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SUPPORTING INFORMATION

A Bottleable Super-Electron-Donor for Catalytic Borylation of Aryl Halides

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I. General Information

Super-electron-donor catalyst **G** were prepared based on previous report.[1] Other reagents were purchased from Sigma-Aldrich, Alfa-Aesar, TCI, Energy-Chemical or Bidepharm, and were checked for purity by GC-MS and/or ^{1}H NMR spectroscopy and used as received. HPLC grade solvents were argon saturated, dried using an Innovative Technology Inc. Solvent Purification System, and further deoxygenated by using the freeze-pump-thaw method. $CDCl_3$ was purchased from Cambridge Isotope Laboratories. All manipulations in this paper were performed in an argon-filled glove box unless otherwise stated.

GC-MS analyses were performed using an Agilent 7820A gas chromatograph [column: HP-5MS 5% phenyl methyl siloxane, 30 m, ø 0.25 mm, film 0.25 μm; injector: 250 °C; oven: 60 °C (2 min), 60 °C to 280 °C (55 °C min^{-1}), 280 °C (2 min); carrier gas: He (1.2 mL min^{-1})] equipped with an Agilent 5977B inert MSD with triple-axis detector operating in EI mode. High resolution mass spectrometry (HRMS) was performed with a Thermo Fisher Scientific Q-Exactive MS System.

All oxygen or moisture-free operation were conducted under argon atmosphere in Schlenk line or in a glove box. Automated flash chromatography was performed using a Biotage® Isolera One system on boric acid-impregnated silica gel[2]. The removal of solvent was performed on a rotary evaporator in vacuo at a maximum temperature of 40 °C.

NMR spectra were recorded at ambient temperature using a Bruker Avance III HD 400 NMR (^{1}H, 400 MHz; $^{13}C\{^{1}H\}$, 101 MHz; ^{11}B, 128 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonance of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas $^{13}C\{^{1}H\}$ NMR spectra are reported relative to TMS via the carbon signal of the deuterated solvent ($CDCl_3$: 77.00 ppm). ^{11}B NMR chemical shifts are quoted relative to $BF_3{\cdot}Et_2O$ as the external standard. ^{19}F NMR chemical shifts are quoted relative to $CFCl_3$ as the external standard.

II. Detailed Optimization Studies

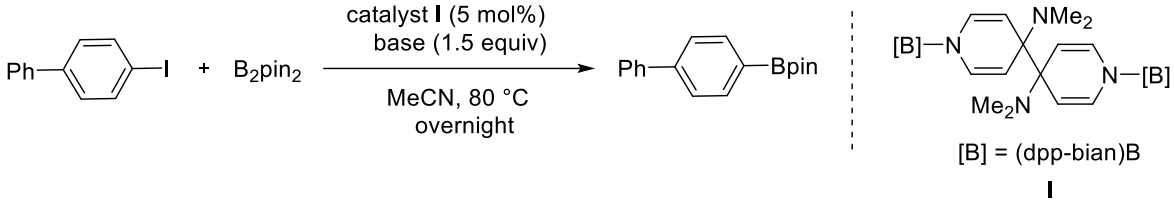
General procedures for optimization

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, 4-iodobiphenyl (**1a**, 1.0 equiv, 0.2 mmol, 56.0 mg), catalyst (5 mol %, 0.01 mmol), B_2pin_2 (1.5 equiv, 0.3 mmol, 76.2 mg), base (1.5 equiv, 0.3 mmol), and solvent (1 mL) were added in this order. Then, the tube was sealed with a Teflon cap and stirred at a certain temperature overnight. GC yields of product **2a** were determined by GC-MS using naphthalene as the internal calibration standard. The reaction mixture was then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm) in air with copious washing (Et_2O). The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (hexane: Et_2O = 500:1). Isolated yields are given in parentheses.

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, iodobenzene (**1i**, 1.0 equiv, 0.2 mmol, 40.0 mg), catalyst (5 mol %, 0.01 mmol), Bpin-Bdan (1.5 equiv, 0.3 mmol, 88 mg), base (1.5 equiv, 0.3 mmol), and solvent (1 mL) were added in this order. Then, the tube was sealed with a Teflon cap and stirred at certain temperature for overnight. GC yields of product **3a** were determined by GC-MS using naphthalene as the internal calibration standard. The reaction mixture was then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm) in air with copious washing (Et_2O). The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (pentane: Et_2O = 500:1). Isolated yields are given in parentheses.

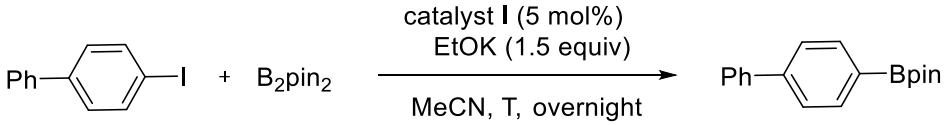
Optimization tables

Table S1. Screening of bases for the SED-catalyzed borylation of aryl iodides

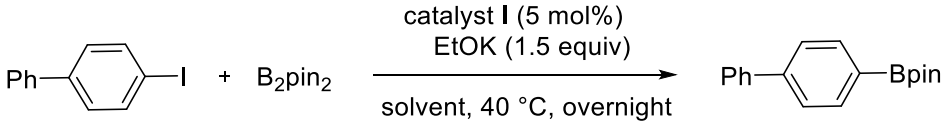


Entry	base	yield (%)
1	MeOK	38
2	EtOK	47
3	^{t}BuOK	25
4	EtONa	4
5	KF	0
6	MeONa	31
7	^{t}BuONa	13
8	^{t}BuOLi	5
9	KOH	trace
10	K_2CO_3	7

Table S2. Screening of reaction temperatures and solvent for the SED-catalyzed borylation of aryl iodides.



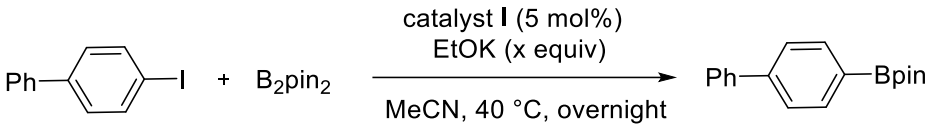
Entry	T (°C)	yield (%)
1	80	47
2	60	64
3	40	95 (86)
4	rt	88



Entry	solvent	yield (%)
1	DCM	0
2	THF	0
3	MTBE	0
4	toluene	0
5	hexane	0
6	DMF	13

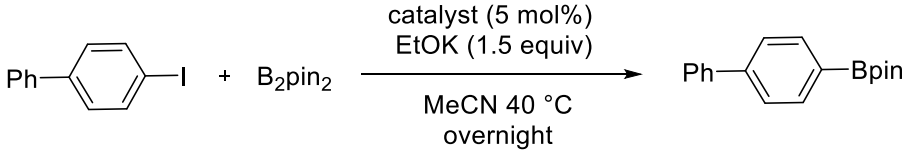
Table S3. Screening of the amount of B_2pin_2 and base for the SED-catalyzed

borylation of aryl iodides



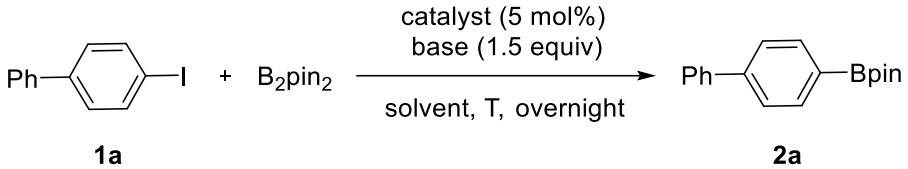
Entry	B_2pin_2	EtOK	yield (%)
1	1.1 equiv	1.1 equiv	72
2	1.2 equiv	1.2 equiv	76

Table S4. Screening of the type of catalyst for the SED-catalyzed borylation of aryl iodides



Entry	catalyst	yield (%)
1	DMAP	0
2	-	0

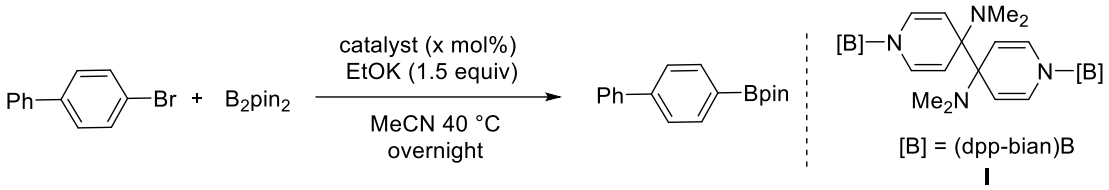
Table S5. Screening of the reaction condition optimization for the SED-Catalyzed borylation of aryl iodides



Entry	Catalyst	T (°C)	Base	Solvent	Yield (%)[a]
1	**I**	80	MeOK	MeCN	38
2	**I**	80	EtOK	MeCN	47
3	**I**	80	^{t}BuOK	MeCN	25
4	**I**	80	EtONa	MeCN	4
5	**I**	80	KF	MeCN	0
6	**I**	60	EtOK	MeCN	64
7	**I**	40	EtOK	MeCN	95 (86)
8	**I**	rt	EtOK	MeCN	88
9	**I**	40	EtOK	THF	0
10	**I**	40	EtOK	toluene	0
11	DMAP	40	EtOK	MeCN	0
12	-	40	EtOK	MeCN	0

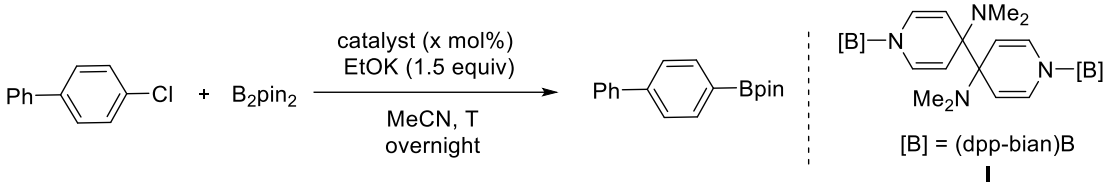
Reaction conditions: **1a** (0.2 mmol), catalyst (5 mol%), B_2pin_2 (1.5 equiv, 0.3 mmol, 76.2 mg), base (1.5 equiv, 0.3 mmol), solvent (1 mL). [a]Yields were determined by GC-MS using naphthalene as the internal calibration standard, and isolated yields are given in parentheses.

Table S6. Optimization of the SED-Catalyzed borylation of aryl bromides



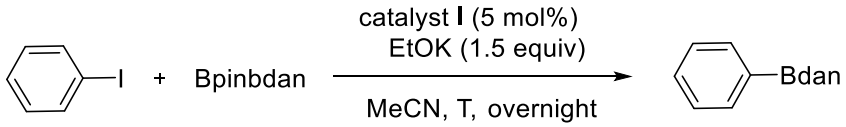
Entry	catalyst	T (°C)	yield (%)
1	**I** (5 mol%)	40	63
2	**I** (5 mol%)	60	79
3	**I** (5 mol%)	80	59
4	**I** (5 mol%)	100	38
5	**I** (10 mol%)	60	89

Table S7. Optimization of the SED-Catalyzed borylation of aryl chlorides



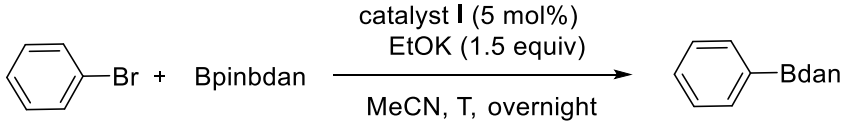
Entry	catalyst	T (°C)	yield (%)
1	**I** (5 mol%)	40	21
2	**I** (5 mol%)	60	37
3	**I** (5 mol%)	80	62
4	**I** (5 mol%)	100	41
5	**I** (10 mol%)	80	78

Table S8 Screening of reaction temperatures for the SED-catalyzed B(dan)-installing reaction of aryl iodides



Entry	T (°C)	yield (%)
1	40	80
2	60	76
3	80	87
4	100	89
5	120	83

Table S9 Screening of reaction temperatures for the SED-catalyzed B(dan)-installing reaction of aryl bromides



Entry	T (°C)	yield (%)
1	60	50
2	80	76
3	100	82
4	120	80

III. Substrate Scope

Experimental Procedures

General procedures for the SED-catalyzed borylation of (hetero)aryl iodides and alkyl iodides

In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, aryl iodides (1.0 equiv, 0.2 mmol), catalyst **I** (5 mol %, 0.01 mmol, 12.7 mg), B_2pin_2 (1.5 equiv, 0.3 mmol, 76.2 mg), EtOK (1.5 equiv, 0.3 mmol, 25.2 mg), and MeCN (1 mL) were added in this order. Then, the tube was sealed with a Teflon cap and stirred at 40 °C for overnight. The reaction mixture was then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm) in air with copious washing (Et_2O).

Preparation of **2a**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (hexane: Et_2O = 500:1 v/v).

Preparation of **2b**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (hexane: Et_2O = 500:1 v/v).

Preparation of **2c**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (pentane).

Preparation of **2d**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (pentane: Et_2O = 500:1 v/v).

Preparation of **2e**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (hexane: Et_2O = 250:1 v/v).

Preparation of **2f**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (hexane: Et_2O = 500:1 v/v).

Preparation of **2g**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (pentane).

Preparation of **2h**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (hexane: Et_2O = 500:1 v/v).

Preparation of **2i**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (hexane: Et_2O = 500:1 v/v).

Preparation of **2j**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (hexane: Et_2O = 250:1 v/v).

Preparation of **2k**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (hexane).

Preparation of **2l**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (hexane).

Preparation of **2n**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (pentane: Et_2O = 500:1 v/v).

Preparation of **2o**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (pentane: Et_2O = 500:1 v/v).

Preparation of **2p**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (pentane: Et_2O = 500:1 v/v).

Preparation of **3a**. The reaction was performed following the general procedure (The reaction temperature was elevated to 100 °C). The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (pentane: Et_2O = 500:1 v/v).

Preparation of **3b**. The reaction was performed following the general procedure (The reaction temperature was elevated to 100 °C). The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (pentane: Et_2O = 500:1 v/v).

Preparation of **3c**. The reaction was performed following the general procedure (The reaction temperature was elevated to 100 °C). The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (pentane).

Preparation of **3d**. The reaction was performed following the general procedure (The reaction temperature was elevated to 100 °C). The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (pentane: Et_2O = 500:1 v/v).

Preparation of **3e**. The reaction was performed following the general procedure (The reaction temperature was elevated to 100 °C). The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (pentane: Et_2O = 500:1 v/v).

General procedures for the SED-catalyzed borylation of aryl bromides

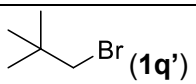
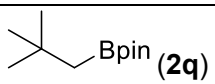
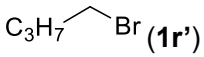
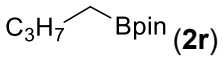
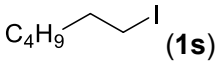
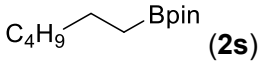
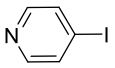
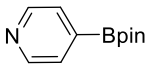
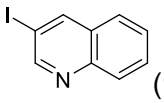
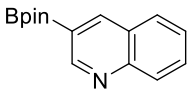
In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, aryl iodides (1.0 equiv, 0.2 mmol), catalyst **I** (5 mol %, 0.01 mmol, 12.7 mg), B_2pin_2 (1.5 equiv, 0.3 mmol, 76.2 mg), EtOK (1.5 equiv, 0.3 mmol, 25.2 mg), and MeCN (1 mL) were added in this order. Then, the tube was sealed with a Teflon cap and stirred at 60 °C for overnight. The reaction mixture was then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm) in air with copious washing (Et_2O).

Preparation of **2m**. The reaction was performed following the general procedure. The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (hexane).

General procedures for the SED-catalyzed borylation of aryl chlorides

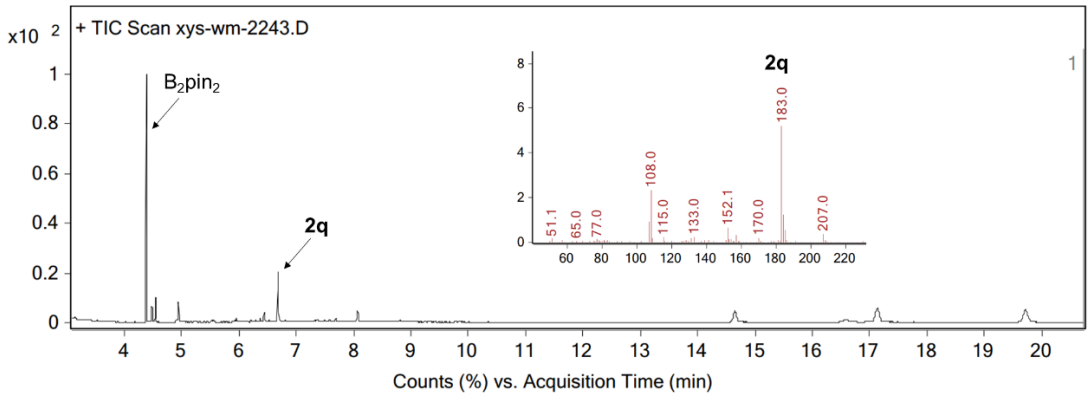
In a 10 mL thick-walled reaction tube equipped with a magnetic stirring bar, aryl iodides (1.0 equiv, 0.2 mmol), catalyst **I** (5 mol %, 0.01 mmol, 12.7 mg), B_2pin_2 (1.5 equiv, 0.3 mmol, 76.2 mg), EtOK (1.5 equiv, 0.3 mmol, 25.2 mg), and MeCN (1 mL) were added in this order. Then, the tube was sealed with a Teflon cap and stirred at 80 °C for overnight. The reaction mixture was then diluted with Et_2O (2 mL) and filtered through a plug of celite (Ø 3 mm × 8 mm) in air with copious washing (Et_2O). The solvents were removed in vacuo, and the residue was purified by column chromatography on boric acid-impregnated silica gel[2] (hexane:Et_2O = 500:1).

Table S10 SED-catalyzed borylation of heteroaryl and alkyl halides 1q'-1u

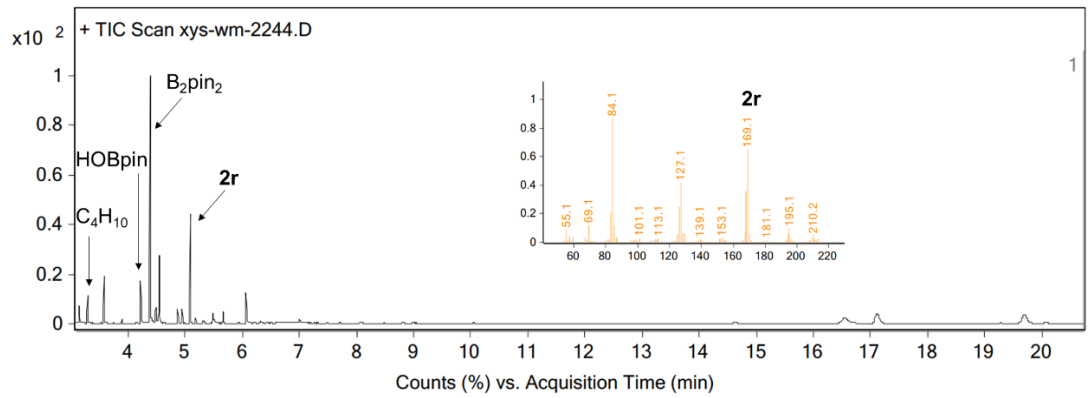
Entry	Substrate	Target product	Yield (%)[a]
1	 (**1q'**)	 (**2q**)	25%
2	 (**1r'**)	 (**2r**)	27%
3	 (**1s**)	 (**2s**)	6%
4	 (**1t**)	 (**2t**)	59%[b]
5	 (**1u**)	 (**2u**)	58%[b]

[a]Yields were determined by GC-MS using naphthalene as the internal calibration standard. Standard conditions: **1** or **1'** (0.2 mmol), catalyst **I** (5 or 10 mol%, 0.01 mmol), B_2pin_2 (1.5 equiv, 0.3 mmol), EtOK (1.5 equiv, 0.3 mmol), MeCN (1 mL), 40-80 °C, overnight.

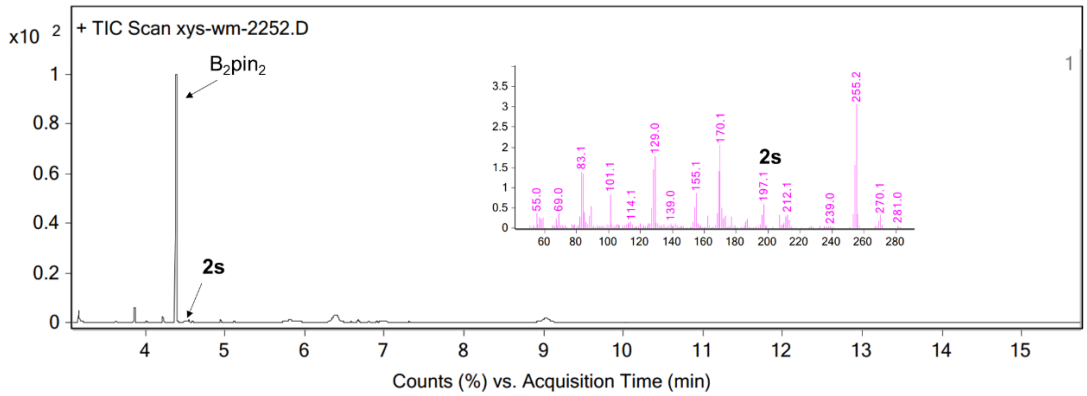
[b]Relative low yield due to incomplete conversion of halide substrate.



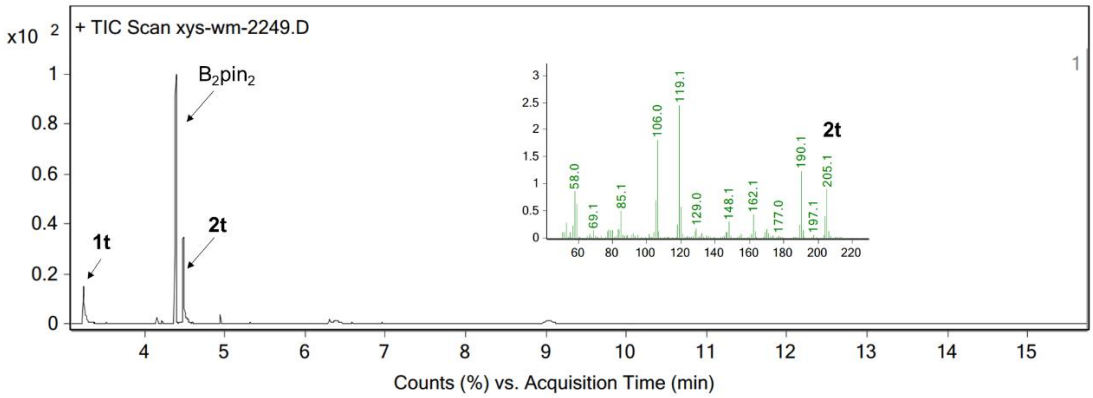
GC-MS spectrum for entry 1 of Table S10



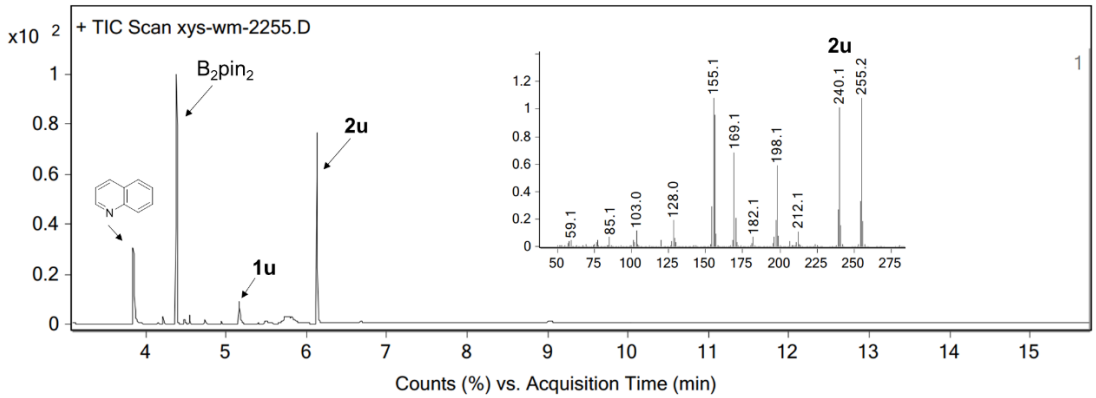
GC-MS spectrum for entry 2 of Table S10



GC-MS spectrum for entry 3 of Table S10

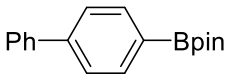


GC-MS spectrum for entry 4 of Table S10



GC-MS spectrum for entry 5 of Table S10

Compound Characterization

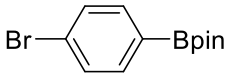


2-([1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.1 Hz, 2H), 7.67–7.58 (m, 4H), 7.50–7.42 (m, 2H), 7.41–7.32 (m, 1H), 1.38 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.0, 141.2, 135.4, 128.9, 127.7, 127.4, 126.6, 84.0, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.0.

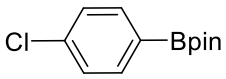


2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 1.34 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.4, 131.1, 126.4, 84.2, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.9.



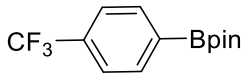
2-(4- chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2c**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 7.2 Hz, 2H), 1.34 (s,

12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 137.5, 136.1, 128.0, 84.0, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6.



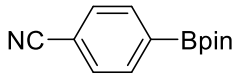
2-(4- (trifluoromethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2d**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.2 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 1.35 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 135.1, 133.0 (C–F, q, J_{CF} = 30.3 Hz), 124.4 (C–F, q, J_{CF} = 10 Hz), 124.4 (C–F, q, J_{CF} = 10 Hz), 124.2 (C–F, q, J_{CF} = 272.7 Hz), 84.2, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7.

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ – 63.1.

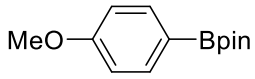


4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (**2e**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 1.35 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 135.1, 131.1, 118.9, 114.5, 84.5, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6.

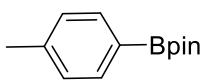


2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2f**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 162.3, 136.6, 113.4, 83.7, 55.2, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5.



2-(p-tolyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2g**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8 Hz, 2H), 7.19 (d, J = 7.6 Hz, 2H), 2.36 (s, 3H), 1.34 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.4, 134.8, 128.5, 83.6, 24.8, 21.7.

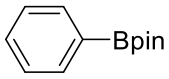
^{11}B NMR (128 MHz, $CDCl_3$) δ 30.8.

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**2h**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 6.66 (d, J = 8.5 Hz, 2H), 3.83 (s, 2H), 1.32 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.4, 136.6, 114.2, 83.4, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.8.

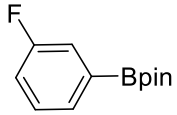


4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (**2i**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.1 Hz, 2H), 7.45 (t, 8.2 Hz, 1H), 7.35 (t, 7.4 Hz, 2H), 1.34 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 134.9, 131.4, 127.8, 83.9, 25.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.9.



