Supporting Information

Cu-catalyzed borylative cyclization of *N*-(*o*-alkynylaryl)imines

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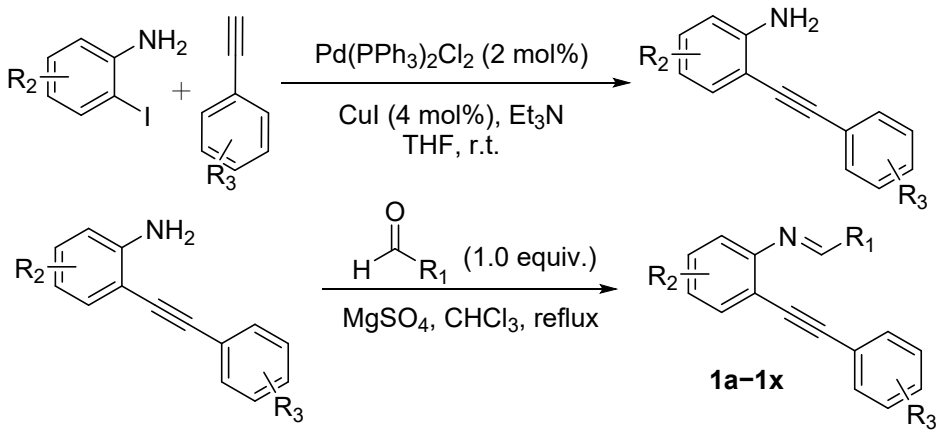
1. General Information

All reactions were carried out under the argon atmosphere in flame-dried glassware. Unless otherwise noted, all the reagents were obtained from commercial supplier and used as received without further purification. The solvents used in the reactions were distilled from appropriate drying agents prior to use. Flash column chromatography was performed using 200−300 mesh silica gel. **^{1}H NMR** and **^{13}C NMR** spectra were recorded on a Bruker Advance 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz). Chemical shifts (δ) are reported in parts per million (ppm) relative to residual chloroform (δ = 7.26 ppm, ^{1}H; 77.16 ppm, ^{13}C). High resolution mass spectra were obtained on Bruker Compass DataAnalysis 4.0 spectrometer in ESI mode. The X-ray single-crystal determination was performed on Bruker D8 VENTURE X-ray single crystal diffractometer.

2. Preparation of *N*-(*o*-alkynylaryl)imines

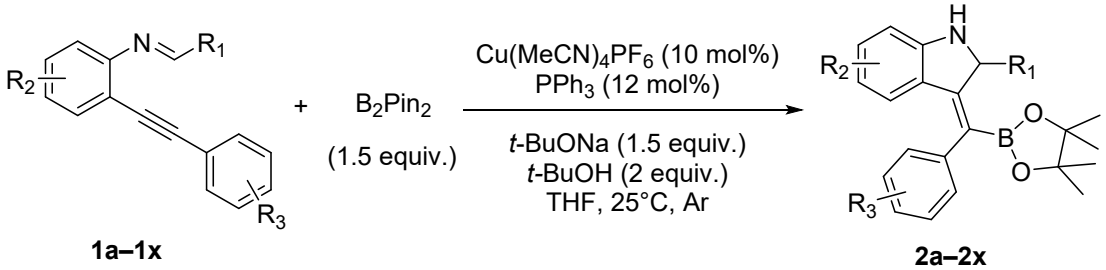


Step 1: In an argon atmosphere, terminal alkynes (6 mmol) was added to a solution of 2-iodoaniline (5 mmol), $Pd(PPh_3)_2Cl_2$ (0.125 mmol, 87.8 mg) and CuI (0.25 mmol, 47.6 mg) in Et_3N (5 mL). The reaction was stirred at room temperature and monitored by TLC. Upon completion, the reaction was quenched with aqueous NH_4Cl and extracted with EtOAc (3 x 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to afford the *o*-alkynylanilines.

Step 2: The product (2 mmol) obtained in the first step, arylaldehyde (2 mmol), anhydrous $MgSO_4$ (50 mmol, 6.0 g) and chloroform (50 mL) were added to a round bottom flask that attached with a water separator and condenser. The resulting suspension was refluxed at 110°C and monitored by **^{1}H NMR**. Upon completion, the suspension was filtered, and the filter cake washed with chloroform twice. The filtrate was concentrated under reduced pressure to give the *N*-(*o*-alkynylaryl)imines **1a–1x** without further purification.

3. Cu-catalyzed borylative cyclization of *N*-(*o*-alkynylaryl)imines

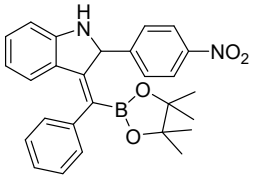
3.1 Typical Procedure



In an argon atmosphere, the *N*-(*o*-alkynylaryl)imines **1a–1x** (0.1 mmol) was added to a solution of B_2pin_2 (0.15 mmol, 38 mg), $Cu(MeCN)_4PF_6$ (0.01 mmol, 4 mg), PPh_3 (0.012 mmol, 3 mg), *t*-BuONa (0.15 mmol, 15 mg), *t*-BuOH (0.2 mmol, 19 μL) in THF (2 mL). The reaction was stirred at room temperature and monitored by TLC. Upon completion, the resulting solution was diluted with DCM, filtered through a short plug of silica, and concentrated *in vacuo*. The residue was purified by flash column chromatography to give products **2a–2x**.[1-4]

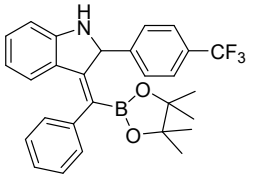
3.2 Characterization Data for the Products of 2a–2x

(*E*)-2-(4-Nitrophenyl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl -ene)indoline (2a)



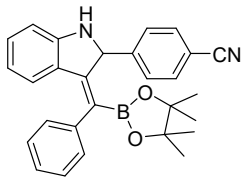
Yellow solid, 38.6 mg, 85% yield, m.p. = 134.0 ℃ – 135.4 ℃. R_f = 0.4 (petroleum ether/ethyl acetate = 20:1), **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.1 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 6.43 (t, *J* = 7.6 Hz, 1H), 6.17 (d, *J* = 7.9 Hz, 1H), 6.07 (s, 1H), 2.96 (br, 1H), 1.09 (s, 6H), 1.03 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.9, 153.5, 152.3, 147.1, 142.0, 131.2, 128.8, 128.3, 126.6, 126.5, 126.4, 123.9, 119.0, 110.9, 83.4, 65.4, 24.8, 24.3. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{27}H_{28}BN_2O_4^+$ 455.2137, found 455.2139.

(*E*)-3-(Phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-2-(4-(trifluoromethyl)phenyl)indoline (2b)



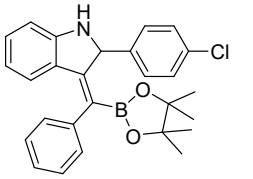
Yellow solid, 43.9 mg, 92% yield, m.p. = 182.1 ℃ – 182.6 ℃. R_f = 0.5 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.52 (s, 2H), 7.42 (dd, *J* = 12.5, 7.6 Hz, 3H), 7.36 – 7.30 (m, 1H), 7.22 (d, *J* = 7.1 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 1H), 6.40 (t, *J* = 7.6 Hz, 1H), 6.18 (d, *J* = 7.9 Hz, 1H), 6.03 (s, 1H), 4.24 (s, 1H), 1.06 (s, 6H), 1.01 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 154.0, 146.6, 142.4, 131.0, 130.3, 130.1, 129.3, 128.7, 128.5, 128.4, 127.0 (q, *J* = 559 Hz), 126.6, 126.3, 126.2, 124.6 (dd, *J* = 115, 4 Hz), 118.5, 110.6, 83.2, 65.8, 24.7, 24.1. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{28}H_{28}BF_3NO_2^+$ 478.2160, found 478.2161.

