = 6.2 Hz, 2H), 2.47 (t, *J* = 6.1 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7 (d, $J_{C\text{-}F}$ = 253.6 Hz), 165.4, 141.6, 132.1 (d, $J_{C\text{-}F}$ = 9.3 Hz), 126.7 (d, $J_{C\text{-}F}$ = 2.8 Hz), 115.4 (d, $J_{C\text{-}F}$ = 22.0 Hz), 112.4, 63.2, 36.8, 22.4.



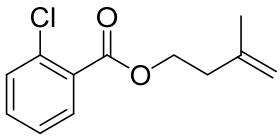
3-Methylbut-3-en-1-yl 4-chlorobenzoate (3c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 4.84 (s, 1H), 4.80 (s, 1H), 4.43 (t, *J* = 6.7 Hz, 2H), 2.47 (t, *J* = 6.6 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 141.6, 139.4, 131.0, 128.9, 128.8, 112.6, 63.4, 36.9, 22.6.



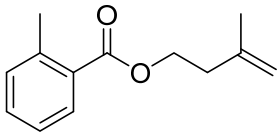
3-Methylbut-3-en-1-yl 4-(trifluoromethyl)benzoate (3d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 4.84 (s, 1H), 4.80 (s, 1H), 4.47 (t, *J* = 6.6 Hz, 2H), 2.49 (t, *J* = 6.4 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 141.6, 134.5 (q, J_{C-F} = 32.6 Hz), 133.7, 130.1, 125.5 (q, J_{C-F} = 7.1, 3.5 Hz), 123.78 (q, J_{C-F} = 272.6 Hz), 112.7, 63.7, 36.9, 22.5.



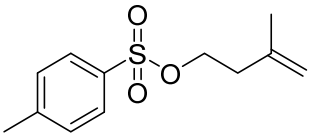
3-Methylbut-3-en-1-yl 3-chlorobenzoate(3e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 4.84 (s, 1H), 4.80 (s, 1H), 4.43 (t, *J* = 6.6 Hz, 2H), 2.47 (t, *J* = 6.4 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.3, 141.5, 134.5, 132.9, 132.2, 129.7, 129.70, 127.68, 112.6, 63.6, 36.8, 22.6.



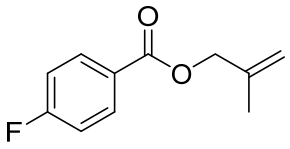
3-Methylbut-3-en-1-yl 2-chlorobenzoate (3f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.34 (m, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 4.85 (s, 1H), 4.81 (s, 1H), 4.46 (t, *J* = 6.6 Hz, 2H), 2.49 (t, *J* = 6.4 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6, 141.5, 133.7, 132.5, 131.4, 131.0, 130.3, 126.6, 112.6, 63.6, 36.7, 22.5.



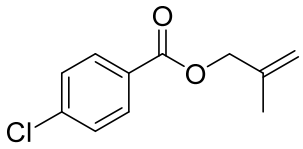
3-Methylbut-3-en-1-yl 2-methylbenzoate (3g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.1 Hz, 1H), 7.29 – 7.17 (m, 2H), 4.84 (s, 1H), 4.81 (s, 1H), 4.42 (t, *J* = 6.6 Hz, 2H), 2.59 (s, 3H), 2.48 (t, *J* = 6.4 Hz, 2H), 1.81 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.7, 141.8, 140.2, 132.0, 131.7, 130.7, 129.9, 125.8, 112.5, 63.0, 36.9, 22.5, 21.8.



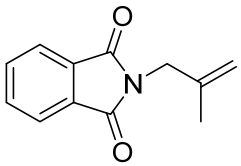
3-Methylbut-3-en-1-yl 4-methylbenzenesulfonate (3h): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 4.74 (s, 1H), 4.64 (s, 1H), 4.09 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 2.31 (t, *J* = 6.8 Hz, 2H), 1.61 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.8, 140.1, 133.1, 129.8, 127.8, 113.0, 68.5, 36.7, 22.2, 21.6.



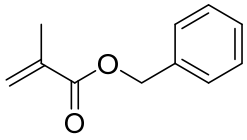
2-Methylallyl 4-fluorobenzoate (3i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.06 (m, 2H), 7.15 – 7.05 (m, 2H), 5.06 (s, 1H), 4.98 (s, 1H), 4.73 (s, 2H), 1.83 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0 (d, J_{C-F} = 208.6 Hz), 165.1, 140.0, 132.3 (d, J_{C-F} = 9.4 Hz), 126.5 (d, J_{C-F} = 2.8 Hz), 115.6 (d, *J* = 22.0 Hz), 113.2, 68.4, 19.7.



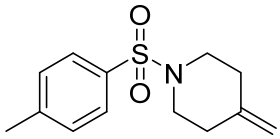
2-Methylallyl 4-chlorobenzoate (3j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 5.06 (s, 1H), 4.99 (s, 1H), 4.74 (s, 2H), 1.83 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 139.9, 139.6, 131.1, 128.9, 128.8, 113.3, 68.5, 19.7.



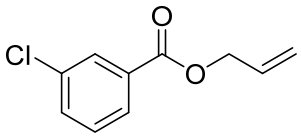
2-(2-Methylallyl)isoindoline-1,3-dione (3k): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.72 – 7.68 (m, 2H), 4.86 (s, 1H), 4.79 (s, 1H), 4.19 (s, 2H), 1.75 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 139.3, 134.1, 132.1, 123.4, 112.0, 43.3, 20.5.



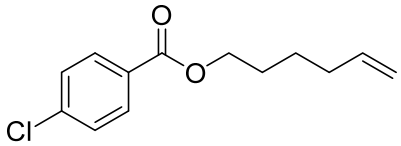
Benzyl methacrylate (3l): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 6.19 (s, 1H), 5.60 (s, 1H), 5.22 (s, 2H), 2.00 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 136.3, 136.2, 128.6, 128.2, 128.1, 125.8, 66.4, 18.4.



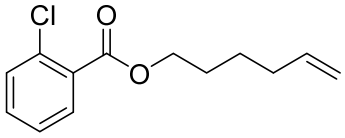
1-Tosyl-4-(2,2,2-trifluoroethyl)piperidin-4-ol (3m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 4.69 (s, 2H), 3.08 – 2.98 (m, 4H), 2.42 (s, 3H), 2.33 – 2.26 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 143.4, 133.4, 129.6, 127.6, 110.0, 47.7, 33.8, 21.5.



Allyl 3-chlorobenzoate (3n): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.0 Hz, 1H), 7.93 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.51 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 6.10 – 5.95 (m, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.29 (d, *J* = 10.5 Hz, 1H), 4.81 (dd, *J* = 5.7, 1.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, overlapping peaks) δ 165.1, 134.6, 133.1, 132.0, 132.0, 129.8, 127.8, 118.7, 66.0.

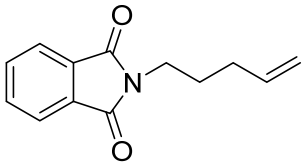


Hex-5-en-1-yl 4-chlorobenzoate （3o）: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 5.95 – 5.71 (m, 1H), 5.11 – 4.93 (m, 2H), 4.31 (t, *J* = 6.5 Hz, 2H), 2.12 (q, *J* = 6.9 Hz, 2H), 1.87 – 1.68 (m, 2H), 1.64 – 1.43 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 139.4, 138.3, 131.0, 129.0, 128.8, 115.0, 65.2, 33.4, 28.2, 25.4.

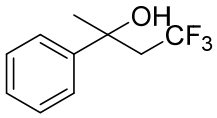


Hex-5-en-1-yl 2-chlorobenzoate (3p): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.36 (m, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 5.89 – 5.73 (m, 1H), 5.09 – 4.91 (m, 2H), 4.34 (t, *J* = 6.5 Hz, 2H), 2.12 (q, *J* = 7.0 Hz, 2H), 1.85 – 1.72 (m, 2H),

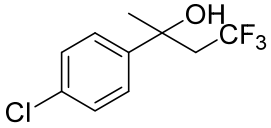
1.62 – 1.49 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 138.4, 133.7, 132.5, 131.4, 131.1, 130.6, 126.6, 115.0, 65.6, 33.4, 28.1, 25.4.



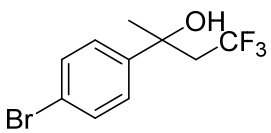
2-(Pent-4-en-1-yl)isoindoline-1,3-dione (3q): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.72 – 7.68 (m, 2H), 5.84 – 5.76 (m, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 4.96 (d, *J* = 10.2 Hz, 1H), 3.69 (t, *J* = 7.3 Hz, 2H), 2.13 – 2.08 (m, 2H), 1.81 – 1.74 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 137.4, 134.0, 132.3, 123.3, 115.4, 37.7, 31.1, 27.8.



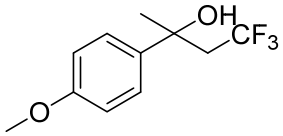
4,4,4-Trifluoro-2-phenylbutan-2-ol (2a): Colorless oil; 61% yield (100 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.40 – 7.36 (m, 2H), 7.32 – 7.28 (m, 1H), 2.83 (s, 1H), 2.75 – 2.57 (m, 2H), 1.72 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.3, 128.6, 127.5, 125.9 (q, $J_{C\text{-}F}$ = 278.4 Hz), 124.5, 72.2, 46.7 (q, $J_{C\text{-}F}$ = 25.7 Hz), 29.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.11 (t, *J* = 10.9 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3442, 2984, 1120, 700, 609; HRMS (CI) calcd $C_{10}H_{12}F_3O$ $[M + H]^+$: 205.0840, found: 205.0849.



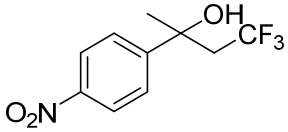
2-(4-Chlorophenyl)-4,4,4-trifluorobutan-2-ol (2b): Colorless oil; 69% yield (132 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 2.73 – 2.53 (m, 2H), 2.35 (s, 1H), 1.69 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.7, 133.4, 128.7, 126.2, 125.8 (q , $J_{C\text{-}F}$ = 278.4 Hz), 71.8, 46.7 (q, $J_{C\text{-}F}$ = 25.8 Hz), 29.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.12 (t, *J* = 10.9 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3443, 2986, 1258, 1119, 832; HRMS (CI) calcd $C_{10}H_{11}{}^{35}ClF_3O$ $[M + H]^+$: 239.0451, found: 239.0447.



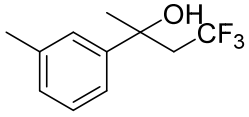
2-(4-Bromophenyl)-4,4,4-trifluorobutan-2-ol (2c): Colorless oil; 75% yield (170 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 2.74 – 2.51 (m, 2H), 2.29 (s, 1H), 1.68 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.3, 131.6, 126.5, 125.7 (q, $J_{C\text{-}F}$ = 278.5 Hz), 121.5, 71.8, 46.6 (q, $J_{C\text{-}F}$ = 25.8 Hz), 29.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.08 (t, J = 10.8 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3442, 2985, 1259, 1118, 622; HRMS (CI) calcd $C_{10}H_{11}{}^{79}BrF_3O$ $[M + H]^+$: 282.9945, found: 282.9953.



4,4,4-Trifluoro-2-(4-methoxyphenyl)butan-2-ol (2d): Colorless oil; 54% yield (101 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 3.81 (s, 3H), 2.75 – 2.48 (m, 2H), 2.13 (s, 1H), 1.70 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.7, 138.3, 125.7 (d, $J_{C\text{-}F}$ = 278.4 Hz), 125.6, 113.6, 71.6, 55.3, 46.7 (q, $J_{C\text{-}F}$ = 25.6 Hz), 29.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.21 (t, J = 11.0 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3445, 2929, 1510, 1174, 831; HRMS (ESI) calcd $C_{11}H_{14}F_3O_2$ $[M + H]^+$: 235.0940, found: 235.0946.

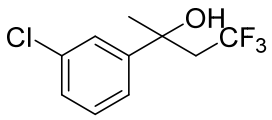


4,4,4-Trifluoro-2-(4-nitrophenyl)butan-2-ol (2e): White solid; m.p. 89-94 ℃; 75% yield (149 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H), 2.69 (m, 2H), 2.47 (s, 1H), 1.73 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.2, 147.2, 125.9, 125.6 (q, $J_{C\text{-}F}$ = 278.4 Hz), 123.8, 72.0, 46.4 (q, $J_{C\text{-}F}$ = 26.1 Hz), 30.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -59.98 (t, J = 10.5 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3535, 2938, 1519, 1348, 1104; HRMS (CI) calcd $C_{10}H_{11}F_3NO_3$ $[M + H]^+$: 250.0691, found: 250.0692.

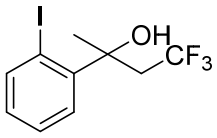


4,4,4-Trifluoro-2-(m-tolyl)butan-2-ol (2f): Colorless oil; 56% yield (98 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 3H), 7.10 (d, J = 5.9 Hz, 1H), 2.72 – 2.56 (m, 2H), 2.37 (s, 3H), 2.21 (s, 1H), 1.69 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 138.2, 128.5, 128.2, 126.0 (q, $J_{C\text{-}F}$ = 278.4 Hz), 125.2, 121.6, 72.0, 46.7 (q, $J_{C\text{-}F}$ = 25.6 Hz), 29.7, 21.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.09 (t, J = 11.0 Hz, 3F); FT-IR

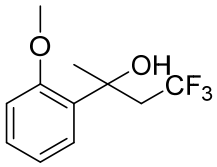
(thin film, KBr): ν (cm^{-1}) 3357, 2958, 1469, 1125, 704; HRMS (CI) calcd $C_{11}H_{13}F_3O$ $[M]^+$: 218.0918, found: 218.0925.



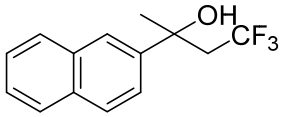
2-(3-Chlorophenyl)-4,4,4-trifluorobutan-2-ol (2g): Colorless oil; 49% yield (93 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.34 – 7.25 (m, 3H), 2.70 – 2.56 (m, 2H), 2.29 (s, 1H), 1.69 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.3, 134.6, 129.9, 127.7, 125.8 (q, J_{C-F} = 278.4 Hz), 125.1, 122.8, 71.8, 46.6 (q, J_{C-F} = 25.9 Hz), 29.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.09 (t, J = 10.8 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3357, 2958, 1724, 1265, 712; HRMS (CI) calcd $C_{10}H_{11}{}^{35}ClF_3O$ $[M + H]^+$: 239.0451, found: 239.0451.



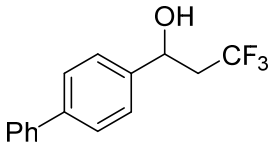
4,4,4-Trifluoro-2-(2-iodophenyl)butan-2-ol (2h): Colorless oil; 65% yield (171 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.7 Hz, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 3.25 – 3.10 (m, 1H), 3.08 – 2.94 (m, 1H), 2.70 (s, 1H), 1.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.2, 142.9, 129.4, 128.6, 127.2, 125.9 (q, J_{C-F} = 278.5 Hz), 93.2, 72.9, 43.1 (q, J_{C-F} = 25.7 Hz), 28.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.09 (t, J = 11.0 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3456, 1256, 1172, 758, 608; HRMS (CI) calcd $C_{10}H_{10}F_3IO$ $[M]^+$: 329.9729, found: 329.9736.



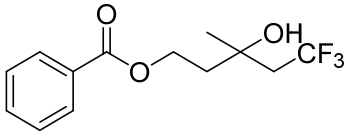
4,4,4-Trifluoro-2-(2-methoxyphenyl)butan-2-ol (2i): Colorless oil; 49% yield (92 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.2 Hz, 1H), 7.29 (t, J = 7.3 Hz, 1H), 6.99 (t, J = 6.7 Hz, 1H), 6.93 (d, J = 7.7 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 1H), 2.96 – 2.71 (m, 2H), 1.73 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.4, 133.0, 128.8, 126.4, 126.0 (q, J_{C-F} = 278.2 Hz), 121.2, 111.3, 71.8, 55.4, 44.6 (q, J_{C-F} = 25.4 Hz), 27.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.71 (t, J = 11.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3359, 2921, 1633, 1470, 1064; HRMS (CI) calcd $C_{11}H_{12}F_3O$ $[M - OH]^+$: 217.0840, found: 217.0847.



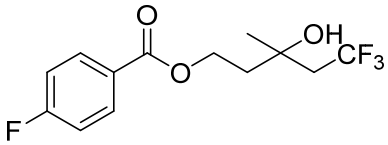
4,4,4-Trifluoro-2-(naphthalen-2-yl)butan-2-ol (2j): Colorless oil; 48% yield (98 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.90 – 7.83 (m, 3H), 7.58 – 7.46 (m, 3H), 2.88 – 2.65 (m, 2H), 2.39 (s, 1H), 1.81 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, overlapping peaks) δ 143.6, 133.2, 132.6, 128.4, 127.7, 126.5, 126.3, 125.9 (t, J_{C-F} = 278.5 Hz), 123.1, 123.0, 72.3, 46.5 (q, J_{C-F} = 25.7 Hz), 29.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.02 (t, J = 10.9 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3444, 3059, 1259, 1113, 818; HRMS (CI) calcd $C_{14}H_{14}F_3O$ $[M + H]^+$: 255.0997, found: 255.0996.



1-([1,1'-Biphenyl]-4-yl)-3,3,3-trifluoropropan-1-ol (2k): White solid; m.p. 96-98 ℃; 35% yield (74 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 4H), 7.48 – 7.44 (m, 4H), 7.37 (t, J = 7.3 Hz, 1H), 5.16 – 5.12 (m, 1H), 2.74 – 2.62 (m, 1H), 2.56 – 2.46 (m, 1H), 2.27 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.5, 141.4, 140.6, 129.0, 127.70, 127.67, 127.2, 126.3, 126.0 (d, J_{C-F} = 277.5 Hz), 68.7, 43.0 (q, J_{C-F} = 26.9 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.71 (t, J = 10.6 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3349, 2921, 1122, 1100, 764; HRMS (CI) calcd $C_{15}H_{14}F_3O$ $[M + H]^+$: 267.0997, found: 267.0998.

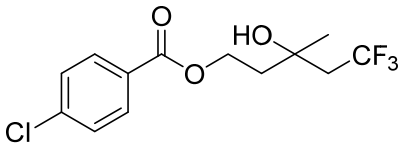


5,5,5-Trifluoro-3-hydroxy-3-methylpentyl benzoate (4a): Colorless oil; 82% yield (45 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.4 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 4.53 (t, J = 6.4 Hz, 2H), 2.49 – 2.38 (m, 2H), 2.27 (s, 1H), 2.15 – 2.04 (m, 2H), 1.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 133.3, 130.1, 129.6, 128.6, 126.1 (q, J_{C-F} = 277.9 Hz), 69.7, 61.1, 45.1 (q, J_{C-F} = 26.0 Hz), 40.5, 27.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.21 (t, J = 11.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3476, 2925, 1704, 1102, 712; HRMS (CI) calcd $C_{13}H_{16}F_3O_3$ $[M + H]^+$: 277.1052, found: 277.1046.

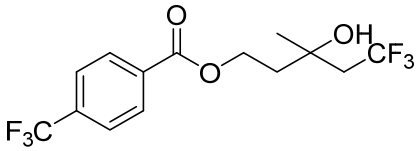


5,5,5-Trifluoro-3-hydroxy-3-methylpentyl 4-fluorobenzoate (4b): White solid; m.p. 46-48 ℃; 89% yield (52 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 2H),

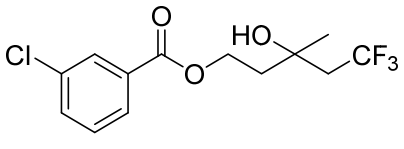
7.13 – 7.06 (m, 2H), 4.51 (t, J = 6.5 Hz, 2H), 2.46 – 2.38 (m, 2H), 2.25 (s, 1H), 2.14 – 2.04 (m, 2H), 1.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0 (d, J_{C-F} = 254.3 Hz), 165.8, 132.2 (d, J_{C-F} = 9.4 Hz), 126.3 (d, J_{C-F} = 2.6 Hz), 126.1 (q, J_{C-F} = 277.9 Hz), 115.8 (d, J_{C-F} = 22.0 Hz), 69.7, 61.2, 45.1 (q, J_{C-F} = 26.0 Hz), 40.4, 27.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.23 (t, J = 11.3 Hz, 3F), -105.33 – -105.40 (m, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3459, 2972, 1702, 1104, 763; HRMS (CI) calcd $C_{13}H_{15}F_4O_3$ $[M + H]^+$: 295.0957, found: 295,0962.



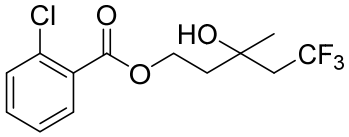
5,5,5-Trifluoro-3-hydroxy-3-methylpentyl 4-chlorobenzoate (4c): Colorless oil; 95% yield (59 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 4.52 (t, J = 6.6 Hz, 2H), 2.42 (q, J = 11.3 Hz, 2H), 2.25 (s, 1H), 2.16 – 2.00 (m, 2H), 1.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 139.7, 131.0, 128.9, 128.5, 126.1 (q, J_{C-F} = 277.9 Hz), 69.6, 61.4, 45.1 (q, J_{C-F} = 26.0 Hz), 40.4, 27.4.; ^{19}F NMR (564 MHz, $CDCl_3$) δ -69.72 (t, J = 11.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3478, 2978, 1707, 1263, 759; HRMS (CI) calcd $C_{13}H_{15}{}^{35}ClF_3O_3$ $[M + H]^+$: 311.0662, found: 311.0664.



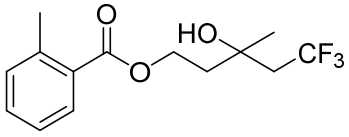
5,5,5-Trifluoro-3-hydroxy-3-methylpentyl 4-(trifluoromethyl)benzoate (4d): Colorless oil; 80% yield (55 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.9 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 4.56 (t, J = 6.5 Hz, 2H), 2.44 (q, J = 11.3 Hz, 2H), 2.17 – 2.05 (m, 3H), 1.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 134.8 (q, J_{C-F} = 32.6 Hz), 133.4, 130.1, 126.1 (q, J_{C-F} = 277.9 Hz), 125.7 (q, J_{C-F} = 7.2, 3.5 Hz), 123.7 (q, J_{C-F} = 272.8 Hz), 69.7, 61.6, 45.2 (q, J_{C-F} = 26.1 Hz), 40.4, 27.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.22 (t, J = 11.3 Hz, 3F), -63.21 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3483, 2958, 1714, 1124, 775; HRMS (CI) calcd $C_{14}H_{15}F_6O_3$ $[M + H]^+$: 345.0925, found: 345.0927.



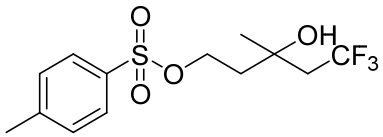
5,5,5-Trifluoro-3-hydroxy-3-methylpentyl 3-chlorobenzoate (4e): Colorless oil; 93% yield (58 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 4.53 (t, *J* = 6.7 Hz, 2H), 2.43 (q, *J* = 11.3 Hz, 2H), 2.24 (s, 1H), 2.17 – 2.00 (m, 2H), 1.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 134.8, 133.3, 131.9, 129.9, 129.8, 127.8, 126.1 (q, J_{C-F} = 278.0 Hz), 69.7, 61.5, 45.1 (q, J_{C-F} = 26.0 Hz), 40.4, 27.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.22 (t, *J* = 11.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3476, 2978, 1716, 1252, 747; HRMS (CI) calcd $C_{13}H_{15}{}^{35}ClF_3O_3$ $[M + H]^+$: 311.0662, found: 311.0663.



5,5,5-Trifluoro-3-hydroxy-3-methylpentyl 2-chlorobenzoate (4f): Colorless oil; 84% yield (52 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.32 (t, *J* = 6.7 Hz, 1H), 4.54 (t, *J* = 6.6 Hz, 2H), 2.42 (q, *J* = 11.3 Hz, 2H), 2.27 (s, 1H), 2.17 – 2.01 (m, 2H), 1.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 134.8, 133.3, 131.9, 129.9, 129.8, 127.8, 126.1 (q, J_{C-F} = 278.0 Hz), 69.7, 61.5, 45.2 (q, J_{C-F} = 26.0 Hz), 40.4, 27.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.23 (t, *J* = 11.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3476, 2980, 1710, 1101, 748; HRMS (CI) calcd $C_{13}H_{15}{}^{35}ClF_3O_3$ $[M + H]^+$: 311.0662, found: 311.0665.

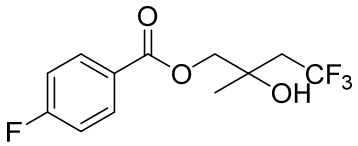


5,5,5-Trifluoro-3-hydroxy-3-methylpentyl 2-methylbenzoate (4g): Colorless oil; 91% yield (53 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 6.7 Hz, 1H), 7.29 – 7.19 (m, 2H), 4.50 (t, *J* = 6.2 Hz, 2H), 2.60 (s, 3H), 2.49 – 2.37 (m, 2H), 2.32 (s, 1H), 2.16 – 2.03 (m, 2H), 1.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.6, 140.5, 132.3, 131.9, 130.5, 129.4, 126.1 (q, J_{C-F} = 278.0 Hz), 125.9, 69.8, 60.8, 45.1 (q, J_{C-F} = 26.0 Hz), 40.5, 27.4, 21.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.23 (t, *J* = 11.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3477, 2976, 1703, 1081, 754; HRMS (CI) calcd $C_{14}H_{18}F_3O_3$ $[M + H]^+$: 291.1208, found: 291.1218.

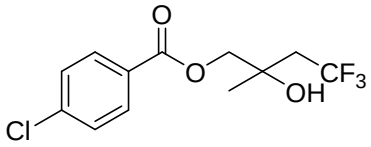


5,5,5-Trifluoro-3-hydroxy-3-methylpentyl 4-methylbenzenesulfonate (4h): Colorless oil; 64% yield (42 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.27 – 4.19 (m, 2H), 2.46 (s, 3H), 2.36 – 2.27 (m, 2H),

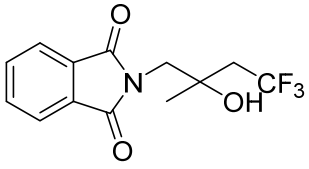
2.01 – 1.91 (m, 3H), 1.34 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.2, 132.9, 130.1, 128.1, 126.0 (q, J_{C-F} = 277.9 Hz), 69.4, 66.5, 45.0 (q, J_{C-F} = 26.1 Hz), 40.5, 27.3, 21.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.26 (t, J = 11.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3523, 2958, 1171, 1097, 663; HRMS (CI) calcd $C_{13}H_{18}F_3O_4S$ $[M + H]^+$: 327.0878, found: 327.0871.



4,4,4-Trifluoro-2-hydroxy-2-methylbutyl 4-fluorobenzoate (4i): Colorless oil; 84% yield (47 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H), 7.17 – 7.10 (m, 2H), 4.32 (d, J = 11.5 Hz, 1H), 4.28 (d, J = 11.5 Hz, 1H), 2.50 (q, J = 11.3 Hz, 2H), 2.45 (s, 1H), 1.46 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.2 (d, J_{C-F} = 254.8 Hz), 165.6, 132.4 (d, J_{C-F} = 9.4 Hz), 125.9 (q, J_{C-F} = 277.5 Hz), 125.8 (d, J_{C-F} = 2.7 Hz), 115.9 (d, J_{C-F} = 22.0 Hz), 70.9, 69.9, 42.1 (q, J_{C-F} = 27.1 Hz), 24.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.44 (t, J = 11.3 Hz, 3F), -104.59 – -104.65 (m, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3475, 2958, 1708, 1260, 766; HRMS (CI) calcd $C_{12}H_{13}F_4O_3$ $[M + H]^+$: 281.0801, found: 281.0811.

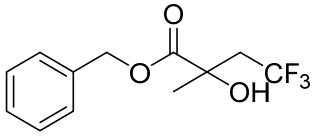


4,4,4-Trifluoro-2-hydroxy-2-methylbutyl 4-chlorobenzoate (4j): Colorless oil; 65% yield (39 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 4.36 – 4.25 (m, 2H), 2.60 – 2.34 (m, 3H), 1.46 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 140.1, 131.2, 129.1, 128.0, 125.9 (q, J_{C-F} = 277.6 Hz), 71.0, 69.9, 42.2 (q, J_{C-F} = 27.1 Hz), 24.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.44 (t, J = 11.2 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3479, 2930, 1712, 1259, 758; HRMS (CI) calcd $C_{12}H_{13}{}^{35}ClF_3O_3$ $[M + H]^+$: 297.0505, found: 297.0503.

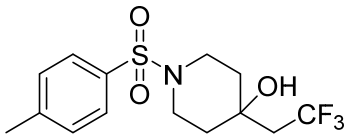


2-(4,4,4-Trifluoro-2-hydroxy-2-methylbutyl)isoindoline-1,3-dione (4k): White solid; m.p. 115-119 ℃; 69% yield (40 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.78 – 7.76 (m, 2H), 3.86 (s, 2H), 3.18 (s, 1H), 2.42 (q, J = 11.2 Hz, 2H), 1.37 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.3, 134.6, 131.8, 126.0 (q, J_{C-F} = 277.8 Hz), 123.9, 71.2, 48.3, 43.4 (q, J_{C-F} = 26.9 Hz), 25.2; ^{19}F NMR (564 MHz,

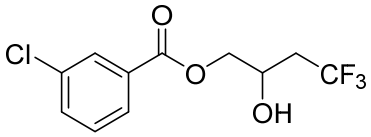
$CDCl_3$) δ -59.94 (t, *J* = 11.2 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3525, 2921, 1712, 1382, 713; HRMS (CI) calcd $C_{13}H_{13}F_3NO_3$ $[M + H]^+$: 288.0848, found: 288.0849.



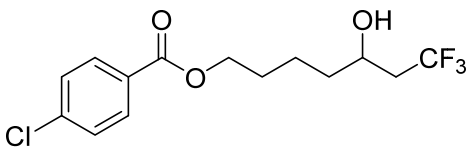
Benzyl 4,4,4-trifluoro-2-hydroxy-2-methylbutanoate (4l): Colorless oil; 46% yield (24 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 5H), 5.27 (d, *J* = 12.1 Hz, 1H), 5.19 (d, *J* = 12.1 Hz, 1H), 3.45 (s, 1H), 2.76 – 2.64 (m, 1H), 2.62 – 2.50 (m, 1H), 1.49 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.0, 134.8, 128.91, 128.86, 128.6, 125.3 (q, J_{C-F} = 278.0 Hz), 71.3, 68.6, 43.0 (q, J_{C-F} = 27.4 Hz), 27.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ -61.64 (t, *J* = 10.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3421, 2975, 1735, 1152, 701; HRMS (CI) calcd $C_{12}H_{14}F_3O_3$ $[M + H]^+$: 263.0895, found: 263.0884.



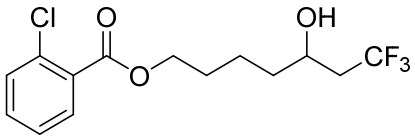
1-Tosyl-4-(2,2,2-trifluoroethyl)piperidin-4-ol (4m): White solid; m.p. 124-129 ℃; 38% yield (25 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 3.63 – 3.51 (m, 2H), 2.70 – 2.59 (m, 2H), 2.43 (s, 3H), 2.29 (q, *J* = 11.3 Hz, 2H), 1.88 – 1.71 (m, 4H), 1.66 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.8, 133.2, 129.8, 127.8, 126.1 (q, J_{C-F} = 278.3 Hz), 66.9, 45.6 (q, J_{C-F} = 25.7 Hz), 41.7, 36.2, 21.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -59.59 (t, *J* = 11.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3503, 2932, 1335, 1169, 724; HRMS (CI) calcd $C_{14}H_{19}F_3NO_3S$ $[M + H]^+$: 338.1038, found: 338.1034.



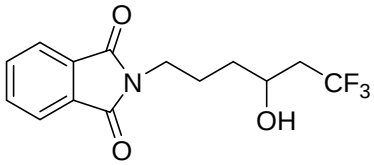
4,4,4-Trifluoro-2-hydroxybutyl 3-chlorobenzoate (4n): Colorless oil; 47% yield (27 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 4.47 – 4.31 (m, 3H), 2.52 – 2.38 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 134.9, 133.7, 131.2, 130.0, 129.9, 128.0, 126.1 (q, J_{C-F} = 276.8 Hz), 68.2, 64.9, 38.1 (q, J_{C-F} = 28.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.53 (t, *J* = 10.7 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3457, 2948, 1720, 1127, 746; HRMS (CI) calcd $C_{11}H_{11}{}^{35}ClF_3O_3$ $[M + H]^+$: 283.0349, found: 283.0360.



7,7,7-Trifluoro-5-hydroxyheptyl 4-chlorobenzoate (4o): Colorless oil; 55% yield (36 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 4.33 (t, J = 6.4 Hz, 2H), 4.13 – 3.94 (m, 1H), 2.36 – 2.18 (m, 2H), 1.99 (s, 1H), 1.87 – 1.74 (m, 2H), 1.69 – 1.49 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 146.1, 139.5, 131.1, 128.9, 126.5 (q, $J_{C\text{-}F}$ = 277.0 Hz), 66.1, 65.1, 41.4 (q, $J_{C\text{-}F}$ = 26.4 Hz), 36.8, 28.6, 21.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.53 (t, J = 11.0 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3444, 2946, 1717, 1271, 760; HRMS (CI) calcd $C_{14}H_{17}{}^{35}ClF_3O_3$ $[M + H]^+$: 325.0818, found: 325.0821.



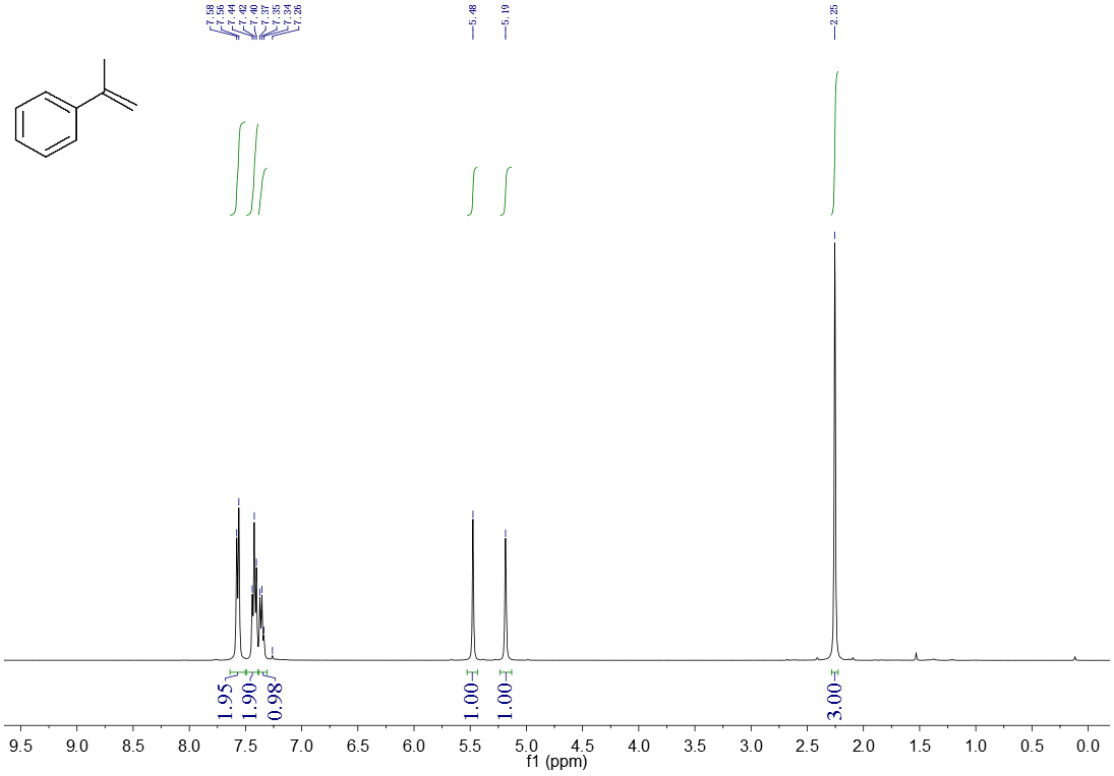
7,7,7-Trifluoro-5-hydroxyheptyl 2-chlorobenzoate (4p): Colorless oil; 54% yield (35 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.5 Hz, 1H), 7.48 – 7.37 (m, 2H), 7.31 (t, J = 7.0 Hz, 1H), 4.34 (t, J = 6.2 Hz, 2H), 4.09 – 3.96 (m, 1H), 2.35 – 2.18 (m, 2H), 2.12 (s, 1H), 1.86 – 1.71 (m, 2H), 1.68 – 1.50 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.1, 133.7, 132.6, 131.4, 131.2, 130.5, 126.7, 126.5 (q, $J_{C\text{-}F}$ = 277.1 Hz), 66.1, 65.4, 41.4 (q, $J_{C\text{-}F}$ = 26.4 Hz), 36.8, 28.5, 21.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.53 (t, J = 11.0 Hz 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3441, 2948, 1715, 1249, 747; HRMS (CI) calcd $C_{14}H_{17}{}^{35}ClF_3O_3$ $[M + H]^+$: 325.0818, found: 325.0811.



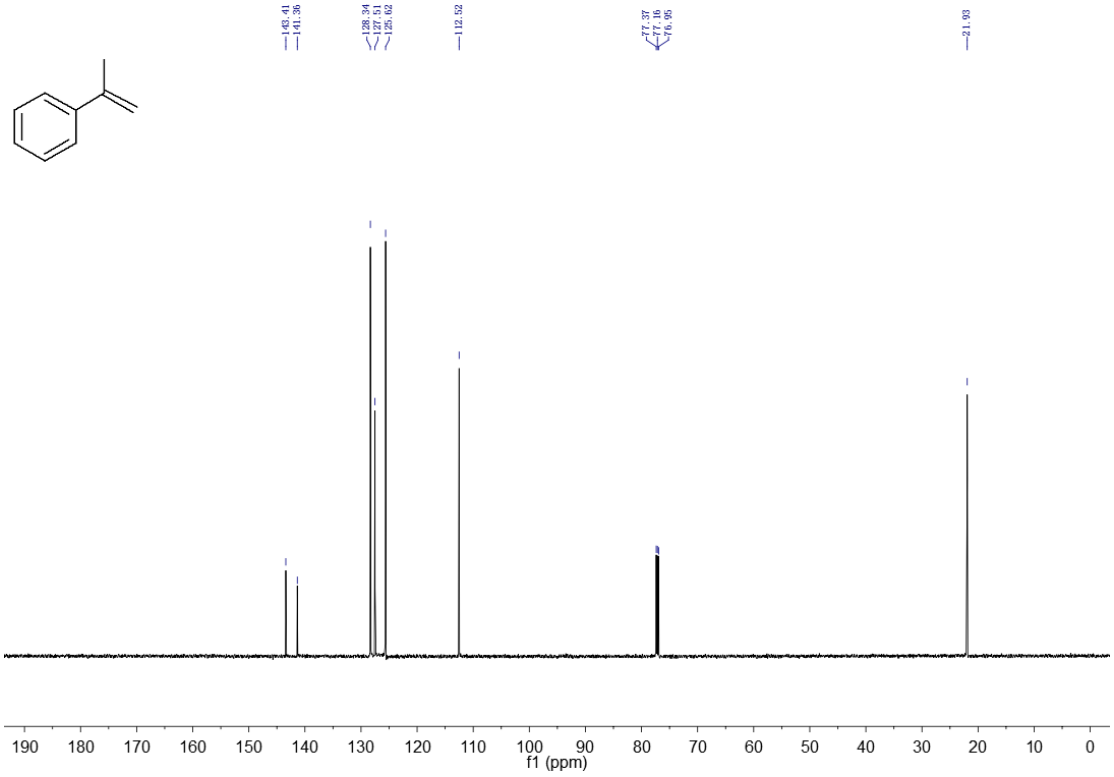
2-(6,6,6-Trifluoro-4-hydroxyhexyl)isoindoline-1,3-dione (4q): White solid; m.p. 83-86 ℃; 63% yield (38 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 2H), 7.75 – 7.68 (m, 2H), 4.20 – 3.99 (m, 1H), 3.75 (t, J = 6.8 Hz, 2H), 2.36 – 2.15 (m, 3H), 1.94 – 1.74 (m, 2H), 1.62 – 1.54 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6, 134.2, 132.1, 126.5 (q, $J_{C\text{-}F}$ = 277.1 Hz), 123.4, 65.9, 41.4 (q, $J_{C\text{-}F}$ = 26.4 Hz), 37.7, 34.2, 24.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.56 (t, J = 10.9 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3468, 2953, 171, 1132, 720; HRMS (CI) calcd $C_{14}H_{15}F_3NO_3$ $[M + H]^+$: 302.1004, found: 302.1006.