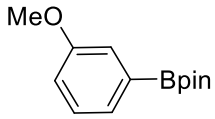
2-(3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2j**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.2 Hz, 1H), 7.50 (q, J = 2.4 Hz, 1H), 7.36 (dd, J = 13.2, 7.6 Hz, 1H), 7.16 (t, J = 8 Hz, 1H), 1.37 (s, 12H). (The peaks at 1.2 and 0.8 ppm are from the residual hexane.)

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 130.3 (C–F, d, J_{CF} = 30.3 Hz), 129.5 (C–F, d, J_{CF} = 70.7 Hz), 123.1 (C–F, d, J_{CF} = 74.7 Hz), 120.9 (C–F, d, J_{CF} = 19.2 Hz), 118.2 (C–F, d, J_{CF} = 21.2 Hz), 84.1, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7.

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ – 114.2.

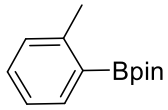


2-(3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2k**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 7.2 Hz, 1H), 7.31 (d, J = 2.8 Hz, 1H), 7.29 (t, J = 8 Hz, 1H), 7.01 (q, J = 2 Hz, 1H), 3.83 (s, 3H), 1.34 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 159.0, 128.9, 127.1, 118.6, 117.9, 83.8, 55.2, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.0.

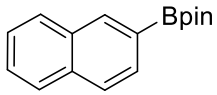


2-(o-tolyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2l**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.19 (t, J = 6 Hz, 2H), 2.58 (s, 3H), 1.38 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 144.8, 135.8, 130.8, 129.8, 124.7, 83.4, 24.9, 22.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.3.

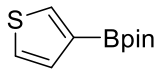


2-(naphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2m**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.83 (s, 3H), 7.49 (m, J = 8 Hz, 2H), 1.40 (s, 12H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 136.1, 134.9, 132.7, 130.3, 128.5, 127.6, 126.8, 125.7, 83.8, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.2.

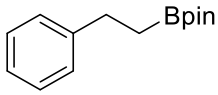


4,4,5,5-tetramethyl-2-(thiophen-3-yl)-1,3,2-dioxaborolane (**2n**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.0 Hz, 1H), 7.41 (d, *J* = 4.8 Hz, 1H), 7.35 (d, *J* = 2.8 Hz, 3H), 1.34 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.5, 132.0, 125.3, 83.7, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.1.

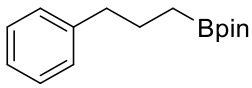


4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (**2o**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.2 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 2.78 (t, *J* = 8.4 Hz, 2H), 1.25 (s, 12H), 1.18 (t, *J* = 8.4 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.4, 128.2, 128.0, 125.5, 83.1, 30.0, 29.7, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.0.

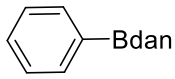


4,4,5,5-tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (**2p**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 3H), 2.63 (t, *J* = 7.6 Hz, 1H), 2.78 (t, *J* = 8.4 Hz, 2H), 1.76 (m, 2H), 1.27 (s, 12H), 0.85 (t, *J* = 8.0 Hz, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.3, 128.9, 128.0, 125.6, 83.0, 39.0, 26.1, 24.9, 15.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 34.2.



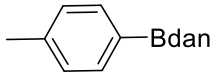
2-phenyl-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (**3a**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J*=1.6, 7.6 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.43 (dd, *J*=7.2, 8.0 Hz, 2H), 6.04 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.1, 136.3, 131.4, 130.3, 128.3, 127.6, 119.8, 117.8, 106.0.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.3.

HRMS $[M+H]^+$, $C_{16}H_{14}N_2B$: 245.12421 (calc.: 245.12500).



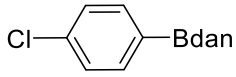
2-(p-tolyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (**3b**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 6.8 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 6.42 (dd, *J*= 0.8, 7.2 Hz, 2H), 6.03 (s, 2H), 2.41 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.2, 140.4, 136.4, 131.5, 129.1, 127.6, 119.8, 117.7, 106.0, 29.7.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.4.

HRMS $[M+H]^+$, $C_{17}H_{16}N_2B$: 259.13980 (calc.: 259.14065).



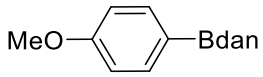
2-(4-chlorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (**3c**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J*= 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.42 (dd, *J* = 0.8, 7.2 Hz, 2H), 5.99 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.8, 135.4, 135.3, 131.8, 127.5, 126.6, 118.8, 117.0, 105.1.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.6.

HRMS $[M+H]^+$, $C_{16}H_{13}N_2BCl$: 279.08484 (calc.: 279.08603).



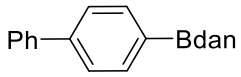
2-(4-methoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (**3d**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J*= 8.8 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 8.0 Hz, 2H), 6.02 (s, 2H), 3.89 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.4, 141.2, 136.3, 133.0, 127.6, 119.6, 117.6, 113.9, 105.9, 55.2.

^{11}B NMR (128 MHz, $CDCl_3$) δ 29.1.

HRMS $[M+H]^+$, $C_{17}H_{16}ON_2B$: 275.13440 (calc.: 275.13557).



2-([1,1'-biphenyl]-4-yl)-2,3-dihydro-1*H*-naphtho[1,8-*de*][1,3,2]diazaborinine (**3e**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 20.4, 8.0 Hz, 4H), 7.64 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.2 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.16 (t, J = 8.0 Hz, 2H), 7.07 (d, J = 7.6 Hz, 2H), 6.44 (d, J = 7.6 Hz, 2H), 6.08 (s, 2H), 3.89 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.0, 141.1, 136.4, 135.3, 132.0, 128.9, 127.6, 127.2, 127.0, 126.5, 119.9, 117.9, 106.1.

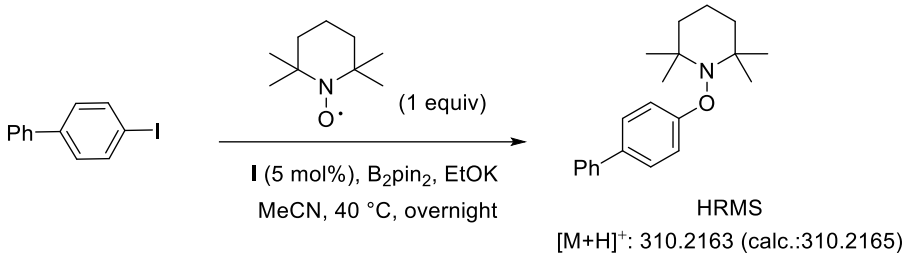
^{11}B NMR (128 MHz, $CDCl_3$) δ 29.7.

HRMS $[M+H]^+$, $C_{22}H_{18}BN_2$: 321.15553 (calc.: 321.15630).

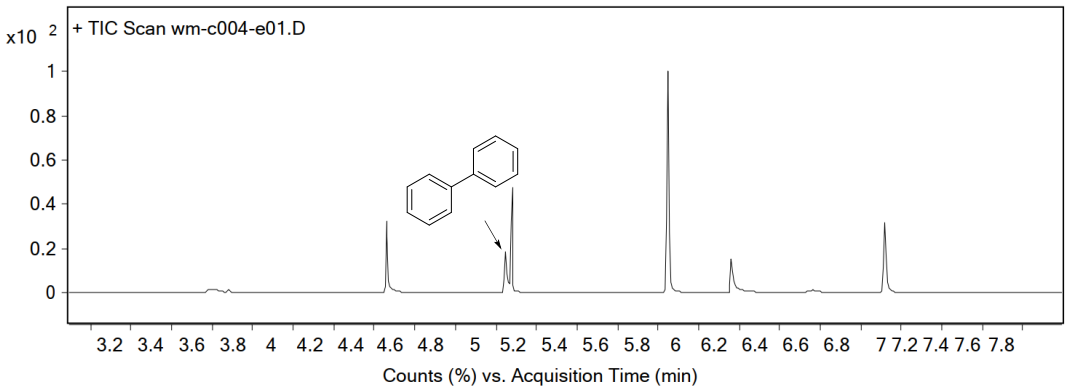
IV. Studies of the Reaction Mechanism

Radical trapping experiment

In radical trapping experiments, stoichiometric TEMPO was added and largely suppressed the reaction, the aryl-TEMPO species was detected by high resolution mass spectroscopy (HRMS) (Table 1 entry 3, Scheme S1). Stoichiometric 9,10-dihydroanthracene was added into the reaction (Table 1 entry 7) diminished the yield of **2a** to 45% and found the formation of diphenyl. Reported the GC-MS spectra for this (Scheme S2).



Scheme S1. The aryl-TEMPO species was detected by HRMS after stoichiometric TEMPO was added into the reaction (Table 1 entry 3)

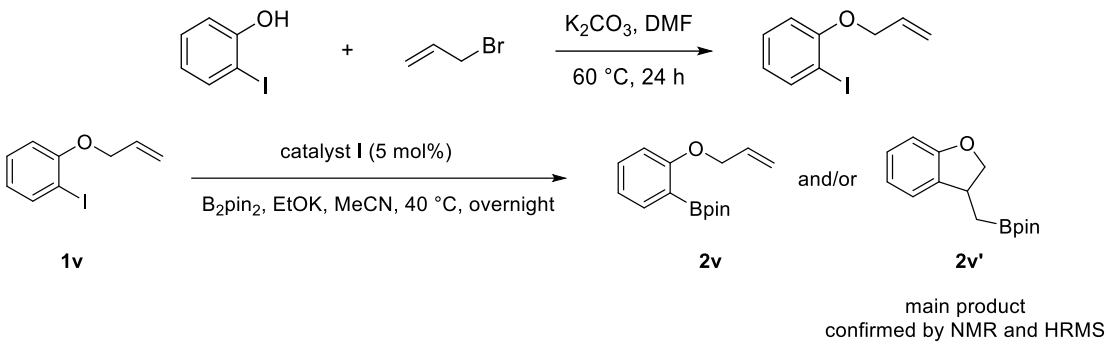


Scheme S2. GC-MS spectrum for radical trapping experiments (Table 1 entry 7)

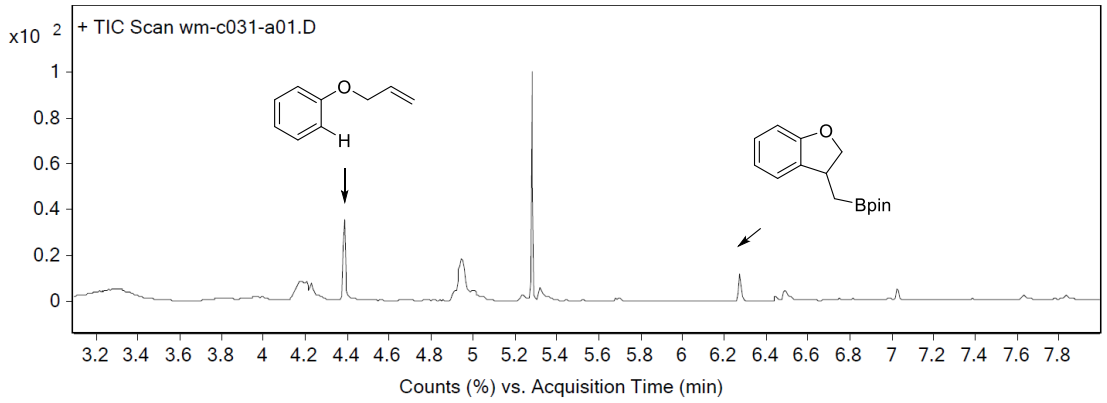
Radical clock experiment

Radical clock substrate **1v** was prepared based on a reported method (Scheme S3, top). Then **1v** was used as a radical substrate for testing the SED-catalyzed borylation under the general procedures (page S7). After the reaction finish, the reaction mixture was diluted with Et_2O (2 mL) and filtered through a plug of celite (ø 3 mm × 8 mm) in air with copious

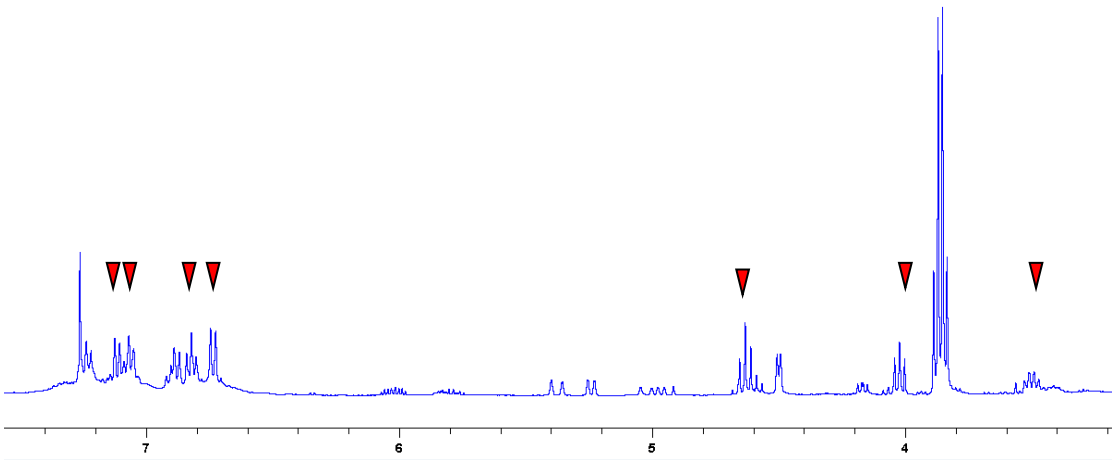
washing (Et_2O). The solvents were removed in vacuo, and GC-MS and NMR were measured for the residue. Reported spectra for **2v**[3] and **2v'**[4].



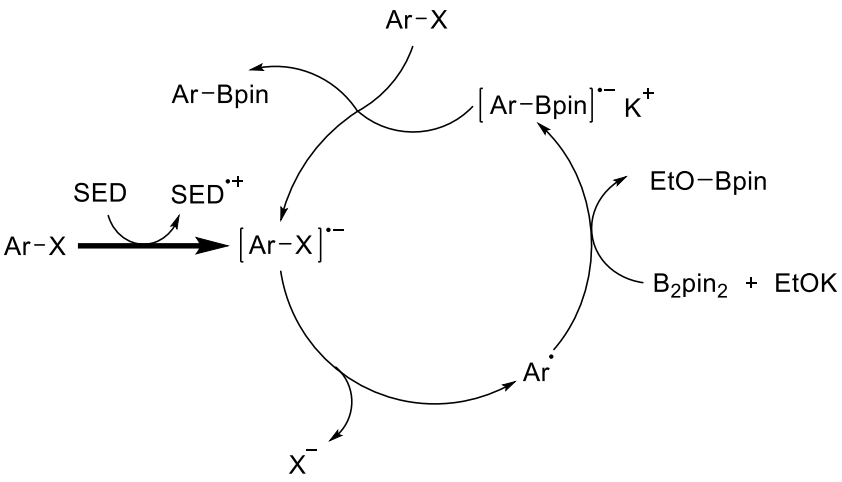
Scheme S3. The preparation of radical clock substrate **1v** and radical clock experiment.

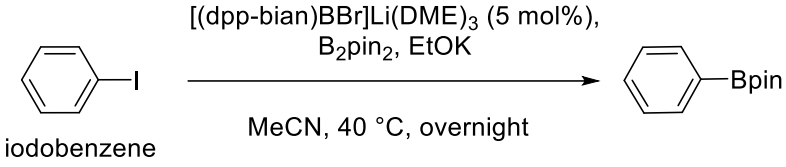


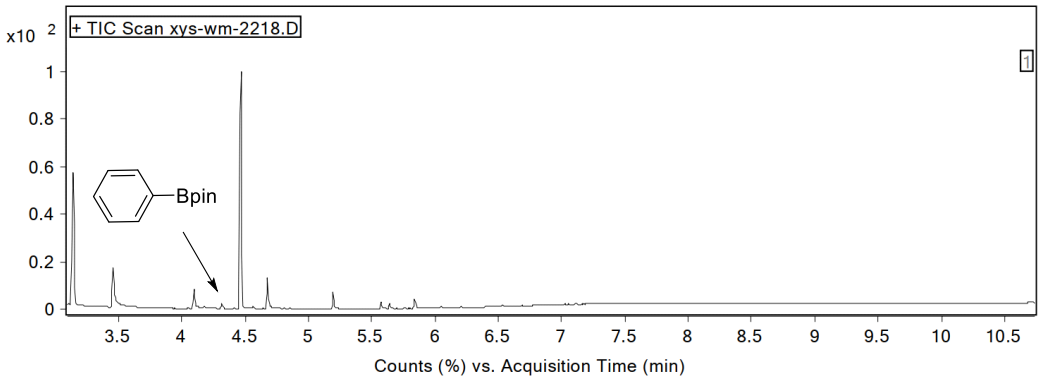
Scheme S4. GC-MS spectrum for radical clock experiment



Scheme S5. ^{1}H-NMR spectrum for radical clock experiment



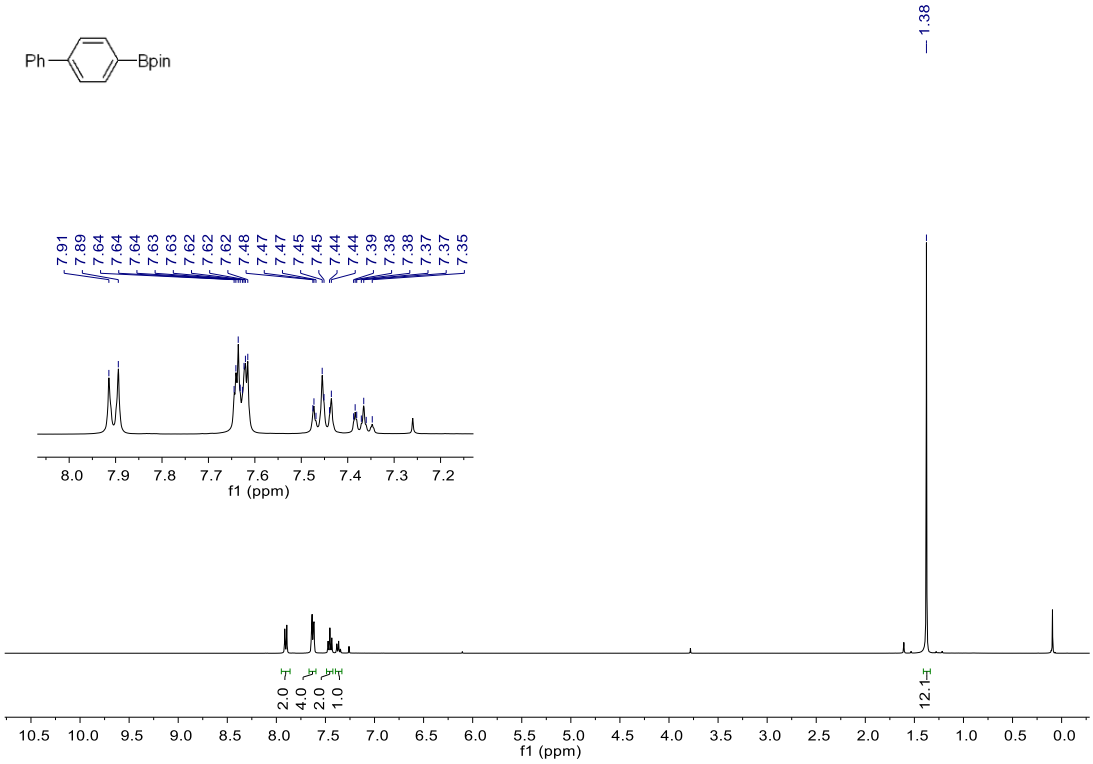




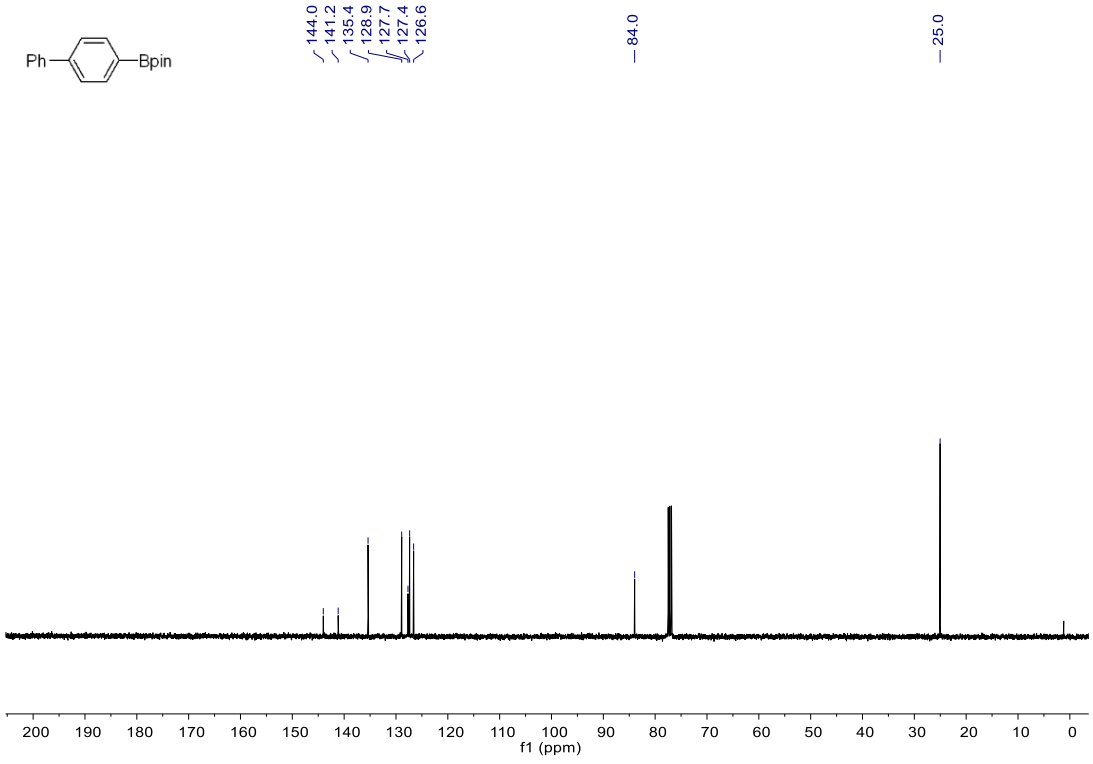
Scheme S6. Another possible mechanism and the control experiment

V. NMR Spectra of Products

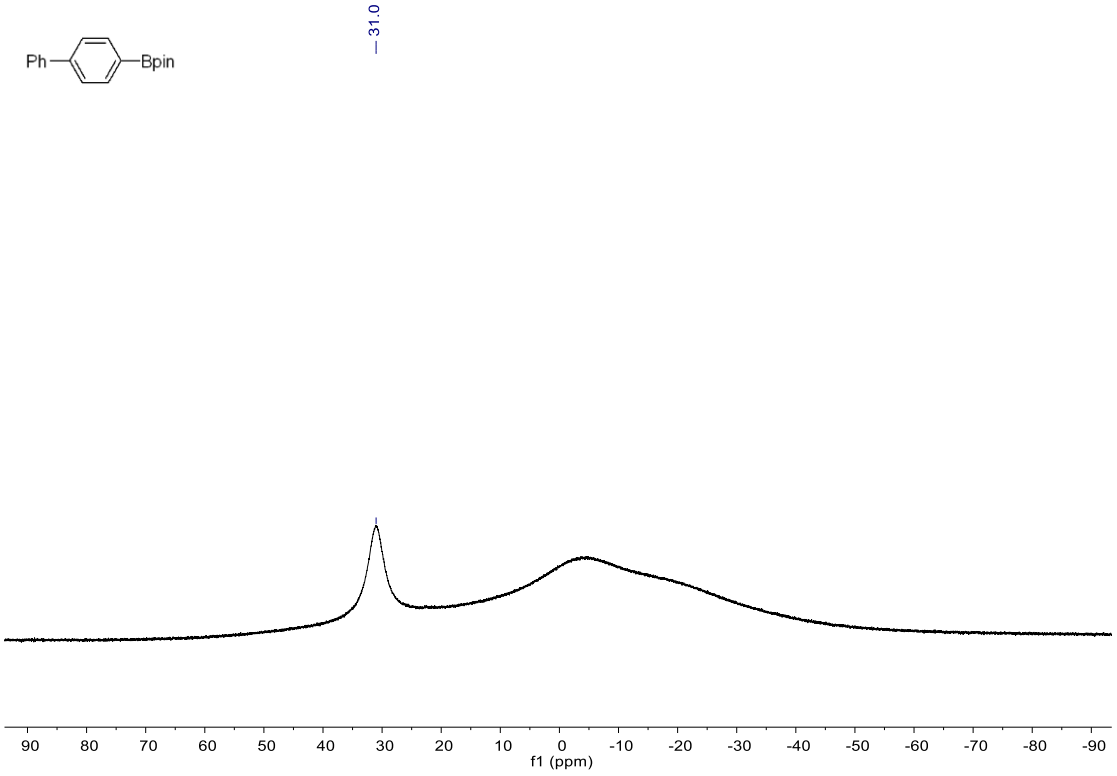
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2a**



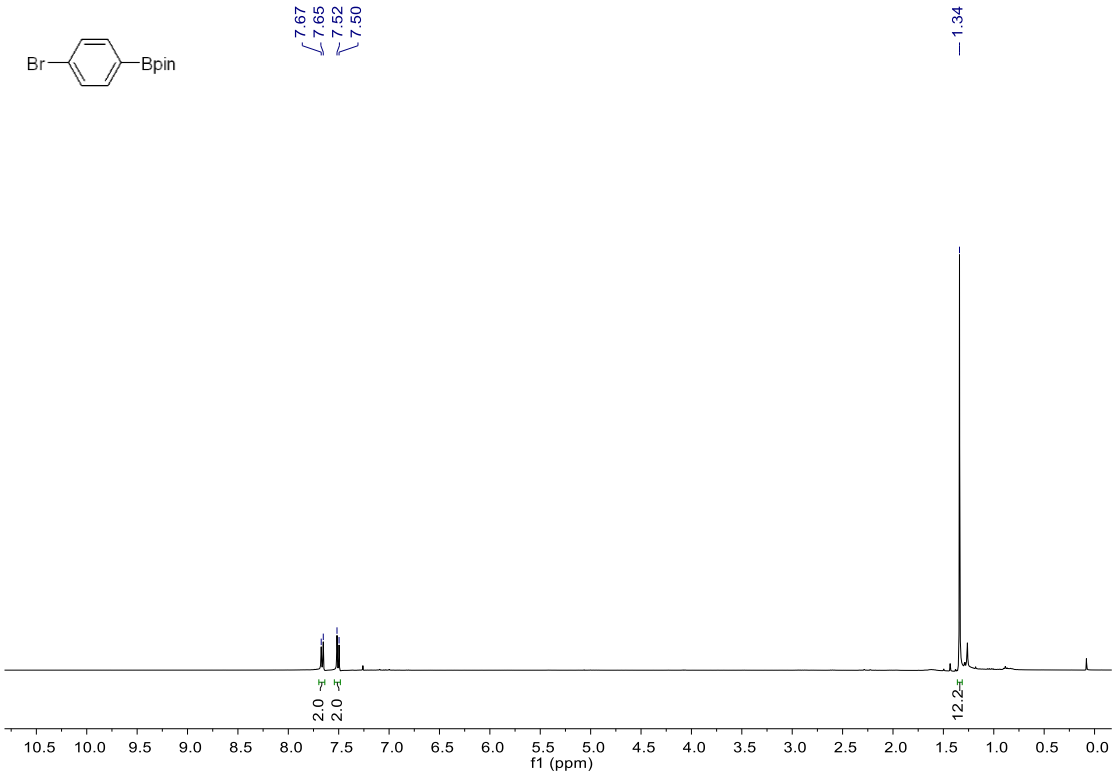
$^{13}C\{^1H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2a**