(*E*)-4-(3-(Phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)indolin-2-yl)benzonitrile (2c)



Yellow solid, 36.1 mg, 83% yield, m.p. = 147.4 ℃ – 148.5 ℃. R_f = 0.3 (petroleum ether/ethyl acetate = 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.3 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.38 – 7.30 (m, 1H), 7.21 (d, *J* = 6.6 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.41 (t, *J* = 7.6 Hz, 1H), 6.17 (d, *J* = 7.9 Hz, 1H), 6.00 (s, 1H), 4.24 (s, 1H), 1.08 (s, 6H), 1.02 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.0, 153.9, 150.6, 142.2, 132.5, 131.1, 128.8, 128.4, 128.2, 126.6, 126.4, 126.3, 118.9, 118.7, 111.0, 110.7, 83.34, 65.7, 24.8, 24.3. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{28}H_{28}BN_2O_2^+$ 435.2238, found 435.2239.

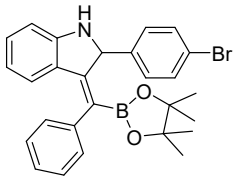
(*E*)-2-(4-Chlorophenyl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methylene)indoline (2d)



Yellow solid, 38.2 mg, 86% yield, m.p. = 135.9 ℃ – 136.5 ℃. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.4 Hz, 2H), 7.32 (m, 6H), 7.23 (d, *J* = 7.0 Hz, 2H), 7.04 (m, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 6.39 (t, *J* = 7.6 Hz,

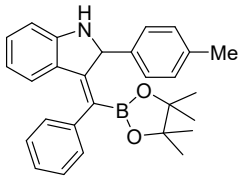
1H), 6.17 (d, *J* = 7.8 Hz, 1H), 5.95 (s, 1H), 4.17 (s, 1H), 1.08 (s, 6H), 1.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.4, 154.1, 144.2, 142.5, 132.9, 130.9, 128.9, 128.7, 128.6, 128.4, 126.7, 126.3, 126.2, 118.4, 110.6, 83.2, 65.5, 24.8, 24.3. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{27}H_{28}BClNO_2^+$ 444.1896, found 444.1901.

(*E*)-2-(4-Bromophenyl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methylene)indoline (2e)



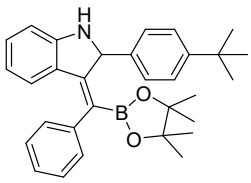
Yellow solid, 42.5 mg, 87% yield, m.p. = 160.1 ℃ – 162.4 ℃. R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 16.5, 7.9 Hz, 4H), 7.38 – 7.32 (m, 1H), 7.26 (dd, *J* = 16.9, 7.7 Hz, 4H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 6.40 (t, *J* = 7.6 Hz, 1H), 6.20 (d, *J* = 8.7 Hz, 1H), 5.95 (s, 1H), 4.19 (s, 1H), 1.10 (s, 6H), 1.06 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.4, 154.1, 144.7, 142.5, 131.6, 130.9, 129.3, 128.8, 128.5, 126.7, 126.3, 126.2, 121.1, 118.4, 110.6, 83.2, 65.6, 24.8, 24.7, 24.3. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{27}H_{28}BBrNO_2^+$ 488.1391, found 488.1396.

(*E*)-3-(Phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-2-(p-tolyl) indoline (2f)



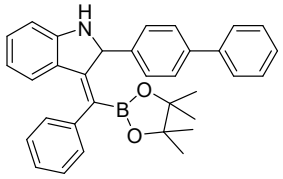
Yellow solid, 34.7 mg, 82% yield, m.p. = 138.2 ℃ – 140.1 ℃. R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.3 Hz, 1H), 7.29 – 7.20 (m, 4H), 7.12 (d, *J* = 7.8 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.37 (t, *J* = 7.6 Hz, 1H), 6.18 (d, *J* = 7.9 Hz, 1H), 5.95 (s, 1H), 4.15 (s, 1H), 2.34 (s, 3H), 1.05 (s, 6H), 1.03 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.6, 154.4, 142.8, 142.7, 136.8, 130.6, 129.1, 128.7, 128.5, 127.4, 127.0, 126.1, 126.1, 118.1, 110.6, 83.1, 65.9, 24.7, 24.3, 21.1. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{28}H_{31}BNO_2^+$ 424.2442, found 424.2446.

(*E*)-2-(4-(*tert*-Butyl)phenyl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methylene)indoline (2g)



Yellow solid, 37.2 mg, 80% yield, m.p. = 147.4 ℃ – 148.5 ℃. R_f = 0.5 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.24 (m, 7H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 6.38 (t, *J* = 7.6 Hz, 1H), 6.21 (d, *J* = 7.9 Hz, 1H), 5.95 (s, 1H), 4.16 (s, 1H), 1.32 (s, 9H), 1.00 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 154.3, 150.2, 142.8, 130.6, 128.7, 128.6 127.4, 127.0, 126.2, 126.1, 125.4, 118.1, 110.7, 83.0, 65.9, 34.5, 31.4, 24.7, 24.1. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{31}H_{37}BNO_2^+$ 466.2912, found 466.2912.

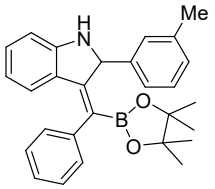
(*E*)-2-([1,1'-Biphenyl]-4-yl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methylene)indoline (2h)



Yellow solid, 34.0 mg, 70% yield, m.p. = 89.4 ℃ – 90.6 ℃. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1). **^{1}H NMR** (400

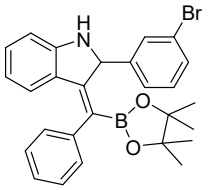
MHz, $CDCl_3$) δ 7.59 (dd, *J* = 13.5, 7.9 Hz, 4H), 7.51 – 7.41 (m, 6H), 7.37 (dd, *J* = 11.5, 7.2 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 6.41 (t, *J* = 7.5 Hz, 1H), 6.23 (d, *J* = 7.8 Hz, 1H), 6.05 (s, 1H), 4.26 (s, 1H), 1.07 (s, 6H), 1.05 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.5, 154.3, 144.8, 142.7, 141.1, 140.2, 130.8, 128.8, 128.7, 128.6, 128.0, 127.3, 127.2, 127.1, 127.0, 126.2, 126.2, 118.3, 110.7, 83.2, 66.0, 24.7, 24.3. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{33}H_{33}BNO_2^+$ 486.2599, found 486.2605.

(*E*)-3-(Phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-2-(m-tolyl) indoline (2i)



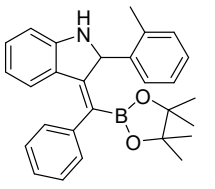
Yellow solid, 36.4 mg, 86% yield, m.p. = 72.7 ℃ – 74.1 ℃. R_f = 0.5 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.31 (m, 1H), 7.27 (d, *J* = 6.9 Hz, 2H), 7.25 – 7.16 (m, 3H), 7.09 (d, *J* = 6.8 Hz, 1H), 7.04 (dd, *J* = 11.1, 4.1 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 6.39 (t, *J* = 7.5 Hz, 1H), 6.21 (d, *J* = 7.8 Hz, 1H), 5.97 (s, 1H), 4.19 (s, 1H), 2.37 (s, 3H), 1.06 (s, 6H), 1.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.5, 154.4, 145.6, 142.8, 137.9, 130.7, 128.7, 128.4, 128.5, 127.9, 127.0, 126.2, 126.1, 124.4, 118.1, 110.6, 83.1, 66.2, 24.7, 24.6, 24.2, 21.5. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{28}H_{31}BNO_2^+$ 424.2442, found 424.2445.

