Supplementary Information

Dispersion-controlled C6-selective C–H borylation of indoles

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1. General Information

All reagents, unless otherwise stated, were used as supplied from *J&K* and others commercial sources without further purification. $[Ir(COD)OMe]_2$ was purchased from TCI, B_2pin_2 was purchased from *J&K* and HBpin was purchased from Energy Chemical used as received and stored in a glovebox filled with argon. Extra dry 1,4-dioxane with molecular sieves was also purchased from *J&K* and used without further purification. All borylation reactions were carried out in extra dry and degassed 1,4-dioxane in a glove box filled with argon.

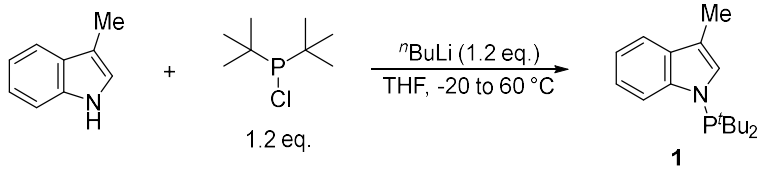
NMR spectra were recorded on *Bruker Avance III* 400 MHz (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR, 128 MHz for ^{11}B NMR, and 162 MHz for ^{31}P NMR) or 500 MHz (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR, 470 MHz for ^{19}F NMR, 160 MHz for ^{11}B NMR, and 202 MHz for ^{31}P NMR). Chemical shifts are reported in parts per million (ppm) and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent ($CDCl_3$: 7.26 ppm). ^{13}C NMR spectra were recorded on the same spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm).

Data are reported as follows: chemical shift δ/ppm, integration (^{1}H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet or combinations, ^{13}C signals are singlets unless otherwise stated), coupling constants J in Hz, assignment. The C atom attached to B atom was generally not observed by ^{13}C spectroscopy due to quadrupolar relaxation.

High resolution mass spectrometry (HRMS) analyses were performed on a *Thermo Fisher Q Exactive* mass spectrometer, and measured values are reported to 4 decimal places.

2. Synthesis of substrates

2.1 Synthesis of 1-(di-*tert*-butylphosphaneyl)-3-methyl-1*H*-indole (1)



1

Under N_2 atmosphere, a 50 mL Schlenk flask was charged with a stir bar and 0.328 g 3-methyl-1*H*-indole (2.5 mmol, 1.0 equiv.) and 8 mL anhydrous THF. Then ^{n}BuLi (2.4 M solution in hexane, 1.25 mL, 1.2 equiv.) was added slowly at -20 °C. The mixture was allowed to stir and warm to room temperature over two hours. Then the solution of 0.542 g di-*tert*-butylchlorophosphane (3.0 mmol, 1.2 equiv.) in 8 mL anhydrous THF was added at room temperature and the reaction was heated at 60 °C for 4 h. The reaction was monitored by TLC, cooled to room temperature and quenched with ethanol when finished. The mixture was poured into 40 mL H_2O and extracted with ethyl acetate (3 × 25 mL). The combined organics were dried with Na_2SO_4 and evaporated. Further purification was carried out by flash chromatography on silica gel with petroleum ether/ ethyl acetate (5:1) to afford the pure product **1** (0.525 g, 76%).

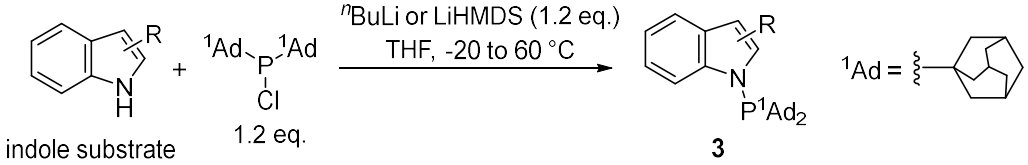
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.80 (m, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 2.33 (s, 3H), 1.21 (d, *J* = 12.6 Hz, 18H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.2 (d, *J* = 21.4 Hz), 129.4 (d, *J* = 3.4 Hz), 127.9 (d, *J* = 9.1 Hz), 121.8 (d, *J* = 1.8 Hz), 119.5, 118.2, 114.3 (d, *J* = 2.1 Hz), 112.9 (d, *J* = 20.4 Hz), 35.1 (d, *J* = 25.0 Hz), 29.2 (d, *J* = 16.3 Hz), 10.0.

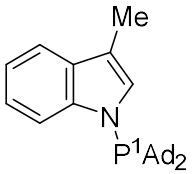
^{31}P NMR (162 MHz, Chloroform-*d*) δ 70.0.

2.2 Synthesis of substrates 3

General procedure A:



Under N_2 atmosphere, a 50 mL Schlenk flask was charged with a stir bar and indole substrate (2.5 mmol, 1.0 equiv.) and 8 mL anhydrous THF. Then ^{n}BuLi or LiHMDS (1.2 equiv) was added slowly at -20 °C. The mixture was allowed to stir and warm to room temperature over two hours. Then the solution of di(1-adamantyl)chlorophosphine (1.2 equiv.) in 5 mL anhydrous THF was added at room temperature and the reaction was heated at 60 °C for 12 h. The reaction was monitored by TLC, cooled to room temperature and quenched with ethanol when finished. The mixture was poured into 40 mL H_2O and extracted with ethyl acetate (3 × 25 mL). The combined organics were dried with Na_2SO_4 and evaporated. Further purification was carried out by flash chromatography on silica gel with petroleum ether/ ethyl acetate to afford the pure product **3**.



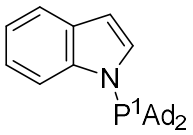
1-(Di(adamantan-1-yl)phosphanyl)-3-ethyl-1*H*-indole (3a)

According to **general procedure A** with ^{n}BuLi used, compound **3a** was prepared from 3-methyl-1*H*-indole and di(1-adamantyl)chlorophosphine in 74% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.78 (m, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.22 – 7.16 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 2.36 (s, 3H), 2.02 – 1.96 (m, 6H), 1.93 – 1.84 (m, 12H), 1.68 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.3 (d, *J* = 20.9 Hz), 129.3 (d, *J* = 8.5 Hz), 125.5, 121.6 (d, *J* = 1.9 Hz), 119.4, 118.1, 113.7 (d, *J* = 2.3 Hz), 113.0 (d, *J* = 20.3 Hz), 40.2 (d, *J* = 13.4 Hz), 39.3 (d, *J* = 24.8 Hz), 36.8, 28.4 (d, *J* = 9.2 Hz), 10.0.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 67.7.



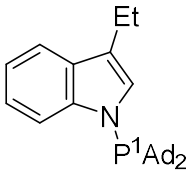
1-(Di(adamantan-1-yl)phosphaneyl)-1*H*-indole (3b)

According to **general procedure A** with ^{n}BuLi used, compound **3b** was prepared from 1*H*-indole and di(1-adamantyl)chlorophosphine in 61% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.83 (m, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 3.3 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 2.8 Hz, 1H), 2.02 – 1.97 (m, 6H), 1.92 – 1.85 (m, 12H), 1.68 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.9 (d, *J* = 20.8 Hz), 132.2 (d, *J* = 8.5 Hz), 128.7 (d, *J* = 3.0 Hz), 121.6 (d, *J* = 1.8 Hz), 120.0 (d, *J* = 16.0 Hz), 113.2, 113.0, 104.8 (d, *J* = 2.2 Hz), 40.2 (d, *J* = 13.6 Hz), 39.4 (d, *J* = 25.7 Hz), 36.8, 28.4 (d, *J* = 9.2 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 68.9.



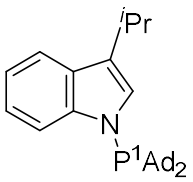
1-(Di(adamantan-1-yl)phosphanyl)-3-ethyl-1*H*-indole (3c)

According to **general procedure A** with ^{n}BuLi used, compound **3c** was prepared from 3-ethyl-1*H*-indole and di(1-adamantyl)chlorophosphine in 59% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 2.81 (q, *J* = 7.5 Hz, 2H), 2.02 – 1.96 (m, 6H), 1.93 – 1.84 (m, 12H), 1.68 (m, 12H), 1.36 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.5 (d, *J* = 20.9 Hz), 128.5 (d, *J* = 3.5 Hz), 128.2 (d, *J* = 8.5 Hz), 121.6 (d, *J* = 1.8 Hz), 120.8 (d, *J* = 2.3 Hz), 119.3, 118.3, 113.1 (d, *J* = 20.0 Hz), 40.3 (d, *J* = 13.6 Hz), 39.4 (d, *J* = 24.9 Hz), 36.8, 28.4 (d, *J* = 9.1 Hz), 18.5, 14.5.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 68.0.



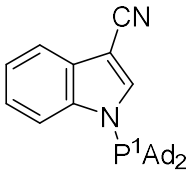
1-(Di(adamantan-1-yl)phosphaneyl)-3-isopropyl-1*H*-indole (3d)

According to **general procedure A** with ^{n}BuLi used, compound **3d** was prepared from 3-isopropyl-1*H*-indole [1] and di(1-adamantyl)chlorophosphine in 26% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.79 (m, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.10 (t, *J* = 6.9 Hz, 1H), 3.28 – 3.15 (m, 1H), 2.01 – 1.95 (m, 6H), 1.93 – 1.84 (m, 12H), 1.68 (m, 12H), 1.39 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.7 (d, *J* = 20.9 Hz), 127.9 (d, *J* = 3.3 Hz), 127.1 (d, *J* = 8.6 Hz), 125.8 (d, *J* = 2.2 Hz), 121.5 (d, *J* = 1.8 Hz), 119.2, 118.7, 113.2 (d, *J* = 20.2 Hz), 40.3 (d, *J* = 13.6 Hz), 39.4 (d, *J* = 25.1 Hz), 36.8, 28.4 (d, *J* = 9.1 Hz), 25.6, 23.4.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 68.5.



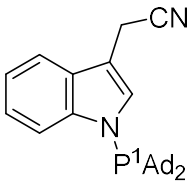
1-(Di(adamantan-1-yl)phosphanyl)-1*H*-indole-3-carbonitrile (3e)

According to **general procedure A** with LiHMDS used, compound **3e** was prepared from 1*H*-indole-3-carbonitrile and di(1-adamantyl)chlorophosphine in 67% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.27 (m, 2H), 1.97 – 1.92 (m, 12H), 1.86 – 1.81 (m, 6H), 1.70 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.0 (d, *J* = 19.6 Hz), 139.5 (d, *J* = 9.0 Hz), 127.4, 123.9, 122.3, 119.2, 116.0, 114.1 (d, *J* = 19.6 Hz), 89.6 (d, *J* = 3.8 Hz), 40.1 (d, *J* = 13.6 Hz), 39.5 (d, *J* = 27.7 Hz), 36.5, 28.2 (d, *J* = 9.1 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 75.4.



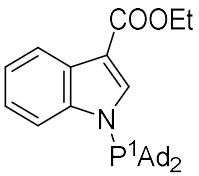
2-(1-(Di(adamantan-1-yl)phosphanyl)-1*H*-indol-3-yl)acetonitrile (3f)

According to **general procedure A** with LiHMDS used, compound **3f** was prepared from 2-(1*H*-indol-3-yl)acetonitrile and di(1-adamantyl)chlorophosphine in 45% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.45 (s, 1H), 7.29 – 7.23 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 3.88 (s, 2H), 2.00 – 1.92 (m, 12H), 1.88 – 1.82 (m, 6H), 1.69 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.5 (d, *J* = 20.8 Hz), 130.3 (d, *J* = 8.8 Hz), 126.8 (d, *J* = 3.1 Hz), 122.7 (d, *J* = 1.8 Hz), 120.4, 118.1, 117.5, 113.6 (d, *J* = 20.3 Hz), 106.8 (d, *J* = 2.8 Hz), 40.2 (d, *J* = 13.6 Hz), 39.4 (d, *J* = 25.9 Hz), 36.7, 28.3 (d, *J* = 9.1 Hz), 14.7.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 70.5.



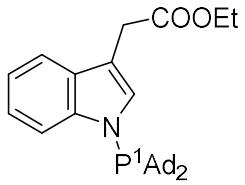
Ethyl 1-(di(adamantan-1-yl)phosphanyl)-1*H*-indole-3-carboxylate (3g)

According to **general procedure A** with LiHMDS used, compound **3g** was prepared from ethyl 1*H*-indole-3-carboxylate and di(1-adamantyl)chlorophosphine in 53% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 8.14 – 8.10 (m, 1H), 7.90 – 7.83 (m, 1H), 7.28 – 7.23 (m, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.00 – 1.92 (m, 12H), 1.89 – 1.83 (m, 6H), 1.69 (m, 12H), 1.47 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.4, 146.1 (d, *J* = 44.3 Hz), 138.9 (d, *J* = 8.7 Hz), 126.3, 122.8, 121.9, 121.0, 116.2, 113.6 (d, *J* = 20.3 Hz), 59.9, 40.1 (d, *J* = 13.6 Hz), 39.3 (d, *J* = 27.1 Hz), 36.6, 28.3 (d, *J* = 9.2 Hz), 14.6.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 73.3.



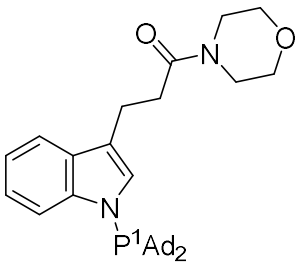
Ethyl 2-(1-(di(adamantan-1-yl)phosphanyl)-1*H*-indol-3-yl)acetate (3h)

According to **general procedure A** with LiHMDS used, compound **3h** was prepared from ethyl 2-(1*H*-indol-3-yl)acetate and di(1-adamantyl)chlorophosphine in 42% yield.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 – 7.79 (m, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.44 (s, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 6.9 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 2H), 2.01 – 1.96 (m, 6H), 1.93 – 1.84 (m, 12H), 1.68 (m, 12H), 1.23 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 144.1 (d, *J* = 20.7 Hz), 130.8 (d, *J* = 8.6 Hz), 128.2 (d, *J* = 3.2 Hz), 121.9 (d, *J* = 1.8 Hz), 119.8, 118.2, 113.2 (d, *J* = 20.0 Hz), 110.6 (d, *J* = 2.6 Hz), 60.7, 40.2 (d, *J* = 13.6 Hz), 39.3 (d, *J* = 25.5 Hz), 36.7, 31.6, 28.4 (d, *J* = 9.1 Hz), 14.2.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 69.1.



1-(1-(Di(adamantan-1-yl)phosphaneyl)-1*H*-indol-3-yl)-1-morpholinopropan-1-one (3i)

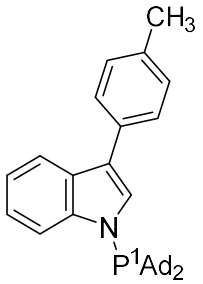
According to **general procedure A** with LiHMDS used, compound **3i** was prepared from 3-(1*H*-indol-3-yl)-1-morpholinopropan-1-one [2] and di(1-adamantyl)chlorophosphine in 85% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.79 (m, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.28 (s, 1H), 7.19 (t, *J* = 7.0 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 3.60 (m, 4H), 3.46 (t, *J* = 4.8 Hz, 2H), 3.33 (t, *J* = 4.8 Hz, 2H), 3.16 (t, *J* = 7.5 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.00 – 1.90 (m, 12H), 1.87 – 1.82 (m, 6H), 1.68 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.4, 144.4 (d, *J* = 20.9 Hz), 129.7 (d, *J* = 8.6 Hz),

128.2, 121.8, 119.6, 118.0, 117.2, 113.3 (d, J = 20.1 Hz), 66.8, 66.5, 46.0, 41.9, 40.2 (d, J = 13.6 Hz), 39.3 (d, J = 25.4 Hz), 36.7, 33.8, 28.4 (d, J = 9.0 Hz), 21.3.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 68.7.



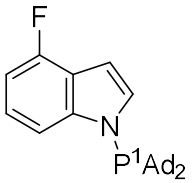
1-(Di(adamantan-1-yl)phosphaneyl)-3-(*p*-tolyl)-1*H*-indole (3j)

According to **general procedure A** with ^{n}BuLi used, compound **3i** was prepared from 3-(*p*-tolyl)-1*H*-indole [3] and di(1-adamantyl)chlorophosphine in 63% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.89 (m, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.56 (s, 1H), 7.29 (d, J = 7.8 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.18 (t, J = 7.7 Hz, 1H), 2.42 (s, 3H), 2.06 – 2.01 (m, 6H), 1.94 – 1.89 (m, 12H), 1.69 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.8 (d, J = 20.5 Hz), 135.8, 132.6, 129.4 (d, J = 3.5 Hz), 129.3, 127.6, 126.9, 122.0, 120.3, 120.0, 119.1, 113.4 (d, J = 20.4 Hz), 40.3 (d, J = 13.5 Hz), 39.4 (d, J = 25.9 Hz), 36.8, 28.4 (d, J = 9.1 Hz), 21.2.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 69.3.



1-(Di(adamantan-1-yl)phosphaneyl)-4-fluoro-1*H*-indole (3k)

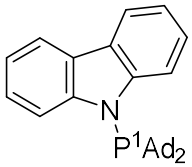
According to **general procedure A** with ^{n}BuLi used, compound **3k** was prepared from 4-fluoro-1*H*-indole and di(1-adamantyl)chlorophosphine in 54% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.59 (m, 1H), 7.42 (d, J = 3.3 Hz, 1H), 7.12 – 7.06 (m, 1H), 6.81 – 6.75 (m, 1H), 6.73 (d, J = 4.4 Hz, 1H), 2.00 – 1.92 (m, 12H), 1.88 – 1.83 (m, 6H), 1.69 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.2 (d, *J* = 248.1 Hz), 140.2 (d, *J* = 10.9 Hz), 132.1 (d, *J* = 8.3 Hz), 121.9 (d, *J* = 7.7 Hz), 117.7, 109.2 (dd, *J* = 20.4, 3.5 Hz), 104.7 (d, *J* = 18.7 Hz), 100.7 (d, *J* = 2.4 Hz), 40.2 (d, *J* = 13.6 Hz), 39.4 (d, *J* = 25.9 Hz), 36.7, 28.3 (d, *J* = 9.1 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 71.6.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -123.3.



9-(Di(adamantan-1-yl)phosphaneyl)-9*H*-carbazole (3l)

According to **general procedure A** with ^{n}BuLi used, compound **3l** was prepared from 9*H*-carbazole and di(1-adamantyl)chlorophosphine in 37% yield.

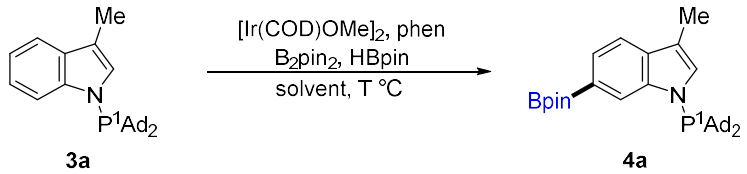
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.15 (m, 1H), 8.08 – 8.05 (m, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.28 – 7.21 (m, 2H), 2.15 – 2.00 (m, 12H), 1.93 – 1.88 (m, 6H), 1.67 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.3 (d, *J* = 26.2 Hz), 144.0 (d, *J* = 13.2 Hz), 126.0 (d, *J* = 1.9 Hz), 125.4 (d, *J* = 2.8 Hz), 124.8, 124.6 (d, *J* = 3.2 Hz), 120.0, 119.9 (d, *J* = 2.0 Hz), 119.8, 119.2, 115.8, 114.3 (d, *J* = 30.0 Hz), 41.4 (d, *J* = 15.3 Hz), 40.5 (d, *J* = 31.4 Hz), 36.7, 28.6 (d, *J* = 9.7 Hz).

^{31}P NMR (162 MHz, Chloroform-*d*) δ 77.3.

3. Screening of C6-borylation reactions of indoles

All screening reactions were performed on a 0.1 mmol scale using dry solvents. Conversion and the C6:C5 regioselectivity ratio were determined from crude ^{1}H NMR spectra.

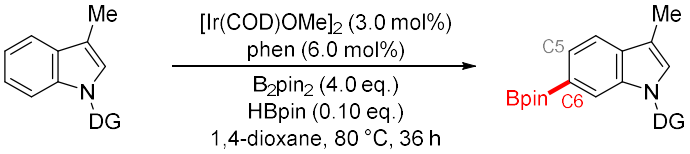


3a **4a**

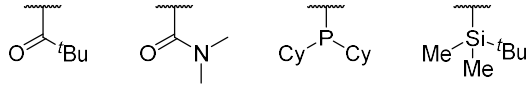
Table S1. Optimization of borylation of 3a

Entry	[Ir] (mol%)	phen (mol%)	B_2pin_2 (eq.)	HBpin (eq.)	Solvent (1 mL)	Temp. (°C)	Time (h)	Conv. (%)	**C6:C5**
1	5	10	1.0	0	*n*-Hexane	80	24	14	85:15
2	5	10	2.0	0	*n*-Hexane	80	24	18	85:15
3	5	10	4.0	0	*n*-Hexane	80	24	53	86:14
4	5	10	4.0	0.10	*n*-Hexane	80	24	73	88:12
5	5	10	4.0	0.25	*n*-Hexane	80	24	67	88:12
6	5	10	4.0	0.50	*n*-Hexane	80	24	55	87:13
7	5	10	4.0	0.10	Cyclohexane	80	24	44	89:11
8	5	10	4.0	0.10	1,4-Dioxane	80	24	84	88:12
9	5	10	4.0	0.10	THF	80	24	43	83:17
10	5	10	4.0	0.10	1,4-Dioxane	60	24	54	88:12
11	5	10	4.0	0.10	1,4-Dioxane	100	24	83	87:13
12	3	6	4.0	0.10	1,4-Dioxane	80	24	67	87:13
13	1.5	3	4.0	0.10	1,4-Dioxane	80	24	51	87:13
14	3	6	4.0	0.10	1,4-Dioxane	80	36	81	88:12
15	3	6	4.0	0.10	1,4-Dioxane	80	48	79	88:12
16	**3**	**6**	**4.0**	**0.10**	**1,4-Dioxane (0.5 mL)**	**80**	**36**	**89**	**90:10**
17	3	6	4.0	0.10	1,4-Dioxane (1.5 mL)	80	36	85	87:13

Table S2. Screening of directing groups for C6-borylation

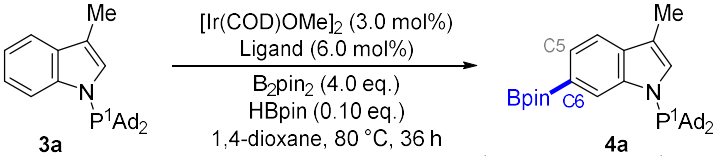


DG	conv.	C6:C5
DG1	91%	45:55
DG2	99%	31:69
DG3	messy	-
DG4	97%	83:17

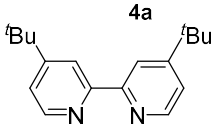


DG1 **DG2** **DG3** **DG4**

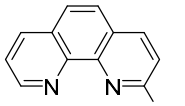
Table S3. Screening of ligands for C6-borylation



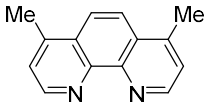
Ligand	conv.	C6:C5
dtbpy	20%	67:33
phen-1	38%	76:24
phen-2	41%	56:44
phen-3	78%	79:21
phen-4	34%	83:17
phen-5	82%	86:14
phen-6	87%	88:12
phen-7	10%	78:22
phen-8	2%	88:12



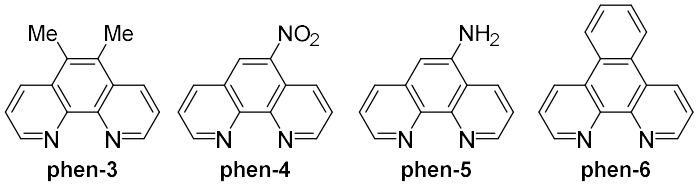
dtbpy



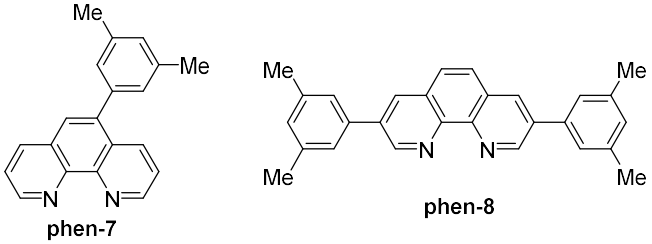
phen-1



phen-2



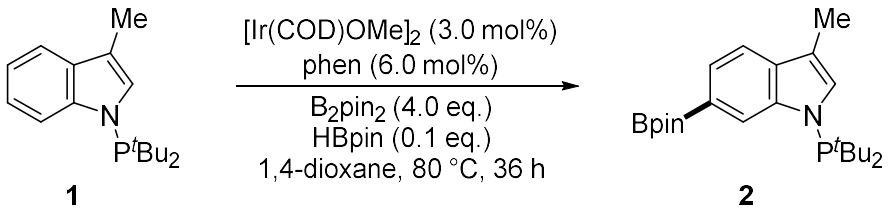
phen-3 **phen-4** **phen-5** **phen-6**



phen-7 **phen-8**

4. General procedure of borylation reactions and characterization of products

4.1 Borylation of 1-(di-*tert*-butylphosphaneyl)-3-methyl-1*H*-indole



1 **2**

1-(Di-*tert*-butylphosphaneyl)-3-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (2)

In an argon-filled glove box, a 4 mL vial was charged with 3.3 mg $[Ir(COD)OMe]_2$ (0.005 mmol, 3.0 mol%), 1.8 mg 1,10-phenanthroline (0.010 mmol, 6.0 mol%), 101.7 mg B_2pin_2 (0.4 mmol, 4.0 equiv.), 0.5 mL 1,4-dioxane and 1.5 μL HBpin (0.01 mmol, 0.1 equiv.). To the vial was added a magnetic stir bar, and the vial was sealed with a Teflon-lined cap and stirred at 25 °C for minutes. Then, 27.5 mg **1** (0.1 mmol) was added to the reaction system and stirred at 80 °C for 24 hours. The mixture was concentrated in vacuo. The crude residue was purified by chromatography on silica gel with petroleum ether/ DCM (2:1) to afford 13.6 mg **2** (34% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.26 (m, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.25 (s, 1H), 2.33 (s, 3H), 1.36 (s, 12H), 1.21 (d, *J* = 12.6 Hz, 18H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 143.8 (d, *J* = 21.1 Hz), 131.8 (d, *J* = 3.4 Hz), 129.4 (d, *J* = 8.7 Hz), 125.7, 119.6 (d, *J* = 19.2 Hz), 117.6, 114.3, 83.4, 35.1 (d, *J* = 25.8 Hz), 29.2 (d, *J* = 16.5 Hz), 24.9, 9.9.

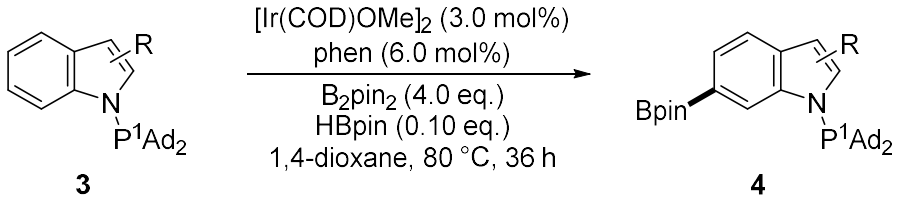
^{31}P NMR (202 MHz, Chloroform-*d*) δ 69.4.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 36.6.

HRMS m/z: $[M+H]^+$ calculated for $[C_{23}H_{38}BNO_2P]^+$ 402.2728, found 402.2714.

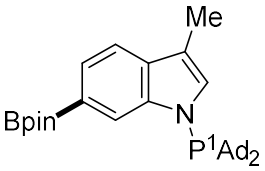
4.2 General procedure of borylation of 3

General procedure B:



3 **4**

In an argon-filled glove box, a 4 mL vial was charged with 2.0 mg $[Ir(COD)OMe]_2$ (0.003mmol, 3.0 mol%), 1.1 mg 1,10-phenanthroline (0.006 mmol, 6.0 mol%), 101.7 mg B_2pin_2 (0.4 mmol, 4.0 equiv.), 0.5 mL 1,4-dioxane and 1.5 μL HBpin (0.01 mmol, 0.1 equiv.). To the vial was added a magnetic stir bar, and the vial was sealed with a Teflon-lined cap and stirred at 25 °C for minutes. Then, substrate (0.1 mmol, 1.0 equiv.) was added to the reaction system and stirred at 80 °C for 36 hours. The mixture was concentrated in vacuo. The crude residue was purified by chromatography on silica gel to afford the pure product.



1-(Di(adamantan-1-yl)phosphaneyl)-3-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (4a)

Following the **general procedure B** using **3a** (43.2 mg, 0.1 mmol), $[Ir(COD)OMe]_2$ (2.0 mg, 3.0 mol%) , 1,10-phenanthroline (1.1 mg, 6.0 mol%) , B_2pin_2 (101.7 mg, 4.0 equiv.) , HBpin (1.5 μL, 0.1 equiv.) and 0.5 mL 1,4-dioxane. The reaction was stirred at 80 °C for 36 hours before the solvents removed. The crude product was passed through a short pad of silica gel with petroleum ether/ DCM (2:1) as the eluent to afford 43.5 mg **4a** (78% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 – 8.24 (m, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.25 (s, 1H), 2.36 (s, 3H), 2.02 – 1.98 (m, 6H), 1.92 – 1.84 (m, 12H), 1.68 (m, 12H), 1.37 (s, 12H).

