Supporting Information

For

Photoredox-catalysed chloro-, bromo- and trifluoromethylthio-trifluoromethylation of unactivated alkenes with sodium triflinate

Jing Fang,[†,#] Zhong-Kui Wang,[†,#] Shu-Wei Wu,[†] Wei-Guo Shen,[†] Gui-Zhen Ao[†] and Feng Liu*[,†,§]

[†]Jiangsu Key Laboratory of Translational Research and Therapy for Neuro-Psycho-Diseases and Department of Medicinal Chemistry, College of Pharmaceutical Sciences, Soochow University, 199 Ren-Ai Road, Suzhou, Jiangsu 215123, People's Republic of China

[§]Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

[#]These authors contributed equally to this work.

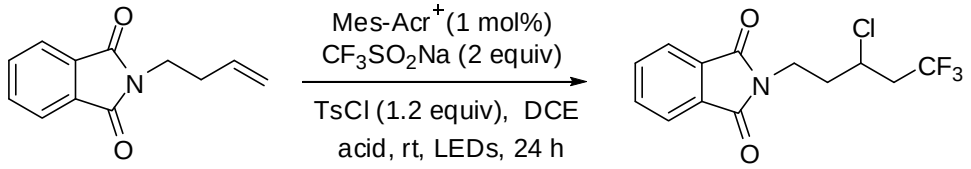
E-mail: fliu2@suda.edu.cn

Table of Contents

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). Mass spectroscopy data of the products were collected on a GCT PremierTM (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 were purchased or readily prepared according to known methods (*J. Org. Chem*. **2009**, 74, 2854; *Org. Lett.* **2016**. 18, 5368; *Angew. Chem., Int. Ed.* **2011.** 50, 5541).

2. Screening of organic acids and solvents

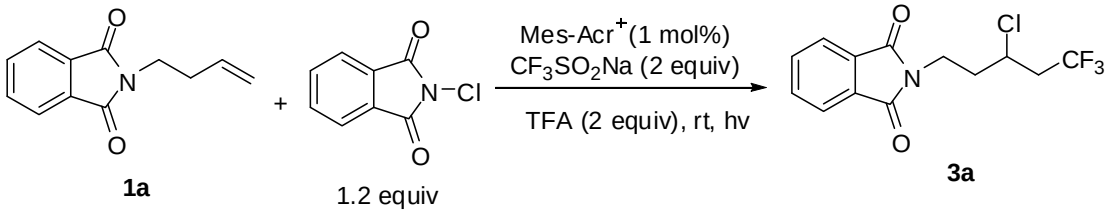


1a **3a**

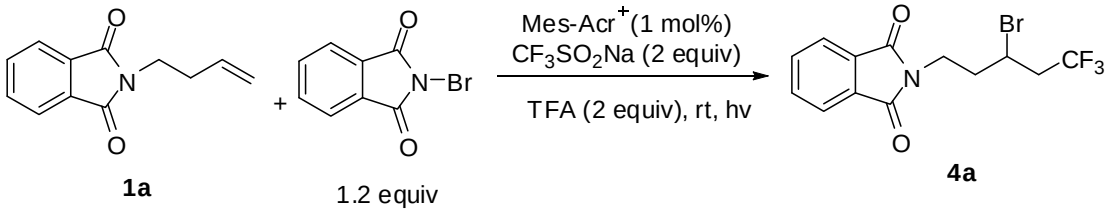
Entry[a]	LEDs	Catalyst	Acid (equiv)	Solvent	Yield (%)[b]
1	White	Mes-Acr$^+$	---	DCE	34
2	White	Mes-Acr$^+$	HCO_2H (2)	DCE	42
3	White	Mes-Acr$^+$	$PhCO_2H$ (2)	DCE	27
4	White	Mes-Acr$^+$	AcOH (2)	DCE	55
5	White	Mes-Acr$^+$	TsOH (2)	DCE	25
6	White	Mes-Acr$^+$	TfOH (2)	DCE	<5
7	**White**	**Mes-Acr$^+$**	**TFA (2)**	**DCE**	**62**
8	White	Mes-Acr$^+$	TFA (4)	DCE	55
9	White	Mes-Acr$^+$	TFA (8)	DCE	33
10	White	Mes-Acr$^+$	TFA (2)	DMSO	<5
11	White	Mes-Acr$^+$	TFA (2)	DMF	<5
12	White	Mes-Acr$^+$	TFA (2)	CH_3CN	23
13	White	Mes-Acr$^+$	TFA (2)	Acetone	27

[a]**1a** (0.4 mmol), Mes-Acr$^+$ (1 mol%), TsCl (0.48 mmol), CF_3SO_2Na (0.8 mmol), Acid (0.8 mmol), solvent (4 mL), Argon balloon, 5 W LEDs. [b]Isolated yield.

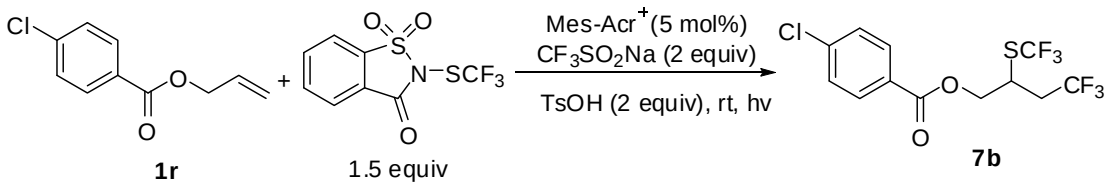
3. Typical experimental procedure



To a suspension of **1a** (80.4 mg, 0.4 mmol), CF_3SO_2Na (124.8 mg, 0.8 mmol) and *N*-Methyl-9-mesityl acridinium perchlorate (1.6 mg, 0.004 mmol) in DCE (4 mL) was added *N*-chlorophthalimide (87 mg, 0.48 mmol) and TFA (91.2 mg, 0.8 mmol) at rt. The resulting mixture was stirred upon 5W white LEDs irradiation under argon balloon. 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 **3a** as a white solid (89.0 mg, 73% yield).



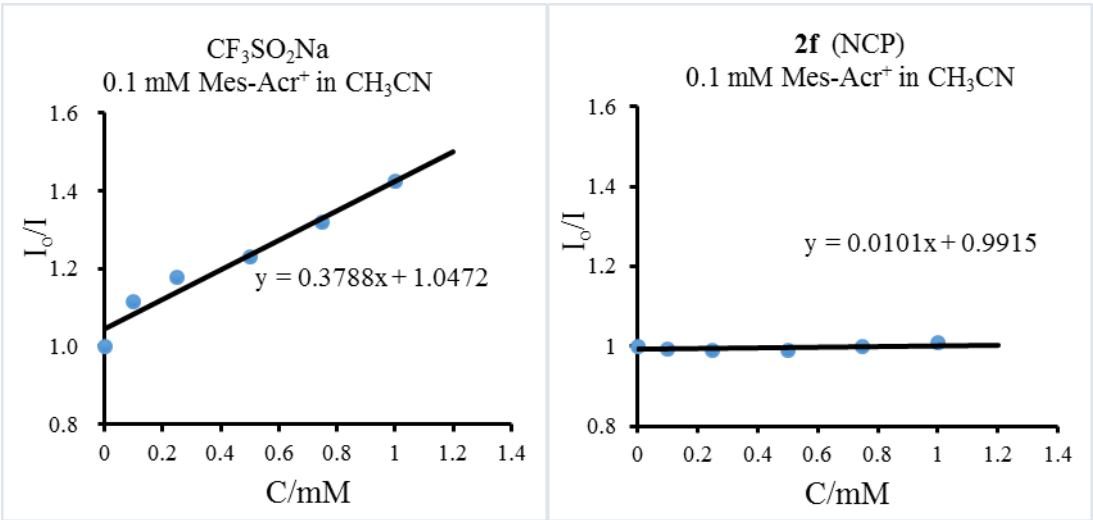
To a suspension of **1a** (80.4 mg, 0.4 mmol), CF_3SO_2Na (124.8 mg, 0.8 mmol) and *N*-Methyl-9-mesityl acridinium perchlorate (1.6 mg, 0.004 mmol) in DCE (4 mL) was added *N*-bromophthalimide (108.4 mg, 0.48 mmol) and TFA (91.2 mg, 0.8 mmol) at rt. The resulting mixture was stirred upon 5W white LEDs irradiation under argon balloon. 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 **4a** as a white solid (100.6 mg, 72% yield).

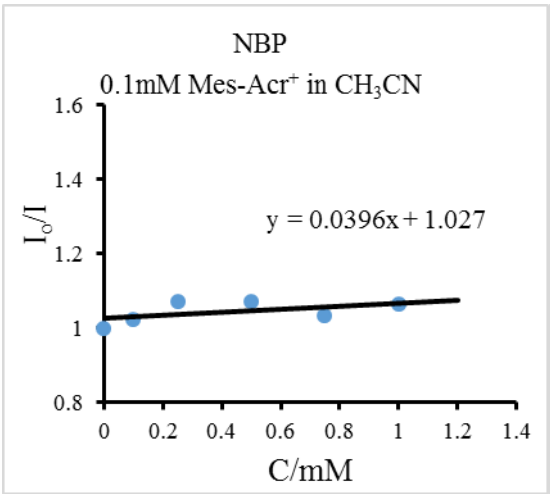


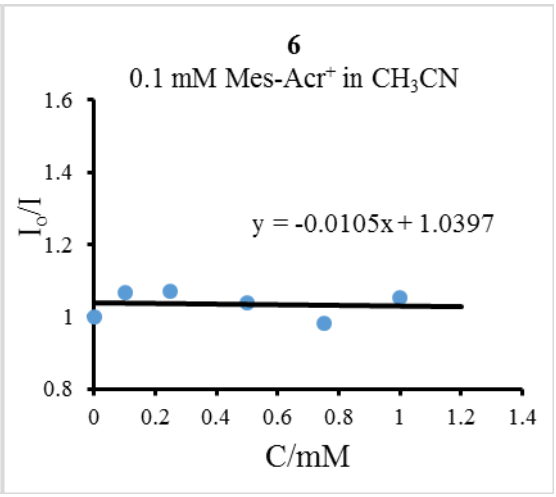
To a suspension of **1r** (78.4 mg, 0.4 mmol), CF_3SO_2Na (124.8 mg, 0.8 mmol) and *N*-Methyl-9-mesityl acridinium perchlorate (8 mg, 0.02 mmol) in DCE (4 mL) was added *N*-trifluoromethylthiosaccharin (170 mg, 0.6 mmol) and TsOH (137.6 mg, 0.8 mmol) at rt. The resulting mixture was stirred upon 5W white LEDs irradiation under argon balloon. 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 **7b** as a white solid (105.4 mg, 72% yield).

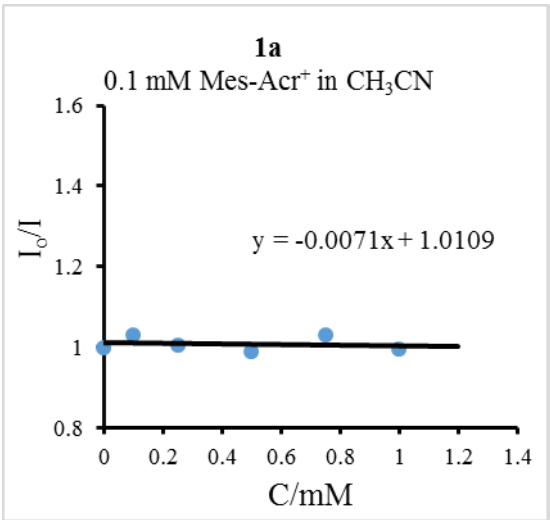
4. Fluorescence quenching experiments

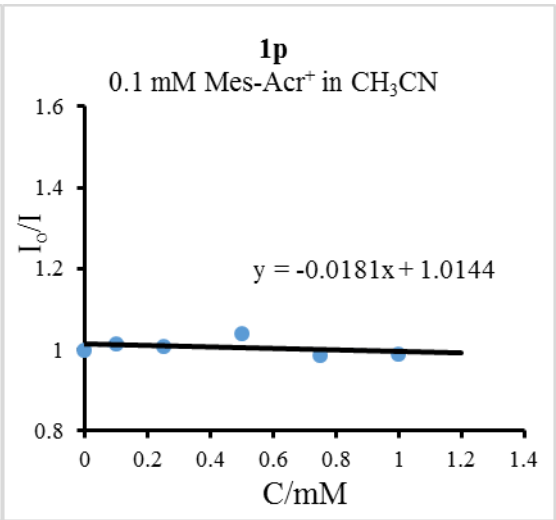
Emission intensities were recorded using LS55 Luminescence Spectrometer for all experiments. All Mes-Acr^+ solutions were excited at 450 nm and the emission intensity was collected at 500-550 nm. In a typical experiment, the CH_3CN solution of Mes-Acr^+ (0.1 mM) was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing with nitrogen for 10 min, the emission spectra of the samples were collected. The results showed that CF_3SO_2Na quenched the photoexcited Mes-Acr^+ effectively.

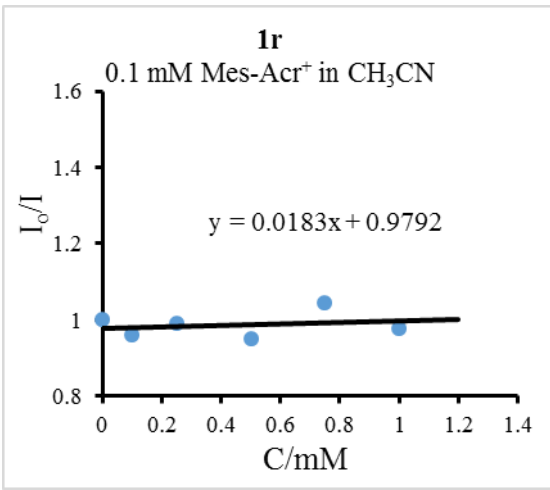


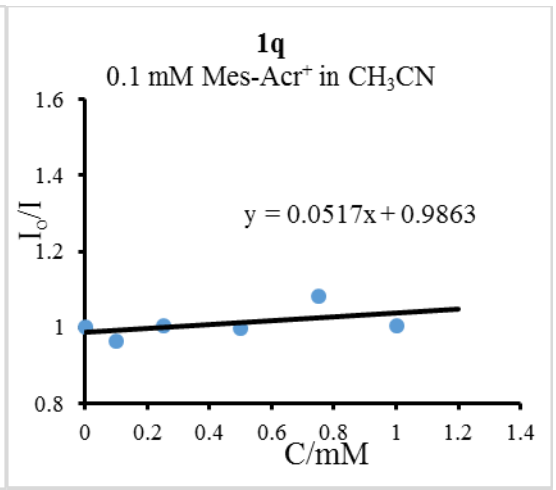

NBP
0.1mM Mes-Acr+ in CH3CN
y = 0.0396x + 1.027
I0/I
C/mM


6
0.1 mM Mes-Acr+ in CH3CN
y = -0.0105x + 1.0397
I0/I
C/mM


1a
0.1 mM Mes-Acr+ in CH3CN
y = -0.0071x + 1.0109
I0/I
C/mM


1p
0.1 mM Mes-Acr+ in CH3CN
y = -0.0181x + 1.0144
I0/I
C/mM

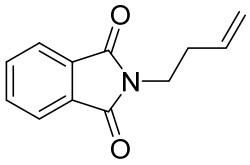

1r
0.1 mM Mes-Acr+ in CH3CN
y = 0.0183x + 0.9792
I0/I
C/mM


1q
0.1 mM Mes-Acr+ in CH3CN
y = 0.0517x + 0.9863
I0/I
C/mM

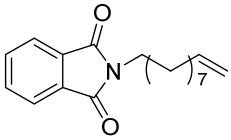
5. References for known products

Entry	Reference	Compound
1	S. H. Oh; S. B. Han. *Org. Lett*., **2014**, 16, 1310.	**3a, 3k, 3q**
2	W. An; S. B. Han. *Adv. Synth. Catal*., **2015**, 18, 3949.	**4a**
3	S. Mizuta; V. Gouverneu; *J. Am. Chem. Soc*., **2013**, 135, 2505.	**3s**

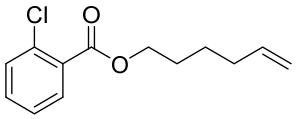
6. Characterization of the substrates and products



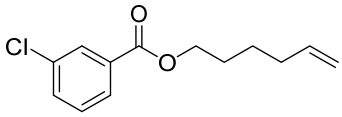
2-(But-3-en-1-yl)isoindoline-1,3-dione (1a): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.77 (m, 2H), 7.75 – 7.66 (m, 2H), 5.87 – 5.70 (m, 1H), 5.14 – 4.93 (m, 2H), 3.77 (t, *J* = 7.1 Hz, 2H), 2.52 – 2.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 134.6, 134.0, 132.2, 123.3, 117.7, 37.4, 33.0.



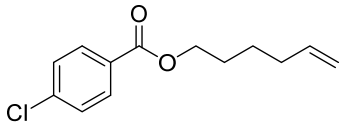
2-(Dec-9-en-1-yl)isoindoline-1,3-dione (1b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 2H), 7.75 – 7.63 (m, 2H), 5.87 – 5.69 (m, 1H), 5.03 – 4.82 (m, 2H), 3.66 (t, *J* = 7.3 Hz, 2H), 2.09 – 1.95 (m, 2H), 1.69 – 1.60 (m, 2H), 1.44 – 1.15 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.5, 139.3, 133.9, 132.2, 123.2, 114.2, 38.2, 33.9, 29.4, 29.2, 29.1, 29.0, 28.7, 26.9.



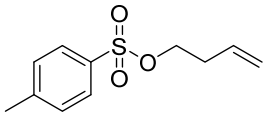
Hex-5-en-1-yl 2-chlorobenzoate (1c)： ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.35 (m, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 5.90 – 5.71 (m, 1H), 5.00 (dd, *J* = 22.4, 13.7 Hz, 2H), 4.34 (t, *J* = 6.5 Hz, 2H), 2.12 (q, *J* = 7.0 Hz, 2H), 1.87 – 1.71 (m, 2H), 1.64 – 1.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 138.4, 133.7, 132.5, 131.4, 131.1, 130.6, 126.7, 115.0, 65.6, 33.4, 28.1, 25.4.



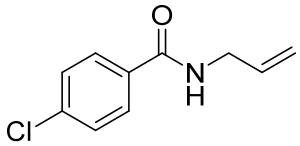
Hex-5-en-1-yl 3-chlorobenzoate (1d)： ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 5.94 – 5.72 (m, 1H), 5.01 (dd, *J* = 21.6, 13.7 Hz, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 2.13 (q, *J* = 7.0 Hz, 2H), 1.89 – 1.69 (m, 2H), 1.61 – 1.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 138.3, 134.5, 132.9, 132.3, 129.78, 129.74, 127.7, 115.0, 65.3, 33.4, 28.2, 25.3.



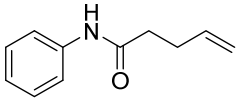
Hex-5-en-1-yl 4-chlorobenzoate (1e)： ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 5.90 – 5.72 (m, 1H), 5.10 – 4.90 (m, 2H), 4.31 (t, *J* = 6.5 Hz, 2H), 2.12 (q, *J* = 6.9 Hz, 2H), 1.86 – 1.69 (m, 2H), 1.62 – 1.47 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 139.4, 138.3, 131.0, 129.0, 128.8, 115.0, 65.2, 33.4, 28.2, 25.4.



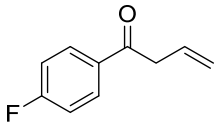
But-3-en-1-yl 4-methylbenzenesulfonate (1f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 5.72 – 5.56 (m, 1H), 5.10 – 4.98 (m, 2H), 4.03 (t, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 2.40 – 2.32 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.8, 133.1, 132.5, 129.9, 127.9, 118.2, 69.5, 33.2, 21.7.



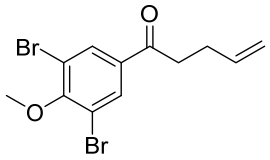
***N*-allyl-4-chlorobenzamide (1g)：** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 6.21 (brs, 1H), 6.02 – 5.83 (m, 1H), 5.38 – 5.10 (m, 2H), 4.08 (t, *J* = 5.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 137.9, 134.1, 132.9, 129.0, 128.5, 117.1, 42.7.



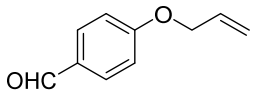
***N*-phenylpent-4-enamide (1h):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 5.94 – 5.76 (m, 1H), 5.20 – 4.94 (m, 2H), 2.54 – 2.36 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 138.0, 137.0, 129.0, 124.4, 120.1, 116.0, 36.9, 29.6.



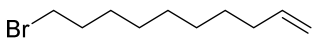
1-(4-Fluorophenyl)but-3-en-1-one (1i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.12 (t, *J* = 8.5 Hz, 2H), 6.15 – 5.98 (m, 1H), 5.29 – 5.13 (m, 2H), 3.72 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.5, 165.9 (d, J_{C-F} = 254.6 Hz), 133.1 (d, J_{C-F} = 3.0 Hz), 131.0 (d, J_{C-F} = 9.1 Hz), 130.9 , 119.0, 115.8 (d, J_{C-F} = 22.0 Hz), 43.5.



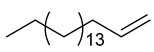
1-(3,5-Dibromo-4-methoxyphenyl)pent-4-en-1-one (1j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 2H), 5.96 – 5.77 (m, 1H), 5.16 – 4.93 (m, 2H), 3.93 (s, 3H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.47 (q, *J* = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ196.1, 158.1, 136.9, 135.0, 132.8, 118.8, 115.8, 60.9, 37.8, 28.0.



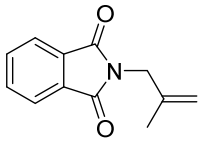
4-(Allyloxy)benzaldehyde (1k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.11 – 5.93 (m, 1H), 5.49 – 5.25 (m, 2H), 4.59 (d, *J* = 4.9 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.8, 163.6, 132.3, 132.0, 130.1, 118.3, 115.0, 69.0.



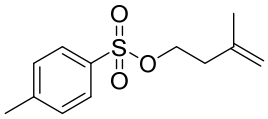
10-Bromodec-1-ene (1l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 – 5.70 (m, 1H), 5.07 – 4.86 (m, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.04 (q, *J* = 13.7, 6.8 Hz, 2H), 1.91 – 1.77 (m, 2H), 1.51 – 1.22 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.2, 114.3, 34.1, 33.9, 33.0, 29.4, 29.1, 29.0, 28.9, 28.3.



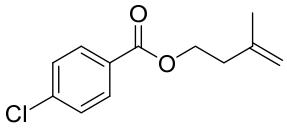
Octadec-1-ene (1m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 – 5.73 (m, 1H), 5.07 – 4.87 (m, 2H), 2.11 – 1.96 (m, 2H), 1.48 – 1.15 (m, 28H), 0.88 (t, *J* = 6.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, overlapping peaks) δ 139.4, 114.2, 34.0, 32.1, 29.9, 29.85, 29.81, 29.7, 29.6, 29.3, 29.1, 22.9, 14.3.



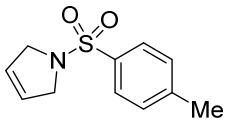
2-(2-Methylallyl)isoindoline-1,3-dione (1n)： ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.77 – 7.69 (m, 2H), 4.89 (s, 1H), 4.82 (s, 1H), 4.22 (s, 2H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 139.4, 134.1, 132.1, 123.5, 112.1, 43.4, 20.5.



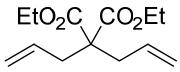
3-Methylbut-3-en-1-yl 4-methylbenzenesulfonate (1o): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.77 (s, 1H), 4.66 (s, 1H), 4.11 (t, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 2.33 (t, *J* = 6.7 Hz, 2H), 1.64 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.8, 140.2, 133.2, 129.9, 127.9, 113.1, 68.6, 36.8, 22.3, 21.7.



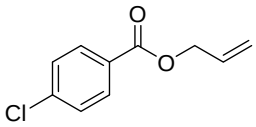
3-Methylbut-3-en-1-yl 4-chlorobenzoate (1p):^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 4.84 (s, 2H), 4.80 (s, 2H), 4.43 (t, *J* = 6.7 Hz, 2H), 2.47 (t, *J* = 6.7 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 141.7, 139.4, 131.1, 129.0, 128.8, 112.6, 63.5, 36.9, 22.6.



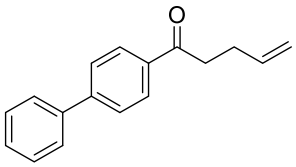
1-Tosyl-2,5-dihydro-1H-pyrrole (1r): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 5.64 (s, 2H), 4.11 (s, 4H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.6, 134.4, 129.9, 127.5, 125.6, 55.0, 21.6.



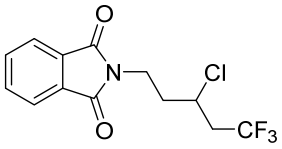
Diethyl 2,2-diallylmalonate (1s): ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.77 – 5.54 (m, 2H), 5.14 – 5.02 (m, 4H), 4.21 – 4.10 (m, 4H), 2.62 (d, *J* = 7.4 Hz, 4H), 1.29 – 1.17 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 132.4, 119.2, 61.3, 57.4, 36.9, 14.2.



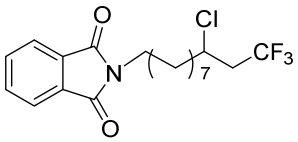
Allyl 4-chlorobenzoate (1t): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 6.10 – 5.95 (m, 1H), 5.48 – 5.23 (m, 2H), 4.81 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 139.5, 132.1, 131.1, 128.8, 128.7, 118.6, 65.9.



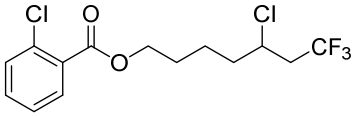
1-([1,1'-Biphenyl]-4-yl)pent-4-en-1-one (1u): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.44 – 7.38 (m, 1H), 6.06 – 5.85 (m, 1H), 5.24 – 4.98 (m, 2H), 3.11 (t, *J* = 7.3 Hz, 2H), 2.61 – 2.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 145.8, 140.0, 137.5, 135.8, 129.1, 128.8, 128.3, 127.38, 127.36, 115.4, 37.9, 28.4.



2-(3-Chloro-5,5,5-trifluoropentyl)isoindoline-1,3-dione (3a): White solid; m.p. 64-66 ℃; 73% yield (89 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.80 (m, 2H), 7.80 – 7.67 (m, 2H), 4.25 – 4.09 (m, 1H), 4.01 – 3.79 (m, 2H), 2.76 – 2.55 (m, 2H), 2.38 – 2.21 (m, 1H), 2.21 – 2.05 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 134.3, 132.1, 125.2 (q, J_{C-F} =277.6), 123.6, 51.5 (q, J_{C-F} = 3.1 Hz), 42.4 (q, J_{C-F} = 28.6 Hz), 36.6, 35.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.65 (t, *J* = 10.1 Hz, 3F).

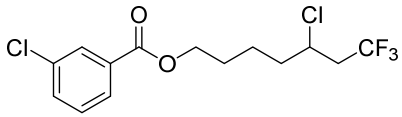


2-(9-Chloro-11,11,11-trifluoropentyl)isoindoline-1,3-dione (3b): White solid; m.p. 49-51 ℃; 84% yield (131 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.77 (m, 2H), 7.77 – 7.62 (m, 2H), 4.23 – 4.02 (m, 1H), 3.66 (t, *J* = 7.1 Hz, 2H), 2.71 – 2.41 (m, 2H), 1.91 – 1.60 (m, 4H), 1.60 – 1.38 (m, 2H), 1.36 – 1.17 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 134.0, 132.3, 125.4 (q, J_{C-F} = 277.5 Hz), 123.2, 54.3 (q, J_{C-F} = 3.1 Hz), 42.5 (q, J_{C-F} = 28.3 Hz), 38.12, 38.08, 29.3, 29.1, 28.8, 28.6, 26.8, 25.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.83 (t, *J* = 10.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2919, 2850, 1688, 1600, 831; HRMS (CI) calcd $C_{19}H_{24}NO_2F_3Cl^{35}$ $[M + H]^+$: 390.1448, found: 390.1454.

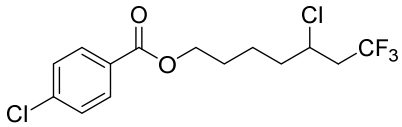


5-Chloro-7,7,7-trifluoroheptyl 2-chlorobenzoate (3c): Colorless oil; 74% yield (101 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.38 (m, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 4.36 (t, *J* = 6.1 Hz, 2H), 4.22 – 4.03 (m, 1H), 2.75 – 2.43 (m, 2H), 1.99 – 1.69 (m, 5H), 1.69 – 1.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 133.7, 132.7, 131.5, 131.2, 130.4, 126.7, 125.3 (d, J_{C-F} = 277.6 Hz), 65.2,

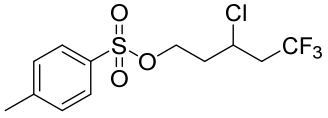
54.0 (q, J_{C-F} = 3.1 Hz), 42.6 (q, J_{C-F} = 28.4 Hz), 37.7, 28.0, 22.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.78 (t, J = 10.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2960, 1728, 1436, 1118, 747; HRMS (CI) calcd $C_{14}H_{16}O_2F_3Cl^{35}_2$ $[M + H]^+$: 343.0479, found: 343.0480.



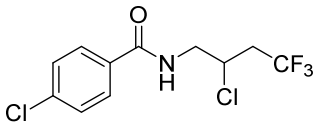
5-Chloro-7,7,7-trifluoroheptyl 3-chlorobenzoate (3d): Colorless oil; 65% yield (90 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.92 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 4.35 (t, J = 6.1 Hz, 2H), 4.21 – 4.08 (m, 1H), 2.74 – 2.47 (m, 2H), 2.00 – 1.68 (m, 5H), 1.68 – 1.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 134.7, 133.1, 132.1, 129.9, 129.8, 127.8, 125.3 (q, J_{C-F} = 277.6 Hz), 65.0, 54.0 (q, J_{C-F} = 3.1 Hz), 42.6 (q, J_{C-F} = 28.5 Hz), 37.7, 28.1, 22.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.76 (t, J = 10.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2957, 1720, 1427, 1279, 748; HRMS (CI) calcd $C_{14}H_{16}O_2F_3Cl^{35}_2$ $[M + H]^+$: 343.0479, found: 343.0485.



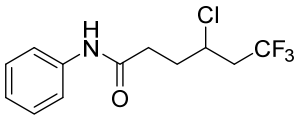
5-Chloro-7,7,7-trifluoroheptyl 4-chlorobenzoate (3e): Colorless oil; 64% yield (88 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 4.34 (t, J = 6.1 Hz, 2H), 4.22 – 4.06 (m, 1H), 2.75 – 2.46 (m, 2H), 2.00 – 1.87 (m, 1H), 1.88 – 1.69 (m, 4H), 1.68 – 1.56 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$, overlapping peaks) δ 165.8, 139.5, 131.1, 128.9, 125.3 (q, J_{C-F} = 277.6 Hz), 64.9, 54.0, 42.6 (q, J_{C-F} = 28.5 Hz), 37.7, 28.1, 22.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -59.07 (t, J = 10.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2957, 1718, 1390, 1241, 759; HRMS (CI) calcd $C_{14}H_{16}O_2F_3Cl^{35}_2$ $[M + H]^+$: 343.0479, found: 343.0483.



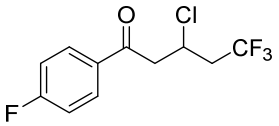
3-Chloro-5,5,5-trifluoropentyl 4-methylbenzenesulfonate (3f): Yellow oil; 86% yield (114 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.9 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 4.29 – 4.21 (m, 2H), 4.21 – 4.14 (m, 1H), 2.68 – 2.48 (m, 2H), 2.46 (s, 3H), 2.35 – 2.18 (m, 1H), 2.03 – 1.87 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.3, 132.7, 130.1 , 128.1, 125.0 (q, J_{C-F} = 277.7 Hz), 66.4, 50.0, 42.4 (q, J_{C-F} = 28.9 Hz), 37.2, 21.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.63 (t, J = 10.0 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2962, 2923, 1598, 1175, 775; HRMS (CI) calcd $C_{12}H_{15}O_3F_3SCl^{35}$ $[M + H]^+$: 311.0383, found: 331.0381.



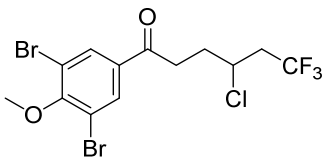
4-Chloro-N-(2-chloro-4,4,4-trifluorobutyl)benzamide (3g): White solid; m.p. 132-134 ℃; 69% yield (83 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.53 (brs, 1H), 4.46 – 4.29 (m, 1H), 4.04 – 3.92 (m, 1H), 3.72 – 3.59 (m, 1H), 2.78 – 2.55 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.8, 138.5, 132.1, 129.2, 128.6, 125.2 (q, J_{C-F} = 277.4 Hz), 53.7, 46.0, 40.2 (q, J_{C-F} = 29.4 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.68 (t, *J* = 10.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3302, 2922, 1637, 1185, 759; HRMS (CI) calcd $C_{11}H_{11}NOF_3Cl^{35}{}_2$ $[M + H]^+$: 300.0170, found: 300.0172.



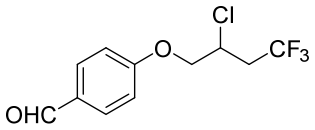
4-Chloro-6,6,6-trifluoro-N-phenylhexanamide (3h): Colorless oil; 74% yield (83 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 2H), 7.41 (brs, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 4.31 – 4.17 (m, 1H), 2.79 – 2.47 (m, 4H), 2.45 – 2.26 (m, 1H), 2.16 – 1.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 137.7, 129.2, 125.2 (q, J_{C-F} = 277.7 Hz), 124.7, 120.1, 53.8 (q, J_{C-F} = 3.1 Hz), 42.8 (q, J_{C-F} = 28.7 Hz), 33.7, 33.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.62 (t, *J* = 10.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3301, 2924, 1773, 1543, 692; HRMS (CI) calcd $C_{12}H_{14}NOF_3Cl^{35}$ $[M + H]^+$: 280.0716, found: 280.0711.



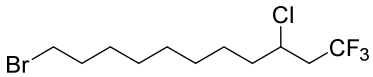
3-Chloro-5,5,5-trifluoro-1-(4-fluorophenyl)pentan-1-one (3i): Colorless oil; 54% yield (58 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.2, 5.6 Hz, 2H), 7.17 (t, *J* = 8.4 Hz, 2H), 4.82 – 4.71 (m, 1H), 3.60 (dd, J = 17.6, 7.0 Hz, 1H), 3.40 (dd, J = 17.6, 6.0 Hz, 1H), 2.91 – 2.63 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 193.9, 166.3 (d, J_{C-F} = 256.2 Hz), 132.78 (d, J_{C-F} = 2.9 Hz), 130.6 (d, J_{C-F} = 9.4 Hz), 125.3 (q, J_{C-F} = 277.8 Hz), 116.2 (d, J_{C-F} = 22.0 Hz), 48.4, 46.1, 41.7 (q, J_{C-F} = 28.8 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.48 (t, *J* = 10.1 Hz, 3F), -103.68 – -103.74 (m, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 2961, 2924, 1686, 1598, 669; HRMS (CI) calcd $C_{11}H_{10}OF_4Cl^{35}$ $[M + H]^+$: 269.0356, found: 269.0351.



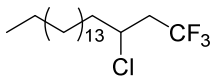
4-Chloro-1-(3,5-dibromo-4-methoxyphenyl)-6,6,6-trifluorohexan-1-one (3j): Yellow oil; 53% yield (95 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 2H), 4.35–4.16 (m, 1H), 3.95 (s, 3H), 3.18 (t, J = 6.8 Hz, 2H), 2.86 – 2.54 (m, 2H), 2.46 – 2.31 (m, 1H), 2.13–1.95 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.2, 158.4, 134.6, 132.8, 125.2 (q, J_{C-F} = 277.7 Hz), 118.9, 61.0, 53.7, 42.9 (q, J_{C-F} = 28.7 Hz), 35.0, 32.1; ^{19}F NMR (564 MHz,$CDCl_3$) δ -58.98 (t, J = 10.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2930, 1689, 1382, 737; HRMS (CI) calcd $C_{13}H_{13}O_2F_3Cl^{35}Br^{79}_2$ $[M + H]^+$: 450.8923, found: 450.8925.



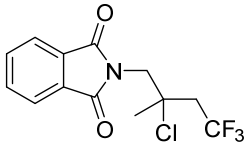
4-(2-Chloro-4,4,4-trifluorobutoxy)benzaldehyde (3k): Colorless oil; 62% yield (66 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.87 (d, J = 8.5 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 4.48 – 4.38 (m, 1H), 4.32 (dd, J = 9.9, 4.8 Hz, 1H), 4.20 (dd, J = 9.8, 6.5 Hz, 1H), 3.05 – 2.84 (m, 1H), 2.79 – 2.56 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.7, 162.7, 132.2, 131.0, 125.3 (q, J_{C-F} = 277.3 Hz), 115.0, 70.6, 50.3, 39.1 (q, J_{C-F} = 29.4 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -61.32 (t, J = 10.1 Hz, 3F).



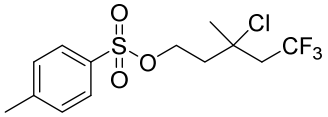
11-Bromo-3-chloro-1,1,1-trifluoroundecane (3l): Colorless oil; 65% yield (84 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.15 – 4.07 (m, 1H), 3.40 (t, J = 6.8 Hz, 2H), 2.66 – 2.48 (m, 2H), 1.89 – 1.79 (m, 3H), 1.79 – 1.70 (m, 1H), 1.59 – 1.41 (m, 4H), 1.37 – 1.30 (m, 4H), 0.90 – 0.85 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 125.4 (q, J_{C-F} = 277.5 Hz), 54.3, 42.6 (q, J_{C-F} = 28.4 Hz), 38.2, 34.0, 32.9, 29.3, 28.9, 28.8, 28.2, 26.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.90 (t, J = 10.3 Hz, 3F).



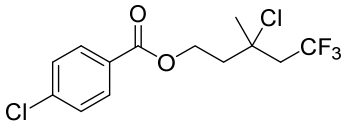
3-Chloro-1,1,1-trifluorononadecane (3m): Colorless oil; 72% yield (103 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.14 – 4.08 (m, 1H), 2.67 – 2.49 (m, 2H), 1.86 – 1.79 (m, 1H), 1.78 – 1.72 (m, 1H), 1.59 – 1.51 (m, 2H), 1.49 – 1.40 (m, 2H), 1.37 – 1.24 (m, 24H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$, overlapping peaks) δ 125.5 (q, J_{C-F} = 277.5 Hz), 54.3, 42.6 (q, J_{C-F} = 28.3 Hz), 38.3, 32.1, 29.89, 29.87, 29.81, 29.79, 29.7, 29.6, 29.5, 29.1, 26.1, 22.9, 14.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.94 (t, J = 10.3 Hz, 3F).



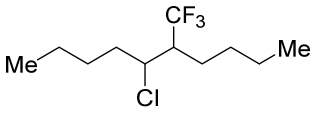
2-(2-Chloro-4,4,4-trifluoro-2-methylbutyl)isoindoline-1,3-dione (3n): White solid; m.p. 104-106 ℃; 60% yield (73 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.80 – 7.75 (m, 2H), 4.04 (s, 2H), 2.89 – 2.60 (m, 2H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 134.6, 131.8, 125.2 (q, J_{C-F} = 278.4 Hz), 123.9, 65.3, 49.5, 45.5 (q, J_{C-F} = 28.4 Hz), 28.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.00 (t, J = 10.5Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2989, 1712, 1384, 1098, 715; HRMS (CI) calcd $C_{13}H_{12}NO_2F_3Cl^{35}$ $[M + H]^+$: 306.0509, found: 306.0514.



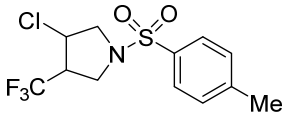
3-Chloro-5,5,5-trifluoro-3-methylpentyl 4-methylbenzenesulfonate (3o): Yellow oil; 85% yield (117 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 4.29 (t, J = 6.4 Hz, 2H), 2.64 (q, J = 10.6 Hz, 2H), 2.45 (s, 3H), 2.34 – 2.14 (m, 2H), 1.67 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.3, 132.8, 130.1, 128.0, 124.8 (q, J_{C-F} = 278.7 Hz), 66.6, 64.9, 47.1 (q, J_{C-F} = 27.9 Hz), 42.3, 30.3, 21.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.66 (t, J = 10.6 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2928, 1598, 1364, 1210, 764; HRMS (CI) calcd $C_{13}H_{17}O_3F_3SCl^{35}$ $[M + H]^+$: 345.0539, found: 345.0545.



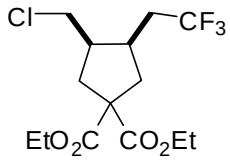
3-Chloro-5,5,5-trifluoro-3-methylpentyl 4-chlorobenzoate (3p): Colorless oil; 88% yield (115 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 4.68 – 4.49 (m, 2H), 2.88 – 2.65 (m, 2H), 2.48 – 2.25 (m, 2H), 1.78 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.7, 139.7, 131.1, 128.9, 127.7, 125.0 (q, J_{C-F} = 278.7 Hz), 65.4, 61.7, 47.2 (q, J_{C-F} = 27.8 Hz), 42.1, 30.5; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.61 (t, J = 10.7 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2972, 1720, 1595, 1268, 758; HRMS (CI) calcd $C_{13}H_{14}O_2F_3Cl^{35}{}_2$ $[M + H]^+$: 329.0323, found: 329.0328.



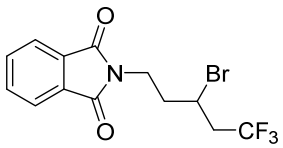
5-Chloro-6-(trifluoromethyl)decane (3q): yield: 63% (1.2:1 dr); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.25 – 4.13 (m, 1H), 2.59 – 2.47 (m, 0.66H), 2.38 – 2.29 (m, 0.55H), 1.89 – 1.17 (m, 12H), 0.98 – 0.88 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 127.1 (q, J_{C-F} = 281.5 Hz), 126.9 (q, J_{C-F} = 282.2 Hz), 60.0, 59.2, 49.5 (q, J_{C-F} = 24.1 Hz), 48.5 (q, J_{C-F} = 24.6 Hz), 36.1, 33.7, 30.1, 29.9, 29.7, 29.3, 29.0, 24.3, 24.0, 22.7, 22.6, 22.0, 21.9, 13.9, 13.8, 13.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -65.66 (d, J = 9.4 Hz, 1.64F), -67.44 (d, J = 9.2 Hz, 1.36F).



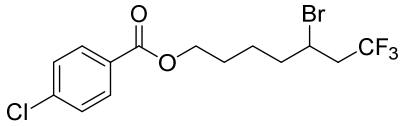
3-Chloro-1-tosyl-4-(trifluoromethyl)pyrrolidine (3r): yield: 41%; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 4.32 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.79 (dd, *J* = 11.2, 6.2 Hz, 1H), 3.65 (dd, *J* = 10.8, 9.1 Hz, 1H), 3.46 (dd, *J* = 11.0, 5.5 Hz, 1H), 3.41 (dd, *J* = 11.2, 5.1 Hz, 1H), 3.08 – 2.98 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.6, 132.8, 130.1, 127.8, 125.2 (q, $J_{C\text{-}F}$ = 279.0 Hz), 56.2, 52.8, 51.9 (q, $J_{C\text{-}F}$ = 28.7 Hz), 46.0, 21.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -70.66 (d, *J* = 8.6 Hz, 3F).



Diethyl 3-(chloromethyl)-4-(2,2,2-trifluoroethyl)cyclopentane-1,1-dicarboxylate (3s): Colorless oil; 41% yield (56 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.19 (q, *J* = 7.1 Hz, 4H), 3.50 (dd, *J* = 11.1, 6.2 Hz, 1H), 3.43 (dd, *J* = 11.1, 7.5 Hz, 1H), 2.56 – 2.46 (m, 4H), 2.34 – 2.27 (m, 2H), 2.23 – 2.07 (m, 2H), 1.27 – 1.22 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.2, 172.1, 126.9 (q, $J_{C\text{-}F}$ = 277.1 Hz), 62.0, 61.9, 58.6, 44.4, 44.0, 38.6, 37.1, 35.6, 33.4 (q, $J_{C\text{-}F}$ = 28.3 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -64.49 (t, *J* = 10.8 Hz, 3F).

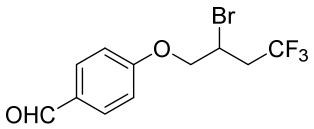


2-(3-Bromo-5,5,5-trifluoropentyl)isoindoline-1,3-dione (4a): White solid; m.p. 58-60 ℃; 72% yield (101 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.81 (m, 2H), 7.78 – 7.69 (m, 2H), 4.23 – 4.09 (m, 1H), 4.02 – 3.81 (m, 2H), 2.93 – 2.67 (m, 2H), 2.45 – 2.29 (m, 1H), 2.29 – 2.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 134.3, 132.1, 125.2 (q, $J_{C\text{-}F}$ = 278.2 Hz), 123.5, 43.0 (q, $J_{C\text{-}F}$ = 28.7 Hz), 41.2 (q, $J_{C\text{-}F}$ = 3.2 Hz), 37.0, 36.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.61 (t, *J* = 10.1 Hz, 3F).

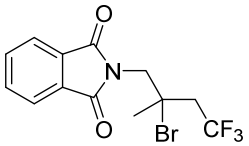


5-Bromo-7,7,7-trifluoroheptyl 4-chlorobenzoate (4b): Colorless oil; 71% yield (110 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 4.34 (t, *J* = 6.0 Hz, 2H), 4.25 – 4.09 (m, 1H), 2.95 – 2.56 (m, 2H), 2.05 – 1.70 (m, 5H), 1.69 – 1.59 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 139.6, 131.1, 128.9, 128.8, 125.4 (q, $J_{C\text{-}F}$ = 278.1 Hz), 64.8, 44.8, 43.3 (q, $J_{C\text{-}F}$ = 28.5 Hz), 38.1, 28.0, 24.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.82 (t, *J* = 10.2 Hz, 3F); FT-IR (thin film, KBr): ν

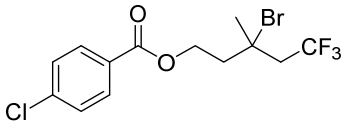
(cm^{-1}) 2957, 1718, 1595, 1241, 760; HRMS (CI) calcd $C_{14}H_{16}O_2F_3Cl^{35}Br^{79}$ $[M + H]^+$: 386.9974, found: 386.9975.



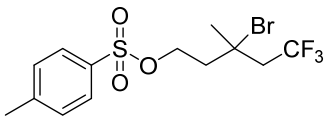
4-(2-Bromo-4,4,4-trifluorobutoxy)benzaldehyde (4c): Colorless oil; 60% yield (74 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.86 (d, J = 7.9 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 4.47 – 4.33 (m, 2H), 4.31 – 4.21 (m, 1H), 3.17 – 2.99 (m, 1H), 2.87 – 2.70 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.8, 162.6, 132.2, 131.0, 125.3 (q, $J_{C\text{-}F}$ = 277.6 Hz), 115.5, 70.8, 39.6 (q, $J_{C\text{-}F}$ = 29.4 Hz), 39.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.99 (t, J = 10.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3056, 3005, 1693, 1596, 771; HRMS (CI) calcd $C_{11}H_{11}O_2F_3Br^{79}$ $[M + H]^+$: 310.9895, found: 310.9890.



2-(2-Bromo-4,4,4-trifluoro-2-methylbutyl)isoindoline-1,3-dione (4d): White solid; m.p. 63-65 ℃; 76% yield (106 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 2H), 7.82 – 7.75 (m, 2H), 4.20 – 4.09 (m, 2H), 3.06 – 2.72 (m, 2H), 1.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.4, 134.6, 131.8, 125.2 (q, $J_{C\text{-}F}$ = 278.8 Hz), 123.9, 58.2, 50.4, 46.6 (q, $J_{C\text{-}F}$ = 28.4 Hz), 29.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.01 (t, J = 10.6 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2933, 1774, 1387, 1260, 713; HRMS (CI) calcd $C_{13}H_{12}NO_2F_3Br^{79}$ $[M + H]^+$: 350.0003, found: 350.0004.

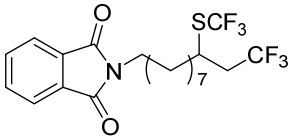


3-Bromo-5,5,5-trifluoro-3-methylpentyl 4-chlorobenzoate (4e): Colorless oil; 82% yield (122 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 4.71 – 4.53 (m, 2H), 3.05 – 2.84 (m, 2H), 2.53 – 2.32 (m, 2H), 1.98 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 139.6, 130.9, 128.8, 128.3, 124.9 (q, $J_{C\text{-}F}$ = 279.5 Hz), 62.9, 59.3, 48.3 (q, $J_{C\text{-}F}$ = 27.7 Hz), 42.9, 32.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.52 (t, J = 10.7 Hz, 3F).

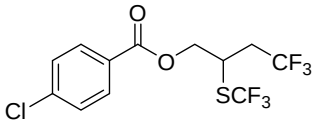


3-Bromo-5,5,5-trifluoro-3-methylpentyl 4-methylbenzenesulfonate (4f): Colorless oil; 75% yield (116 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 2H), 7.36

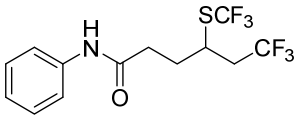
(d, J = 7.9 Hz, 2H), 4.32 (t, J = 6.5 Hz, 2H), 2.80 (q, J = 10.6 Hz, 2H), 2.45 (s, 3H), 2.35 – 2.22 (m, 2H), 1.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.3, 132.8, 130.1, 128.0, 124.9 (q, $J_{C\text{-}F}$ = 279.4 Hz), 67.9, 58.7, 48.3 (q, $J_{C\text{-}F}$ = 27.9 Hz), 43.3, 32.0, 21.8; ^{19}F NMR (564 MHz, $CDCl_3$) δ -60.60 (t, J = 10.6 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2920, 2850, 1598, 1362, 762; HRMS (CI) calcd $C_{13}H_{17}O_3F_3SBr^{79}$ $[M + H]^+$: 389.0034, found: 389.0024.



2-(11,11,11-Trifluoro-9-((trifluoromethyl)thio)undecyl)isoindoline-1,3-dione (7a): Colorless oil; 78% yield (142 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, J = 5.1, 3.1 Hz, 2H), 7.70 (dd, J = 5.2, 3.0 Hz, 2H), 3.67 (t, J = 7.2 Hz, 2H), 3.45 – 3.34 (m, 1H), 2.71 – 2.41 (m, 2H), 1.90 – 1.76 (m, 1H), 1.73 – 1.62 (m, 3H), 1.57 – 1.44 (m, 1H), 1.43 – 1.26 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 134.0, 132.3, 130.8 (q, $J_{C\text{-}F}$ = 306.7 Hz), 125.6 (q, $J_{C\text{-}F}$ = 278.0 Hz), 123.3, 40.3 (q, $J_{C\text{-}F}$ = 28.1 Hz), 39.7, 38.1, 34.4, 29.3, 29.1, 29.0, 28.7, 26.9, 26.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.66 (s, 3F), -63.72 (t, J = 11.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2932, 2859, 1711, 1396, 718; HRMS (CI) calcd $C_{20}H_{24}NO_2F_6S$ $[M + H]^+$: 456.1432, found: 456.1428.

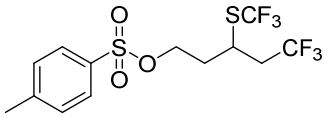


4,4,4-Trifluoro-2-((trifluoromethyl)thio)butyl 4-chlorobenzoate (7b): Colorless oil; 72% yield (105 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 4.62 (dd, J = 11.7, 5.0 Hz, 1H), 4.53 (dd, J = 11.7, 5.5 Hz, 1H), 3.88 – 3.76 (m, 1H), 2.84 – 2.58 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.0, 140.4, 131.2, 130.4 (q, $J_{C\text{-}F}$ = 307.2 Hz), 129.2, 127.6, 125.3 (q, $J_{C\text{-}F}$ = 277.7 Hz), 65.7, 37.9, 37.2 (q, $J_{C\text{-}F}$ = 29.5 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -40.03 (s, 3F), -64.02 (t, J = 10.2 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2965, 1728, 1595, 1256, 757; HRMS (CI) calcd $C_{12}H_{10}O_2F_6SCl^{35}$ $[M + H]^+$: 366.9994, found: 366.9987.

