Supporting Information

Activation of perfluoroalkyl iodides by anions: Extending the scope of halogen bond activation to C(sp^3)-H amidation, C(sp^2)-H iodination and perfluoroalkylation reactions

Yaxin Wang,*[†ab] Zehui Cao,[†a] Qin He,[†a] Xin Huang,[c] Jiaxi Liu,[a] Helfried Neumann,*[b] Gong Chen*[c] and Matthias Beller,*[b]

[a] College of Pharmacy, Nanjing University of Chinese Medicine, Nanjing 210023 (China).
Email: 300500@njucm.edu.cn, Yaxin.Wang@catalysis.de

[b] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein Straße 29a, 18059 Rostock (Germany).
E-mail: Matthias.Beller@catalysis.de

[c] State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071 (China).

Content

1. Reagents

All commercial materials were used as received unless otherwise noted. Dry solvents and deuterated solvents were purchased from *J&K* Chemical. Perfluoroalkyl iodides were purchased from Energy Chemical. Starting materials for this study were purchased from TCI or were synthesized according to reported procedures. $Pd(OAc)_2$ and Cs_2CO_3 (≥99%, Aladdin), K_2CO_3, Rb_2CO_3, AgOAc, Ag_2CO_3, KOH, $KHCO_3$, K_3PO_4, $NaOCH_3$, $NaSCH_3$, CsOH, NaO*t*Bu (99%, Energy Chemical), and NaH (60% dispersion in mineral oil, Energy Chemical) were used in the reactions of $C(sp^3)$-H amidation or $C(sp^2)$-H iodination and perfluoroalkylation.

TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max} = 254 nm). Flash chromatography was performed using silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., China.

2. Instruments

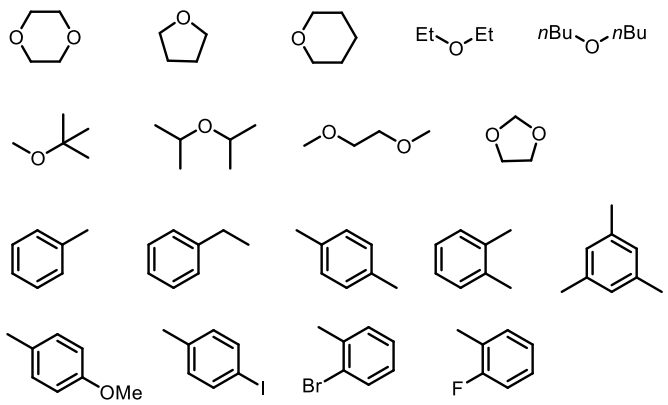
NMR spectra were recorded on Bruker AVANCE AV 400 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, br = broad singlet, m = multiplet. High resolution ESI mass experiments were operated on a Waters LCT Premier instrument. All reactions were carried out in a 4 mL glass vial (Thermo SCIENTIFIC National B7999-2, made from superior quality 33 expansion borosilicate clear glass), sealed with a PTEF cap on bench top if necessary.

Lights: PHILIPS TORNADO 25W CFL

3. Synthesis of substrates

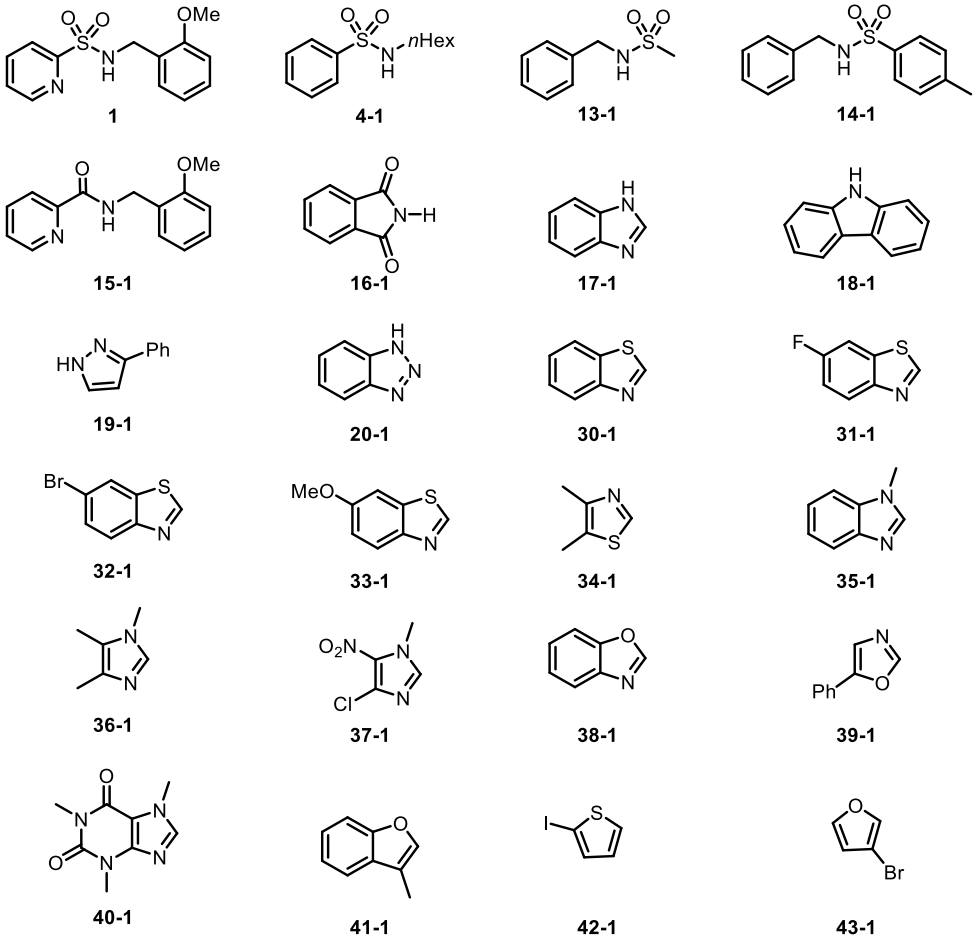
Compounds **1**[1], **4-1**[1], **13-1**[2], **14-1**[2], **15-1**[2], isonitrile compounds (**44-1 to 80-1**)[3], alkenes (**86-1 to 89-1**)[3], alkynes (**102-1 to 104-1**)[3], and biologically active molecules (**90-1 to**

Ethers and arenes:

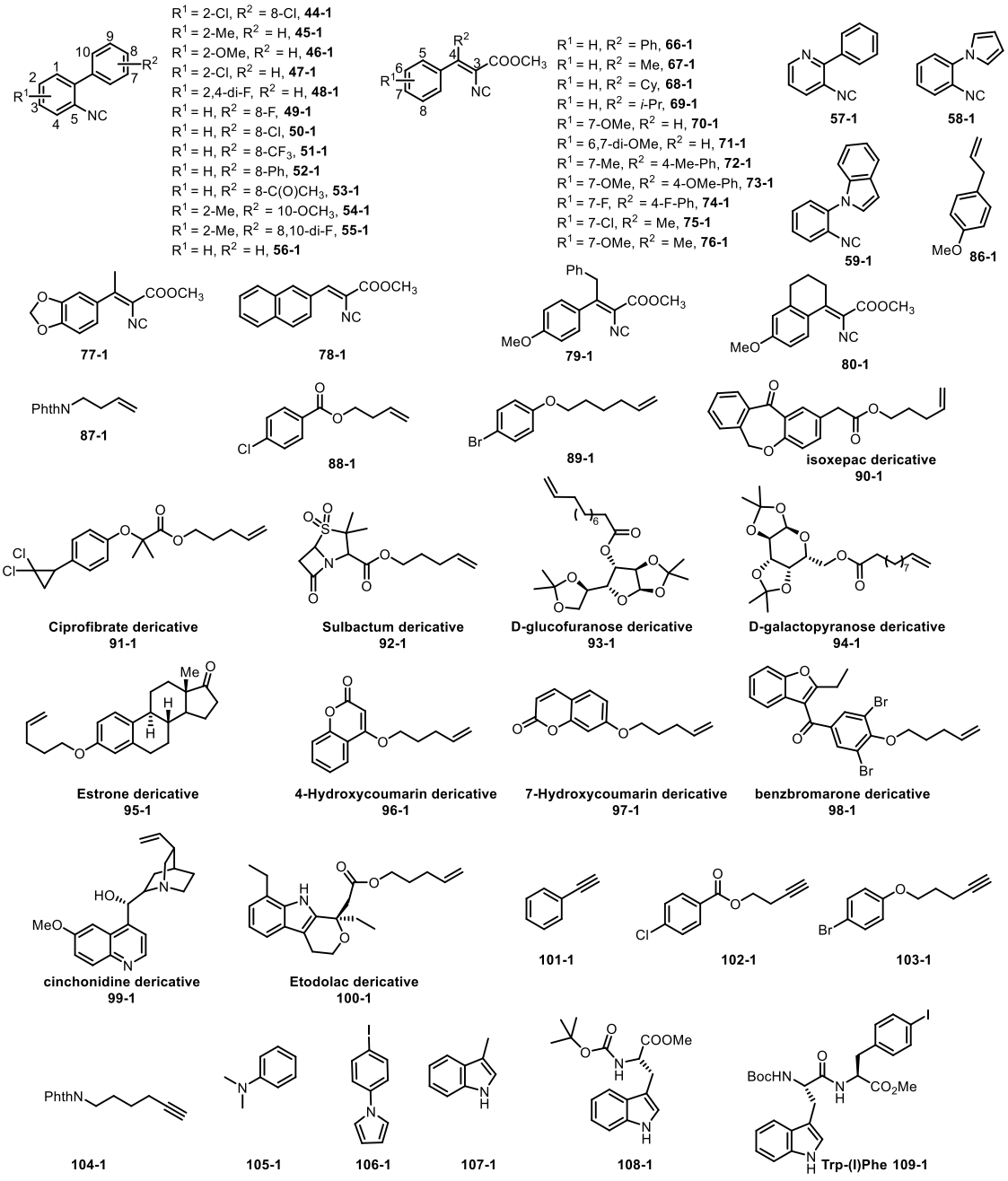


Scheme S1. Ethers and arenes used in this study

Substrates :



Scheme S2. Substrates used in amidation and iodination

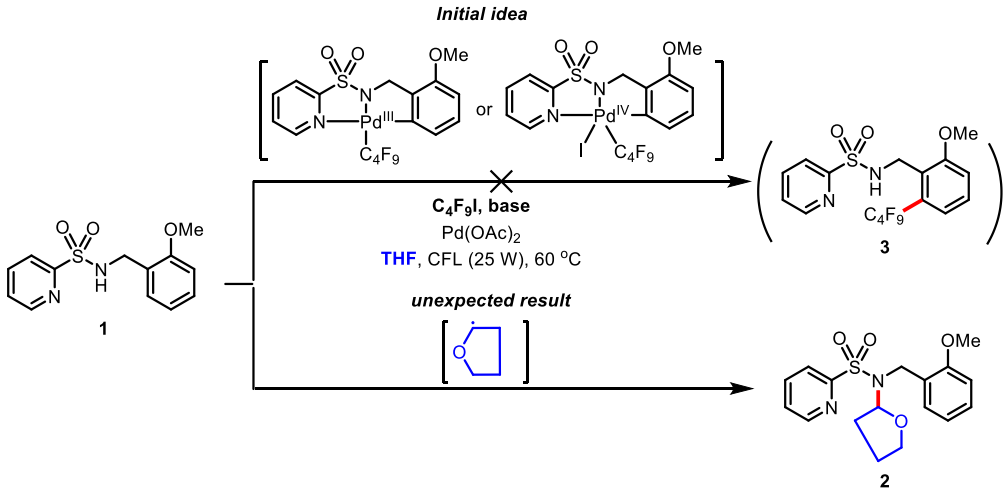


Scheme S3. Substrates used in perfluoroalkylation

100-1 and 108-1, 109-1)[3] are known compounds and were synthesized following the reported procedures. Other compounds for this study are commercially available and used as received.

4. Reaction optimization for the halogen-bond-promoted reaction of C(sp^3)-H amidation of N-(2-methoxybenzyl)-pyridine-2-sulfonamide

All screening reactions were carried out at a 0.2 mmol scale in a 4 mL glass vial (Thermo Scientific, National B7999-2) sealed with PTEF cap and stirred on bench top. The amidation reaction was discovered while aiming for a selective perfluoroalkylation of N-(2-methoxybenzyl)-pyridine-2-sulfonamide (see below).



Sulfonyl amide **1** (55.6 mg, 0.2 mmol, 1.0 equiv) and other specified reagents were dispersed in specific solvent and the resulting mixture was vigorously stirred at specified temperature with or without light irradiation for 12 hours. After removal of the solvent *in vacuo*, the resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (20 uL) as an internal standard for ^1H NMR analysis. The composition of the reaction mixture was analyzed based on the –(N)CH(O)- peak at 5.89 (t, J = 6.2 Hz, 1H) for compound **2**.

Table S1. Reaction optimization for the halogen-bond-promoted reaction of C(sp3)-H amidation of N-(2-methoxybenzyl)-pyridine-2-sulfonamide

entry	reagent (equiv), reaction time, temp	solvent	**2** %
1	C_4F_9I (2), $Pd(OAc)_2$ (0.1), TEEDA (3), CFL (25 W), 60 °C, 12 h, Ar	THF	23
2	C_4F_9I (2), $Pd(OAc)_2$ (0.1), Cs_2CO_3 (3), 60 °C, 12	THF	62

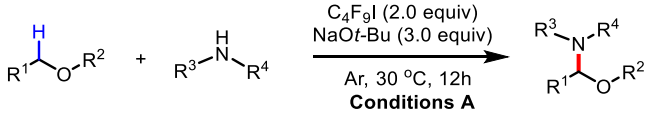
	h, Ar,		
3	C_4F_9I (2), Cs_2CO_3 (3), $Pd(OAc)_2$ (10 mol%), AgOAc (3), 12 h, 60 °C, Ar, CFL (25 W)	THF	62 (55 [b])
4	C_4F_9I (2), Cs_2CO_3 (3), 60 °C, 12 h, Ar	THF	65 (56 [b])
5	C_4F_9I (2), Cs_2CO_3 (3), 30 °C, 12 h, Ar	THF	<2
6	C_4F_9I (2), K_2CO_3 (3), 60 °C, 12 h, Ar	THF	10
7	C_4F_9I (2), Na_2CO_3 (3), 60 °C, 12 h, Ar	THF	<2
8	C_4F_9I (2), Rb_2CO_3 (3), 12 h, 60 °C, Ar	THF	56
9	C_4F_9I (2), Ag_2CO_3 (3), 12 h, 60 °C, Ar	THF	<2
10	C_4F_9I (2), $KHCO_3$ (3), 12 h, 60 °C, Ar	THF	10
11	C_4F_9I (2), K_3PO_4 (3), 12 h, 60 °C, Ar	THF	35
12	C_4F_9I (2), $NaOCH_3$ (3), 60 °C, 12 h, Ar	THF	33
13	C_4F_9I (2), $NaSCH_3$ (3), 12 h, 60 °C, Ar	THF	44
14	C_4F_9I (2), CsOH (3), 12 h, 60 °C, Ar	THF	46
15	C_4F_9I (2), KO*t*Bu (3), 60 °C, 12 h, Ar	THF	<2
16	C_4F_9I (2), KO*t*Bu (3), 30 °C, 12 h, Ar	THF	<2
17	C_4F_9I (2), NaO*t*Bu (3), 12 h, 60 °C, Ar	THF	99 (90 [b])
18	C_4F_9I (2), NaO*t*Bu (3), 12 h, 30 °C, Ar	THF	99 (90 [b])
19	C_4F_9I (2), NaO*t*Bu (2), 12 h, 30 °C, Ar	THF	81
20	C_4F_9I (2), NaO*t*Bu (1), 12 h, 30 °C, Ar	THF	58
21	C_4F_9I (2), NaO*t*Bu (3), 12 h, 30 °C, Ar, in darkness	THF	99 (90 [b])
22	C_4F_9I (2), NaO*t*Bu (3), 12 h, 30 °C, Air	THF	28
23	C_4F_9I (2), NaO*t*Bu (3), 12 h, 30 °C, O_2	THF	26
24[c]	THF (10), C_4F_9I (2), NaO*t*Bu (3), 12 h, 30 °C, Ar	CH_3CN	<2
25[c]	THF (10), C_4F_9I (2), NaO*t*Bu (3), 12 h, 30 °C, Ar	$PhCF_3$	67

26[c]	THF (10), C_4F_9I (2), NaO*t*Bu (3), 12 h, 30 °C, Ar	CCl_4	71
27	TEEDA (3), CFL (25 W), 30 °C, 12 h, Ar	THF	21
29	Et_3N (3), CFL (25 W), 30 °C, 12 h, Ar	THF	18
28	Et_3N (3), 30 °C, 12 h, Ar, in darkness	THF	<2
30	C_4F_9I (2), NaH (3), 30 °C, 12 h, Ar	THF	<2
31	Bu_4NCl (3), 30 °C, 12 h, Ar	THF	<2
32	Bu_4NBr (3), 30 °C, 12 h, Ar	THF	<2
33	Bu_4NI (3), 30 °C, 12 h, Ar	THF	<2
34	Bu_4NCl (3), NaH (1), 30 °C, 12 h, Ar	THF	65
35	Bu_4NBr (3), NaH (1), 30 °C, 12 h, Ar	THF	63
37	Bu_4NI (3), NaH (1), 30 °C, 12 h, Ar	THF	64

Halogen-bond promoted amination of dioxane. All screening reactions were carried out on a 0.2 mmol scale at 0.1 M concentration; the reaction vial is purged with Ar. a) Yield are based on ^1H NMR analysis on 0.2 mmol scale in 4 mL glass vial. b) Isolated yield. c) 10 equiv THF were added.

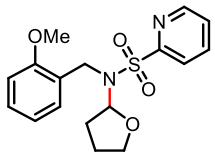
5. General procedures and substrate scope of halogen-bond-promoted reactions for C(sp^3)-H amidation

5.1 Halogen-bond-promoted reaction system for the alkyl ethers C(sp^3)-H amidation



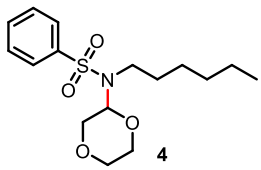
Scheme S4. Halogen-bond-promoted reaction system for the alkyl ethers C(sp^3)-H amidation

Conditions A: Amide (0.2 mmol, 1.0 equiv), C_4F_9I (0.4 mmol, 2.0 equiv) and NaO*t*Bu (0.6 mmol, 3.0 equiv) were dispersed in 2 mL of ethers. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C for 12 hours. Then, the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the desired product.



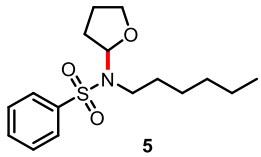
2

Compound **2** was isolated in 90% yield (crude ^{1}H NMR yield: 99%) following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 4.6 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.86 (td, *J* = 7.7, 1.5 Hz, 1H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.50 – 7.39 (m, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.89 (t, *J* = 6.2 Hz, 1H), 4.67 (d, *J* = 18.2 Hz, 1H), 4.48 (d, *J* = 18.2 Hz, 1H), 3.84 – 3.74 (m, 4H), 3.71 – 3.61 (m, 1H), 2.11 – 1.92 (m, 1H), 1.83 – 1.66 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.05, 156.14, 150.08, 137.80, 128.33, 127.95, 126.74, 126.59, 122.61, 120.66, 109.68, 89.27, 68.52, 55.21, 41.76, 30.06, 24.87. **HRMS** Calcd for $C_{17}H_{20}N_2O_4S$ [M+H$^+$]: 349.1217; Found: 349.1218.



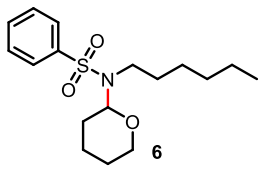
4

Compound **4** was isolated in 84% yield following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 5.32 (dd, *J* = 9.7, 2.5 Hz, 1H), 3.88 – 3.59 (m, 4H), 3.54 – 3.41 (m, 2H), 3.19 – 3.05 (m, 1H), 3.05 – 2.90 (m, 1H), 1.85 – 1.67 (m, 1H), 1.52 – 1.36 (m, 1H), 1.25 (s, 6H), 0.87 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.90, 132.79, 128.93, 127.76, 82.83, 69.21, 66.94, 65.74, 44.45, 31.87, 31.45, 26.62, 22.67, 14.11. **HRMS** Calcd for $C_{16}H_{26}NO_4S$ [M+H$^+$]: 328.1577; Found: 328.1578.



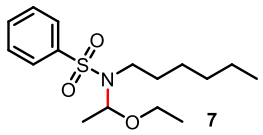
5

Compound **5** was isolated in 90% yield following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.57 – 7.51 (m, 1H), 7.51 – 7.44 (m, 2H), 5.78 (t, *J* = 5.9 Hz, 1H), 3.87 (q, *J* = 7.5 Hz, 1H), 3.73 (q, *J* = 7.4 Hz, 1H), 3.07 – 2.84 (m, 2H), 2.22 – 2.07 (m, 1H), 1.96 – 1.76 (m, 4H), 1.66 – 1.45 (m, 1H), 1.24 (s, 6H), 0.86 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.19, 132.48, 128.86, 127.72, 88.85, 68.11, 43.52, 31.47, 30.36, 26.94, 25.03, 22.67, 14.10. **HRMS** Calcd for $C_{16}H_{26}NO_3S$ [M+H$^+$]: 312.1628; Found: 312.1628.



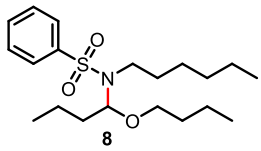
6

Compound **6** was isolated in 91% yield following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.9 Hz, 2H), 7.58 – 7.49 (m, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 5.13 (d, *J* = 9.1 Hz, 1H), 3.85 (d, *J* = 11.7 Hz, 1H), 3.58 – 3.37 (m, 1H), 3.16 – 3.03 (m, 1H), 3.03 – 2.89 (m, 1H), 2.00 – 1.87 (m, 1H), 1.88 – 1.69 (m, 2H), 1.66 – 1.38 (m, 5H), 1.24 (s, 6H), 0.86 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.25, 132.49, 128.71, 127.86, 86.28, 68.06, 43.92, 31.67, 31.49, 31.08, 26.77, 25.06, 23.82, 22.71, 14.13. **HRMS** Calcd for $C_{17}H_{28}NO_3S$ [M+H$^+$]: 326.1784; Found: 326.1780.



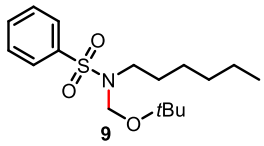
7

Compound **7** was isolated in 85% yield following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 2H), 7.57 – 7.51 (m, 1H), 7.51 – 7.44 (m, 2H), 5.23 (q, *J* = 6.0 Hz, 1H), 3.61 - 3.53 (m, 1H), 3.40 - 3.33 (m, 1H), 3.26 – 3.08 (m, 1H), 3.07 – 2.94 (m, 1H), 1.66 - 1.57 (m, 2H), 1.34 – 1.20 (m, 6H), 1.17 (d, *J* = 6.1 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.19, 132.43, 129.08, 126.92, 84.24, 63.12, 42.47, 31.49, 30.77, 26.95, 22.68, 19.97, 14.86, 14.10. **HRMS** Calcd for $C_{16}H_{28}NO_3S$ [M+H$^+$]: 314.1784; Found: 314.1787.



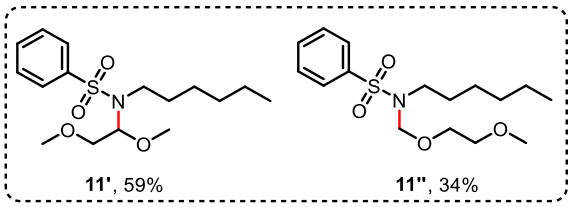
8

Compound **8** was isolated in 84% yield following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 2H), 7.58 – 7.51 (m, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 4.99 (dd, *J* = 8.3, 4.3 Hz, 1H), 3.44 – 3.38 (m, 1H), 3.27 – 3.21 (m, 1H), 3.21 – 3.08 (m, 1H), 3.06 – 2.91 (m, 1H), 1.72 – 1.51 (m, 3H), 1.50 – 1.41 (m, 2H), 1.40 – 1.14 (m, 11H), 0.86 (dt, *J* = 12.0, 5.8 Hz, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.34, 132.41, 129.00, 127.06, 88.18, 68.04, 42.71, 36.49, 31.54, 31.50, 30.77, 27.02, 22.70, 19.44, 19.07, 14.12, 13.98, 13.83. **HRMS** Calcd for $C_{20}H_{36}NO_3S$ [M+H$^+$]: 370.2410; Found: 370.2415.



9

Compound **9** was isolated in 90% yield following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.81 (m, 2H), 7.56 – 7.48 (m, 1H), 7.48 – 7.39 (m, 2H), 4.75 (s, 2H), 3.24 – 2.95 (m, 2H), 1.71 – 1.41 (m, 2H), 1.31 – 1.22 (m, 6H), 1.14 (s, 9H), 0.85 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.44, 132.28, 128.49, 127.90, 72.91, 70.84, 45.88, 31.47, 28.40, 27.62, 26.35, 22.58, 14.06. **HRMS** Calcd for $C_{17}H_{30}NO_3S$ [M+H$^+$]: 328.1941; Found: 328.1940.

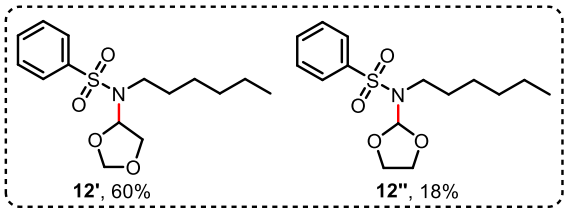


11', 59% **11"**, 34%

Compound **11'** was isolated in 59% yield and compound **11"** was isolated in 34% yield following the condition A.

Compound **11'**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.58 – 7.52 (m, 1H), 7.51 – 7.44 (m, 2H), 5.15 (t, *J* = 6.1 Hz, 1H), 3.46 (dd, *J* = 10.2, 6.4 Hz, 1H), 3.30 (dd, *J* = 10.2, 5.9 Hz, 1H), 3.27 (s, 3H), 3.25 (s, 3H), 3.20 – 2.98 (m, 2H), 1.63 – 1.48 (m, 2H), 1.30 – 1.17 (m, 6H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.97, 132.50, 128.82, 127.36, 87.47, 72.52, 59.04, 55.95, 42.97, 31.38, 30.46, 26.81, 22.62, 14.06. **HRMS** Calcd for $C_{16}H_{28}NO_4S$ [M+H$^+$]: 330.1734; Found: 330.1734.

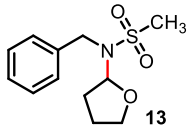
Compound **11''**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 2H), 7.59 – 7.53 (m, 1H), 7.52 – 7.44 (m, 2H), 4.83 (s, 2H), 3.68 – 3.61 (m, 2H), 3.54 – 3.47 (m, 2H), 3.37 (s, 3H), 3.14 – 3.18 (m, 2H), 1.58 – 1.48 (m, 2H), 1.27 – 1.16 (m, 6H), 0.85 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.63, 132.58, 129.04, 127.20, 78.80, 71.68, 67.25, 59.05, 47.23, 31.42, 28.52, 26.40, 22.57, 14.05. **HRMS** Calcd for $C_{16}H_{28}NO_4S$ [M+H$^+$]: 330.1734; Found: 330.1733.



Compound **12'** was isolated in 60% yield and compound **12''** was isolated in 18% yield following the condition A.

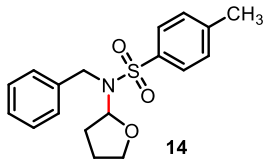
Compound **12'**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 2H), 6.02 (dd, *J* = 6.4, 2.9 Hz, 1H), 5.15 (s, 1H), 4.72 (s, 1H), 3.99 (dd, *J* = 9.7, 2.8 Hz, 1H), 3.89 (dd, *J* = 9.6, 6.7 Hz, 1H), 3.07 – 2.99 (m, 1H), 2.99 – 2.87 (m, 1H), 1.88 – 1.69 (m, 1H), 1.65 – 1.44 (m, 1H), 1.24 (s, 6H), 0.86 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.65, 132.82, 129.04, 127.73, 95.81, 84.71, 68.57, 43.74, 31.42, 31.11, 26.92, 22.67, 14.12. **HRMS** Calcd for $C_{15}H_{23}NO_4S$ [M+H$^+$]: 314.1421; Found: 314.1424.

Compound **12''**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.62 – 7.53 (m, 1H), 7.50 (t, *J* = 7.1 Hz, 2H), 6.47 (s, 1H), 4.07 – 3.98 (m, 2H), 3.98 – 3.88 (m, 2H), 3.15 – 2.87 (m, 2H), 1.76 – 1.57 (m, 2H), 1.23 (s, 6H), 0.86 (t, *J* = 5.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.29, 132.72, 129.04, 127.40, 107.19, 64.76, 42.77, 31.47, 30.78, 26.85, 22.67, 14.14. **HRMS** Calcd for $C_{15}H_{23}NO_4S$ [M+H$^+$]: 314.1421; Found: 314.1425.



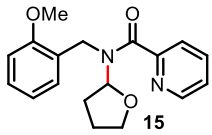
13

Compound **13** was isolated in 51% yield following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.1 Hz, 1H), 5.69 (t, *J* = 6.8 Hz, 1H), 4.55 (d, *J* = 16.7 Hz, 1H), 4.25 (d, *J* = 16.7 Hz, 1H), 4.02 (q, *J* = 6.8 Hz, 1H), 3.80 (q, *J* = 7.3 Hz, 1H), 2.96 (s, 3H), 2.05 – 1.77 (m, 3H), 1.76 – 1.57 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.38, 128.68, 127.45, 127.08, 88.82, 68.42, 46.47, 39.52, 29.51, 24.92. **HRMS** Calcd for $C_{12}H_{18}NO_3S$ [M+H$^+$]: 256.1002; Found: 256.1000.



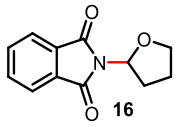
14

Compound **14** was isolated in 88% yield following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.34 – 7.17 (m, 5H), 5.90 (t, *J* = 6.6 Hz, 1H), 4.41 (d, *J* = 17.0 Hz, 1H), 4.11 (d, *J* = 17.0 Hz, 1H), 3.86 (q, 7.0 Hz, 1H), 3.72 (q, *J* = 7.3 Hz, 1H), 2.41 (s, 3H), 2.05 – 1.90 (m, 1H), 1.83 – 1.57 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.41, 138.54, 136.90, 129.57, 128.53, 127.87, 127.28, 127.14, 88.92, 68.52, 46.03, 30.22, 24.85, 21.66. **HRMS** Calcd for $C_{18}H_{22}NO_3S$ [M+H$^+$]: 332.1315; Found: 332.1317.



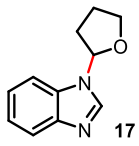
15

Compound **15** was isolated in 33% yield following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 2.8 Hz, 1H), 7.79 (t, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 6.6 Hz, 2H), 7.20 (t, *J* = 7.1 Hz, 1H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 5.79 (s, 1H), 4.92 (d, *J* = 17.3 Hz, 1H), 4.54 (d, *J* = 17.2 Hz, 1H), 3.94 (q, *J* = 7.3 Hz, 1H), 3.86 (s, 3H), 3.76 – 3.58 (m, 1H), 2.07 (q, *J* = 8.4 Hz, 1H), 1.96 – 1.70 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.00, 156.38, 154.67, 148.61, 137.02, 127.54, 126.74, 126.29, 124.51, 123.83, 120.68, 109.85, 89.57, 68.28, 55.28, 39.21, 29.20, 25.47. **HRMS** Calcd for $C_{18}H_{21}N_2O_3$ [M+H$^+$]: 313.1547; Found: 313.1547.



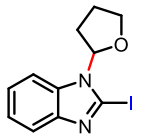
16

Compound **16** was isolated in 90% yield following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 – 7.78 (m, 2H), 7.75 – 7.66 (m, 2H), 6.03 (dd, *J* = 7.9, 4.9 Hz, 1H), 4.18 (q, *J* = 7.7 Hz, 1H), 3.94 (td, *J* = 7.8, 4.6 Hz, 1H), 2.60 – 2.47 (m, 1H), 2.43 – 2.32 (m, 1H), 2.32 – 2.21 (m, 1H), 2.08 – 1.91 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.96, 134.26, 132.03, 123.45, 80.98, 69.90, 29.21, 26.13. **HRMS** Calcd for $C_{12}H_{12}NO_3$ [M+H$^+$]: 218.0812; Found: 218.0815.



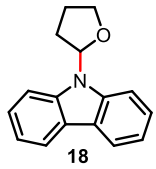
17

Compound **17** was isolated in 59% yield (Crude ^{1}H-NMR yield: 78%) following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.86 – 7.76 (m, 1H), 7.50 – 7.41 (m, 1H), 7.29 (dt, *J* = 9.8, 5.1 Hz, 2H), 6.18 (t, *J* = 4.1 Hz, 1H), 4.19 (q, *J* = 7.3 Hz, 1H), 4.05 (q, *J* = 7.8 Hz, 1H), 2.53 – 2.30 (m, 2H), 2.24 – 1.99 (m, 2H).[4]



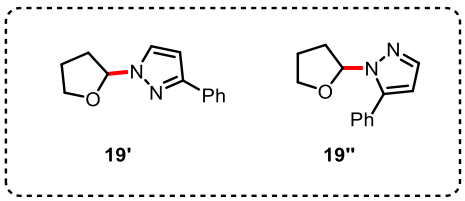
17'

Compound **17'** was isolated in 20% yield following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.4 Hz, 1H), 7.55 – 7.41 (m, 1H), 7.25 – 7.17 (m, 2H), 6.21 (t, *J* = 6.5 Hz, 1H), 4.39 (q, *J* = 15.2, 6.9 Hz, 1H), 4.09 (q, *J* = 13.7, 8.0 Hz, 1H), 2.49 – 2.20 (m, 4H).[4]



18

Compound **18** was isolated in 32% yield following the condition A. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.47 – 7.38 (m, 2H), 7.28 – 7.17 (m, 2H), 6.48 (t, *J* = 6.7 Hz, 1H), 4.49 – 4.30 (m, 1H), 4.13 – 4.00 (m, 1H), 2.56 – 2.44 (m, 1H), 2.42 – 2.28 (m, 2H), 2.28 – 2.17 (m, 1H).[5]



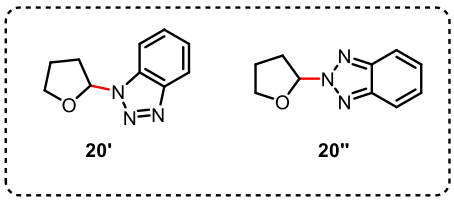
19' 19''

Compound **19'** was isolated in 35% yield and compound **19''** was isolated in 25% yield following the condition A.

Compound **19': ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 2H), 7.58 (d, *J* = 2.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 2.4 Hz, 1H), 6.03 (dd, *J* = 6.6, 2.5 Hz, 1H), 4.24 -4.12 (m, 1H), 4.01 (q, *J* = 7.4 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.42 – 2.28 (m, 1H), 2.29 – 2.16 (m, 1H), 2.12 – 1.96 (m, 1H).[6]

Compound **19'': ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 3H), 7.50 – 7.37 (m, 3H), 6.32 (d, *J* = 1.8 Hz, 1H), 5.97 (dd, *J* = 7.3, 3.3 Hz, 1H), 4.21 (q, *J* = 7.5 Hz, 1H),

4.03 - 3.90 (m, 1H), 2.84 – 2.68 (m, 1H), 2.56 – 2.40 (m, 1H), 2.31 – 2.15 (m, 1H), 2.11 – 1.93 (m, 1H).[6]

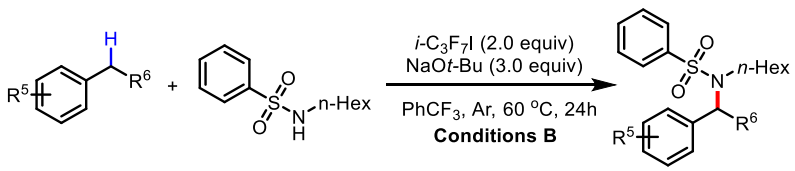


Compound **20'** was isolated in 80% yield and compound **20''** was isolated in 9% yield following the condition A.

Compound **20': ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 6.50 (dd, *J* = 6.8, 2.3 Hz, 1H), 4.15 – 3.97 (m, 2H), 3.23 – 3.06 (m, 1H), 2.57 – 2.46 (m, 1H), 2.45 – 2.31 (m, 1H), 2.24 – 2.10 (m, 1H).[6]

Compound **20'': ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 – 7.82 (m, 2H), 7.44 – 7.31 (m, 2H), 6.60 (dd, *J* = 6.4, 2.2 Hz, 1H), 4.40 – 4.28 (m, 1H), 4.21 – 4.07 (m, 1H), 2.85 – 2.67 (m, 1H), 2.61 – 2.42 (m, 2H), 2.21 – 2.09 (m, 1H).[6]

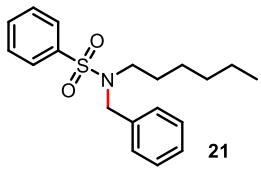
5.2 Halogen-bond-promoted reaction system for benzyl hydrocarbon C(sp^3)-H amidation



Scheme S5. Halogen-bond-promoted reaction system for benzyl hydrocarbon C(sp^3)-H amidation

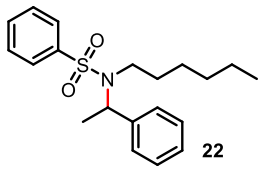
General conditions B: Amide (0.2 mmol, 1.0 equiv), *i*-C_3F_7I (0.4 mmol, 2.0 equiv), arenes (2.0 mmol, 10.0 equiv) and NaO*t*Bu (0.6 mmol, 3.0 equiv) were dispersed in 1 mL of $PhCF_3$. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 60 °C for 24 hours. Then, the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash

chromatography to give the desired product.



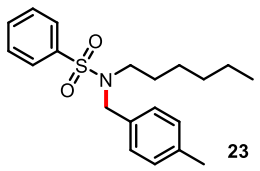
21

Compound **21** was isolated in 79% yield following the condition B. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.22 (m, 5H), 4.34 (s, 2H), 3.19 – 2.98 (m, 2H), 1.38 – 1.23 (m, 2H), 1.22 – 1.01 (m, 6H), 0.80 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.33, 136.57, 132.52, 129.19, 128.64, 128.36, 127.84, 127.21, 51.86, 48.13, 31.32, 27.92, 26.37, 22.52, 14.05. **HRMS** Calcd for $C_{19}H_{26}NO_2S$ [M+H$^+$]: 332.1679; Found: 332.1673.



22

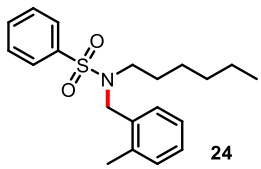
Compound **22** was isolated in 33% yield following the condition B. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.80 (m, 2H), 7.63 – 7.55 (m, 1H), 7.55 – 7.47 (m, 2H), 7.33 – 7.18 (m, 5H), 5.19 (q, *J* = 7.0 Hz, 1H), 3.10 – 2.90 (m, 2H), 1.46 – 1.34 (m, 4H), 1.21 – 1.09 (m, 3H), 1.10 – 0.98 (m, 4H), 0.79 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.52, 140.34, 132.38, 129.15, 128.43, 127.73, 127.67, 127.20, 55.48, 44.48, 31.30, 30.76, 26.66, 22.56, 17.01, 14.07. **HRMS** Calcd for $C_{20}H_{28}NO_2S$ [M+H$^+$]: 346.1835; Found: 346.1839.



23

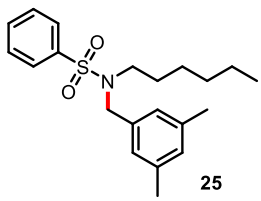
Compound **23** was isolated in 75% yield following the condition B. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 2H),

7.13 (q, *J* = 8.0 Hz, 4H), 4.30 (s, 2H), 3.20 – 2.95 (m, 2H), 2.33 (s, 3H), 1.39 – 1.25 (m, 2H), 1.22 – 1.01 (m, 6H), 0.80 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.40, 137.51, 133.38, 132.45, 129.29, 129.15, 128.35, 127.18, 51.49, 47.84, 31.31, 27.85, 26.35, 22.51, 21.21, 14.04. **HRMS** Calcd for $C_{20}H_{28}NO_2S$ [M+H$^+$]: 346.1835; Found: 346.1836.



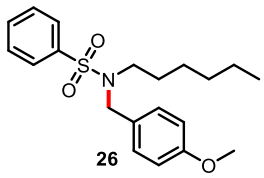
24

Compound **24** was isolated in 63% yield following the condition B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 2H), 7.64 – 7.57 (m, 1H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.08 (m, 4H), 4.32 (s, 2H), 3.13 – 2.92 (m, 2H), 2.37 (s, 3H), 1.27 – 0.96 (m, 8H), 0.79 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.58, 137.23, 133.90, 132.57, 130.68, 129.31, 129.19, 128.03, 127.34, 126.06, 50.73, 48.28, 31.26, 28.18, 26.37, 22.47, 19.34, 14.03. **HRMS** Calcd for $C_{20}H_{28}NO_2S$ [M+H$^+$]: 346.1835; Found: 346.1836.



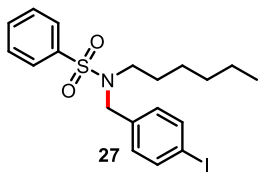
25

Compound **25** was isolated in 67% yield following the condition B. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.77 (m, 2H), 7.63 – 7.55 (m, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 6.89 (s, 1H), 6.81 (s, 2H), 4.28 (s, 2H), 3.18 – 2.95 (m, 2H), 2.26 (s, 6H), 1.43 – 1.26 (m, 2H), 1.25 – 1.01 (m, 6H), 0.81 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.55, 138.12, 136.22, 132.43, 129.39, 129.13, 127.18, 126.12, 51.56, 47.82, 31.35, 27.78, 26.37, 22.54, 21.31, 14.06. **HRMS** Calcd for $C_{21}H_{30}NO_2S$ [M+H$^+$]: 360.1992; Found: 360.1991.



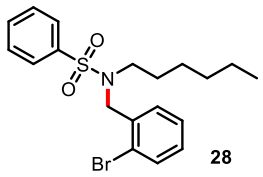
26

Compound **26** was isolated in 90% yield following the condition B. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.76 (m, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.27 (s, 2H), 3.78 (s, 3H), 3.13 – 2.98 (m, 2H), 1.38 – 1.22 (m, 2H), 1.22 – 1.02 (m, 6H), 0.80 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.31, 140.41, 132.45, 129.72, 129.14, 128.43, 127.17, 113.99, 55.36, 51.25, 47.80, 31.31, 27.93, 26.36, 22.51, 14.03. **HRMS** Calcd for $C_{20}H_{28}NO_3S$ [M+H$^+$]: 362.1784; Found: 362.1782.



27

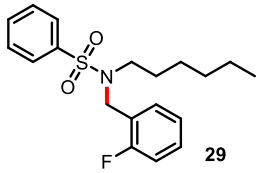
Compound **27** was isolated in 48% yield following the condition B. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 4.27 (s, 2H), 3.17 – 2.94 (m, 2H), 1.37 – 1.22 (m, 2H), 1.21 – 1.02 (m, 6H), 0.80 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.08, 137.74, 136.52, 132.66, 130.21, 129.26, 127.18, 93.35, 51.43, 48.39, 31.32, 27.96, 26.36, 22.53, 14.07. **HRMS** Calcd for $C_{19}H_{25}INO_2S$ [M+H$^+$]: 458.0645; Found: 458.0640.



28

Compound **28** was isolated in 33% yield following the condition B. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.66 – 7.43 (m, 5H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 4.46 (s, 2H), 3.23 – 3.07 (m, 2H), 1.39 – 1.26 (m, 2H), 1.22 –

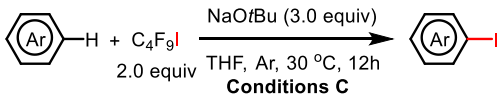
1.04 (m, 6H), 0.80 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.05, 136.13, 132.75, 132.69, 130.19, 129.29, 129.18, 127.85, 127.26, 123.04, 51.77, 49.32, 31.36, 28.14, 26.47, 22.54, 14.06. **HRMS** Calcd for $C_{19}H_{25}BrNO_2S$ [M+H$^+$]: 410.0784; Found: 410.0784.



29

Compound **29** was isolated in 32% yield following the condition B. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.75 (m, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.55 – 7.42 (m, 3H), 7.31 – 7.20 (m, 1H), 7.12 (t, J = 7.2 Hz, 1H), 7.04 – 6.93 (m, 1H), 4.42 (s, 2H), 3.25 – 3.00 (m, 2H), 1.43 – 1.27 (m, 2H), 1.23 – 1.02 (m, 6H), 0.81 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.04, 159.59, 140.15, 132.59, 130.94, 130.90, 129.57, 129.49, 129.20, 127.22, 124.52, 124.49, 123.87, 123.73, 115.42, 115.20, 48.77, 44.87, 44.82, 31.35, 28.03, 26.40, 22.54, 14.06. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.50. HRMS Calcd for $C_{19}H_{25}BrNO_2S$ [M+Na$^+$]: 372.1404; Found: 372.1406.

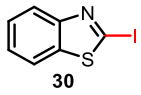
6. General procedure and substrate scope of halogen-bond-promoted reactions for C(sp^2)-H iodination



Scheme S6. Halogen-bond-promoted reactions for C(sp^2)-H iodination

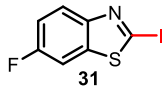
Conditions C: Heteroarene (0.2 mmol, 1.0 equiv), C_4F_9I (0.4 mmol, 2.0 equiv) and NaO*t*Bu (0.6 mmol, 3.0 equiv) were dispersed in 2 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C for 12 hours. Then, the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the desired product.

Conditions D: Heteroarene (0.2 mmol, 1.0 equiv), C_4F_9I (0.8 mmol, 4.0 equiv) and NaO*t*Bu (0.8 mmol, 4.0 equiv) were dispersed in 2 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C for 12 hours. Then, the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the desired product.



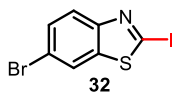
30

Compound **30** was isolated in 90% yield following the condition C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 1H), 7.88 – 7.78 (m, 1H), 7.50 – 7.34 (m, 2H).[7]



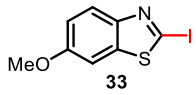
31

Compound **31** was isolated in 56% yield following the condition C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.9, 4.8 Hz, 1H), 7.52 (dd, *J* = 7.9, 2.3 Hz, 1H), 7.17 (td, *J* = 8.9, 2.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.07, 159.61, 151.15, 151.14, 140.20, 140.09, 123.63, 123.54, 115.30, 115.06, 107.10, 106.83, 104.56, 104.54. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.83. **HRMS** Calcd for C_7H_4FINS [M+H$^+$]: 279.9088; Found: 279.9080.



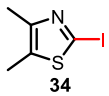
32

Compound **32** was isolated in 60% yield following the condition C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.28, 140.82, 130.07, 123.67, 123.14, 119.93, 106.16. **HRMS** Calcd for C_7H_4BrINS [M+H$^+$]: 339.8287; Found: 339.8288.



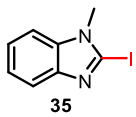
33

Compound **33** was isolated in 90% yield following the condition C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 9.0 Hz, 1H), 7.26 (d, *J* = 2.5 Hz, 1H), 7.02 (dd, *J* = 8.9, 2.4 Hz, 1H), 3.85 (s, 3H).[7]



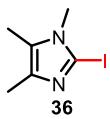
34

Compound **34** was isolated in 92% yield following the condition C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.32 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.07, 132.95, 95.09, 14.67, 11.22.[7]



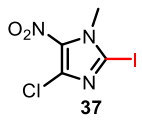
35

Compound **35** was isolated in 85% yield following the condition C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 1H), 7.34 (dd, *J* = 6.8, 1.9 Hz, 1H), 7.28 – 7.19 (m, 2H), 3.77 (s, 3H).[7]



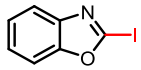
36

Compound **36** was isolated in 13% yield (Crude ^{1}H-NMR yield: 80%) following the condition C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.60 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H).[7]



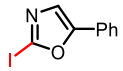
37

Compound **37** was isolated in 35% yield (Crude ^{1}H-NMR yield: 90%) following the condition C. **^{1}H NMR** (400 MHz, DMSO) δ 3.60 (s, 3H). **^{13}C NMR** (101 MHz, DMSO) δ 143.23, 120.77, 95.37, 35.71. HRMS Calcd for $C_4H_4ClIN_3O_2$ [M+H$^+$]: 287.9031; Found: 287.9035.



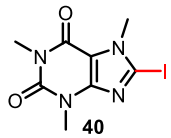
38

Compound **38** was isolated in 74% yield following the condition C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.66 (m, 1H), 7.57 – 7.48 (m, 1H), 7.37 – 7.28 (m, 2H).[7]



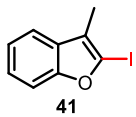
39

Compound **39** was isolated in 84% yield following the condition C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.28 (s, 1H).[7]



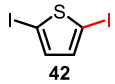
40

Compound **40** was isolated in 85% yield following the condition C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 3.56 (s, 3H), 3.39 (s, 3H).[7]



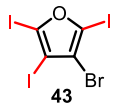
41

Compound **41** was isolated in 87% yield following the condition D. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.39 (m, 2H), 7.25 – 7.17 (m, 2H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.04, 129.04, 124.23, 123.22, 122.81, 118.68, 110.97, 97.55, 10.60. **HRMS** Calcd for C_9H_8IO [M+H$^+$]: 258.9614; Found: 258.9617.



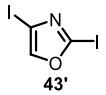
42

Compound **42** was isolated in 84% yield following the condition C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.94 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.92. **HRMS** Calcd for $C_4H_3I_2S$ [M+H$^+$]: 336.8039; Found: 336.8043.



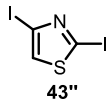
43

Compound **43** was isolated in 86% yield following the condition D. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 119.21, 102.04, 94.55, 87.80. **HRMS** Calcd for C_4HBrI_3O [M+H$^+$]: 524.6339; Found: 524.6333.



43'

Compound **43'** was isolated in 75% yield following the condition C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (s, 1H).[7]



43"

Compound **43"** was isolated in 78% yield following the condition C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, J = 1.0 Hz, 1H).[7]

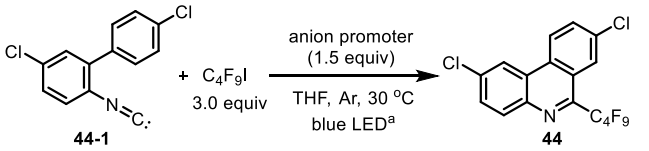
7. Evaluation of anion promoters for synthesis of compound 44 under blue LED irradiation

All screening reactions were carried out at a 0.1 mmol scale in a 4 mL glass vial (Thermo Scientific, National B7999-2) sealed with PTEF cap and stirred on bench top. 4',5-Dichloro-2-isocyano-1,1'-biphenyl **44-1** (27.7 mg, 0.1 mmol, 1.0 equiv), C_4F_9I (103.8 mg, 0.3 mmol, 3.0 equiv) and inorganic salts were dispersed in THF (1 mL) and the resulting mixture was vigorously stirred at 30 ^{o}C with blue LED (25 W) irradiation for 36 hours. After removal of the solvent *in vacuo*, the resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (20 uL) as an internal standard for ^{1}H NMR analysis. The composition of reaction mixture was analyzed based on the Ar-H peak at δ 8.55 – 8.35 (m, 3H) for compound **44**.

Procedure of phenanthridine synthesis using UV light (254 nm): **44-1** (27.7 mg, 0.1 mmol, 1.0 equiv), C_4F_9I (103.8 mg, 0.3 mmol, 3.0 equiv) and KOH (8.4 mg, 0.15 mmol,

1.5 equiv) were dispersed in 1 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C in **UV light (254 nm)** for 36 hours. Then, THF was removed under reduced pressure. The resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (20 μL) as an external standard for ^1H NMR analysis.

Procedure of phenanthridine synthesis using sunlight: **44-1** (27.7 mg, 0.1 mmol, 1.0 equiv), C_4F_9I (103.8 mg, 0.3 mmol, 3.0 equiv) and KOH (8.4 mg, 0.15 mmol, 1.5 equiv) were dispersed in 1 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C in **sunlight** for 9 hours. Then, THF was removed under reduced pressure. The resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (20 μL) as an external standard for ^1H NMR analysis.

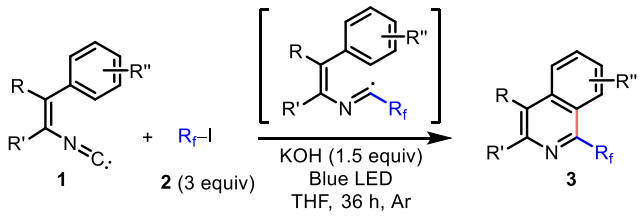


NaO*t*Bu	NaOH	NaH	Na_2CO_3	$NaNO_3$
72%	65%	53%	15%	12%
NaF	NaCl	NaBr	NaI	NaOAc
20%	15%	12%	<10%	<10%
KO*t*Bu	**KOH**	LiO*t*Bu	LiOH	CsOH
80%	95% (87%)[b] [CFL, 36 h] 95% [UV 254nm[c], 36 h] 90% [sunlight[d], 9 h]	65%	75%	64%
n-Bu_4NF	*n*-Bu_4NCl	*n*-Bu_4NBr	*n*-Bu_4NI	*n*-$Bu_4N(OH)$
81%	38%	10%	<10%	85%

Scheme S7. Reaction optimization for the halogen-bond-promoted perfluoroalkylation reaction

a) Yields are based on ^1H-NMR analysis of crude reaction mixture on a 0.1 mmol scale; b) Isolated yield on 0.2 mmol scale. c) UV (254 nm): low-pressure Hg-vapor lamp, 25 W. d) Sunlight: direct irradiation for 6 h.

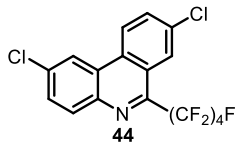
8. General procedures and substrate scope of phenanthridine and isoquinoline synthesis



Scheme S8. Halogen-bond-promoted reaction system for the synthesis of perfluoroalkylated phenanthridines and isoquinolines

Conditions E: 2-Isocyanobiaryl compound (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide (0.6 mmol, 3.0 equiv) and KOH (0.3 mmol, 1.5 equiv) were dispersed in 2 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C under irradiation of blue LED (25W) for 36 hours. Then, the mixture was concentrated in vacuo, and the residue was purified by silica gel flash chromatography to give the desired product.

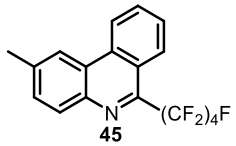
Conditions F: 2-Isocyanobiaryl compound (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide (1.2 mmol, 6.0 equiv) and KOH (0.6 mmol, 3.0 equiv) were dispersed in 1 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C under irradiation of blue LED (25W) for 36 h. Then, the mixture was concentrated in vacuo, and the residue was purified by silica gel flash chromatography to give the desired product.



44

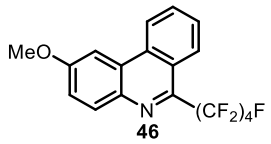
Compound **44** was isolated in 87% yield (Crude ^{1}H-NMR yield: 95%) following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 – 8.35 (m, 3H), 8.20 – 8.13 (m, 1H), 7.87 –7.83 (m, 1H), 7.76 – 7.71 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.93 (t), 140.06, 136.38, 135.22, 132.83, 132.32, 131.38, 130.48, 125.65, 125.36, 124.37, 123.90, 121.71. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.99 (t, J = 10.6 Hz, 3F), -105.07 (dd, J = 21.2, 7.8 Hz, 2F), -119.87 – -119.94 (m, 2F), -122.56 – -125.30 (m, 2F). **HRMS**

Calcd for $C_{17}H_7Cl_{12}F_9N$ [M+H$^+$]: 465.9806; Found: 465.9808. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



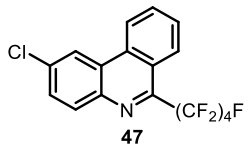
45

Compound **45** was isolated in 80% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.4 Hz, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.35 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.87 (dd, *J* = 11.3, 4.0 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.61 (dd, *J* = 8.3, 1.5 Hz, 1H), 2.65 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -81.00 (t, *J* = 10.7 Hz, 3F), -104.53 – -105.38 (m, 2F), -119.80 – -119.87 (m, 2F), -123.70 – -123.77 (m, 2F).[8b]



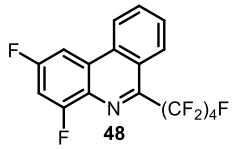
46

Compound **46** was isolated in 85% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.4 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 9.0 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.43 (dd, *J* = 9.0, 2.6 Hz, 1H), 4.06 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.98 (t, *J* = 10.0 Hz, 3F), -104.85 (t, *J* = 12.4 Hz, 2F), -119.90 (dd, *J* = 6.6, 2.9 Hz, 2F), -123.75 – -123.82 (m, 2F).[8b]



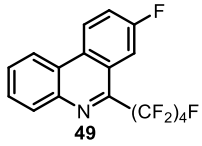
47

Compound **47** was isolated in 68% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.4 Hz, 1H), 8.58 (d, *J* = 2.1 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.7 Hz, 1H), 8.00 – 7.90 (m, 1H), 7.84 – 7.78 (m, 1H), 7.75 (dd, *J* = 8.7, 2.2 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -70.36 – -90.67 (m, 3F), -105.06 (dd, *J* = 20.6, 7.4 Hz, 2F), -115.08 – -121.77 (m, 2F), -122.27 – -129.48 (m, 2F).[8b]



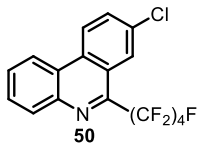
48

Compound **48** was isolated in 50% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 23.5, 8.5 Hz, 2H), 7.99 –7.93 (m, 2H), 7.88 – 7.77 (m, 1H), 7.35 – 7.20 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.70, 163.58, 161.41, 161.27, 161.20, 161.08, 158.79, 158.66, 146.32, 131.88, 129.48, 126.60, 123.51, 123.24, 105.40, 105.18, 105.12, 104.89, 103.23, 103.18, 103.00, 102.95. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -81.08 (dd, *J* = 22.4, 10.7 Hz, 3F), -102.56 – -107.69 (m, 3F), -114.43 – -117.48 (m, 1F), -119.82 (dd, *J* = 11.8, 8.2 Hz, 2F), -122.70 – -125.83 (m, 2F). **HRMS** Calcd for $C_{17}H_7F_{11}N$ [M+H$^+$]: 434.0397; Found: 434.0399. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



49

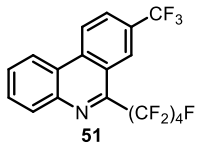
Compound **49** was isolated in 55% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 9.2, 5.4 Hz, 1H), 8.61 – 8.52 (m, 1H), 8.36 – 8.21 (m, 1H), 8.09 (d, J = 10.1 Hz, 1H), 7.92 – 7.73 (m, 2H), 7.72 – 7.53 (m, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.97 (t, *J* = 10.6 Hz, 3F), -105.64 (dd, *J* = 21.2, 7.8 Hz, 2F), -109.36 – -110.55 (m, 1F), -119.67 – -120.31 (m, 2F), -123.46 – -124.21 (m, 2F).[8b]



50

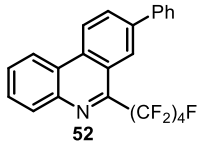
Compound **50** was isolated in 81% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.71 – 8.46 (m, 2H), 8.41 (s, 1H), 8.32 – 8.14 (m, 1H), 7.94 – 7.68 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.68 (t), 141.69, 134.37, 132.41, 131.97, 131.40,

130.01, 129.76, 125.49, 124.34, 124.29, 123.69, 121.96. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.98 (t, *J* = 10.6 Hz, 3F), -100.39 – -110.24 (m, 2F), -114.74 – -121.83 (m, 2F), -122.14 – -129.43 (m, 2F). **HRMS** Calcd for $C_{17}H_8ClF_9N$ [M+H$^+$]: 432.0196; Found: 432.0190. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



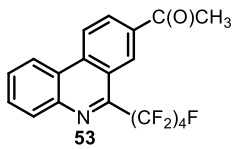
51

Compound **51** was isolated in 77% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.8 Hz, 1H), 8.74 (s, 1H), 8.67 – 8.60 (m, 1H), 8.36 – 8.26 (m, 1H), 8.12 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.92 – 7.85 (m, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.65 (s, 3F), -80.08 – -82.48 (m, 3F), -103.11 – -106.97 (m, 2F), -119.85 – -119.92 (m, 2F), -122.41 – -125.81 (m, 2F).[3i]



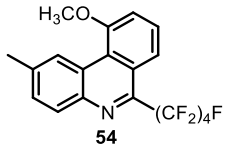
52

Compound **52** was isolated in 84% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.7 Hz, 1H), 8.66 (s, 1H), 8.61 (dd, *J* = 6.8, 2.8 Hz, 1H), 8.28 (dd, *J* = 6.0, 3.5 Hz, 1H), 8.15 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.90 – 7.77 (m, 2H), 7.76 – 7.72 (m, 2H), 7.56 (t, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.83 (t), 141.75, 140.89, 140.00, 133.04, 131.30, 130.59, 129.62, 129.36, 129.32, 128.33, 127.59, 124.74, 124.09, 123.42, 123.27, 122.12. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.93 (t, *J* = 10.8 Hz, 3F), -103.93 – -105.33 (m, 2F), -118.06 – -120.81 (m, 2F), -123.49 (d, *J* = 8.7 Hz, 2F). **HRMS** Calcd for $C_{17}H_8ClF_9N$ [M+H$^+$]: 474.0899; Found: 474.0900. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



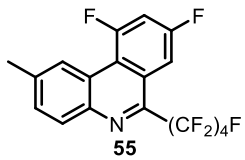
53

Compound **53** was isolated in 40% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.05 (s, 1H), 8.81 (d, *J* = 8.7 Hz, 1H), 8.67 (d, *J* = 7.9 Hz, 1H), 8.49 (dd, *J* = 8.7, 1.4 Hz, 1H), 8.31 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.89 (dd, *J* = 8.0, 1.6 Hz, 2H), 2.79 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.93, 147.11 (t), 142.58, 136.90, 135.99, 131.44, 130.66, 130.03, 129.55, 127.40 (t), 124.17, 123.35, 122.73, 122.47, 26.62. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.93 (t, *J* = 10.7 Hz, 3F), -102.41 – -107.10 (m, 2F), -119.77 – -119.83 (m, 2F), -122.33 – -126.76 (m, 2F). **HRMS** Calcd for $C_{19}H_{11}F_9NO$ [M+H$^+$]: 440.0691; Found: 440.0697. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



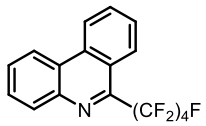
54

Compound **54** was isolated in 30% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.35 (s, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.69 (t, *J* = 8.2 Hz, 1H), 7.62 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 4.17 (s, 3H), 2.66 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.53, 140.69, 139.56, 130.76, 130.36, 128.09, 127.68, 125.08, 124.65, 124.56, 118.20, 112.01, 56.02, 22.79. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -81.06 (t, *J* = 10.8 Hz, 3F), -104.10 (t, *J* = 13.6 Hz, 2F), -119.21 (dd, *J* = 18.1, 7.8 Hz, 2F), -122.71 – -123.47 (m, 2F). **HRMS** Calcd for $C_{19}H_{13}F_9NO$ [M+H$^+$]: 442.0848; Found: 442.0845. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



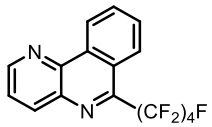
55

Compound **55** was isolated in 35% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 8.00 – 7.97 (m, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.34 (m, 1H), 2.66 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.68, 162.54, 161.82, 161.68, 160.09, 159.98, 159.33, 159.18, 144.37 (t), 141.25, 140.14, 131.33, 131.10, 126.02, 125.78, 125.07, 122.09, 120.41, 120.30, 108.23, 107.96, 107.68, 22.58. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -81.03 (t, *J* = 10.7 Hz, 3F), -101.13 – -103.72 (m, 1F), -104.05 – -106.43 (m, 2F), -106.76 – -109.47 (m, 1F), -117.20 – -121.53 (m, 2F), -121.98 – -125.87 (m, 2F). **HRMS** Calcd for $C_{18}H_9F_{11}N$ [M+H$^+$]: 448.0554; Found: 448.0554. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



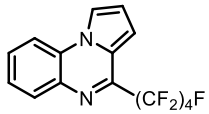
56

Compound **56** was isolated in 80% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.4 Hz, 1H), 8.61 (dd, *J* = 6.3, 3.1 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.31 – 8.25 (m, 1H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.83 – 7.73 (m, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.99 (t, *J* = 10.7 Hz, 3F), -102.58 – -106.65 (m, 2F), -119.77 – -119.84 (m, 2F), -123.65 – -123.72 (m, 2F).[8b]



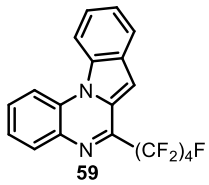
57

Compound **57** was isolated in 70% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.37 (d, *J* = 8.3 Hz, 1H), 9.11 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.55 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.47 (d, *J* = 8.5 Hz, 1H), 8.01 (t, *J* = 7.7 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.75 (dd, *J* = 8.3, 4.3 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.95 (dd, *J* = 16.7, 6.2 Hz, 3F), -104.69 – -105.95 (m, 2F), -119.34 – -120.90 (m, 2F), -123.21 – -125.04 (m, 2F).[8b]



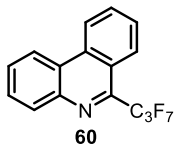
58

Compound **58** was isolated in 56% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 – 8.02 (m, 2H), 7.92 – 7.88 (m, 1H), 7.67 – 7.60 (m, 1H), 7.54 – 7.48 (m, 1H), 7.14 (d, *J* = 3.0 Hz, 1H), 6.98 (dd, *J* = 4.1, 2.8 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -79.69 – -82.52 (m, 3F), -112.89 – -114.33 (m, 2F), -121.08 – -122.88 (m, 2F), -124.64 – -126.52 (m, 2F).[8b]



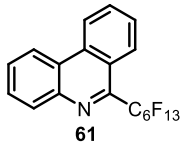
59

Compound **59** was isolated in 52% yield following the conditions E. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.4 Hz, 1H), 8.47 (d, *J* = 8.7 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.71 (m, 1H), 7.65 – 7.58 (m, 1H), 7.54 – 7.41 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -78.47 – -83.51 (m, 3F), -110.94 – -115.05 (m, 2F), -120.61 – -122.93 (m, 2F), -124.01 – -126.61 (m, 2F).[8b]



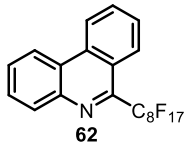
60

Compound **60** was isolated in 72% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.4 Hz, 1H), 8.65 – 8.61 (m, 1H), 8.47 (d, *J* = 8.3 Hz, 1H), 8.31 – 8.27 (m, 1H), 7.95 – 7.90 (m, 1H), 7.84 – 7.74 (m, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.48 – -79.64 (m, 3F), -105.51 – -106.41 (m, 2F), -123.26 – -124.07 (m, 2F).[8b]



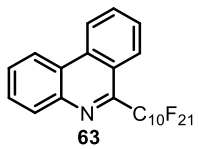
61

Compound **61** was isolated in 83% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.4 Hz, 1H), 8.65 – 8.56 (m, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.33 – 8.25 (m, 1H), 7.98 – 7.86 (m, 1H), 7.86 – 7.72 (m, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.04 – -81.63 (m, 3F), -104.48 – -105.62 (m, 2F), -118.46 – -119.35 (m, 2F), -119.92 (dd, *J* = 16.8, 6.3 Hz, 2F), -121.95 – -123.21 (m, 2F), -125.41 – -126.99 (m, 2F).[8b]



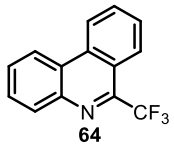
62

Compound **62** was isolated in 85% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.73 (d, J = 8.4 Hz, 1H), 8.65 – 8.60 (m, 1H), 8.47 (d, J = 8.4 Hz, 1H), 8.33 – 8.26 (m, 1H), 7.95 – 7.89 (m, 1H), 7.84 – 7.74 (m, 3H). **^{19}F NMR** (471 MHz, CDCl3) δ -80.77 (t, J = 10.8 Hz, 3F), -104.66 – -105.26 (m, 2F), -119.03 (dd, J = 17.8, 14.2 Hz, 2F), -119.75 (s, 2F), -121.04 – -122.47 (m, 4F), -122.73 (d, J = 7.0 Hz, 2F), -125.79 – -126.73 (m, 2F).[8b]



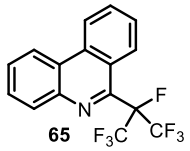
63

Compound **63** was isolated in 85% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.4 Hz, 1H), 8.67 – 8.57 (m, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.34 – 8.23 (m, 1H), 7.92 (t, *J* = 7.7 Hz, 1H), 7.85 – 7.67 (m, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.75 (dd, *J* = 53.9, 43.2 Hz, 3F), -104.31 – -105.78 (m, 2F), -119.03 (s, 2F), -119.65 (d, *J* = 100.8 Hz, 7F), -120.47 – -122.61 (m, 3F), -122.75 (s, 2F), -125.44 – -127.24(m, 2F).[8b]



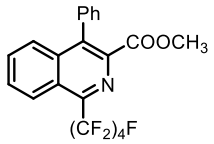
64

2-Isocyanobiaryl compound (0.2 mmol, 1.0 equiv) and KOH (0.3 mmol, 1.5 equiv) were dispersed in 2 mL of THF. The reaction vial was then purged with CF_3I for 5 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C under irradiation of blue LED (25W) for 36 hours. Then, the mixture was concentrated in vacuo, and the residue was purified by silica gel flash chromatography to give the compound **64** in 65% isolated yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.4 Hz, 1H), 8.64 – 8.59 (m, 1H), 8.43 – 8.36 (m, 1H), 8.34 – 8.26 (m, 1H), 7.98 – 7.90 (m, 1H), 7.86 – 7.74 (m, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.44 (d, *J* = 2.8 Hz, 3F).[8b]



65

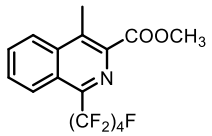
Compound **65** was isolated in 80% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.4 Hz, 1H), 8.65 – 8.60 (m, 2H), 8.27 – 8.19 (m, 1H), 7.91 (t, *J* = 7.7 Hz, 1H), 7.83 – 7.73 (m, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -72.50 (d, *J* = 6.1 Hz, 6F), -175.04 – -175.26 (m, 1F).[8b]



66

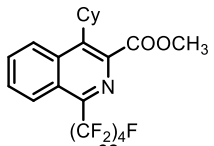
Compound **66** was isolated in 78% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.5 Hz, 1H), 7.83 – 7.70 (m, 3H), 7.57 – 7.48 (m, 3H), 7.41 – 7.31 (m, 2H), 3.71 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.61, 145.53 (t), 140.70, 137.28, 137.16, 135.03, 131.30, 129.91, 129.64, 128.73, 128.55, 127.66, 126.68, 125.09 (t), 52.69. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.93 (dd, *J* = 16.8, 5.9 Hz, 3F), -103.24 – -108.07 (m, 2F), -118.07 – -122.24 (m, 2F), -122.69 – -128.17 (m, 2F). **HRMS**

Calcd for $C_{21}H_{13}F_9NO_2$ [M+H$^+$]: 482.0797; Found: 482.0799. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



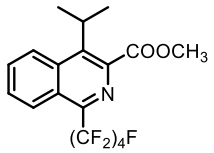
67

Compound **67** was isolated in 54% yield following the conditions F. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.6 Hz, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.81 – 7.78 (m, 1H), 4.03 (s, 3H), 2.92 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.23, 144.09, 140.48, 137.43, 133.40, 131.21, 129.76, 126.30, 125.62, 125.22, 52.99, 14.92. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.40 – -81.57 (m, 3F), -104.86 – -105.97 (m, 2F), -119.67 – -121.08 (m, 2F), -123.93 – -124.93 (m, 2F). **HRMS** Calcd for $C_{16}H_{11}F_9NO_2$ [M+H$^+$]: 420.0641; Found: 420.0643. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



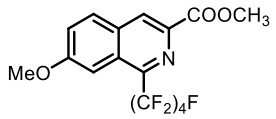
68

Compound **68** was isolated in 40% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50 – 8.42 (m, 2H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.76 – 7.71 (m, 1H), 4.02 (s, 3H), 2.13 – 1.83 (m, 8H), 1.53 – 1.37 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.59, 144.27, 142.25, 138.18, 136.60, 130.54, 128.92, 126.68, 125.83, 52.93, 31.75, 27.51, 26.18, 0.14. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.98 (t, *J* = 10.5 Hz, 3F), -103.61 – -106.65 (m, 2F), -120.18 (dd, *J* = 13.7, 6.4 Hz, 2F), -122.56 – -125.98 (m, 2F). **HRMS** Calcd for $C_{21}H_{19}F_9NO_2$ [M+H$^+$]: 488.1267; Found: 488.1260. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



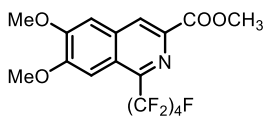
69

Compound **69** was isolated in 60% yield following the conditions F. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 9.1 Hz, 2H), 7.85 – 7.80 (m, 1H), 7.77 – 7.72 (m, 1H), 4.02 (s, 3H), 3.84 – 3.78 (m, 1H), 1.59 (d, *J* = 7.2 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.43, 144.36 (t), 141.93, 139.52, 136.28, 130.55, 128.99, 126.77, 125.94, 125.59, 53.03, 29.86, 22.07. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.99 (t, *J* = 10.5 Hz, 3F), -103.98 – -105.64 (m, 2F), -119.32 – -121.11 (m, 2F), -123.06 – -125.34 (m, 2F). **HRMS** Calcd for $C_{18}H_{15}F_9NO_2$ [M+H$^+$]: 448.0954; Found: 448.0956. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



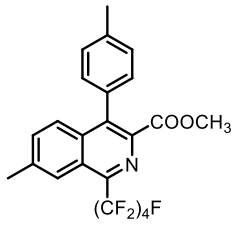
70

Compound **70** was isolated in 70% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.65 (s, 1H), 7.49 (dd, *J* = 9.0, 2.4 Hz, 1H), 4.04 (s, 3H), 3.99 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.62, 161.27, 144.51 (t), 138.43, 133.01, 130.79, 129.35, 127.26, 124.80, 103.20, 55.77, 53.05. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.48 – -81.39 (m, 3F), -106.34 – -107.16 (m, 2F), -120.03 – -121.25 (m, 2F), -124.13 – -125.37 (m, 2F). **HRMS** Calcd for $C_{18}H_{15}F_9NO_2$ [M+H$^+$]: 436.0590; Found: 436.0599. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



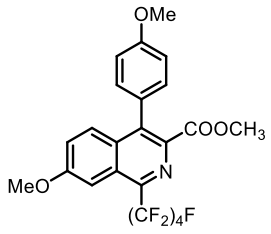
71

Compound **71** was isolated in 72% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.64 (s, 1H), 7.27 (s, 1H), 4.07 (s, 3H), 4.06 (s, 3H), 4.03 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.78, 153.64, 152.99, 143.72 (t), 139.16, 134.70, 125.90, 124.32, 106.65, 103.39, 56.44, 56.29, 53.04. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.90 (dd, *J* = 16.8, 6.3 Hz, 3F), -106.56 – -107.04 (m, 2F), -120.37 – -120.95 (m, 2F), -124.35 – -125.01 (m, 2F). **HRMS** Calcd for $C_{17}H_{13}F_9NO_4$ [M+H$^+$]: 466.0695; Found: 466.0698. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



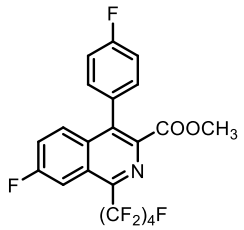
72

Compound **72** was isolated in 72% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 3.74 (s, 3H), 2.61 (s, 3H), 2.47 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.79, 144.50, 140.44, 139.87, 138.44, 137.31, 135.75, 133.42, 132.18, 129.50, 129.24, 127.52, 126.95, 123.82, 52.67, 22.48, 21.57. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.92 (dd, *J* = 16.8, 6.3 Hz,3F), -105.11 – -105.62 (m,2F), -120.23 – -120.29 (m, 2F), -123.94 – -124.62 (m,2F). **HRMS** Calcd for $C_{23}H_{17}F_9NO_2$ [M+H$^+$]: 510.1110; Found: 510.1111. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



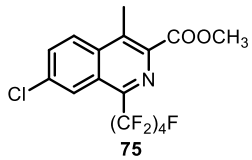
73

Compound **73** was isolated in 85% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 2H), 7.35 (dd, *J* = 9.4, 2.4 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.07 – 7.02 (m, 2H), 3.98 (s, 3H), 3.90 (s, 3H), 3.74 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.87, 160.19, 159.86, 143.24 (t), 139.19, 137.17, 133.09, 130.84, 129.28, 128.48, 127.24, 124.19, 114.00, 102.77 (t), 55.69, 55.42, 52.64. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.93 (t, *J* = 10.6 Hz, 3F), -105.29 – -107.26 (m, 2F), -119.13 – -121.37 (m, 2F), -124.34 – -124.42 (m, 2F). **HRMS** Calcd for $C_{23}H_{17}F_9NO_4$ [M+H$^+$]: 542.1008; Found: 542.1011. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



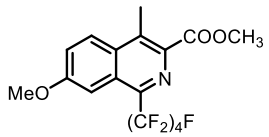
74

Compound **74** was isolated in 70% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 10.0 Hz, 1H), 7.76 (dd, *J* = 9.4, 5.6 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.33 (dd, *J* = 8.5, 5.3 Hz, 2H), 7.24 (t, *J* = 8.7 Hz, 2H), 3.75 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.21, 164.11, 163.43, 162.13, 161.41, 145.18, 140.47, 136.31, 134.55, 131.43, 131.36, 130.56, 130.53, 130.48, 127.85, 127.78, 122.33, 122.13, 116.02, 115.84, 109.53, 109.34, 52.87. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.91 (t, *J* = 10.6 Hz, 3F), -104.92 – -105.50 (m, 1F), -106.09 – -106.57 (m, 2F), -111.84 – -112.76 (m, 1F), -120.13 – -120.84 (m, 2F), -124.24 – -125.04 (m, 2F). **HRMS** Calcd for $C_{21}H_{11}F_{11}NO_2$ [M+H$^+$]: 518.0609; Found: 518.0610. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



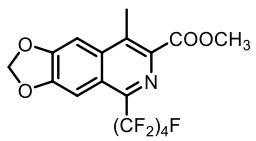
75

Compound **75** was isolated in 65% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.21 (d, *J* = 9.1 Hz, 1H), 7.82 (dd, *J* = 9.1, 1.9 Hz, 1H), 4.03 (s, 3H), 2.92 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.86, 140.73, 136.39, 135.82, 133.48, 132.30, 126.96, 126.88, 124.60, 100.13, 53.08, 14.93. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.94 (t, *J* = 10.4 Hz, 3F), -105.38 – -105.90 (m,2F), -120.29 – -120.91 (m,2F), -124.31 – -124.38 (m, 2F). **HRMS** Calcd for $C_{16}H_{10}ClF_9NO_2$ $[M+H^+]$: 454.0251; Found: 454.0257. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



76

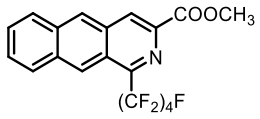
Compound **76** was isolated in 78% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 9.4 Hz, 1H), 7.63 (s, 1H), 7.49 (dd, *J* = 9.4, 2.4 Hz, 1H), 4.01 (s, 3H), 3.98 (s, 3H), 2.90 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.27, 160.11, 142.16 (t), 138.65, 133.87, 132.90, 128.15, 126.90, 124.07, 103.32, 55.66, 52.86, 14.89. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.98 (t, *J* = 10.6 Hz, 3F), -105.51 – -106.67 (m, 2F), -119.82 – -120.78 (m, 2F), -123.89 – -124.97 (m, 2F). **HRMS** Calcd for $C_{17}H_{13}F_9NO_3$ $[M+H^+]$: 450.0746; Found: 450.0749. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



77

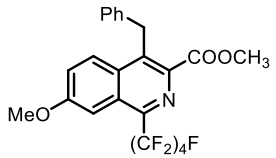
Compound **77** was isolated in 62% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.45 (s, 1H), 6.20 (s, 2H), 4.00 (s, 3H), 2.79 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.40, 151.65, 150.48, 142.04, 140.09, 136.44, 132.14, 124.31, 102.67, 101.67, 101.36, 52.91, 15.32. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -79.49 –

-82.23 (m, 3F), -105.28 – -107.34 (m, 2F), -119.94 – -121.36 (m, 2F), -123.62 – -125.92 (m, 2F). **HRMS** Calcd for $C_{17}H_{11}F_9NO_4$ [M+H$^+$]: 464.0539; Found: 464.0531. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



78

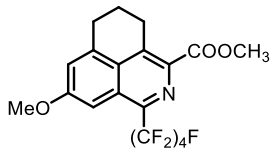
Compound **78** was isolated in 69% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.94 – 8.89 (m, 1H), 8.67 (s, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 8.01 – 7.97 (m, 1H), 7.85 – 7.74 (m, 3H), 4.06 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.07, 140.41, 139.50, 134.61, 133.80, 129.39, 129.26, 129.17, 128.94, 127.78, 127.19, 127.01, 126.60, 125.72, 53.08. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -81.30 (t, *J* = 11.2 Hz, 3F), -102.40 (t, *J* = 13.7 Hz, 2F), -115.73 – -116.77 (m, 2F), -121.21 – -122.56 (m, 2F). **HRMS** Calcd for $C_{19}H_{11}F_9NO_2$ [M+H$^+$]: 456.0641; Found: 456.0641. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



79

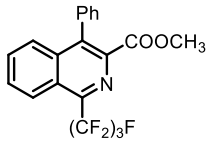
Compound **79** was isolated in 56% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.4 Hz, 1H), 7.64 (s, 1H), 7.38 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.24 (t, *J* = 7.4 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.1 Hz, 2H), 4.79 (s, 2H), 3.95 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.07, 160.07, 143.14, 139.50, 139.30, 135.20, 132.79, 128.81, 128.72, 128.34, 127.64, 126.53, 124.39, 103.42, 55.67, 52.97, 33.98. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.94 (t, *J* = 10.5 Hz, 3F), -105.69 – -106.93 (m, 2F), -119.71 – -120.84 (m, 2F), -123.49 – -125.01 (m, 2F). **HRMS** Calcd for $C_{23}H_{17}F_9NO_3$ [M+H$^+$]: 526.1059; Found: 526.1062. The ^{13}C peaks of the perfluoroalkyl

moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



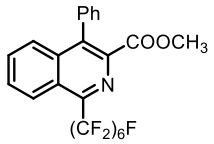
80

Compound **80** was isolated in 76% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.22 – 7.20 (m, 1H), 3.99 (s, 3H), 3.95 (s, 3H), 3.44 (t, *J* = 6.2 Hz, 2H), 3.09 (t, *J* = 6.1 Hz, 2H), 2.11 – 2.04 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.87, 160.05, 141.66 (t), 140.28, 136.98, 136.03, 130.59, 128.91, 121.69, 101.23, 55.55, 52.70, 30.76, 27.74, 22.45. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.98 (dd, *J* = 16.8, 6.3 Hz, 3F), -105.28 – -107.34 (m, 2F), -119.56 – -121.25 (m, 2F), -123.63 – -125.30 (m, 2F). **HRMS** Calcd for $C_{19}H_{15}F_9NO_3$ [M+H$^+$]: 476.0903; Found: 476.0906. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



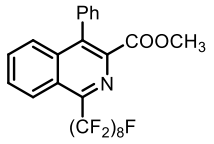
81

Compound **81** was isolated in 70% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.6 Hz, 1H), 7.82 – 7.71 (m, 3H), 7.56 – 7.50 (m, 3H), 7.39 – 7.34 (m, 2H), 3.71 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.63, 145.42 (t), 140.76, 137.28, 137.15, 135.04, 131.30, 129.89, 129.64, 128.72, 128.54, 127.65, 126.67, 125.11 (t), 52.71. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -79.43 (t, *J* = 10.1 Hz, 3F), -105.81 – -107.08 (m, 2F), -123.71 – -124.74 (m, 2F). **HRMS** Calcd for $C_{20}H_{13}F_7NO_2$ [M+H$^+$]: 432.0829; Found: 432.0823. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



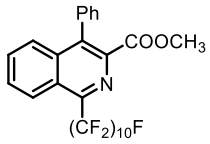
82

Compound **82** was isolated in 77% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.5 Hz, 1H), 7.84 – 7.70 (m, 3H), 7.60 – 7.50 (m, 3H), 7.41 – 7.34 (m, 2H), 3.72 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.62, 145.56 (t), 140.76, 137.31, 137.17, 135.05, 131.28, 129.91, 129.66, 128.73, 128.55, 127.66, 126.75, 125.12 (t), 52.68. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.24 – -83.38 (m, 3F), -104.04 – -107.36 (m, 2F), -117.60 – -119.94 (m, 2F), -120.42 (d, *J* = 90.4 Hz, 2F), -122.68 (s, 2F), -124.77 – -131.75 (m, 2F). **HRMS** Calcd for $C_{23}H_{13}F_{13}NO_2$ [M+H$^+$]: 582.0733; Found: 582.0736. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



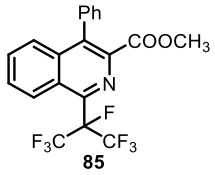
83

Compound **83** was isolated in 78% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.5 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.55 – 7.51 (m, 3H), 7.38 – 7.34 (m, 2H), 3.71 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.62, 145.58, 140.77 (t), 137.32, 137.16, 135.06, 131.28, 129.91, 129.66, 128.73, 128.55, 127.66, 126.76, 125.13, 52.67. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.81 (t, *J* = 10.7 Hz, 3F), -105.35 – -105.80 (m,2F), -119.44 (dd, *J* = 23.7, 15.2 Hz, 2F), -120.34 (s,2F), -121.78 (dd, *J* = 37.7, 17.2 Hz,4F), -122.75 (s,2F), -125.80 – -126.39 (m,2F). **HRMS** Calcd for $C_{25}H_{13}F_{17}NO_2$ [M+H$^+$]: 682.0669; Found: 682.0671. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



84

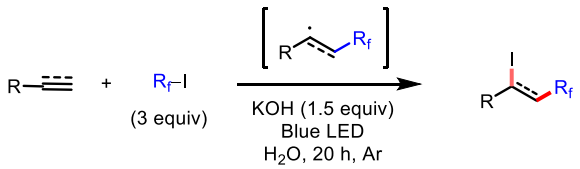
Compound **84** was isolated in 78% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.5 Hz, 1H), 7.84 – 7.70 (m, 3H), 7.59 – 7.49 (m, 3H), 7.42 – 7.34 (m, 2H), 3.72 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.63, 145.58, 140.76, 137.31, 137.17, 135.06, 131.28, 129.91, 129.66, 128.73, 128.55, 127.66, 126.76, 125.13, 52.68. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.80 (t, *J* = 10.6 Hz, 3F), -105.17 – -106.07 (m, 2F), -119.44 (s, 3F), -120.33 (s, 2F), -121.73 (dd, *J* = 94.3, 59.3 Hz, 6F), -122.75 (s, 3F), -125.64 – -126.96 (m, 2F). **HRMS** Calcd for $C_{27}H_{13}F_{21}NO_2$ [M+H$^+$]: 782.0605; Found: 782.0609. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



85

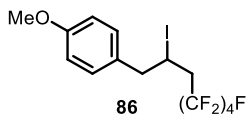
Compound **85** was isolated in 50% yield following the conditions E. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.5 Hz, 1H), 7.79 – 7.69 (m, 3H), 7.53 (dd, *J* = 8.3, 3.1 Hz, 3H), 7.36 (dd, *J* = 7.0, 2.2 Hz, 2H), 3.70 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.52, 144.73, 144.54, 140.10, 137.50, 136.40, 135.11, 131.11, 129.76, 129.73, 129.71, 128.66, 128.52, 127.84, 125.27, 125.10, 52.62. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -72.76 (d, *J* = 6.3 Hz, 6F), -175.28 – -175.89 (m, 1F). **HRMS** Calcd for $C_{20}H_{13}F_7NO_2$ [M+H$^+$]: 432.0829; Found: 432.0837. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.

9. General procedure and substrate scope for addition of perfluorobutyl iodide to alkenes and alkynes



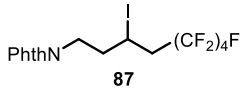
Scheme 9 Addition of perfluoroalkyl iodide to alkenes and alkynes

Conditions G: Substrate (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide (0.6 mmol, 3.0 equiv) and KOH (0.3 mmol, 1.5 equiv) were dispersed in 2 mL of H_2O. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30°C under irradiation of blue LED (25W) for 20 h. Then, the reaction mixture was extracted with EtOAc (3 x 2 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography to afford fluorination compounds.



86

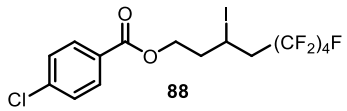
Compound **86** was isolated in 66% yield following the conditions G. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 9.2 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 4.54 – 4.35 (m, 1H), 3.81 (s, 3H), 3.27 – 3.11 (m, 2H), 3.00 – 2.52 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.96, 130.79, 130.18, 114.13, 55.37, 46.39, 46.37, 40.65 (t), 20.27. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.57 – -81.63 (m, 3F), -111.57 – -114.63 (m, 2F), -124.56 (d, *J* = 10.0 Hz, 2F), -125.65 – -126.35 (m, 2F). **HRMS** Calcd for $C_{14}H_{13}F_9IO$ [M+H$^+$]: 494.9862; Found: 494.9860. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



87

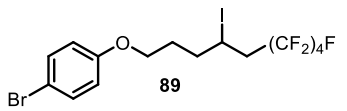
Compound **87** was isolated in 85% yield following the conditions G. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.33 – 4.27 (m, 1H), 3.95 – 3.79 (m, 2H), 3.03 – 2.79 (m, 2H), 2.34 – 2.19 (m, 2H). **^{13}C NMR**

(126 MHz, $CDCl_3$) δ 168.28, 134.27, 132.09, 123.55, 41.63 (t), 38.83, 38.43, 14.62. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.03 – -81.92 (m, 3F), -111.02 – -112.47 (m, 1F), -113.56 – -116.40 (m, 1F), -124.54 (d, *J* = 10.5 Hz, 2F), -125.37 – -127.69 (m, 2F). **HRMS** Calcd for $C_{16}H_{12}F_9INO_2$ [M+H$^+$]: 547.9764; Found: 547.9767. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



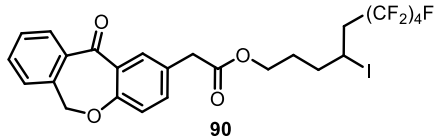
88

Compound **88** was isolated in 81% yield following the conditions G. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 – 7.91 (m, 2H), 7.45 – 7.38 (m, 2H), 4.60 – 4.54 (m, 1H), 4.51 – 4.39 (m, 2H), 3.11 – 2.78 (m, 2H), 2.39 – 2.32 (m, 1H), 2.28 – 2.18 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.51, 139.84, 131.08, 128.96, 128.34, 64.96, 41.98 (t), 39.01 (d), 15.00. **^{13}C NMR** (126 MHz, $CDCl_3$) (108.32 – 119.91, m) are signal peaks of perfloro-substituted carbons (-$CF_2CF_2CF_2CF_3$). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.23 – -81.85 (m,3F), -110.12 – -112.48 (m,1F), -113.66 – -116.02 (m,1F), -124.48 (dd, *J* = 10.0, 3.7 Hz,2F), -125.40 – -127.28 (m,2F). **HRMS** Calcd for $C_{15}H_{12}ClF_9IO_2$ [M+H$^+$]: 556.9421; Found: 556.9420.



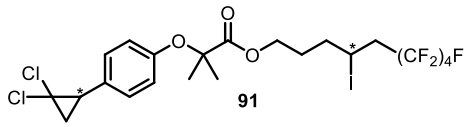
89

Compound **89** was isolated in 79% yield following the conditions G. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 6.79 – 6.75 (m, 2H), 4.43 – 4.36 (m, 1H), 3.97 (t, *J* = 5.6 Hz, 2H), 3.02 – 2.75 (m, 2H), 2.11 – 1.88 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.03, 132.43, 116.41, 113.16, 66.94, 41.80, 37.16, 29.59, 19.82. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.26 – -81.97 (m, 3F), -110.75 – -113.06 (m, 1F), -113.87 – -116.36 (m, 1F), -123.87 – -125.02 (m, 2F), -125.49 – -127.16 (m, 2F). **HRMS** Calcd for $C_{15}H_{14}BrF_9IO$ [M+H$^+$]: 586.9124; Found: 586.9130. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



90

Compound **90** was isolated in 73% yield following the conditions G. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.1 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.55 (dd, *J* = 10.7, 4.1 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.18 (s, 2H), 4.35 – 4.27 (m, 1H), 4.16 (td, *J* = 6.3, 1.8 Hz, 2H), 3.64 (s, 2H), 2.98 – 2.70 (m, 2H), 1.95 – 1.74 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 190.89, 171.41, 160.63, 140.53, 136.39, 135.68, 132.90, 132.56, 129.61, 129.36, 127.93, 127.80, 125.31, 121.21, 73.75, 63.73, 41.64, 40.34, 36.93, 28.99. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -81.01 (s, 3F), -110.65 – -112.77 (m, 1F), -113.83 – -115.47 (m, 1F), -123.79 – -125.16 (m, 2F), -125.27 – -127.43 (m, 2F). **HRMS** Calcd for $C_{25}H_{21}F_9IO_4$ [M+H$^+$]: 683.0335; Found: 683.0338. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.

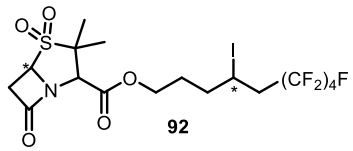


91

Compound **91** was isolated in 85% yield following the conditions G (dr = 1:1).

The dr ratio of compound **91** is determined by ^{19}F NMR (see ^{19}F NMR analysis).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 4.30-4.20 (m, 3H), 2.93 – 2.79 (m, 2H), 2.75 – 2.60 (m, 1H), 1.95 – 1.85 (m, 2H), 1.79 – 1.69 (m, 4H), 1.66 – 1.55 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.25, 155.11, 155.10, 129.78, 128.22, 128.19, 118.47, 118.43, 79.22, 64.15, 64.14, 41.60, 36.73, 34.91, 28.91, 25.90, 25.63, 25.57, 25.44, 25.39, 19.32. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.75 – -81.41 (m, 3F), -111.31 – -113.11 (m, 1F), -113.89 – -115.96 (m, 1F), -124.52 (s, 2F), -125.64 – -126.26 (m, 2F). **HRMS** Calcd for $C_{22}H_{23}Cl_2F_9IO_3$ [M+H$^+$]: 702.9920; Found: 702.9931. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.

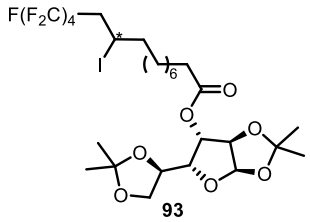


92

Compound **92** isolated in 60% yield following the conditions G (dr = 1:1).

The dr ratio of compound **92** is determined by ^{1}H NMR (see ^{1}H NMR analysis).

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.66 – 4.62 (m, 1H), 4.41 (s, 1H), 4.37 (dd, J = 8.6, 4.0 Hz, 1H), 4.29 (t, J = 6.1 Hz, 2H), 3.49 (dd, J = 5.4, 3.2 Hz, 2H), 3.06 – 2.75 (m, 2H), 2.05 – 1.85 (m, 3H), 1.64 (s, 3H), 1.45 (d, J = 2.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.78, 167.06, 65.27, 65.21, 63.43, 62.81, 61.28, 61.27, 38.50, 38.49, 36.73, 36.64, 31.58, 30.35, 29.84, 28.95, 28.92, 20.52, 19.24, 18.99, 18.75. **^{19}F NMR** (471 MHz, CDCl3) δ -80.20 – -81.92 (m, 3F), -109.68 – -112.83 (m, 1F), -114.88 (m, 1F), -123.14 – -124.98 (m, 2F), -125.36 – -128.12 (m, 2F). **HRMS** Calcd for $C_{17}H_{20}F_9INO_5S$ [M+H$^+$]: 647.9958; Found: 647.9950. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



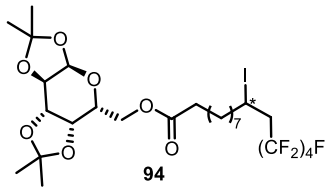
93

Compound **93** was isolated in 78% yield following the conditions G (dr = 1:1).

The dr ratio of compound **93** is determined by ^{1}H NMR and HPLC (see ^{1}H NMR and HPLC analysis).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (d, *J* = 3.7 Hz, 1H), 5.26 (s, 1H), 4.47 (d, *J* = 3.7 Hz, 1H), 4.35 – 4.29 (m, 1H), 4.22 – 4.18 (m, 2H), 4.10 – 4.06 (m, 1H), 4.03 – 3.99 (m, 1H), 2.98 – 2.68 (m, 2H), 2.38 – 2.30 (m, 2H), 1.86 – 1.71 (m, 2H), 1.66 – 1.62 (m, 2H), 1.46 (d, *J* = 56.8 Hz, 9H), 1.31 (t, *J* = 6.7 Hz, 13H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.45, 112.44, 109.46, 105.22, 83.57, 80.05, 76.01, 72.61, 67.45, 41.75 (t), 40.44, 34.38, 29.67, 29.30, 29.26, 29.12, 28.58, 26.95, 26.89, 26.35, 25.43, 24.98, 20.86. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.74 – -81.40 (m, 3F), -111.47 – -112.88 (m, 1F), -113.65

– -115.78 (m, 1F), -124.29 – -124.84 (m, 2F), -125.92 (m, 2F). **HRMS** Calcd for $C_{27}H_{37}F_9IO_7$ [M+H$^+$]: 771.1435; Found: 771.1437. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.