6. NMR Spectra for the substrates and products

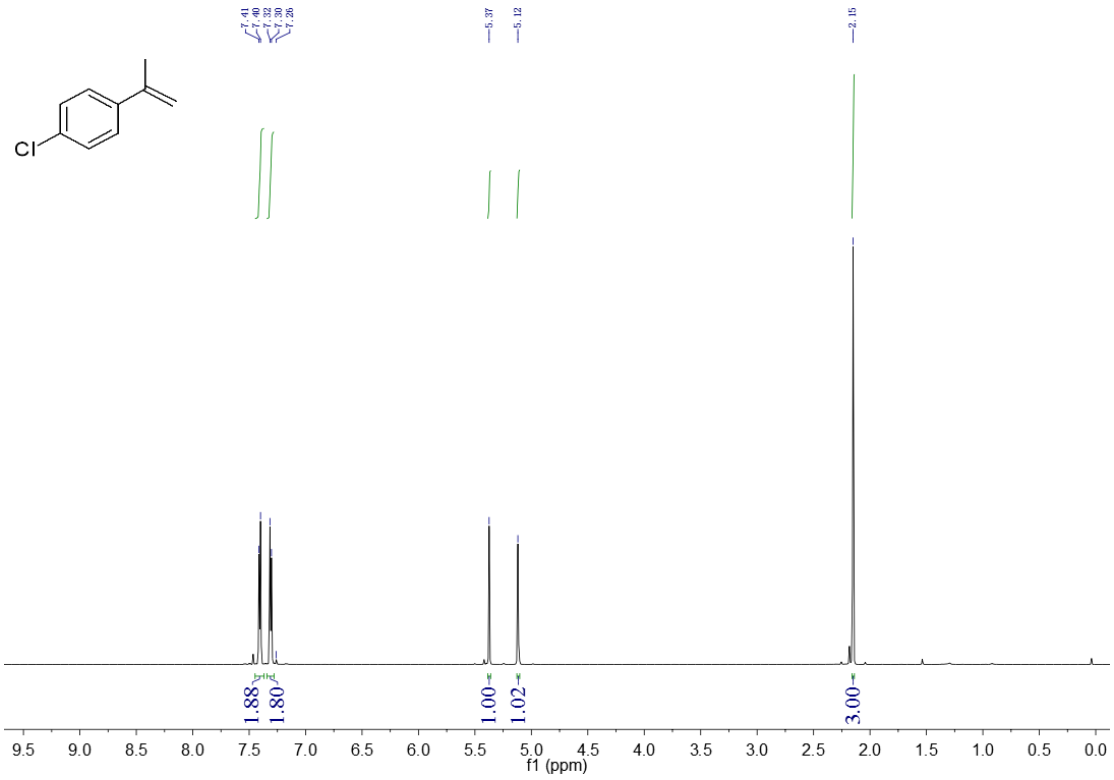
^{1}H NMR of **1a**



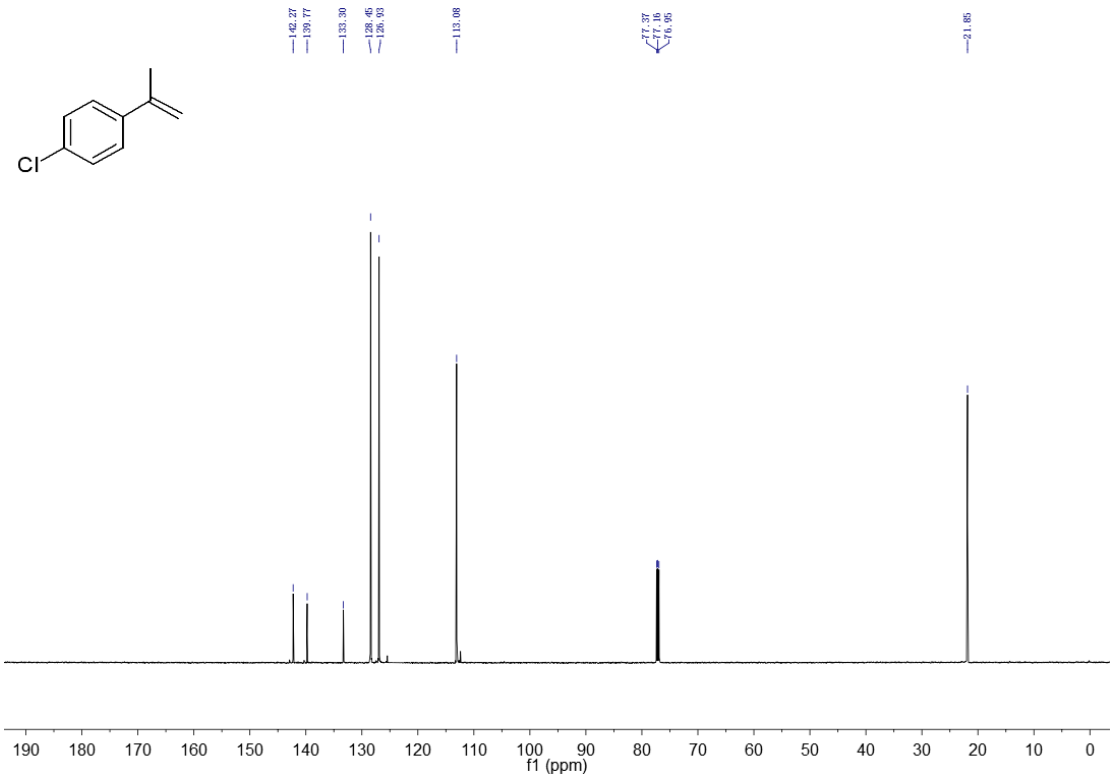
^{13}C NMR of **1a**



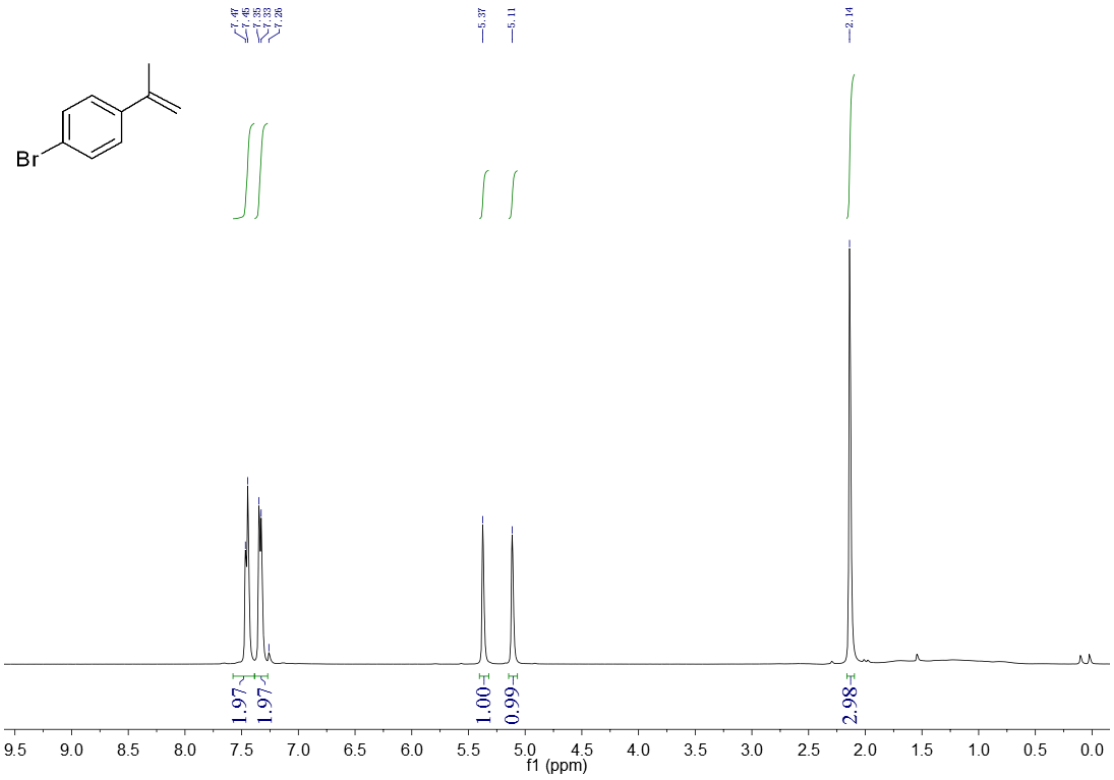
^{1}H NMR of **1b**



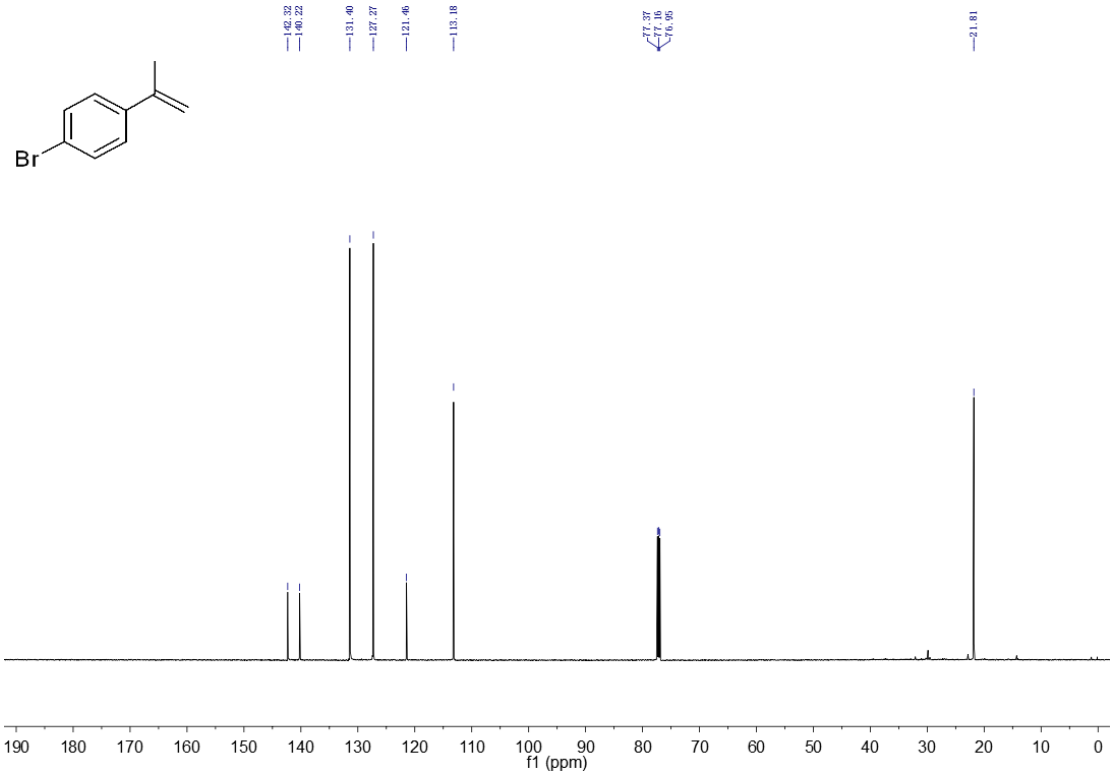
^{13}C NMR of **1b**



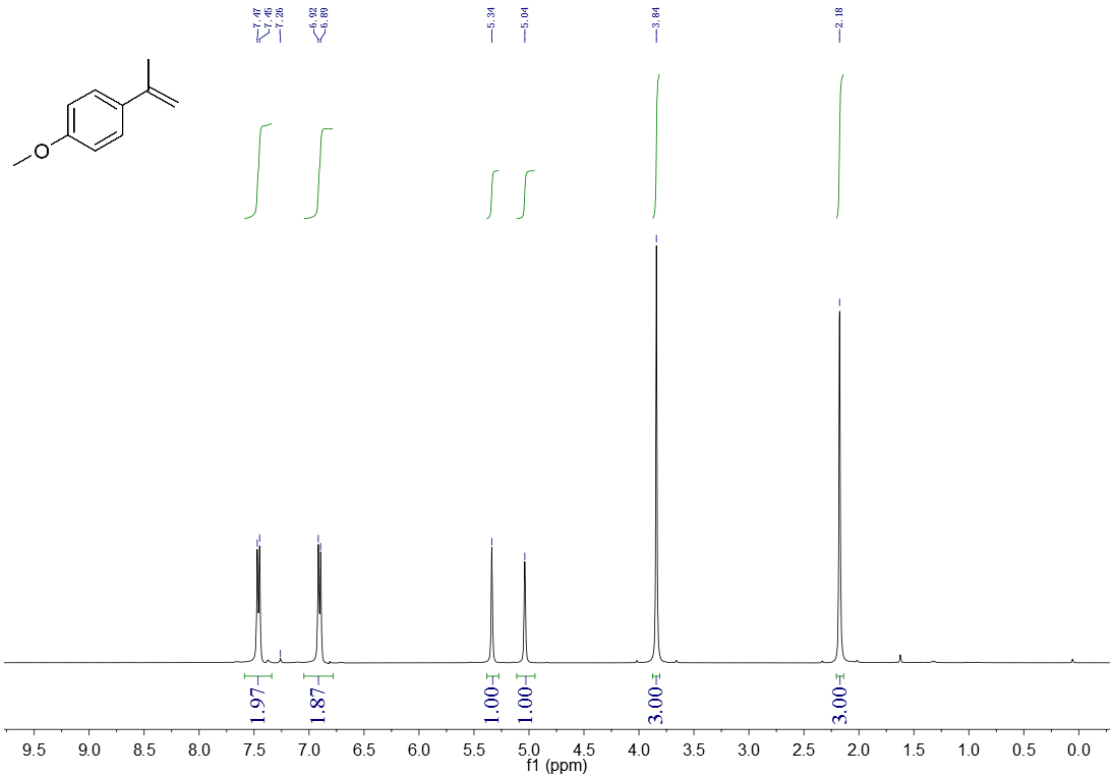
^{1}H NMR of **1c**



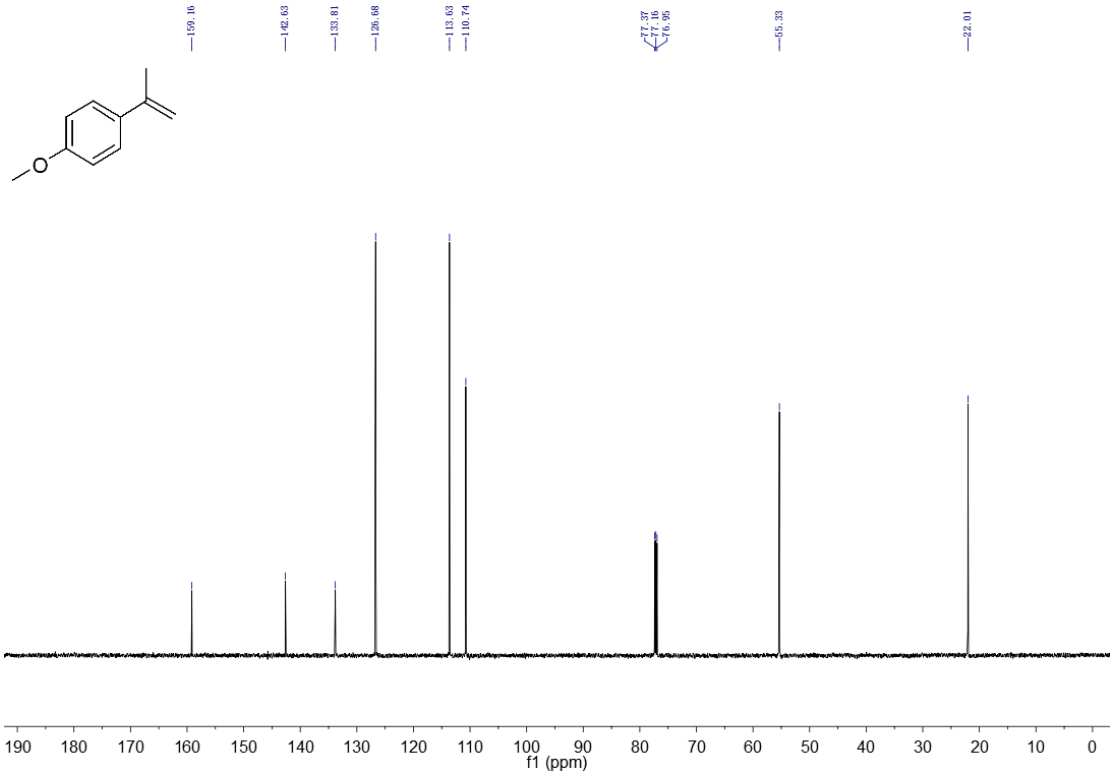
^{13}C NMR of **1c**



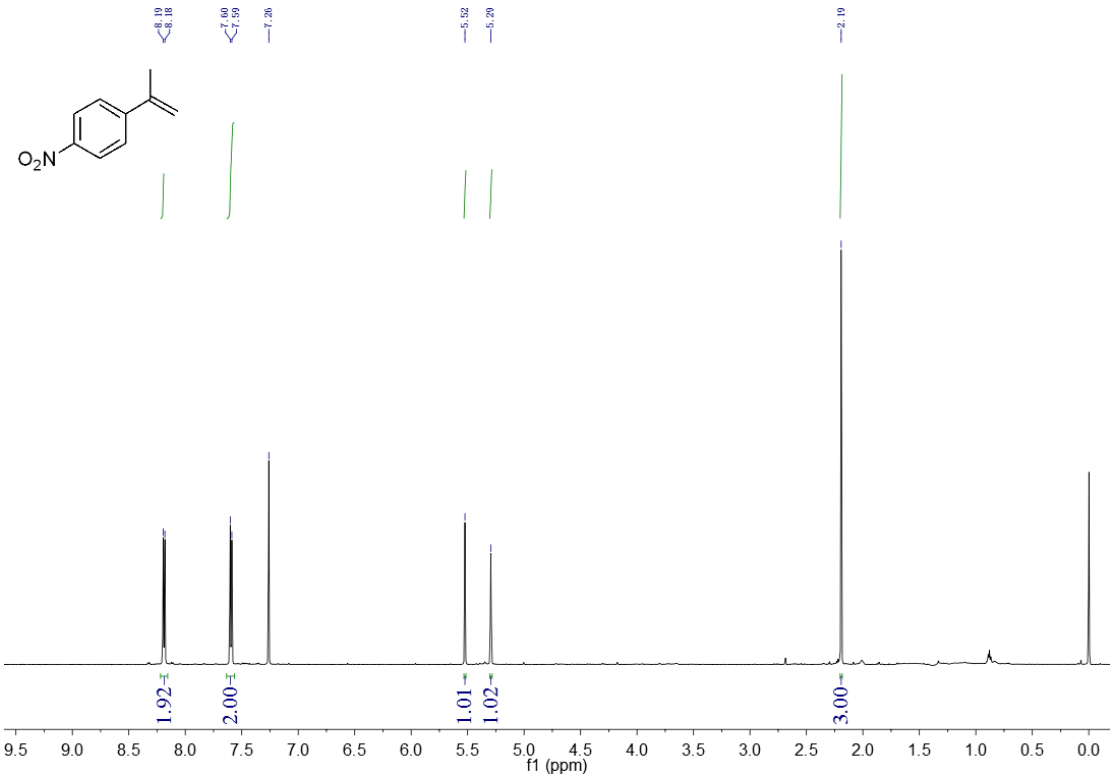
^{1}H NMR of **1d**



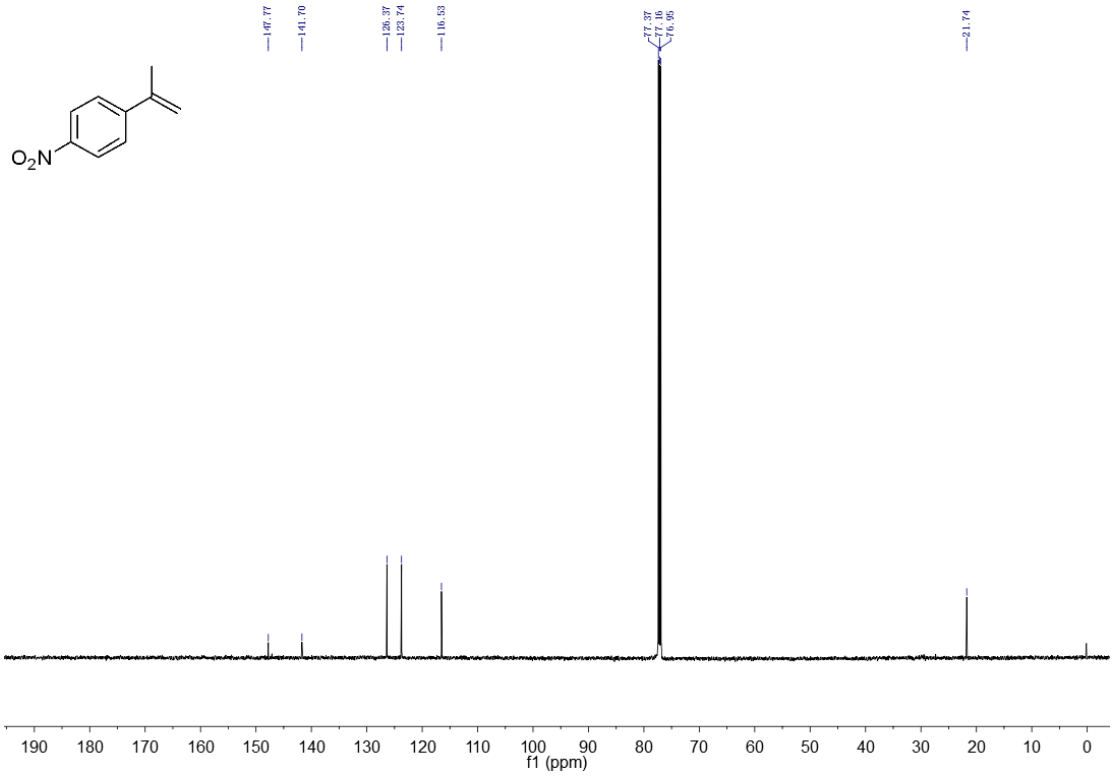
^{13}C NMR of **1d**



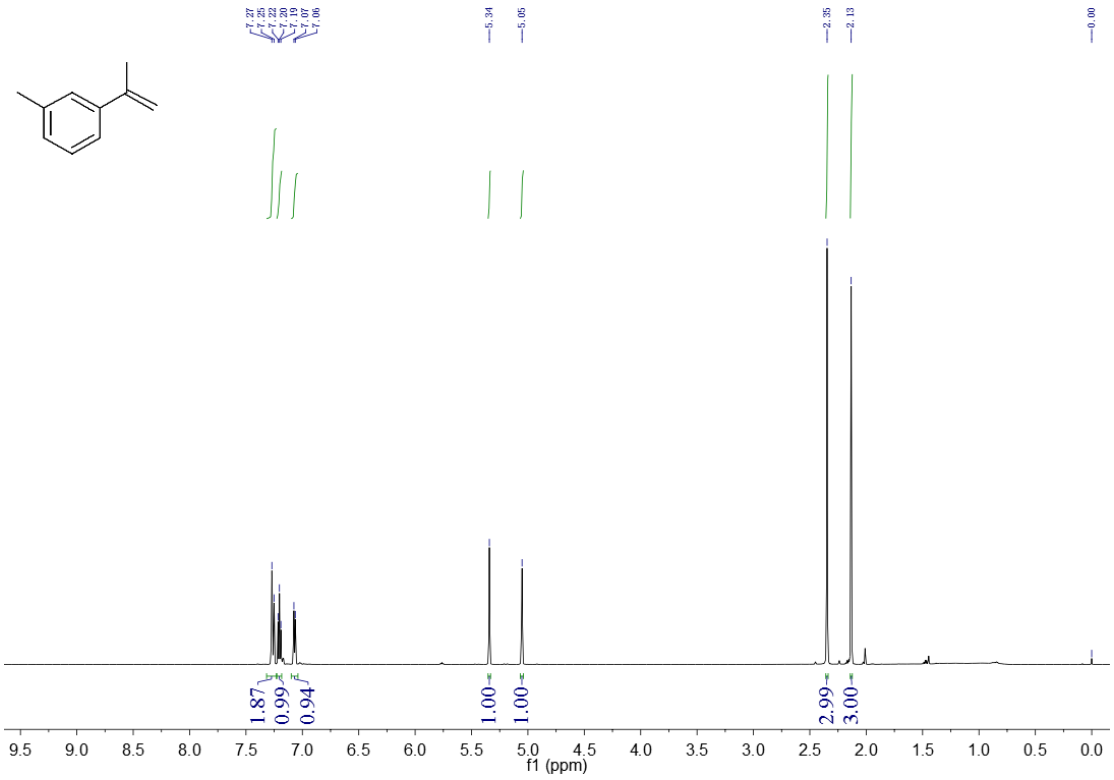
^{1}H NMR of **1e**



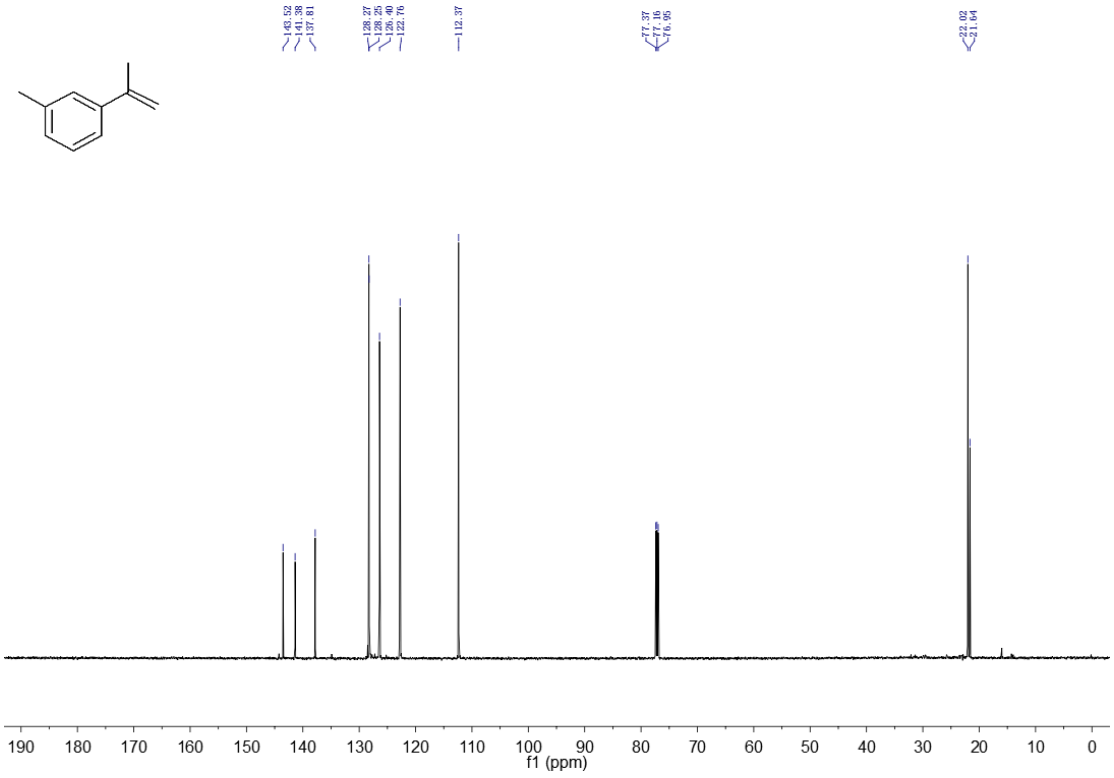
^{13}C NMR of **1e**



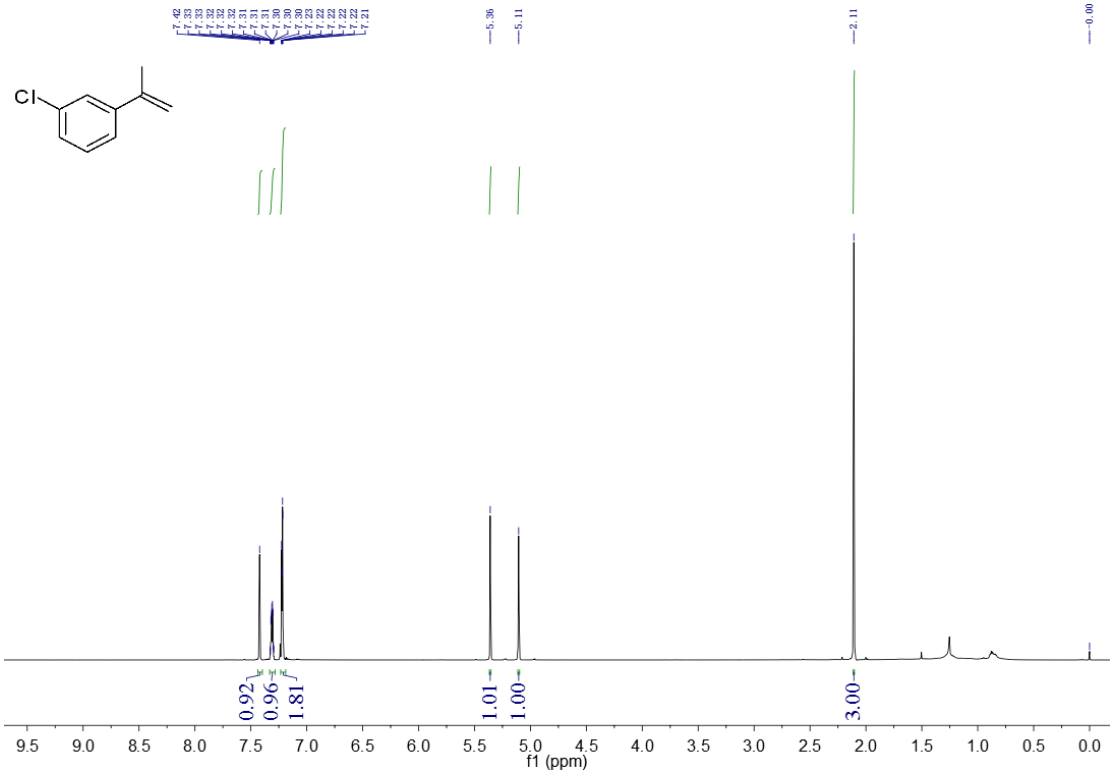
^{1}H NMR of **1f**



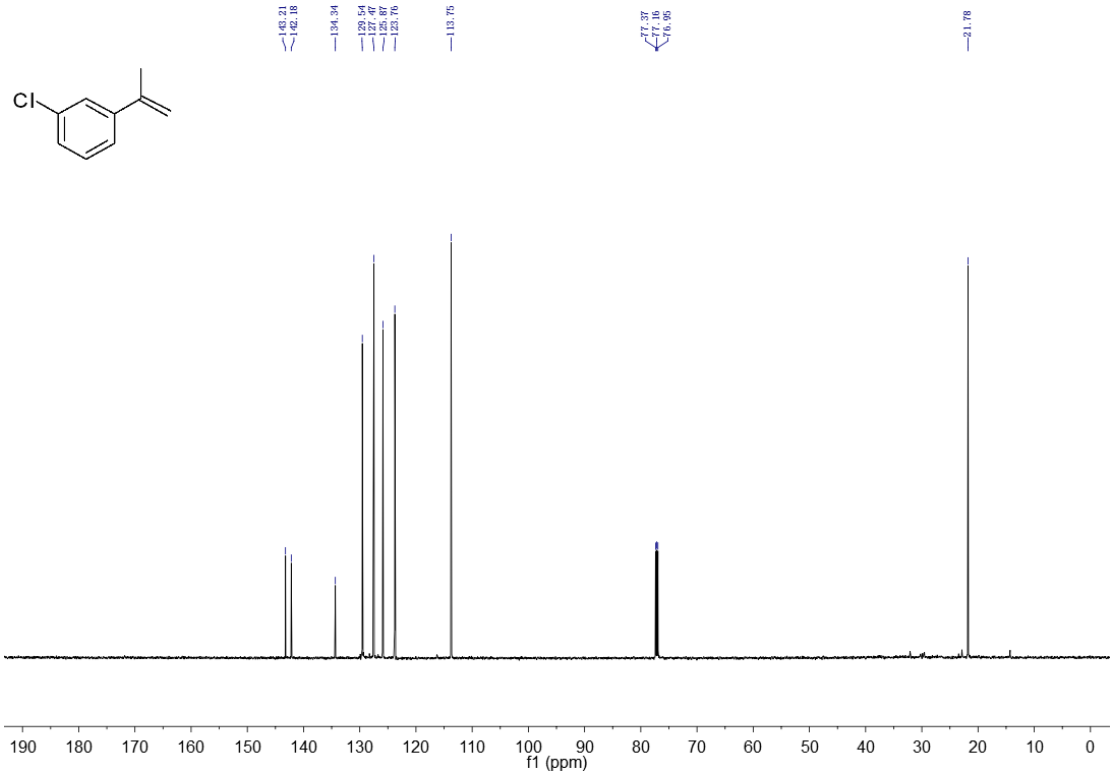
^{13}C NMR of **1f**



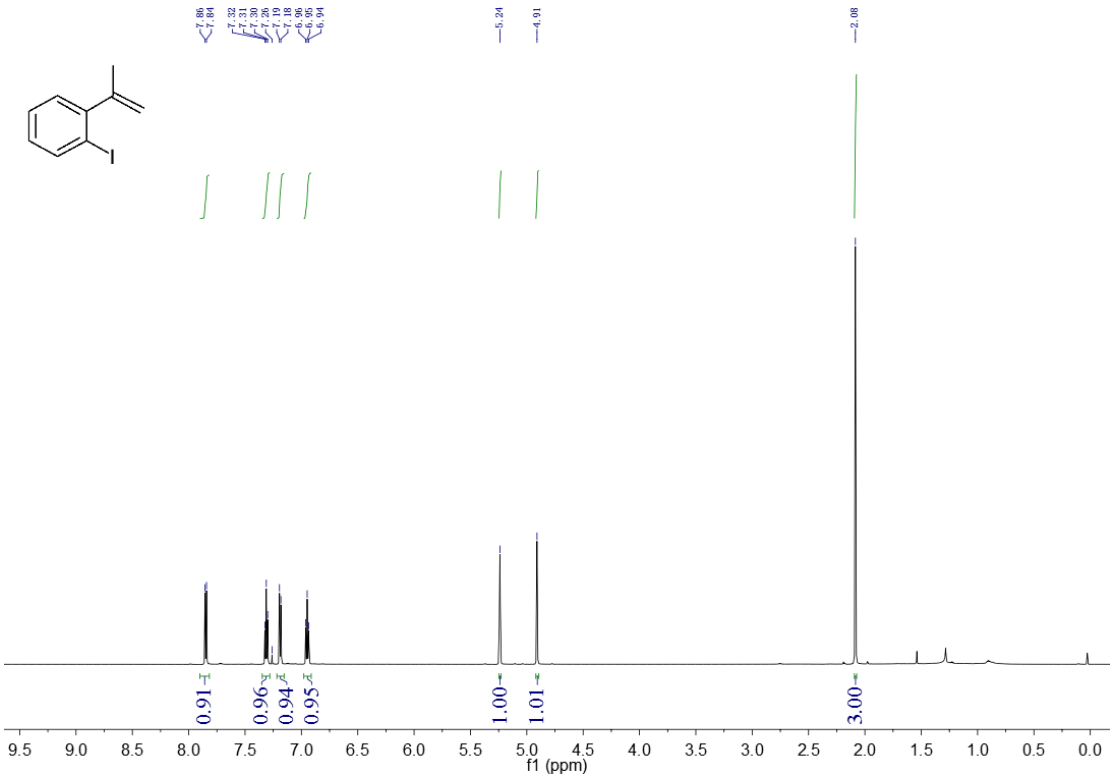
^{1}H NMR of **1g**



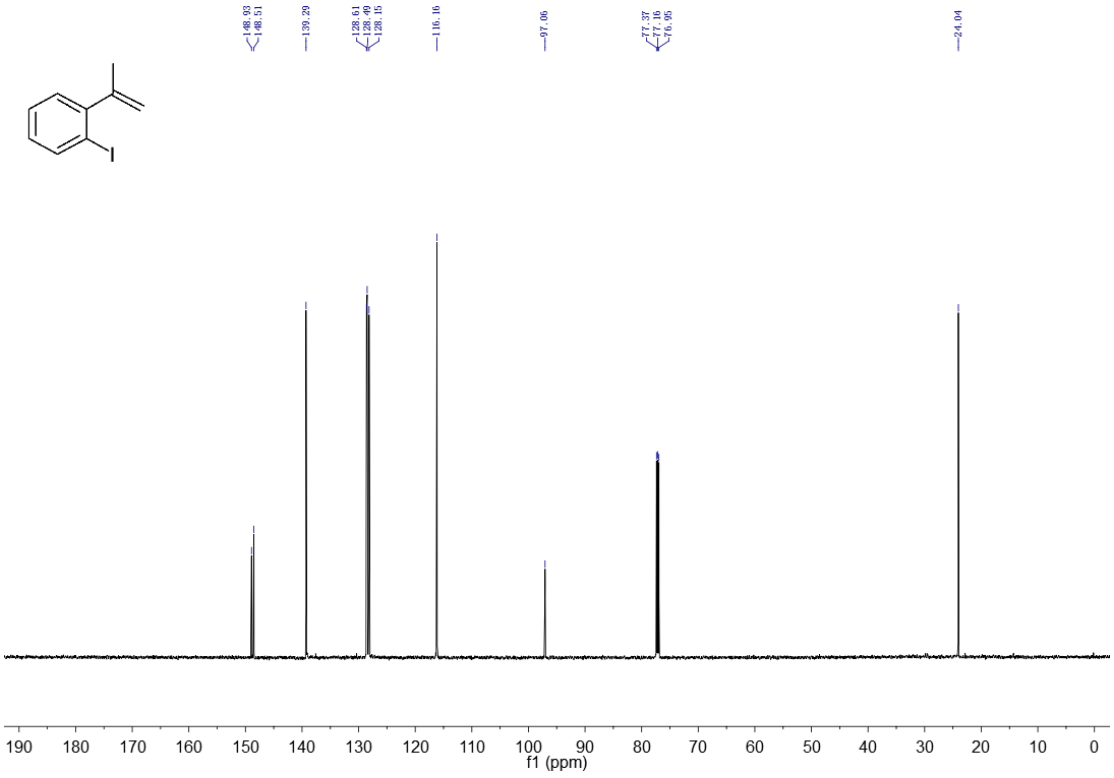
^{13}C NMR of **1g**



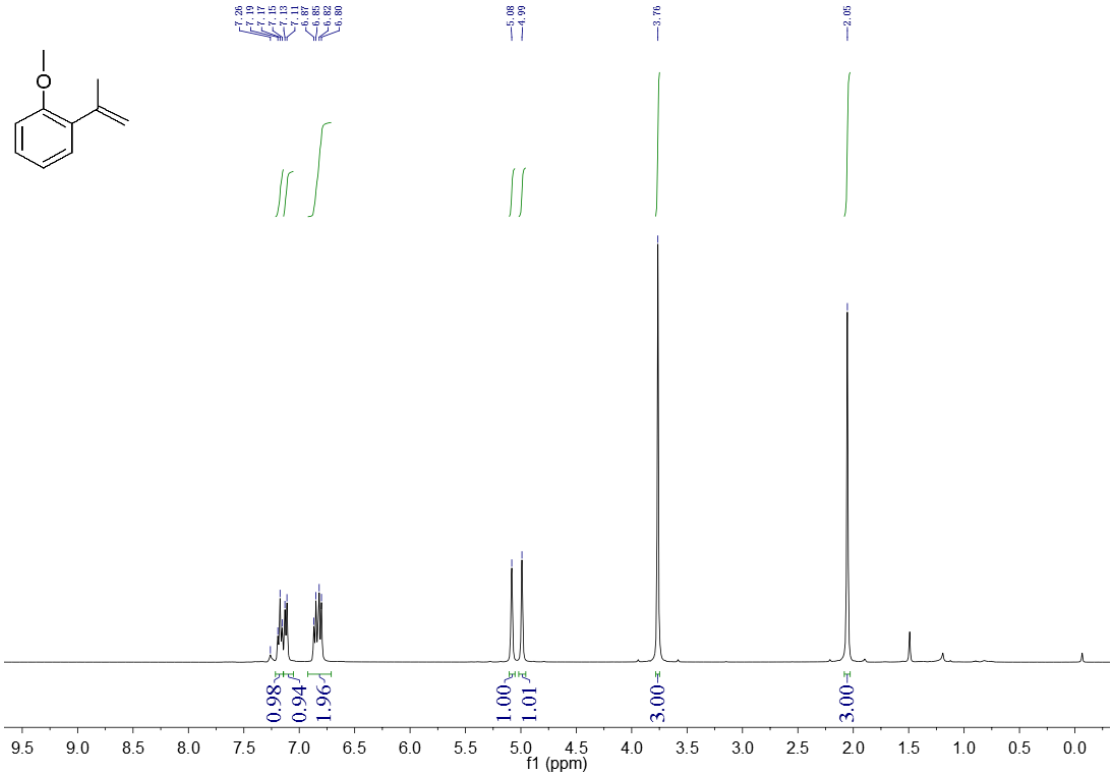
^{1}H NMR of **1h**



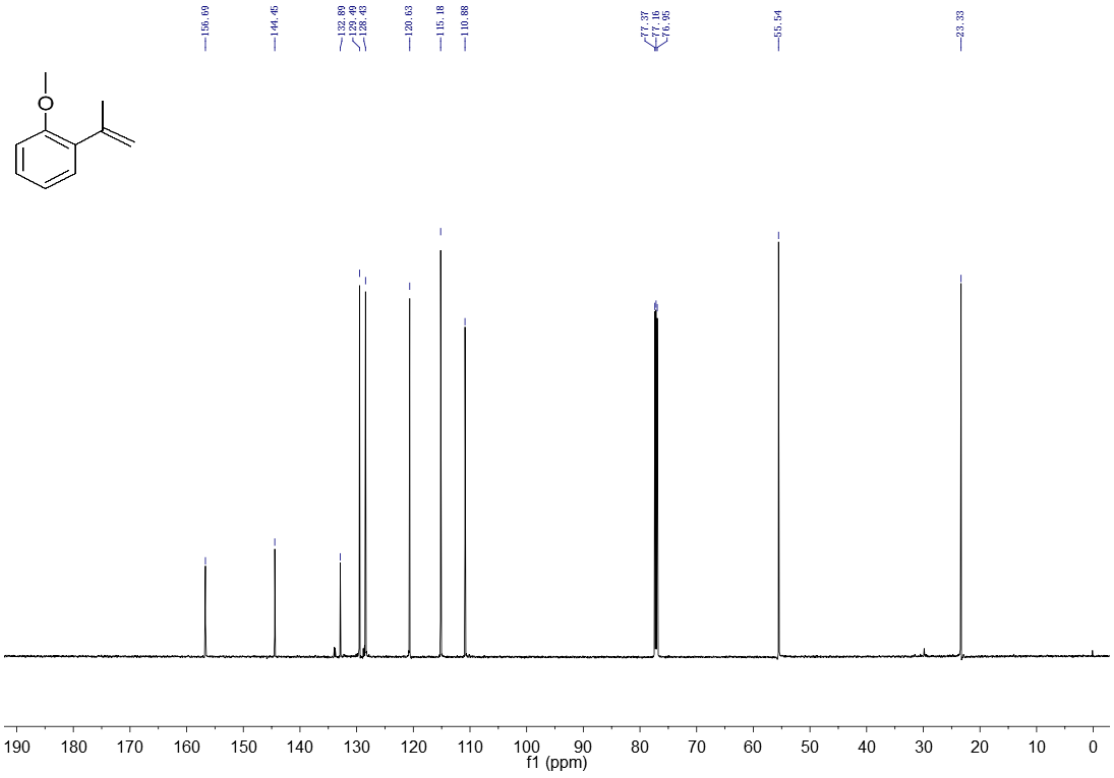
^{13}C NMR of **1h**



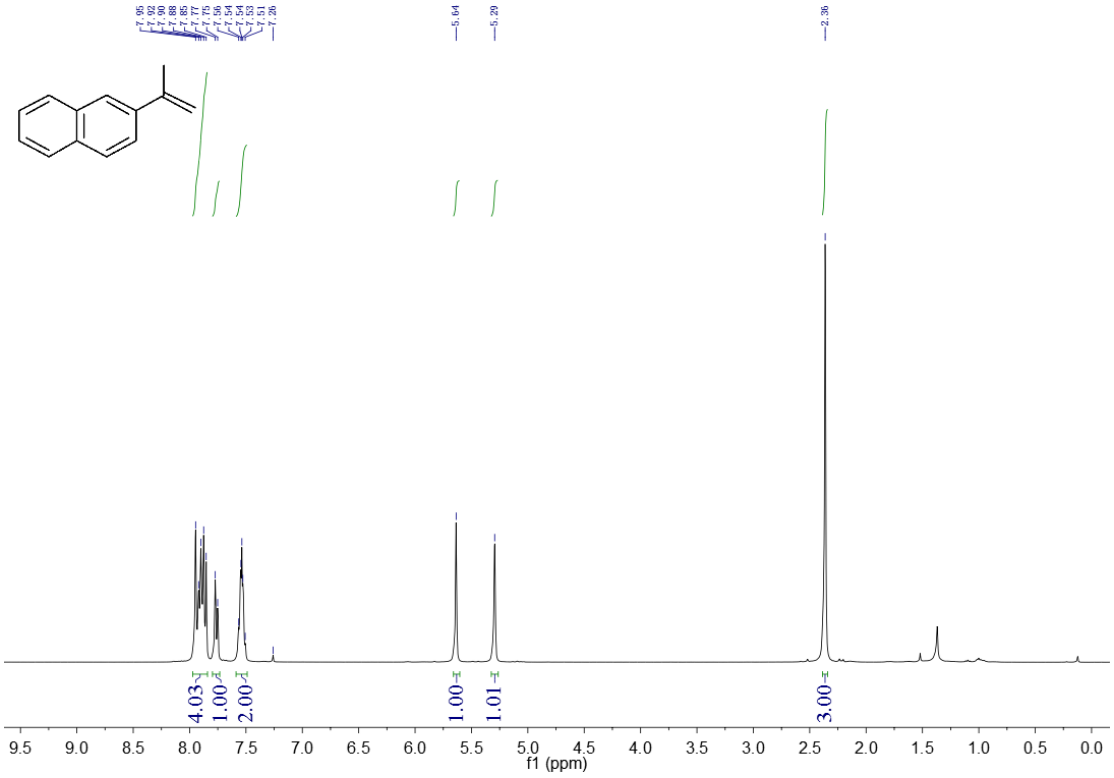
^{1}H NMR of **1i**



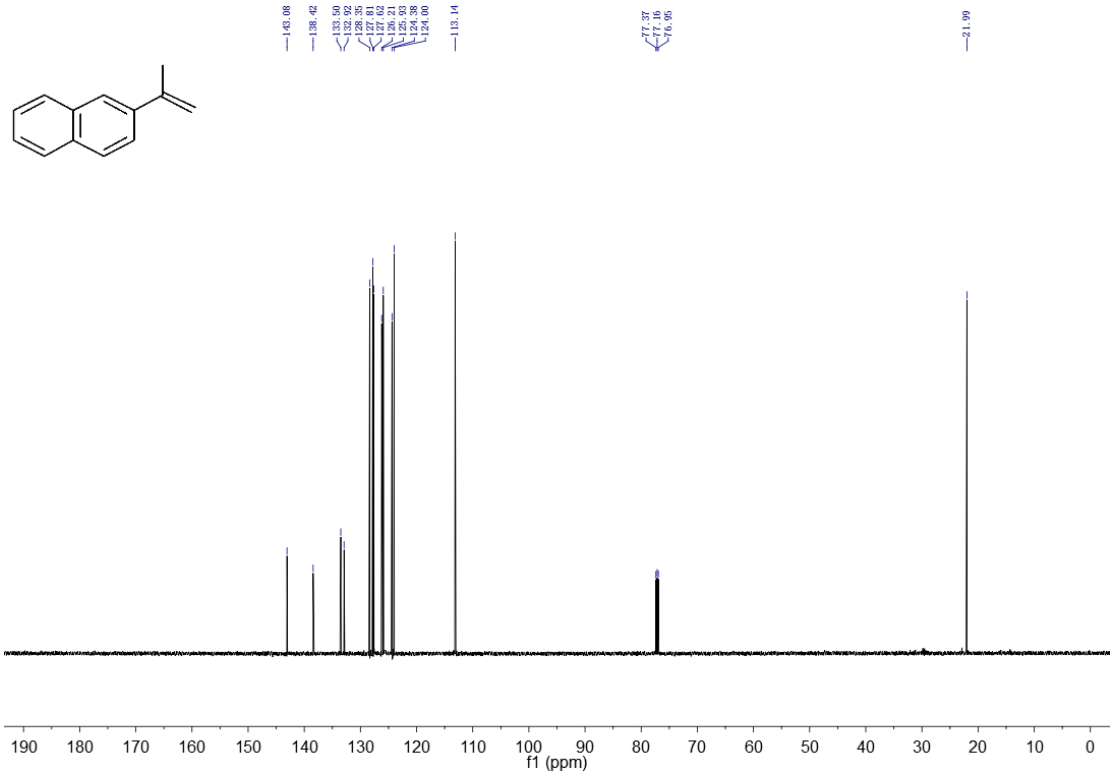
^{13}C NMR of **1i**



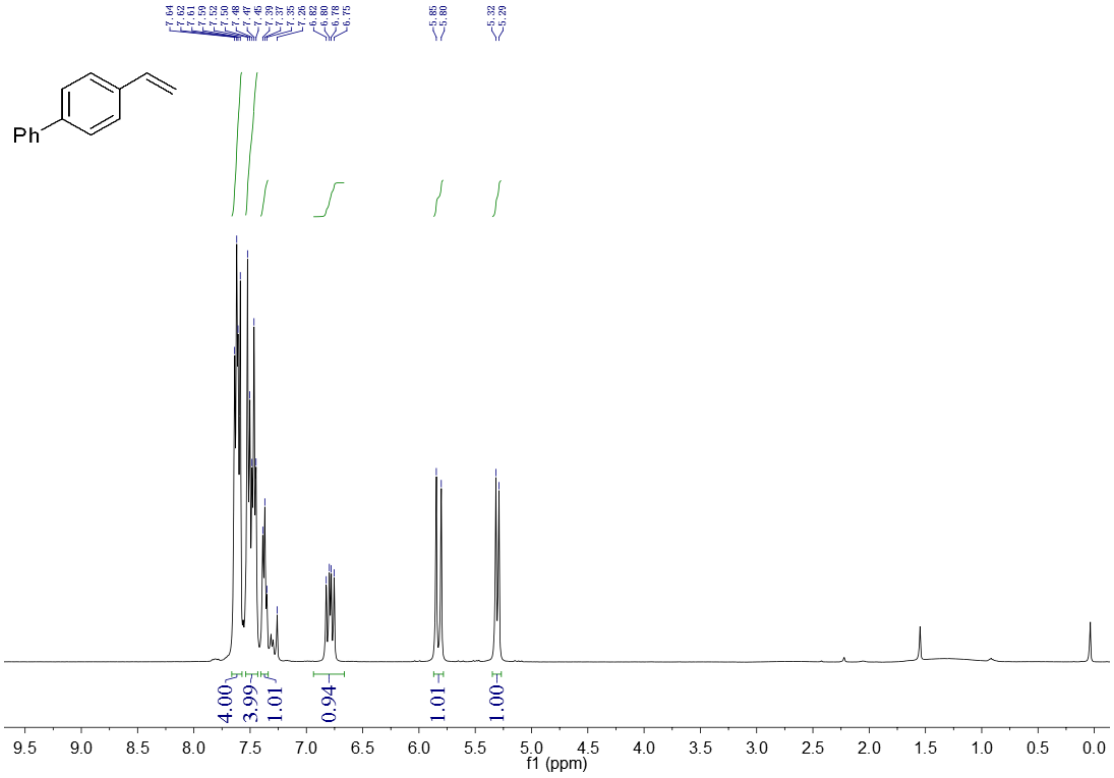
^{1}H NMR of **1j**



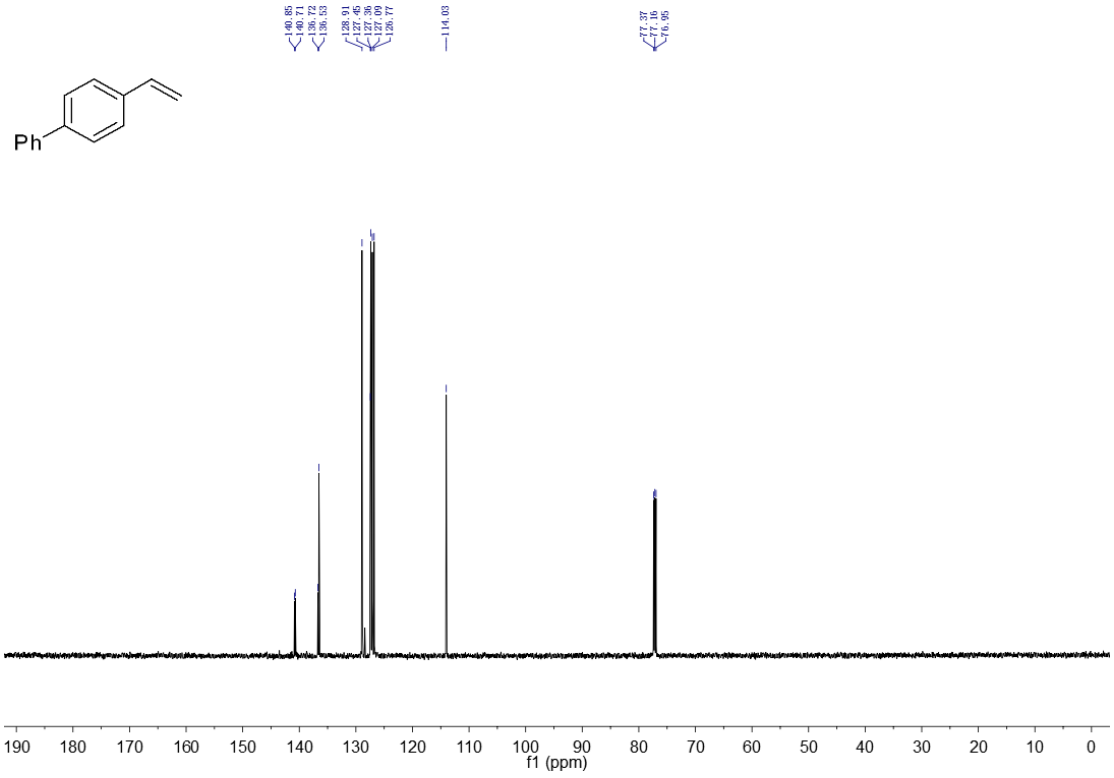
^{13}C NMR of **1j**



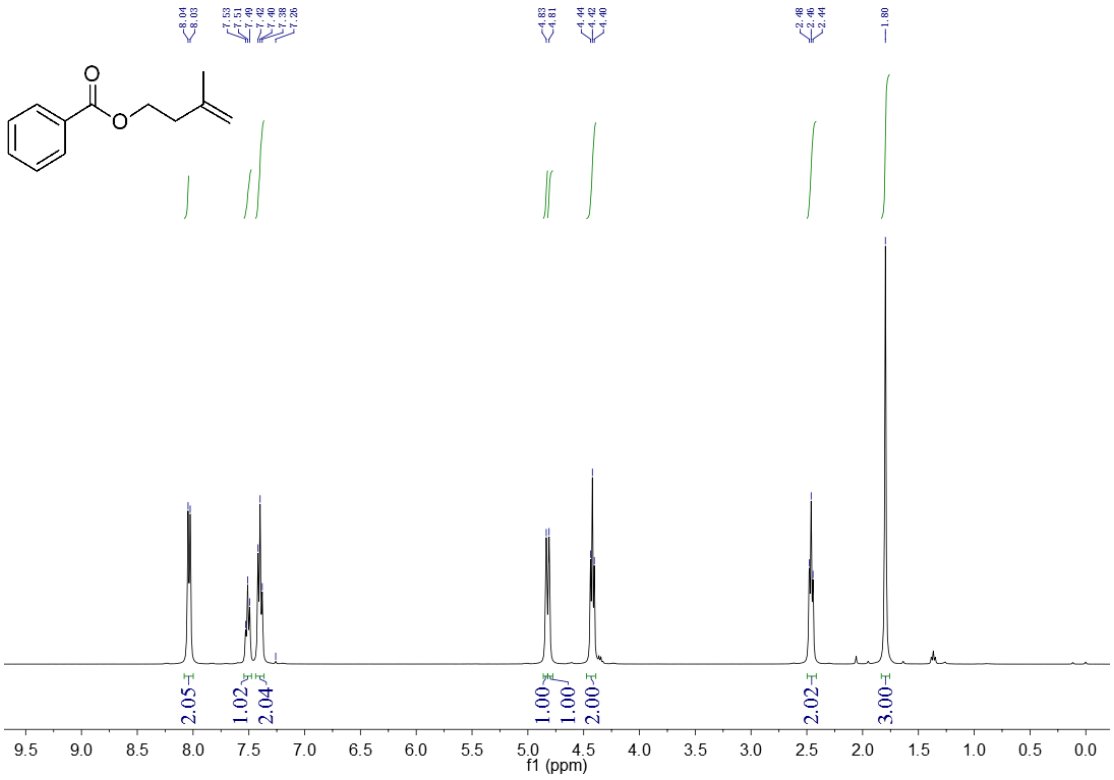