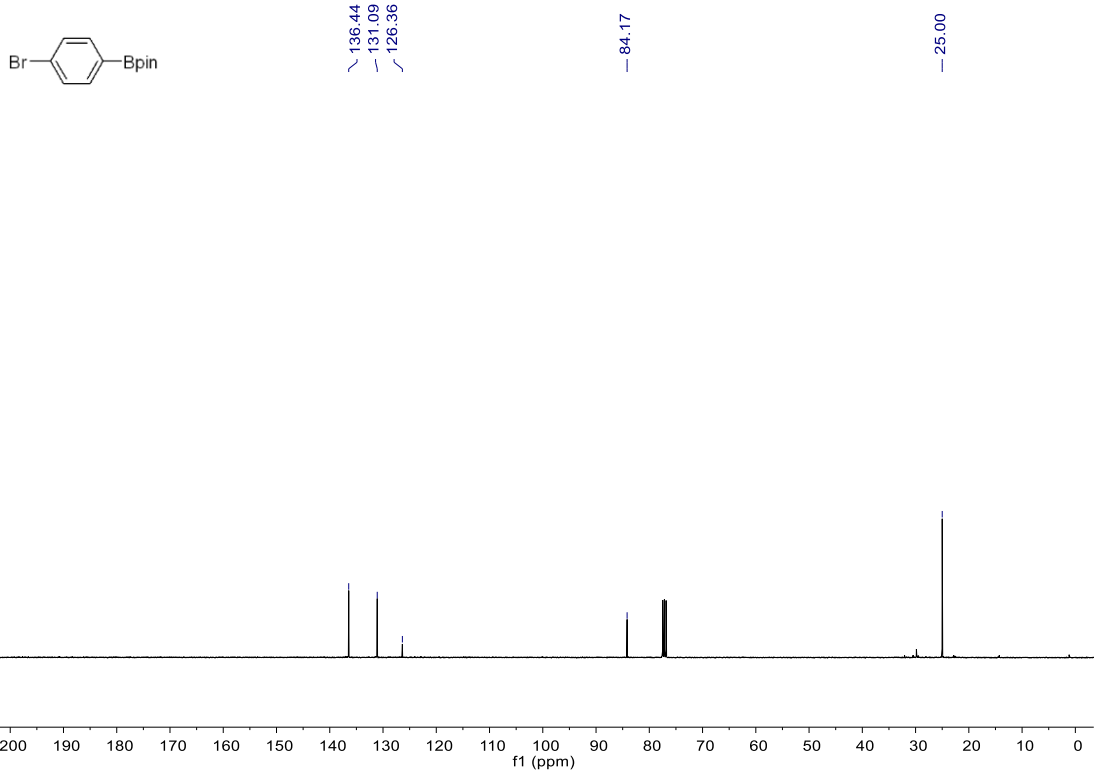
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2a**



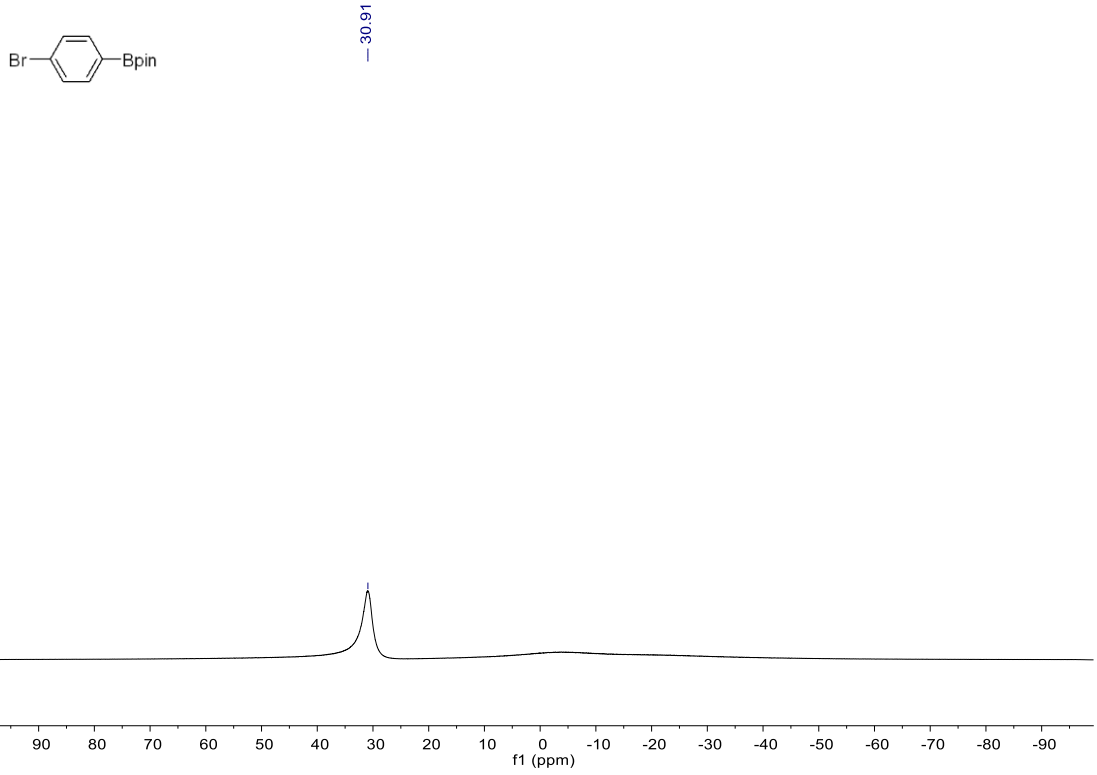
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2b**



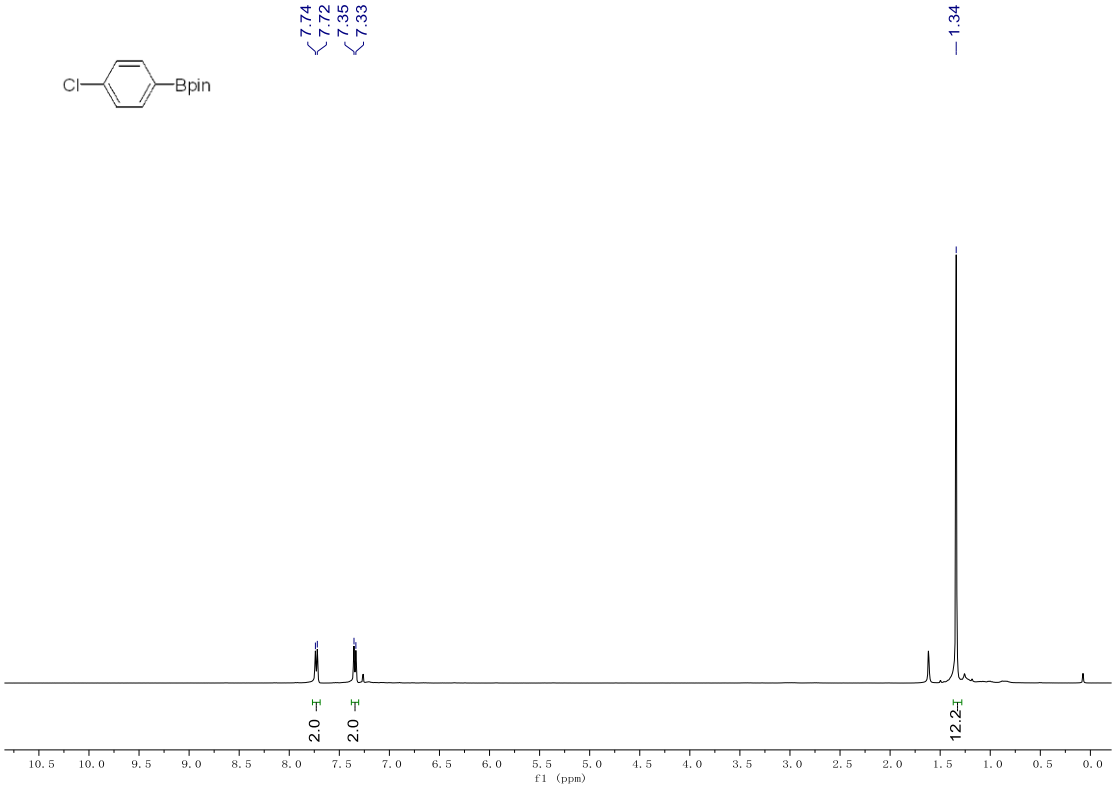
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2b**



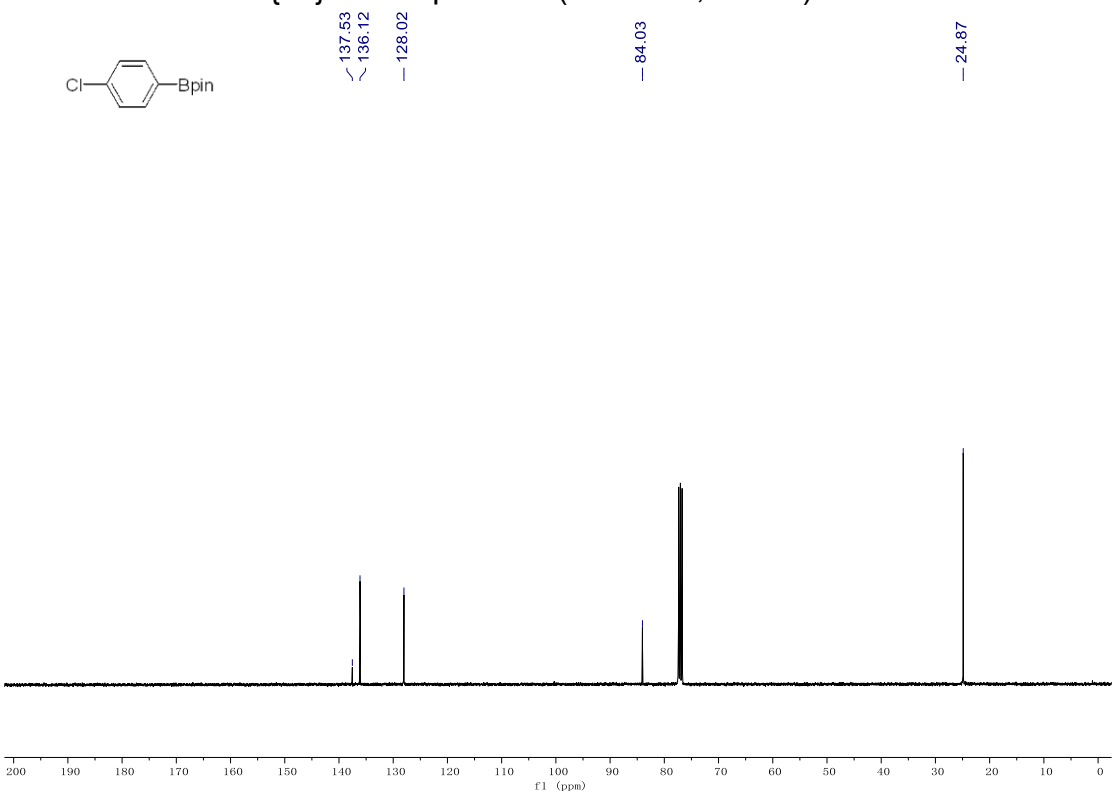
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2b**



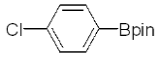
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2c**



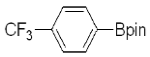
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2c**



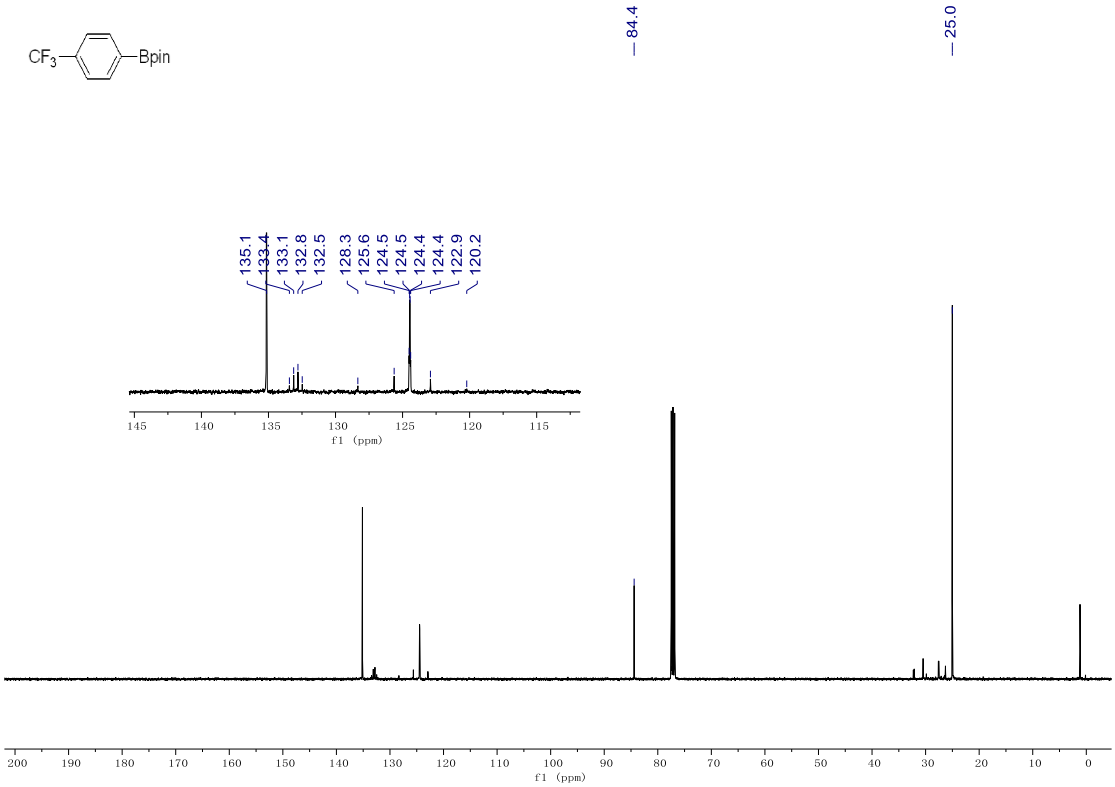
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2c**



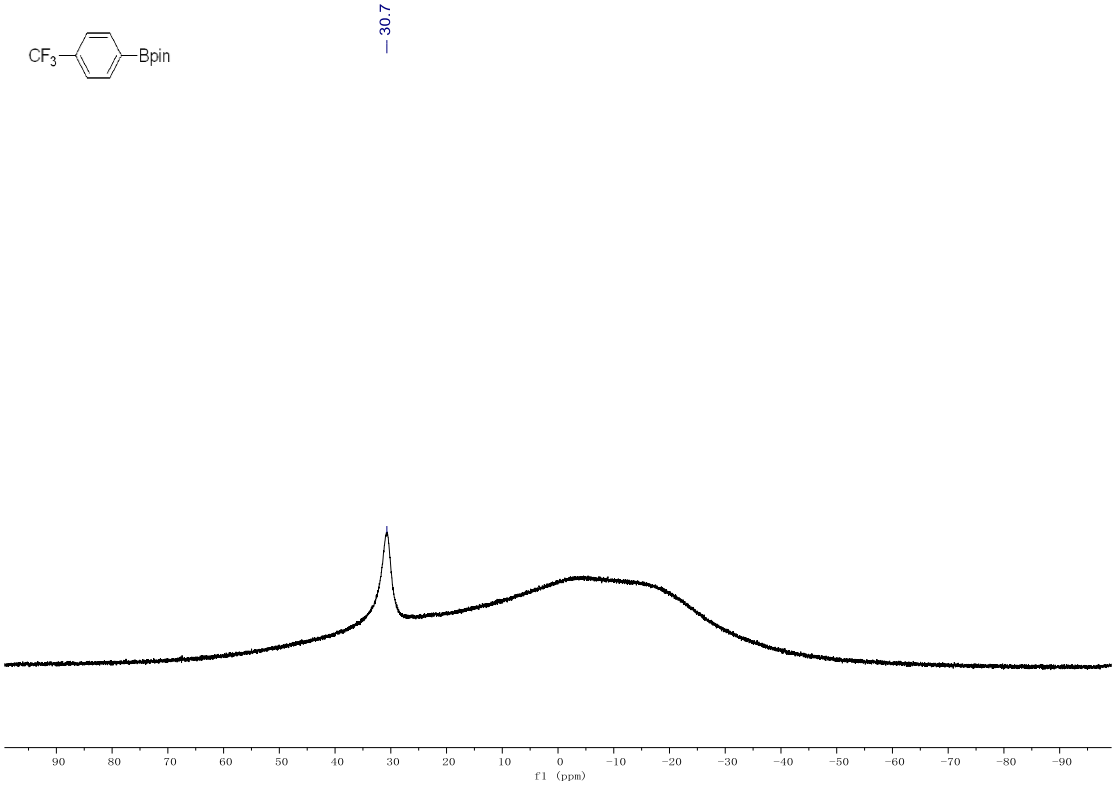
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2d**



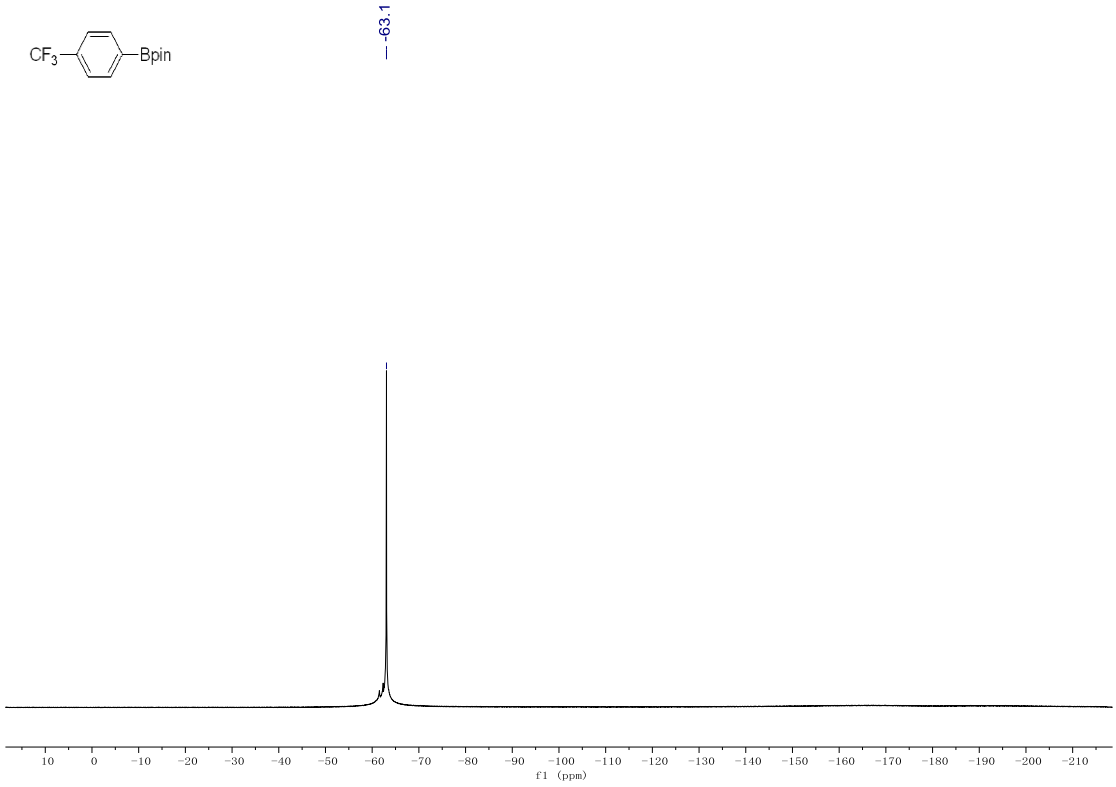
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2d**



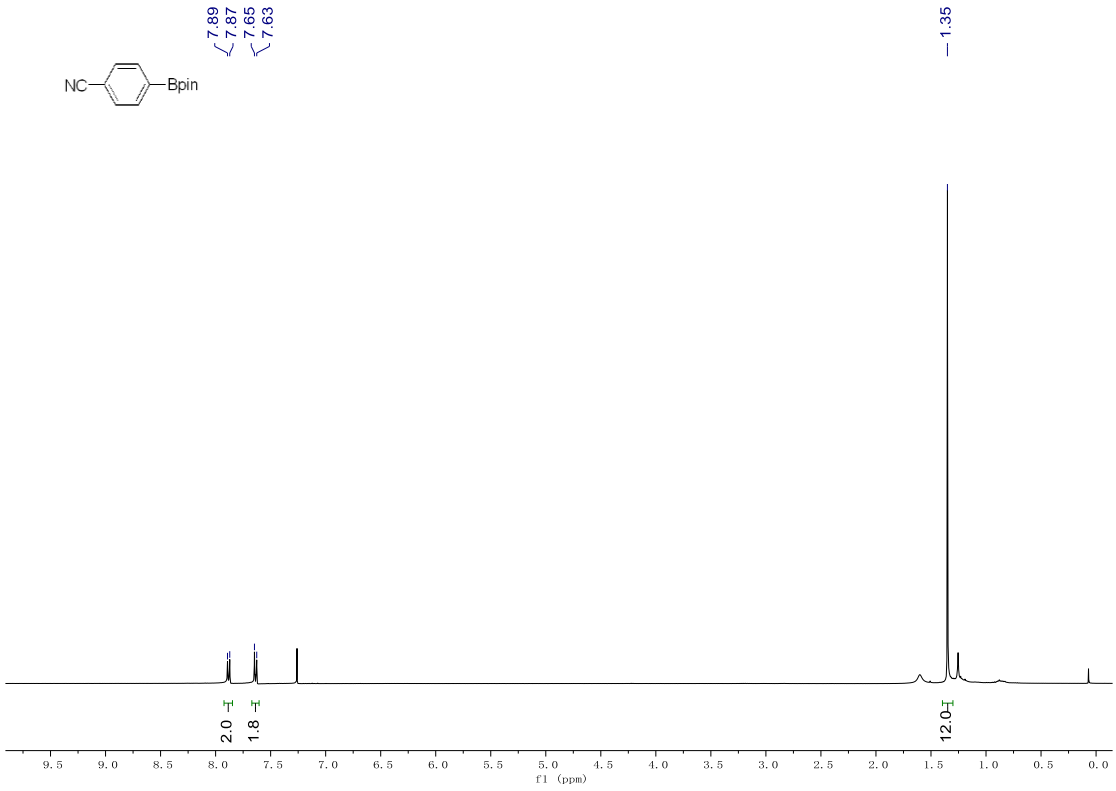
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2d**



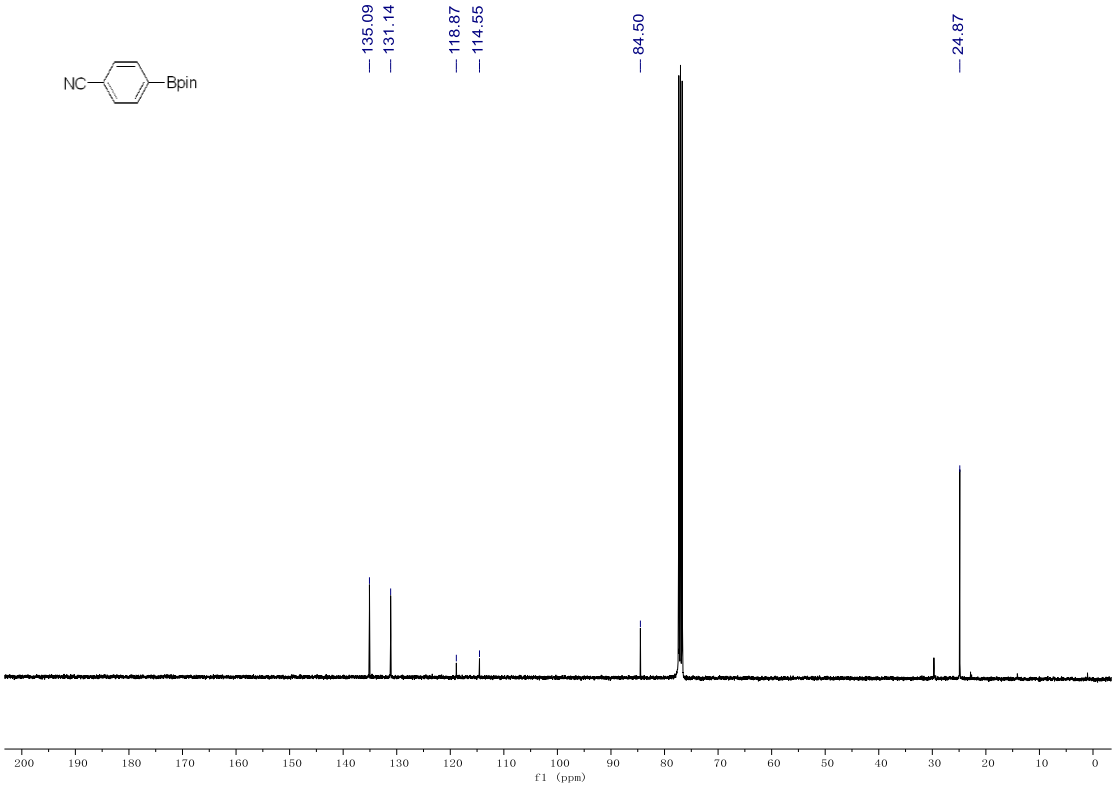
$^{19}F\{^{1}H\}$ NMR spectrum (376 MHz, $CDCl_3$) of **2d**



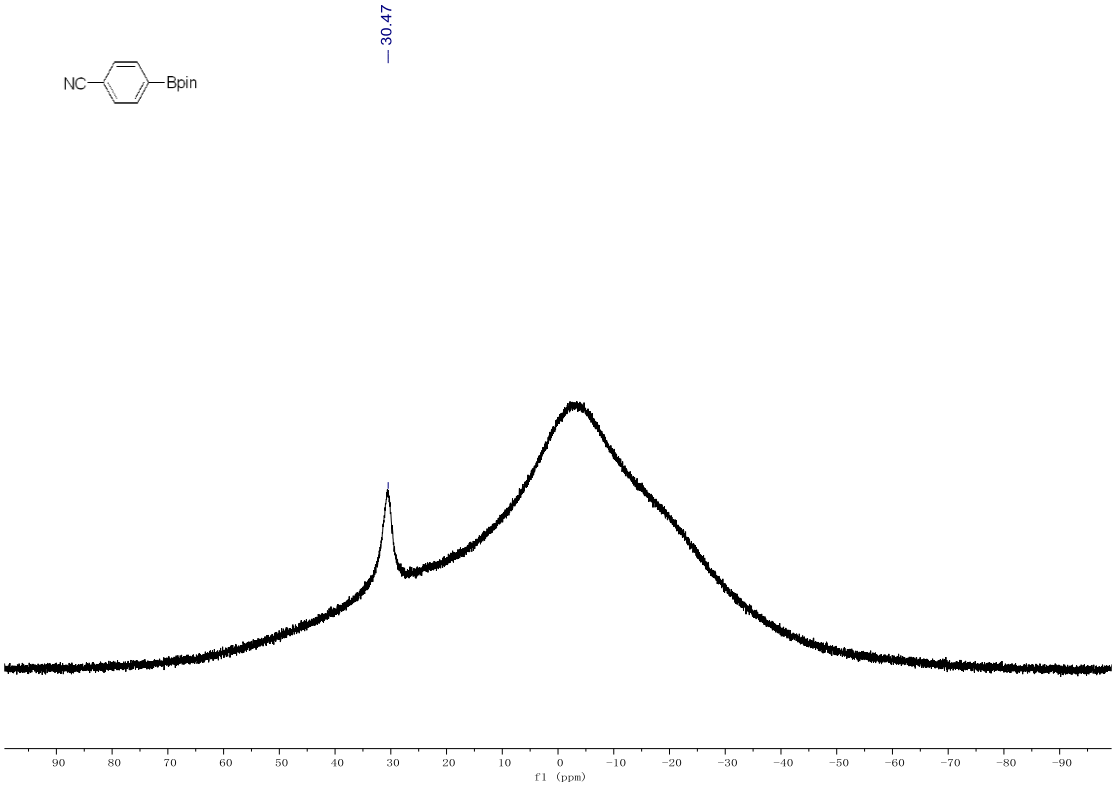
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2e**



