Supporting Information

Metal-free *meta*-halogenation of cyclic diaryliodonium salts via aryne intermediates

Hongqiang Jiang,[a,†] Min Liu,[c,†] Zenghui Ye,[b] Zongqiang Song,[a] Yanqi Wu*[b,c] and Fengzhi Zhang*[b,c]

[a] *School of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou, 310014, P.R.China.*

[b] *School of Pharmaceutical Science, Hangzhou Medical College, Hangzhou, 311399, P.R.China.*

[c] *Zhejiang University of Technology, Hangzhou, 310014, P.R.China.*

*E-mail:zhangfengzhi@hmc.edu.cn

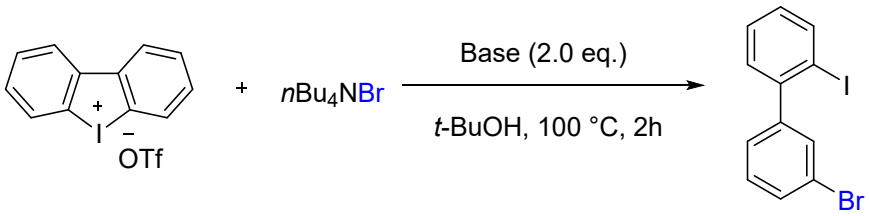
Contents

1. General information

Unless otherwise noted, all chemicals were obtained from commercial suppliers and used without further treatment. The cyclic diaryliodoniums were prepared according to the literature work.[1] The yields of all compounds were purified by flash column chromatography which was used silica gel (200−300 mesh), and reactions were monitor by thin layer chromatography (TLC) which was carried out on UV-254 silica gel plates using appropriate eluents. The ^{1}H nuclear magnetic resonance (NMR) spectra were obtained at 400 or 500 MHz, ^{13}C NMR were obtained at 101 or 126 MHz NMR spectra were obtained at 400 or 500 MHz, in $CDCl_3$ or *d*-DMSO as solvent with TMS as internal standard. Chemical shifts (δ) are given in parts per million. The residual solvent signals were used as references (for $CDCl_3$, δ_H = 7.26 ppm and δ_C = 77.03 ppm. For *d*-DMSO, δ_H = 2.50 ppm and δ_C = 39.00 ppm.). Coupling constants (*J*) were reported in hertz. The peak splitting patterns are described as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublet (dd), doublet of triplet (dt). Melting points were measured on an SGW® X-4B apparatus and uncorrected. HRMS were recorded on Agilent 6210TOF LC/MS mass spectrometer. HRMS were recorded in the EI（or CI） mode on Agilent 8890 GC / 7250 Q-TOF MS.

2. Optimization of reaction conditions.

Table S1: Optimization of bases

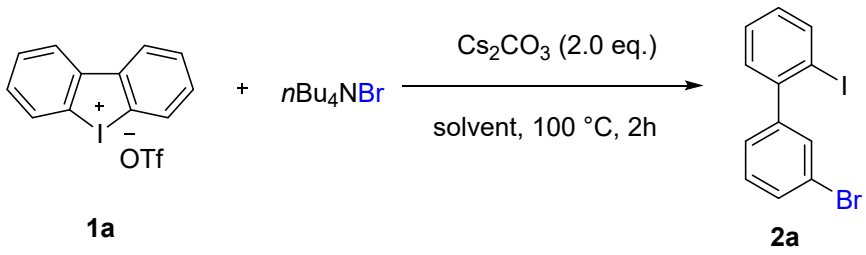


1a **2a**

Entry[a]	Base	Yield (%)[b]
1	NaOH	85
2	K_2CO_3	60
3	*t*-BuOK	34
4	LiH	46
6	LiOH	messy
7	CaO	N.R.
8	Cs_2CO_3	90
9	Et_3N	N.D.
10	DBU	N.D.

[a] Reaction conditions: cyclic diaryliodonium salt **1a** (0.2 mmol), nBu_4NBr (3.0 eq.), and base (2.0 eq.) in *t*-BuOH (2.0 mL) at 100 °C for 2 h. [b] Isolated yields. N.R. = No reaction. N.D. = Not detected.

Table S2: Optimization of solvents

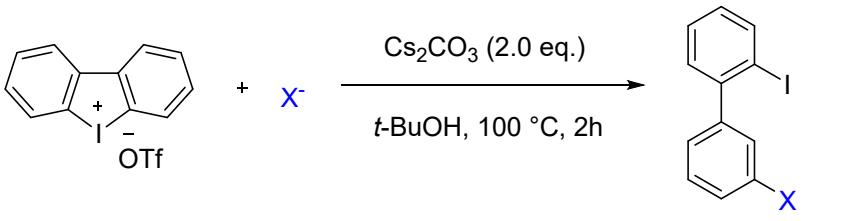


1a **2a**

Entry[a]	Solvent	Yield (%)[b]
1	DCM	N.D.
2	1, 3-propanediol	N.D.
3	toluene	trace
4	1, 4-dioxane	N.D.
6	MTBE	45
7	*t*-BuOH	90
8	*t*-BuOH/H_2O (2/1)	trace
9	DMF	N.D.
10	THF	N.D.

[a] Reaction conditions: cyclic diaryliodonium salt **1a** (0.2 mmol), nBu$_4$NBr (3.0 eq.), and Cs_2CO_3 (2.0 eq.) in solvent (2.0 mL) at 100 °C for 2 h. [b] Isolated yields. N.D. = Not detected.

Table S3: Optimization of X$^-$ sources



1a

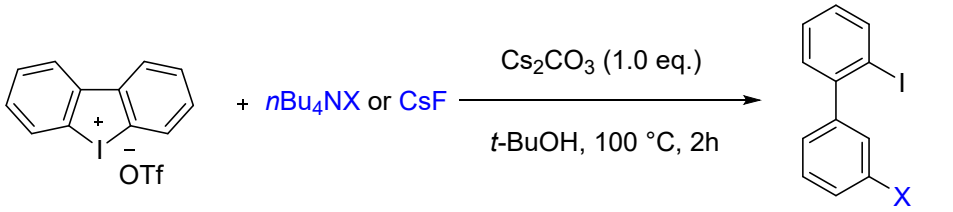
2a, X=Br **3a**, X=Cl
4a, X=F **5a**, X=I

Entry[a]	X$^-$ source	Yield (%)[b]
1	nBu$_4$NF	30
2	nBu$_4$NF·3H_2O	26
3	CsF	33
4	KCl	trace

5	NCS	N.D.
6	nBu$_4$NCl	83
7	NaBr	messy
8	KBr	messy
9	NBS	trace
10	nBu$_4$NBr	90
11	KI	trace
12	I_2	N.D.
13	nBu$_4$NI	93

[a] Reaction conditions: cyclic diaryliodonium salt **1a** (0.2 mmol), X^- source (3.0 eq.), and Cs_2CO_3 (2.0 eq.) in *t*-BuOH (2.0 mL) at 100 °C for 2 h. [b] Isolated yields. N.D. = Not detected.

Table S4: Optimization of amount of Cs_2CO_3



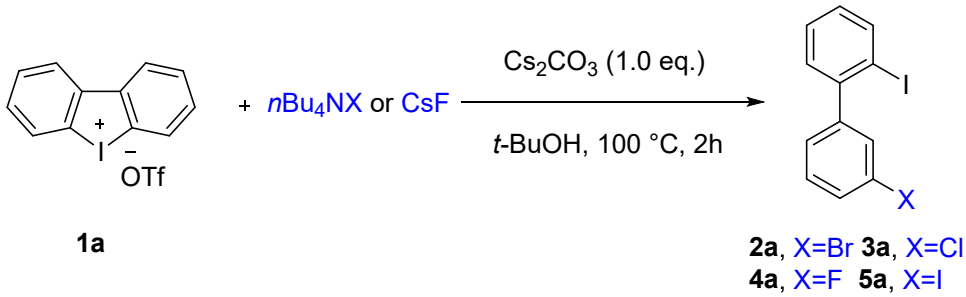
1a

2a, X=Br **3a**, X=Cl
4a, X=F **5a**, X=I

Entry[a]	**1a**/Cs_2CO_3	Yield (%)[b]
1	1:1	88
2[c]	1:1	82
3[d]	1:1	31
4[e]	1:1	89

[a] Reaction conditions: cyclic diaryliodonium salt **1a** (0.2 mmol), nBu$_4$NBr (3.0 eq.), and Cs_2CO_3 (1.0 eq.) in *t*-BuOH (2.0 mL) at 100 °C for 2 h. [b] Isolated yields. [c] nBu$_4$NCl (3.0 eq.) instead of nBu$_4$NBr (3.0 eq.). [d] CsF (3.0 eq.) instead of nBu$_4$NBr (3.0 eq.). [e] nBu$_4$NI (3.0 eq.) instead of nBu$_4$NBr (3.0 eq.).

Table S5: Optimization of amount of X^- source



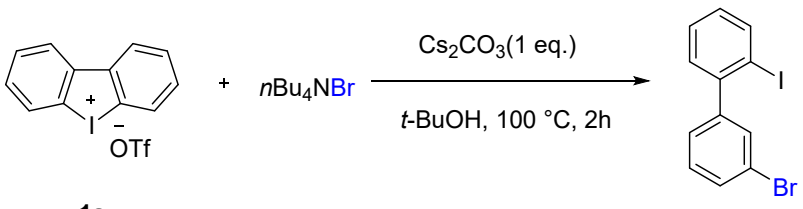
1a

2a, X=Br **3a**, X=Cl
4a, X=F **5a**, X=I

Entry[a]	**1a/X⁻ source**	Yield (%)[b]
1	1:2	85
2	1:1.5	67
3[c]	1:1.5	80
4[c]	1:1	60
5[d]	1:2	20
6[e]	1:2	81
7[e]	1:1.5	69

[a] Reaction conditions: cyclic diaryliodonium salt **1a** (0.2 mmol), nBu$_4$NBr, and Cs_2CO_3 (1.0 eq.) in *t*-BuOH (2.0 mL) at 100 °C for 2 h. [b] Isolated yields. [c] nBu$_4$NCl instead of nBu$_4$NBr. [d] CsF instead of nBu$_4$NBr. [e] nBu$_4$NI instead of nBu$_4$NBr.

Table S6: Optimization of temperature

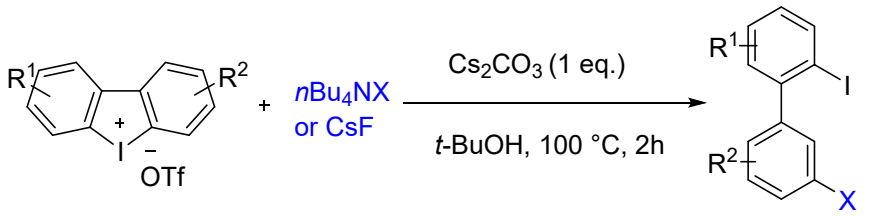


1a **2a**

Entry[a]	Temp. (°C)	Yield (%)[b]
1[c]	30	0
2[c]	60	14
3[c]	80	83
4	100	85
5	120	82

[a] Reaction conditions: cyclic diaryliodonium salt **1a** (0.2 mmol), nBu$_4$NBr (2 eq.) and Cs_2CO_3 (1.0 eq.) in *t*-BuOH (2.0 mL) at 100 °C for 2 h. [b] Isolated yields. [c] 6h.

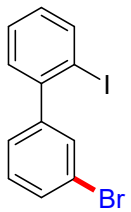
3. Synthesis and characterization of 2, 3, 4, 5.



1

2, X=Br **3**, X=Cl
4, X=F **5**, X=I

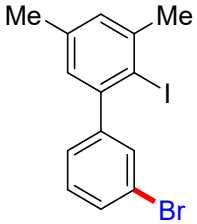
General procedure: To a 15 mL pressure vessel equipped with a stir bar were added cyclic diaryliodonium salts **1** (0.2 mmol), nBu$_4$NBr (2.0 eq.) or nBu$_4$NCl (1.5 eq.) or CsF (2.0 eq.) or nBu$_4$NI (2.0 eq.), Cs_2CO_3 (65.2 mg, 0.2 mmol) and *t*-BuOH (2 mL) as solvent. After the reaction mixture was stirred at 100 °C in oil bath for 2 h, it was allowed to cool to ambient temperature. The reaction was passed through a diatomite pad washing with DCM. The filtrate was concentrated in vacuum and the resulting residue purified by column chromatography on silica gel to give the targeted products.



2a

3'-bromo-2-iodo-1,1'-biphenyl (2a)

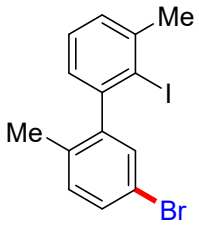
Following the general procedure, **2a** was purified by petroleum ether and obtained as a colourless oil (61.2 mg, 85%). (Regioisomers ratio determined by ^{1}H NMR *m:o* >99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.56 (dt, *J* = 6.7, 2.2 Hz, 1H), 7.53 (d, *J* = 1.4 Hz, 1H), 7.43 (td, *J* = 7.5, 1.2 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.09 (td, *J* = 7.7, 1.7 Hz, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.0, 145.1, 139.6, 132.3, 130.7, 130.0, 129.5, 129.3, 128.2, 128.1, 121.9, 98.2. HRMS m/z (ESI) calcd for $C_{12}H_9BrI$ [M + H] $^+$ 358.8927; found 358.8937. The spectra data matched with values reported in the literature[2].



2b

3'-bromo-2-iodo-3,5-dimethyl-1,1'-biphenyl (2b)

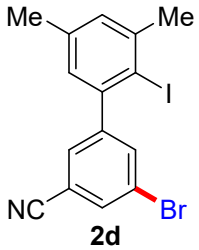
Following the general procedure, **2b** was purified by petroleum ether and obtained a slight yellow oil (63.4 mg, 82%). (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.54 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.49 (t, *J* = 1.5 Hz, 1H), 7.35 – 7.25 (m, 2H), 7.11 (d, *J* = 2.2 Hz, 1H), 6.93 (d, *J* = 2.2 Hz, 1H), 2.54 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.5, 146.0, 142.3, 137.6, 132.4, 130.4, 130.0, 129.4, 128.2, 128.1, 121.8, 101.5, 29.9, 20.7. HRMS m/z (ESI) calcd for $C_{14}H_{12}BrIK$ [M + K] $^{+}$ 424.8799; found 424.8799.



2c

5'-bromo-2-iodo-2',3-dimethyl-1,1'-biphenyl (2c)

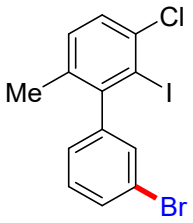
Following the general procedure, **2c** was purified by petroleum ether and obtained as a white solid (47.2 mg, 63%). **Mp** = 79.3 - 80.2 ℃; (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.25 (d, *J* = 2.1 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.98 (dd, *J* = 7.2, 1.5 Hz, 1H), 2.56 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.3, 146.2, 142.5, 134.8, 132.0, 131.5, 130.7, 128.6, 127.8, 126.7, 118.9, 106.5, 29.7, 19.5. HRMS m/z (ESI) calcd for $C_{14}H_{12}BrIK$ [M + K] $^{+}$ 424.8799; found 424.8810.



2d

5-bromo-2'-iodo-3',5'-dimethyl-[1,1'-biphenyl]-3-carbonitrile(2d)

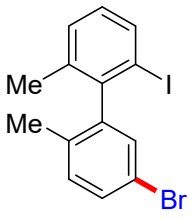
Following the general procedure, **2d** was purified by PE/EtOAc (100:1) and obtained as a white solid (46.2 mg, 56%). **MP** = 96.4 - 97.8 ℃; (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.81 (t, *J* = 1.6 Hz, 1H), 7.71 (t, *J* = 1.7 Hz, 1H), 7.57 (t, *J* = 1.5 Hz, 1H), 7.14 (d, *J* = 2.1 Hz, 1H), 6.87 (d, *J* = 2.1 Hz, 1H), 2.52 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 148.2, 143.7, 142.8, 138.0, 137.1, 133.4, 131.8, 130.8, 128.0, 122.3, 117.4, 113.6, 100.7, 29.7, 20.7. HRMS (EI) calcd for $C_{15}H_{11}BrIN$ $[M]^{+}$ 410.9120; found 410.9111.



2e

3'-bromo-3-chloro-2-iodo-6-methyl-1,1'-biphenyl (2e)

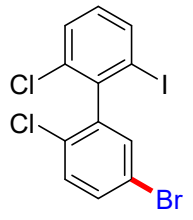
Following the general procedure, **2e** was purified by petroleum ether and obtained as a yellow oil (37.4 mg, 47%). (Regioisomers ratio determined by ^{1}H NMR *m:o* = 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.54 (m, 1H), 7.41 – 7.34 (m, 2H), 7.28 (d, *J* = 1.8 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.5, 146.9, 136.6, 135.3, 131.8, 130.9, 130.8, 130.3, 128.4, 127.6, 122.5, 104.7, 21.9. HRMS (EI) calcd for $C_{13}H_9BrICl$ $[M]^+$ 405.8621; found 405.8615.



2f

5-bromo-2'-iodo-2,6'-dimethyl-1,1'-biphenyl (2f)

Following the general procedure, **2f** was purified by petroleum ether and obtained as a white solid (40.7 mg, 52%). **MP** = 78.5 - 79.3 °C; (Regioisomers ratio determined by ^{1}H NMR *m:o* = 15:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.45 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.18 (d, *J* = 2.1 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 2.06 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.7, 144.3, 137.6, 136.6, 134.7, 131.8, 131.6, 130.9, 129.9, 129.3, 119.4, 100.5, 21.8, 19.1. HRMS m/z (ESI) calcd for $C_{14}H_{12}BrIK$ $[M + K]^+$ 424.8799; found 424.8805.

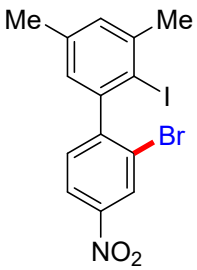


2g

5-bromo-2,2'-dichloro-6'-iodo-1,1'-biphenyl (2g)

Following the general procedure, **2g** was purified by petroleum ether and obtained as a white solid (69.3 mg, 81%). **MP** = 156.8 - 157.7 °C; (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.59 – 7.47 (m, 2H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.35 (d, *J* = 2.3 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz,

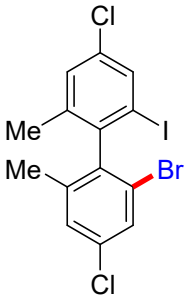
Chloroform-*d*) δ 142.9, 141.4, 137.6, 133.6, 133.5, 132.9, 132.5, 131.1, 130.9, 129.4, 120.3, 100.0. HRMS m/z (ESI) calcd for $C_{12}H_7BrCl_2I$ $[M + H]^+$ 426.8147; found 426.8141.



2h

2'-bromo-2-iodo-3,5-dimethyl-4'-nitro-1,1'-biphenyl (2h)

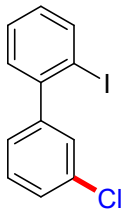
Following the general procedure (MTBE as solvent), **2h** was purified by PE/EtOAc (100:1) and obtained as a yellow solid (66.0 mg, 76%). **MP** = 138.2 - 139.6 °C; (Regioisomers ratio determined by ^{1}H NMR *o:m* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 2.3 Hz, 1H), 8.26 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 2.5 Hz, 1H), 6.82 (d, *J* = 2.2 Hz, 1H), 2.53 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.4, 147.6, 144.9, 142.4, 138.0, 131.7, 130.7, 127.8, 127.3, 124.3, 122.2, 100.6, 29.2, 20.8. HRMS (EI) calcd for $C_{14}H_{11}BrINO_2$ $[M]^+$ 430.9018; found 430.9008.



2i

2-bromo-4,4'-dichloro-2'-iodo-6,6'-dimethyl-1,1'-biphenyl (2i)

Following the general procedure, **2i** was purified by petroleum ether and obtained as a white solid (74.3 mg, 83%). **MP** = 113.6 - 114.5 °C; (Regioisomers ratio determined by ^{1}H NMR *o:m* = 4:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 1.6 Hz, 1H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.32 (d, *J* = 2.0 Hz, 1H), 7.30 (d, *J* = 2.1 Hz, 1H), 2.02 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.2, 141.4, 139.5, 138.9, 136.2, 134.3, 134.2, 130.2, 130.1, 129.5, 124.3, 100.2, 21.3, 20.6. HRMS (EI) calcd for $C_{14}H_{10}BrCl_2I$ $[M]^+$ 453.8388; found 453.8387. The spectra data matched with values reported in the literature[3].

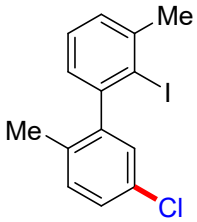


3a

3'-chloro-2-iodo-1,1'-biphenyl (3a)

Following the general procedure, **3a** was purified by petroleum ether and obtained as a colourless oil (50.0 mg, 80%). (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.47 – 7.38 (m, 3H), 7.37 (d, *J* = 1.6 Hz, 1H), 7.31 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.12 – 7.06 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.8, 145.2, 139.6, 133.8, 130.0, 129.4, 129.3, 129.2, 128.2, 127.8, 127.6, 98.2. HRMS m/z (ESI) calcd for $C_{12}H_8ClINa$ [M + Na] $^+$ 336.9251; found 336.9256. The spectra data matched with values reported in the literature[4].

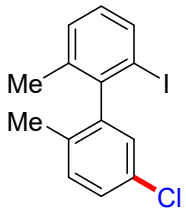
Gram scale procedure: A 100 mL pressure vessel equipped with a magnetic stir bar was charged with basic cyclic diaryliodonium salt (2.14 g, 5.0 mmol), *n*Bu_4NCl (2.09 g, 7.5 mmol), Cs_2CO_3 (1.65 g, 5.0 mmol) and *t*-BuOH (30 mL) as solvent. After the reaction mixture was stirred at 100 °C in oil bath for 4 h, it was allowed to cool to ambient temperature. The reaction was passed through a diatomite pad washing with DCM. The filtrate was concentrated in vacuum and the resulting residue purified by column chromatography on silica gel using petroleum ether as an eluent to give the targeted **3a** as colorless oil (1.23 g, 78%).



3b

5'-chloro-2-iodo-2',3-dimethyl-1,1'-biphenyl (3b)

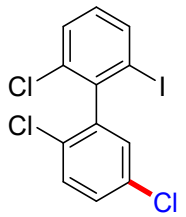
Following the general procedure, **3b** was purified by petroleum ether and obtained as a colourless oil (46.1 mg, 67%). (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.25 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.10 (d, *J* = 2.2 Hz, 1H), 6.99 (dd, *J* = 7.2, 1.9 Hz, 1H), 2.56 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.9, 146.3, 142.5, 134.3, 131.2, 131.0, 129.1, 128.6, 127.8, 127.8, 126.7, 106.5, 29.7, 19.4. HRMS m/z (ESI) calcd for $C_{14}H_{13}ClI$ [M + H] $^+$ 342.9745; found 342.9735



3c

5-chloro-2'-iodo-2,6'-dimethyl-1,1'-biphenyl (3c)

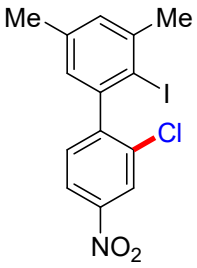
Following the general procedure, **3c** was purified by petroleum ether and obtained as a colourless oil (34.3 mg, 50%). (Regioisomers ratio determined by ^{1}H NMR *m:o* = 33:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.31 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 2.2 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 2.06 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.3, 144.4, 137.6, 136.6, 134.1, 131.5, 131.5, 129.9, 129.3, 128.7, 127.9, 100.4, 21.7, 19.0. HRMS m/z (ESI) calcd for $C_{14}H_{12}ClINa$ [M + Na] $^+$ 364.9564; found 364.9563.



3d

2,2',5-trichloro-6'-iodo-1,1'-biphenyl (3d)

Following the general procedure, **3d** was purified by petroleum ether and obtained as a white solid (37.2 mg, 63%). **MP** = 85.6 - 86.8 ℃; (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.51 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.38 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.6, 141.4, 137.6, 133.5, 132.7, 131.8, 130.8, 130.7, 129.9, 129.4, 100.0. HRMS m/z (ESI) calcd for $C_{12}H_7Cl_3I$ [M + H] $^+$ 382.8653; found 382.8662.

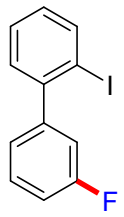


3e

2'-chloro-2-iodo-3,5-dimethyl-4'-nitro-1,1'-biphenyl (3e)

Following the general procedure (MTBE as solvent), **3e** was purified by PE/EtOAc (100:1) and obtained as a yellow solid （36.2 mg, 46%）. **MP** = 136.3 - 137.6 ℃; (Regioisomers ratio

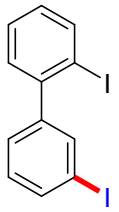
determined by ^{1}H NMR *o:m* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.38 (d, *J* = 2.3 Hz, 1H), 8.21 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 1.9 Hz, 1H), 6.83 (d, *J* = 2.1 Hz, 1H), 2.53 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.5, 147.7, 143.3, 142.4, 138.0, 134.7, 131.9, 130.8, 127.4, 124.8, 121.7, 100.7, 29.2, 20.8. HRMS m/z (ESI) calcd for $C_{14}H_{11}ClINO_2$ [M + H] $^+$ 387.9596; found 387.9591.



4a

3'-fluoro-2-iodo-1,1'-biphenyl (4a)

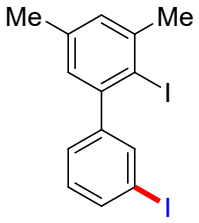
Following the general procedure, **4a** was purified by petroleum ether and obtained as a colourless oil (12.0 mg, 20%). (Regioisomers ratio determined by ^{1}H NMR *m:o* = 17:1); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.41 (td, *J* = 7.8, 6.5 Hz, 2H), 7.31 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.15 – 7.04 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3 (d, $J_{C\text{-}F}$ = 247.6 Hz), 146.1 (d, $J_{C\text{-}F}$ = 8.0 Hz), 145.4 (d, $J_{C\text{-}F}$ = 1.6 Hz), 139.6, 130.0, 129.5 (d, $J_{C\text{-}F}$ = 8.2 Hz), 129.2, 128.2, 125.1 (d, $J_{C\text{-}F}$ = 2.9 Hz), 116.5 (d, $J_{C\text{-}F}$ = 22 Hz), 114.6 (d, $J_{C\text{-}F}$ = 21.3 Hz), 98.1. The spectra data matched with values reported in the literature[5].



5a

2,3'-diiodo-1,1'-biphenyl (5a)

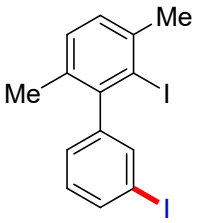
Following the general procedure, **5a** was purified by petroleum ether and obtained as a colourless oil (66.0 mg, 81%). (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.78 – 7.74 (m, 1H), 7.72 (d, *J* = 2.8 Hz, 1H), 7.42 (td, *J* = 7.5, 1.1 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.08 (td, *J* = 7.7, 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 145.0, 139.6, 138.1, 136.6, 130.0, 129.6, 129.3, 128.7, 128.3, 98.2, 93.7. HRMS m/z (ESI) calcd for $C_{12}H_8I_2Na$ [M + Na] $^+$ 428.8608; found 428.8618.