^{1}H NMR of **1k**



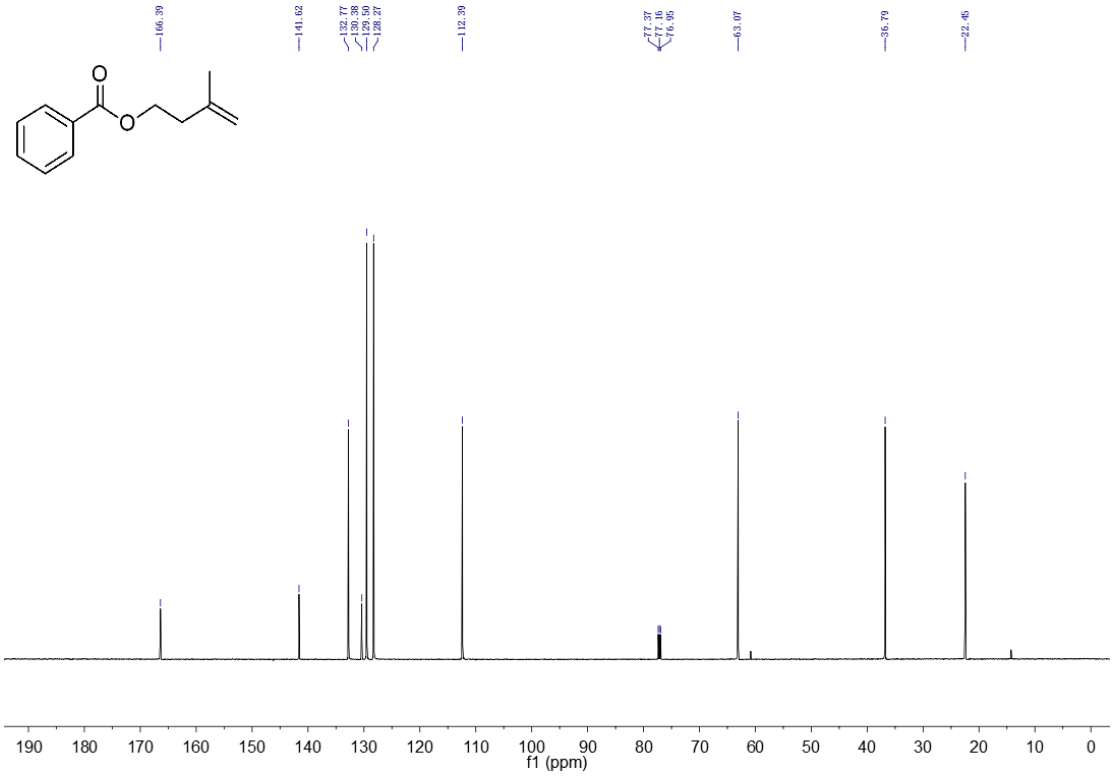
^{13}C NMR of **1k**



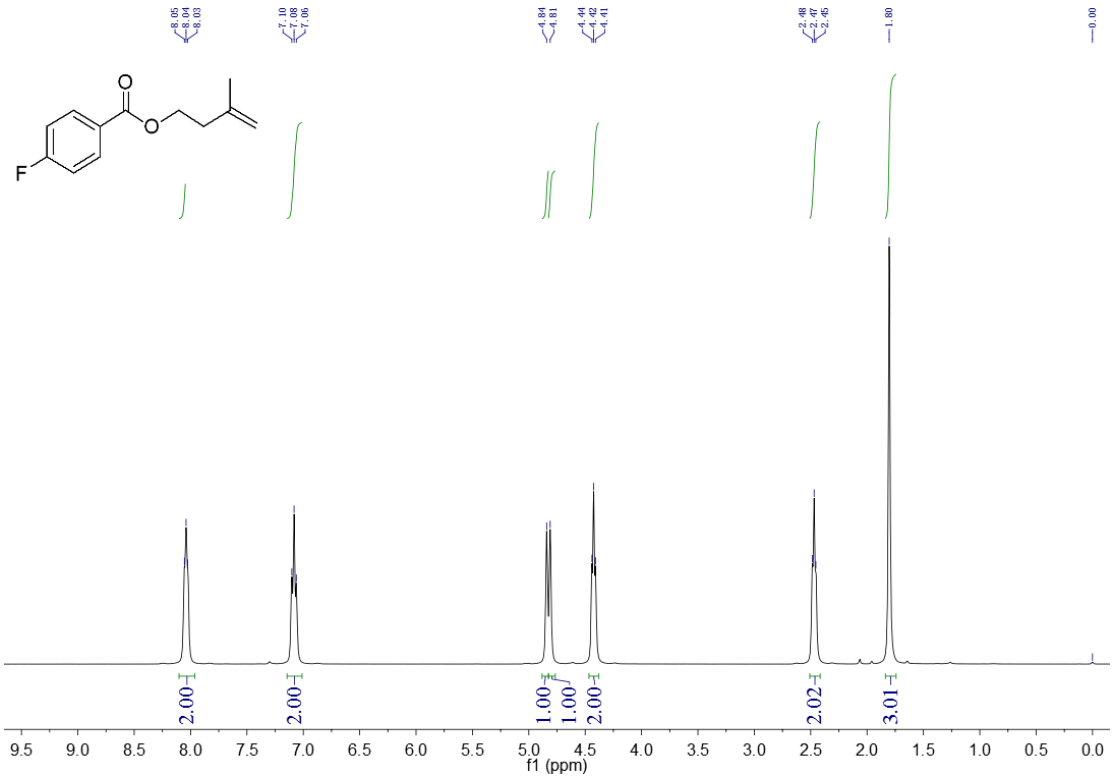
^{1}H NMR of **3a**



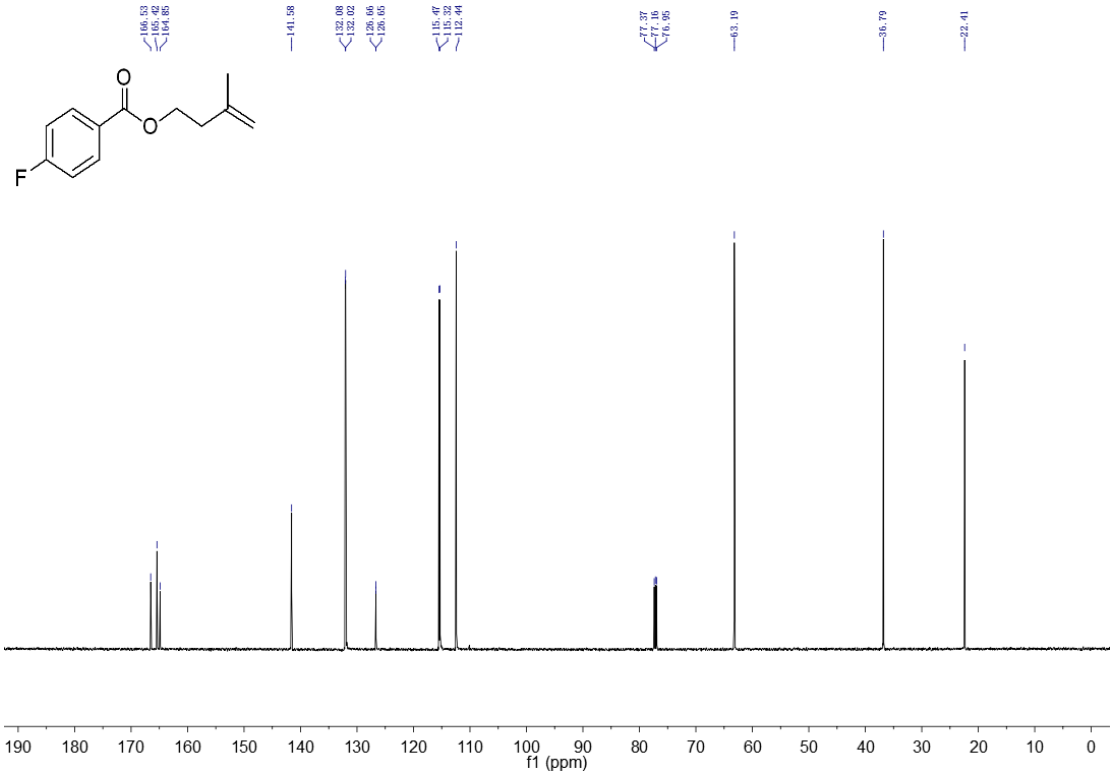
^{13}C NMR of **3a**



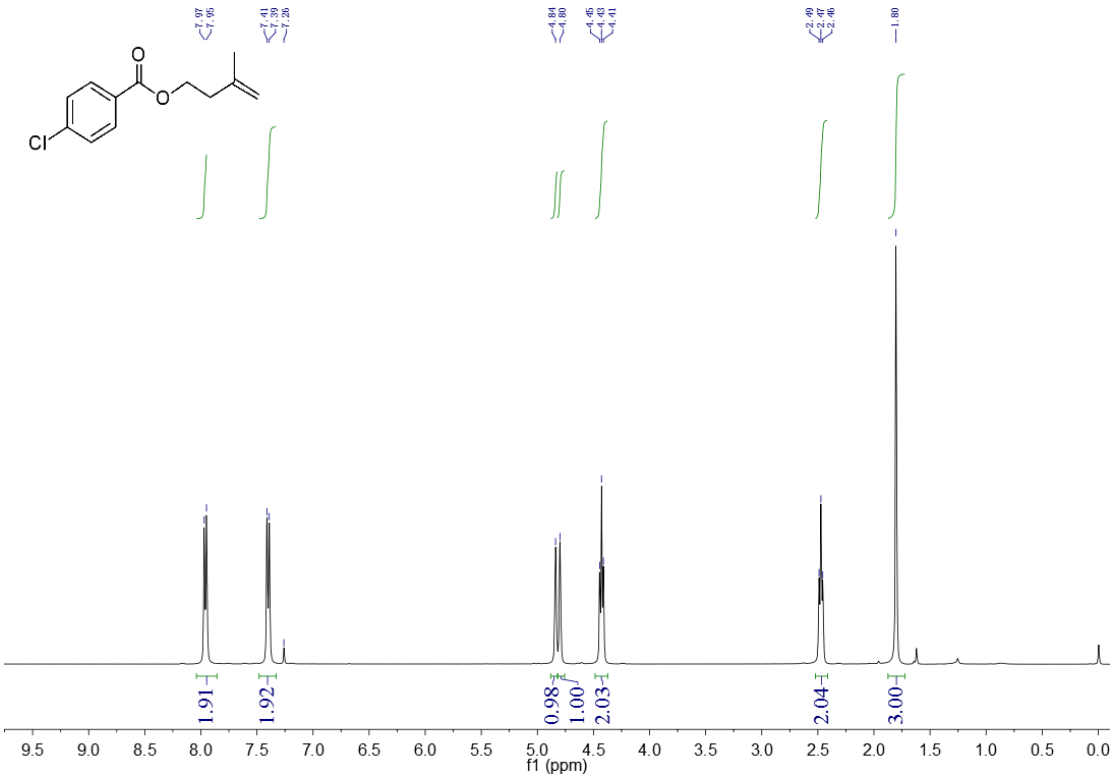
^{1}H NMR of **3b**



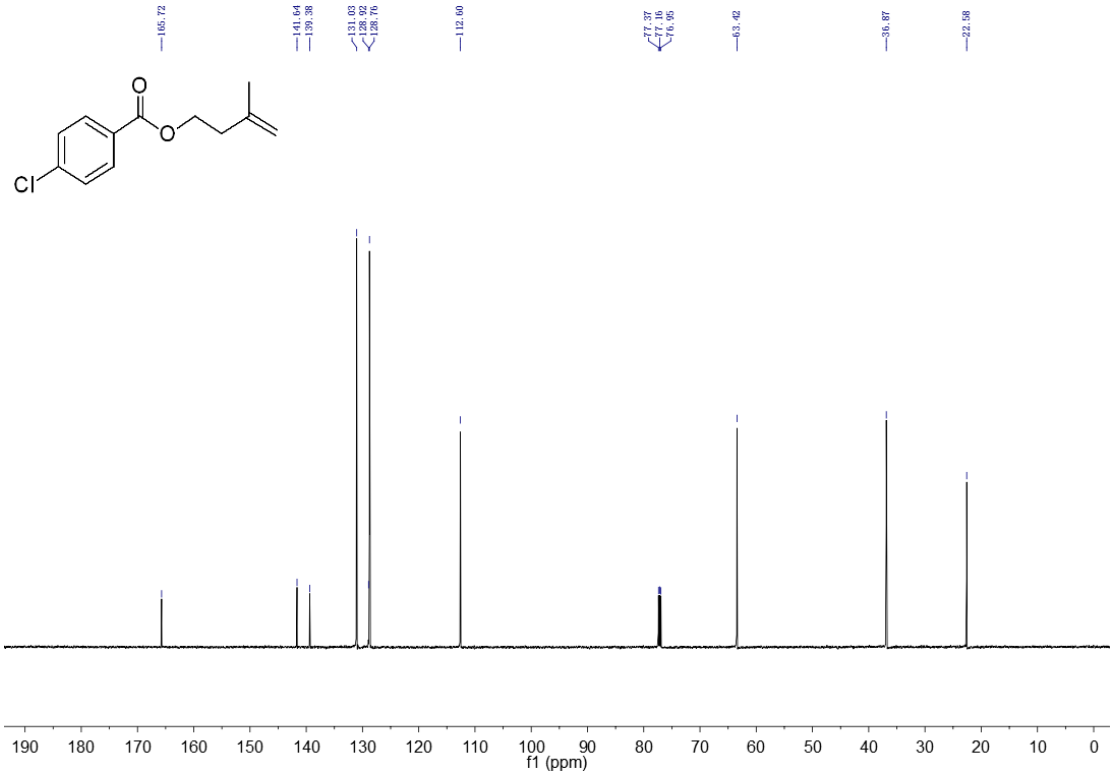
^{13}C NMR of **3b**



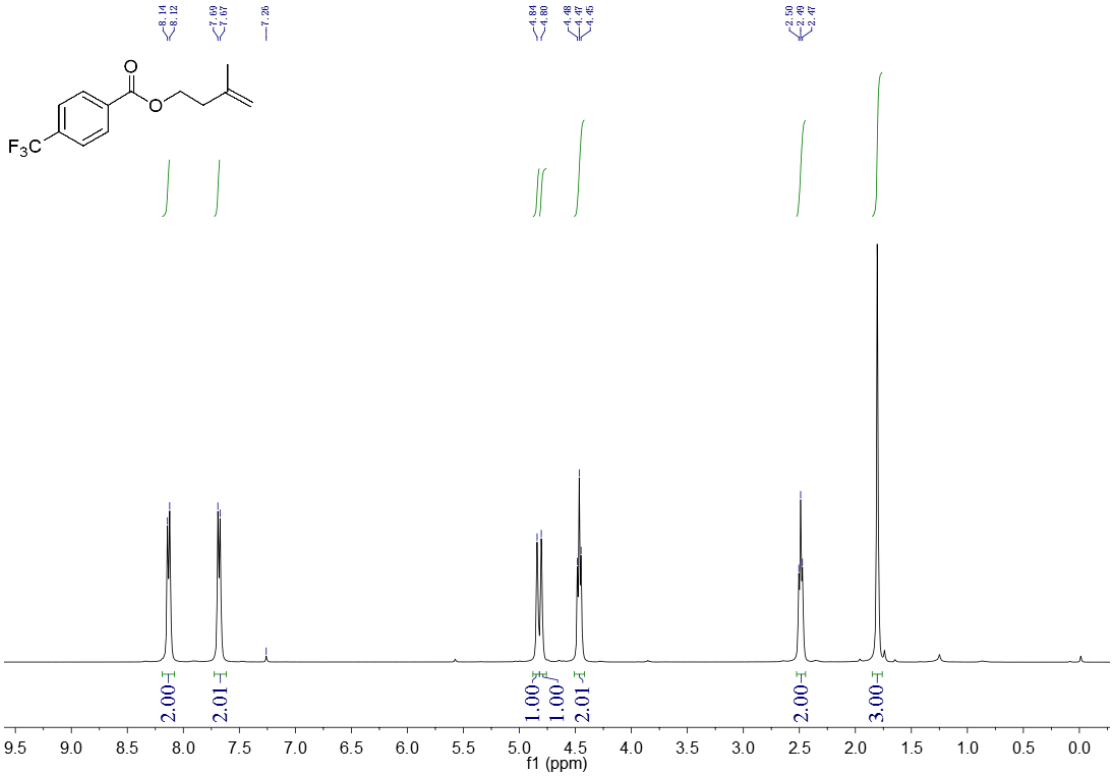
^{1}H NMR of **3c**



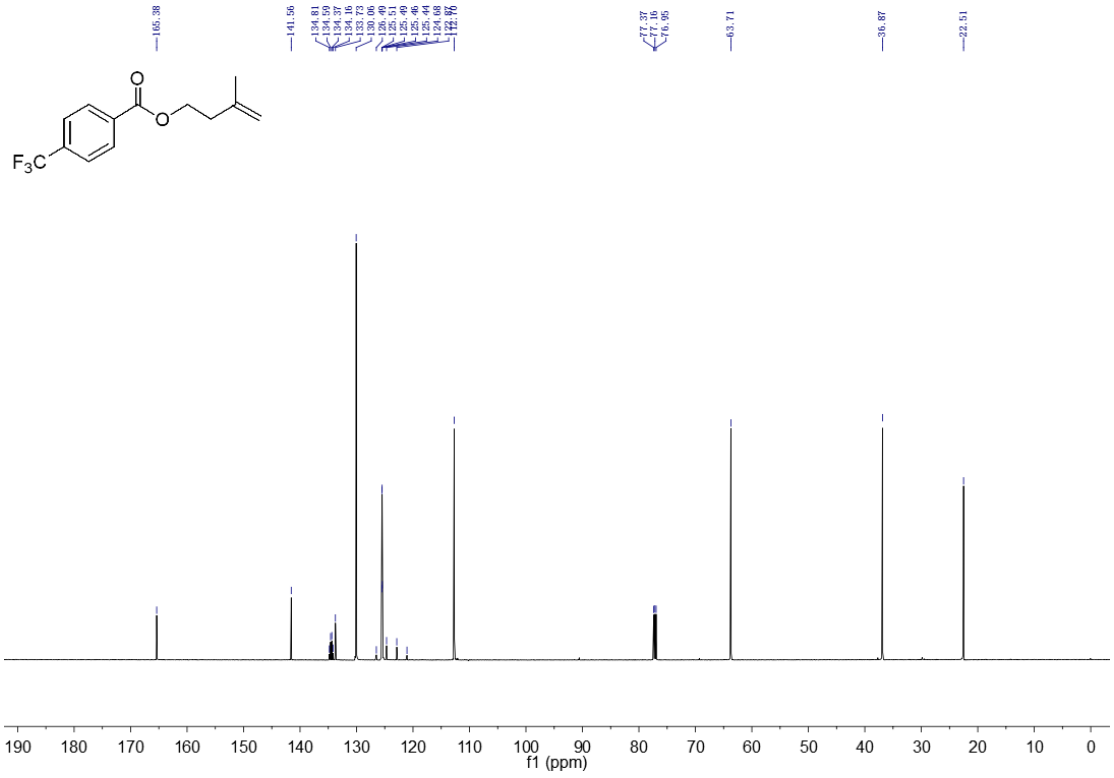
^{13}C NMR of **3c**



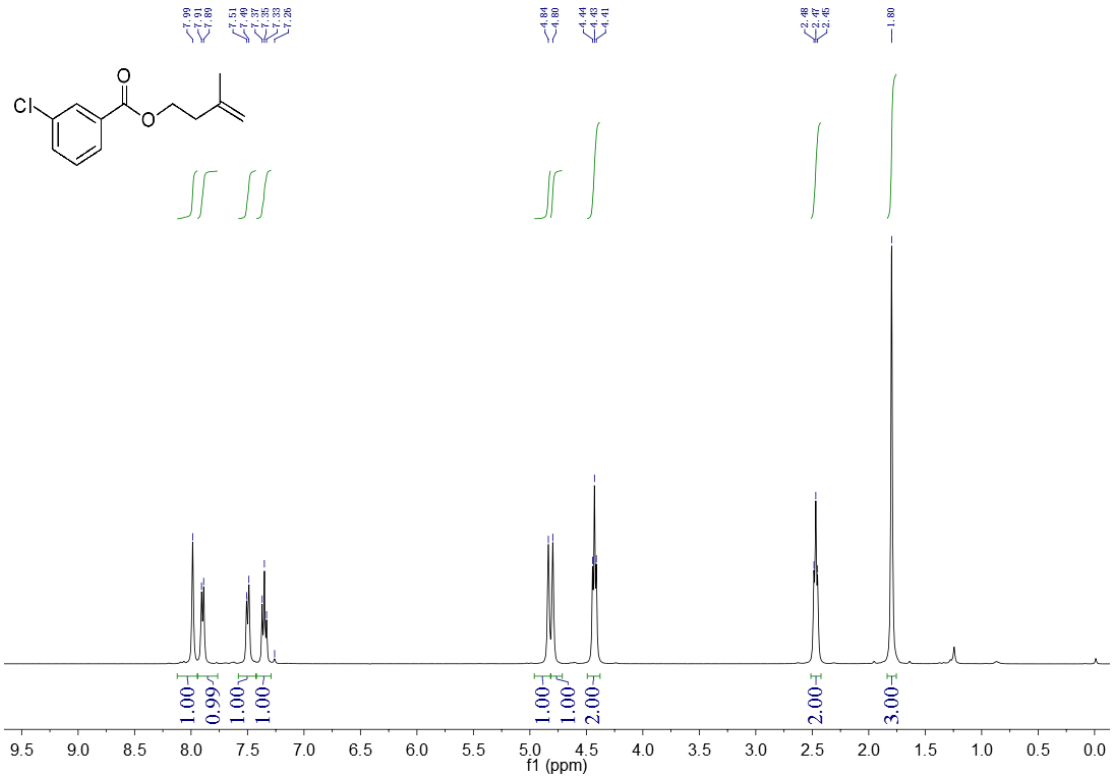
^{1}H NMR of **3d**



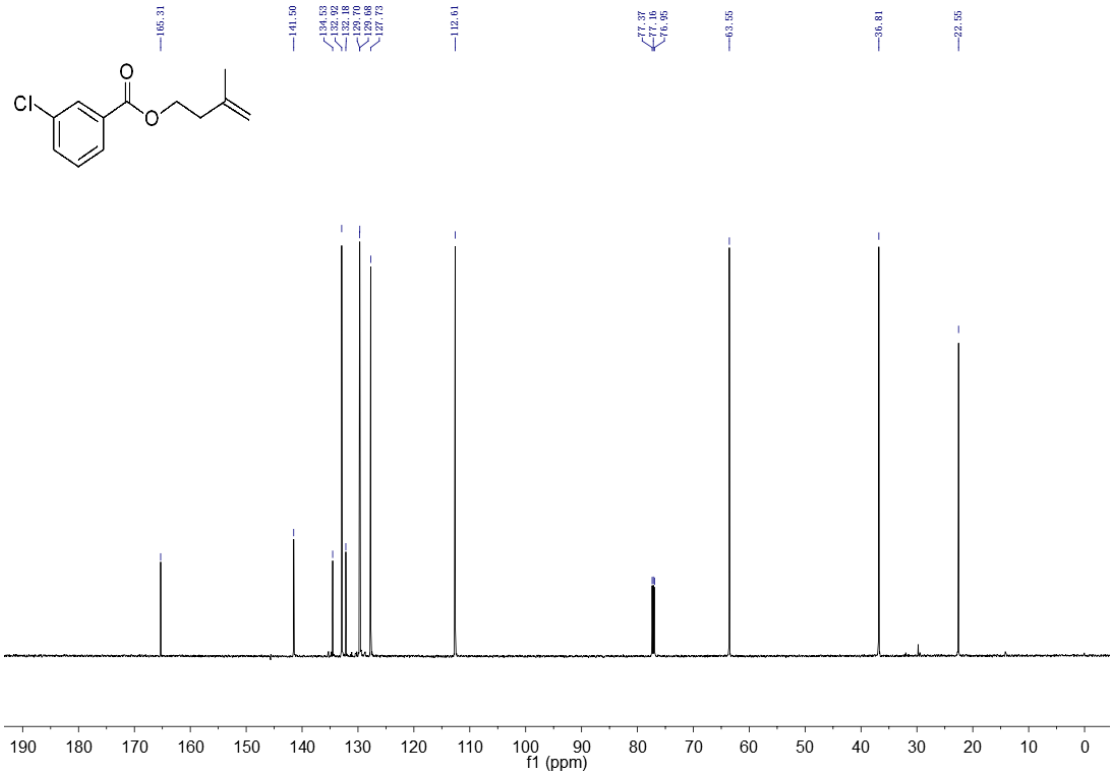
^{13}C NMR of **3d**



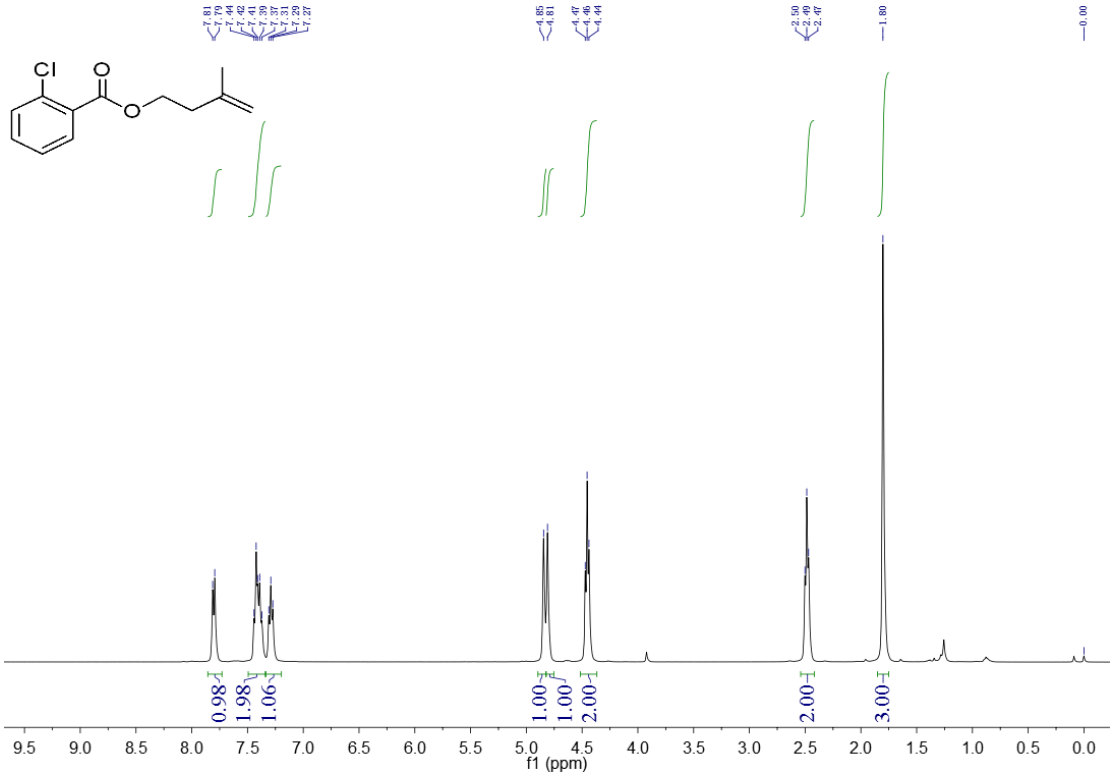
^{1}H NMR of **3e**



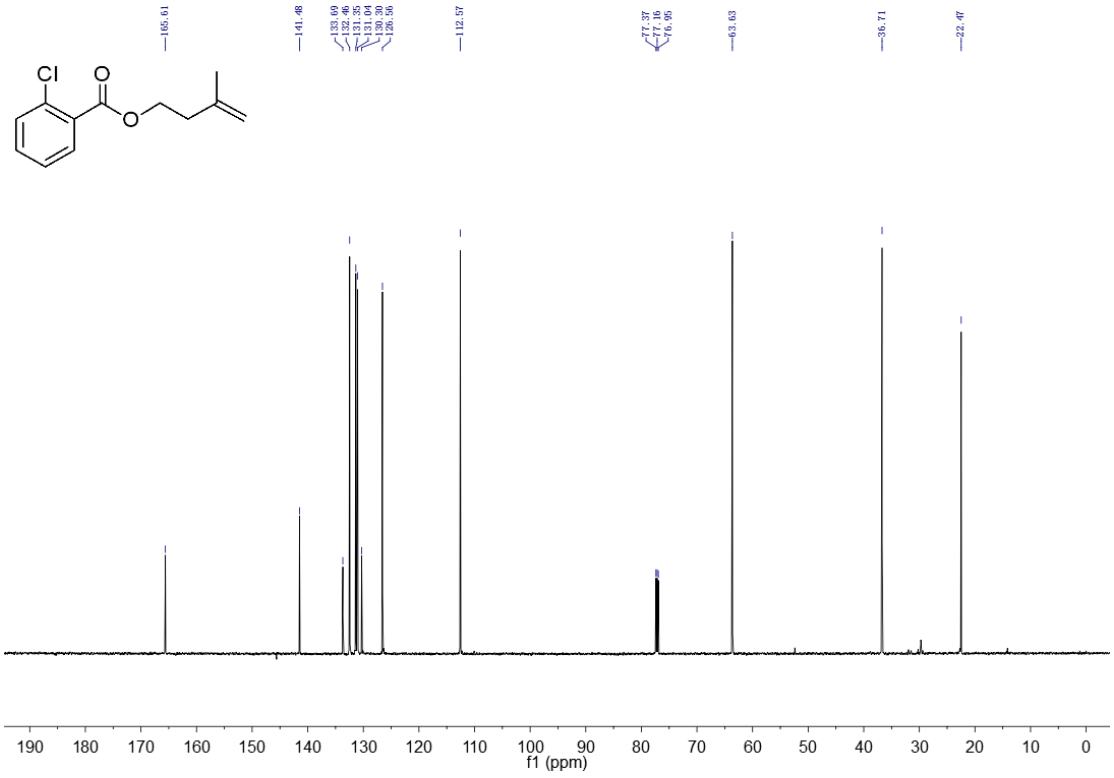
^{13}C NMR of **3e**



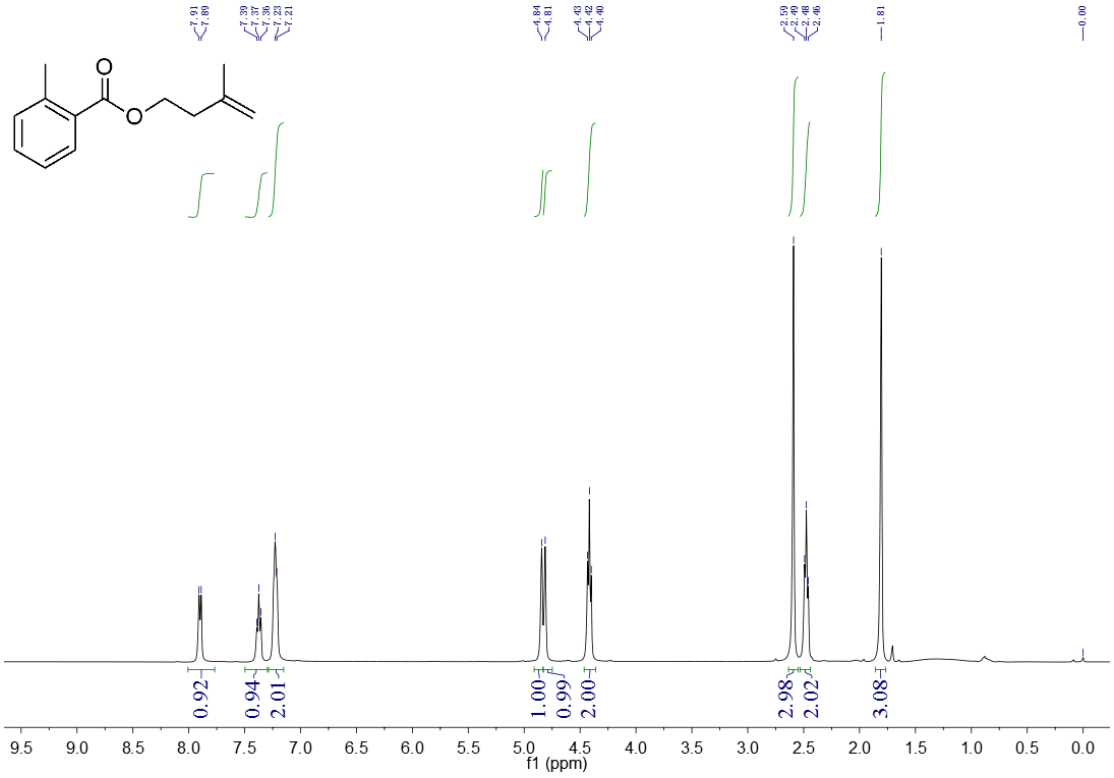
^{1}H NMR of **3f**



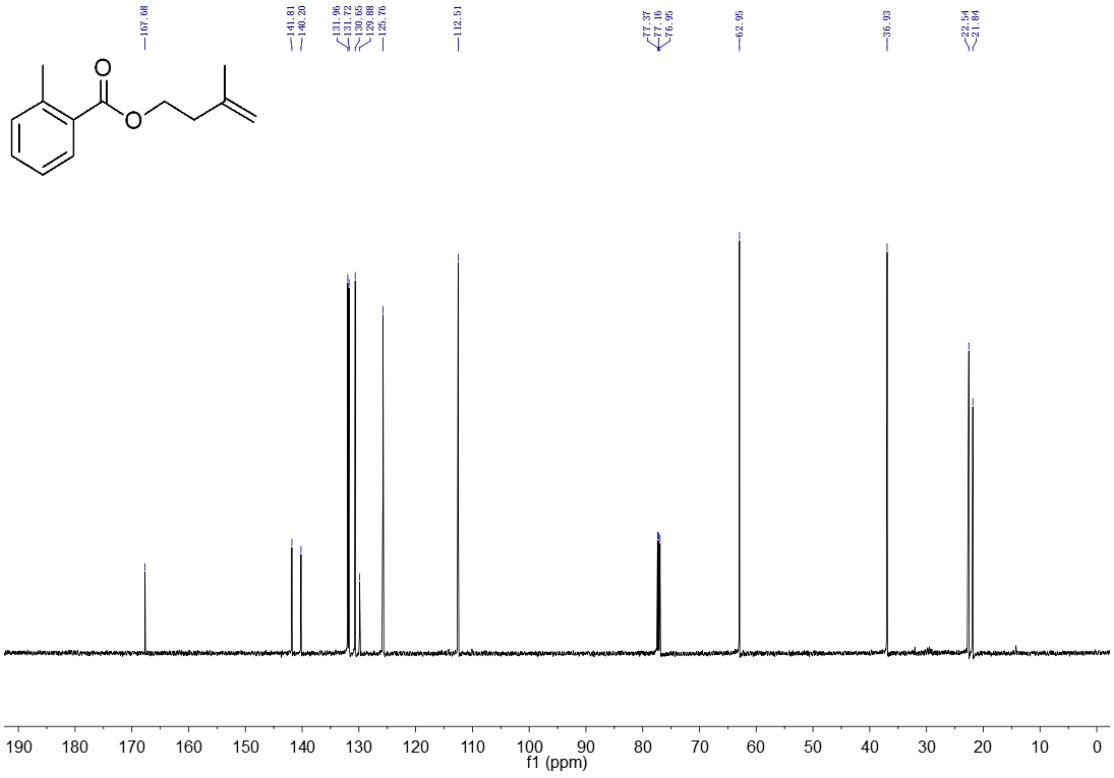
^{13}C NMR of **3f**



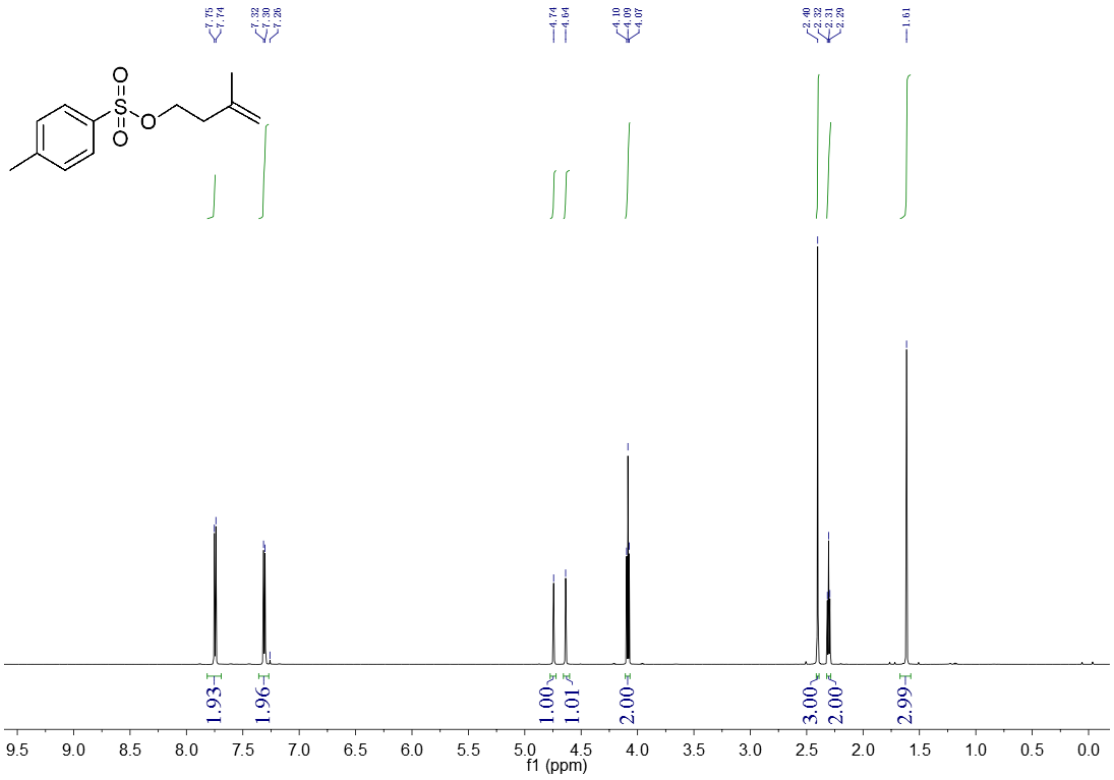
^{1}H NMR of **3g**



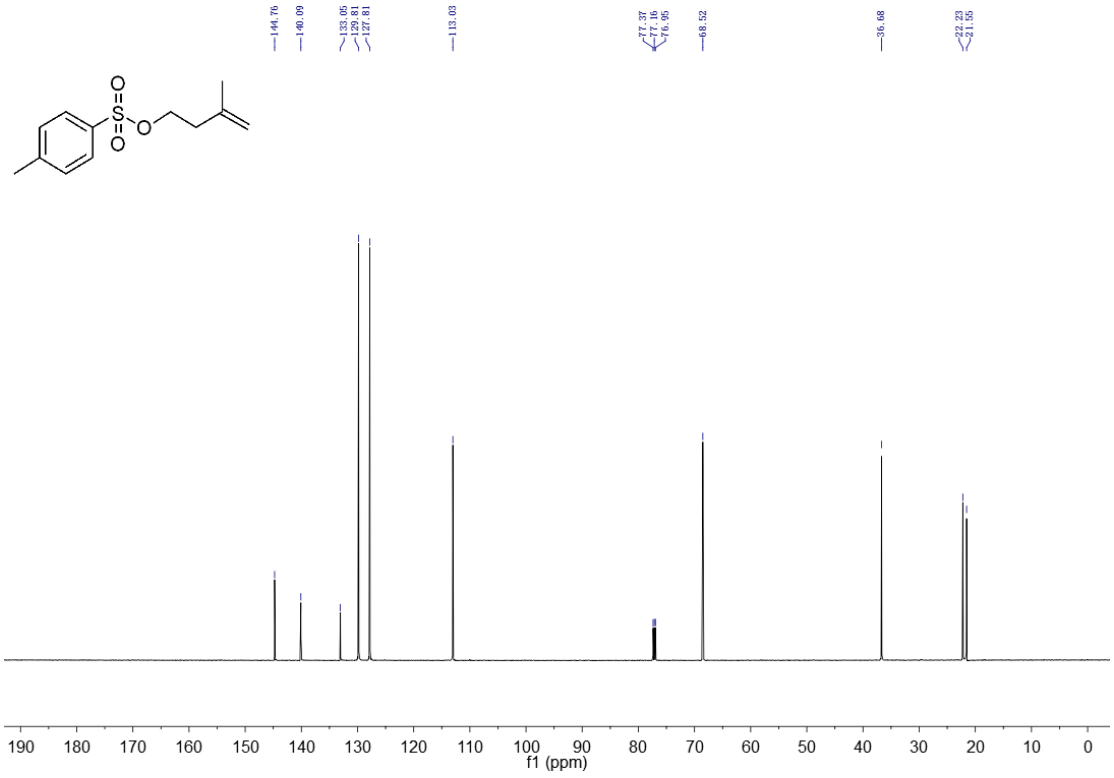
^{13}C NMR of **3g**



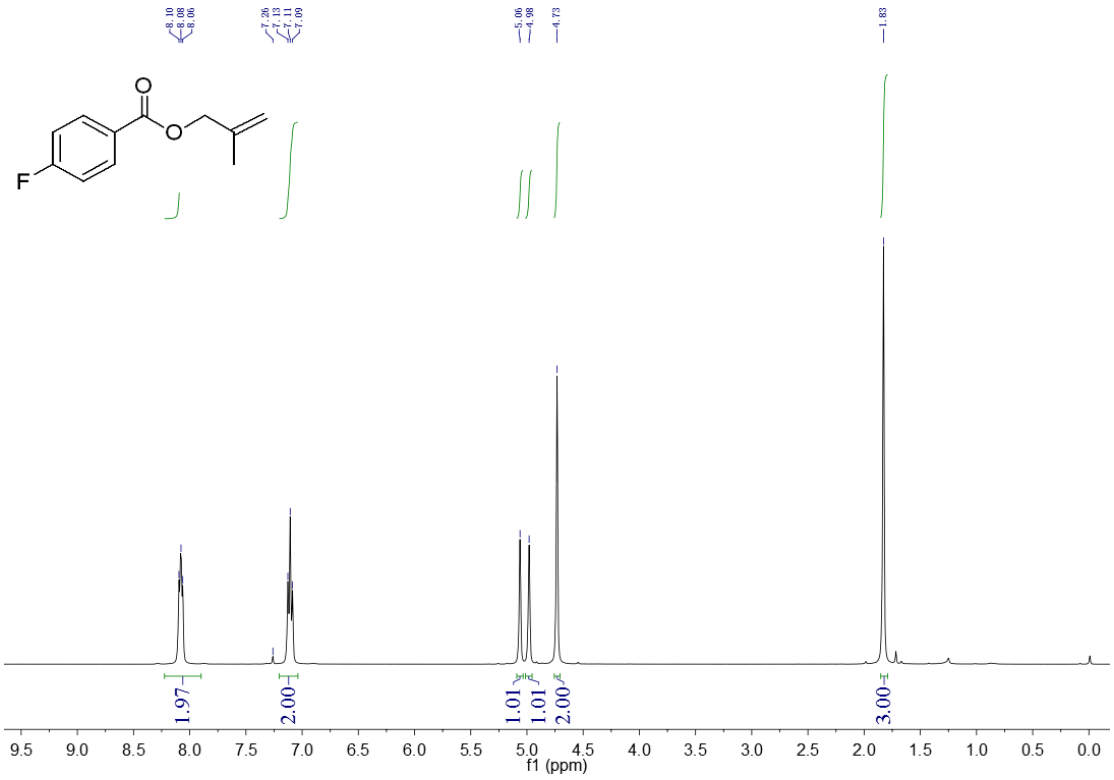
^{1}H NMR of **3h**



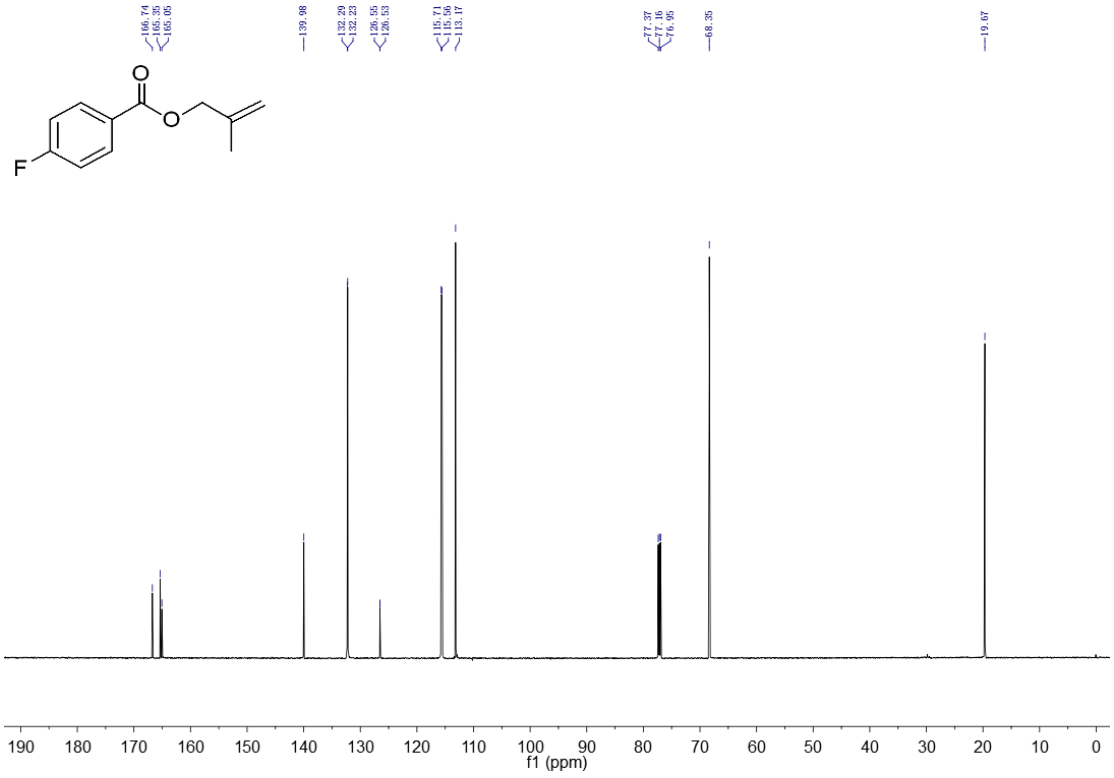
^{13}C NMR of **3h**



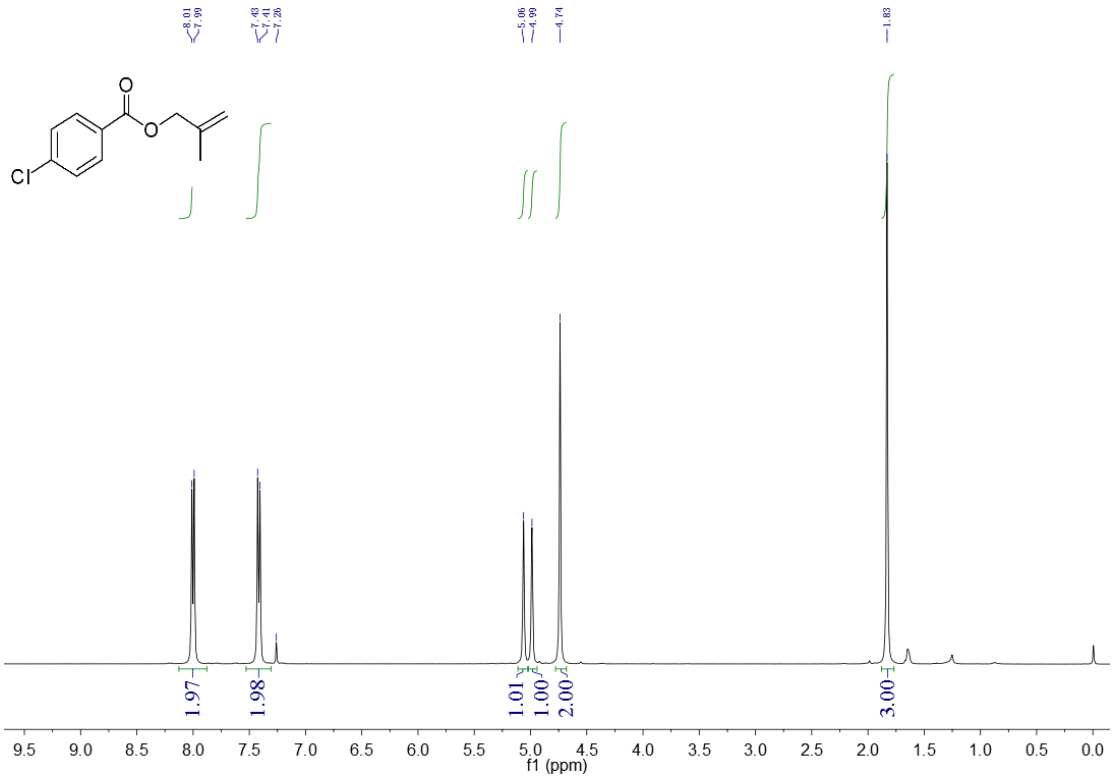
^{1}H NMR of **3i**



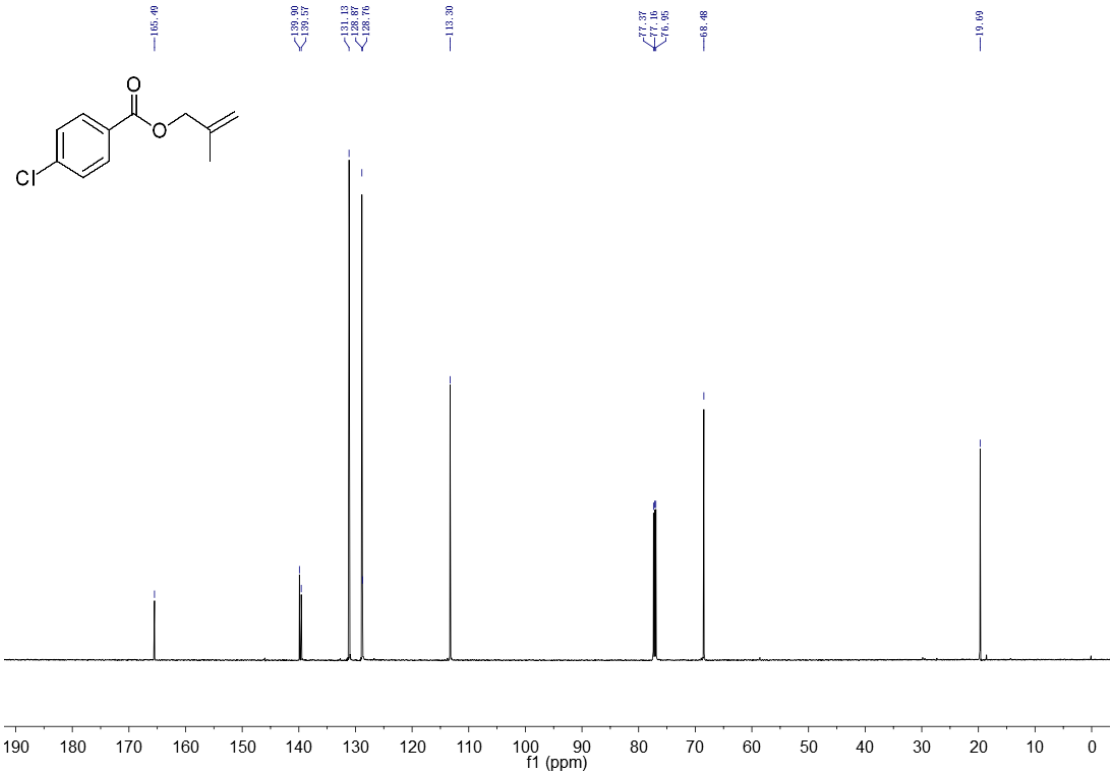
^{13}C NMR of **3i**



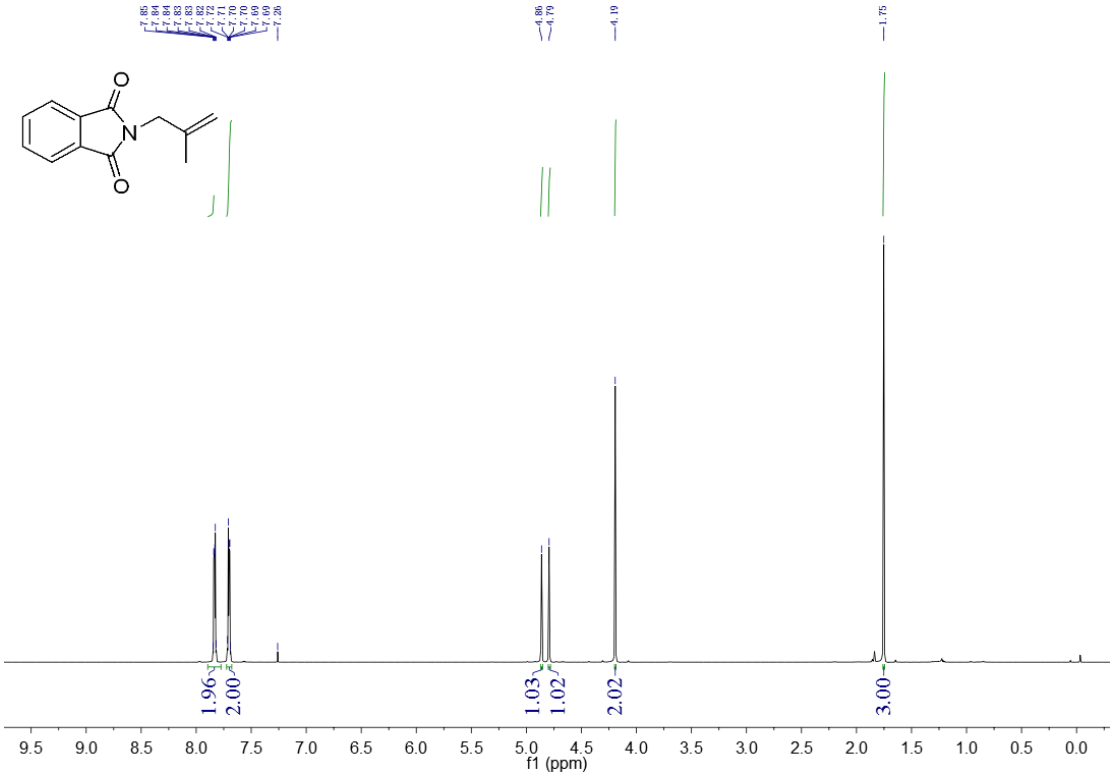
^{1}H NMR of **3j**



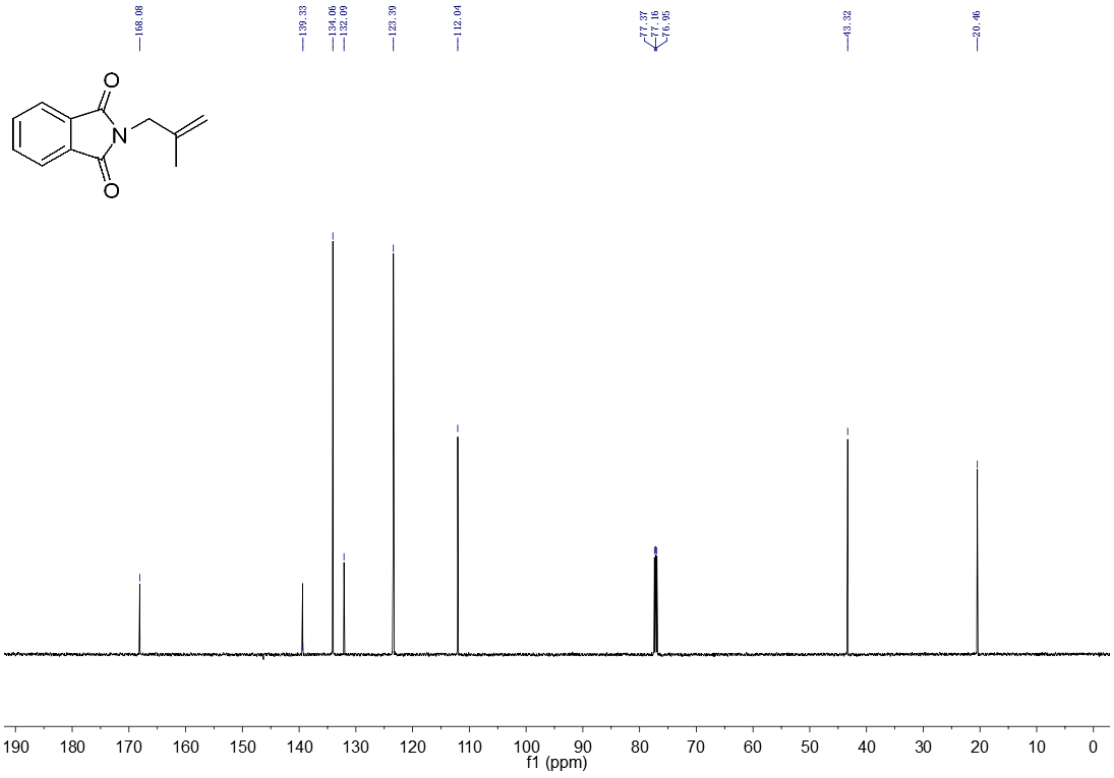
^{13}C NMR of **3j**



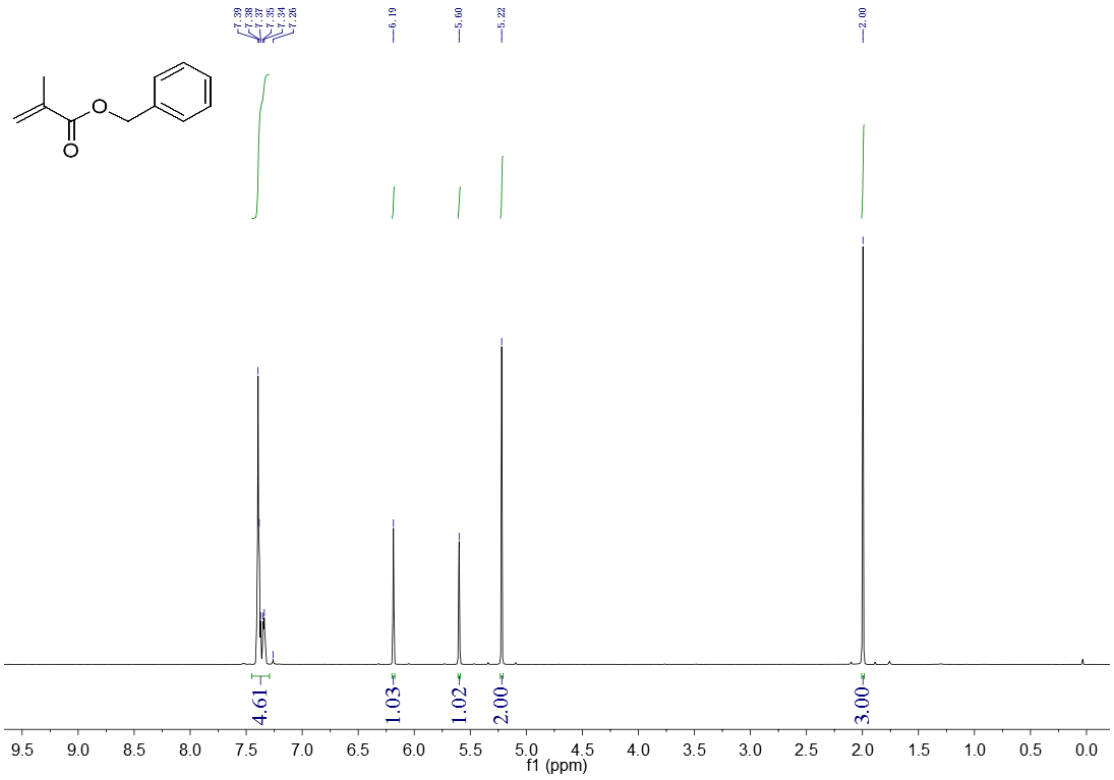