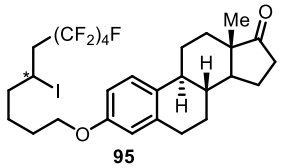


94

Compound **94** was isolated in 87% yield following the conditions G (dr = 1:1).

The dr ratio of compound **94** is determined by ^{1}H NMR (see ^{1}H NMR analysis).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.51 (d, *J* = 5.0 Hz, 1H), 4.59 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.32 – 4.27 (m, 3H), 4.21 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.14 (dd, *J* = 11.6, 7.8 Hz, 1H), 4.02 – 3.98 (m, 1H), 2.96 – 2.68 (m, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 1.84 – 1.69 (m, 2H), 1.59 (dd, *J* = 14.4, 7.1 Hz, 2H), 1.45 (d, *J* = 27.9 Hz, 7H), 1.33 – 1.26 (m, 15H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.77, 173.73, 109.73, 109.71, 108.82, 108.80, 96.42, 71.22, 70.84, 70.58, 66.16, 63.35, 41.86, 41.69, 41.53, 40.43, 34.26, 34.25, 29.79, 29.62, 29.23, 29.08, 28.53, 26.10, 26.08, 26.03, 26.02, 25.03, 24.57, 24.55, 20.70. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.59 – -81.74 (m, 3F), -112.09 (dd, *J* = 272.8, 33.6 Hz, 1F), -114.01 – -116.01 (m, 1F), -124.64 (s, 2F), -125.54 – -126.64 (m, 2F). **HRMS** Calcd for $C_{29}H_{45}F_9IO_7$ [M+H$^+$]: 803.2061; Found: 803.2059. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



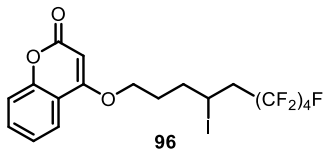
95

Compound **95** was isolated in 64% yield following the conditions G (dr = 1:1).

The dr ratio of compound **95** is determined by ^{1}H NMR (see ^{1}H NMR analysis).

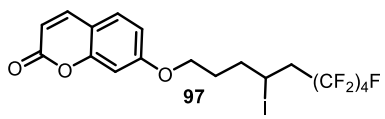
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 1H), 6.71 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.65 (d, *J* = 2.6 Hz, 1H), 4.38 – 4.32 (m, 1H), 3.96 (t, *J* = 6.1 Hz, 2H), 3.01 – 2.74 (m,

4H), 2.50 (dd, *J* = 19.0, 8.6 Hz, 1H), 2.42 – 2.37 (m, 1H), 2.29 – 2.22 (m, 1H), 2.19 – 1.71 (m, 10H), 1.63 – 1.46 (m, 6H), 0.91 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.08, 137.89, 132.23, 126.46, 114.73, 112.24, 67.54, 50.57, 48.15, 44.13, 41.89, 41.73, 41.56, 40.16, 38.53, 36.01, 31.74, 29.78, 28.38, 26.70, 26.62, 26.07, 21.72, 20.35, 13.99. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.57 – -81.44 (m, 3F), -111.94 (dd, *J* = 271.5, 42.6 Hz, 1F), -114.73 (dd, *J* = 272.7, 36.6 Hz, 1F), -124.52 (d, *J* = 5.1 Hz, 2F), -125.27 – -127.51 (m, 2F). **HRMS** Calcd for $C_{28}H_{33}F_9IO_2$ [M+H$^+$]: 699.1376; Found: 699.1379. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



96

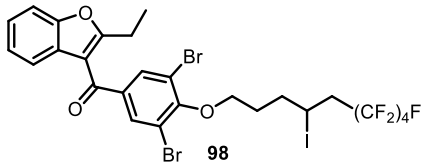
Compound **96** was isolated in 78% yield following the conditions G. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.34 – 7.27 (m, 2H), 5.67 (s, 1H), 4.46 – 4.40 (m, 1H), 4.19 (t, *J* = 5.6 Hz, 2H), 3.07 – 2.78 (m, 2H), 2.26 – 2.05 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.57, 162.94, 153.47, 132.62, 124.07, 122.97, 116.96, 115.69, 90.78, 68.10, 41.71 (t), 36.76, 28.93, 19.26. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.57 – -81.44 (m, 3F), -110.81 – -112.44 (m, 1F), -113.84 – -115.98 (m, 1F), -124.45 (dd, *J* = 9.9, 4.0 Hz, 2F), -125.49 – -126.60 (m, 2F). **HRMS** Calcd for $C_{18}H_{15}F_9IO_3$ [M+H$^+$]: 576.9917; Found: 576.9921. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



97

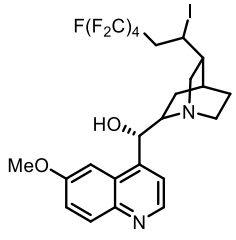
Compound **97** was isolated in 71% yield following the conditions G. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 9.5 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.79 (d, *J* = 2.3 Hz, 1H), 6.24 (d, *J* = 9.5 Hz, 1H), 4.43 – 4.36 (m, 1H), 4.10 – 4.04 (m, 2H), 3.03 – 2.75 (m, 2H), 2.14 – 1.93 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$)

δ 162.09, 161.31, 156.01, 143.50, 128.93, 113.35, 113.03, 112.81, 101.48, 67.33, 41.78 (t), 37.04, 29.43, 19.59. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.62 – -81.42 (m, 3F), -111.82 (dd, *J* = 276.1, 40.1 Hz, 1F), -113.75 – -115.94 (m, 1F), -124.51 (d, *J* = 10.0 Hz, 2F), -125.51 – -126.32 (m, 2F). **HRMS** Calcd for $C_{18}H_{15}F_9IO_3$ [M+H$^+$]: 576.9917; Found: 576.9921. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



98

Compound **98** was isolated in 71% yield following the conditions G. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.32 (dd, *J* = 8.1, 7.4 Hz, 1H), 7.24 (d, *J* = 7.4 Hz, 1H), 4.52 – 4.44 (m, 1H), 4.21 – 4.12 (m, 2H), 3.05 – 2.82 (m, 4H), 2.27 – 2.02 (m, 4H), 1.36 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 188.15, 167.09, 156.77, 153.85, 137.40, 133.78, 126.53, 124.87, 124.02, 121.16, 118.72, 115.48, 111.30, 72.32, 41.88, 37.12, 30.61, 22.18, 20.04, 12.32. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.49 – -81.55 (m, 3F), -111.19 – -112.44 (m, 1F), -113.83 – -115.30 (m, 1F), -123.85 – -124.74 (m, 2F), -125.08 – -126.56 (m, 2F). **HRMS** Calcd for $C_{26}H_{21}Br_2F_9IO_3$ [M+H$^+$]: 836.8753; Found: 836.8756. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.

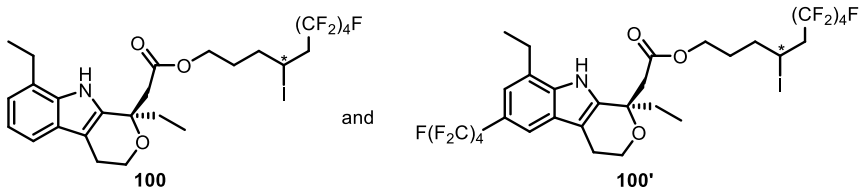


99

Compound **99** was isolated in 70% yield following the conditions G (dr = 1:1). The spectra data are consistent with those reported in literature.[8b]

The dr ratio of compound **99** is determined by ^{1}H NMR (see ^{1}H NMR analysis).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 3.8 Hz, 1H), 8.00 (d, J = 9.1 Hz, 1H), 7.54 (d, J = 3.8 Hz, 1H), 7.44-7.32 (m, 1H), 5.65 (s, 1H), 4.11-4.02 (m, 1H), 4.01-3.90 (m, 3H), 3.59 (s, 1H), 3.30-3.09 (m, 2H), 3.08-2.78 (m, 2H), 2.70 (d, J = 11.5 Hz, 1H), 2.59 (d, J = 10.1 Hz, 1H), 2.14 (s, 2H), 1.88 (s, 2H), 1.53 (s, 1H), 1.44-1.24 (m, 2H).



Compound **100** was isolated in 40% yield and compound **100'** was isolated in 32% yield following the conditions G.

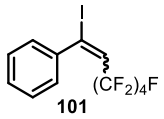
Compound **100** (dr = 1:1): The dr ratio of compound **100** is determined by ^{1}H NMR (see ^{1}H NMR analysis).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (s, 0.5H), 8.98 (d, *J* = 7.2 Hz, 0.5H), 7.37 (d, *J* = 7.7 Hz, 0.5H), 7.32 (d, *J* = 7.7 Hz, 0.5H), 7.22 – 6.96 (m, 2H), 4.35 – 4.29 (m, 1H), 4.25 – 4.20 (m, 1H), 4.17 – 4.11 (m, 1H), 4.08 – 4.02 (m, 1H), 3.98 – 3.90 (m, 1H), 2.98 – 2.73 (m, 8H), 2.17 (td, *J* = 14.1, 7.0 Hz, 1H), 2.02 (dt, *J* = 14.6, 7.4 Hz, 1H), 1.91 – 1.74 (m, 4H), 1.42 – 1.37 (m, 3H), 0.84 (dt, *J* = 6.6, 3.6 Hz, 3H).[8b]

Compound **100'** (dr = 1:1): The dr ratio of compound **100'** is determined by ^{19}F NMR and HPLC (see ^{19}F NMR and HPLC analysis).

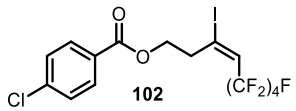
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 4.34 (dd, *J* = 8.2, 4.5 Hz, 1H), 4.24 (dd, *J* = 7.5, 3.8 Hz, 1H), 4.16 (dd, *J* = 11.2, 6.0 Hz, 1H), 4.02 (dd, *J* = 10.7, 5.7 Hz, 1H), 3.92 (dd, *J* = 7.4, 4.2 Hz, 1H), 3.12 – 2.74 (m, 8H), 2.23 – 2.13 (m, 1H), 2.03 – 1.77 (m, 5H), 1.40 (t, *J* = 7.6 Hz, 3H), 0.83 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.35, 138.62, 135.40, 130.95, 123.51, 120.81, 119.37, 117.41, 114.21, 108.06, 74.48, 64.00, 63.89, 61.16, 43.17, 43.15, 41.76, 36.84, 36.79, 32.09, 31.59, 30.91, 30.36, 29.86, 29.52, 28.97, 28.93, 24.72, 24.19, 22.85, 19.35, 19.28, 14.26, 13.40, 7.59, 1.18, 0.13. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.21 – -82.05 (m, 6F), -102.12 – -105.20 (m, 2F), -110.83 – -115.89 (m, 2F), -120.24

– -121.50 (m, 2F), -124.51 (d, J = 9.8 Hz, 2F), -125.07 – -127.30 (m, 4F). **HRMS** Calcd for $C_{30}H_{29}F_{18}INO_3$ [M+H$^+$]: 920.0899; Found: 920.0900. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



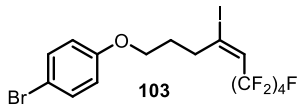
101

Compound **101** was isolated in 70% yield following the conditions G (E:Z = 3:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 – 7.27 (m, 5H), 6.56 (dt, J = 40.0, 13.4 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 141.46, 130.36, 129.44, 128.69, 128.37, 128.15, 127.22, 127.05, 126.99, 126.97, 126.87, 124.12. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.31 – -81.46 (m, 3F), -104.35 – -106.41 (m, 2F), -123.81 (dd, J = 19.4, 9.7 Hz, 2F), -125.38 – -126.30 (m, 2F). **HRMS** Calcd for $C_{12}H_7F_9I$ [M+H$^+$]: 448.9443; Found: 448.9441. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



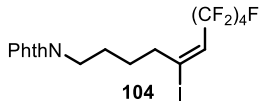
102

Compound **102** was isolated in 85% yield following the conditions G. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.43 – 7.39 (m, 2H), 6.52 (t, J = 14.3 Hz, 1H), 4.53 (t, J = 6.1 Hz, 2H), 3.14 (t, J = 5.8 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.50, 139.82, 131.16, 129.42, 128.89, 128.28, 116.11, 63.54, 40.04. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.40 – -81.70 (m, 3F), -105.49 (dd, J = 29.5, 14.5 Hz, 2F), -124.07 (dd, J = 20.0, 9.8 Hz, 2F), -125.07 – -126.94 (m, 2F). **HRMS** Calcd for $C_{15}H_{10}ClF_9IO_2$ [M+H$^+$]: 554.9265; Found: 554.9265. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



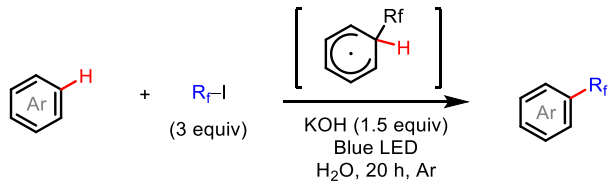
103

Compound **103** was isolated in 68% yield following the conditions G. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 6.78 – 6.74 (m, 2H), 6.39 (t, *J* = 14.4 Hz, 1H), 3.96 (t, *J* = 6.1 Hz, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.12 – 2.04 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.93, 132.40, 127.45 (t), 121.21, 116.37, 113.17, 66.37, 38.11, 29.82. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.30 – -81.60 (m, 3F), -105.78 (dd, *J* = 29.8, 14.7 Hz, 2F), -124.13 (dd, *J* = 19.9, 9.8 Hz, 2F), -125.45 – -126.34 (m, 2F). **HRMS** Calcd for $C_{15}H_{12}BrF_9IO$ [M+H$^+$]: 584.8967; Found: 584.8969. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.



Compound **104** was isolated in 75% yield following the conditions G. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.72 – 7.68 (m, 2H), 6.32 (t, *J* = 14.4 Hz, 1H), 3.70 (t, *J* = 7.0 Hz, 2H), 2.66 (t, *J* = 7.0 Hz, 2H), 1.73 – 1.61 (m, 4H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.35 – -81.74 (m, 3F), -104.62 – -106.40 (m, 2F), -123.85 – -124.74 (m, 2F), -125.30 – -126.61 (m, 2F).[8b]

10. General procedure and substrate scope for C-H perfluorobutylation of electron-rich arenes and heteroarenes

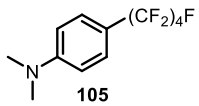


Scheme 10 C–H perfluoroalkylation of aniline and heteroarenes

Conditions H: Substrate (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide (0.6 mmol, 3.0 equiv) and KOH (0.3 mmol, 1.5 equiv) were dispersed in 2 mL of H_2O. The reaction vial was purged with Ar for 1 min then sealed with PTEF cap. The reaction mixture was vigorously stirred at 30°C under irradiation of blue LED (25W) for 20 h. Then, the

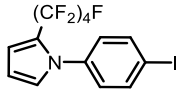
mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the desired product.

Conditions I: Substrate (0.2 mmol, 1.0 equiv), perfluoroalkyl iodide (0.6 mmol, 3.0 equiv) and KOH (0.3 mmol, 1.5 equiv) were dispersed in 2 mL of CH_2Cl_2. The reaction vial was purged with Ar for 1 min then sealed with PTEF cap. The reaction mixture was vigorously stirred at 30°C under irradiation of blue LED (25W) for 20 h. Then, the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the desired product.



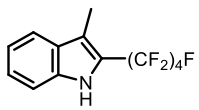
105

Compound **105** was isolated in 66% yield following the conditions H. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.0 Hz, 2H), 6.67 (d, *J* = 9.3 Hz, 2H), 3.12 (s, 6H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.08 – -81.95 (m, 3F), -107.18 – -108.84 (m, 1F), -110.27 (dd, *J* = 16.4, 13.8 Hz, 1F), -121.55 – -123.47 (m, 2F), -124.96 – -127.22 (m, 2F).[8b]



106

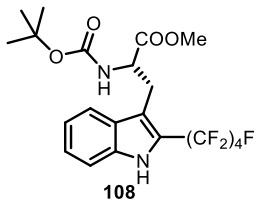
Compound **106** was isolated in 57% yield following the conditions H. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 – 7.71 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.89 – 6.81 (m, 1H), 6.75 (d, *J* = 2.8 Hz, 1H), 6.39 – 6.30 (m, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -78.86 – -82.87 (m, 3F), -99.93 – -102.66 (m, 2F), -121.46 (d, *J* = 9.7 Hz, 2F), -125.86 (dd, *J* = 15.8, 11.3 Hz, 2F).[8b]



107

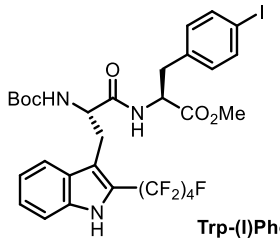
Compound **107** was isolated in 54% yield following the conditions H. **^{1}H NMR** (500

MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 2.45 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.66 – -81.46 (m, 3F), -108.36 – -109.16 (m, 2F), -122.25 – -123.45 (m, 2F), -125.53 – -126.44 (m, 2F).



108

Compound **108** was isolated in 60% yield following the conditions I. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 5.13 (d, *J* = 8.3 Hz, 1H), 4.66 (dd, *J* = 14.9, 7.1 Hz, 1H), 3.64 (s, 3H), 3.37 – 3.25 (m, 2H), 1.36 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.55, 155.07, 136.21, 127.69, 125.37, 121.10, 120.54, 115.61, 111.85, 80.00, 54.23, 52.39, 29.85, 28.31, 28.07. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -80.31 – -81.74 (m, 3F), -105.29 – -109.79 (m, 2F), -122.76 (dd, *J* = 18.4, 7.9 Hz, 2F), -124.54 – -127.41 (m, 2F). **HRMS** Calcd for $C_{21}H_{22}F_9N_2O_4$ [M+H$^+$]: 537.1430; Found: 537.1436. The ^{13}C peaks of the perfluoroalkyl moiety is not visible due to ^{19}F-^{13}C coupling and are not reported.

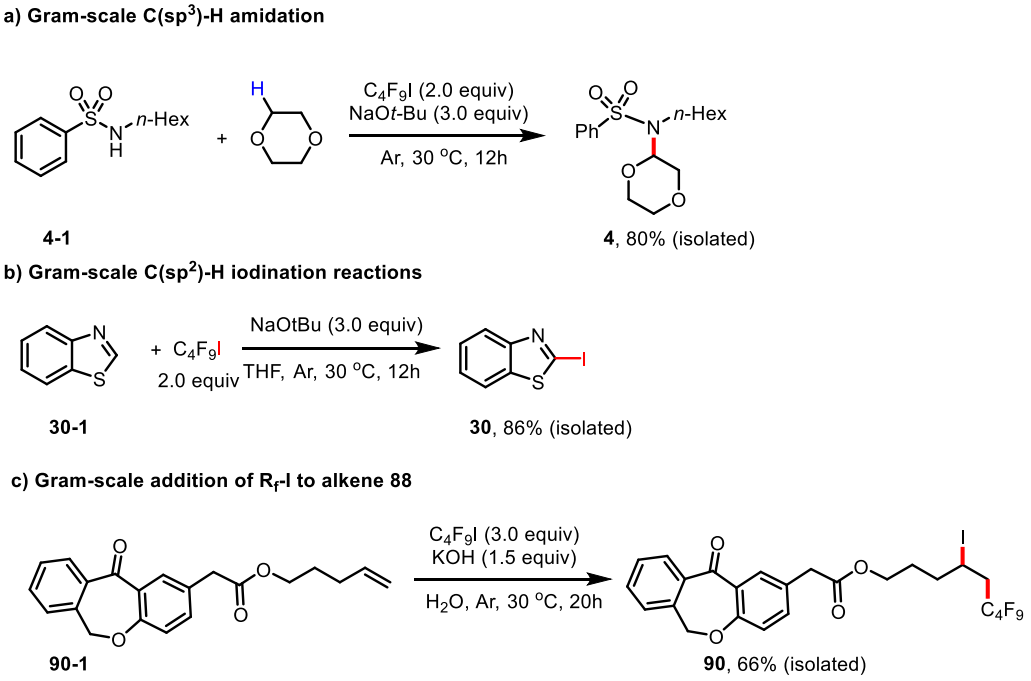


Trp-(I)Phe 109

Compound **109** was isolated in 65% yield following the conditions I. The spectra data are consistent with those reported in literature.[8b] **^{1}H NMR** (400 MHz, CDCl3) δ 8.51 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 2H), 6.08 (d, *J* = 6.7 Hz, 1H), 5.16 (s, 1H), 4.67 (q, *J* = 12.2, 1H), 4.50-4.30 (m, 1H), 3.58 (s, 3H), 3.28 (d, *J* = 5.2 Hz, 2H), 3.06-2.83 (m, 2H), 1.37 (s, 9H). **^{19}F NMR** (376 MHz, CDCl3) δ -79.81 – - 81.92 (m, 3F), -105.42 – -109.99 (m, 2F), -122.70 (d, *J* = 10.3 Hz, 2F), -124.60 – -

127.32 (m, 2F).[8b]

11. Gram-scale C(sp^3)-H amidation, C(sp^2)-H iodination and perfluoroalkylation reactions



Scheme S11. Gram-scale C(sp^3)-H amidation, C(sp^2)-H iodination and perfluoroalkylation reactions

Gram-scale C(sp^3)-H amidation: Compound **4-1** (10.0 mmol, 1.0 equiv), C_4F_9I (20.0 mmol, 2.0 equiv) and NaO*t*Bu (30.0 mmol, 3.0 equiv) were dispersed in 100 mL of ethers. The reaction vial was then purged with Ar for 5 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C for 12 hours. Then, the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the desired product **4** in 80% isolated yield.

Gram-scale C(sp^2)-H iodination: Compound **30-1** (10.0 mmol, 1.0 equiv), C_4F_9I (20.0 mmol, 2.0 equiv) and NaO*t*Bu (30.0 mmol, 3.0 equiv) were dispersed in 100 mL of THF. The reaction vial was then purged with Ar for 5 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C for 12 hours. Then, the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash

chromatography to give the desired product **30** in 86% isolated yield.

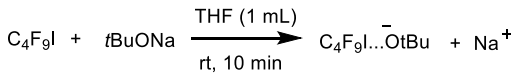
Gram-scale perfluoroalkylation reactions: Compound **90-1** (10.0 mmol, 1.0 equiv), perfluoroalkyl iodide (30.0 mmol, 3.0 equiv) and KOH (15.0 mmol, 1.5 equiv) were dispersed in 100 mL of H_2O. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30°C under irradiation of blue LED (25W) for 20 h. Then, the reaction mixture was extracted with EtOAc (3 x 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography to afford fluorination compound **90** in 66 % isolated yield.

12. Mechanistic studies

12.1 Titration experiment of C_4F_9I with *t*BuONa[8]

^{19}F NMR spectra of nine samples of mixtures of C_4F_9I and *t*BuONa in THF were recorded at 298 K. Fluorobenzene ($\delta_{CF3\text{-}Ph}$ = -63.72) was used as internal standard.

The formation of a halogen bonding complex between NaO*t*Bu and C_4F_9I is supported by ^{19}F NMR titration experiments. The resonance corresponding to the F of the CF_2I group is shifted to the upfield region when NaO*t*Bu was added to the THF solution of C_4F_9I (Table S2 and Scheme S12).

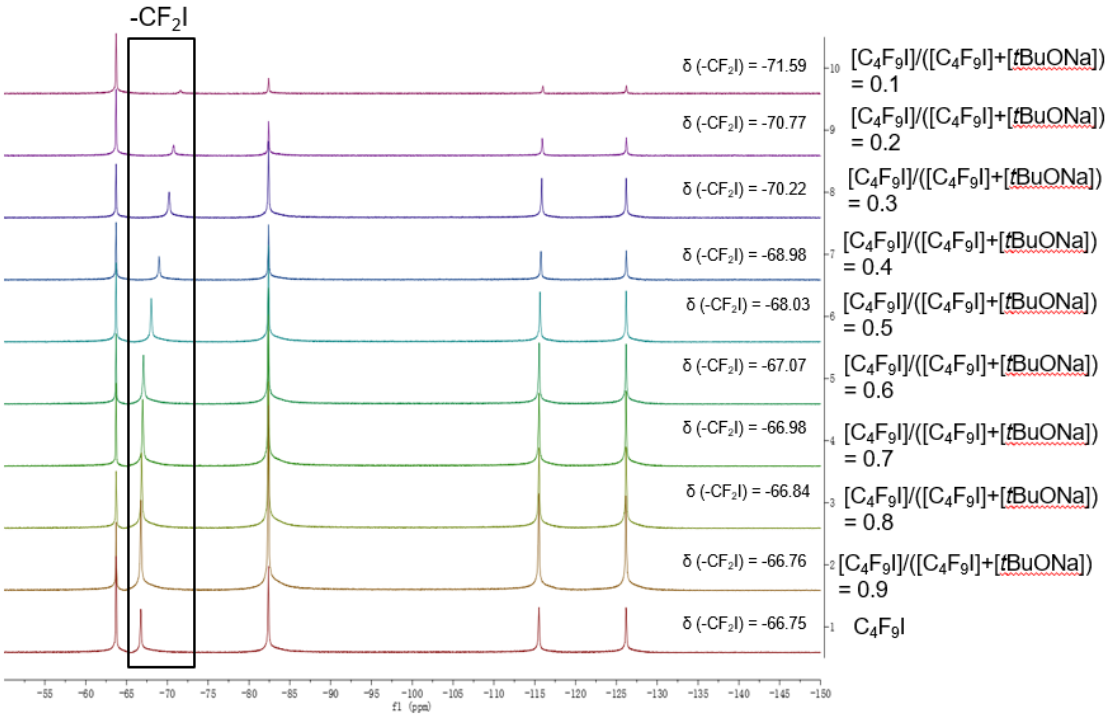


[C_4F_9I] + [*t*BuONa] = 0.25 M

[C_4F_9I]/([C_4F_9I]+[tBuONa])	△δ
0.1	4.84
0.2	4.02
0.3	3.47
0.4	2.23
0.5	1.28
0.6	0.32
0.7	0.23
0.8	0.09

0.9	0.01

Table S2. The ^{19}F-NMR signals for the mixture of C_4F_9I with NaO*t*Bu shifted downfield when the ratio of C_4F_9I to NaO*t*Bu increased

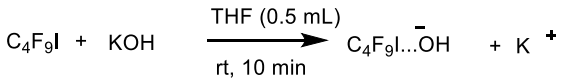


Scheme S12. The ^{19}F-NMR signals for the mixture of C_4F_9I with NaO*t*Bu shifted downfield when the ratio of C_4F_9I to NaO*t*Bu increased

12.2Titration experiment of C_4F_9I with KOH[8]

^{19}F NMR spectra of seven samples of mixtures of C_4F_9I and KOH in THF were recorded at 298 K. Fluorobenzene ($\delta_{F\text{-}Ph} = -113.07$) was used as internal standard.

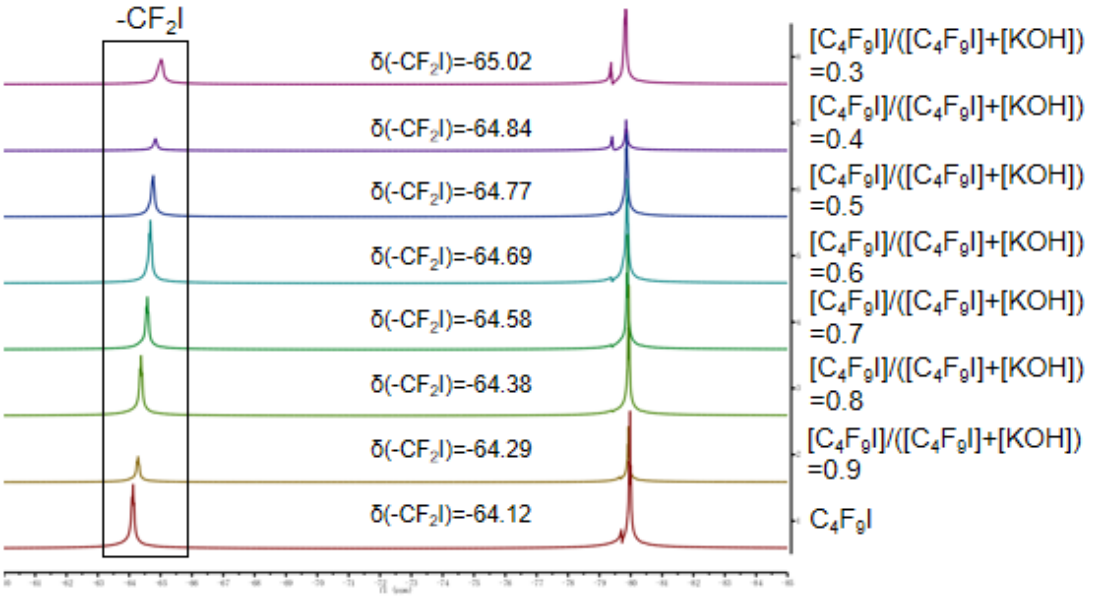
The formation of a halogen bonding complex between KOH and C_4F_9I is supported by ^{19}F NMR titration experiments. The resonance corresponding to the F of the CF_2I group is shifted to the upfield region when KOH was added to the THF solution of C_4F_9I (Table S3 and Scheme S9).



$[C_4F_9I] + [KOH] = 0.5$ M

$[C_4F_9I] / ([C_4F_9I]+[KOH])$	$\triangle\delta$ (ppm)
0.3	0.90
0.4	0.72
0.5	0.65
0.6	0.57
0.7	0.46
0.8	0.26
0.9	0.17

Table S3. The ^{19}F NMR signals for the mixture of C_4F_9I with KOH shifted downfield when the ratio of C_4F_9I to KOH increased

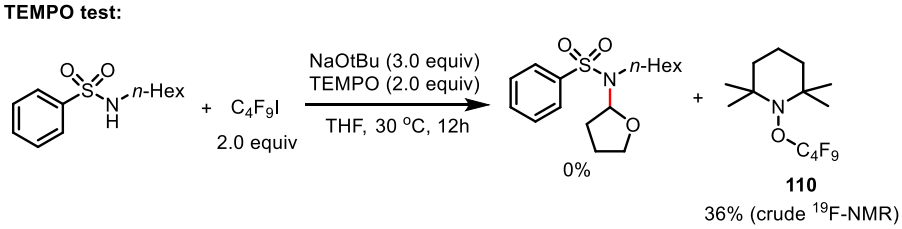


Scheme S13. The ^{19}F NMR signals for the mixture of C_4F_9I with KOH shifted downfield when the ratio of C_4F_9I to KOH increased

Note: The binding constant of the halogen bond complex (R_f-I···O*t*Bu) or (R_f-I···OH) could not be accurately measured because the NaO*t*Bu or KOH was not completely soluble in the solvent and the substrate R_f-I is converted to perfluorobutane over time.

12.3 Reaction of C_4F_9I with TEMPO

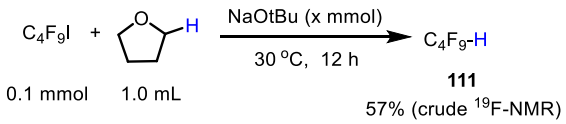
Perfluorobutyl iodide (0.1 mmol, 1.0 equiv) and *t*BuONa (0.2 mol, 2.0 equiv) were dispersed in 1.0 mL of THF in a 4 mL glass vial. The vial was purged with Ar for 1 min and the reaction mixture was stirred at 30 °C for 12 h. Fluorobenzene (10 μL) was used as an internal standard ($\delta_{CF3\text{-}Ph}$ = -63.72) for ^{19}F NMR analysis. The composition of reaction mixture was identified based on the chemical shift of -OCF_2 group at -78.90 ppm for compound **110.**[11]

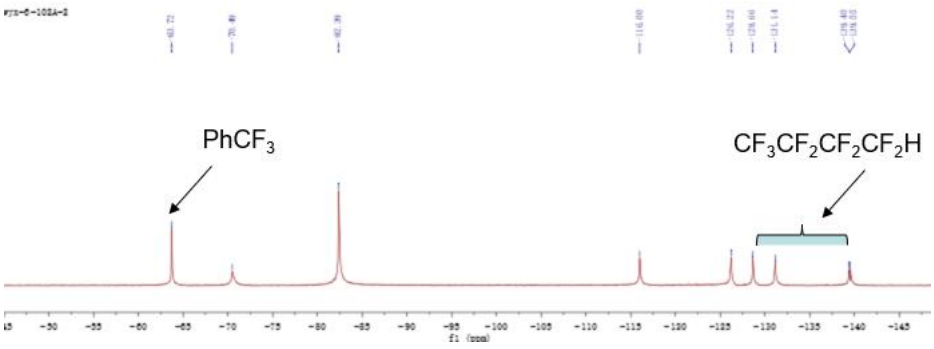


Scheme S14. Reaction of C_4F_9I with TEMPO

12.4 Reaction of C_4F_9I with THF

Perfluorobutyl iodide (0.2 mmol, 1.0 equiv) and *t*BuONa (0.6 mol, 3.0 equiv) were dispersed in 2.0 mL of THF in a 4 mL glass vial. The vial was purged with Ar for 1 min and the reaction mixture was stirred at 30 °C for 12 h. Fluorobenzene (10 μL) was used as an internal standard ($\delta_{CF3\text{-}Ph}$ = -63.72) for ^{19}F NMR analysis. The composition of reaction mixture was identified based on the chemical shift of -CF_2- group at -126.22 ppm for compound **111.**[10]

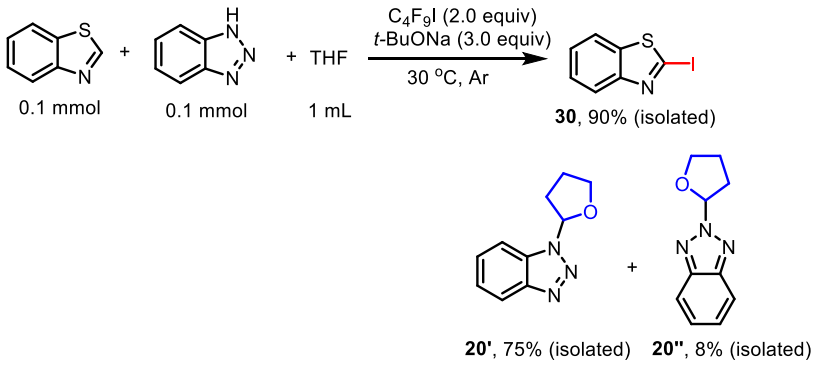




Scheme S15. Reaction of C_4F_9I with THF

12.5 Reaction of C_4F_9I with benzothiazole and benzotriazole

Benzothiazole (0.1 mmol, 1.0 equiv) and benzotriazole (0.1 mmol, 1.0 equiv), C_4F_9I (0.2 mmol, 2.0 equiv) and NaO*t*Bu (0.3 mmol, 3.0 equiv) were dispersed in 1 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C for 12 hours. Then the mixture was concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography to give the desired products, iodination product was isolated in 90% yield and amidation products were isolated in 83% yield (75%+8%).

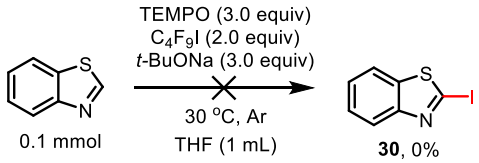


Scheme S16. Reaction of C_4F_9I with benzothiazole and benzotriazole

12.6 Iodination reaction of benzothiazole with TEMPO

Benzothiazole (0.1 mmol, 1.0 equiv), TEMPO (0.3 mmol, 3.0 equiv), C_4F_9I (0.2 mmol,

2.0 equiv) and NaO*t*Bu (0.3 mmol, 3.0 equiv) were dispersed in 1 mL of THF. The reaction vial was then purged with Ar for 1 min and sealed with PTEF cap. The reaction mixture was vigorously stirred at 30 °C for 12 hours. Iodination product was not observed by GCMS, which proved that the iodination process was involved in free radical intermediate.



Scheme S17. Iodination reaction of benzothiazole with BHT

13 References

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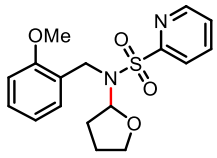
14. ^{1}H-NMR, ^{13}C-NMR spectra and ^{19}F-NMR



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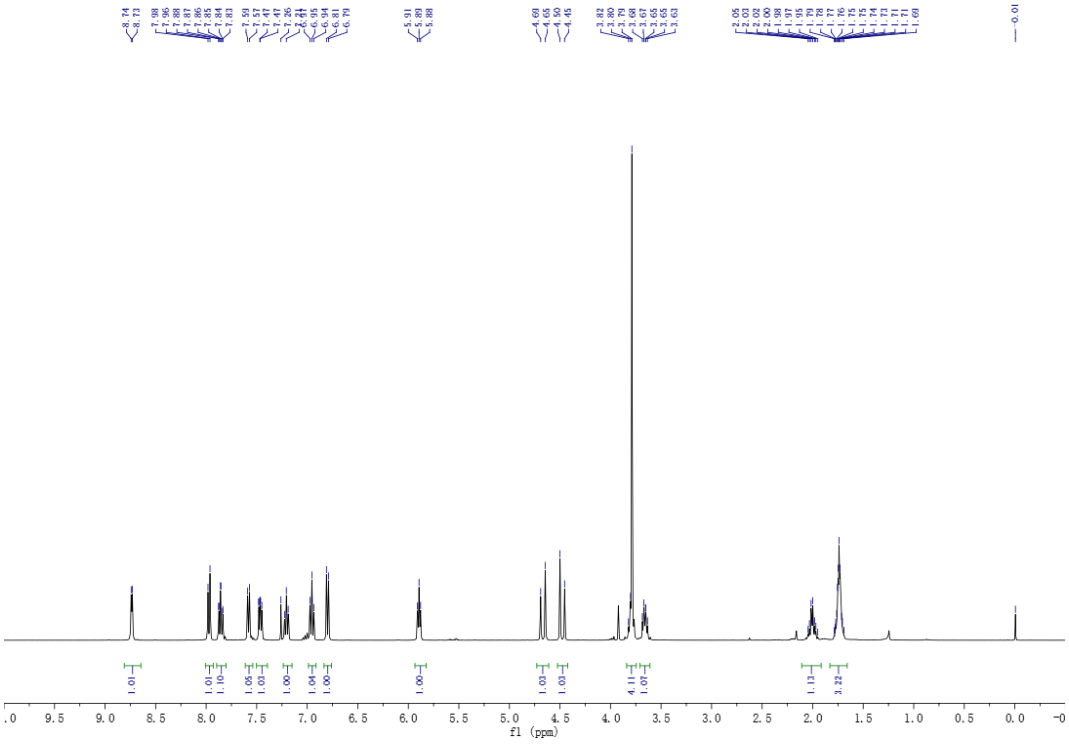
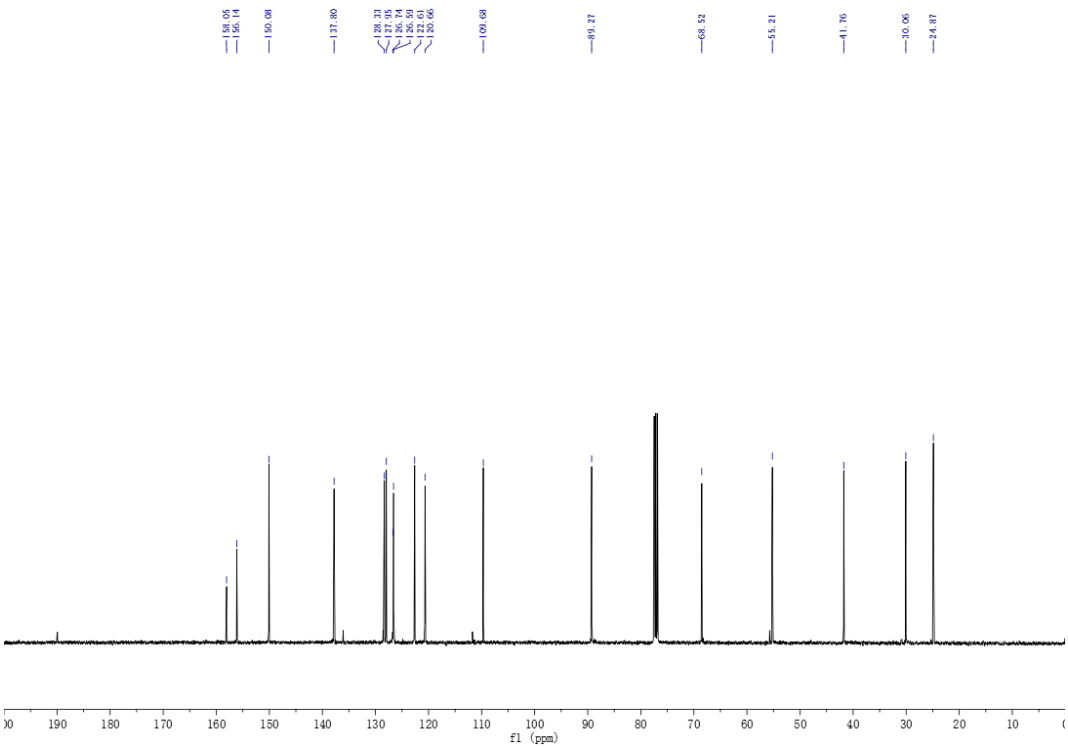
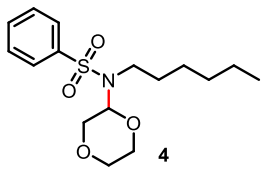


^{1}H NMR of compound **2**



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



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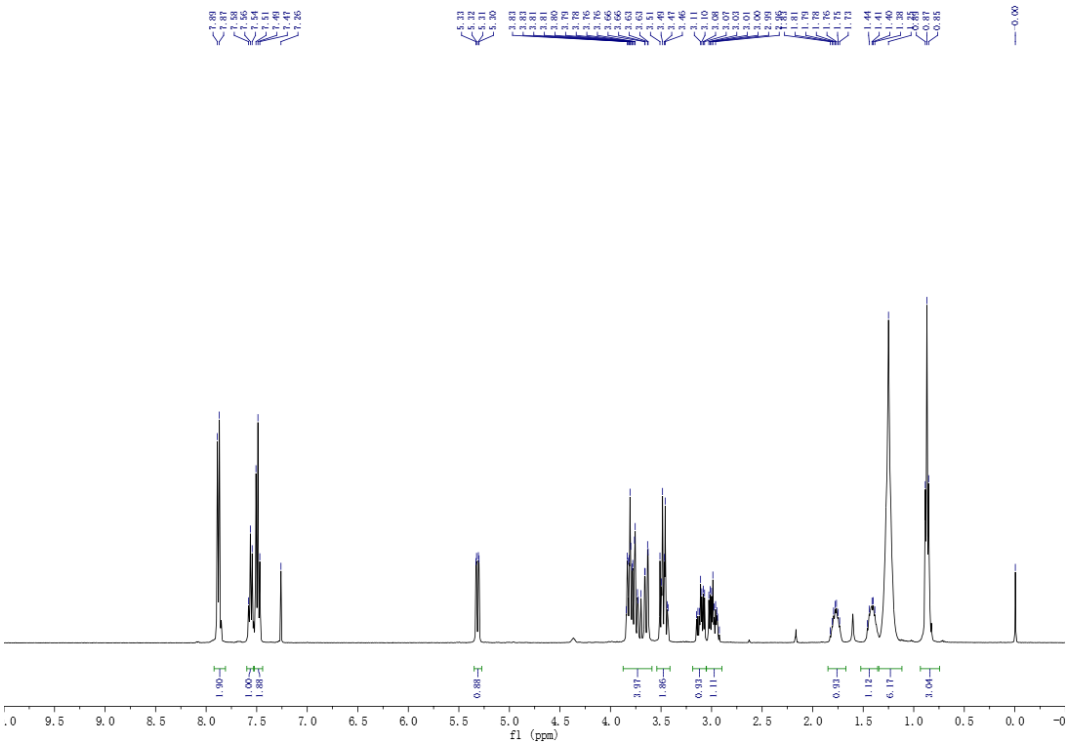
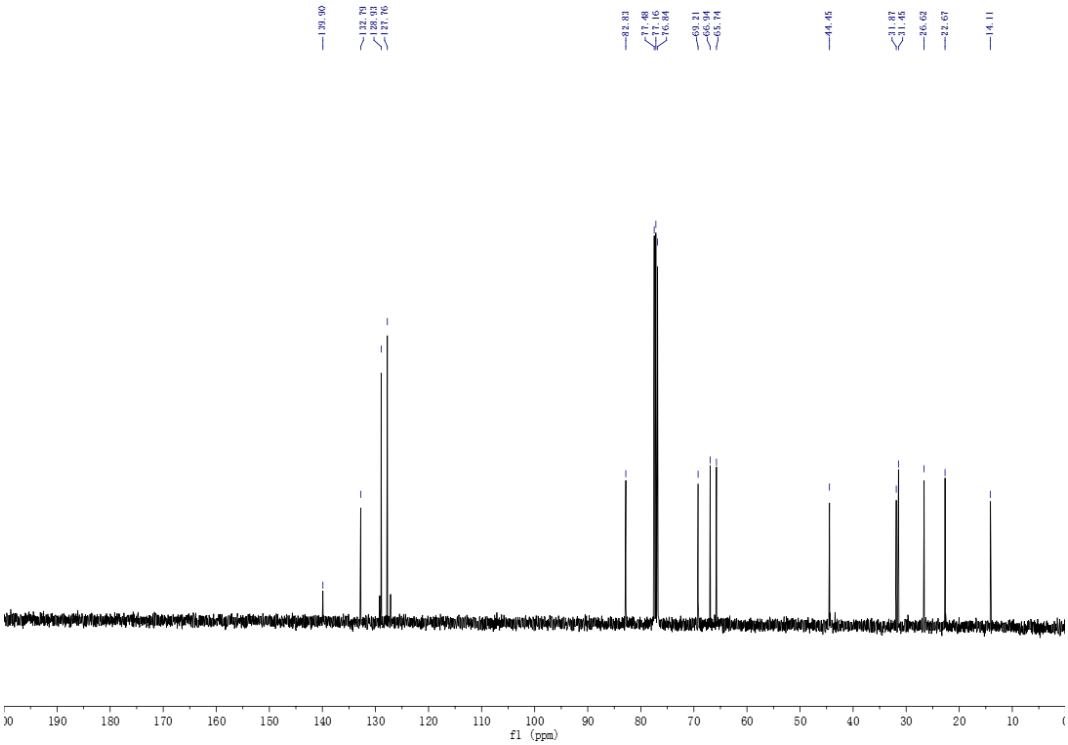
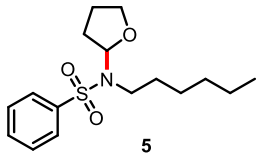


^{1}H NMR of compound **4**



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



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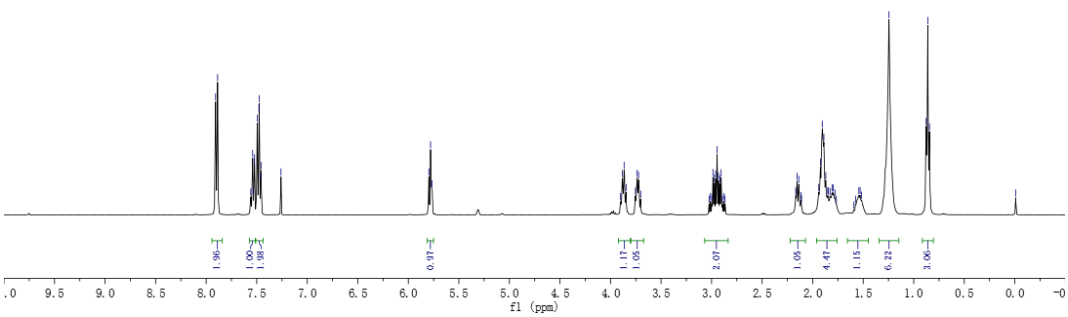
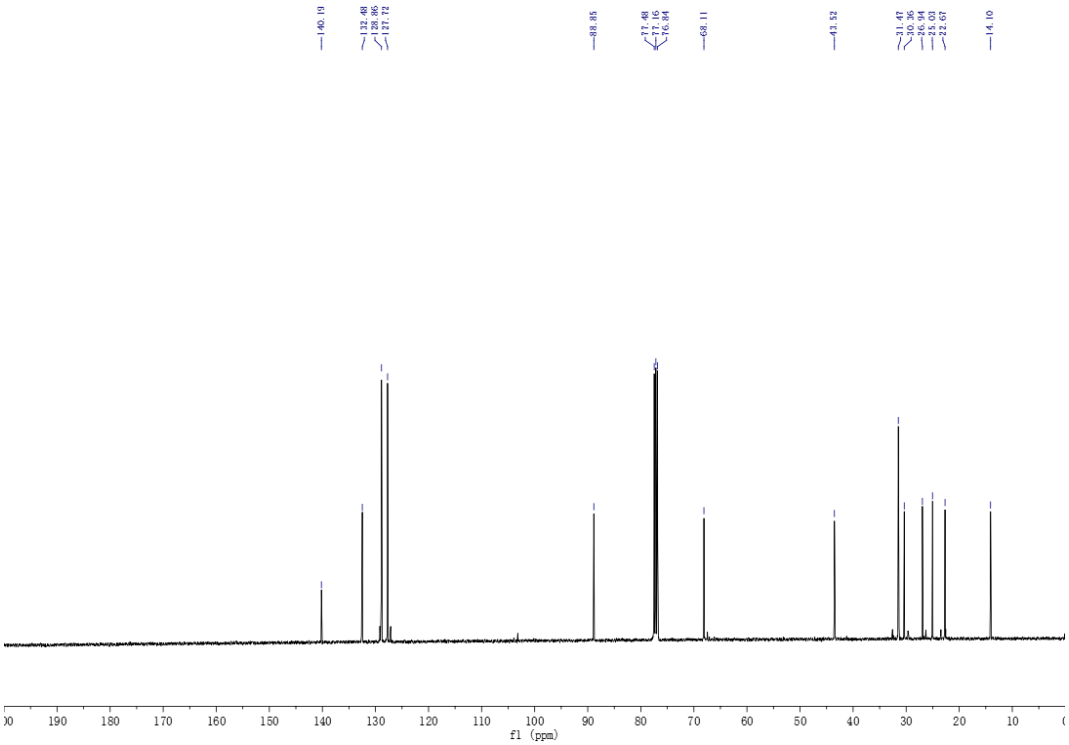


^{1}H NMR of compound **5**



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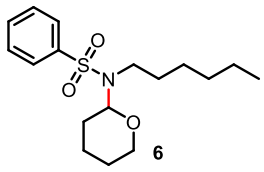

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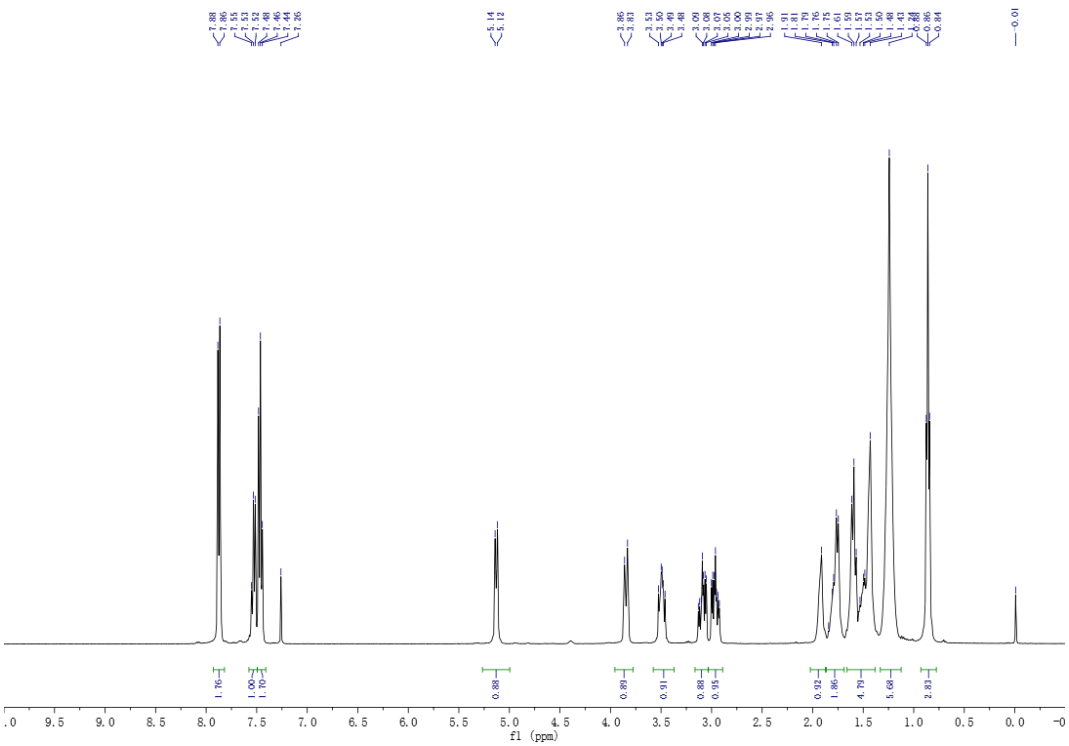

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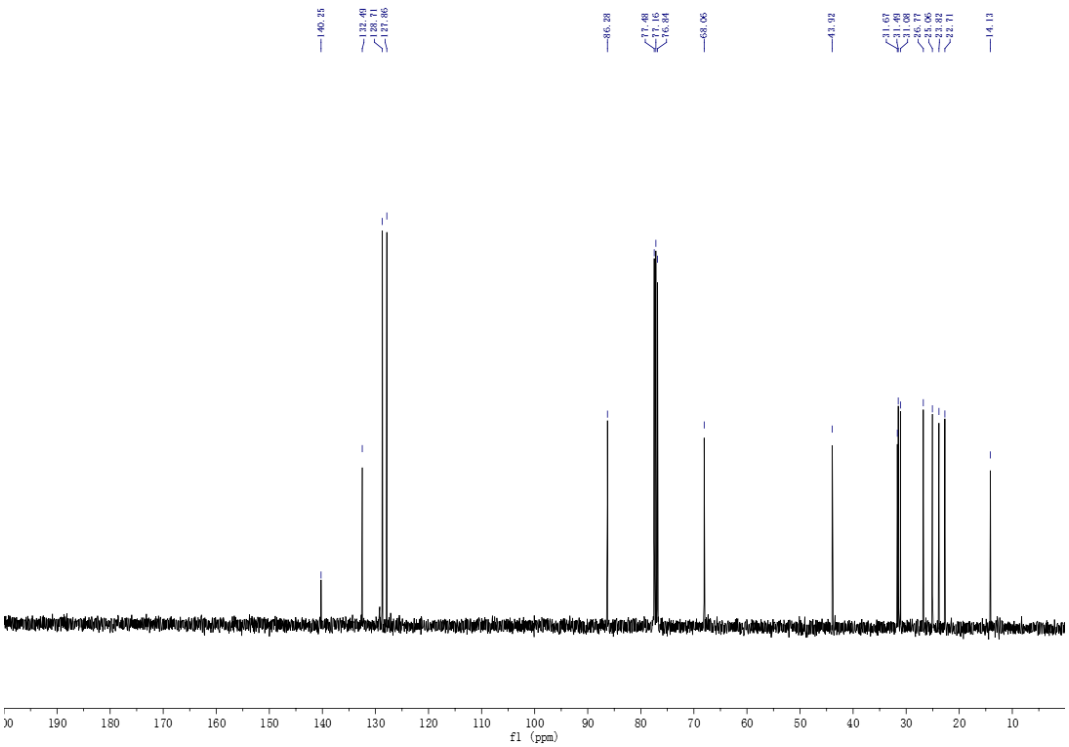
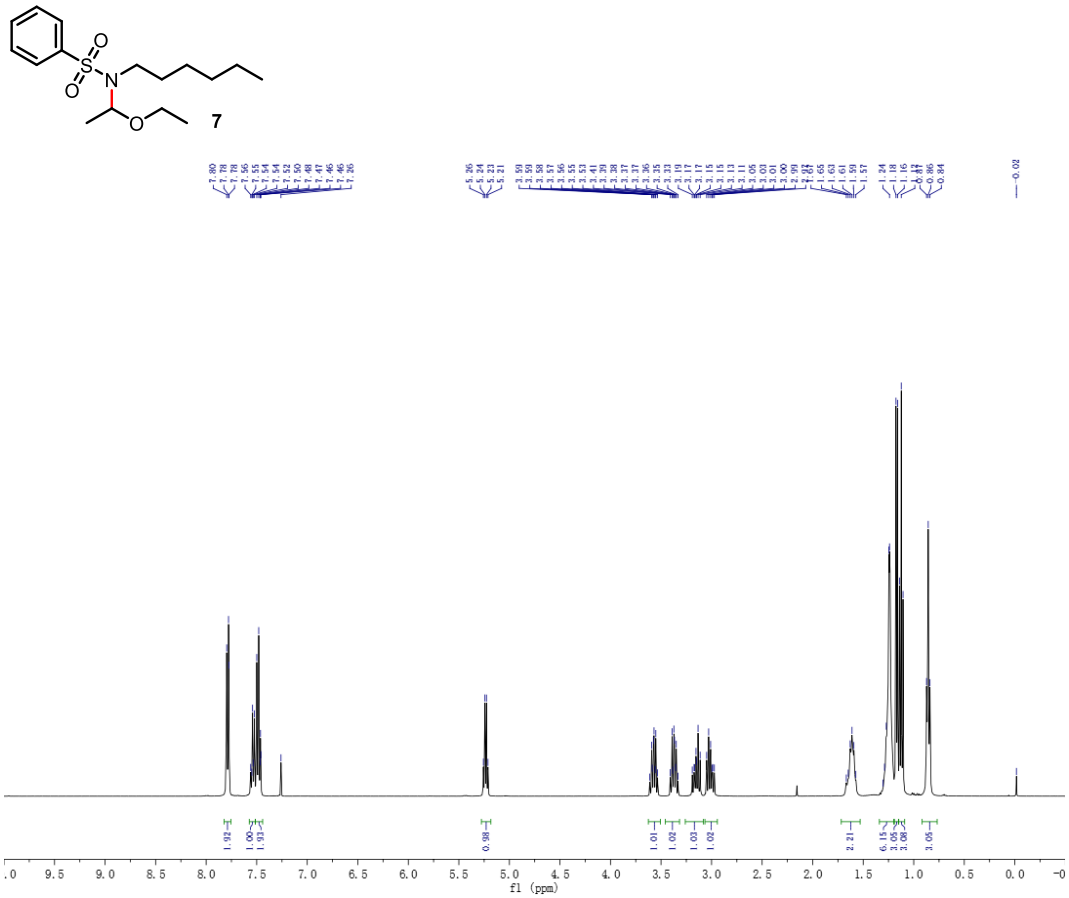
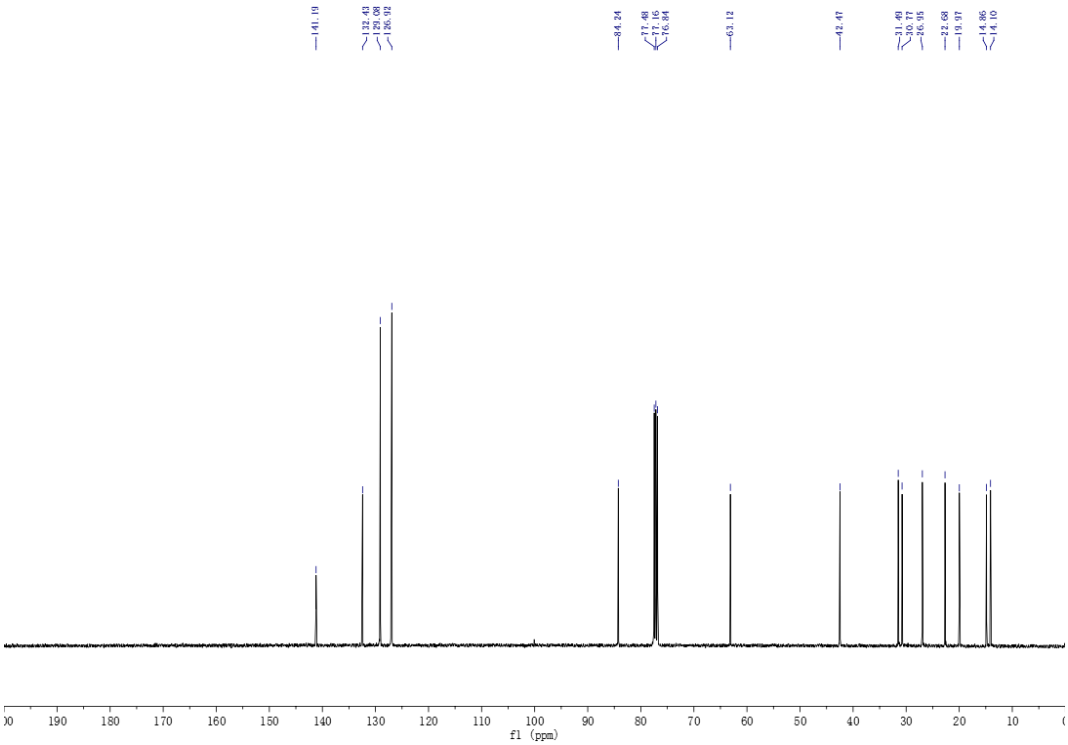


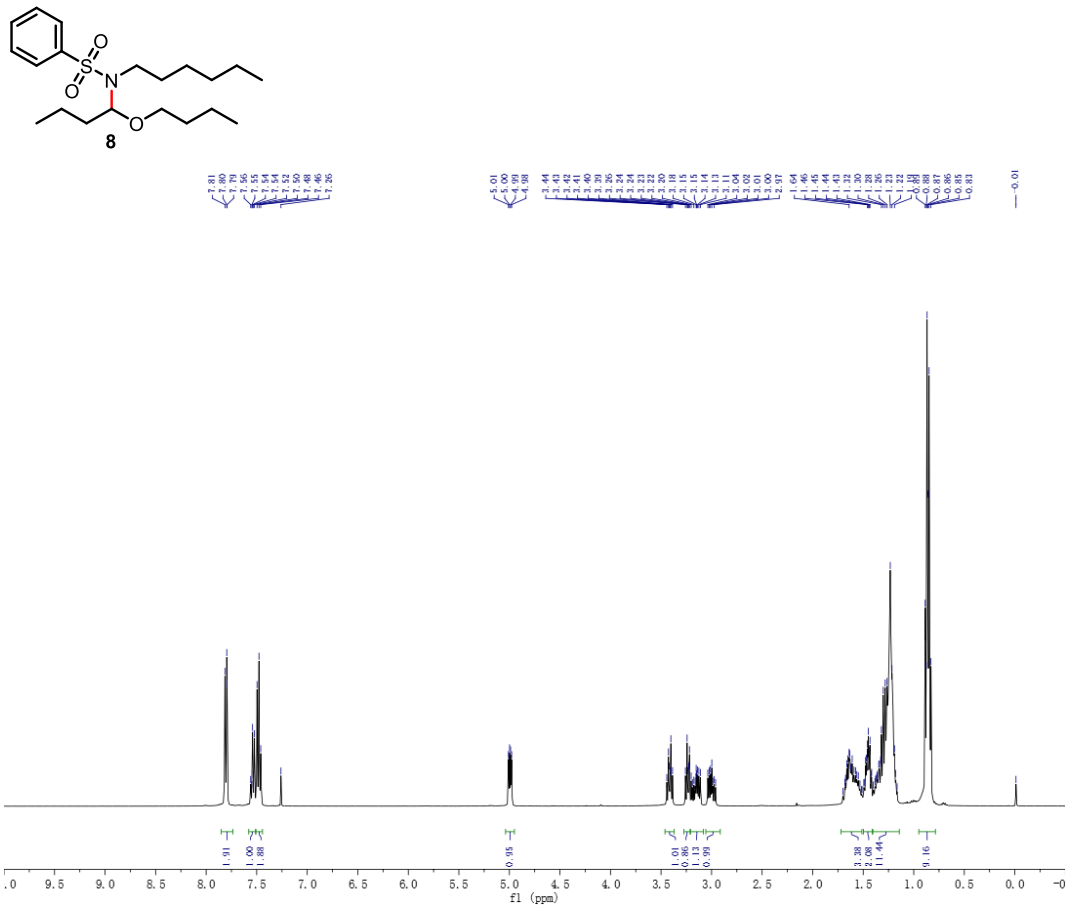
^{13}C NMR of compound **6**



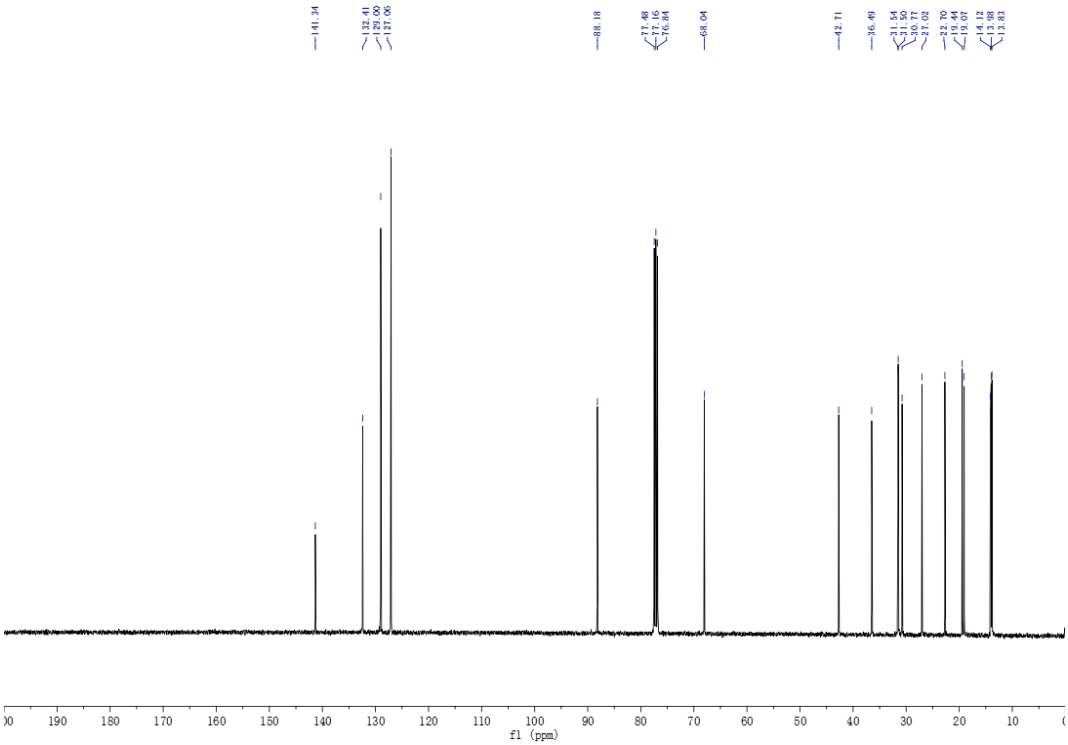
^{1}H NMR of compound **7**



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



^{1}H NMR of compound **8**



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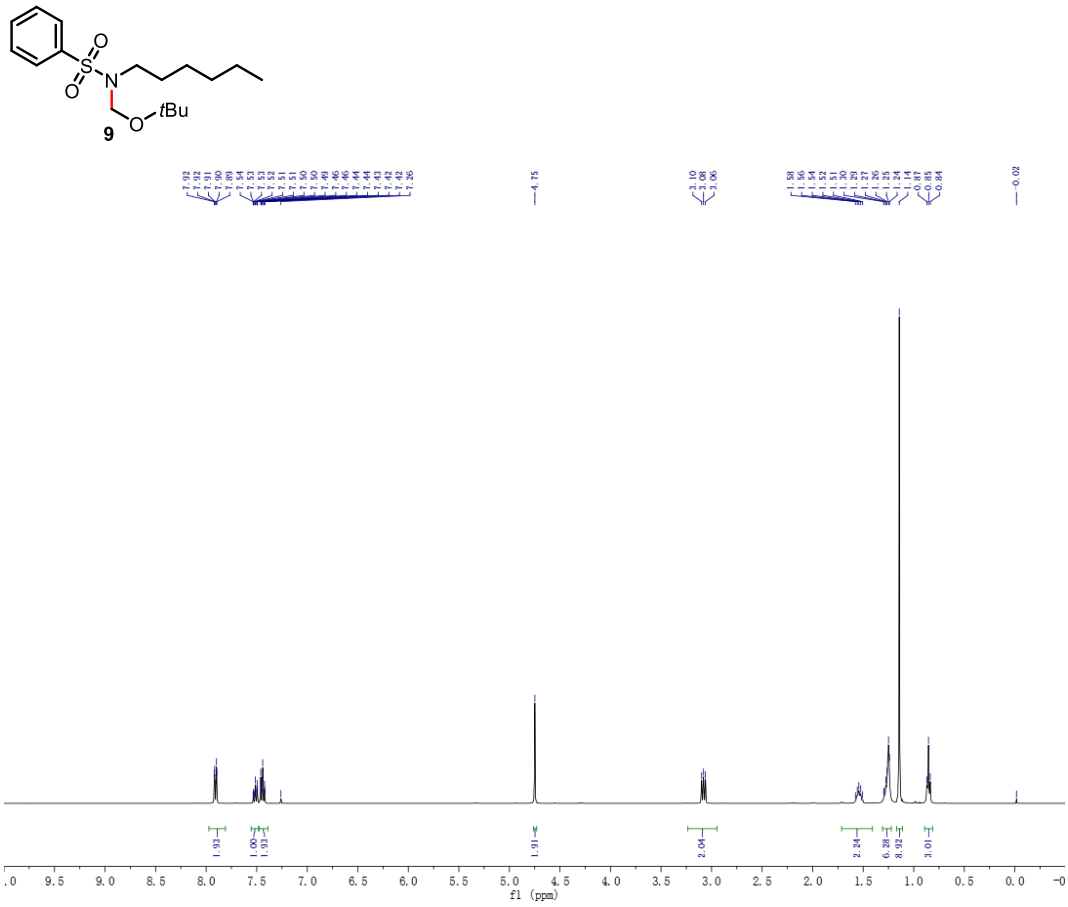
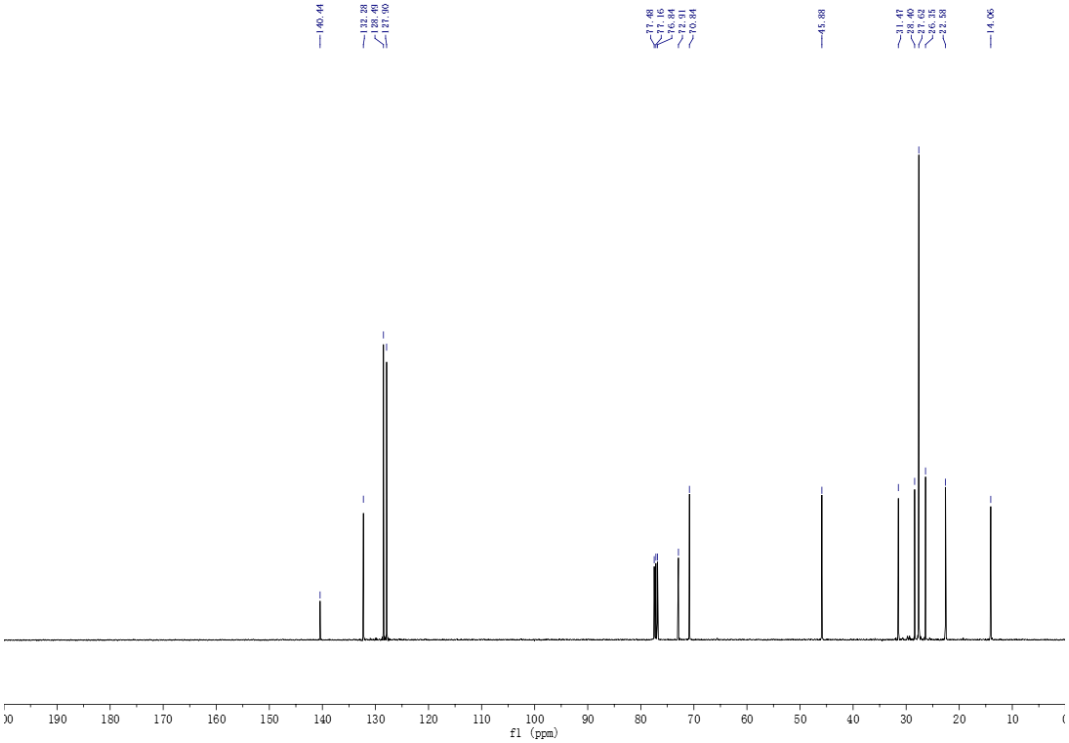
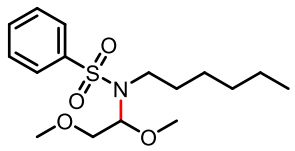


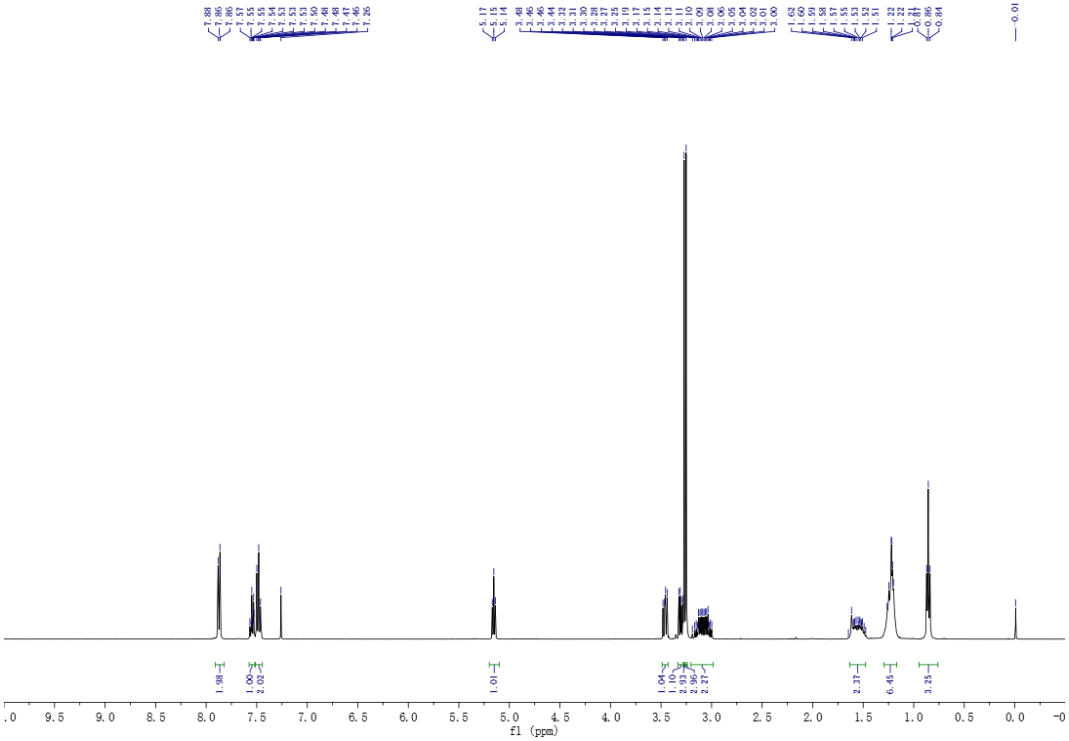
^{1}H NMR of compound **9**



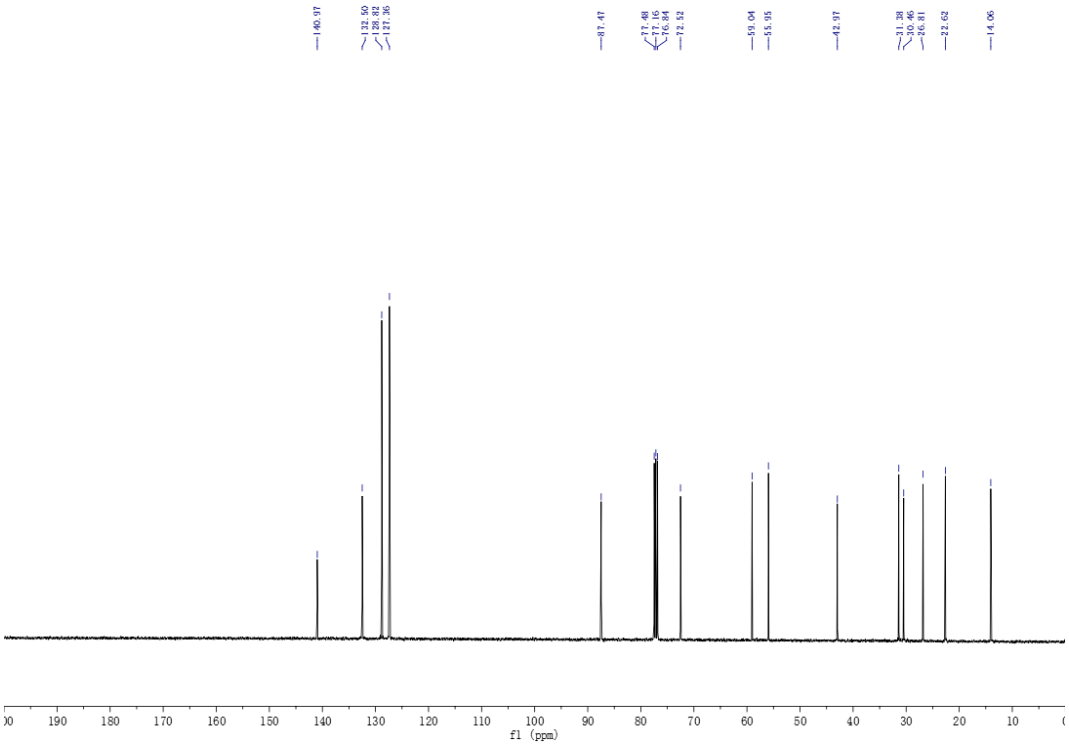
^{13}C NMR of compound **9**



11', 59%



^{1}H NMR of compound **11'**



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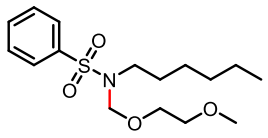
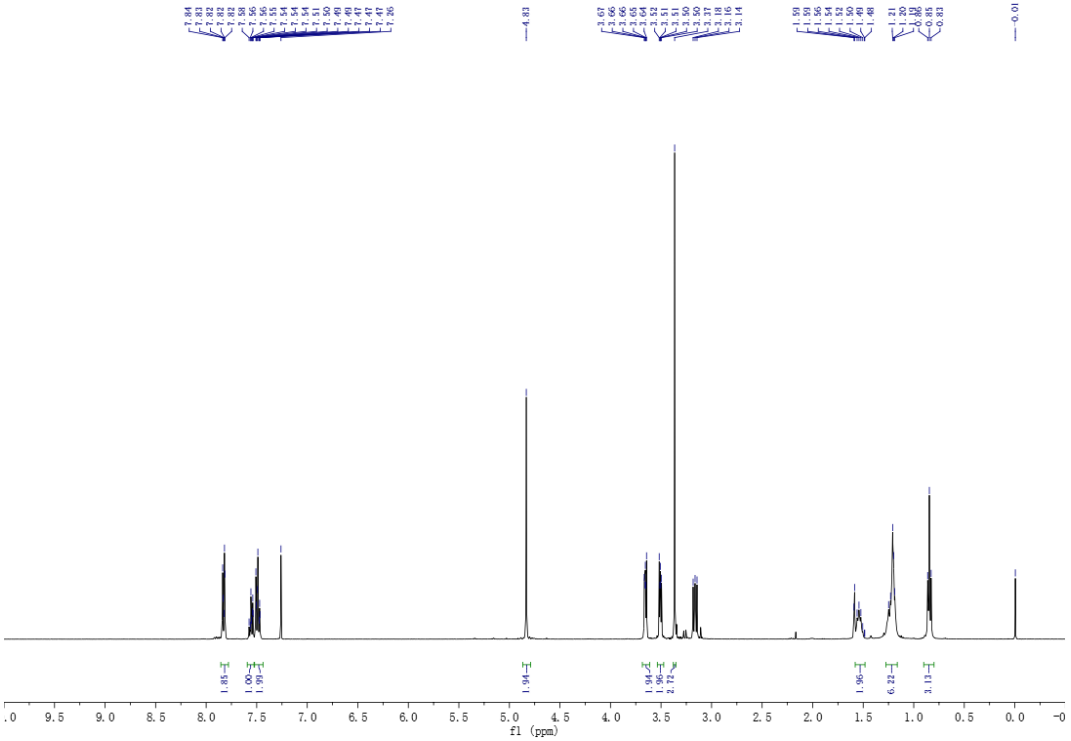
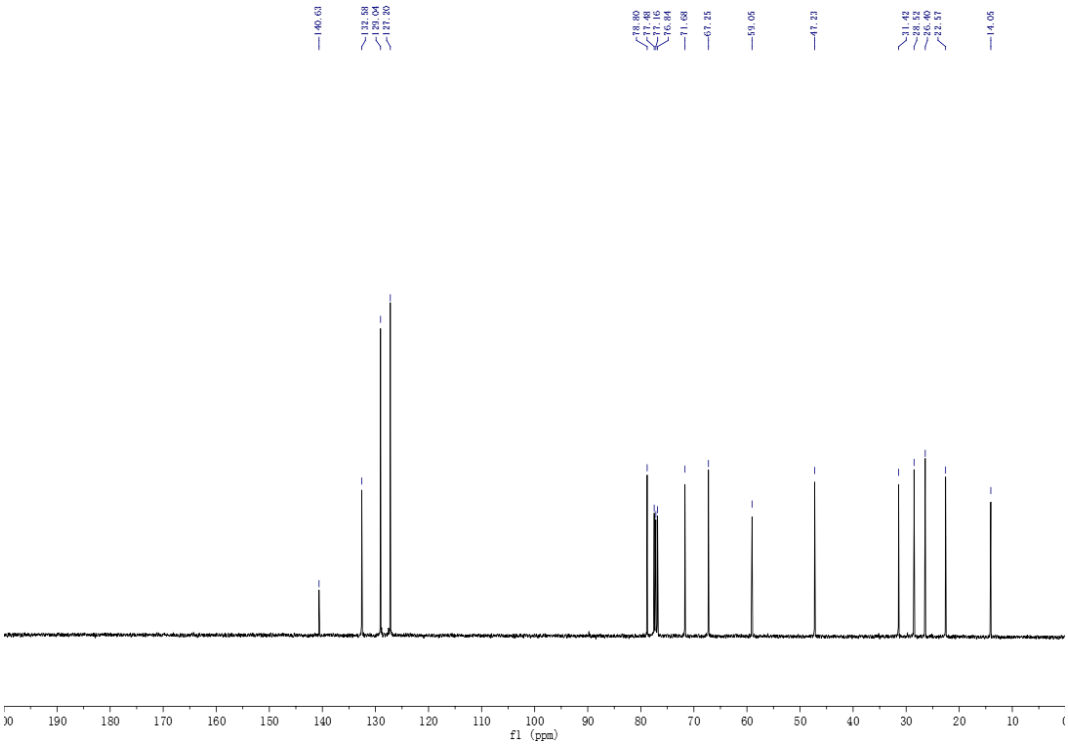