5b

2,3'-diiodo-3,5-dimethyl-1,1'-biphenyl (5b)

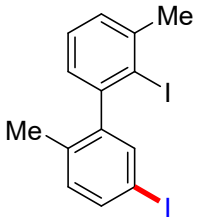
Following the general procedure, **5b** was purified by petroleum ether and obtained as a white solid (61.2 mg, 71%). **MP** = 69.4 - 69.8 ℃; (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.68 (s, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 2.2 Hz, 1H), 6.91 (d, *J* = 2.2 Hz, 1H), 2.53 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 145.9, 142.3, 138.2, 137.6, 136.3, 129.9, 129.5, 128.8, 128.1, 101.5, 93.6, 29.8, 20.7. HRMS m/z (ESI) calcd for $C_{14}H_{13}I_2$ $[M + H]^+$ 434.9101; found 434.9108.



5c

2,3'-diiodo-3,6-dimethyl-1,1'-biphenyl (5c)

Following the general procedure, **5c** was purified by petroleum ether and obtained as a white solid (53.1 mg, 61%). **MP** = 69.6 - 70.3 ℃; (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.50 (t, *J* = 1.7 Hz, 1H), 7.26 – 7.07 (m, 4H), 2.51 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 145.4, 139.7, 138.0, 136.4, 134.3, 130.2, 129.5, 128.9, 128.5, 107.5, 94.1, 29.7, 22.0. HRMS (EI) calcd for $C_{14}H_{12}I_2$ $[M]^+$ 433.9028; found 433.9032.

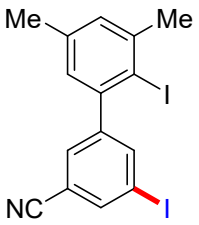


5d

2,5'-diiodo-2',3-dimethyl-1,1'-biphenyl (5d)

Following the general procedure, **5d** was purified by petroleum ether and obtained as a white solid (64.3 mg, 75%). **MP** = 70.2 - 71.3 ℃ ; (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 8.1, 1.9 Hz, 1H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.25 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.98 (dd, *J* =

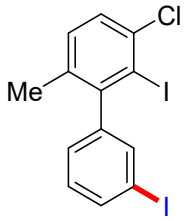
7.2, 1.6 Hz, 1H), 2.56 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 146.1, 142.4, 137.8, 136.7, 135.5, 131.8, 128.6, 127.8, 126.7, 106.5, 90.1, 29.7, 19.6. HRMS m/z (ESI) calcd for $C_{14}H_{13}I_2$ $[M + H]^+$ 434.9101; found 434.9094.



5e

2',5-diiodo-3',5'-dimethyl-[1,1'-biphenyl]-3-carbonitrile (5e)

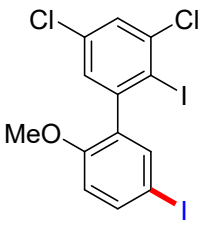
Following the general procedure, **5e** was purified by PE/EtOAc (100:1) and obtained as a white solid (57.3 mg, 57%). **MP** = 136.4 - 137.6 °C; (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (t, *J* = 1.6 Hz, 1H), 7.91 (t, *J* = 1.6 Hz, 1H), 7.60 (t, *J* = 1.5 Hz, 1H), 7.14 (d, *J* = 2.2 Hz, 1H), 6.87 (d, *J* = 2.2 Hz, 1H), 2.52 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.0, 143.6, 142.8, 142.8, 139.1, 138.0, 132.4, 130.7, 127.9, 117.2, 113.6, 100.8, 93.2, 29.7, 20.7.HRMS (EI) calcd for $C_{15}H_{11}I_2N$ $[M]^+$ 458.8981; found 458.8963.



5f

3-chloro-2,3'-diiodo-6-methyl-1,1'-biphenyl (5f)

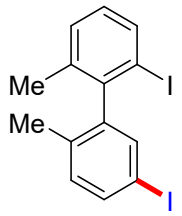
Following the general procedure, **5f** was purified by petroleum ether and obtained as a yellow solid (46.2 mg, 51%). **MP** = 77.3 - 78.6 °C; (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 1H), 7.48 (t, *J* = 1.7 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.17 (m, 2H), 7.11 – 7.06 (m, 1H), 2.13 – 2.02 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 147.0, 137.6, 136.8, 136.6, 135.3, 130.8, 130.4, 128.4, 128.1, 104.8, 94.2, 21.9. HRMS (EI) calcd for $C_{13}H_9ClI_2$ $[M]^+$ 453.8482; found 453.8480.



5g

3,5-dichloro-2,5'-diiodo-2'-methoxy-1,1'-biphenyl (5g)

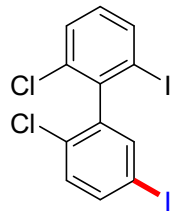
Following the general procedure, **5g** was purified by petroleum ether and obtained as a white solid (35.1 mg, 36%). **MP** = 130.3 - 131.4 °C; (Regioisomers ratio determined by ^{1}H NMR *m:o* = 30:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.47 (d, *J* = 2.4 Hz, 1H), 7.38 (d, *J* = 2.3 Hz, 1H), 7.11 (d, *J* = 2.4 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 146.6, 140.0, 138.7, 138.4, 135.1, 134.5, 128.2, 127.9, 113.4, 102.6, 82.2, 55.7. HRMS (EI) calcd for $C_{13}H_8Cl_2I_2O$ $[M]^+$ 503.8042; found 503.8033.



5h

2',5-diiodo-2,6'-dimethyl-1,1'-biphenyl (5h)

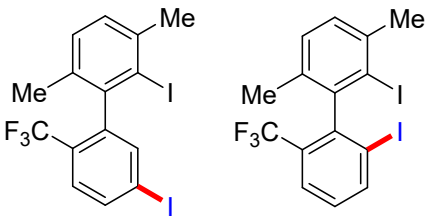
Following the general procedure, **5h** was purified by petroleum ether and obtained as a white solid (45.0 mg, 58%). **MP** = 68.3 – 69.0 °C; (Regioisomers ratio determined by ^{1}H NMR *m:o* = 12:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.77 (m, 1H), 7.65 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.37 (d, *J* = 1.9 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 2.06 (s, 3H), 1.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.0, 144.2, 137.6, 137.4, 136.8, 136.6, 135.3, 132.1, 129.8, 129.3, 100.5, 90.6, 21.8, 19.2. HRMS (EI) calcd for $C_{14}H_{12}I_2$ $[M]^+$ 433.9028; found 433.9032.



5i

2,2'-dichloro-5,6'-diiodo-1,1'-biphenyl (5i)

Following the general procedure, **5i** was purified by petroleum ether and obtained as a white solid (66.0 mg, 70%). **MP** = 148.4 - 149.5 °C; (Regioisomers ratio determined by ^{1}H NMR *m:o* > 99:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.71 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.52 (d, *J* = 2.1 Hz, 1H), 7.50 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 141.3, 139.3, 138.8, 137.5, 133.5, 133.5, 131.3, 130.8, 129.4, 100.1, 91.1. HRMS (EI) calcd for $C_{12}H_6Cl_2I_2$ $[M]^+$ 473.7936; found 473.7931.



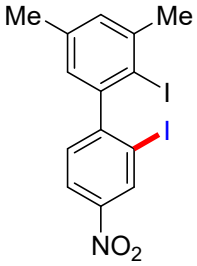
5j **5j'**

2,5'-diiodo-3,6-dimethyl-2'-(trifluoromethyl)-1,1'-biphenyl(5j)

Following the general procedure, **5j** was purified by PE/EtOAc (100:1) and obtained as a white solid (44 mg, 44%). **MP** = 143.6 - 144.8 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.85 (m, 1H), 7.52 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 2.47 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 142.5, 140.3, 139.5, 137.2, 134.9, 129.4, 128.0 (q, $J_{C\text{-}F}$ = 5.5 Hz), 127.8, 127.7, 123.6 (q, $J_{C\text{-}F}$ = 275.4 Hz), 107.2, 98.7, 29.5, 21.6. HRMS (EI) calcd for $C_{15}H_{11}F_3I_2$ $[M]^+$ 501.8902; found 501.8896.

2,2'-diiodo-3,6-dimethyl-6'-(trifluoromethyl)-1,1'-biphenyl (5j')

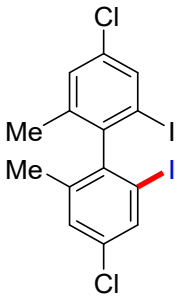
Following the general procedure, **5j'** was purified by PE/EtOAc (100:1) and obtained as a white solid (35.2 mg, 35%). **MP** = 143.3 - 144.5 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 2.52 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 145.5, 143.1, 139.7, 135.2, 129.6, 129.5, 129.2, 126.7 (q, $J_{C\text{-}F}$ = 5.5 Hz), 122.7 (q, $J_{C\text{-}F}$ = 275.4 Hz), 107.8, 104.4, 29.4, 21.3. HRMS (EI) calcd for $C_{15}H_{11}F_3I_2$ $[M]^+$ 501.8902; found 501.8904.



5k

2,2'-diiodo-3,5-dimethyl-4'-nitro-1,1'-biphenyl (5k)

Following the general procedure, **5k** was purified by PE/EtOAc (100:1) and obtained as a white solid (91.5 mg, 95%). **MP** = 113.4 - 114.5 °C; (Regioisomers ratio determined by ^{1}H NMR *o:m* = 10:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.80 (d, *J* = 2.2 Hz, 1H), 8.29 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.20 – 7.14 (m, 1H), 6.78 (d, *J* = 2.1 Hz, 1H), 2.53 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 147.8, 147.1, 142.4, 138.1, 133.8, 130.7, 130.4, 127.2, 123.1, 100.6, 99.7, 29.2, 20.8. HRMS (EI) calcd for $C_{14}H_{11}I_2NO_2$ $[M]^+$ 478.8879; found 478.8874.



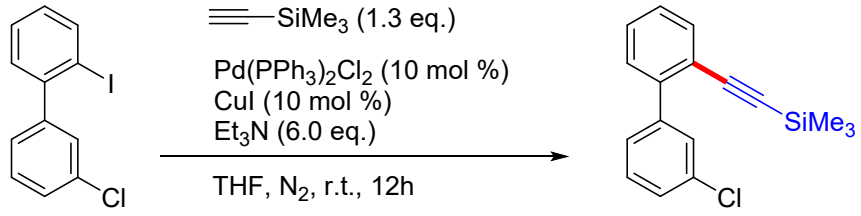
5l

4,4'-dichloro-2,2'-diiodo-6,6'-dimethyl-1,1'-biphenyl (5l)

Following the general procedure, **5l** was purified by petroleum ether and obtained as a white solid (90.6 mg, 90%). **MP** = 132.3 - 133.4 ℃; (Regioisomers ratio determined by ^{1}H NMR *o:m* = 6:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 2.1 Hz, 2H), 7.32 (d, *J* = 2.1 Hz, 2H), 2.01 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 138.7, 136.3, 134.3, 130.3, 100.5, 21.4. HRMS (EI) calcd for $C_{14}H_{10}Cl_2I_2$ $[M]^+$ 501.8249; found 501.8239. The spectra data matched with values reported in the literature[3].

4. Diversity oriented transformations of product 2a

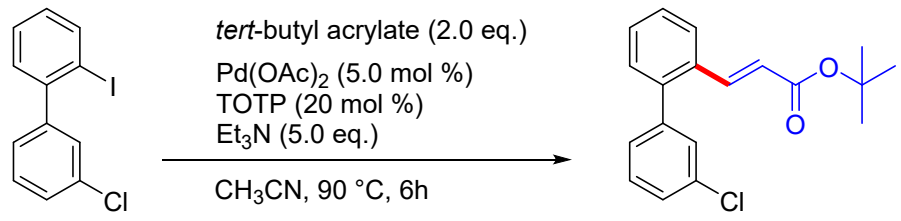
(1) Synthesis of ((3'-chloro-[1,1'-biphenyl]-2-yl) ethynyl) trimethylsilane 6



2a **6**

Following the modified procedure described by Ding et al[6]. Compound **2a** (62.8 mg, 0.2 mmol), 2-TMS-acetylene (35.8 μL, 0.26 mmol), $Pd(PPh_3)_2Cl_2$ (13.4 mg, 10 mol %), and Et_3N (0.3 mL, 1.2 mmol) were dissolved in THF (2 mL). The reaction mixture was degassed and stirred under a N_2 atmosphere for 20 min before the addition of CuI (2.1 mg, 10 mol %). The reaction was then stirred at rt for 12 h before it was diluted with diethyl ether (10 mL). The content was poured into a separate funnel and washed with 0.1 M HCl (10 mL), H_2O (10 mL), and brine (10 mL) respectively. The organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 100:1) on silica gel to provide the product **6** as a slight yellow oil (45.0 mg, 80%).^{1}H NMR (400 MHz, Chloroform-d) δ 7.69 (q, *J* = 1.4 Hz, 1H), 7.61 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.42 – 7.35 (m, 4H), 7.35 – 7.30 (m, 1H), 0.19 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 142.0, 133.5, 133.4, 129.6, 129.2, 129.1, 128.9, 127.5, 127.5 (2C), 121.4, 104.1, 98.3, -0.3 (3C). HRMS m/z (ESI) calcd for $C_{17}H_{18}ClSi$ $[M + H]^+$ 285.0861; found 285.0867.

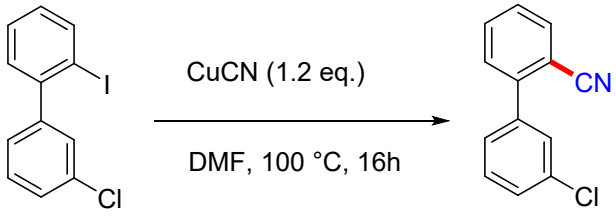
(2) Synthesis of tert-butyl-3-(3'-chloro-[1,1'-biphenyl]-2-yl) acrylate 7



2a **7**

Following the modified procedure described by Ding et al[6]. A dry Schlenk tube equipped with a stir bar was charged with **2a** (62.8 mg, 0.2 mmol), *tert*-butyl acrylate (58 µL 0.4 mmol), Et_3N (0.14 mL, 1.0 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol), tri-*o*-tolylphopine (TOTP, 12.2 mg, 0.04 mmol) and CH_3CN (1.5 mL). The reaction mixture was stirred at 90 °C in oil bath for 6 h. After completion, the reaction mixture was filtered through celite pad and washed with dichloromethane, evaporated solvent under reduced pressure. The residue was purified by column chromatography (PE/EtOAc =80:1) on silica gel to provide the product **7** as yellow oil (46 mg, 73%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.61 (d, *J* = 15.9 Hz, 1H), 7.48 – 7.33 (m, 6H), 7.24 – 7.17 (m, 1H), 6.36 (d, *J* = 15.9 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 141.8, 141.8, 141.3, 134.2, 132.7, 130.3, 129.7, 129.7, 129.4, 128.1 (2C), 127.6, 126.7, 121.5, 80.5, 28.2(3C). HRMS m/z (ESI) calcd for $C_{19}H_{20}ClO_2$ $[M + H]^+$ 315.1146; found 315.1139. The spectra data matched with values reported in the literature[7].

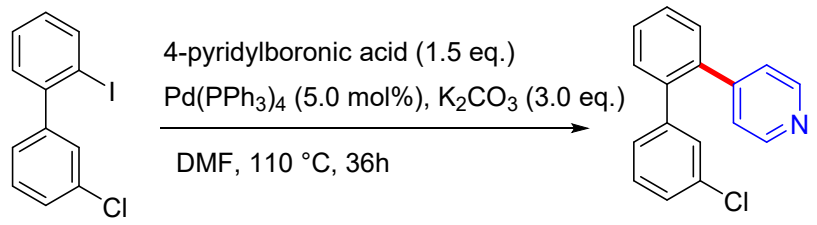
(3) Synthesis of 3'-chloro-[1,1'-biphenyl]-2-carbonitrile 8



2a **8**

Following the modified procedure described by Berliner et al[8]. Compound **2a** (62.8 mg, 0.2 mmol) and CuCN (21.5 mg, 0.24mmol) were dissolved in anhydrous *N, N*-dimethylformamide (0.3 mL). The reaction mixture was refluxed at 100 °C for 16 h before it was cooled to rt and diluted with water (10 mL). The mixture was extracted with EtOAc (3 × 10 mL), and the combined organic phase was washed with H_2O (3 × 10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (PE/EtOAc = 50:1) on silica gel to provide the product **8** as white solid (41.7 mg, 98% yield). **MP** = 89.3 - 90.2 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.69 (td, *J* = 7.7, 1.4 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.50 (m, 2H), 7.46 (td, *J* = 4.9, 4.1, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 139.8, 134.7, 133.8, 133.0, 130.0 (2C), 128.9 (2C), 128.2, 127.1, 118.3, 111.3. HRMS m/z (ESI) calcd for $C_{13}H_8ClNNa$ $[M + Na]^+$ 236.0237; found 236.0230. The spectra data matched with values reported in the literature[9].

(4) synthesis of 4-(3'-chloro-[1,1'-biphenyl]-2-yl) pyridine 9

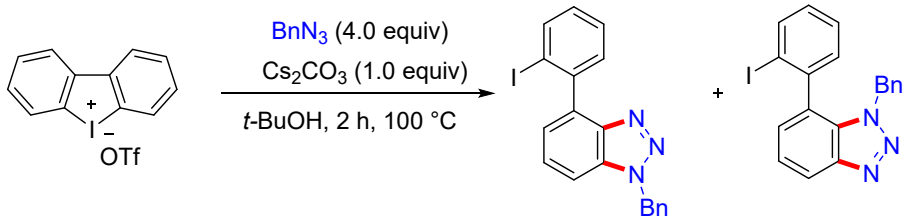


2a **9**

Following the modified procedure described by Zhu et al[10]. An oven-dried Schlenk tube equipped with a teflon cap and a magnetic stir bar was charged with compound **2a** (62.8 mg, 0.2 mmol), 4-pyridylboronic acid (36.9 mg, 0.3 mmol), K_2CO_3 (82.9 mg, 0.6 mmol) and $Pd(PPh_3)_4$ (11.6 mg, 5 mol%). The contents were placed under nitrogen with three vacuum/refill cycles, and then DMF (2.0 mL) was added. The mixture was allowed to be stirred at 110 °C for 36 h. After cooling to room temperature, the mixture was quenched with water and extracted with ethyl acetate. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography (PE/EtOAc = 50:1) on silica gel to provide the product **9** as yellow solid (46.2 mg, 87%). **MP** = 70.2 - 71.3 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.55 – 8.46 (m, 2H), 7.55 – 7.48 (m, 2H), 7.45 (m, 2H), 7.25 (m, 2H), 7.15 (t, J = 7.7 Hz, 1H), 7.11 – 7.07 (m, 2H), 6.94 (dt, J = 7.7, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4 (2C), 149.1, 142.4, 139.2, 137.7, 134.1, 130.7, 130.3, 129.6, 129.4, 128.9, 128.3, 128.2, 127.2, 124.7 (2C). HRMS m/z (ESI) calcd for $C_{17}H_{13}ClN$ $[M + H]^+$ 266.0731; found 266.0726.

5. Control experiments

(1) Benzyne trapping experiment



1a **10**, 25% **11**, 16%

To a 15 mL pressure vessel equipped with a stir bar were added **1a** (171.2 mg, 0.4 mmol), BnN_3 (213 mg, 1.6 mmol), Cs_2CO_3 (132 mg, 0.4 mmol) and *t*-BuOH (3 mL) as solvent. After the reaction mixture was stirred at 100 °C in oil bath for 2 h, it was allowed to cool to ambient temperature. The reaction was passed through a diatomite pad washing with DCM. The filtrate was concentrated in vacuum and the resulting residue purified by column chromatography on silica gel using PE/EtOAc = 50:1 as an eluent to give the targeted **10** (41.3 mg, 25%) and **11** (26.4 mg, 16%) both as yellow oil.

1-benzyl-4-(2-iodophenyl)-1H-benzo[d][1,2,3]triazole 10

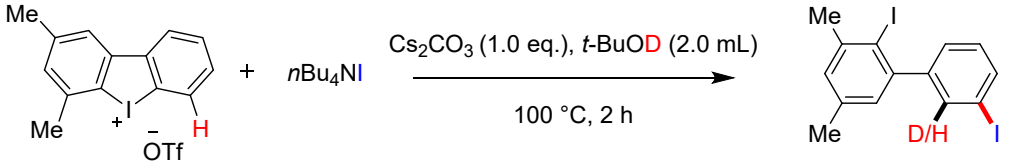
^{1}H NMR (400 MHz, Chloroform-d) δ 8.05 (dd, J = 8.0, 1.2 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.43 – 7.32 (m, 7H), 7.15 (m, 1H), 5.91 (s, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 144.6, 141.9, 139.7,

136.0, 134.8, 133.1, 131.2, 129.7, 129.1, 128.5, 128.1, 127.7, 127.0, 125.1, 109.5, 98.9, 52.5. HRMS (EI) calcd for $C_{19}H_{14}IN_3$ $[M]^+$ 411.0232; found 411.0223.

1-benzyl-7-(2-iodophenyl)-1H-benzo[d][1,2,3]triazole 11

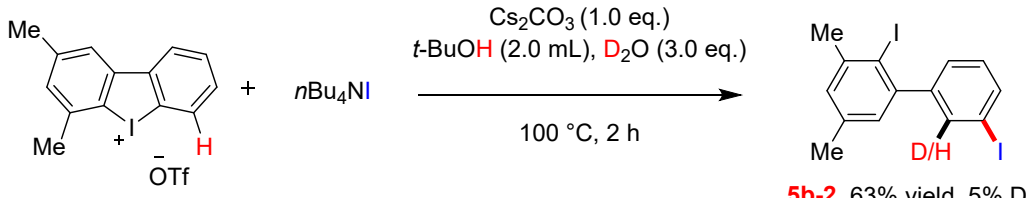
^{1}H NMR (400 MHz, Chloroform-d) δ 8.17 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.96 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.43 (dd, *J* = 8.4, 7.1 Hz, 1H), 7.25 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.20 (dd, *J* = 7.1, 1.0 Hz, 1H), 7.16 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.10 (dd, *J* = 8.2, 6.7 Hz, 2H), 6.97 (dd, *J* = 7.5, 1.8 Hz, 1H), 6.56 – 6.43 (m, 2H), 5.72 (d, *J* = 15.9 Hz, 1H), 5.33 (d, *J* = 15.9 Hz, 1H); ^{13}C NMR (101 MHz, CDCl3) δ 142.0, 138.8, 135.7, 130.9, 129.9, 129.2, 129.0, 128.7, 128.4 (2C), 128.3, 128.0, 127.8, 126.5 (2C), 123.9, 119.9, 100.9, 53.1. HRMS (EI) calcd for $C_{19}H_{14}IN_3$ $[M]^+$ 411.0232; found 411.0215.

(2) Deuterium labeling reaction



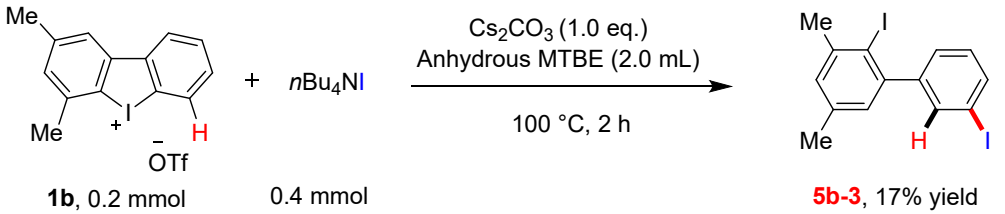
1b, 0.2 mmol 0.4 mmol **5b-1**, 74% yield, 93% D

To a 15 mL pressure vessel equipped with a stir bar were added cyclic diaryliodonium salts **1b** (91.2 mg, 0.2 mmol), nBu$_4$NI (147.8 mg, 0.4 mmol, 2.0 eq.), Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 eq.) and *t*-BuOD (2 mL) as solvent. After the reaction mixture was stirred at 100 °C in oil bath for 2 h, it was allowed to cool to ambient temperature. The reaction was passed through a diatomite pad washing with DCM. The filtrate was concentrated in vacuum and the resulting residue purified by column chromatography on silica gel to give the targeted product **5b-1** (64.5 mg, 74%, 93% D) as a white solid.



1b, 0.2 mmol 0.4 mmol **5b-2,** 63% yield, 5% D

To a 15 mL pressure vessel equipped with a stir bar were added cyclic diaryliodonium salts **1b** (91.2 mg, 0.2 mmol), nBu$_4$NI (147.8 mg, 0.4 mmol, 2.0 eq.), Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 eq.), then added *t*-BuOH (2 mL) and D_2O (11 μL, 3.0 eq.) as solvent. After the reaction mixture was stirred at 100 °C in oil bath for 2 h, it was allowed to cool to ambient temperature. The reaction was passed through a diatomite pad washing with DCM. The filtrate was concentrated in vacuum and the resulting residue purified by column chromatography on silica gel to give the targeted product **5b-2** (54.9 mg, 63%, 5% D) as a white solid.



To a 15 mL flame dry pressure vessel equipped with a stir bar were added cyclic diaryliodonium salts **1b** (91.2 mg, 0.2 mmol), nBu$_4$NI (147.8 mg, 0.4 mmol, 2.0 eq.), Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 eq.) and anhydrous MTBE (2 mL) as solvent. After the reaction mixture was stirred at 100 °C in oil bath for 2 h, it was allowed to cool to ambient temperature. The reaction was passed through a diatomite pad washing with DCM. The filtrate was concentrated in vacuum and the resulting residue purified by column chromatography on silica gel to give the targeted product **5b-3** (14.8 mg, 17%) as a white solid.

6. References

[1] (a) Z. Liu, D. Zhu, B. Luo, N. Zhang, Q. Liu, Y. Hu, R. Pi, P. Huang and S. Wen, Mild Cu(I)-Catalyzed Cascade Reaction of Cyclic Diaryliodoniums, Sodium Azide, and Alkynes: Efficient Synthesis of Triazolophenanthridines, *Org Lett*, 2014, **16**, 5600-5603. (b) F. Heinen, E. Engelage, A. Dreger, R. Weiss and S. M. J. A. C. I. E. Huber, Iodine (III) derivatives as halogen bonding organocatalysts, *Angew. Chem. Int. Ed.*, 2018, 57, 3830–3833. (c) K. Zhao, L. Duan, S. Xu, J. Jiang, Y. Fu and Z. Gu, Enhanced Reactivity by Torsional Strain of Cyclic Diaryliodonium in Cu-Catalyzed Enantioselective Ring-Opening Reaction, *Chem-Us*, 2018, **4**, 599-612. (d) J. Ke, B. Zu, Y. Guo, Y. Li and C. J. O. L. He, Hexafluoroisopropanol-enabled copper-catalyzed asymmetric halogenation of cyclic diaryliodoniums for the synthesis of axially chiral 2, 2′-dihalobiaryls, *Org. Lett.,* 2021, 23, 329−333.

[2] M. Gioanola, R. Leardini, D. Nanni, P. Pareschi and G. Zanardi, Intramolecular addition of aryl radicals to carbon-nitrogen double bonds, *Tetrahedron*, 1995, **51**, 2039-2054.

[3] K. Zhu, Z. Song, Y. Wang and F. Zhang, Synthesis of 2,2′-Dihalobiaryls via Cu-Catalyzed Halogenation of Cyclic Diaryliodonium Salts, *Org Lett*, 2020, **22**, 9356-9359.

[4] S. Pan, H. Jiang, Y. Zhang, D. Chen and Y. Zhang, Synthesis of Triphenylenes Starting from 2-Iodobiphenyls and Iodobenzenes via Palladium-Catalyzed Dual C–H Activation and Double C–C Bond Formation, *Org Lett*, 2016, **18**, 5192-5195.

