# Zinc catalyzed C3–H borylation of indoles and 1,1-diboration of terminal alkynes

Binfeng Zhang, Youliang Zou, Li Wang and Hua Zhang*

Key Laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education and Hubei Key Laboratory of Catalysis and Materials Science, School of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430074, China

and

College of Chemistry, Nanchang University, Nanchang 330031, China

huazhang@scuec.edu.cn

# Supplementary Information

## Table of Contents

## 1. General information

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. $Zn(OTf)_2$ was obtained from TCI. Alkynes, HBpin, $BH_3$•DMS (2.0 M in DMS), 3,4,5-trichloropyridine were obtained from Energy Chemical. $CDCl_3$ was obtained from J&K Chemical. *n*Octane and THF were obtained from Sinopharm and purified by distillation with sodium. Otherwise noted, all reactions were performed with dry solvents under an atmosphere of nitrogen gas (99.999%) in dried glassware using standard Schlenk techniques. All *N*-methyl indoles[1] were prepared from the corresponding N-H indoles according to the procedures reported in the literature. **1b**,[2] 1**i**,[3],[1] **1j**,[4],[1] **1n**[5],[1] and **1o**[2] were prepared according to the procedures reported in the literature. All reactions were performed in a 25-mL Schlenk tube (with a Teflon high-pressure valve and side arm) and heated in a heating module (heater + magnetic stirrer). All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using Huang Hai HSGF254 (0.2 mm) precoated plates. The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with silica gel (200–300 mesh). GCMS analysis was conducted on a Shimadzu GCMS-QP2010 instrument equipped with a Restec-5HT column (30 m × 0.25 mm, Hewlett-Packard). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Advance III (400 MHz) spectrometers with tetramethyl silane as an internal standard. Chemical shifts for $^1H$ NMR are expressed in parts per million (ppm) relative to tetramethyl silane (δ 0.00 ppm) or residual peak of $CDCl_3$ (δ 7.26 ppm). Chemical shifts for $^{13}C$ NMR are expressed in ppm relative to $CDCl_3$ (δ 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet), coupling constant (Hz), and integration. High resolution mass spectra (HRMS) were obtained from Agilent 6545 Q-TOF LCMS with electrospray ionization (ESI).

## 2. Reaction optimization

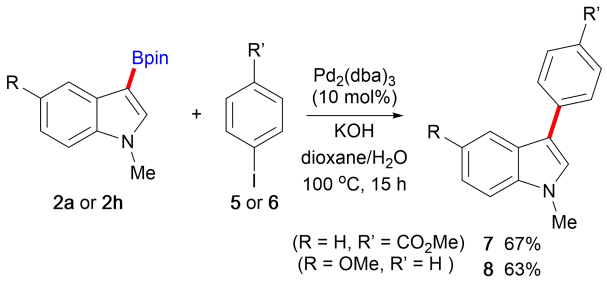
An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar and flushed with nitrogen gas. **1a** (0.2 mmol, 26.2 mg), HBpin (0.6 mmol, 76.8 mg), $Zn(OTf)_2$ (0.0004 mmol, 0.04 M in THF, 10.0 μL) and $^{n}$octane (0.5 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 °C for 24 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the solvent was evaporated under reduced pressure. The yield of **2a** was determined by $^{1}$H NMR using 3,4,5-trichloropyridine as internal standard.

## 3. General procedures

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was flushed with nitrogen gas. **1** or **3** (0.2 mmol), HBpin (0.6 mmol, 76.8 mg), $Zn(OTf)_2$ (0.0004 mmol, 0.04 M in THF, 10 μL) and $^{n}$octane (0.5 mL) were added to the tube under nitrogen atmosphere. The sealed tubes were heated at 160 °C (indole) or 140 °C (terminal alkynes) for 24 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the solvent was evaporated under reduced pressure and the residue was directly purified by flash column chromatography over silica gel eluting with petroleum ether/methylene chloride (indole) or petroleum ether/ethyl acetate (terminal alkynes) to afford the product.
*Note:* **2c** and **2j** were purified by recrystallition (petroleum ether).

*Hazardous statement*: These reactions were performed at a temperature that is well above the boiling point of $^{n}$octane (approximately 126 $^{o}$C), leading to substantial pressure buildup in the sealed reaction vessel. As such, proper precautions should be taken when performing these experiments. All reactions were performed in a 25-mL Schlenk tube (with a Teflon high-pressure valve and side arm) and heated in a heating module (heater + magnetic stirrer).

## 4. Synthetic application

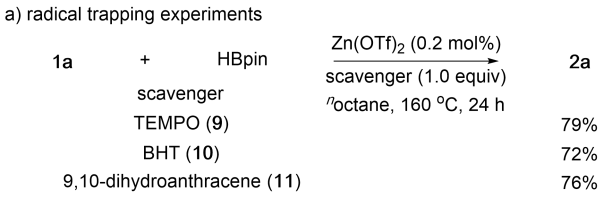



Compound **7** was prepared according to the modified procedures reported in the literature.[6] An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **2a** (0.4 mmol, 102.9 mg), **5** (0.2 mmol, 52.4 mg) and KOH (0.4 mmol, 22.4 mg). The tube was then introduced to a nitrogen-atmosphere glovebox and charged with $Pd_2(dba)_3$ (0.02 mmol, 18.3 mg). After the tube was taken out of the glovebox, 1,4-dioxane/$H_2O$ (0.7 mL/0.3 mL) were added to the vessel under nitrogen atmosphere. The sealed tube was heated at 100 °C for 15 h in a heating module with stirring. After cooling the reaction mixture to room temperature, water (10.0 mL) was added. Then the mixture was extracted with ethyl acetate and dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography over silica gel eluting with petroleum ether/ethyl acetate to afford product **7** (35.5 mg, 67%) as a white solid.

Compound **8** was prepared according to the modified procedures reported in the literature.[6] An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **2h** (0.4 mmol, 114.9 mg) and KOH (0.4 mmol, 22.4 mg). The tube was then introduced to a nitrogen-atmosphere glovebox and charged with $Pd_2(dba)_3$ (0.02 mmol, 18.3 mg). After the tube was taken out of the glovebox, **6** (0.2 mmol, 40.8 mg) and 1,4-dioxane/$H_2O$ (0.7 mL/0.3 mL) were added to the vessel under nitrogen atmosphere. The sealed tube was heated at 100 °C for 15 h in a heating module with stirring. After cooling the reaction mixture to room temperature, water (10.0 mL) was added. Then the mixture was extracted with ethyl acetate and dried over $Na_2SO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography over silica gel eluting with petroleum ether/ethyl acetate to afford product **8** (29.9 mg, 63%) as a white solid.

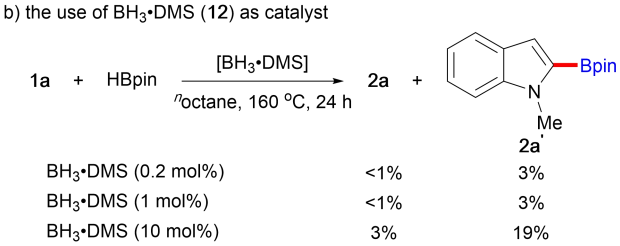
## 5. Control experiments

a) Radical trapping experiment



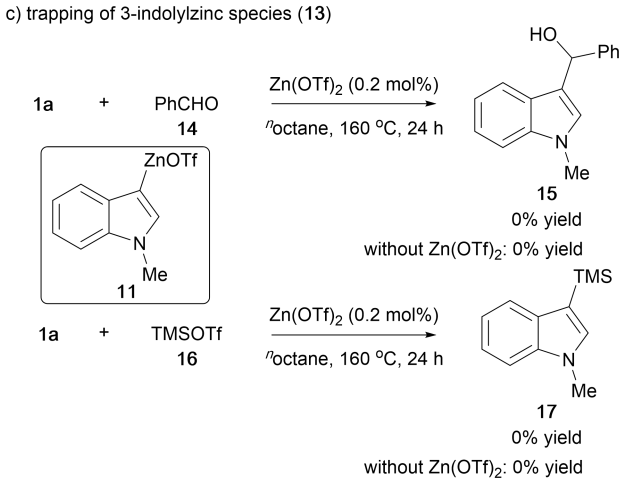

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar, and then flushed with nitrogen gas. **1a** (0.2 mmol, 26.2 mg), HBpin (0.6 mmol, 76.8 mg), radical scavenger (TEMPO, **9**, 0.2 mmol, 31.2 mg; BHT, **10**, 0.2 mmol, 44.1 mg; 9,10-dihydroanthracene, **11**, 0.2 mmol, 36.0 mg), $Zn(OTf)_2$ (0.0004 mmol, 0.04 M in THF, 10.0 μL) and $^n$octane (0.5 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 °C for 24 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the solvent was evaporated under reduced pressure. The yield of **2a** was determined by $^1$H NMR using 3,4,5-trichloropyridine as internal standard.

b) The use of $BH_3$•DMS (**12**) as catalyst




An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar, and then flushed with nitrogen gas. **1a** (0.2 mmol, 26.2 mg), HBpin (0.6 mmol, 76.8 mg), $BH_3$•DMS **12** (0.0004 mmol, 0.1 M in DMS, 4 μL; 0.002 mmol, 0.2 M in DMS, 10 μL; 0.02 mmol, 2.0 M in DMS, 10 μL) and $^n$octane (0.5 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 °C for 24 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the solvent was evaporated under reduced pressure. The yield of **2a** and **2a'** was determined by $^1$H NMR using 3,4,5-trichloropyridine as internal standard.

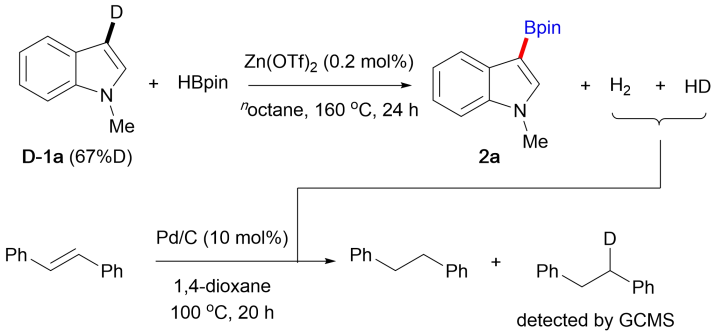
c) Trapping of 3-indolylzinc species (**13**)

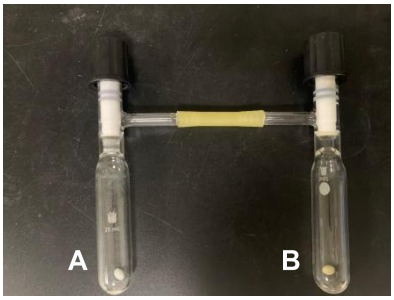



An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar, and then flushed with nitrogen gas. **1a** (0.2 mmol, 26.2 mg), $Zn(OTf)_2$ (0.0004 mmol, 0.04 M in THF, 10 μL), PhCHO (0.2 mmol, 21.2 mg) and $^n$octane (0.5 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 °C for 24 h in a heating module with stirring. After cooling to room temperature, the reaction mixture was monitored by GCMS.

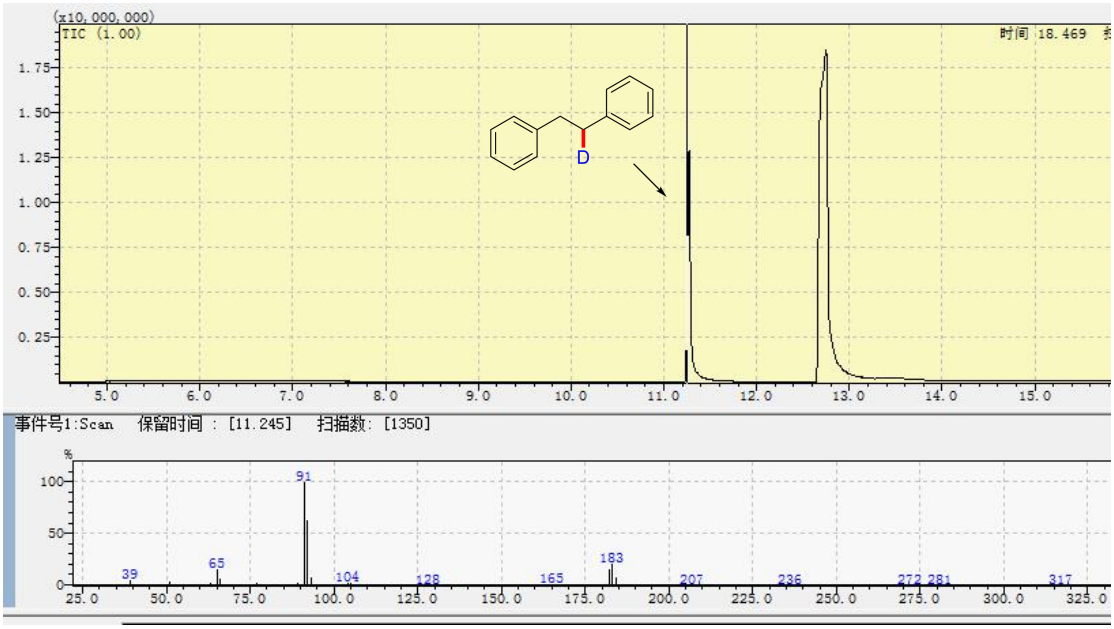
An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar, and then flushed with nitrogen gas. **1a** (0.2 mmol, 26.2 mg), $Zn(OTf)_2$ (0.0004 mmol, 0.04 M in THF, 10 μL), TMSOTf (0.2mmol, 44.5 mg) and $^n$octane (0.5 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 °C for 24 h in a heating module with stirring. After cooling to room temperature, the reaction mixture was monitored by GCMS.

d) Trapping Experiment of Hydrogen Gas

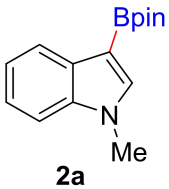





A two-chamber glass equipment was used for this experiment. The picture of the glass equipment used is shown left. At first, an oven-dried 25-mL Schlenk tube A equipped with a magnetic stirring bar was flushed with nitrogen gas. **D-1a** (1 mmol, 132.0 mg, 67% D) (ref. ACS Catalysis, 2019, 9, 6522-6529), HBpin (2 mmol, 256.0 mg), $Zn(OTf)_2$ (0.002 mmol, 0.04 M in THF, 50.0 μL) and n-octane (2.0 mL) were added to tube A under nitrogen atmosphere. The sealed tube A was heated at 160 °C for 24 h in a heating module with stirring. After cooling tube A to room temperature, tube B charged with Pd/C (0.04 mmol, 4.3 mg), 1,2-diphenylethene (0.4 mmol, 72.1 mg) and 1,4-dioxane (0.4 mL) was connected to tube A by a rubber hose in glovebox. Then the two tubes were open allowing the gas flow and then sealed. Tube B was heated at 100 °C for 20 h in a heating module with stirring. After cooling tube B to room temperature, the reaction mixture was monitored by GCMS.



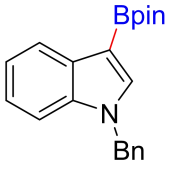
## 6. Analytical data of products




**2a**

**1-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2a)**[7]

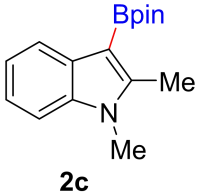
White solid (39.1 mg, 76%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.51 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.25–7.21 (m, 1H), 7.19–7.16 (m, 1H), 3.78 (s, 3H), 1.36 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.5, 137.8, 132.5, 122.7, 121.8, 120.2, 109.2, 82.8, 33.0, 25.0.




**2b**

**1-Benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2b)** [8]

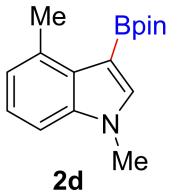
White soild (43.3 mg, 65%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.07–8.05 (m, 1H), 7.59 (s, 1H), 7.27–7.23 (m, 4H), 7.18–7.15 (m, 2H), 7.13–7.11 (m, 2H), 5.28 (s, 2H), 1.35 (s, 12H) ; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 137.9, 137.4, 137.0, 132.8, 128.8, 127.8, 127.1, 122.8, 122.0, 120.5, 109.8, 82.9, 50.4, 25.0.




**2c**

**1,2-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2c)** [7]

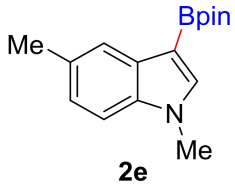
White soild (36.6 mg, 62%). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, $J$ = 8.0 Hz, 1H), 7.22 (d, $J$ = 7.2 Hz, 1H), 7.16–7.10 (m, 2H), 3.63 (s, 3H), 2.62 (s, 3H), 1.35 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 147.6, 138.0, 132.5, 121.8, 120.8, 120.1, 108.5, 82.3, 29.5, 25.1, 12.7.




**2d**

**1,4-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2d)**

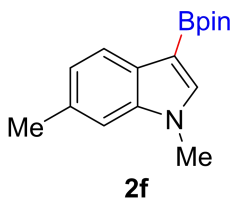
White soild (26.6 mg, 49%). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.14 (d, $J$ = 5.2 Hz, 2H), 6.96–6.94 (m, 1H), 3.75 (s, 3H), 2.76 (s, 3H), 1.34 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.7, 138.4, 133.1, 130.7, 122.0, 121.7, 106.9, 82.9, 33.1, 24.8, 21.3. HRMS (ESI) m/z calcd for $C_{16}H_{22}BNO_2$ $[M+H]^+$ : 272.1816 found 272.1820.




**2e**

**1,5-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2e)** [7]

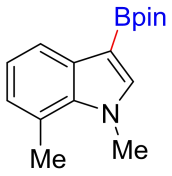
White soild (40.7 mg, 75%). $^1$H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.46 (d, $J$ = 1.2 Hz, 1H), 7.18 (d, $J$ = 8.4 Hz, 1H), 7.04 (d, $J$ = 8.4 Hz, 1H), 3.72 (s, 3H), 2.48 (s, 3H), 1.35 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.6, 136.3, 132.8, 129.6, 123.4, 122.3, 108.9, 82.7, 33.0, 25.0, 21.6.




**2f**

**1,6-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2f)**

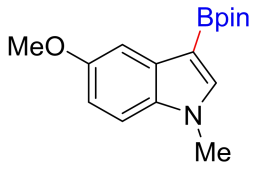
White soild (38.5 mg, 71%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.0 Hz 1H), 7.45 (s, 1H), 7.11 (s, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 2.49 (s, 3H), 1.35 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 138.2, 138.0, 131.6, 130.3, 122.3, 122.0, 109.3, 82.7, 32.9, 25.0, 22.0 . HRMS (ESI) m/z calcd for $C_{16}H_{22}BNO_2$ $[M+H]^+$ : 272.1816 found 272.1821.




**2g**

**1,7-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2g)** [9]

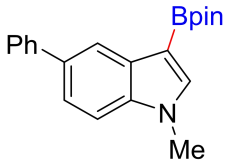
White soild (39.6 mg, 73%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.47–7.43 (m, 1H), 7.09 (s, 1H), 6.94-6.91 (m, 2H), 4.26 (s, 3H), 2.79 (s, 3H), 1.36 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.2, 128.9, 126.0, 121.7, 119.9, 119.5, 115.0, 83.7, 35.7, 24.8, 20.5.




**2h**

**5-Methoxy-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2h)** [8]

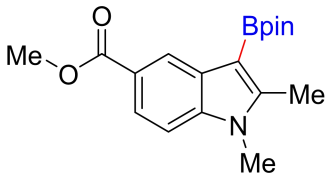
White soild (45.9 mg, 80%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 2.4 Hz, 1H), 7.48 (s, 1H), 7.20 (d, *J* = 8.8 Hz, 1H), 6.90–6.87 (m, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 1.36 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.7, 138.8, 133.2, 133.1, 111.7, 109.8, 104.7, 82.7, 56.0, 33.2, 24.9.




**2i**

**5-Phenyl-1-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2i)**

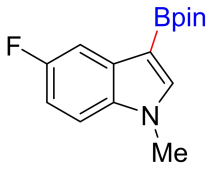
White soild (48.6 mg, 73%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.54 (s, 1H), 7.49–7.43 (m, 3H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 3.81 (s, 3H), 1.36 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 142.9, 139.1, 137.4, 133.9, 132.9, 128.6, 127.7, 126.3, 121.8, 121.3, 109.5, 82.8, 33.1, 25.0. HRMS (ESI) m/z calcd for $C_{21}H_{24}BNO_2$ $[M+H]^+$ : 334.1973 found 334.1979.




**2j**

**Methyl1,2-dimethyl-5-carboxylate-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -1H-indole(2j)**

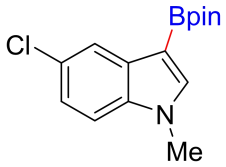
White soild (22.4 mg, 34%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 1H), 3.94 (s, 3H), 3.68 (s, 3H), 2.64 (s, 3 H), 1.37 (s, 12H) ; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 168.6, 149.0, 140.6, 131.9, 124.5, 122.5, 122.0, 108.2, 82.6, 51.8, 29.7, 25.0, 12.7. HRMS (ESI) m/z calcd for $C_{18}H_{24}BNO_4$ $[M+H]^+$ : 330.1871 found 330.1878.




**2k**

**5-Fluoro-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2k)** [8]

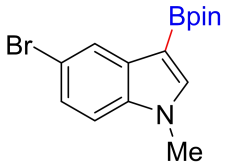
White soild (37.4 mg, 68%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.70–7.67 (m, 1H), 7.53 (s, 1H), 7.23–7.19 (m, 1H), 7.00–6.94 (m, 1H), 3.78 (s, 3H), 1.35 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.6 (d, $J$ = 233.2 Hz), 139.7, 134.4, 133.2 (d, $J$ = 10.6 Hz), 110.1 (d, $J$ = 26.6 Hz), 109.7(d, $J$ = 10.0 Hz), 107.6 (d, $J$ = 23.2 Hz), 82.9, 33.3, 24.9.




**2l**

**5-Chloro-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2l)** [8]

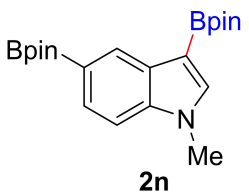
White soild (41.4 mg, 71%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, $J$ = 1.2 Hz, 1H), 7.51 (s, 1H), 7.22–7.16 (m, 2H), 3.76 (s, 3H), 1.35 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.5, 136.3, 133.6, 126.2, 122.1, 122.1, 110.2, 83.0, 33.2, 24.9.




**2m**

**5-Bromo-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2m)** [9]

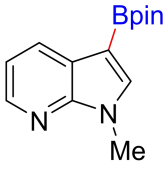
White soild (49.0 mg, 73%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, $J$ = 2.0 Hz, 1H), 7.49 (s, 1H), 7.32–7.30 (m, 1H), 7.17 (d, $J$ = 8.4 Hz, 1H), 3.77 (s, 3H), 1.35 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.3, 136.5, 134.2, 125.1, 124.7, 113.9, 110.7, 83.0, 33.2, 24.9.




**2n**

**1-Methyl-3,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2n)**

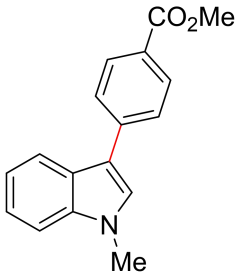
White soild (49.0 mg, 64%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.52 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 1.38 (s, 12H), 1.36 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 139.9, 139.0, 131.9, 130.0, 128.2, 108.7, 83.4, 82.8, 33.0, 24.9. HRMS (ESI) m/z calcd for $C_{21}H_{31}B_2NO_4$ $[M+H]^+$ : 384.2512 found 384.2521.




**2o**

**1-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-aza-1H-indole(2o)**

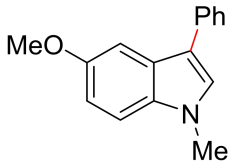
White soild (24.8 mg, 48%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.34-8.33 (m, 1H), 8.28-8.26 (m, 1H), 7.65 (s, 1H), 7.13-7.10 (m, 1H), 3.90 (s, 3H), 1.36 (s, 12H) ; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 149.1, 142.9, 138.5, 130.8, 124.7, 116.4, 83.0, 31.5, 24.9. HRMS (ESI) m/z calcd for $C_{14}H_{19}BN_2O_2$[M+H]$^+$ : 259.1612 found 259.1627.




7

**Methyl 4-(5-methoxy-1-methyl-1H-indol-3-yl)benzoate**

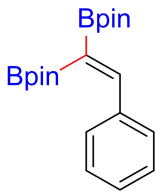
White soild (35.5 mg, 67%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.40-7.37 (m, 2H), 7.36-7.32 (m, 1H), 7.28 (s, 1H), 4.03 (s, 3H), 3.75 (s, 3H) ; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.3, 140.8, 137.8, 130.3, 127.8, 126.9, 126.5, 125.9, 122.4, 120.6, 120.0, 115.5, 110.0, 52.1, 32.9. HRMS (ESI) m/z calcd for $C_{17}H_{15}NO_2$ $[M+H]^+$ : 266.1176 found 266.1167.




**8**

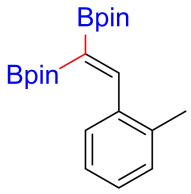
**5-Methoxy-1-methyl-3-phenyl-1H-indole(6)**[10]

White soild (29.9 mg, 63%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.67-7.65 (m, 2H), 7.49-7.45 (m, 2H), 7.42 (s, 1H), 7.32-7.28 (m, 2H), 7.23 (s, 1H), 6.98 (dd, *J* = 8.8 Hz, 1.2 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H) ; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.6, 135.8, 132.9, 128.8, 127.2, 127.2, 126.4, 125.6, 116.3, 112.3, 110.3, 101.7, 55.1, 33.1.



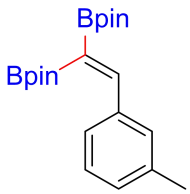

**2,2'-(2-phenylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4a)**[11]

Colorless oil (43.4 mg, 61%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.41 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.22–7.19 (m, 3H), 1.24 (s, 12H), 1.21 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.3, 139.7, 128.6, 128.3, 128.2, 83.8, 83.3, 25.0, 24.8.



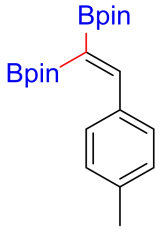

**2,2'-(2-(o-tolyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4b)**[11]

Colorless oil. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.18–7.08 (m, 3H), 2.36 (s, 3H), 1.28 (s, 12H), 1.24 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.4, 139.3, 136.4, 129.9, 128.4, 127.8, 125.6, 83.6, 83.3, 25.0, 24.7, 19.9.



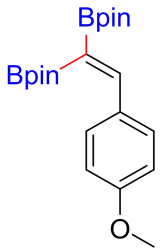

**2,2'-(2-(m-tolyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4c)**[11]

Colorless oil. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.25 (s, 1H), 7.20–7.18 (m, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 2.24 (s, 3H), 1.24 (s, 12H), 1.20 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.5, 139.7, 137.7, 129.4, 128.6, 128.2, 125.7, 83.7, 83.3, 25.0, 24.8, 21.4.



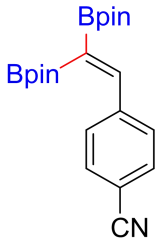

**2,2'-(2-(p-tolyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4d)**[11]

Colorless oil. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 1.32 (s, 12H), 1.27 (s, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.3, 138.5, 136.9, 128.9, 128.3, 83.6, 83.2, 25.0, 24.8, 21.4.



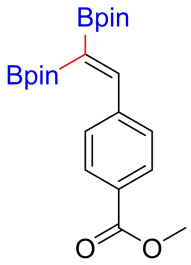

**2,2'-(2-(4-methoxyphenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4e)**[11]

Pale yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 1.32 (s, 12H), 1.27 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 160.1, 154.9, 132.6, 129.9, 113.6, 83.7, 83.2, 55.4, 25.0, 24.8.



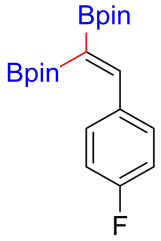

**4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (4f)**

White solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.60–7.54 (m, 4H), 1.30 (s, 12H), 1.28 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.7, 144.1, 132.2, 128.7, 119.0, 111.8, 84.1, 83.8, 25.0, 24.8. HRMS (ESI) m/z calcd for $C_{21}H_{29}B_2NO_4$ $[M+H]^+$: 382.2355 found 382.2352.



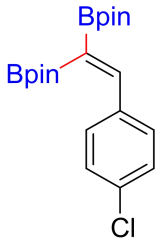

**Methyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (4g)**[12]

White solid (26.5 mg, 32%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, $J$ = 8.4 Hz, 2H), 7.71 (s, 1H), 7.54 (d, $J$ = 8.4 Hz, 2H), 3.90 (s, 3H), 1.31 (s, 12H), 1.28 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.0, 153.8, 144.1, 129.8, 129.7, 128.2, 84.0, 83.9, 52.2, 25.0, 24.8.



