Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

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1. General information

Unless otherwise noted, all reactants or reagents were obtained from commercial suppliers and used as received. $B(OMe)_3$ was obtained from Aladdin (Shanghai, China). B_2pin_2 and ethylmorpholine were obtained from Energy Chemical (Shanghai, China). Et_3N was obtained from Sinopharm Chemical Reagent (Shanghai, China). *n*-Octane was obtained from Sinopharm Chemical Reagent 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 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). Gas chromatography (GC) analysis was conducted on a Aglient 7024A instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard) with naphthalene as an internal standard. 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 tetramethylsilane as an internal standard. Chemical shifts for ^1H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (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. Synthesis of starting materials

Indole, 2-methylindole, 3-methylindole, 4-methylindole, 5-methylindole, 6-methylindole, 7-methylindole, 2-ethylindole, 5-fluoroindole, 5-chloroindole, 5-(trifluoromethyl)indole, 5-methoxyindole, 2,5-dimethylindole, 5-fluoro-2-methylindole, 5-chloro-2-methylindole, 5-methoxy-2-methylindole, phenylboronic acid, *p*-tolylboronic acid, *m*-tolylboronic acid, *o*-tolylboronic acid, (4-(tert-butyl)phenyl)boronic acid, (4-fluorophenyl)boronic acid, (4-(trifluoromethyl)phenyl)boronic acid, (4-(trimethylsilyl)phenyl)boronic acid, [1,1'-biphenyl]-4-ylboronic acid, naphthalen-2-ylboronic acid and (3,4,5-trimethoxyphenyl)boronic acid were purchased from commercial sources and used as received. Unless otherwise noted, all other indole derivatives were prepared according to the procedures reported in the literature. The methylation of indole derivatives was conducted according to the procedures reported in the literature.[1]

1ra[2], **1sa**[2], **1ga**[3][1], **1fa**[3][1], **1ea**[3][1], **1ba**[4][1], **1da**[4][1], **1ia**[5], **1ja**[6][1], **1ma**[7][1], **1na**[8], **1oa**[9], **1pa**[10][11], **1qa**[12], **1hb**[1][14], **1ar**[1][14], **1hc**[1][15], **1hd**[1][13], **1he**[1][13], **1hf**[1][16], **1hg**[1][16], **1hh**[1][16], **1hi**[1][16], **1hj**[1][16], **1hk**[1][16], **1hl**[1][16], **1hm**[1][16], **1hn**[1][16], **1ho**[1][16], **1ap**[1][16], **1fp**[1][16], **1bp**[1][16], **1cp**[1][16], **1dp**[1][16], **1ep**[1][16], **1hp**[1][16], **1jp**[1][16], **1kp**[1][16], **1lp**[1][16], **1op**[1][16], **1qp**[1][16], **1af**[1][16], **1aq**[17], **1as**[1][18], **1at**[19][1], **1tu**[19][20], **1tw**[13][20], **1ta**[20], **3r**[21], **3r’**[21], **3s**[21], **3e**[22] were prepared according to the procedures reported in the literature.

3. Reaction optimization

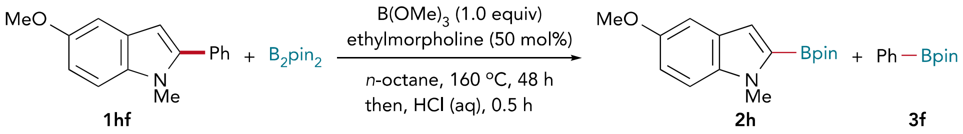
$B(OMe)_3$/B_2pin_2-mediated fragmentation borylation of 1aa

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1aa** (0.20 mmol, 29.4 mg) and B_2pin_2 (0.50 mmol, 127.0 mg), and then flushed with nitrogen gas. $B(OMe)_3$ (0.06 mmol, 6.2 mg), Et_3N (0.06 mmol, 6.1 mg), and *n*-octane (1.0 mL) were added to the tube under nitrogen. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. The reaction mixture was cooled to room temperature, 6.0 M HCl aqueous solution (1.0 mL) was added, and the mixture was stirred for 0.5 h, then the solvent was diluted with ethyl acetate. The yield of **2a** was determined by GC and calibrated using naphthalene as internal standard.

$B(OMe)_3$/B_2pin_2-mediated fragmentation borylation of 1hf

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1hf** (0.20 mmol, 47.4 mg) and B_2pin_2 (0.80 mmol, 203.2 mg), and then flushed with nitrogen gas. $B(OMe)_3$ (0.20 mmol, 20.8 mg), ethylmorpholine (0.10 mmol, 11.5 mg), and *n*-octane (1.0 mL) were added to the tube under nitrogen. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. The reaction mixture was cooled to room temperature, 6.0 M HCl aqueous solution (1.0 mL) was added, and the mixture was stirred for 0.5 h, then the solvent was diluted with ethyl acetate. The yield of **2h** and **3f** were determined by GC and calibrated using naphthalene as internal standard.

Table S1. Effects of varying reaction parameters in $B(OMe)_3$/B_2pin_2-mediated fragmentation borylation of 1hf



Entry	Deviation from standard reaction conditions	Yield of **2h** (%)[a]	Yield of **3f** (%)[a]
1	None	63(57)[b]	68(62)[b]
2	No $B(OMe)_3$	0	0
3	$B(O^iPr)_3$, instead of $B(OMe)_3$	46	48
4	$B(OPh)_3$, instead of $B(OMe)_3$	38	43
5	$B(OCH_2CF_3)_3$, instead of $B(OMe)_3$	48	50
6[c]	$BF_3 \cdot Et_2O$, instead of $B(OMe)_3$	0(34[d])	0(57[d])
7	10 mol% $B(C_6F_5)_3$, instead of $B(OMe)_3$	41	38
8	no ethylmorpholine	48	66
9	Et_3N, instead of ethylmorpholine	62	64

10	*n*-hexane, instead of *n*-octane	63	65
11	1,4-dioxane, instead of *n*-octane	5	6
12	mesitylene, instead of *n*-octane	23	23
13	140 ℃, instead of 160 ℃	39	39
14	16 h, instead of 48 h	51	48

Standard reaction conditions: **1hf** (0.2 mmol), B_2pin_2 (0.8 mmol), $B(OMe)_3$ (1.0 equiv), ethylmorpholine (0.1 mmol), *n*-octane (1.0 mL), 160 ^{o}C, 48 h; HCl (1.0 mL, 6.0 M), 0.5 h. [a]Yields were determined by GC with naphthalene as the internal standard. [b]Isolated yield in parentheses. [c]THF (0.1 mL) was added. [d]No ethylmorpholine.

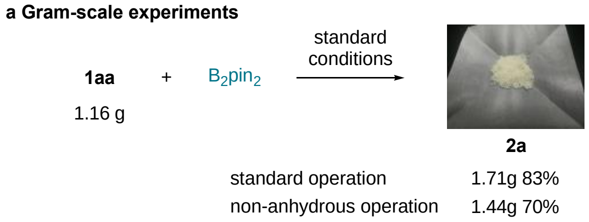
4. $B(OMe)_3/B_2pin_2$-mediated fragmentation borylation of 2-alkyl(aryl) indoles

General Procedure: An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1** (0.20 mmol) and B_2pin_2 (0.50 mmol, 127.0 mg, for 2-alkylindoles; 0.80 mmol, 203.2 mg, for 2-arylindoles), and then flushed with nitrogen gas. $B(OMe)_3$ (0.06 mmol, 6.2 mg, for 2-alkylindoles; 0.20 mmol, 20.8 mg, for 2-arylindoles), Et_3N (0.06 mmol, 6.1 mg, for 2-alkylindoles)/ethylmorpholine (0.10 mmol, 11.5 mg, for 2-arylindoles), and *n*-octane (1.0 mL) were added to the tube under nitrogen. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. The reaction mixture was cooled to room temperature, 6.0 M HCl aqueous solution (1.0 mL) was added, and the mixture was stirred for 0.5 h. After addition of saturated brine, the mixture was extracted with ethyl acetate, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was directly purified by flash column chromatography over silica gel with petroleum ether/ethyl acetate to afford the product.

Note: The reaction of **1fa** was conducted with B_2pin_2 (0.8 mmol, 203.2 mg) and $B(OMe)_3$ (0.2 mmol, 20.8 mg) at 180 ℃. The reactions of **1hb, 1hc, 1hd** and **1he** were conducted with B_2pin_2 (0.8 mmol, 203.2 mg), Et_3N (0.06 mmol, 6.1 mg) and $B(OMe)_3$ (0.2 mmol, 20.8 mg) at 160 ℃. The post-reaction treatment of **1fa**, **1ia** and **1fp** weren't conducted with HCl aqueous solution. Products **2i** and **2p** were purified by preparative thin-layer chromatography (PTLC; petroleum ether/ethyl acetate as the eluent). If **1** was a liquid, it was added with under nitrogen atmosphere.

Hazard statement: These reactions were performed at a temperature that is well above the boiling point of *n*-octane (approximately 125-127 ^{o}C), leading to substantial pressure buildup in the sealed reaction vessel. As such, proper precautions should be taken when performing these experiments.

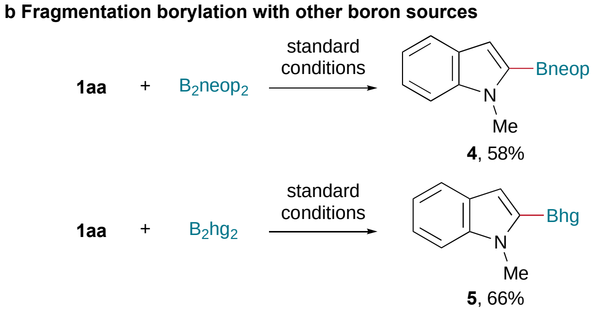
5. Control experiments and mechanistic studies



A Gram-scale experiments

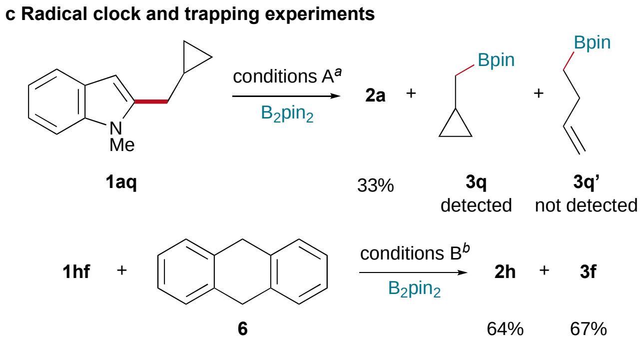
Standard operation. An oven-dried 50-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1aa** (8.0 mmol, 1.16 g) and B_2pin_2 (20.0 mmol, 5.08 g), and then flushed with nitrogen gas. $B(OMe)_3$ (2.4 mmol, 249.4 mg), Et_3N (2.4 mmol, 242.9 mg) and ^{n}octane (10.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the mixture was added 6.0 M HCl aqueous solution (10.0 mL) and stirred for 0.5 h. Then the mixture was added saturated brine, extracted with ethyl acetate and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was directly purified by flash column chromatography over silica gel eluting with petroleum ether/ethyl acetate to afford the product.

Non-anhydrous operation. An undried 50-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1aa** (8.0 mmol, 1.16 g) and B_2pin_2 (20.0 mmol, 5.08 g), and then flushed with nitrogen gas. $B(OMe)_3$ (2.4 mmol, 249.4 mg), Et_3N (2.4 mmol, 242.9 mg) and ^{n}octane (10.0 mL, undried) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the mixture was added 6.0 M HCl aqueous solution (10.0 mL) and stirred for 0.5 h. Then the mixture was added saturated brine, extracted with ethyl acetate and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was directly purified by flash column chromatography over silica gel eluting with petroleum ether/ethyl acetate to afford the product.



B Fragmentation borylation with other boron sources

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1aa** (0.2 mmol, 29.0 mg), B_2neop_2 (0.5 mmol, 112.5 mg) or B_2hg_2 (0.5 mmol, 127.0 mg), and then flushed with nitrogen gas. $B(OMe)_3$ (0.06 mmol, 6.2 mg), Et_3N (0.06 mmol, 6.1 mg), and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the mixture was added 6.0 M HCl aqueous solution (1.0 mL) and stirred for 0.5 h. Then the mixture was added saturated brine, extracted with ethyl acetate and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was directly purified by flash column chromatography over silica gel eluting with petroleum ether/ethyl acetate to afford the product.



c Radical clock and trapping experiments

C Radical clock and trapping experiments

Radical clock experiment. An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with B_2pin_2 (0.5 mmol, 127.0 mg) and flushed with nitrogen gas. **1aq** (0.2 mmol, 37.0 mg), $B(OMe)_3$ (0.2 mmol, 20.8 mg), and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 180 ℃ for 24 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the mixture was added 6.0 M HCl aqueous solution (1.0 mL) and stirred for 0.5 h. Then the mixture was added saturated brine, extracted with ethyl acetate. Compound **3q** can be monitored by GCMS while the isomer of **3q’** was not found. The yield of **2a** was determined by GC and calibrated using naphthalene as internal standard.

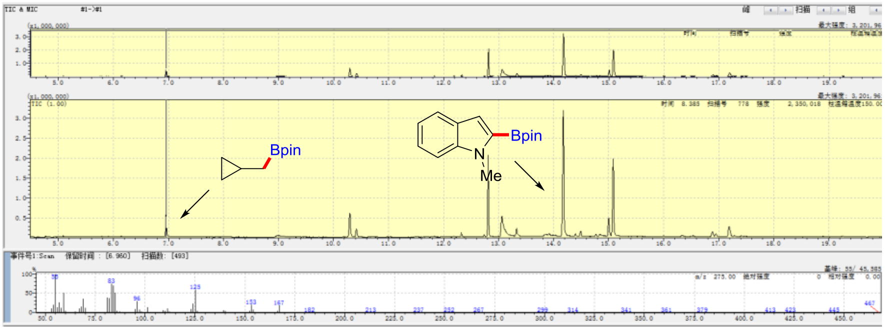
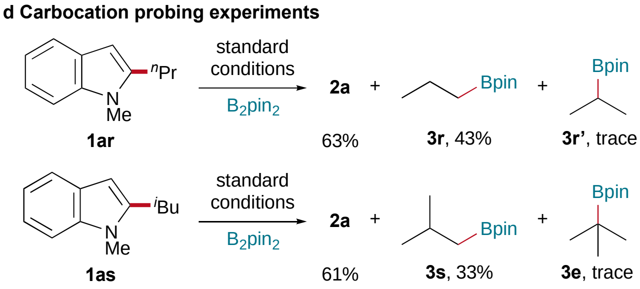


Figure S1. The GCMS analysis of radical clock experiment

Radical trapping experiment. An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1hf** (0.2 mmol, 47.5 mg), 9,10-dihydroanthracene (0.2 mmol, 36.1 mg), B_2pin_2 (0.8 mmol, 203.2 mg) and flushed with nitrogen gas. $B(OMe)_3$ (0.2 mmol, 20.8 mg), ethylmorpholine (0.1 mmol, 11.5 mg) and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the mixture was added 6.0 M HCl aqueous solution (1.0 mL) and stirred for 0.5 h, then the mixture was added saturated brine, extracted with ethyl acetate. The yield of **2h** and **3f** was determined by GC and calibrated using naphthalene as internal standard.



D Carbocation probing experiments

Reaction with 1ar as substrate. An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1ar** (0.2 mmol, 34.7 mg) and B_2pin_2 (0.5 mmol, 127.0 mg), and then flushed with nitrogen gas. $B(OMe)_3$ (0.06 mmol, 6.2 mg), Et_3N (0.06 mmol, 6.1 mg) and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the mixture was added 6.0 M HCl aqueous solution (1.0 mL) and stirred for 0.5 h, then the mixture was added saturated brine, extracted with ethyl acetate. The peak of **3r'** was detected by GCMS. The yield of **2a** and **3r** was determined by GC and calibrated using naphthalene as internal standard.

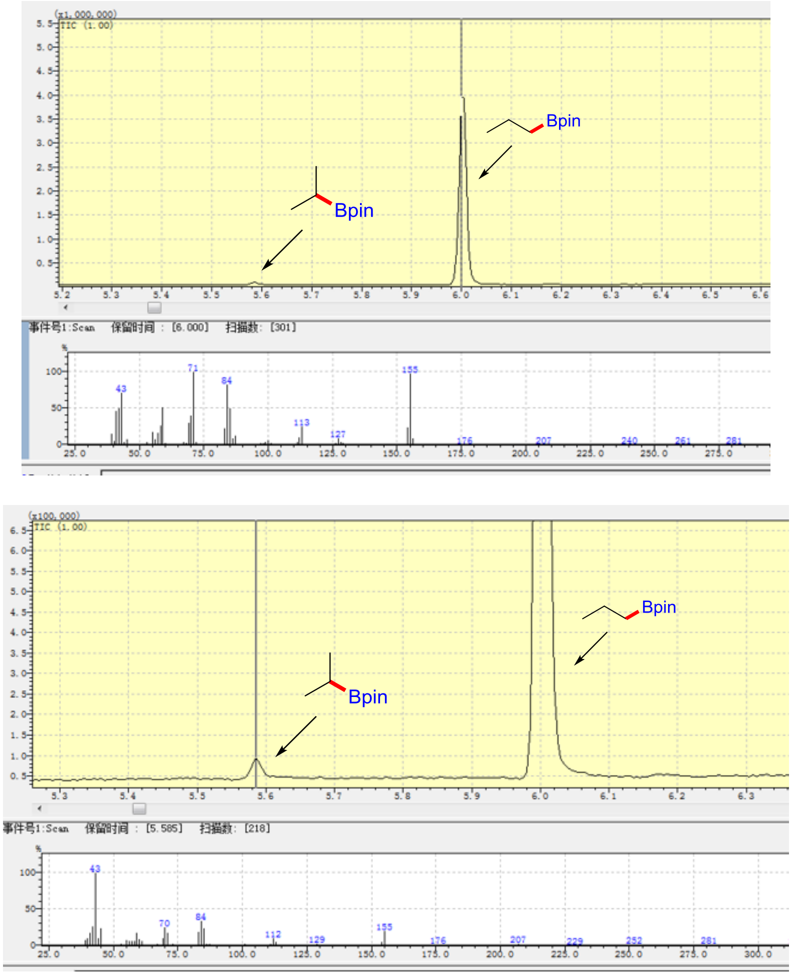


Figure S2. The GCMS analysis of reaction with **1ar** as substrate

Reaction with 1as as substrate. An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1as** (0.2 mmol, 37.5 mg) and B_2pin_2 (0.5 mmol, 127.0 mg), and then flushed with nitrogen gas. $B(OMe)_3$ (0.06 mmol, 6.2 mg), Et_3N (0.06 mmol, 6.1 mg) and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the mixture was added 6.0 M HCl aqueous solution (1.0 mL) and stirred for 0.5 h, then the mixture was added saturated brine, extracted with ethyl acetate. The peak of **3e** was detected by GCMS. The yield of **2a** and **3s** was determined by GC and calibrated using naphthalene as internal standard.

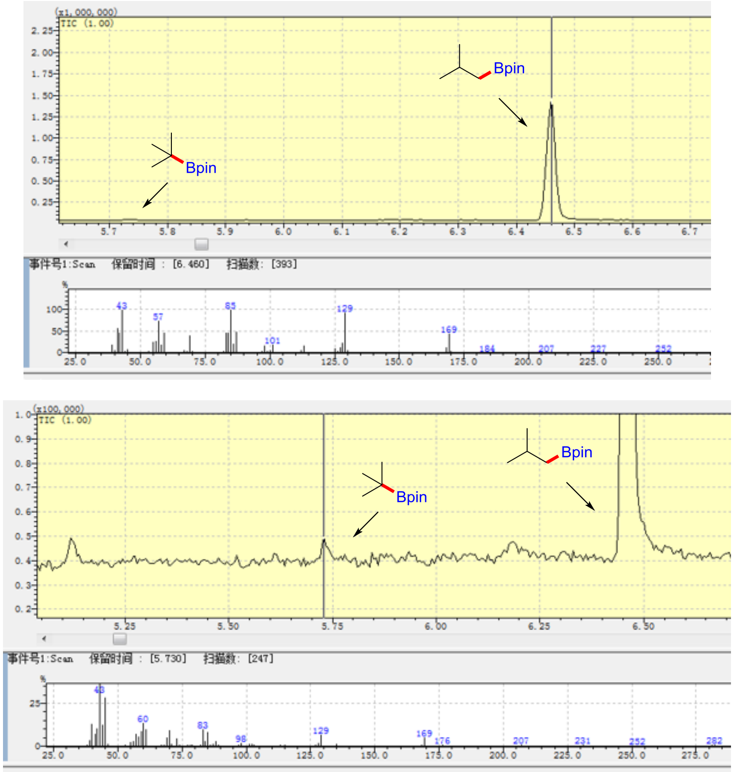
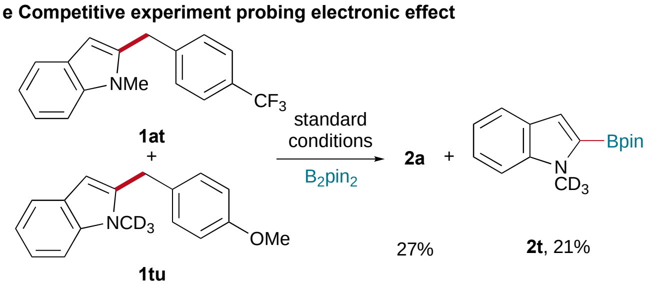


Figure S3. The GCMS analysis of reaction with **1as** as substrate



E Competitive experiment probing electronic effect

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1tu** (0.2 mmol, 50.9 mg), **1at** (0.2 mmol, 57.9 mg) and B_2pin_2 (0.5 mmol, 127.0 mg), and then flushed with nitrogen gas. $B(OMe)_3$ (0.06 mmol, 6.2 mg), Et_3N (0.06 mmol, 6.1 mg) and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the mixture was added 6.0 M HCl aqueous solution (1.0 mL) and stirred for 0.5 h. Then the mixture was added saturated brine, extracted with ethyl acetate. The solvent was evaporated under reduced pressure. The yield of **2a** and **2t** was determined by ^{1}H NMR, and calibrated using 3,4,5-trichloropyridine (25.2 mg) as internal standard.

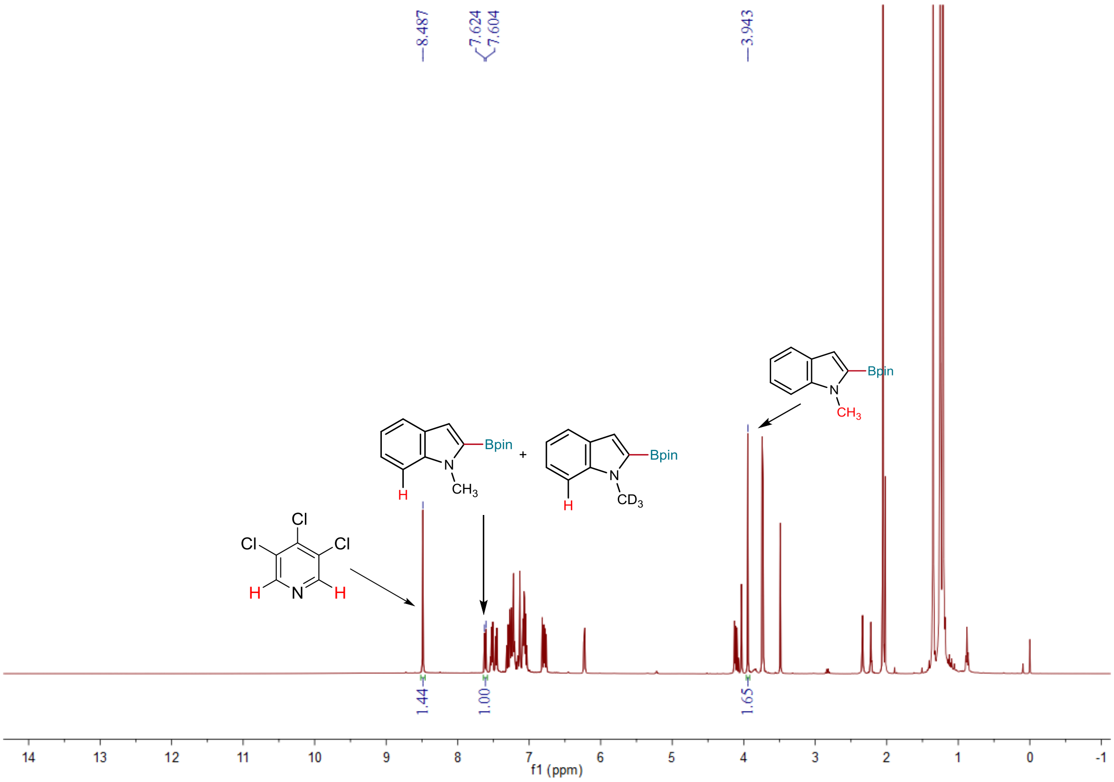
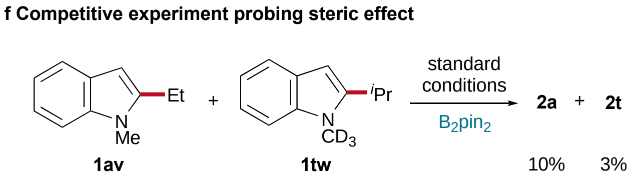


Figure S4. ^{1}H NMR spectrum of reaction with **1at** and **1tu** as substrates



F Competitive experiment probing steric effect

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with B_2pin_2 (0.5 mmol, 127.0 mg) and flushed with nitrogen gas. **1av** (0.2 mmol, 31.8 mg), **1tw** (0.2 mmol, 35.3 mg), $B(OMe)_3$ (0.06 mmol, 6.2 mg), Et_3N (0.06 mmol, 6.1 mg) and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the mixture was added 6.0 M HCl aqueous solution (1.0 mL) and stirred for 0.5 h. Then the mixture was added saturated brine, extracted with ethyl acetate. The solvent was evaporated under reduced pressure. The yield of **2a** and **2t** was determined by ^{1}H NMR, and calibrated using 3,4,5-trichloropyridine (25.1 mg) as internal standard.

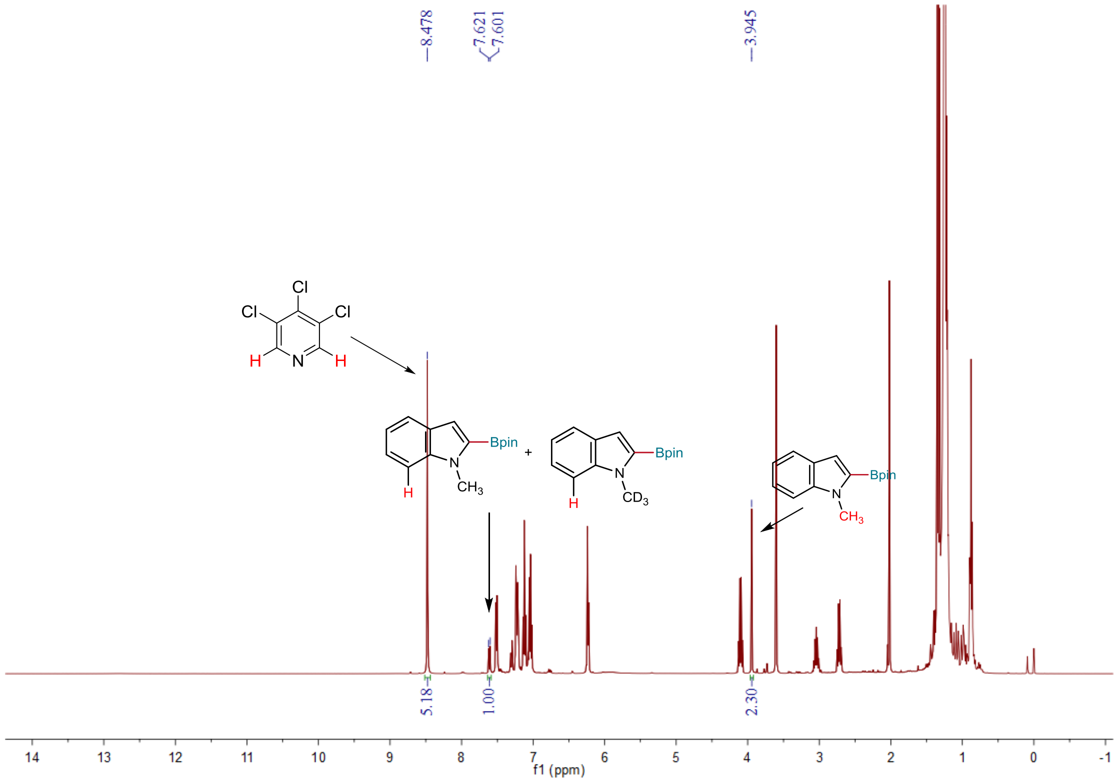
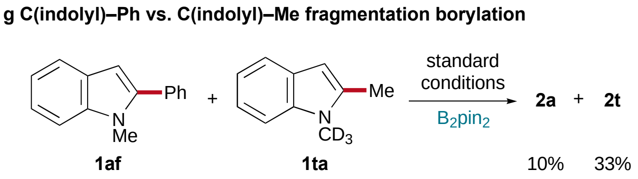


Figure S5. ^{1}H NMR spectrum of reaction with **1av** and **1tw** as substrates



G C(indolyl)–Ph vs C(indolyl)–Me fragmentation borylation

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1ta** (0.2 mmol, 29.6 mg), **1af** (0.2 mmol, 41.5 mg), B$_2$pin$_2$ (0.5 mmol, 127.0 mg) and flushed with nitrogen gas. B(OMe)$_3$ (0.06 mmol, 6.2 mg), Et$_3$N (0.06 mmol, 6.1 mg) and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the mixture was added 6.0 M HCl aqueous solution (1.0 mL) and stirred for 0.5 h. Then the mixture was added saturated brine, extracted with ethyl acetate. The solvent was evaporated under reduced pressure. The yield of **2a** and **2t** was determined by ^{1}H NMR, and calibrated using 3,4,5-trichloropyridine (26.4 mg) as internal standard.

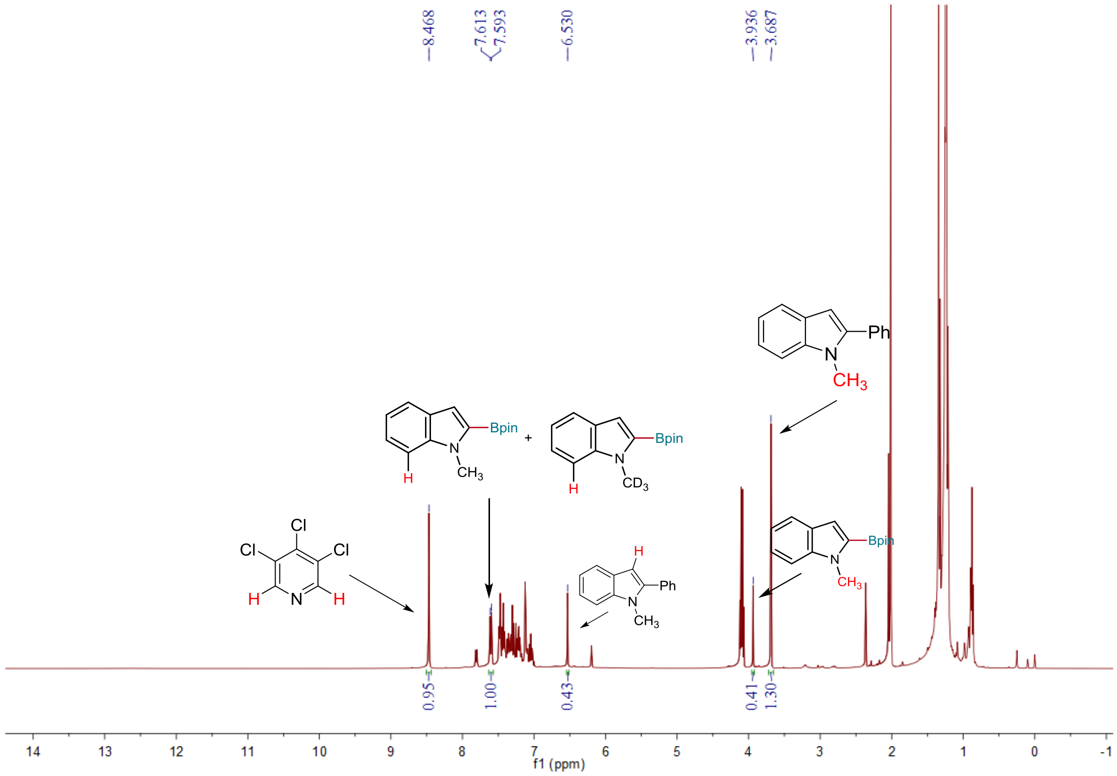
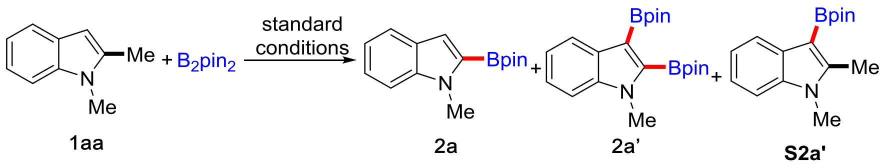


Figure S6. ^{1}H NMR spectrum of reaction with **1af** and **1ta** as substrates

6. The investigations of 2,3-diborylated indoles

(a) The structure of 2a'



Scheme S1. The detection of **2a’** in the reaction of **1aa** and B_2pin_2

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1aa** (0.2 mmol, 29.0 mg) and B_2pin_2 (0.5 mmol, 127.0 mg), and then flushed with nitrogen gas. $B(OMe)_3$ (0.06 mmol, 6.2 mg), Et_3N (0.06 mmol, 6.1 mg) and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 h in a heating module with stirring. After cooling the reaction mixture to room temperature, the solvent was evaporated under reduced pressure. **1aa**, **2a**, **S2a'**, **2a'** were involved in the residue. **2a'** is not particularly stable and it was difficult to obtain a pure compound. The corresponding C2,C3-diborylated indoles were also detected by GCMS in the reaction of **1ba**, **1ca**, **1da**, **1ea** and other substrates. The residue was purified by flash column chromatography over silica gel eluting with petroleum ether/dichloromethane to give the mixture mainly containing **2a** and **2a'** (detected by GCMS). The characteristic peak of **2a'** can be confirmed by eliminating the ^{1}H NMR of known compounds. The HRMS information provides convenience for the structure of **2a'**. HRMS (ESI) m/z calcd for $C_{21}H_{31}B_2NO_4$ [M+H]$^+$: 384.2512 found 384.2521.

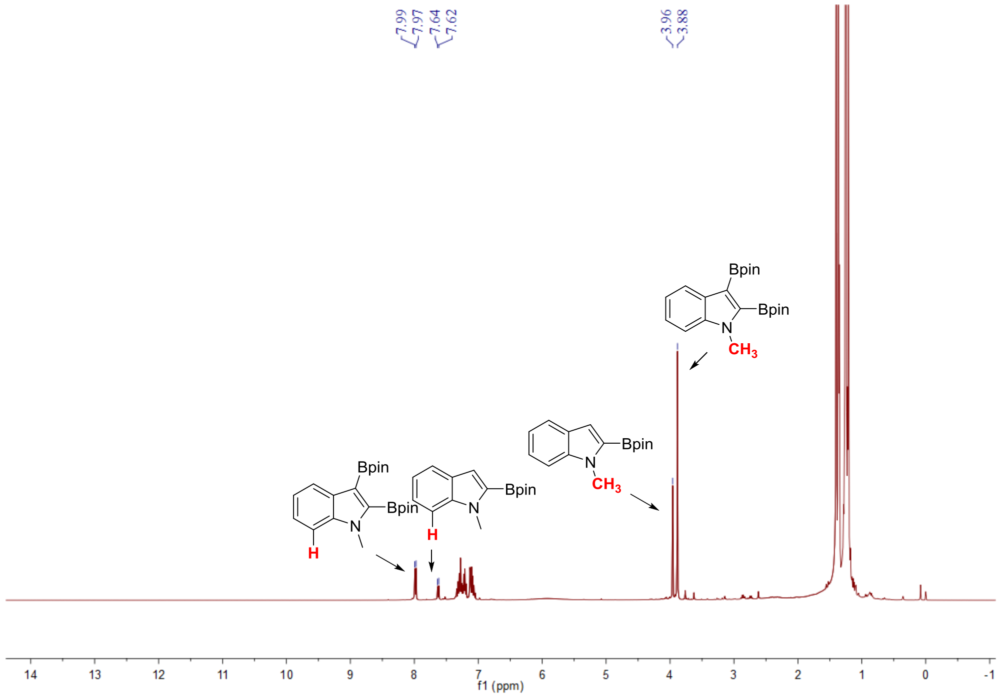


Figure S7. ^{1}H NMR spectrum of reaction residue including **2a’**

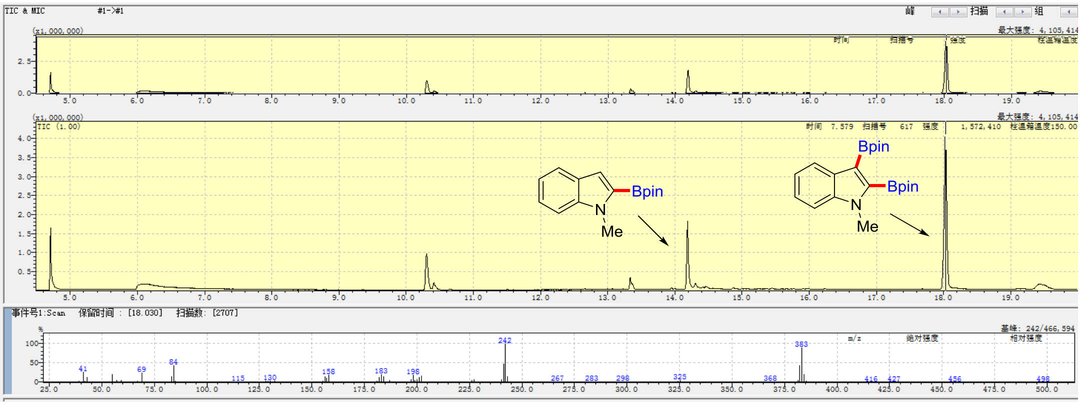
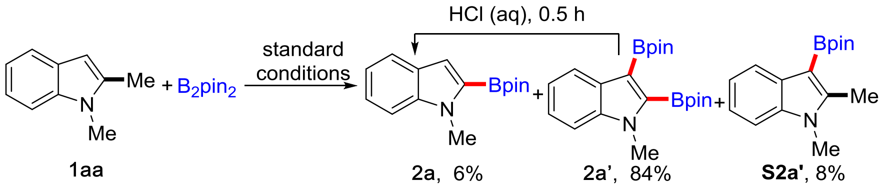


Figure S8. The GCMS analysis of reaction residue including **2a’**

(b) The fragmentation borylation of 1aa and B$_2$pin$_2$ before acidification



Scheme S2. The reaction of **1aa** and B$_2$pin$_2$ before acidification

1aa was converted to C2-borylated indole **2a** (6%), C3-borylated indole **S2a’** (8%) and C2,C3-diborylated indole **2a’** (84%) under standard conditions. **2a’** further occurred C3-protodeboronation by the treatment of aqueous HCl to afford **2a** in 83% GC yield and 75% yield upon isolation.

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1aa** (0.2 mmol, 29.0 mg) and B$_2$pin$_2$ (0.5 mmol, 127.0 mg), and then flushed with nitrogen gas. B(OMe)$_3$ (0.06 mmol, 6.2 mg), Et$_3$N (0.06 mmol, 6.1 mg) and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 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**, **2a'** and **S2a'** was determined by ^{1}H NMR, and calibrated using 3,4,5-trichloropyridine (26.7 mg) as internal standard.

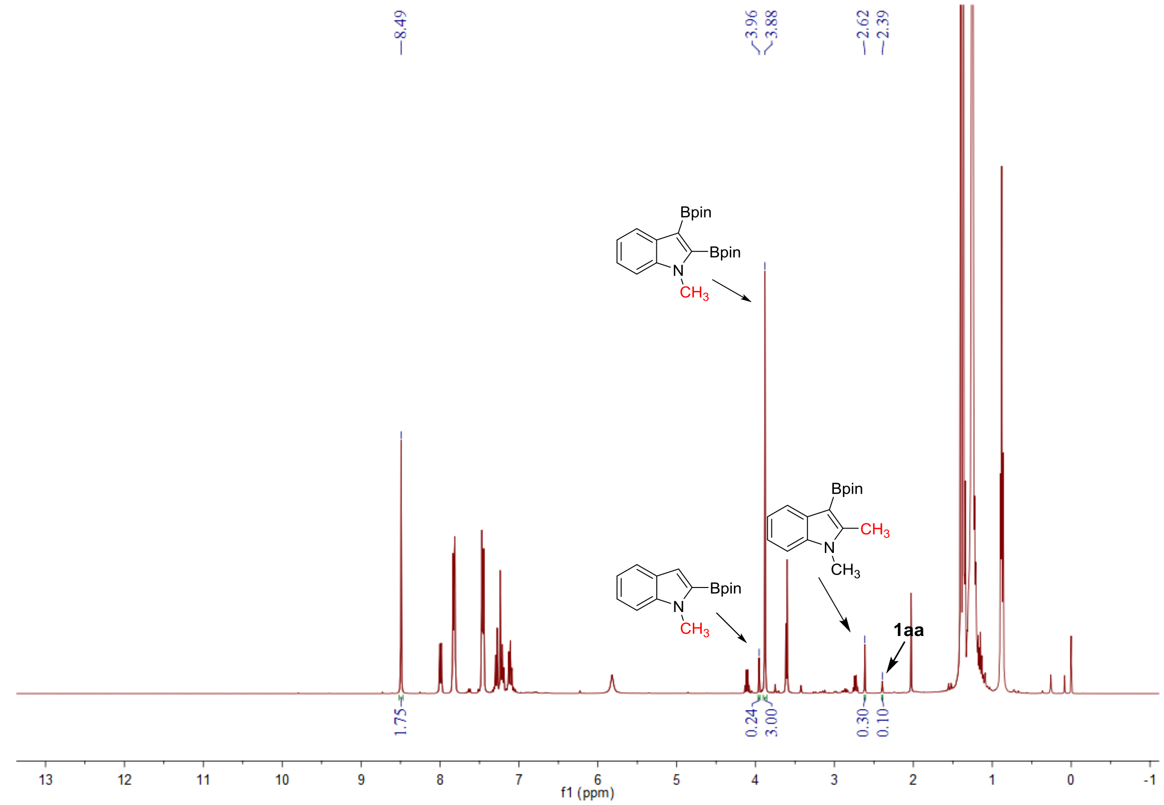
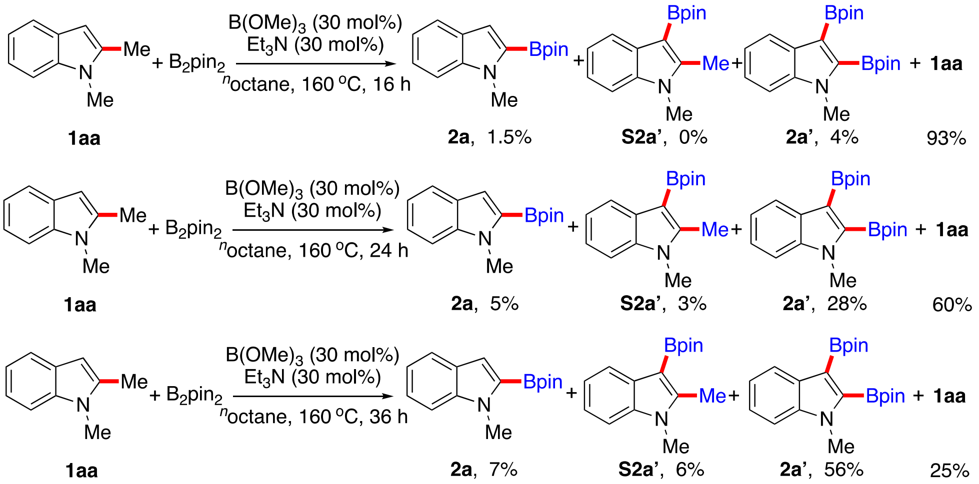


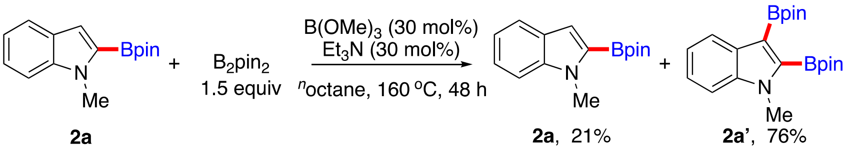
Figure S9. ^{1}H NMR spectrum of reaction of **1aa** and B_2pin_2 before acidification

(c) The generation of 2a'



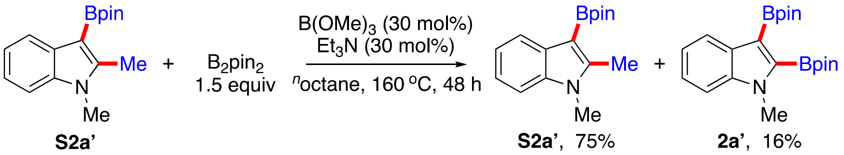
Scheme S3. The reaction of **1aa** and B_2pin_2 in different reaction times

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **1aa** (0.2 mmol, 29.0 mg) and B_2pin_2 (0.5 mmol, 127.0 mg), and then flushed with nitrogen gas. $B(OMe)_3$ (0.06 mmol, 6.2 mg), Et_3N (0.06 mmol, 6.1 mg) and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 16 h or 24 h or 36 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**, **S2a'**, **2a'** and **1aa** was determined by ^{1}H NMR, and calibrated using 3,4,5-trichloropyridine as internal standard.



Scheme S4. The reaction of **2a** and B_2pin_2

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **2a** (0.2 mmol, 51.4 mg) and B_2pin_2 (0.3 mmol, 76.2 mg), and then flushed with nitrogen gas. $B(OMe)_3$ (0.06 mmol, 6.2 mg), Et_3N (0.06 mmol, 6.1 mg) and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 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, and calibrated using 3,4,5-trichloropyridine as internal standard.



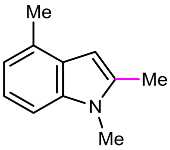
Scheme S5. The reaction of **2a’** and B_2pin_2

An oven-dried 25-mL Schlenk tube equipped with a magnetic stirring bar was charged with **S2a'** (0.2 mmol, 54.2 mg) and B_2pin_2 (0.3 mmol, 76.2 mg), and then flushed with nitrogen gas. $B(OMe)_3$ (0.06 mmol, 6.2 mg), Et_3N (0.06 mmol, 6.1 mg) and ^{n}octane (1.0 mL) were added to the tube under nitrogen atmosphere. The sealed tube was heated at 160 ℃ for 48 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 **S2a'** and **2a'** was determined by ^{1}H NMR, and calibrated using 3,4,5-trichloropyridine as internal standard.

These results showed that **2a’** was probably generated via the C3–H borylation of **2a**.

7. Analytical data of starting materials and products

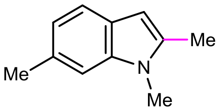
1,2,4-trimethyl-1H-indole (1ba)



1ba

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.06 (m, 2H), 6.89 (d, *J* = 6.4 Hz, 1H), 6.28 (s, 1H), 3.67 (s, 3H), 2.53 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 136.2, 129.2, 127.8, 120.7, 119.6, 106.5, 98.2, 29.6, 18.8, 12.9. HRMS (ESI) *m*/*z* calcd for $C_{11}H_{13}N$ $[M+H]^+$: 160.1121 found 160.1118.

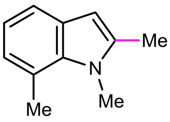
1,2,6-trimethyl-1H-indole (1da)



1da

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.54 (d, *J* = 5.2 Hz, 1H), 7.17 (s, 1H), 7.06-7.04 (m, 1H), 6.32 (s, 1H), 3.69 (s, 3H), 2.64 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.1, 130.1, 125.9, 120.9, 119.3, 108.9, 99.4, 29.3, 22.0, 12.8. HRMS (ESI) *m*/*z* calcd for $C_{11}H_{13}N$ $[M+H]^+$: 160.1121 found 160.1116.

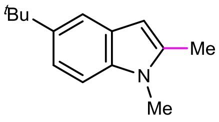
1,2,7-trimethyl-1H-indole (1ea)



1ea

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 1H), 6.94 (m, *J* = 7.2 Hz, 1H), 6.86-6.84 (m, 1H), 6.24 (s, 1H), 3.93 (s, 3H), 2.79 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 136.1, 128.7, 123.7, 120.5, 119.3, 117.9, 100.3, 32.4, 20.2, 13.2. HRMS (ESI) *m*/*z* calcd for $C_{11}H_{13}N$ $[M+H]^+$: 160.1121 found 160.1117.

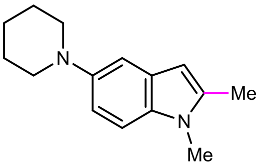
5-(tert-butyl)-1,2-dimethyl-1H-indole (1ga)



1ga

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 3.83 (s, 3H), 2.67 (s, 3H), 1.77 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 136.9, 135.7, 127.9, 118.6, 115.7, 108.3, 99.6, 34.6, 32.1, 29.5, 12.8. HRMS (ESI) *m*/*z* calcd for $C_{14}H_{19}N$ $[M+H]^+$: 202.1591 found 202.1585.

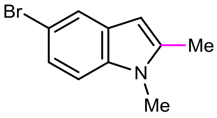
1,2-dimethyl-5-(piperidin-1-yl)-1H-indole (1ia)



1ia

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.22 (m, 2H), 7.06-7.04 (m, 1H), 6.26 (s, 1H), 3.64 (s, 3H), 3.20-3.18 (m, 4H), 2.46 (s, 3H), 1.88 (s, 4H), 1.69-1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 136.8, 133.1, 128.3, 114.7, 108.9, 107.7, 99.3, 53.7, 29.3, 26.5, 24.4, 12.7. HRMS (ESI) *m*/*z* calcd for $C_{15}H_{20}N_2$ $[M+H]^+$: 229.1699 found 229.1703.

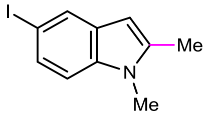
5-bromo-1,2-dimethyl-1H-indole (1ma)



1ma

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.67 (m, 1H), 7.26-7.23 (m, 1H), 7.09-7.06 (m, 1H), 6.21 (s, 1H), 3.58 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 135.8, 129.5, 122.7, 121.7, 112.2, 110.0, 99.0, 29.1, 12.5. HRMS (ESI) *m/z* calcd for $C_{10}H_{10}BrN$ $[M+H]^+$: 224.0069 found 224.0061.

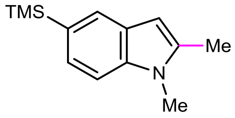
5-iodo-1,2-dimethyl-1H-indole (1na)



1na

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.90 (m, 1H), 7.43-7.41 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.20 (s, 1H), 3.56 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 136.5, 130.6, 128.6, 128.3, 110.8, 99.0, 82.7, 29.5, 12.8. HRMS (ESI) *m/z* calcd for $C_{10}H_{10}IN$ $[M+H]^+$: 271.9931 found 271.9923.

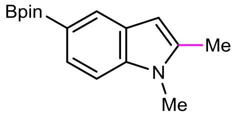
1,2-dimethyl-5-(trimethylsilyl)-1H-indole (1oa)



1oa

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.36 (dd, J_1 = 24.0 Hz, J_2 = 8.4 Hz, 2H), 6.32 (s, 1H), 3.70 (s, 3H), 2.49 (s, 3H), 0.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 136.9, 129.2, 128.1, 125.3, 125.2, 108.5, 99.7, 29.4, 12.8, -0.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{19}NSi$ $[M+H]^+$: 218.1360 found 218.1359.

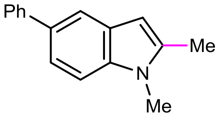
1,2-dimethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (1pa)



1pa

White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.20 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.35 (s, 1H), 3.60 (s, 3H), 2.44 (s, 3H), 1.48 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.3, 136.8, 127.7, 127.4, 126.7, 108.1, 100.1, 83.2, 29.2, 24.9, 12.6. HRMS (ESI) *m*/*z* calcd for $C_{16}H_{22}BNO_2$ [M+H]$^+$: 272.1819 found 272.1817.

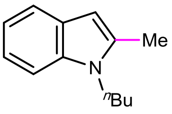
1,2-dimethyl-5-phenyl-1H-indole (1qa)



1qa

White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (s, 1H), 7.92-7.86 (m, 2H), 7.68-7.63 (m, 3H), 7.54-7.44 (m, 2H), 6.51 (s, 1H), 3.73 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.9, 137.5, 137.0, 132.7, 128.7, 128.5, 127.3, 126.1, 120.2, 118.2, 109.0, 100.0, 29.3, 12.7. HRMS (ESI) *m*/*z* calcd for $C_{16}H_{15}N$ [M+H]$^+$: 222.1277 found 222.1275.

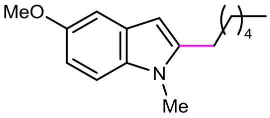
1-butyl-2-methyl-1H-indole (1ra)



1ra

Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69-7.63 (m, 1H), 7.41-7.39 (m, 1H), 7.30-7.19 (m, 2H), 6.38 (s, 1H), 4.17-4.14 (m, 2H), 2.54 (s, 3H), 1.89-1.83 (m, 2H), 1.54-1.44 (m, 2H), 1.11-1.07 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.7, 136.4, 128.2, 120.4, 119.7, 119.2, 109.1, 99.9, 43.0, 32.4, 20.4, 14.0, 12.9. HRMS (ESI) *m*/*z* calcd for $C_{13}H_{17}N$ [M+H]$^+$: 188.1434 found 188.1434.

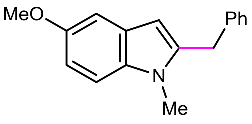
2-hexyl-5-methoxy-1-methyl-1H-indole(1hb)



1hb

Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.16 (d, *J* = 8.8 Hz, 1H), 7.04 (s, 1H), 6.84-6.82 (m, 1H), 6.19 (s, 1H), 3.86 (s, 3H), 3.64 (s, 3H), 2.74-2.70 (m, 2H), 1.76-7.69 (m, 2H), 1.47-1.29 (m, 6H), 0.95-0.92 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.0, 142.2, 132.7, 128.2, 110.3, 109.4, 102.0, 98.3, 56.0, 31.7, 29.5, 29.2, 28.7, 27.0, 22.7, 14.2. HRMS (ESI) *m*/*z* calcd for $C_{16}H_{23}NO$ [M+H]$^+$: 246.1852 found 246.1844.

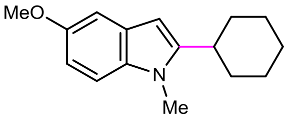
2-benzyl-5-methoxy-1-methyl-1H-indole (1hc)



1hc

White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32-7.28 (m, 2H), 7.25-7.14 (m, 4H), 7.05 (d, *J* = 3.6 Hz, 1H), 6.86-6.83 (m, 1H), 6.21 (s, 1H), 4.13 (s, 2H), 3.85 (s, 3H), 3.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.0, 139.7, 138.4, 133.0, 128.6, 128.5, 128.0, 126.4, 110.8, 109.5, 102.1, 100.8, 55.9, 33.5, 29.8. HRMS (ESI) *m*/*z* calcd for $C_{17}H_{17}NO$ [M+H]$^+$: 252.1383 found 252.1373.

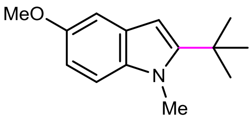
2-cyclohexyl-5-methoxy-1-methyl-1H-indole (1hd)



1hd

White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.16 (d, *J* = 8.8 Hz, 1H), 7.04-7.03 (m, 1H), 6.82-6.80 (m, 1H), 6.17 (s, 1H), 3.84 (s, 3H), 3.66 (s, 3H), 2.68-2.62 (m, 1H), 2.03-2.01 (m, 2H), 1.88-1.86 (m, 2H), 1.80-1.77 (m, 1H), 1.51-1.41 (m, 4H), 1.34-1.26 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.0, 147.4, 132.6, 128.2, 110.4, 109.4, 102.1, 96.2, 56.1, 36.1, 33.2, 29.6, 26.7, 26.2. HRMS (ESI) *m*/*z* calcd for $C_{16}H_{21}NO$ [M+H]$^+$: 244.1696 found 244.1689.

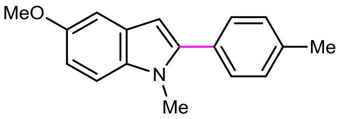
2-(tert-butyl)-5-methoxy-1-methyl-1H-indole (1he)



1he

White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.16 (d, *J* = 8.8 Hz, 1H), 7.04-7.03 (m, 1H), 6.85-6.82 (m, 1H), 6.24 (s, 1H), 3.85-3.85 (m, 6H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.1, 149.8, 134.0, 127.4, 110.8, 109.3, 102.2, 97.7, 56.1, 32.4, 32.4, 30.2. HRMS (ESI) *m*/*z* calcd for $C_{14}H_{19}NO$ [M+H]$^+$: 218.1539 found 218.1532.

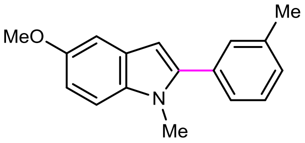
5-methoxy-1-methyl-2-(p-tolyl)-1H-indole (1hg)



1hg

White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26-7.24 (m, 2H), 7.10-7.01 (m, 4H), 6.85-6.83 (m, 1H), 6.37 (s, 1H), 3.71 (s, 3H), 3.45 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.3, 142.0, 137.4, 133.8, 129.9, 129.1, 129.0, 128.3, 111.6, 110.2, 102.0, 101.0, 55.6, 30.9, 21.1. HRMS (ESI) *m*/*z* calcd for $C_{17}H_{17}NO$ [M+H]$^+$: 252.1383 found 252.1383.

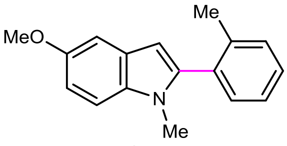
5-methoxy-1-methyl-2-(m-tolyl)-1H-indole (1hh)



1hh

White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40-7.23 (m, 5H), 7.14 (d, *J* = 2.4 Hz, 1H), 6.95-6.93 (m, 1H), 6.51 (s, 1H), 3.90 (s, 3H), 3.74 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.3, 142.3, 138.2, 133.8, 132.8, 130.0, 128.6, 128.4, 128.3, 126.4, 111.8, 110.3, 102.1, 101.2, 55.9, 31.3, 21.6. HRMS (ESI) *m*/*z* calcd for $C_{17}H_{17}NO$ [M+H]$^+$: 252.1383 found 252.1375.

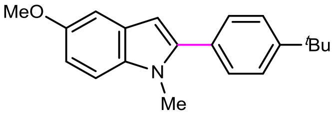
5-methoxy-1-methyl-2-(o-tolyl)-1H-indole (1hi)



1hi

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H), 7.14-7.13 (m, 1H), 6.94-6.91 (m, 1H), 6.38 (s, 1H), 3.89 (s, 3H), 3.50 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 141.1, 138.0, 132.7, 132.6, 131.1, 130.1, 128.6, 128.3, 125.6, 111.5, 110.2, 102.2, 101.2, 56.0, 30.5, 20.1. HRMS (ESI) *m/z* calcd for $C_{17}H_{17}NO$ $[M+H]^+$: 252.1383 found 252.1377.

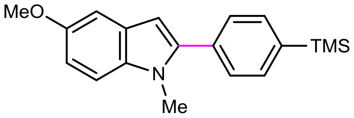
2-(4-(tert-butyl)phenyl)-5-methoxy-1-methyl-1H-indole (1hj)



1hj

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.43 (m, 4H), 7.27-7.24 (m, 1H), 7.11 (s, 1H), 6.91 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 6.48 (s, 1H), 3.87 (s, 3H), 3.73 (s, 3H), 1.39-1.38 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 150.9, 142.2, 133.7, 130.0, 129.0, 128.3, 125.5, 111.7, 110.3, 102.1, 101.0, 56.0, 34.7, 31.4, 31.4. HRMS (ESI) *m/z* calcd for $C_{20}H_{23}NO$ $[M+H]^+$: 294.1852 found 294.1846.

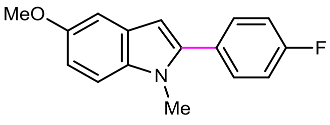
5-methoxy-1-methyl-2-(4-(trimethylsilyl)phenyl)-1H-indole (1hk)



1hk

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.28-7.25 (m, 1H), 7.12-7.11 (m, 1H), 6.94-6.91 (m, 1H), 6.51 (s, 1H), 3.88 (s, 3H), 3.75 (s, 3H), 0.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 143.3, 141.2, 135.0, 134.6, 134.3, 129.6, 129.4, 113.1, 111.5, 103.2, 102.5, 57.0, 32.5, 0.00. HRMS (ESI) *m/z* calcd for $C_{19}H_{23}NOSi$ $[M+H]^+$: 310.1622 found 310.1613.

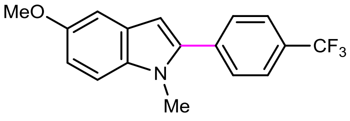
2-(4-fluorophenyl)-5-methoxy-1-methyl-1H-indole (1hl)



1hl

White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 (s, 2H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.26-7.24 (m, 3H), 7.07-7.05 (m, 1H), 6.57 (s, 1H), 3.98 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 162.5 (d, *J* = 246.0 Hz), 154.5, 141.0, 133.8, 130.9 (d, *J* = 8.0 Hz), 129.0 (d, *J* = 3.0 Hz), 128.2, 115.5 (d, *J* = 22.0 Hz), 112.0, 110.4, 102.2, 101.4, 55.8, 31.1. HRMS (ESI) *m*/*z* calcd for $C_{16}H_{14}FNO$ [M+H]$^+$: 256.1132 found 256.1130.

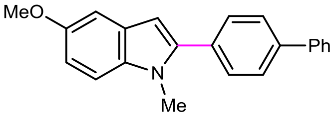
5-methoxy-1-methyl-2-(4-(trifluoromethyl)phenyl)-1H-indole (1hm)



1hm

White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.62-7.60 (m, 2H), 7.48-7.46 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.06 (m, 1H), 6.93-6.91 (m, 1H), 6.48 (s, 1H), 3.79 (s, 3H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.7, 140.3, 136.4, 134.3, 129.5 (q, *J* = 32.0 Hz), 129.3, 128.3, 125.5 (q, *J* = 4.0 Hz), 124.3 (q, *J* = 270.0 Hz), 112.8, 110.6, 102.6, 102.3, 55.7, 31.3. HRMS (ESI) *m*/*z* calcd for $C_{17}H_{14}F_3NO$ [M+H]$^+$: 306.1100 found 306.1097.

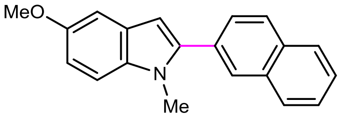
2-([1,1'-biphenyl]-4-yl)-5-methoxy-1-methyl-1H-indole (1hn)



1hn

White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.71-7.65 (m, 4H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.50-7.46 (m, 2H), 7.41-7.37 (m, 1H), 7.29-7.25 (m, 1H), 7.13-7.12 (m, 1H), 6.94-6.92 (m, 1H), 6.55 (s, 1H), 3.88 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.4, 141.8, 140.6, 140.6, 134.0, 131.8, 129.6, 128.9, 128.3, 127.6, 127.2, 127.1, 112.0, 110.4, 102.2, 101.4, 56.0, 31.5. HRMS (ESI) *m*/*z* calcd for $C_{22}H_{19}NO$ [M+H]$^+$: 314.1539 found 314.1533.

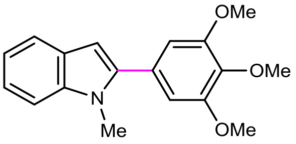
5-methoxy-1-methyl-2-(naphthalen-2-yl)-1H-indole (1ho)



1ho

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.92 (m, 4H), 7.67-7.55 (m, 3H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.17 (s, 1H), 6.99-6.97 (m, 1H), 6.63 (s, 1H), 3.92 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 142.2, 134.1, 133.4, 132.8, 130.4, 128.5, 128.3, 128.3, 128.2, 127.9, 127.3, 126.7, 126.5, 112.2, 110.5, 102.4, 101.9, 56.1, 31.6. HRMS (ESI) *m/z* calcd for $C_{20}H_{17}NO$ $[M+H]^+$: 288.1383 found 288.1380.

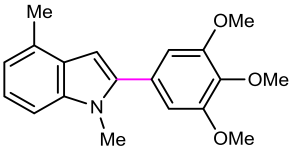
1-methyl-2-(3,4,5-trimethoxyphenyl)-1H-indole (1ap)



1ap

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.38-7.36 (m, 1H), 7.28-7.24 (m, 1H), 7.17-7.13 (m, 1H), 6.71 (s, 2H), 6.55 (s, 1H), 3.93 (s, 3H), 3.91 (s, 6H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 141.6, 138.3, 138.0, 128.4, 127.9, 121.8, 120.5, 120.0, 109.7, 106.7, 101.5, 61.0, 56.3, 31.3. HRMS (ESI) *m/z* calcd for $C_{18}H_{19}NO_3$ $[M+H]^+$: 298.1438 found 298.1431.

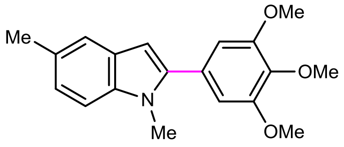
1,4-dimethyl-2-(3,4,5-trimethoxyphenyl)-1H-indole (1bp)



1bp

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.15 (m, 2H), 6.96 (d, *J* = 6.8 Hz, 1H), 6.72 (s, 2H), 6.56 (s, 1H), 3.93 (s, 3H), 3.92 (s, 6H), 3.76 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 141.0, 138.0, 138.0, 130.0, 128.5, 127.7, 122.0, 120.2, 107.3, 106.7, 100.1, 61.0, 56.3, 31.4, 18.7. HRMS (ESI) *m/z* calcd for $C_{19}H_{21}NO_3$ $[M+H]^+$: 312.1594 found 312.1586.

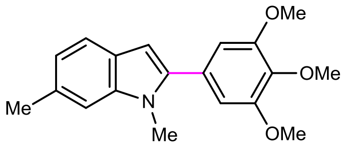
1,5-dimethyl-2-(3,4,5-trimethoxyphenyl)-1H-indole (1cp)



1cp

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.26-7.24 (m, 1H), 7.09-7.07 (m, 1H), 6.71 (s, 2H), 6.47 (s, 1H), 3.93 (s, 3H), 3.91 (s, 6H), 3.74 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 141.6, 137.9, 136.8, 129.2, 128.6, 128.1, 123.4, 120.1, 109.3, 106.7, 101.0, 61.0, 56.3, 31.3, 21.5. HRMS (ESI) *m/z* calcd for $C_{19}H_{21}NO_3$ $[M+H]^+$: 312.1594 found 312.1586.

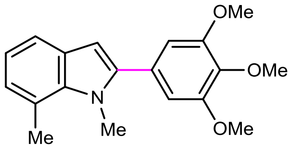
1,6-dimethyl-2-(3,4,5-trimethoxyphenyl)-1H-indole (1dp)



1dp

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, $J = 8.0$ Hz, 1H), 7.15 (s, 1H), 6.98 (d, $J = 8.0$ Hz, 1H), 6.70 (s, 2H), 6.49 (s, 1H), 3.92 (s, 3H), 3.90 (s, 6H), 3.72 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 141.0, 138.8, 137.9, 131.6, 128.6, 125.7, 121.7, 120.1, 109.7, 106.7, 101.3, 61.0, 56.3, 31.2, 22.0. HRMS (ESI) *m/z* calcd for $C_{19}H_{21}NO_3$ $[M+H]^+$: 312.1594 found 312.1586.

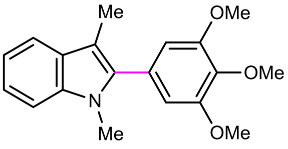
1,7-dimethyl-2-(3,4,5-trimethoxyphenyl)-1H-indole (1ep)



1ep

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, $J = 7.6$ Hz, 1H), 7.02-6.93 (m, 2H), 6.68 (s, 2H), 6.50 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.91 (s, 6H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 142.7, 137.9, 137.6, 128.8, 128.6, 124.8, 121.5, 120.2, 118.6, 106.9, 102.2, 61.0, 56.3, 34.6, 20.2. HRMS (ESI) *m/z* calcd for $C_{19}H_{21}NO_3$ $[M+H]^+$: 312.1594 found 312.1585.

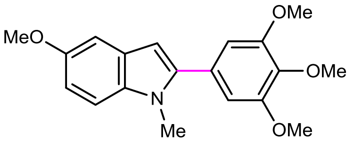
1,3-dimethyl-2-(3,4,5-trimethoxyphenyl)-1H-indole (1fp)



1fp

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.34-7.32 (m, 1H), 7.28-7.24 (m, 1H), 7.18-7.14 (m, 1H), 6.61 (s, 2H), 3.95 (s, 3H), 3.89 (s, 6H), 3.64 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 137.7, 137.7, 137.1, 128.3, 127.6, 121.9, 119.2, 118.8, 109.3, 108.4, 107.8, 61.0, 56.2, 31.0, 9.5. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{21}NO_3$ $[M+H]^+$: 312.1594 found 312.1586.

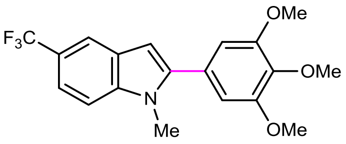
5-methoxy-1-methyl-2-(3,4,5-trimethoxyphenyl)-1H-indole (1hp)



1hp

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.24 (m, 1H), 7.10-7.09 (m, 1H), 6.92-6.90 (m, 1H), 6.69 (s, 2H), 6.47 (s, 1H), 3.92 (s, 3H), 3.92 (s, 6H), 3.87(s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 153.2, 142.1, 138.0, 133.7, 128.4, 128.2, 112.0, 110.4, 106.7, 102.2, 101.1, 61.0, 56.3, 55.9, 31.4. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{21}NO_4$ $[M+H]^+$: 328.1543 found 328.1536.