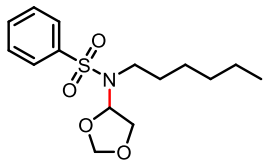
11", 34%



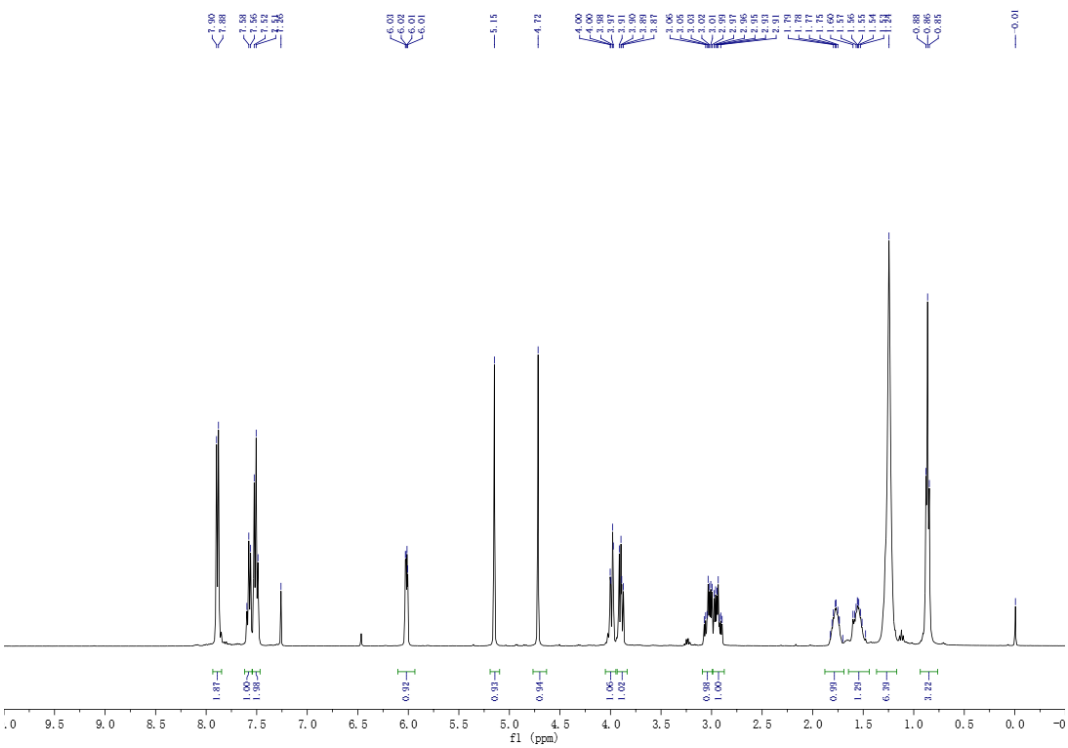
^{1}H NMR of compound **11''**



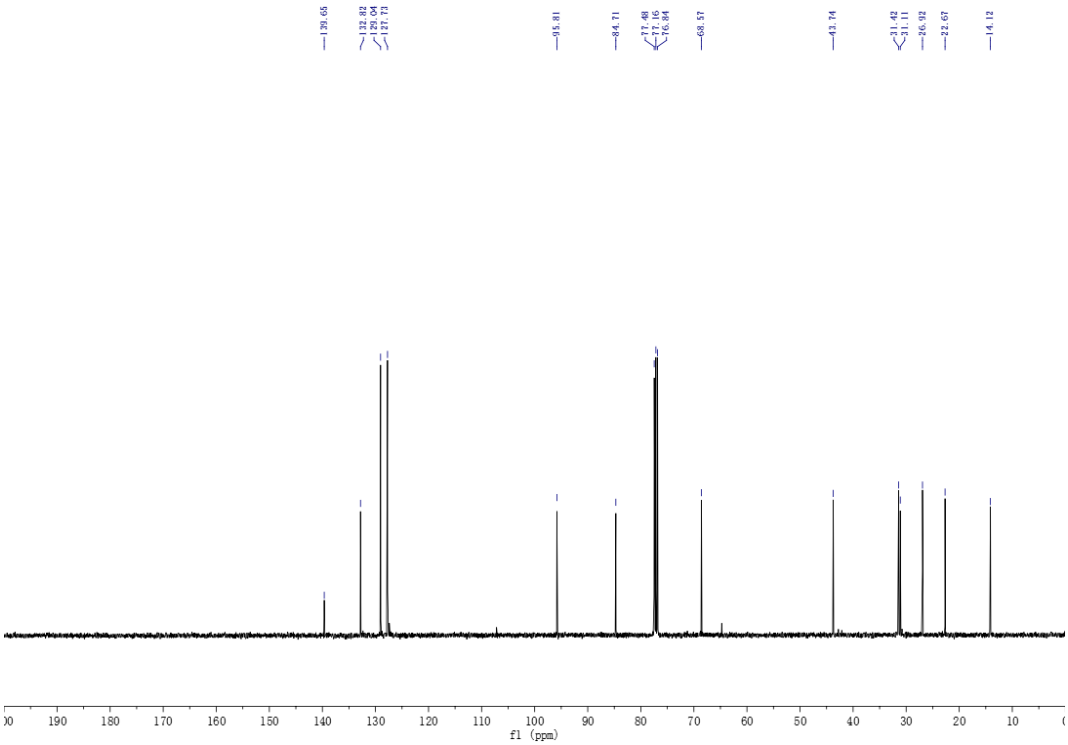
^{13}C NMR of compound **11''**



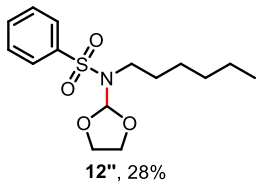
12', 65%



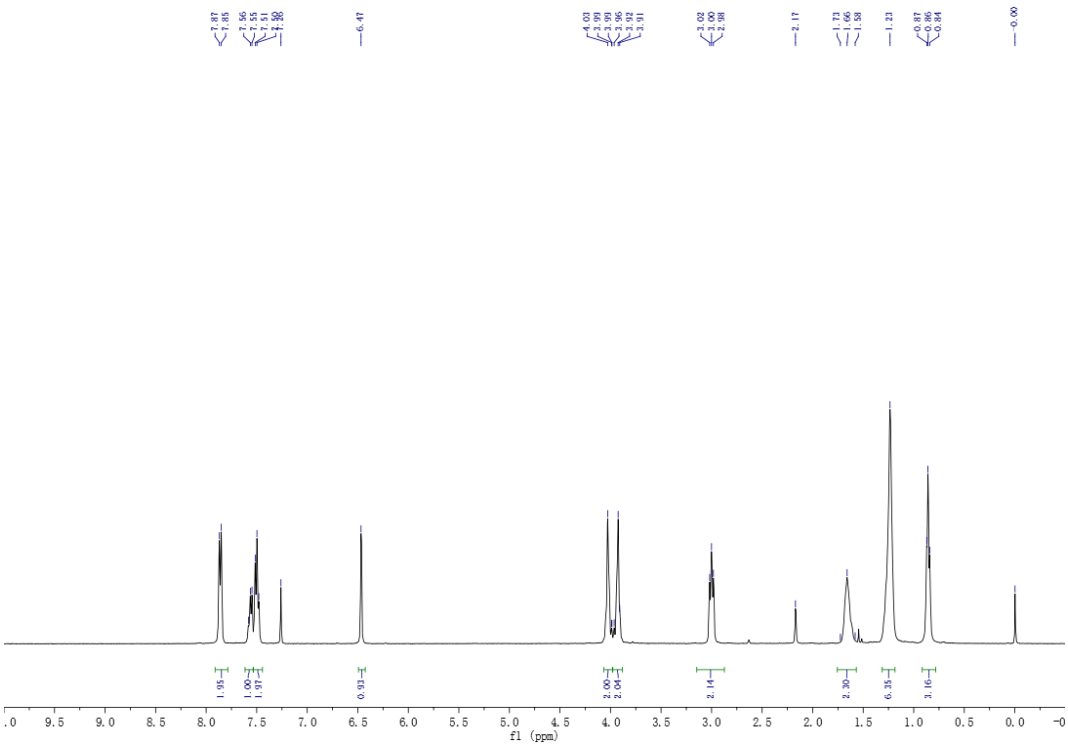
^{1}H NMR of compound **12'**



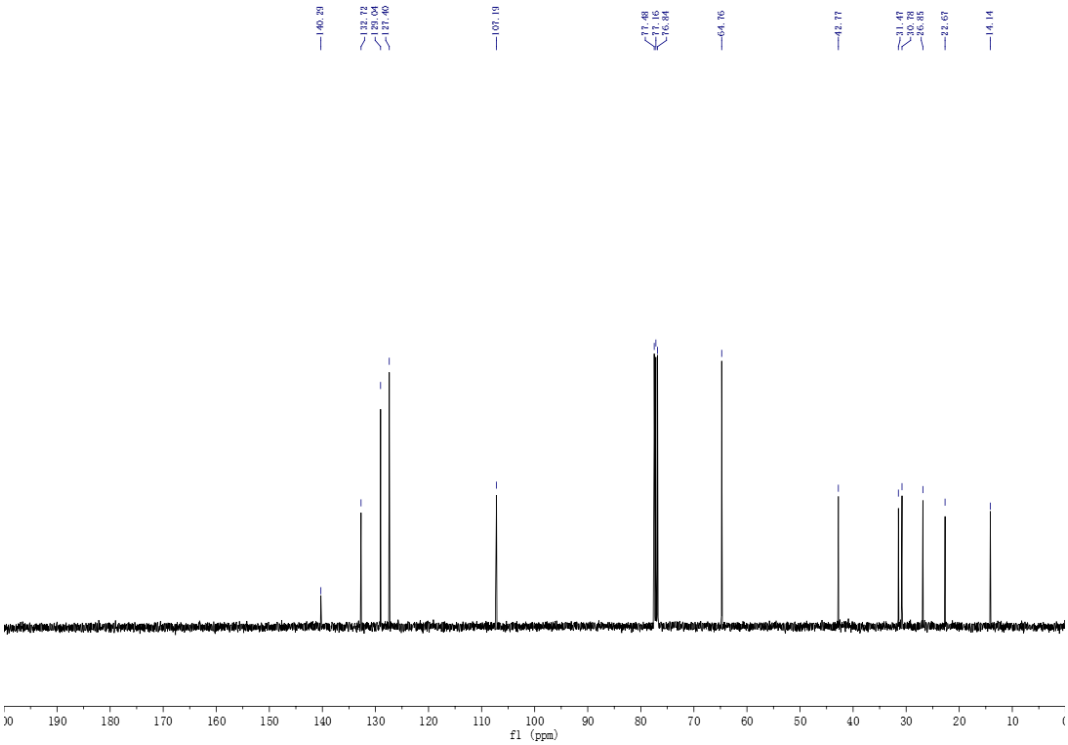
^{13}C NMR of compound **12'**



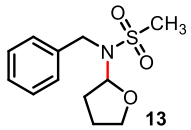
12'', 28%



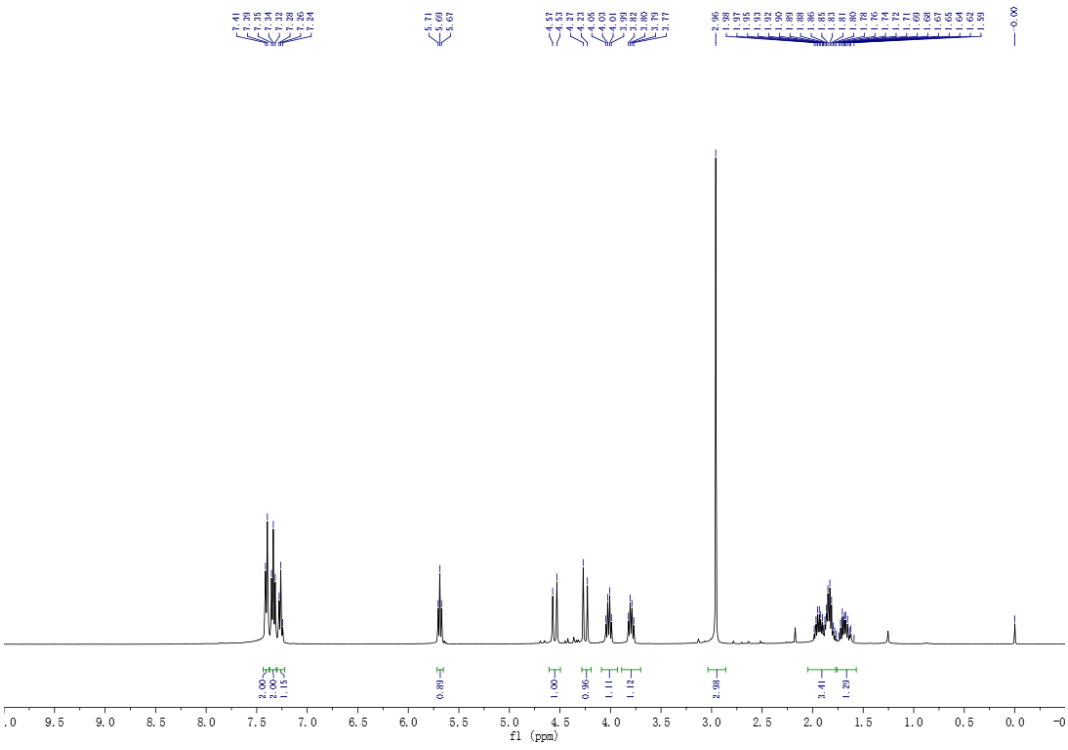
^{1}H NMR of compound **12''**



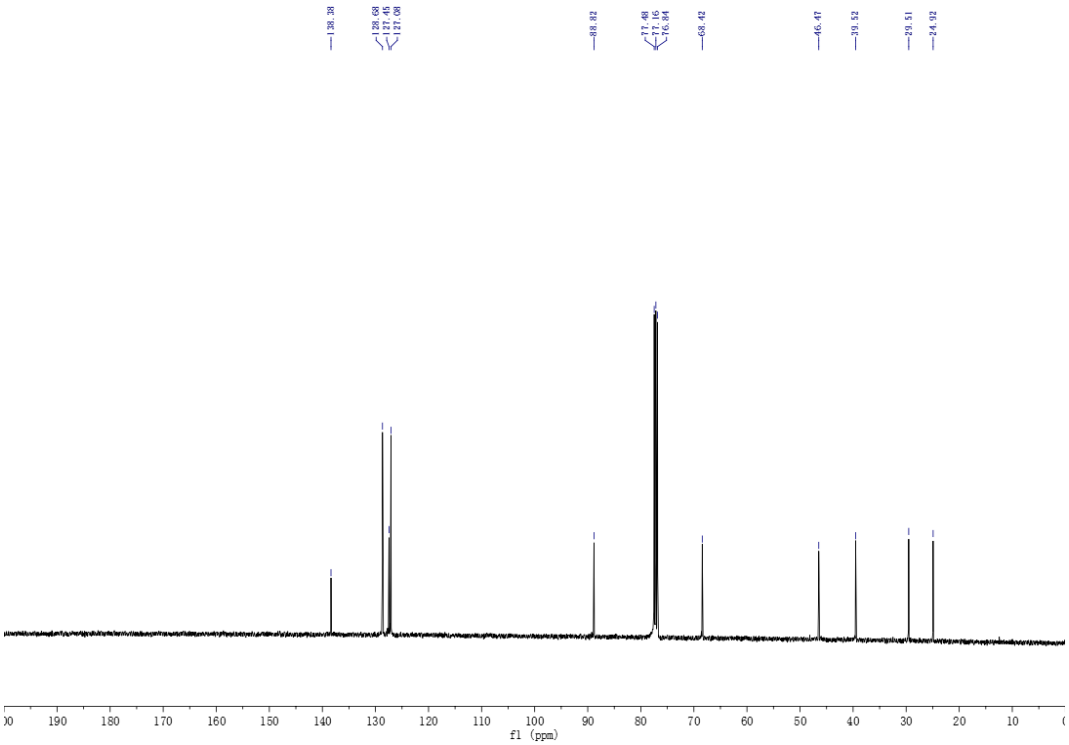
^{13}C NMR of compound **12''**



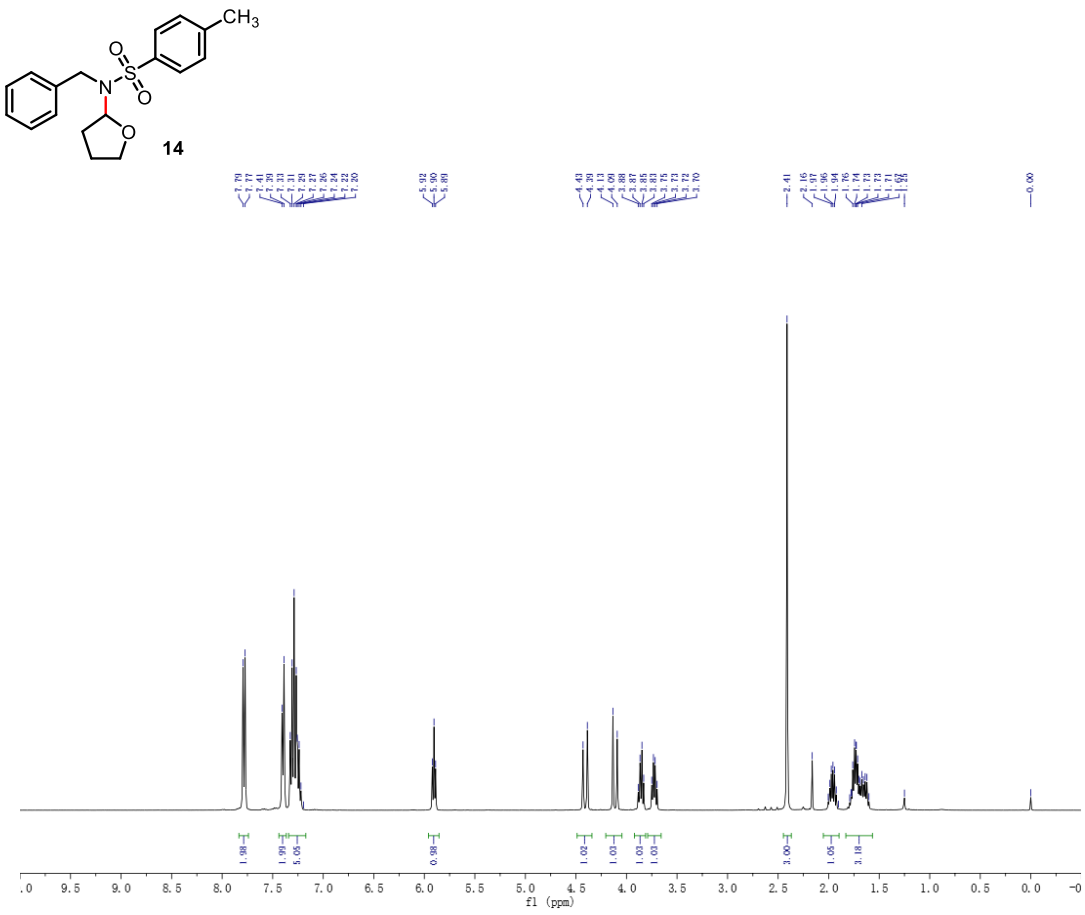
13



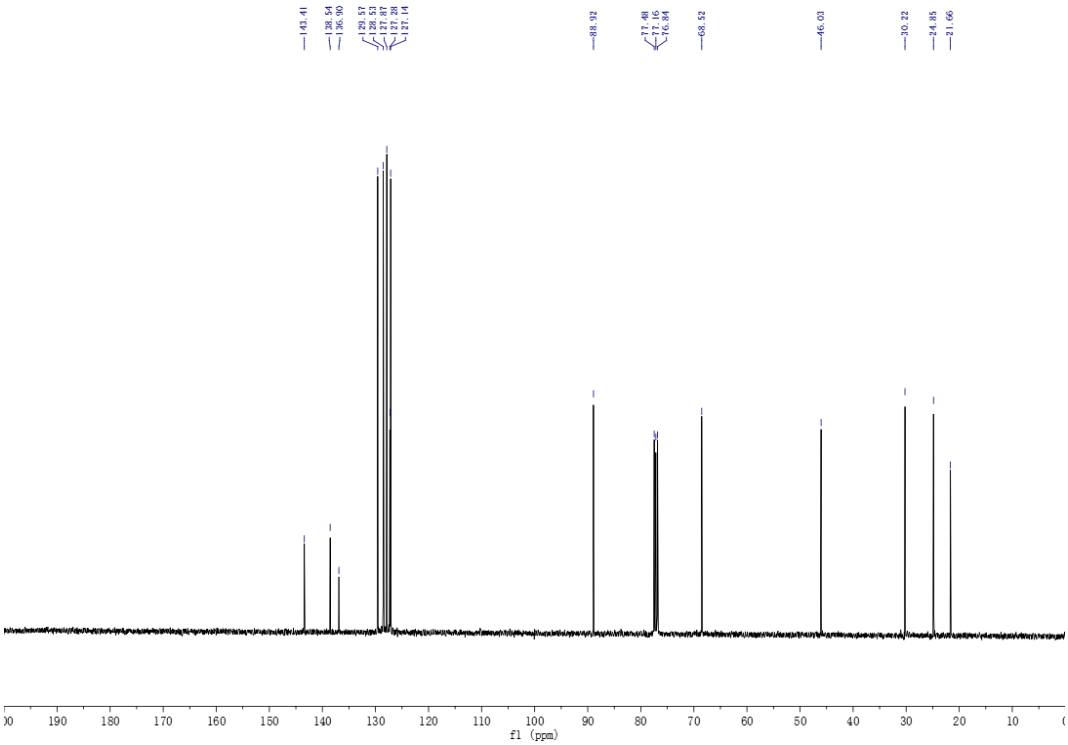
^{1}H NMR of compound **13**



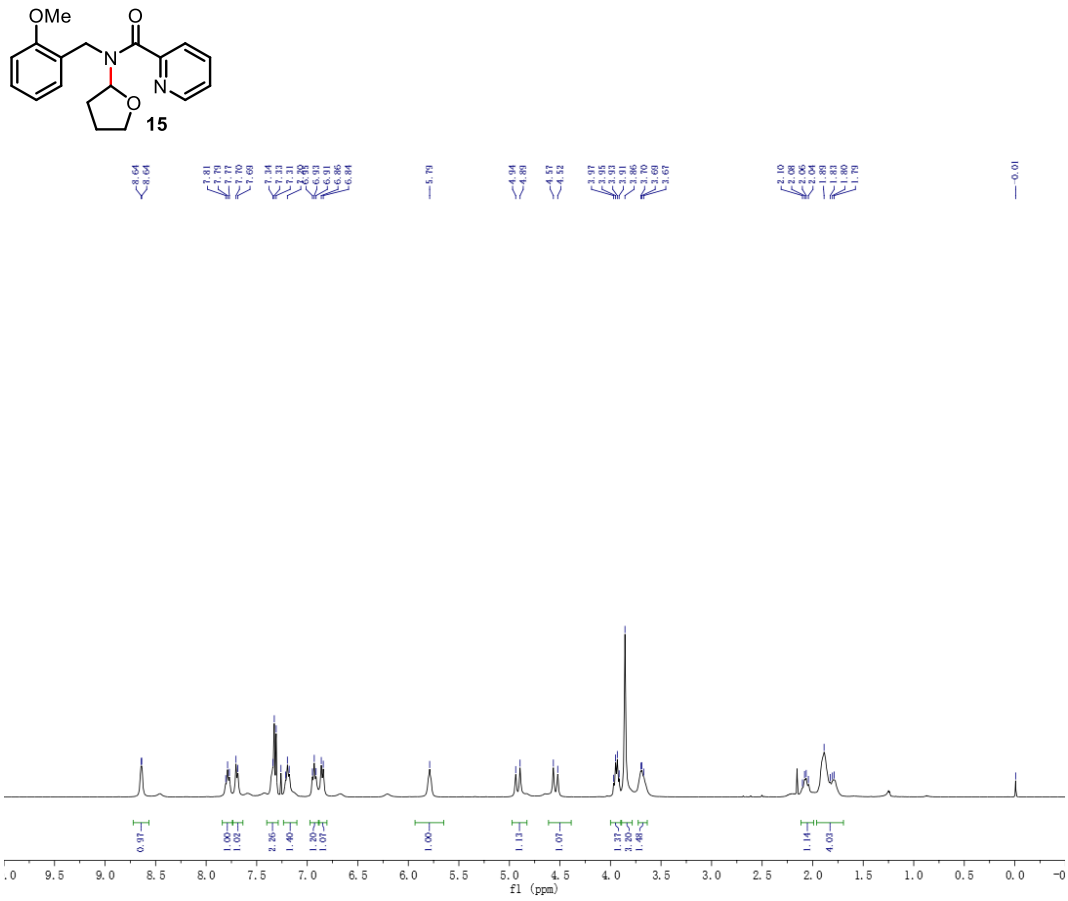
^{13}C NMR of compound **13**



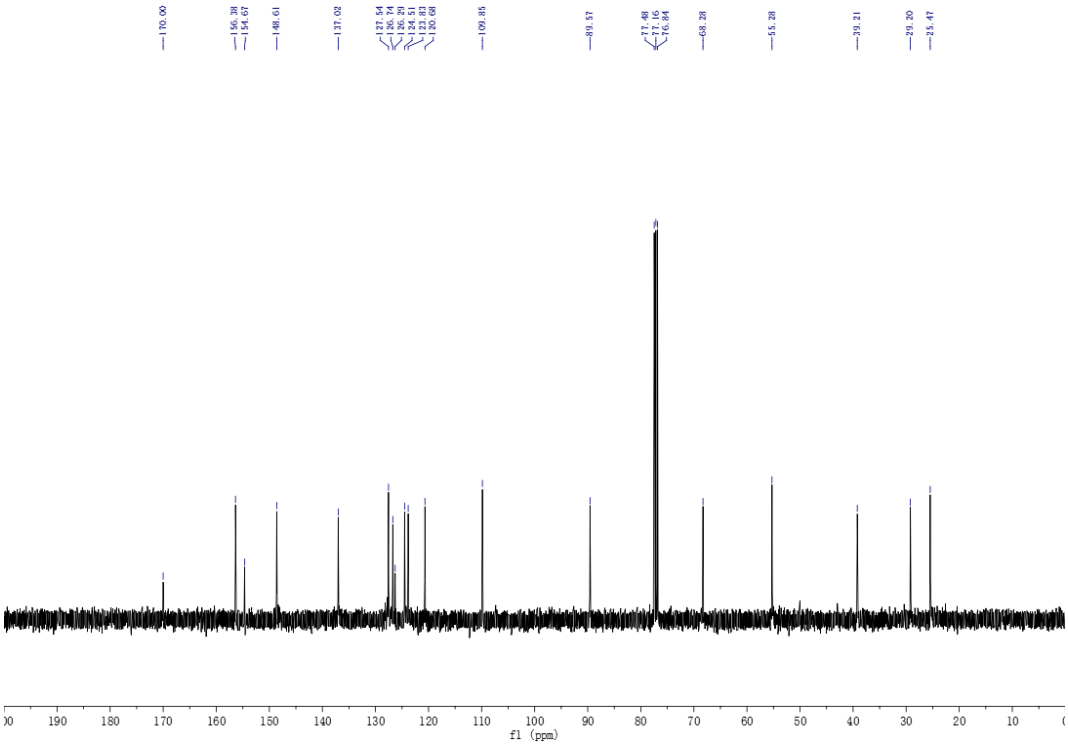
^{1}H NMR of compound **14**



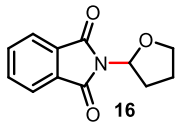
^{13}C NMR of compound **14**



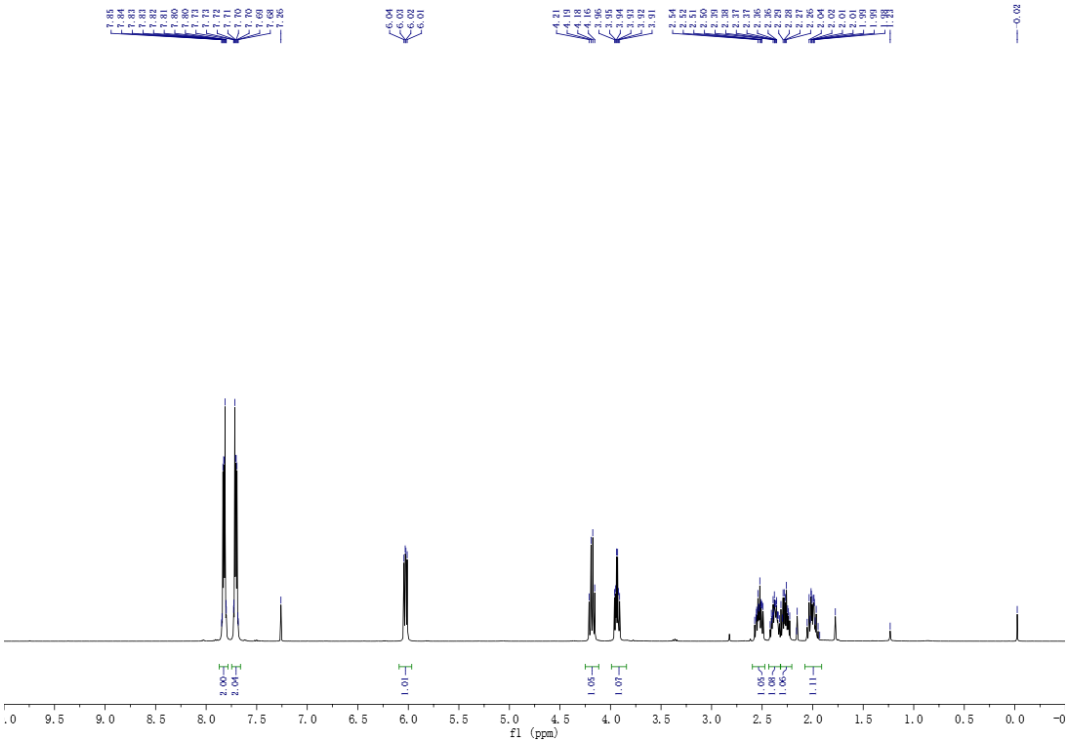
^{1}H NMR of compound **15**



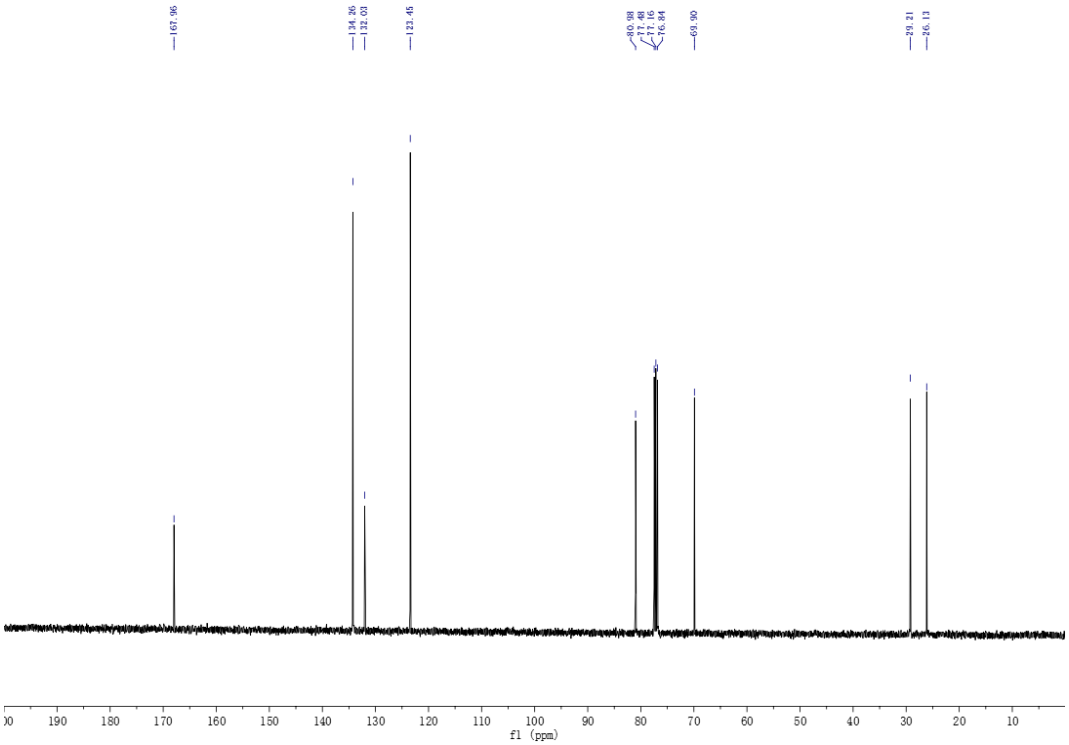
^{13}C NMR of compound **15**



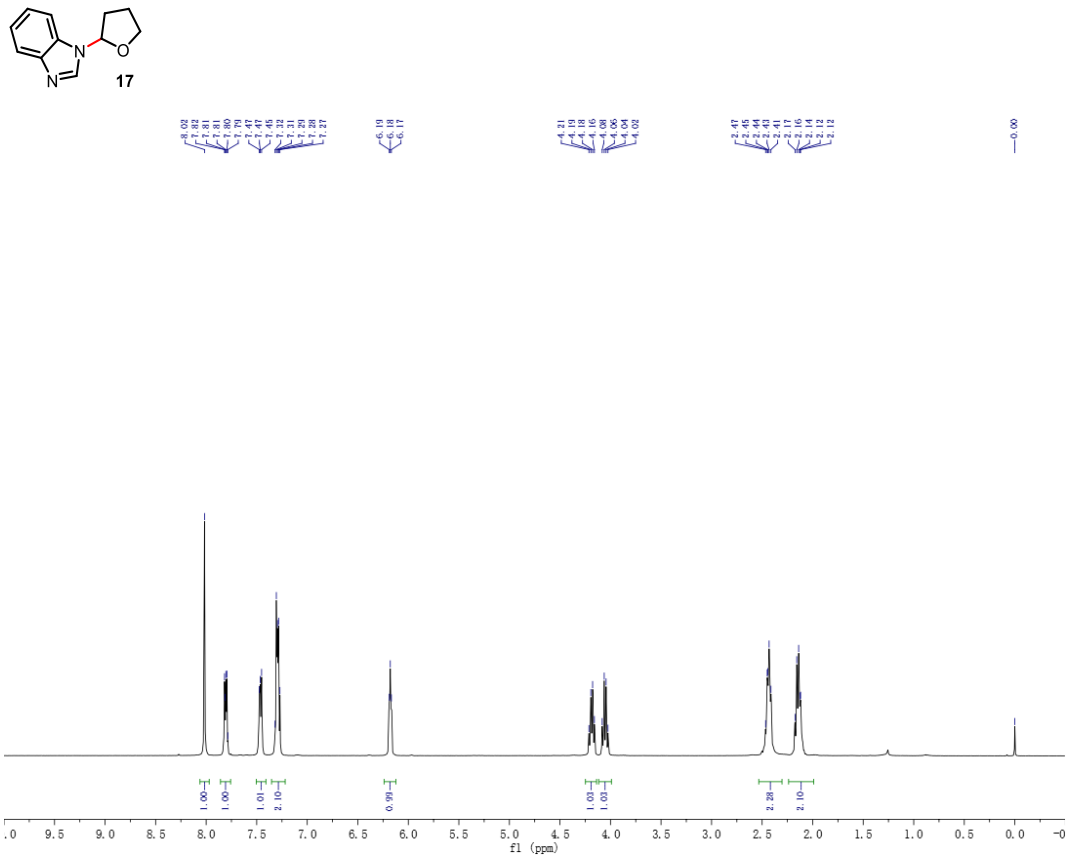
16



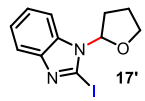
^{1}H NMR of compound **16**

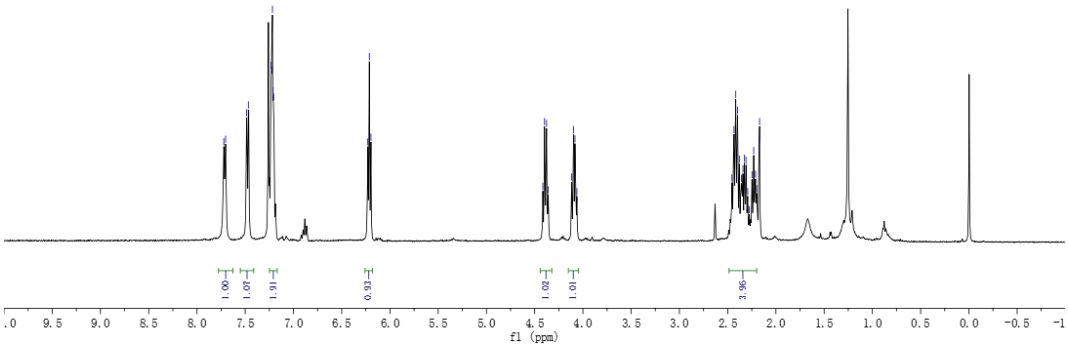


^{13}C NMR of compound **16**

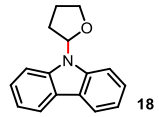


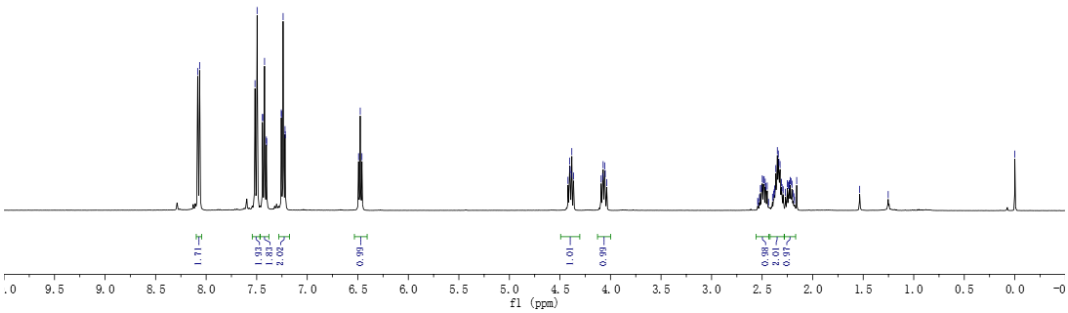
^{1}H NMR of compound **17**



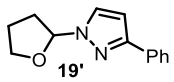


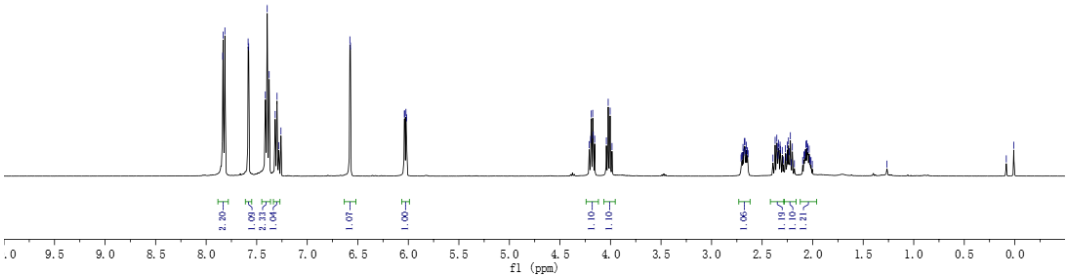
^{1}H NMR of compound **17'**



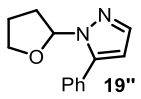


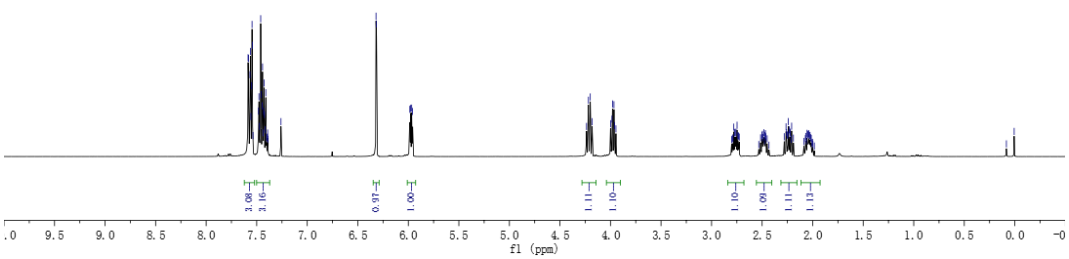
^{1}H NMR of compound **18**



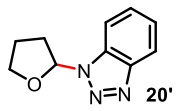


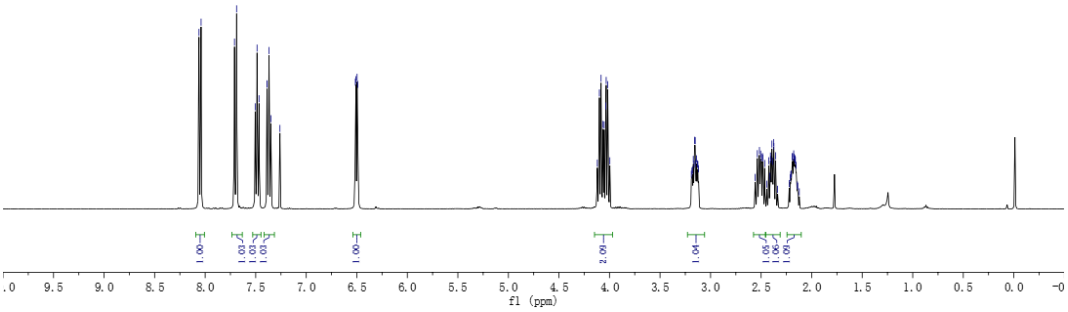
^{1}H NMR of compound **19'**



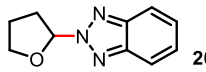


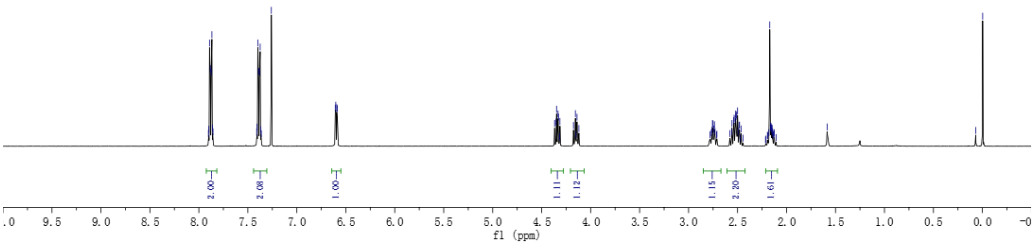
^{1}H NMR of compound **19''**



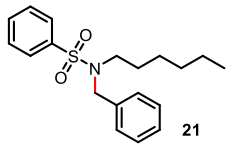


^{1}H NMR of compound **20'**





^{1}H NMR of compound **20''**



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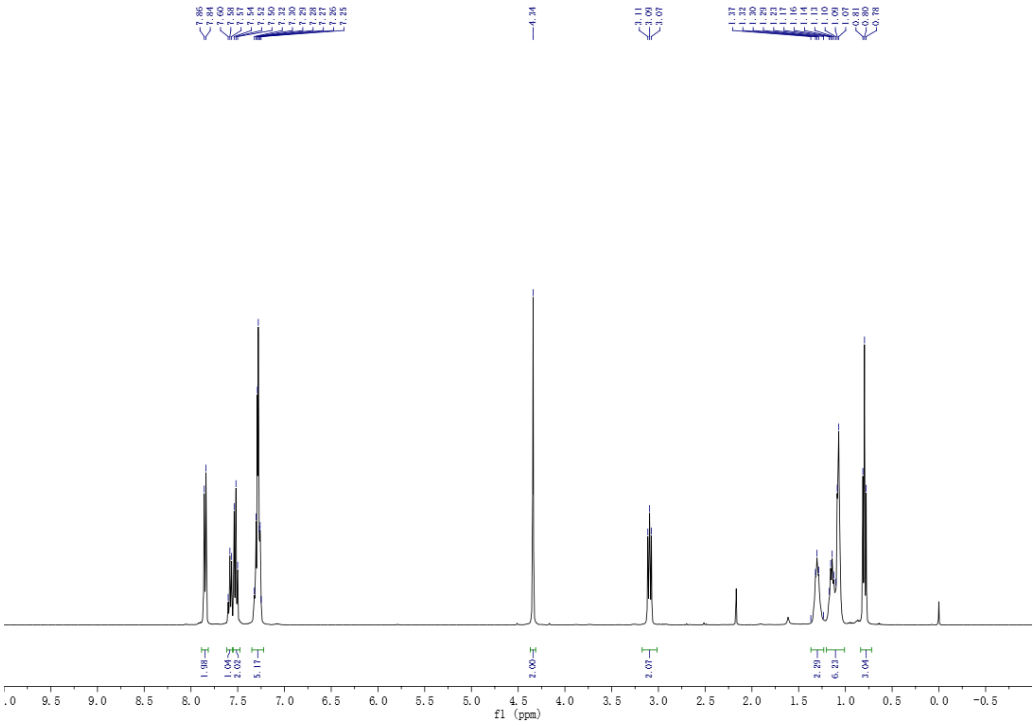
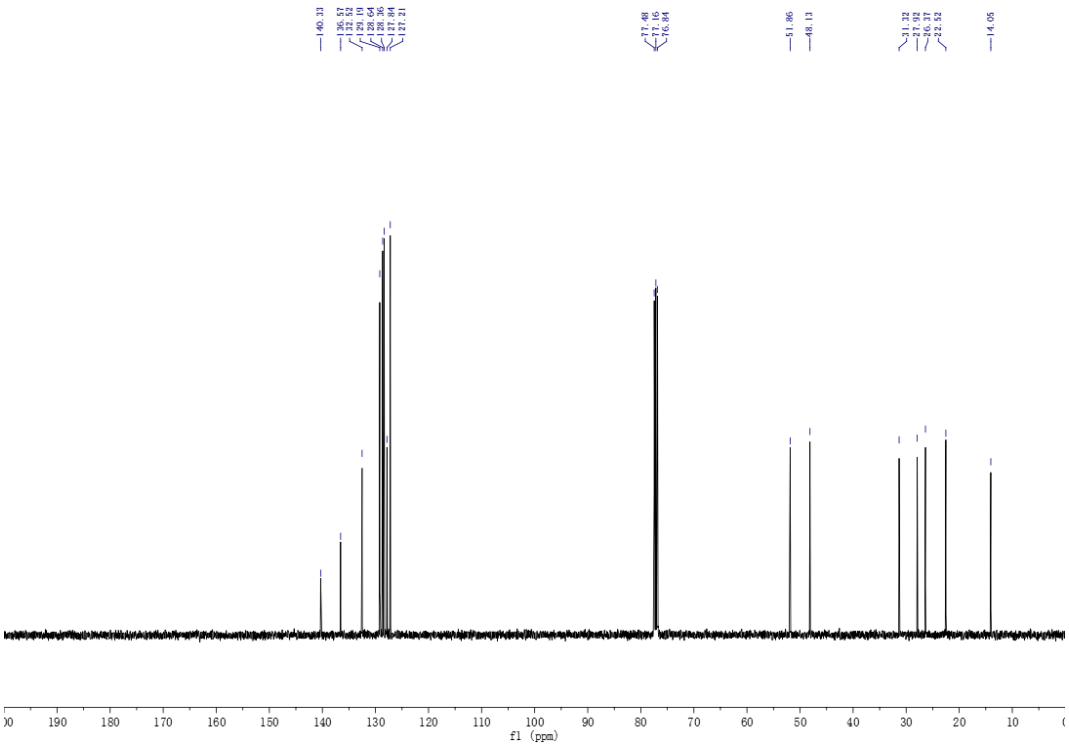
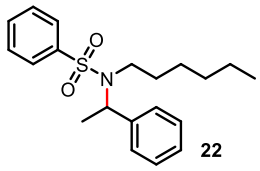


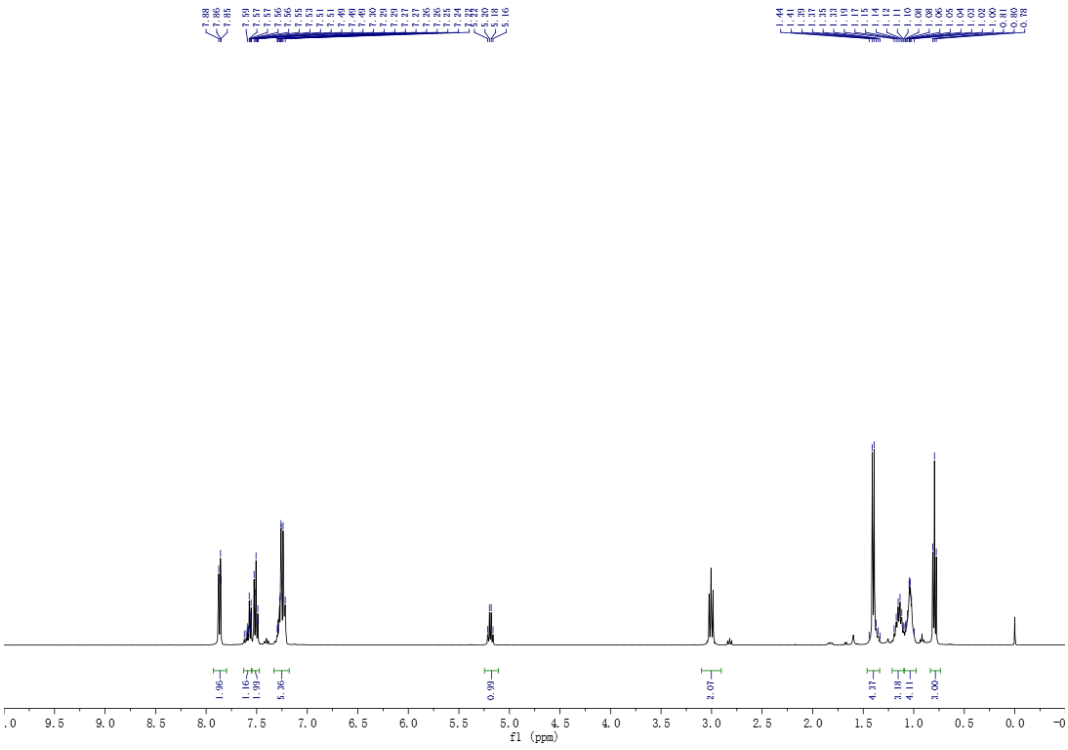
^{1}H NMR of compound **21**



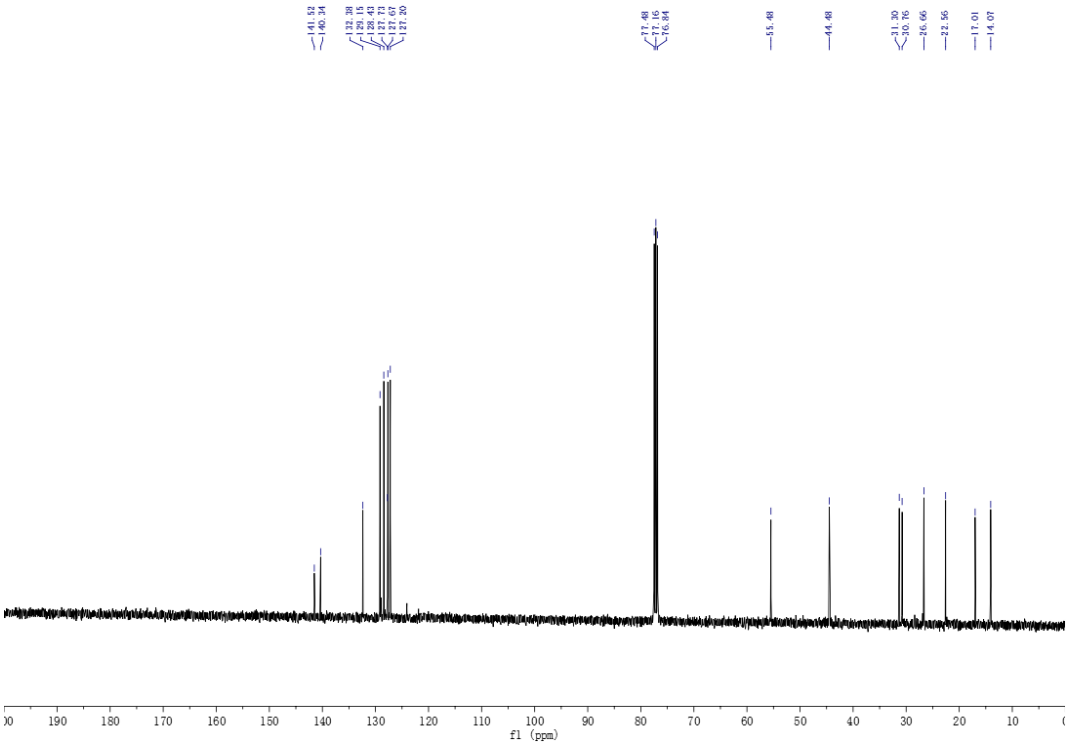
^{13}C NMR of compound **21**



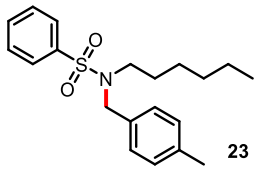
22



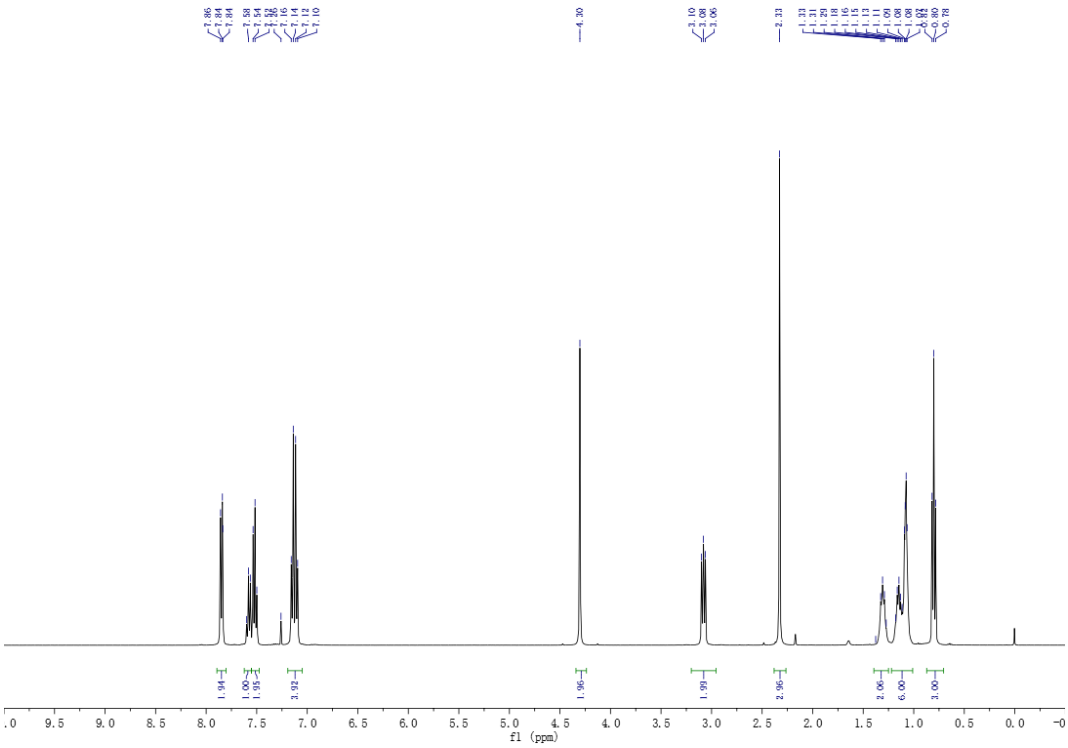
^{1}H NMR of compound **22**



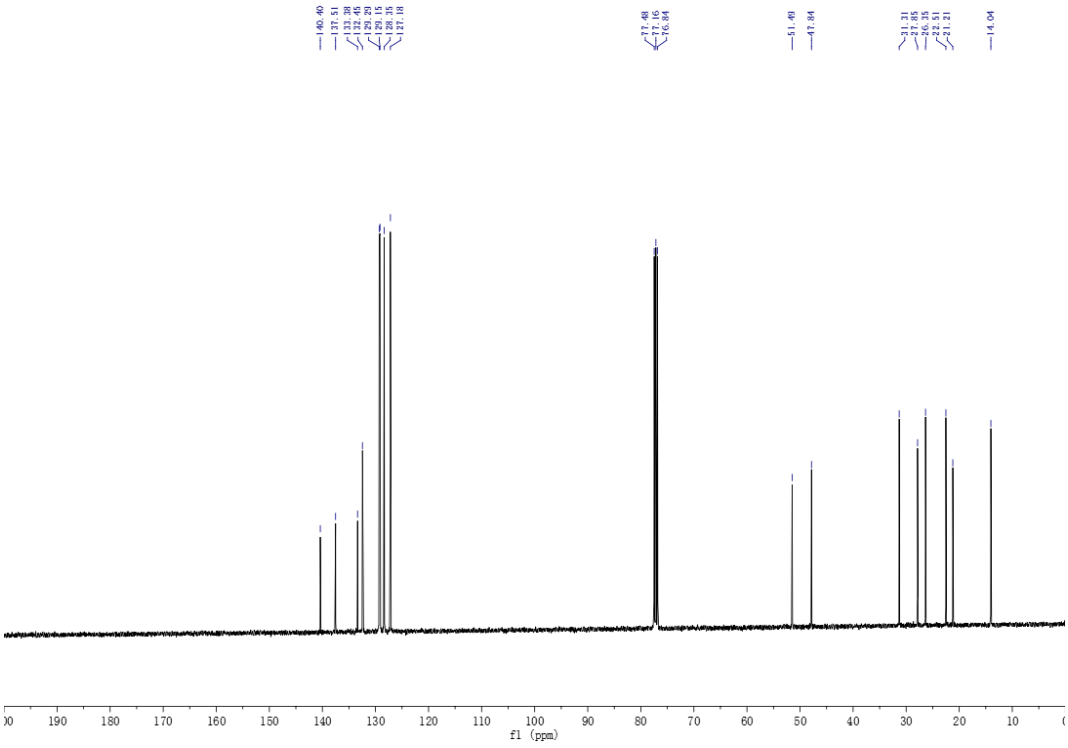
^{13}C NMR of compound **22**



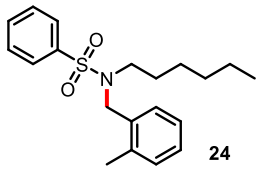
23



^{1}H NMR of compound **23**



^{13}C NMR of compound **23**



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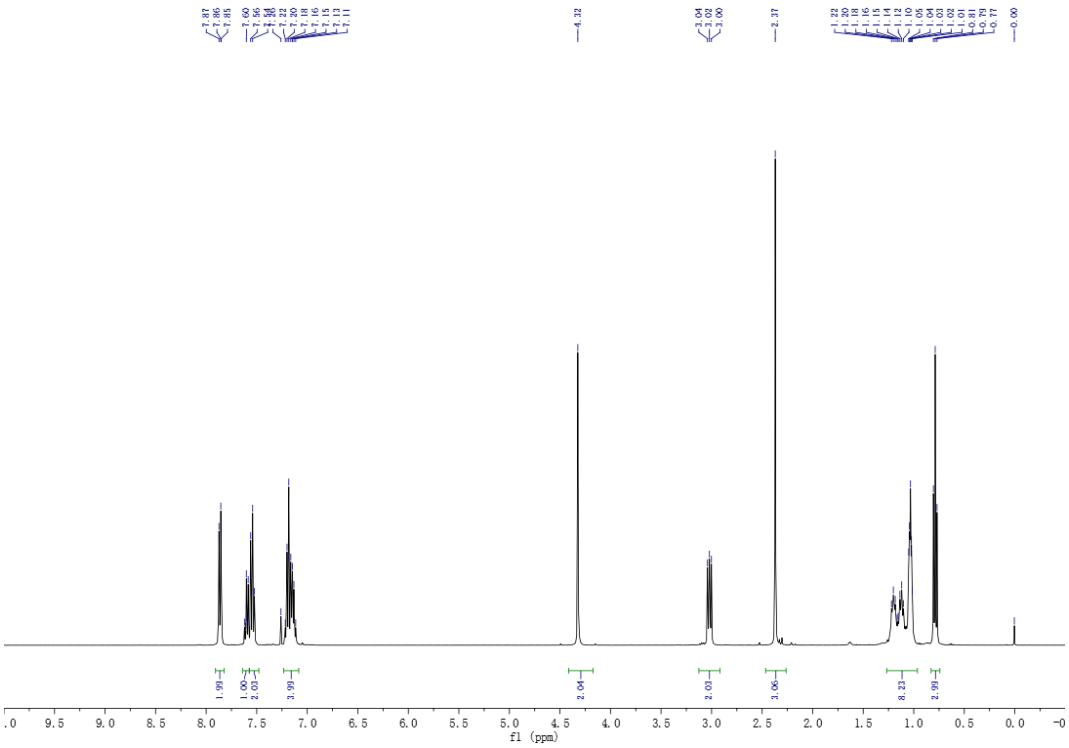
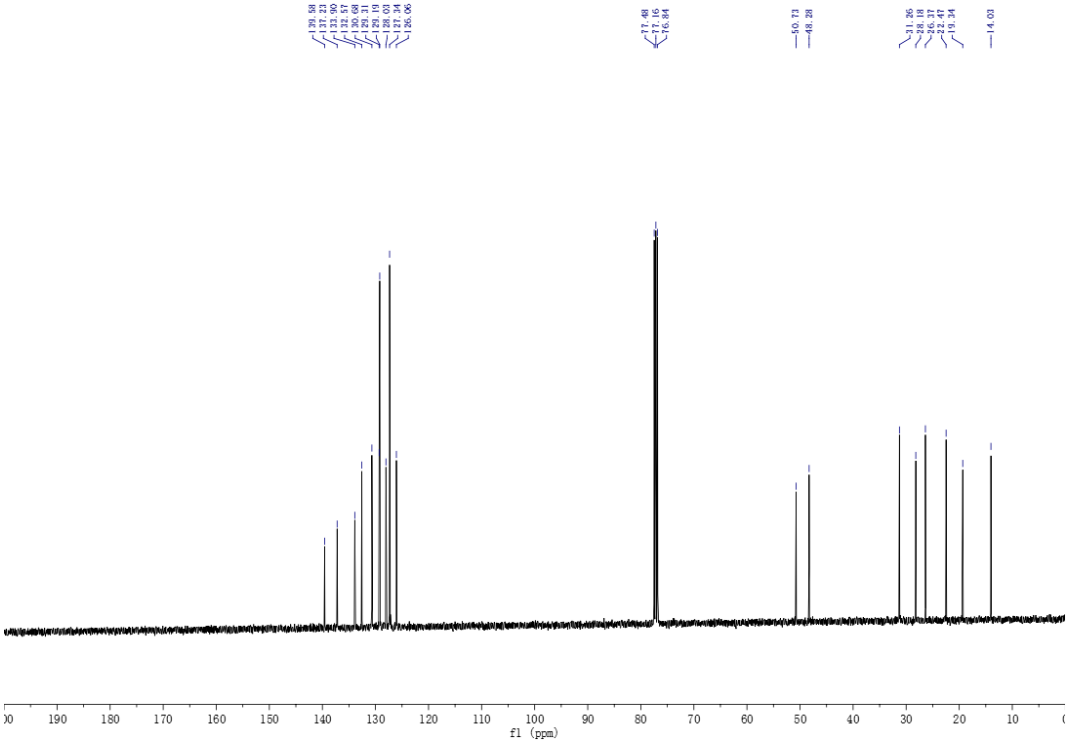
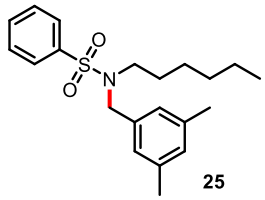


^{1}H NMR of compound **24**



^{13}C NMR of compound **24**



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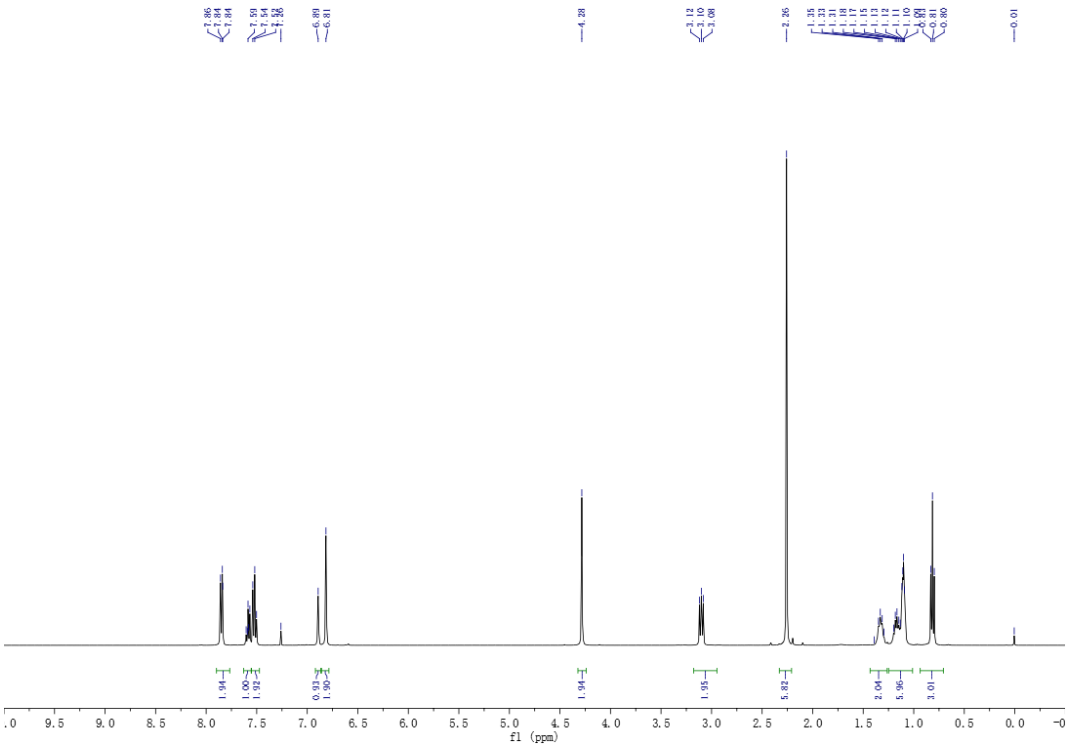
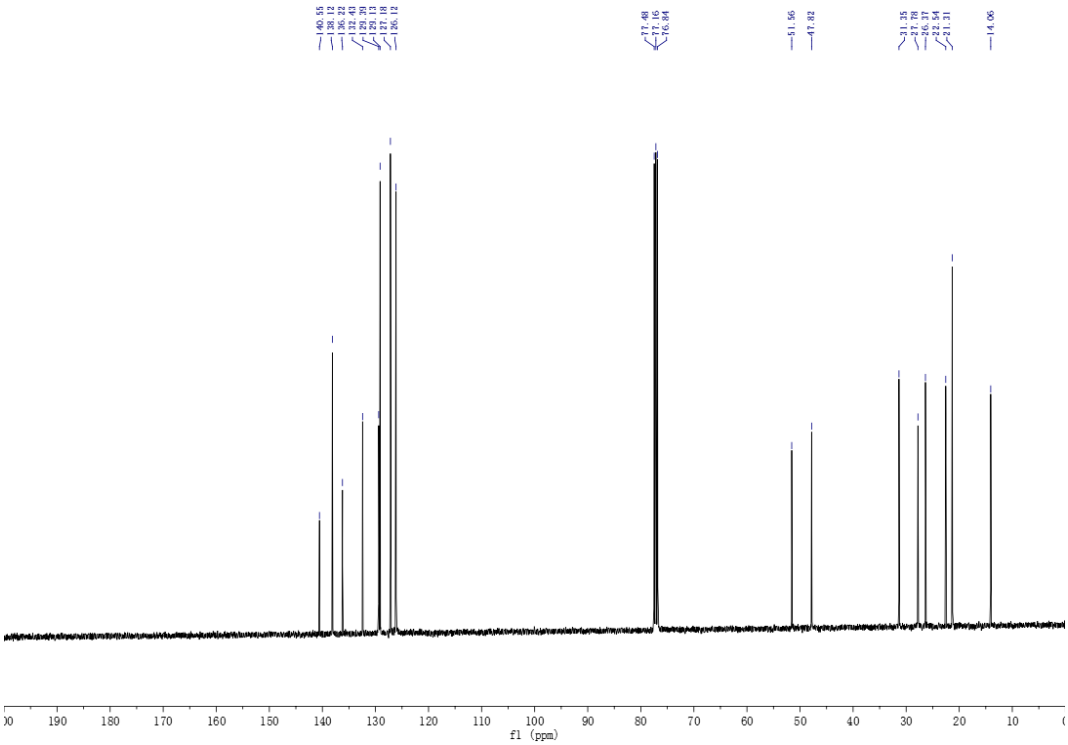
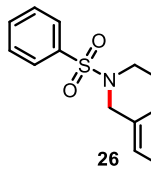
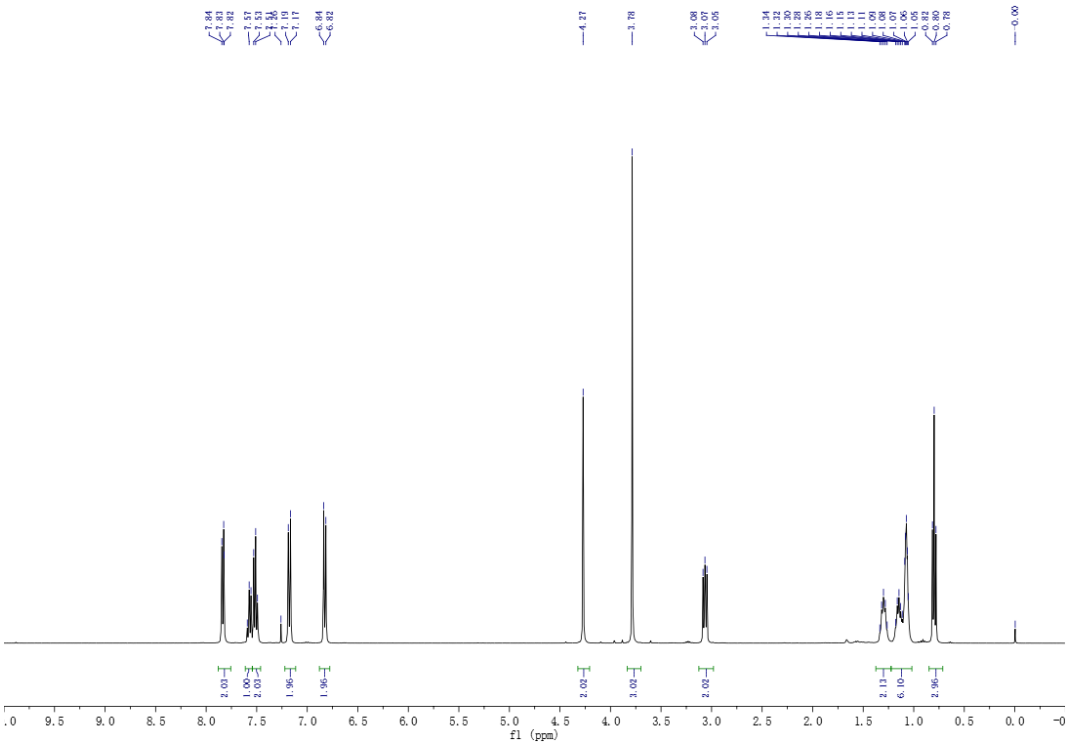


^{1}H NMR of compound **25**

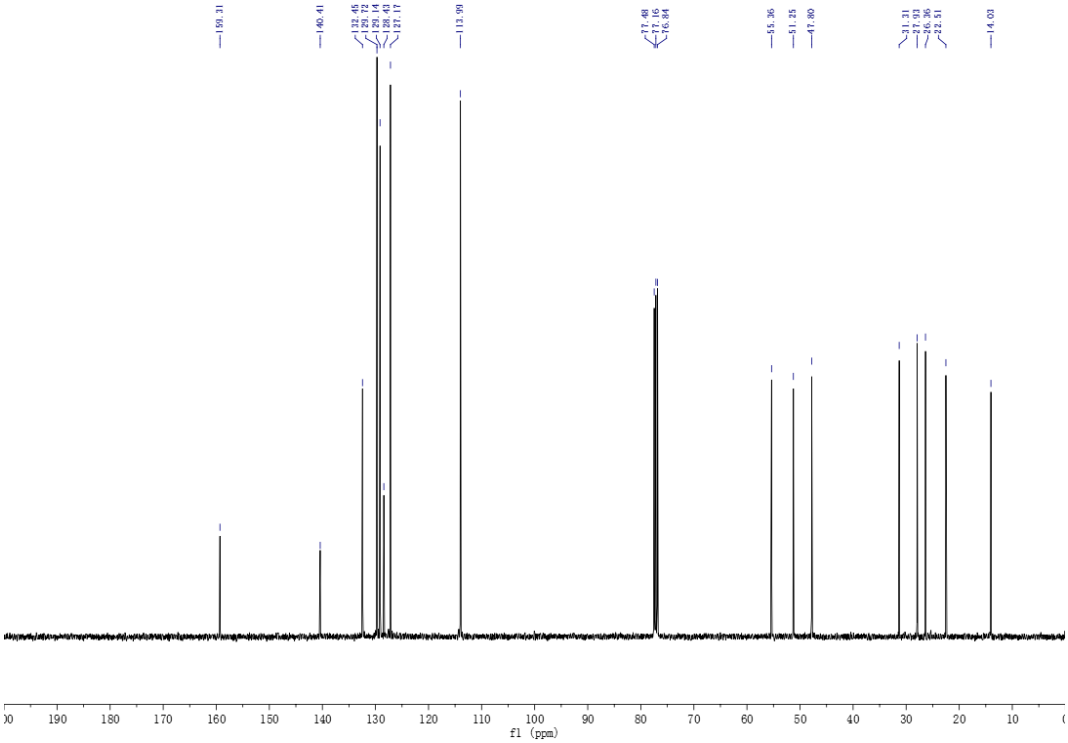


^{13}C NMR of compound **25**

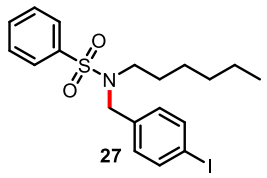


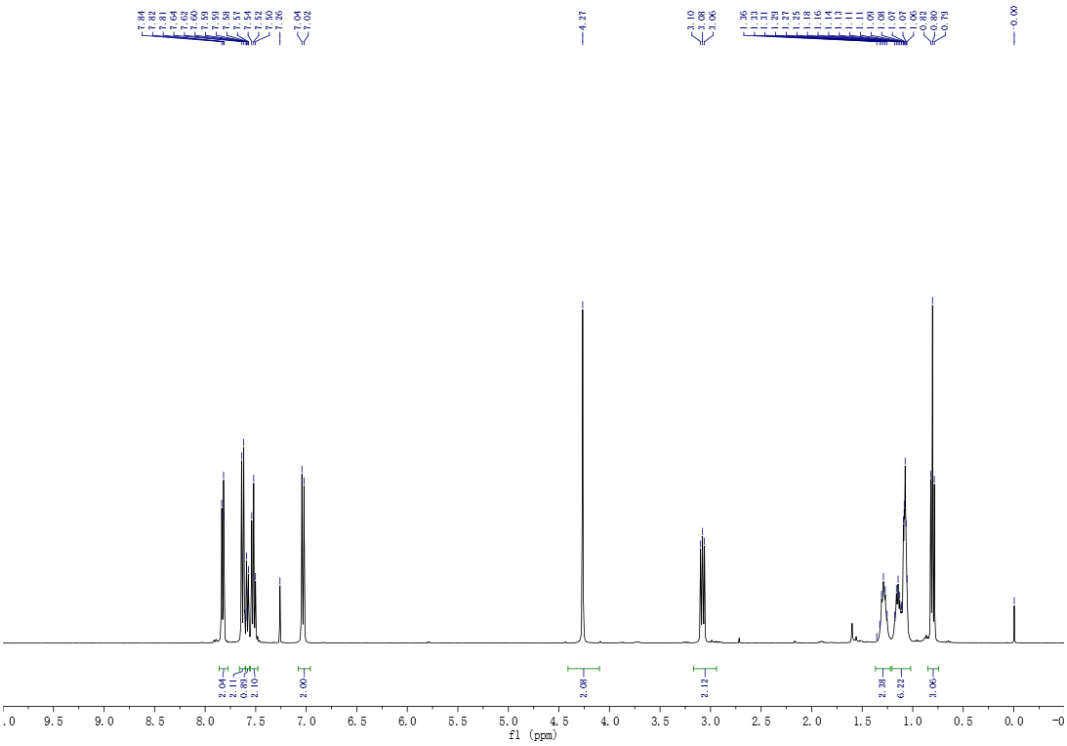


^{1}H NMR of compound **26**

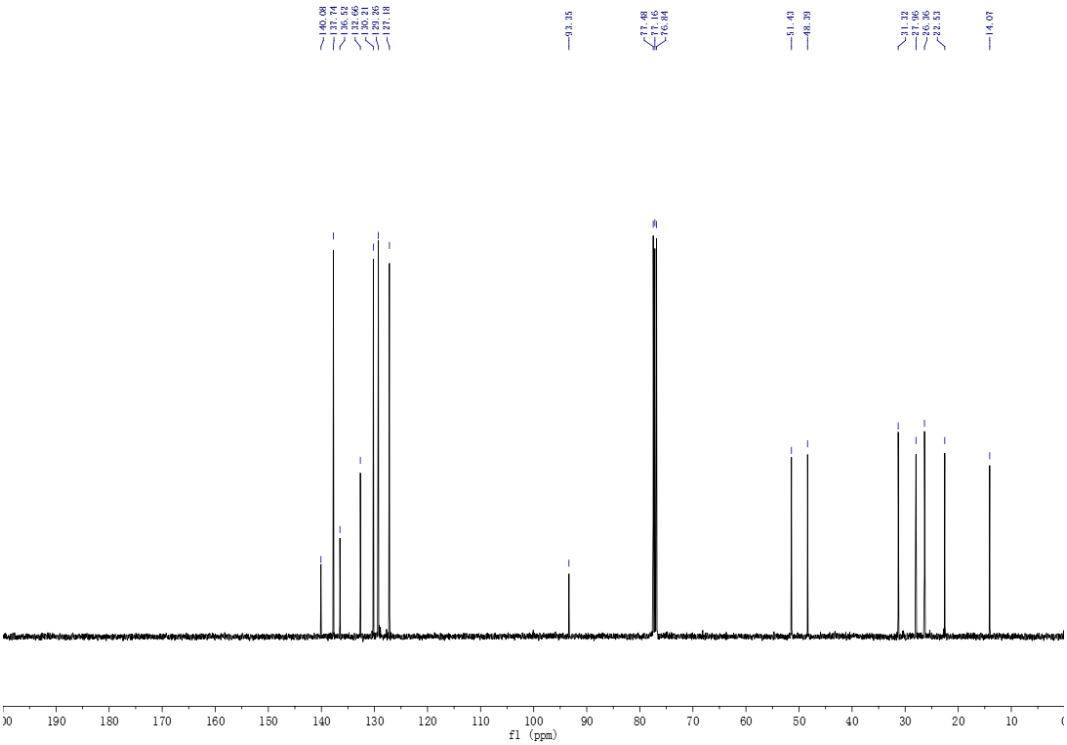


^{13}C NMR of compound **26**

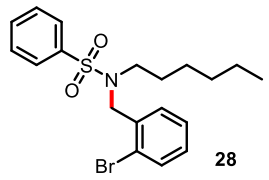




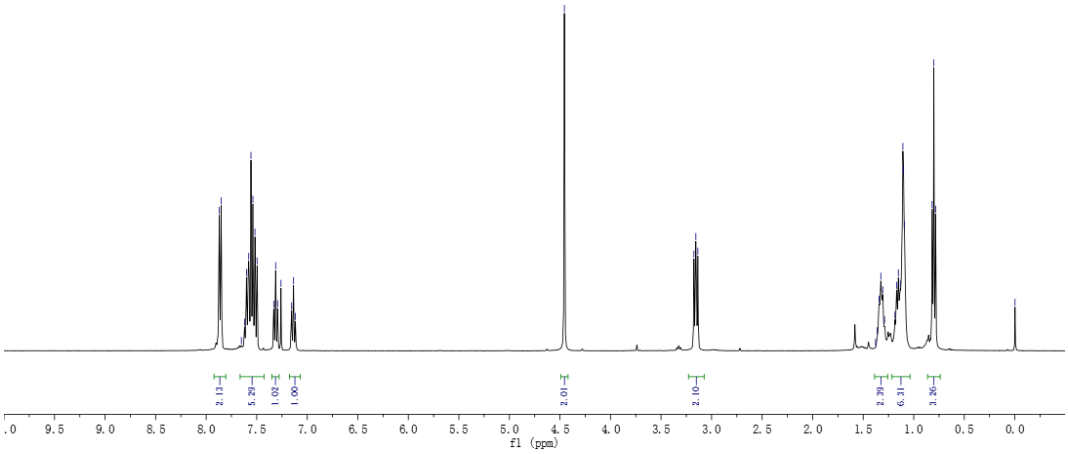
^{1}H NMR of compound **27**



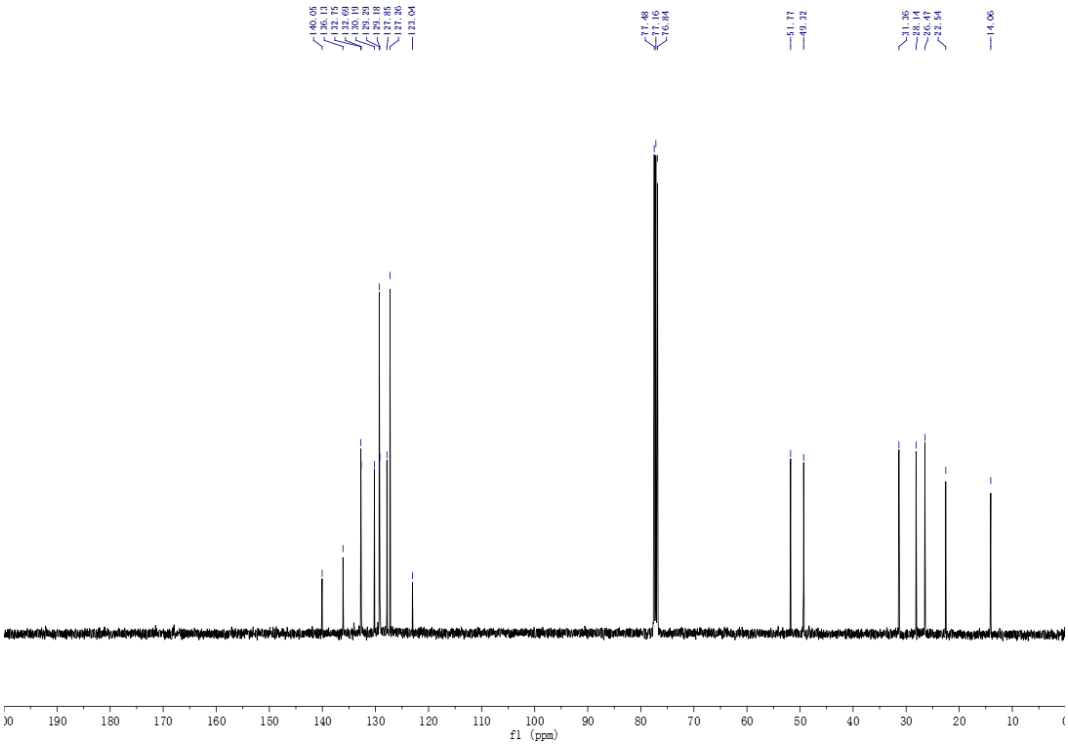
^{13}C NMR of compound **27**



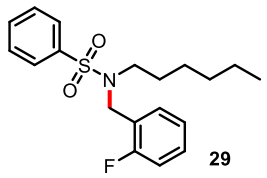
28



^{1}H NMR of compound **28**



^{13}C NMR of compound **28**



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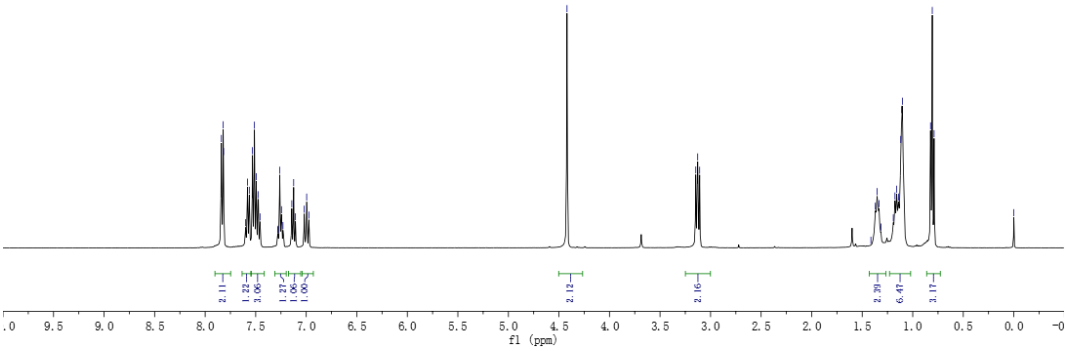
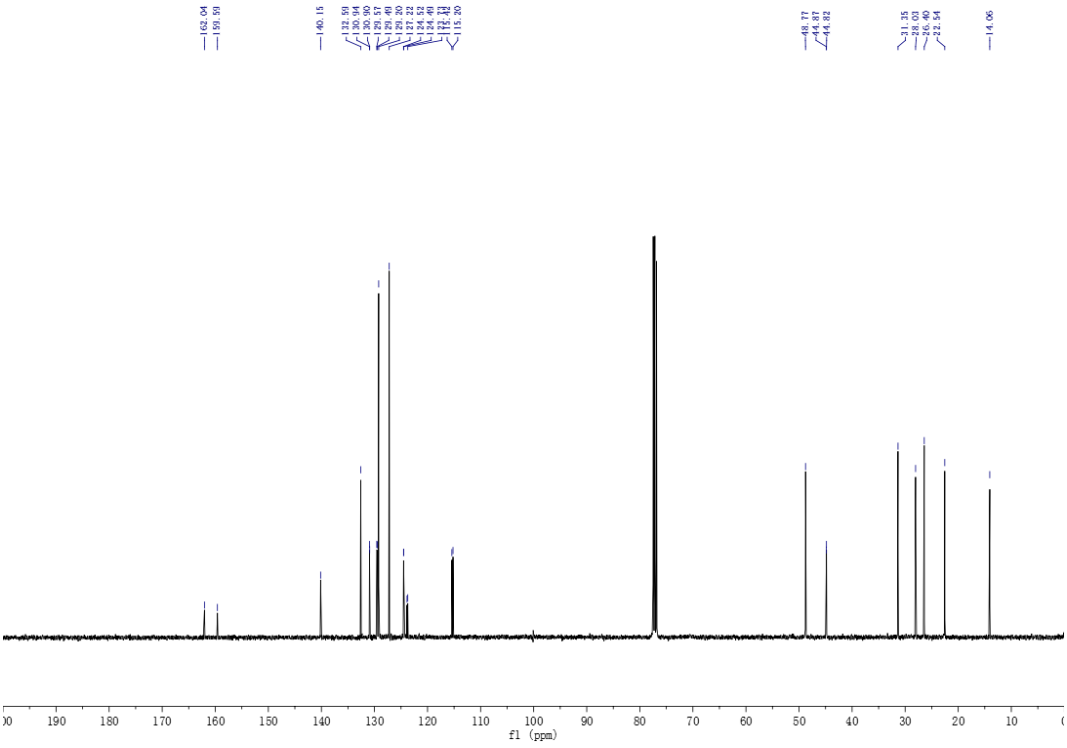
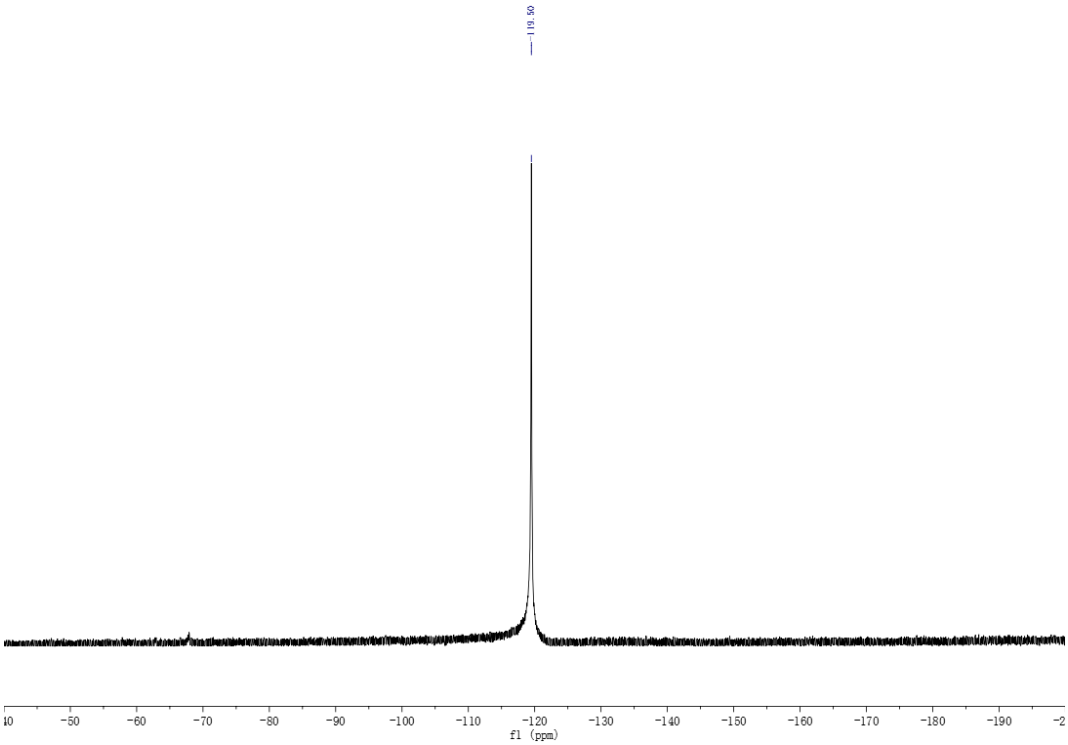


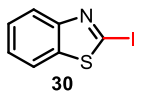
^{1}H NMR of compound **29**



^{13}C NMR of compound **29**



^{19}F NMR of compound **29**



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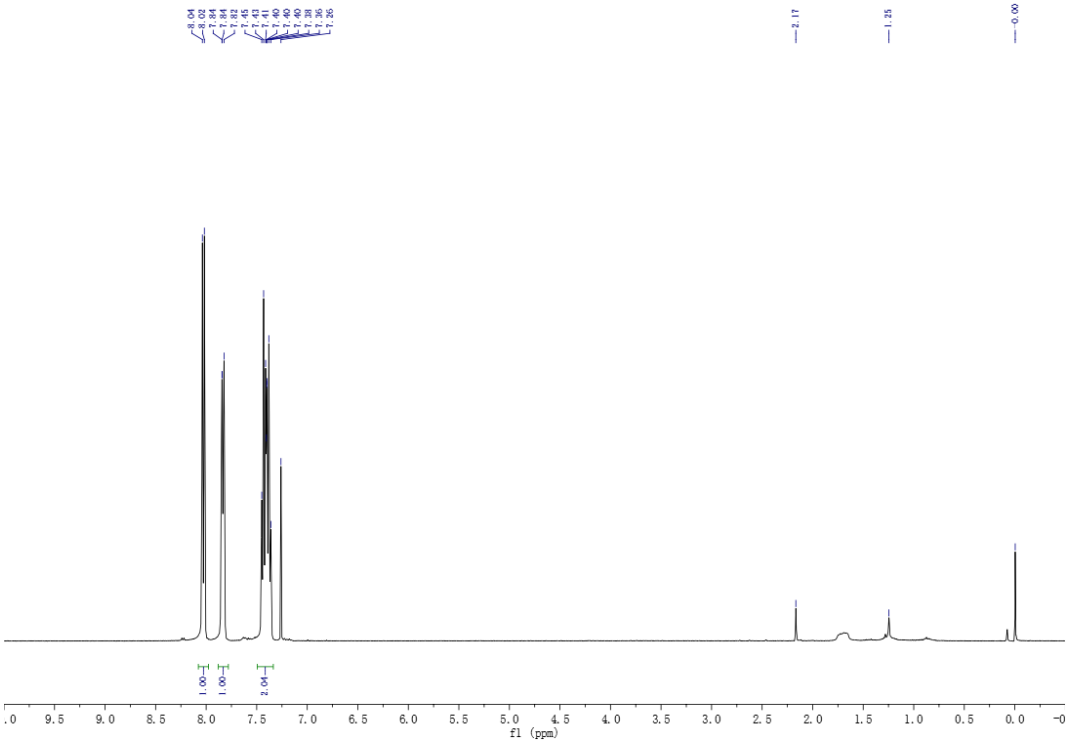
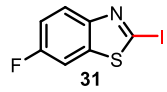
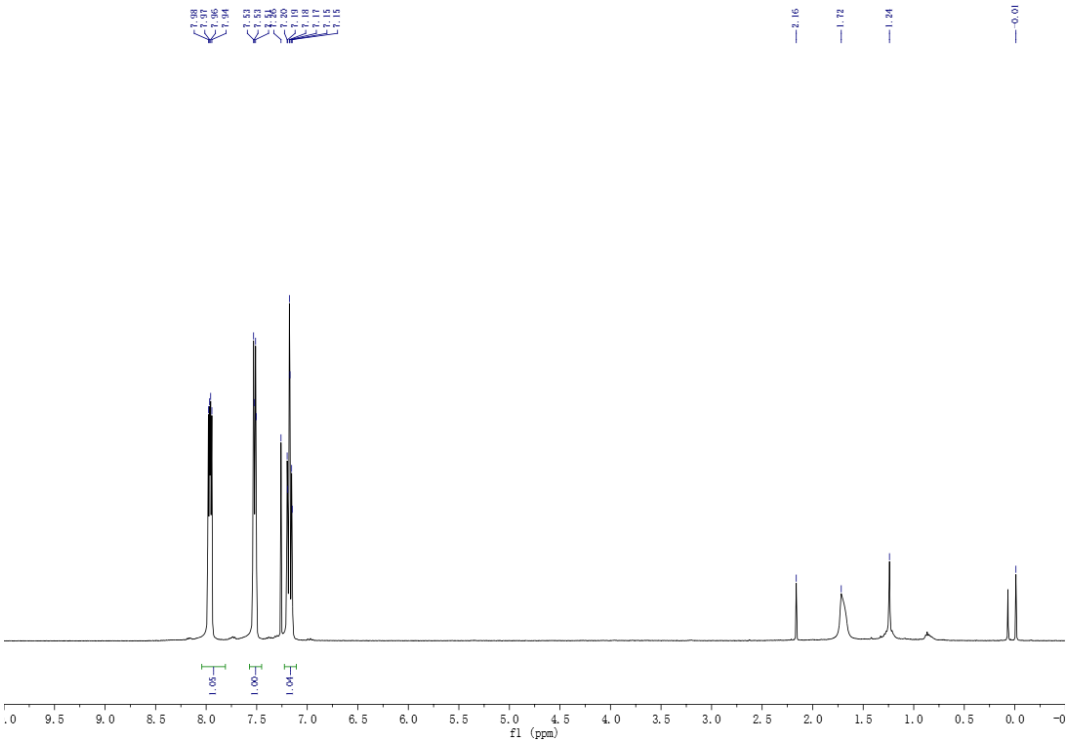


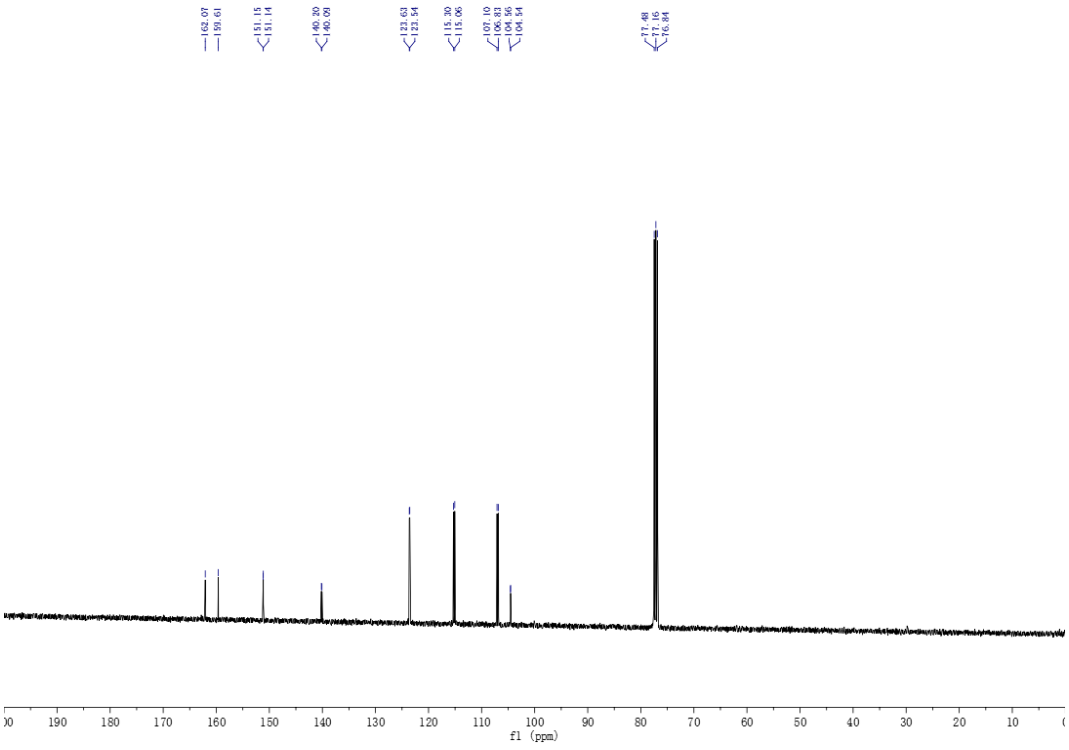
^{1}H NMR of compound **30**



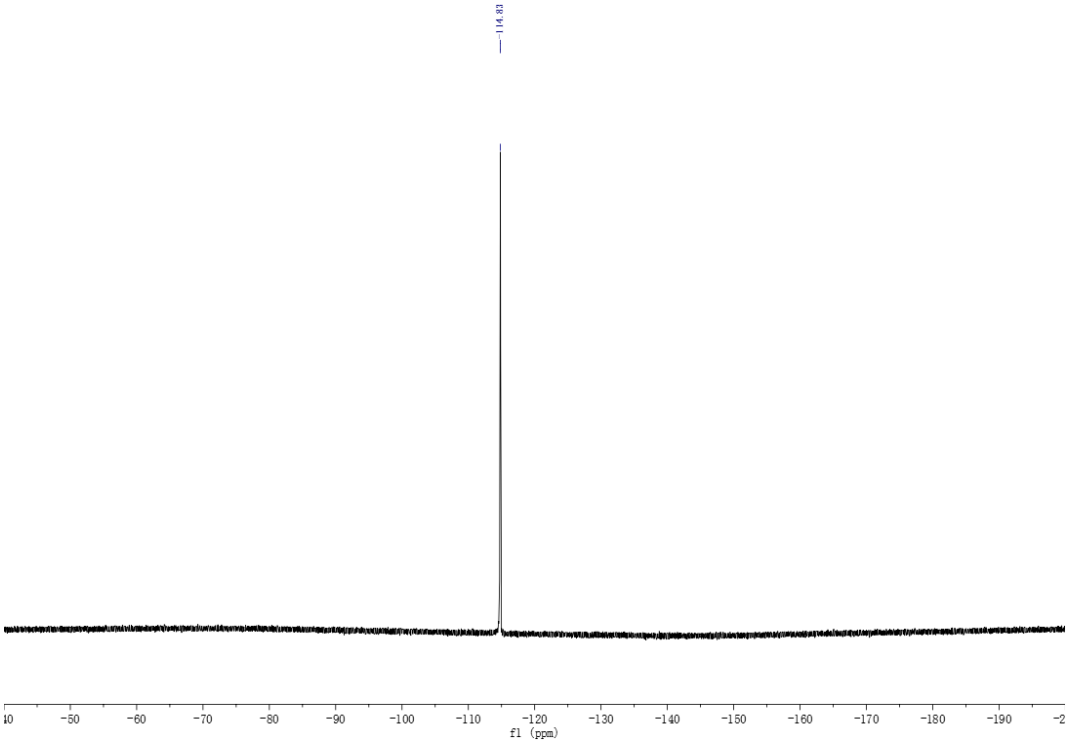
31



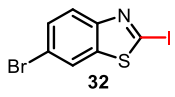
^{1}H NMR of compound **31**



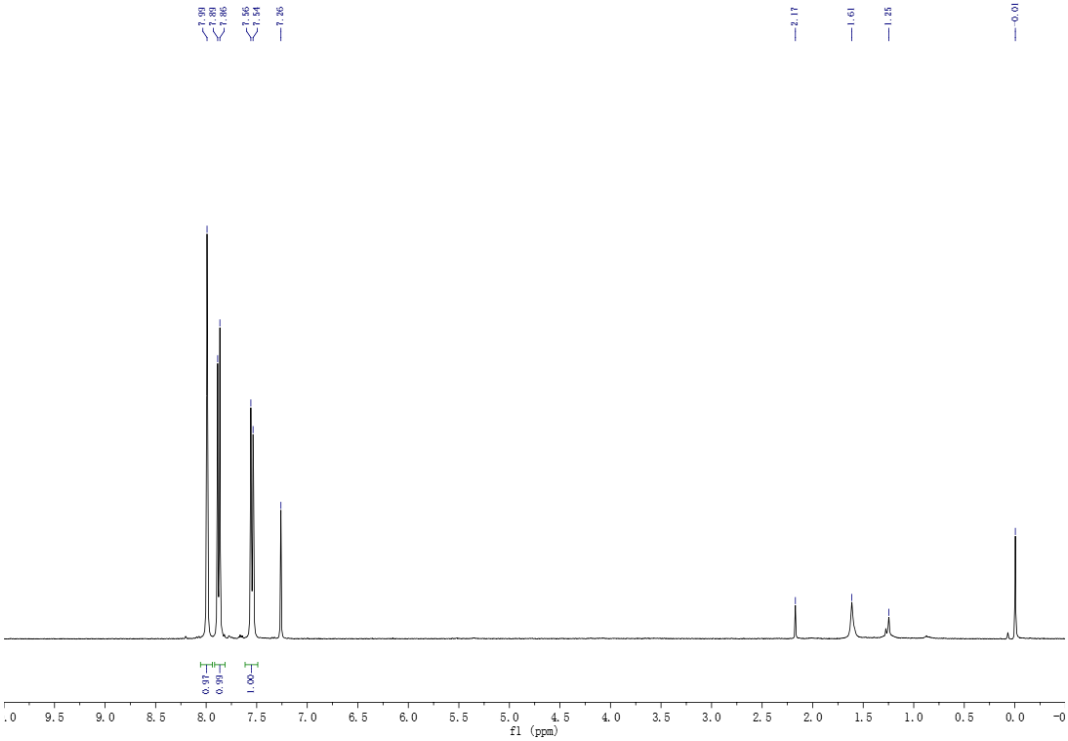
^{13}C NMR of compound **31**



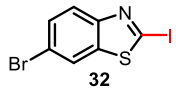
^{19}F NMR of compound **31**



32



^{1}H NMR of compound **32**



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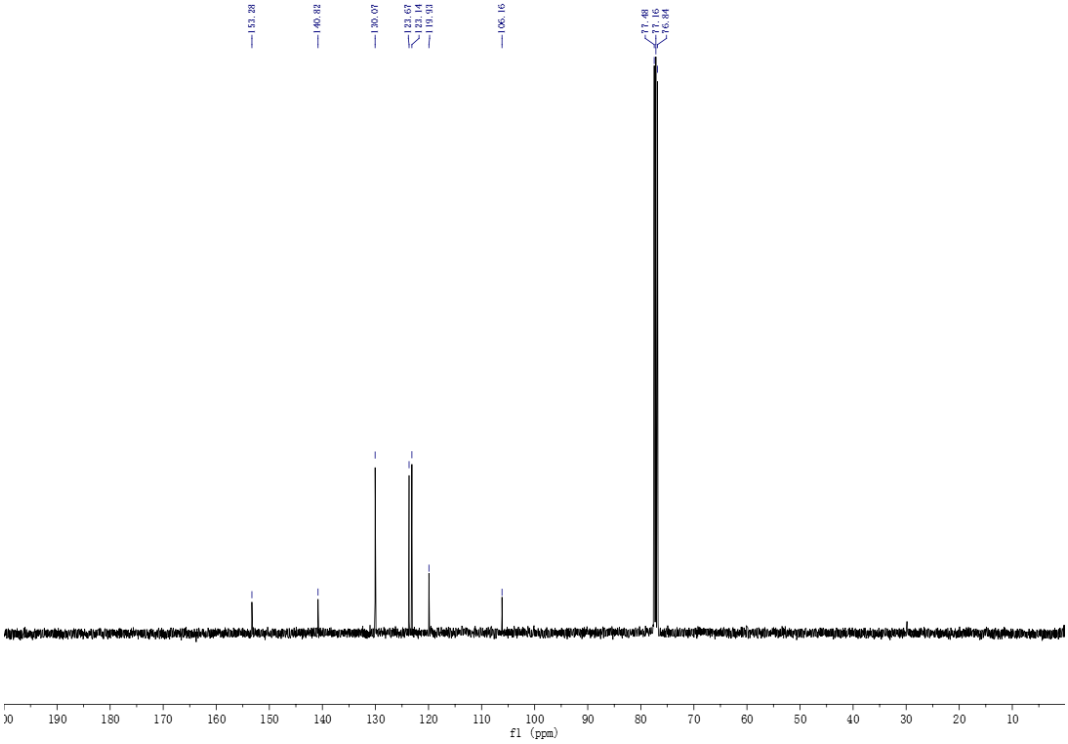
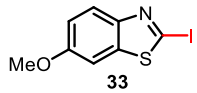
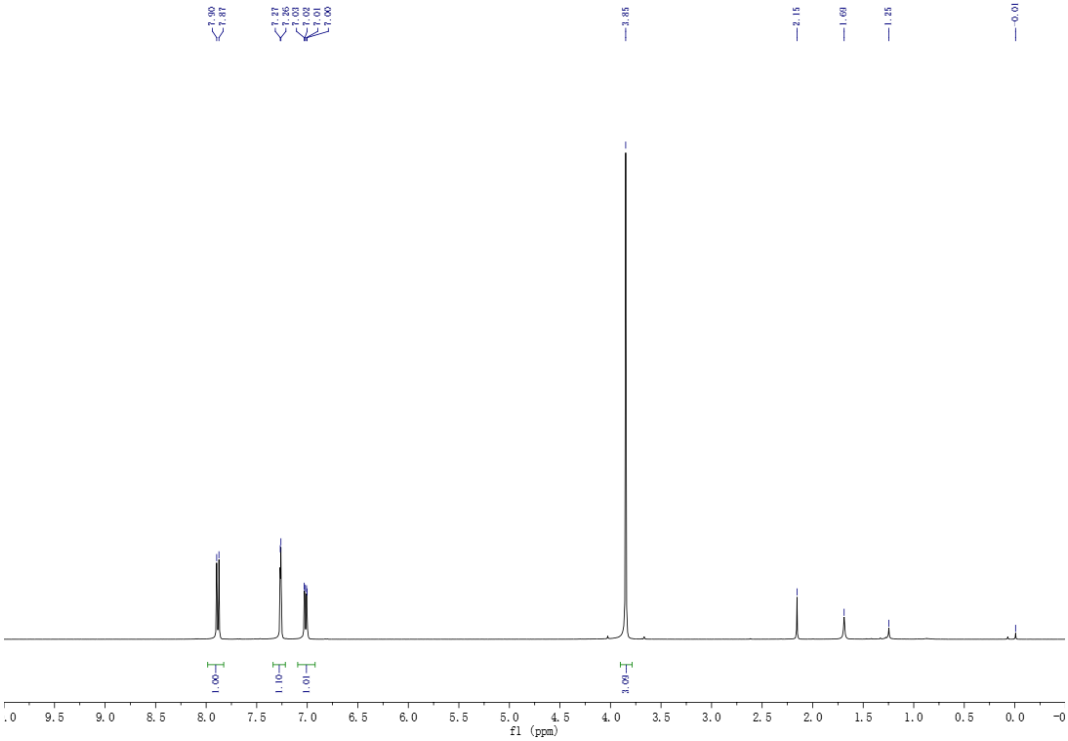