^{1}H NMR of **3k**



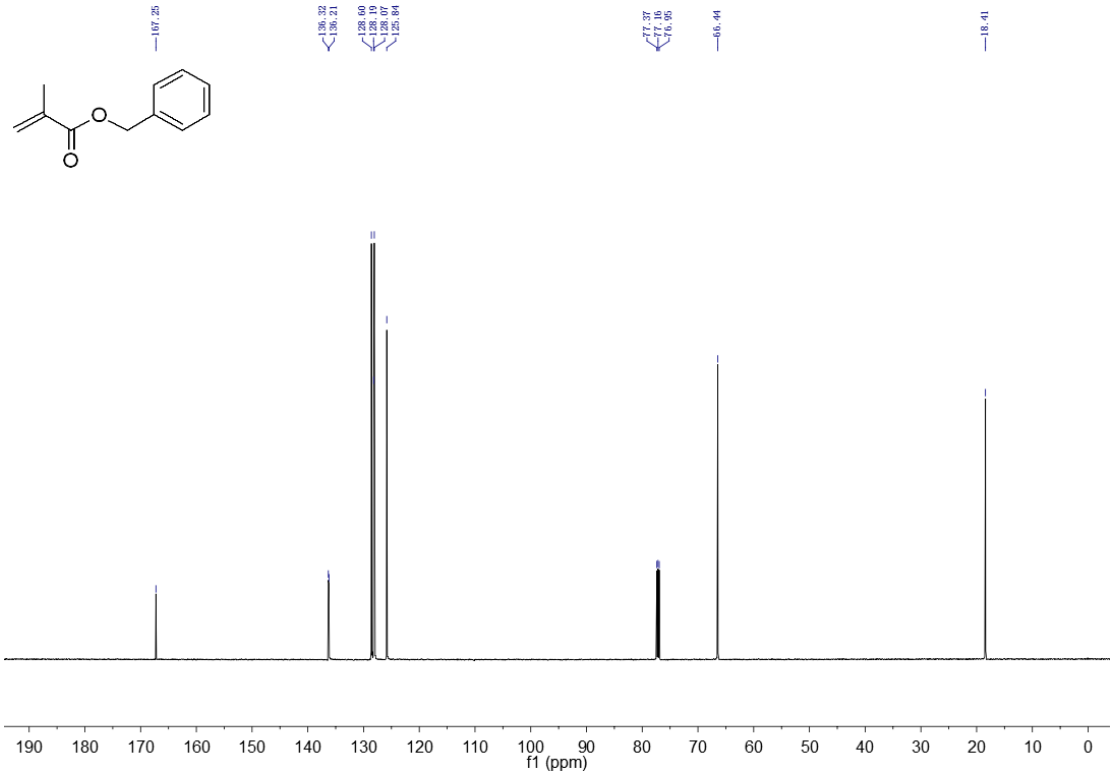
^{13}C NMR of **3k**



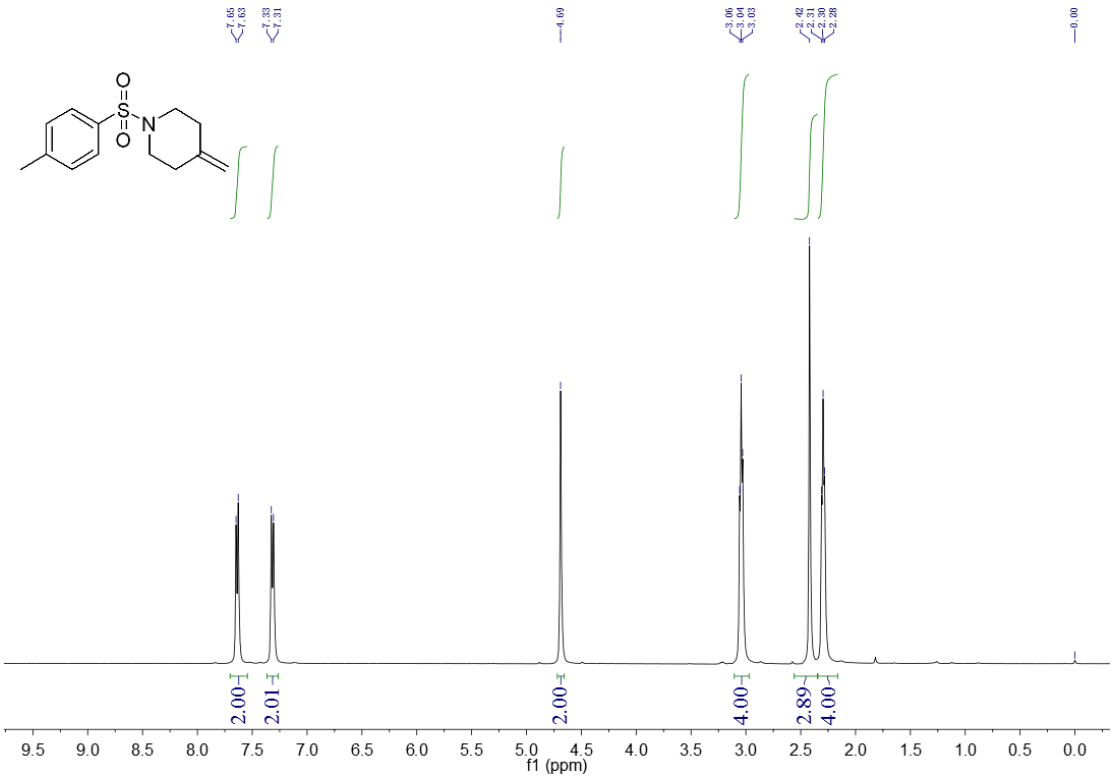
^{1}H NMR of **3l**



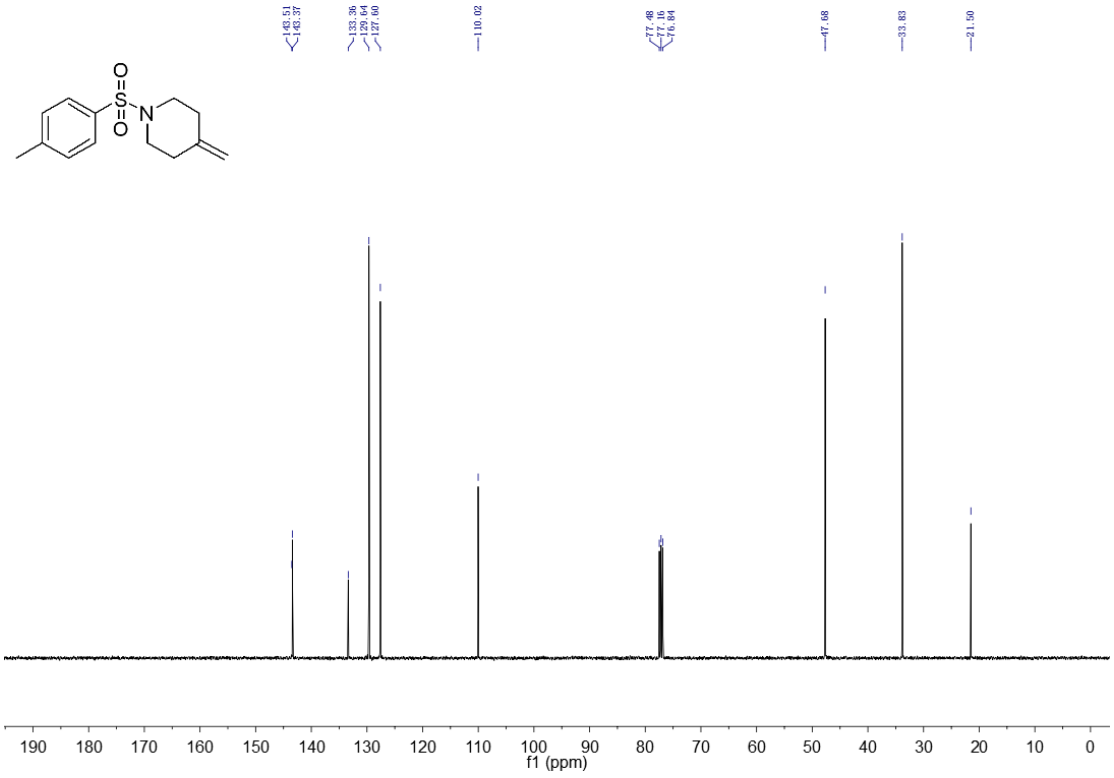
^{13}C NMR of **3l**



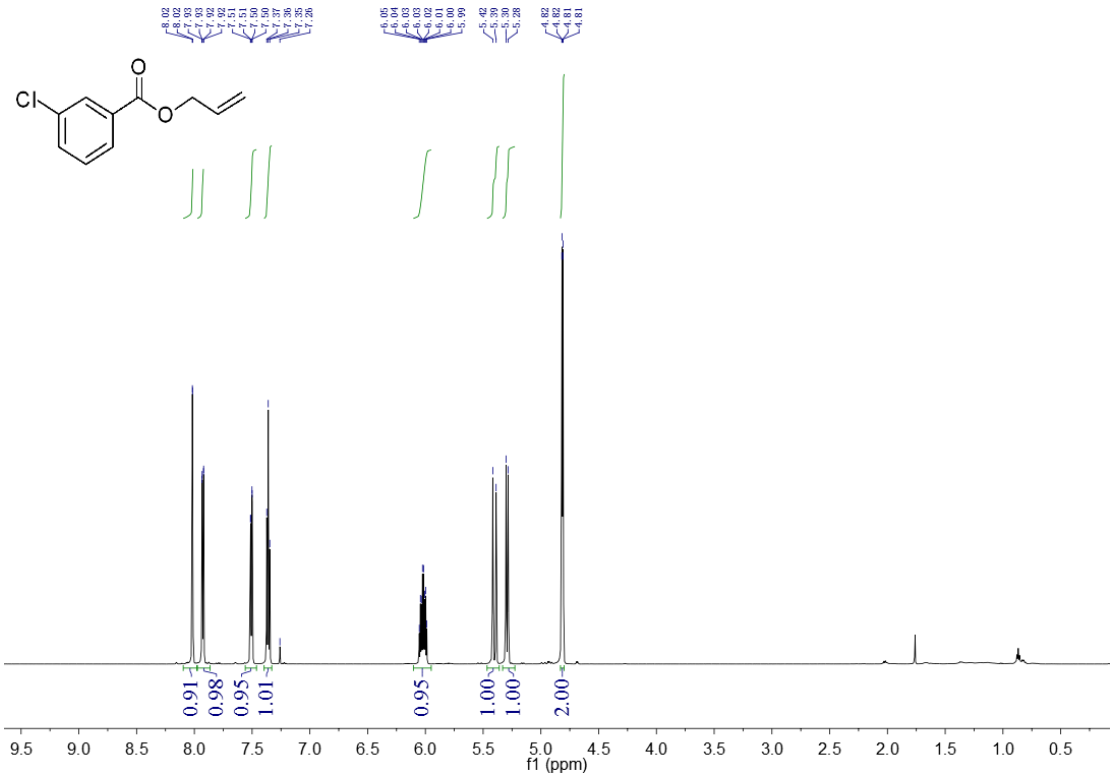
^{1}H NMR of **3m**



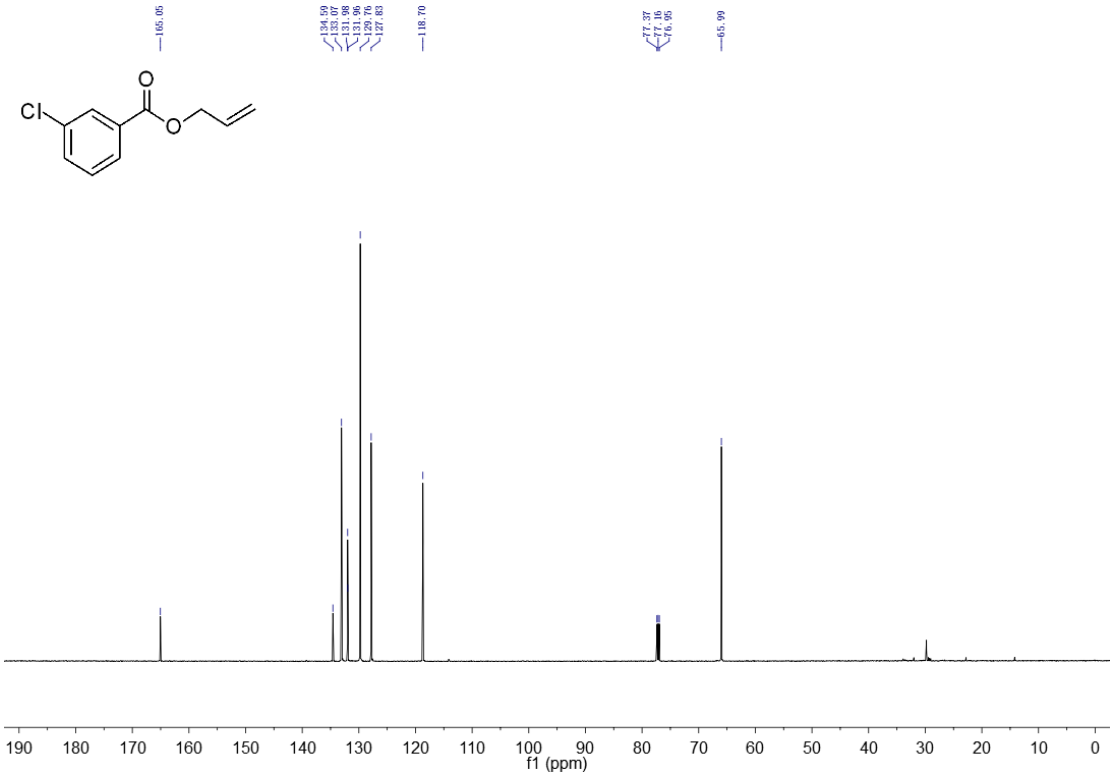
^{13}C NMR of **3m**



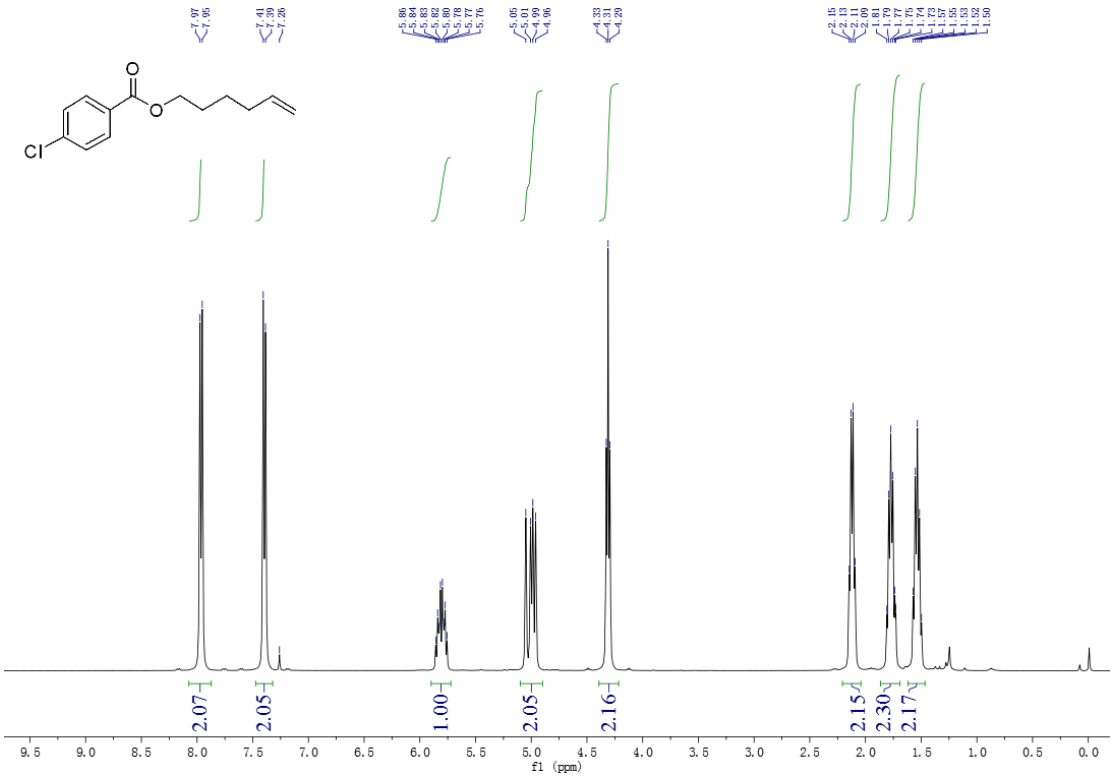
^{1}H NMR of **3n**



^{13}C NMR of **3n**



^{1}H NMR of **3o**



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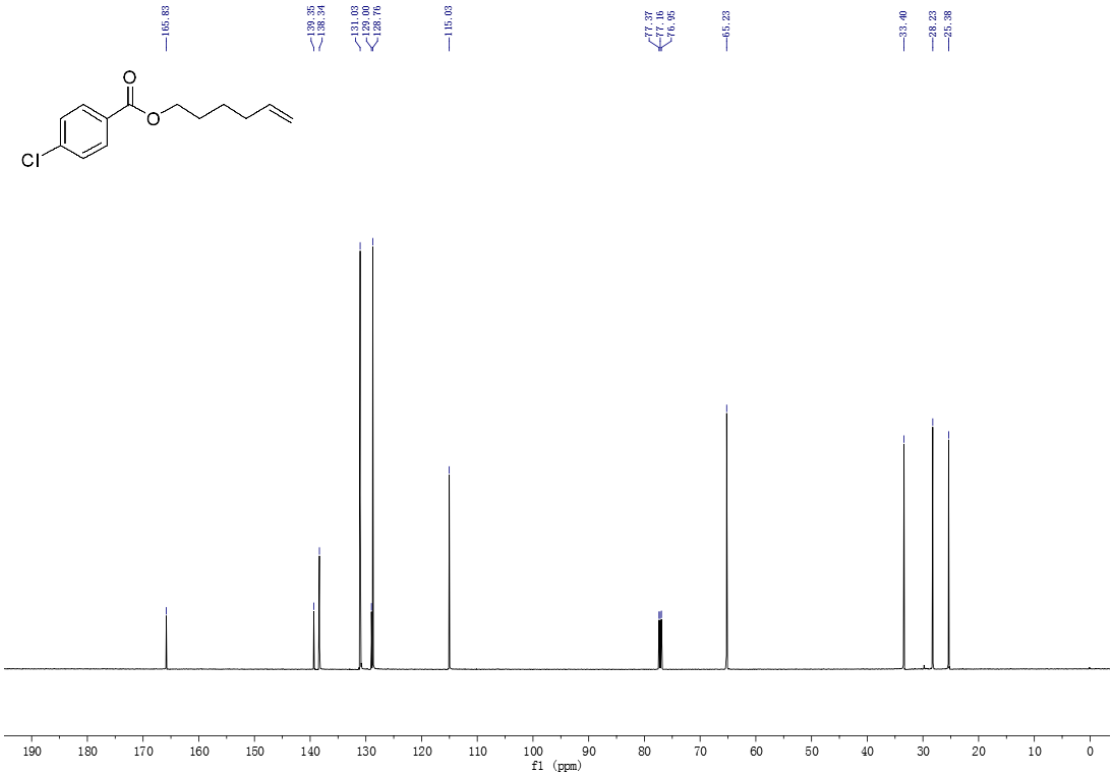
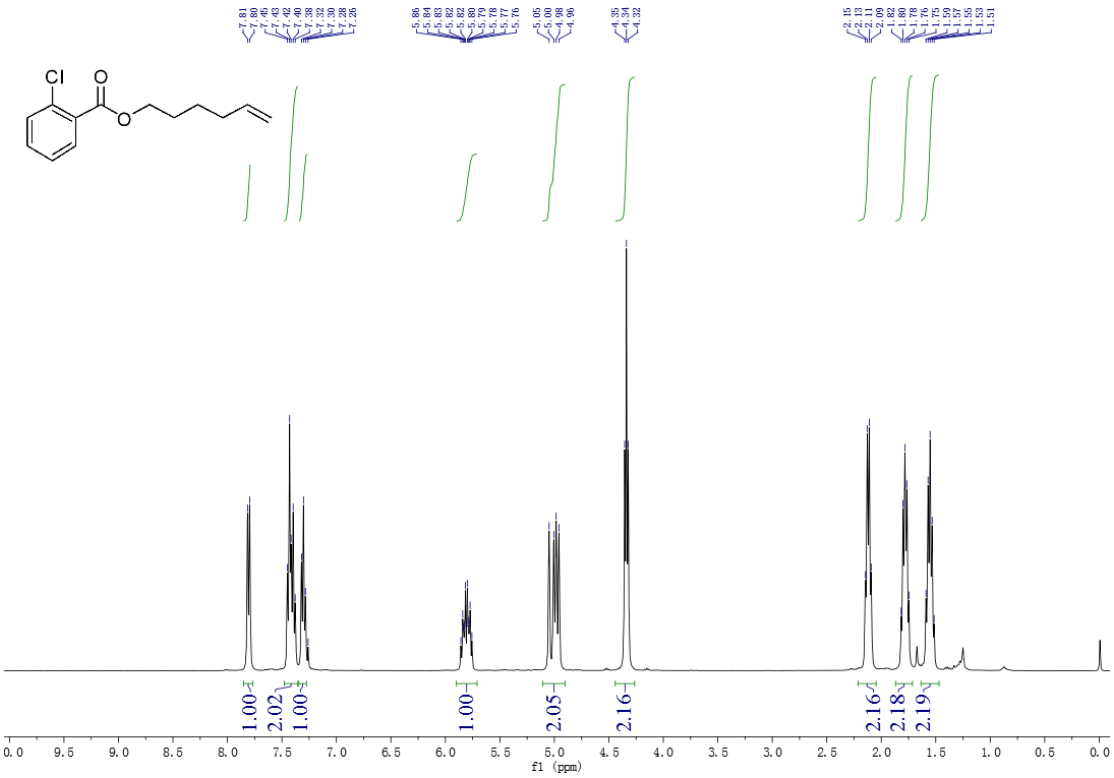
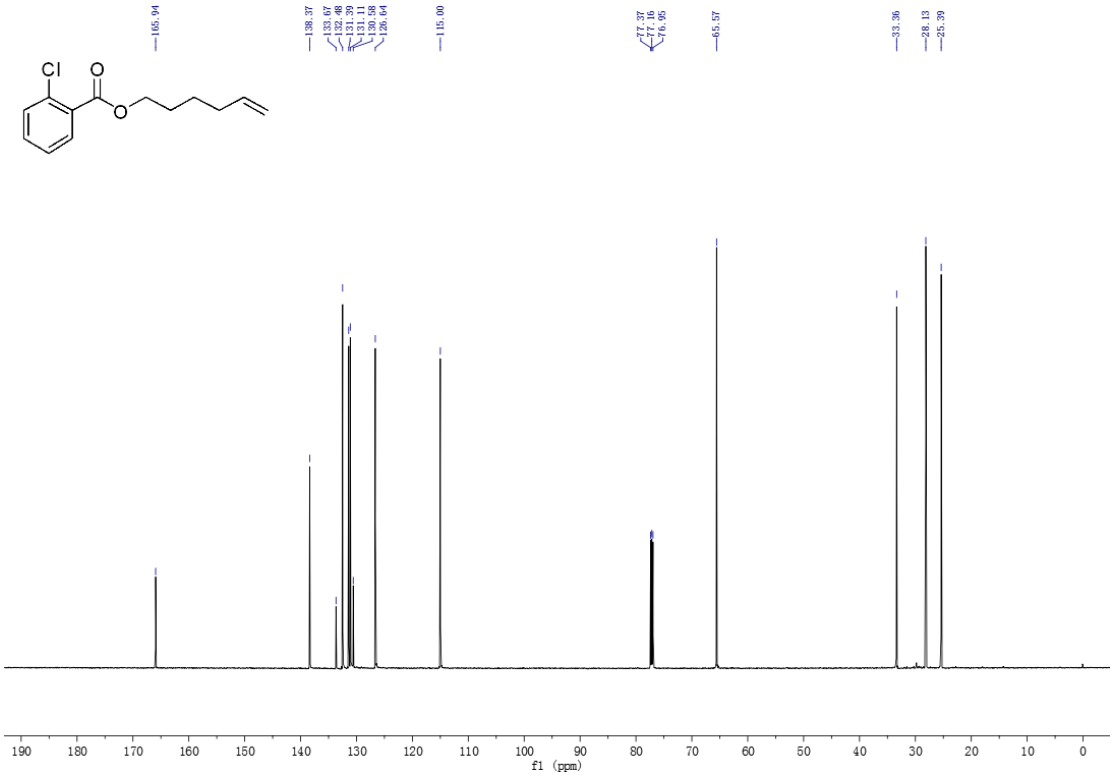


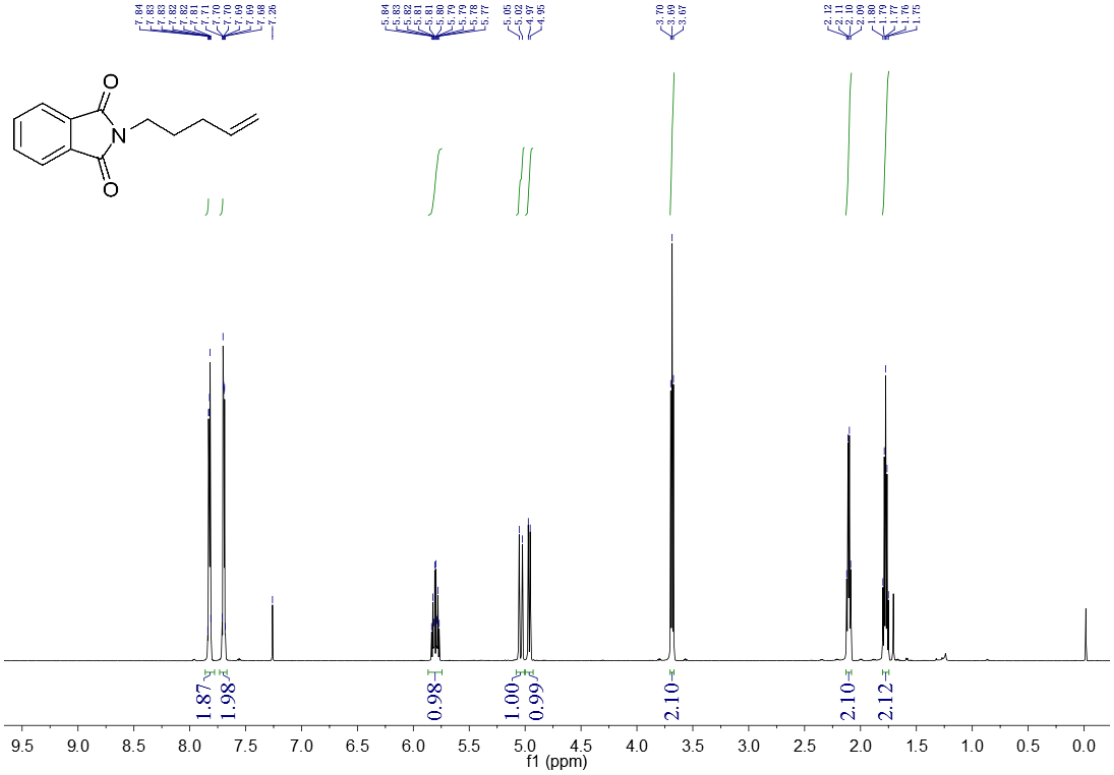
^{1}H NMR of **3p**



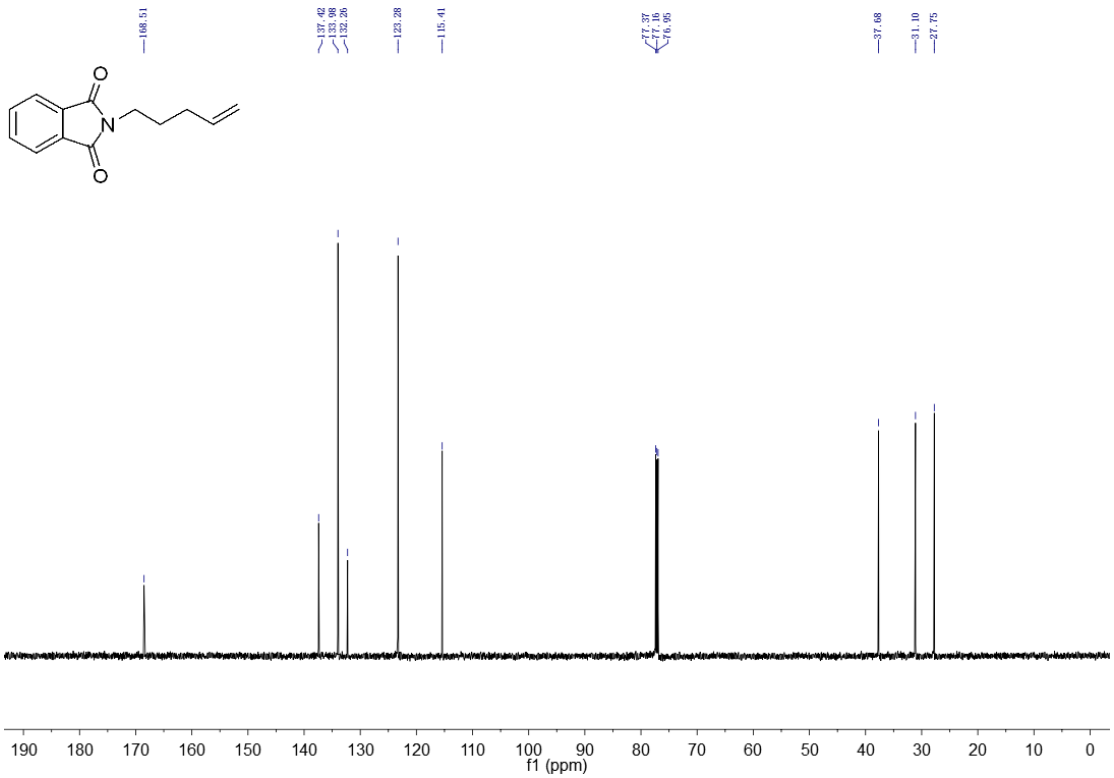
^{13}C NMR of **3p**



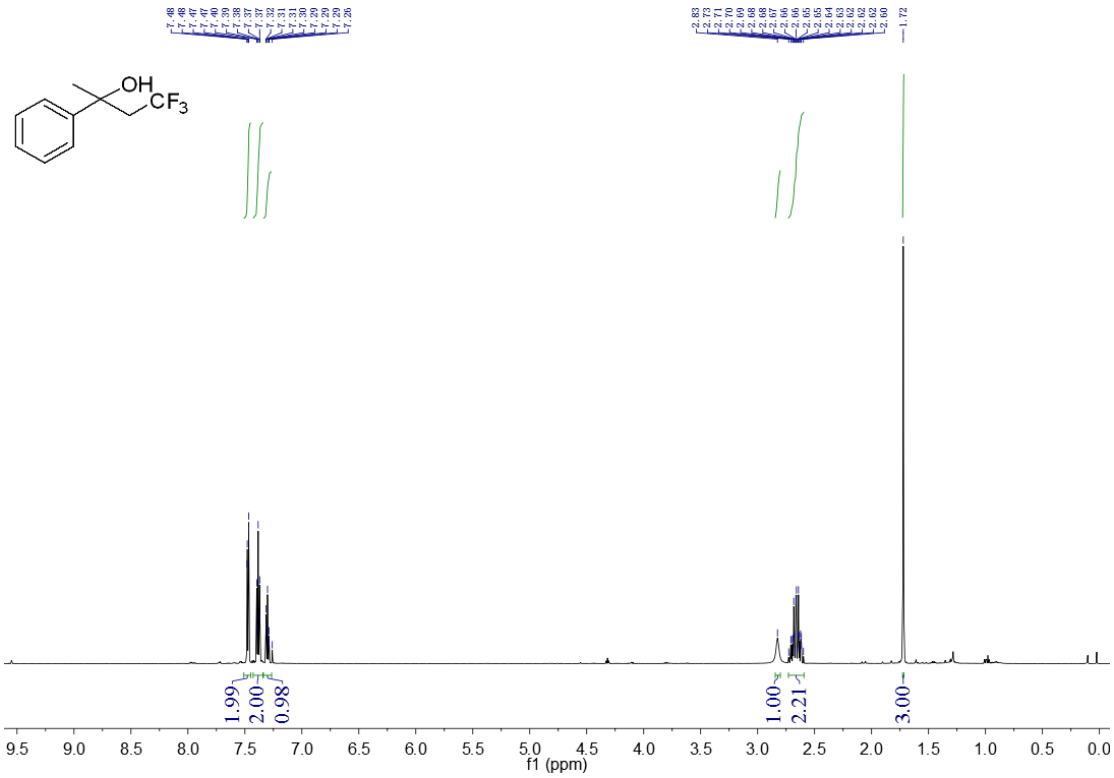
^{1}H NMR of **3q**



^{13}C NMR of **3q**



^{1}H NMR of **2a**



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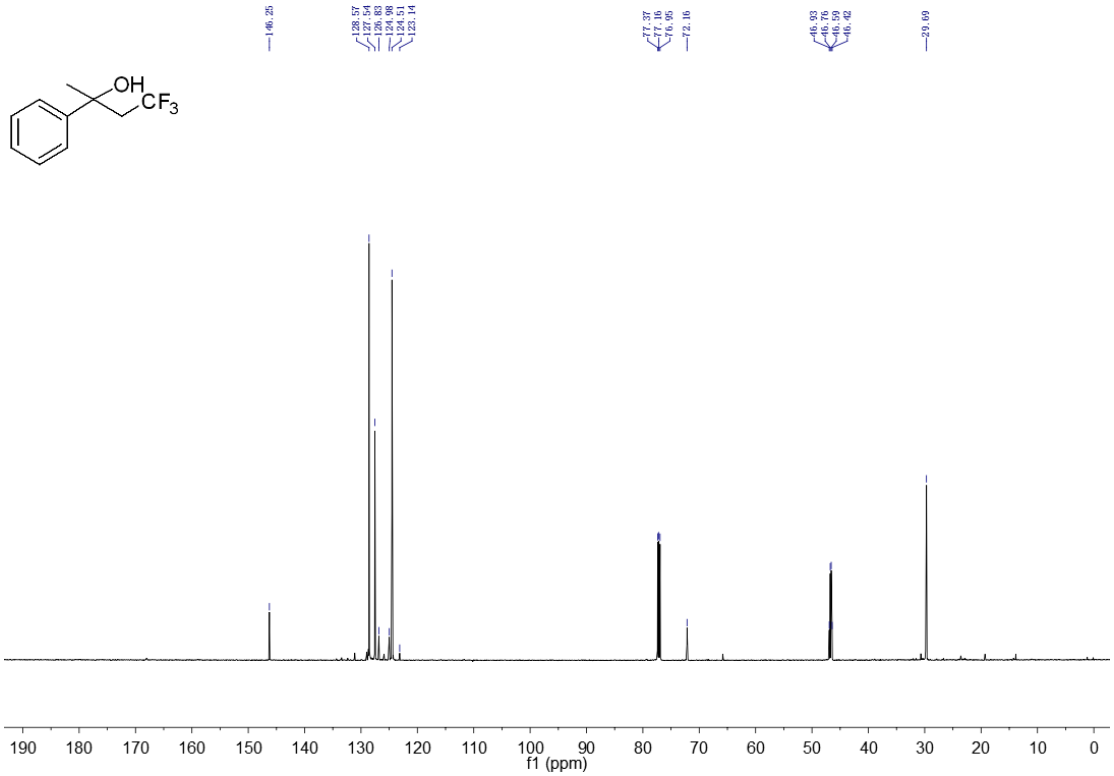
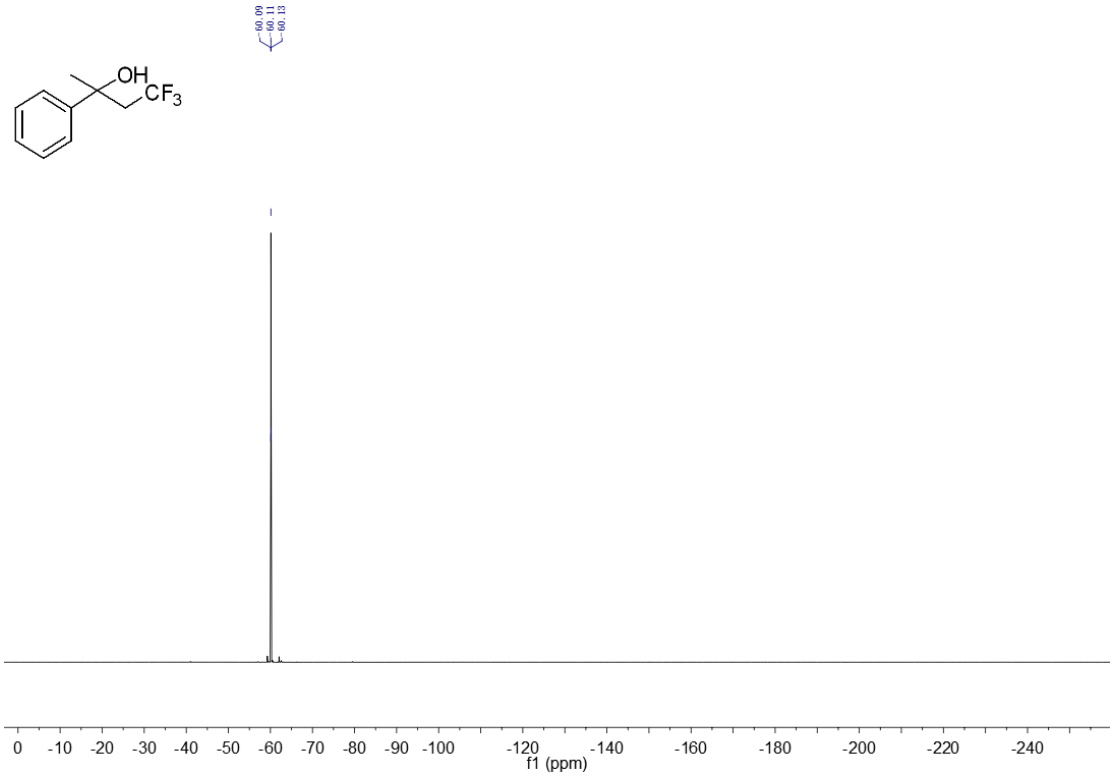
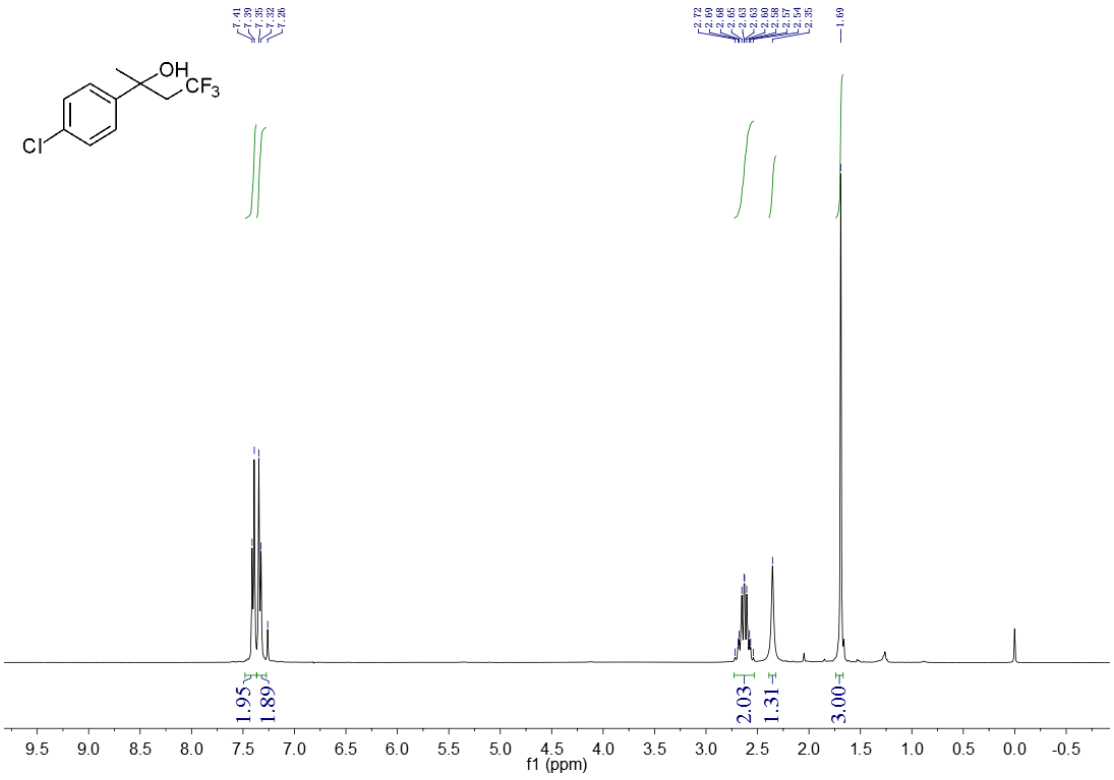


^{19}F NMR of **2a**



^{1}H NMR of **2b**



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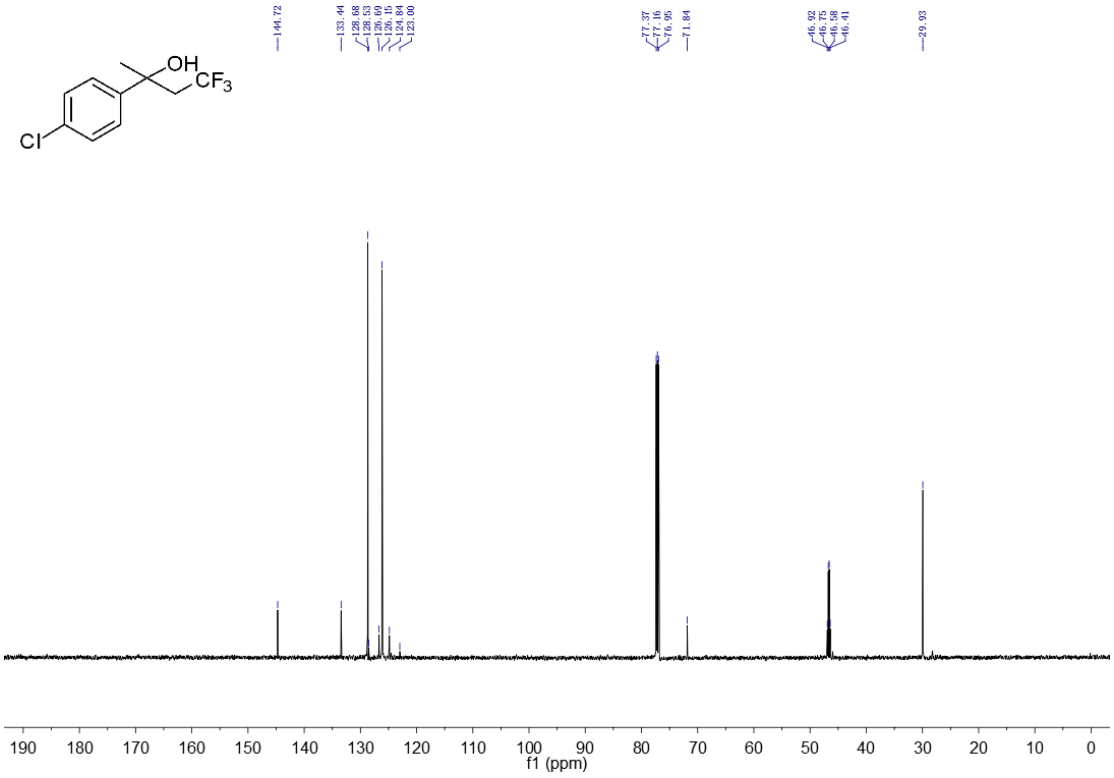

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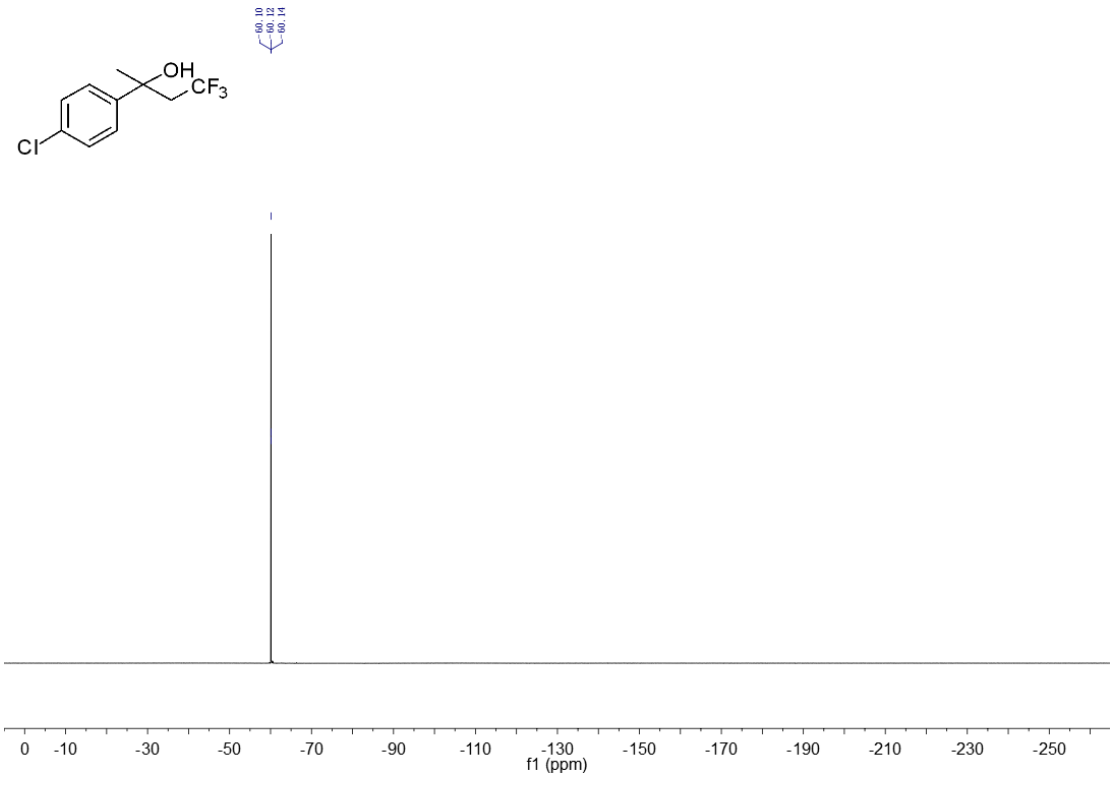
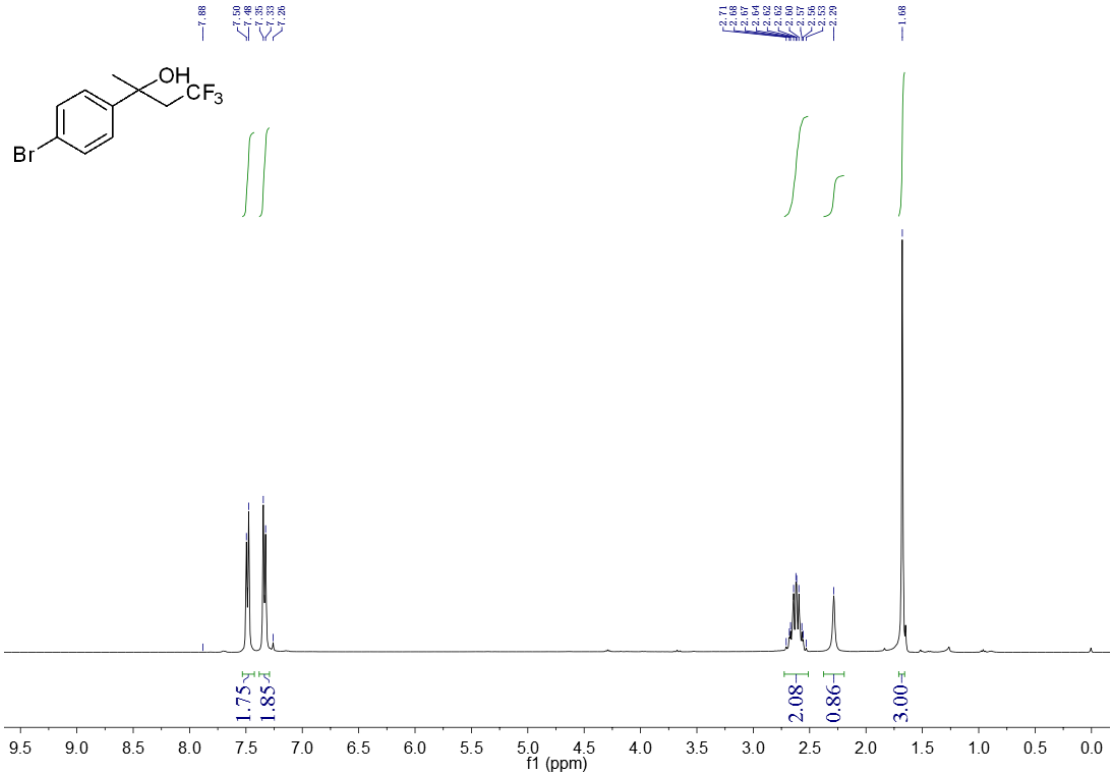
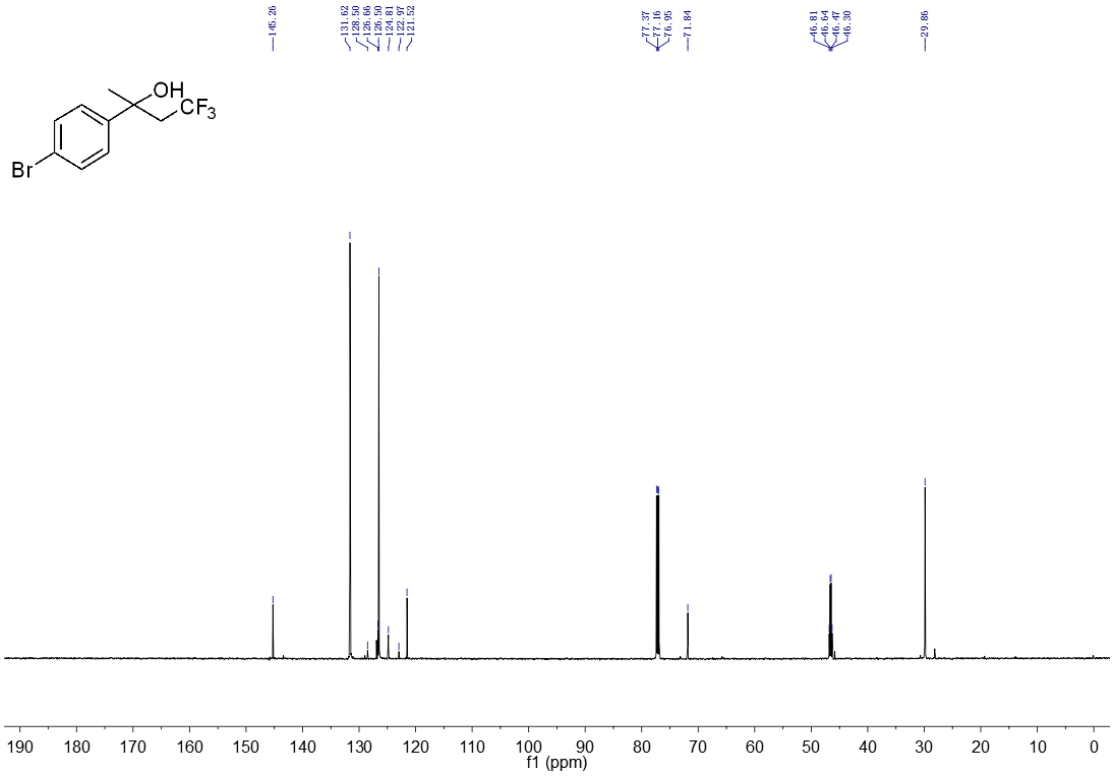