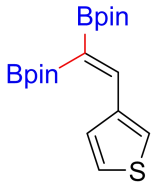

**2,2'-(2-(4-fluorophenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4h)**[11]

Colorless oil. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.48–7.44 (m, 2H), 7.00–6.95 (m, 2H), 1.31 (s, 12H), 1.27 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 164.3, 161.8, 154.0, 136.0, 136.0, 130.1, 130.0, 115.3, 115.1, 83.8, 83.4, 25.0, 24.8.




**2,2'-(2-(4-chlorophenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4i)**[11]

White solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.20–7.18 (m, 2H), 1.24 (s, 12H), 1.20 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 153.7, 138.2, 134.4, 129.5, 128.5, 83.9, 83.5, 25.0, 24.8.




**2,2'-(2-(thiophen-3-yl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4j)**[13]

Colorless solid. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.44 (d, *J* = 2.8 Hz, 1H), 7.31 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.22 (dd, *J* = 5.2, 3.2 Hz, 1H), 1.33 (s, 12H), 1.27 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.4, 142.6, 127.4, 125.8, 125.5, 83.8, 83.3, 25.0, 24.9.

## 7. Scope of $Zn(OTf)_2$-catalysed 1,1-diboration of terminal alkynes

### 2,2'-(2-phenylethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4a)

The title compound was prepared following above general procedure from phenylacetylene (20.4 mg, 0.2 mmol). Yield (74%) was determined by integration against $CH_2Br_2$ (33.3 mg, 0.19 mmol) as internal standard (Figure S1). Purification by flash chromatography afforded the 1,1- diborylalkene product (43.4 mg, 61%) as colourless oil. The product contained two minor impurities (5% of 1,1-diborylalkane[14] and 2% of monoborylolefin[11]) as judged by $^1H$ NMR analysis using $CH_2Br_2$ (17.7 mg, 0.1 mmol) as internal standard (Figure S2).

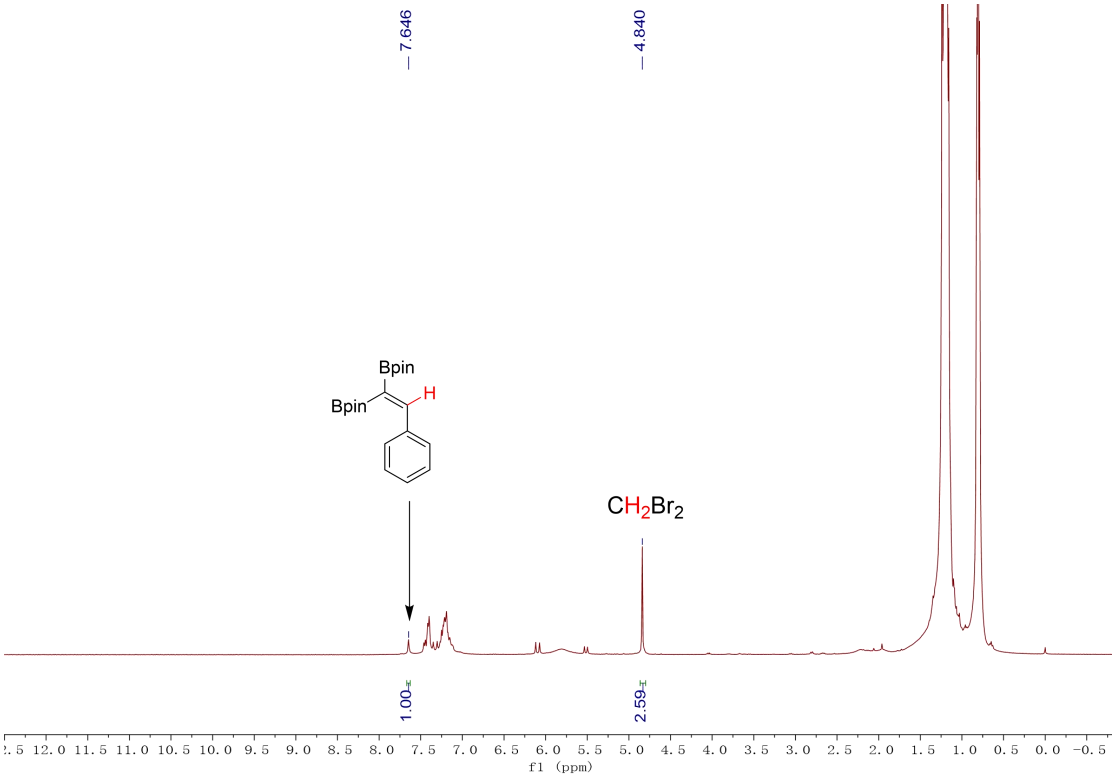



**Figure S1**. $^1H$ NMR spectrum of the reaction of phenylacetylene with HBPin catalyzed by $Zn(OTf)_2$ affording **4a** with $CH_2Br_2$ (33.3mg, 0.19 mmol) added as internal standard.

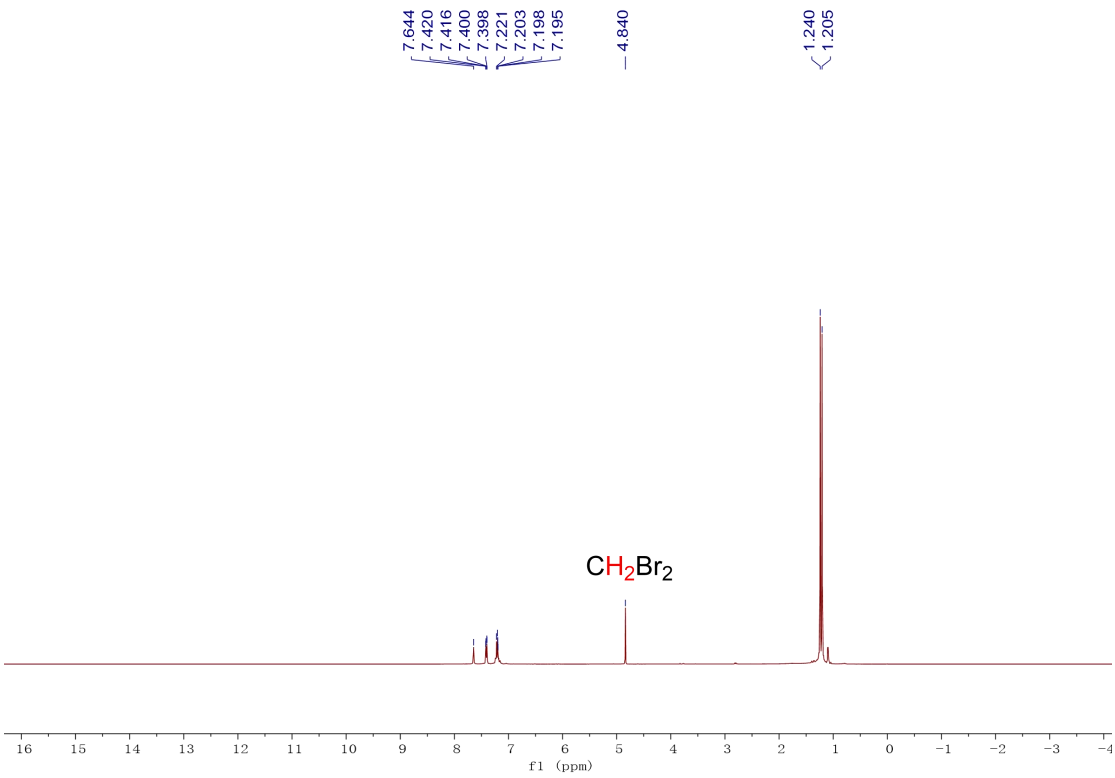



**Figure S2.** $^{1}$H NMR of isolated **4a** with $CH_2Br_2$ (17.7 mg, 0.1 mmol).

**2,2'-(2-(o-tolyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4b)**

The title compound was prepared following above general procedure from 1-ethynyl-2-methy-lbenzene (23.2 mg, 0.2 mmol). Yield (75%) was determined by integration against $CH_2Br_2$ (18.1mg, 0.1 mmol) as internal standard (Figure S3).

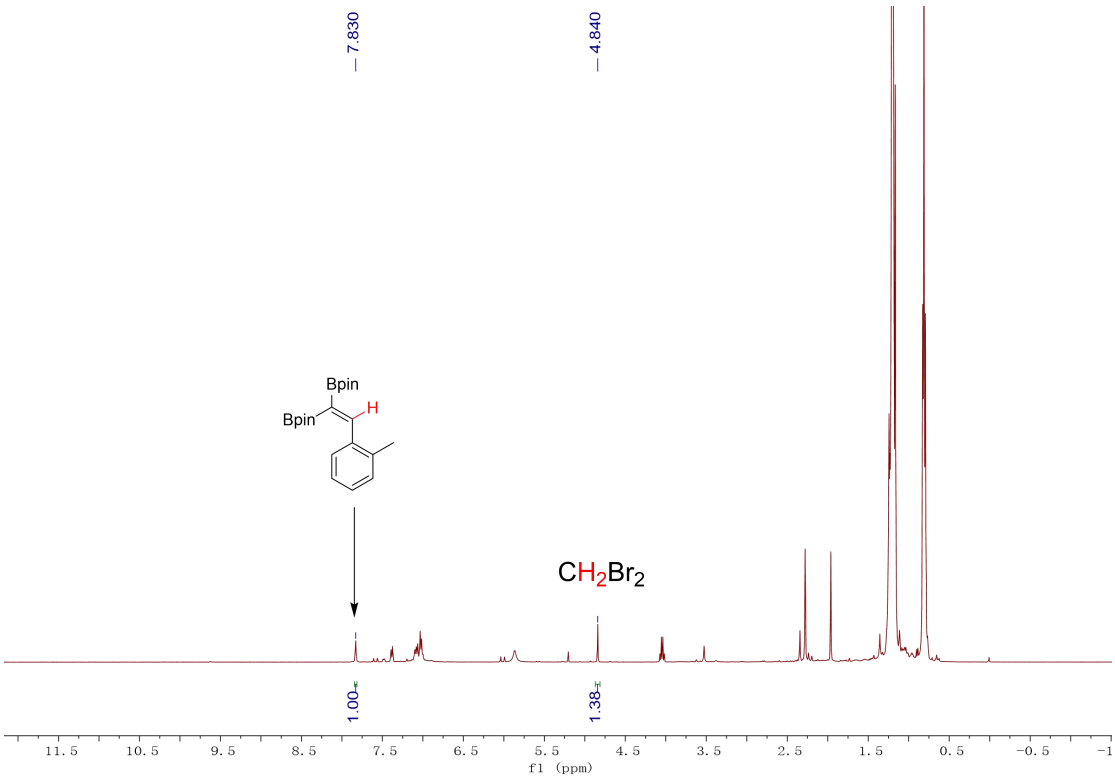



**Figure S3**. $^{1}$H NMR spectrum of the reaction of 1-ethynyl-2-methylbenzene with HBPin catalyzed by $Zn(OTf)_2$ affording **4b** with $CH_2Br_2$ (18.1mg, 0.1 mmol) added as internal standard.

**2,2'-(2-(m-tolyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4c)**

The title compound was prepared following above general procedure from 1-ethynyl-3-methylbenzene (23.2 mg, 0.2 mmol). Yield (76%) was determined by integration against $CH_2Br_2$ (12.5 mg, 0.07 mmol) as internal standard (Figure S4).

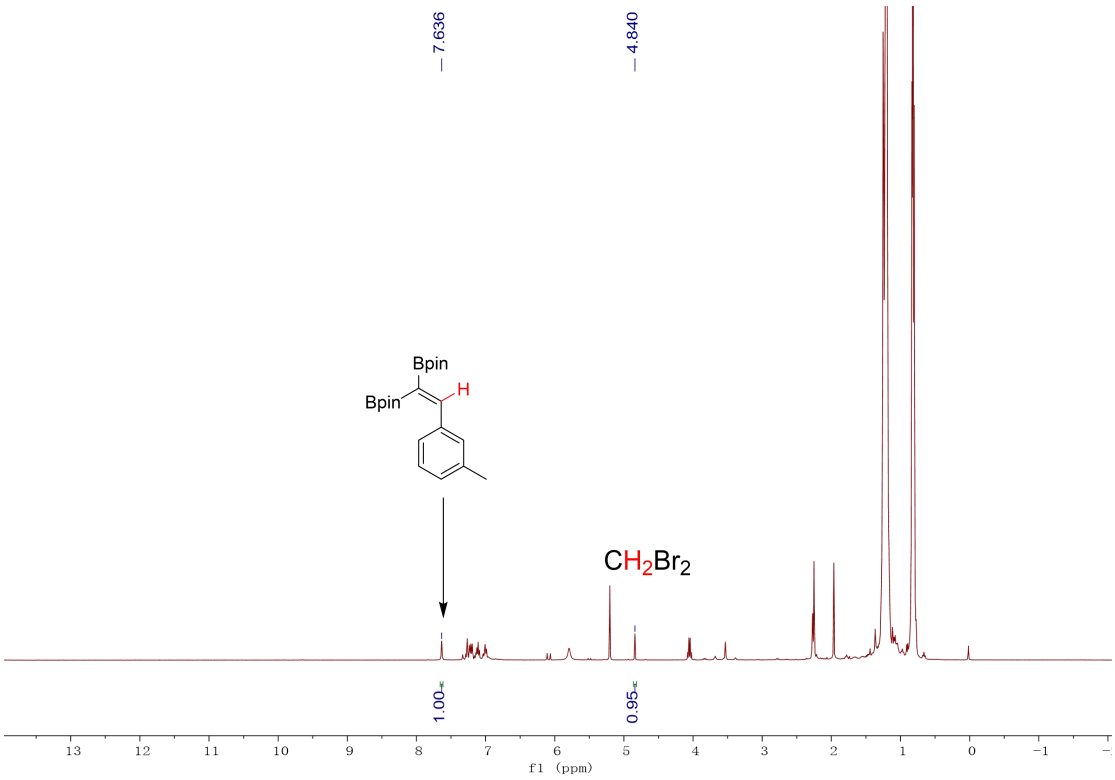



**Figure S4**. $^{1}$H NMR spectrum of the reaction of 1-ethynyl-3-methylbenzene with HBPin catalyzed by $Zn(OTf)_2$ affording **4c** with $CH_2Br_2$ (12.5mg, 0.07 mmol) added as internal standard.

**2,2'-(2-(p-tolyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4d)**

The title compound was prepared following above general procedure from 1-ethynyl-4-methylbenzene (23.2 mg, 0.2 mmol). Yield (77%) was determined by integration against $CH_2Br_2$ (28.7 mg, 0.16 mmol) as internal standard (Figure S5).

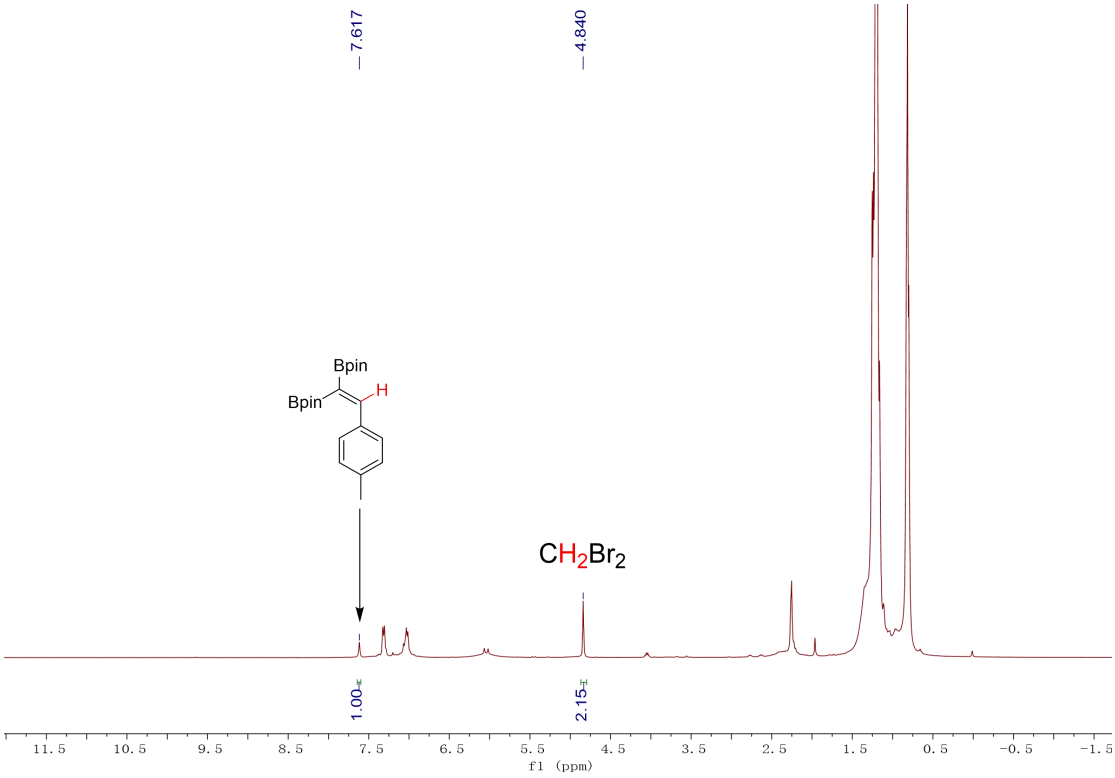



**Figure S5**. $^{1}$H NMR spectrum of the reaction of 1-ethynyl-4-methylbenzene with HBPin catalyzed by $Zn(OTf)_2$ affording **4d** with $CH_2Br_2$ (28.7mg, 0.16 mmol) added as internal standard.

**2,2'-(2-(4-methoxyphenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4e)**

The title compound was prepared following above general procedure from 1-ethynyl-4-methoxybenzene (26.4 mg, 0.2 mmol). Yield (88%) was determined by integration against $CH_2Br_2$ (31.0 mg, 0.18 mmol) as internal standard (Figure S6).

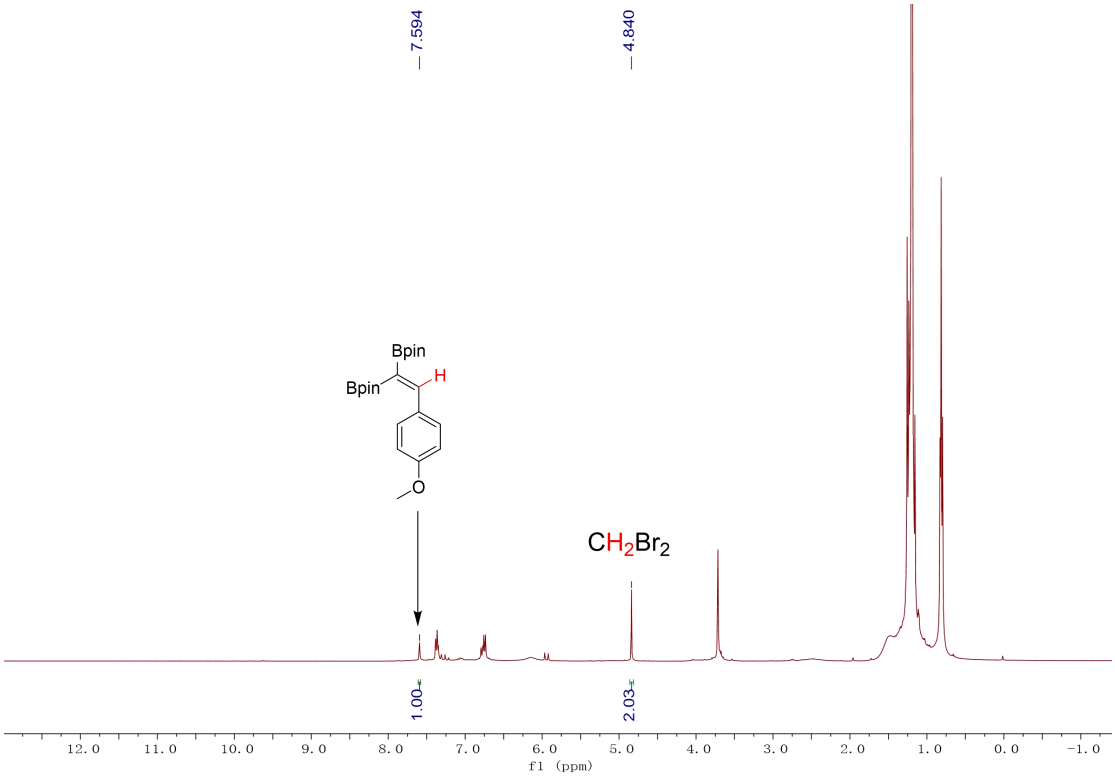



**Figure S6**. $^{1}$H NMR spectrum of the reaction of 1-ethynyl-4-methoxybenzene with HBPin catalyzed by $Zn(OTf)_2$ affording **4e** with $CH_2Br_2$ (31.0 mg, 0.18 mmol) added as internal standard.

### 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzonitrile (4f)

The title compound was prepared following above general procedure from 4-ethynylbenzonitrile (25.4 mg, 0.2 mmol). Yield (36%) was determined by integration against $CH_2Br_2$ (25.0 mg, 0.14 mmol) as internal standard (Figure S7).

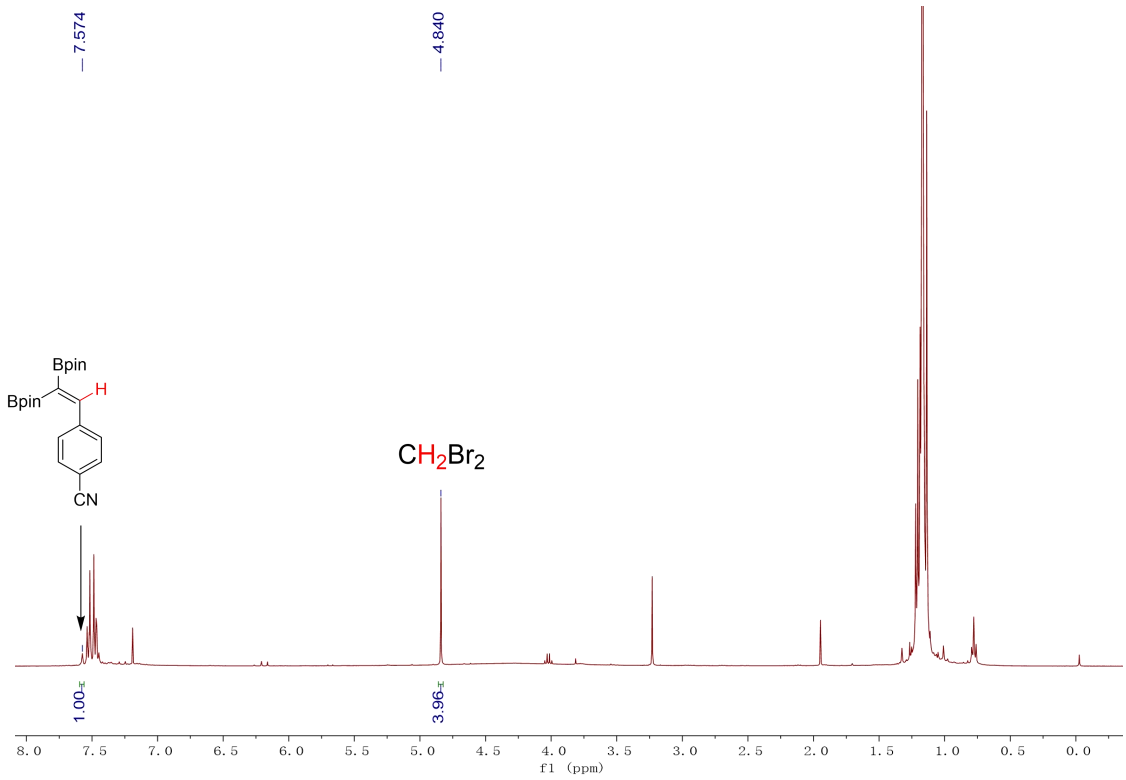



**Figure S7**. $^{1}$H NMR spectrum of the reaction of 4-ethynylbenzonitrile with HBPin catalyzed by $Zn(OTf)_2$ affording **4f** with $CH_2Br_2$ (25.0 mg, 0.14 mmol) added as internal standard.

**Methyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzoate (4g)**

The title compound was prepared following above general procedure from methyl4-ethynylbenzoate (32.0 mg, 0.2 mmol). Yield (62%) was determined by integration against $CH_2Br_2$ (20.5 mg, 0.12 mmol) as internal standard (Figure S8). Purification by flash chromatography afforded the 1,1-diborylalkene product (26.5 mg, 32%) as white solid. The product contained one minor impurities (1% of 1,1-diborylalkane[15]) as judged by $^{1}$H NMR analysis using $CH_2Br_2$ (15.5 mg, 0.09 mmol) as internal standard (Figure S9).

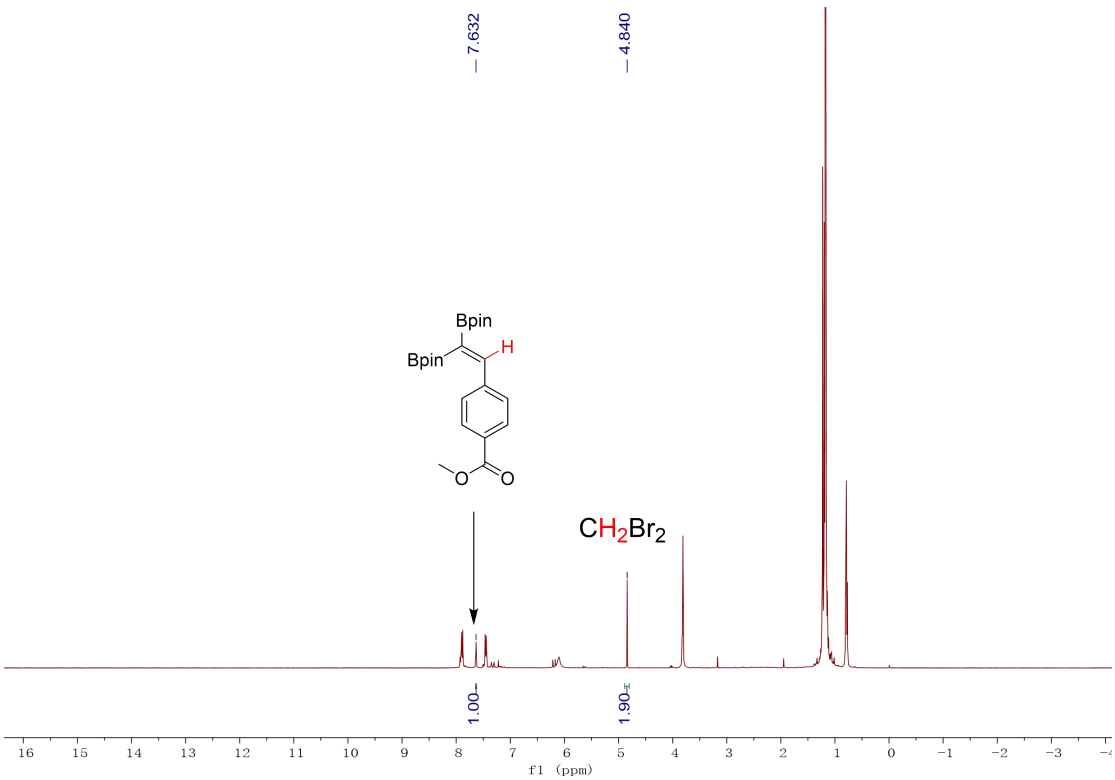



**Figure S8**. $^{1}$H NMR spectrum of the reaction of methyl 4-ethynylbenzoate with HBPin catalyzed by $Zn(OTf)_2$ affording **4g** with $CH_2Br_2$ (20.5 mg, 0.12 mmol) added as internal standard.

