Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Cr-catalyzed borylation of C(aryl)–F bonds using terpyridine ligand

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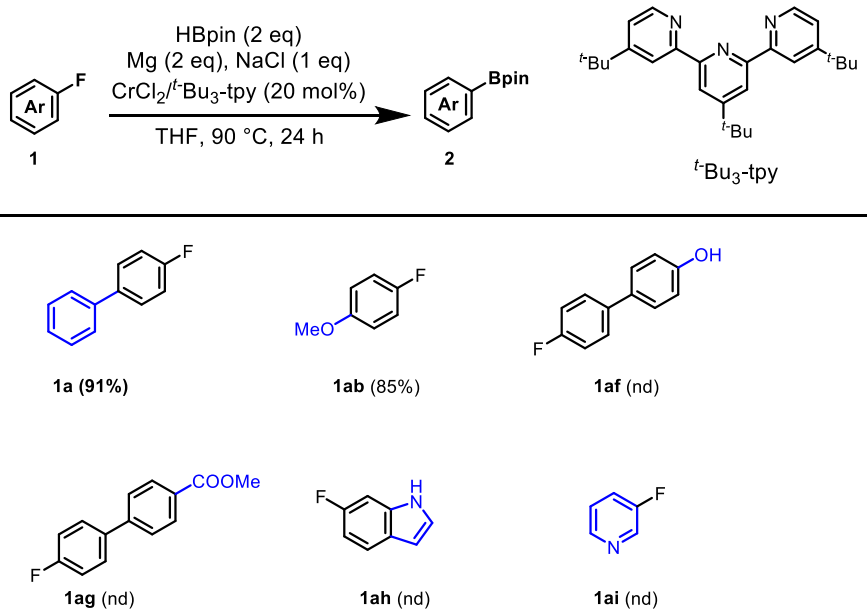
1. General Information

General. All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Flash silica gel column chromatography was performed on silica gel 60N (spherical and neutral, 140–325 mesh) as described by Still. NMR spectra were measured on a Bruker AV- 400 spectrometer and reported in parts per million. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ were referenced internally to tetramethylsilane as an internal standard, ^{13}C NMR spectra were recorded at 101 MHz and ^{11}B NMR spectra were recorded at 128 MHz and referenced to the solvent resonance. Analytical gas chromatography (GC) was carried out on a Thermo Trace 1300 gas chromatograph, equipped with a flame ionization detector. Mass spectra (GC-MS) were taken at Thermo Trace 1300 gas chromatograph mass spectrometer. High resolution mass spectra (HRMS) were recorded on the Exactive Mass Spectrometer (Thermo Scientific, USA) equipped with ESI ionization source. Melting points were determined with a Hanon MP-300.

Materials. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, Adamas-beta, and other commercial suppliers and used as received. Solvents were dried over sodium (for THF) by refluxing overnight and freshly distilled prior to use.

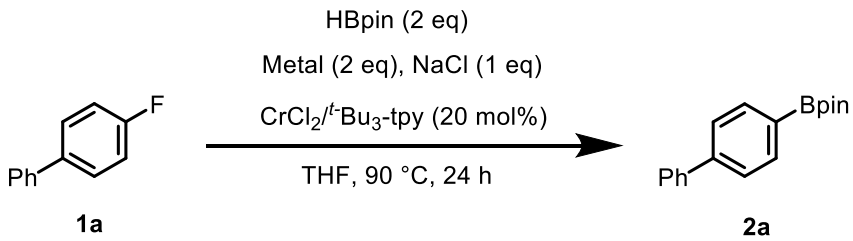
2. Optimization of Reaction Parameters

Table S1. **Studying the Effect of Substituents of Fluoroarenes on the Borylation**[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), HBpin (0.4 mmol), $CrCl_2$ (20 mol %), $^{t}Bu_3$-tpy (20 mol %), Mg (0.4 mmol) and NaCl (0.2 mmol), THF (2 mL), 90 °C, 24 h. [b]The yields are determined by GC analysis using *n*-tridecane as internal standard. n.d. = Not detected.

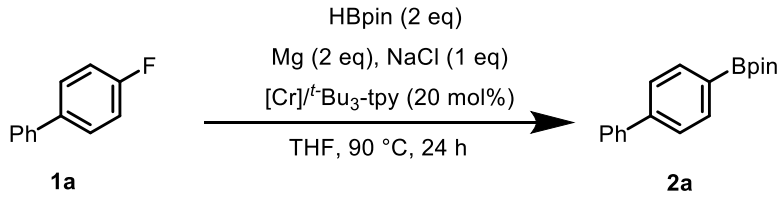
Table S2. **Studying the Effect of Metallic Reductants**[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), HBpin (0.4 mmol), $CrCl_2$ (20 mol %), $^{t}Bu_3$-tpy (20 mol %), Metal (0.4 mmol) and NaCl (0.2 mmol), THF (2 mL), 90 °C, 24 h. [b]The yields are determined by GC analysis using *n*-tridecane as internal standard. n.d. = Not detected.

Entry	.Metal	Yield (%)[b]
1	...Na	35
2	...Zn	nd
3	...Al	nd
4	...Mn	nd
5	...Fe	nd
6	**...Mg**	**.91**

***Table S3*. Studying the Effect of Chromium Salts[a,b]**

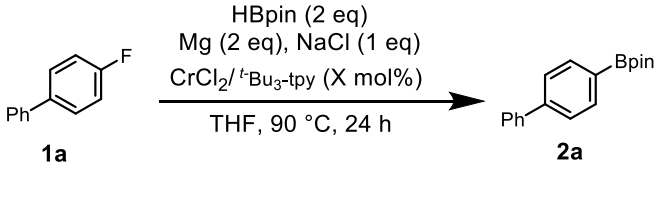


1a **2a**

Entry	Catalyst	..Yield (%)[b]
1	--	nd
2	$Cr(CO)_6$	nd
3	**$CrCl_2$**	**91**
4	$CrBr_3$	nd
5	$Cr(OAc)_3$	nd

[a]Reaction conditions: **1a** (0.2 mmol), HBpin (0.4 mmol), Chromium salt (20 mol %), ^{t}-Bu$_3$-tpy (20 mol %), Mg (0.4 mmol) and NaCl (0.2 mmol), THF (2 mL), 90 °C, 24 h. [b]The yields are determined by GC analysis using *n*-tridecane as internal standard. n.d. = Not detected.

***Table S4*. Studying the Effect of the Amounts of $CrCl_2$ on the Borylation[a,b]**

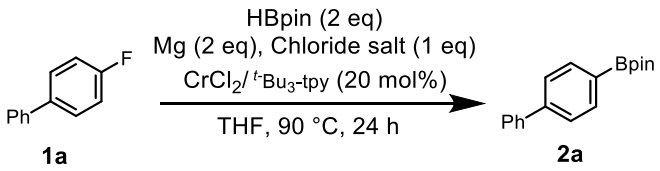


1a **2a**

..Entry	$CrCl_2$ (X mol%)	Yield (%)[b]
1	none	**nd**
2	5 mol%	38
3	10 mol%	71
4	15 mol%	79
5	**20 mol%**	**91**

[a]Reaction conditions: **1a** (0.2 mmol), HBpin (0.4 mmol), $CrCl_2$ (X mol %), ^{t}-Bu$_3$-tpy (X mol %), Mg (0.4 mmol) and NaCl (0.2 mmol), THF (2 mL), 90 °C, 24 h. [b]The yields are determined by GC analysis using n-tridecane as internal standard. n.d. = Not detected.

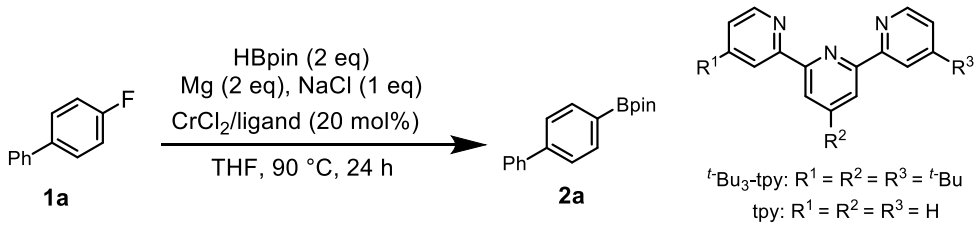
***Table S5*. Studying the Effect of Chloride Salts on the Borylation[a,b]**



..Entry	Chloride salt	Yield (%)[b]
1	none	**76**
2	NaCl	91
3	LiCl	88
4	KCl	83
5	TBAC	58

[a]Reaction conditions: **1a** (0.2 mmol), HBpin (0.4 mmol), $CrCl_2$ (20 mol %), ^{t}-Bu_3-tpy (20 mol %), Mg (0.4 mmol) and Chloride salt (0.2 mmol), THF (2 mL), 90 °C, 24 h. [b]The yields are determined by GC analysis using n-tridecane as internal standard. n.d. = Not detected.

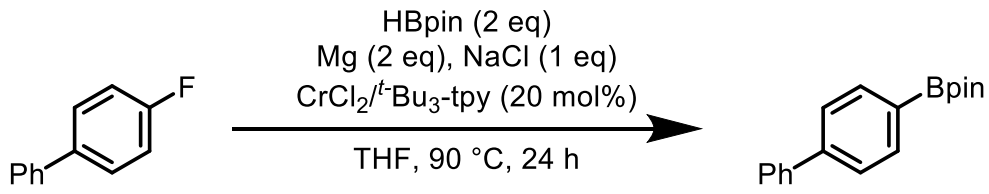
***Table S6*. Studying the Effect of Ligands[a,b]**



..Entry	Ligand	Yield (%)[b]
1	^{t}-Bu_3-tpy	**91**
2	dtbpy	nd
3	bpy	nd
4	1,10-phen	nd
5	tpy	62

[a]Reaction conditions: **1a** (0.2 mmol), HBpin (0.4 mmol), $CrCl_2$ (20 mol %), Ligand (20 mol %), Mg (0.4 mmol) and NaCl (0.2 mmol), THF (2 mL), 90 °C, 24 h. [b]The yields are determined by GC analysis using n-tridecane as internal standard. n.d. = Not detected.

***Table S7*. Optimization of Reaction Parameters[a]**



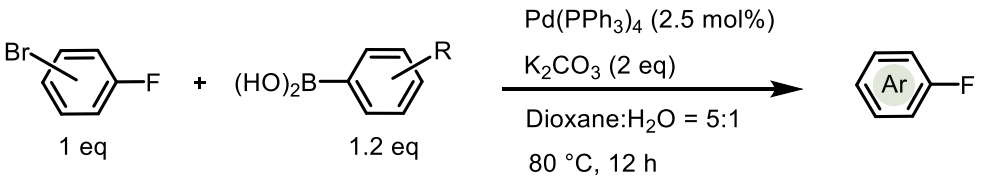
1a **2a**

Entry	Variation from standard conditions	Yield (%)[a]
1	**none**	**91**
2	25 °C instead of 90 °C	trace
3	40 °C instead of 90 °C	21
4	120 °C instead of 90 °C	88
5	12 h instead of 24 h	68

[a]The yields are determined by GC analysis using *n*-tridecane as internal standard. Reaction conditions: **1a** (0.2 mmol), HBpin (0.4 mmol), $CrCl_2$ (20 mol %), $^{t}Bu_3$-tpy (20 mol %), Mg (0.4 mmol) and NaCl (0.2 mmol), THF (2 mL), 90 °C, 24 h.

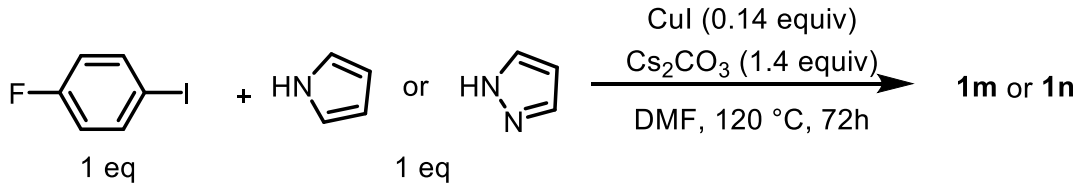
3. General Procedure for the Synthesis of Fluoroarenes

Method A for the synthesis of compouds 1a-1l, 1x, 1aa, 1ab, 1ae:



Fluoroarenes were prepared by modifying the reported procedure.[1] To a solution of corresponding phenylboronic acid (1.2 equiv) and corresponding bromo-substituted fluorobenzene (1.0 equiv), $Pd(PPh_3)_4$ (0.025 equiv), and potassium carbonate (2.0 equiv) in 1,4-dioxane:water (5:1) at room temperature under N_2 with stirring. After stirring for 12 h at 80 °C, the mixture was cooled to room temperature and filtered through a plug of Celite with diethyl ether (Et_2O) (100 mL). The combined organic extracts were washed with brine (30 mL) and dried over sodium sulfate (Na_2SO_4). After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by passing through a pad of silica gel to get the product **1a-1l, 1x, 1aa, 1ab, 1ae.**

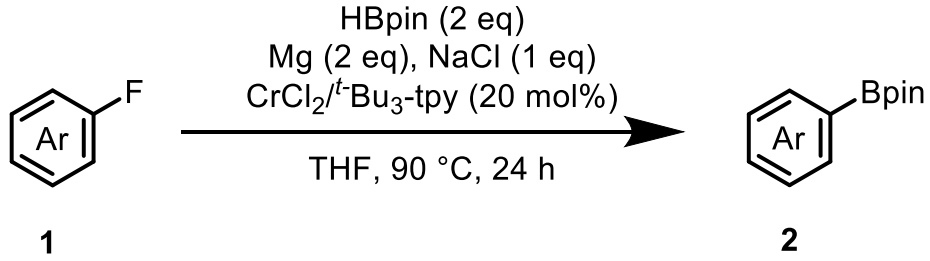
Method B for the synthesis of compounds 1m and 1n:



1m and **1n** were prepared by modifying the reported procedure.[1] To a suspension of copper iodide (0.14 equiv), cesium carbonate (1.4 equiv) in DMF (1M) were added 1-fluoro-4-iodobenzene (1.0 equiv) and pyrazole or pyrrole (1.0 equiv) at room temperature. After stirring for 72 h at 120 °C, the mixture was cooled to room temperature and water (10 mL) was added then filtered through a plug of Celite with EtOAc (20 mL) and then extracted with EtOAc (20 mL × 3). The combined organic extract was washed with brine (10 mL) and dried over Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by passing through a short pad of silica gel (PE/EtOAc = 10/1) to give the product **1m, 1n**.

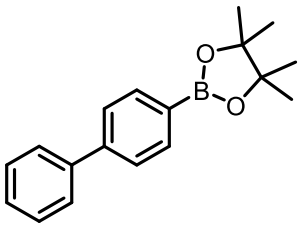
1o, 1p, 1q, 1r, 1s, 1t, 1u, 1v, 1w, 1y, 1z, 1ac, 1ad were all commercially available.

4. Cr-catalyzed Borylation of C(aryl)–F Bonds Using Terpyridine Ligand



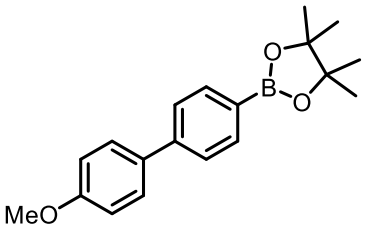
A dried Schlenk tube were placed fluoroarenes **1** (0.2 mmol), $CrCl_2$ (4.9 mg, 0.04 mmol), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.4 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) was added dropwise by syringe under atmosphere of nitrogen. After stirring for 24 h at 90 °C, the resulting mixture was quenched by an aqueous solution of NH_4Cl and extracted with ethyl acetate (3 x 10 mL). The combined organic phase

was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel chromatography to give the desired coupling product.



2a: 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl

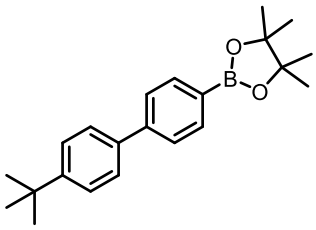
The general procedure was applied to **1a** (34.4 mg, 0.2 mmol), $CrCl_2$ (4.9 mg, 0.04 mmol), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 30/1) to give **2a** (47.6 mg, 85% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.1 Hz, 2H), 7.67 – 7.62 (m, 4H), 7.47 (t, J = 7.5 Hz, 2H), 7.40 – 7.35 (m, 1H), 1.39 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 141.1, 135.3, 128.8, 127.6, 127.3, 126.5, 83.9, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.9. Spectroscopic data are in accordance with those described in the literature.[1]



2b: 4-Methoxy-4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)biphenyl

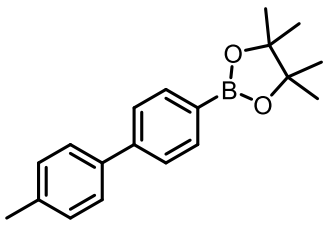
The general procedure was applied to **1b** (40.4mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column

chromatography on silica gel (PE/EtOAc = 15:1) to give **2b** (50.2 mg, 81% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.1 Hz, 2H), 7.60 – 7.55 (m, 4H), 7.01 – 6.97 (m, 2H), 3.86 (s, 3H), 1.37 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 143.6, 135.4, 133.6, 128.4, 126.1, 114.4, 83.9, 55.5, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.6. Spectroscopic data are in accordance with those described in the literature.[1]



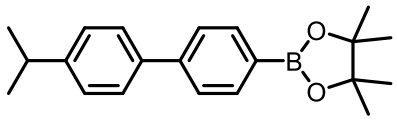
2c: 2-(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure was applied to **1c** (45.6mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 30/1) to give **2c** (48.8 mg, 76% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.1 Hz, 2H), 7.60 (dd, J = 15.8, 8.3 Hz, 4H), 7.48 (d, J = 8.5 Hz, 2H), 1.38 (s, 12H + 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 143.7, 138.1, 135.2, 126.9, 126.3,125.8, 83.8, 34.6, 31.4, 29.7, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6. Spectroscopic data are in accordance with those described in the literature.[1]



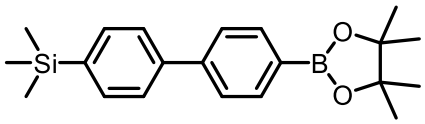
2d: 4,4,5,5-tetramethyl-2-(4'-methyl-[1,1'-biphenyl]-4-yl)-1,3,2-dioxaborolane

The general procedure was applied to **1d** (37.2 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}Bu$_3$-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 30/1) to give **2d** (48.8 mg, 83% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.9 Hz, 2H), 7.61 – 7.58 (m, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 4.2 Hz, 2H), 2.39 (s, 3H), 1.36 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 138.3, 137.5, 135.4, 129.6, 127.2, 126.4, 83.92, 25.0, 21.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6. Spectroscopic data are in accordance with those described in the literature.[1]



2e: 2-(4'-isopropyl-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure was applied to **1e** (42.8 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}Bu$_3$-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 30/1) to give **2e** (50.2 mg, 78% yield) as white solid. Mp 123 - 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.62 – 7.55 (m, 4H), 7.31 (d, J = 8.2 Hz, 2H), 2.93 – 3.00 (m, J = 6.9 Hz, 1H), 1.37 (s, 12H), 1.30 (d, J = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 144.0, 138.7, 135.4, 127.2, 127.0, 126.5, 83.9, 34.0, 25.0, 24.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.8. IR $\tilde{\nu}$ = 2973, 2898, 2262, 1999, 1612, 1395, 1361, 1361, 1048, 822, 654 cm^{-1}. HRMS (ESI+) calcd for $C_{21}H_{28}BO_2$ $[M+H]^+$: 323.2177, found 323.2180 .



2f: trimethyl(4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-yl)silane

The general procedure was applied to **1f** (48.8 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}Bu$_3$-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 30/1) to give **2f** (54.9 mg, 78% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 6.8 Hz, 6H), 1.37 (s, 12H), 0.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 141.5, 139.8, 135.4, 134.0, 126.7, 126.6, 84.0, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6. Spectroscopic data are in accordance with those described in the literature.[2]

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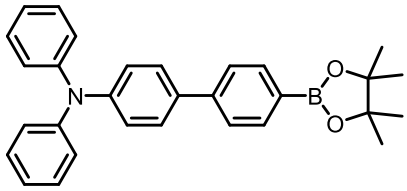
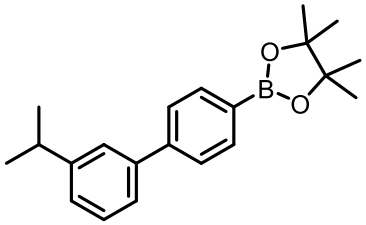


2g: *N*,*N*-diphenyl-4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]- 4-amine

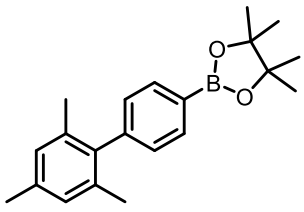
The general procedure was applied to **1g** (67.8 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}Bu$_3$-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 30/1) to give **2g** (64.3 mg, 72% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.8 Hz, 2H), 7.60 (d, J = 7.8 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.31 – 7.26 (m, 4H), 7.17 – 7.12 (m, 6H), 7.05 (t, J = 7.3 Hz, 2H), 1.37 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 147.6, 135.4, 129.4,

128.0, 126.0, 124.6, 123.9, 123.1, 83.9, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.0. Spectroscopic data are in accordance with those described in the literature.[3]



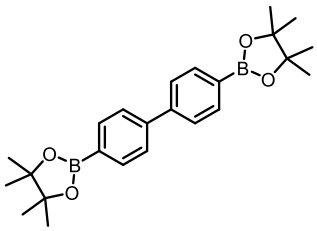
2h: 2-(3'-isopropyl-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure was applied to **1h** (42.8 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 ºC for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to give **2h** (48.4 mg, 75% yield) as white solid. Mp 114 - 116 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.25 (t, J = 7.6 Hz, 1H), 7.11 (dt, J = 7.5, 1.6 Hz, 1H), 2.83 – 2.90 (m, J = 6.9 Hz, 1H), 1.25 (s, 12H), 1.19 (d, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 144.4, 141.2, 135.4, 128.9, 126.7, 125.8, 125.6, 124.9, 83.9, 34.4, 25.0, 24.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7. IR $\tilde{\nu}$ = 2977, 2902, 2356, 1610, 1393, 1359, 1260, 1145, 1057, 795, 659 cm^{-1}. HRMS (ESI+) calcd for $C_{21}H_{28}BO_2$ $[M+H]^+$: 323.2177, found 323.2180.



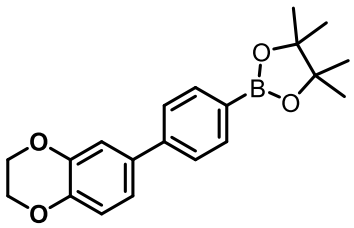
2i:4,4,5,5-tetramethyl-2-(2',4',6'-trimethyl-[1,1'-biphenyl]-4-yl)-1,3,2-dioxaborolane

The general procedure was applied to **1i** (42.8 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), $^{t}Bu_3$-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to give **2i** (41.9 mg, 65% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.93 (s, 2H), 2.33 (s, 3H), 1.99 (s, 6H), 1.37 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 135.0, 128.9, 128.2, 83.9, 25.0, 21.2, 20.8. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.1. Spectroscopic data are in accordance with those described in the literature.[1]



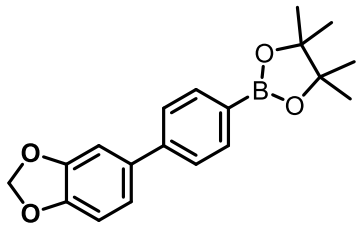
2j: 4,4'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1'-biphenyl

The general procedure was applied to **1j** (38 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), $^{t}Bu_3$-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (4 equiv, 0.8 mmol, 116 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 15/1) to give **2j** (48.8 mg, 58% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 4H), 7.63 (d, J = 8.2 Hz, 4H), 1.36 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 135.4, 126.7, 84.0, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7. Spectroscopic data are in accordance with those described in the literature.[4]



2k: 2-(4-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

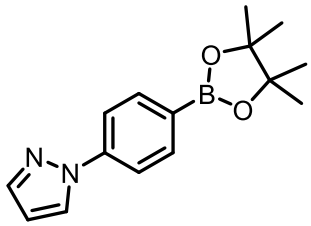
The general procedure was applied to **1k** (46 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 ºC for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 15/1) to give **2k** (53.4 mg, 79% yield) as white solid. Mp 161 - 162 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.16 – 7.10 (m, 2H), 6.94 (d, J = 8.3 Hz, 1H), 4.30 (s, 4H), 1.36 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 143.6, 143.4, 135.4, 134.7, 126.2, 120.4, 117.7, 116.1, 83.9, 64.6, 64.6, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.7. IR $\tilde{\nu}$ = 2918, 2243, 2157, 1609, 1394, 1352, 1306, 1141, 1092, 815, 660, 601 cm^{-1}. HRMS (ESI+) calcd for $C_{20}H_{24}BO_4$ $[M+H]^+$: 339.1762, found 339.1762.



2l: 2-(4-(benzo[*d*][1,3]dioxol-5-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

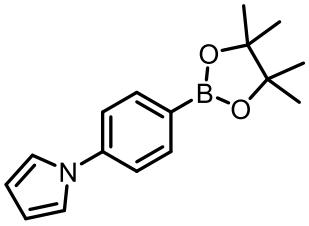
The general procedure was applied to **1l** (43.2 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 ºC for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 15/1) to give **2l** (52.5 mg, 81% yield) as

white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.11 – 7.08 (m, 2H), 6.89 (d, J = 8.5 Hz, 1H), 6.00 (s, 2H), 1.36 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 147.5, 143.1, 135.5, 135.4, 126.3, 121.0, 108.7, 107.8, 101.3, 84.0, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7. Spectroscopic data are in accordance with those described in the literature.[1]



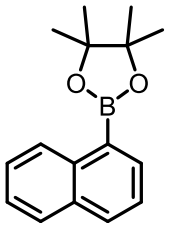
2m: 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1*H*-pyrazole

The general procedure was applied to **1m** (32.2 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 10/1) to give **2m** (36.7 mg, 68% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 2.5 Hz, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.74 – 7.70 (m, 3H), 6.47 (t, J = 2.1 Hz, 1H), 1.36 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 141.5, 136.3, 126.9, 118.1, 108.0, 84.1, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.5. Spectroscopic data are in accordance with those described in the literature.[1]



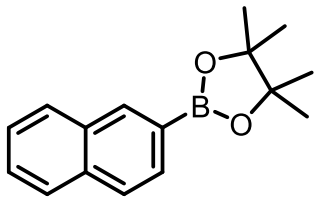
2n: 1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1*H*-pyrrole

The general procedure was applied to **1n** (32 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 10/1) to give **2n** (42.5 mg, 79% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.16 (t, J = 2.2 Hz, 2H), 6.38 (t, J = 2.2 Hz, 2H), 1.38 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 136.4, 119.3, 119.2, 110.9, 84.0, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.2. Spectroscopic data are in accordance with those described in the literature.[1]



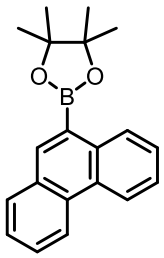
2o: 4,4,5,5-tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane

The general procedure was applied to **1o** (29.2 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to give **2o** (40.6 mg, 80% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 – 8.76 (m, 1H), 8.09 (dd, J = 6.8, 1.4 Hz, 1H), 7.94 (dt, J = 8.3, 1.0 Hz, 1H), 7.87 – 7.82 (m, 1H), 7.57 – 7.52 (m, 1H), 7.48 (dd, J = 8.2, 6.8 Hz, 2H), 1.44 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 135.8, 133.4, 131.7, 128.6, 128.5, 126.5, 125.6, 125.1, 83.9, 25.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.1. Spectroscopic data are in accordance with those described in the literature.[4]



2p: 4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane

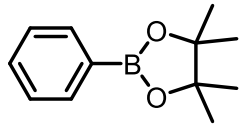
The general procedure was applied to **1p** (29.2 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE /EtOAc= 20/1) to give **2p** (41.1 mg, 81% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 – 8.76 (m, 1H), 8.09 (dd, J = 6.8, 1.4 Hz, 1H), 7.94 (dt, J = 8.3, 1.0 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.55 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.48 (dd, J = 8.2, 6.8 Hz, 2H), 1.44 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 135.8, 133.4, 131.7, 128.6, 128.5, 126.5, 125.6, 125.1, 83.9, 25.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.54. Spectroscopic data are in accordance with those described in the literature.[5]



2q: 4,4,5,5-tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane

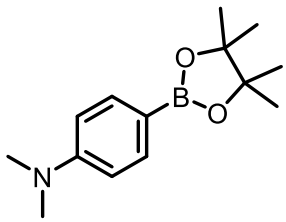
The general procedure was applied to **1q** (39.2 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 30/1) to give **2q** (47.7 mg, 78% yield) as

white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 – 8.89 (m, 1H), 8.76 – 8.69 (m, 2H), 8.47 (s, 1H), 8.00 (dd, J = 7.9, 1.4 Hz, 1H), 7.75 – 7.67 (m, 3H), 7.66 – 7.60 (m, 1H), 1.50 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 134.6, 132.0, 131.2, 130.1, 129.5, 129.3, 127.9, 126.9, 126.6, 126.3, 122.8, 122.6, 84.0, 25.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.2. Spectroscopic data are in accordance with those described in the literature.[6]



2r: 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane

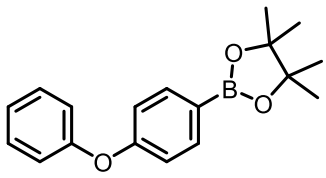
The general procedure was applied to **1r** (19.2 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to give **2r** (28.9 mg, 71% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 2H), 7.50 – 7.44 (m, 1H), 7.41 – 7.35 (m, 2H), 1.36 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9, 131.4, 127.8, 83.9, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.1. Spectroscopic data are in accordance with those described in the literature.[4]



2s: *N,N*-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline

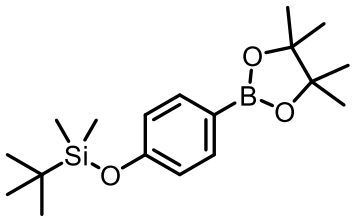
The general procedure was applied to **1s** (27.8 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4

mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 40/1) to give **2s** (35.6 mg, 72% yield) as brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 6.70 (d, J = 8.8 Hz, 2H), 3.00 (s, 6H), 1.34 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 136.2, 111.3, 83.2, 40.2, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.9. Spectroscopic data are in accordance with those described in the literature.[5]



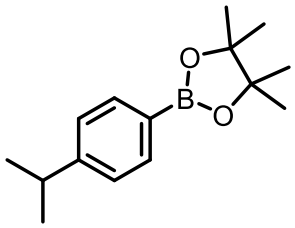
2t: 4,4,5,5-tetramethyl-2-(4-phenoxyphenyl)-1,3,2-dioxaborolane

The general procedure was applied to **1t** (37.6 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 30/1) to give **2t** (42 mg, 71% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.13 (td, J = 7.3, 1.2 Hz, 1H), 7.06 – 6.97 (m, 4H), 1.35 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 156.7, 136.8, 129.9, 123.8, 119.6, 117.8, 83.9, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.4. Spectroscopic data are in accordance with those described in the literature.[7]



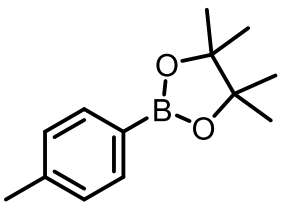
2u: *tert*-butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)- silane

The general procedure was applied to **1u** (45.2 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 40/1) to give **2u** (44.7 mg, 67% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 1.33 (s, 12H), 0.98 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 136.6, 119.8, 83.7, 25.8, 25.0, 18.4, -4.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6. Spectroscopic data are in accordance with those described in the literature.[1]



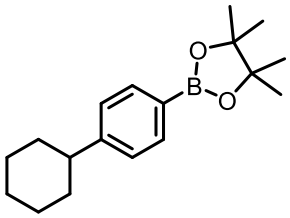
2v: 2-(4-isopropylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure was applied to **1v** (27.6 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to give **2v** (34.4 mg, 70% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 1.9 Hz, 2H), 7.36 – 7.30 (m, 2H), 2.94 (p, J = 6.9 Hz, 1H), 1.36 (s, 12H), 1.28 (d, J = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 133.0, 132.5, 129.5, 127.9, 83.8, 34.3, 25.0, 24.2. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.0. Spectroscopic data are in accordance with those described in the literature.[8]



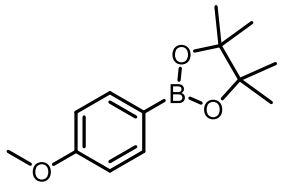
2w: 4,4,5,5-tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane

The general procedure was applied to **1w** (22.0 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to give **2w** (32.3 mg, 74% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.7 Hz, 2H), 7.20 (d, J = 7.5 Hz, 2H), 2.38 (s, 3H), 1.35 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 134.9, 128.7, 83.7, 25.0, 21.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.1. Spectroscopic data are in accordance with those described in the literature.[1]



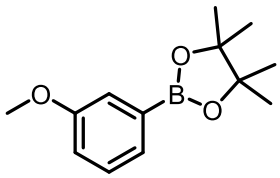
2x: 2-(4-cyclohexylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure was applied to **1x** (35.6 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 50/1) to give **2x** (39.5 mg, 69% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 2.56 – 2.47 (m, 1H), 1.86 (td, J = 9.9, 9.1, 5.5 Hz, 4H), 1.76 (ddd, J = 12.4, 2.9, 1.5 Hz, 1H), 1.50 – 1.36 (m, 5H), 1.34 (s, 12H).^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 135.0, 126.5, 83.7, 45.0, 34.4, 27.0, 26.3, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6. Spectroscopic data are in accordance with those described in the literature.[6]



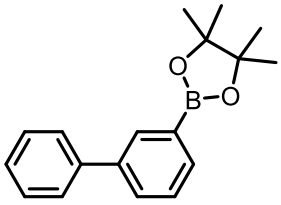
2y: 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure was applied to **1y** (25.2 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 30/1) to give **2y** (37.9 mg, 81% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 12H). ^{13}C 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 31.0. Spectroscopic data are in accordance with those described in the literature.[4]



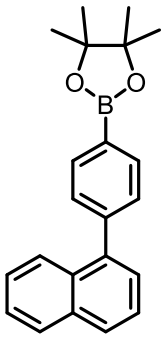
2z: 2-(3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure was applied to **1z** (25.2 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 30/1) to give **2z** (32.3 mg, 69% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dt, J = 7.2, 1.1 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.01 (ddd, J = 8.2, 2.8, 1.2 Hz, 1H), 3.84 (s, 3H), 1.35 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 129.1, 127.3, 118.8, 118.0, 84.0, 55.4, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.6. Spectroscopic data are in accordance with those described in the literature.[4]



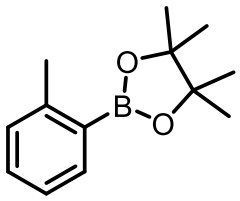
2aa: 2-([1,1'-biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure was applied to **1aa** (34.4 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to give **2aa** (39.2 mg, 70% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (t, J = 1.6 Hz, 1H), 7.82 (dt, J = 7.4, 1.3 Hz, 1H), 7.71 (ddd, J = 7.7, 2.1, 1.3 Hz, 1H), 7.66 (d, J = 1.6 Hz, 1H), 7.65 – 7.63 (m, 1H), 7.46 (ddd, J = 10.0, 8.7, 7.0 Hz, 3H), 7.39 – 7.32 (m, 1H), 1.38 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 135.4, 129.4, 128.0, 126.0, 124.6, 124.6, 123.9, 123.1, 83.9, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.4. Spectroscopic data are in accordance with those described in the literature.[9]



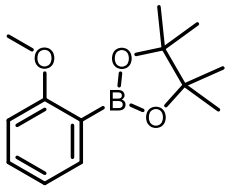
2ab: 4,4,5,5-tetramethyl-2-(4-(naphthalen-1-yl)phenyl)-1,3,2-dioxaborolane

The general procedure was applied to **1ab** (44.4 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to give **2ab** (50.8 mg, 77% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.9 Hz, 2H), 7.92 (dd, J = 8.1, 1.5 Hz, 2H), 7.90 – 7.87 (m, 1H), 7.57 – 7.51 (m, 4H), 7.45 (dd, J = 7.0, 1.4 Hz, 2H), 1.42 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 140.3, 134.9, 133.9, 131.6, 129.6, 128.4, 127.9, 127.0, 126.2, 126.1, 125.9, 125.5, 84.0, 25.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7. Spectroscopic data are in accordance with those described in the literature.[10]



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

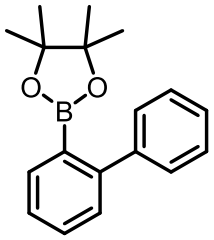
The general procedure was applied to **1ac** (22.0 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE /EtOAc= 30/1) to give **2ac** (26.2 mg, 66% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.30 – 7.27 (m, 2H), 2.37 (s, 3H), 1.36 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 135.5, 132.2, 131.9, 127.8, 83.8, 25.0, 21.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.1. Spectroscopic data are in accordance with those described in the literature.[4]



2ad: 2-(2-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure was applied to **1aa** (25.2 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 30/1) to give **2aa** (28.5 mg, 61% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 7.3, 1.9 Hz, 1H), 7.39 (ddd, J = 8.2, 7.4, 1.9 Hz, 1H), 6.94 (td, J = 7.3, 0.9 Hz, 1H), 6.86 (d, J = 8.3 Hz, 1H), 3.83 (s, 3H), 1.36 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 136.8, 132.6 120.3, 110.6,

83.6, 55.9, 25.0. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.7. Spectroscopic data are in accordance with those described in the literature.[4]

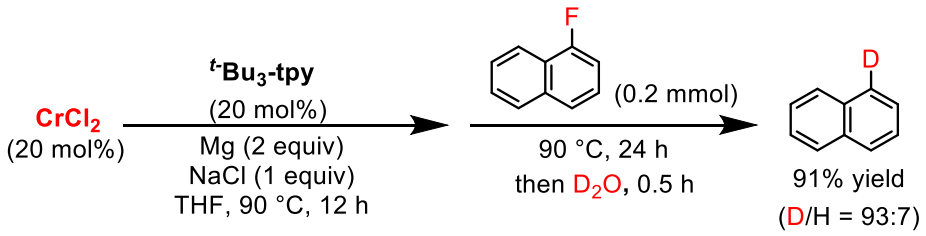


2ae: 2-([1,1'-biphenyl]-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

The general procedure was applied to **1ae** (34.4 mg, 0.2 mmol), $CrCl_2$ (0.04 mmol, 4.9 mg), ^{t}Bu$_3$-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.8 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) at 90 °C for 24 h. The crude product was purified by column chromatography on silica gel (PE/EtOAc = 20/1) to give **2ae** (36.9 mg, 66% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.3, 1.5 Hz, 1H), 7.51 – 7.33 (m, 9H), 1.24 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 143.4, 134.6, 130.2, 129.3, 129.1, 127.9, 126.9, 126.4, 24.7. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.9. Spectroscopic data are in accordance with those described in the literature.[5]

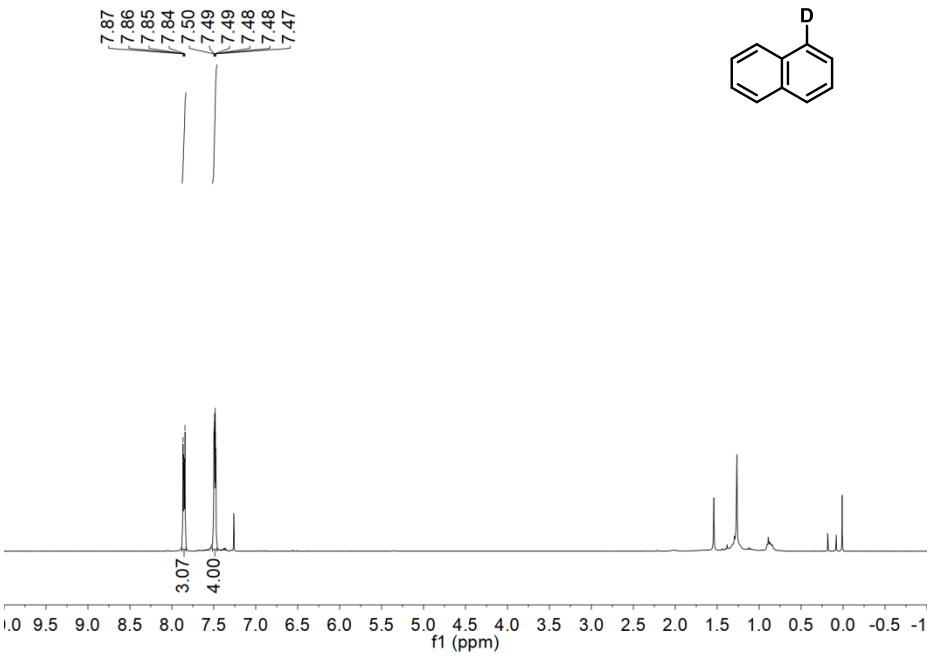
5. Mechanistic Studies

5.1 Deuterium-labeling experiment

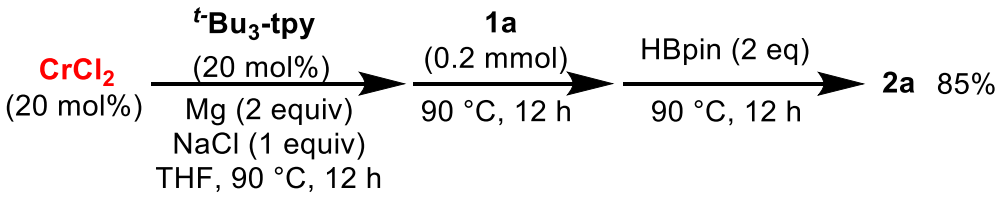


In a dried Schlenk tube was placed metallic magnesium (9.7 mg, 0.4 mmol). The tube was heated to around 630 °C under vacuum for 15 min using a heat gun. After cooling to room temperature, $CrCl_2$ (4.9 mg, 0.04 mmol), ^{t}Bu$_3$-tpy (16.0 mg, 0.04 mmol), NaCl (11.6 mg, 0.2 mmol) and dry THF (2 mL) were added under atmosphere

of nitrogen, the resulting mixture was stirred at 90 °C for 12 h. After cooling to room temperature, 1-fluoronaphthalene (29.2 mg, 0.2 mmol) was added and stirred at 90 °C in an oil bath for 24 h. After treatment of the reaction with 0.5 mL of D_2O at room temperature for 0.5 h, the mixture was filtered through a Celite to assure collecting all products. The organic layer was extracted with ethyl acetate and dried over anhydrous Na_2SO_4 and the product was purified by column chromatography (PE) to afford 1-deuteronaphthalene (23.5 mg, 91% yield) with a trace amount of **1o** as white solid. All C–F bonds were cleaved and converted to C–H or C–D bonds to form the product. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 3H), 7.52 – 7.46 (m, 4H).

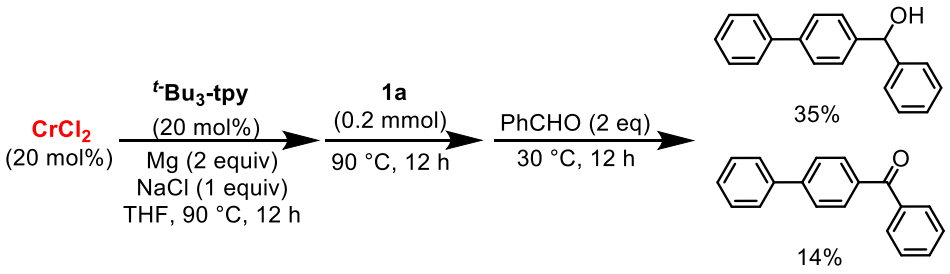


5.2 Intermediate experiments



In a dried Schlenk tube was placed metallic magnesium (9.7 mg, 0.4 mmol). The tube was heated to around 630 °C under vacuum for 15 min using a heat gun. After cooling to room temperature, $CrCl_2$ (4.9 mg, 0.04 mmol), ^{t}Bu$_3$-tpy (16.0 mg, 0.04 mmol), NaCl (11.6 mg, 0.2 mmol) and dry THF (2 mL) were added under atmosphere of nitrogen, the resulting mixture was stirred at 90 °C for 12 h. After cooling to room

temperature, **1a** (34.4 mg, 0.2 mmol) was added and stirred at 90 °C in an oil bath for 12 h. After 12 h, HBpin (58 μL, 0.4 mmol) was added. The mixture was stirred at 90 °C for 12 hours, and then filtered through a pad of Celite. Ethyl acetate (3×10 mL) and water (3×5 mL) were added to the Celite to assure collecting all products. The organic layer was extracted and dried over anhydrous Na_2SO_4 and the product was purified by column chromatography (PE/EA = 30/1) to afford **2a** (43.1 mg, 85% yield) as white solid.