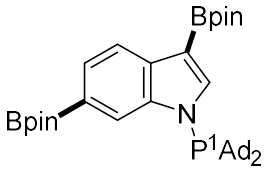
^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.9 (d, *J* = 20.8 Hz), 131.8 (d, *J* = 3.2 Hz), 130.9 (d,

J = 8.4 Hz), 125.5, 119.6 (d, *J* = 19.3 Hz), 117.5, 113.7 (d, *J* = 2.4 Hz), 83.3, 40.2 (d, *J* = 13.7 Hz), 39.3 (d, *J* = 25.7 Hz), 36.8, 28.4 (d, *J* = 9.1 Hz), 24.9, 10.0.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 67.1.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.9.

HRMS m/z: $[M+H]^+$ calculated for $[C_{35}H_{50}BNO_2P]^+$ 558.3667, found 558.3685.



1-(Di(adamantan-1-yl)phosphaneyl)-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -1*H*-indole (4b)

Following the **general procedure B** using **3b** (41.8 mg, 0.1 mmol), $[Ir(COD)OMe]_2$ (2.0 mg, 3.0 mol%) , 1,10-phenanthroline (1.1 mg, 6.0 mol%) , B_2pin_2 (101.7 mg, 4.0 equiv.) , HBpin (1.5 μL, 0.1 equiv.) and 0.5 mL 1,4-dioxane. The reaction was stirred at 80 °C for 36 hours before the solvents removed. The crude product was passed through a short pad of silica gel with petroleum ether/ DCM (2:1) as the eluent to afford 44.9 mg **4b** (67% yield).

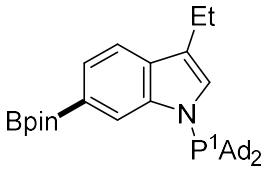
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 – 8.25 (m, 1H), 7.99 (d, *J* = 7.8 Hz, 1H), 7.87 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 2.02 – 1.97 (m, 6H), 1.92 – 1.83 (m, 12H), 1.67 (m, 12H), 1.39 (s, 12H), 1.37 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.6 (d, *J* = 20.2 Hz), 142.8 (d, *J* = 8.4 Hz), 135.2, 126.8, 121.2, 119.7 (d, *J* = 19.6 Hz), 83.3, 82.8, 40.1 (d, *J* = 13.7 Hz), 39.3 (d, *J* = 26.7 Hz), 36.7, 28.3 (d, *J* = 9.1 Hz), 25.0, 24.9.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 69.9.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.1.

HRMS m/z: $[M+H]^+$ calculated for $[C_{40}H_{59}B_2NO_4P]^+$ 670.4362, found 670.4347.



1-(Di(adamantan-1-yl)phosphaneyl)-3-ethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (4c)

Following the **general procedure B** using **3c** (44.6 mg, 0.1 mmol), $[Ir(COD)OMe]_2$ (2.0 mg, 3.0 mol%) , 1,10-phenanthroline (1.1 mg, 6.0 mol%) , B_2pin_2 (101.7 mg, 4.0 equiv.) , HBpin (1.5 μL, 0.1 equiv.) and 0.5 mL 1,4-dioxane. The reaction was stirred at 80 °C for 36 hours before the solvents removed. The crude product was passed through a short pad of silica gel with petroleum ether/ DCM (2:1) as the eluent to afford 33.7 mg **4c** (59% yield).

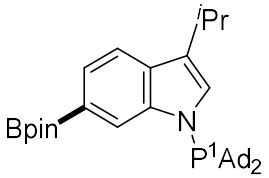
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 – 8.25 (m, 1H), 7.58 – 7.53 (m, 2H), 7.26 (s, 1H), 2.81 (q, *J* = 7.5 Hz, 2H), 2.03 – 1.97 (m, 6H), 1.93 – 1.84 (m, 12H), 1.68 (m, 12H), 1.37 – 1.33 (m, 15H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.1 (d, *J* = 20.7 Hz), 131.0 (d, *J* = 3.4 Hz), 129.8 (d, *J* = 8.5 Hz), 125.5, 120.8 (d, *J* = 2.3 Hz), 119.8 (d, *J* = 19.1 Hz), 117.6, 83.3, 40.2 (d, *J* = 13.7 Hz), 39.4 (d, *J* = 25.7 Hz), 36.8, 28.4 (d, *J* = 9.1 Hz), 24.9, 18.4, 14.6.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 67.4.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.8.

HRMS m/z: $[M+H]^+$ calculated for $[C_{36}H_{52}BNO_2P]^+$ 572.3823, found 572.3817.



1-(Di(adamantan-1-yl)phosphaneyl)-3-isopropyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (4d)

Following the **general procedure B** using **3d** (46.0 mg, 0.1 mmol), $[Ir(COD)OMe]_2$ (2.0 mg, 3.0 mol%) , 1,10-phenanthroline (1.1 mg, 6.0 mol%) , B_2pin_2 (101.7 mg, 4.0 equiv.) , HBpin (1.5 μL, 0.1 equiv.) and 0.5 mL 1,4-dioxane. The reaction was stirred at 80 °C for 36 hours

before the solvents removed. The crude product was passed through a short pad of silica gel with petroleum ether/ DCM (2:1) as the eluent to afford 27.1 mg **4d** (46% yield).

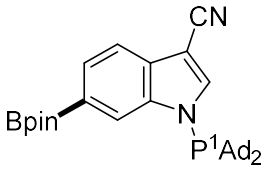
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.26 (m, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.24 (s, 1H), 3.29 – 3.17 (m, 1H), 2.03 – 1.97 (m, 6H), 1.93 – 1.85 (m, 12H), 1.69 (m, 12H), 1.40 – 1.36 (m, 18H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.3 (d, *J* = 20.5 Hz), 130.4 (d, *J* = 3.3 Hz), 128.6 (d, *J* = 8.5 Hz), 125.9 (d, *J* = 2.3 Hz), 125.4, 119.9 (d, *J* = 19.0 Hz), 118.0, 83.3, 40.3 (d, *J* = 13.8 Hz), 39.5 (d, *J* = 25.8 Hz), 36.8, 28.4 (d, *J* = 9.1 Hz), 25.5, 24.9, 23.4.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 67.7.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.8.

HRMS m/z: $[M+H]^+$ calculated for $[C_{37}H_{54}BNO_2P]^+$ 586.3980, found 586.3974.



1-(Di(adamantan-1-yl)phosphaneyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-3-carbonitrile (4e)

Following the **general procedure B** using **3e** (44.3 mg, 0.1 mmol), $[Ir(COD)OMe]_2$ (2.0 mg, 3.0 mol%) , 1,10-phenanthroline (1.1 mg, 6.0 mol%) , B_2pin_2 (101.7 mg, 4.0 equiv.) , HBpin (1.5 μL, 0.1 equiv.) and 0.5 mL 1,4-dioxane. The reaction was stirred at 80 °C for 36 hours before the solvents removed. The crude product was passed through a short pad of silica gel with petroleum ether/ DCM (1:1) as the eluent to afford 32.7 mg **4e** (57% yield).

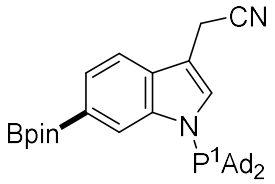
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 – 8.28 (m, 1H), 7.98 (s, 1H), 7.76 – 7.71 (m, 2H), 1.97 – 1.93 (m, 12H), 1.86 – 1.81 (m, 6H), 1.70 (m, 12H), 1.37 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.6, 140.4 (d, *J* = 8.5 Hz), 129.9, 128.3, 120.5 (d, *J* = 18.9 Hz), 118.5, 115.9, 89.6, 83.8, 40.1 (d, *J* = 13.5 Hz), 39.5 (d, *J* = 28.2 Hz), 36.5, 28.2 (d, *J* = 9.1 Hz), 24.9.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 74.7.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.3.

HRMS m/z: $[M+H]^+$ calculated for $[C_{35}H_{47}BN_2O_2P]^+$ 569.3463, found 569.3446.



2-(1-(Di(adamantan-1-yl)phosphaneyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl)acetonitrile (4f)

Following the **general procedure B** using **3f** (45.7 mg, 0.1 mmol), $[Ir(COD)OMe]_2$ (2.0 mg, 3.0 mol%) , 1,10-phenanthroline (1.1 mg, 6.0 mol%) , B_2pin_2 (101.7 mg, 4.0 equiv.) , HBpin (1.5 μL, 0.1 equiv.) and 0.5 mL 1,4-dioxane. The reaction was stirred at 80 °C for 36 hours before the solvents removed. The crude product was passed through a short pad of silica gel with petroleum ether/ DCM (1:1) as the eluent to afford 29.7 mg **4f** (51% yield).

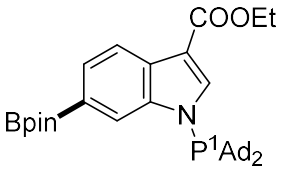
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 – 8.28 (m, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.49 (m, 2H), 3.88 (s, 2H), 2.00 – 1.92 (m, 12H), 1.88 – 1.83 (m, 6H), 1.69 (m, 12H), 1.37 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.0 (d, *J* = 20.3 Hz), 131.6 (d, *J* = 8.6 Hz), 129.2, 126.5, 120.2 (d, *J* = 19.1 Hz), 118.1, 116.7, 106.8, 83.6, 40.2 (d, *J* = 13.7 Hz), 39.4 (d, *J* = 26.6 Hz), 36.7, 28.3 (d, *J* = 9.1 Hz), 24.9, 14.6.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 69.9.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.9.

HRMS m/z: $[M+H]^+$ calculated for $[C_{36}H_{49}BN_2O_2P]^+$ 583.3619, found 583.3608.



Ethyl 1-(di(adamantan-1-yl)phosphaneyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-3-carboxylate (4g)

Following the **general procedure B** using **3g** (49.0 mg, 0.1 mmol), $[Ir(COD)OMe]_2$ (2.0 mg, 3.0 mol%) , 1,10-phenanthroline (1.1 mg, 6.0 mol%) , B_2pin_2 (101.7 mg, 4.0 equiv.) , HBpin

(1.5 μL, 0.1 equiv.) and 0.5 mL 1,4-dioxane. The reaction was stirred at 80 °C for 36 hours before the solvents removed. The crude product was passed through a short pad of silica gel with petroleum ether/ DCM (1:1) as the eluent to afford 44.3 mg **4g** (71% yield).

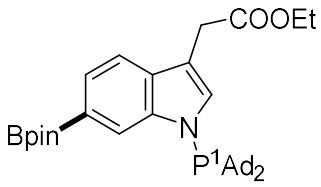
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 – 8.27 (m, 1H), 8.18 (s, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.01 – 1.92 (m, 12H), 1.88 – 1.83 (m, 6H), 1.68 (m, 12H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.37 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.3, 144.1 (d, *J* = 19.5 Hz), 140.0 (d, *J* = 8.4 Hz), 128.8 (d, *J* = 2.3 Hz), 128.1, 120.3, 120.1 (d, *J* = 19.4 Hz), 111.0 (d, *J* = 2.8 Hz), 83.6, 59.9, 40.1 (d, *J* = 13.6 Hz), 39.4 (d, *J* = 27.6 Hz), 36.6, 28.3 (d, *J* = 9.1 Hz), 24.9, 14.6.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 72.6.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.9.

HRMS m/z: $[M+H]^+$ calculated for $[C_{37}H_{52}BNO_4P]^+$ 616.3722, found 616.3708.



Ethyl 2-(1-(di(adamantan-1-yl)phosphaneyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan -2-yl)-1*H*-indol-3-yl)acetate (4h)

Following the **general procedure B** using **3h** (50.4 mg, 0.1 mmol), $[Ir(COD)OMe]_2$ (2.0 mg, 3.0 mol%) , 1,10-phenanthroline (1.1 mg, 6.0 mol%) , B_2pin_2 (101.7 mg, 4.0 equiv.) , HBpin (1.5 μL, 0.1 equiv.) and 0.5 mL 1,4-dioxane. The reaction was stirred at 80 °C for 36 hours before the solvents removed. The crude product was passed through a short pad of silica gel with petroleum ether/ DCM (1:1) as the eluent to afford 37.1 mg **4h** (59% yield).

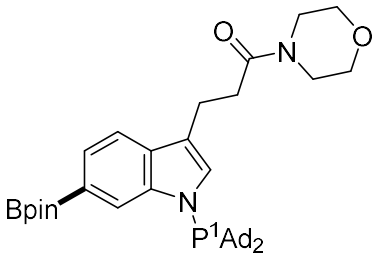
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.29 – 8.25 (m, 1H), 7.61 – 7.55 (m, 2H), 7.51 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 2H), 2.02 – 1.97 (m, 6H), 1.92 – 1.84 (m, 12H), 1.68 (m, 12H), 1.36 (s, 12H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 143.7 (d, *J* = 20.6 Hz), 132.3 (d, *J* = 8.5 Hz), 130.7, 126.0, 119.8 (d, *J* = 19.1 Hz), 117.5, 110.7 (d, *J* = 2.7 Hz), 83.4, 60.7, 40.2 (d, *J* = 13.8 Hz), 39.4 (d, *J* = 26.0 Hz), 36.7, 31.6, 28.4 (d, *J* = 9.1 Hz), 24.9, 14.2.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 68.3.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.4.

HRMS m/z: $[M+H]^+$ calculated for $[C_{38}H_{54}BNO_4P]^+$ 630.3878, found 630.3864.



3-(1-(Di(adamantan-1-yl)phosphaneyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indol-3-yl)-1-morpholinopropan-1-one (4i)

Following the **general procedure B** using **3i** (55.9 mg, 0.1 mmol), $[Ir(COD)OMe]_2$ (2.0 mg, 3.0 mol%) , 1,10-phenanthroline (1.1 mg, 6.0 mol%) , B_2pin_2 (101.7 mg, 4.0 equiv.) , HBpin (1.5 μL, 0.1 equiv.) and 0.5 mL 1,4-dioxane. The reaction was stirred at 80 °C for 36 hours before the solvents removed. The crude product was passed through a short pad of silica gel with petroleum ether/ ethyl acetate (2:1) as the eluent to afford 44.3 mg **4i** (65% yield).

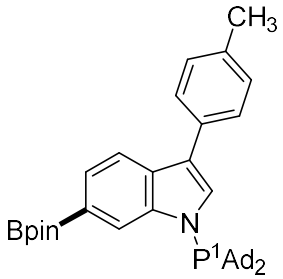
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 – 8.25 (m, 1H), 7.58 – 7.52 (m, 2H), 7.26 (s, 1H), 3.72 (m, *J* = 4.7 Hz, 4H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.45 – 2.38 (m, 6H), 2.02 – 1.97 (m, 6H), 1.92 – 1.84 (m, 12H), 1.68 (m, 12H), 1.36 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.4, 144.0 (d, *J* = 20.6 Hz), 131.4 (d, *J* = 8.4 Hz), 130.6 (d, *J* = 3.2 Hz), 125.7, 120.0 (d, *J* = 19.1 Hz), 117.6, 117.3, 83.4, 66.8, 66.5, 46.0, 41.9, 40.2 (d, *J* = 13.7 Hz), 39.4 (d, *J* = 25.9 Hz), 36.7, 33.7, 28.4 (d, *J* = 9.1 Hz), 24.9, 21.2.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 67.2.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 36.6.

HRMS m/z: $[M+H]^+$ calculated for $[C_{41}H_{59}BN_2O_4P]^+$ 685.4300, found 685.4280.



1-(Di(adamantan-1-yl)phosphaneyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(*p*-tolyl)-1*H*-indole (4j)

Following the **general procedure B** using **3j** (50.8 mg, 0.1 mmol), $[Ir(COD)OMe]_2$ (2.0 mg, 3.0 mol%) , 1,10-phenanthroline (1.1 mg, 6.0 mol%) , B_2pin_2 (101.7 mg, 4.0 equiv.) , HBpin (1.5 μL, 0.1 equiv.) and 0.5 mL 1,4-dioxane. The reaction was stirred at 80 °C for 48 hours before the solvents removed. The crude product was passed through a short pad of silica gel with petroleum ether/ DCM (3:1) as the eluent to afford 27.3 mg **4j** (43% yield).

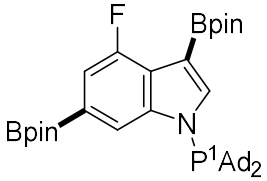
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.36 – 8.33 (m, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.64 – 7.58 (m, 4H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.42 (s, 3H), 2.06 – 2.01 (m, 6H), 1.94 – 1.89 (m, 12H), 1.69 (m, 12H), 1.38 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.4 (d, *J* = 20.2 Hz), 135.8, 132.5, 130.8 (d, *J* = 8.4 Hz), 129.5, 129.3 (d, *J* = 2.8 Hz), 127.6, 126.5, 120.2, 120.0 (d, *J* = 2.4 Hz), 118.4, 83.5, 40.3 (d, *J* = 13.7 Hz), 39.5 (d, *J* = 26.4 Hz), 36.7, 28.4 (d, *J* = 9.1 Hz), 24.9, 21.2.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 68.8.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 34.8.

HRMS m/z: $[M+H]^+$ calculated for $[C_{41}H_{54}BNO_2P]^+$ 634.3980, found 634.3965.



1-(Di(adamantan-1-yl)phosphaneyl)-4-fluoro-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (4k)

Following the **general procedure B** using **3k** (43.6 mg, 0.1 mmol), $[Ir(COD)OMe]_2$ (2.0 mg, 3.0 mol%) , 1,10-phenanthroline (1.1 mg, 6.0 mol%) , B_2pin_2 (101.7 mg, 4.0 equiv.) , HBpin

(1.5 μL, 0.1 equiv.) and 0.5 mL 1,4-dioxane. The reaction was stirred at 80 °C for 36 hours before the solvents removed. The crude product was passed through a short pad of silica gel with petroleum ether/ ethyl acetate (20:1) as the eluent to afford 42.6 mg **4k** (62% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 8.02 (m, 1H), 7.84 (s, 1H), 7.21 (d, *J* = 10.8 Hz, 1H), 2.01 – 1.92 (m, 12H), 1.88 – 1.83 (m, 6H), 1.68 (m, 12H), 1.38 (s, 12H), 1.36 (s, 12H).

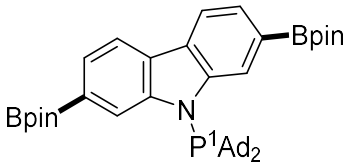
^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.7 (d, J = 250.5 Hz), 147.9, 143.5 (d, J = 8.2 Hz), 122.9, 115.9 (d, J = 20.2 Hz), 111.3 (d, J = 18.1 Hz), 83.6, 83.2, 40.1 (d, J = 13.7 Hz), 39.4 (d, J = 27.0 Hz), 36.7, 28.3 (d, J = 9.1 Hz), 24.9, 24.8.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 72.3.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 36.0.

^{19}F NMR (470 MHz, Chloroform-*d*) δ -118.3.

HRMS m/z: $[M+H]^+$ calculated for $[C_{40}H_{58}B_2FNO_4P]^+$ 688.4268, found 688.4257.



9-(Di(adamantan-1-yl)phosphaneyl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) -9*H*-carbazole (4l)

Following the **general procedure B** using **3l** (41.8 mg, 0.1 mmol), $[Ir(COD)OMe]_2$ (2.0 mg, 3.0 mol%) , 1,10-phenanthroline (1.1 mg, 6.0 mol%) , B_2pin_2 (101.7 mg, 4.0 equiv.) , HBpin (1.5 μL, 0.1 equiv.) and 0.5 mL 1,4-dioxane. The reaction was stirred at 80 °C for 36 hours before the solvents removed. The crude product was passed through a short pad of silica gel with petroleum ether/ ethyl acetate (20:1) as the eluent to afford 46.5 mg **4l** (65% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (s, 2H), 8.07 (d, *J* = 7.7 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 2.18 – 2.03 (m, 12H), 1.92 – 1.88 (m, 6H), 1.67 (m, 12H), 1.41 (s, 12H), 1.37 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.1 (d, *J* = 25.7 Hz), 144.0 (d, *J* = 12.6 Hz), 127.8 (d, *J* = 2.1 Hz), 127.1 (d, *J* = 3.0 Hz), 126.2, 125.4, 123.3, 120.7, 120.4, 119.2 (d, *J* = 50.0 Hz), 83.6 (d, *J* = 5.9 Hz), 41.1 (d, *J* = 15.4 Hz), 40.5 (d, *J* = 31.8 Hz), 36.7, 28.7 (d, *J* = 9.8 Hz), 25.0 (d, *J* = 1.6 Hz).

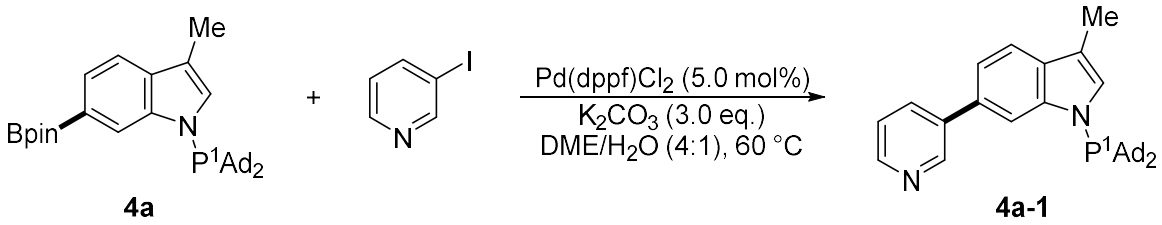
^{31}P NMR (162 MHz, Chloroform-*d*) δ 76.5.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 31.6.

HRMS m/z: $[M+H]^+$ calculated for $[C_{44}H_{61}B_2NO_4P]^+$ 720.4519, found 720.4511.

5. Synthetic applications

5.1 Derivatization of Bpin group



1-(Di(adamantan-1-yl)phosphaneyl)-3-methyl-6-(pyridin-3-yl)-1*H*-indole (4a-1)

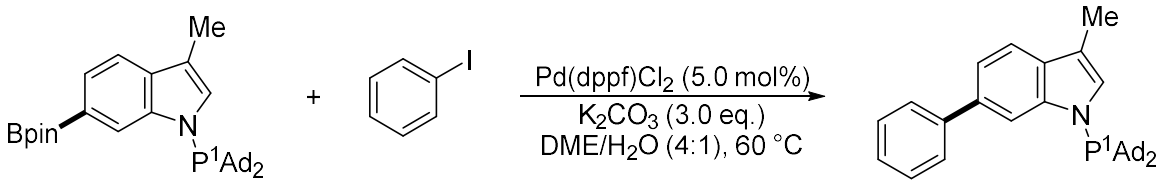
According to the reported procedure [4], a 10 mL Schlenk tube was charged with a magnetic stirring bar, 7.3 mg $Pd(dppf)Cl_2$ (0.01 mmol, 5.0 mol%), 82.8 mg K_2CO_3 (0.6 mmol, 3.0 equiv.), 111.6 mg **4a** (0.2 mmol) and then flushed with nitrogen. The mixture was stirred during the addition of 2.5 mL DME/H_2O (4:1) and 45.1 mg 3-iodopyridine (0.22 mmol, 1.1 equiv.), then the mixture was stirred at 60 °C overnight. The reaction was monitored by TLC and extracted with ethyl acetate, the organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography on silica gel (petroleum ether / 1,4-dioxane = 5:1) gave the title compound **4a-1** (83.9 mg, 82%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.94 (d, *J* = 2.4 Hz, 1H), 8.56 – 8.53 (m, 1H), 8.06 – 8.04 (m, 1H), 7.99 – 7.96 (m, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.25 (s, 1H), 2.39 (s, 3H), 2.03 – 1.98 (m, 6H), 1.95 – 1.87 (m, 12H), 1.71 – 1.68 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 148.7, 147.5, 144.9 (d, *J* = 21.0 Hz), 138.1, 134.6, 131.5 (d, *J* = 1.8 Hz), 130.5 (d, *J* = 8.7 Hz), 129.3 (d, *J* = 3.4 Hz), 123.4, 118.8, 113.7 (d, *J* = 2.4 Hz), 111.8, 111.6, 40.3 (d, *J* = 13.5 Hz), 39.4 (d, *J* = 25.5 Hz), 36.7, 28.4 (d, *J* = 9.2 Hz), 10.0.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 68.0.

HRMS m/z: $[M+H]^+$ calculated for $[C_{34}H_{42}N_2P]^+$ 509.3080, found 509.3066.



4a **4a-2**

1-(Di(adamantan-1-yl)phosphaneyl)-3-methyl-6-phenyl-1*H*-indole (4a-2)

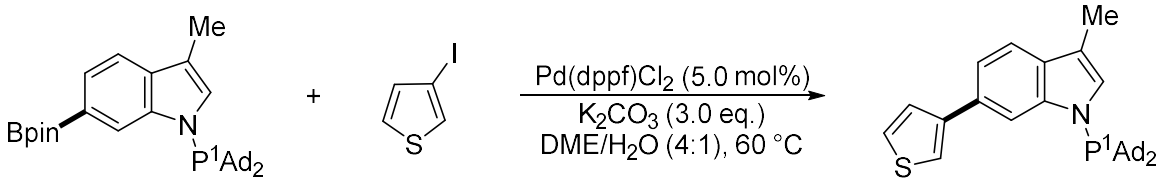
A 10 mL Schlenk tube was charged with a magnetic stirring bar, 11.0 mg $Pd(dppf)Cl_2$ (0.015 mmol, 5.0 mol%), 124.4 mg K_2CO_3 (0.9 mmol, 3.0 equiv.), 167.3 mg **4a** (0.3 mmol) and then flushed with nitrogen. The mixture was stirred during the addition of 4.0 mL DME/H_2O (4:1) and 67.3 mg iodobenzene (0.33 mmol, 1.1 equiv.), then the mixture was stirred at 60 °C overnight. The reaction was monitored by TLC and extracted with ethyl acetate, the organic layer washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography on silica gel (petroleum ether / DCM = 2:1) gave the title compound **4a-2** (121.2 mg, 80%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.04 (m, 1H), 7.71 (d, *J* = 6.9 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.41 – 7.38 (m, 1H), 7.33 – 7.28 (m, 1H), 7.22 (s, 1H), 2.38 (s, 3H), 2.03 – 1.98 (m, 6H), 1.93 – 1.86 (m, 12H), 1.69 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.0, 144.8, 142.7, 135.1, 130.1 (d, *J* = 8.7 Hz), 128.7, 128.6, 127.6, 126.4, 119.1, 118.4, 113.6, 111.7, 111.5, 40.3 (d, *J* = 13.4 Hz), 39.4 (d, *J* = 25.3 Hz), 36.8, 28.4 (d, *J* = 9.0 Hz), 10.0.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 67.5.

HRMS m/z: $[M+H]^+$ calculated for $[C_{35}H_{43}NP]^+$ 508.3128, found 508.3117.



4a **4a-3**

1-(Di(adamantan-1-yl)phosphaneyl)-3-methyl-6-(thiophen-3-yl)-1*H*-indole (4a-3)

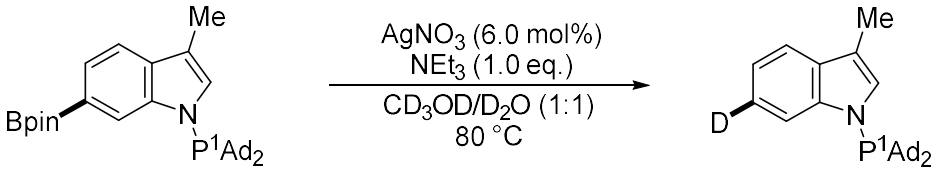
A 10 mL Schlenk tube was charged with a magnetic stirring bar, 3.7 mg Pd(dppf)Cl_2 (0.005 mmol, 5.0 mol%), 41.4 mg K_2CO_3 (0.3 mmol, 3.0 equiv.), 55.8 mg **4a** (0.1 mmol) and then flushed with nitrogen. The mixture was stirred during the addition of 1.5 mL DME/H_2O (4:1) and 23.1 mg 3-iodothiophene (0.11 mmol, 1.1 equiv.), then the mixture was stirred at 60 °C overnight. The reaction was monitored by TLC and extracted with ethyl acetate, the organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography on silica gel (petroleum ether / DCM = 10:1) gave the title compound **4a-3** (39.1 mg, 76%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 8.04 (m, 1H), 7.55 – 7.47 (m, 3H), 7.42 – 7.36 (m, 2H), 7.21 (s, 1H), 2.38 (s, 3H), 2.03 – 1.99 (m, 6H), 1.94 – 1.87 (m, 12H), 1.71 – 1.68 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.8 (d, *J* = 20.8 Hz), 143.9, 130.0 (d, *J* = 8.6 Hz), 129.8, 128.7 (d, *J* = 3.6 Hz), 127.1, 125.6, 119.2, 118.5 (d, *J* = 24.3 Hz), 113.7 (d, *J* = 2.4 Hz), 111.0, 110.8, 40.3 (d, *J* = 13.6 Hz), 39.4 (d, *J* = 25.3 Hz), 36.8, 28.4 (d, *J* = 9.2 Hz), 10.0.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 67.5.

HRMS m/z: $[M+H]^+$ calculated for $[C_{33}H_{41}NPS]^+$ 514.2692, found 514.2678.