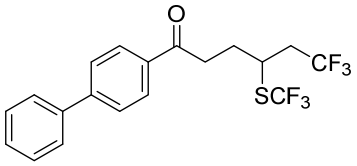


6,6,6-Trifluoro-N-phenyl-4-((trifluoromethyl)thio)hexanamide (7c): Yellowish solid; m.p. 67-69 ℃; 64% yield (88 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.8 Hz, 2H), 7.32 (t, J = 7.5 Hz, 3H), 7.12 (t, J = 7.2 Hz, 1H), 3.59 – 3.46 (m, 1H), 2.79 – 2.51 (m, 4H), 2.47 – 2.33 (m, 1H), 2.04 – 1.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 137.6, 130.6 (q, $J_{C\text{-}F}$ = 307.0 Hz), 129.2, 125.5 (q, $J_{C\text{-}F}$ = 278.0 Hz), 124.8, 120.2, 41.0 (q, $J_{C\text{-}F}$ = 28.4 Hz), 39.4, 34.0, 29.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.29 (s, 3F), -63.41 (t, J = 11.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3245,

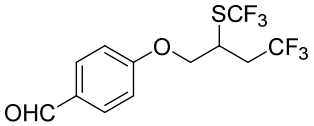
2924, 1654, 1445, 757; HRMS (CI) calcd $C_{13}H_{14}NOF_6S$ $[M + H]^+$: 346.0700, found: 346.0686.



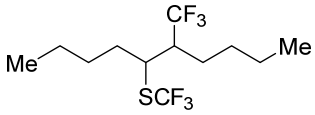
5,5,5-Trifluoro-3-((trifluoromethyl)thio)pentyl 4-methylbenzenesulfonate (7d): Colorless oil; 64% yield (101 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.22 (t, J = 5.4 Hz, 2H), 3.56 – 3.42 (m, 1H), 2.74 – 2.58 (m, 1H), 2.58 – 2.49 (m, 1H), 2.45 (s, 3H), 2.33 – 2.21 (m, 1H), 2.00 – 1.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 132.6, 130.3 (q, J_{C-F} = 307.4 Hz), 130.1, 128.1, 125.3 (q, J_{C-F} = 278.0 Hz), 66.4, 40.3 (q, J_{C-F} = 28.7 Hz), 36.0, 33.5, 21.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.15 (s, 3F), -63.42 (t, J = 10.9 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2962, 1599, 1360, 1176, 757; HRMS (CI) calcd $C_{13}H_{15}O_3F_6S_2$ $[M + H]^+$: 397.0367, found: 397.0385.



1-([1,1'-Biphenyl]-4-yl)-6,6,6-trifluoro-4-((trifluoromethyl)thio)hexan-1-one (7e): White solid; m.p. 101-103 ℃; 74% yield (120 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.9 Hz, 2H), 7.71 (d, J = 7.9 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.3 Hz, 2H), 7.45 – 7.38 (m, 1H), 3.67 – 3.52 (m, 1H), 3.29 (t, J = 6.9 Hz, 2H), 2.86 – 2.68 (m, 1H), 2.70 – 2.55 (m, 1H), 2.54 – 2.38 (m, 1H), 2.11 – 1.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 146.3, 139.9, 135.3, 130.7 (q, J_{C-F} = 307.0 Hz), 129.1, 128.7, 128.5, 127.5, 127.4, 125.5 (q, J_{C-F} = 278.1 Hz), 41.1 (q, J_{C-F} = 28.5 Hz), 39.5, 35.3, 28.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -39.31 (s, 3F), -63.44 (t, J = 10.4 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2909, 1680, 1389, 1243, 697; HRMS (CI) calcd $C_{19}H_{17}OF_6S$ $[M + H]^+$: 407.0904, found: 407.0912.



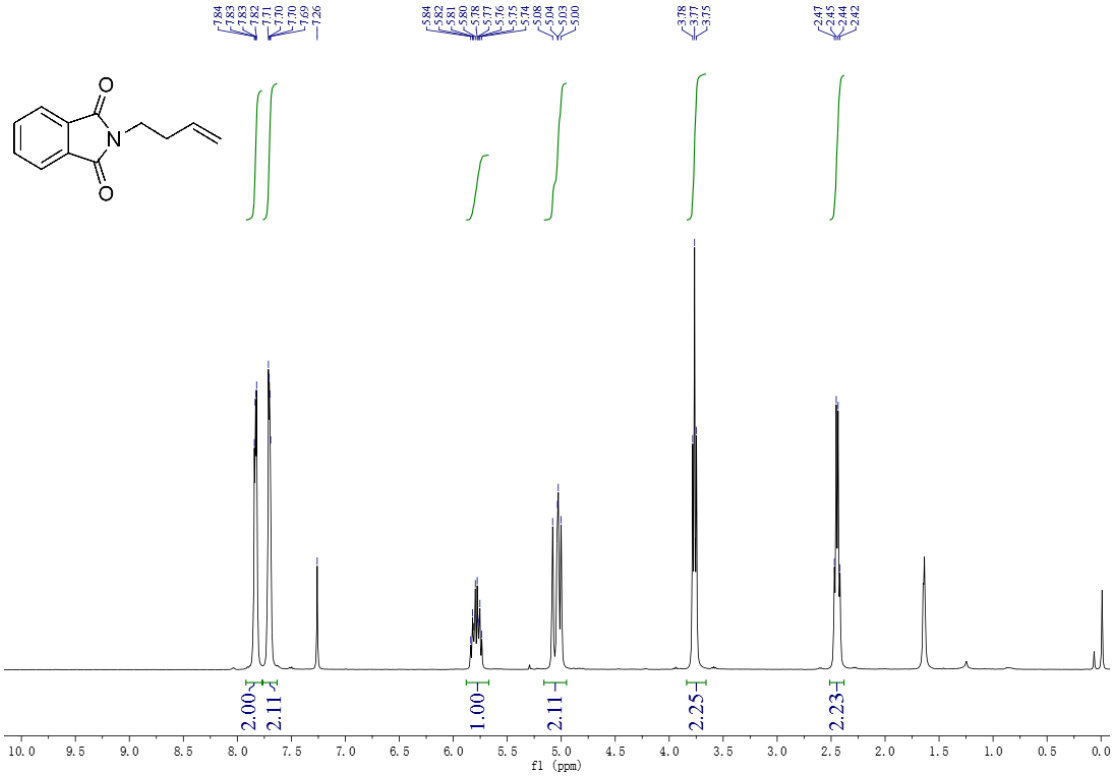
4-(4,4,4-Trifluoro-2-((trifluoromethyl)thio)butoxy)benzaldehyde (7f): White solid; m.p. 68-70 ℃; 69% yield (92 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.87 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 8.2 Hz, 2H), 4.49 – 4.16 (m, 2H), 3.88 – 3.74 (m, 1H), 3.05 – 2.56 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.6, 162.4, 132.0, 130.9, 130.4 (q, J_{C-F} = 307.1 Hz), 125.2 (q, J_{C-F} = 277.9 Hz), 114.8, 69.2, 38.0, 36.5 (q, J_{C-F} = 29.5 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -40.41 (s, 3F), -64.07 (t, J = 10.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 2949, 1673, 1425, 1148, 758; HRMS (CI) calcd $C_{12}H_{11}O_2F_6S$ $[M + H]^+$: 333.0384, found: 333.0382.



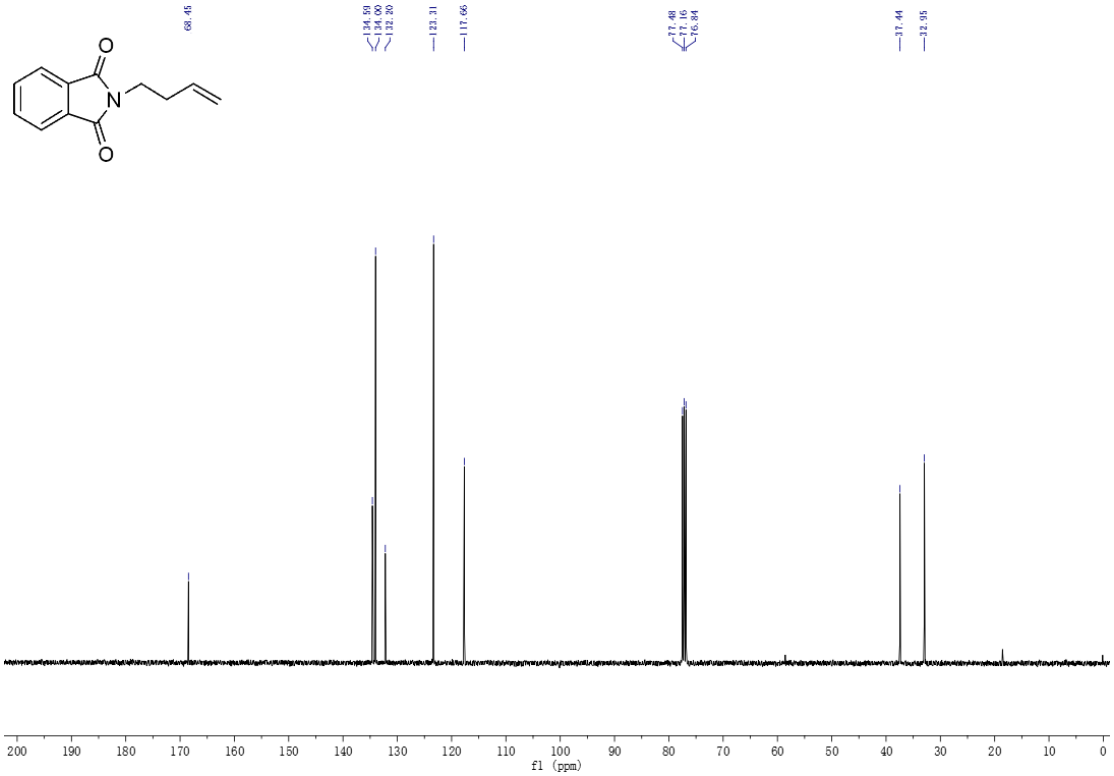
(Trifluoromethyl)(6-(trifluoromethyl)decan-5-yl)sulfane (7g): yield: 58% (1.2:1 dr); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 – 3.41 (m, 0.45H), 3.35 – 3.24 (m, 0.55H), 2.67 – 2.50 (m, 1H), 1.89 – 1.20 (m, 12H), 1.03 – 0.83 (m,6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.3 (d, J_{C-F} = 306.1 Hz), 131.0 (q, J_{C-F} = 306.5 Hz), 127.6 (q, J_{C-F} = 281.8 Hz), 127.4 (q, J_{C-F} = 282.3 Hz), 48.6 (q, J_{C-F} = 24.4 Hz), 45.1, 44.4, 32.1, 30.2, 29.8, 29.7, 29.6, 26.3, 24.4, 22.7, 22.6, 22.2, 22.2, 14.0, 13.9, 13.9, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -40.65 (s, 1.36F), -40.74 (s, 1.64F), -66.23 (d, J = 10.4 Hz, 1.36F), -66.52 (d, J = 10.6 Hz, 1.64F).