(*E*)-2-(3-Bromophenyl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methylene)indoline (2j)



Yellow solid, 41.0 mg, 84% yield, m.p. = 89.4 ℃ – 91.6 ℃. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.42 (t, *J* = 7.2 Hz, 3H), 7.37 – 7.14 (m, 5H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.40 (t, *J* = 7.4 Hz, 1H), 6.17 (d, *J* = 7.8 Hz, 1H), 5.94 (s, 1H), 4.18 (s, 1H), 1.10 (s, 6H), 1.07 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.4, 154.2, 147.9, 142.4, 131.3, 130.9, 130.4, 130.2, 128.8, 128.5, 126.6, 126.3, 126.3, 125.5, 122.2, 118.4, 110.6, 83.3, 65.7, 24.8, 24.3. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{27}H_{28}BBrNO_2^+$ 488.1391, found 488.1396.

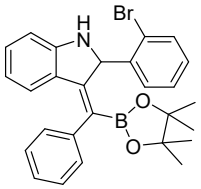
(*E*)-3-(Phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-2-(o-tolyl) indoline (2k)



Yellow solid, 36.0 mg, 85% yield, m.p. = 177.2 ℃ – 178.7 ℃. R_f = 0.5 (petroleum ether/ethyl acetate = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.26 (d, *J* = 1.4 Hz, 1H), 7.18 (ddd, *J* = 12.7, 9.7, 6.1 Hz, 3H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.40 (t, *J* = 7.6 Hz, 1H), 6.23 (d, *J* = 7.9 Hz, 1H), 6.16 (s, 1H), 4.07 (s, 1H), 2.61 (br, 3H), 0.99 (s, 6H), 0.88 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.6, 154.2, 144.5, 142.7, 136.3, 130.7, 129.9, 128.8, 128.5, 127.4, 127.1, 126.8, 126.3, 126.2, 123.0, 118.3, 111.2, 82.9, 63.1, 24.4, 24.0, 19.7. **HRMS(ESI)**: $[M+H]^+$ calcd. for $C_{28}H_{31}BNO_2^+$ 424.2442, found 424.2447.

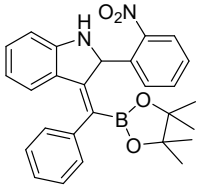
(*E*)-2-(2-Bromophenyl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)

methylene)indoline (2l)



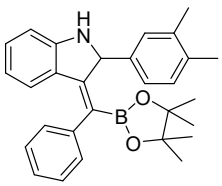
Yellow solid, 43.0 mg, 88% yield, m.p. = 87.5 ℃ – 89.3 ℃. R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (t, *J* = 9.6 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.30 (m, 4H), 7.30 – 7.23 (m,1H), 7.13 (td, *J* = 7.8, 1.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.38 (t, *J* = 7.5 Hz, 1H), 6.33 (s, 1H), 6.26 (d, *J* = 7.9 Hz, 1H), 4.51 (s, 1H), 1.05 (s, 6H), 0.89 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.5, 153.7, 145.3, 142.4, 132.4, 131.0, 128.8, 128.5, 128.5, 128.1, 128.1, 126.8, 126.3, 126.1, 125.3, 118.0, 110.7, 83.1, 65.5, 24.3, 24.2. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{27}H_{28}BBrNO_2^+$ 488.1391, found 488.1396.

(*E*)-2-(2-Nitrophenyl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methylene)indoline (2m)



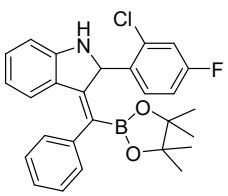
Yellow solid, 37.2 mg, 82% yield, m.p. = 193.9 ℃ – 195.5 ℃. R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.61 – 7.51 (m, 2H), 7.47 – 7.38 (m, 3H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 20.4 Hz, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.36 (t, *J* = 7.6 Hz, 1H), 6.19 (d, *J* = 7.9 Hz, 1H), 6.16 (s, 1H), 5.02 (s, 1H), 0.99 (s, 6H), 0.86 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.7, 153.6, 145.0, 142.3, 140.9, 133.9, 131.4, 128.8, 128.5, 128.4, 127.6, 126.4, 126.3, 126.1, 123.6, 117.9, 110.2, 83.3, 61.7, 24.2, 24.1. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{27}H_{28}BN_2O_4^+$ 455.2137, found 455.2138.

(*E*)-2-(3,4-Dimethylphenyl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methylene)indoline (2n)



Yellow solid, 36.3 mg, 83% yield, m.p. = 147.4 ℃ – 148.5 ℃. R_f = 0.5 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.3 Hz, 2H), 7.32 (dd, *J* = 8.0, 6.7 Hz,1H), 7.27 (dd, *J* = 11.1, 4.3 Hz, 2H), 7.18 (s, 1H), 7.09 (q, *J* = 7.8 Hz, 2H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.38 (t, *J* = 7.5 Hz, 1H), 6.19 (d, *J* = 7.9 Hz, 1H), 5.93 (d, *J* = 1.1 Hz, 1H), 4.16 (s, 1H), 2.26 (s, 6H), 1.06 (s, 6H), 1.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.7, 154.5, 143.3, 142.8, 136.3, 135.4, 130.6, 129.8, 129.1, 128.7, 128.6, 127.0, 126.1, 126.1, 124.7, 118.1, 110.6, 83.0, 66.0, 24.7, 24.3, 19.8, 19.4. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{29}H_{33}BNO_2^+$ 438.2599, found 438.2601.

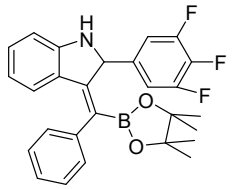
(*E*)-2-(2-Chloro-4-fluorophenyl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)indoline (2o)



Yellow solid, 39.2 mg, 85% yield, m.p. = 79.7 ℃ – 80.5 ℃. R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.5 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.30 (d, *J* = 6.7 Hz, 2H), 7.20 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.04 (t, *J* = 7.3 Hz, 1H), 6.95 (td, *J* = 8.4, 2.5 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.39 (t, *J* = 7.5 Hz, 1H), 6.31 (s, 1H), 6.25 (d, *J* = 7.9 Hz, 1H), 4.35 (br, 1H), 1.07 (s, 6H), 0.92 (s,

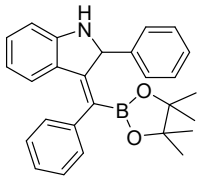
6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.7, 160.3, 154.5, 153.7, 142.2, 139.9 (d, *J* = 4 Hz), 135.0 (d, *J* = 10 Hz), 131.1, 128.9, 128.8, 128.4, 126.5, 126.1, 118.2, 116.3 (d, *J* = 25 Hz), 114.4 (d, *J* = 21 Hz), 110.8, 83.2, 62.5, 24.3, 24.2. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{27}H_{27}BClFNO_2^+$ 462.1802, found 462.1804.

(*E*)-3-(Phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-2-(3,4,5-trifluorophenyl)indoline (2p)



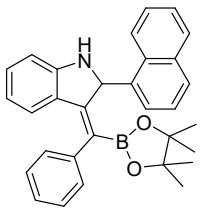
Yellow solid, 39.4 mg, 85% yield, m.p. = 64.1 ℃ – 64.4 ℃. R_f = 0.5 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 6.7 Hz, 1H), 7.35 (d, *J* = 5.8 Hz, 1H), 7.21 (s, 2H), 7.10 – 6.98 (m, 3H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.40 (d, *J* = 7.5 Hz, 1H), 6.15 (d, *J* = 7.6 Hz, 1H), 5.91 (s, 1H), 3.47 (s, 1H), 1.14 (s, 6H), 1.11 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.9, 153.8, 151.0 (ddd, *J* = 250, 10, 4 Hz), 141.8 (q, *J* = 6 Hz), 138.9 (dt, *J* = 251, 15 Hz), 131.1, 128.8, 128.4, 126.4, 126.4, 126.1, 118.8, 111.5 (d, *J* = 6 Hz), 111.3 (d, *J* = 5 Hz), 110.6, 83.4, 65.0, 24.8, 24.4. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{27}H_{26}BF_3NO_2^+$ 464.2003, found 464.2008.