4a **4a-4**

1-(Di(adamantan-1-yl)phosphaneyl)-3-methyl-1*H*-indole-6-*d* (4a-4)

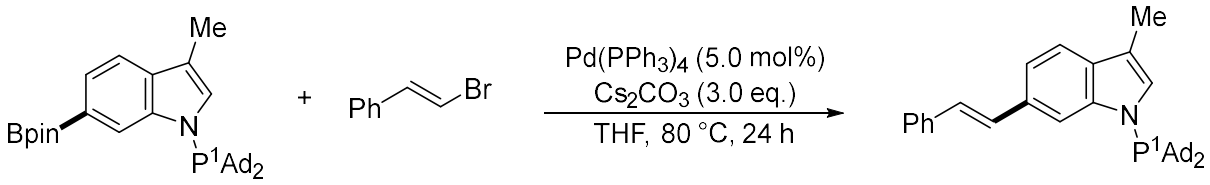
According to the reported procedure [5], a 4 mL vial was charged with a magnetic stirring bar, 1.0 mg $AgNO_3$ (0.006 mmol, 6.0 mol%), 10.1 mg NEt_3 (0.1 mmol, 1.0 equiv.), 55.8 mg **4a** (0.1 mmol) and 0.5 mL CD_3OD/D_2O (1:1). The mixture was stirred at 80 °C, monitored by TLC and extracted with ethyl acetate, the organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography on silica gel (petroleum ether / DCM = 2:1) gave the title compound **4a-4** (41.3 mg, 95%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.79 (m, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.19 (s, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 2.36 (s, 3H), 2.01 – 1.96 (m, 6H), 1.92 – 1.84 (m, 12H), 1.68 (m, 12H).

^{13}C NMR (125 MHz, Chloroform-*d*) δ 144.3 (d, *J* = 21.2 Hz), 129.3 (d, *J* = 8.3 Hz), 121.3 (t, *J* = 24.3 Hz), 119.2, 118.1, 113.7, 113.0, 112.8, 40.2 (d, *J* = 13.5 Hz), 39.3 (d, *J* = 25.1 Hz), 36.8, 28.4 (d, *J* = 8.9 Hz), 10.0.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 67.8.

HRMS m/z: $[M+H]^+$ calculated for $[C_{29}H_{38}DNP]^+$ 433.2877, found 433.2879.



4a **4a-5**

(E)-1-(di(adamantan-1-yl)phosphaneyl)-3-methyl-6-styryl-1*H*-indole (4a-5)

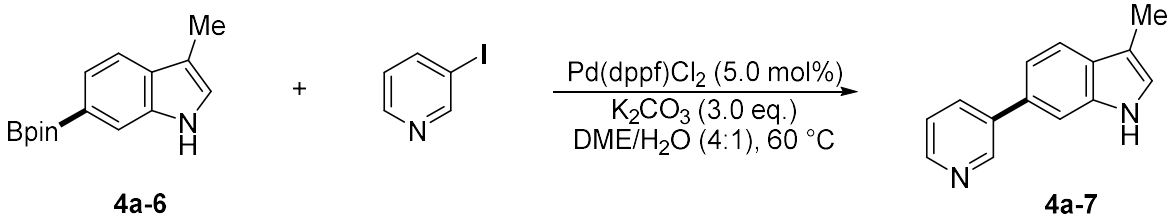
According to the reported procedure [4], in an argon-filled glove box, a 4 mL vial charged with 5.8 mg $Pd(PPh_3)_4$ (0.005 mmol, 5.0 mol%), 97.7 mg Cs_2CO_3 (0.3 mmol, 3.0 equiv.), 55.8 mg **4a** (0.1 mmol), 22.0 mg β-bromostyrene (0.12 mmol, 1.2 equiv.) and 1.0 mL THF. To the vial was added a magnetic stir bar, and sealed with a Teflon-lined cap then stirred at 80 °C for 24 h. The reaction mixture was extracted with ethyl acetate, the organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude residue was purified by chromatography on silica gel with petroleum ether / DCM (2:1) to give the title compound **4a-5** (18.4 mg, 34%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.91 (m, 1H), 7.55 – 7.47 (m, 3H), 7.39 – 7.30 (m, 4H), 7.25 – 7.19 (m, 2H), 7.15 (d, *J* = 16.3 Hz, 1H), 2.36 (s, 3H), 2.04 – 1.98 (m, 6H), 1.94 – 1.87 (m, 12H), 1.70 (m, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.7 (d, *J* = 19.1 Hz), 138.1, 130.4, 130.3, 129.7 (d, *J* = 6.8 Hz), 129.0, 128.6, 128.0, 126.9, 126.3, 122.0, 121.8, 119.9, 118.4, 40.3 (d, *J* = 13.6 Hz), 39.4 (d, *J* = 25.4 Hz), 36.8, 28.4 (d, *J* = 9.1 Hz), 10.0.

^{31}P NMR (162 MHz, Chloroform-*d*) δ 67.6.

HRMS m/z: $[M+H]^+$ calculated for $[C_{37}H_{45}NP]^+$ 534.3284, found 534.3275.



4a-6 **4a-7**

3-Methyl-6-(pyridin-3-yl)-1*H*-indole (4a-7)

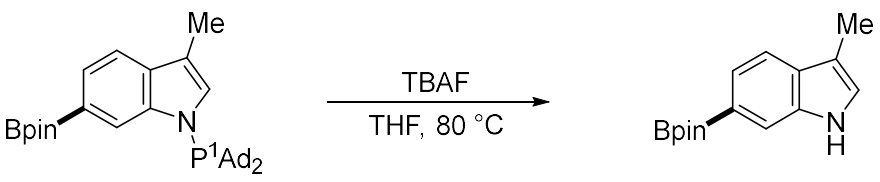
A 10 mL Schlenk tube was charged with a magnetic stirring bar, 1.0 mg $Pd(dppf)Cl_2$ (0.0013 mmol, 5.0 mol%), 10.4 mg K_2CO_3 (0.075 mmol, 3.0 equiv.), 6.4 mg **4a-6** (0.025 mmol) and then flushed with nitrogen. The mixture was stirred during the addition of 1.0 mL DME/H_2O (4:1) and 5.7 mg 3-iodopyridine (0.028 mmol, 1.1 equiv.), then the mixture was stirred at 60 °C overnight. The reaction was monitored by TLC and extracted with ethyl acetate, the organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography on silica gel (petroleum ether / 1,4-dioxane = 3:1) gave the title compound **4a-7** (4.6 mg, 88%).

^{1}H NMR (400 MHz, Chloroform-d) δ 9.0 – 8.9 (m, 1H), 8.6 – 8.6 (m, 1H), 8.5 (br, 1H), 8.0 – 7.9 (m, 1H), 7.7 (d, J = 8.2 Hz, 1H), 7.6 (d, J = 1.6 Hz, 1H), 7.4 – 7.3 (m, 2H), 7.1 – 7.0 (m, 1H), 2.4 (s, 3H).

^{13}C NMR (100 MHz, Chloroform-d) δ 148.4, 147.6, 138.0, 136.9, 134.6, 131.6, 128.3, 123.6, 123.0, 119.5, 118.6, 111.7, 109.7, 9.7.

HRMS m/z: $[M+H]^+$ calculated for $[C_{14}H_{13}N_2]^+$ 209.1073, found 209.1066

5.2 Directing group removal



4a **4a-6**

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

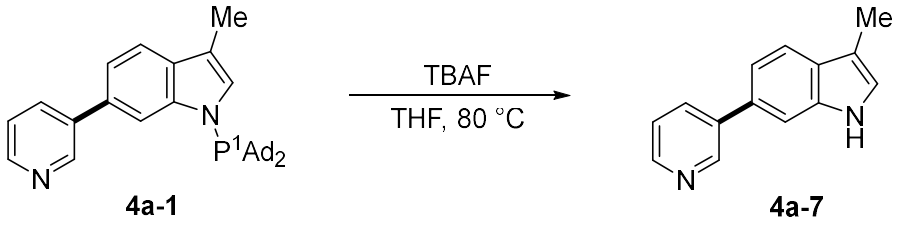
According to the reported procedure [6], a 4 mL vial was charged with a magnetic stirring bar, 55.8 mg **4a** (0.1 mmol), TBAF (0.8 mmol, 8.0 equiv.) and 2.0 mL THF. The mixture was stirred at 80 °C, monitored by TLC extracted with ethyl acetate, the organic layer washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography on silica gel (petroleum ether/ ethyl acetate = 4:1) gave the title compound **4a-6** (13.2 mg, 51%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (br, 1H), 7.85 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.02 (s, 1H), 2.33 (s, 3H), 1.37 (s, 12H).

^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.0, 130.7, 124.9, 123.1, 118.2, 117.9, 111.9, 83.5, 24.9, 9.6.

^{11}B NMR (160 MHz, Chloroform-*d*) δ 36.9.

HRMS m/z: $[M+H]^+$ calculated for $[C_{15}H_{21}BNO_2]^+$ 258.1660, found 258.1650.

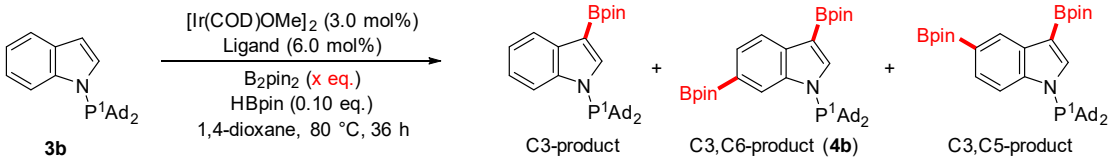


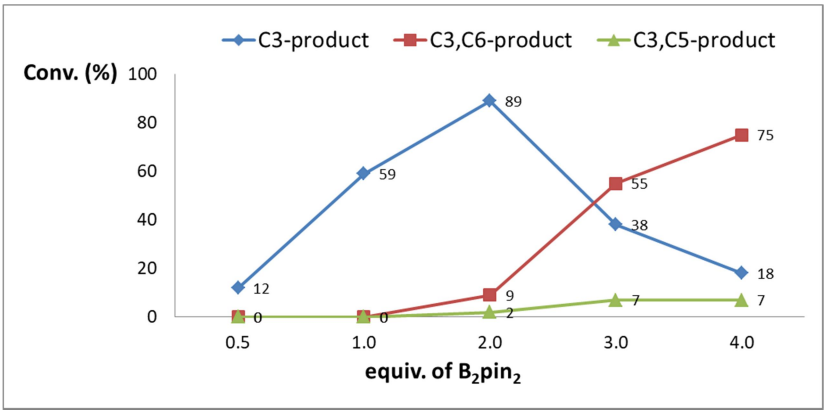
2-Methyl-6-(pyridin-3-yl)-1*H*-indole (4a-7)

A 4 mL vial was charged with a magnetic stirring bar, 50.9 mg **4a-1** (0.1 mmol), TBAF (0.8 mmol, 8.0 equiv.) and 2.0 mL THF. The mixture was stirred at 80 °C, monitored by TLC extracted with ethyl acetate, the organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography on silica gel (petroleum ether / 1,4-dioxane = 3:1) gave the title compound **4a-7** (20.4 mg, 98%). NMR and HRMS data is shown above.

6. Further discussion on substrate scope

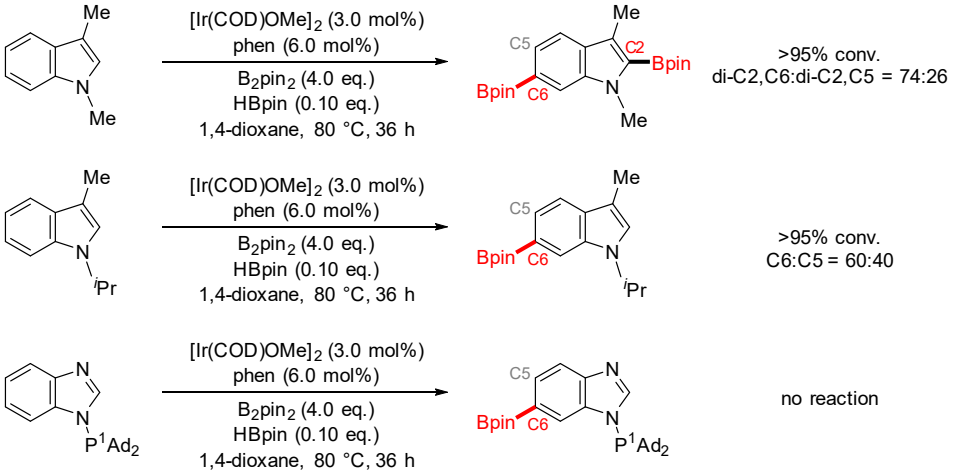
6.1 Borylation of C3-unsubstituted indole 3b with a range of B_2pin_2 equivalents





Scheme S1 Borylation of **3b** with a range of B_2pin_2 equivalents. All borylation reactions were performed on a 0.1 mmol scale using extra dry solvents. Conversion and the site-selectivity ratio were determined from crude ^{1}H NMR spectra.

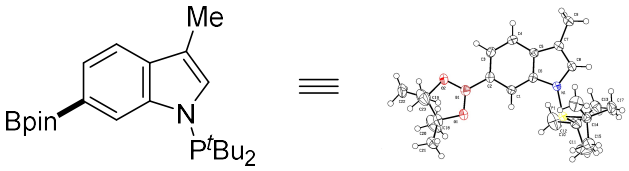
6.2 Control experiments for C6-borylation



Scheme S2 Control experiments for C6-borylation. All borylation reactions were performed on a 0.1 mmol scale using extra dry solvents. Conversion and the site-selectivity ratio were determined from crude ^{1}H NMR spectra.

7. X-ray crystallographic data

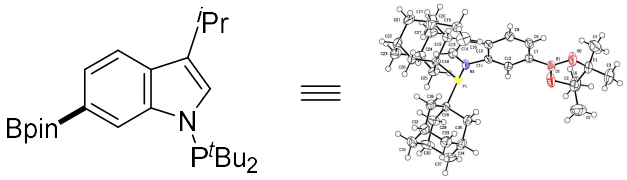
7.1 X-ray crystal structure of 2 (CCDC 2258140)



2 ≡ CCDC 2258140

Identification code	**2**
Empirical formula	$C_{23}H_{37}BNO_2P$
Formula weight	401.31
Temperature/K	193.0
Crystal system	triclinic
Space group	P-1
a/Å	7.7665(3)
b/Å	11.5656(6)
c/Å	13.5181(6)
α/°	80.546(2)
β/°	88.085(2)
γ/°	87.299(2)
Volume/Å^3	1196.02(9)
Z	2
ρ_{calc}g/cm^3	1.114
μ/mm^{-1}	0.132
F(000)	436.0
Crystal size/mm^3	0.14 × 0.13 × 0.11
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.066 to 54.962
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -17 ≤ l ≤ 14
Reflections collected	11404
Independent reflections	5447 [R_{int} = 0.0450, R_{sigma} = 0.0701]
Data/restraints/parameters	5447/0/264
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0564, wR_2 = 0.1144
Final R indexes [all data]	R_1 = 0.0974, wR_2 = 0.1338
Largest diff. peak/hole / e Å^{-3}	0.32/-0.22

7.2 X-ray crystal structure of 4d (CCDC 2258141)



4d CCDC 2258141

Identification code	**4d**
Empirical formula	$C_{37}H_{50}BNO_2P$
Formula weight	582.56
Temperature/K	193.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.0888(7)
b/Å	12.8677(6)
c/Å	20.7793(11)
α/°	90
β/°	108.194(2)
γ/°	90
Volume/Å^3	3324.7(3)
Z	4
ρ_{calc}g/cm^3	1.164
μ/mm^{-1}	0.115
F(000)	1260.0
Crystal size/mm^3	0.21 × 0.2 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.126 to 54.976
Index ranges	-17 ≤ h ≤ 13, -16 ≤ k ≤ 16, -26 ≤ l ≤ 26
Reflections collected	31263
Independent reflections	7584 [R_{int} = 0.0520, R_{sigma} = 0.0502]
Data/restraints/parameters	7584/0/384
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0568, wR_2 = 0.1349
Final R indexes [all data]	R_1 = 0.0853, wR_2 = 0.1516
Largest diff. peak/hole / e Å^{-3}	0.50/-0.27

8. Computational details

All DFT calculations were performed with Gaussian 09 [7] program. Geometry optimizations were performed using M06 [8] functionals, while LANL2DZ [9] pseudo-potential was set for Ir and 6-31G(d) basis set was set for all other atoms. After optimization, frequency calculations were subsequently performed at the same level of theory to confirm that all stationary points had correct number of imaginary frequencies (zero for minima and one for transition states) and to provide thermodynamic corrections at 298 K, 1 atm. For all transition states, Intrinsic Reaction Coordinate (IRC) [10] were calculated to confirm that they indeed connected between two correct minima. Single-point energies of the optimized structures were calculated using ωB97X-D [11] functionals with SDD [12] for Ir and 6-311+G(d,p) for all other atoms. SMD [13] solvation model (solvent = *n*-hexane) was used in single-point energy calculations to consider solvent effect. The final Gibbs free energy was calculated as the sum of Gibbs free energy correction (from frequency calculation) and the single point energy in solution. For each species, extensive conformational search was done and the reported value is from the conformer with the lowest Gibbs free energy. Previous reports [14-16] showed that the rate-determining step of Ir-catalyzed C-H borylation of arenes is C-H activation. Therefore, the relative free energies of C-H activation transition states were represented and discussed. The absolute barriers were regarded as the $\Delta G^{\ddagger}$ of: Ir(phen)(Bpin)$_3$(COD) + substrate → COD + TS(C-H activation). Graphics of the transition states were rendered using CYLview [17].

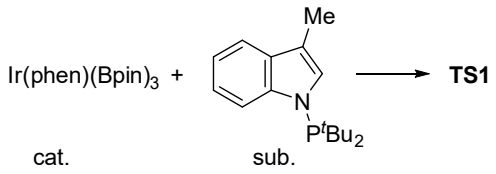
Noncovalent interaction (NCI) analysis of transition states

Noncovalent interaction (NCI) analysis [18] was processed using Multiwfn 3.8 [19] program. The wavefunctions used for analysis were generated using Gaussian 09 at SMD(*n*-hexane)-6-311+G(d,p)[SDD for Ir] as .fchk files. The center of grid was set as the P atom of the substrate and extend for 6 Å (11.3 Bohr) in all *x*/*y*/*z* directions. The grid spacing was set as 0.10 Bohr. For visualization, the reduced density gradient (RDG) isosurface was set as 0.5 a.u., while the sign(λ_2)ρ color range was set from -0.035 a.u. (blue) to 0.020 a.u. (red). The visualization was performed using VMD 1.9.4 [20].

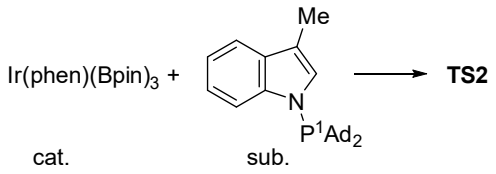
Natural bond orbital (NBO) analysis of transition states

The analysis was performed using NBO 3.1[21-22] attached in the Gaussian program package at SMD(*n*-hexane)-ωB97X-D/6-311G(d,p)[SDD for Ir] of theory (the diffusion functional should be removed to avoid numerical noises). The second-order perturbation energy [*E*(2)] between the directing group (-PR_2) and the catalyst [Ir(phen)$(Bpin)_3$] were collected. The printing threshold was set as 0.05 kcal/mol, and irrelevant (e.g. Ir-B as donor) or noise-like (e.g. between very-far-away atoms) interactions were removed.

Table S4. Distortion/Interaction analysis



E (kcal/mol)	TS1-C5	TS1-C6
ΔE	8.6	6.0
$\Delta E_{\text{dist-cat.}}$	11.3	11.4
$\Delta E_{\text{dist-sub.}}$	71.0	71.5
ΔE_{int}	-73.7	-76.9



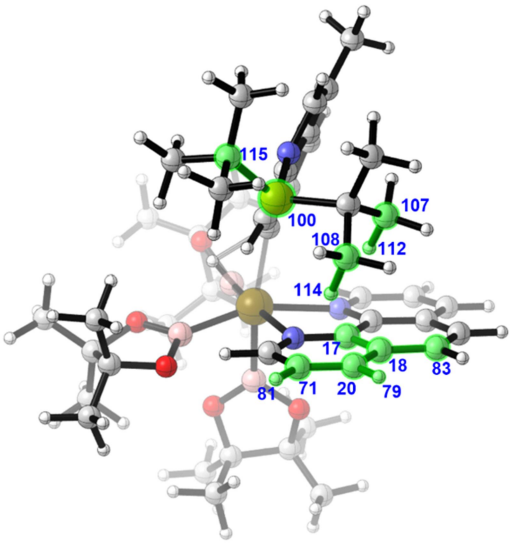
E (kcal/mol)	TS2-C5	TS2-C6
ΔE	8.2	4.3
$\Delta E_{\text{dist-cat.}}$	11.4	11.2
$\Delta E_{\text{dist-sub.}}$	70.8	69.9
ΔE_{int}	-74.0	-76.8

Distortion/Interaction analysis shows greater interaction energies for both C6-transition states compared with the corresponding C5-transition states. For **TS2-C6**, less distortion of the substrate ($\Delta E_{\text{dist-sub}}$) may also contribute to the greater energetic preference over **TS2-C5**.

Table S5. NBO analysis

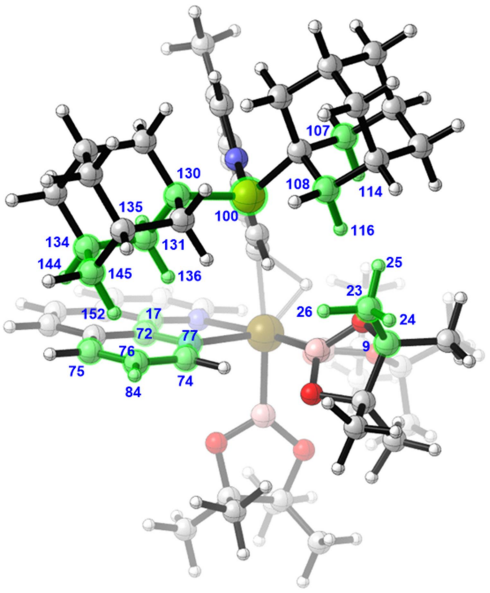
TS1-C6

Donor	**Acceptor**	***E*(2)** (kcal/mol)
BD(1) C18-C20	RY*(1) H112	0.30
BD(1) C107-H112	LP(1) C18	0.22
BD(1) C17-C18	RY*(1) H112	0.18
LP(1) C71	BD*(1) C108-H114	0.18
BD(1) C18-C83	RY*(1) H112	0.16
BD(1) C108-H114	LP*(1) C20	0.16
BD(1) C20-C71	RY*(1) H114	0.15
BD(1) C107-H112	LP*(1) C20	0.14
LP(1) C18	BD*(1) C107-H112	0.14
LP(1) P100	LP(1) C71	0.13
LP*(1) C20	BD*(1) C108-H114	0.11
BD(1) C108-H114	LP(1) C71	0.08
BD(1) C20-C71	RY*(1) H112	0.06
BD(1) C108-H114	RY*(1) H81	0.06
LP(1) C18	RY*(1) H112	0.06
LP*(1) C20	BD*(1) C107-H112	0.06
LP(1) C71	BD*(1) P100-C115	0.06
BD(1) C108-H114	RY*(1) H79	0.05
Total	18	2.30



TS2-C6

Donor	**Acceptor**	***E*(2)** (kcal/mol)
BD(1) C131-H136	BD*(2) C75-C76	0.27
BD(1) C23-H25	BD*(1) C107-H114	0.25
LP(1) P100	BD*(1) C23-H26	0.21
BD(1) C107-H114	BD*(1) C23-H25	0.17
BD(1) C74-C76	RY*(1) H136	0.16
BD(1) C145-H152	RY*(1) H84	0.14
BD(1) C23-H24	RY*(2) H116	0.11
BD(2) C75-C76	BD*(1) C130-C131	0.11
BD(1) C23-H25	BD*(1) P100-C130	0.10
LP(1) P100	BD*(1) C9-C23	0.09
BD(1) C23-H25	RY*(1) H114	0.08
BD(1) C23-H26	BD*(1) P100-C130	0.08
BD(1) C75-C76	RY*(4) C131	0.08
BD(2) C75-C76	BD*(1) C134-H144	0.08
LP(1) N78	RY*(1) H135	0.08
BD(1) C17-C72	RY*(1) H135	0.07
BD(1) C23-H25	RY*(2) H114	0.07
BD(1) C75-C76	RY*(1) H144	0.07
BD(1) C108-H116	BD*(1) C9-C23	0.07
BD(1) C131-C134	RY*(3) C76	0.07
BD(1) C72-N78	RY*(1) H135	0.06
BD*(2) C75-C76	BD*(1) C131-H136	0.05
Total	22	2.47



The atoms involved in the non-covalent interactions are highlighted in green. The NBO analysis shows more and stronger interactions in **TS2-C6** than those in **TS1-C6**. Several ^{1}Ad···Bpin interactions (marked in red) are found in **TS2-C6**.

Table S6. Cartesian coordinates of the computed structures

COD			
G(*n*-hexane) = -313.084501 Hartree			

C	-0.753594	-1.182061	-0.798345
C	1.794895	0.390338	-0.178476
C	0.372315	-1.753458	0.060959
C	1.336566	-0.757489	0.717074
H	-1.244957	-2.021275	-1.314331
H	2.109510	-0.017956	-1.157022
H	0.968097	-2.419097	-0.584818
H	2.229550	-1.319280	1.029820
H	0.919286	-0.348134	1.646019
C	-1.326069	0.828409	0.724251
H	-2.199478	1.405579	1.059226
C	-1.828383	-0.385302	-0.070965
H	-2.376925	-1.048383	0.617993
H	-2.563820	-0.042487	-0.815735
C	-0.414353	1.736559	-0.057035
H	-0.867527	2.672561	-0.393621
C	0.854436	1.534380	-0.430878
H	1.311147	2.332760	-1.024297
H	-0.841394	0.481009	1.645525
H	2.719228	0.817883	0.245025
H	-0.321284	-0.558337	-1.595558
H	-0.056316	-2.403109	0.842266

Ir(phen)(Bpin)$_3$(COD)			
G(*n*-hexane) = -1909.241222 Hartree			

Ir	-0.174805	0.267544	-0.271172
O	0.897521	-1.936616	1.623409
O	-0.443062	-2.753681	-0.027724
O	1.072004	1.165303	2.364661
O	2.685850	0.806288	0.802489
C	0.990613	-3.365288	1.695790
C	-0.292816	-3.802035	0.937266
C	2.325430	1.236414	3.060544
C	3.334485	1.459390	1.896362
B	0.158078	-1.603128	0.492432
B	1.312486	0.748325	1.047239
B	1.396316	-0.178390	-1.459329
O	1.786616	0.573671	-2.577933
O	2.239961	-1.282161	-1.335998
C	3.099208	0.146483	-2.967548
C	3.140314	-1.321261	-2.443561
C	3.504060	2.923716	1.508271
H	4.073492	3.490709	2.257689
H	4.047774	2.973843	0.554821
H	2.534040	3.418769	1.360520
C	4.698236	0.831244	2.108639
H	5.349147	1.052036	1.251124
H	5.184818	1.232887	3.009515
H	4.628029	-0.258710	2.201810
C	2.264133	2.359334	4.077685
H	1.522020	2.118137	4.850809
H	3.234490	2.492055	4.578446
H	1.975601	3.315549	3.624639
C	2.530077	-0.094033	3.774408
H	3.437468	-0.090699	4.394431
H	1.667603	-0.280860	4.428856
H	2.576453	-0.921966	3.056592
C	2.586227	-2.333013	-3.438566
H	3.266999	-2.504102	-4.284104
H	2.435893	-3.289694	-2.919886
H	1.611686	-2.014346	-3.831737
C	4.499140	-1.781361	-1.949318
H	4.442591	-2.828531	-1.621492
H	5.257766	-1.721172	-2.743795
H	4.834751	-1.183776	-1.093384
C	3.245046	0.292712	-4.469461
H	2.450335	-0.232852	-5.011829
H	3.192940	1.354480	-4.744952
H	4.215545	-0.094856	-4.812565
C	4.091483	1.064142	-2.262471
H	5.130024	0.857155	-2.556536
H	3.860465	2.103001	-2.537190
H	3.995209	0.977432	-1.172322
C	-1.535458	-3.775412	1.820851
H	-1.609752	-2.821607	2.362487
H	-2.428401	-3.873641	1.187029