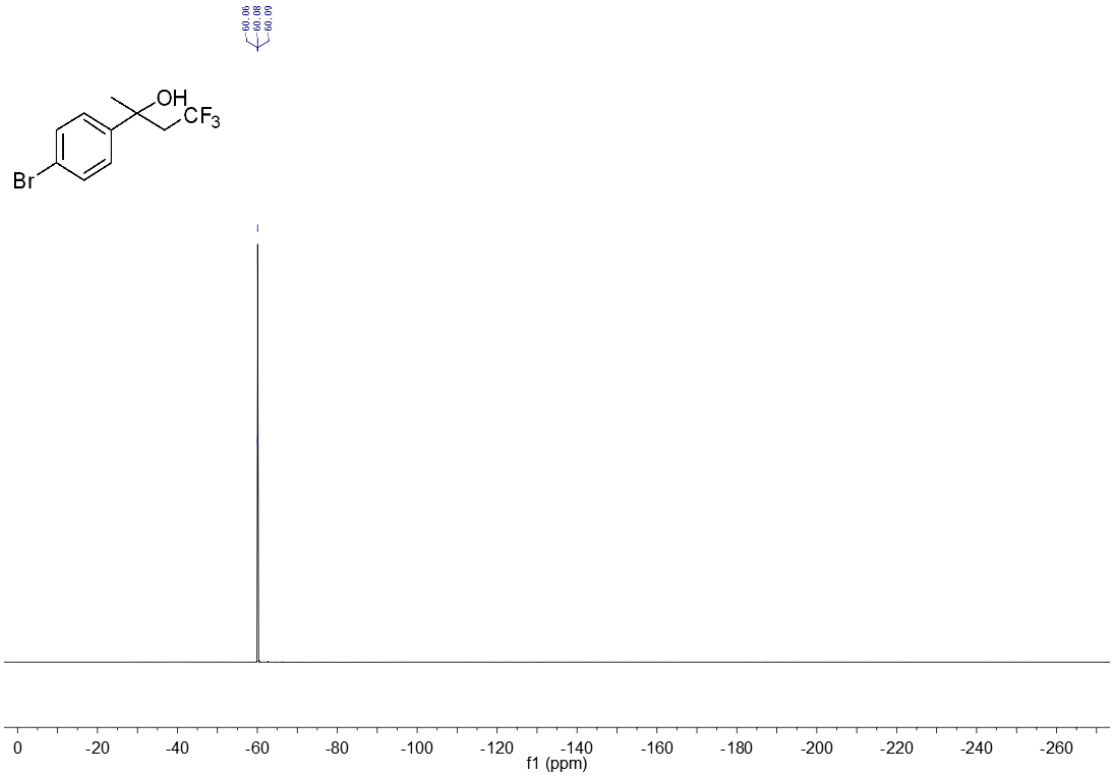
^{1}H NMR of **2c**



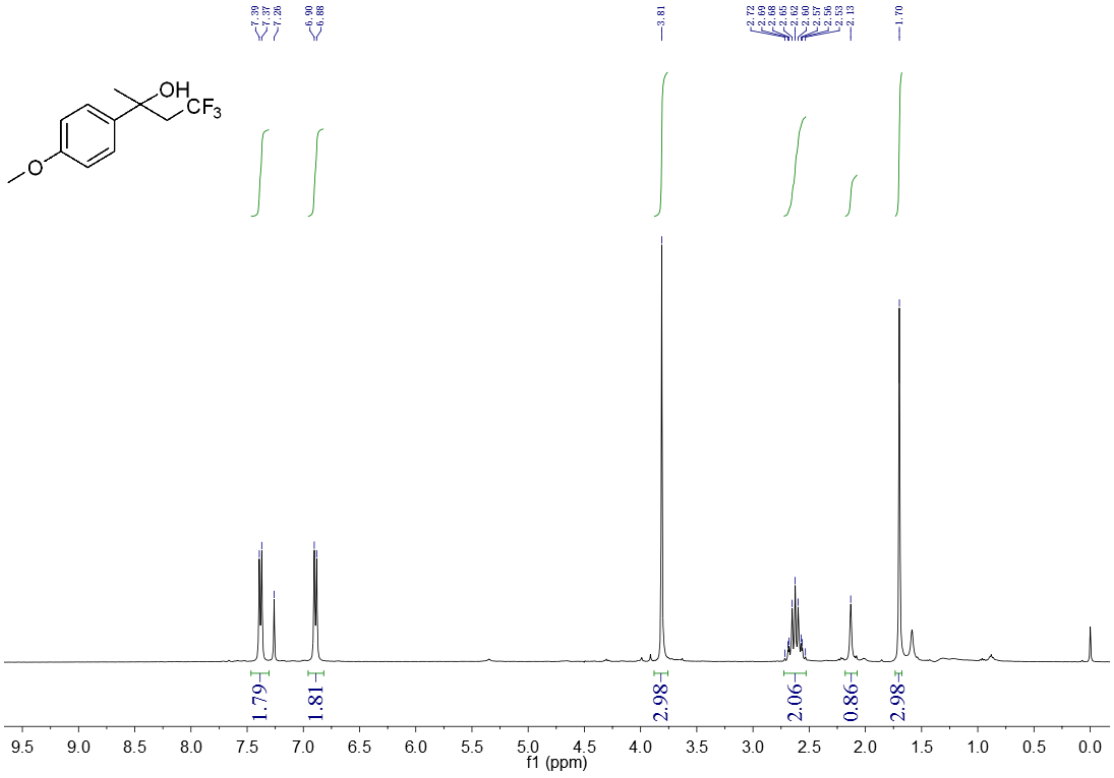
^{13}C NMR of **2c**



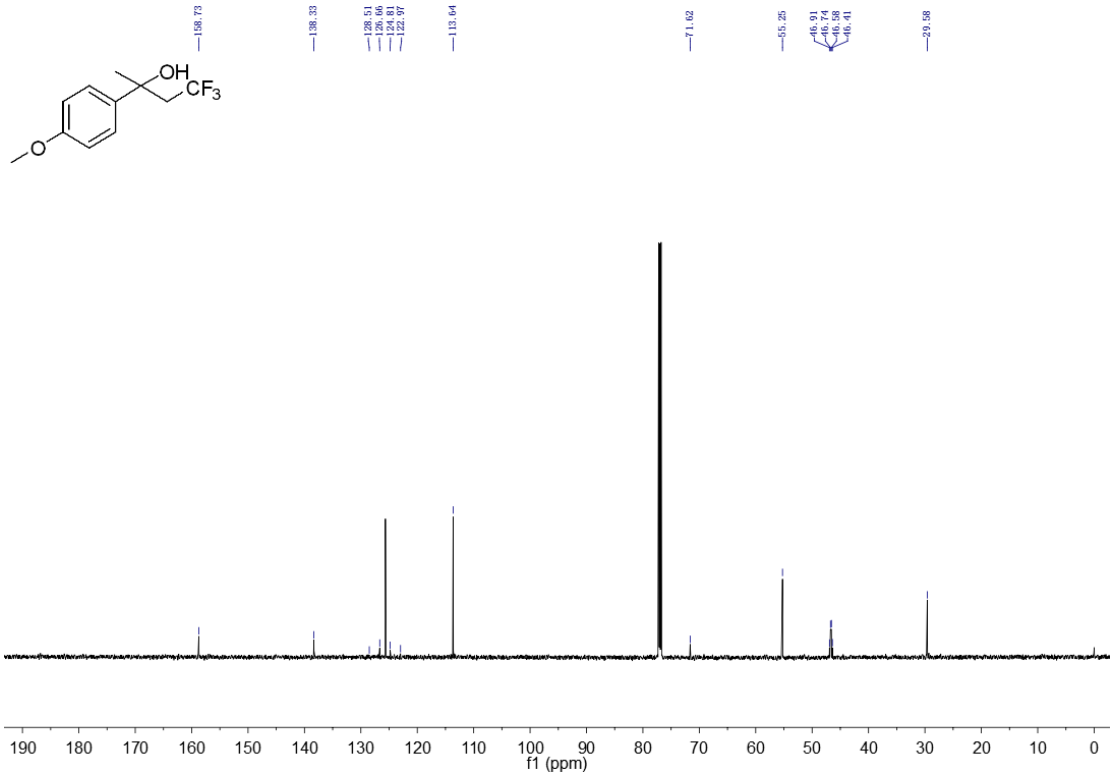
^{19}F NMR of **2c**



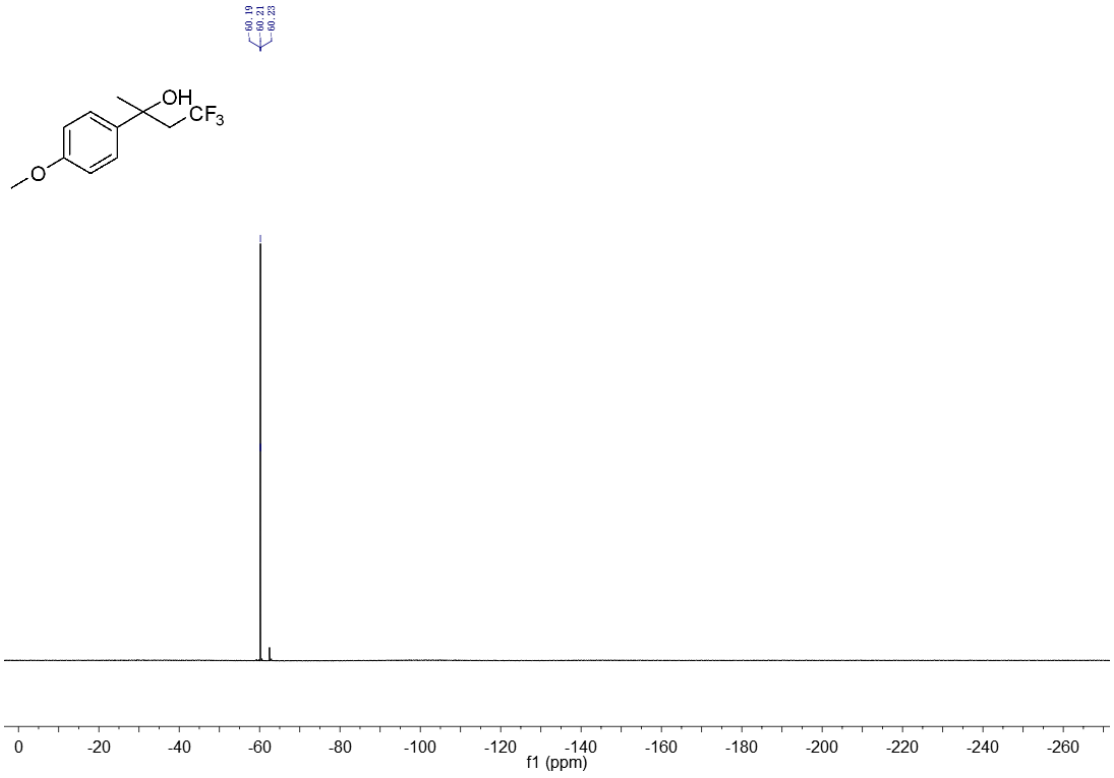
^{1}H NMR of **2d**



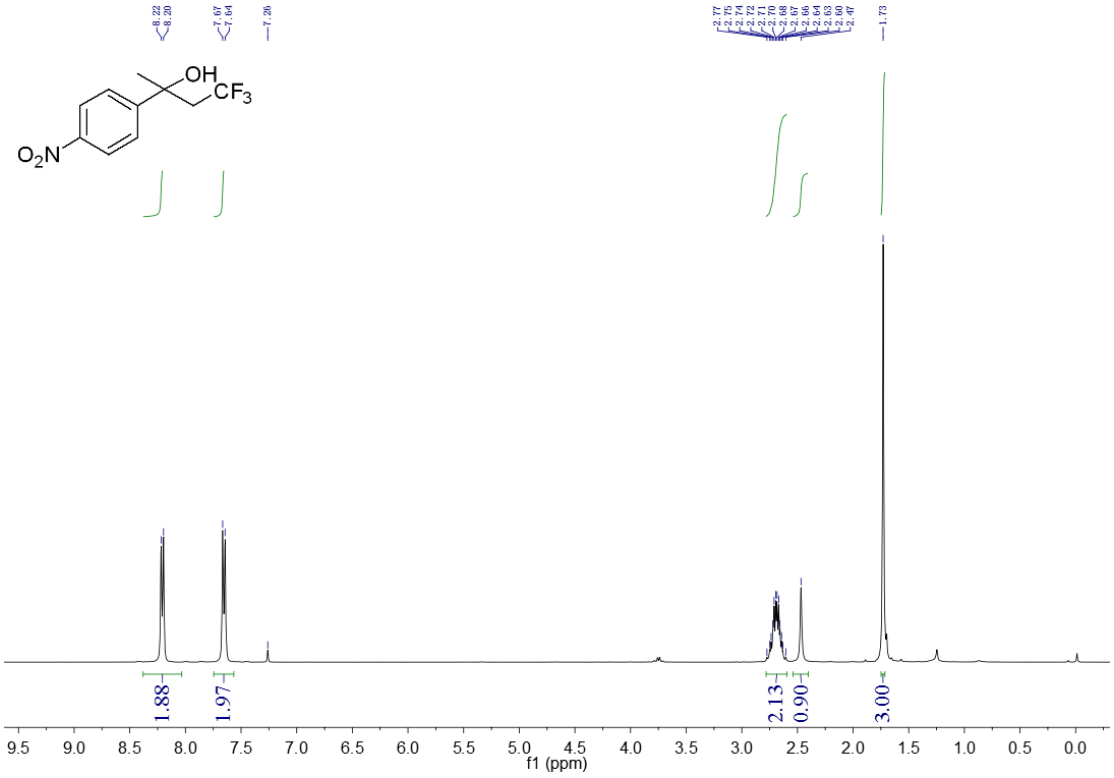
^{13}C NMR of **2d**



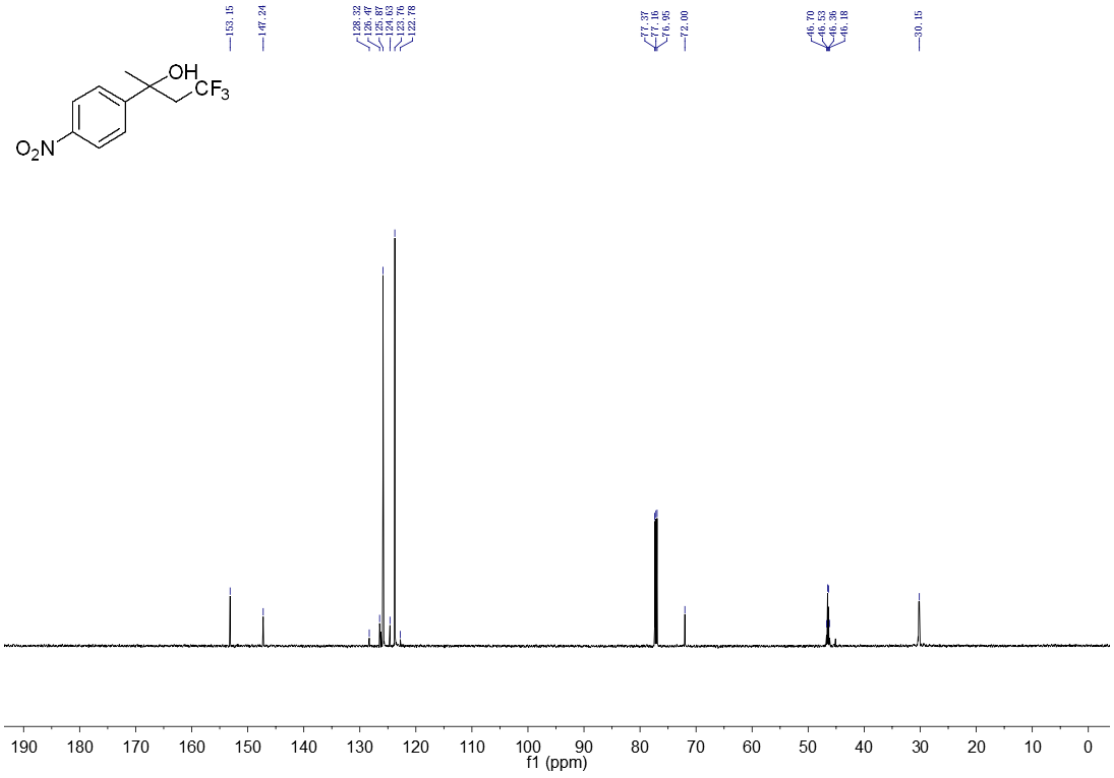
^{19}F NMR of **2d**



^{1}H NMR of **2e**



^{13}C NMR of **2e**



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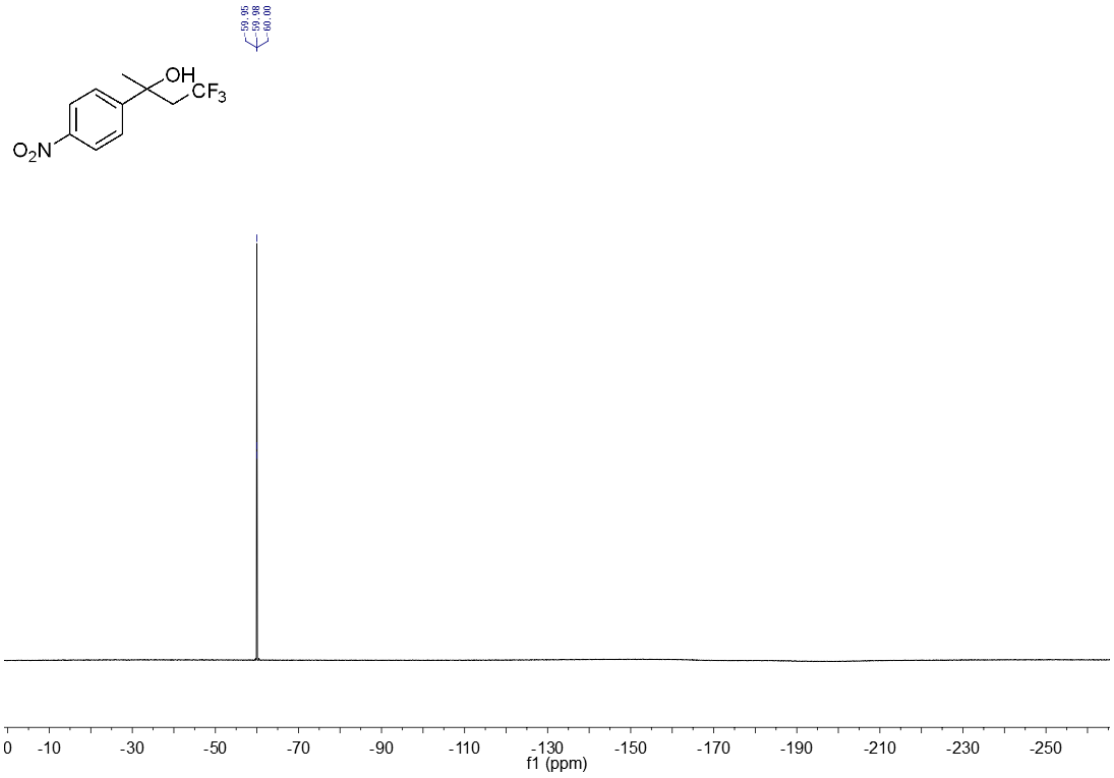
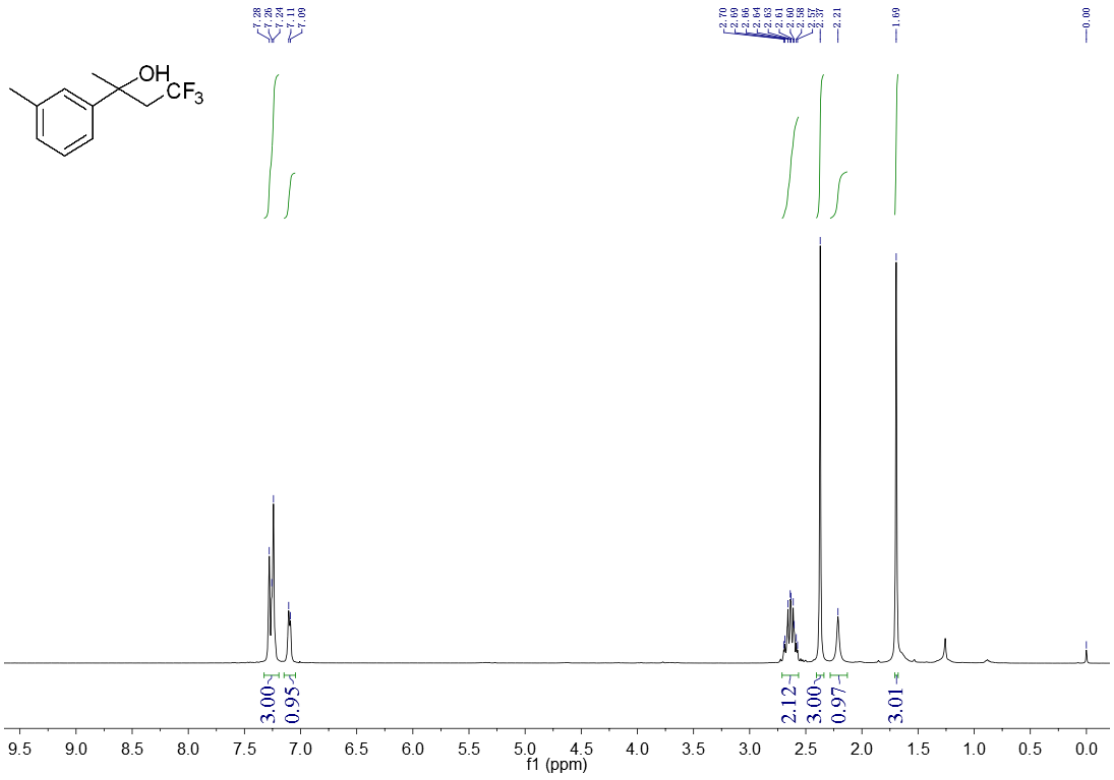
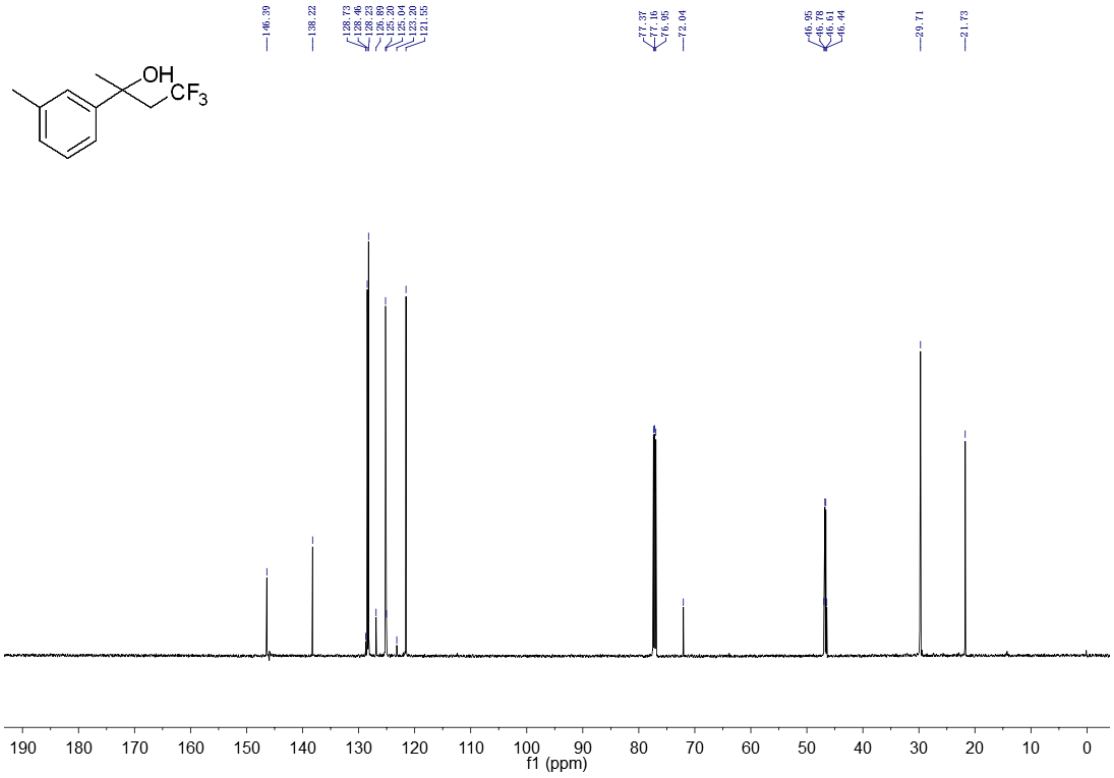


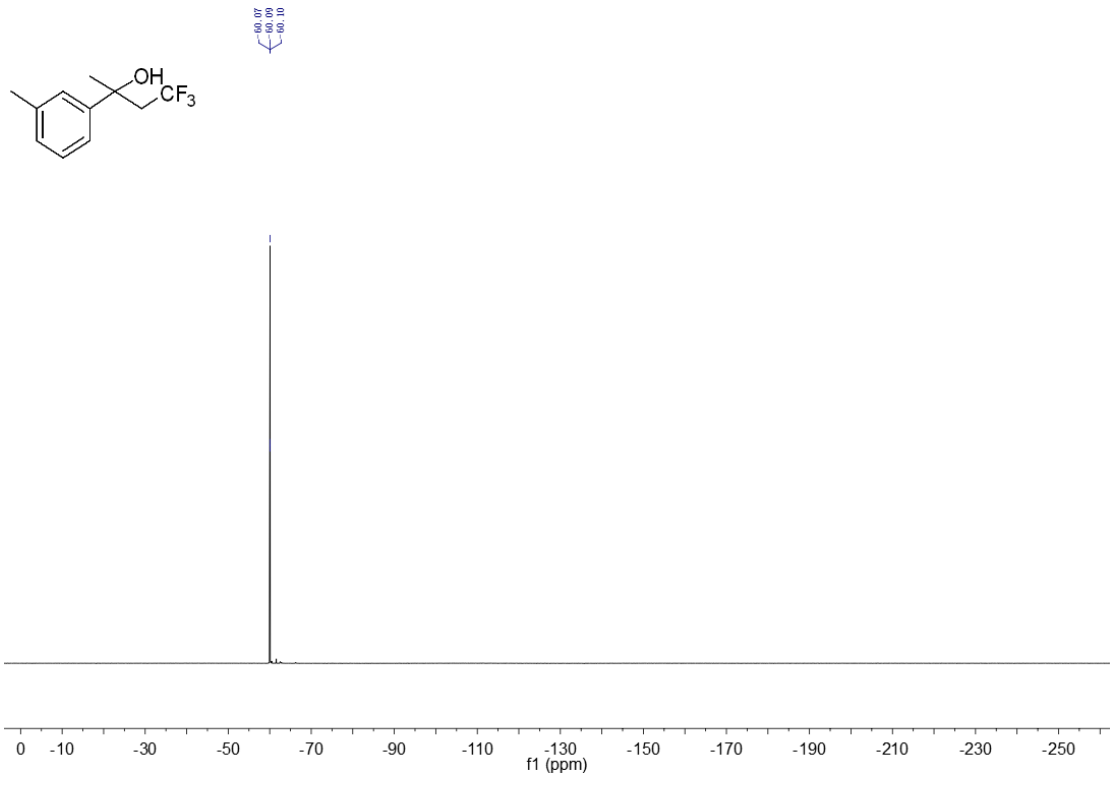
^{1}H NMR of **2f**



^{13}C NMR of **2f**



^{19}F NMR of **2f**



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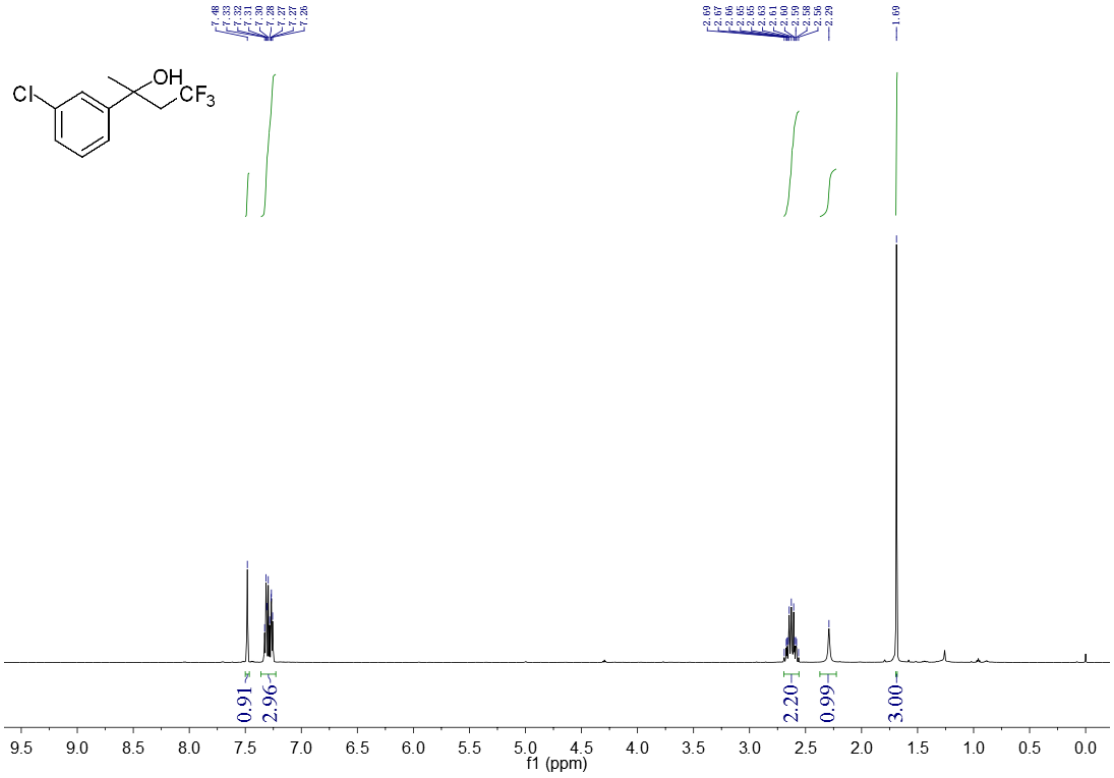
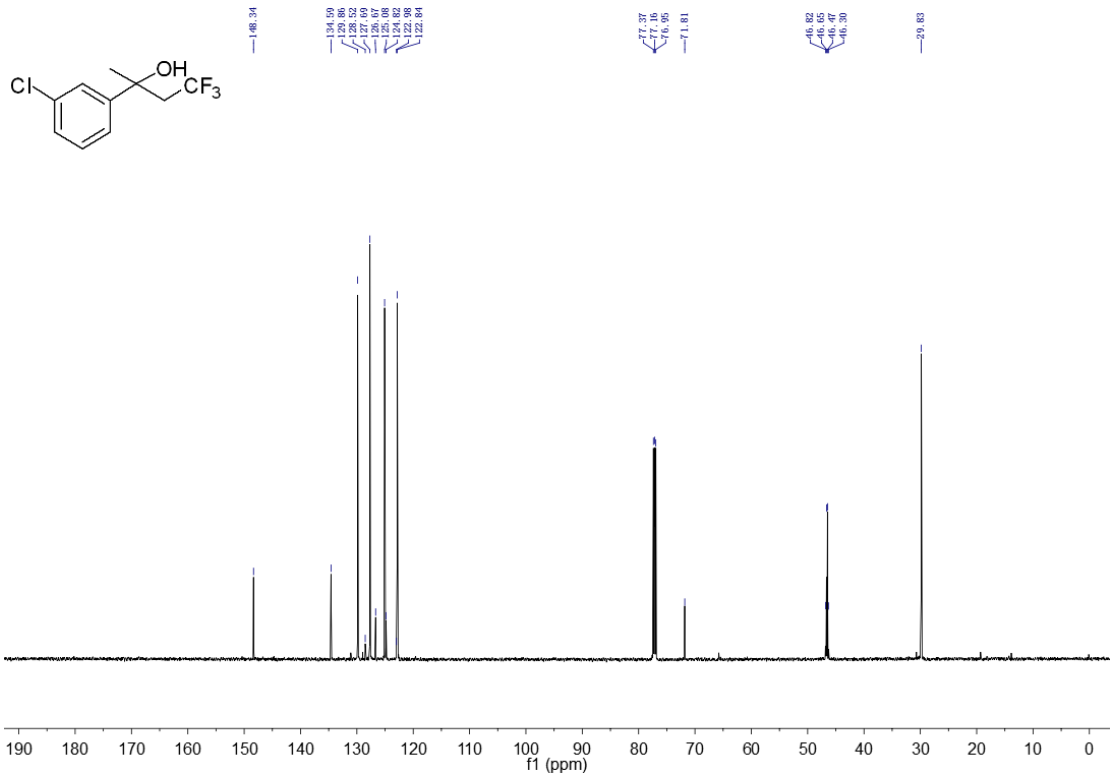
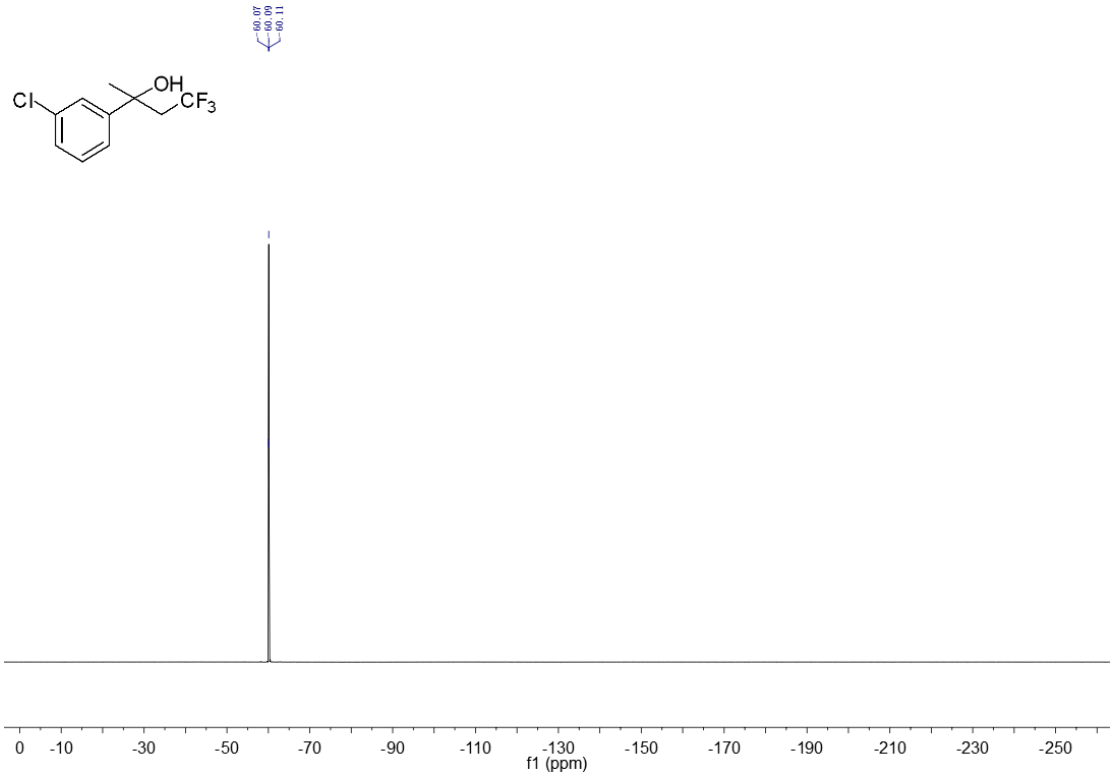


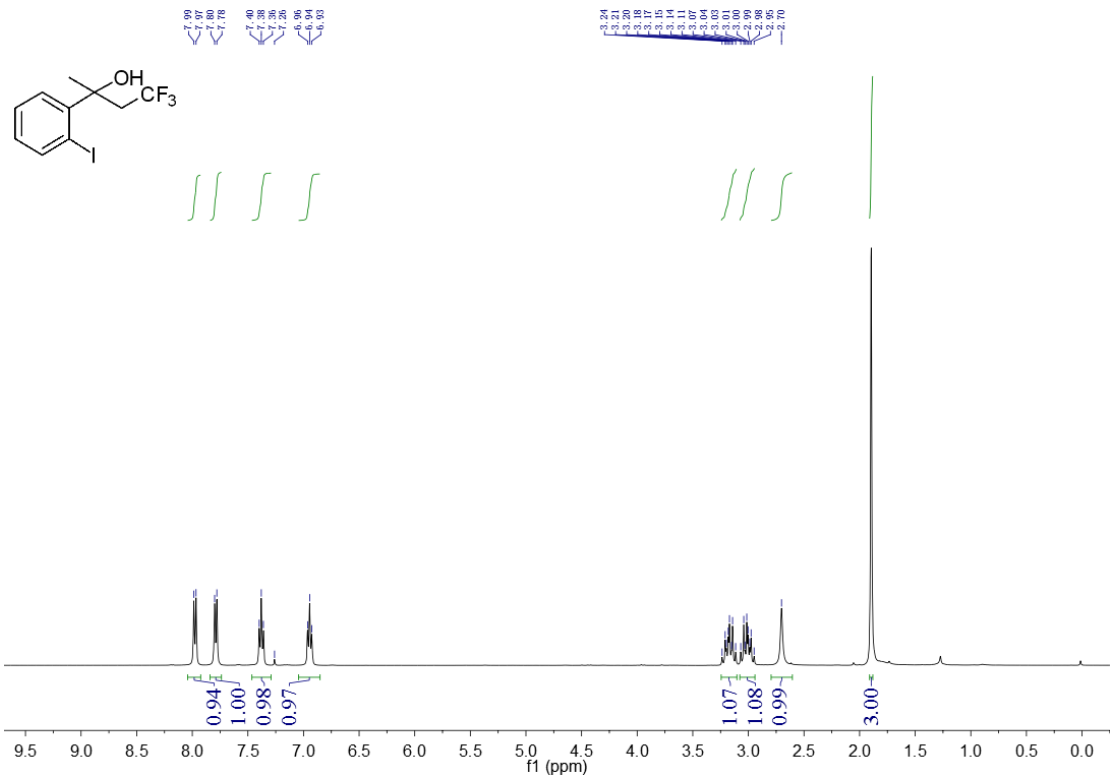
^{13}C NMR of **2g**



^{19}F NMR of **2g**



^{1}H NMR of **2h**



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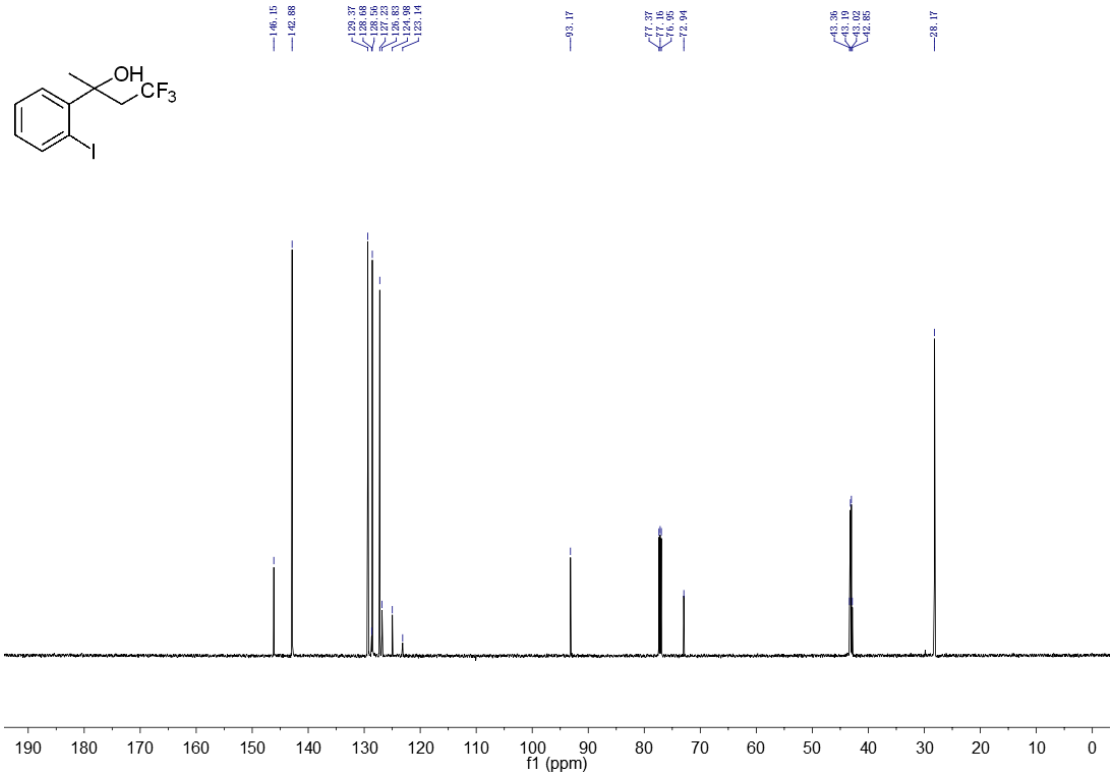
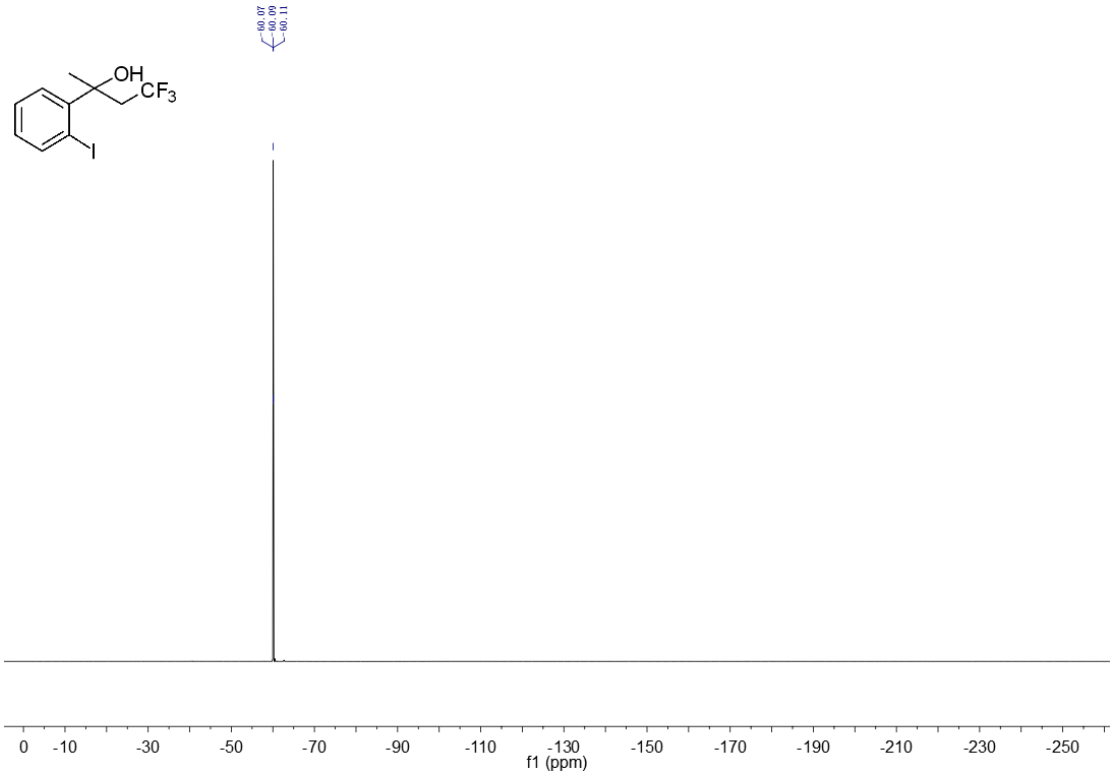
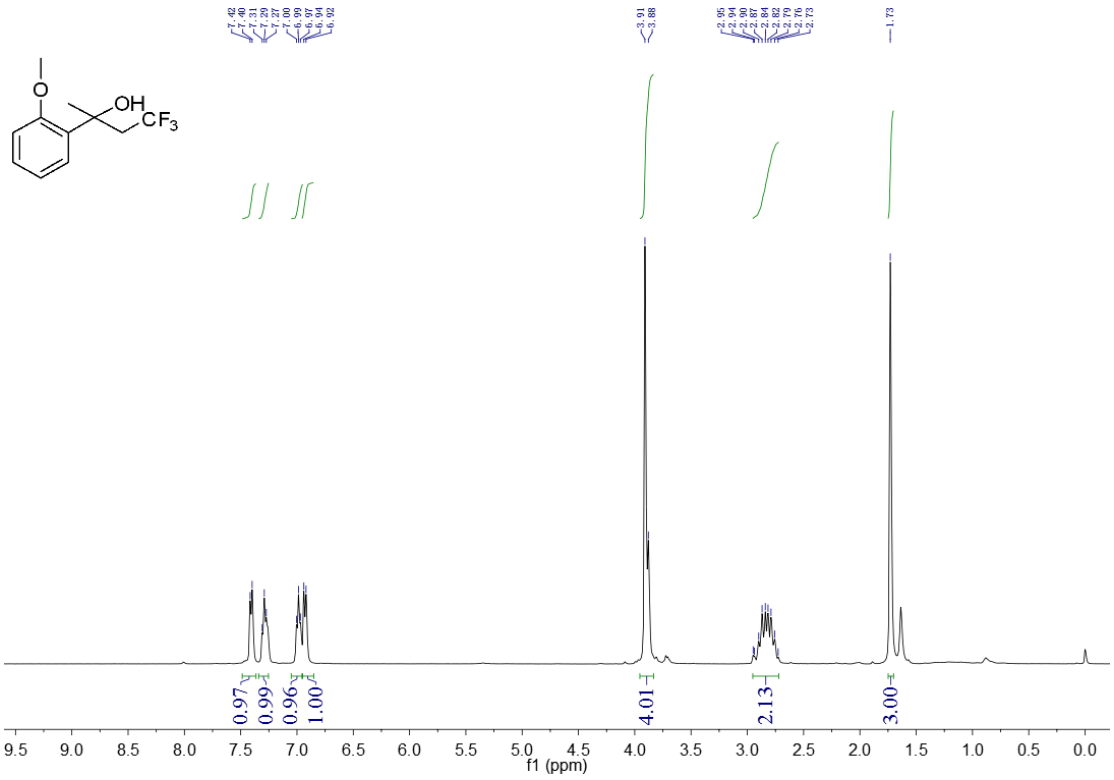