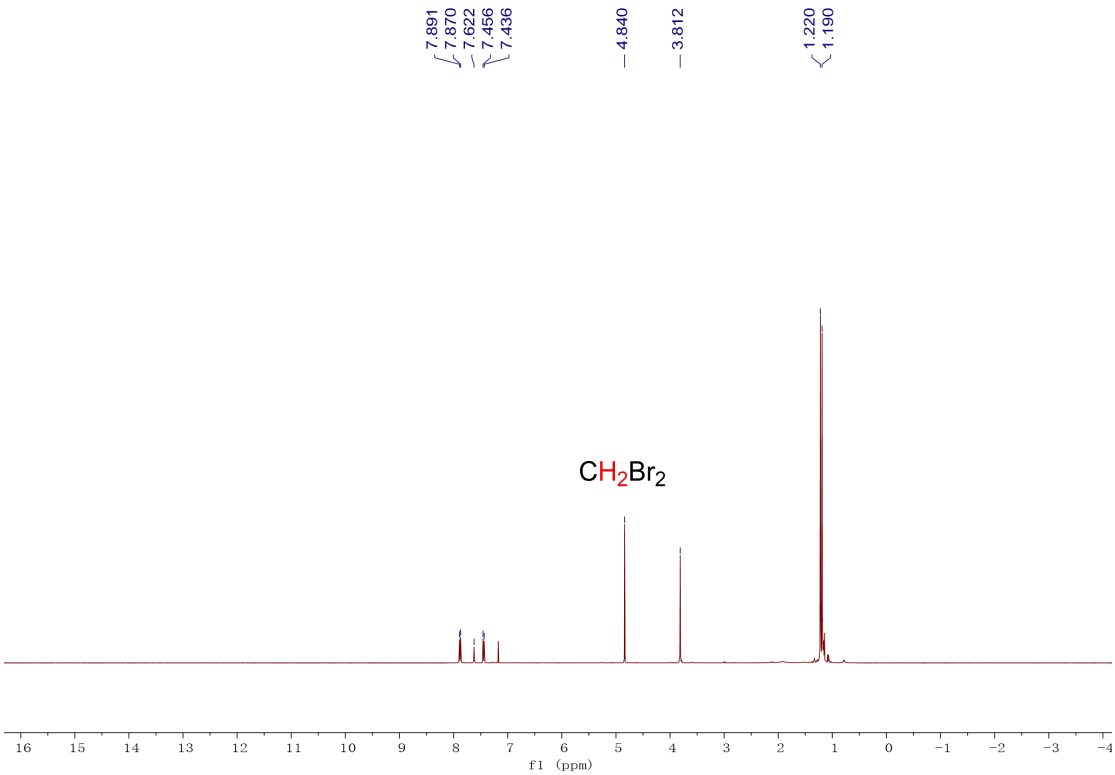



**Figure S9.** $^{1}$H NMR of isolated **4g** with $CH_2Br_2$ (15.5 mg, 0.09 mmol).

**2,2'-(2-(4-fluorophenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4h)**

The title compound was prepared following above general procedure from 1-ethynyl-4-fluorobenzene (24.0 mg, 0.2 mmol). Yield (64%) was determined by integration against $CH_2Br_2$ (19.2 mg, 0.11 mmol) as internal standard (Figure S10).

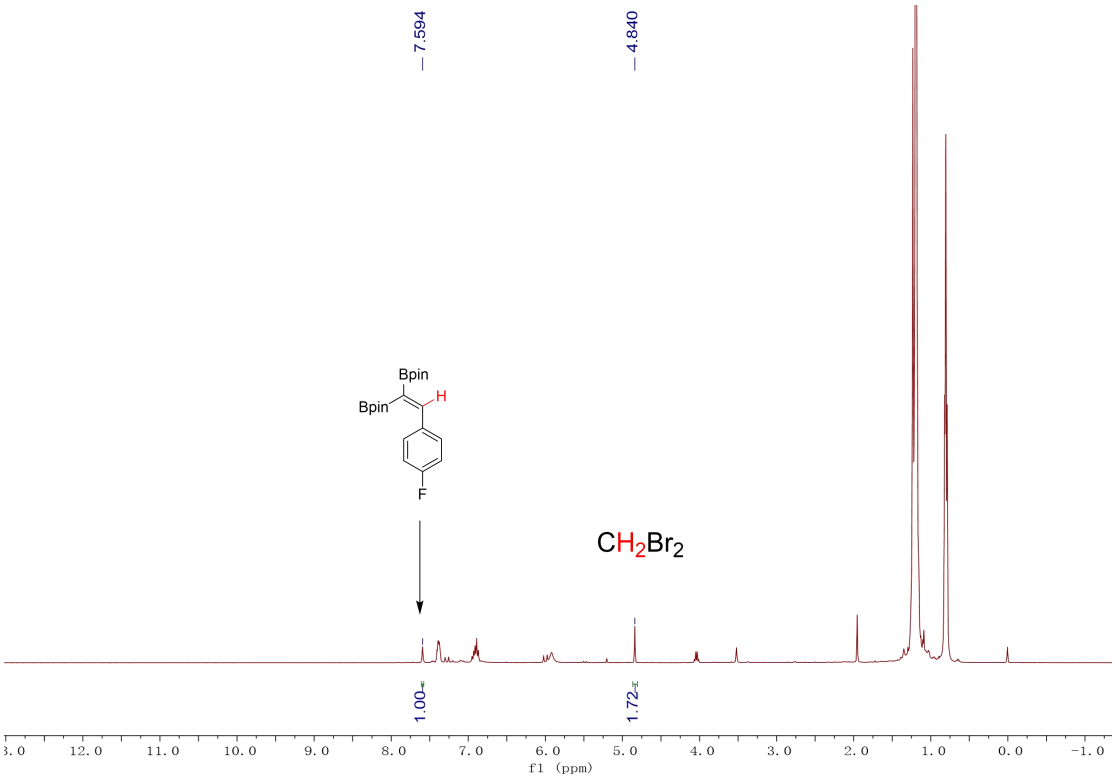



**Figure S10**. $^1$H NMR spectrum of the reaction of 1-ethynyl-4-fluorobenzene with HBPin catalyzed by $Zn(OTf)_2$ affording **4h** with $CH_2Br_2$ (19.2 mg, 0.11 mmol) added as internal standard.

**2,2'-(2-(4-chlorophenyl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4i)**

The title compound was prepared following above general procedure from 1-chloro-4-ethynylbenzene (27.3 mg, 0.2 mmol). Yield (31%) was determined by integration against $CH_2Br_2$ (16.6 mg, 0.1 mmol) as internal standard (Figure S11).

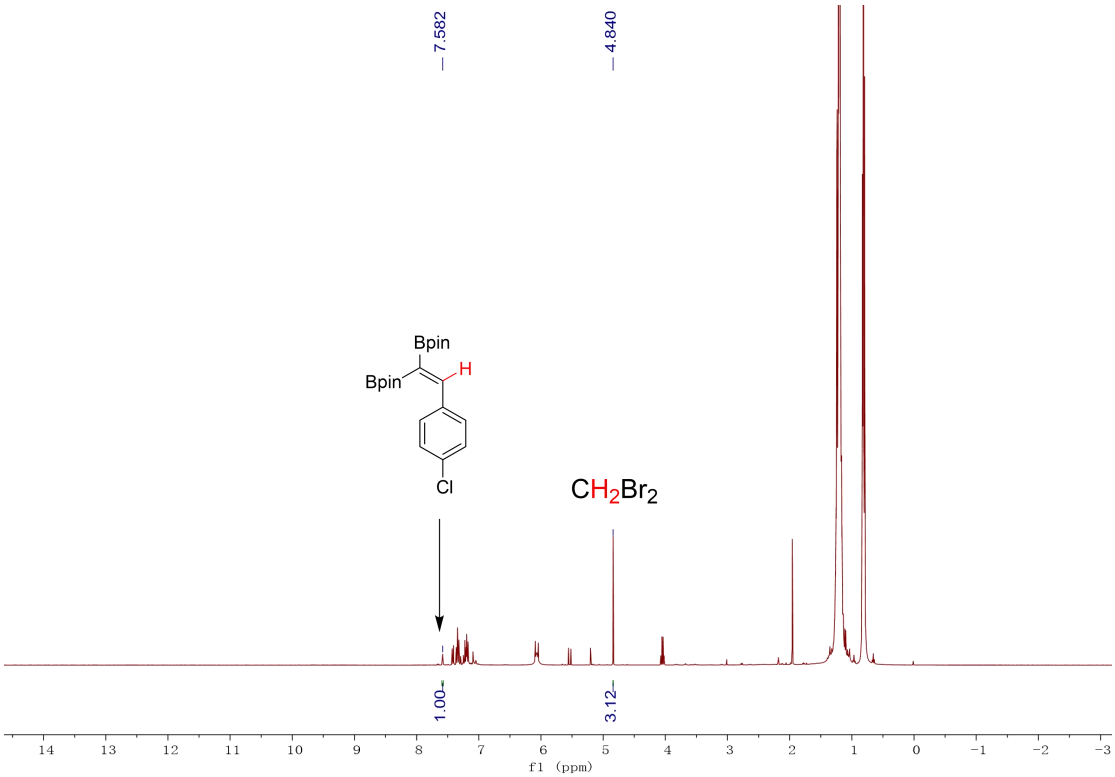



**Figure S11**. $^{1}$H NMR spectrum of the reaction of 1-chloro-4-ethynylbenzene with HBPin catalyzed by $Zn(OTf)_2$ affording **4i** with $CH_2Br_2$ (16.6 mg, 0.1 mmol) added as internal standard.

**2,2'-(2-(thiophen-3-yl)ethene-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4j)**

The title compound was prepared following above general procedure from 3-ethynylthiophene (21.6 mg, 0.2 mmol). Yield (58%) was determined by integration against $CH_2Br_2$ (26.0 mg, 0.15 mmol) as internal standard (Figure S12).

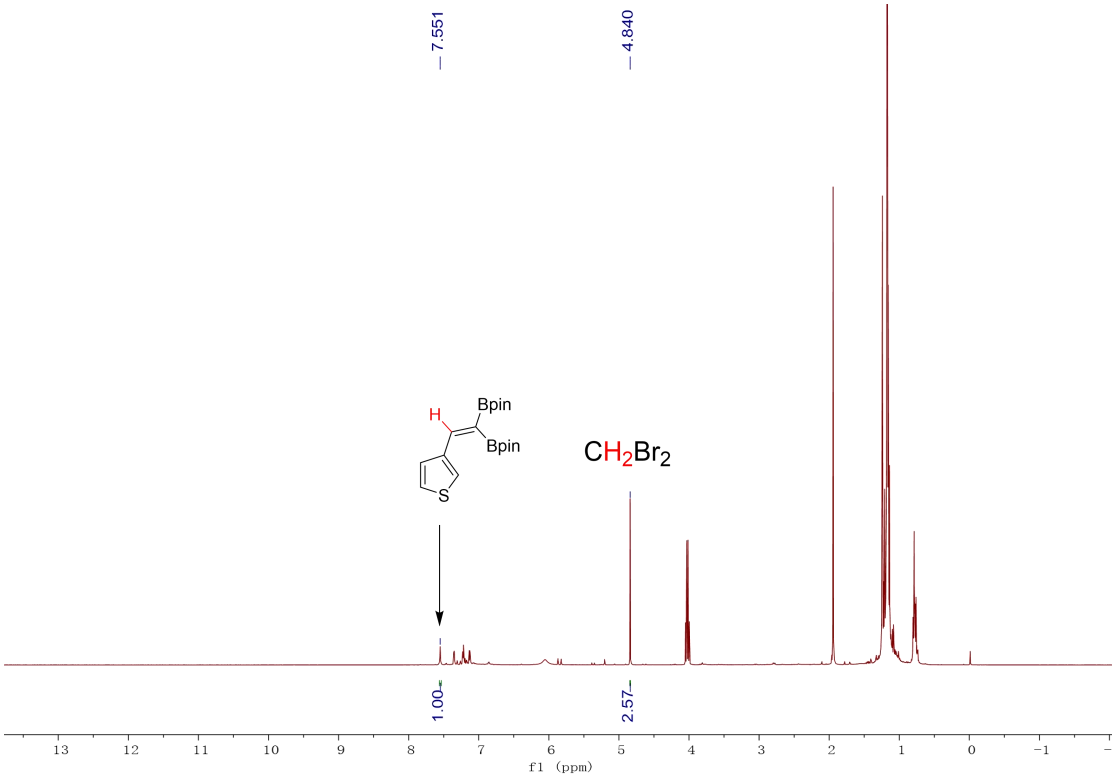



**Figure S12**. $^{1}$H NMR spectrum of the reaction of 3-ethynylthiophene with HBPin catalyzed by $Zn(OTf)_2$ affording **4j** with $CH_2Br_2$ (26.0 mg, 0.15 mmol) added as internal standard.

## 8. Reference


[1] Klare, H. F. T.; Oestreich, M.; Ito, J.-i.; Nishiyama, H.; Ohki, Y.; Tatsumi, K. *J. Am. Chem. Soc.* **2011**, *133*, 3312.

[2] Das, D.; Bhutia, Z. T.; Chatterjee, A.; Banerjee, M. *J. Org. Chem.* **2019**, *84*, 10764.

[3] Ramgren, S. D.; Hie, L.; Ye, Y. X.; Garg, N. K. *Org. Lett*. **2013**, *15*, 3950.

[4] Wang, T. C.; Wei, J. Z.; Guo, C. S.; Zhang, H. B.; Fan, H. X. *Chinese. Chem. Lett*. **2010**, *21*, 1407.

[5] Prieto, M.; Zurita, E.; Rosa, E.; Munoz, L.; Lloyd-Williams, P.; Giralt, E. *J. Org. Chem*. **2004**, *69*, 6812.

[6] Tian, Y. M.; Guo, X. N.; Wu, Z.; Friedrich, A.; Westcott, S. A.; Braunschweig, H.; Radius, U.; Marder, T. B. *J. Am. Chem. Soc*. **2020**, *142,* 13136.

[7] Stahl, T.; Muther, K.; Ohki, Y.; Tatsumi, K.; Oesteich, M. *J. Am. Chem. Soc*. **2013**, *135,* 10978.

[8] Jayaraman, A.; Fontaine, F. G. *Org. Process. Res. Dev.* **2018**, *22*, 1489.

[9] Rochette, É.; Desrosiers, V.; Soltani, Y.; Fontaine, F. G. *J. Am. Chem. Soc*. **2019**, *141*, 12305.

[10] Vasquez-Cespedes, S.; Chepiga, K. M.; Moller, N.; Schaefer, A. H.; Glorius, F.; *ACS Catal.* **2016***, 6,* 5954.

[11] Wen, H. N.; Zhang, L.; Zhu, S. Z.; Liu, G. X.; Huang, Z. *ACS Catal.* **2017**, *7*, 6419−6425.

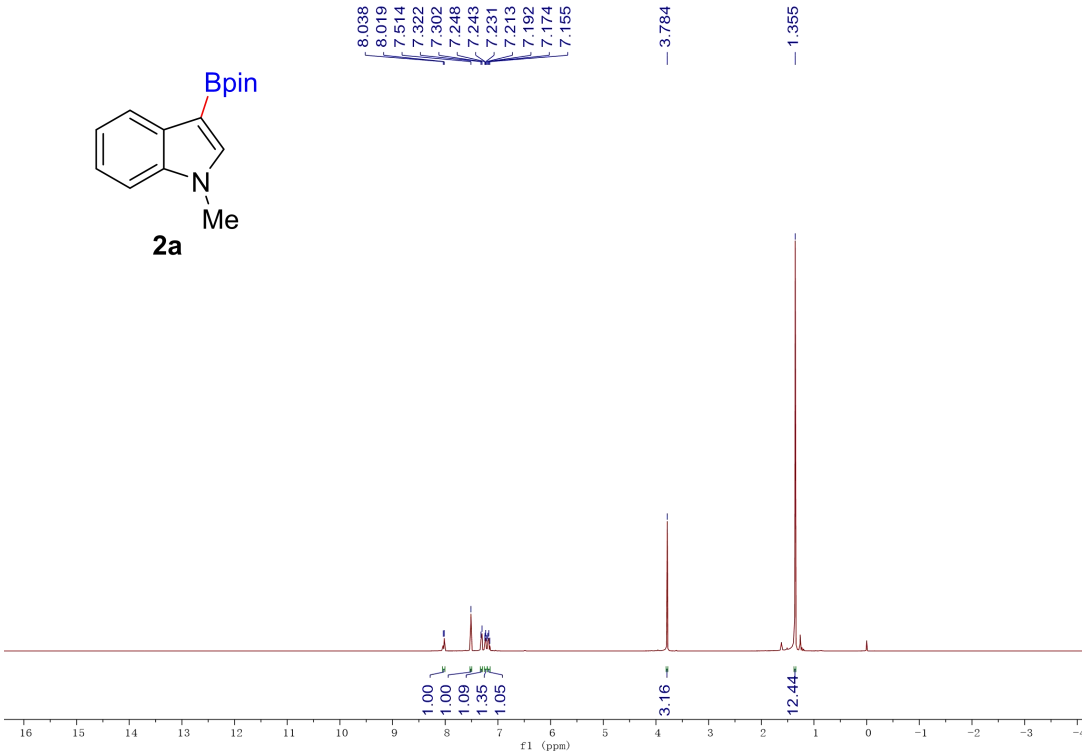
[12] Tao, L.; Guo, X. Y.; Li, J.; Li, R. L.; Lin, Z. Y.; Zhao, W. X. *J. Am. Chem. Soc.* **2020**, *142*, 18118−18127.

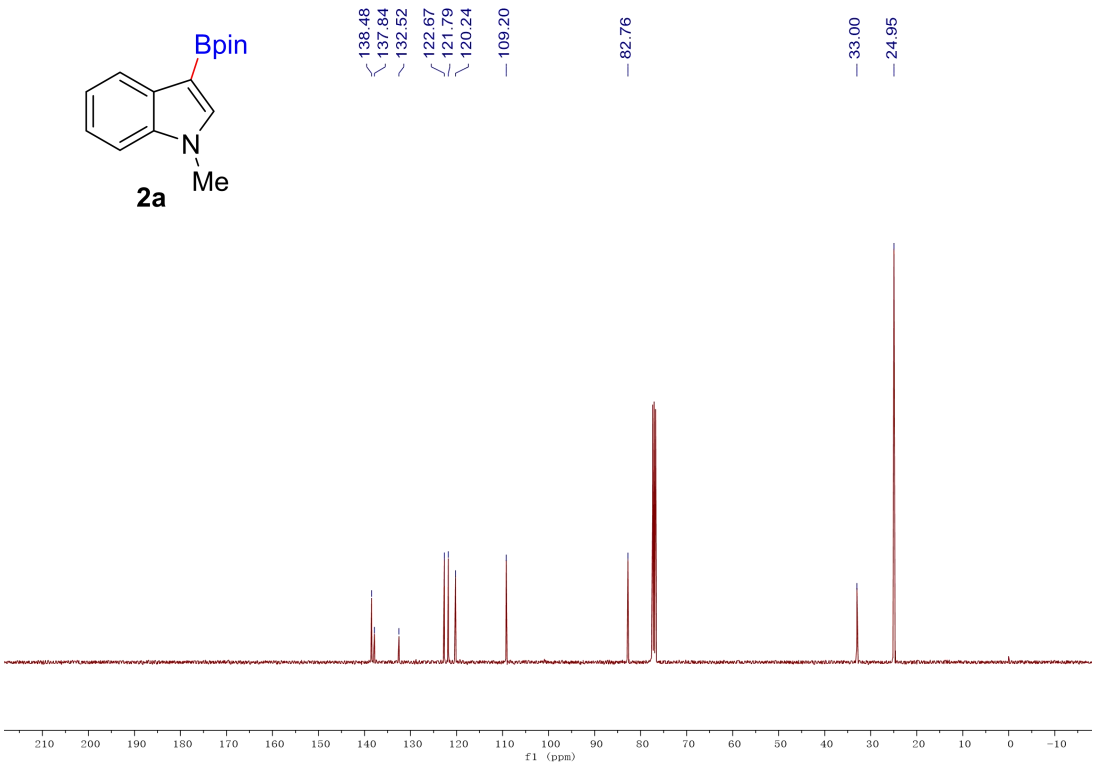
[13] Procter, R. J.; Uzelac, M.; Cid, J.; Rushworth, P. J.; Ingleson, M. J. *ACS Catal.* **2019**, *9*, 5760−5771.

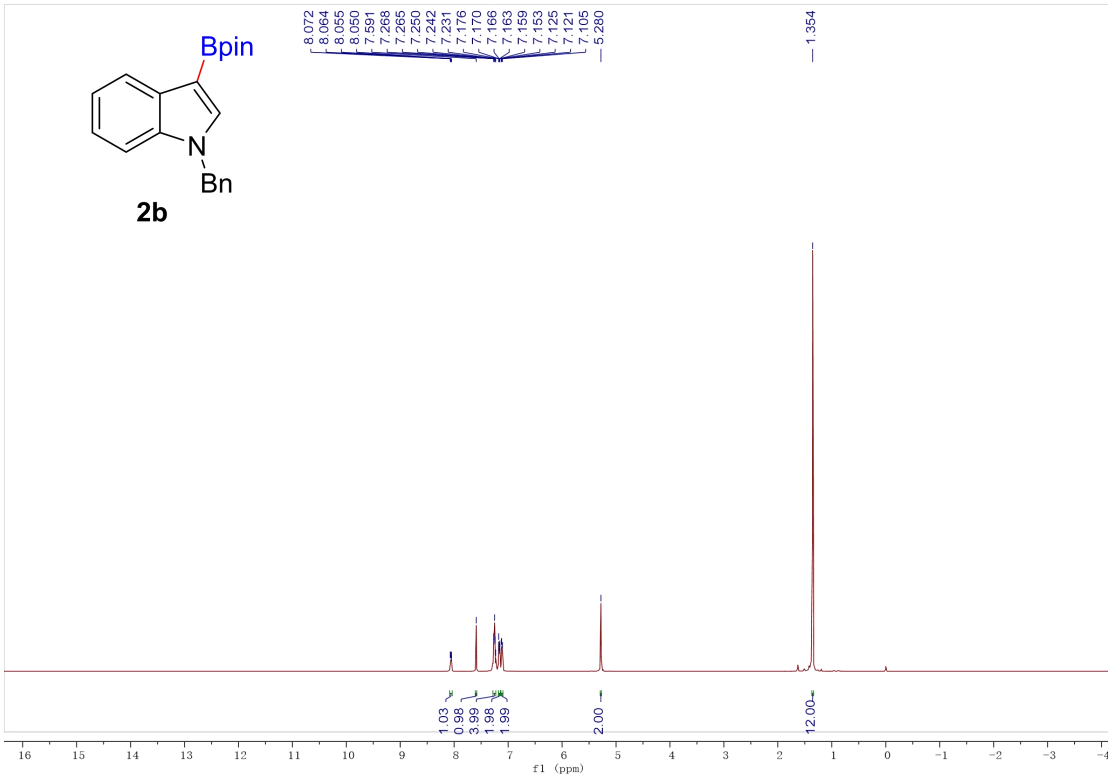
[14] Wang, X. J.; Cui, X.; Li, S.; Wang, W.; Xia, C. G.; Jiao, H. J.; Wu, L. P. *Angew. Chem. Int. Ed.* **2020**, *59*, 13608 – 13612.

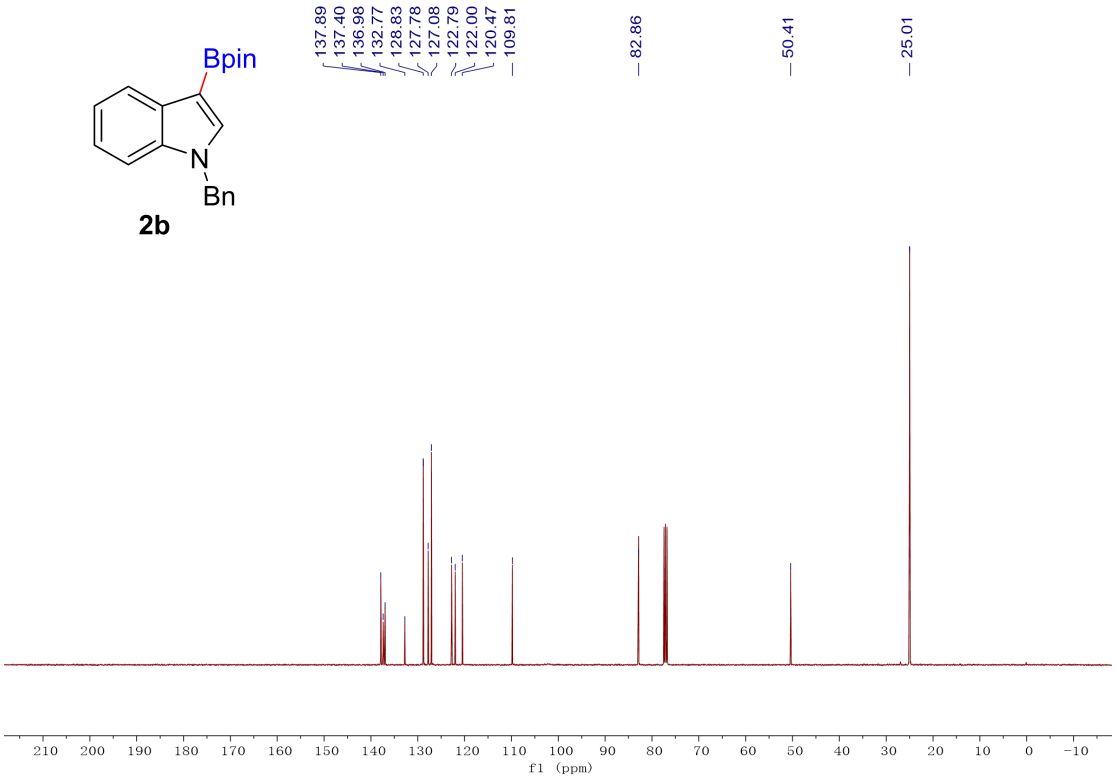
[15] Gao, G. L.; Kuang, Z. J.; Song, Q. L. *Org. Chem. Front.* **2018**, *5*, 2249.