H	-1.545128	-4.594670	2.553278
C	-0.192978	-5.131589	0.218600
H	0.018469	-5.949186	0.923224
H	-1.144635	-5.356846	-0.281651
H	0.591279	-5.116884	-0.547118
C	1.051896	-3.783431	3.151510
H	0.998718	-4.877529	3.252589
H	2.002150	-3.454249	3.593756
H	0.240581	-3.336773	3.738649
C	2.271838	-3.770474	0.979534
H	3.112872	-3.223423	1.428944
H	2.472919	-4.847547	1.067452
H	2.231131	-3.487374	-0.079069
C	-1.377737	5.280174	-0.940534
C	-2.157524	2.523205	-1.965128
C	-2.808353	4.751146	-0.831928
C	-3.021054	3.231934	-0.923969
H	-1.429885	6.374503	-1.049486
H	-2.165669	3.135140	-2.887096
H	-3.385530	5.216723	-1.647485
H	-4.075762	3.064796	-1.193178
H	-2.900179	2.748444	0.053852
C	-0.330575	3.472776	0.561724
H	0.397300	3.342552	1.374215
C	-0.455502	4.961423	0.229096
H	-0.810818	5.488156	1.130410
H	0.545760	5.369436	0.010771
C	0.093912	2.634917	-0.617223
H	1.170861	2.632835	-0.816317
C	-0.705767	2.222952	-1.666862
H	-0.162025	1.866964	-2.545532
H	-1.278733	3.111293	0.976548
H	-2.658209	1.589000	-2.264466
H	-0.921940	4.916195	-1.874382
H	-3.261989	5.122685	0.102254
C	-3.123821	-0.272452	0.611757
C	-4.298964	-0.473354	1.369911
C	-2.080449	0.818380	2.357648
C	-4.317629	0.021964	2.685993
H	-1.169331	1.295139	2.719986
N	-2.040959	0.380397	1.104438
C	-3.204669	0.662714	3.181600
C	-3.052104	-0.787118	-0.728539
C	-4.166663	-1.459495	-1.278082
C	-1.828279	-1.066513	-2.662972
C	-4.058024	-1.933445	-2.597145
C	-2.888172	-1.728979	-3.293868
H	-0.888365	-0.883553	-3.184080
N	-1.899017	-0.612621	-1.418850
H	-5.209373	-0.116407	3.296926
H	-4.901035	-2.453855	-3.051123
H	-3.178752	1.046960	4.198412
C	-5.344633	-1.636956	-0.485222
C	-5.405974	-1.167746	0.787313
H	-2.770300	-2.074699	-4.317846
H	-6.301142	-1.311509	1.391757
H	-6.189704	-2.163741	-0.927634

TS1-C5

G(*n*-hexane) = -2968.435798 Hartree

Ir	1.184670	0.099931	0.084135
O	4.340762	-0.190365	-0.139764
O	3.529285	1.748581	-1.014746
O	2.288938	-1.398867	-2.309067
O	1.007566	-2.743760	-0.983635
C	5.478669	0.629183	-0.437724
C	4.888896	1.633600	-1.462687
C	2.572863	-2.750709	-2.706799
C	1.347633	-3.520153	-2.134224
B	3.193693	0.561545	-0.367031
B	1.525279	-1.470143	-1.132274
B	2.313685	-0.910473	1.480096
O	2.752758	-0.289436	2.651252
O	2.660662	-2.249430	1.486575
C	3.133813	-1.322622	3.571913
C	3.496363	-2.503838	2.621148
C	0.383392	3.078577	0.444668
C	-0.012031	4.332130	0.961358
C	0.948162	2.291654	2.537898
C	0.075760	4.515849	2.353022
H	1.361511	1.462761	3.114200
N	0.849961	2.083106	1.233610
C	0.143732	-3.501201	-3.067572
H	0.283307	-4.160461	-3.935307
H	-0.737876	-3.841196	-2.509291

H	-0.060680	-2.483748	-3.431080
C	1.637995	-4.939129	-1.685892
H	0.714364	-5.402898	-1.316600
H	2.019635	-5.551748	-2.515716
H	2.366433	-4.948687	-0.867052
C	2.723230	-2.805652	-4.213162
H	3.599402	-2.217618	-4.517389
H	2.875232	-3.839600	-4.555180
H	1.846611	-2.394569	-4.726864
C	3.883382	-3.142299	-2.034534
H	4.182639	-4.168388	-2.287915
H	4.673589	-2.460432	-2.375869
H	3.804725	-3.043089	-0.942982
C	4.943917	-2.476753	2.149828
H	5.641818	-2.728708	2.960042
H	5.064881	-3.217561	1.348194
H	5.200755	-1.498080	1.730159
C	3.165585	-3.881649	3.163018
H	3.435606	-4.638728	2.415354
H	3.732927	-4.093542	4.081155
H	2.096444	-3.990968	3.374201
C	4.273871	-0.819427	4.434035
H	5.107883	-0.450463	3.826180
H	3.925335	0.009629	5.064147
H	4.645981	-1.613727	5.097074
C	1.912454	-1.607240	4.439143
H	2.118734	-2.354762	5.216852
H	1.606099	-0.675841	4.934715
H	1.067270	-1.957972	3.831139
C	4.840684	1.076279	-2.880004
H	4.341067	0.097437	-2.892806
H	4.251293	1.760539	-3.504604
H	5.841530	0.983736	-3.323513
C	5.530993	3.006137	-1.461385
H	6.598119	2.940339	-1.719097
H	5.042175	3.642864	-2.210090
H	5.434622	3.499452	-0.487814
C	6.595217	-0.250158	-0.962913
H	7.468445	0.352480	-1.252855
H	6.911863	-0.952468	-0.180410
H	6.273270	-0.838273	-1.829350
C	5.906140	1.297535	0.864144
H	6.124848	0.523179	1.611504

H	6.807960	1.911159	0.734362
H	5.100996	1.927259	1.265226
C	0.559996	3.497175	3.141914
C	0.311869	2.845030	-0.972041
C	-0.116117	3.881849	-1.828392
C	0.685364	1.416613	-2.750610
C	-0.125557	3.623250	-3.210345
C	0.286412	2.394044	-3.672413
H	1.036316	0.434886	-3.072451
N	0.681712	1.631133	-1.443177
H	-0.233453	5.466850	2.786759
H	-0.452472	4.403410	-3.897637
H	0.651094	3.611870	4.219260
C	-0.515740	5.137312	-1.270510
C	-0.472335	5.351562	0.069247
H	0.303131	2.165246	-4.734955
C	-3.139891	0.326740	1.276840
C	-3.812419	-0.208883	0.162341
C	-3.104237	-0.765501	-0.902720
C	-1.718079	-0.763661	-0.830215
C	-1.004996	-0.203360	0.255294
C	-1.739875	0.319118	1.316083
C	-4.140612	0.799852	2.193188
C	-5.346986	0.538734	1.614733
H	-3.621628	-1.196790	-1.759429
H	-1.162388	-1.219912	-1.650528
H	0.335516	-1.018558	0.925627
H	-1.234938	0.719136	2.199595
H	-6.338812	0.753091	1.997125
N	-5.190703	-0.070808	0.364859
C	-3.878921	1.462515	3.499896
H	-3.351365	0.792523	4.194789
H	-3.241589	2.351733	3.377801
H	-4.809517	1.780960	3.986351
H	-0.780413	6.307928	0.490994
P	-6.341162	-0.901951	-0.657091
C	-7.163477	-2.119487	0.547461
C	-7.531711	0.493023	-1.131428
C	-8.160544	-1.587171	1.570522
C	-6.000132	-2.802536	1.272551
C	-7.860129	-3.167599	-0.327626
C	-8.015941	1.444184	-0.041901
H	-7.715833	-0.845408	2.246170

H	-9.045713	-1.141287	1.096922
H	-5.493962	-2.125162	1.972933
H	-5.245449	-3.179573	0.566455
H	-8.719774	-2.756042	-0.873344
H	-7.168651	-3.601897	-1.062609
H	-7.182421	1.998392	0.407192
H	-8.565237	0.933236	0.758885
H	-0.857004	5.918333	-1.949432
C	-6.732614	1.302826	-2.158782
H	-5.810946	1.711157	-1.720462
H	-6.451412	0.690518	-3.026717
H	-7.338768	2.148369	-2.520003
C	-8.731564	-0.141610	-1.834440
H	-9.312215	0.638354	-2.350799
H	-8.422682	-0.877655	-2.591770
H	-9.411593	-0.639642	-1.129277
H	-6.381871	-3.662597	1.844241
H	-8.236130	-3.986059	0.305677
H	-8.516282	-2.420827	2.197457
H	-8.699275	2.185435	-0.487077

TS1-C6			
G(*n*-hexane) = -2968.438293 Hartree			

Ir	0.974250	-0.080909	0.164964
O	3.807408	0.256995	-1.250481
O	2.873718	-1.802723	-1.520085
O	3.522321	-0.484101	1.755221
O	2.183220	1.104734	2.697545
C	4.636697	-0.444732	-2.186849
C	4.247961	-1.923992	-1.917767
C	4.348179	0.260295	2.665248
C	3.284537	0.912240	3.591680
B	2.701593	-0.535675	-0.966486
B	2.318000	0.225097	1.636193
B	1.593858	1.711461	-0.626944
O	1.200479	2.130383	-1.899508
O	2.320095	2.705714	0.004055
C	1.410380	3.549991	-1.962733
C	2.560788	3.760865	-0.934202
C	-0.804883	-2.060860	-1.448990
C	-1.748770	-2.653671	-2.315021
C	-1.047202	0.002876	-2.448222
C	-2.356776	-1.825441	-3.276722
H	-0.720254	1.043026	-2.471515
N	-0.466363	-0.752657	-1.529649
C	2.812880	-0.019795	4.700061
H	3.569255	-0.144417	5.487186
H	1.907171	0.403507	5.152881
H	2.557616	-1.011393	4.299894
C	3.683334	2.254340	4.171837
H	2.880913	2.631085	4.818990
H	4.597515	2.167133	4.777121
H	3.850082	2.992796	3.379574
C	5.314629	-0.684549	3.349158
H	6.019693	-1.090379	2.610908
H	5.899047	-0.159356	4.118597
H	4.798000	-1.529004	3.820248
C	5.111716	1.285958	1.834499
H	5.819590	1.860503	2.447979
H	5.672363	0.759627	1.050744
H	4.421825	1.977708	1.331537
C	3.944901	3.548048	-1.532198
H	4.221955	4.362092	-2.215998
H	4.681006	3.514606	-0.718067
H	3.999184	2.589171	-2.059136
C	2.522836	5.082356	-0.191140
H	3.355729	5.119210	0.523357
H	2.631361	5.929472	-0.884185
H	1.593474	5.204761	0.375496
C	1.745205	3.936387	-3.388663
H	2.587345	3.352262	-3.776269
H	0.879366	3.748968	-4.037414
H	1.994674	5.004945	-3.458339
C	0.100783	4.205257	-1.537163
H	0.140930	5.300223	-1.612432
H	-0.703488	3.847499	-2.194653
H	-0.162906	3.933396	-0.505730
C	4.996060	-2.532710	-0.737908
H	4.896780	-1.897369	0.153485
H	4.548697	-3.509056	-0.508313
H	6.060500	-2.691202	-0.959400
C	4.337846	-2.841330	-3.120668
H	5.369843	-2.895859	-3.496966
H	4.029697	-3.855309	-2.834456
H	3.684905	-2.509893	-3.935699

C	6.087850	-0.099373	-1.915701
H	6.757734	-0.661286	-2.583049
H	6.253933	0.971653	-2.093323
H	6.371587	-0.312149	-0.878694
C	4.243566	0.023943	-3.583014
H	4.371210	1.112551	-3.648234
H	4.868155	-0.436002	-4.360680
H	3.189950	-0.202918	-3.793308
C	-2.006842	-0.496165	-3.343180
C	-0.155443	-2.870055	-0.453706
C	-0.457735	-4.246142	-0.367298
C	1.411492	-3.022065	1.238208
C	0.236157	-5.005582	0.591600
C	1.180703	-4.396311	1.385676
H	2.167430	-2.502408	1.829120
N	0.748664	-2.281005	0.362246
H	-3.099677	-2.249144	-3.953622
H	0.023506	-6.070405	0.685520
H	-2.459274	0.172534	-4.071932
C	-1.435916	-4.808972	-1.246440
C	-2.058660	-4.043753	-2.179267
H	1.746076	-4.957706	2.125106
H	0.304762	1.223119	0.886931
H	-2.802795	-4.474748	-2.848869
C	-3.245996	-0.313515	2.835342
C	-3.236150	0.247708	1.543906
C	-2.049016	0.448758	0.841024
C	-0.840825	0.063941	1.418039
C	-0.848155	-0.445920	2.735965
C	-2.025712	-0.645505	3.438917
C	-4.618917	-0.406076	3.250241
C	-5.367125	0.084493	2.221811
H	-2.074442	0.899057	-0.152680
H	0.103641	-0.688792	3.211466
H	-2.004742	-1.054092	4.450848
H	-6.445745	0.179934	2.163467
N	-4.557543	0.511765	1.161190
P	-4.945397	0.882513	-0.502590
C	-5.109939	-0.923197	4.556743
H	-4.776433	-1.956450	4.732137
H	-4.732338	-0.323660	5.397934
H	-6.205946	-0.913217	4.607890
C	-5.936667	-0.646003	-1.042890
C	-7.364076	-0.820683	-0.536416
C	-5.084167	-1.836494	-0.591053
C	-5.951571	-0.618897	-2.574635
H	-7.421644	-0.845368	0.559030
H	-8.035552	-0.031863	-0.902539
H	-5.110330	-1.971607	0.498465
H	-4.029948	-1.718221	-0.884714
H	-6.559468	0.203963	-2.973734
H	-4.935675	-0.515537	-2.982104
C	-6.065485	2.397733	-0.327344
C	-5.081713	3.521965	0.017246
C	-7.162714	2.374129	0.731292
H	-4.560161	3.323367	0.964191
H	-4.321121	3.650309	-0.765773
H	-6.743957	2.294636	1.741961
H	-7.880525	1.556829	0.584403
H	-1.666879	-5.869530	-1.150641
C	-6.678362	2.681372	-1.698579
H	-7.121532	3.689113	-1.703263
H	-5.926099	2.649142	-2.501001
H	-7.480188	1.972557	-1.949451
H	-5.461033	-2.759252	-1.061351
H	-7.766055	-1.779605	-0.902697
H	-6.378815	-1.558872	-2.958740
H	-7.728159	3.318921	0.686989
H	-5.624170	4.474392	0.123525

TS2-C5			
G(*n*-hexane) = -3432.763328 Hartree			

Ir	-2.336170	0.008838	-0.201890
O	-5.501501	-0.048643	0.030539
O	-4.612623	2.046549	0.117424
O	-3.562473	-0.445588	2.530965
O	-2.343299	-2.248493	1.846597
C	-6.603488	0.866921	-0.034650
C	-5.977298	2.159965	0.549383
C	-3.926583	-1.534466	3.394136
C	-2.733776	-2.513015	3.196238
B	-4.324602	0.690367	-0.020069
B	-2.785873	-0.986580	1.493247
B	-3.499545	-1.388844	-1.167647
O	-3.886854	-1.219031	-2.499466

O	-3.923803	-2.618201	-0.697289
C	-4.311241	-2.499002	-2.991374
C	-4.760729	-3.226104	-1.687823
C	-1.426421	2.616626	-1.629844
C	-1.012467	3.585496	-2.570072
C	-1.992080	1.116179	-3.288681
C	-1.102056	3.246188	-3.932074
H	-2.412557	0.135963	-3.520069
N	-1.900012	1.404044	-1.998894
C	-1.540966	-2.183782	4.086673
H	-1.712938	-2.469316	5.133617
H	-0.666162	-2.732989	3.713989
H	-1.304707	-1.110314	4.052917
C	-3.083733	-3.982646	3.320517
H	-2.179022	-4.588941	3.184586
H	-3.501474	-4.210333	4.312222
H	-3.804197	-4.281905	2.551144
C	-4.105230	-1.015354	4.806257
H	-4.955351	-0.321010	4.840923
H	-4.314378	-1.839846	5.503090
H	-3.217343	-0.478360	5.159152
C	-5.244737	-2.093825	2.871768
H	-5.597156	-2.939200	3.478098
H	-6.005516	-1.303095	2.913269
H	-5.148815	-2.409399	1.823241
C	-6.210618	-2.948264	-1.313940
H	-6.909470	-3.458018	-1.991599
H	-6.386246	-3.317741	-0.294604
H	-6.417846	-1.872300	-1.312646
C	-4.510498	-4.722389	-1.676366
H	-4.847010	-5.139584	-0.718533
H	-5.069038	-5.223409	-2.480534
H	-3.445963	-4.956294	-1.786300
C	-5.403860	-2.293569	-4.020920
H	-6.229192	-1.694089	-3.620151
H	-4.996387	-1.764374	-4.892551
H	-5.804289	-3.256965	-4.368315
C	-3.095285	-3.145239	-3.644980
H	-3.333364	-4.118231	-4.095184
H	-2.726389	-2.483165	-4.440293
H	-2.282586	-3.284180	-2.919211
C	-5.956819	2.177834	2.073228
H	-5.504781	1.256388	2.466617
H	-5.335345	3.021456	2.402785
H	-6.961774	2.304123	2.499450
C	-6.565167	3.451902	0.019239
H	-7.637964	3.517000	0.252466
H	-6.065085	4.307828	0.490645
H	-6.436034	3.543385	-1.064905
C	-7.767547	0.298793	0.751085
H	-8.613662	1.001419	0.763990
H	-8.108781	-0.635062	0.284636
H	-7.487300	0.071593	1.785475
C	-6.982785	1.007220	-1.505162
H	-7.224559	0.015281	-1.909257
H	-7.858790	1.654459	-1.647647
H	-6.143412	1.407458	-2.088973
C	-1.596910	2.013681	-4.292375
C	-1.369934	2.924773	-0.226524
C	-0.915750	4.194321	0.190074
C	-1.797172	2.269984	1.948289
C	-0.917249	4.465450	1.569541
C	-1.368500	3.507282	2.448244
H	-2.183359	1.489618	2.605704
N	-1.780486	1.983320	0.655058
H	-0.783269	3.967766	-4.684265
H	-0.569219	5.435676	1.923823
H	-1.686188	1.724561	-5.336658
C	-0.487004	5.145869	-0.788686
C	-0.531452	4.853332	-2.113567
H	-0.127165	6.114724	-0.443268
H	-1.396647	3.690421	3.519380
C	1.853781	-0.525487	1.211007
C	2.638895	-0.447512	0.043640
C	2.043932	-0.371275	-1.214994
C	0.656069	-0.357116	-1.271173
C	-0.164342	-0.410501	-0.121486
C	0.457063	-0.524222	1.118772
C	2.754547	-0.605045	2.327789
C	4.013936	-0.576788	1.808789
H	2.648152	-0.333897	-2.121349
H	0.184850	-0.314081	-2.255757
H	-1.519081	-1.375840	-0.509961
H	-0.136107	-0.607748	2.031820
H	4.959331	-0.616578	2.338842
N	3.988673	-0.491217	0.411999

C	2.361644	-0.712917	3.758918
H	1.737742	0.138178	4.070766
H	1.768488	-1.620138	3.948021
H	3.238628	-0.743235	4.417874
P	5.266018	-0.179946	-0.741466
C	6.143124	1.328822	-0.008723
C	6.325927	-1.735043	-0.575555
C	7.071552	1.154432	1.202220
C	5.029729	2.333521	0.355774
C	6.961285	1.940590	-1.168810
C	5.508957	-2.811953	-1.325961
C	6.632373	-2.270678	0.831314
C	7.646312	-1.525200	-1.337648
C	7.672354	2.504892	1.615572
H	6.518498	0.728307	2.053630
H	7.887361	0.452995	0.961993
C	5.635029	3.680063	0.765716
H	4.416134	1.936181	1.178872
H	4.352518	2.466966	-0.505941
H	7.762841	1.252266	-1.480737
H	6.307019	2.078237	-2.045360
C	7.572635	3.283260	-0.756632
C	6.289198	-4.127212	-1.406933
H	4.544685	-2.968448	-0.814602
H	5.274183	-2.455136	-2.342757
C	7.430915	-3.577510	0.744091
H	5.690424	-2.462171	1.365982
H	7.198466	-1.530680	1.417738
H	7.438611	-1.138708	-2.351084
H	8.266693	-0.769698	-0.827910
C	8.430854	-2.839422	-1.425246
C	6.546414	3.475635	1.978800
H	8.327013	2.352578	2.487712
C	8.486727	3.077804	0.453435
H	4.819717	4.372182	1.027693
C	6.451738	4.257996	-0.391961
H	8.156000	3.685152	-1.599553
C	6.601372	-4.628884	0.004534
H	5.680921	-4.873015	-1.941187
C	7.598509	-3.890614	-2.163450
H	7.650423	-3.928988	1.764292
C	8.740304	-3.334604	-0.009538
H	9.370873	-2.659011	-1.969534
H	5.964131	3.078833	2.826151
H	6.969938	4.440533	2.302321
H	8.945840	4.035191	0.748682
H	9.310375	2.392171	0.194496
H	5.801696	4.430205	-1.264939
H	6.875937	5.234585	-0.106858
H	5.665836	-4.825894	0.552093
H	7.152977	-5.581899	-0.044792
H	8.166333	-4.831734	-2.244111
H	7.387154	-3.552546	-3.190815
H	9.353064	-2.590452	0.525974
H	9.330744	-4.264117	-0.054459
H	-0.206410	5.581444	-2.856307

TS2-C6			
G(*n*-hexane) = -3432.768626 Hartree			

Ir	2.048671	0.078101	0.413136
O	4.404372	-0.717059	-1.577326
O	3.704361	1.441112	-1.777365
O	1.320728	-1.301046	-2.185696
O	0.789184	-2.580785	-0.373048
C	5.328850	-0.069247	-2.462893
C	4.511185	1.164152	-2.931756
C	1.099580	-2.633316	-2.676241
C	0.280767	-3.270464	-1.518140
B	3.530549	0.245821	-1.082999
B	1.354252	-1.387941	-0.785447
B	3.531022	-1.232042	0.970606
O	4.631618	-0.807281	1.721249
O	3.566105	-2.604229	0.803002
C	5.208575	-1.974284	2.325846
C	4.805073	-3.096869	1.325068
C	2.202549	3.105822	1.121482
C	2.450538	4.354290	1.732169
C	3.617875	2.011074	2.576600
C	3.331007	4.376437	2.828958
H	4.075059	1.060058	2.853191
N	2.781735	1.960459	1.551294
C	-1.210811	-2.971100	-1.601047
H	-1.707489	-3.546514	-2.395716
H	-1.672393	-3.237792	-0.639841
H	-1.401094	-1.900999	-1.769142

C	0.502586	-4.758257	-1.328240
H	-0.120149	-5.120705	-0.500329
H	0.227687	-5.319371	-2.233539
H	1.547848	-4.972741	-1.079055
C	0.384821	-2.561325	-4.009602
H	1.034692	-2.077302	-4.751051
H	0.142378	-3.568044	-4.379700
H	-0.543500	-1.981932	-3.943951
C	2.474145	-3.269679	-2.846309
H	2.407159	-4.287252	-3.254856
H	3.060989	-2.654645	-3.540905
H	3.018405	-3.291992	-1.891360
C	5.773667	-3.234279	0.159613
H	6.724931	-3.690278	0.466835
H	5.313183	-3.873236	-0.605842
H	5.963532	-2.258483	-0.299765
C	4.563213	-4.454764	1.955468
H	4.288638	-5.176359	1.175361
H	5.470539	-4.824615	2.454926
H	3.745060	-4.425743	2.683084
C	6.700146	-1.763590	2.487662
H	7.170068	-1.477236	1.540060
H	6.886391	-0.960643	3.213224
H	7.187318	-2.675686	2.861499
C	4.550615	-2.130581	3.692589
H	4.966417	-2.973427	4.260835
H	4.718164	-1.213113	4.273257
H	3.465818	-2.274462	3.594508
C	3.553357	0.843236	-4.073613
H	2.918679	-0.017091	-3.816709
H	2.896349	1.708515	-4.234064
H	4.084288	0.639600	-5.013718
C	5.334014	2.391288	-3.267879
H	6.023004	2.186932	-4.100321
H	4.668667	3.209095	-3.573523
H	5.916456	2.736947	-2.406537
C	5.727226	-1.037889	-3.557376
H	6.415610	-0.563330	-4.271887
H	6.239065	-1.903516	-3.115430
H	4.857815	-1.410992	-4.108651
C	6.552940	0.310611	-1.637082
H	6.974286	-0.596749	-1.184592
H	7.336798	0.775900	-2.249898

H	6.282305	0.996428	-0.823426
C	3.917917	3.205284	3.249899
C	1.321899	3.037186	-0.013446
C	0.735184	4.220680	-0.511429
C	0.338918	1.755108	-1.666604
C	-0.084824	4.113063	-1.648588
C	-0.276941	2.881251	-2.231615
H	0.230189	0.762369	-2.106643
N	1.103798	1.830871	-0.586837
H	3.540218	5.323470	3.326500
H	-0.547649	5.010536	-2.059832
H	4.608021	3.189287	4.089884
C	0.997207	5.466887	0.140252
C	1.818704	5.530796	1.219178
H	-0.898613	2.766234	-3.117412
H	1.559462	-0.986819	1.554059
H	2.018256	6.482112	1.711848
C	-2.050198	0.586757	3.246303
C	-2.110633	0.202906	1.891127
C	-0.963202	-0.062800	1.145677
C	0.284423	0.110233	1.739791
C	0.343262	0.491805	3.099859
C	-0.796592	0.726587	3.853134
C	-3.402101	0.748542	3.706093
C	-4.206280	0.482673	2.637372
H	-1.050792	-0.392446	0.109661
H	1.321589	0.590030	3.576919
H	-0.720511	1.010833	4.904226
H	-5.290066	0.498396	2.588775
N	-3.453678	0.152966	1.505759
P	-3.915940	-0.283128	-0.120665
C	-3.822553	1.132514	5.081271
H	-3.463559	0.410920	5.829764
H	-3.416482	2.113206	5.370152
H	-4.915030	1.186187	5.168889
C	-5.172045	-1.669258	0.136906
C	-6.586936	-1.348524	0.643427
C	-4.503892	-2.650060	1.124541
C	-5.290506	-2.381817	-1.230035
C	-7.410489	-2.638172	0.772144
H	-6.541943	-0.848358	1.623929
H	-7.098272	-0.659087	-0.048864
C	-5.325368	-3.936176	1.245975

H	-4.403426	-2.178818	2.114222
H	-3.478656	-2.880966	0.785804
H	-5.756694	-1.713436	-1.971589
H	-4.283144	-2.620704	-1.609556
C	-6.118402	-3.663602	-1.105090
C	-6.726572	-3.589791	1.757115
H	-8.416439	-2.383075	1.140512
C	-7.519346	-3.315630	-0.595775
H	-4.827261	-4.611596	1.958044
C	-5.433610	-4.613902	-0.121338
H	-6.191274	-4.140663	-2.094818
H	-6.660005	-3.121617	2.752542
H	-7.326757	-4.507039	1.872190
H	-8.132698	-4.227901	-0.518181
H	-8.026248	-2.646752	-1.310949
H	-4.429963	-4.880770	-0.491510
H	-6.006852	-5.551499	-0.037669
C	-4.739854	1.304203	-0.722978
C	-3.547450	2.255044	-0.974054
C	-5.733326	2.027985	0.197702
C	-5.417081	1.018578	-2.074520
C	-4.020976	3.559361	-1.620340
H	-3.028418	2.463418	-0.022329
H	-2.809785	1.758921	-1.628692
C	-6.219337	3.327076	-0.459944
H	-5.244351	2.265090	1.154750
H	-6.596501	1.383534	0.424450
H	-4.716056	0.490064	-2.744497
H	-6.283513	0.352535	-1.930069
C	-5.889226	2.322013	-2.726306
C	-5.025389	4.254317	-0.698771
H	-3.149893	4.215180	-1.784362
C	-4.690980	3.245579	-2.960297
H	-6.940600	3.818231	0.211466
C	-6.893086	3.010506	-1.797404
H	-6.371885	2.089587	-3.688194
H	-4.546063	4.508272	0.260065
H	-5.365103	5.200102	-1.151973
H	-5.022859	4.177312	-3.446827
H	-3.969925	2.764751	-3.642711
H	-7.765602	2.356276	-1.635704
H	-7.267340	3.937005	-2.262244
H	0.524450	6.365835	-0.254427

Ir(phen)(Bpin)$_3$			
G(*n*-hexane) = -1909.241222 Hartree			

Ir	0.462538	0.145903	-0.446163
O	-1.638429	-2.127674	-0.298622
O	-1.392657	-1.183521	-2.360872
O	-2.392405	1.296700	-0.707907
O	-0.827616	2.882329	-0.237606
C	-2.728495	-2.608410	-1.095422
C	-2.210042	-2.345126	-2.538460
C	-3.073706	2.550625	-0.760187
C	-2.102423	3.493824	0.008307
B	-0.979784	-1.129535	-1.024419
B	-1.035951	1.510943	-0.478110
B	-0.309800	-0.392296	1.303780
O	0.271132	-1.388893	2.090049
O	-1.371225	0.197910	1.989399
C	-0.573450	-1.602435	3.230018
C	-1.303360	-0.233002	3.353911
C	3.507906	0.853601	-0.436898
C	4.740160	1.538986	-0.472442
C	2.304246	2.828008	-0.495049
C	4.698011	2.945257	-0.527524
H	1.314708	3.288023	-0.485261
N	2.316410	1.502144	-0.447271
C	-2.074470	4.924921	-0.491482
H	-3.061272	5.399524	-0.388389
H	-1.360667	5.511933	0.102420
H	-1.768366	4.986891	-1.542273
C	-2.324699	3.477936	1.515808
H	-1.491970	4.007464	1.998898
H	-3.259740	3.980962	1.799272
H	-2.334333	2.448524	1.897697
C	-3.228313	2.915531	-2.231112
H	-3.726927	2.083143	-2.745607
H	-3.833093	3.821908	-2.375145
H	-2.251148	3.063078	-2.709664
C	-4.440919	2.385313	-0.123806
H	-4.958983	3.350616	-0.024057
H	-5.065251	1.735072	-0.752213
H	-4.365880	1.917512	0.865399
C	-2.709388	-0.294291	3.916628