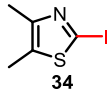
^{13}C NMR of compound **32**



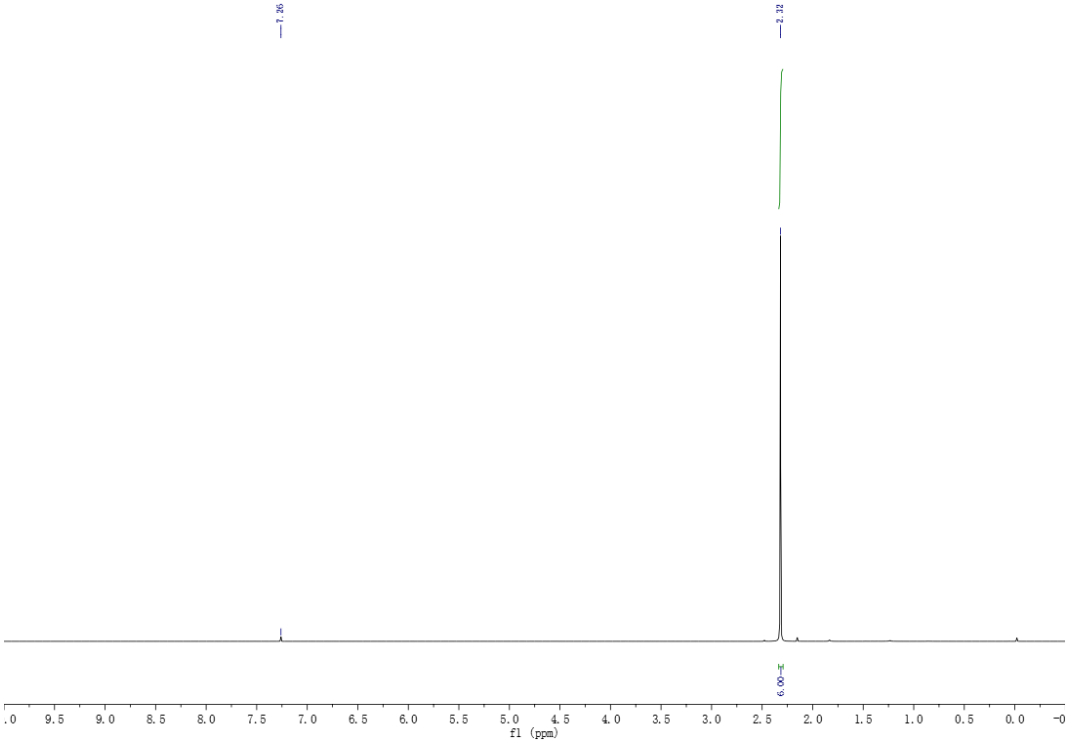
33



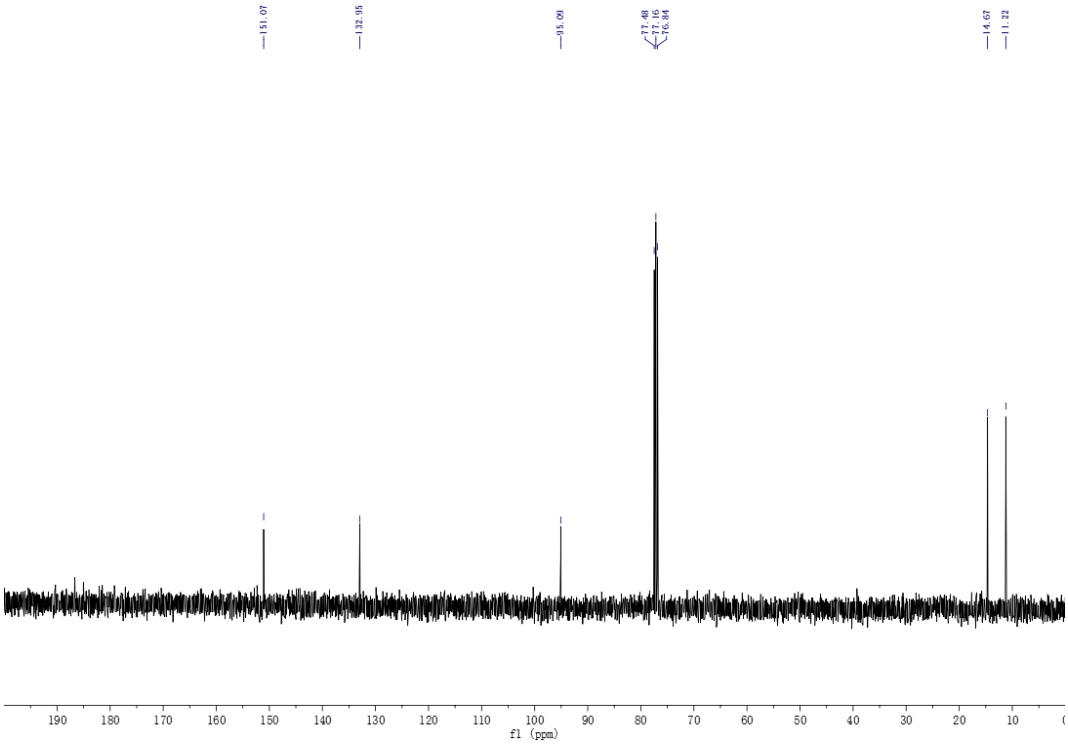
^{1}H NMR of compound **33**



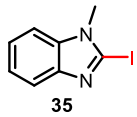
34



^{1}H NMR of compound **34**



^{13}C NMR of compound **34**



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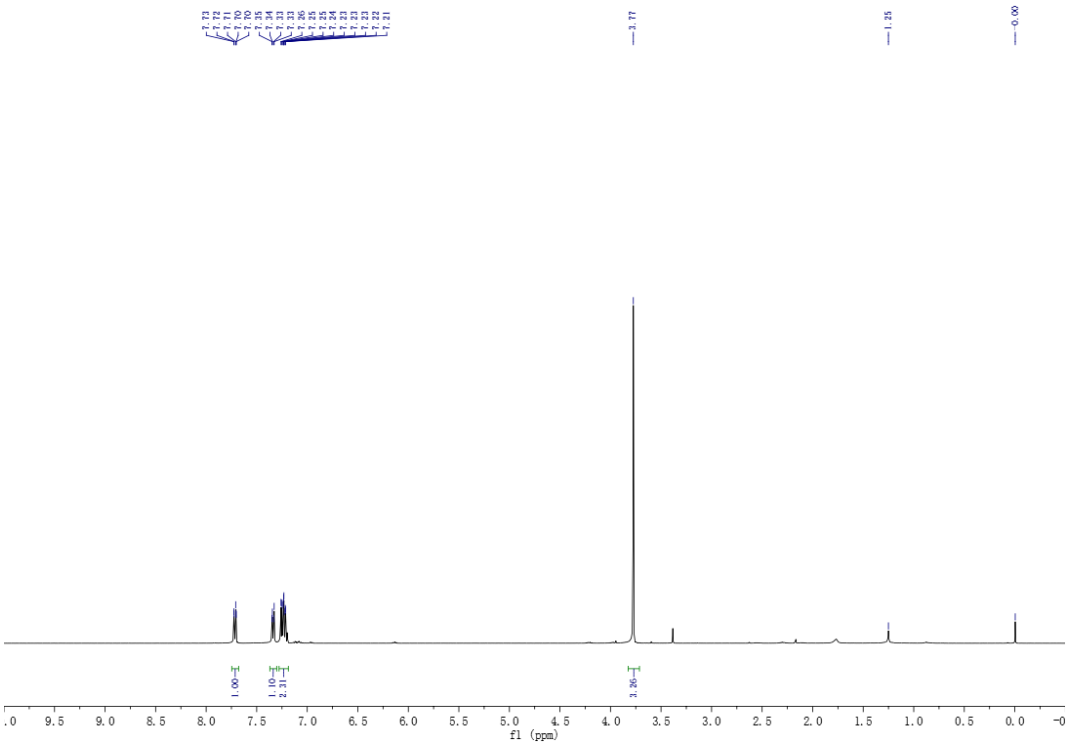
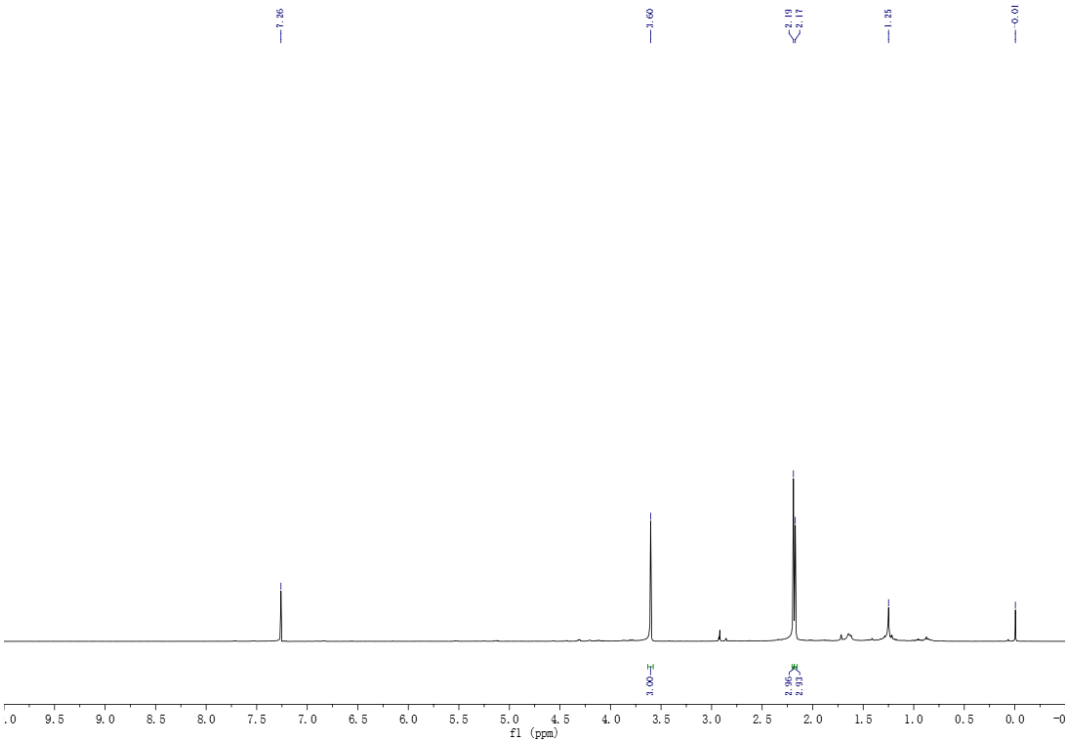
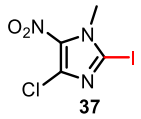


^{1}H NMR of compound **35**

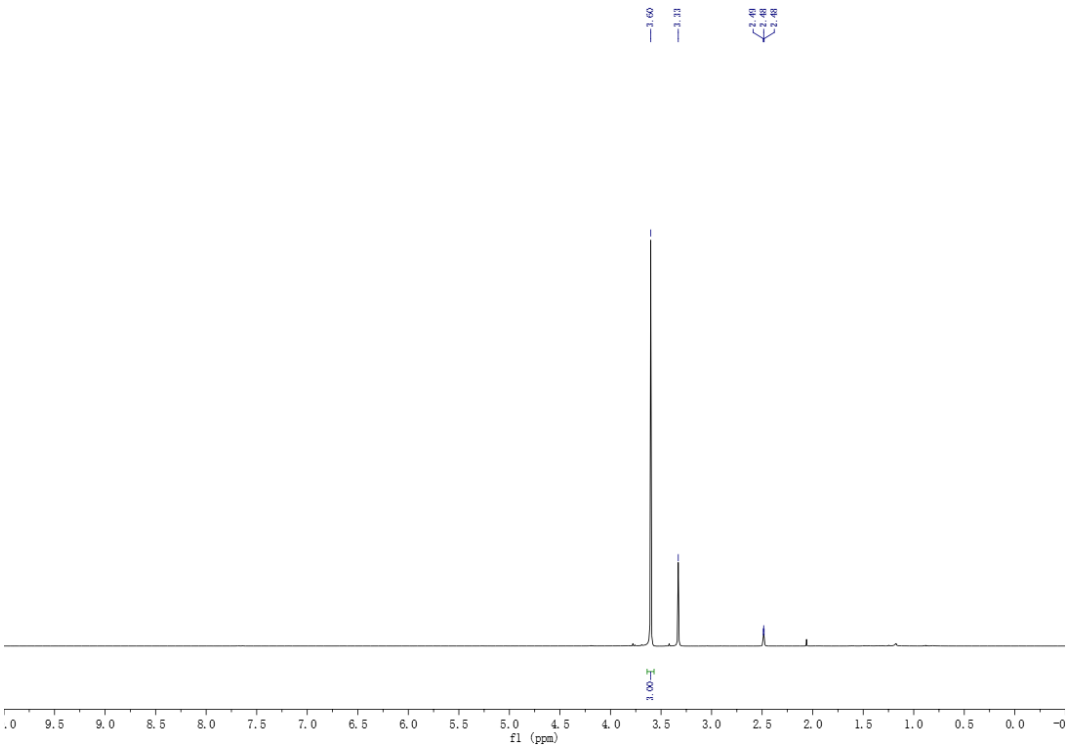
36



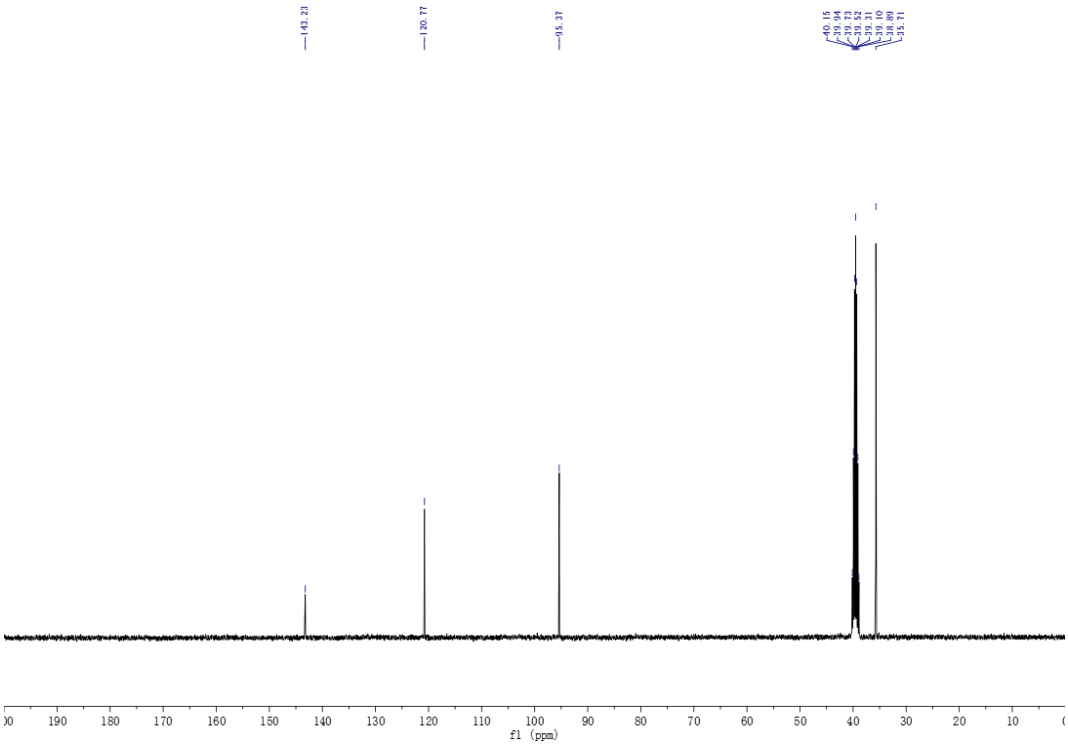
^{1}H NMR of compound **36**



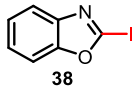
37



^{1}H NMR of compound **37**



^{13}C NMR of compound **37**



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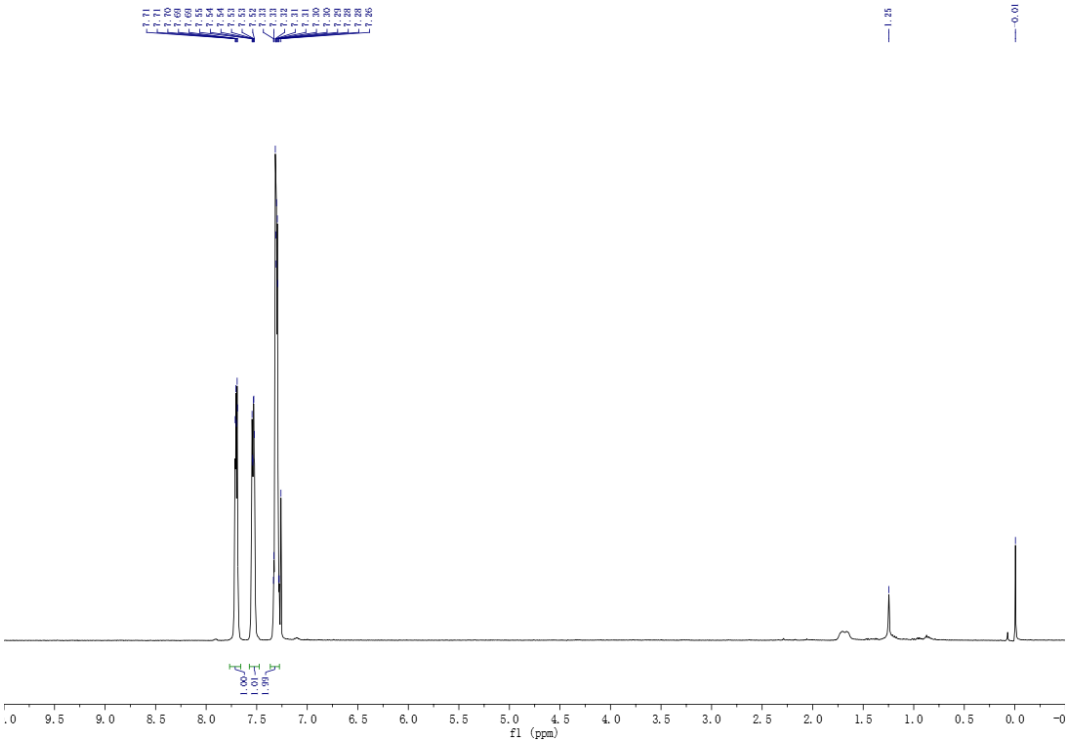
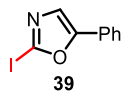


^{1}H NMR of compound **38**



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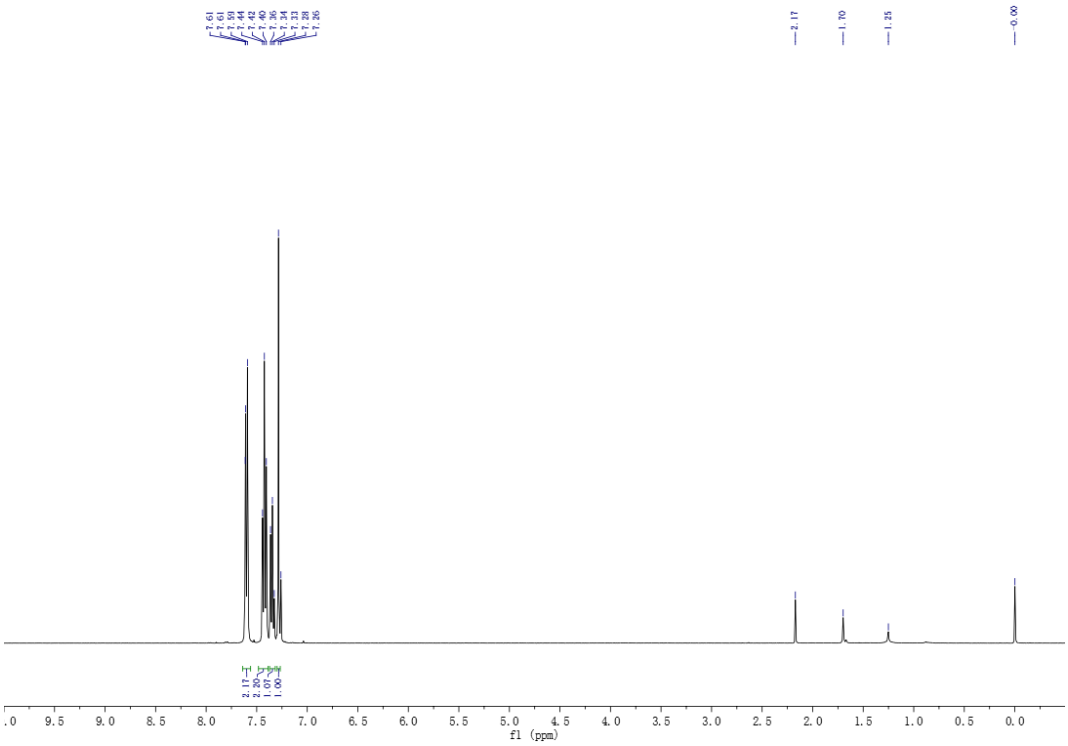
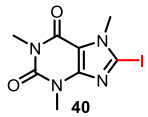


^{1}H NMR of compound **39**



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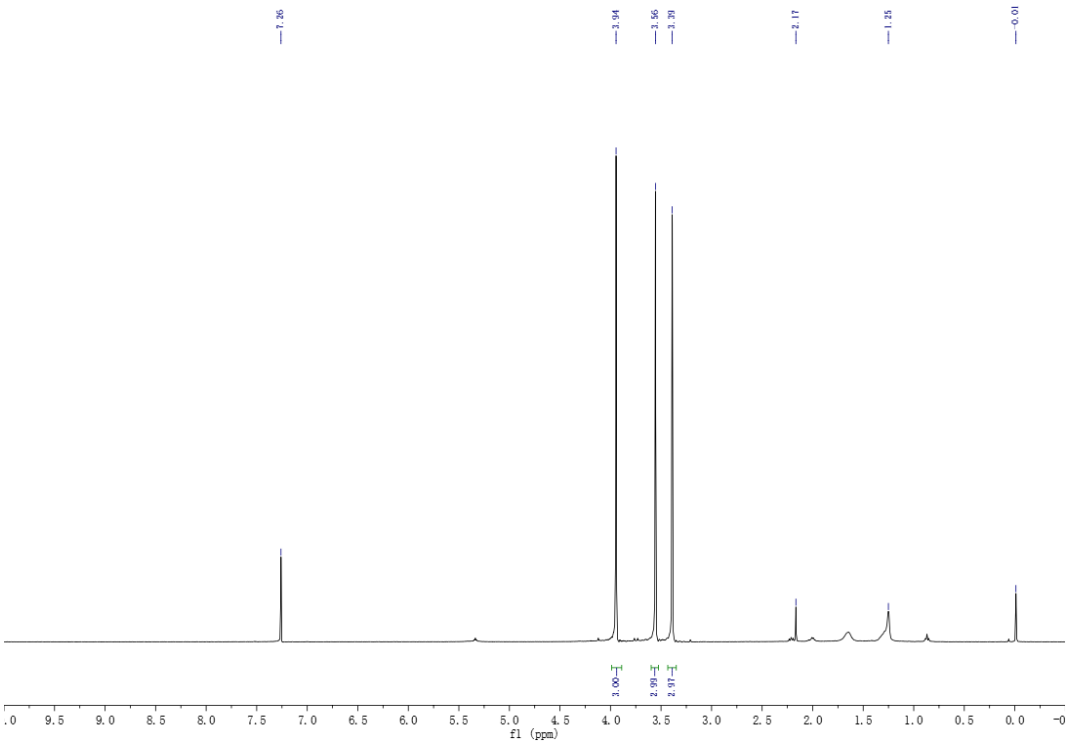
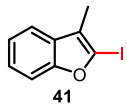


^{1}H NMR of compound **40**



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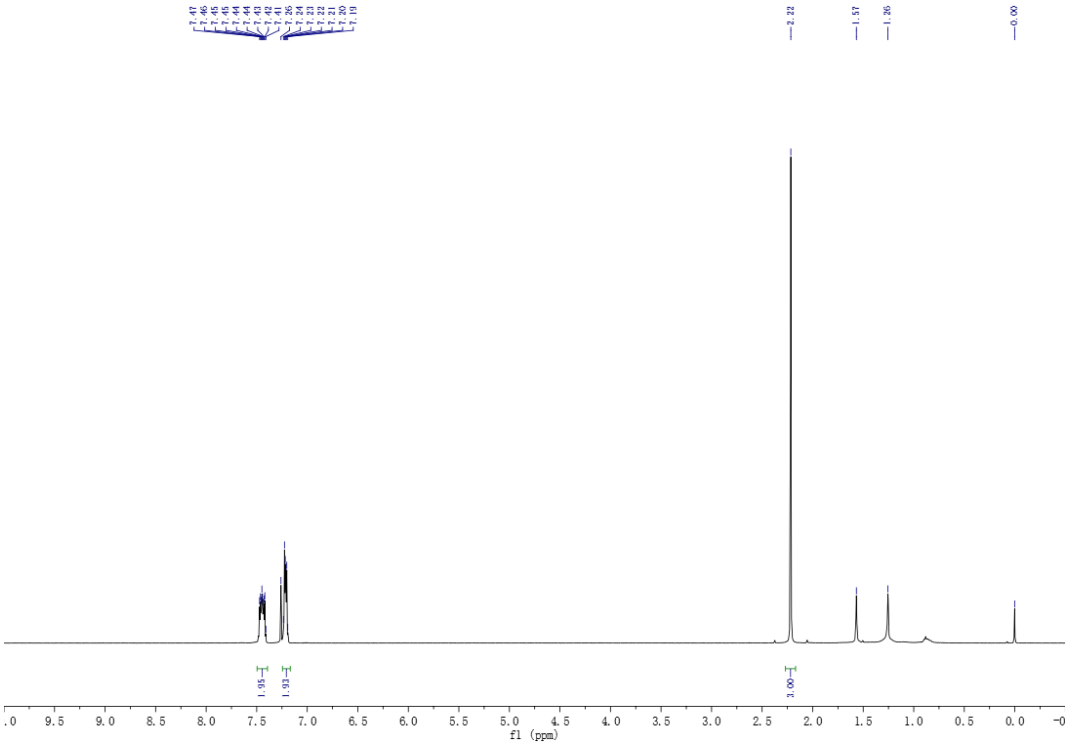
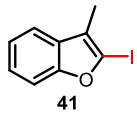
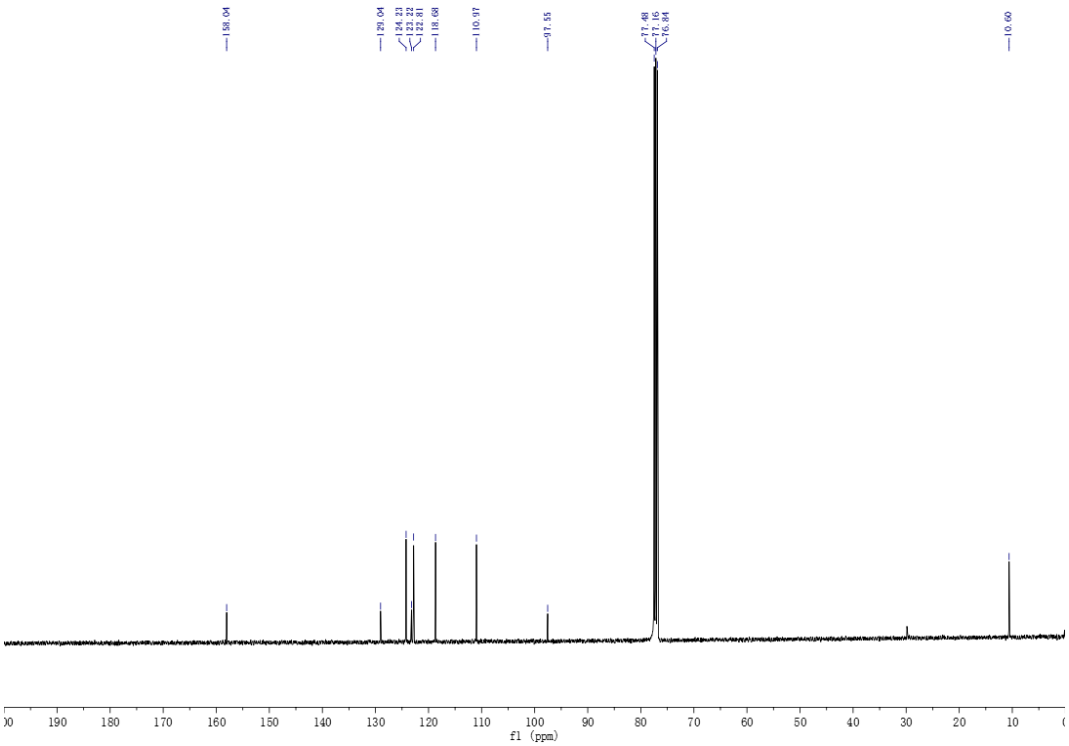


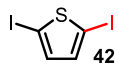
^{1}H NMR of compound **41**

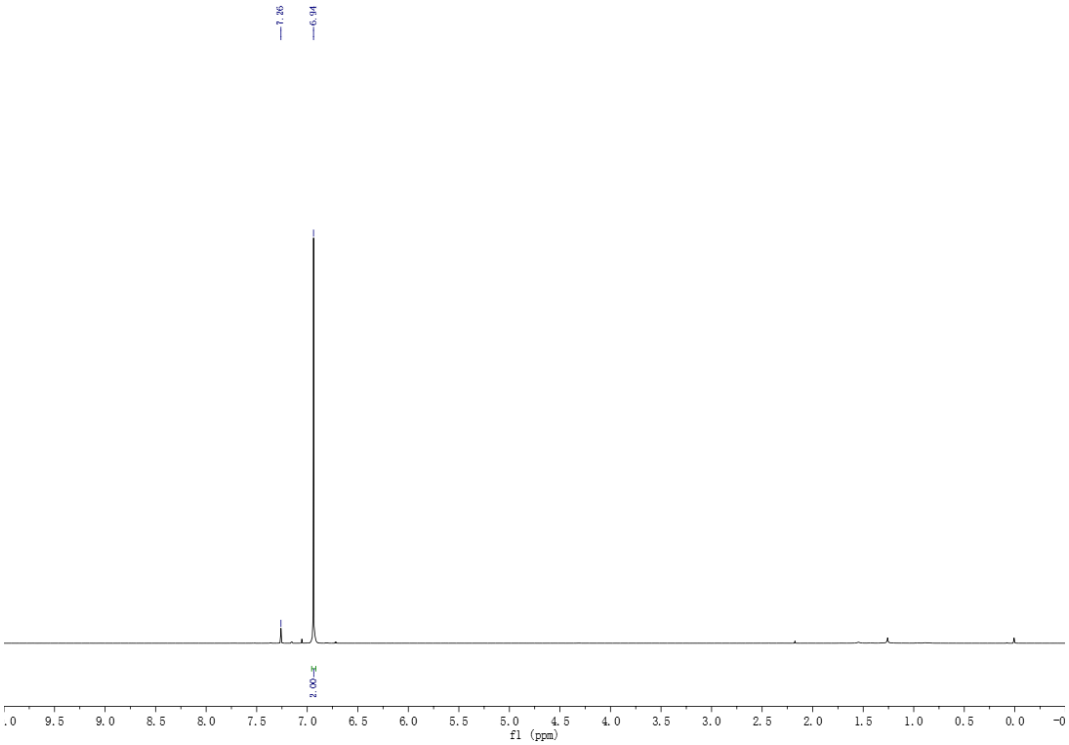


41

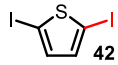


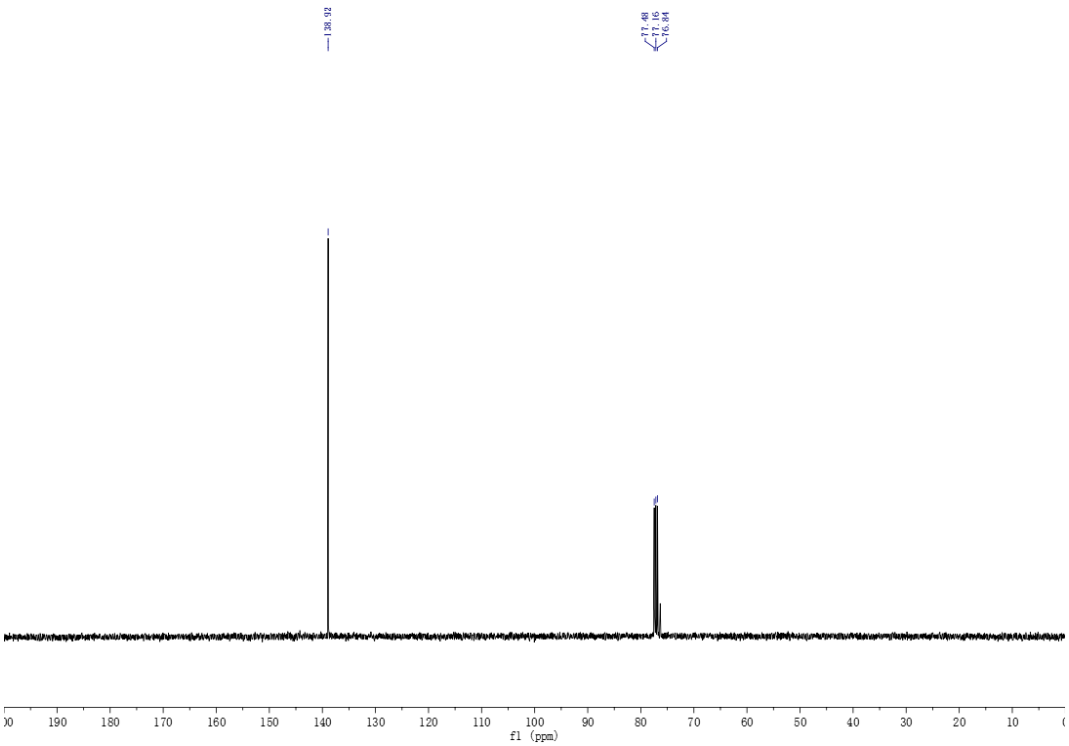
^{13}C NMR of compound **41**



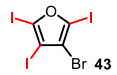


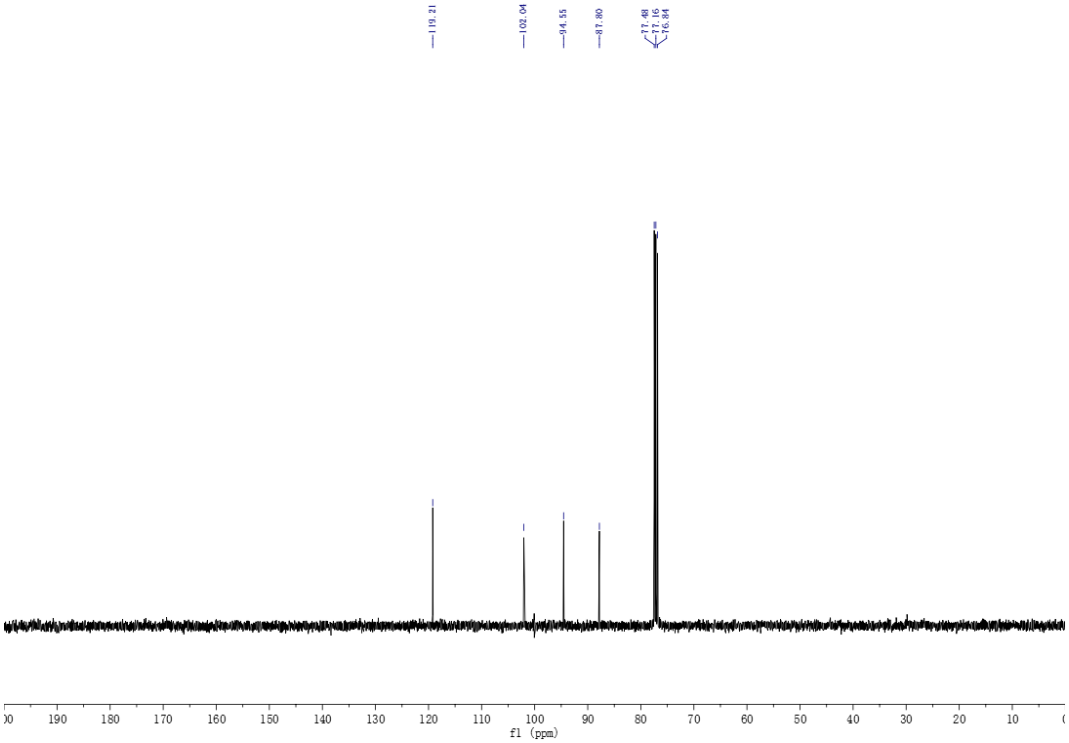
^{1}H NMR of compound **42**



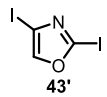


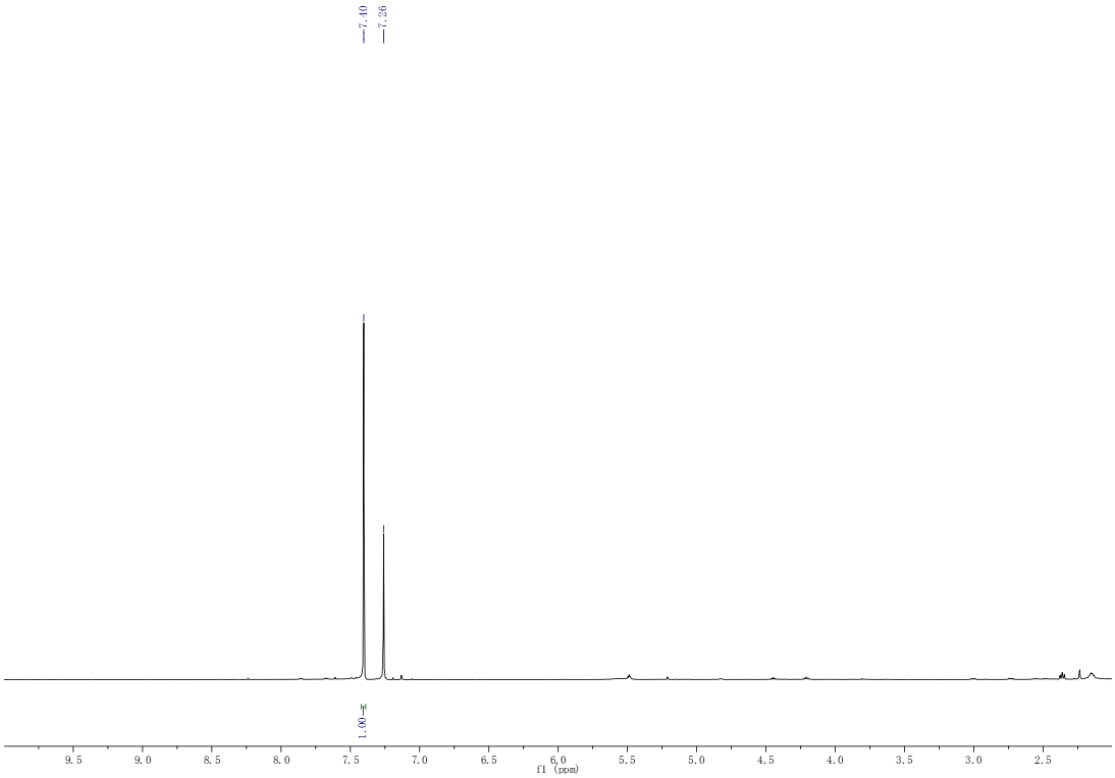
^{13}C NMR of compound **42**



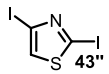


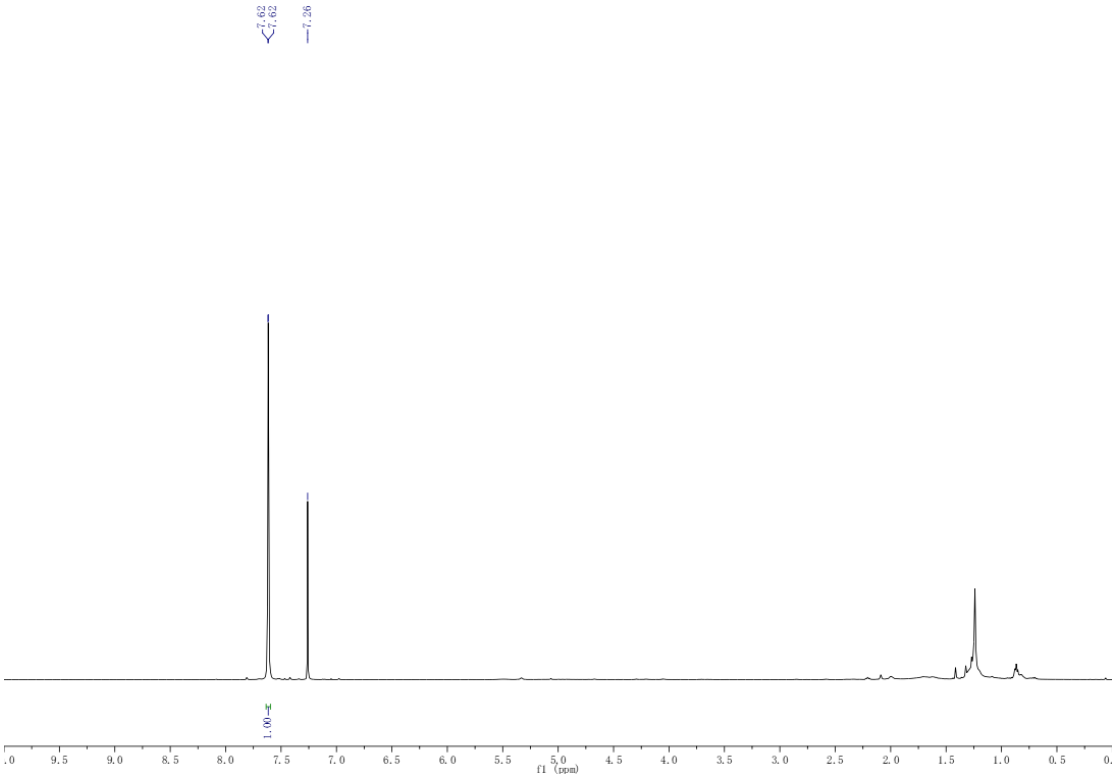
^{13}C NMR of compound **43**



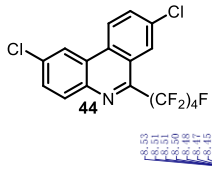


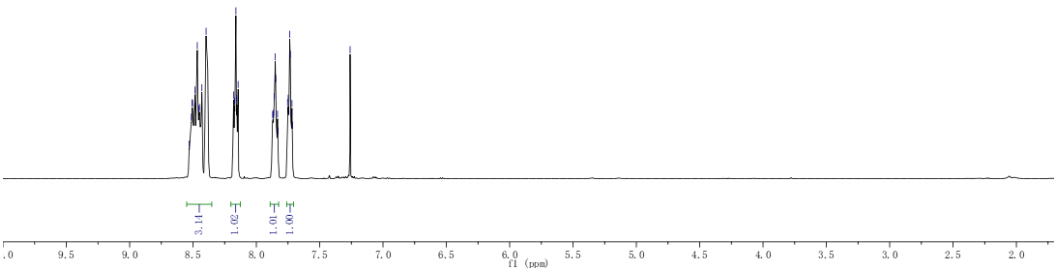
^{1}H NMR of compound **43'**



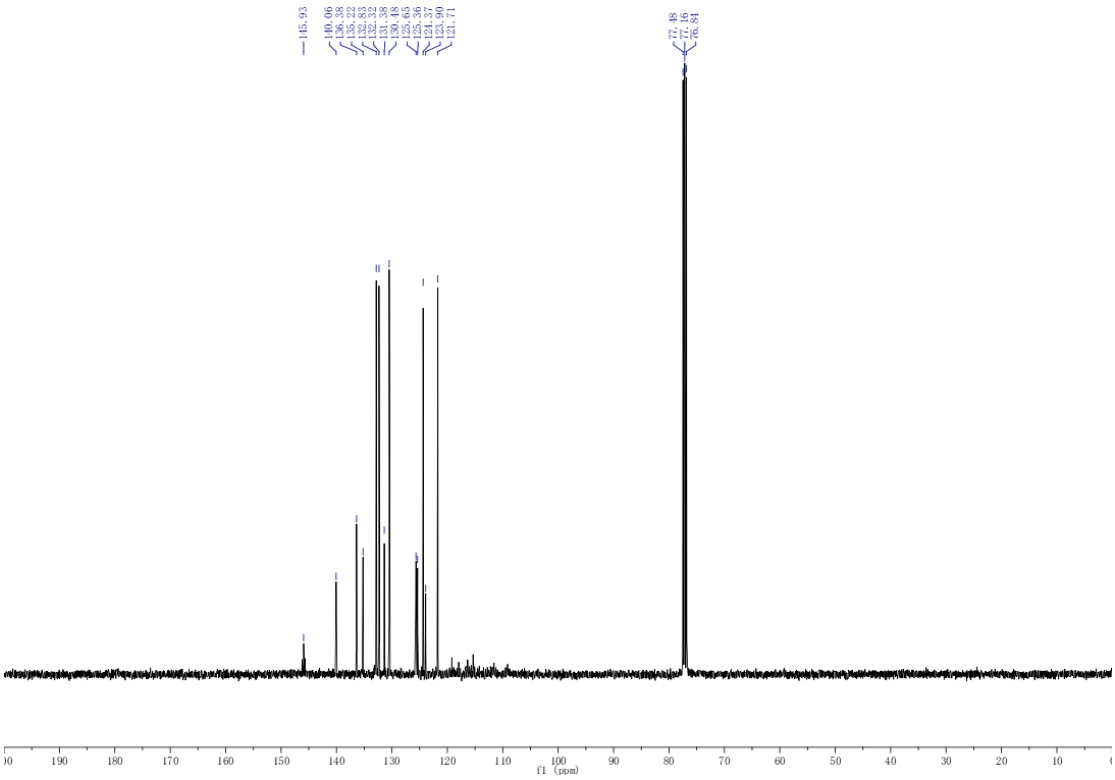


^{1}H NMR of compound **43''**

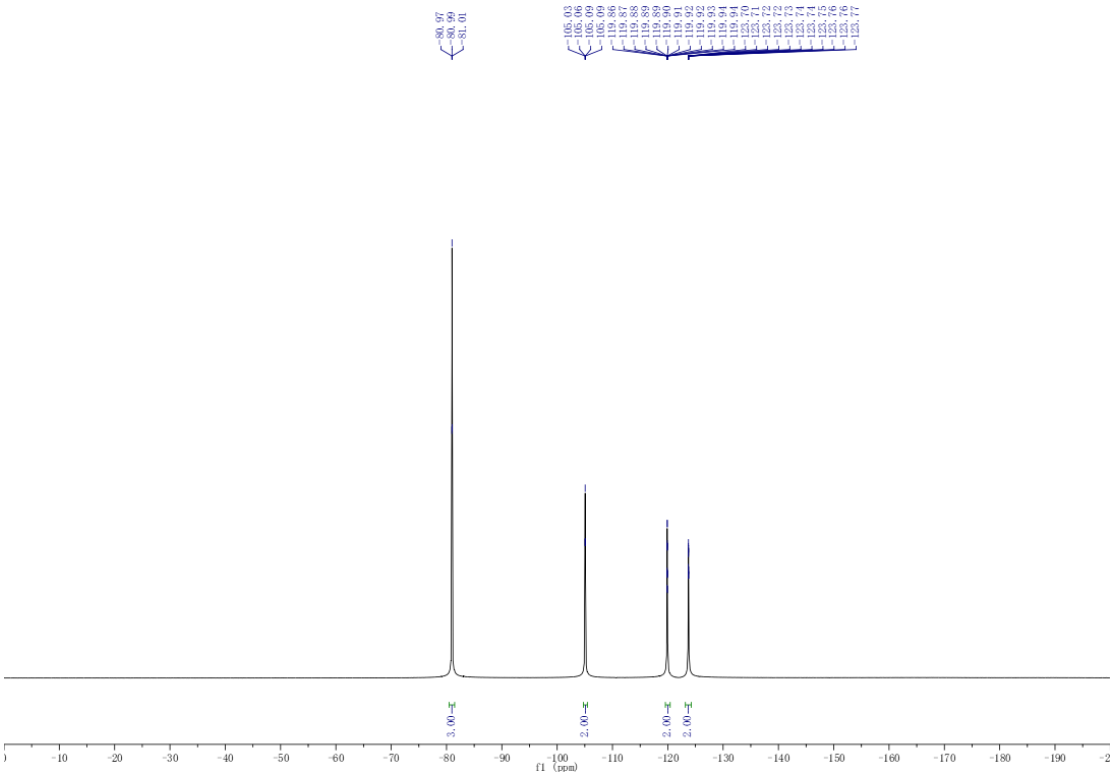




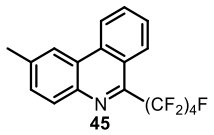
^{1}H NMR of compound **44**

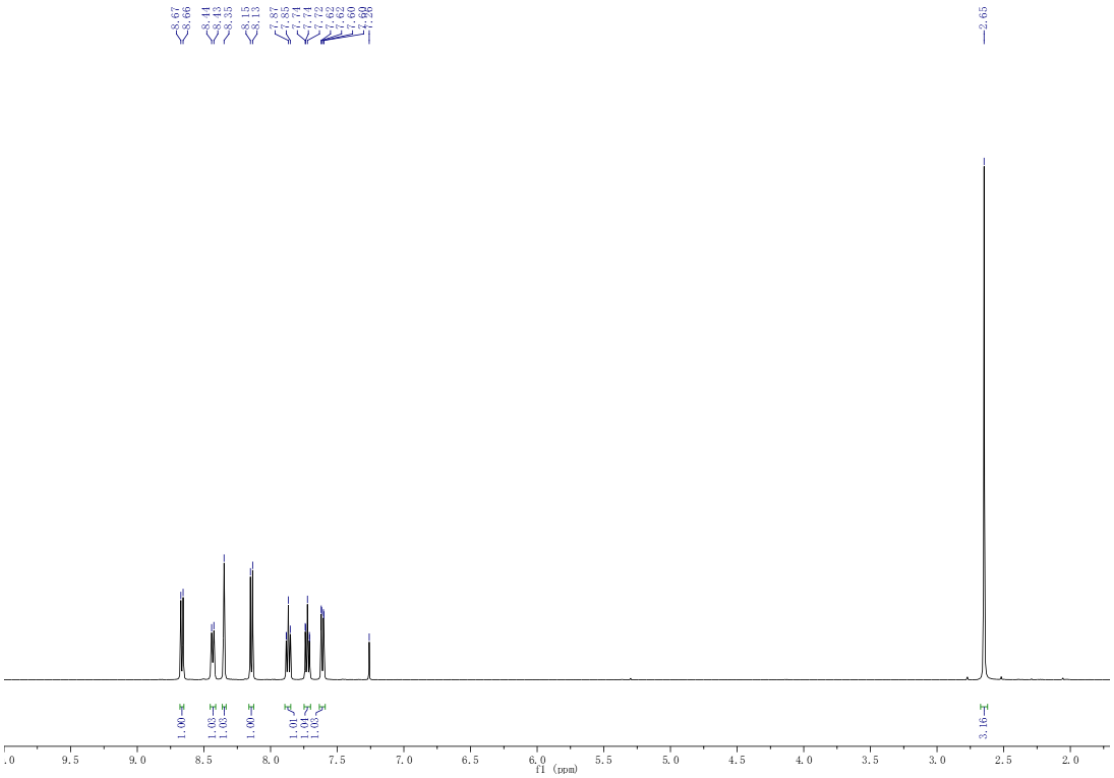


^{13}C NMR of compound **44**

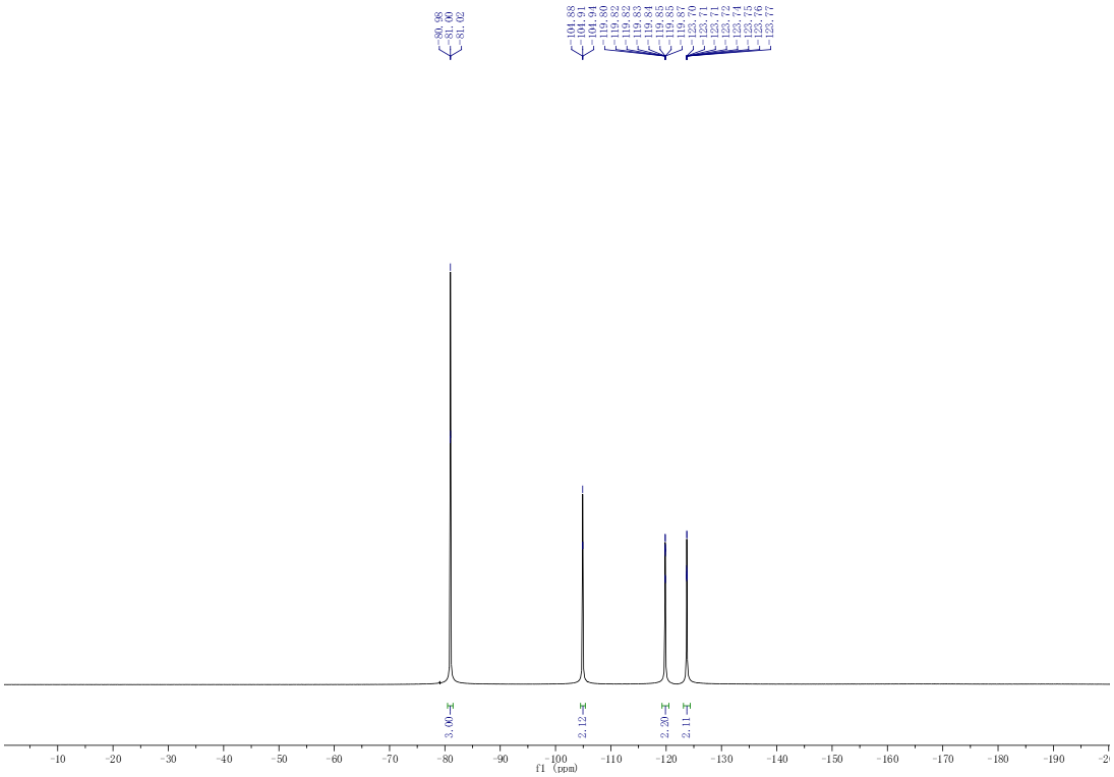


^{19}F NMR of compound **44**

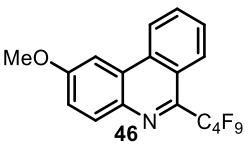


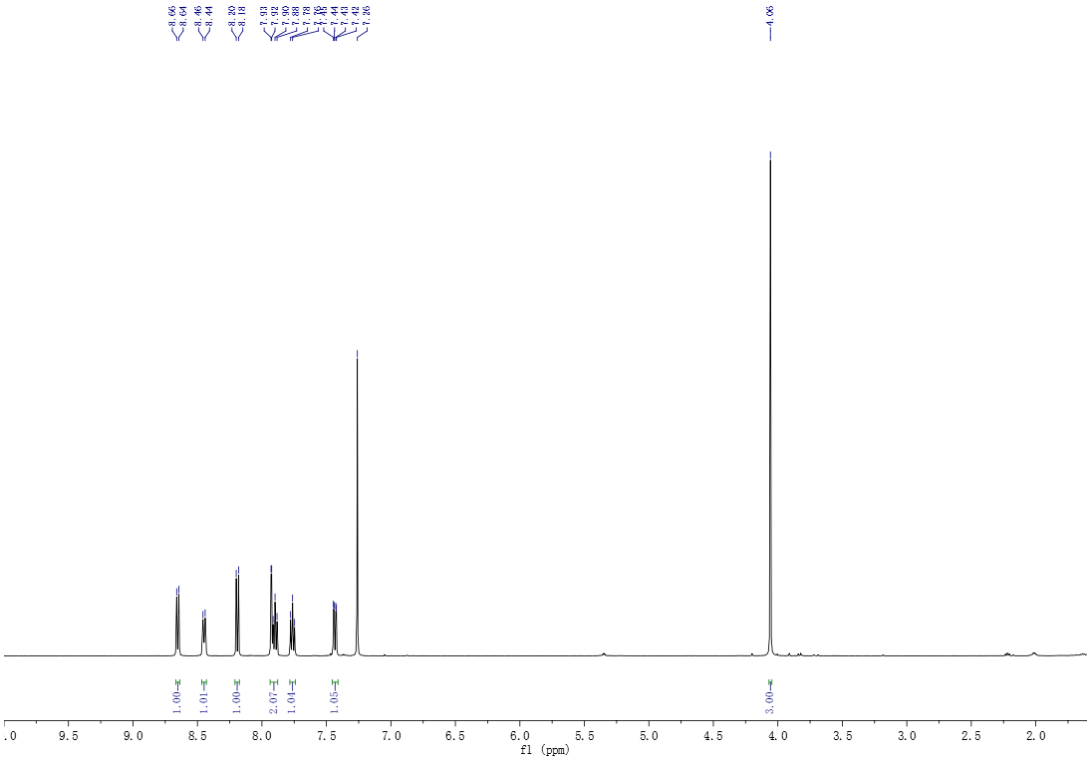


^{1}H NMR of compound **45**

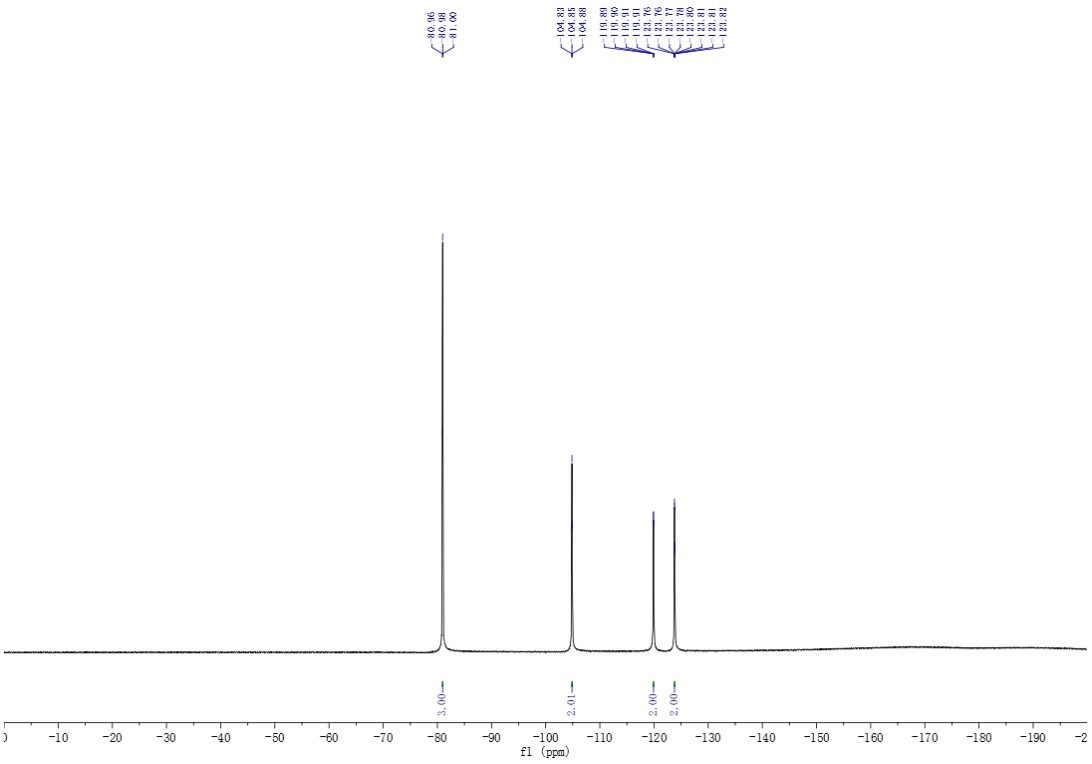


^{19}F NMR of compound **45**

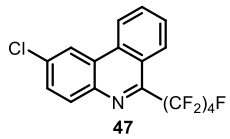


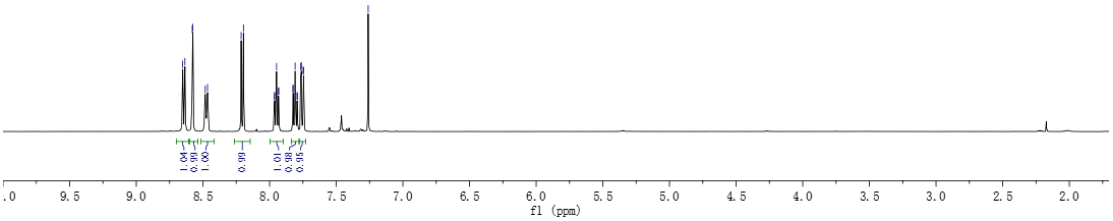


^{1}H NMR of compound **46**

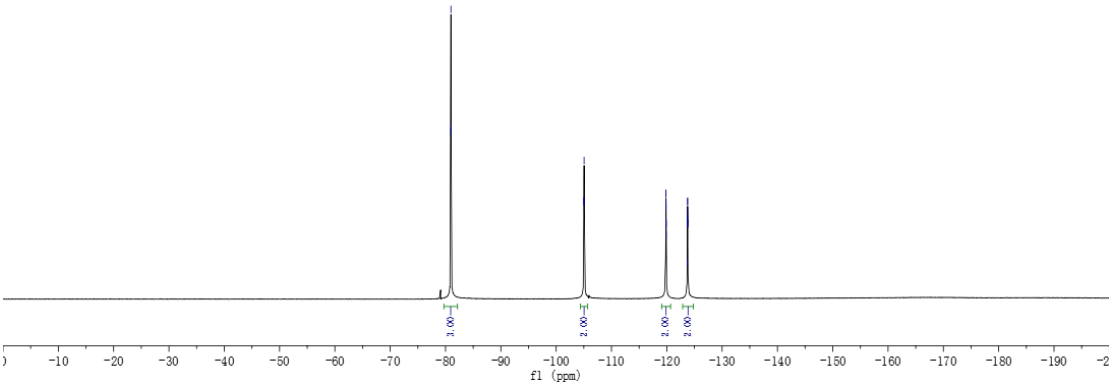


^{19}F NMR of compound **46**

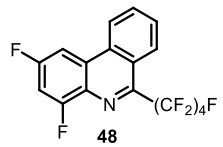




^{1}H NMR of compound **47**



^{19}F NMR of compound **47**



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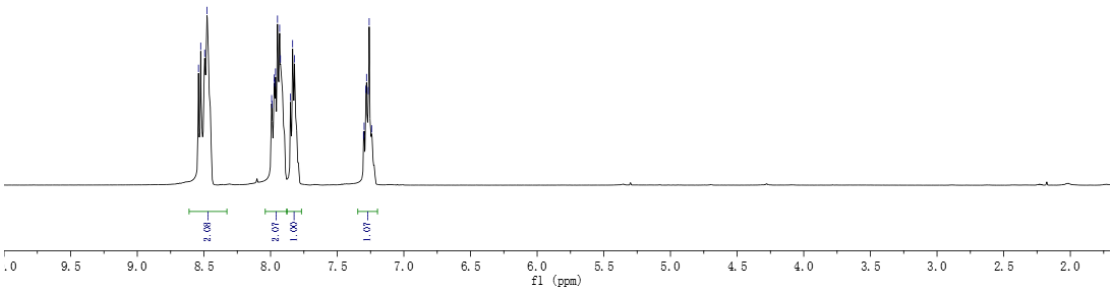
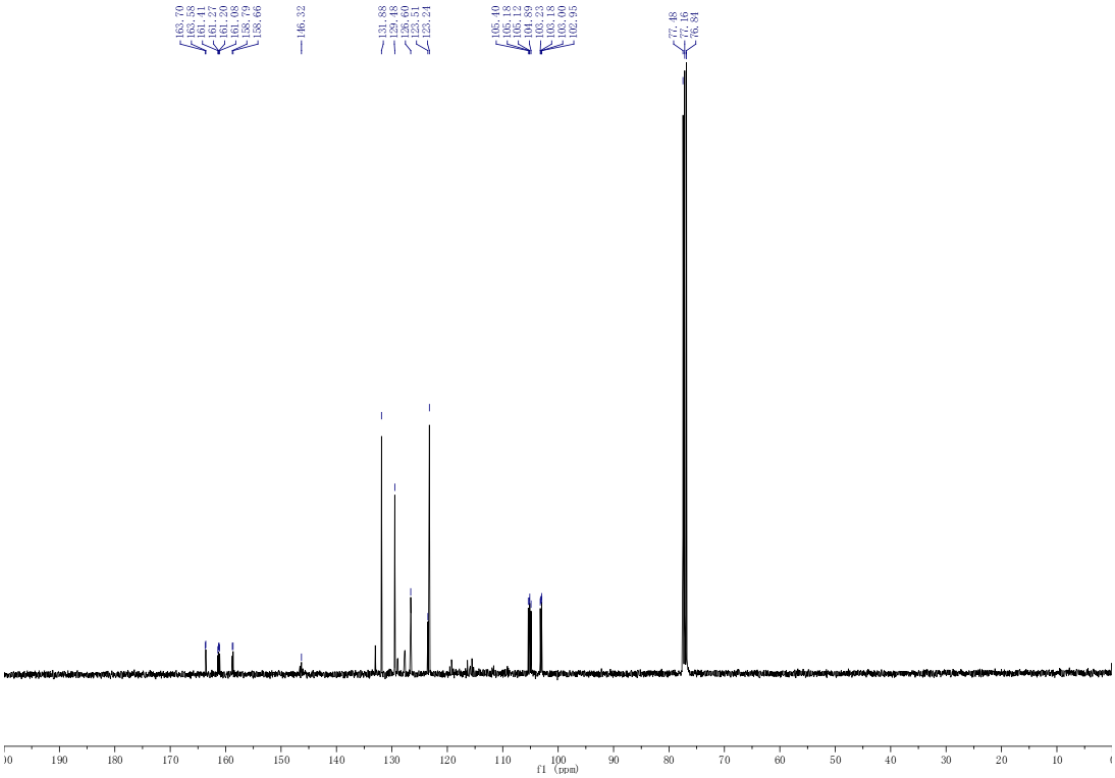
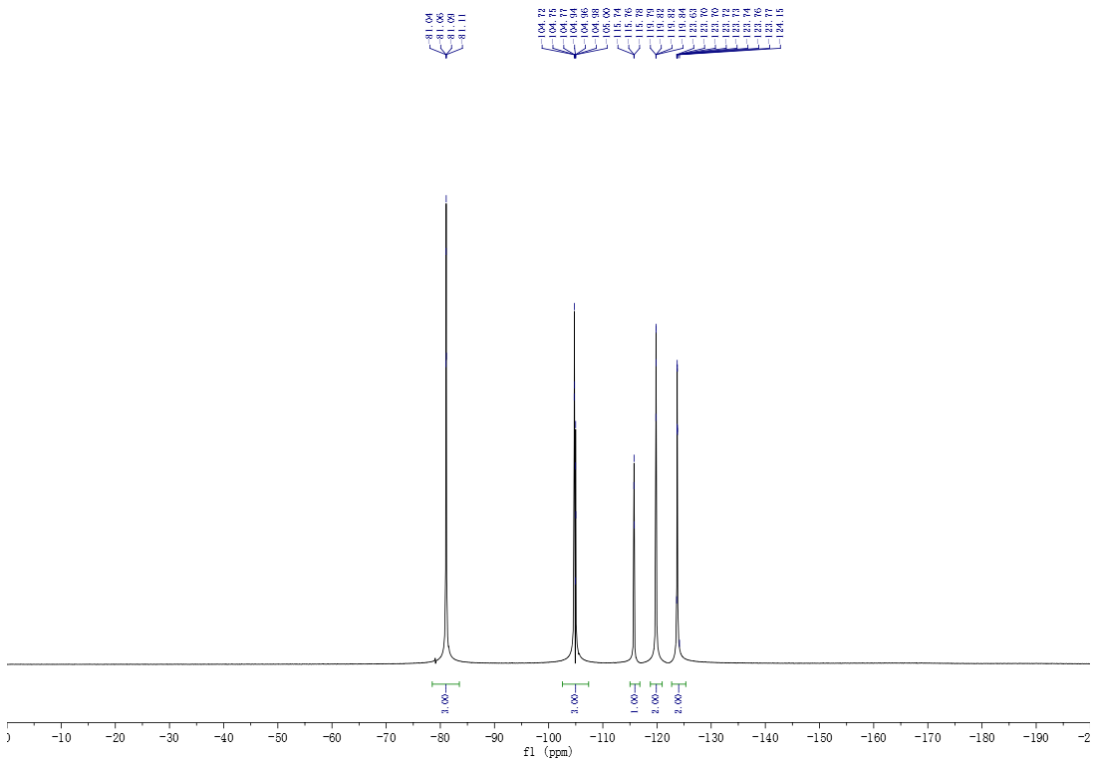


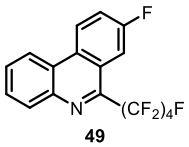
^{1}H NMR of compound **48**



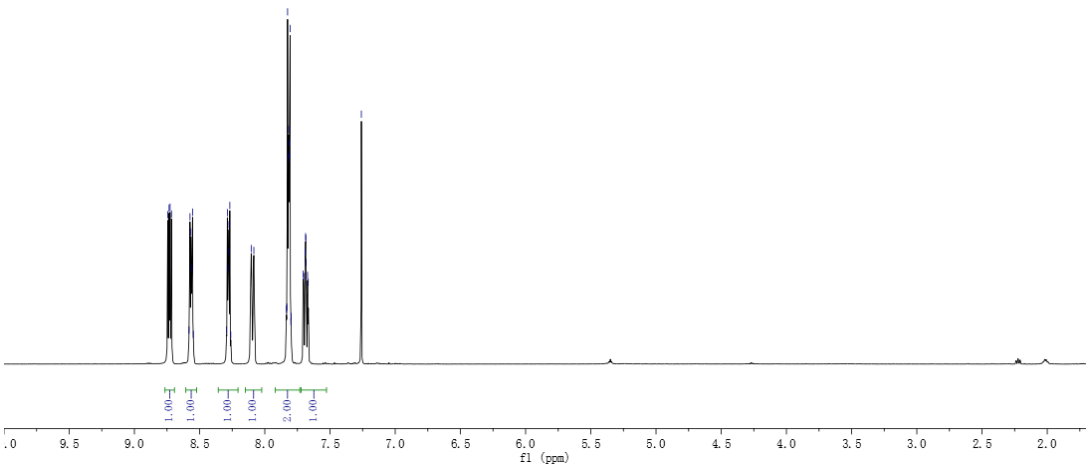
^{13}C NMR of compound **48**



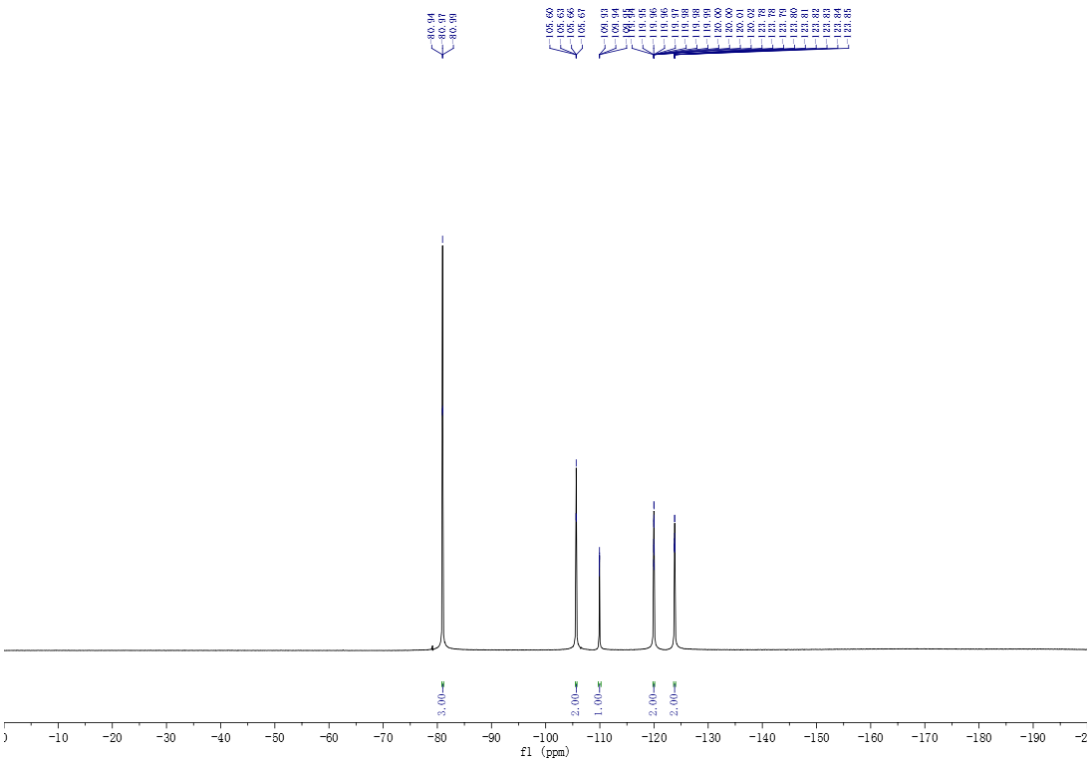
^{1919}F NMR of compound **48**



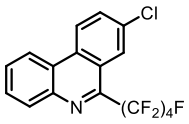
49



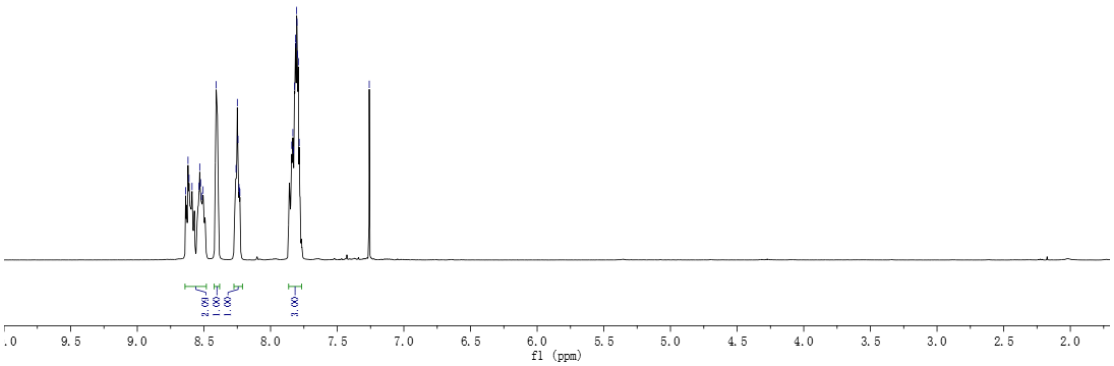
^{1}H NMR of compound **49**



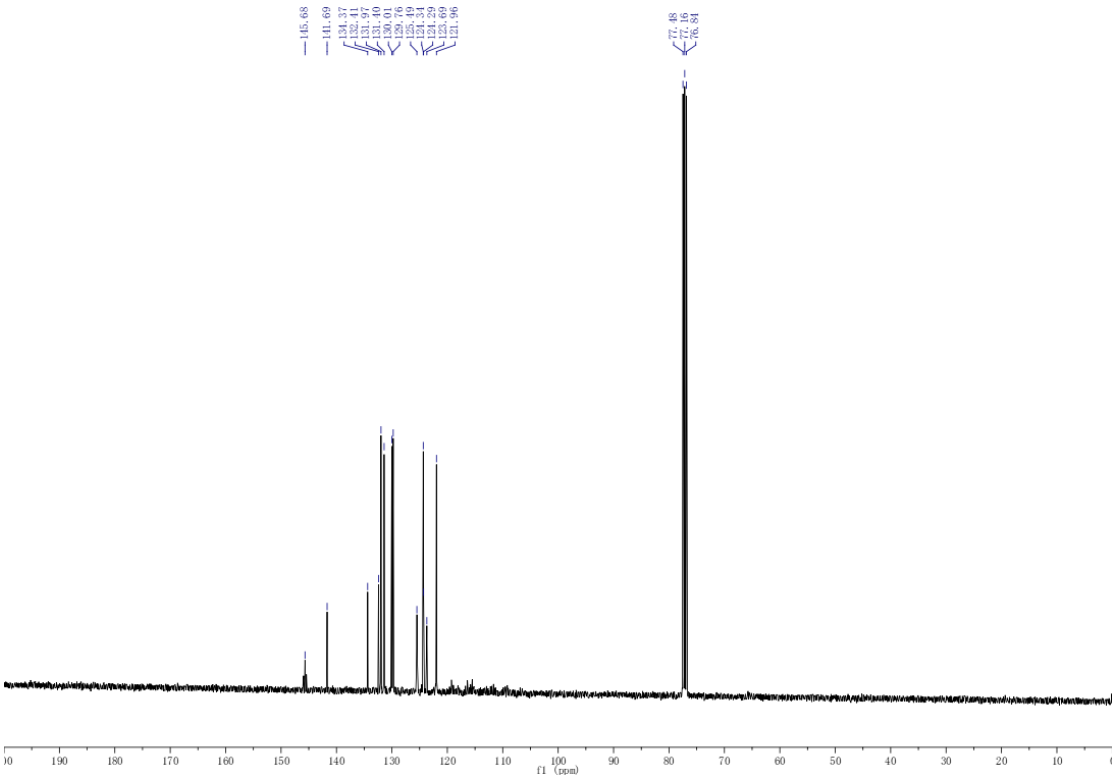
^{19}F NMR of compound **49**



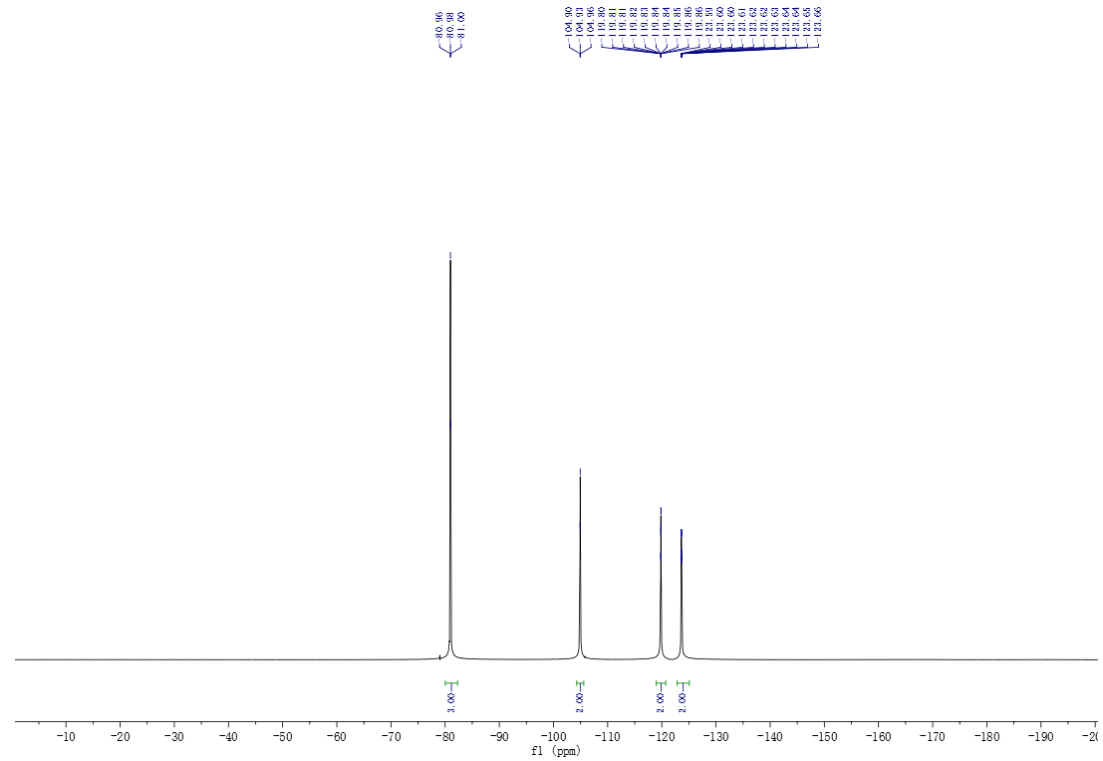
50



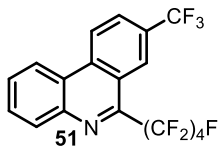
^{1}H NMR of compound **50**

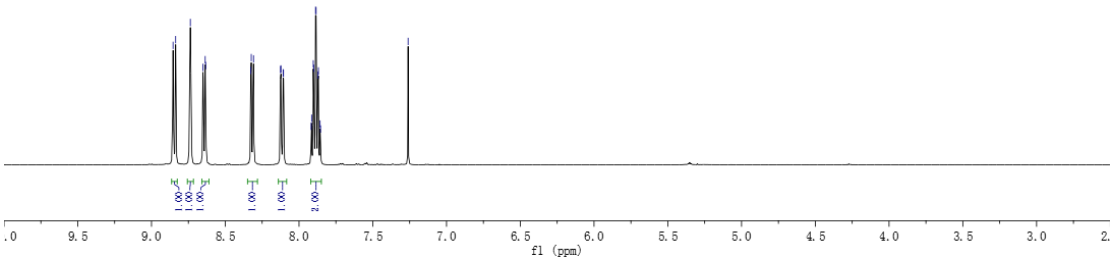


^{13}C NMR of compound **50**

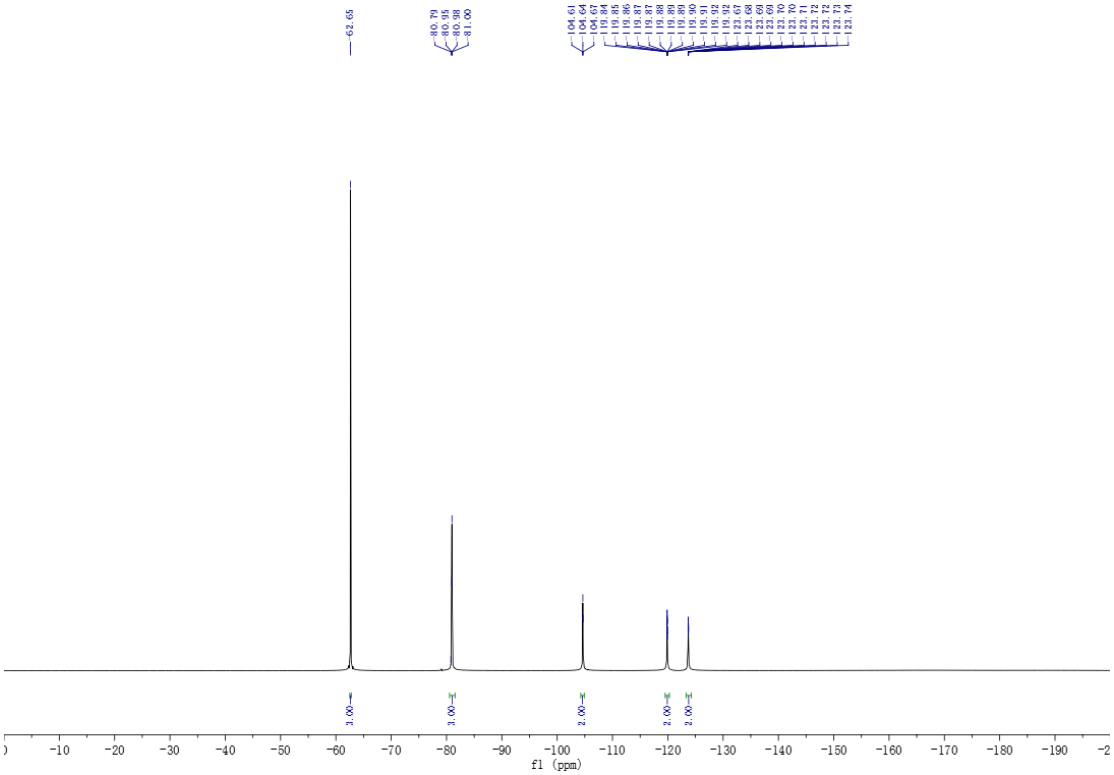


^{19}F NMR of compound **50**

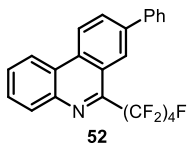




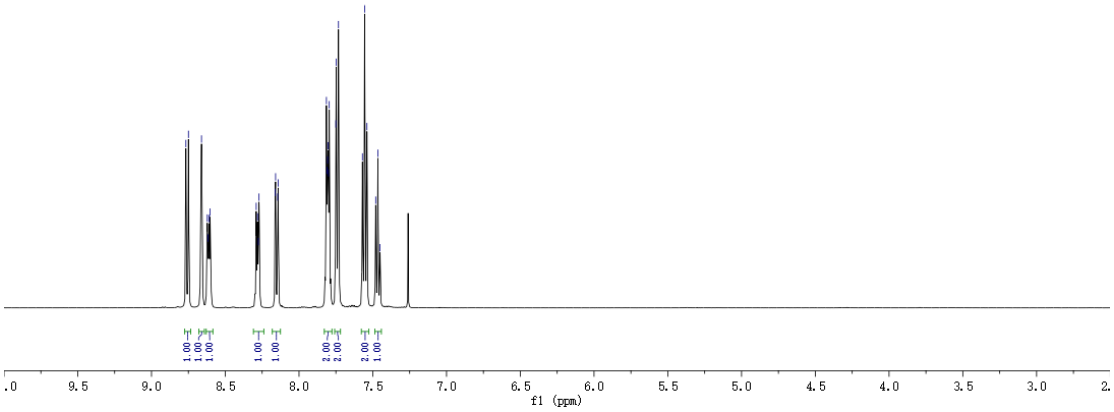
^{1}H NMR of compound **51**



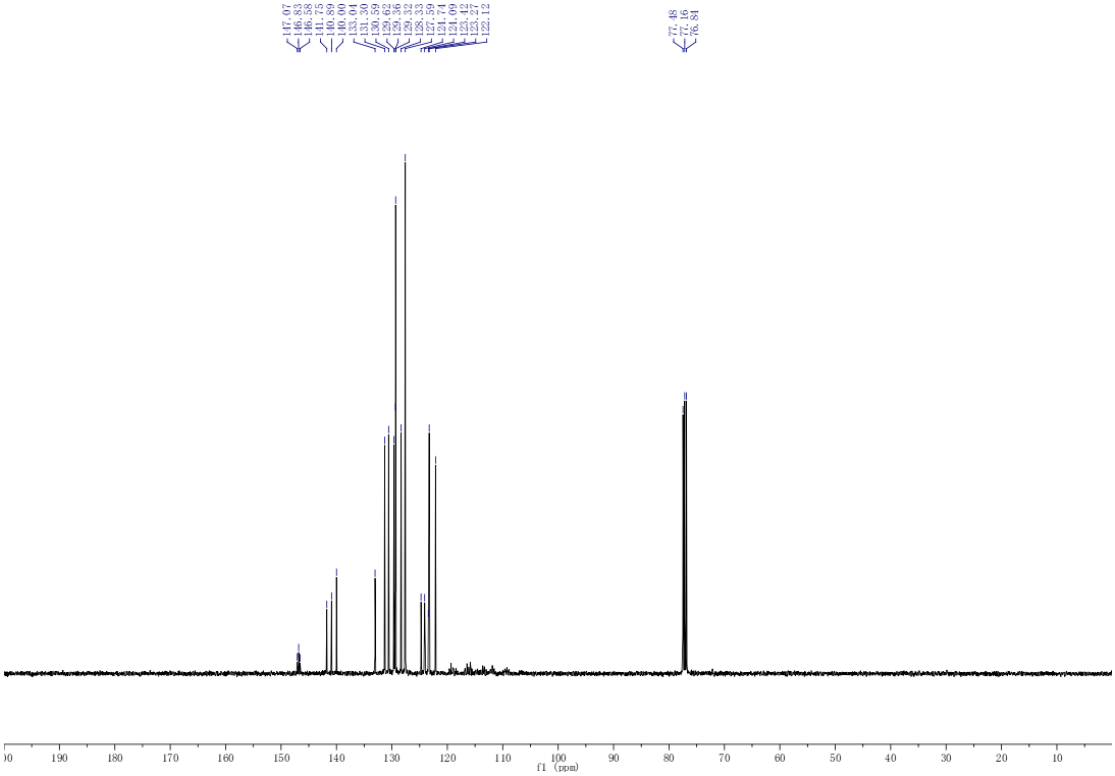
^{19}F NMR of compound **51**



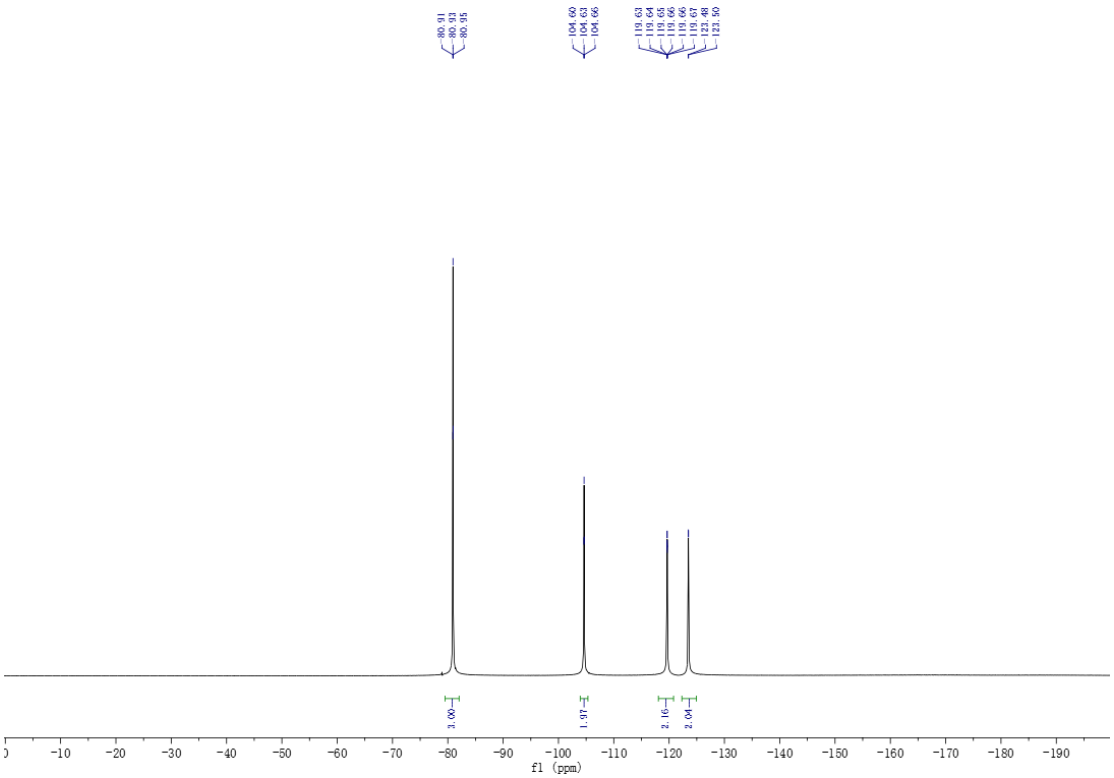
52



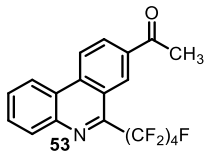
^{1}H NMR of compound **52**

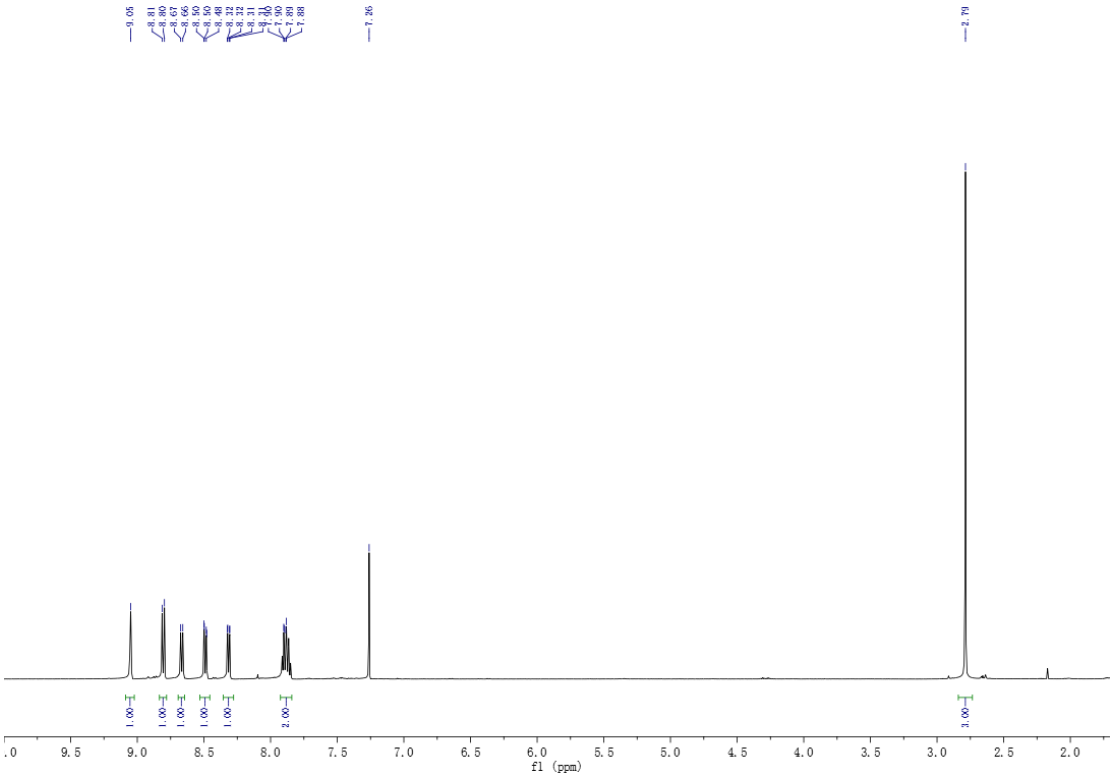


^{13}C NMR of compound **52**

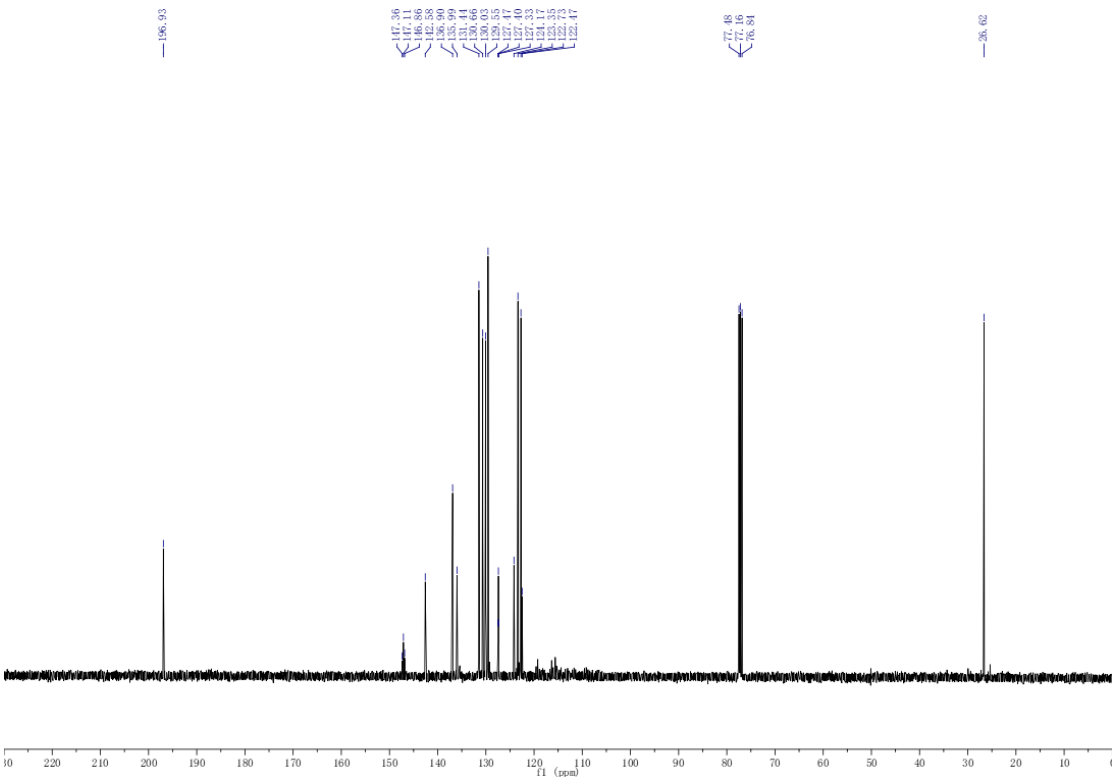


^{19}F NMR of compound **52**

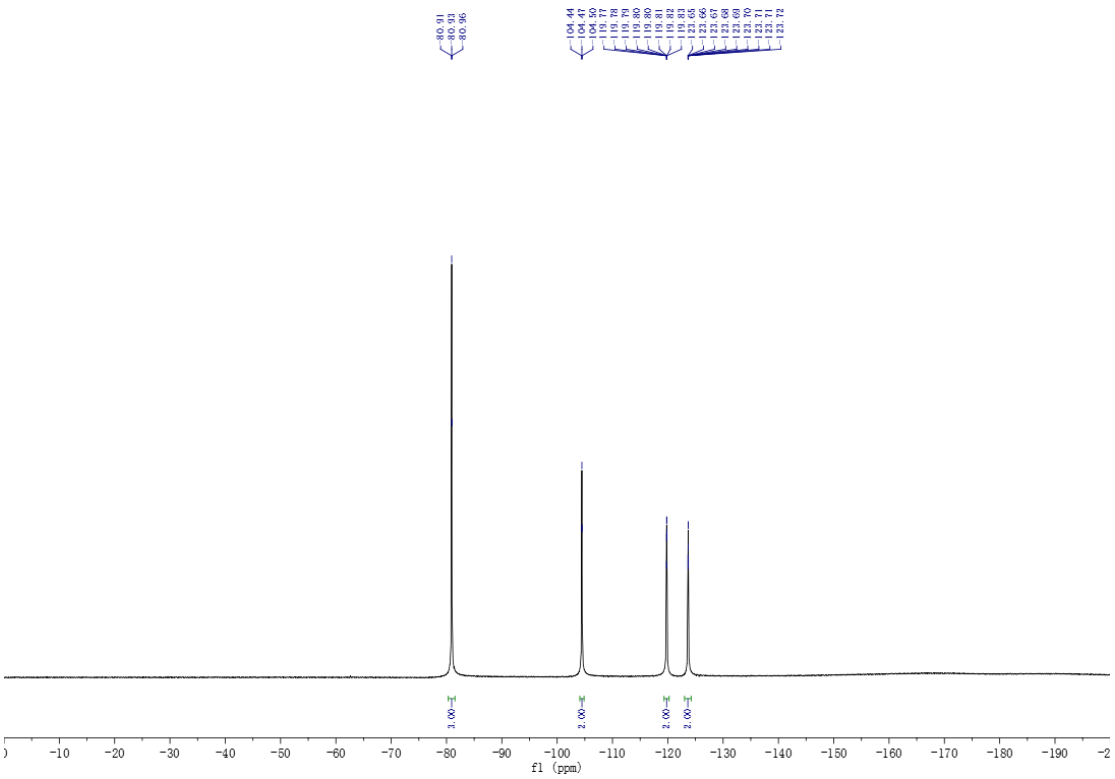




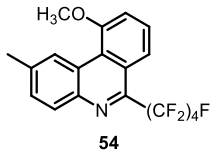
^{1}H NMR of compound **53**



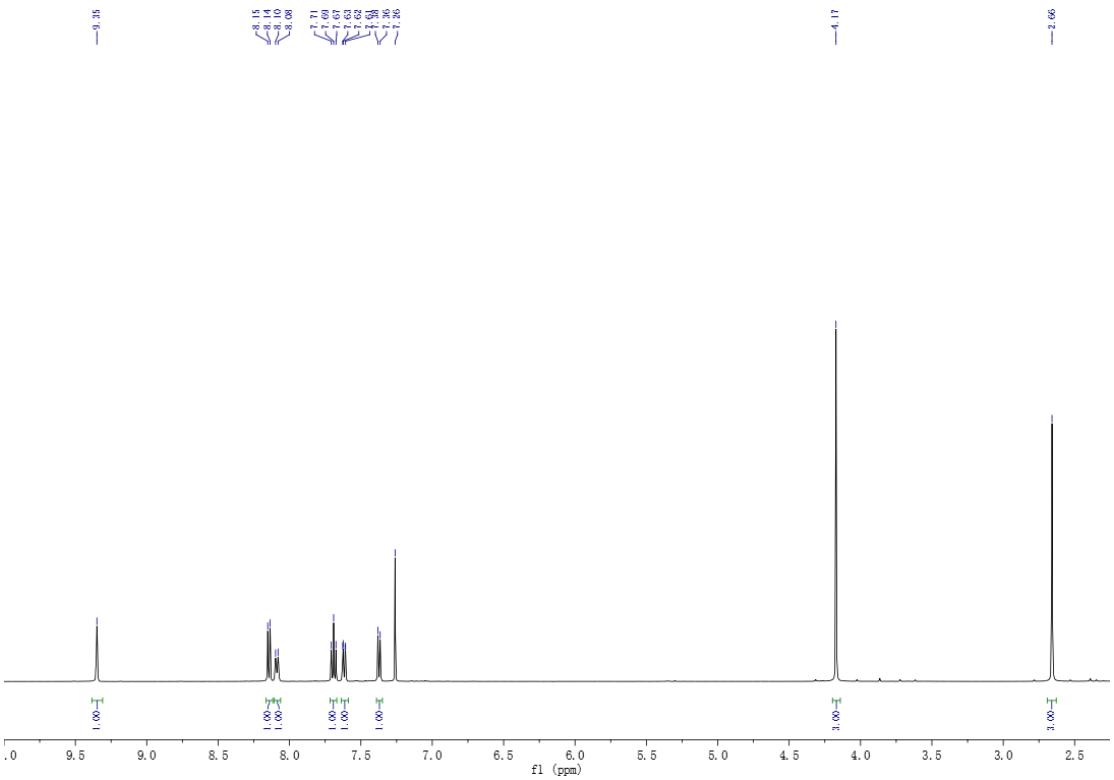
^{13}C NMR of compound **53**



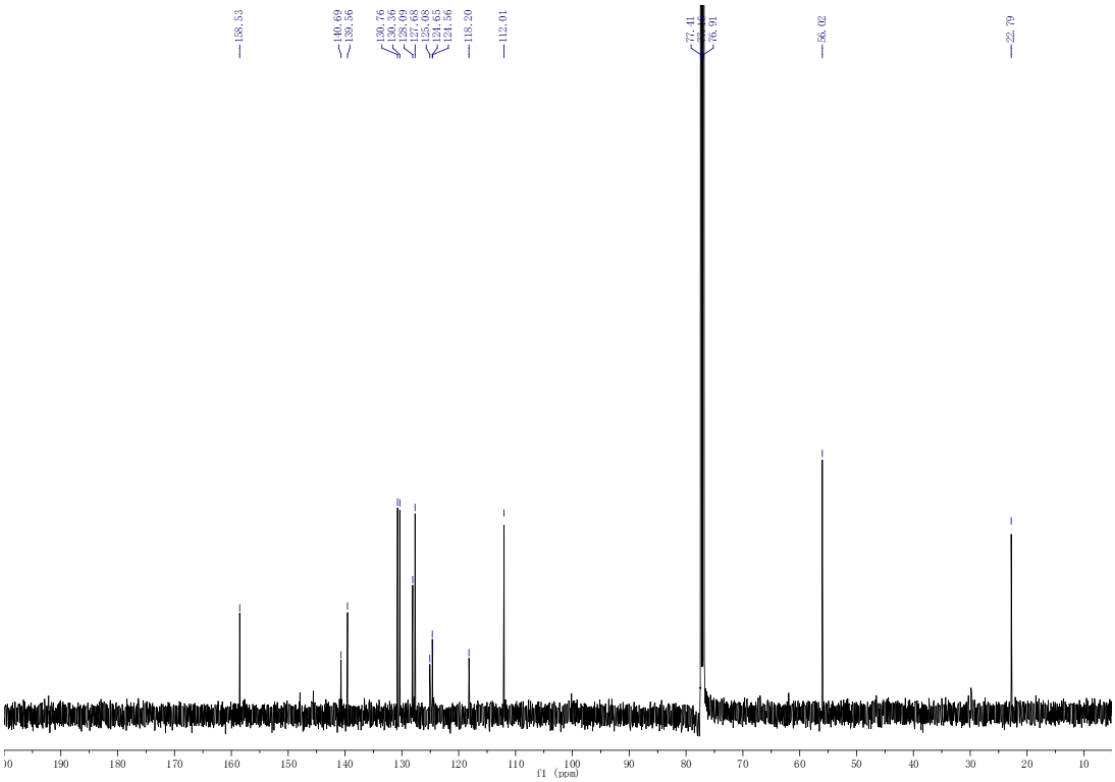
^{19}F NMR of compound **53**



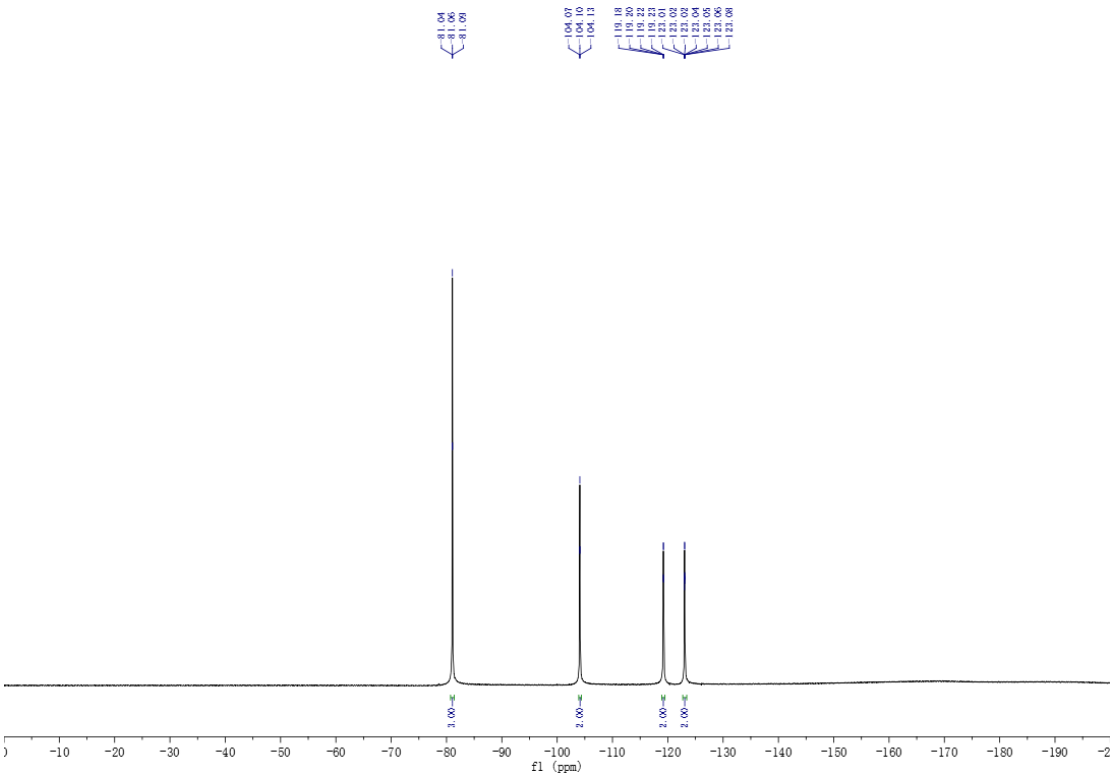
54



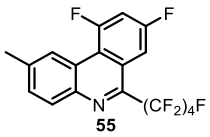
^{1}H NMR of compound **54**



^{13}C NMR of compound **54**



^{19}F NMR of compound **54**



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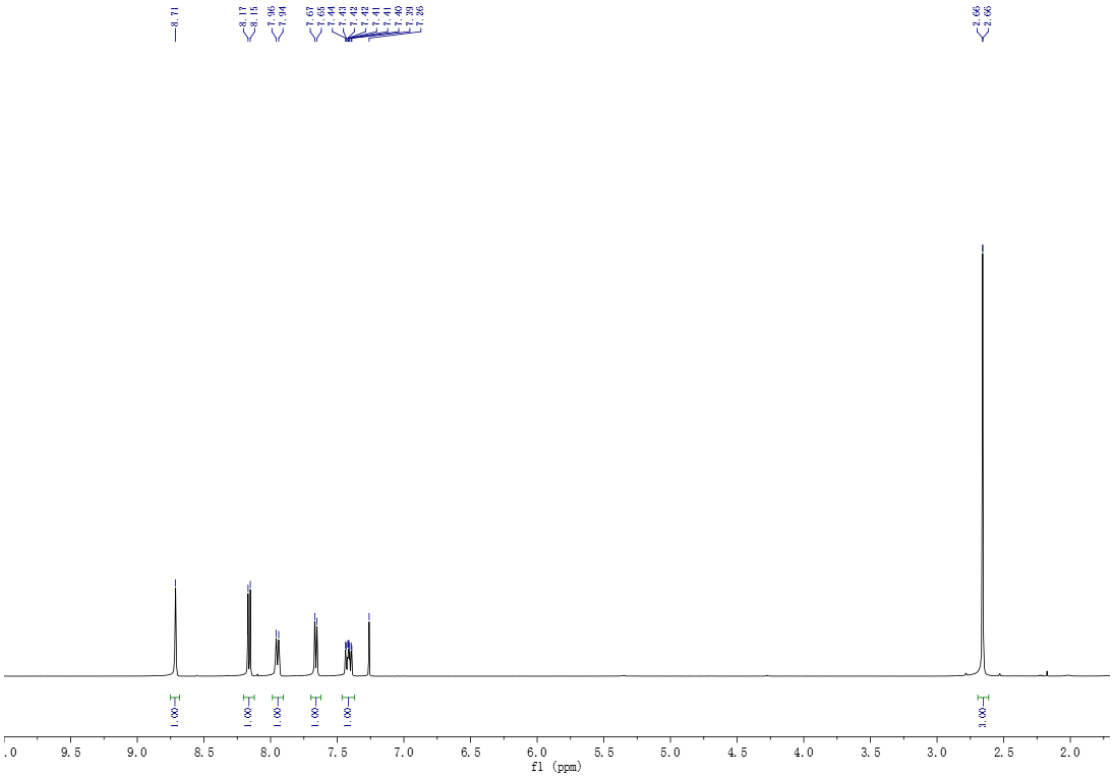
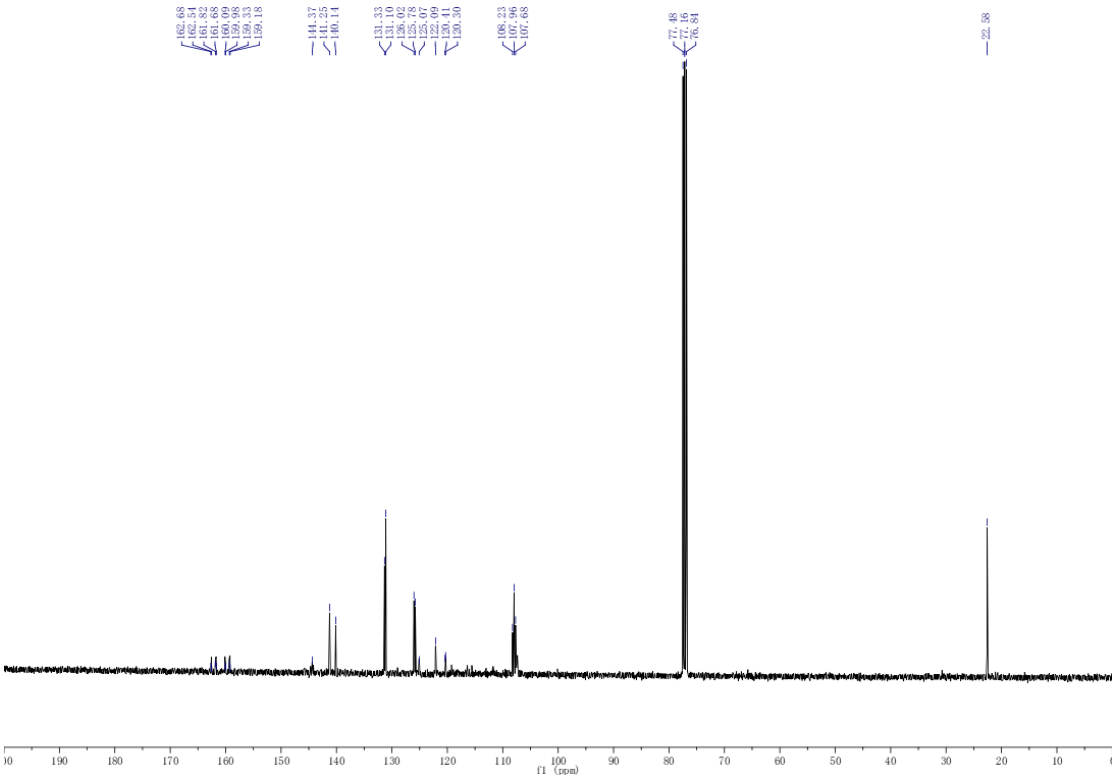