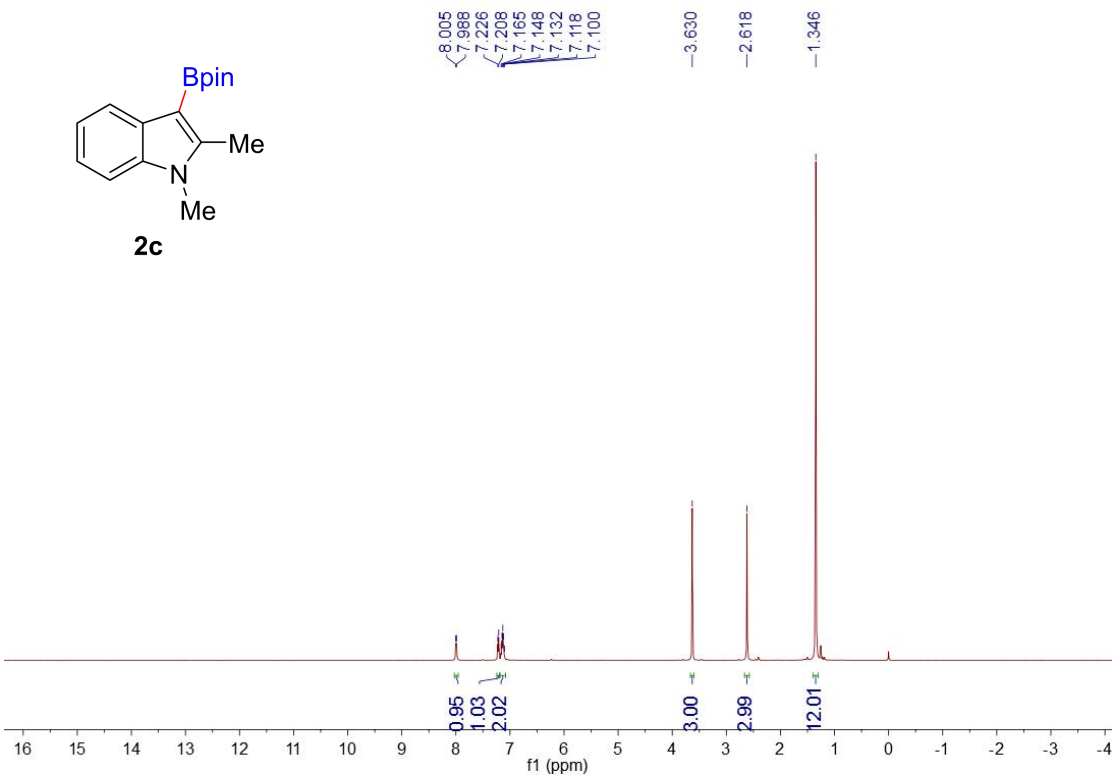
## 9. NMR spectra of products

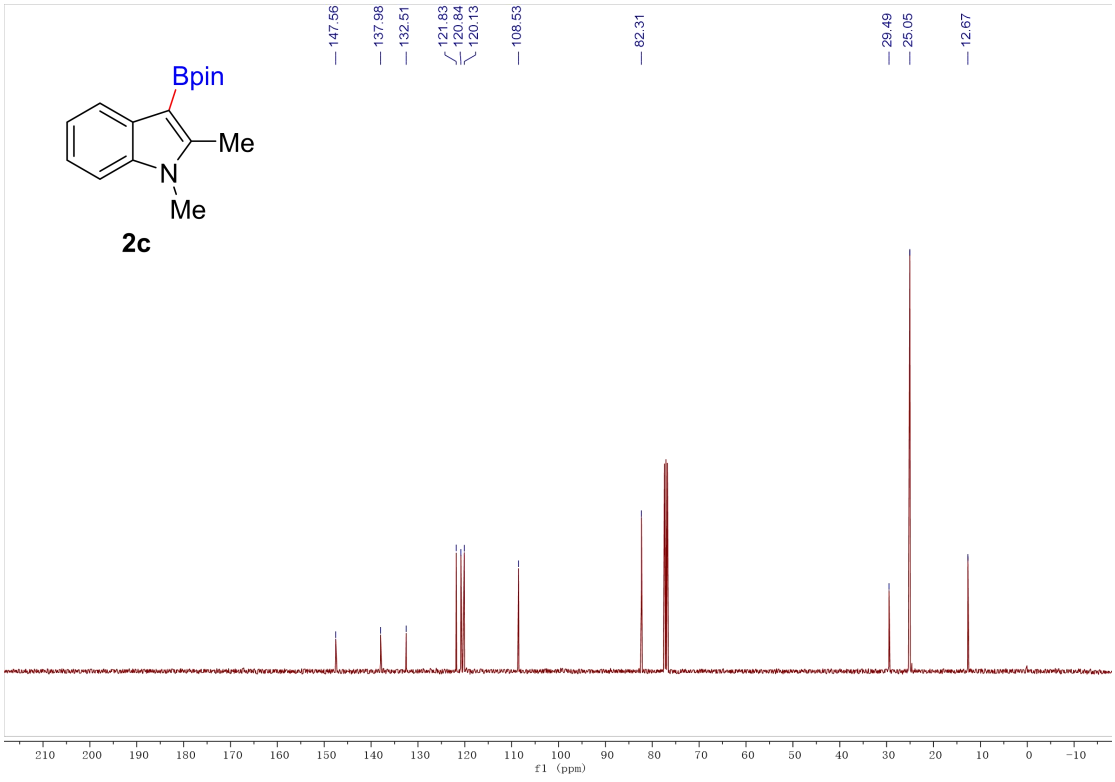


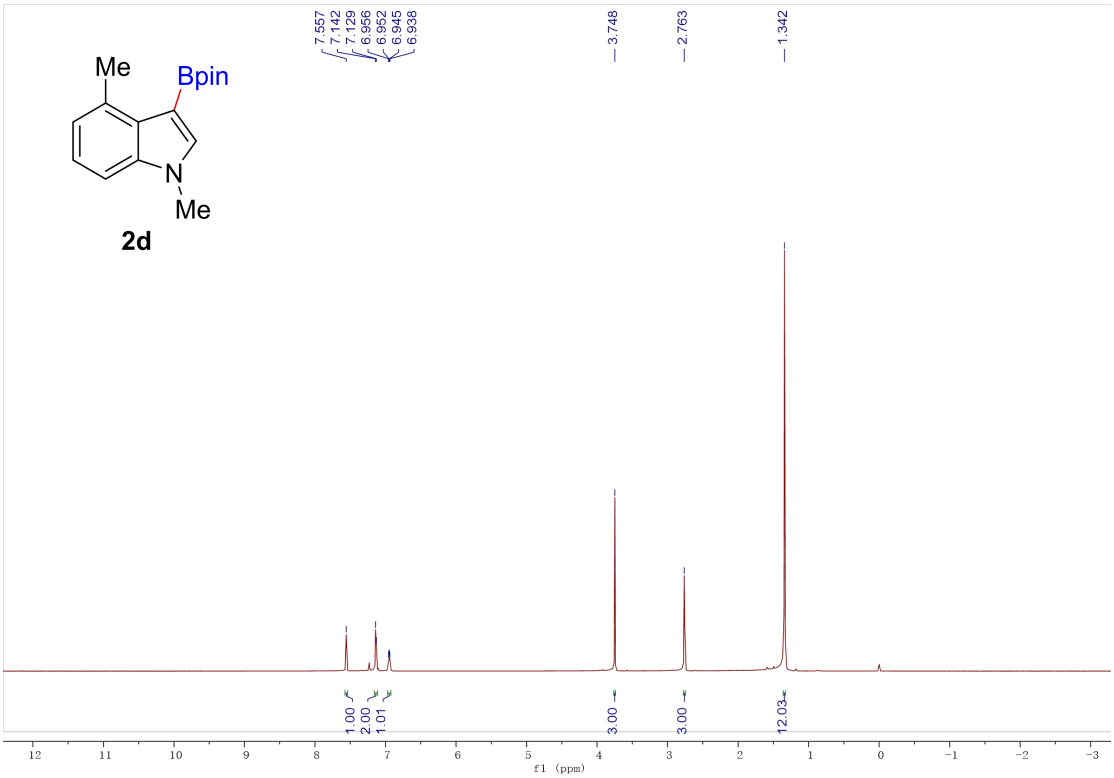



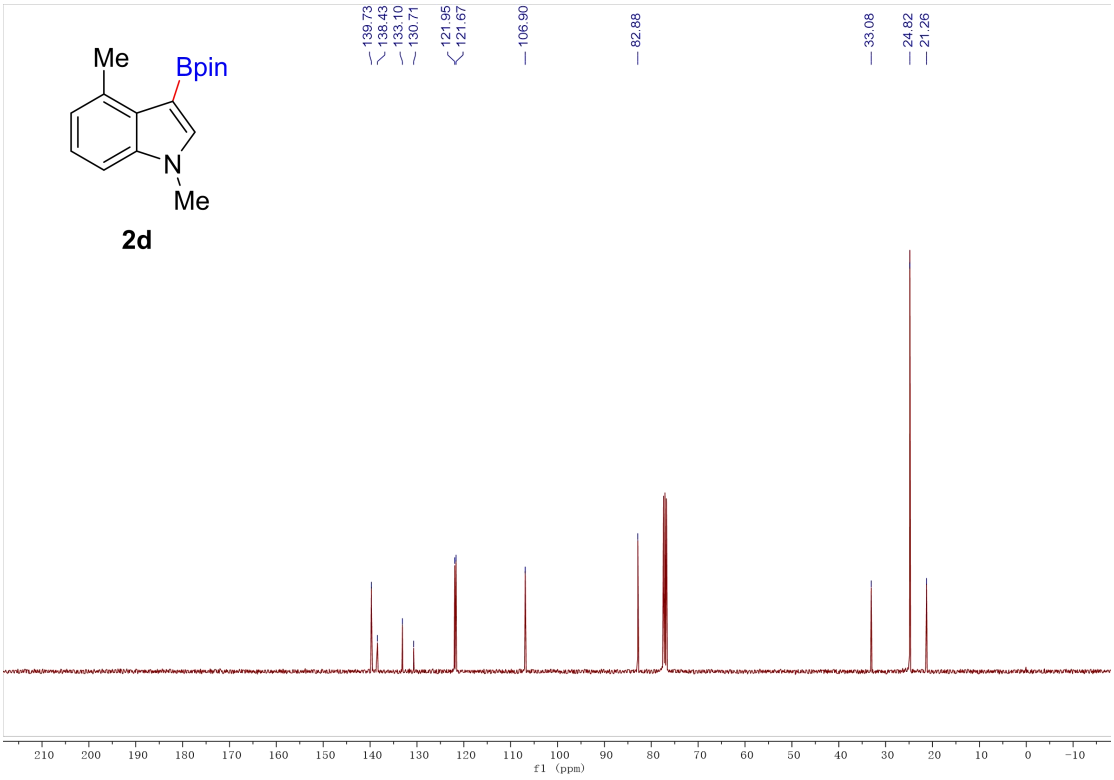

Bpin
N
Bn
2b
8.072
8.064
8.055
8.050
7.591
7.268
7.265
7.250
7.242
7.231
7.176
7.170
7.166
7.163
7.159
7.153
7.125
7.121
7.105
5.280
1.354
1.03
0.98
3.99
1.98
1.99
2.00
12.00
f1 (ppm)

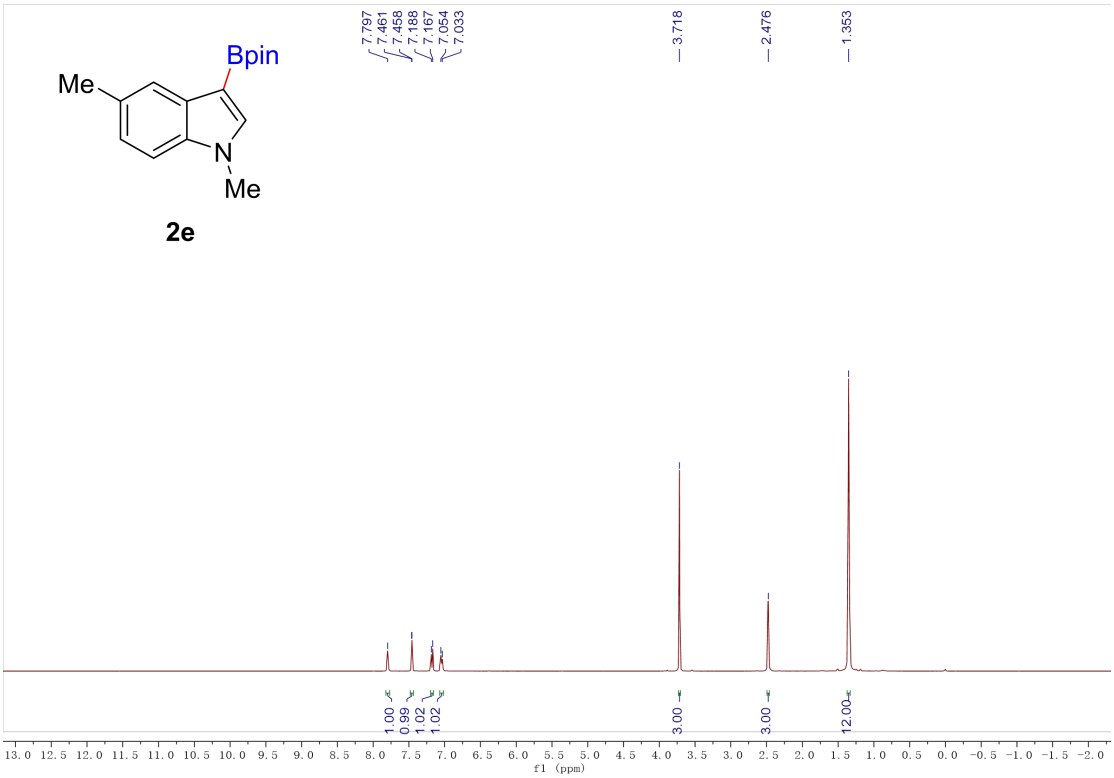

Bpin
N
Bn
2b
137.89
137.40
136.98
132.77
128.83
127.78
127.08
122.79
122.00
120.47
109.81
82.86
50.41
25.01
f1 (ppm)

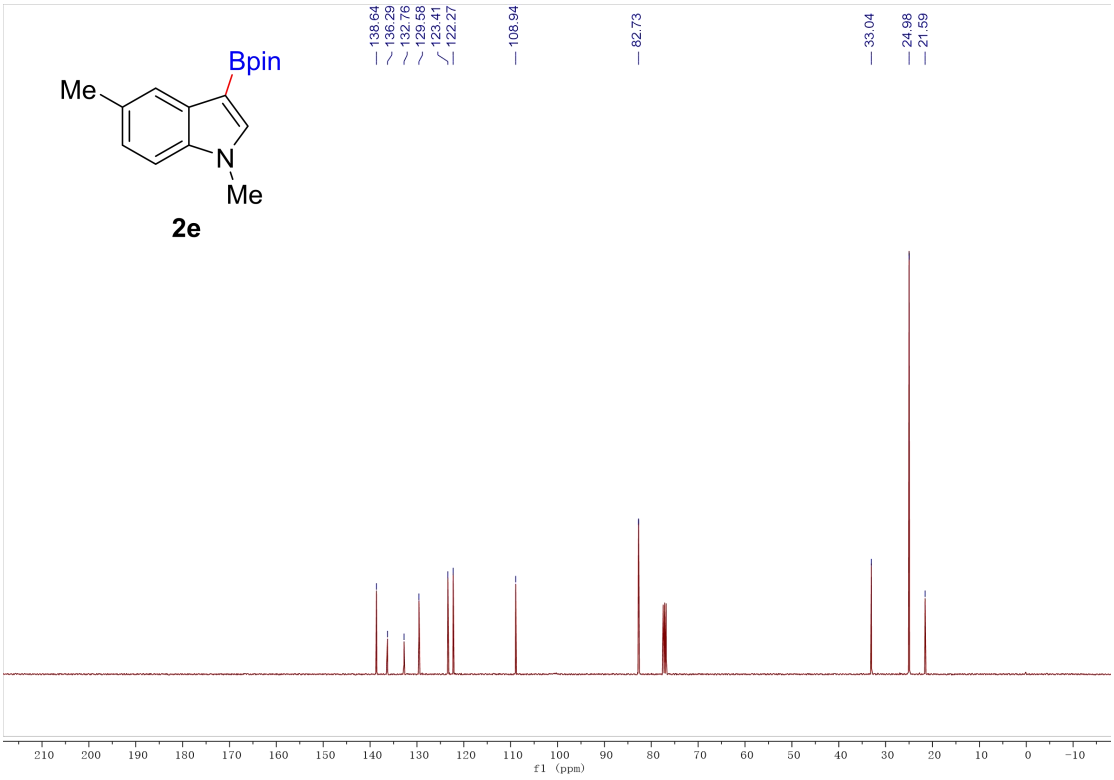

Bpin
Me
N
Me
2c
8.005
7.988
7.226
7.208
7.165
7.148
7.132
7.118
7.100
3.630
2.618
1.346
0.95
1.03
2.02
3.00
2.99
12.01
f1 (ppm)

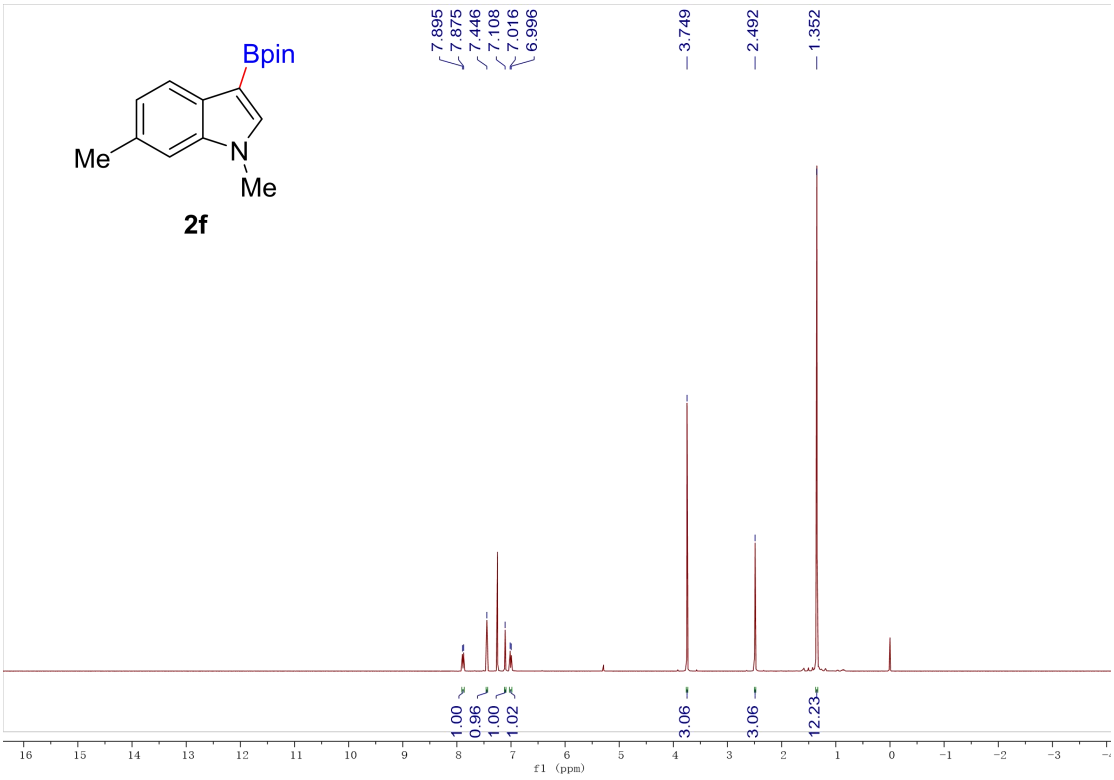

Bpin
Me
N
Me
2c
147.56
137.98
132.51
121.83
120.84
120.13
108.53
82.31
29.49
25.05
12.67
f1 (ppm)

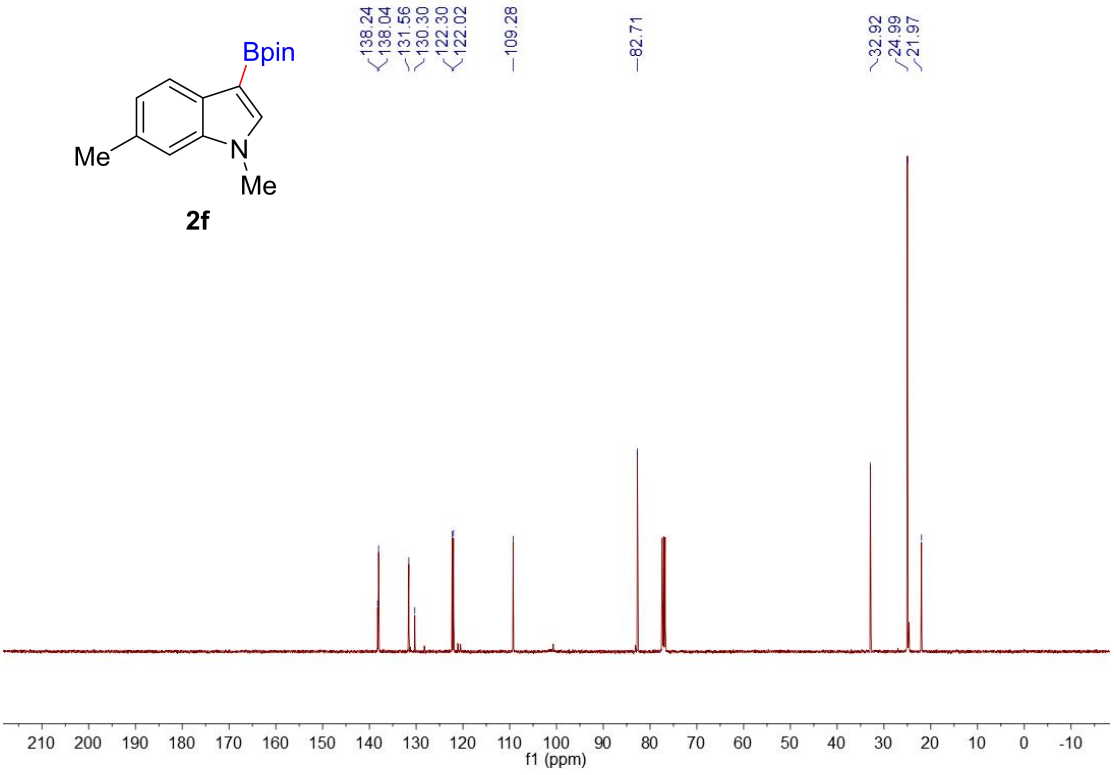

Me
Bpin
N
Me
2d
7.557
7.142
7.129
6.956
6.952
6.945
6.938
3.748
2.763
1.342
1.00
2.00
1.01
3.00
3.00
12.03
f1 (ppm)

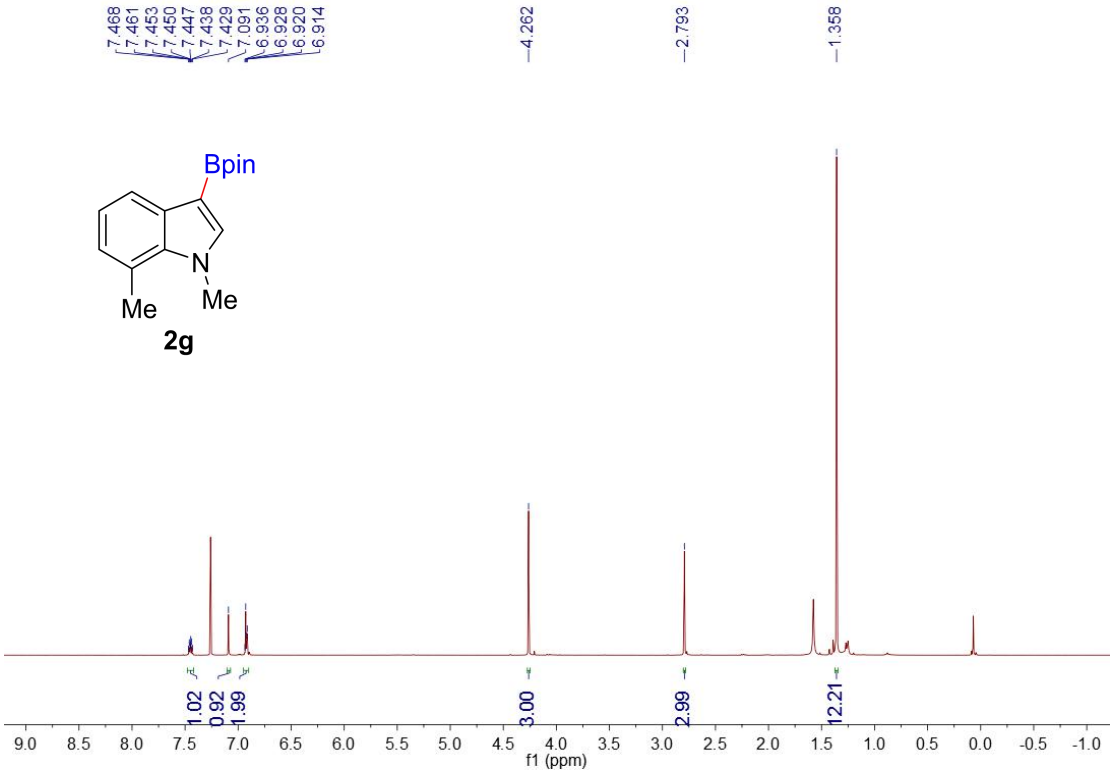

Me
Bpin
N
Me
2d
139.73
138.43
133.10
130.71
121.95
121.67
106.90
82.88
33.08
24.82
21.26
f1 (ppm)

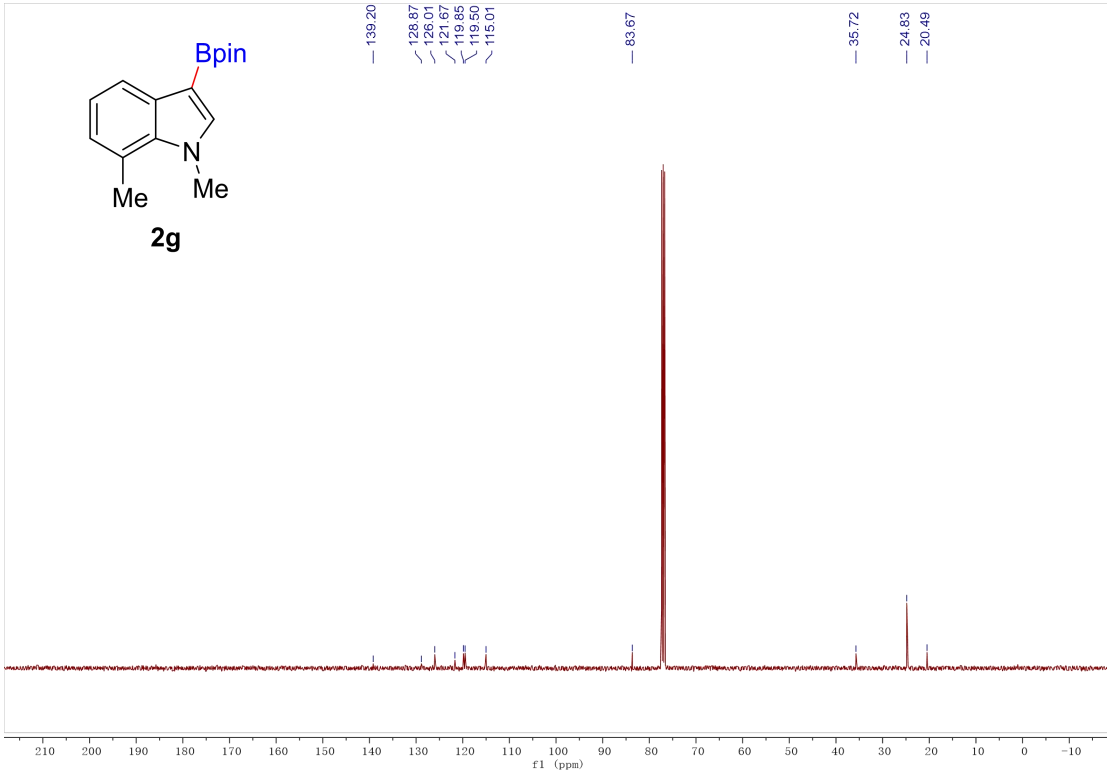

Bpin
Me
N
Me
2e
7.797
7.461
7.458
7.188
7.167
7.054
7.033
3.718
2.476
1.353
1.00
0.99
1.02
1.02
3.00
3.00
12.00
f1 (ppm)

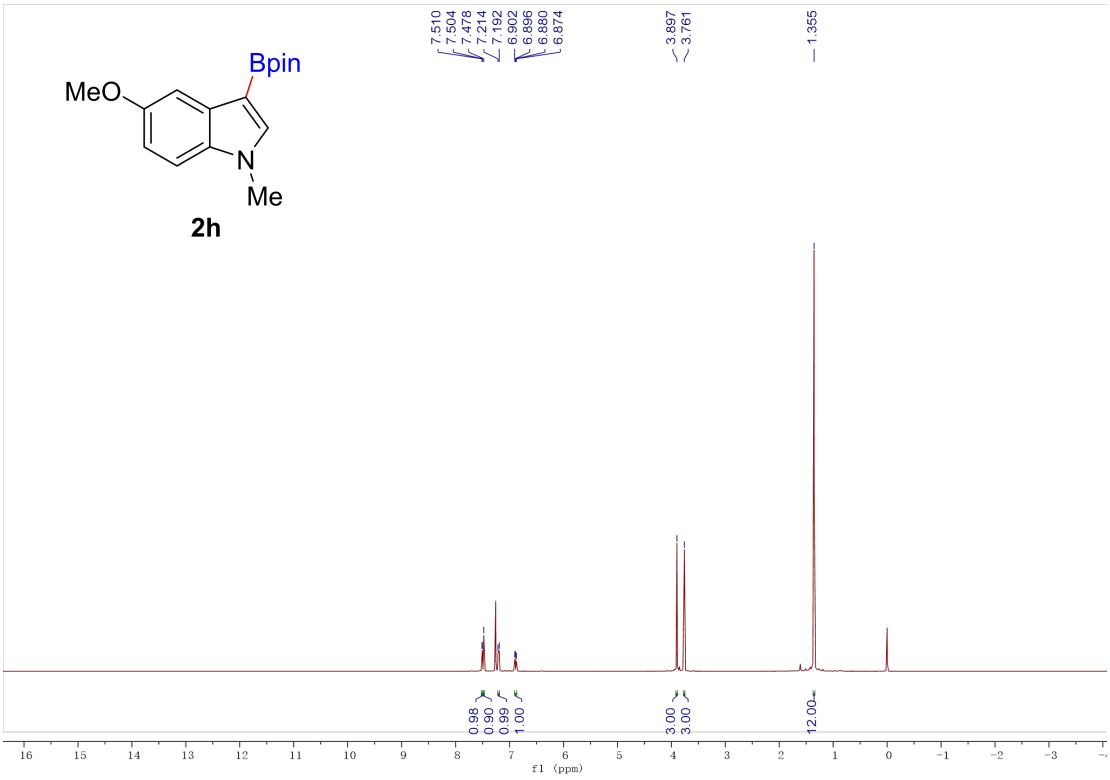

Bpin
Me
N
Me
2e
138.64
136.29
132.76
129.58
123.41
122.27
108.94
82.73
33.04
24.98
21.59
f1 (ppm)