H	-2.713404	-0.704400	4.937016
H	-3.133421	0.718590	3.962044
H	-3.371894	-0.902662	3.290975
C	-0.488805	0.803806	4.119061
H	-0.953151	1.790011	3.987464
H	-0.449820	0.586422	5.195485
H	0.538670	0.865825	3.736388
C	-1.521881	-2.748398	2.902464
H	-2.178632	-2.488762	2.064536
H	-0.929645	-3.620377	2.592649
H	-2.129263	-3.034918	3.772618
C	0.291628	-1.978915	4.417068
H	-0.307923	-2.055412	5.335983
H	0.755921	-2.958321	4.239318
H	1.097022	-1.254503	4.583796
C	-3.289472	-2.035732	-3.556947
H	-3.842622	-1.126734	-3.293700
H	-2.834186	-1.874397	-4.543403
H	-4.001989	-2.868827	-3.648008
C	-1.312428	-3.459097	-3.061675
H	-1.875990	-4.370619	-3.304885
H	-0.815721	-3.111031	-3.976762
H	-0.530882	-3.714319	-2.332986
C	-3.946959	-1.765113	-0.742763
H	-4.854550	-2.115159	-1.254537
H	-4.117472	-1.827508	0.341206
H	-3.771709	-0.709790	-0.987527
C	-2.984457	-4.062751	-0.754376
H	-3.349762	-4.142801	0.278825
H	-3.750838	-4.496852	-1.413314
H	-2.073529	-4.668015	-0.831711
C	3.482321	3.589495	-0.537838
C	3.498261	-0.583089	-0.366410
C	4.721262	-1.285733	-0.323152
C	2.268244	-2.529406	-0.225094
C	4.658560	-2.689171	-0.229179
C	3.431850	-3.310561	-0.171805
H	1.276838	-2.978713	-0.168060
N	2.297232	-1.208734	-0.330835
H	5.632008	3.506293	-0.556994
H	5.583258	-3.264870	-0.197794
H	3.418117	4.674022	-0.575230
C	5.953895	-0.560218	-0.370988
C	5.962874	0.796125	-0.444511
H	6.886616	-1.122775	-0.344655
H	3.348902	-4.391265	-0.088939
H	6.902605	1.346573	-0.478275

1			
G(*n*-hexane) = -1059.231355 Hartree			

C	-2.621730	0.317855	0.266275
C	-1.586345	-0.479694	-0.270980
C	-1.860680	-1.584935	-1.078496
C	-3.190848	-1.877825	-1.340145
C	-4.231547	-1.095280	-0.813004
C	-3.957010	-0.000511	-0.010678
C	-2.003010	1.356075	1.042472
C	-0.658098	1.149916	0.949564
H	-1.057158	-2.195362	-1.487790
H	-5.264295	-1.357472	-1.038859
H	-4.763524	0.606147	0.402448
H	0.141588	1.723995	1.405205
N	-0.363631	0.035659	0.160551
P	1.165401	-0.567584	-0.457679
C	-2.709041	2.426105	1.798428
H	-3.343981	3.035730	1.138817
H	-3.368356	2.009327	2.574100
H	-2.001531	3.102408	2.294346
C	1.935044	0.970381	-1.260352
C	2.508062	2.061930	-0.363775
C	0.833254	1.557889	-2.145784
C	3.047793	0.444068	-2.173687
H	1.757818	2.499230	0.307594
H	3.350872	1.704167	0.243182
H	0.033199	2.029602	-1.560026
H	0.372649	0.793329	-2.789463
H	3.886607	0.013278	-1.610883
H	2.676341	-0.324405	-2.865939
C	2.070333	-1.040131	1.136257
C	1.366707	-2.327763	1.577235
C	2.050875	-0.055221	2.299871
H	0.302166	-2.156978	1.792986
H	1.434449	-3.112689	0.810630
H	1.033452	0.106499	2.677729
H	2.488494	0.919675	2.048254

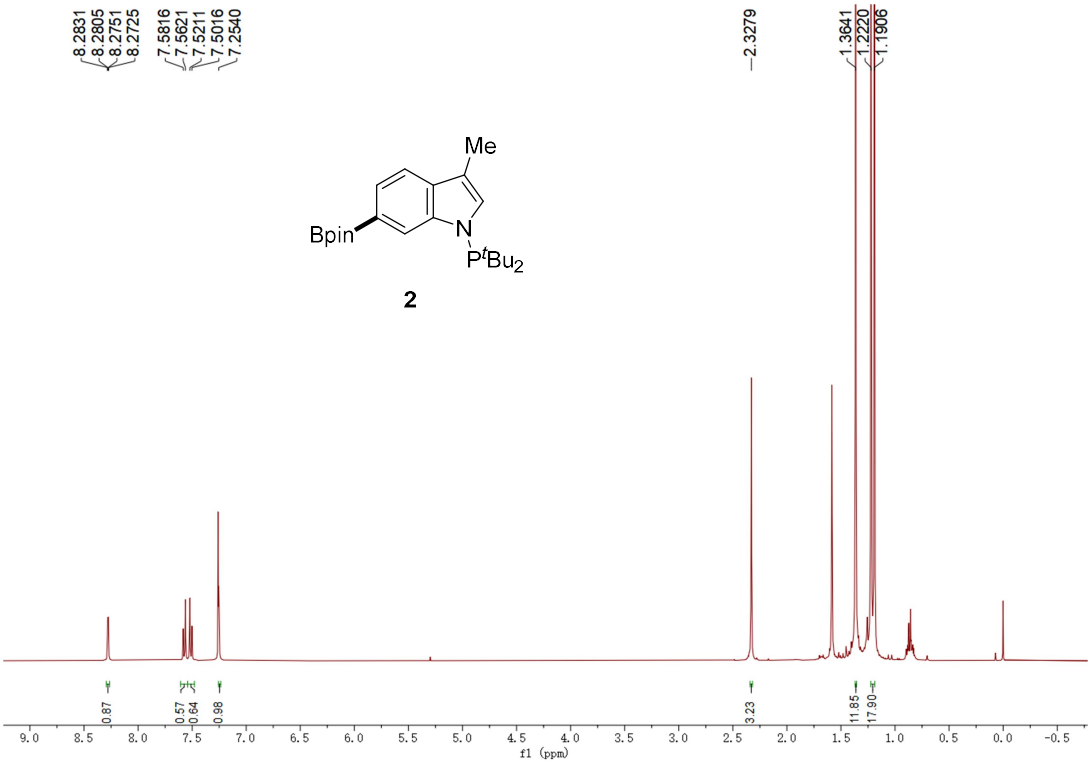
C	3.514826	-1.372098	0.764069
H	3.999942	-1.894181	1.603304
H	3.575426	-2.034925	-0.112296
H	4.108160	-0.470580	0.556608
H	1.265915	2.327120	-2.804095
H	2.890536	2.882513	-0.992379
H	3.450816	1.271962	-2.777397
H	2.640888	-0.470785	3.132800
H	1.834960	-2.713265	2.496455
H	-3.432537	-2.734779	-1.967609

3a			
G(*n*-hexane) = -1523.561067 Hartree			

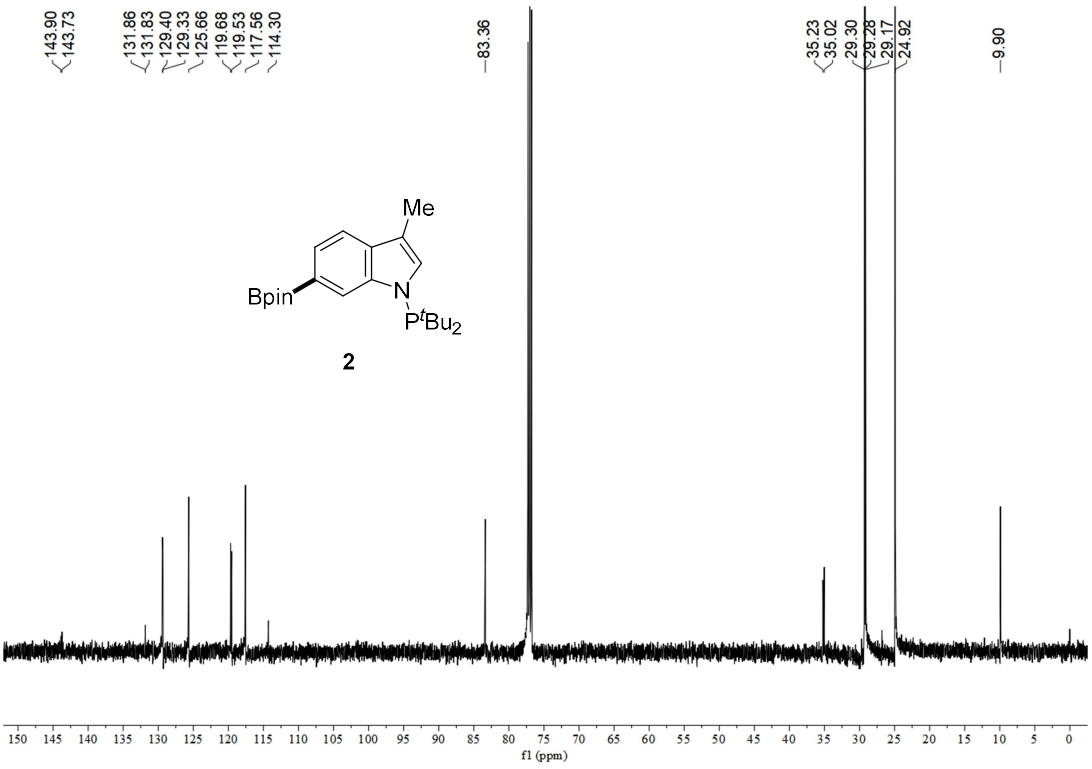
C	-2.524065	-2.702950	0.467427
C	-1.745802	-2.081818	-0.535541
C	-1.867709	-2.438864	-1.879572
C	-2.784892	-3.427936	-2.203429
C	-3.564997	-4.055439	-1.217943
C	-3.439837	-3.702014	0.115178
C	-2.156982	-2.109534	1.722582
C	-1.197313	-1.183118	1.438325
H	-1.261613	-1.956597	-2.645085
H	-4.273629	-4.829428	-1.509565
H	-4.042471	-4.190003	0.882012
H	-0.672946	-0.528800	2.126376
N	-0.914019	-1.140429	0.071628
P	0.059046	-0.019110	-0.869562
C	-2.718187	-2.457454	3.056293
H	-3.808055	-2.312298	3.087086
H	-2.532365	-3.510480	3.314901
H	-2.279867	-1.840453	3.850830
C	-0.555746	1.673450	-0.292386
C	-0.154765	2.201611	1.093858
C	-2.096473	1.612083	-0.376085
C	-0.072308	2.679660	-1.362221
C	-0.768245	3.588528	1.333250
H	-0.498647	1.515277	1.883171
H	0.942064	2.269598	1.178649
C	-2.705539	2.996978	-0.134230
H	-2.490179	0.901838	0.367561
H	-2.400424	1.232089	-1.367103
H	1.026170	2.753432	-1.353498
H	-0.357844	2.317775	-2.363816
C	-0.676581	4.066051	-1.117793
C	-2.294027	3.493665	1.254316
H	-0.469496	3.941300	2.332450
C	-0.261280	4.563847	0.268741
H	-3.801738	2.917546	-0.190504
C	-2.201465	3.976791	-1.195199
H	-0.303365	4.758004	-1.888341
H	-2.671269	2.806338	2.028907
H	-2.744053	4.479971	1.452330
H	-0.673914	5.569478	0.449718
H	0.836282	4.651321	0.326821
H	-2.510315	3.640666	-2.198095
H	-2.648341	4.971633	-1.036909
C	1.799321	-0.384791	-0.239119
C	2.176046	-1.712705	-0.933345
C	2.015491	-0.561910	1.271108
C	2.743390	0.713756	-0.760709
C	3.633938	-2.083035	-0.641882
H	1.502792	-2.514729	-0.587708
H	2.026568	-1.618476	-2.021932
C	3.481053	-0.915882	1.560856
H	1.368288	-1.369523	1.645183
H	1.741825	0.355159	1.815396
H	2.595769	0.855092	-1.845796
H	2.510936	1.676509	-0.276714
C	4.203205	0.346091	-0.473130
C	3.832492	-2.233770	0.867779
H	3.871342	-3.031423	-1.147257
C	4.549519	-0.973592	-1.165722
H	3.611440	-1.022779	2.648734
C	4.393142	0.196801	1.038760
H	4.855039	1.147791	-0.852685
H	3.196540	-3.046029	1.254638
H	4.876802	-2.509907	1.086522
H	5.603724	-1.232503	-0.975499
H	4.435632	-0.870255	-2.256882
H	4.159089	1.147924	1.545267
H	5.445285	-0.038162	1.266982
H	-2.900927	-3.724232	-3.245106
---			

9. ^{1}H and ^{13}C NMR spectra

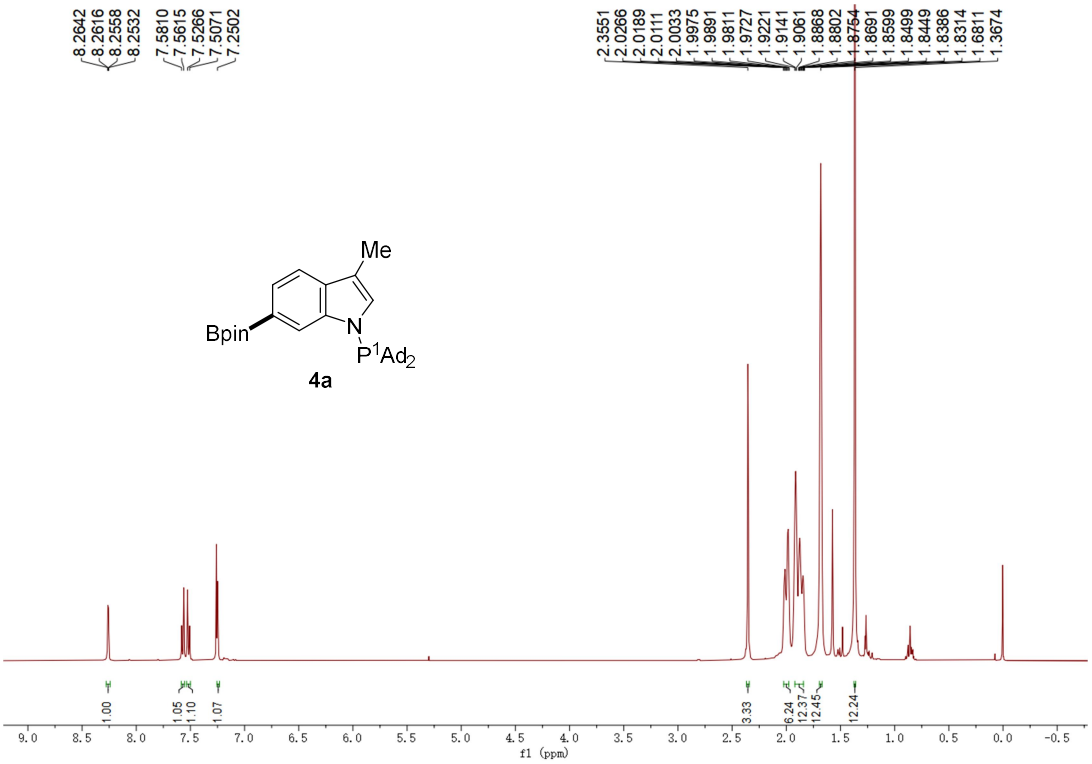
^{1}H NMR spectrum of **2** (400 MHz, Chloroform-*d*)



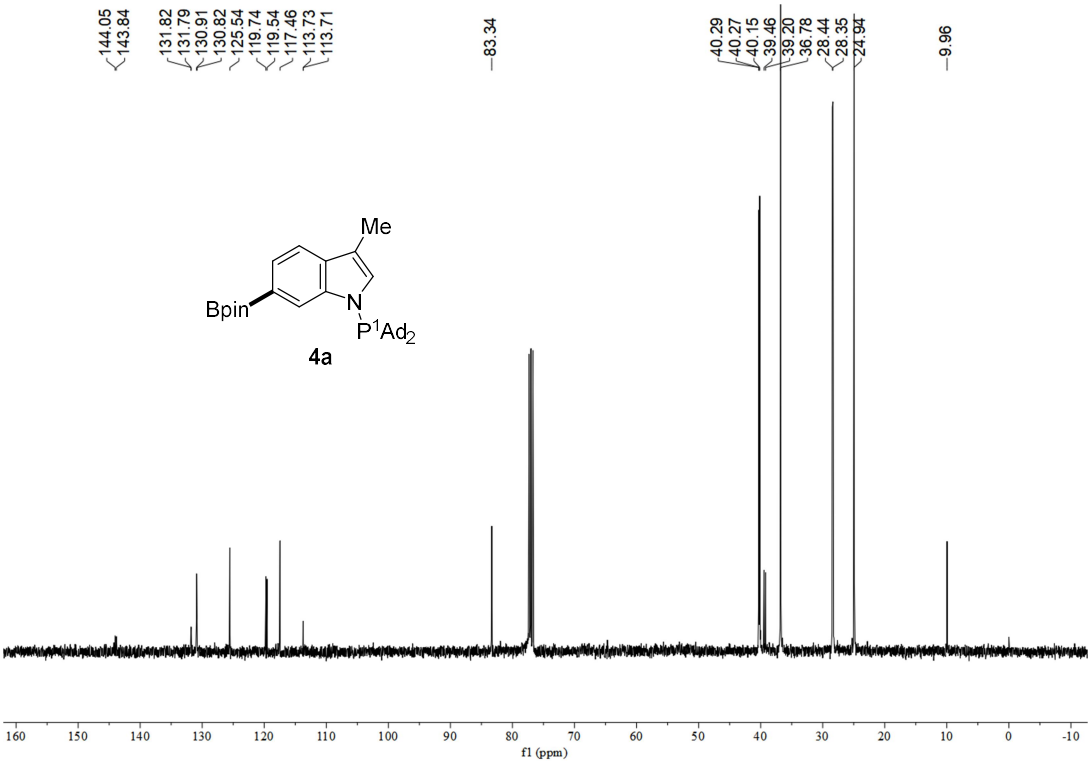
^{13}C NMR spectrum of **2** (125 MHz, Chloroform-*d*)



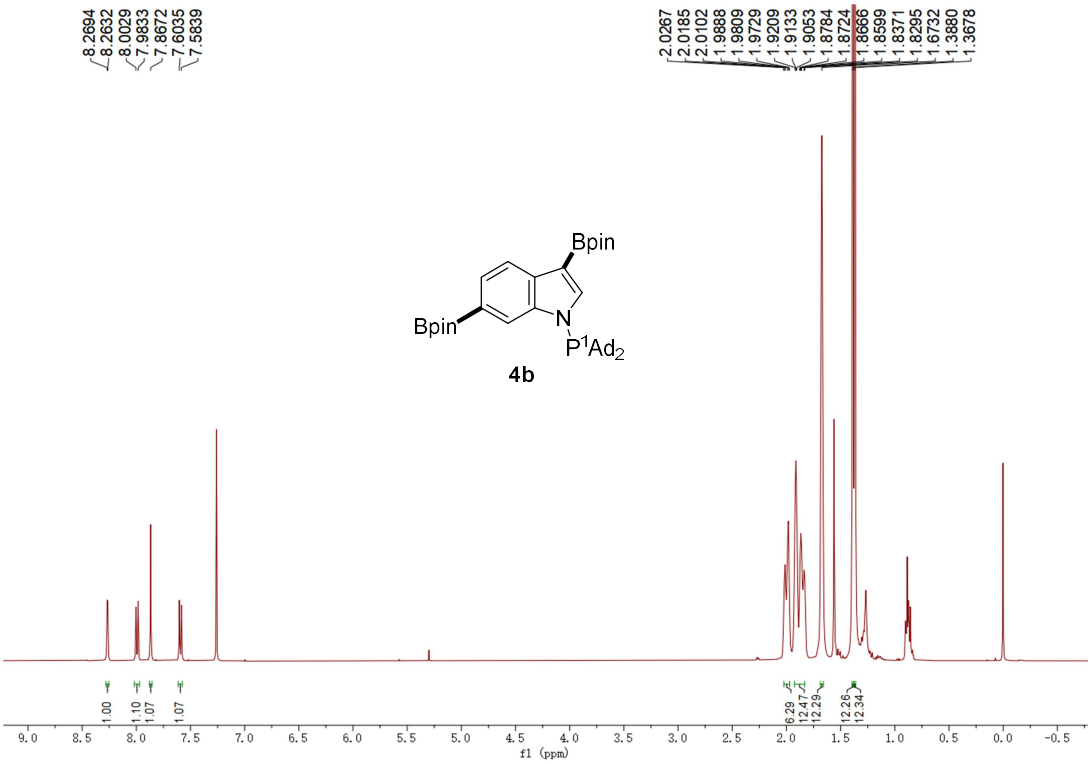
^{1}H NMR spectrum of **4a** (400 MHz, Chloroform-*d*)



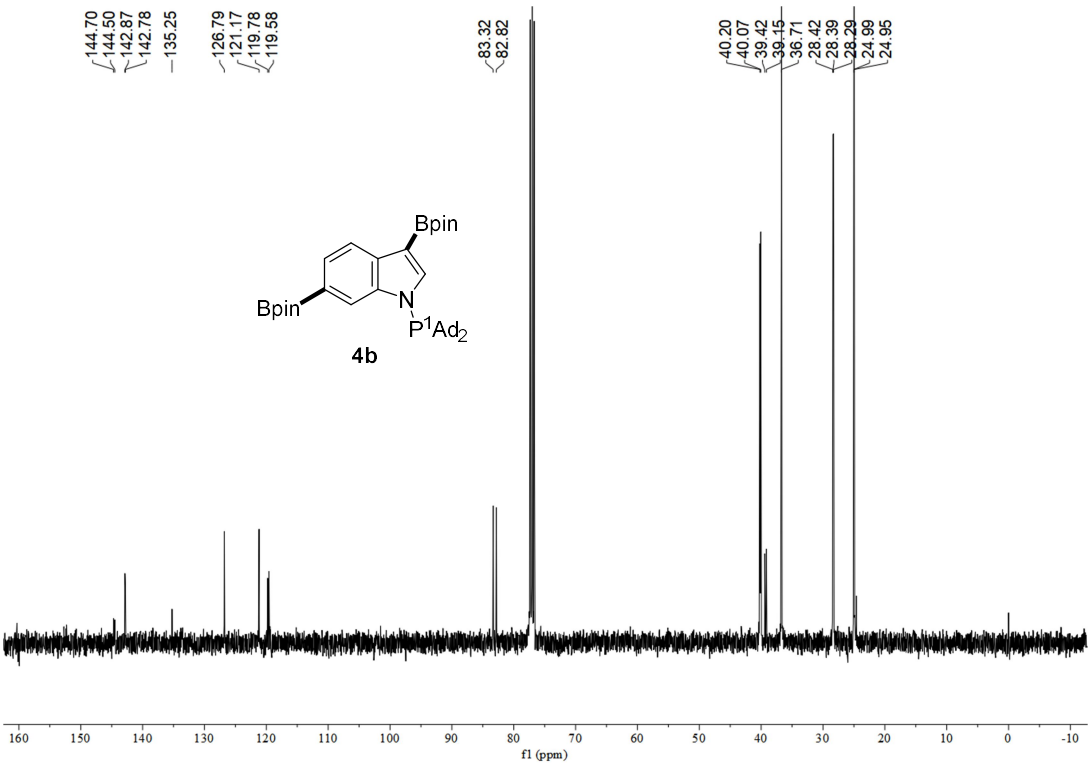
^{13}C NMR spectrum of **4a (**100 MHz, Chloroform-*d***)**



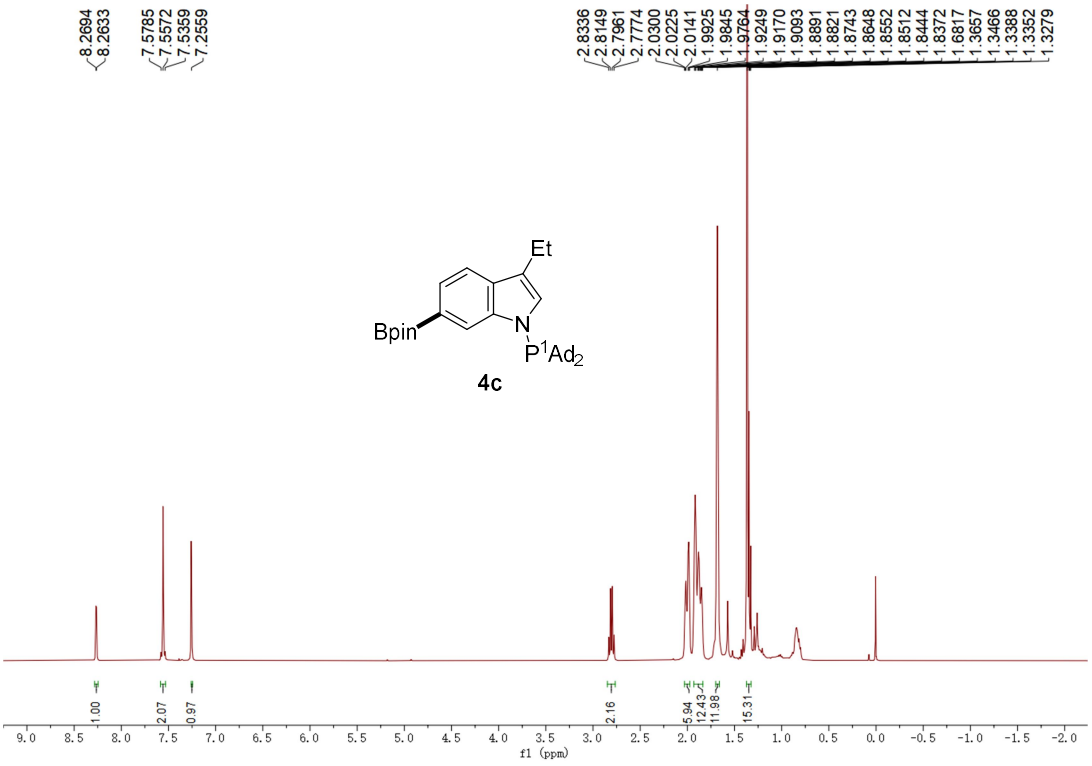
^{1}H NMR spectrum of **4b** (400 MHz, Chloroform-*d*)



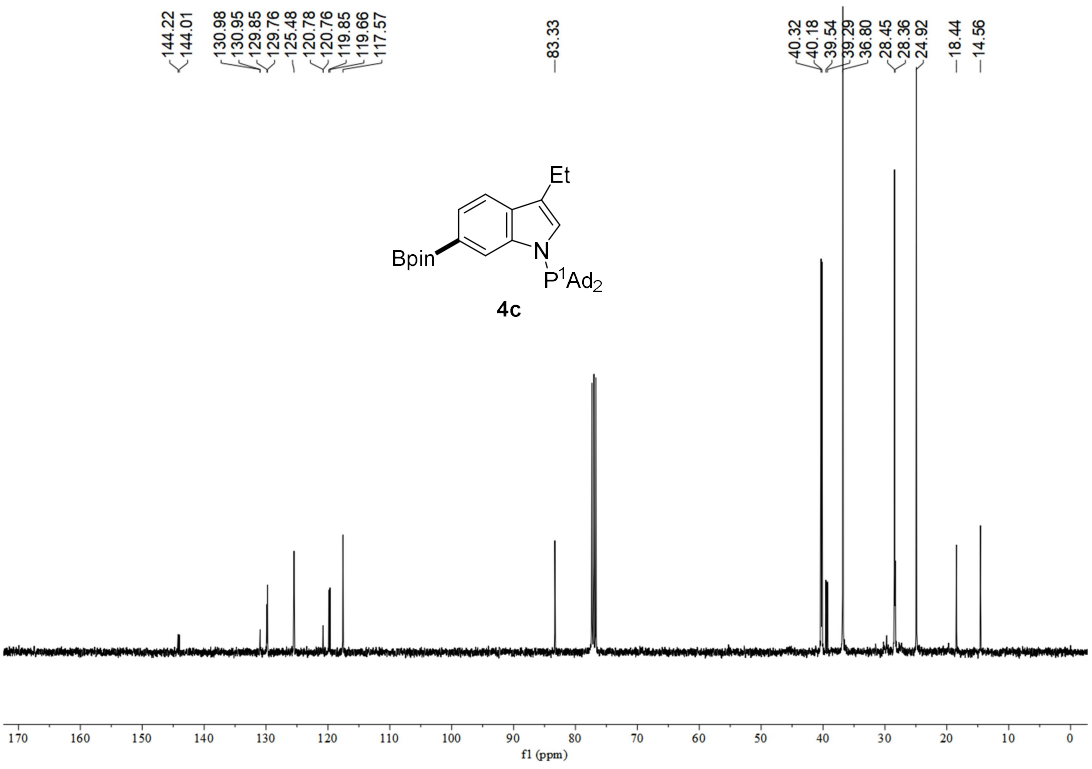
^{13}C NMR spectrum of **4b** (100 MHz, Chloroform-*d*)