^{1}H NMR of compound **55**



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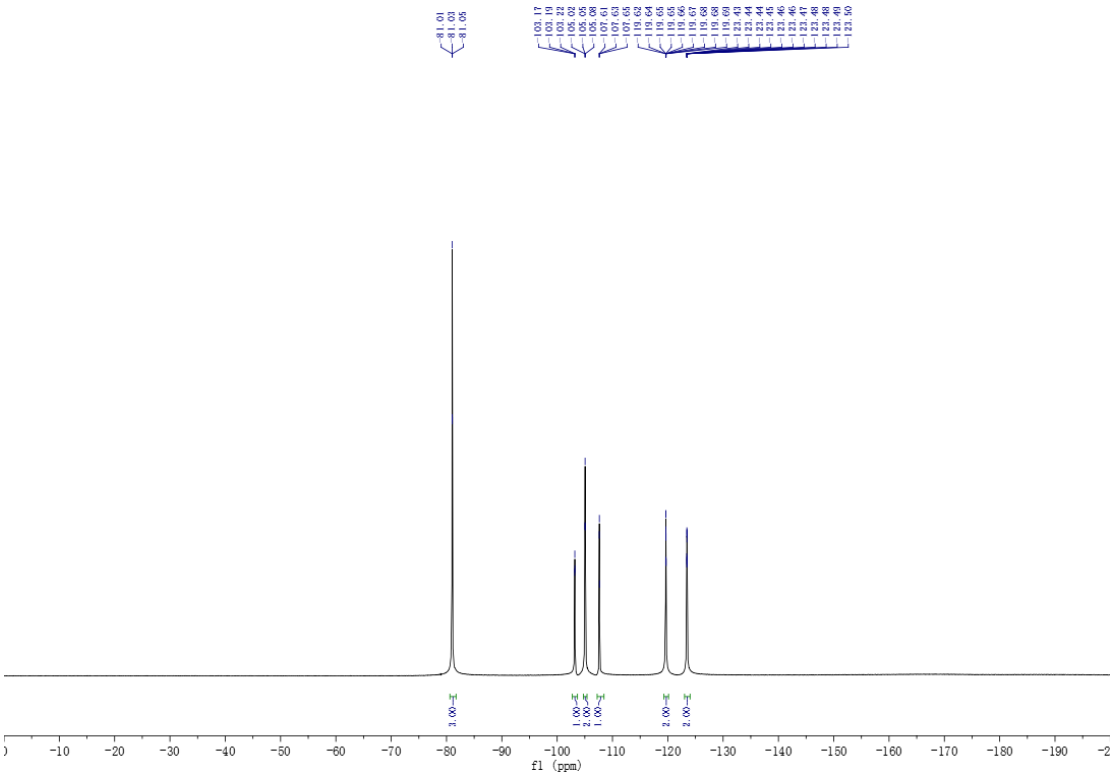

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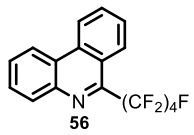
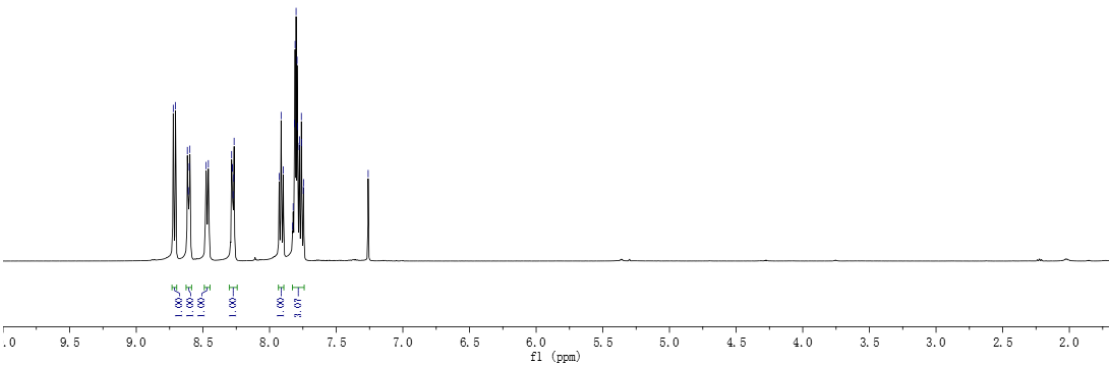
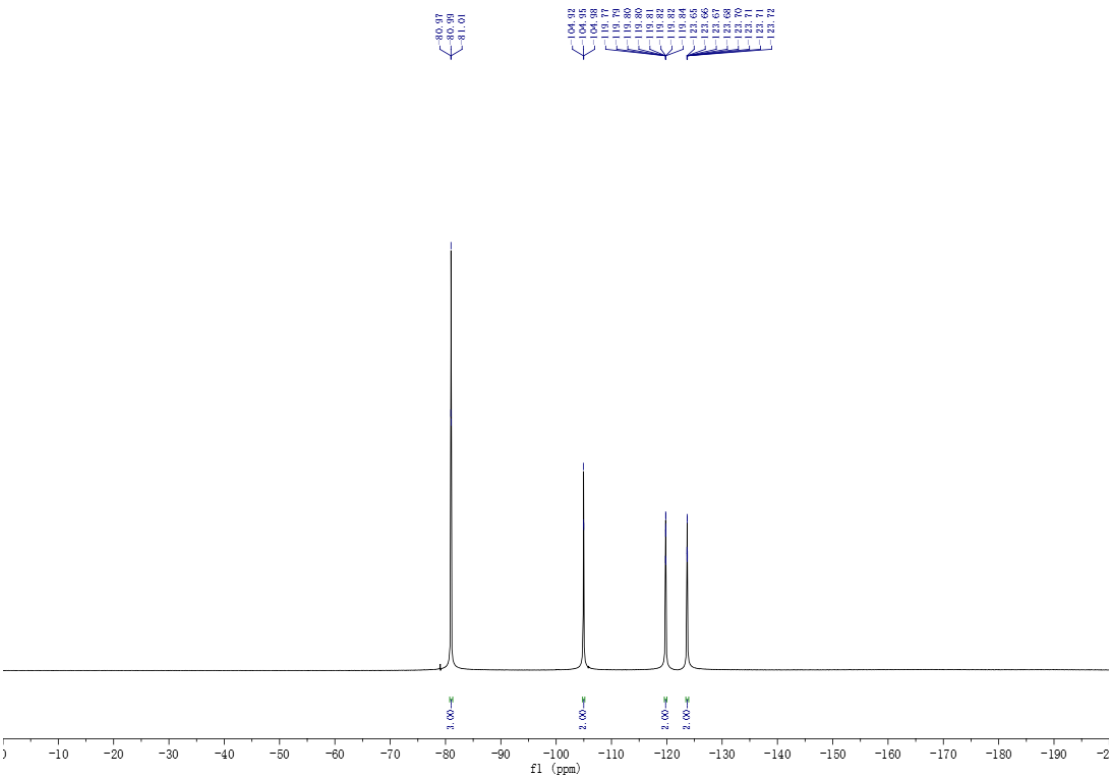
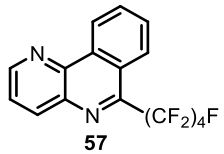




^{1}H NMR of compound **56**



^{19}F NMR of compound **56**



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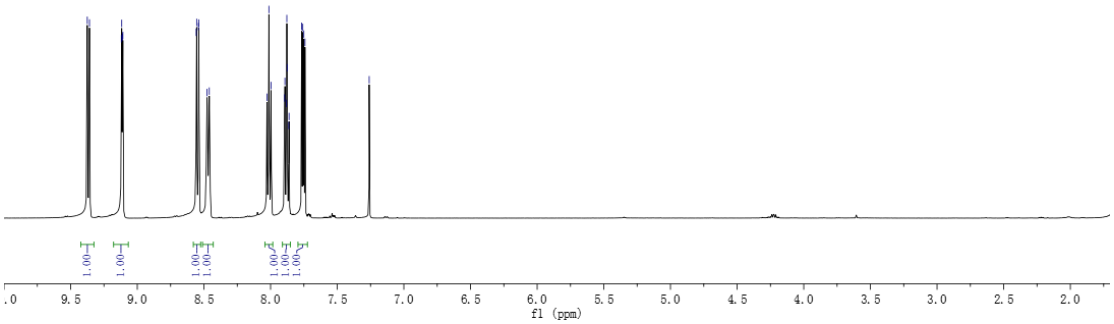
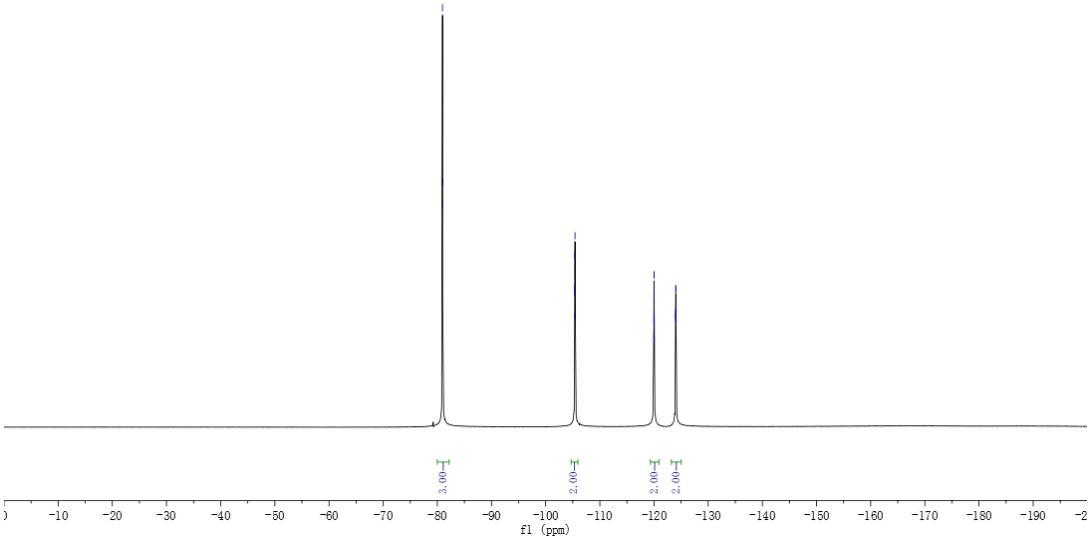
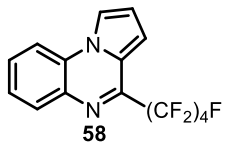


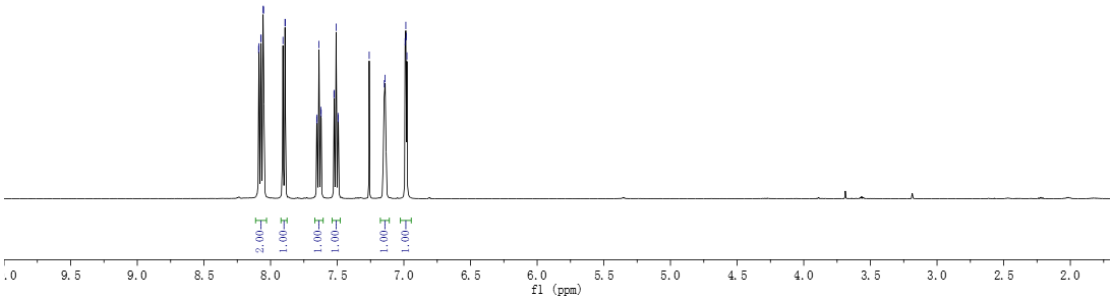
^{1}H NMR of compound **57**



^{19}F NMR of compound **57**



58



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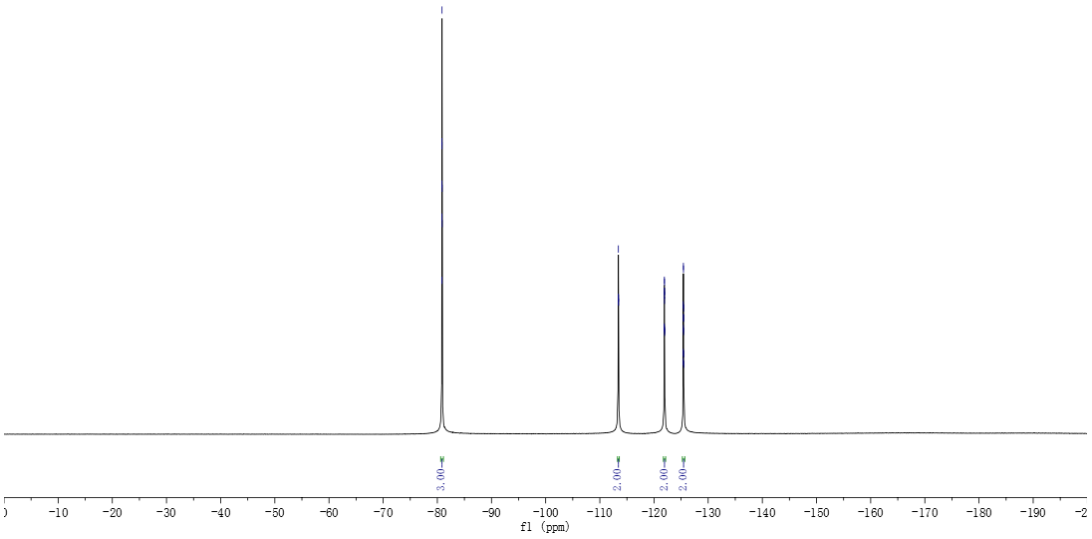
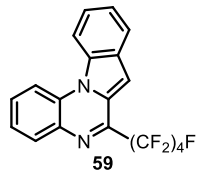
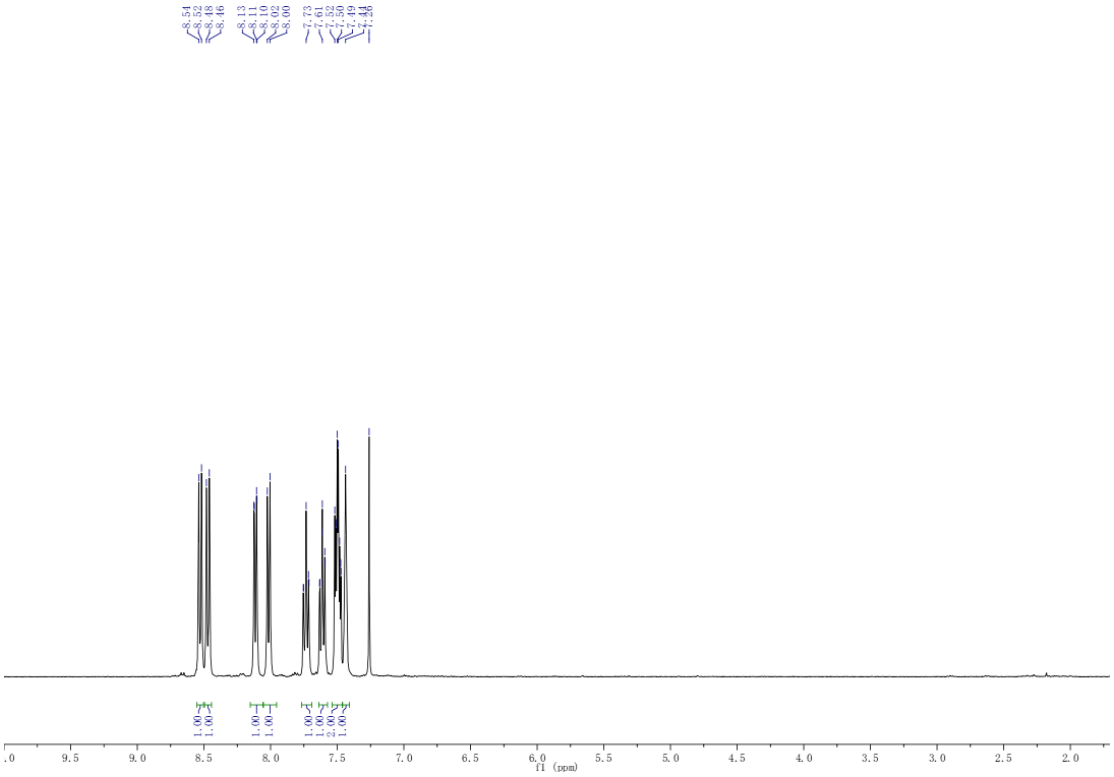


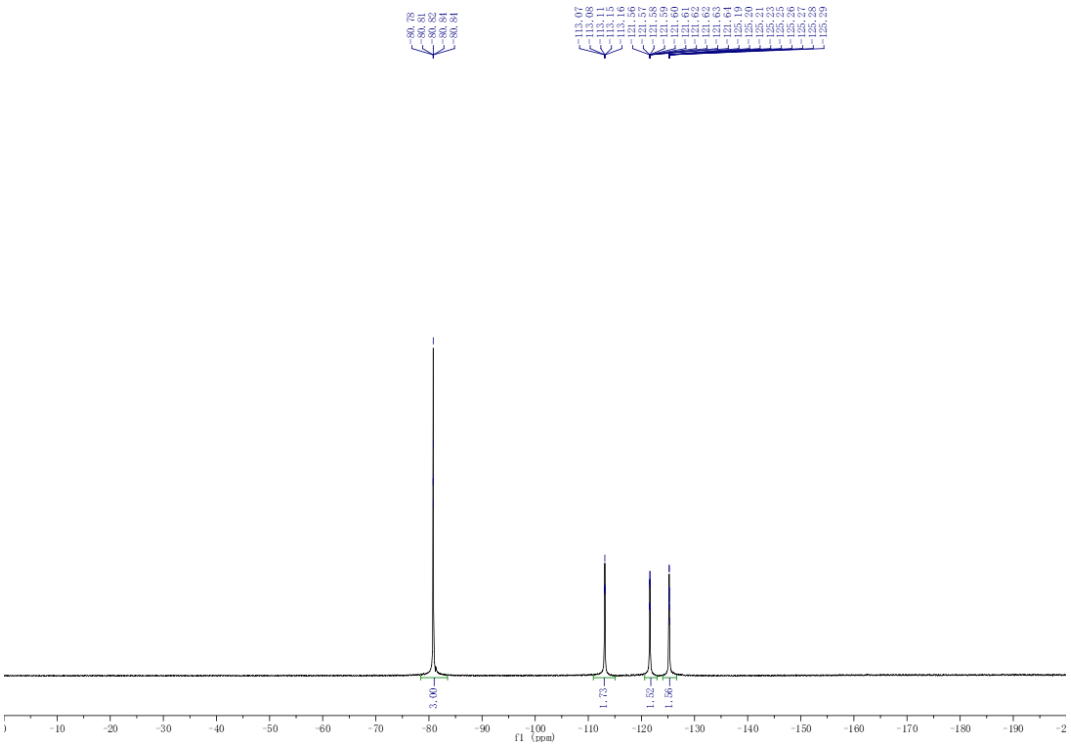
^{19}F NMR of compound **58**



59



^{1}H NMR of compound **59**



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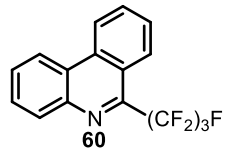

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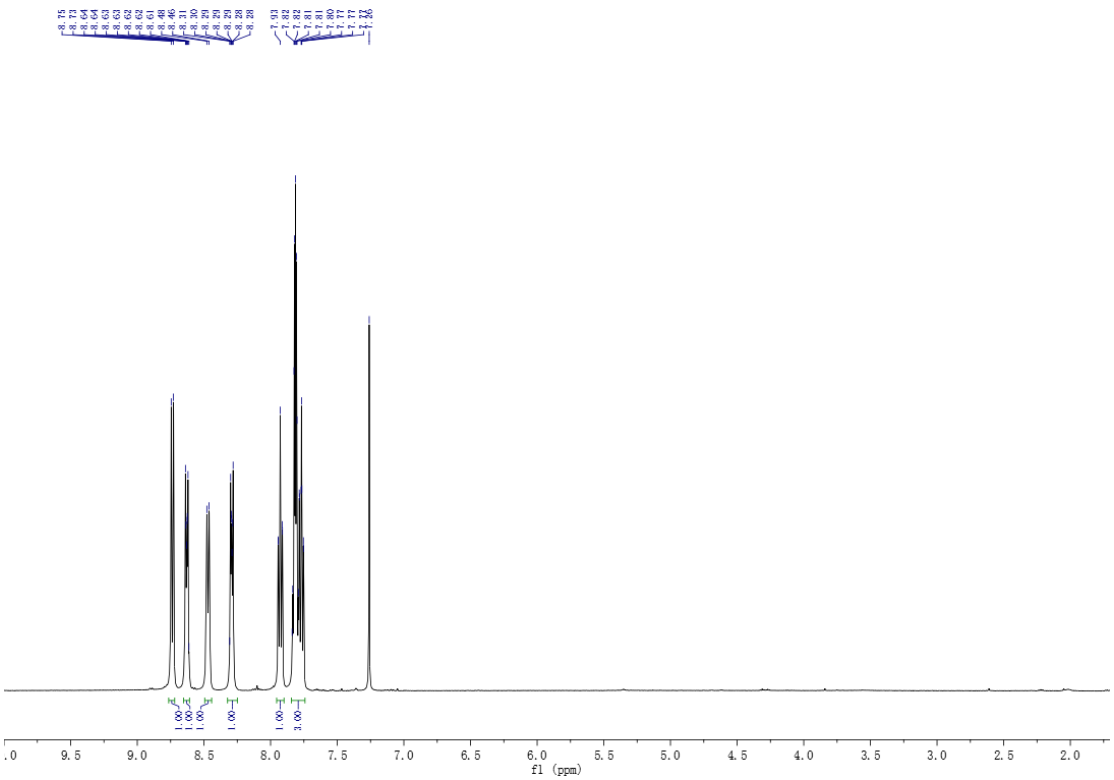

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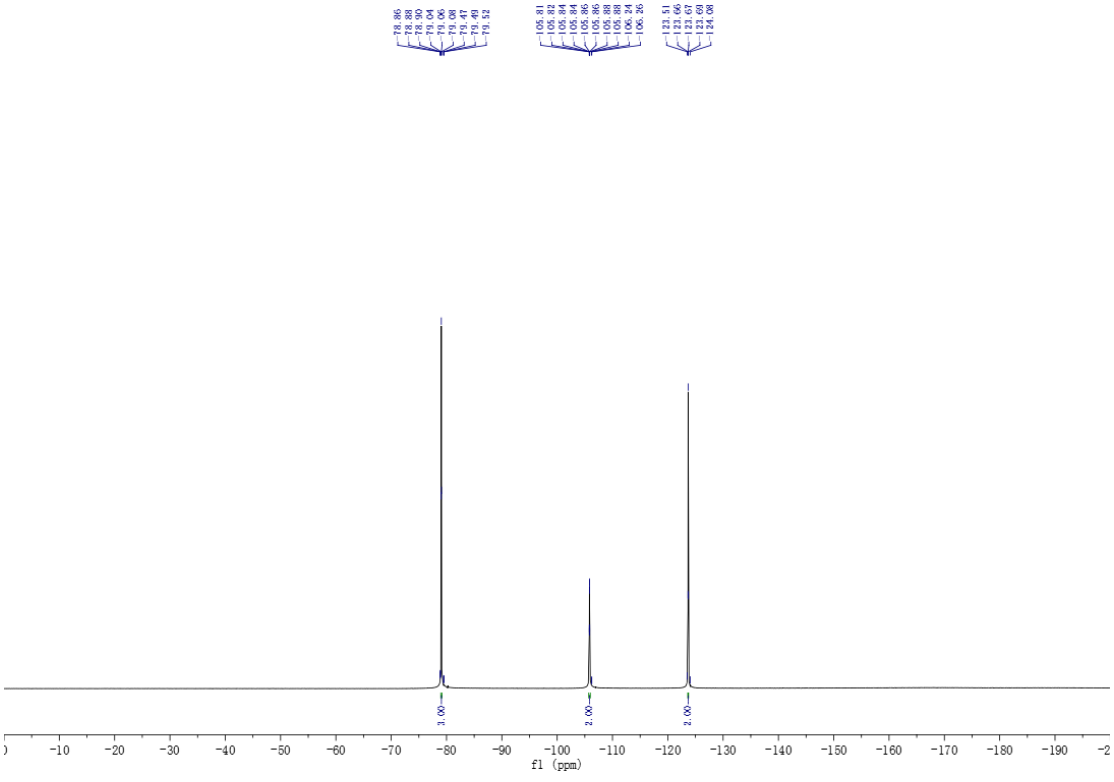
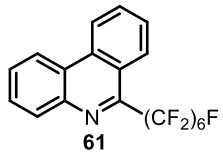
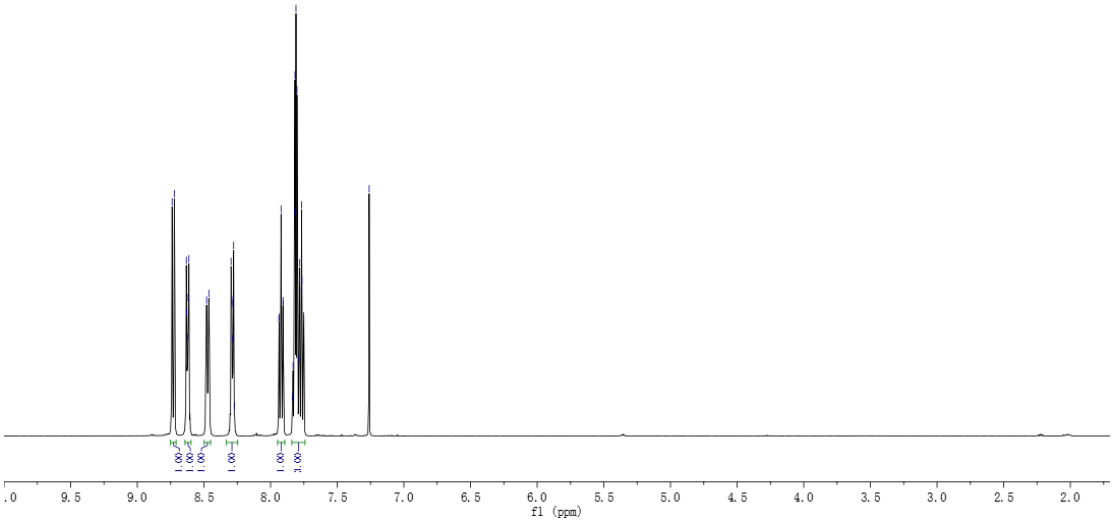


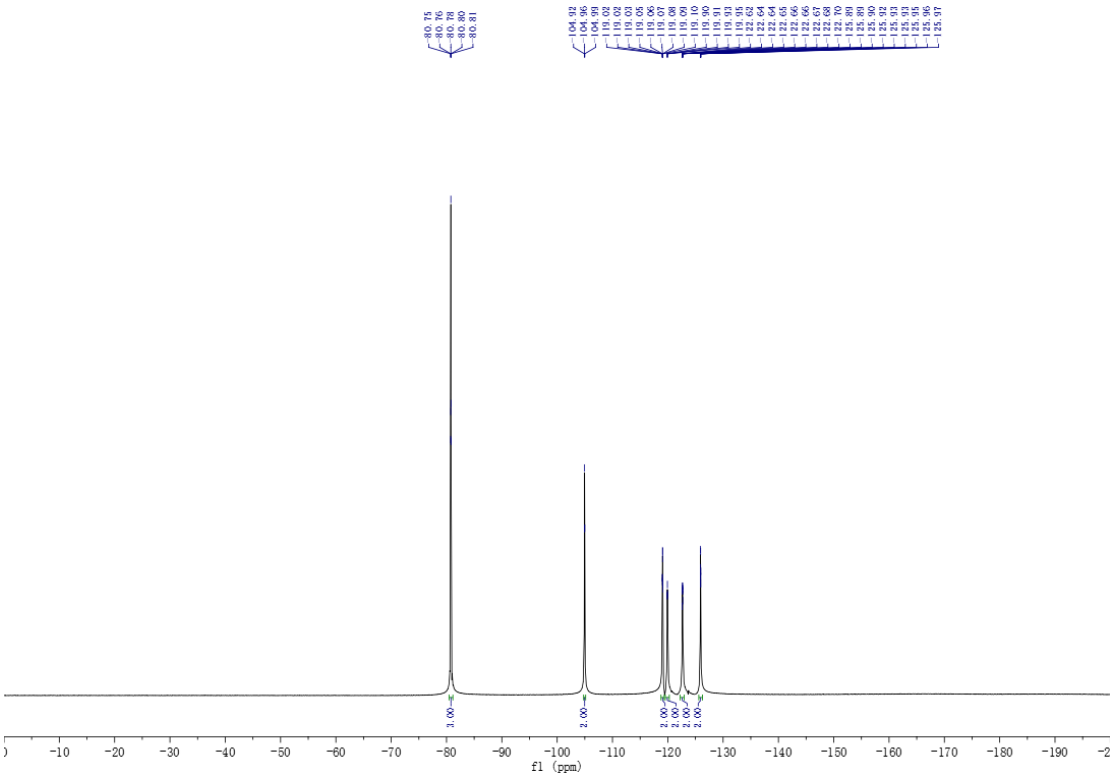
^{19}F NMR of compound **60**



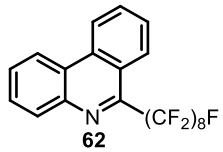
61

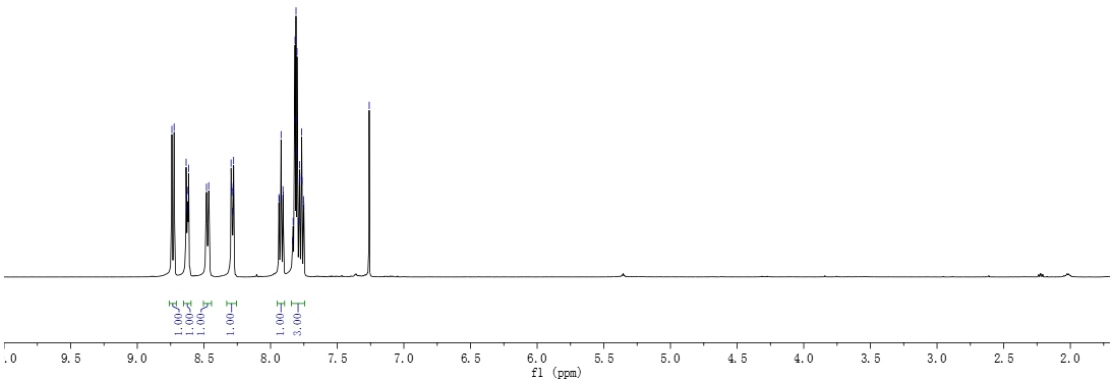


^{1}H NMR of compound **61**

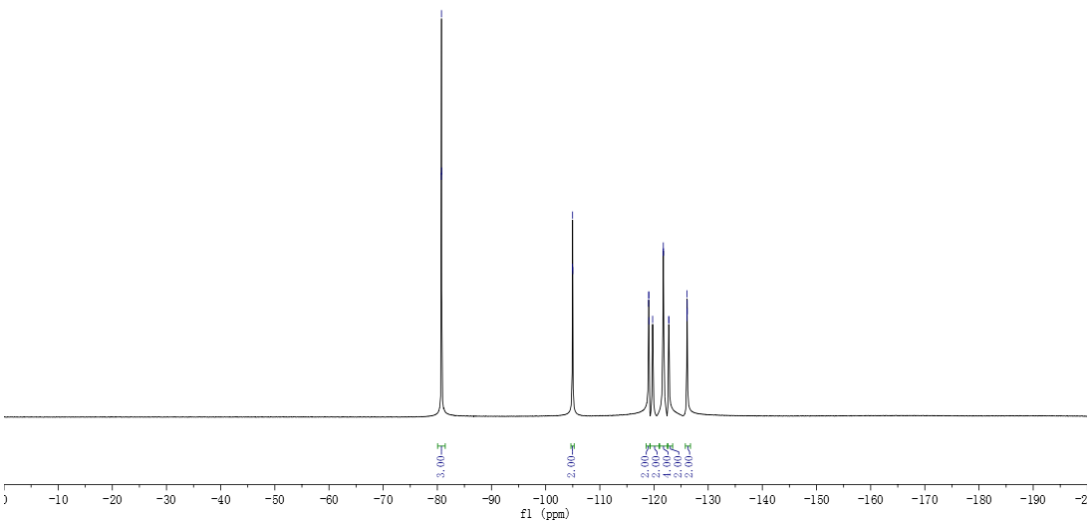


^{19}F NMR of compound **61**

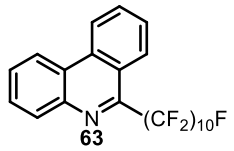


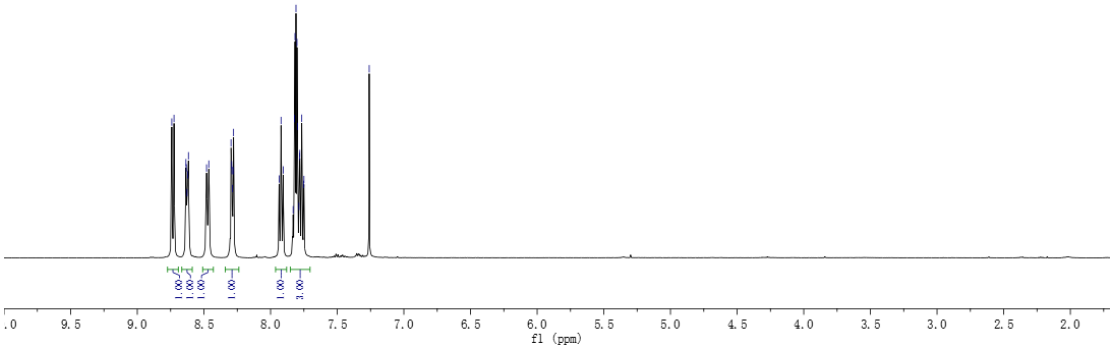


^{1}H NMR of compound **62**

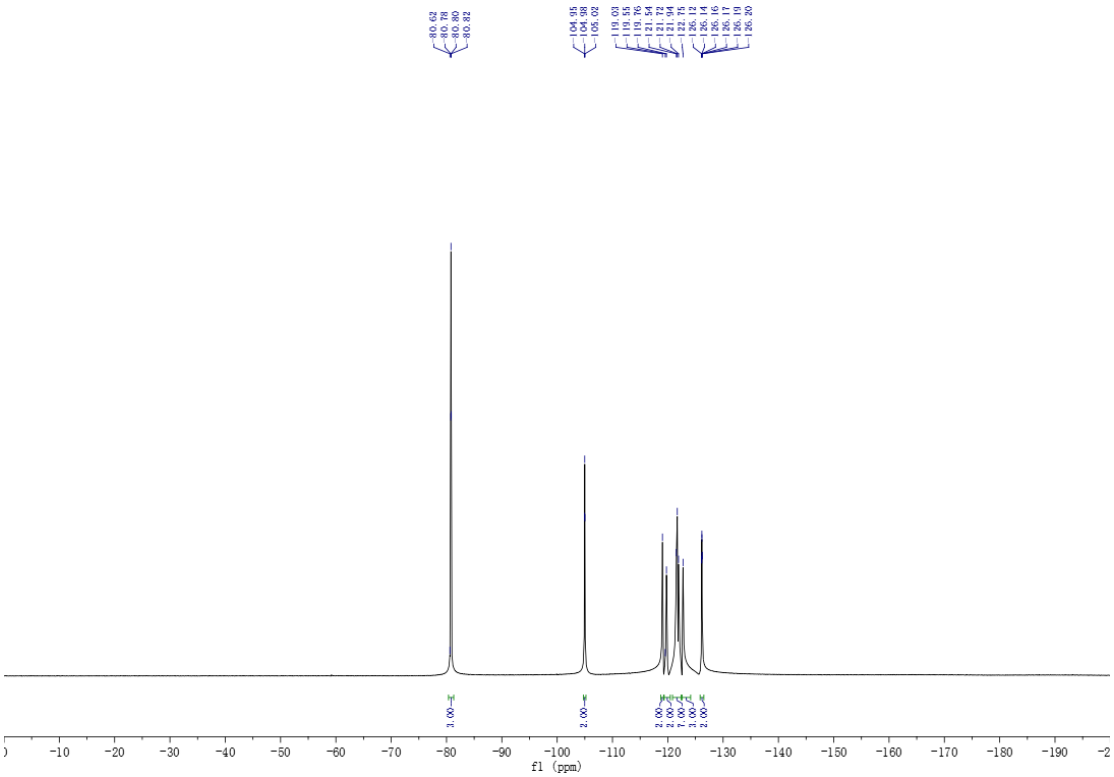


^{19}F NMR of compound **62**

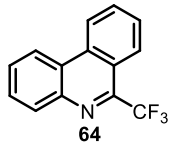




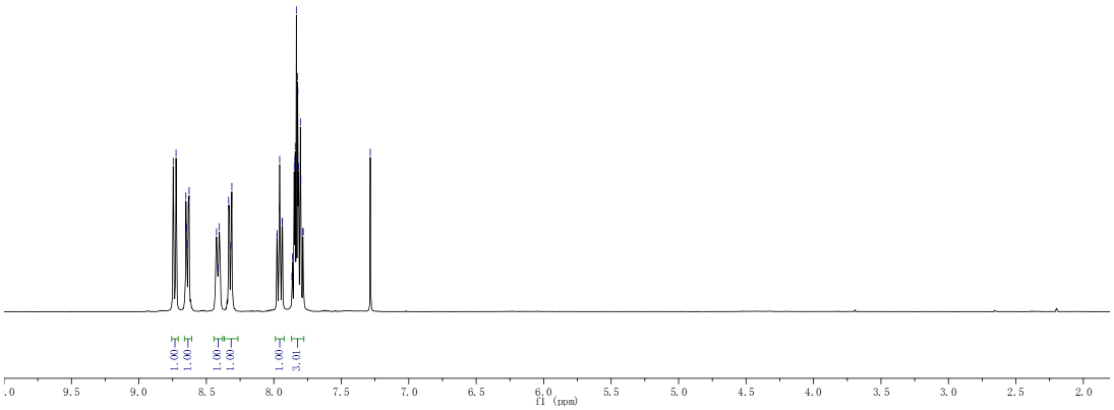
^{1}H NMR of compound **63**



^{19}F NMR of compound **63**



64



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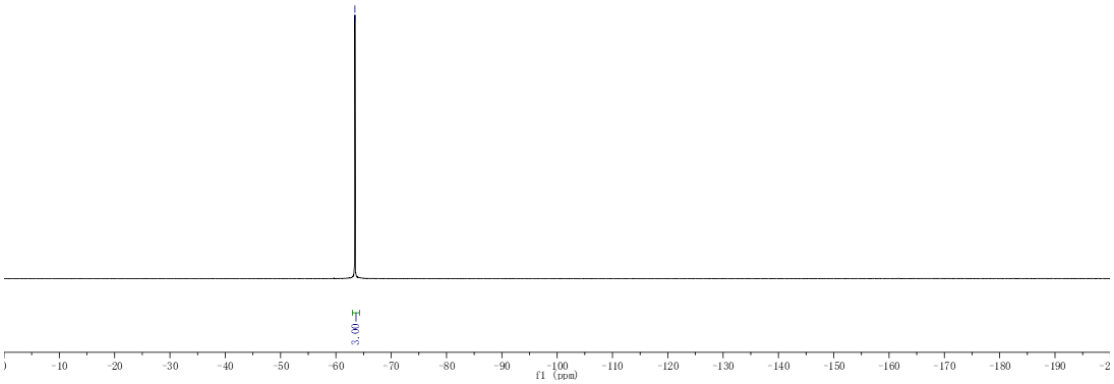
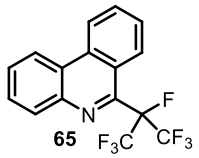
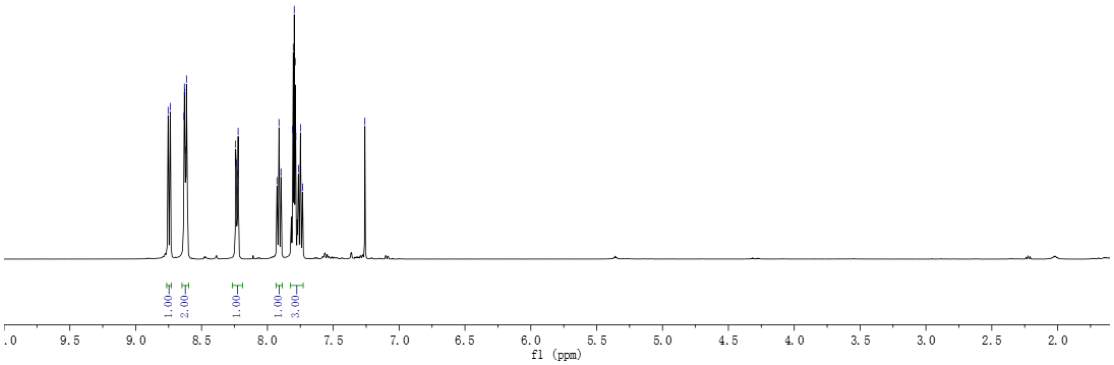
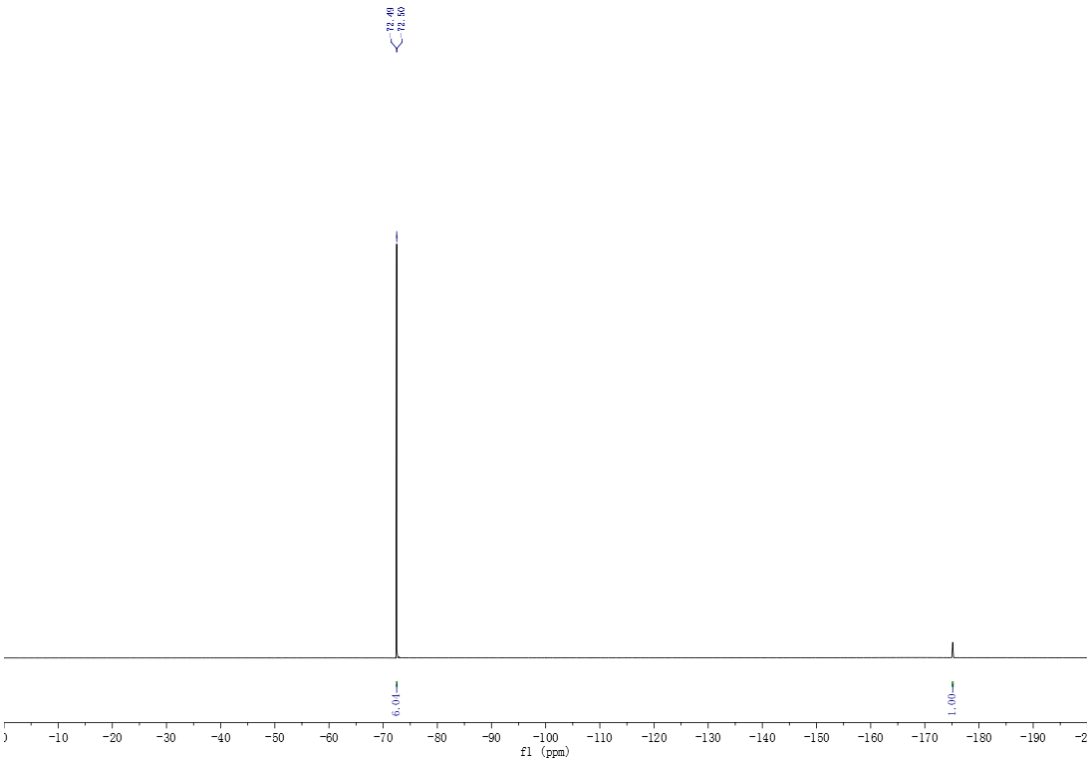