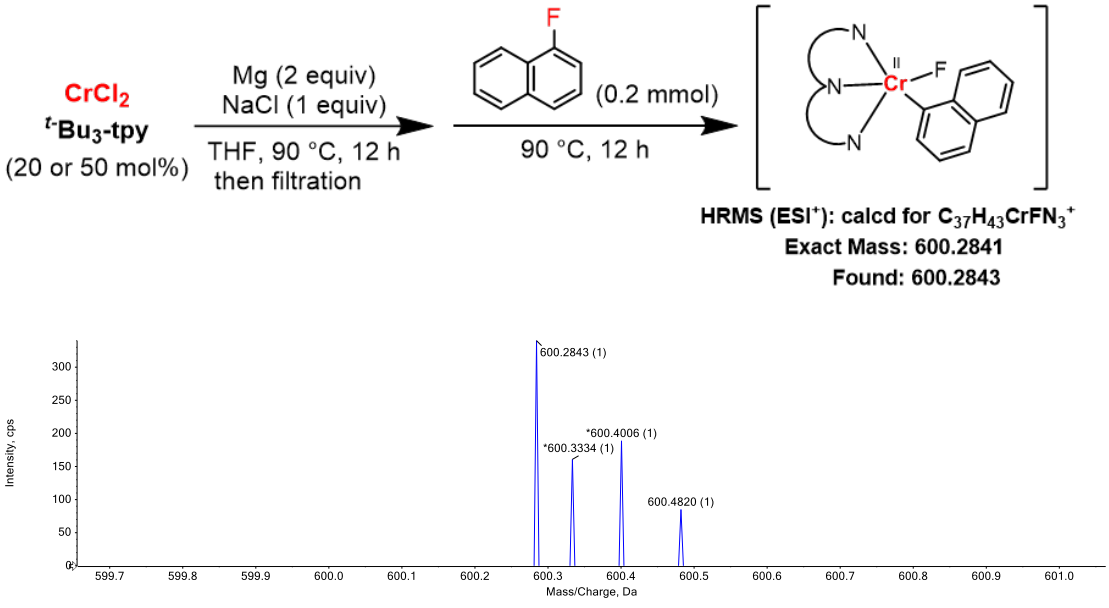


In a dried Schlenk tube was placed metallic magnesium (9.7 mg, 0.4 mmol). The tube was heated to around 630 °C under vacuum for 15 min using a heat gun. After cooling to room temperature, $CrCl_2$ (4.9 mg, 0.04 mmol), ^{t}Bu$_3$-tpy (16.0 mg, 0.04 mmol), NaCl (11.6 mg, 0.2 mmol), and dry THF (2 mL) were added under atmosphere of nitrogen, the resulting mixture was stirred at 90 °C for 12 h. After cooling to room temperature, **1a** (34.4 mg, 0.2 mmol) was added and stirred at 90 °C in an oil bath for 12 h, benzaldehyde (42.4 mg, 0.4 mmol) was added under inert condition. The mixture was stirred at 30 °C for 12 h, and then filtered through a pad of Celite. Ethyl acetate (3×10 mL) and water (3×5 mL) were added to the Celite to assure collecting all products. The organic layer was extracted and dried over anhydrous Na_2SO_4 and the product was purified by column chromatography (PE/EA = 100/1 to PE/EA = 10/1) to afford [1,1'-biphenyl]-4-yl(phenyl)methanol (18.2 mg, 35% yield) and [1,1'-biphenyl]-4-yl(phenyl)methanone (7.2 mg, 14% yield) as white solids.

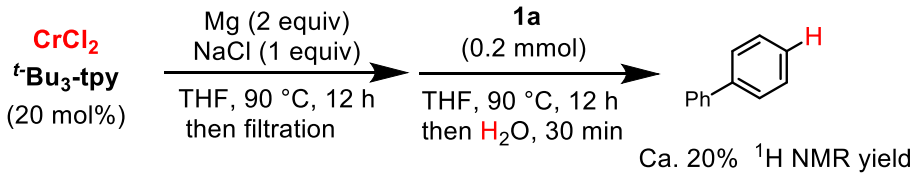
[1,1'-biphenyl]-4-yl(phenyl)methanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, J = 7.9, 2.4 Hz, 4H), 7.48 – 7.42 (m, 6H), 7.40 – 7.35 (m, 3H), 7.31 (d, J = 7.2 Hz, 1H), 5.90 (s, 1H), 2.33 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.88, 142.96, 140.92, 140.64, 128.90, 128.71, 127.80, 127.44, 127.40, 127.22, 127.11, 126.69, 76.20. Spectroscopic data are in accordance with those described in the literature.[11]

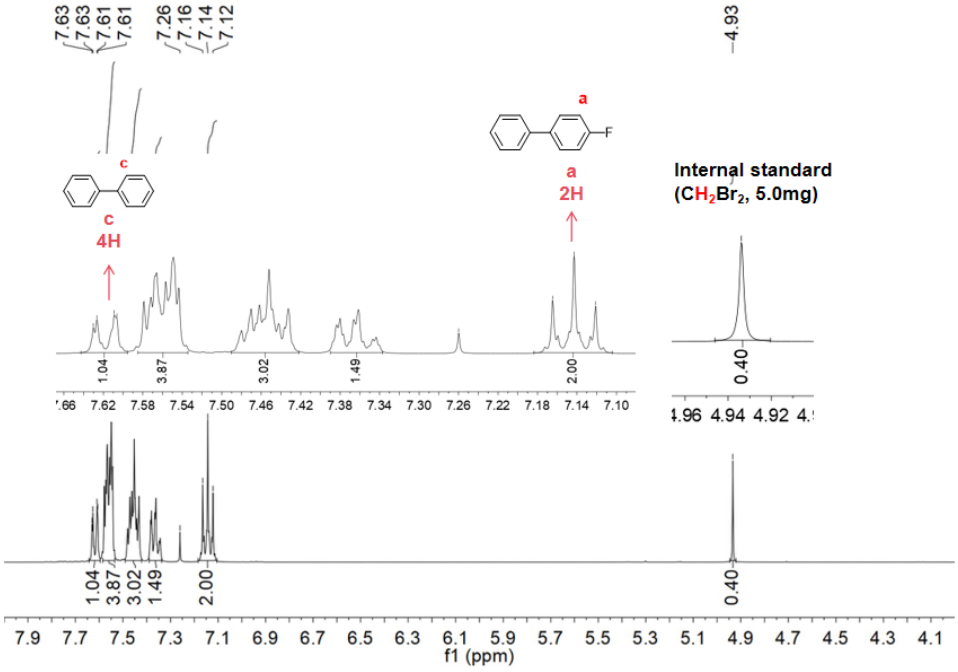
[1,1'-biphenyl]-4-yl(phenyl)methanone. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2H), 7.86 – 7.83 (m, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.68 – 7.64 (m, 2H), 7.63 – 7.58 (m, 1H), 7.50 (q, J = 7.8 Hz, 4H), 7.44 – 7.39 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.52, 145.39, 140.14, 137.91, 136.39, 132.52, 130.88, 130.15, 129.12, 128.46, 128.33, 127.46, 127.12. Spectroscopic data are in accordance with those described in the literature.[12]

5.3 Filtration experiments

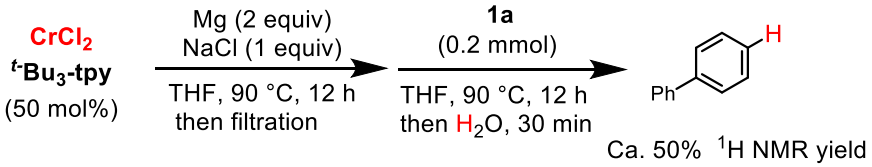


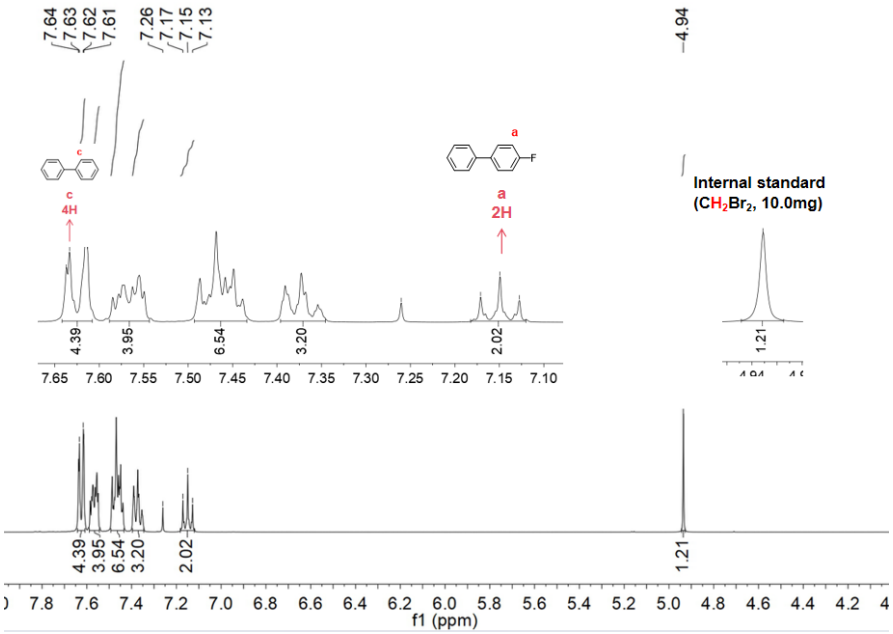
In a dried Schlenk tube was placed metallic magnesium (9.7 mg, 0.4 mmol). The tube was heated to around 630 °C under vacuum for 15 min using a heat gun. After cooling to room temperature, $CrCl_2$ (4.9 mg, 0.04 mmol), ^{t}-Bu$_3$-tpy (16.0 mg, 0.04 mmol), NaCl (11.6 mg, 0.2 mmol) and dry THF (2 mL) were added under atmosphere of nitrogen, the resulting mixture was stirred at 90 °C for 12 h. After cooling to room temperature, and filtration, **1o** (29.2 mg, 0.2 mmol) was added and stirred at 90 °C in an oil bath for 12 h. The THF solution was filtered and the filtrate was washed with hexane (3×5 mL). HRMS (ESI+): calcd for $C_{37}H_{43}CrFN_3^+$ [M+H] + 600.2841, found 600.2843.





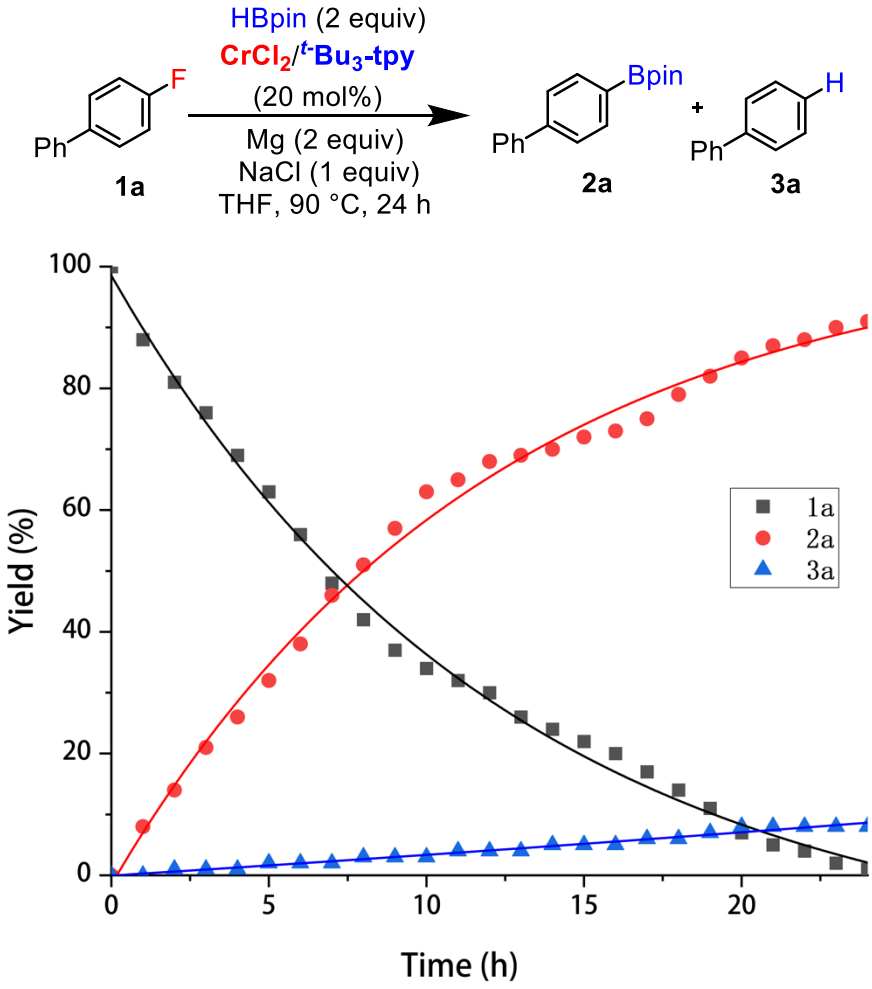
In a dried Schlenk tube was placed metallic magnesium (9.7 mg, 0.4 mmol). The tube was heated to around 630 °C under vacuum for 15 min using a heat gun. After cooling to room temperature, $CrCl_2$ (4.9 mg, 0.04 mmol), $^{t}Bu_3$-tpy (16.0 mg, 0.04 mmol), NaCl (11.6 mg, 0.2 mmol) and dry THF (2 mL) were added under atmosphere of nitrogen, the resulting mixture was stirred at 90 °C for 12 h. After cooling to room temperature, and filtration, **1a** (34.4 mg, 0.2 mmol) was added and stirred at 90 °C in an oil bath for 12 h. After treatment of the reaction with 0.5 mL of H_2O at room temperature for 0.5 h, the mixture was filtered through a pad of Celite. Ethyl acetate (3×10 mL) and water (3×5 mL) were added to the Celite to assure collecting all products. The organic layer was extracted and dried over anhydrous Na_2SO_4 and the product was purified by column chromatography (PE) to afford a mixture, where the C-F bond cleavage was approximately the same amount of chromium catalyst analysed by ^{1}H NMR spectroscopy, dibromomethane (5 mg) was used as an internal standard.





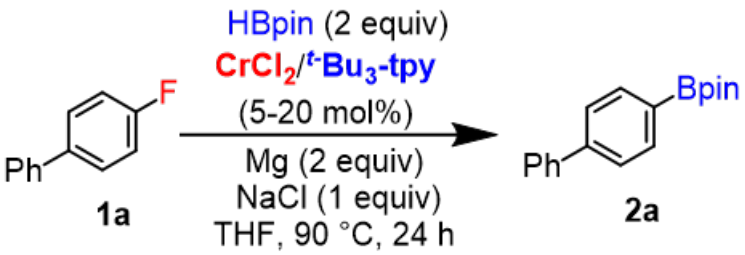
In a dried Schlenk tube was placed metallic magnesium (9.7 mg, 0.4 mmol). The tube was heated to around 630 °C under vacuum for 15 min using a heat gun. After cooling to room temperature, $CrCl_2$ (12.29 mg, 0.1 mmol), ^{t}Bu$_3$-tpy (40.2 mg, 0.1 mmol), NaCl (11.6 mg, 0.2 mmol) and dry THF (2 mL) were added under atmosphere of nitrogen, the resulting mixture was stirred at 90 °C for 12 h. After cooling to room temperature, and filtration, **1a** (34.4 mg, 0.2 mmol) was added and stirred at 90 °C in an oil bath for 12 h. After treatment of the reaction with 0.5 mL of H_2O at room temperature for 0.5 h, the mixture was filtered through a pad of Celite. Ethyl acetate (3×10 mL) and water (3×5 mL) were added to the Celite to assure collecting all products. The organic layer was extracted and dried over anhydrous Na_2SO_4 and the product was purified by column chromatography (PE) to afford a mixture, where the C-F bond cleavage was approximately the same amount of chromium catalyst analysed by ^{1}H NMR spectroscopy, dibromomethane (10 mg) was used as an internal standard.

5.4 Time Course of the Borylation of Fluoroarenes



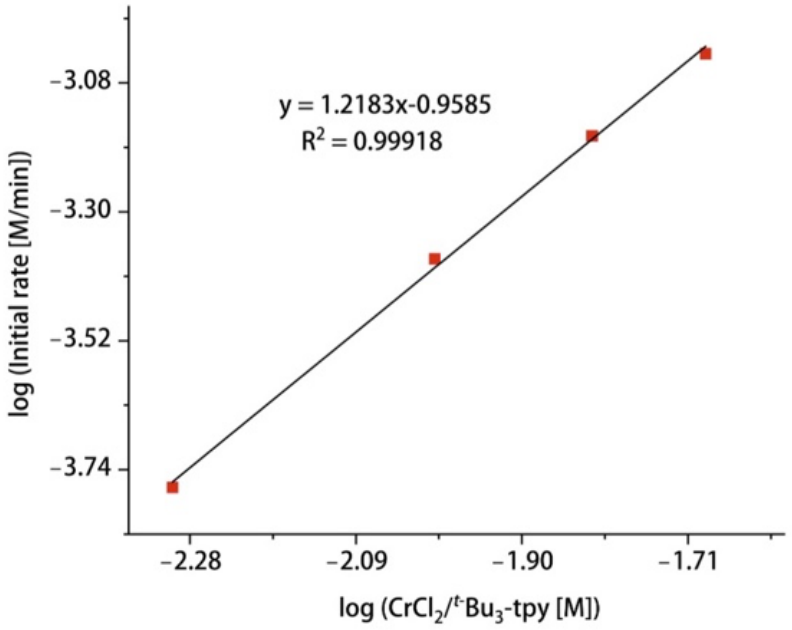
A dried Schlenk tube were placed **1a** (0.2 mmol), $CrCl_2$ (4.9 mg, 0.04 mmol), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.4 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) was added dropwise by syringe under atmosphere of nitrogen. During the reaction stirring for 24 h at 90 °C, periodic aliquots (25 μL) were removed by a syringe and quenched by an aqueous solution of NH_4Cl for a continuous stirring for another 0.5 h. The resulting mixture was extracted with ethyl acetate (1.0 mL) and the organic phase was analyzed by GC using n-tridecane as the internal standard

5.5 Controlled variable experiments



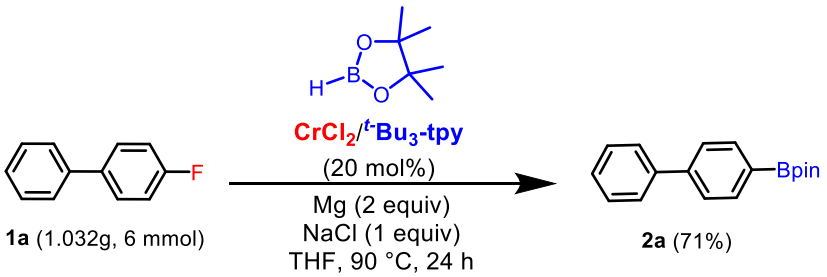
A dried Schlenk tube were placed **1a** (0.2 mmol) and different amounts of $CrCl_2$ (0.01, 0.02, 0.03, 0.04 mmol), ^{t}-Bu_3-tpy (16.0 mg, 0.04 mmol), NaCl (1 equiv, 0.2 mmol, 11.6 mg), magnesium (2 equiv, 0.4 mmol, 9.7 mg), and freshly distilled THF (2 mL), HBpin (2 equiv, 0.4 mmol, 58 μL) was added dropwise by syringe under atmosphere of nitrogen. After the reaction stirring for 8 h at 90 °C, periodic aliquots (25 μL) were removed by a syringe and quenched by an aqueous solution of NH_4Cl for a continuous stirring for another 0.5 h. The resulting mixture was extracted with ethyl acetate (1.0 mL) and the organic phase was analyzed by GC using *n*-tridecane as the internal standard.

Entry	Mol %	$CrCl_2$/ ^{t}-Bu_3-tpy [M]	Initial rate [M/min]
1	5	0.005	1.67×10^{-4}
2	10	0.010	4.16×10^{-4}
3	15	0.015	6.67×10^{-4}
4	20	0.020	9.16×10^{-4}



6. Synthetic Procedures for the Reactions Described in Scheme 5

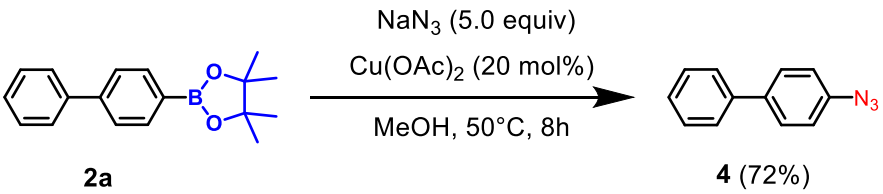
6.1 Gram-scale synthesis



In a dried Schlenk tube were placed **1a** (1.032 g, 6.0 mmol), $CrCl_2$ (147 mg, 1.2 mmol), ^{t}Bu$_3$-tpy (482 mg, 1.2 mmol), Mg (291 mg, 12.0 mmol), NaCl (350 mg, 6.0 mmol) and HBpin (1.7 ml, 12.0 mmol) under atmosphere of nitrogen, after the addition of freshly distilled THF (15 mL) by syringe. Stirring for 24 h at 90 °C, the resulting mixture was quenched by an aqueous solution of NH_4Cl and extracted with ethyl acetate (3 x 10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by silica gel chromatography (PE/EA = 30/1) to give the **2a** as white solid (1.19 g, 71% yield).

6.2 Transformations of aryl boronate esters

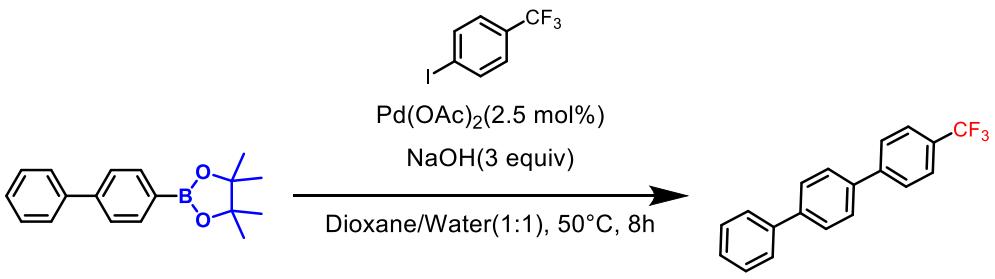
Preparation of 4



2a **4** (72%)

To an oven dried sealed tube, aryl boronate ester **2a** (56 mg, 0.2 mmol), NaN_3 (65 mg, 1.0 mmol), $Cu(OAc)_2$ (72 mg, 0.4 mmol) and MeOH (6 mL) were added. The mixture was initially stirred at room temperature to complete the mixing. The flask was sealed under air, and the reaction mixture was heated at 50 °C in an oil bath for 8 h. The resulting mixture was extracted with Et_2O (3×15 mL). The combined organic phases were washed with brine (10 mL), and dried over anhydrous $MgSO_4$. The ethyl acetate was evaporated under reduced pressure and the crude was purified by column chromatography (PE/EtOAc = 50/1) to give **4** (28 mg, 73% yield) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.44 (t, J = 7.6 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.12 (s, 1H), 7.09 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.29, 139.29, 138.15, 129.01, 128.59, 127.51, 127.01, 119.54. Spectroscopic data are in accordance with those described in the literature.[13]

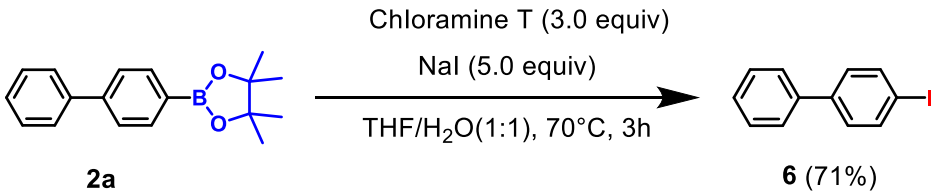
Preparation of 5



2a **5** (67%)

2a (56.0 mg, 0.2 mmol), 4-iodobenzotrifluoride (25.4 μL, 0.2 mmol (1 eq)), palladium(II) acetate (1.6 mg, 0.005 mmol (2.5 mol%)), sodium hydroxide (24.0 mg, 0.6 mmol (3 eq)) were added to a 8 mL vial. Then dioxane (1 mL) and water (1 mL) were added. The mixture was refluxed at 50 °C for 8 h. After the reaction, ethyl acetate (10 mL) and water (10 mL) were added and the solution was shaken vigorously. The organic layer was extracted and dried over anhydrous Na_2SO_4. The solution was concentrated under vacuum and the product was purified by column chromatography (PE) to afford **5** (39.9 mg, 67%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 5.7 Hz, 4H), 7.71 – 7.68 (m, 4H), 7.67 – 7.63 (m, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.41 – 7.36 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.4, 141.2, 140.4, 138.7, 129.5 (q, J = 32.5 Hz), 129.1(2C), 127.9, 127.8, 127.7, 127.4, 127.2, 125.9 (q, J = 3.8 Hz). Spectroscopic data are in accordance with those described in the literature.[14]

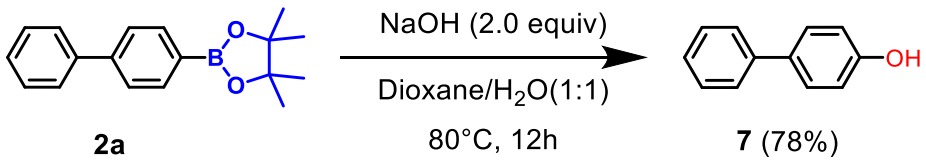
Preparation of 6



2a **6** (71%)

To a solution of aryl boronate ester **2a** (56 mg, 0.2 mmol) in THF/H_2O (3 mL/3 mL) were added NaI (150 mg, 1.0 mmol), and chloramine T (137 mg, 0.6 mmol). The mixture was heated at 70 °C in an oil bath for 3 h, and then diluted with water (10 mL). The resulting mixture was extracted with Et_2O (3×15 mL). The combined organic phases were washed with brine (10 mL), and dried over anhydrous $MgSO_4$. The ethyl acetates were evaporated under reduced pressure and the crude was purified by column chromatography (PE/EtOAc = 100/1) to give **6** (39.8 mg, 71% yield) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.42 (t, J = 7.7 Hz, 2H), 7.34 – 7.29 (m, 1H), 6.94 – 6.89 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.26, 140.91, 134.11, 128.86, 128.52, 126.85, 126.83, 115.79. Spectroscopic data are in accordance with those described in the literature.[15]

Preparation of 7



2a **7** (78%)

In a 20 mL vial, the configured sodium hydroxide aqueous solution (0.2 M) was added to the mixed solution of aryl boronate ester **2a** (56 mg, 0.2 mmol) and 1,4-dioxane (2.0 mL) at room temperature. The reaction mixture was heated to 80 °C and continuously stirred for 12 h. After the reaction was completed, the reaction mixture was neutralized by 1M dilute hydrochloric acid and then extracted with ethyl acetate. The organic layer was collected, dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The product was purified by column chromatography (PE/EtOAc = 20/1) to obtain aryl phenolic compounds **7** (26.52 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.49 (d, J = 8.6 Hz, 2H), 7.42 (t, J = 7.7 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 8.6 Hz, 2H), 4.88 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.22, 140.90, 134.18, 128.87, 128.54, 126.87, 126.85, 115.78. Spectroscopic data are in accordance with those described in the literature.[16]

7. References

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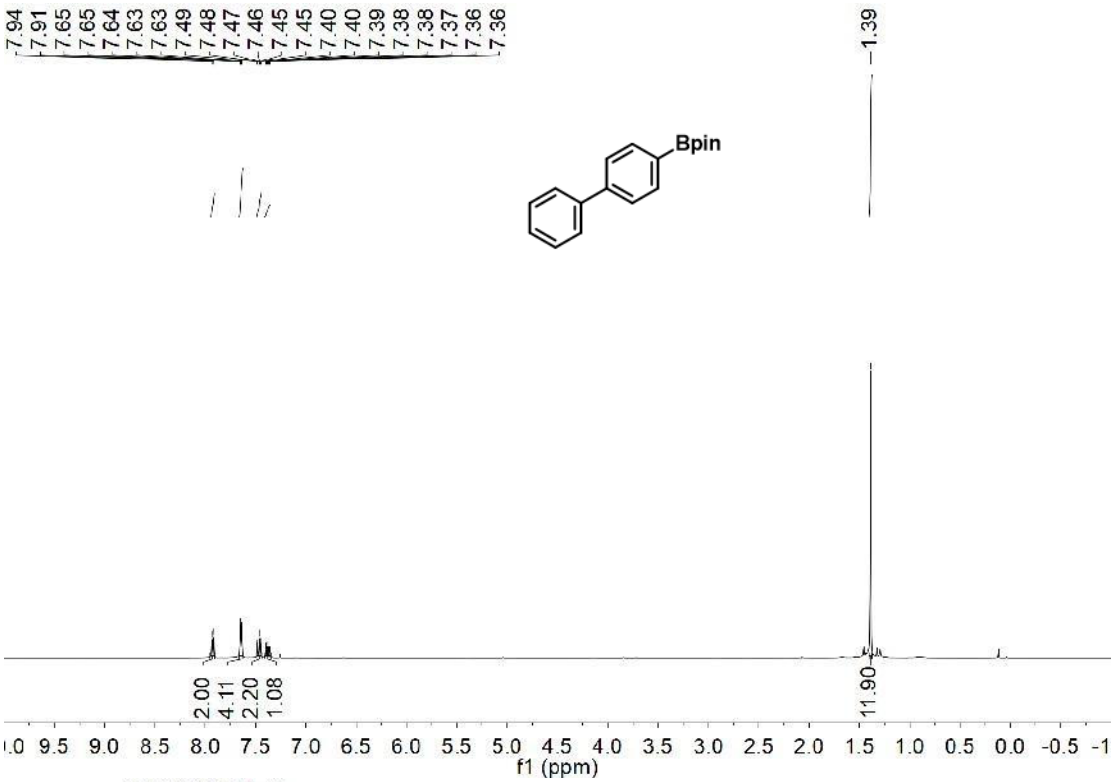
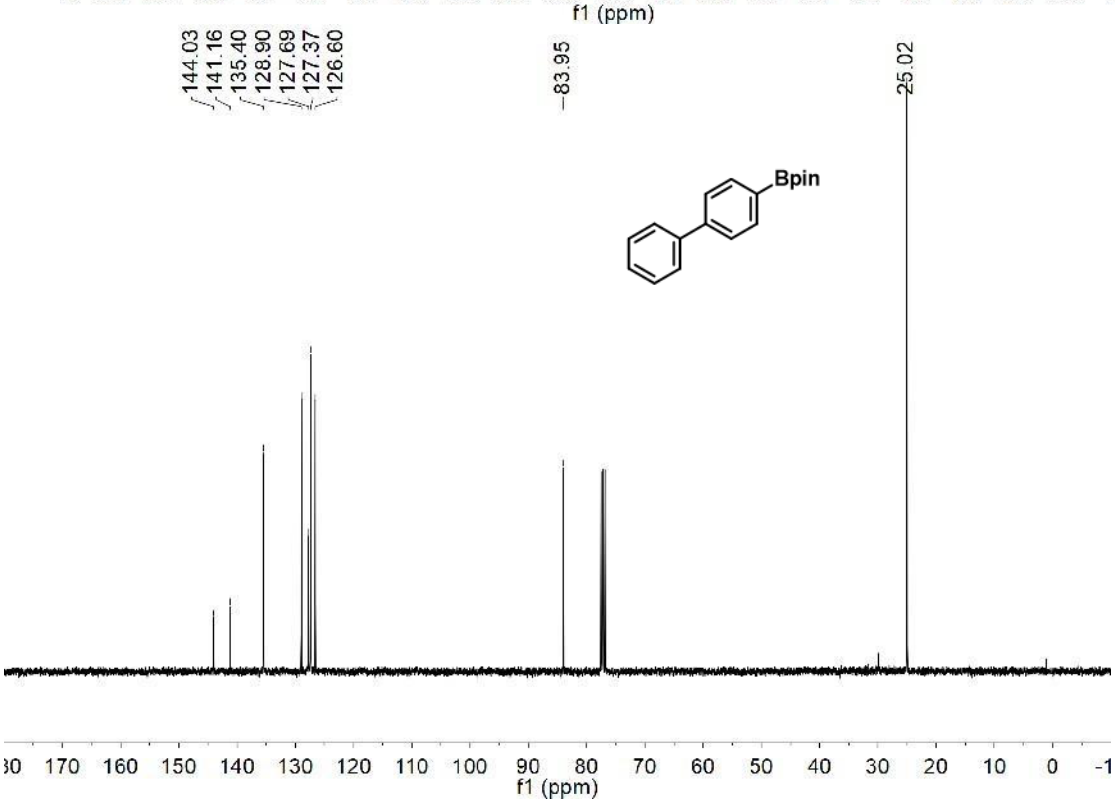
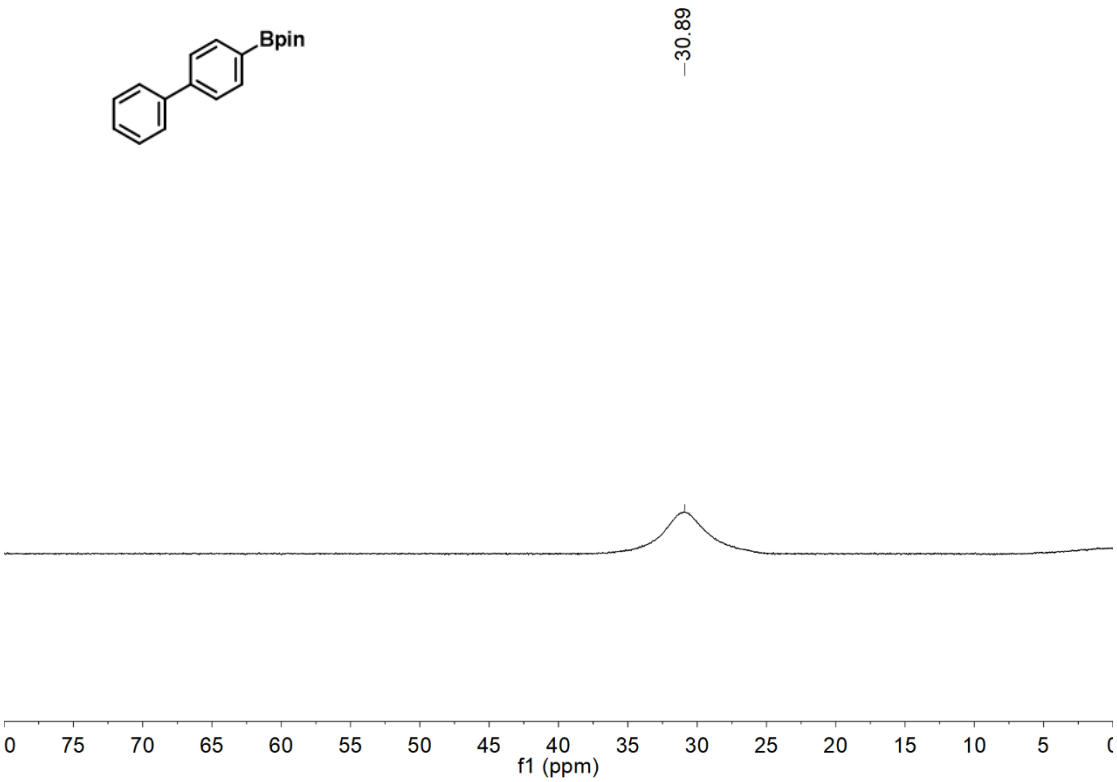
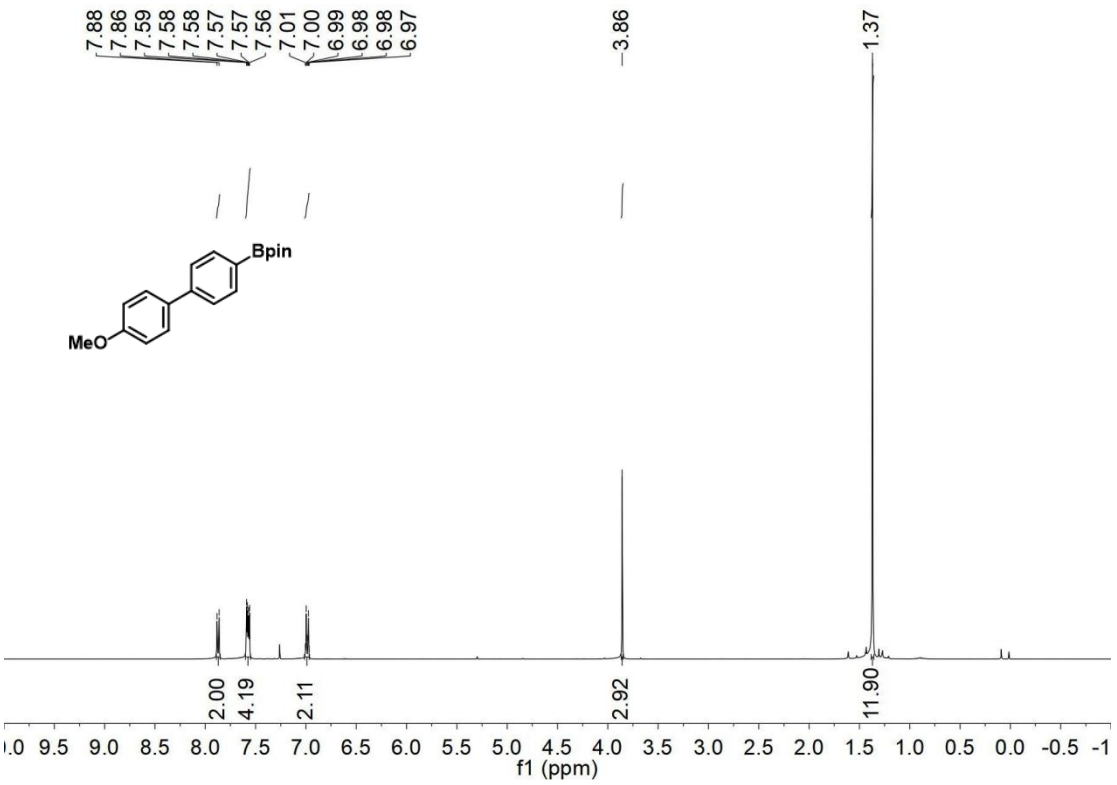
8. ^{1}H, ^{13}C and ^{11}B NMR Spectra

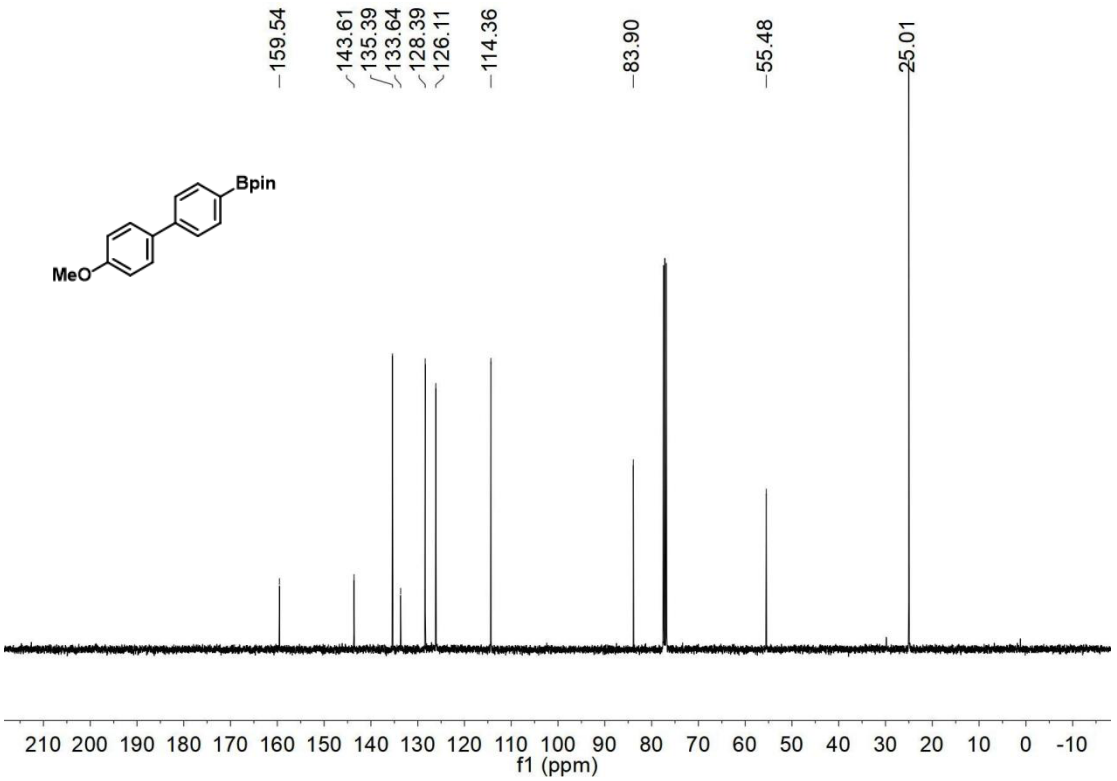


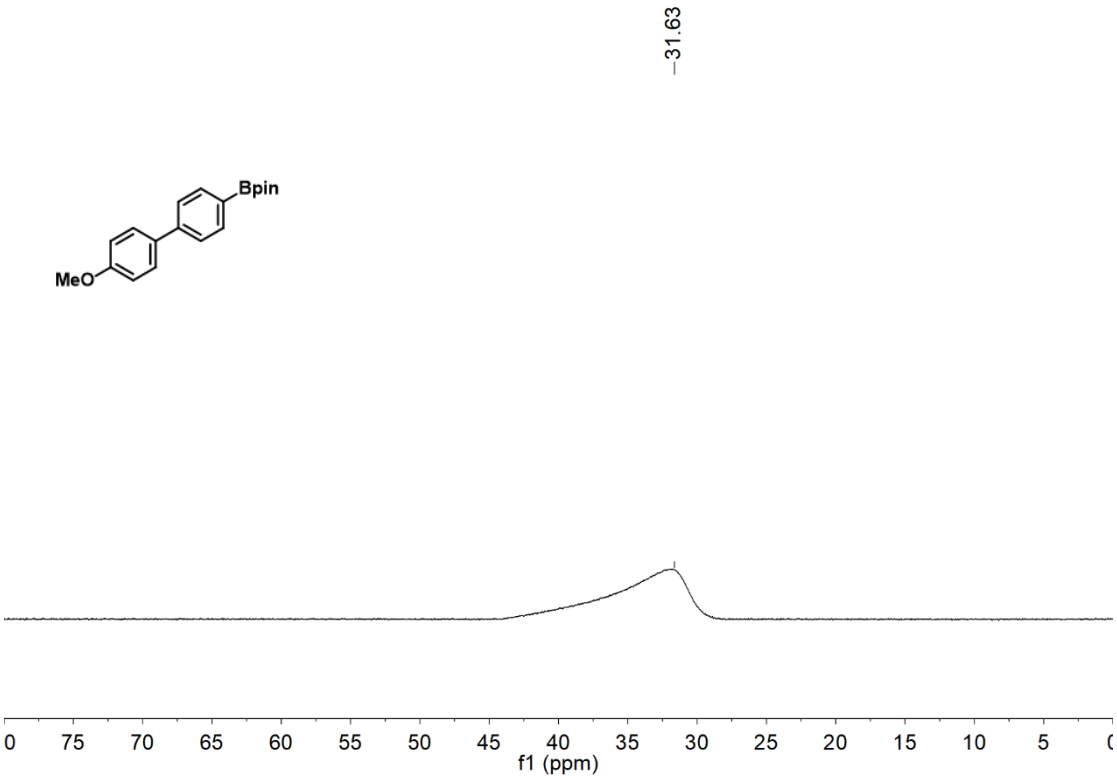




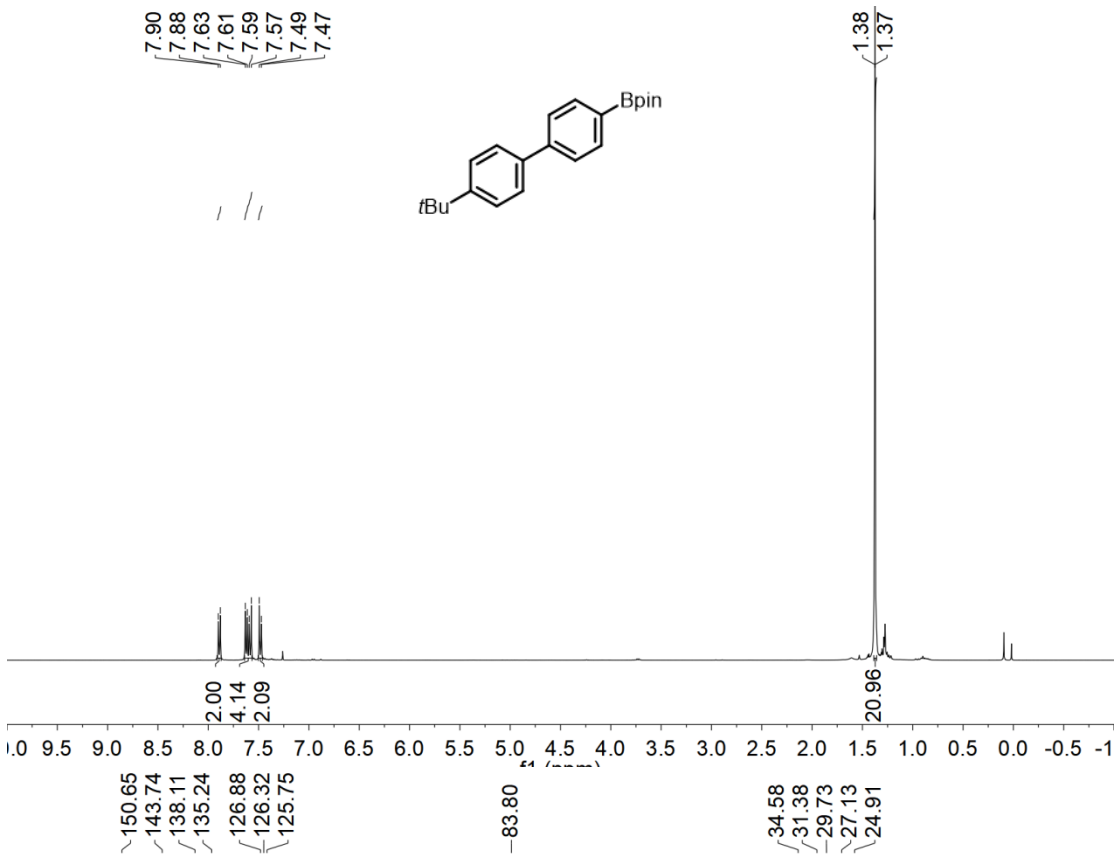
^{1}H, ^{13}C and ^{11}B NMR spectra for **2a**