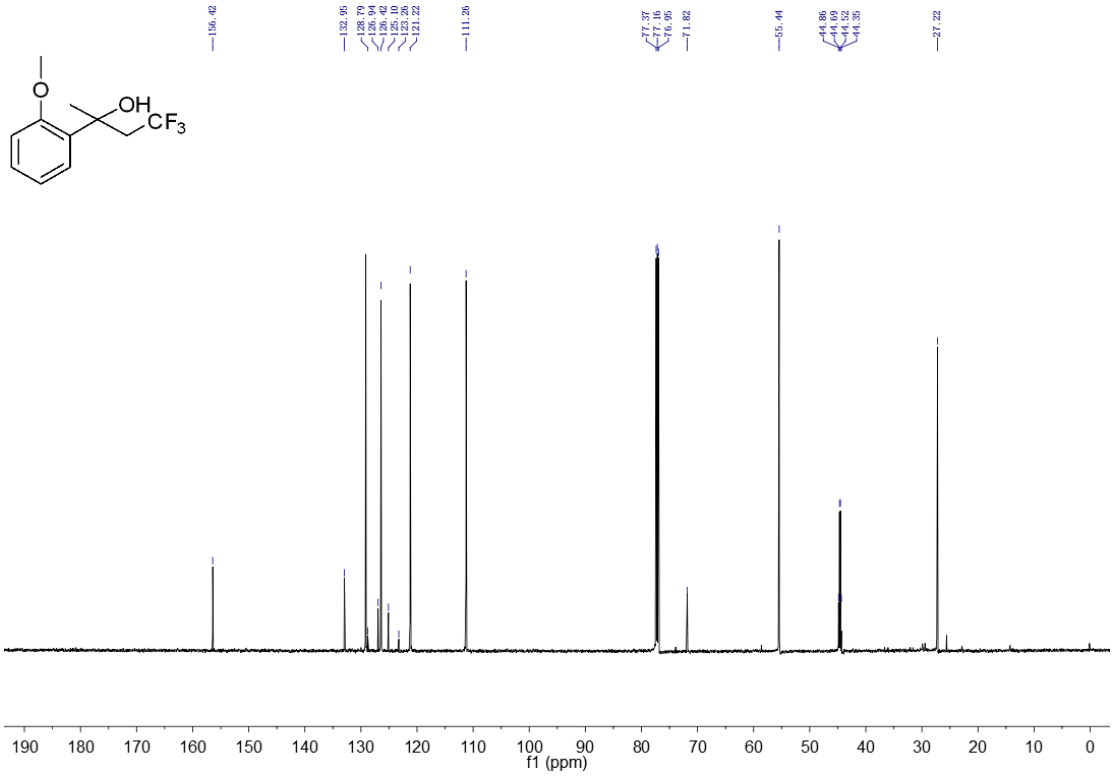
^{19}F NMR of **2h**



^{1}H NMR of **2i**



^{13}C NMR of **2i**



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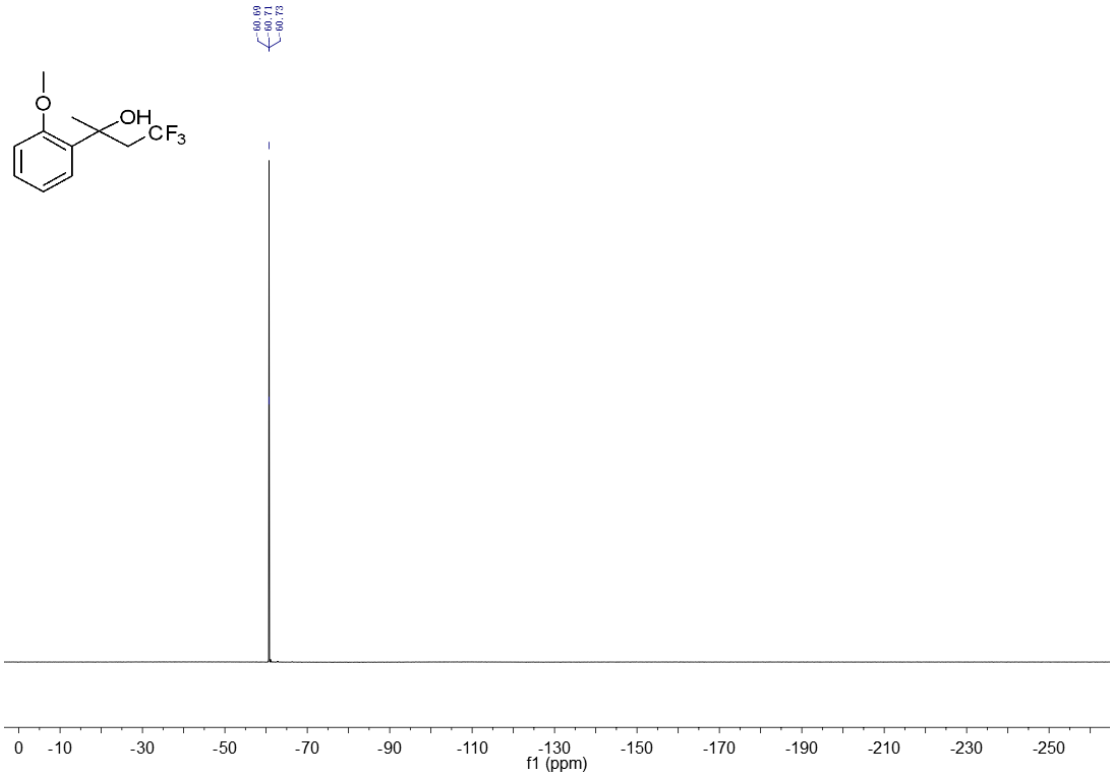
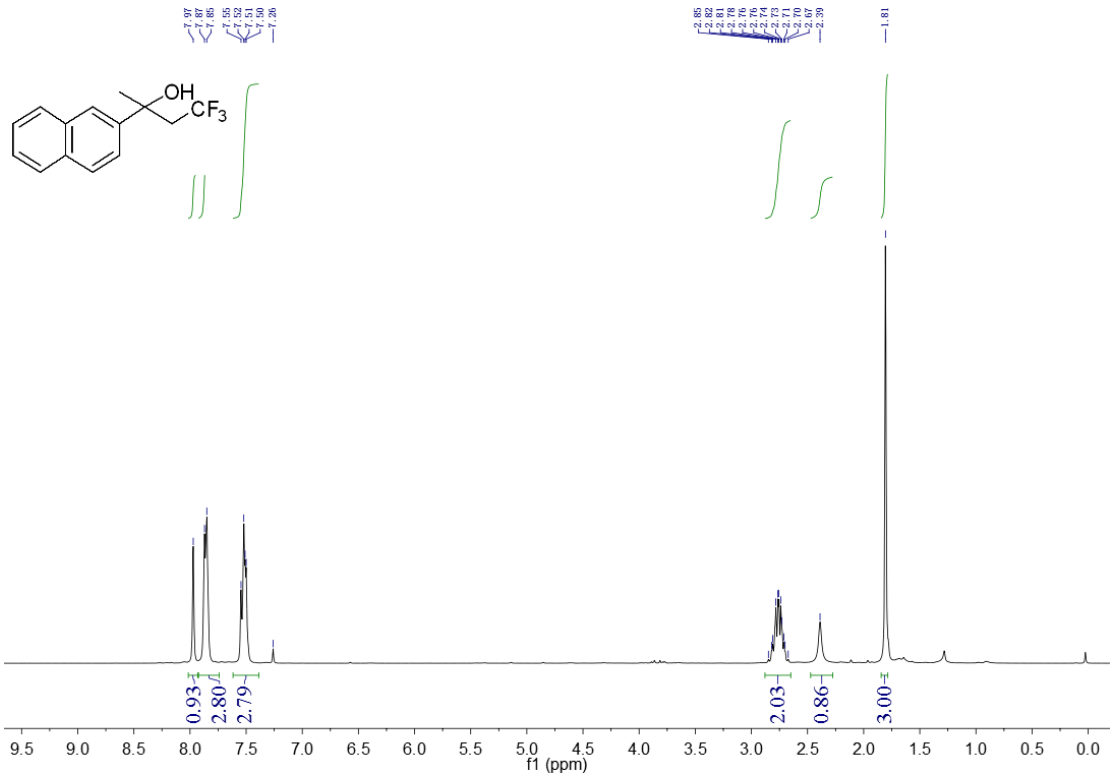
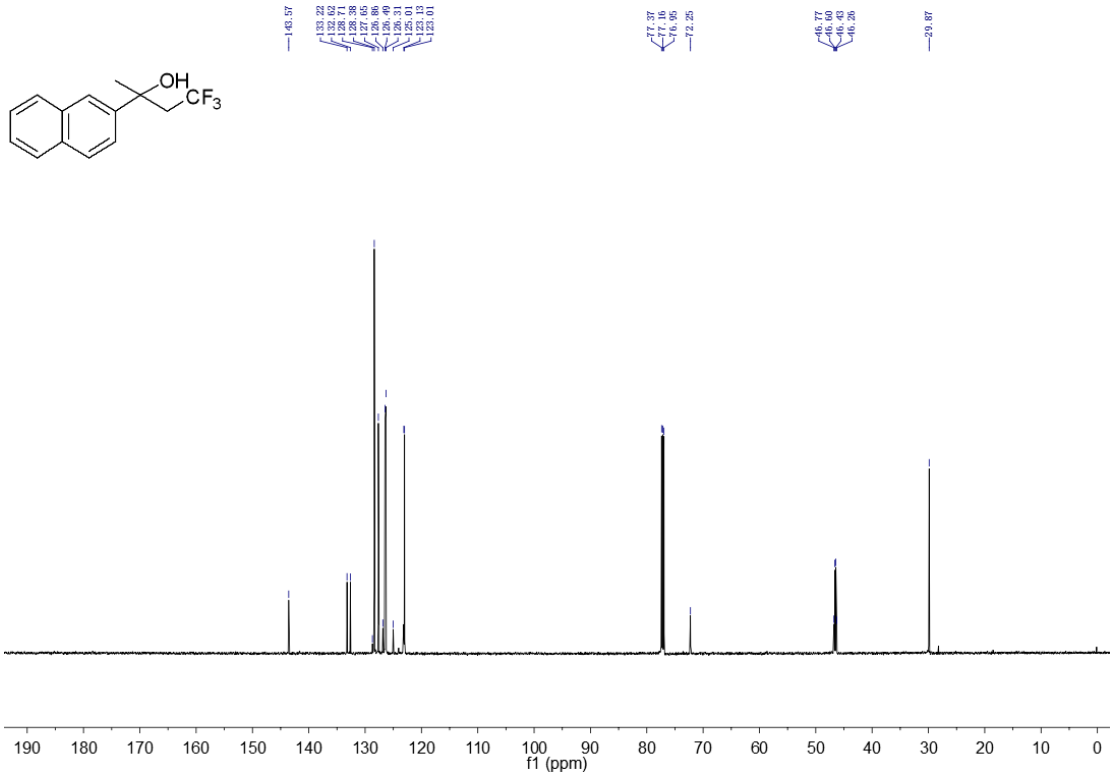


^{1}H NMR of **2j**



^{13}C NMR of **2j**



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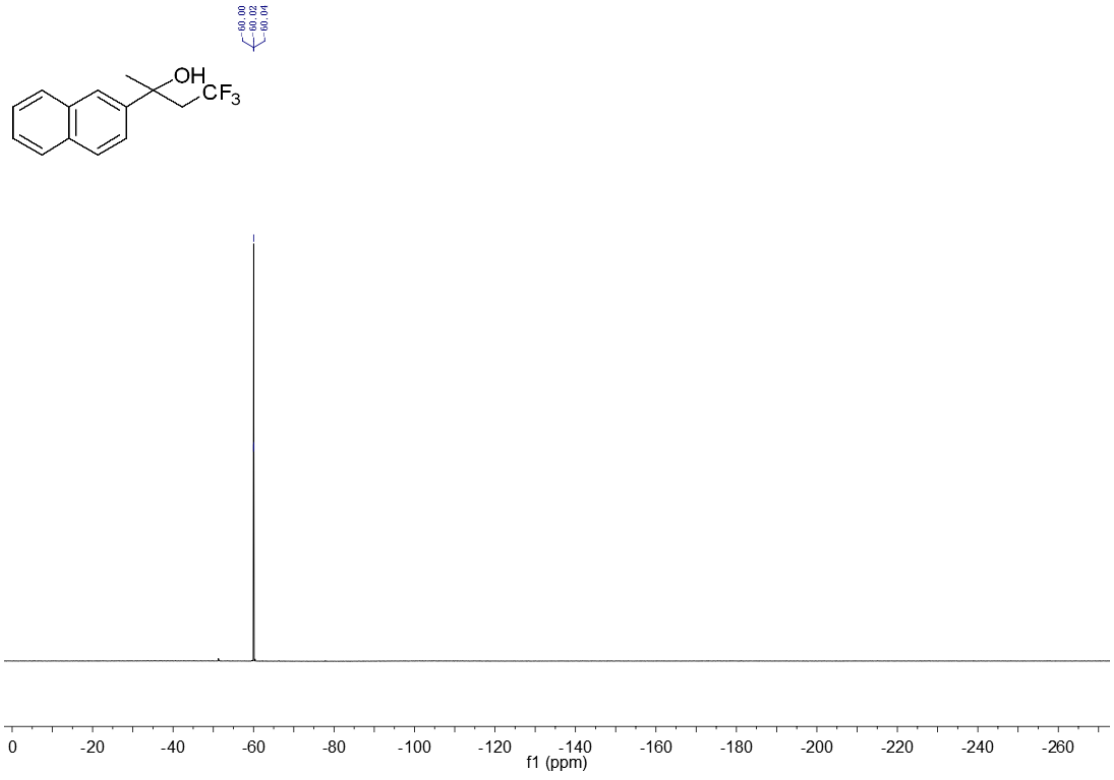
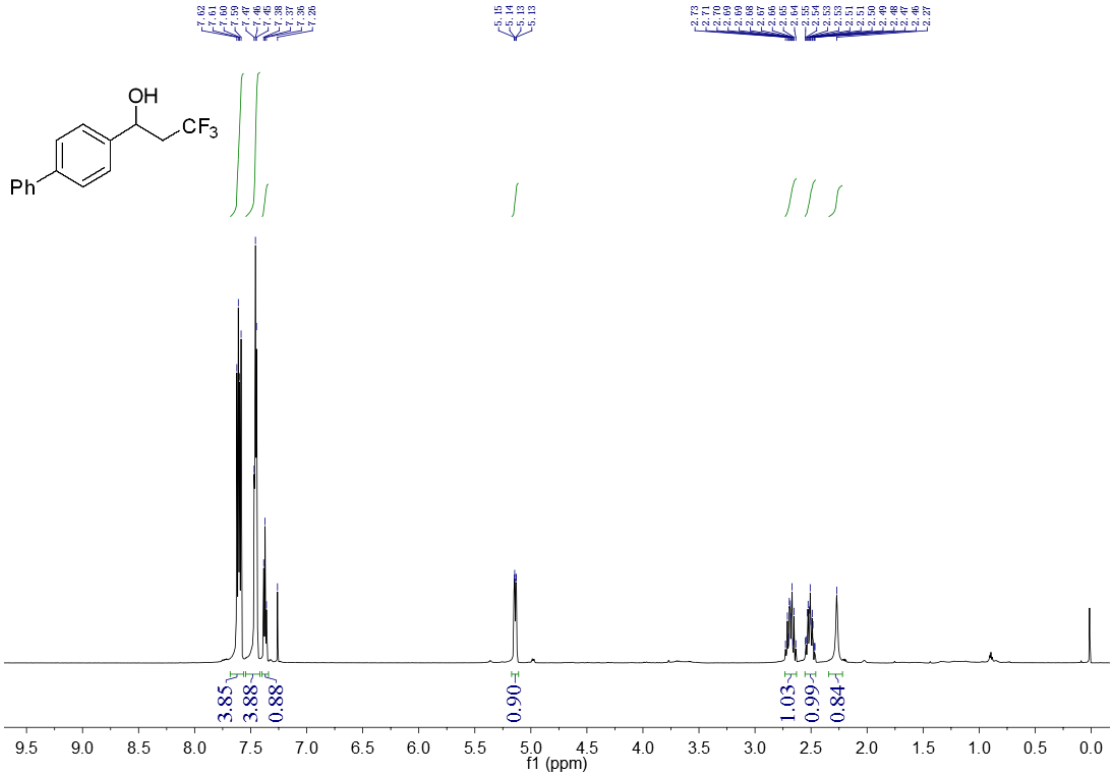
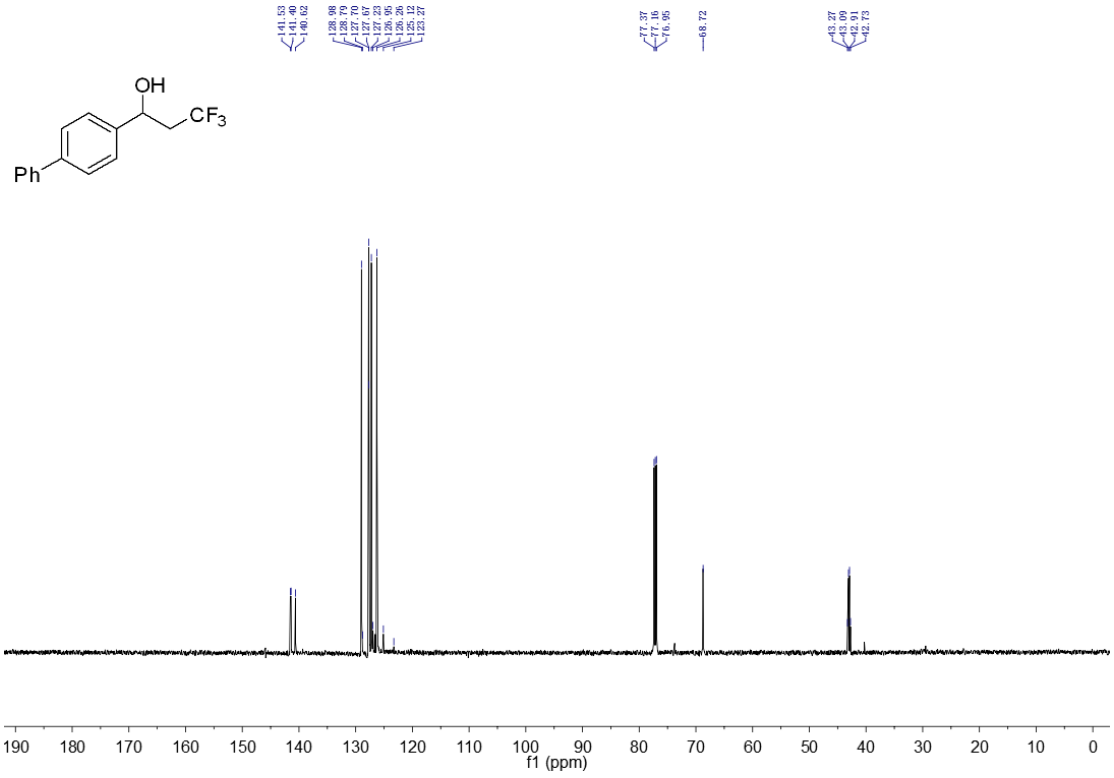


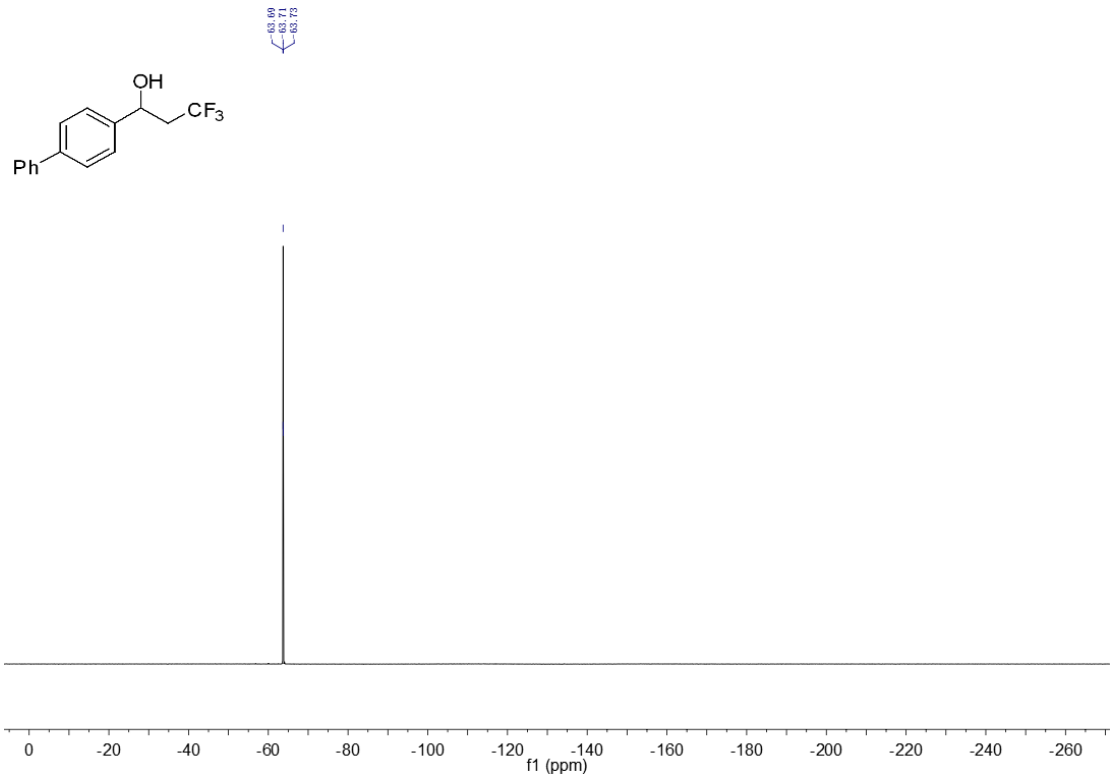
^{1}H NMR of **2k**



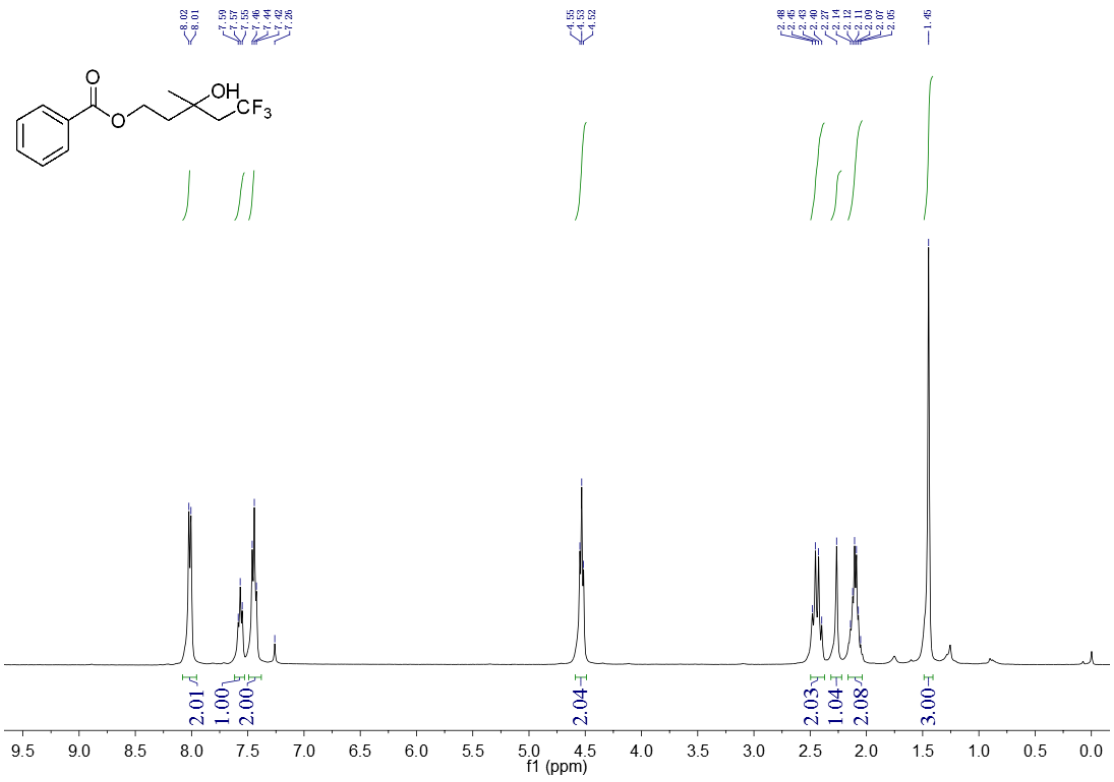
^{13}C NMR of **2k**



^{19}F NMR of **2k**



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



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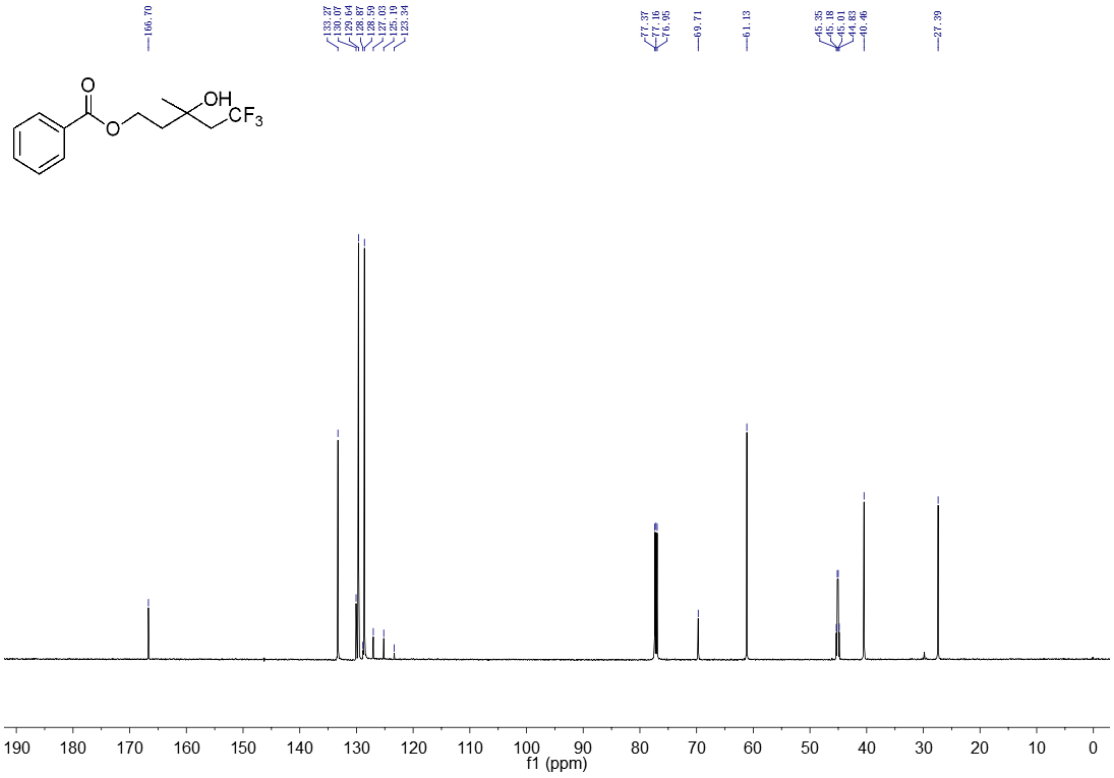
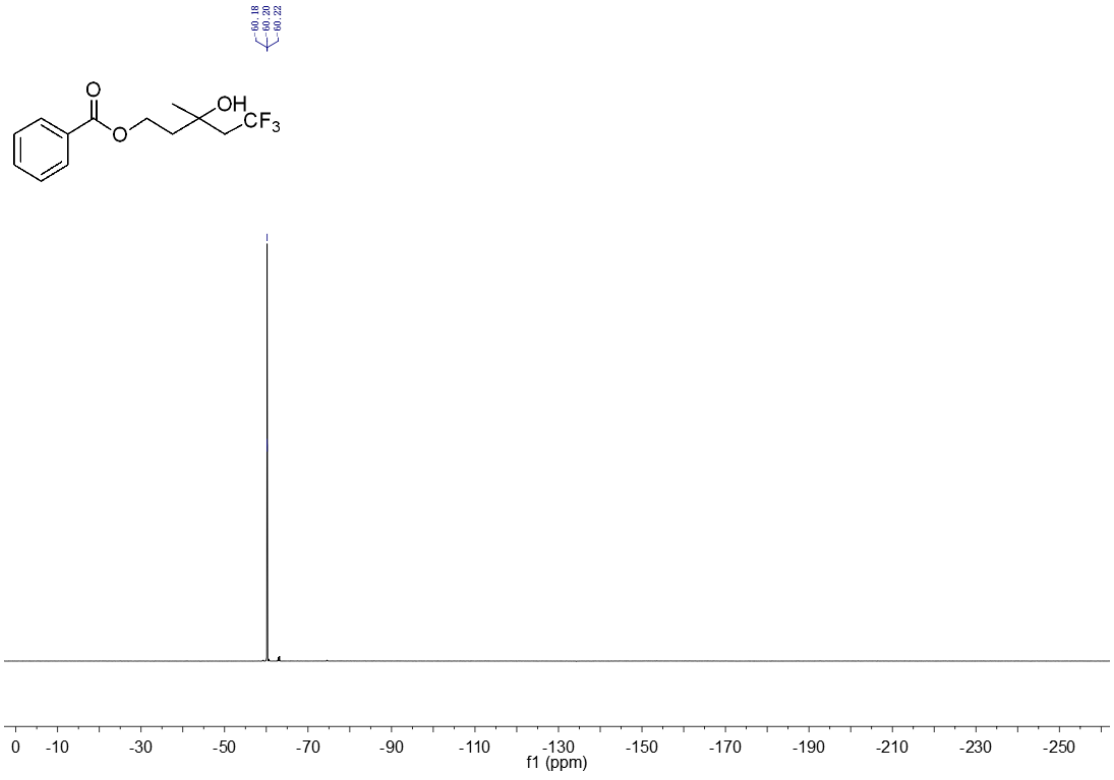
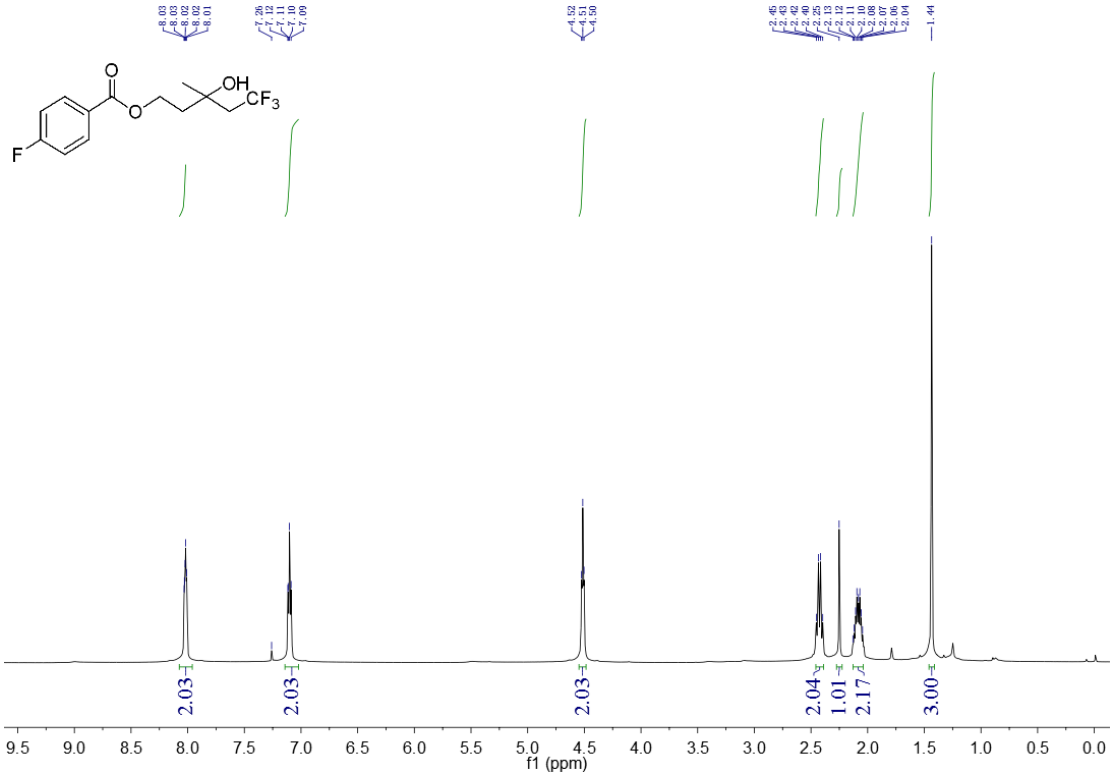


^{19}F NMR of **4a**



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



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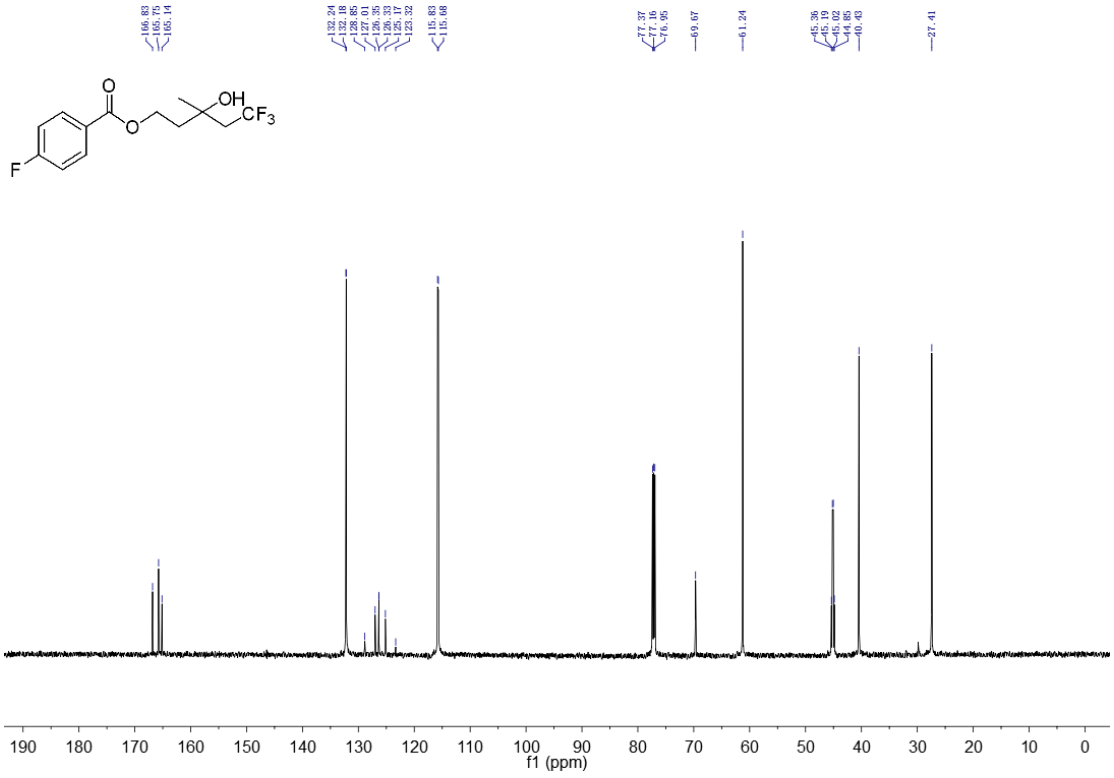
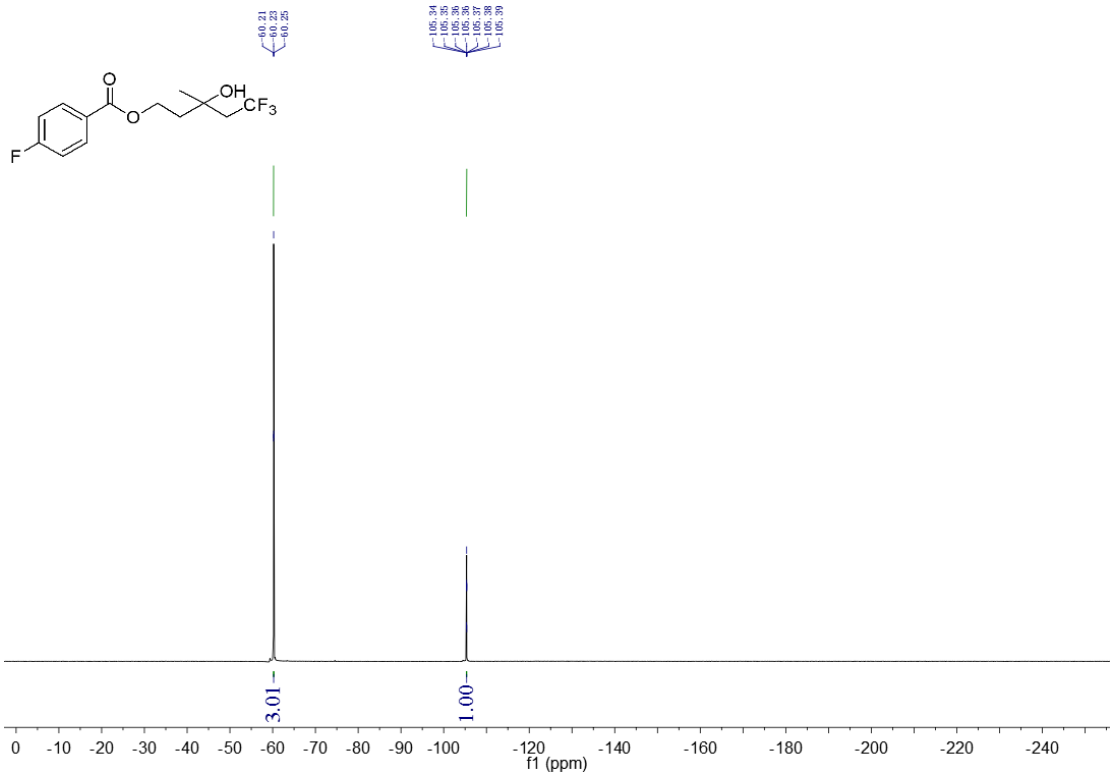
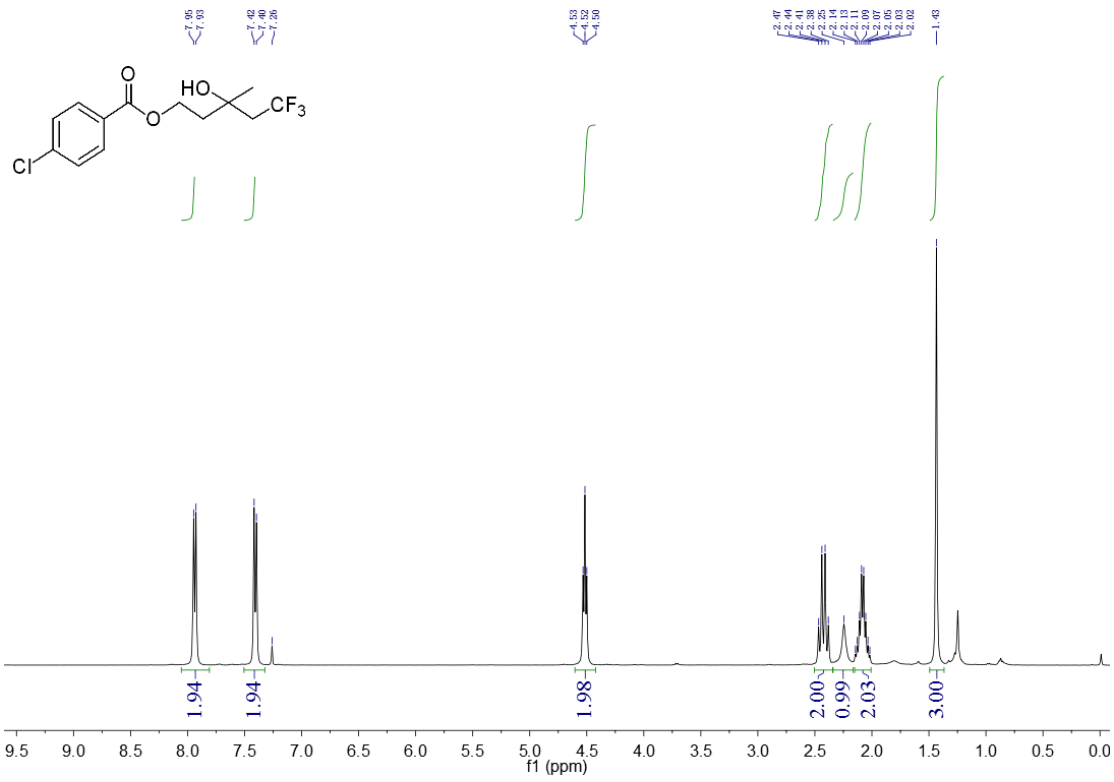


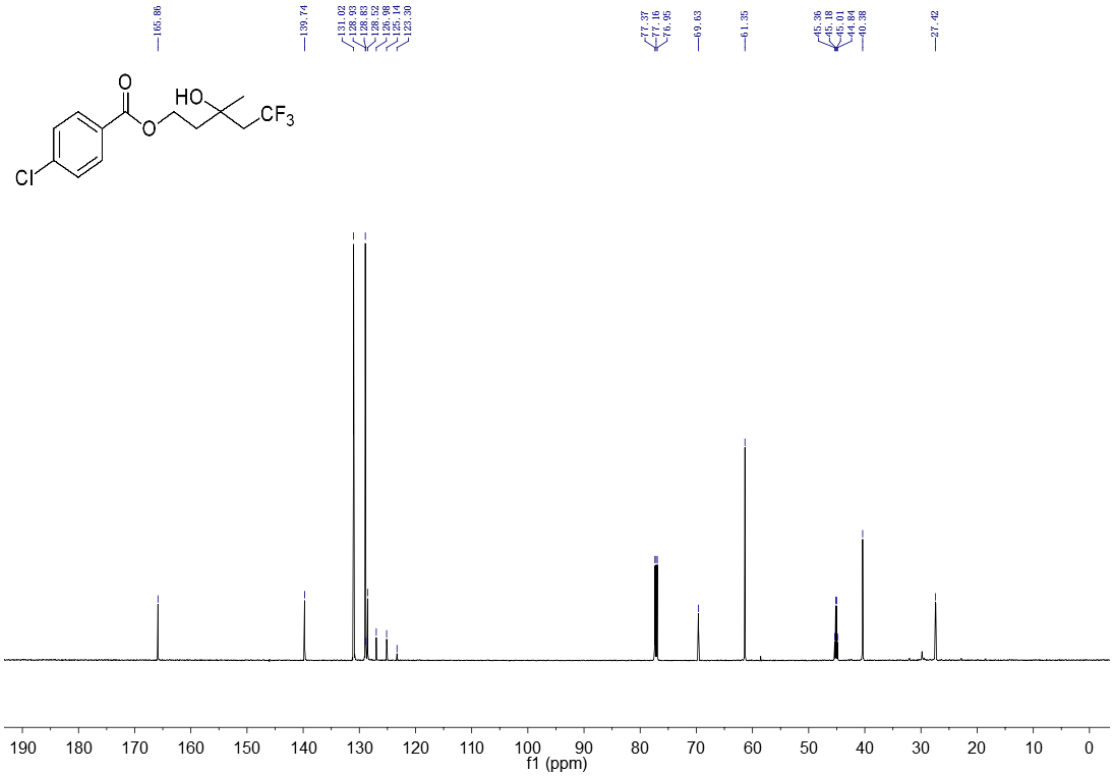
^{19}F NMR of **4b**



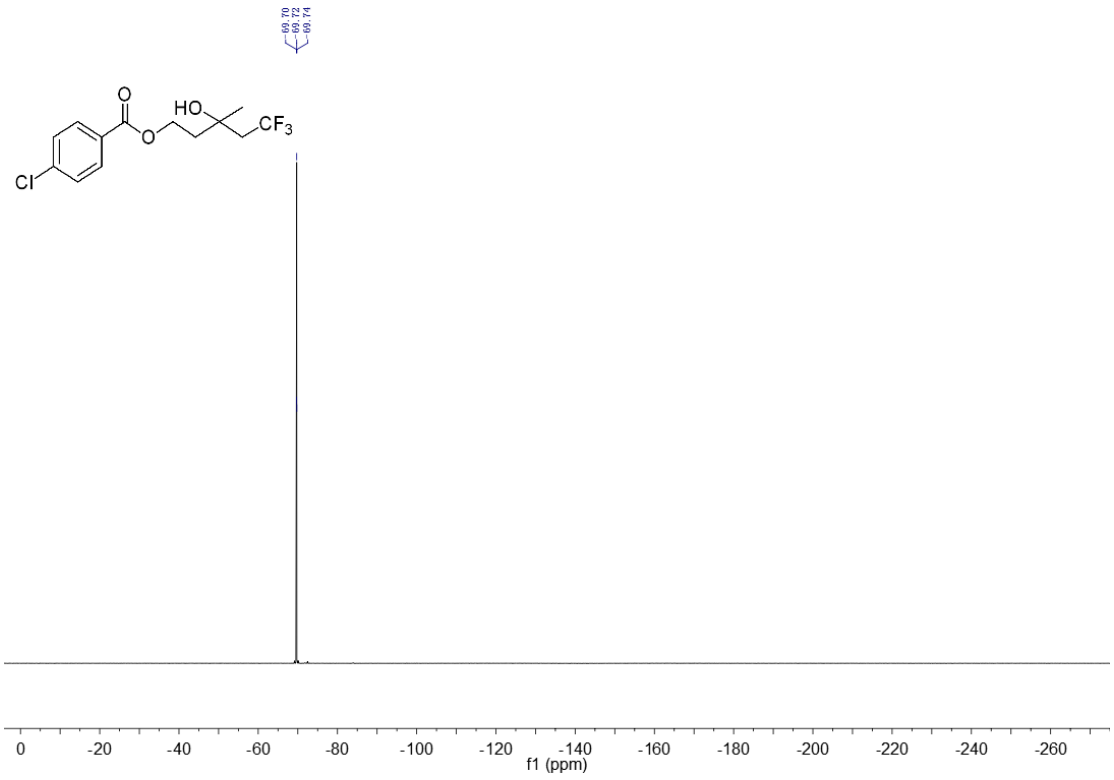
^{1}H NMR of **4c**



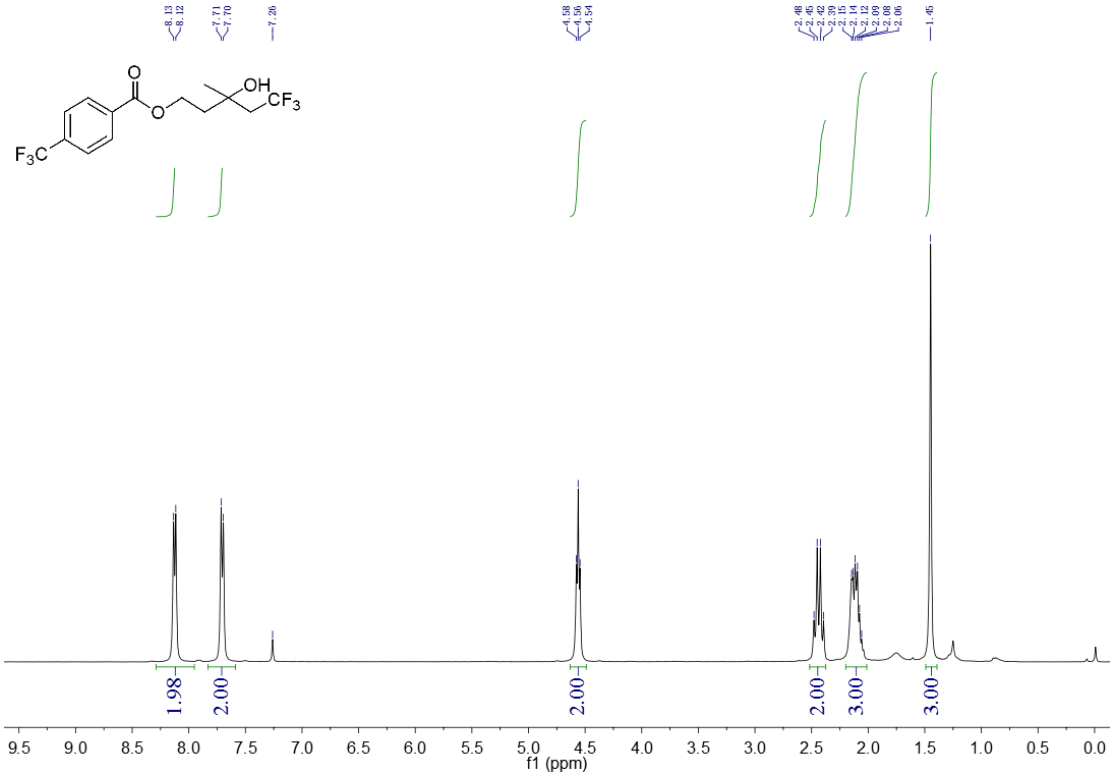
^{13}C NMR of **4c**



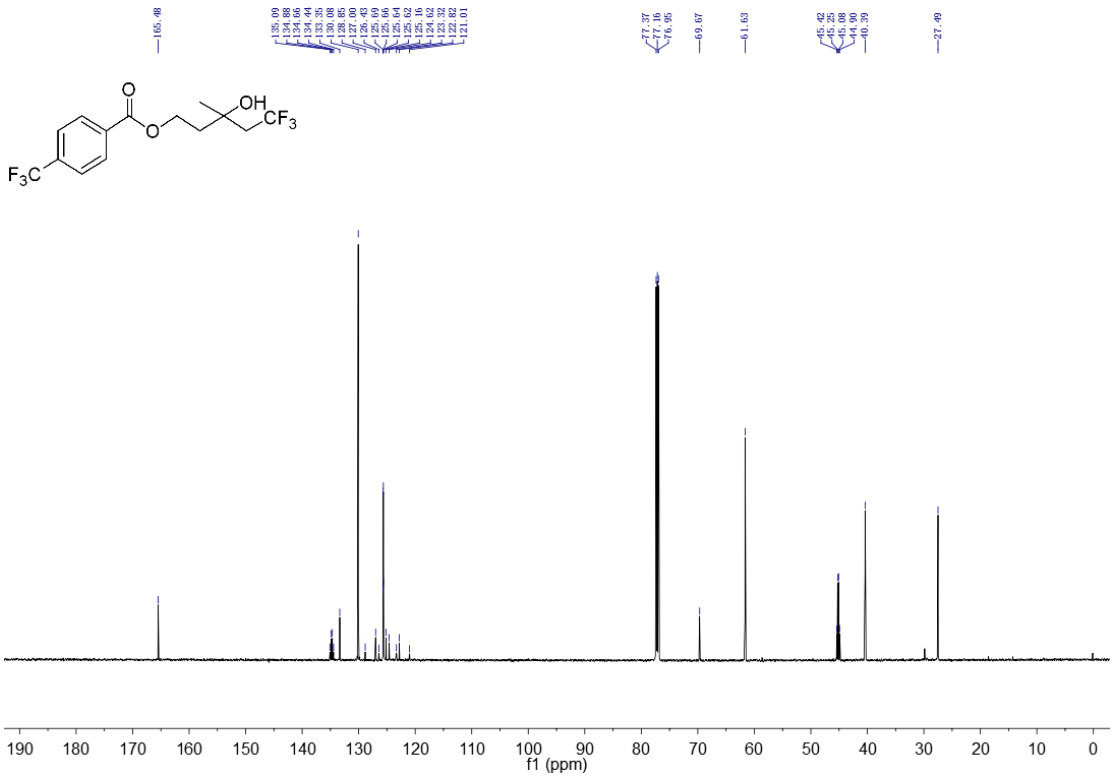
^{19}F NMR of **4c**



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



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



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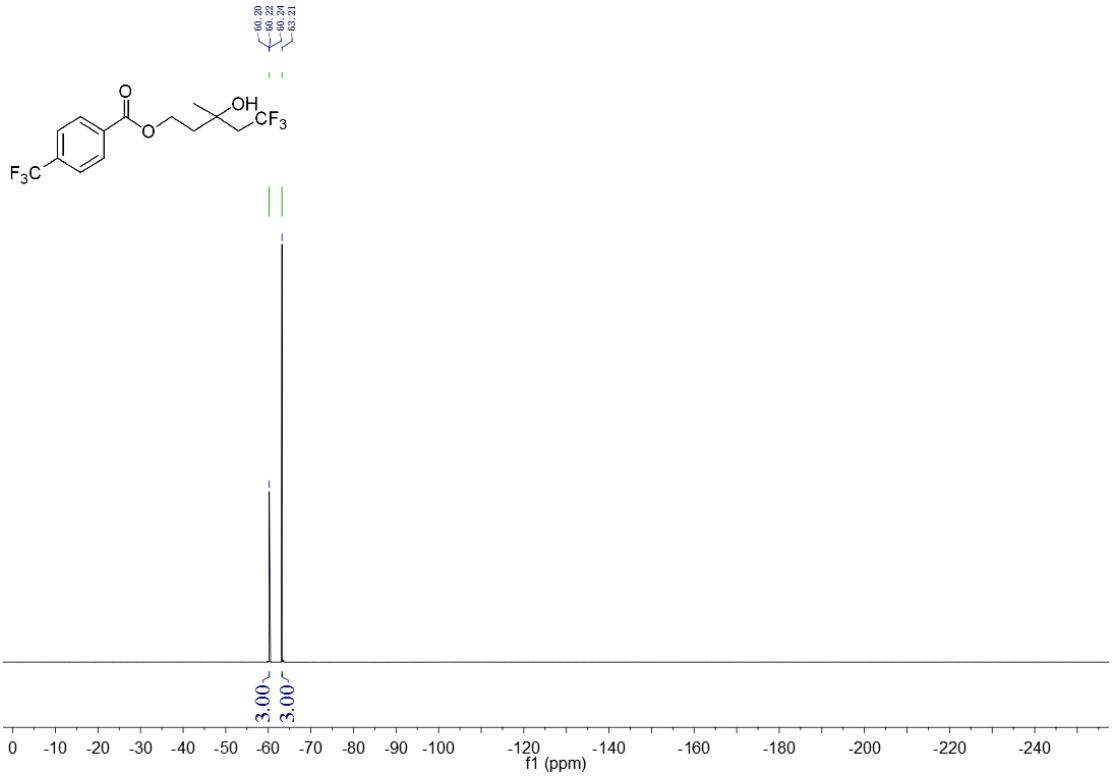