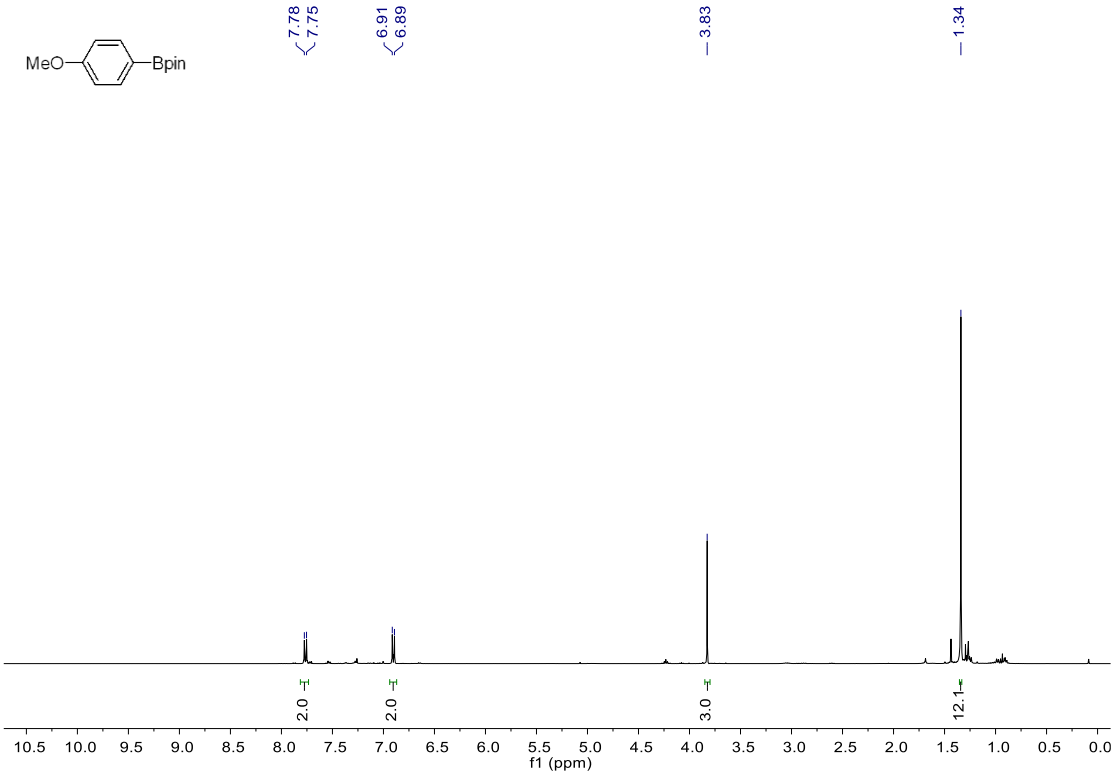
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2e**



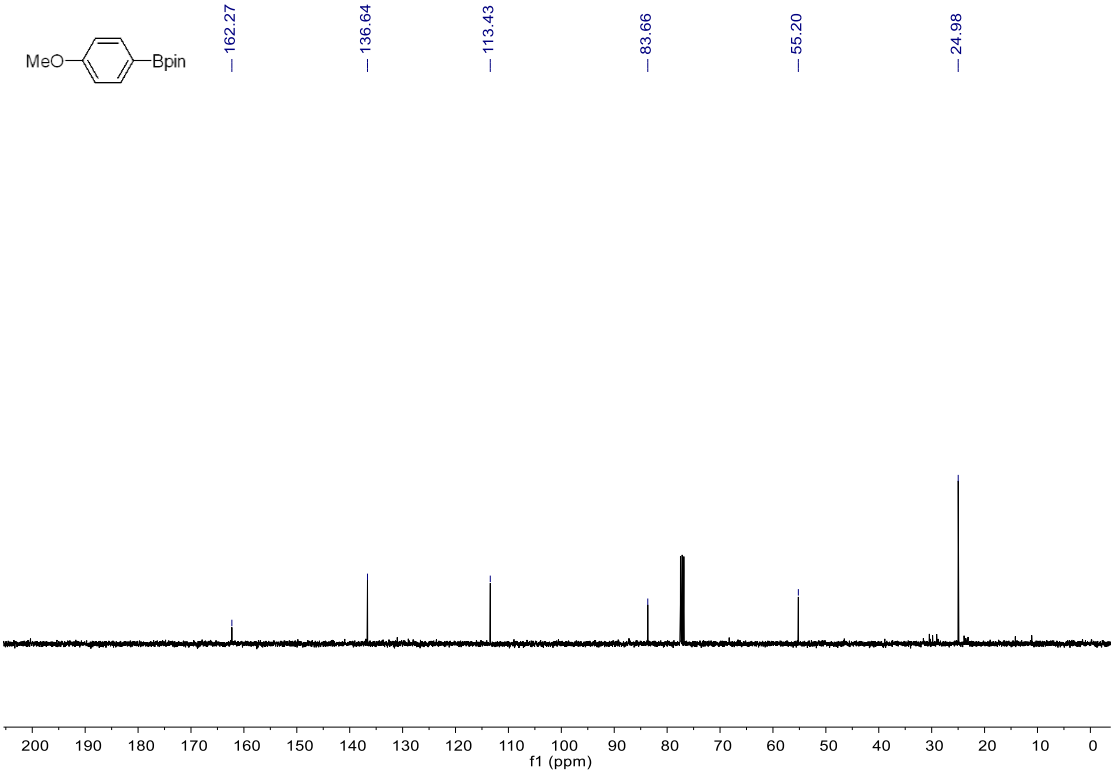
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2e**



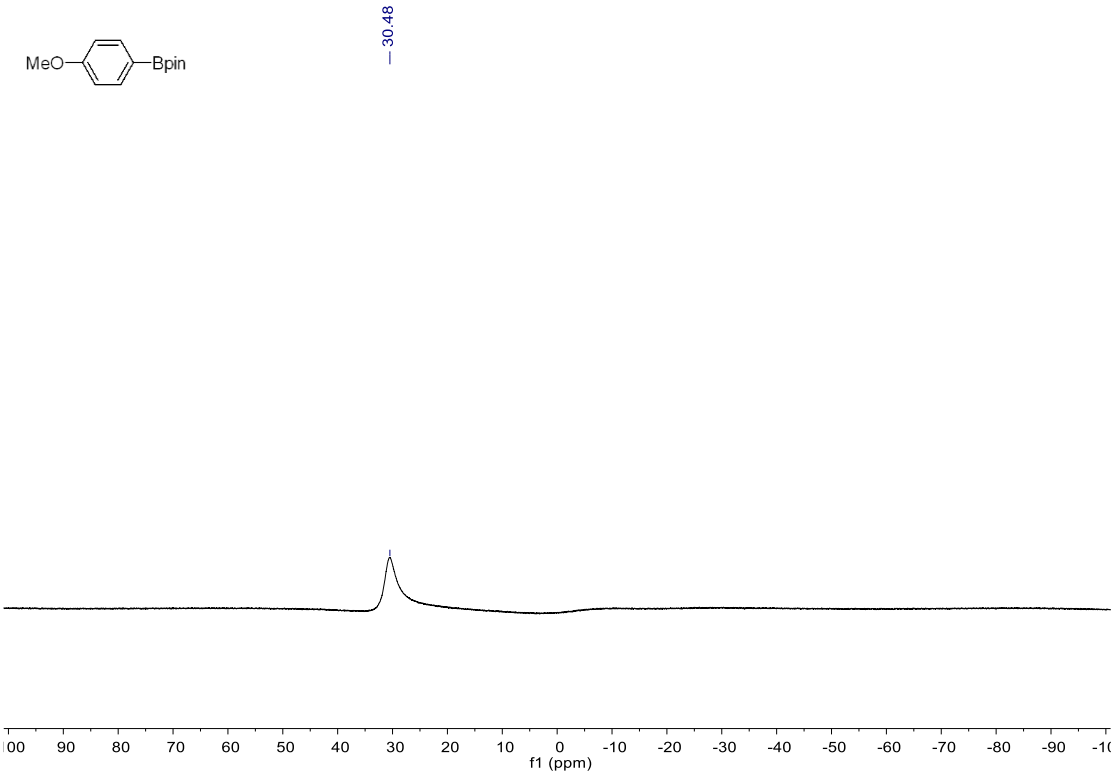
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2f**



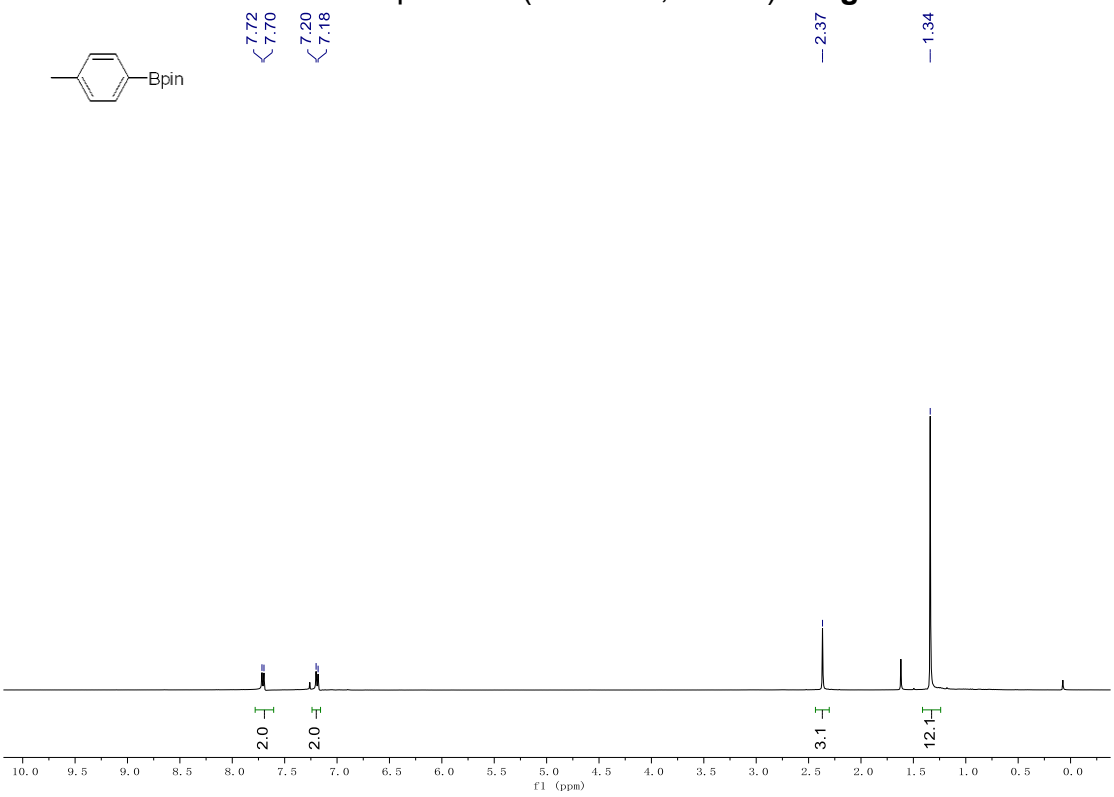
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2f**



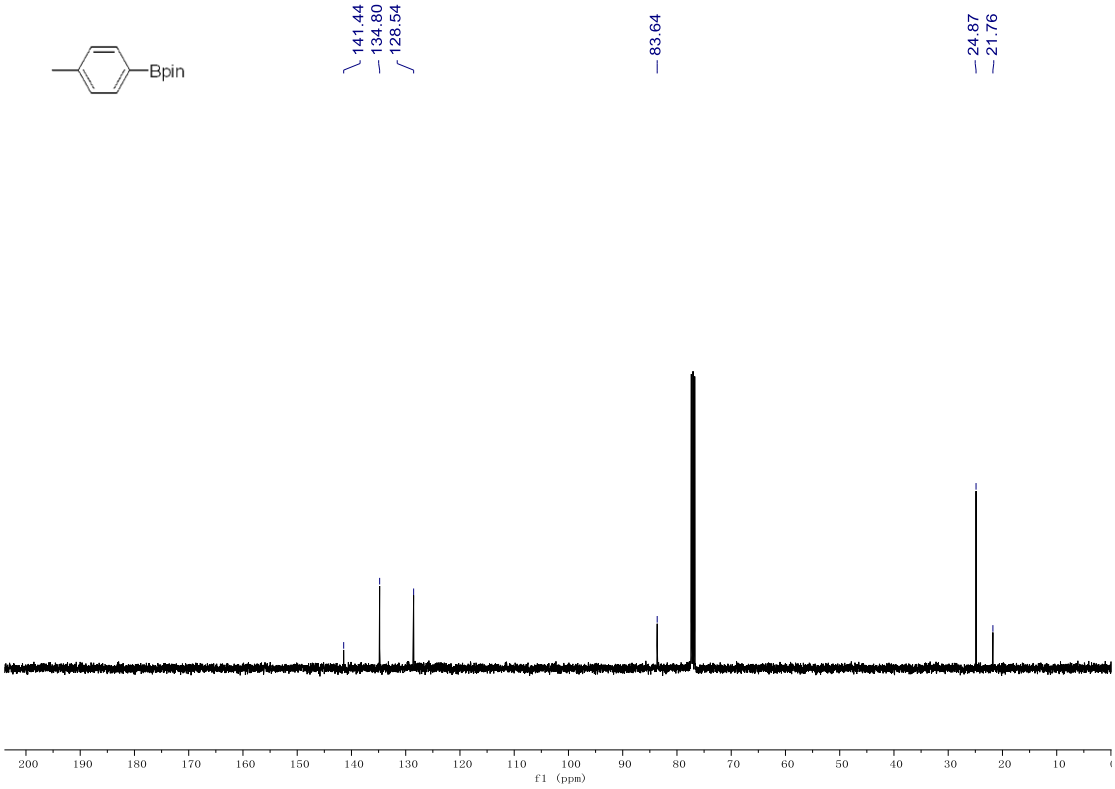
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2f**



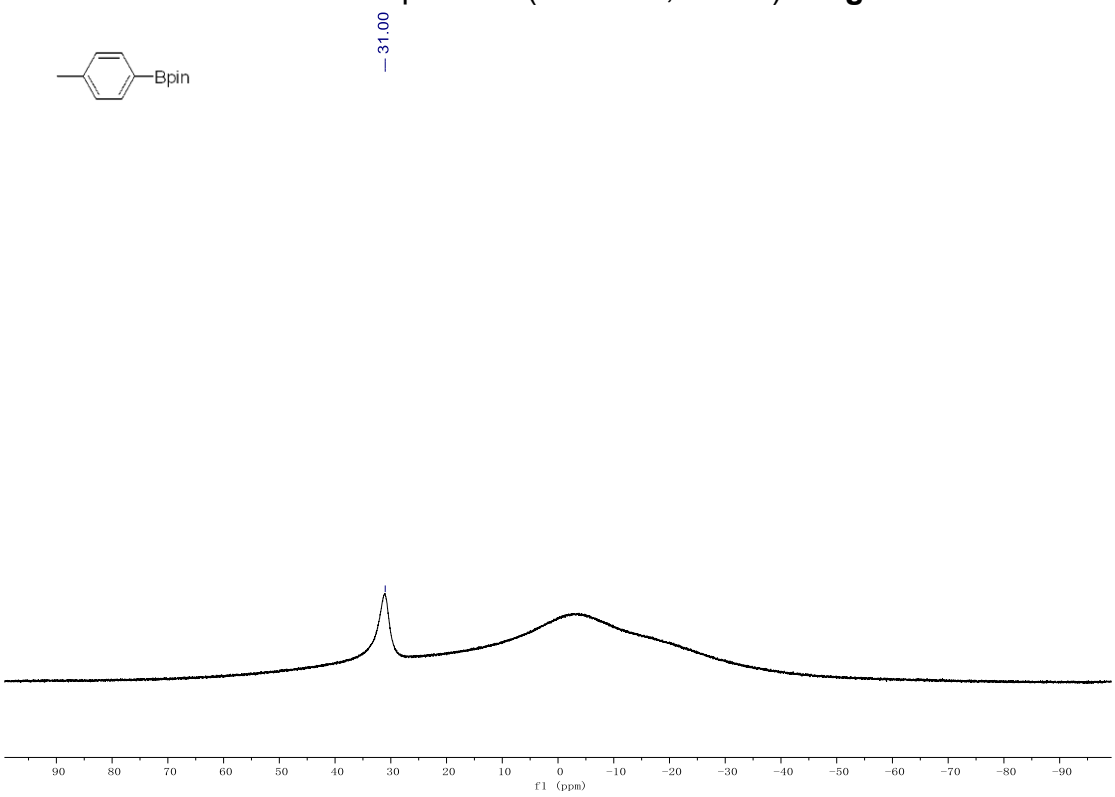
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2g**



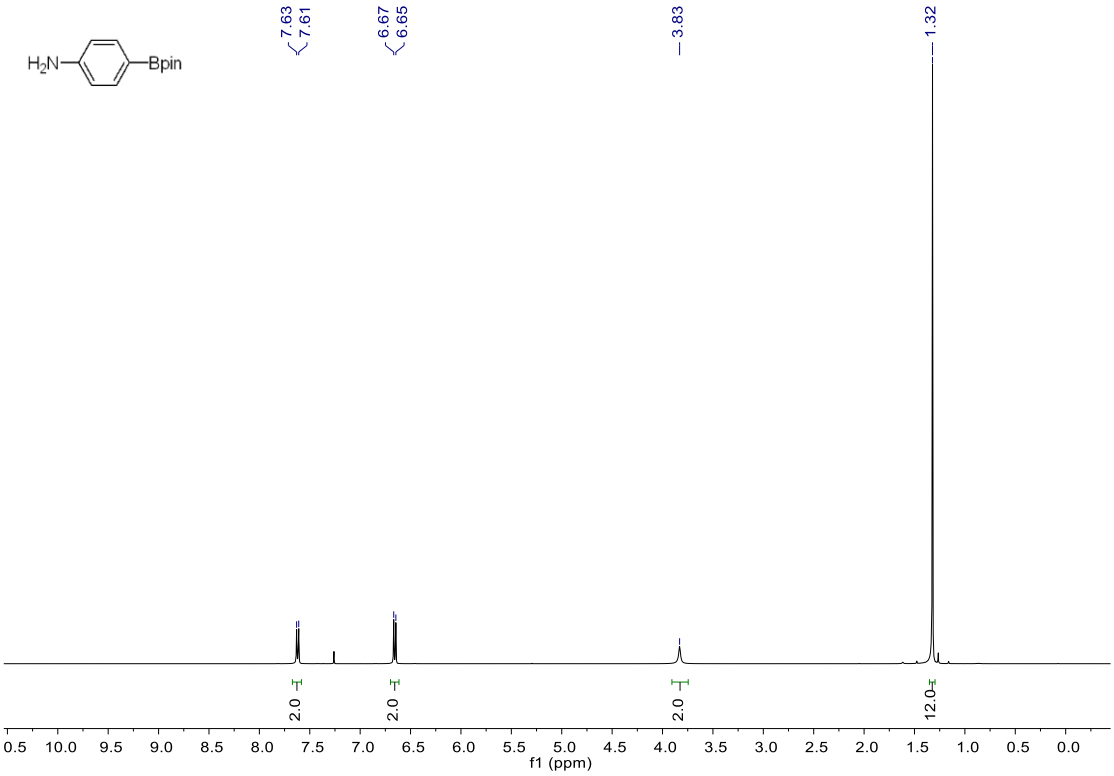
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2g**



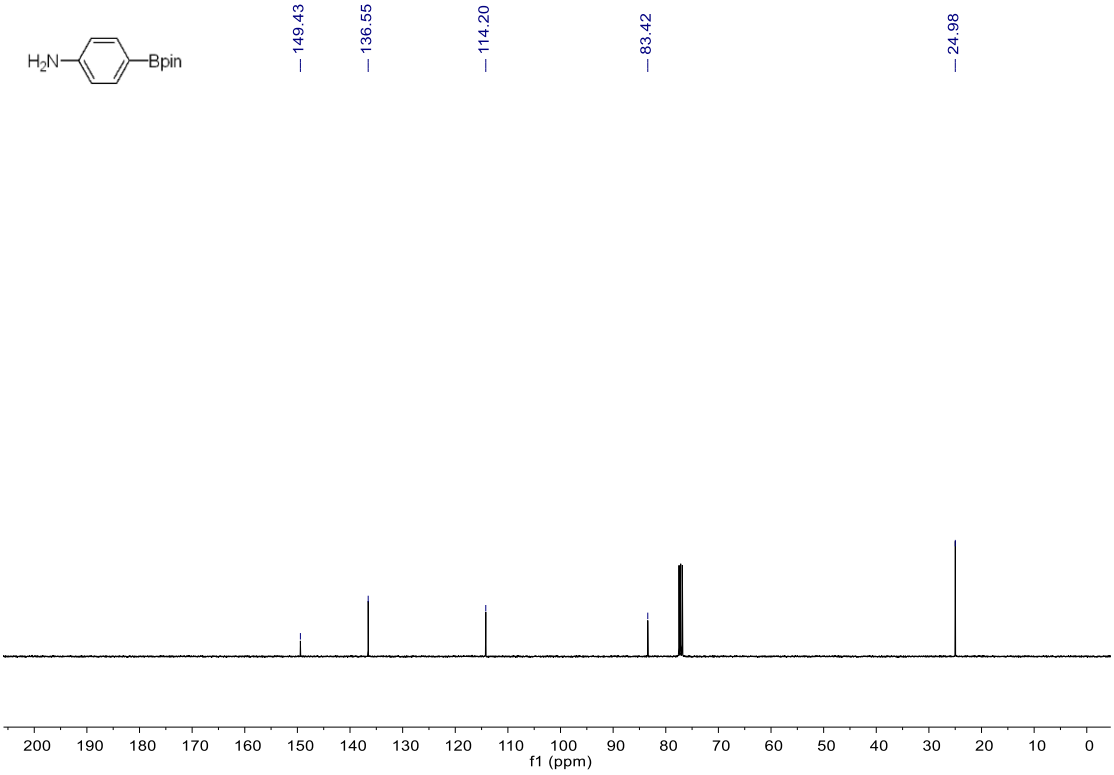
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2g**



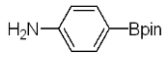
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2h**



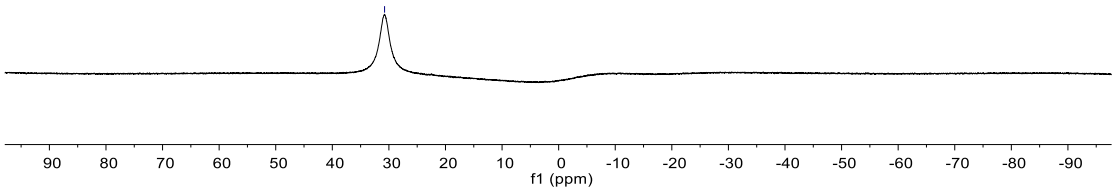
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2h**



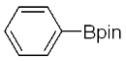
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2h**