7. NMR Spectra for the substrates and products

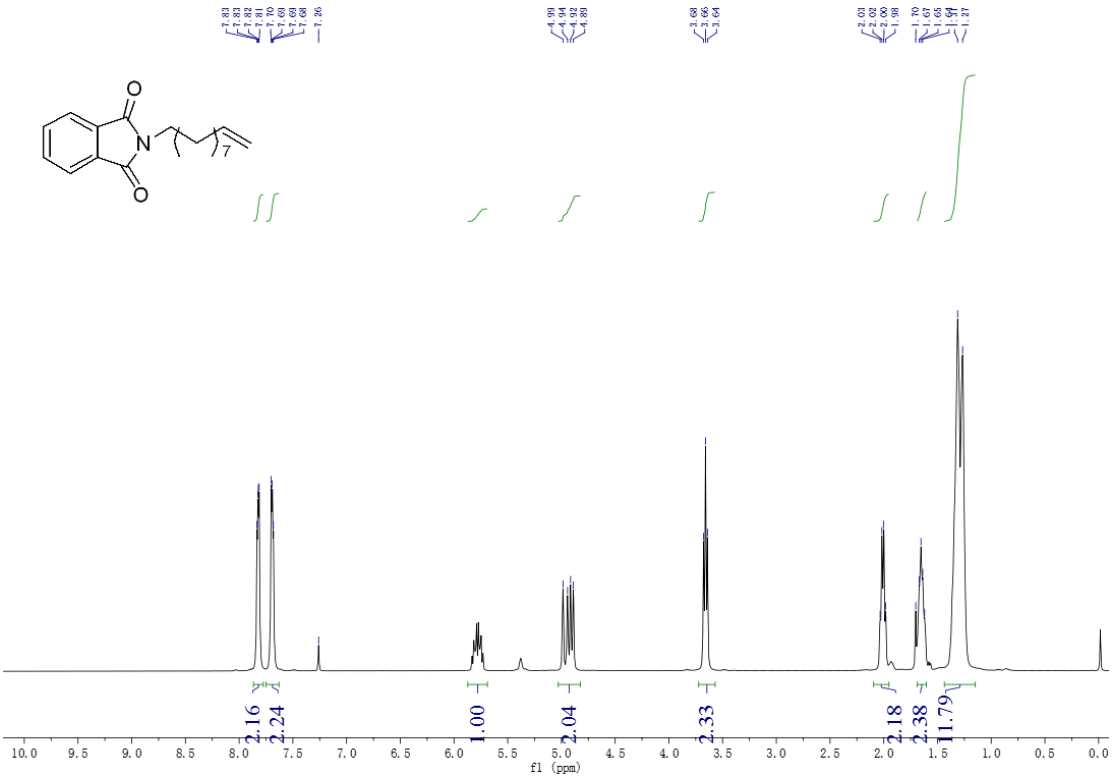
^{1}H NMR of **1a**



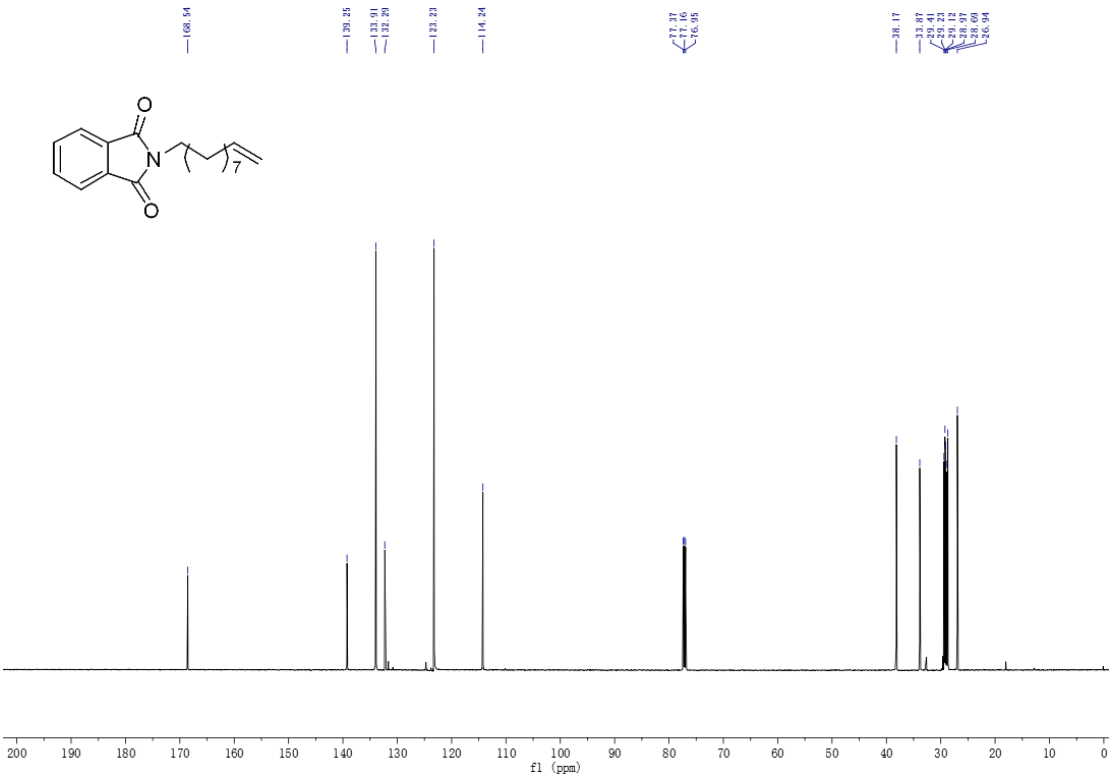
^{13}C NMR of **1a**



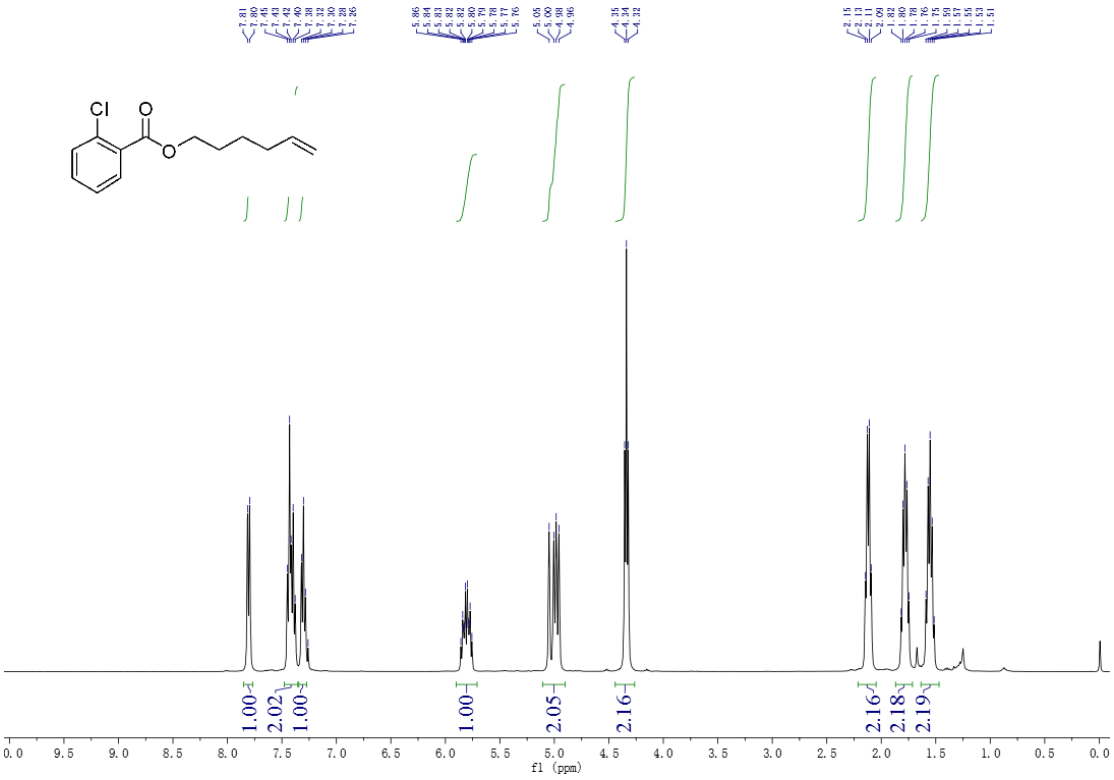
^{1}H NMR of **1b**



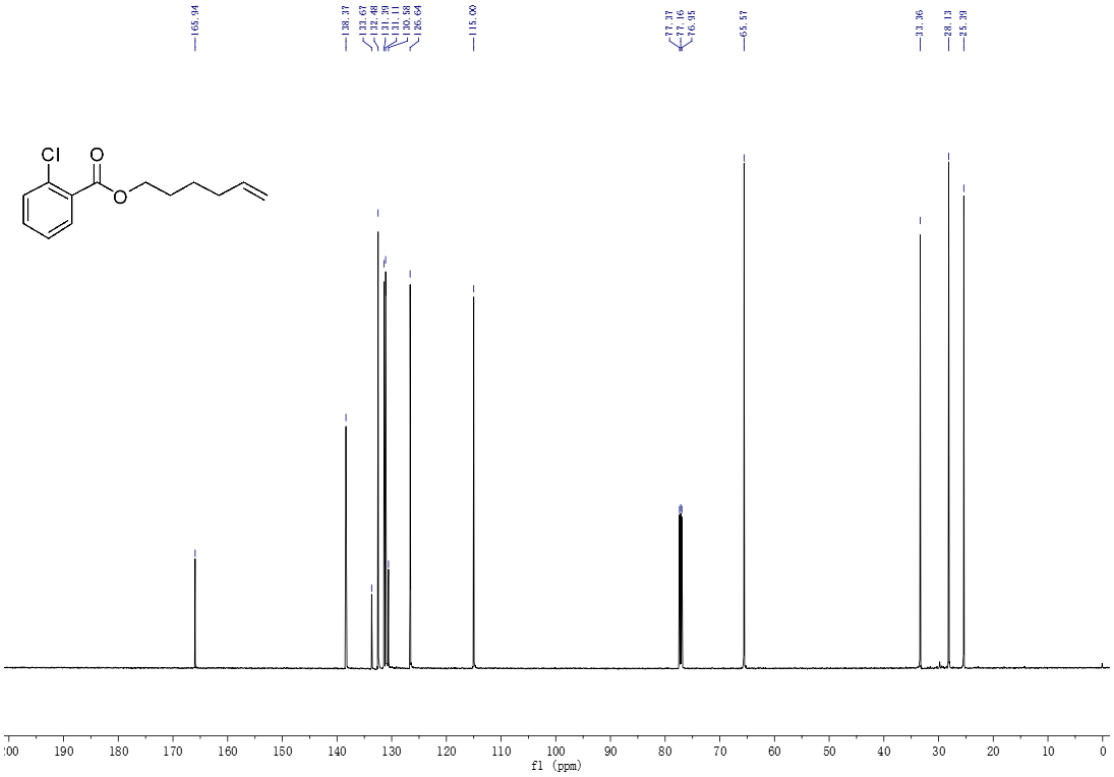
^{13}C NMR of **1b**



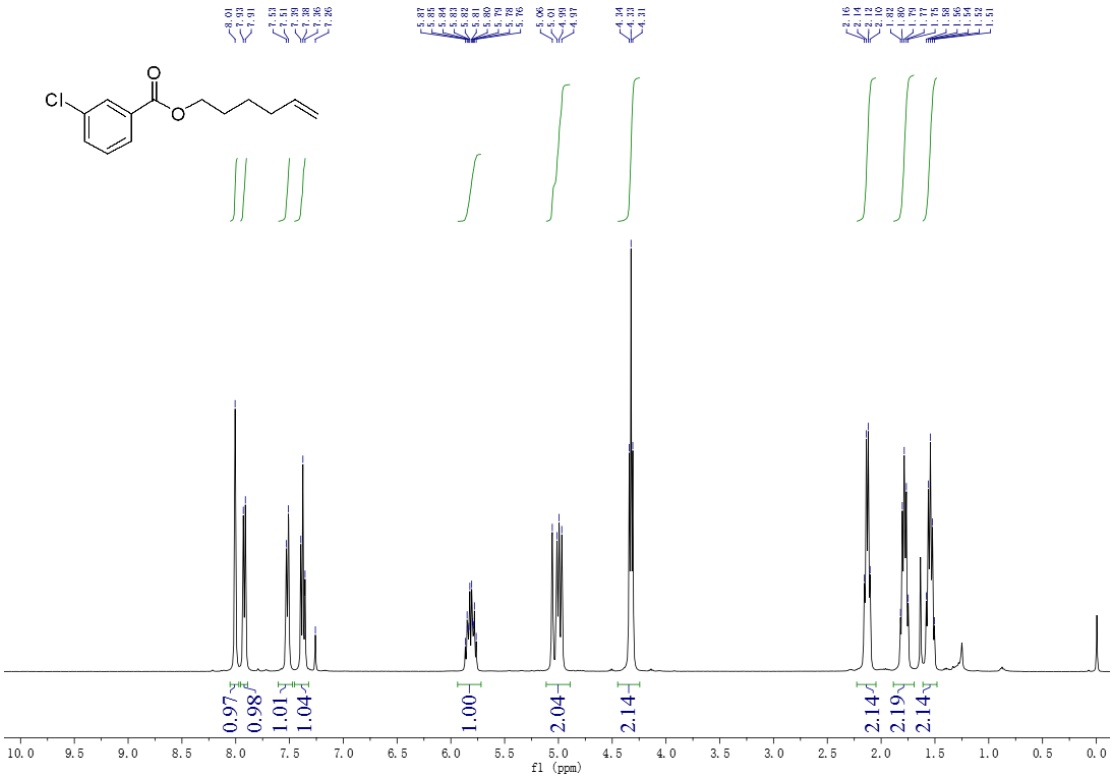
^{1}H NMR of **1c**



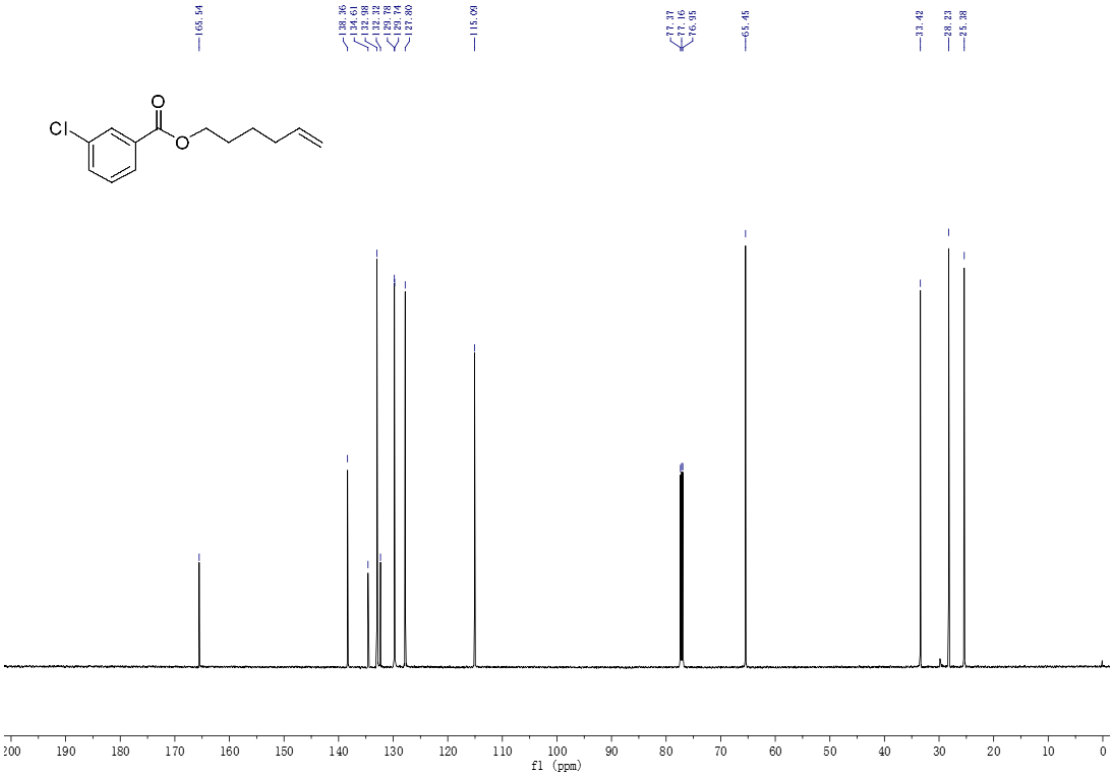
^{13}C NMR of **1c**



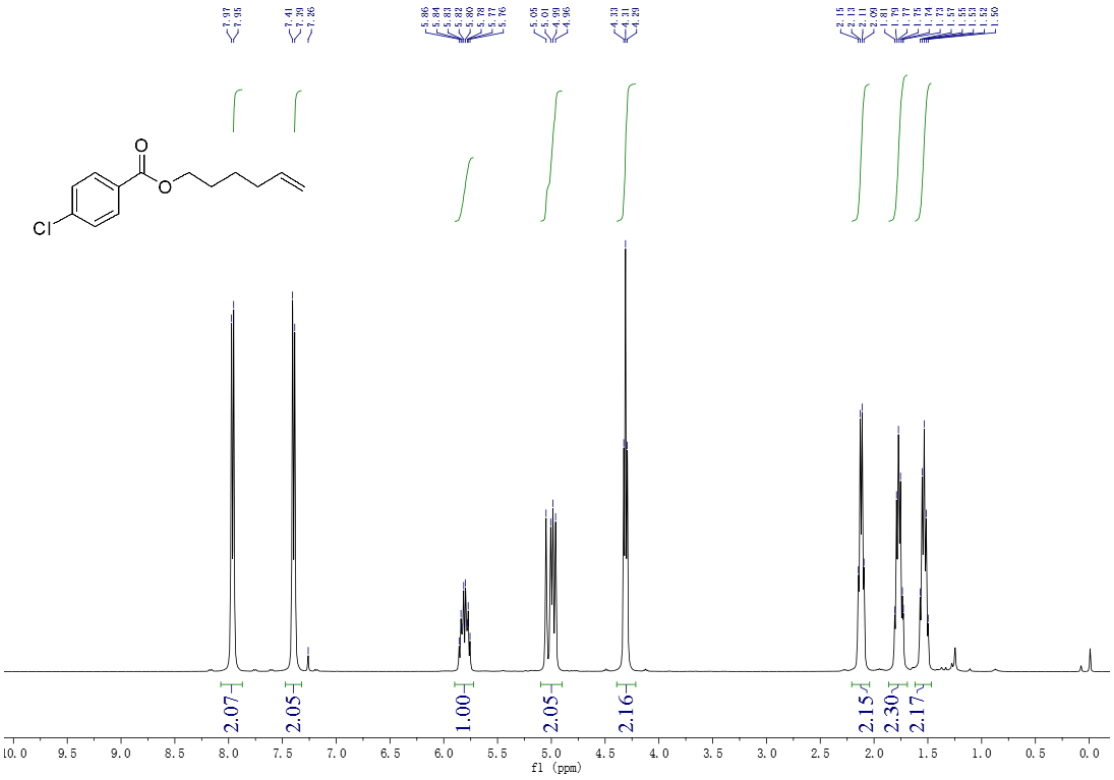
^{1}H NMR of **1d**



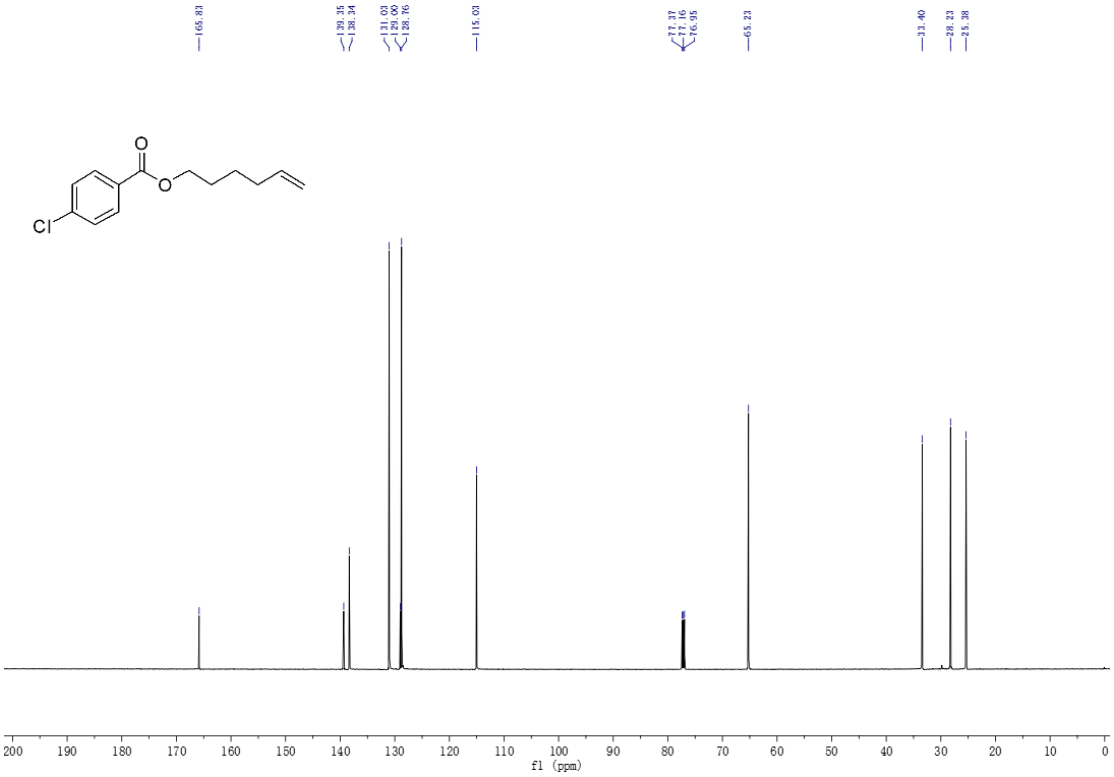
^{13}C NMR of **1d**



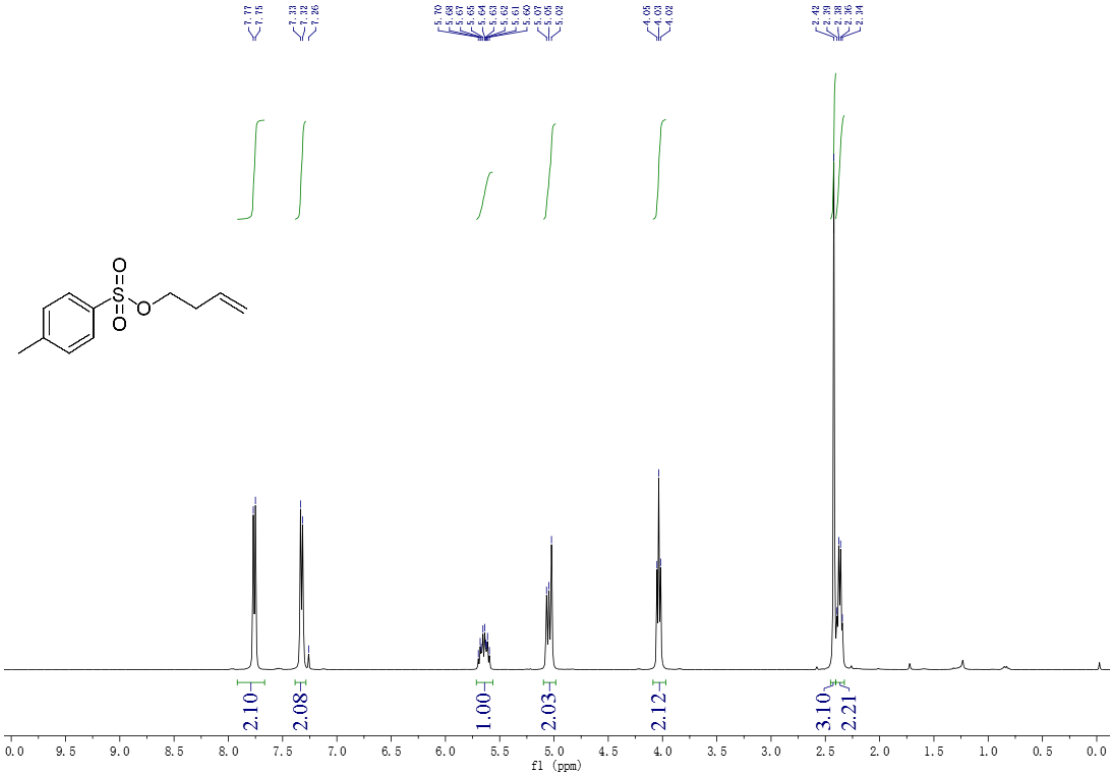
^{1}H NMR of **1e**



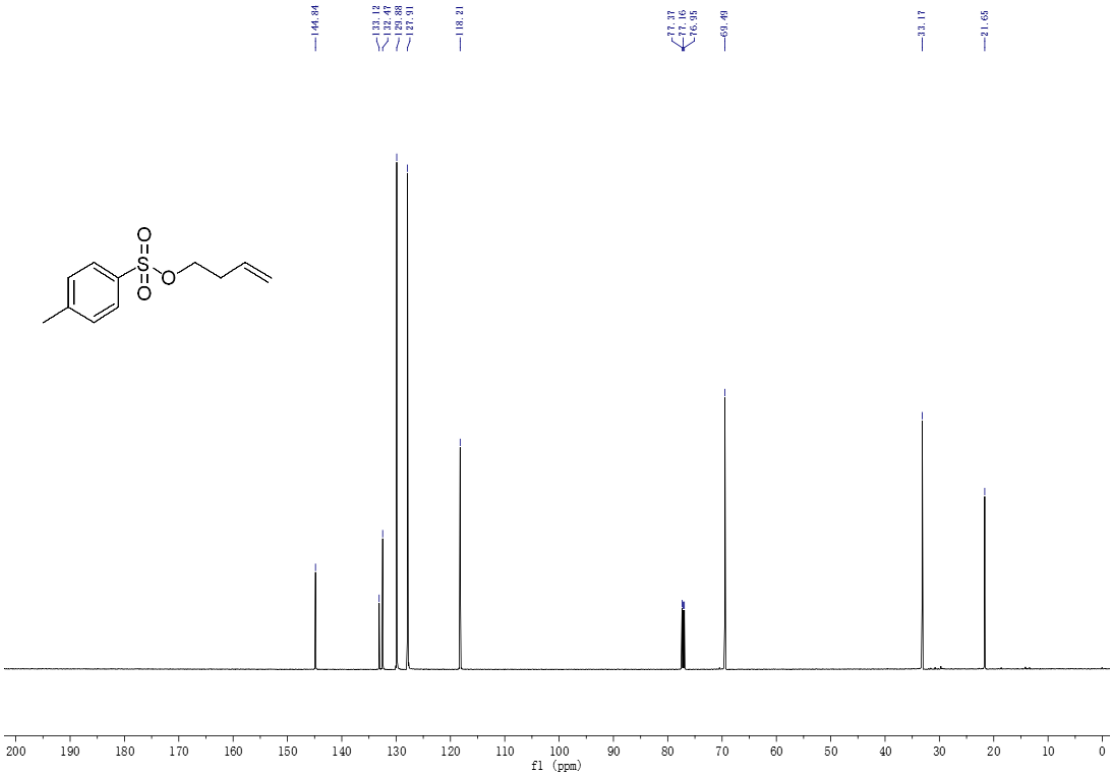
^{13}C NMR of **1e**



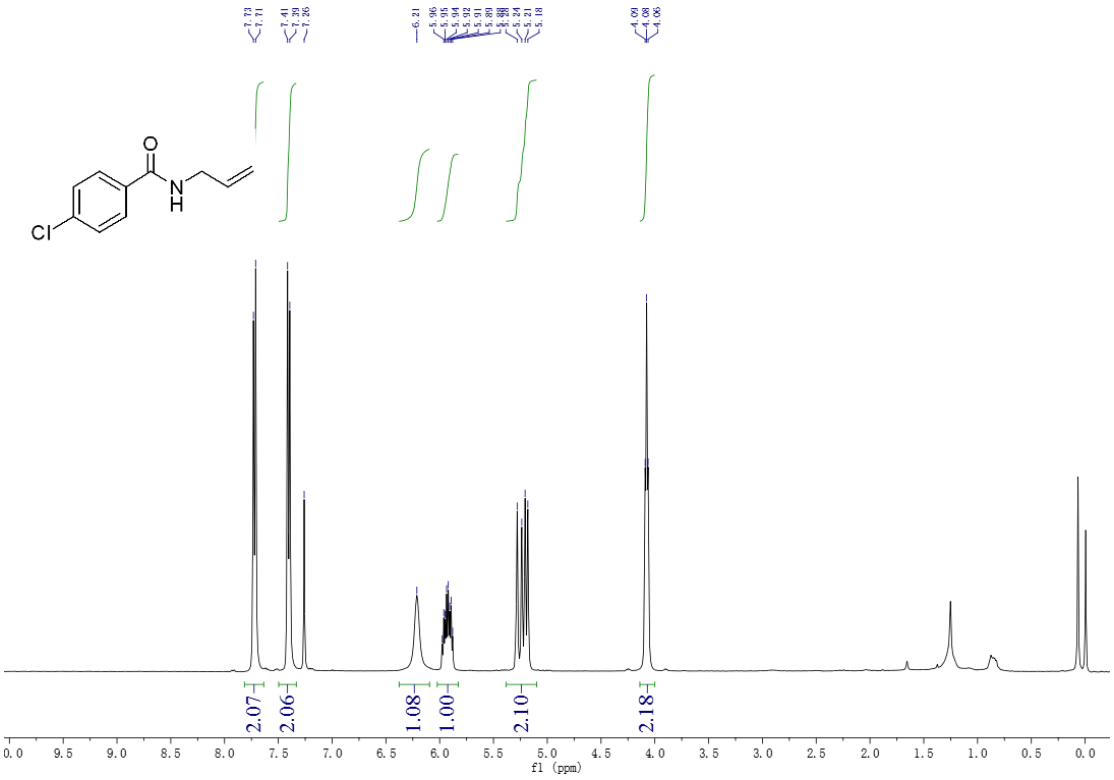
^{1}H NMR of **1f**



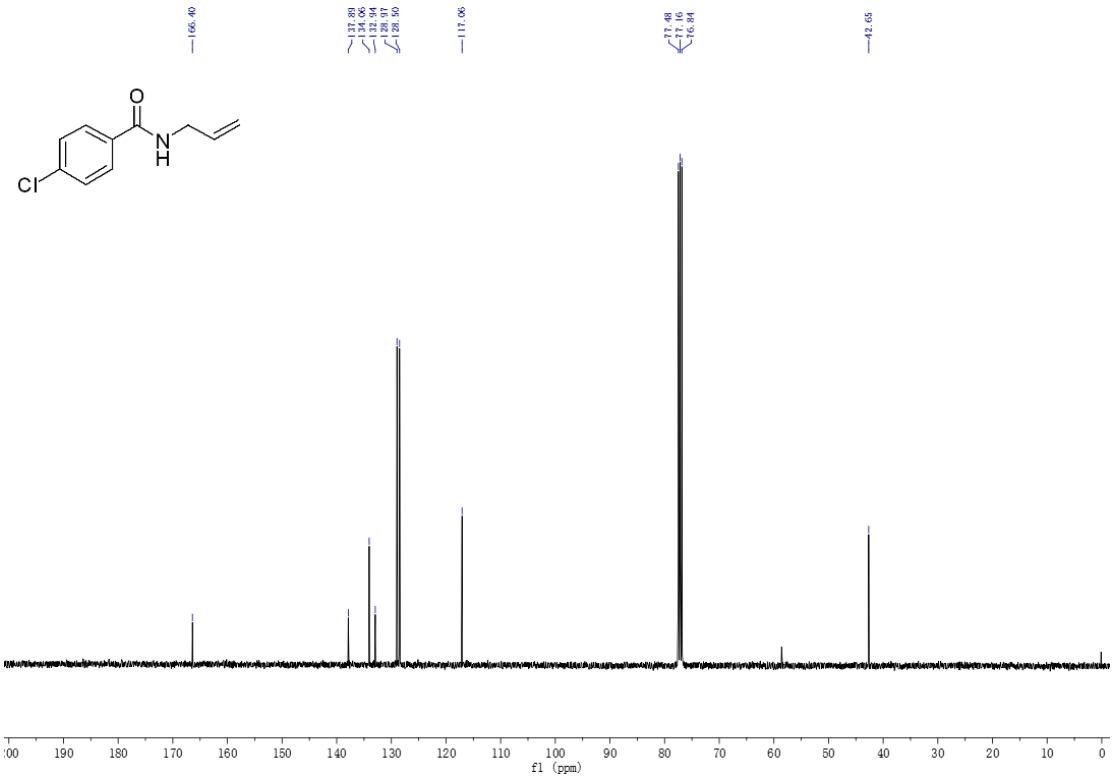
^{13}C NMR of **1f**



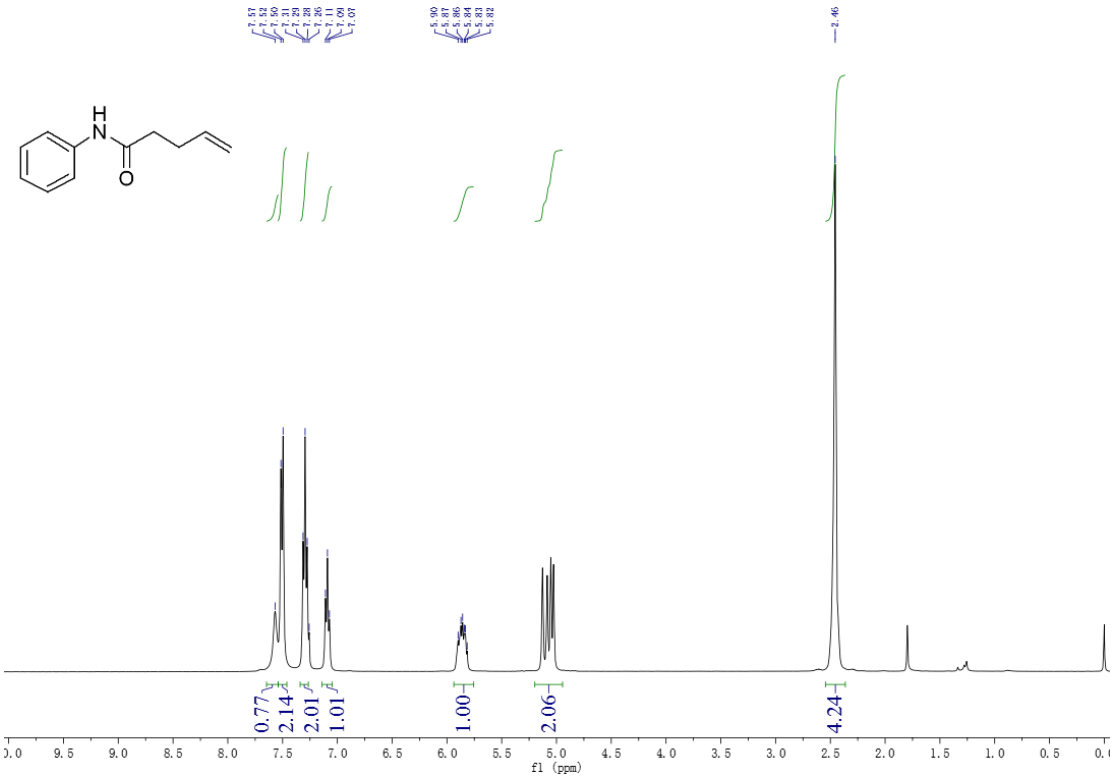
^{1}H NMR of **1g**



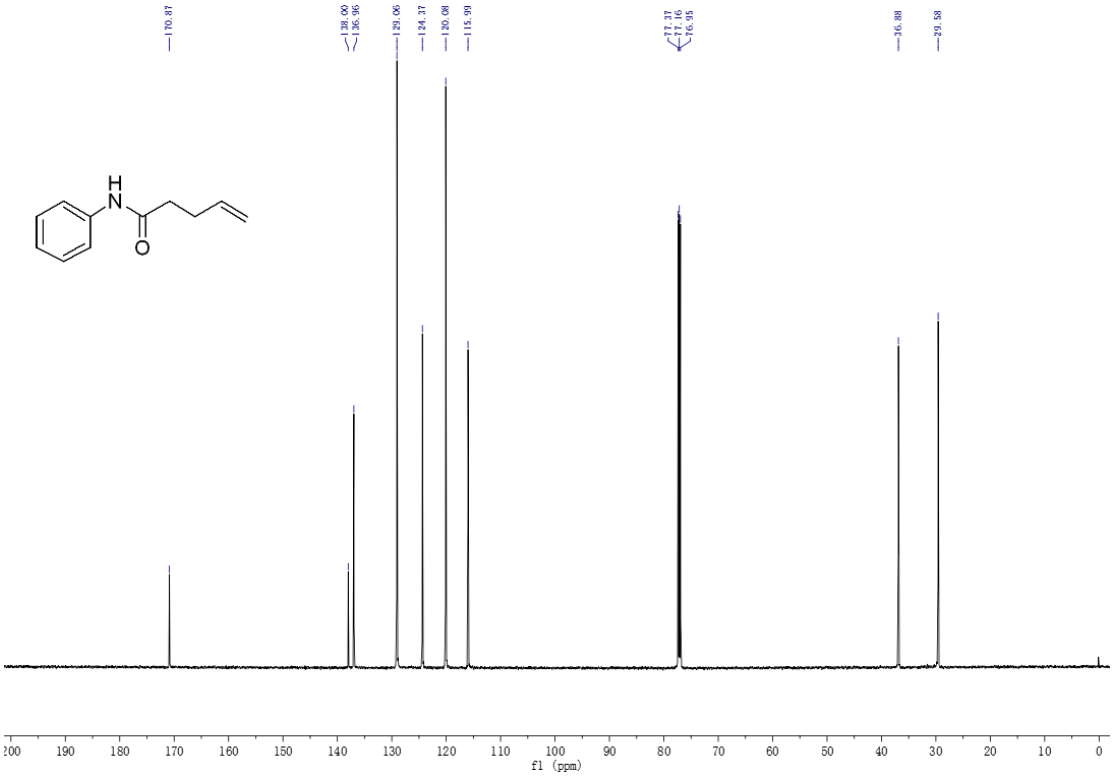
^{13}C NMR of **1g**



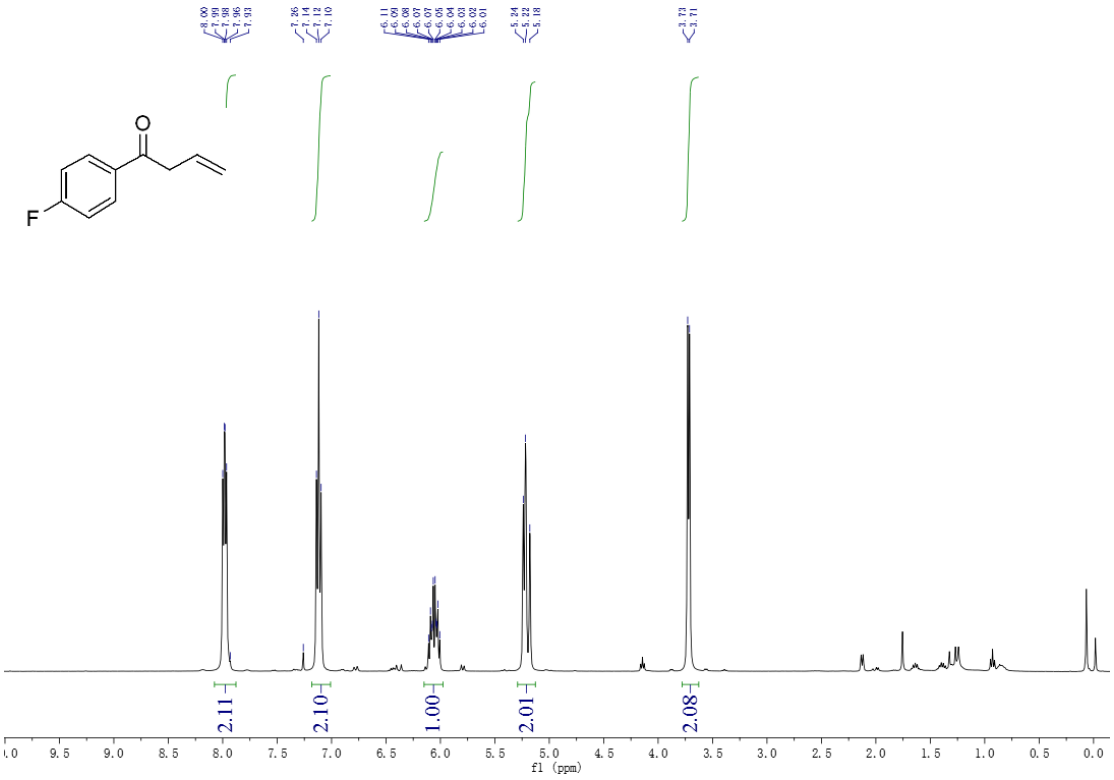
^{1}H NMR of **1h**



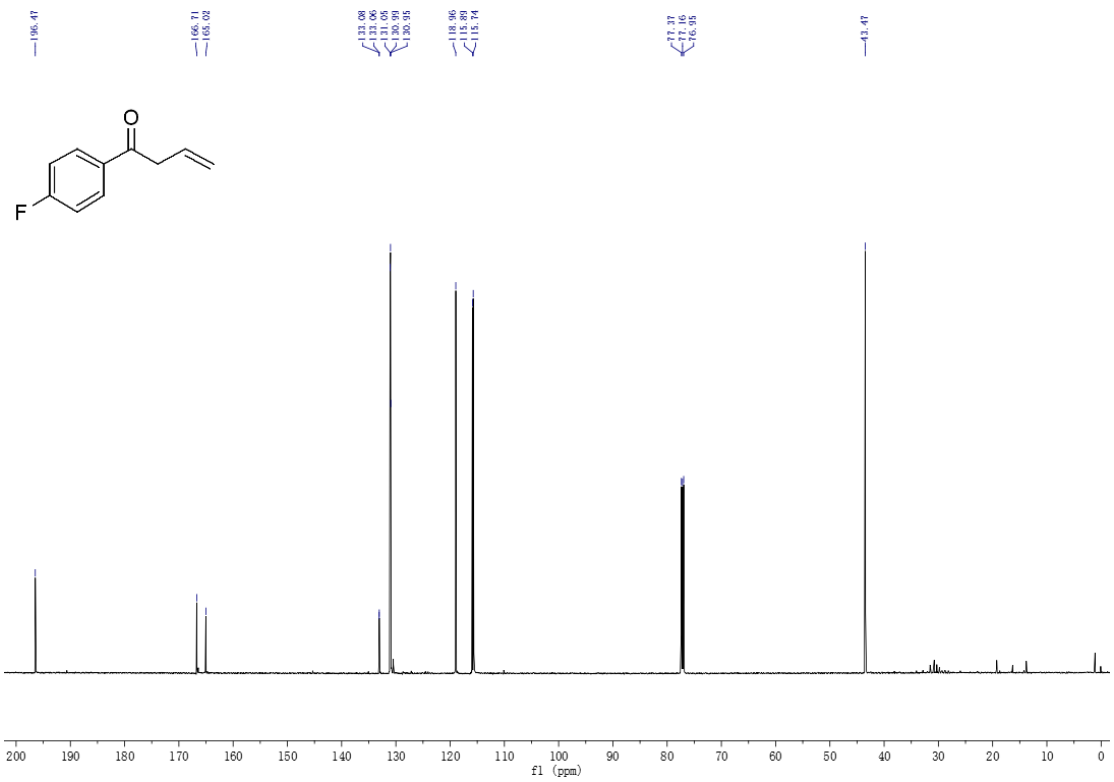
^{13}C NMR of **1h**



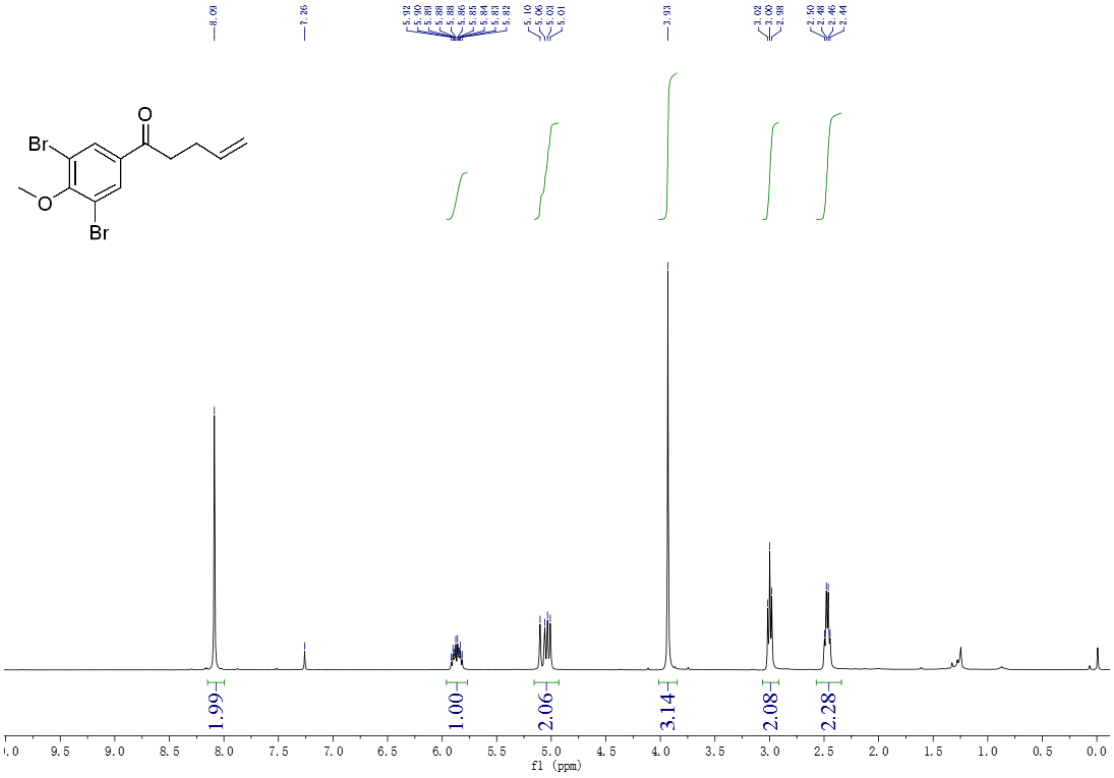
^{1}H NMR of **1i**



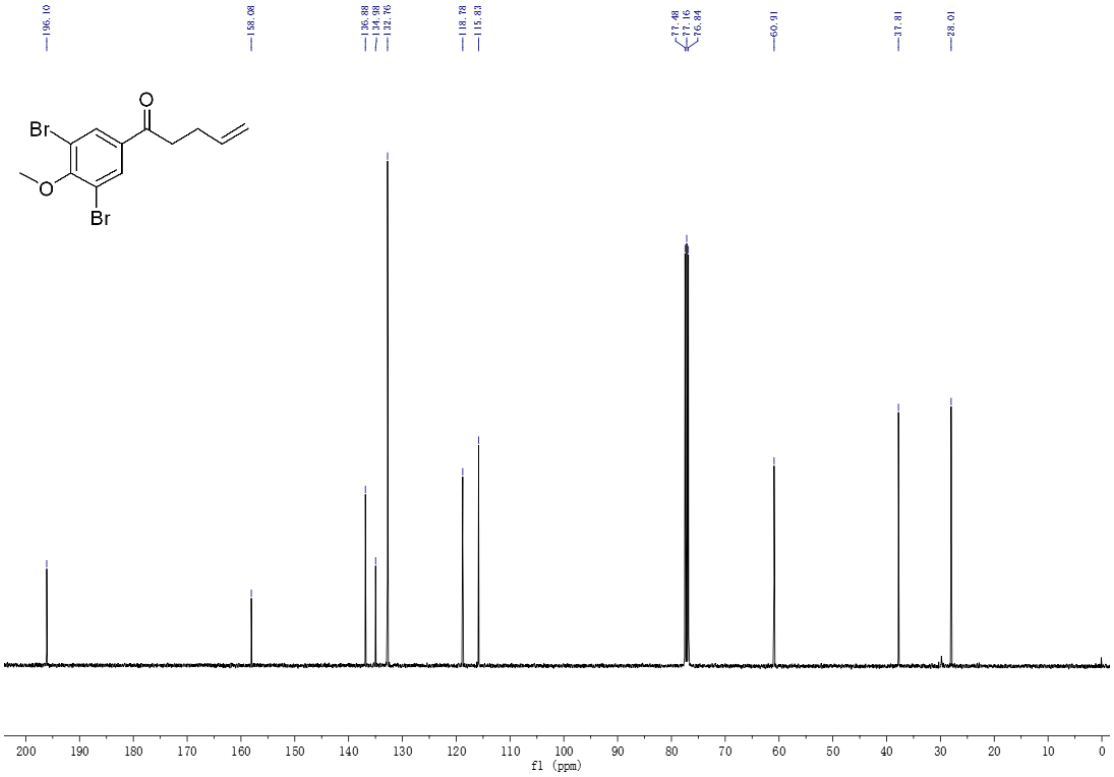
^{13}C NMR of **1i**



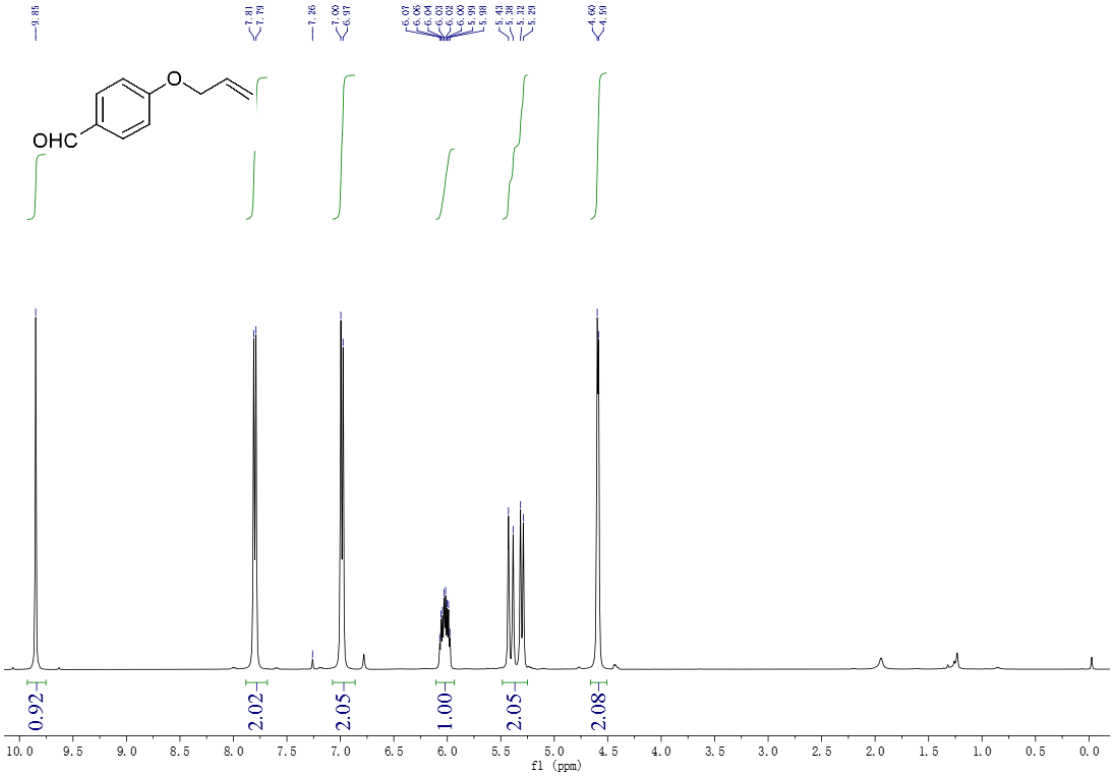
^{1}H NMR of **1j**



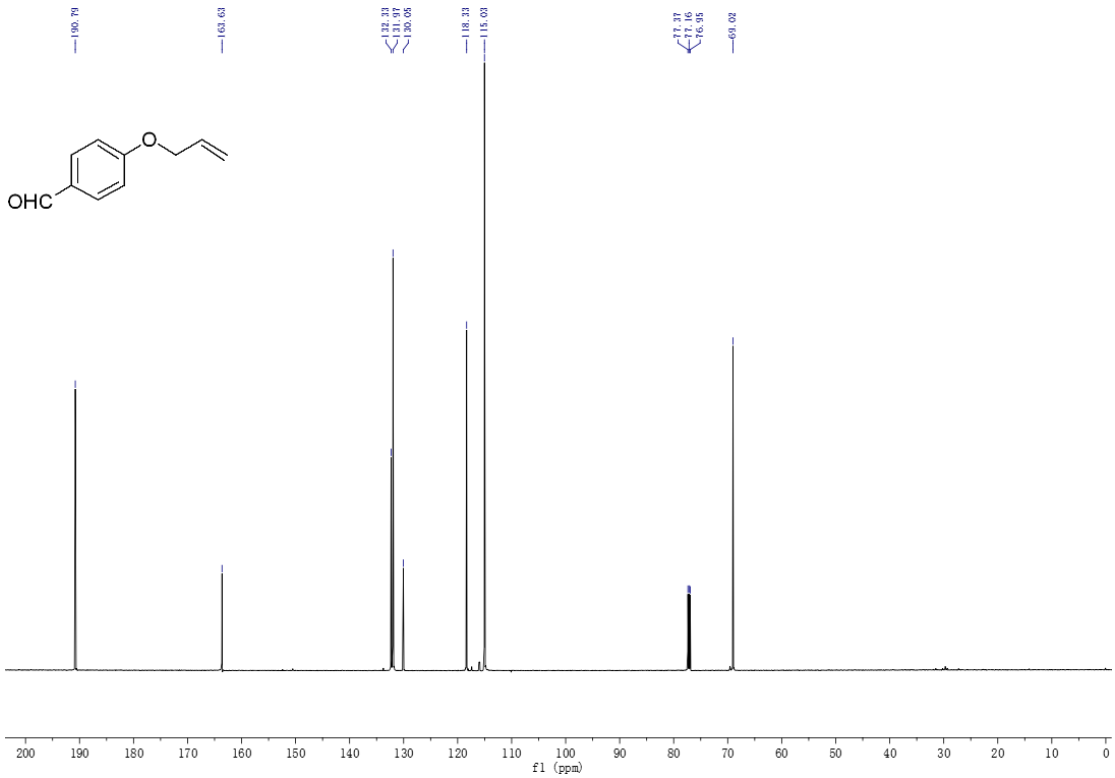
^{13}C NMR of **1j**



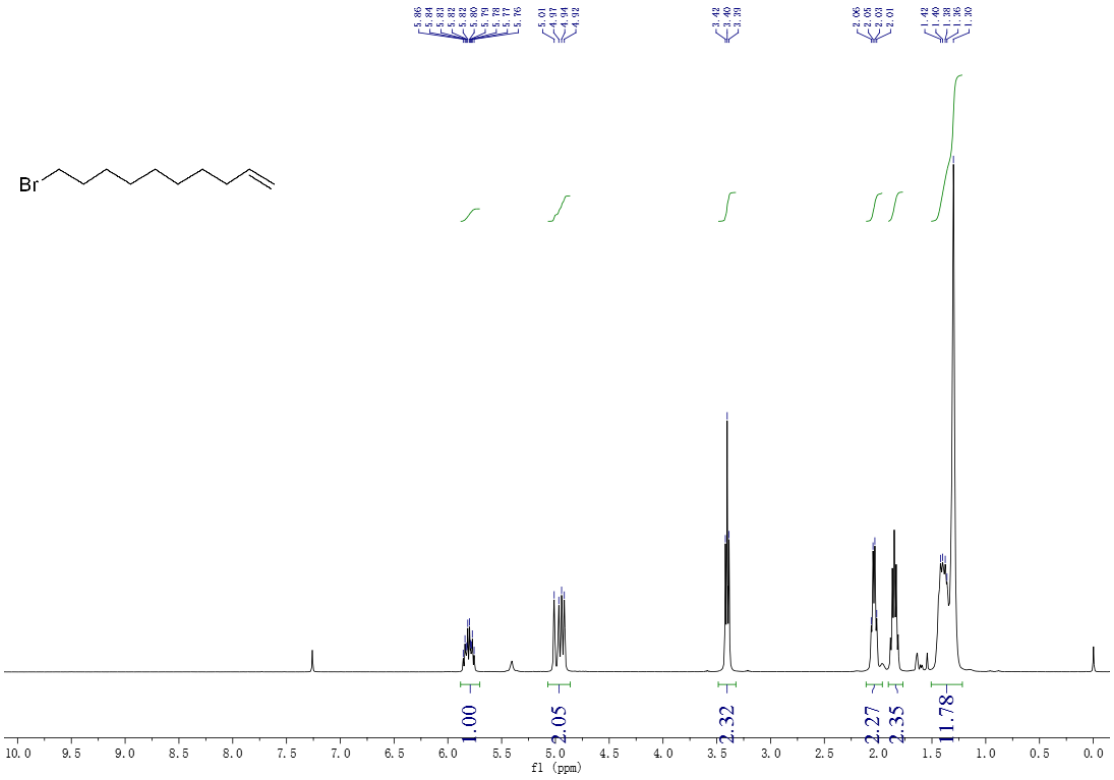
^{1}H NMR of **1k**



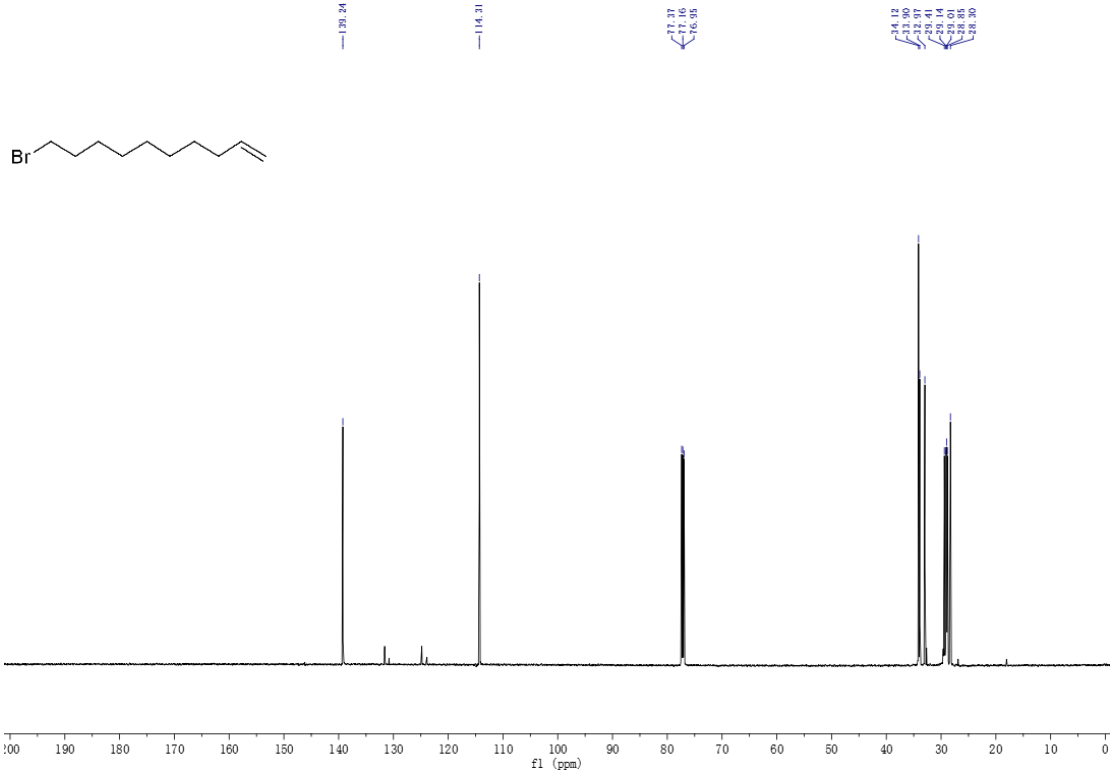