^{1}H, ^{13}C and ^{11}B NMR spectra for **2b**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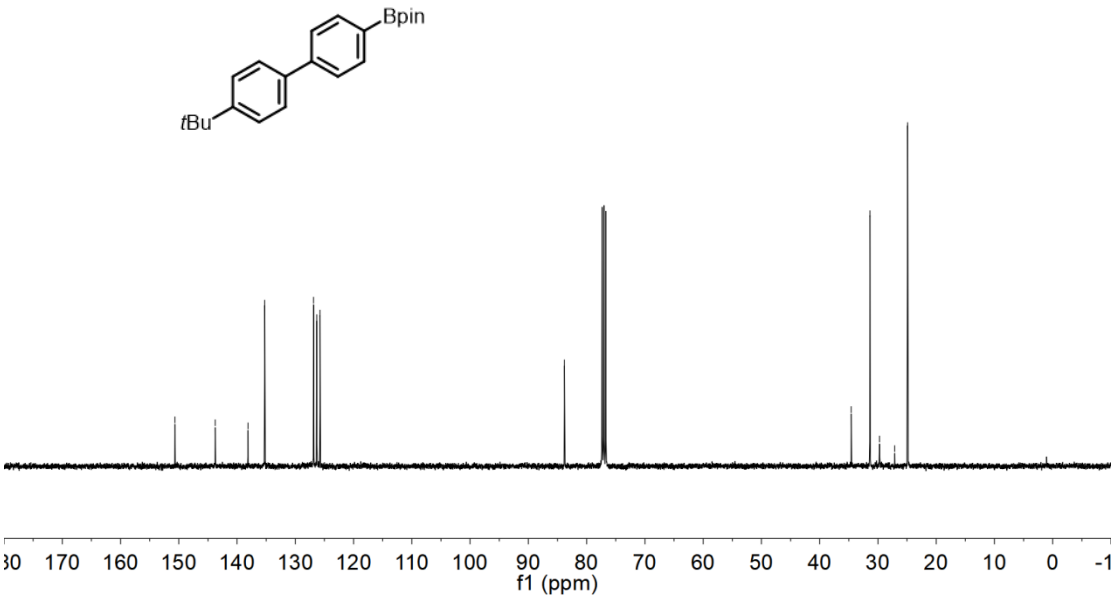
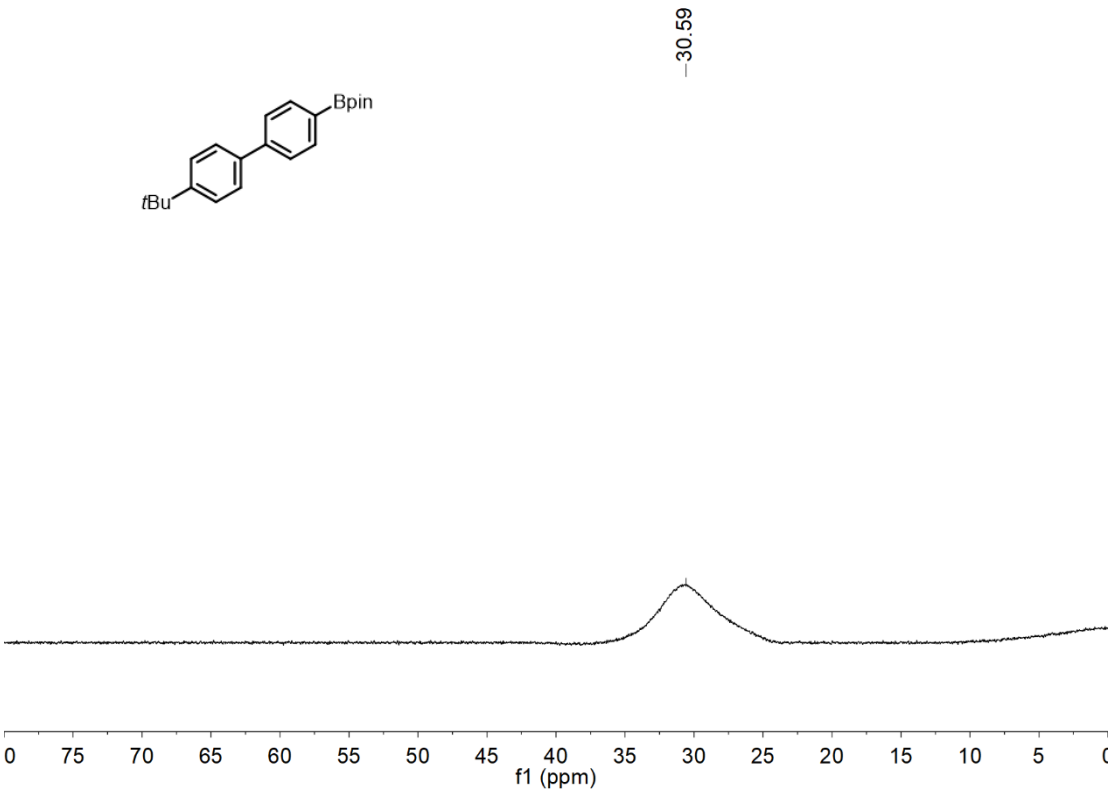
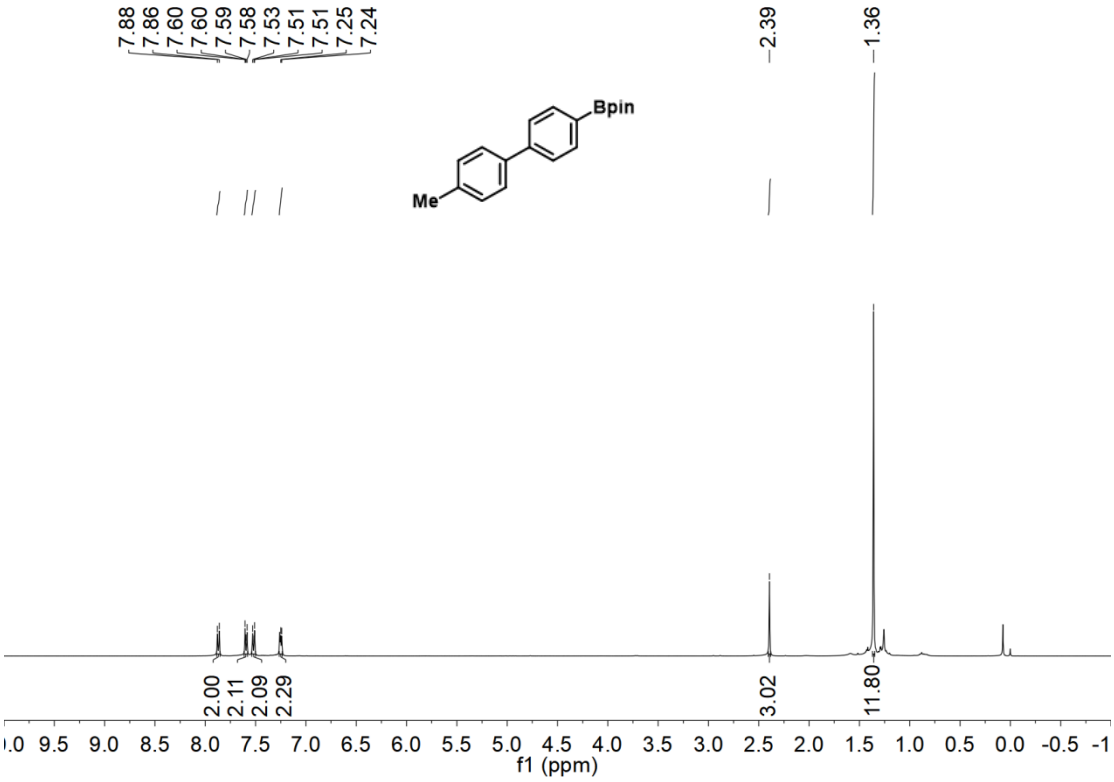
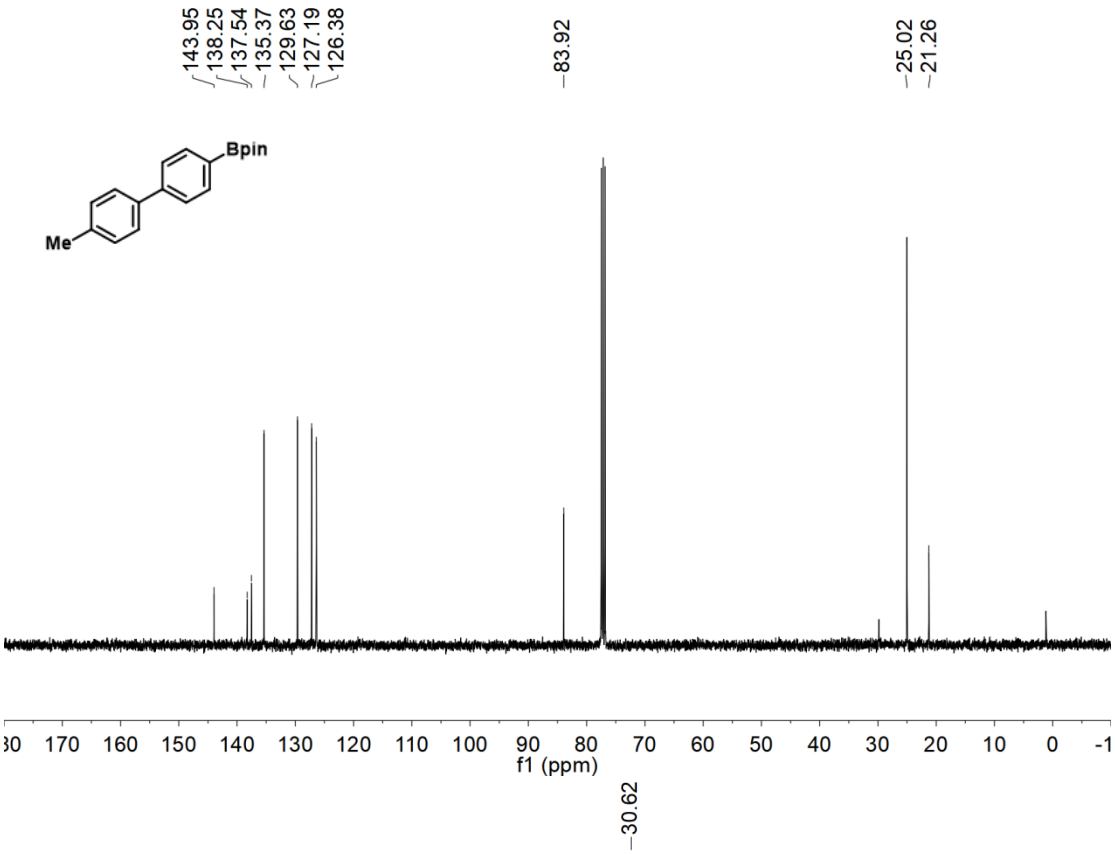
7.63
7.61
7.59
7.57
7.49
7.47
1.38
1.37
Bpin
tBu
2.00
4.14
2.09
20.96
150.65
143.74
138.11
135.24
126.88
126.32
125.75
83.80
34.58
31.38
29.73
27.13
24.91

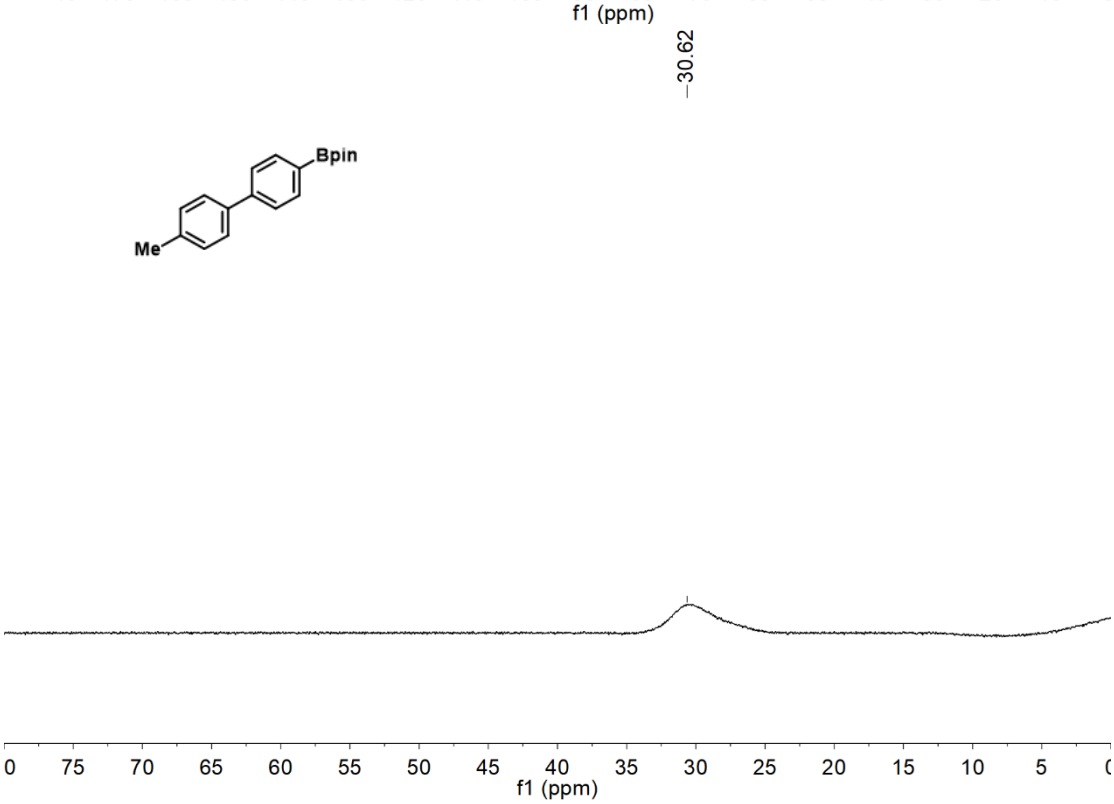

Bpin
tBu
f1 (ppm)



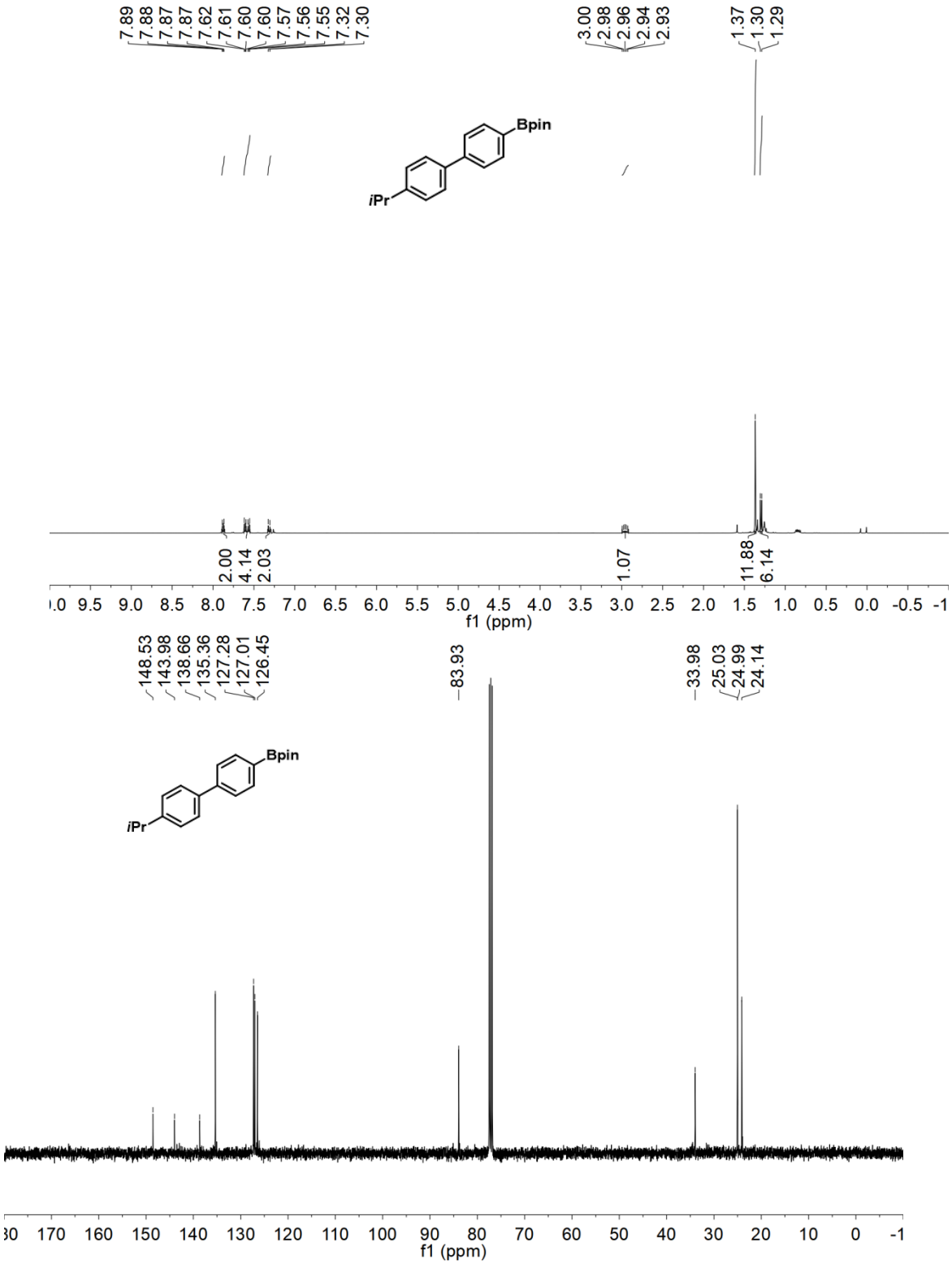
^{1}H, ^{13}C and ^{11}B NMR spectra for **2c**







^{1}H, ^{13}C and ^{11}B NMR spectra for **2d**


7.89
7.88
7.87
7.87
7.62
7.61
7.60
7.60
7.57
7.56
7.55
7.32
7.30
3.00
2.98
2.96
2.94
2.93
1.37
1.30
1.29
Bpin
iPr
2.00
4.14
2.03
1.07
11.88
6.14
f1 (ppm)
148.53
143.98
138.66
135.36
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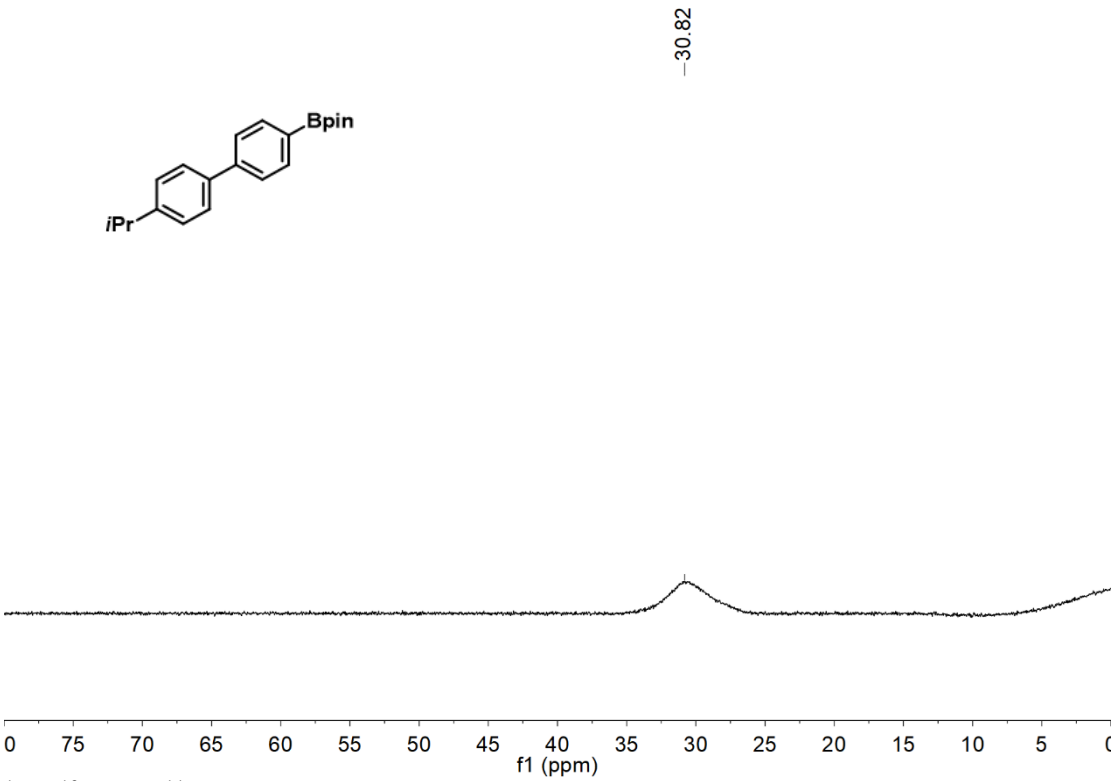
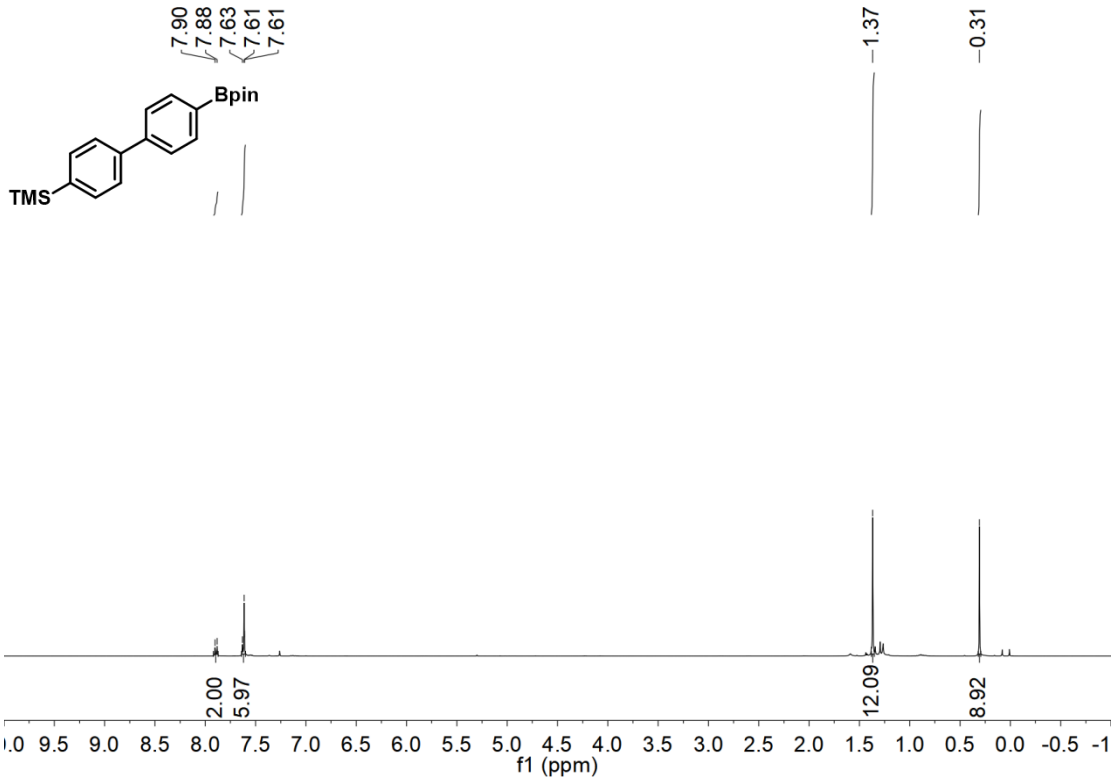
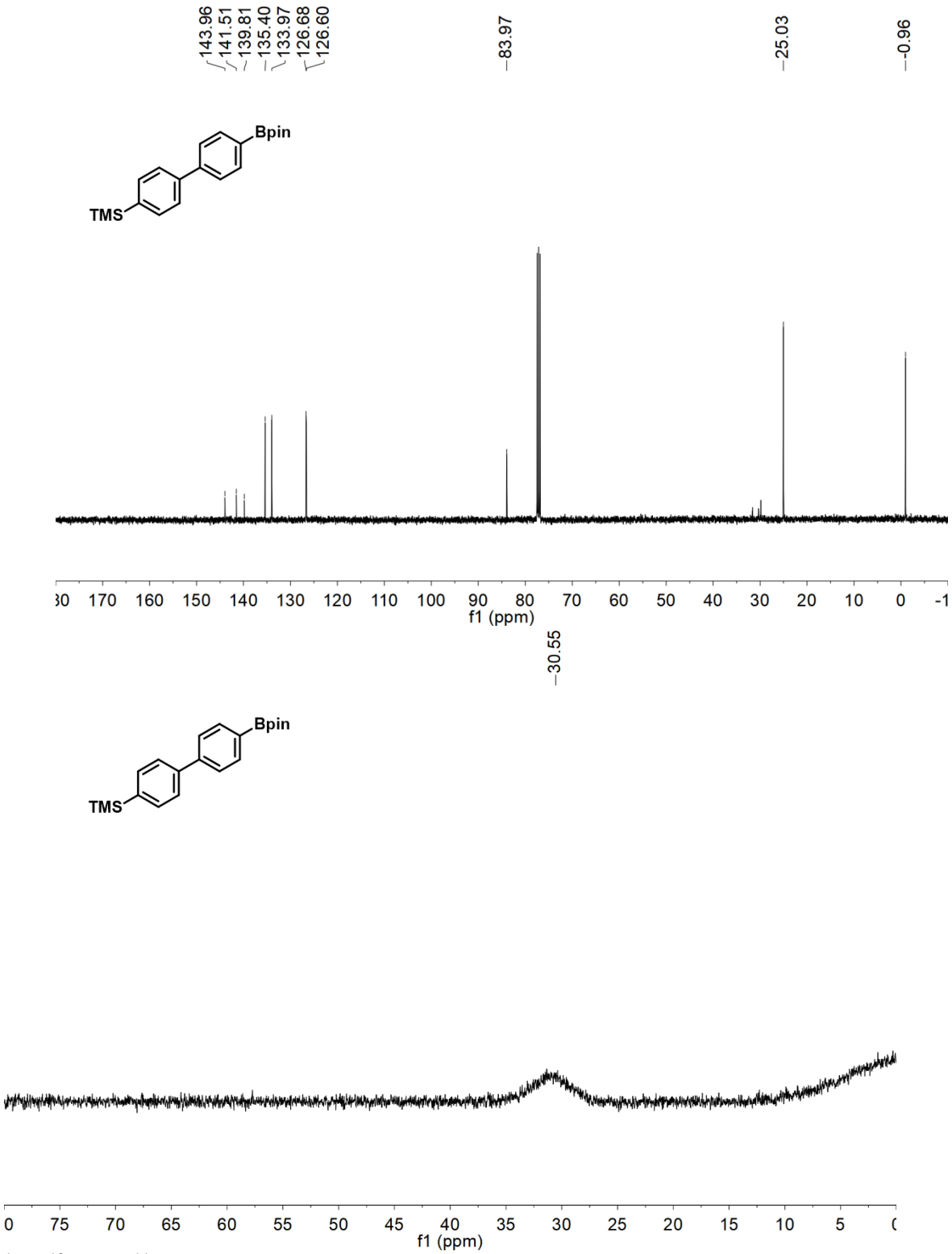
24.14
Bpin
iPr
f1 (ppm)

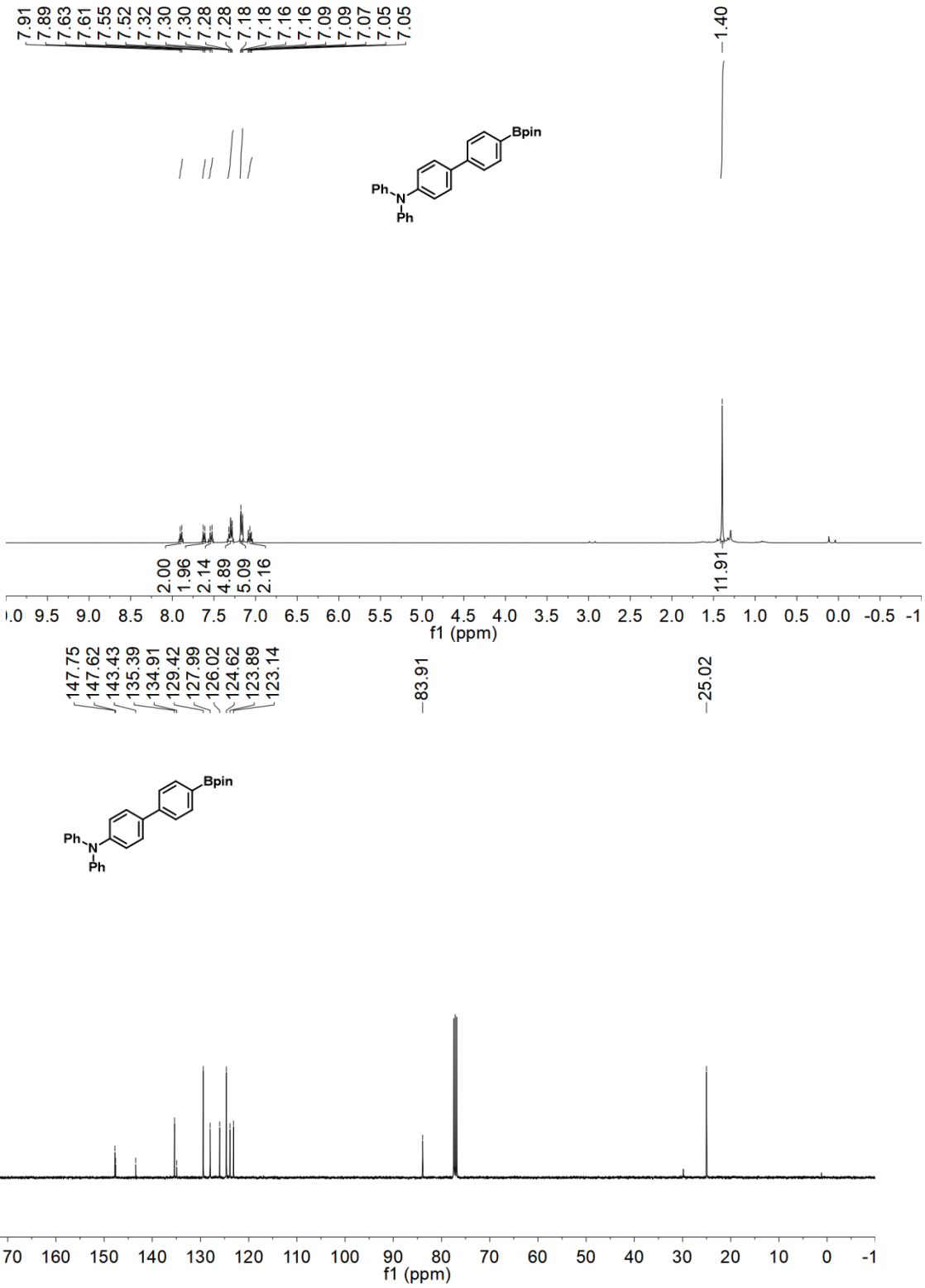


^{1}H, ^{13}C and ^{11}B NMR spectra for **2e**





^{1}H, ^{13}C and ^{11}B NMR spectra for **2f**


7.91
7.89
7.63
7.61
7.55
7.52
7.32
7.30
7.30
7.28
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7.18
7.18
7.16
7.16
7.09
7.09
7.07
7.05
7.05
1.40
Bpin
Ph
N
Ph
2.00
1.96
2.14
4.89
5.09
2.16
11.91
f1 (ppm)
147.75
147.62
143.43
135.39
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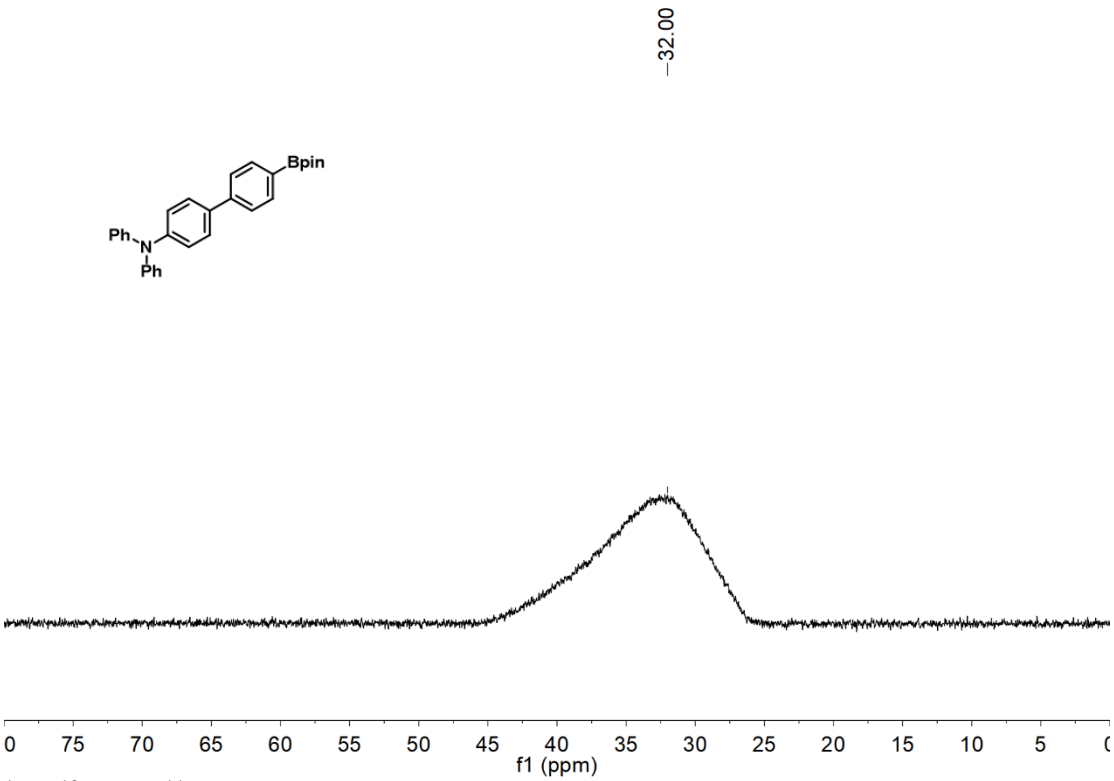
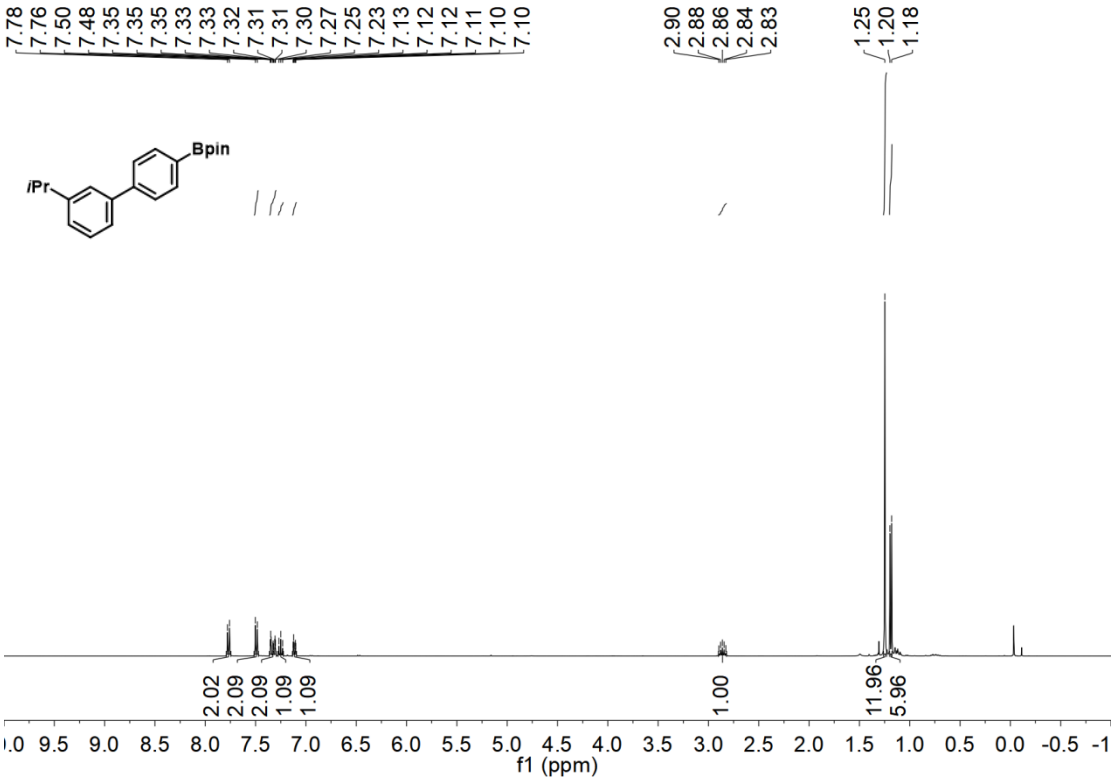
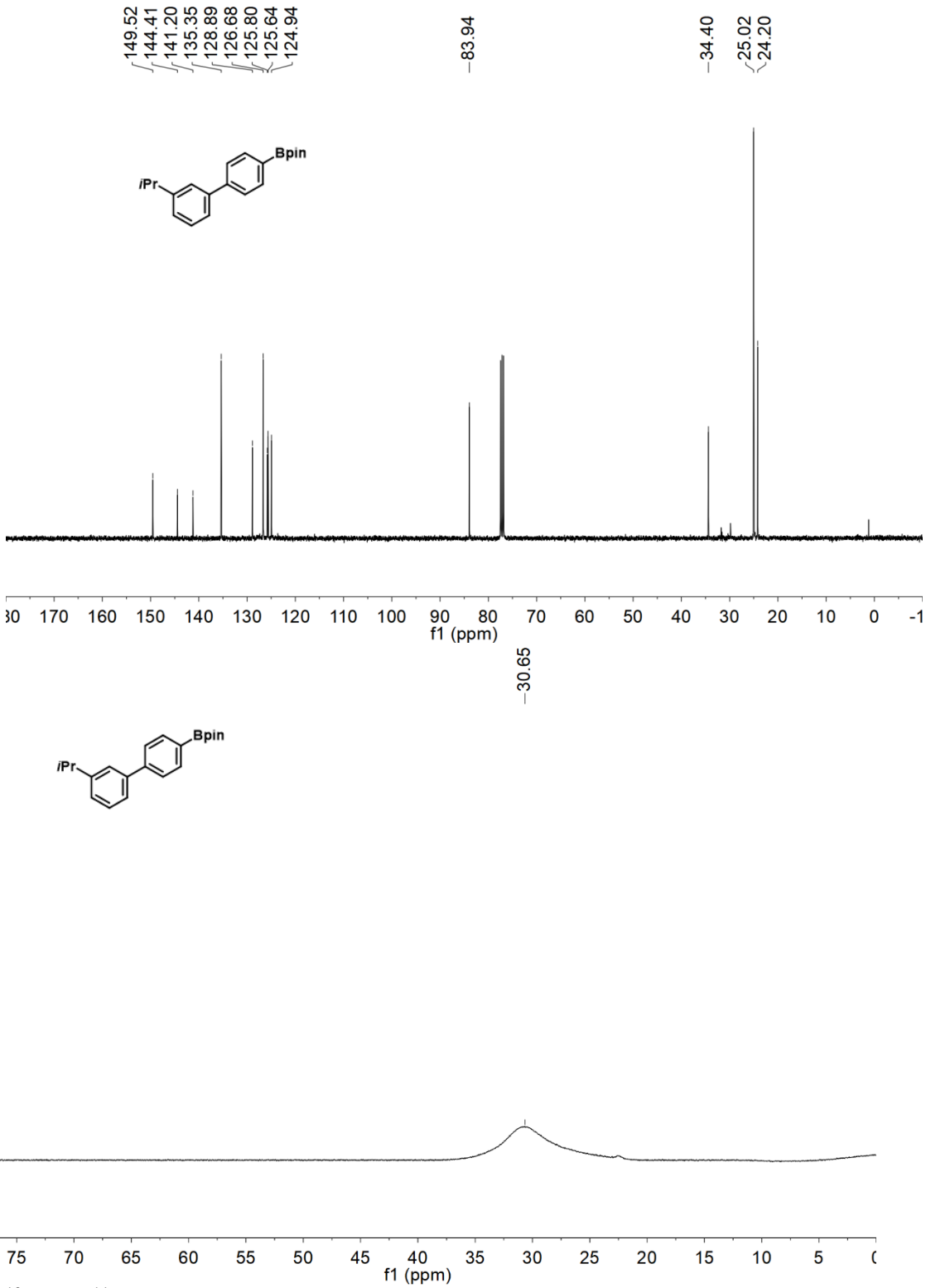
25.02
Bpin
Ph
N
Ph
f1 (ppm)