30.77

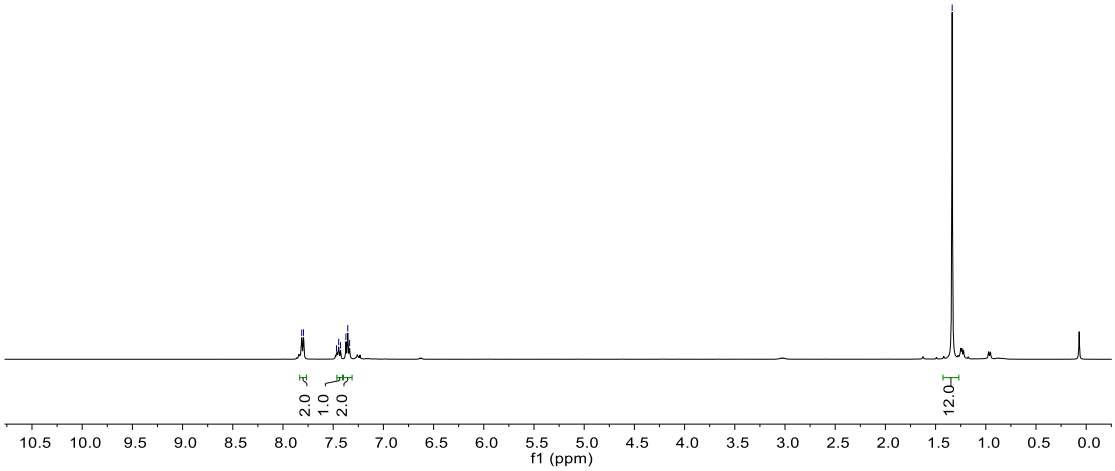


^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2i**

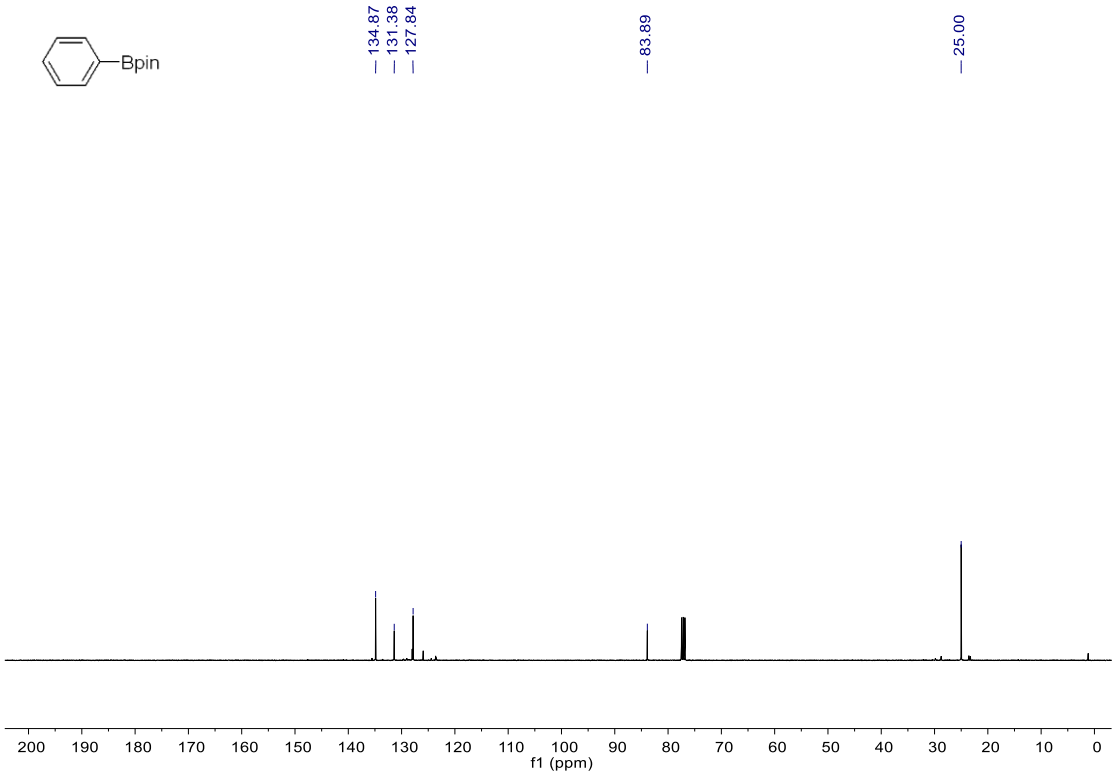


7.81
7.80
7.47
7.45
7.43
7.37
7.35
7.34

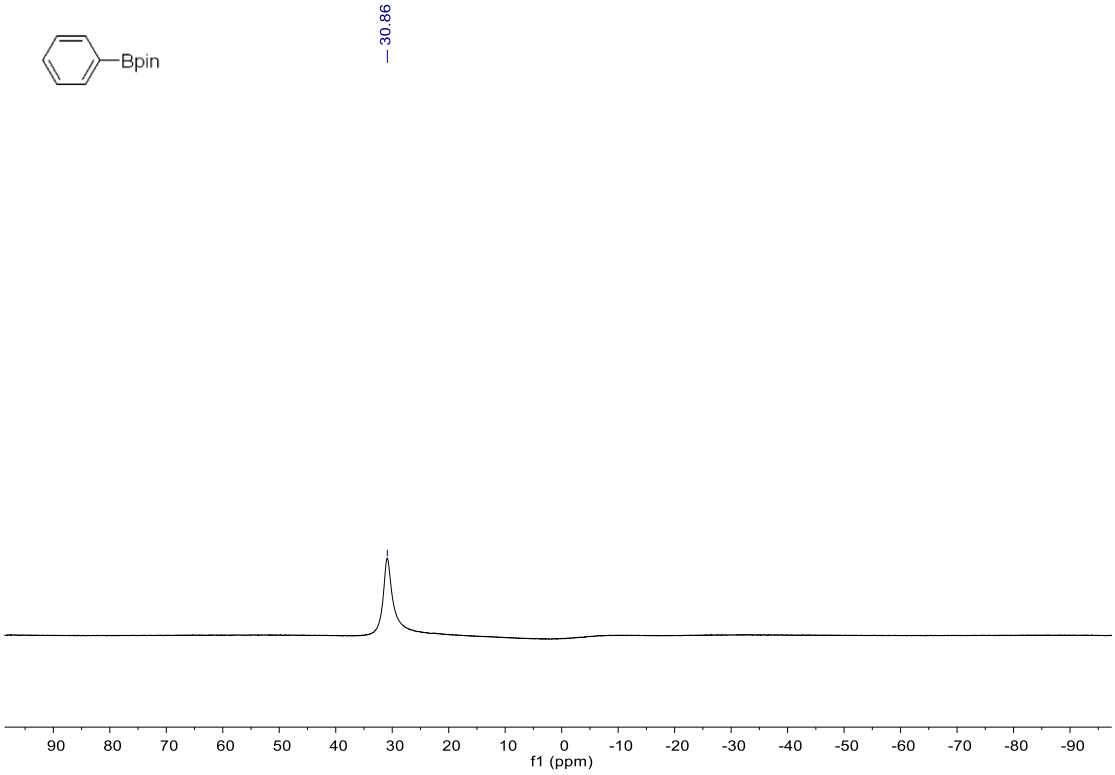
1.34



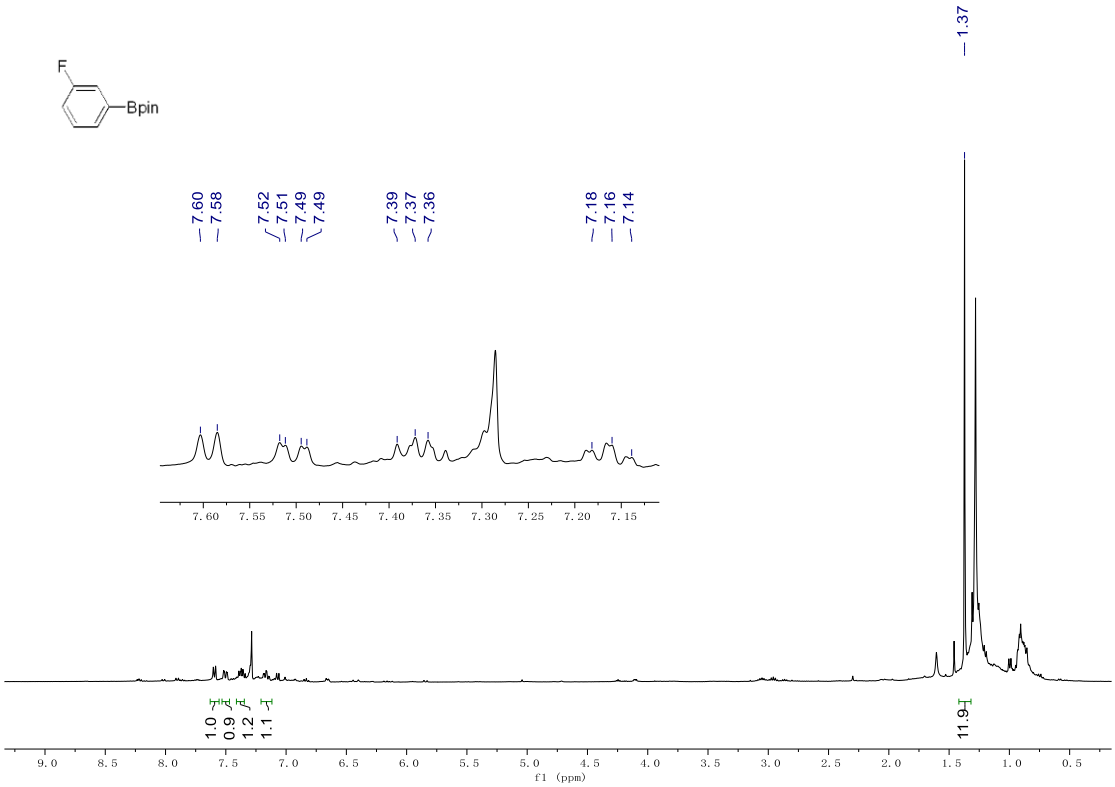
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2i**



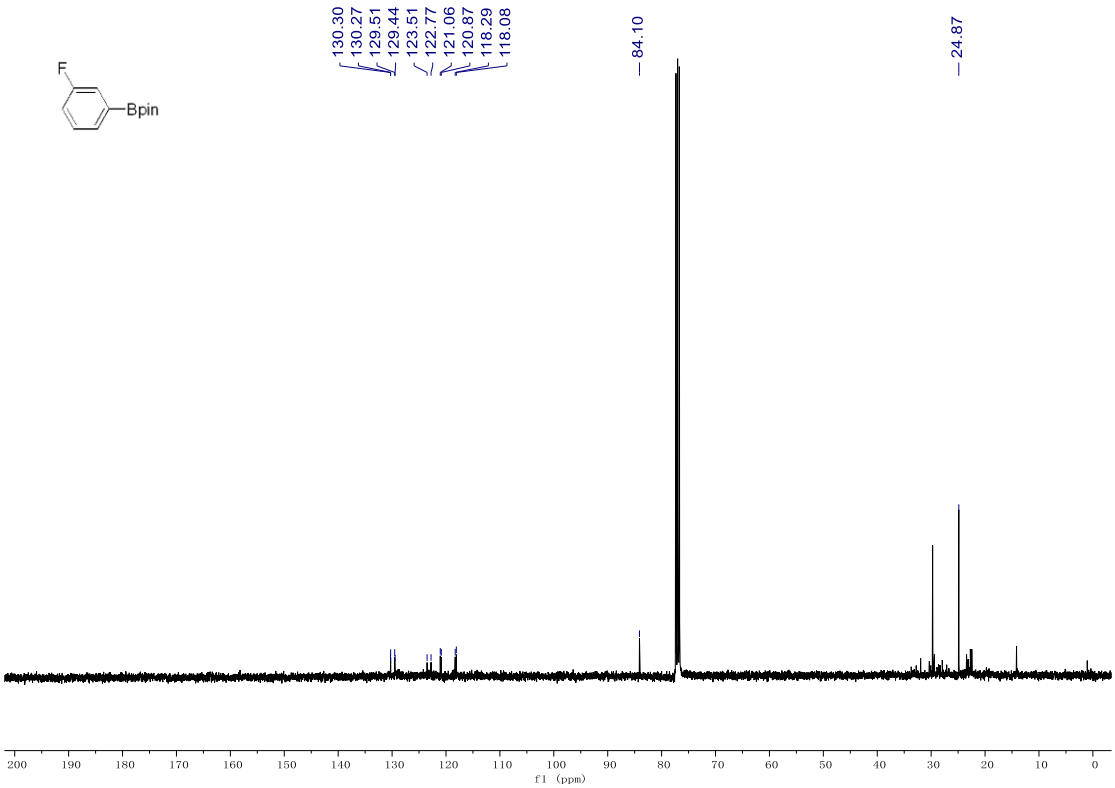
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2i**



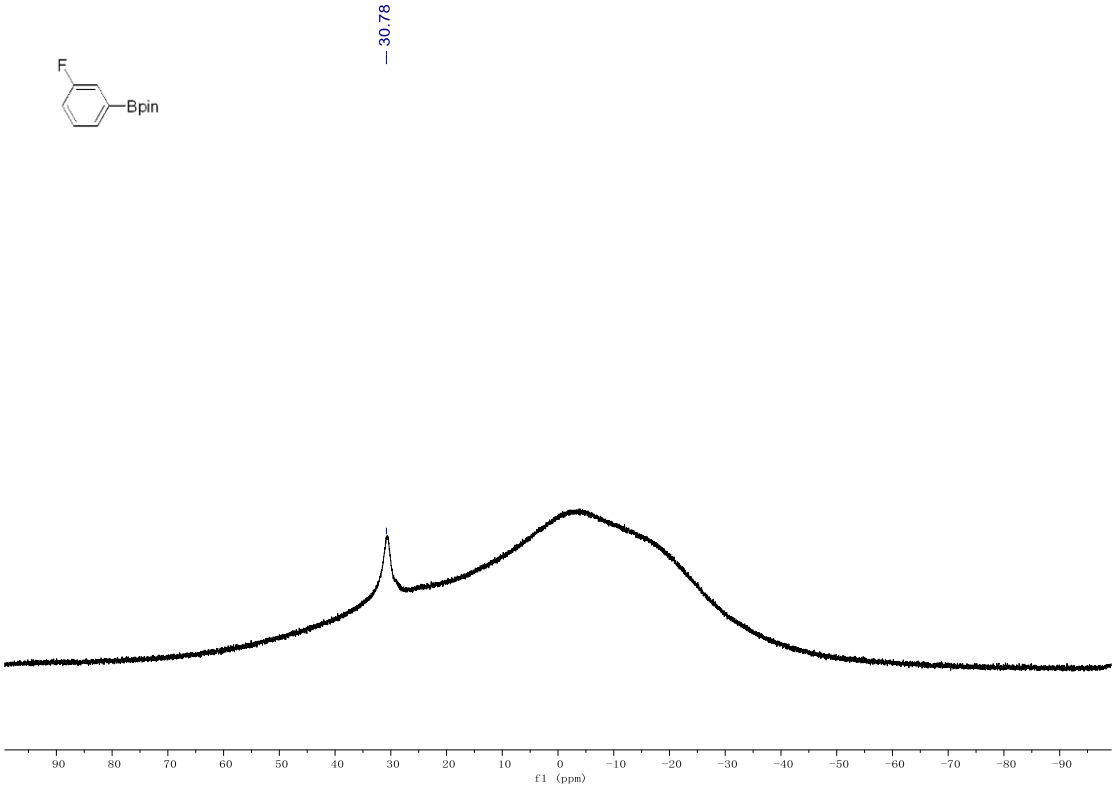
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2j**



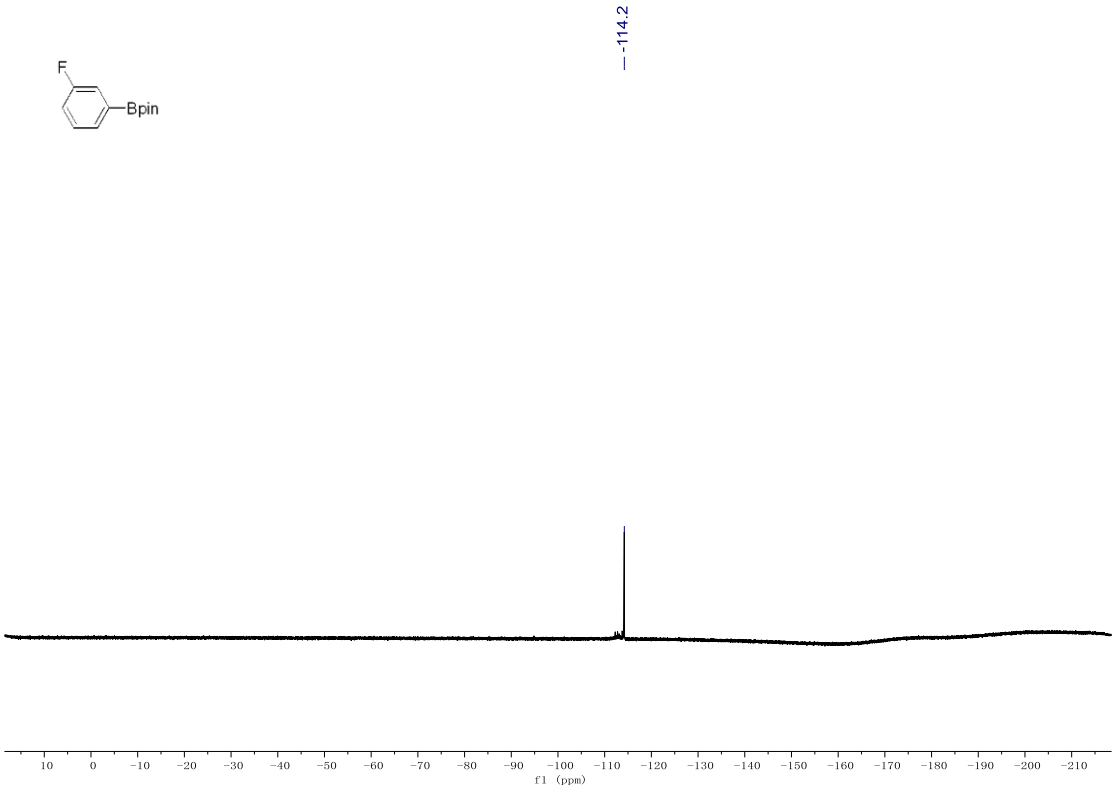
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **2j**



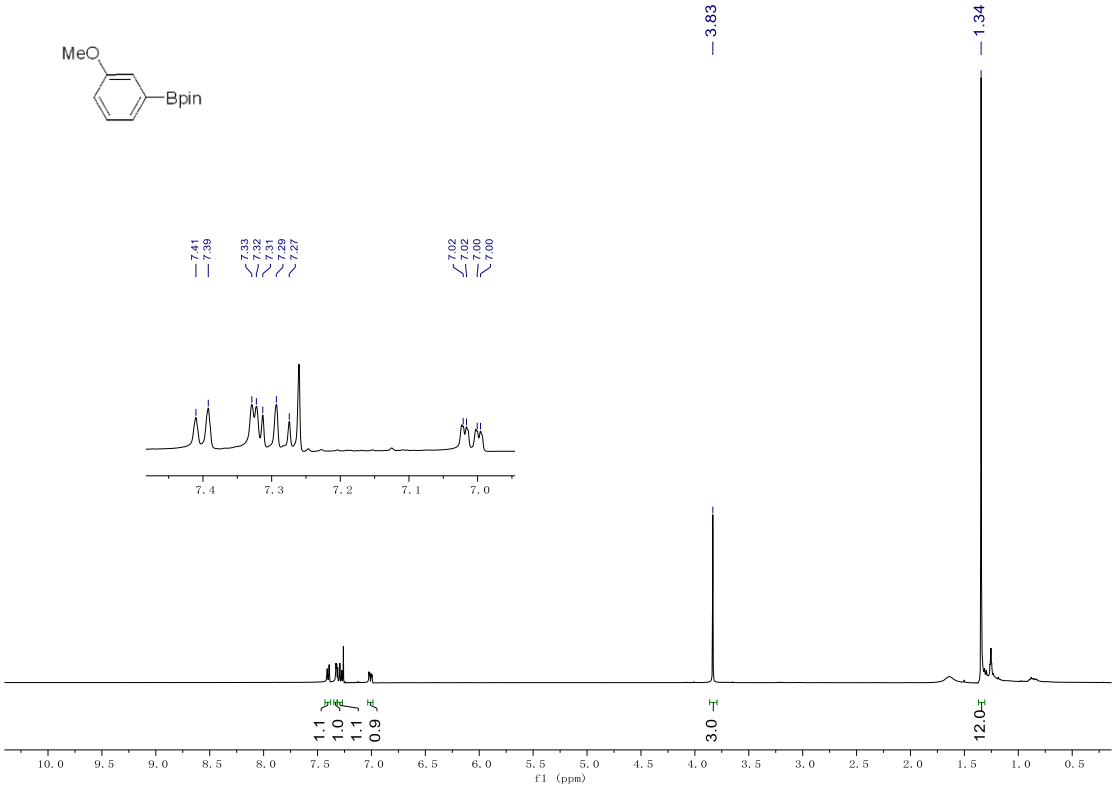
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2j**



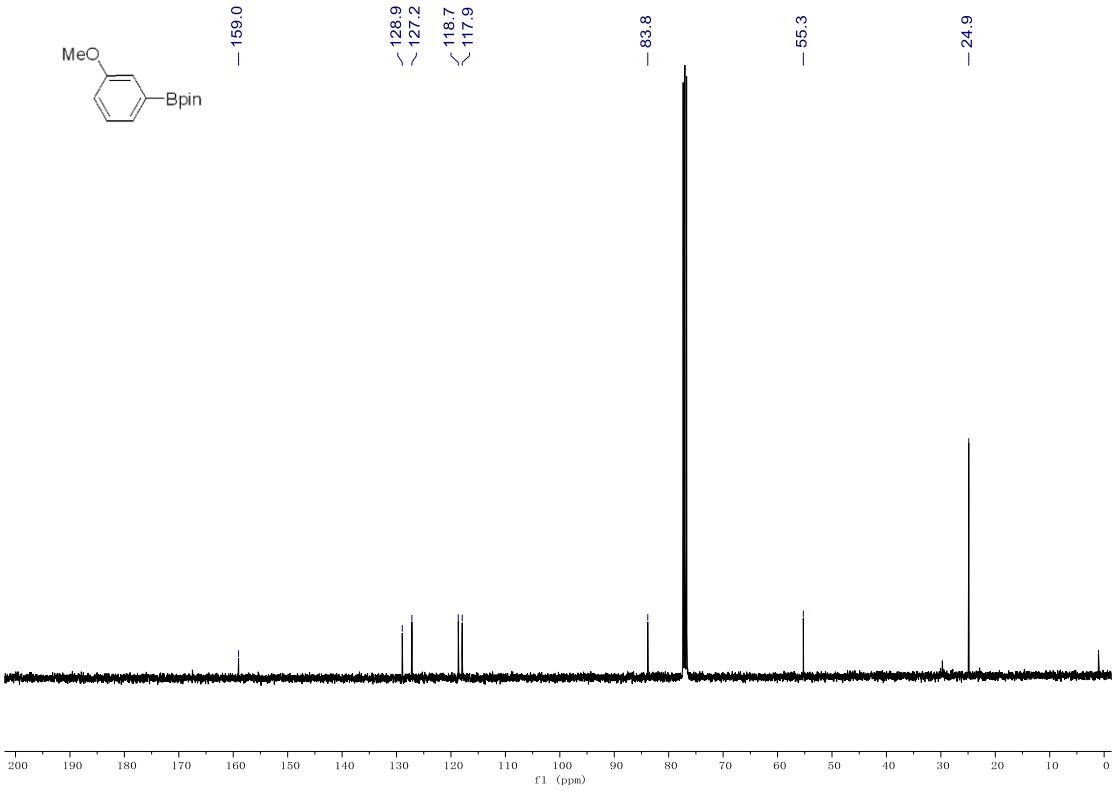
^{19}F{^{1}H} NMR spectrum (376 MHz, $CDCl_3$) of **2j**



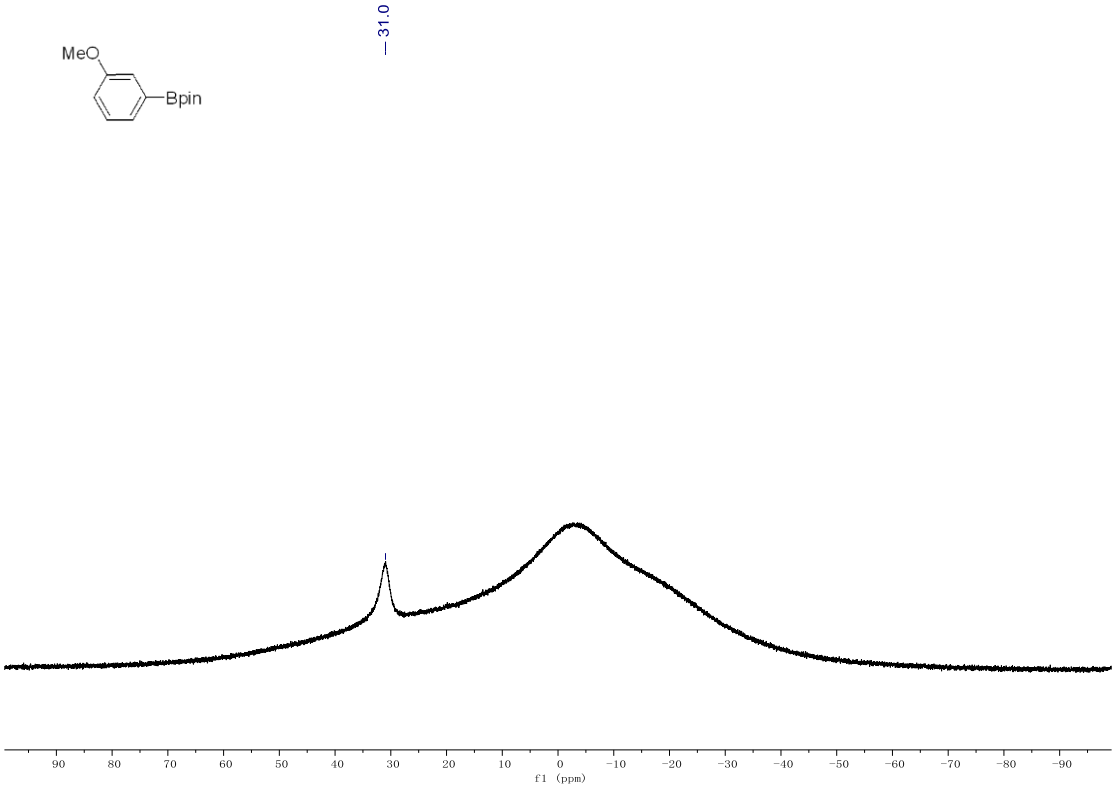
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2k**



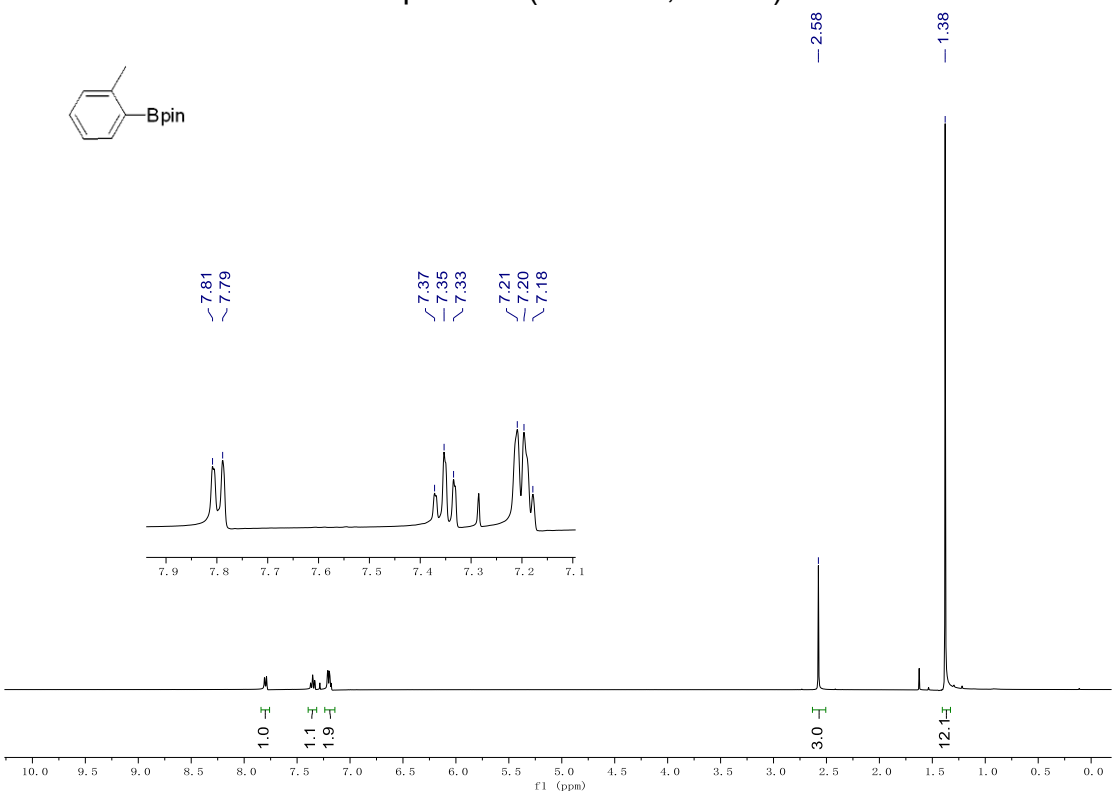
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **2k**