(*E*)-2-Phenyl-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene) indoline (2q)



Yellow solid, 34.4 mg, 84% yield (1.120 g, 84% yield for its gram scale reaction), m.p. = 127.7 ℃ – 128.9 ℃. R_f = 0.4 (petroleum ether/ethyl acetate = 20:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 5H), 7.36 – 7.30 (m, 3H), 7.28 – 7.24 (m, 2H), 7.03 (dd, *J* = 11.1, 4.1 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 6.39 (t, *J* = 7.6 Hz, 1H), 6.20 (d, *J* = 7.9 Hz, 1H), 6.00 (s, 1H), 4.20 (br, 1H), 1.05 (s, 6H), 1.02 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.5, 154.3, 145.7, 142.7, 130.7, 128.7, 128.6, 127.5, 127.3, 127.0, 126.2, 126.1, 118.2, 110.7, 83.1, 66.3, 24.7, 24.2. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{27}H_{29}BNO_2^+$ 410.2286, found 410.2291.

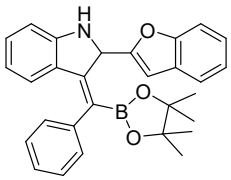
(*E*)-2-(Naphthalen-1-yl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methylene)indoline (2r)



Yellow solid, 36.8 mg, 80% yield, m.p. = 96.8 ℃ – 98.0 ℃. R_f = 0.5 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.52 – 7.32 (m, 7H), 7.02 (t, *J* = 7.3 Hz, 1H), 6.78 (s, 1H), 6.56 (d, *J* = 7.9 Hz, 1H), 6.42 (t, *J* = 7.5 Hz, 1H), 6.35 (d, *J* = 7.8 Hz, 1H), 4.19 (s, 1H), 0.81 (s, 6H), 0.47 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 154.5, 142.5, 142.1, 133.8, 132.0, 130.8, 128.8, 128.7, 128.5, 127.5, 127.3, 126.3, 126.2, 126.1, 126.0, 125.7, 123.4, 118.3, 111.3, 82.8, 76.7, 62.3, 24.1, 23.9. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{31}H_{31}BNO_2^+$ 460.2442, found 460.2444.

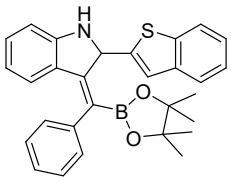
(*E*)-2-(Benzofuran-2-yl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)

methylene)indoline (2s)



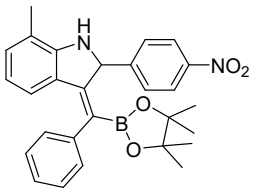
Yellow solid, 41.3 mg, 92% yield, m.p. = 86.5 ℃ – 87.1 ℃. R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.42 (m, 4H), 7.35 (dd, *J* = 13.9, 6.7 Hz, 3H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.9 Hz, 1H), 6.61 (s, 1H), 6.41 (t, *J* = 7.5 Hz, 1H), 6.29 (d, *J* = 7.9 Hz, 1H), 6.25 (s, 1H), 4.59 (s, 1H), 1.11 (s, 6H), 0.95 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1, 154.9, 154.1, 151.8, 142.0, 130.8, 128.8, 128.5, 128.4, 126.4, 126.2, 126.2, 123.9, 122.7, 121.1, 118.6, 111.0, 102.5, 83.3, 60.0, 24.6, 24.4. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{29}H_{29}BNO_3^+$ 450.2235, found 450.2237.

(*E*)-2-(Benzo[b]thiophen-2-yl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)indoline (2t)



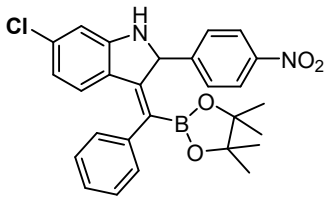
Yellow solid, 41.9 mg, 90% yield, m.p. = 78.5 ℃ – 80.1 ℃. R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.28 (d, *J* = 2.4 Hz, 3H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 6.43 (t, *J* = 7.5 Hz, 1H), 6.23 (d, *J* = 7.8 Hz, 1H), 4.34 (s, 1H), 1.12 (s, 5H), 1.08 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.5, 153.9, 149.4, 142.2, 139.4, 139.3, 130.9, 128.7, 128.4, 126.4, 126.3, 125.9, 124.2, 124.1, 123.3, 122.4, 121.3, 118.8, 111.0, 83.3, 62.0, 24.7, 24.4. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{29}H_{29}BNO_2S^+$ 466.2007, found 466.2008.

(*E*)-7-Methyl-2-(4-nitrophenyl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)indoline (2u)



Yellow solid, 27.8 mg, 57% yield, m.p. = 94.1 ℃ – 94.8 ℃. R_f = 0.3 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.36 – 7.27 (m, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 6.45 (s, 1H), 6.25 (d, *J* = 8.1 Hz, 1H), 6.08 – 6.01 (m, 1H), 4.21 (s, 1H), 2.21 (s, 3H), 1.08 (s, 6H), 1.02 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.2, 154.1, 152.6, 147.0, 142.3, 141.9, 129.7, 128.7, 128.5, 128.2, 126.3, 126.0, 124.1, 123.8, 120.1, 111.2, 83.3, 65.7, 24.8, 24.3, 21.7. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{28}H_{30}BN_2O_4^+$ 469.2293, found 469.2298.

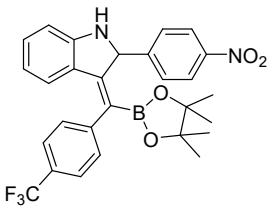
(*E*)-6-Chloro-2-(4-nitrophenyl)-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)indoline (2v)



Yellow solid, 19.6 mg, 40% yield, m.p. = 110 ℃ – 111 ℃. R_f = 0.4 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.34 – 7.31 (m, 1H), 7.15 (d, *J* = 7.0 Hz, 2H), 6.56 (d, *J* = 1.8 Hz, 1H), 6.34 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.05 (s, 1H), 6.01 (d, *J* = 8.5 Hz, 1H), 4.31 (s, 1H), 1.06 (s, 6H), 1.01 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.5, 153.6,

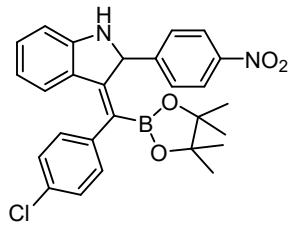
152.0, 147.2, 141.8, 136.9, 128.9, 128.2, 127.0, 126.7, 125.0, 124.0, 118.9, 110.3, 83.5, 77.2, 65.8, 24.8, 24.3. **HRMS (ESI)**: $[M+K]^+$ calcd. for $C_{28}H_{26}BF_3N_2O_4K^+$ 527.1306, found 527.1310.

(*E*)-2-(4-Nitrophenyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(4-(trifluoro-methyl)phenyl)methylene)indoline (2w)



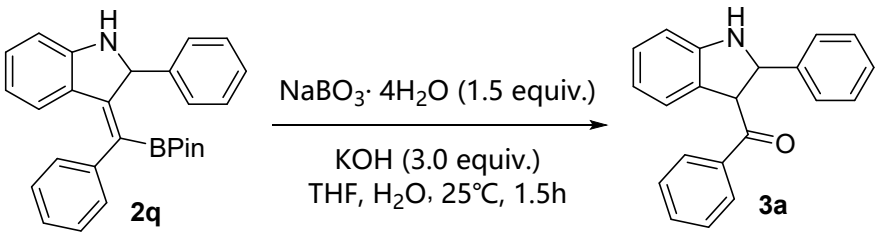
Yellow solid, 35.5 mg, 68% yield, m.p. = 73.1 ℃ – 74.9 ℃. R_f = 0.4 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 8.1 Hz, 1H), 6.45 (t, *J* = 7.6 Hz, 1H), 6.17 (d, *J* = 7.9 Hz, 1H), 6.07 (s, 1H), 4.30 (s, 1H), 1.10 (s, 6H), 1.04 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.0, 154.2, 152.1, 147.1, 146.1, 131.7, 128.9, 128.5(dd, *J* = 33, 5 Hz), 128.2, 127.2 (q, *J* = 721 Hz), 126.2, 125.9, 125.7(q, *J* =4 Hz), 123.9, 118.9, 110.9, 83.6, 65.6, 24.8, 24.3. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{28}H_{27}BF_3N_2O_4^+$ 523.2010, found 523.2011.