[5] G. Shi, D. Chen, H. Jiang, Y. Zhang and Y. Zhang, Synthesis of Fluorenes Starting from 2-Iodobiphenyls and CH2Br2 through Palladium-Catalyzed Dual C–C Bond Formation, *Org Lett*, 2016, **18**, 2958-2961.

[6] M. Ding, W. Hua, M. Liu and F. Zhang, Pd-Catalyzed C(sp3)–H Biarylation via Transient Directing Group Strategy, *Org Lett*, 2020, **22**, 7419-7423.

[7] J. L. Henderson, A. S. Edwards and M. F. Greaney, Biaryl Synthesis via Palladium-Catalyzed Aryne Multicomponent Coupling, *Org Lett*, 2007, **9**, 5589-5592.

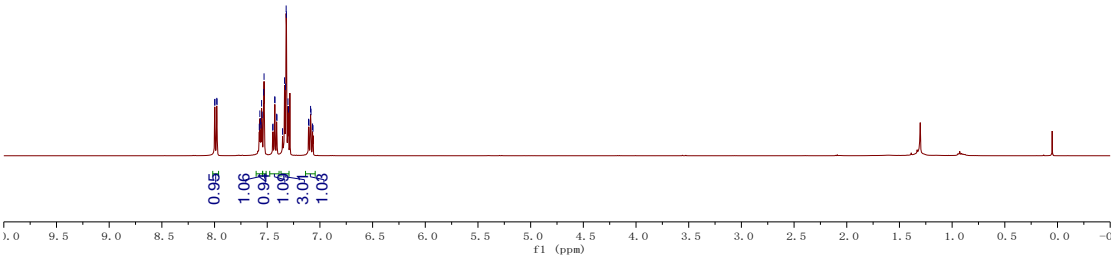
[8] M. A. Berliner, S. P. A. Dubant, T. Makowski, K. Ng, B. Sitter, C. Wager and Y. Zhang, Use of an Iridium-Catalyzed Redox-Neutral Alcohol-Amine Coupling on Kilogram Scale for the Synthesis of a GlyT1 Inhibitor, *Organic Process Research & Development*, 2011, **15**, 1052-1062.

[9] S. Sarkar, M. Jana and T. Narender, Metal-Free Directed ortho C–H Iodination: Synthesis of 2′-Iodobiaryl-2-carbonitriles, *Eur J Org Chem*, 2013, **2013**, 6491-6495.

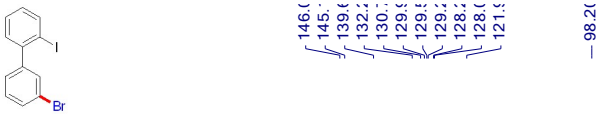
[10] K. Zhu, K. Xu, Q. Fang, Y. Wang, B. Tang and F. J. A. C. Zhang, Enantioselective synthesis of axially chiral biaryls via Cu-catalyzed acyloxylation of cyclic diaryliodonium salts, *ACS Catalysis*, **2019**, 9, 4951-4957.

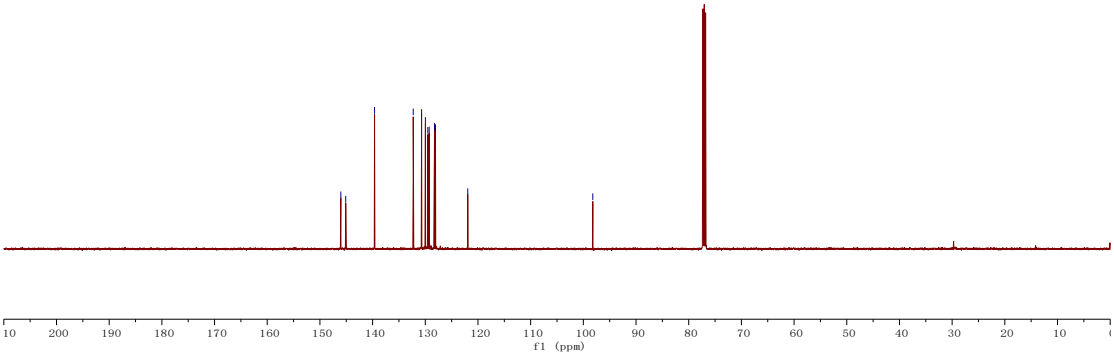
7. Copies of NMR spectra

^{1}H NMR of **2a** (400 MHz, $CDCl_3$)

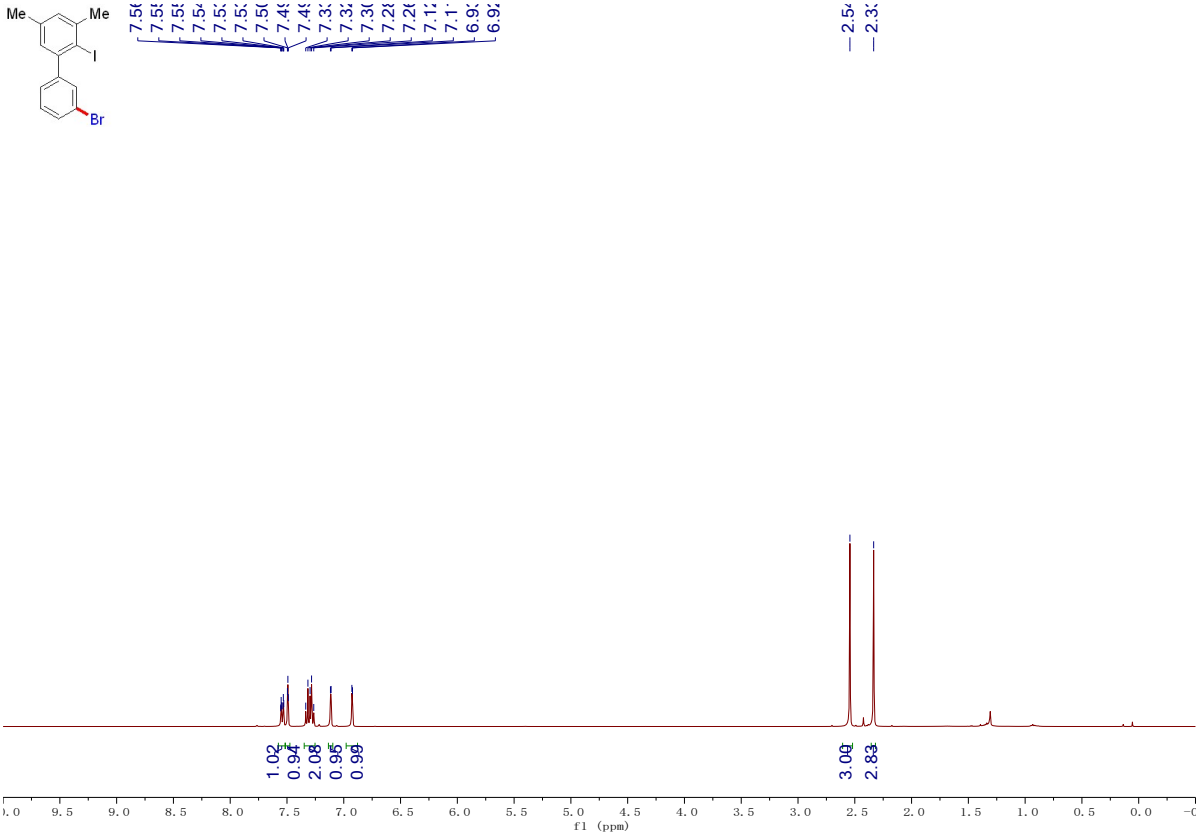


^{13}C NMR of **2a** (126 MHz, $CDCl_3$)

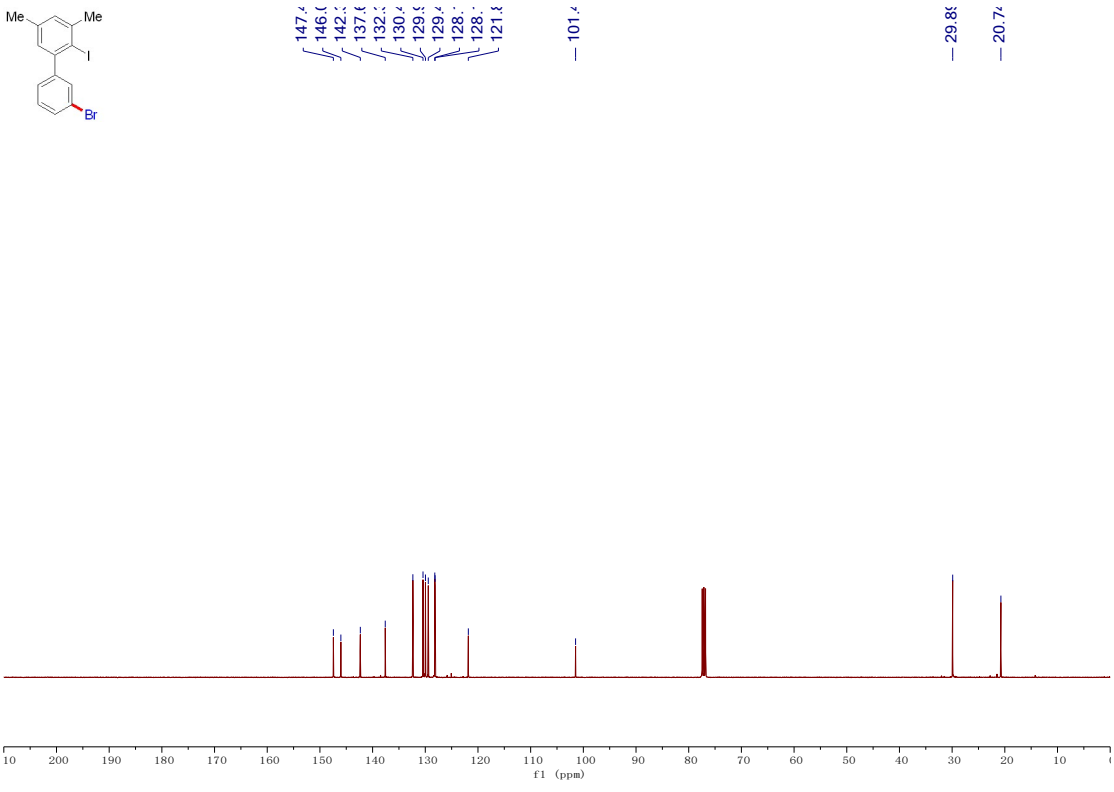




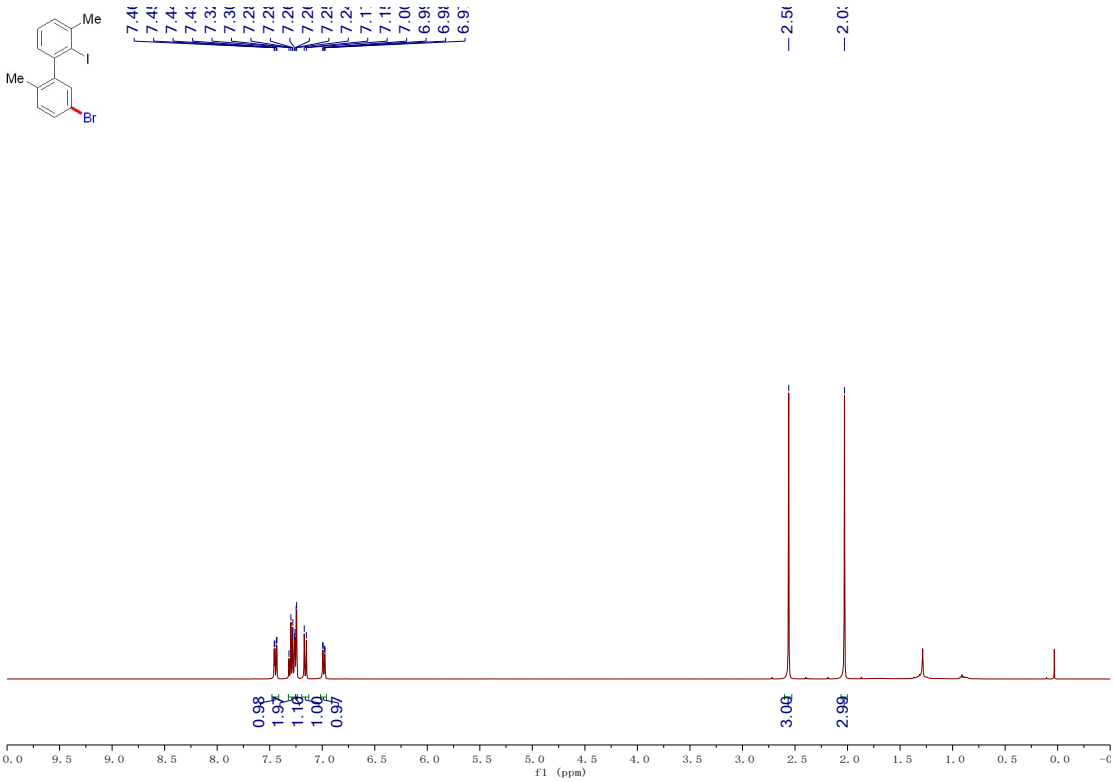
^{1}H NMR of **2b** (400 MHz, $CDCl_3$)



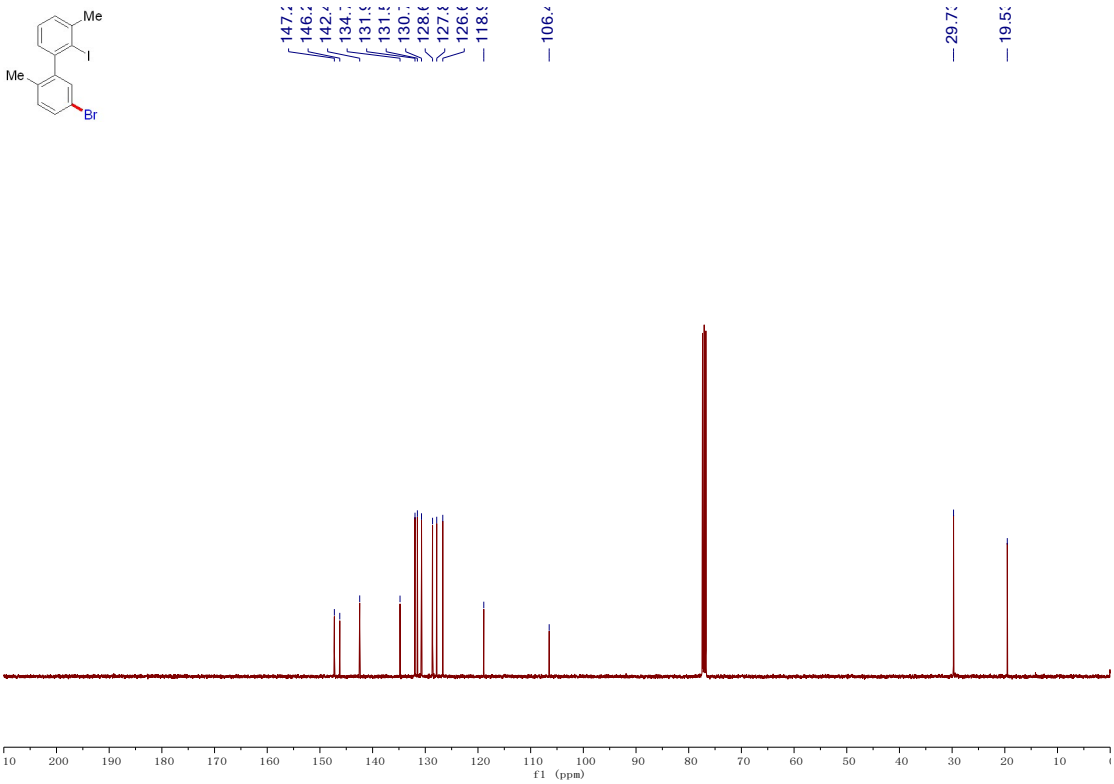
^{13}C NMR of **2b** (101 MHz, $CDCl_3$)



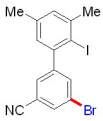
^{1}H NMR of **2c** (400 MHz, $CDCl_3$)

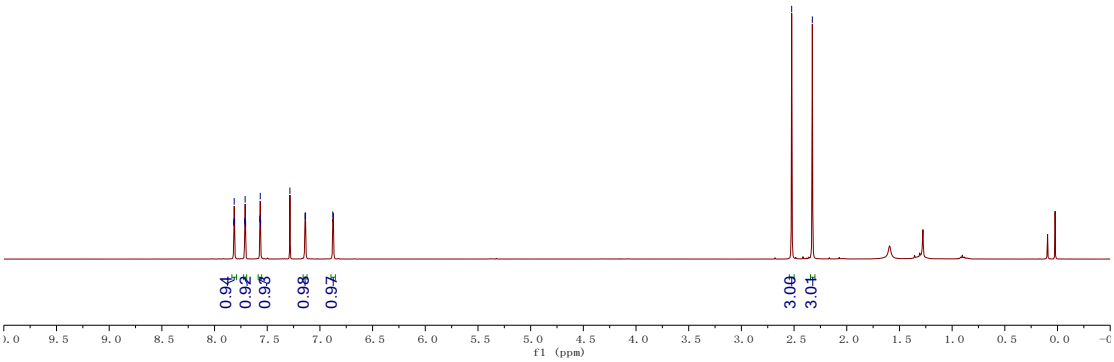


^{13}C NMR of **2c** (101 MHz, $CDCl_3$)

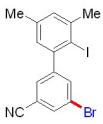


^{1}H NMR of **2d** (400 MHz, $CDCl_3$)

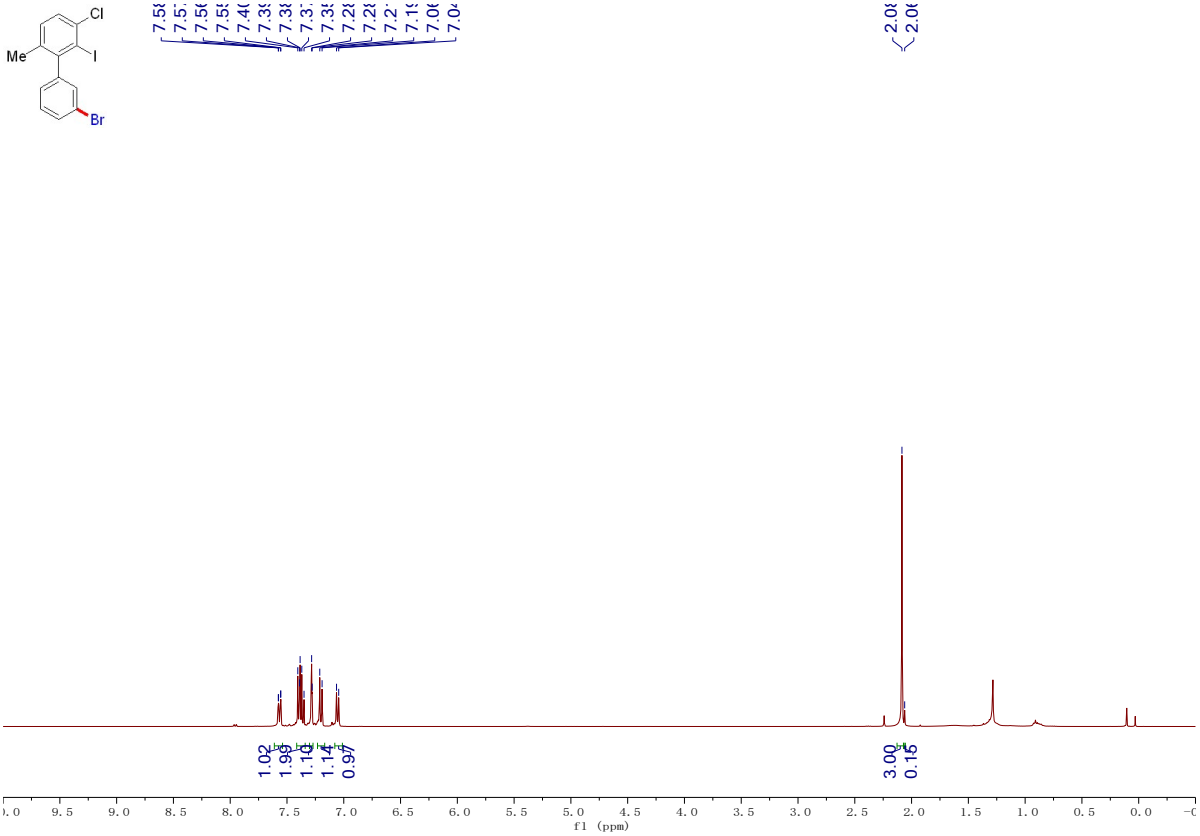




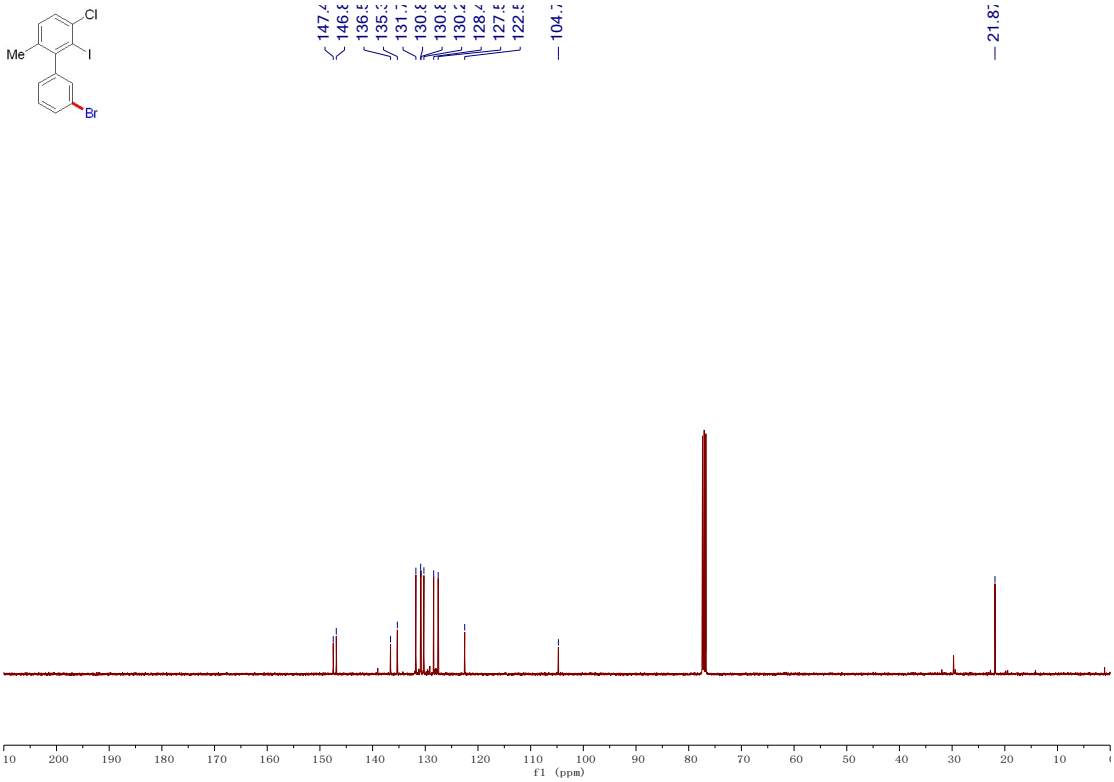
^{13}C NMR of **2d** (101 MHz, $CDCl_3$)



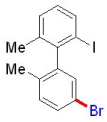
^{1}H NMR of **2e** (400 MHz, $CDCl_3$)

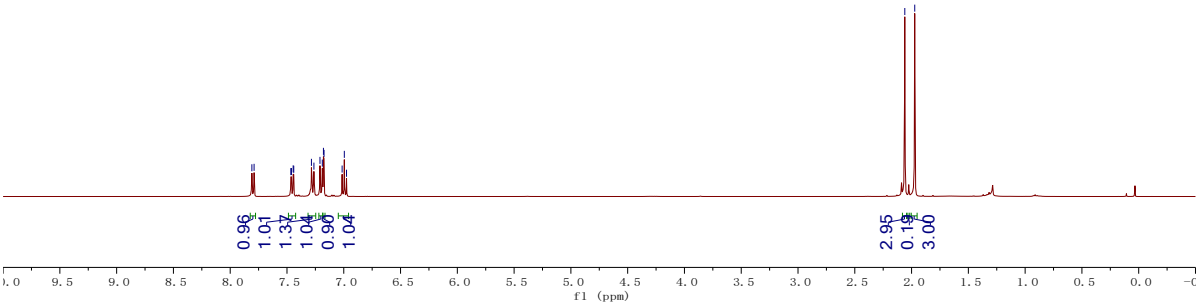


^{13}C NMR of **2e** (101 MHz, $CDCl_3$)

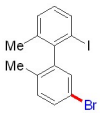


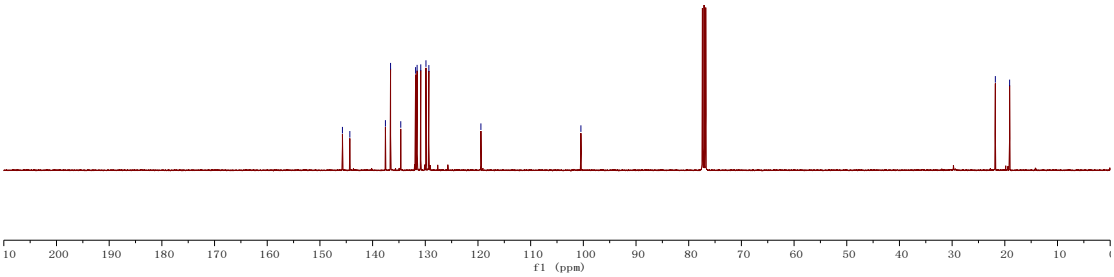
^{1}H NMR of **2f** (400 MHz, $CDCl_3$)



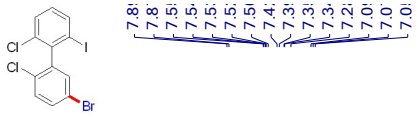


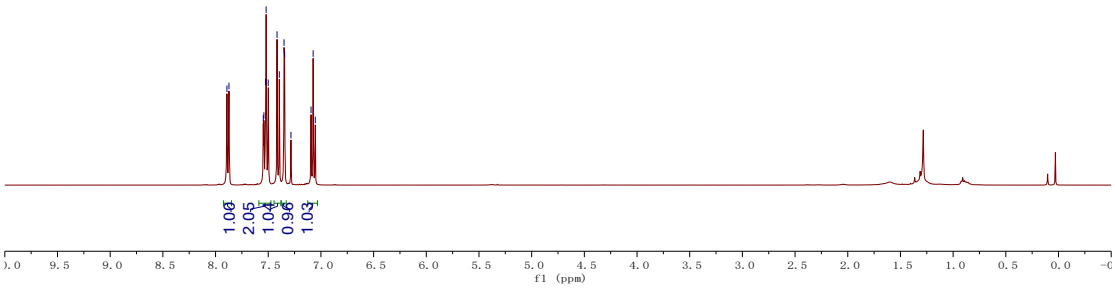
^{13}C NMR of **2f** (101 MHz, $CDCl_3$)