^{13}C NMR of **1k**



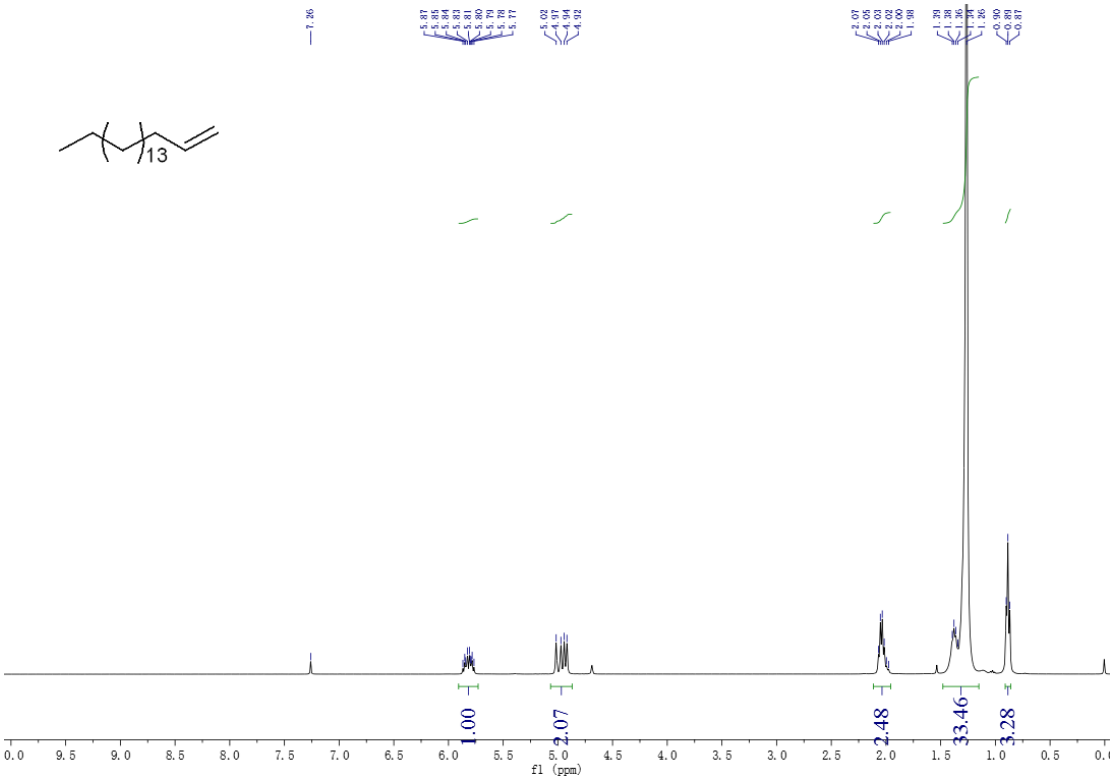
^{1}H NMR of **1l**



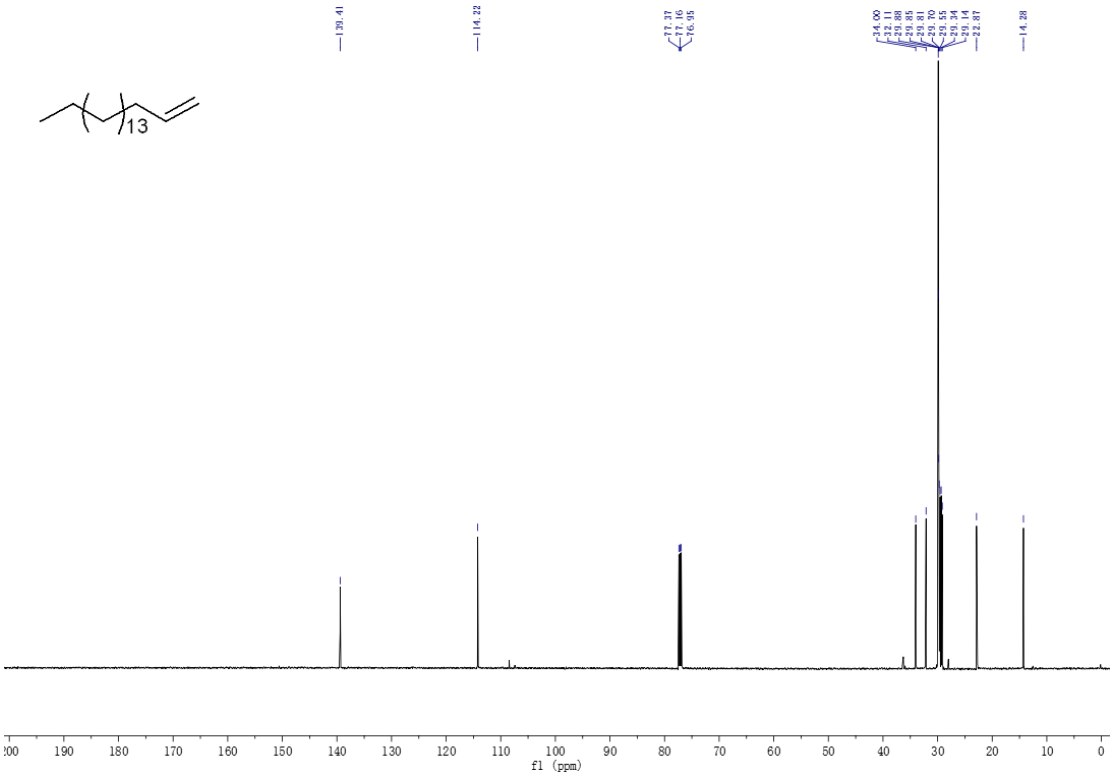
^{13}C NMR of **1l**



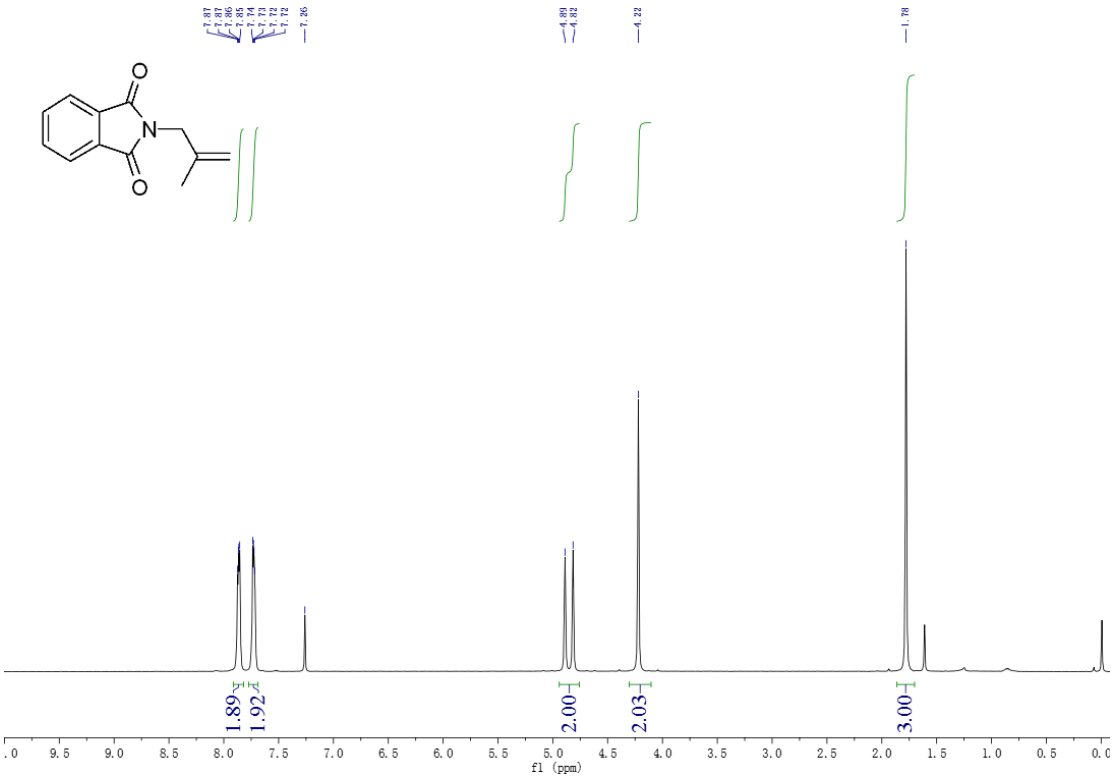
^{1}H NMR of **1m**



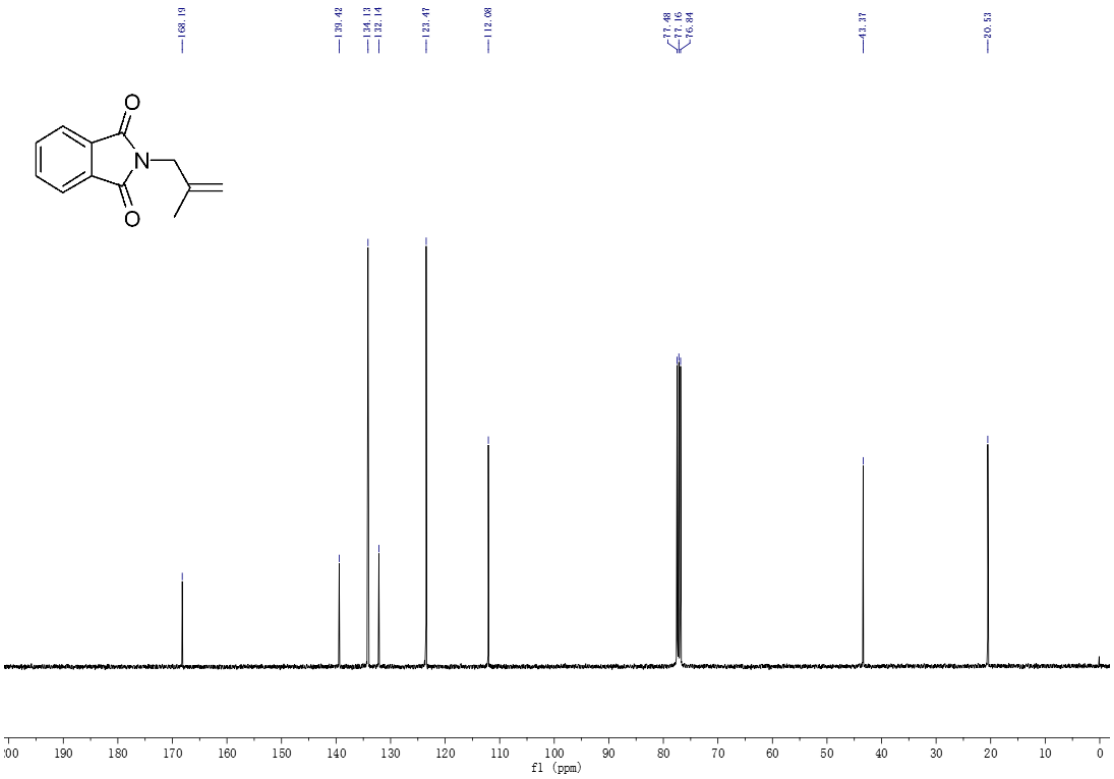
^{13}C NMR of **1m**



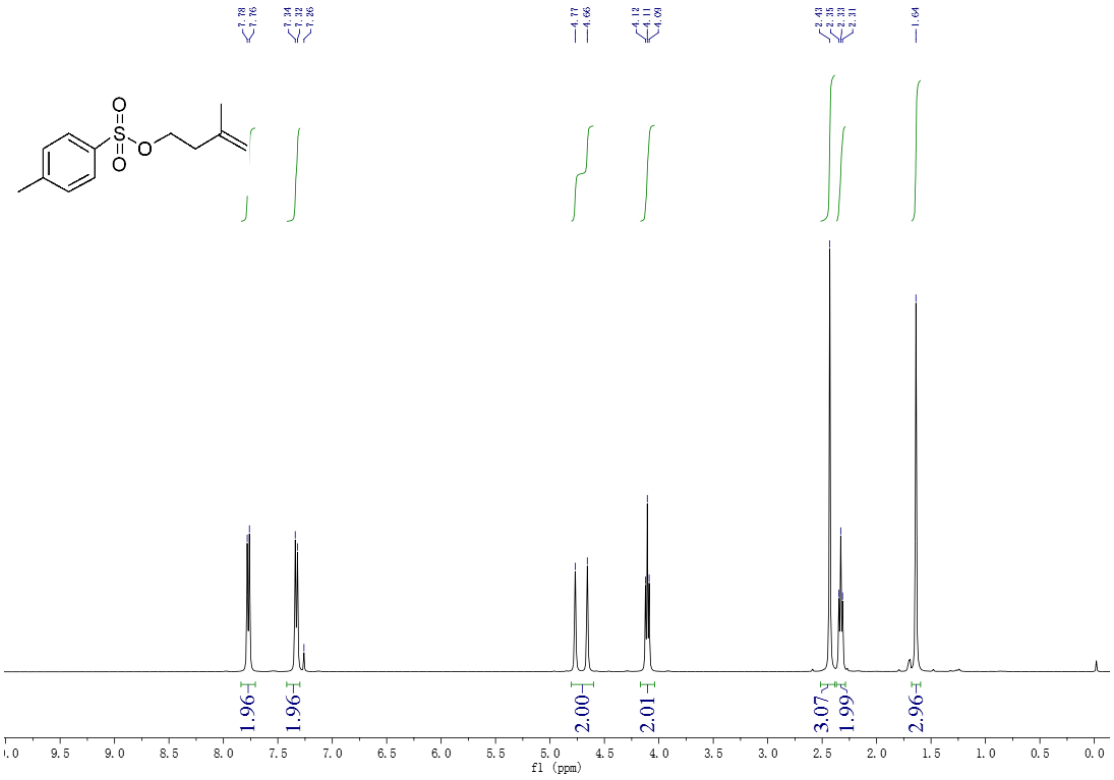
^{1}H NMR of **1n**



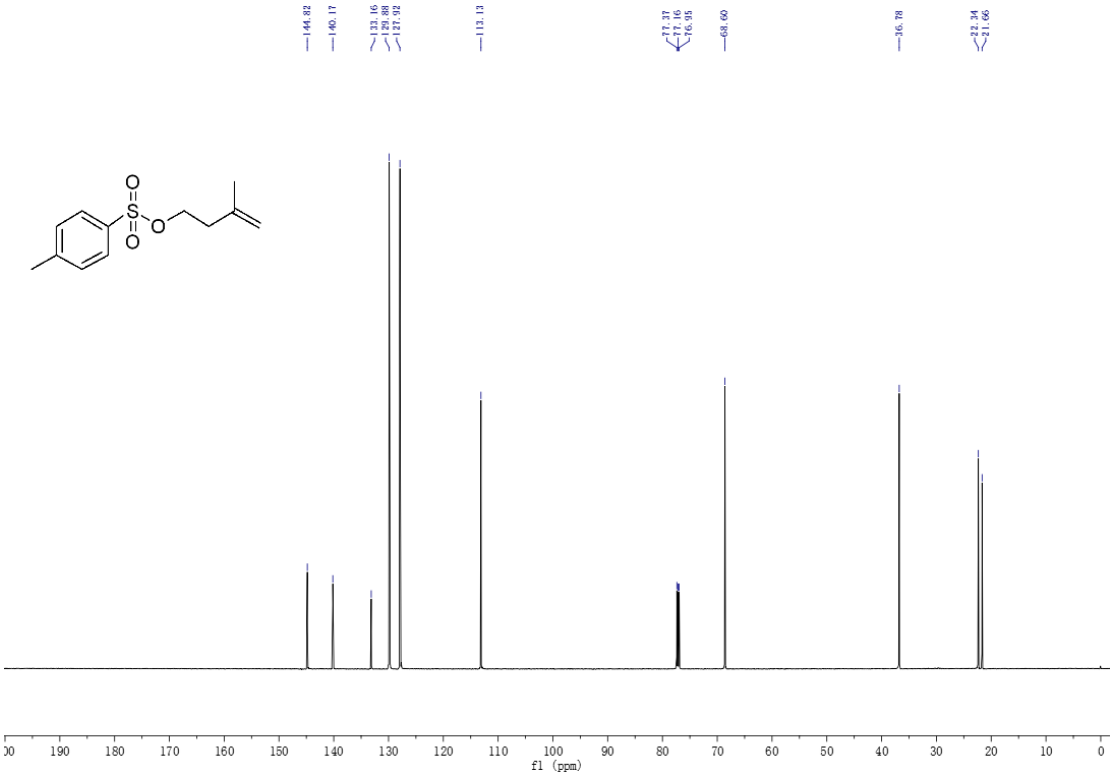
^{13}C NMR of **1n**



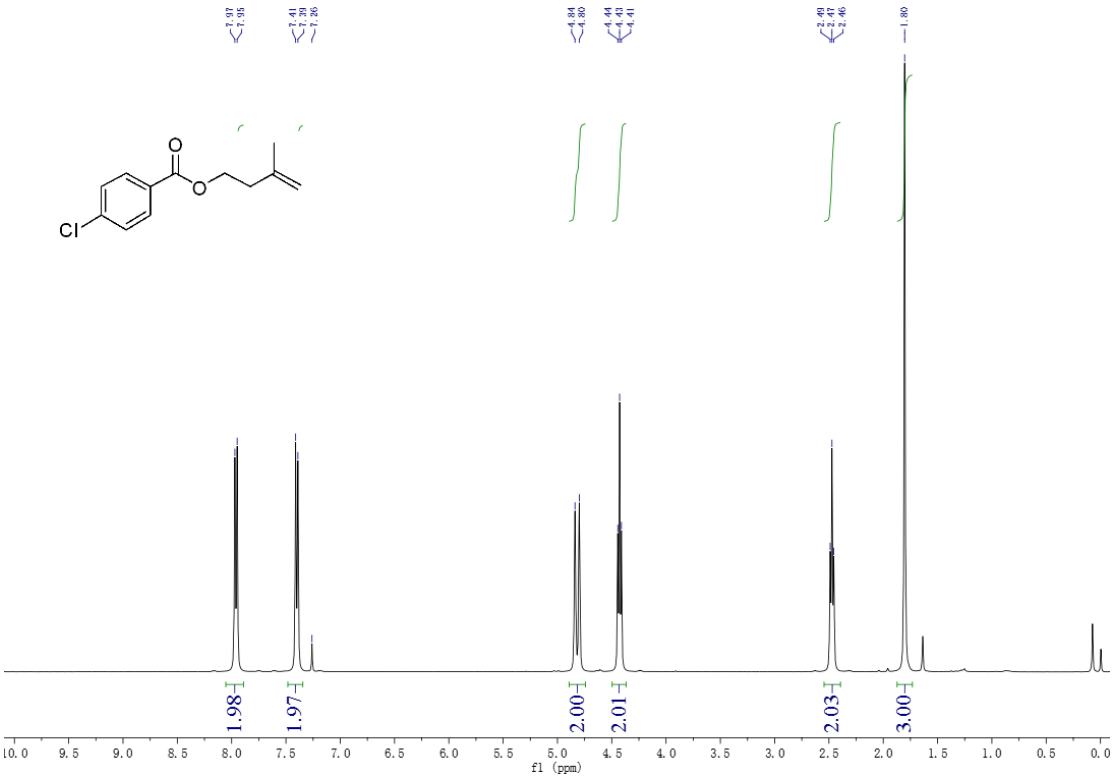
^{1}H NMR of **1o**



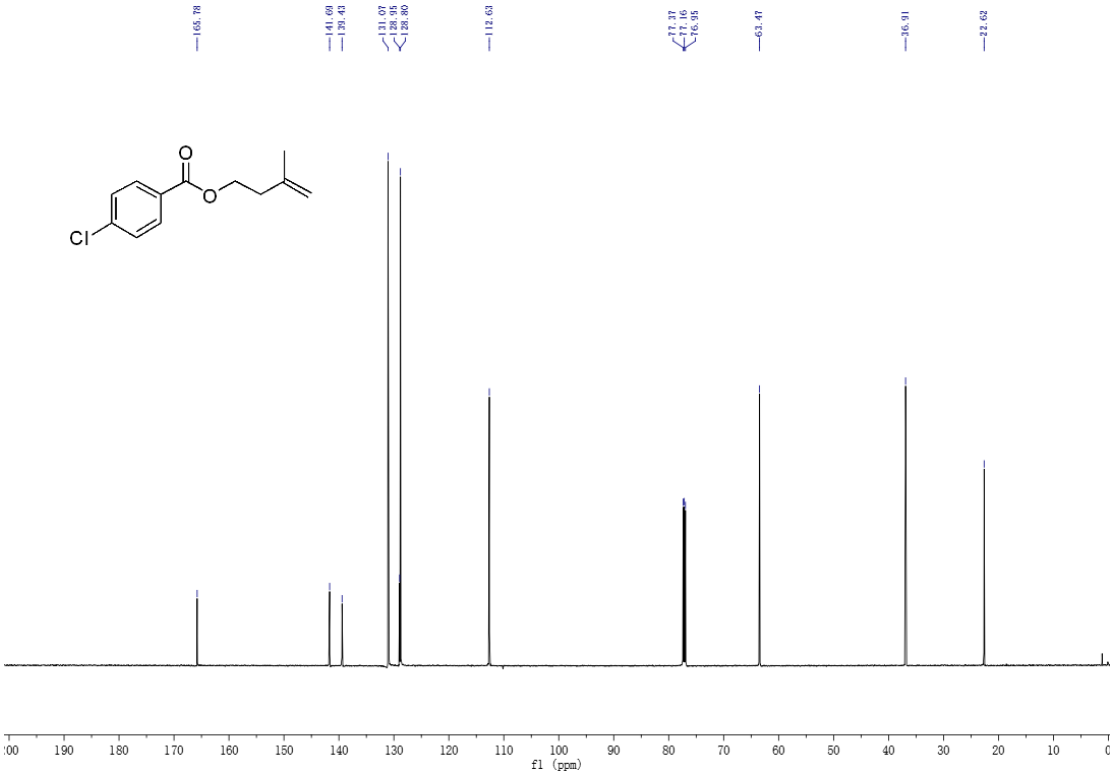
^{13}C NMR of **1o**



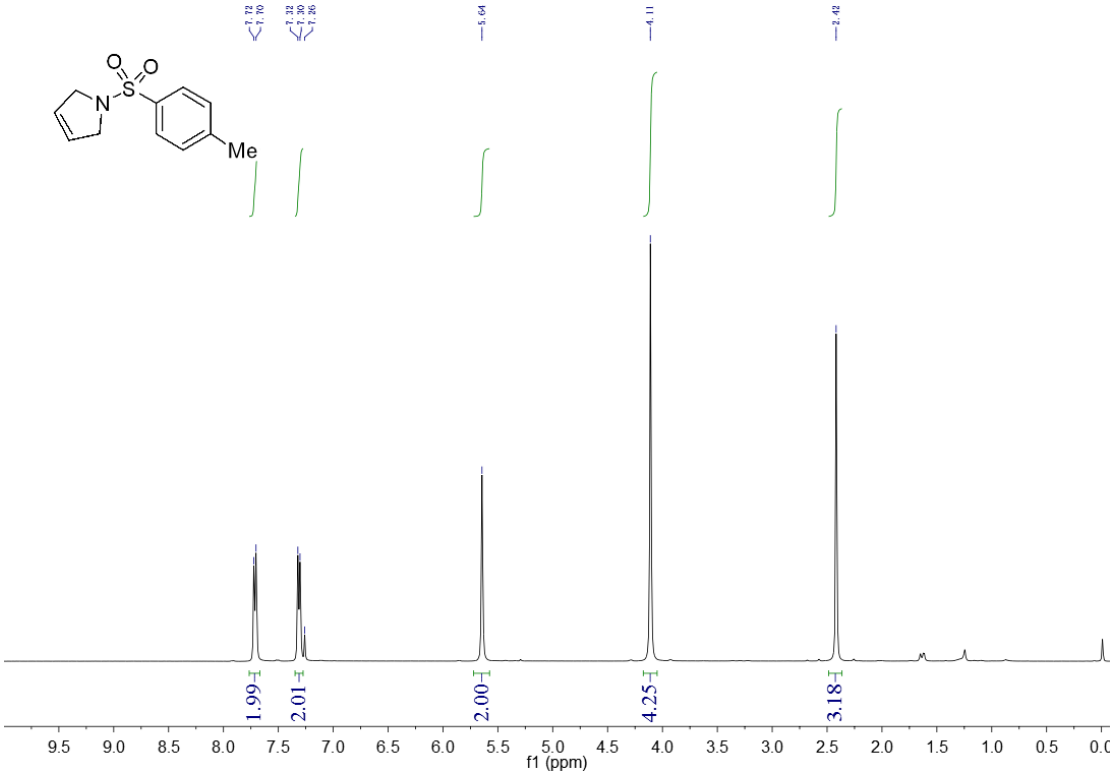
^{1}H NMR of **1p**



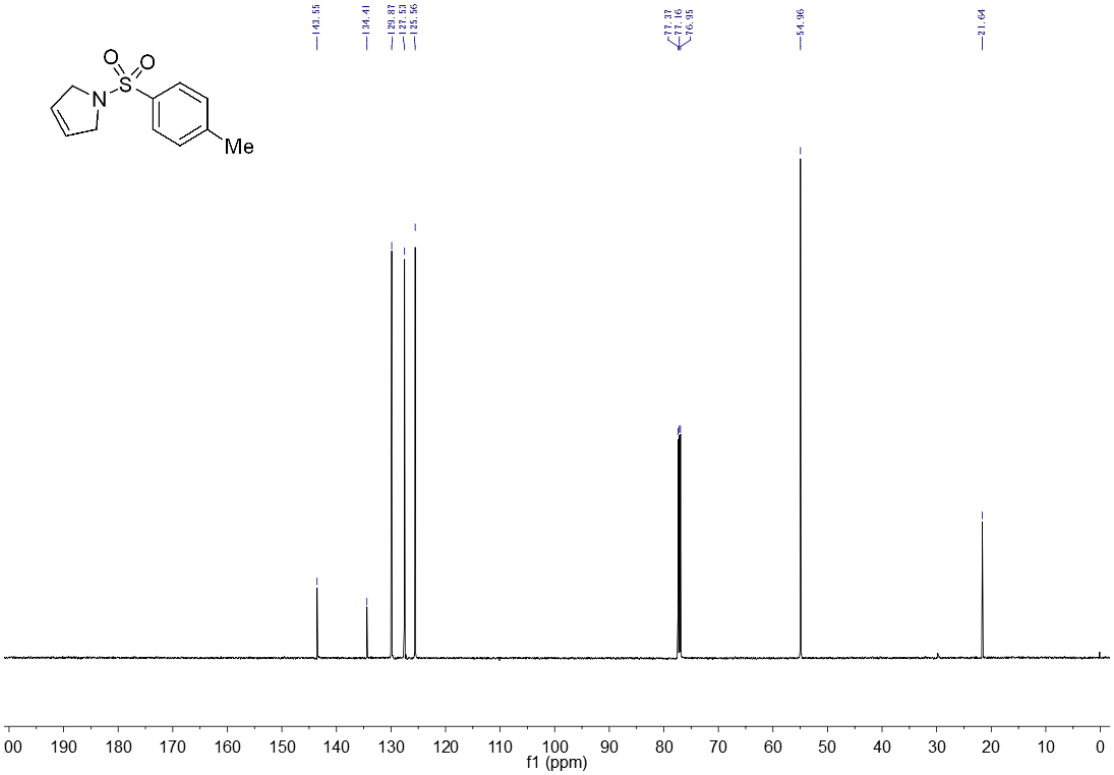
^{13}C NMR of **1p**



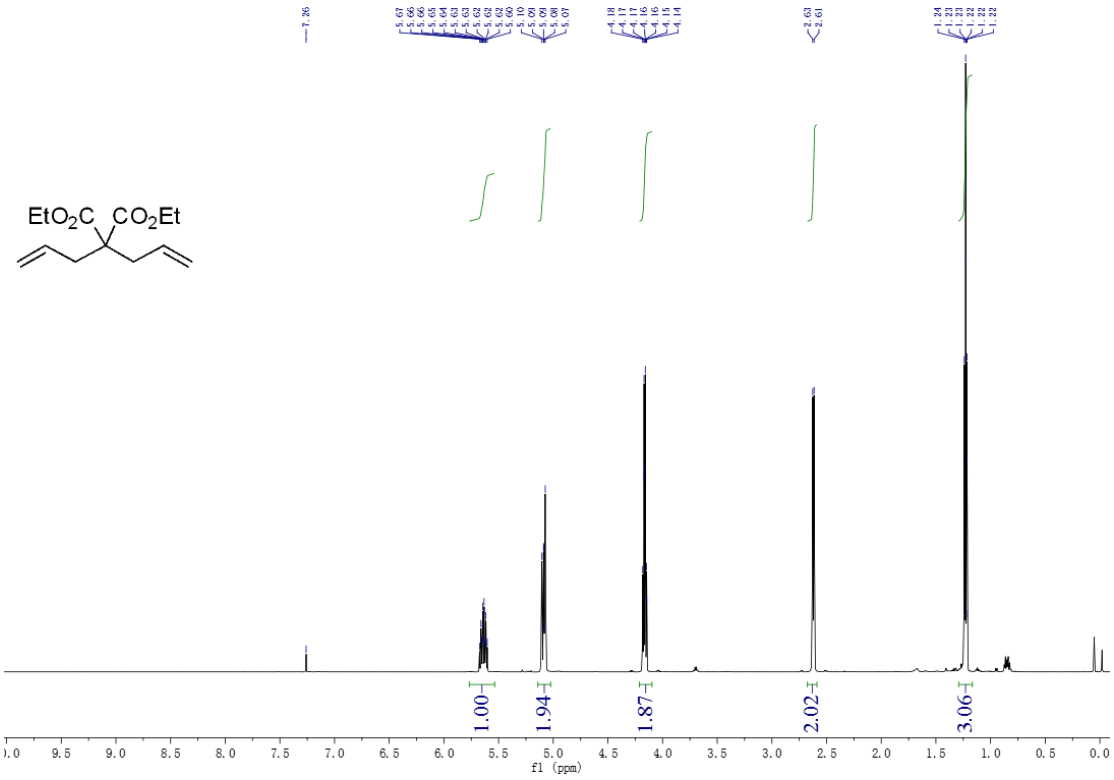
^{1}H NMR of **1r**



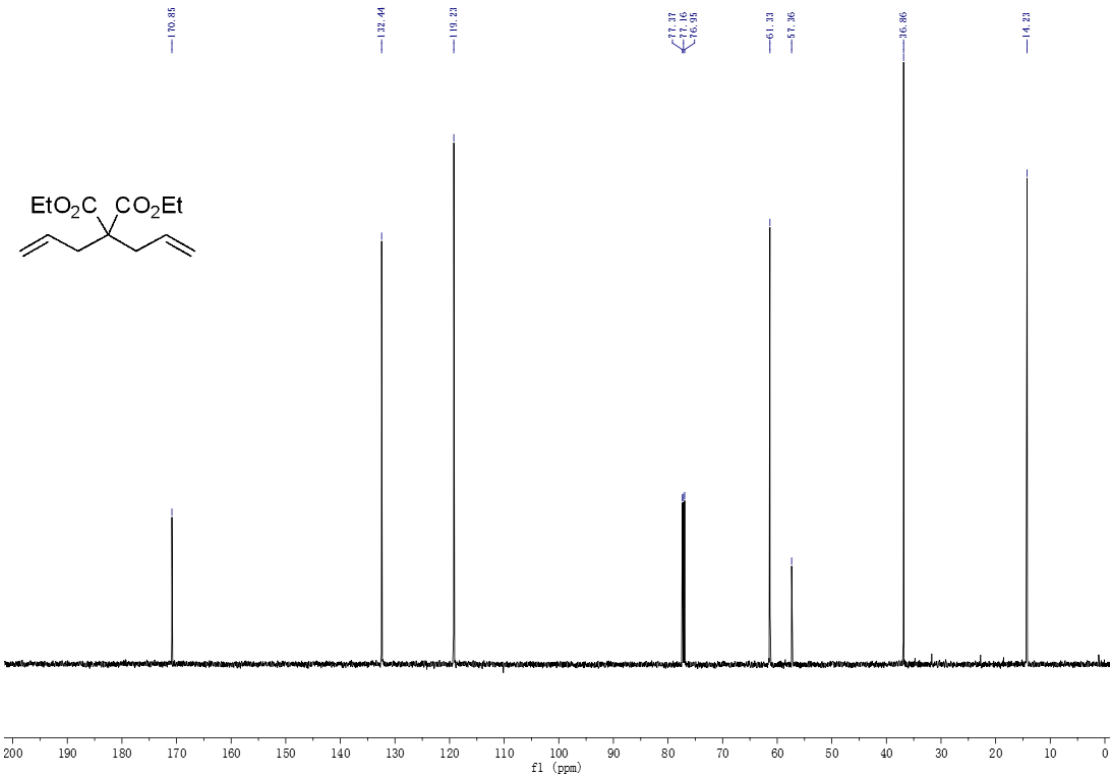
^{13}C NMR of **1r**



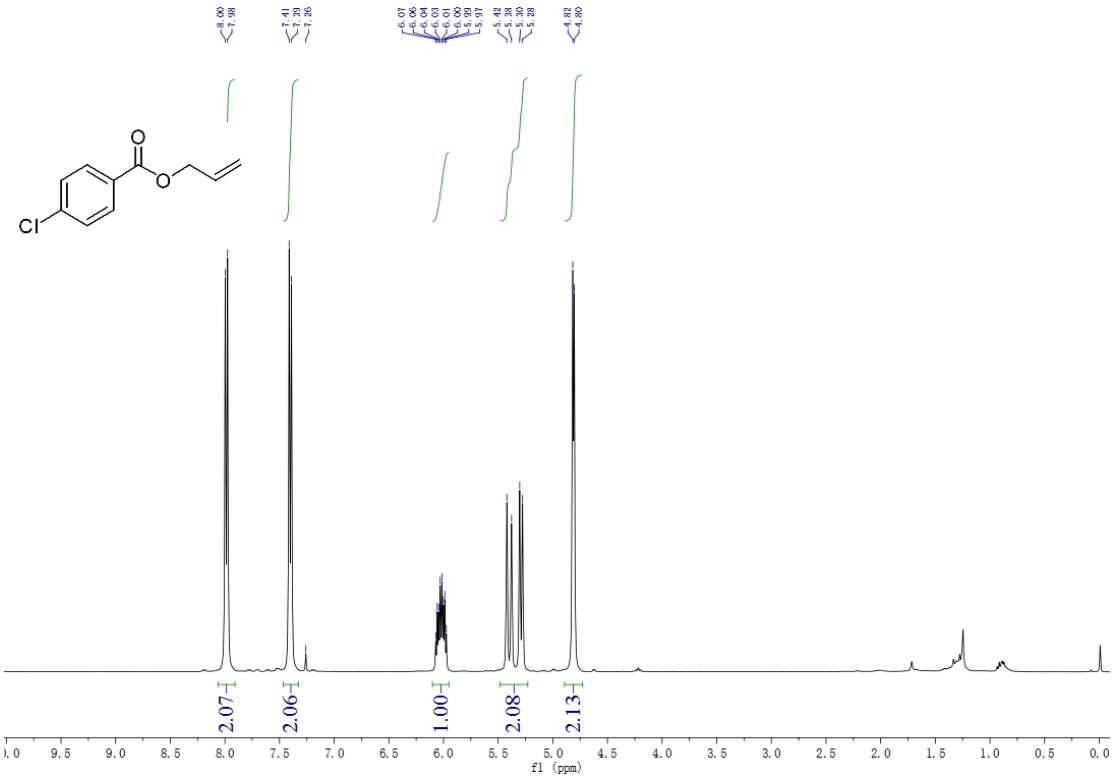
^{1}H NMR of **1s**



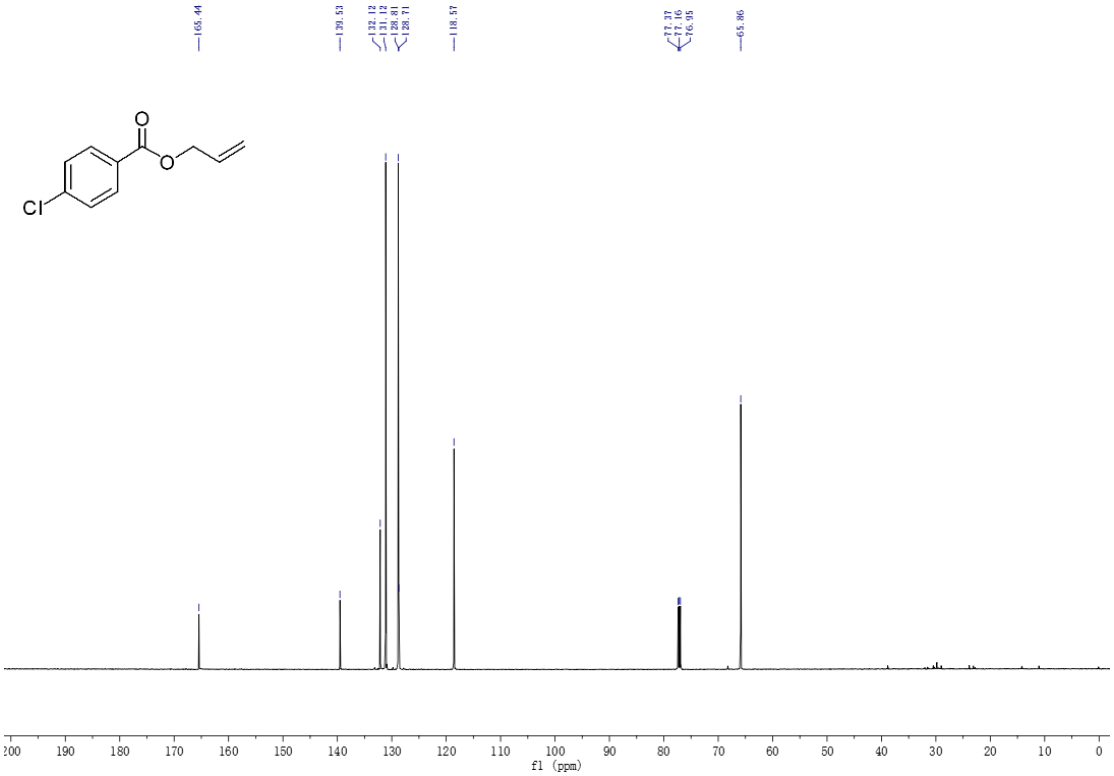
^{13}C NMR of **1s**



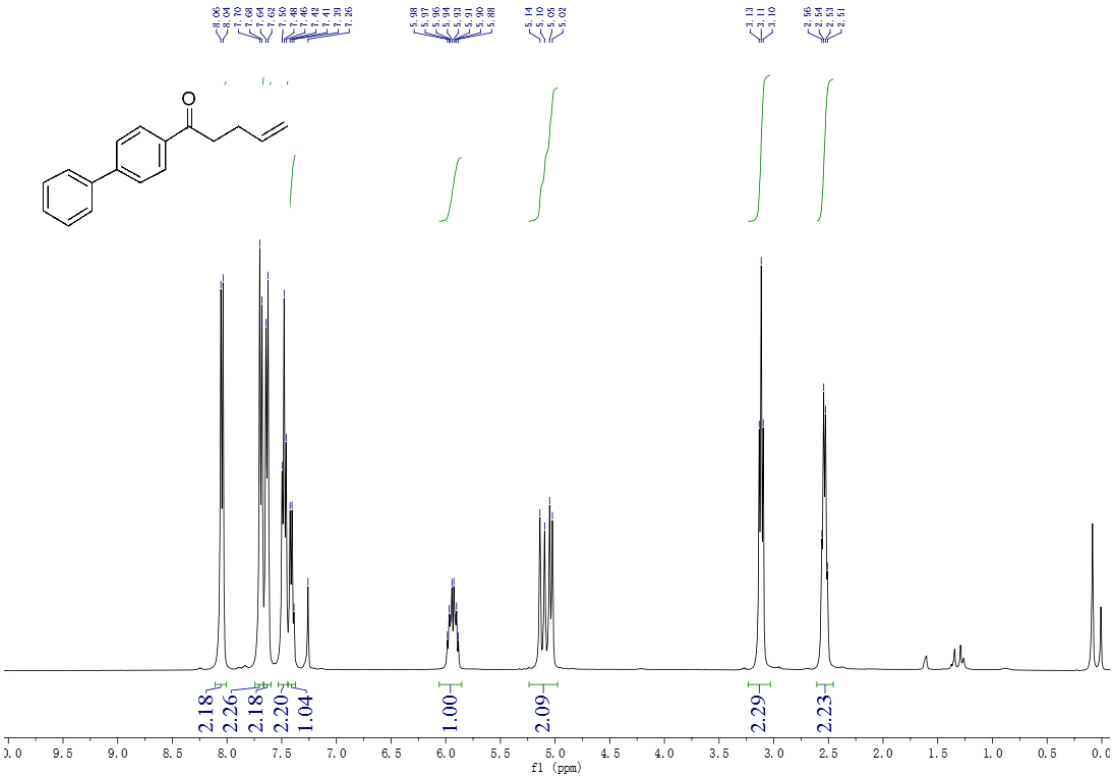
^{1}H NMR of **1t**



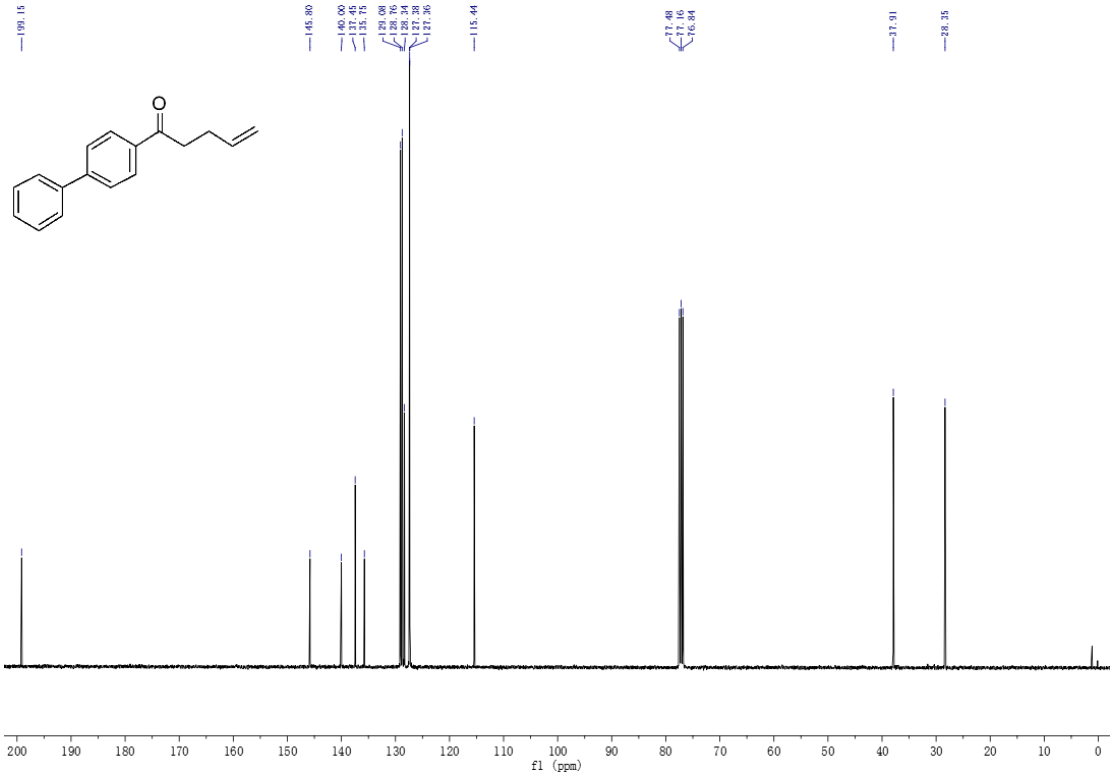
^{13}C NMR of **1t**



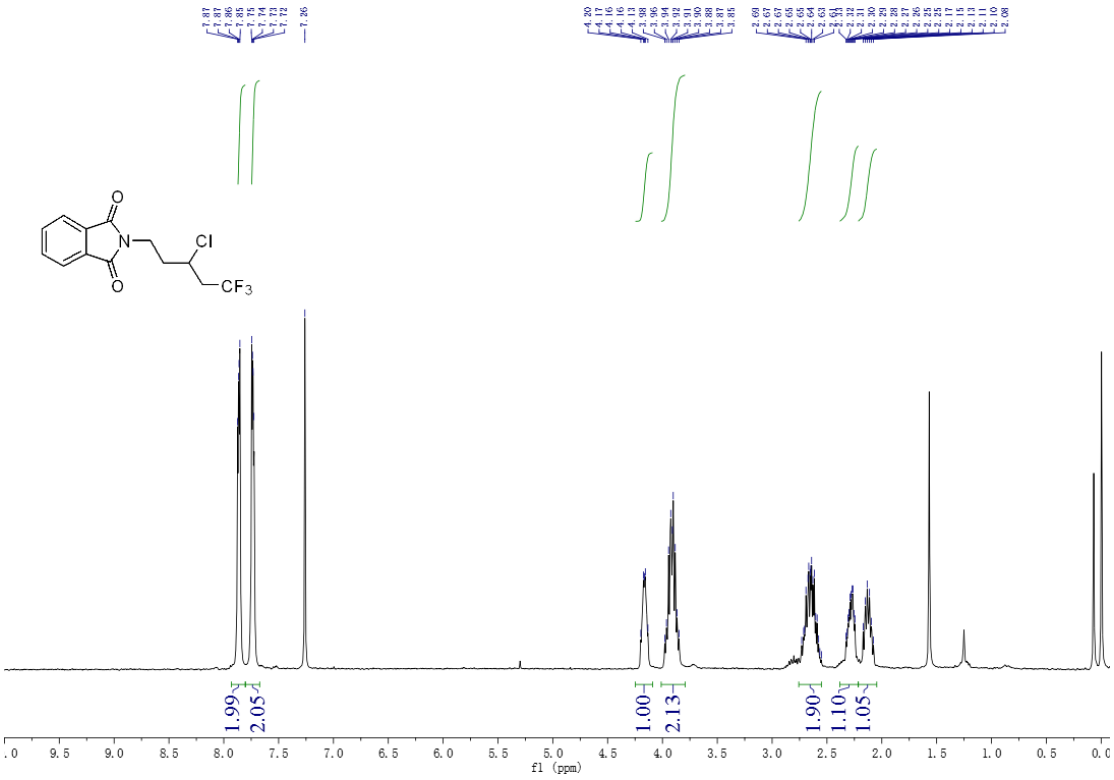
^{1}H NMR of **1u**



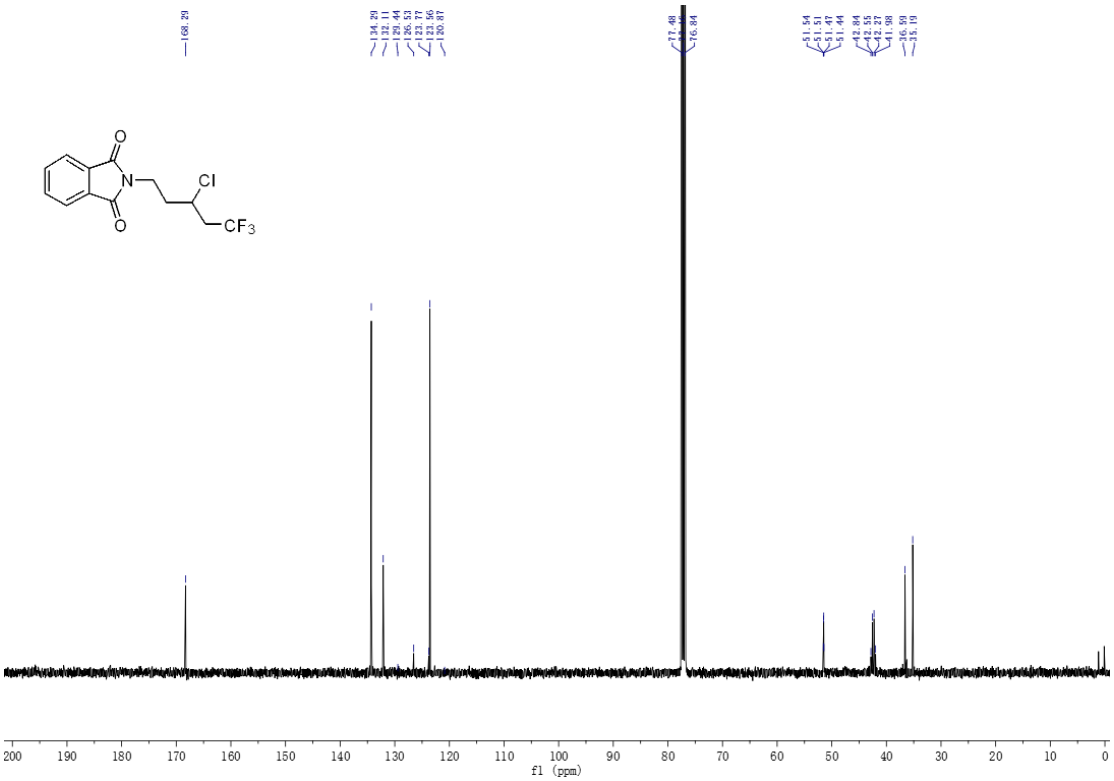
^{13}C NMR of **1u**



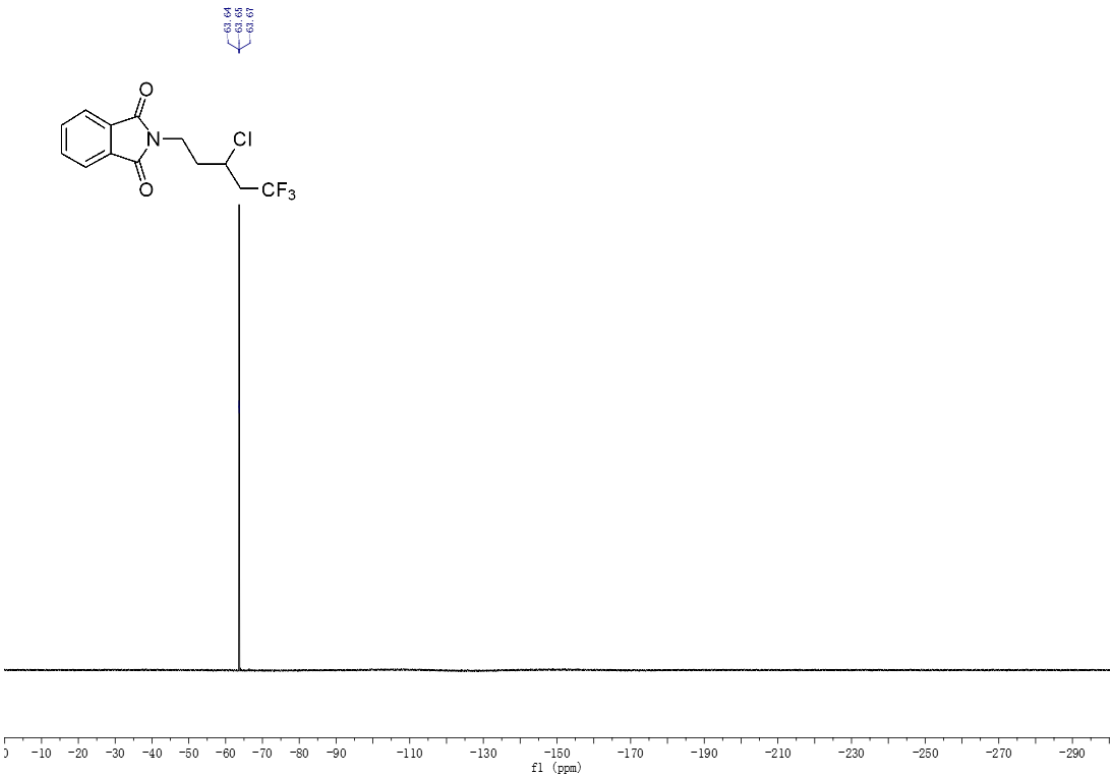
^{1}H NMR of **3a**



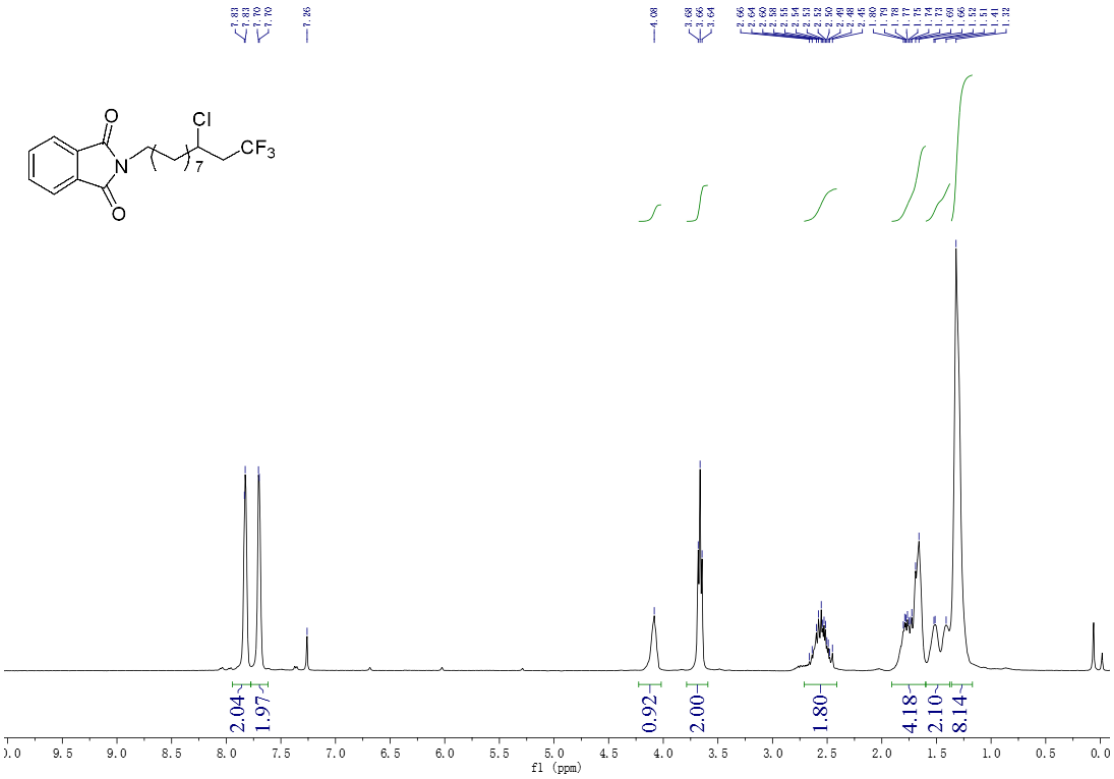
^{13}C NMR of **3a**



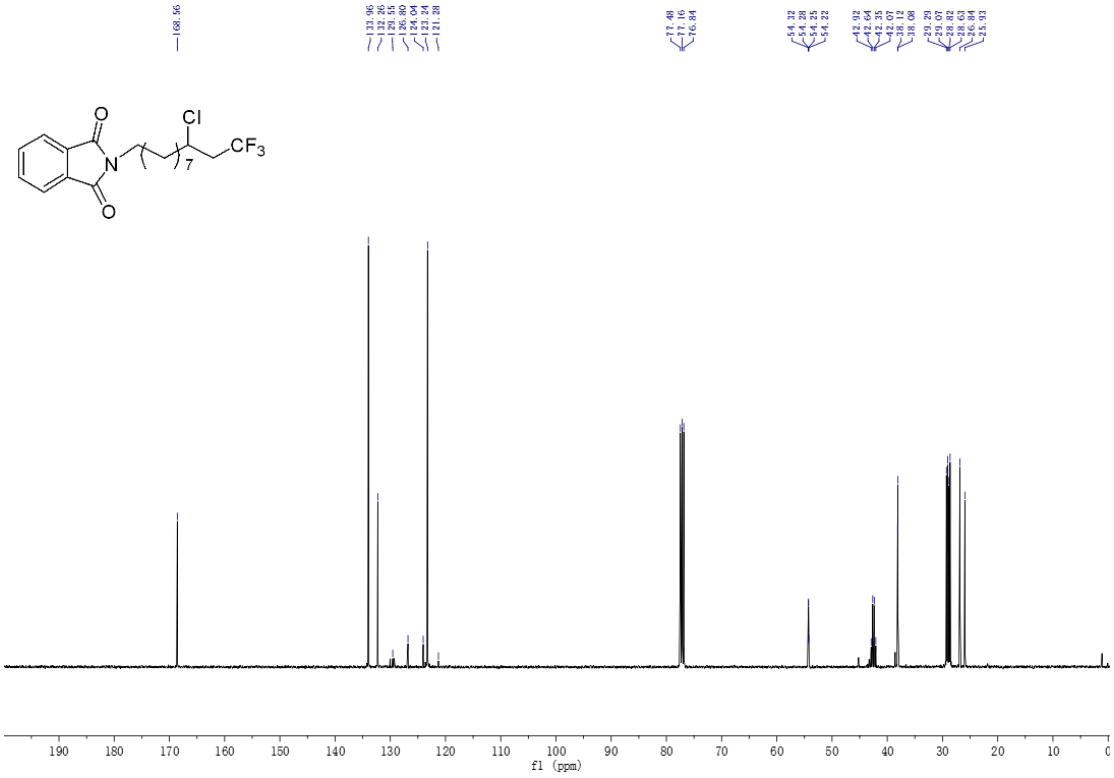
^{19}F NMR of **3a**



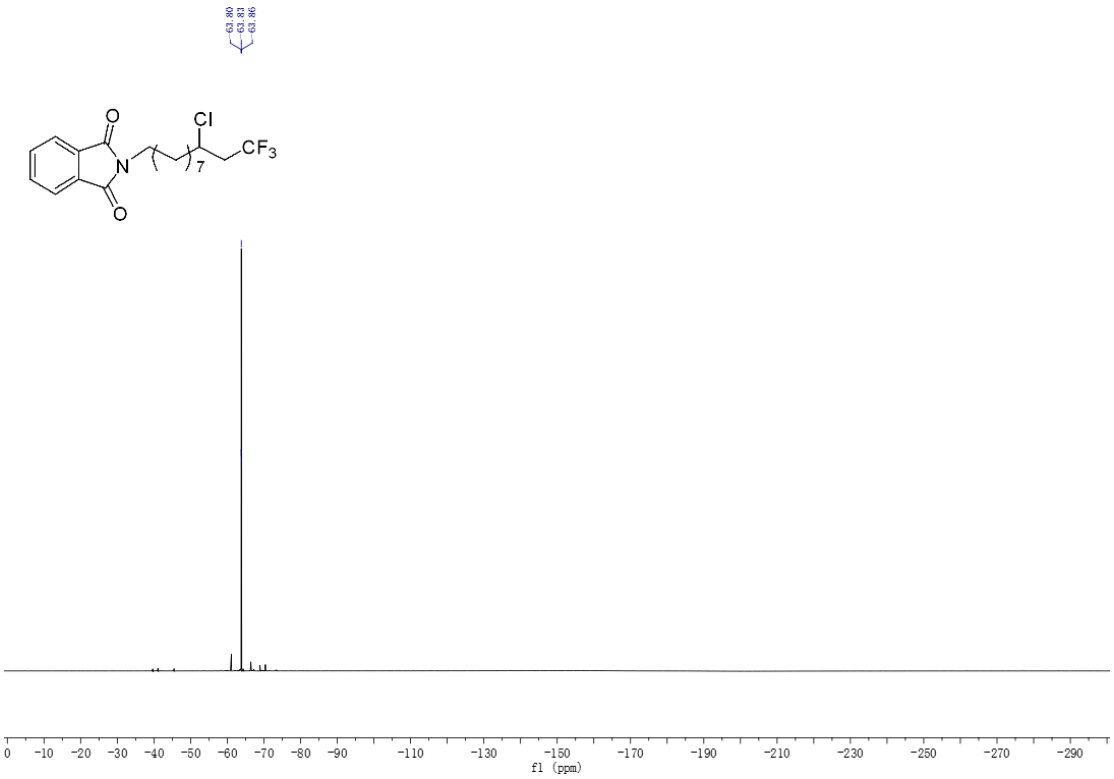
^{1}H NMR of **3b**