(*E*)-3-((4-Chlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-2-(4-nitrophenyl)indoline (2x)



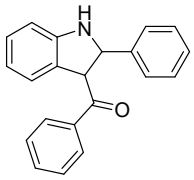
Yellow oil, 22.0 mg, 45% yield, R_f = 0.4 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 7.7 Hz, 2H), 7.03 – 6.95 (m, 1H), 6.55 (d, J = 7.9 Hz, 1H), 6.38 (t, 1H), 6.19 (d, J = 7.8 Hz, 1H), 5.95 (s, 1H), 4.17 (s, 1H), 1.00 (s, 6H), 0.94 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.6, 153.0, 151.2, 146.0, 139.4, 131.2, 130.4, 128.0, 127.1, 125.2, 125.1, 122.9, 117.9, 109.8, 82.5, 64.5, 23.8, 23.3. **HRMS (ESI)**: $[M+K]^+$ calcd. for $C_{27}H_{26}BClN_2O_4K^+$ 527.1306, found 527.1310.

4. Synthetic Transformations



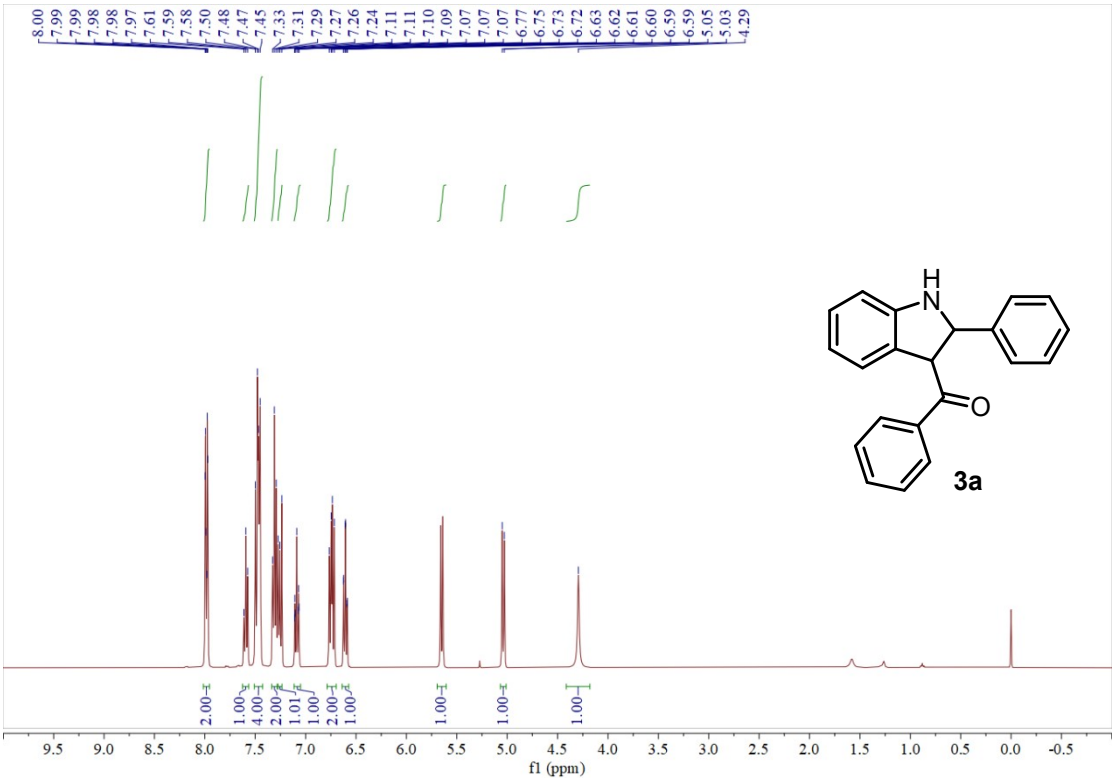
In an argon atmosphere, **2q** (0.1 mmol, 40.9 mg) was added to a solution of $NaBO_3 \cdot 4H_2O$ (0.15 mmol, 23.6 mg), KOH (0.3 mmol, 16.8 mg) in THF (2 mL) and H_2O (0.4 mL). After the reaction was stirred at room temperature for 1.5 h, the resulting mixture was extract with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford **3a** as white solid.

Phenyl(2-phenylindolin-3-yl)methanone (3a)

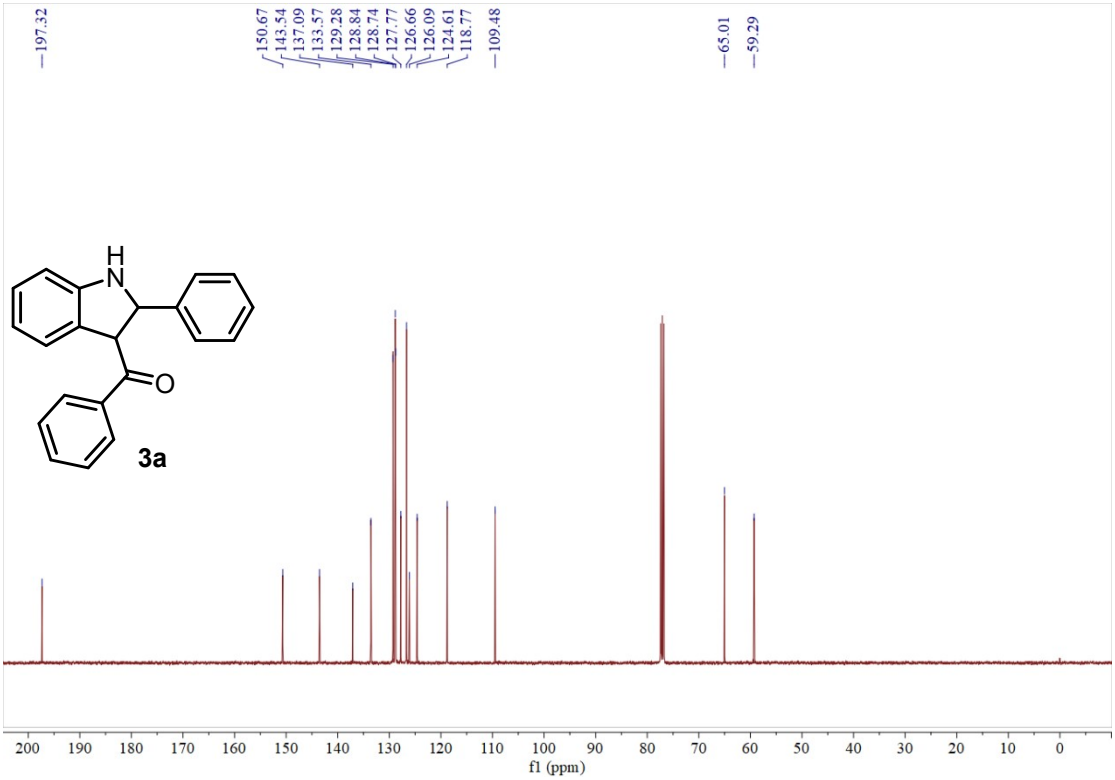


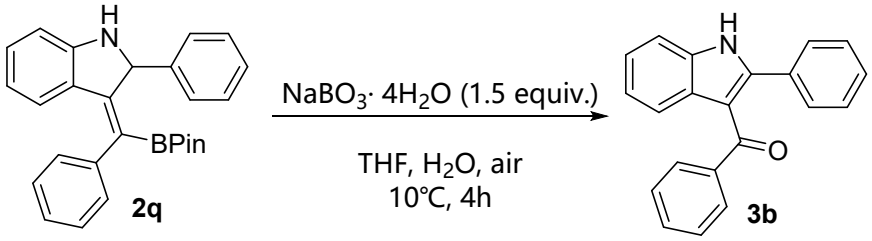
White solid, 27.8 mg, 82% yield, dr = 16:1, m.p. = 177.1 ℃ – 178.6 ℃. R_f = 0.5 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.74 – 7.59 (m, 1H), 7.54 – 7.42 (m, 4H), 7.43 – 7.21 (m, 3H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.78 (t, *J* = 8.3 Hz, 2H), 6.64 (t, *J* = 7.4 Hz, 1H), 5.69 (d, *J* = 8.4 Hz, 1H), 5.07 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.3, 150.6, 143.5, 137.1, 133.6, 129.3, 128.8, 128.7, 127.8, 126.6, 126.1, 124.6, 118.8, 109.5, 65.0, 59.3. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{21}H_{18}NO^+$ 300.1383, found 300.1383.