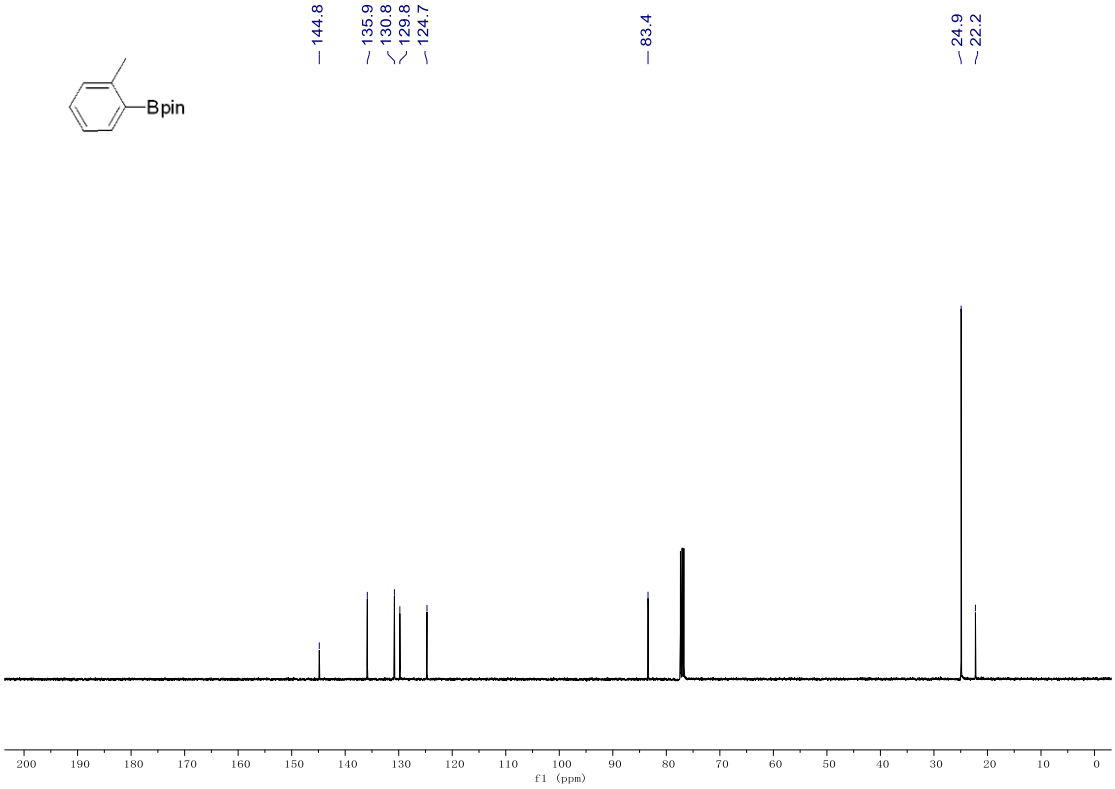
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2k**



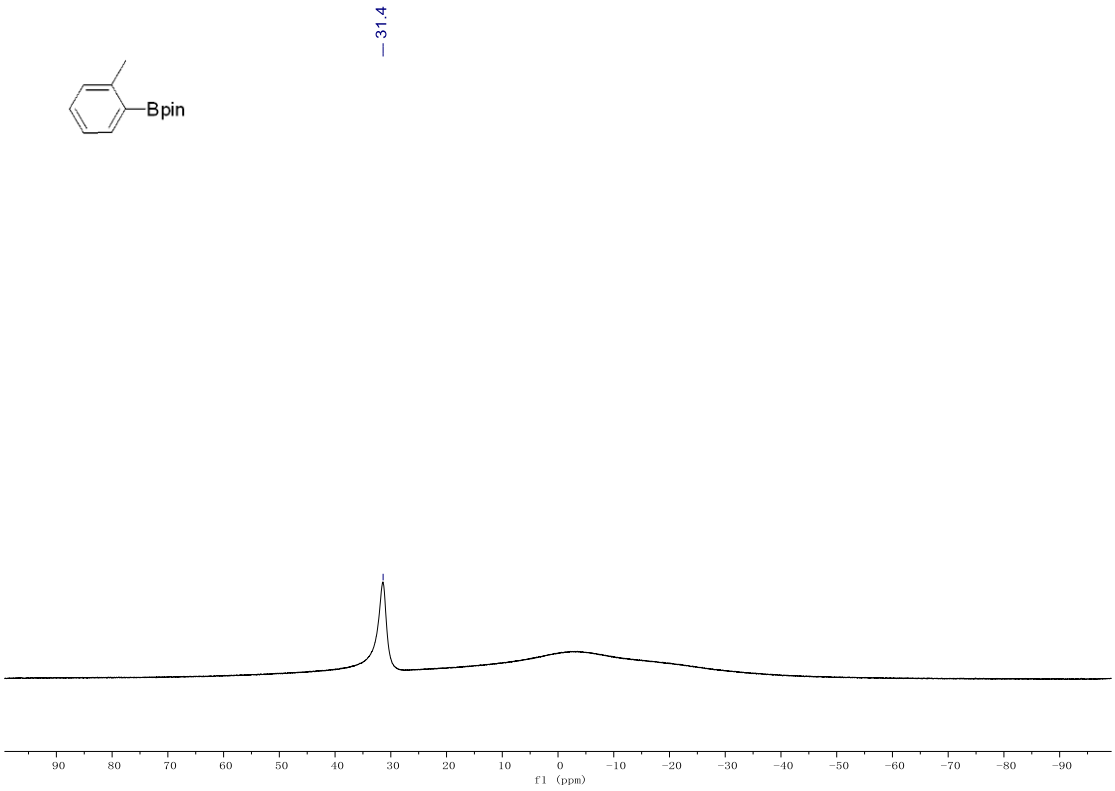
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2l**



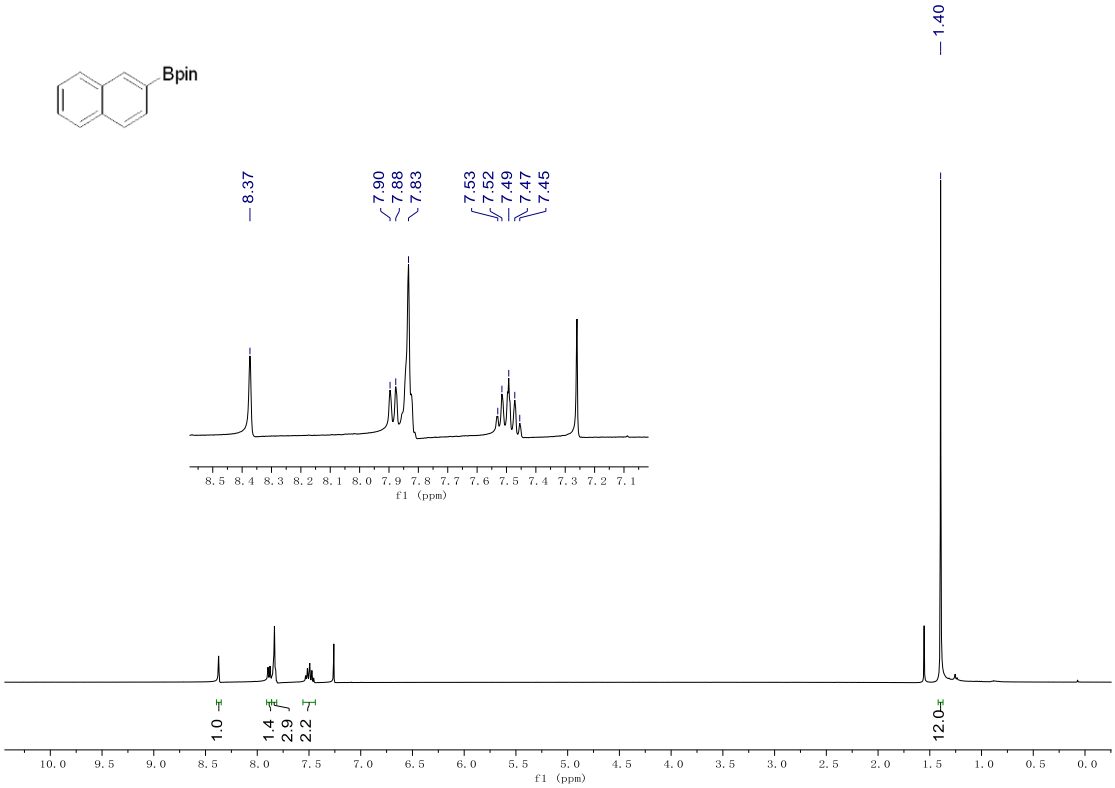
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2l**



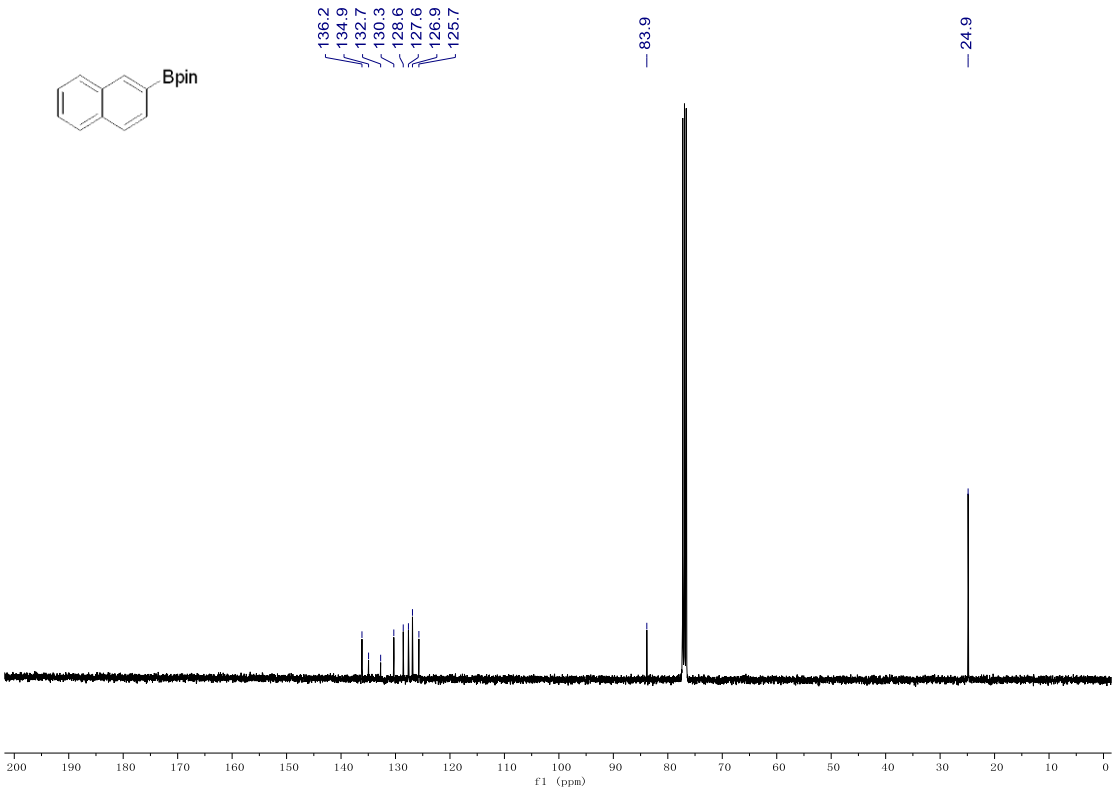
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2l**



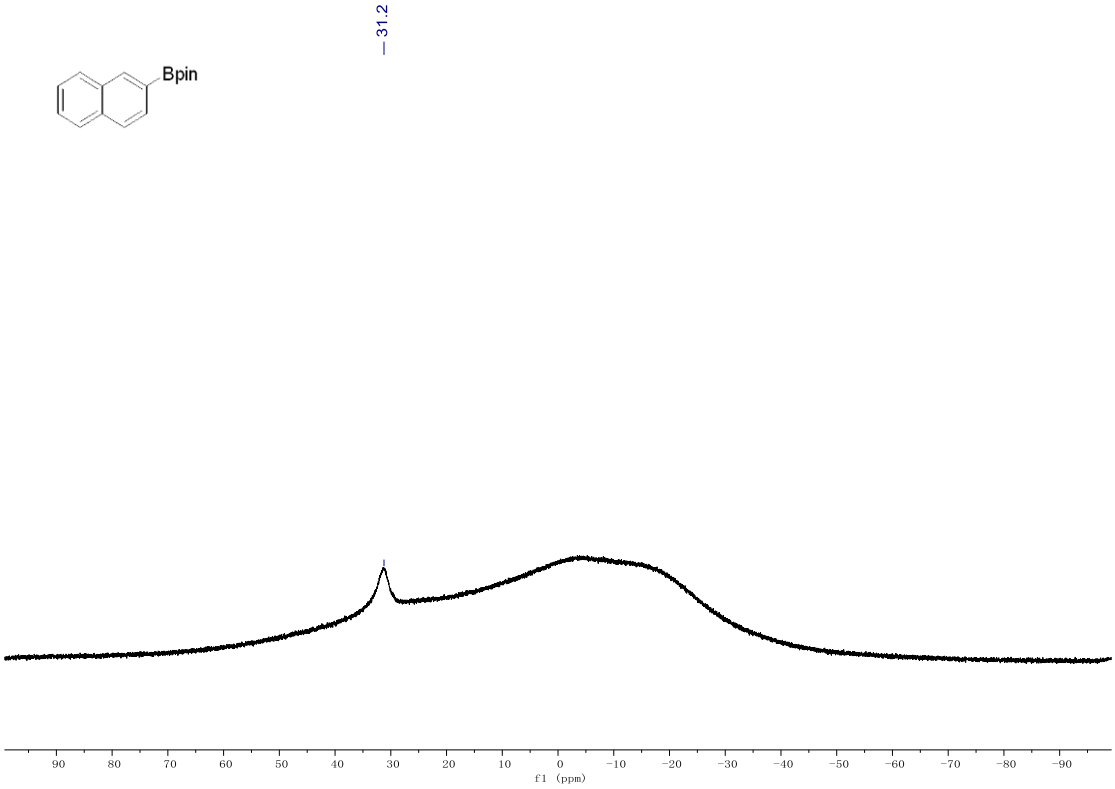
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2m**



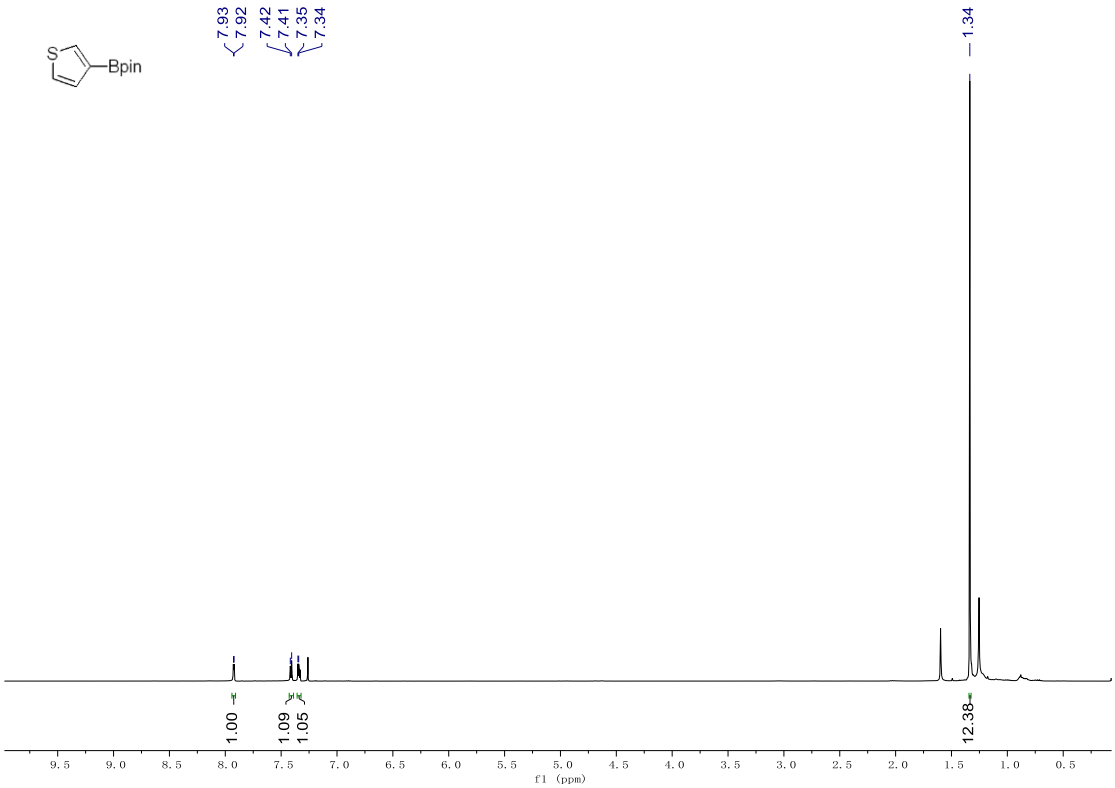
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **2m**



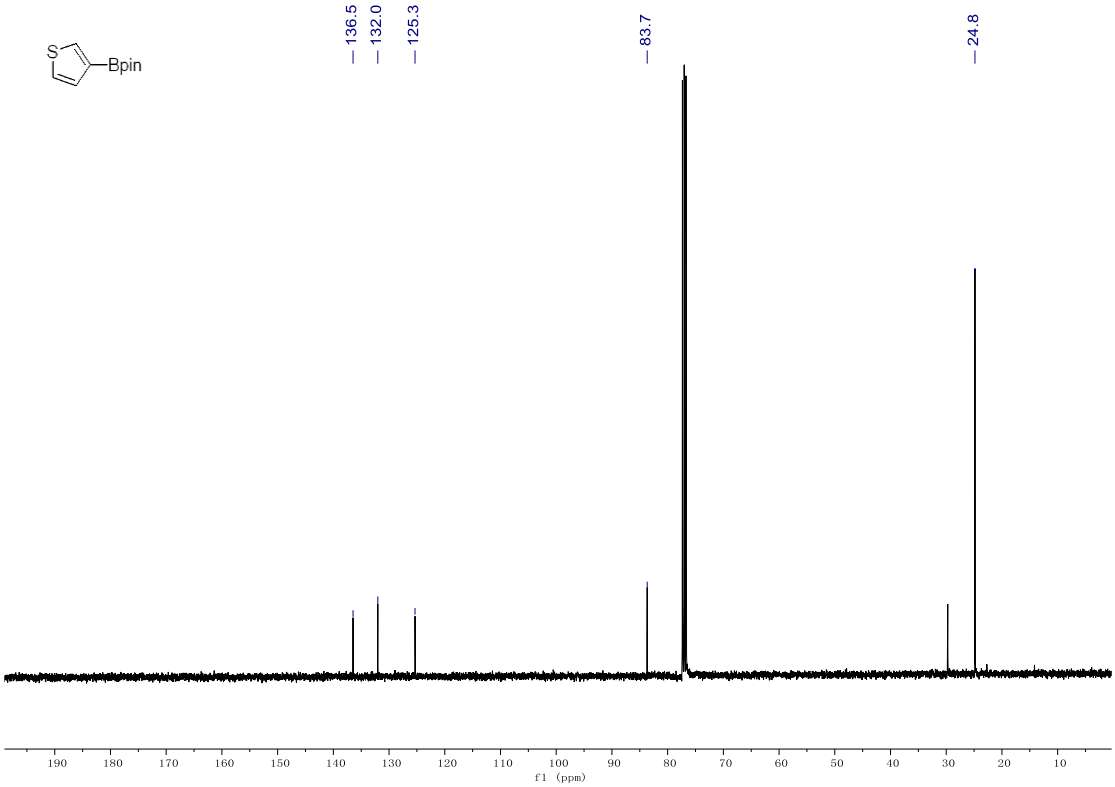
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2m**



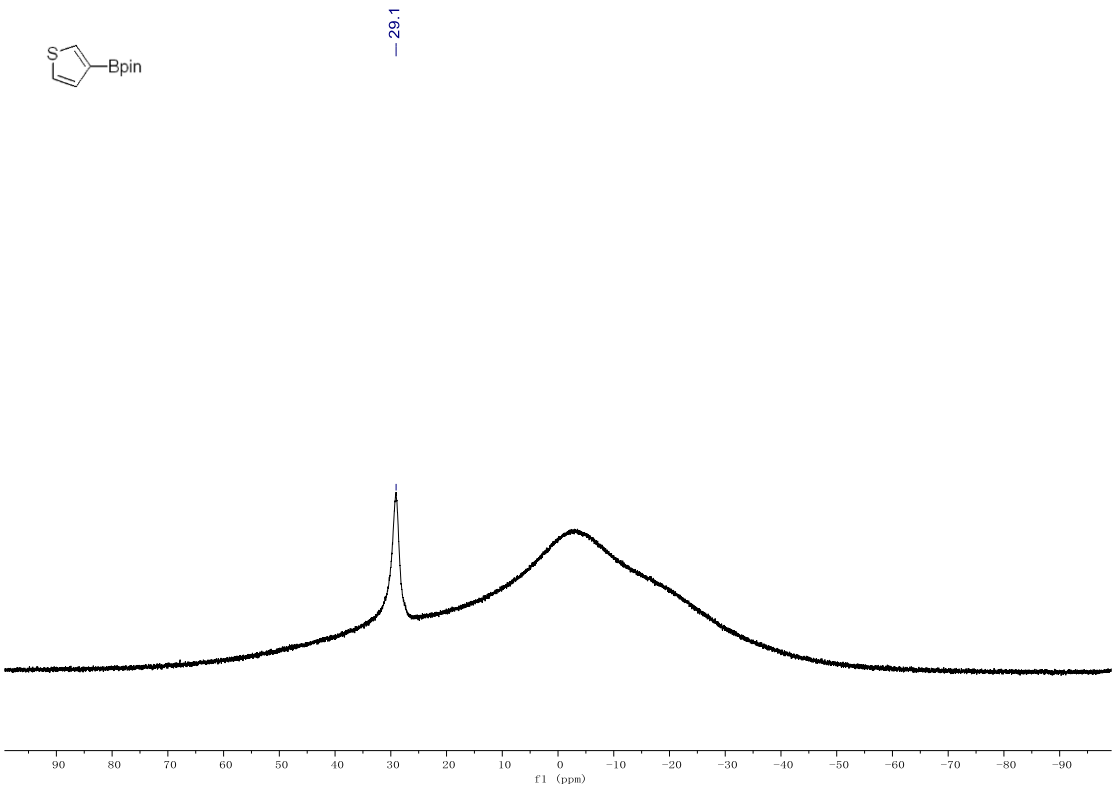
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2n**



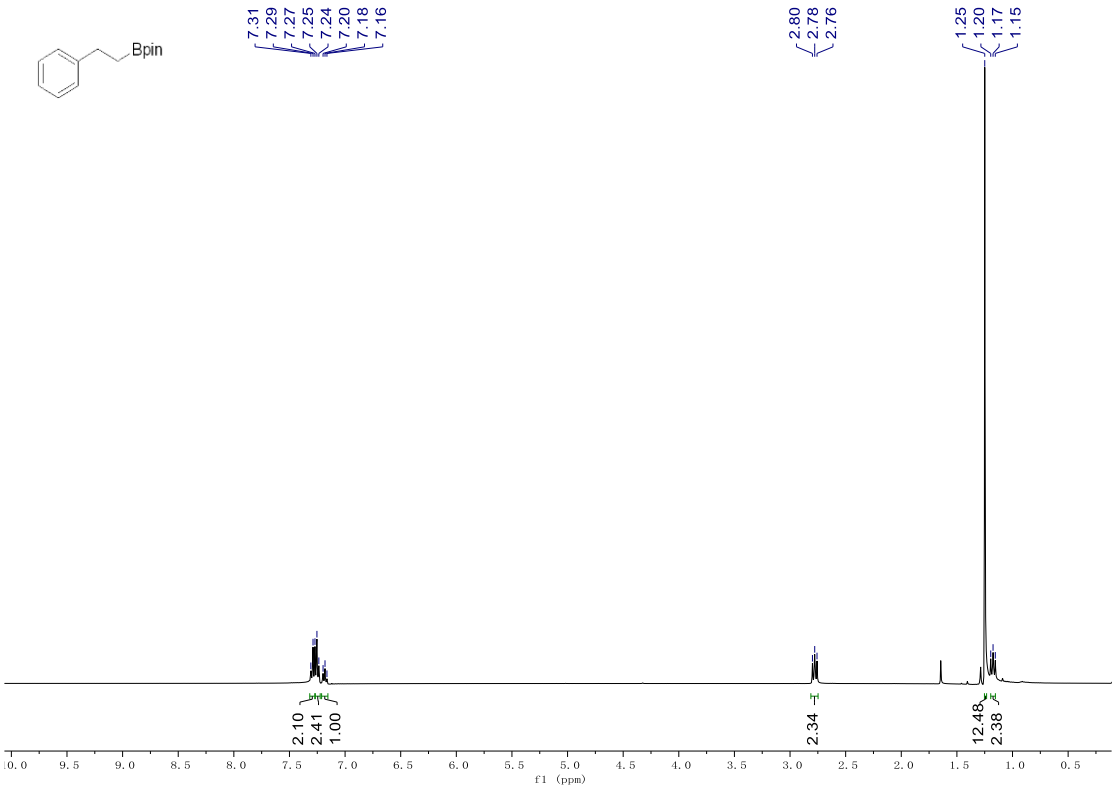
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2n**



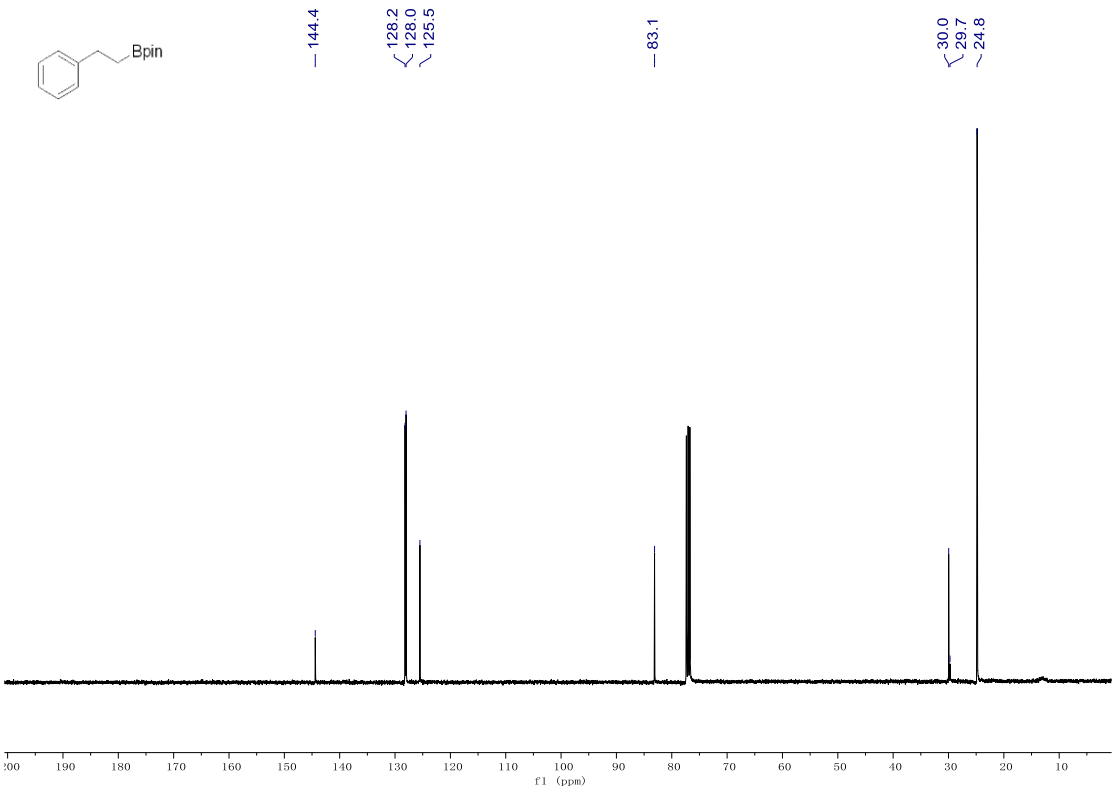
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2n**