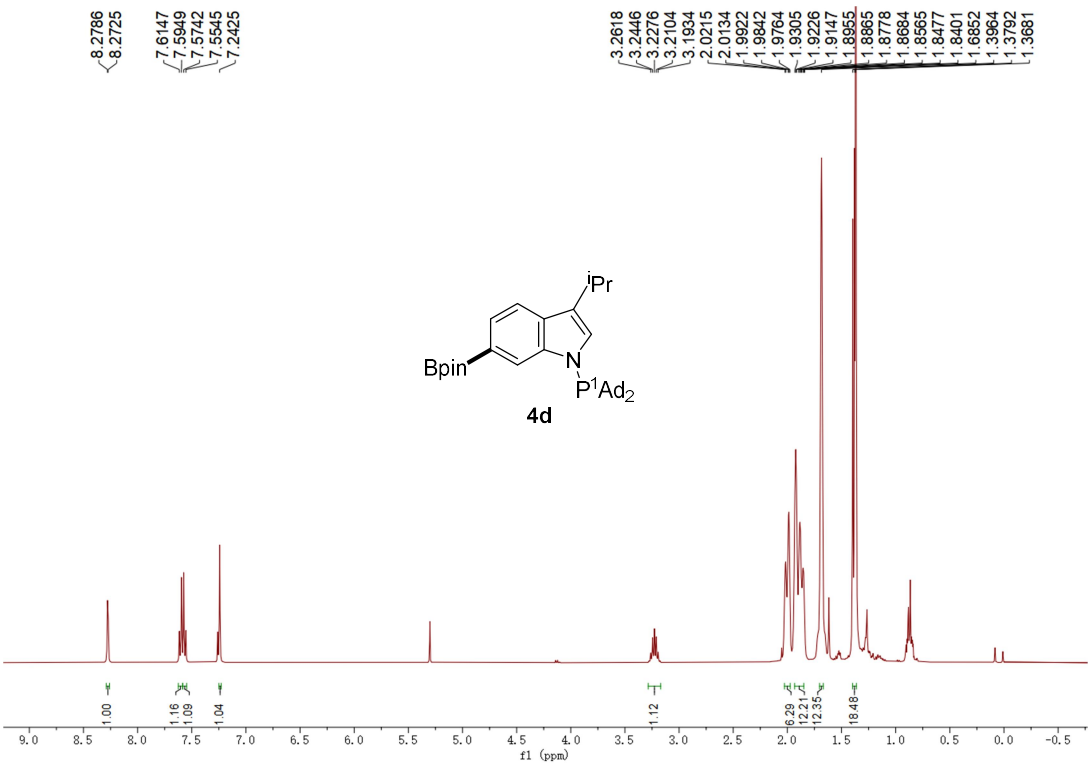
^{1}H NMR spectrum **of 4c** (400 MHz, Chloroform-*d*)



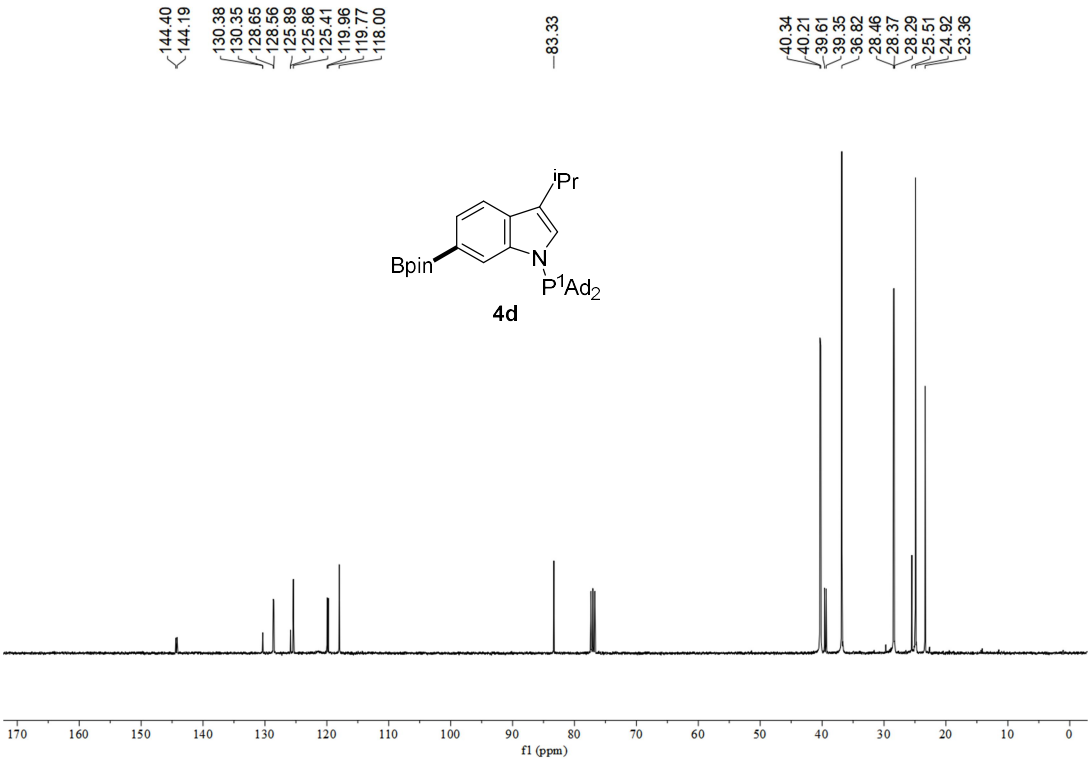
^{13}C NMR spectrum **of 4c** (100 MHz, Chloroform-*d*)



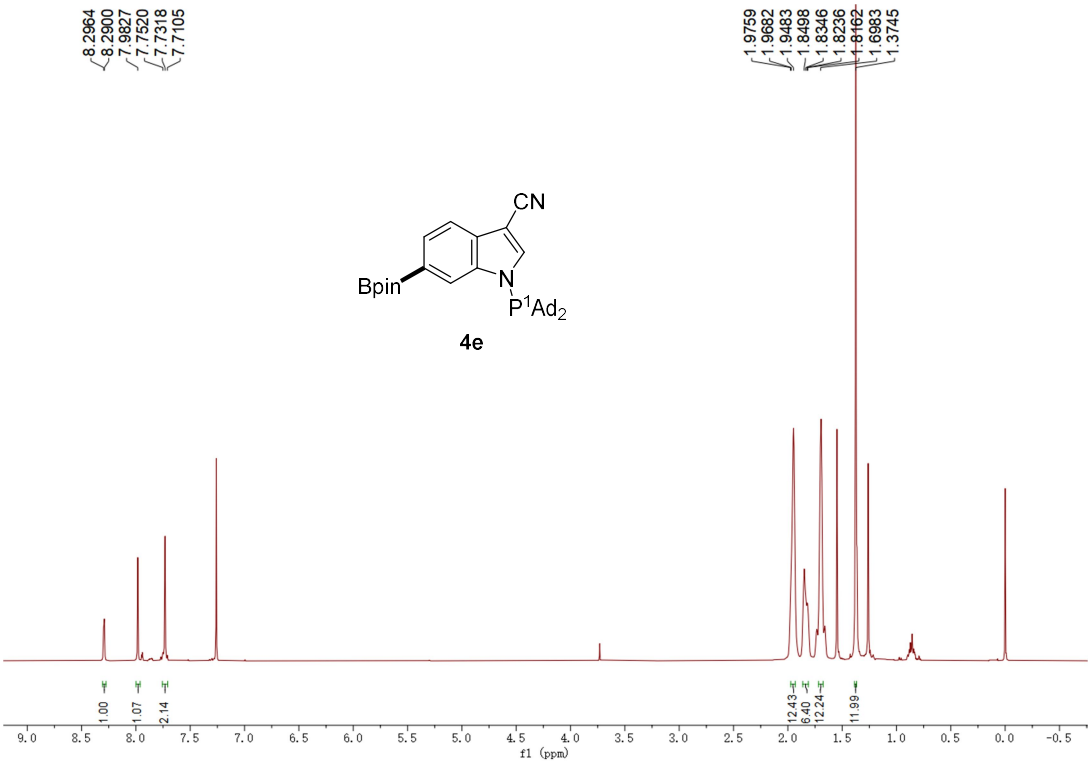
^{1}H NMR spectrum of **4d** (400 MHz, Chloroform-*d*)



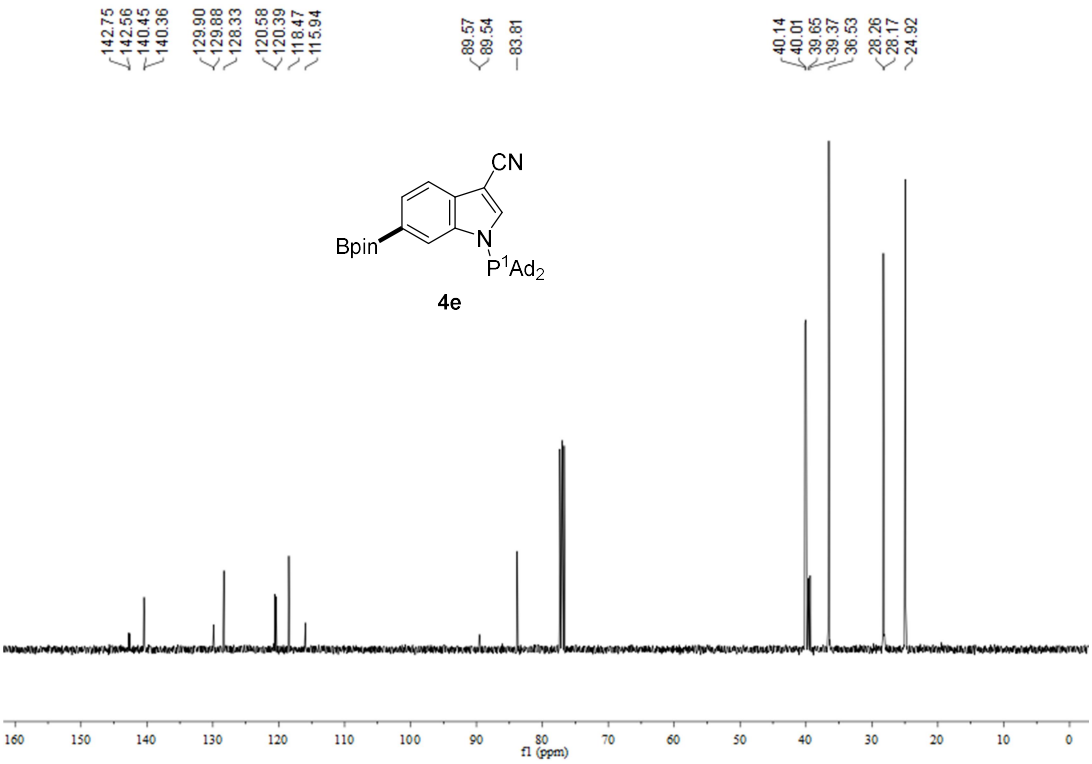
^{13}C NMR spectrum of **4d** (100 MHz, Chloroform-*d*)



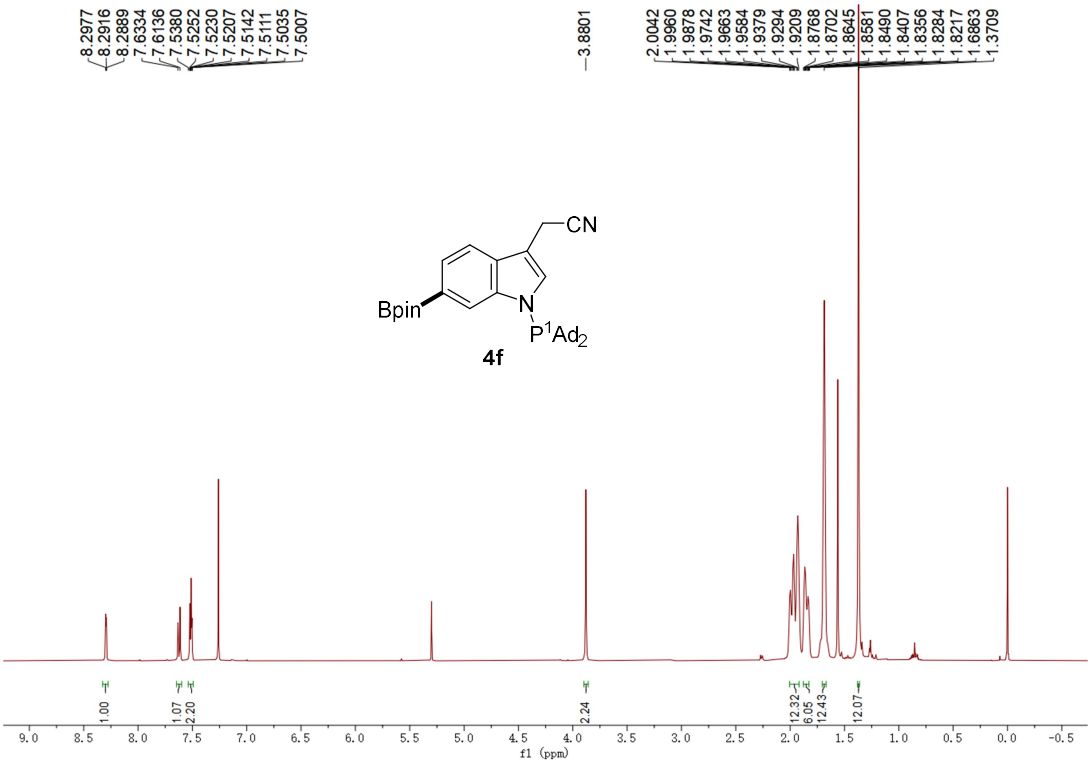
^{1}H NMR spectrum of **4e** (400 MHz, Chloroform-*d*)



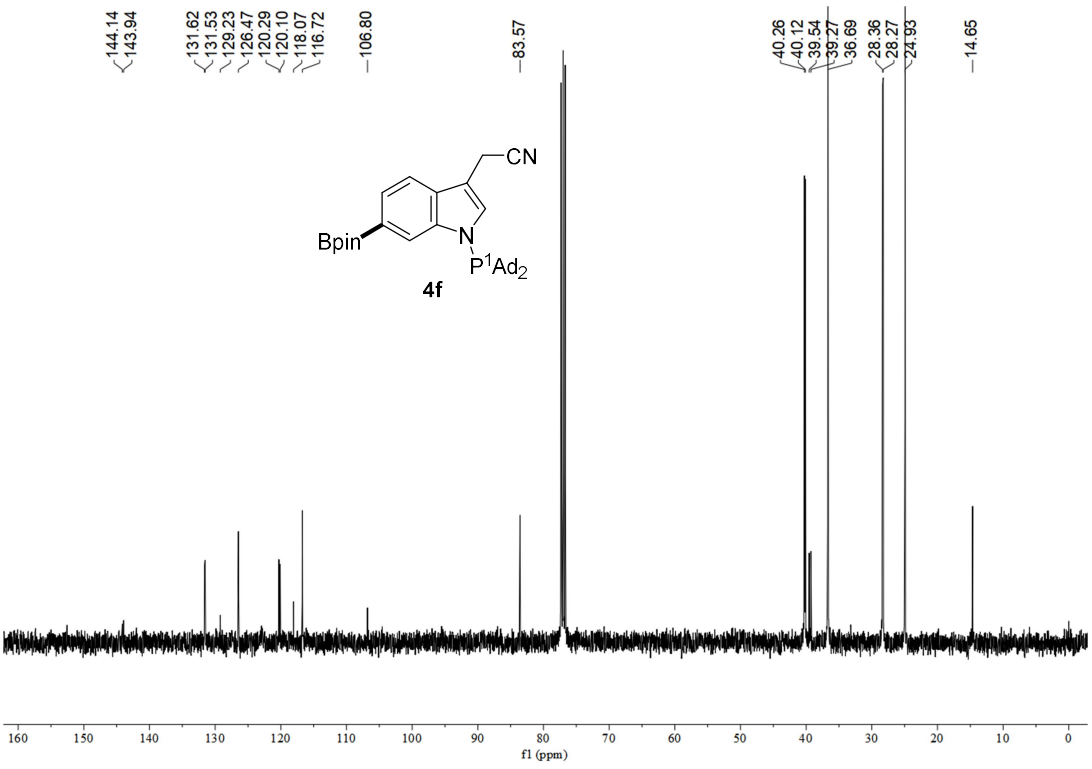
^{13}C NMR spectrum of **4e** (100 MHz, Chloroform-*d*)



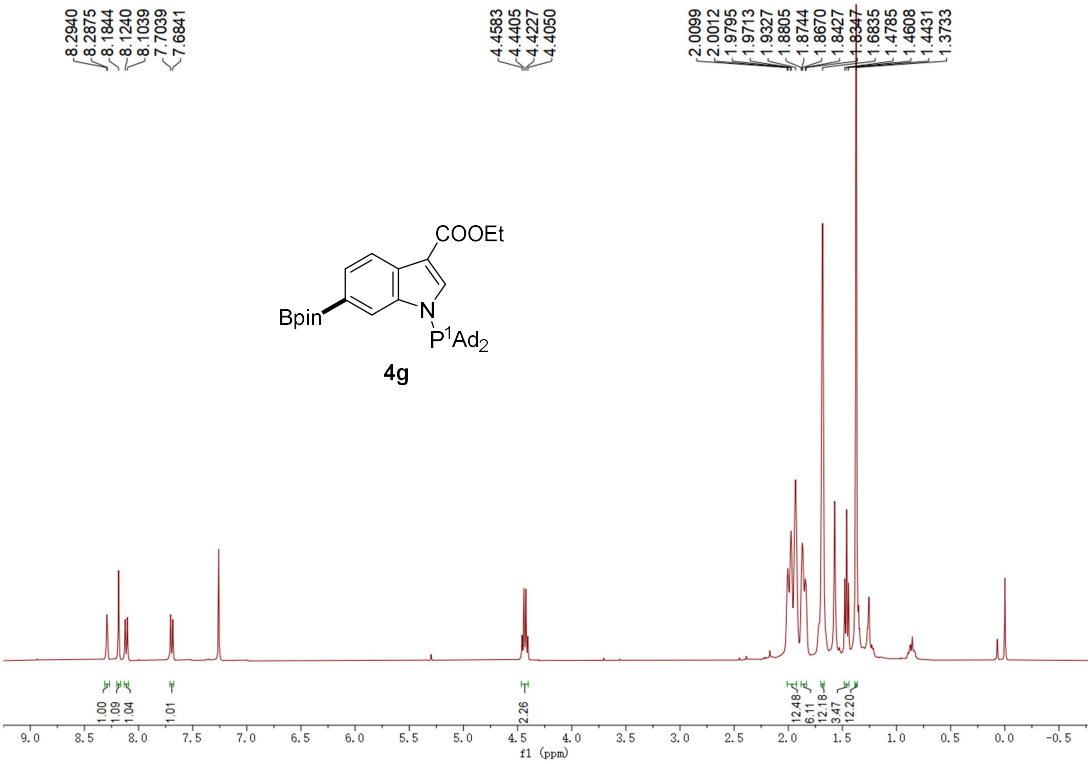
^{1}H NMR spectrum of **4f** (400 MHz, Chloroform-*d*)



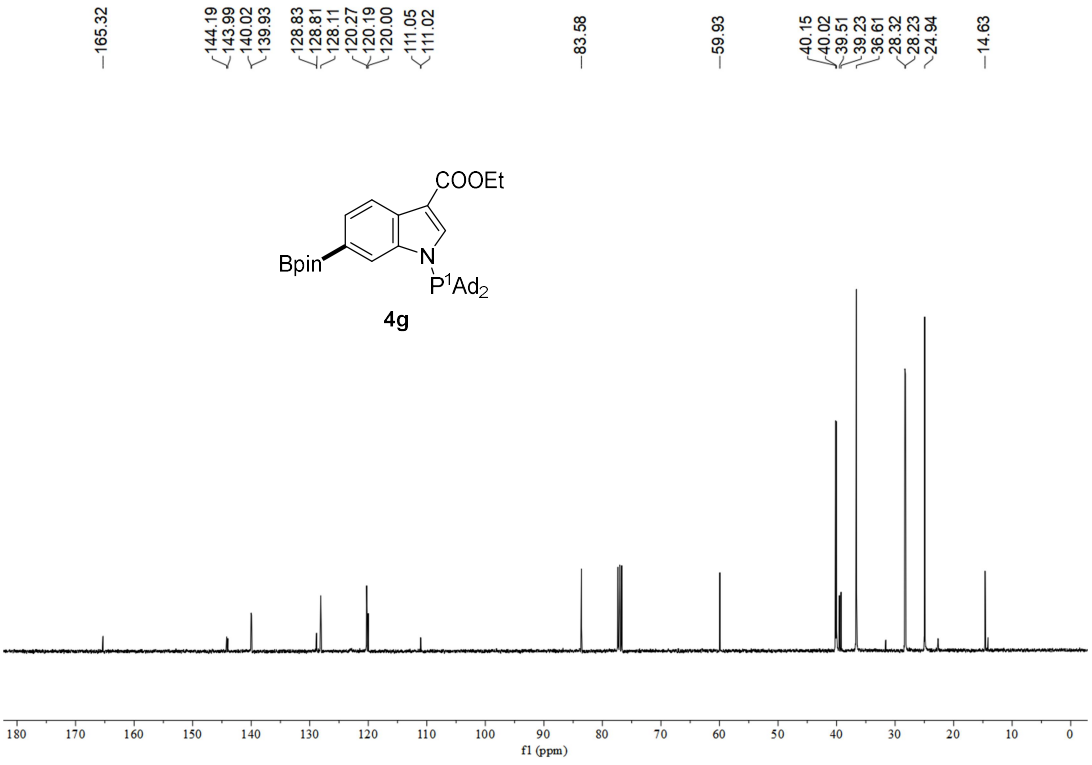
^{13}C NMR spectrum of **4f** (100 MHz, Chloroform-*d*)



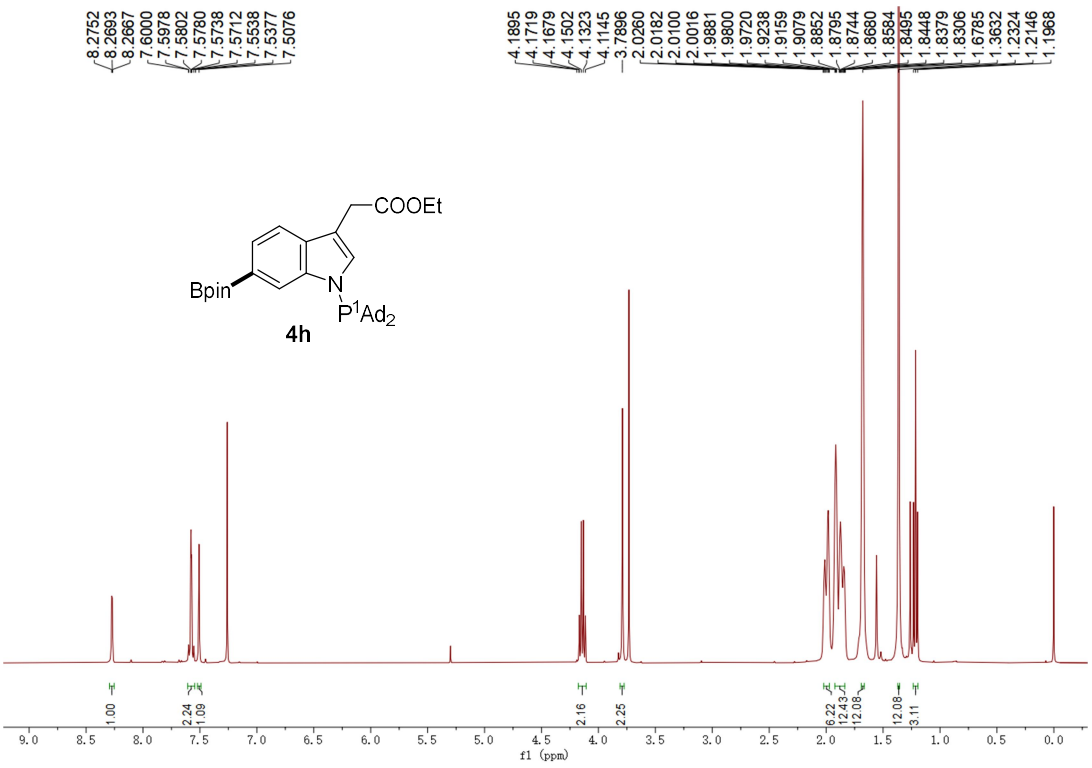
^{1}H NMR spectrum of **4g** (400 MHz, Chloroform-*d*)



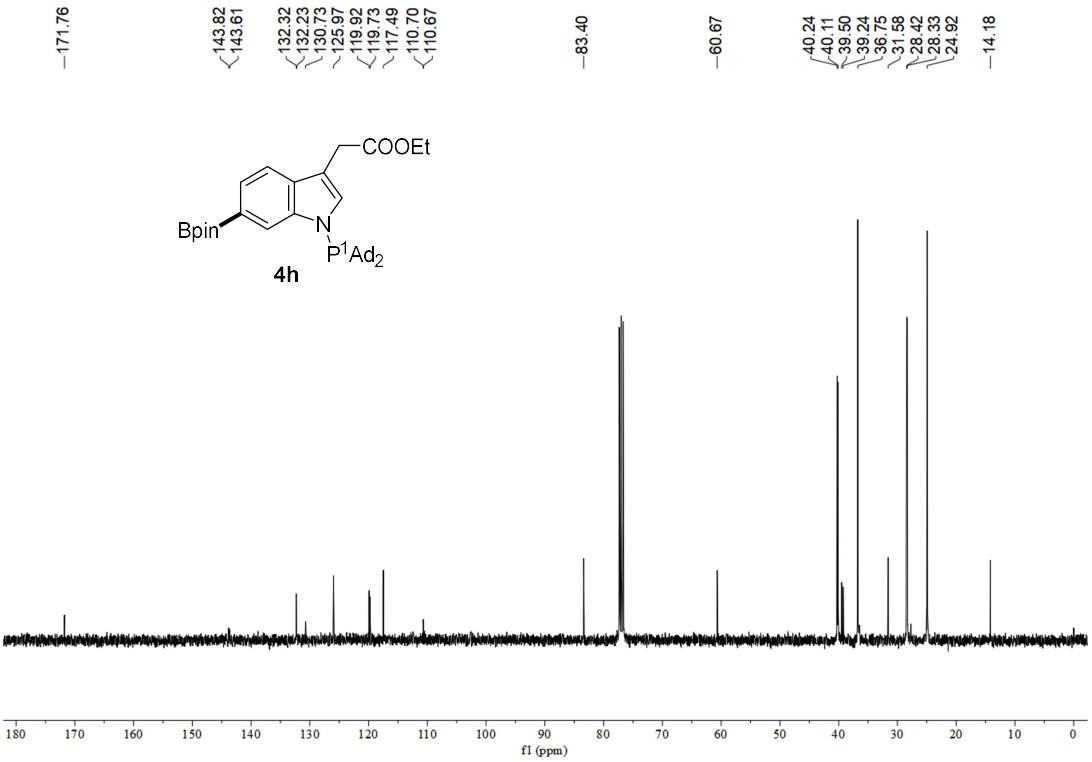
^{13}C NMR spectrum of **4g** (100 MHz, Chloroform-*d*)



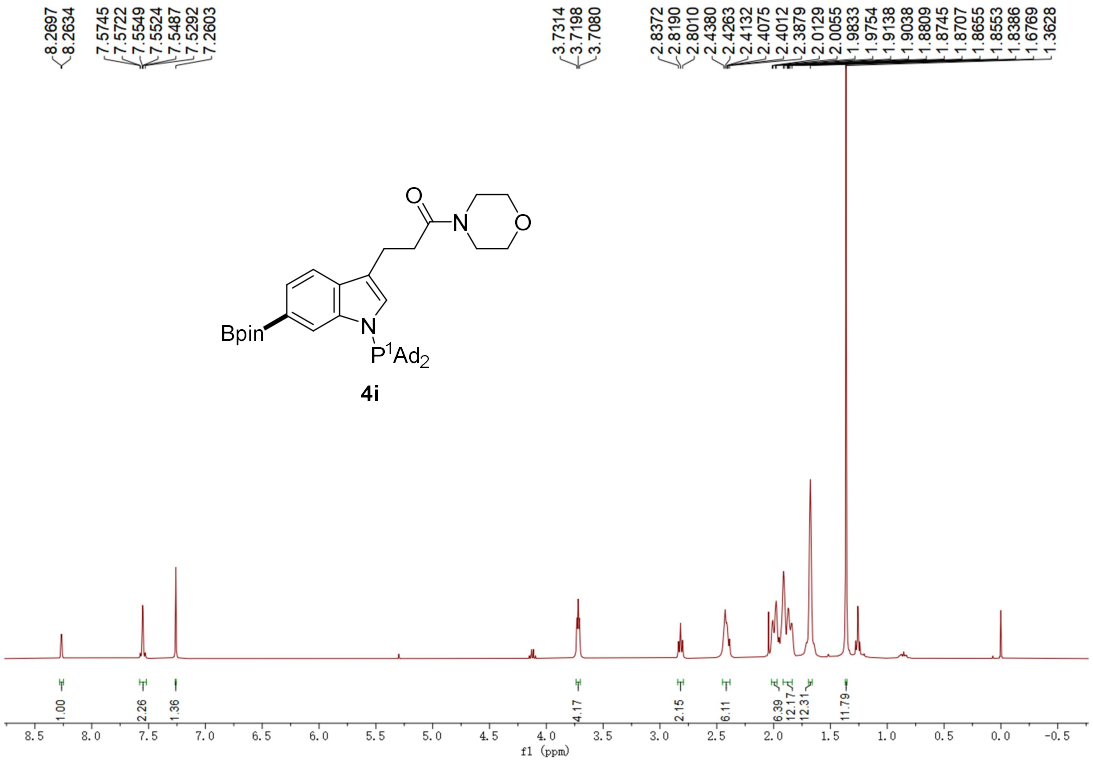
^{1}H NMR spectrum of **4h** (400 MHz, Chloroform-*d*)