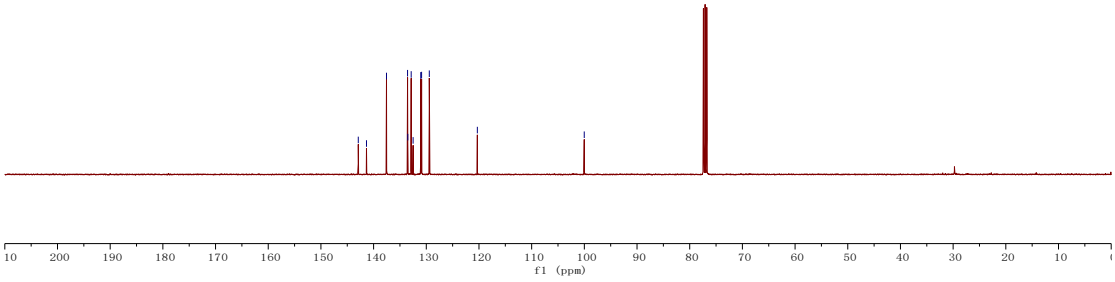


^{1}H NMR of **2g** (400 MHz, $CDCl_3$)

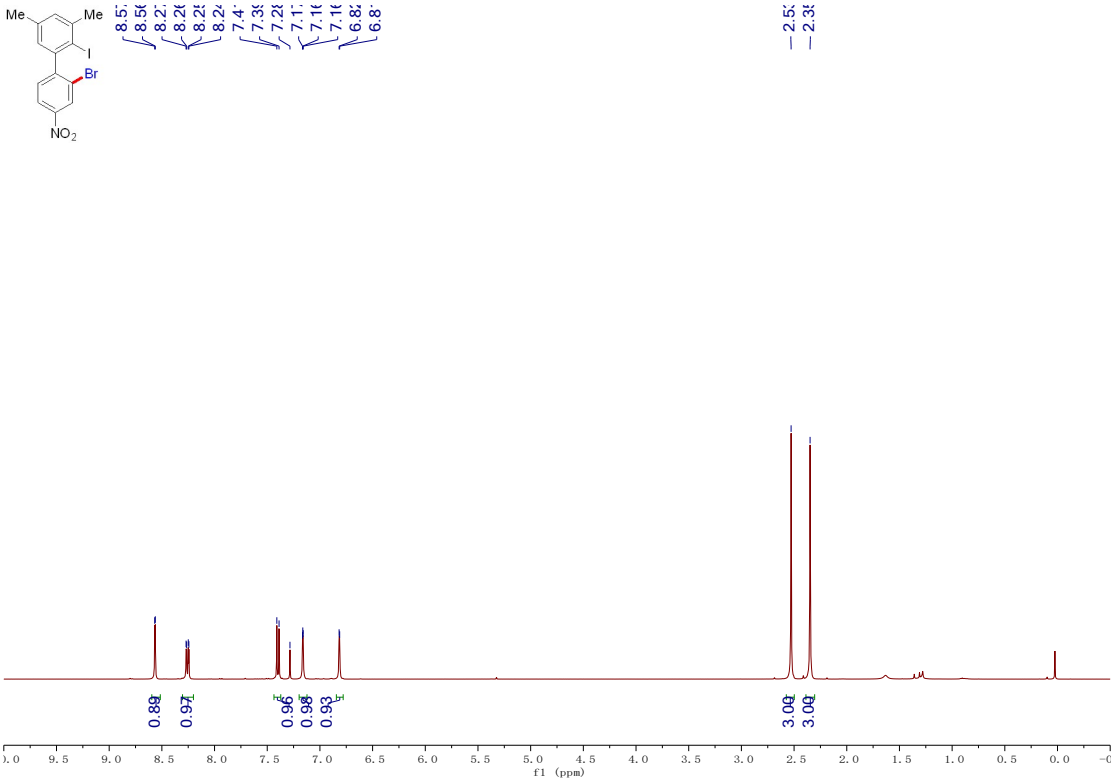




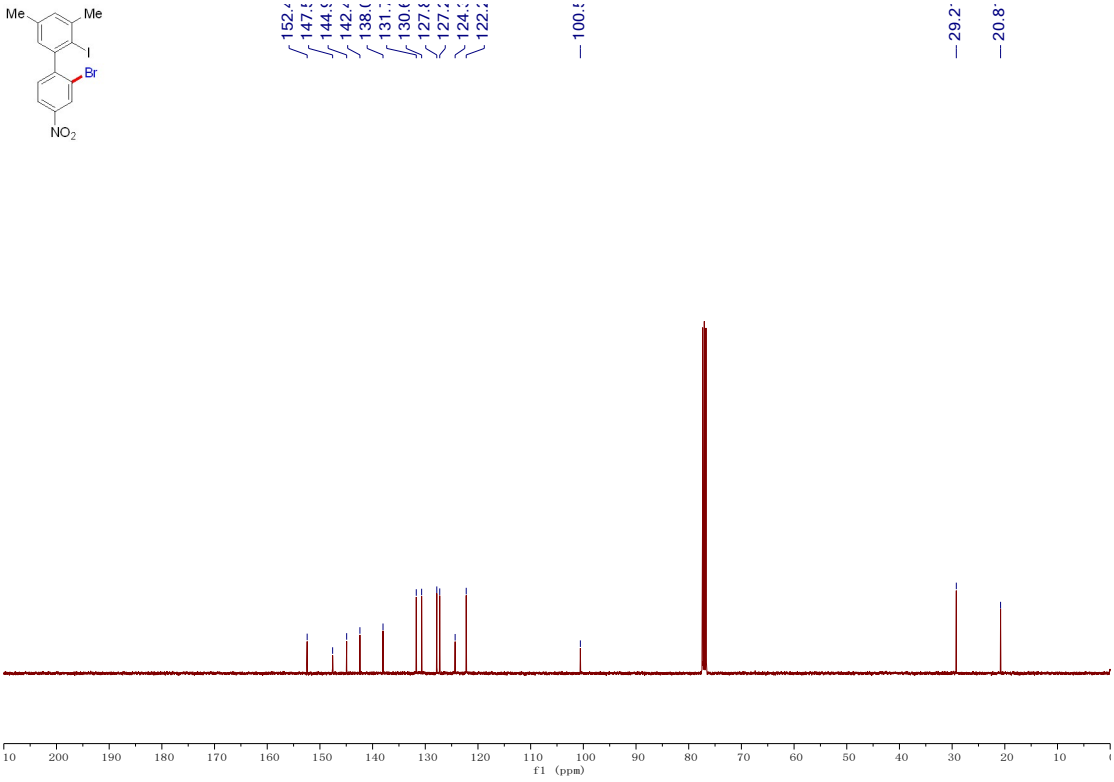
^{13}C NMR of **2g** (101 MHz, $CDCl_3$)



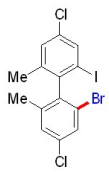
^{1}H NMR of **2h** (400 MHz, $CDCl_3$)



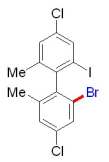
^{13}C NMR of **2h** (101 MHz, $CDCl_3$)



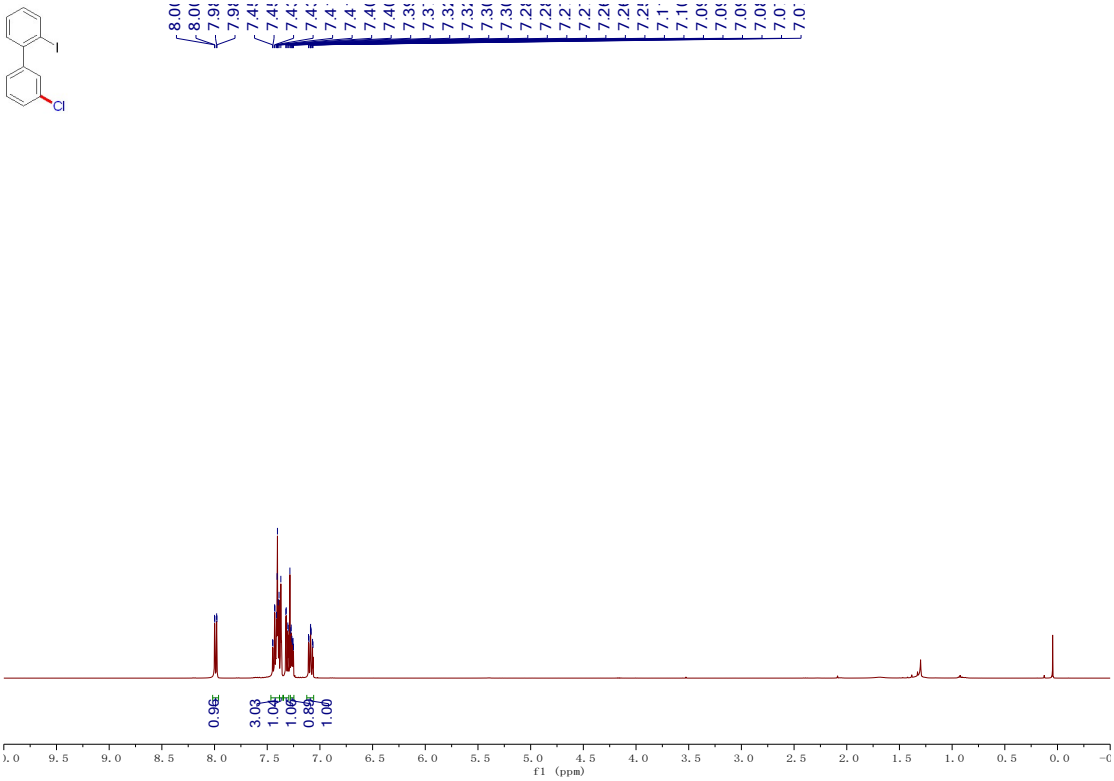
^{1}H NMR of **2i** (400 MHz, $CDCl_3$)



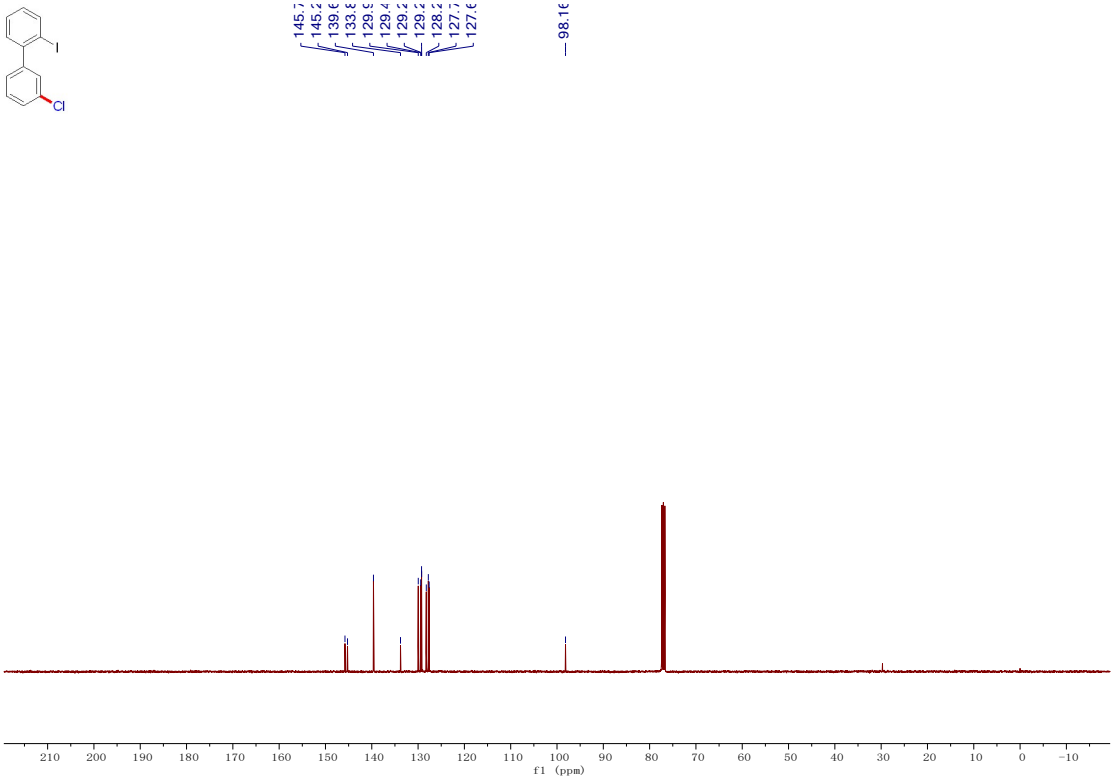
^{13}C NMR of **2i** (101 MHz, $CDCl_3$)



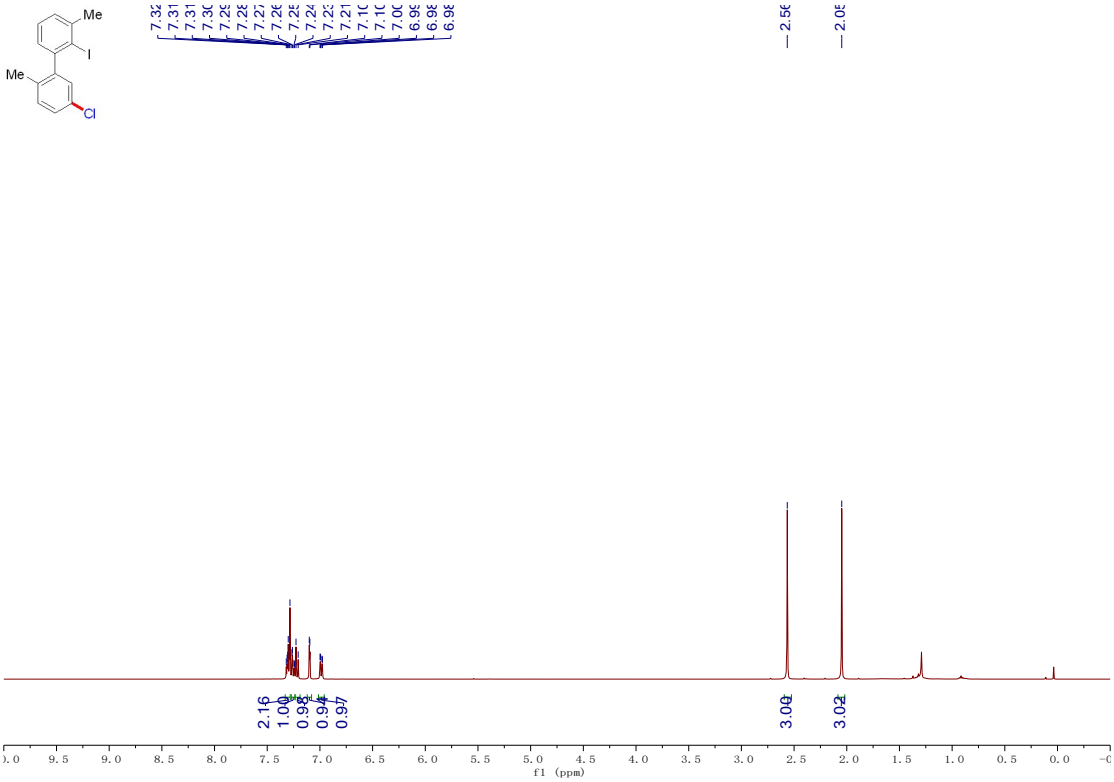
^{1}H NMR of **3a** (400 MHz, $CDCl_3$)



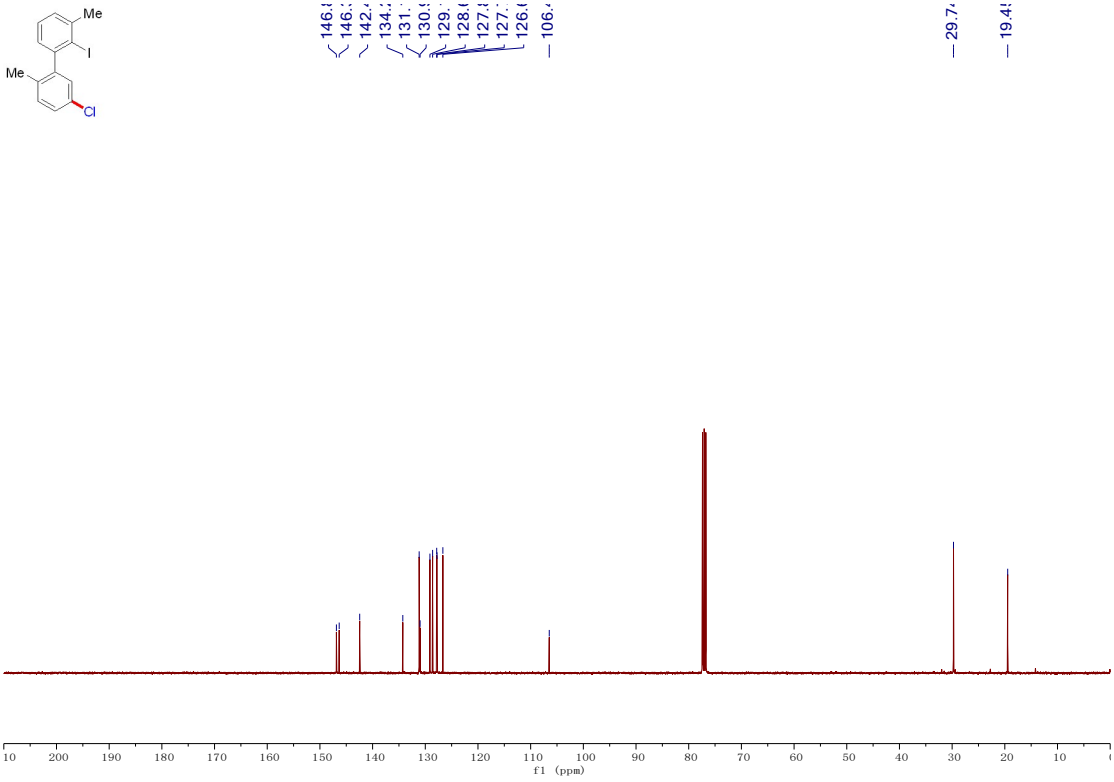
^{13}C NMR of **3a** (101 MHz, $CDCl_3$)



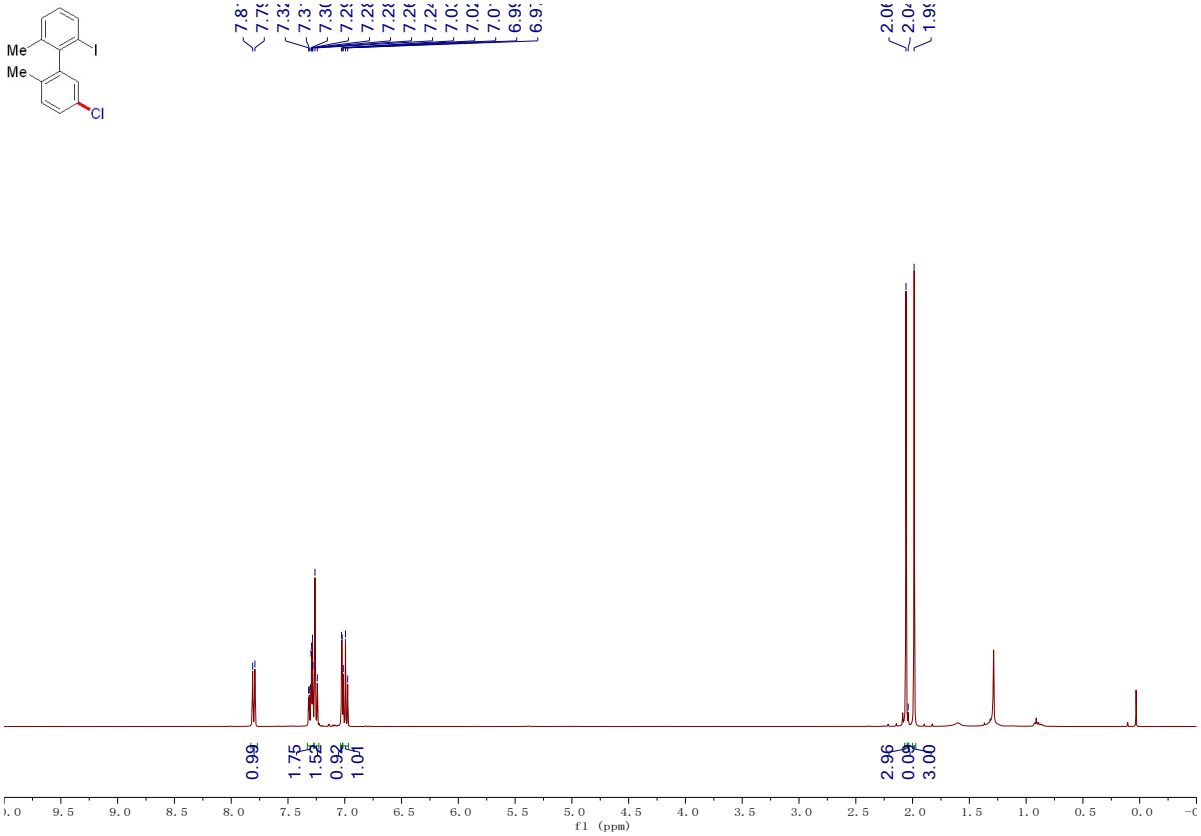
^{1}H NMR of **3b** (400 MHz, $CDCl_3$)



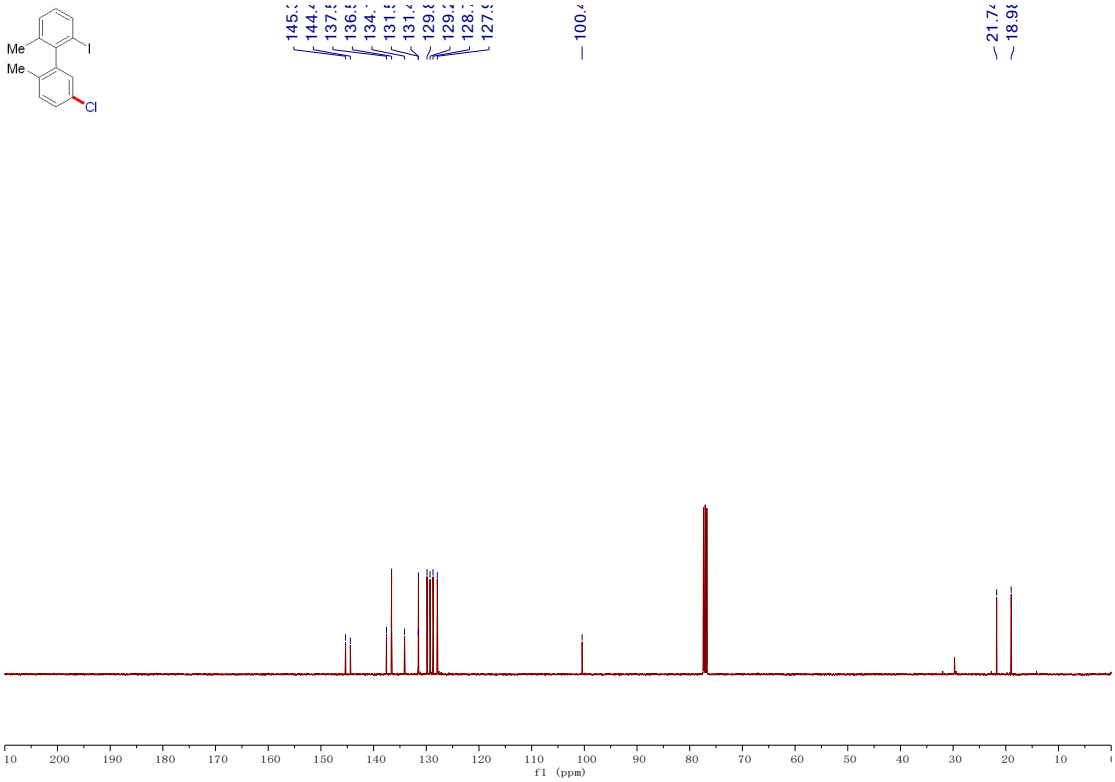
^{13}C NMR of **3b** (101 MHz, $CDCl_3$)



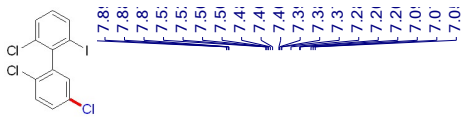
^{1}H NMR of **3c** (400 MHz, $CDCl_3$)

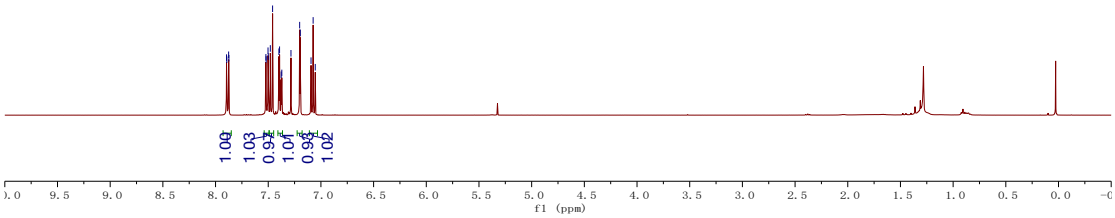


^{13}C NMR of **3c** (101 MHz, $CDCl_3$)

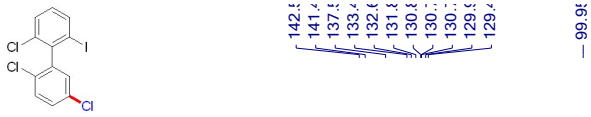


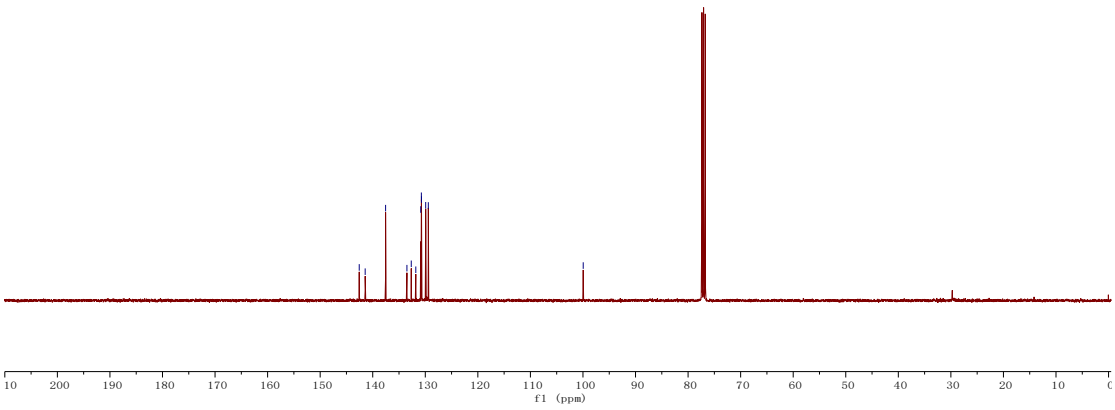
^{1}H NMR of **3d** (400 MHz, $CDCl_3$)