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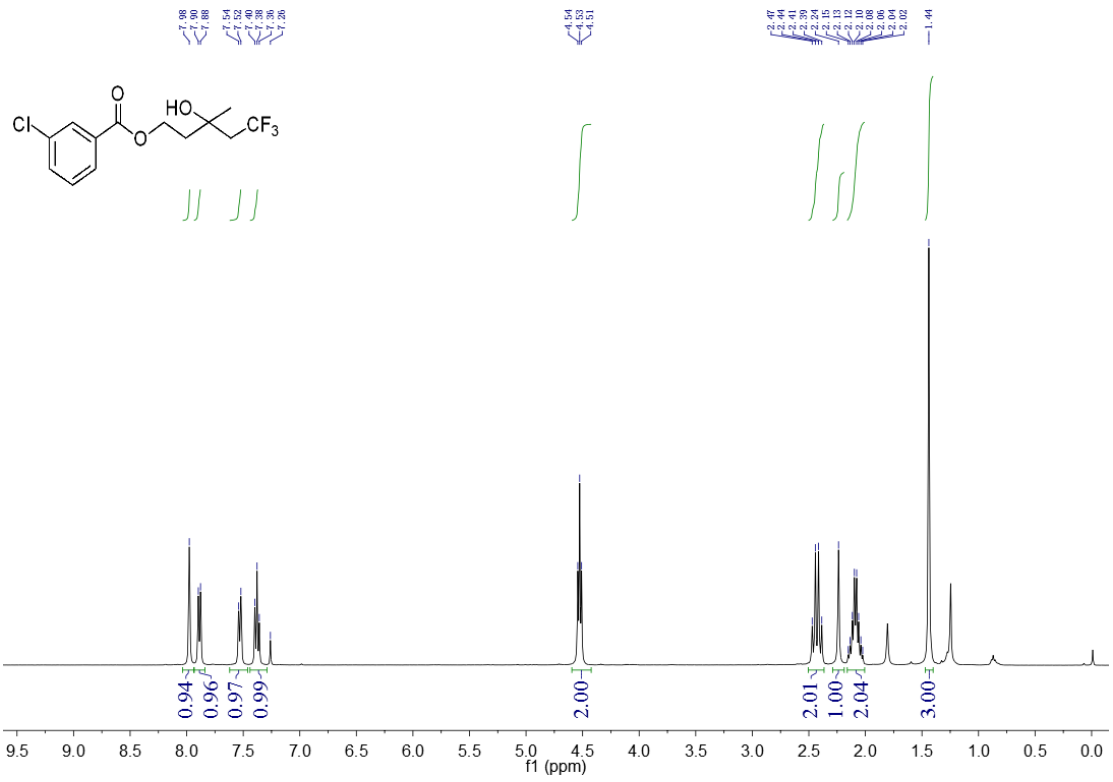

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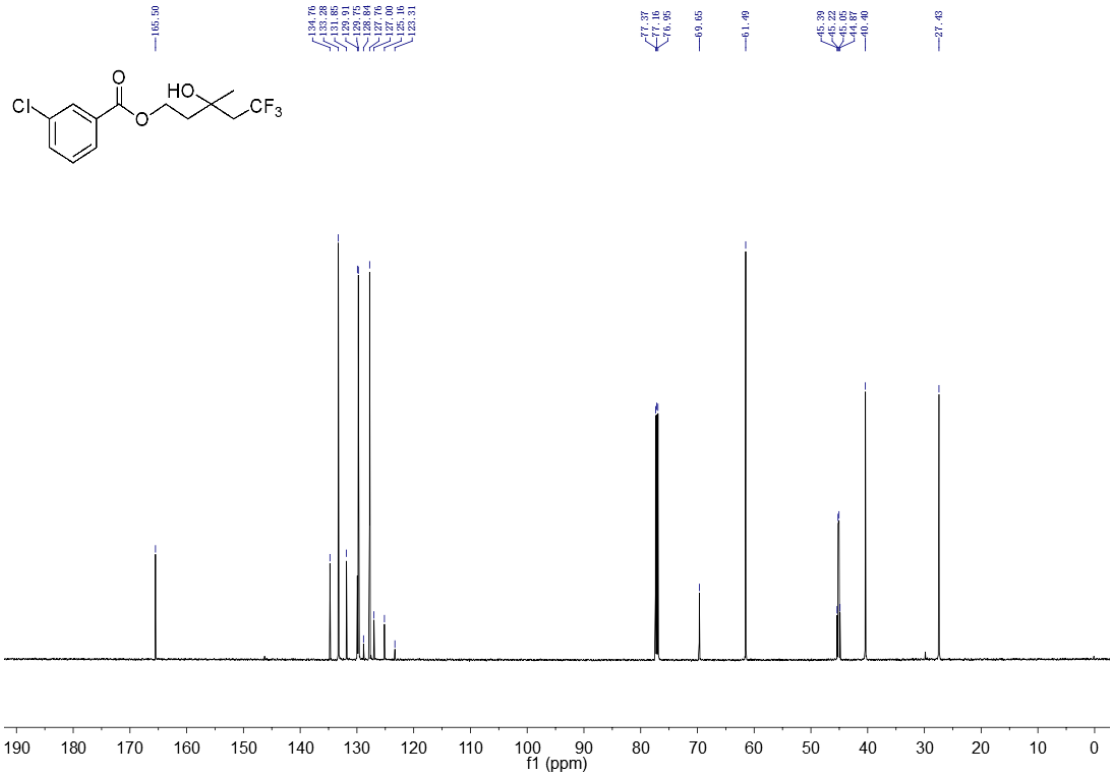

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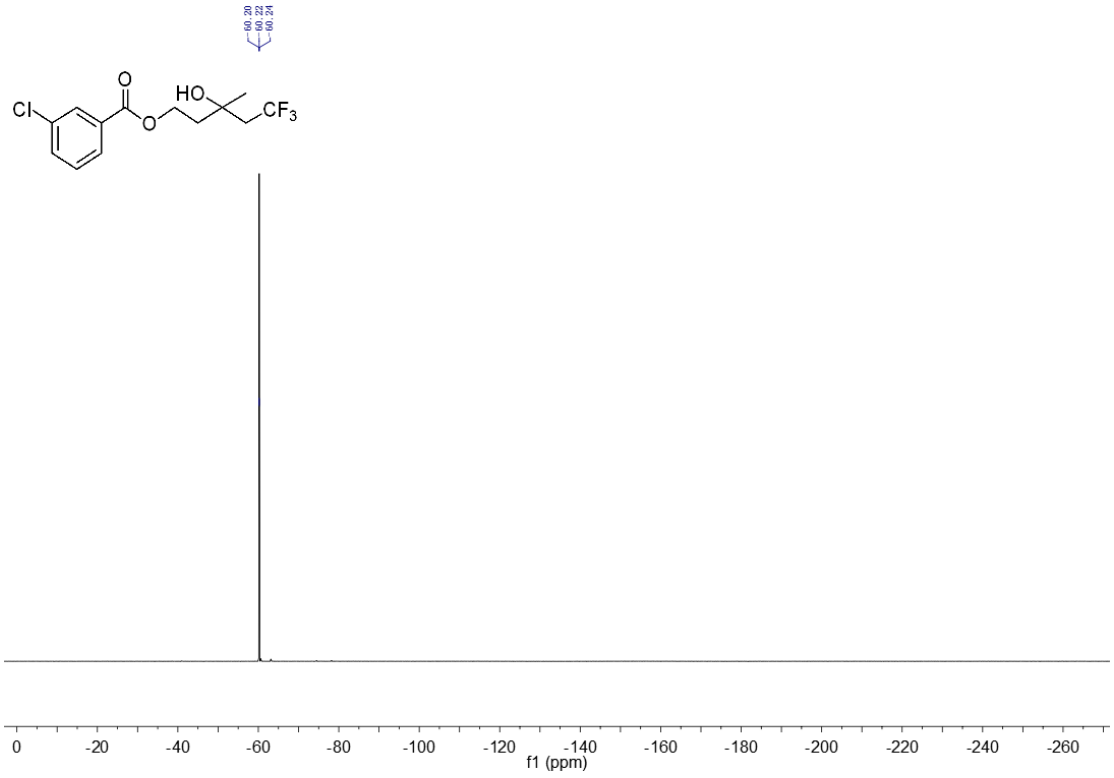

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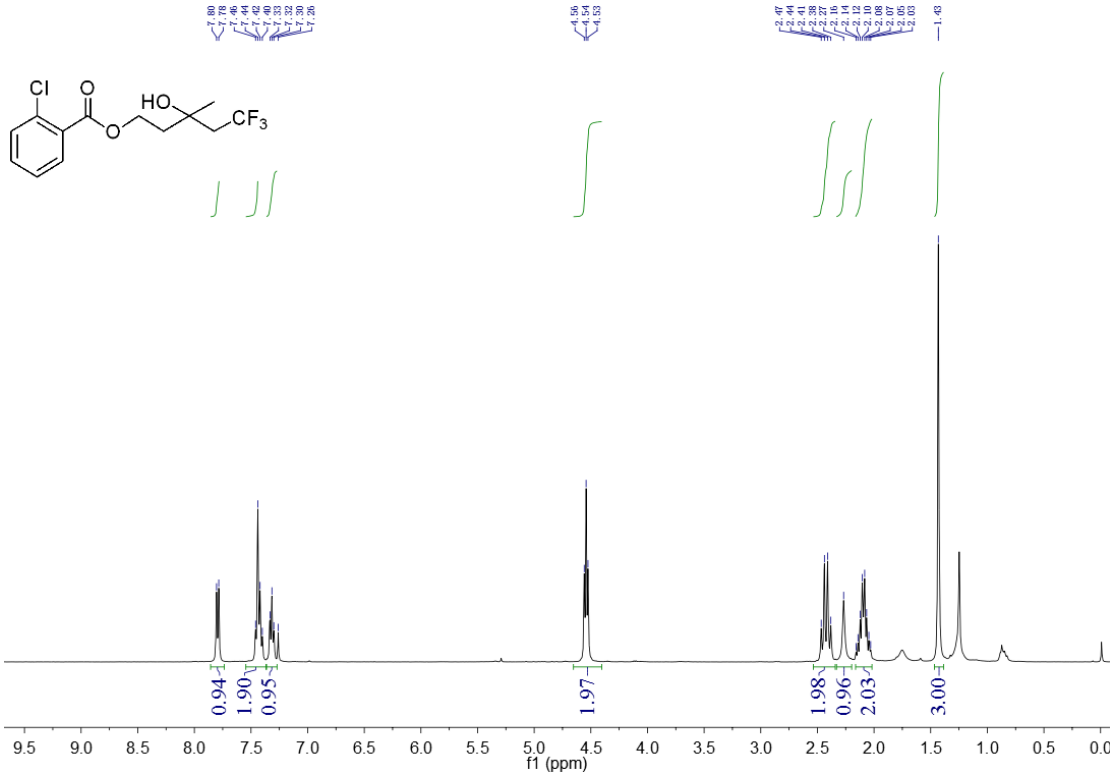
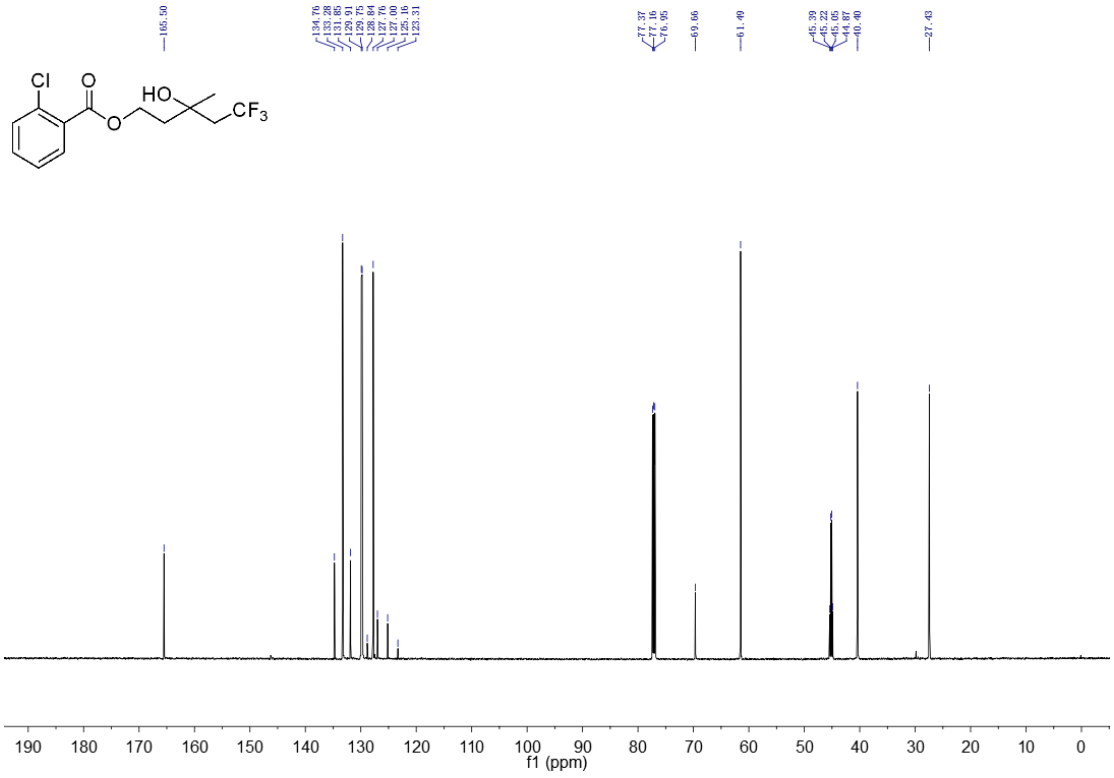
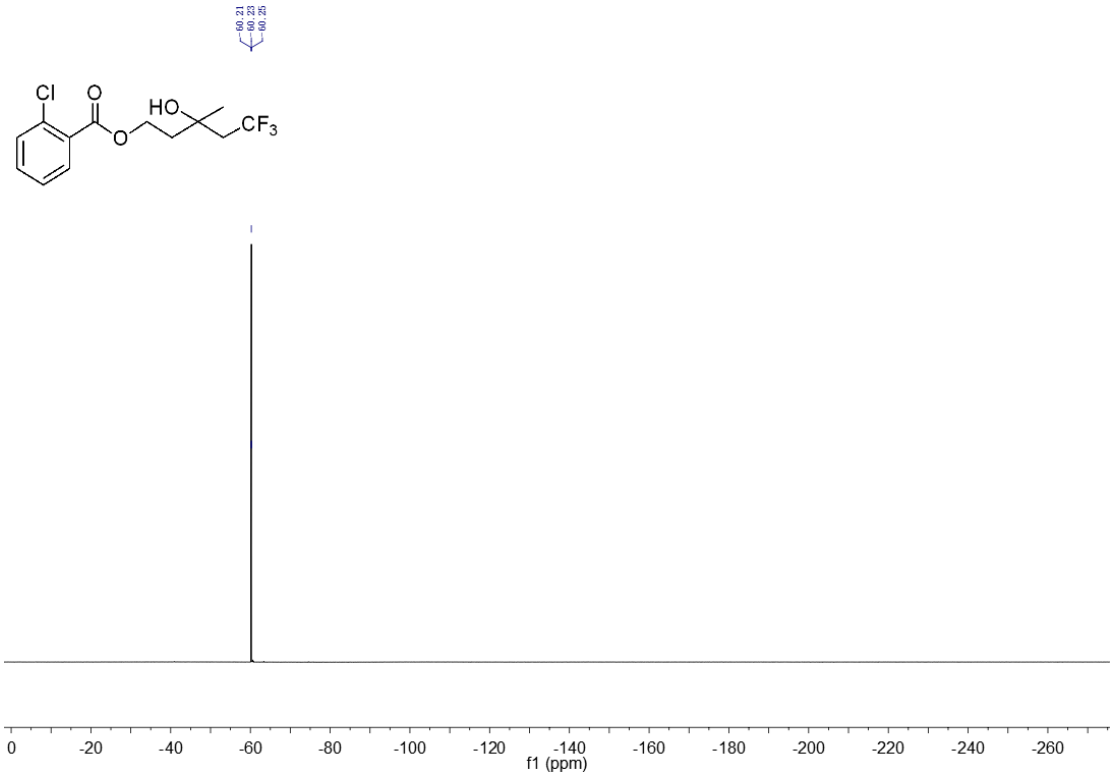


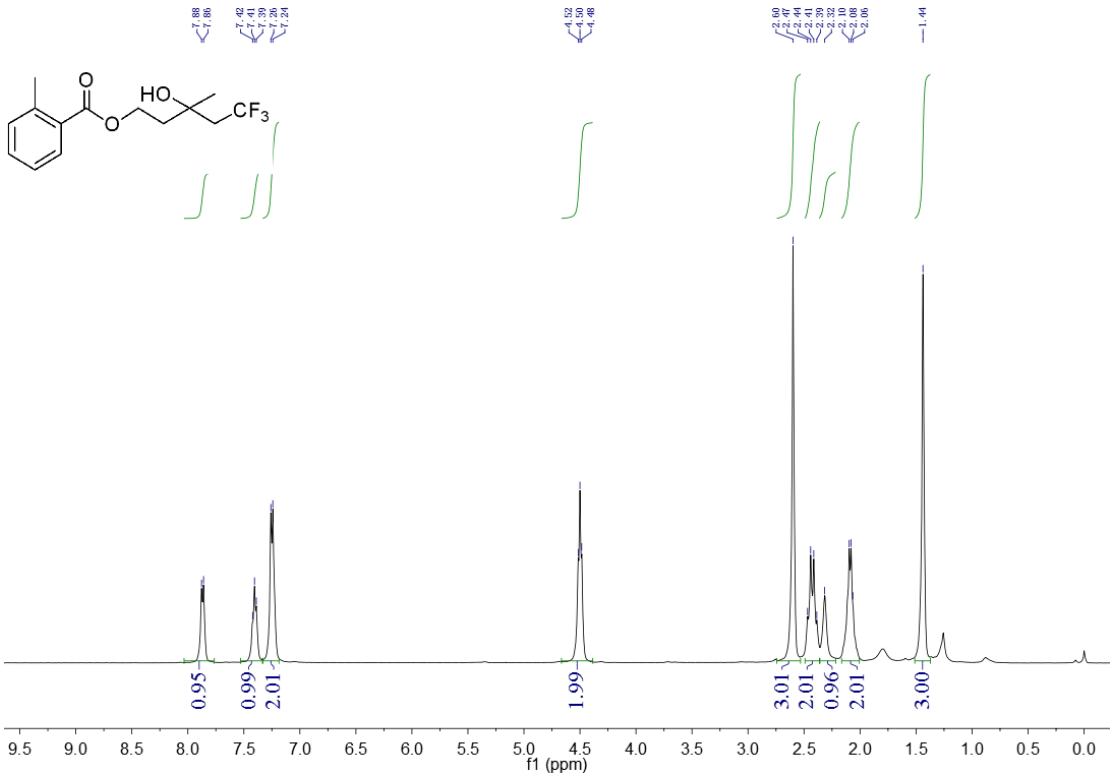
^{13}C NMR of **4f**



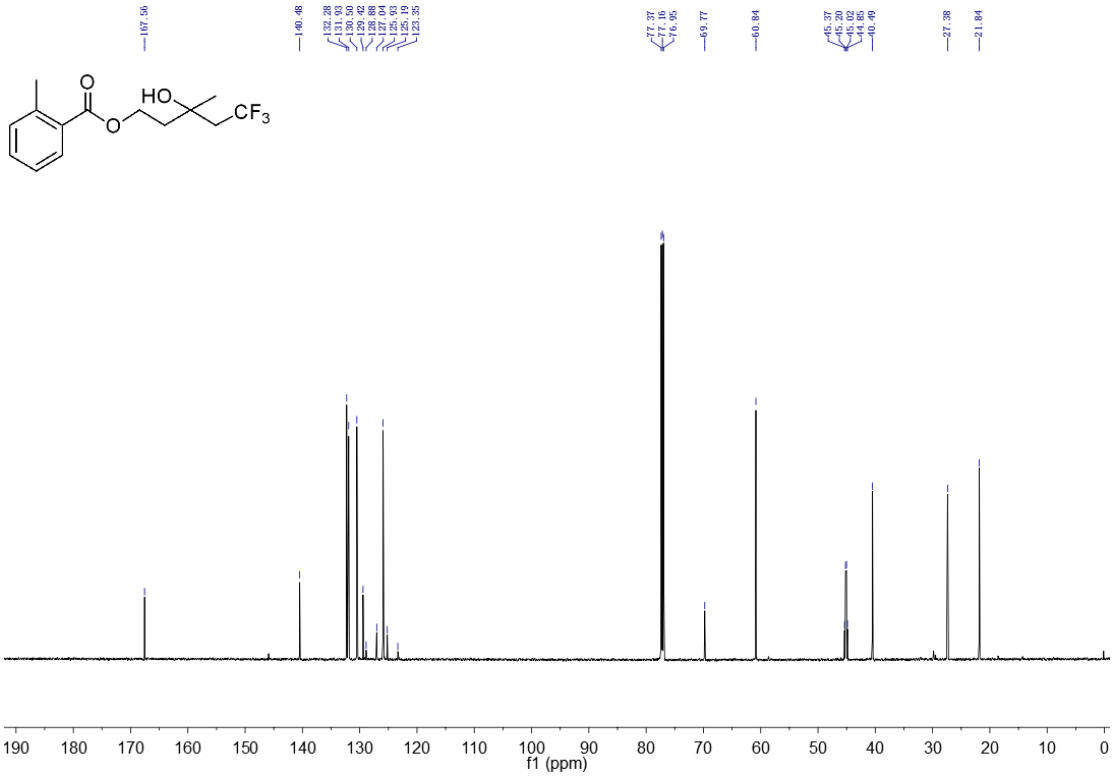
^{19}F NMR of **4f**



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



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



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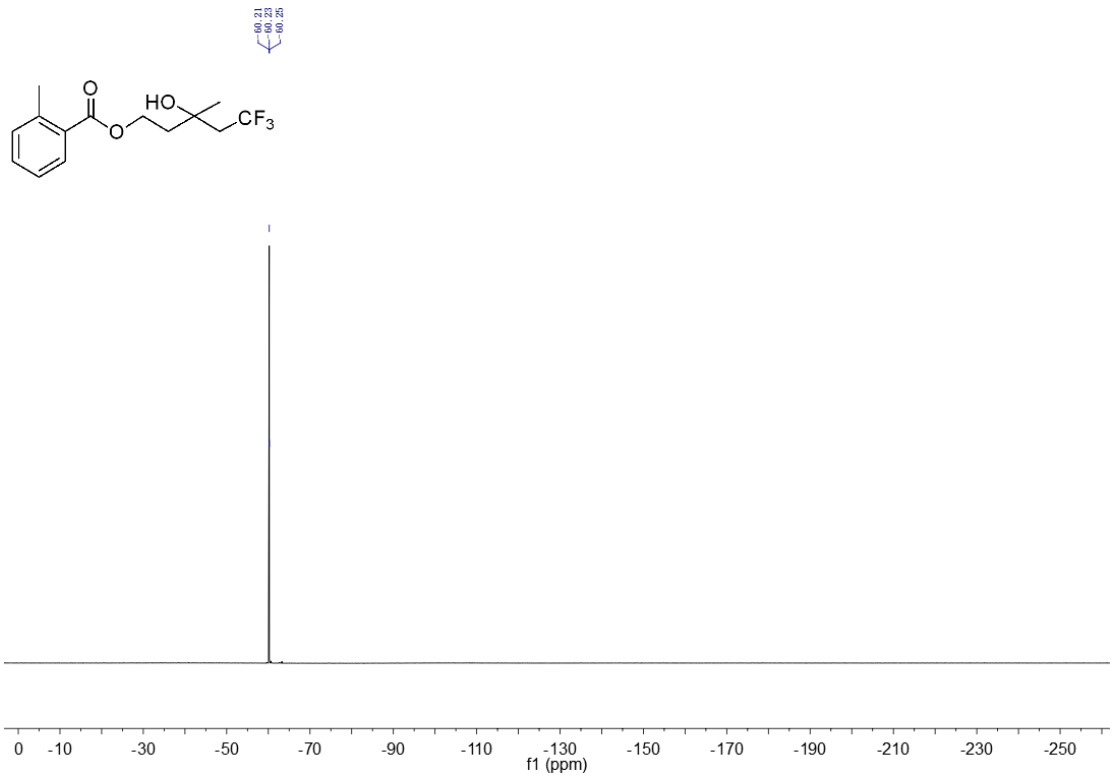
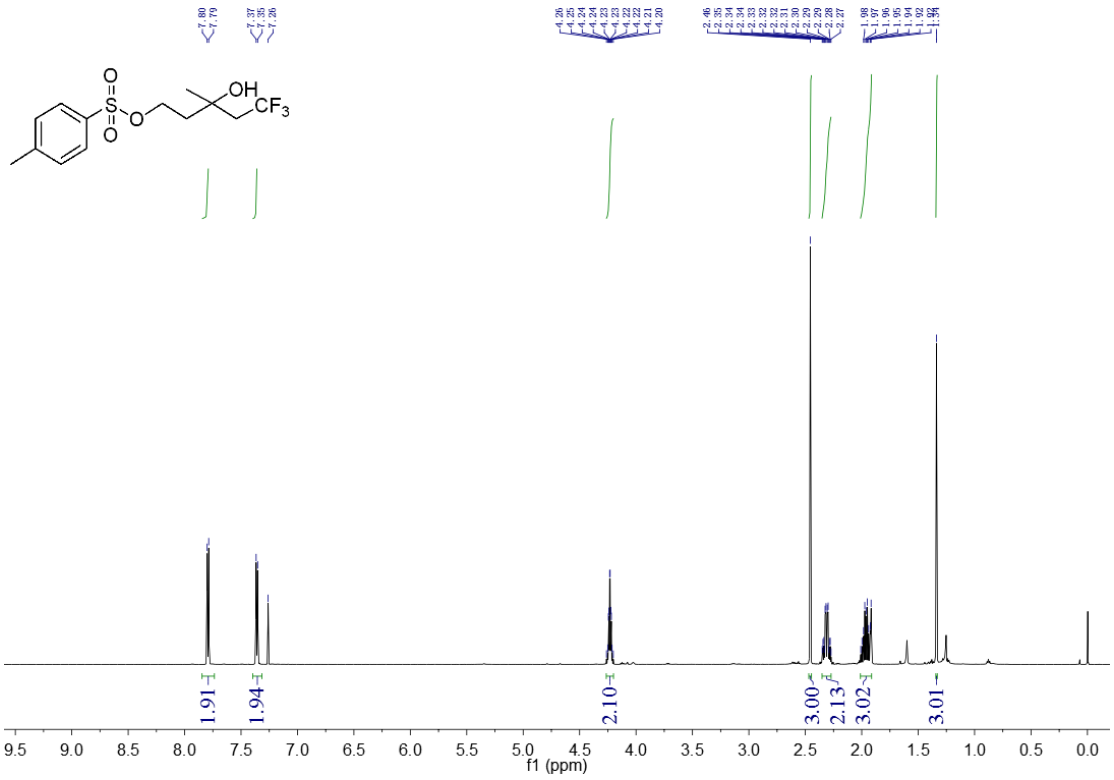
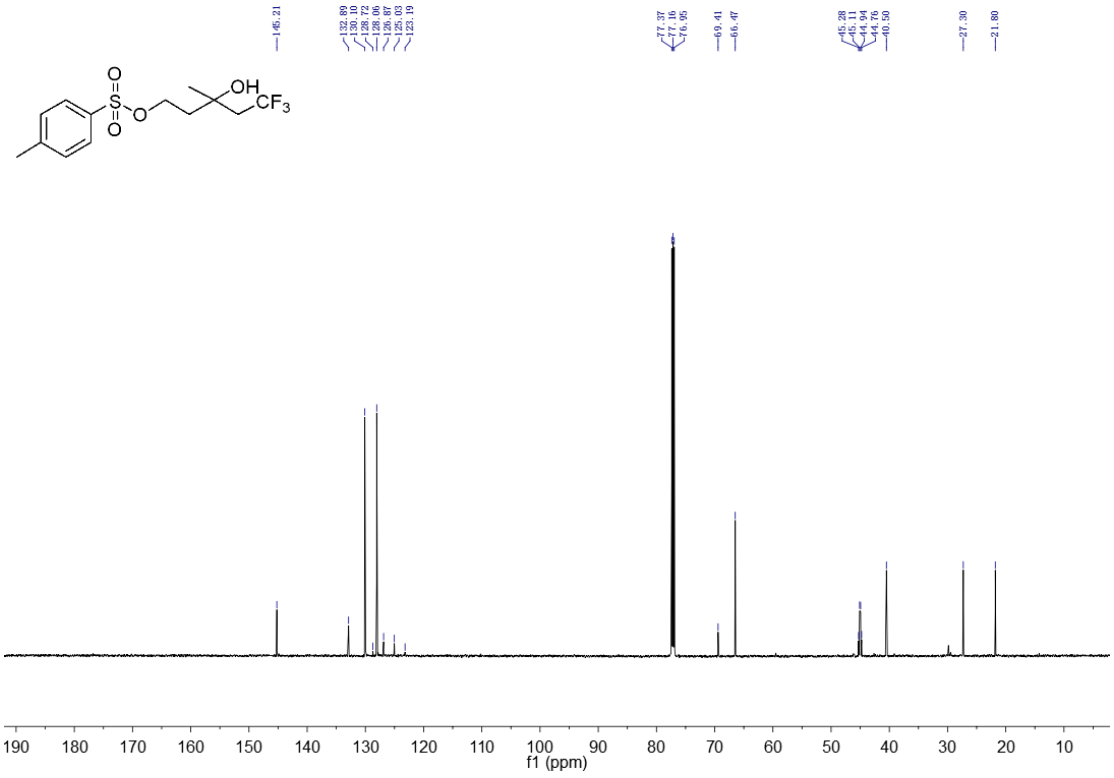


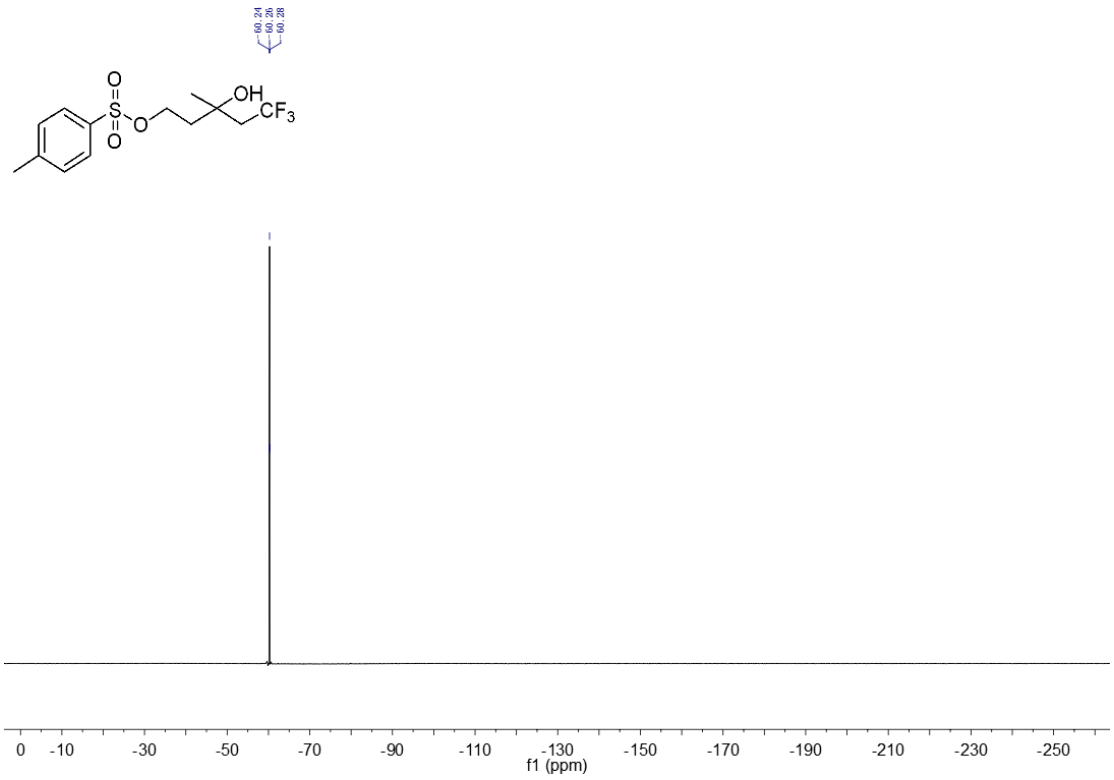
^{1}H NMR of **4h**



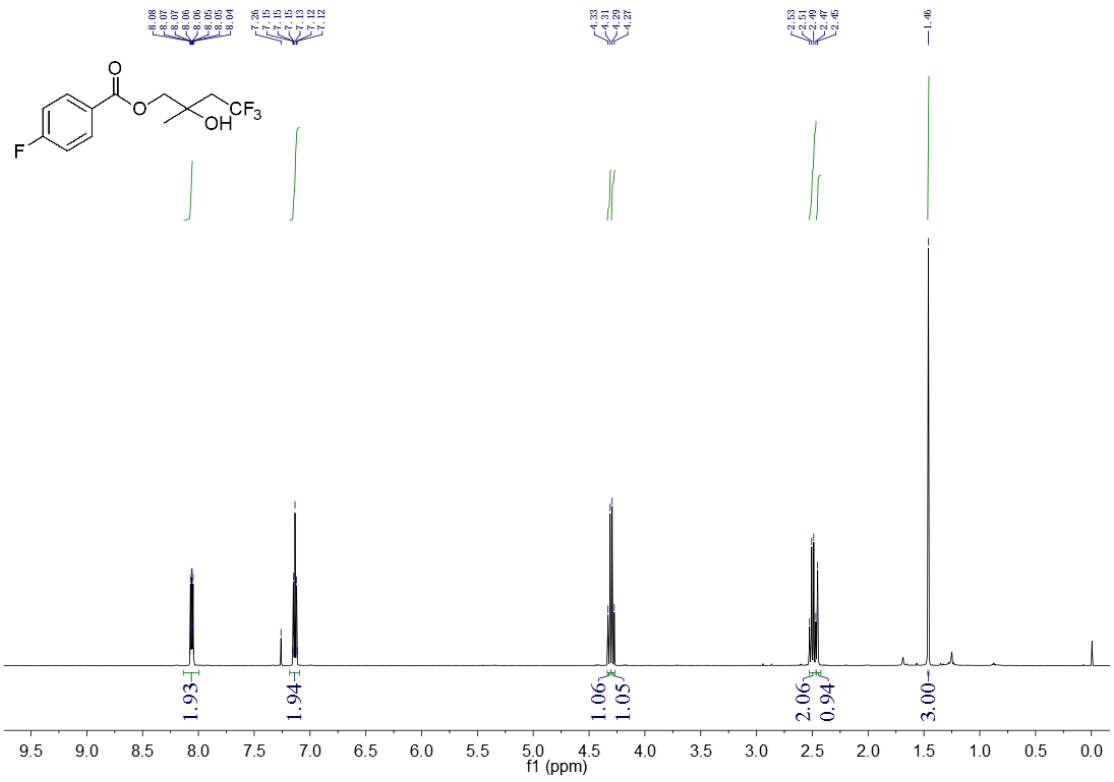
^{13}C NMR of **4h**



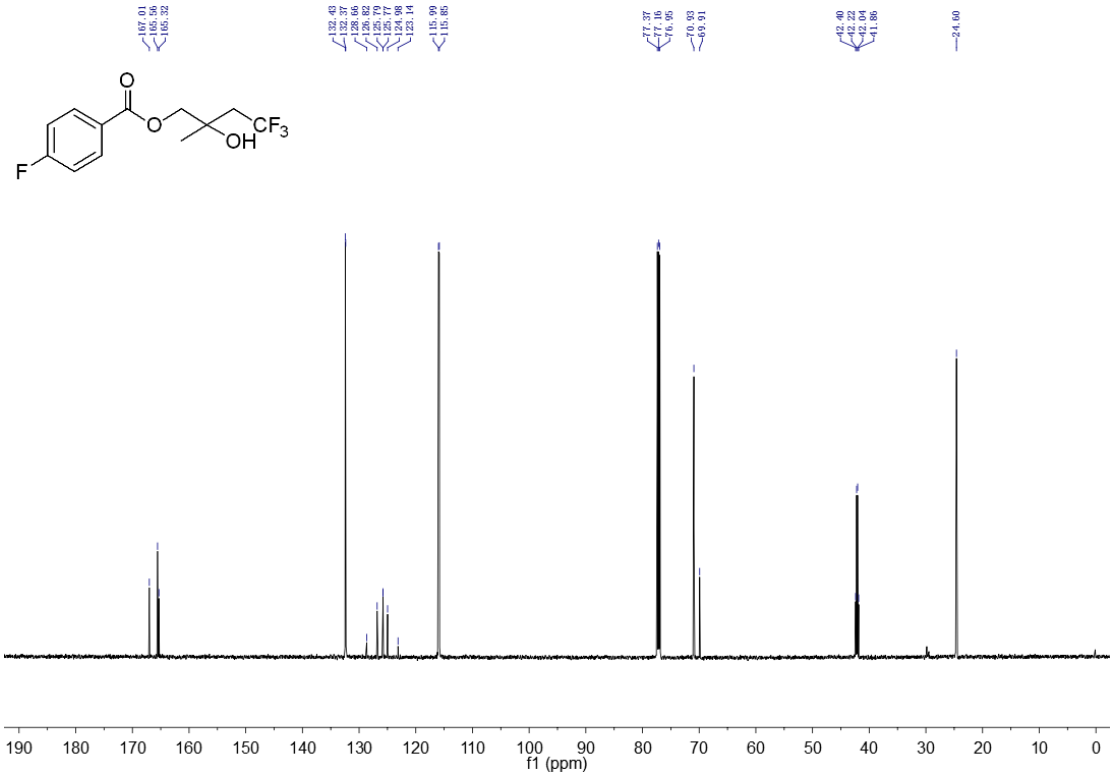
^{19}F NMR of **4h**



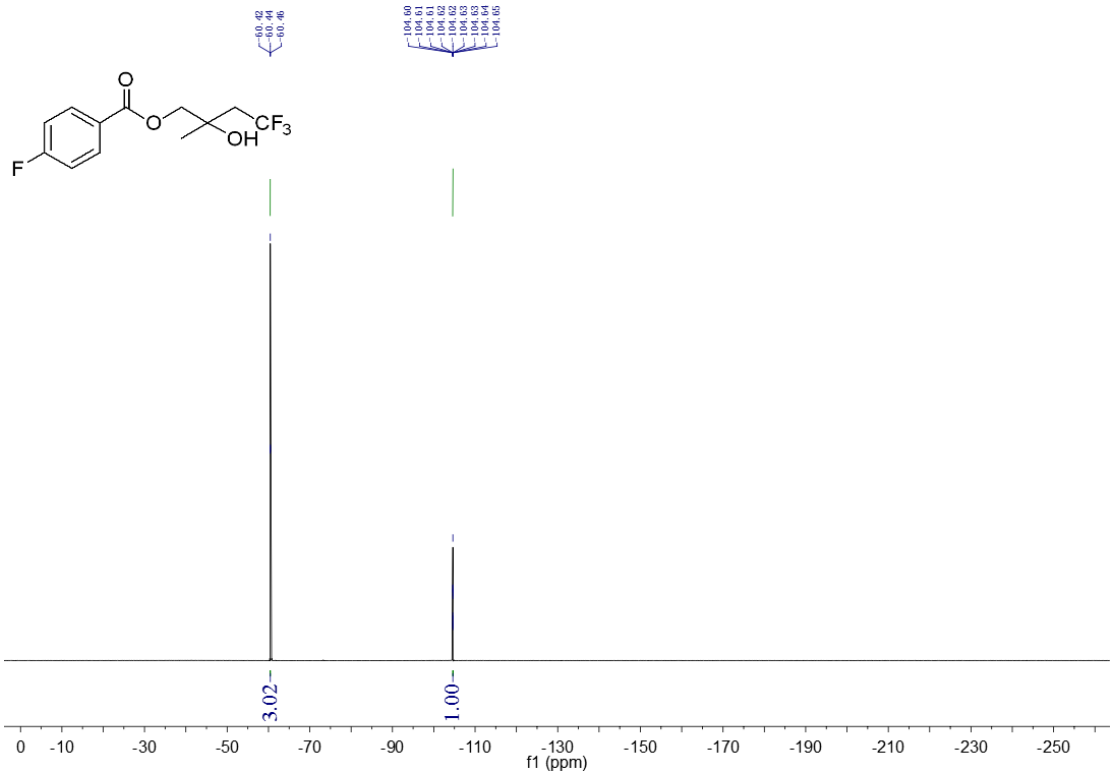
^{1}H NMR of **4i**



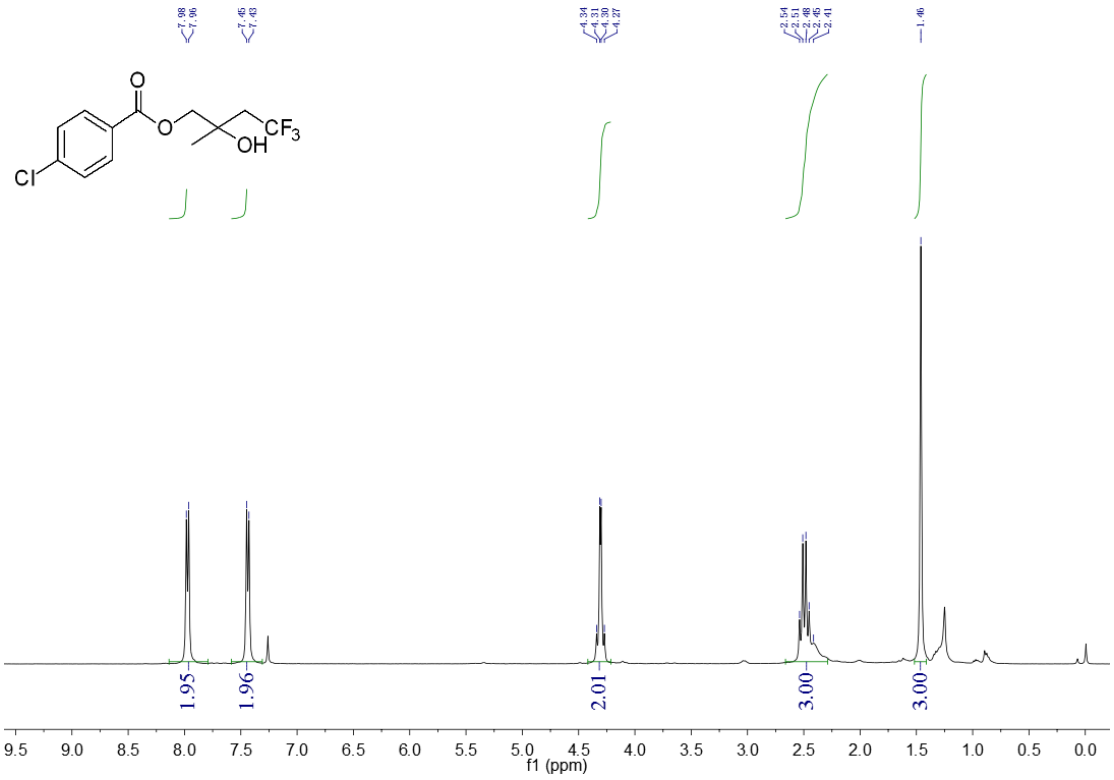
^{13}C NMR of **4i**



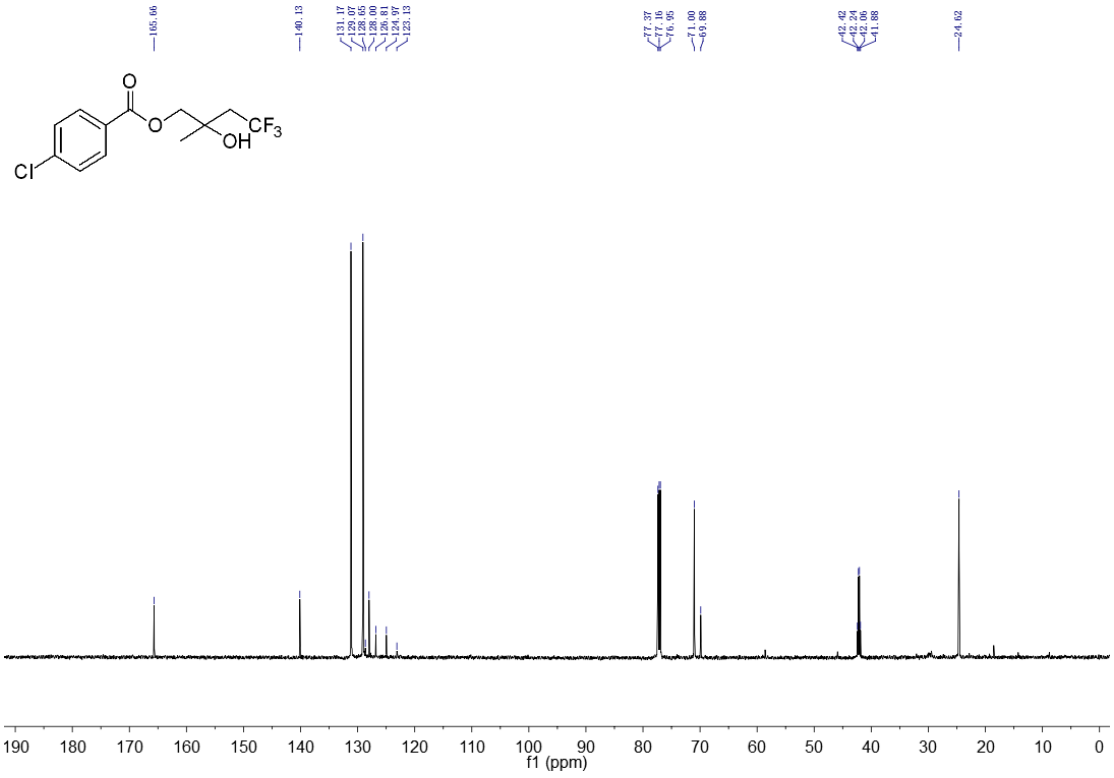
^{19}F NMR of **4i**



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



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



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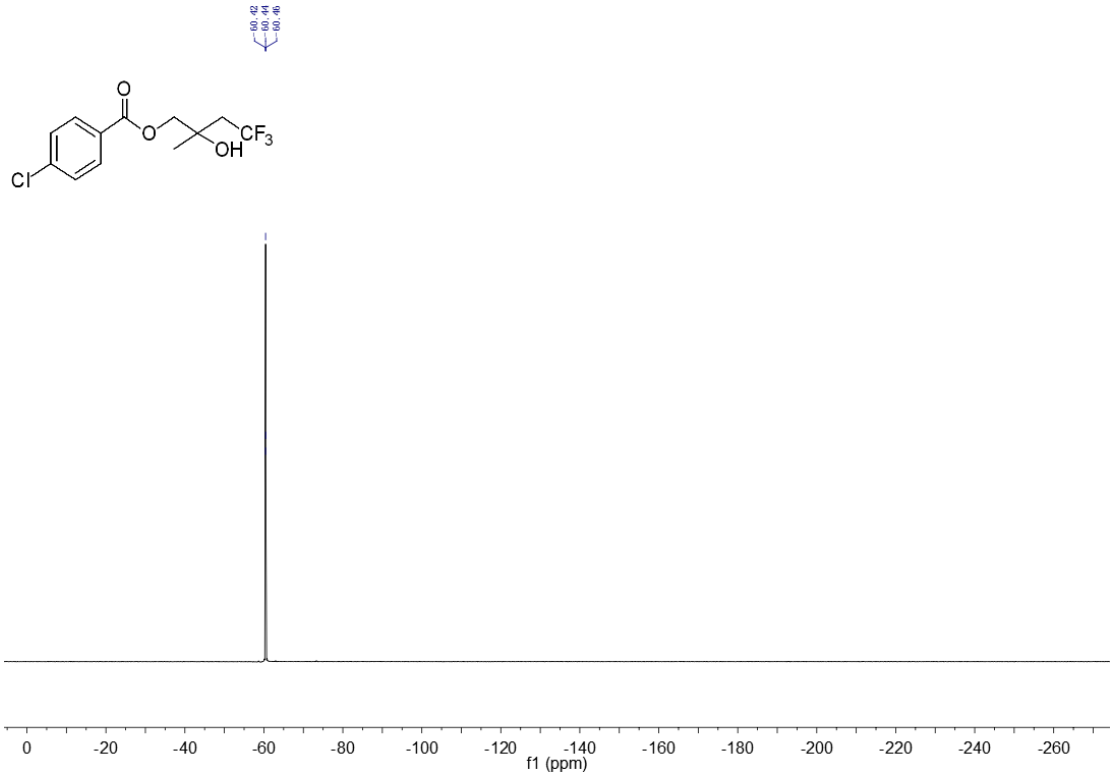