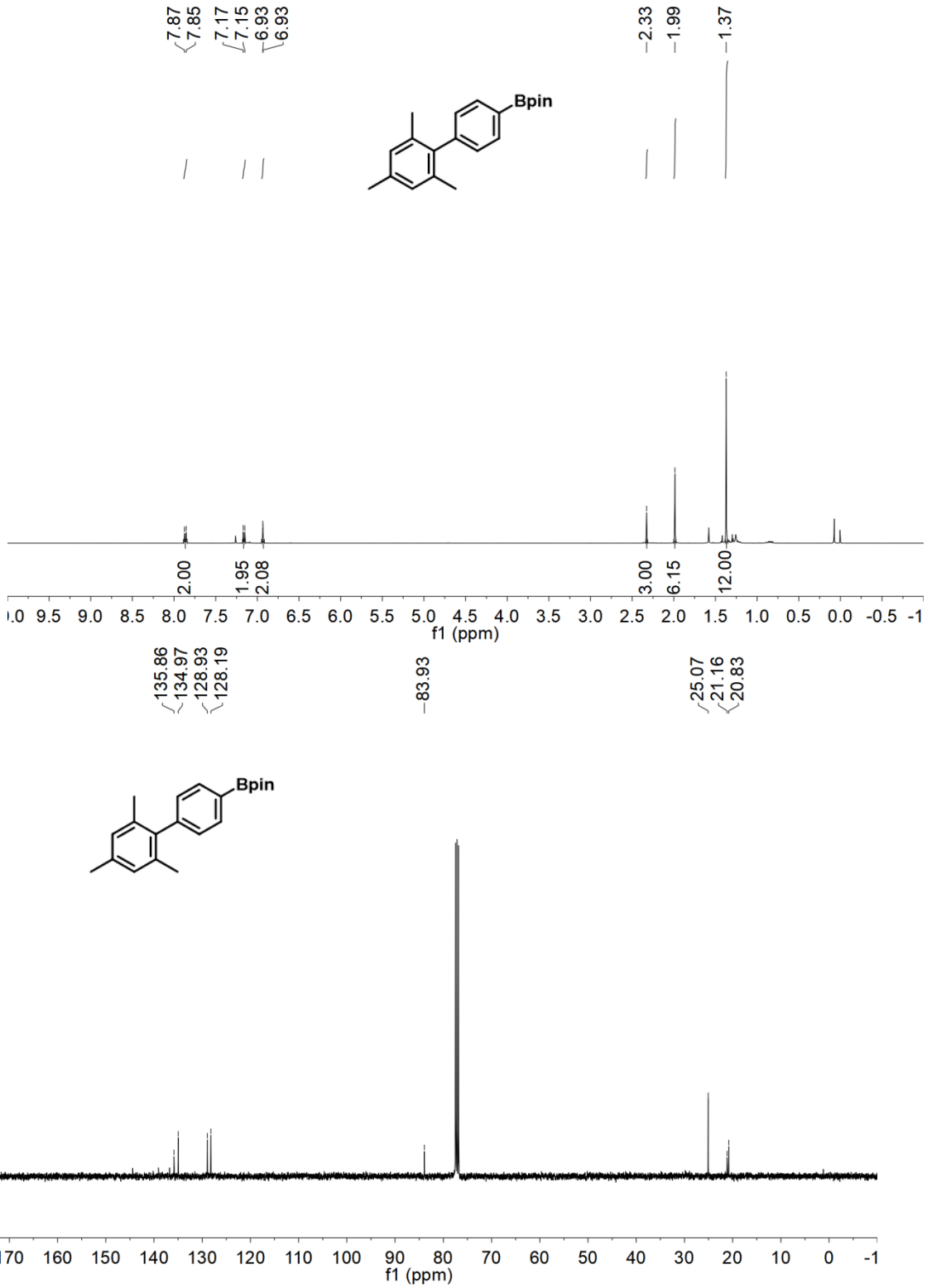


^{1}H, ^{13}C and ^{11}B NMR spectra for **2g**





^{1}H, ^{13}C and ^{11}B NMR spectra for **2h**


7.87
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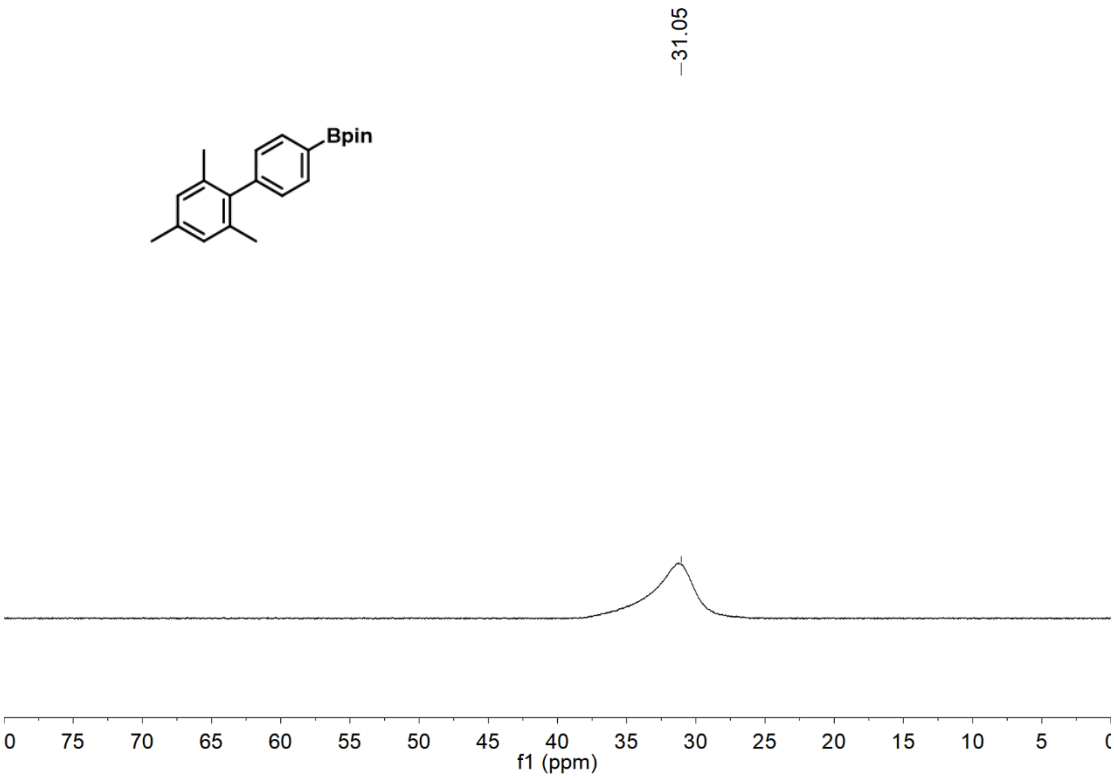
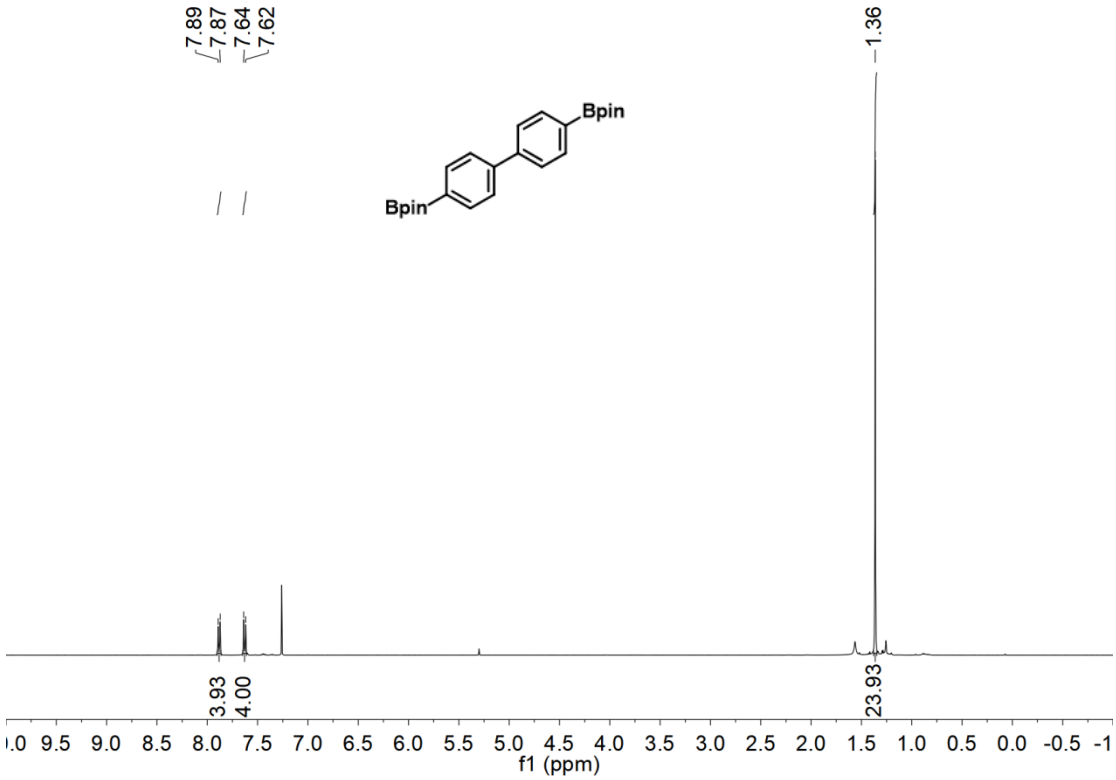
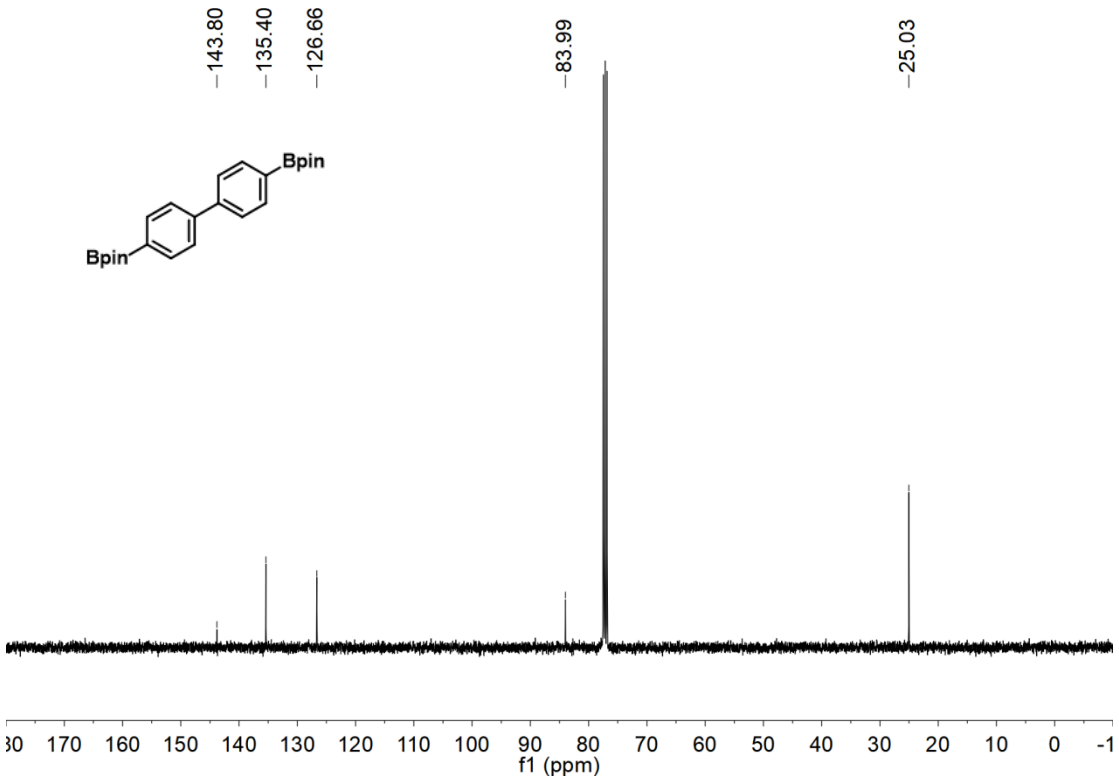
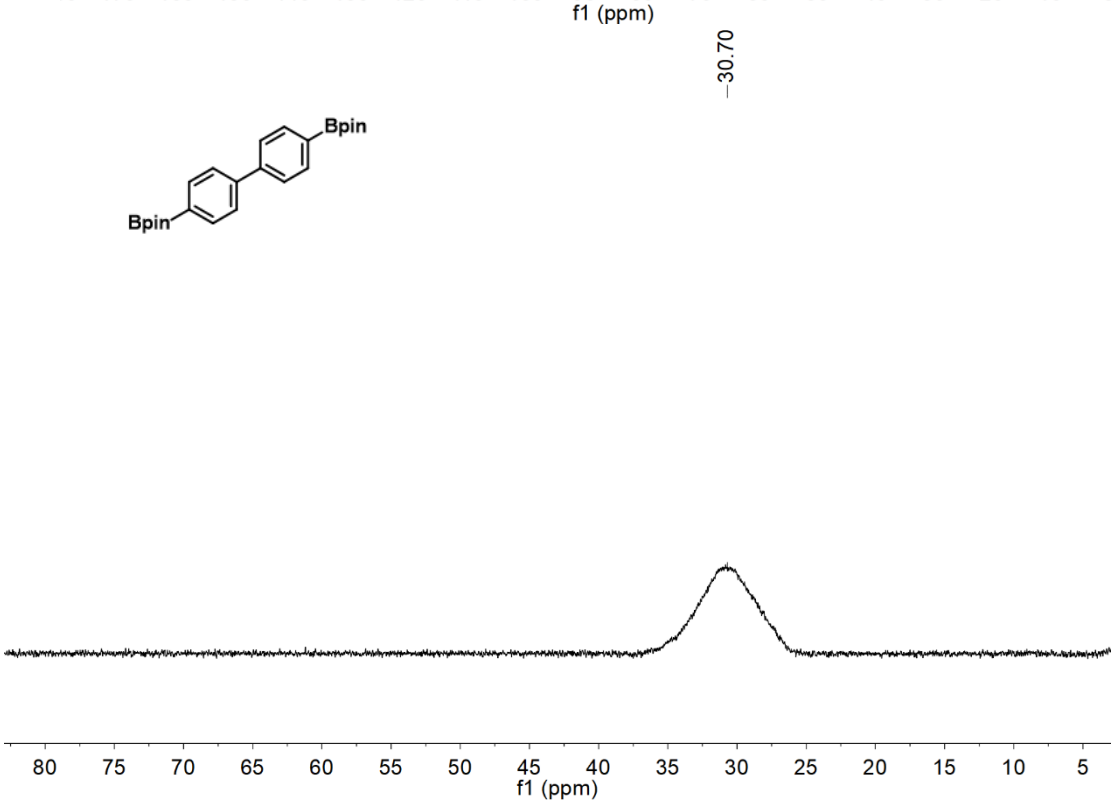
1.99
1.37
Bpin
2.00
1.95
2.08
3.00
6.15
12.00
f1 (ppm)
135.86
134.97
128.93
128.19
83.93
25.07
21.16
20.83
Bpin
f1 (ppm)



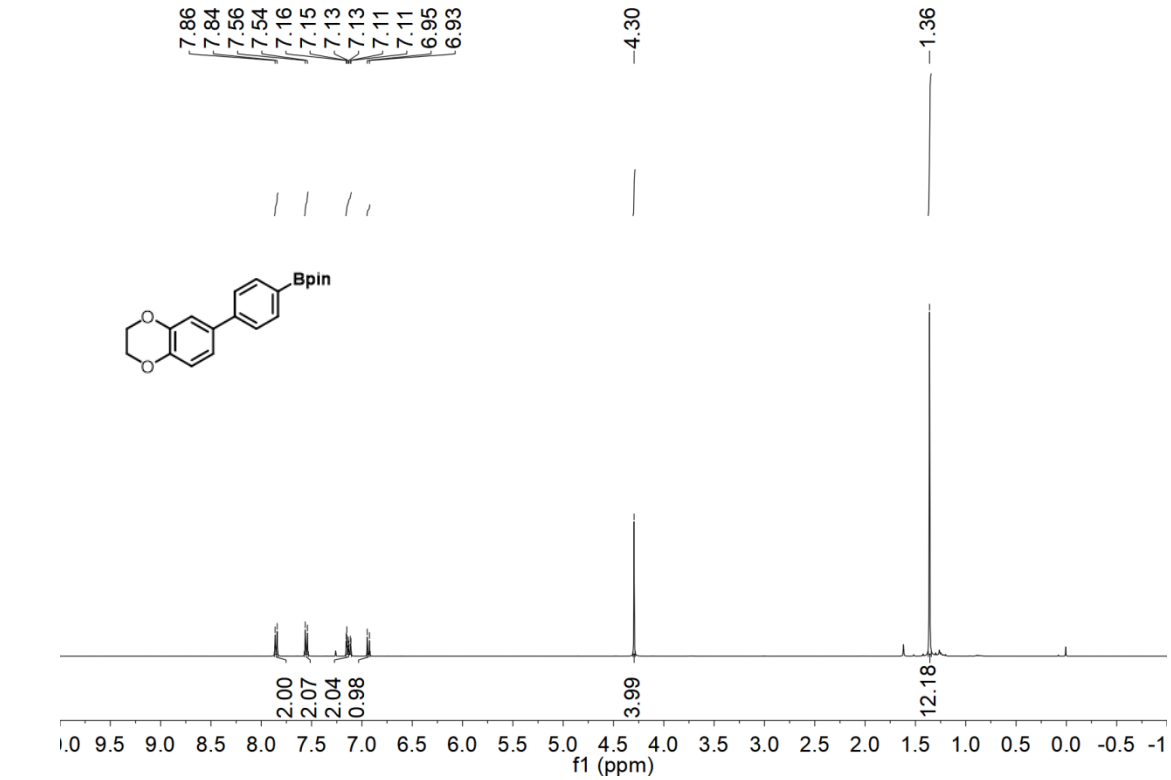
^{1}H, ^{13}C and ^{11}B NMR spectra for **2i**

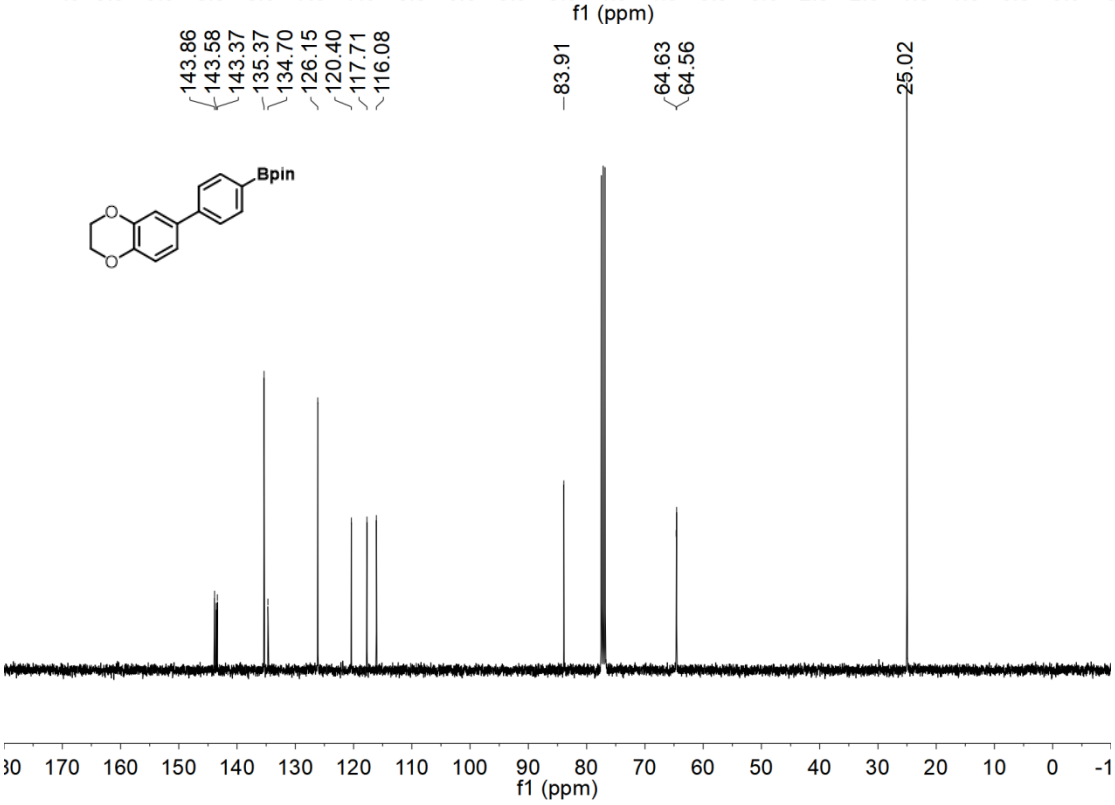


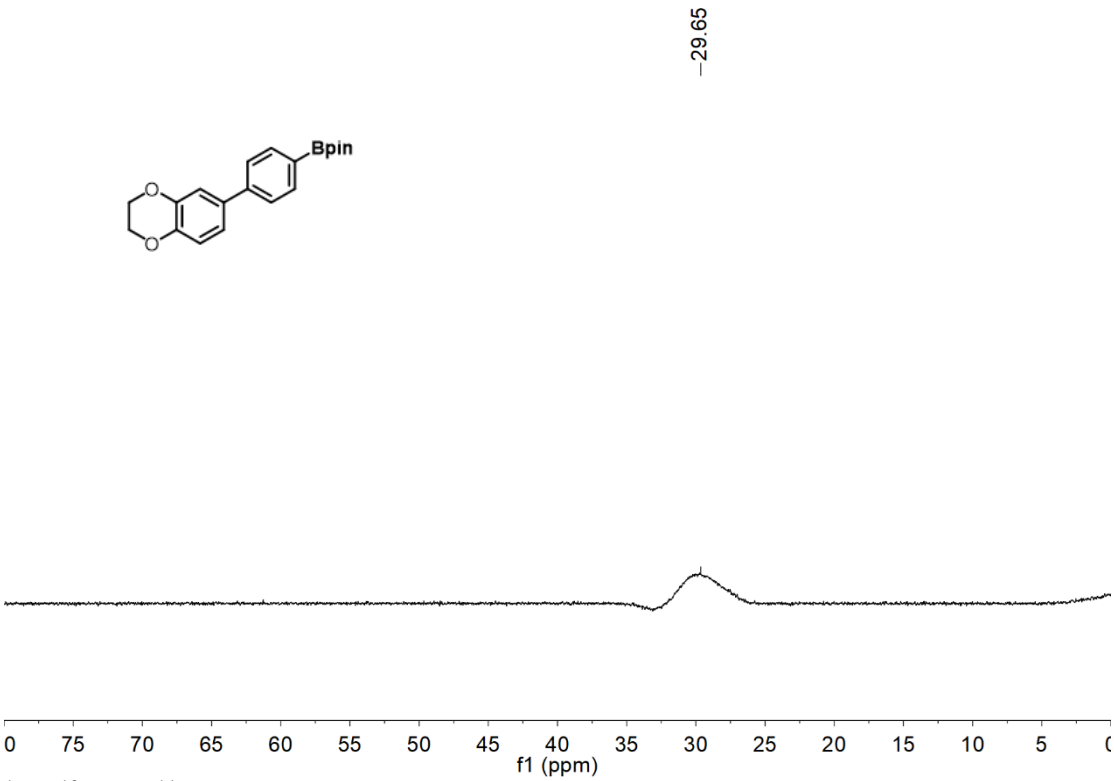




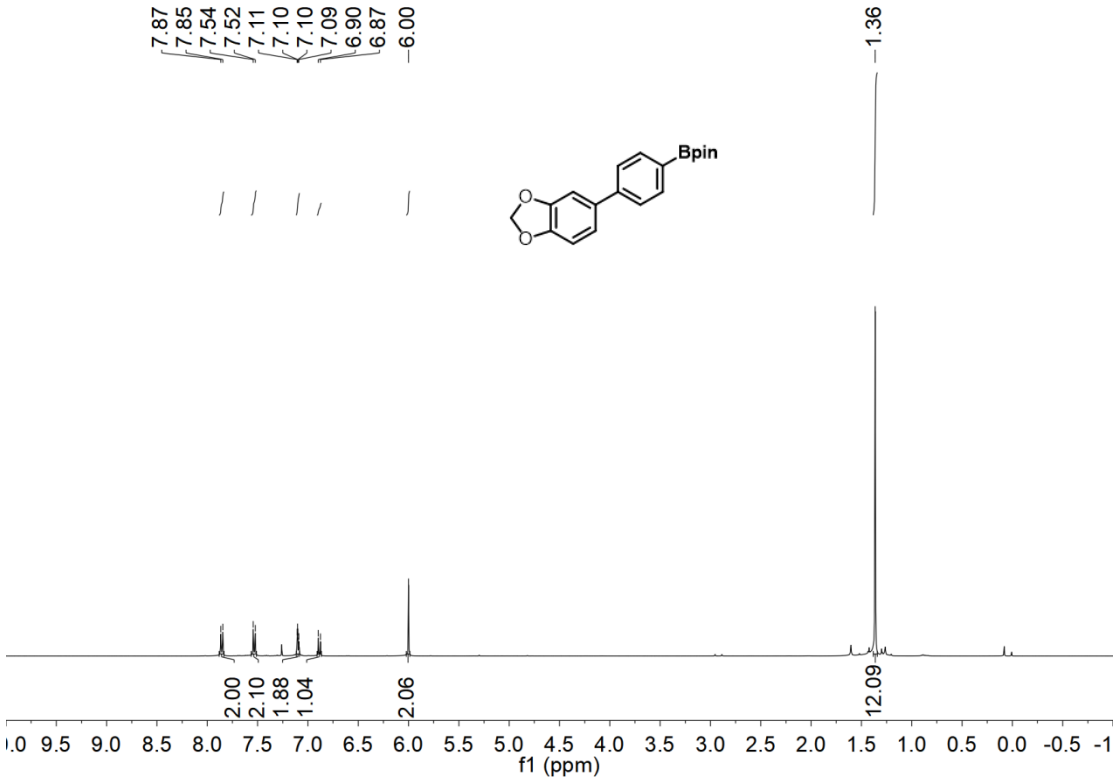
^{1}H, ^{13}C and ^{11}B NMR spectra for **2j**

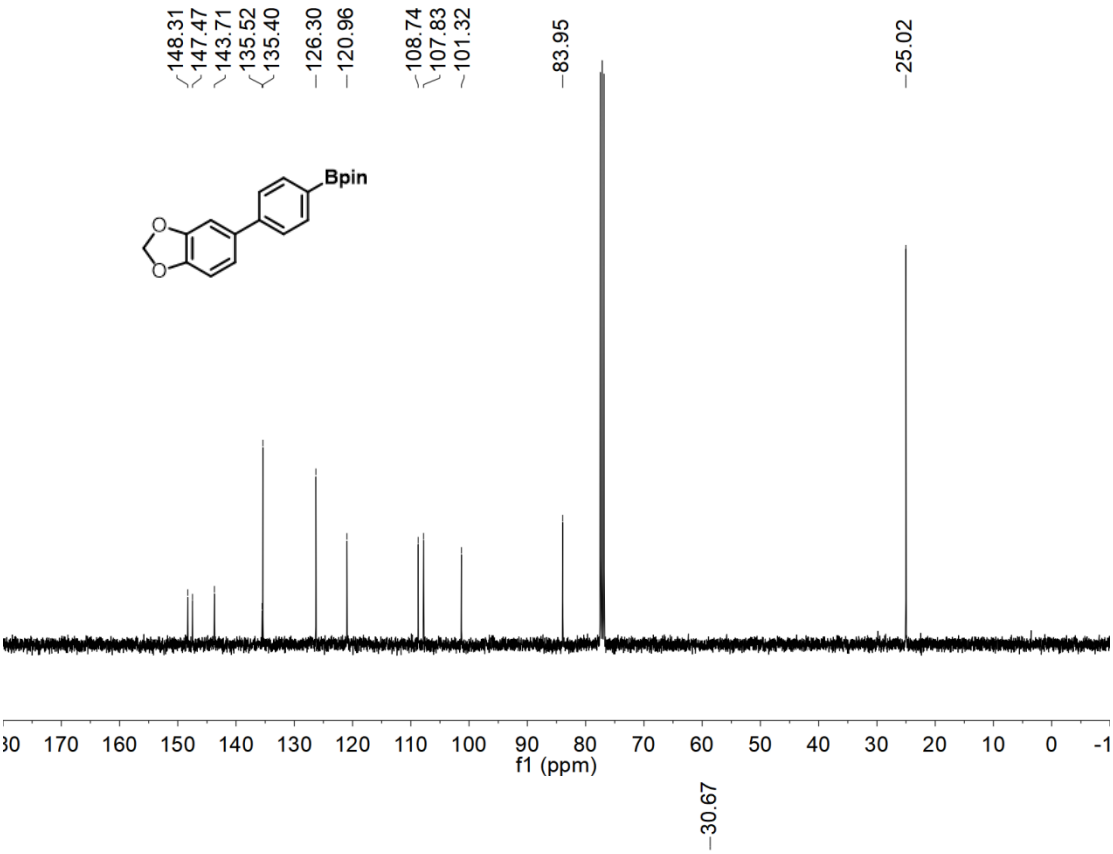

7.86
7.84
7.56
7.54
7.16
7.15
7.13
7.13
7.11
7.11
6.95
6.93
4.30
1.36
Bpin
2.00
2.07
2.04
0.98
3.99
12.18
f1 (ppm)

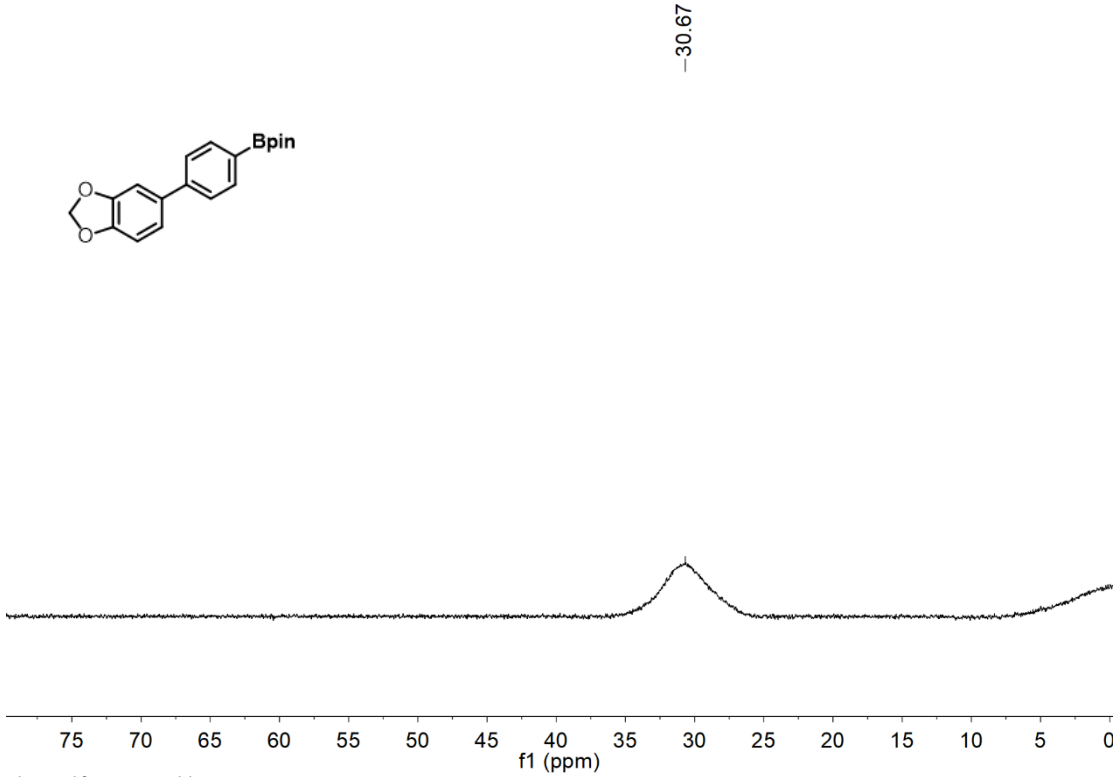

143.86
143.58
143.37
135.37
134.70
126.15
120.40
117.71
116.08
83.91
64.63
64.56
25.02
Bpin
f1 (ppm)



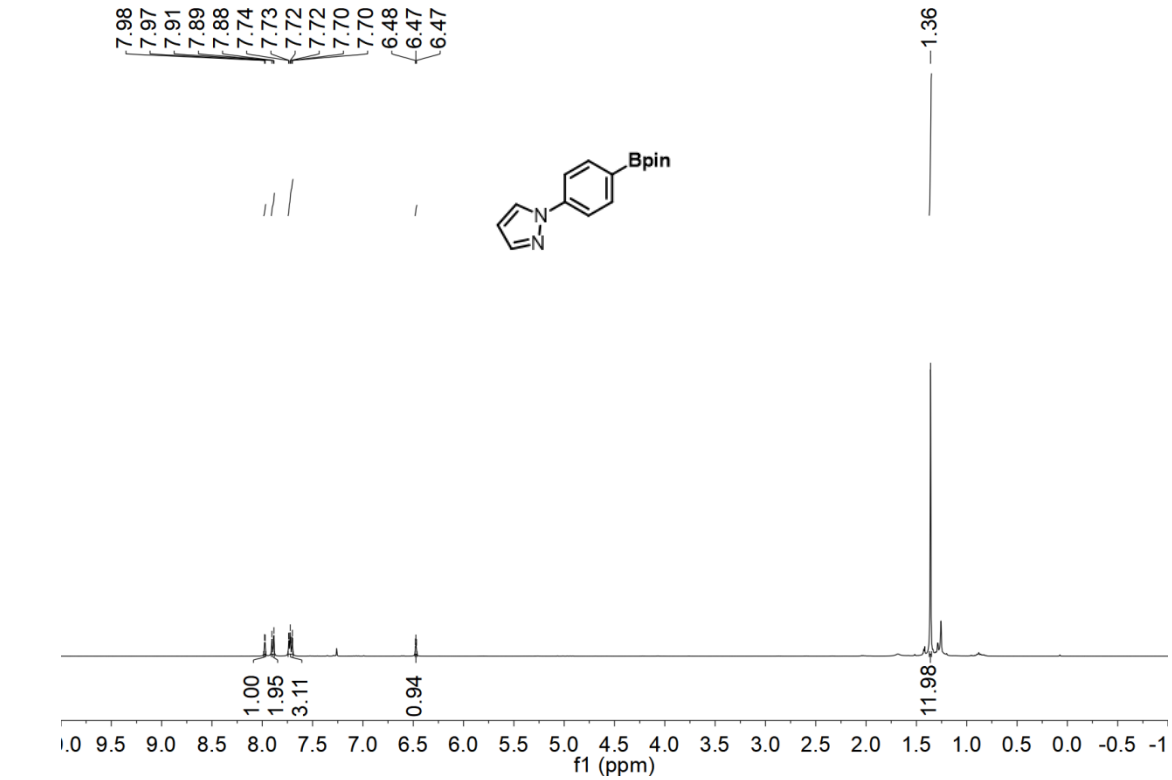
^{1}H, ^{13}C and^{11} B NMR spectra for **2k**

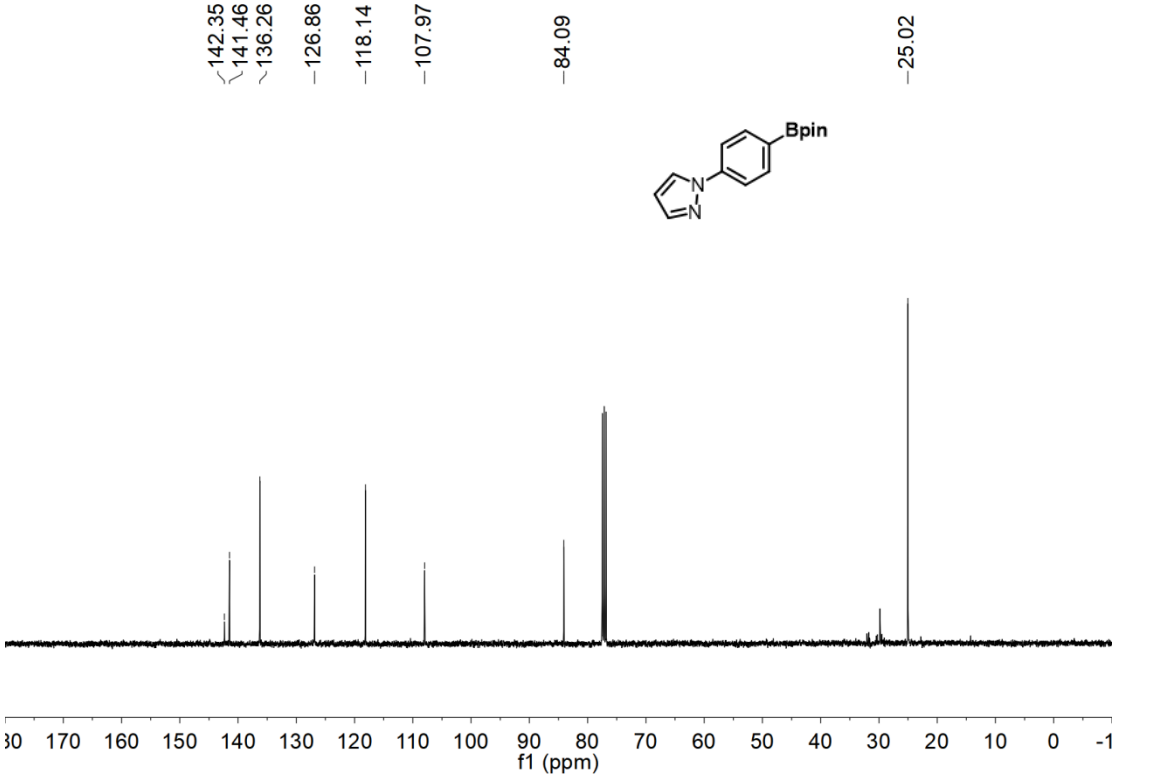


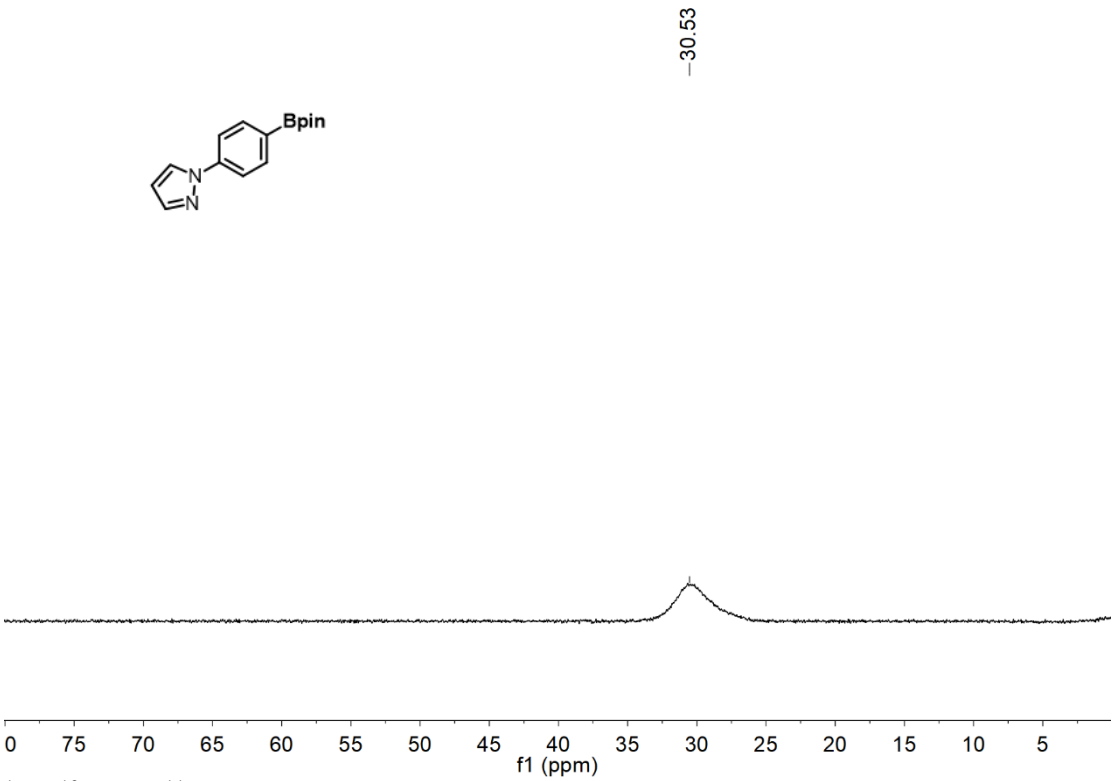




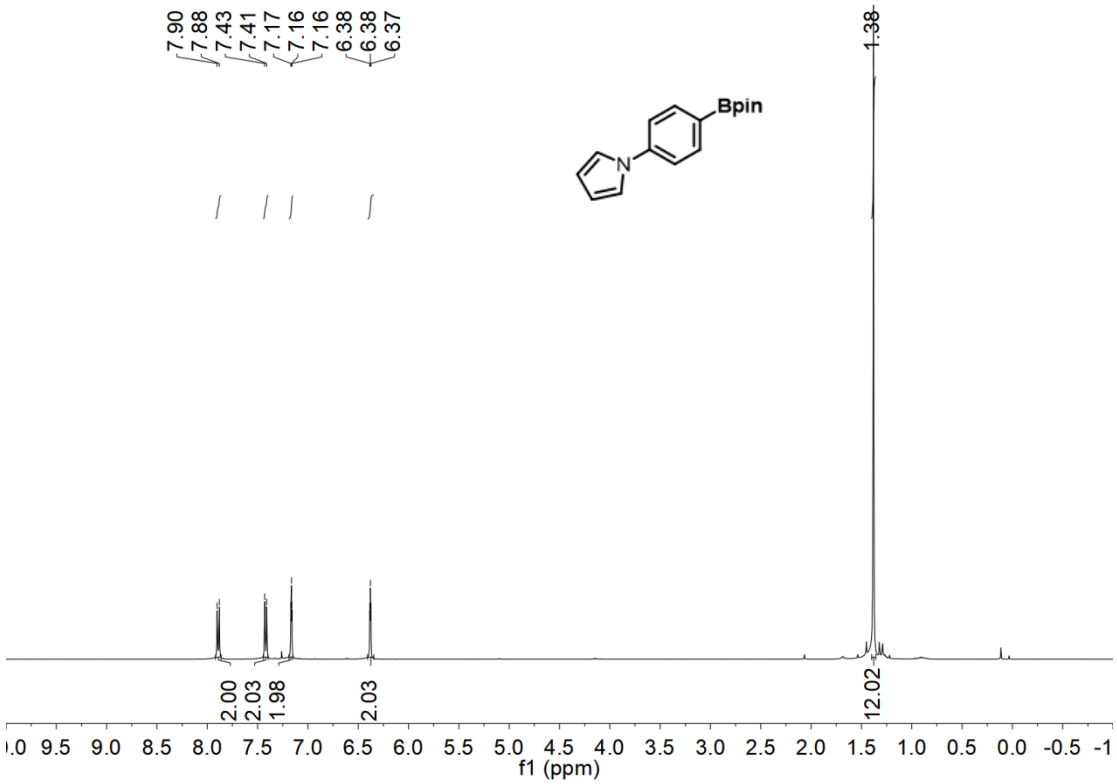
^{1}H, ^{13}C and ^{11}B NMR spectra for **2l**