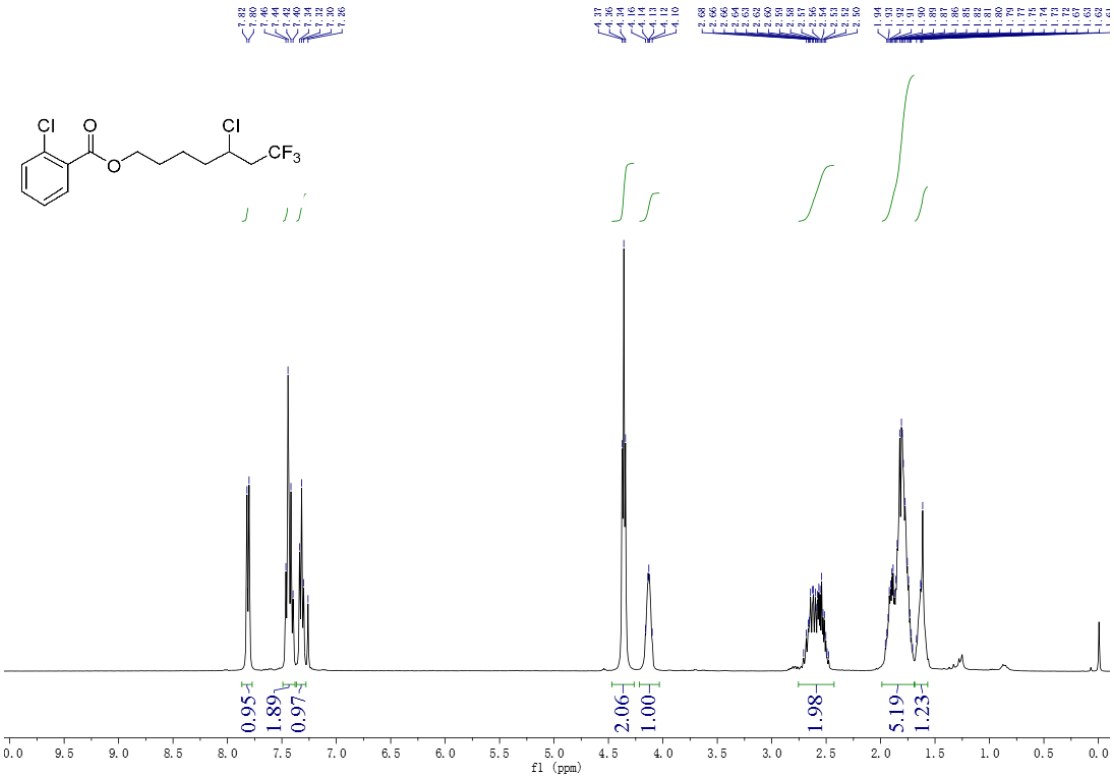
^{13}C NMR of **3b**



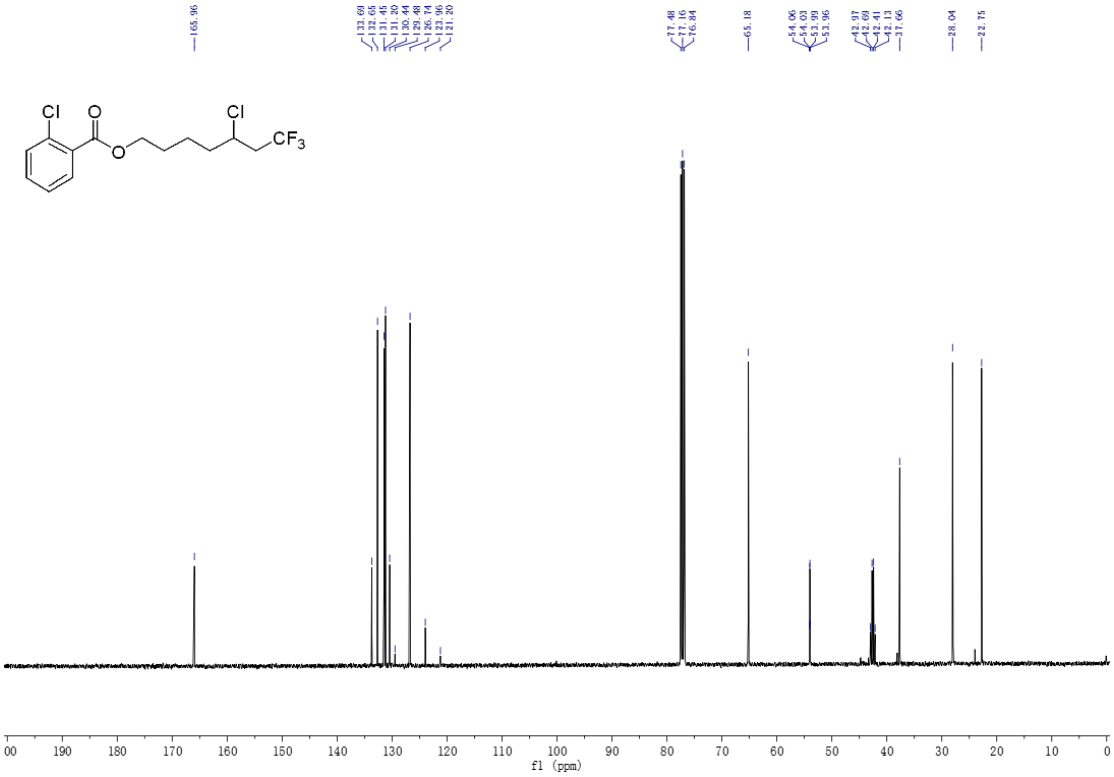
^{19}F NMR of **3b**



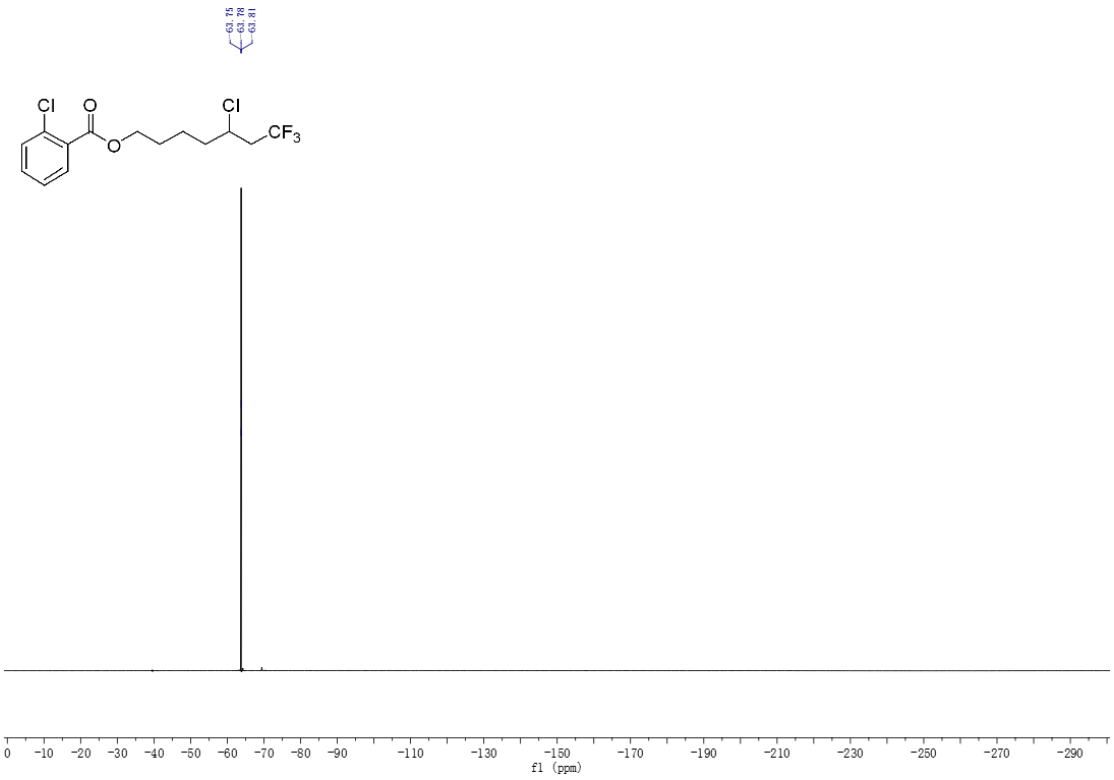
^{1}H NMR of **3c**



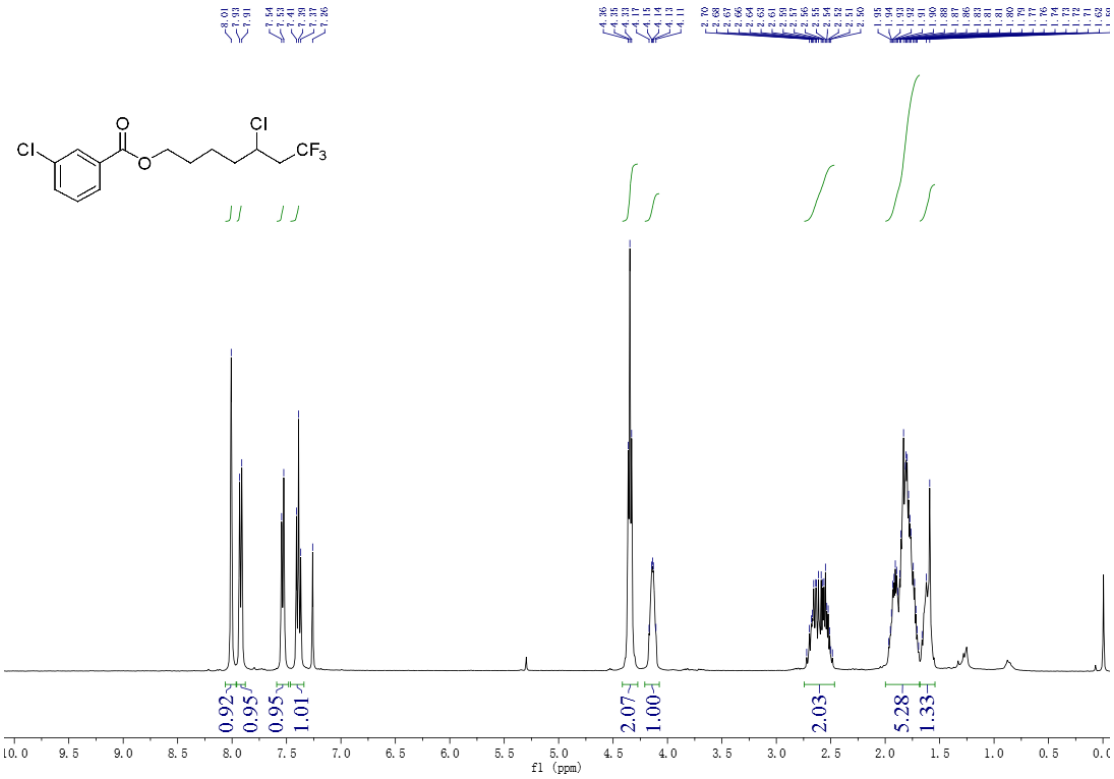
^{13}C NMR of **3c**



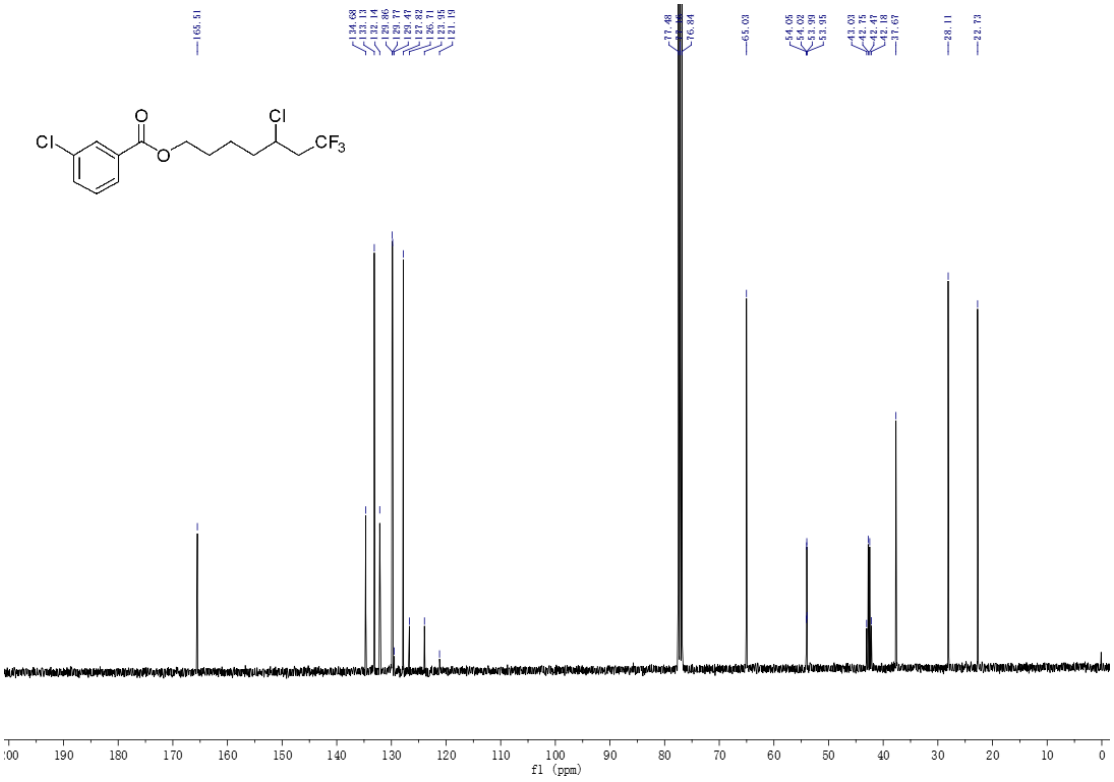
^{19}F NMR of **3c**



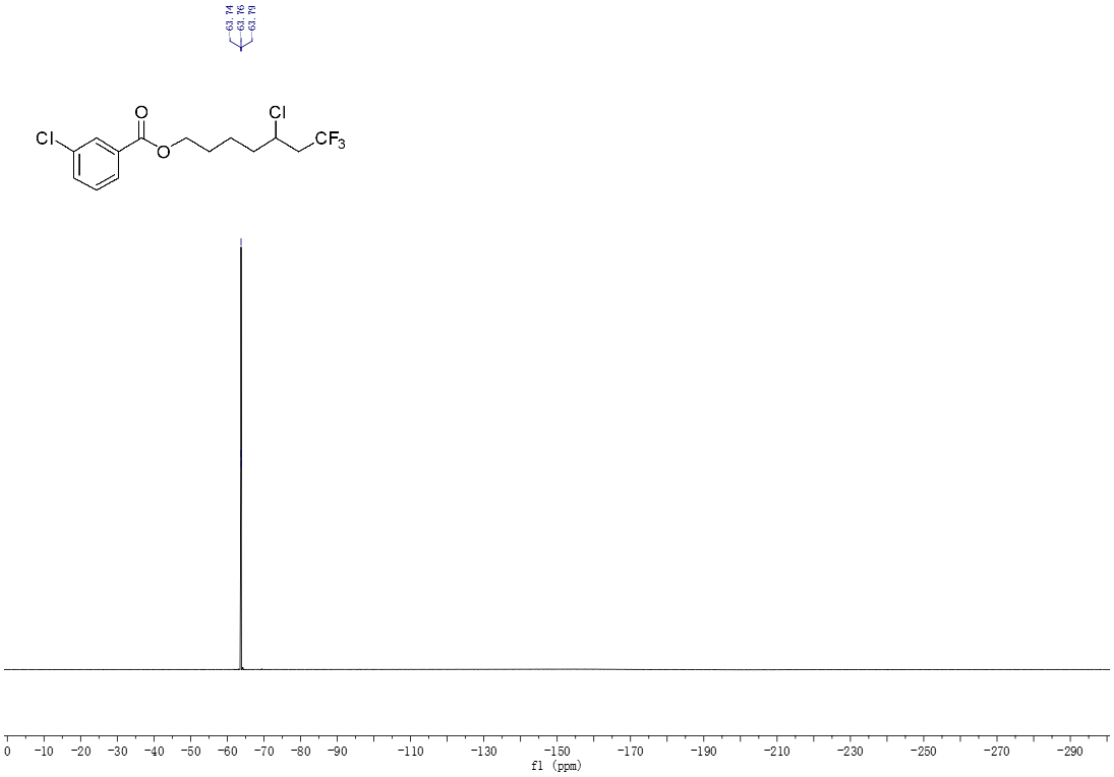
^{1}H NMR of **3d**



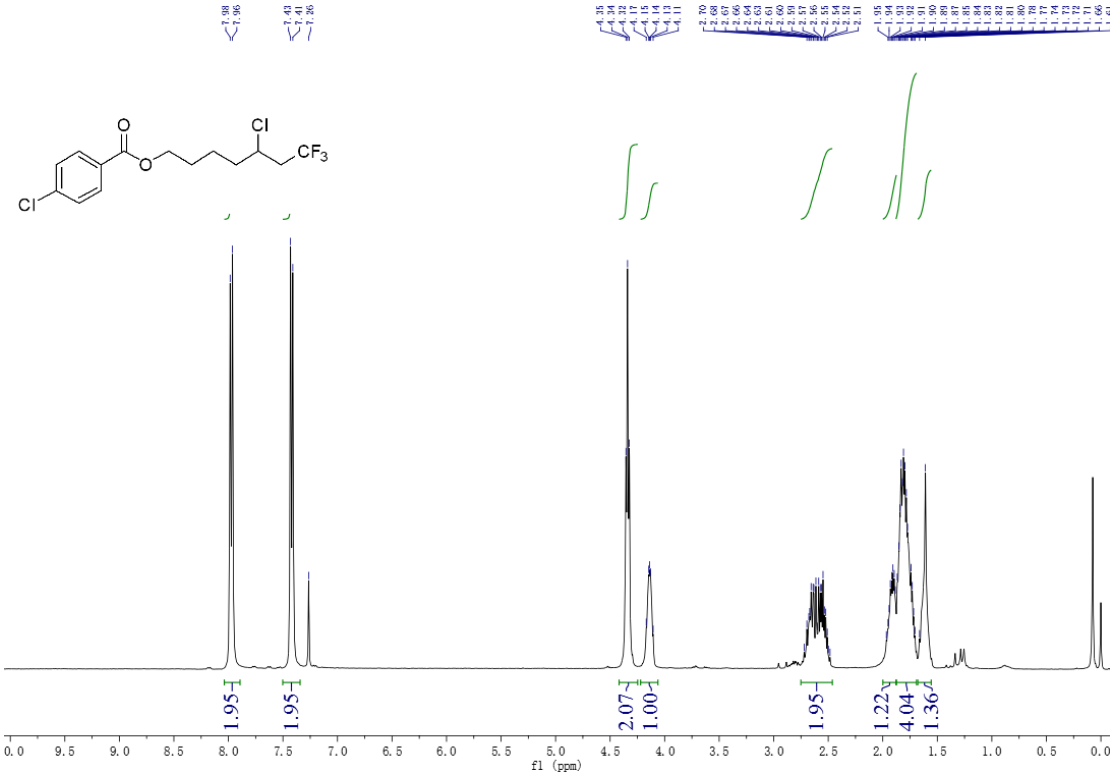
^{13}C NMR of **3d**



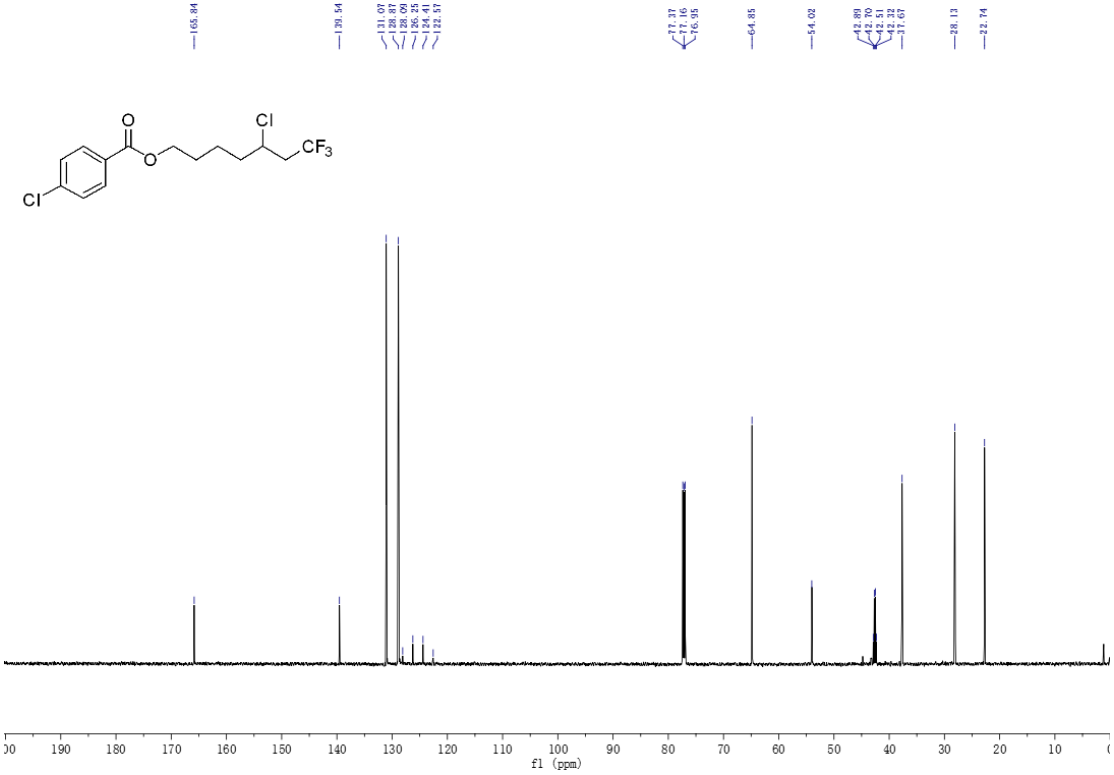
^{19}F NMR of **3d**



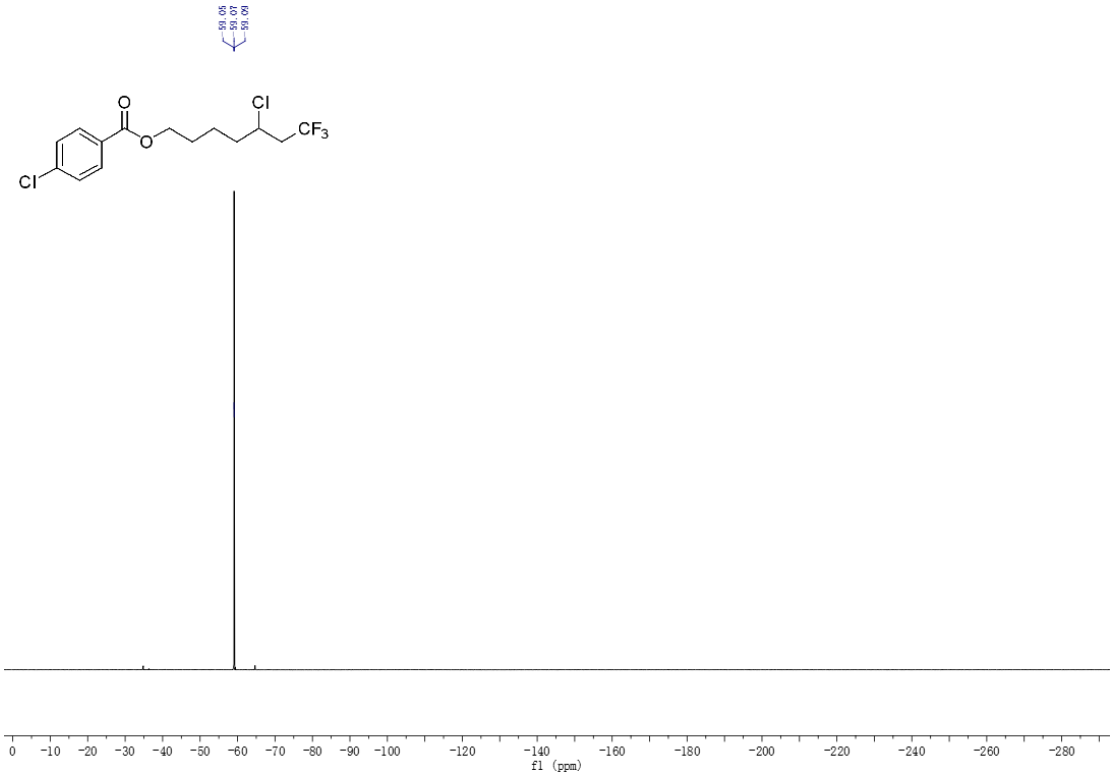
^{1}H NMR of **3e**



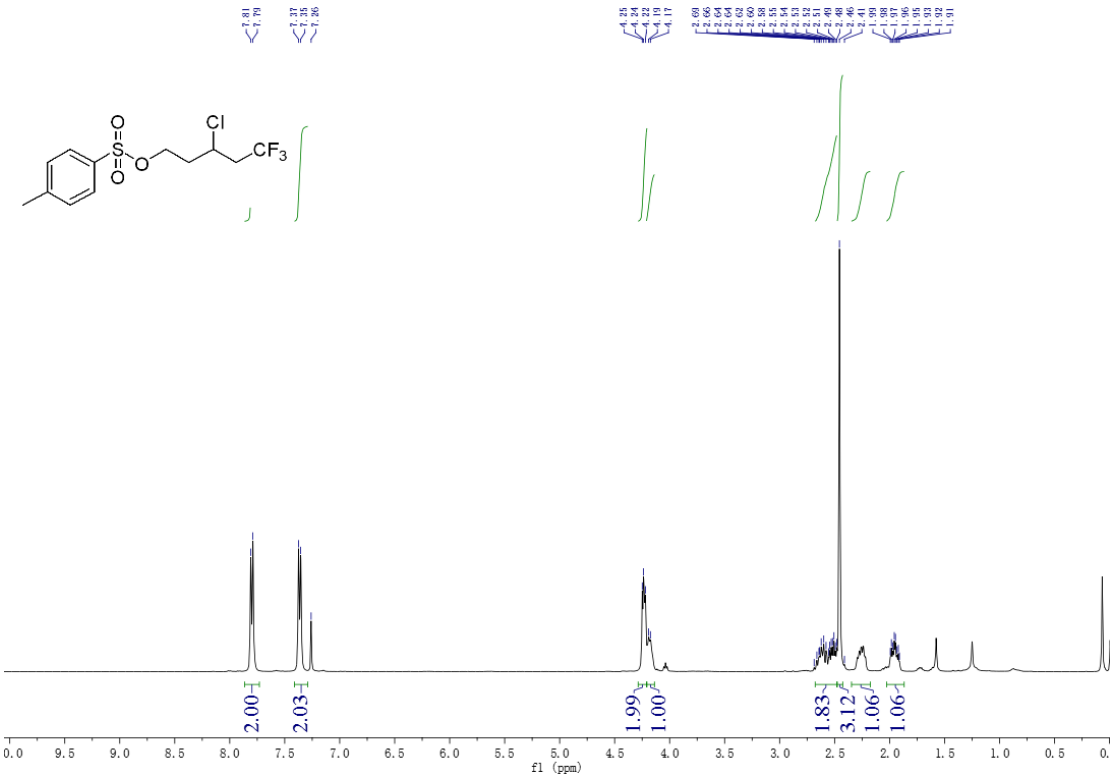
^{13}C NMR of **3e**



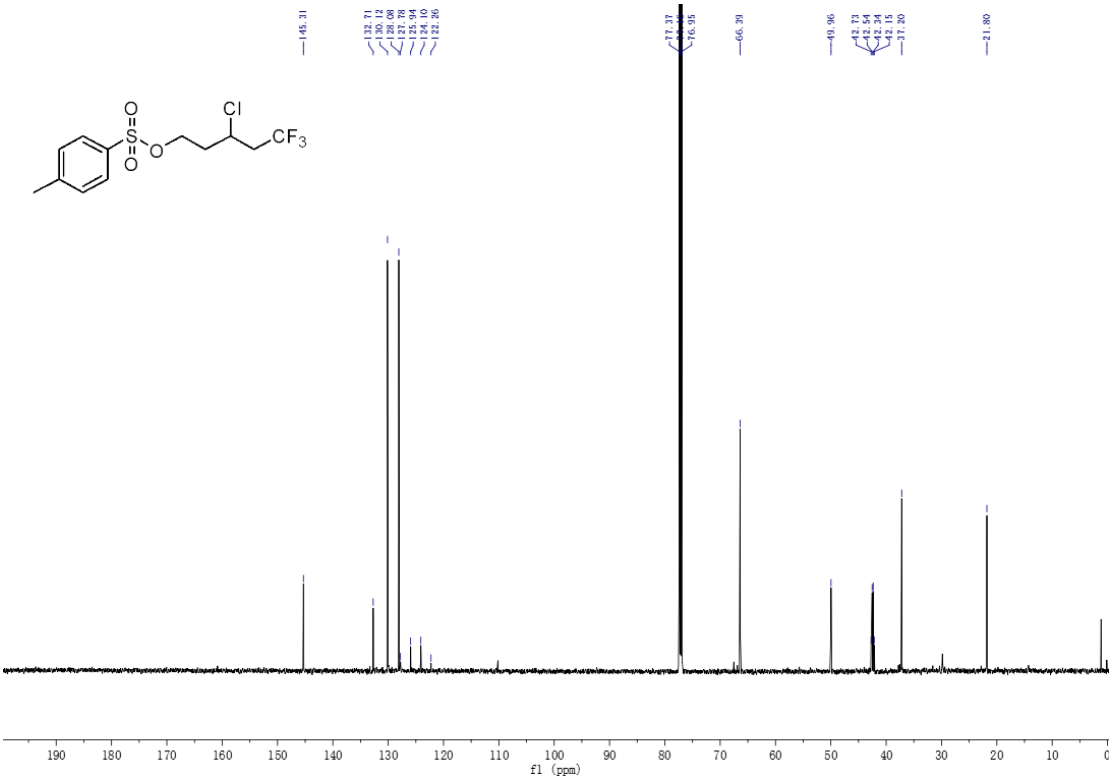
^{19}F NMR of **3e**



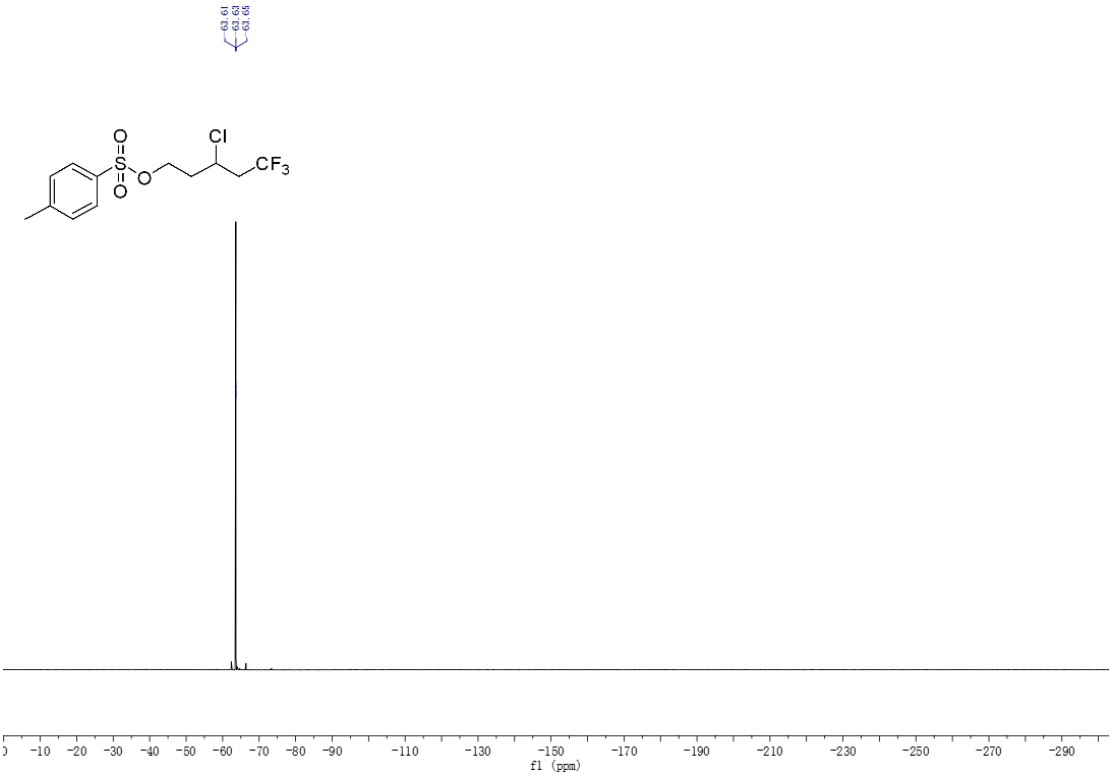
^{1}H NMR of **3f**



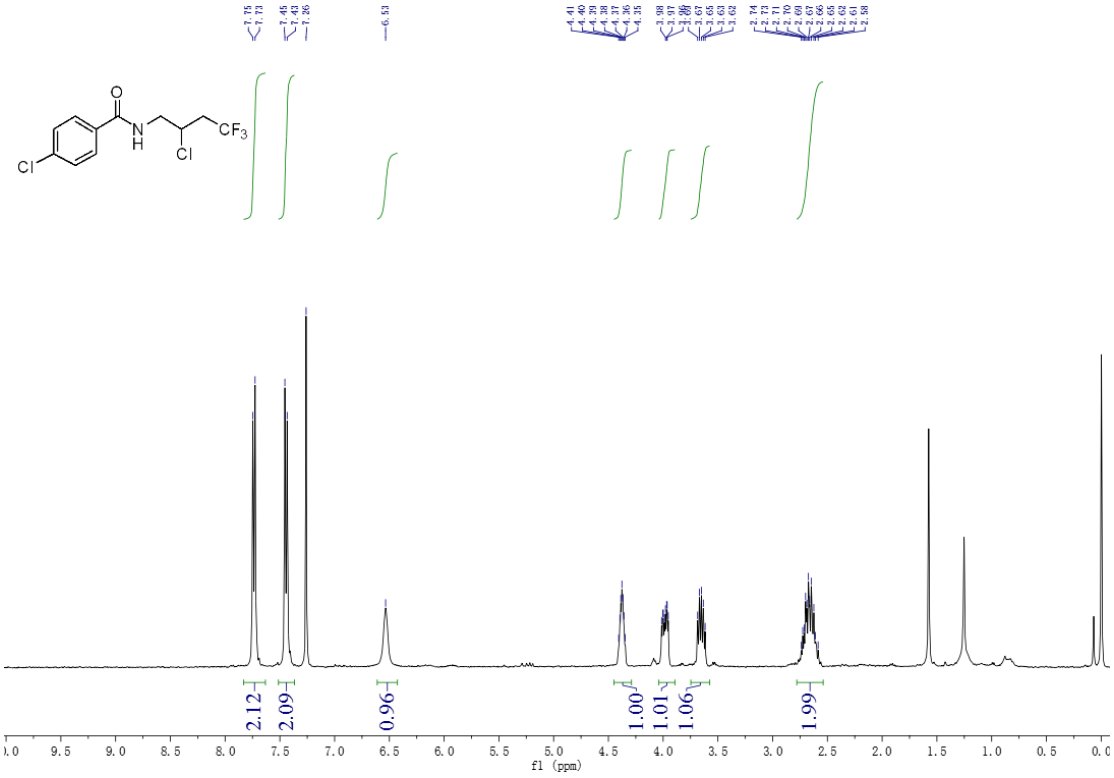
^{13}C NMR of **3f**



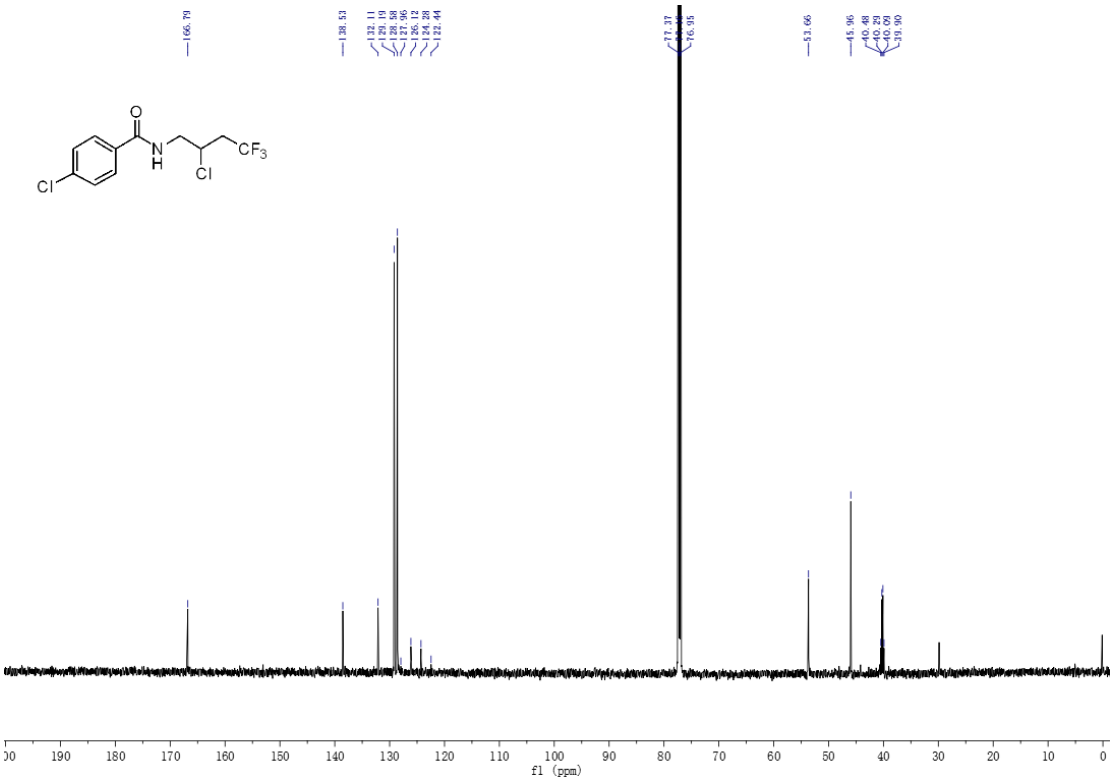
^{19}F NMR of **3f**



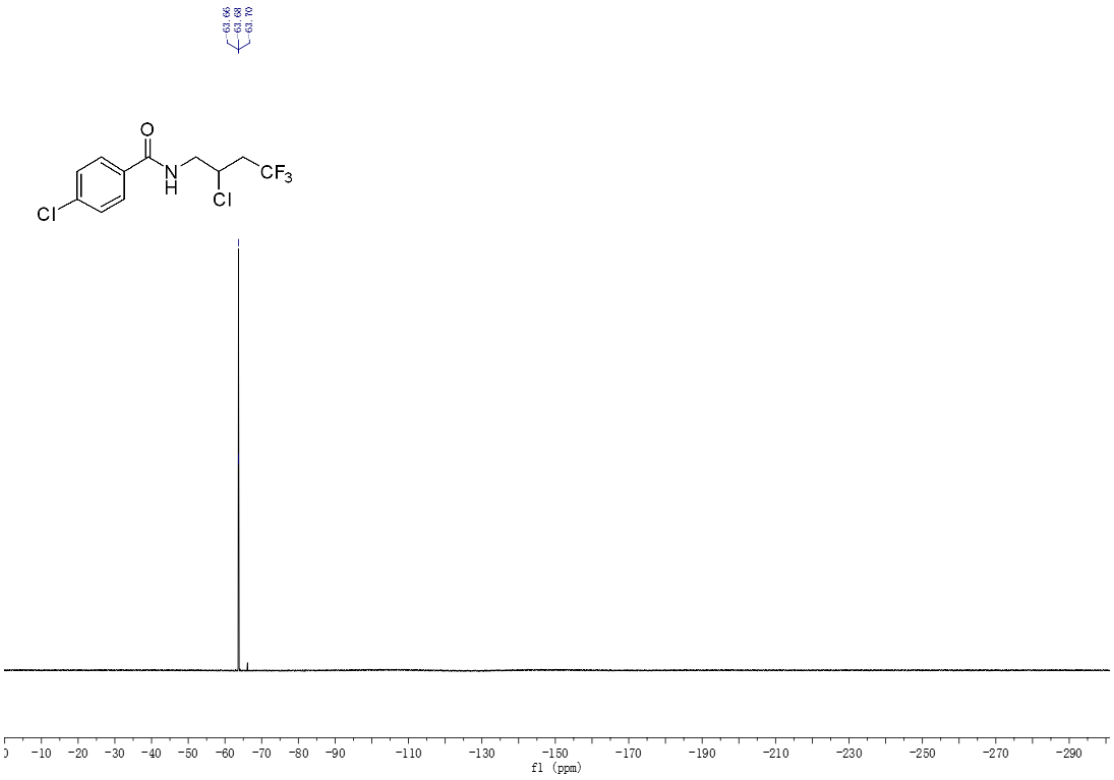
^{1}H NMR of **3g**



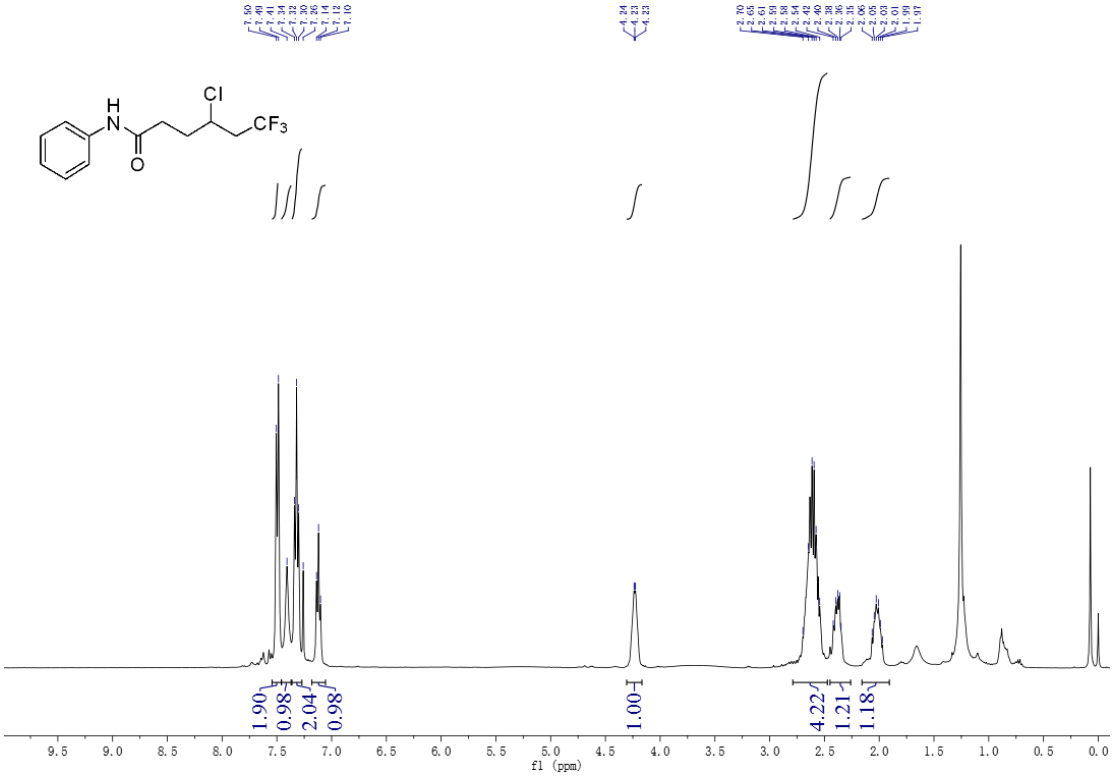
^{13}C NMR of **3g**



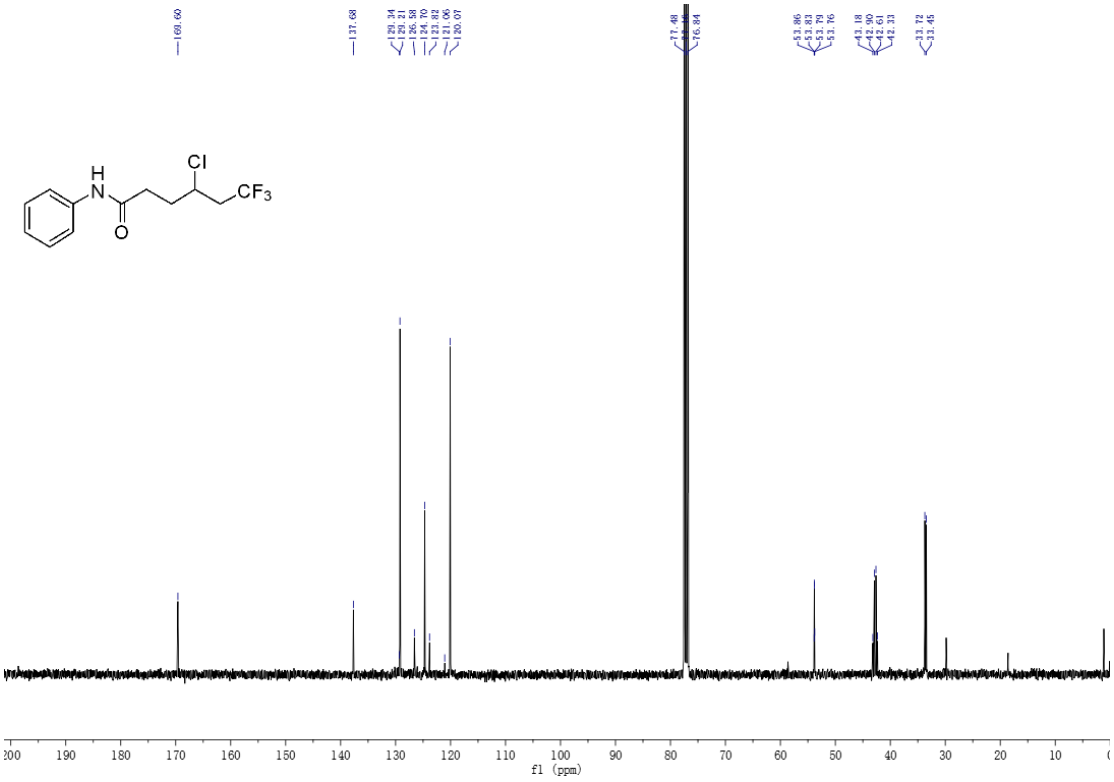
^{19}F NMR of **3g**



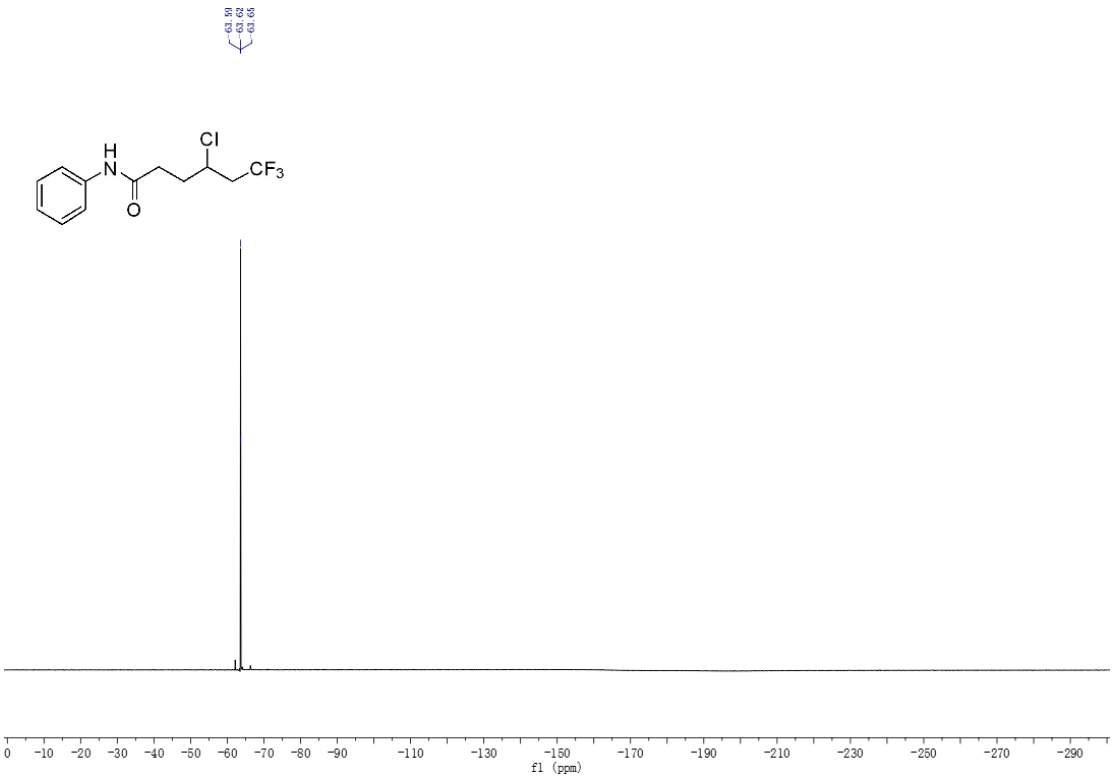
^{1}H NMR of **3h**



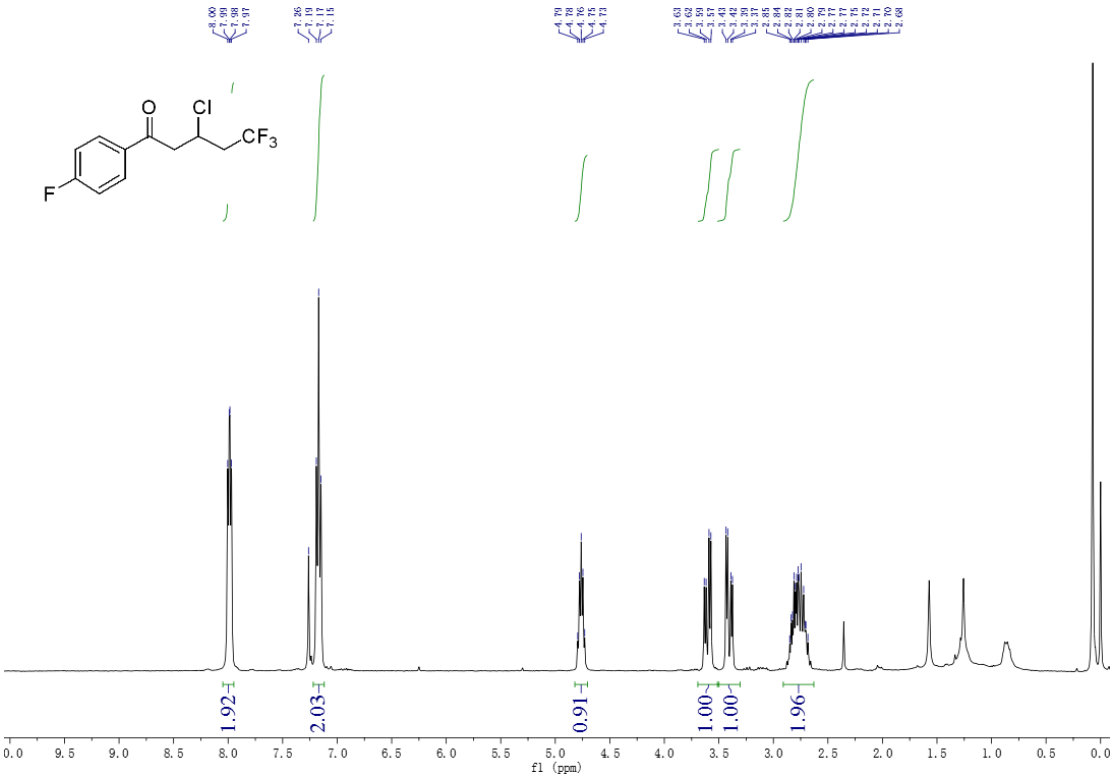
^{13}C NMR of **3h**



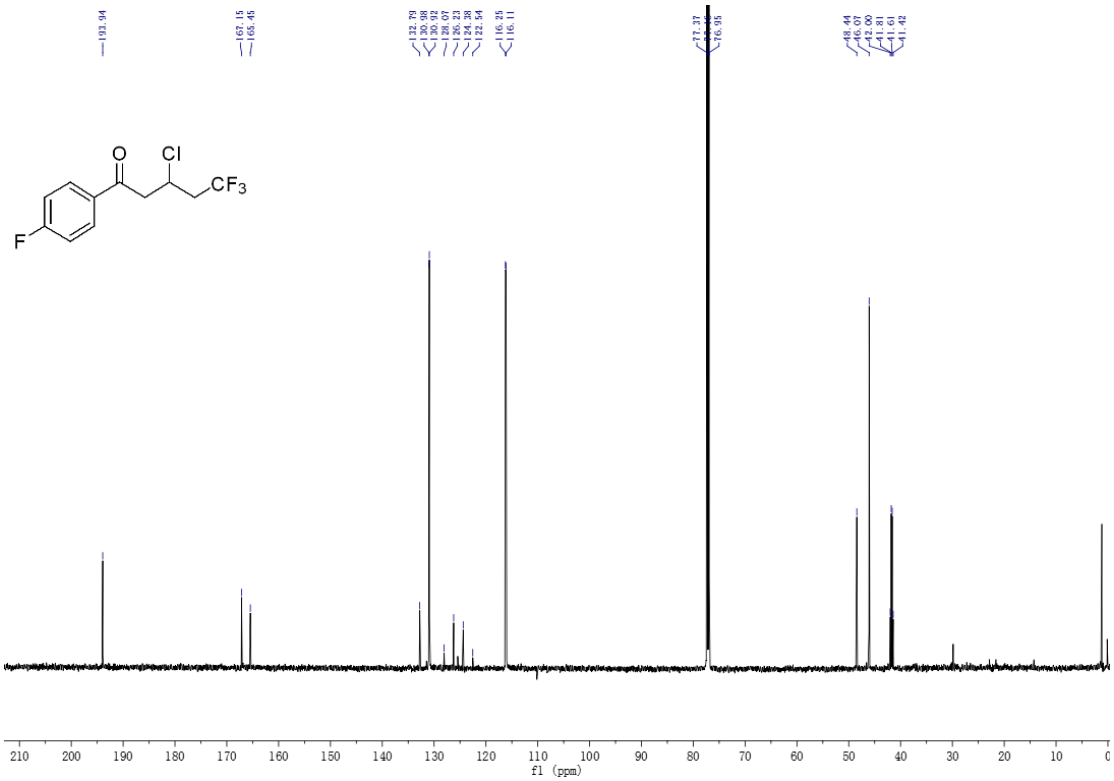
^{19}F NMR of **3h**



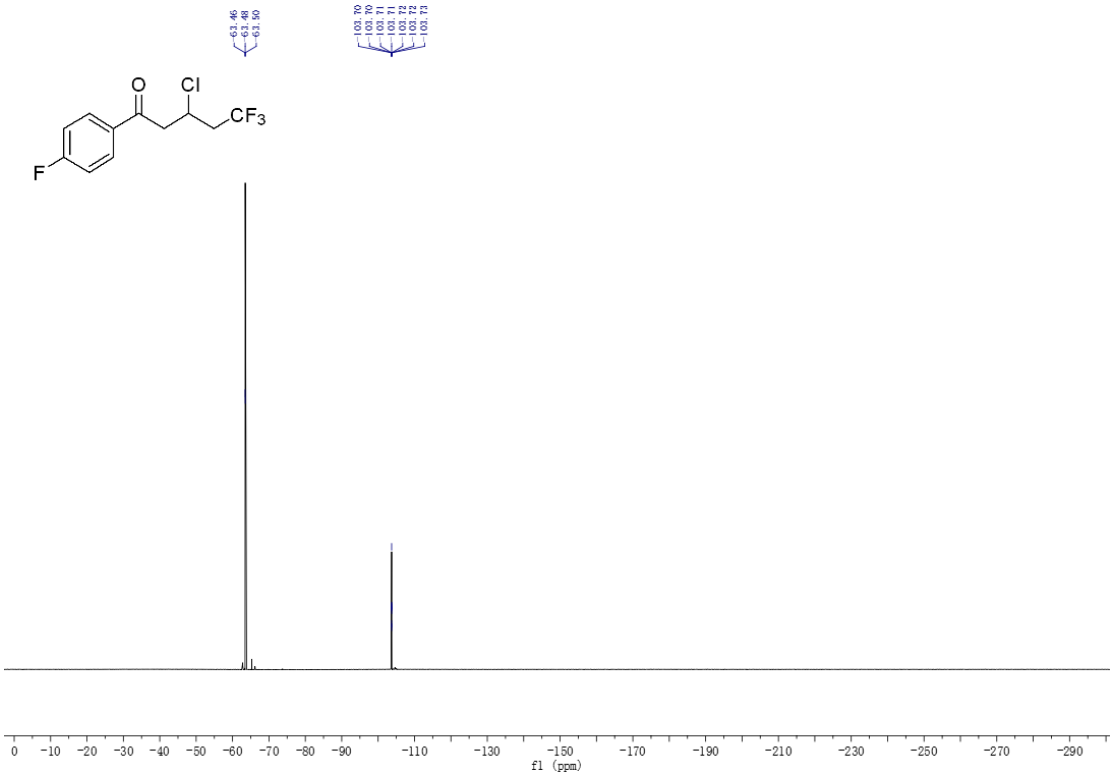
^{1}H NMR of **3i**



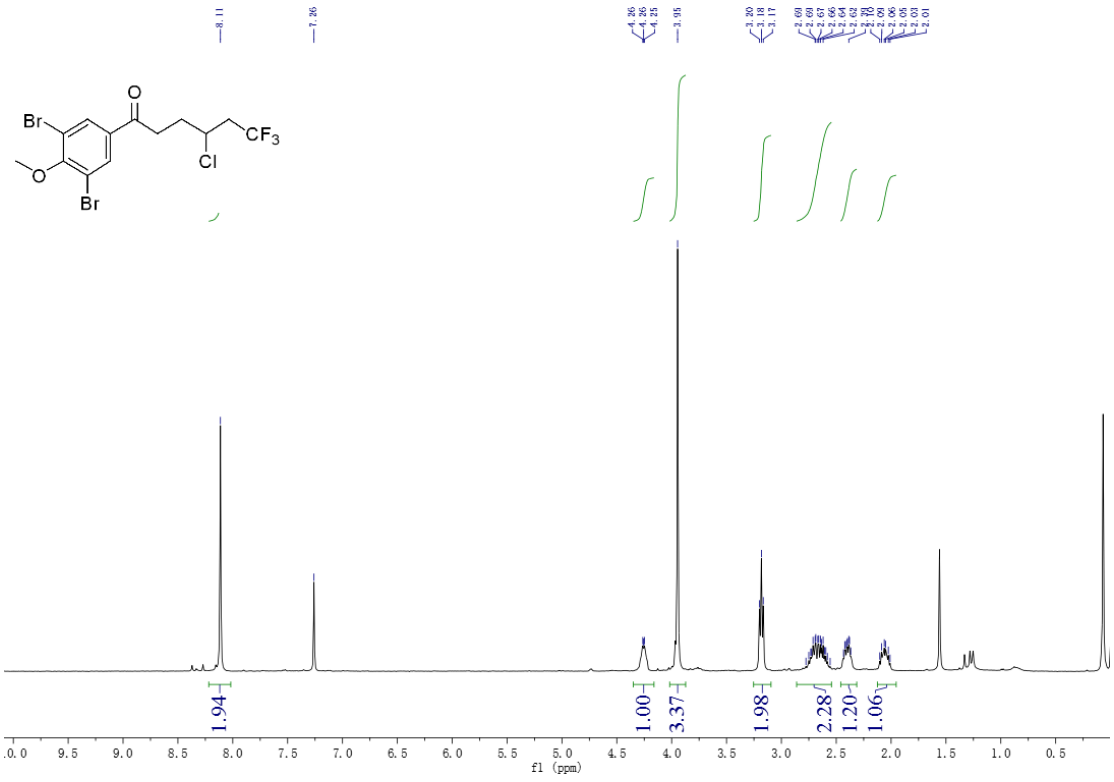
^{13}C NMR of **3i**



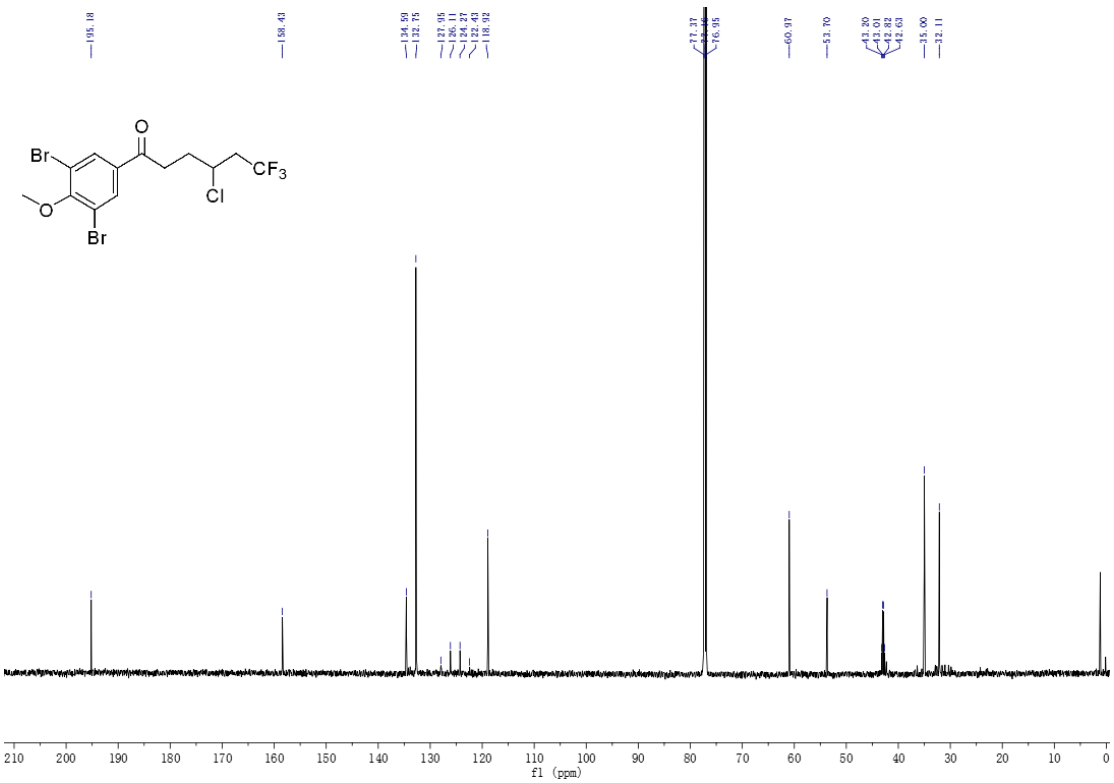