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



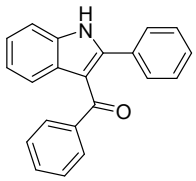
^{13}C NMR Spectra of **3a** (100 MHz, $CDCl_3$)





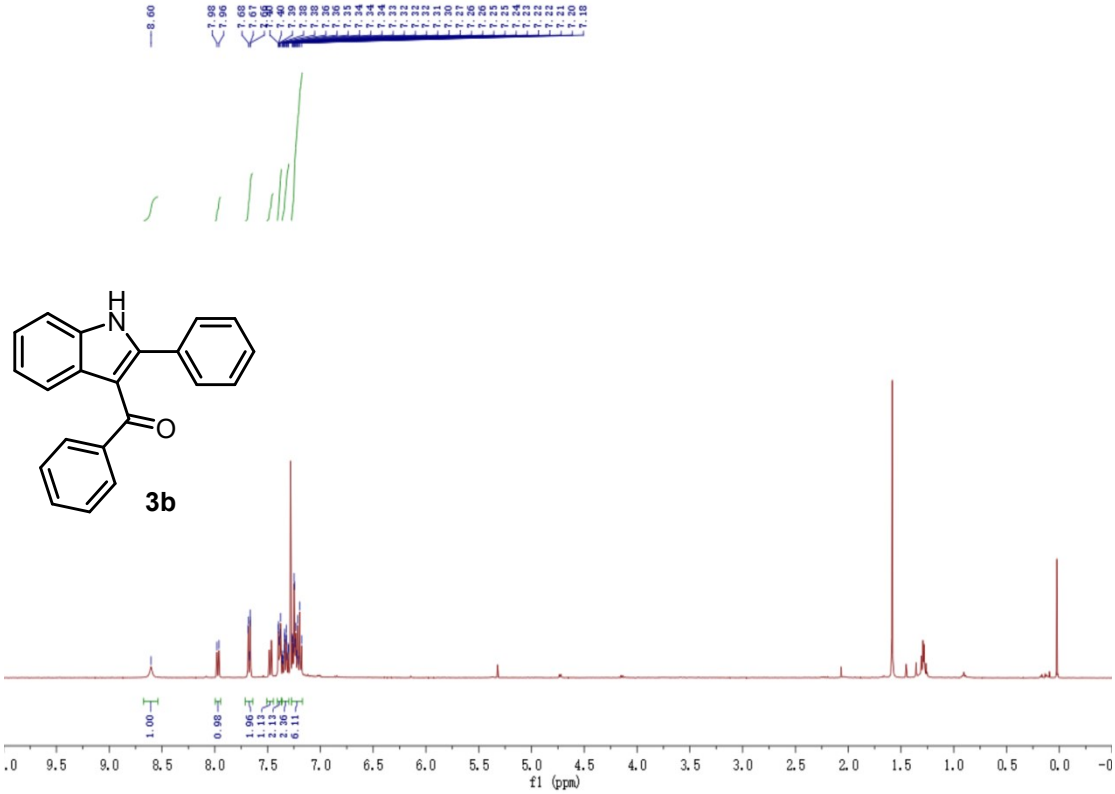
Under an ambient atmosphere, **2q** (0.1 mmol, 40.9 mg) was added to a solution of $NaBO_3 \cdot 4H_2O$ (0.15 mmol, 23.6 mg) in THF (2 mL) and H_2O (0.4 mL). The reaction was open to air and stirred at 10 ℃ for 4 h. The resulting mixture was extract with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford **3b** as gray solid.

Phenyl(2-phenyl-1H-indol-3-yl)methanone (3b)

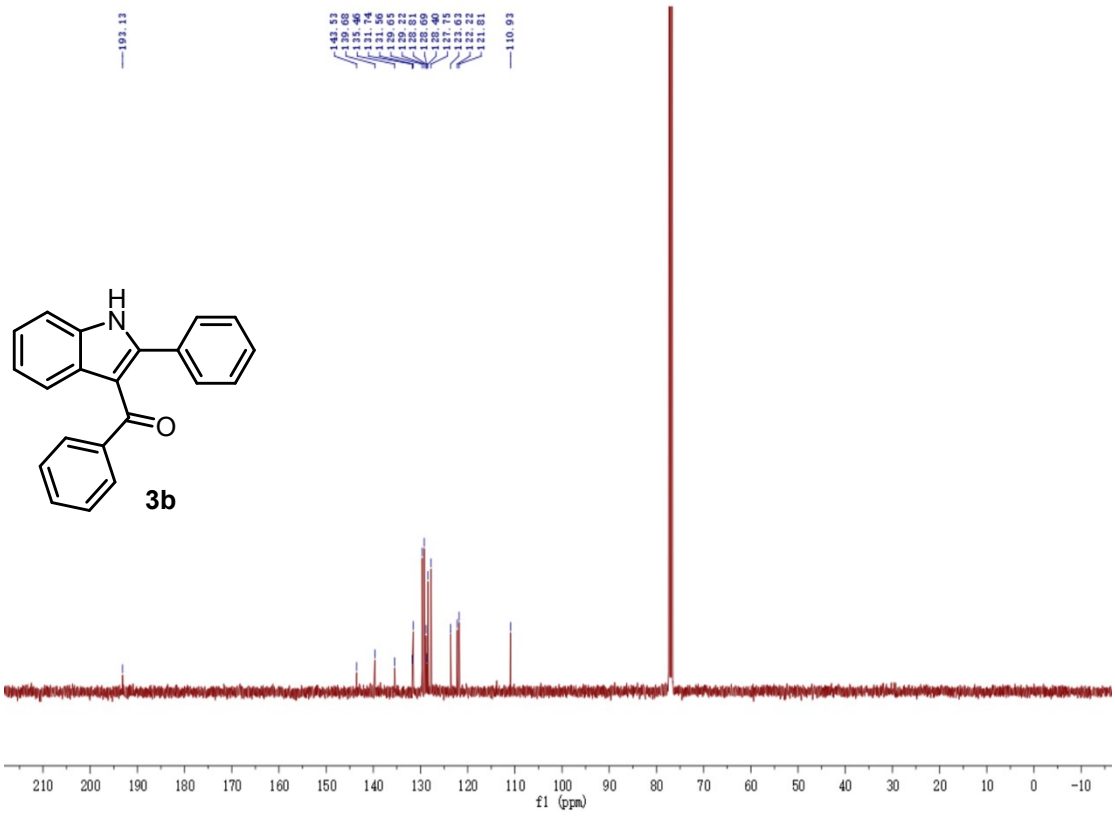


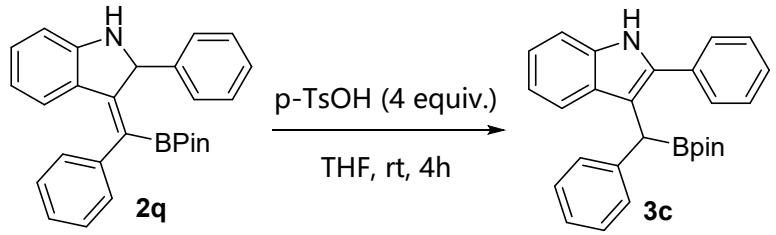
Gray solid, 23.2 mg, 69% yield, m.p. = 178.1 ℃ – 179.4 ℃. R_f = 0.2 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.67 (m, 2H), 7.47 (d, *J* = 7.9 Hz, 1H), 7.39 (m, 2H), 7.33 (m, 2H), 7.23 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.1, 143.5, 139.7, 135.5, 131.7, 131.6, 129.7, 129.2, 128.8, 128.7, 128.4, 127.8, 123.6, 122.2, 121.8, 110.9. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{21}H_{16}NO^+$ 298.1226, found 298.1226.