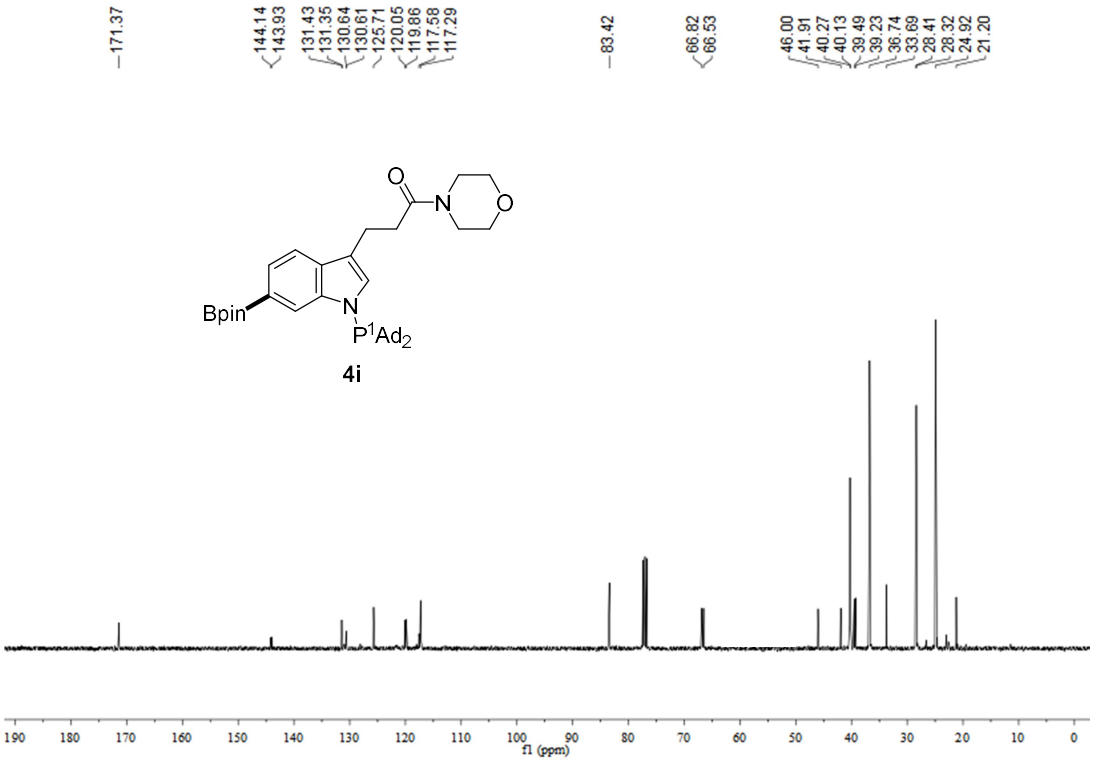
^{13}C NMR spectrum of **4h** (100 MHz, Chloroform-*d*)



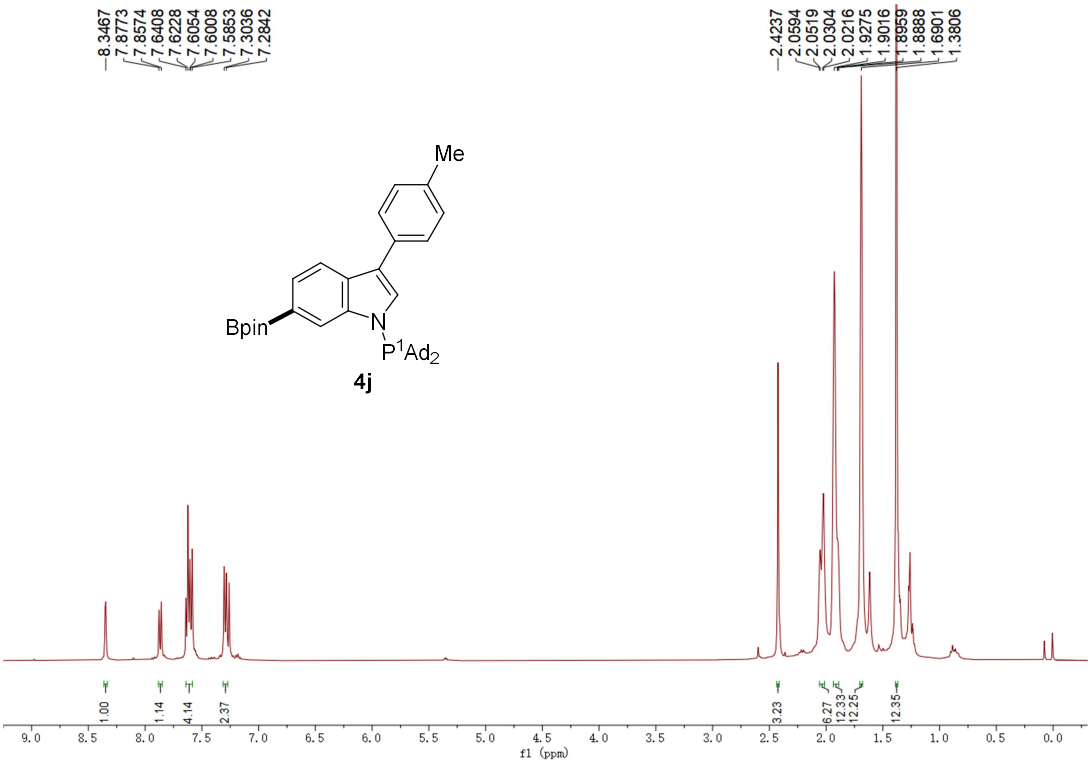
^{1}H NMR spectrum of **4i** (400 MHz, Chloroform-*d*)



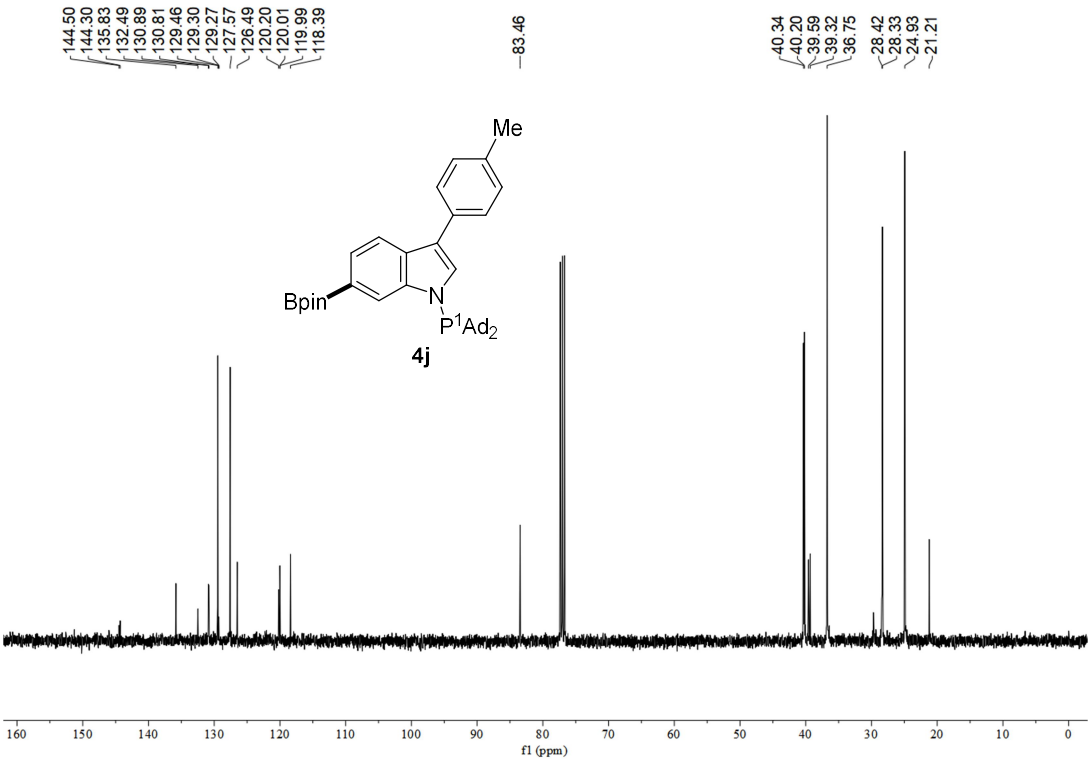
^{13}C NMR spectrum of **4i** (100 MHz, Chloroform-*d*)



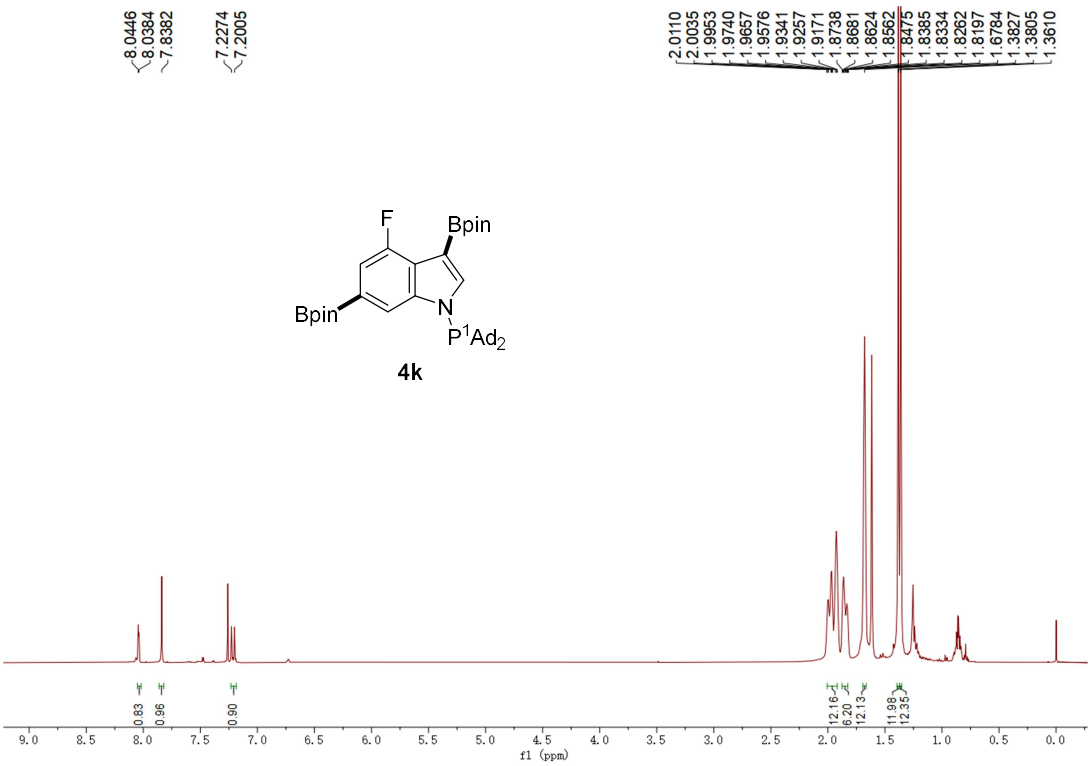
^{1}H NMR spectrum of **4j** (400 MHz, Chloroform-*d*)



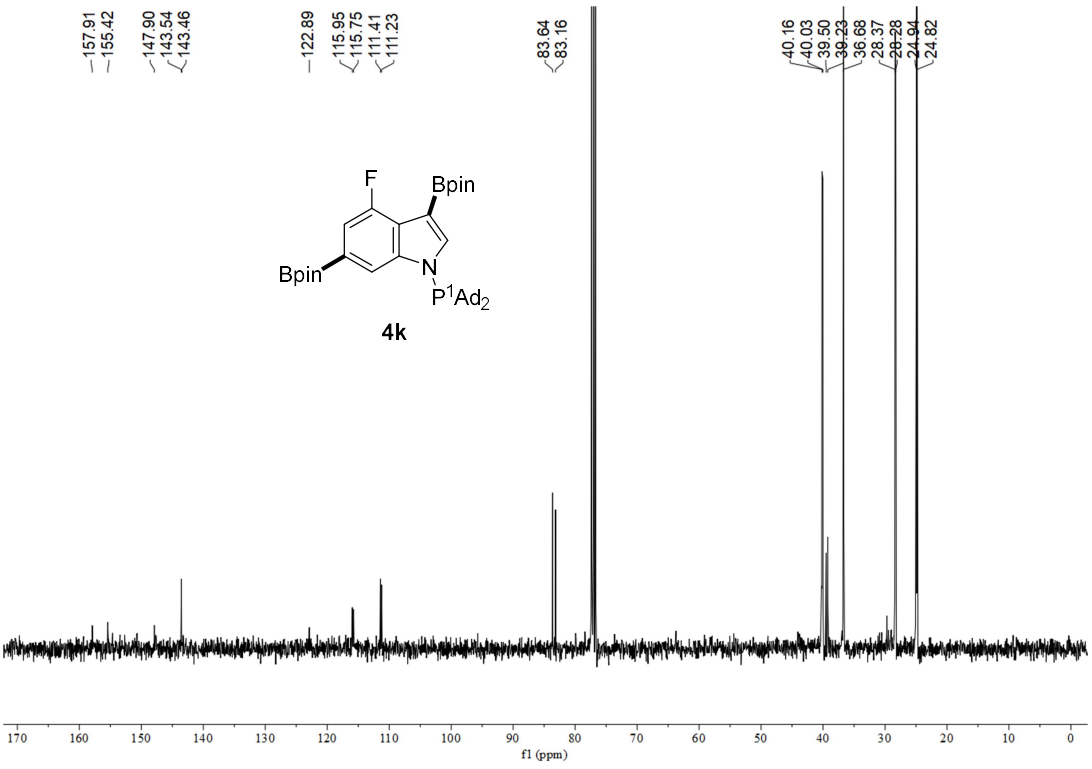
^{13}C NMR spectrum of **4j** (100 MHz, Chloroform-*d*)



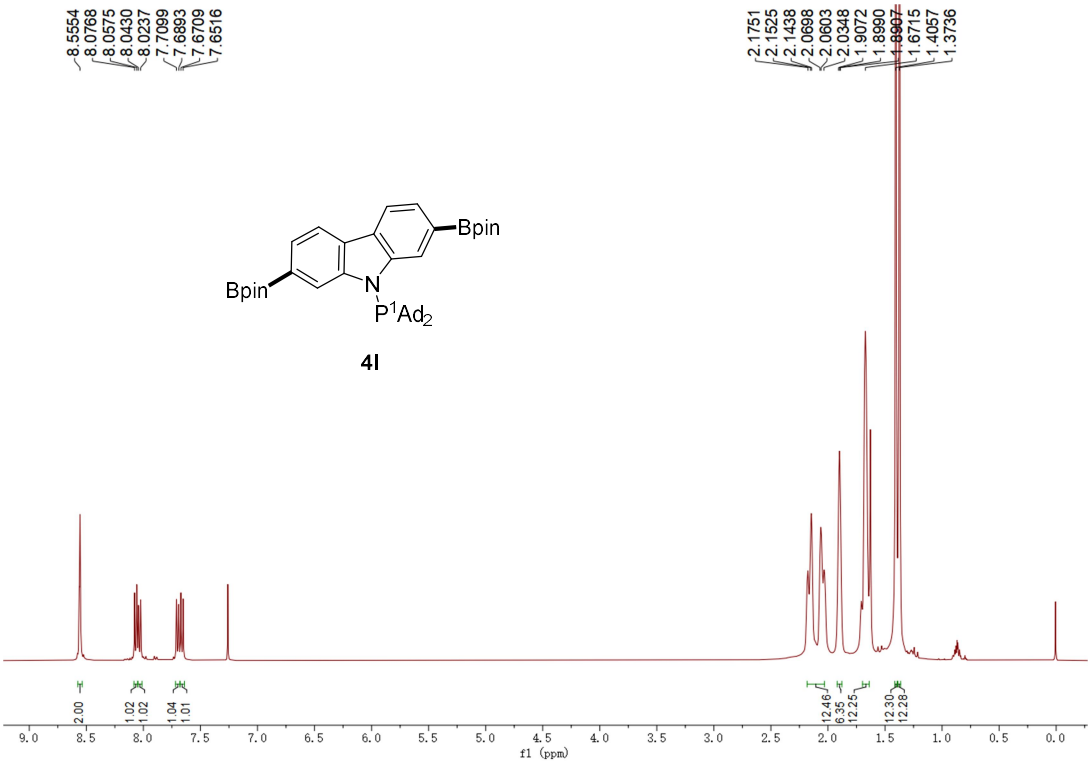
^{1}H NMR spectrum of **4k** (400 MHz, Chloroform-*d*)



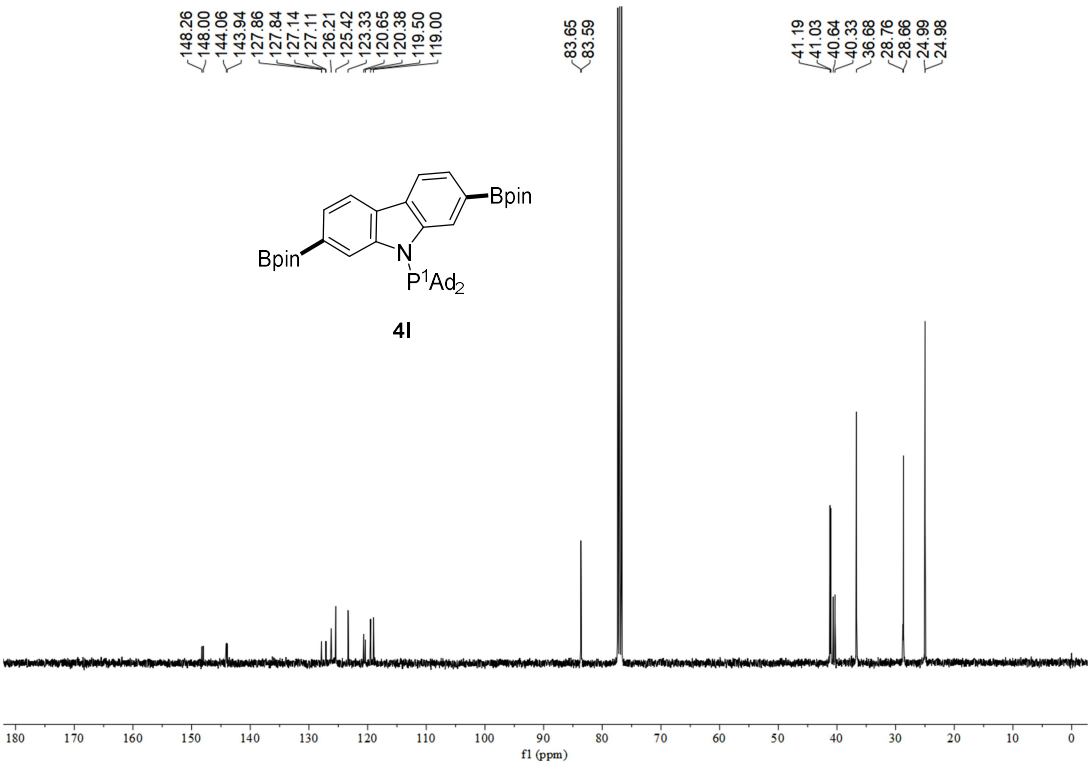
^{13}C NMR spectrum of **4k** (100 MHz, Chloroform-*d*)



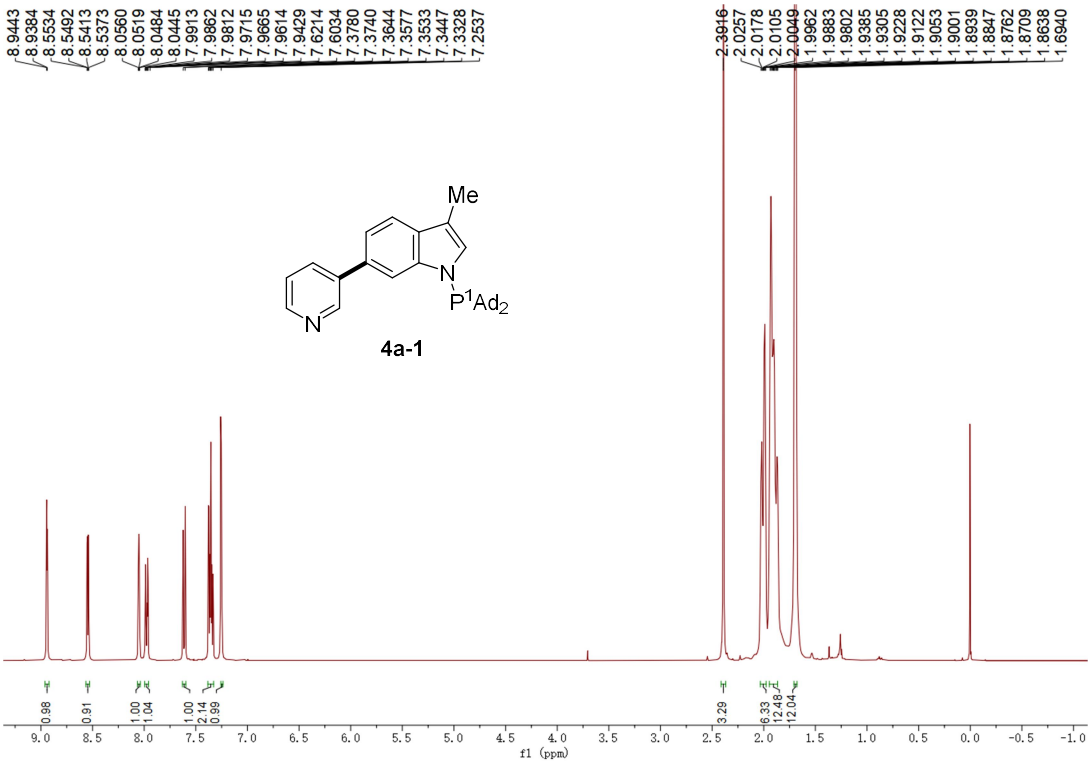
^{1}H NMR spectrum of **4l** (400 MHz, Chloroform-*d*)



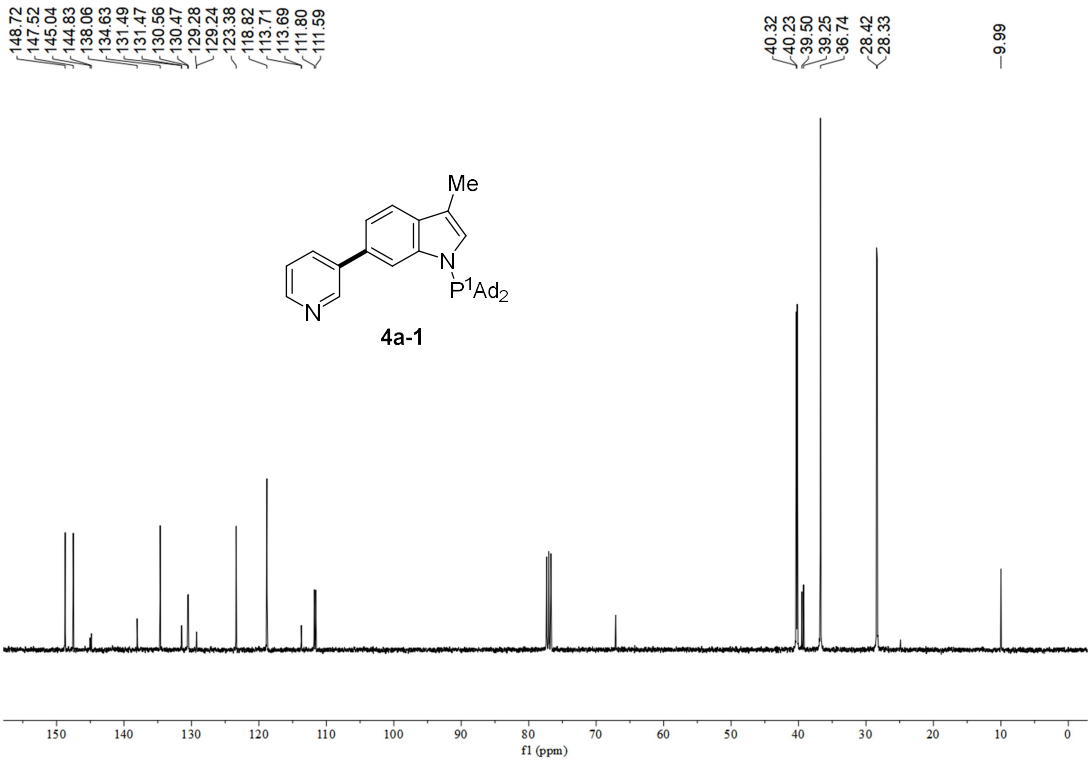
^{13}C NMR spectrum of **4l** (100 MHz, Chloroform-*d*)



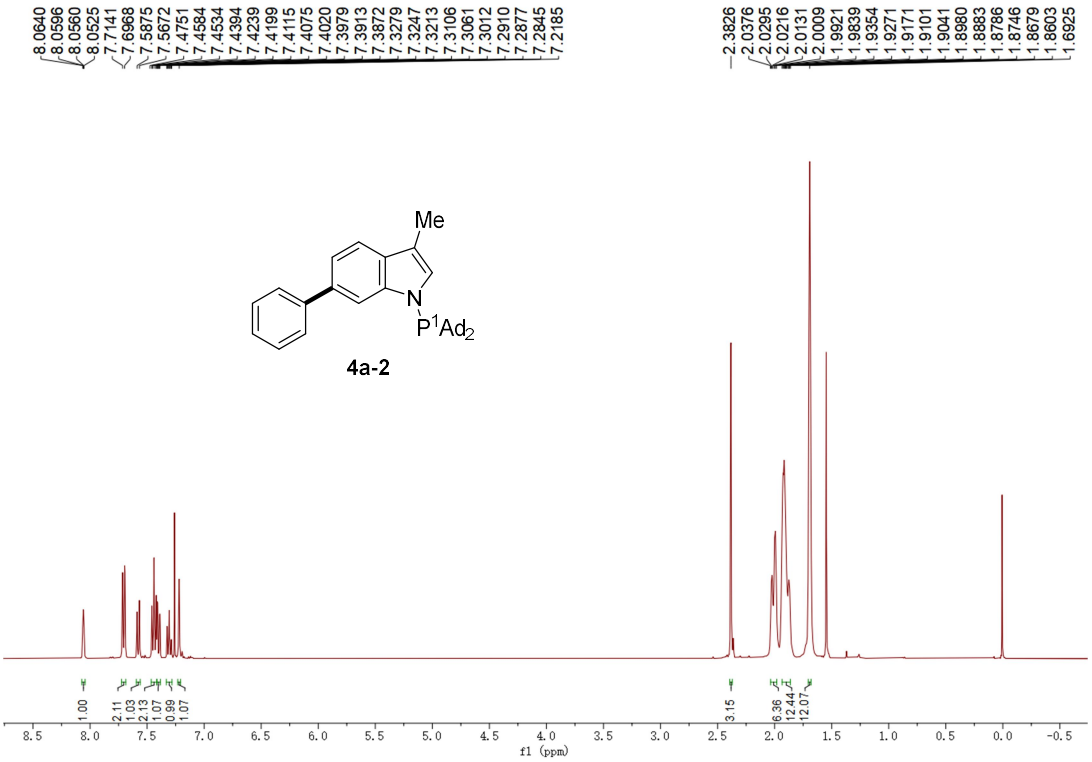
^{1}H NMR spectrum of **4a-1** (400 MHz, Chloroform-*d*)



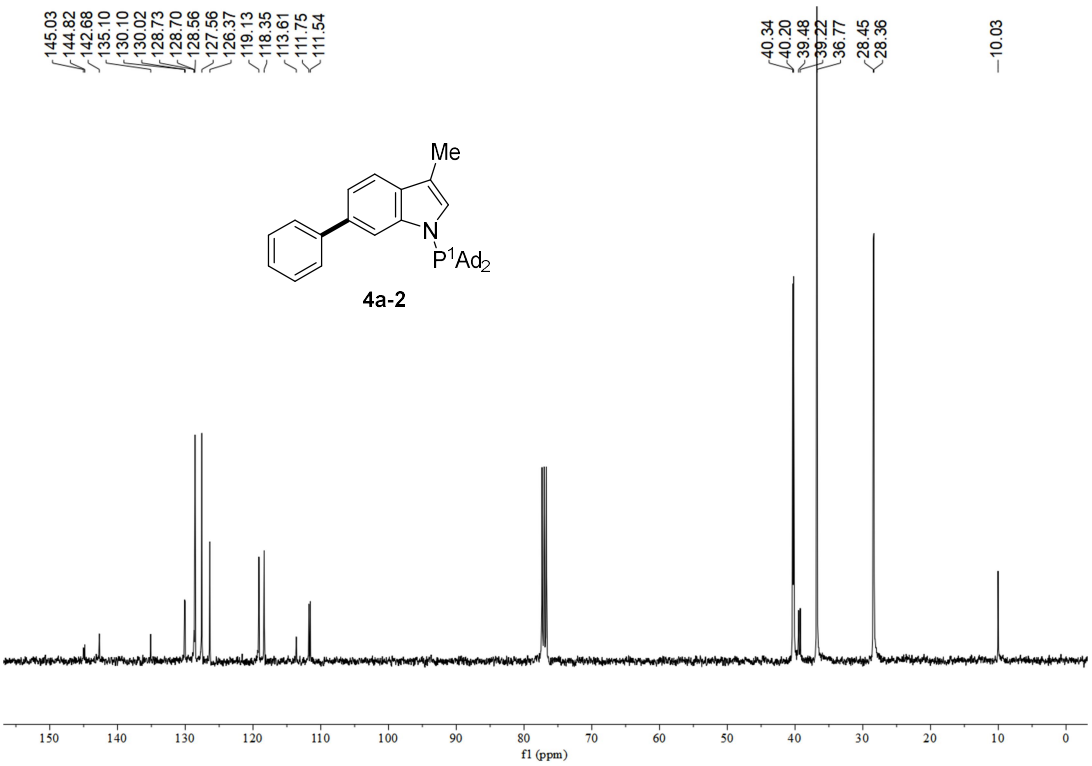
^{13}C NMR spectrum of **4a-1** (100 MHz, Chloroform-*d*)