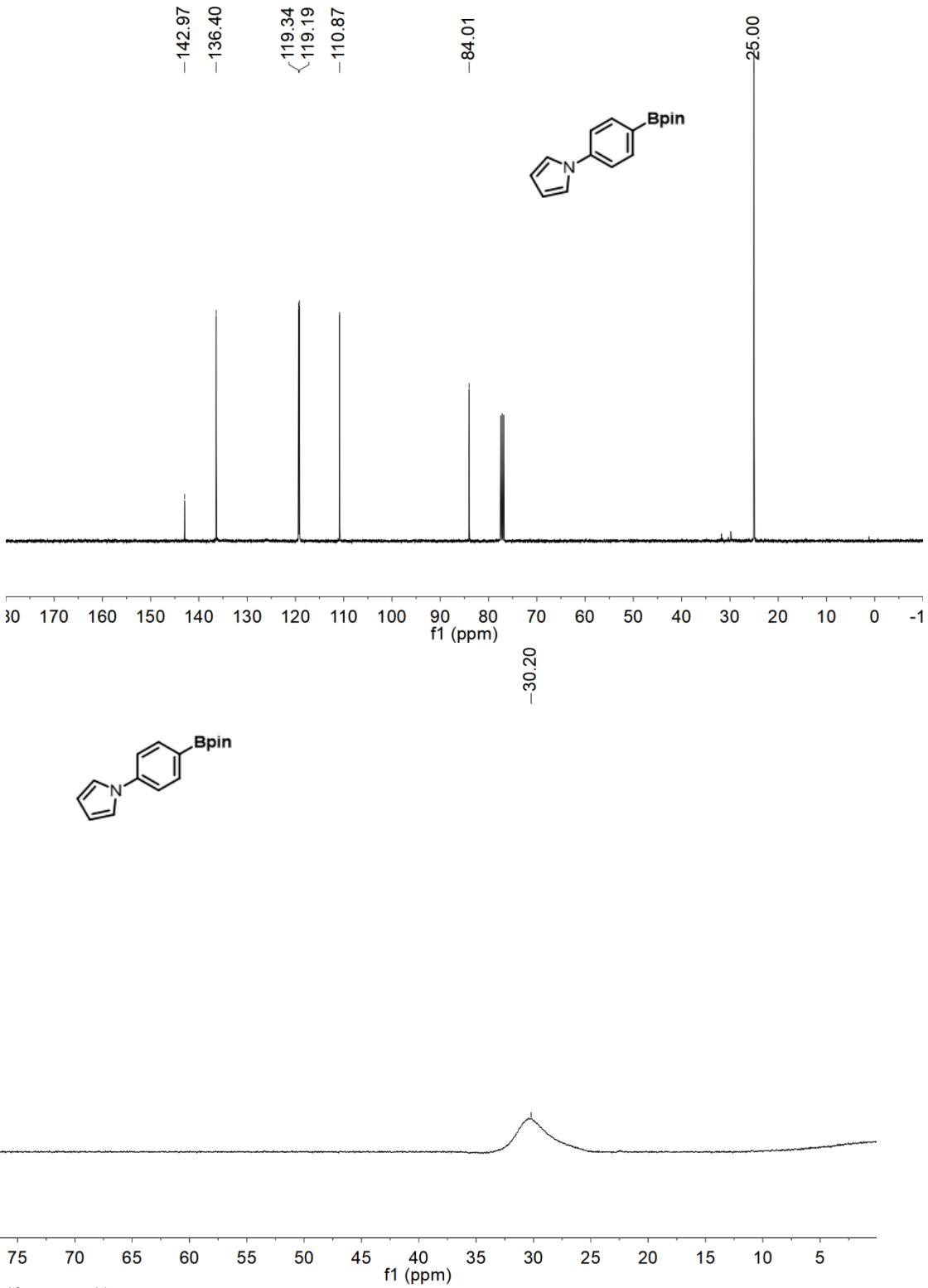

7.98
7.97
7.91
7.89
7.88
7.74
7.73
7.72
7.72
7.70
7.70
6.48
6.47
6.47
1.36
Bpin
1.00
1.95
3.11
0.94
11.98
f1 (ppm)


142.35
141.46
136.26
126.86
118.14
107.97
84.09
25.02
Bpin
f1 (ppm)

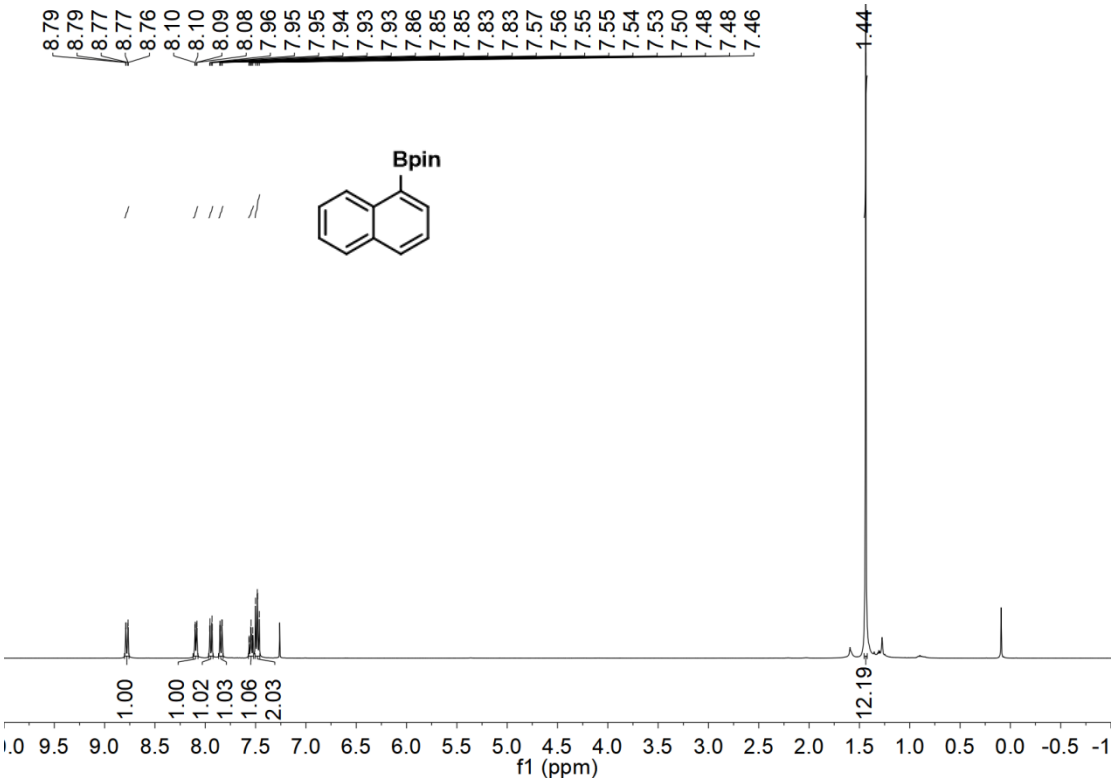


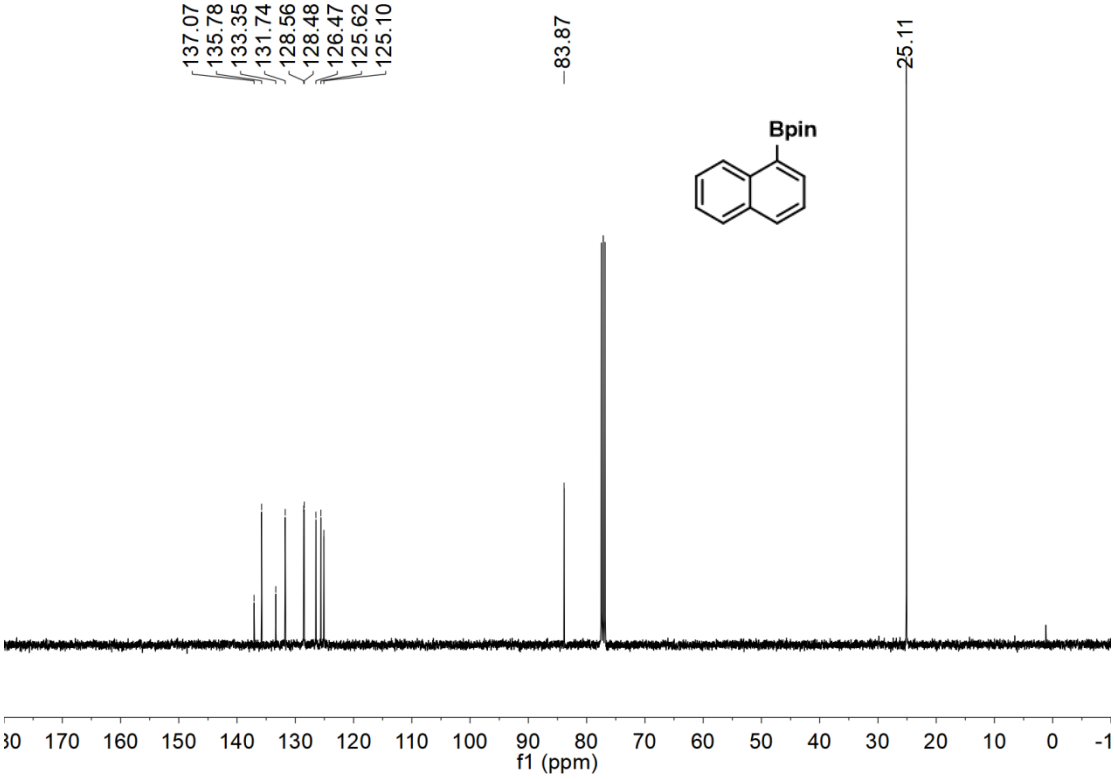
^{1}H, ^{13}C and ^{11}B NMR spectra for **2m**

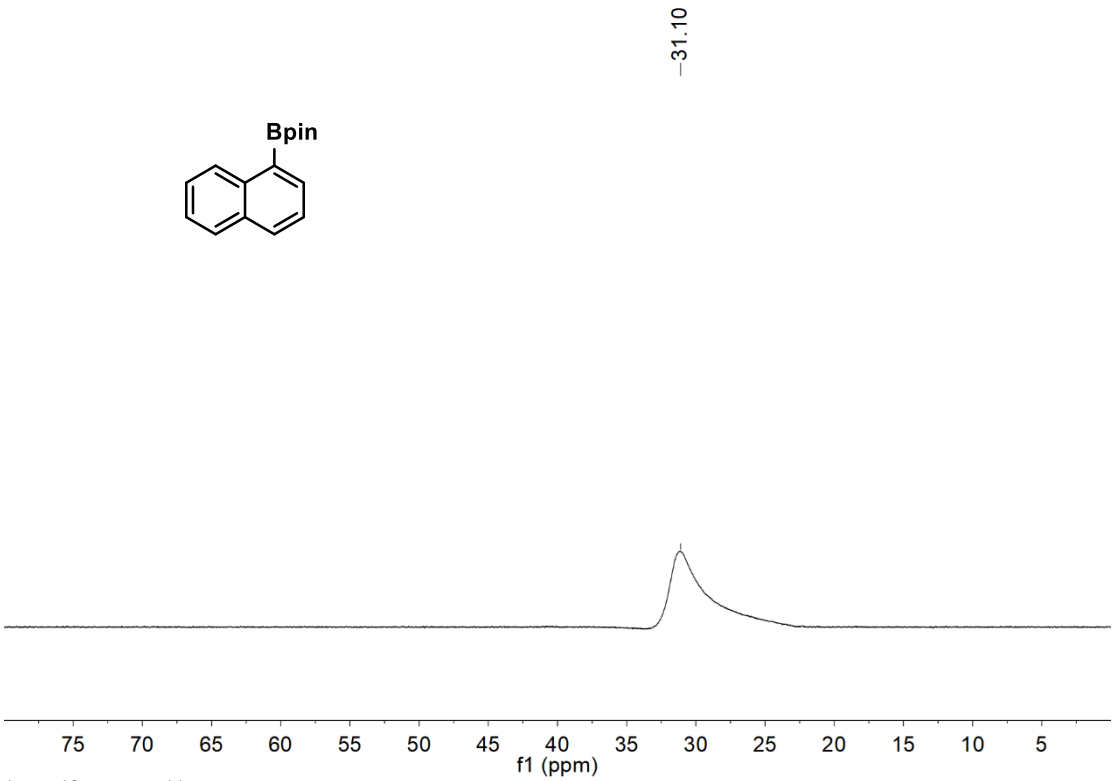




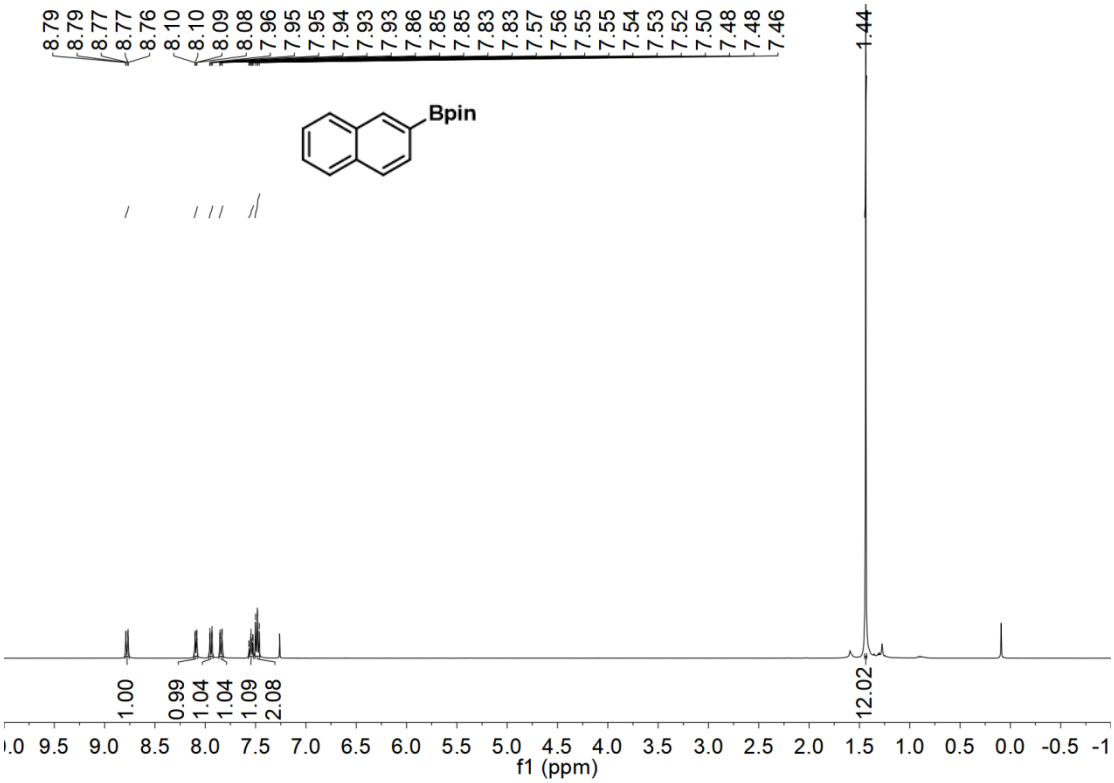
^{1}H, ^{13}C and ^{11}B NMR spectra for **2n**

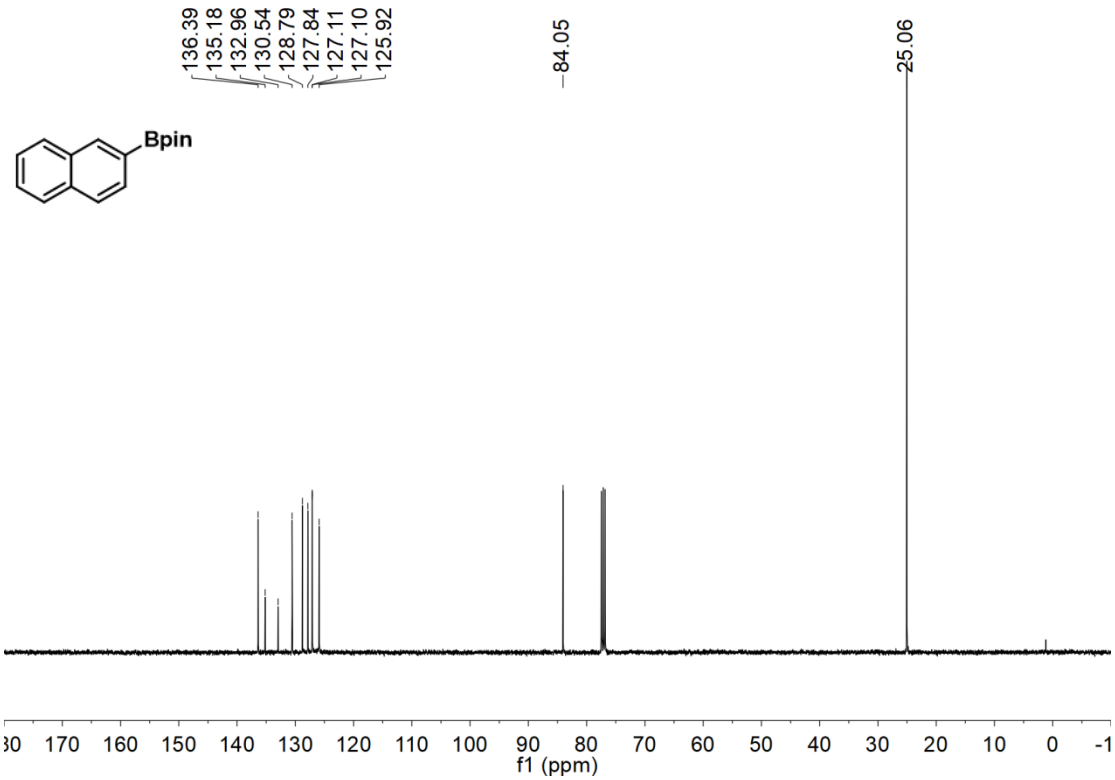

8.79
8.79
8.77
8.77
8.76
8.10
8.10
8.09
8.08
7.96
7.95
7.95
7.94
7.93
7.93
7.86
7.85
7.85
7.83
7.83
7.57
7.56
7.55
7.55
7.54
7.53
7.50
7.48
7.48
7.46
1.44
Bpin
1.00
1.00
1.02
1.03
1.06
2.03
12.19
f1 (ppm)

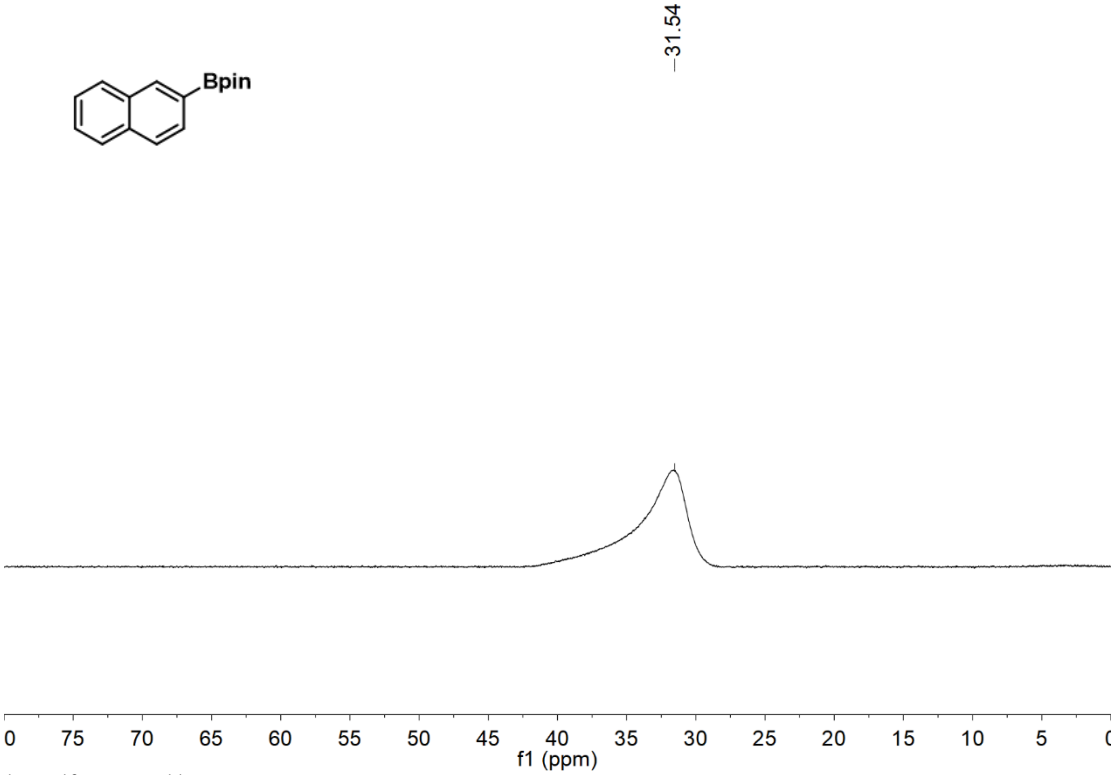

137.07
135.78
133.35
131.74
128.56
128.48
126.47
125.62
125.10
83.87
25.11
Bpin
f1 (ppm)



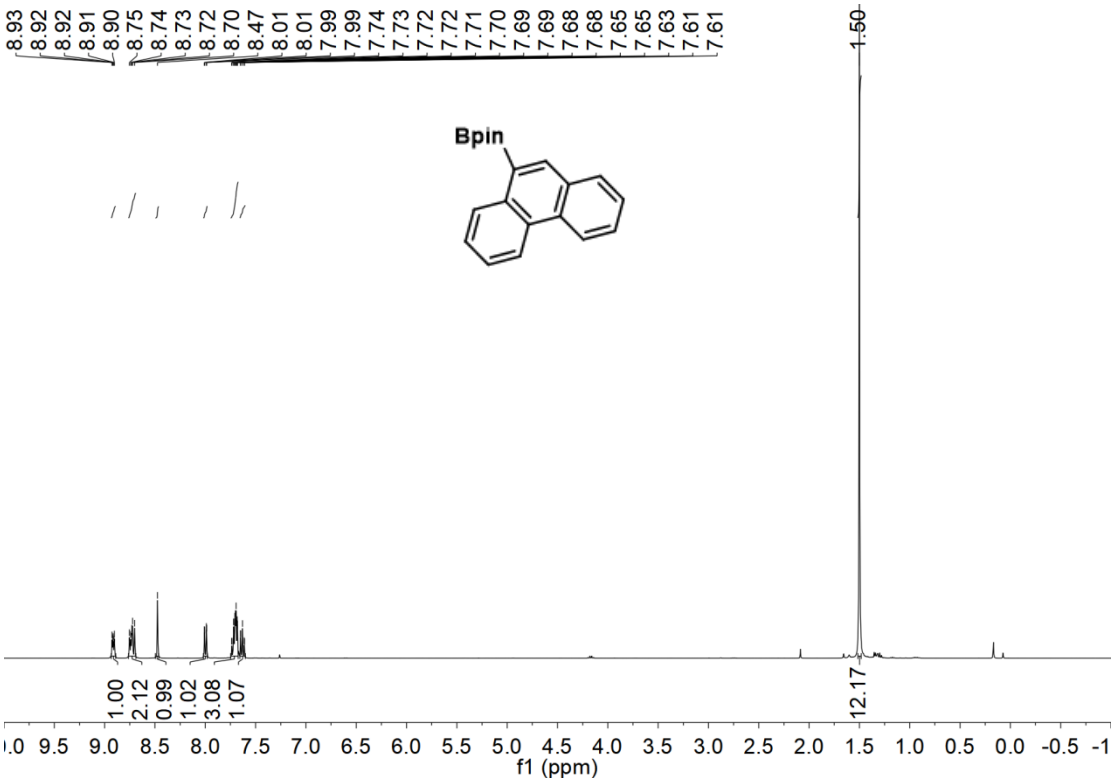
^{1}H, ^{13}C and ^{11}B NMR spectra for **2o**

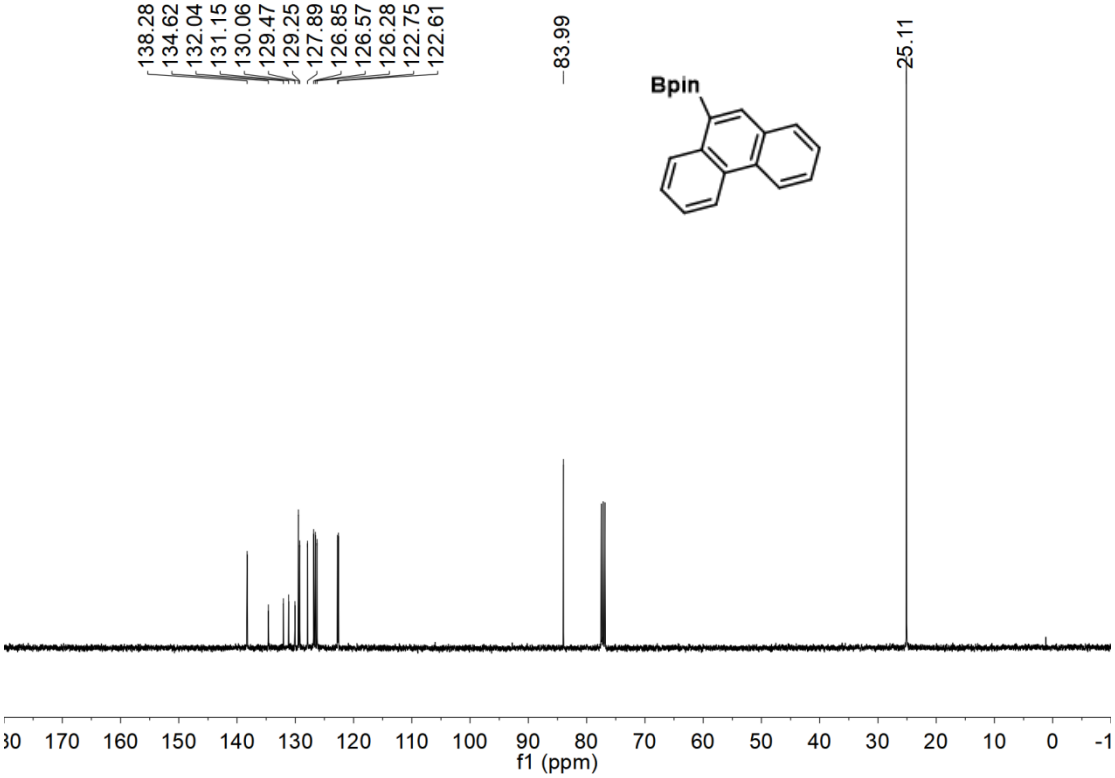


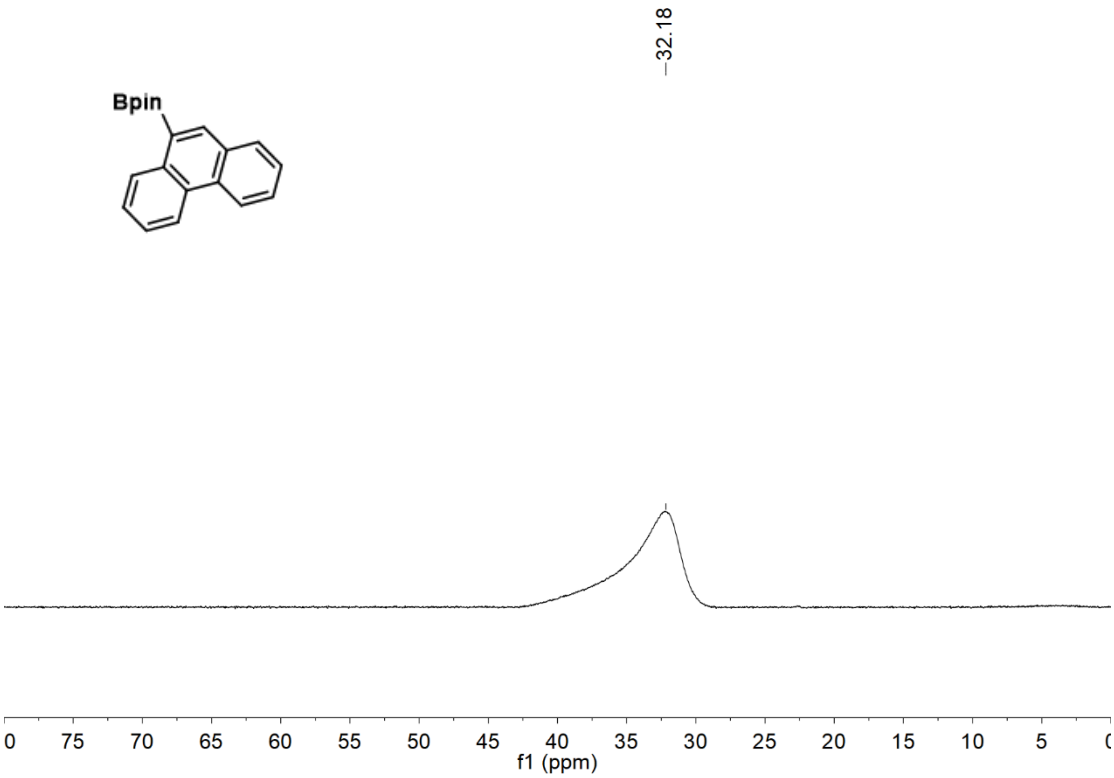




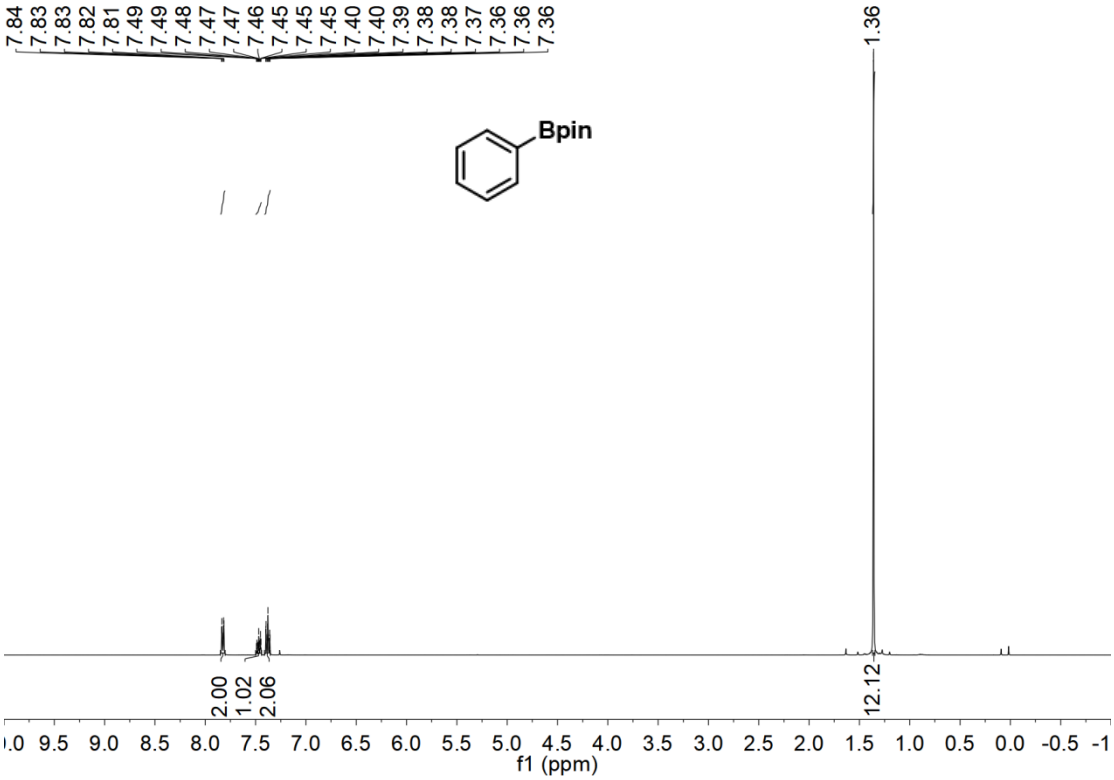
^{1}H, ^{13}C and ^{11}B NMR spectra for **2p**

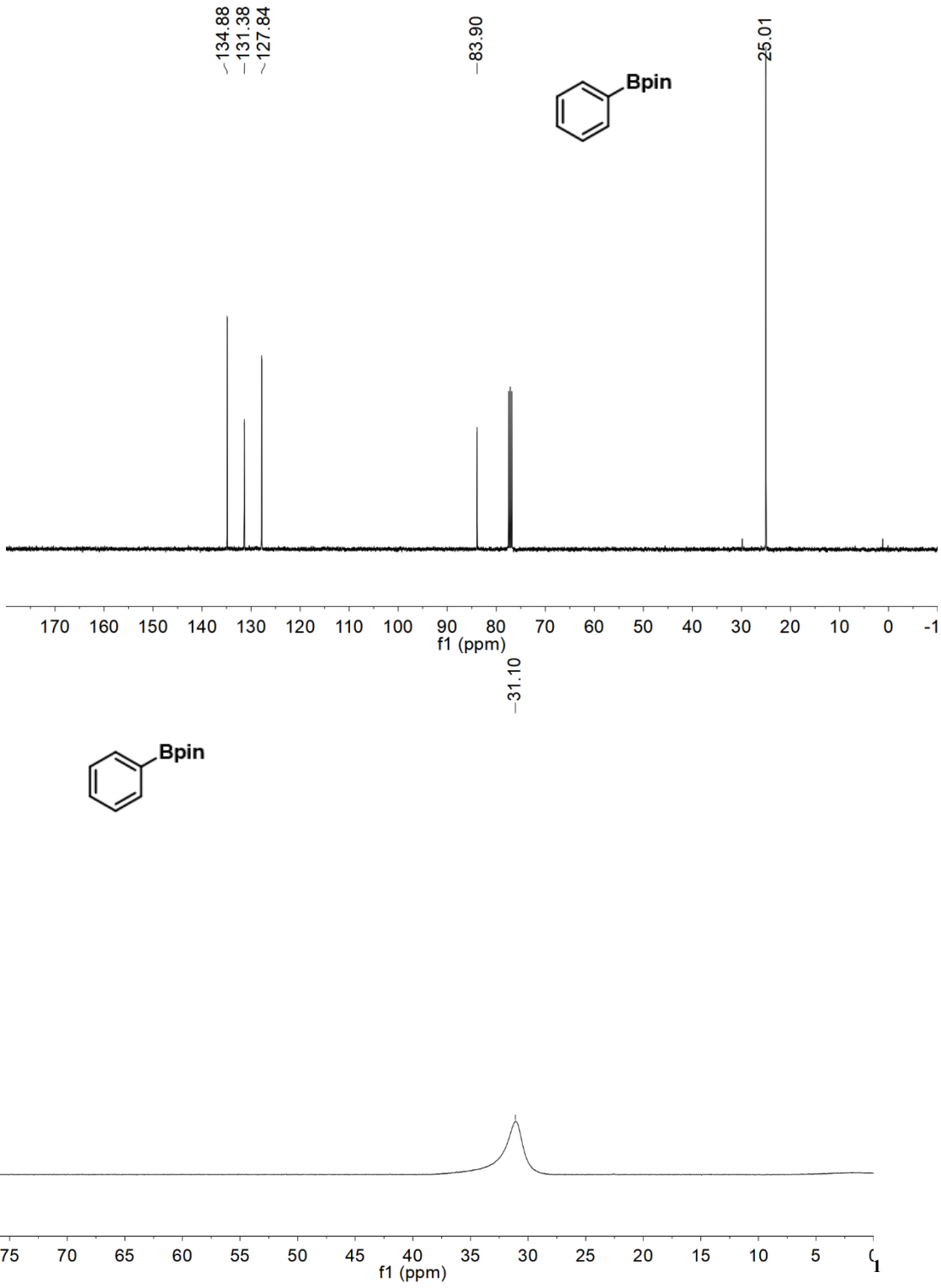

8.93
8.92
8.92
8.91
8.90
8.75
8.74
8.73
8.72
8.70
8.47
8.01
8.01
7.99
7.99
7.74
7.73
7.72
7.72
7.71
7.70
7.69
7.69
7.68
7.68
7.65
7.65
7.63
7.61
7.61
1.50
Bpin
1.00
2.12
0.99
1.02
3.08
1.07
12.17
f1 (ppm)


138.28
134.62
132.04
131.15
130.06
129.47
129.25
127.89
126.85
126.57
126.28
122.75
122.61
83.99
25.11
Bpin
f1 (ppm)

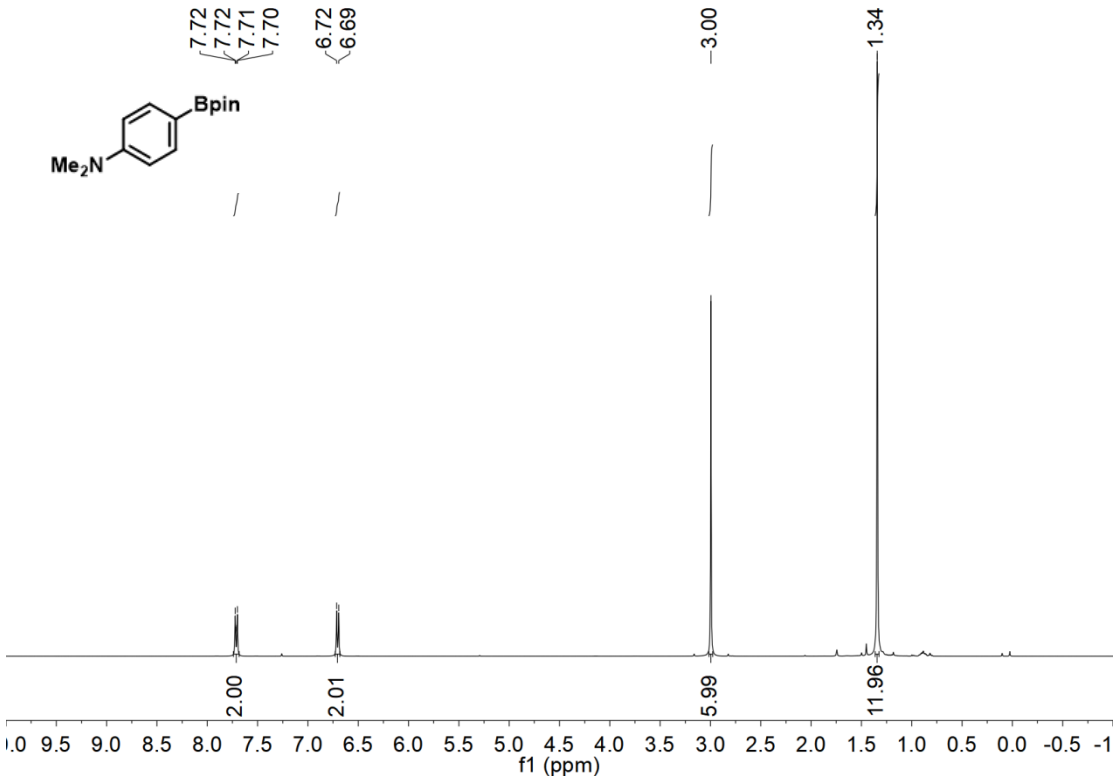


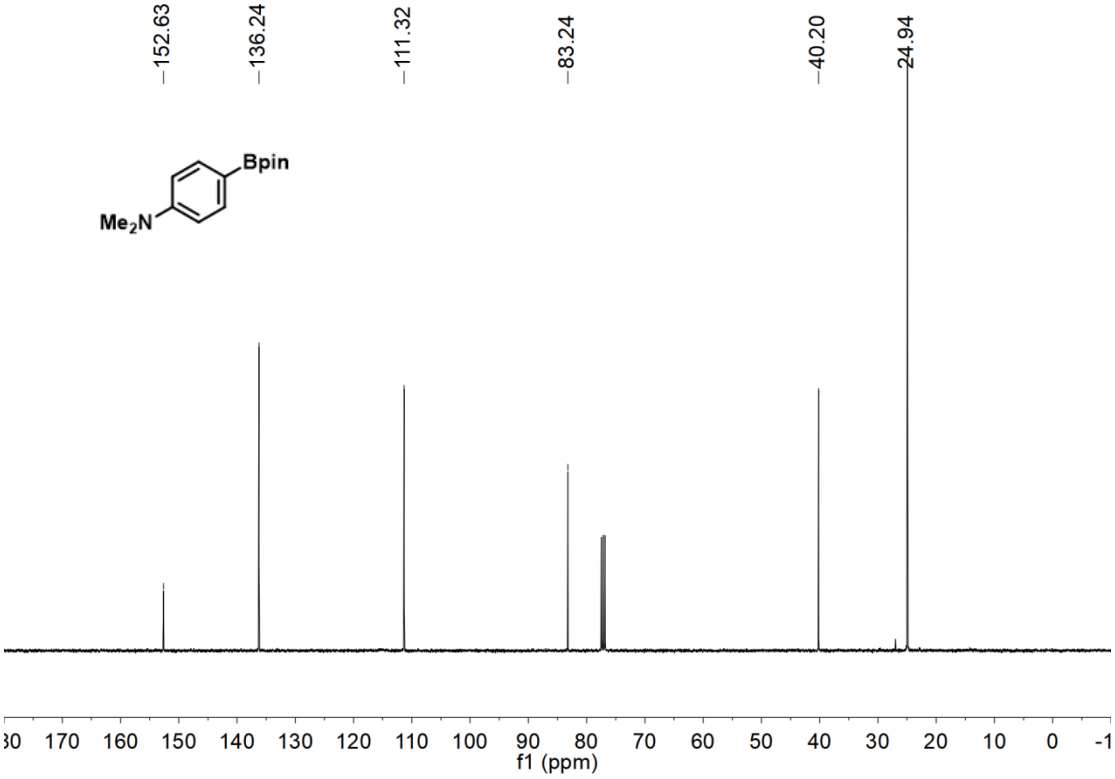
^{1}H, ^{13}C and ^{11}B NMR spectra for **2q**

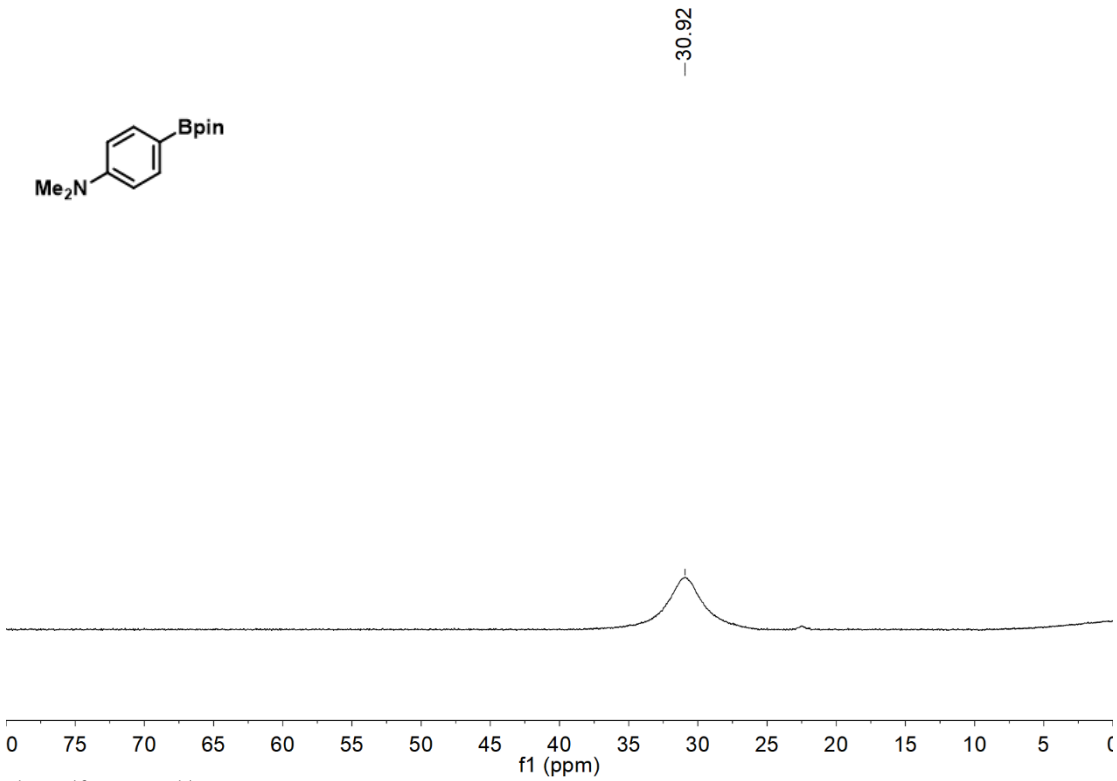




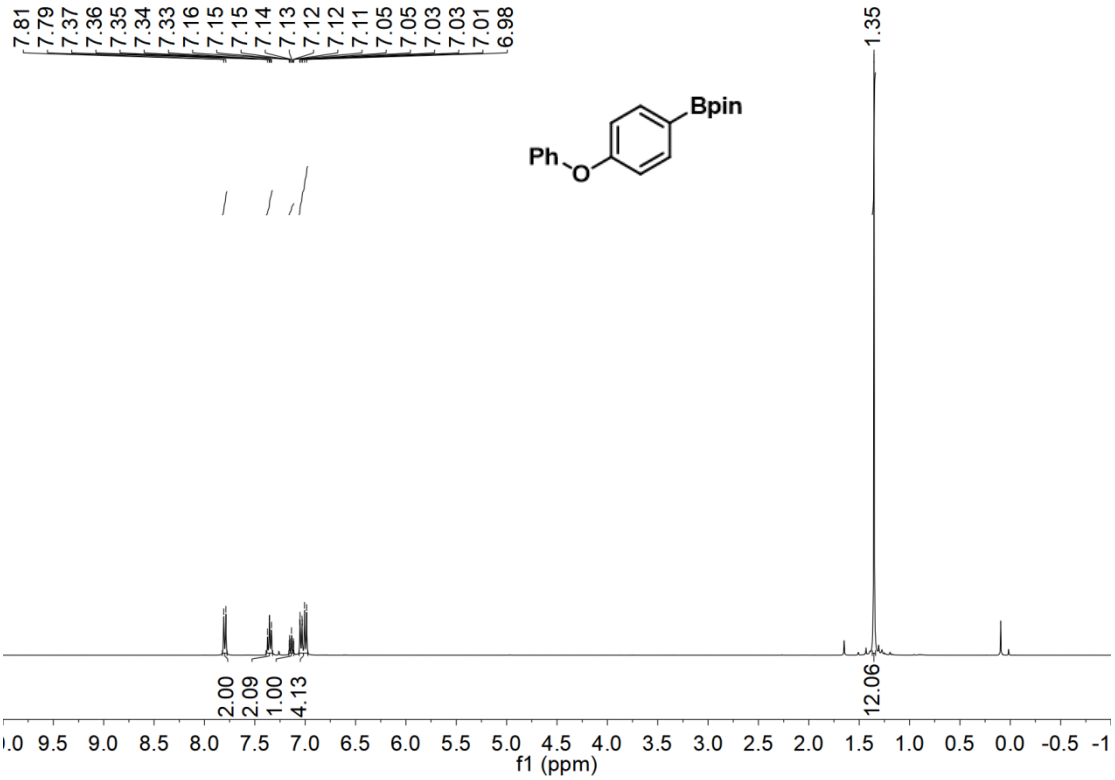
^{1}H, ^{13}C and ^{11}B NMR spectra for **2r**