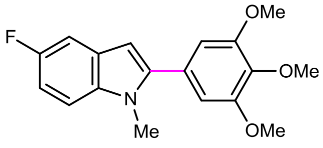
1-methyl-5-(trifluoromethyl)-2-(3,4,5-trimethoxyphenyl)-1H-indole (1jp)



1jp

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.48-7.40 (m, 2H), 6.69 (s, 2H), 6.61 (s, 1H), 3.92 (s, 3H), 3.91 (s, 6H), 3.78 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 143.3, 139.4, 138.3, 127.5, 127.1, 125.4 (q, *J* = 270.0 Hz), 122.2 (q, *J* = 32.0 Hz), 118.3 (q, *J* = 3.0 Hz), 118.0 (q, *J* = 4.0 Hz), 109.8, 106.7, 102.2, 61.0, 56.2, 31.4. HRMS (ESI) *m*/*z* calcd for $C_{19}H_{18}F_3NO_3$ $[M+H]^+$: 366.1312 found 366.1309.

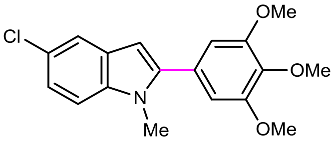
5-fluoro-1-methyl-2-(3,4,5-trimethoxyphenyl)-1H-indole (1kp)



1kp

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.24 (m, 2H), 7.01-6.96 (m, 1H), 6.69 (s, 2H), 6.49 (s, 1H), 3.92 (s, 3H), 3.90 (s, 6H), 3.74 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 157.0, 153.3, 143.2, 138.2, 134.9, 128.0, 110.2 (d, *J* = 3.0 Hz), 110.1 (d, *J* = 39.0 Hz). 106.7, 105.2 (d, *J* = 23.0 Hz), 101.4 (d, *J* = 5.0 Hz), 61.0, 56.3, 31.4. HRMS (ESI) *m*/*z* calcd for $C_{18}H_{18}FNO_3$ $[M+H]^+$: 316.1343 found 316.1340.

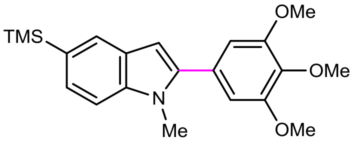
5-chloro-1-methyl-2-(3,4,5-trimethoxyphenyl)-1H-indole(1lp)



1lp

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.6 Hz, 1H), 7.26-7.24 (m, 1H), 7.19-7.16 (m, 1H), 6.69 (s, 2H), 6.47 (s, 1H), 3.92 (s, 3H), 3.90 (s, 6H), 3.73 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 142.9, 138.2, 136.7, 128.8, 127.9, 125.6, 121.9, 119.7, 110.6, 106.7, 101.0, 61.0, 56.3, 31.4. HRMS (ESI) *m*/*z* calcd for $C_{18}H_{18}ClNO_3$ $[M+H]^+$: 332.1048 found 332.1045.

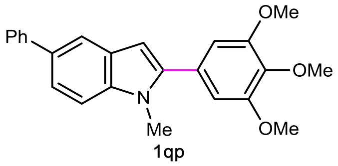
1-methyl-2-(3,4,5-trimethoxyphenyl)-5-(trimethylsilyl)-1H-indole (1op)



1op

White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.82 (s, 1H), 7.42-7.36 (m, 2H), 6.70 (s, 2H), 6.55 (s, 1H), 3.93 (s, 3H), 3.91 (s, 6H), 3.75 (s, 3H), 0.32 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.8, 142.2, 139.4, 138.6, 130.8, 129.0, 128.4, 127.1, 126.5, 109.9, 107.3, 102.0, 61.6, 56.9, 31.8, 0.0. HRMS (ESI) *m*/*z* calcd for $C_{21}H_{27}NO_3Si$ [M+H]$^+$: 370.1833 found 370.1824.

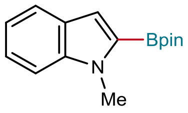
1-methyl-5-phenyl-2-(3,4,5-trimethoxyphenyl)-1H-indole (1qp)



1qp

White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85-7.84 (m, 1H), 7.68-7.66 (m, 2H), 7.53-7.50 (m, 1H), 7.47-7.40 (m, 3H), 7.33-7.30 (m, 1H), 6.72 (s, 2H), 6.59 (s, 1H), 3.93 (s, 3H), 3.91 (s, 6H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 153.3, 142.6, 142.3, 138.1, 137.9, 133.5, 128.7, 128.3, 128.3, 127.4, 126.4, 121.6, 118.9, 109.9, 106.7, 101.8, 61.0, 56.3, 31.4. HRMS (ESI) *m*/*z* calcd for $C_{24}H_{23}NO_3$ [M+H]$^+$: 374.1751 found 374.1743.

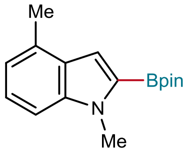
1-Metyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2a) [2]



2a

White solid (38.6 mg, 75%, from **1aa**; 27.8 mg, 54%, from **1ap**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.27-7.22 (m, 1H), 7.13 (s, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 3.96 (s, 3H) , 1.36 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.1, 127.9, 123.2, 121.6, 119.3, 114.3, 109.7, 83.7, 32.2, 24.8.

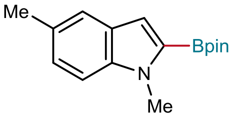
1,4-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2b) [2]



2b

White solid (34.7 mg, 64%, from **1ba**; 24.9 mg, 46%, from 1**bp**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.24-7.20 (m, 3H), 6.94-6.92 (m, 1H), 4.01 (s, 3H), 2.61 (s, 3H), 1.42 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.0, 131.2, 127.9, 123.5, 119.4, 112.9, 107.3, 83.7, 32.4, 24.9, 18,7.

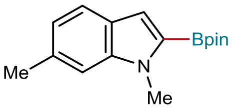
1,5-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2c) [2]



2c

White solid (38.5 mg, 71%, from **1ca**; 28.7 mg, 53%, **1cp**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.41 (s, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.03 (s, 1H), 3.93 (s, 3H), 2.43 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz,CDCl$_3$) δ 138.7, 128.4, 128.1, 125.0, 121.0, 113.6, 109.3, 83.6, 32.2, 24.8, 21.3.

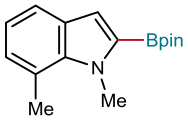
1,6-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2d) [2]



2d

White solid (33.1 mg, 61%, from **1da**; 29.8 mg, 55%, from **1dp**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.15 (s, 1H), 7.11 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 3.96 (s, 3H), 2.52 (s, 3H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.6, 133.1, 125.8, 121.3, 121.2, 114.2, 109.5, 83.6, 32.1, 24.8, 22.1.

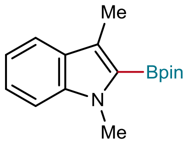
1,7-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2e) [2]



2e

White solid (32.5 mg, 60%, from **1ea**; 34.7 mg, 64%, from **1ep**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 (t, *J* = 4.4 Hz, 1H), 7.11 (s, 1H), 6.94-6.91 (m, 2H), 4.27 (s, 3H), 2.80 (s, 3H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.2, 128.9, 126.0, 121.6, 119.8, 119.5, 115.0, 83.6, 35.7, 24.8, 20.4.

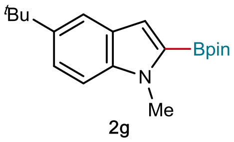
1,3-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2f) [2]



2f

White solid (13.6 mg, 25%, from **1fa**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.38-7.32 (m, 2H), 7.18-7.15 (m, 1H), 4.01 (s, 3H), 2.67 (s, 3H), 1.45 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.9, 128.5, 124.8, 123.3, 119.8, 118.5, 109.5, 83.2, 32.2, 24.9, 10.3.

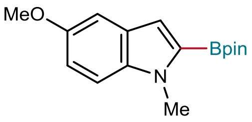
5-(tert-butyl)-1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2g)



2g

White solid (42.6 mg, 68%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, *J* = 1.2 Hz, 1H), 7.40-7.38 (m, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 0.4 Hz, 1H), 3.97 (s, 3H), 1.41 (s, 9H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.1, 138.5, 127.7, 121.7, 117.1, 114.3, 109.1, 83.6, 34.5, 32.2, 31.9, 24.8. HRMS (ESI) *m/z* calcd for $C_{19}H_{28}BNO_2$ $[M+H]^+$: 314.2286 found 314.2289.

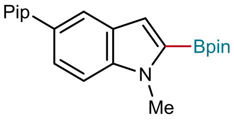
5-Methoxy-1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2h)[2]



2h

White solid (37.9 mg, 66%, from **1ha**; 32.7 mg, 57%, from **1hf**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 9.2 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.95-6.92 (m, 1H), 3.94 (s, 3H), 3.84 (s, 3H), 1.36 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 135.8, 128.0, 114.3, 113.5, 110.4, 102.2, 83.6, 55.8, 32.3, 24.8.

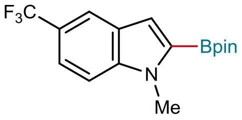
1-methyl-5-(piperidin-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2i)



2i

Light yellow solid (36.7 mg, 54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.8 Hz, 1H), 7.13 (s, 1H), 7.07 (d, *J* = 9.2 Hz, 1H), 7.02 (s, 1H), 3.91 (s, 3H), 3.07 (t, *J* = 4.8 Hz, 4H), 1.76 (s, 4H), 1.56 (d, *J* = 1.2 Hz, 2H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 136.2, 128.2, 118.5, 113.7, 110.0, 108.3, 83.5, 53.5, 32.3, 26.4, 24.8, 24.3. HRMS (ESI) *m*/*z* calcd for $C_{20}H_{29}BN_2O_2$ $[M+H]^+$: 341.2395 found 341.2399.

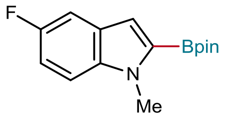
1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl)-1H-indole (2j)



2j

White solid (41.0 mg, 63%, from **1ja**; 24.7 mg, 38%, from **1jp**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.44 (dd, J_1 = 34.0 Hz, J_2 = 8.8 Hz, 2H), 7.22 (s, 1H), 4.00 (s, 3H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 127.2, 125.6 (q, *J* = 272.0 Hz), 121.8 (q, *J* = 31.0 Hz), 119.8 (q, *J* = 4.0 Hz), 119.5 (q, *J* = 5.0 Hz), 115.2, 110.1, 84.2, 32.6, 25.0. HRMS (ESI) *m*/*z* calcd for $C_{16}H_{19}BF_3NO_2$ $[M+H]^+$: 326.1534 found 326.1537.

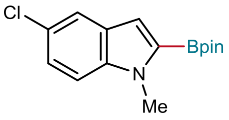
5-Fluoro-1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2k) [2]



2k

White solid (34.1 mg, 62%, from **1ka**; 27.0 mg, 49%, from **1kp**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29-7.22 (m, 2H), 7.08 (s, 1H), 7.02 (td, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H), 3.96 (s, 3H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 157.7 (d, J = 233.0 Hz), 136.9, 127.8 (d, J = 10.0 Hz), 113.8 (d, J = 5.0 Hz), 111.9 (d, J = 27.0 Hz), 110.3 (d, J = 9.0 Hz), 105.7 (d, J = 23.0 Hz), 83.8, 32.4, 24.8.

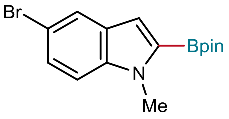
5-Chloro-1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2l) [2]



2l

White solid (35.0 mg, 60%, from **1la**; 23.3 mg, 40%, from **1lp**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, J = 1.2 Hz, 1H), 7.23 (d, J = 8.8 Hz, 1H), 7.19-7.16 (m, 1H), 7.04 (s, 1H), 3.93 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.5, 128.7, 125.0, 123.4, 120.7, 113.5, 110.7, 83.9, 32.4, 24.8.

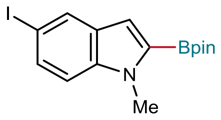
5-Bromo-1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2m) [2]



2m

White solid (48.2 mg, 72%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.77 (s, 1H), 7.32 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 7.05 (s, 1H), 3.95 (s, 3H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 138.7, 129.4, 125.9, 123.8, 113.4, 112.6, 111.1, 83.9, 32.4, 24.8.

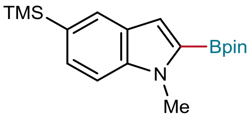
5-iodo-1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2n)



2n

Light yellow solid (40.6 mg, 53%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (s, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.02 (s, 1H), 3.94 (s, 3H), 1.37 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.1, 131.3, 130.4, 130.3, 113.2, 111.6, 83.9, 82.8, 32.3, 24.8. HRMS (ESI) *m/z* calcd for $C_{15}H_{19}BINO_2$ $[M+H]^+$: 384.0625 found 384.0629.

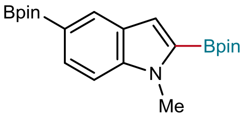
1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trimethylsilyl)-1H-indole (2o)



2o

White solid (35.6 mg, 54%, from **1oa**; 30.3 mg, 46%, from **1op**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80 (s, 1H), 7.36 (dd, J_1 = 24.0 Hz, J_2 = 8.4 Hz, 1H), 7.10 (s, 1H), 3.94 (s, 3H), 1.36 (s, 12H), 0.29 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.6, 129.3, 127.7, 127.2, 123.1, 114.3, 109.2, 83.6, 32.1, 24.8, -0.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{28}BNO_2Si$ $[M+H]^+$: 330.2055 found 330.2059.

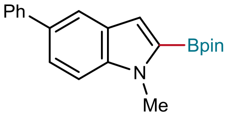
1-methyl-2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (2p)



2p

White solid (43.7 mg, 57%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.18 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 3.40 (s, 3H), 1.38 (s, 24H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.0, 129.7, 129.1, 127.6, 115.1, 109.0, 83.7, 83.4, 32.2, 24.9, 24.8. HRMS (ESI) *m/z* calcd for $C_{21}H_{31}B_2NO_4$ $[M+H]^+$: 384.2512 found 384.2519.

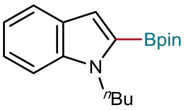
5-Phenyl-1-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2q) [2]



2q

White solid (44.65 mg, 67%, from **1qa**; 33.4 mg, 51%, from **1qp**); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, *J* = 0.8 Hz, 1H), 7.68-7.66 (m, 2H), 7.56-7.53 (m, 1H), 7.46-7.40 (m, 3H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.19 (s, 1H), 4.01 (s, 3H), 1.39 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.4, 139.7, 132.7, 128.6, 128.3, 127.3, 126.2, 123.1, 119.9, 114.6, 109.9, 83.7, 32.3, 24.8.

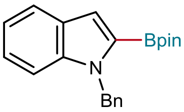
1-Butyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2r) [2]



2r

White solid (41.9 mg, 70%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* =8.4 Hz, 1H), 7.33-7.29 (m, 1H), 7.22 (s, 1H), 7.16-7.12 (m, 1H), 4.49 (t, *J* =8.8 Hz, 1H), 1.87-1.79 (m, 1H), 1.43 (s, 12H), 1.43-1.35 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.4, 128.1, 123. 0, 121.7, 119.2, 114.5, 110.0, 83.6, 45.9, 33.2, 24.8, 20.3, 13.9.

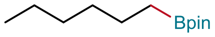
1-Benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2s) [2]



2s

White solid (44.7 mg, 67%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.22-7.13 (m, 5H), 7.08-7.03 (m, 3H), 5.65 (s, 2H), 1.26 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 139.9, 139.3, 128.3, 128.2, 126.9, 126.5, 123.4, 121.7, 119.6, 115.1, 110.3, 83.8, 49.0, 24.7.

2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)[23]



3b

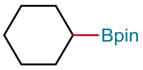
Colourless oil (23.3 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42-1.37 (m, 2H), 1.32-1.26 (m, 6H), 1.24 (s, 12H), 0.89-0.85 (m, 3H), 0.79-0.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.8, 32.1, 31.6, 24.8, 23.9, 22.6, 14.1.

2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(3c)[24]

3c

Colourless oil (27.0 mg, 62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.08 (m, 5H), 2.28 (s, 2H), 1.21 (s, 12H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 129.0, 128.3, 124.8, 83.4, 24,8.

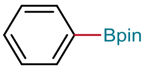
2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)[24]



3d

Colourless oil (8.8 mg, 21%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67-1.58 (m, 4H), 1.35-1.29 (m, 6H), 1.23 (s, 12H), 0.99-0.95 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.7, 28.0, 27.1, 26.8, 24.7.

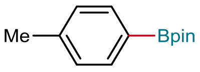
4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (3f)[25]



3f

White solid (25.3 mg, 62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.57-7.46 (m, 3H), 1.43 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 131.2, 127.6, 83.5, 24.8.

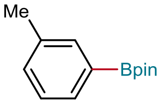
4,4,5,5-tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (3g) [25]



3g

White solid (29.2 mg, 67%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, *J* = 6.4 Hz, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.29 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 141.2, 134.9, 128.5, 83.4, 24.8, 21.7.

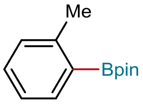
4,4,5,5-tetramethyl-2-(m-tolyl)-1,3,2-dioxaborolane (3h) [25]



3h

White solid (25.3 mg, 58%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.64-7.59 (m, 2H), 7.28-7.25 (m, 2H), 2.35 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 137.2, 135.4, 132.1, 131.8, 127.7, 83.7, 24.9, 21.3.

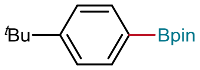
4,4,5,5-tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane (3i) [25]



3i

White solid (17.0 mg, 39%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78-7.76 (m, 1H), 7.31-7.27 (m, 1H), 7.16-7.13 (m, 2H), 2.54 (s, 3H), 1.31 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.9, 136.1, 130.9, 129.9, 124.8, 83.5, 25.0, 22.4.

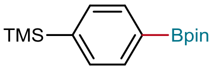
2-(4-(tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)[26]



3j

White solid (36.4 mg, 70%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78-7.76 (d, *J* = 8.4 Hz, 2H), 7.41-7.39 (d, *J* = 8.4 Hz, 2H), 1.33-1.32 (m, 21H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 154.5, 134.8, 124.7, 83.6, 34.9, 31.3, 24.9.

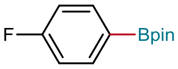
trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (3k)[27]



3k

White solid (34.8 mg, 63%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.78 (d, *J* = 7.6 Hz, 2H), 7.54-7.52 (d, *J* = 7.6 Hz, 2H), 1.34 (s, 12H), 0.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 135.1, 133.9, 85.0, 26.1, 0.00.

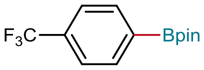
2-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l) [25]



3l

White solid (28.4 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.82 (m, 2H), 7.08-7.04 (m, 2H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2 (d, *J* = 248.0 Hz), 137.1 (d, *J* = 8.0 Hz), 114.8 (d, *J* = 20.0 Hz), 83.8, 24.8.

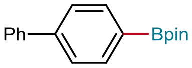
4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (3m) [25]



3m

White solid (35.9 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (m, 2H), 7.63 (m, 2H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 133.0 (q, *J* = 32.0 Hz), 124.4 (q, *J* = 274.0 Hz), 124.4 (q, *J* = 4.0 Hz), 84.3, 24.8.

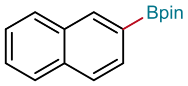
2-([1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n)[28]



3n

White solid (36.4 mg, 65%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91-7.89 (m, 2H), 7.61-7.59 (m, 4H), 7.43-7.39 (m, 2H), 7.34-7.30 (m, 1H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 144.0, 141.1, 135.4, 128.9, 127.7, 127.3, 126.6, 83.9, 25.0.

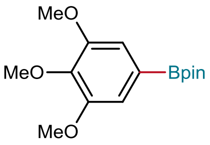
4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (3o) [25]



3o

White solid (32.5 mg, 64%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.43 (s, 1H), 7.93-7.85 (m, 4H), 7.55-7.48 (m, 2H), 1.42 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 136.4, 135.2, 133.0, 130.5, 127.8, 127.1, 127.1, 125.9, 84.0, 25.1.

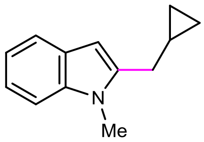
4,4,5,5-tetramethyl-2-(3,4,5-trimethoxyphenyl)-1,3,2-dioxaborolane (3p)[29]



3p

White solid (32.9 mg, 56%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.04 (s, 2H), 3.91 (s, 6H), 3.87 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.9, 140.8, 111.3, 83.9, 60.8, 56.2, 24.9.

2-(cyclopropylmethyl)-1-methyl-1H-indole (1aq)



1aq

Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.27-7.22 (m, 1H), 7.17-7.13 (m, 1H), 7.08-7.05 (m, 1H), 6.39 (s, 1H), 3.65 (s, 3H), 2.67 (d, *J* = 6.8 Hz, 2H), 1.13-1.09 (m, 1H), 0.62-0.58 (m, 2H), 0.25-0.21 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 140.8, 137.4, 127.9, 120.5, 119.8, 119.2, 108.7, 99.1, 31.6, 29.5, 9.6, 4.8. HRMS (ESI) *m/z* calcd for $C_{11}H_{15}N$ [M+H]$^+$: 186.1269 found 186.1267.

4,4,5,5-tetramethyl-2-propyl-1,3,2-dioxaborolane (3r)[30]

3r

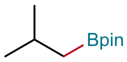
Colourless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.39-1.30 (m, 2H), 1.14 (s, 12H), 0.82 (t, *J* = 7.2 Hz, 3H), 0.66 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 82.6, 24.7, 17.3, 16.7.

2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r')[31]

3r'

Colourless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.21 (s, 12H), 1.06-1.00 (m, 1H), 0.95 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 82.7, 24.6, 17.9.

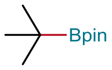
2-isobutyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s)[32]



3s

Colourless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.83-1.73 (m, 1H), 1.17 (s, 12H), 0.85 (d, *J* = 6.8 Hz, 6H), 0.65 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 82.6, 25.1, 24.7, 14.0.

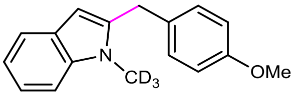
2-(tert-butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)[33]



3e

Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (s, 12H), 0.86 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.7, 26.8, 24.5.

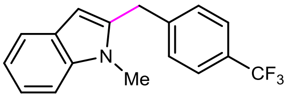
2-(4-methoxybenzyl)-1-(methyl-d3)-1H-indole (1tu)



1tu

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 1H), 7.26-7.23 (m, 1H), 7.16-7.07 (m, 4H), 6.84-6.82 (m, 2H), 6.25 (s, 1H), 4.07 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 139.6, 137.6, 130.4, 129.5, 127.7, 120.8, 120.0, 119.3, 113.9, 108.8, 100.9, 55.3, 32.6. HRMS (ESI) *m*/*z* calcd for $C_{17}H_{14}D_3NO$ $[M+H]^+$: 255.1560 found 255.1559.

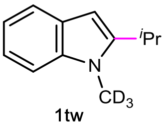
1-methyl-2-(4-(trifluoromethyl)benzyl)-1H-indole (1at)



1at

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.57 (m, 3H), 7.33-7.29 (m, 3H), 7.24-7.21 (m, 1H), 7.15-7.12 (m, 1H), 6.31 (s, 1H), 4.21 (m, 2H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 138.0, 137.8, 129.0, 129.0 (q, *J* = 32.0 Hz), 127.8, 125.6 (q, *J* = 4.0 Hz), 124.4 (q, *J* = 270.0 Hz), 121.3, 120.3, 119.7, 109.1, 101.6, 33.3, 29.8. HRMS (ESI) *m*/*z* calcd for $C_{17}H_{14}F_3N$ $[M+H]^+$: 290.1151 found 290.1151.

2-isopropyl-1-(methyl-d3)-1H-indole (1tw)

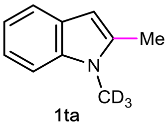


1tw

Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.52 (m, 1H), 7.27-7.22 (m, 1H), 7.19-7.14 (m, 1H), 7.11-7.05 (m, 1H), 6.29-6.25 (m, 1H), 3.09-3.00 (m, 1H), 1.36-1.31 (m, 6H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 147.7, 137.6, 128.0, 120.8, 120.1, 119.4, 108.9, 96.3, 26.1, 22.8. HRMS (ESI) *m/z* calcd for $C_{12}H_{12}D_3N$ $[M+H]^+$: 177.1454 found 177.1453.

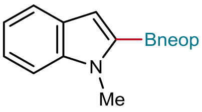
2-methyl-1-(methyl-d3)-1H-indole(1ta)



1ta

White solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.6 Hz, 1H), 7.25-7.21 (m, 1H), 7.16-7.12 (m, 1H), 7.07-7.04 (m, 1H), 6.23 (s, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.8, 128.0, 120.44, 119.6, 119.2, 108.7, 99.6, 12.8. HRMS (ESI) *m/z* calcd for $C_{10}H_8D_3N$ $[M+H]^+$: 149.1153 found 149.1150.

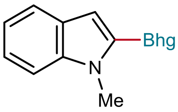
2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-1-methyl-1H-indole (4)[34]



4

White solid (28.1 mg, 58%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.25-7.22 (m, 1H), 7.08-7.05 (m, 2H), 3.96 (s, 3H), 3.79 (s, 4H), 1.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 127.8, 122.7, 121.4, 119.0, 113.0, 109.5, 72.2, 32.1, 31.9, 21.9.

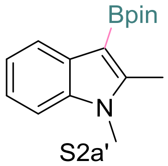
1-methyl-2-(4,4,6-trimethyl-1,3,2-dioxaborinan-2-yl)-1H-indole (5)



5

White solid (33.9 mg, 66%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.31 (d , *J* = 8.0 Hz, 1H), 7.23-7.19 (m, 1H), 7.04 (d, *J* = 9.6 Hz, 2H), 4.37 (s, 1H), 3.95 (s, 3H), 1.87 (d, *J* = 13.6 Hz, 1H), 1.63 (t, *J* = 12.4 Hz, 1H), 1.39 (s, 6H), 1.36 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 127.8, 122.4, 121.2, 118.9, 112.6, 109.5, 71.4, 65.2, 46.0, 32.0, 31.3, 28.2, 23.2. HRMS (ESI) *m*/*z* calcd for $C_{15}H_{20}BNO_2$ $[M+H]^+$: 258.1660 found 258.1663.

1,2-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (S2a')



S2a'

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 6.8 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.16-7.12 (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, 77.4, 77.1, 76.8, 29.5, 25.1, 12.7.

8. Reference

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9. NMR spectra of starting materials and products

Figure S10. ^{1}H NMR spectrum of 1ba in $CDCl_3$ (400 MHz)

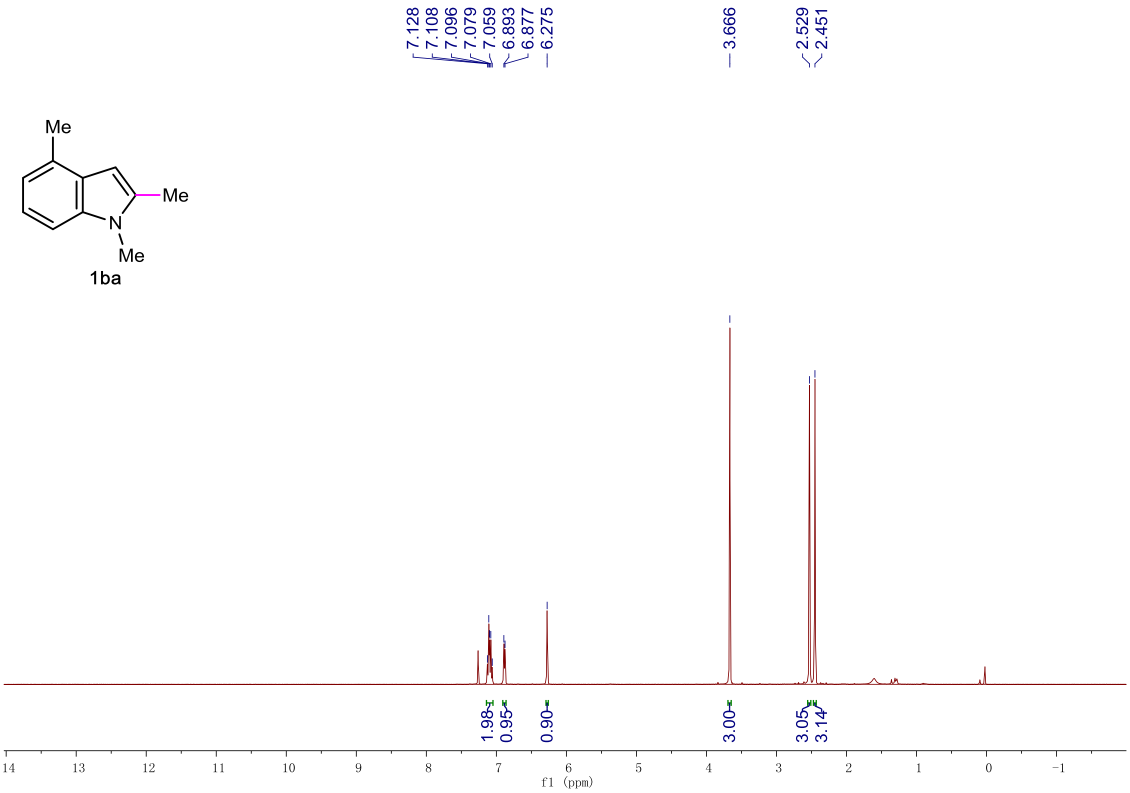

Figure S11. ^{13}C NMR spectrum of 1ba in $CDCl_3$ (100 MHz)

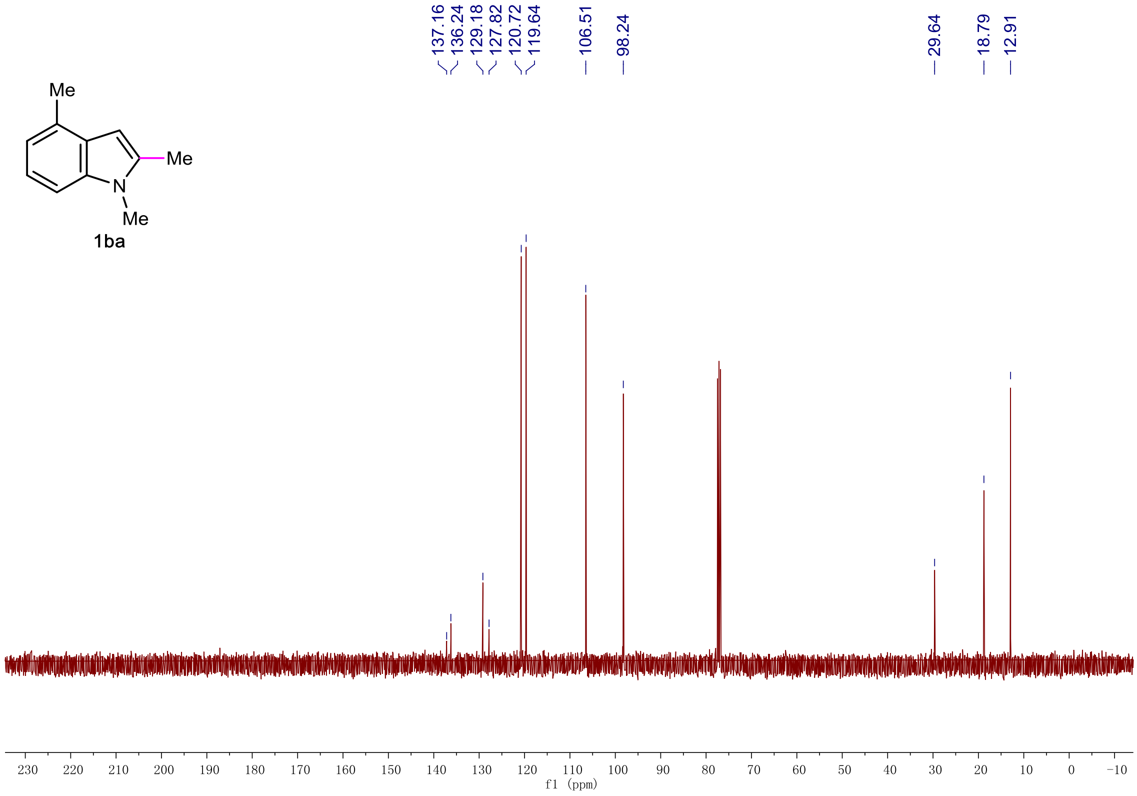

Figure S12. ^{1}H NMR spectrum of 1da in CDCl$_3$ (400 MHz)

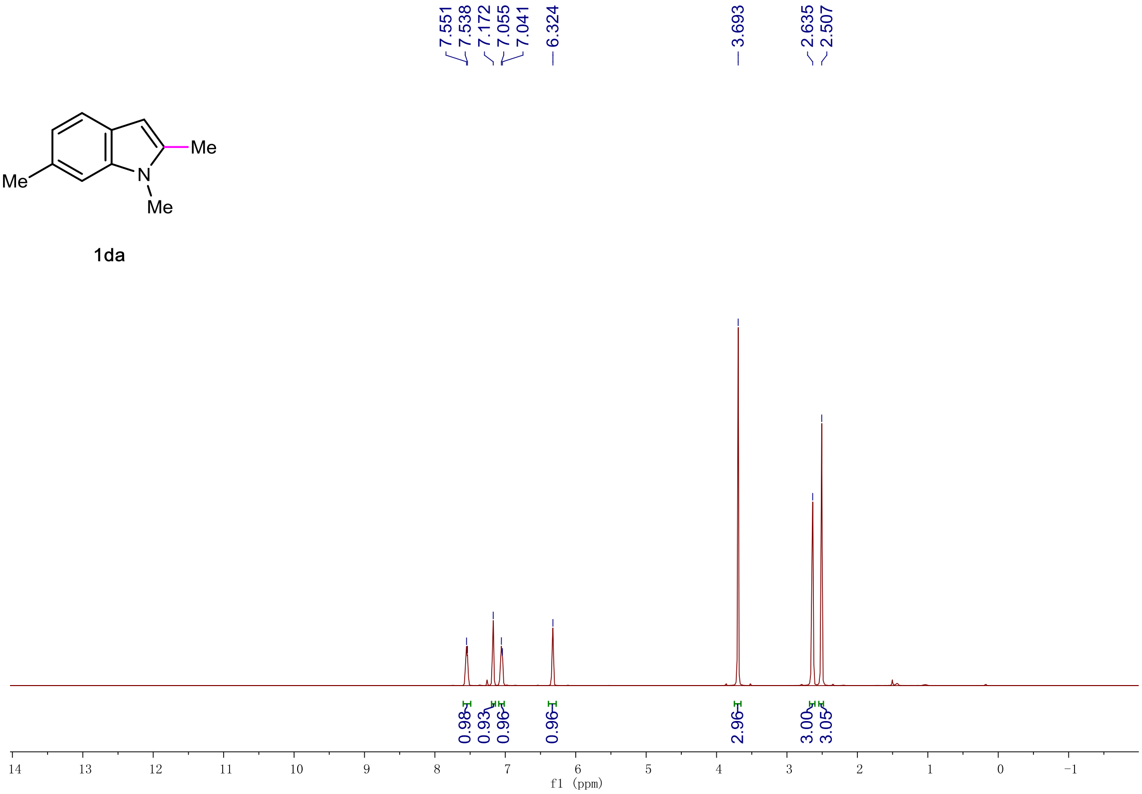

Figure S13. ^{13}C NMR spectrum of 1da in CDCl$_3$ (100 MHz)

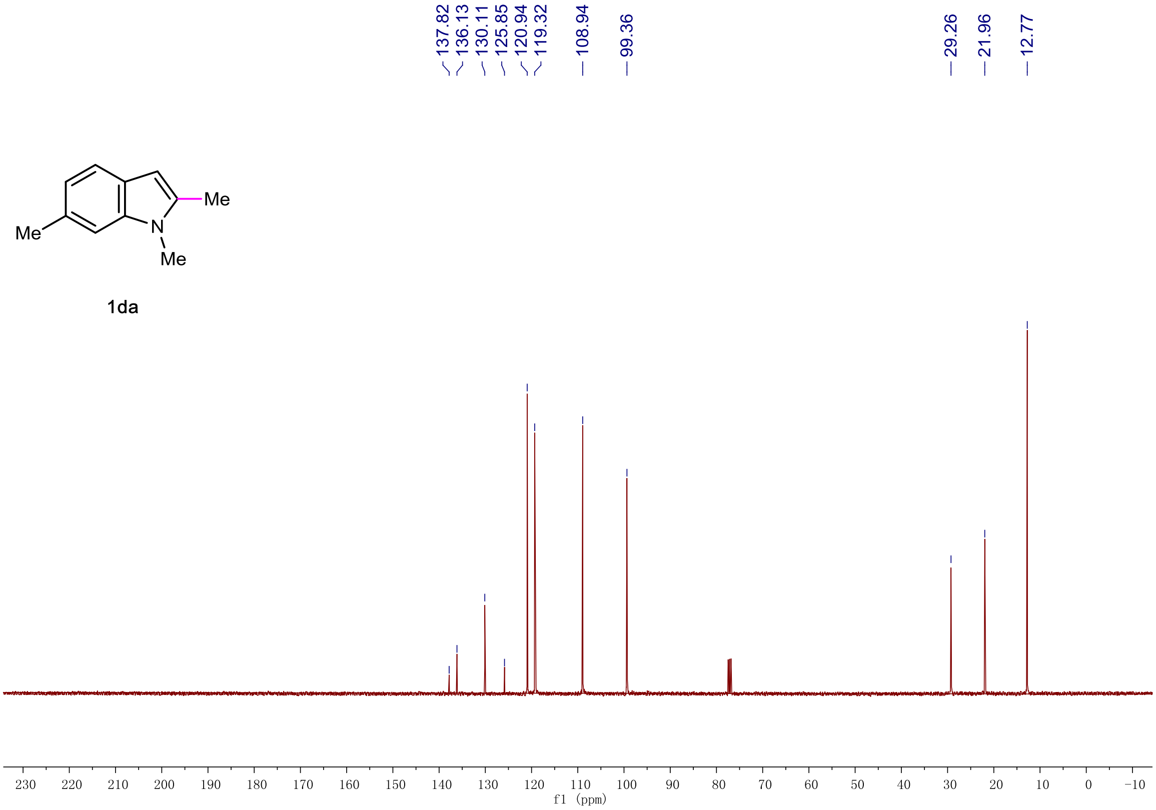

Figure S14. ^{1}H NMR spectrum of 1ea in CDCl$_3$ (400 MHz)

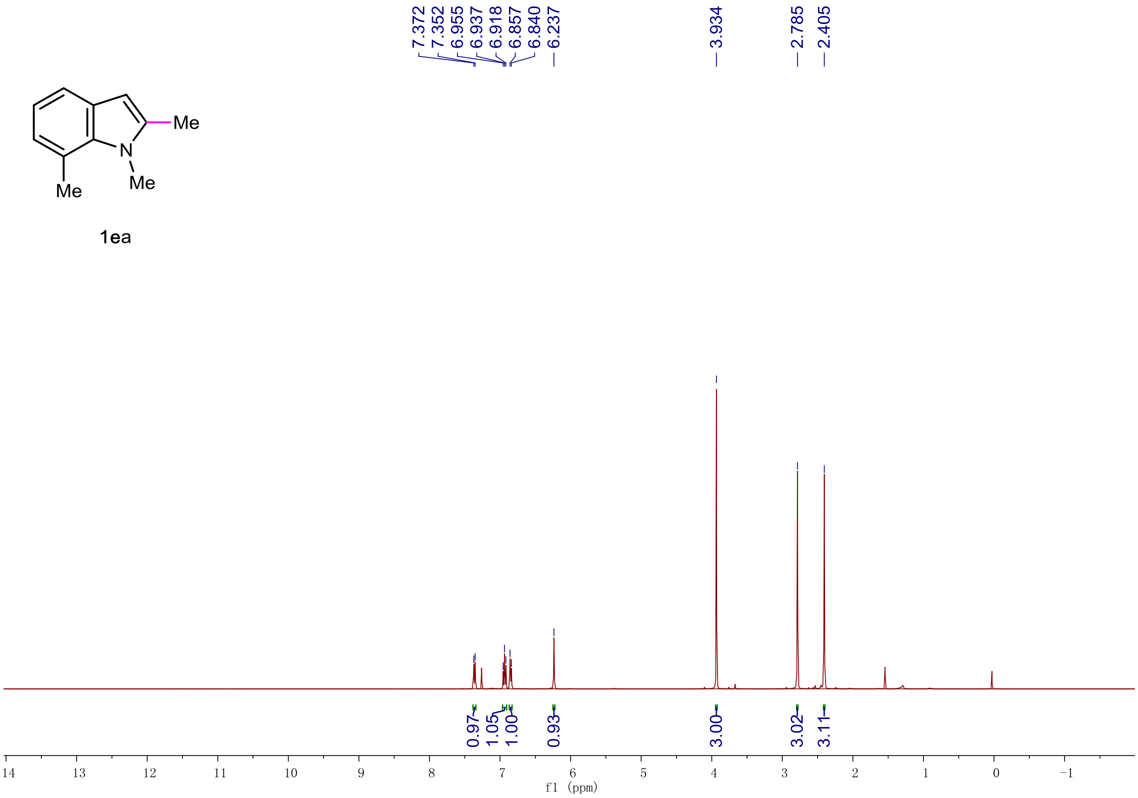
1ea

Figure S15. ^{13}C NMR spectrum of 1ea in CDCl$_3$ (100 MHz)

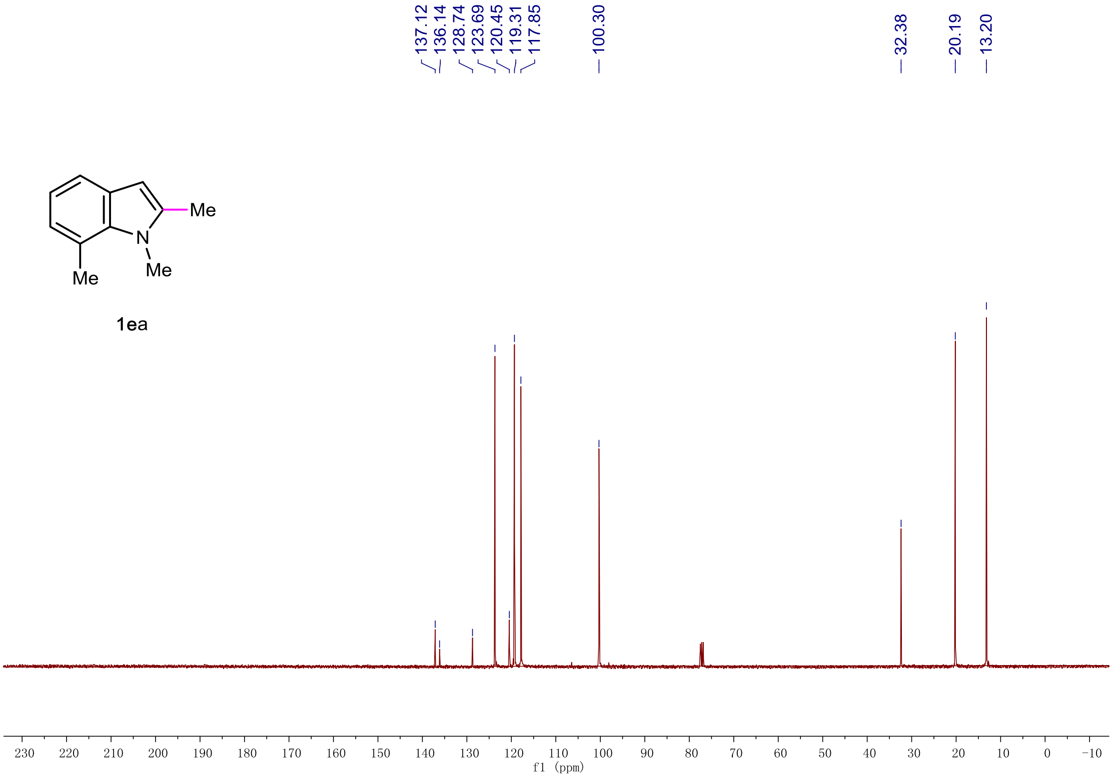
1ea

Figure S16. ^{1}H NMR spectrum of 1ga in $CDCl_3$ (400 MHz)

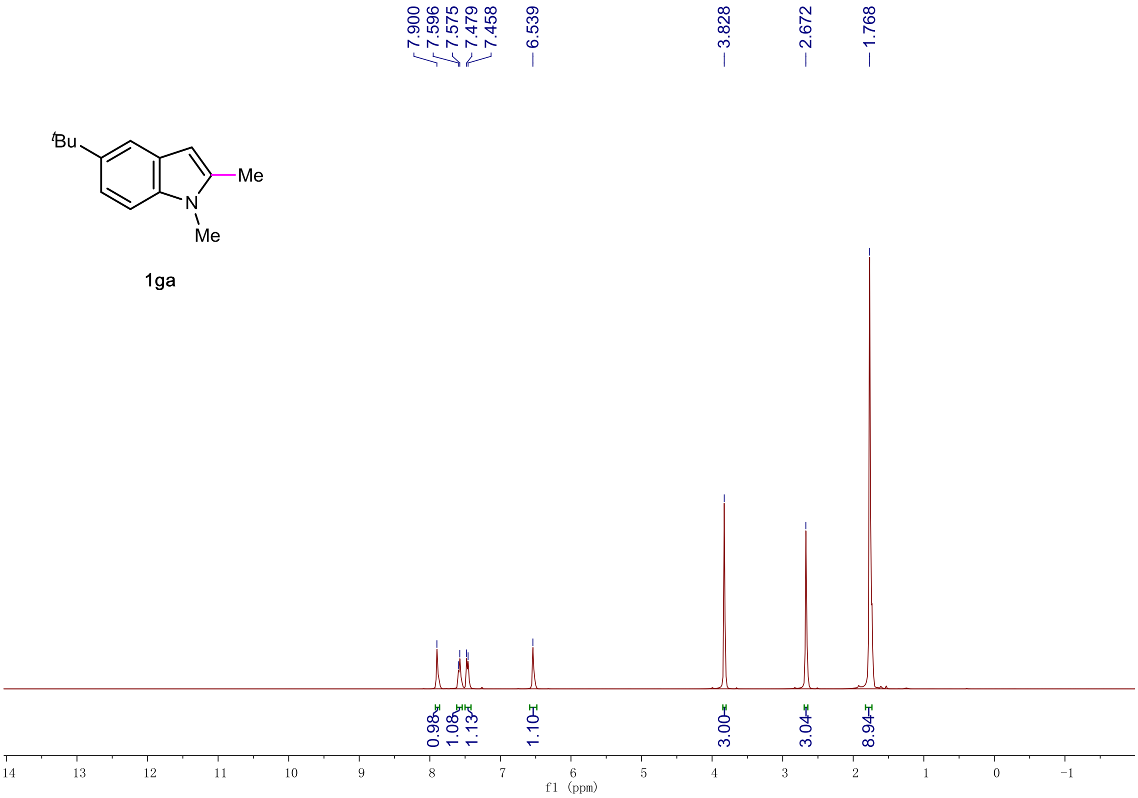

Figure S17. ^{13}C NMR spectrum of 1ga in $CDCl_3$ (100 MHz)

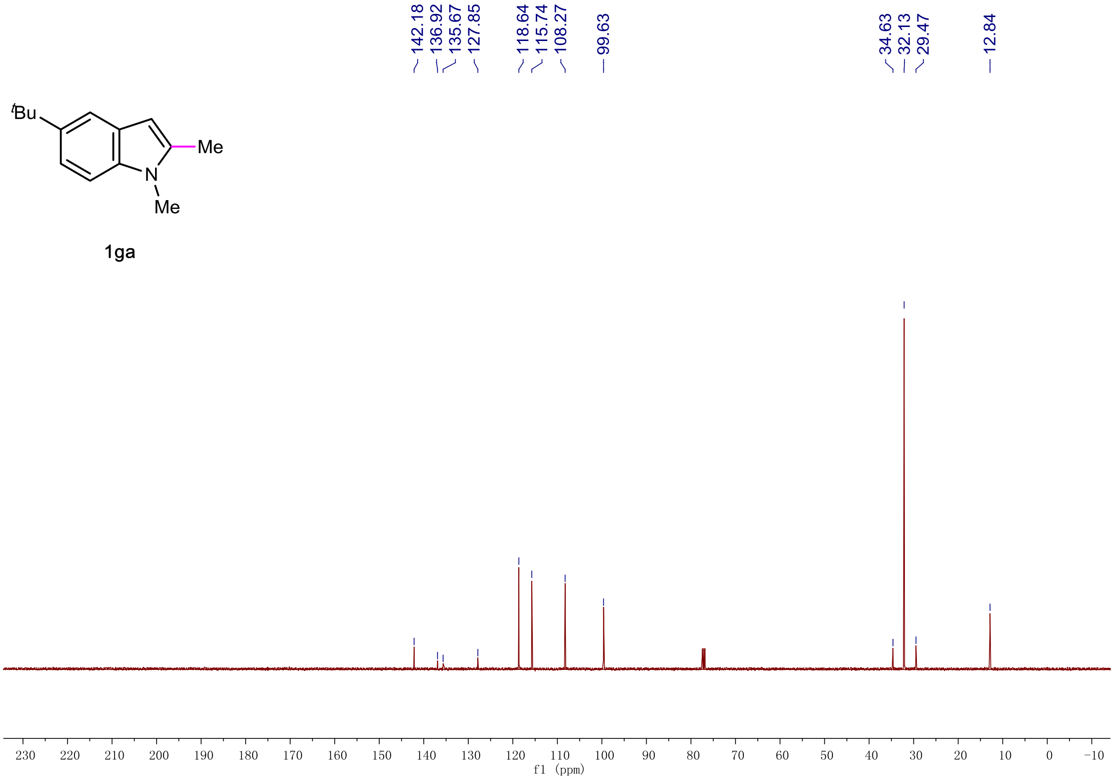

Figure S18. ^{1}H NMR spectrum of 1ia in CDCl$_3$ (400 MHz)

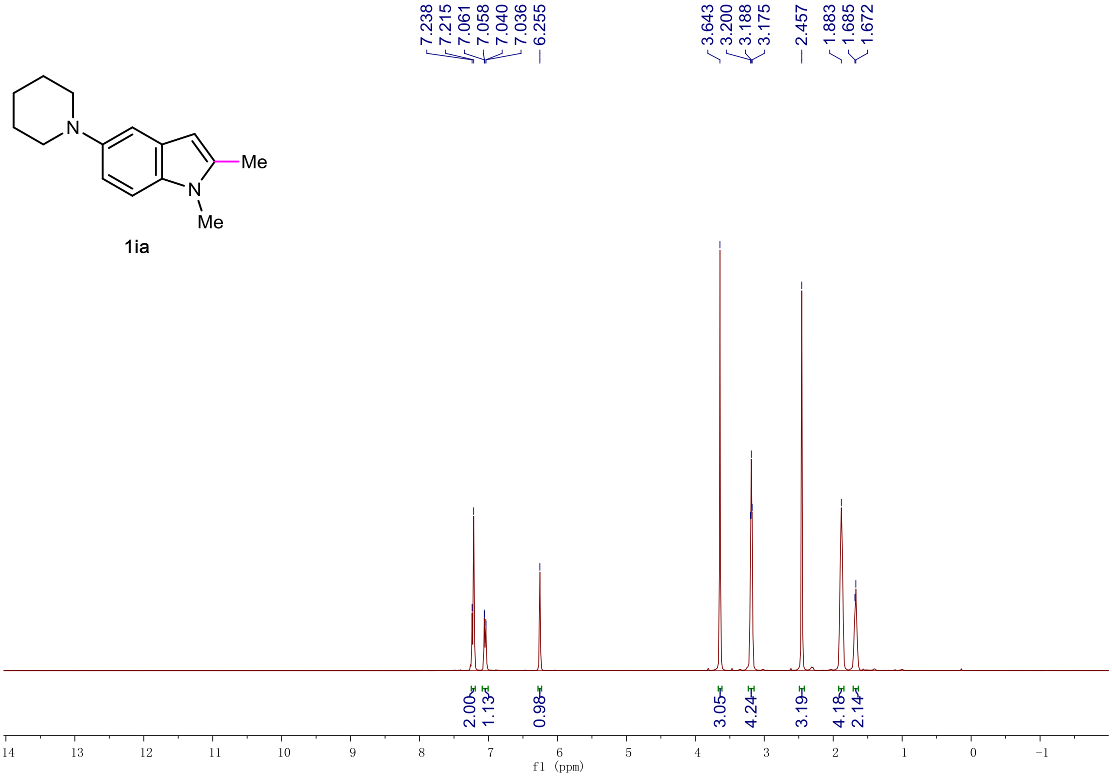

Figure S19. ^{13}C NMR spectrum of 1ia in CDCl$_3$ (100 MHz)

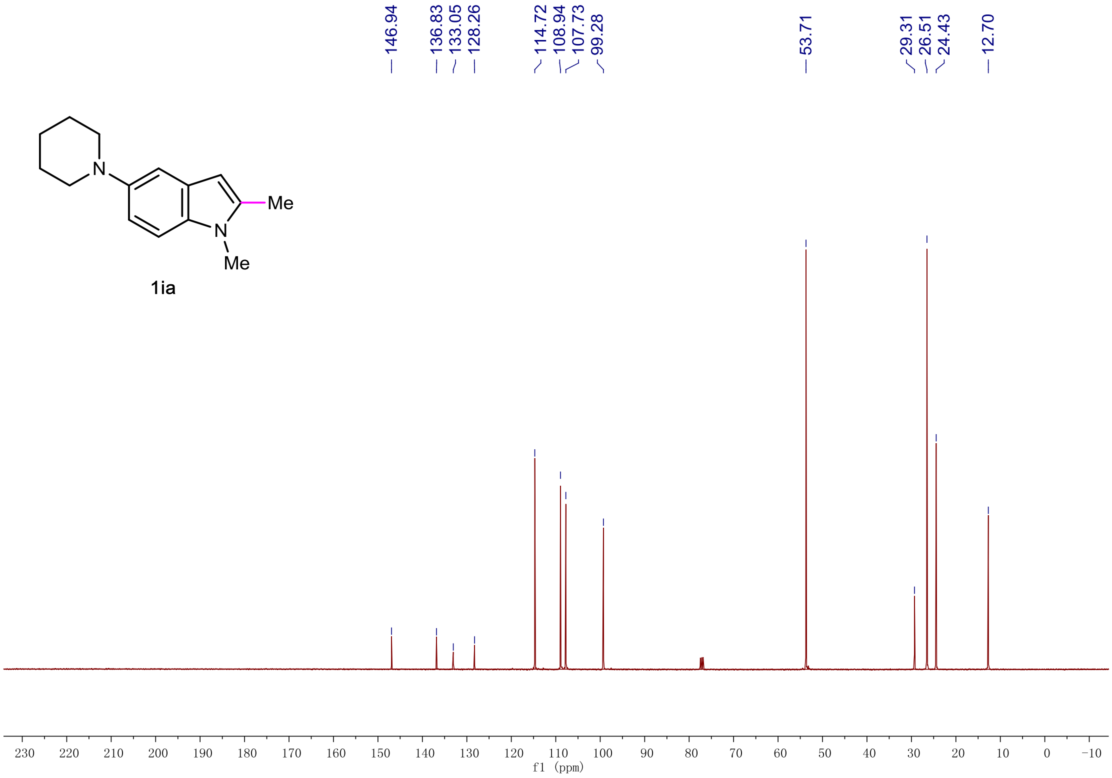

Figure S20. ^{1}H NMR spectrum of 1ma in $CDCl_3$ (400 MHz)

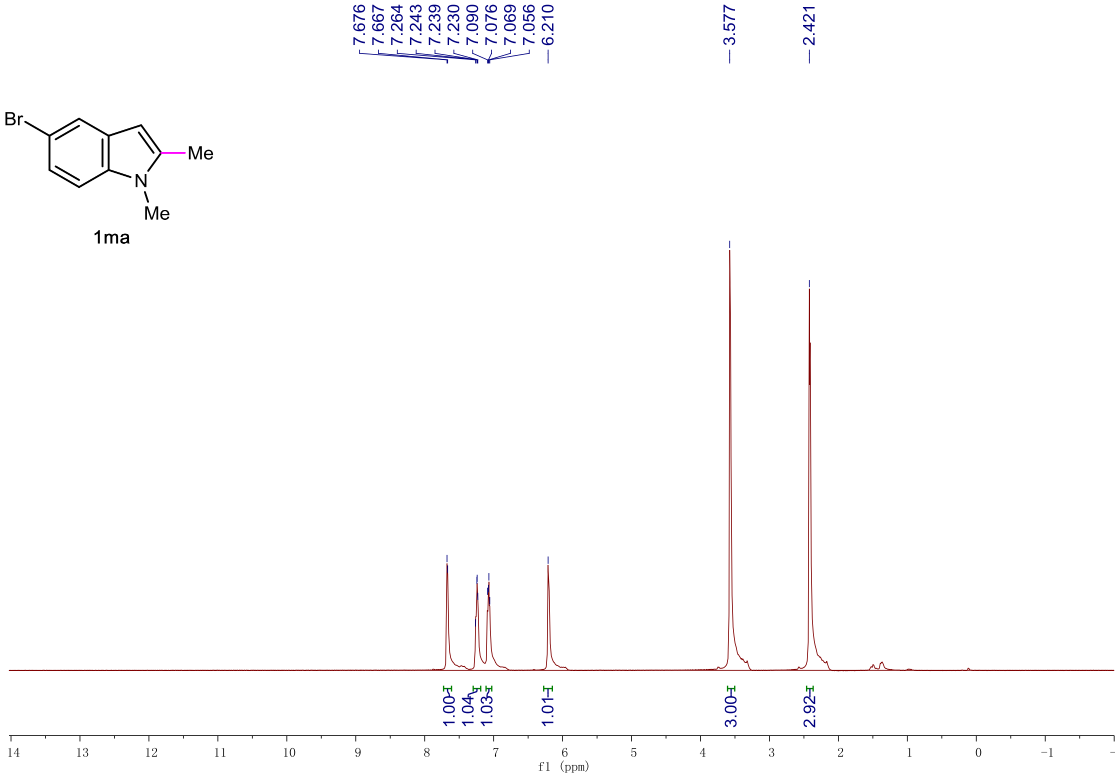

Figure S21. ^{13}C NMR spectrum of 1ma in $CDCl_3$ (100 MHz)

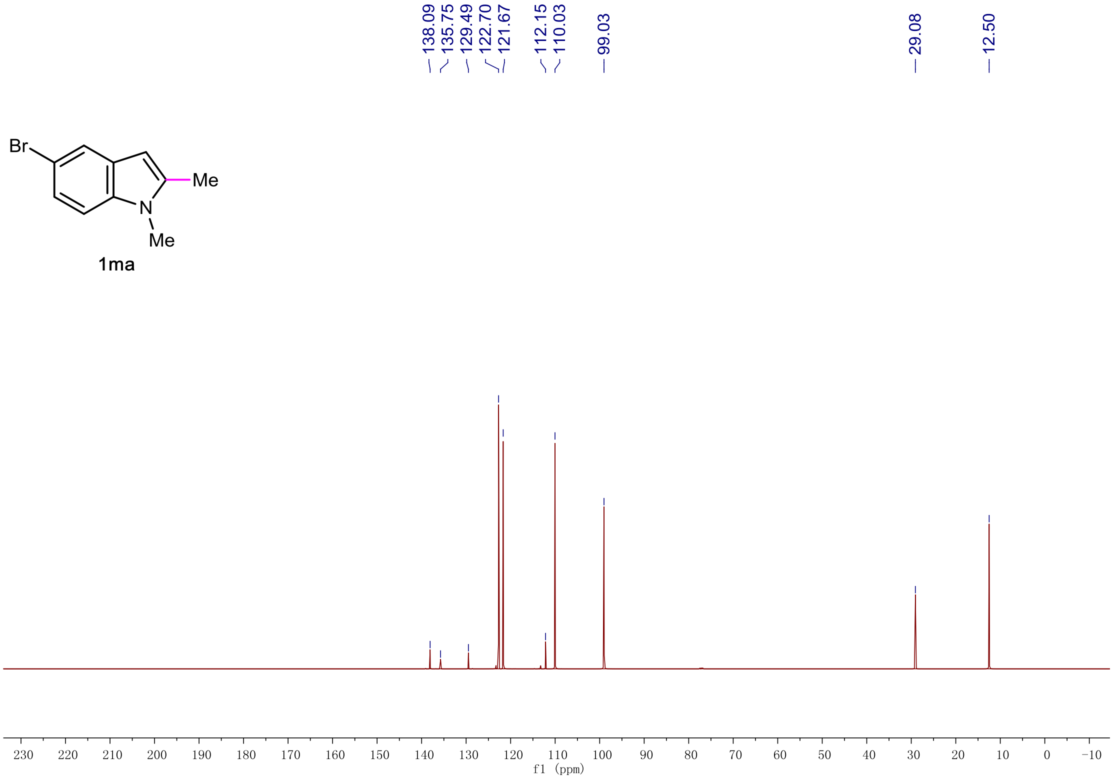

Figure S22. ^{1}H NMR spectrum of 1na in $CDCl_3$ (400 MHz)

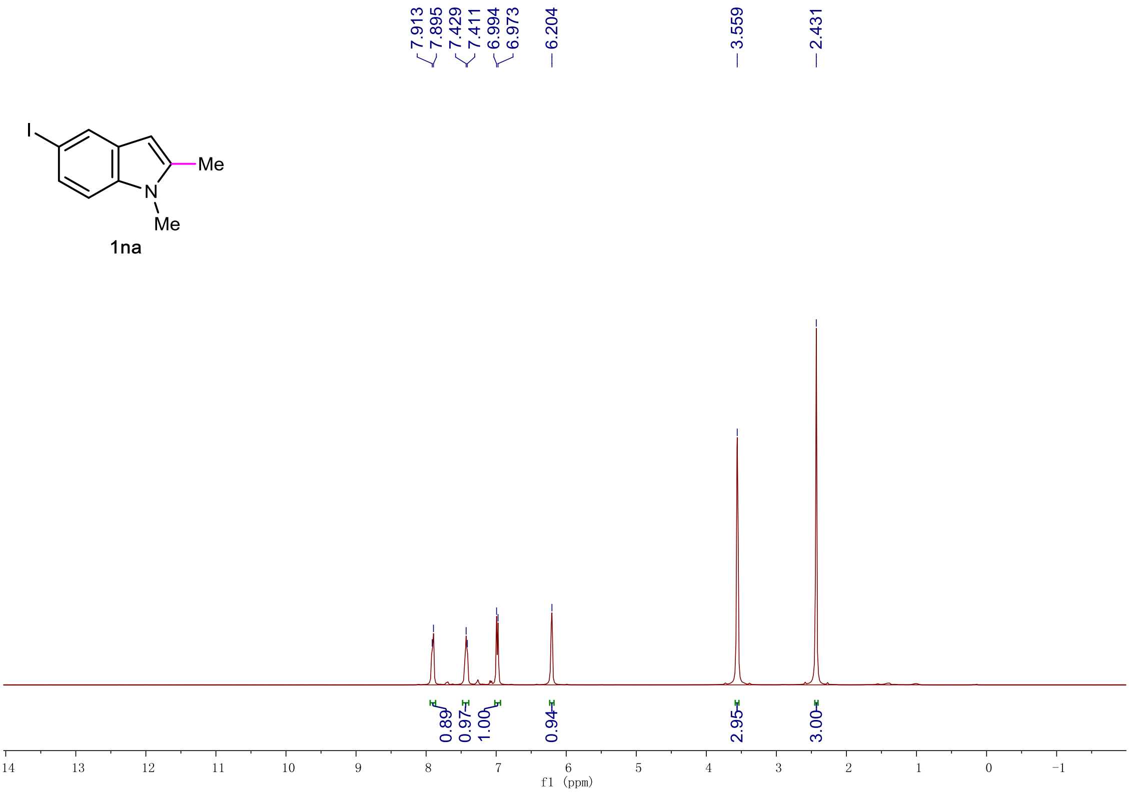

Figure S23. ^{13}C NMR spectrum of 1na in $CDCl_3$ (100 MHz)

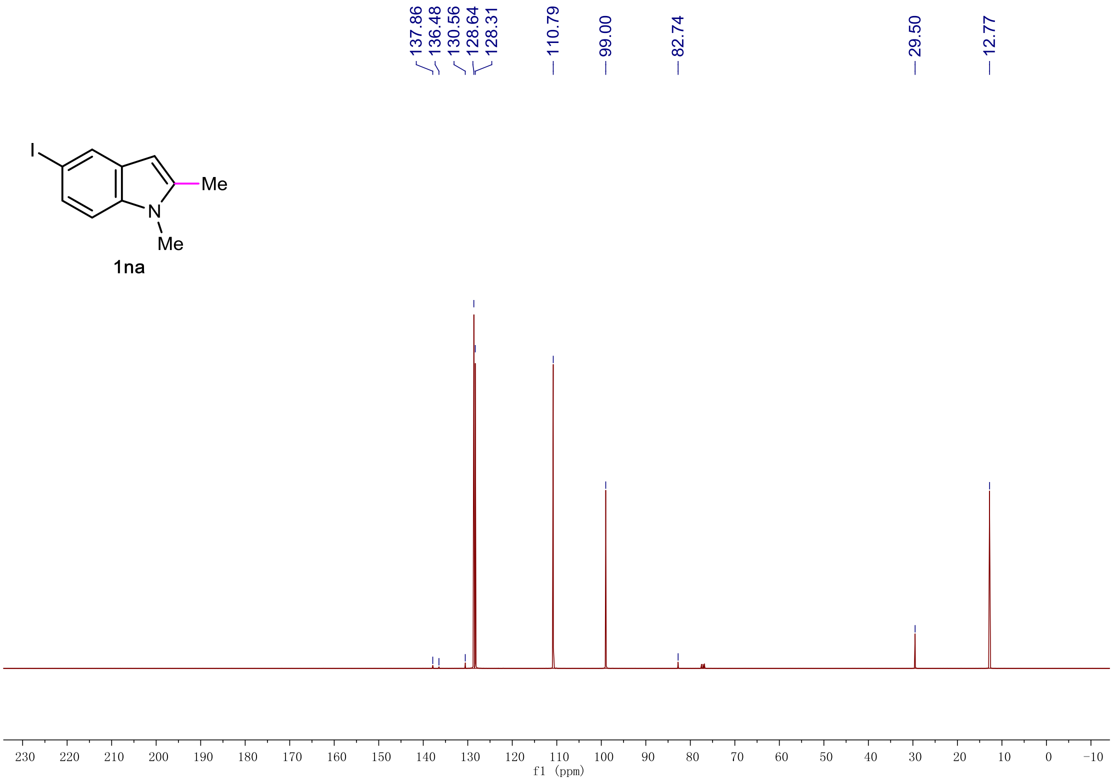

Figure S24. ^{1}H NMR spectrum of 1oa in $CDCl_3$ (400 MHz)

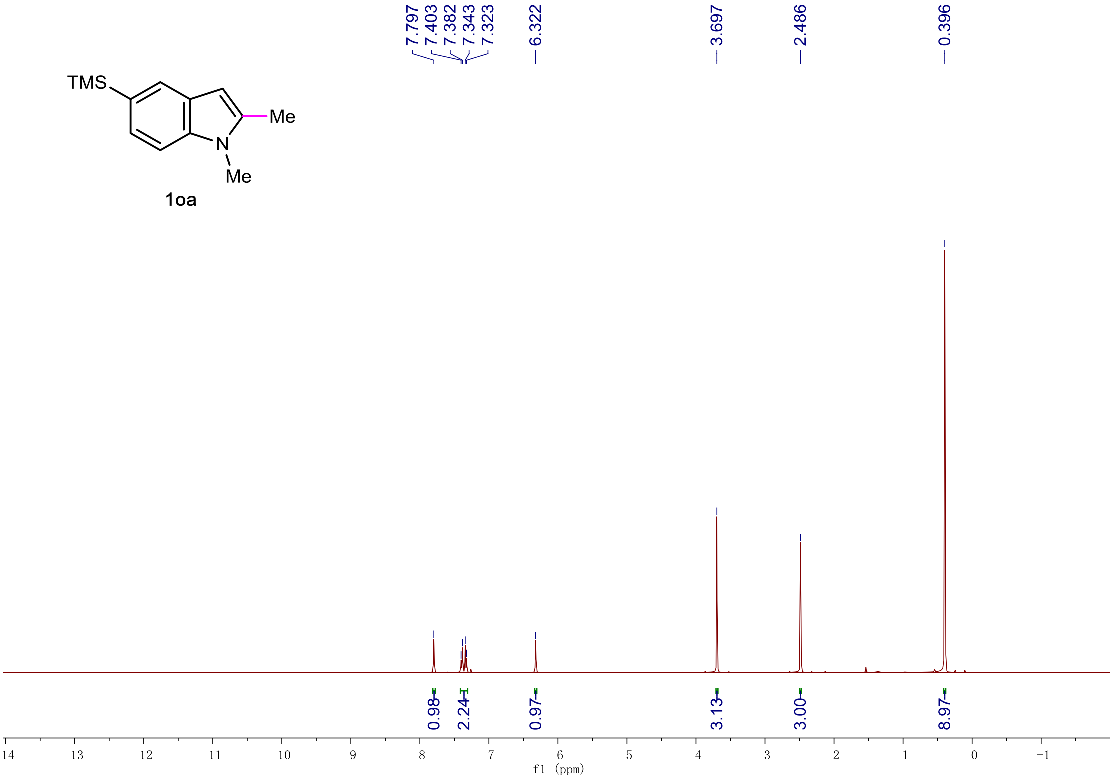

Figure S25. ^{13}C NMR spectrum of 1oa in $CDCl_3$ (100 MHz)