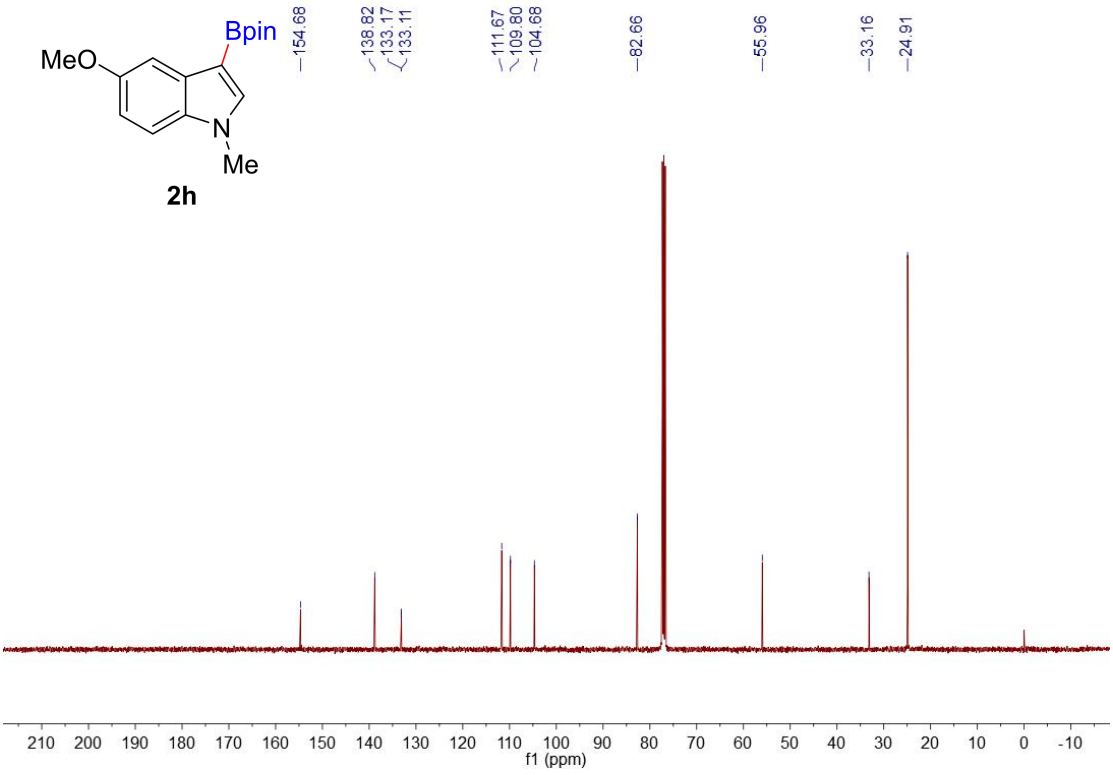

Bpin
Me
N
Me
2f
7.895
7.875
7.446
7.108
7.016
6.996
3.749
2.492
1.352
1.00
0.96
1.00
1.02
3.06
3.06
12.23
f1 (ppm)

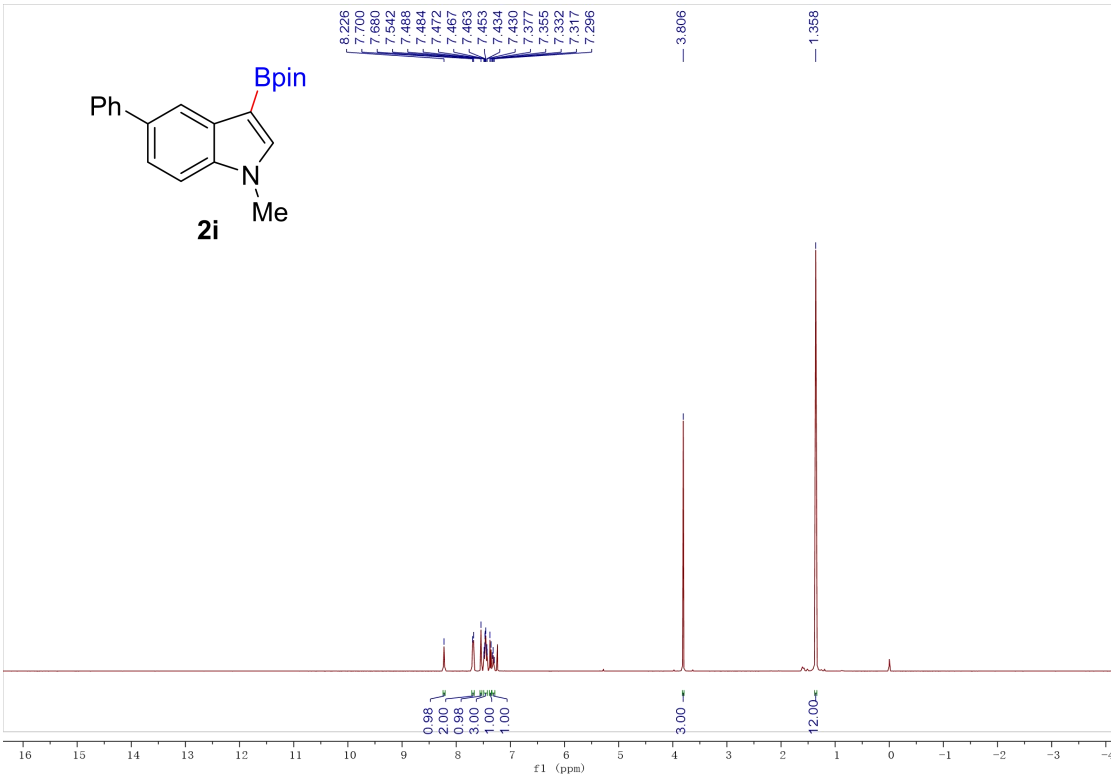

Bpin
Me
N
Me
2f
138.24
138.04
131.56
130.30
122.30
122.02
109.28
82.71
32.92
24.99
21.97
f1 (ppm)

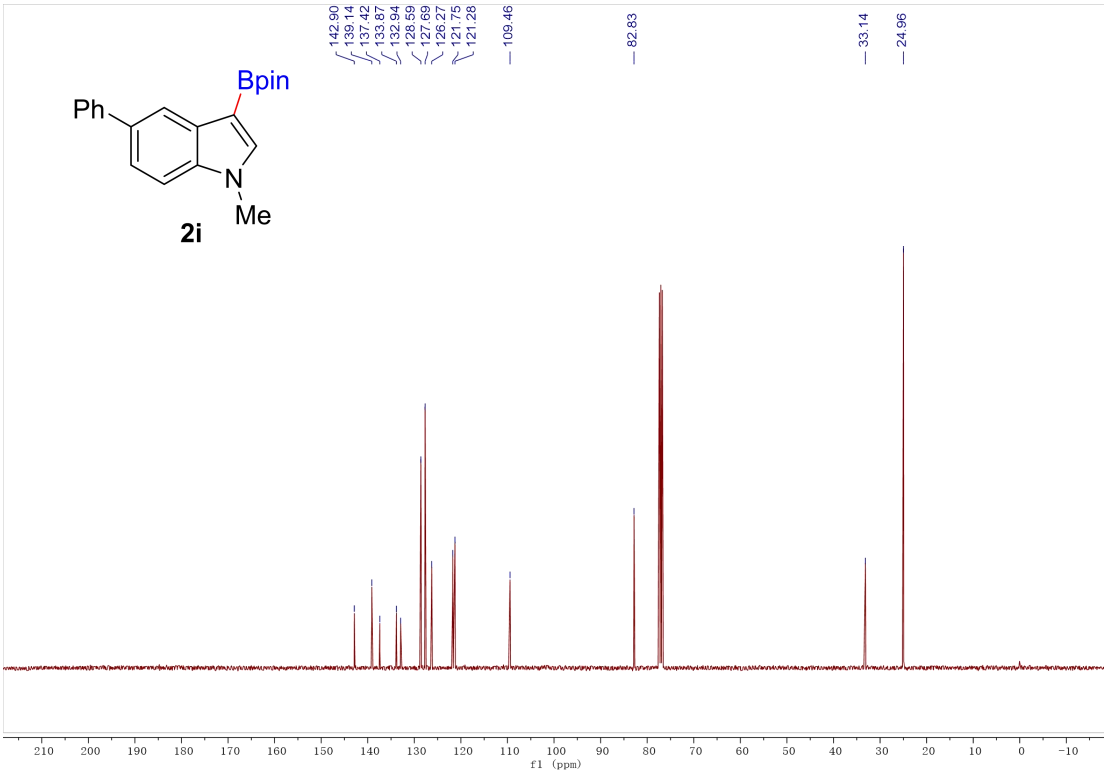

7.468
7.461
7.453
7.450
7.447
7.438
7.429
7.091
6.936
6.928
6.920
6.914
4.262
2.793
1.358
Bpin
N
Me
Me
2g
1.02
0.92
1.99
3.00
2.99
12.21
f1 (ppm)

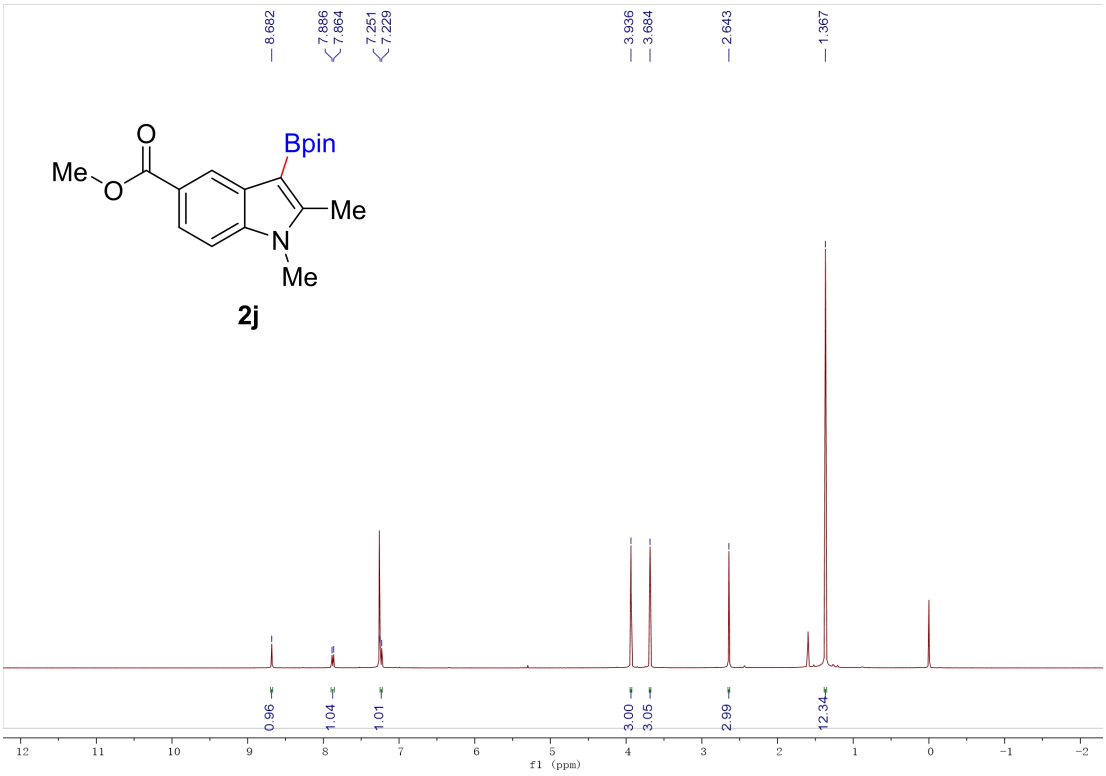

139.20
128.87
126.01
121.67
119.85
119.50
115.01
83.67
35.72
24.83
20.49
Bpin
N
Me
Me
2g
f1 (ppm)


Bpin
MeO
N
Me
2h
7.510
7.504
7.478
7.214
7.192
6.902
6.896
6.880
6.874
3.897
3.761
1.355
0.98
0.90
0.99
1.00
3.00
3.00
12.00
f1 (ppm)

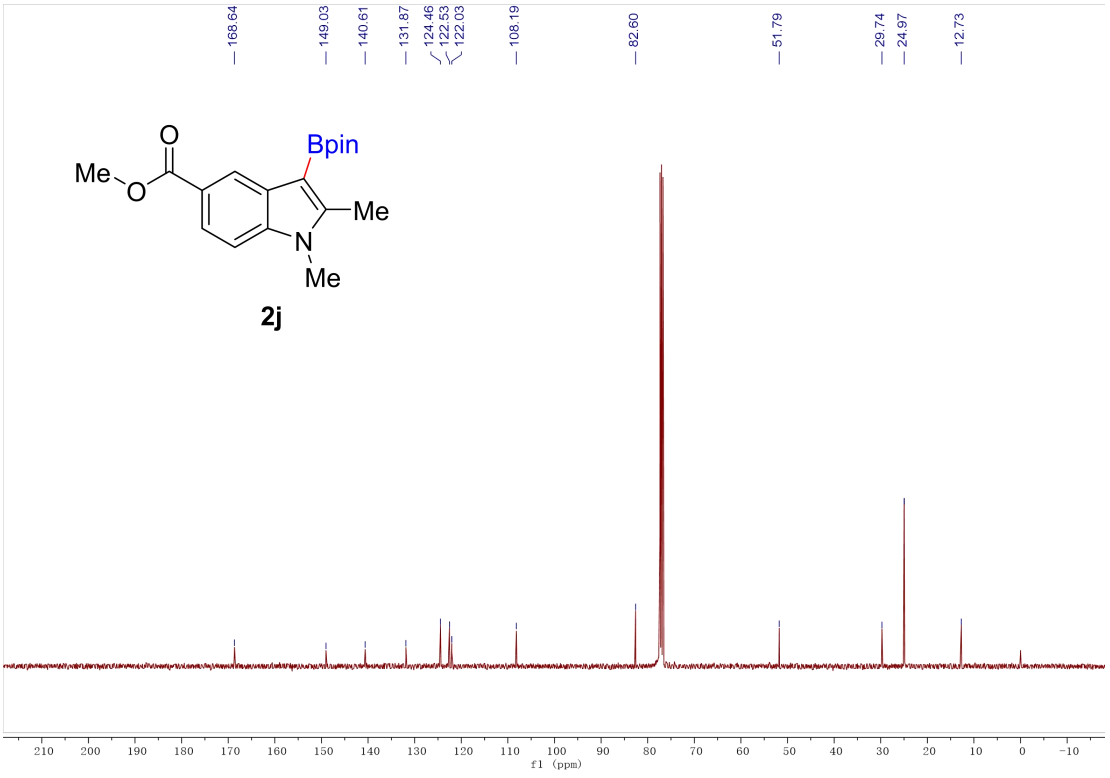

Bpin
MeO
N
Me
2h
154.68
138.82
133.17
133.11
111.67
109.80
104.68
82.66
55.96
33.16
24.91
f1 (ppm)


8.226
7.700
7.680
7.542
7.488
7.484
7.472
7.467
7.463
7.453
7.434
7.430
7.377
7.355
7.332
7.317
7.296
3.806
1.358
Bpin
Ph
N
Me
2i
0.98
2.00
0.98
3.00
1.00
1.00
3.00
12.00
f1 (ppm)

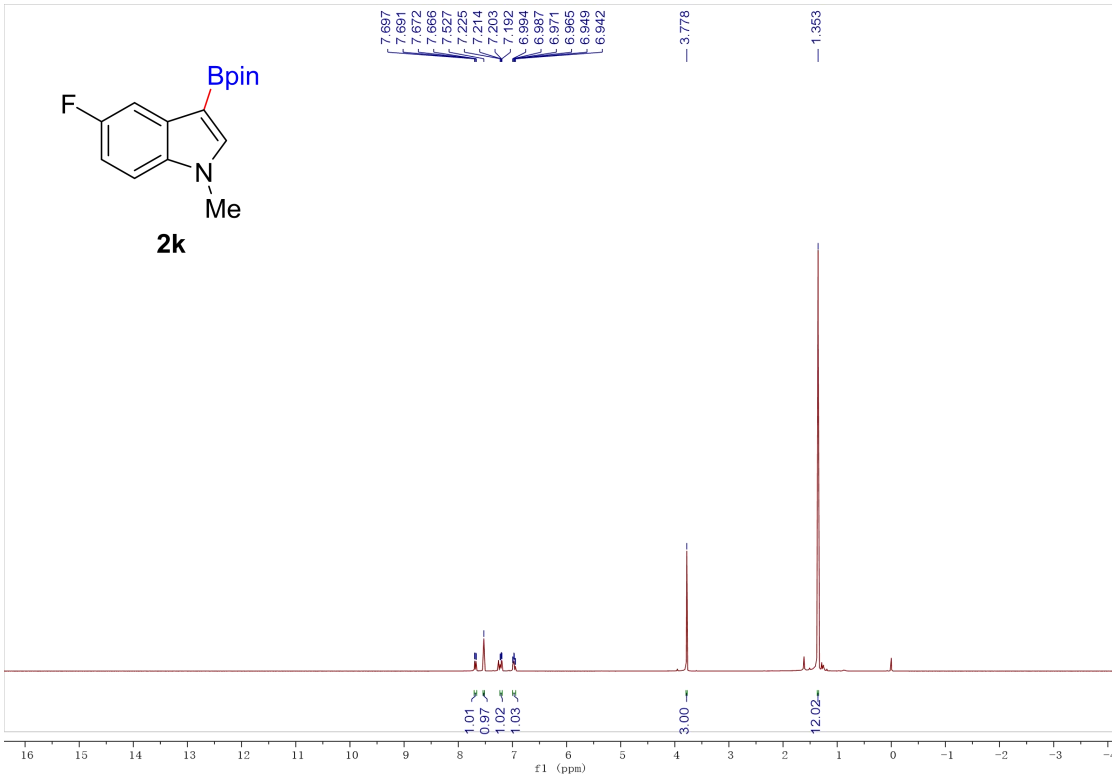

142.90
139.14
137.42
133.87
132.94
128.59
127.69
126.27
121.75
121.28
109.46
82.83
33.14
24.96
Bpin
Ph
N
Me
2i
f1 (ppm)

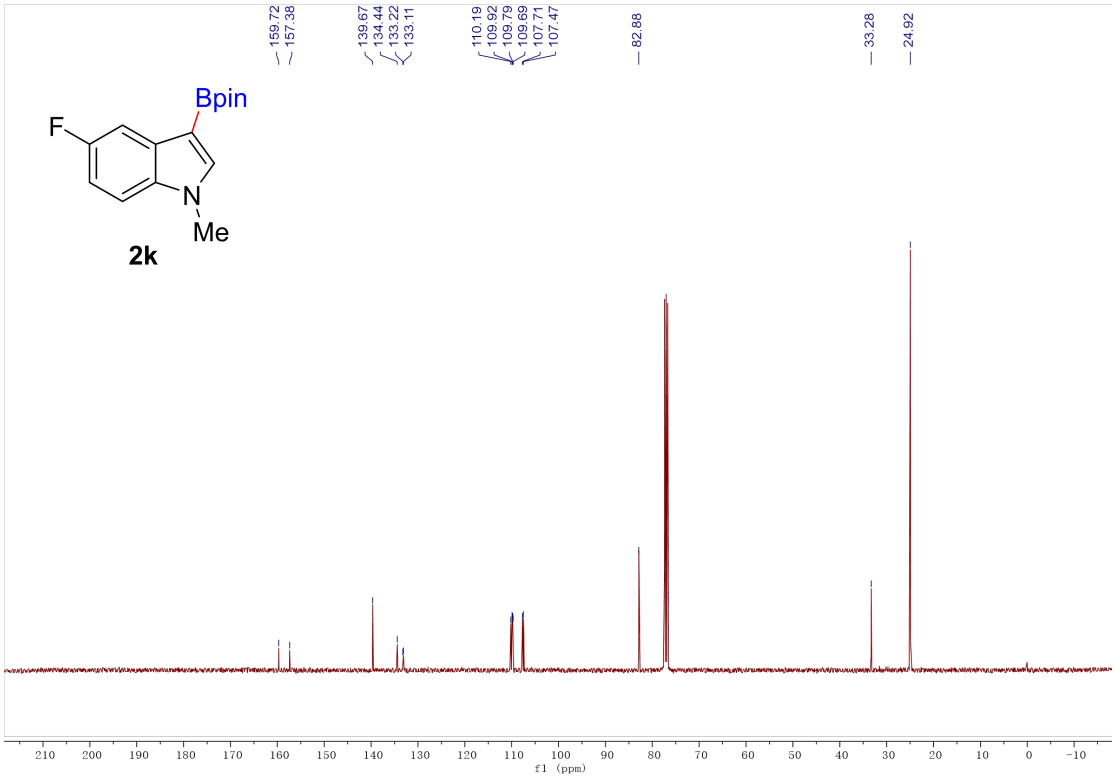

8.682
7.886
7.864
7.251
7.229
3.936
3.684
2.643
1.367
O
Me
O
Bpin
Me
N
Me
0.96
1.04
1.01
3.00
3.05
2.99
12.34
f1 (ppm)

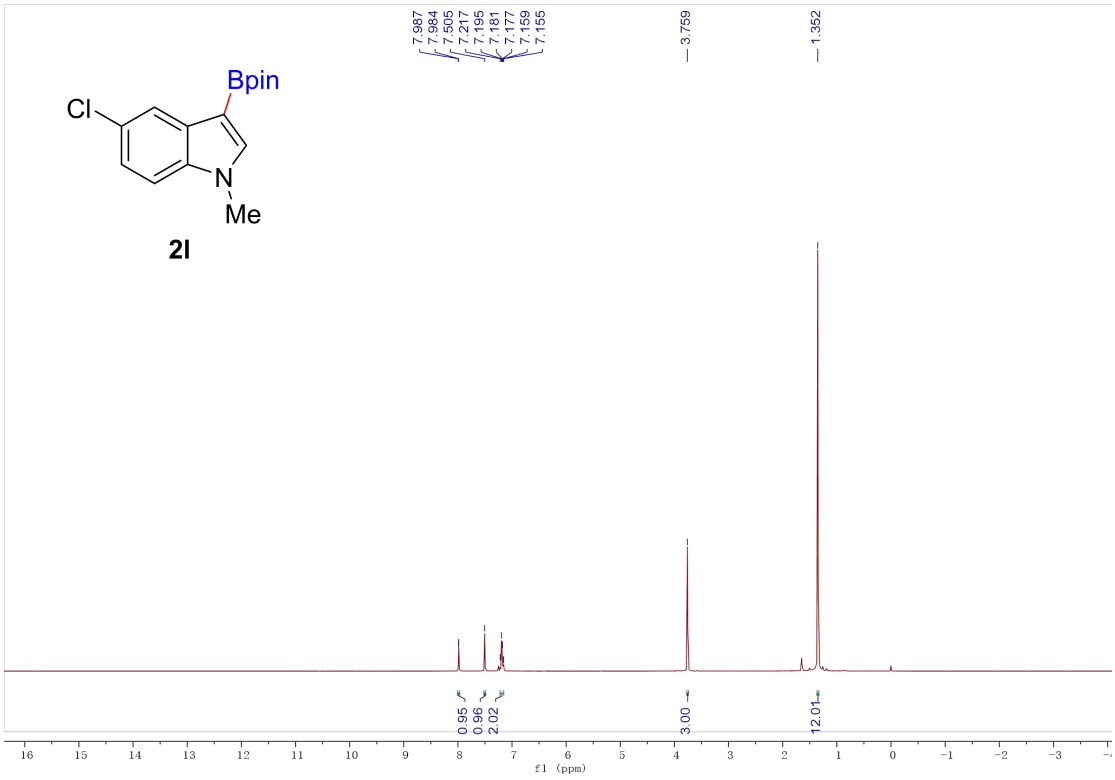
**2j**

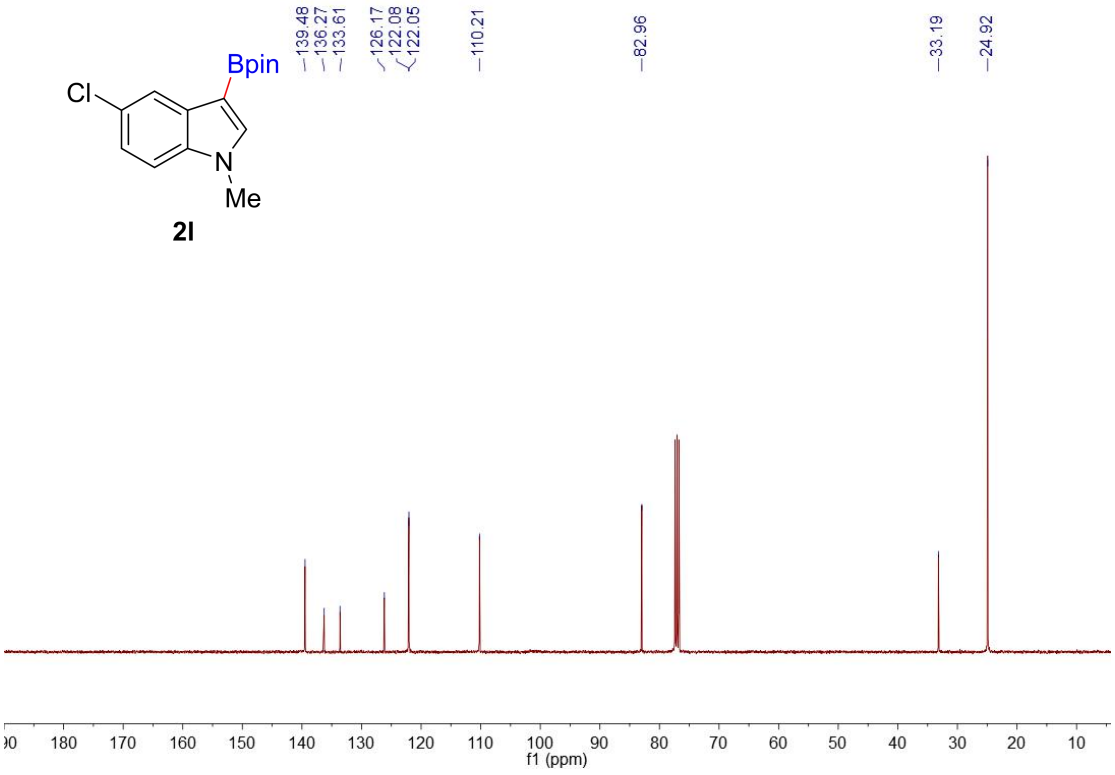

168.64
149.03
140.61
131.87
124.46
122.53
122.03
108.19
82.60
51.79
29.74
24.97
12.73
O
Me
O
Bpin
Me
N
Me
f1 (ppm)