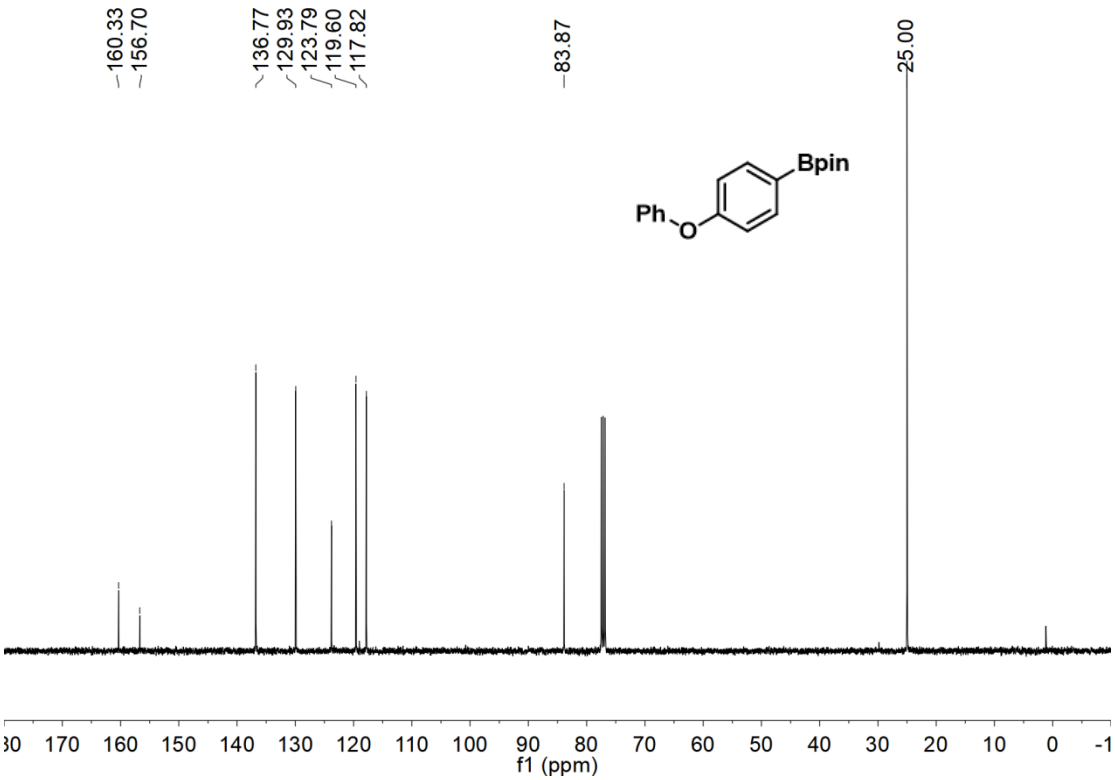

7.72
7.72
7.71
7.70
6.72
6.69
3.00
1.34
Bpin
Me2N
2.00
2.01
5.99
11.96
f1 (ppm)

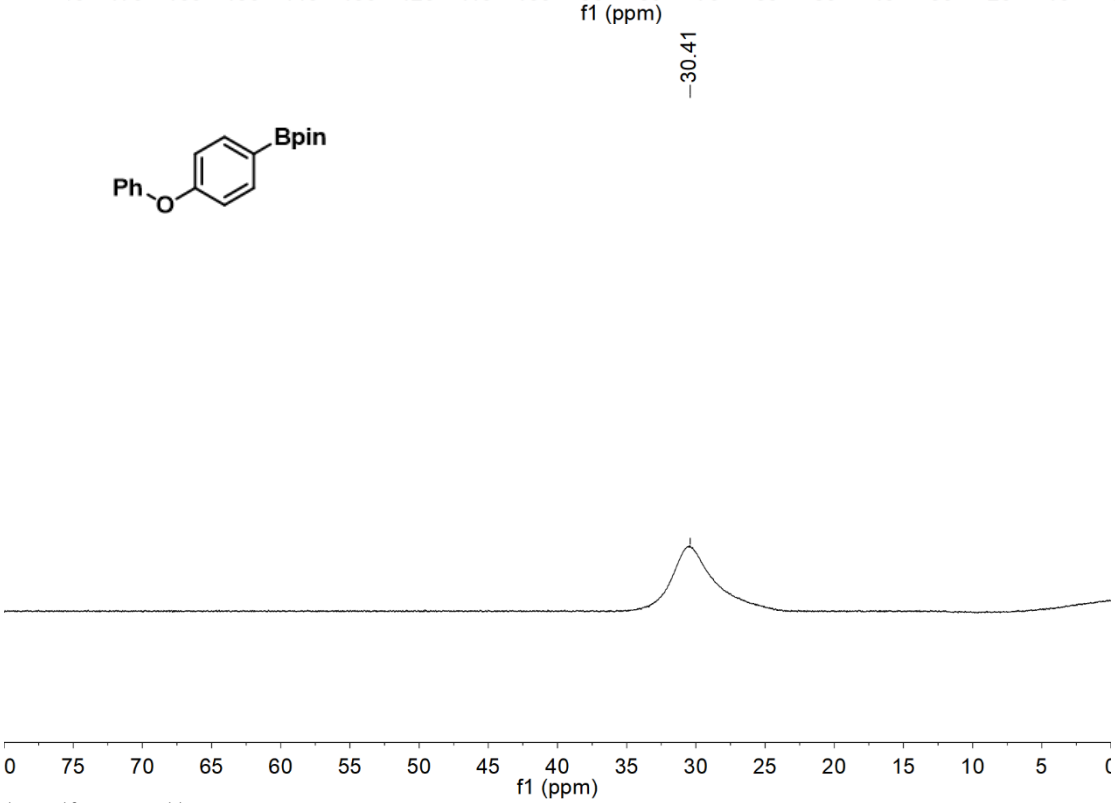

152.63
136.24
111.32
83.24
40.20
24.94
Bpin
Me2N
f1 (ppm)



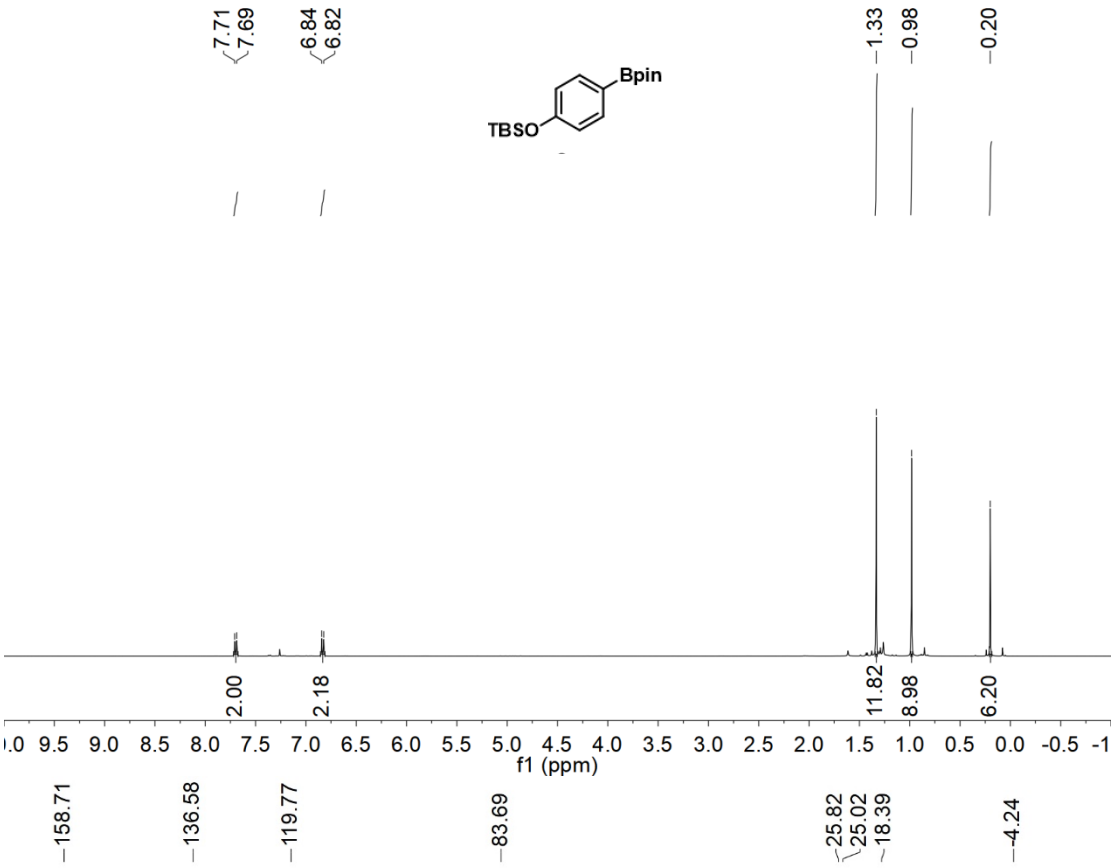
^{1}H, ^{13}C and ^{11}B NMR spectra for **2s**

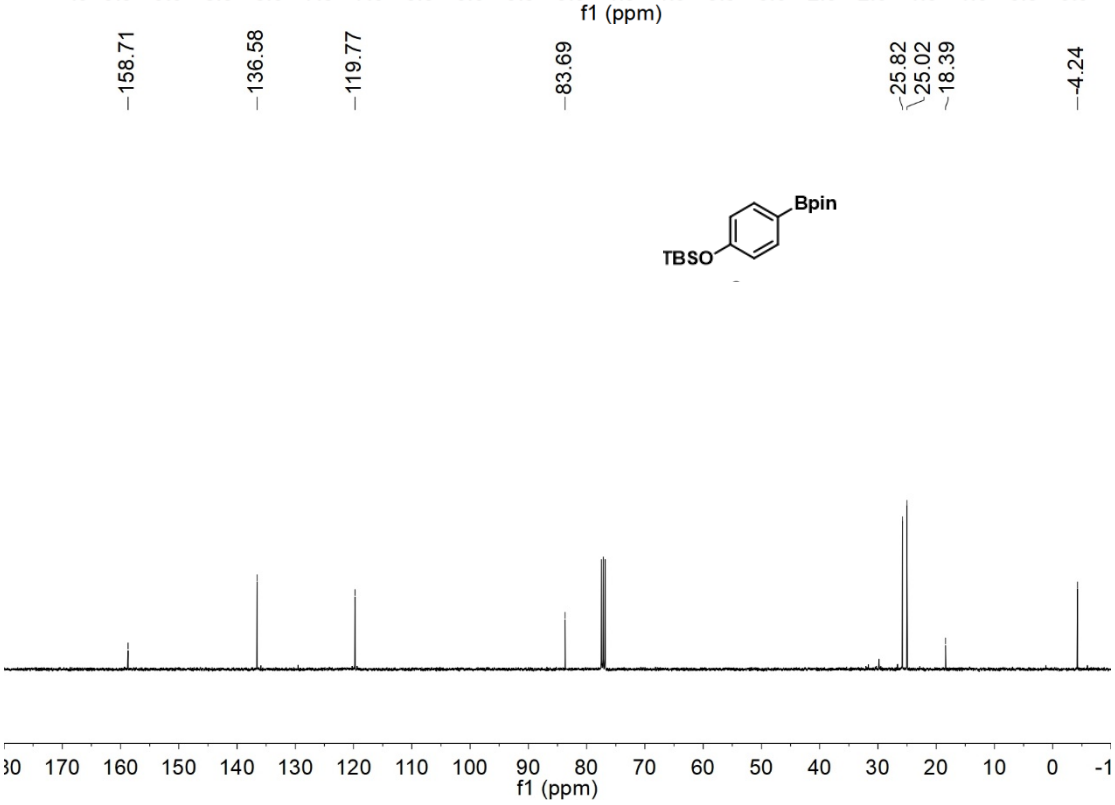


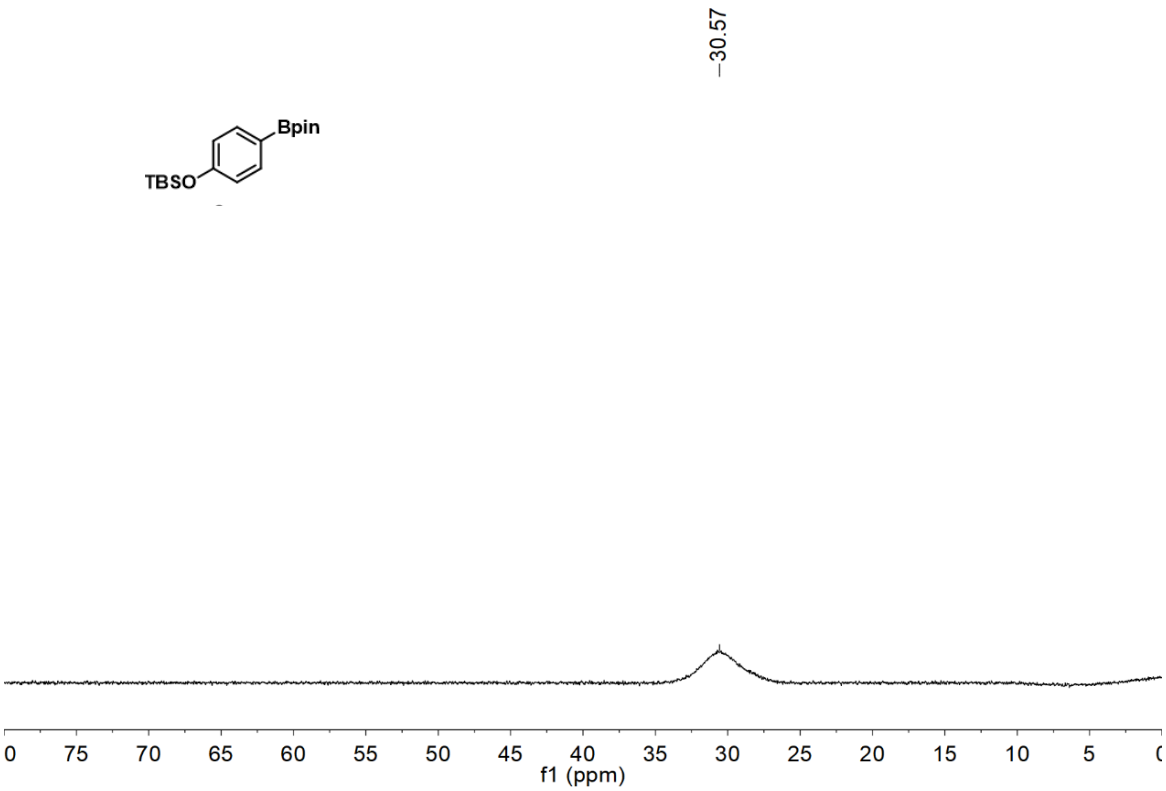




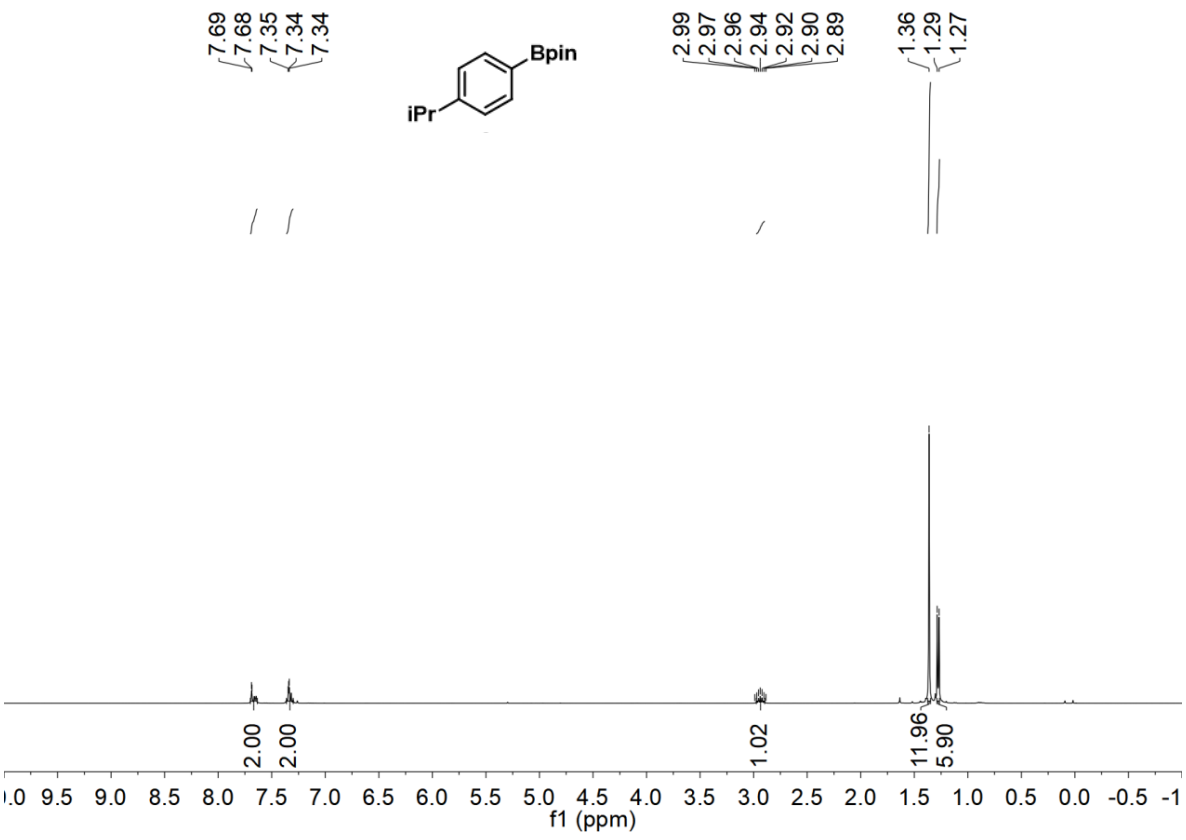
^{1}H, ^{13}C and ^{11}B NMR spectra for **2t**

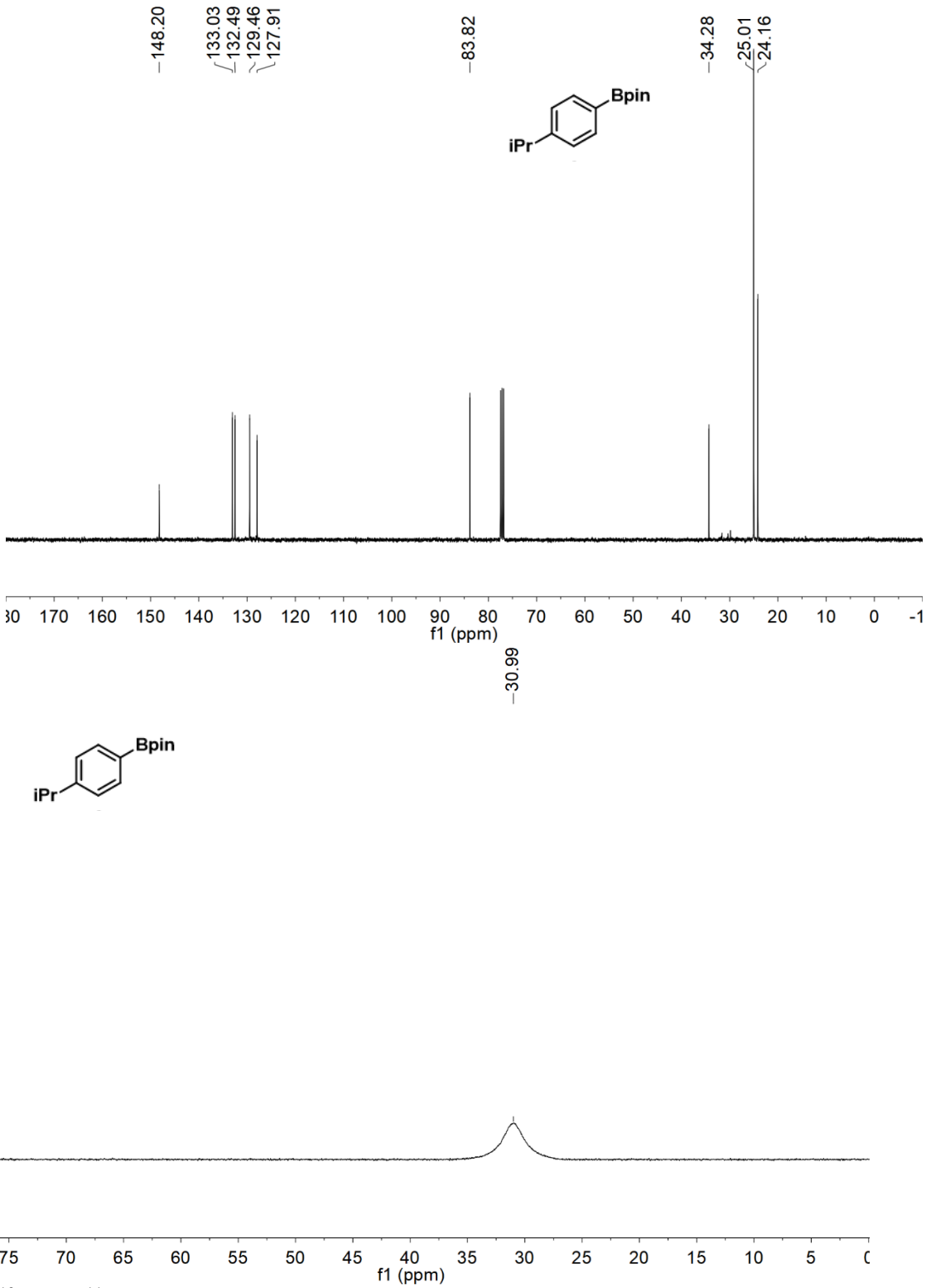

7.71
7.69
6.84
6.82
1.33
0.98
0.20
Bpin
TBSO
2.00
2.18
11.82
8.98
6.20
f1 (ppm)


158.71
136.58
119.77
83.69
25.82
25.02
18.39
4.24
Bpin
TBSO
f1 (ppm)

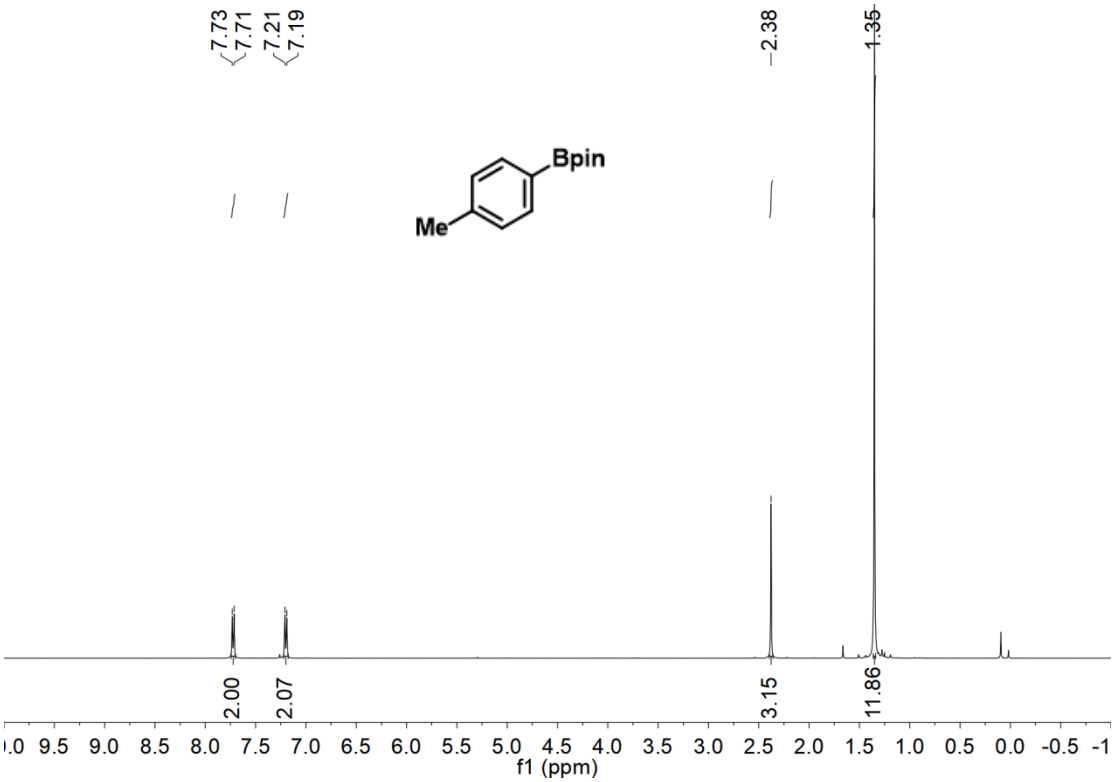


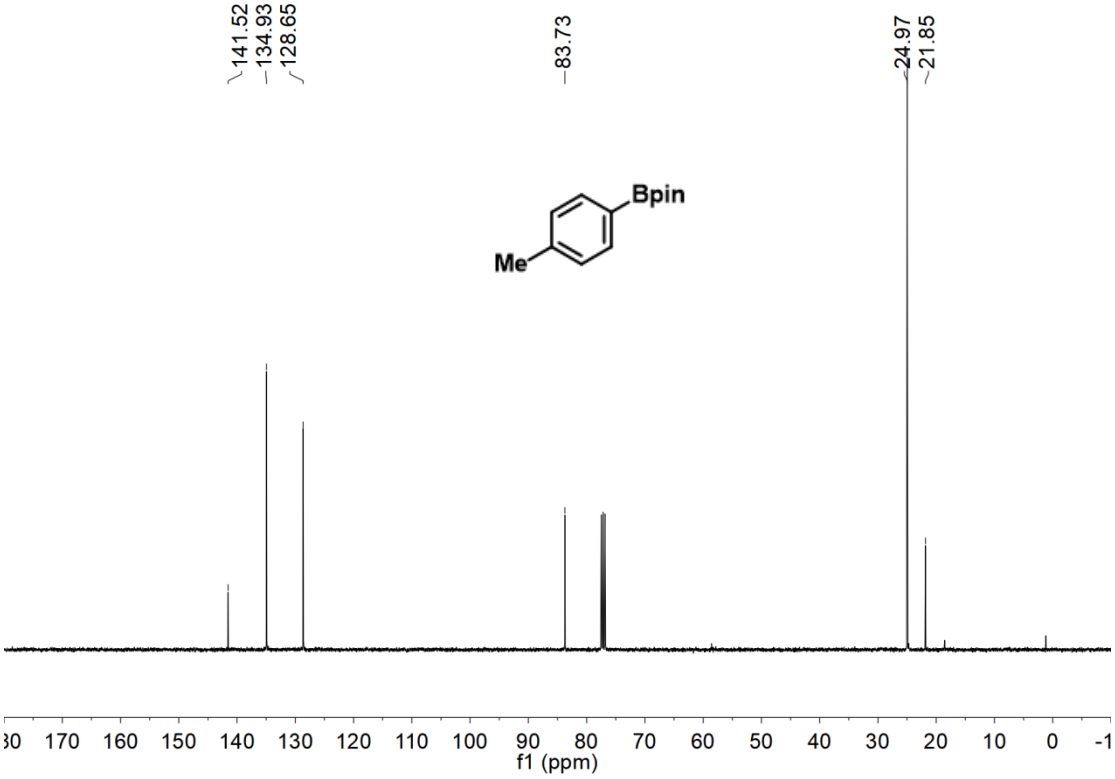
^{1}H, ^{13}C and ^{11}B NMR spectra for **2u**

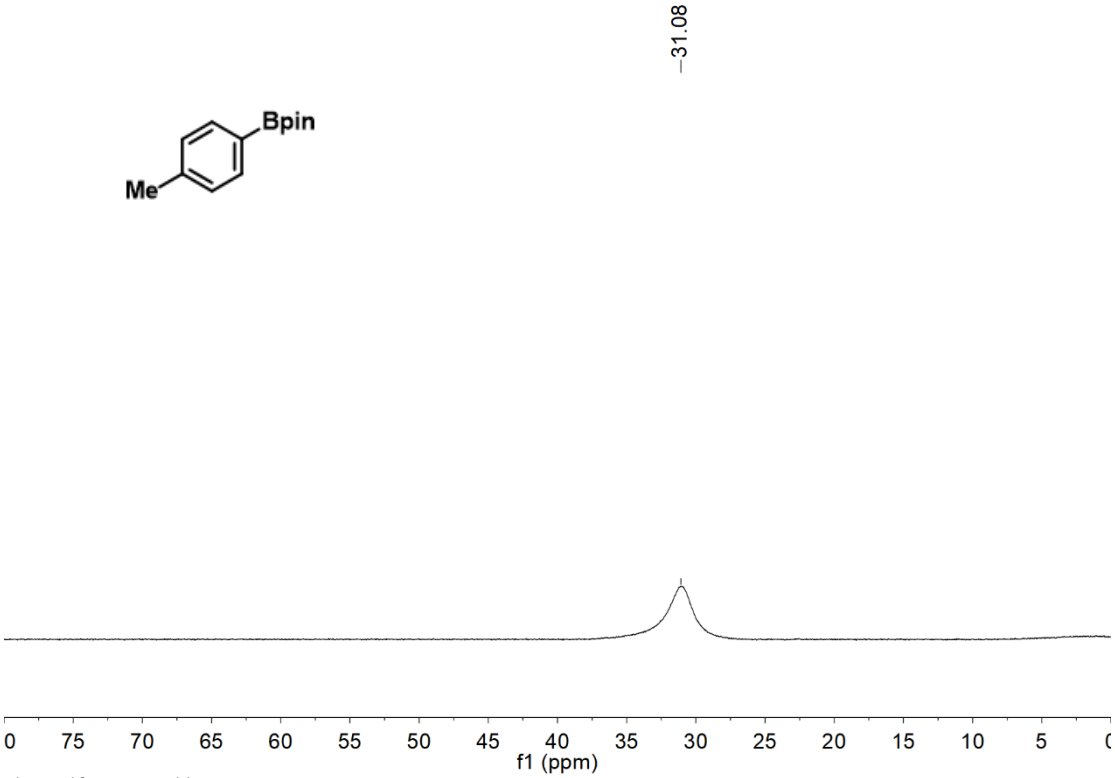




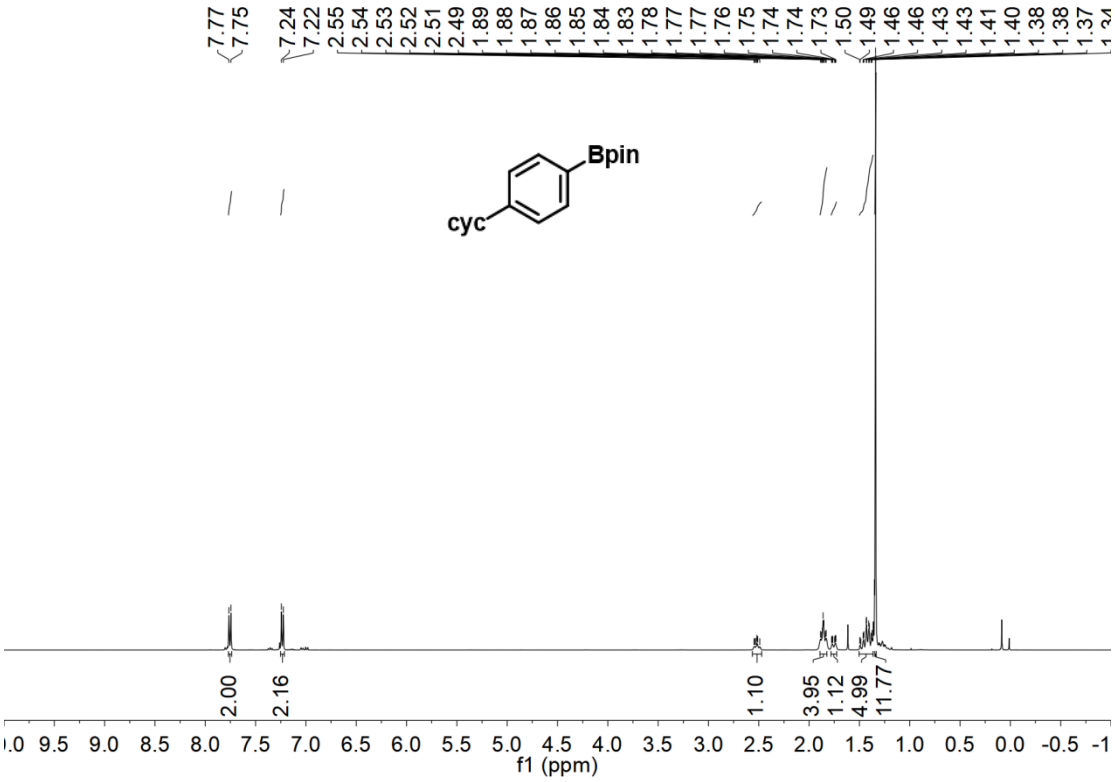
^{1}H, ^{13}C and ^{11}B NMR spectra for **2v**

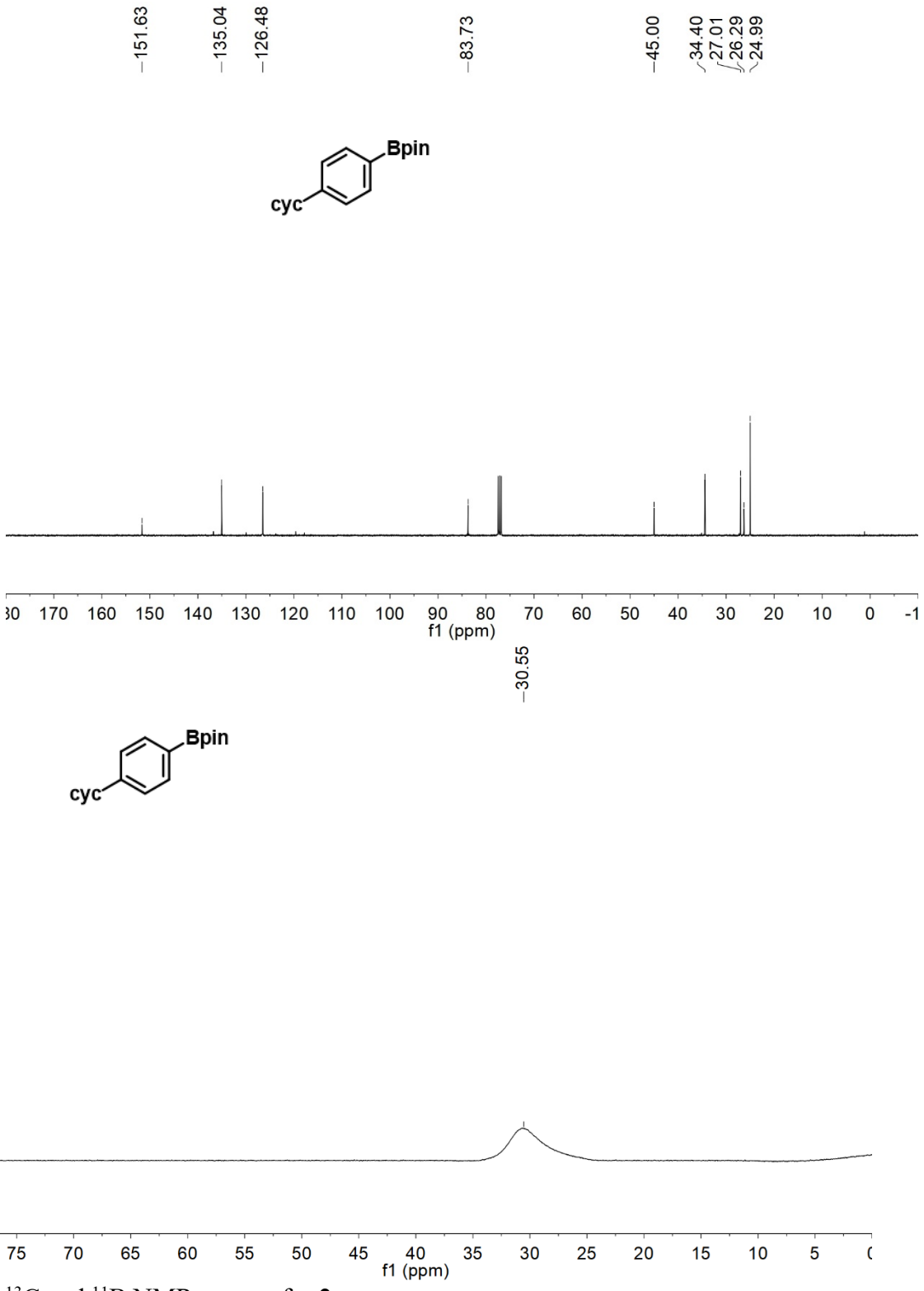

7.73
7.71
7.21
7.19
2.38
1.35
Bpin
Me
2.00
2.07
3.15
11.86
f1 (ppm)


141.52
134.93
128.65
83.73
24.97
21.85
Bpin
Me
f1 (ppm)

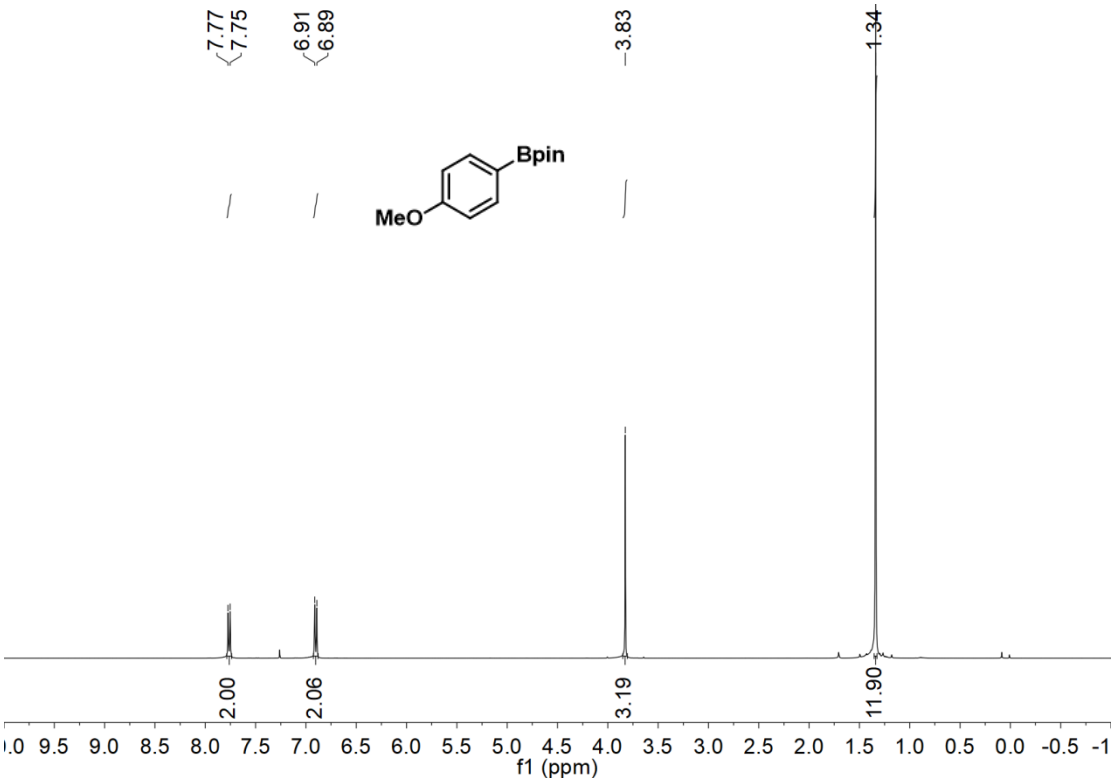


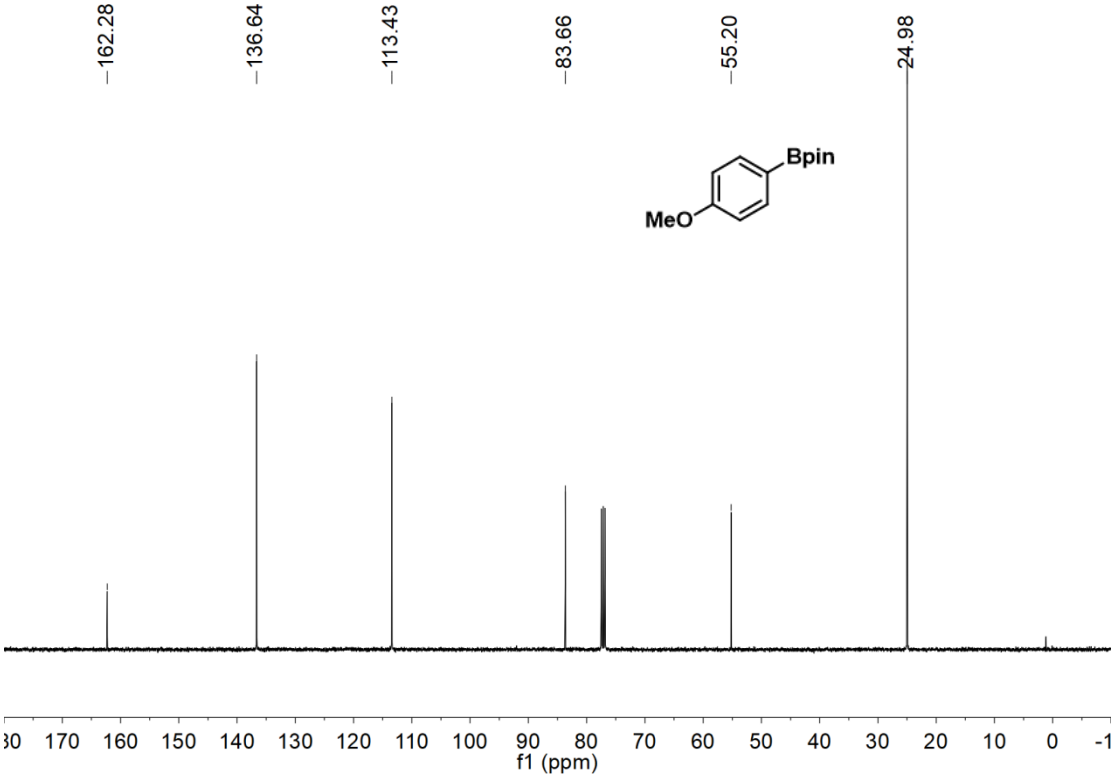
^{1}H, ^{13}C and ^{11}B NMR spectra for **2w**