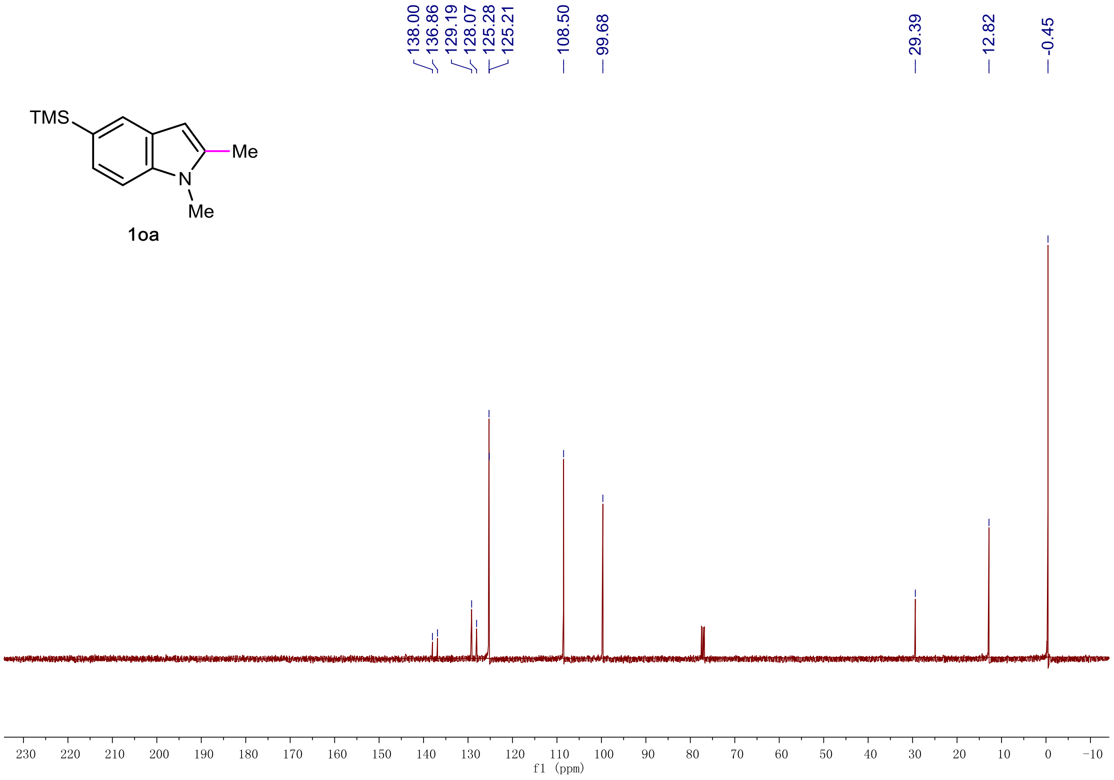

Figure S26. ^{1}H NMR spectrum of 1pa in $CDCl_3$ (400 MHz)

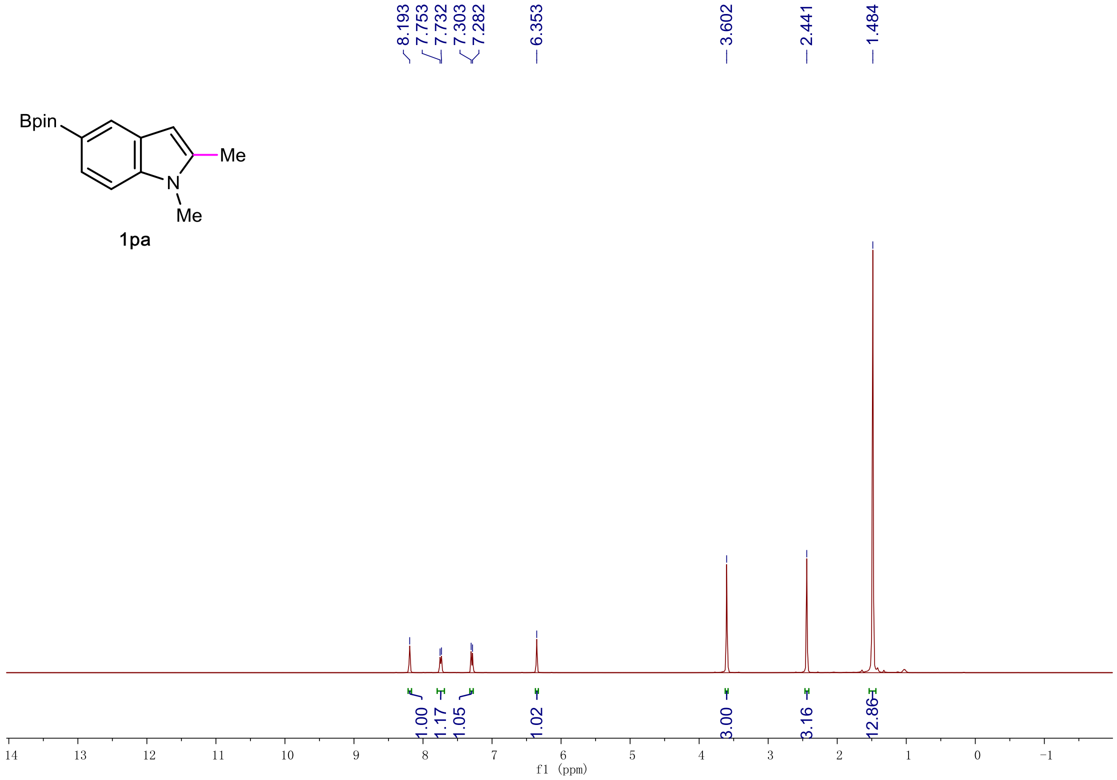

Figure S27. ^{13}C NMR spectrum of 1pa in $CDCl_3$ (100 MHz)

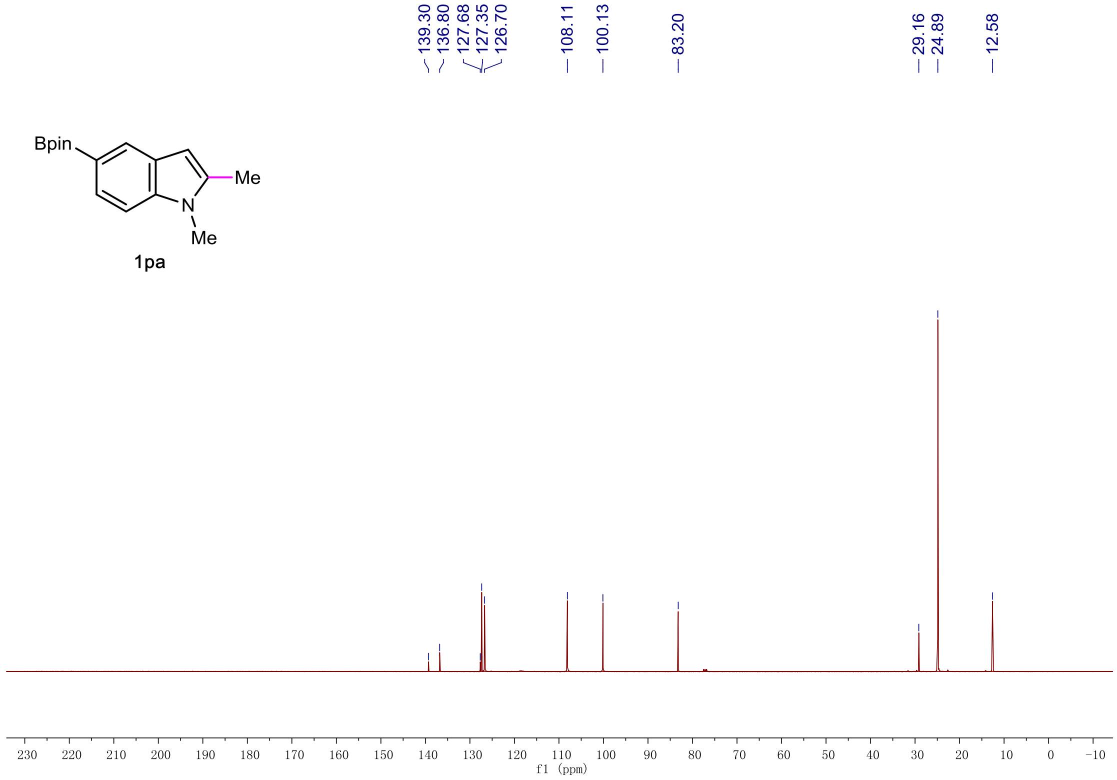

Figure S28. ^{1}H NMR spectrum of 1qa in $CDCl_3$ (400 MHz)

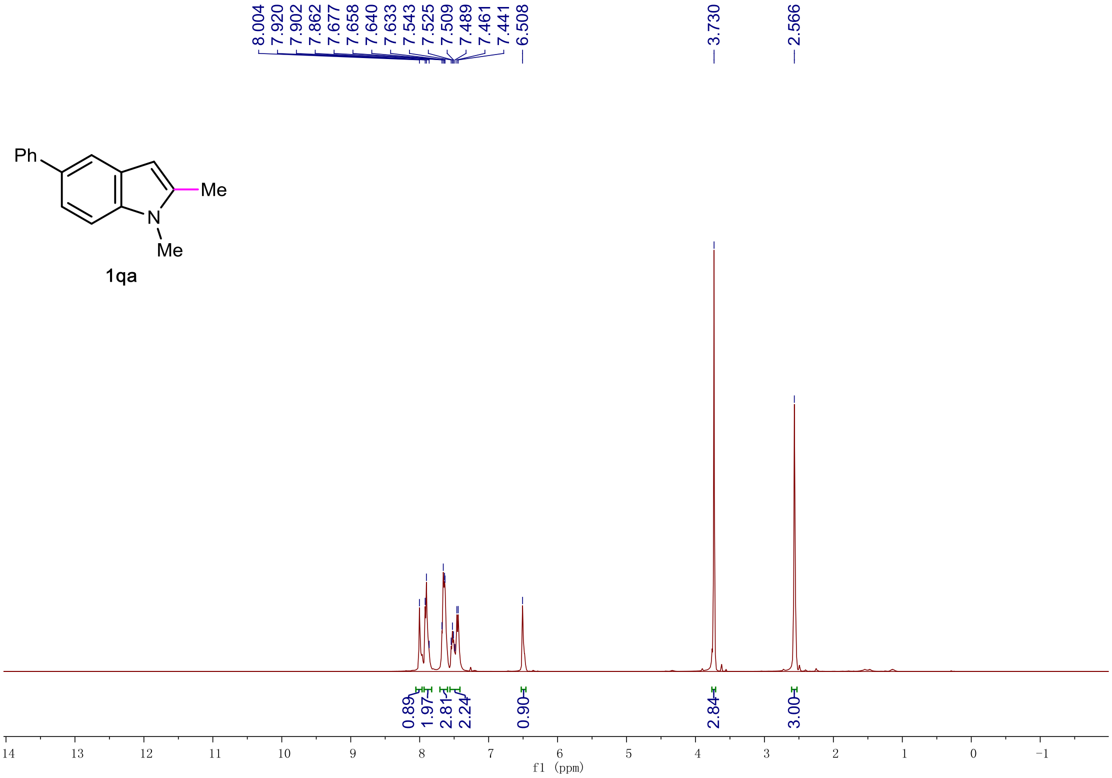

Figure S29. ^{13}C NMR spectrum of 1qa in $CDCl_3$ (100 MHz)

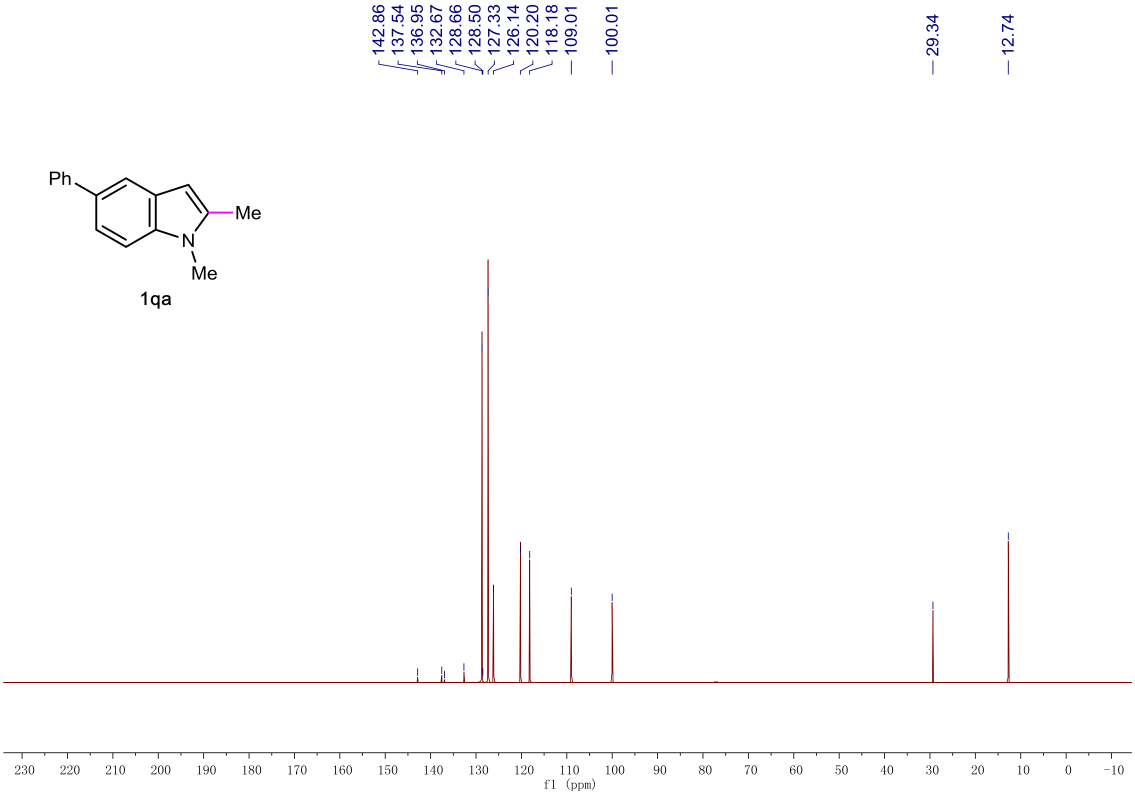

Figure S30. ^{1}H NMR spectrum of 1ra in CDCl$_3$ (400 MHz)

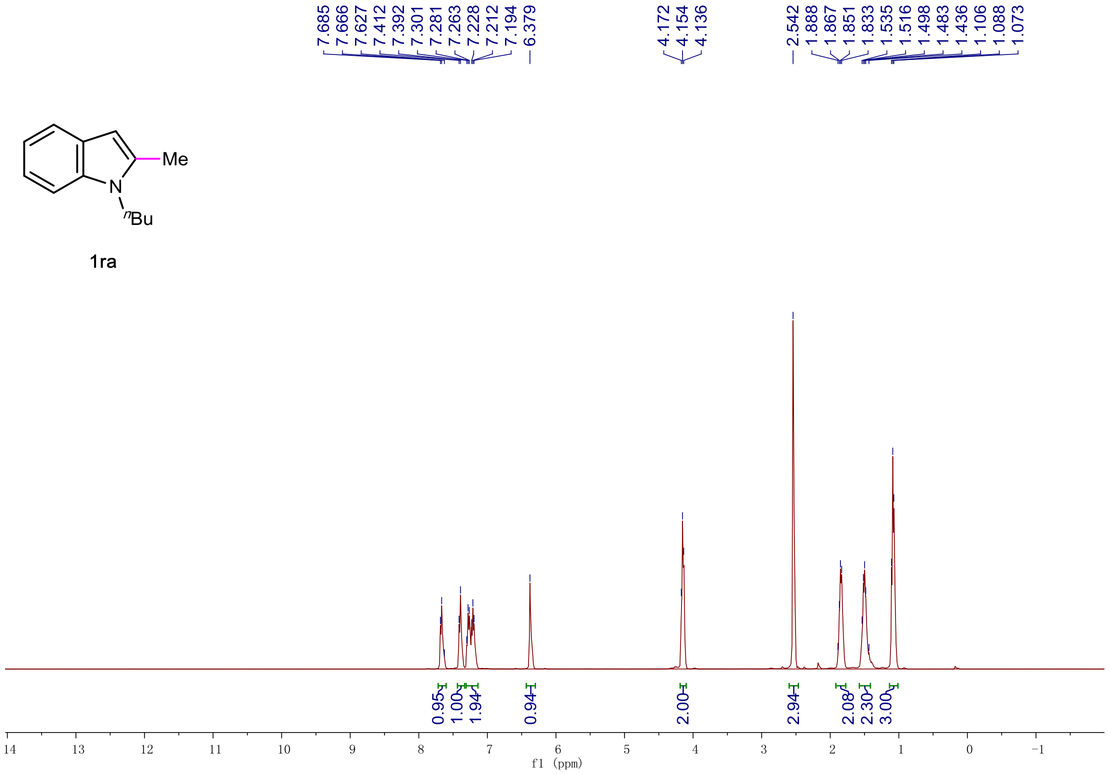

Figure S31. ^{13}C NMR spectrum of 1ra in CDCl$_3$ (100 MHz)

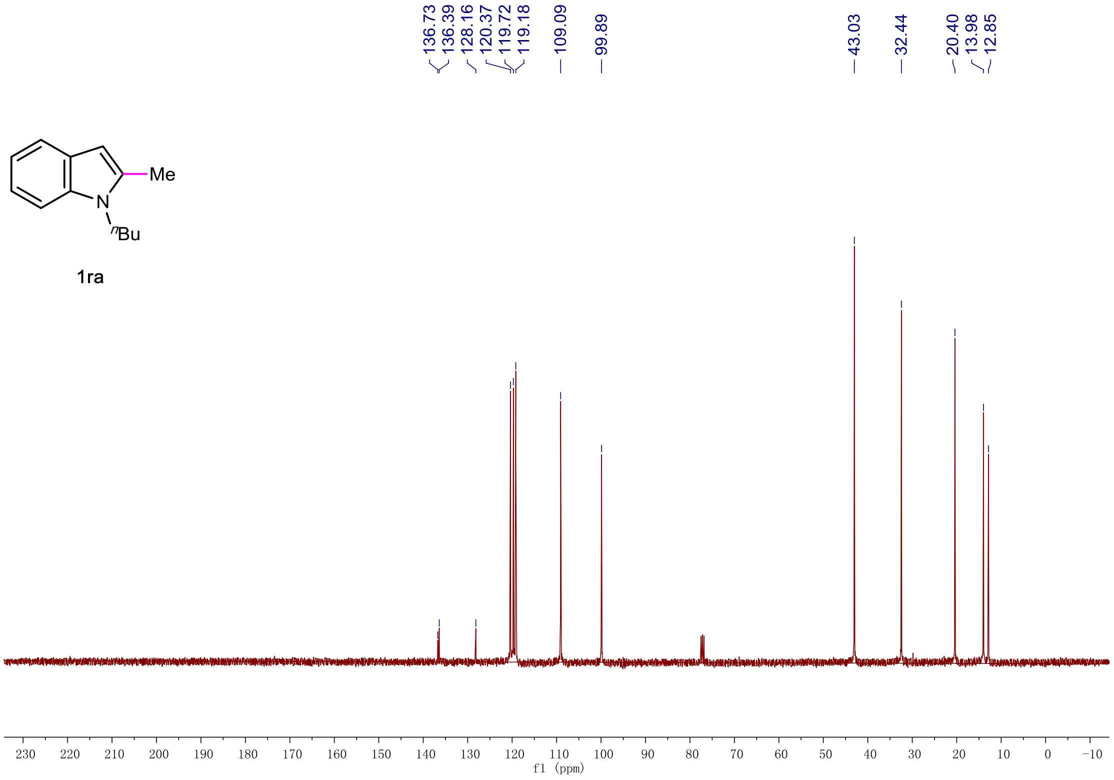

Figure S32. ^{1}H NMR spectrum of 1hb in $CDCl_3$ (400 MHz)

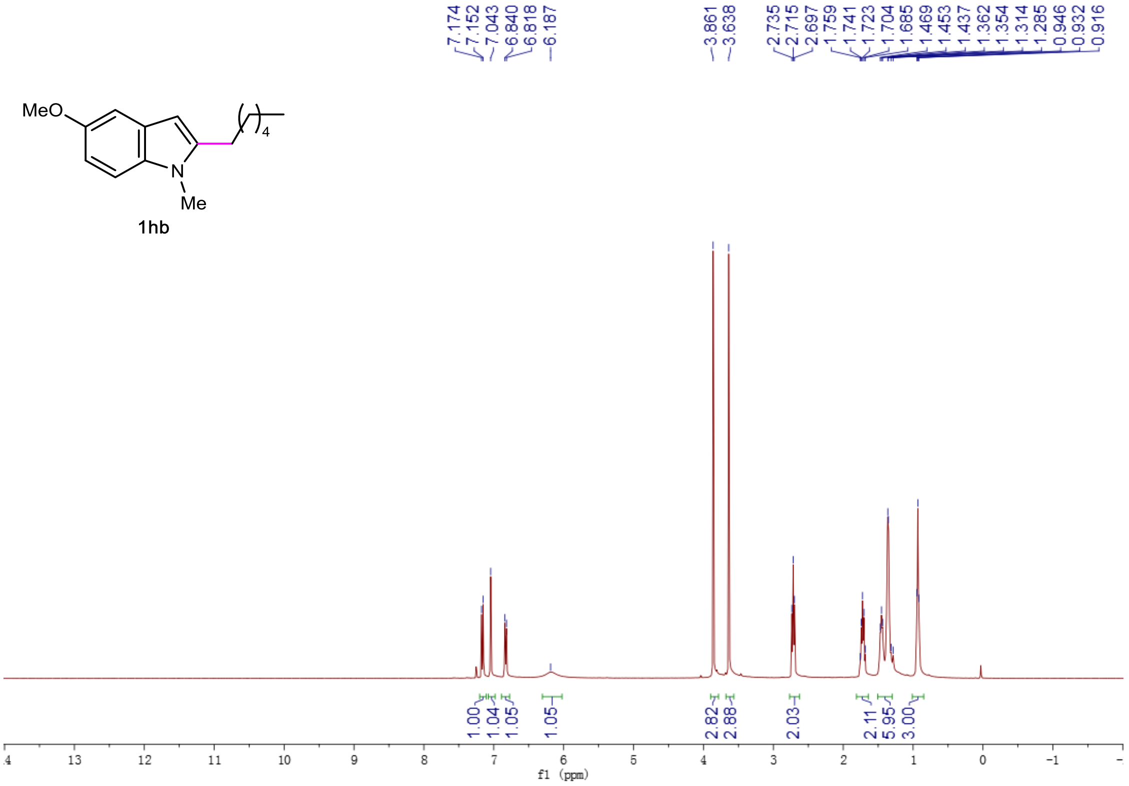

Figure S33. ^{13}C NMR spectrum of 1hb in $CDCl_3$ (100 MHz)

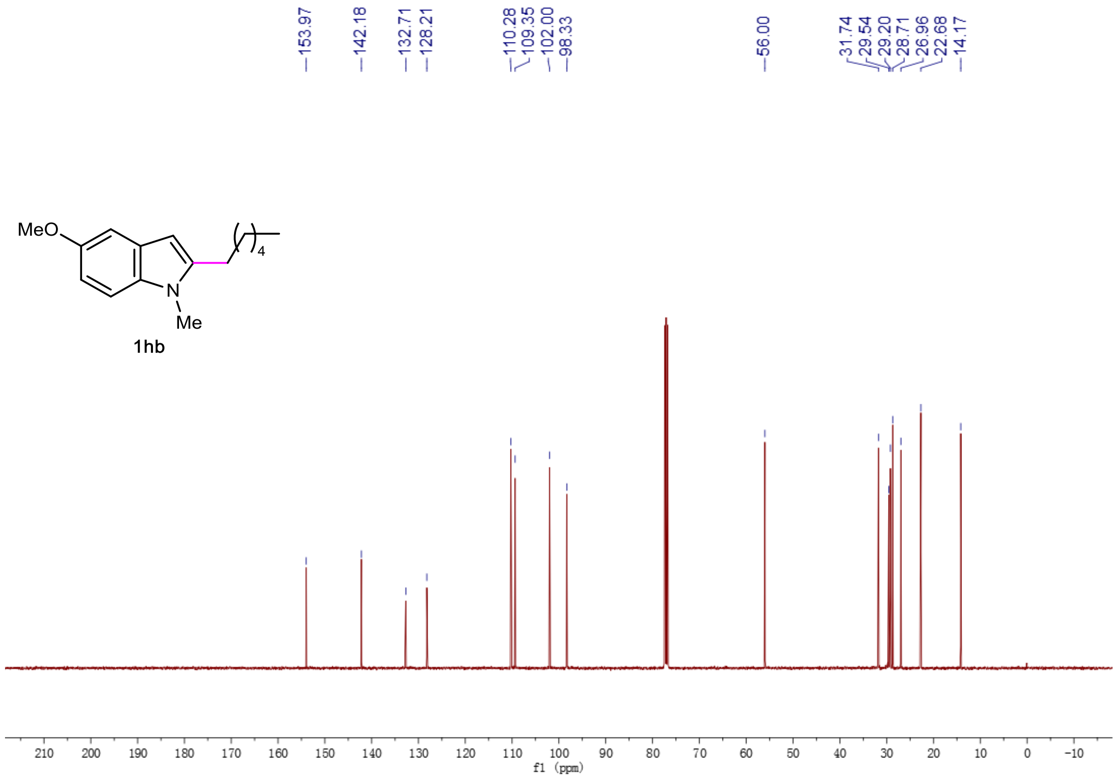

Figure S34. ^{1}H NMR spectrum of 1hc in $CDCl_3$ (400 MHz)

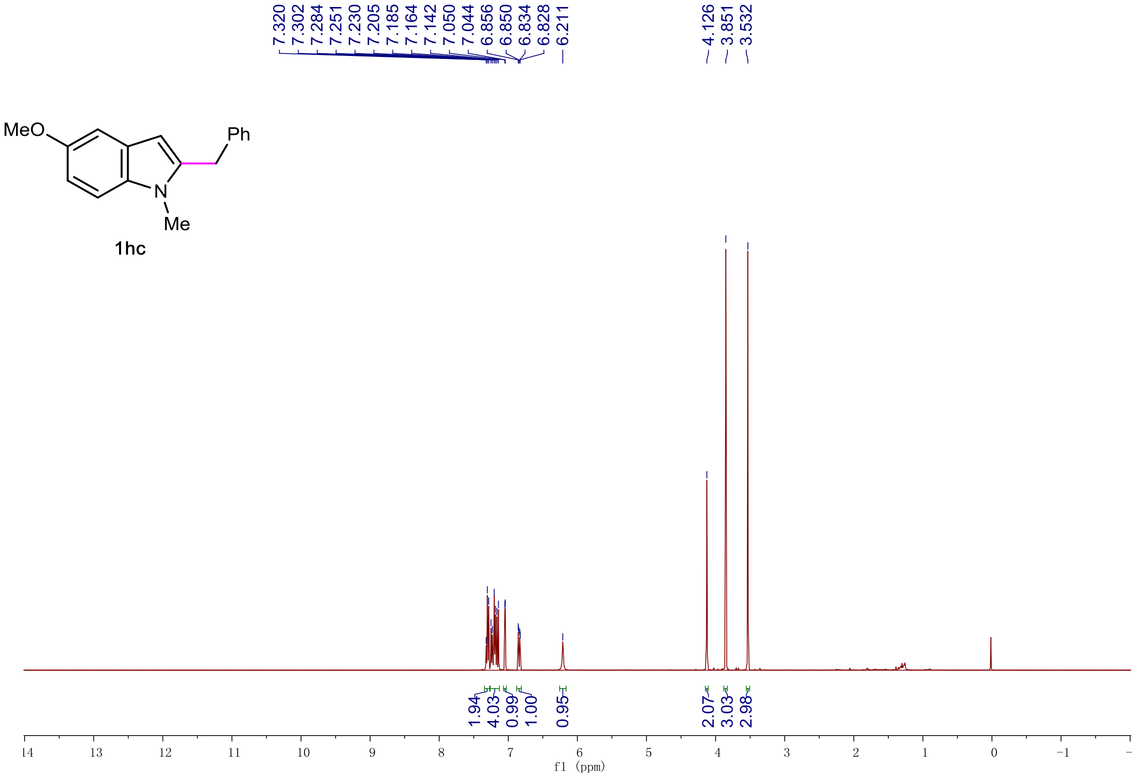

Figure S35. ^{13}C NMR spectrum of 1hc in $CDCl_3$ (100 MHz)

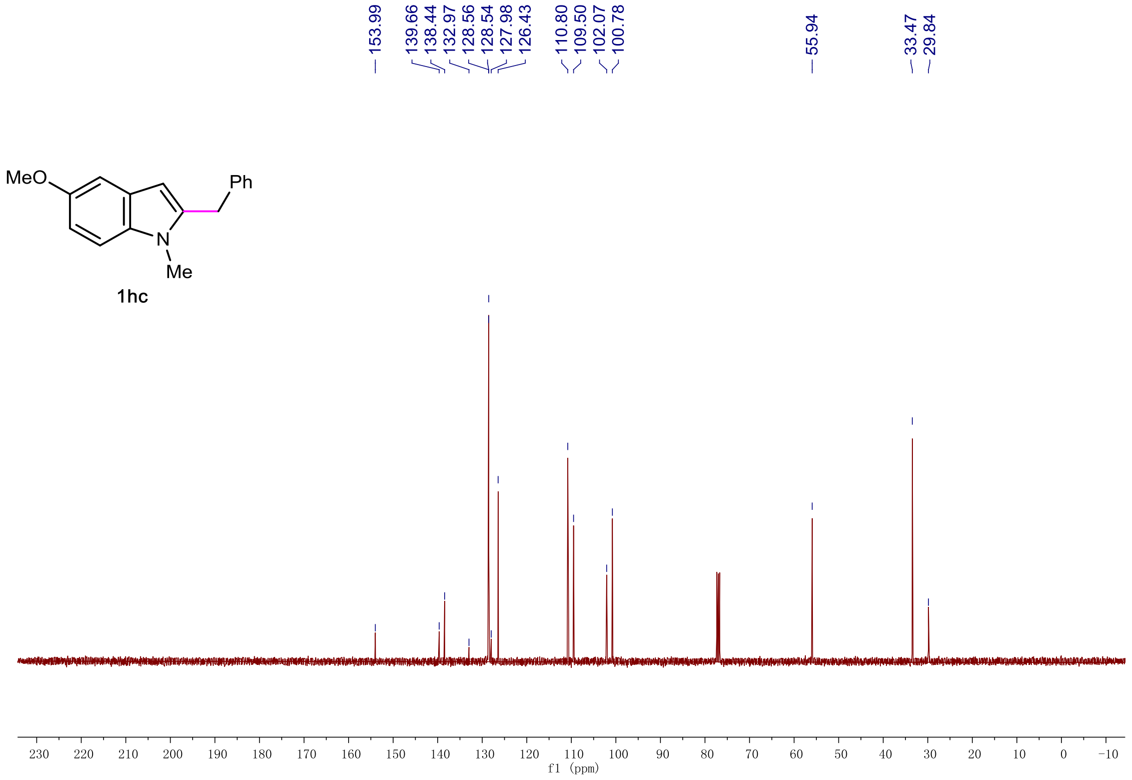

Figure S36. ^{1}H NMR spectrum of 1hd in $CDCl_3$ (400 MHz)

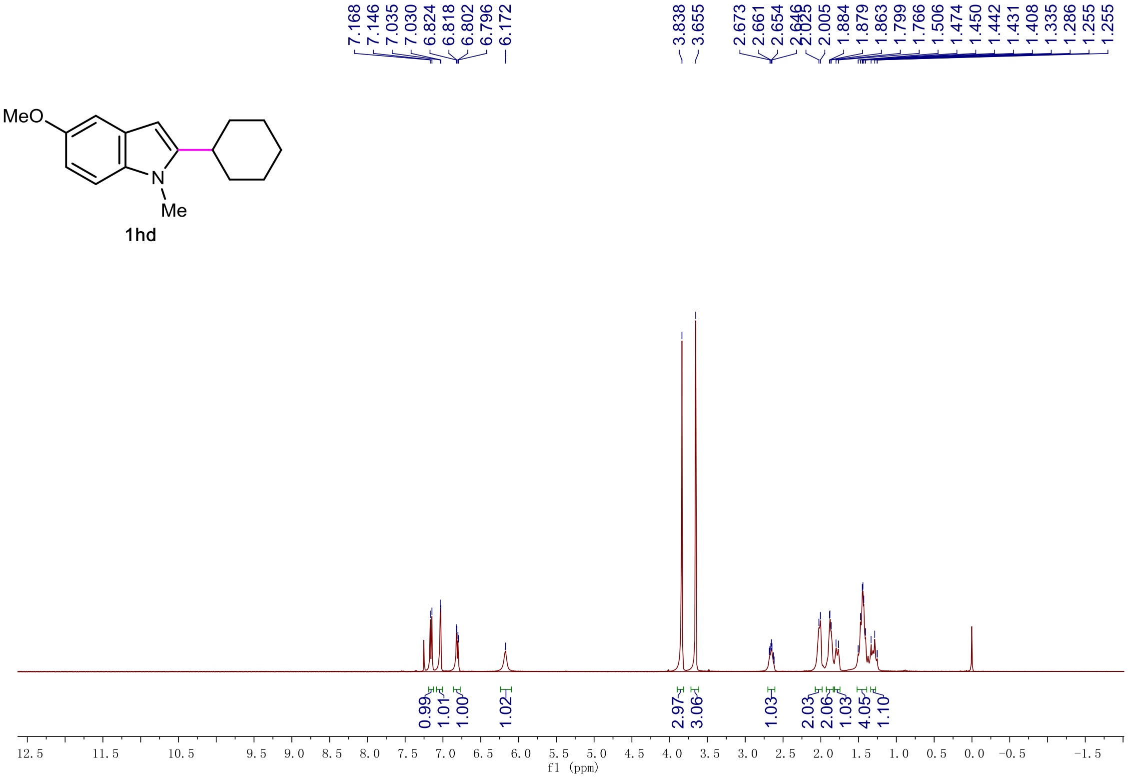

Figure S37. ^{13}C NMR spectrum of 1hd in $CDCl_3$ (100 MHz)

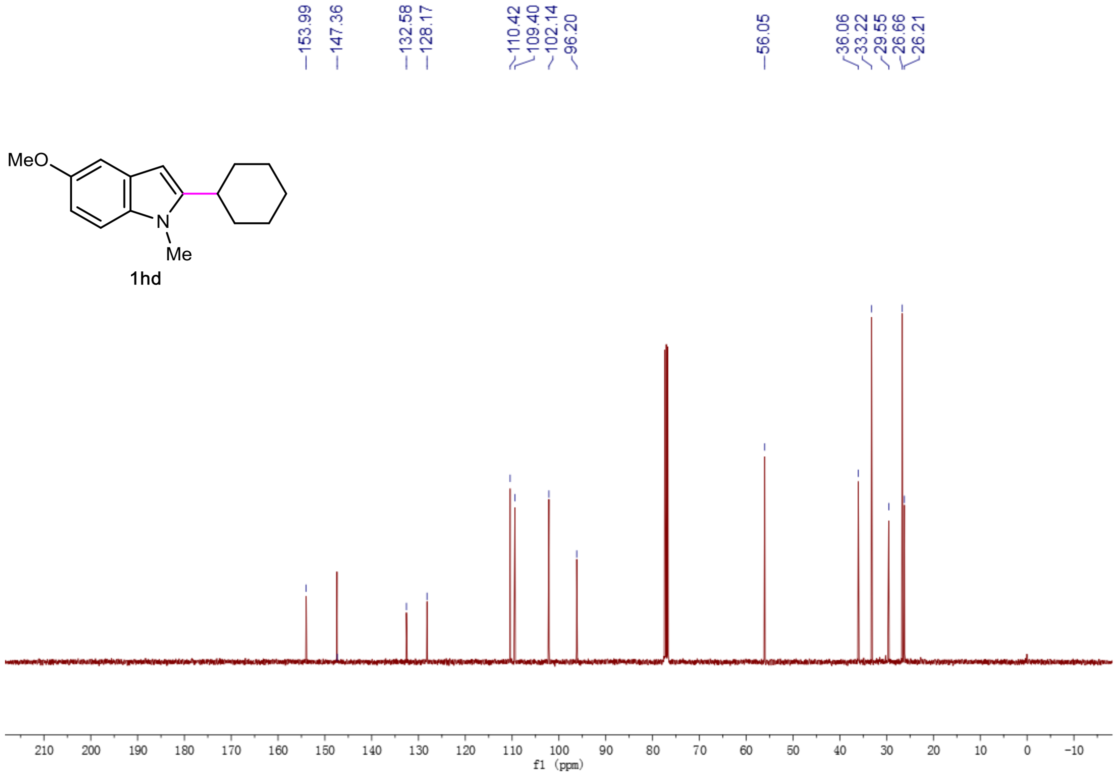

Figure S38. ^{1}H NMR spectrum of 1he in $CDCl_3$ (400 MHz)

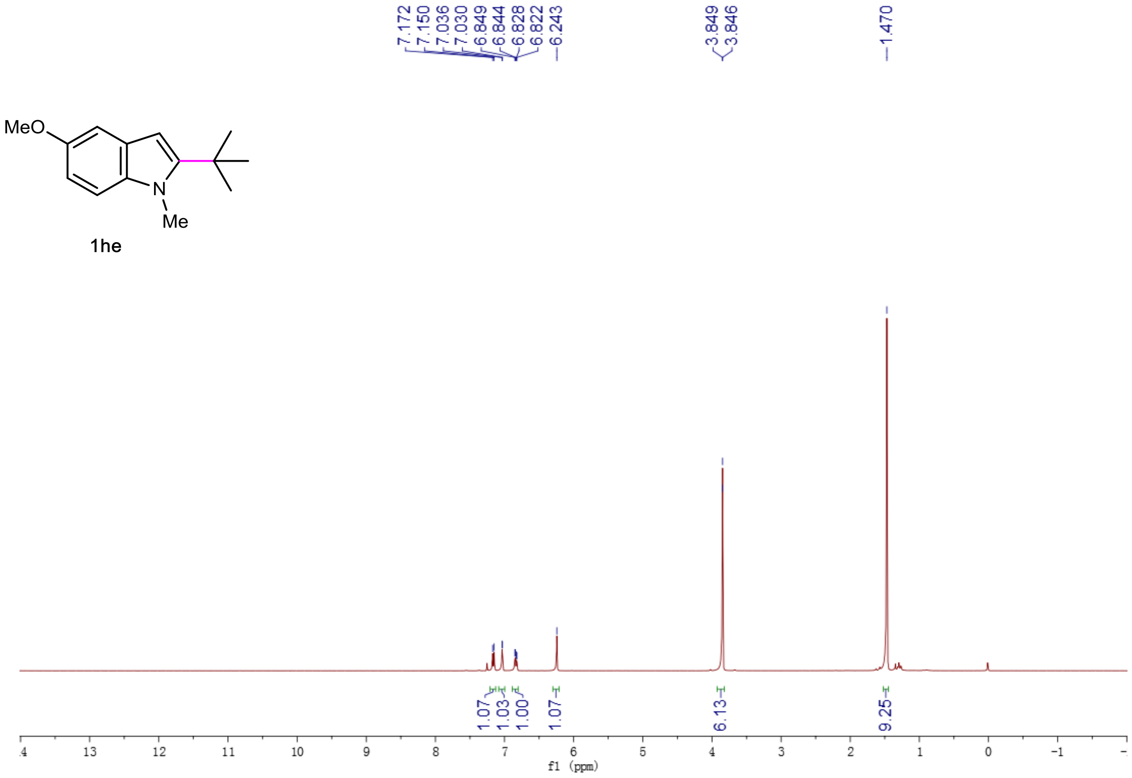

Figure S39. ^{13}C NMR spectrum of 1he in $CDCl_3$ (100 MHz)

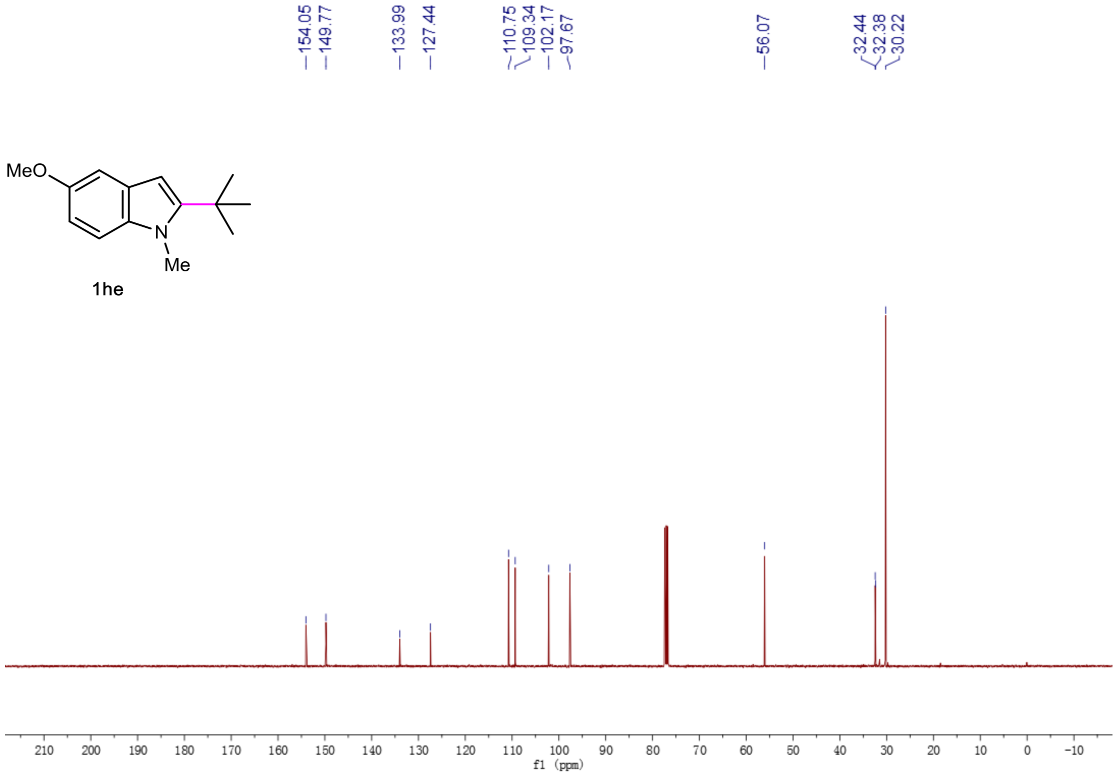

Figure S40. ^{1}H NMR spectrum of 1hg in $CDCl_3$ (400 MHz)

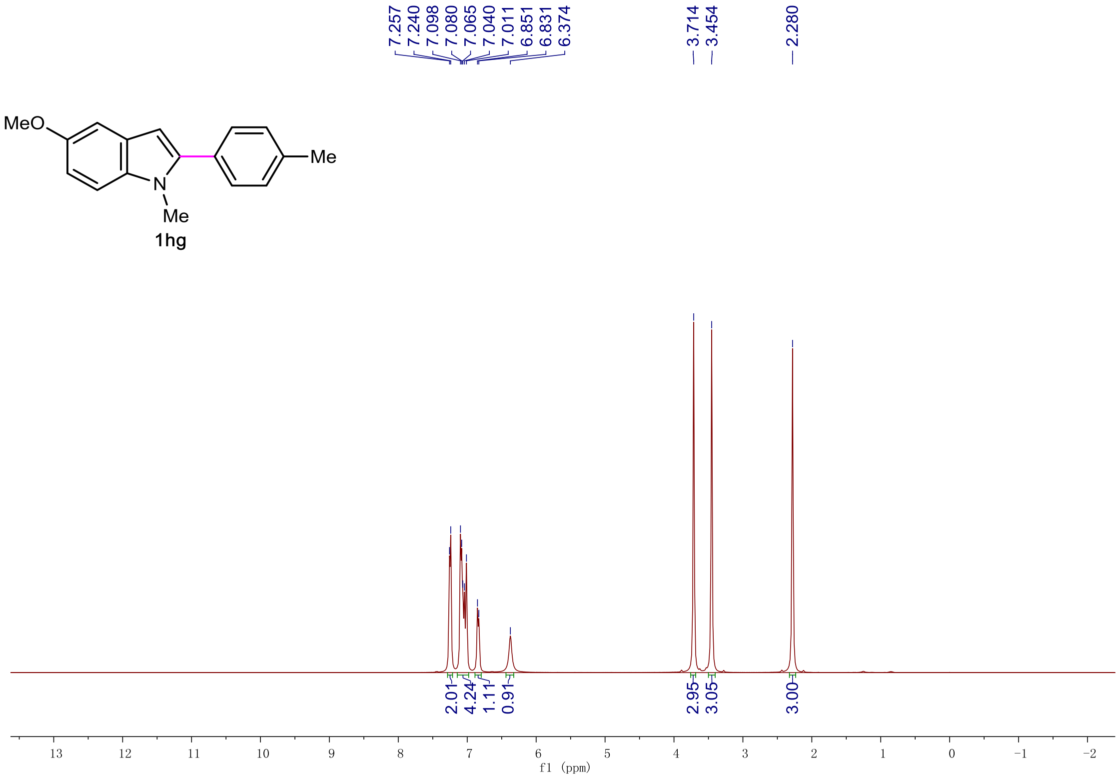

Figure S41. ^{13}C NMR spectrum of 1hg in $CDCl_3$ (100 MHz)

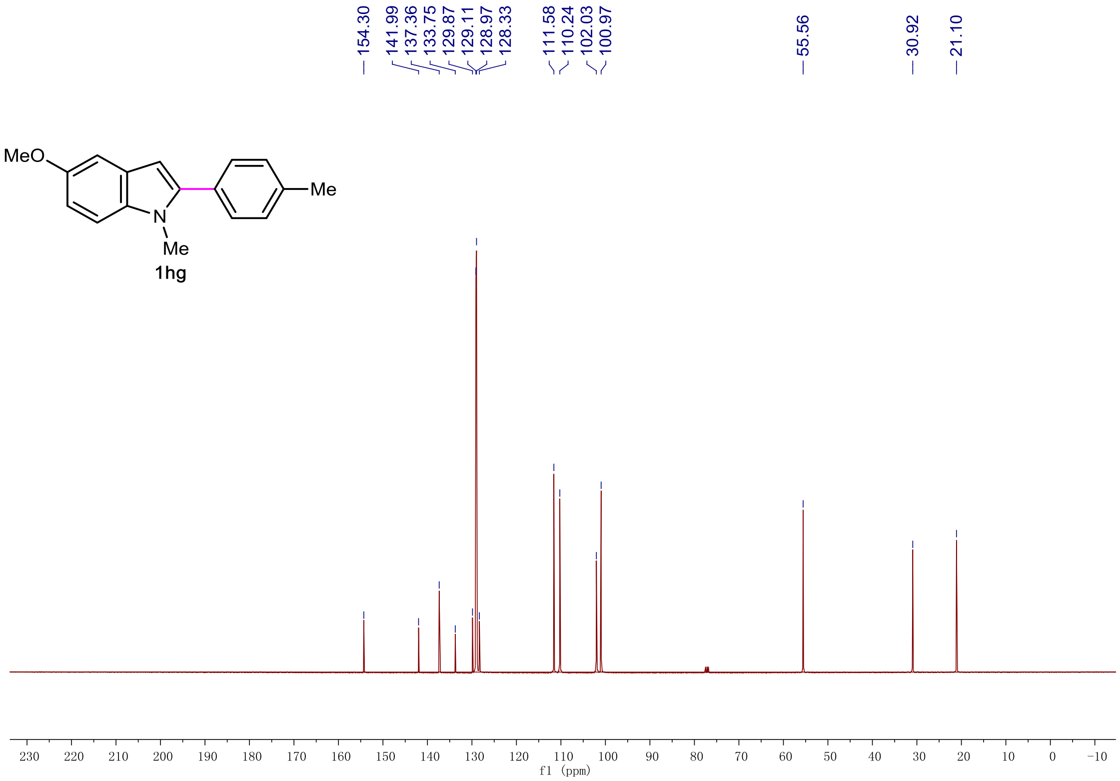

Figure S42. ^{1}H NMR spectrum of 1hh in $CDCl_3$ (400 MHz)

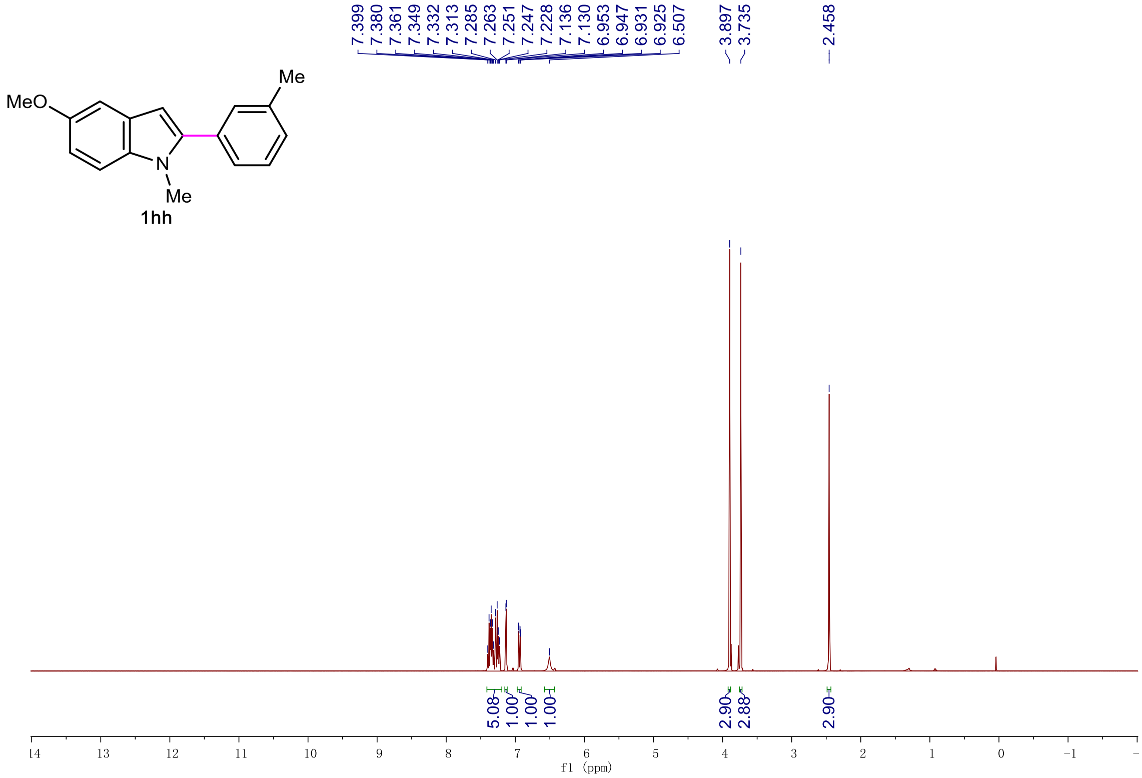

Figure S43. ^{13}C NMR spectrum of 1hh in $CDCl_3$ (100 MHz)

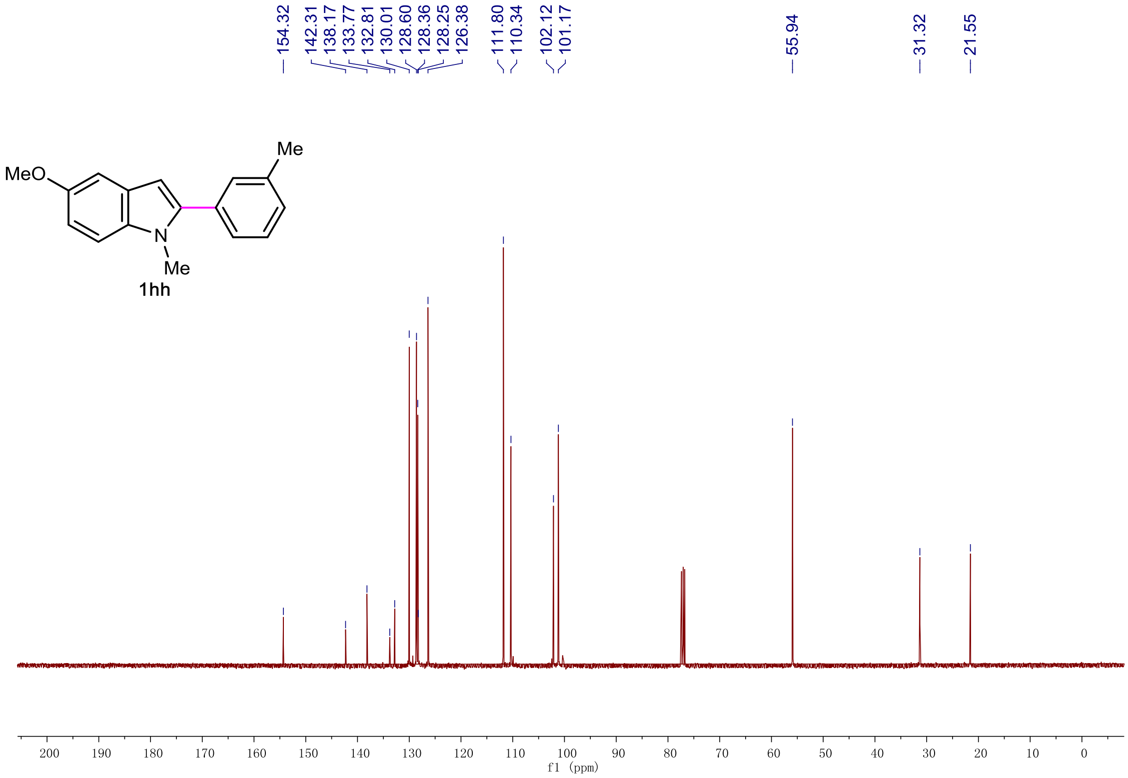

Figure S44. ^{1}H NMR spectrum of 1hi in $CDCl_3$ (400 MHz)

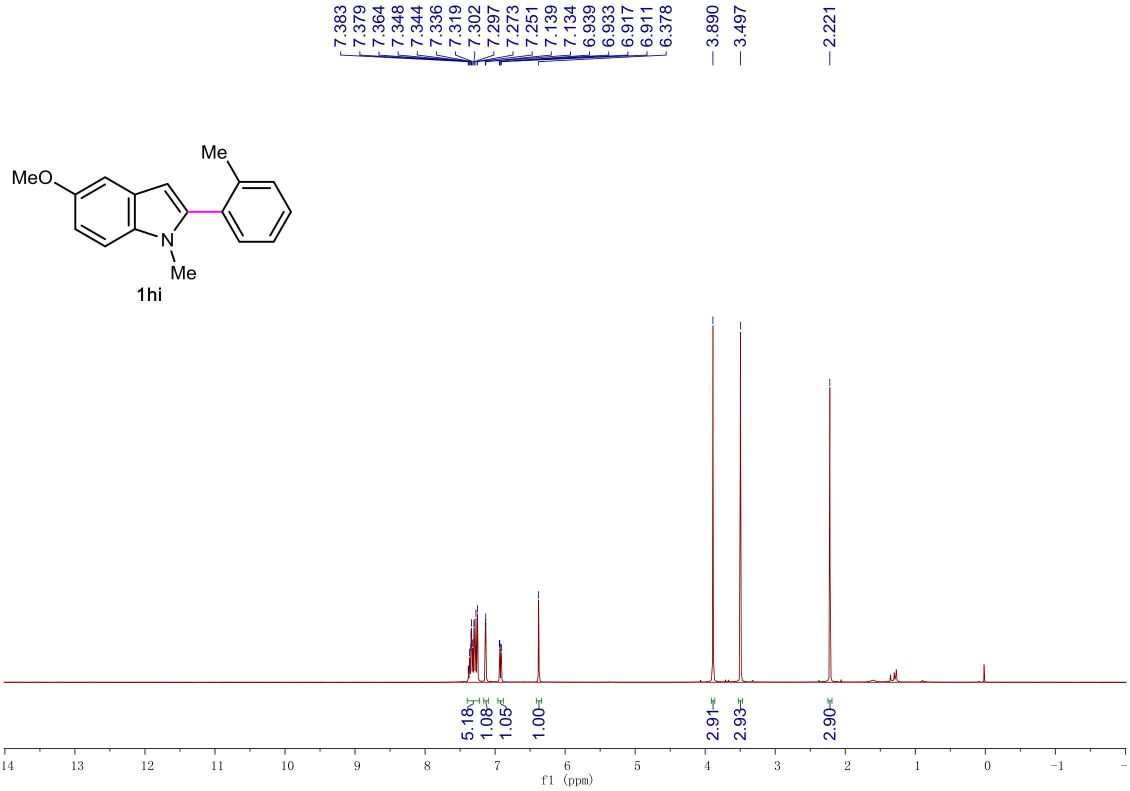

Figure S45. ^{13}C NMR spectrum of 1hi in $CDCl_3$ (100 MHz)

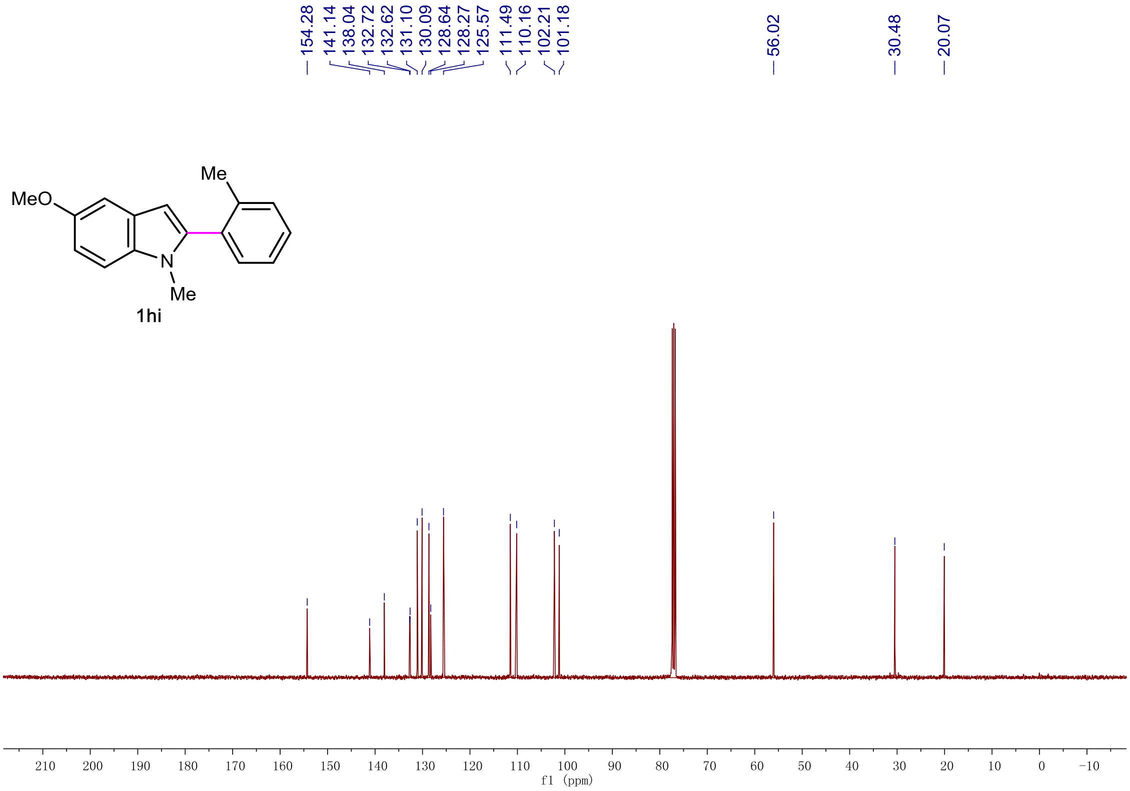

Figure S46. ^{1}H NMR spectrum of 1hj in $CDCl_3$ (400 MHz)

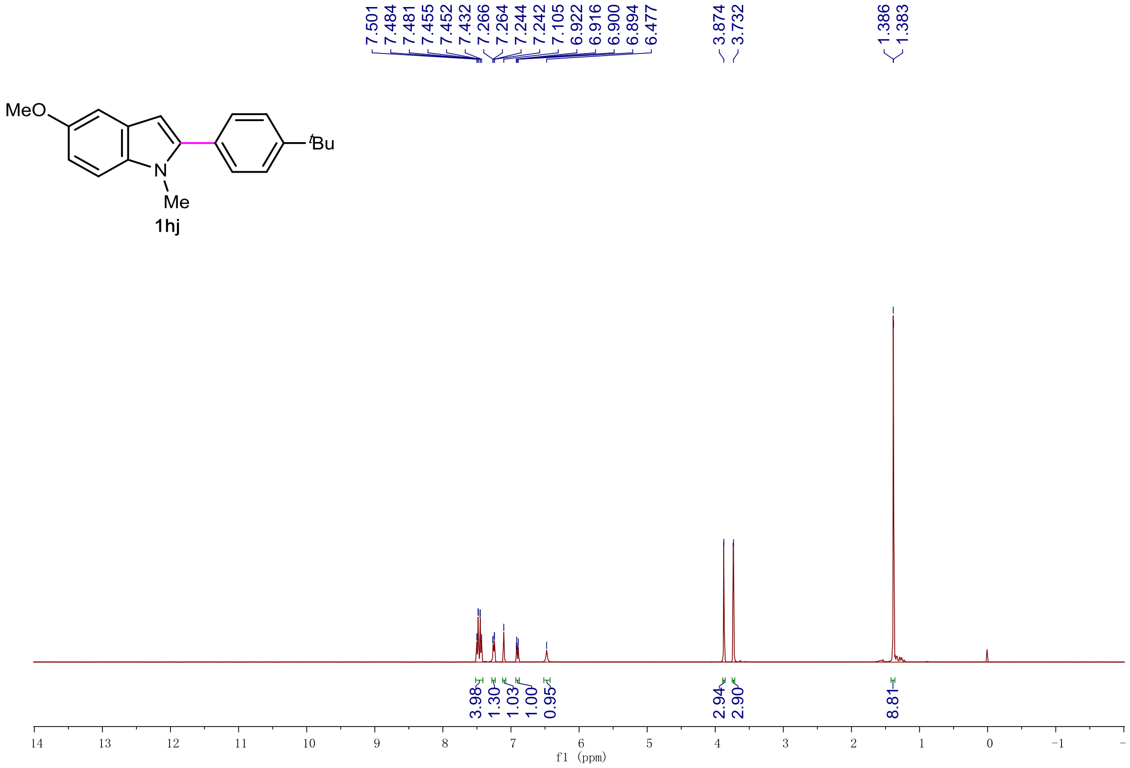

Figure S47. ^{13}C NMR spectrum of 1hj in $CDCl_3$ (100 MHz)

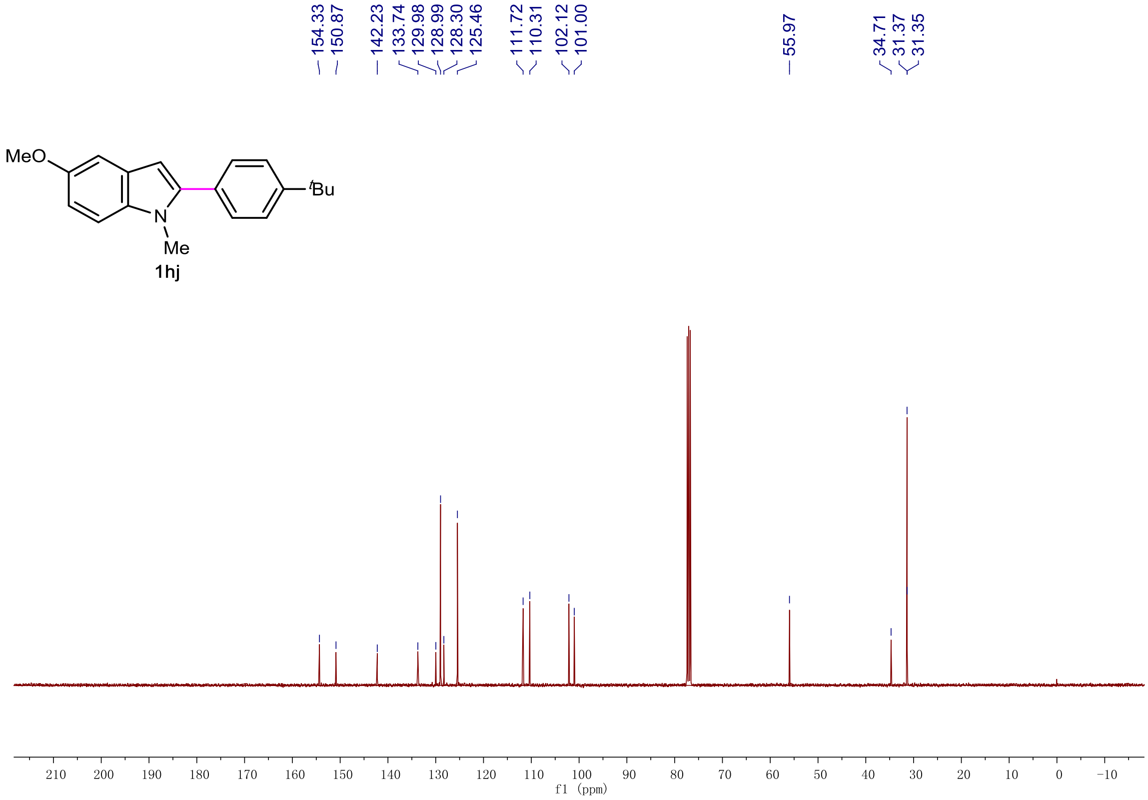

Figure S48. ^{1}H NMR spectrum of 1hk in $CDCl_3$ (400 MHz)

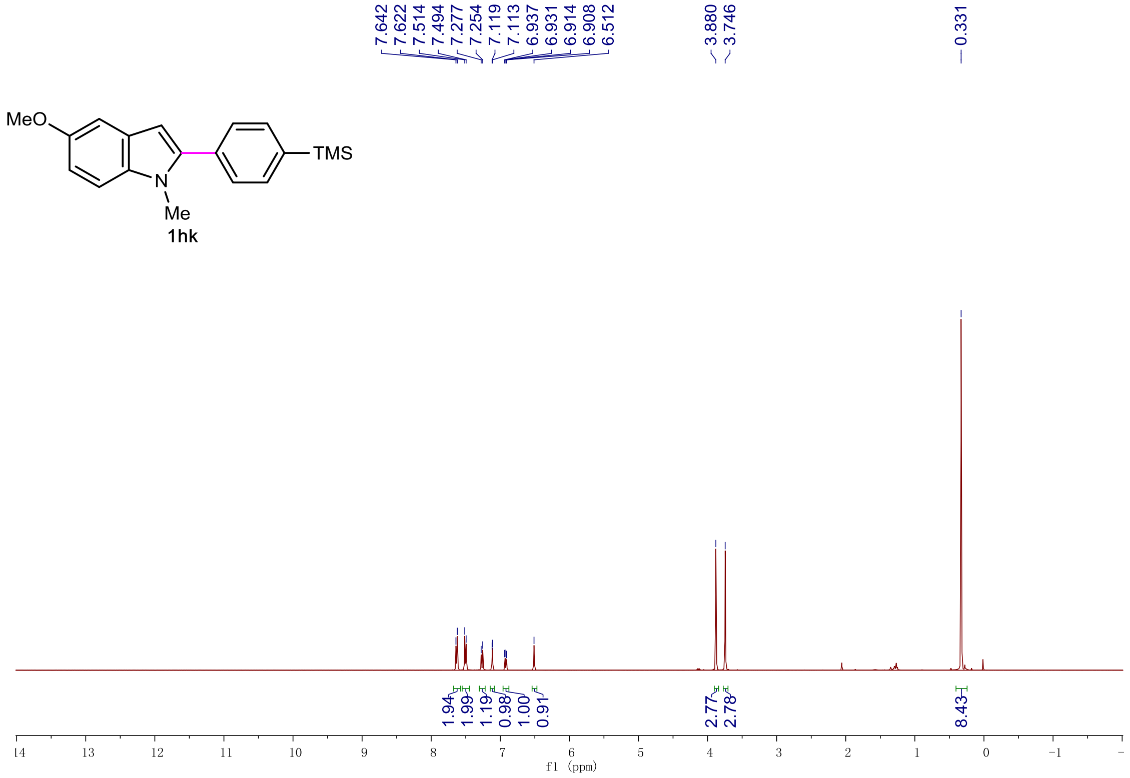

Figure S49. ^{13}C NMR spectrum of 1hk in $CDCl_3$ (100 MHz)

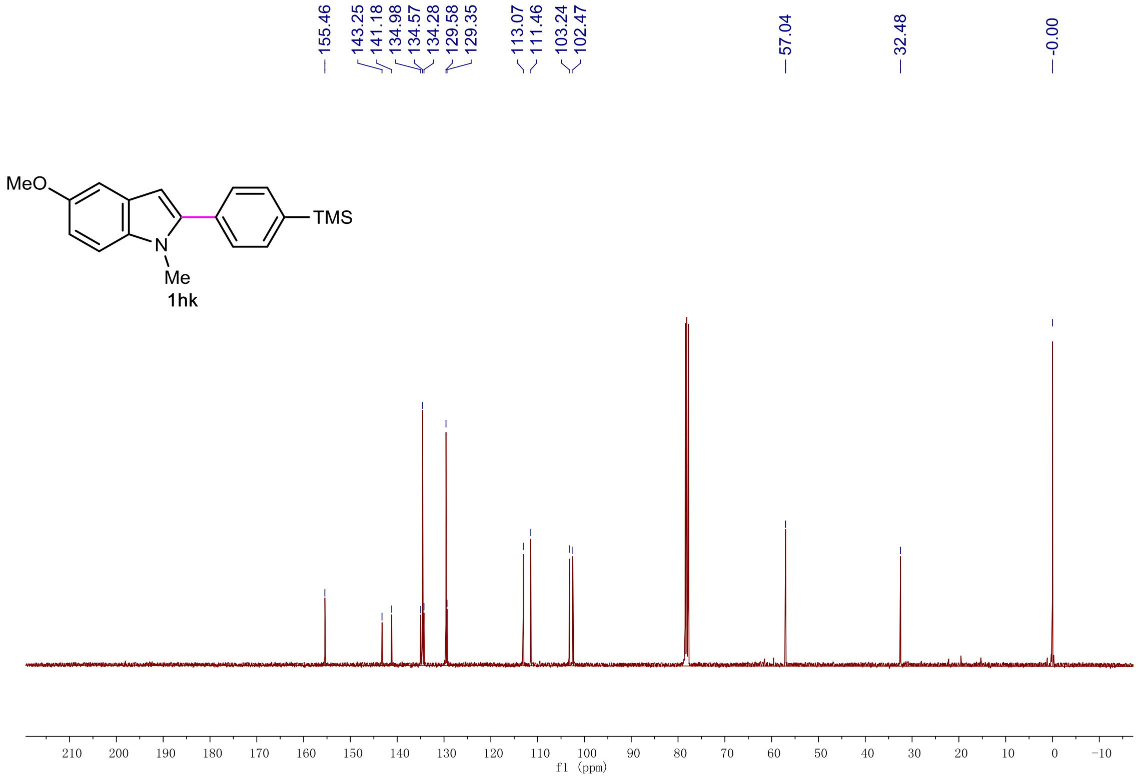

Figure S50. ^{1}H NMR spectrum of 1hl in CDCl$_3$ (400 MHz)