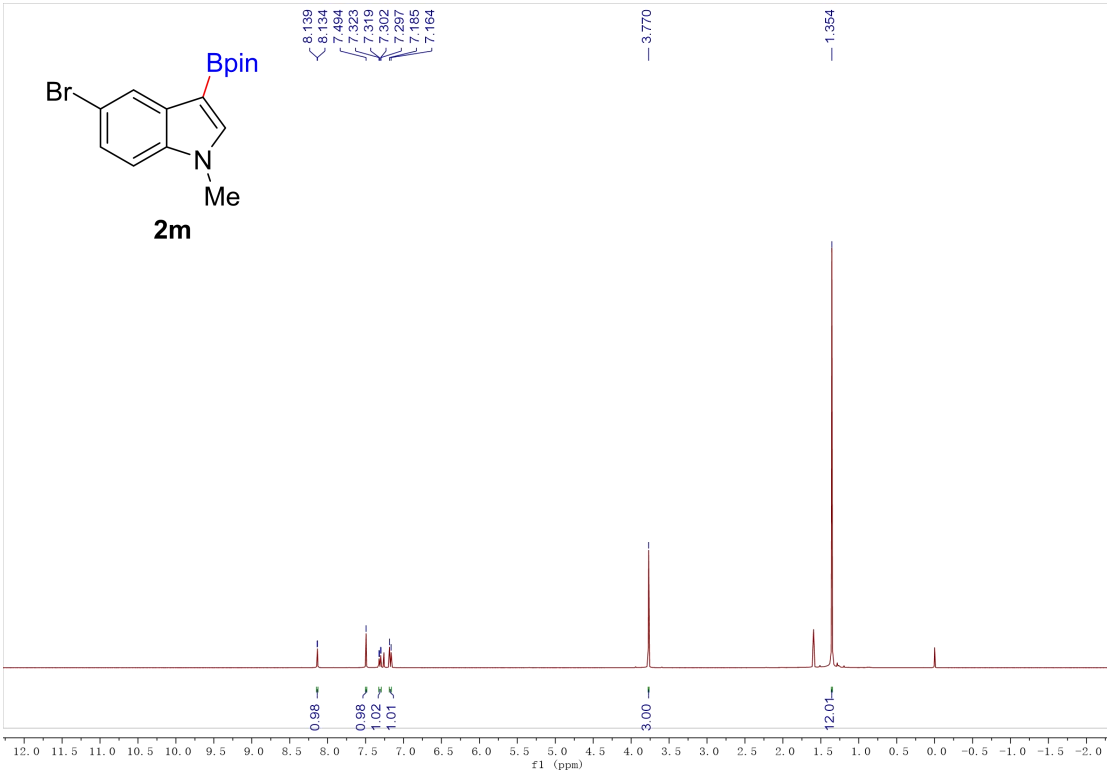
**2j**

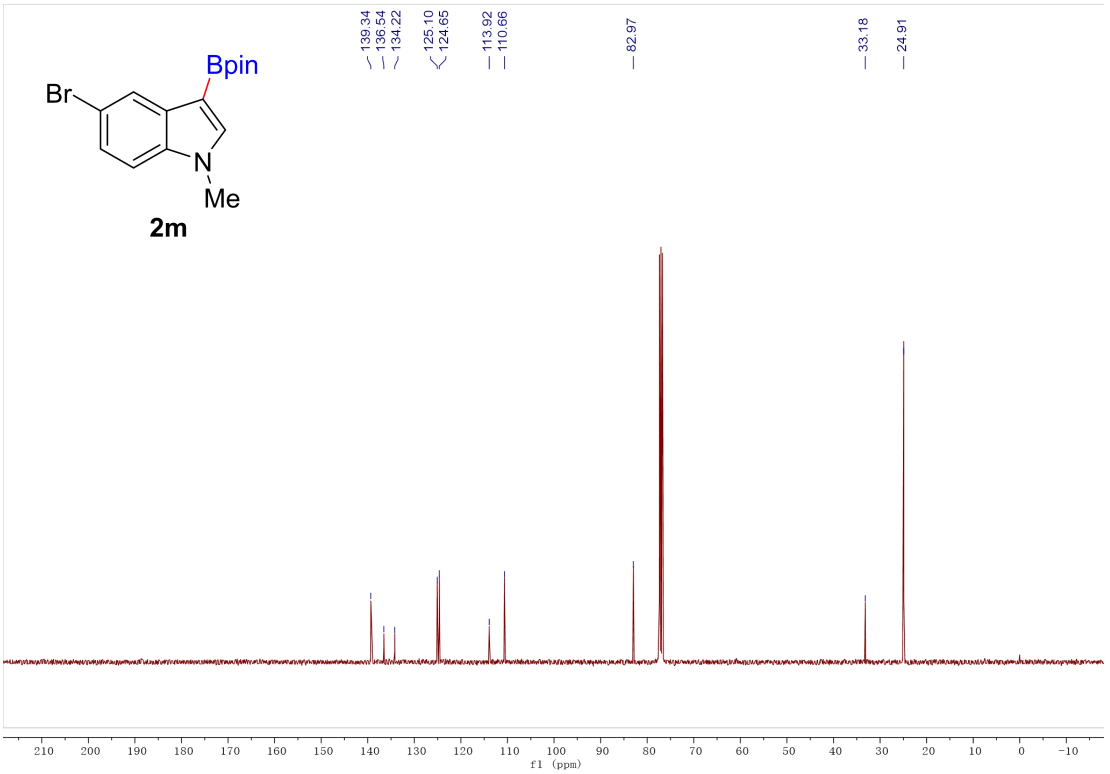

7.697
7.691
7.672
7.666
7.527
7.225
7.214
7.203
7.192
6.994
6.987
6.971
6.965
6.949
6.942
3.778
1.353
Bpin
F
N
Me
2k
1.01
0.97
1.02
1.03
3.00
12.02
f1 (ppm)

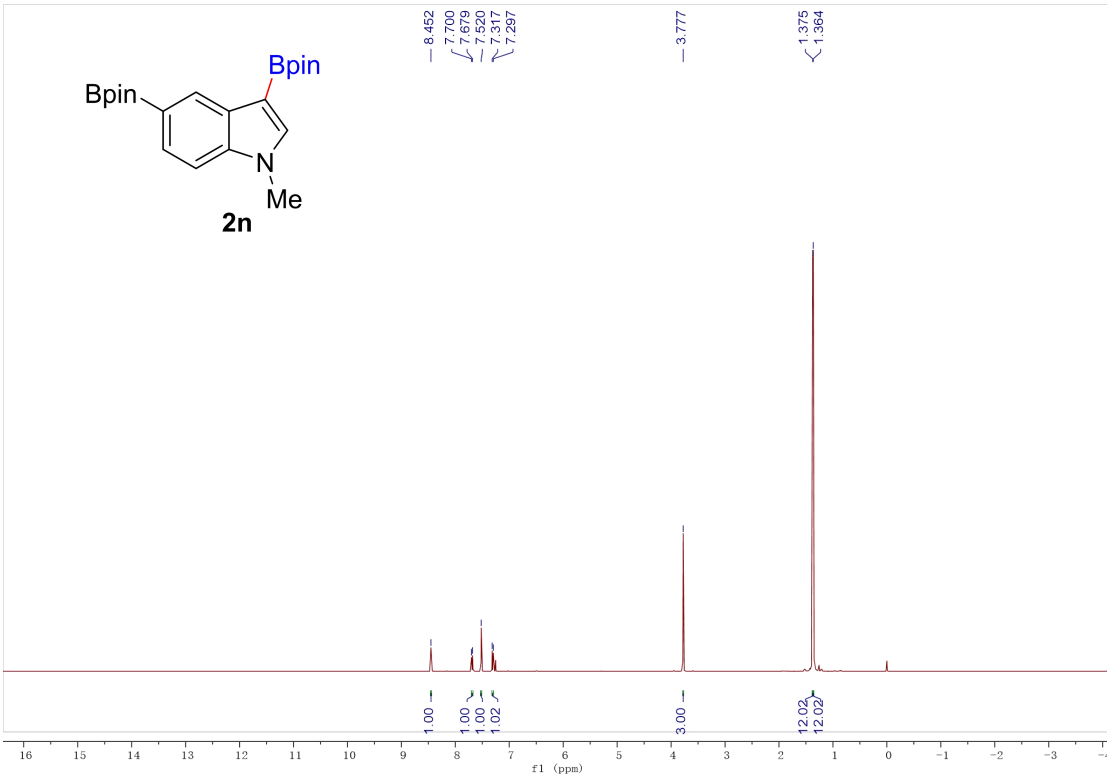

159.72
157.38
139.67
134.44
133.22
133.11
110.19
109.92
109.79
109.69
107.71
107.47
82.88
33.28
24.92
Bpin
F
N
Me
2k
f1 (ppm)

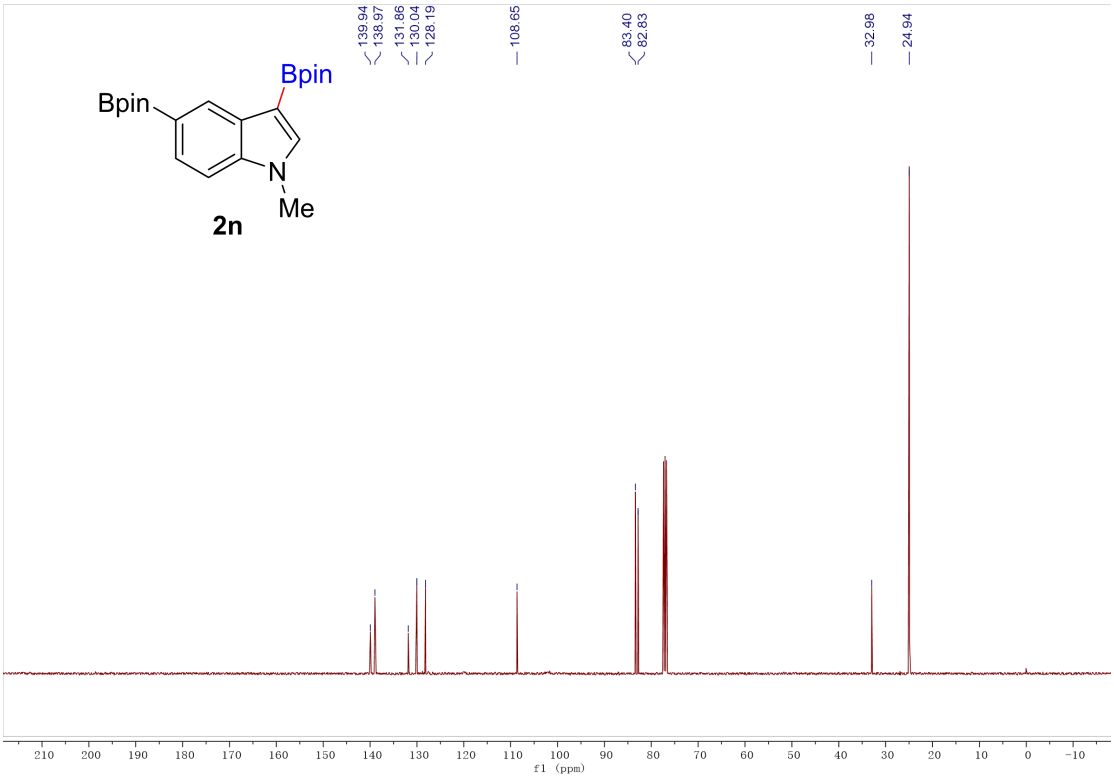

Bpin
Cl
N
Me
2l
7.987
7.984
7.505
7.217
7.195
7.181
7.177
7.159
7.155
3.759
1.352
0.95
0.96
2.02
3.00
12.01
f1 (ppm)

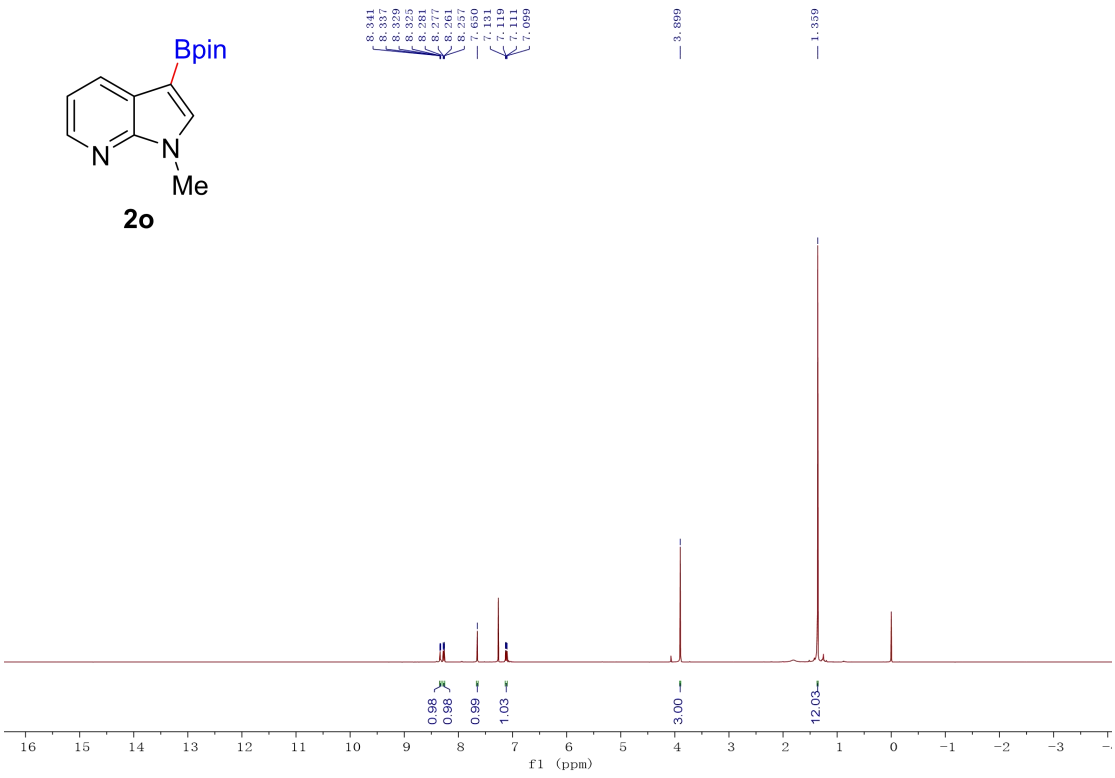

Bpin
Cl
N
Me
2l
139.48
136.27
133.61
126.17
122.08
122.05
110.21
82.96
33.19
24.92
f1 (ppm)

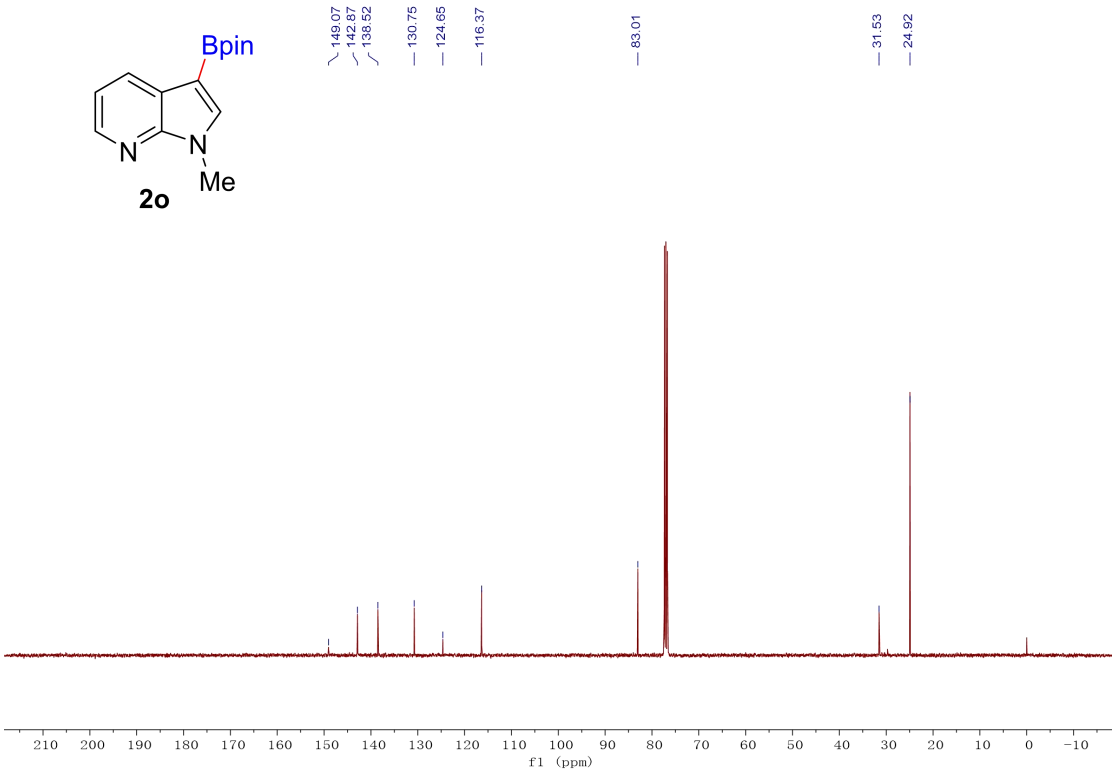

Bpin
Br
N
Me
2m
8.139
8.134
7.494
7.323
7.319
7.302
7.297
7.185
7.164
3.770
1.354
0.98
0.98
1.02
1.01
3.00
12.01
f1 (ppm)

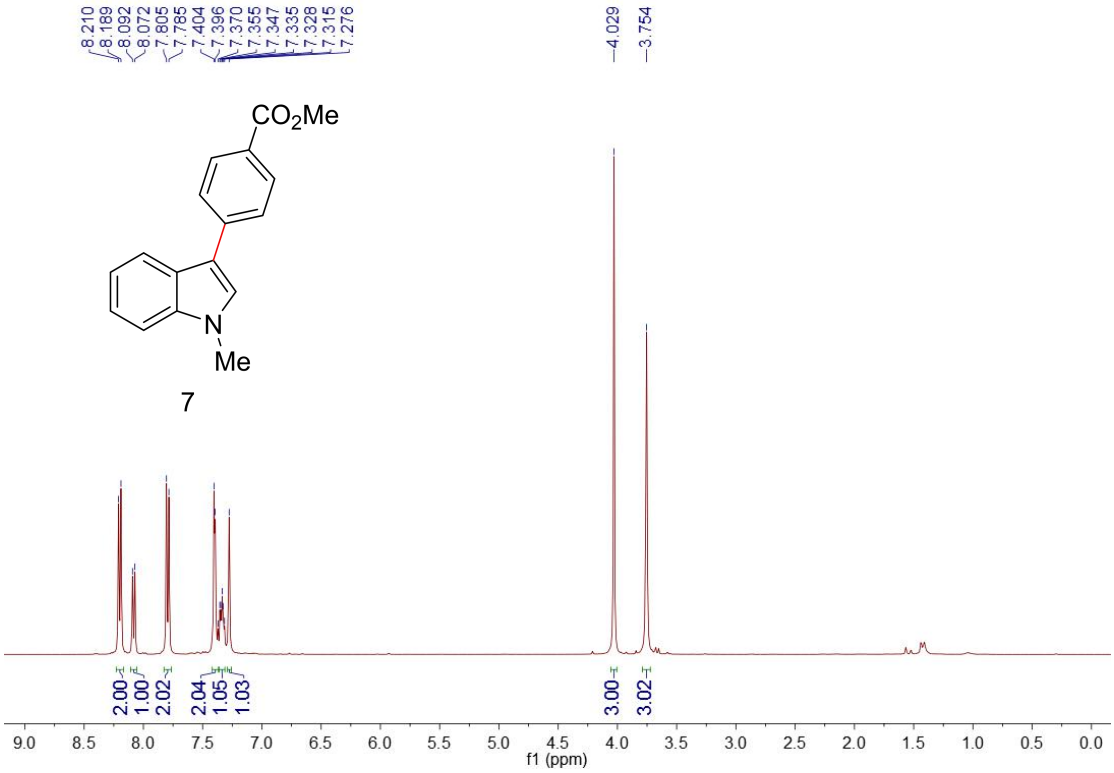

Bpin
Br
N
Me
2m
139.34
136.54
134.22
125.10
124.65
113.92
110.66
82.97
33.18
24.91
f1 (ppm)

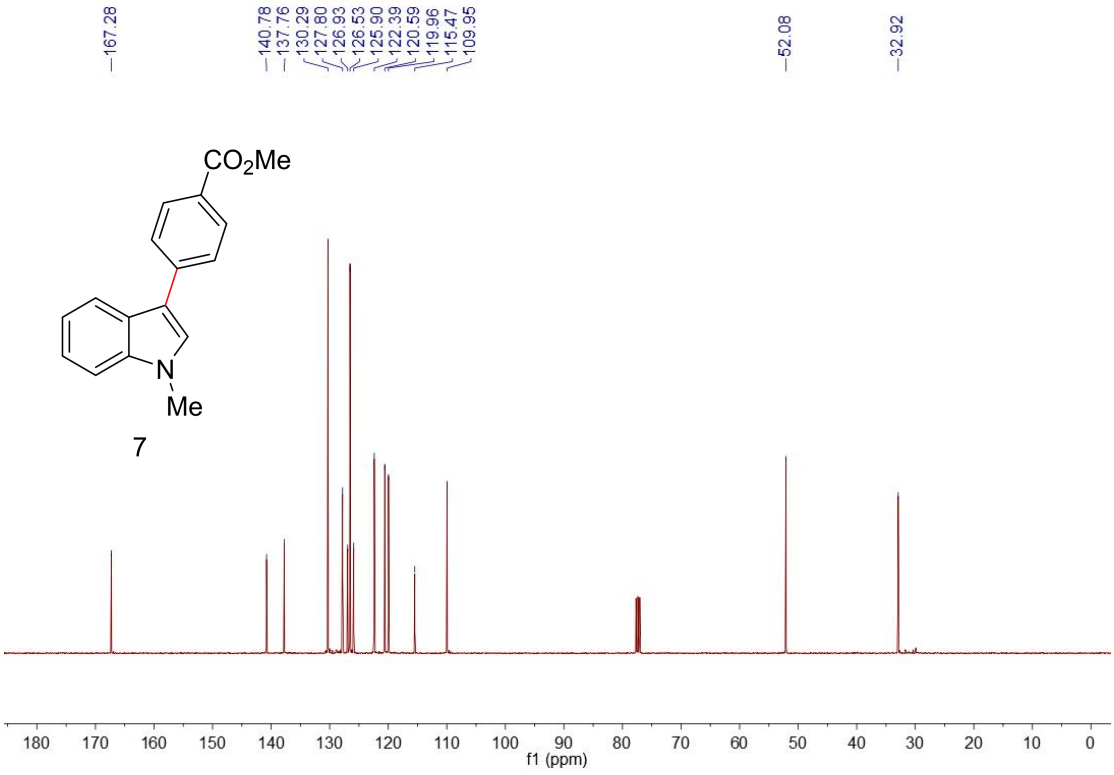

Bpin
Bpin
N
Me
2n
8.452
7.700
7.679
7.520
7.317
7.297
3.777
1.375
1.364
1.00
1.00
1.00
1.02
3.00
12.02
12.02
f1 (ppm)

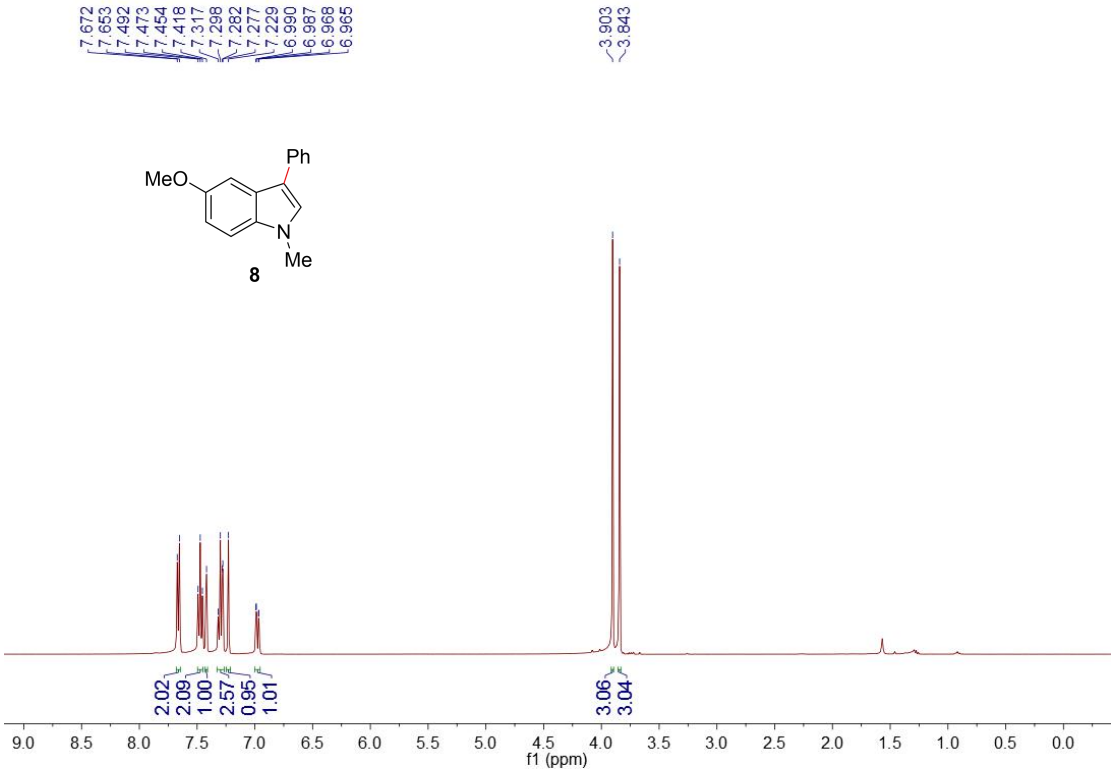

Bpin
Bpin
N
Me
2n
139.94
138.97
131.86
130.04
128.19
108.65
83.40
82.83
32.98
24.94
f1 (ppm)

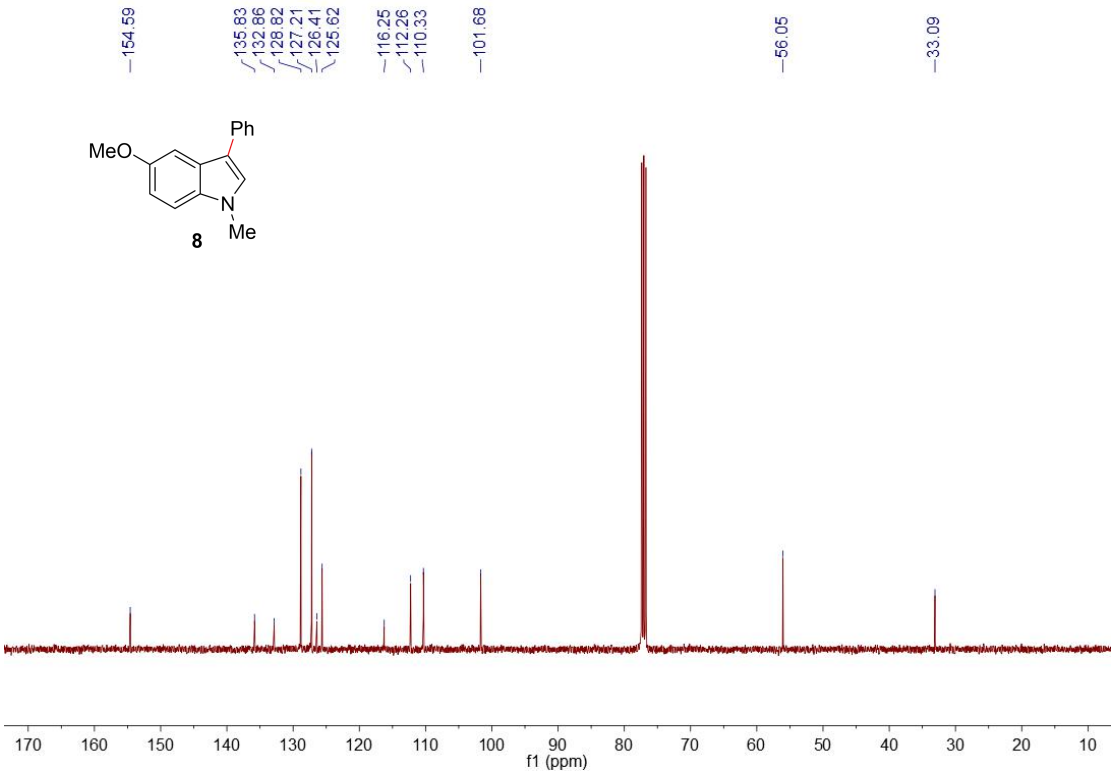

Bpin
N
N
Me
2o
8.341
8.337
8.329
8.325
8.281
8.277
8.261
8.257
7.630
7.131
7.119
7.111
7.099
3.899
1.359
0.98
0.98
0.99
1.03
3.00
12.03
f1 (ppm)

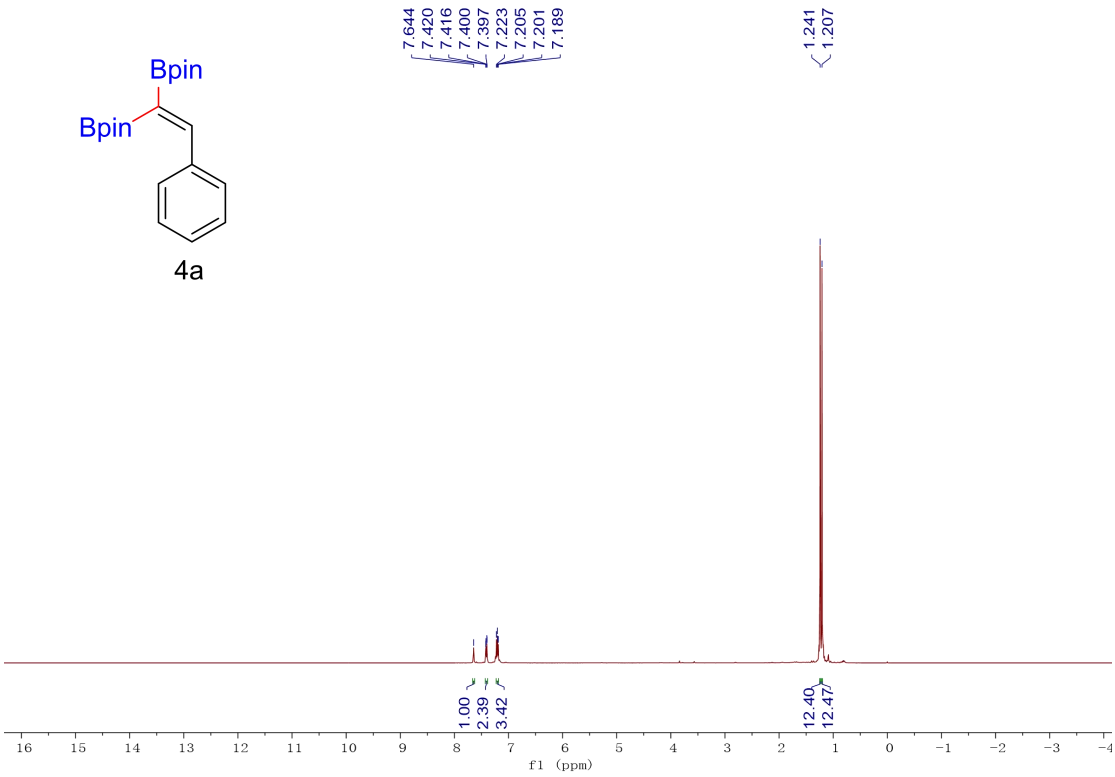

Bpin
N
N
Me
2o
148.07
142.87
138.52
130.75
124.65
116.37
83.01
31.53
24.92
f1 (ppm)