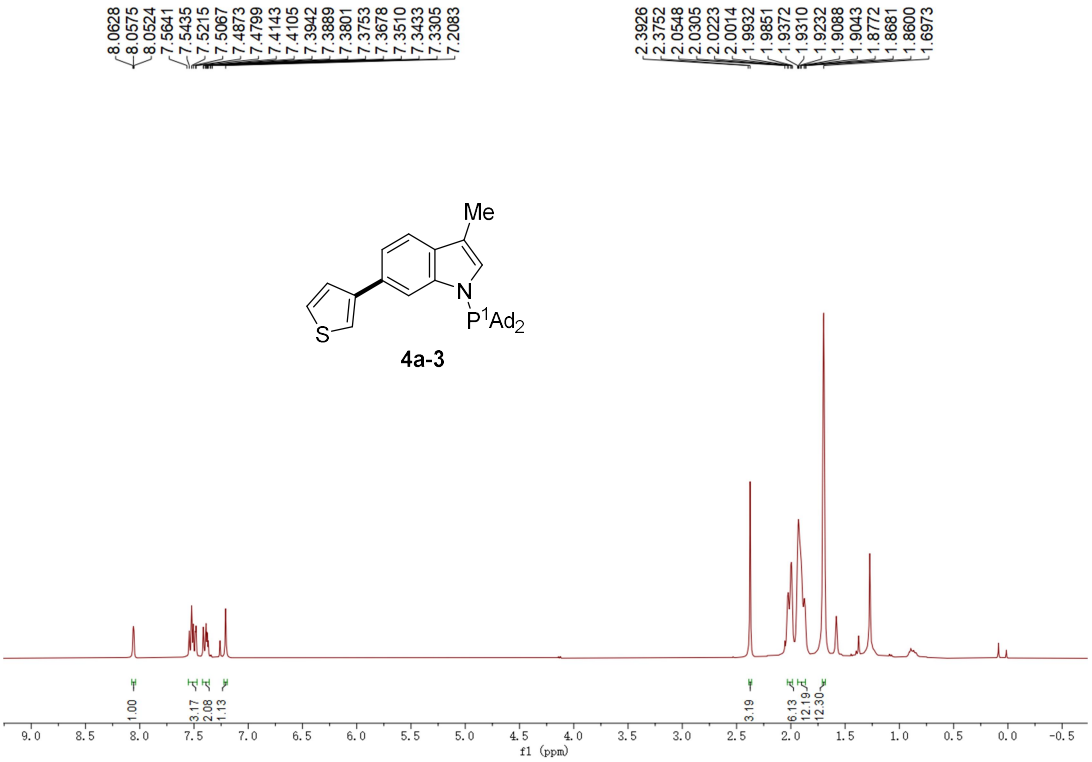
^{1}H NMR spectrum of **4a-2** (400 MHz, Chloroform-*d*)



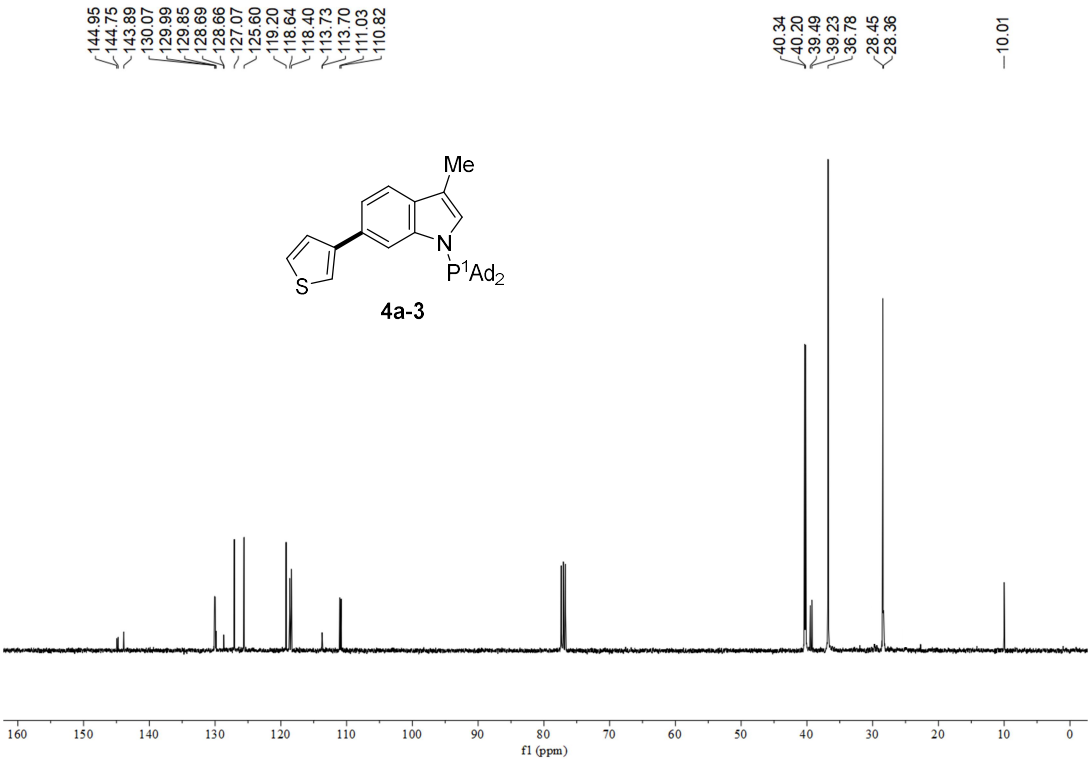
^{13}C NMR spectrum of **4a-2** (100 MHz, Chloroform-*d*)



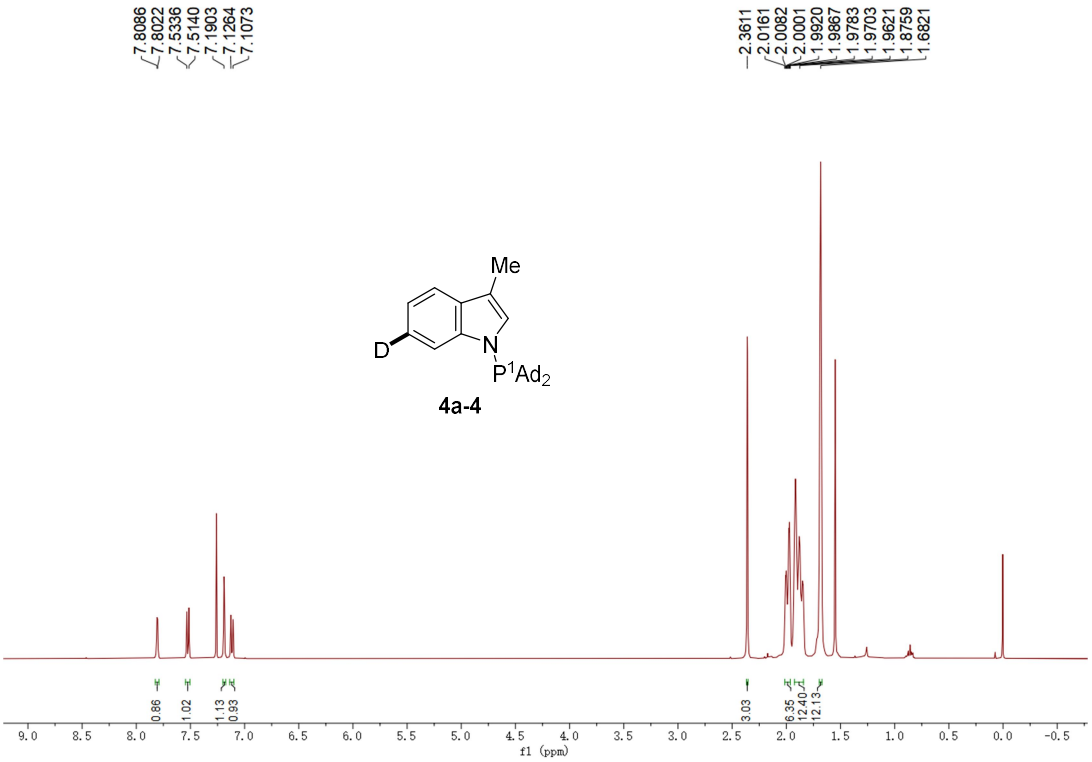
^{1}H NMR spectrum of **4a-3** (400 MHz, Chloroform-*d*)



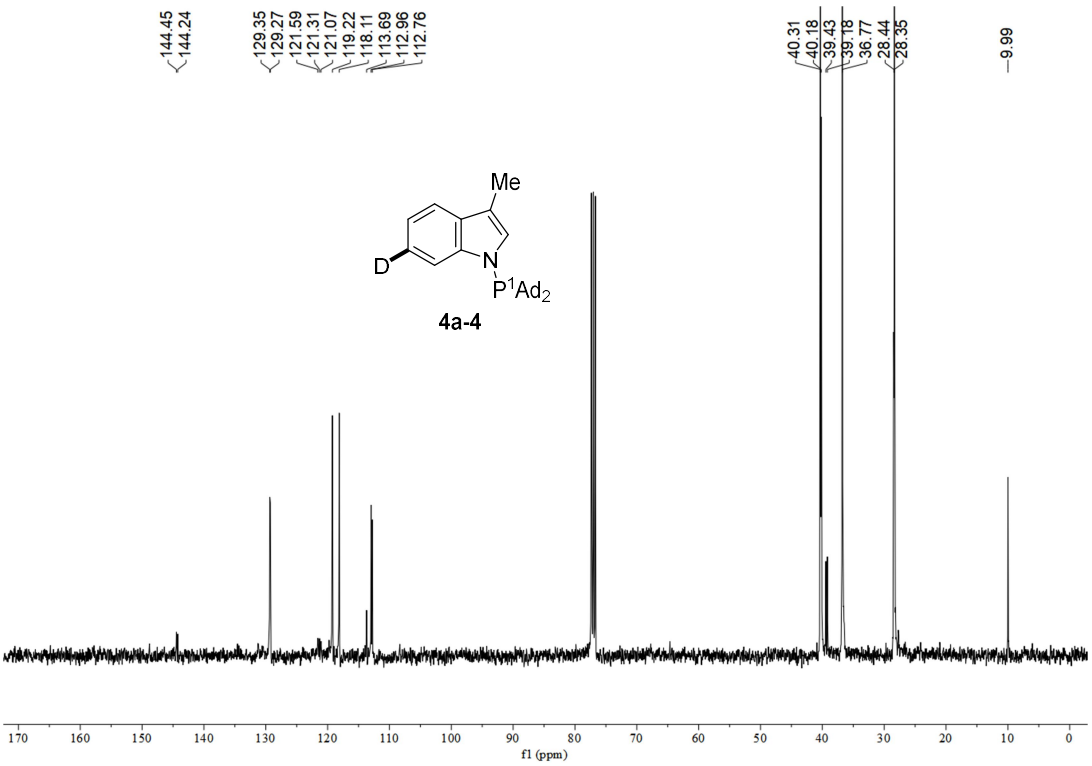
^{13}C NMR spectrum of **4a-3** (100 MHz, Chloroform-*d*)



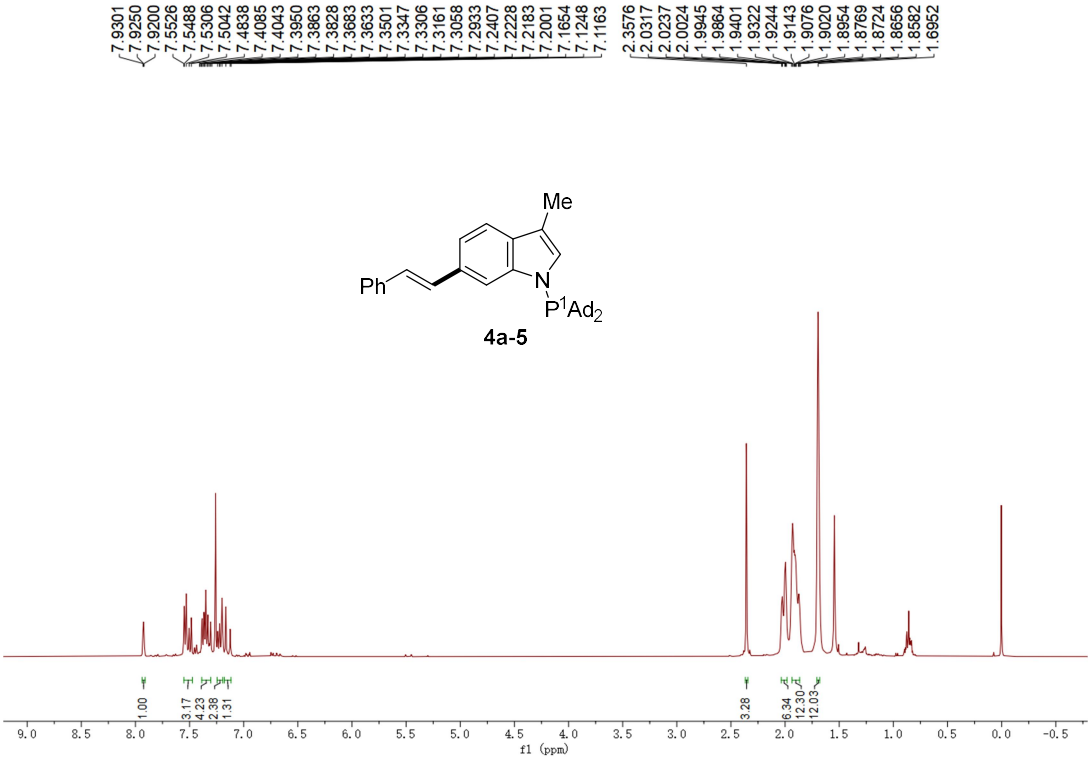
^{1}H NMR spectrum of **4a-4** (400 MHz, Chloroform-*d*)



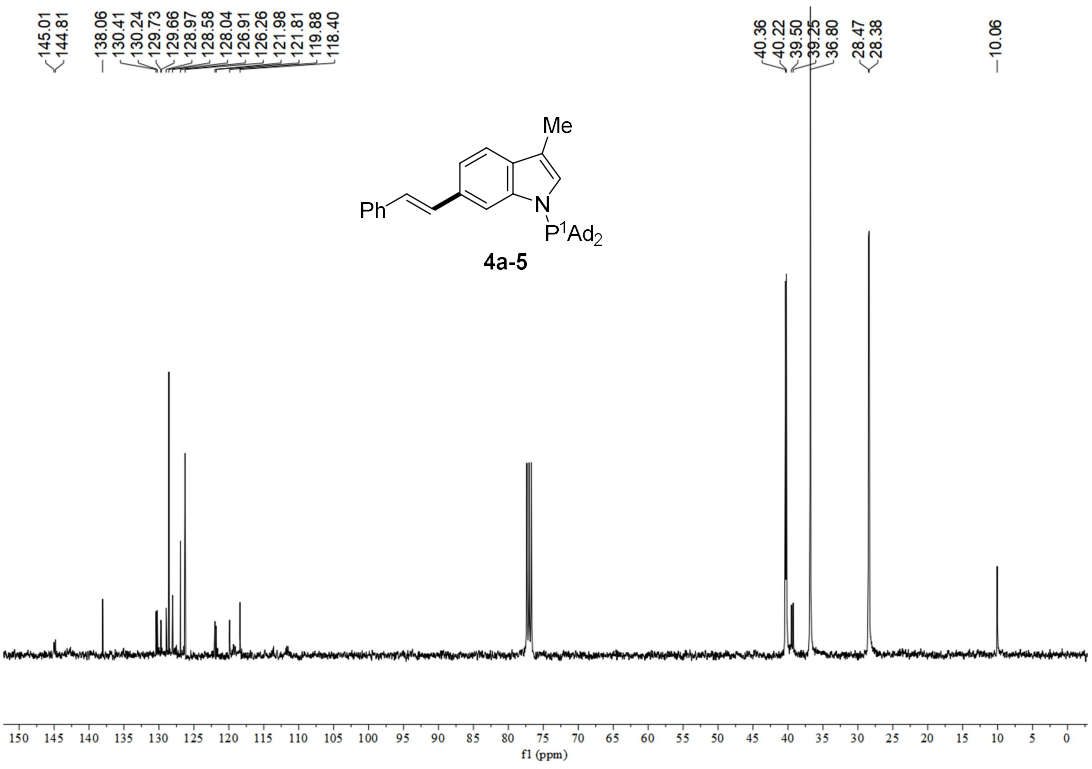
^{13}C NMR spectrum of **4a-4** (100 MHz, Chloroform-*d*)



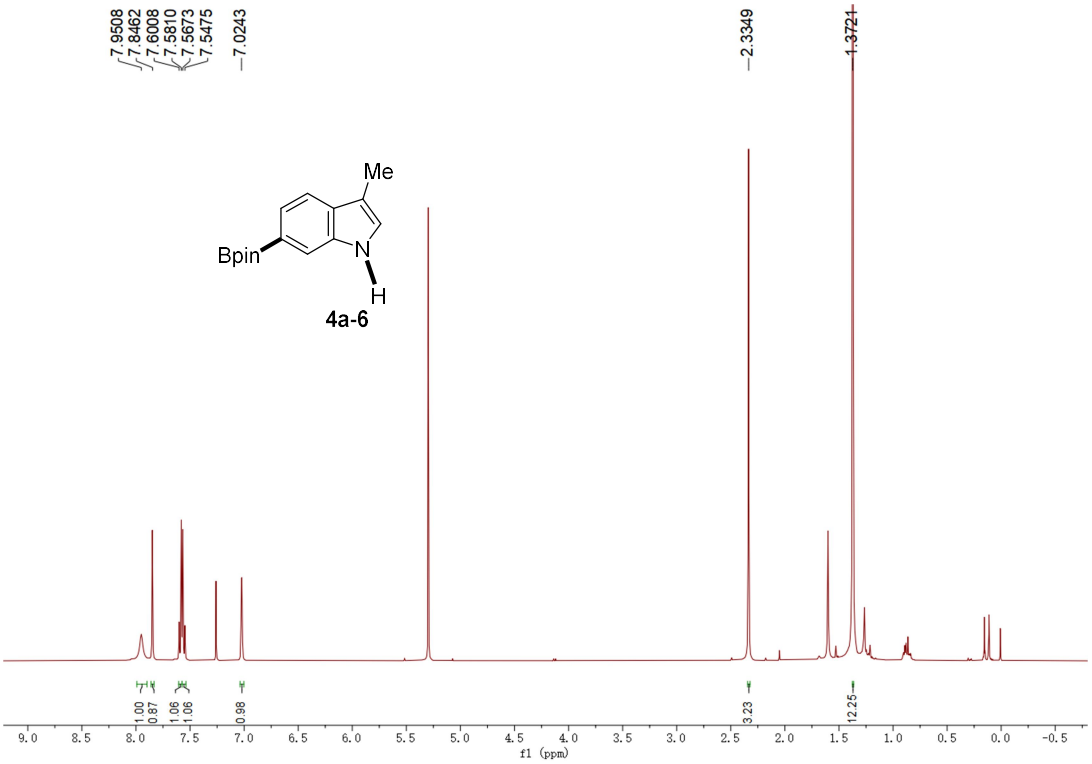
^{1}H NMR spectrum of **4a-5** (400 MHz, Chloroform-*d*)



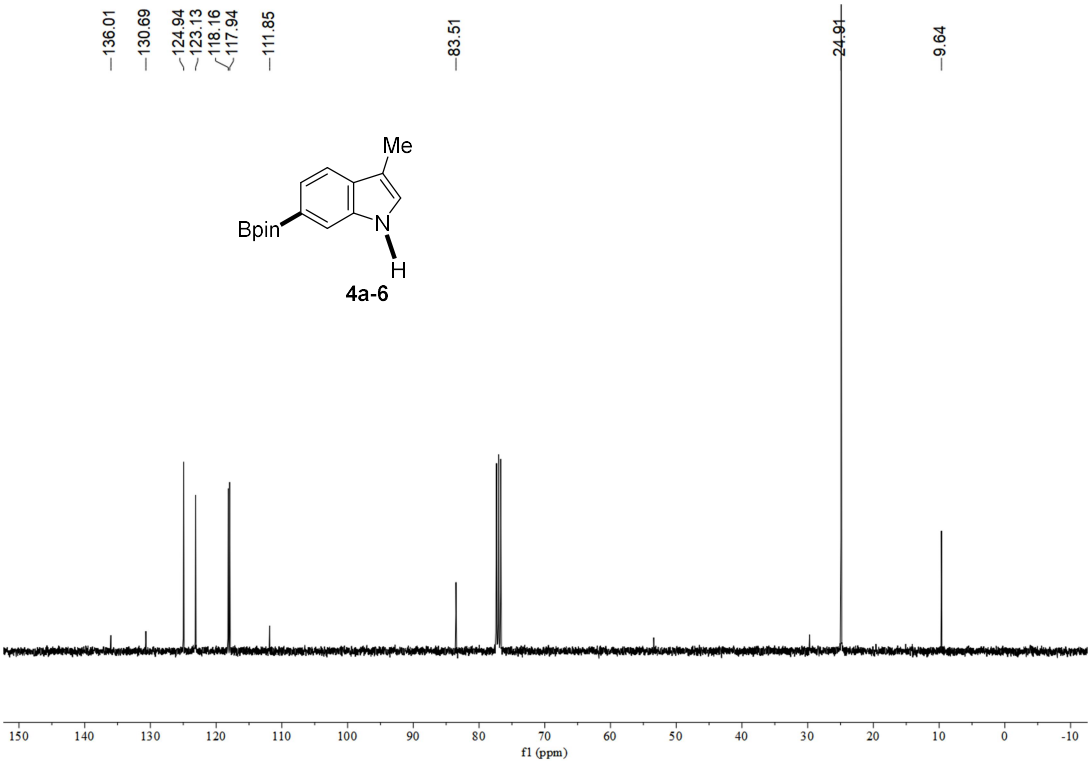
^{13}C NMR spectrum of **4a-5** (100 MHz, Chloroform-*d*)



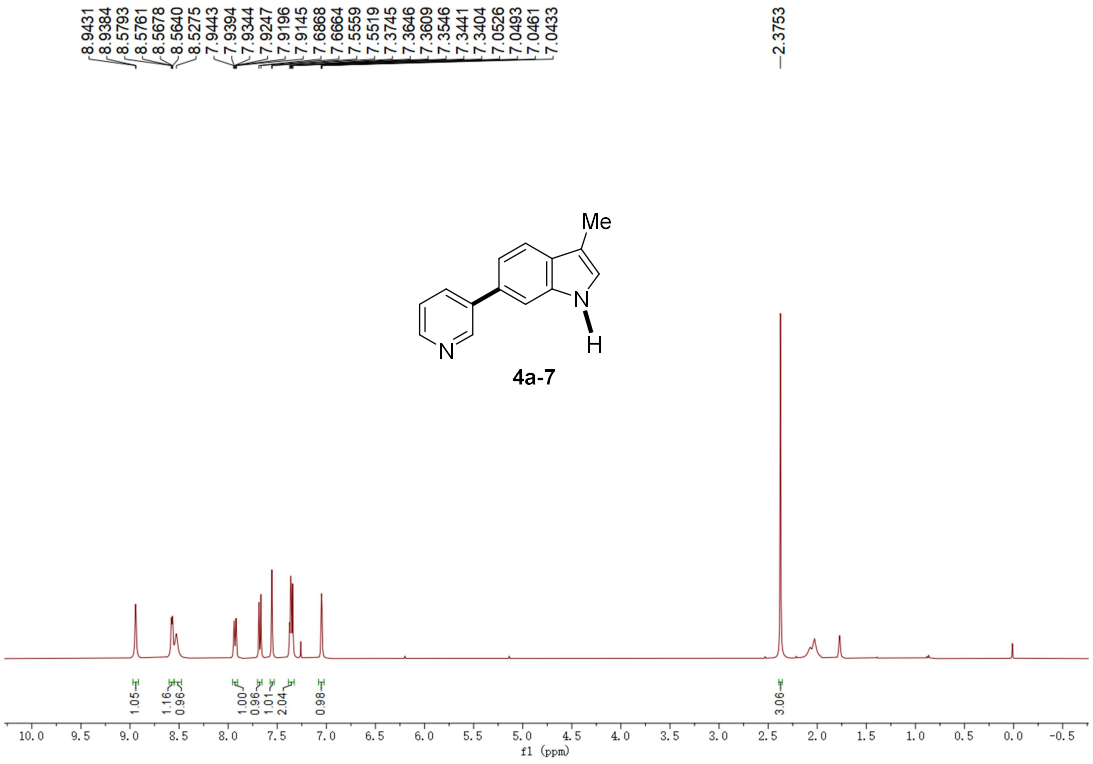
^{1}H NMR spectrum of **4a-6** (400 MHz, Chloroform-*d*)



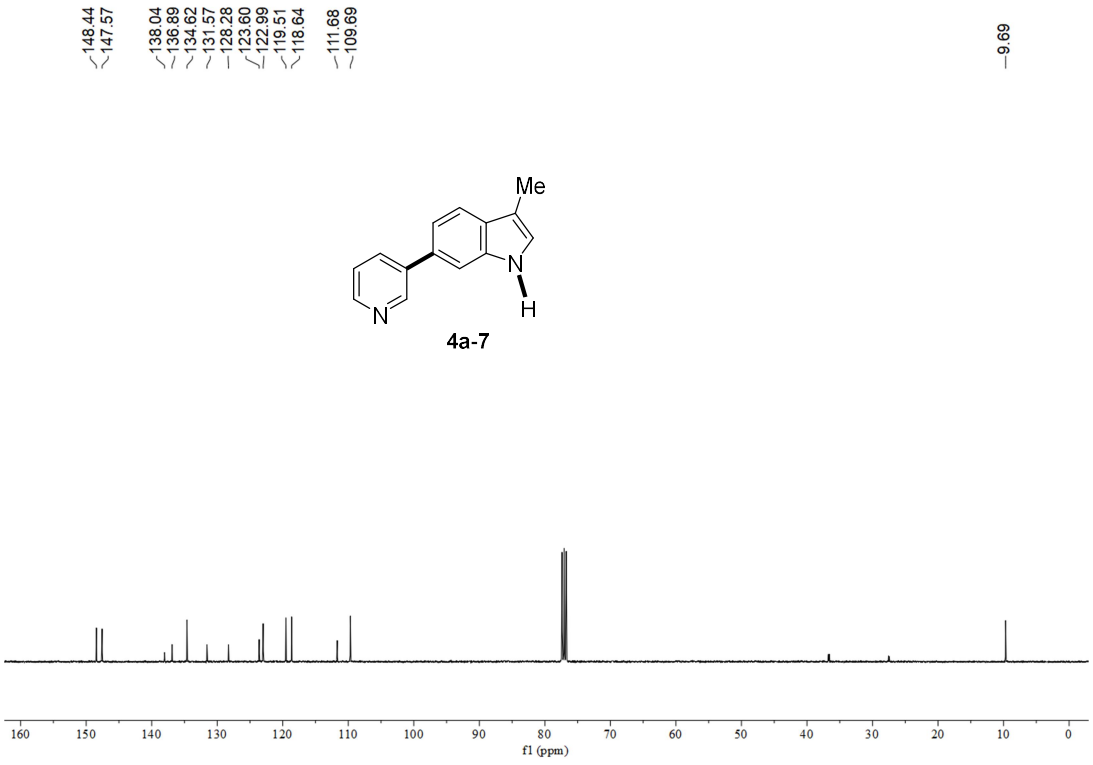
^{13}C NMR spectrum of **4a-6** (100 MHz, Chloroform-*d*)



[1]H NMR spectrum of **4a-7** (400 MHz, Chloroform-*d*)



[13]C NMR spectrum of **4a-7** (100 MHz, Chloroform-*d*)



10. Supplementary references

[1] J. Zhao, T. Shen, Z. Sun, et al., Org. Lett. 23 (2021) 4057-4061.

[2] M. Zheng, M. Zheng, D. Ye, et al., Bioorg. Med. Chem. Lett. 17 (2007) 2414-2420.

[3] Y. Mohr, M. Renom-Carrasco, C. Demarcy, et al., ACS Catal. 10 (2020) 2713-2719.

[4] W. Chang, Y. Chen, S. Lu, et al., Chem 8 (2022) 1775-1788.

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