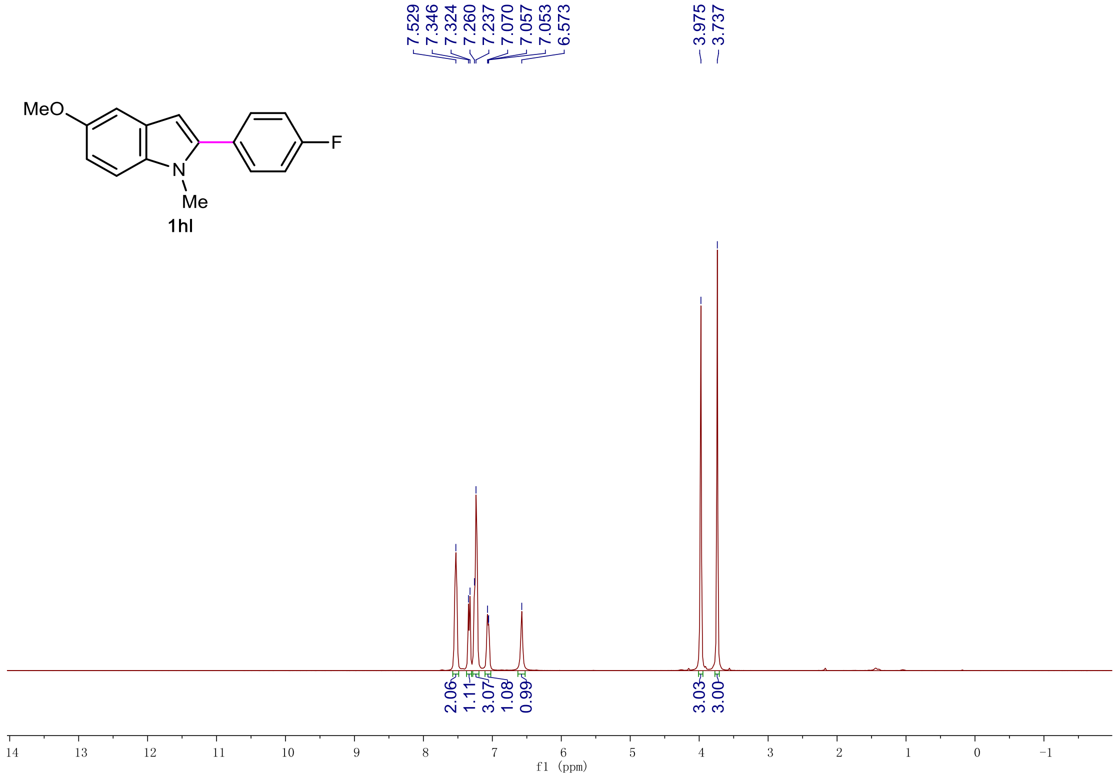

Figure S51. ^{13}C NMR spectrum of 1hl in CDCl$_3$ (100 MHz)

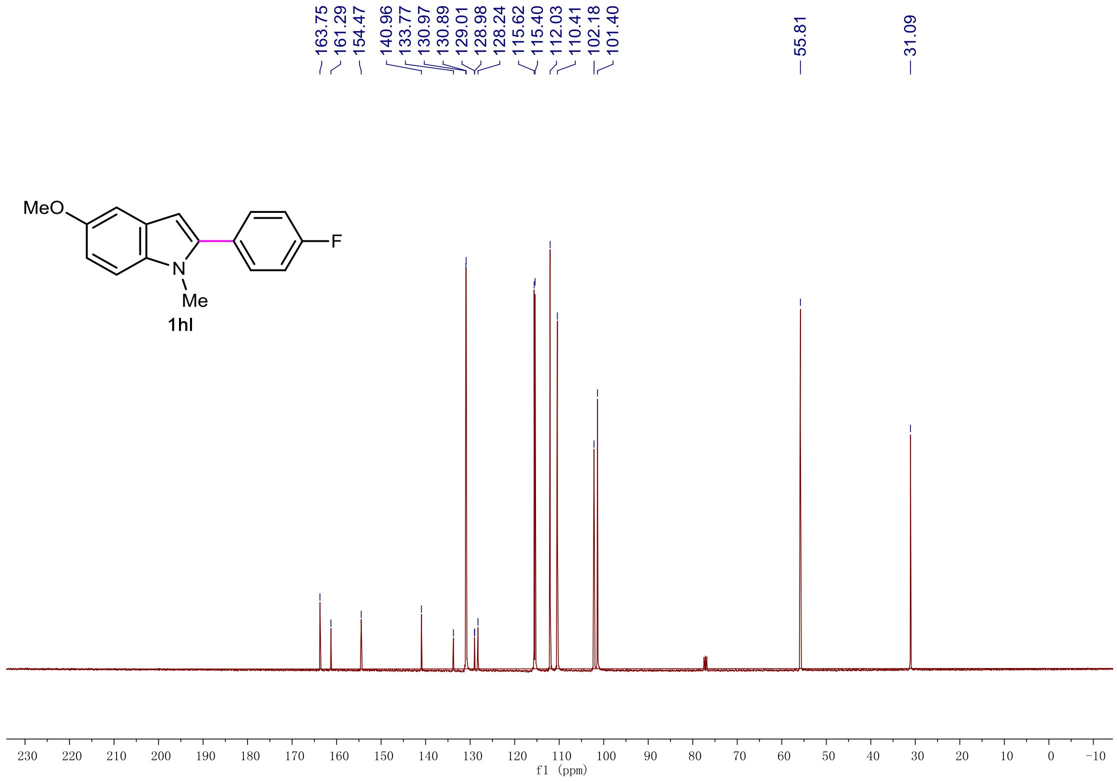

Figure S52. ^{1}H NMR spectrum of 1hm in $CDCl_3$ (400 MHz)

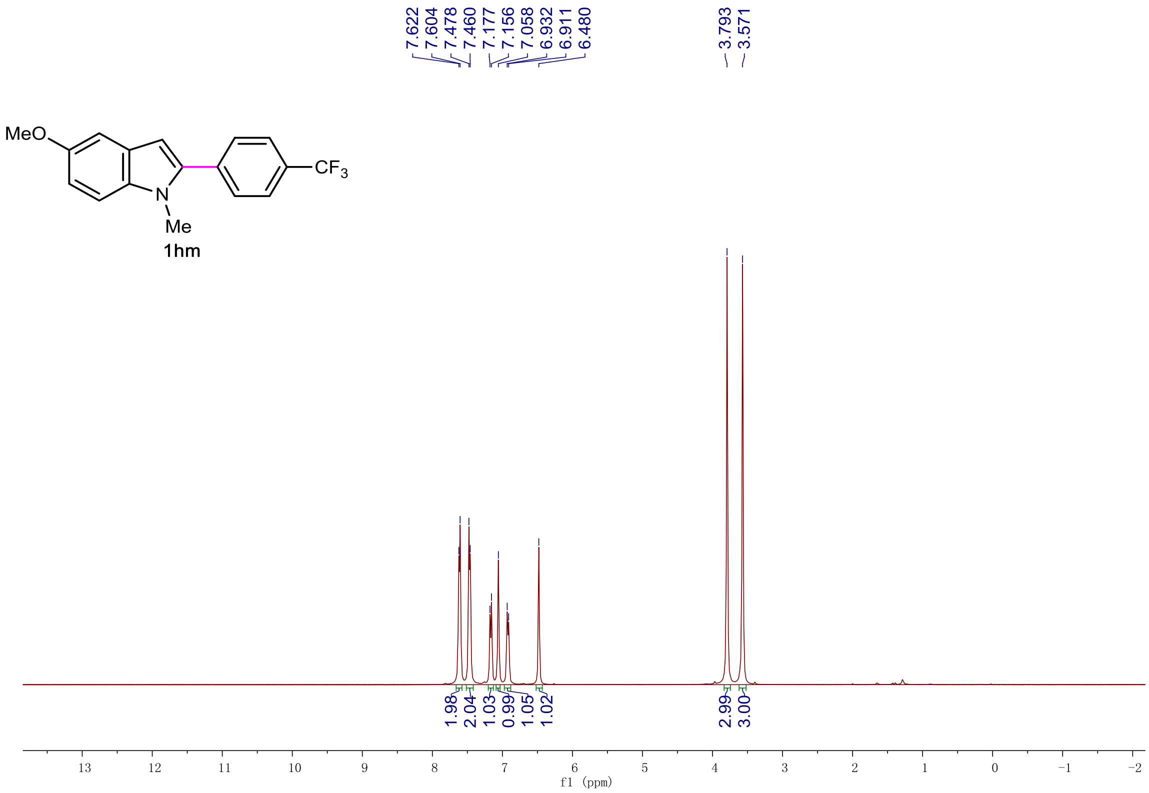

Figure S53. ^{13}C NMR spectrum of 1hm in $CDCl_3$ (100 MHz)

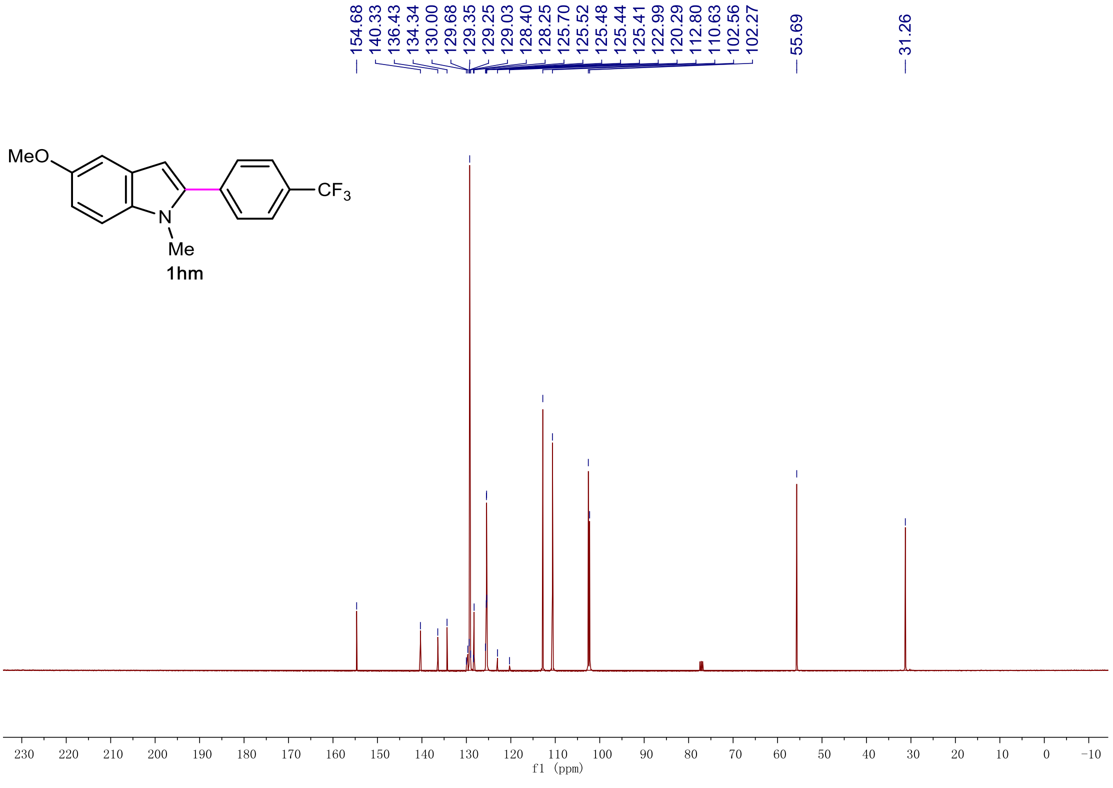

Figure S54. ^{1}H NMR spectrum of 1hn in $CDCl_3$ (400 MHz)

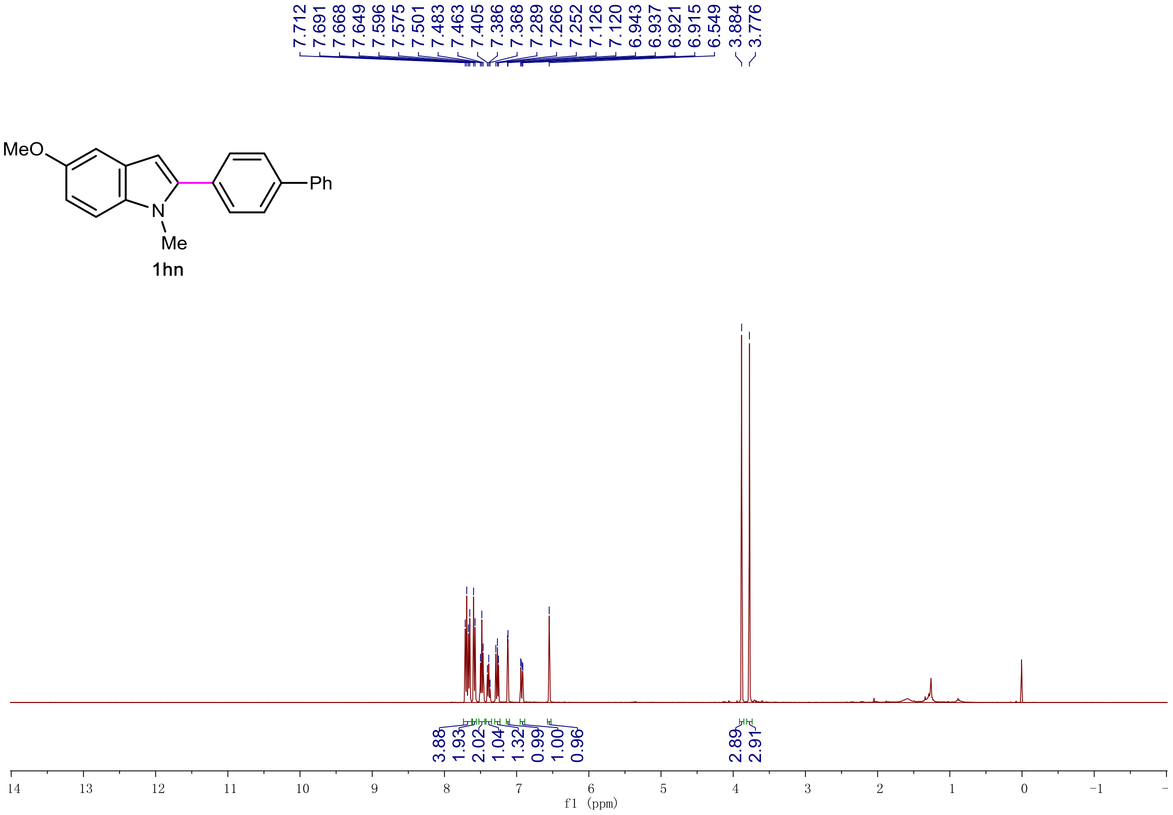

Figure S55. ^{13}C NMR spectrum of 1hn in $CDCl_3$ (100 MHz)

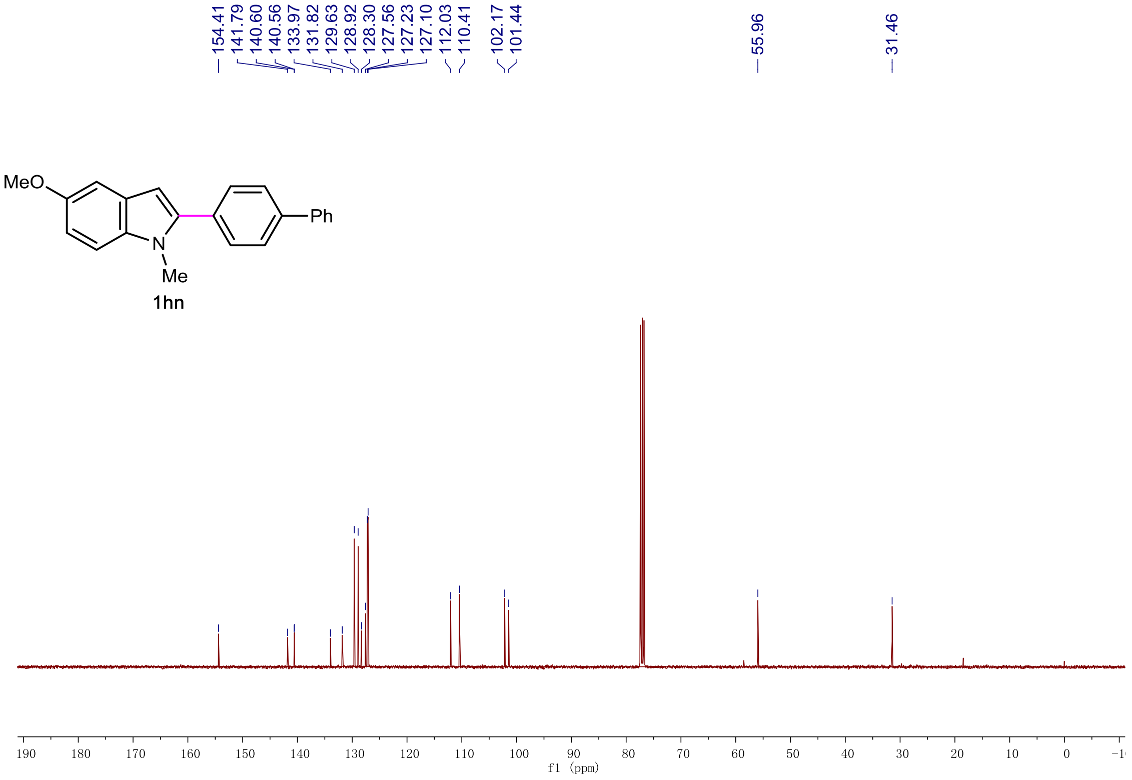

Figure S56. ^{1}H NMR spectrum of 1ho in CDCl$_3$ (400 MHz)

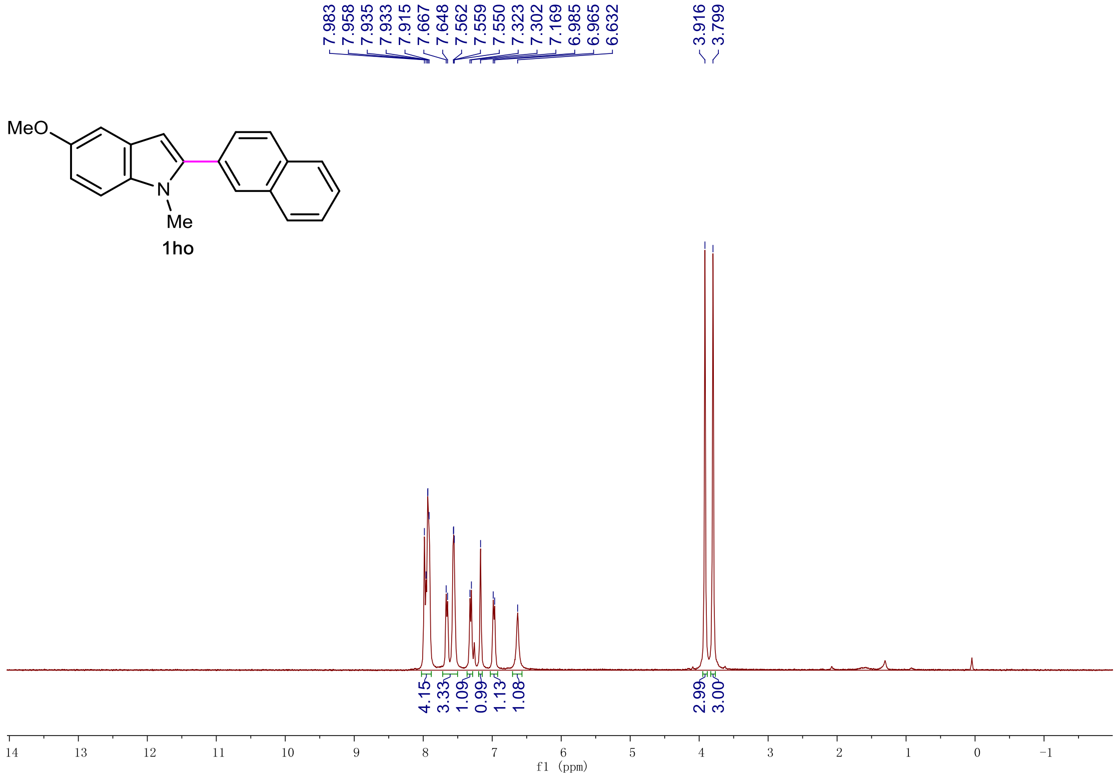

Figure S57. ^{13}C NMR spectrum of 1ho in CDCl$_3$ (100 MHz)

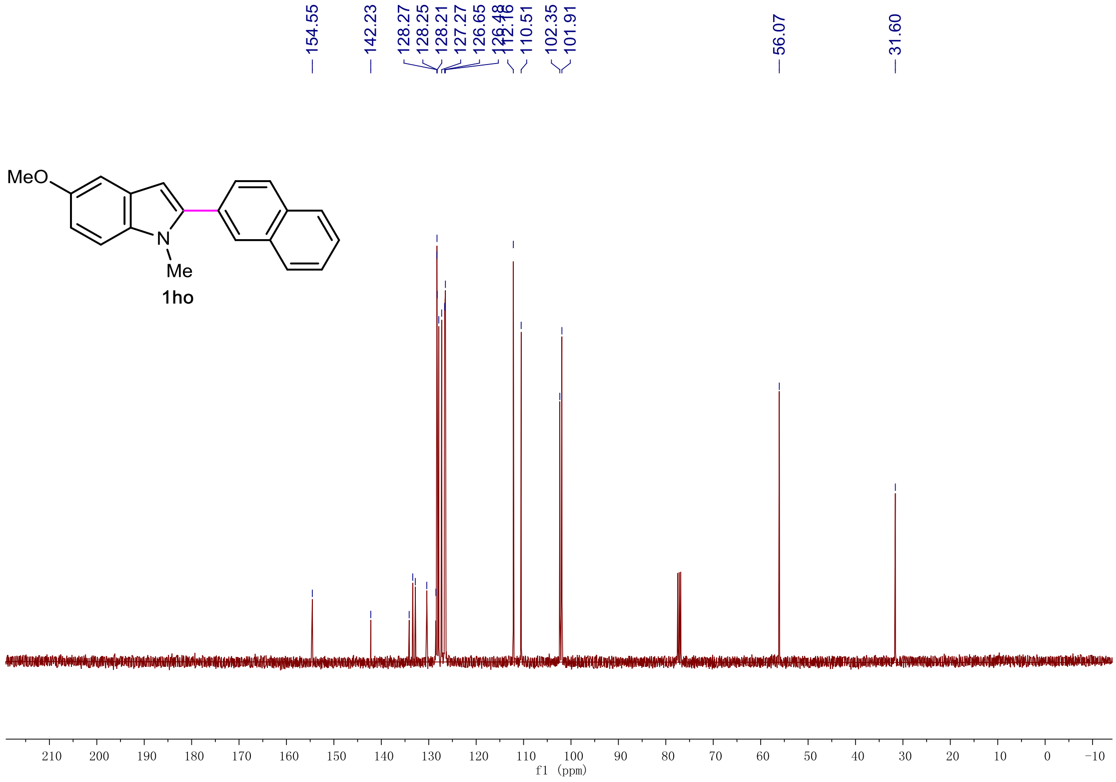

Figure S58. ^{1}H NMR spectrum of 1ap in CDCl$_3$ (400 MHz)

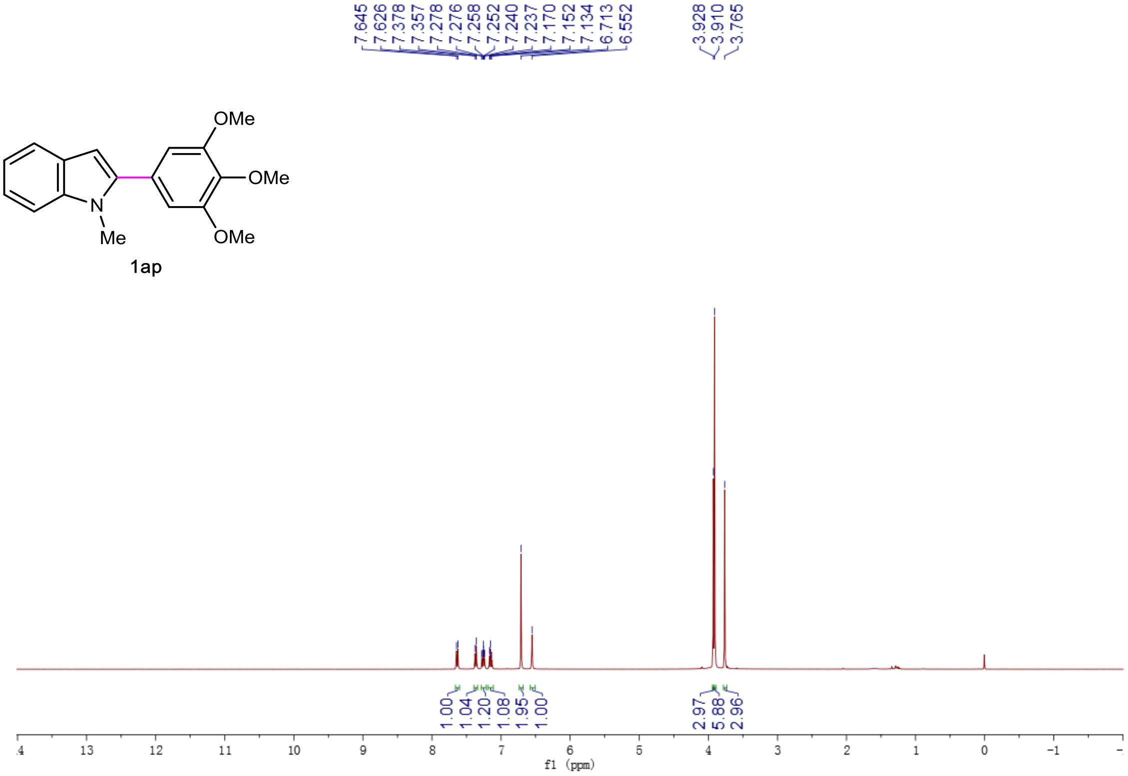

Figure S59. ^{13}C NMR spectrum of 1ap in CDCl$_3$ (100 MHz)

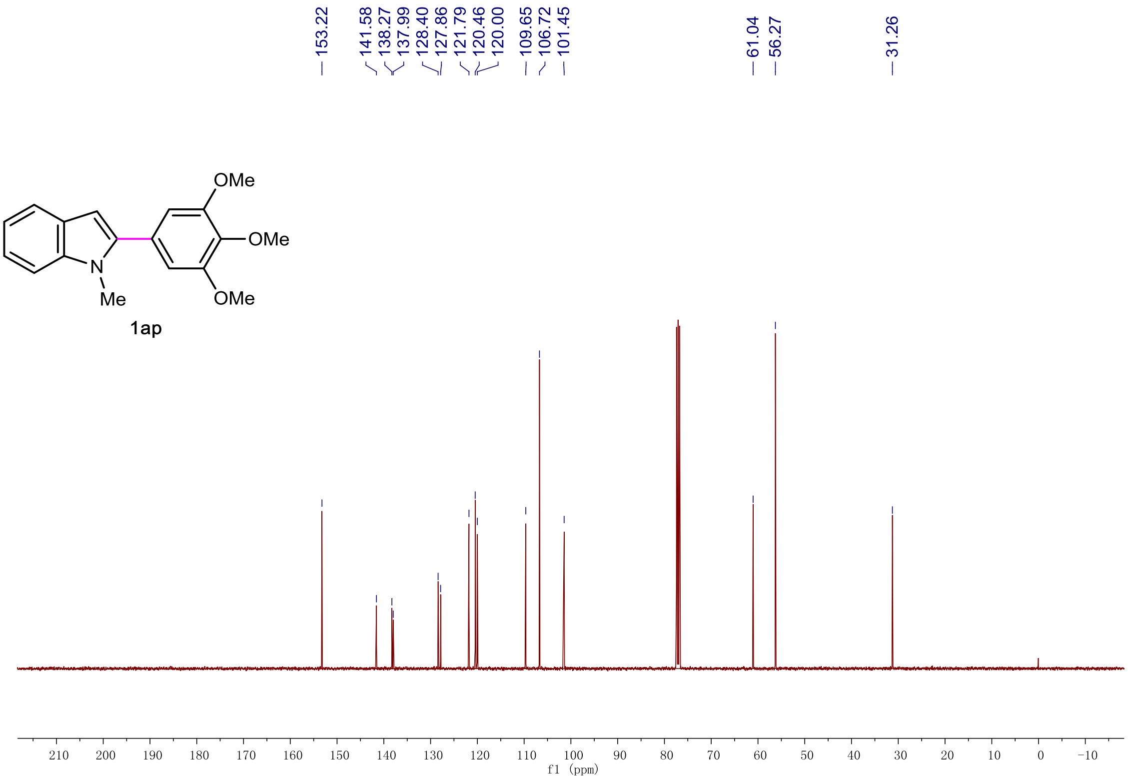

Figure S60. ^{1}H NMR spectrum of 1bp in $CDCl_3$ (400 MHz)

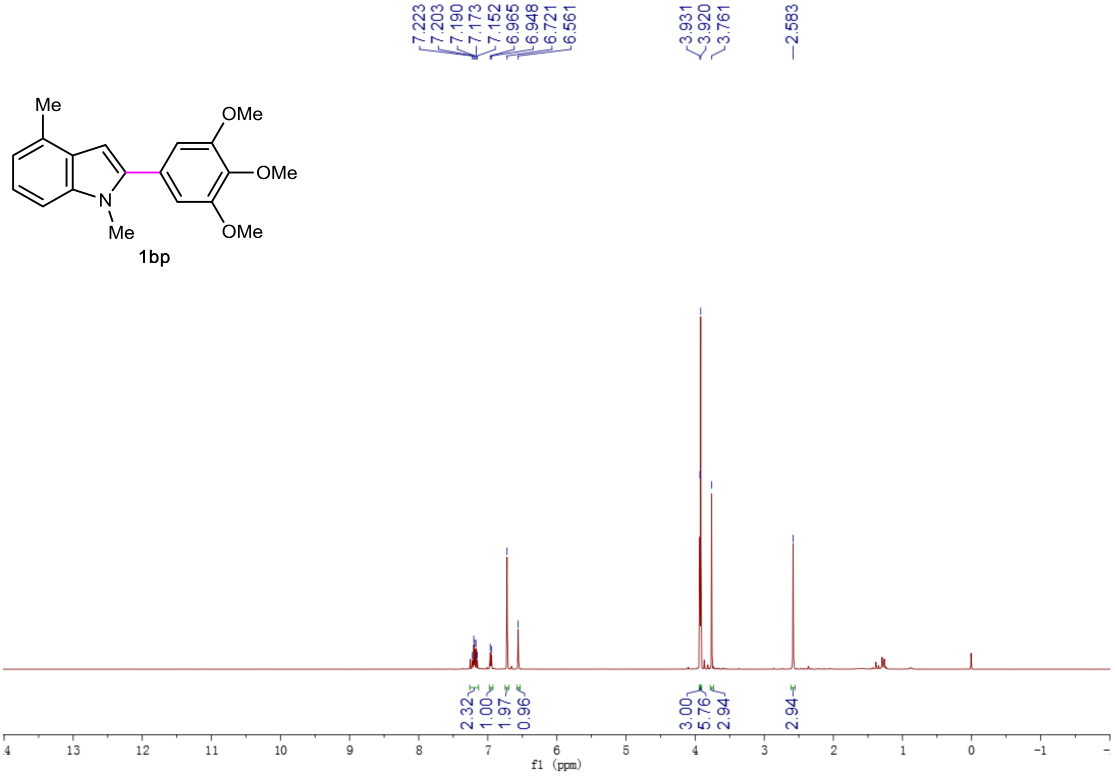

Figure S61. ^{13}C NMR spectrum of 1bp in $CDCl_3$ (100 MHz)

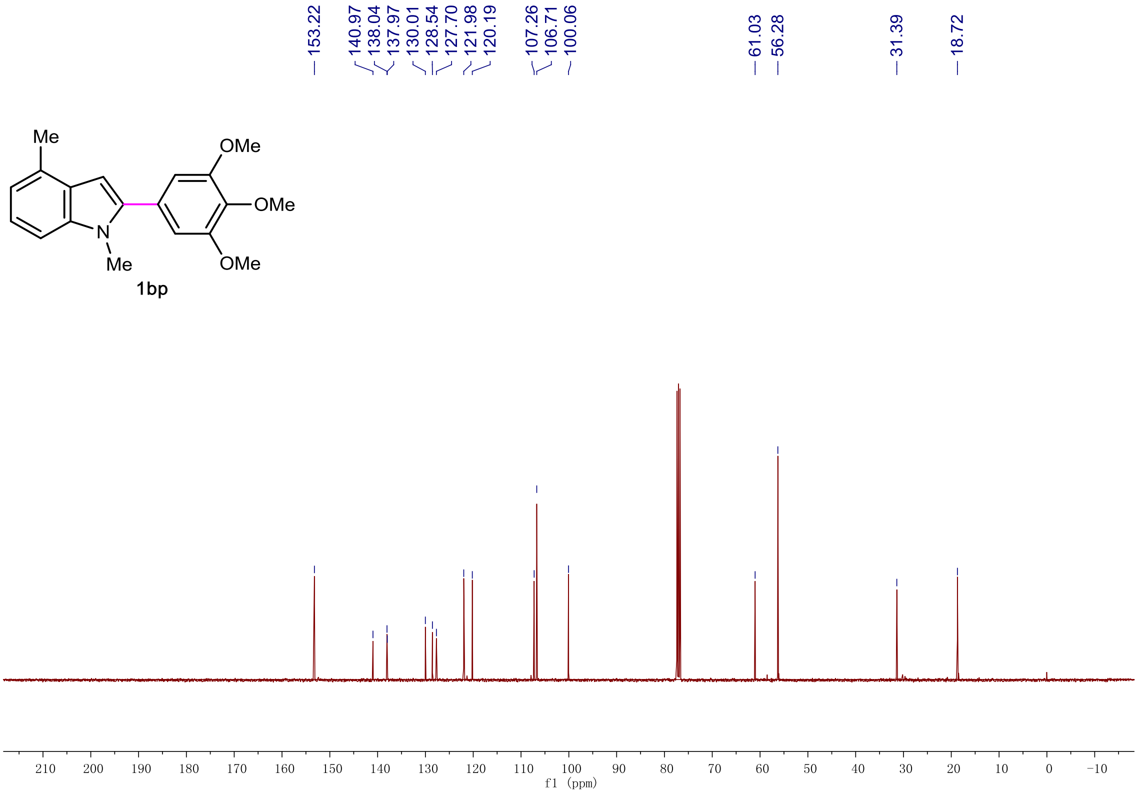

Figure S62. ^{1}H NMR spectrum of 1cp in CDCl$_3$ (400 MHz)

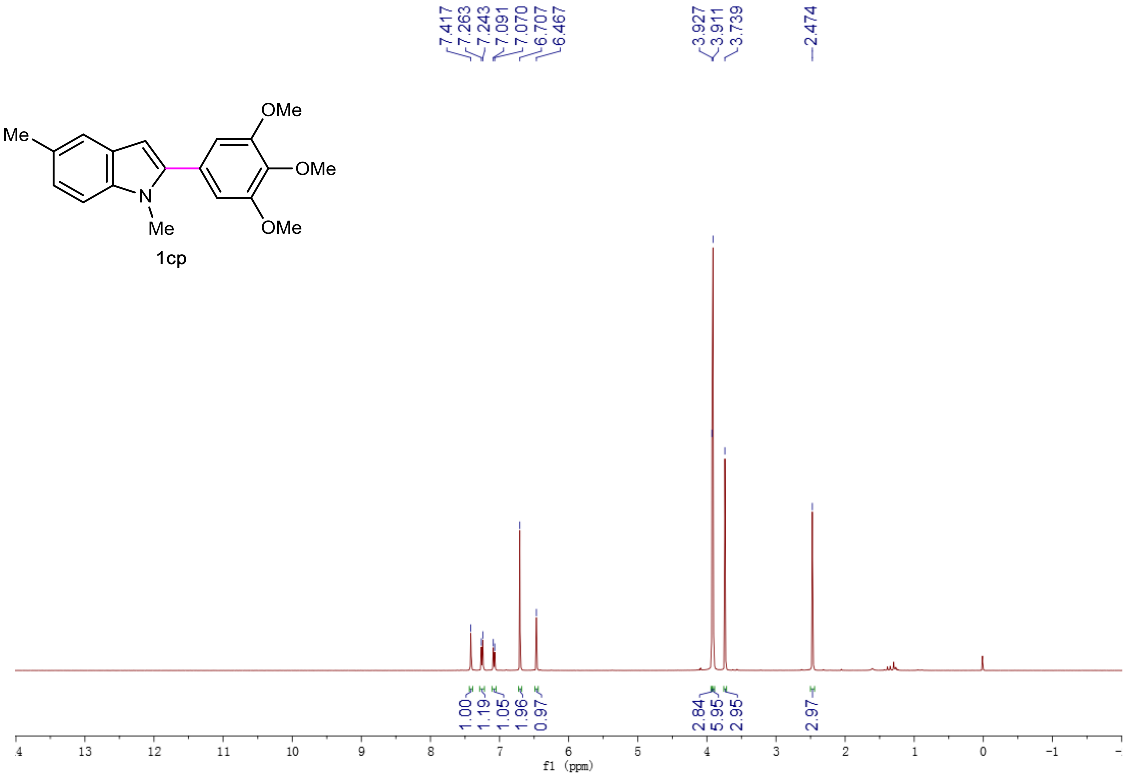

Figure S63. ^{13}C NMR spectrum of 1cp in CDCl$_3$ (100 MHz)

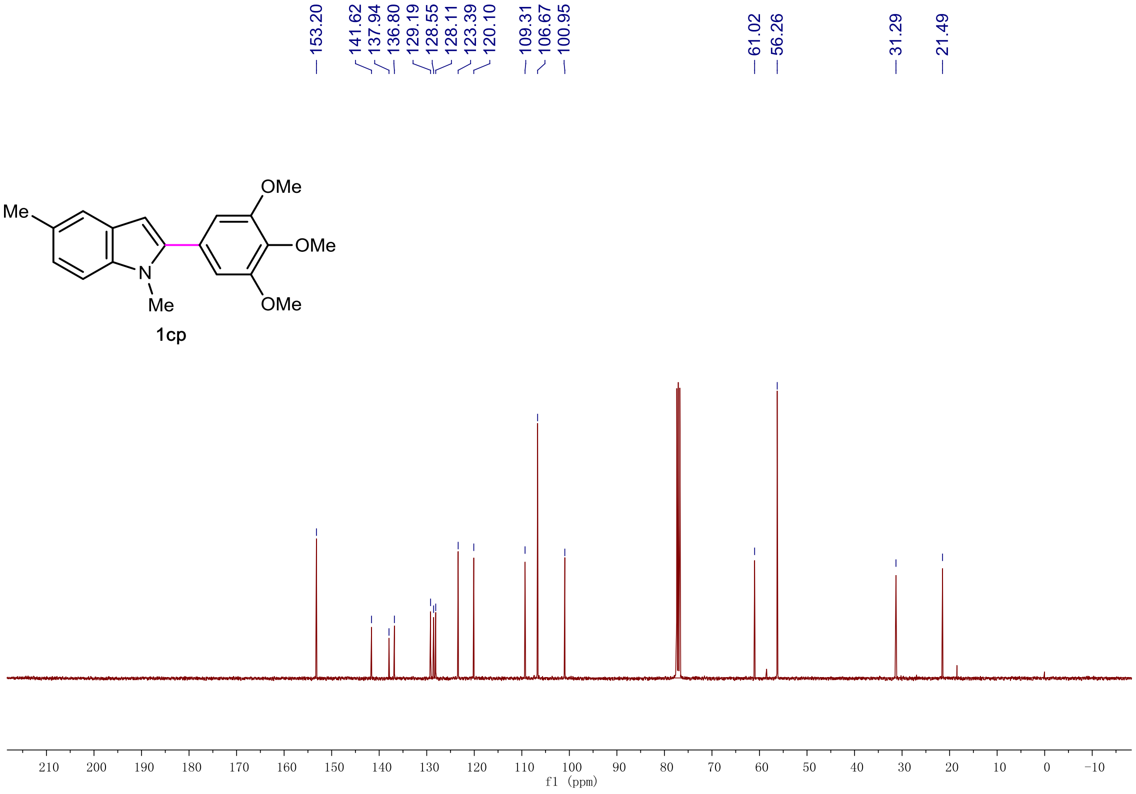

Figure S64. ^{1}H NMR spectrum of 1dp in $CDCl_3$ (400 MHz)

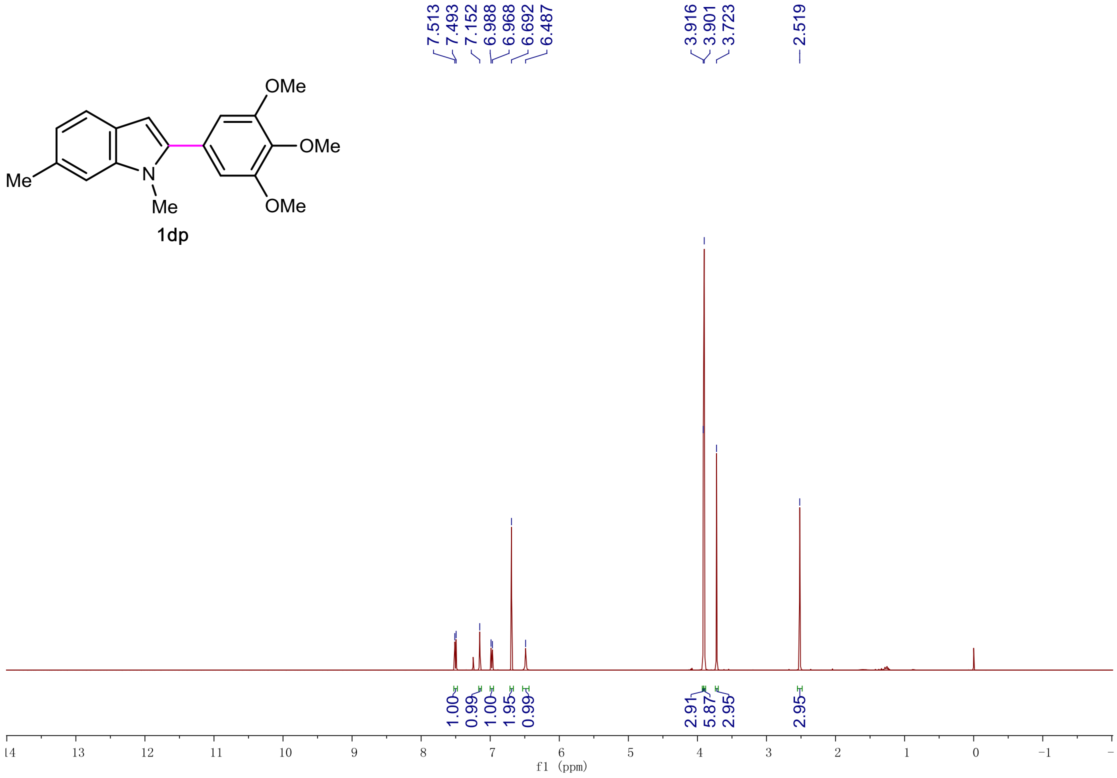

Figure S65. ^{13}C NMR spectrum of 1dp in $CDCl_3$ (100 MHz)

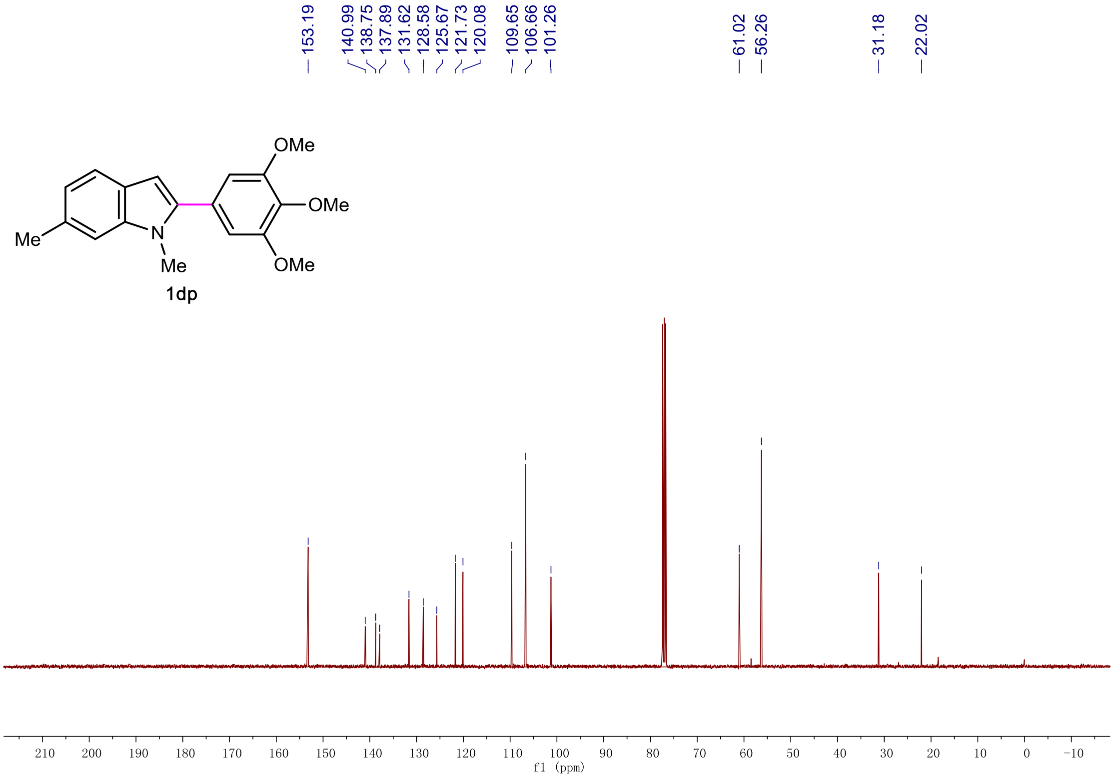

Figure S66. ^{1}H NMR spectrum of 1ep in $CDCl_3$ (400 MHz)

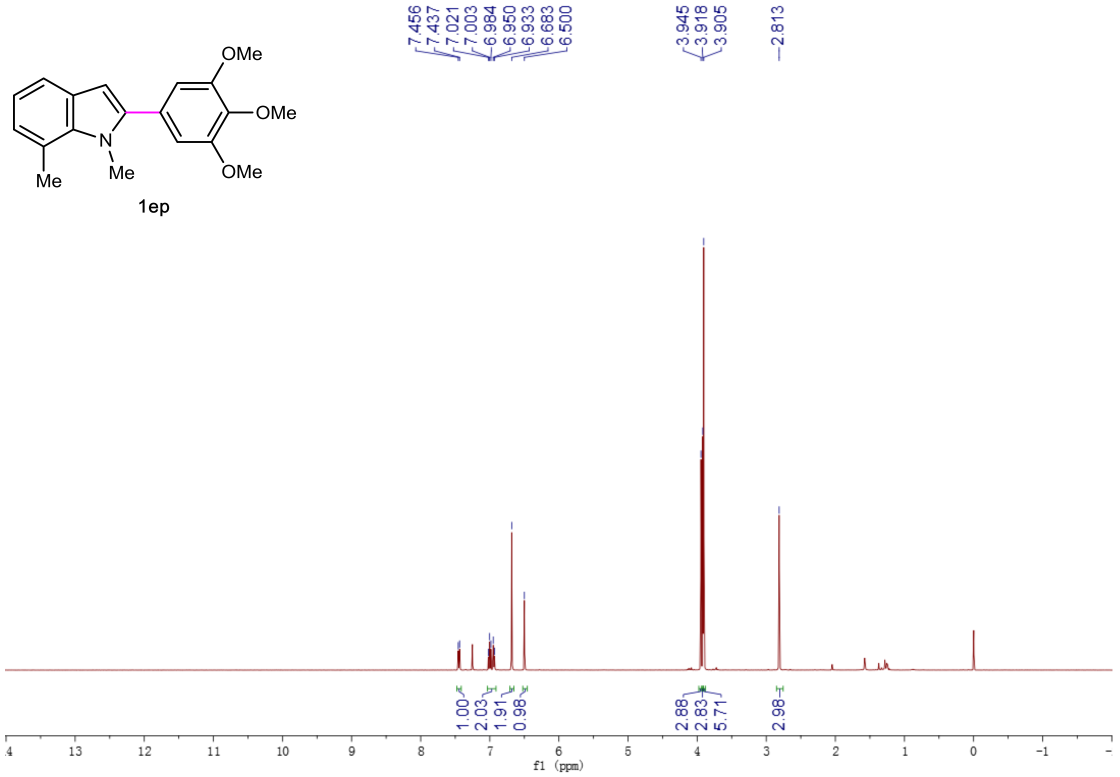

Figure S67. ^{13}C NMR spectrum of 1ep in $CDCl_3$ (100 MHz)

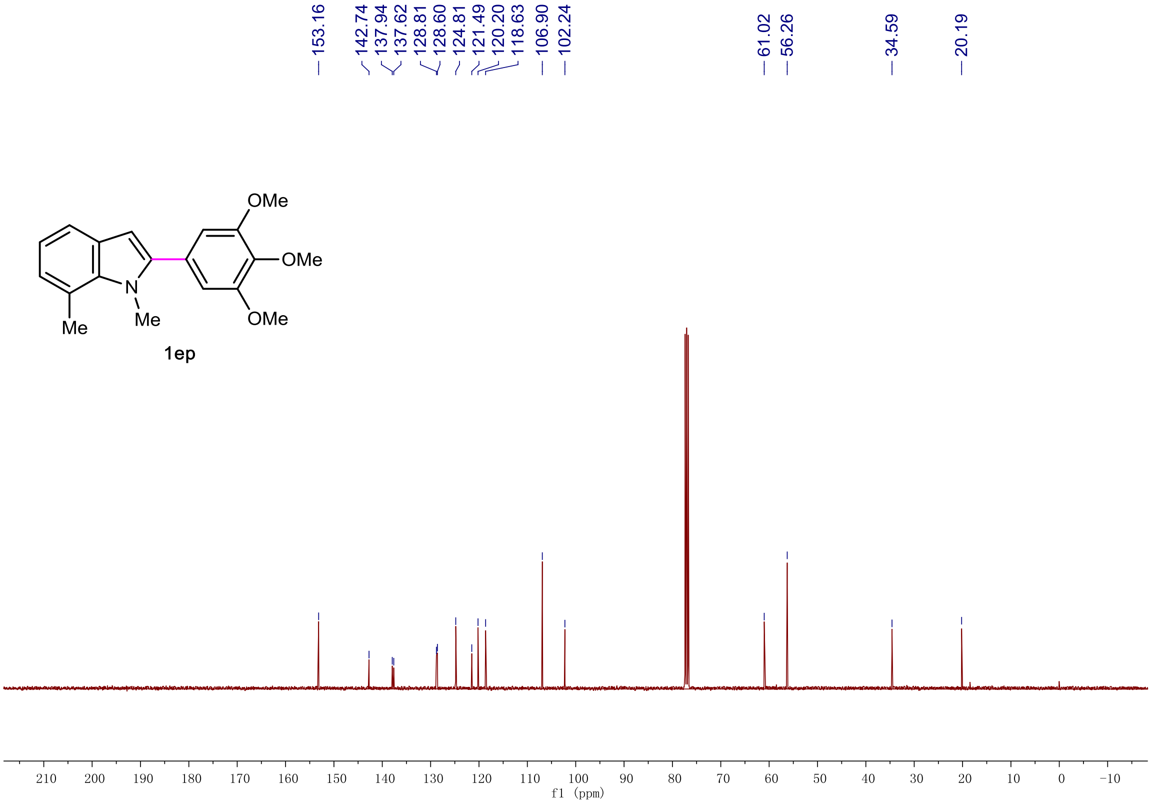

Figure S68. ^{1}H NMR spectrum of 1fp in CDCl$_3$ (400 MHz)

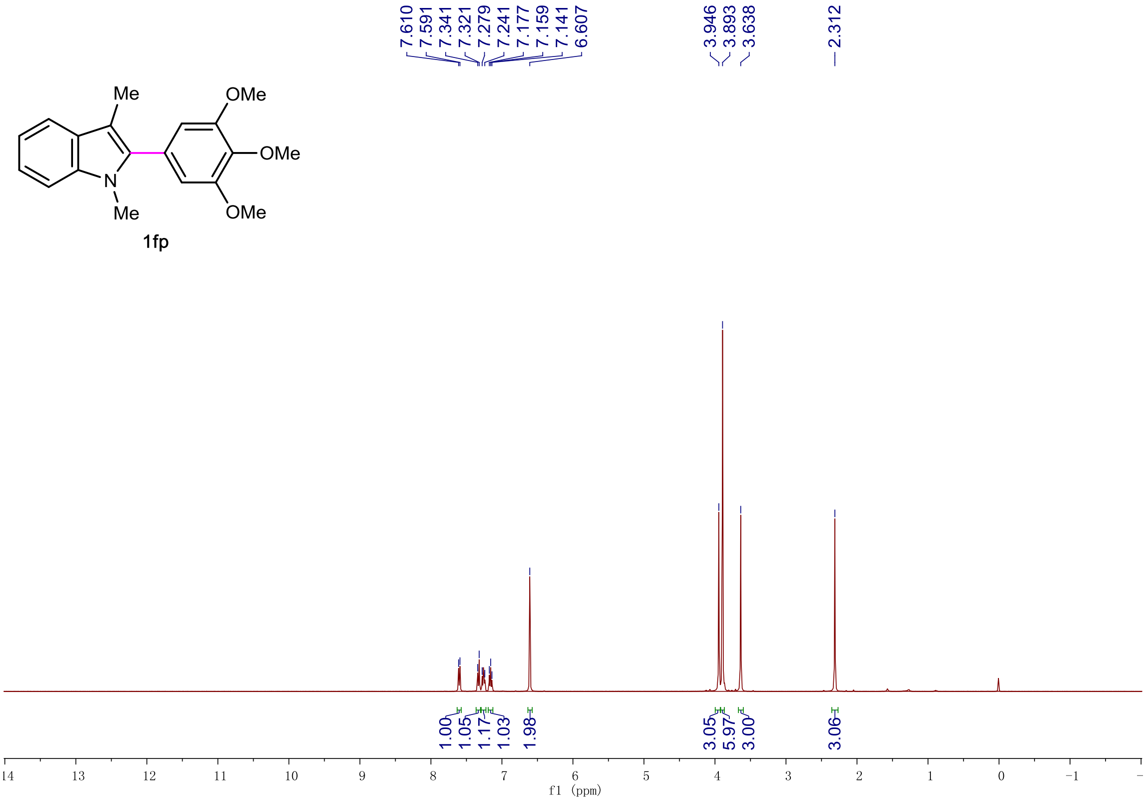

Figure S69. ^{13}C NMR spectrum of 1fp in CDCl$_3$ (100 MHz)

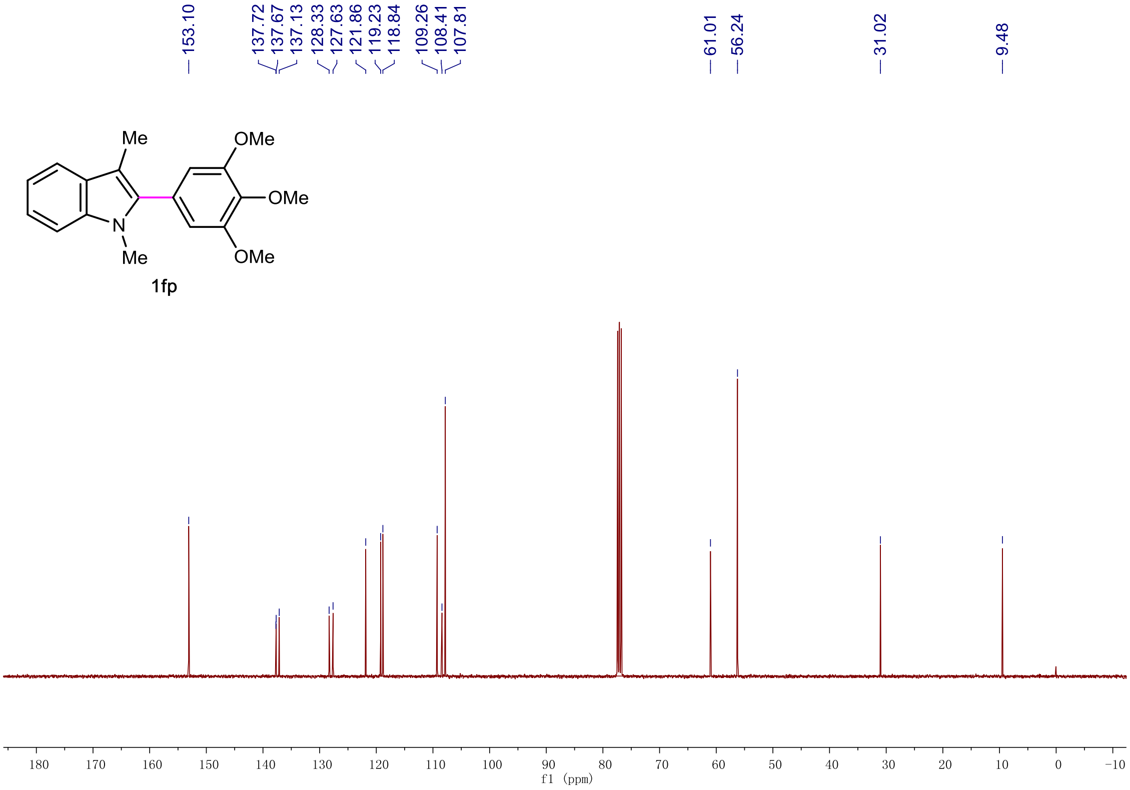

Figure S70. ^{1}H NMR spectrum of 1hp in $CDCl_3$ (400 MHz)

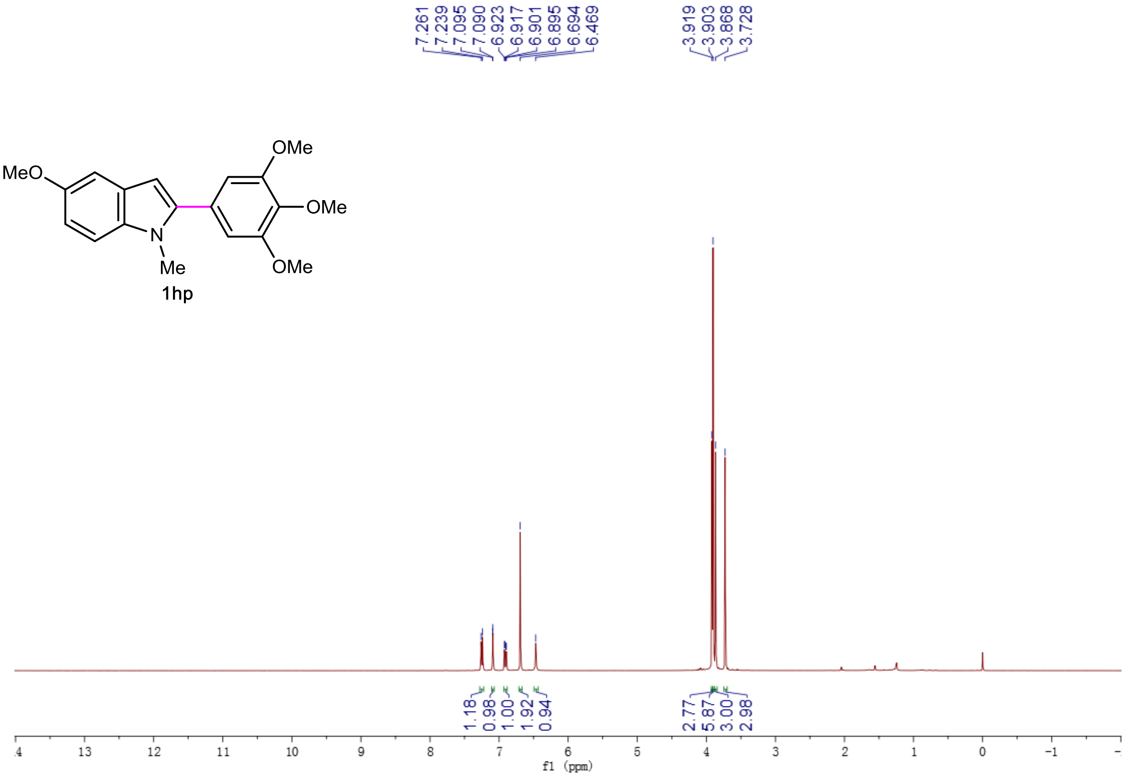

Figure S71. ^{13}C NMR spectrum of 1hp in $CDCl_3$ (100 MHz)

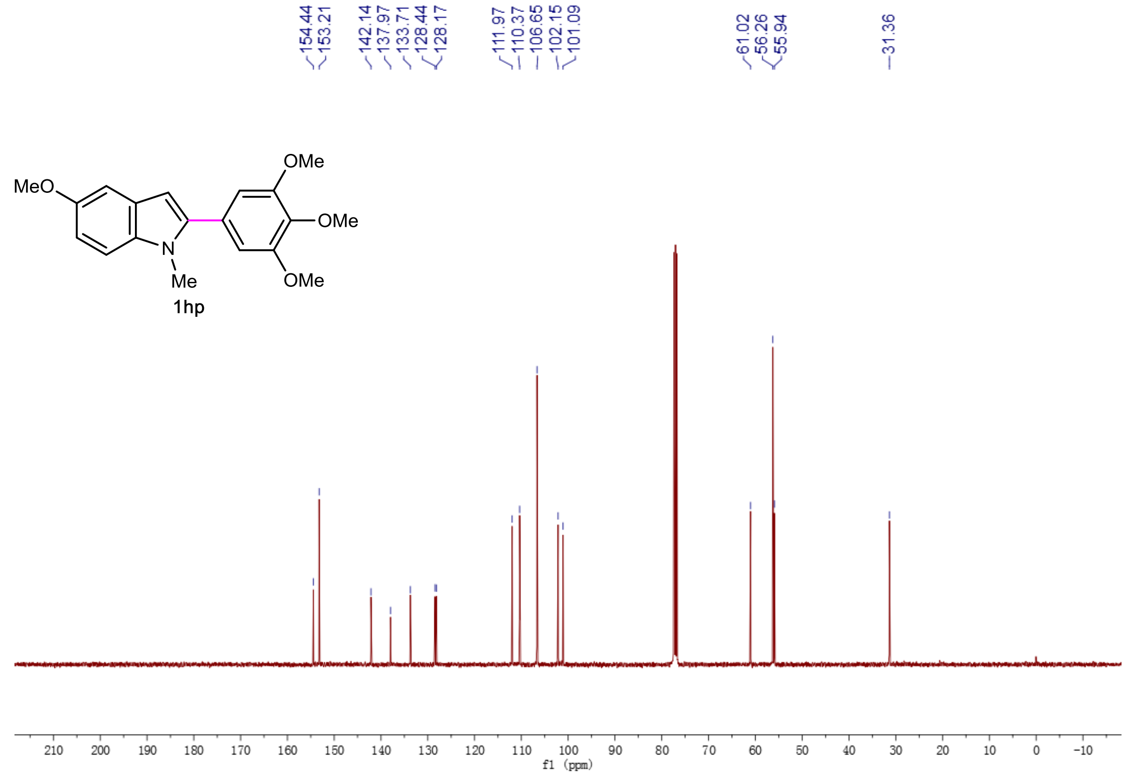

Figure S72. ^{1}H NMR spectrum of 1jp in CDCl$_3$ (400 MHz)

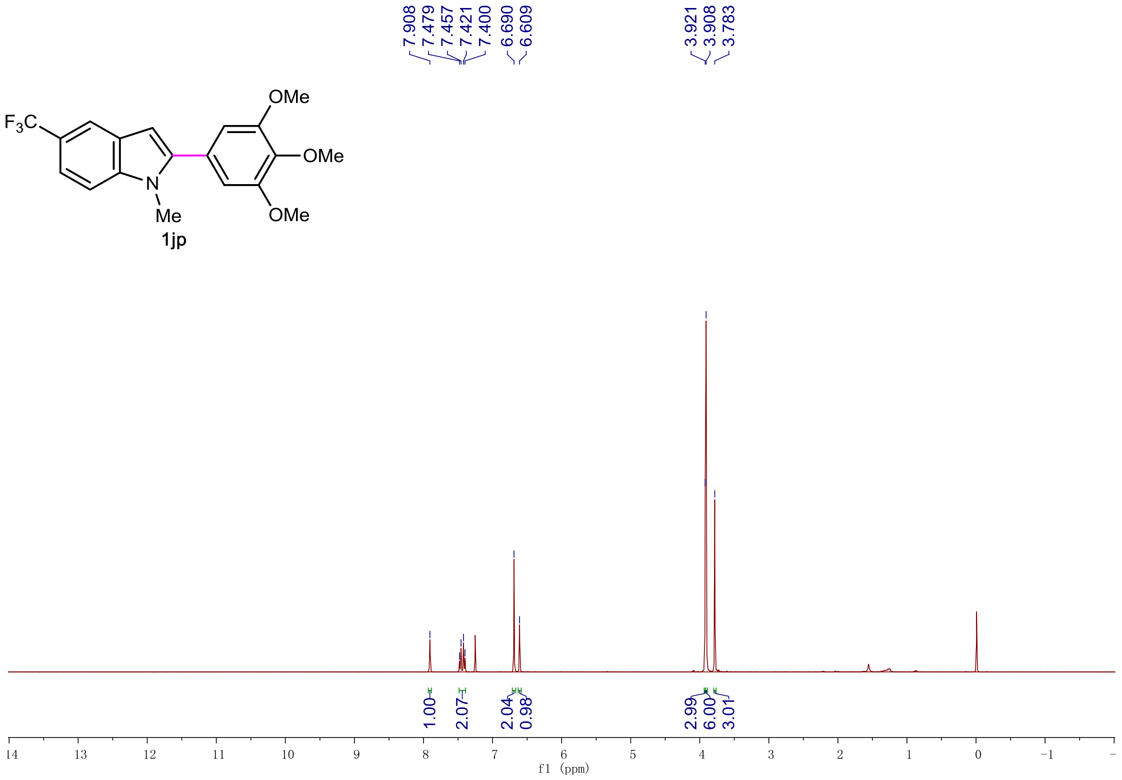

Figure S73. ^{13}C NMR spectrum of 1jp in CDCl$_3$ (100 MHz)

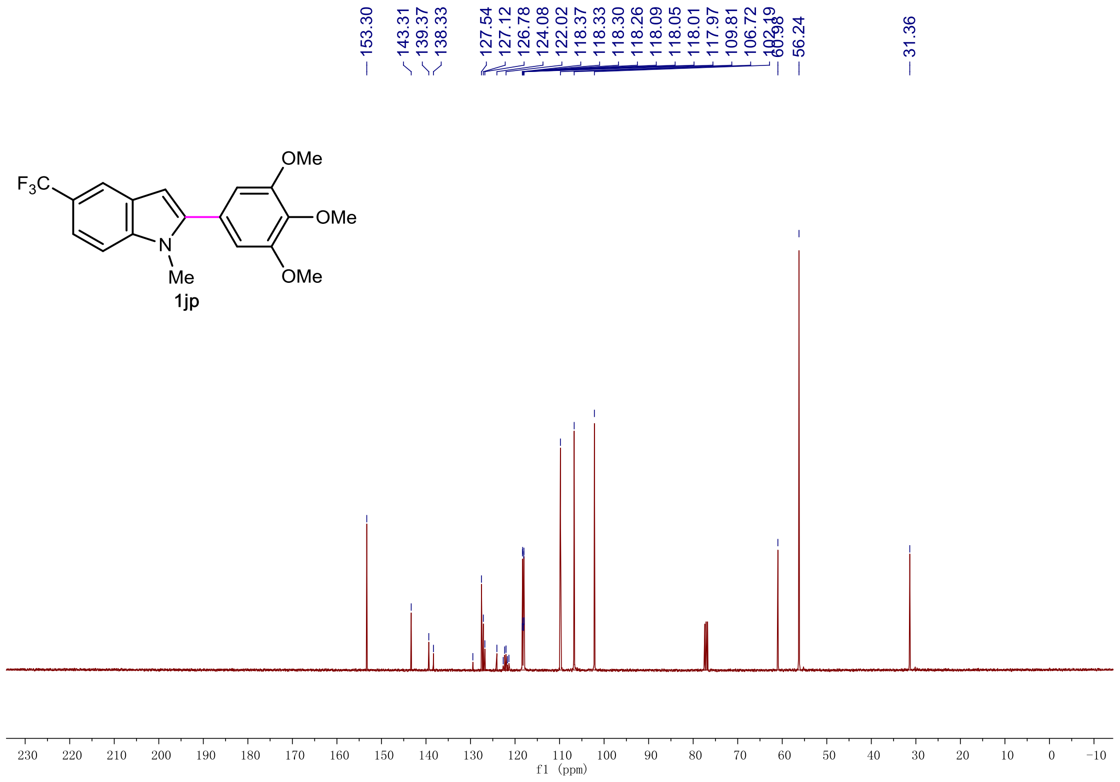

Figure S74. ^{1}H NMR spectrum of 1kp in $CDCl_3$ (400 MHz)