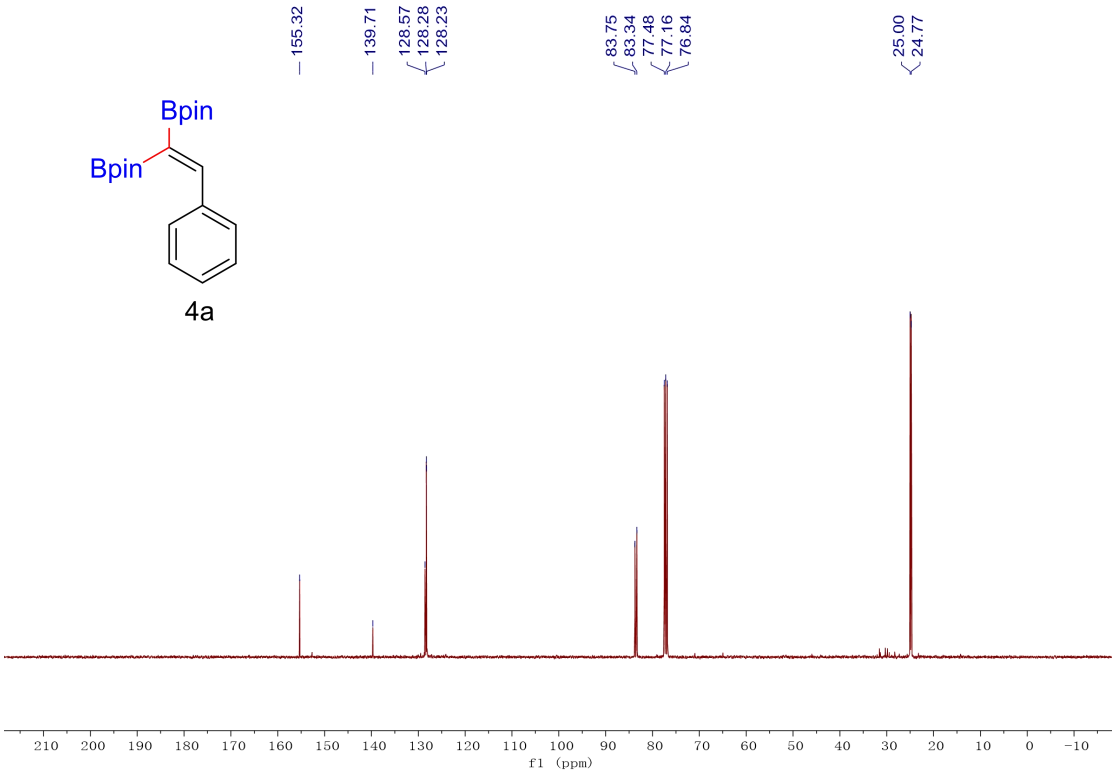

8.210
8.189
8.092
8.072
7.805
7.785
7.404
7.396
7.370
7.355
7.347
7.335
7.328
7.315
7.276
4.029
3.754
CO2Me
N
Me
7
2.00
1.00
2.02
2.04
1.05
1.03
3.00
3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

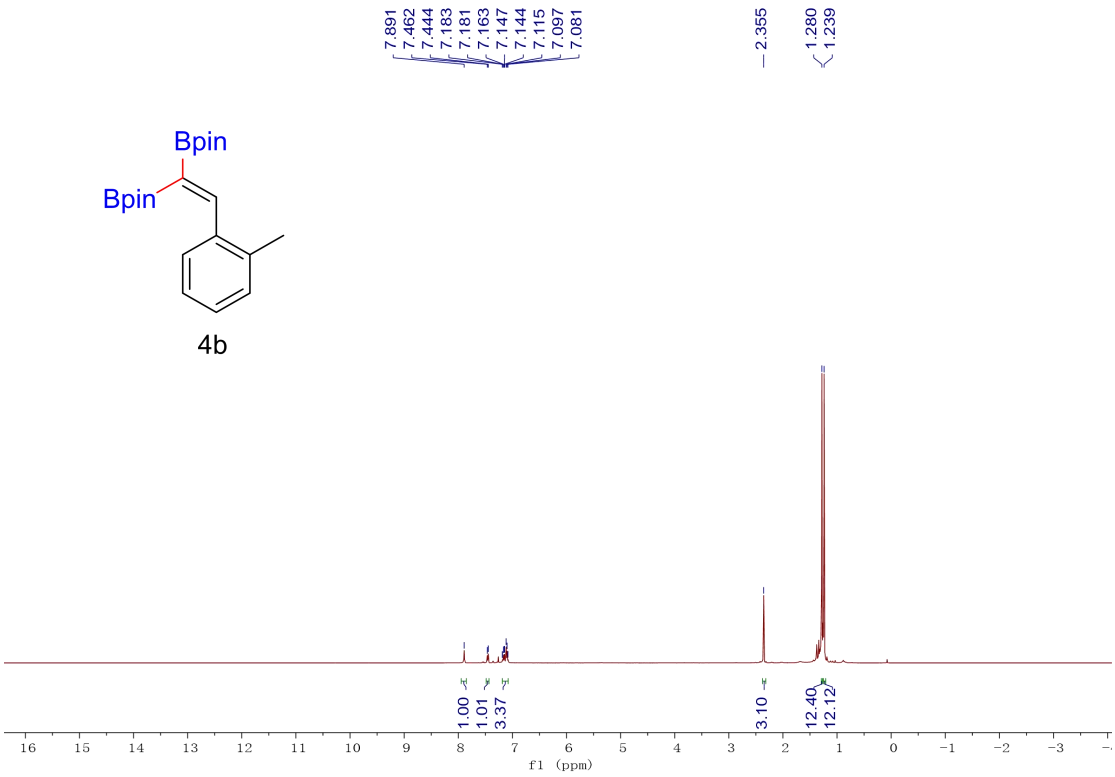

167.28
140.78
137.76
130.29
127.80
126.93
126.53
125.90
122.39
120.59
119.96
115.47
109.95
52.08
32.92
CO2Me
N
Me
7
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

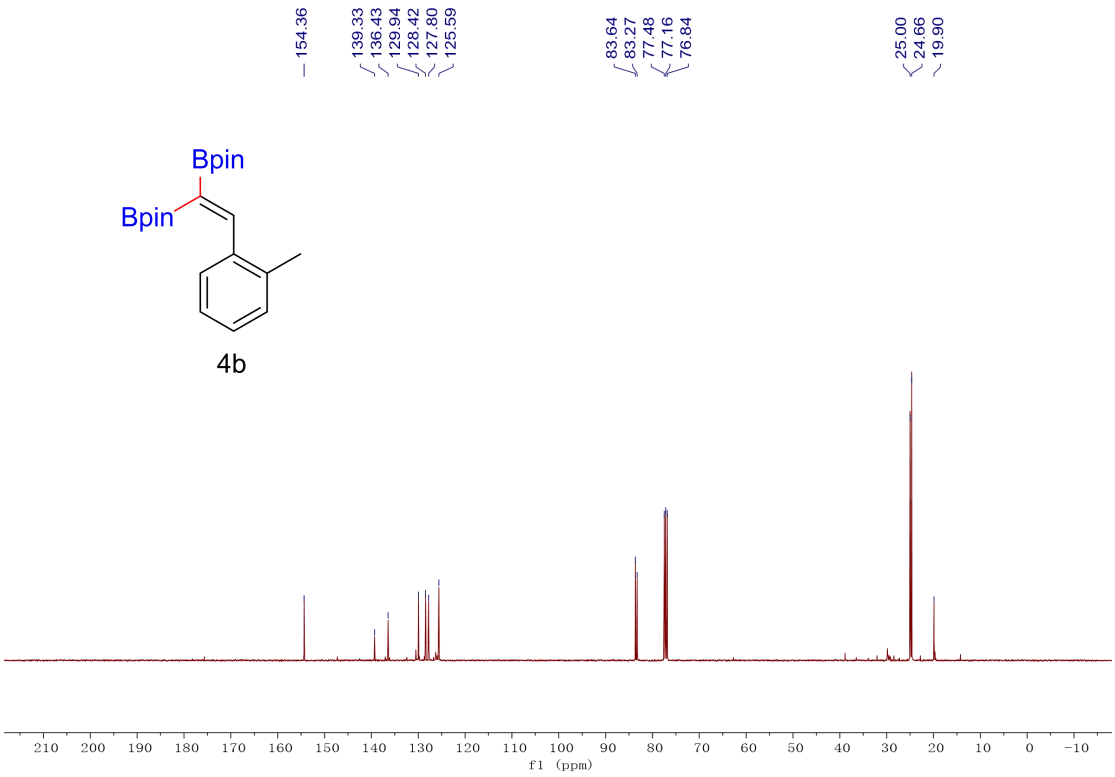

7.672
7.653
7.492
7.473
7.454
7.418
7.317
7.298
7.282
7.277
7.229
6.990
6.987
6.968
6.965
3.903
3.843
Ph
MeO
N
Me
8
2.02
2.09
1.00
2.57
0.95
1.01
3.06
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

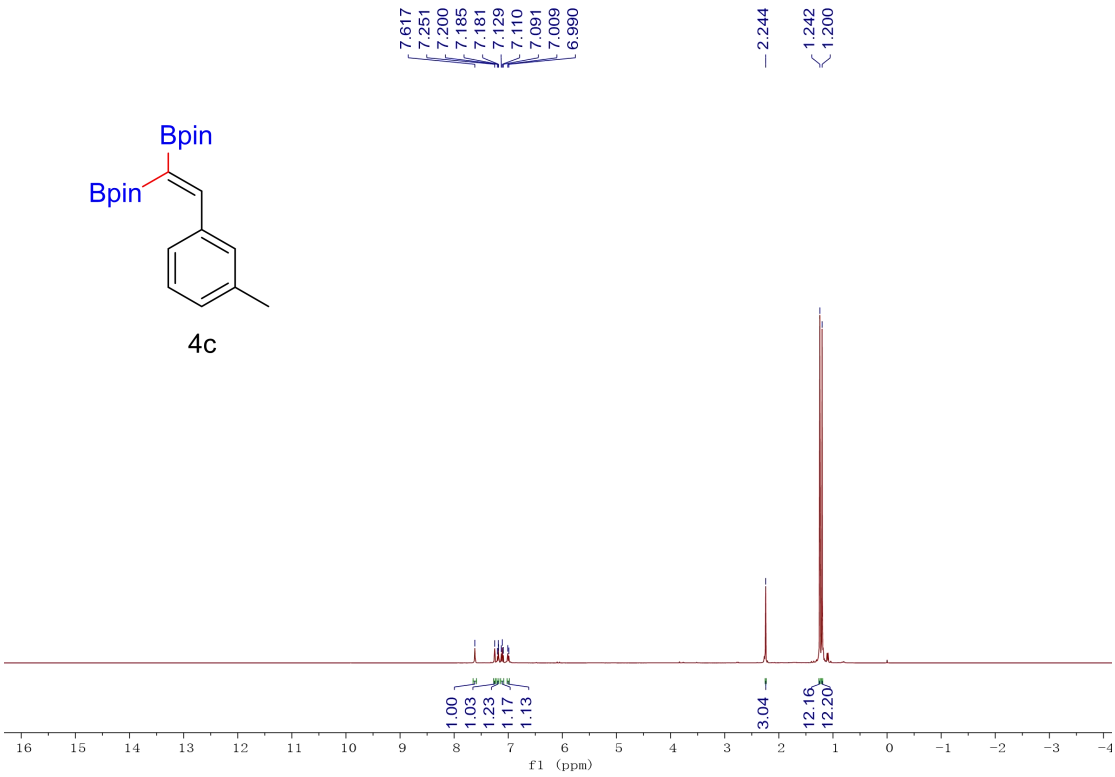

154.59
135.83
132.86
128.82
127.21
126.41
125.62
116.25
112.26
110.33
101.68
56.05
33.09
Ph
MeO
N
Me
8
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

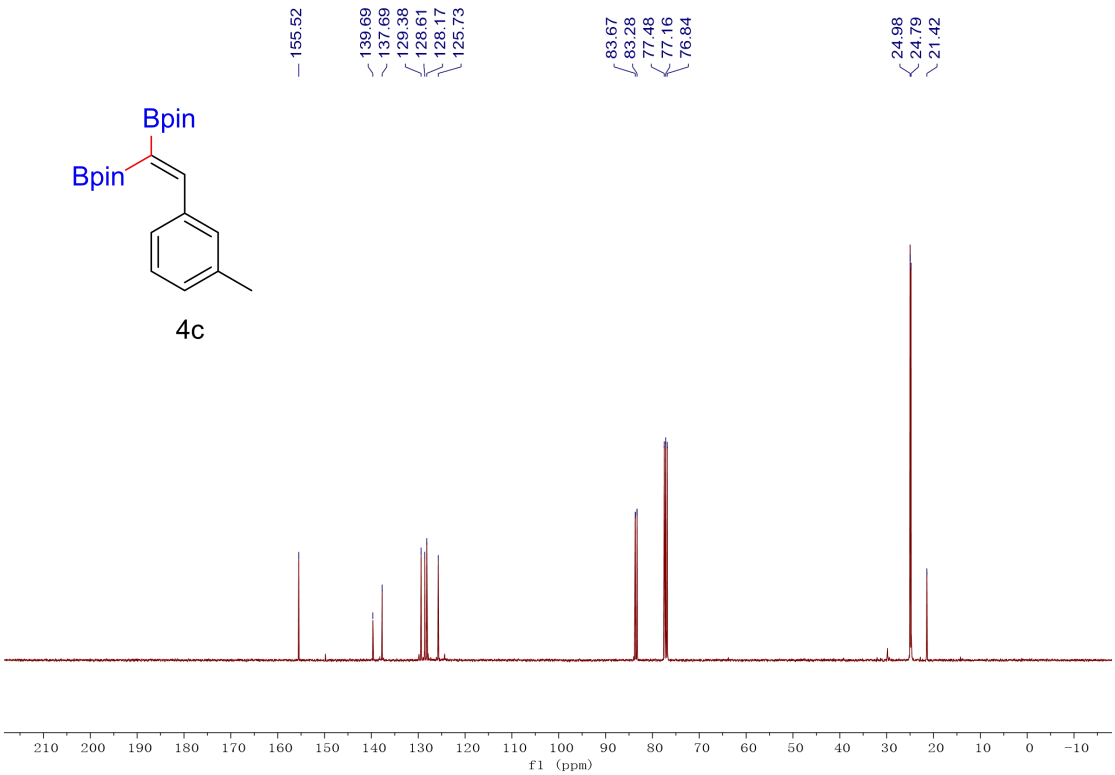

Bpin
Bpin
4a
7.644
7.420
7.416
7.400
7.397
7.223
7.205
7.201
7.189
1.241
1.207
1.00
2.39
3.42
12.40
12.47
f1 (ppm)

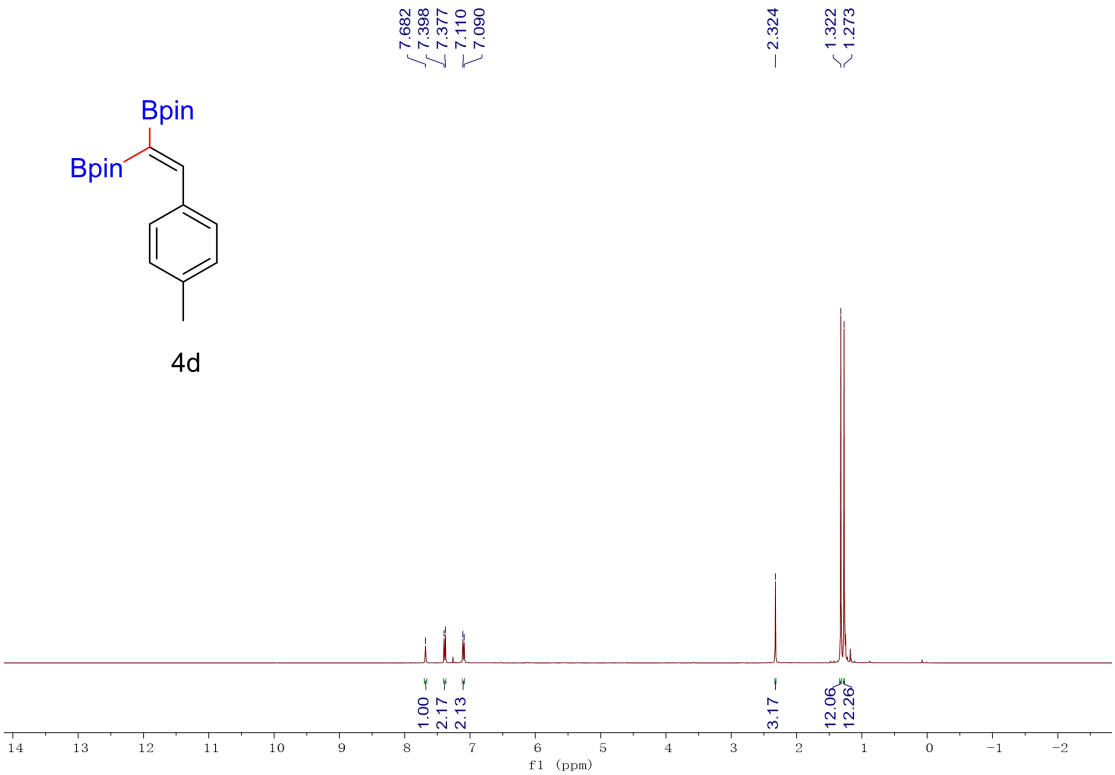

Bpin
Bpin
4a
155.32
139.71
128.57
128.28
128.23
83.75
83.34
77.48
77.16
76.84
25.00
24.77
f1 (ppm)

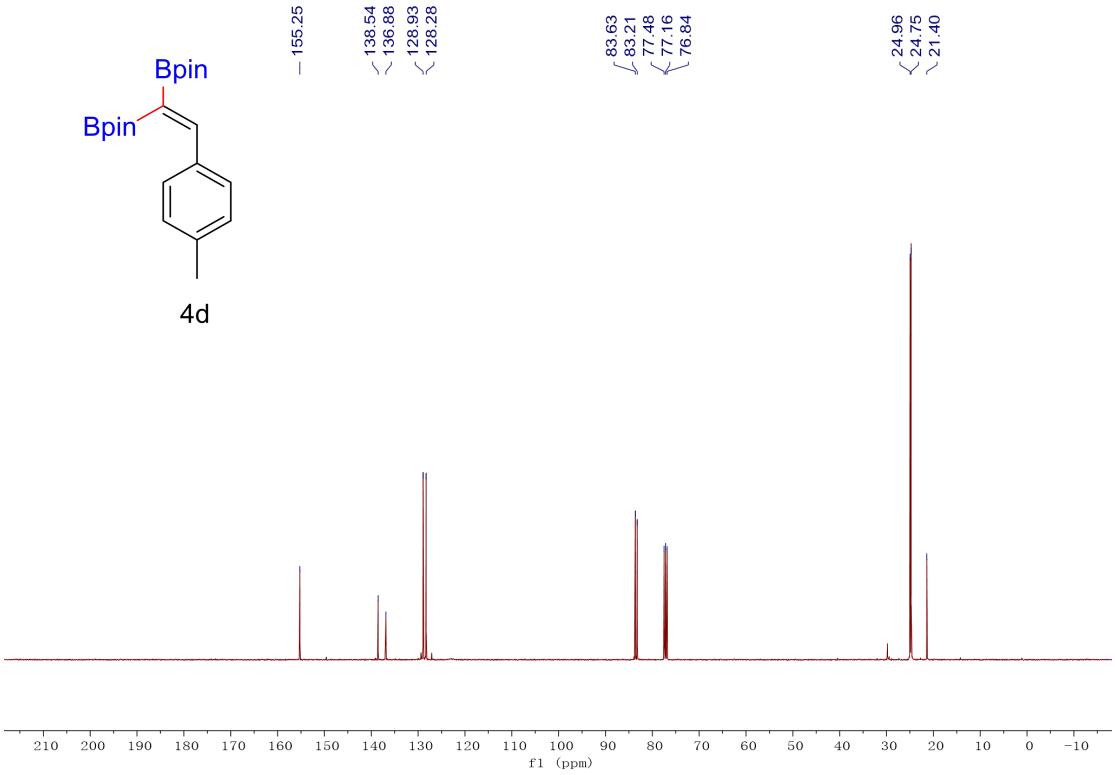

7.891
7.462
7.444
7.183
7.181
7.163
7.147
7.144
7.115
7.097
7.081
2.355
1.280
1.239
Bpin
Bpin
4b
1.00
1.01
3.37
3.10
12.40
12.12
f1 (ppm)

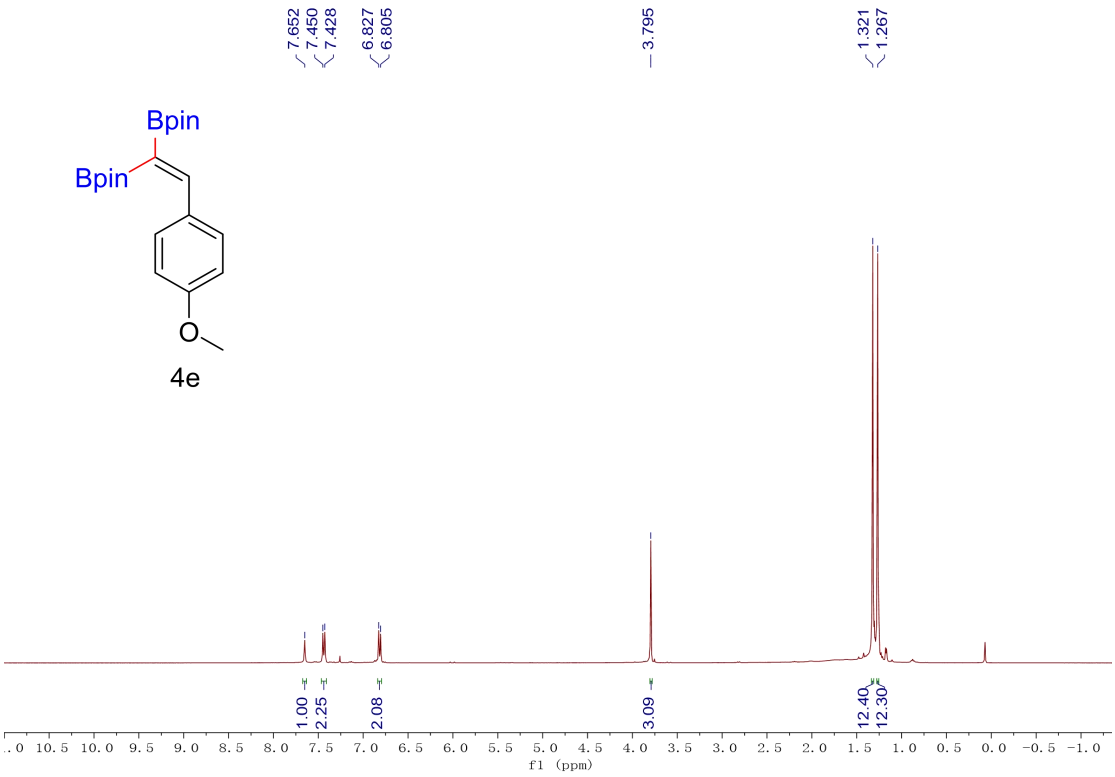

154.36
139.33
136.43
129.94
128.42
127.80
125.59
83.64
83.27
77.48
77.16
76.84
25.00
24.66
19.90
Bpin
Bpin
4b
f1 (ppm)

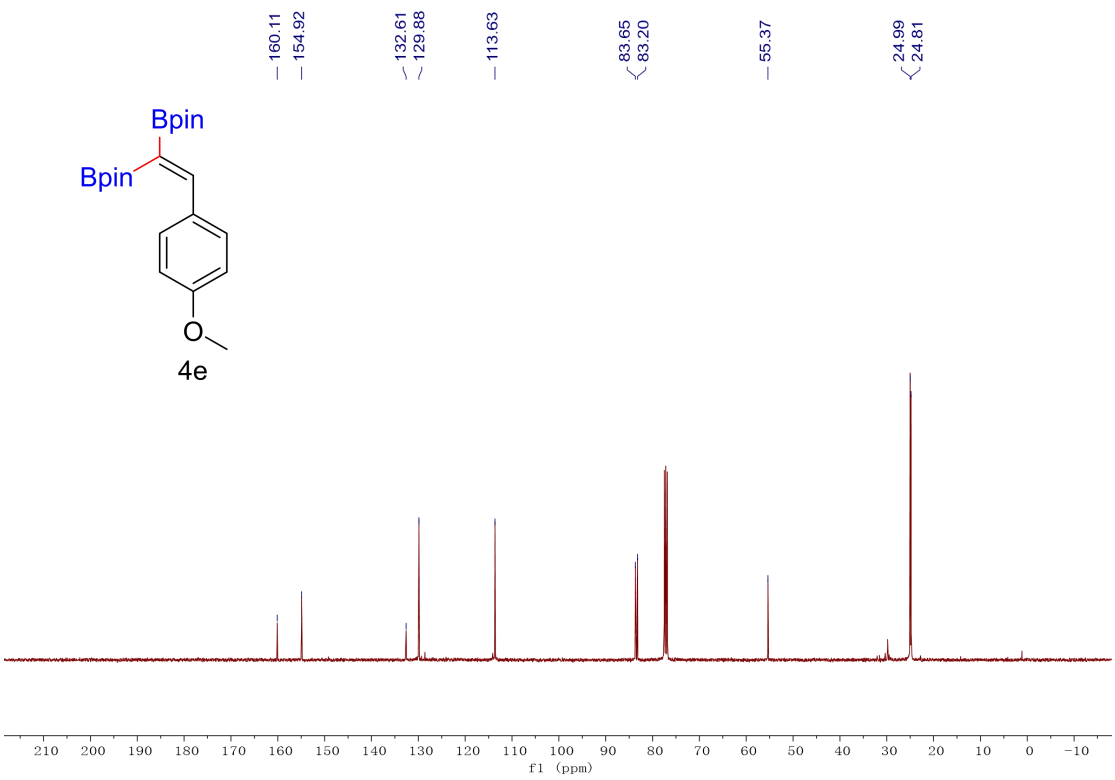

7.617
7.251
7.200
7.185
7.181
7.129
7.110
7.091
7.009
6.990
2.244
1.242
1.200
Bpin
Bpin
4c
1.00
1.03
1.23
1.17
1.13
3.04
12.16
12.20
f1 (ppm)