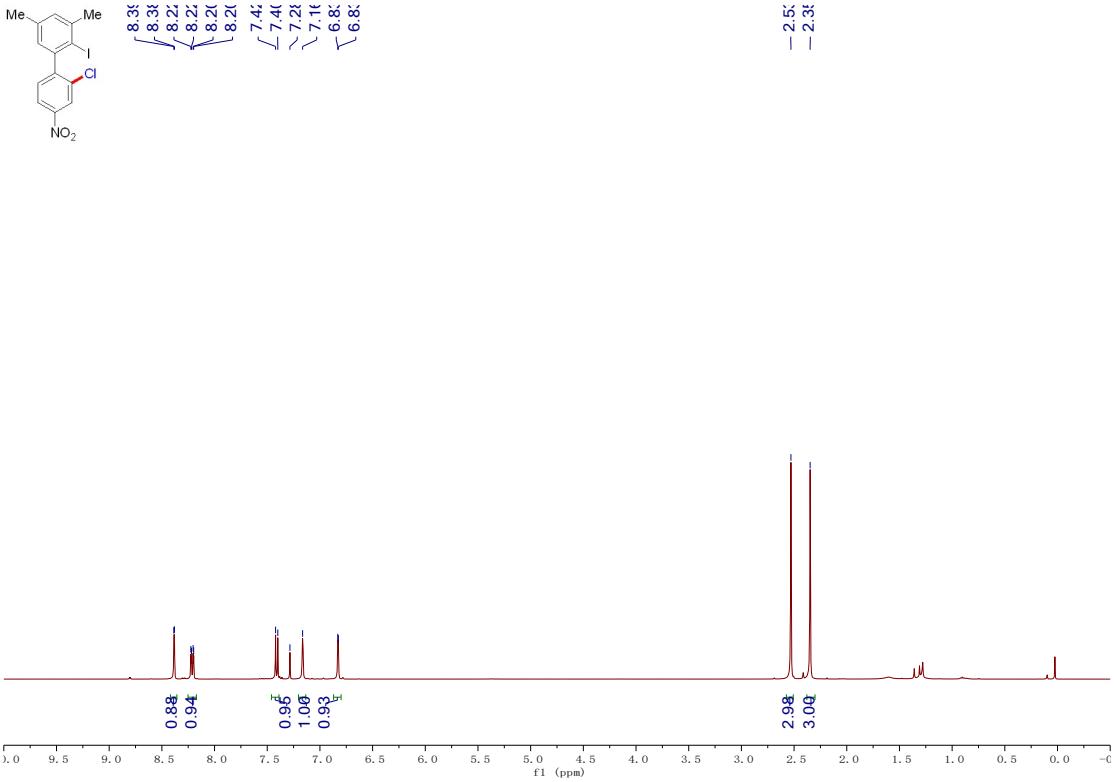


^{13}C NMR of **3d** (101 MHz, $CDCl_3$)

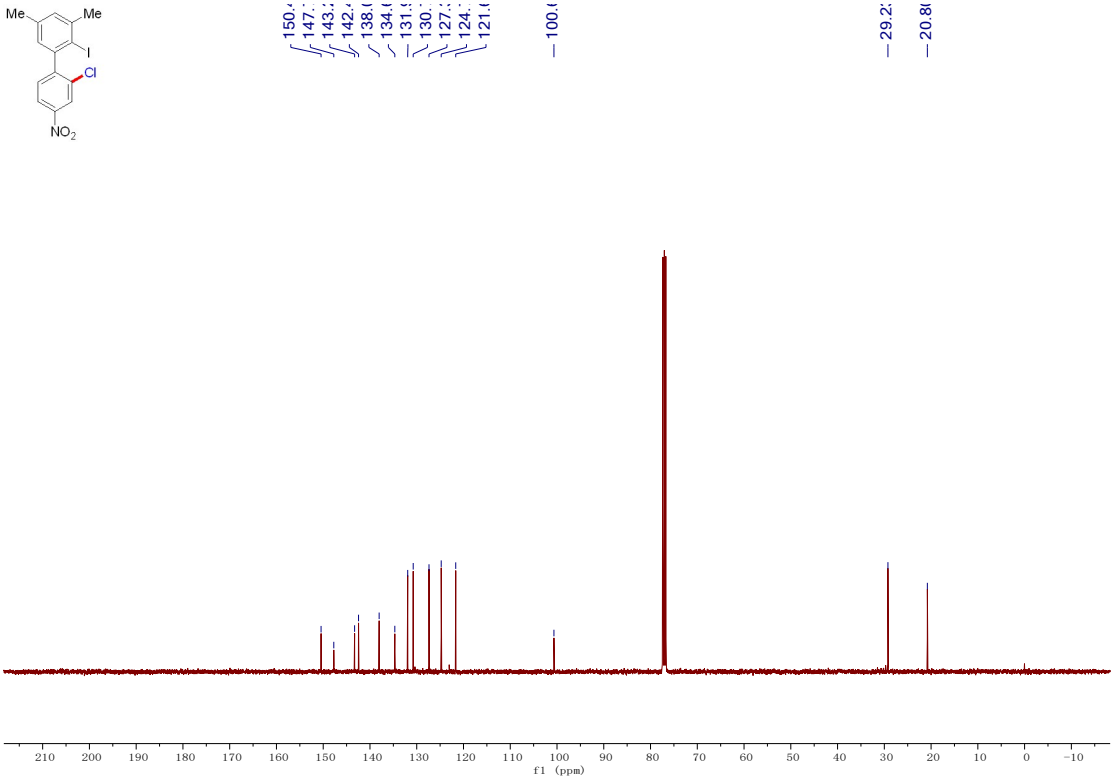




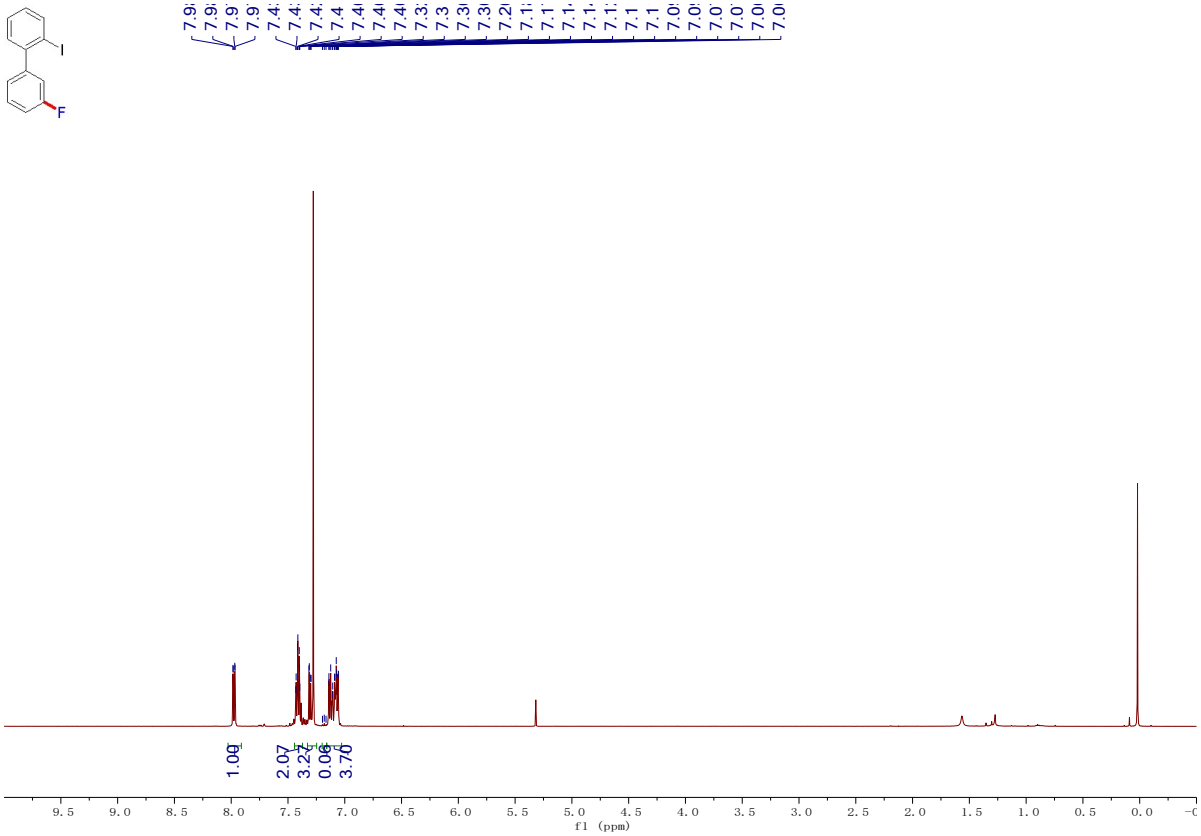
^{1}H NMR of **3e** (400 MHz, $CDCl_3$)



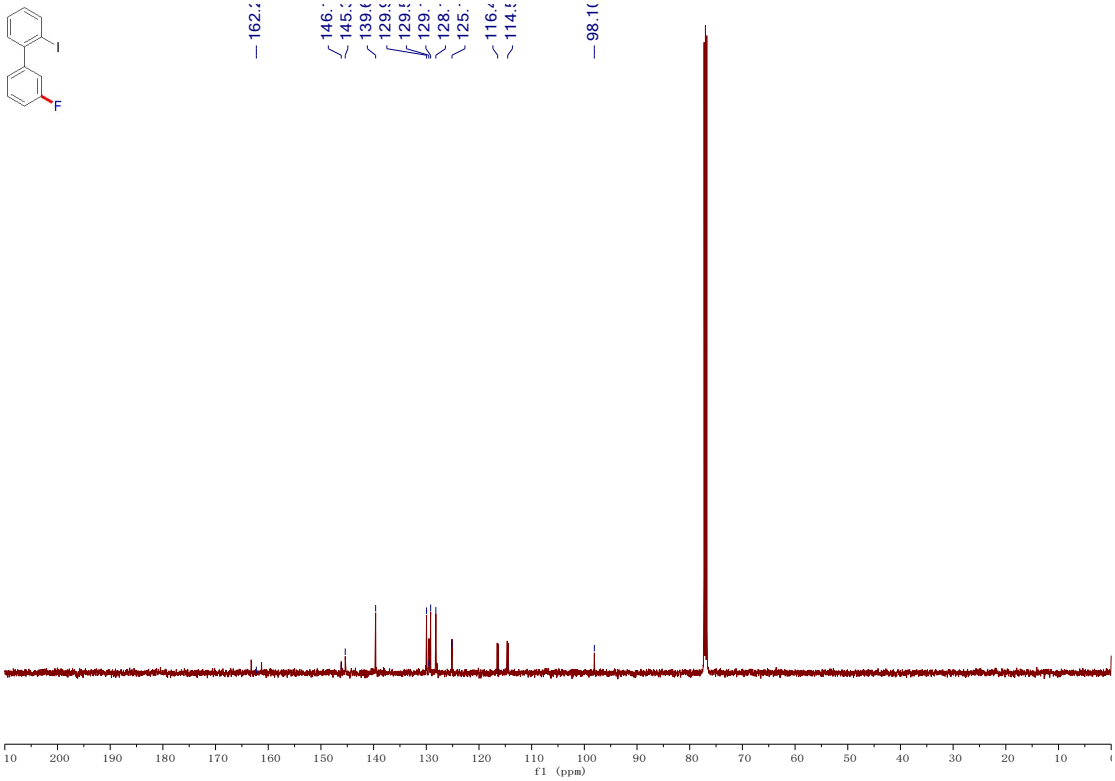
^{13}C NMR of **3e** (101 MHz, $CDCl_3$)



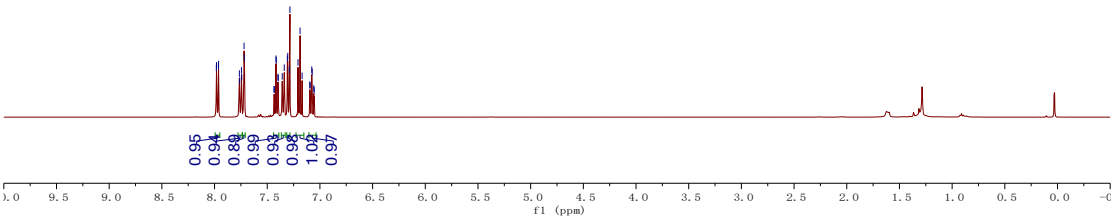
^{1}H NMR of **4a** (500 MHz, $CDCl_3$)



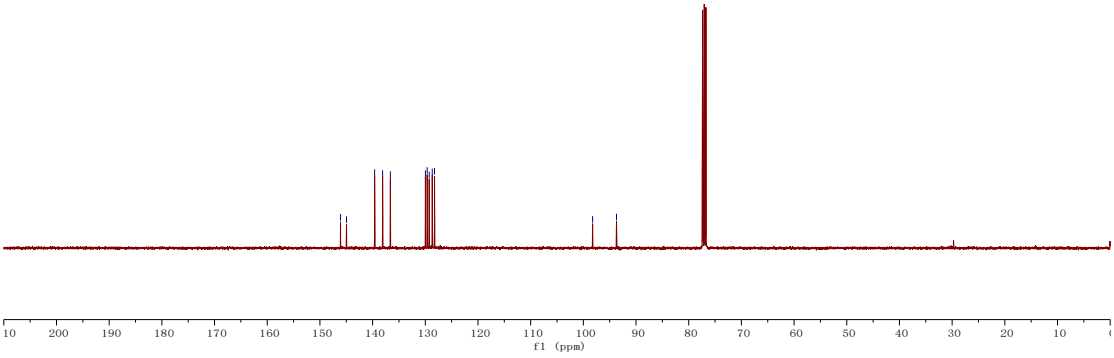
^{13}C NMR of **4a** (126 MHz, $CDCl_3$)



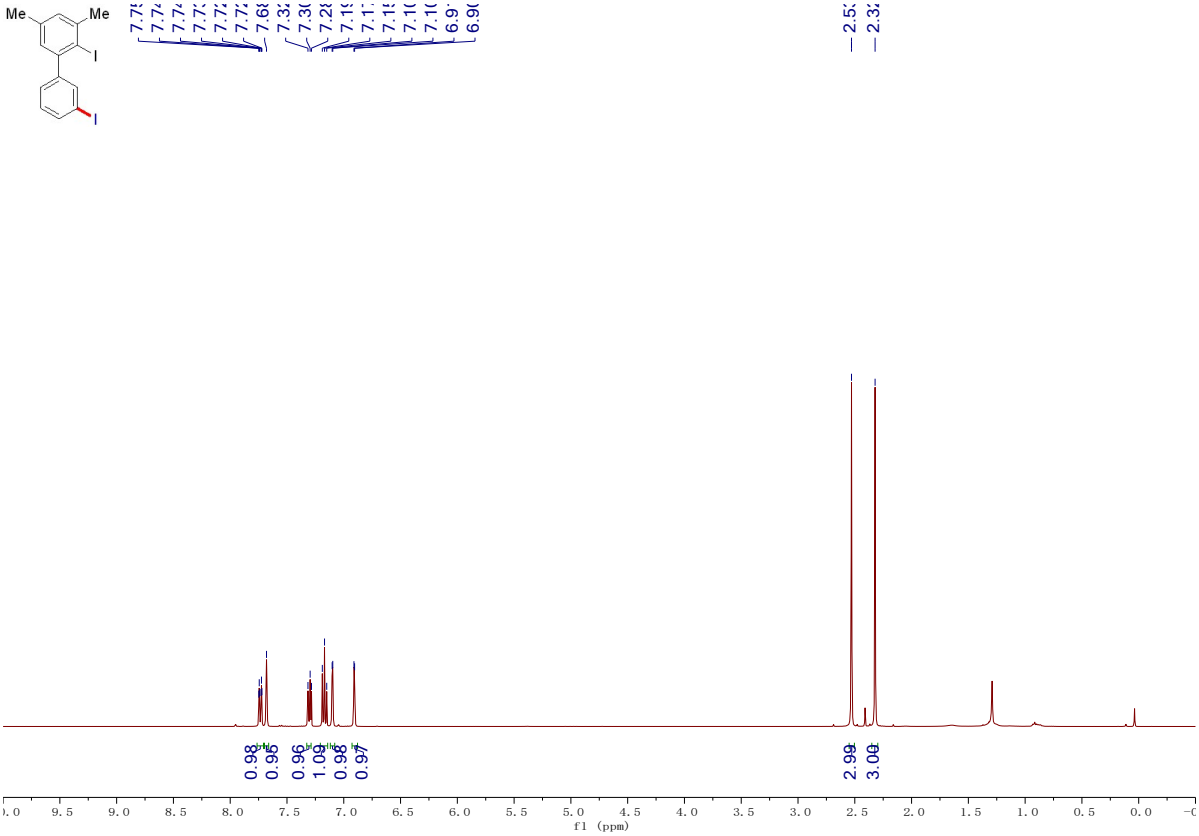
^{1}H NMR of **5a** (400 MHz, $CDCl_3$)



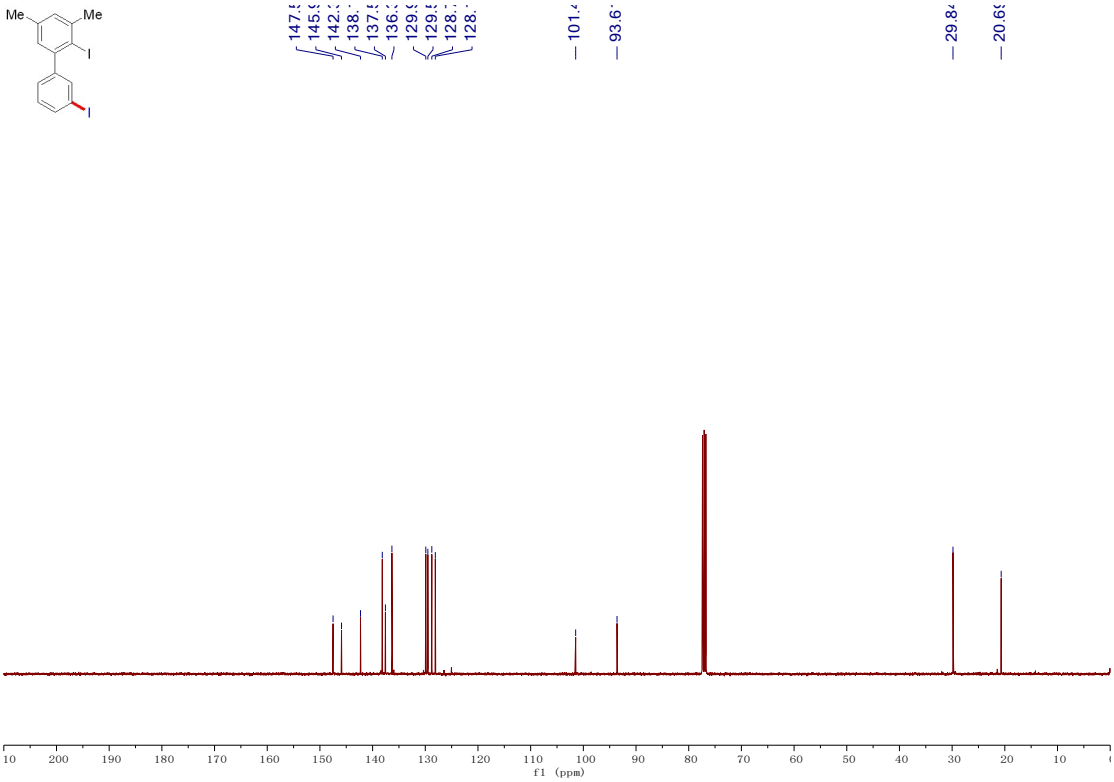
^{13}C NMR of **5a** (101 MHz, $CDCl_3$)



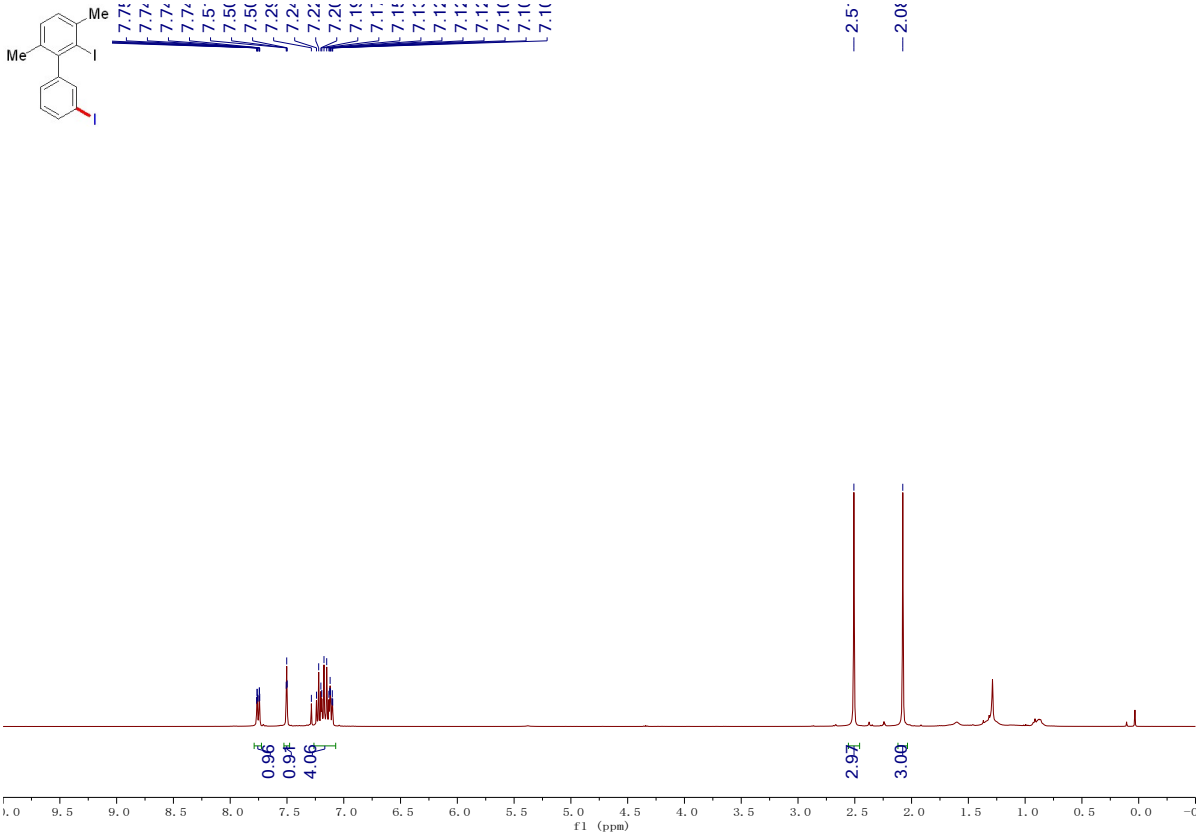
^{1}H NMR of **5b** (400 MHz, $CDCl_3$)



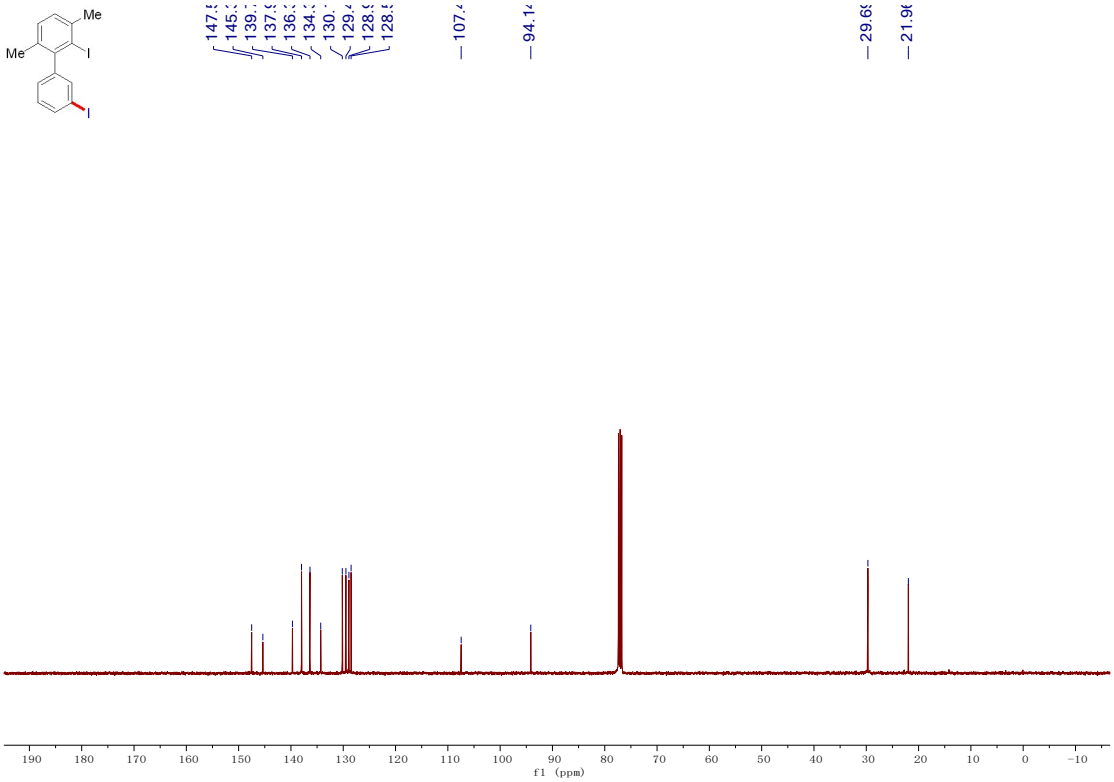
^{13}C NMR of **5b** (101 MHz, $CDCl_3$)



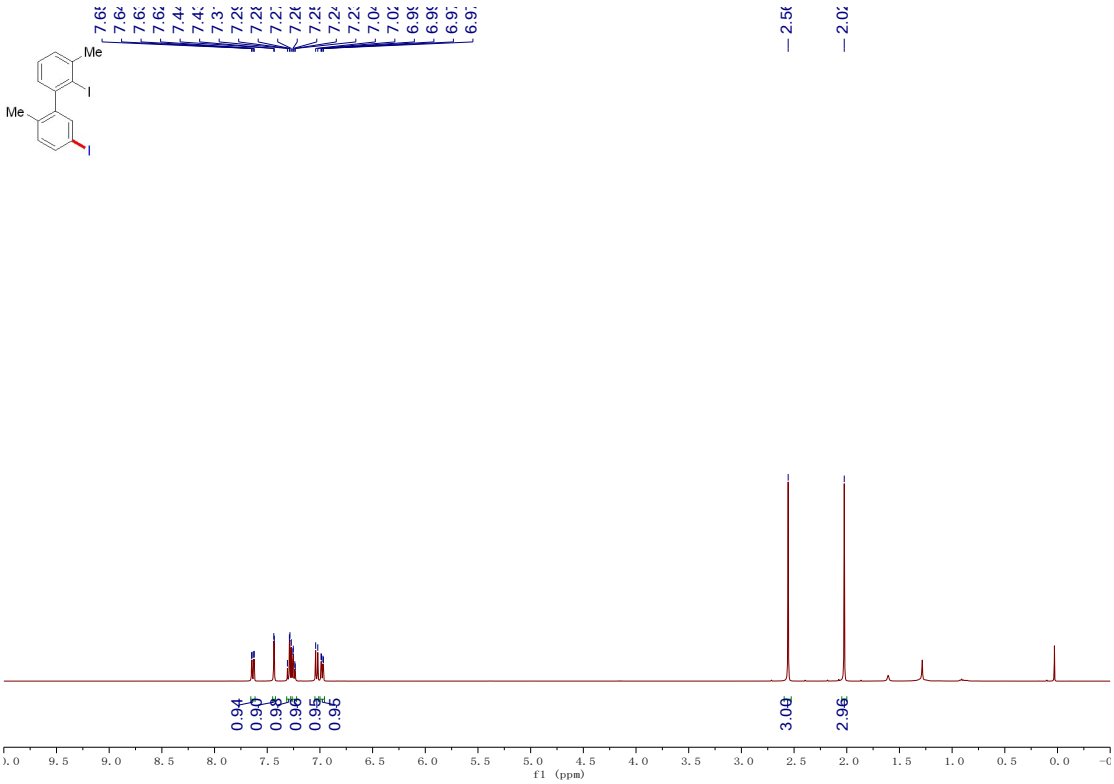
^{1}H NMR of **5c** (400 MHz, $CDCl_3$)