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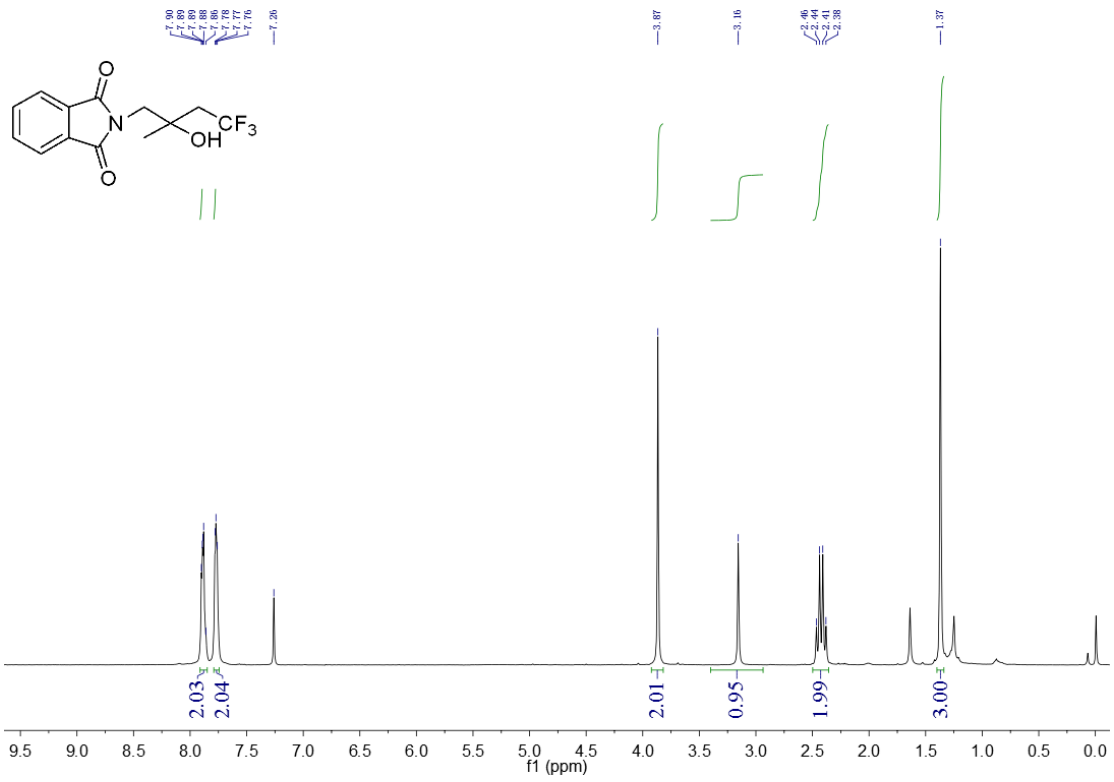
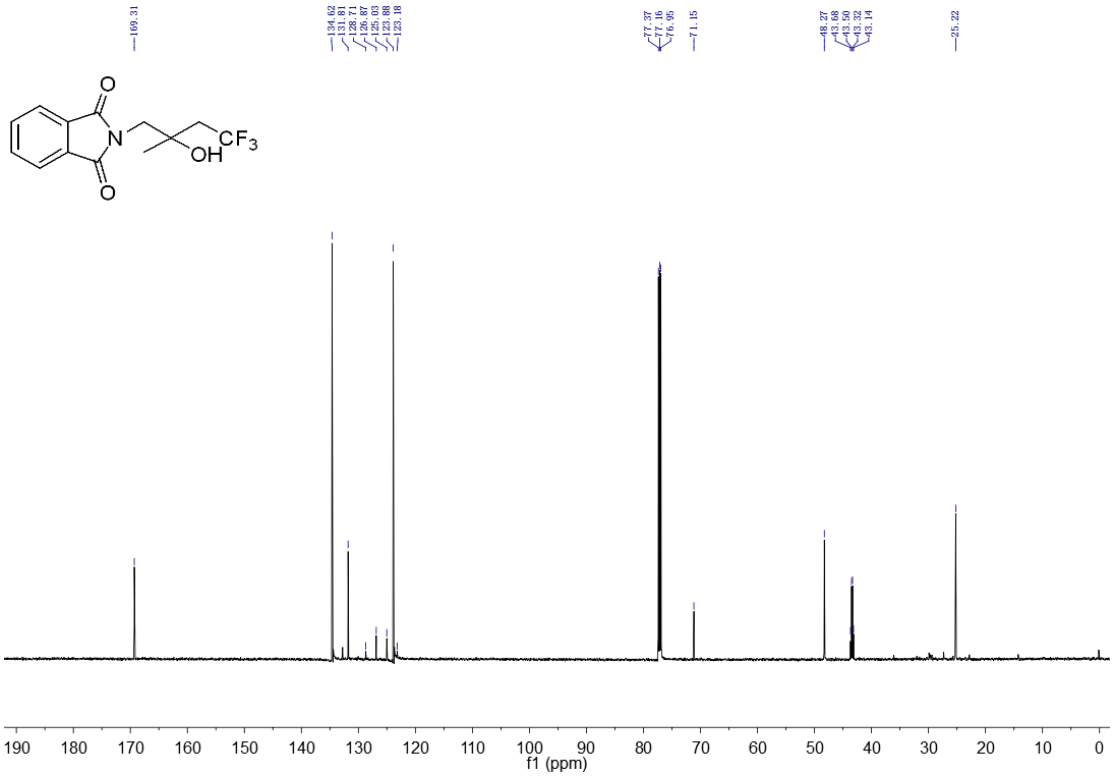
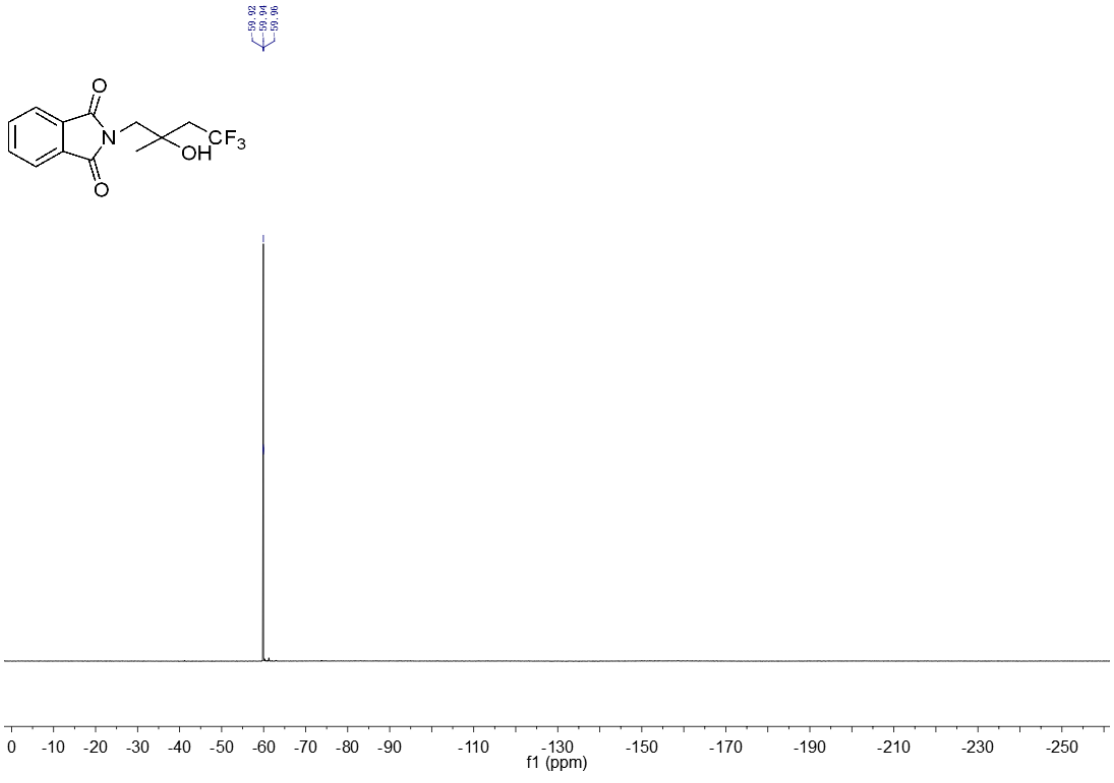


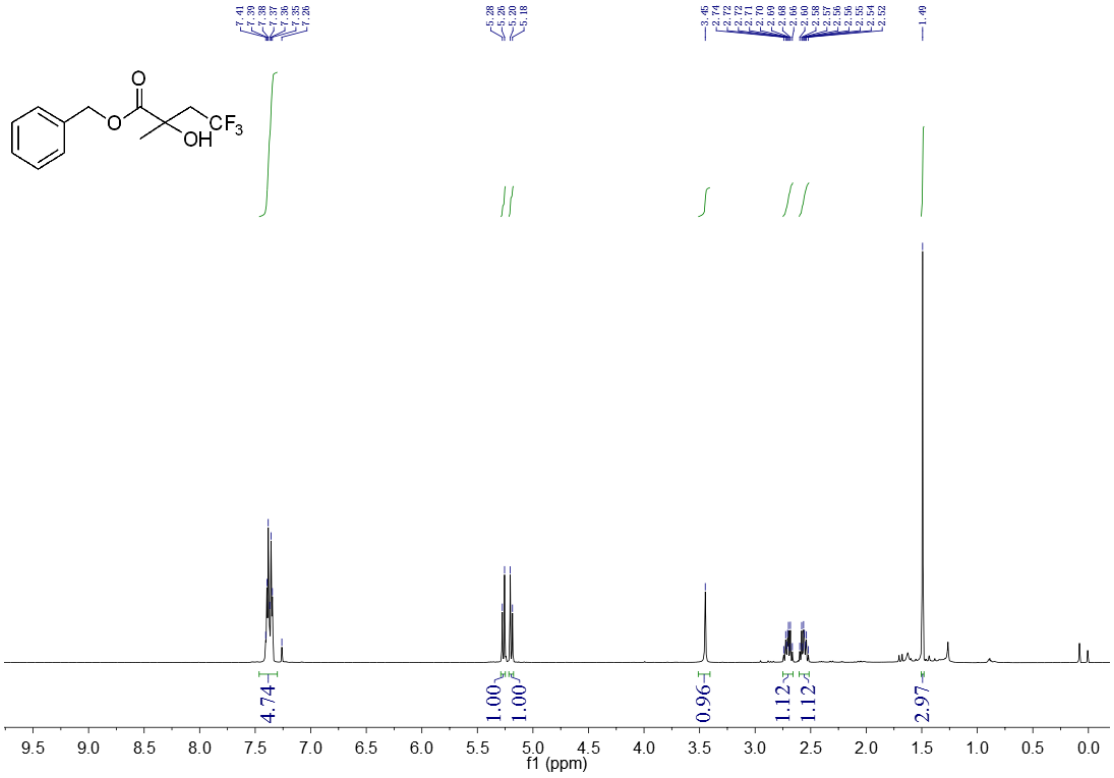
^{13}C NMR of **4k**



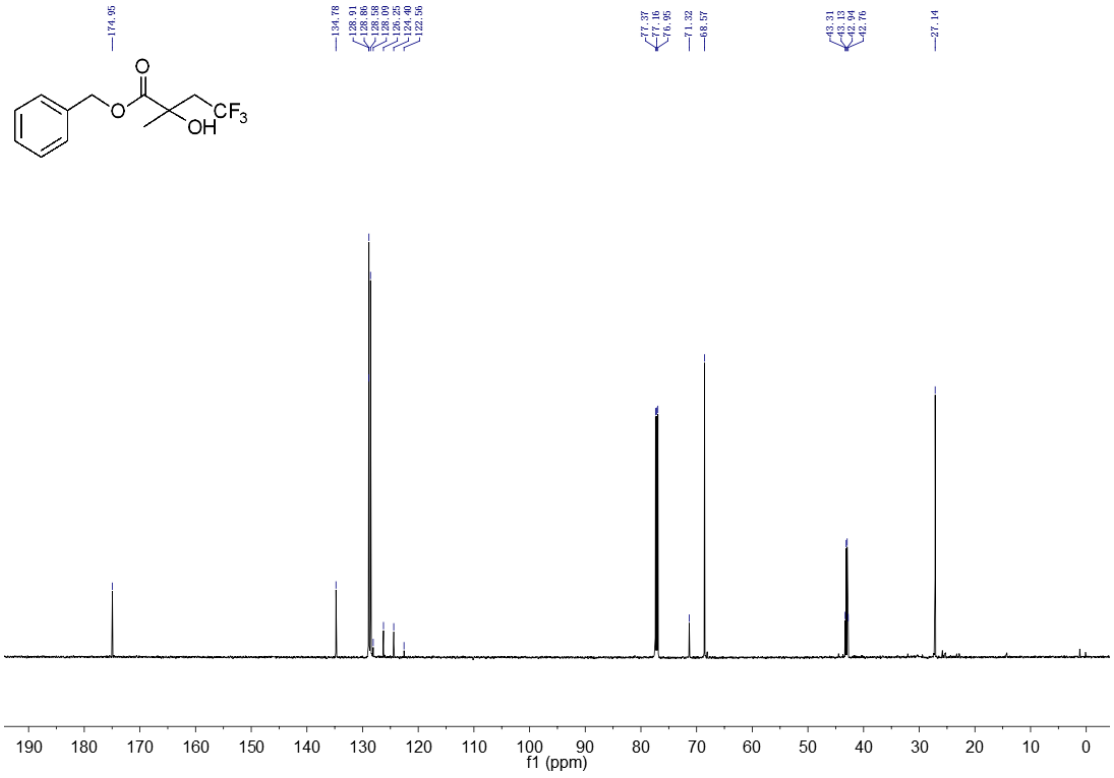
^{19}F NMR of **4k**



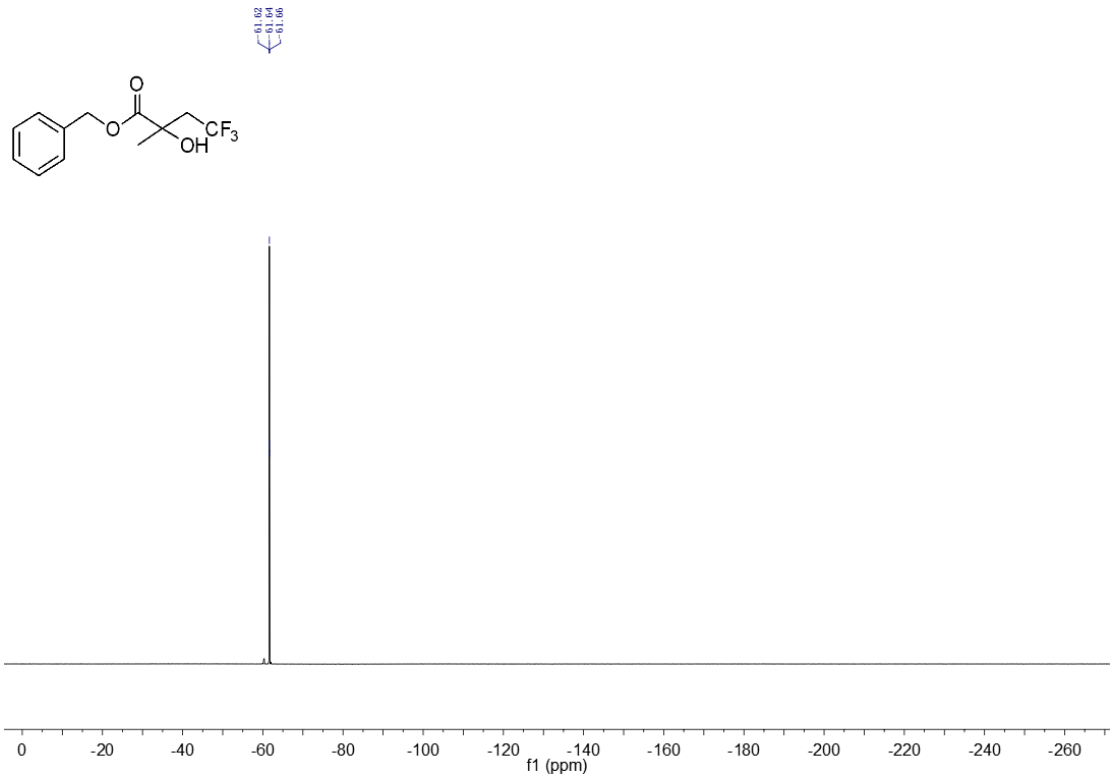
^{1}H NMR of **4l**



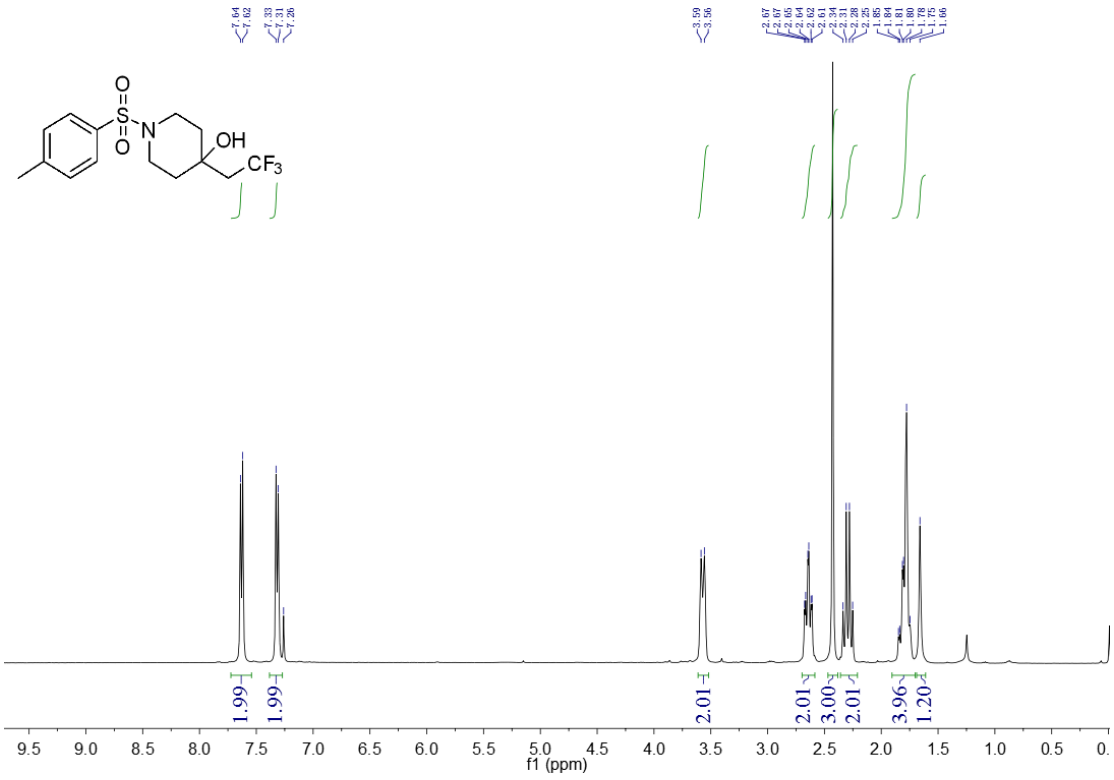
^{13}C NMR of **4l**



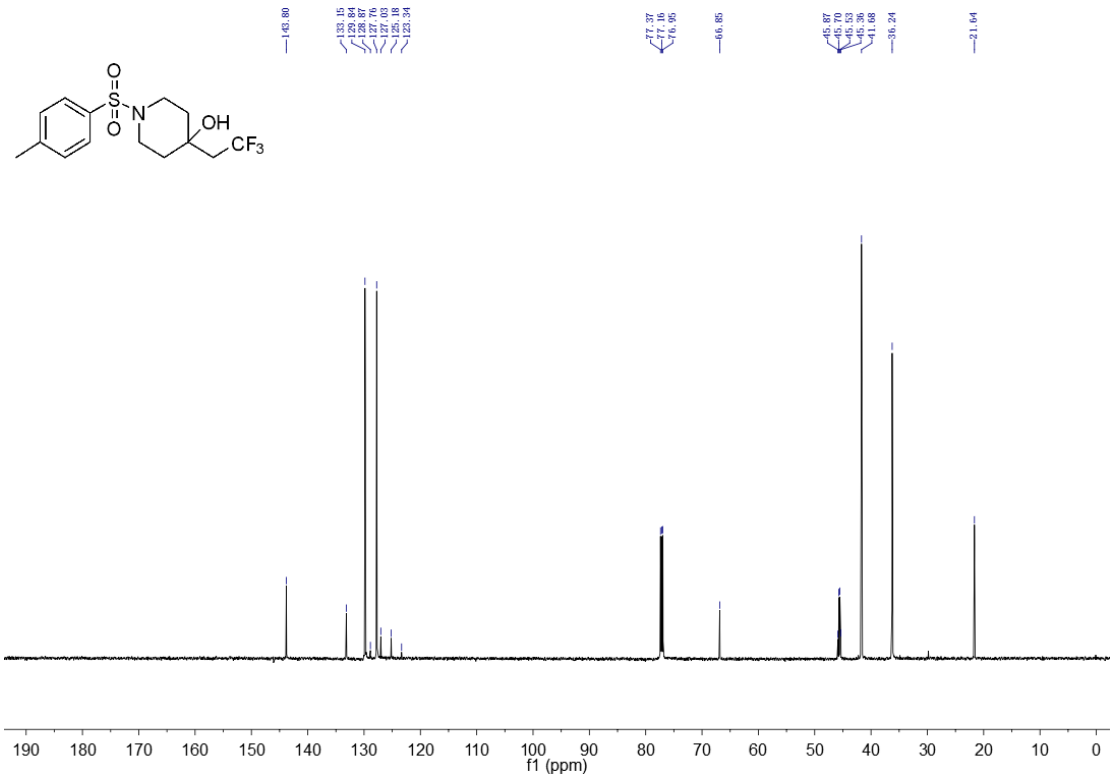
^{19}F NMR of **4l**



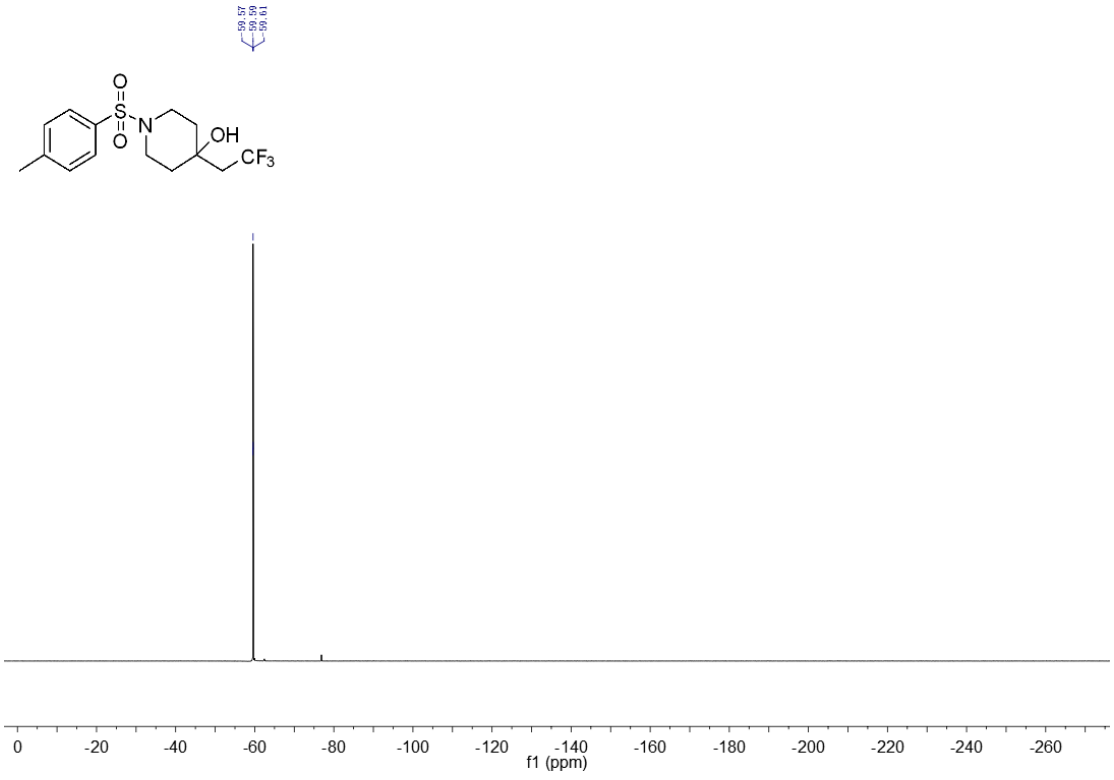
^{1}H NMR of **4m**



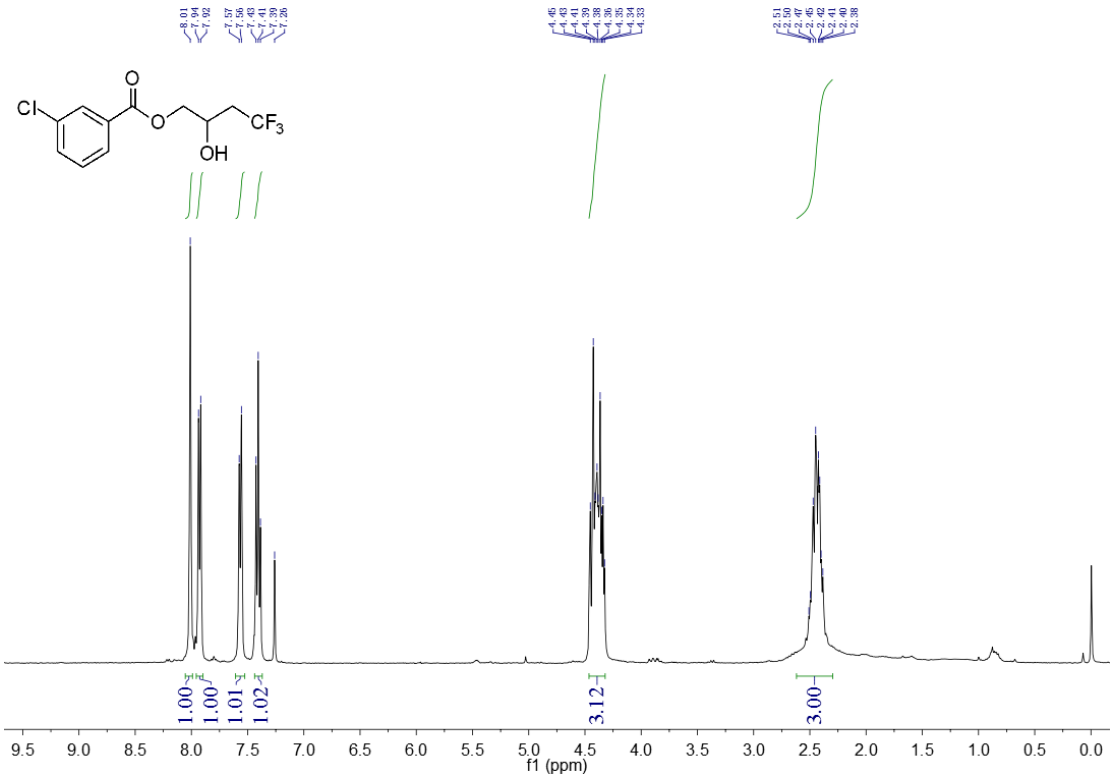
^{13}C NMR of **4m**



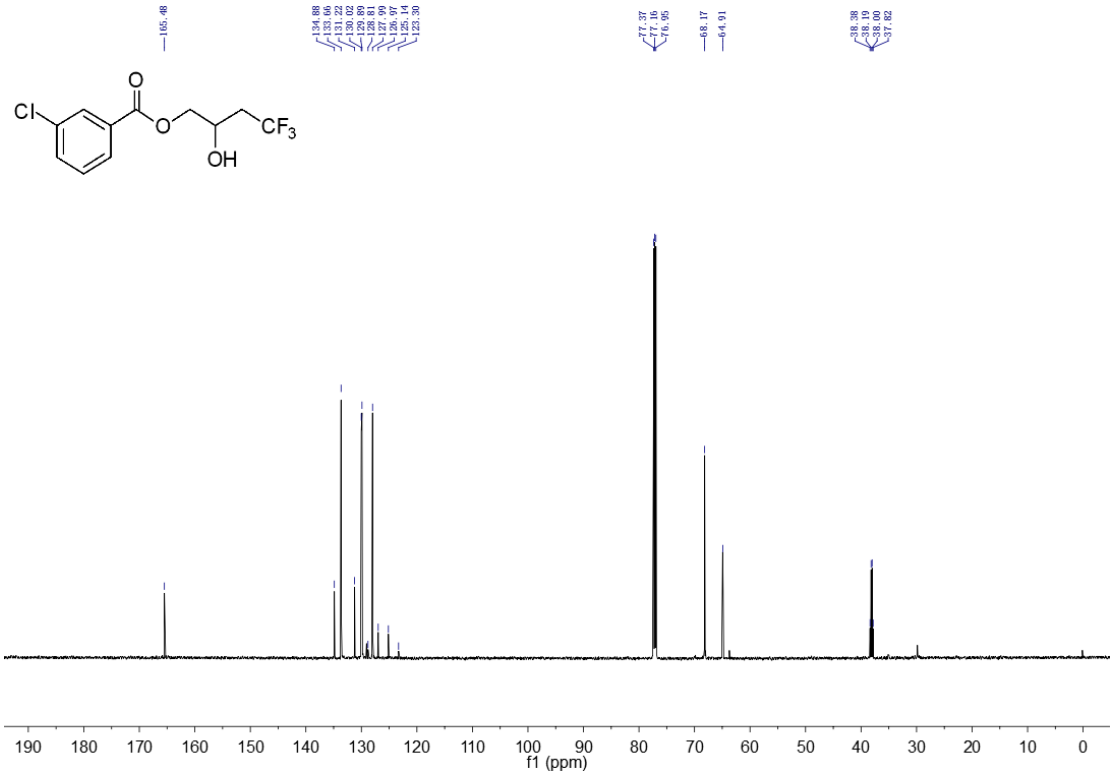
^{19}F NMR of **4m**



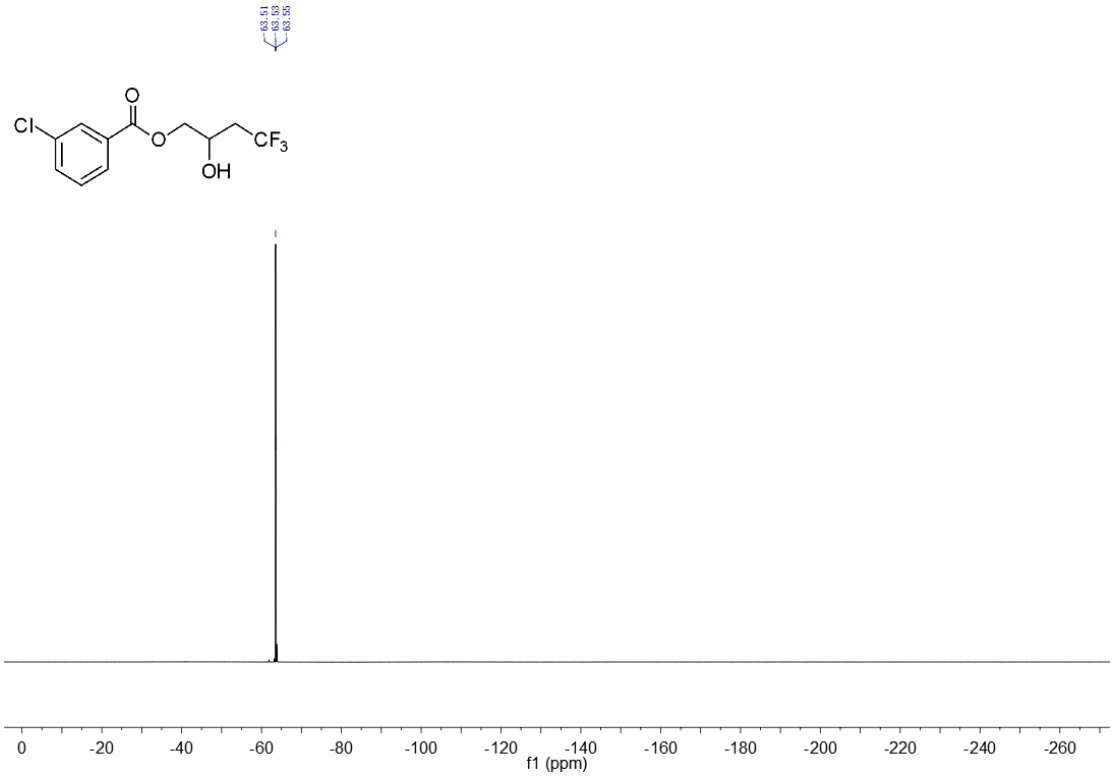
^{1}H NMR of **4n**



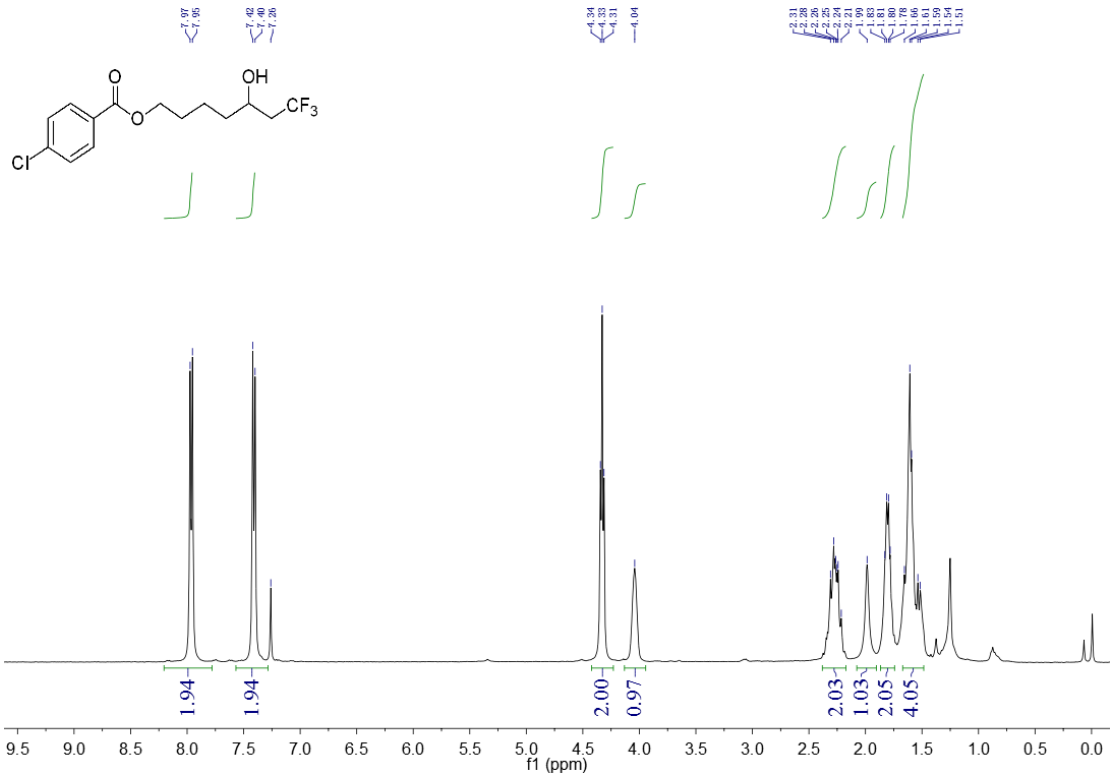
^{13}C NMR of **4n**



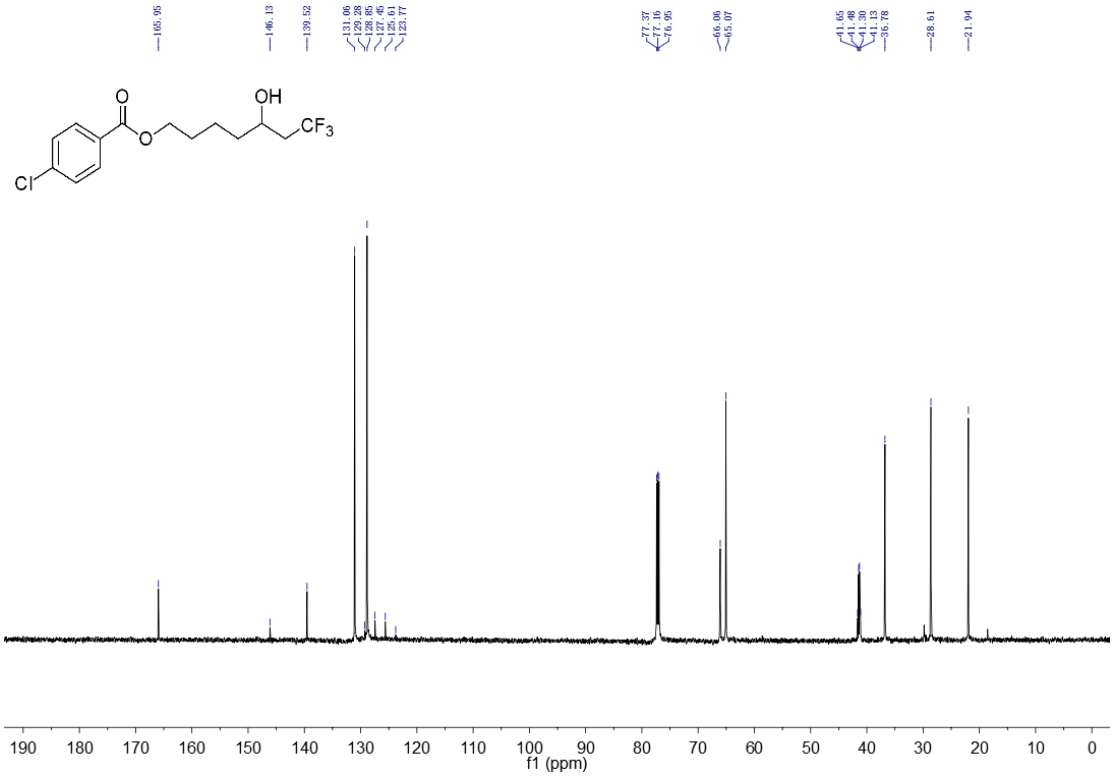
^{19}F NMR of **4n**



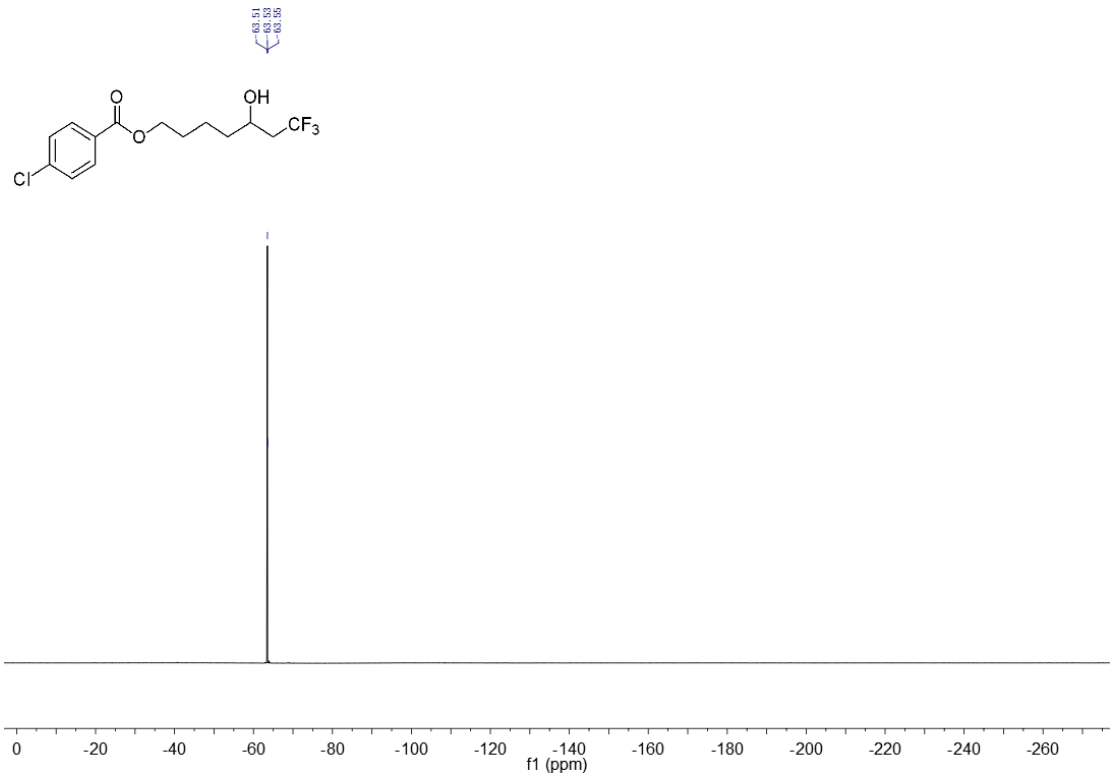
^{1}H NMR of **4o**



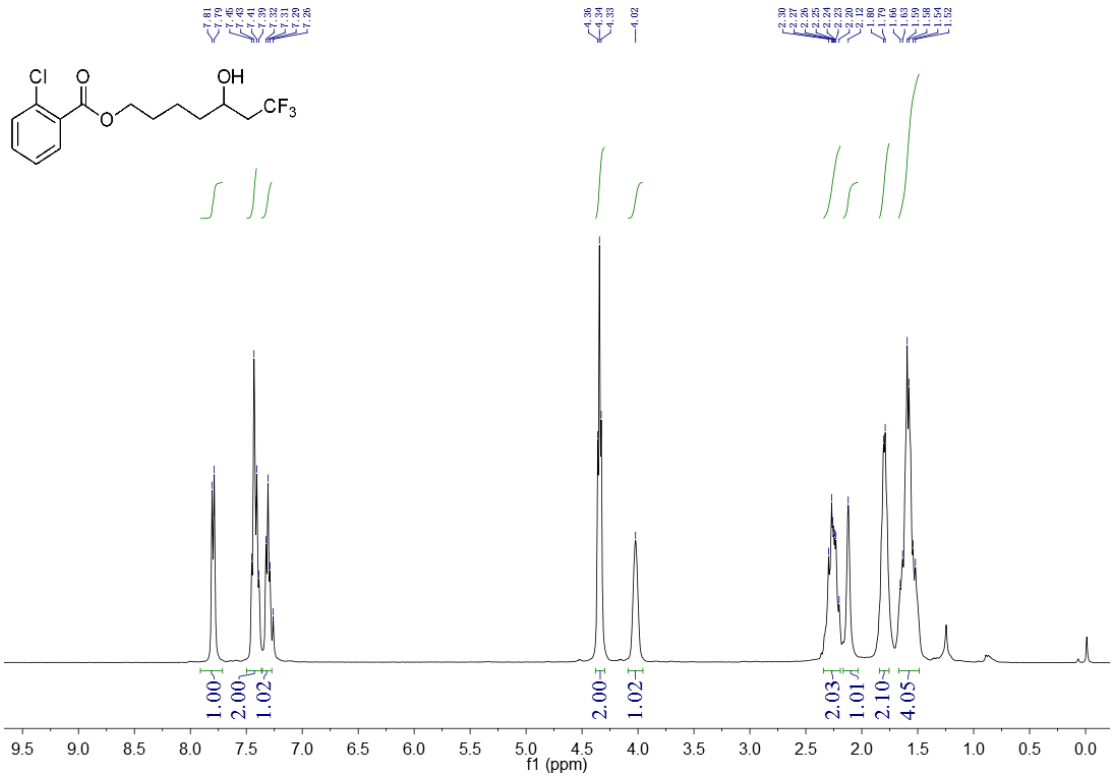
^{13}C NMR of **4o**



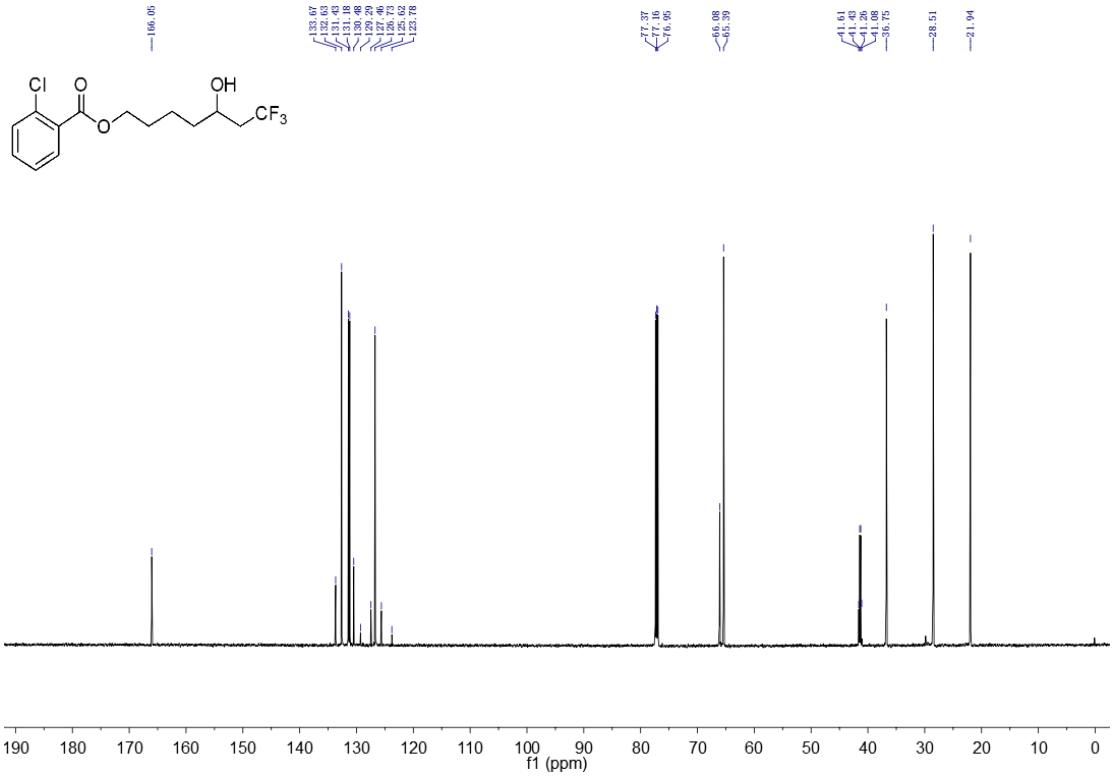
^{19}F NMR of **4o**



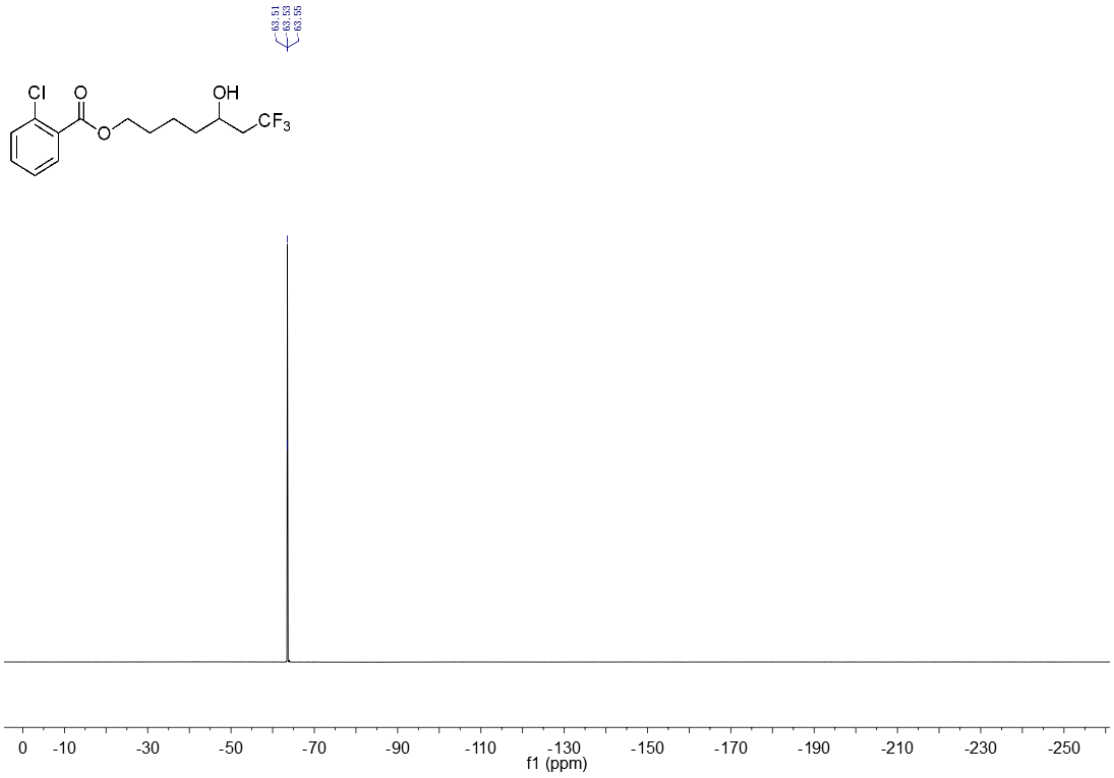
^{1}H NMR of **4p**



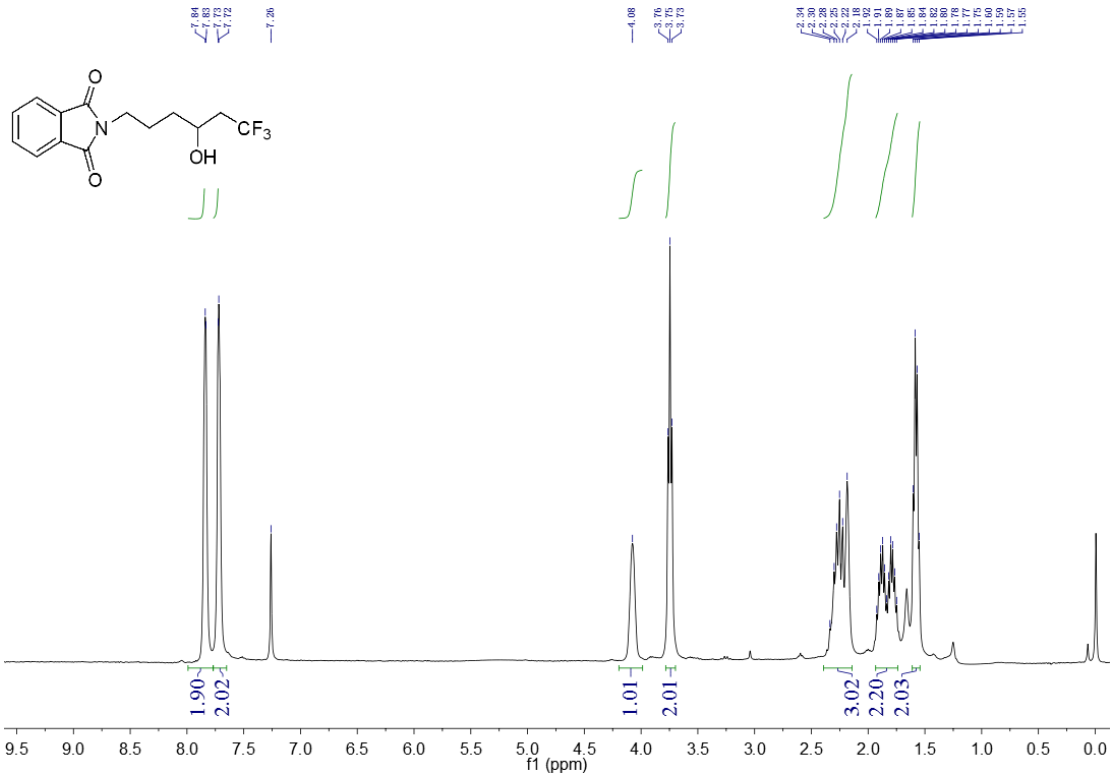
^{13}C NMR of **4p**



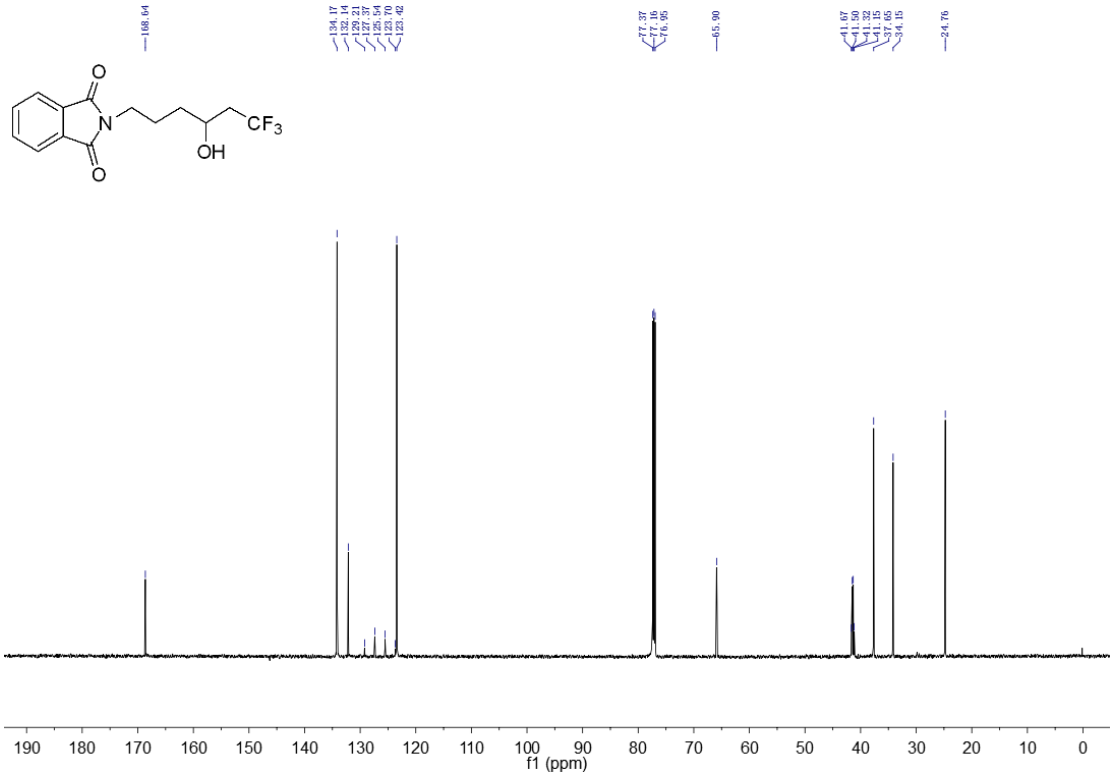
^{19}F NMR of **4p**



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



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



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