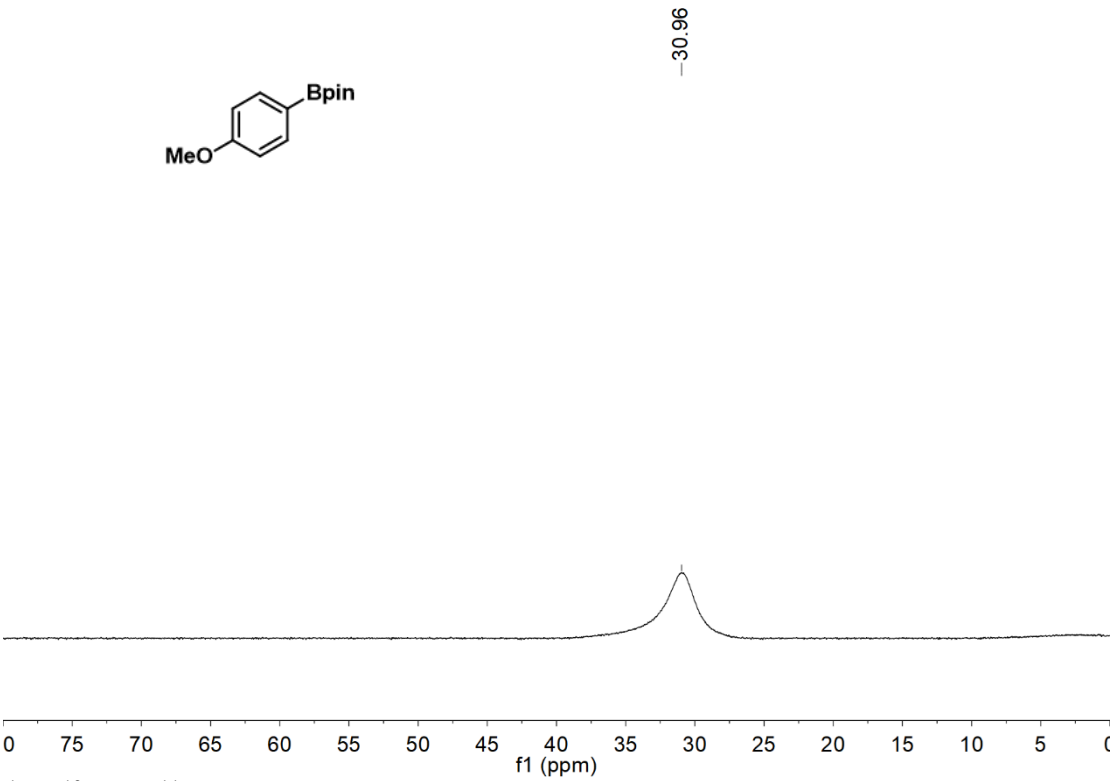




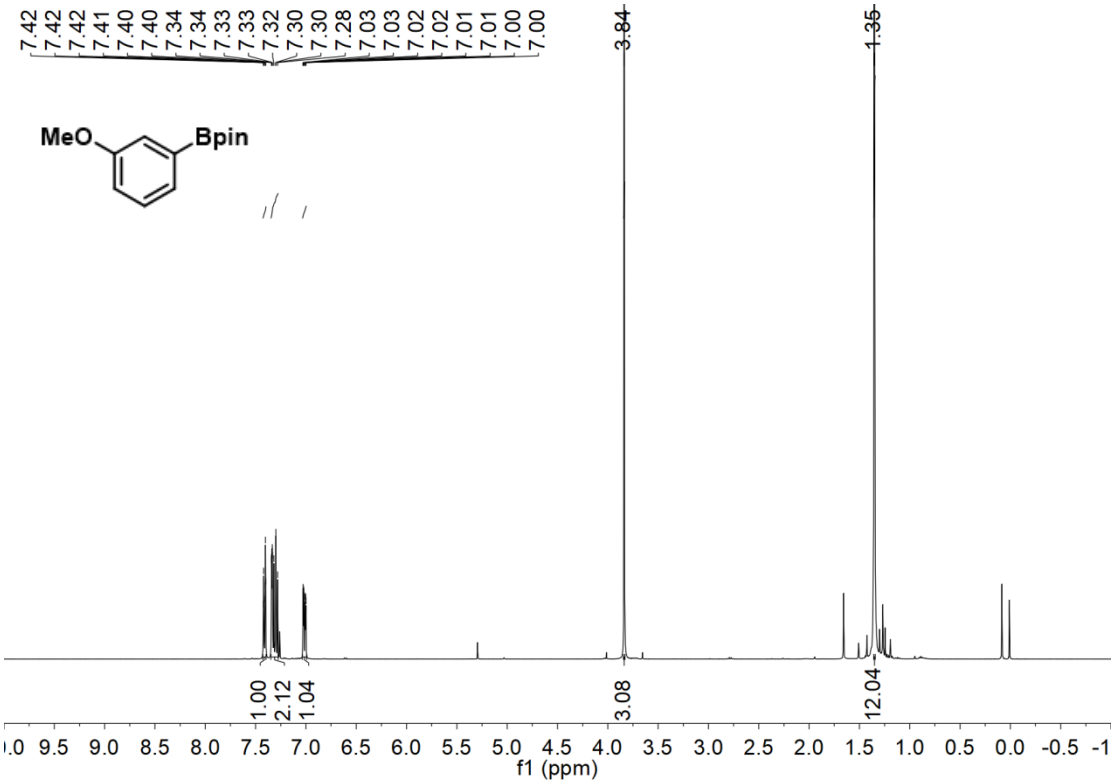
^{1}H, ^{13}C and ^{11}B NMR spectra for **2x**

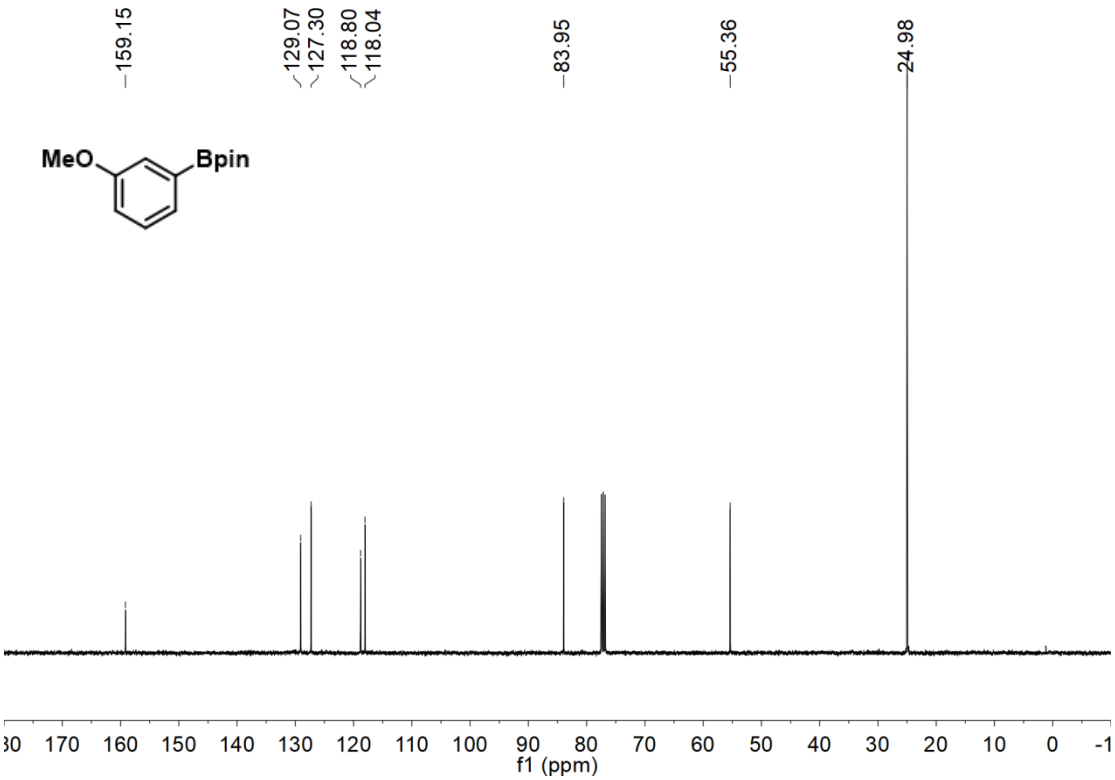

7.77
7.75
6.91
6.89
3.83
1.34
Bpin
MeO
2.00
2.06
3.19
11.90
f1 (ppm)

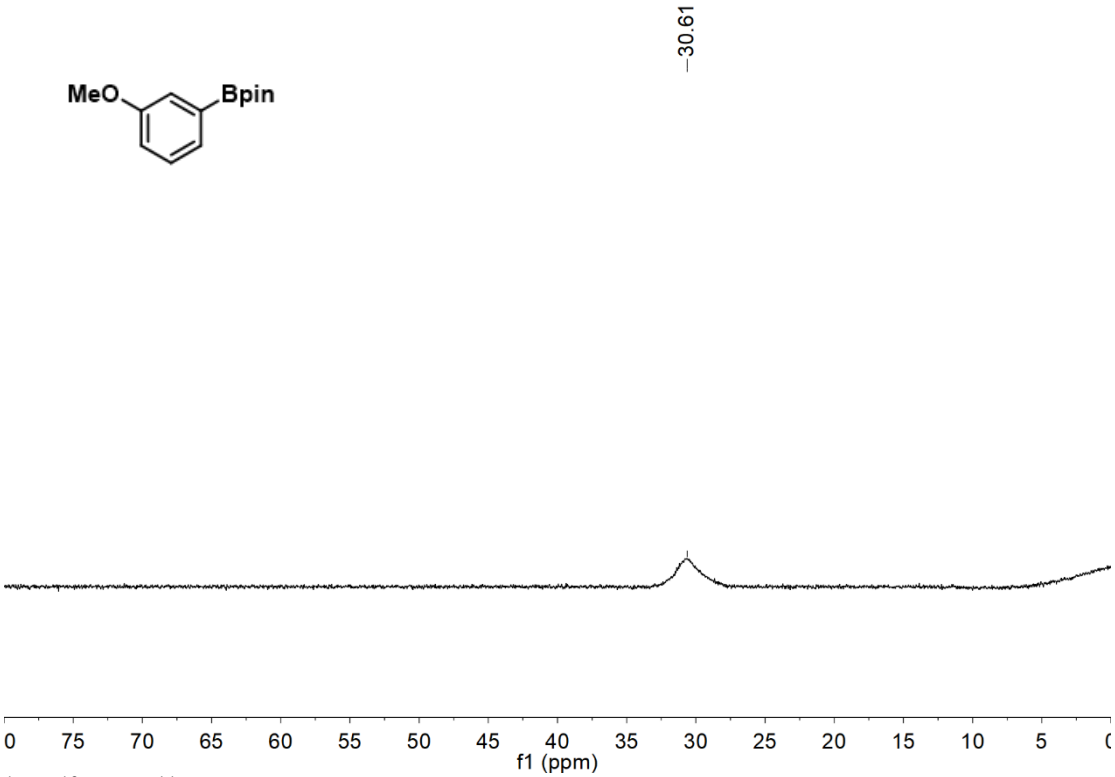

162.28
136.64
113.43
83.66
55.20
24.98
Bpin
MeO
f1 (ppm)



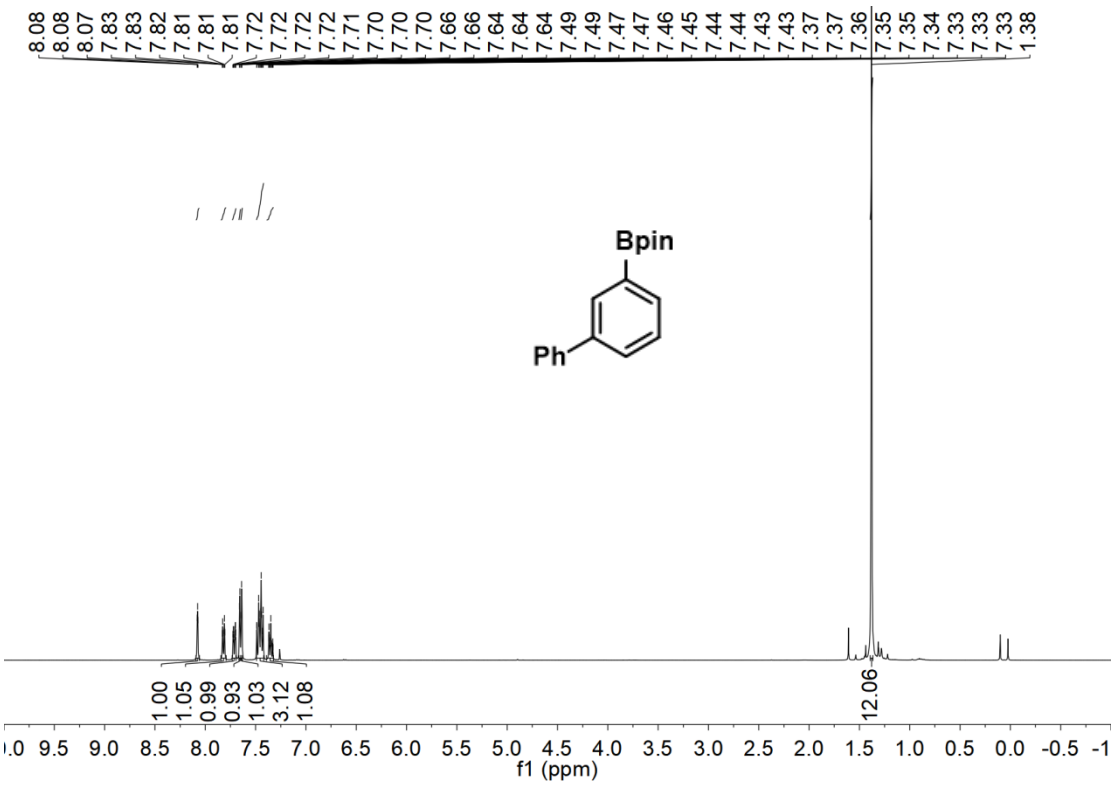
^{1}H, ^{13}C and^{11} B NMR spectra for **2y**

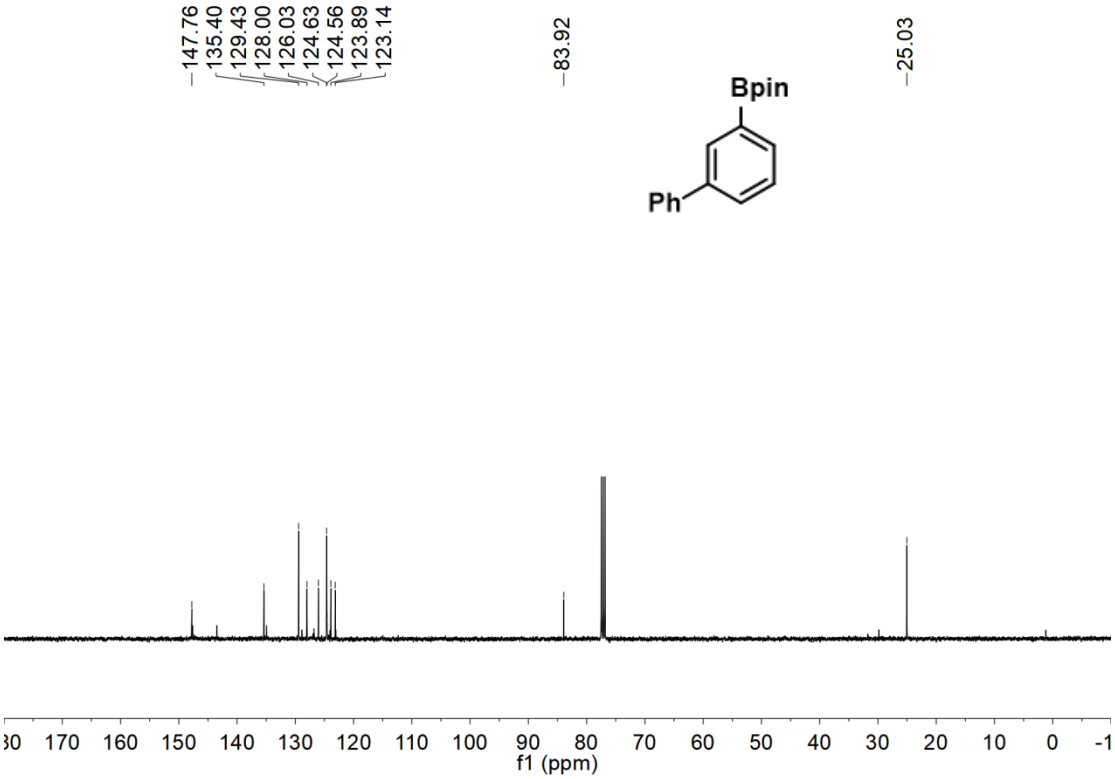


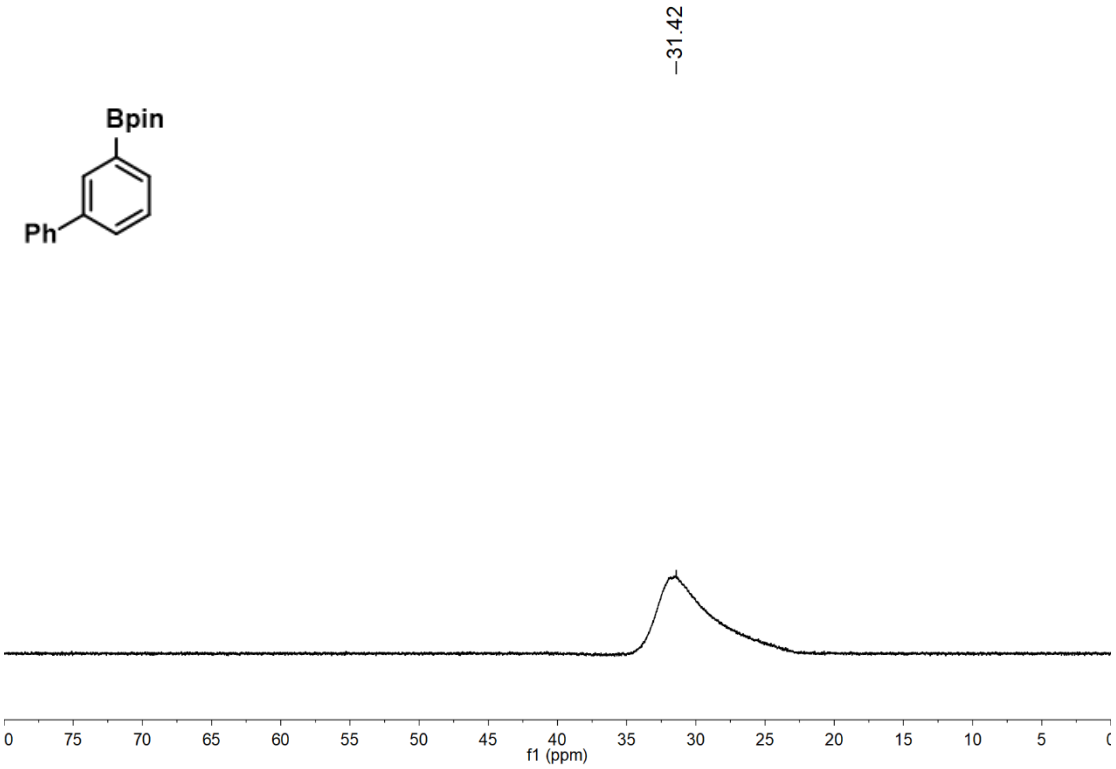




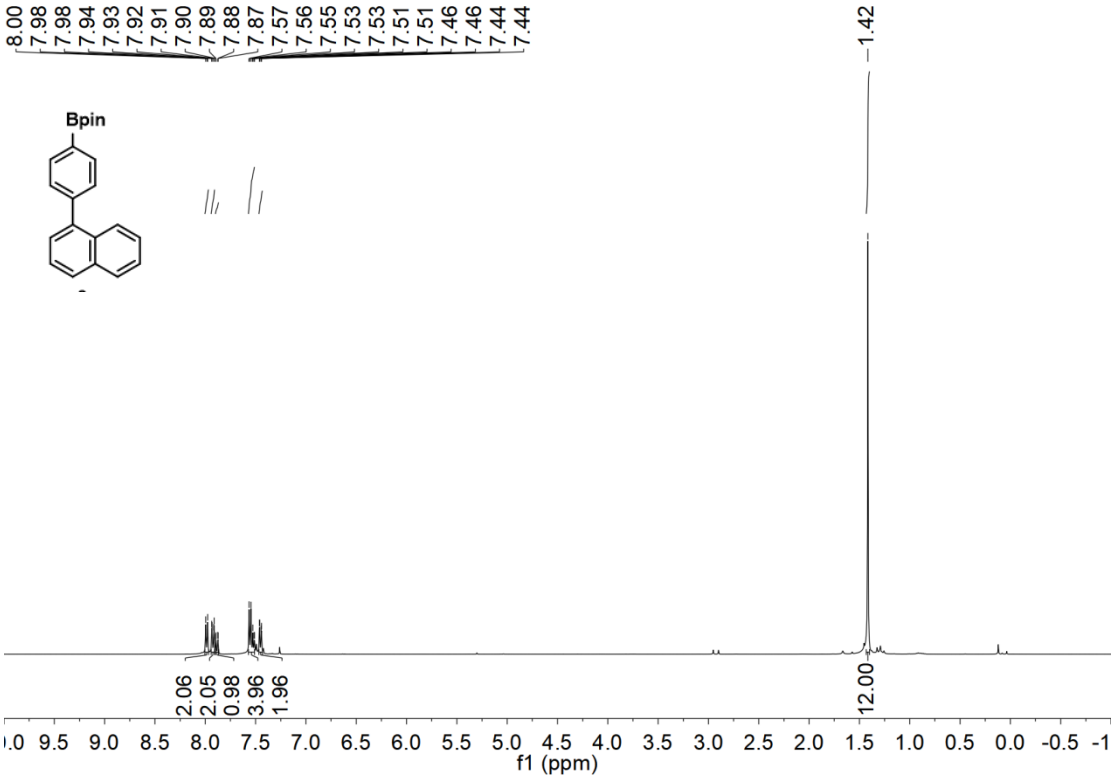
^{1}H, ^{13}C and^{11}B NMR spectra for **2z**

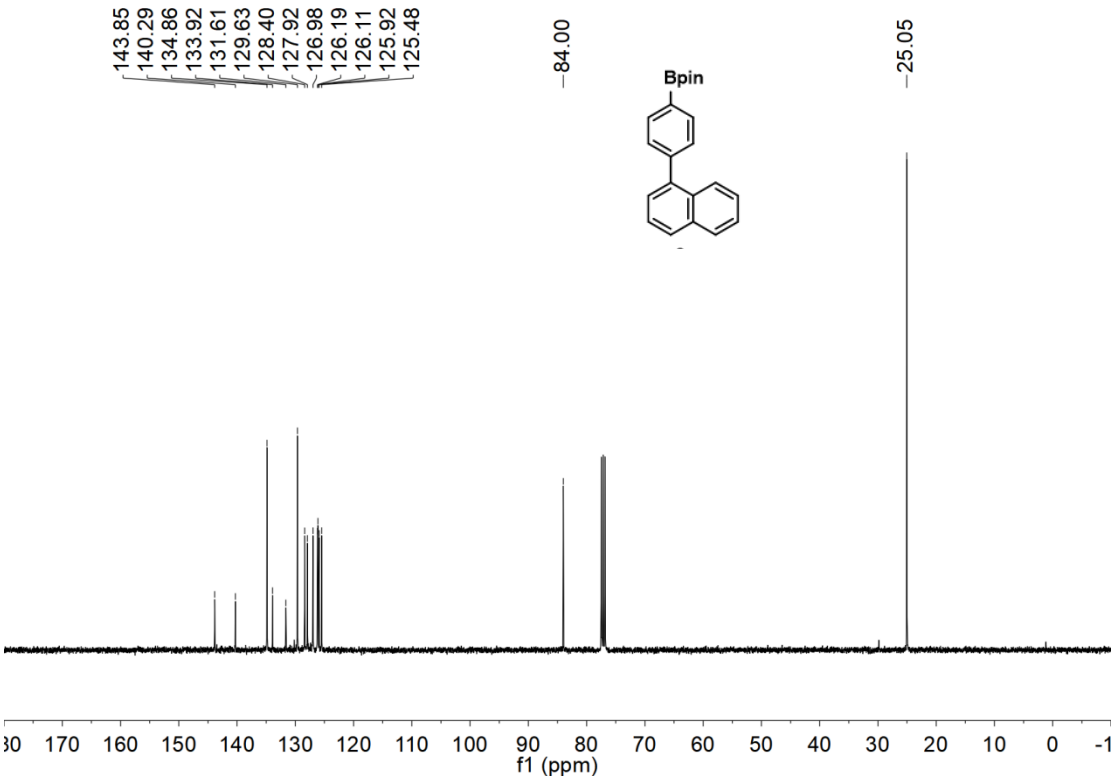

8.08 8.08 8.07 7.83 7.83 7.82 7.81 7.81 7.81 7.72 7.72 7.72 7.72 7.71 7.70 7.70 7.70 7.66 7.66 7.64 7.64 7.64 7.49 7.49 7.47 7.47 7.46 7.45 7.44 7.44 7.43 7.43 7.37 7.37 7.36 7.35 7.35 7.34 7.33 7.33 7.33 1.38
Bpin
Ph
1.00 1.05 0.99 0.93 1.03 3.12 1.08
12.06
f1 (ppm)

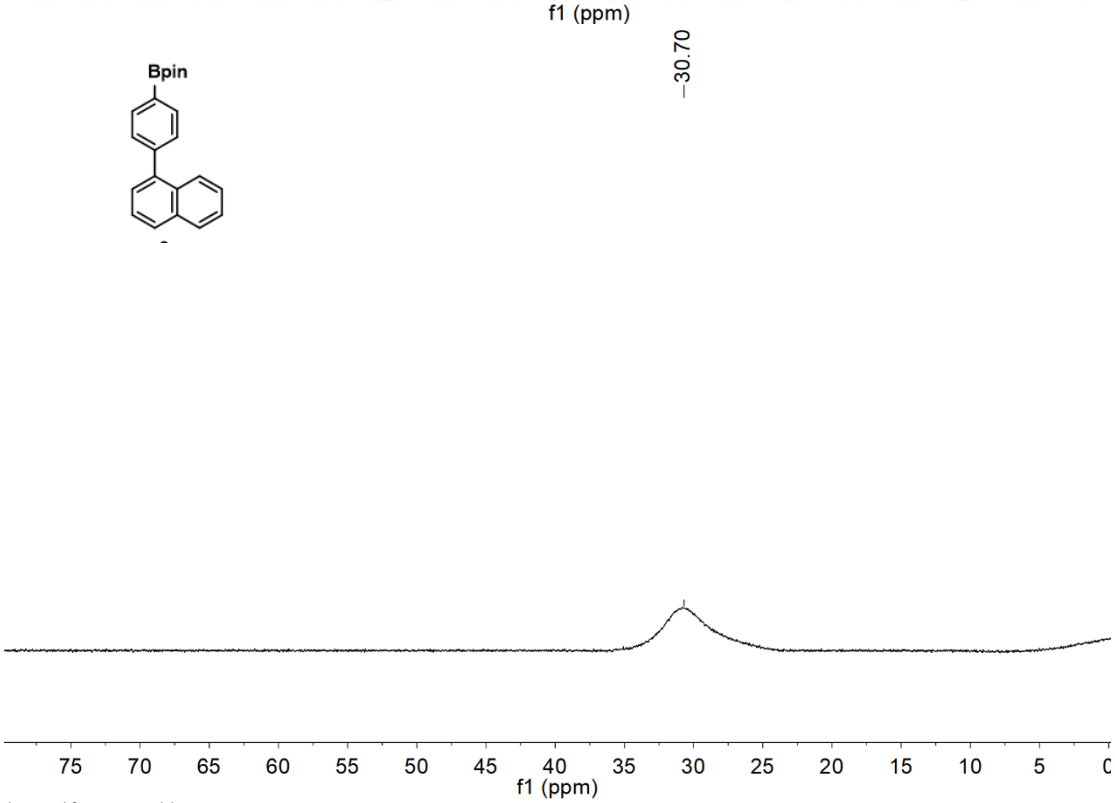

147.76 135.40 129.43 128.00 126.03 124.63 124.56 123.89 123.14
83.92
25.03
Bpin
Ph
f1 (ppm)



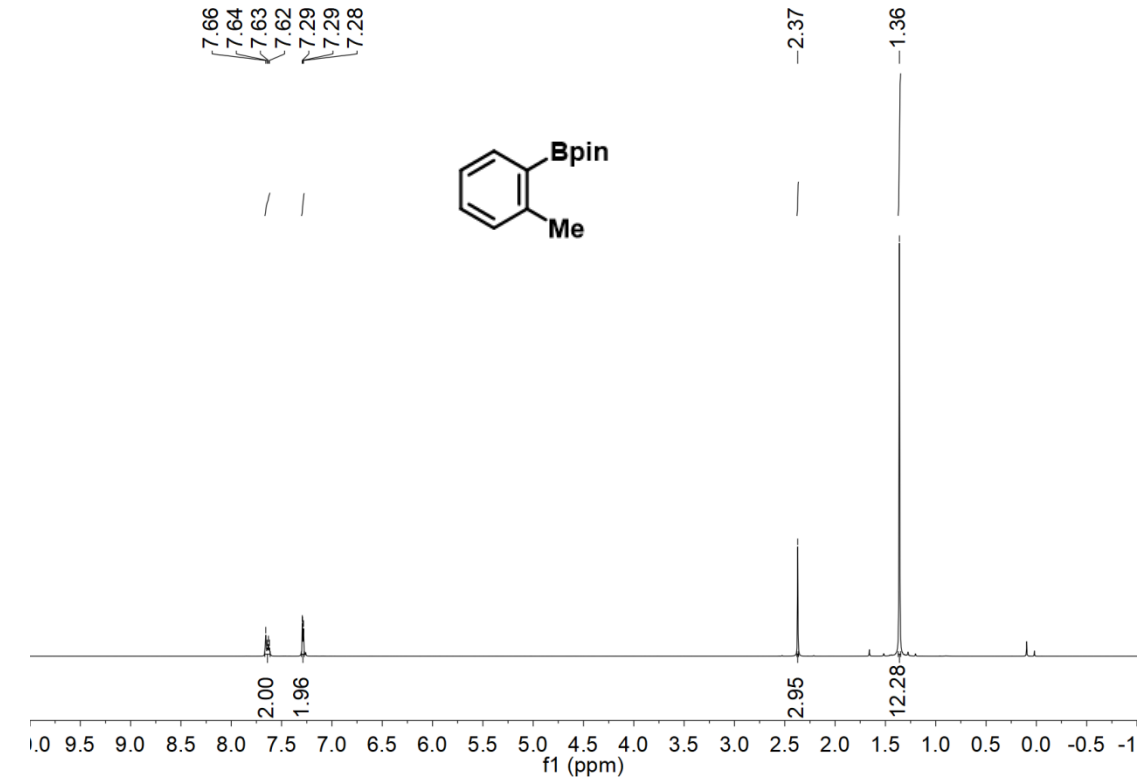
^{1}H, ^{13}C and^{11} B NMR spectra for **2aa**

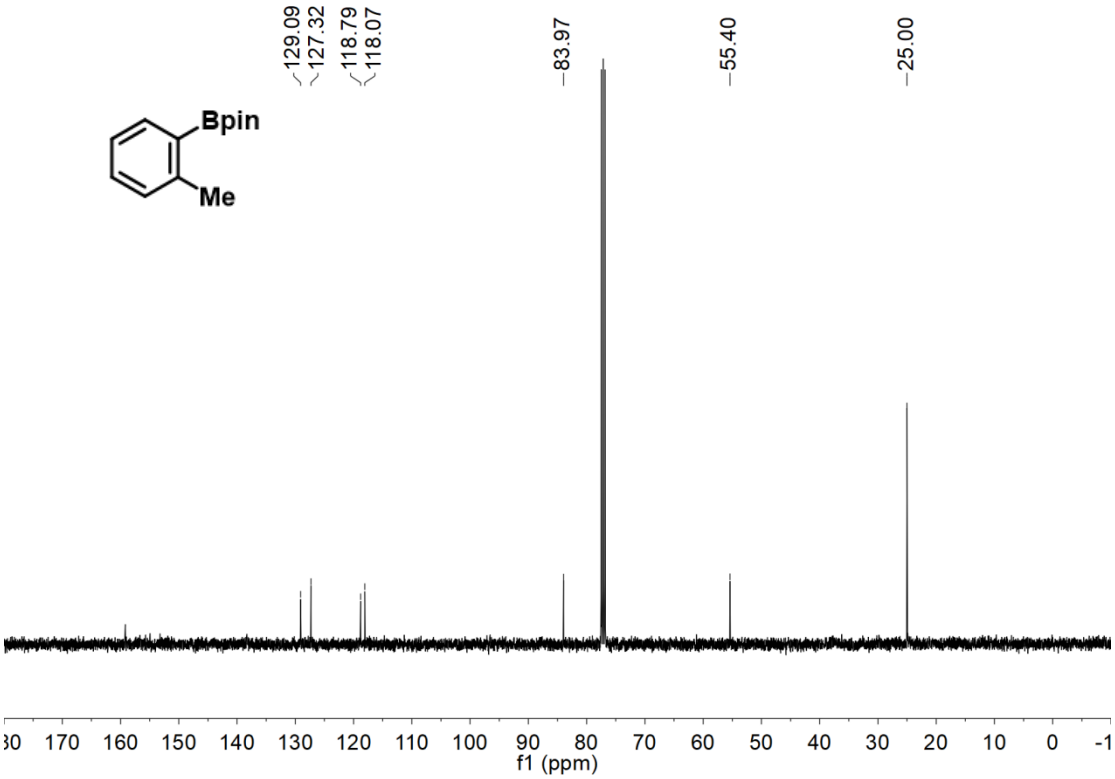


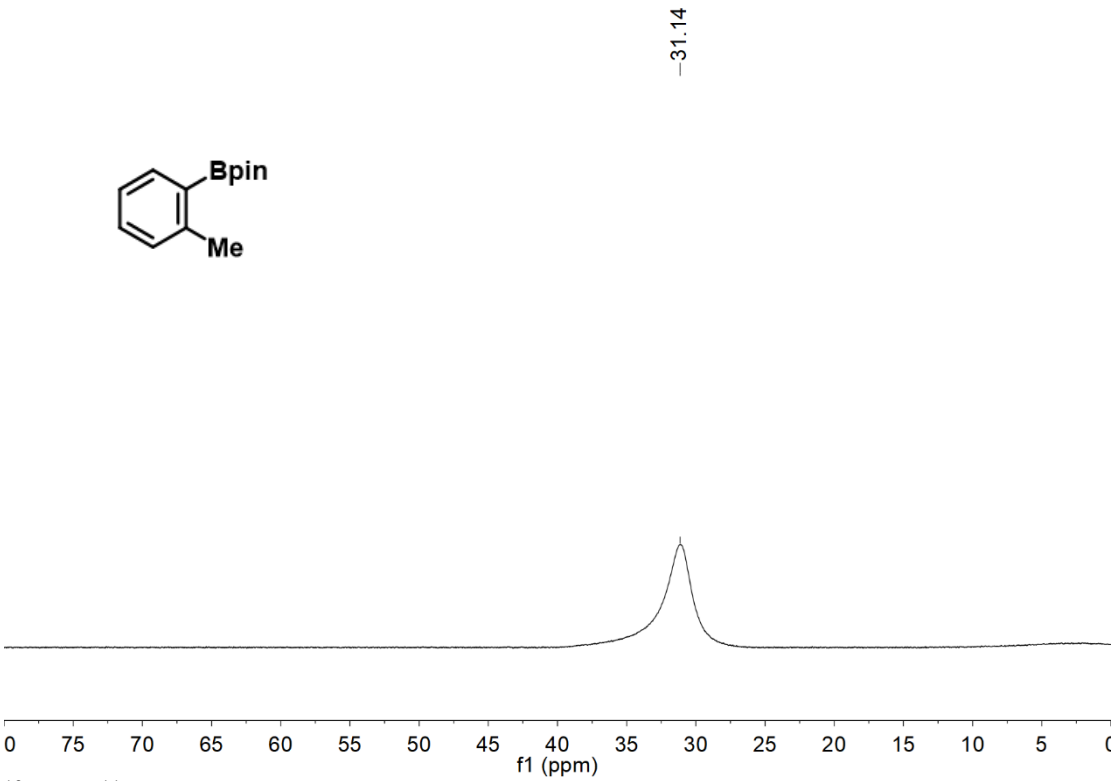




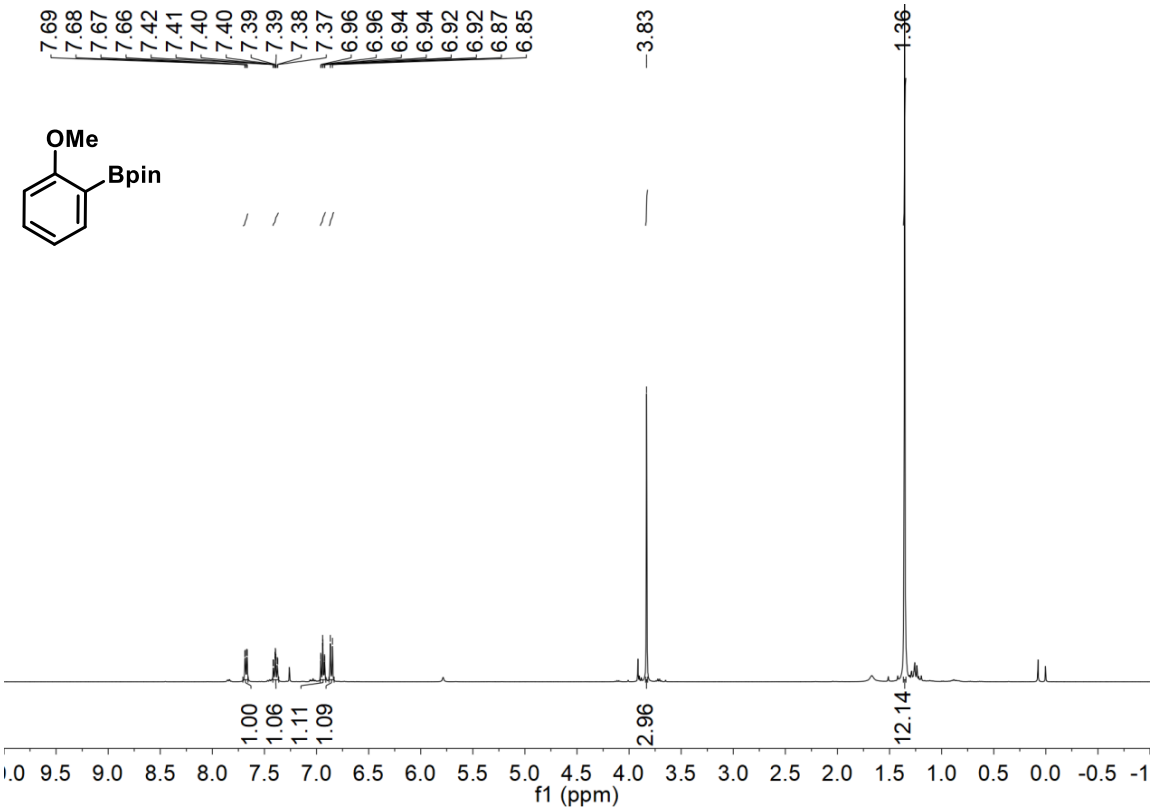
^{1}H, ^{13}C and^{11}B NMR spectra for **2ab**

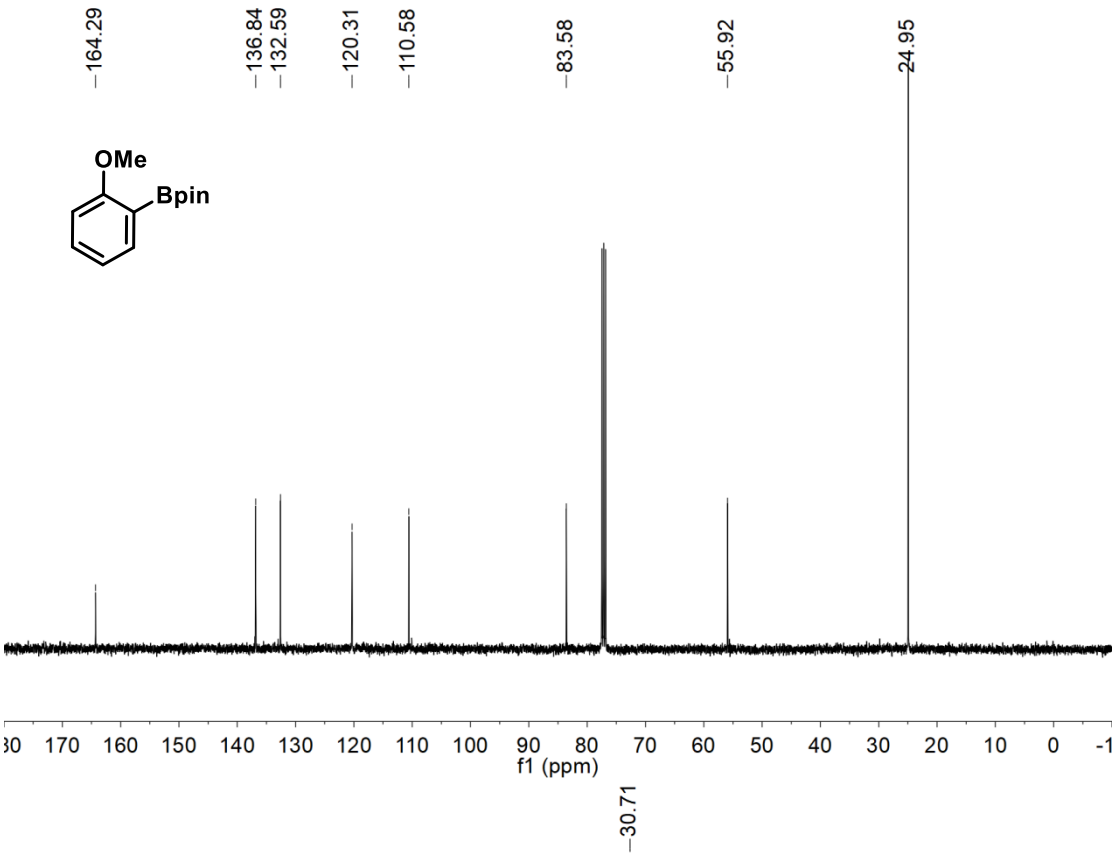

7.66
7.64
7.63
7.62
7.29
7.29
7.28
2.37
1.36
Bpin
Me
2.00
1.96
2.95
12.28
f1 (ppm)