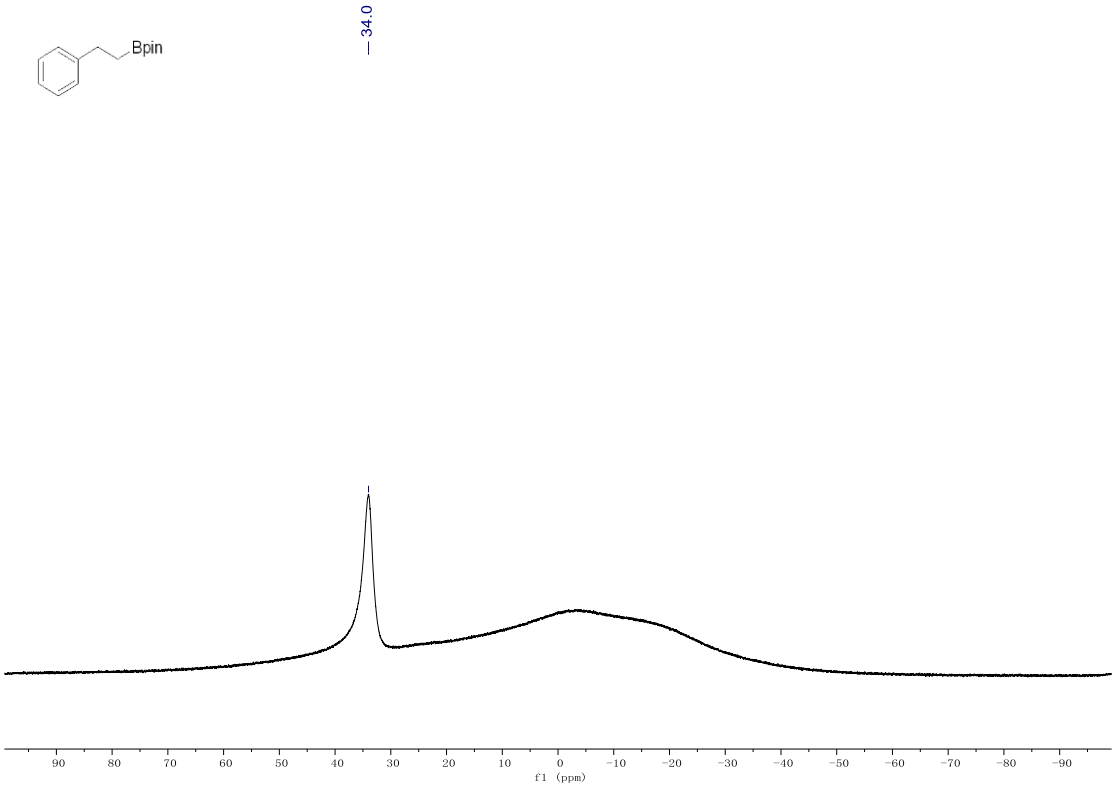
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2o**



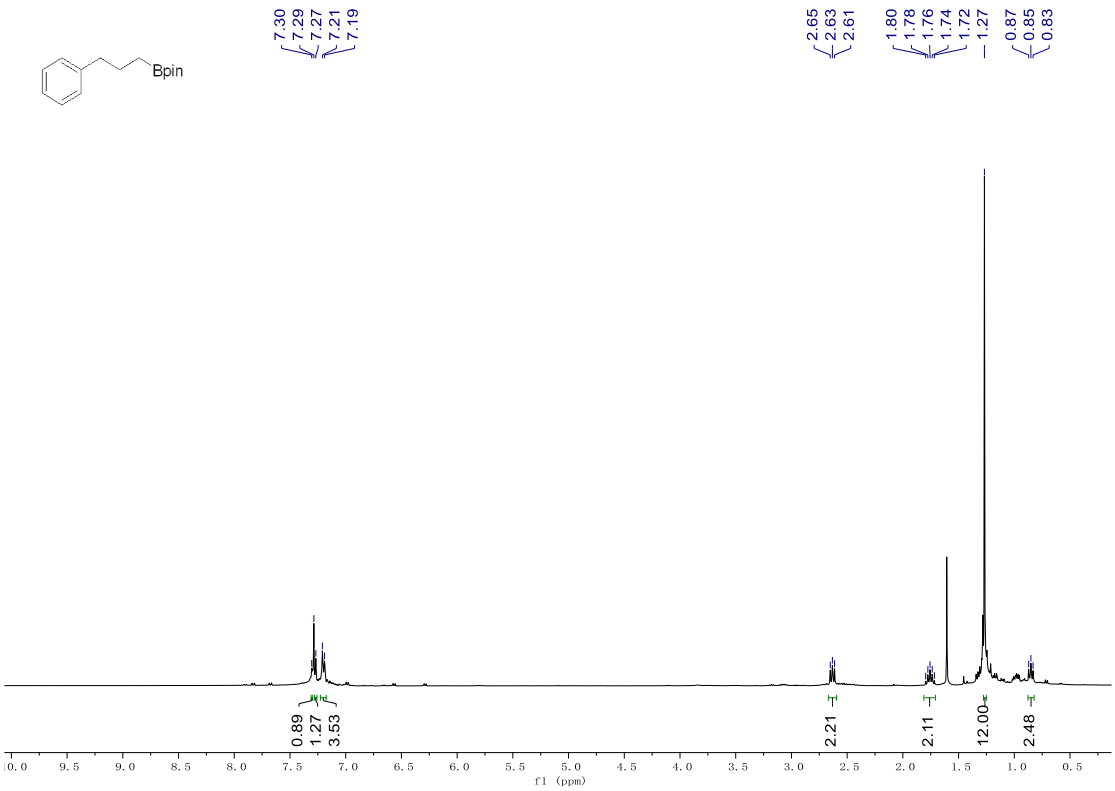
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **2o**



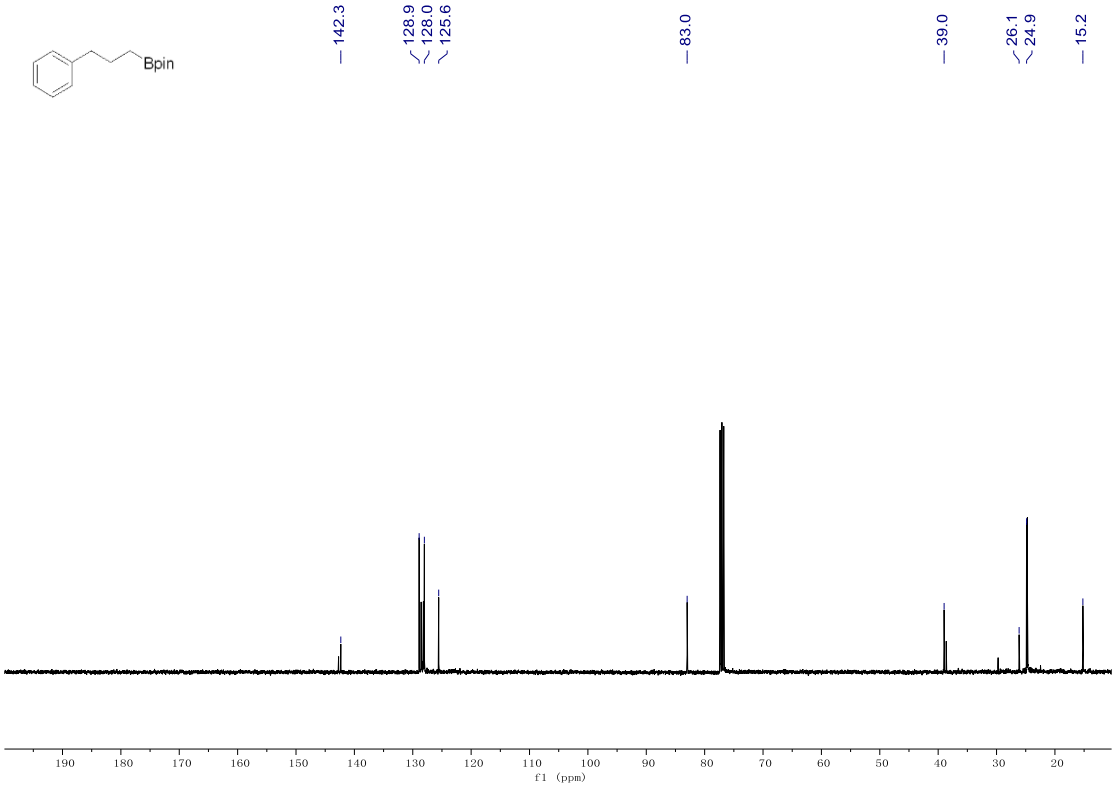
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2o**



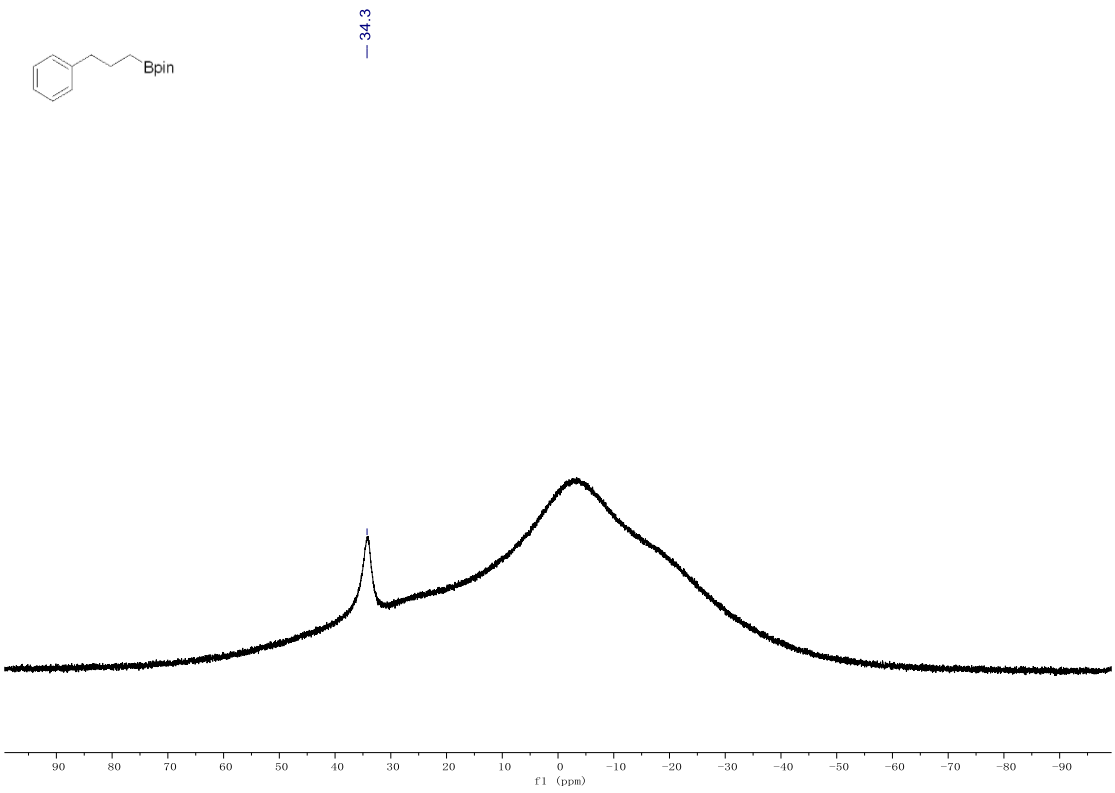
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **2p**



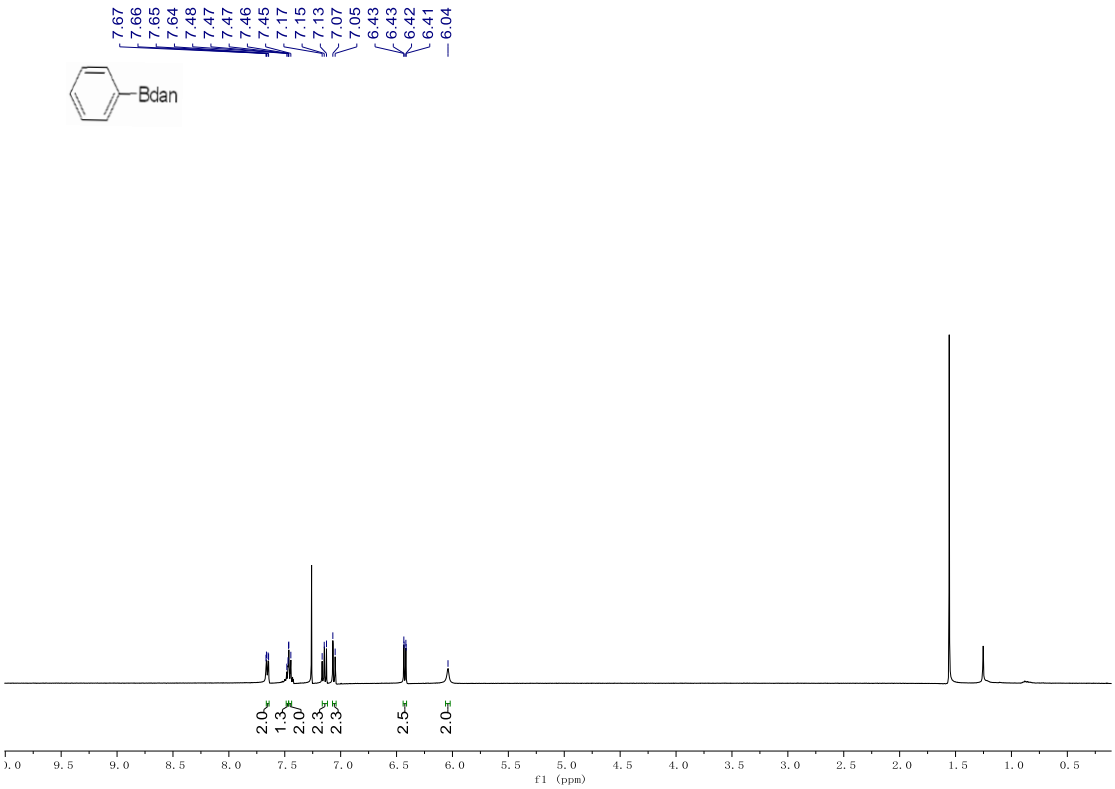
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **2p**



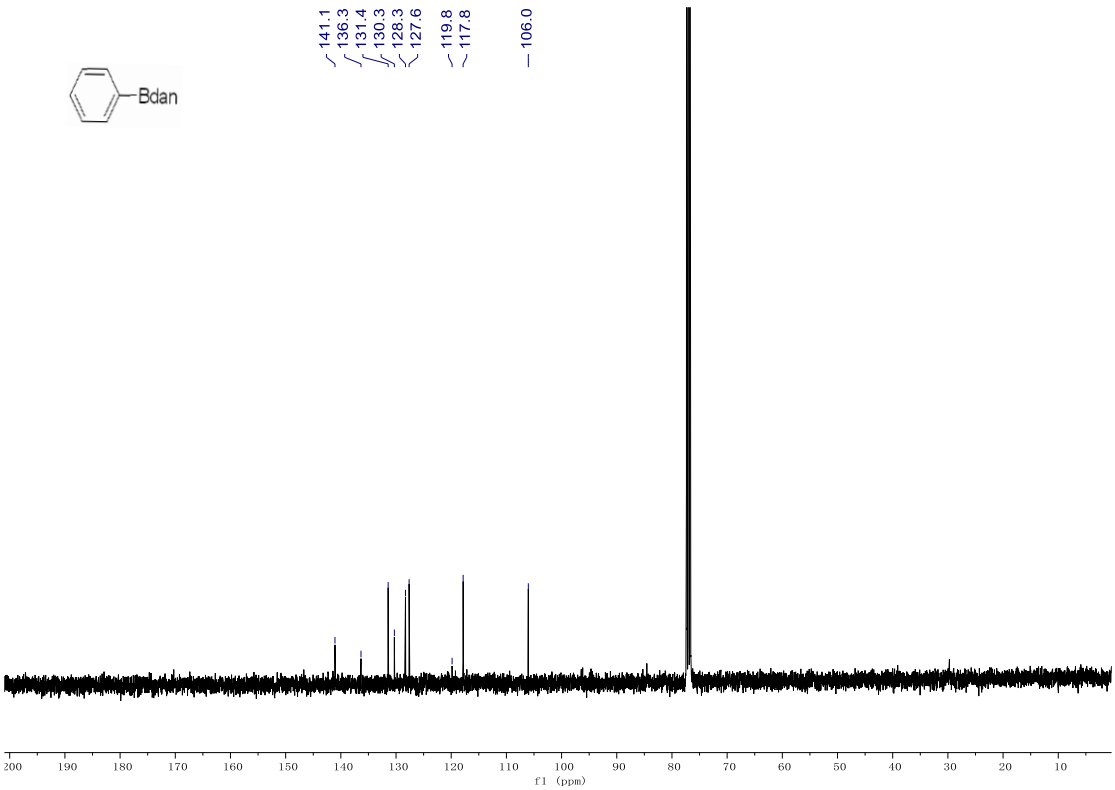
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **2p**



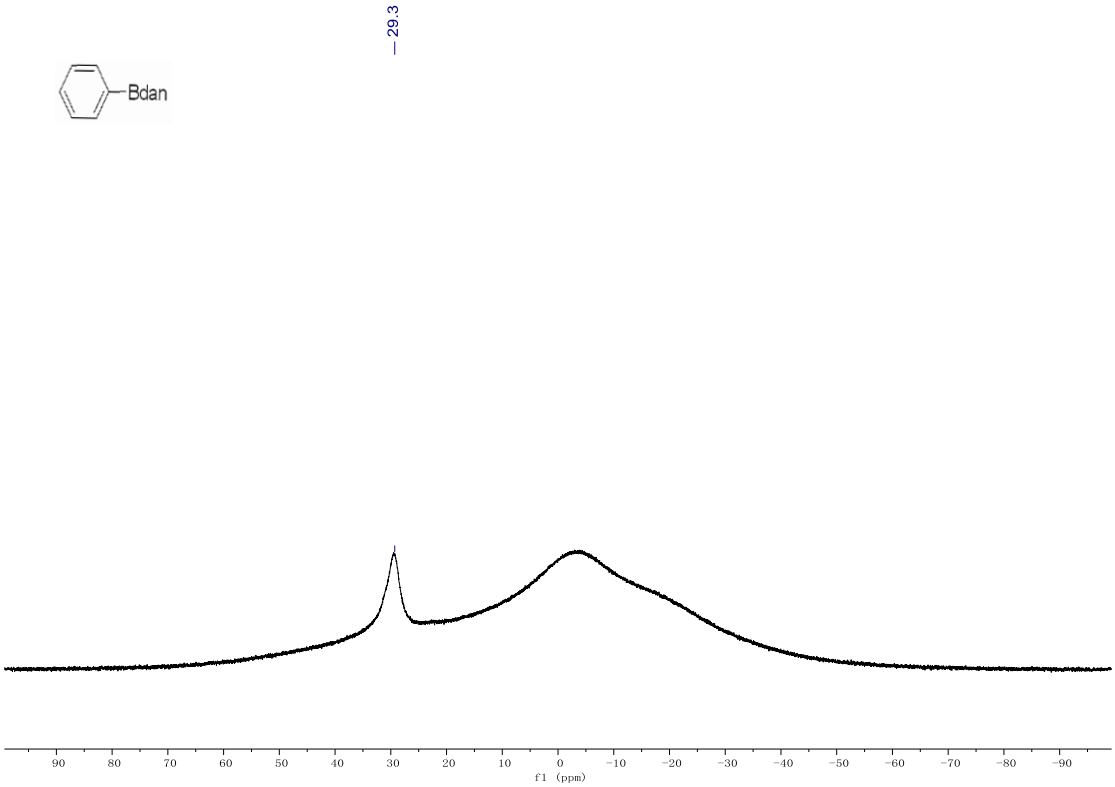
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3a**



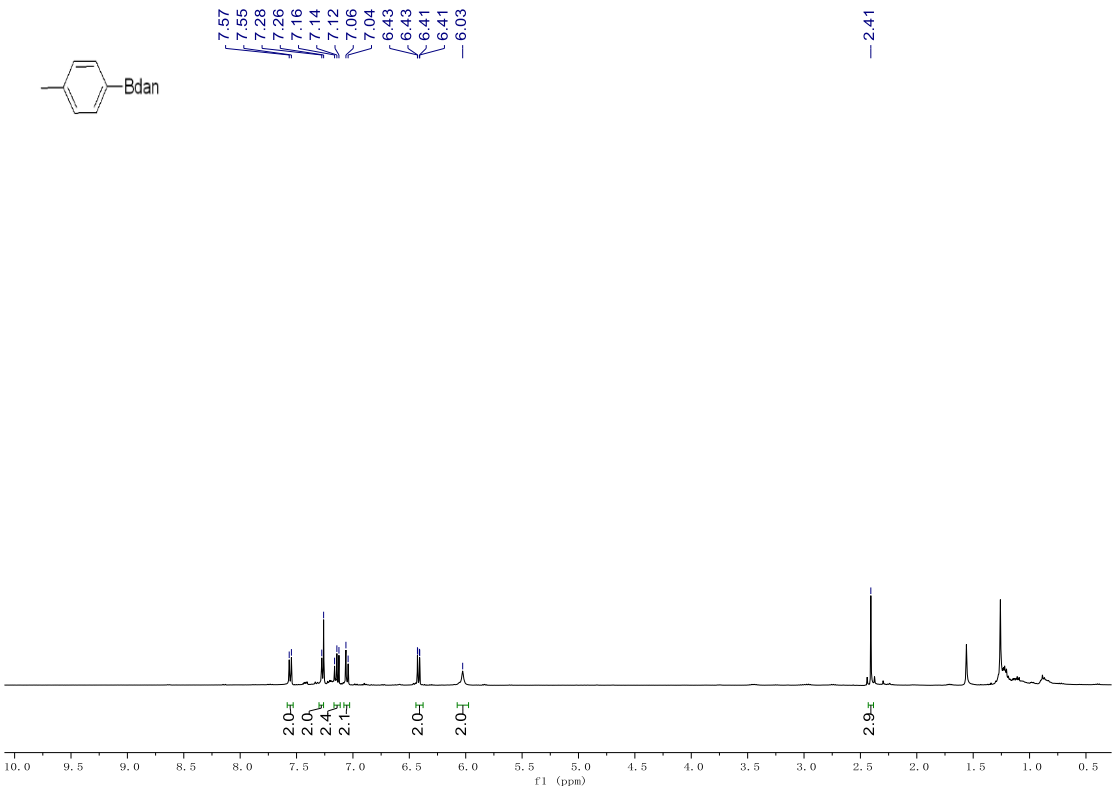
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **3a**



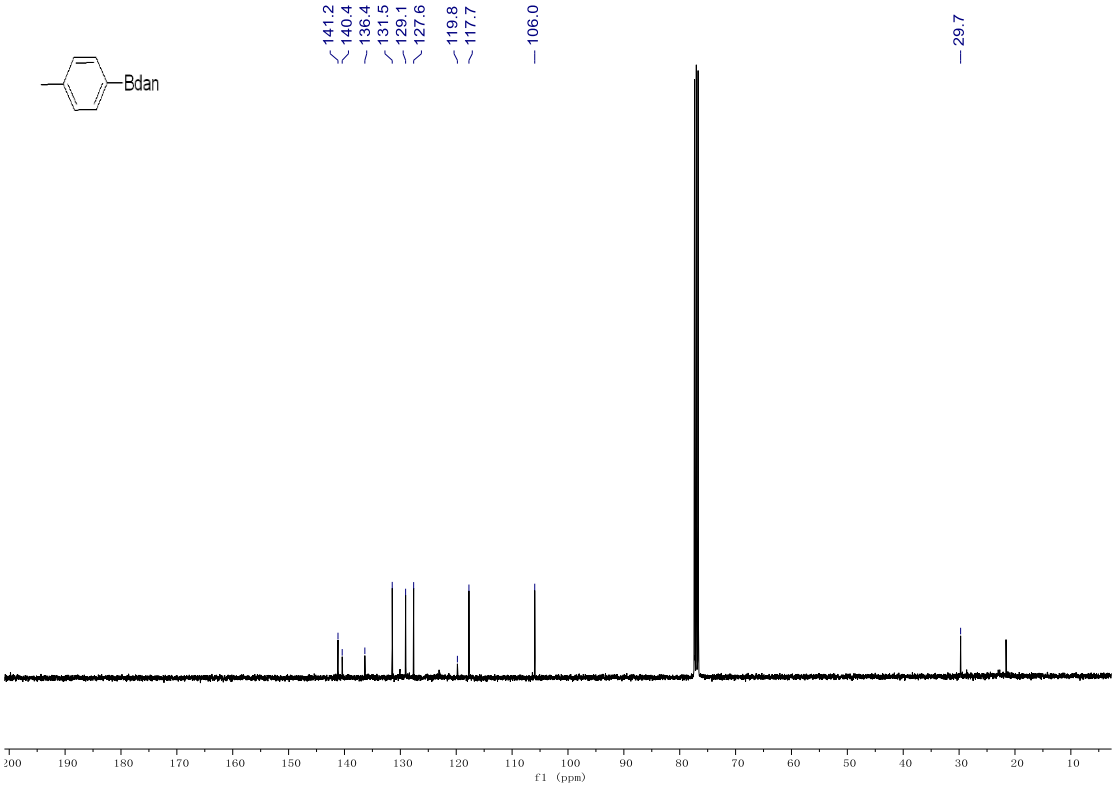
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **3a**



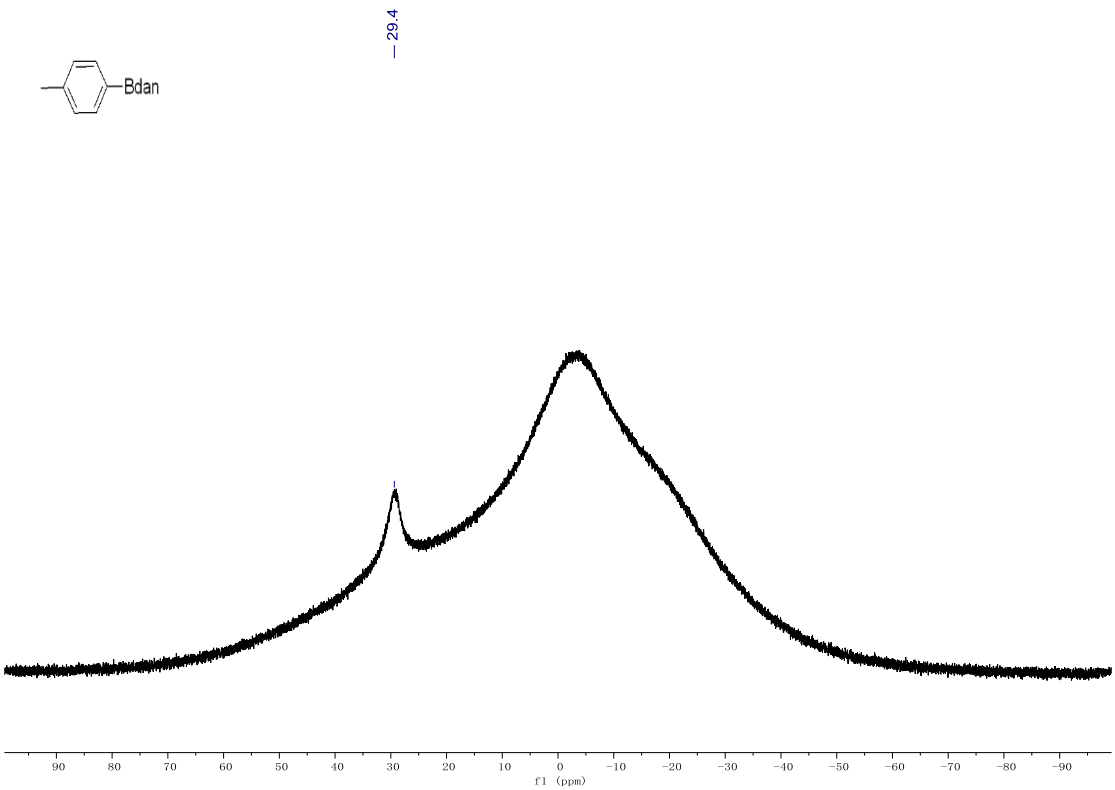
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3b**