^{19}F NMR of compound **64**

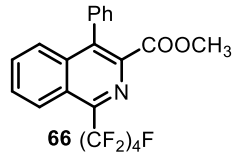


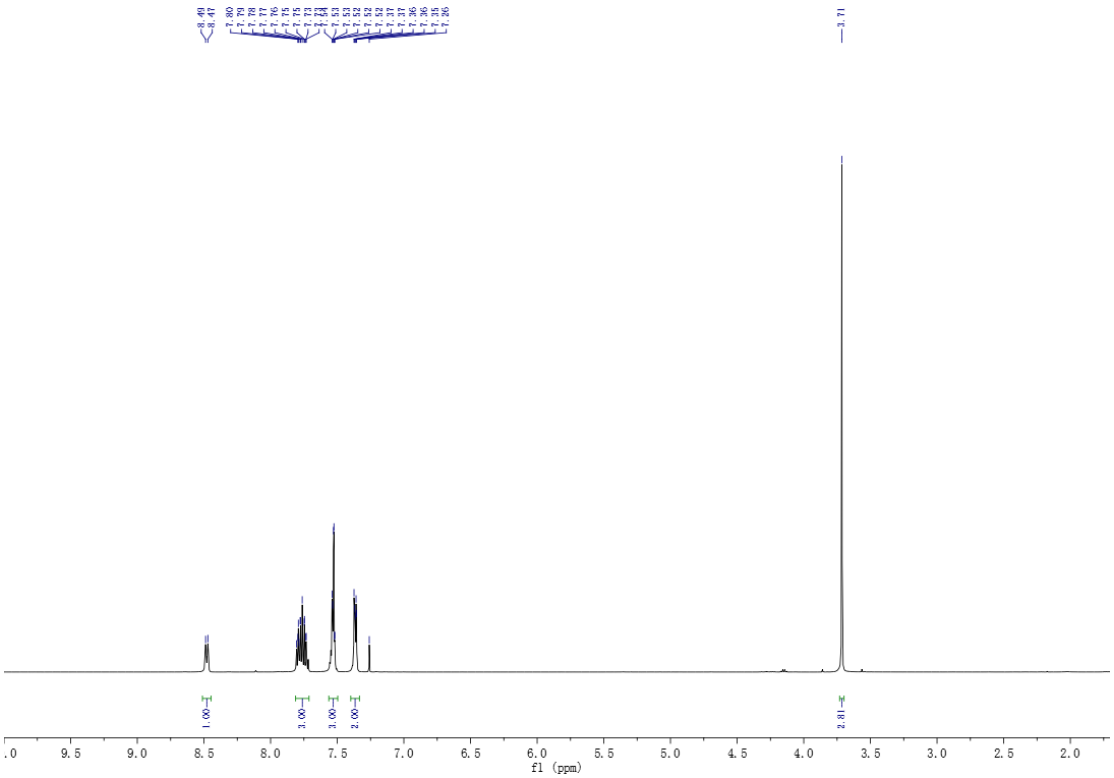


^{1}H NMR of compound **65**

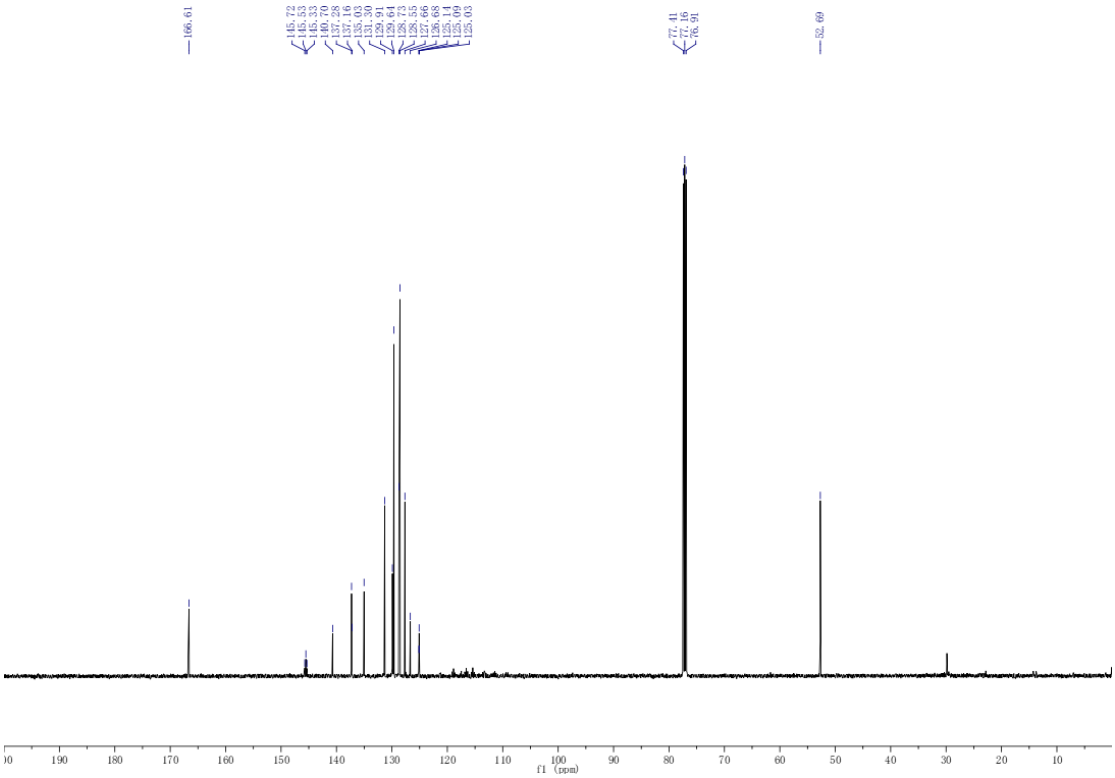


^{19}F NMR of compound **65**

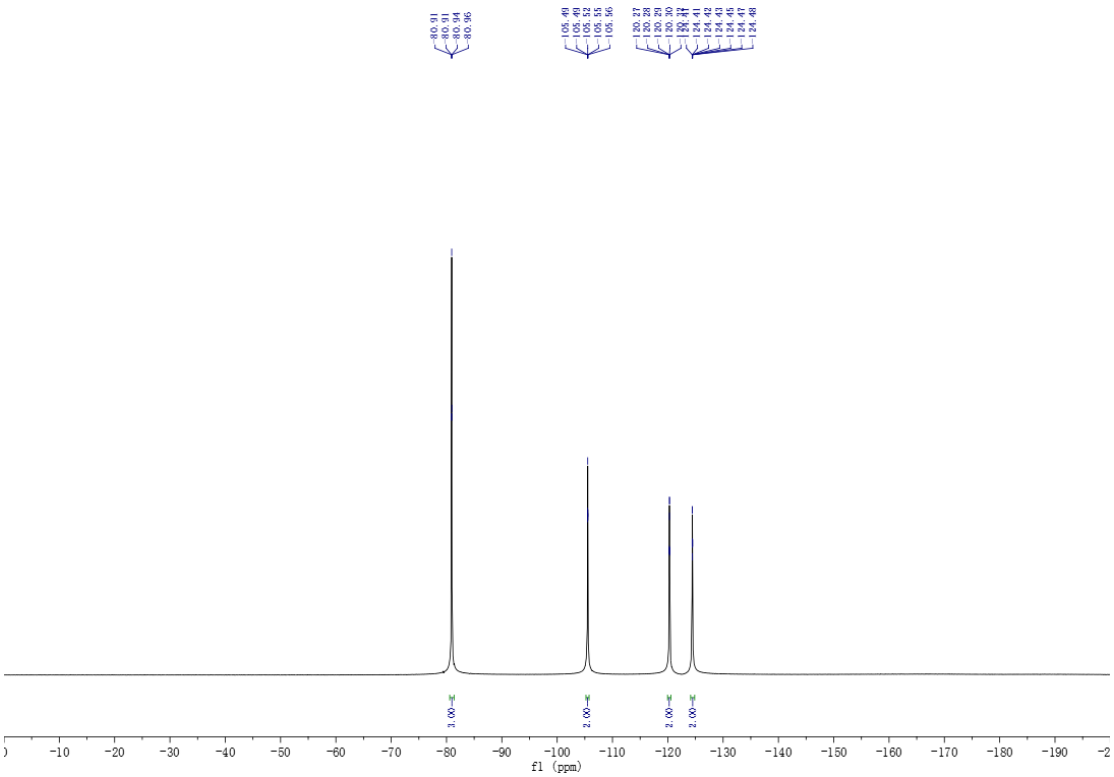




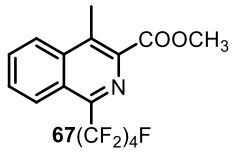
^{1}H NMR of compound **66**

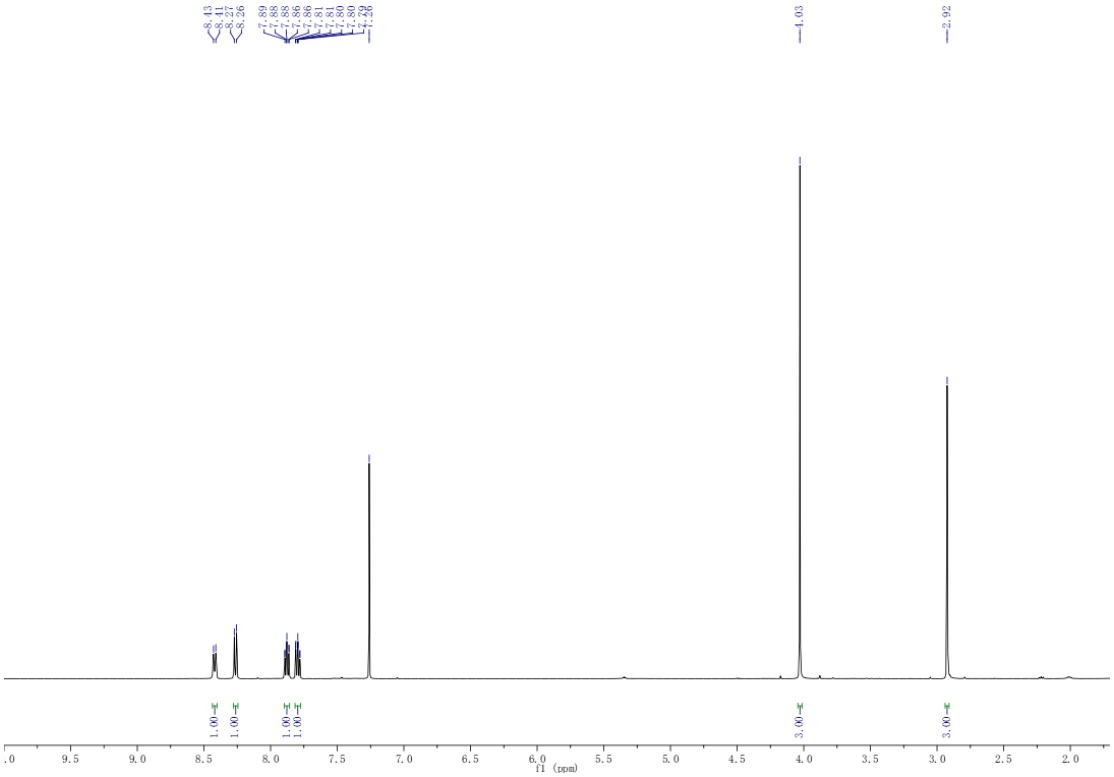


^{13}C NMR of compound **66**

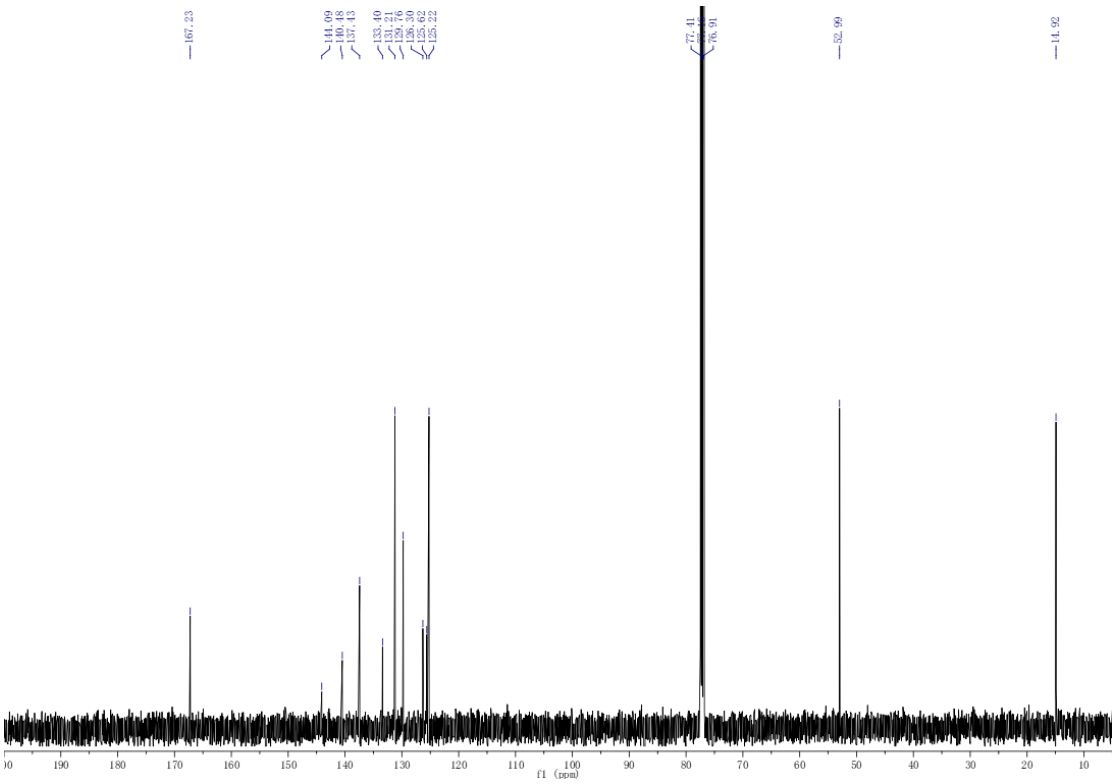


^{19}F NMR of compound **66**

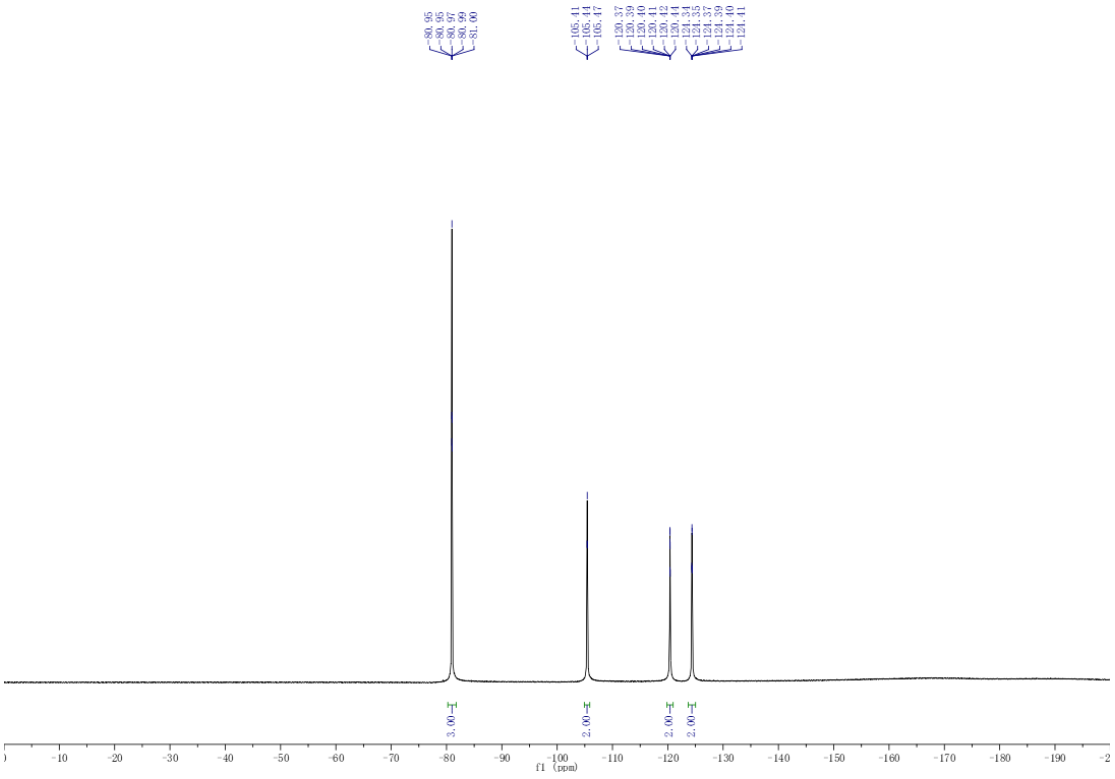




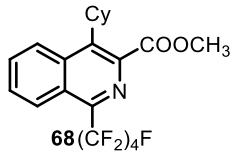
^{1}H NMR of compound **67**

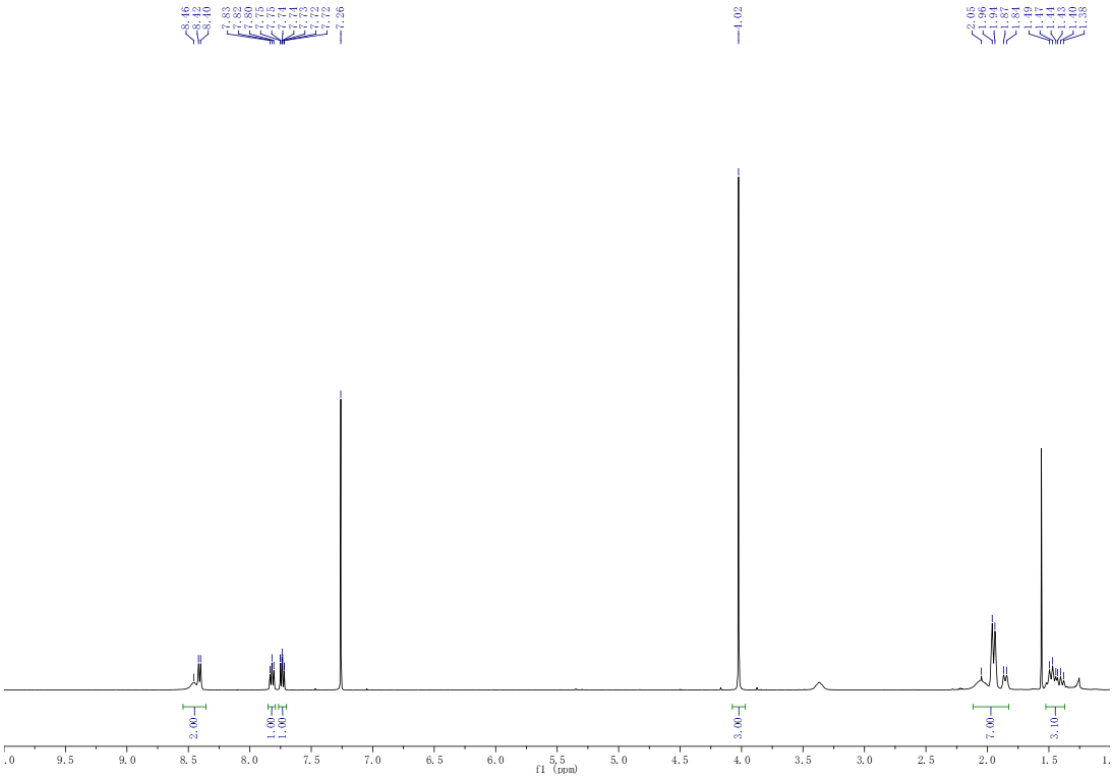


^{13}C NMR of compound **67**

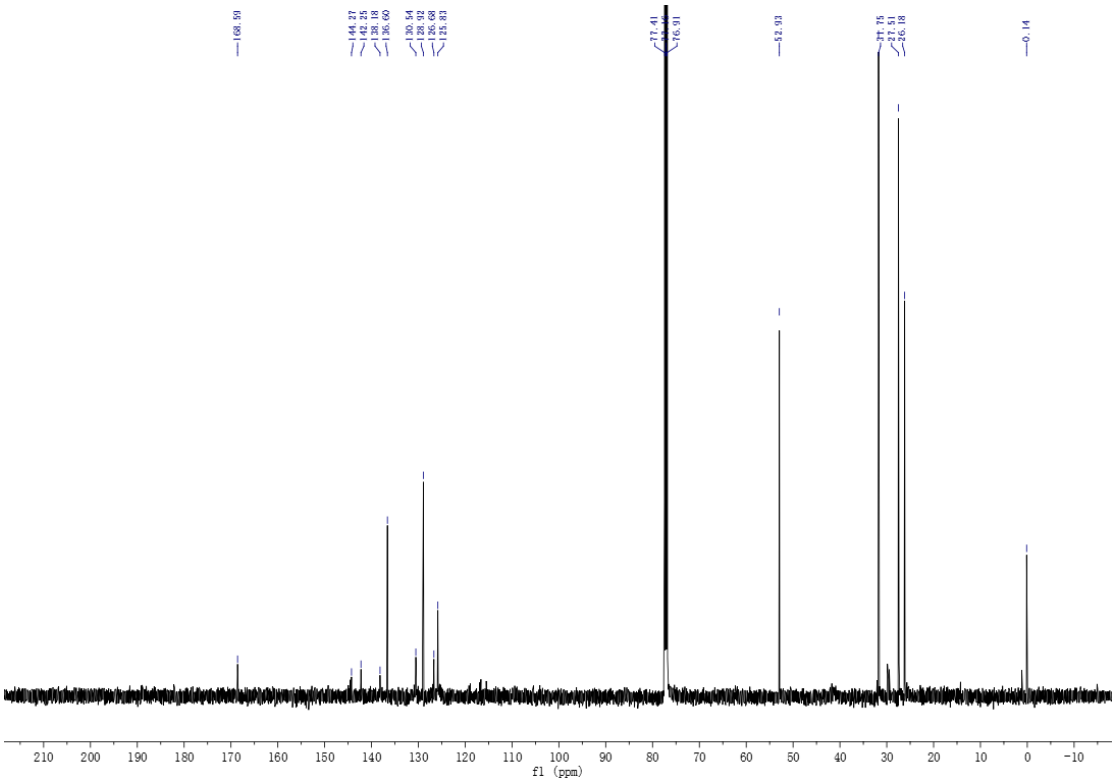


^{19}F NMR of compound **67**

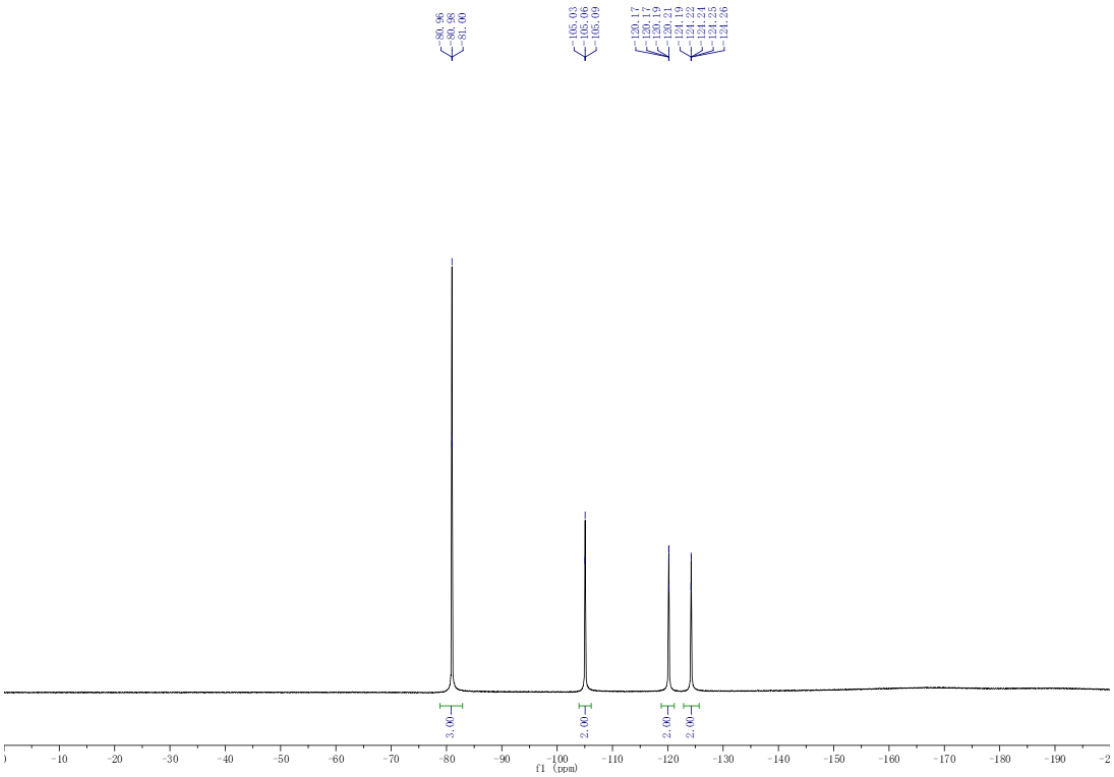




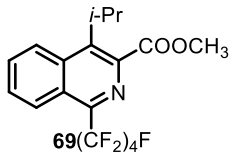
^{1}H NMR of compound **68**

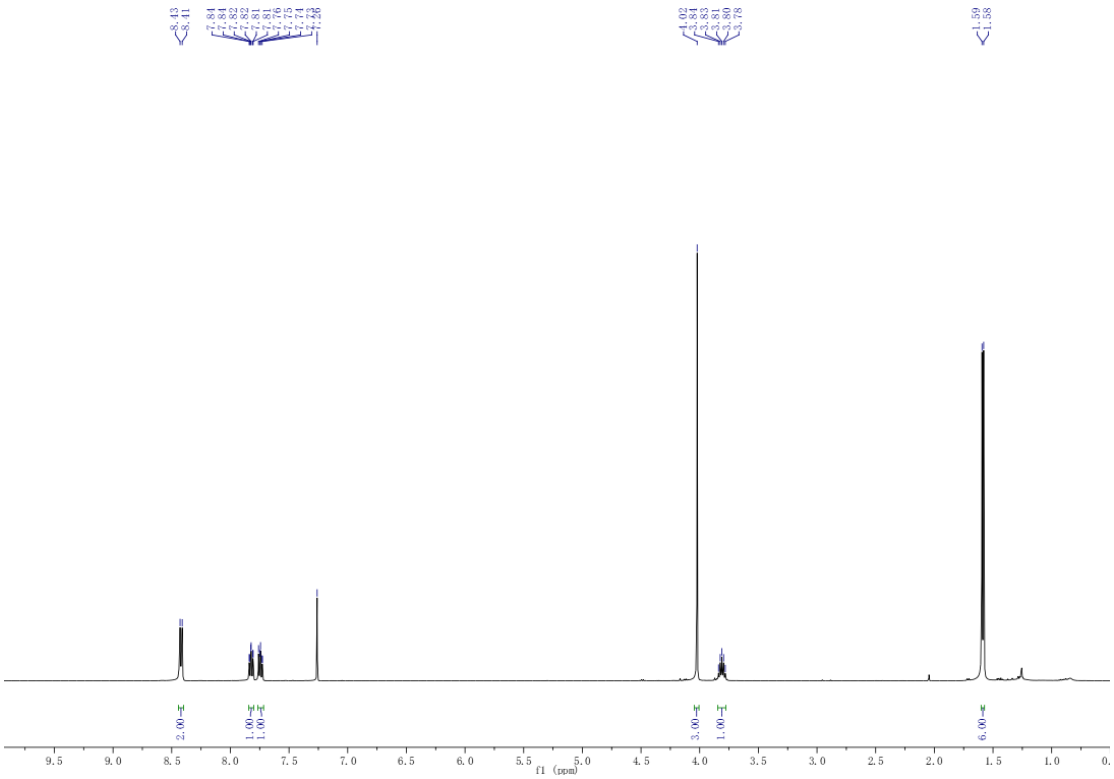


^{13}C NMR of compound **68**

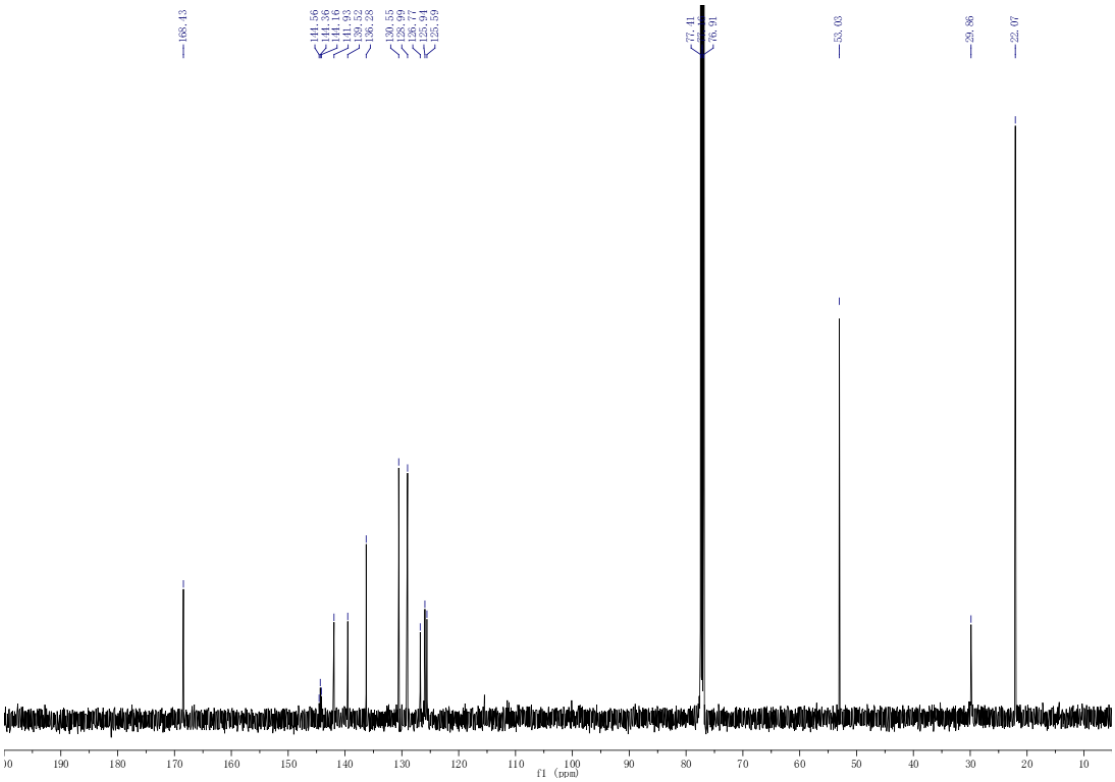


^{19}F NMR of compound **68**

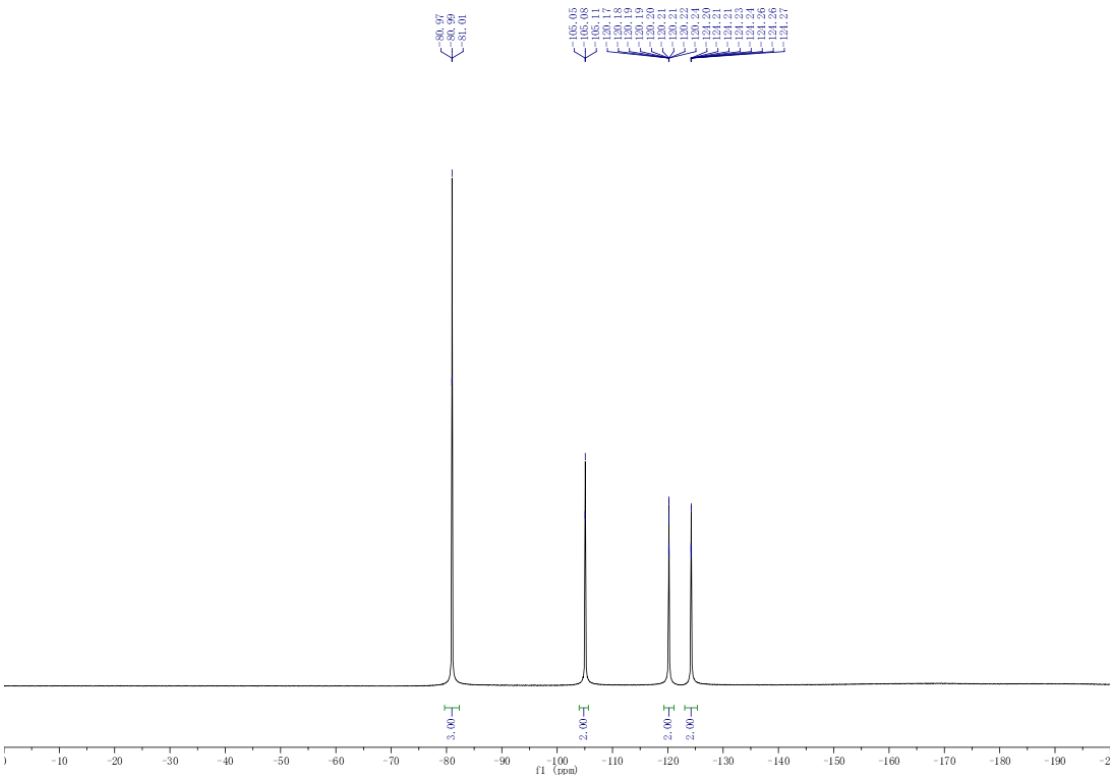




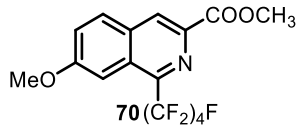
^{1}H NMR of compound **69**

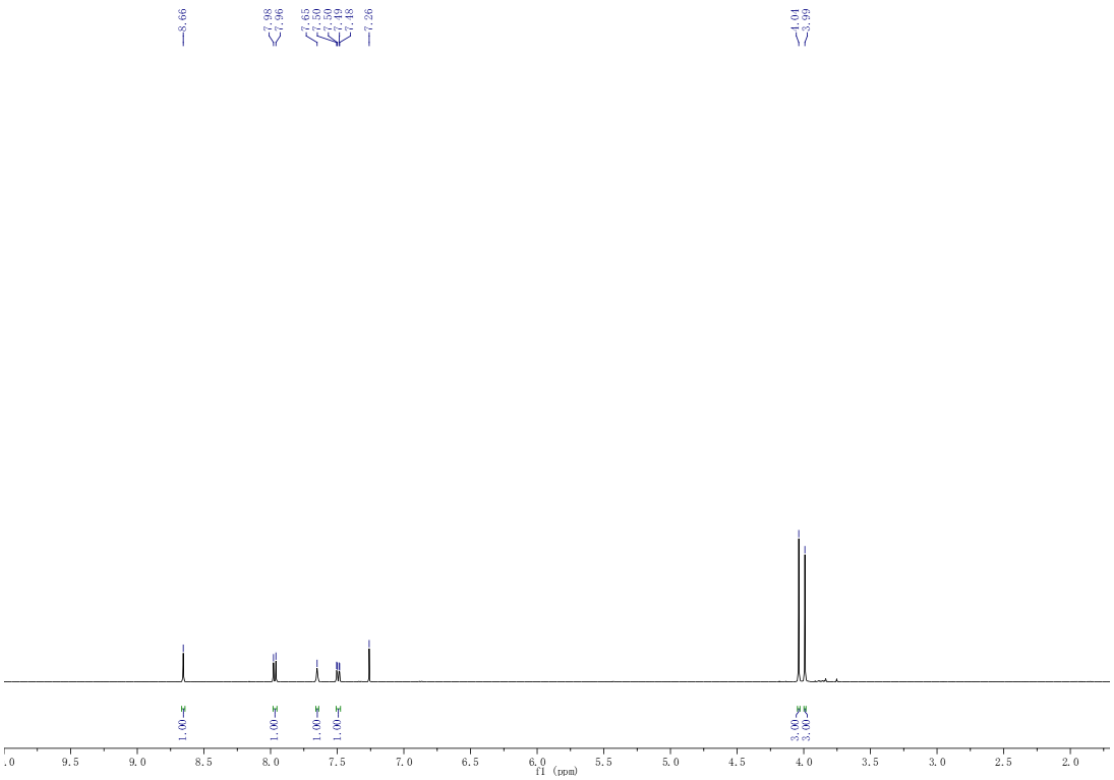


^{13}C NMR of compound **69**

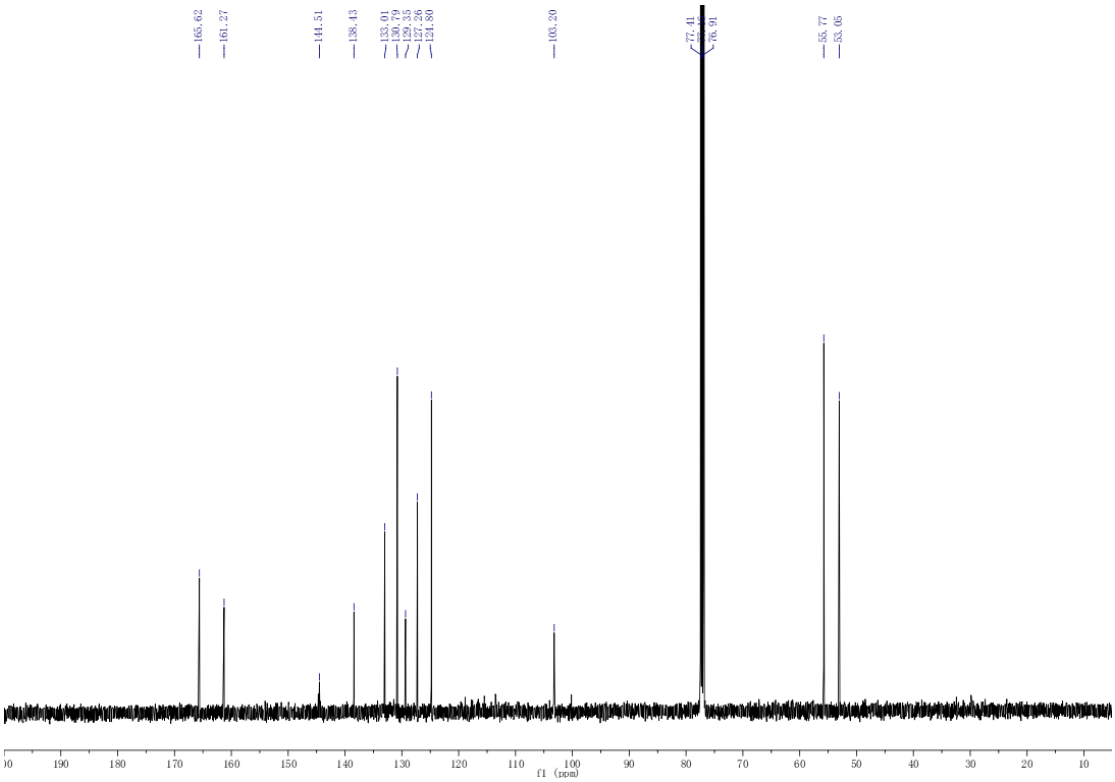


^{19}F NMR of compound **69**

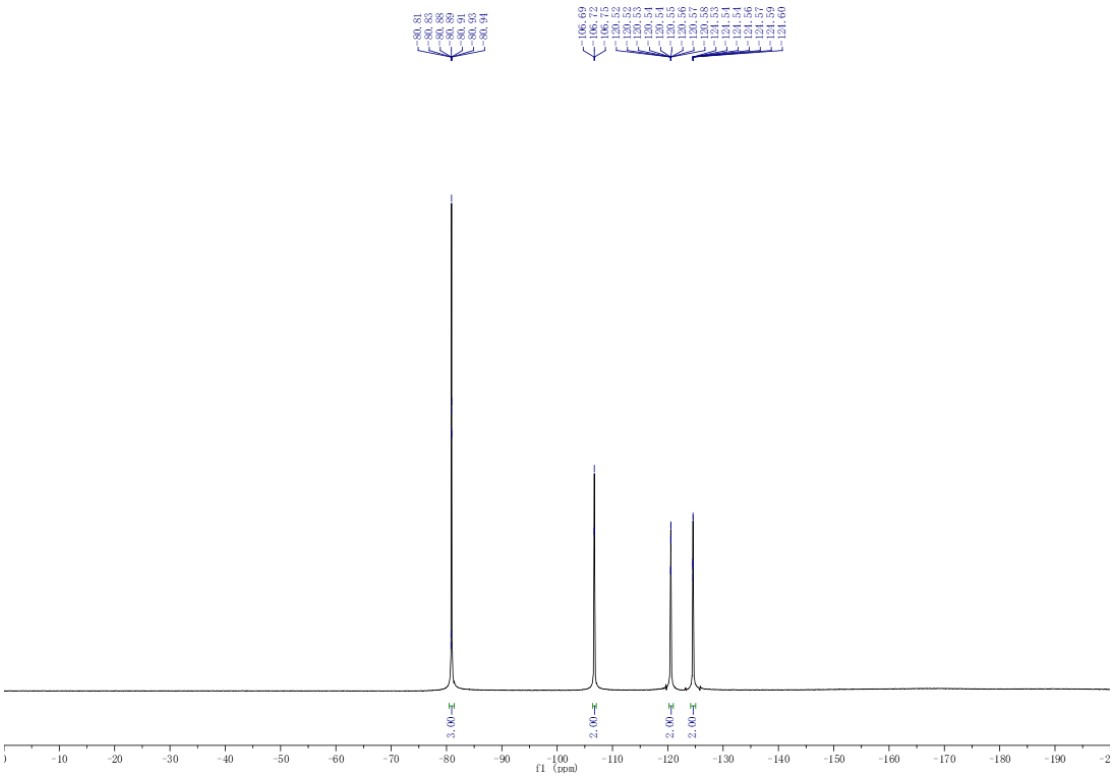




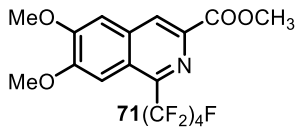
^{1}H NMR of compound **70**

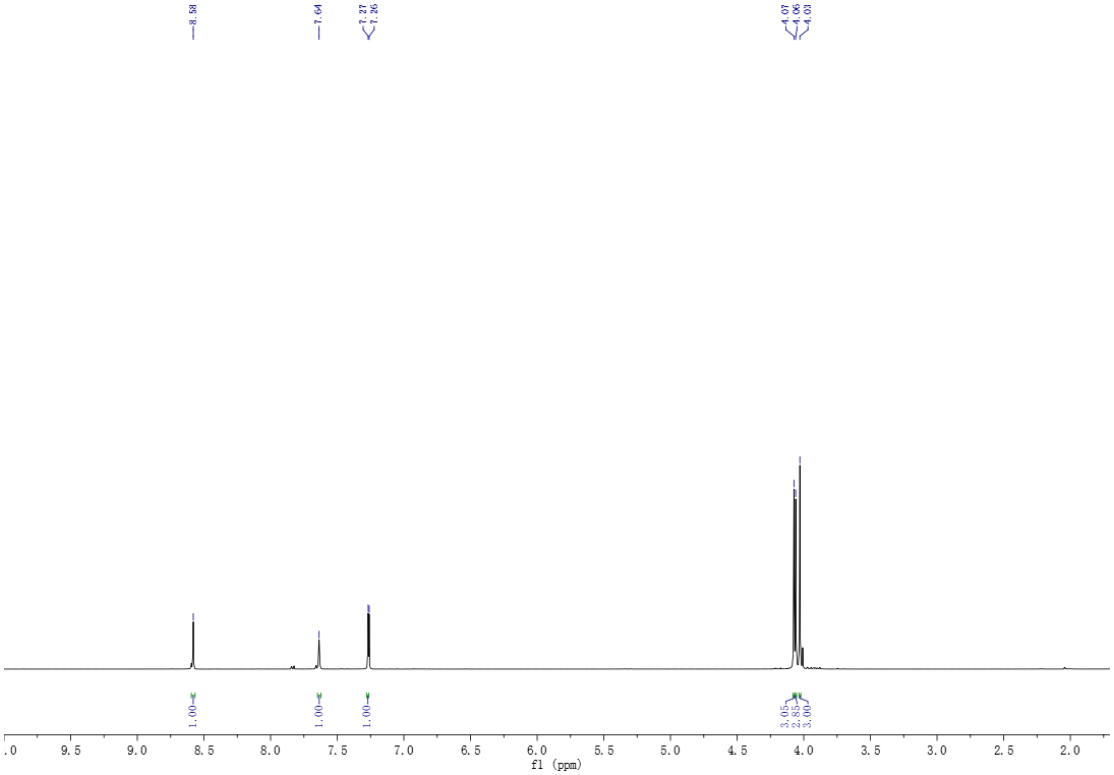


^{13}C NMR of compound **70**

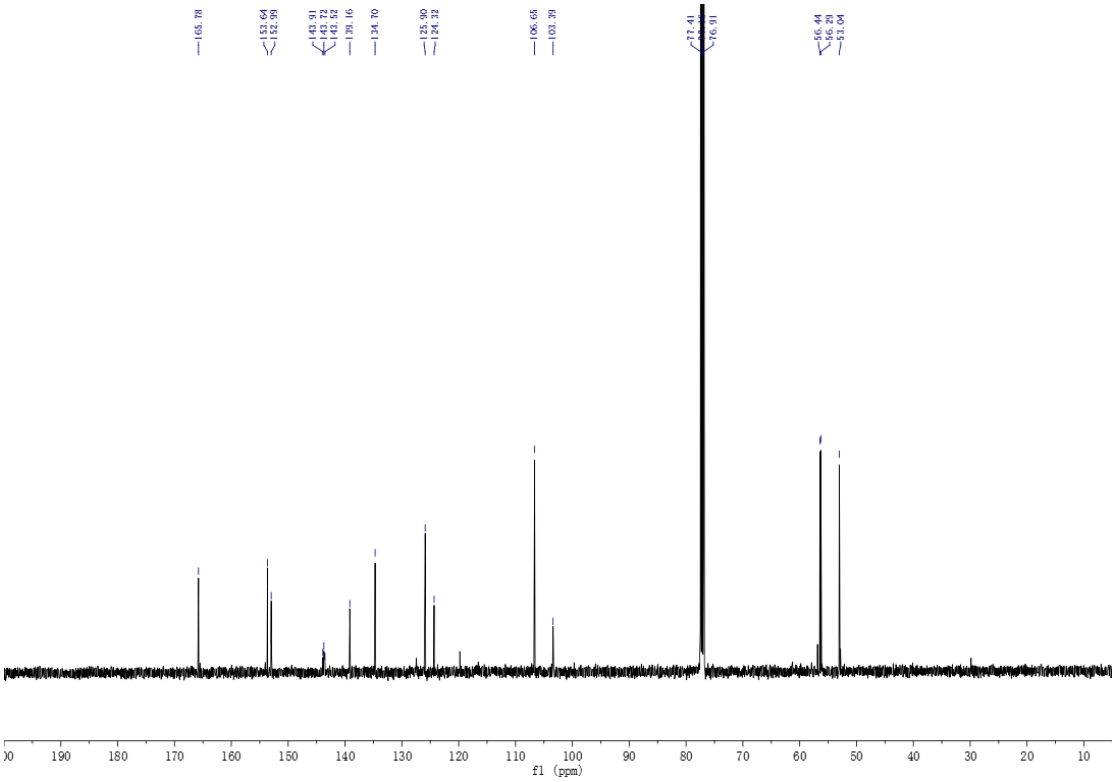


^{19}F NMR of compound **70**

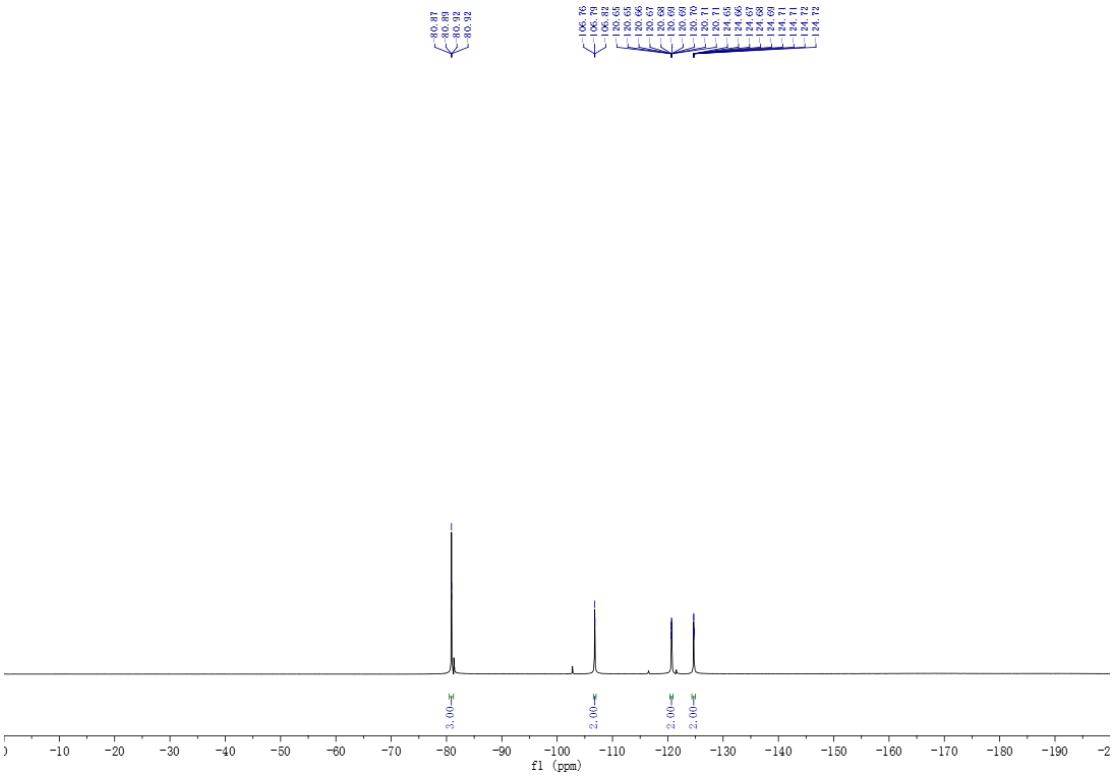




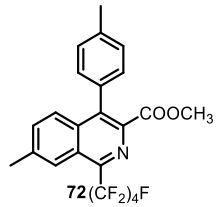
^{1}H NMR of compound **71**

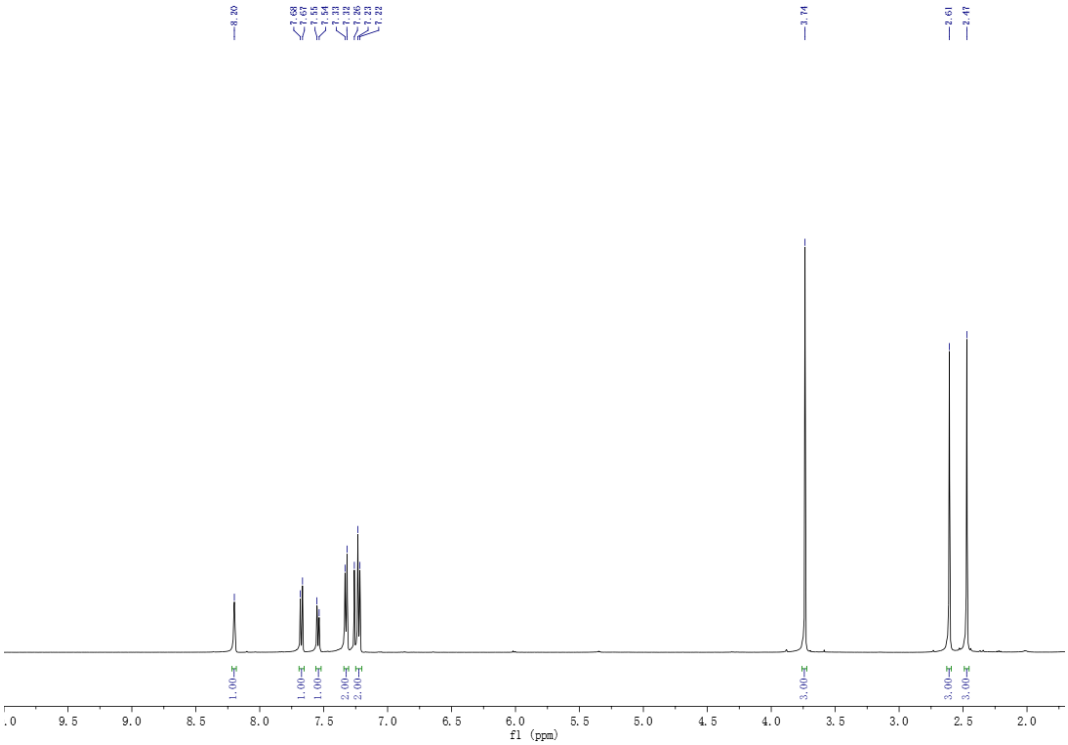


^{13}C NMR of compound **71**

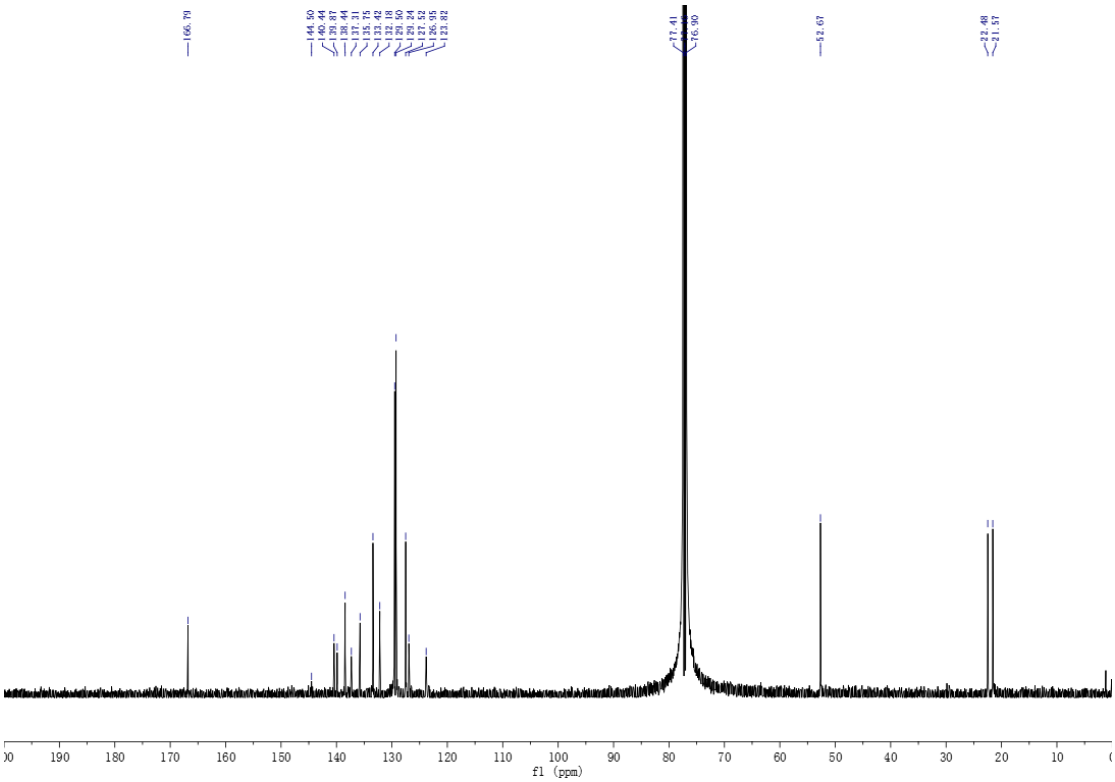


^{19}F NMR of compound **71**

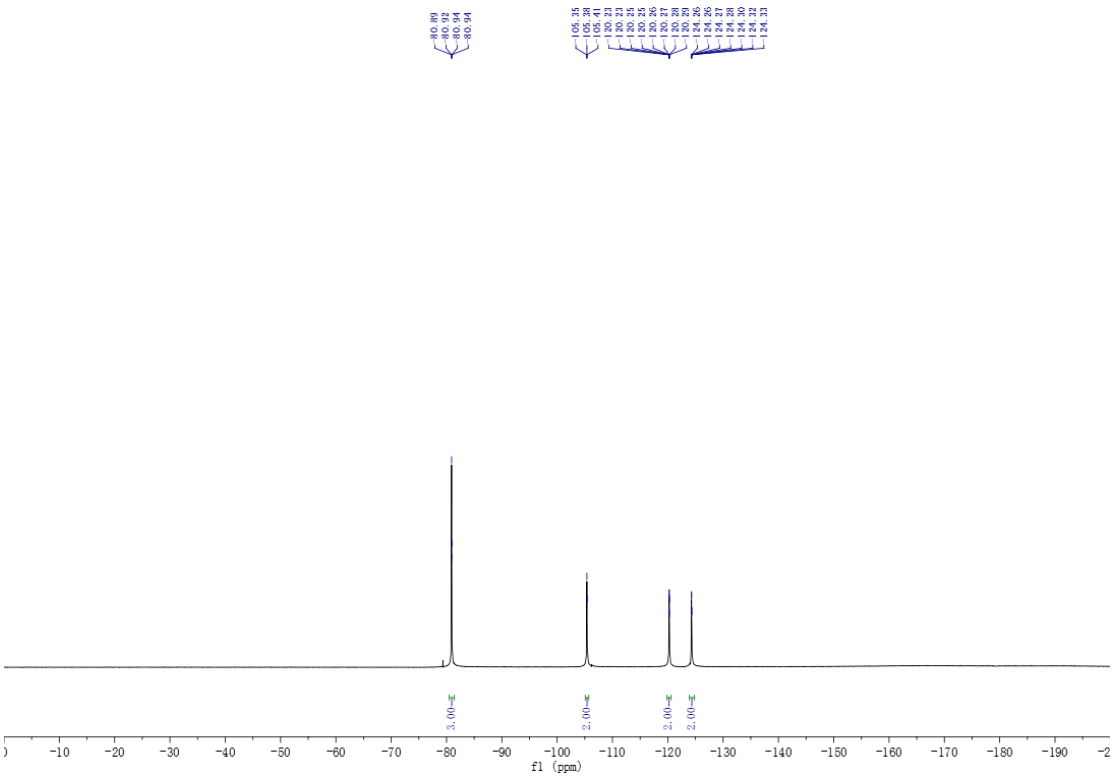




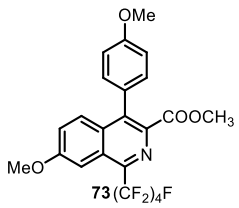
^{1}H NMR of compound **72**

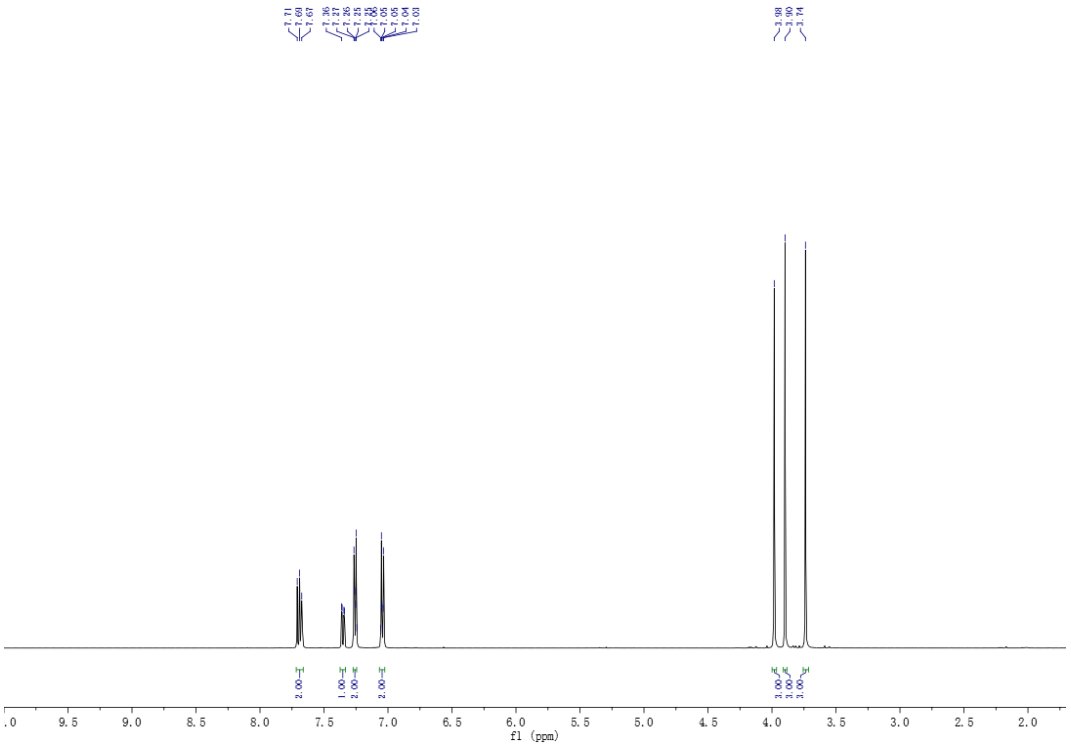


^{13}C NMR of compound **72**

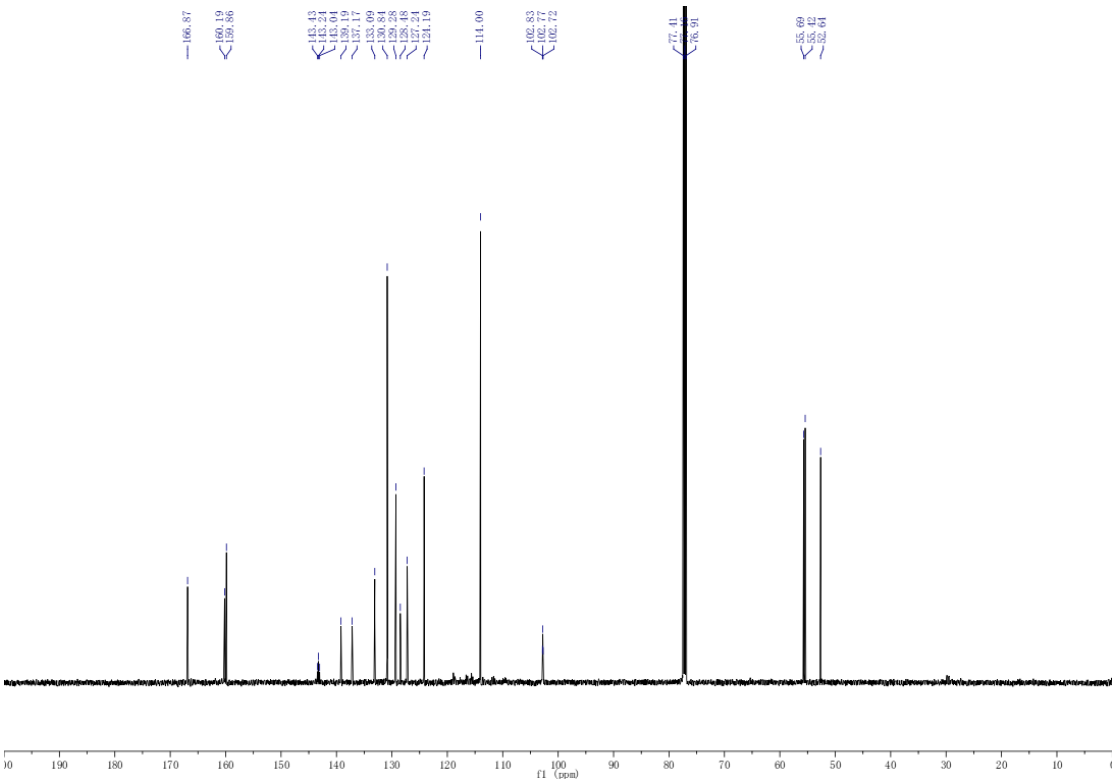


^{19}F NMR of compound **72**

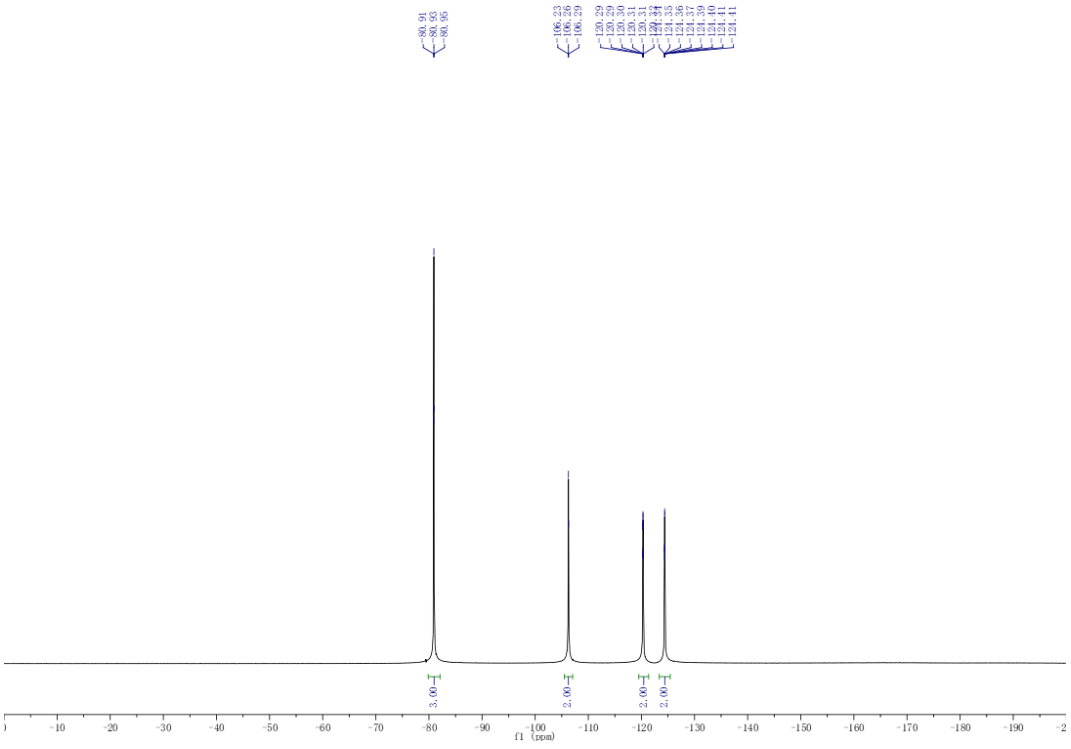




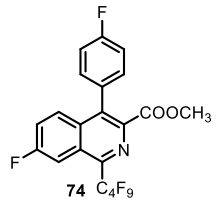
^{1}H NMR of compound **73**

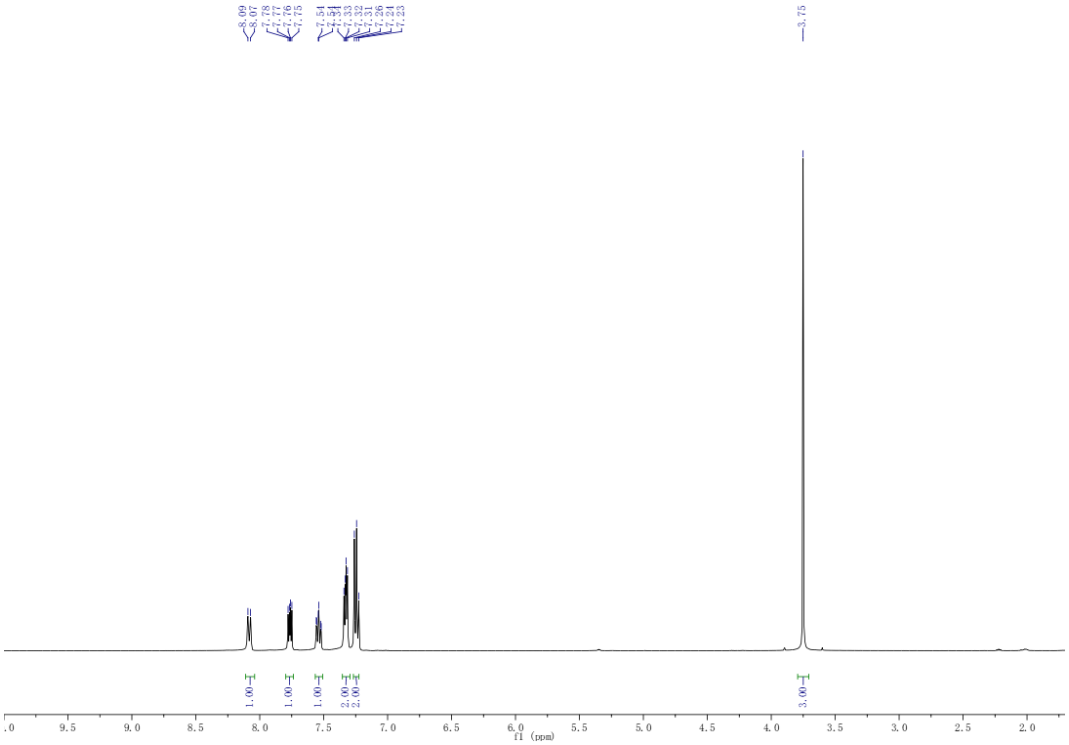


^{13}C NMR of compound **73**

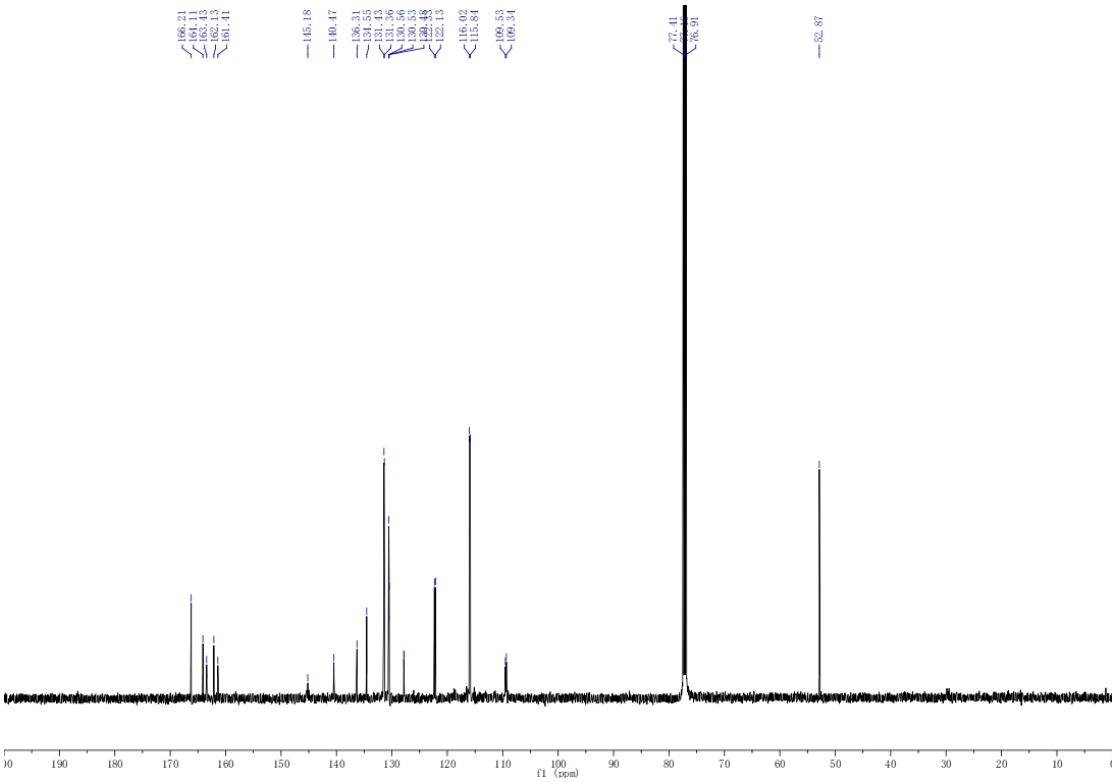


^{19}F NMR of compound **73**





^{1}H NMR of compound **74**



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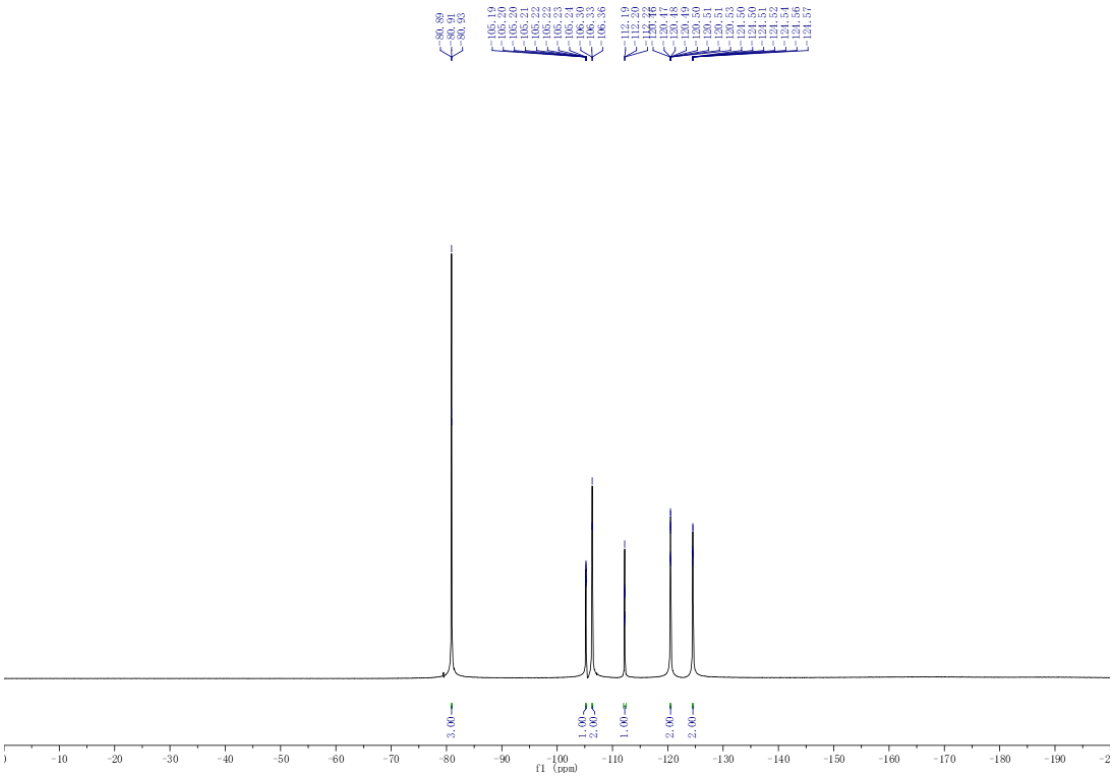
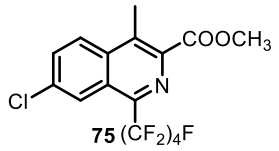
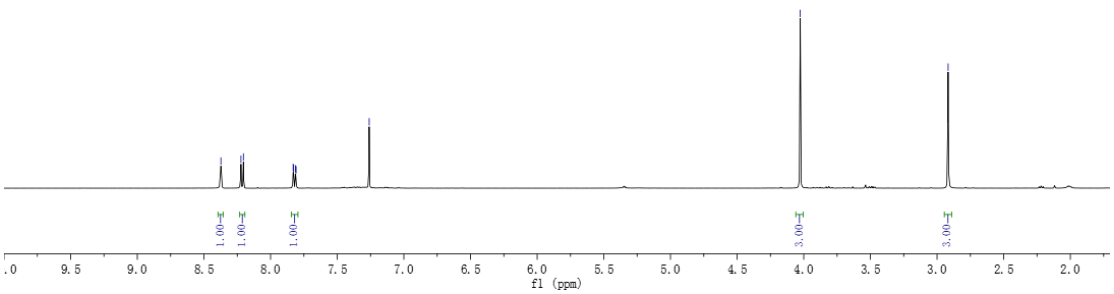
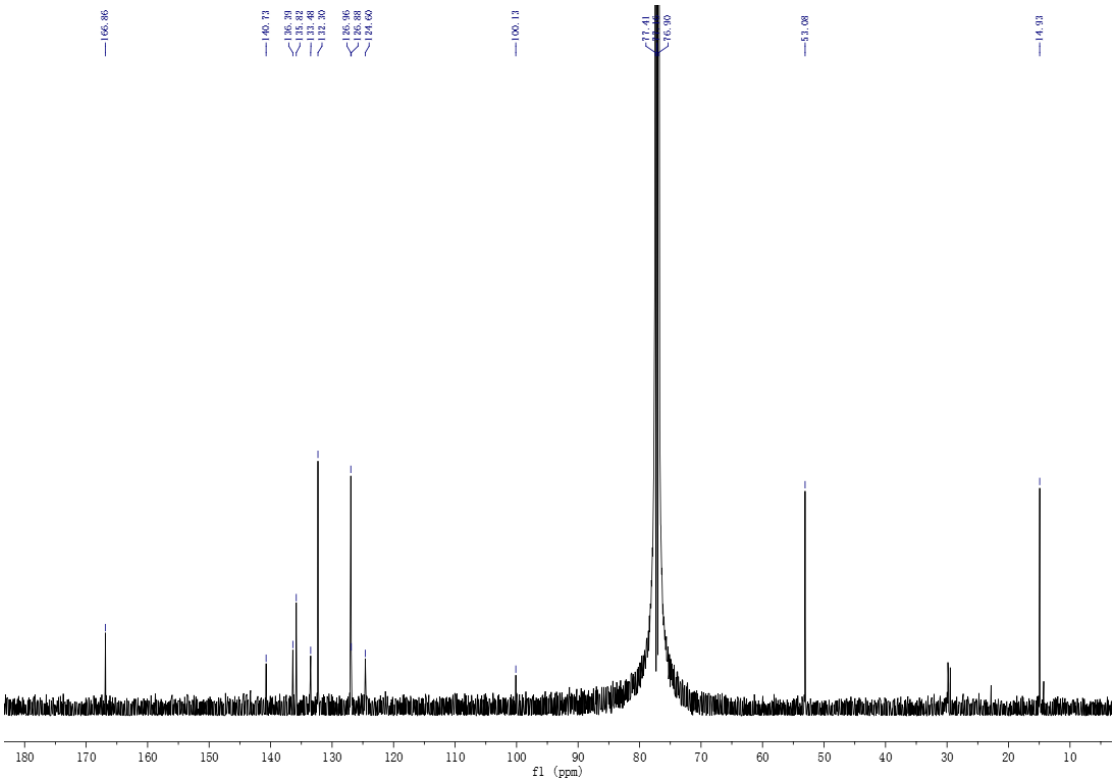