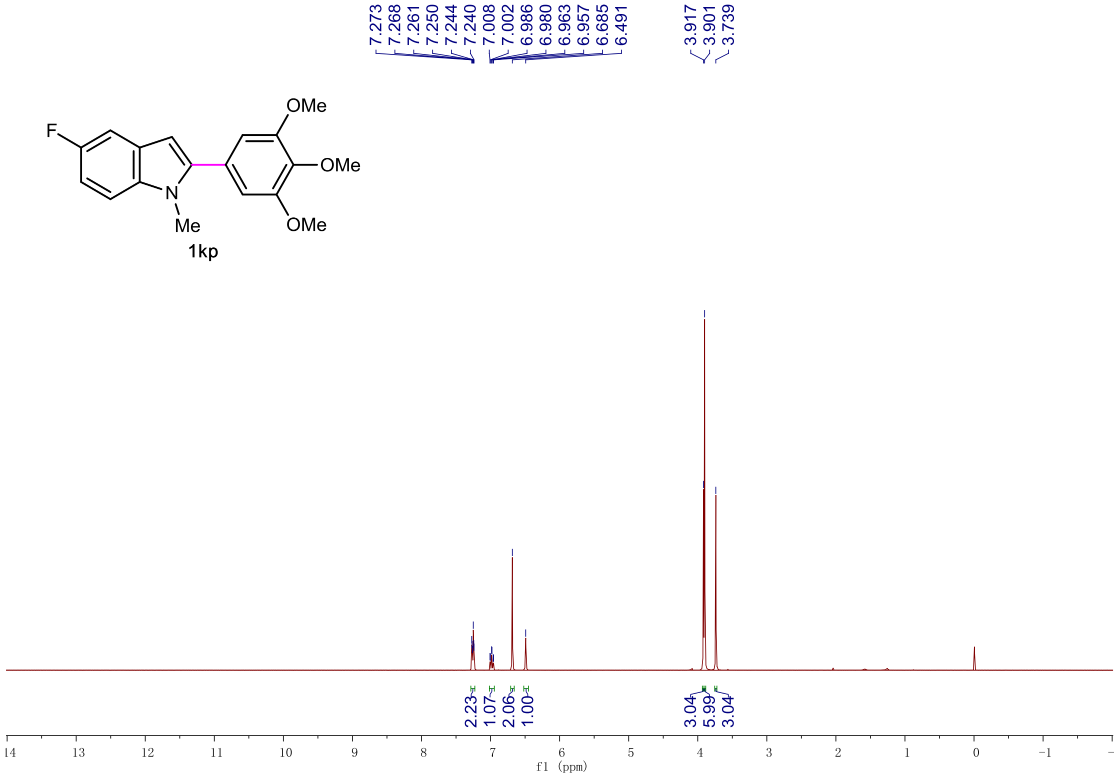

Figure S75. ^{13}C NMR spectrum of 1kp in $CDCl_3$ (100 MHz)

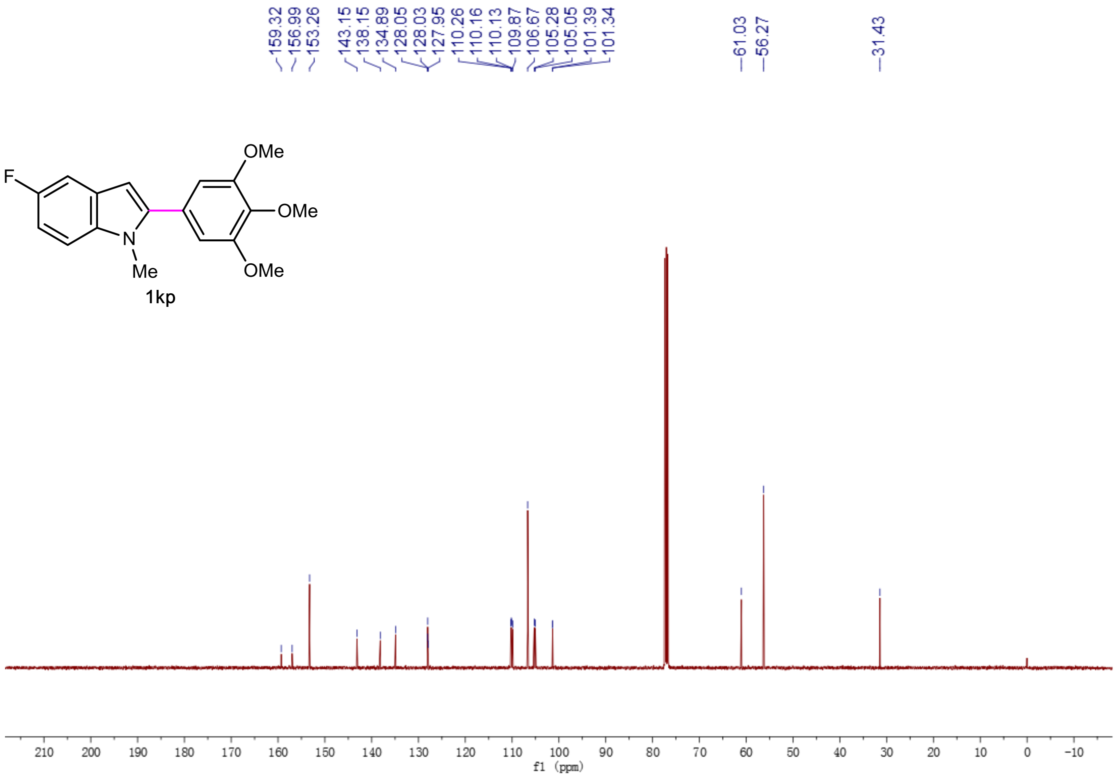

Figure S76. ^{1}H NMR spectrum of 1lp in $CDCl_3$ (400 MHz)

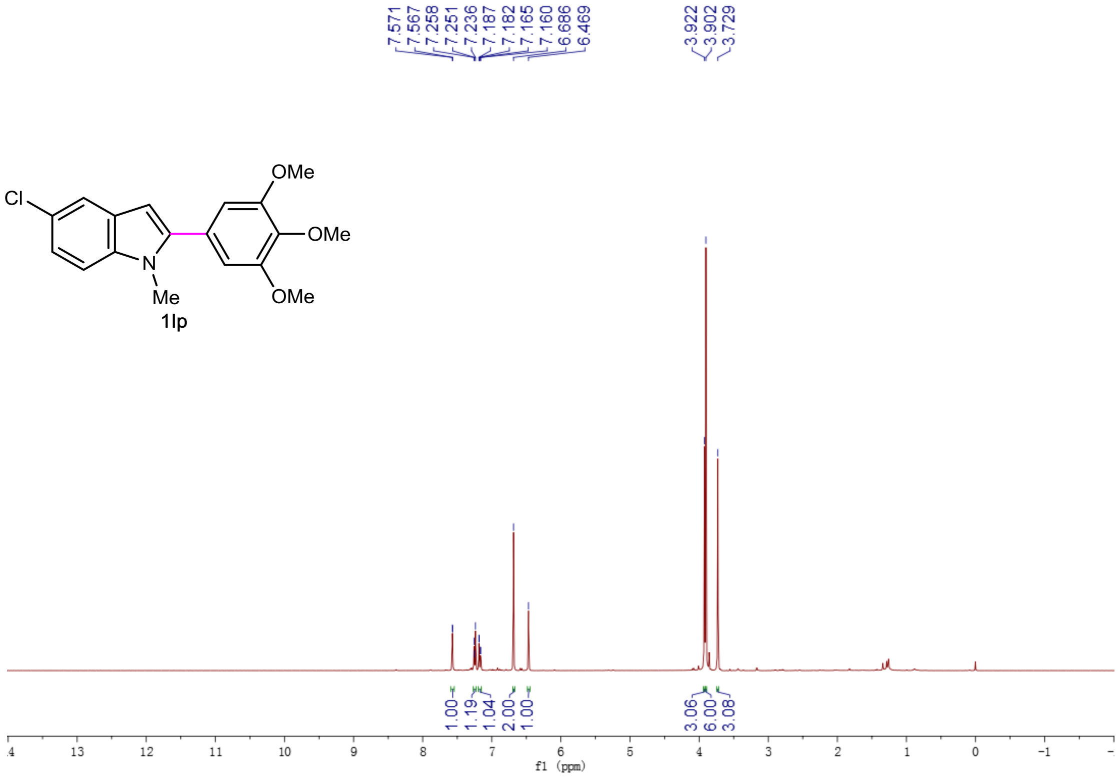

Figure S77. ^{13}C NMR spectrum of 1lp in $CDCl_3$ (100 MHz)

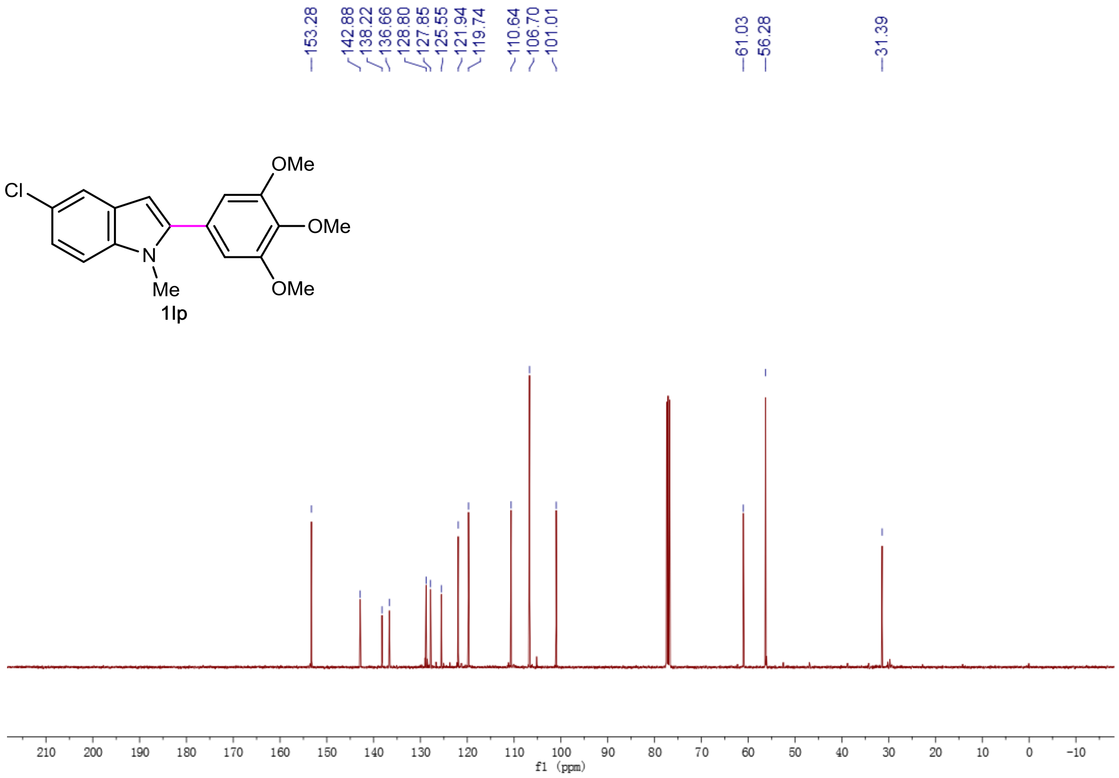

Figure S78. ^{1}H NMR spectrum of 1op in CDCl$_3$ (400 MHz)

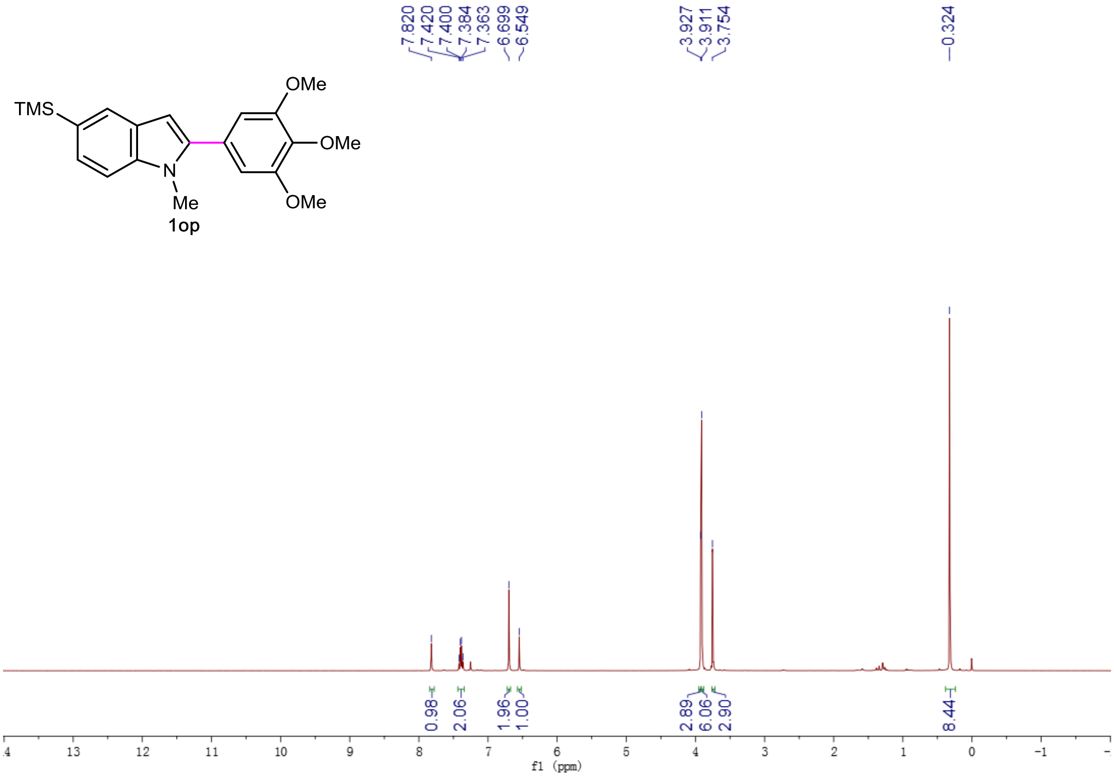

Figure S79. ^{13}C NMR spectrum of 1op in CDCl$_3$ (100 MHz)

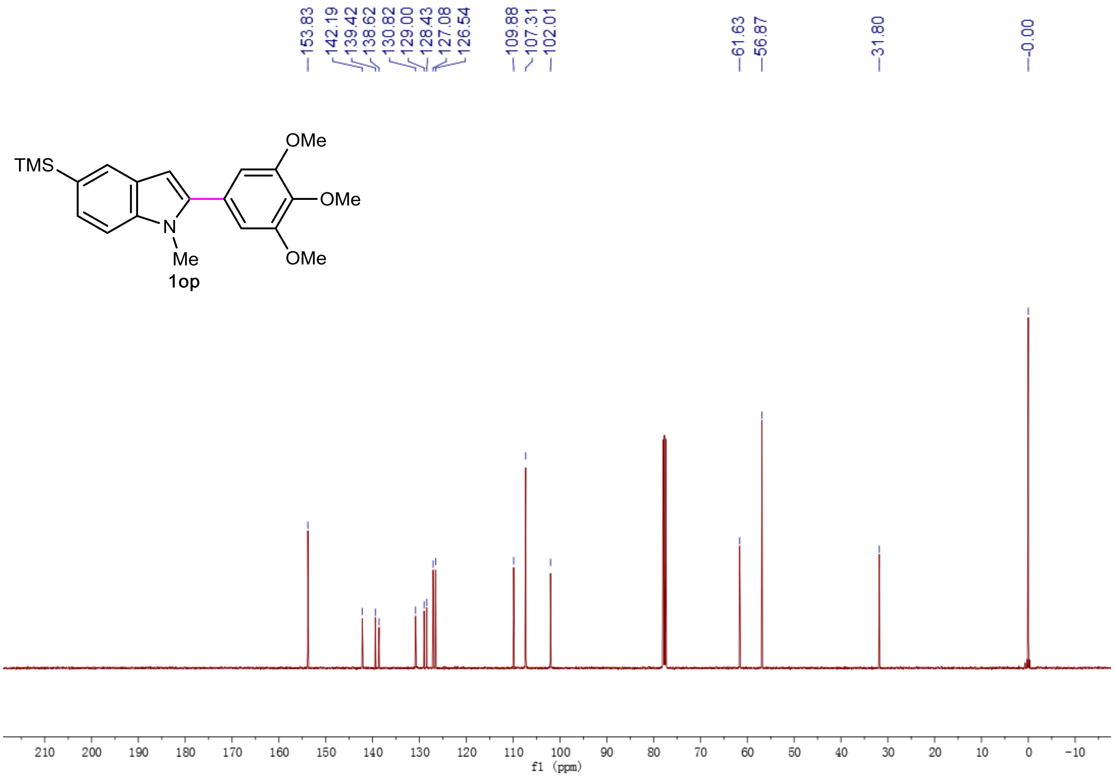

Figure S80. ^{1}H NMR spectrum of 1qp in $CDCl_3$ (400 MHz)

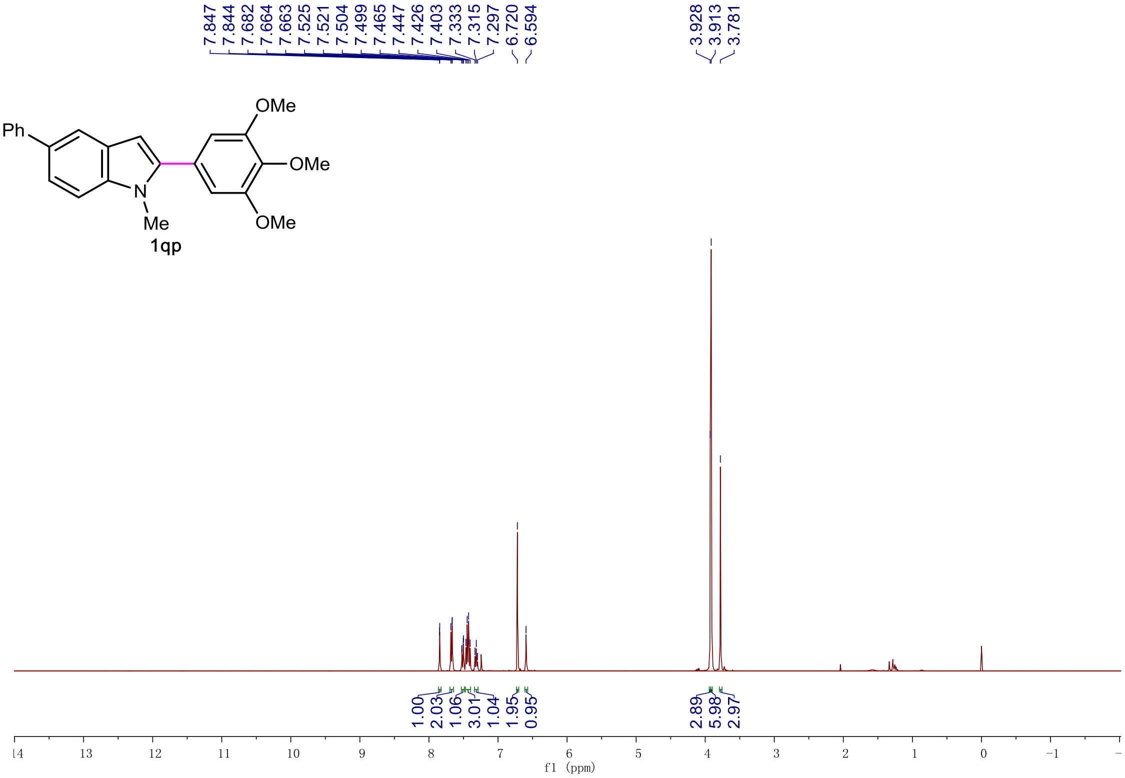

Figure S81. ^{13}C NMR spectrum of 1qp in $CDCl_3$ (100 MHz)

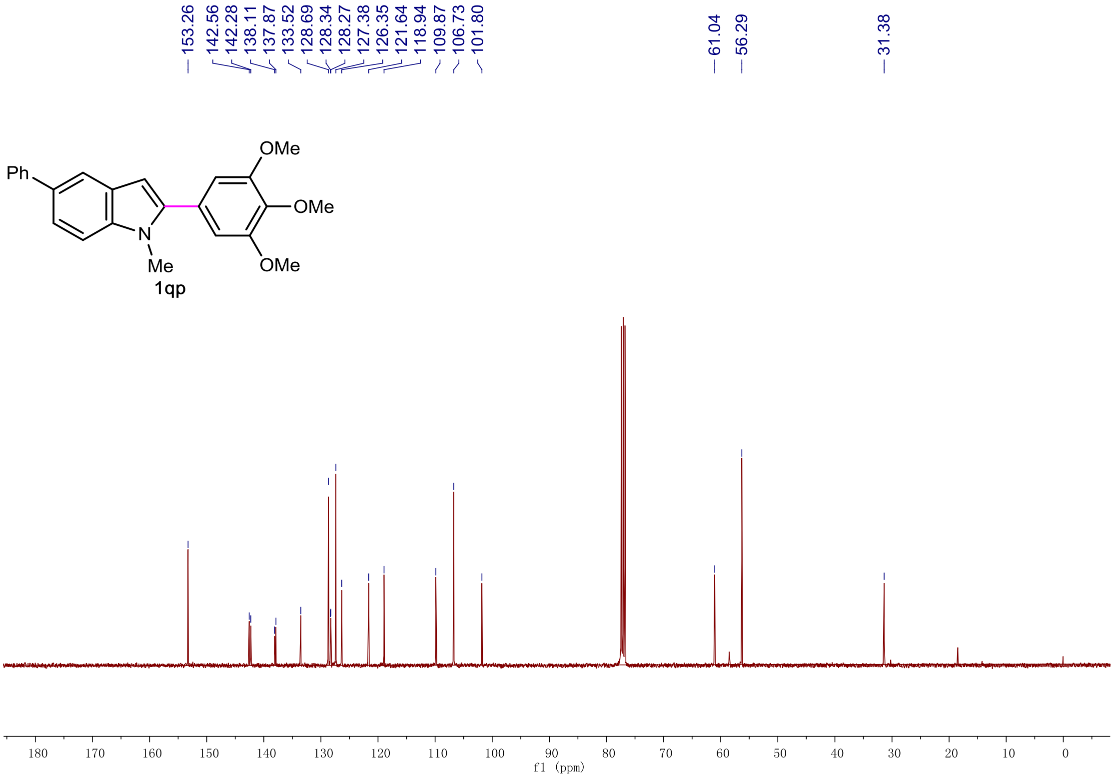

Figure S82. ^{1}H NMR spectrum of 2a in $CDCl_3$ (400 MHz)

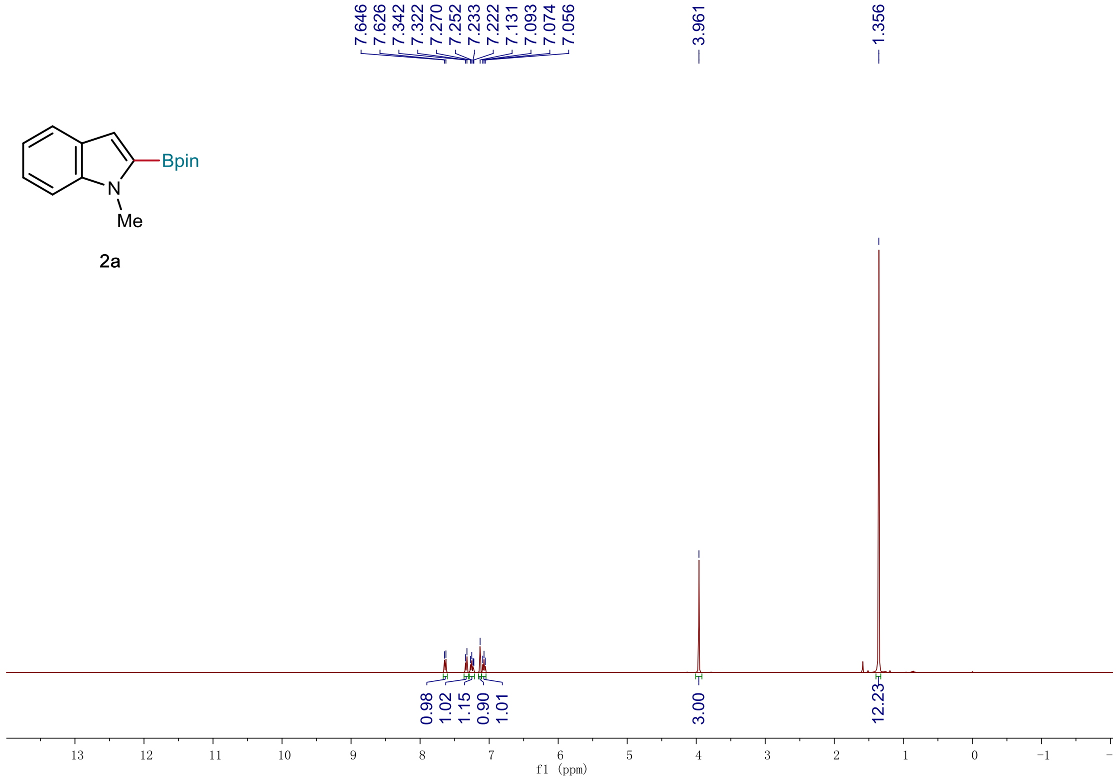

Figure S83. ^{13}C NMR spectrum of 2a in $CDCl_3$ (100 MHz)

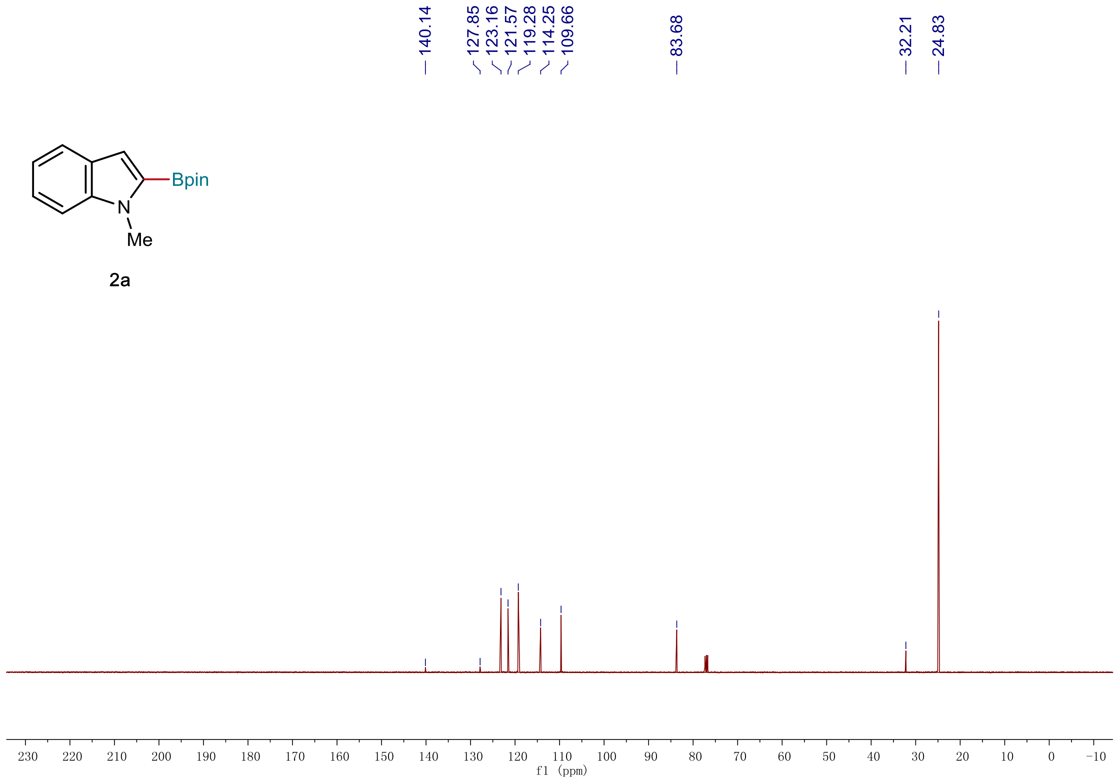

Figure S84. ^{1}H NMR spectrum of 2b in $CDCl_3$ (400 MHz)

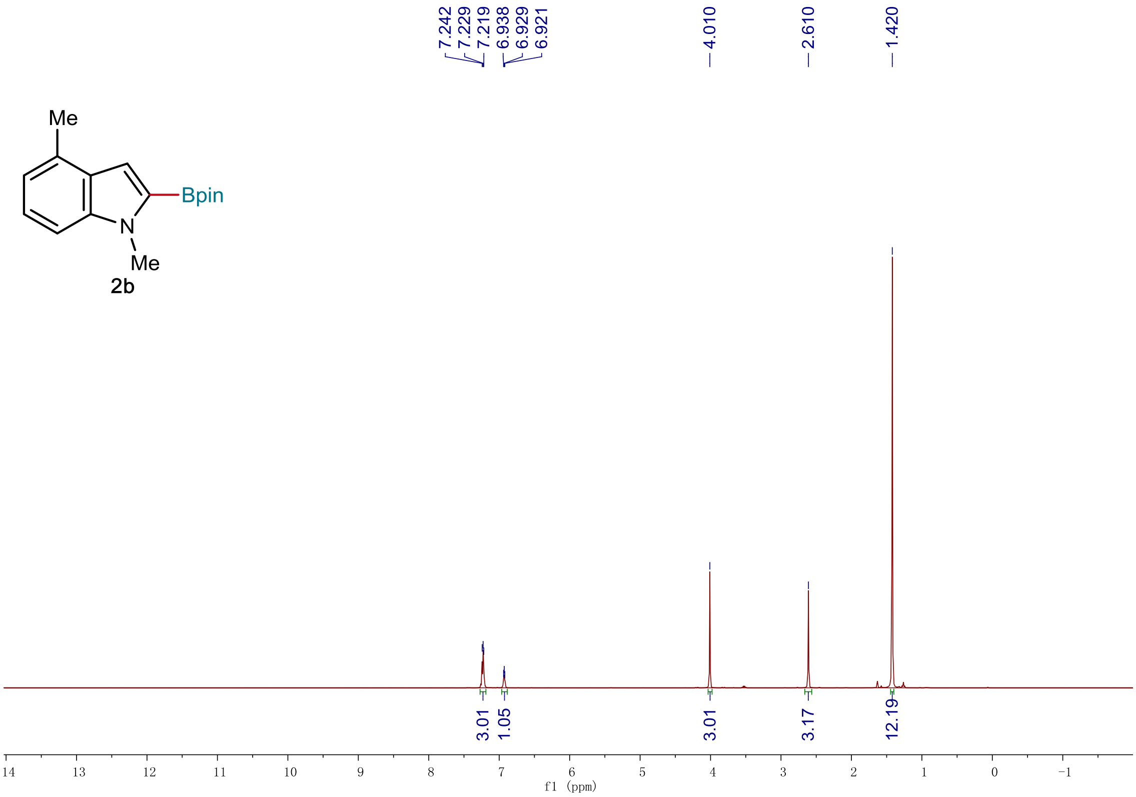

Figure S85. ^{13}C NMR spectrum of 2b in $CDCl_3$ (100 MHz)

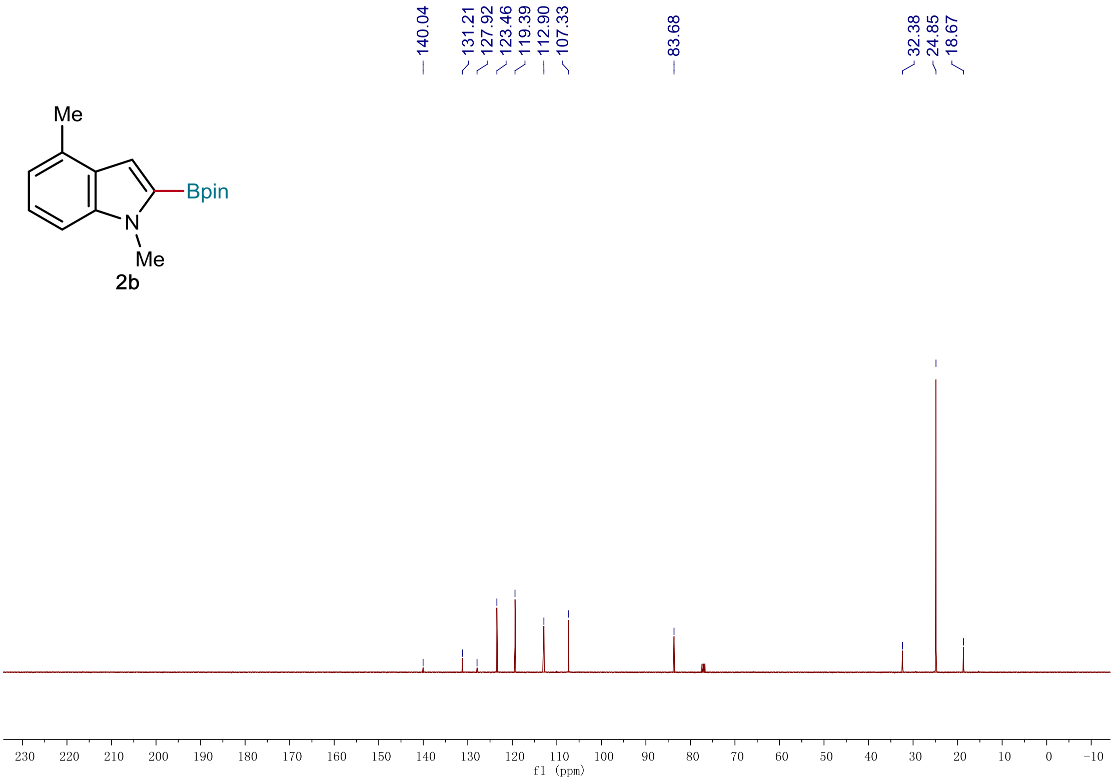

Figure S86. ^{1}H NMR spectrum of 2c in $CDCl_3$ (400 MHz)

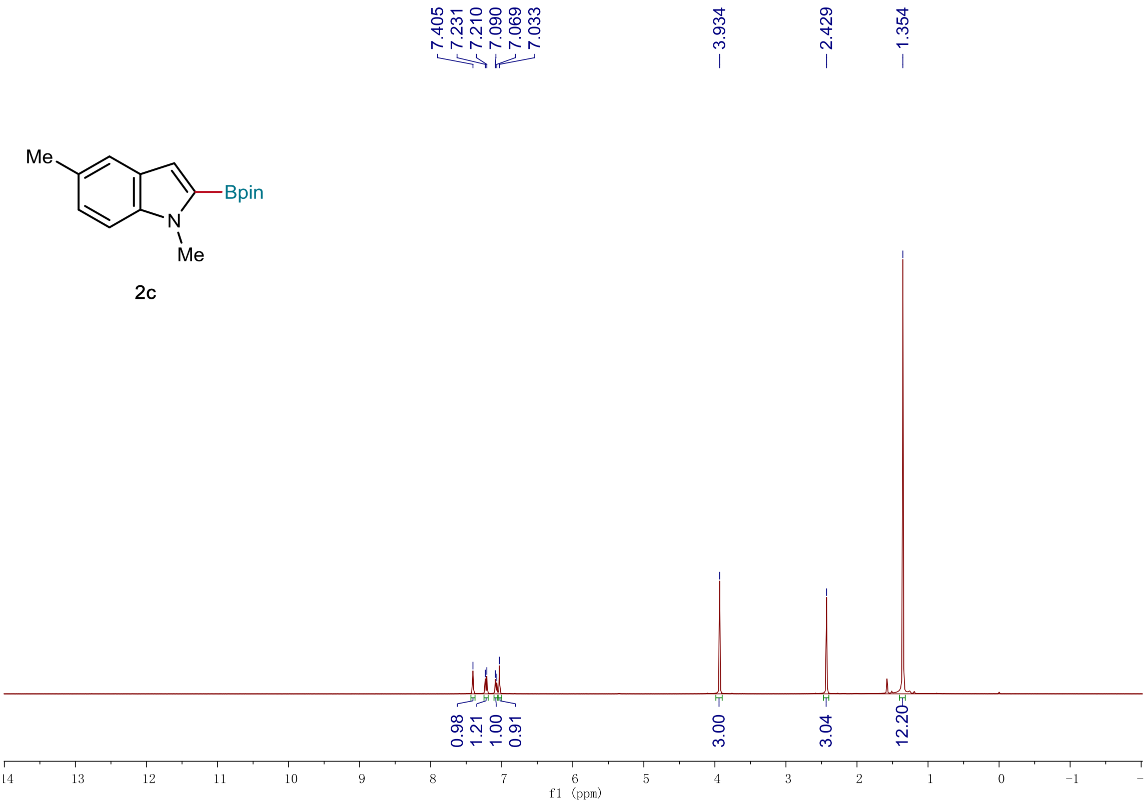

Figure S87. ^{13}C NMR spectrum of 2c in $CDCl_3$ (100 MHz)

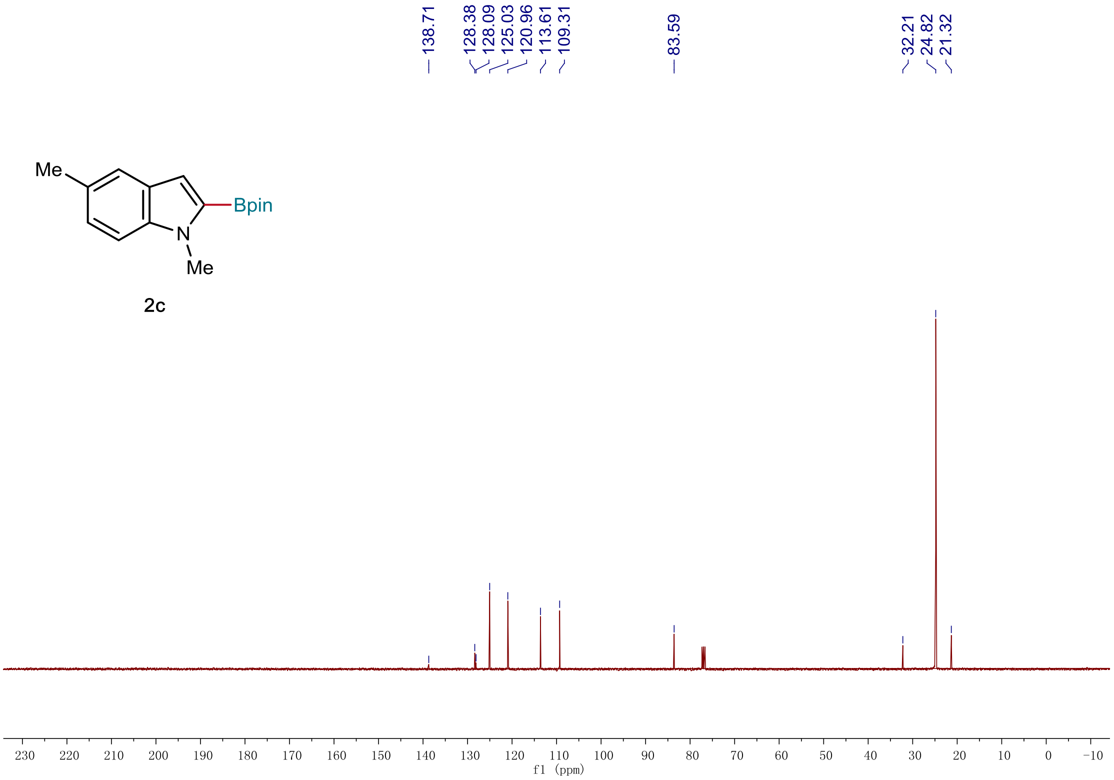

Figure S88. ^{1}H NMR spectrum of 2d in $CDCl_3$ (400 MHz)

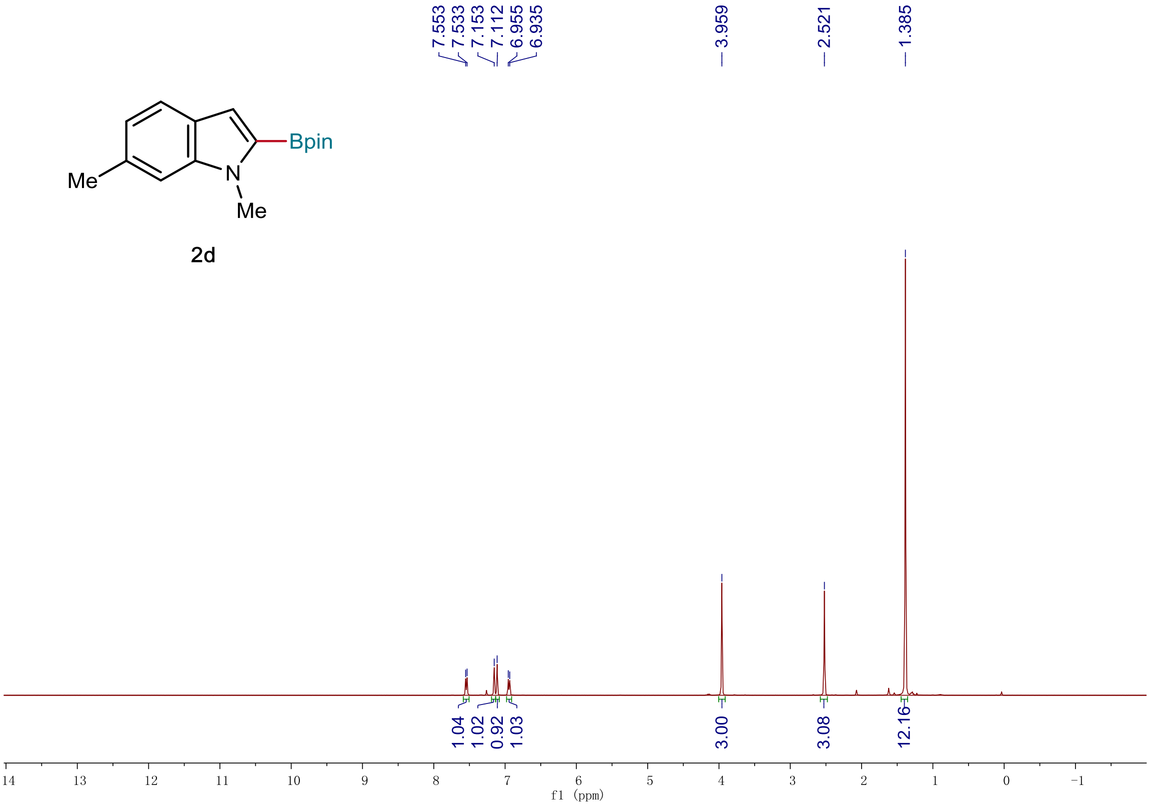

Figure S89. ^{13}C NMR spectrum of 2d in $CDCl_3$ (100 MHz)

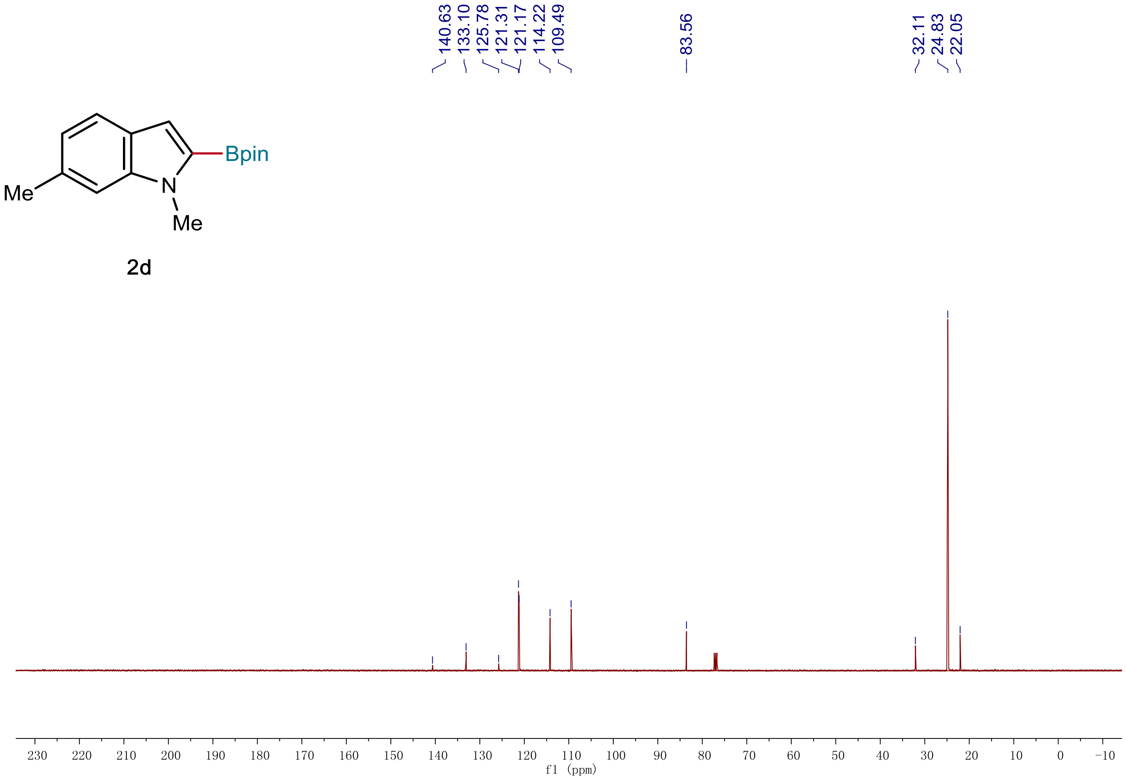

Figure S90. ^{1}H NMR spectrum of 2e in $CDCl_3$ (400 MHz)

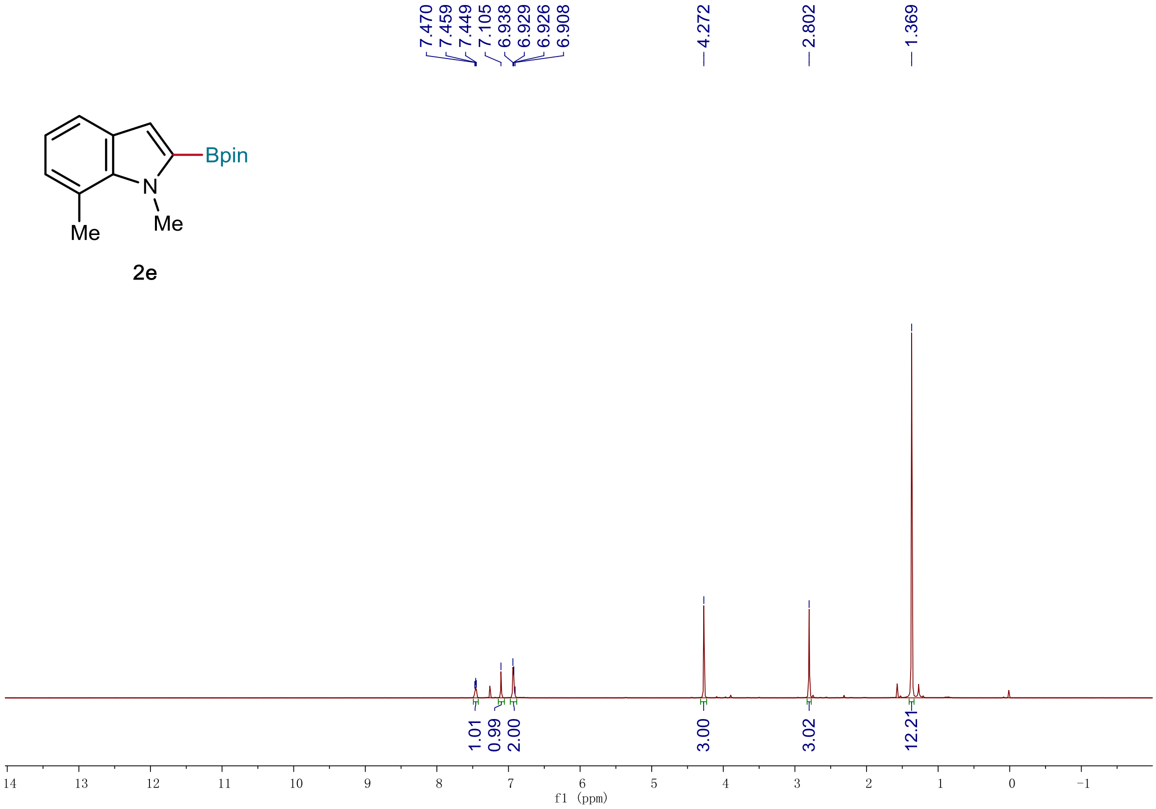

Figure S91. ^{13}C NMR spectrum of 2e in $CDCl_3$ (100 MHz)

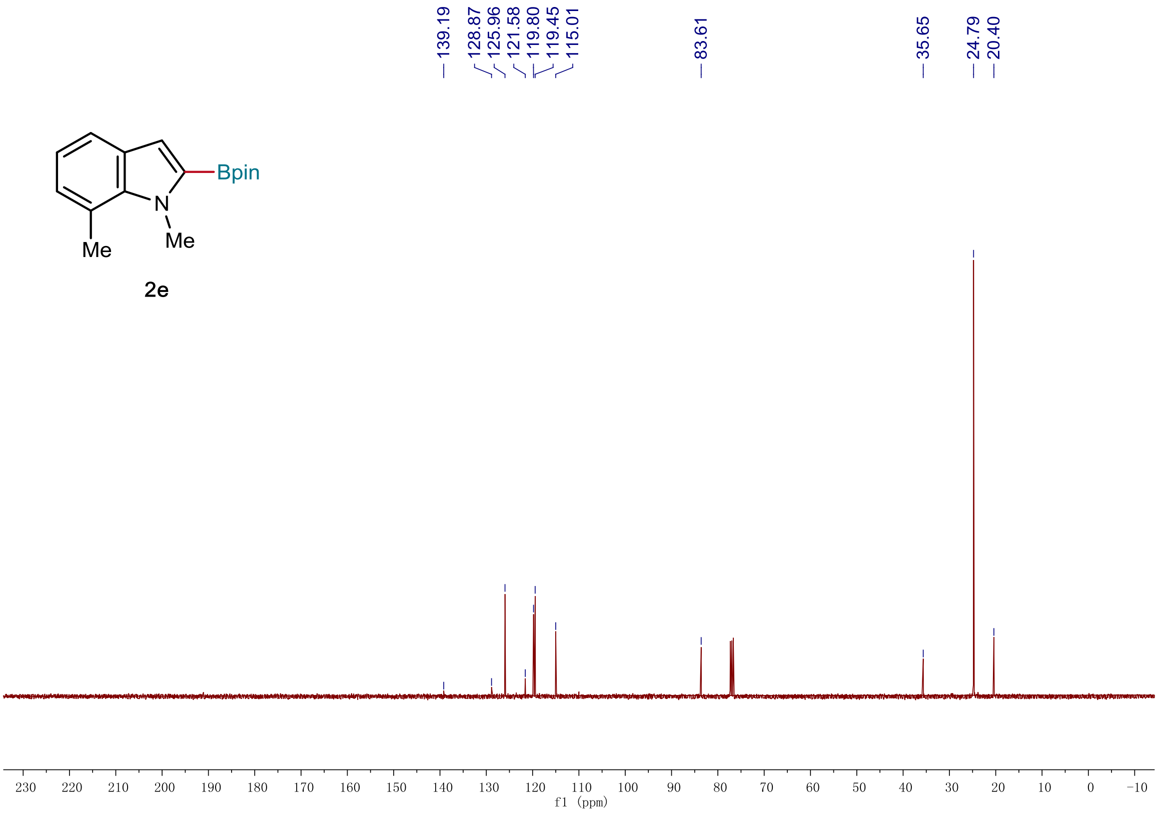

Figure S92. ^{1}H NMR spectrum of 2f in CDCl$_3$ (400 MHz)

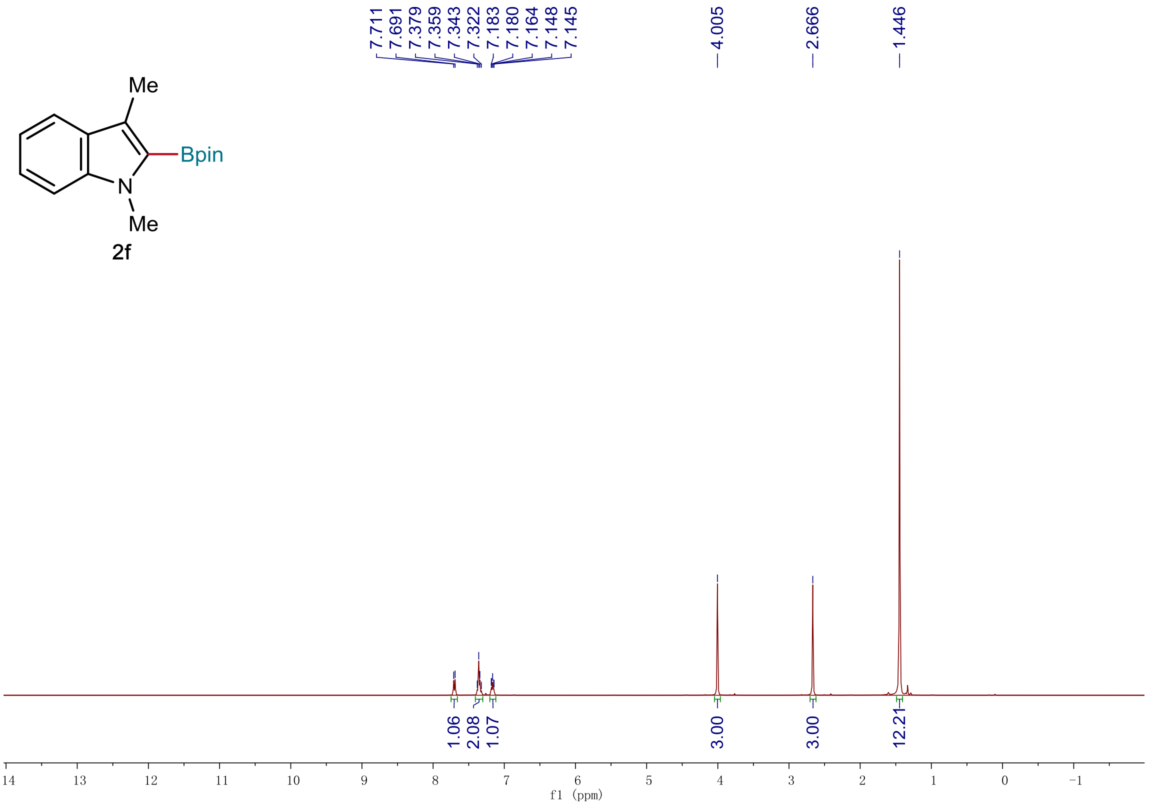

Figure S93. ^{13}C NMR spectrum of 2f in CDCl$_3$ (100 MHz)

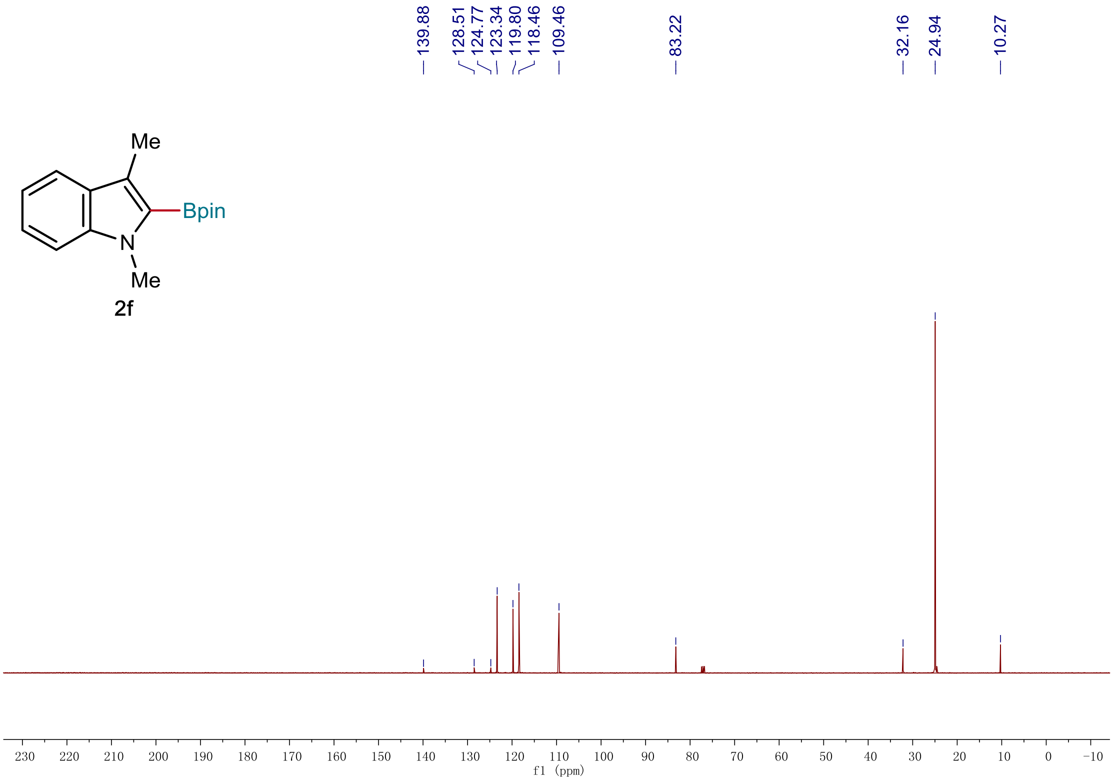

Figure S94. ^{1}H NMR spectrum of 2g in $CDCl_3$ (400 MHz)

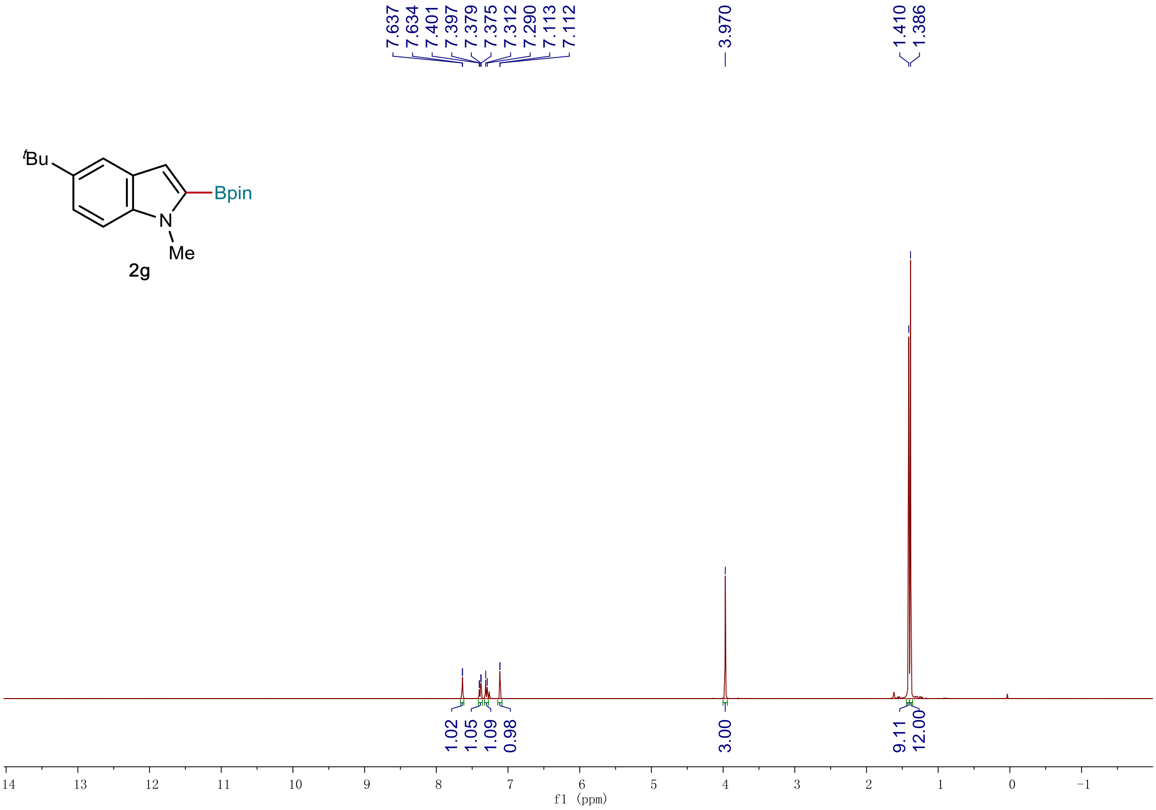

Figure S95. ^{13}C NMR spectrum of 2g in $CDCl_3$ (100 MHz)

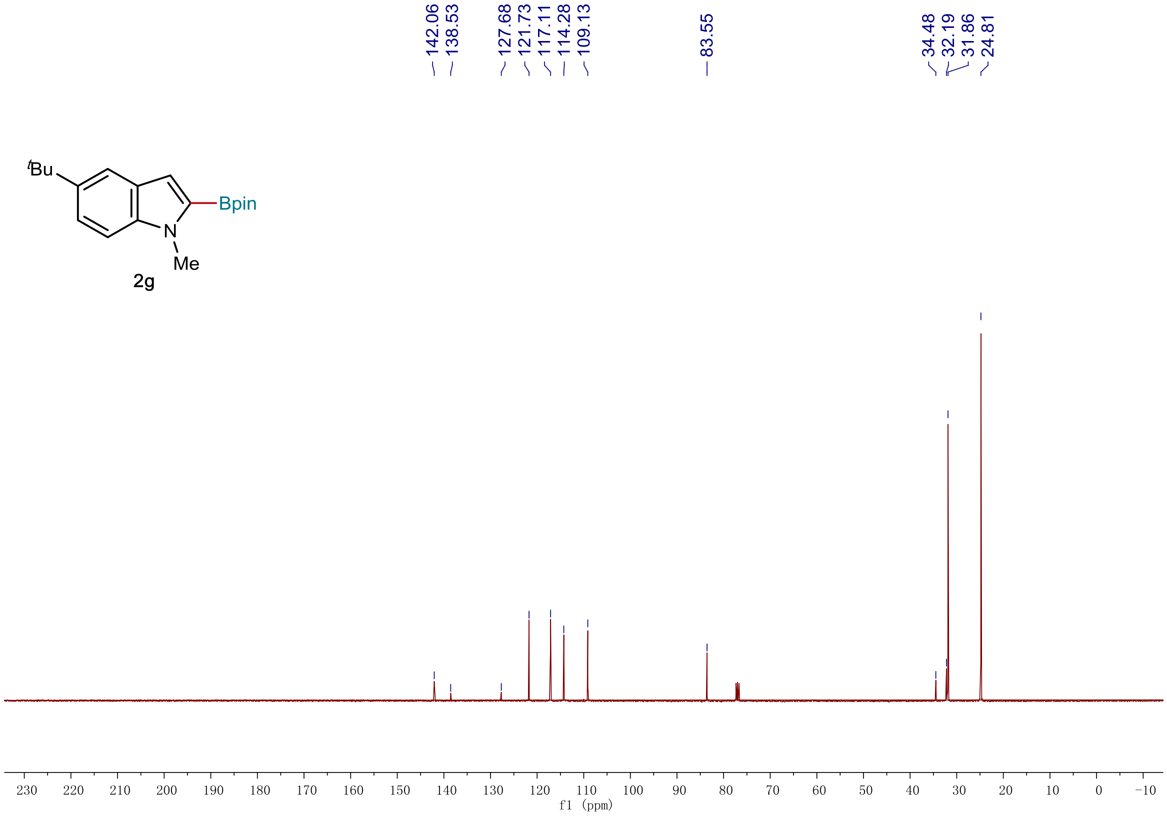

Figure S96. ^{1}H NMR spectrum of 2h in CDCl$_3$ (400 MHz)

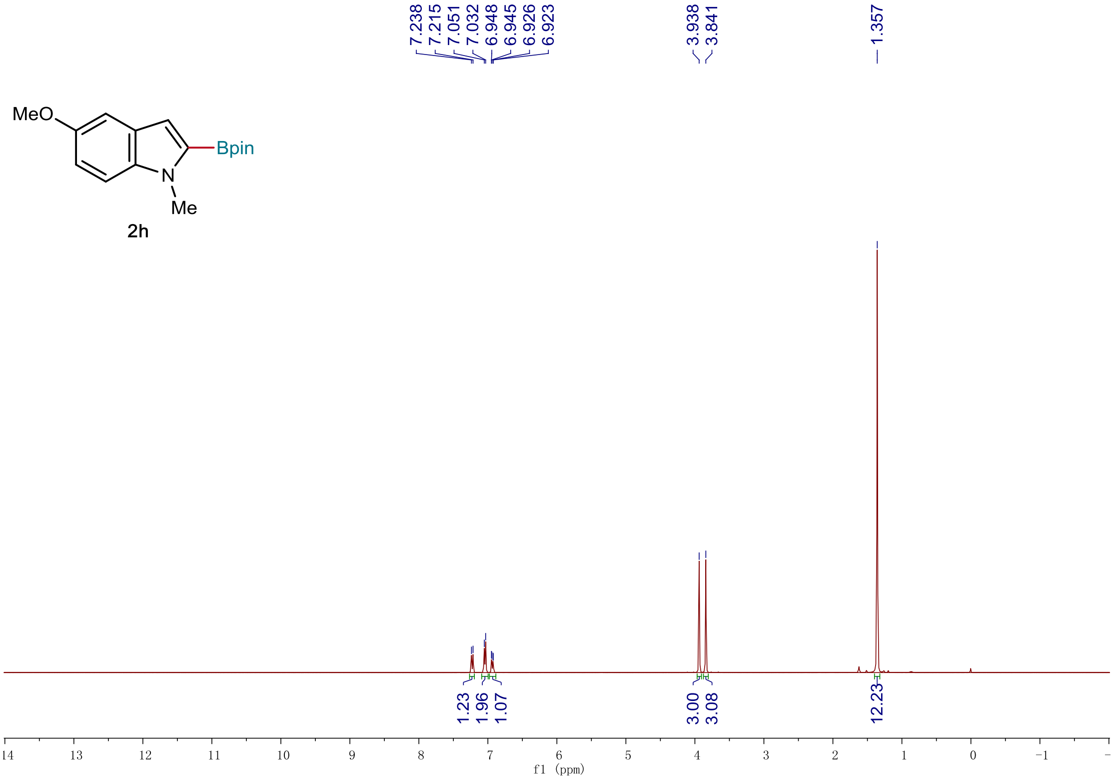

Figure S97. ^{13}C NMR spectrum of 2h in CDCl$_3$ (100 MHz)

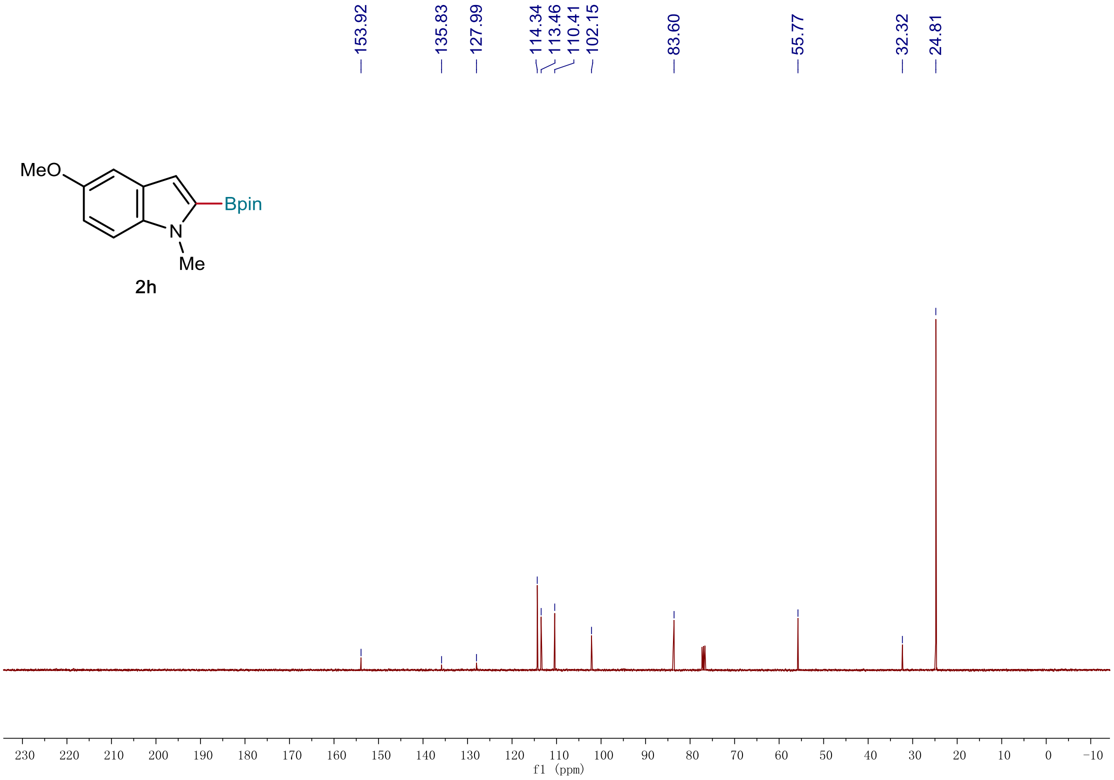

Figure S98. ^{1}H NMR spectrum of 2i in $CDCl_3$ (400 MHz)

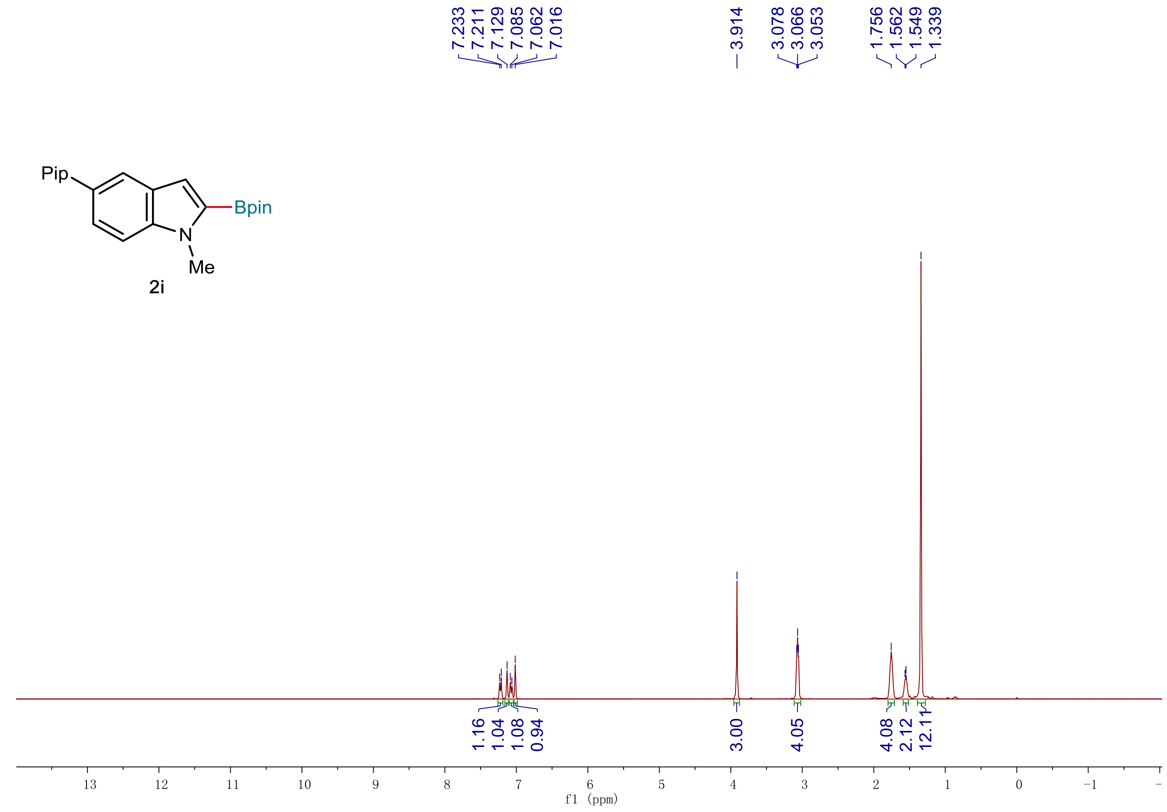

Figure S99. ^{13}C NMR spectrum of 2i in $CDCl_3$ (100 MHz)