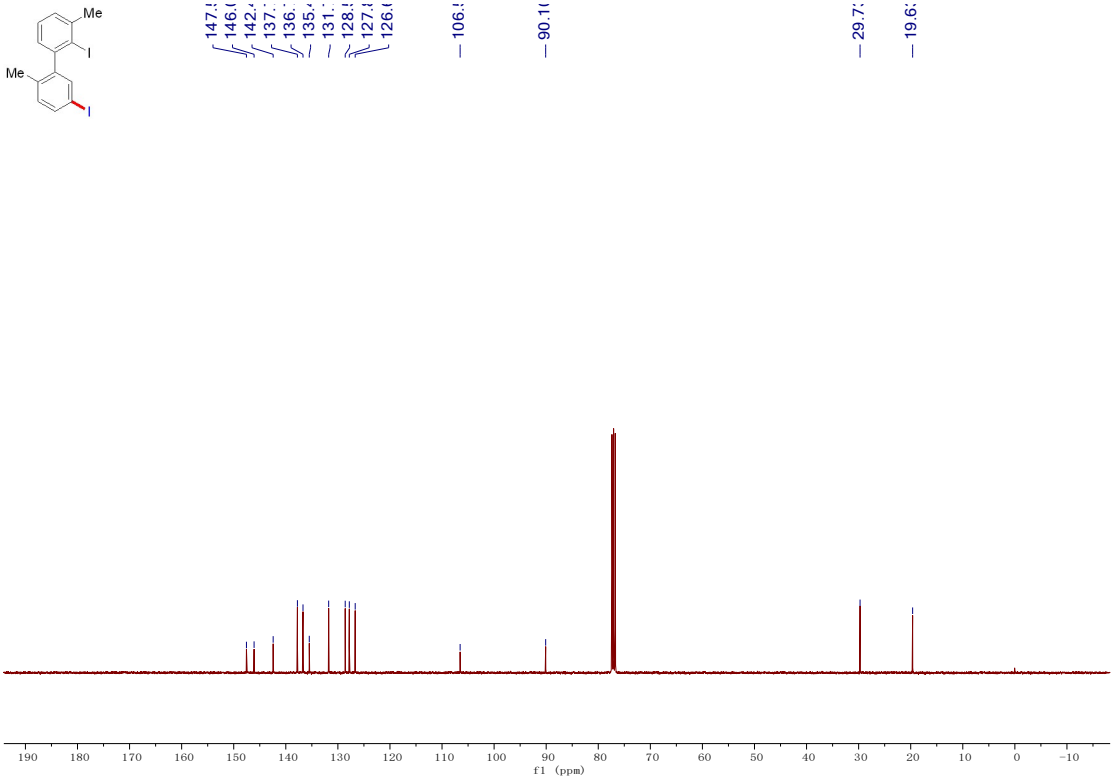
^{13}C NMR of **5c** (101 MHz, $CDCl_3$)



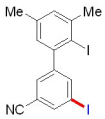
^{1}H NMR of **5d** (400 MHz, $CDCl_3$)

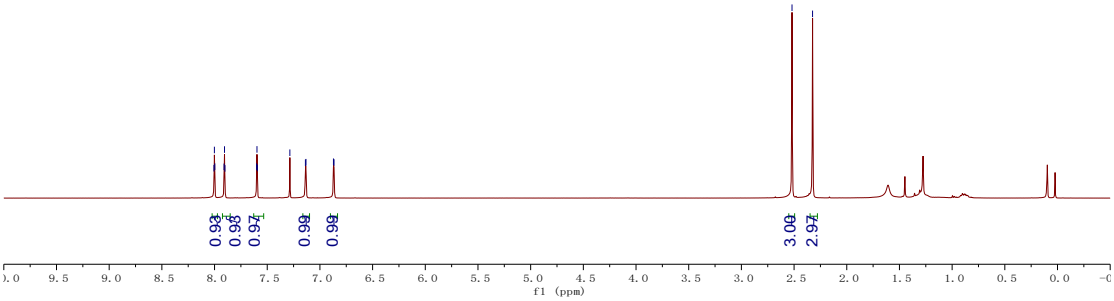


^{13}C NMR of **5d** (101 MHz, $CDCl_3$)

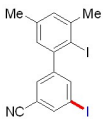


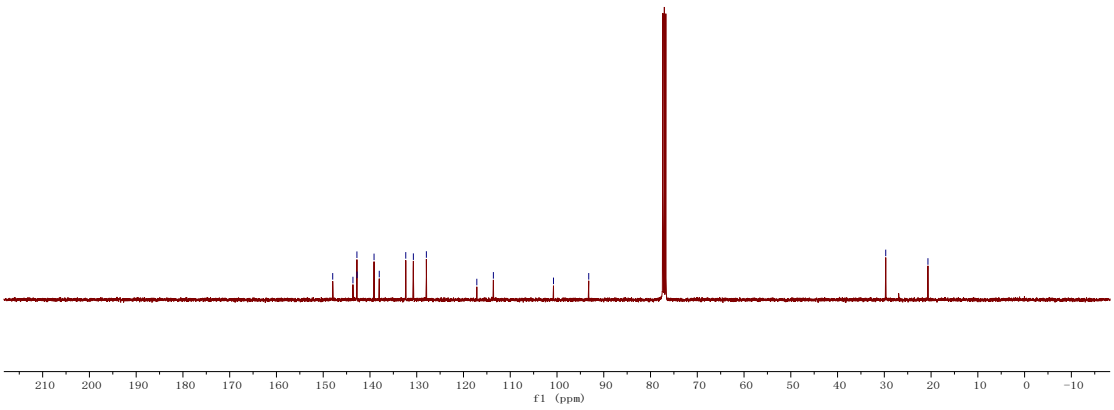
^{1}H NMR of **5e** (400 MHz, $CDCl_3$)



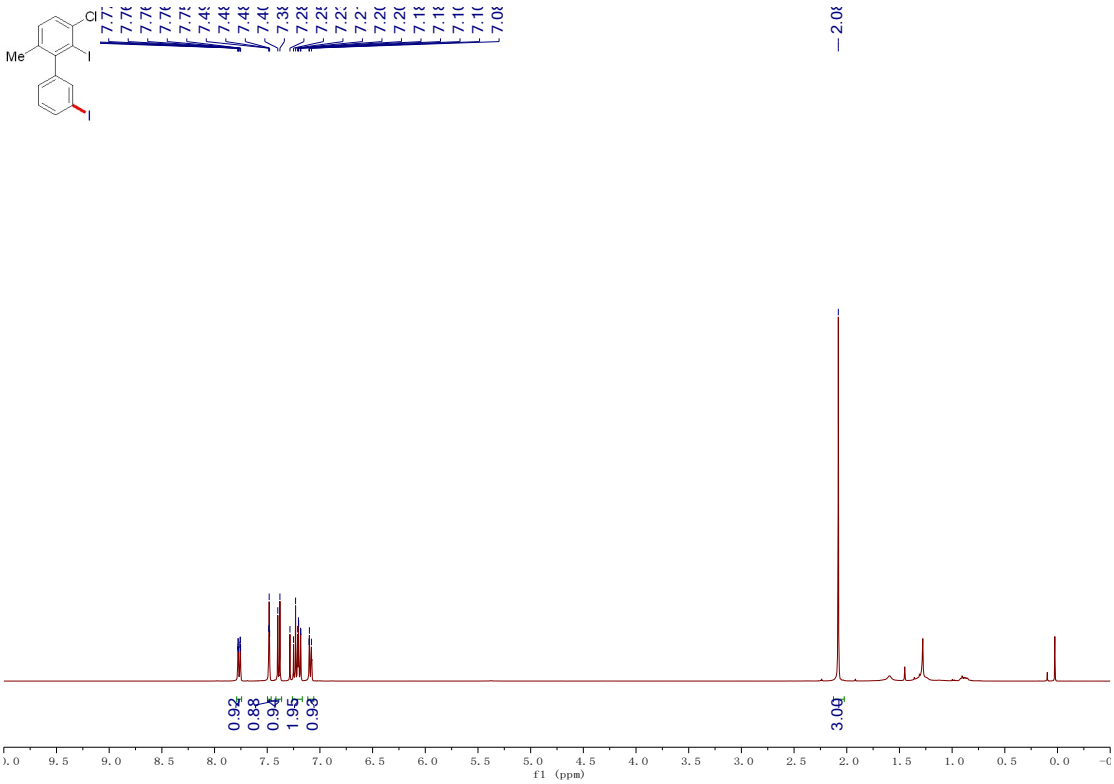


^{13}C NMR of **5e** (101 MHz, $CDCl_3$)

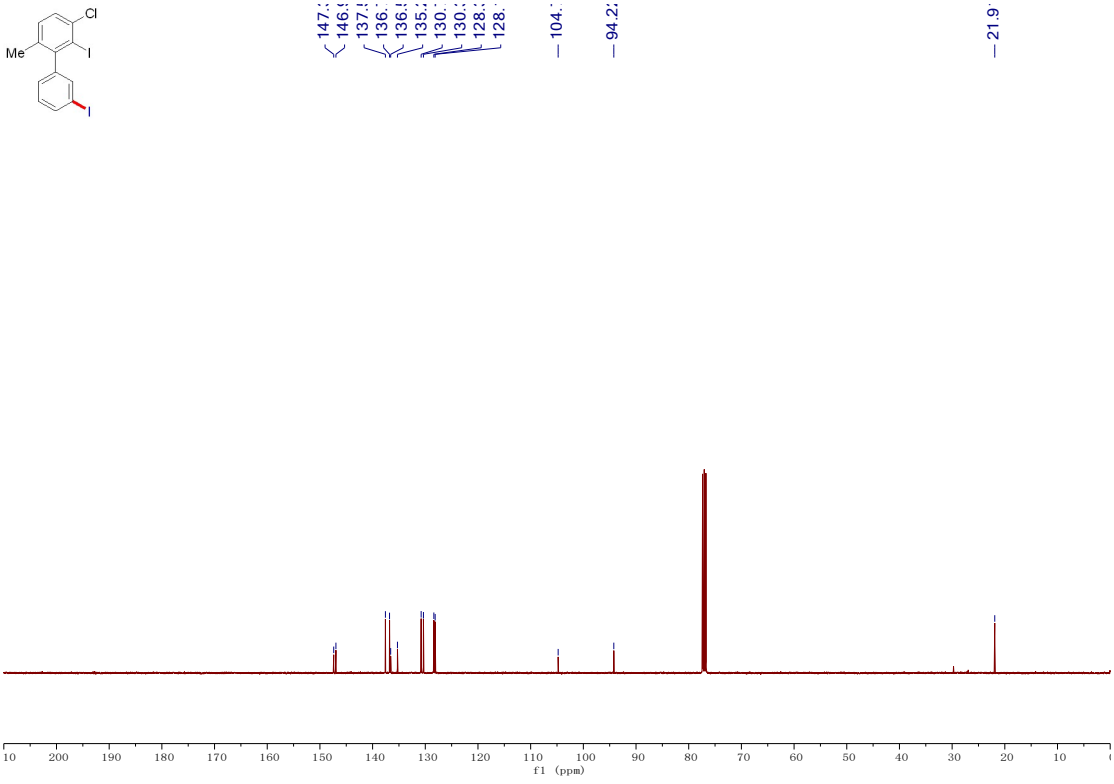




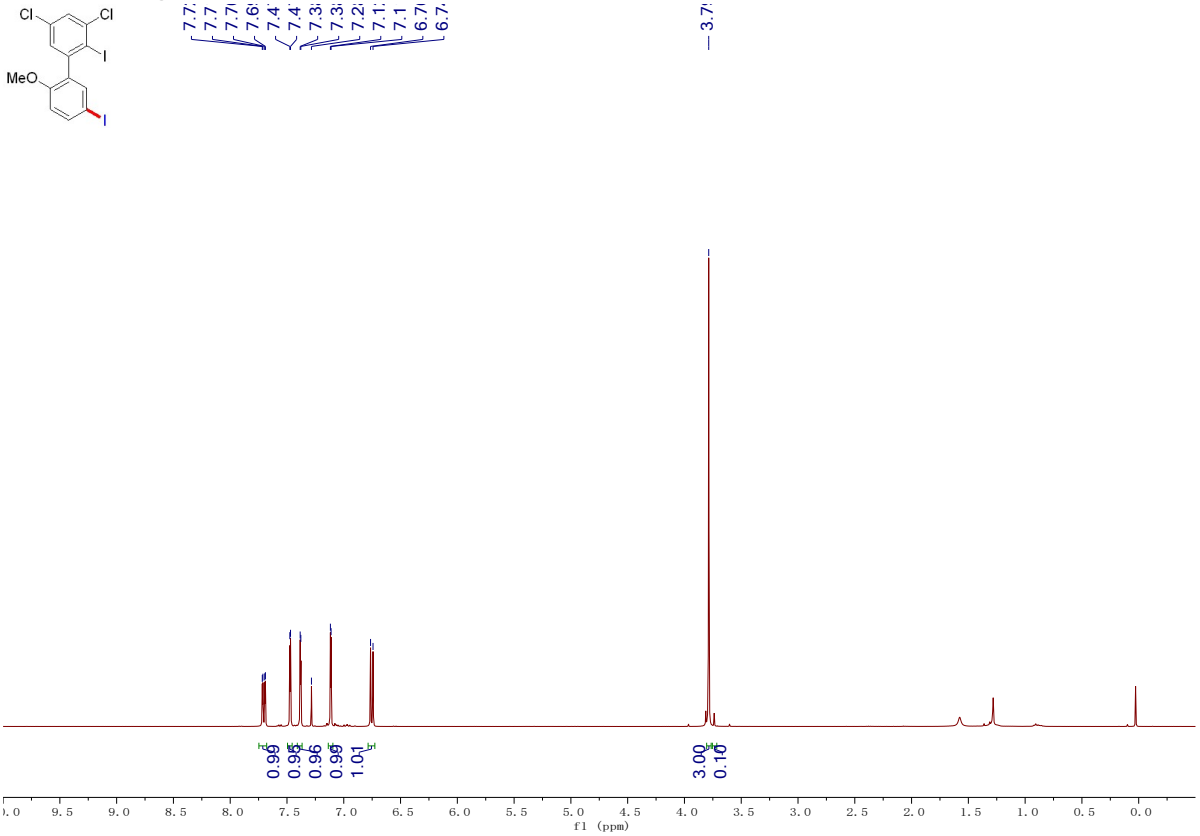
^{1}H NMR of **5f** (400 MHz, $CDCl_3$)



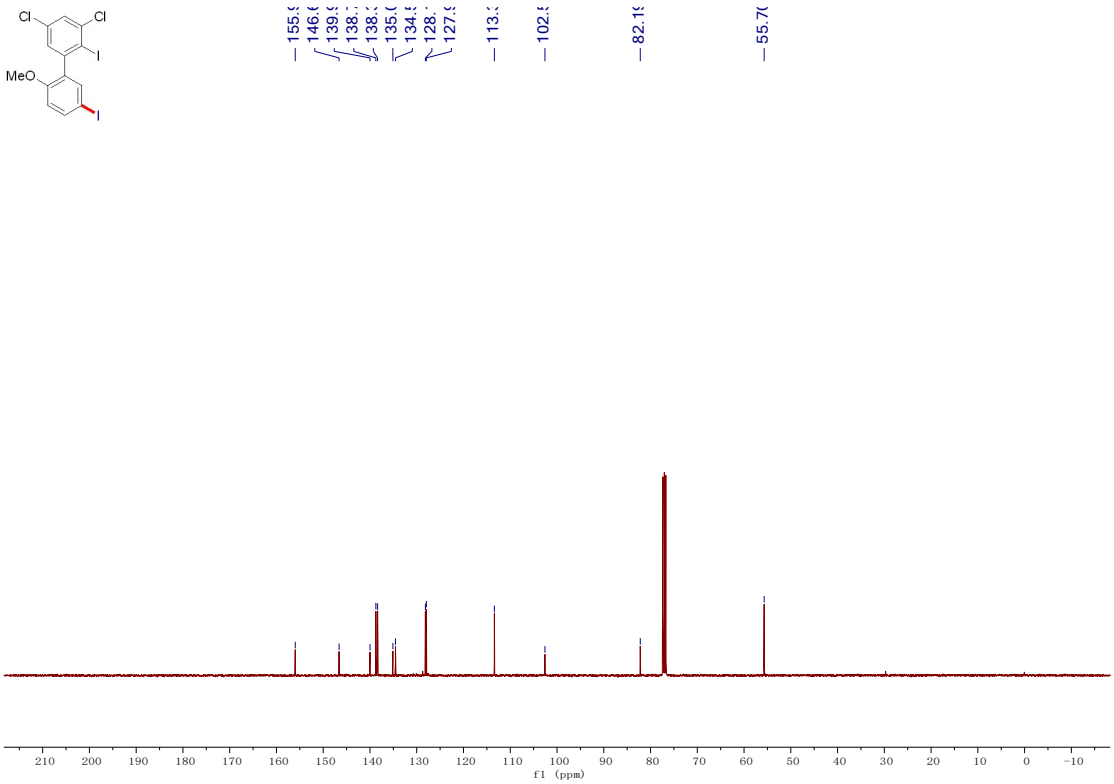
^{13}C NMR of **5f** (101 MHz, $CDCl_3$)



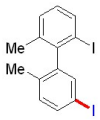
^{1}H NMR of **5g** (400 MHz, $CDCl_3$)



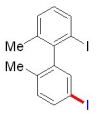
^{13}C NMR of **5g** (101 MHz, $CDCl_3$)



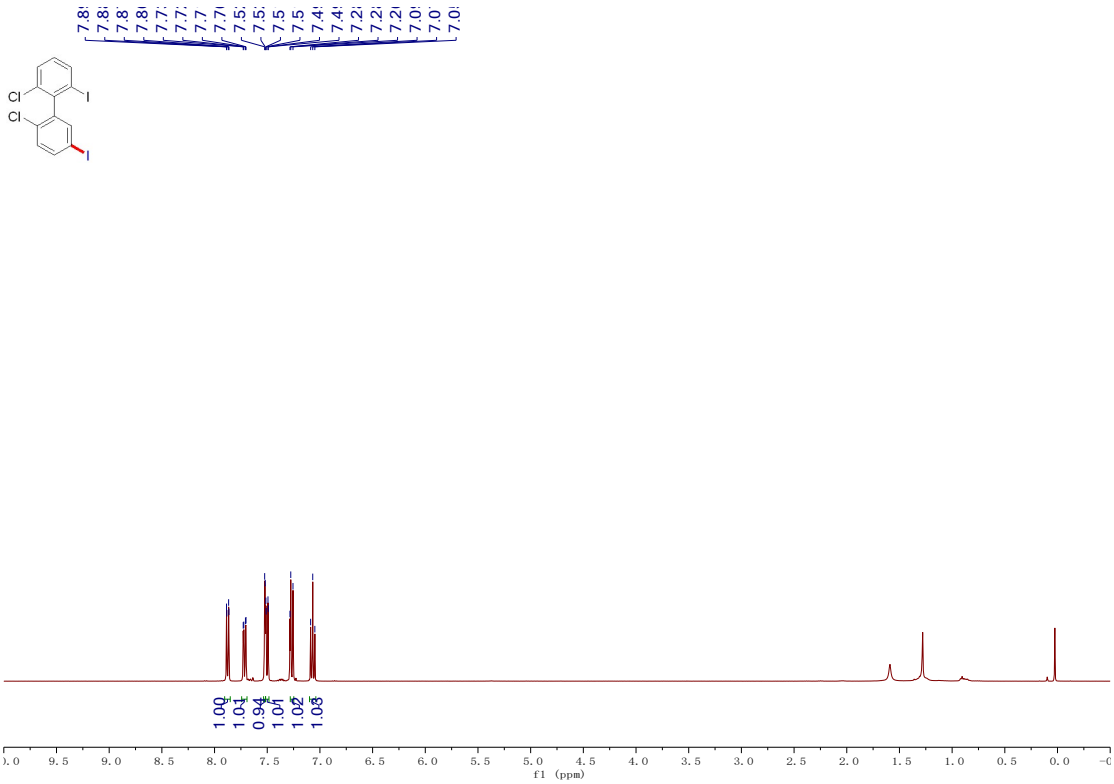
^{1}H NMR of **5h** (400 MHz, $CDCl_3$)



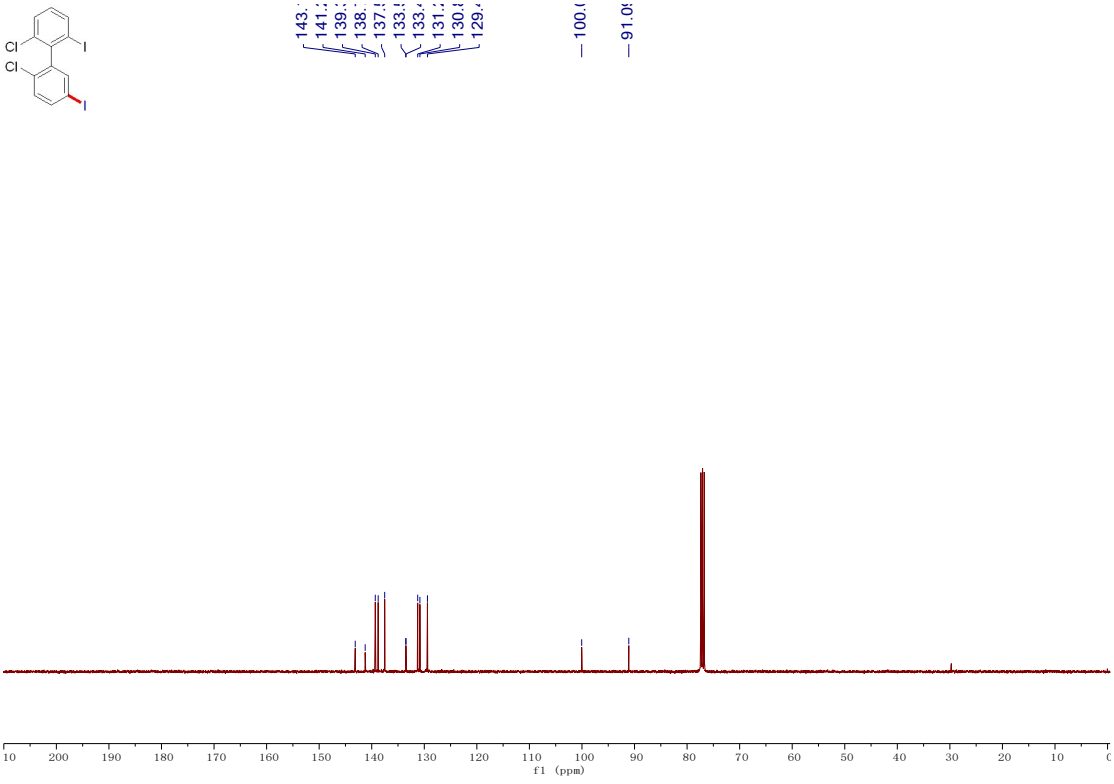
^{13}C NMR of **5h** (101 MHz, $CDCl_3$)



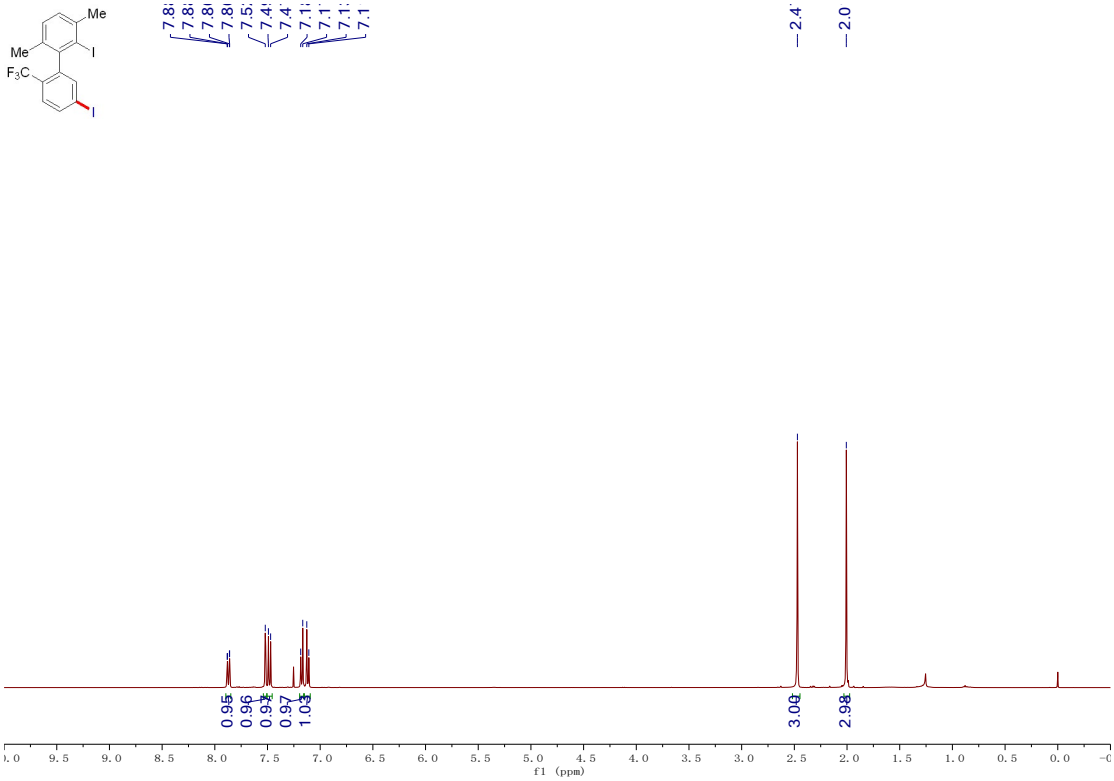
^{1}H NMR of **5i** (400 MHz, $CDCl_3$)



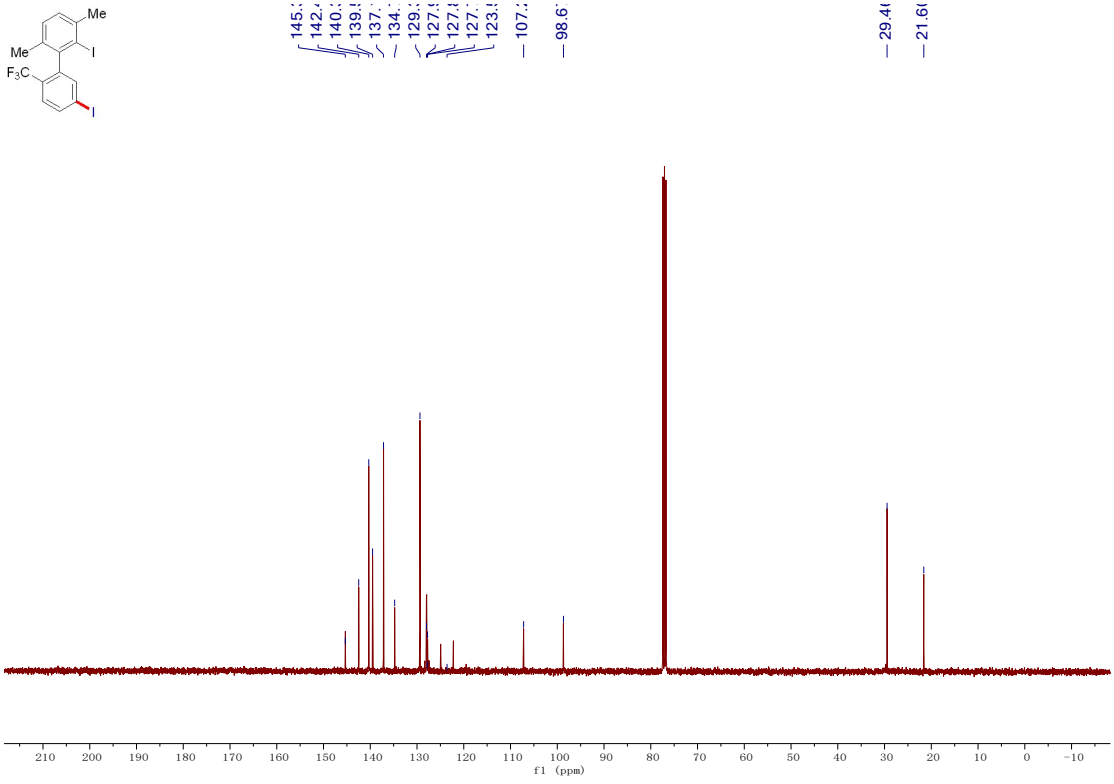
^{13}C NMR of **5i** (101 MHz, $CDCl_3$)