^{19}F NMR of compound **74**

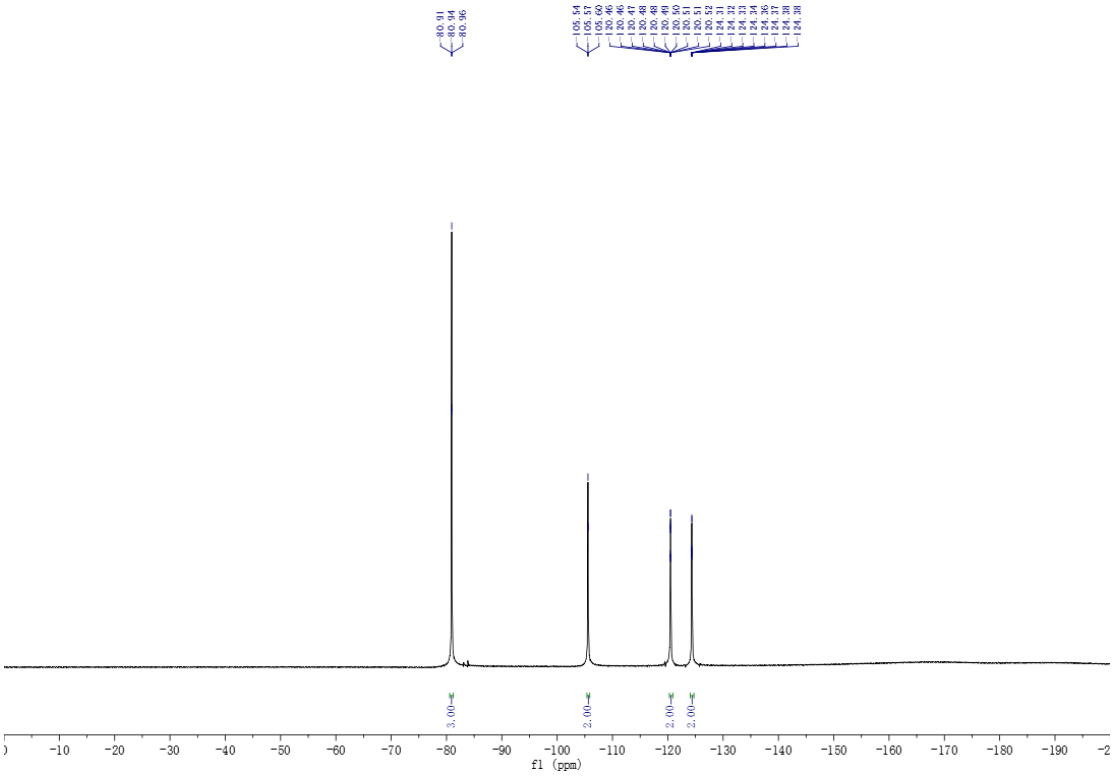




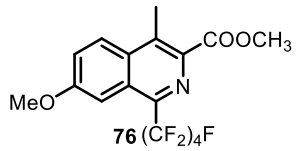
^{1}H NMR of compound **75**

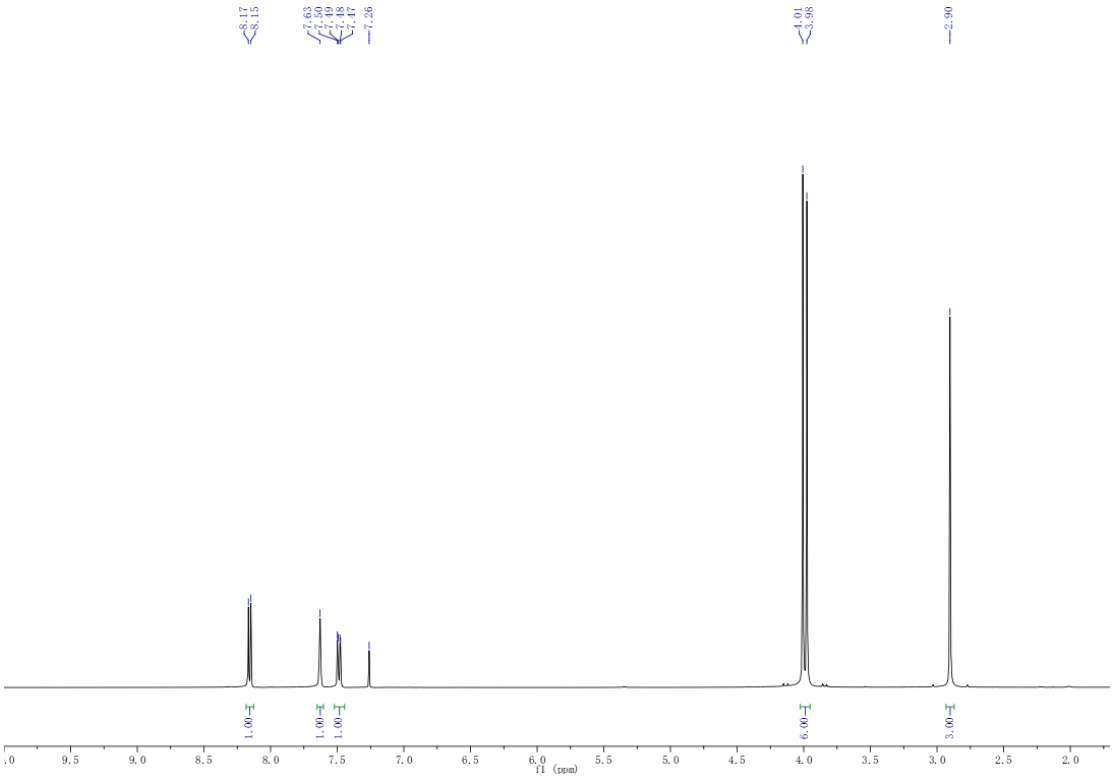


^{13}C NMR of compound **75**

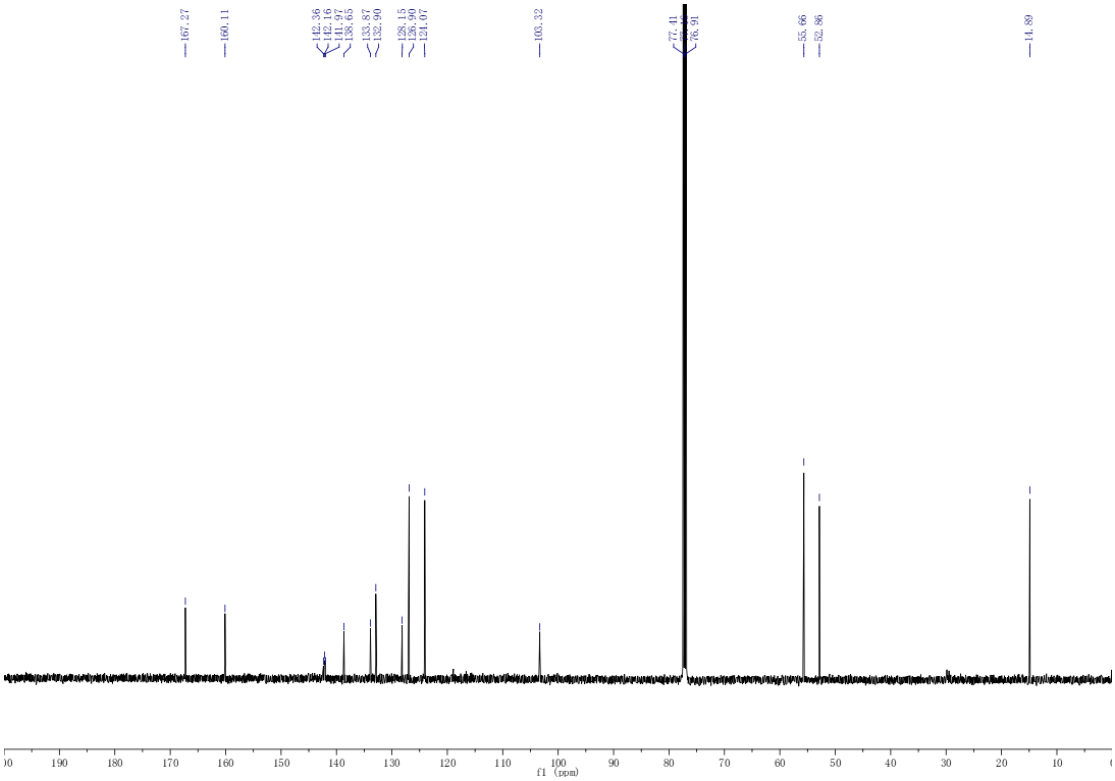


^{19}F NMR of compound **75**

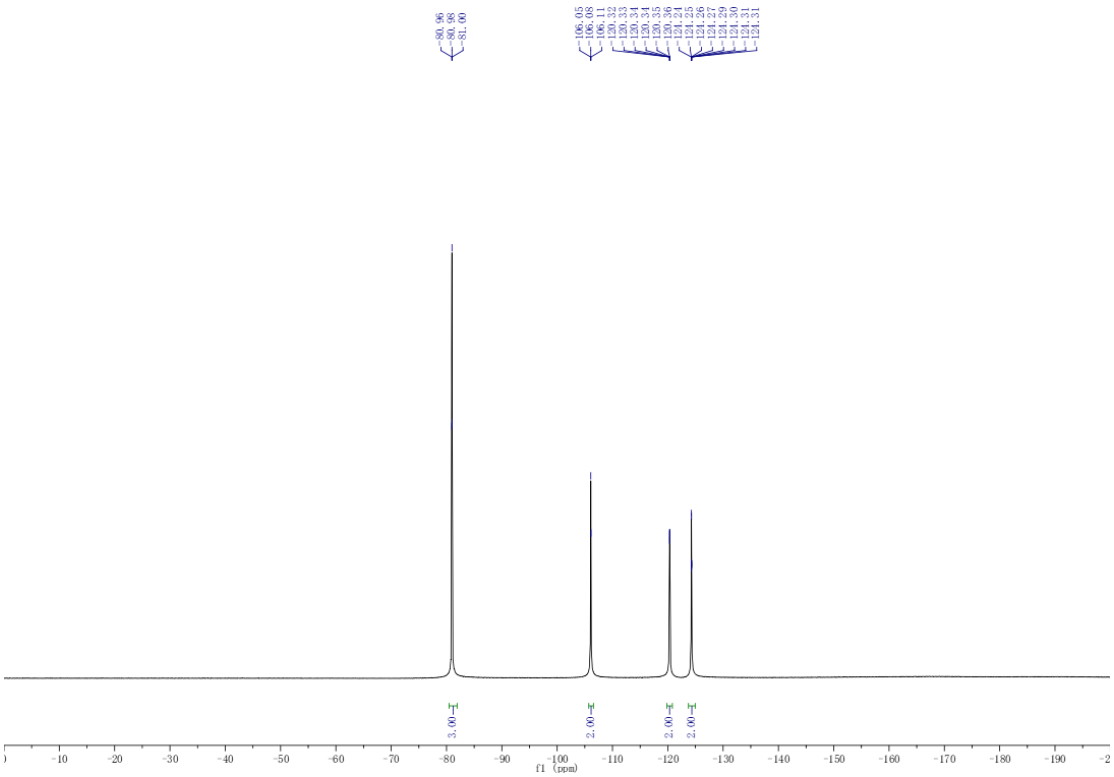




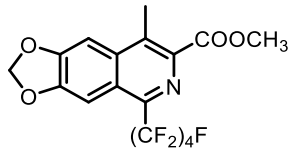
^{1}H NMR of compound **76**



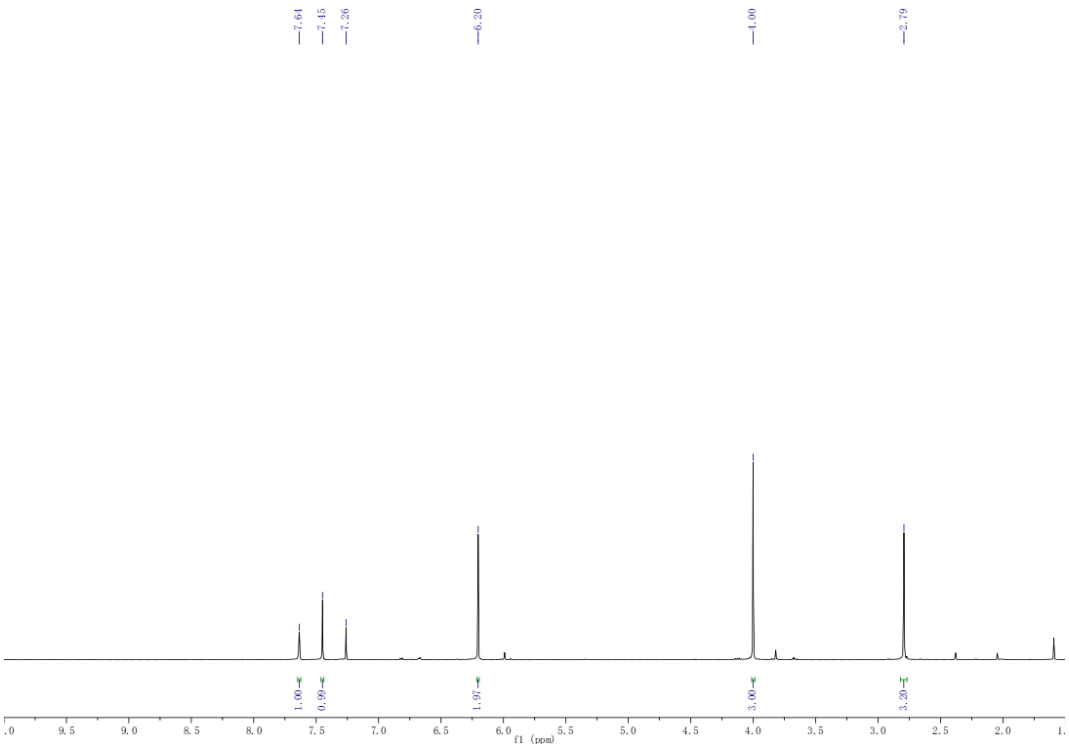
^{13}C NMR of compound **76**



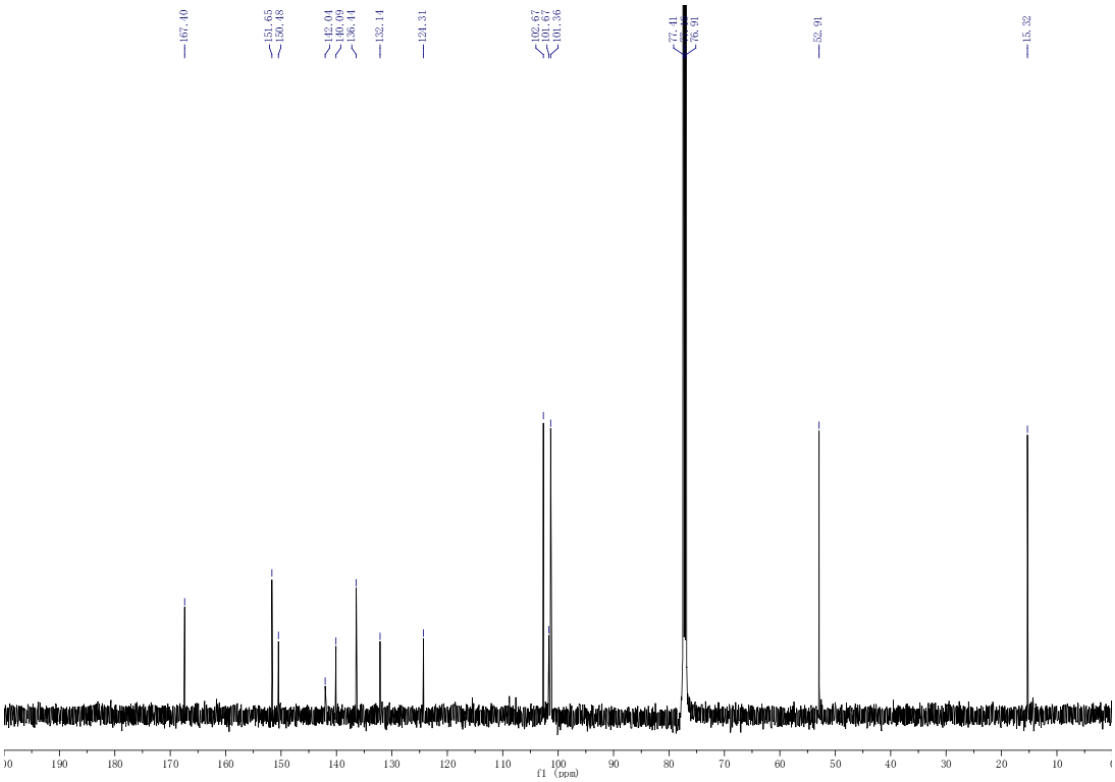
^{19}F NMR of compound **76**



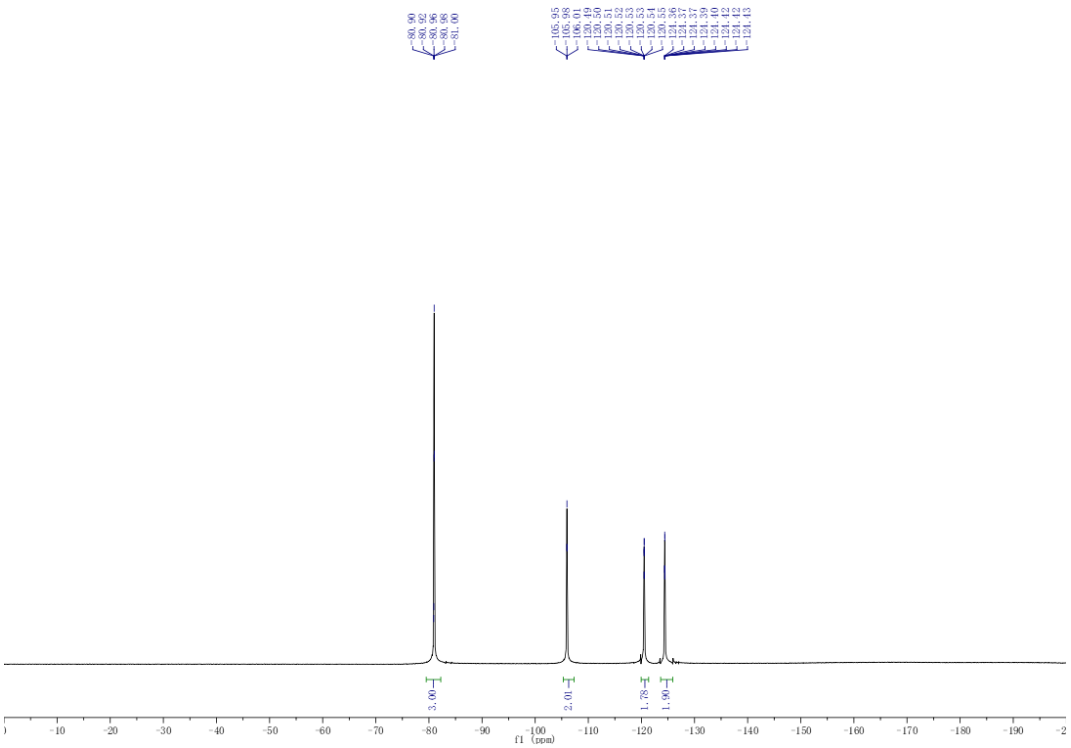
77



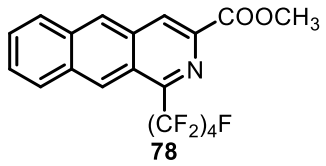
^{1}H NMR of compound **77**



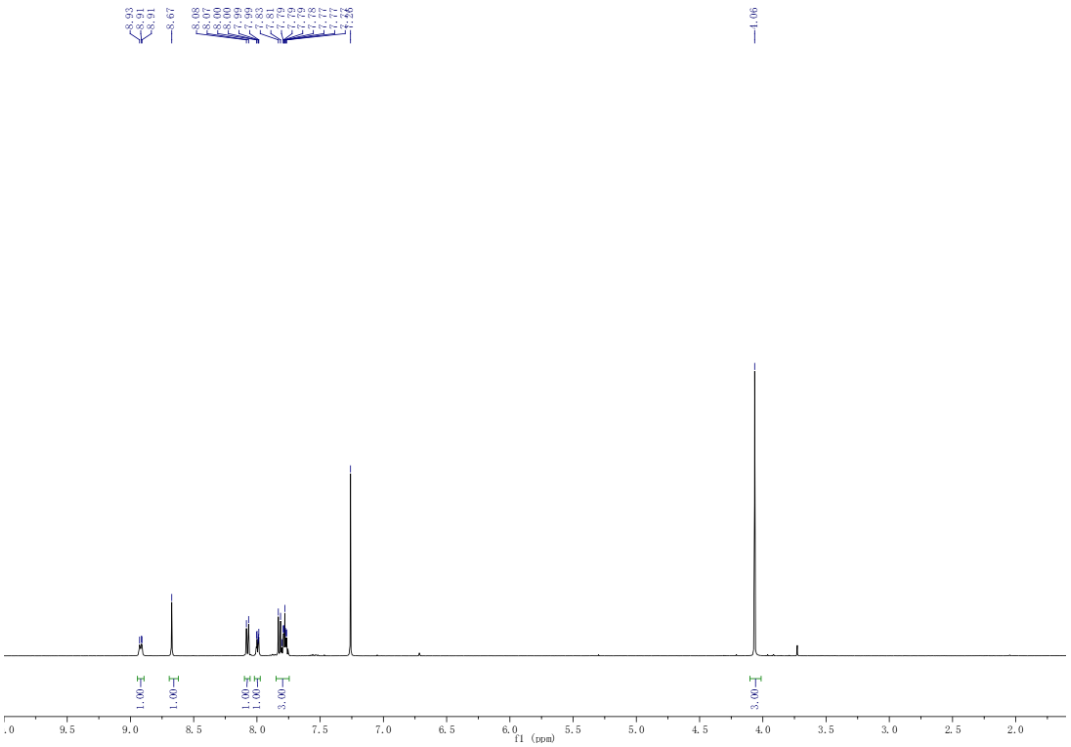
^{13}C NMR of compound **77**



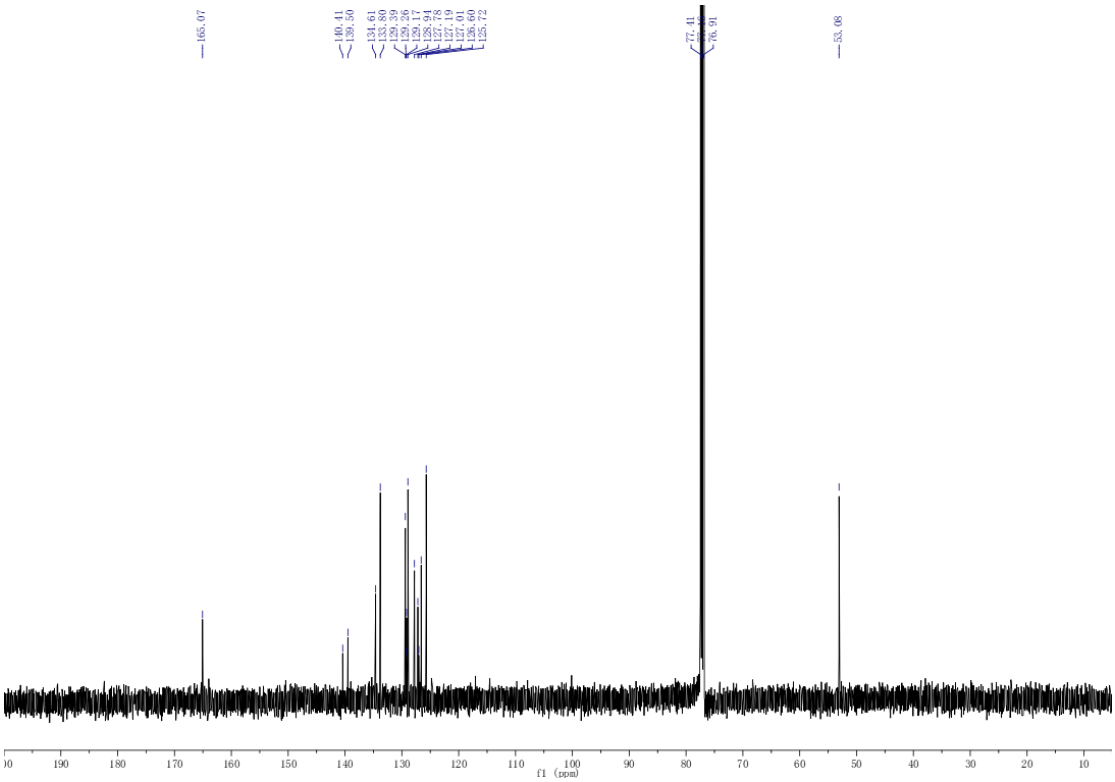
^{19}F NMR of compound **77**



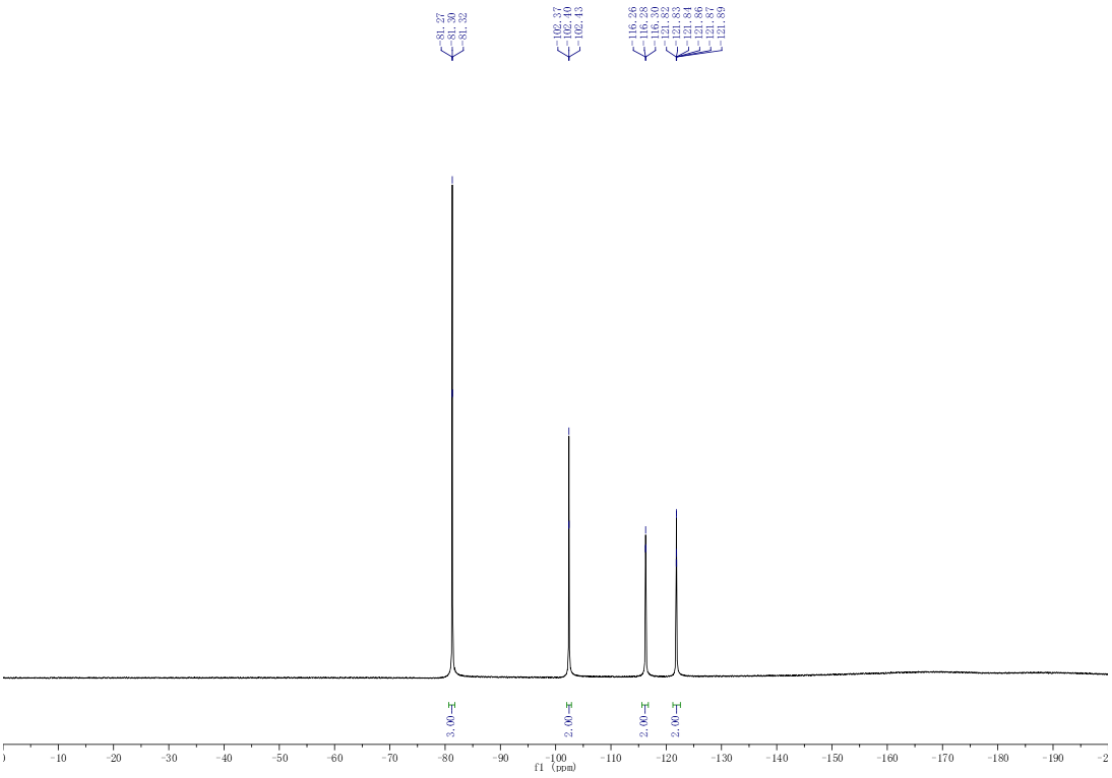
78



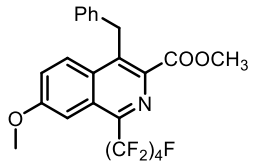
^{1}H NMR of compound **78**



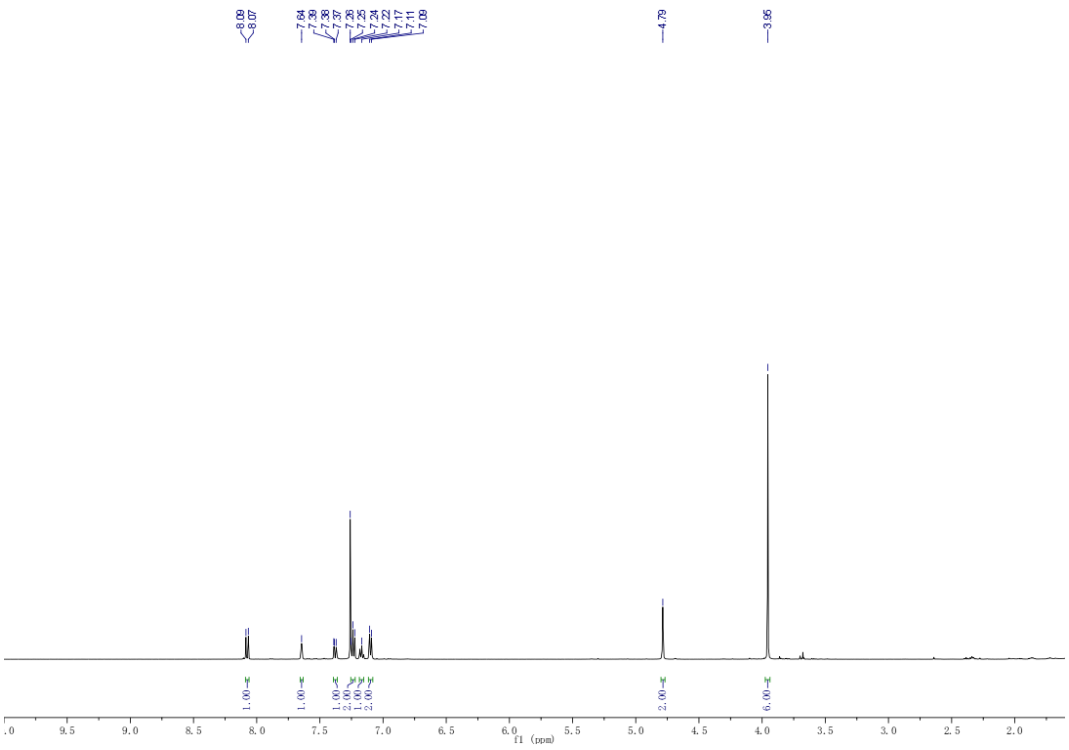
^{13}C NMR of compound **78**



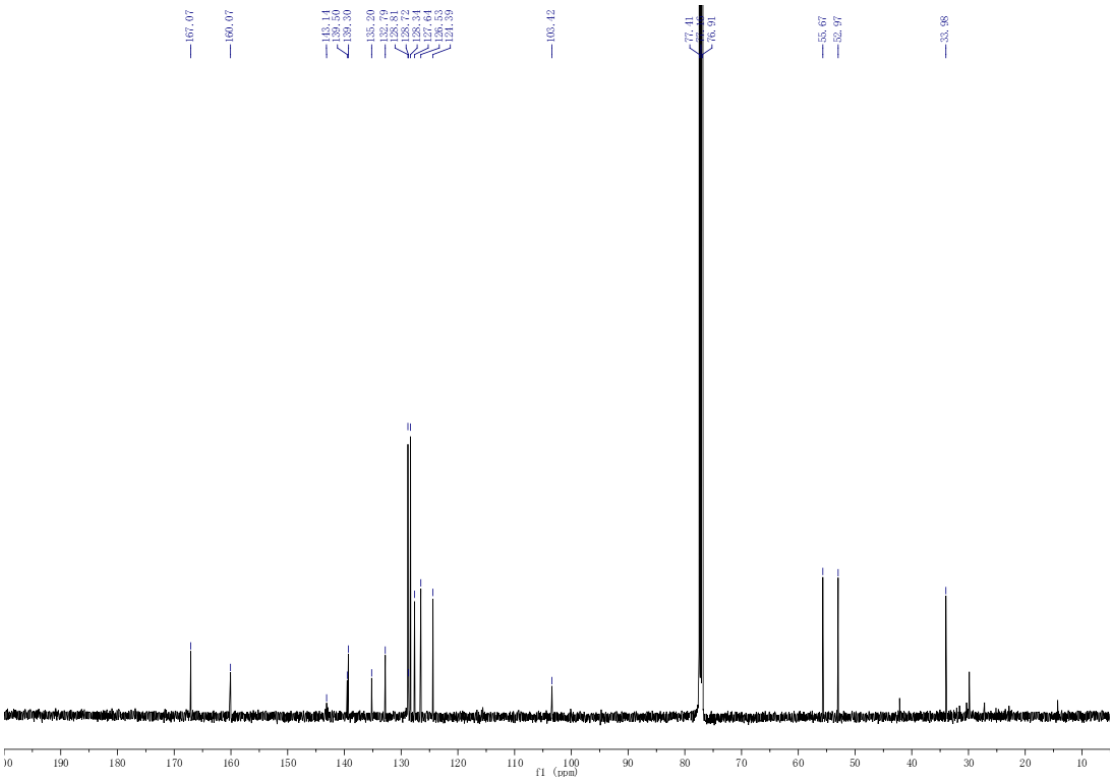
^{19}F NMR of compound **78**



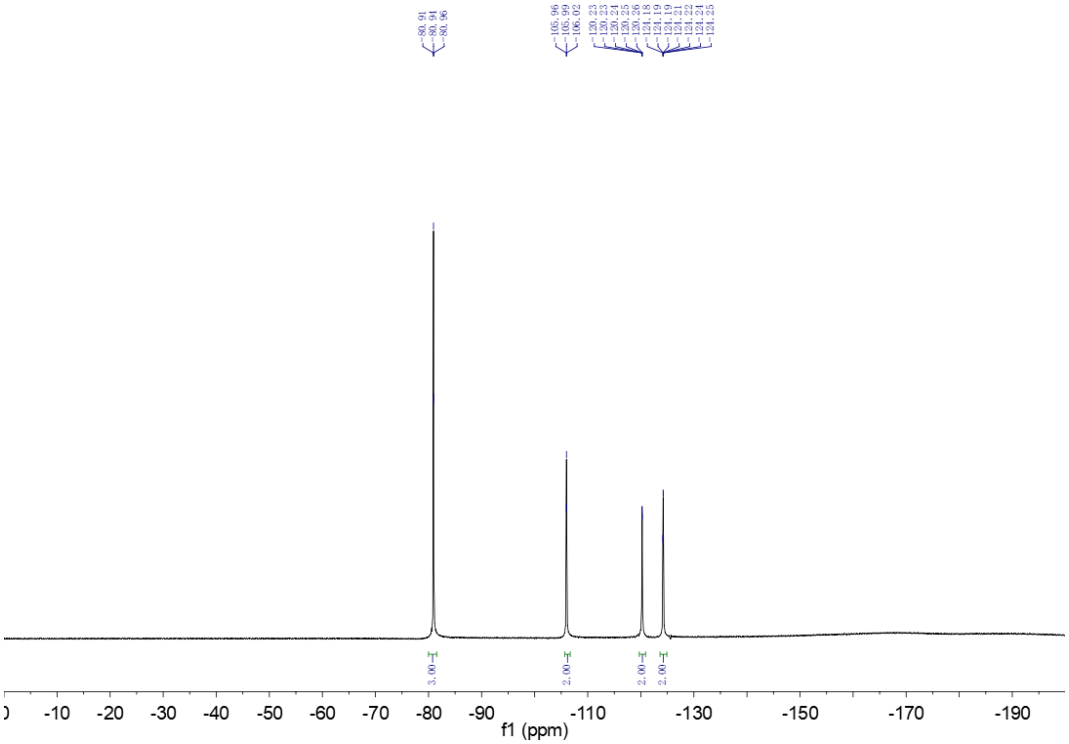
79



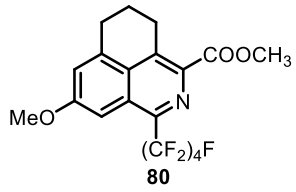
^{1}H NMR of compound **79**



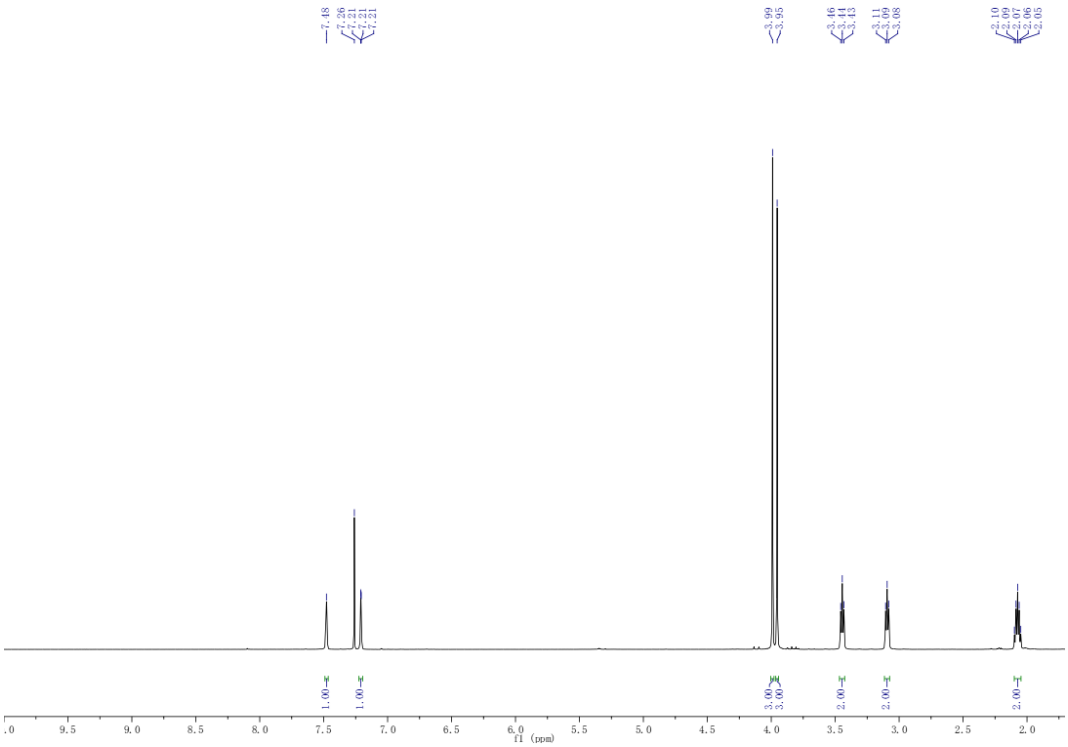
^{13}C NMR of compound **79**



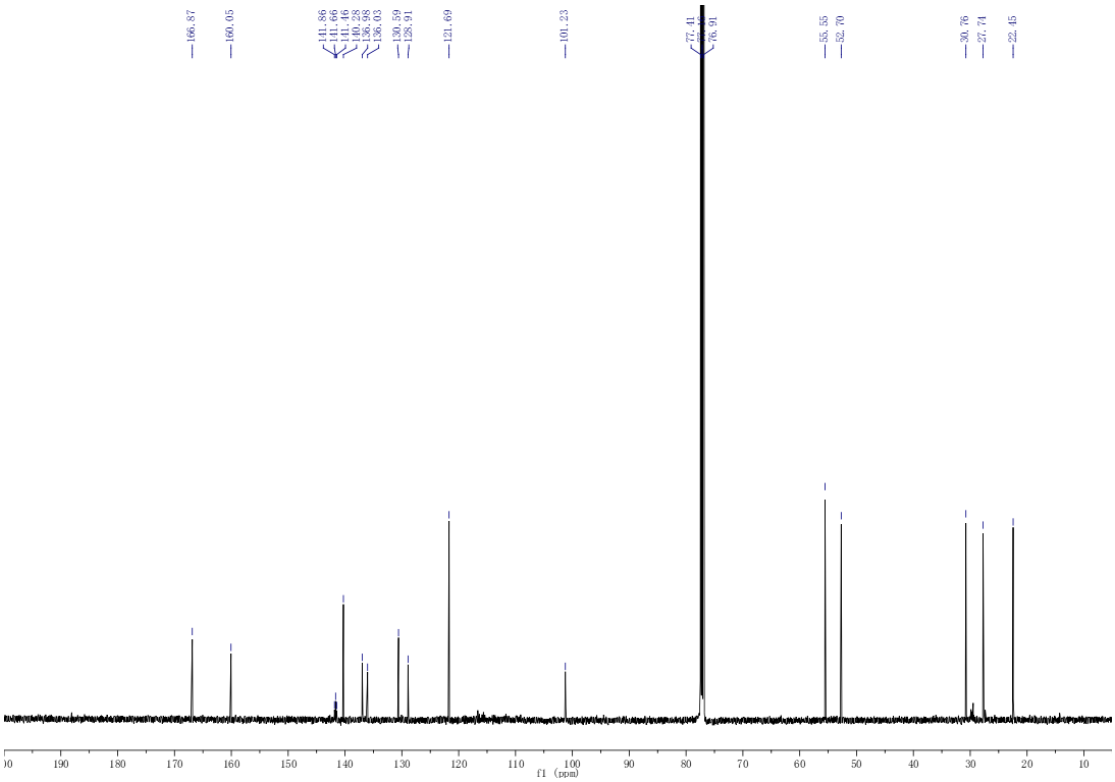
^{19}F NMR of compound **79**



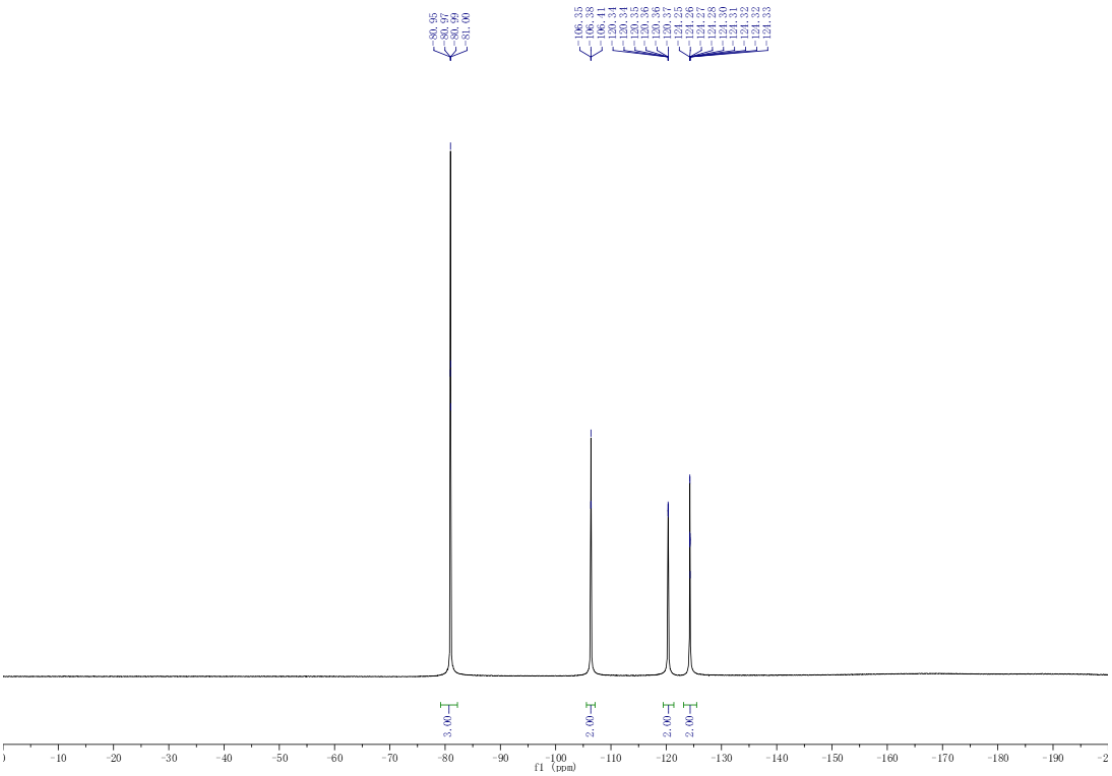
80



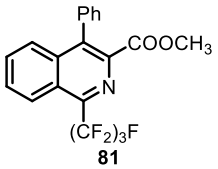
^{1}H NMR of compound **80**



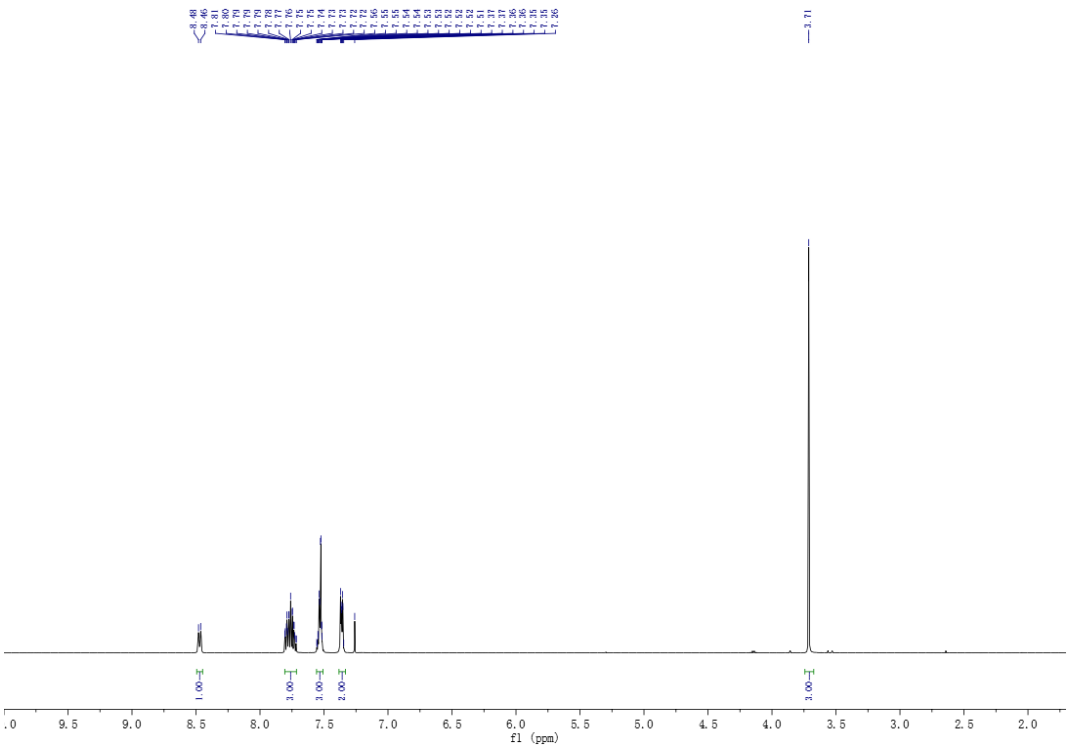
^{13}C NMR of compound **80**



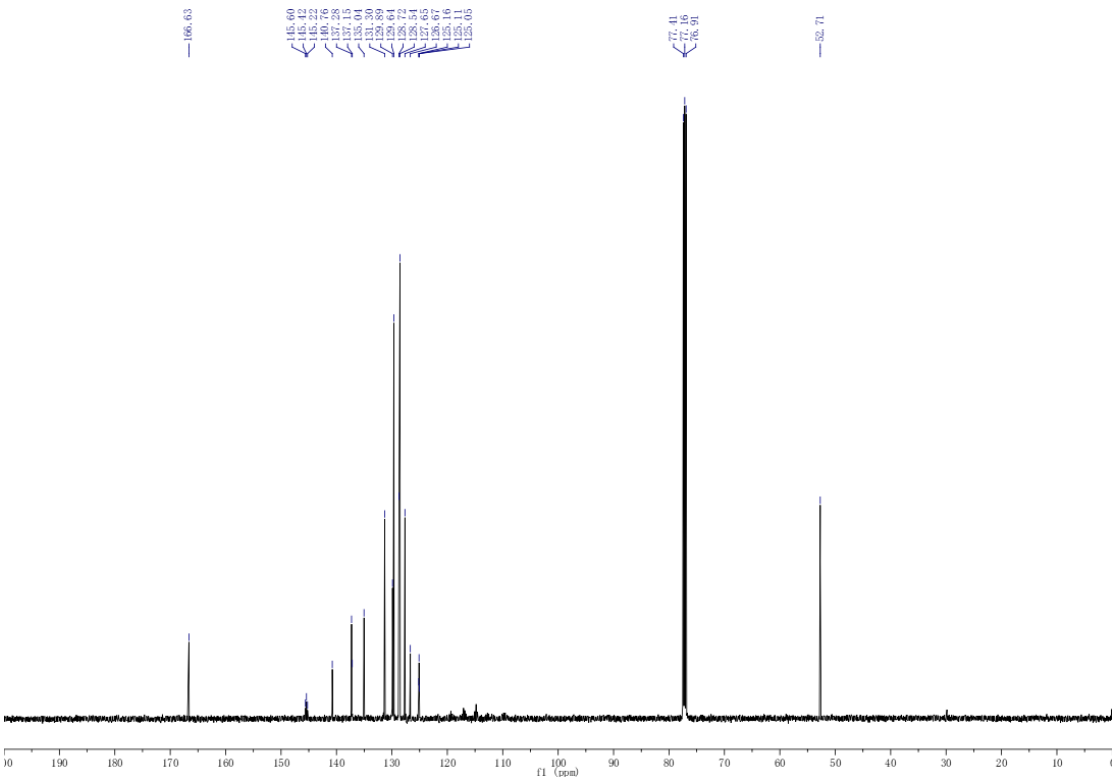
^{19}F NMR of compound **80**



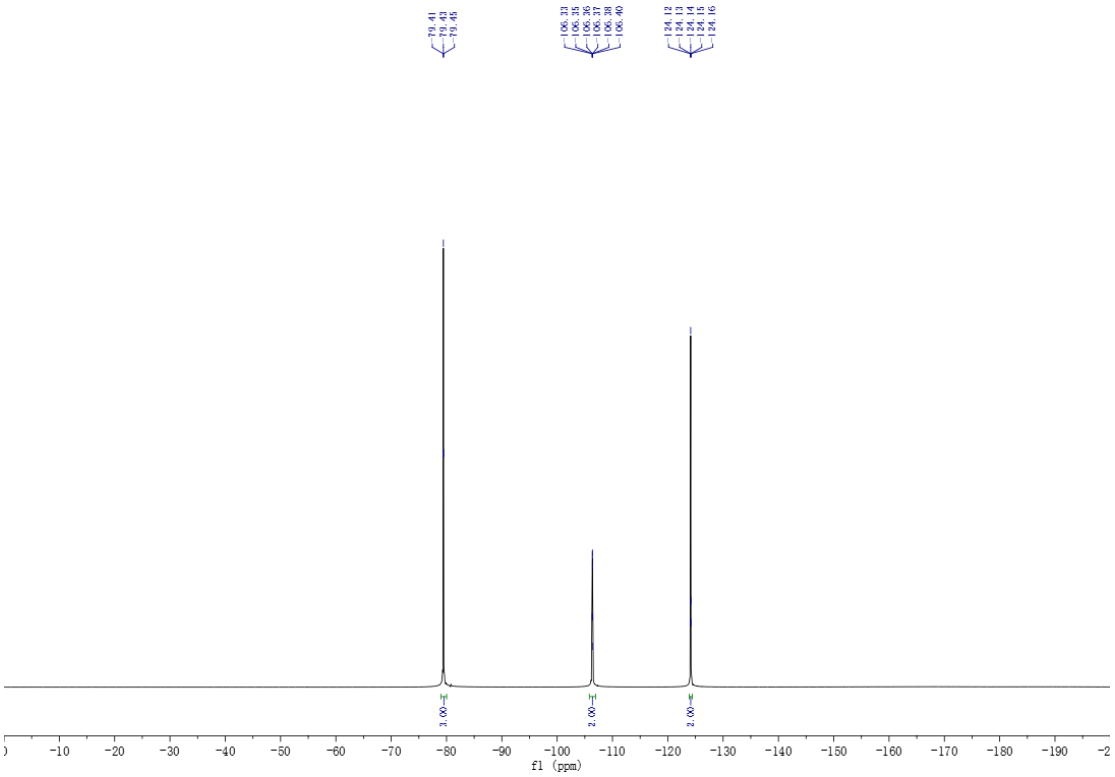
81



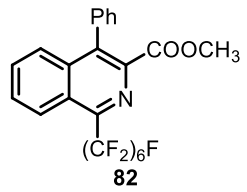
^{1}H NMR of compound **81**



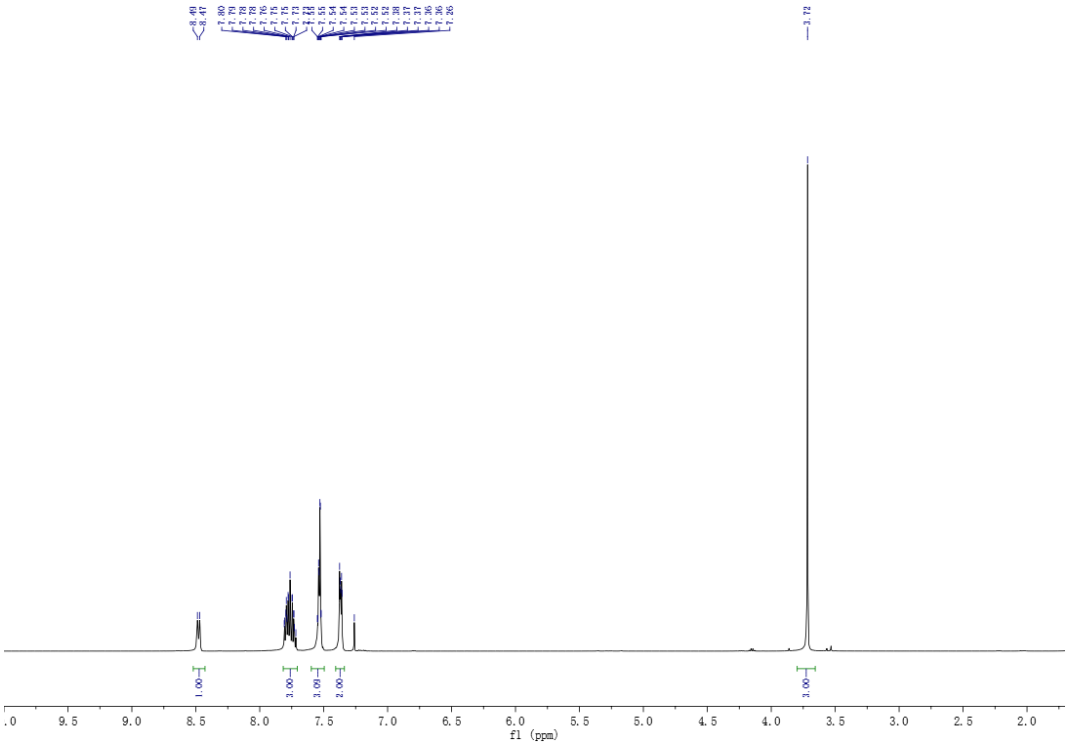
^{13}C NMR of compound **81**



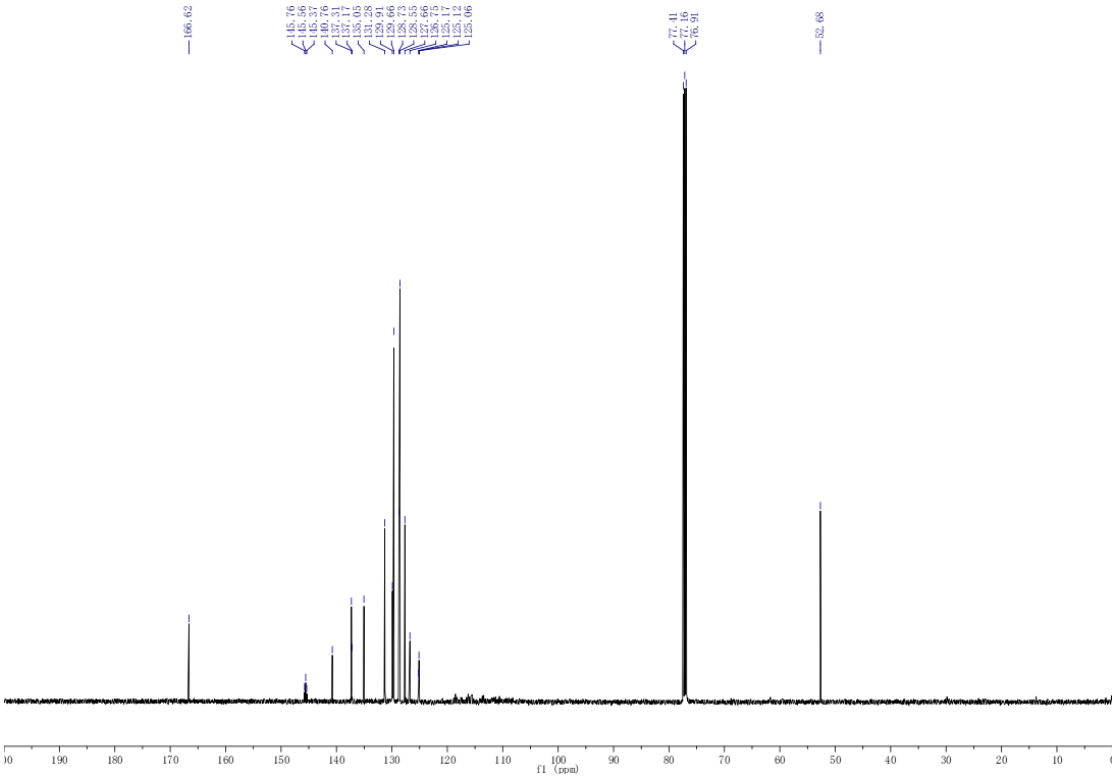
^{19}F NMR of compound **81**



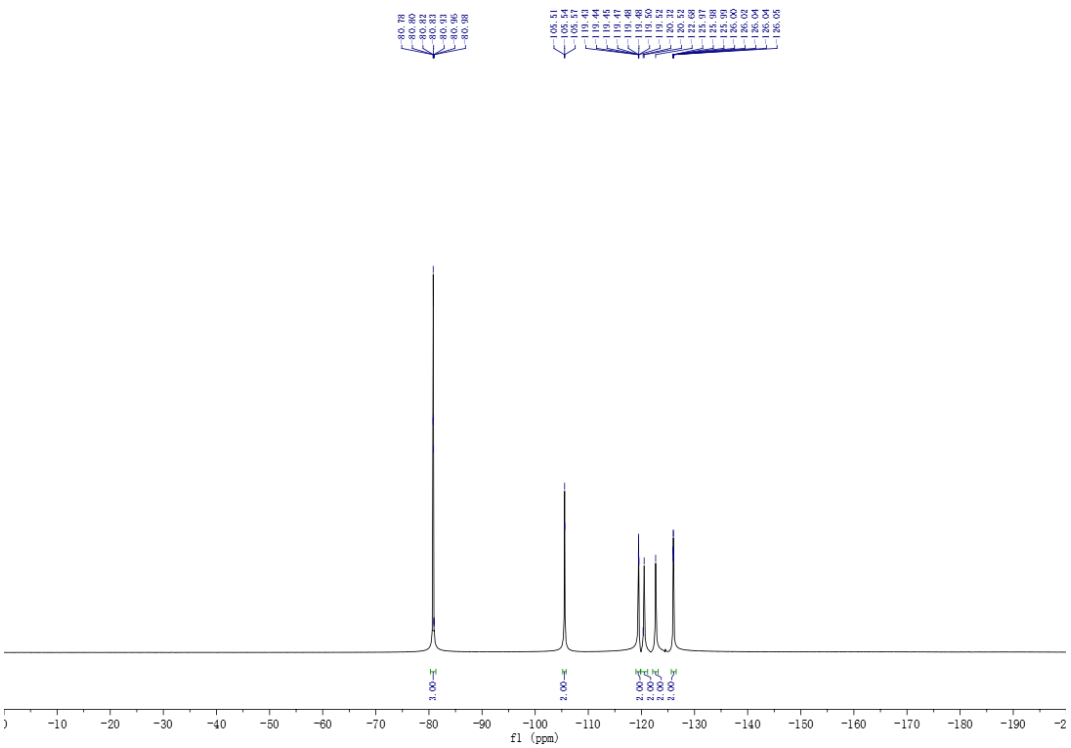
82



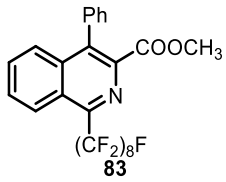
^{1}H NMR of compound **82**



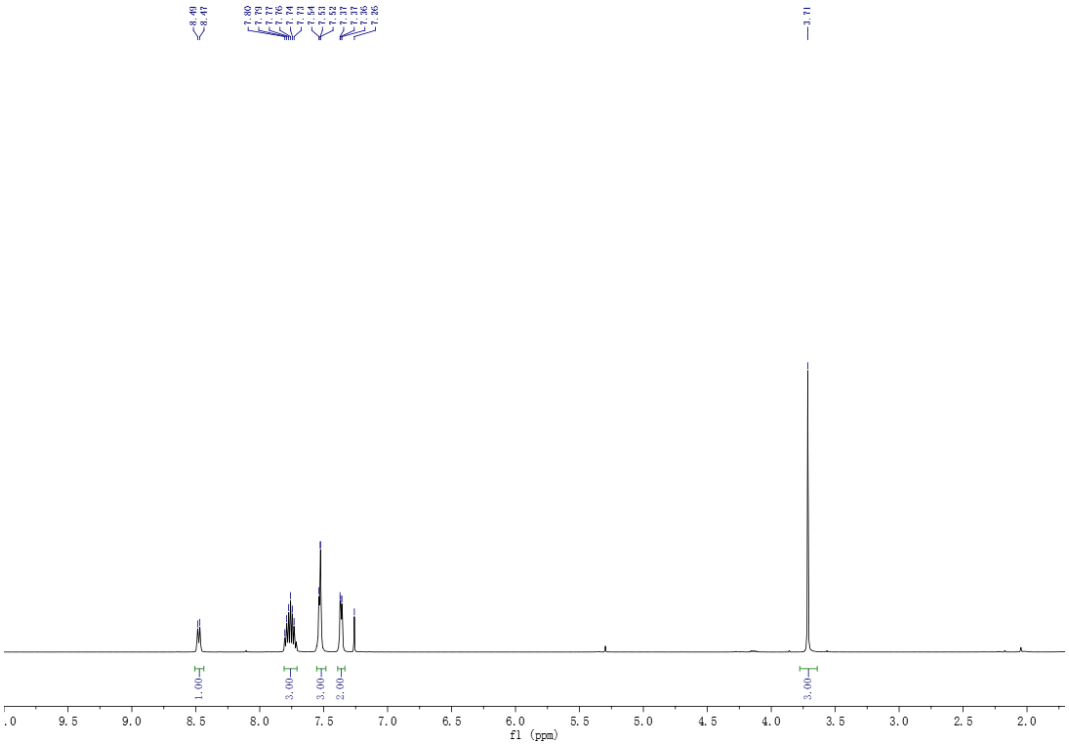
^{13}C NMR of compound **82**



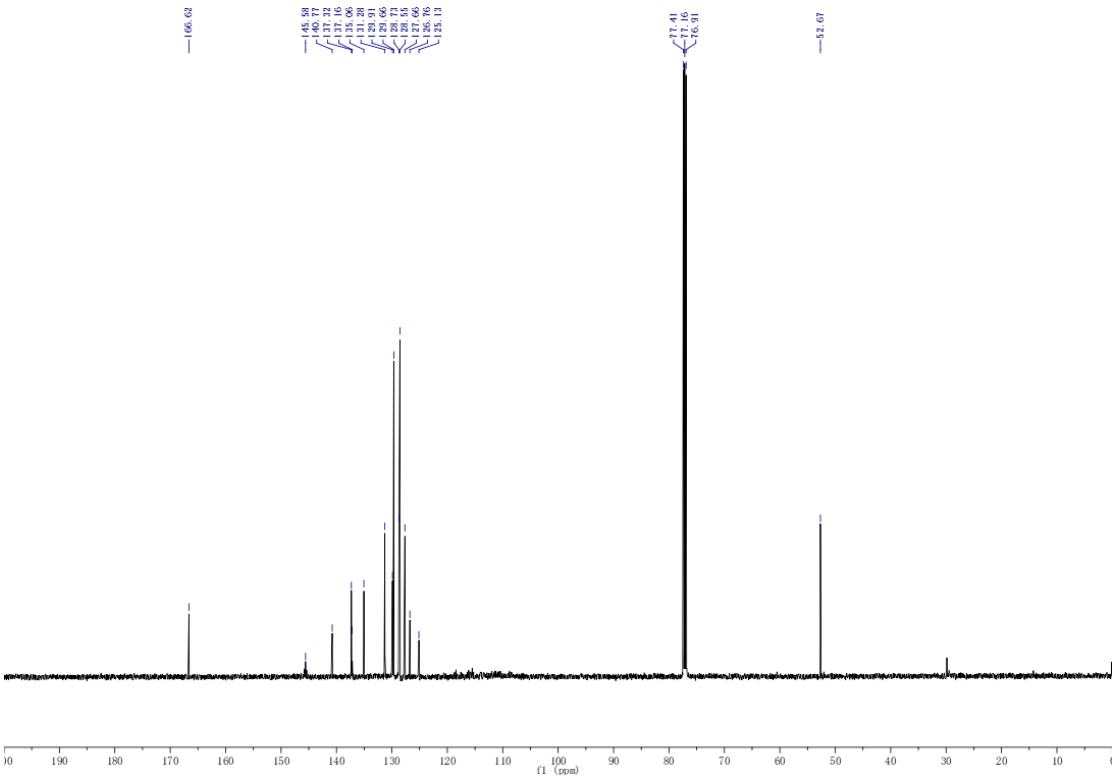
^{19}F NMR of compound **82**



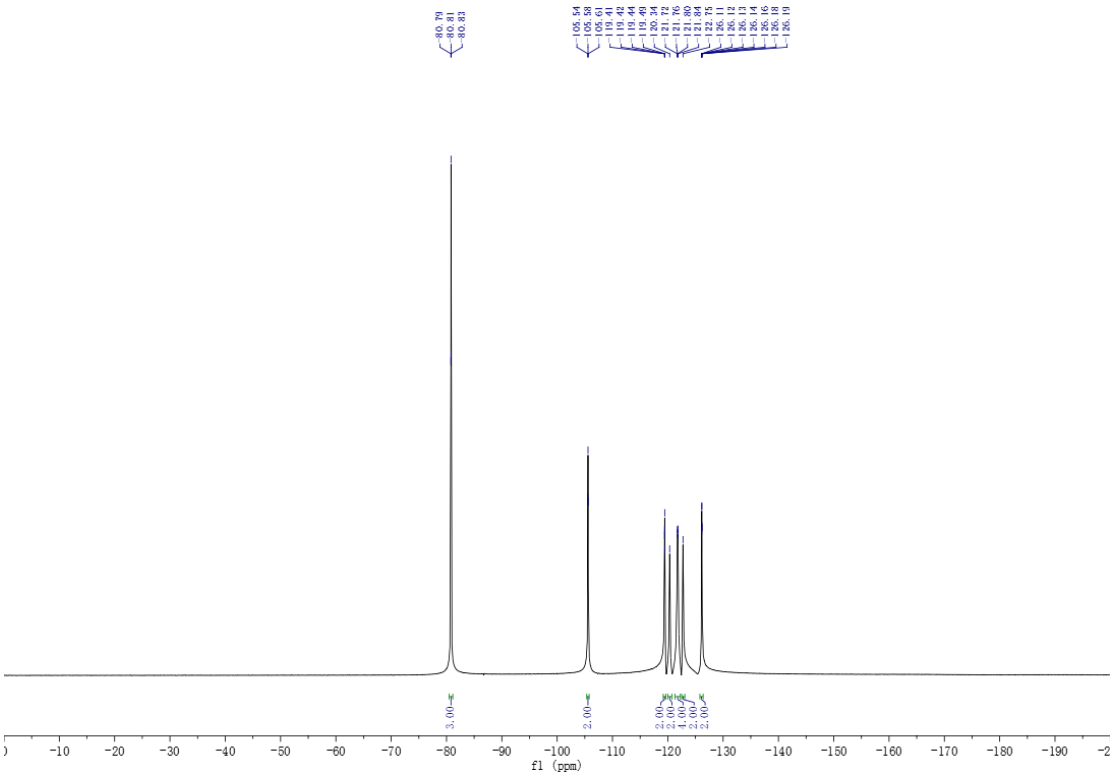
83



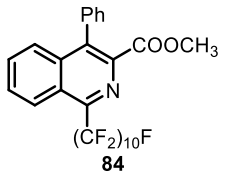
^{1}H NMR of compound **83**



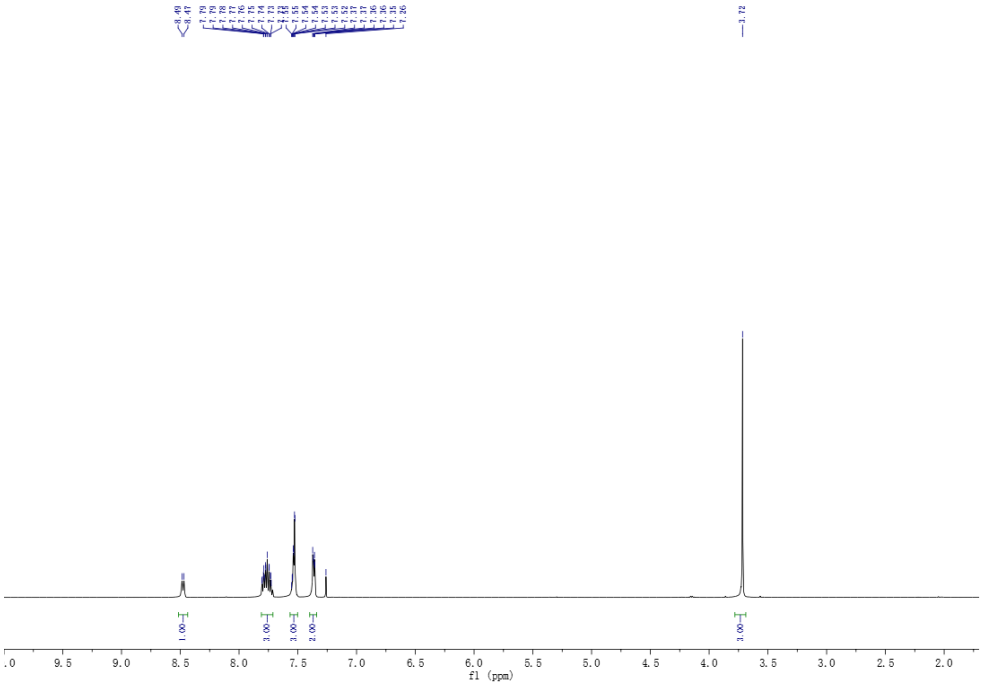
^{13}C NMR of compound **83**



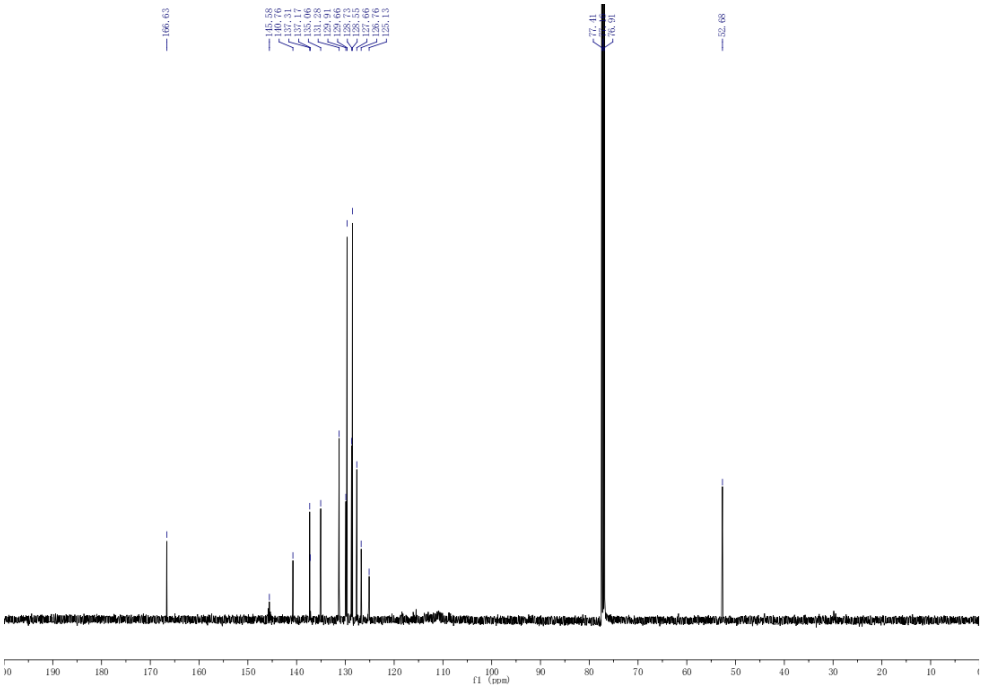
^{19}F NMR of compound **83**



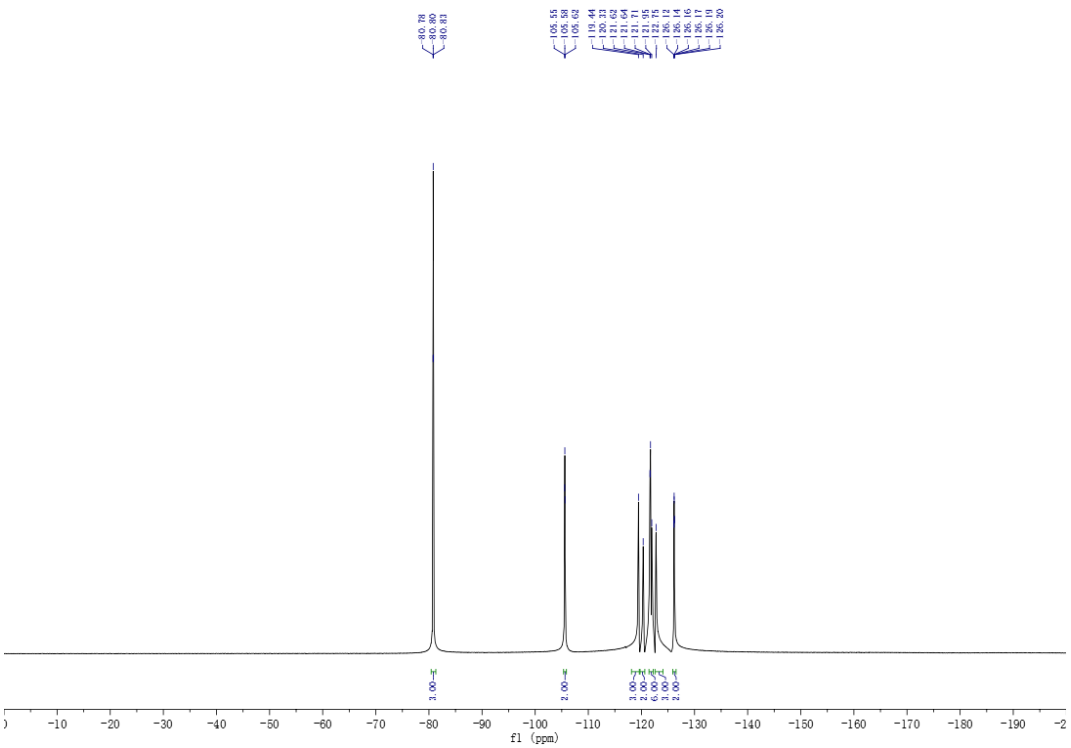
84



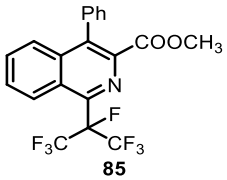
^{1}H NMR of compound **84**



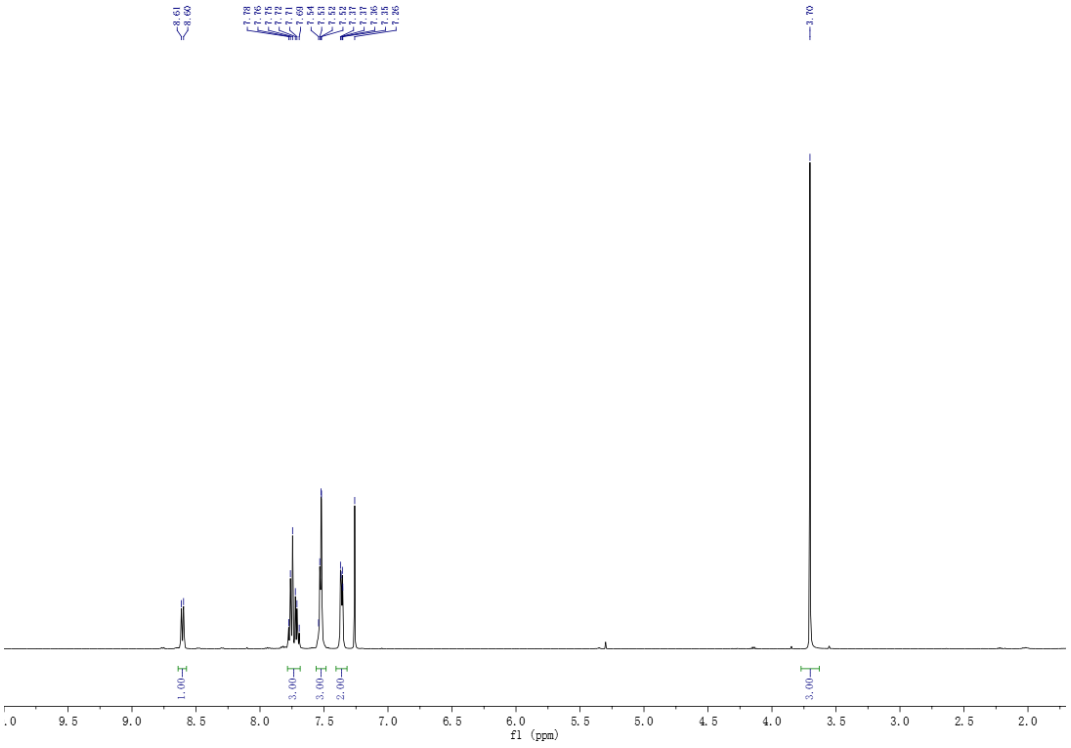
^{13}C NMR of compound **84**



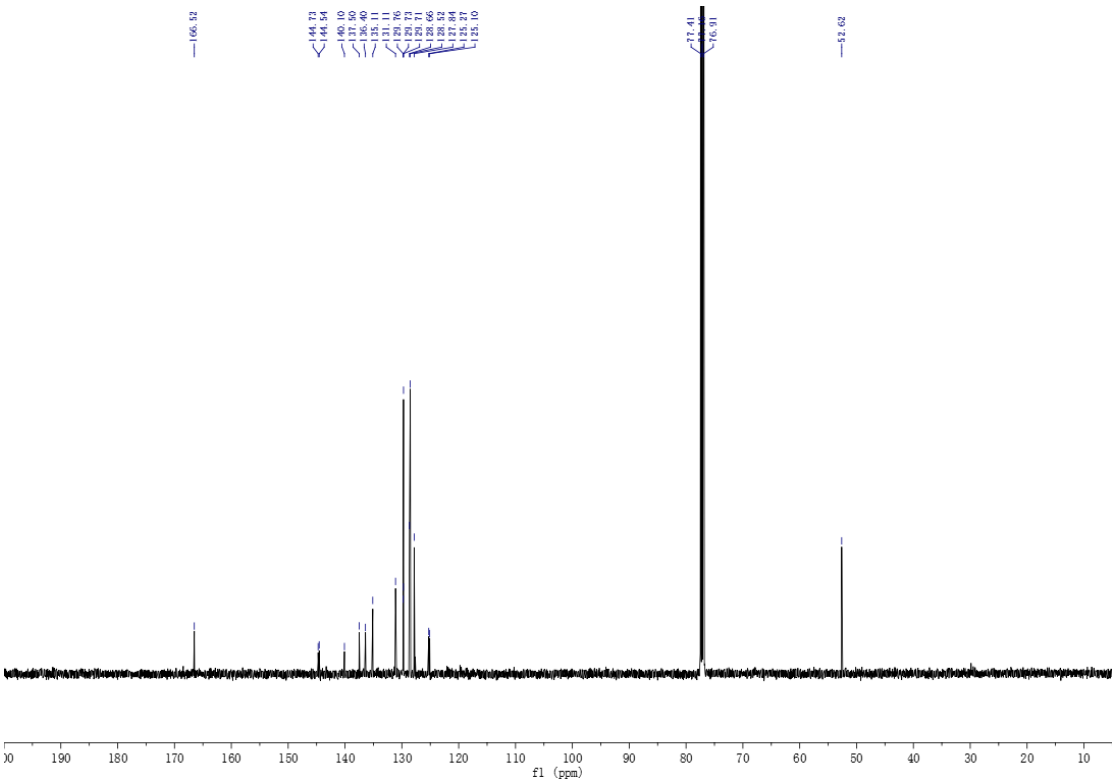
^{19}F NMR of compound **84**



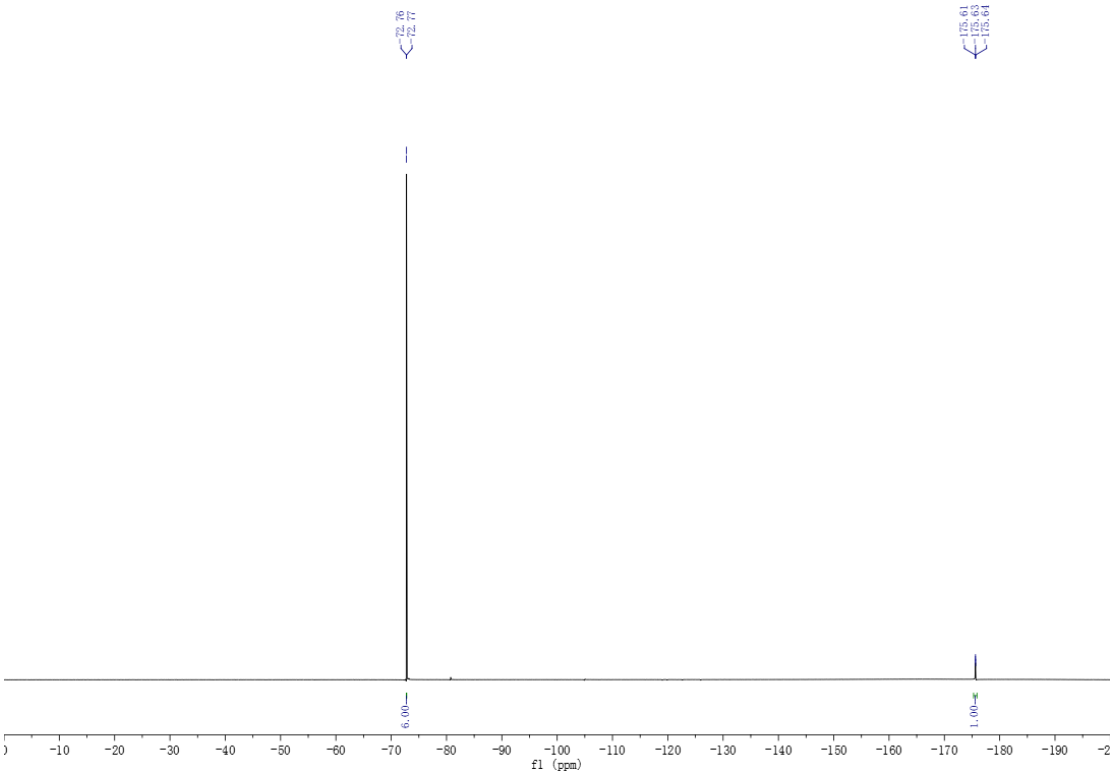
85



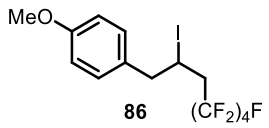
^{1}H NMR of compound **85**

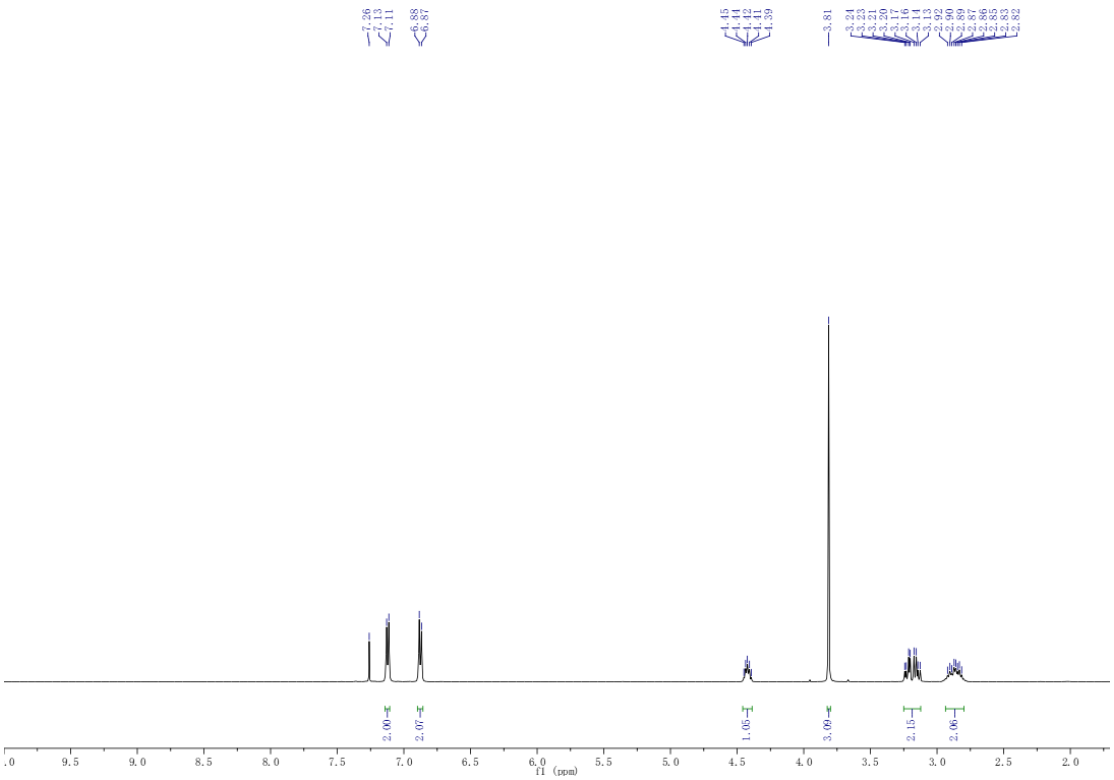


^{13}C NMR of compound **85**

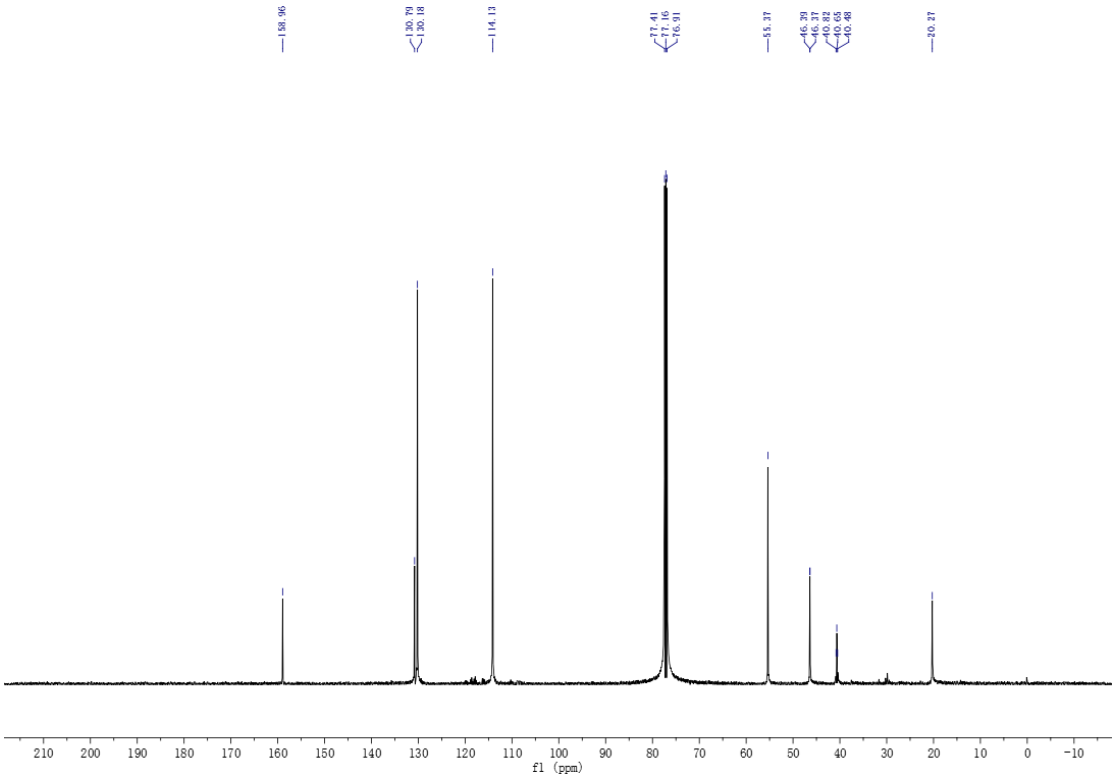


^{19}F NMR of compound **85**

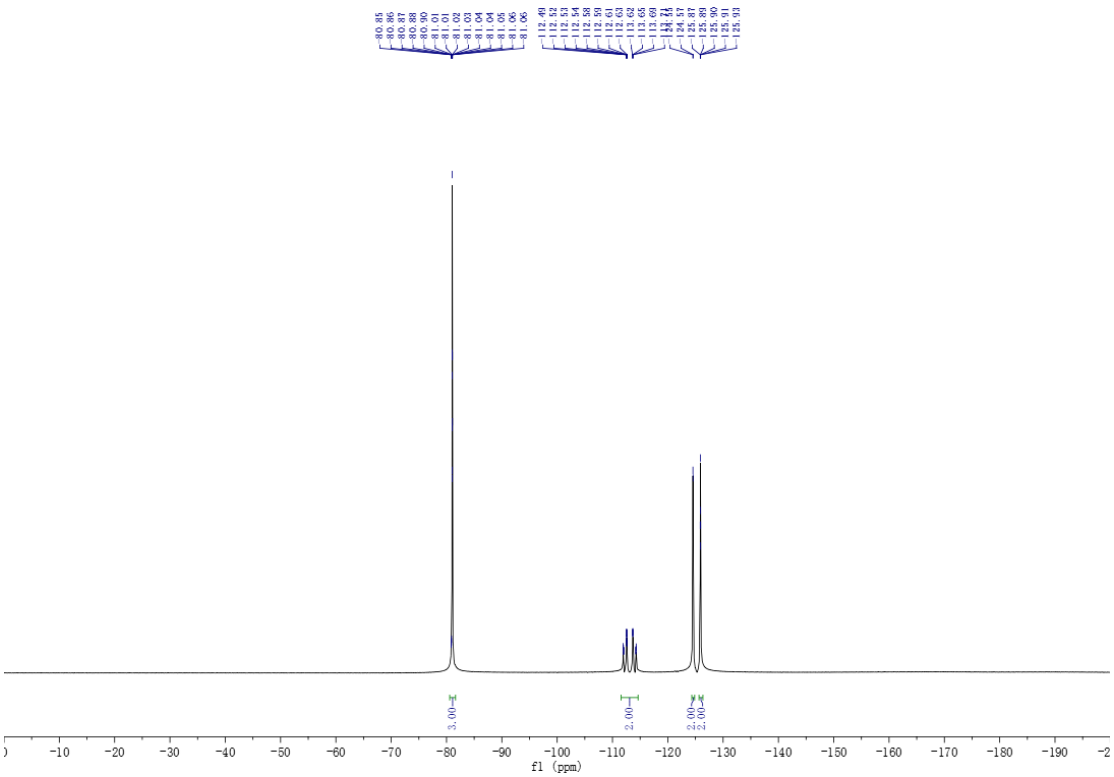




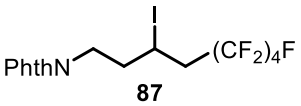
^{1}H NMR of compound **86**



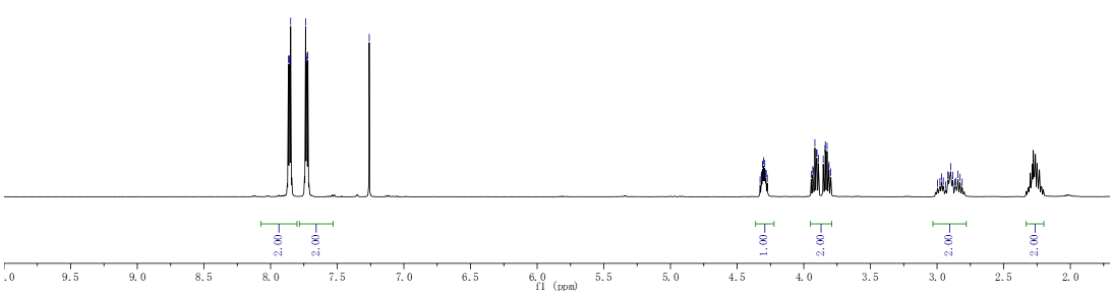
^{13}C NMR of compound **86**



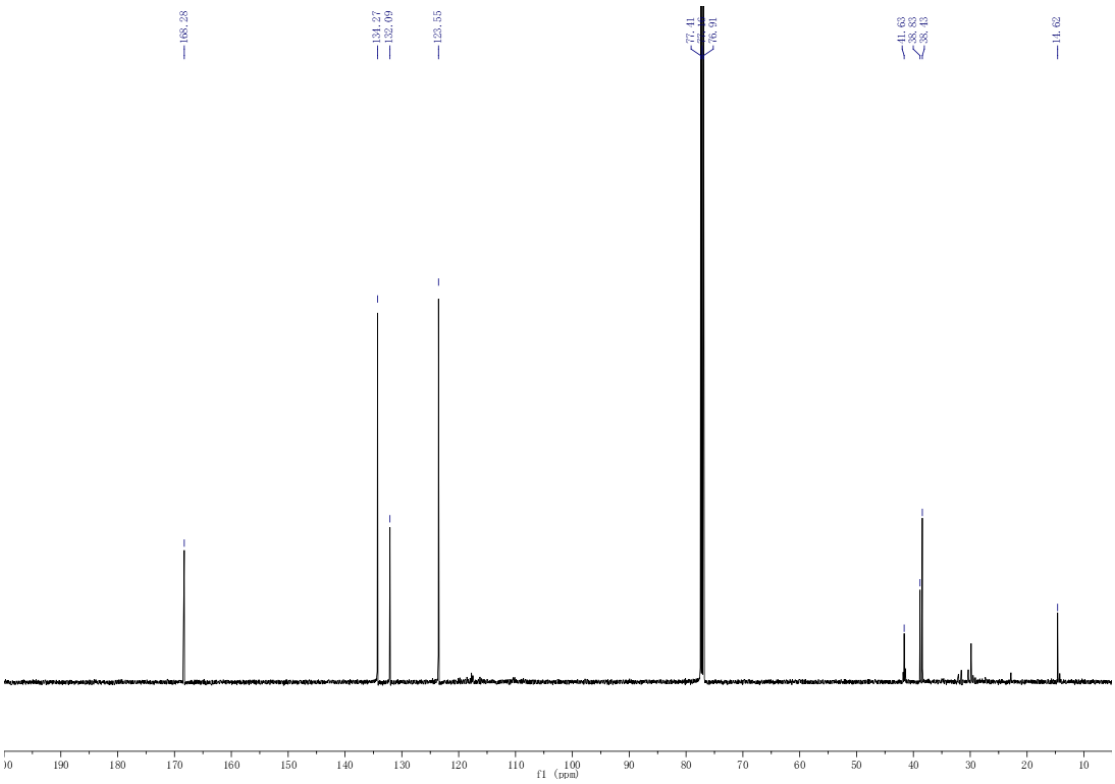
^{19}F NMR of compound **86**



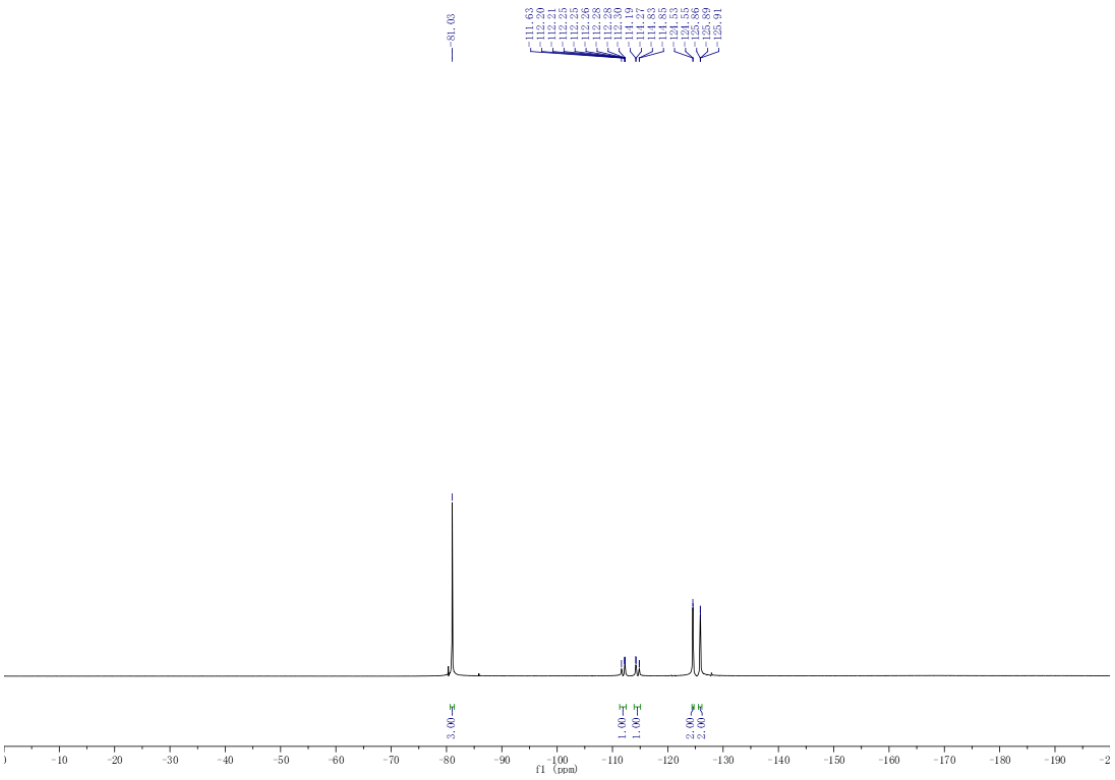
87



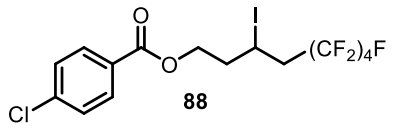
^{1}H NMR of compound **87**



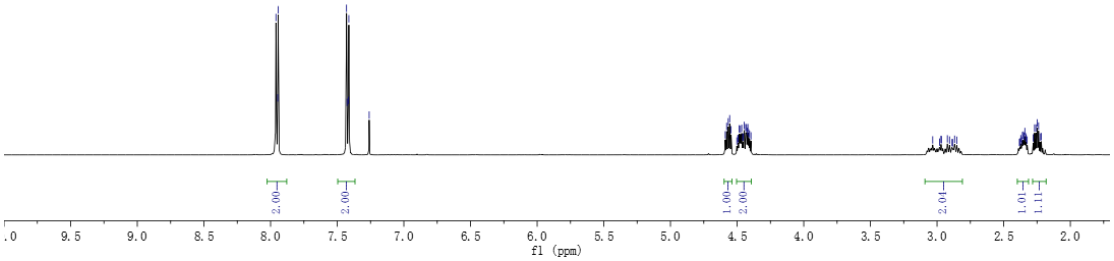
^{13}C NMR of compound **87**



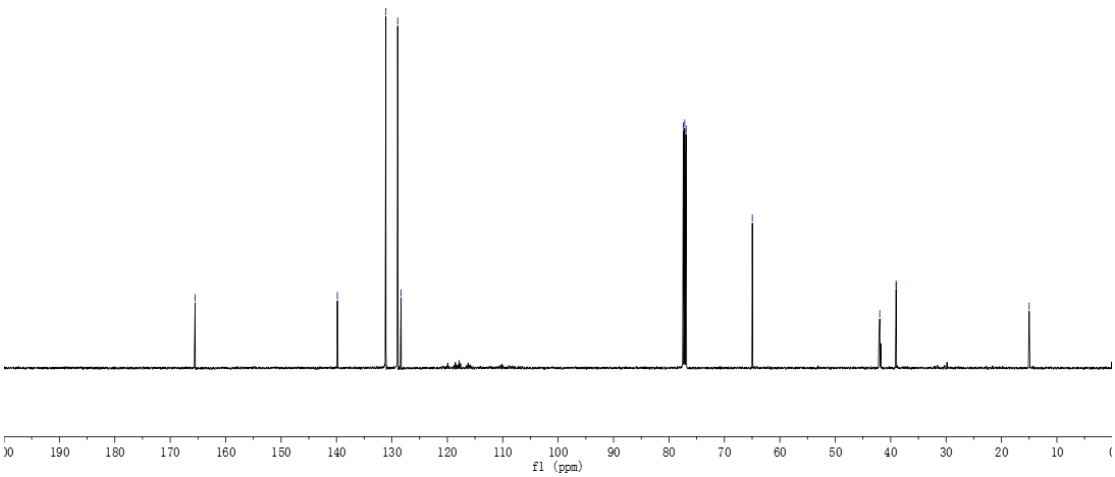
^{19}F NMR of compound **87**



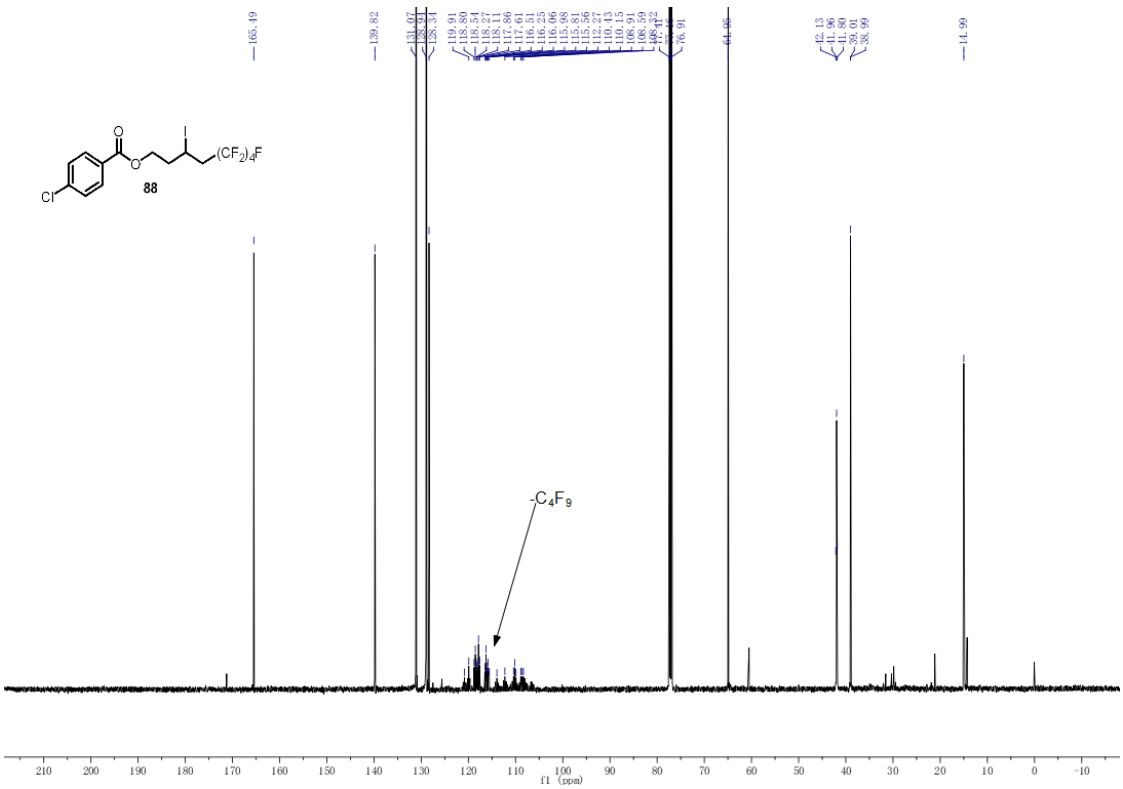
88



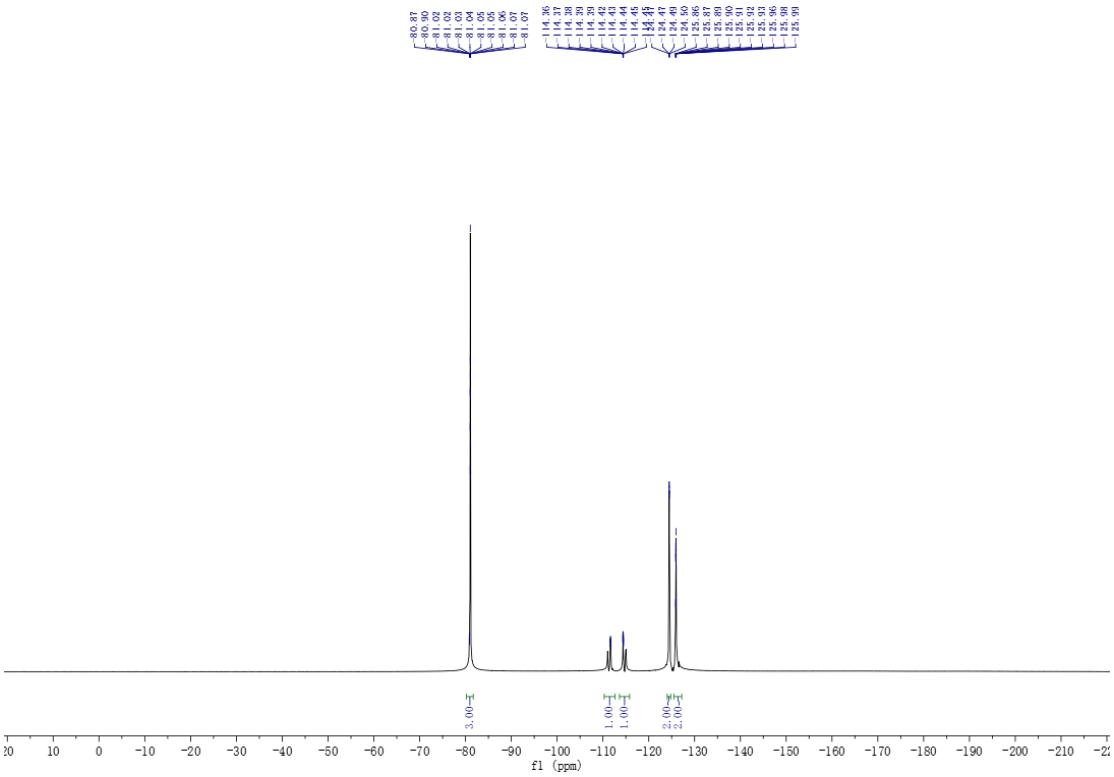
^{1}H NMR of compound **88**



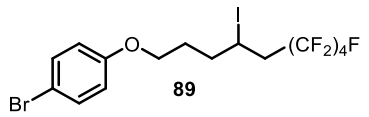
^{13}C NMR of compound **88**

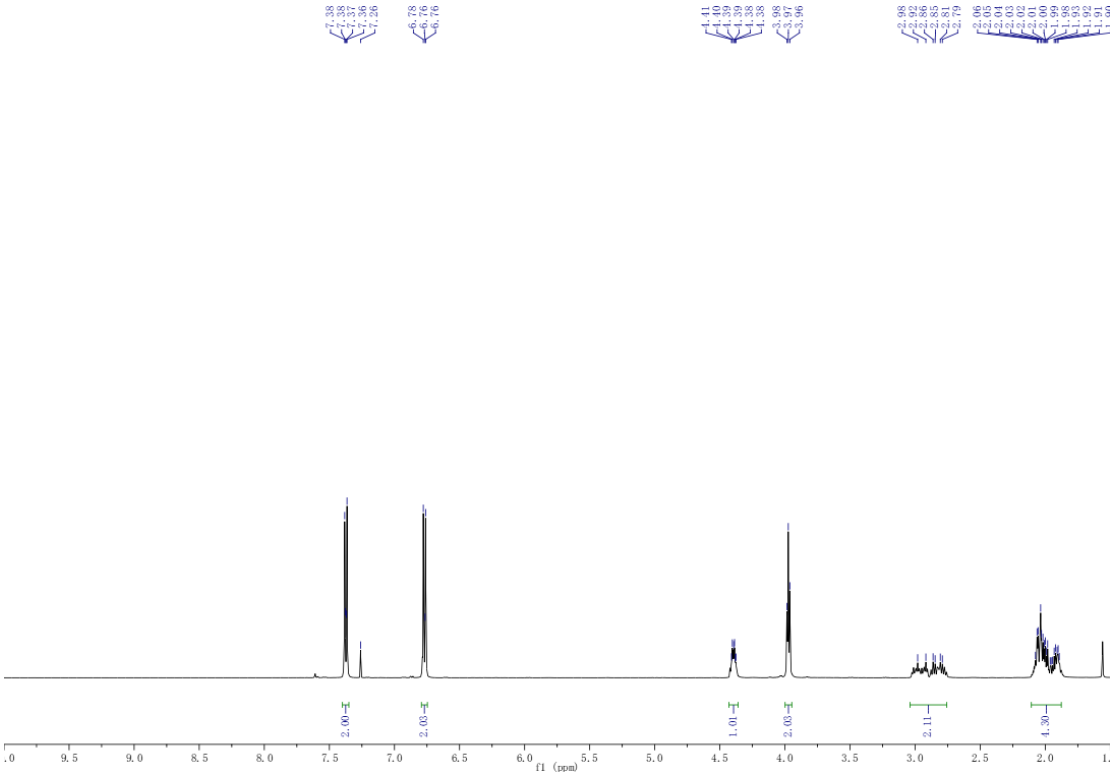


^{13}C NMR of compound **88 (high concentration of product 88 in $CDCl_3$)**

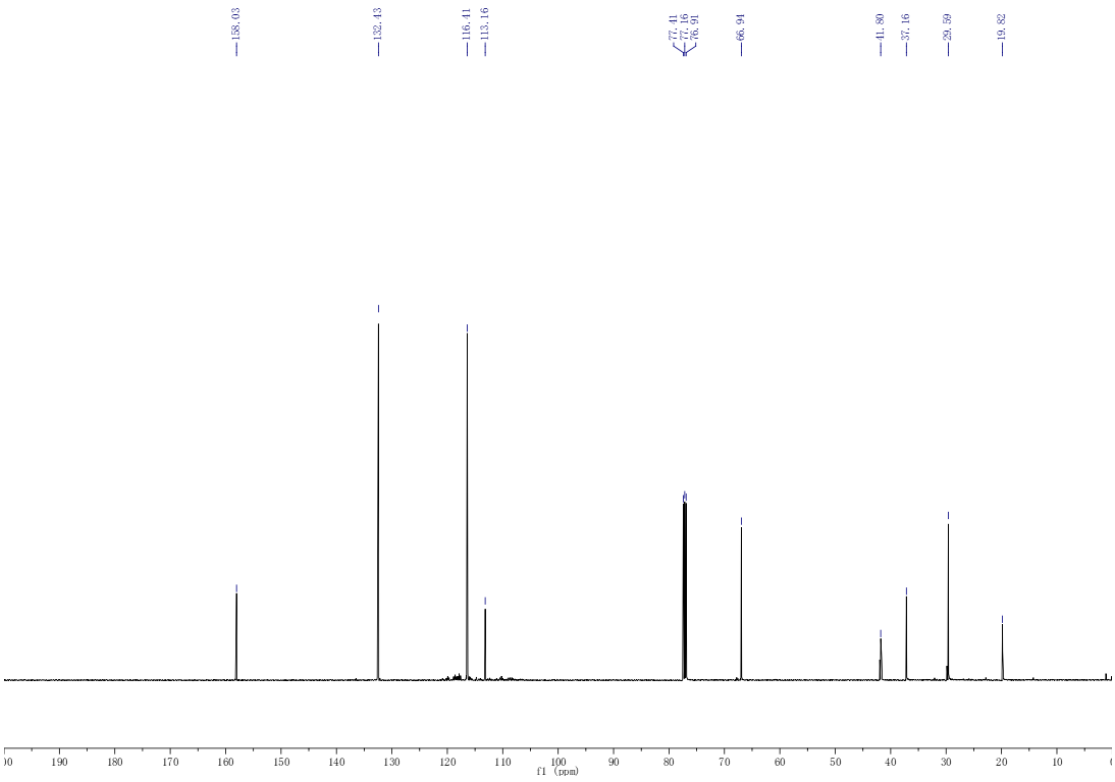


^{19}F NMR of compound **88**

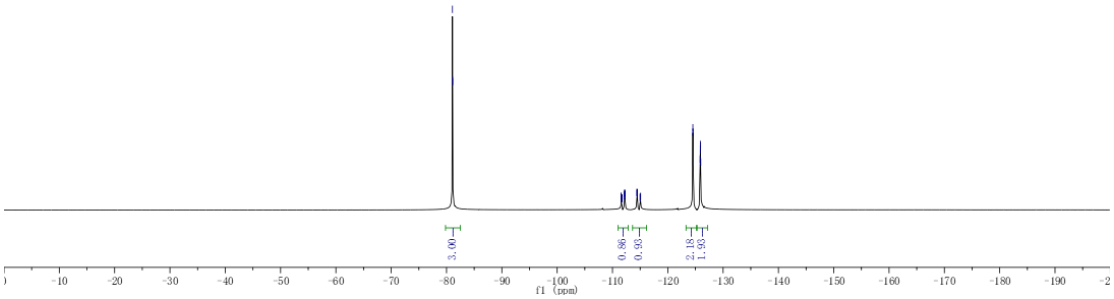




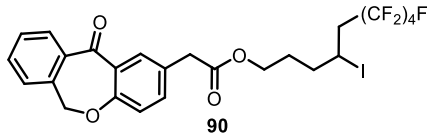
^{1}H NMR of compound **89**



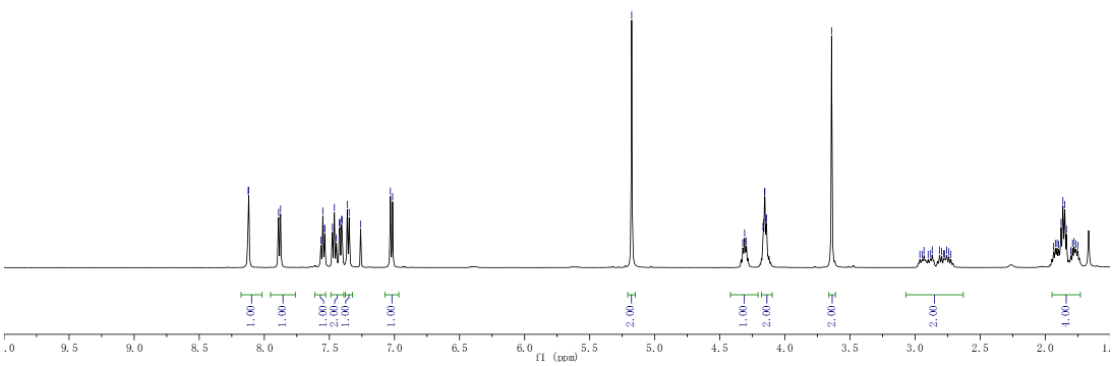
^{13}C NMR of compound **89**



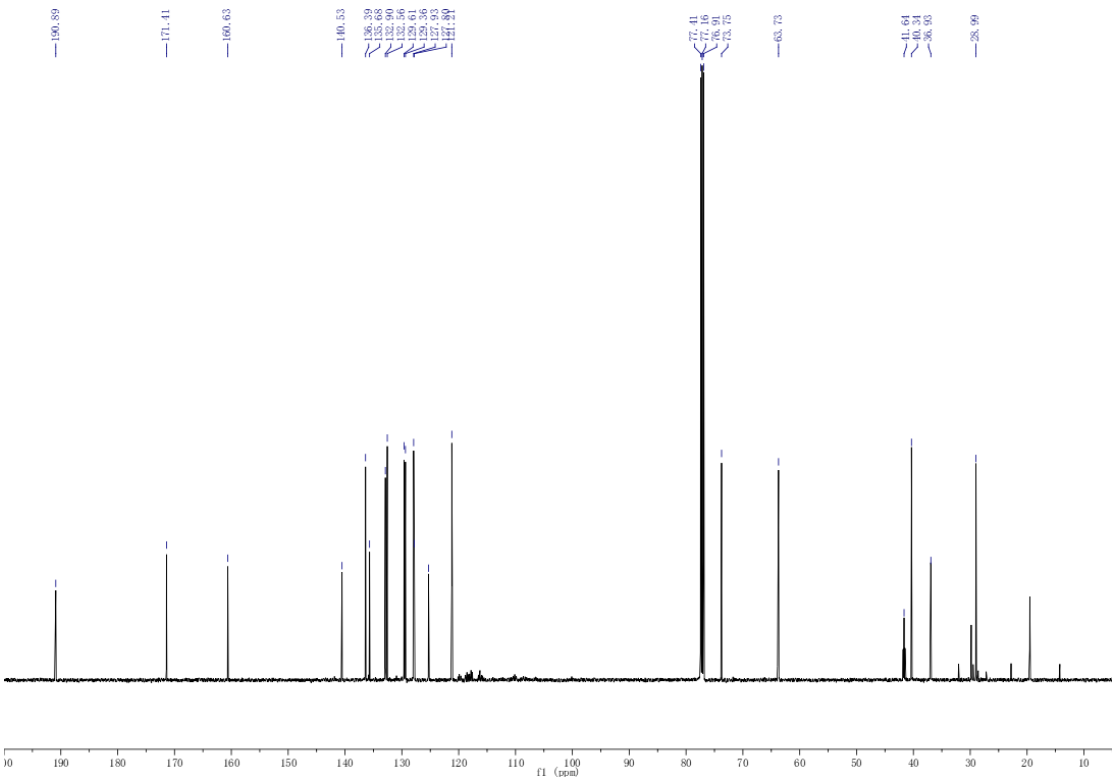
^{19}F NMR of compound **89**



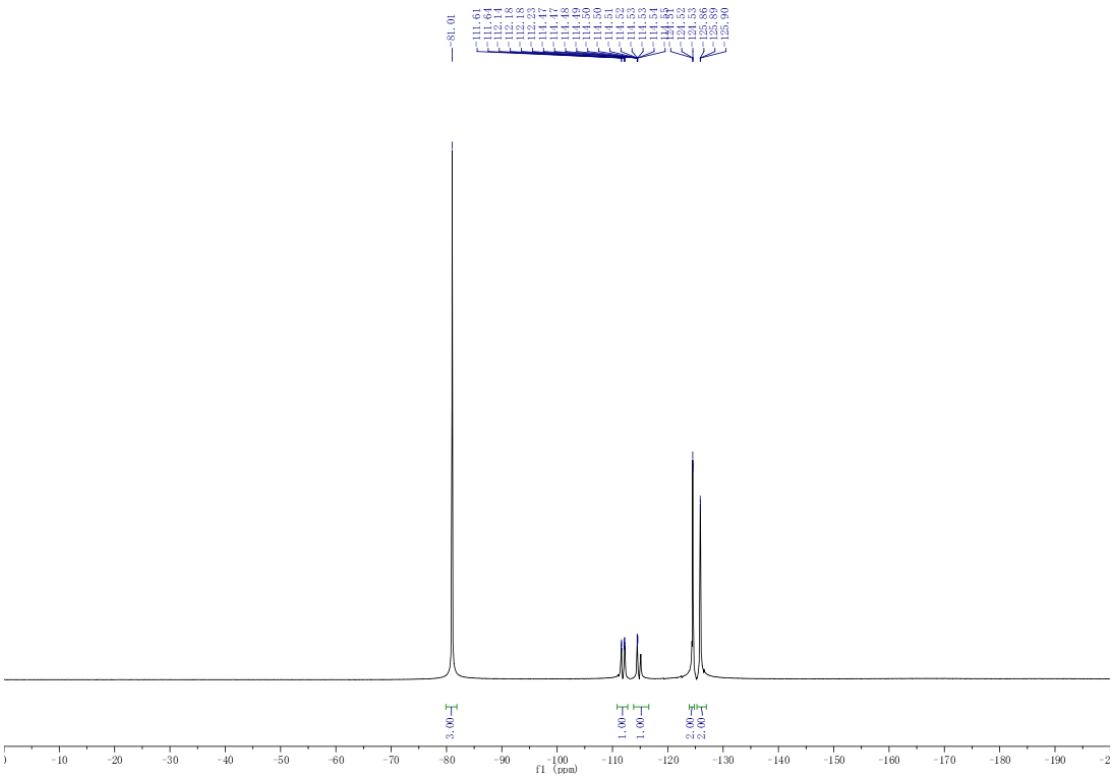
90



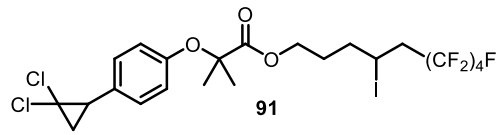
^{1}H NMR of compound **90**



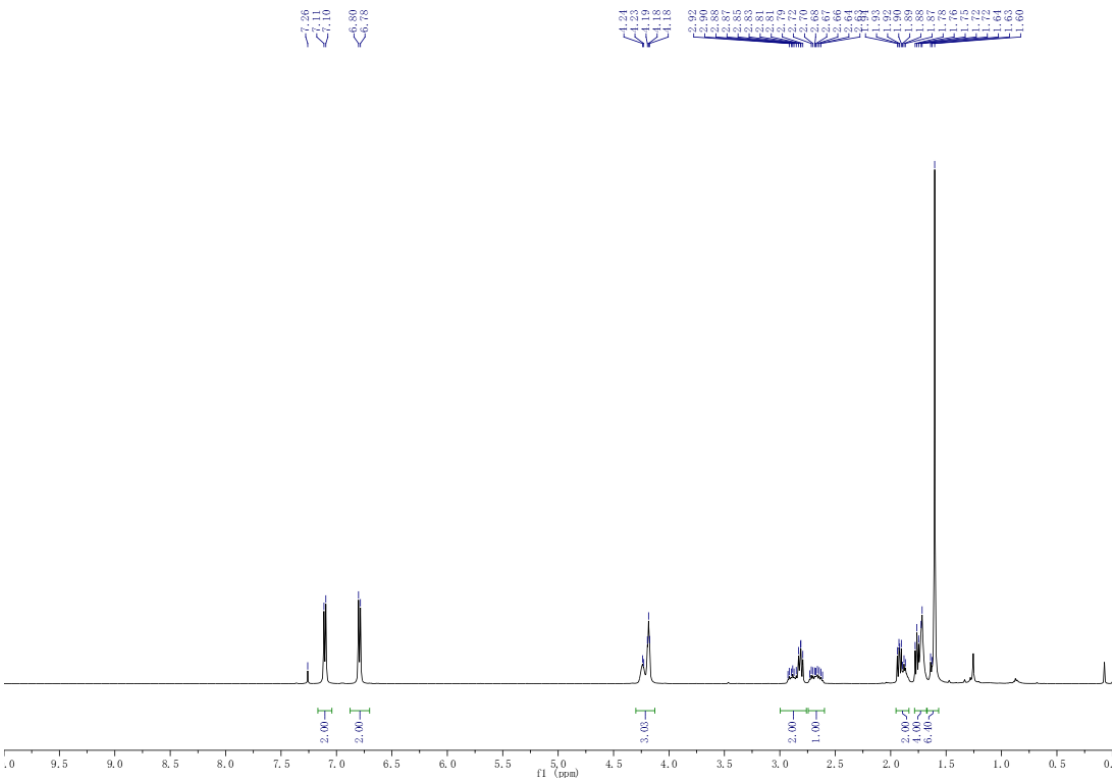
^{13}C NMR of compound **90**



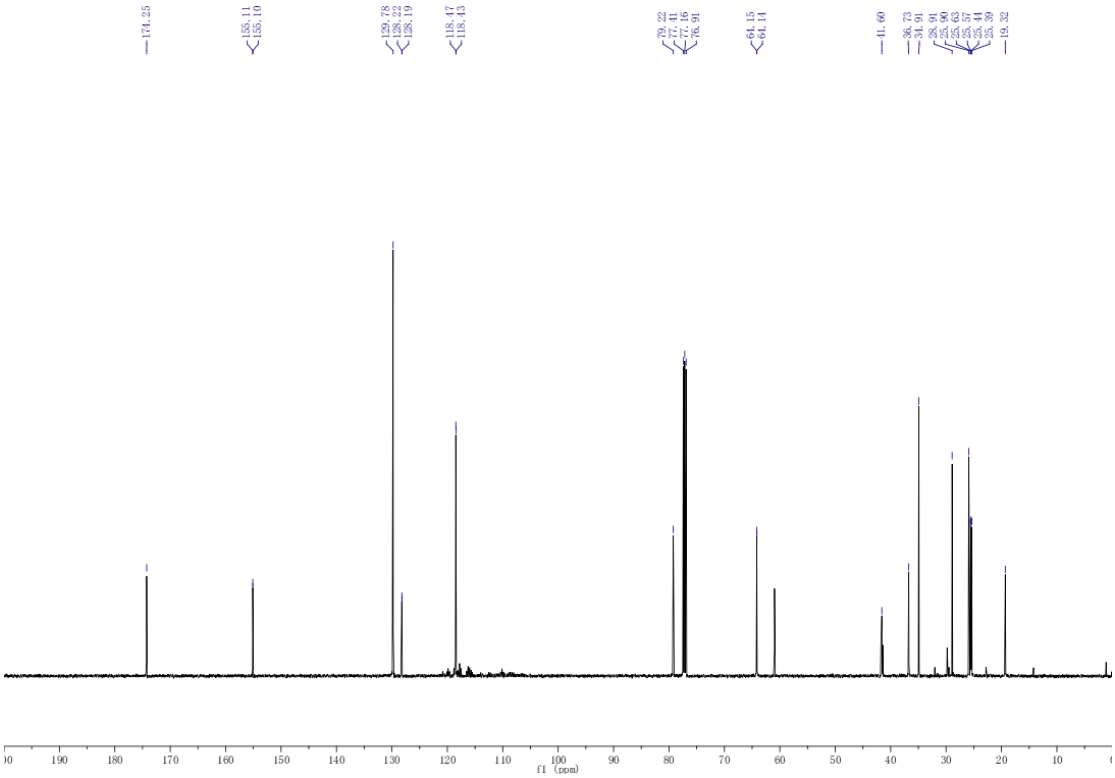
^{19}F NMR of compound **90**



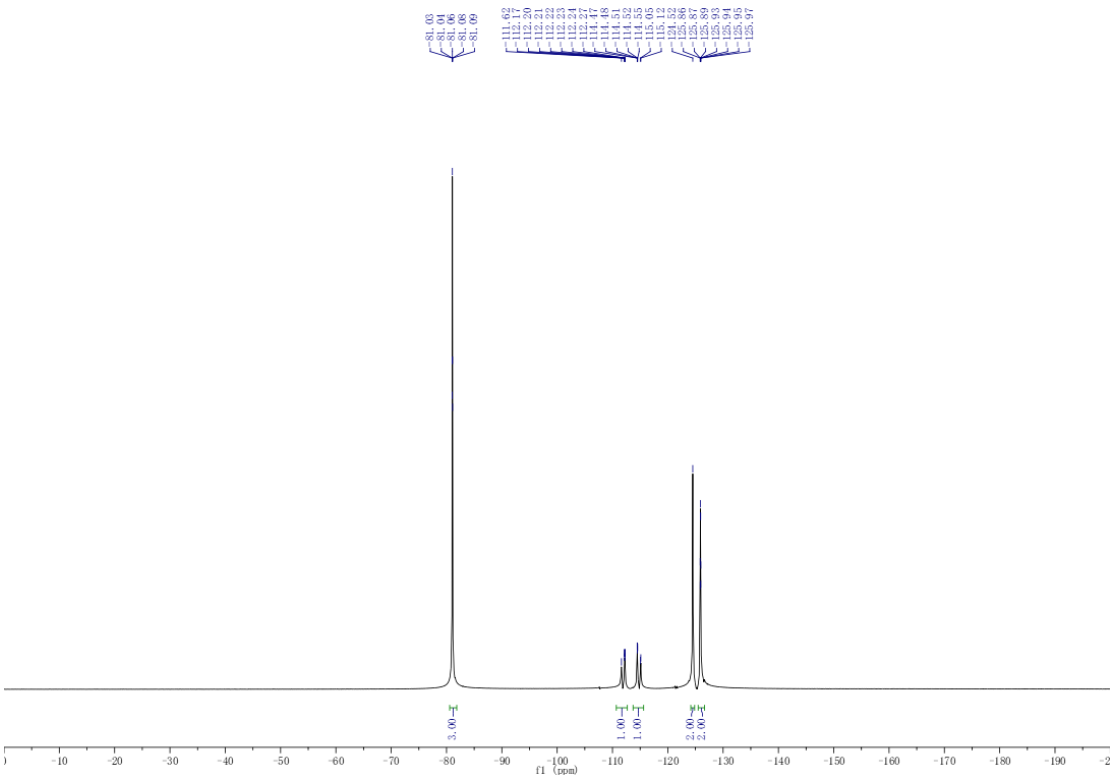
91



^{1}H NMR of compound **91**

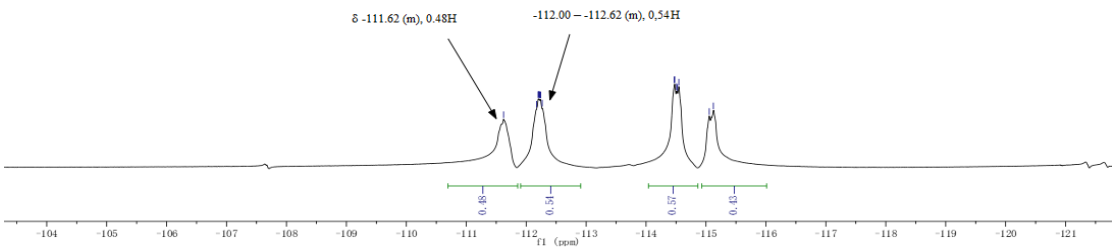


^{13}C NMR of compound **91**

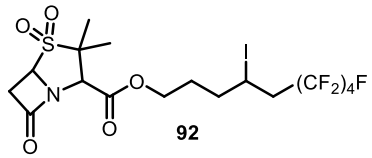


^{19}F NMR of compound **91**

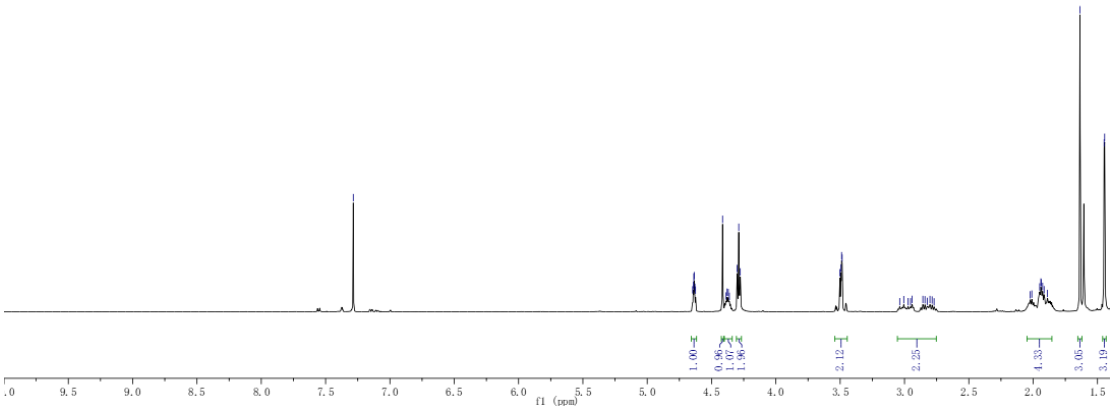
The dr ratio of compound **91** is determined by ^{19}F NMR:



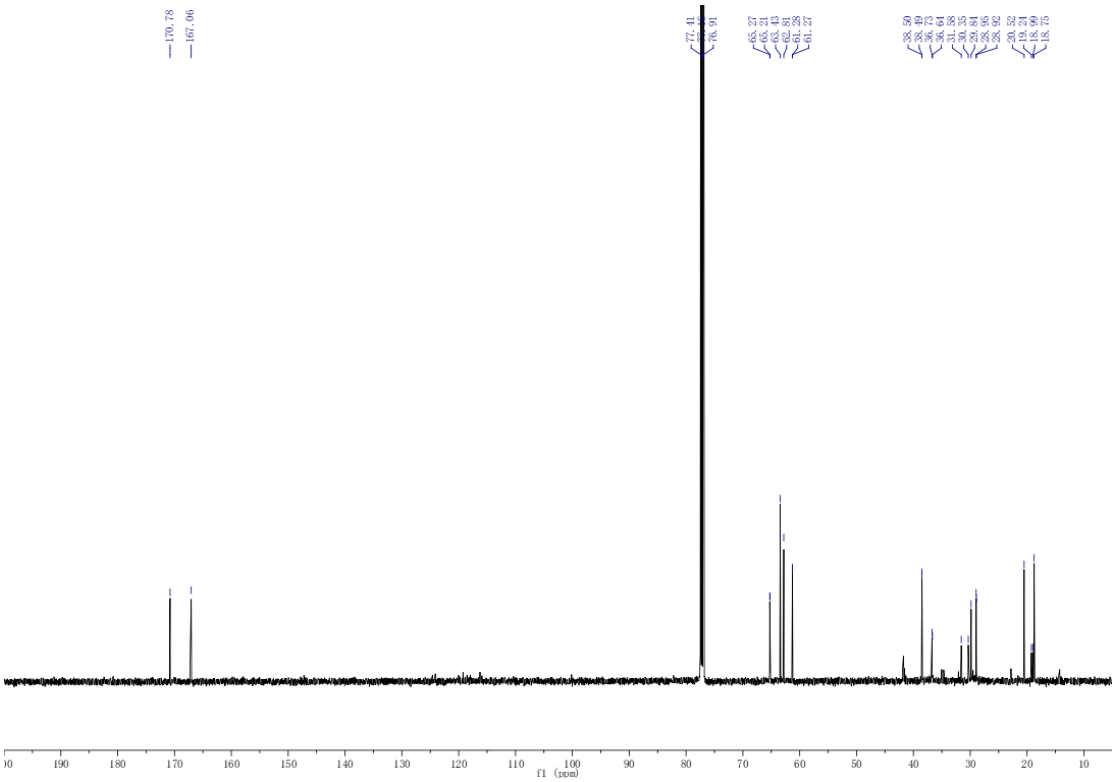
	Chemical shift	Integral area	dr = 1:1
1	-111.62 (m)	0.48	
2	-112.00-112.62 (m)	0.54	



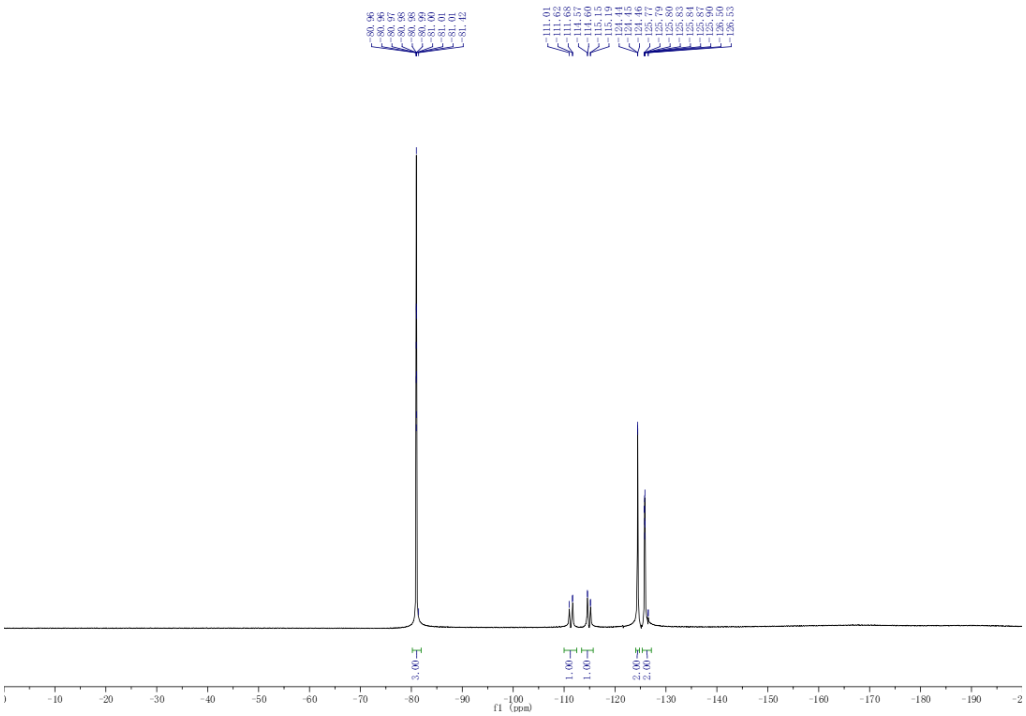
92



^{1}H NMR of compound **92**

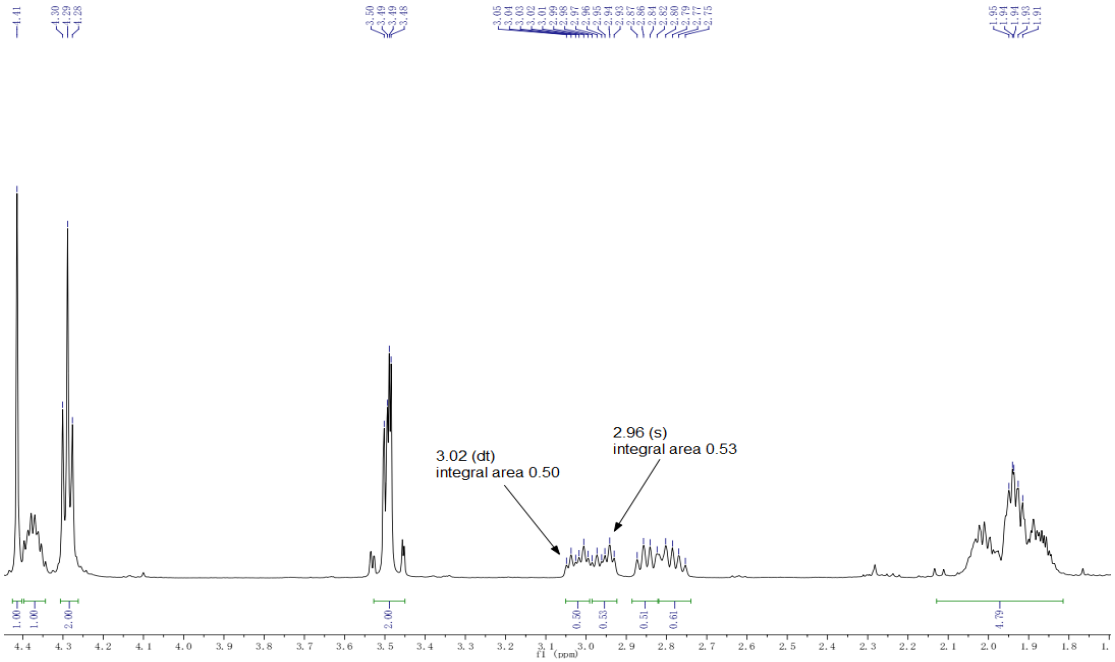


^{13}C NMR of compound **92**

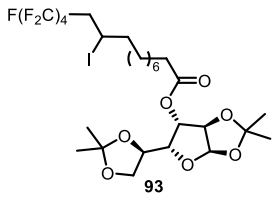


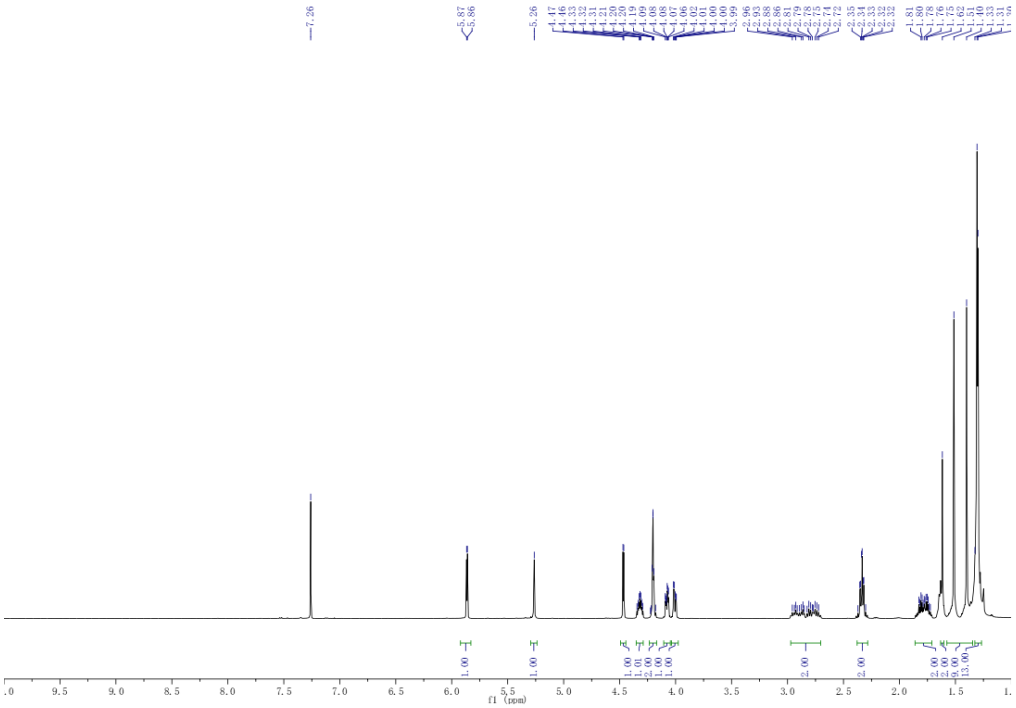
^{19}F NMR of compound **92**

The dr ratio of compound **92** is determined by ^{1}H NMR:

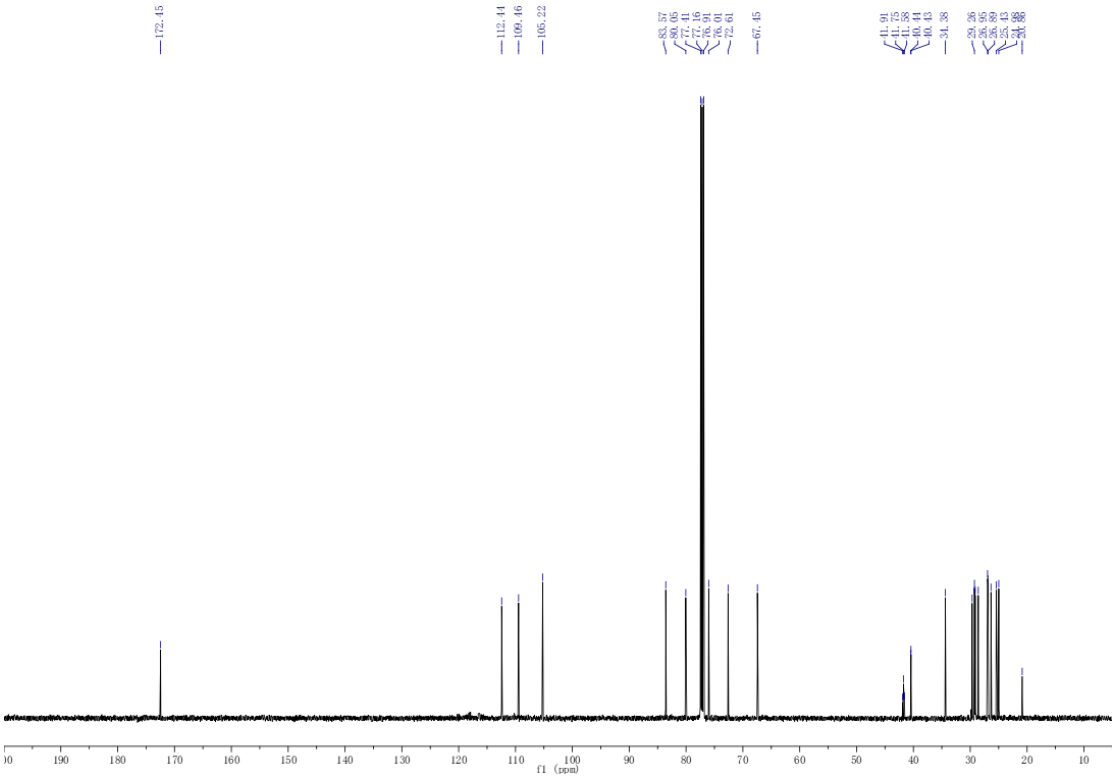


	Chemical shift	Integral area	dr = 1:1
1	2.96 (dt)	0.53	
2	3.02 (dt)	0.50	

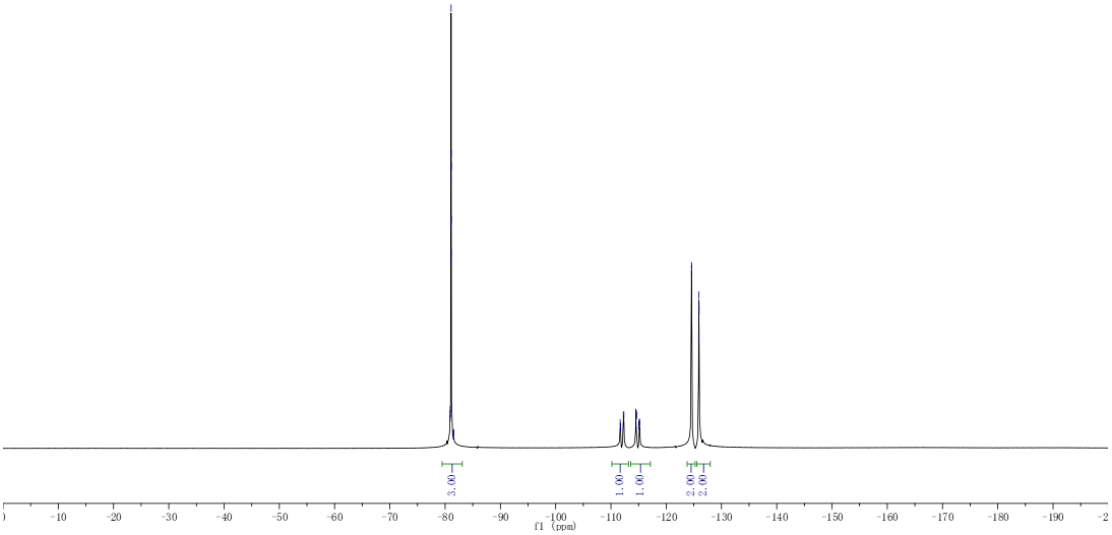




^{1}H NMR of compound **93**

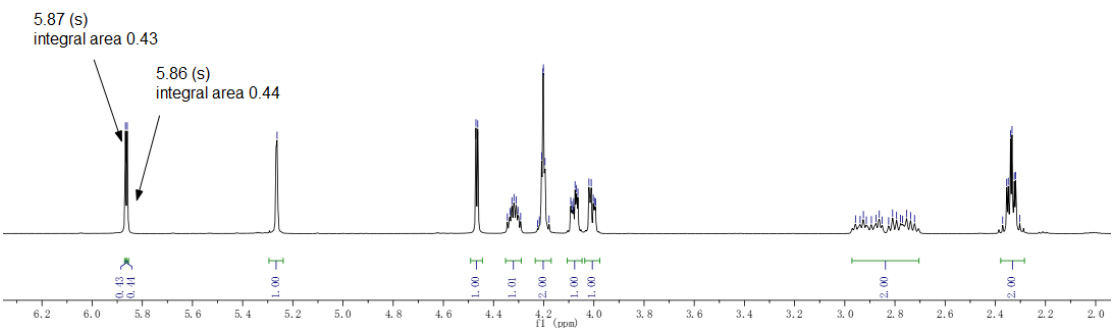


^{13}C NMR of compound **93**

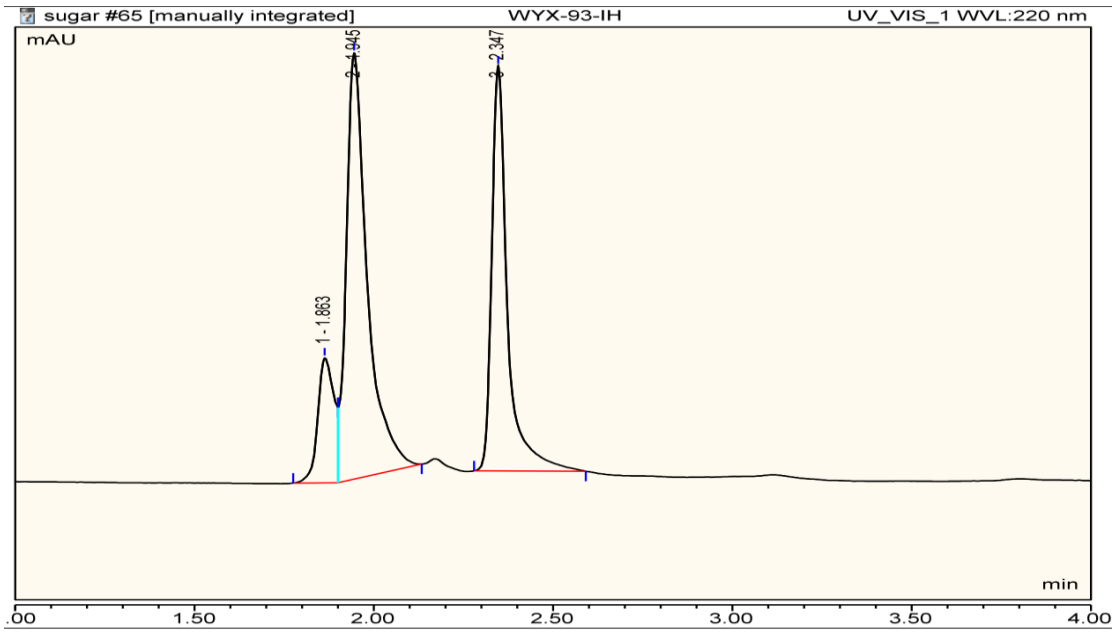


^{19}F NMR of compound **93**

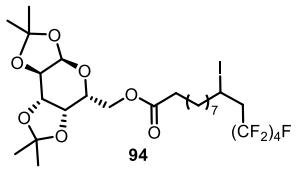
The dr ratio of compound **93** is determined by ^{1}H NMR and HPLC:



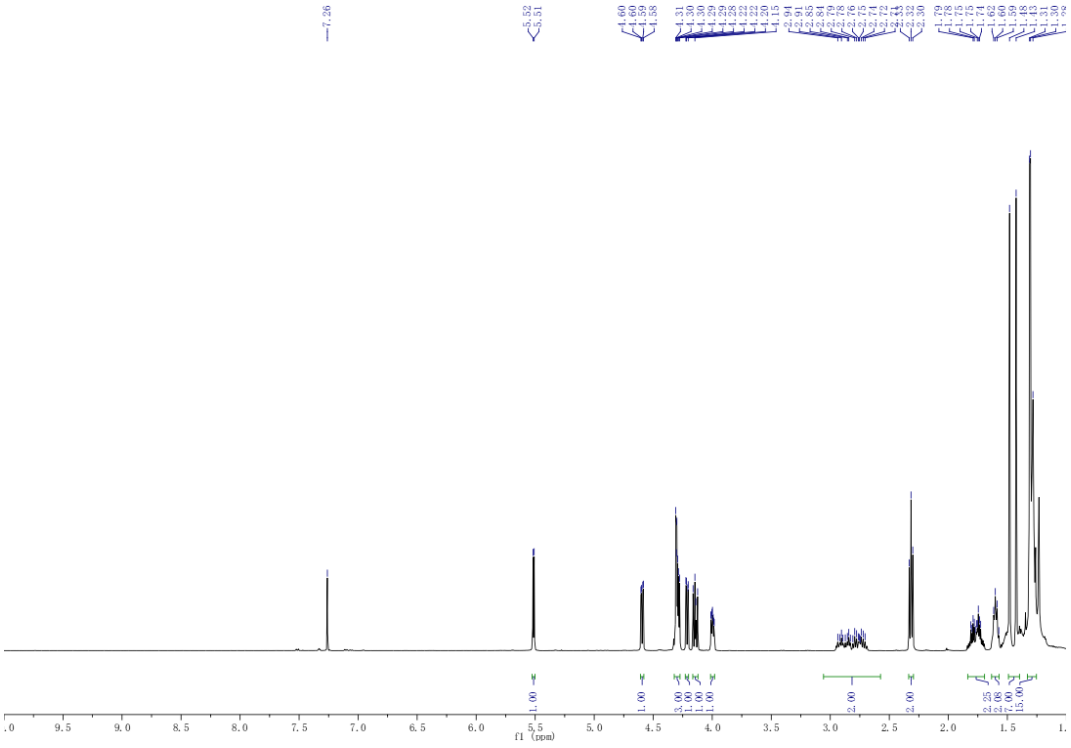
	Chemical shift	Integral area	dr = 1:1
1	5.86 (s)	0.44	
2	5.87 (s)	0.43	



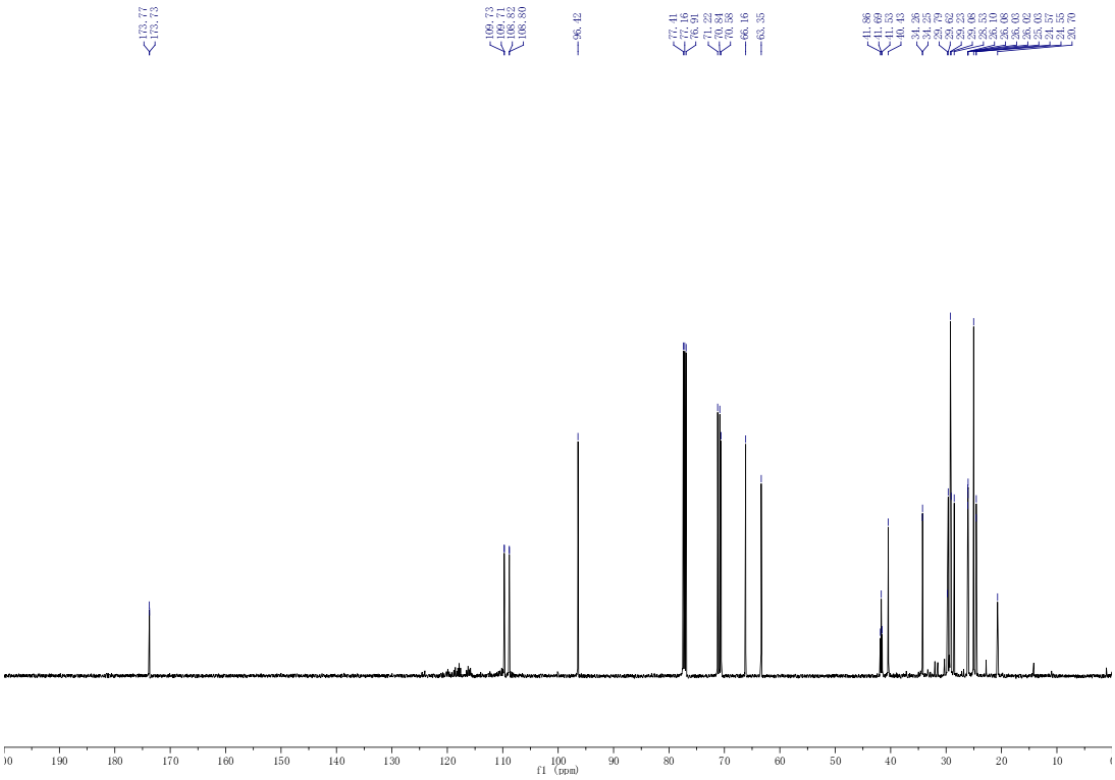
	Retention time (min)	Relative area	dr = 1:1
1	1.945	44.58	
2	2.347	42.36	



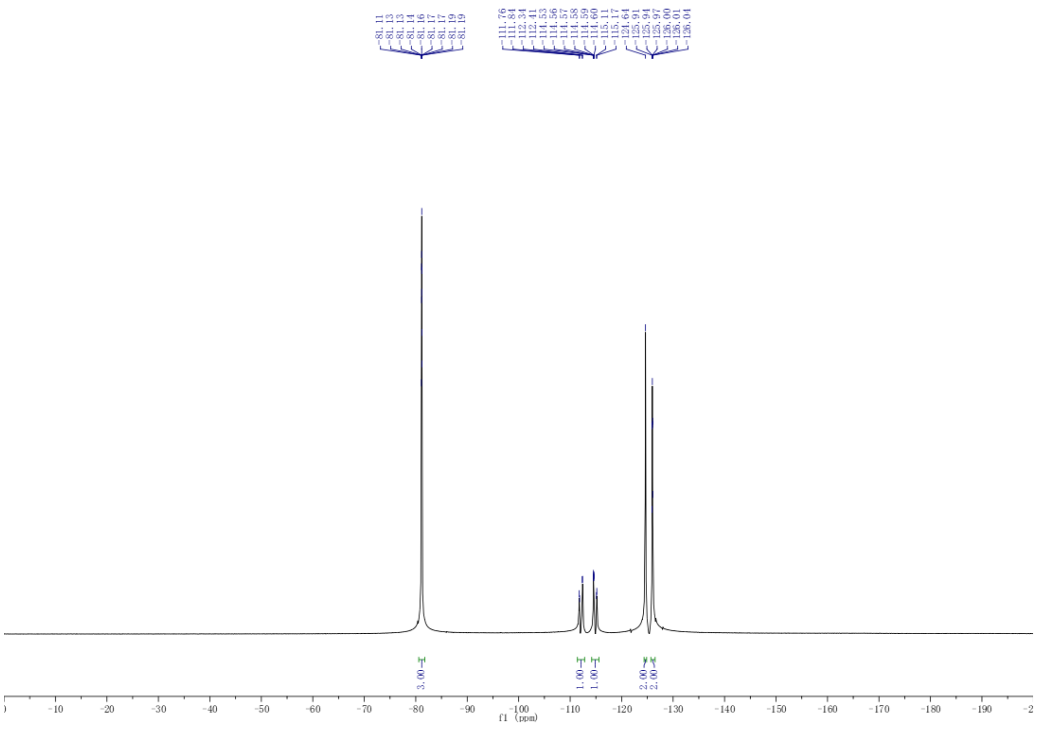
94



^{1}H NMR of compound **94**

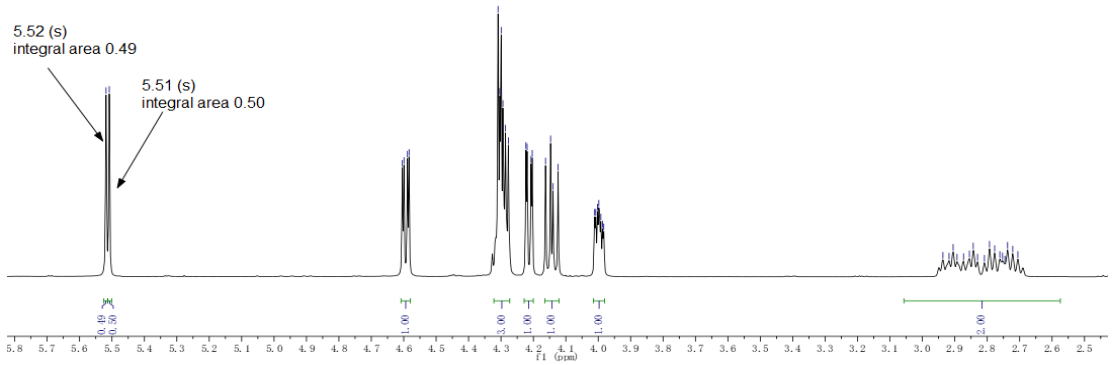


^{13}C NMR of compound **94**

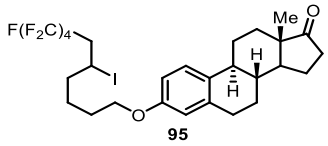


^{19}F NMR of compound **94**

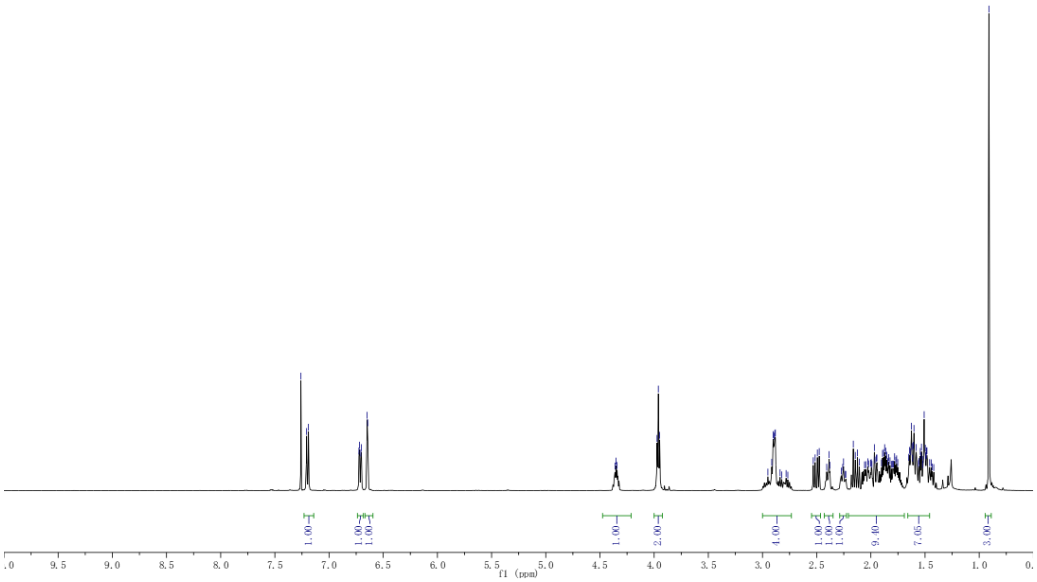
The dr ratio of compound **94** is determined by ^{1}H NMR:



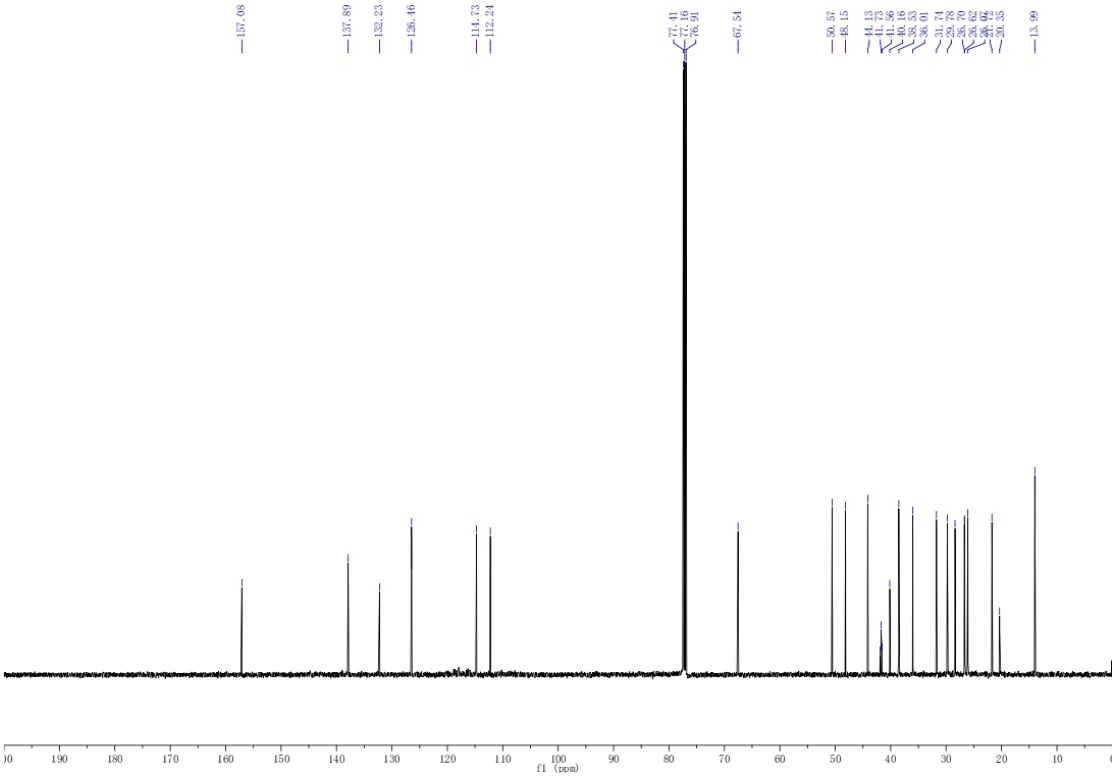
	Chemical shift	Integral area	dr = 1:1
1	5.51 (s)	0.50	
2	5.52 (s)	0.49	



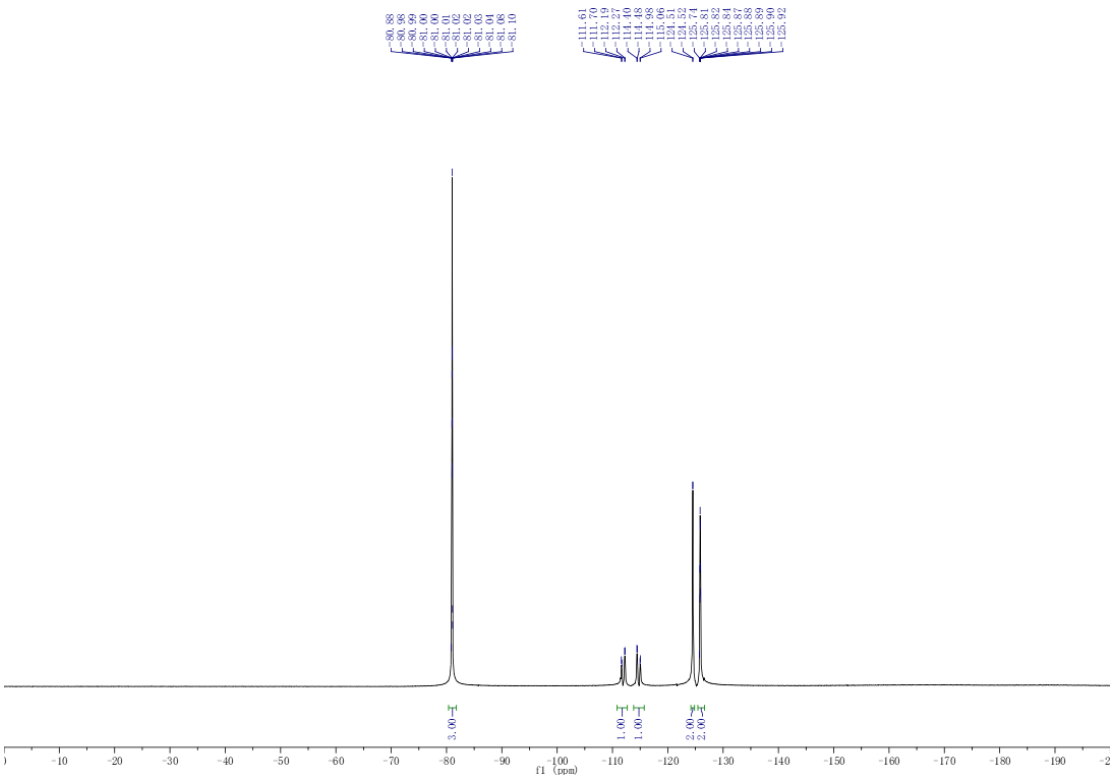
95



^{1}H NMR of compound **95**

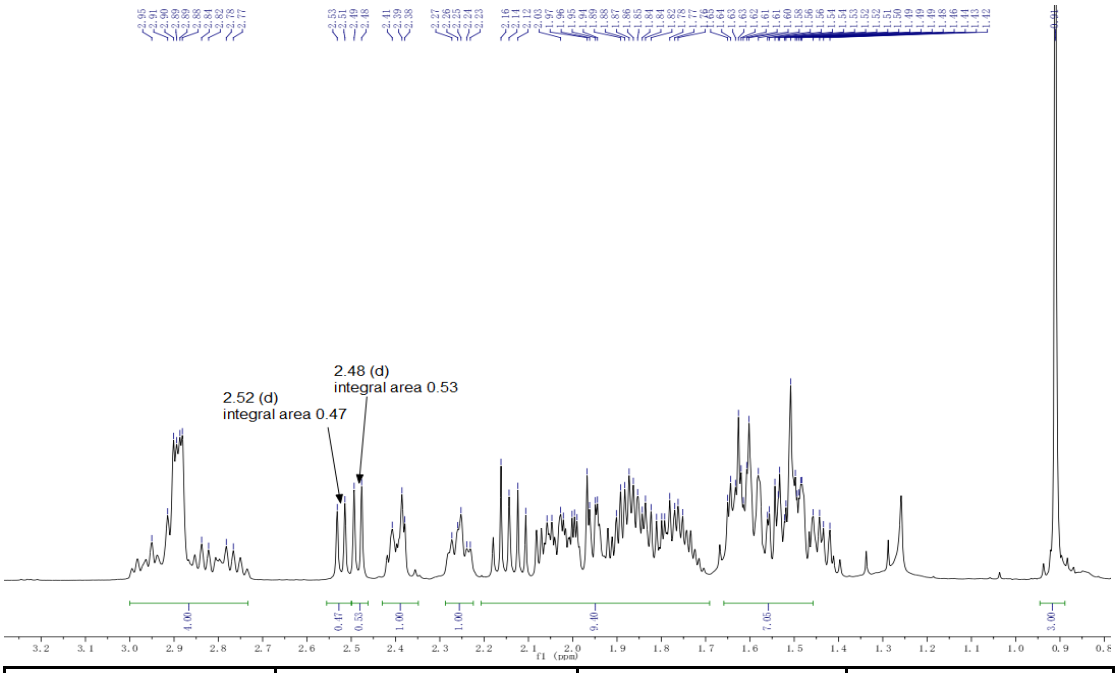


^{13}C NMR of compound **95**

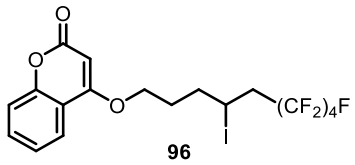


^{19}F NMR of compound **95**

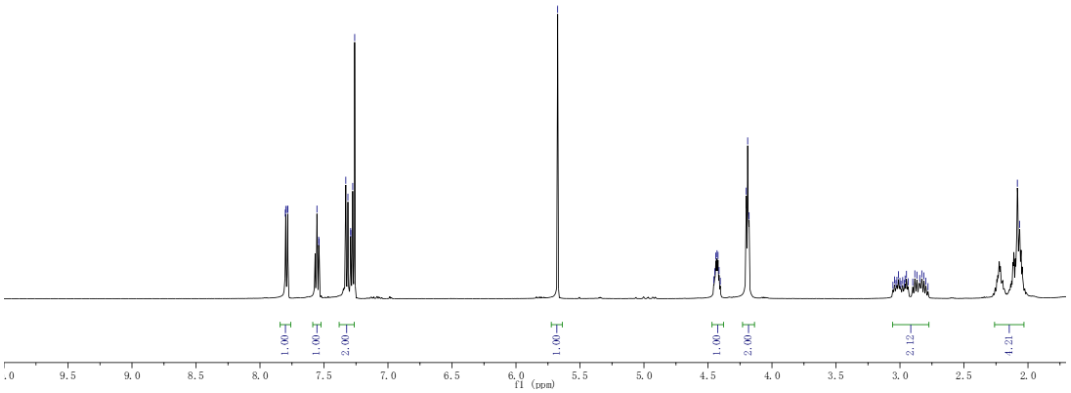
The dr ratio of compound **95** is determined by ^{1}H NMR:



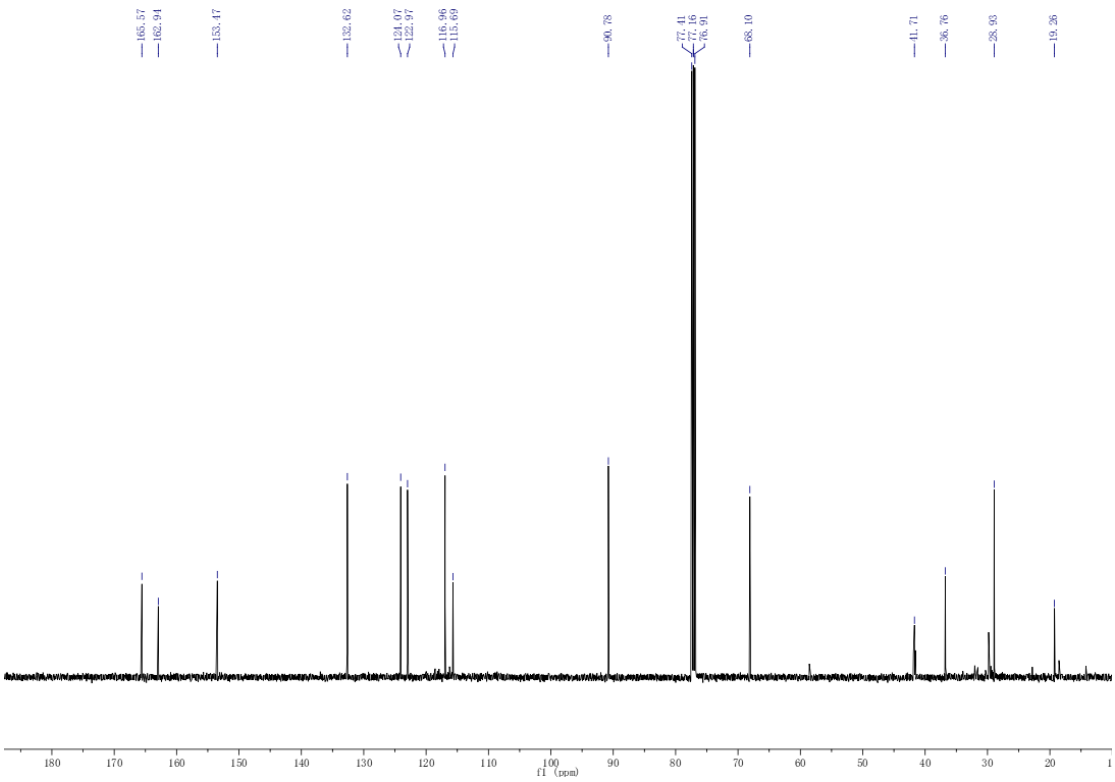
	Chemical shift	Integral area	dr = 1:1
1	2.48 (s)	0.53	
2	2.52 (s)	0.47	



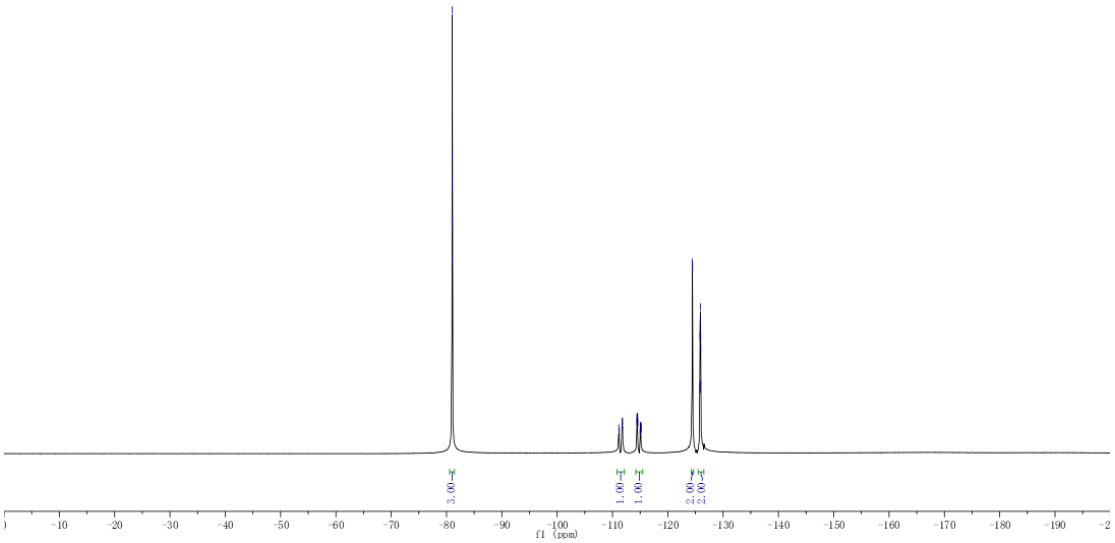
96



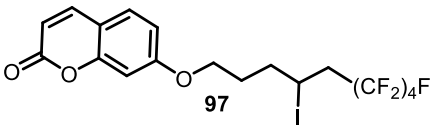
^{1}H NMR of compound **96**



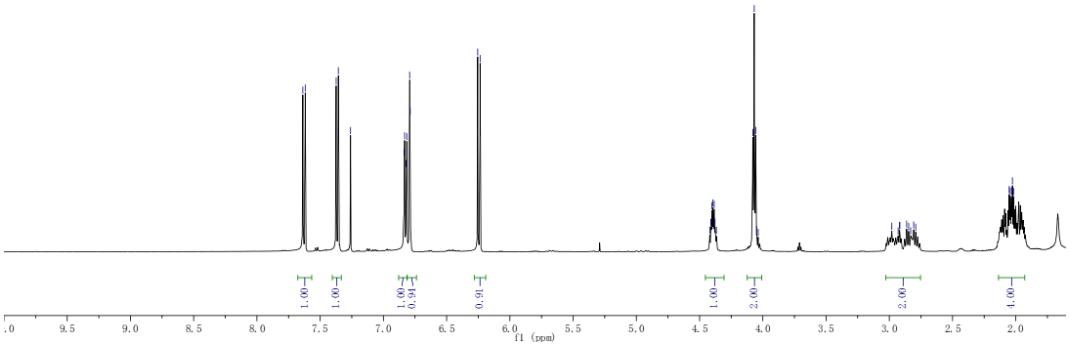
^{13}C NMR of compound **96**



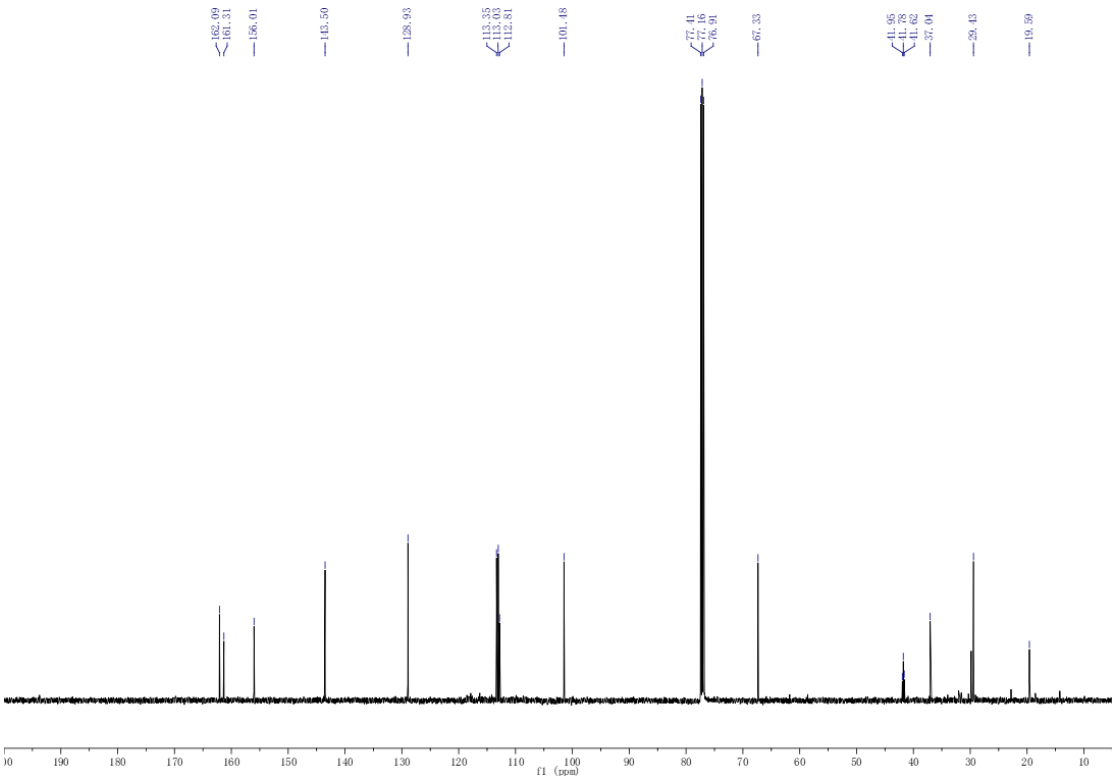
^{19}F NMR of compound **96**



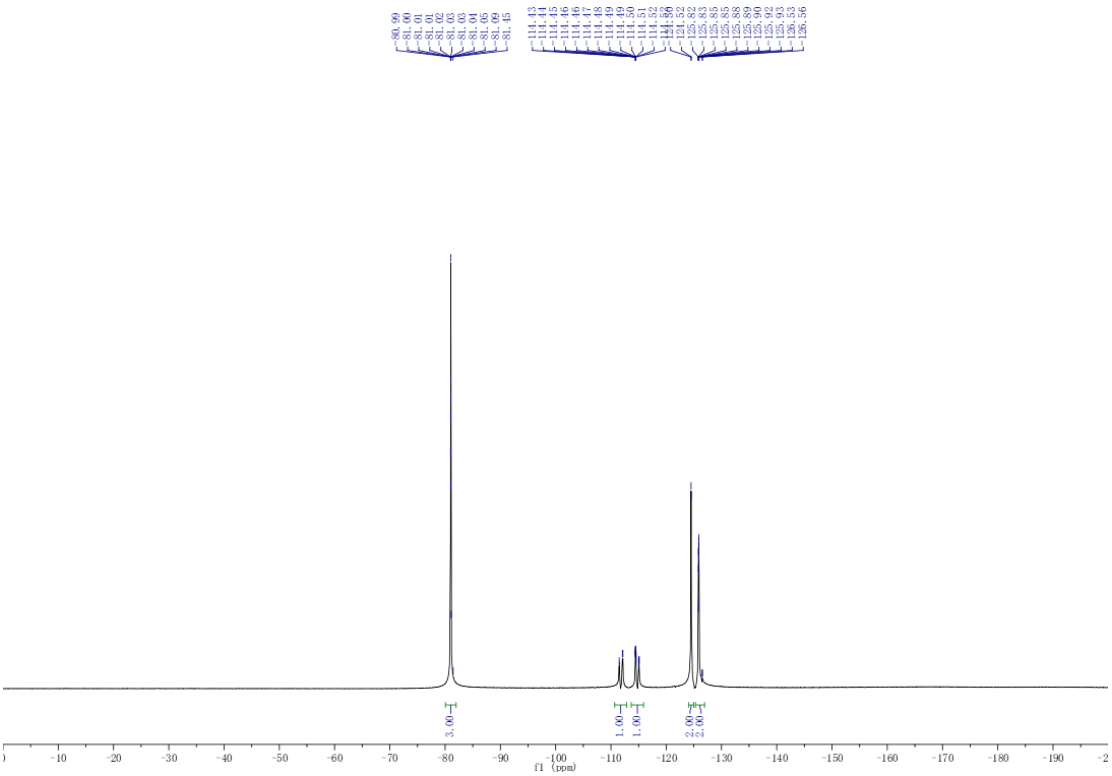
97



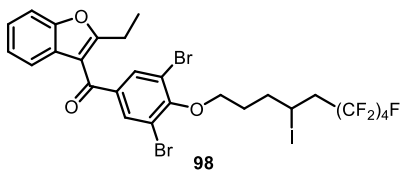
^{1}H NMR of compound **97**



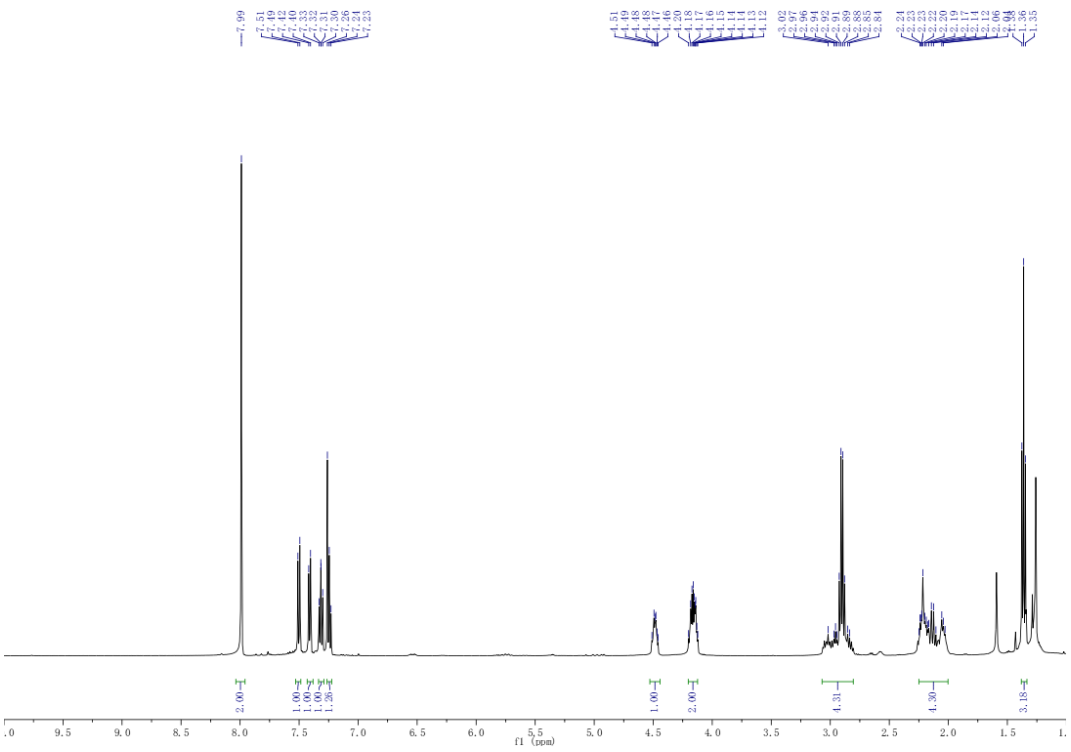
^{13}C NMR of compound **97**



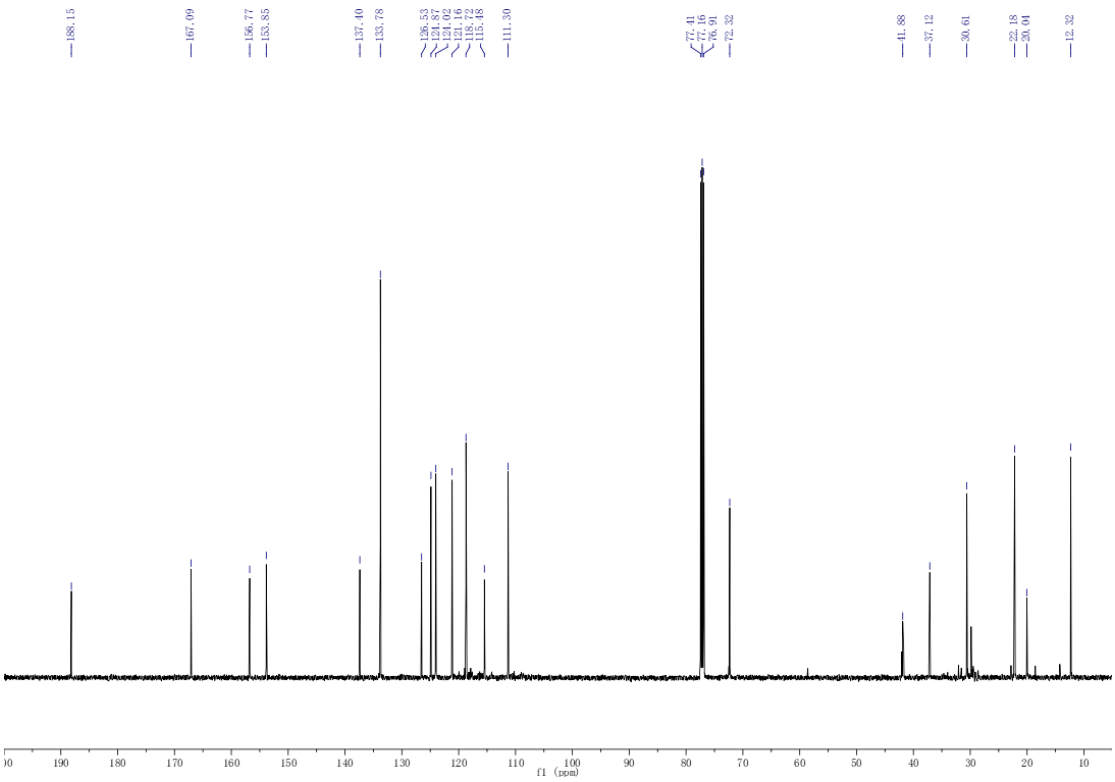
^{19}F NMR of compound **97**



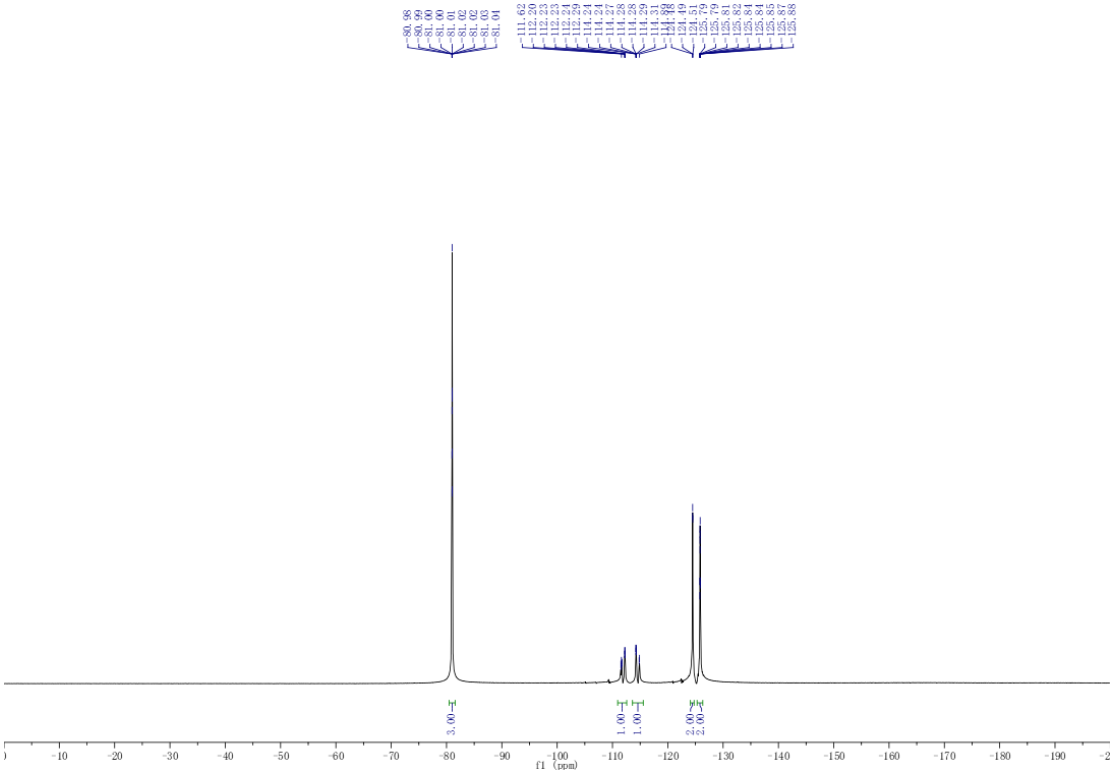
98



^{1}H NMR of compound **98**

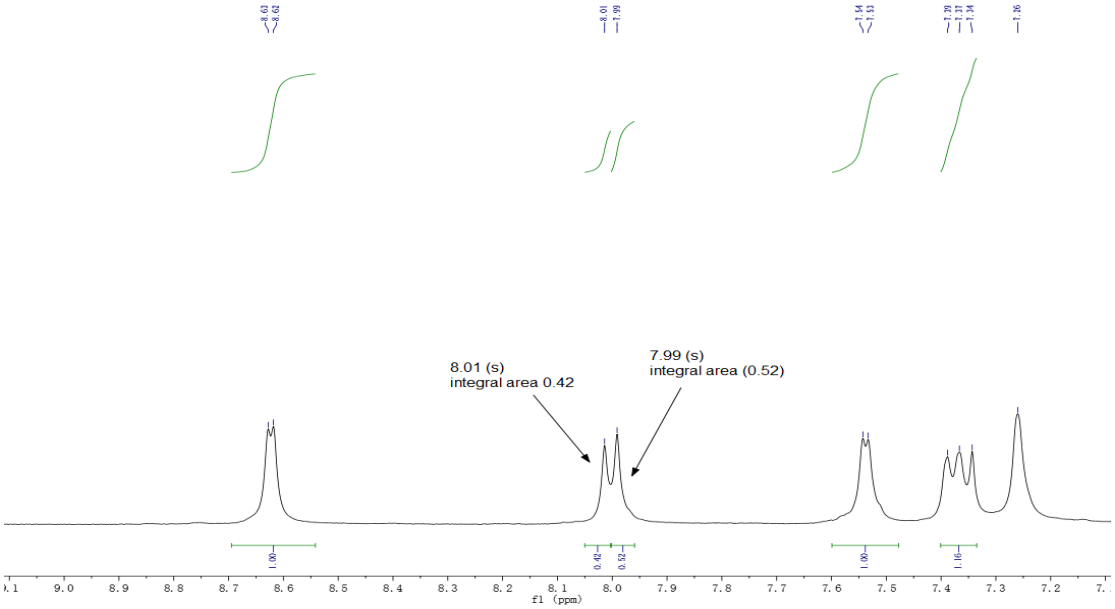


^{13}C NMR of compound **98**

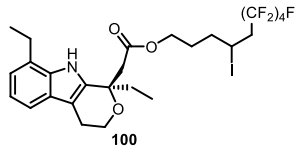


^{19}F NMR of compound **98**

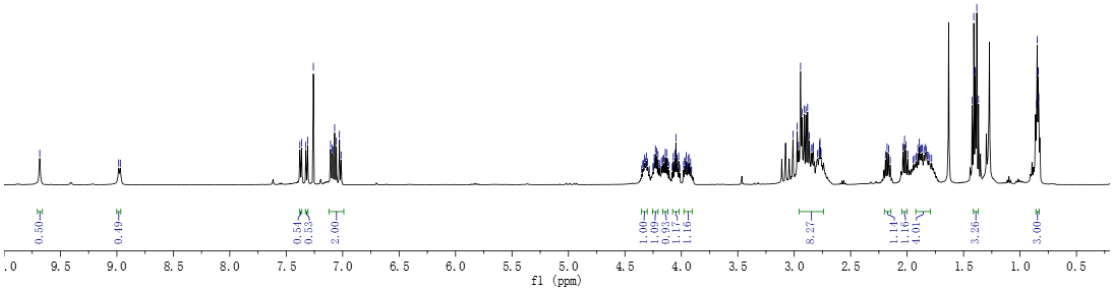
The dr ratio of compound **99** is determined by ^{1}H NMR:



	Chemical shift	Integral area	dr = 1:1
1	7.99 (s)	0.52	
2	8.01 (s)	0.42	

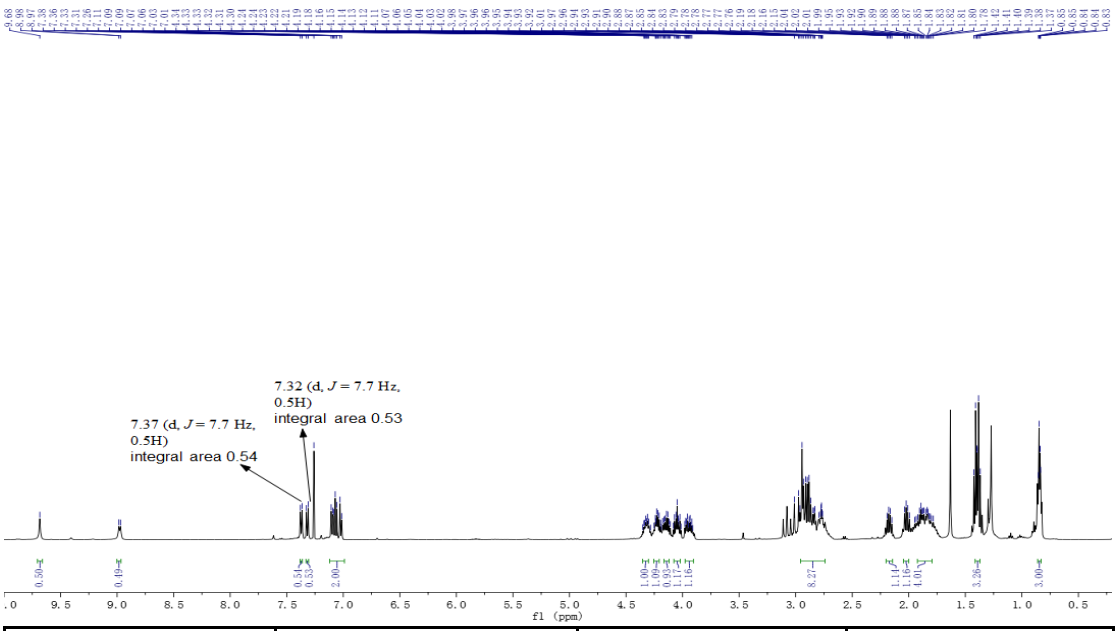


100

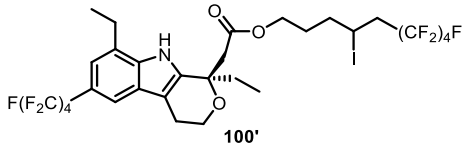


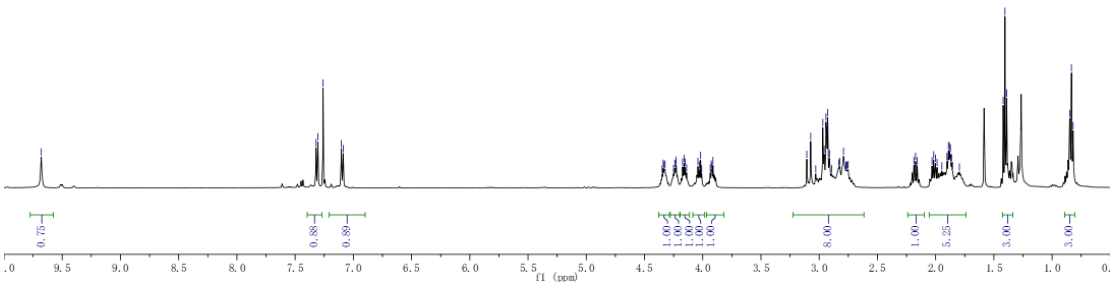
^{1}H NMR of compound **100**

The dr ratio of compound **100** is determined by ^{1}H NMR:

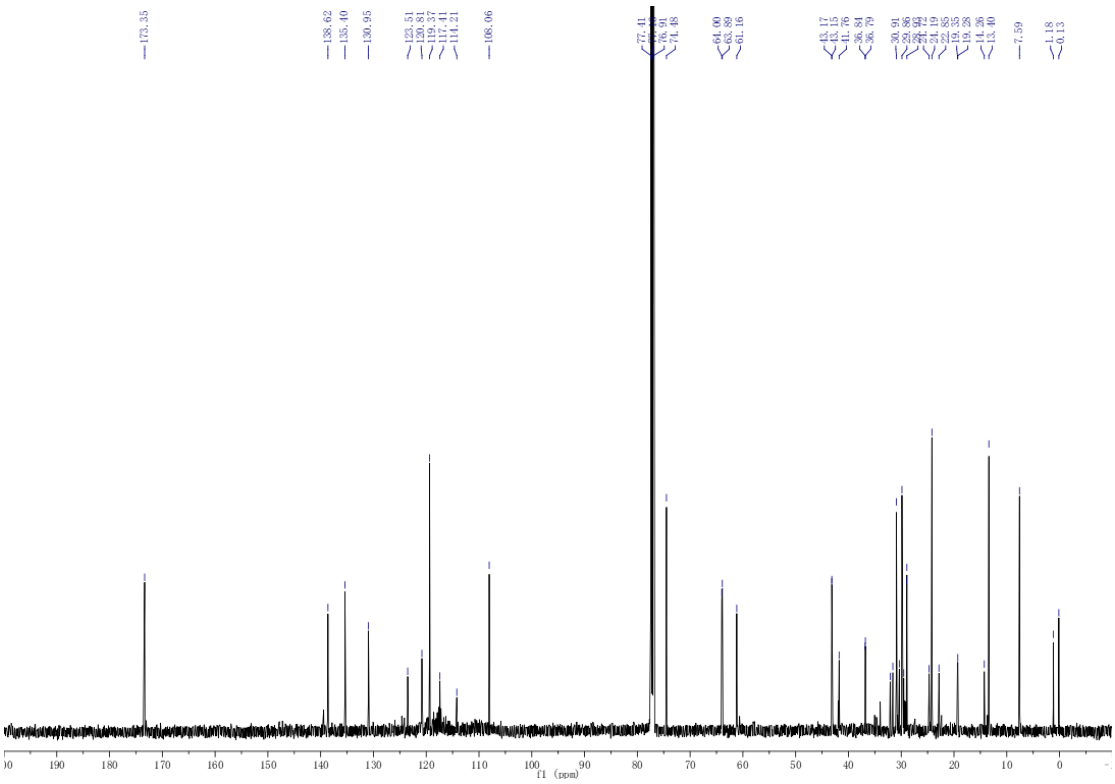


	Chemical shift	Integral area	dr = 1:1
1	7.32 (d)	0.53	
2	7.37 (d)	0.54	

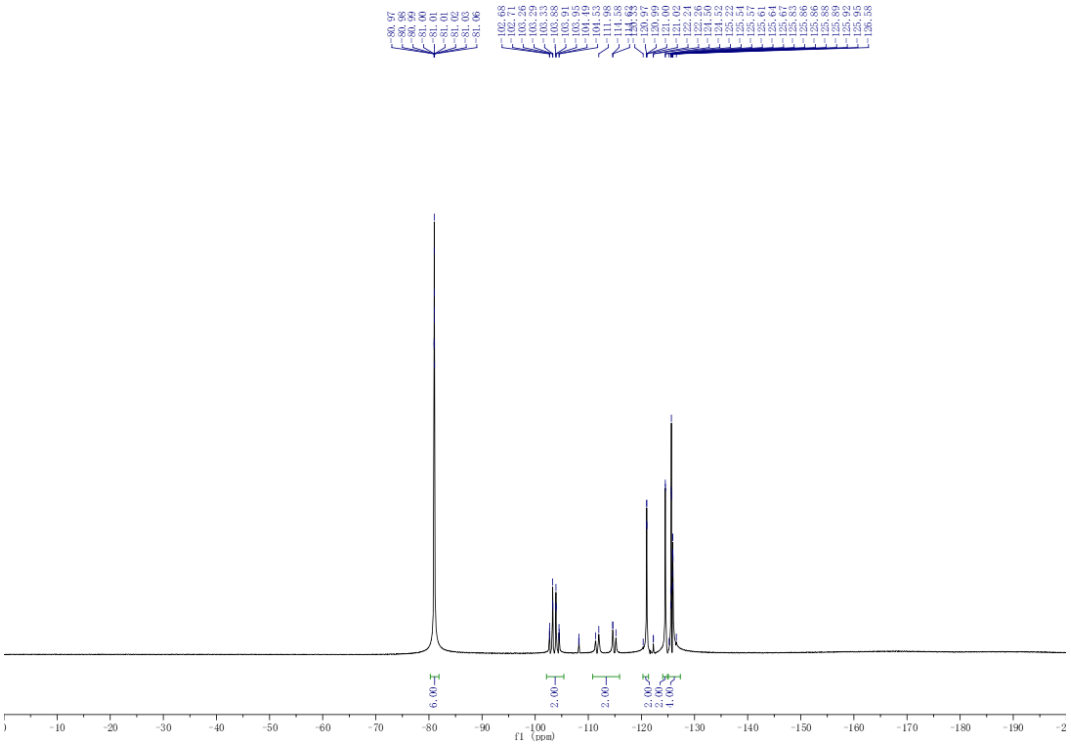




^{1}H NMR of compound **100'**

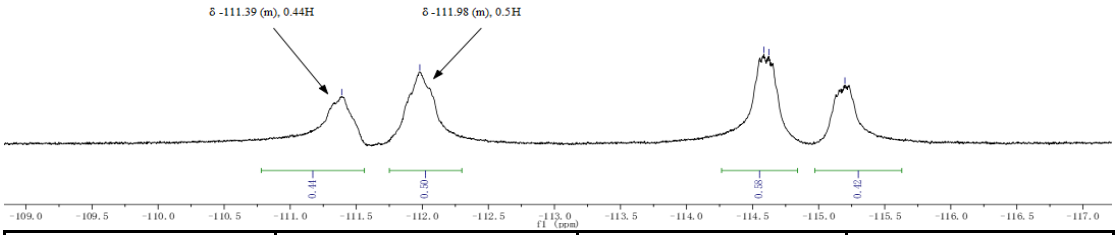


^{13}C NMR of compound **100'**



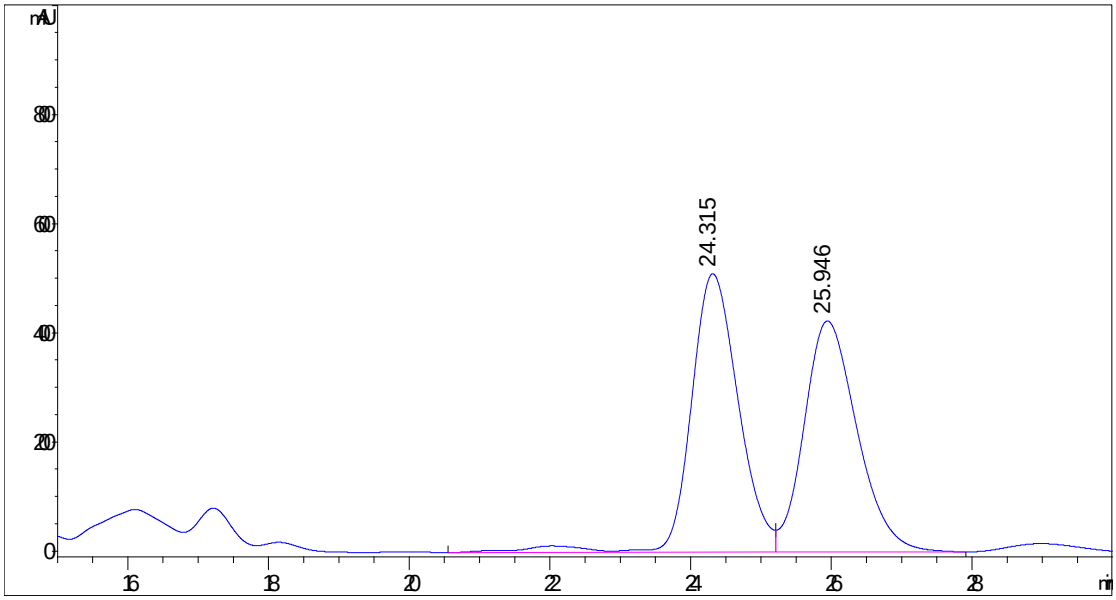
^{19}F NMR of compound **100'**

The dr ratio of compound **100'** is determined by ^{19}F NMR and HPLC:

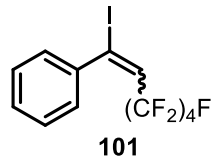


	Chemical shift	Integral area	dr = 1:1
1	-111.39 (m)	0.44	
2	-111.98 (m)	0.50	

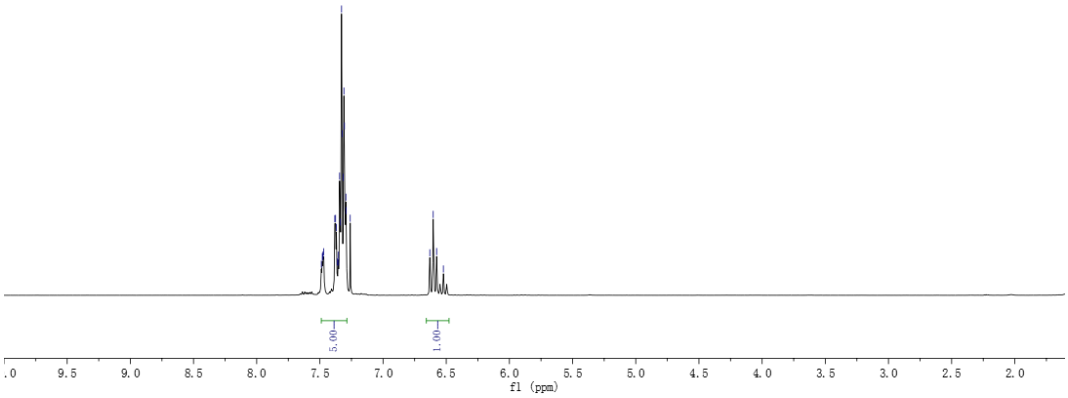
The dr ratio of compound **100'** is determined by HPLC:



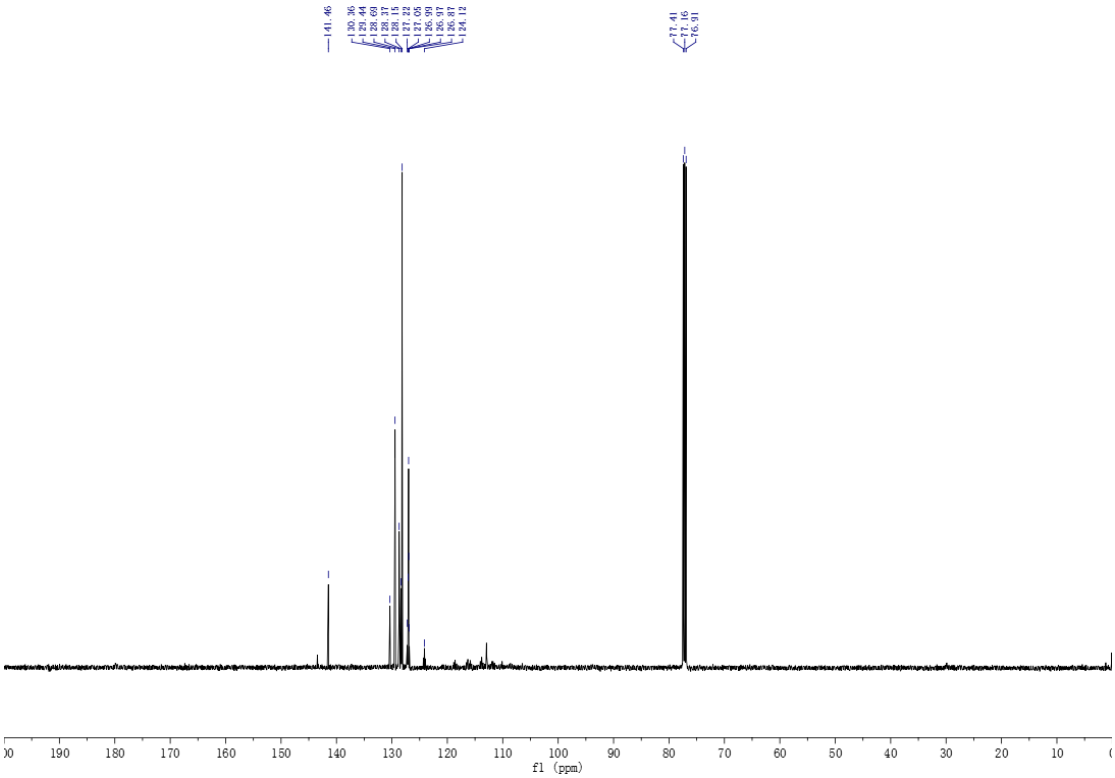
	Retention time (min)	Relative area	dr = 1:1
1	24.315	52.1	
2	25.946	47.9	



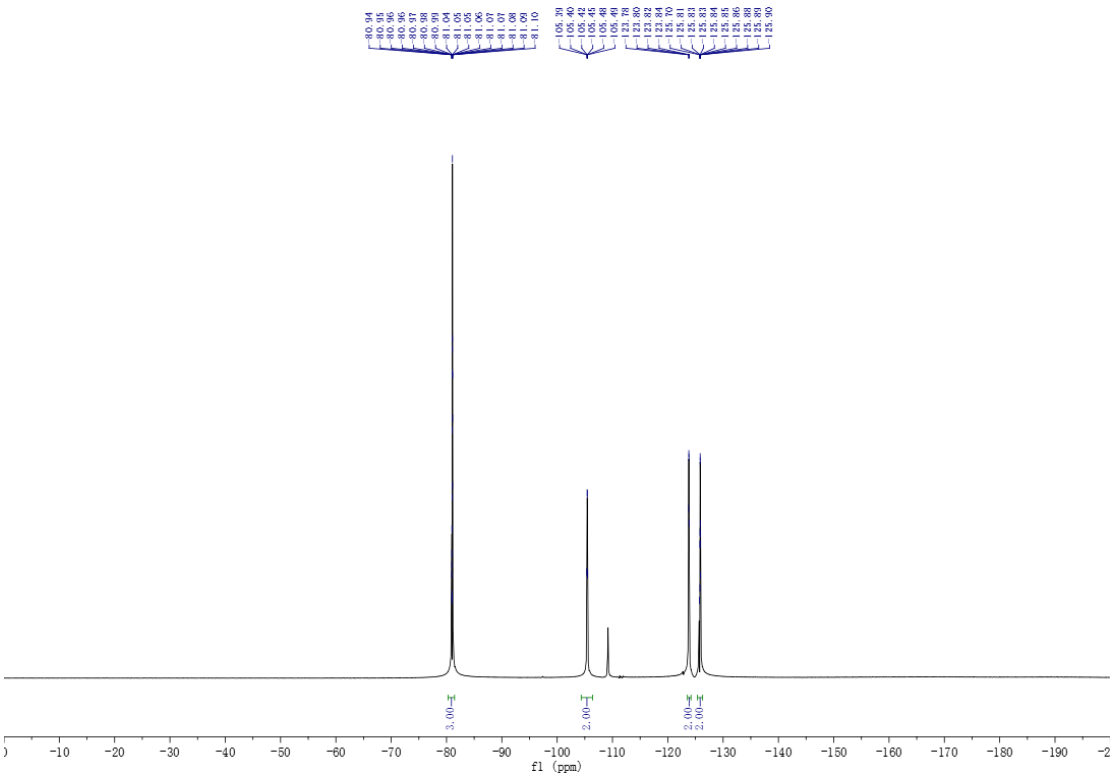
101



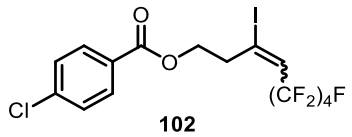
^{1}H NMR of compound **101**



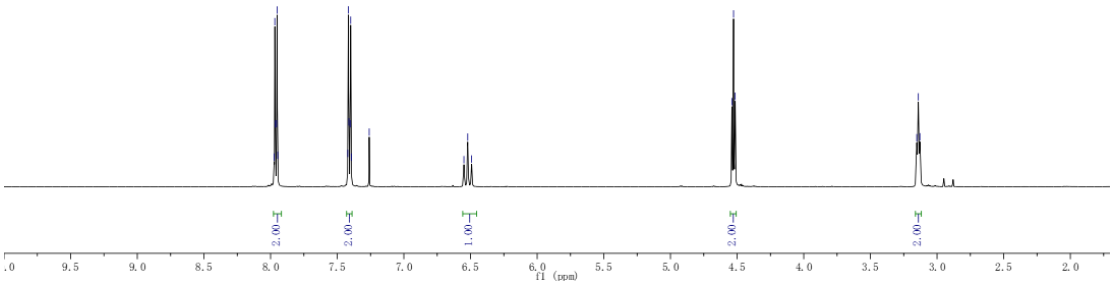
^{13}C NMR of compound **101**



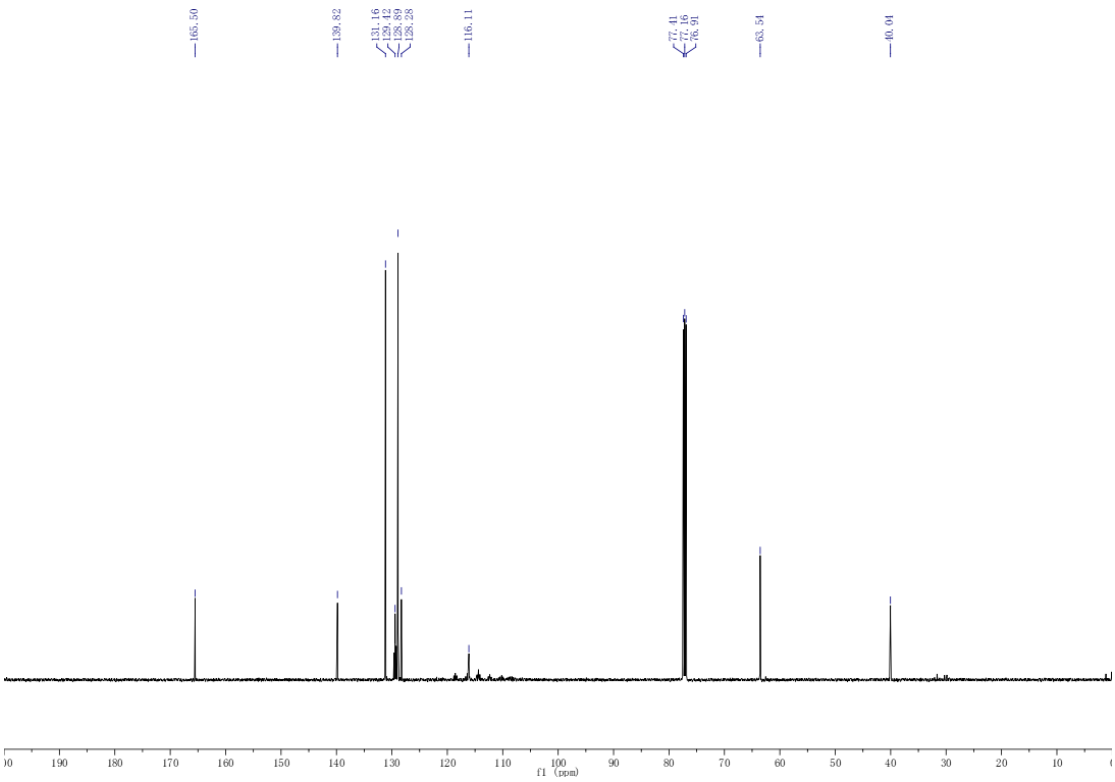
^{19}F NMR of compound **101**



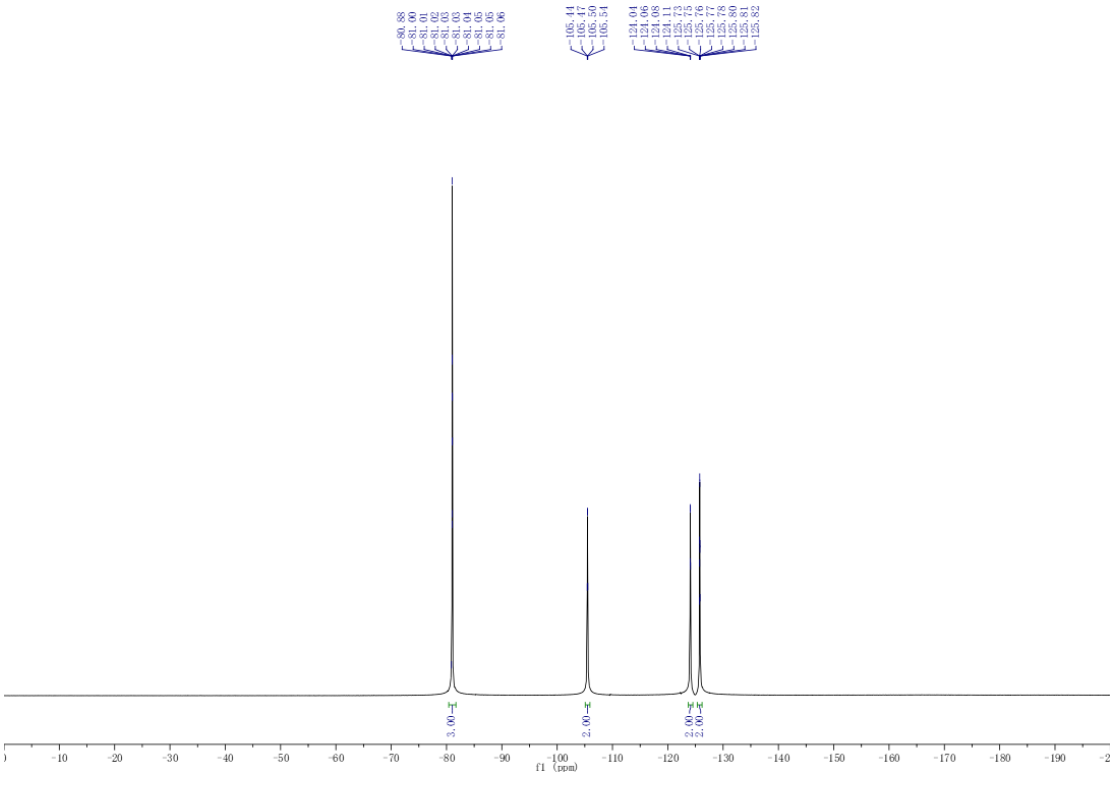
102



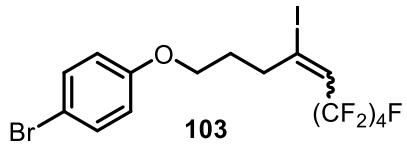
^{1}H NMR of compound **102**



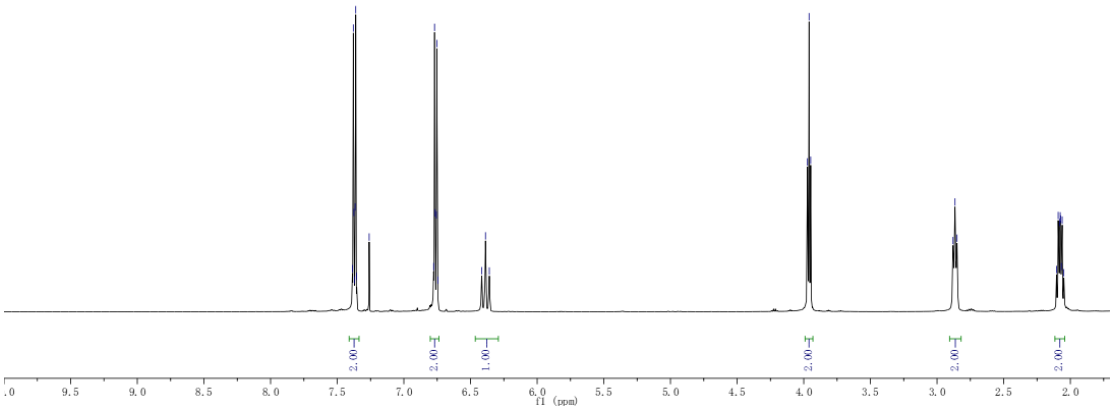
^{13}C NMR of compound **102**



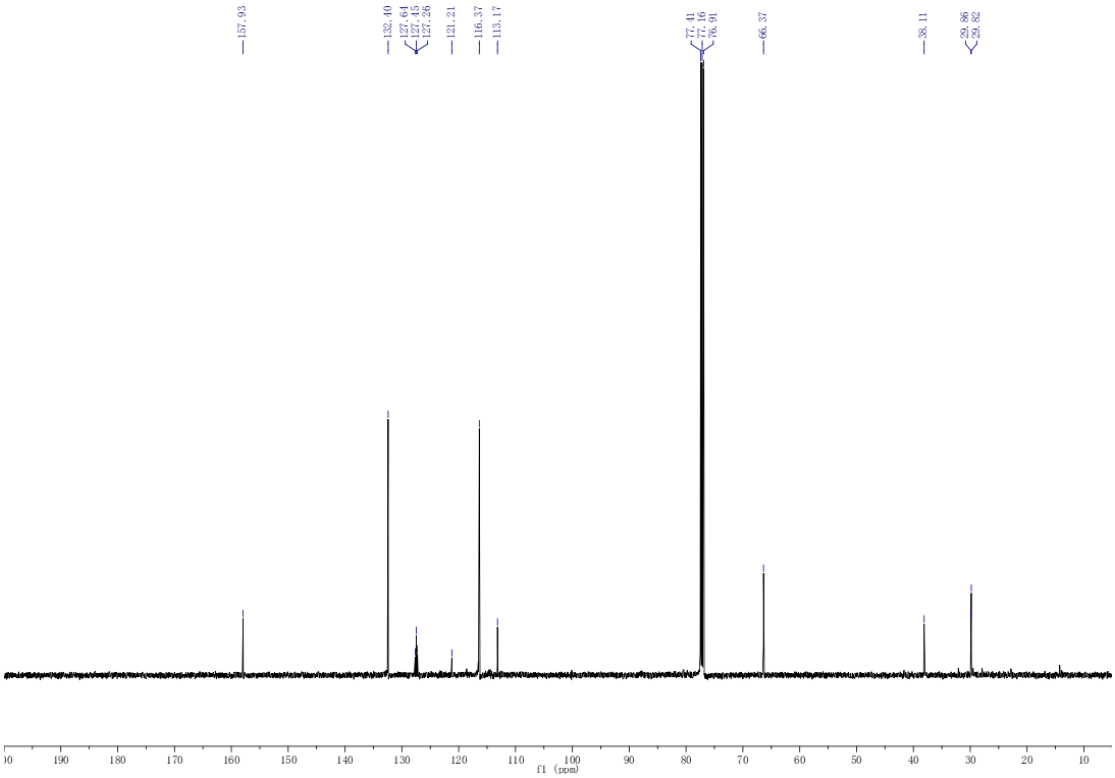
^{19}F NMR of compound **102**



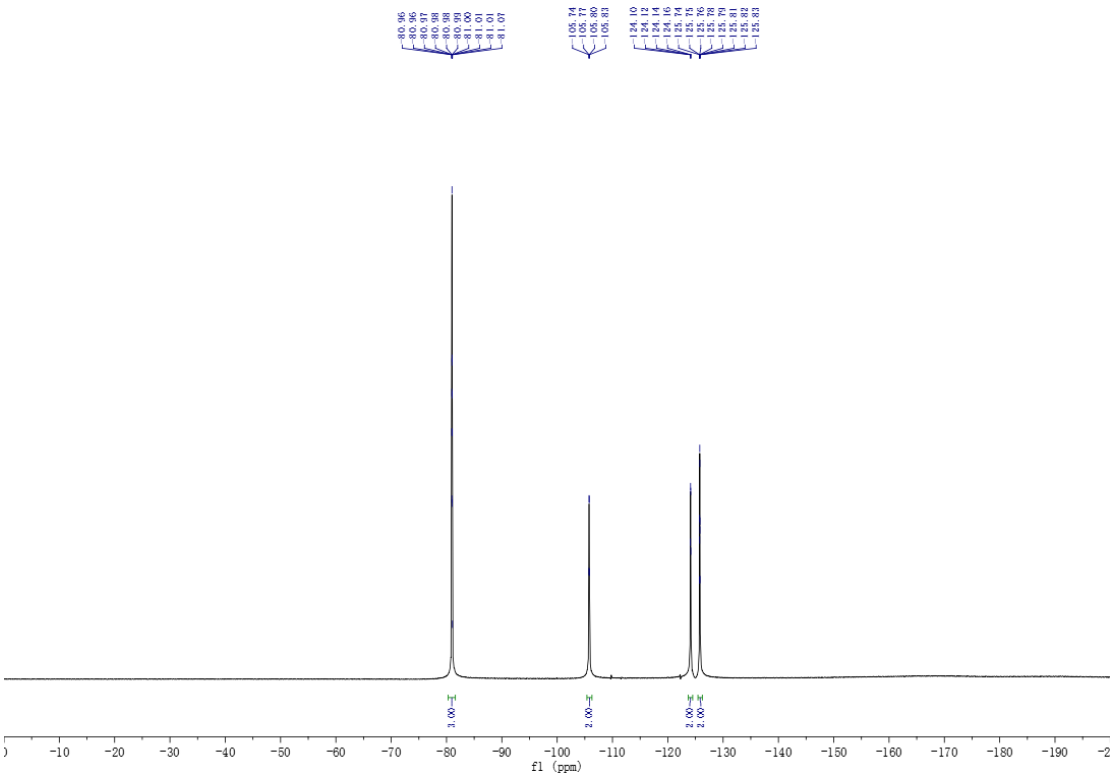
103



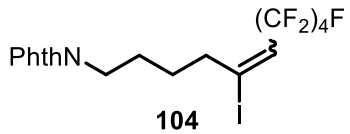
^{1}H NMR of compound **103**

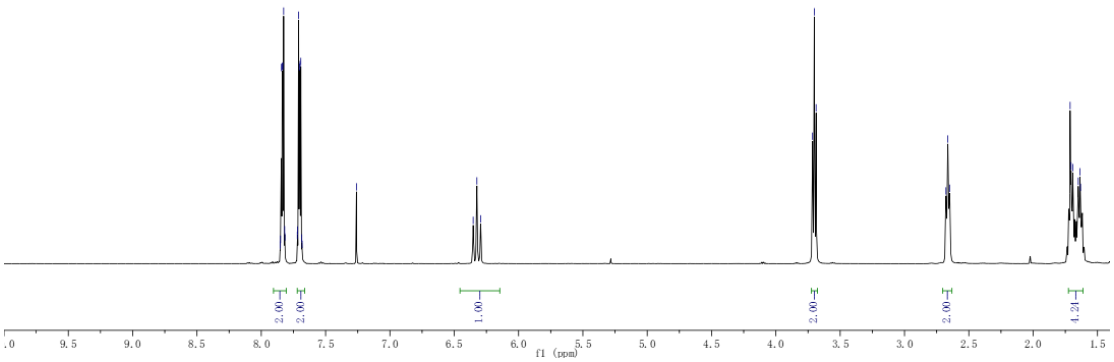


^{13}C NMR of compound **103**

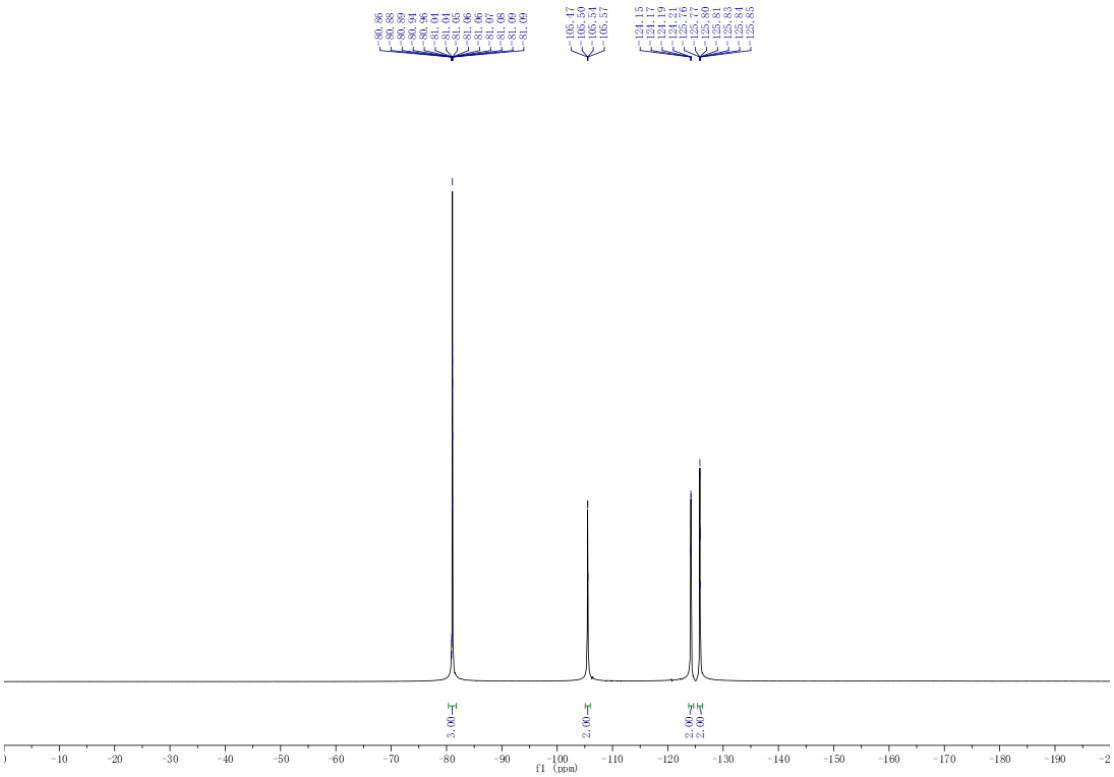


^{19}F NMR of compound **103**

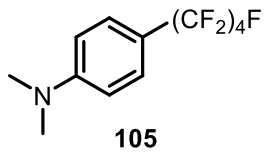




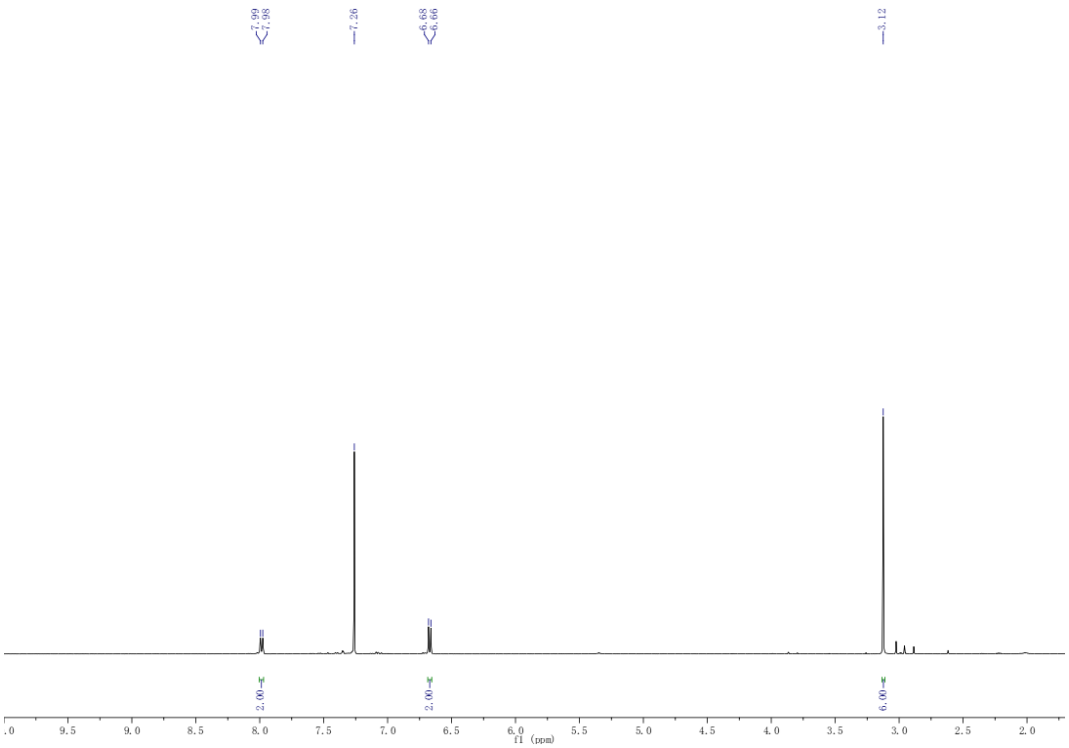
^{1}H NMR of compound **104**



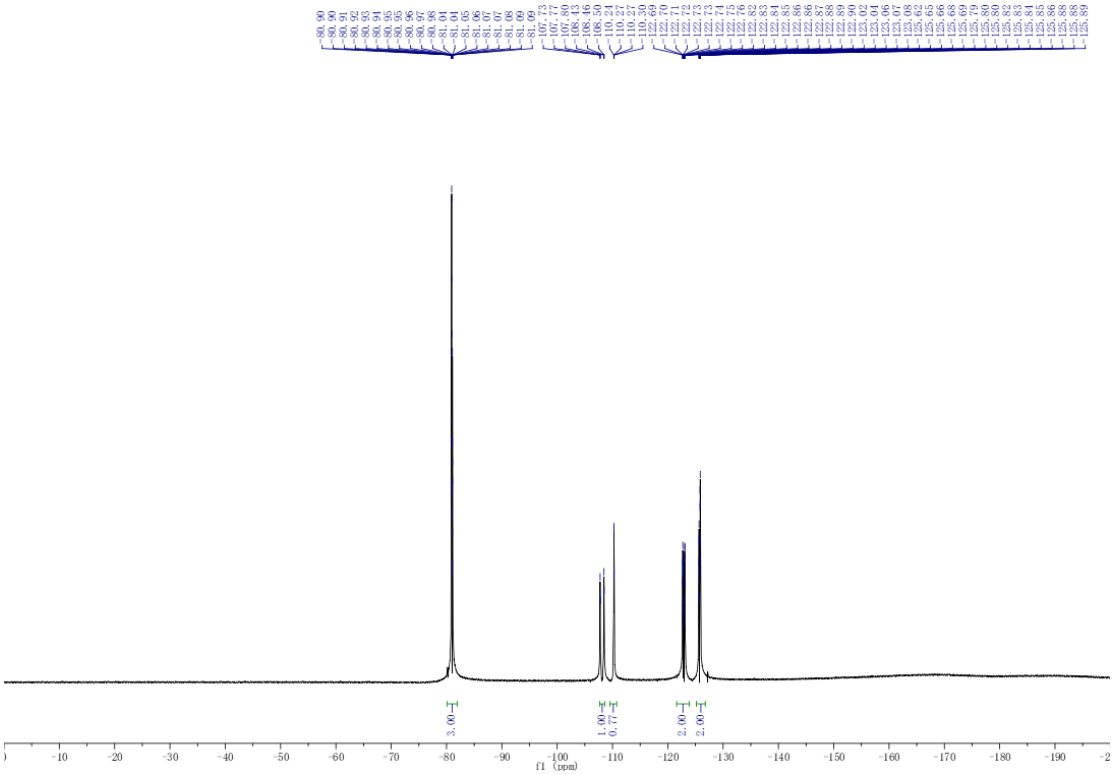
^{19}F NMR of compound **104**



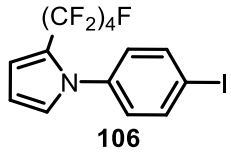
105



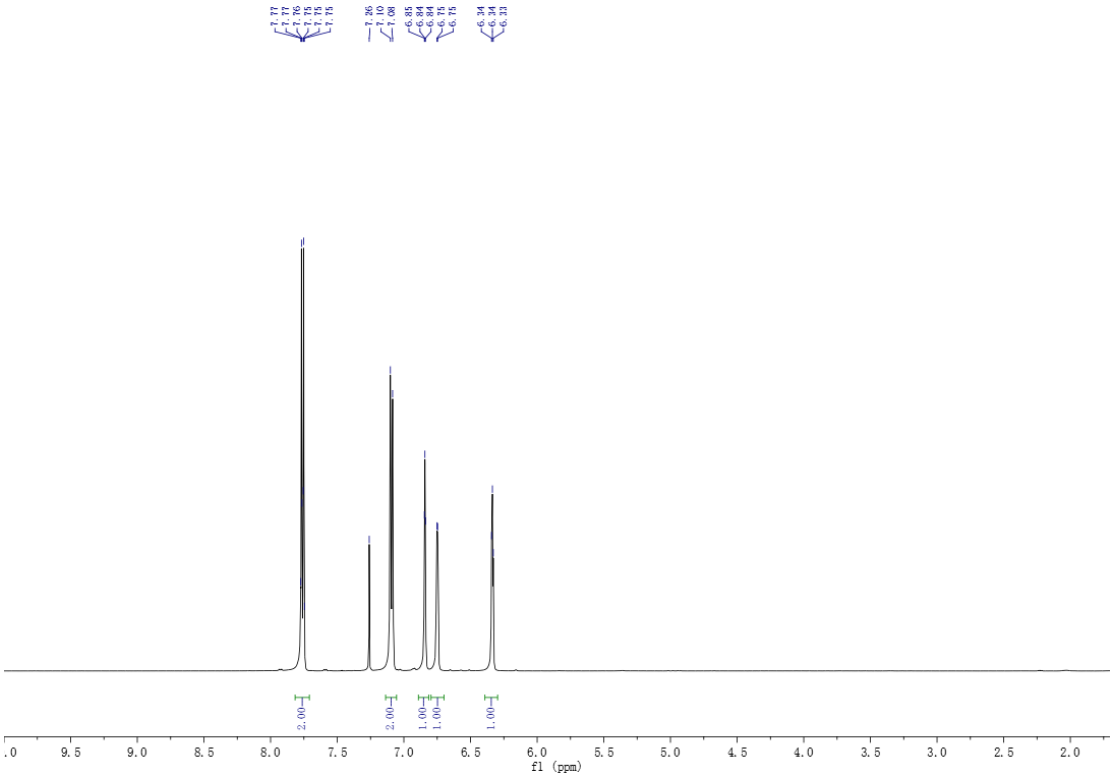
^{1}H NMR of compound **105**



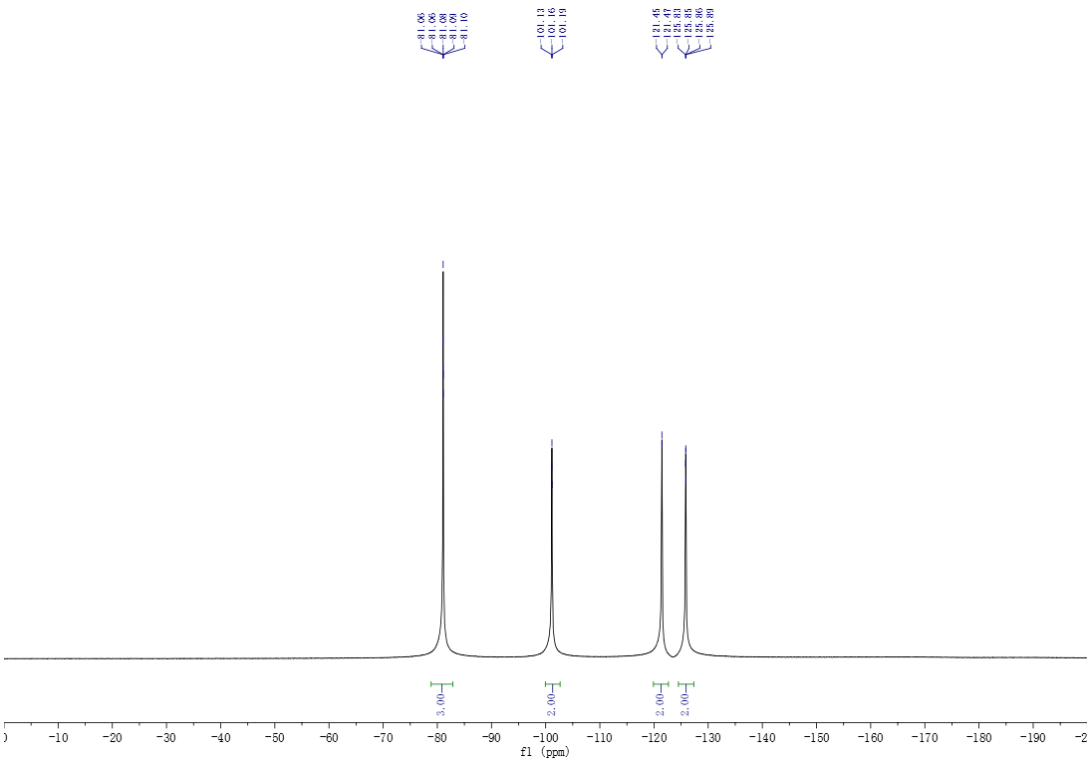
^{19}F NMR of compound **105**



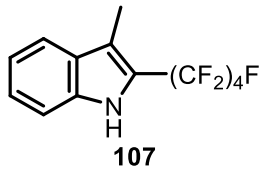
106



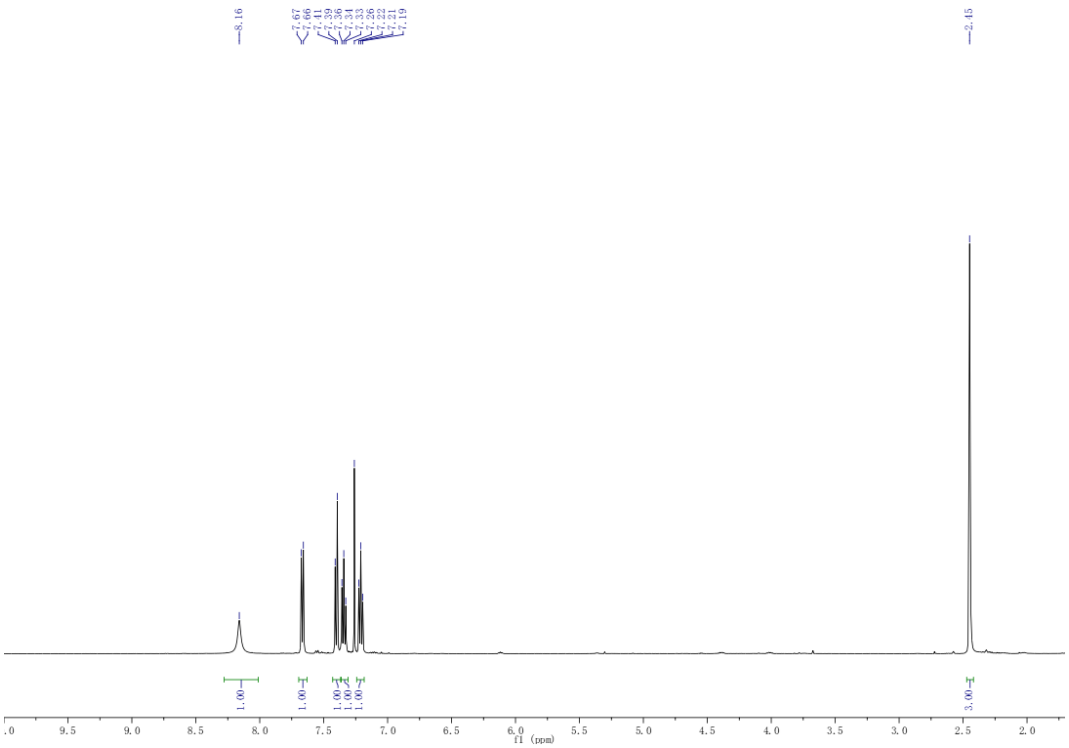
^{1}H NMR of compound **106**



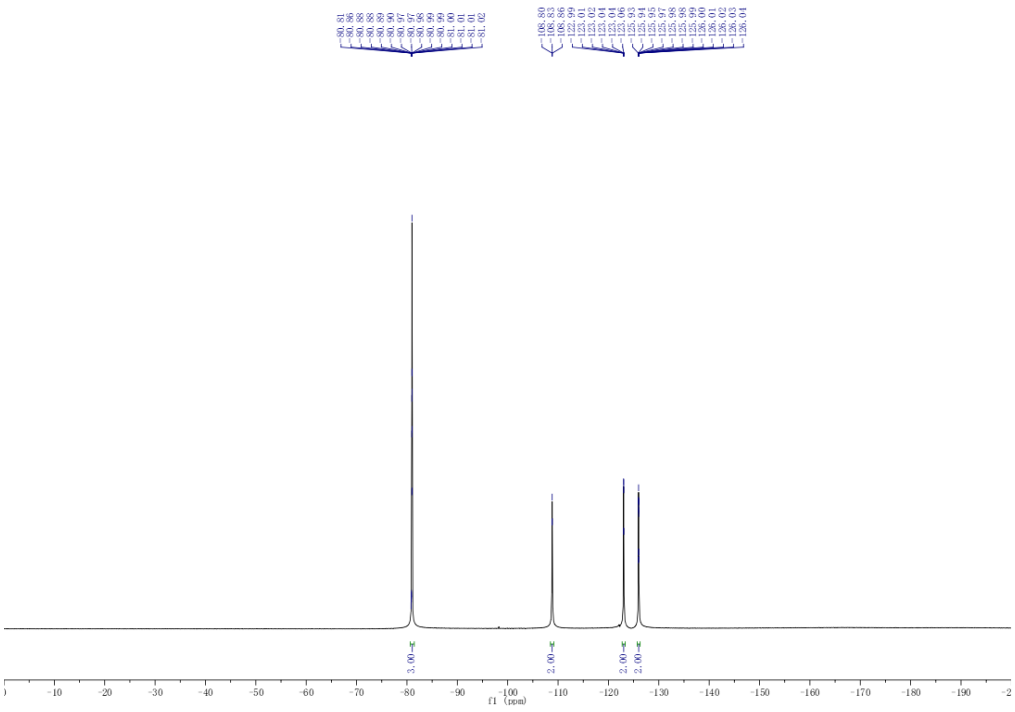
^{1919}F NMR of compound **106**



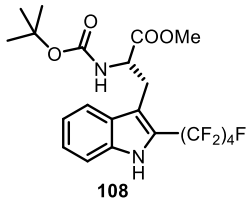
107



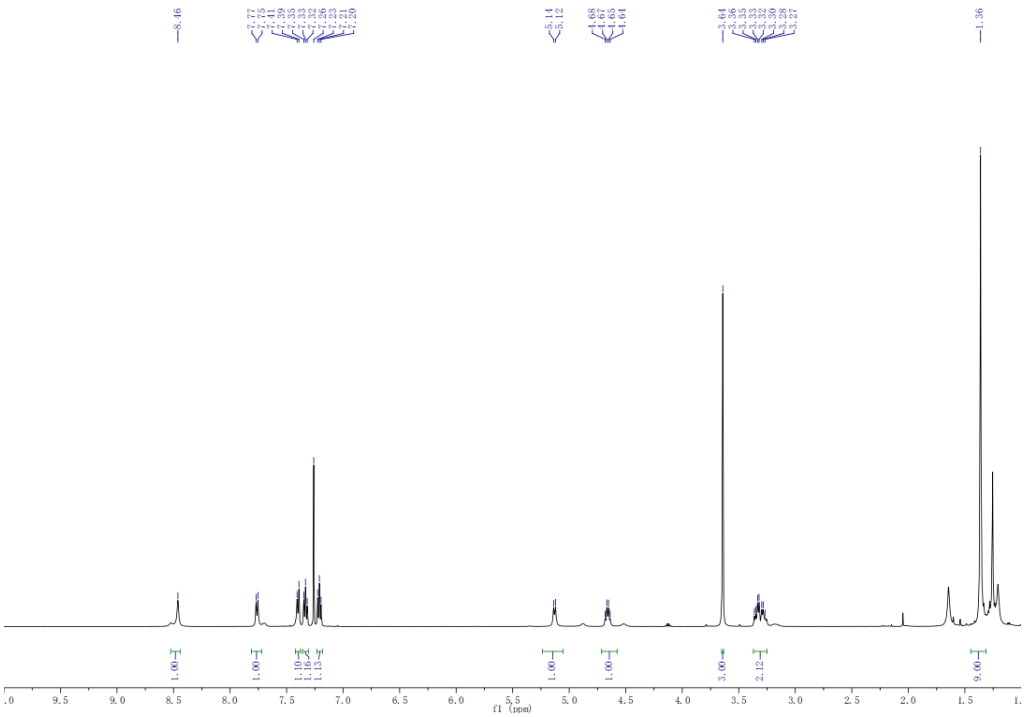
^{1}H NMR of compound **107**



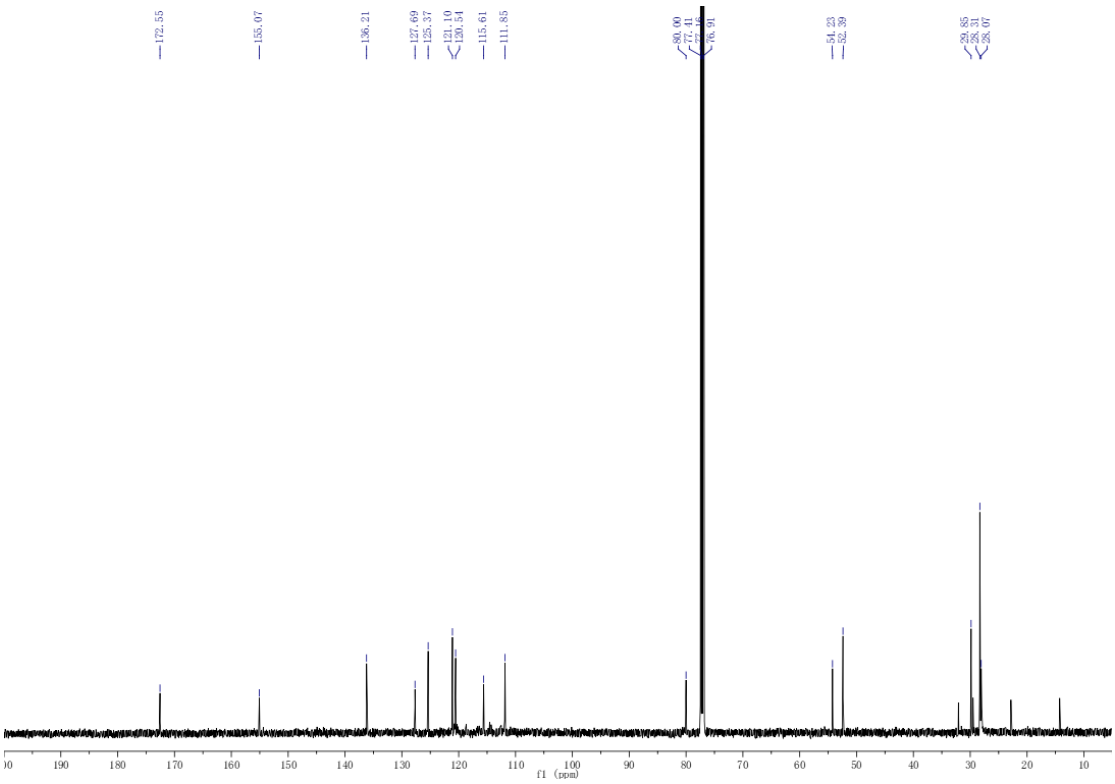
^{19}F NMR of compound **107**



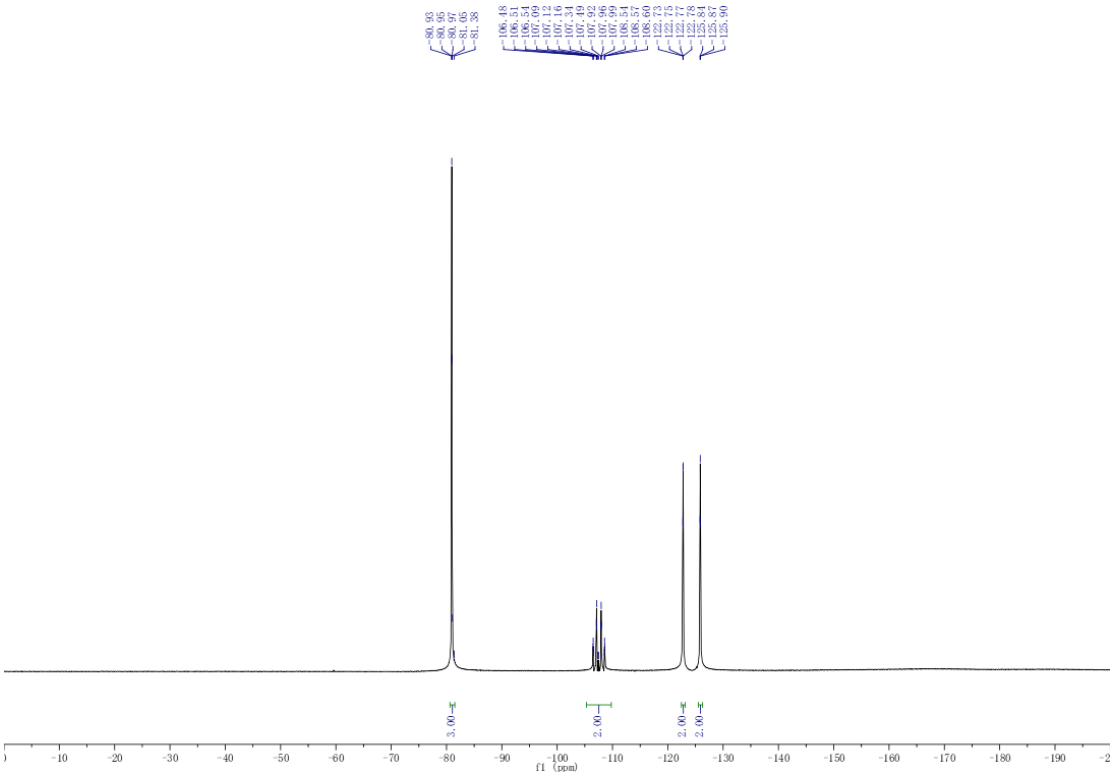
108



^{1}H NMR of compound **108**



^{13}C NMR of compound **108**



^{19}F NMR of compound **108**