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



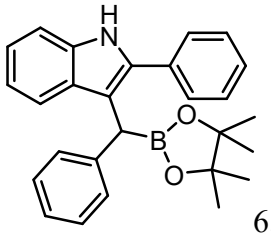
^{13}C NMR Spectra of **3b** (100 MHz, $CDCl_3$)





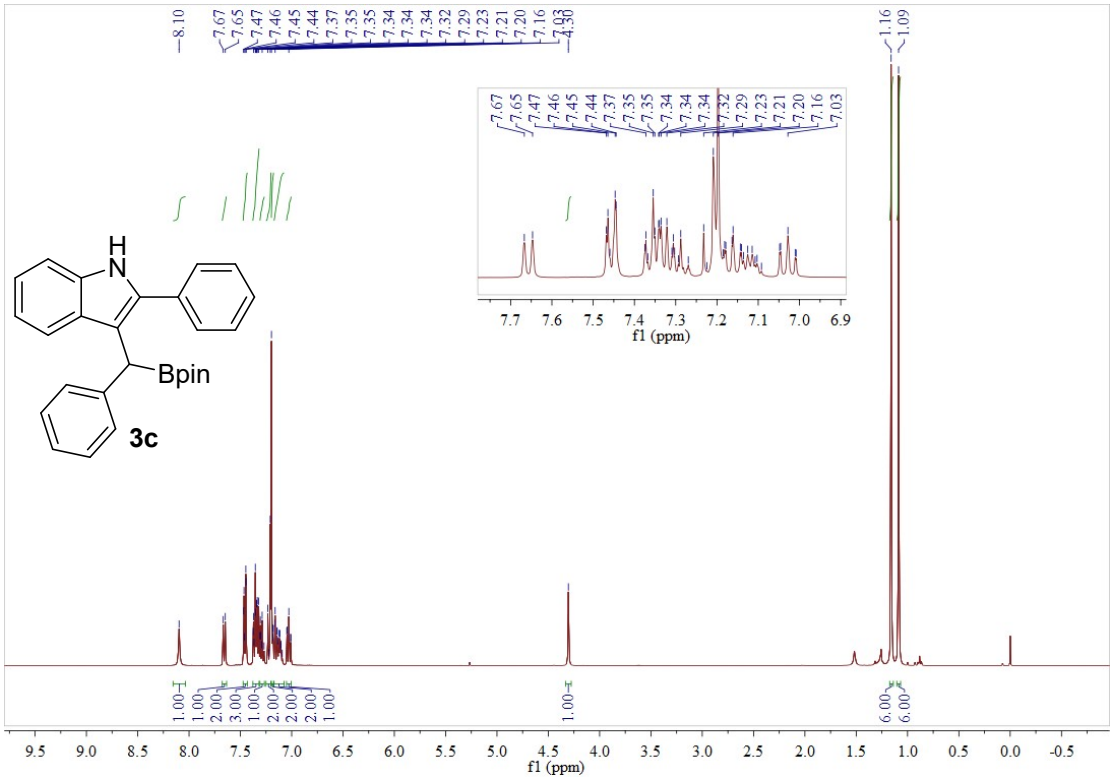
In an argon atmosphere, **2q** (0.1 mmol, 40.9 mg) was added to a solution of *p*-TsOH (0.4 mmol, 72.9 mg) in THF (2 mL). After the reaction was stirred at room temperature for 4 h, the resulting mixture was filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford **3c** as white solid.

2-Phenyl-3-(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indole (3c)

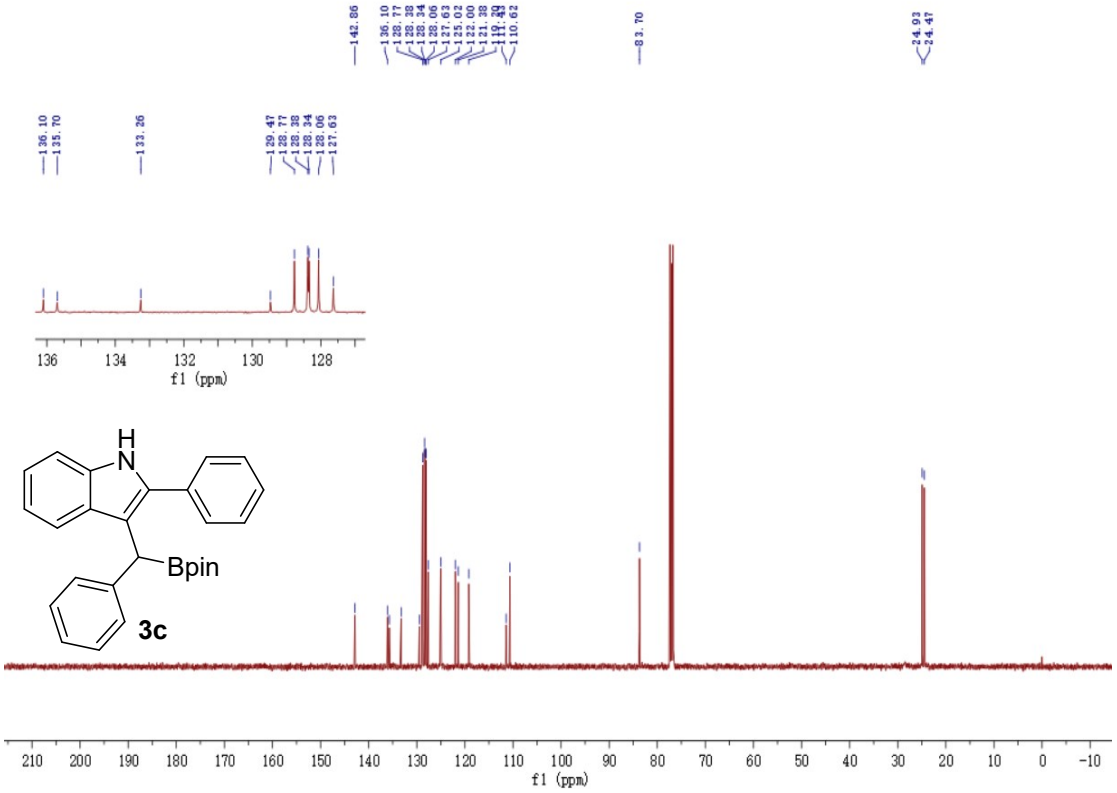


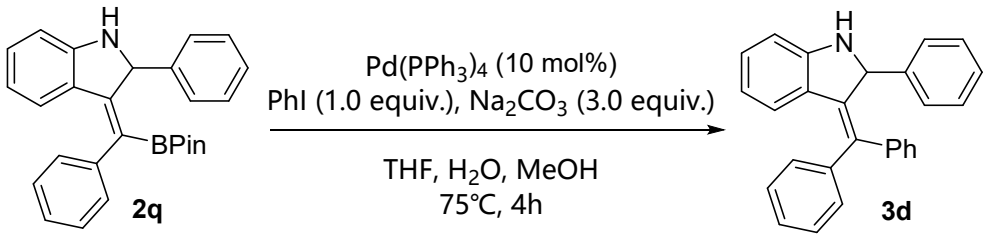
White solid, 36.8 mg, 90% yield, m.p. = 177.8 ℃ – 180.4 ℃. R_f = 0.4 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.39 – 7.32 (m, 3H), 7.29 (dt, J = 9.6, 4.3 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.20 – 7.17 (m, 2H), 7.17 – 7.09 (m, 2H), 7.07 – 6.99 (m, 1H), 4.30 (s, 1H), 1.16 (s, 6H), 1.09 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.9, 136.1, 135.7,133.3, 129.5, 128.8, 128.4, 128.3, 128.1, 127.6, 125.0, 122.0, 121.4, 119.2, 111.4, 110.6, 83.7, 24.9, 24.5. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{27}H_{29}BNO_2^+$ 410.2286, found 410.2291.