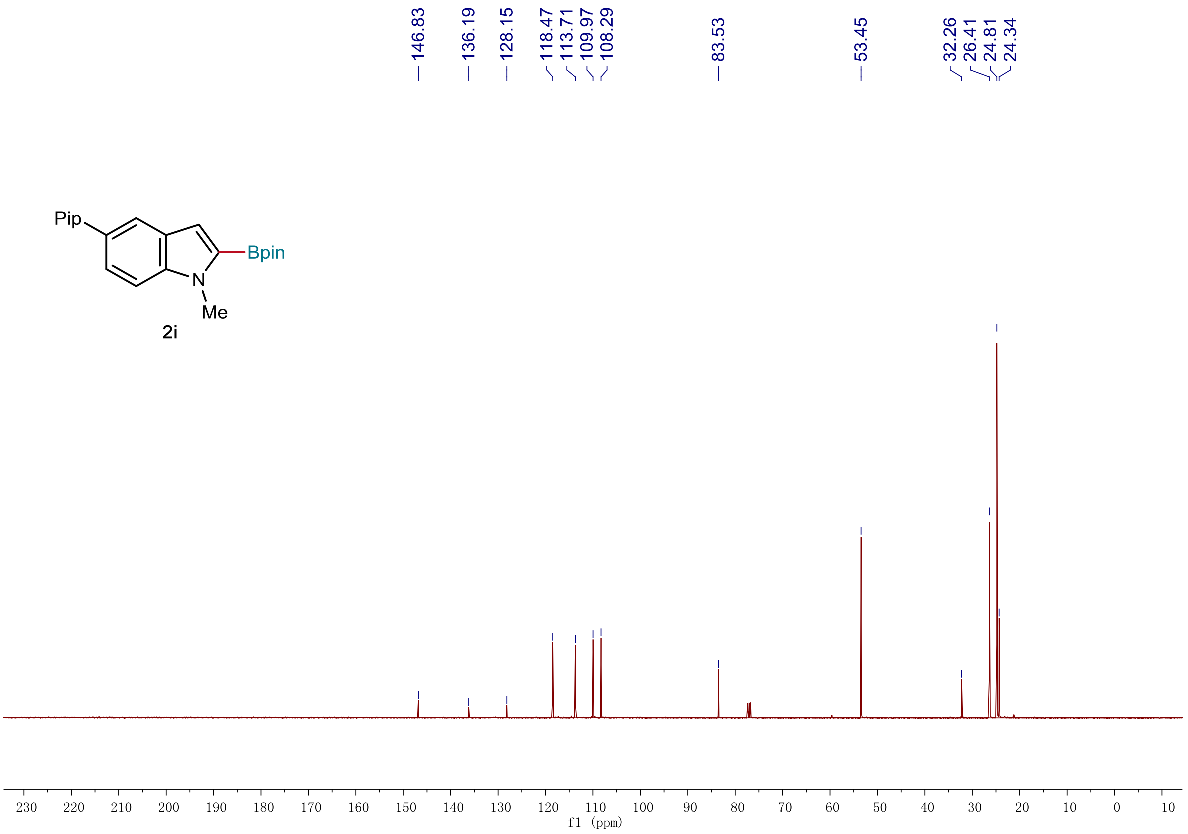

Figure S100. ^{1}H NMR spectrum of 2j in $CDCl_3$ (400 MHz)

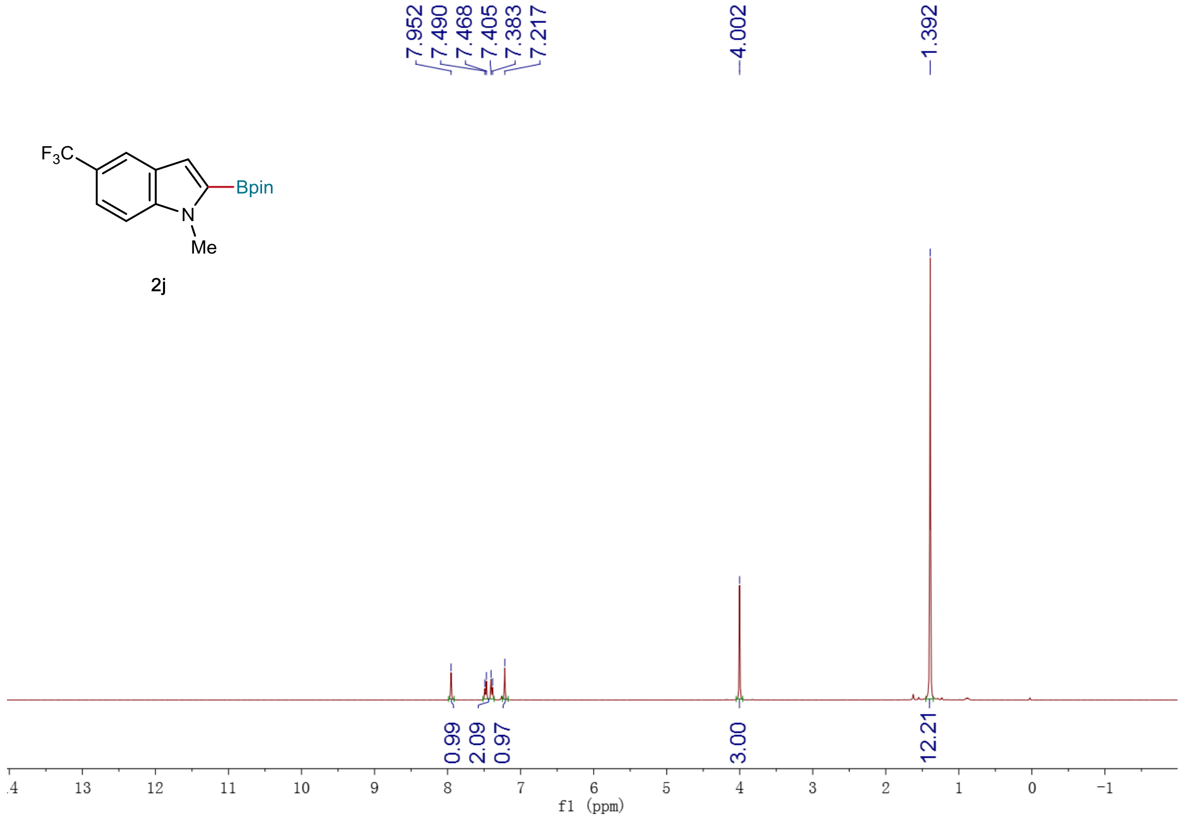

Figure S101. ^{13}C NMR spectrum of 2j in $CDCl_3$ (100 MHz)

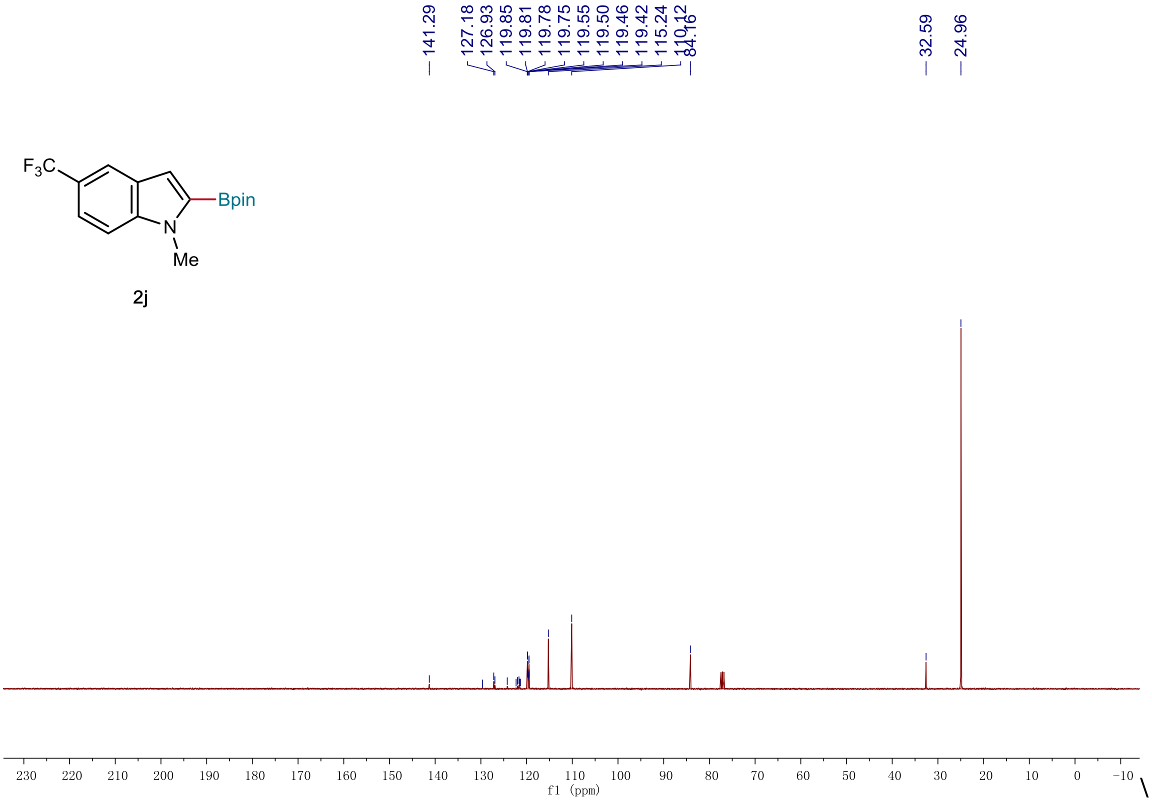

Figure S102. ^{1}H NMR spectrum of 2k in CDCl$_3$ (400 MHz)

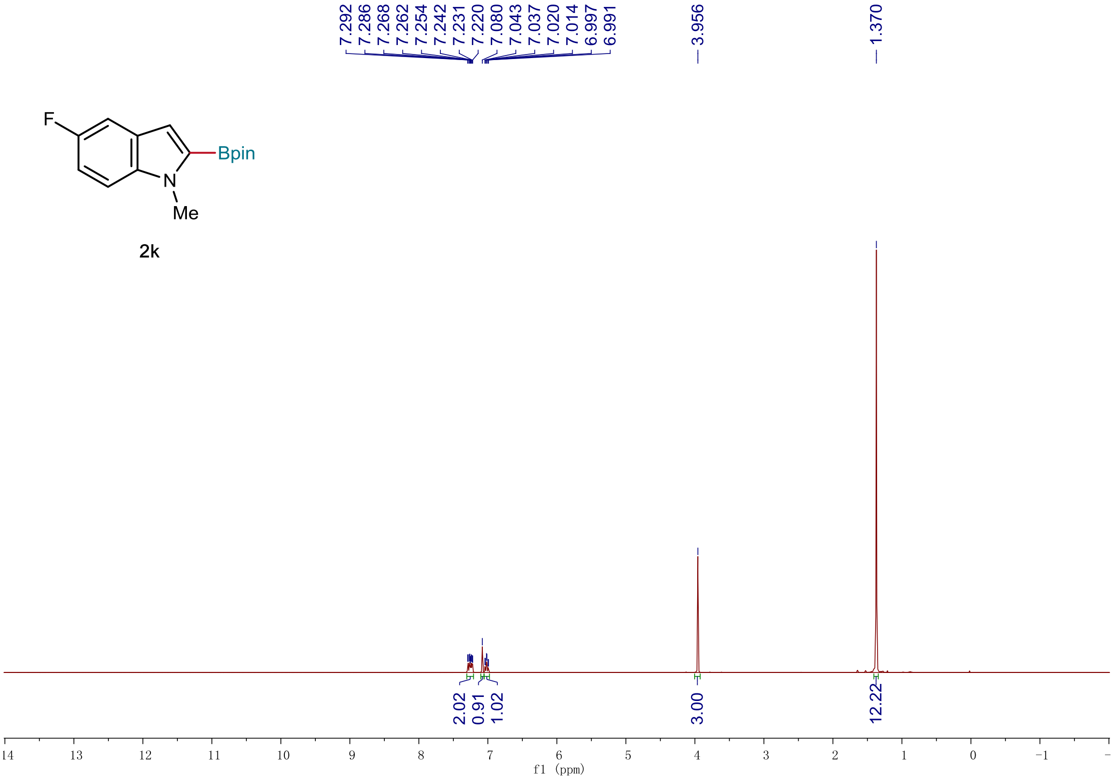

Figure S103. ^{13}C NMR spectrum of 2k in CDCl$_3$ (100 MHz)

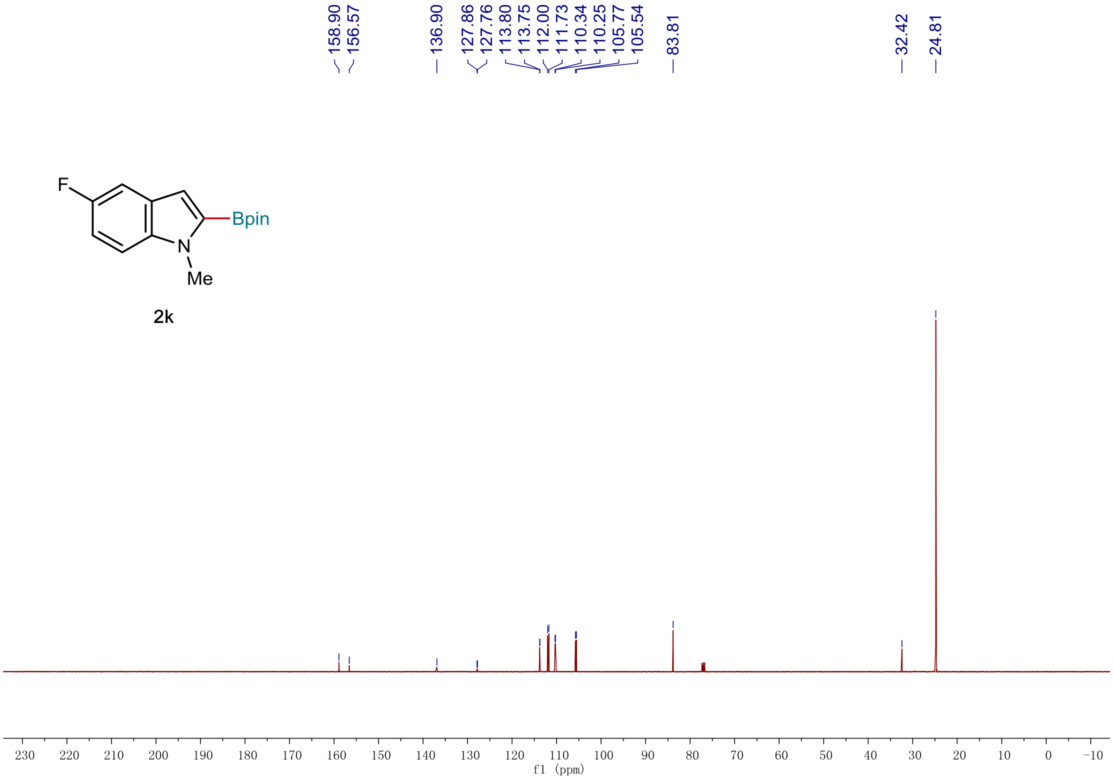

Figure S104. ^{1}H NMR spectrum of 2l in CDCl$_3$ (400 MHz)

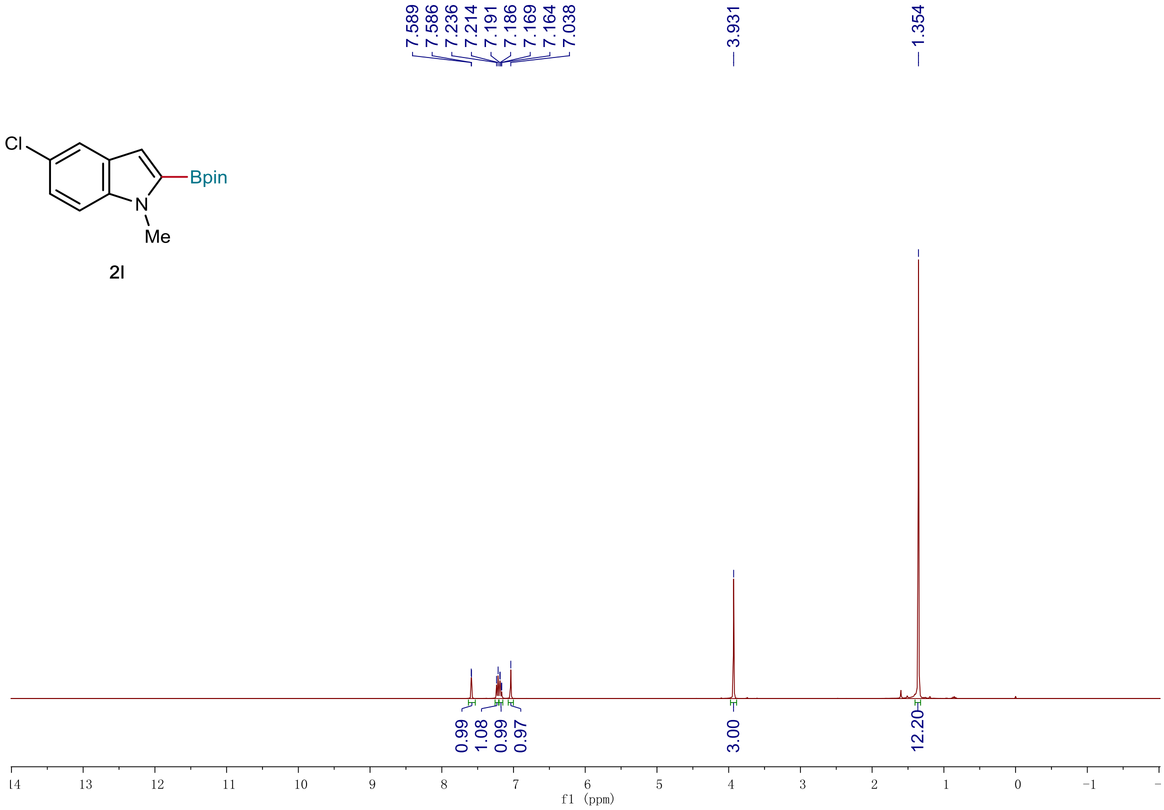

Figure S105. ^{13}C NMR spectrum of 2l in CDCl$_3$ (100 MHz)

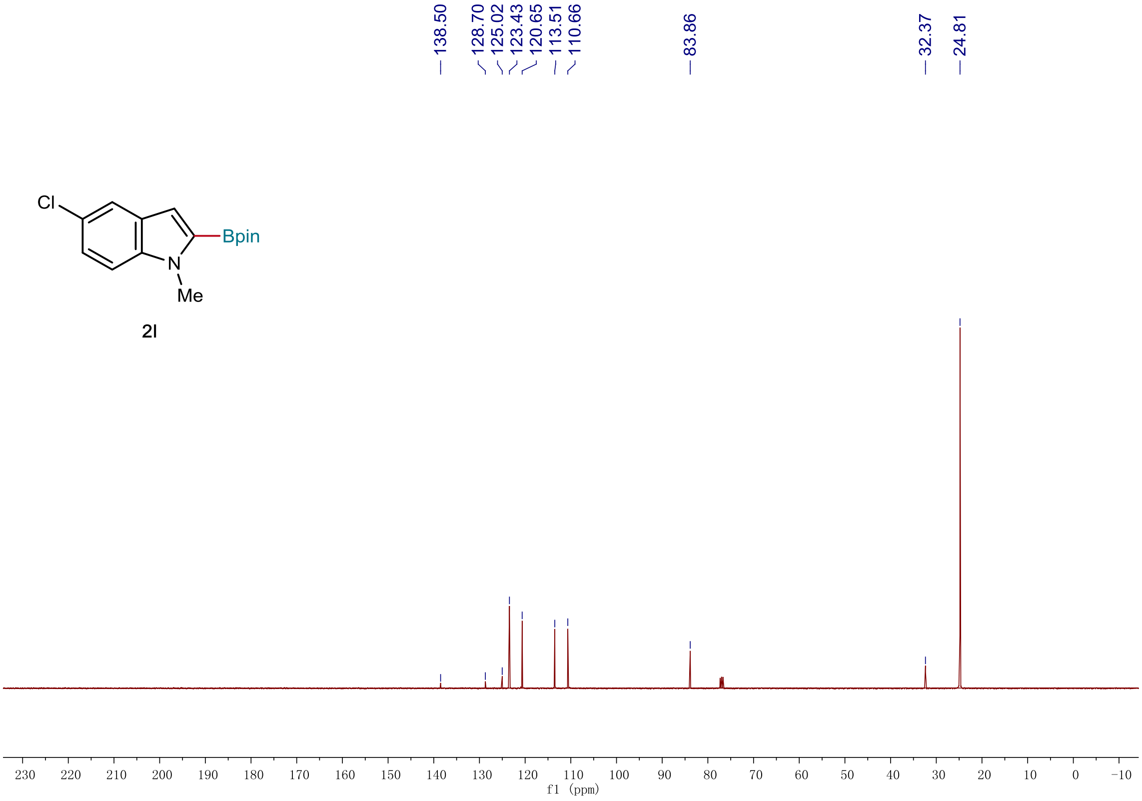

Figure S106. ^{1}H NMR spectrum of 2m in CDCl$_3$ (400 MHz)

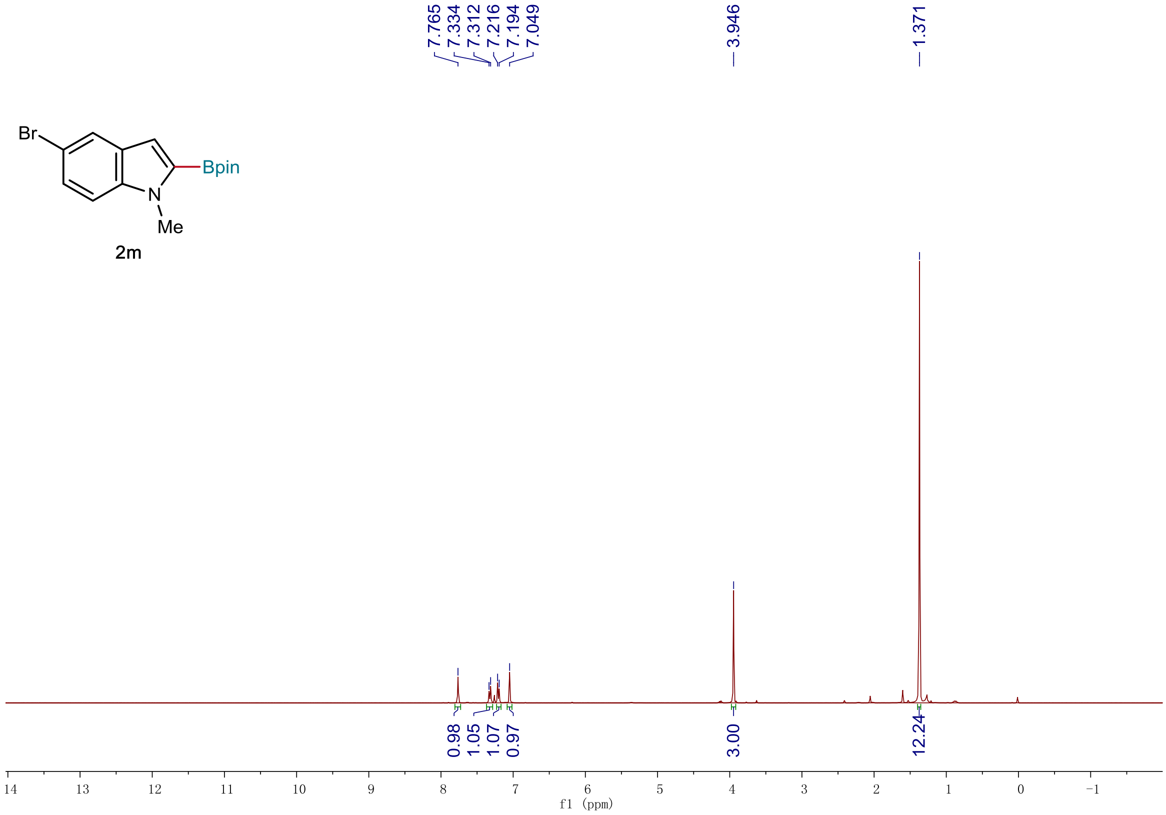

Figure S107. ^{13}C NMR spectrum of 2m in CDCl$_3$ (100 MHz)

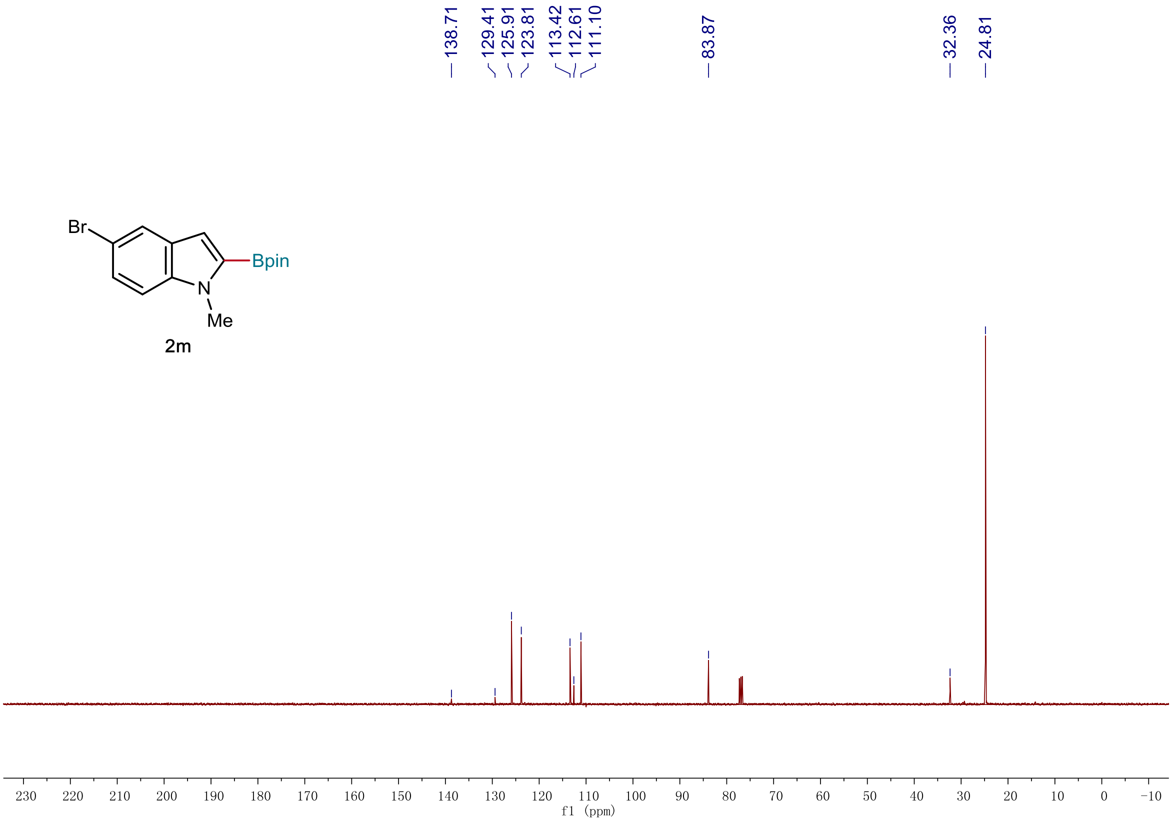

Figure S108. ^{1}H NMR spectrum of 2n in CDCl$_3$ (400 MHz)

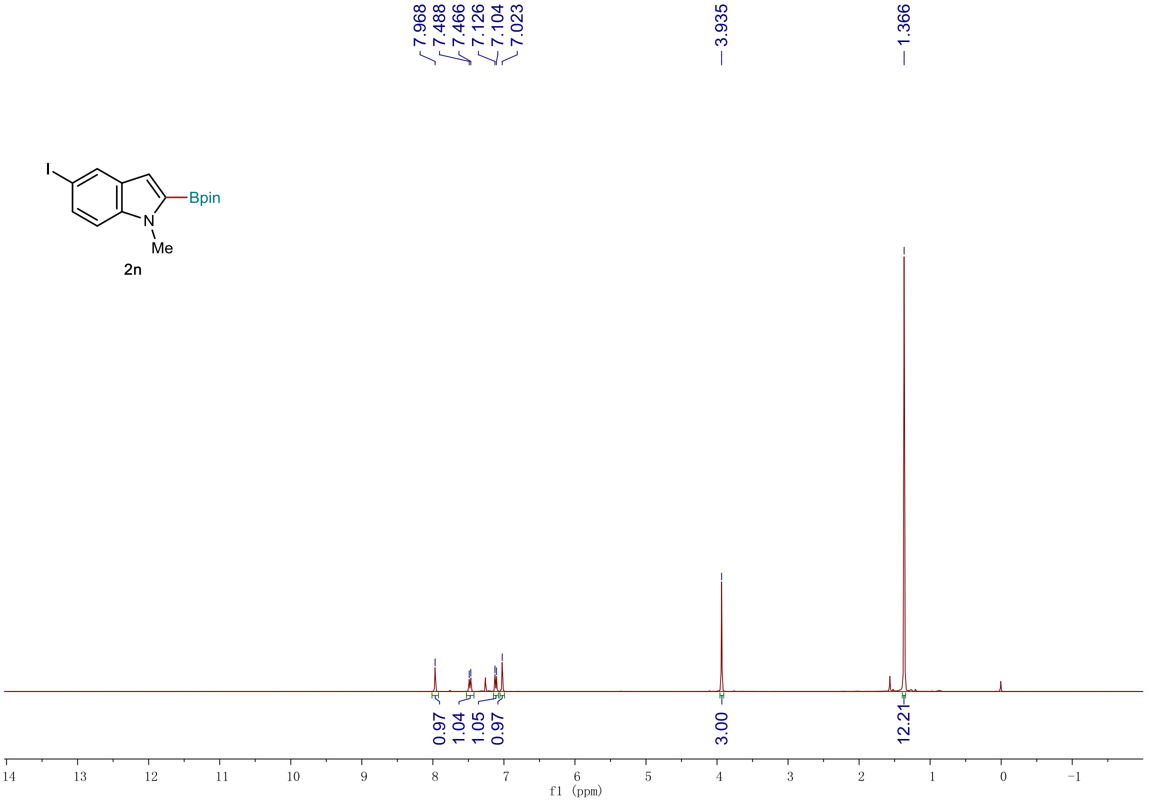

Figure S109. ^{13}C NMR spectrum of 2n in CDCl$_3$ (100 MHz)

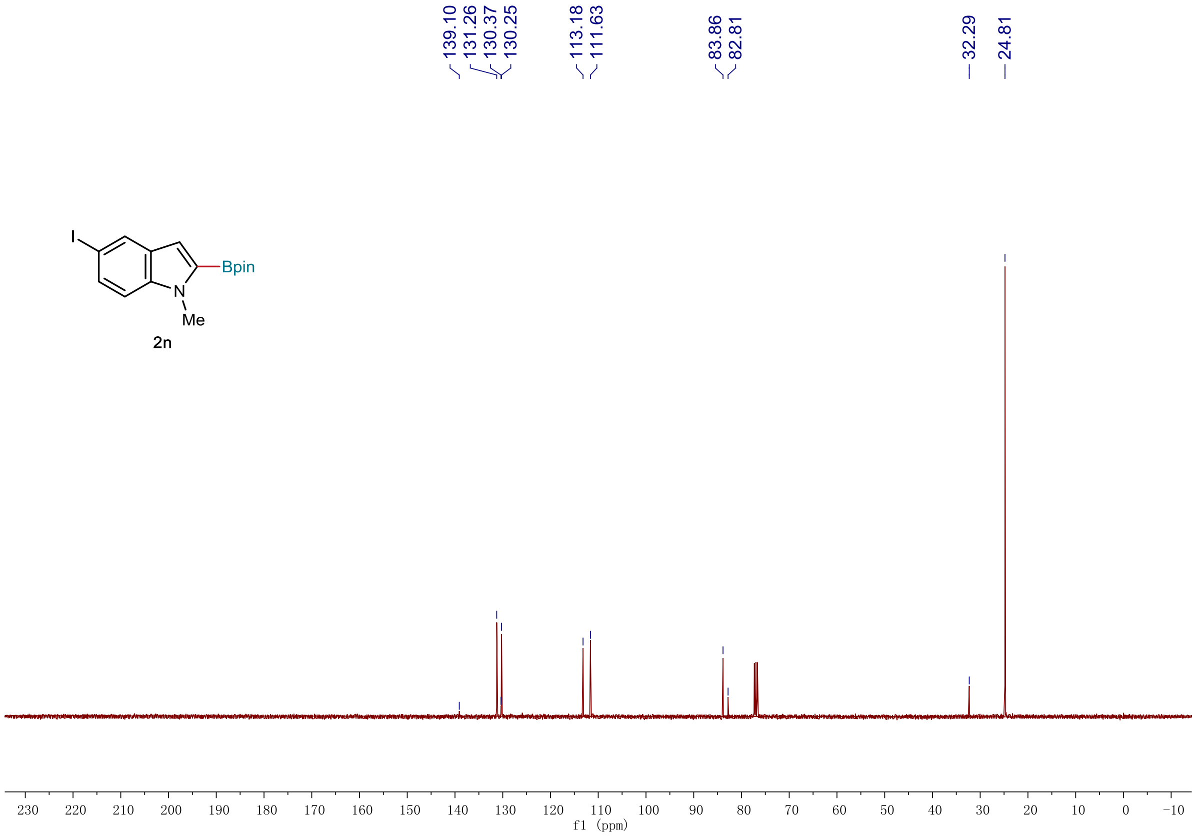

Figure S110. ^{1}H NMR spectrum of 2o in $CDCl_3$ (400 MHz)

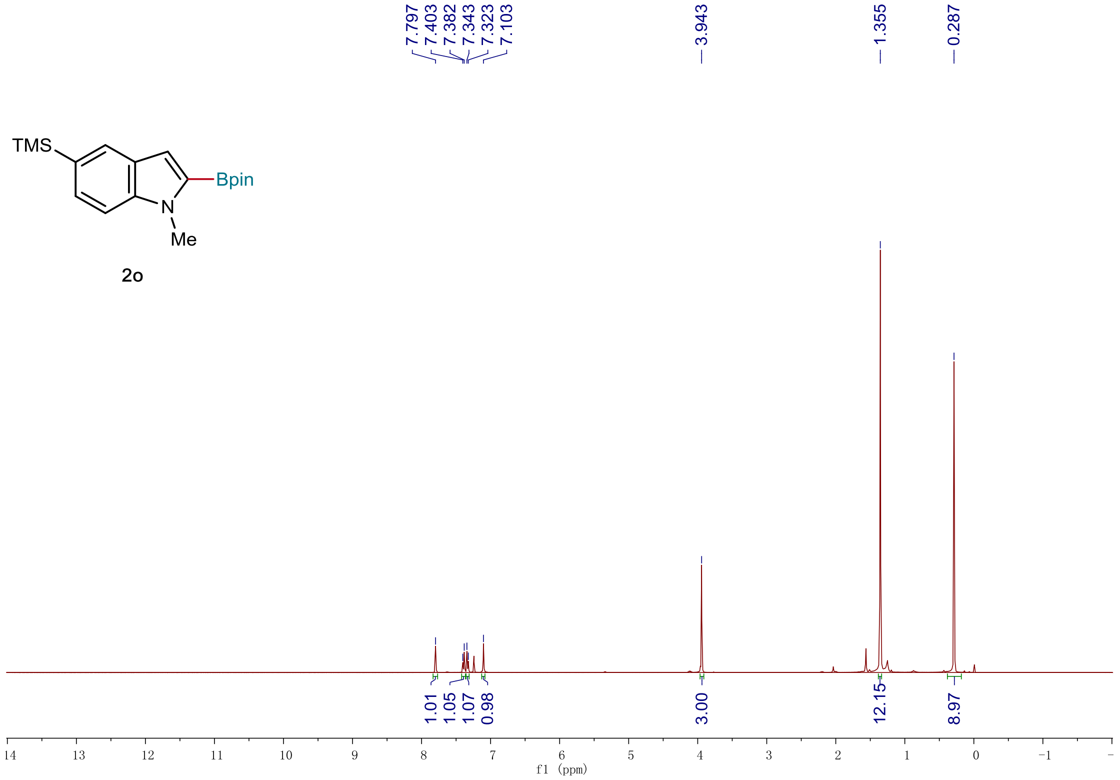

Figure S111. ^{13}C NMR spectrum of 2o in $CDCl_3$ (100 MHz)

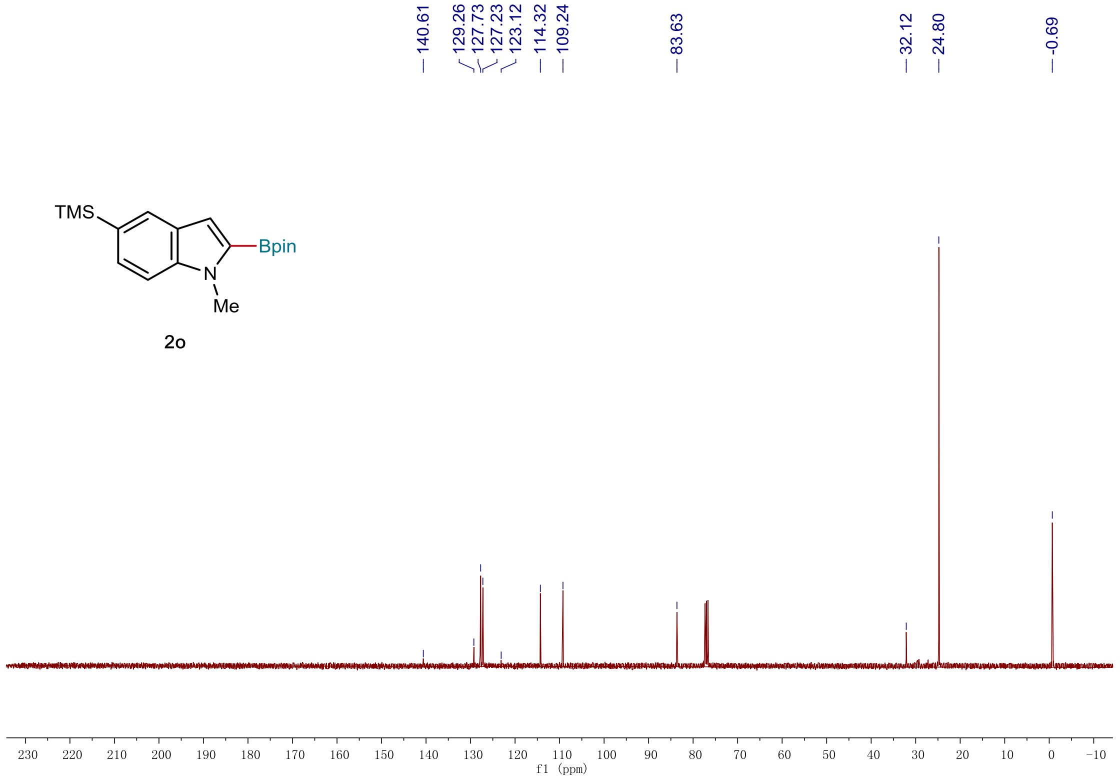

Figure S112. ^{1}H NMR spectrum of 2p in $CDCl_3$ (400 MHz)

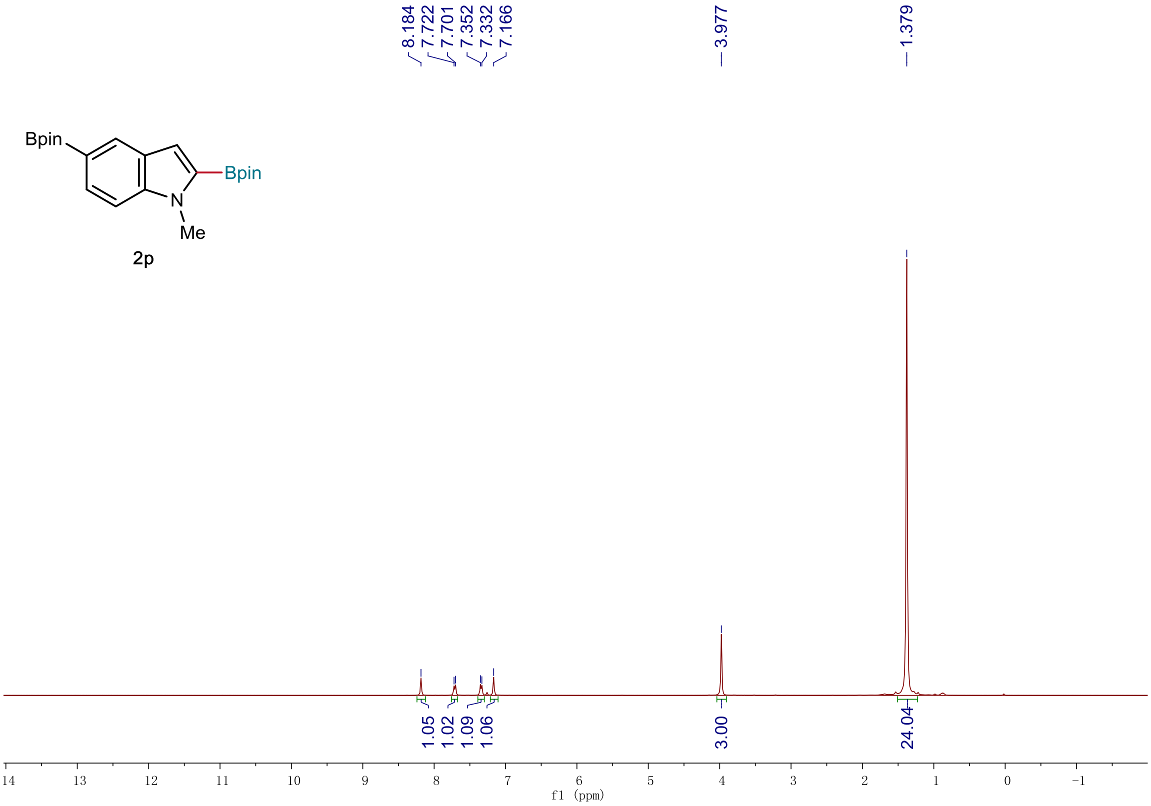

Figure S113. ^{13}C NMR spectrum of 2p in $CDCl_3$ (100 MHz)

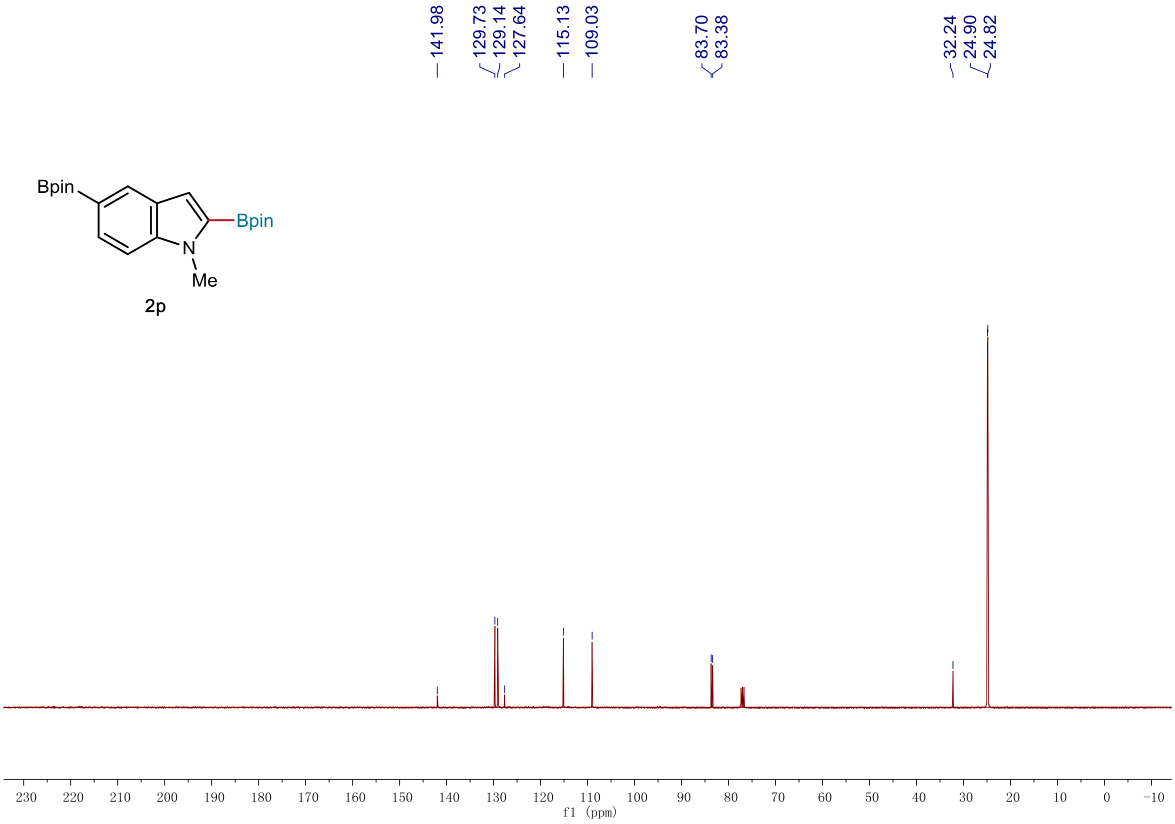

Figure S114. ^{1}H NMR spectrum of 2q in $CDCl_3$ (400 MHz)

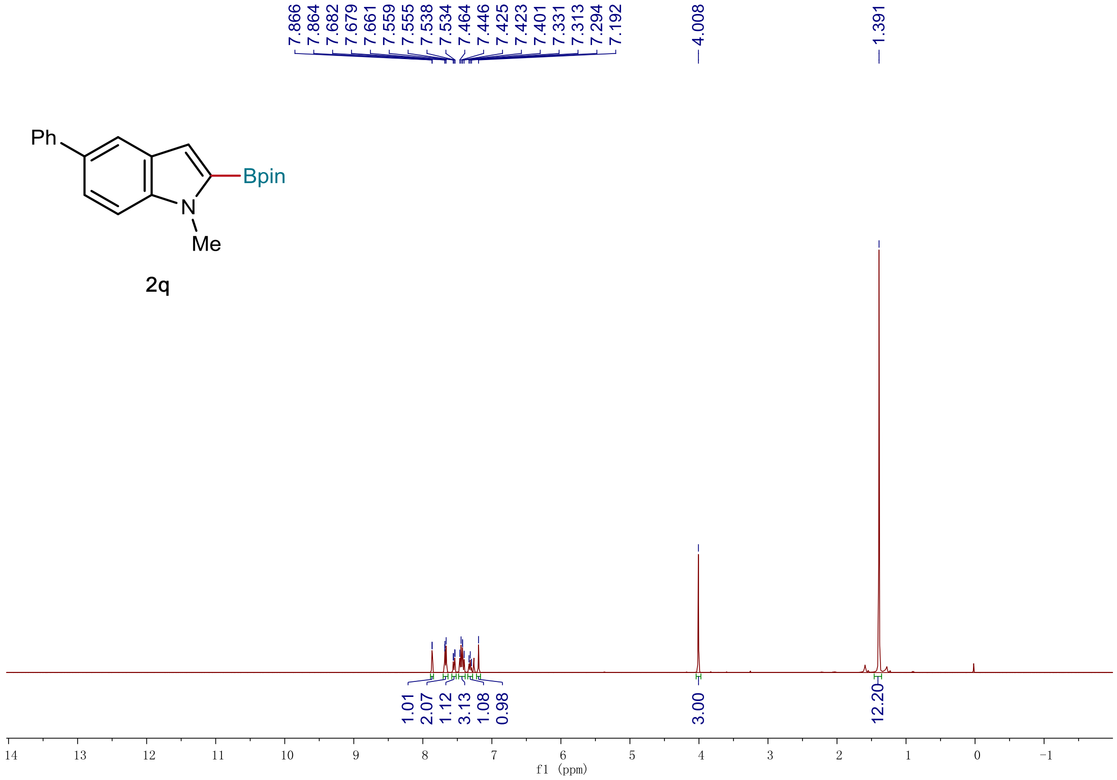

Figure S115. ^{13}C NMR spectrum of 2q in $CDCl_3$ (100 MHz)

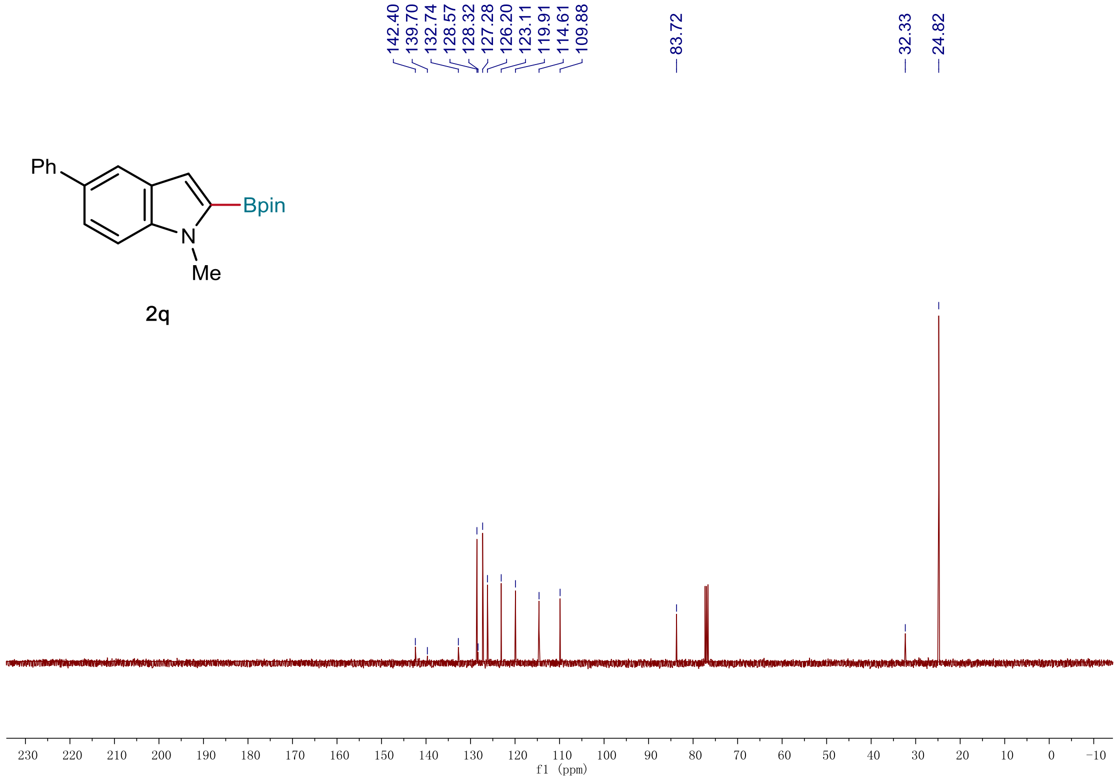

Figure S116. ^{1}H NMR spectrum of 2r in CDCl$_3$ (400 MHz)

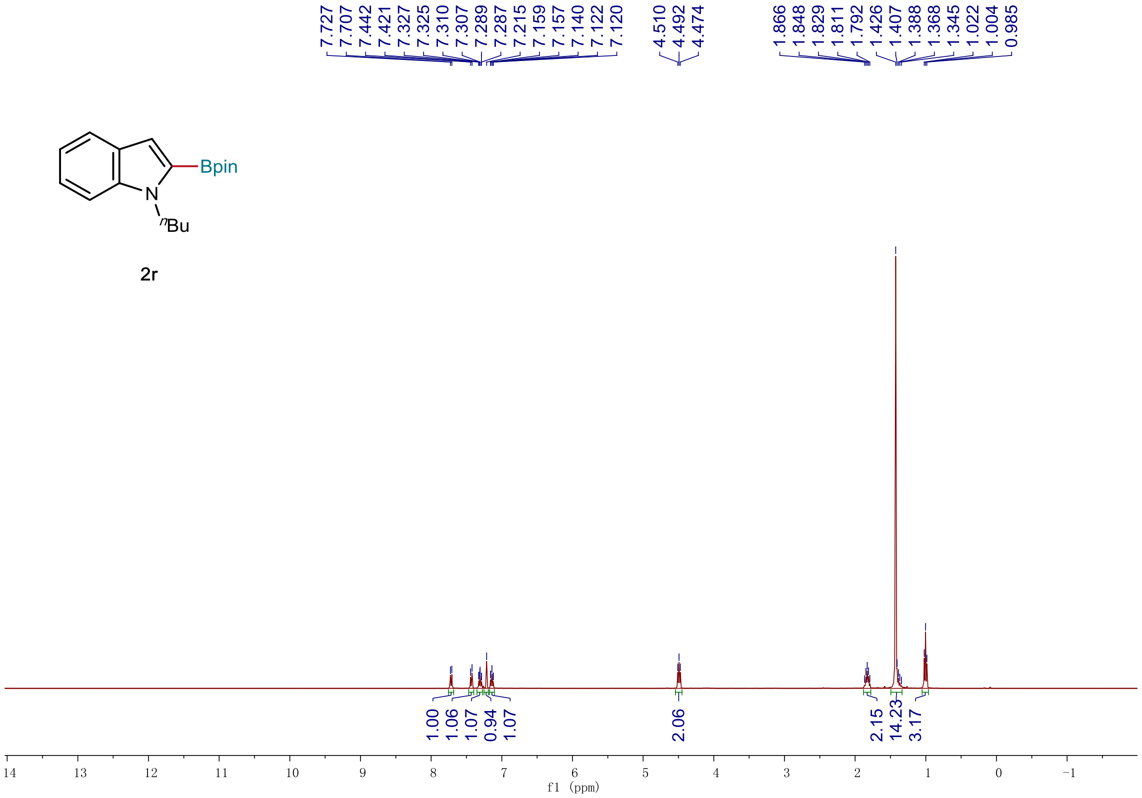

Figure S117. ^{13}C NMR spectrum of 2r in CDCl$_3$ (100 MHz)

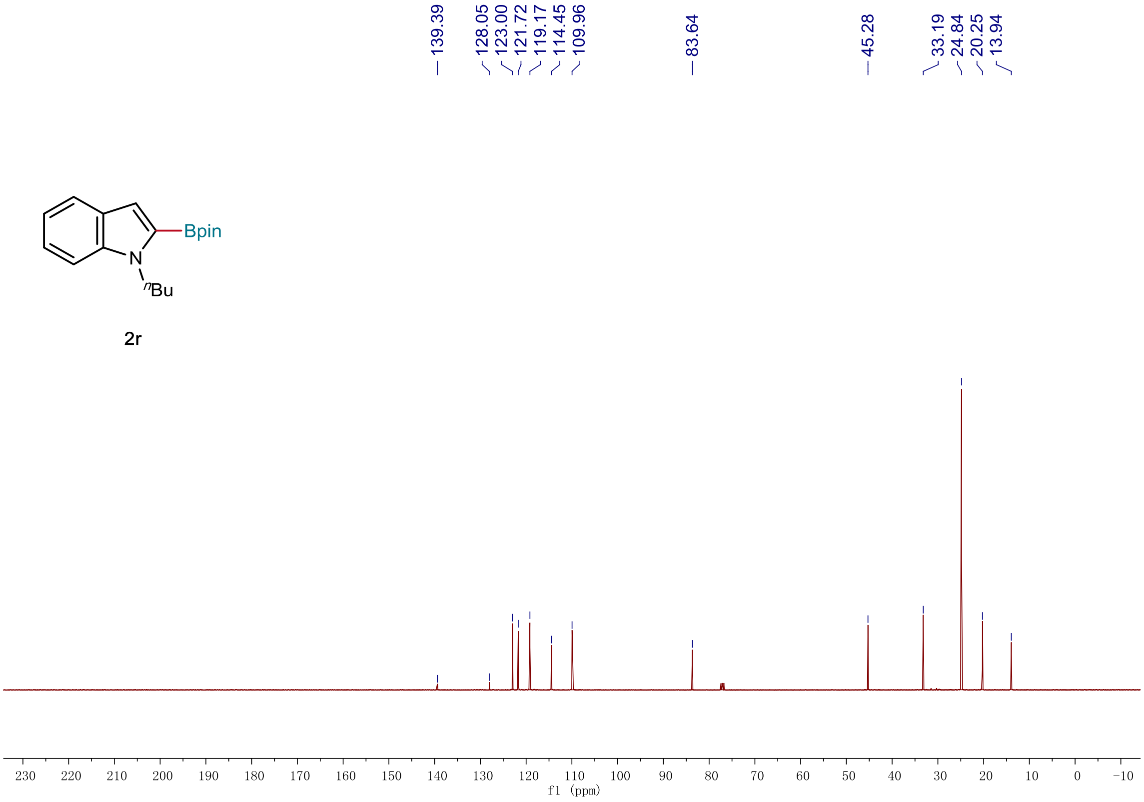

Figure S118. ^{1}H NMR spectrum of 2s in CDCl$_3$ (400 MHz)

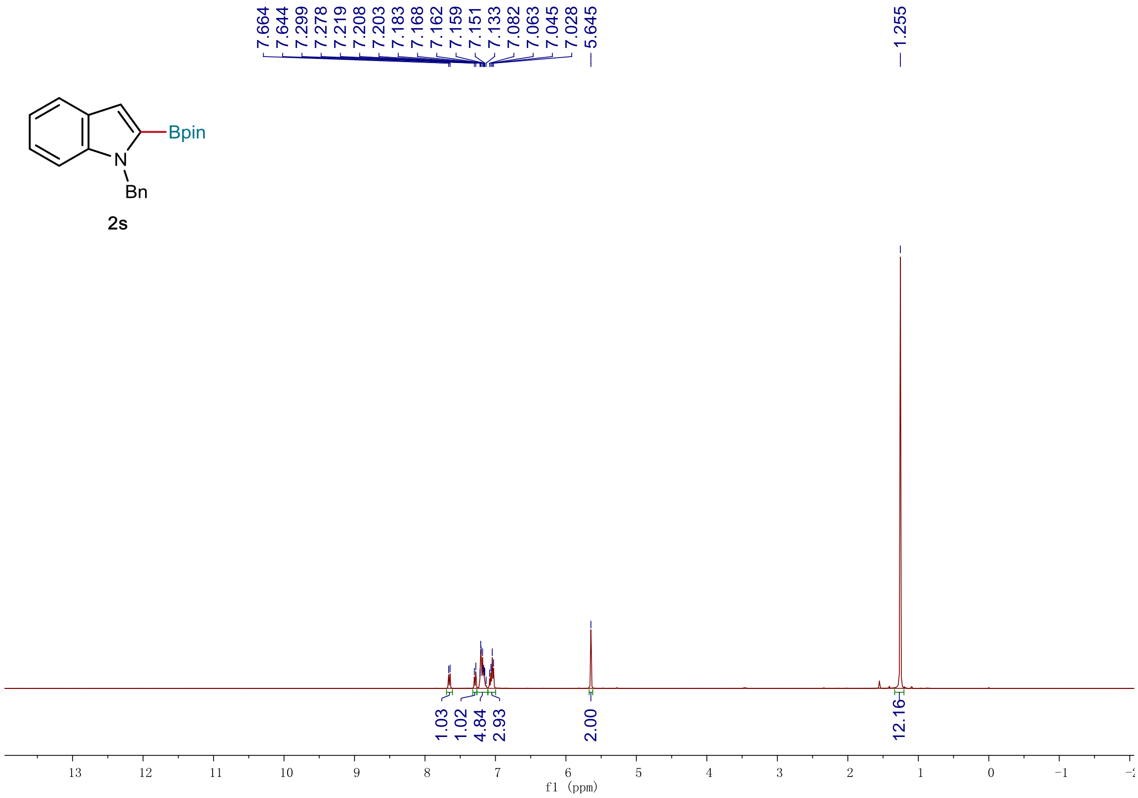

Figure S119. ^{13}C NMR spectrum of 2s in CDCl$_3$ (100 MHz)

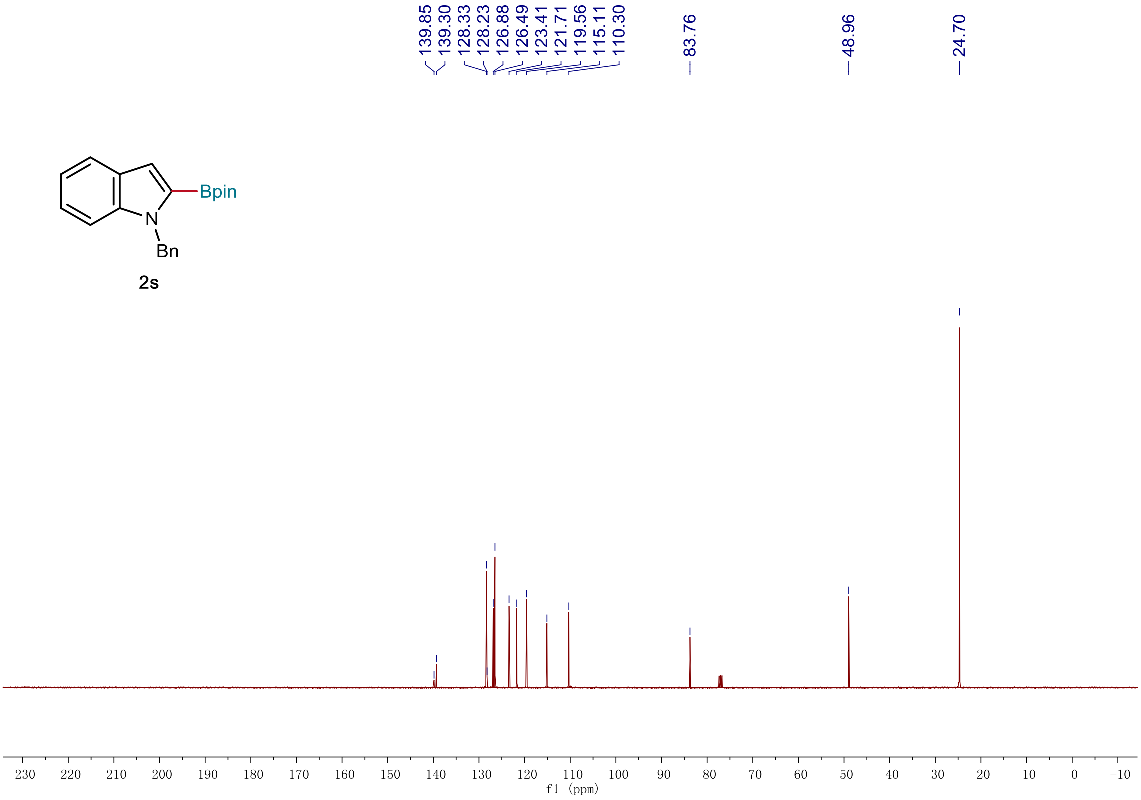

Figure S120. ^{1}H NMR spectrum of 3b in $CDCl_3$ (400 MHz)

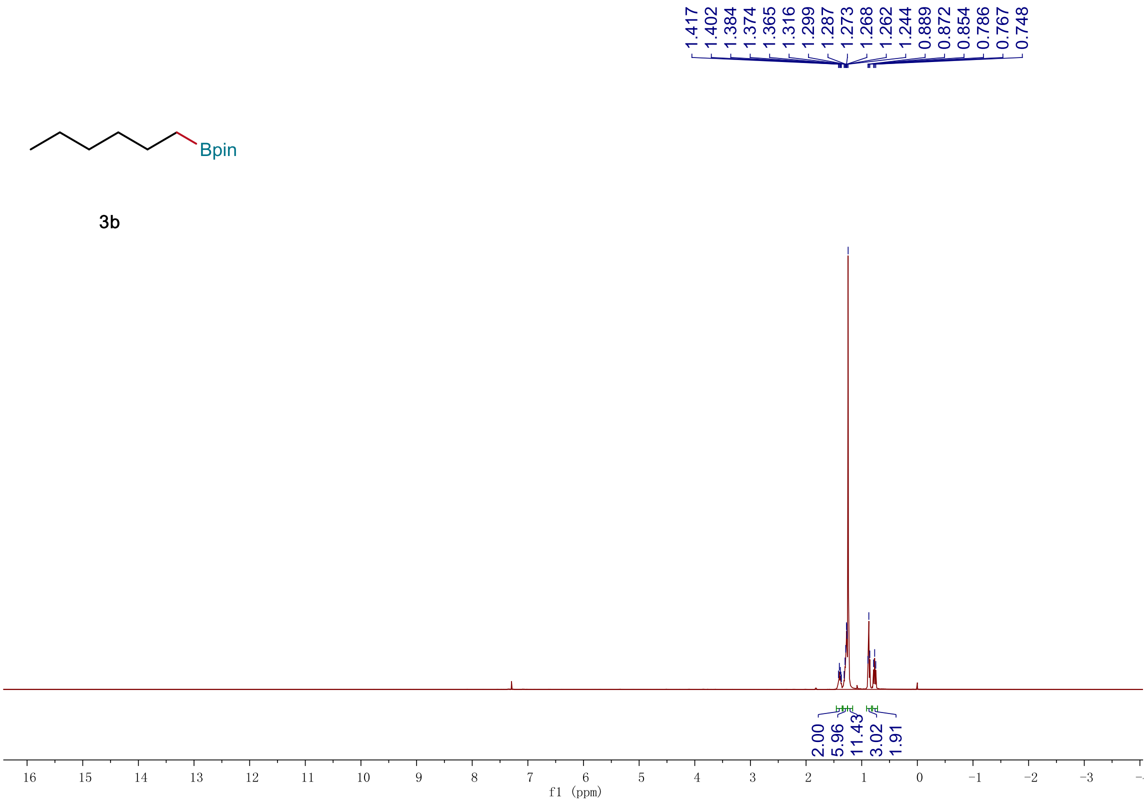

Figure S121. ^{13}C NMR spectrum of 3b in $CDCl_3$ (100 MHz)

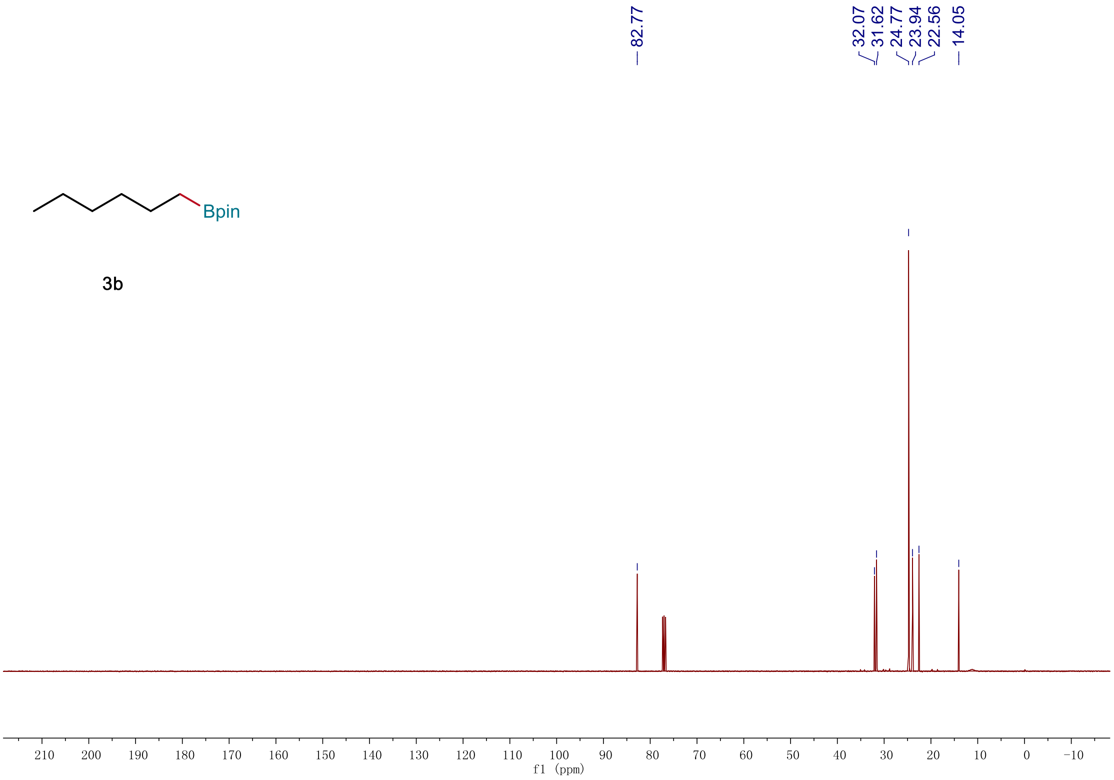

Figure S122. ^{1}H NMR spectrum of 3c in CDCl$_3$ (400 MHz)