^{19}F NMR of **3i**



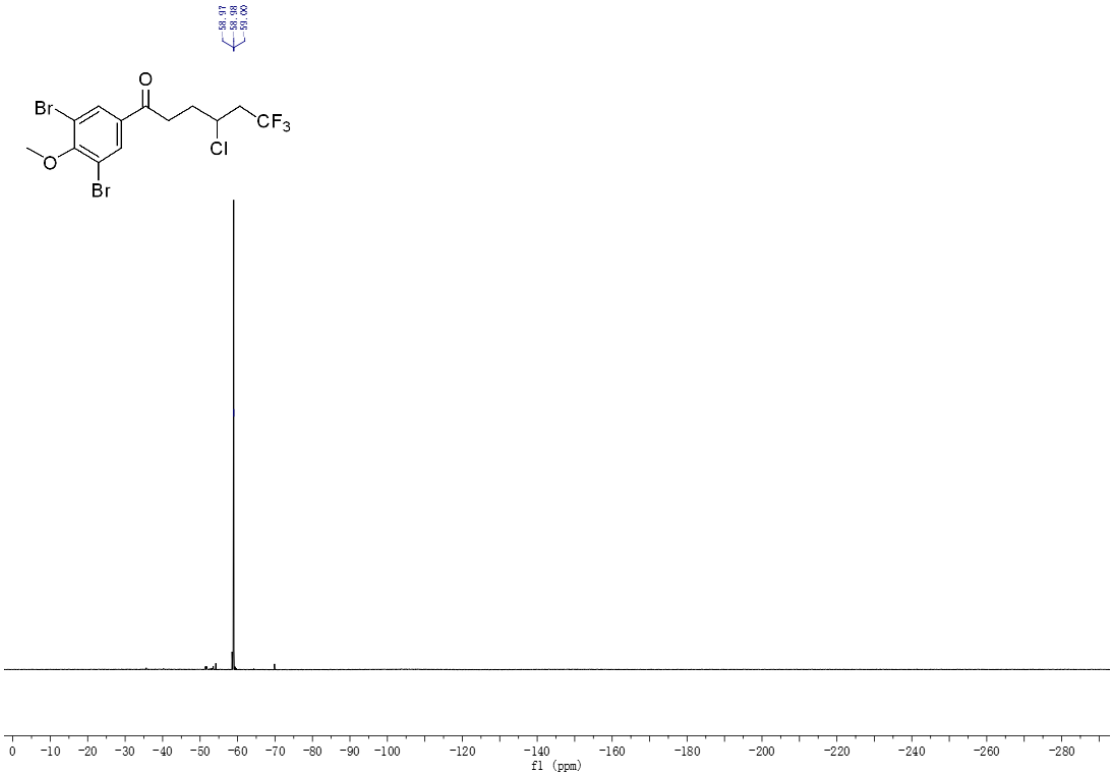
^{1}H NMR of **3j**



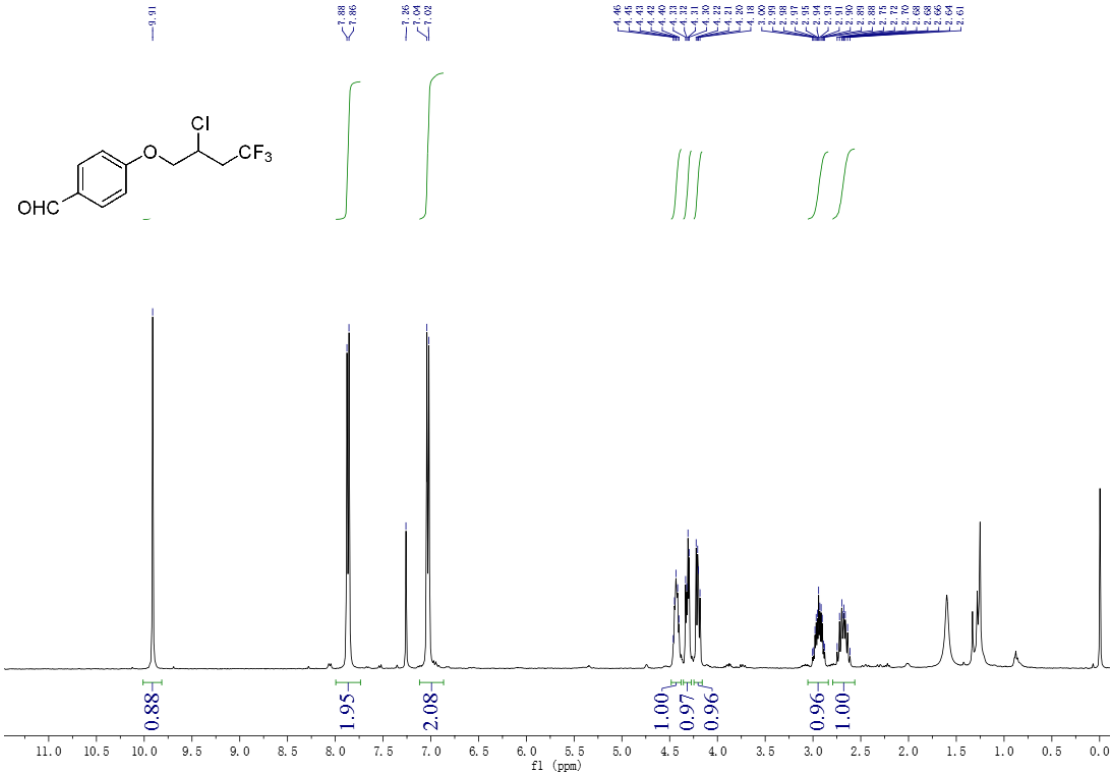
^{13}C NMR of **3j**



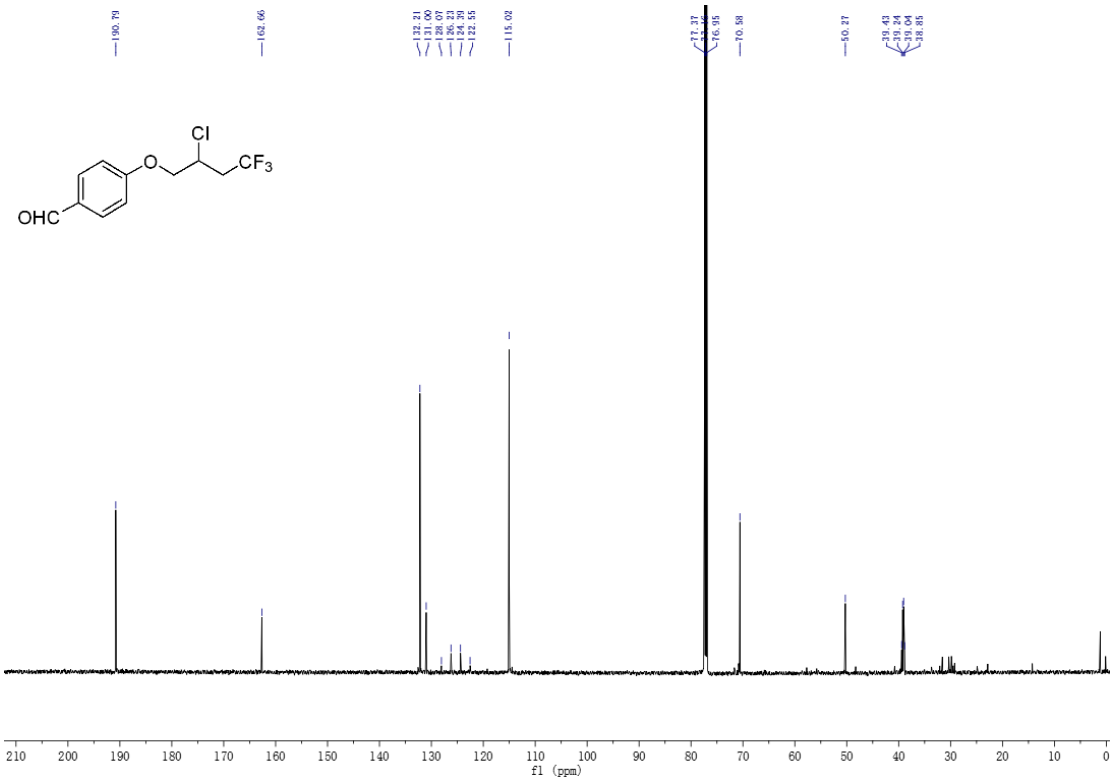
^{19}F NMR of **3j**



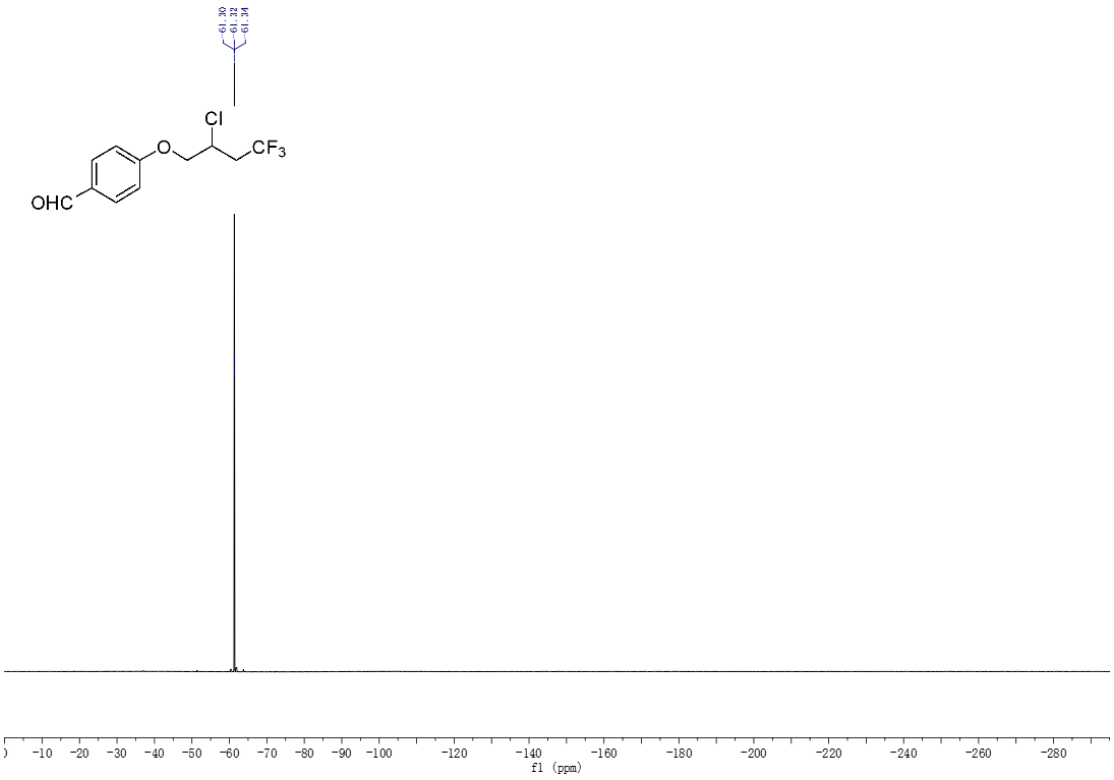
^{1}H NMR of **3k**



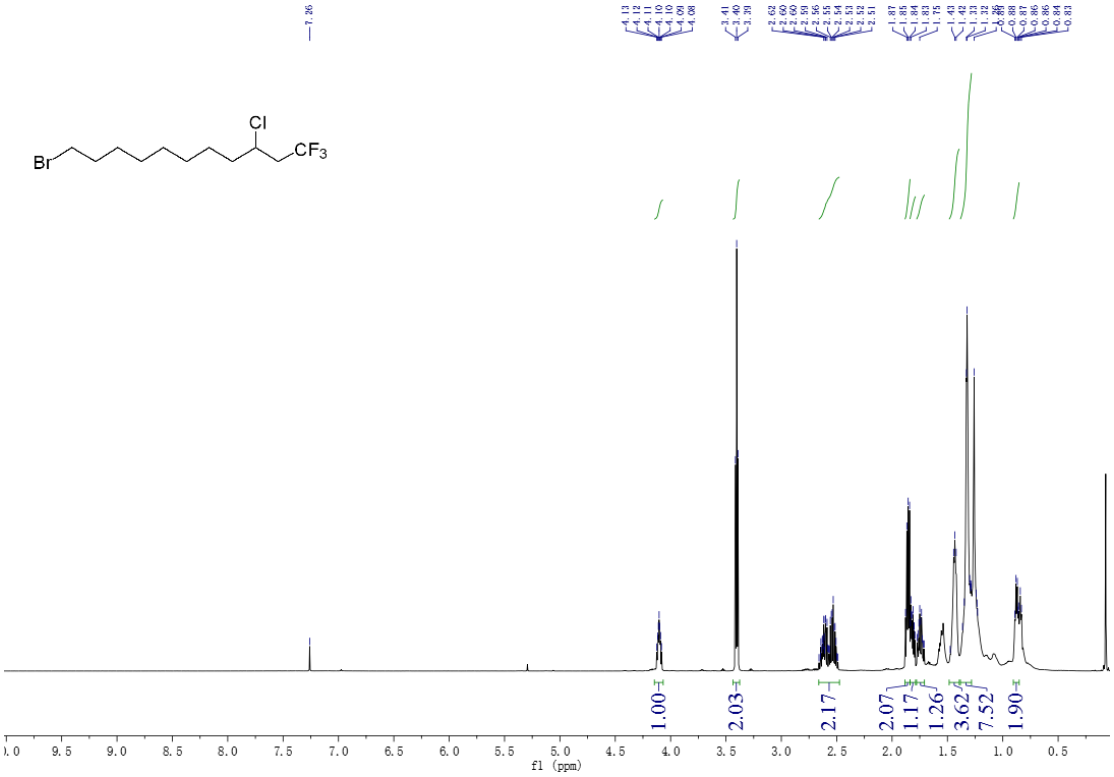
^{13}C NMR of **3k**



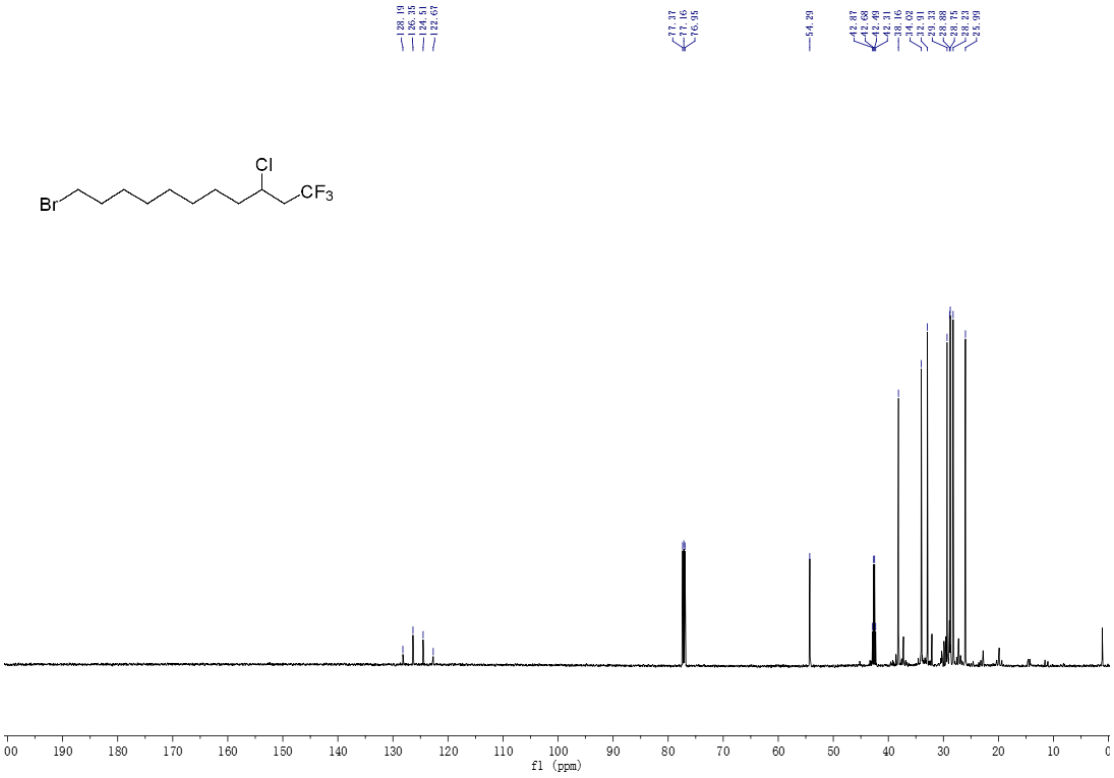
^{19}F NMR of **3k**



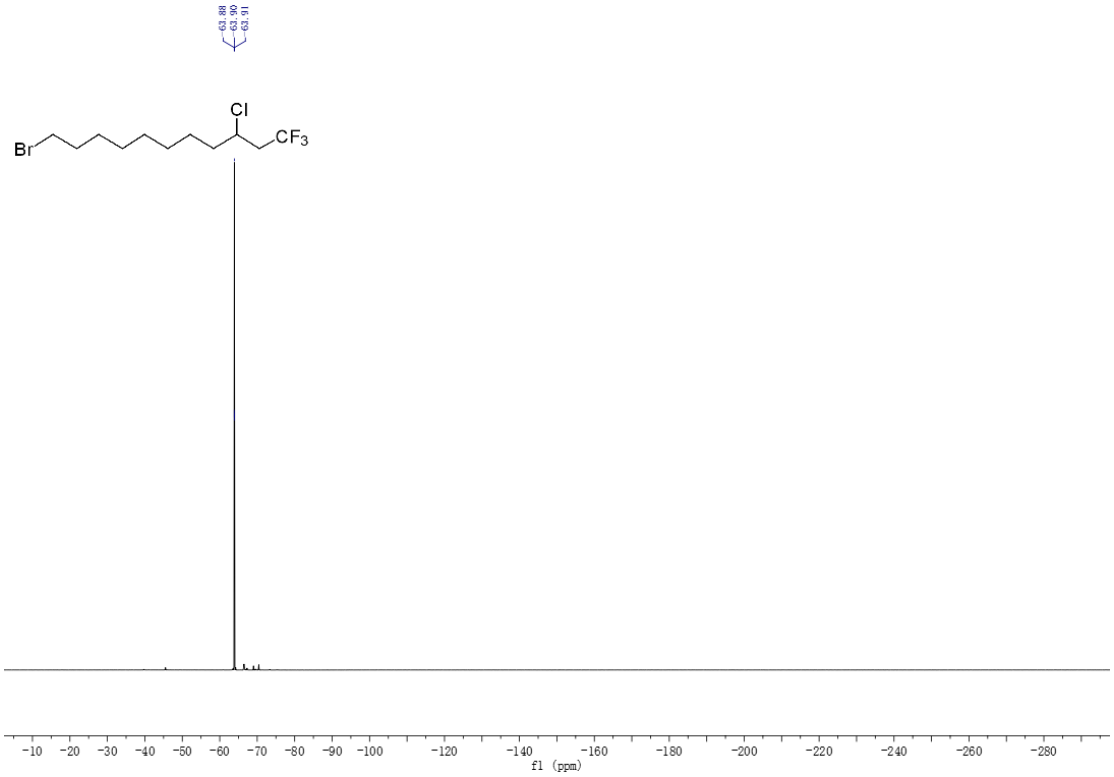
^{1}H NMR of **3l**



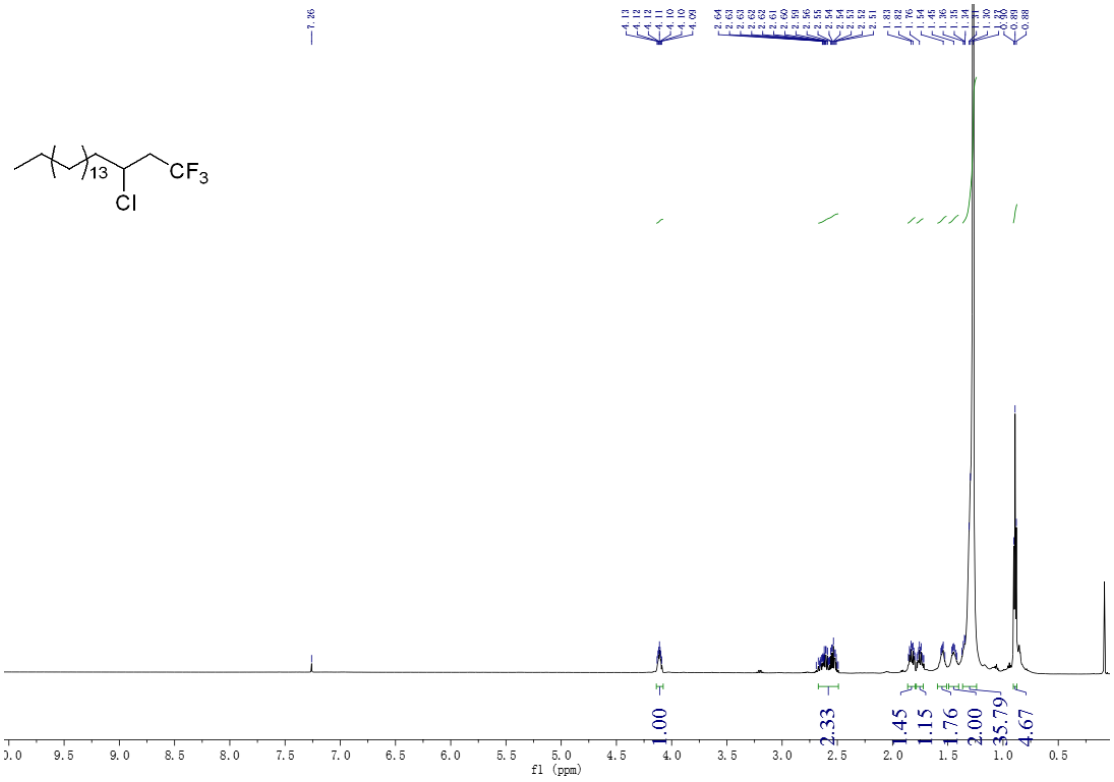
^{13}C NMR of **3l**



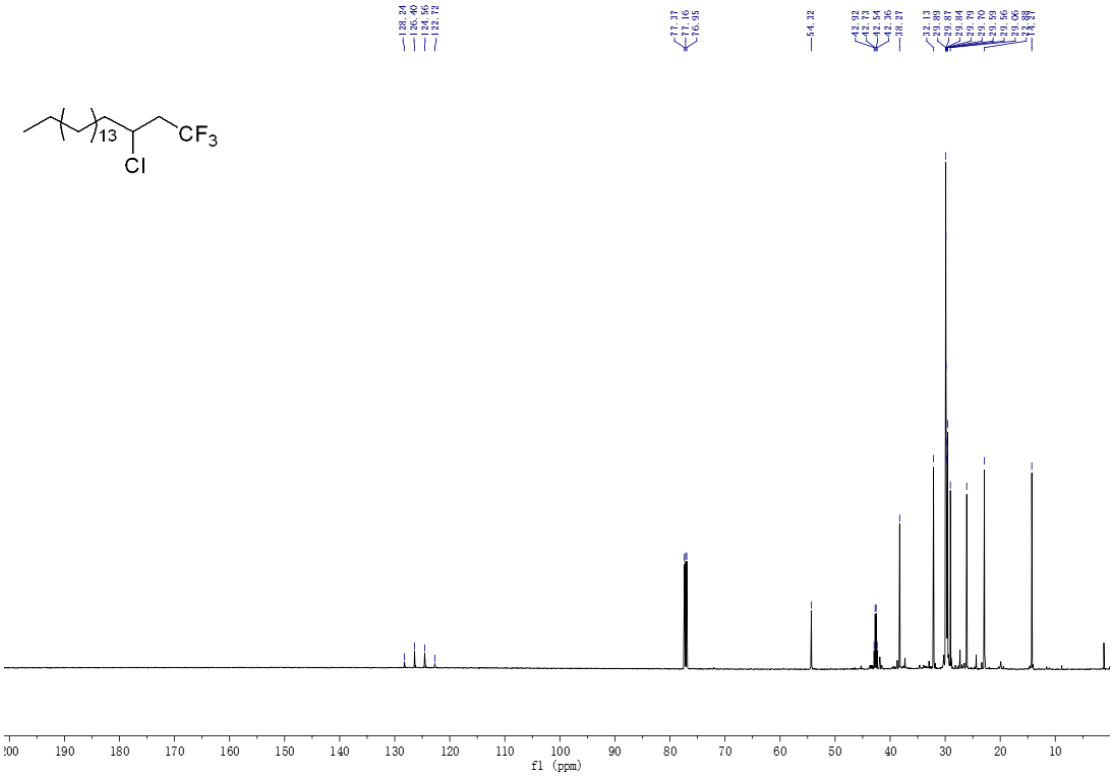
^{19}F NMR of **3l**



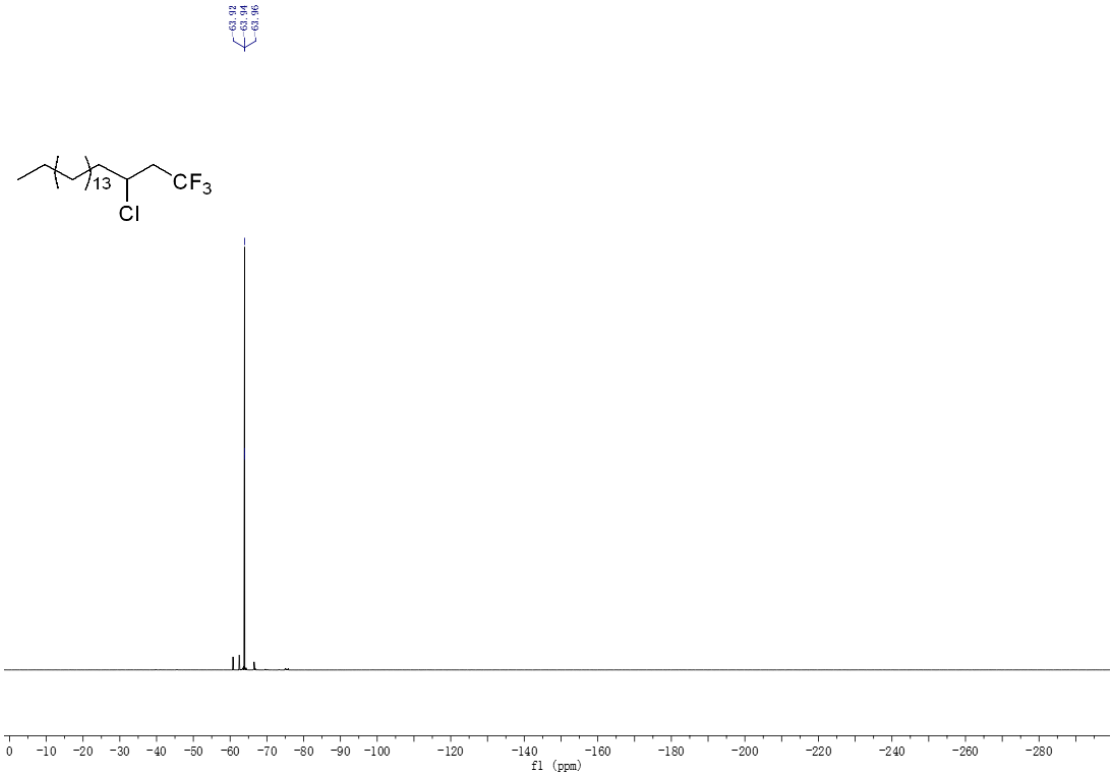
^{1}H NMR of **3m**



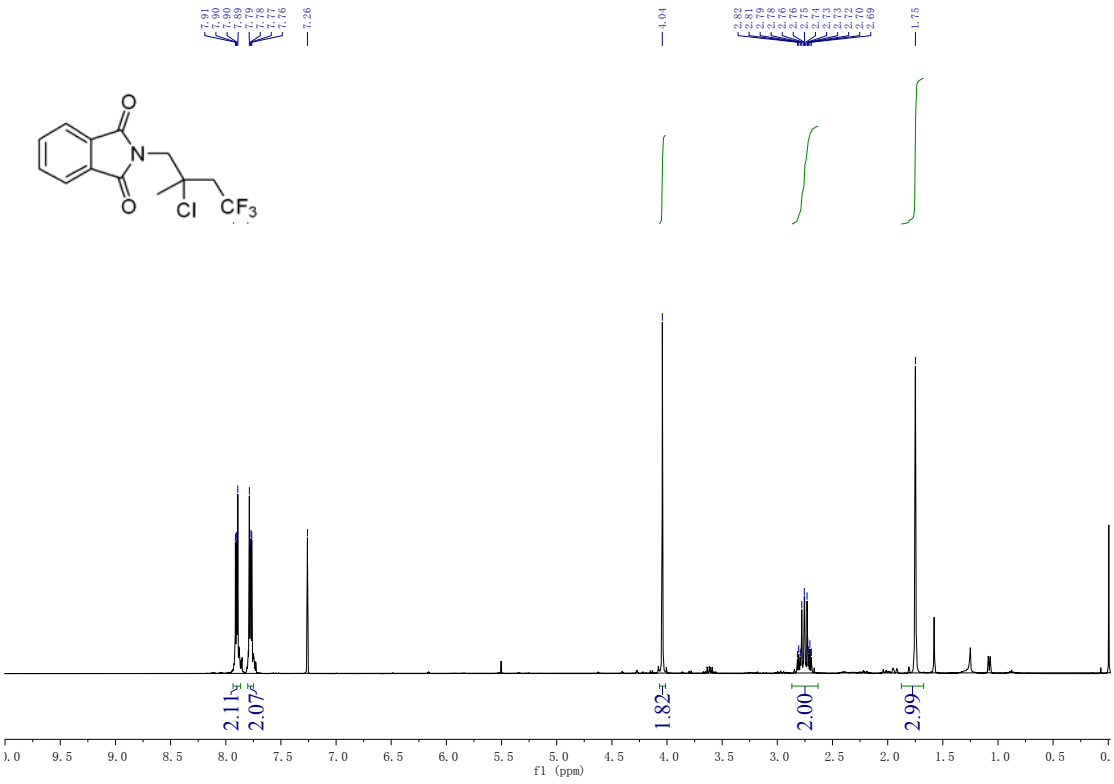
^{13}C NMR of **3m**



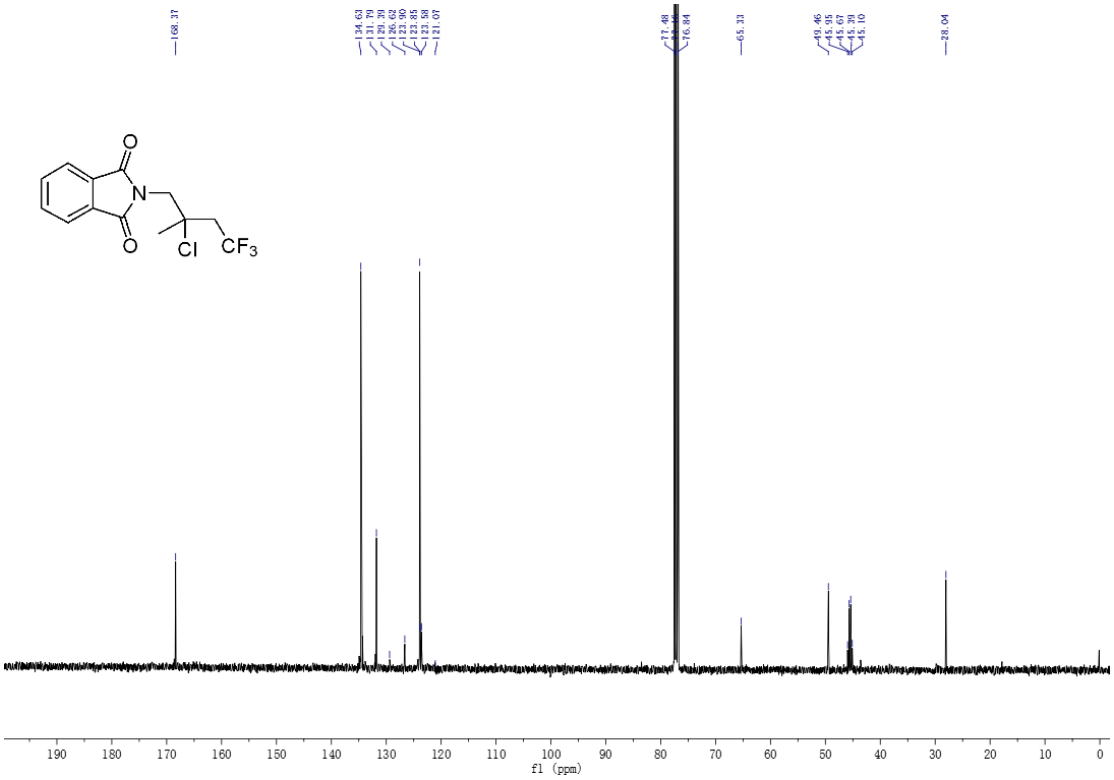
^{19}F NMR of **3m**



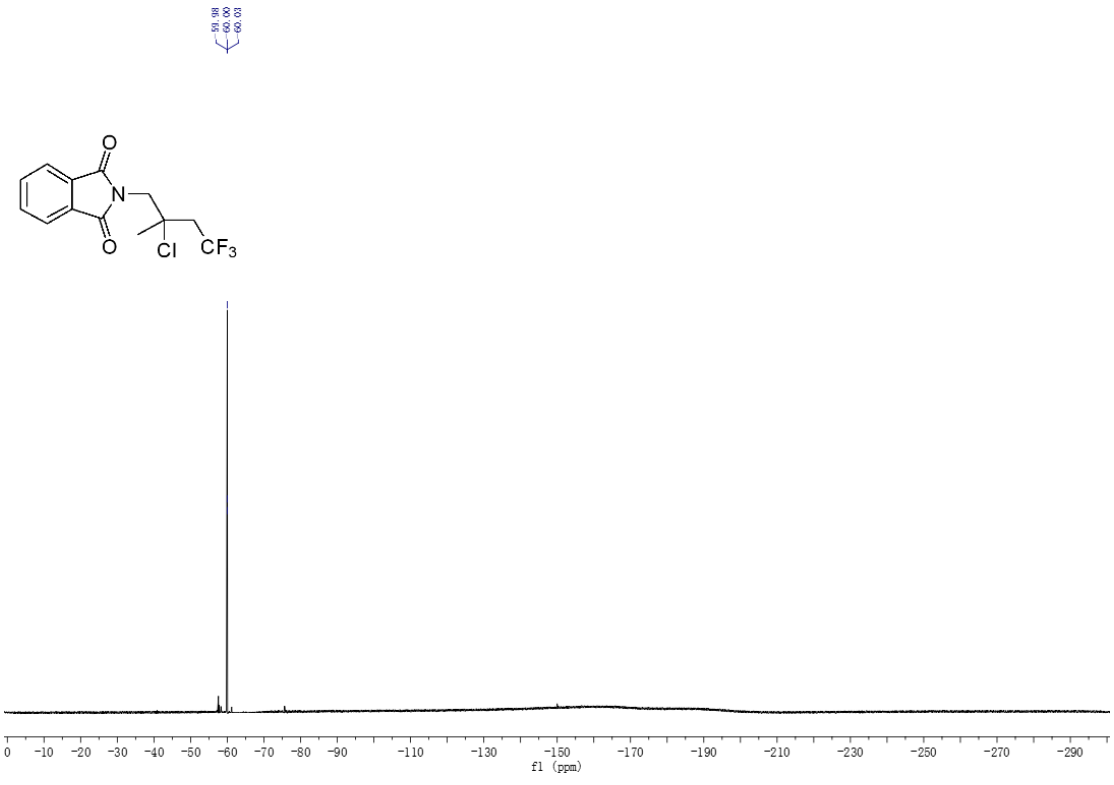
^{1}H NMR of **3n**



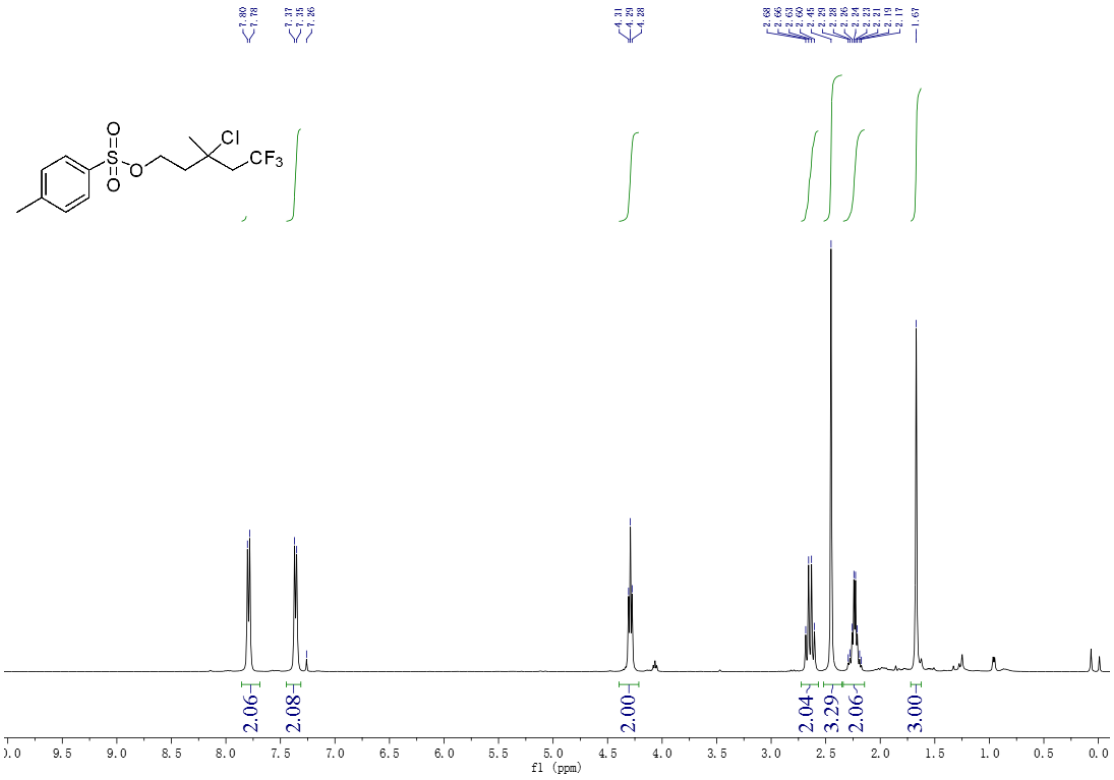
^{13}C NMR of **3n**



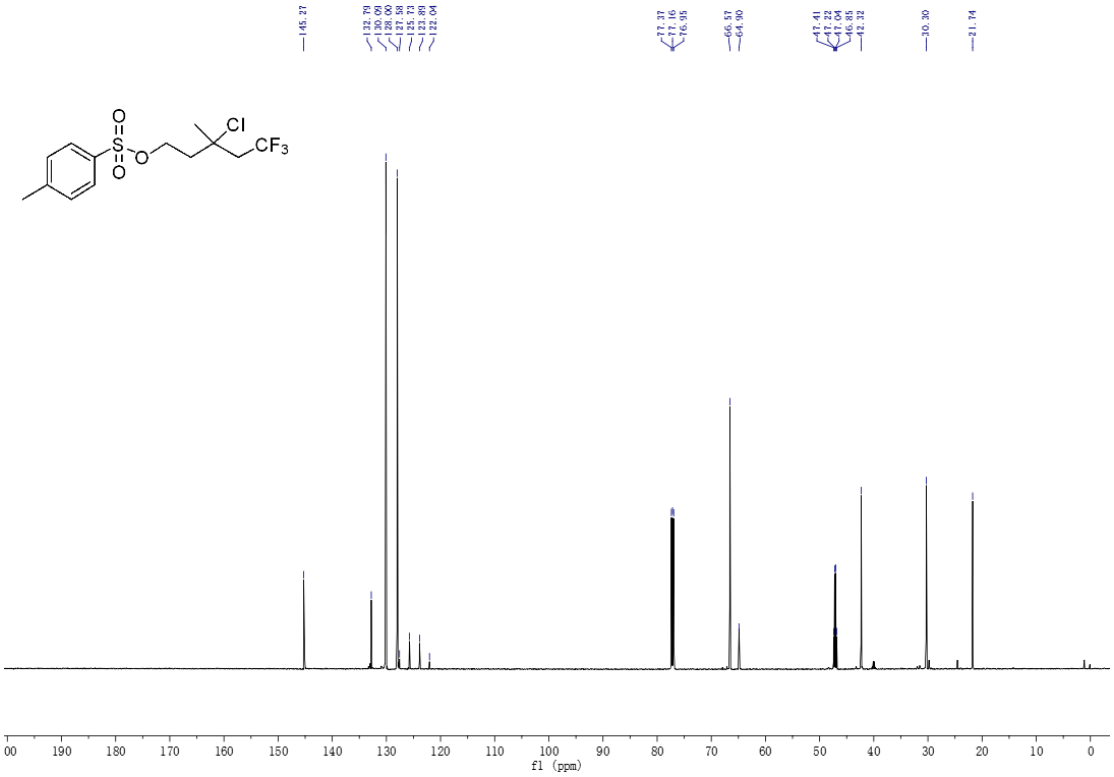
^{19}F NMR of **3n**



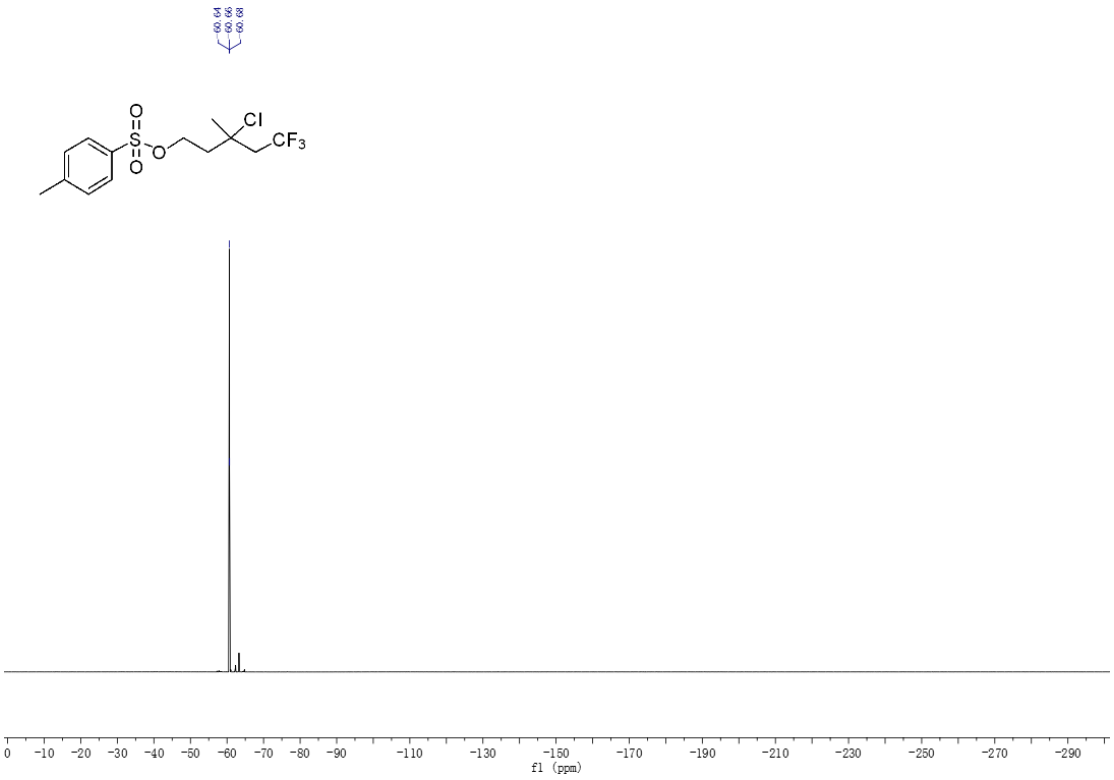
^{1}H NMR of **3o**



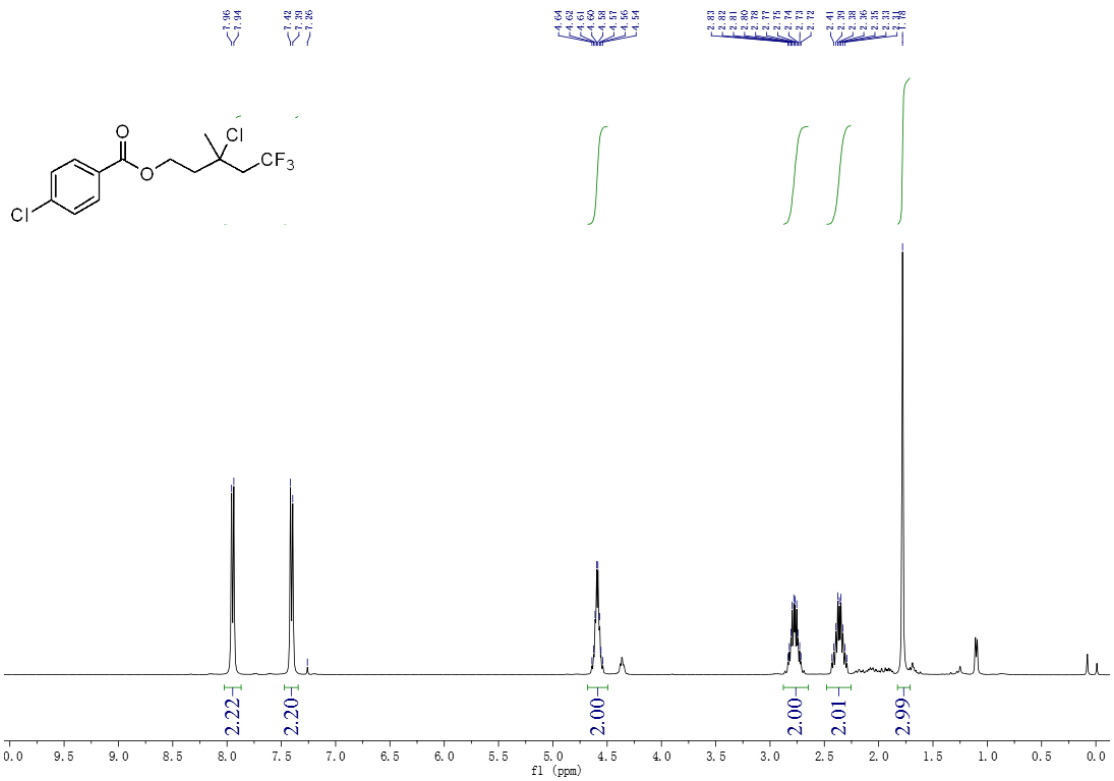
^{13}C NMR of **3o**



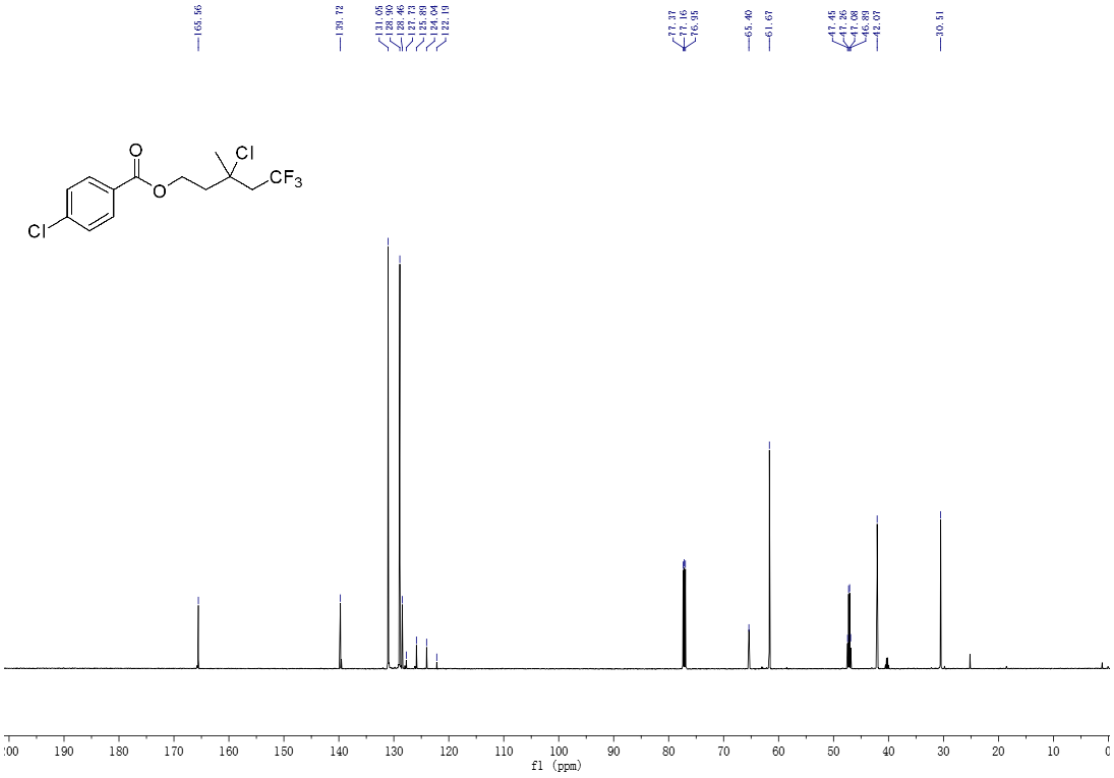
^{19}F NMR of **3o**



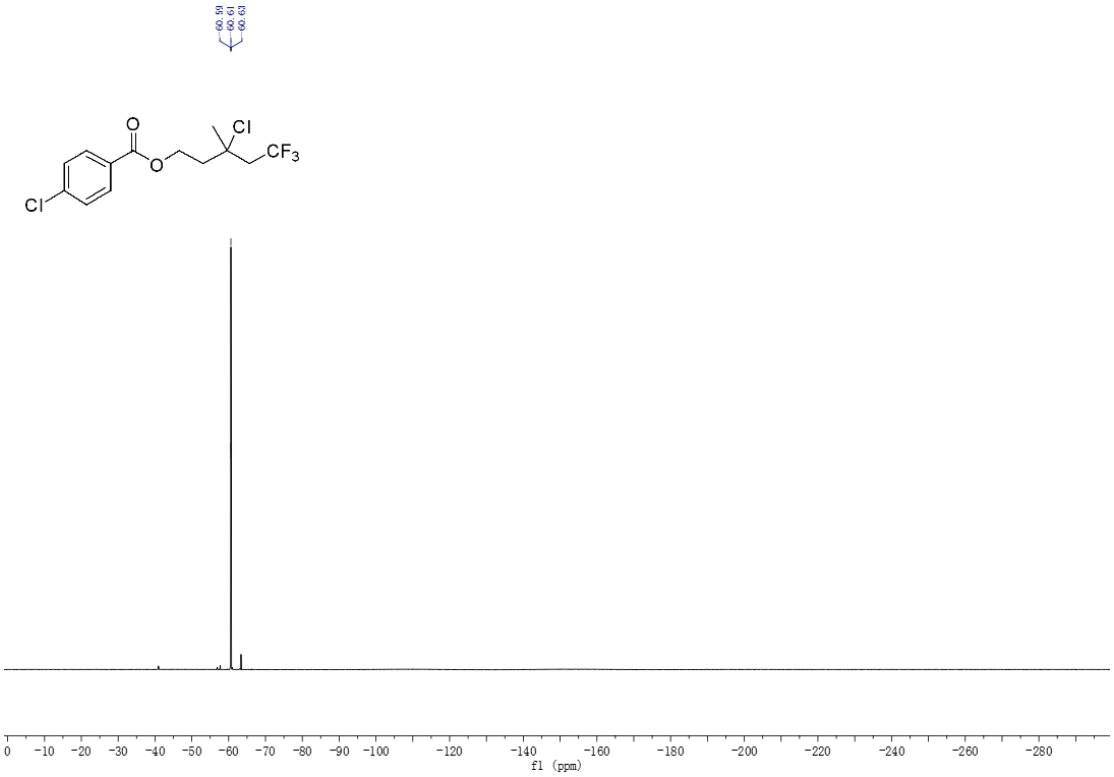
^{1}H NMR of **3p**



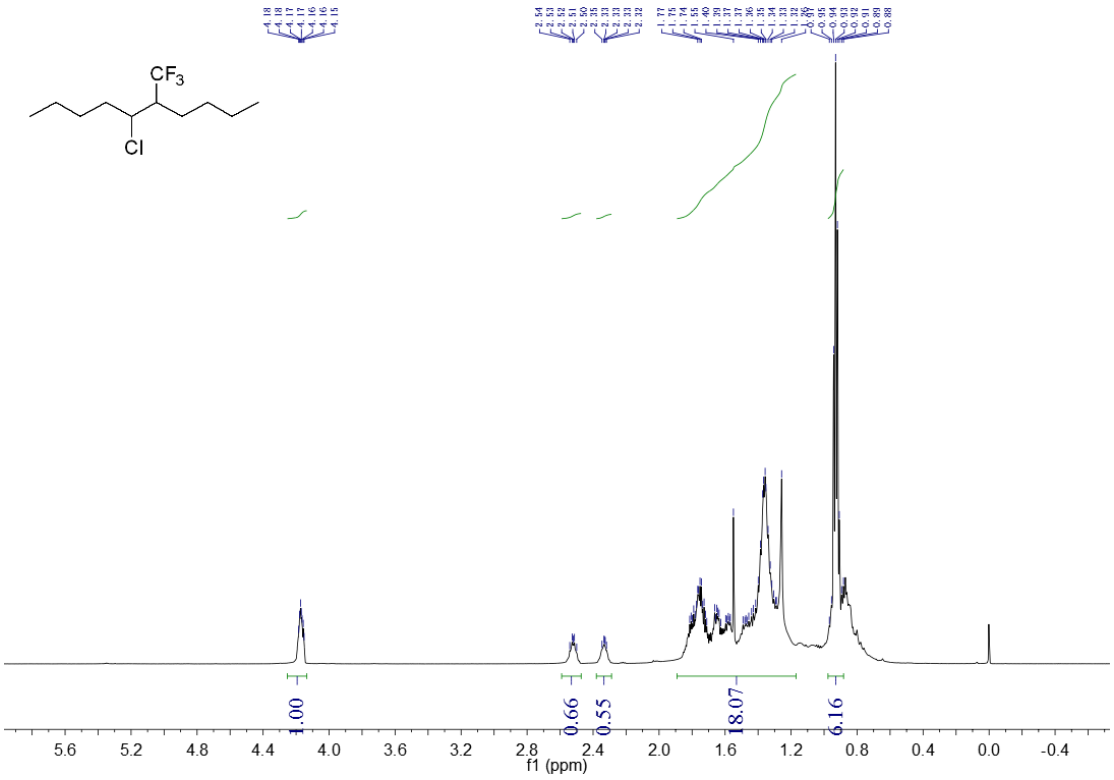
^{13}C NMR of **3p**



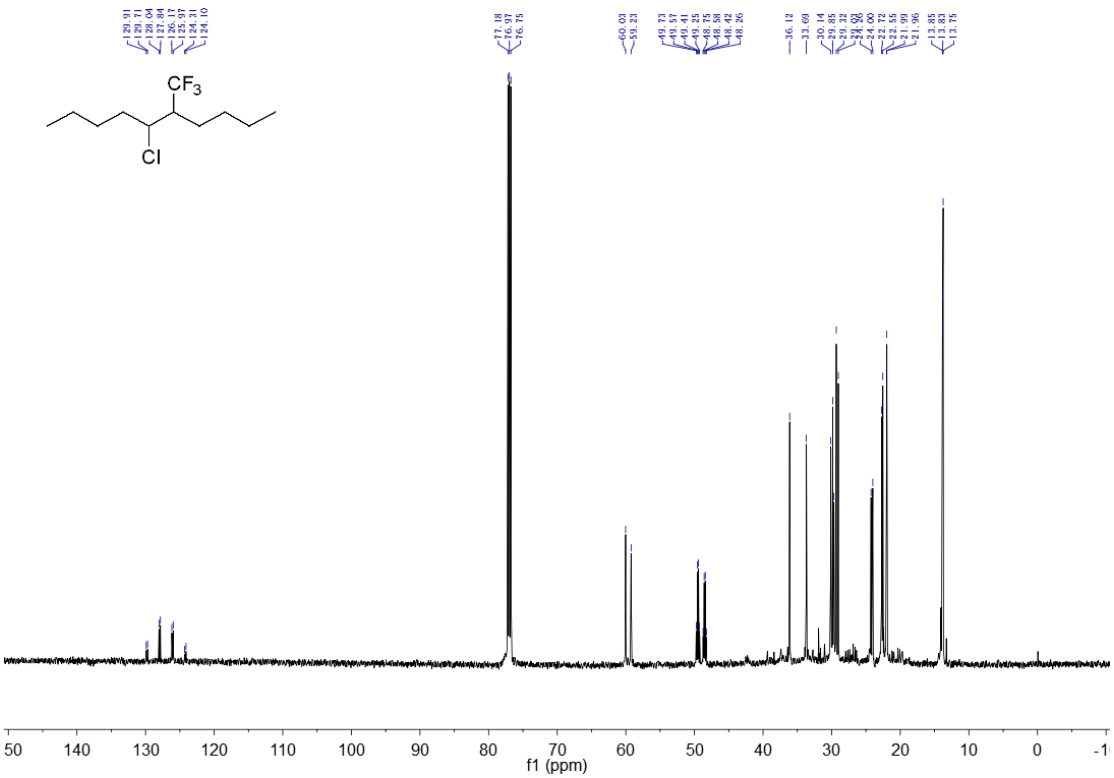
^{19}F NMR of **3p**



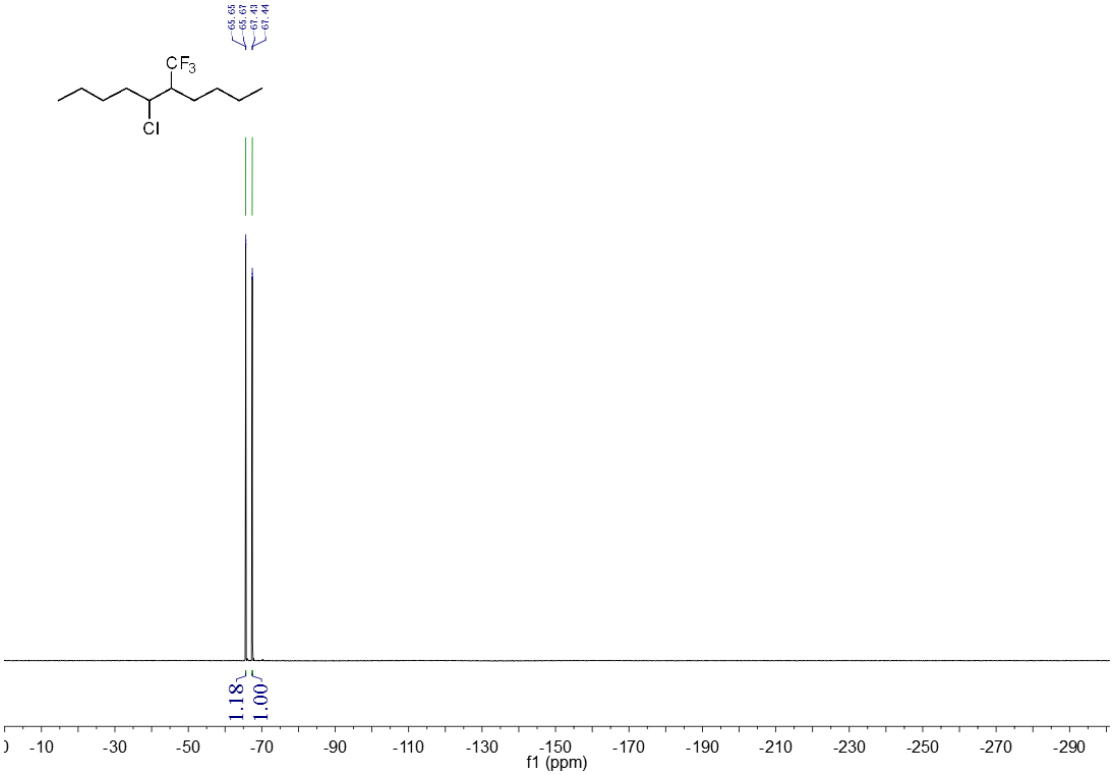
^{1}H NMR of **3q**