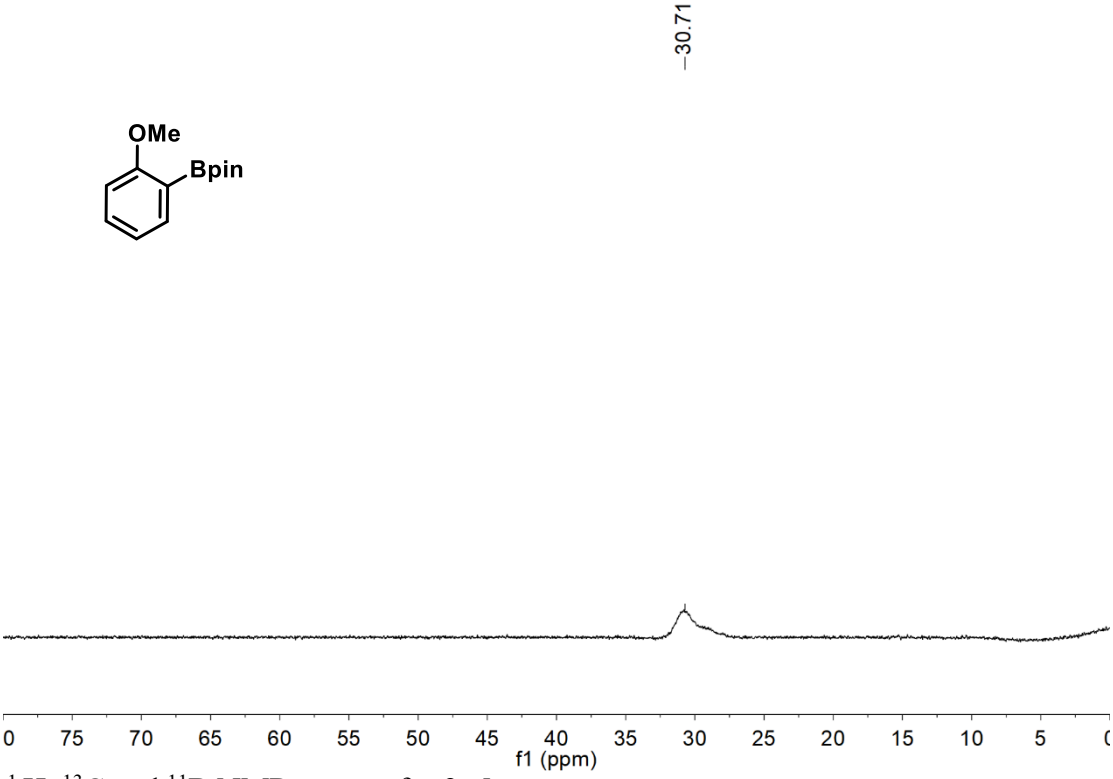

129.09
127.32
118.79
118.07
83.97
55.40
25.00
Bpin
Me
f1 (ppm)



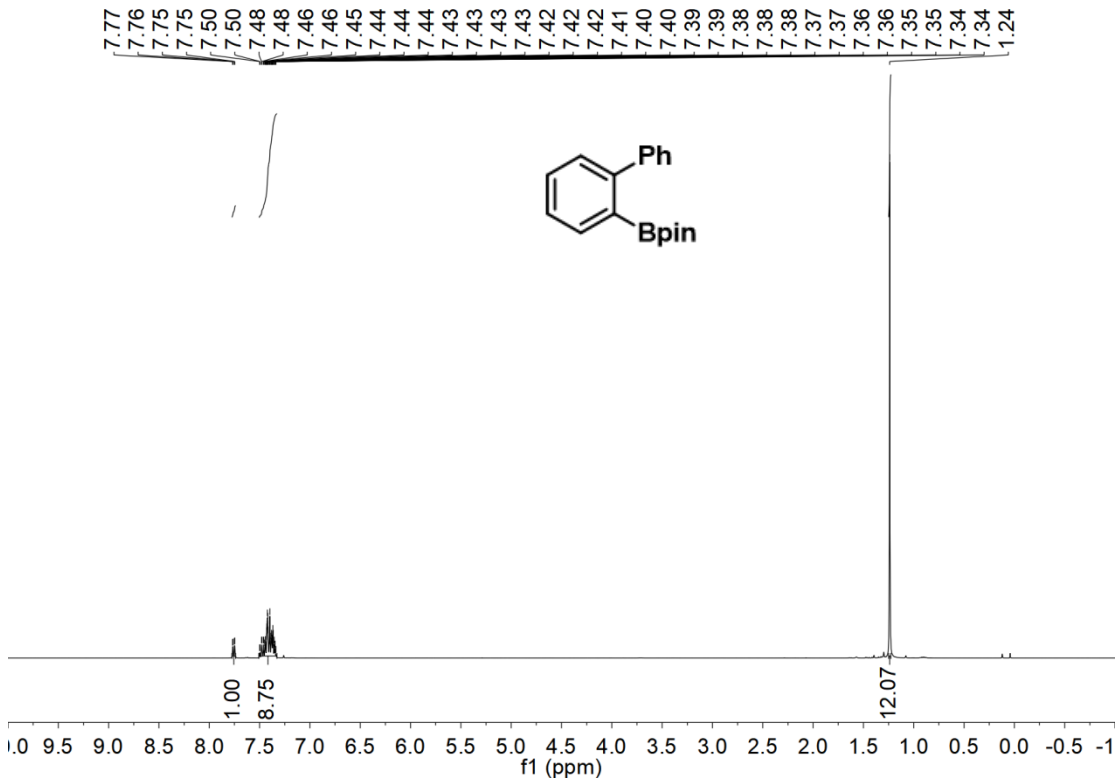
^{1}H, ^{13}C and^{11} B NMR spectra for **2ac**

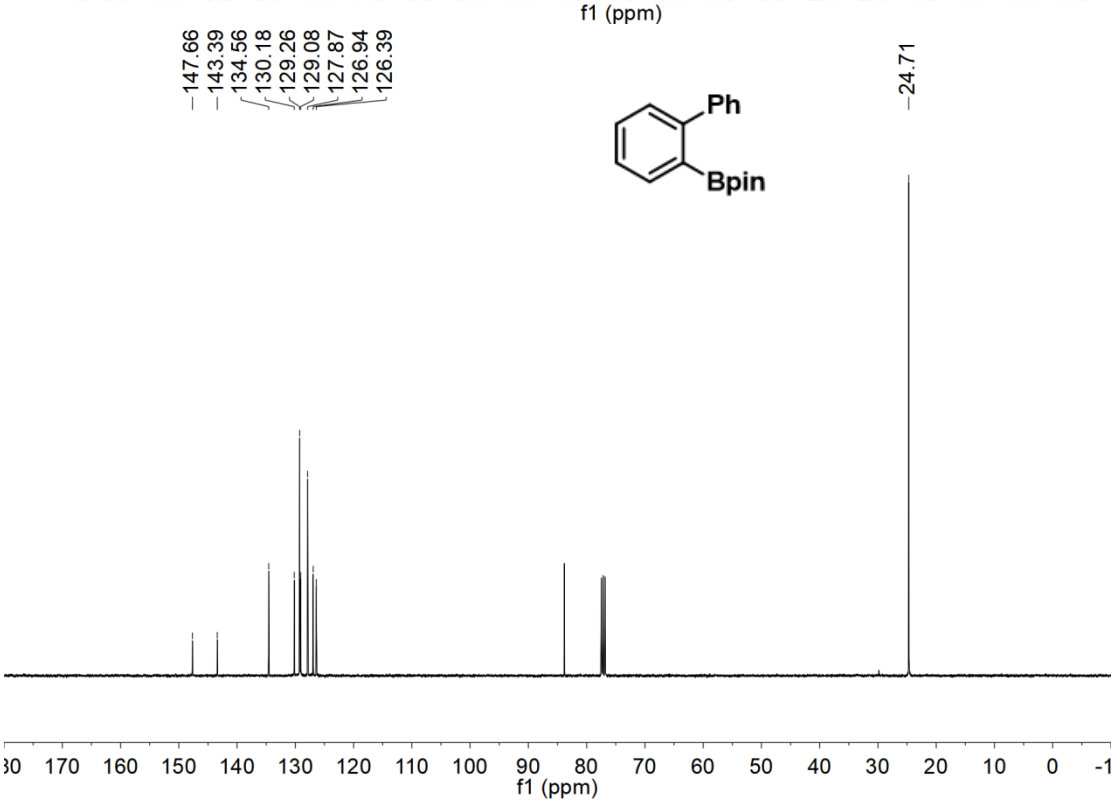


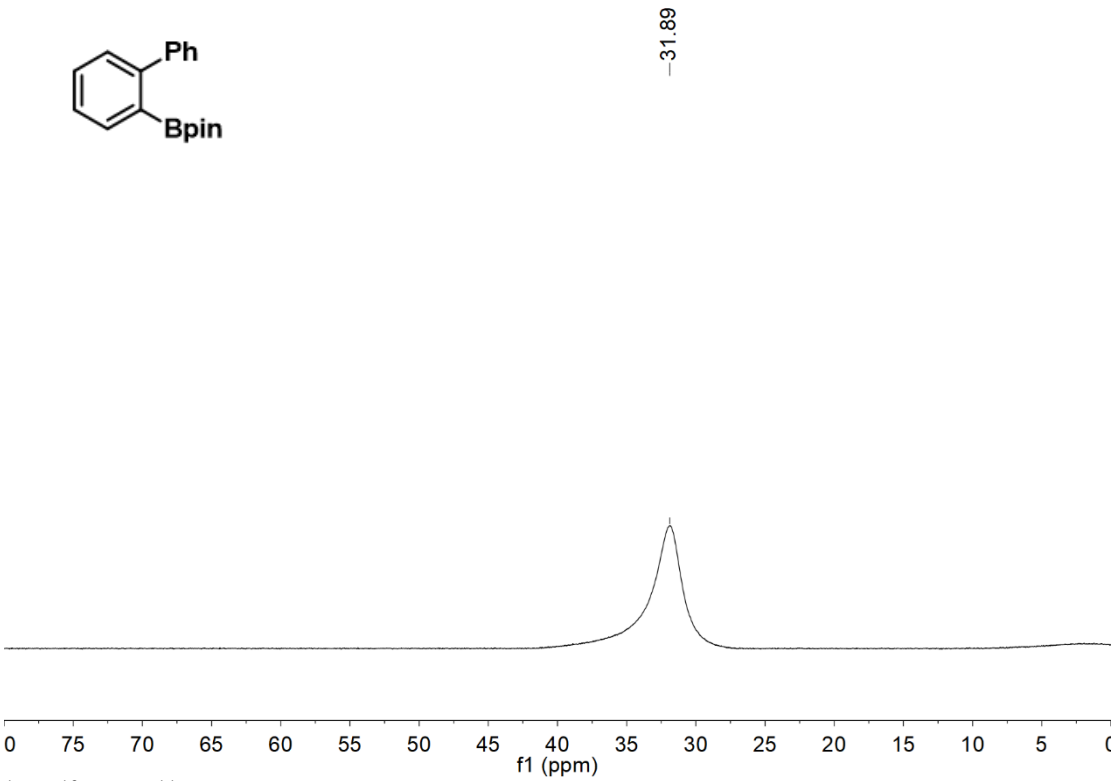




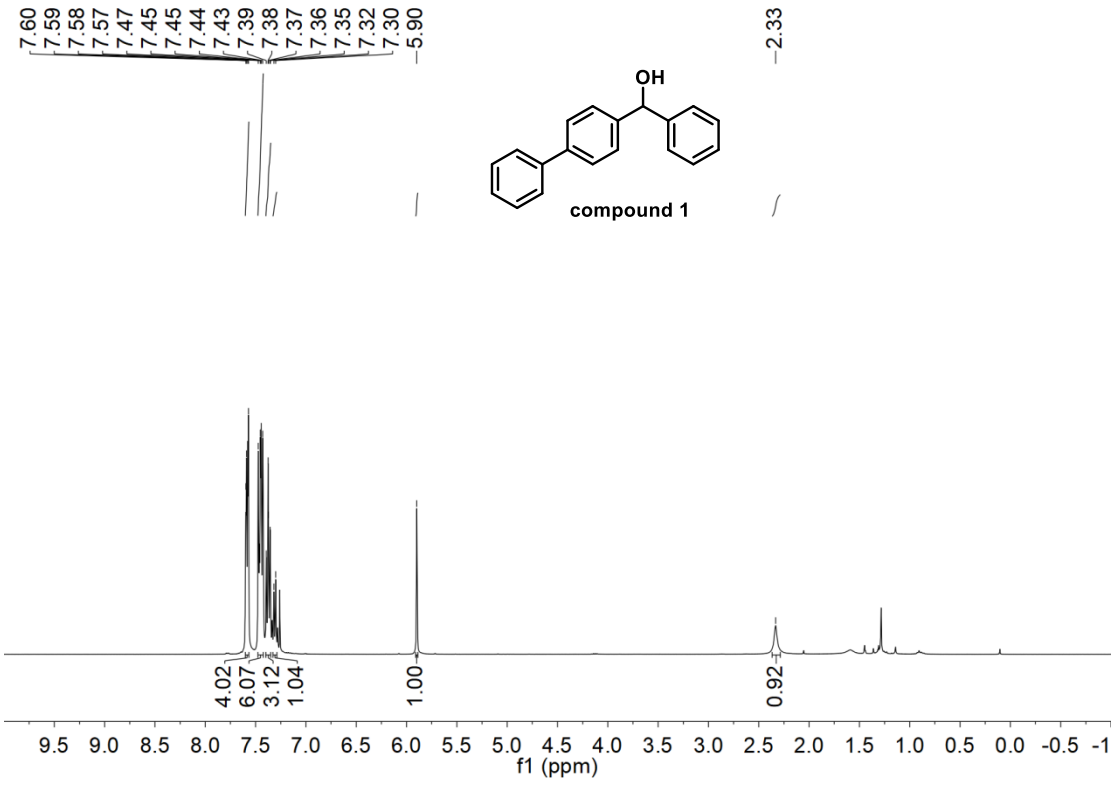
^{1}H, ^{13}C and ^{11}B NMR spectra for **2ad**

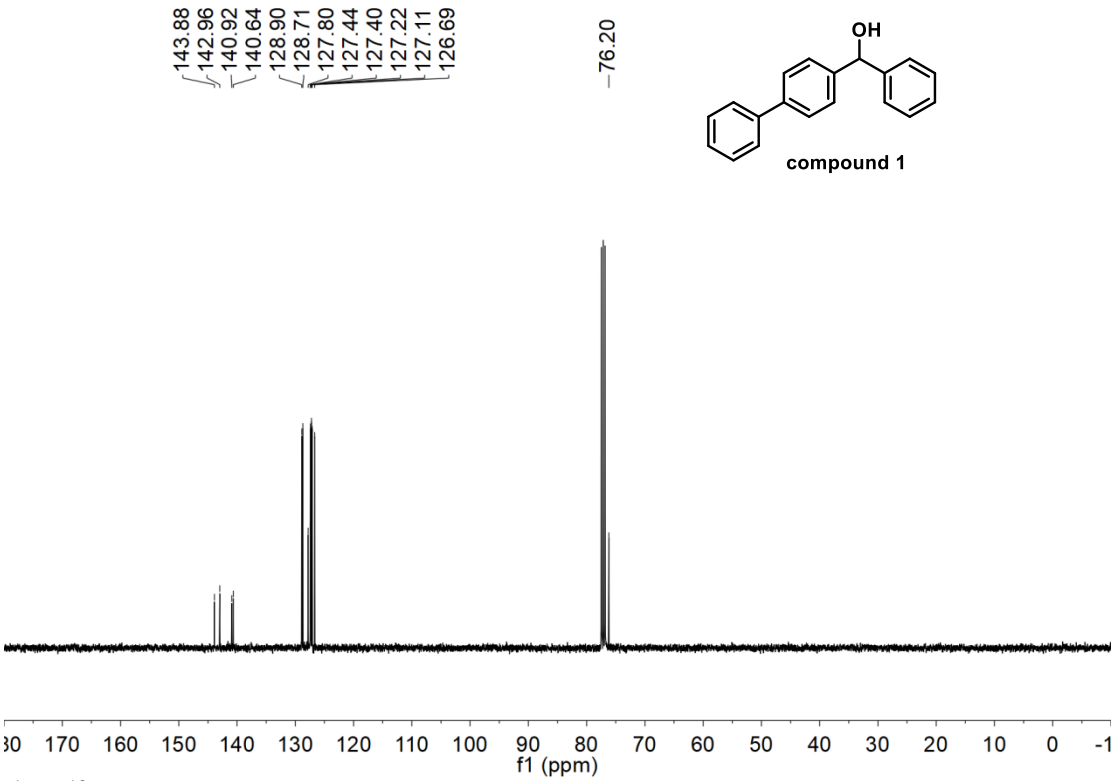

7.77
7.76
7.75
7.75
7.50
7.50
7.48
7.48
7.46
7.46
7.45
7.44
7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
1.24
Ph
Bpin
1.00
8.75
12.07
f1 (ppm)


147.66
143.39
134.56
130.18
129.26
129.08
127.87
126.94
126.39
24.71
Ph
Bpin
f1 (ppm)

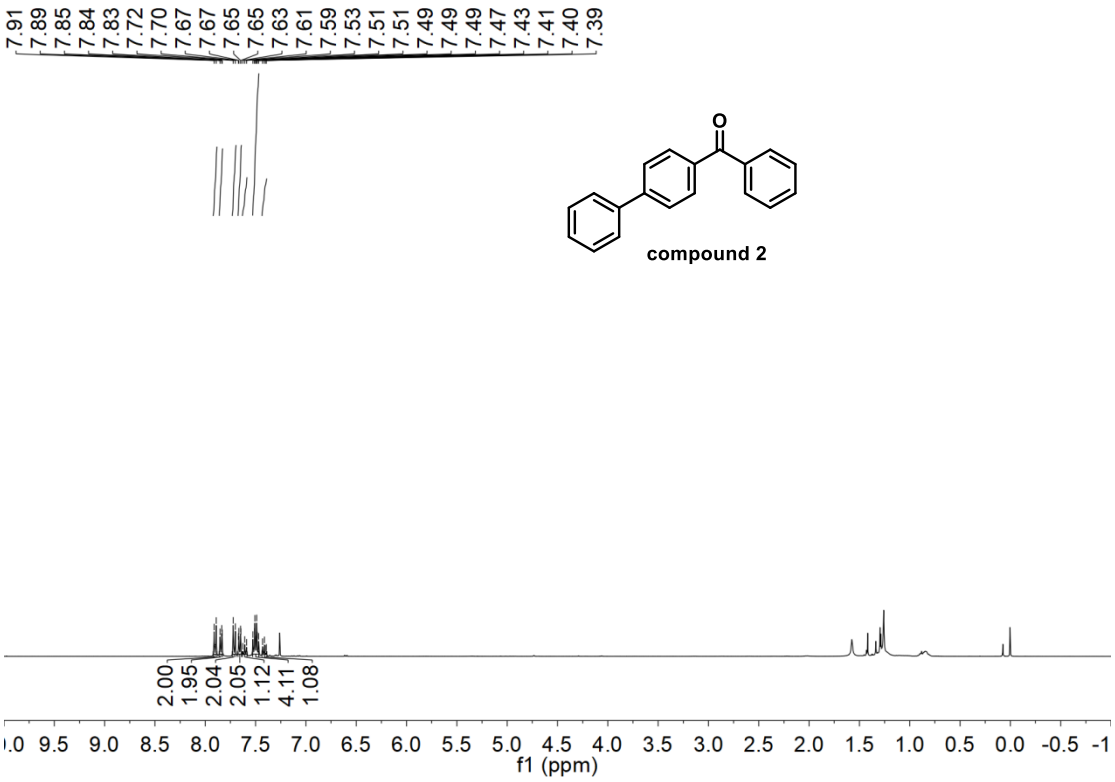


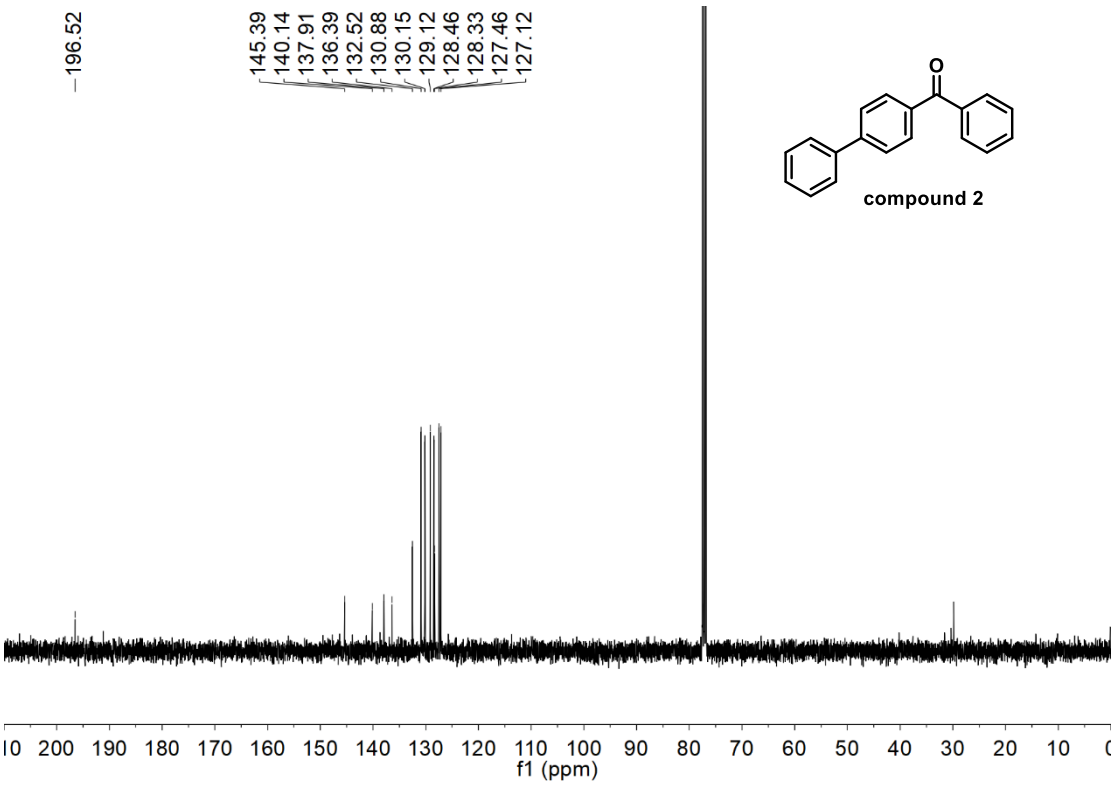
^{1}H, ^{13}C and^{11} B NMR spectra for **2ae**



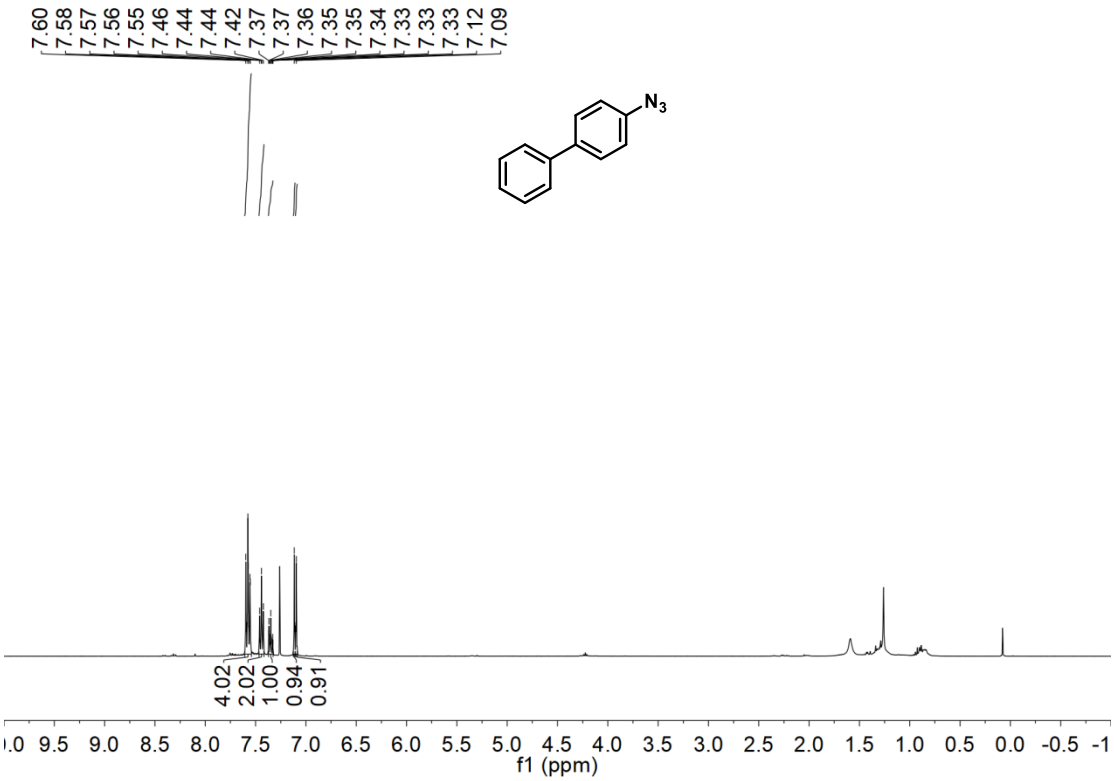


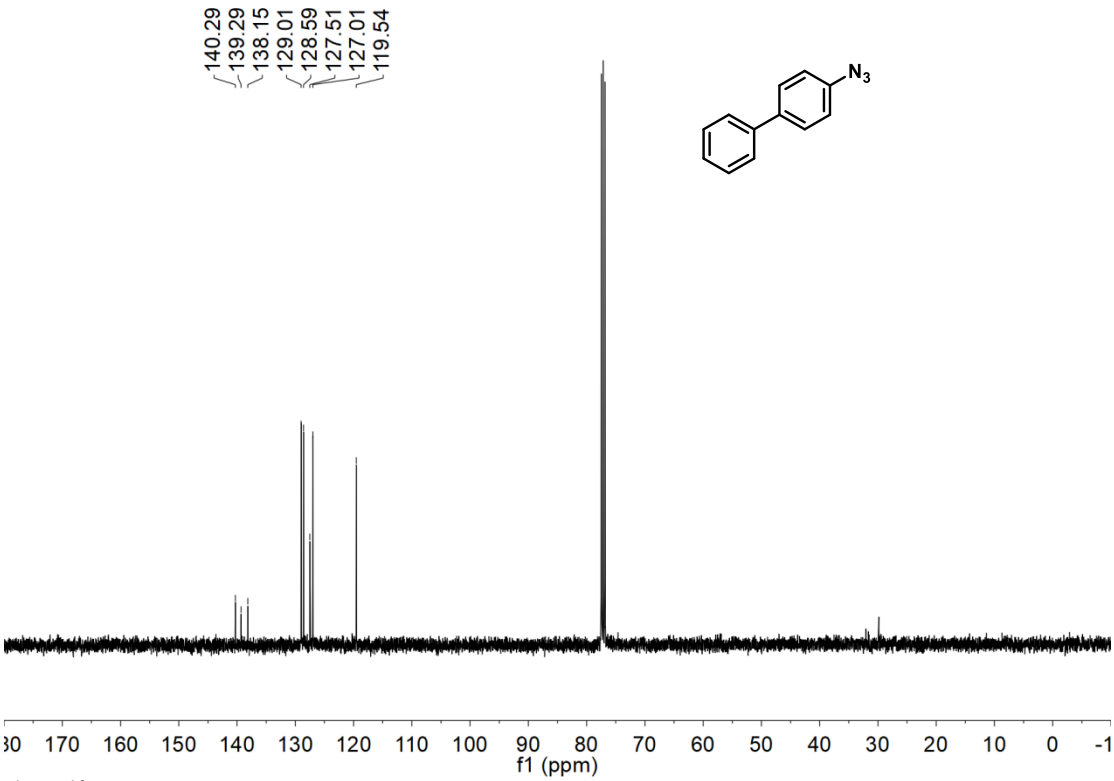
^{1}H, ^{13}C NMR spectra for **compound 1**



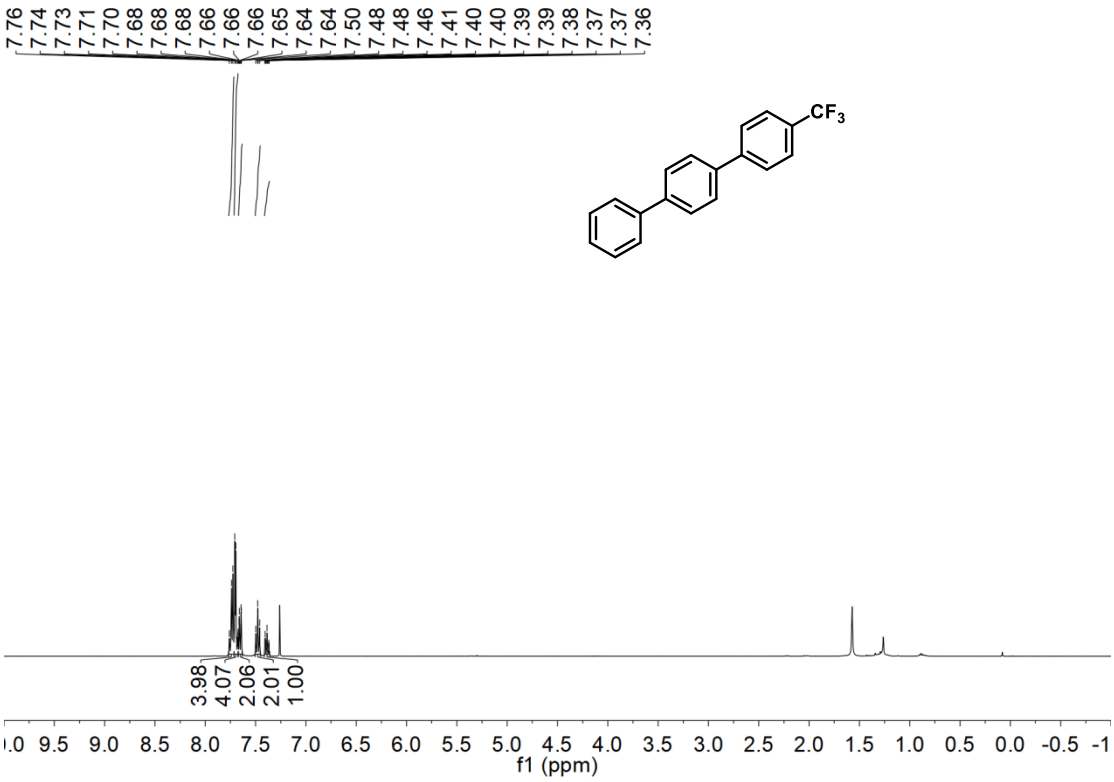


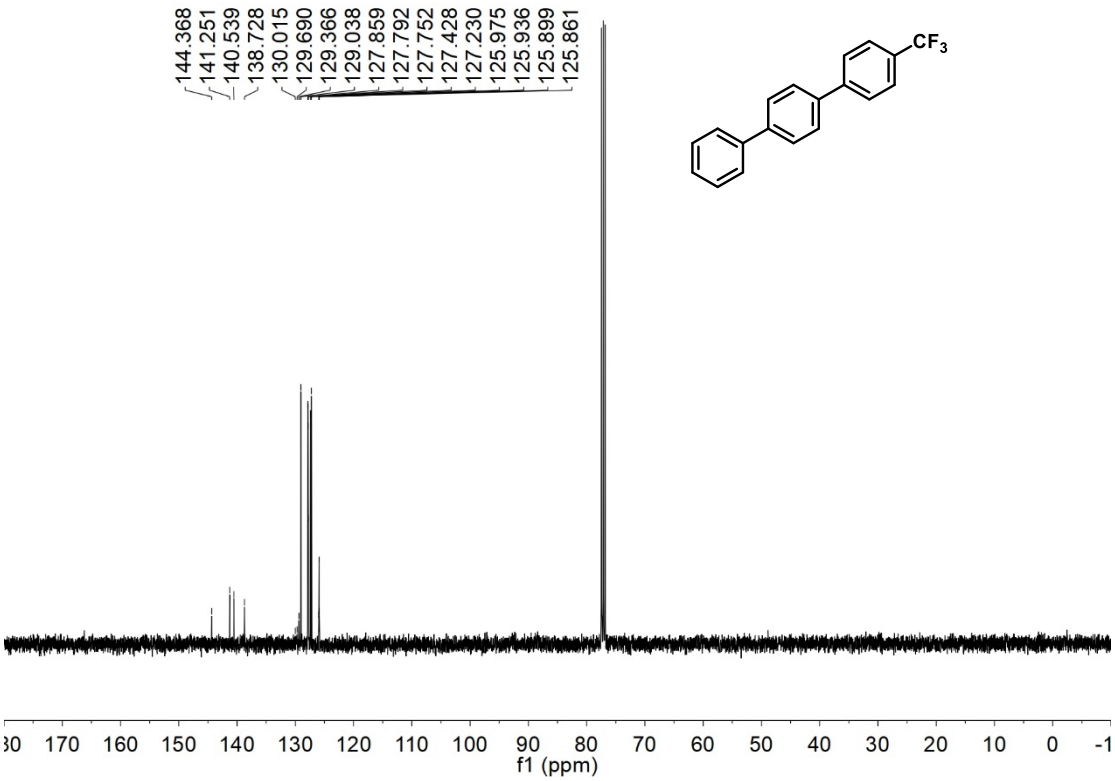
^{1}H, ^{13}C NMR spectra for **compound 2**



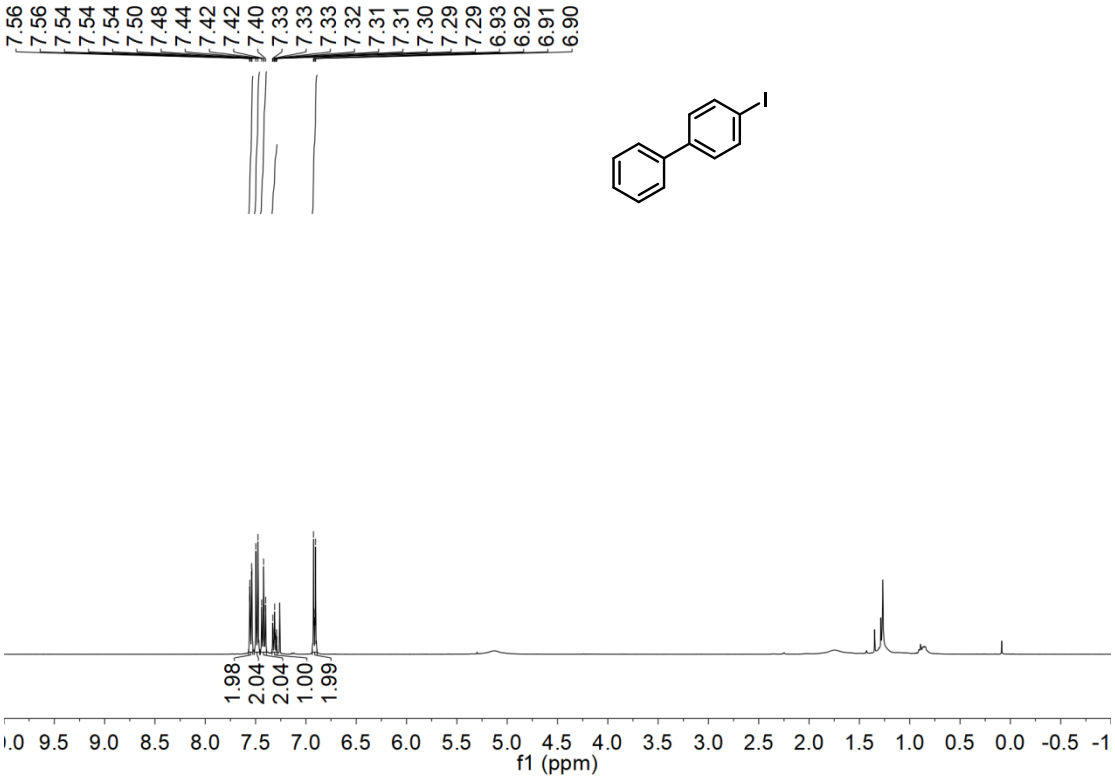


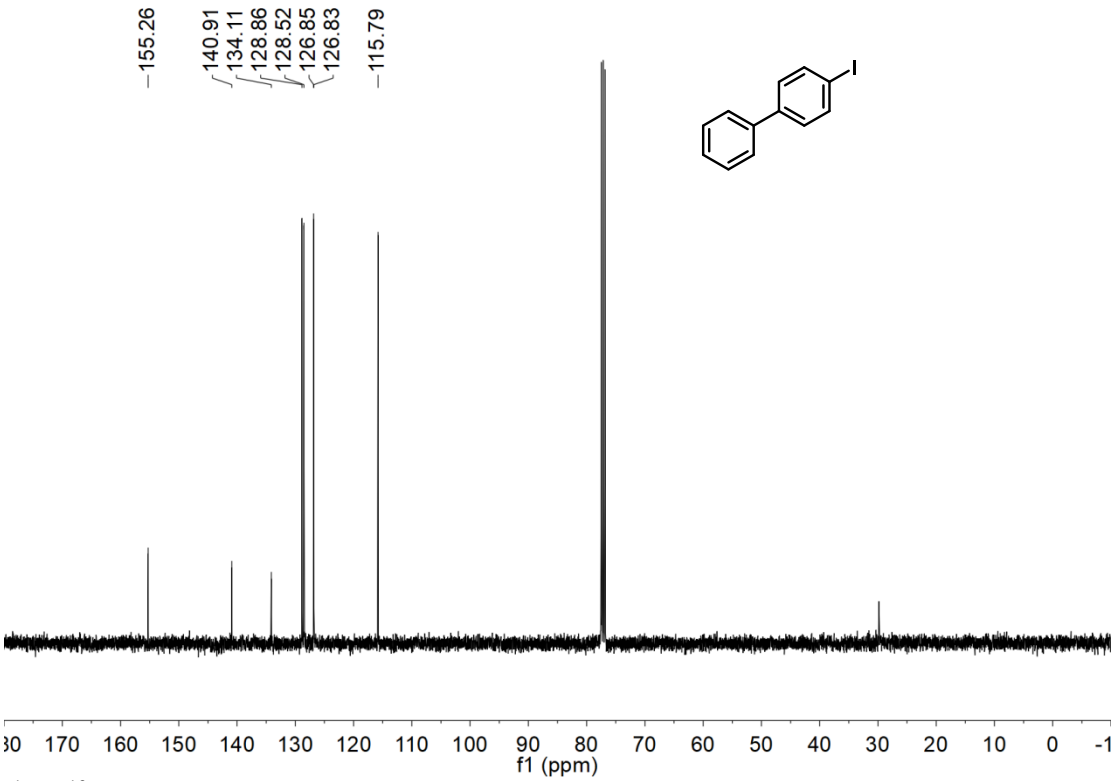
^{1}H, ^{13}C NMR spectra for **4**



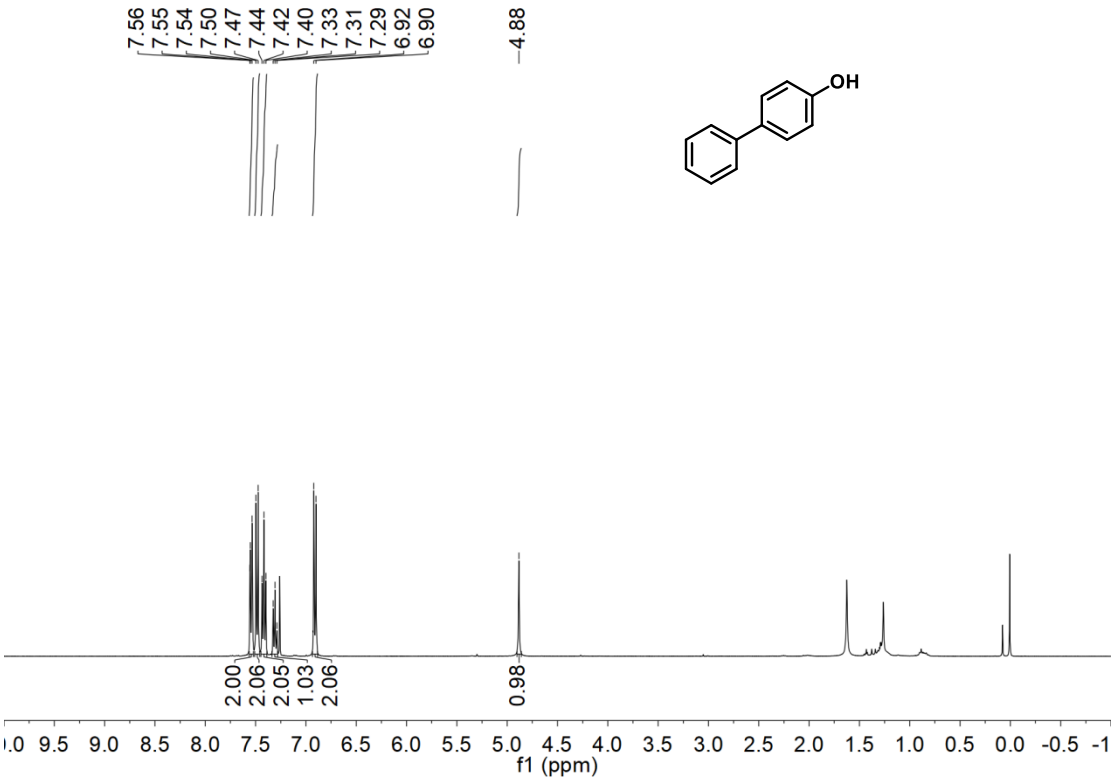


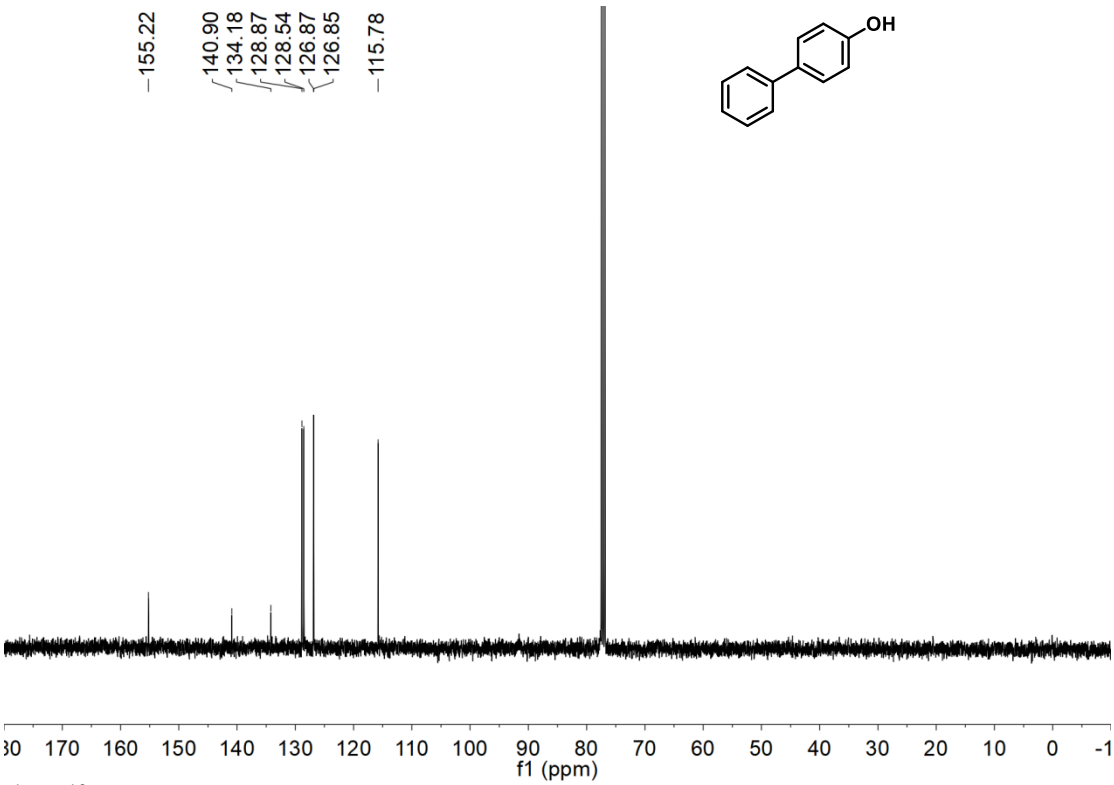
^{1}H, ^{13}C NMR spectra for **5**





^{1}H, ^{13}C NMR spectra for **6**





^{1}H, ^{13}C NMR spectra for **7**