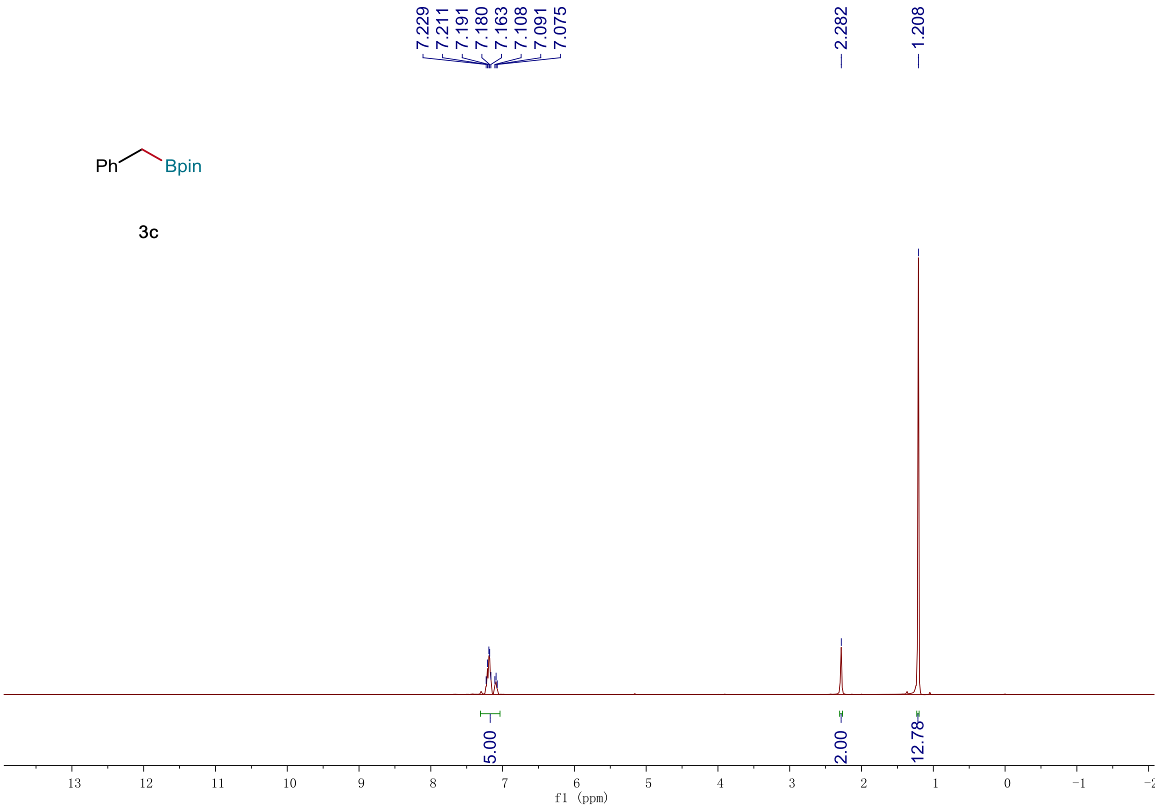

Figure S123. ^{13}C NMR spectrum of 3c in CDCl$_3$ (100 MHz)

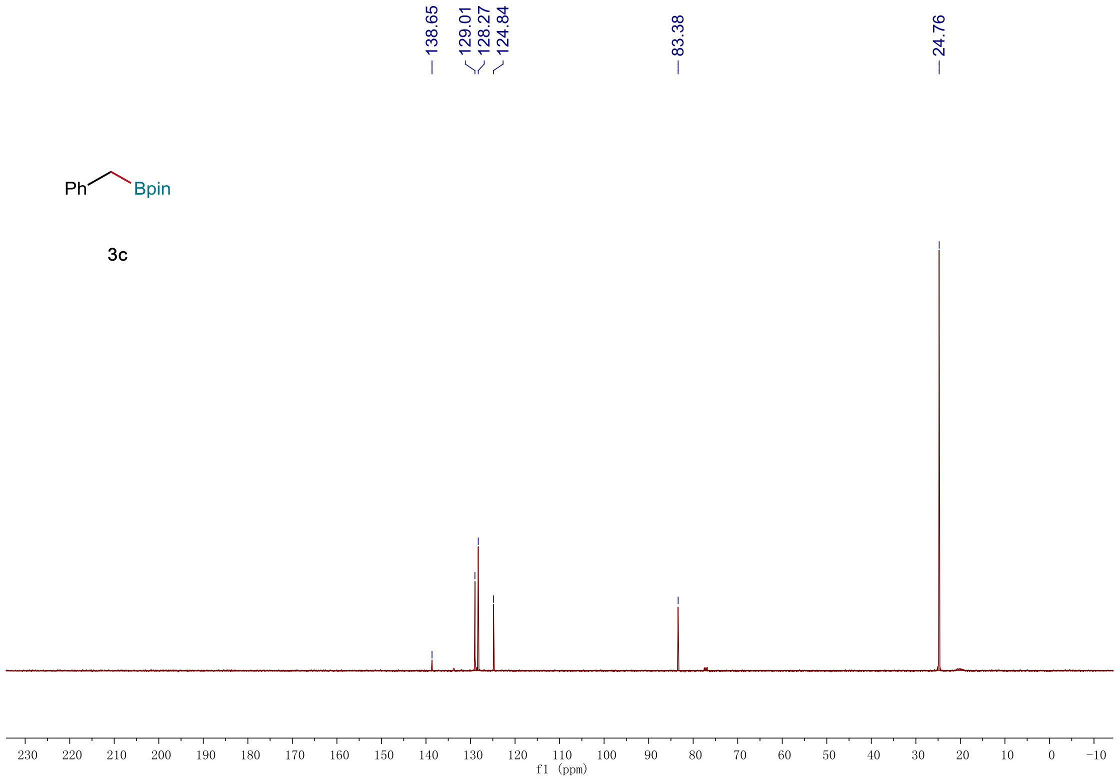

Figure S124. ^{1}H NMR spectrum of 3d in $CDCl_3$ (400 MHz)

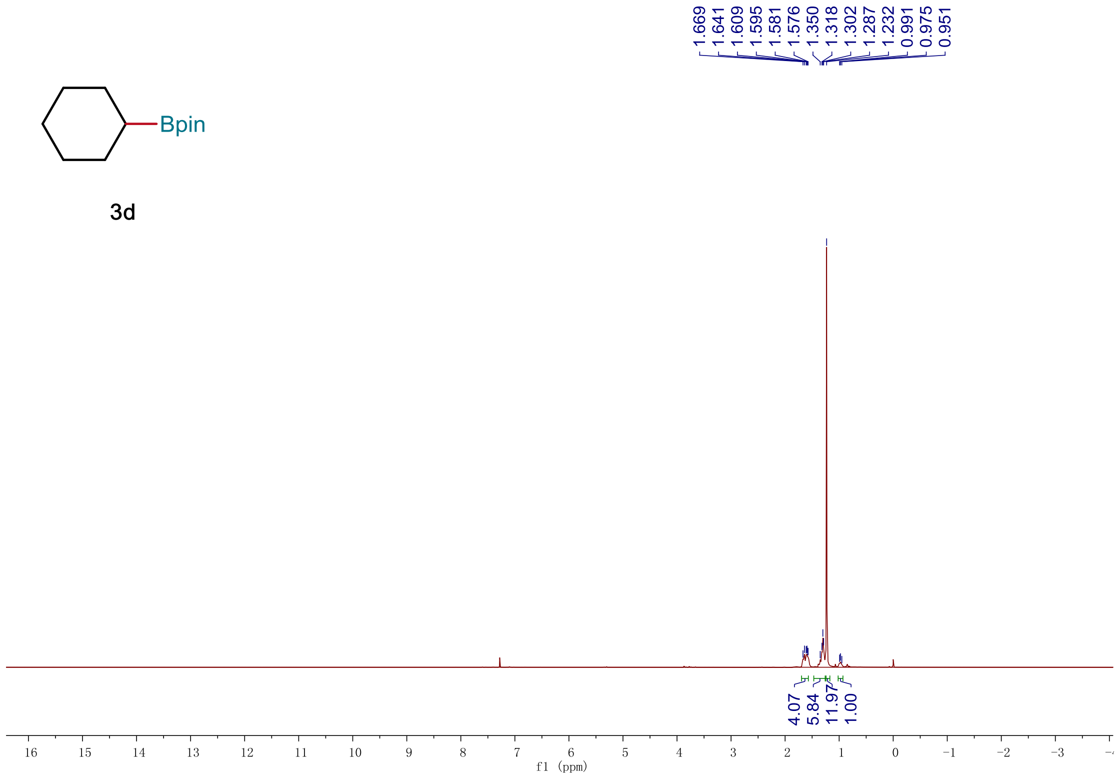

Figure S125. ^{13}C NMR spectrum of 3d in $CDCl_3$ (100 MHz)

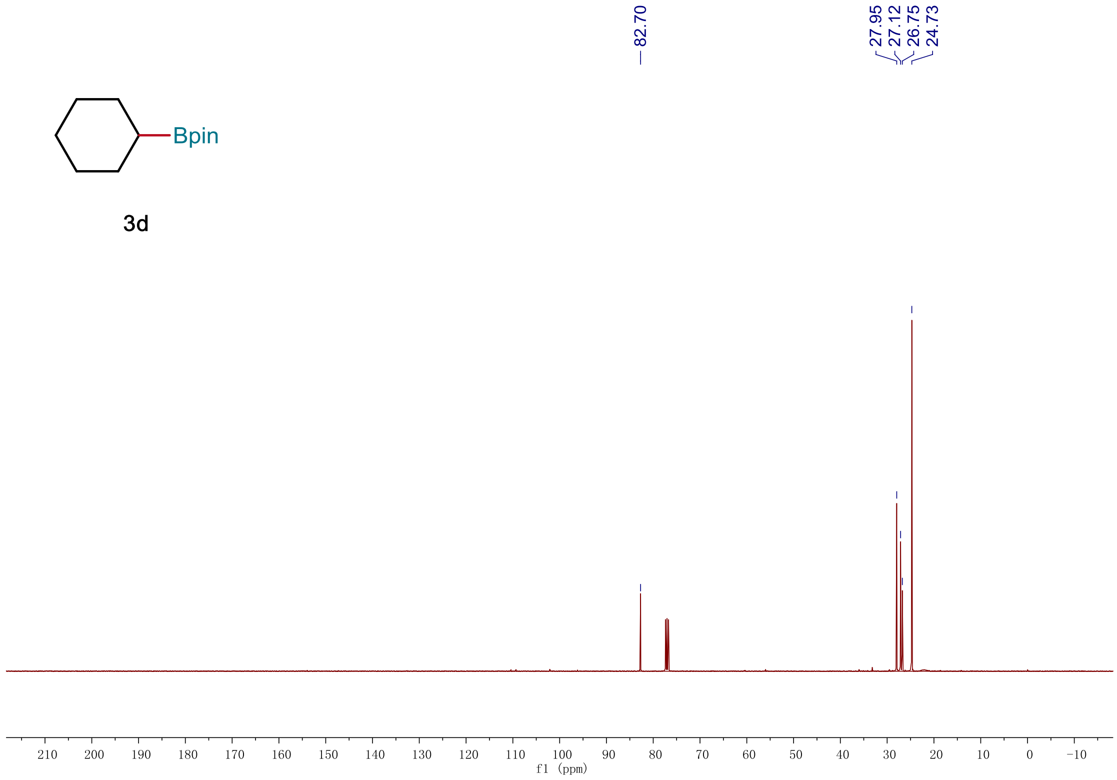

Figure S126. ^{1}H NMR spectrum of 3f in $CDCl_3$ (400 MHz)

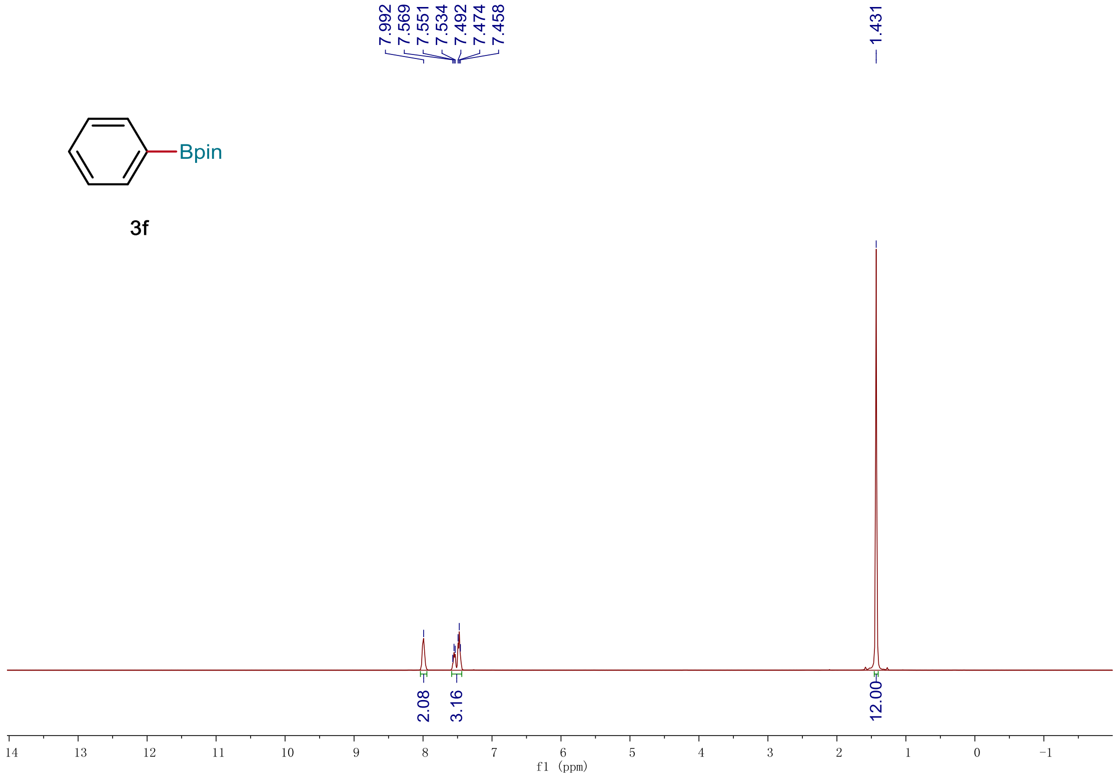

Figure S127. ^{13}C NMR spectrum of 3f in $CDCl_3$ (100 MHz)

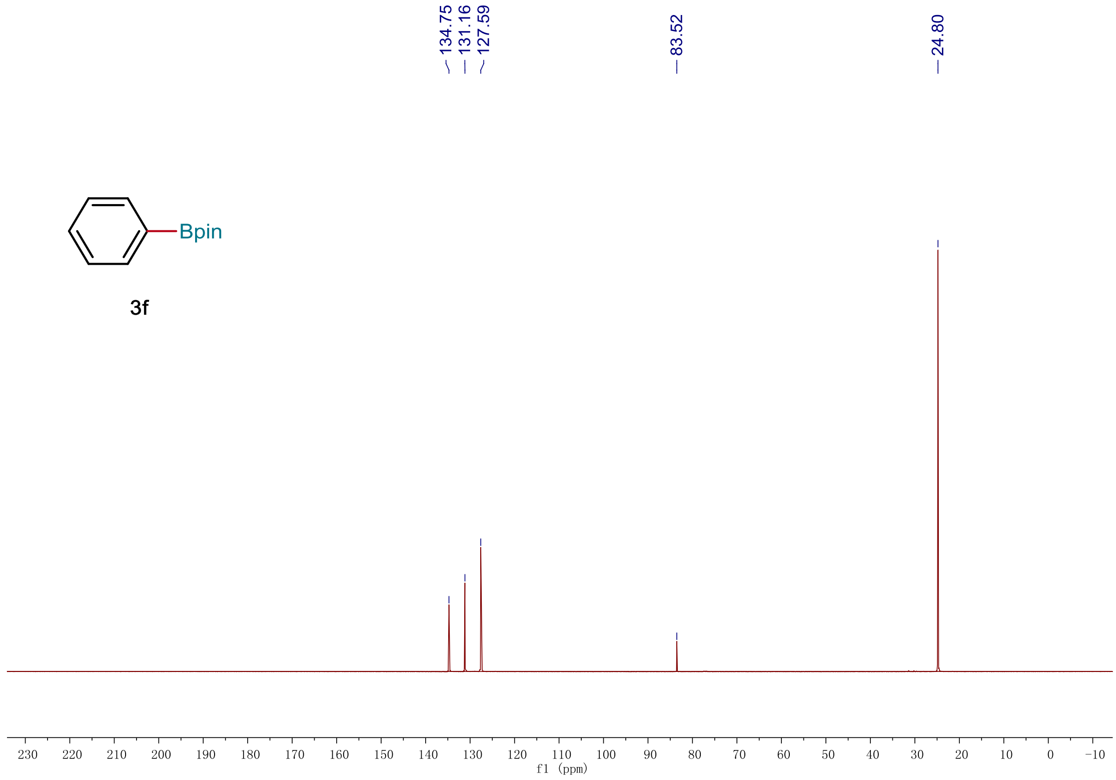

Figure S128. ^{1}H NMR spectrum of 3g in $CDCl_3$ (400 MHz)

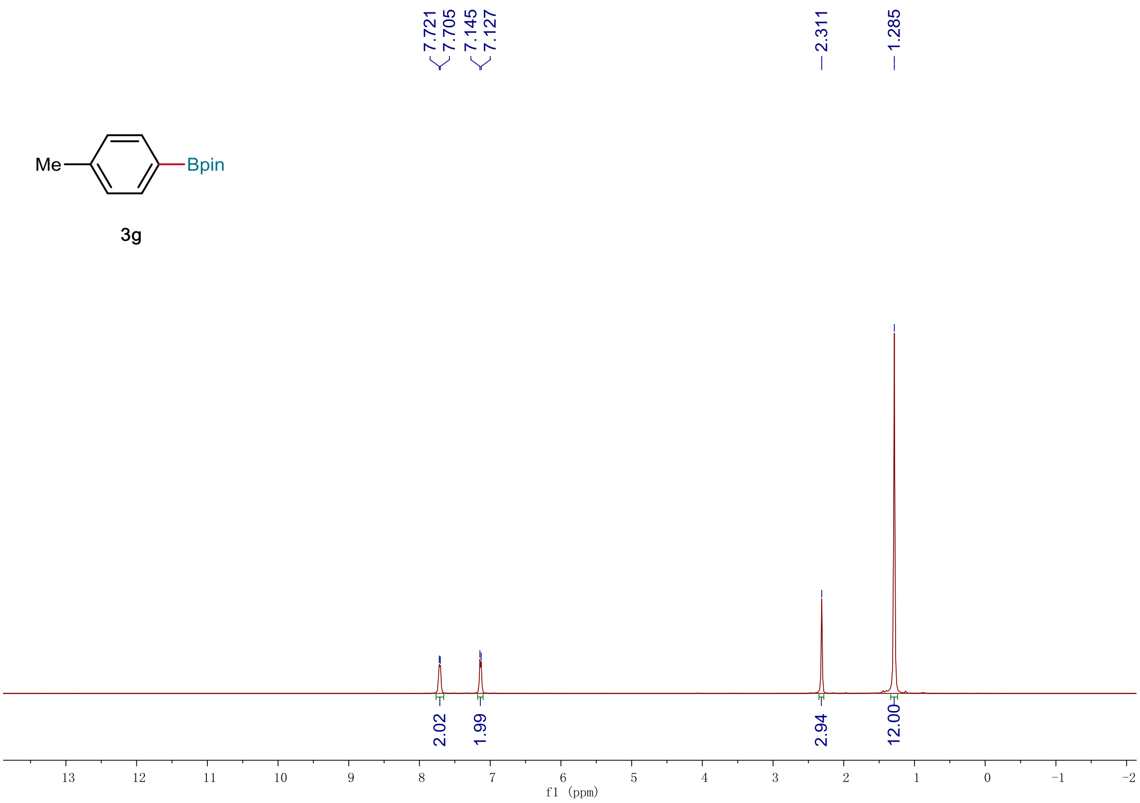

Figure S129. ^{13}C NMR spectrum of 3g in $CDCl_3$ (100 MHz)

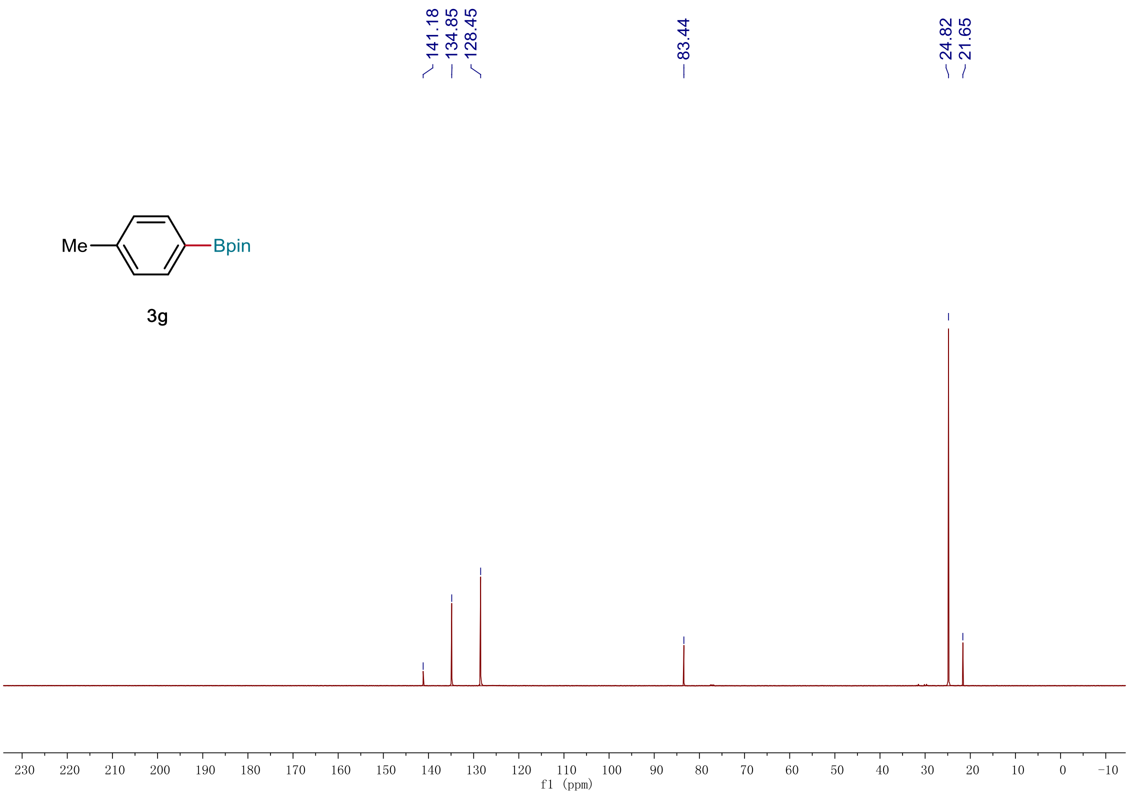

Figure S130. ^{1}H NMR spectrum of 3h in $CDCl_3$ (400 MHz)

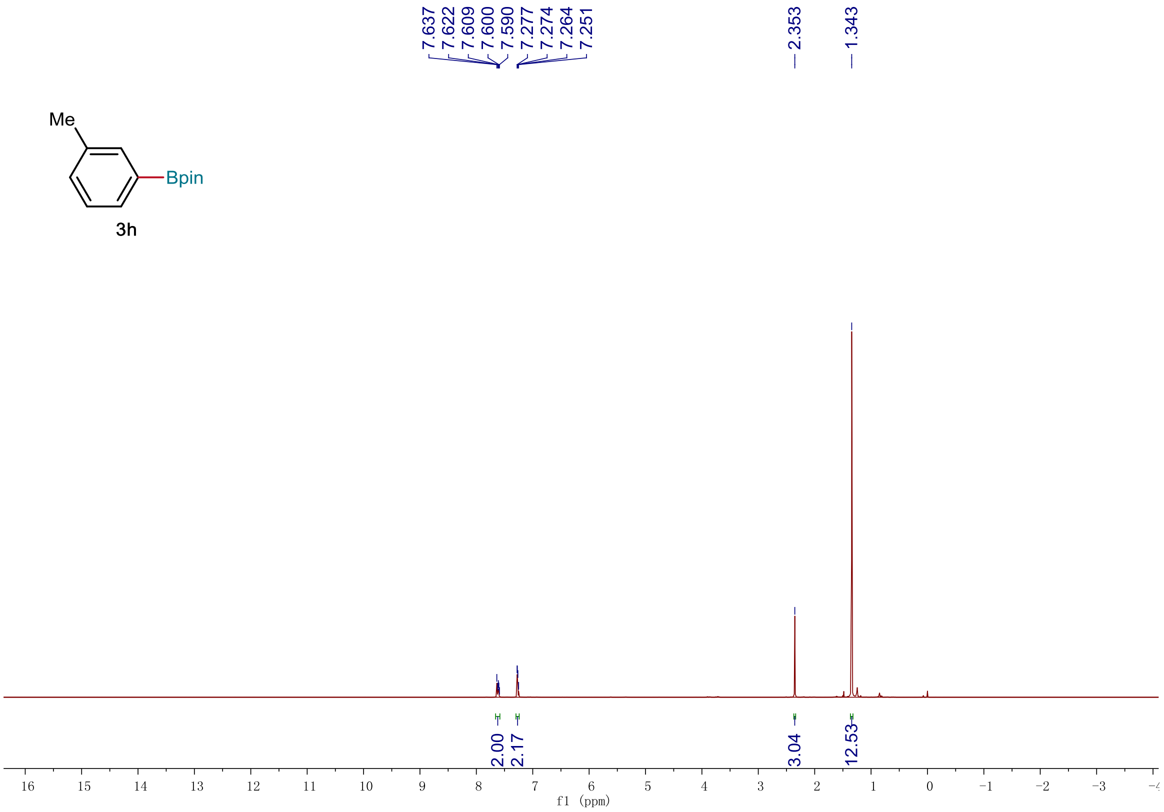

Figure S131. ^{13}C NMR spectrum of 3h in $CDCl_3$ (100 MHz)

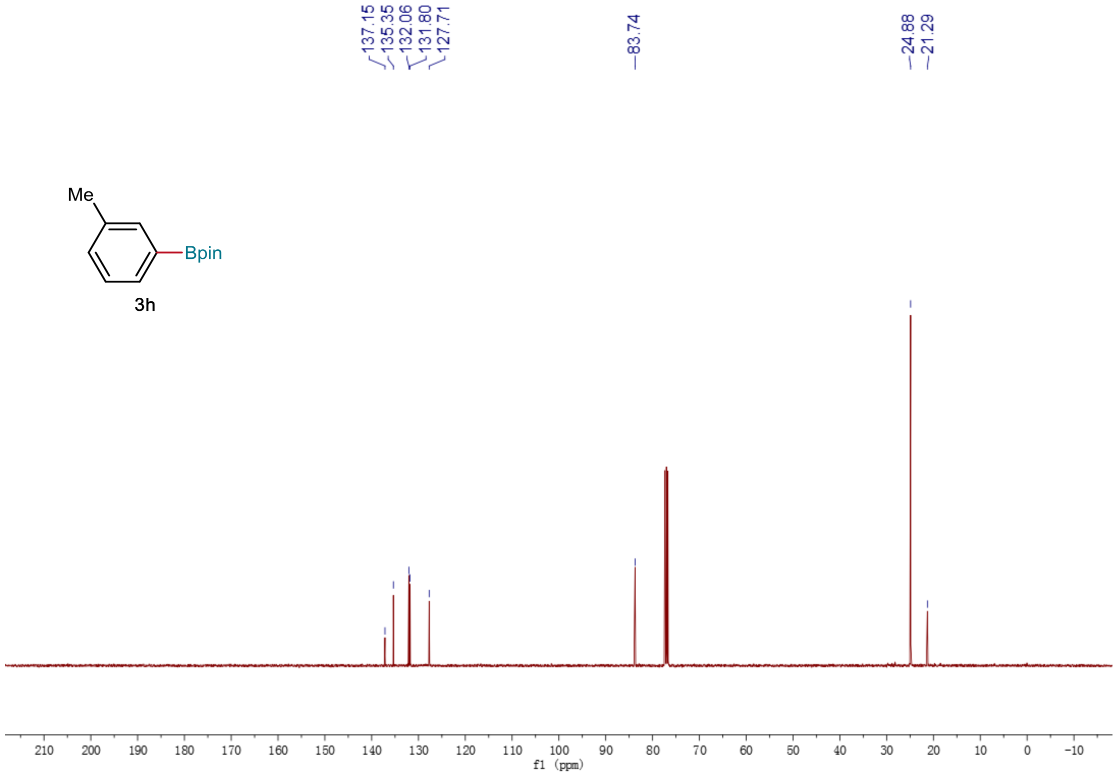

Figure S132. ^{1}H NMR spectrum of 3i in $CDCl_3$ (400 MHz)

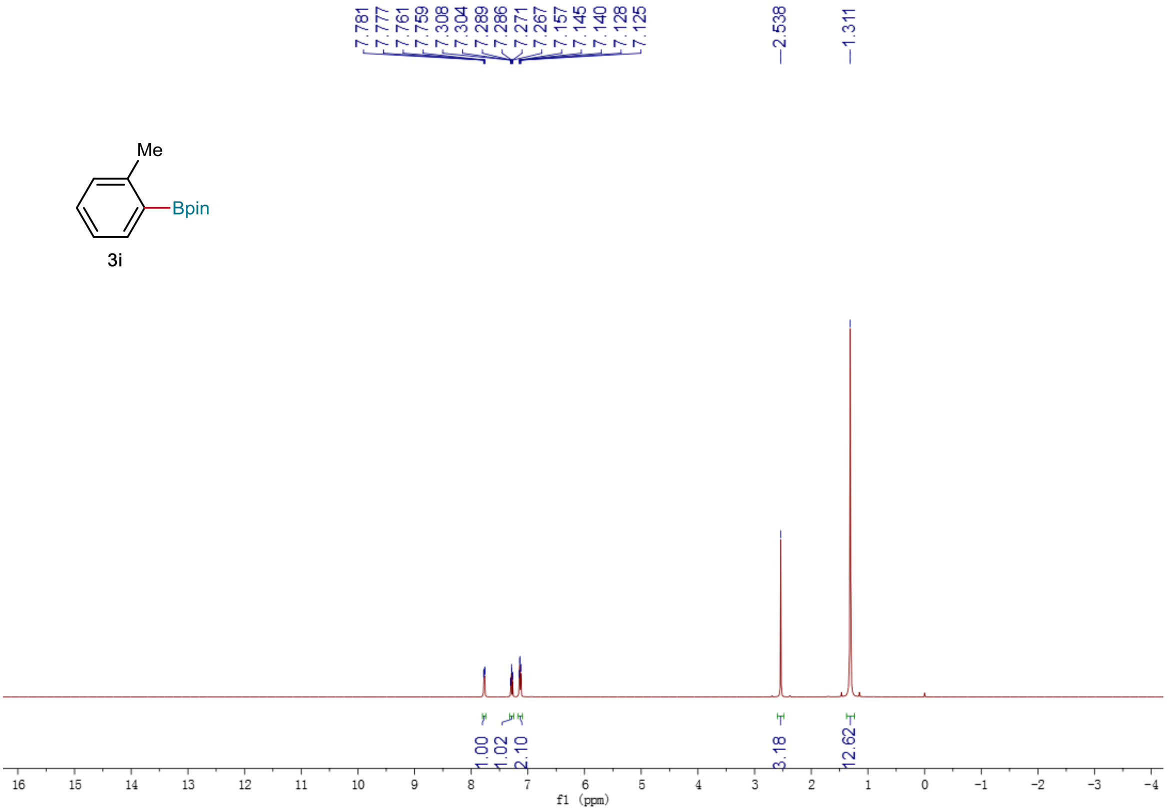

Figure S133. ^{13}C NMR spectrum of 3i in $CDCl_3$ (100 MHz)

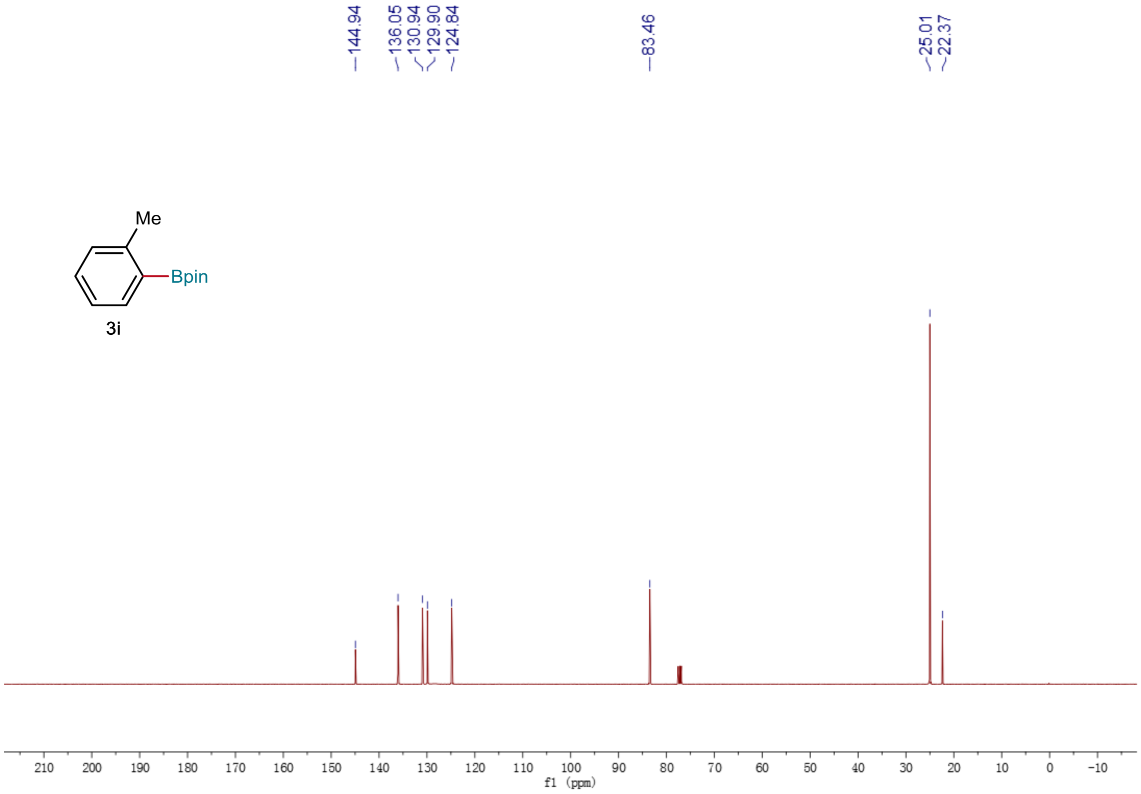

Figure S134. ^{1}H NMR spectrum of 3j in $CDCl_3$ (400 MHz)

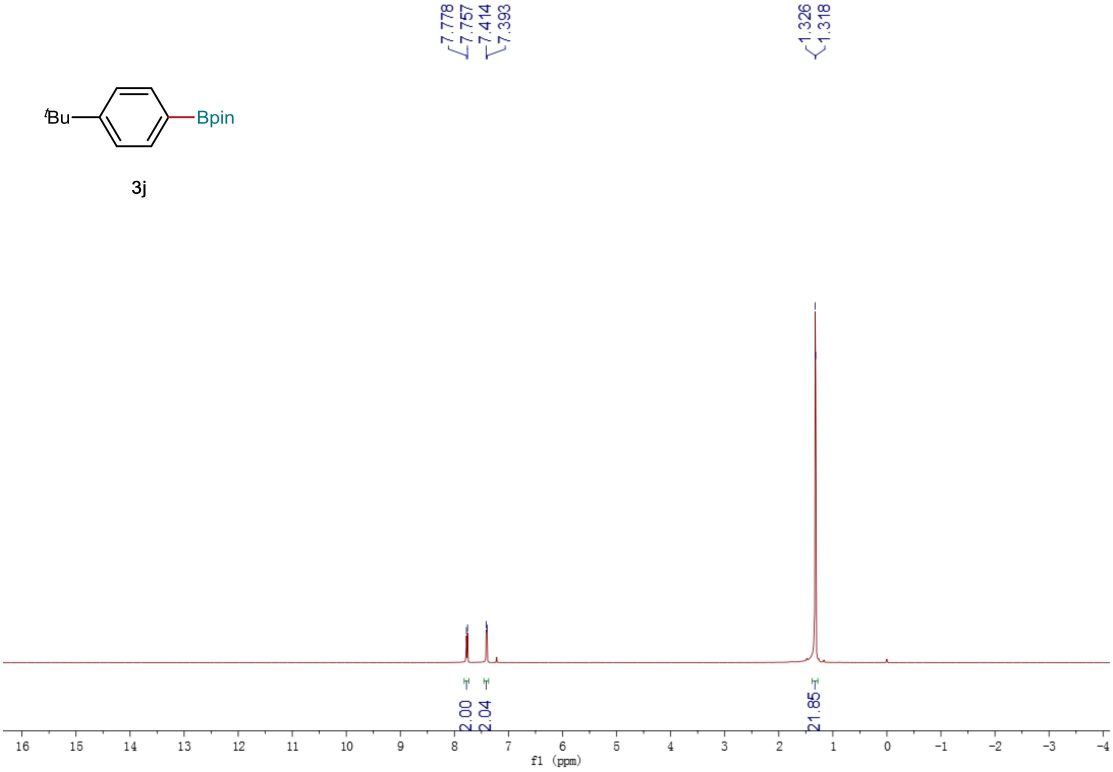

Figure S135. ^{13}C NMR spectrum of 3j in $CDCl_3$ (100 MHz)

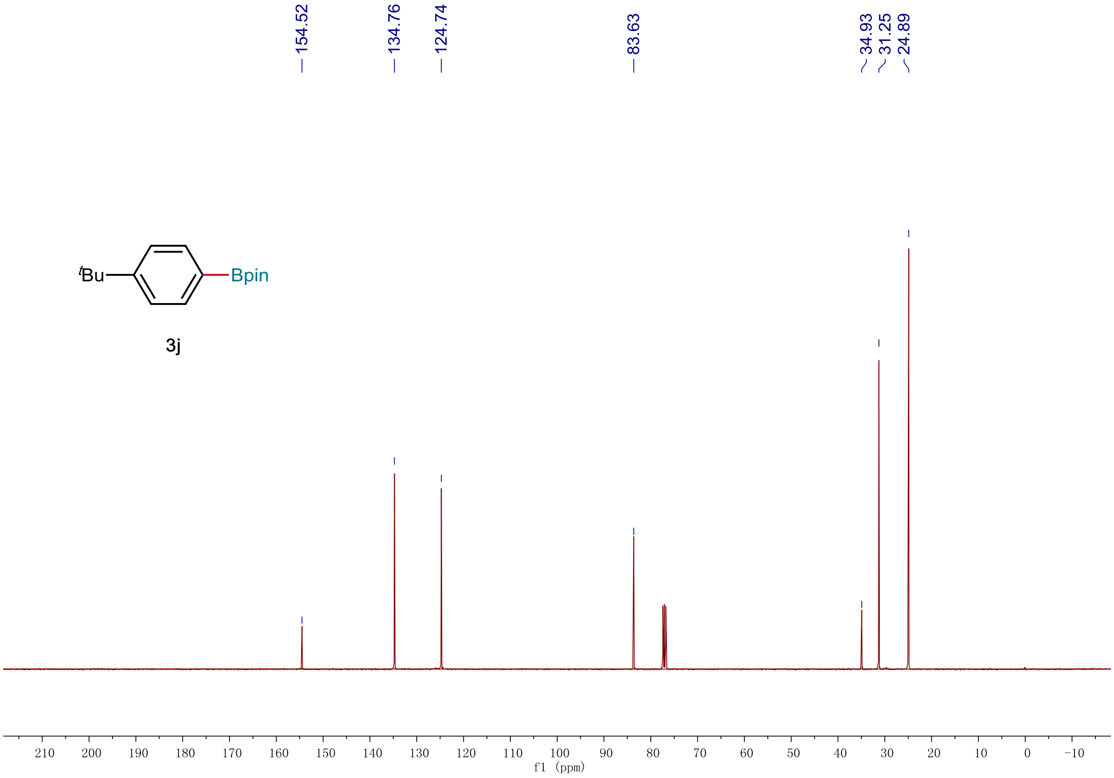

Figure S136. ^{1}H NMR spectrum of 3k in $CDCl_3$ (400 MHz)

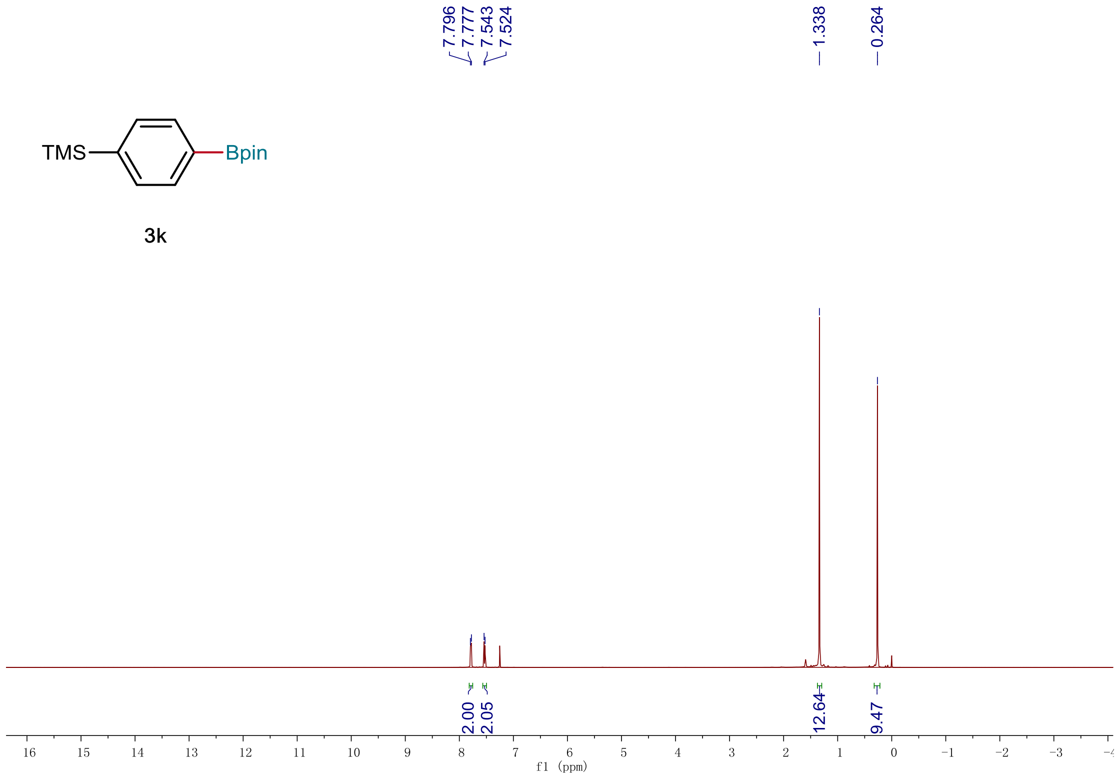

Figure S137. ^{13}C NMR spectrum of 3k in $CDCl_3$ (100 MHz)

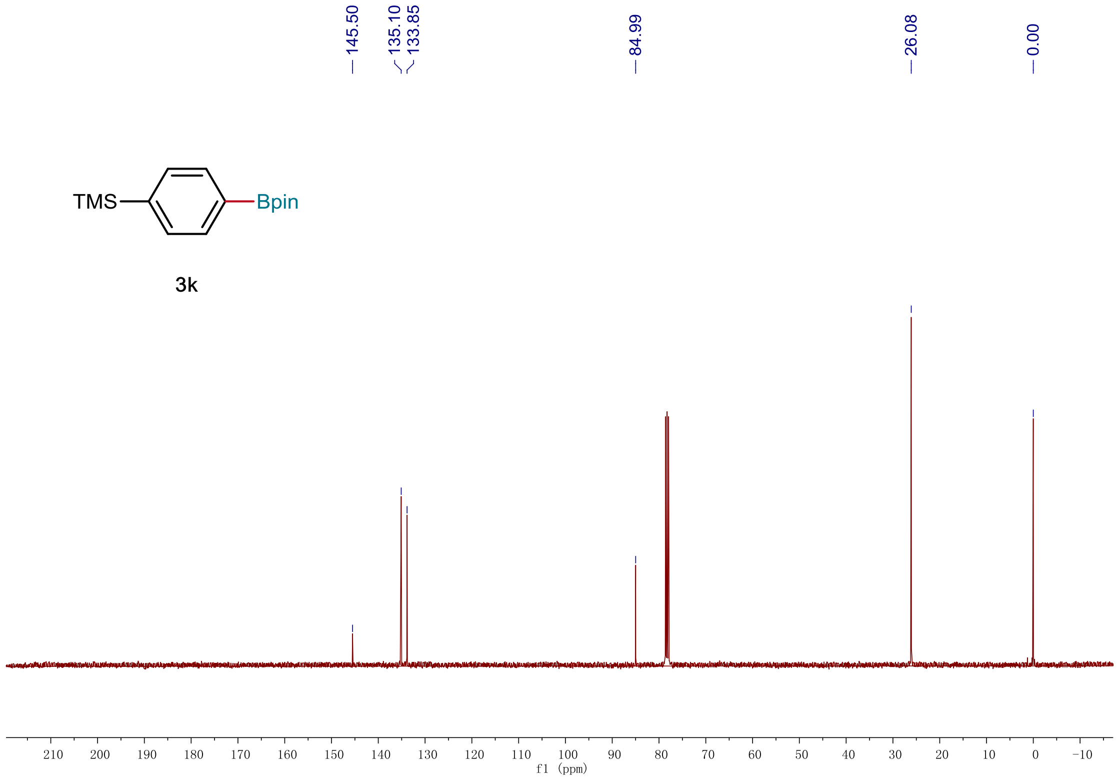

Figure S138. ^{1}H NMR spectrum of 3l in $CDCl_3$ (400 MHz)

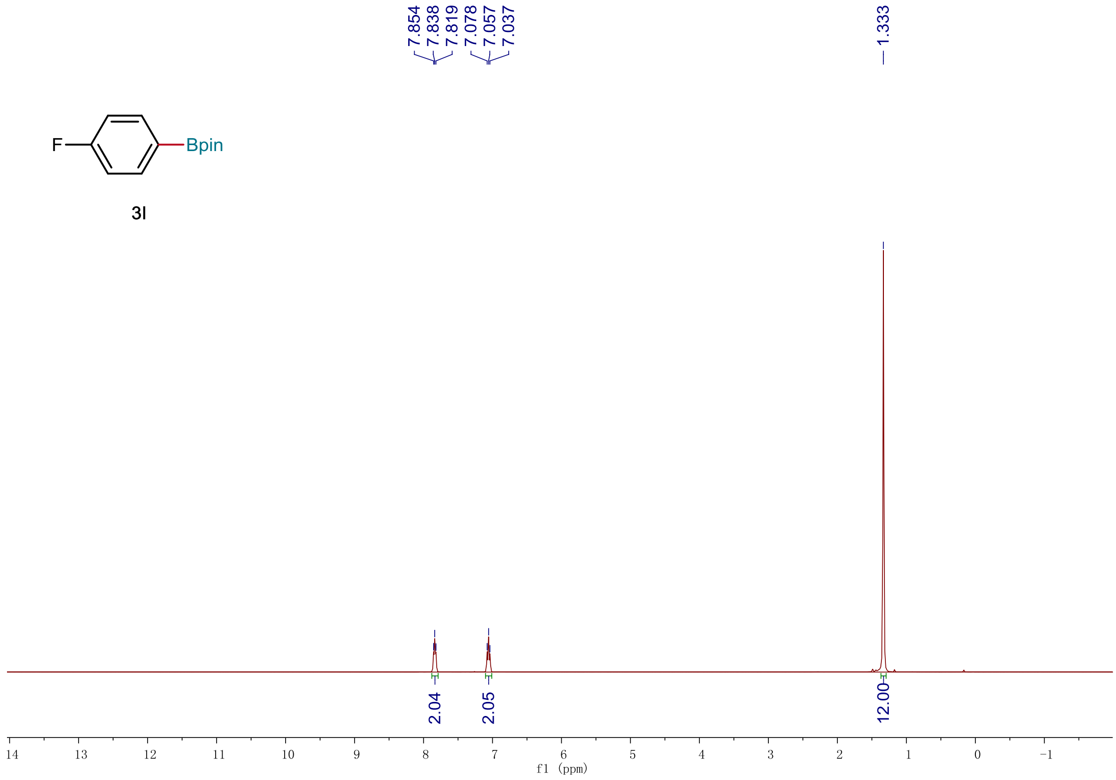

Figure S139. ^{13}C NMR spectrum of 3l in $CDCl_3$ (100 MHz)

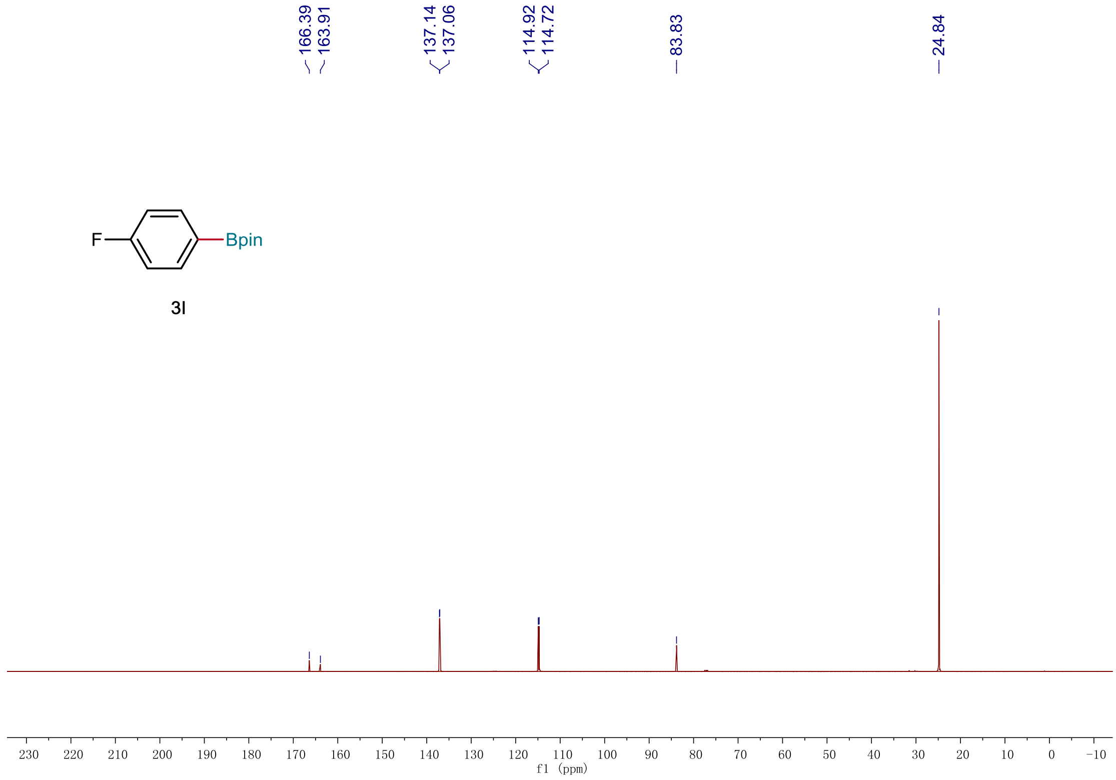

Figure S140. ^{1}H NMR spectrum of 3m in $CDCl_3$ (400 MHz)

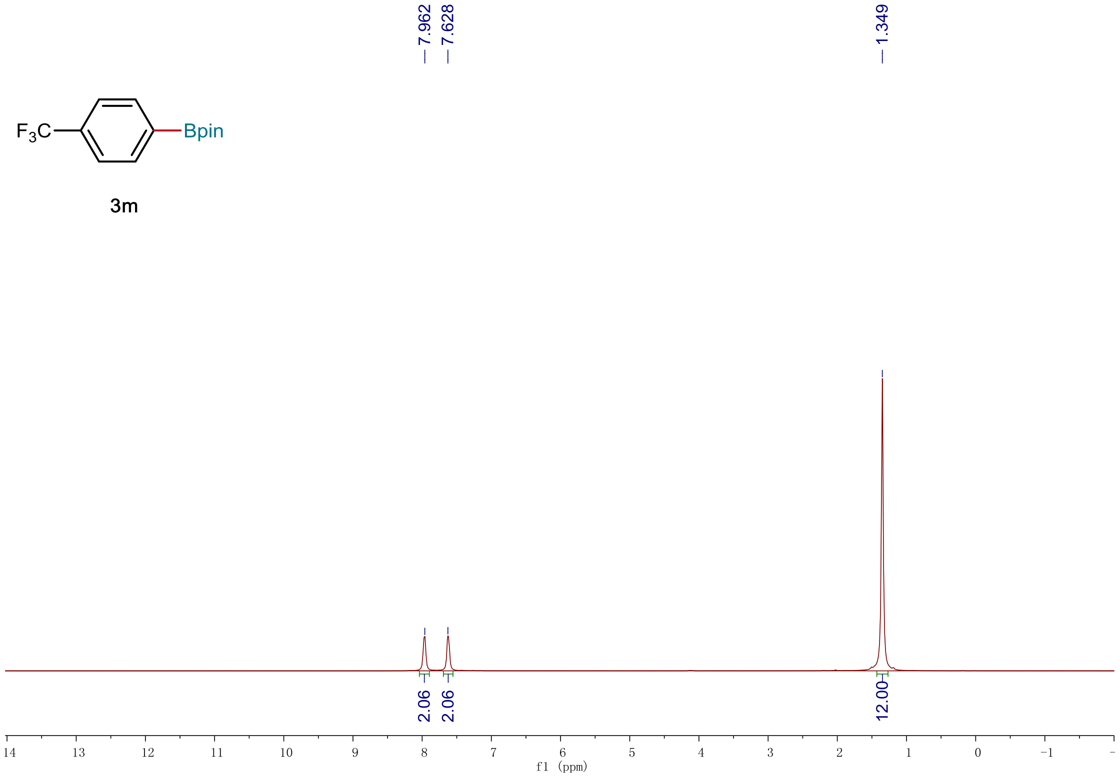

Figure S141. ^{13}C NMR spectrum of 3m in $CDCl_3$ (100 MHz)

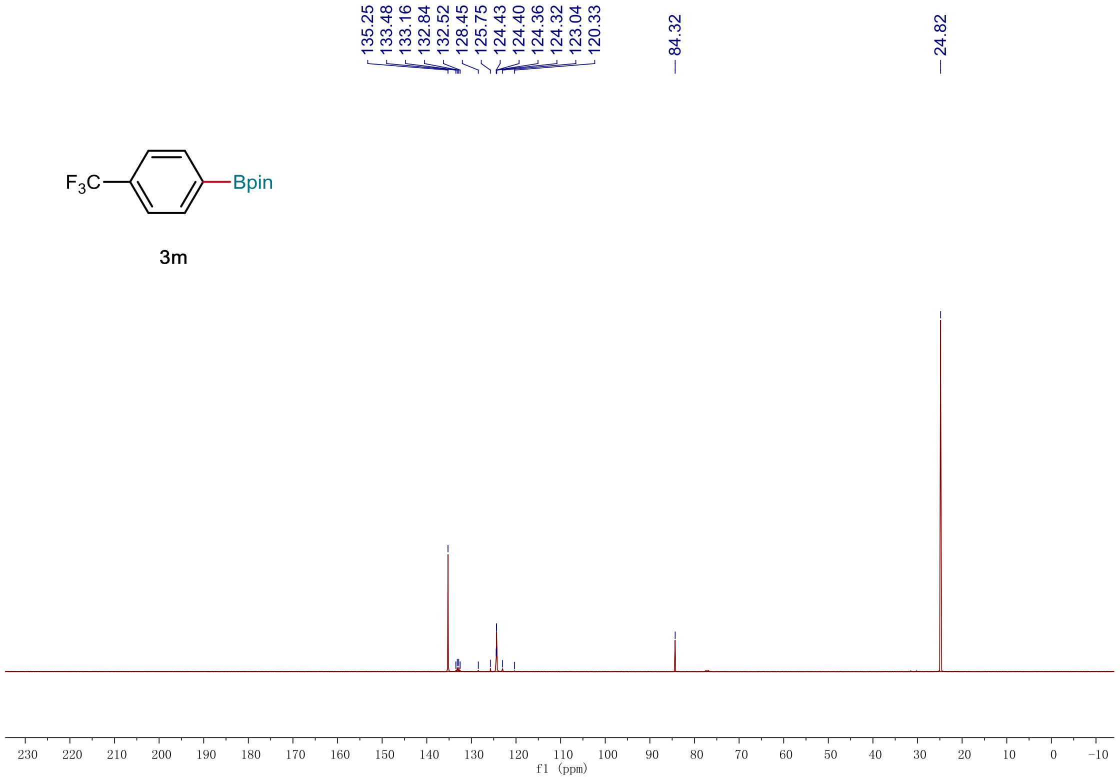

Figure S142. ^{1}H NMR spectrum of 3n in CDCl$_3$ (400 MHz)

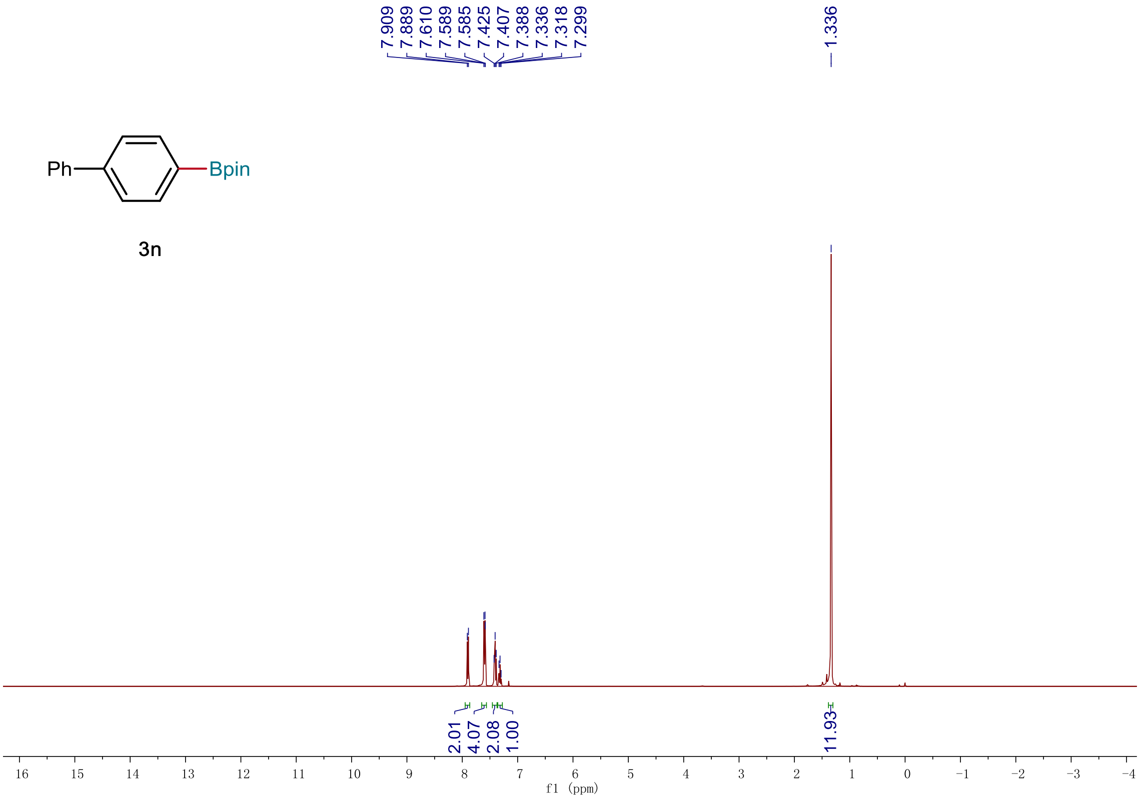

Figure S143. ^{13}C NMR spectrum of 3n in CDCl$_3$ (100 MHz)

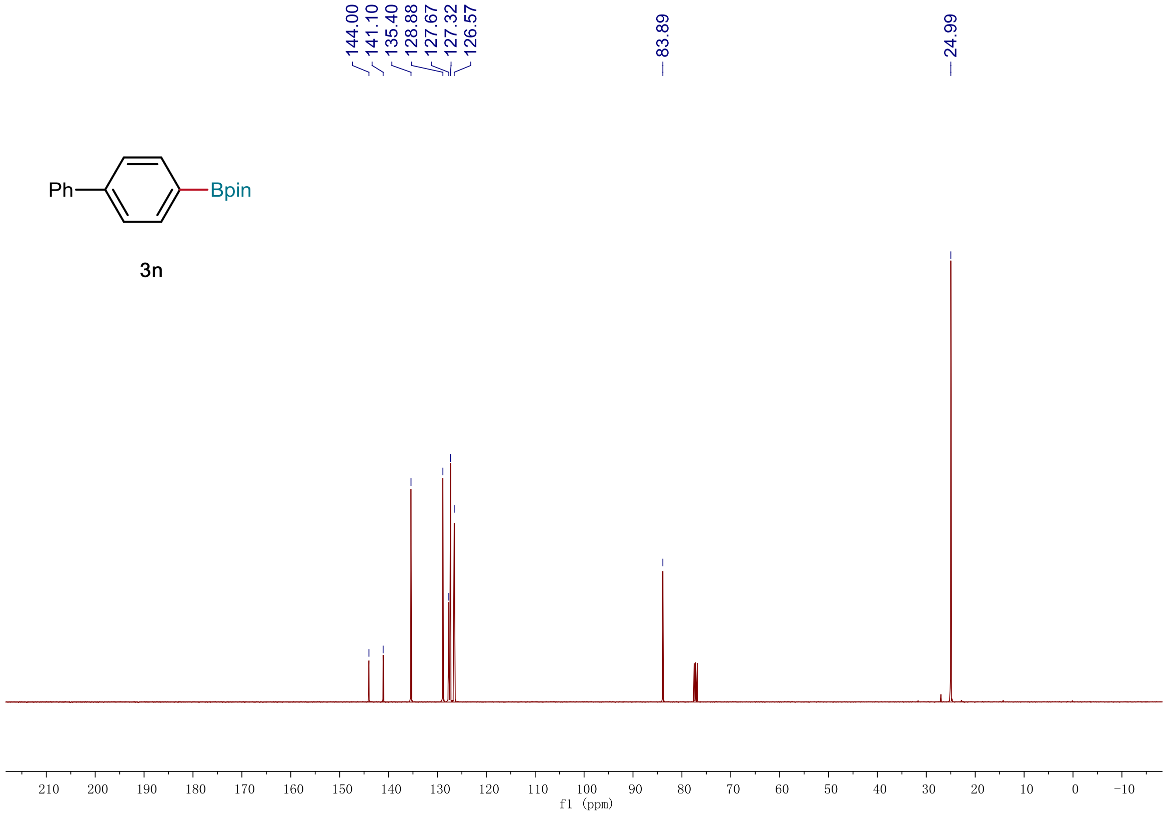

Figure S144. ^{1}H NMR spectrum of 3o in CDCl$_3$ (400 MHz)

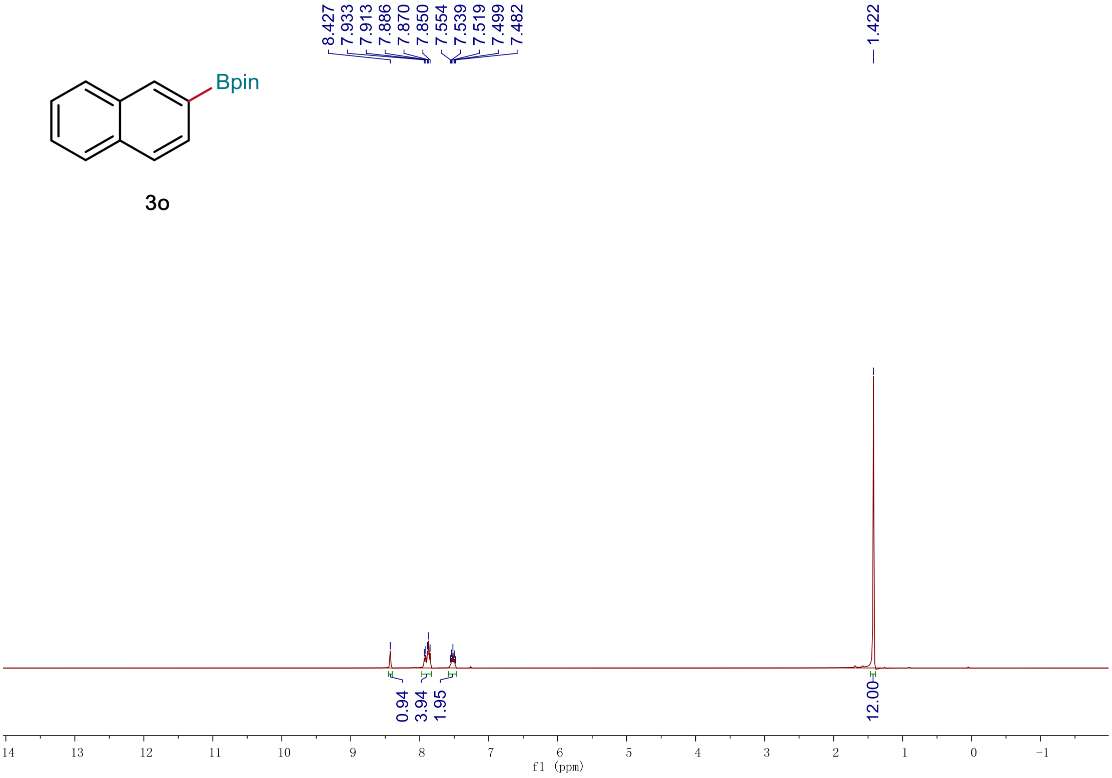

Figure S145. ^{13}C NMR spectrum of 3o in CDCl$_3$ (100 MHz)

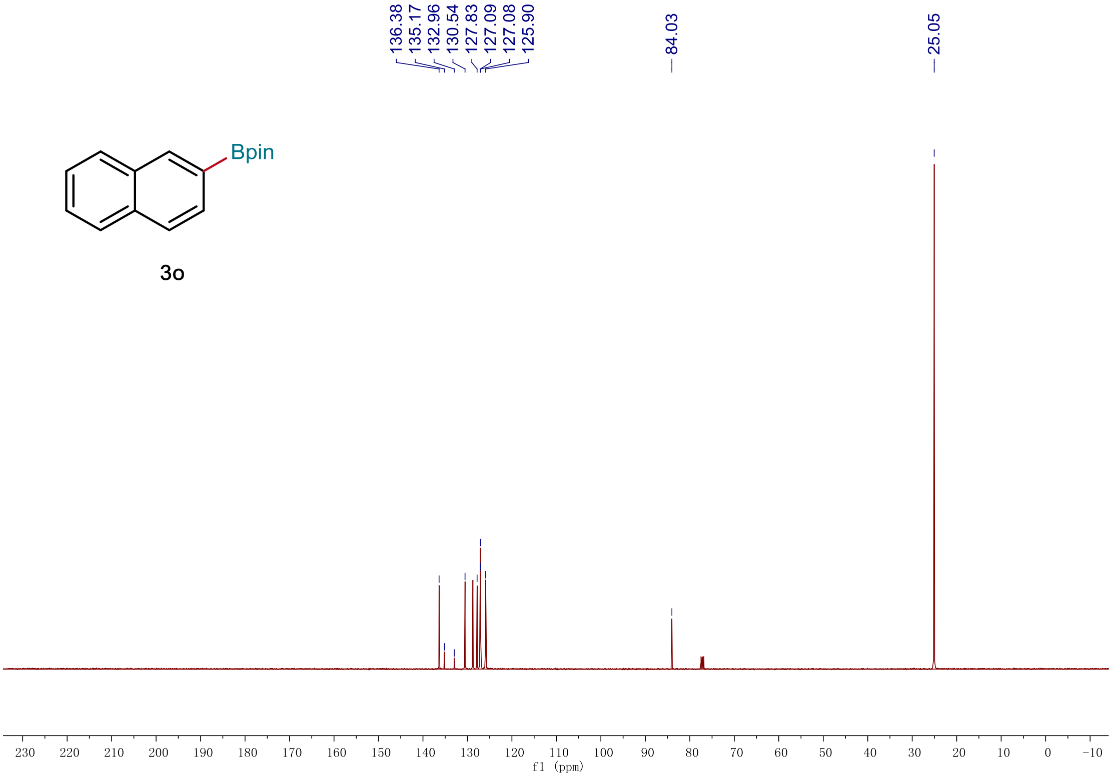

Figure S146. ^{1}H NMR spectrum of 3p in CDCl$_3$ (400 MHz)

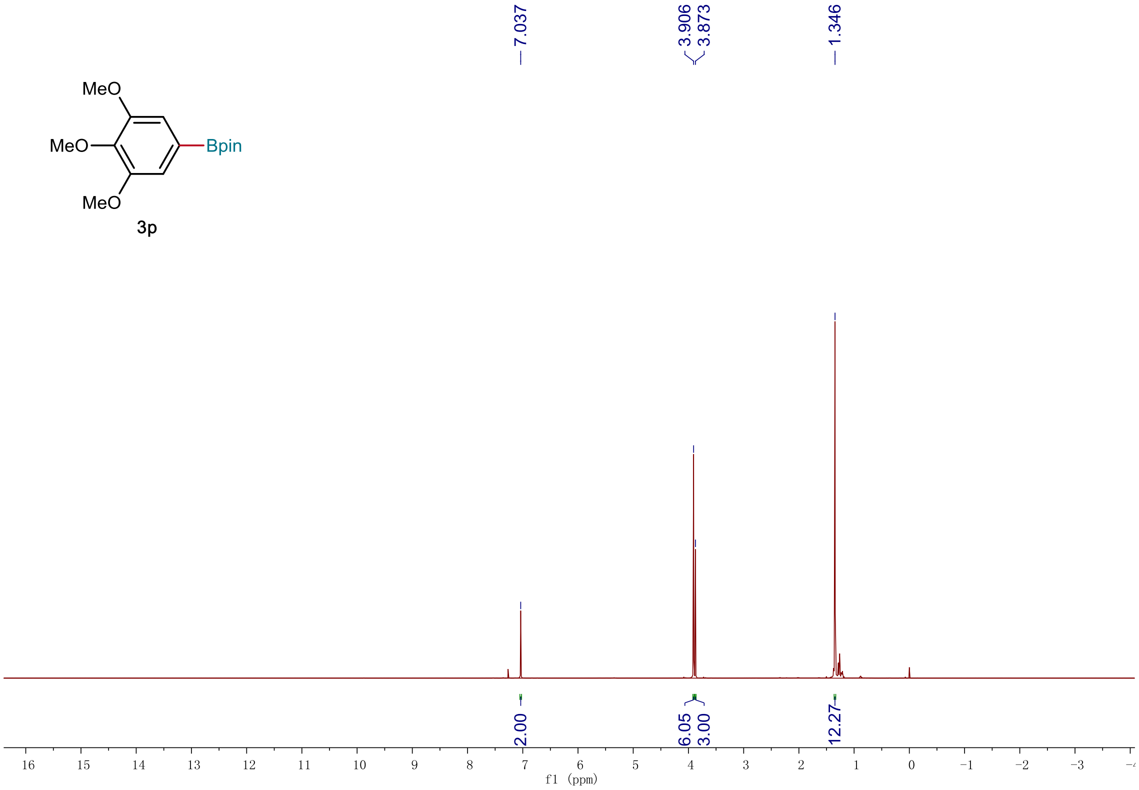

Figure S147. ^{13}C NMR spectrum of 3p in CDCl$_3$ (100 MHz)