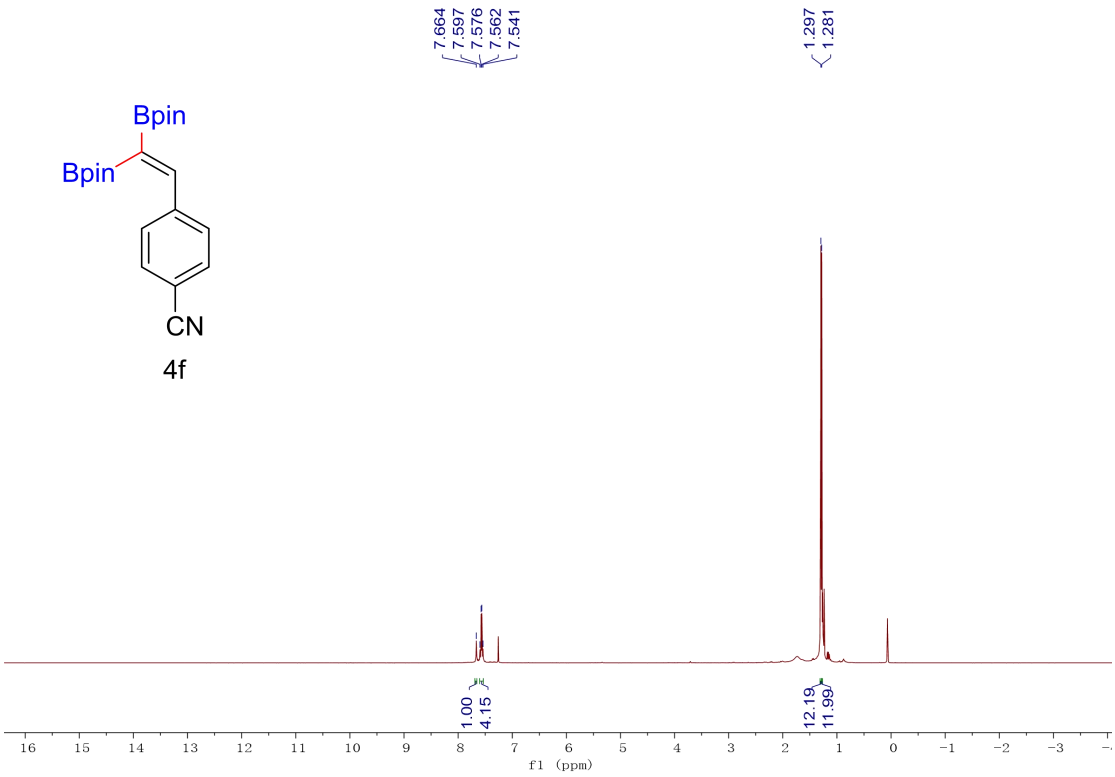

155.52
139.69
137.69
129.38
128.61
128.17
125.73
83.67
83.28
77.48
77.16
76.84
24.98
24.79
21.42
Bpin
Bpin
4c
f1 (ppm)

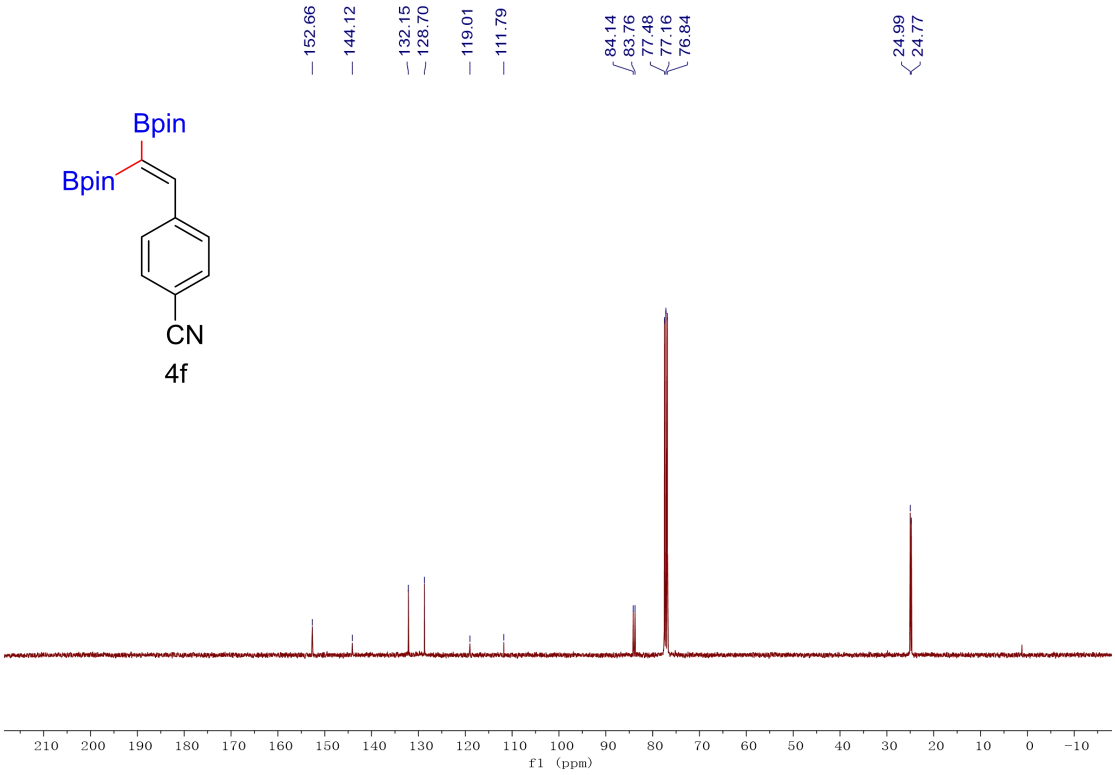

7.682
7.398
7.377
7.110
7.090
2.324
1.322
1.273
Bpin
Bpin
4d
1.00
2.17
2.13
3.17
12.06
12.26
f1 (ppm)

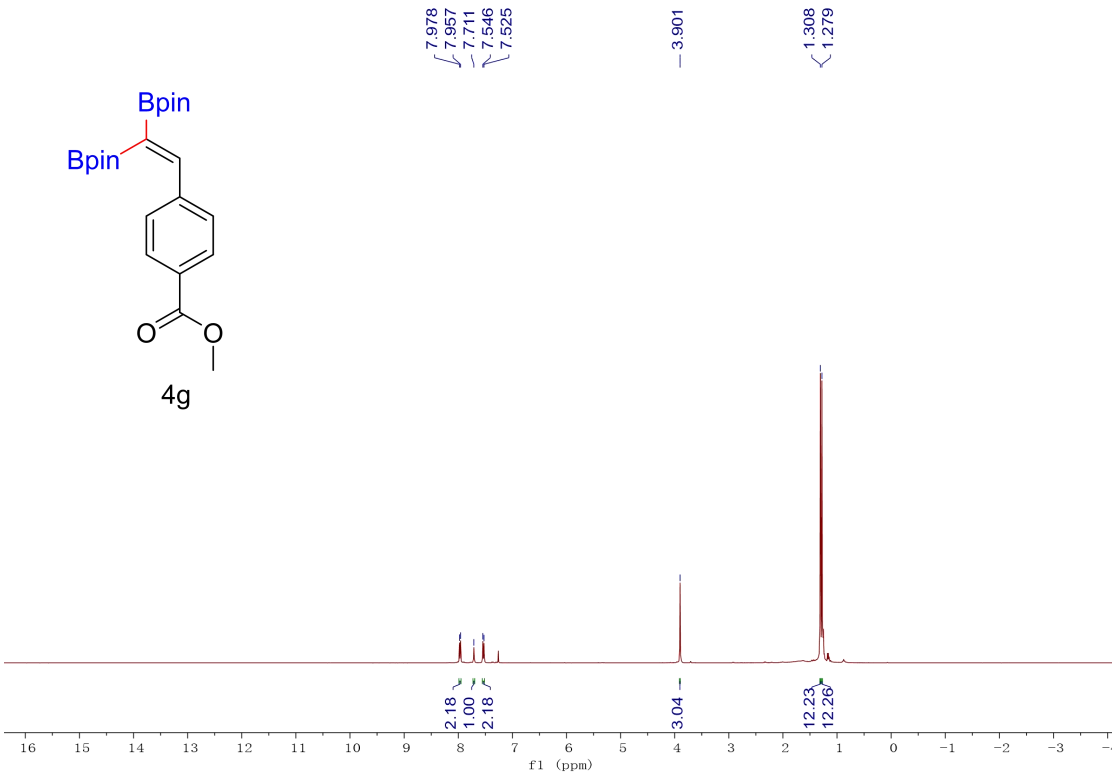

155.25
138.54
136.88
128.93
128.28
83.63
83.21
77.48
77.16
76.84
24.96
24.75
21.40
Bpin
Bpin
4d
f1 (ppm)

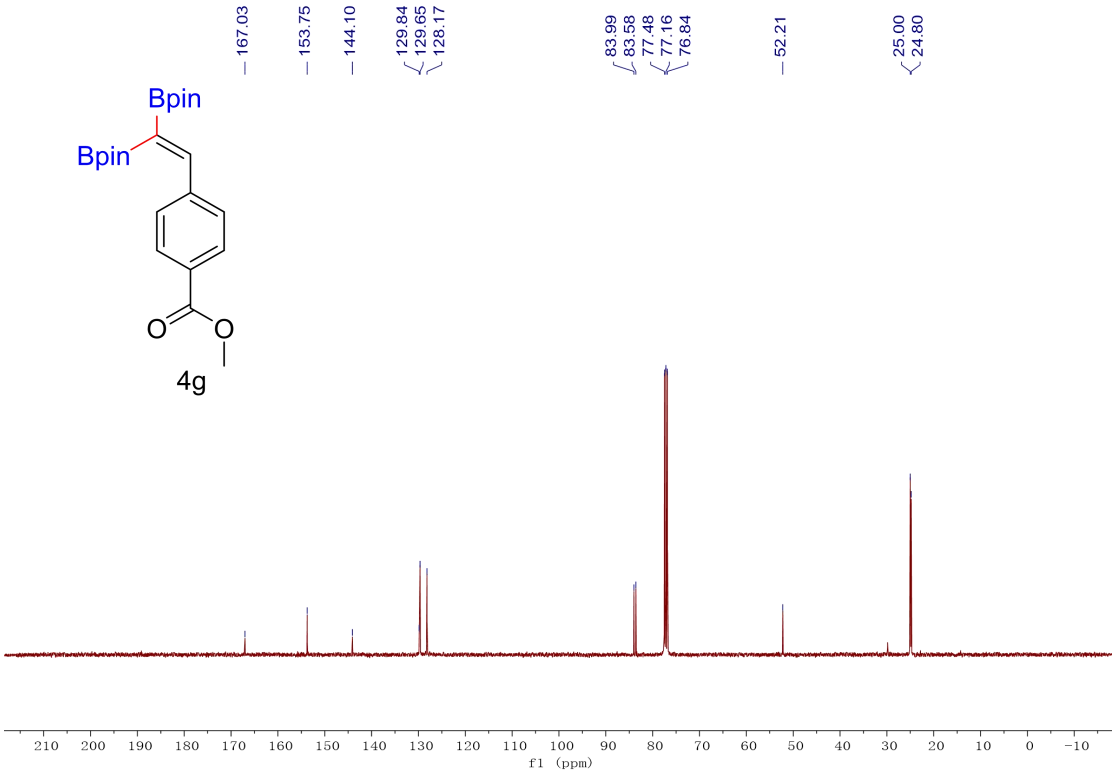

7.652
7.450
7.428
6.827
6.805
3.795
1.321
1.267
Bpin
Bpin
O
4e
1.00
2.25
2.08
3.09
12.40
12.30
f1 (ppm)

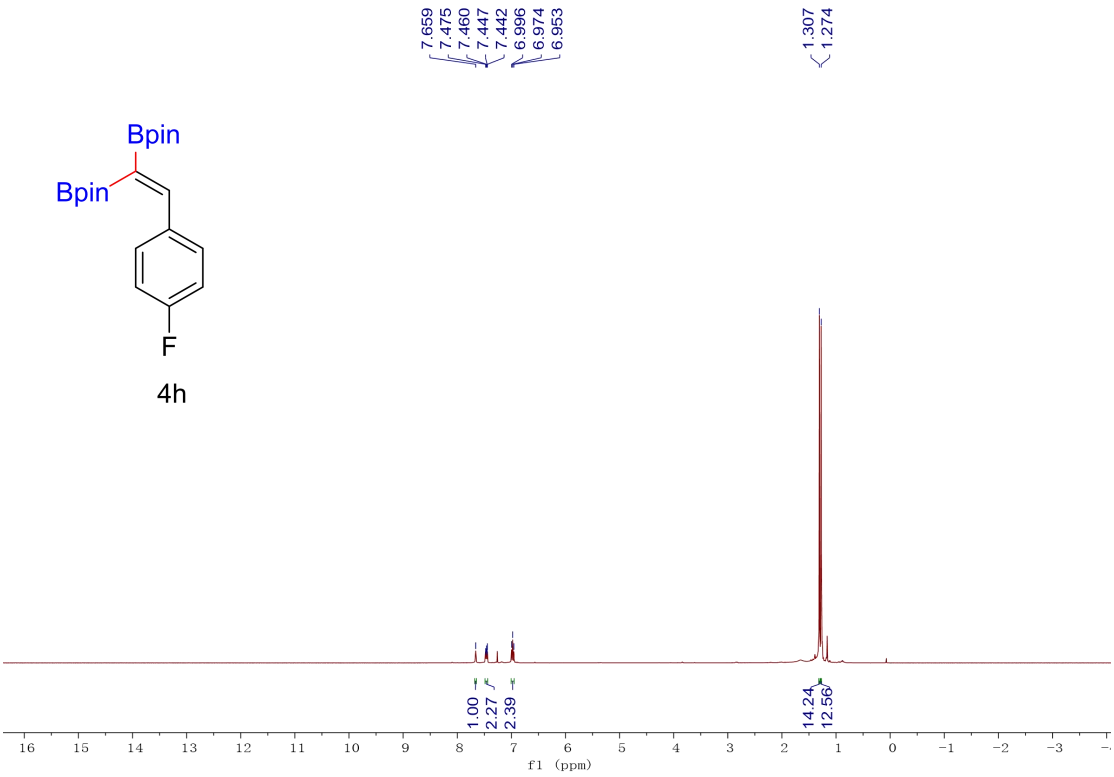

160.11
154.92
132.61
129.88
113.63
83.65
83.20
55.37
24.99
24.81
Bpin
Bpin
O
4e
f1 (ppm)

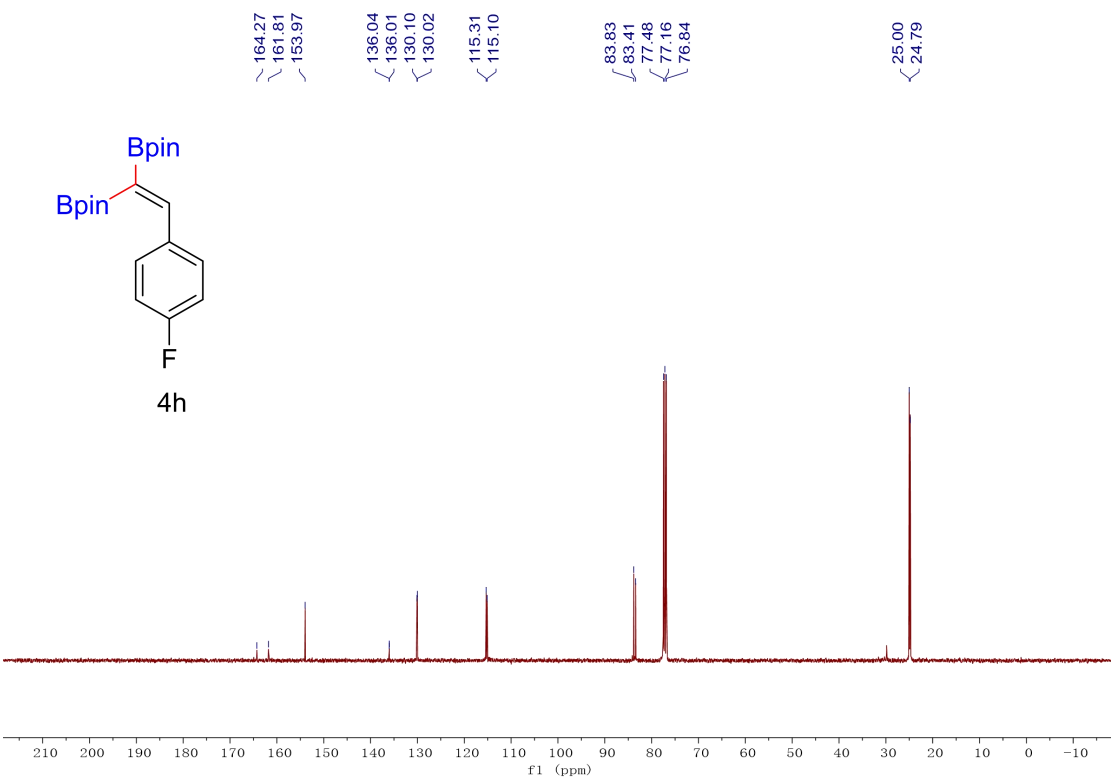

7.664
7.597
7.576
7.562
7.541
1.297
1.281
Bpin
Bpin
CN
4f
1.00
4.15
12.19
11.99
f1 (ppm)

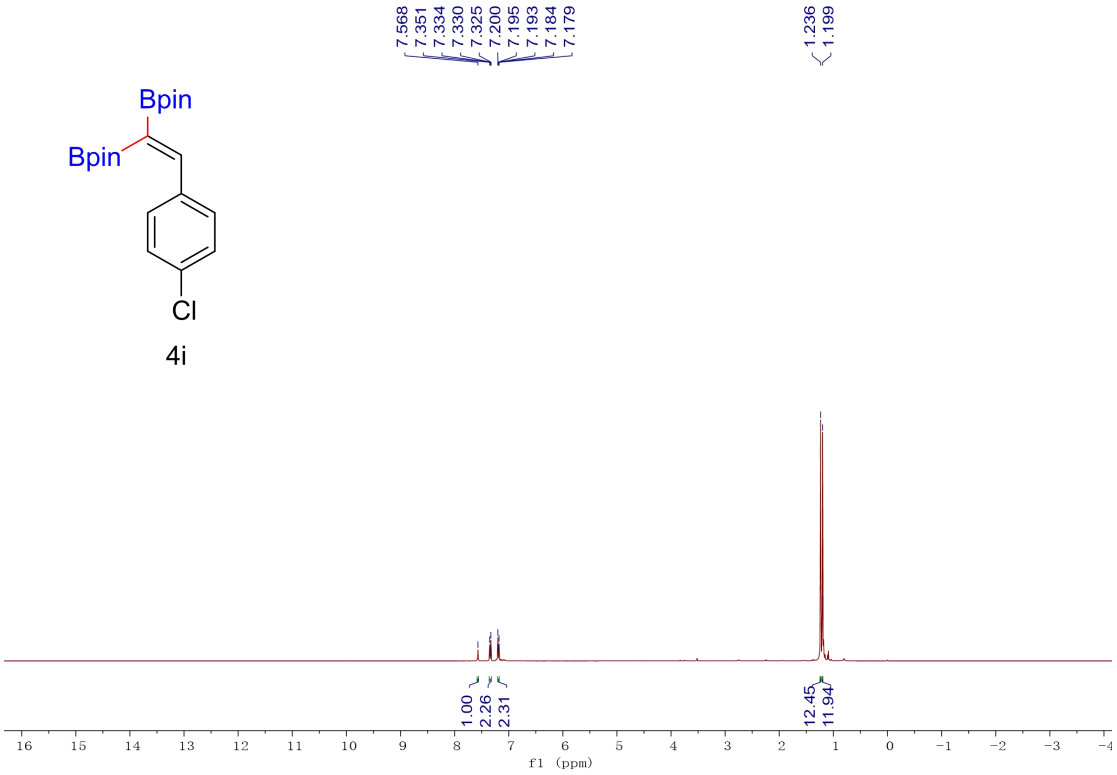

152.66
144.12
132.15
128.70
119.01
111.79
84.14
83.76
77.48
77.16
76.84
24.99
24.77
Bpin
Bpin
CN
4f
f1 (ppm)

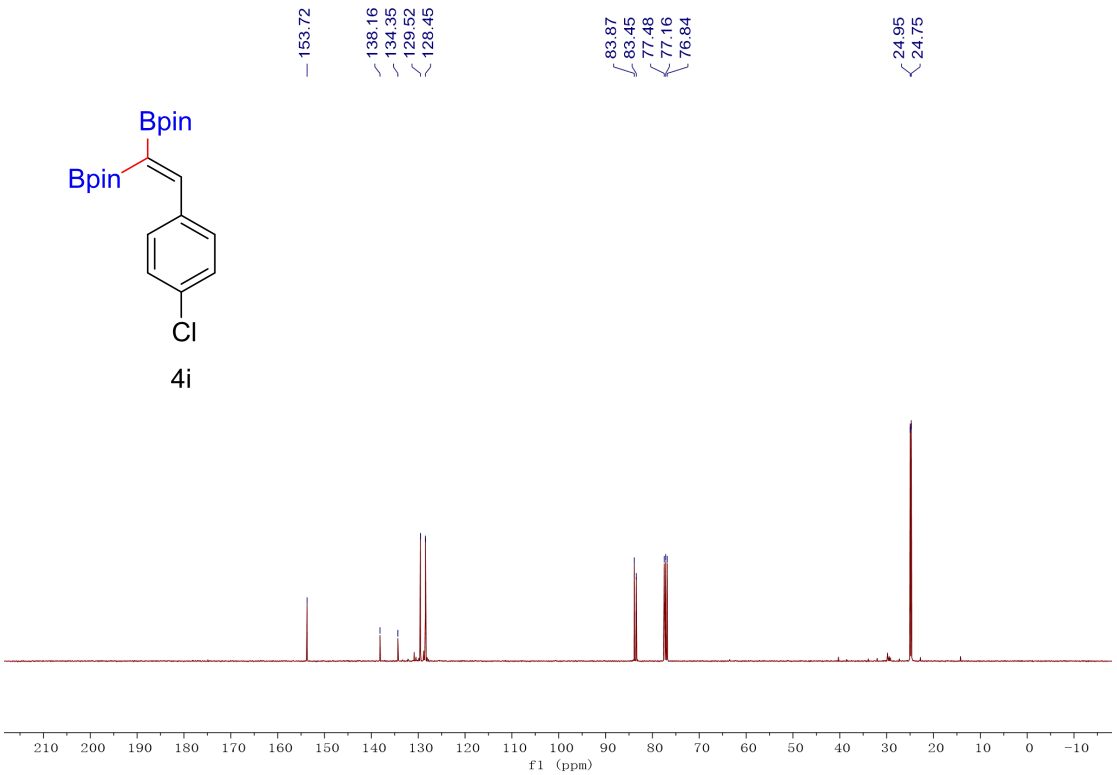

7.978
7.957
7.711
7.546
7.525
3.901
1.308
1.279
Bpin
Bpin
O
O
4g
2.18
1.00
2.18
3.04
12.23
12.26
f1 (ppm)

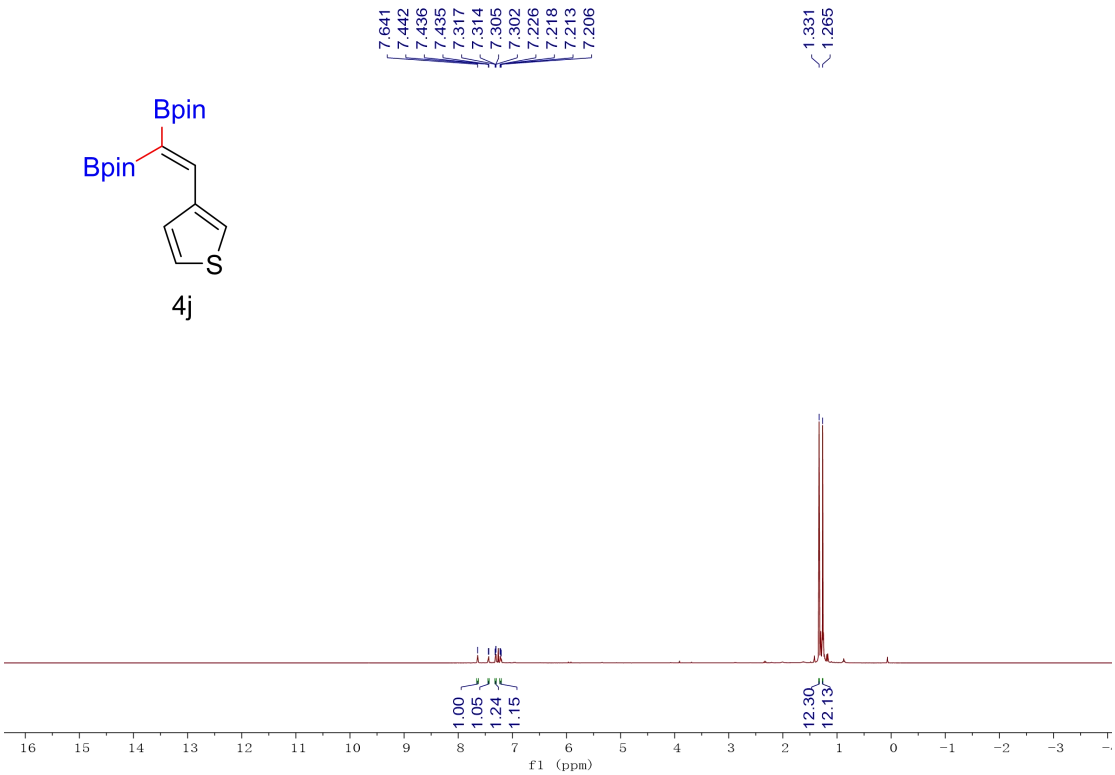

167.03
153.75
144.10
129.84
129.65
128.17
83.99
83.58
77.48
77.16
76.84
52.21
25.00
24.80
Bpin
Bpin
O
O
4g
f1 (ppm)

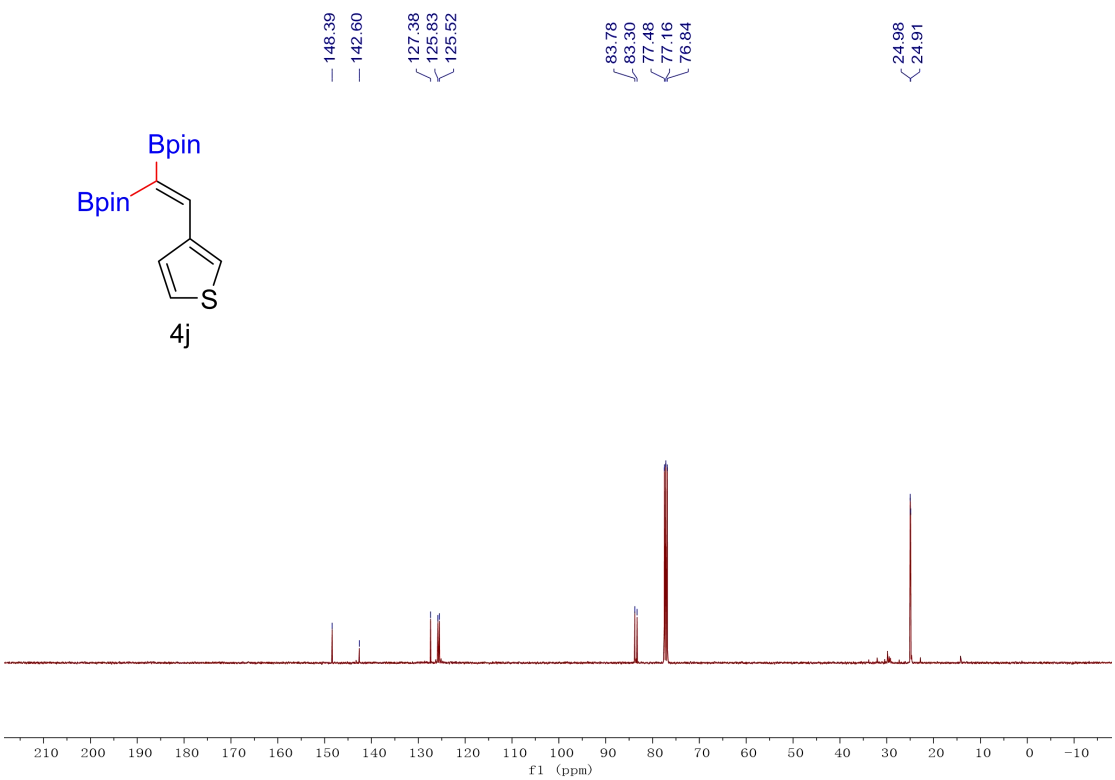

7.659
7.475
7.460
7.447
7.442
6.996
6.974
6.953
1.307
1.274
Bpin
Bpin
F
4h
1.00
2.27
2.39
14.24
12.56
f1 (ppm)


164.27
161.81
153.97
136.04
136.01
130.10
130.02
115.31
115.10
83.83
83.41
77.48
77.16
76.84
25.00
24.79
Bpin
Bpin
F
4h
f1 (ppm)


7.568
7.351
7.334
7.330
7.325
7.200
7.195
7.193
7.184
7.179
1.236
1.199
Bpin
Bpin
Cl
4i
1.00
2.26
2.31
12.45
11.94
f1 (ppm)


153.72
138.16
134.35
129.52
128.45
83.87
83.45
77.48
77.16
76.84
24.95
24.75
Bpin
Bpin
Cl
4i
f1 (ppm)


7.641
7.442
7.436
7.435
7.317
7.314
7.305
7.302
7.226
7.218
7.213
7.206
1.331
1.265
Bpin
Bpin
S
4j
1.00
1.05
1.24
1.15
12.30
12.13
f1 (ppm)


148.39
142.60
127.38
125.83
125.52
83.78
83.30
77.48
77.16
76.84
24.98
24.91
Bpin
Bpin
S
4j
f1 (ppm)