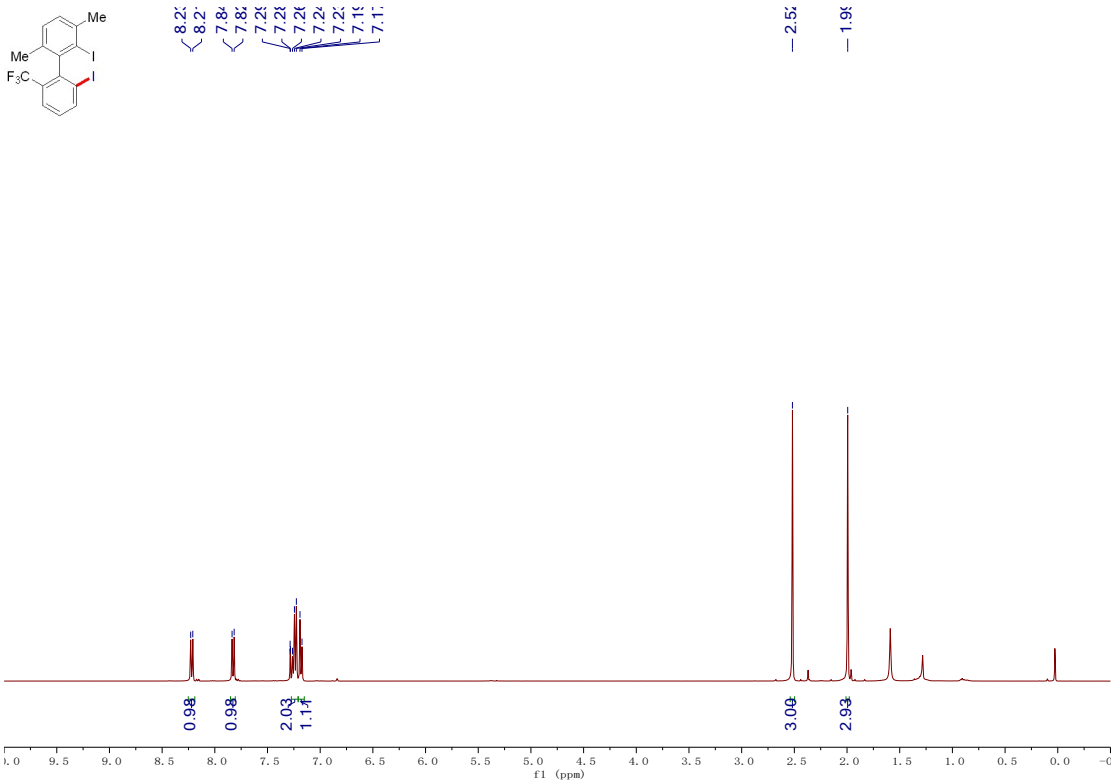
^{1}H NMR of **5j** (400 MHz, $CDCl_3$)



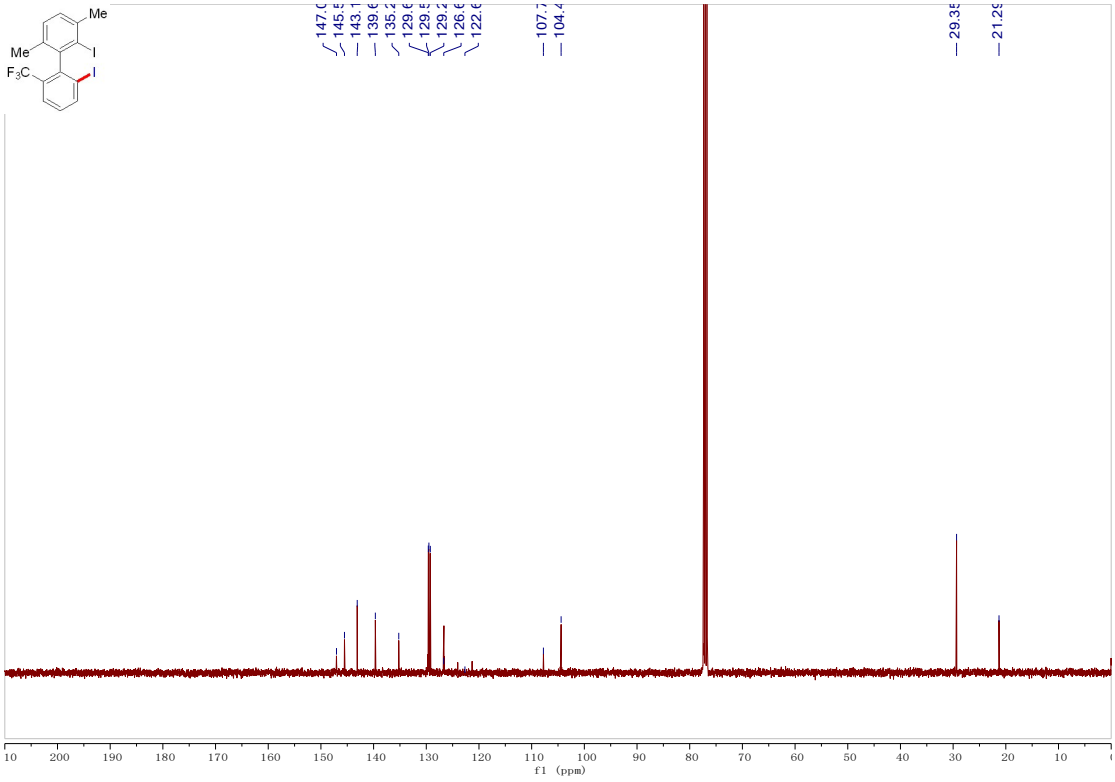
^{13}C NMR of **5j** (101 MHz, $CDCl_3$)



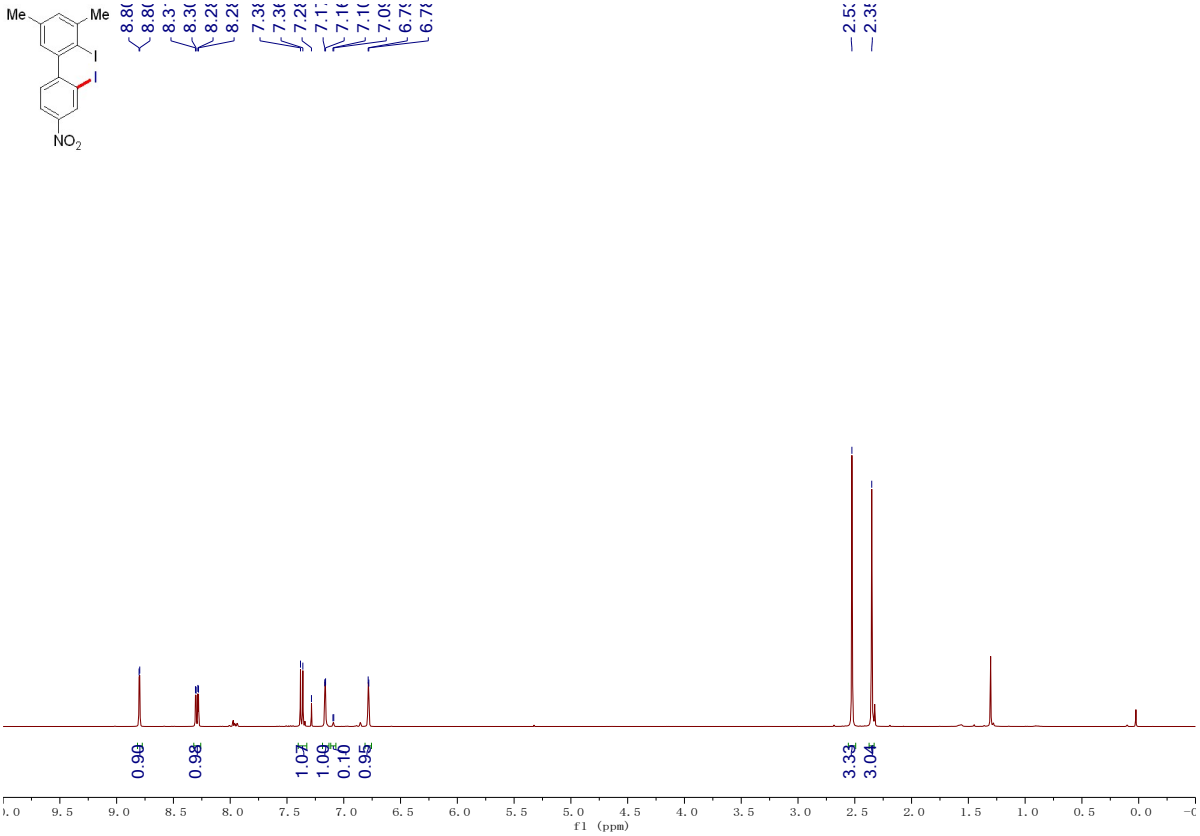
^{1}H NMR of **5j'** (400 MHz, $CDCl_3$)



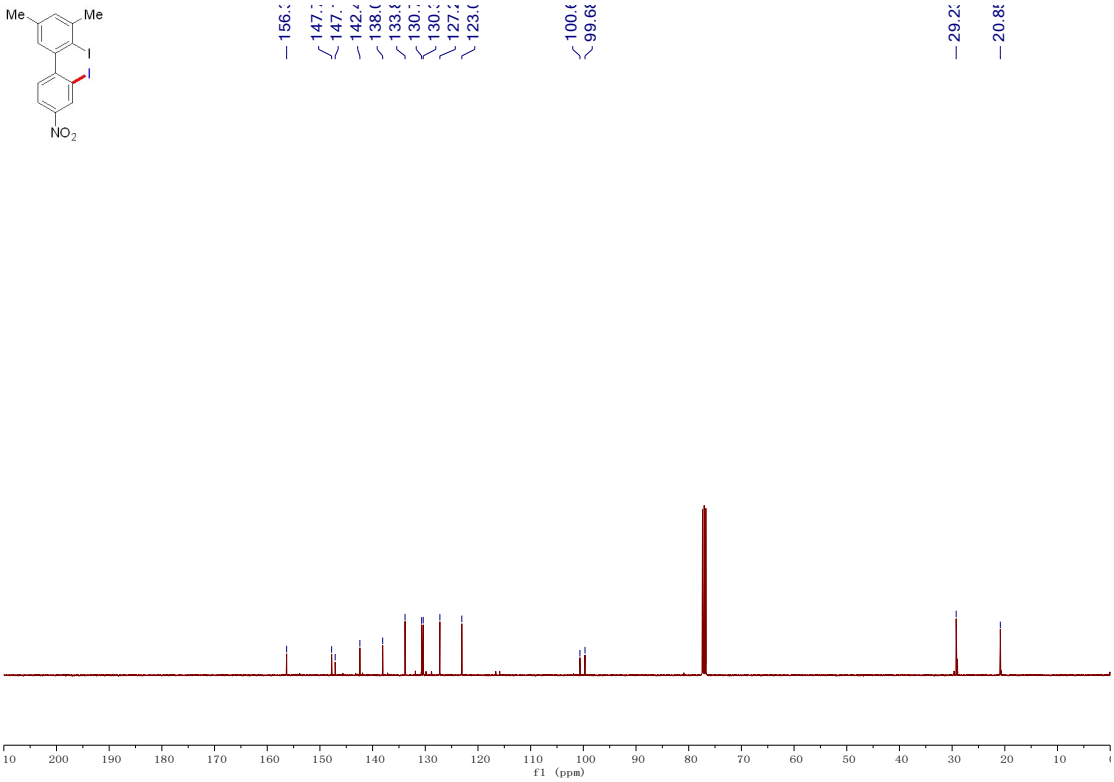
^{13}C NMR of **5j'** (101 MHz, $CDCl_3$)



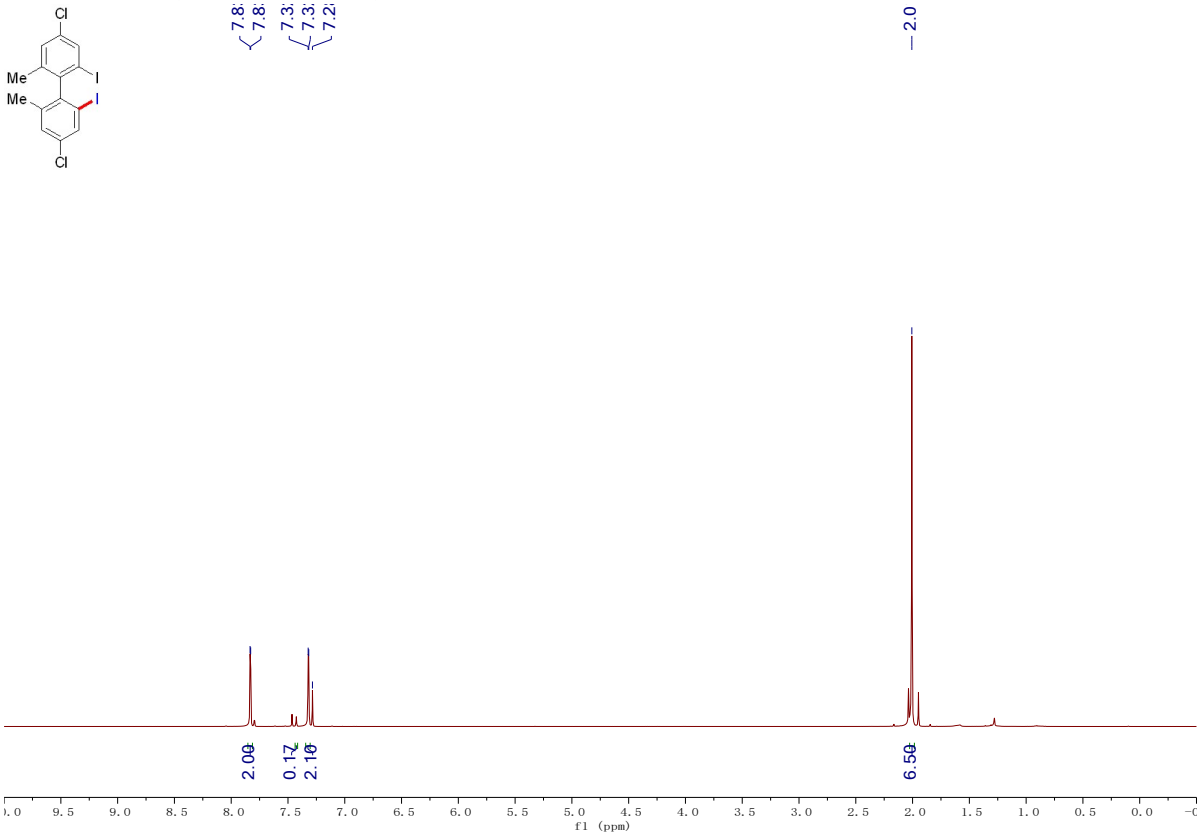
^{1}H NMR of **5k** (400 MHz, $CDCl_3$)



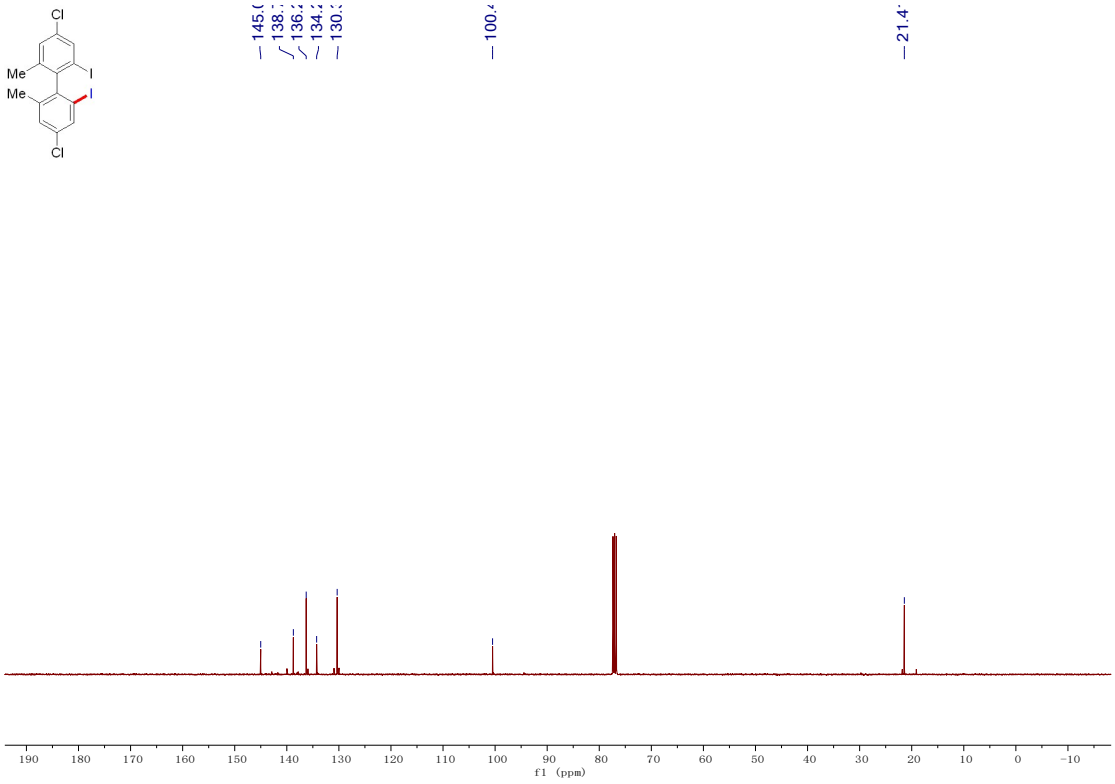
^{13}C NMR of **5k** (101 MHz, $CDCl_3$)



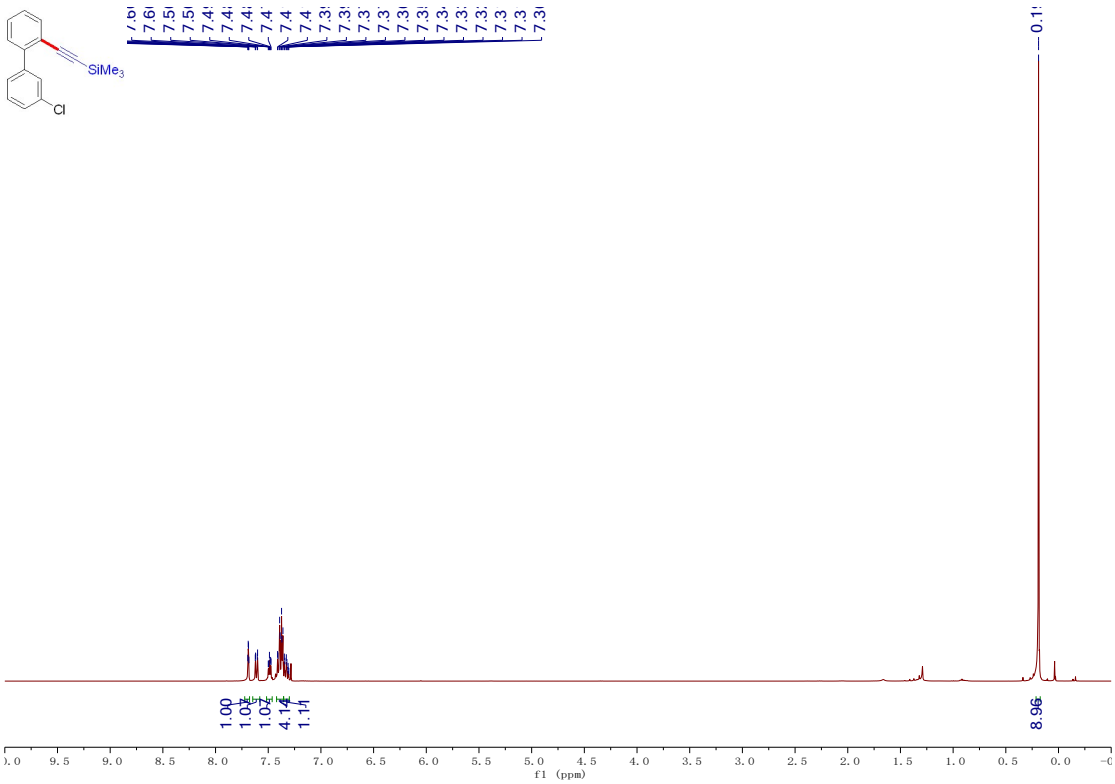
^{1}H NMR of **5l** (400 MHz, $CDCl_3$)



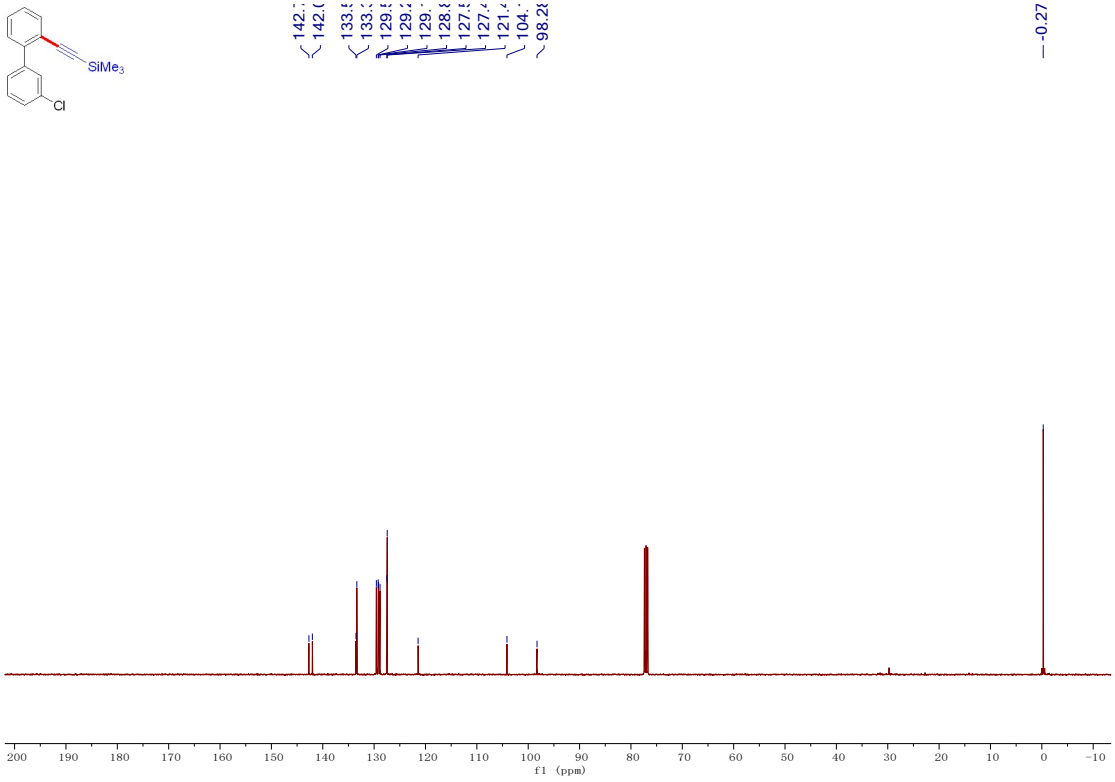
^{13}C NMR of **5l** (101 MHz, $CDCl_3$)



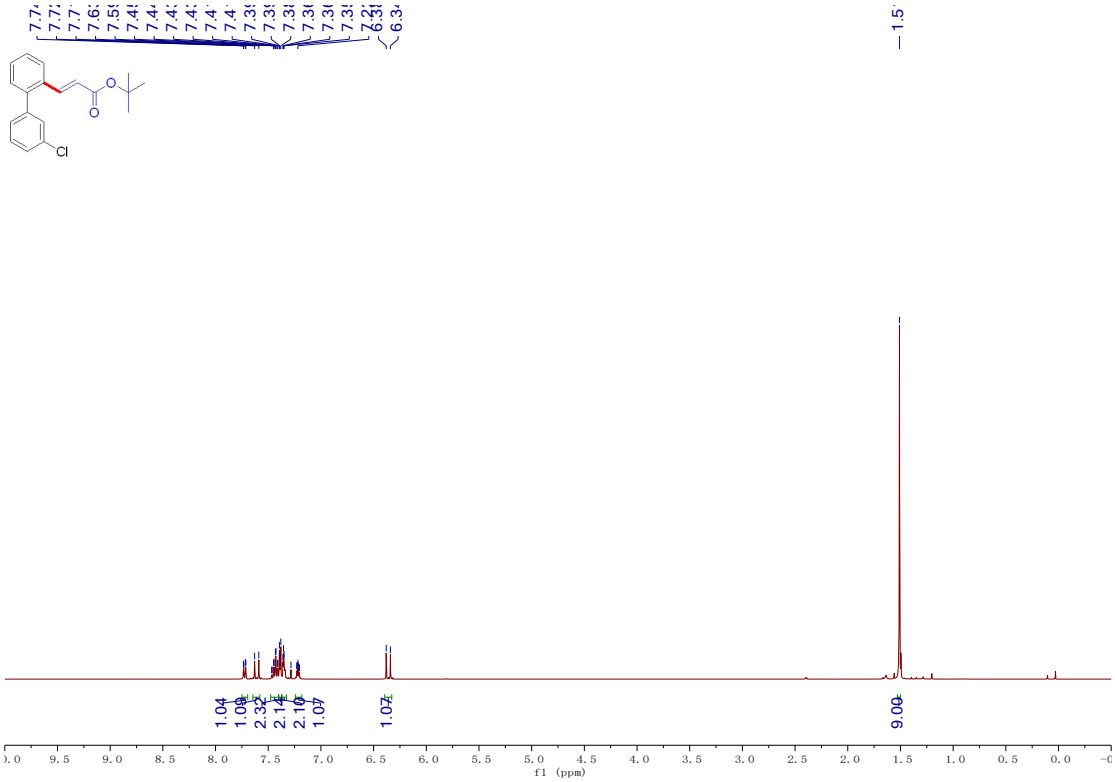
^{1}H NMR of **6** (400 MHz, $CDCl_3$)