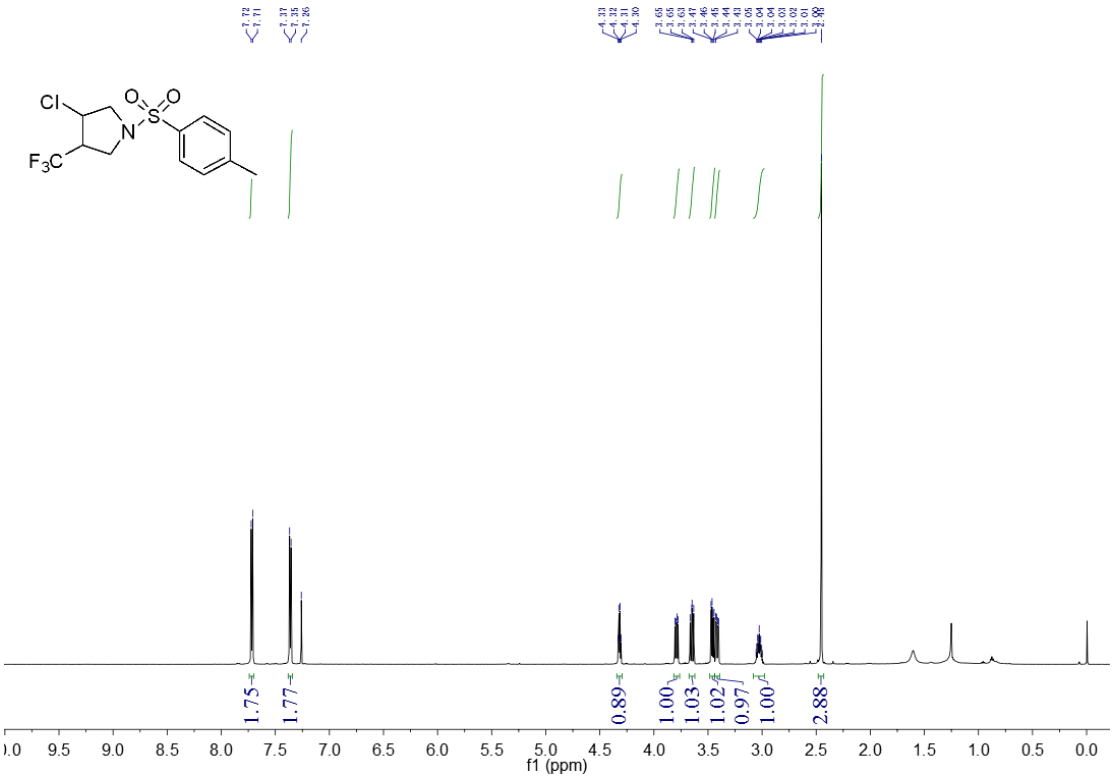
^{13}C NMR of **3q**



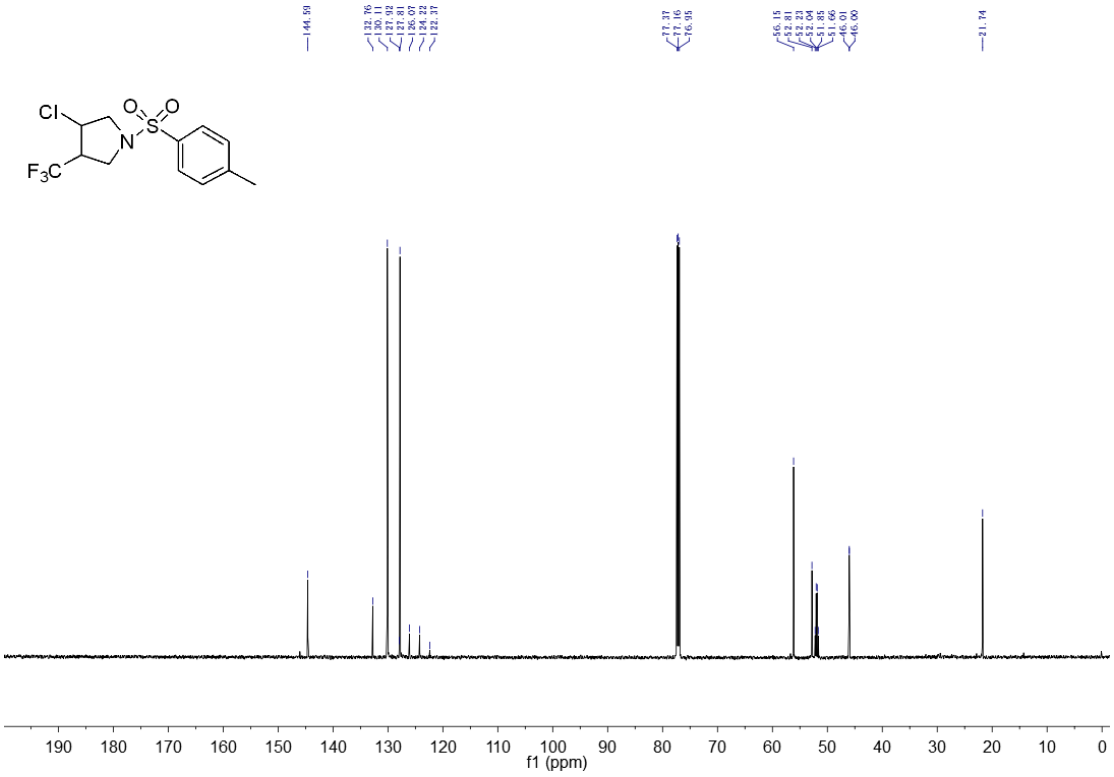
^{19}F NMR of **3q**



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

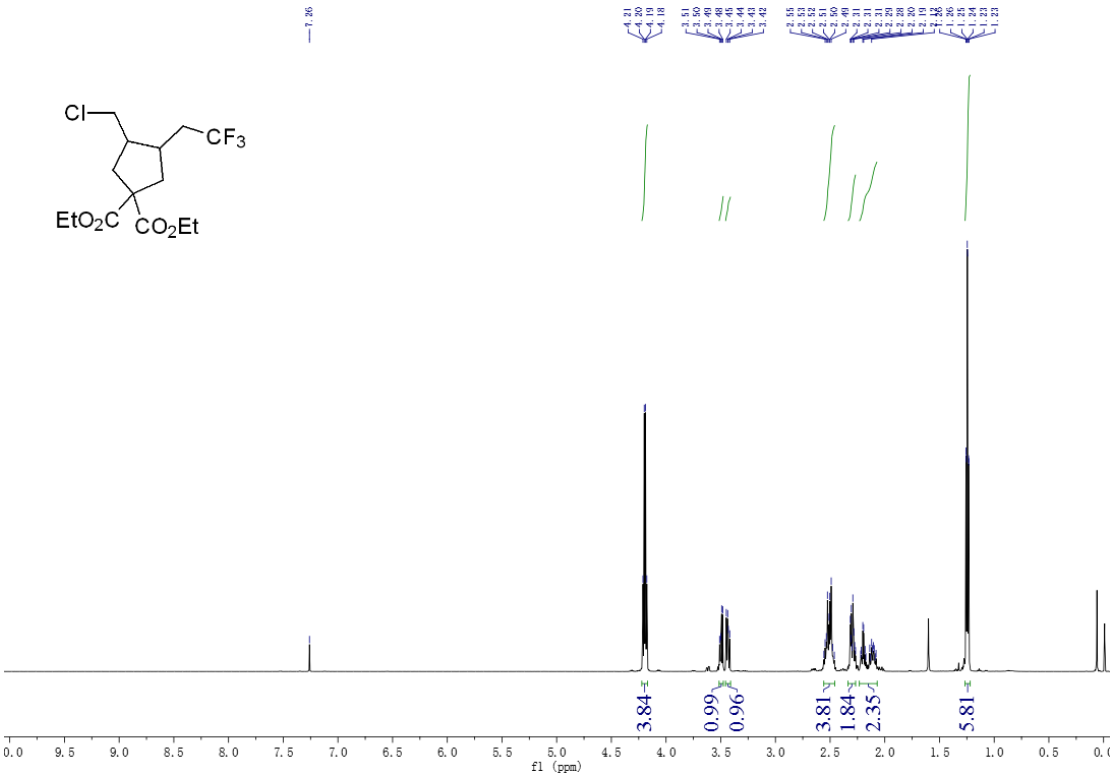


^{13}C NMR of **3r**

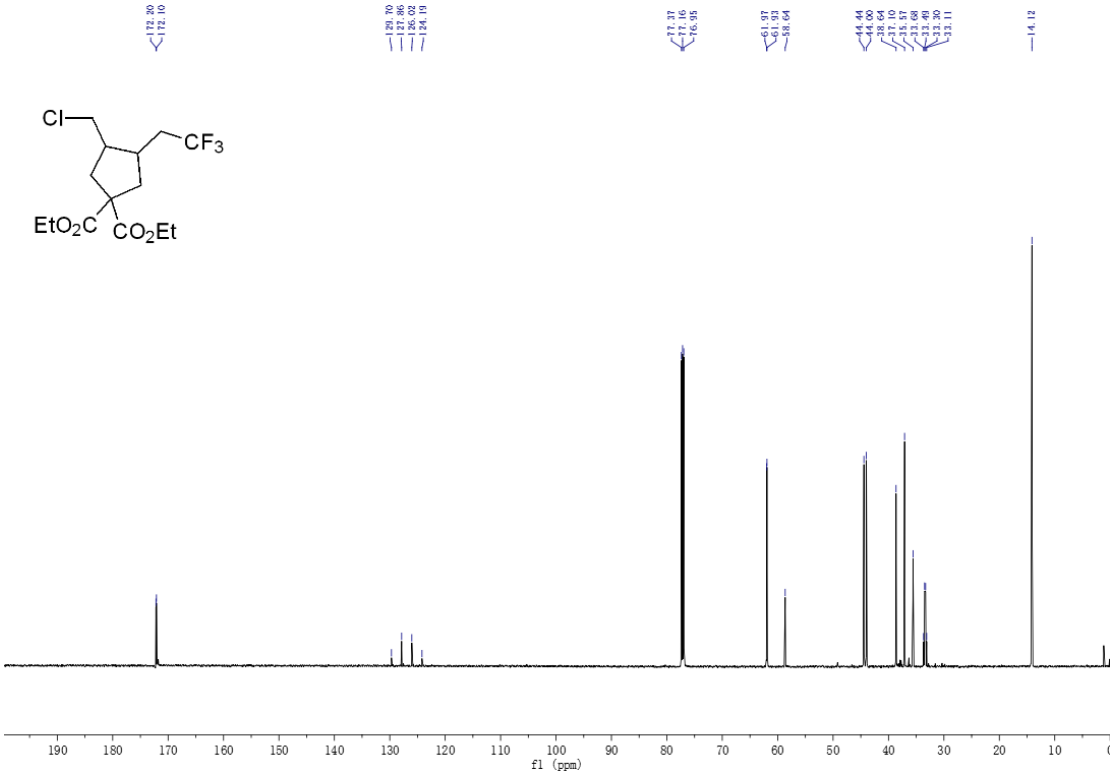


^{19}F NMR of **3r**

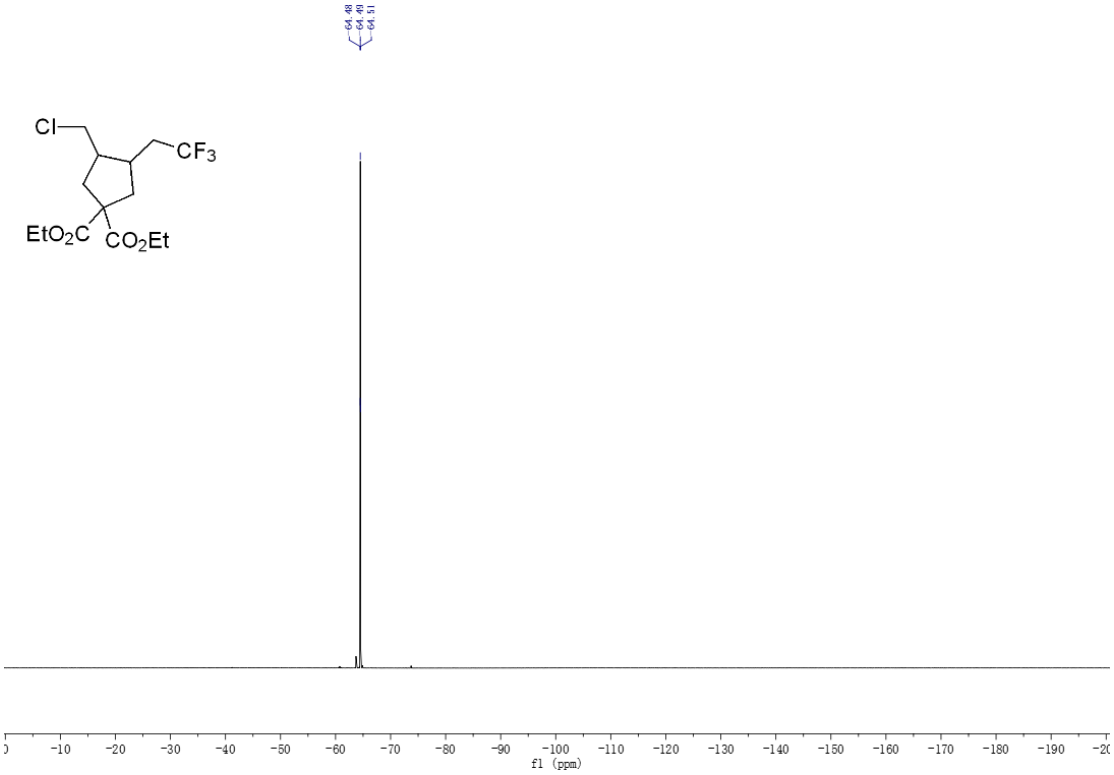
^{1}H NMR of **3s**



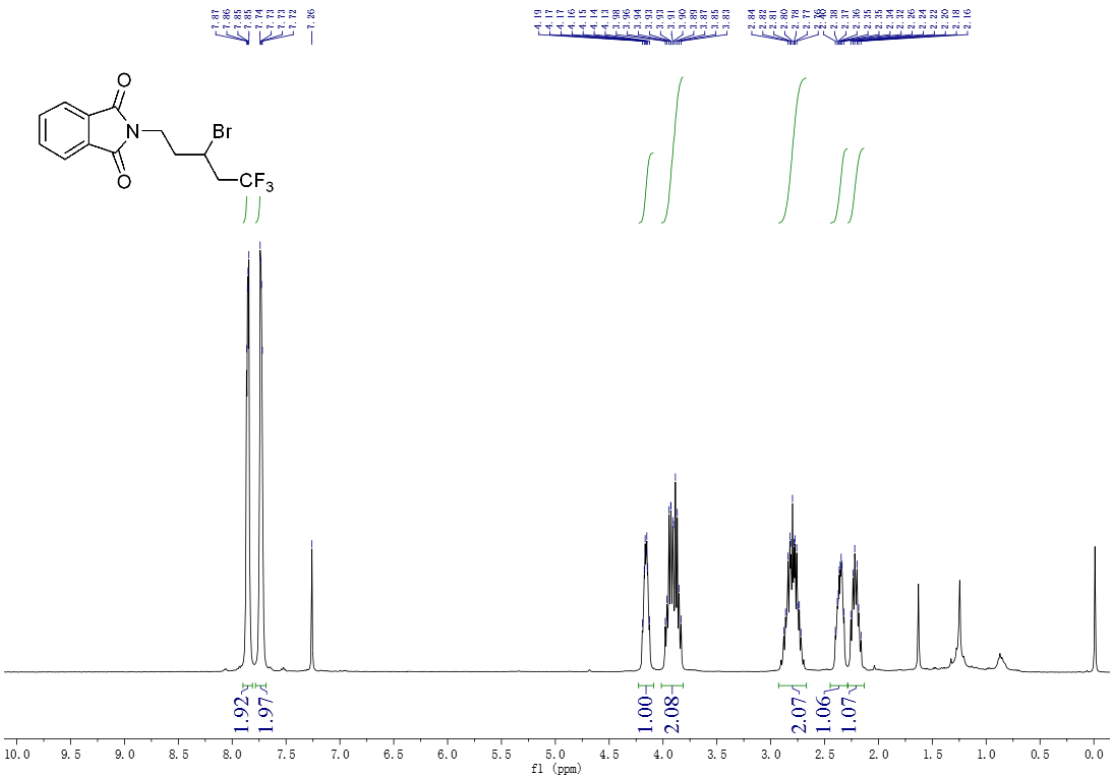
^{13}C NMR of **3s**



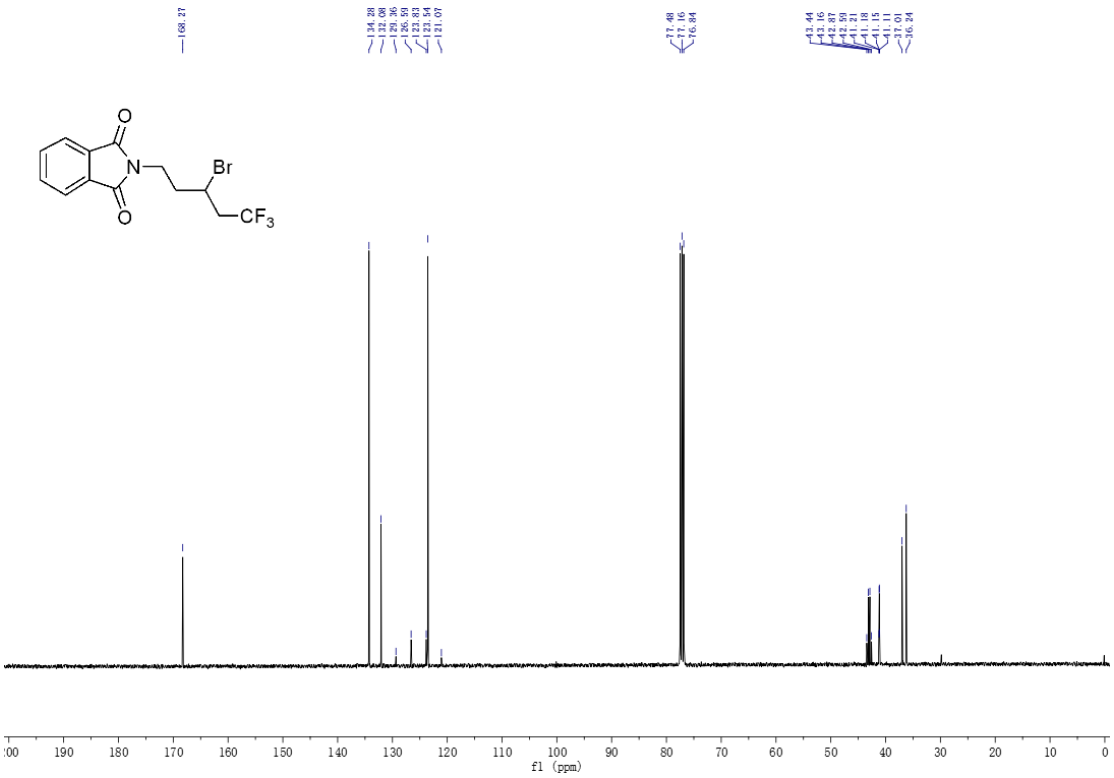
^{19}F NMR of **3s**



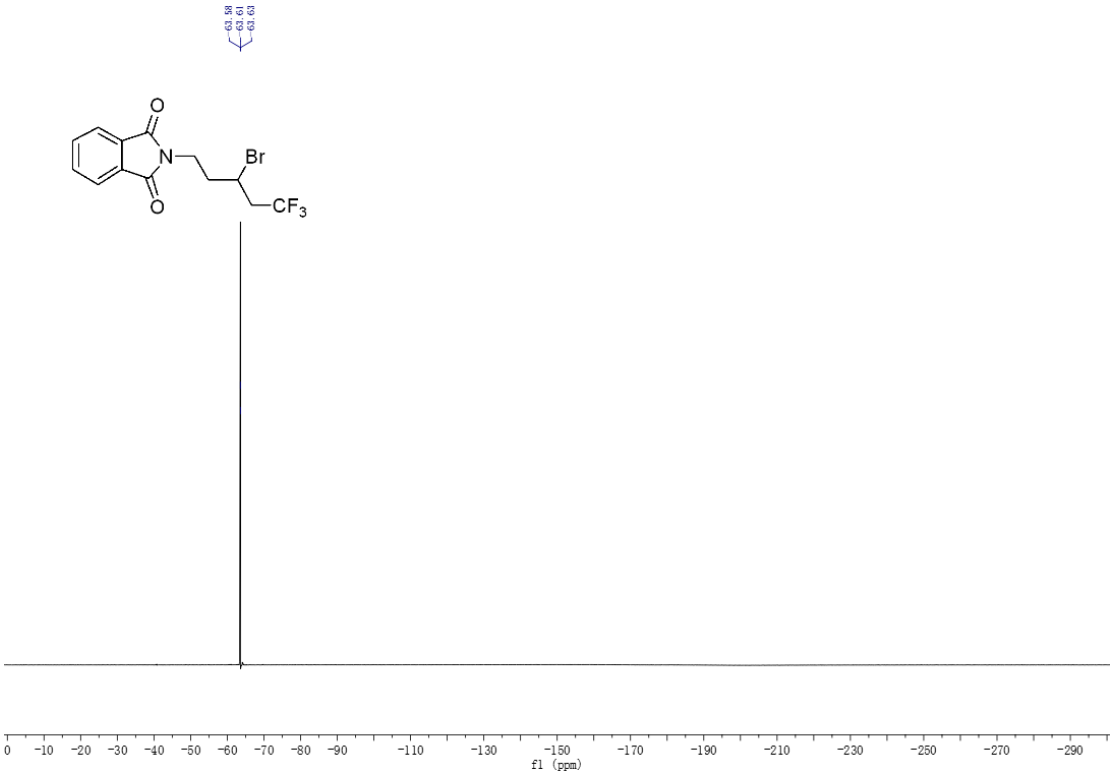
^{1}H NMR of **4a**



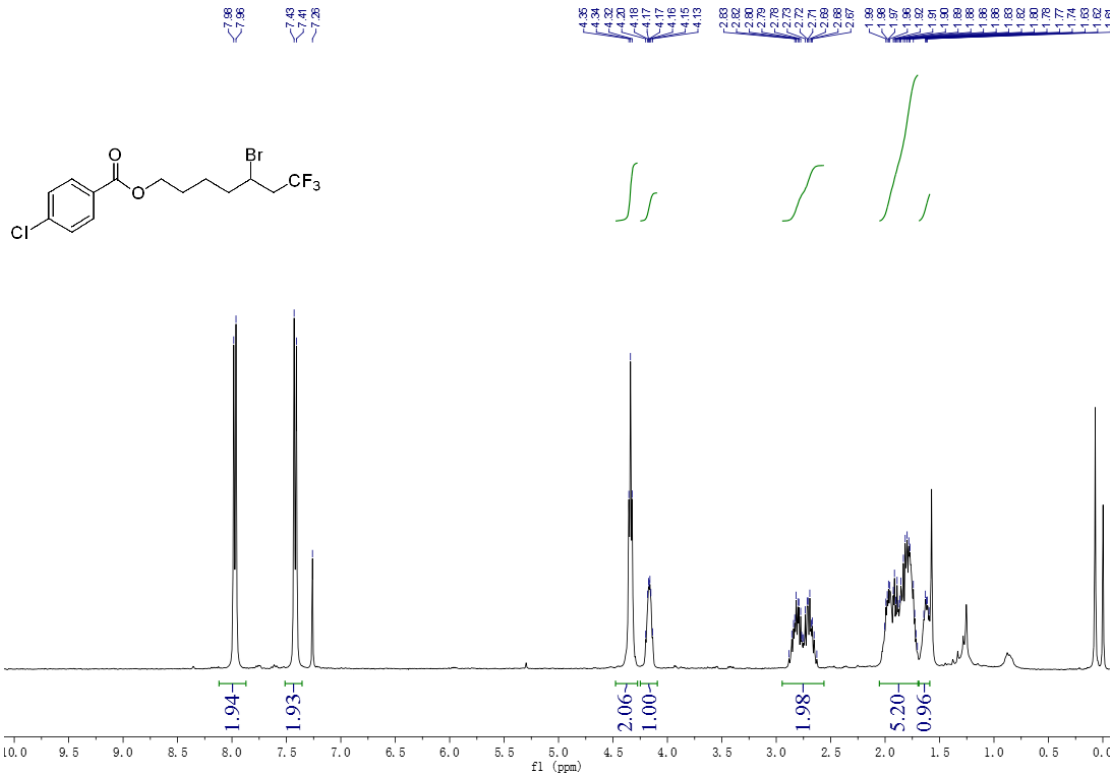
^{13}C NMR of **4a**



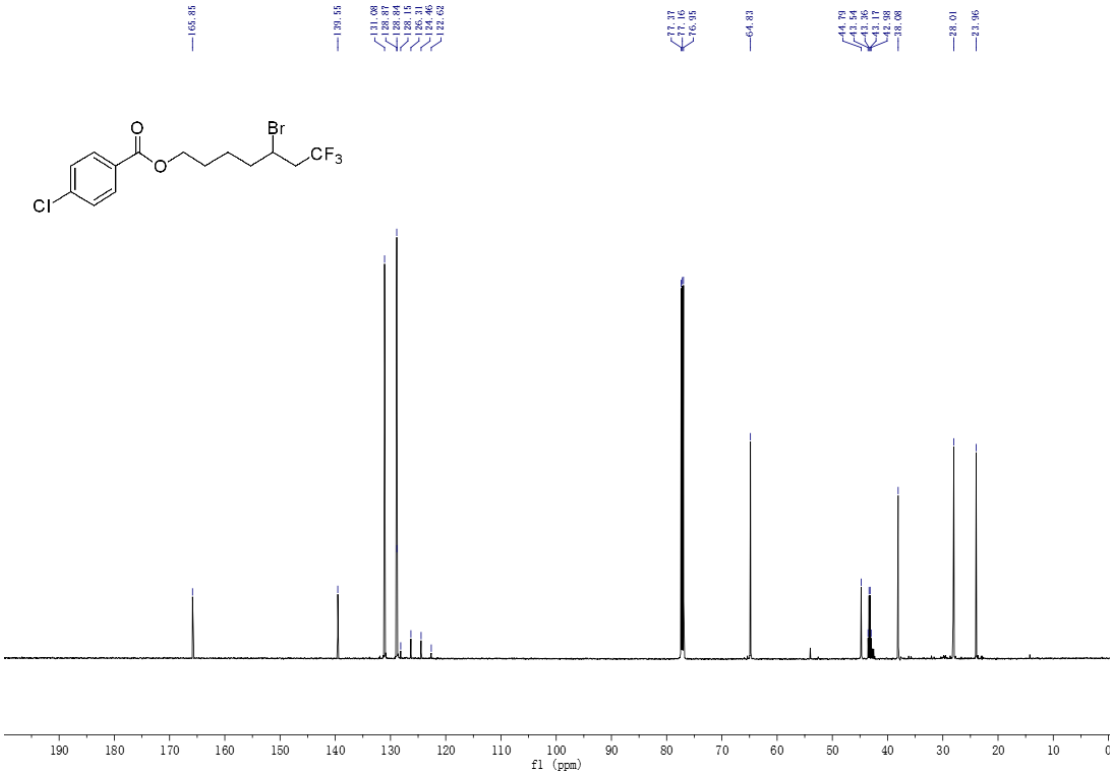
^{19}F NMR of **4a**



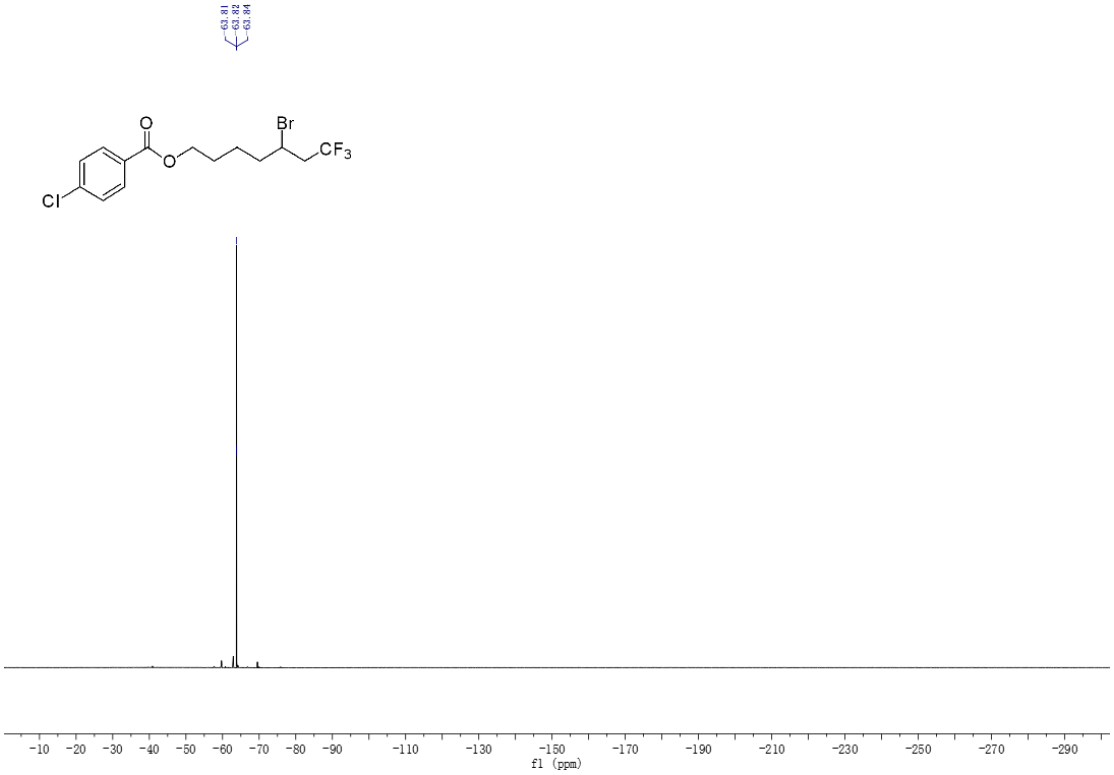
^{1}H NMR of **4b**



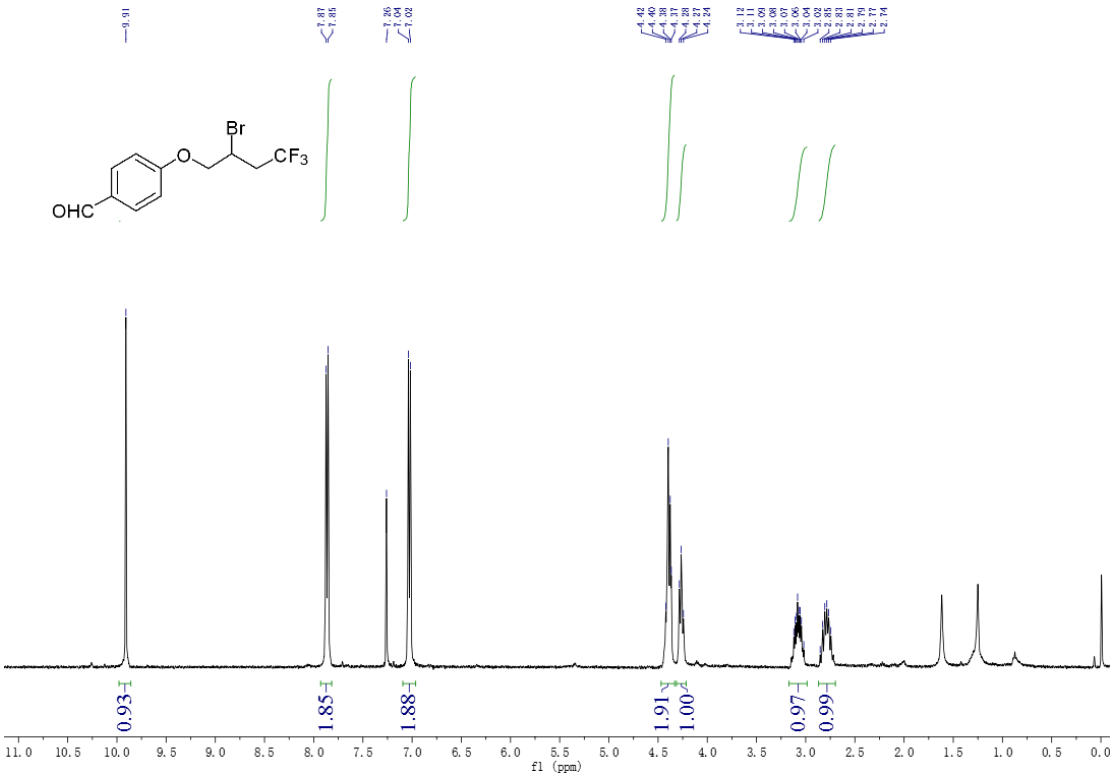
^{13}C NMR of **4b**



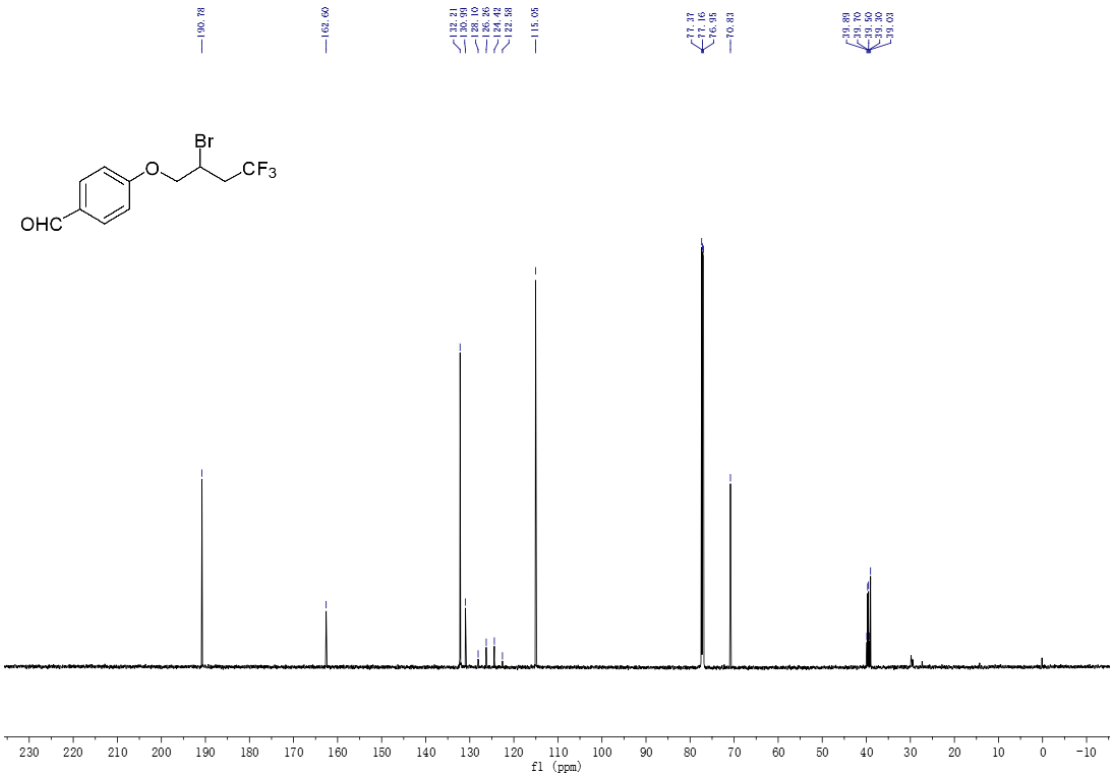
^{19}F NMR of **4b**



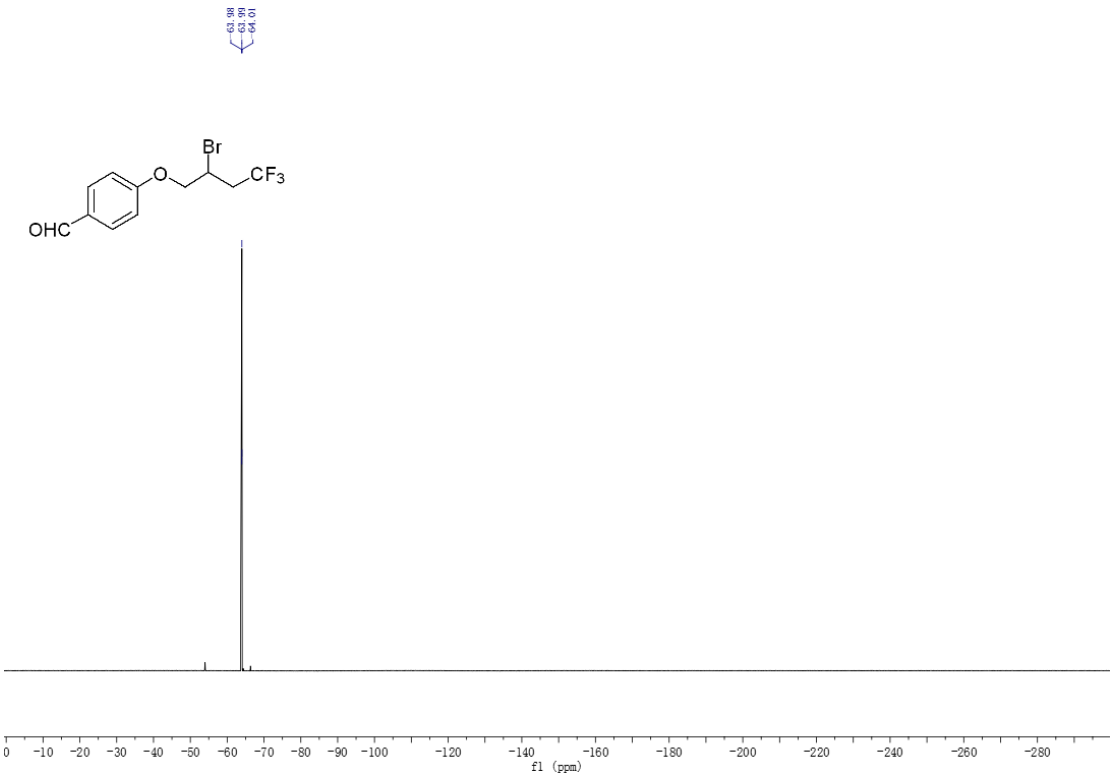
^{1}H NMR of **4c**



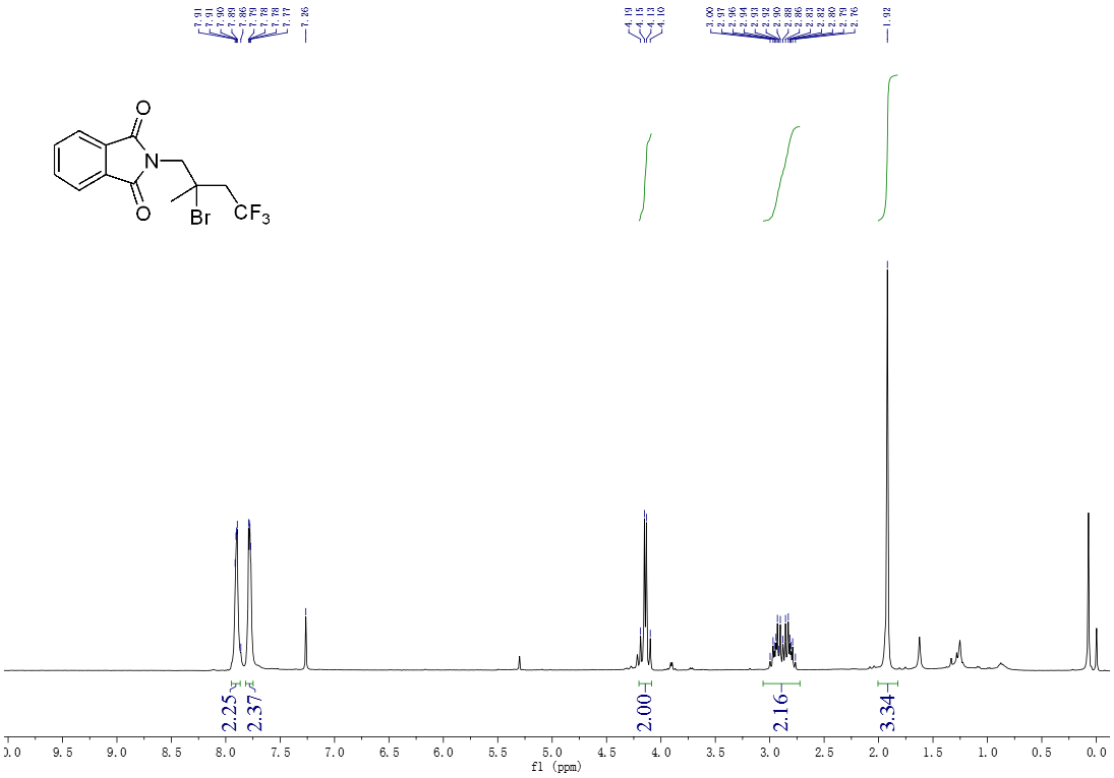
^{13}C NMR of **4c**



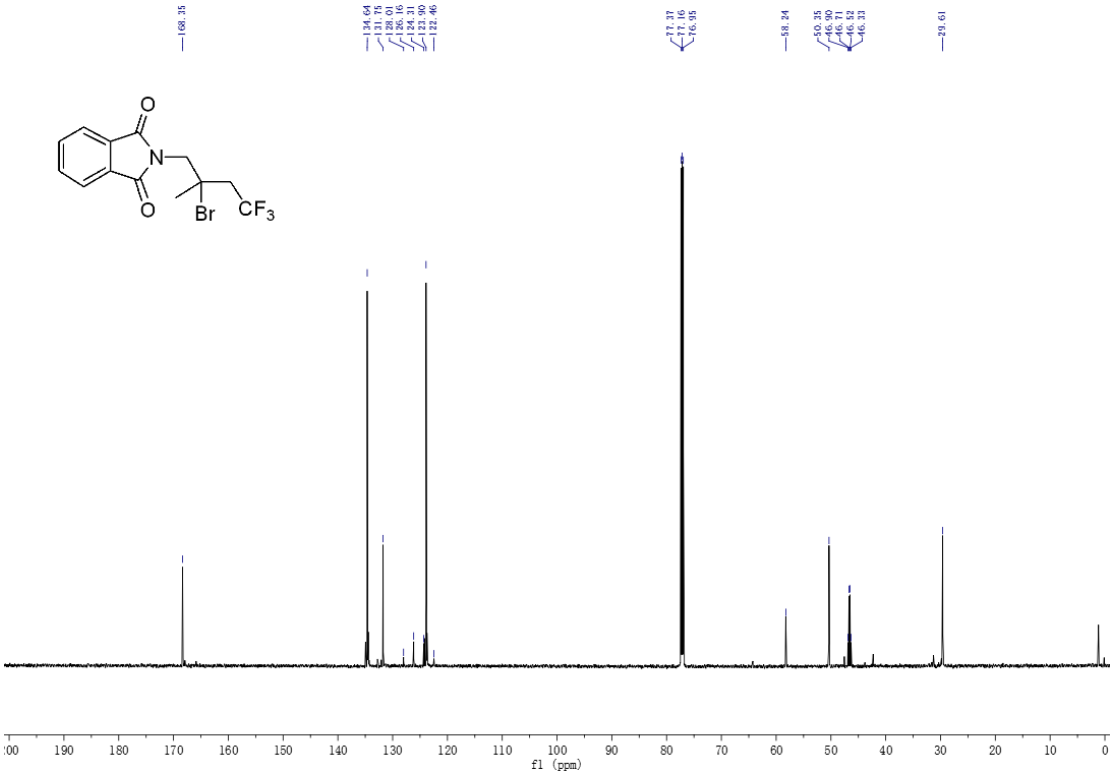
^{19}F NMR of **4c**



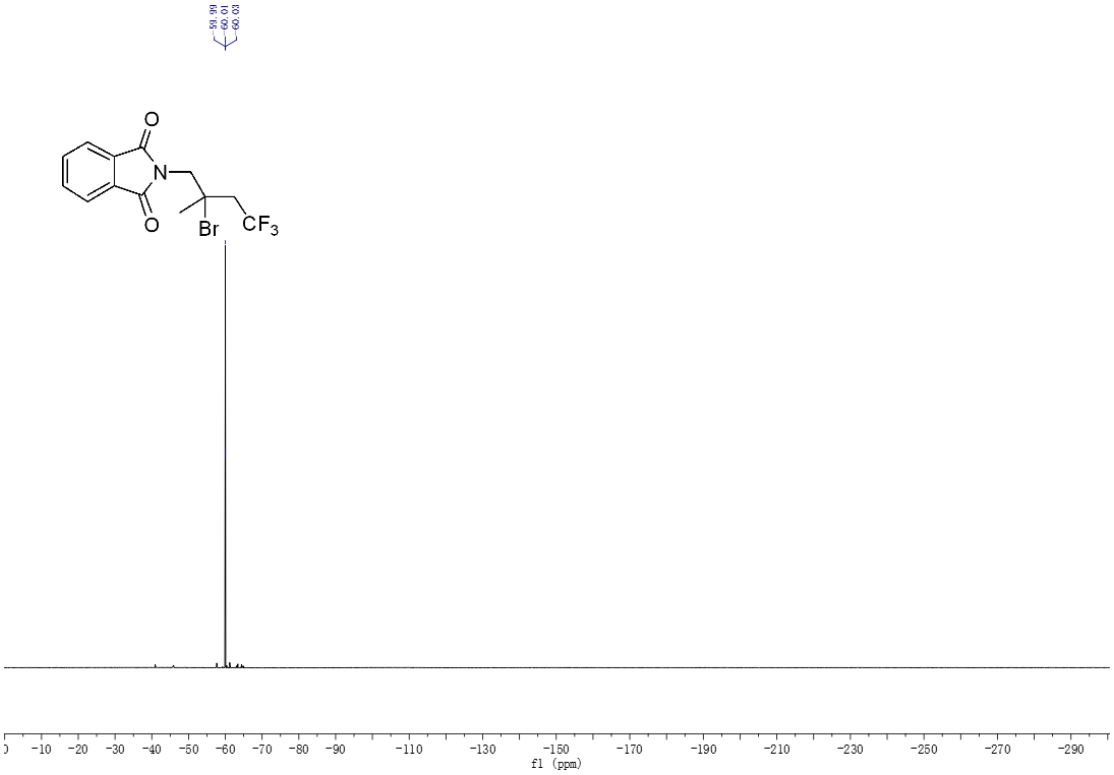
^{1}H NMR of **4d**



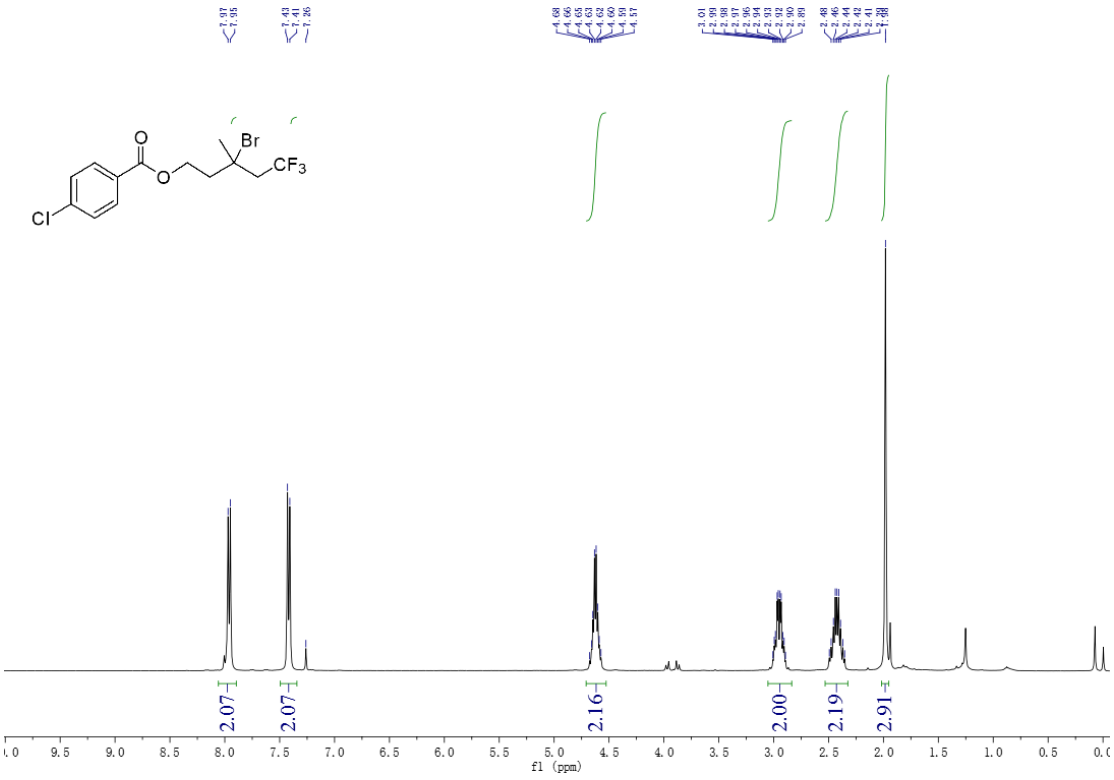
^{13}C NMR of **4d**



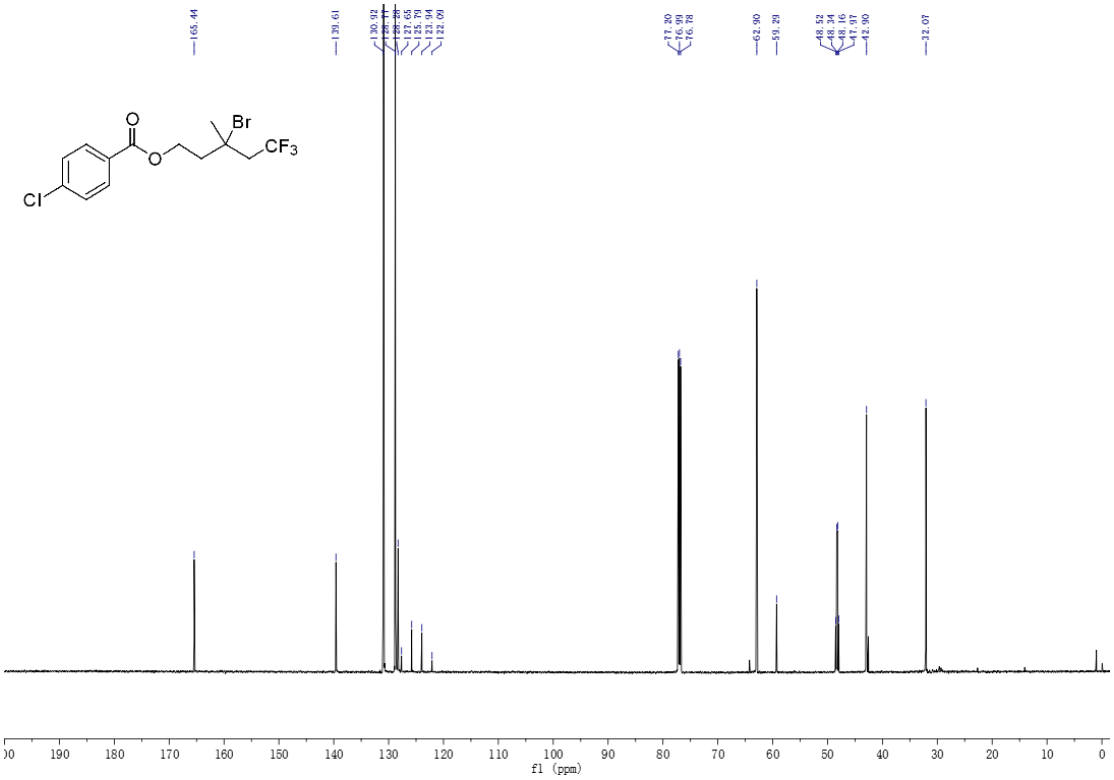
^{19}F NMR of **4d**



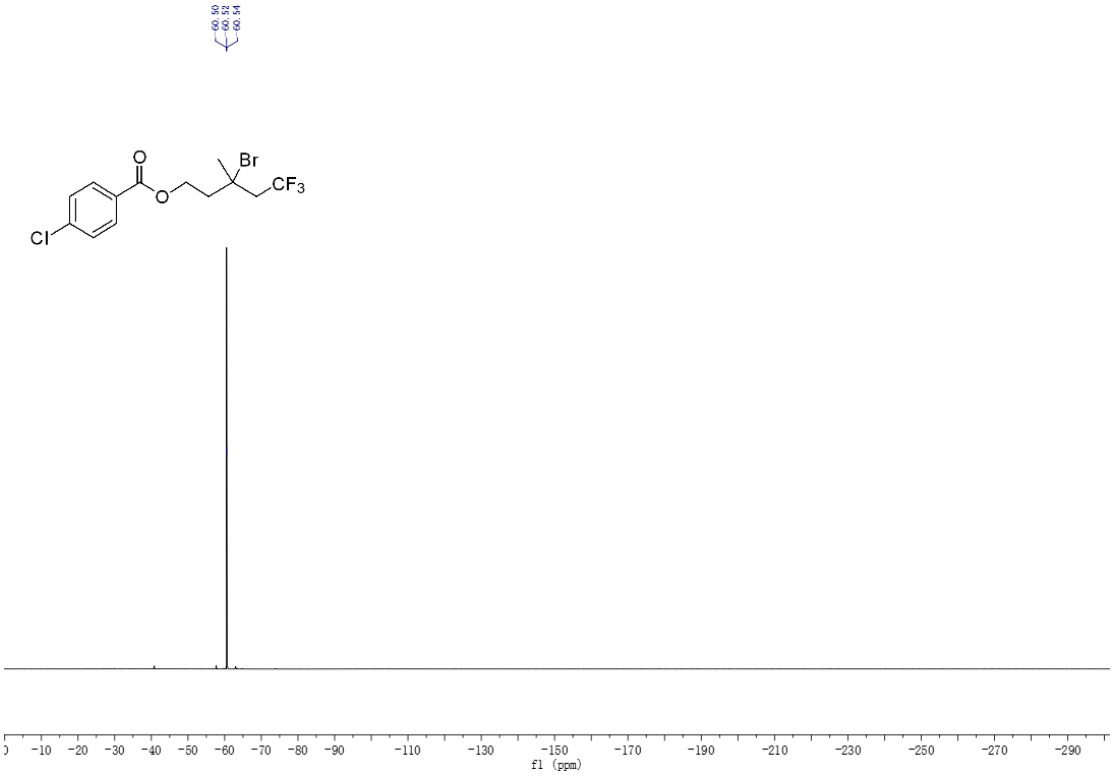
^{1}H NMR of **4e**



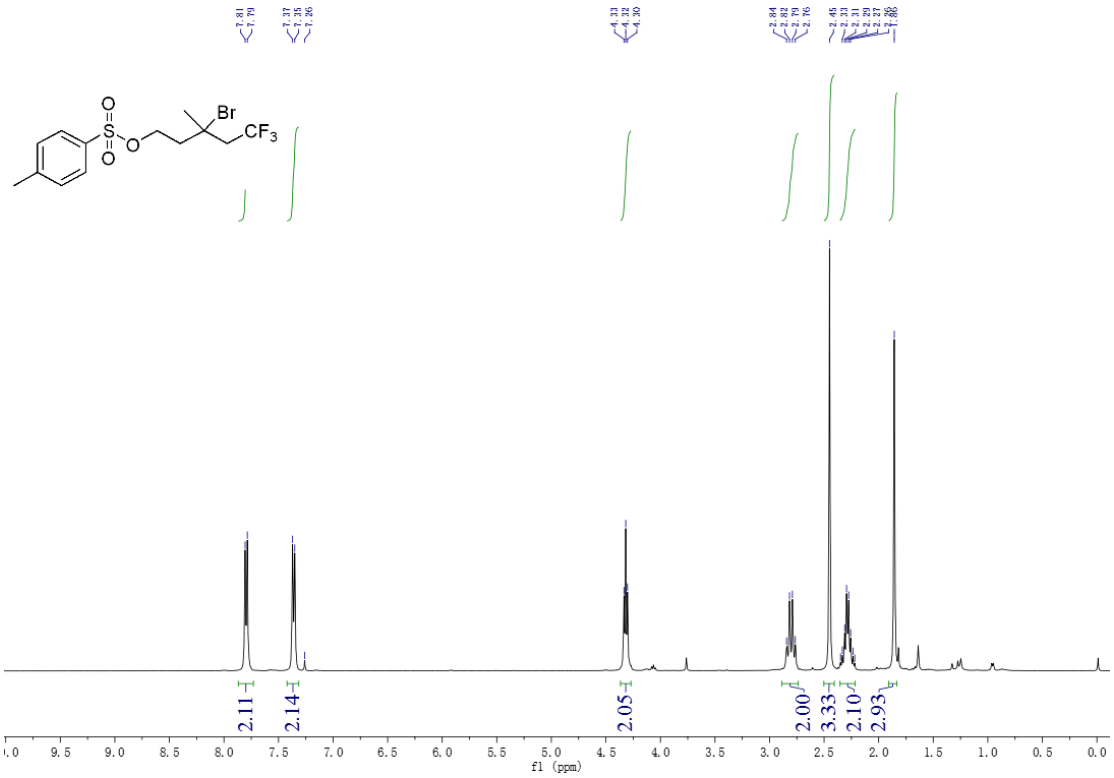
^{13}C NMR of **4e**



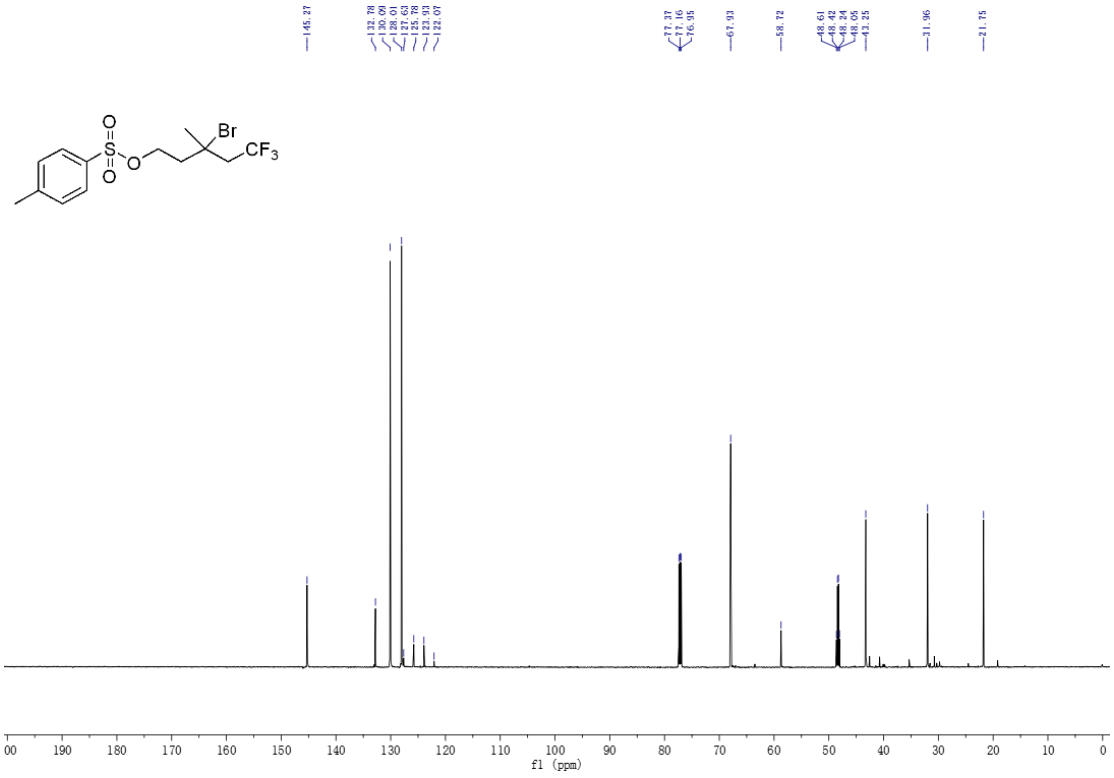