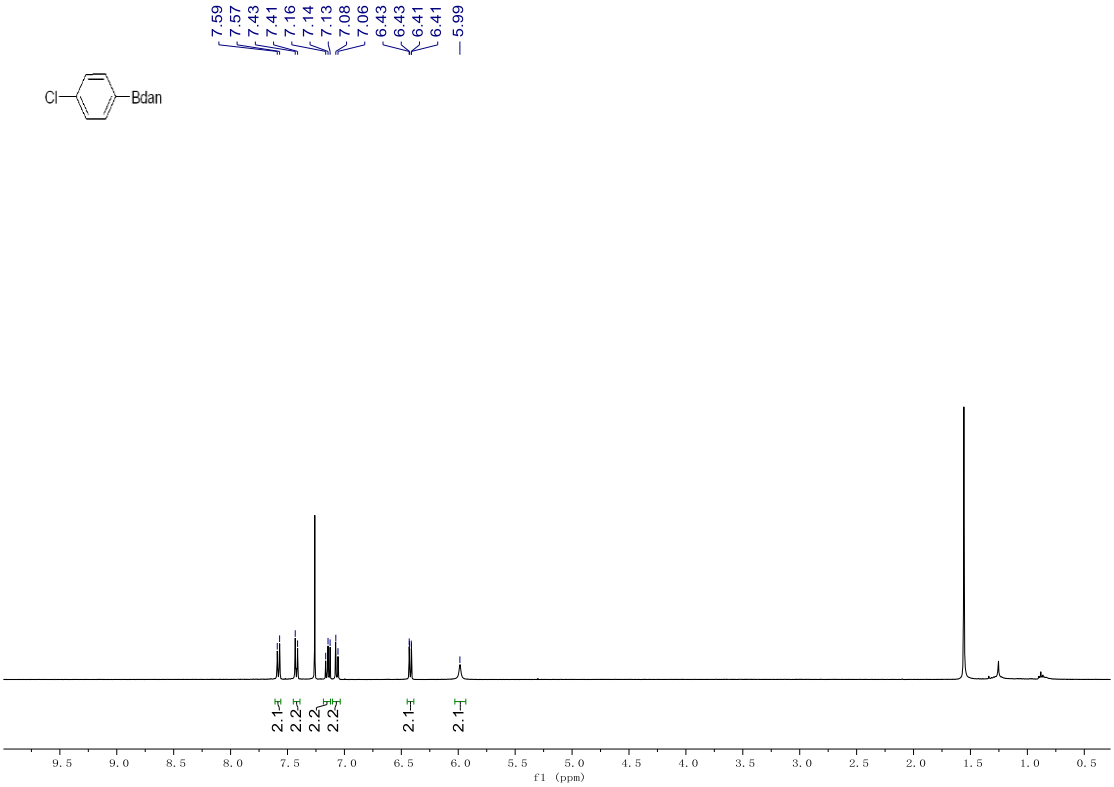
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3b**



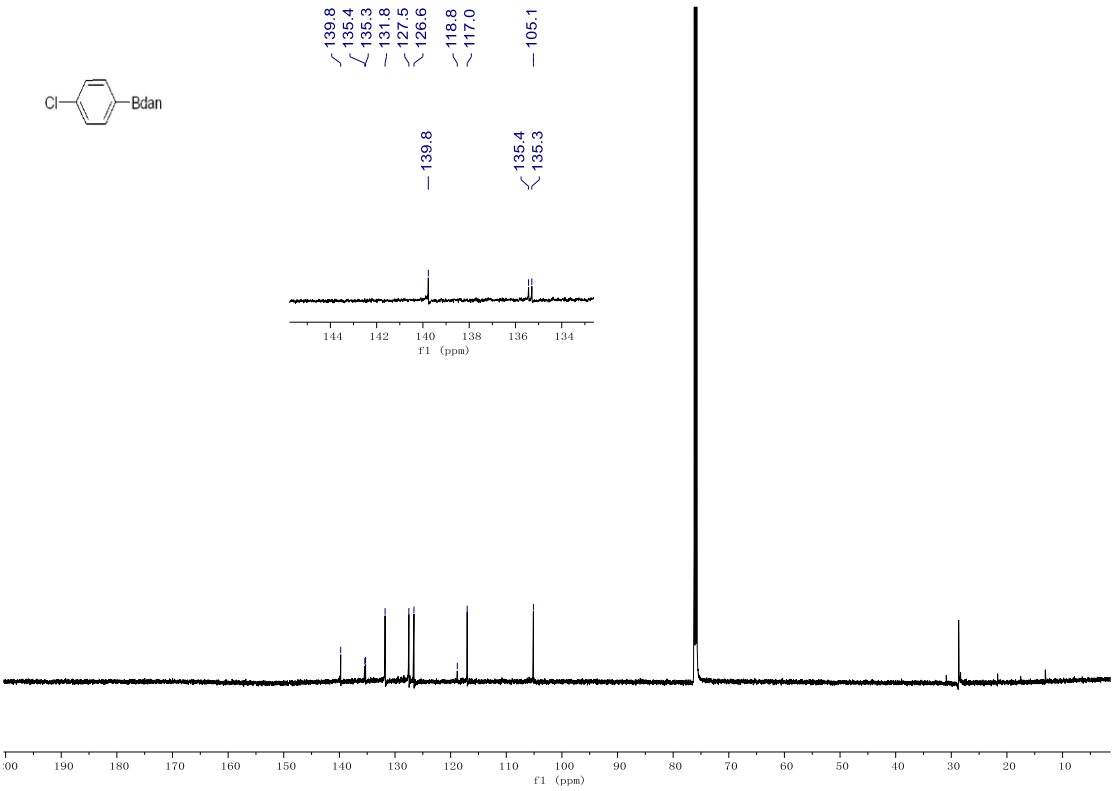
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **3b**



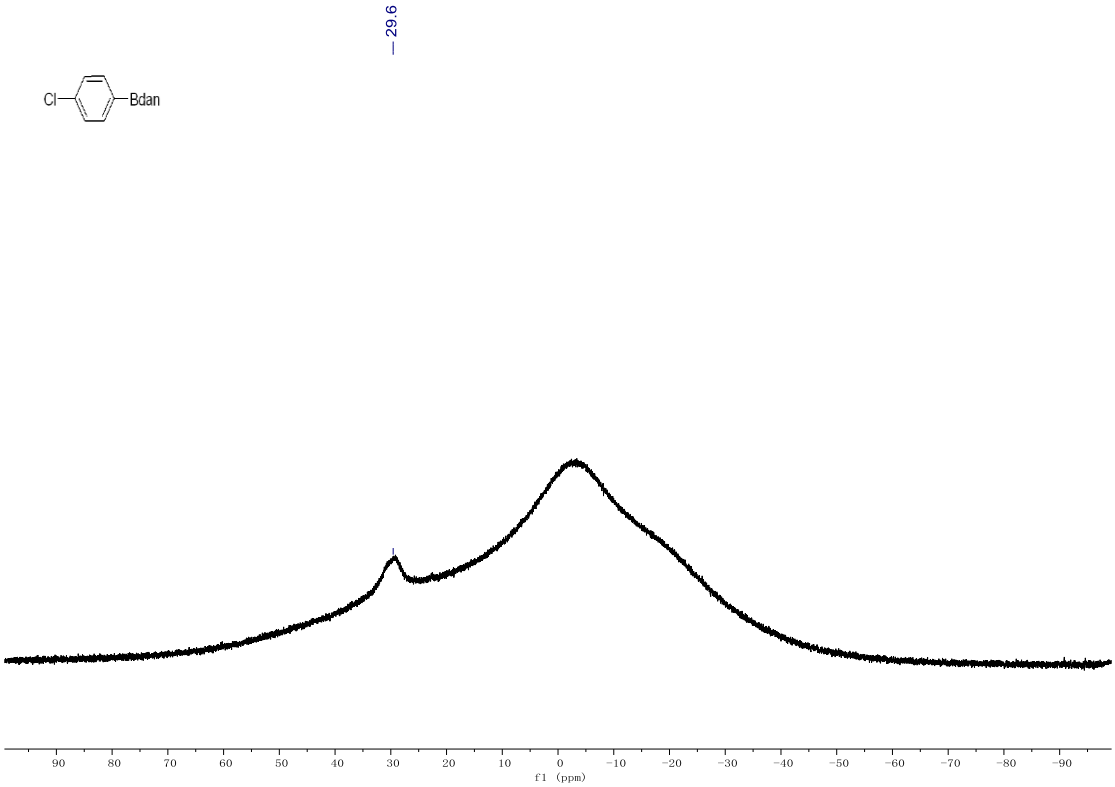
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3c**



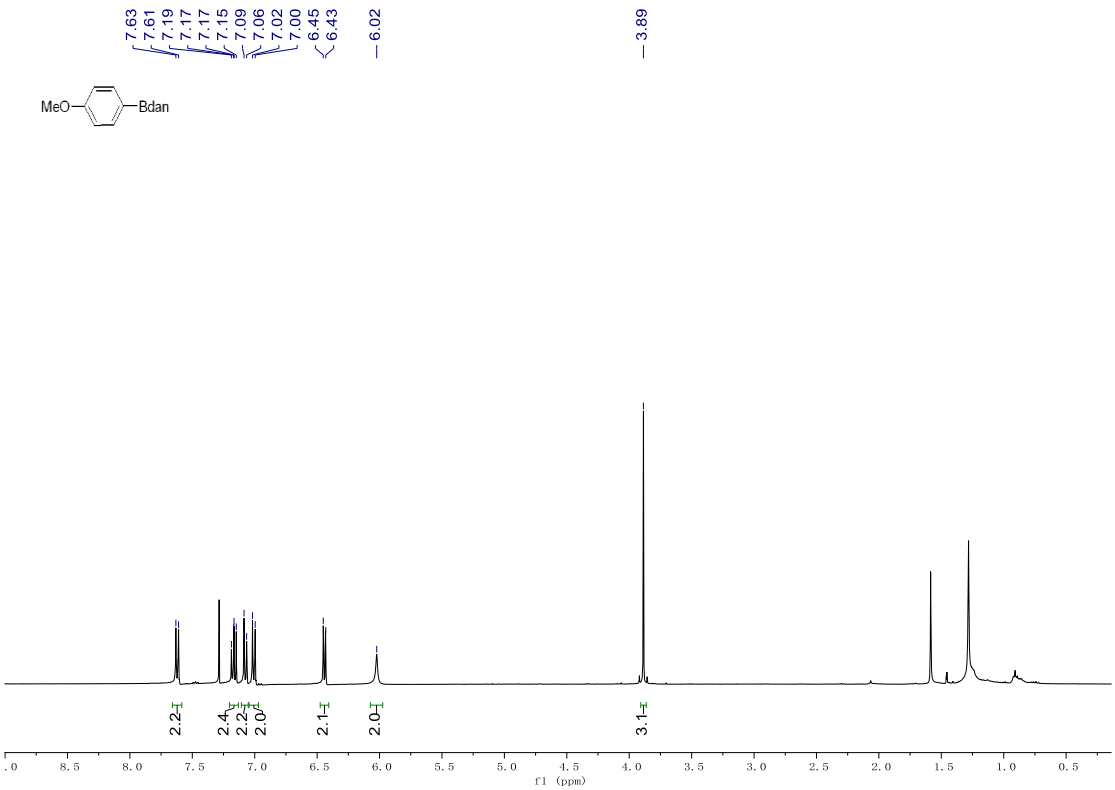
^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of **3c**



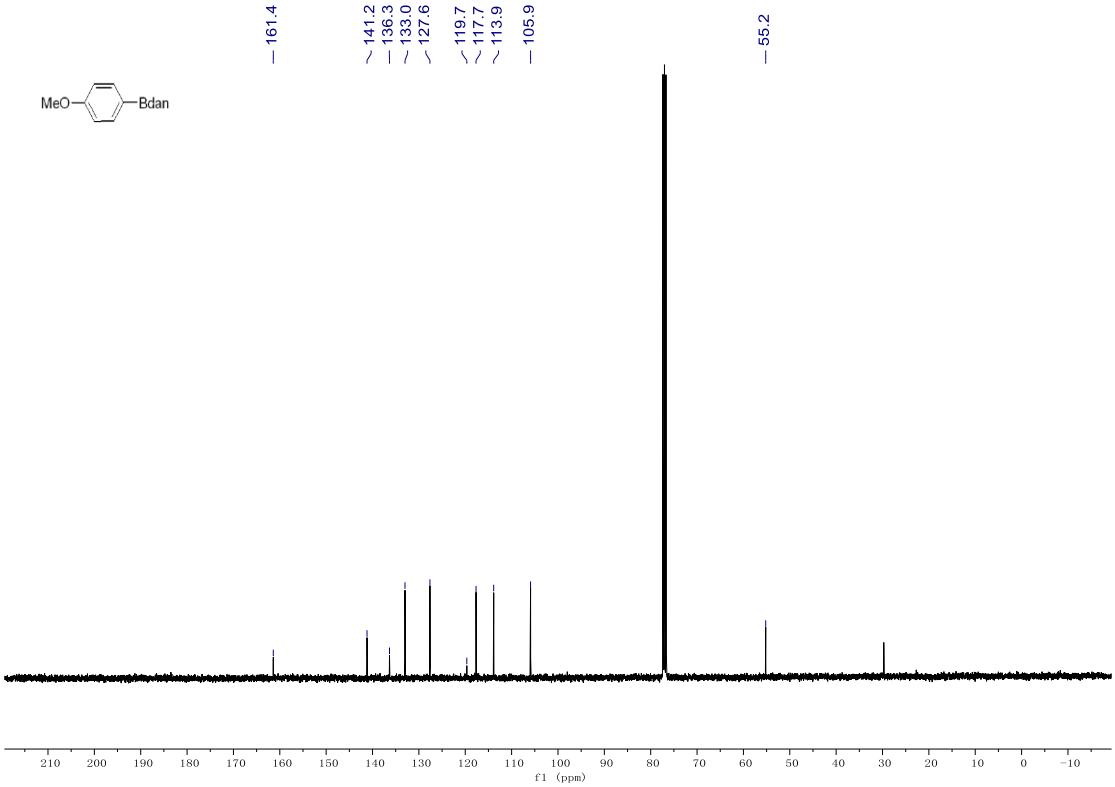
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **3c**



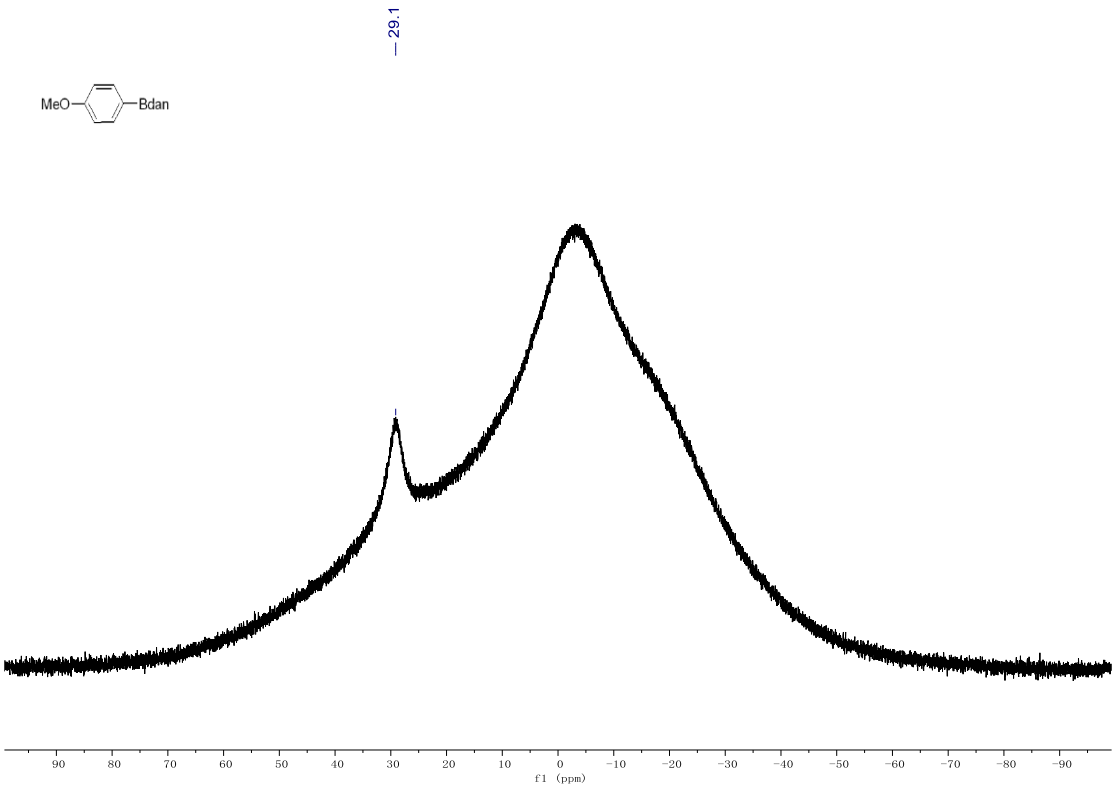
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3d**



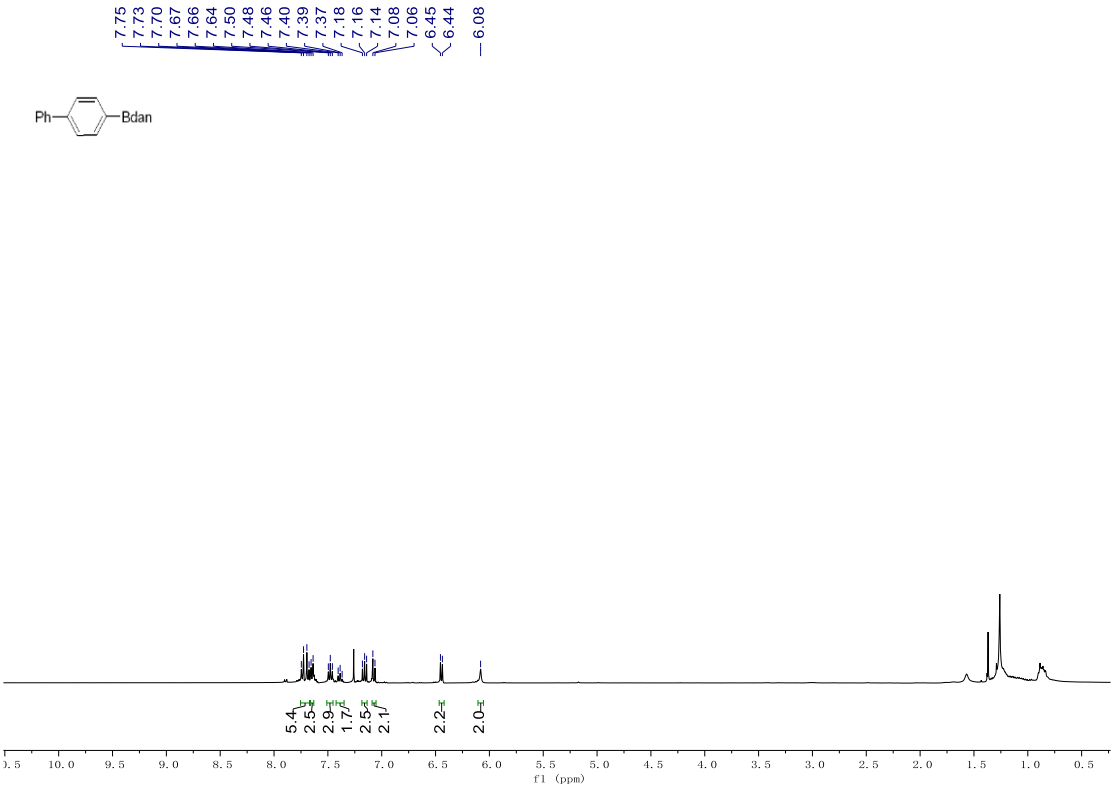
$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3d**



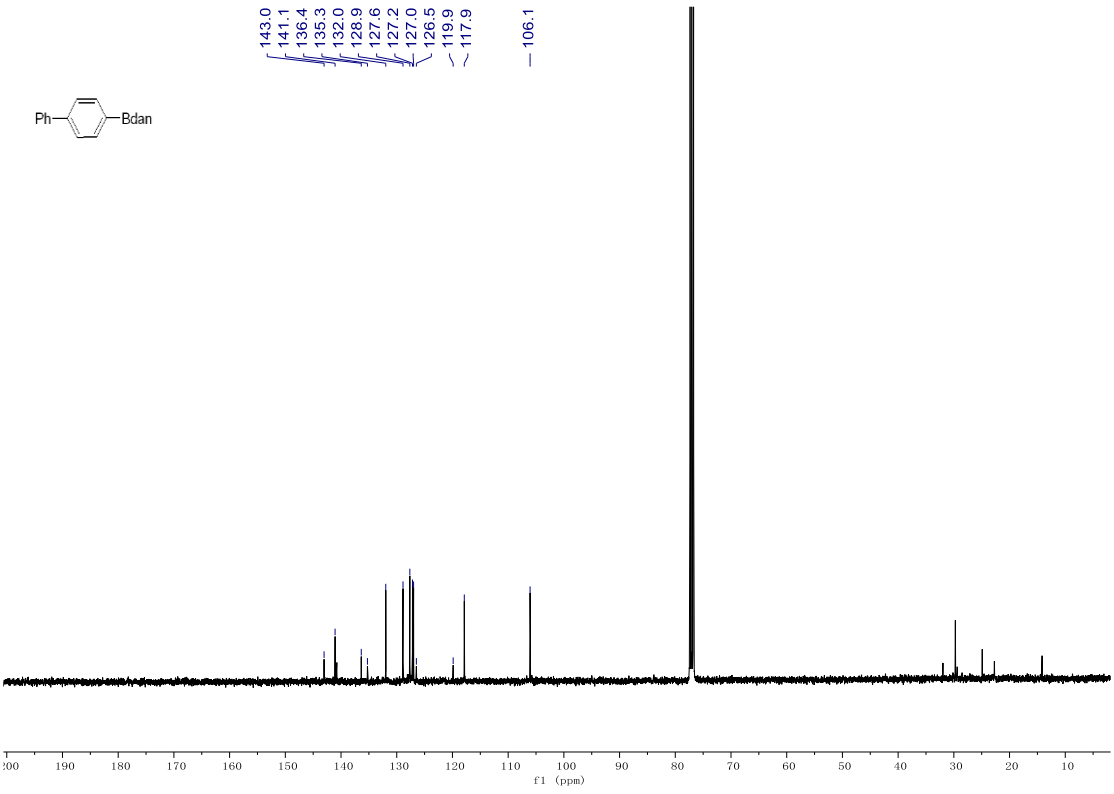
^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **3d**



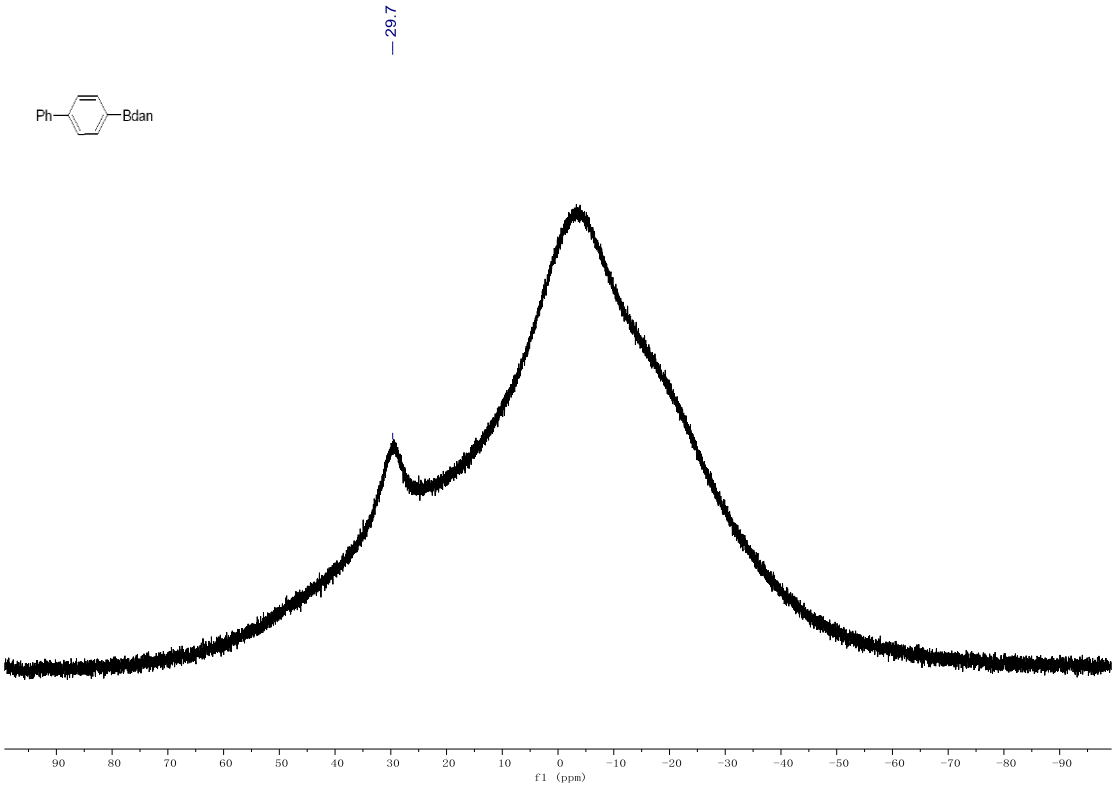
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **3e**



$^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of **3e**



^{11}B NMR spectrum (128 MHz, $CDCl_3$) of **3e**



VI. References

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(4) Zhang, L.; Jiao, L., Pyridine-Catalyzed Radical Borylation of Aryl Halides. *J. Am. Chem. Soc.* **2017,** *139*, 607-610.

Author Contributions

Q.Y. conceived the project. L.X. obtained preliminary results. Y.X. and W.M. completed the main experimental work. Q.Y. wrote the manuscript with input from Y.X. and W.M. All authors read and commented on the manuscript.