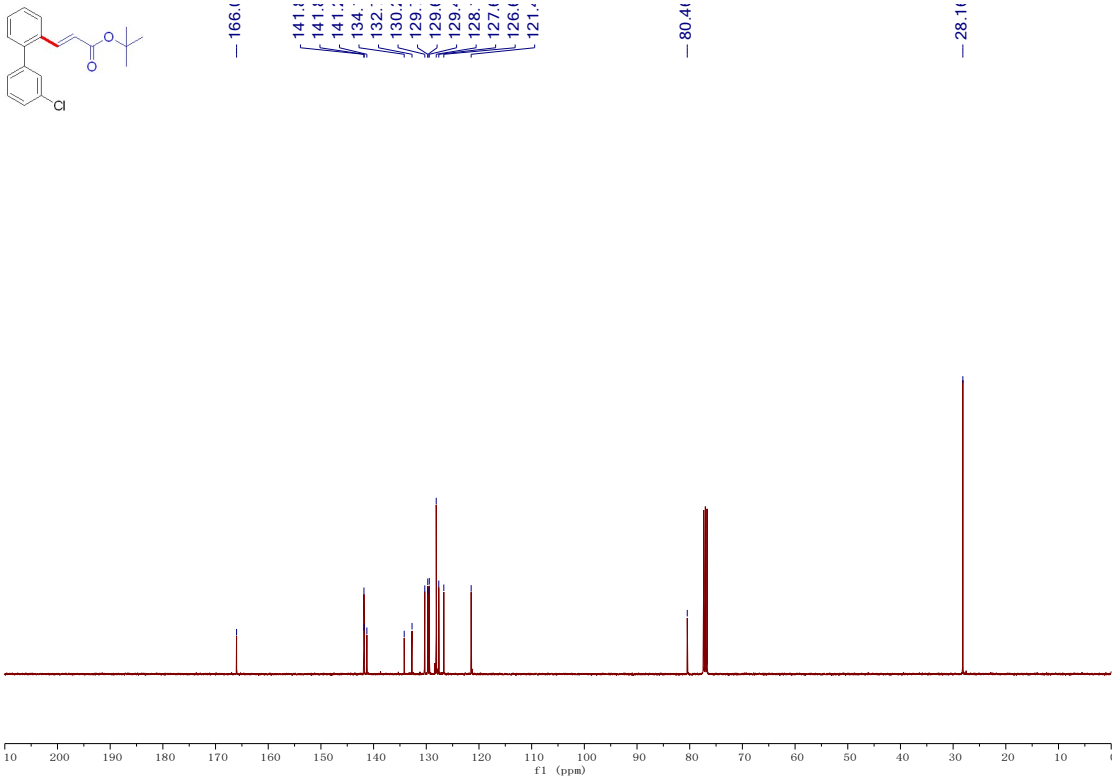
^{13}C NMR of **6** (101 MHz, $CDCl_3$)



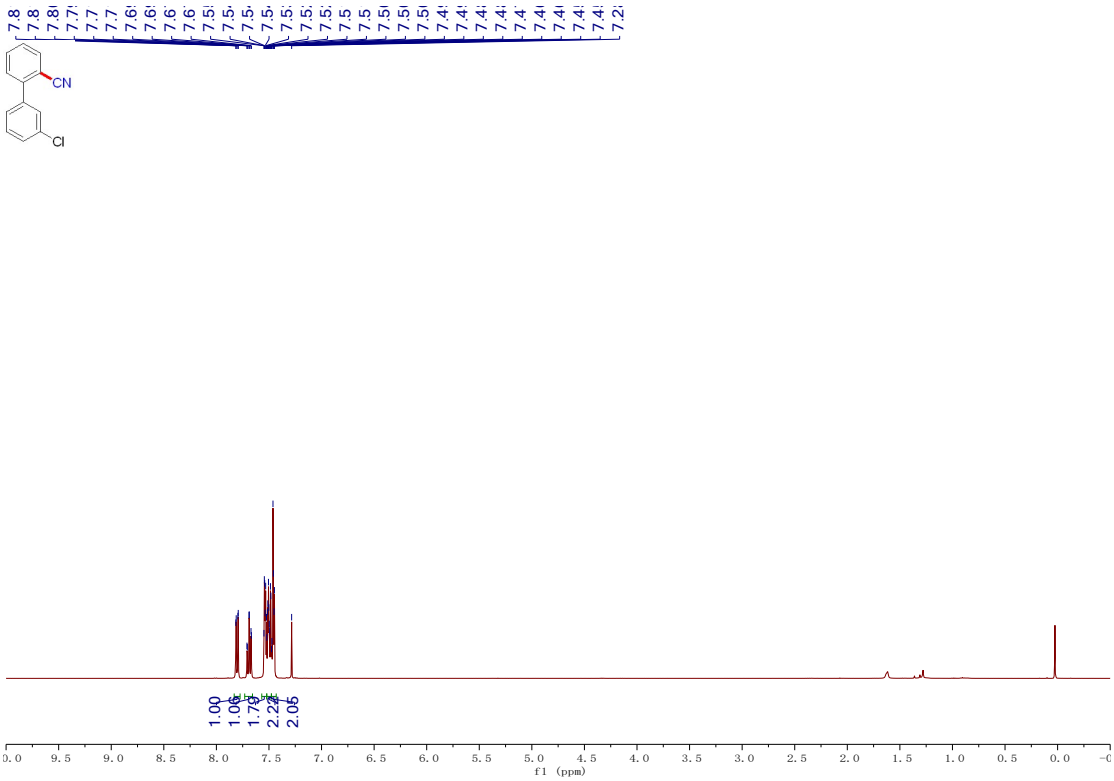
^{1}H NMR of **7** (400 MHz, $CDCl_3$)



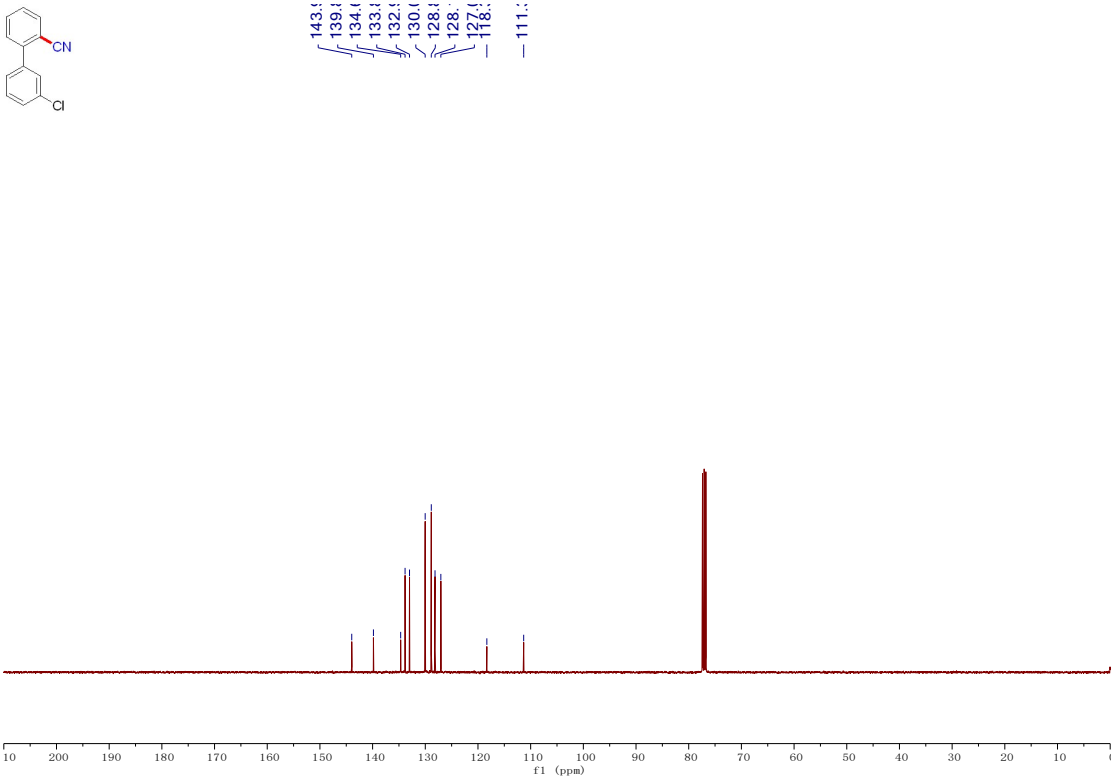
^{13}C NMR of **7** (101 MHz, $CDCl_3$)



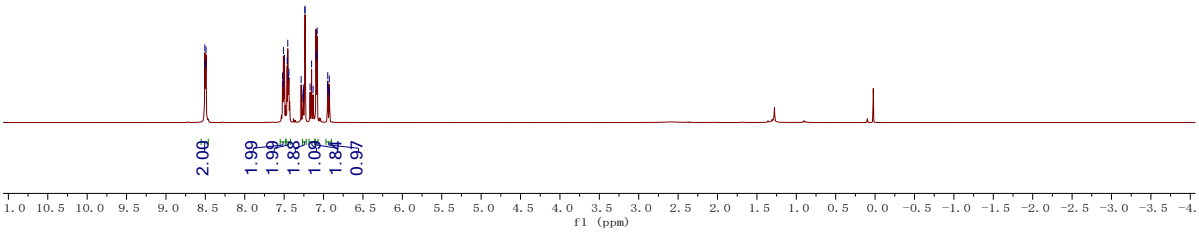
^{1}H NMR of **8** (400 MHz, $CDCl_3$)



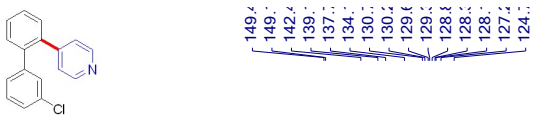
^{13}C NMR of **8** (101 MHz, $CDCl_3$)

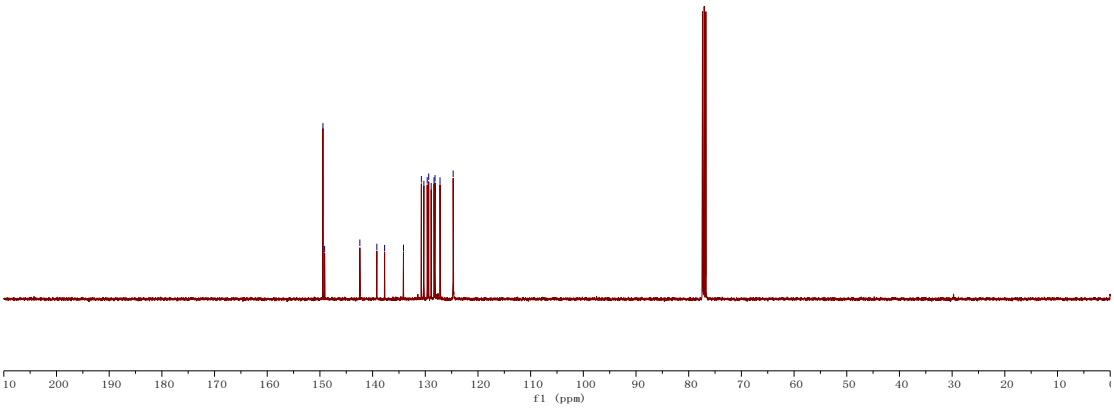


^{1}H NMR of **9** (400 MHz, $CDCl_3$)

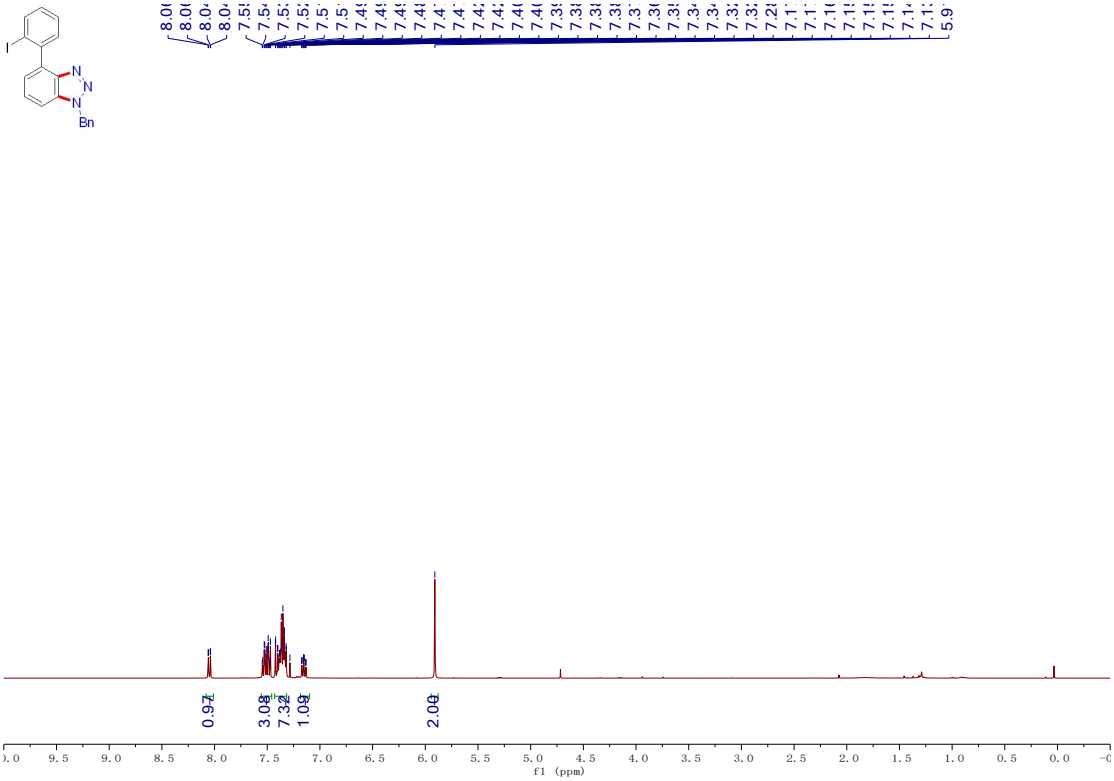


^{13}C NMR of **9** (101 MHz, $CDCl_3$)

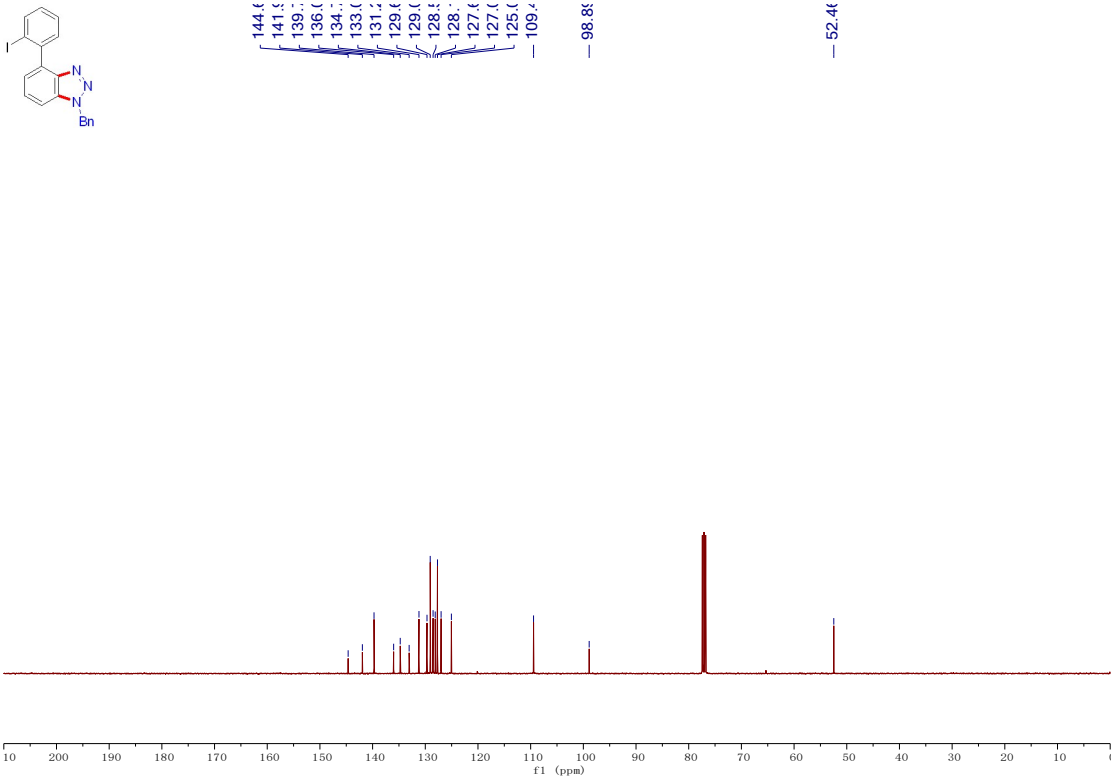




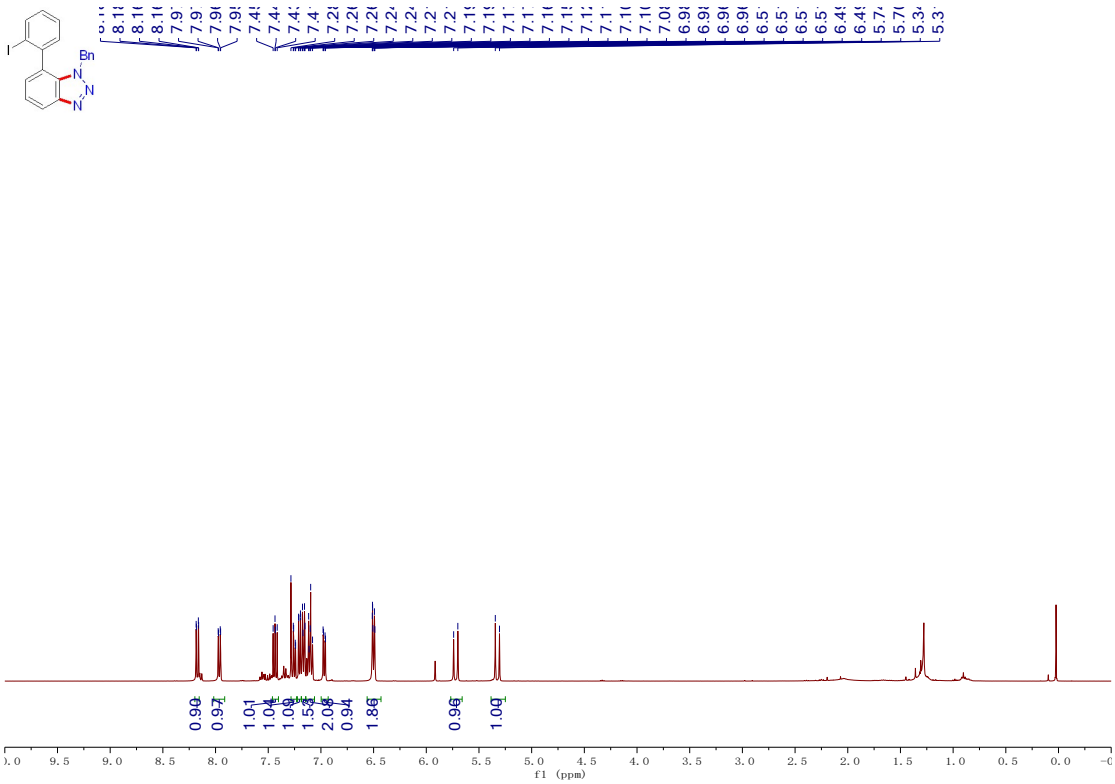
^{1}H NMR of **10** (400 MHz, $CDCl_3$)



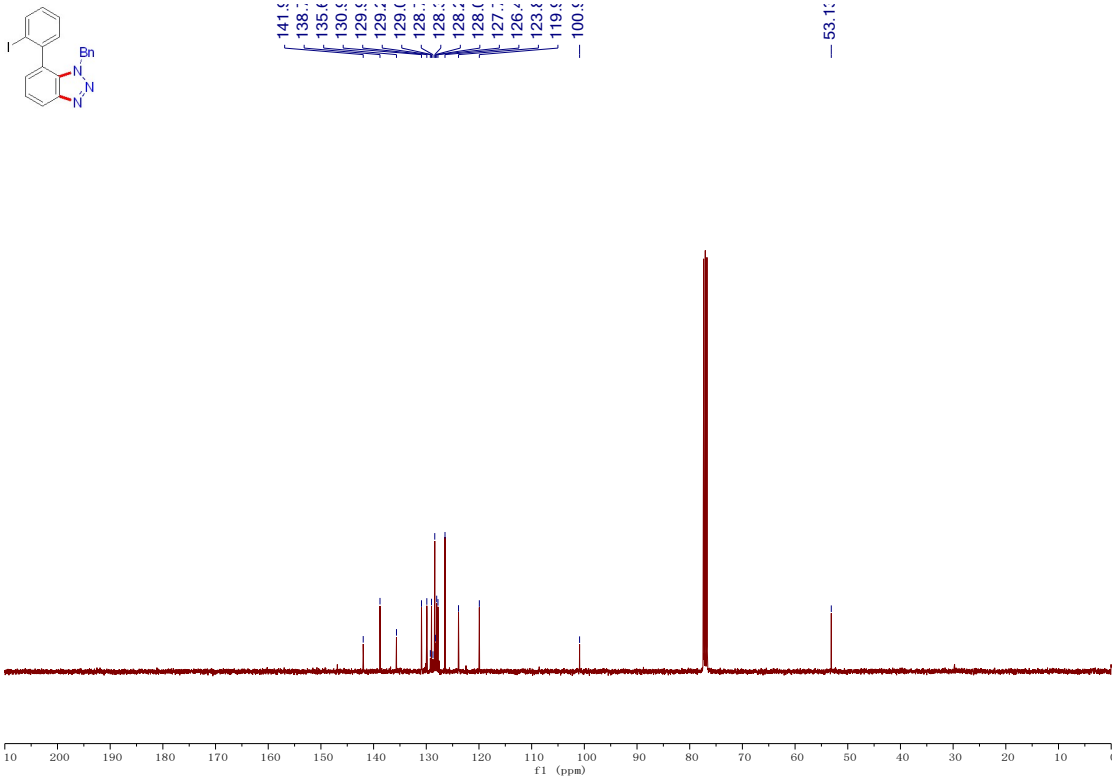
^{13}C NMR of **10** (101 MHz, $CDCl_3$)



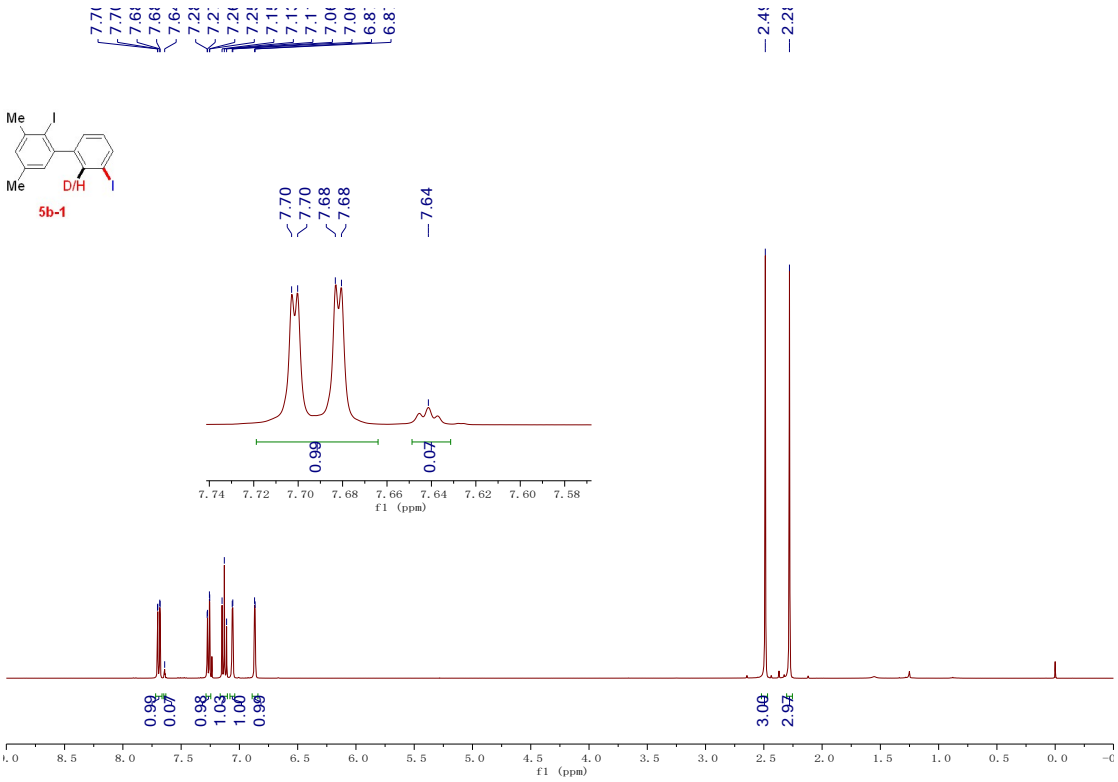
^{1}H NMR of **11** (400 MHz, $CDCl_3$)



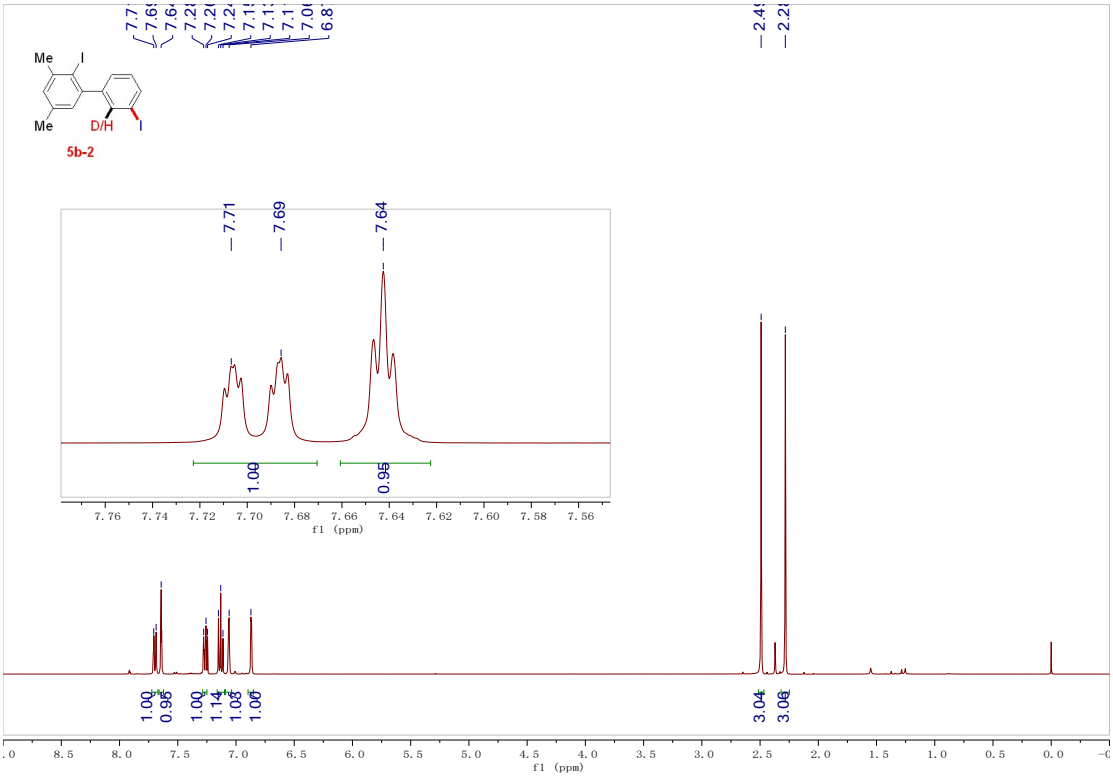
^{13}C NMR of **11** (101 MHz, $CDCl_3$)



^{1}H NMR of **5b-1** (400 MHz, $CDCl_3$)



^{1}H NMR of **5b-2** (400 MHz, $CDCl_3$)



^{1}H NMR of **5b-3** (400 MHz, $CDCl_3$)