^{19}F NMR of **4e**



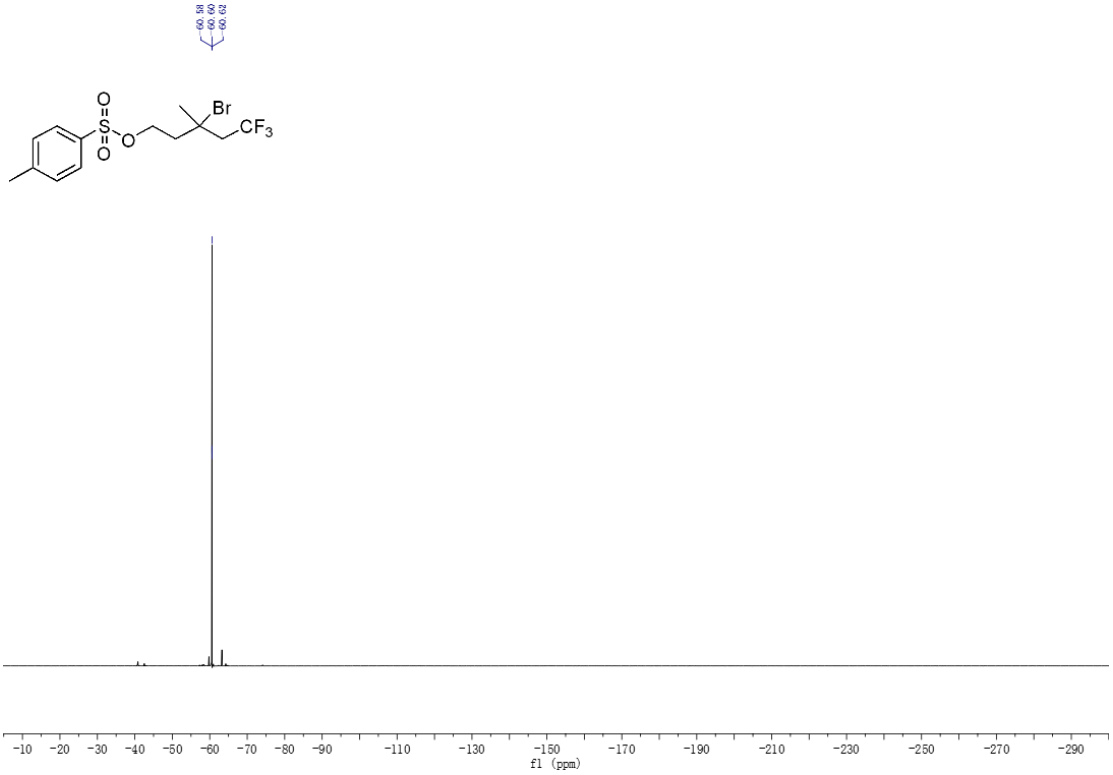
^{1}H NMR of **4f**



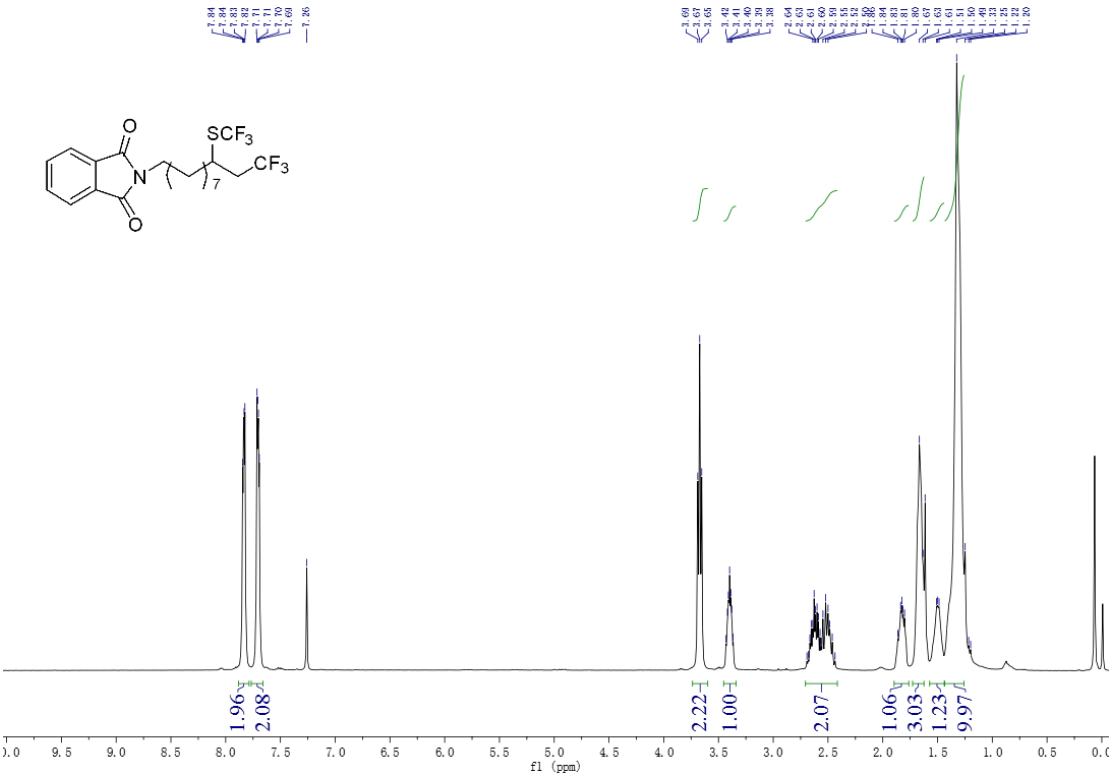
^{13}C NMR of **4f**



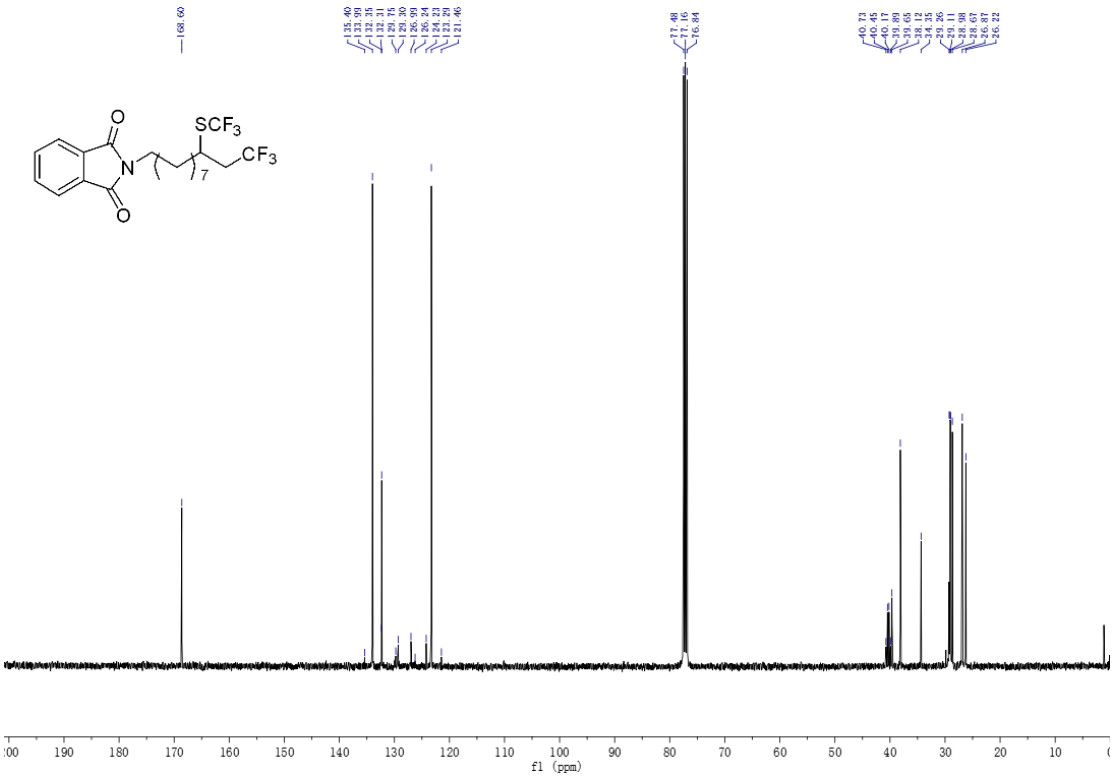
^{19}F NMR of **4f**



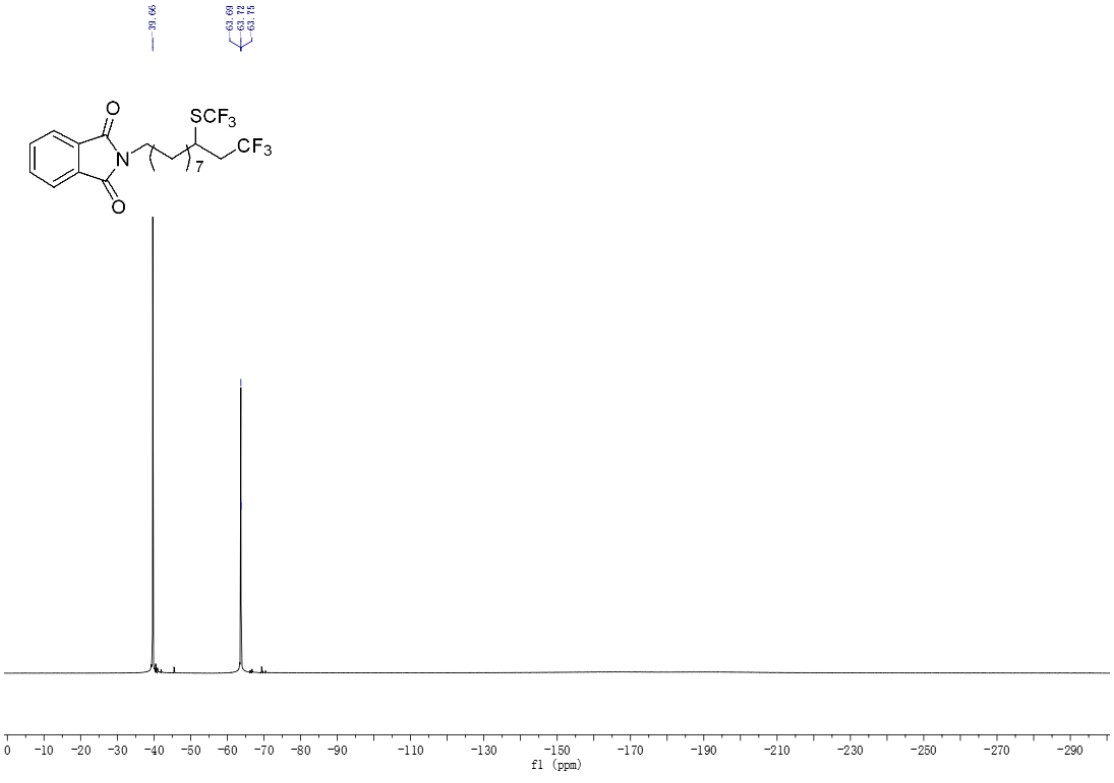
^{1}H NMR of **7a**



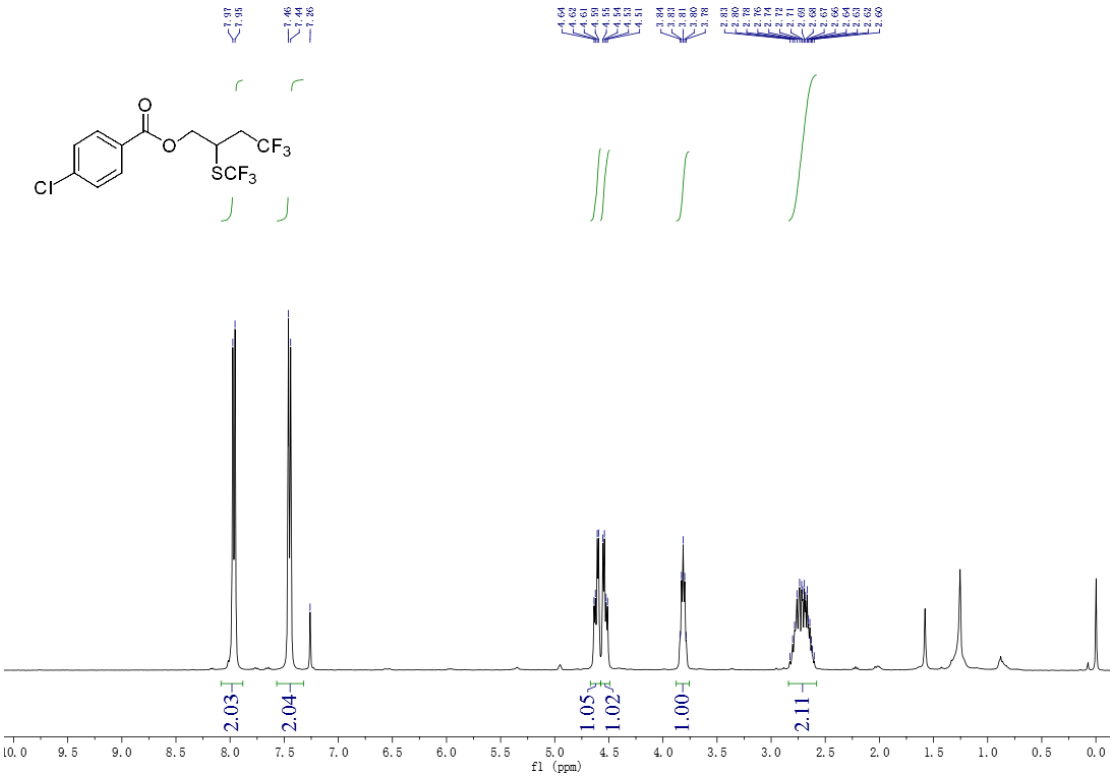
^{13}C NMR of **7a**



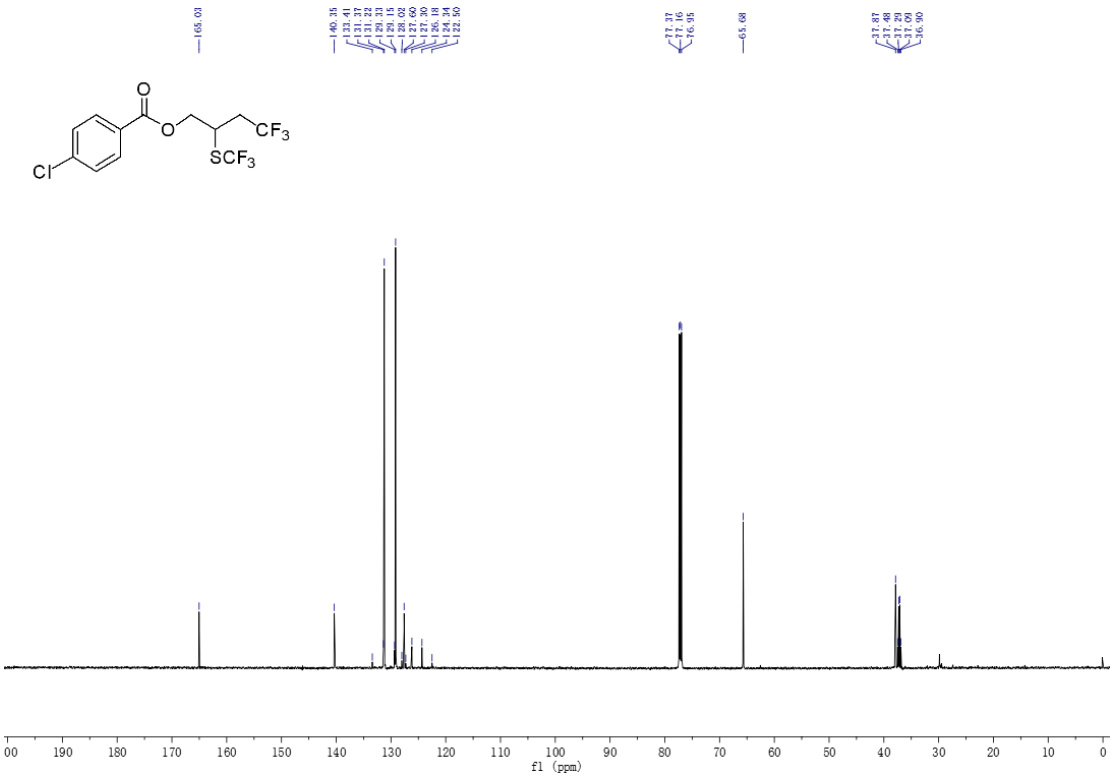
^{19}F NMR of **7a**



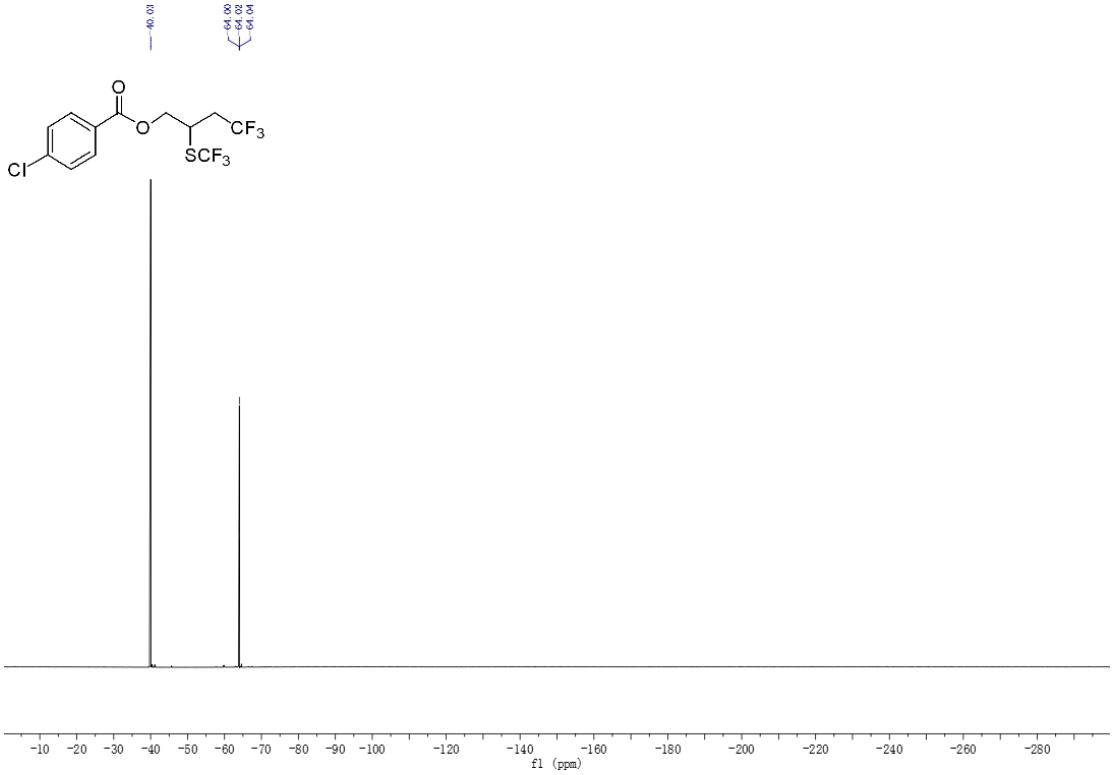
^{1}H NMR of **7b**



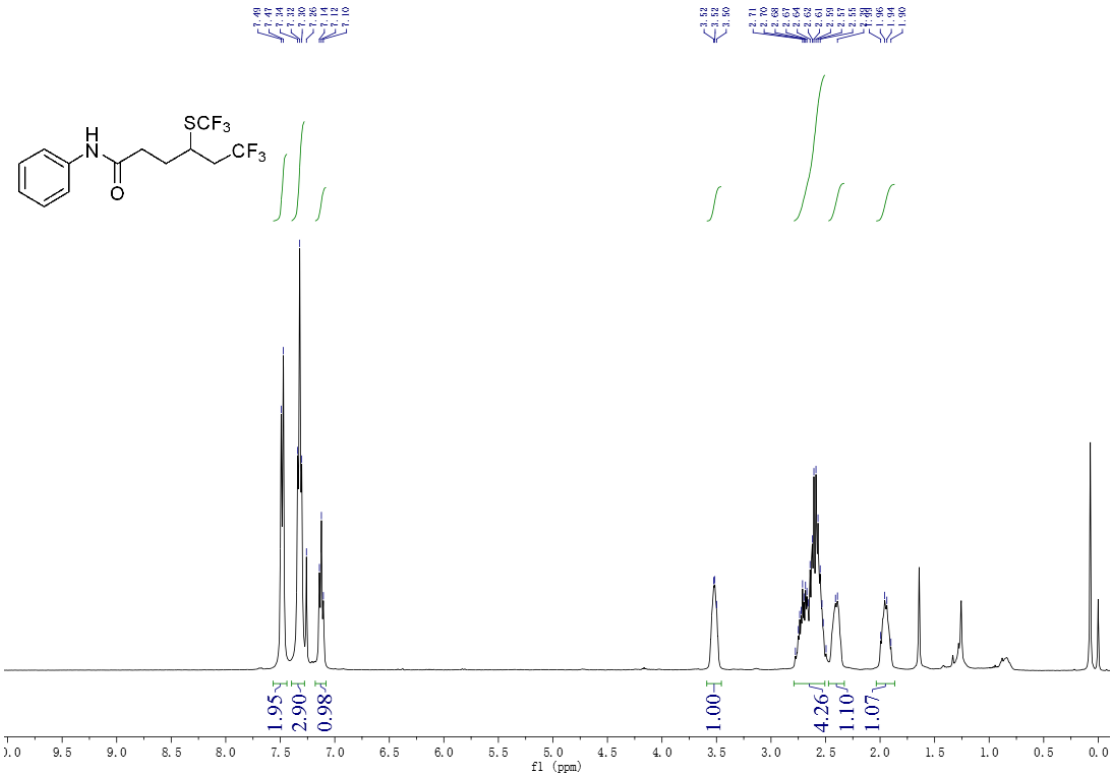
^{13}C NMR of **7b**



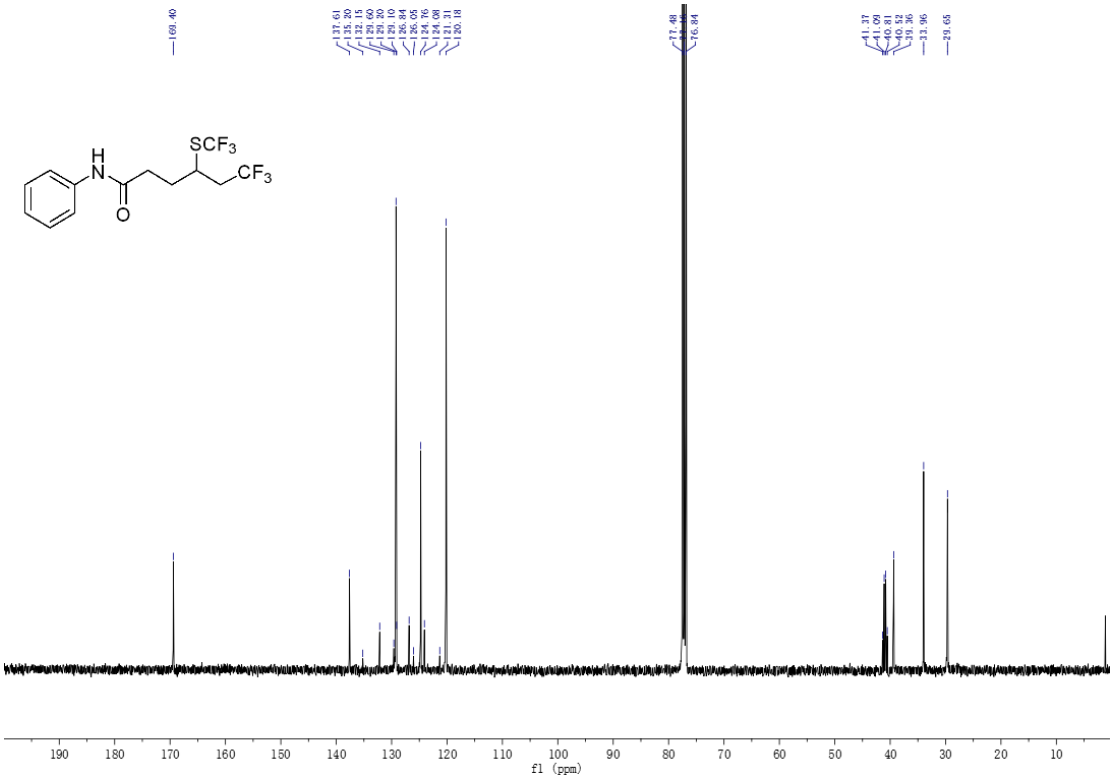
^{19}F NMR of **7b**



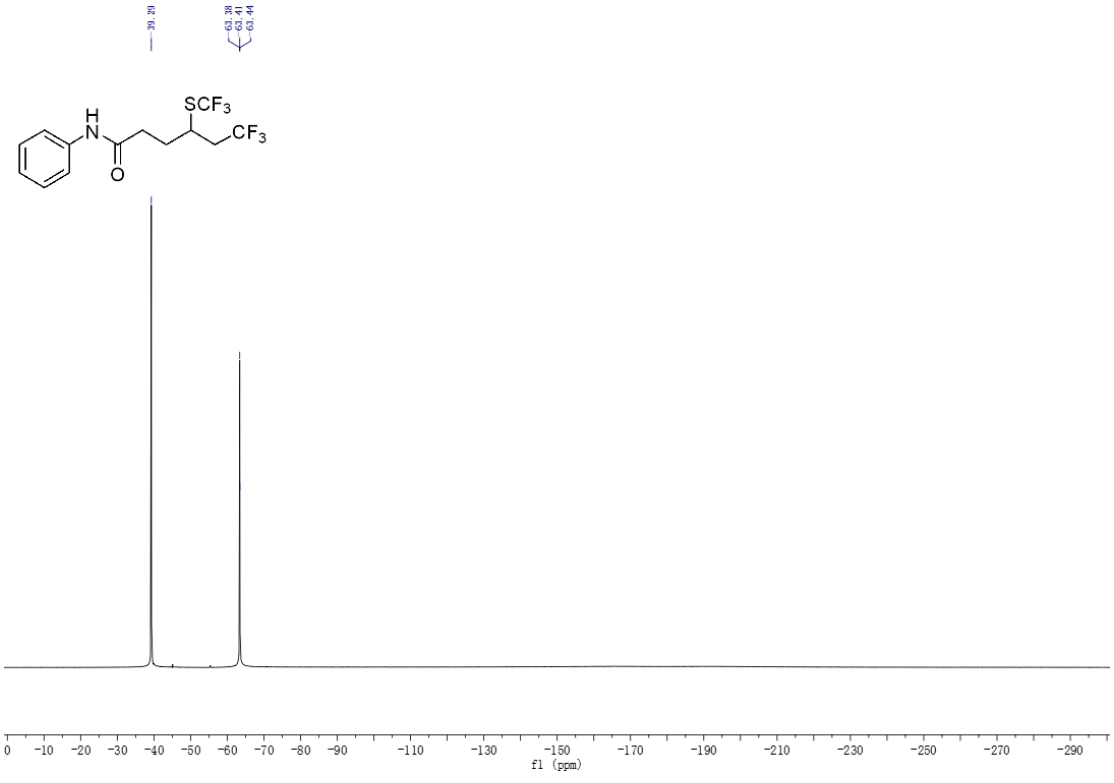
^{1}H NMR of **7c**



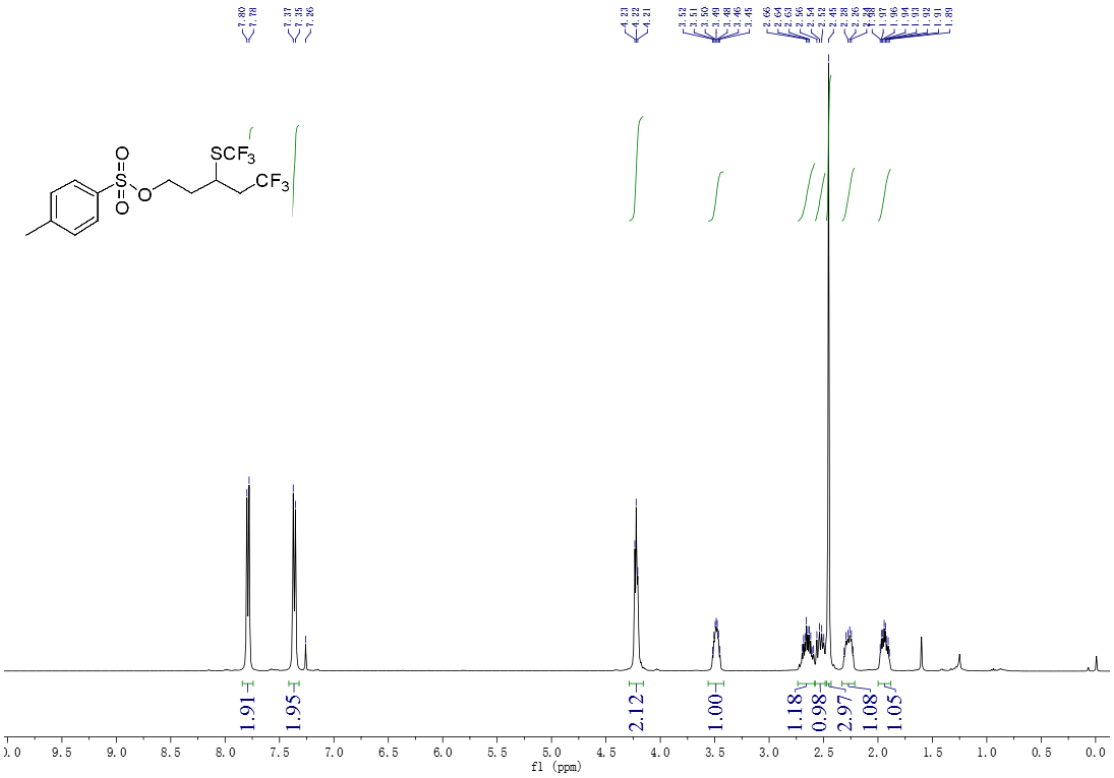
^{13}C NMR of **7c**



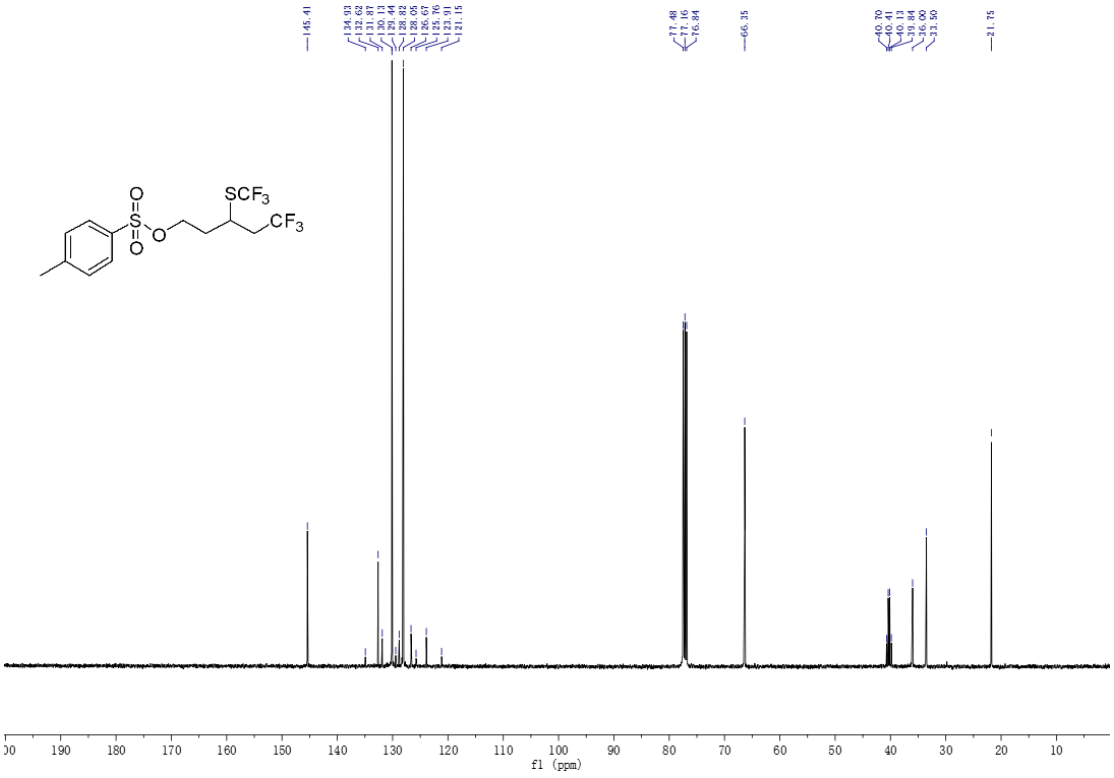
^{19}F NMR of **7c**



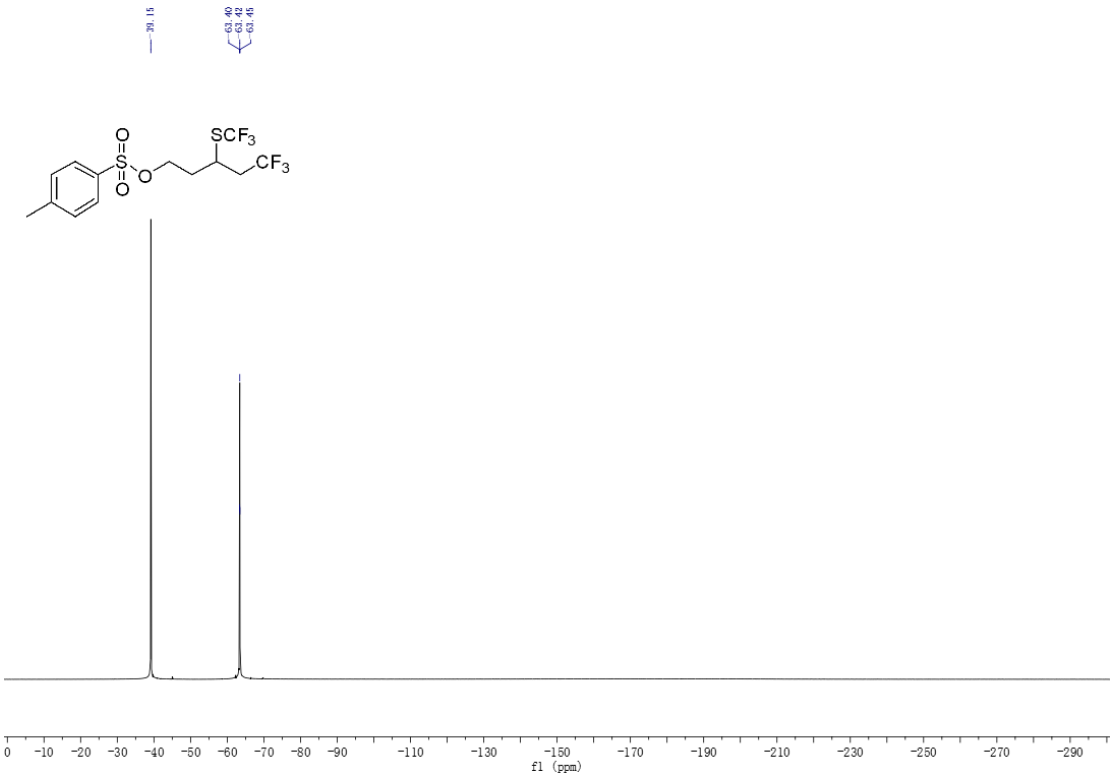
^{1}H NMR of **7d**



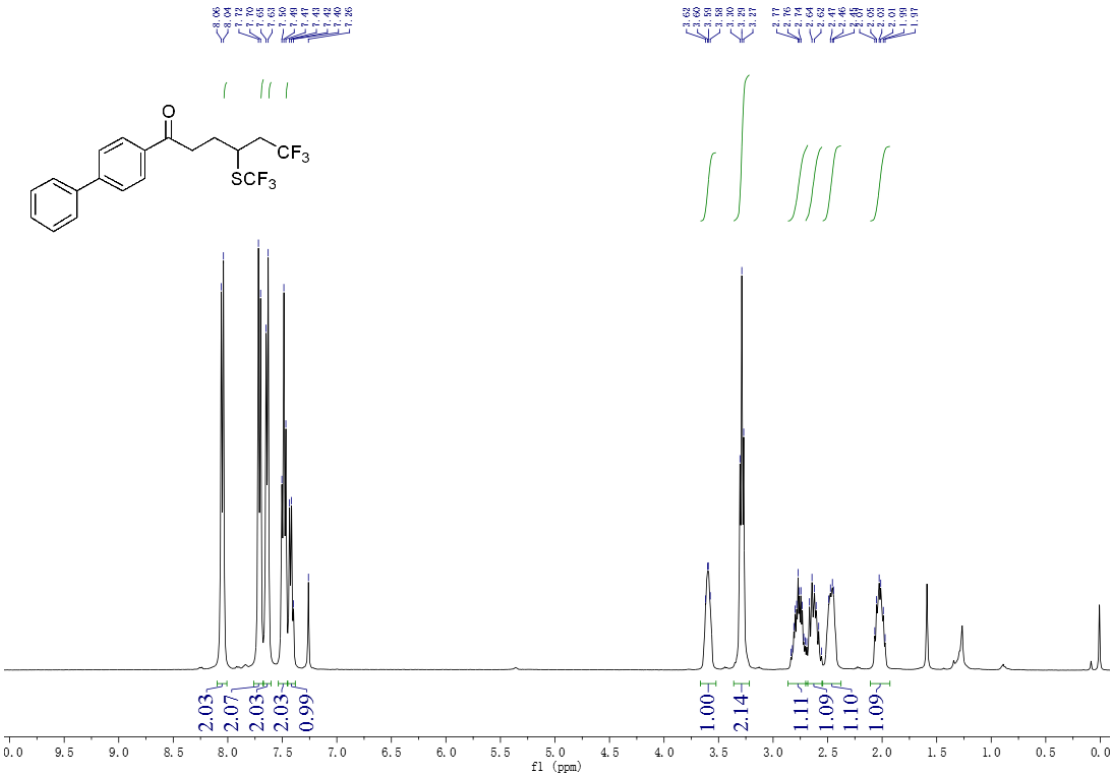
^{13}C NMR of **7d**



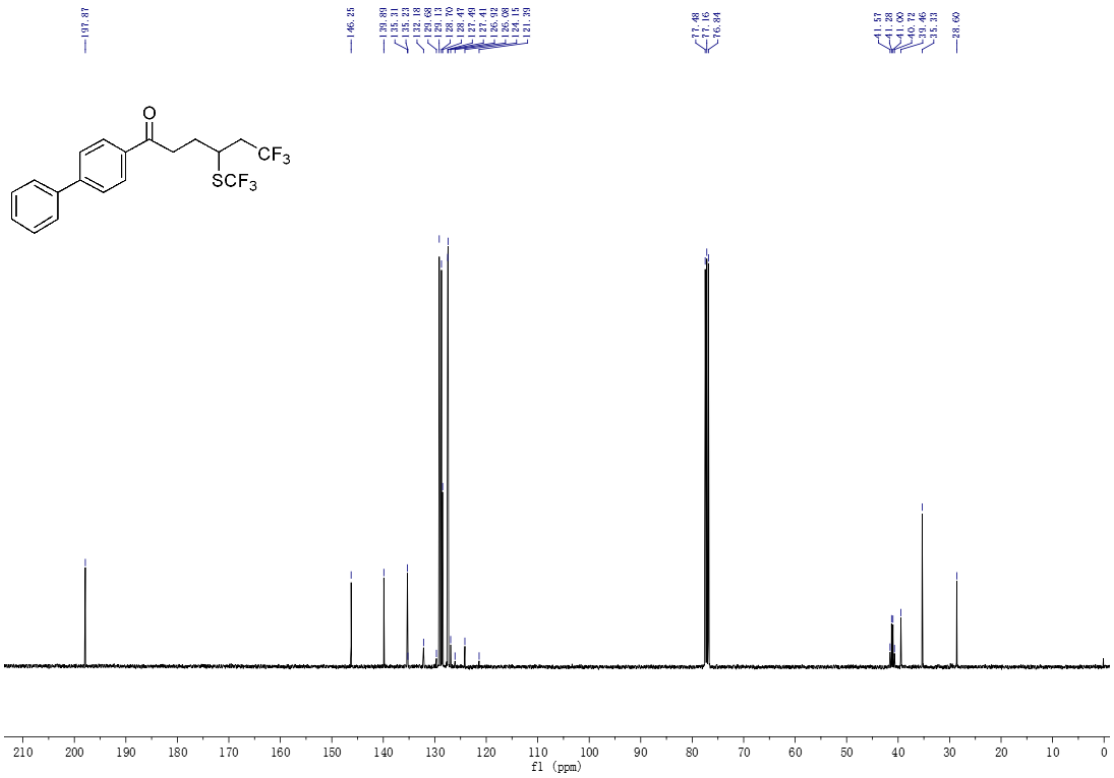
^{19}F NMR of **7d**



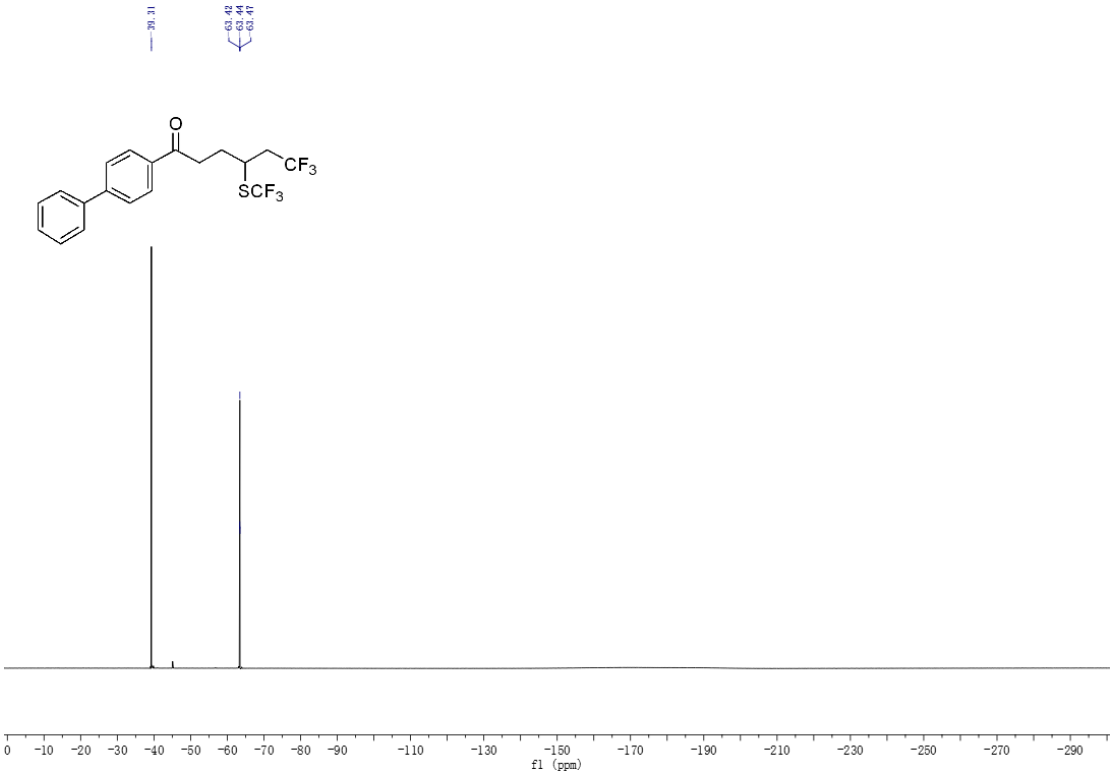
^{1}H NMR of **7e**



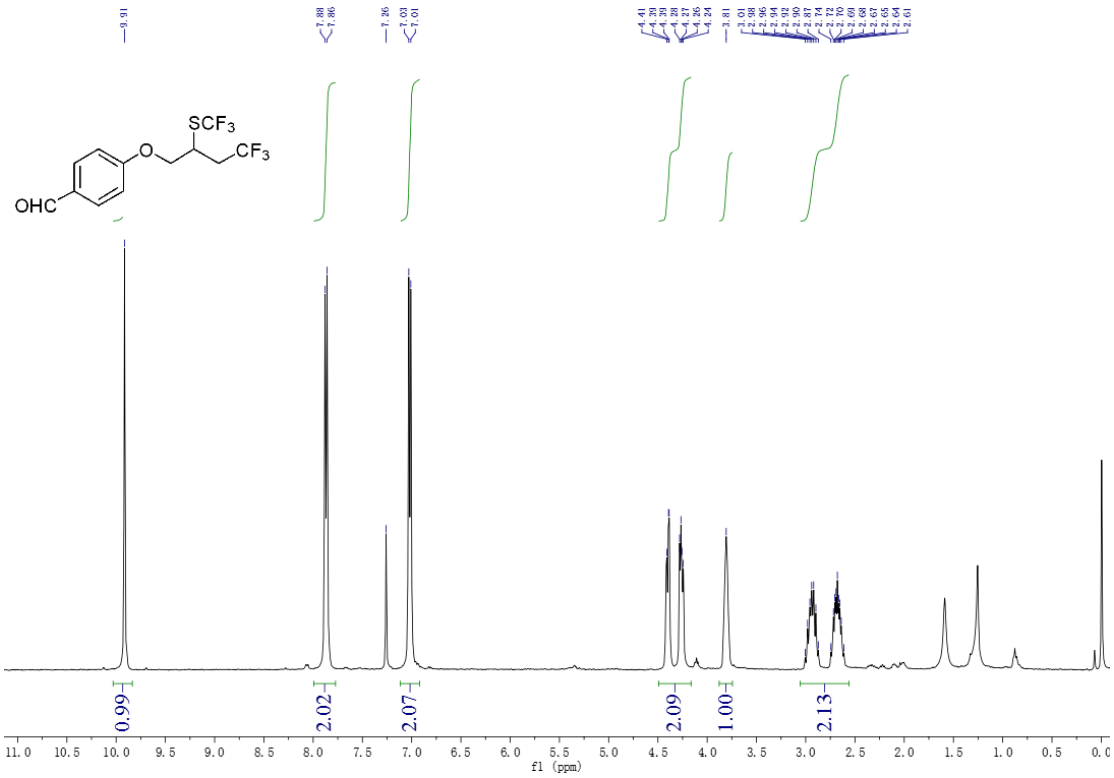
^{13}C NMR of **7e**



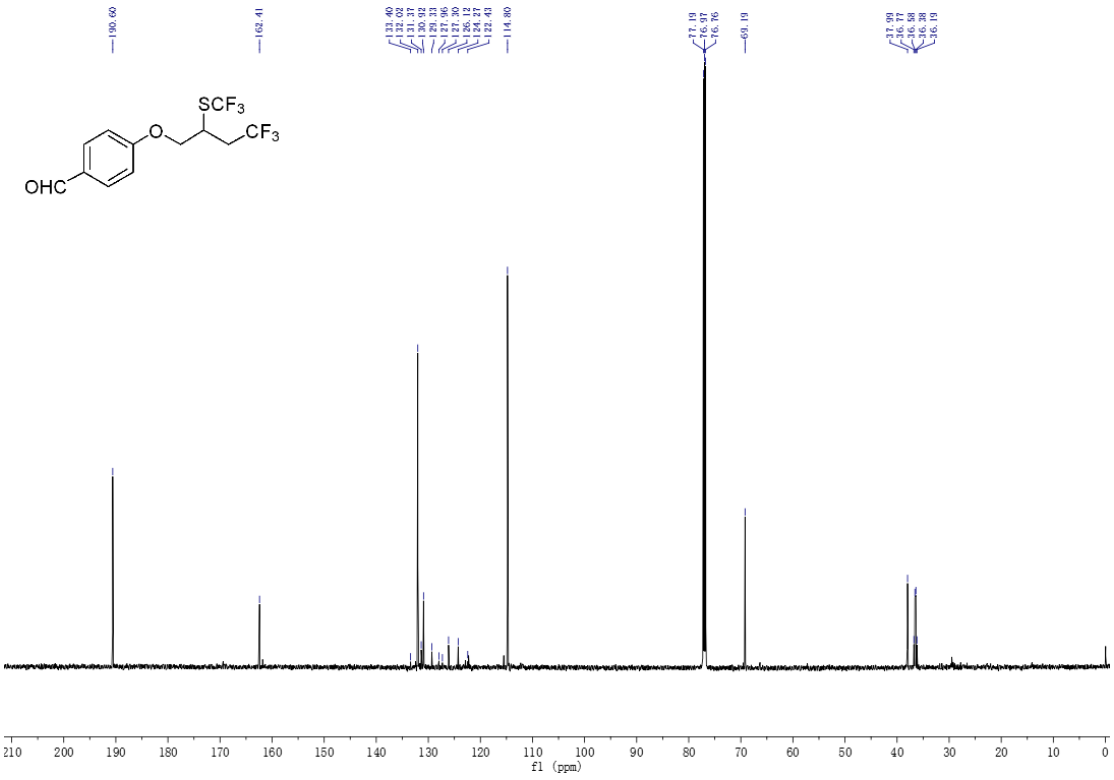
^{19}F NMR of **7e**



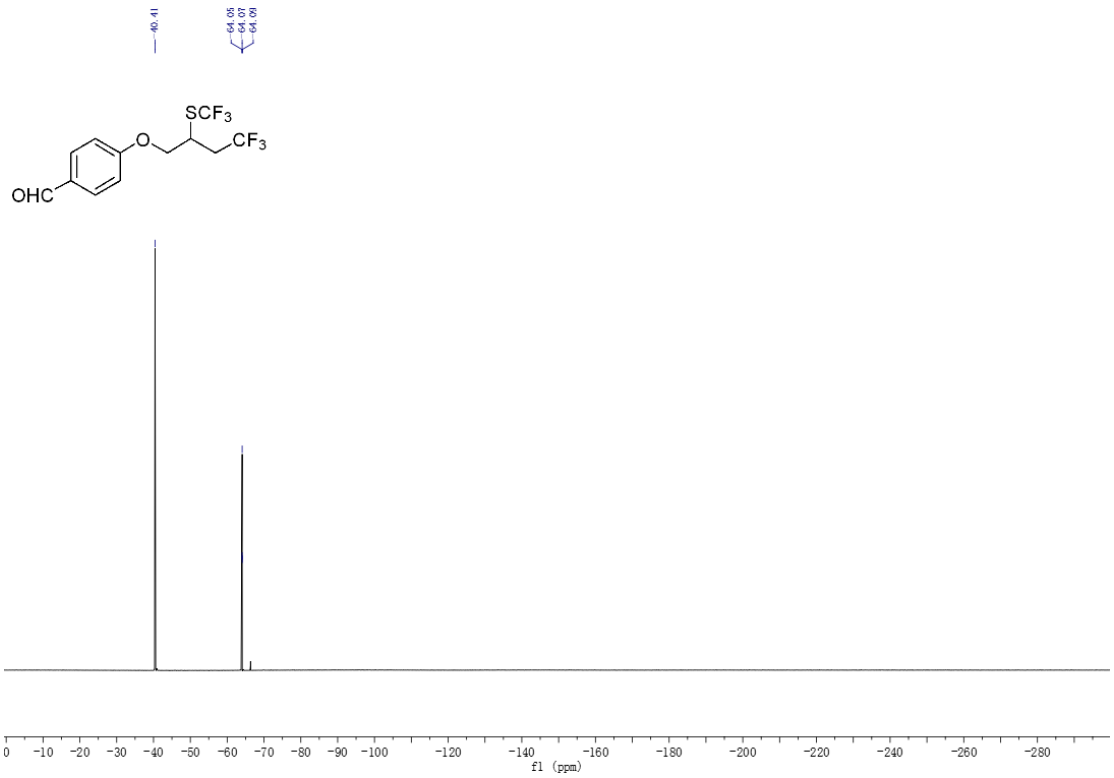
^{1}H NMR of **7f**



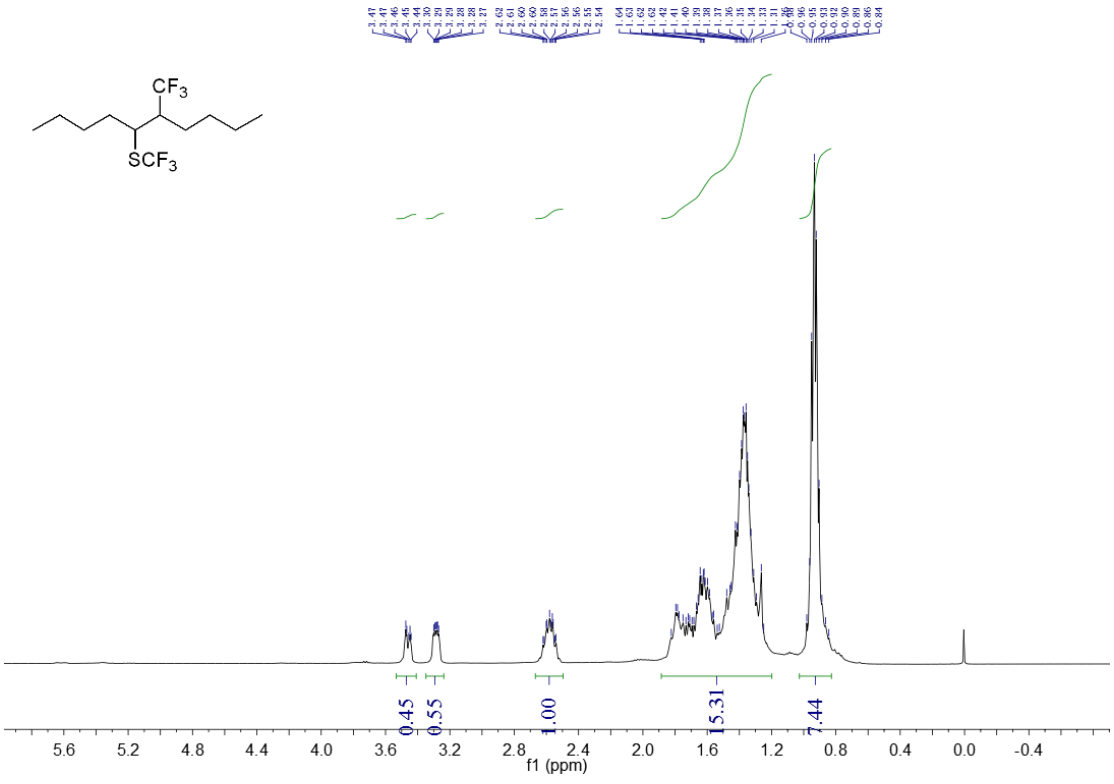
^{13}C NMR of **7f**



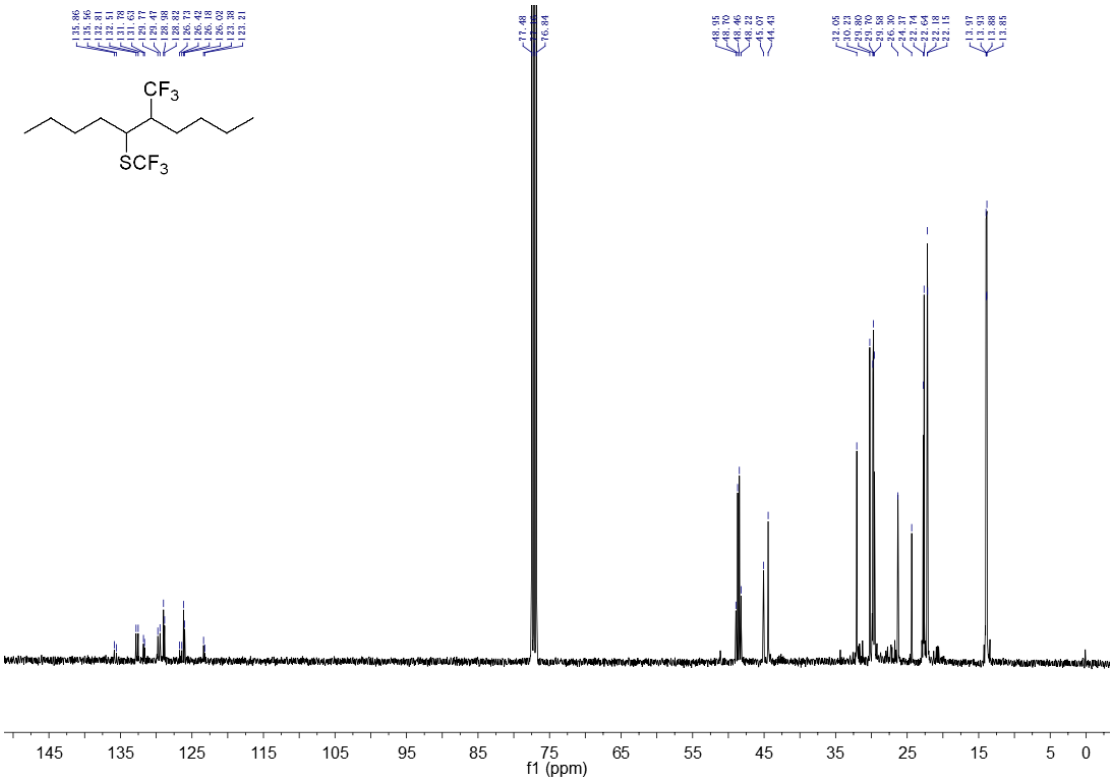
^{19}F NMR of **7f**



^{1}H NMR of **7g**



^{13}C NMR of **7g**



^{19}F NMR of **7g**