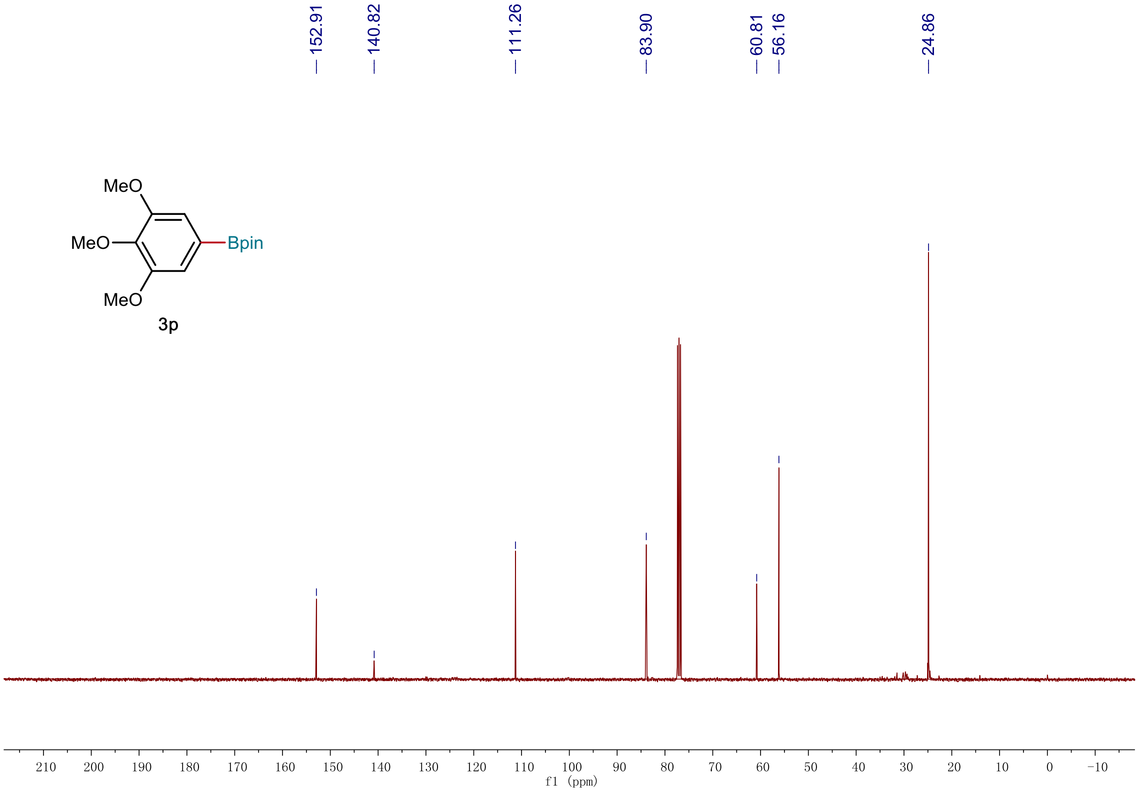

Figure S148. ^{1}H NMR spectrum of 1aq in $CDCl_3$ (400 MHz)

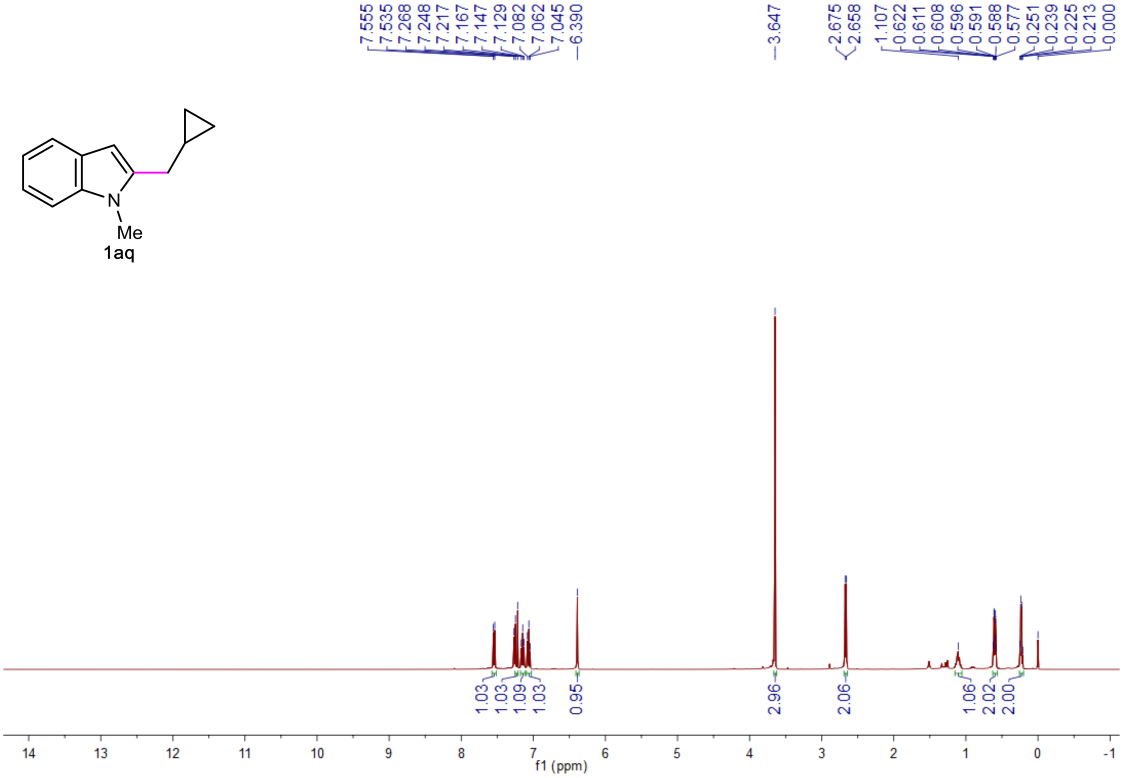

Figure S149. ^{13}C NMR spectrum of 1aq in $CDCl_3$ (100 MHz)

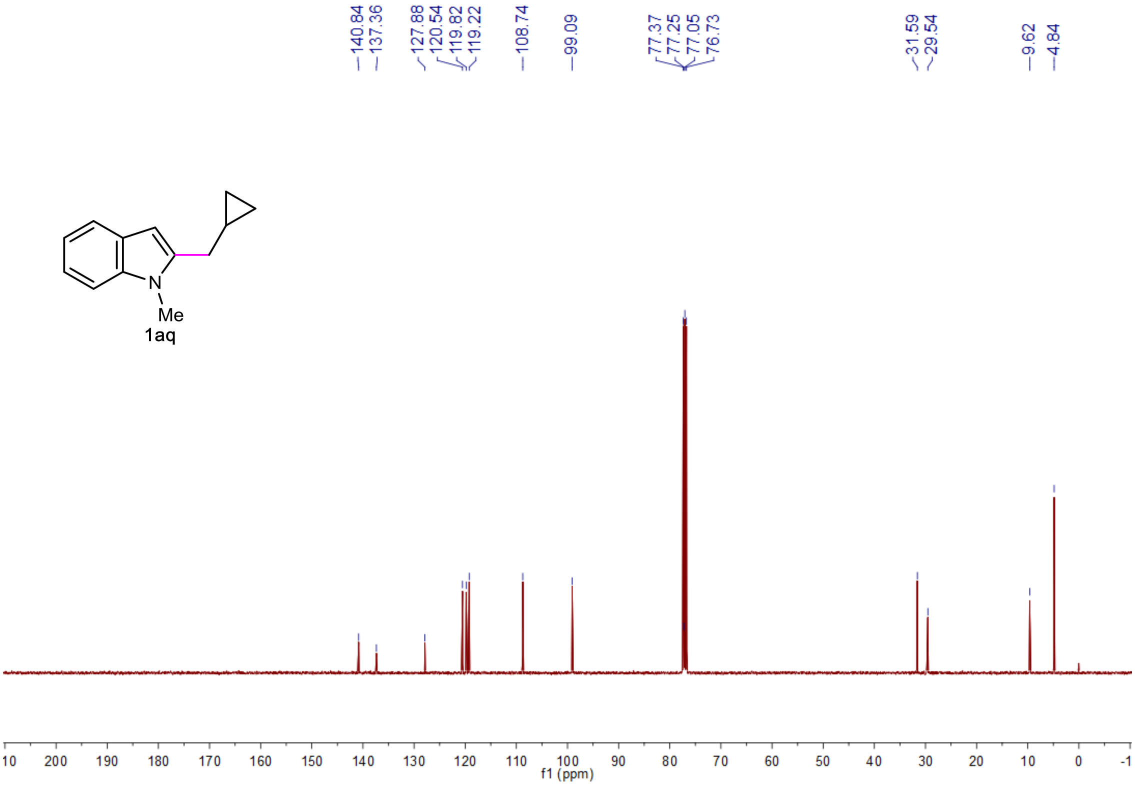

Figure S150. ^{1}H NMR spectrum of 3r in $CDCl_3$ (400 MHz)

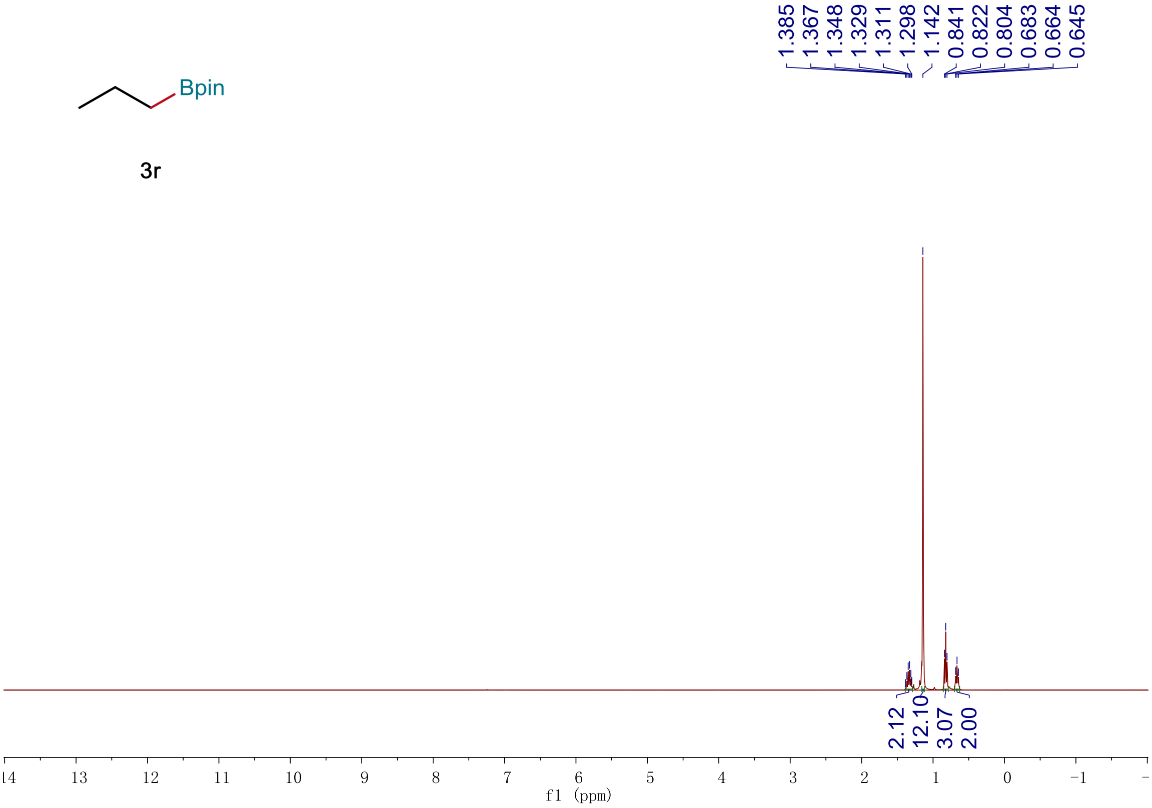

Figure S151. ^{13}C NMR spectrum of 3r in $CDCl_3$ (100 MHz)

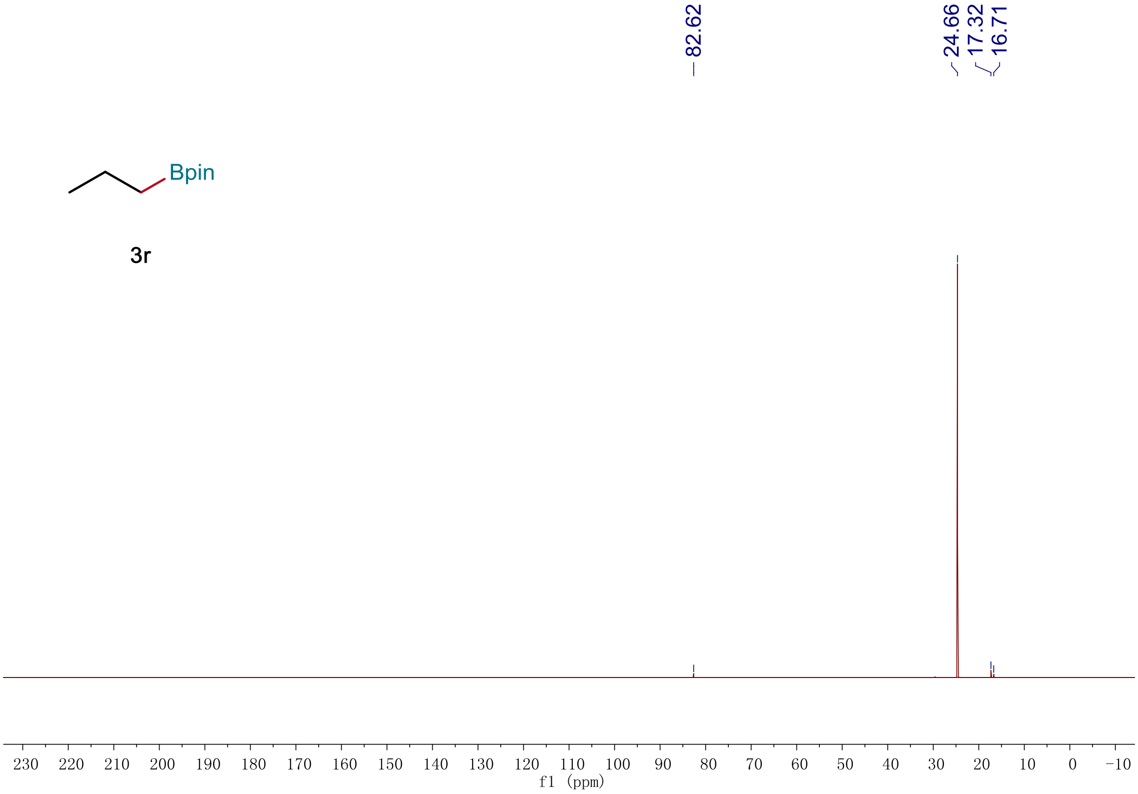

Figure S152. ^{1}H NMR spectrum of 3r' in $CDCl_3$ (400 MHz)

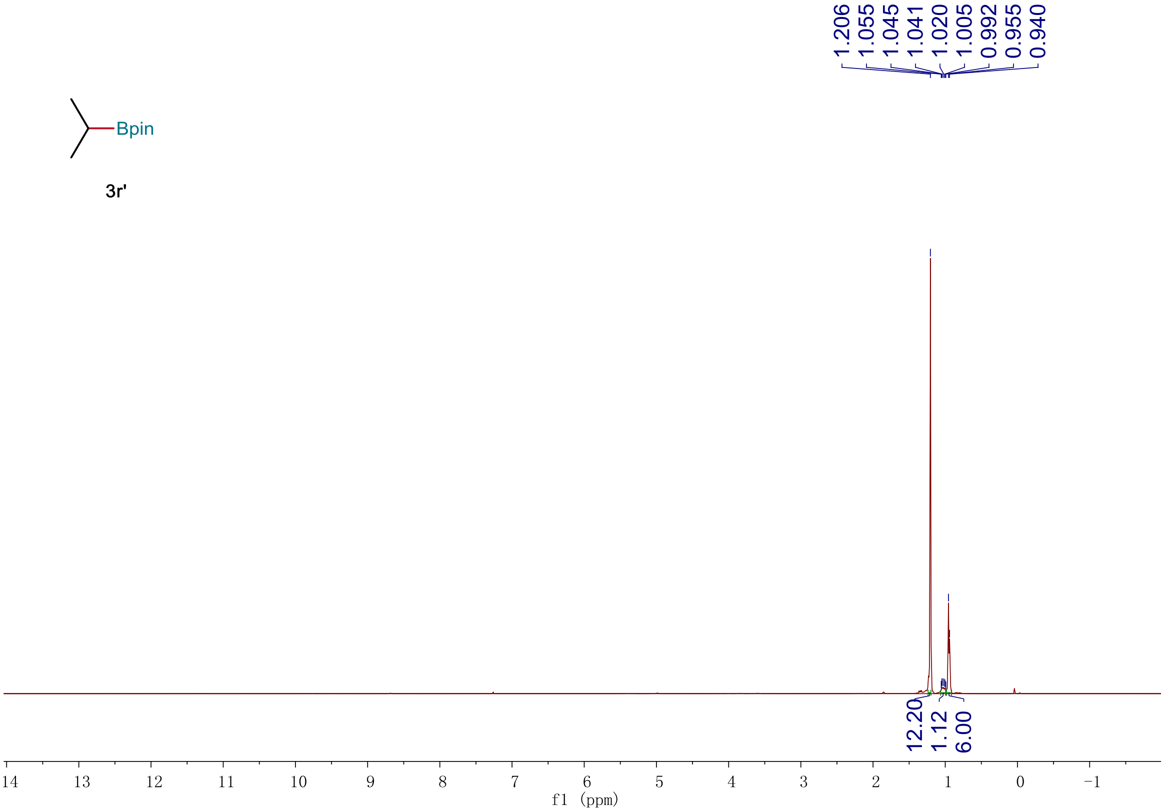

Figure S153. ^{13}C NMR spectrum of 3r' in $CDCl_3$ (100 MHz)

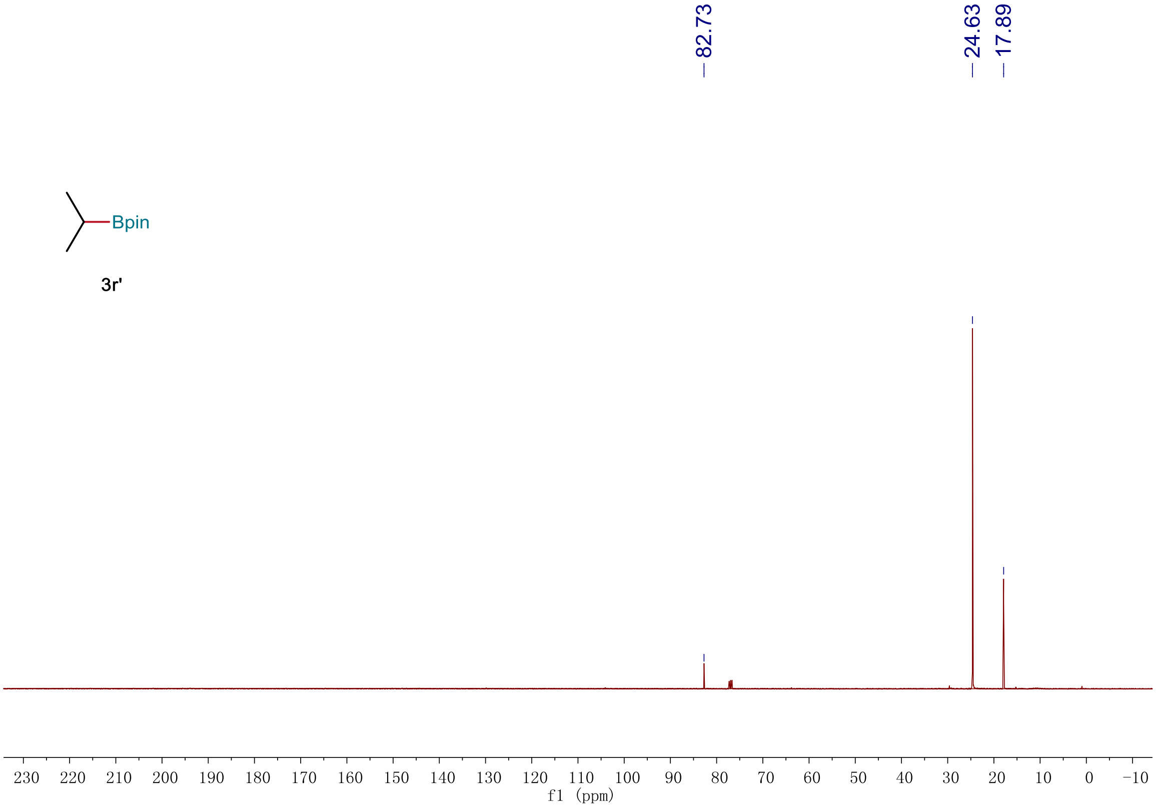

Figure S154. ^{1}H NMR spectrum of 3s in CDCl$_3$ (400 MHz)

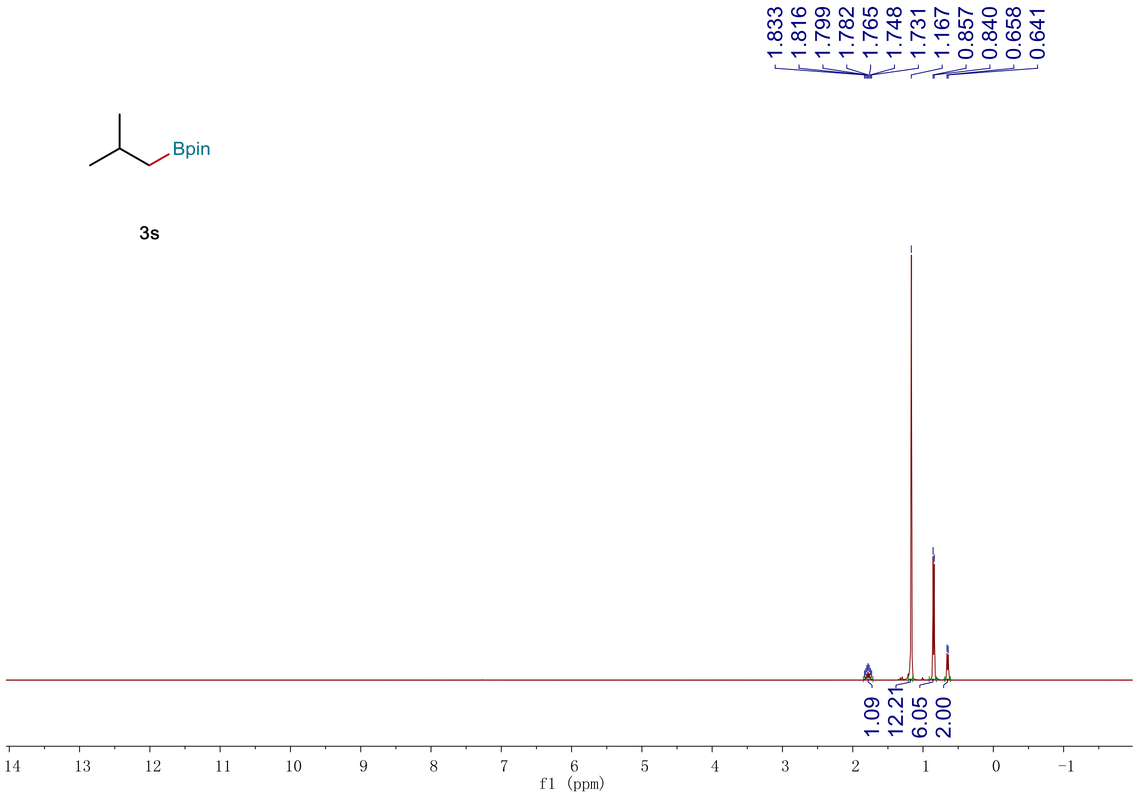

Figure S155. ^{13}C NMR spectrum of 3s in CDCl$_3$ (100 MHz)

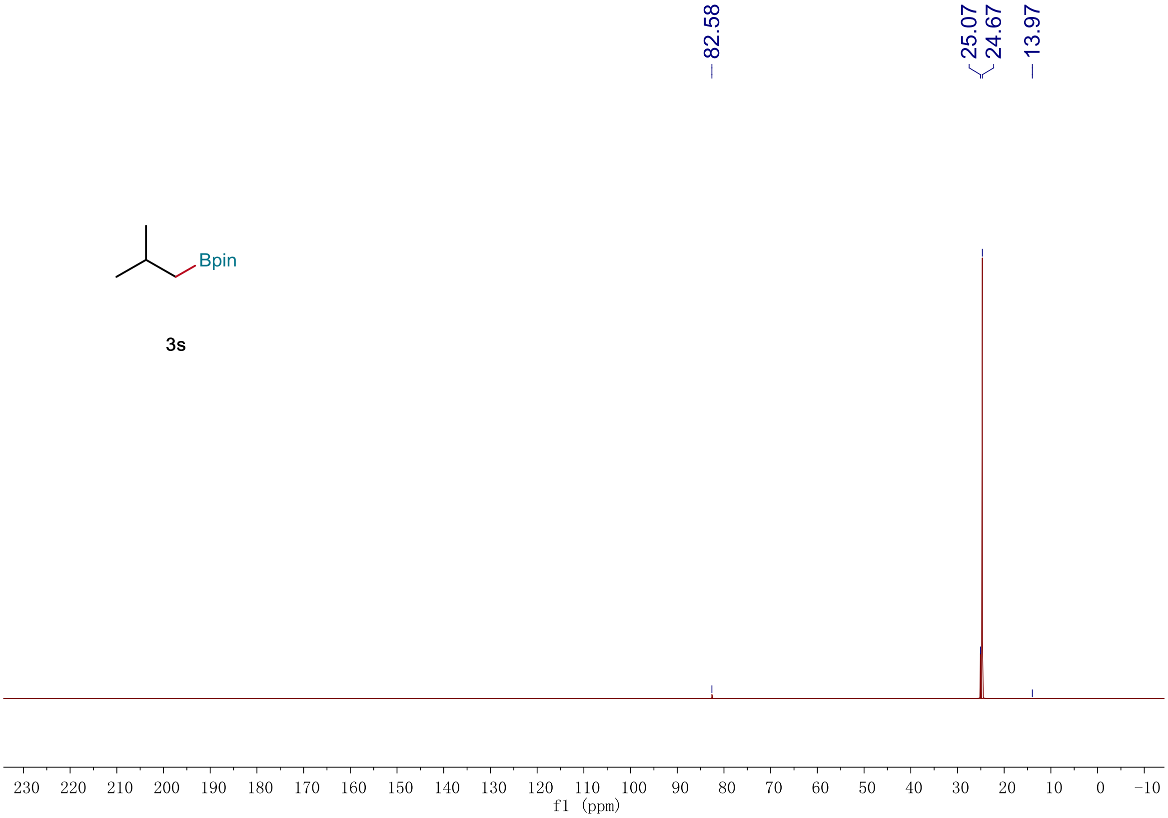

Figure S156. ^{1}H NMR spectrum of 3e in $CDCl_3$ (400 MHz)

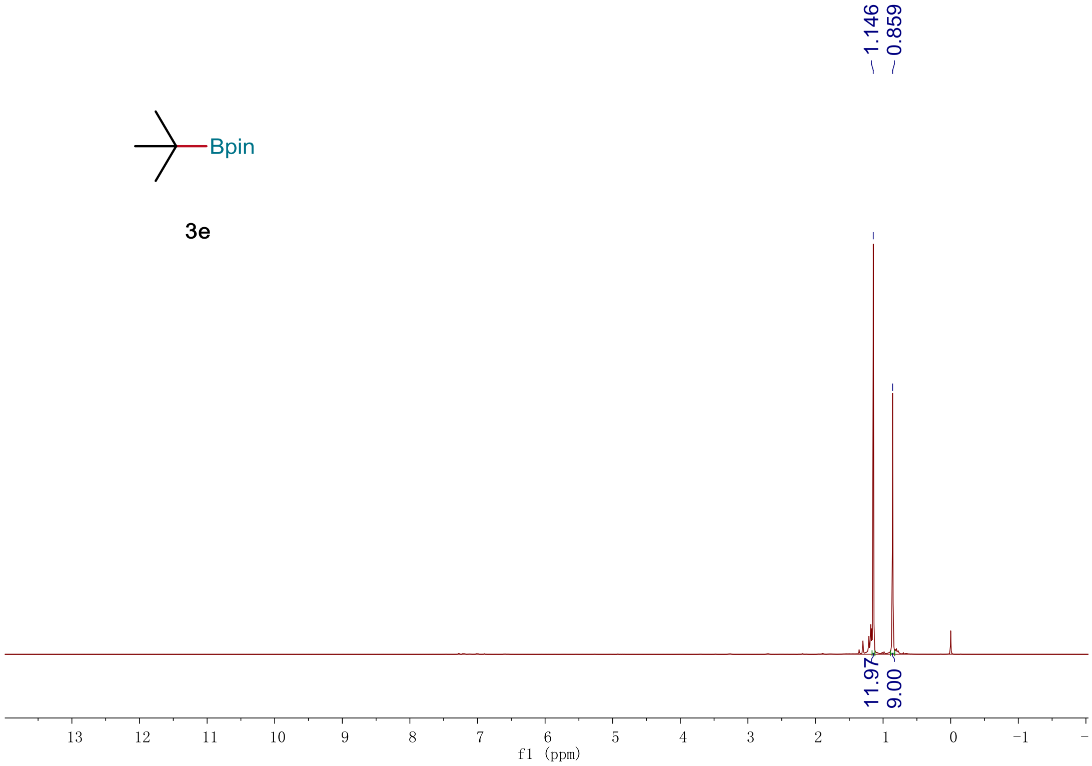

Figure S157. ^{13}C NMR spectrum of 3e in $CDCl_3$ (100 MHz)

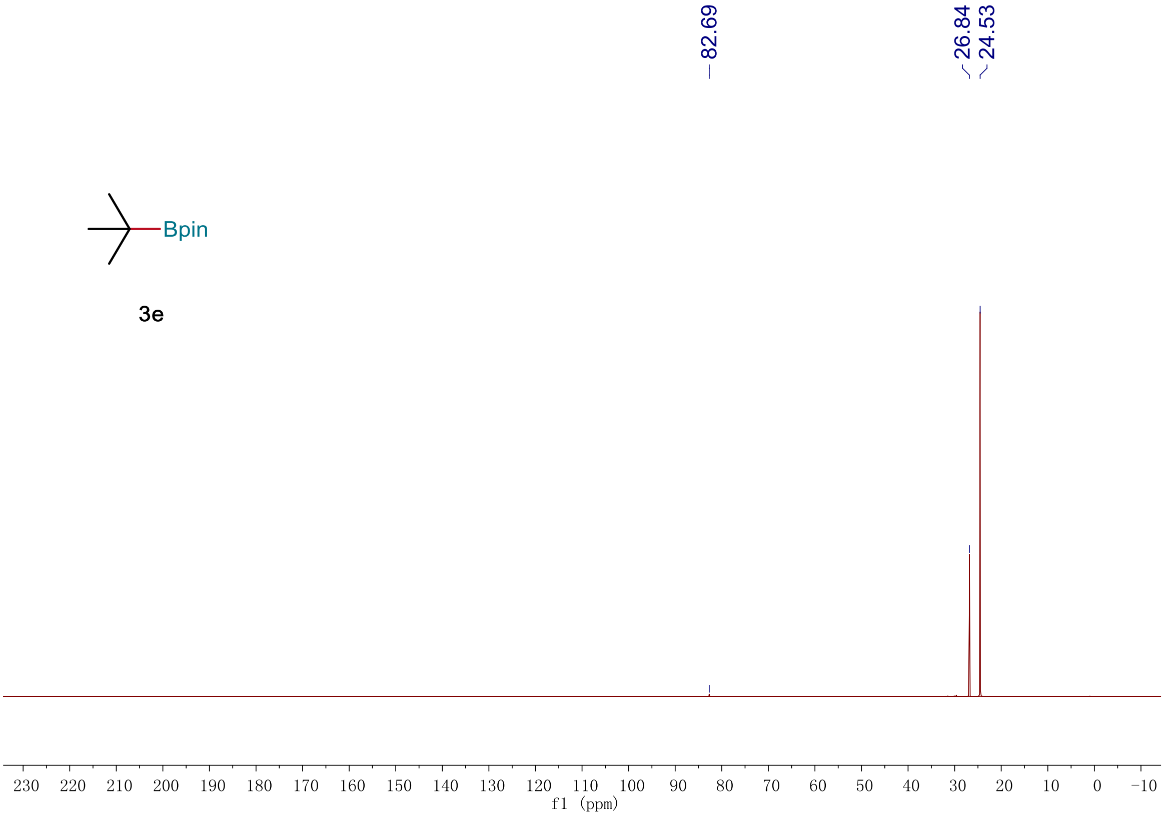

Figure S158. ^{1}H NMR spectrum of 1tu in $CDCl_3$ (400 MHz)

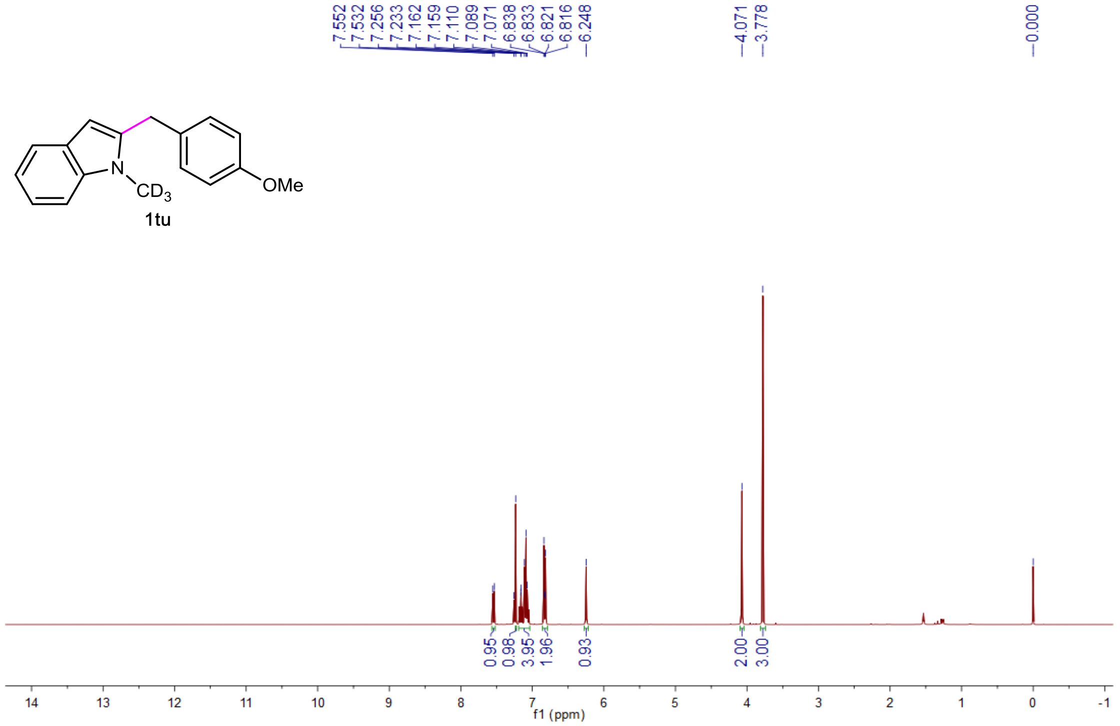

Figure S159. ^{13}C NMR spectrum of 1tu in $CDCl_3$ (100 MHz)

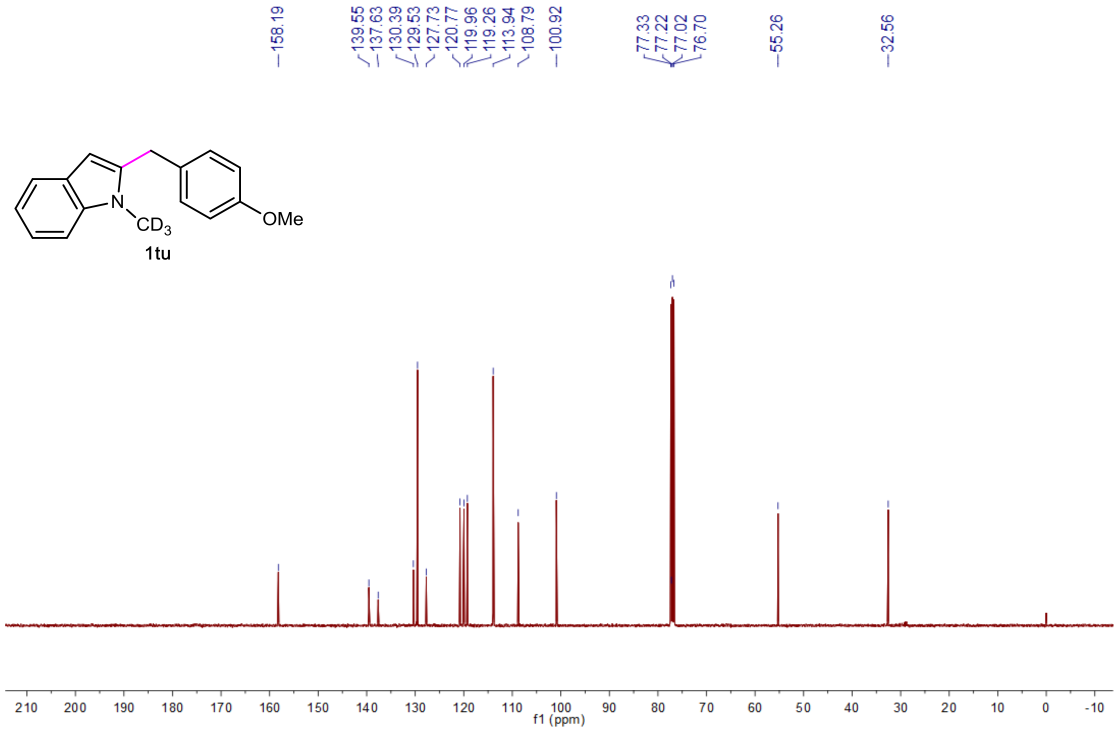

Figure S160. ^{1}H NMR spectrum of 1at in CDCl$_3$ (400 MHz)

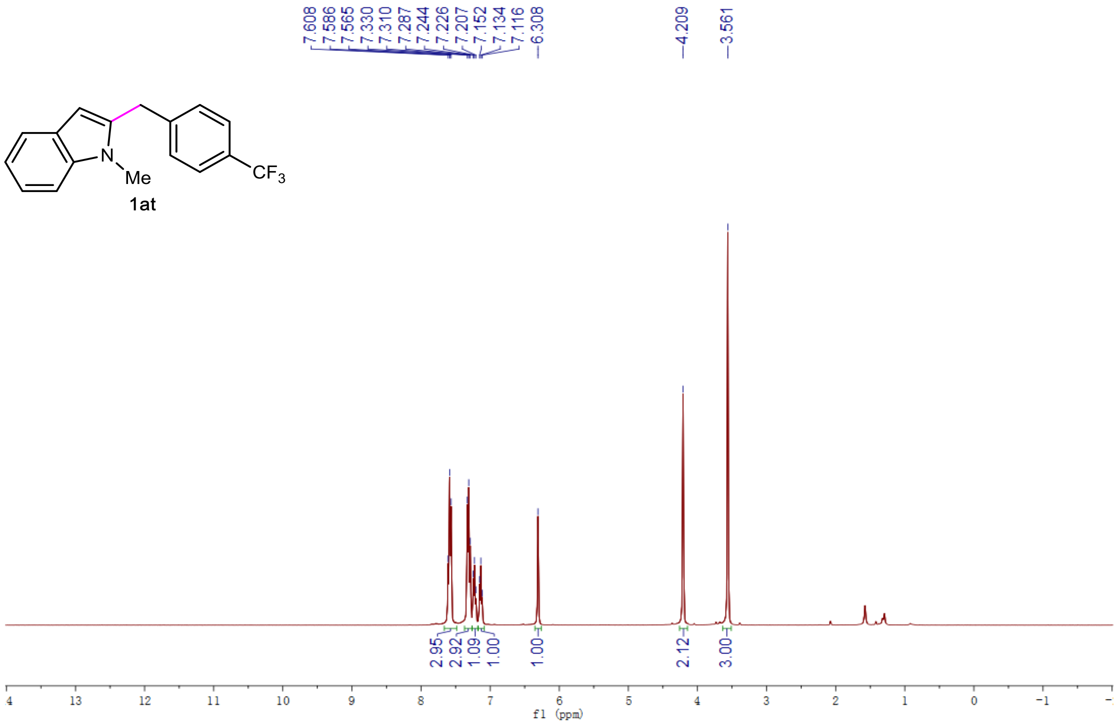

Figure S161. ^{13}C NMR spectrum of 1at in CDCl$_3$ (100 MHz)

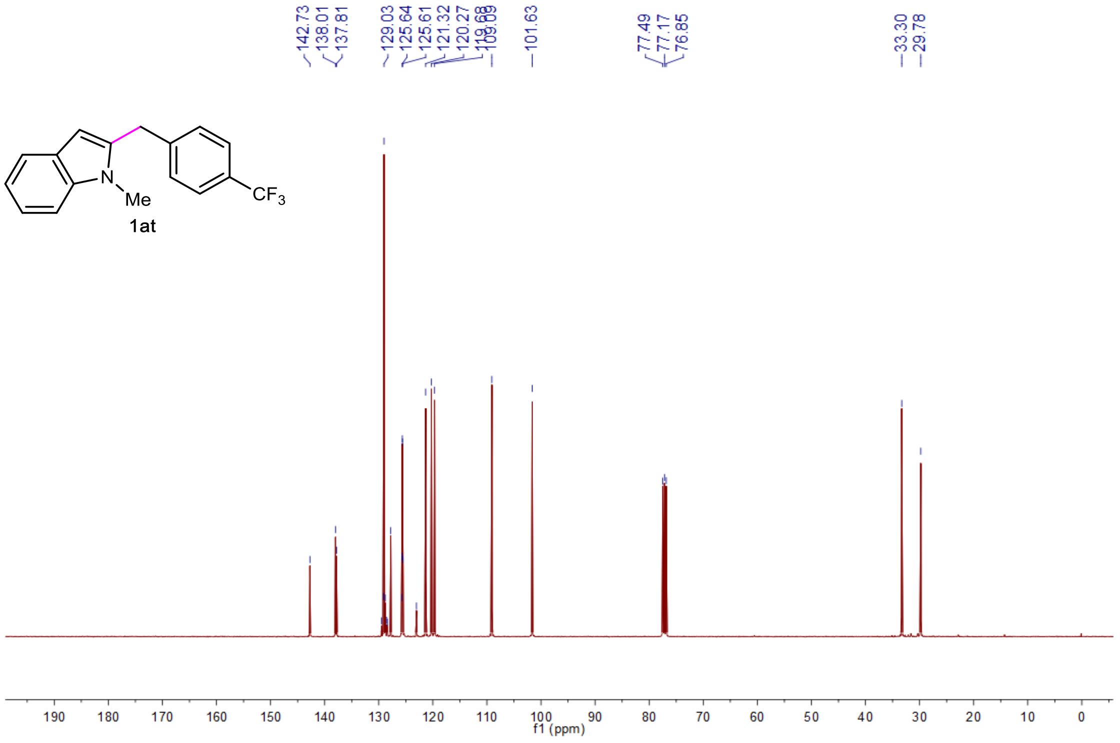

Figure S162. ^{1}H NMR spectrum of 1tw in $CDCl_3$ (400 MHz)

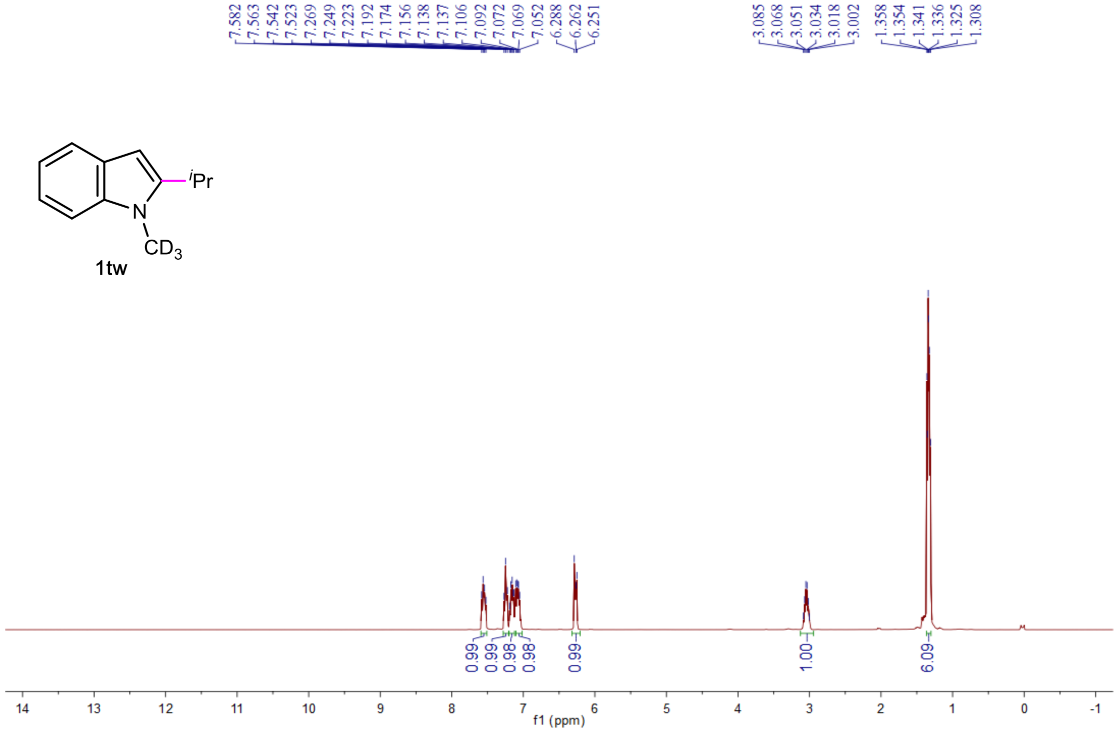

Figure S163. ^{13}C NMR spectrum of 1tw in $CDCl_3$ (100 MHz)

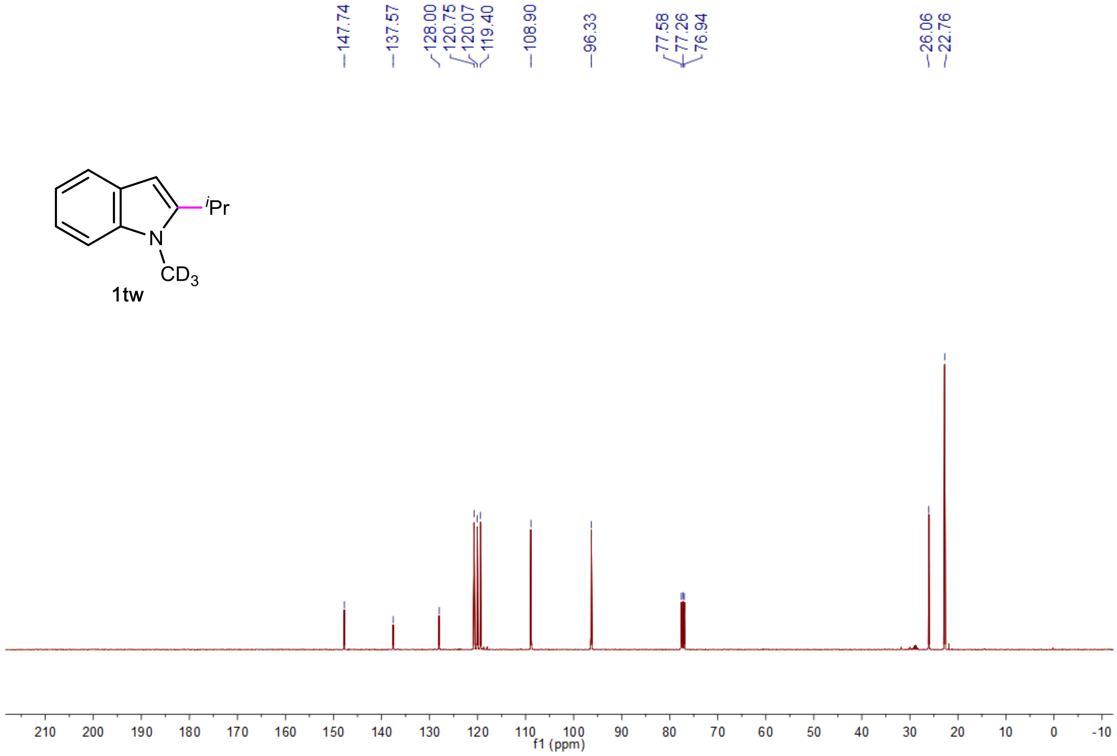

Figure S164. ^{1}H NMR spectrum of 1ta in $CDCl_3$ (400 MHz)

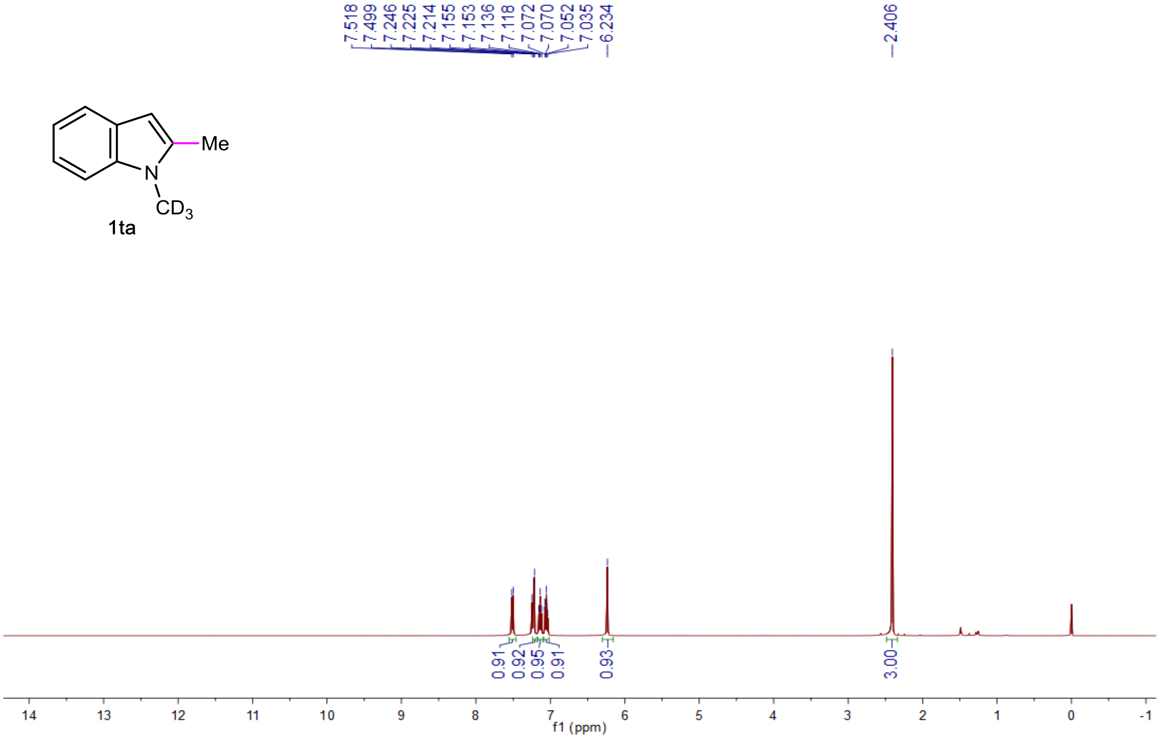

Figure S165. ^{13}C NMR spectrum of 1ta in $CDCl_3$ (100 MHz)

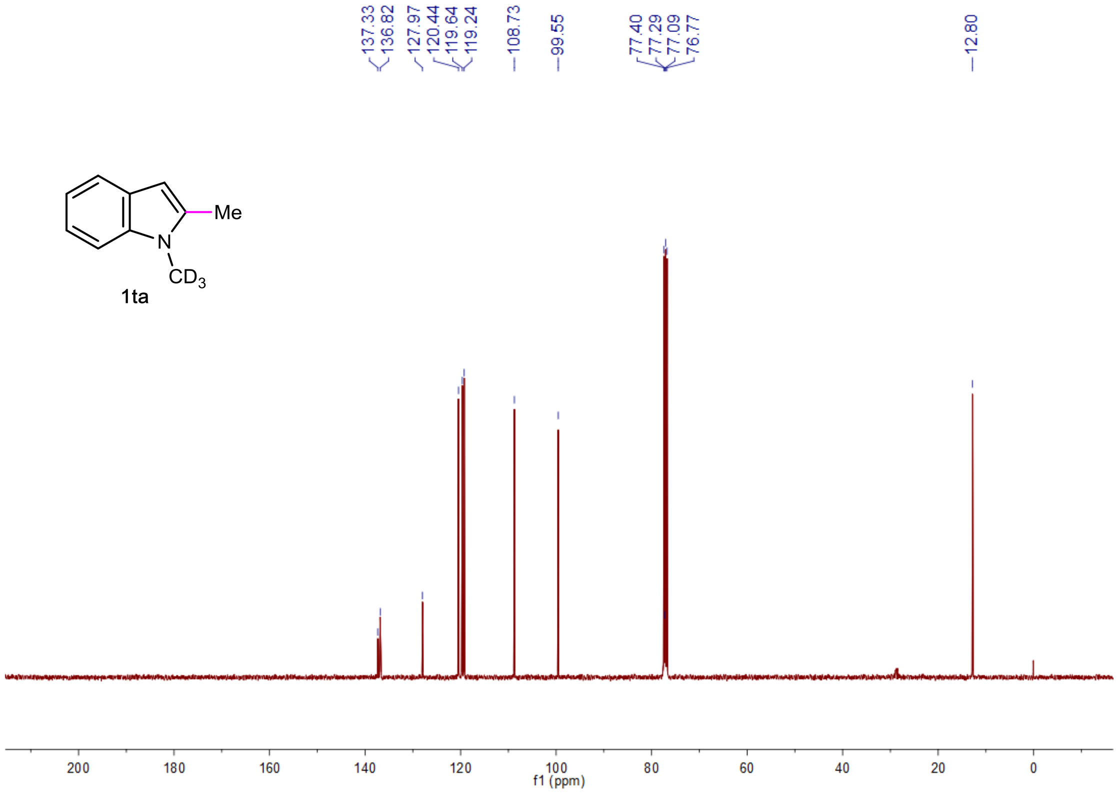

Figure S166. ^{1}H NMR spectrum of 4 in $CDCl_3$ (400 MHz)

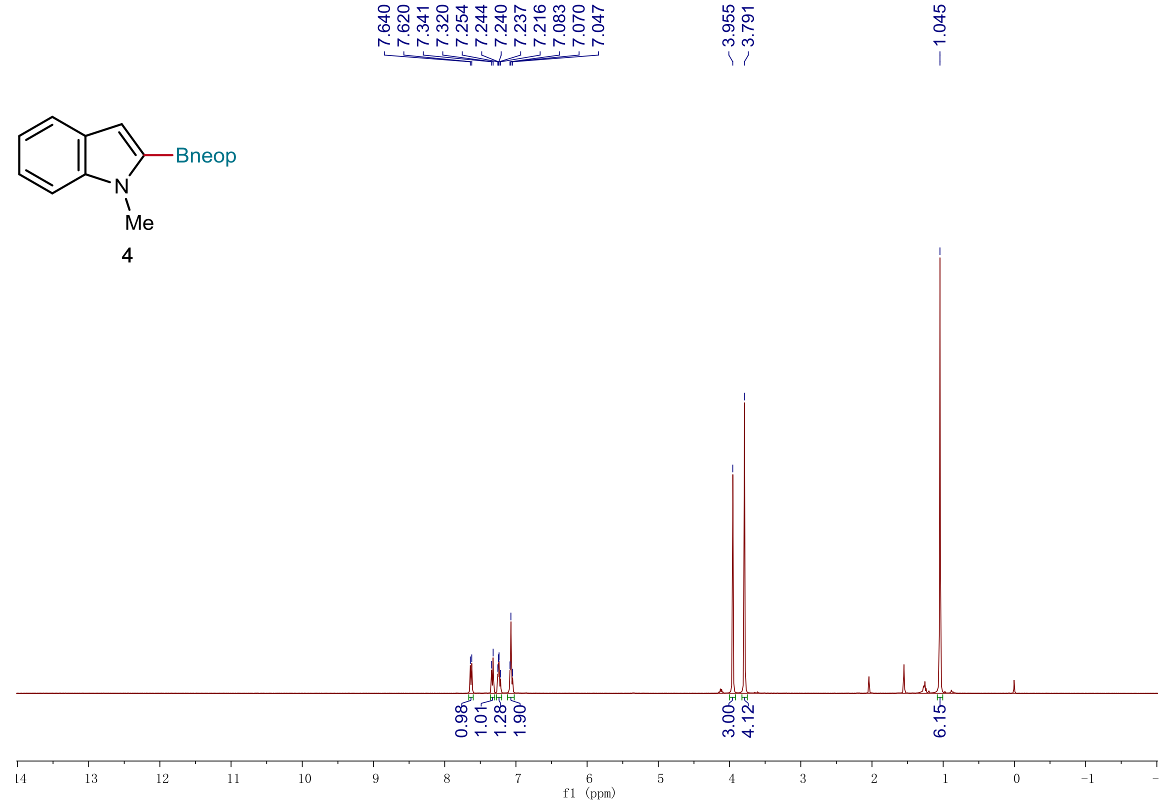

Figure S167. ^{13}C NMR spectrum of 4 in $CDCl_3$ (100 MHz)

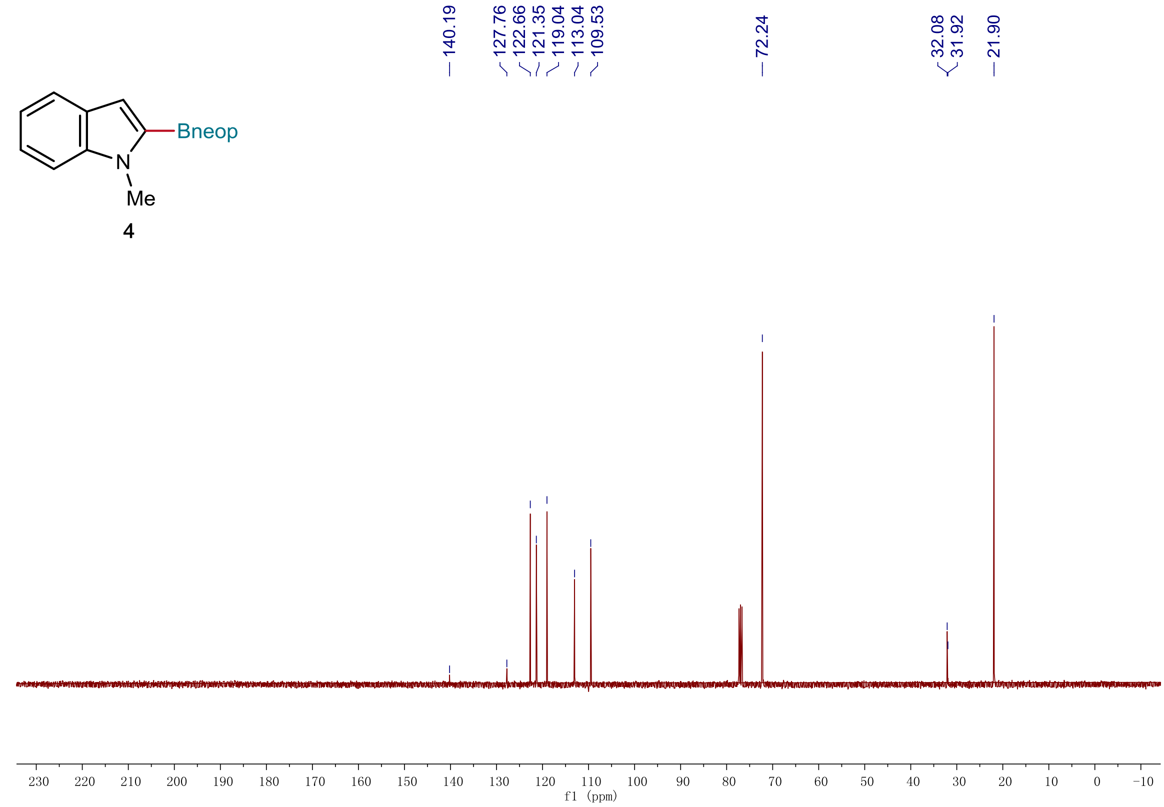

Figure S168. ^{1}H NMR spectrum of 5 in $CDCl_3$ (400 MHz)

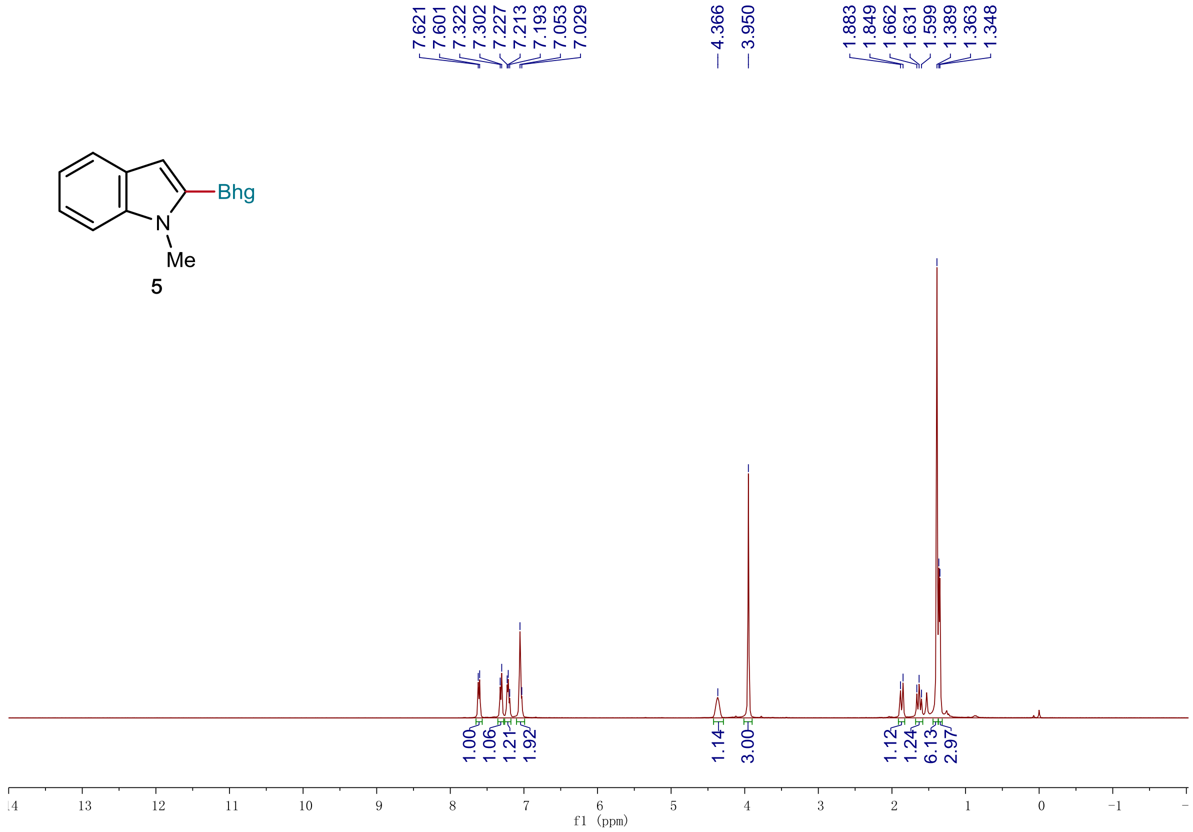

Figure S169. ^{13}C NMR spectrum of 5 in $CDCl_3$ (100 MHz)

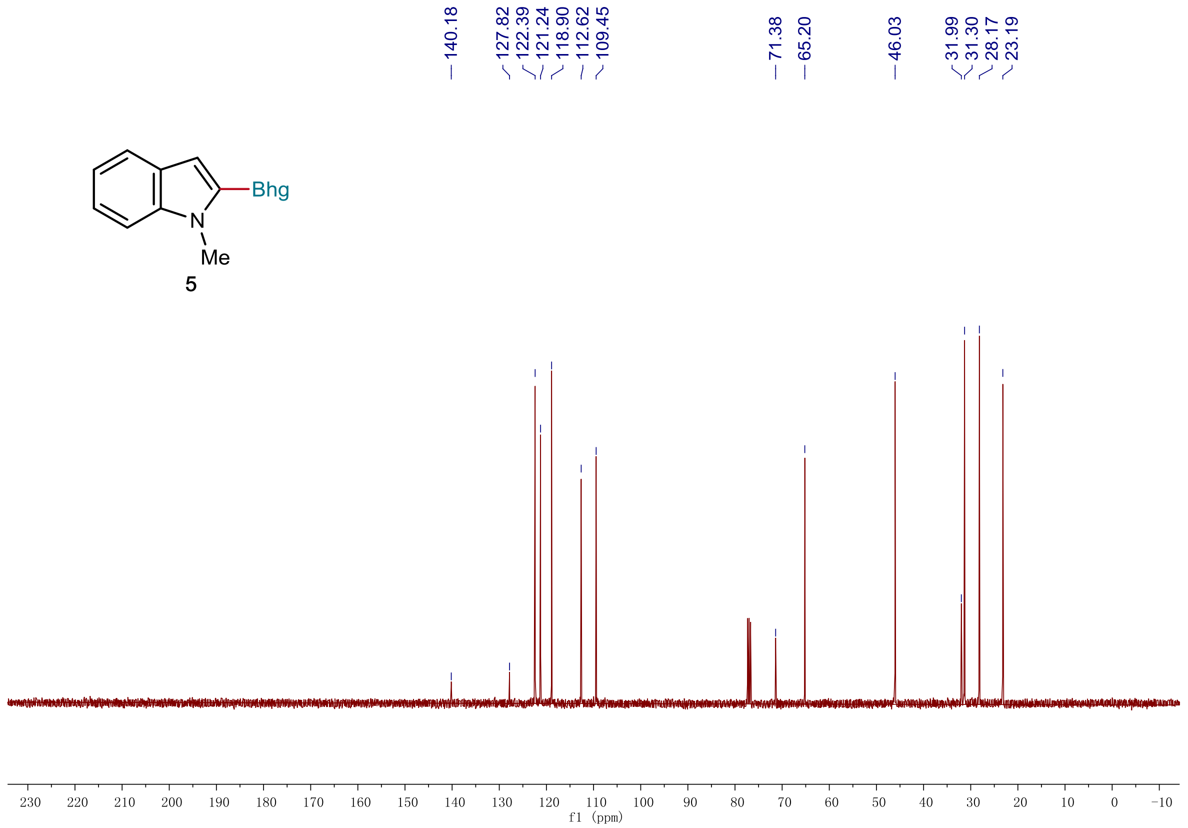

Figure S170. ^{1}H NMR spectrum of S2a’ in CDCl$_3$ (400 MHz)

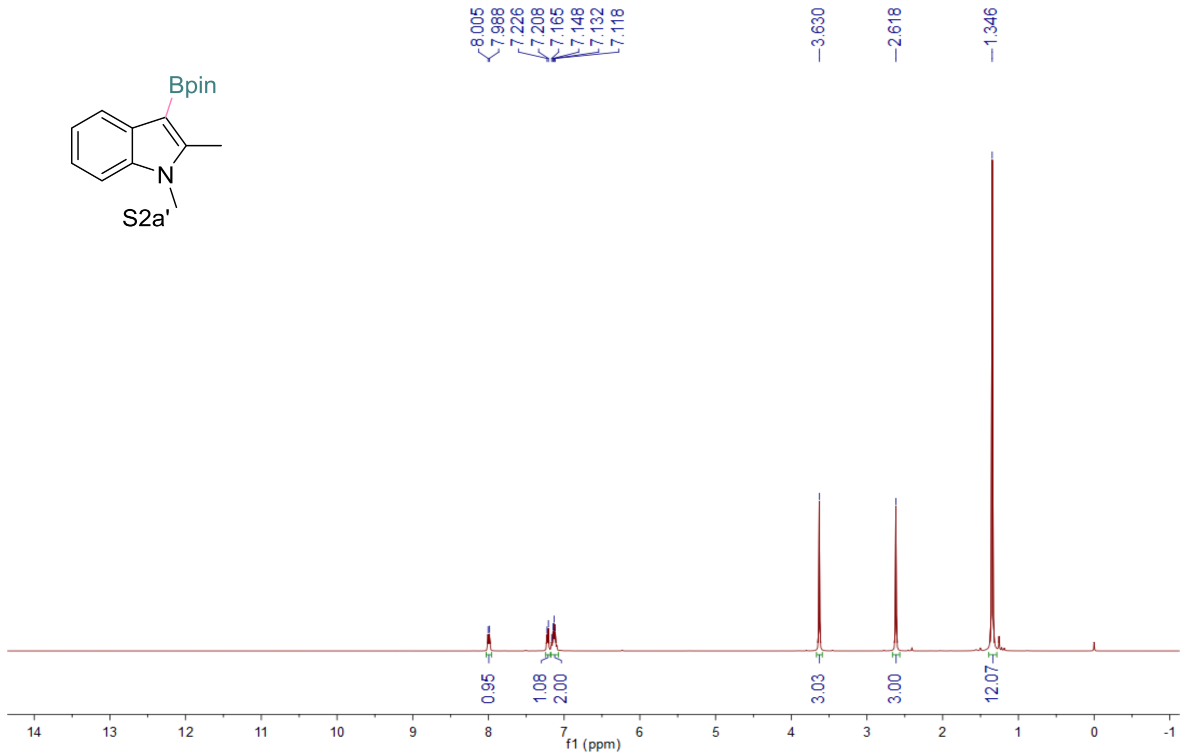

Figure S171. ^{13}C NMR spectrum of S2a’ in CDCl$_3$ (100 MHz)