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



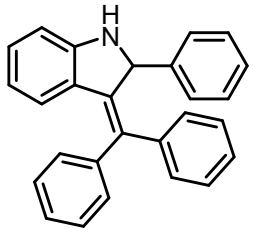
^{13}C NMR Spectra of **3c** (100 MHz, $CDCl_3$)





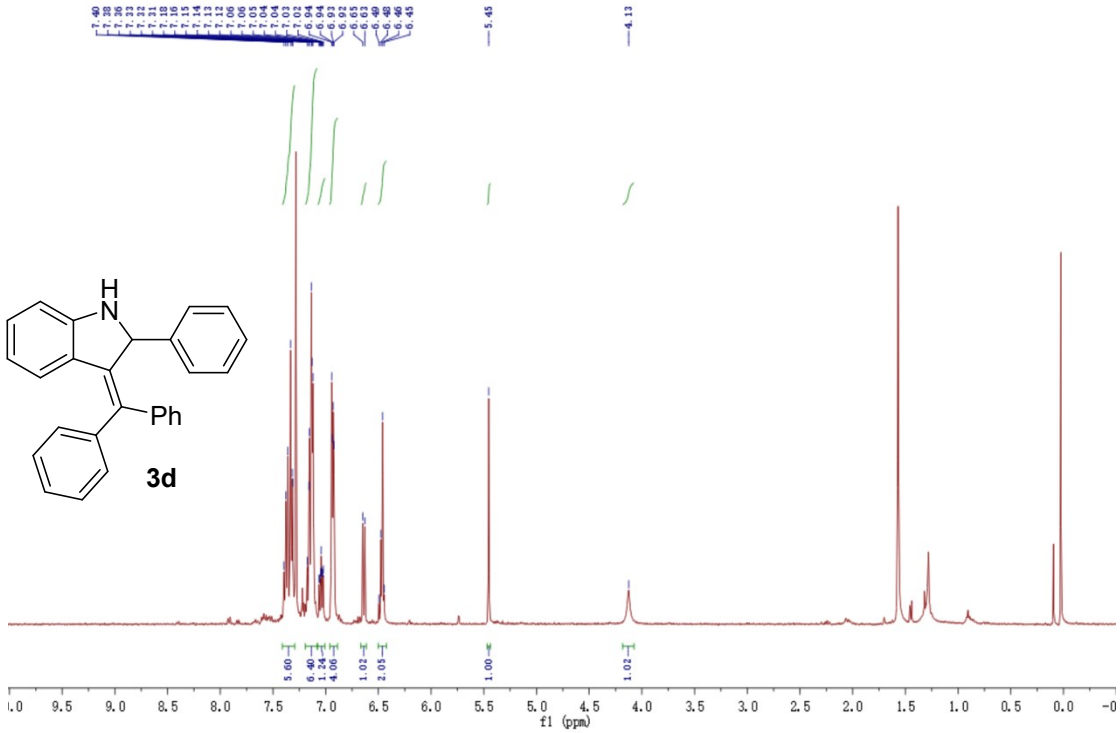
In an argon atmosphere, **2q** (0.1 mmol, 40.9 mg) was added to a solution of $Pd(PPh_3)_4$ (0.01 mmol, 12.0 mg), PhI (0.10 mmol, 11.2μL), Na_2CO_3 (0.30 mmol, 31.8 mg) in THF (1 mL), H_2O (1 mL) and MeOH (0.25 mL). After the reaction was stirred at 75 ℃ for 4 h, the resulting mixture was extract with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford **3d** as yellow oil.

3-(Diphenylmethylene)-2-phenylindoline (3d)

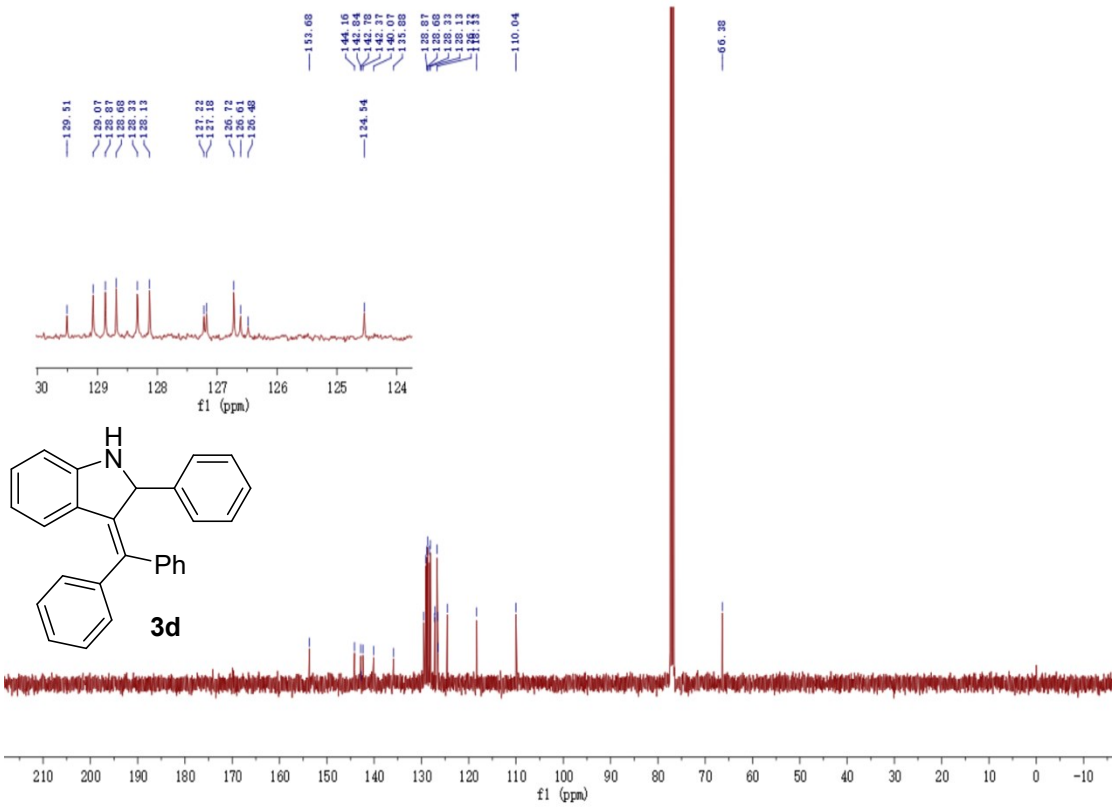


Yellow oil, 21.1 mg, 53% yield, R_f = 0.7 (petroleum ether/ethyl acetate = 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (m, 6H), 7.15 (m, 6H), 7.04 (ddd, J = 8.2, 6.2, 2.4 Hz, 1H), 6.93 (dd, J = 6.2, 2.1 Hz, 4H), 6.64 (d, J = 7.9 Hz, 1H), 6.47 (m, 2H), 5.45 (s, 1H), 4.13 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.6, 144.1, 142.8, 142.7, 142.3, 140.0, 135.8, 129.5, 129.0, 128.8, 128.6, 128.3, 128.1, 127.2, 127.1, 126.7, 126.6, 126.4, 124.5, 118.3, 110.0, 66.3. **HRMS (ESI)**: $[M+H]^+$ calcd. for $C_{27}H_{22}N^+$ 360.1747, found 360.1747.

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

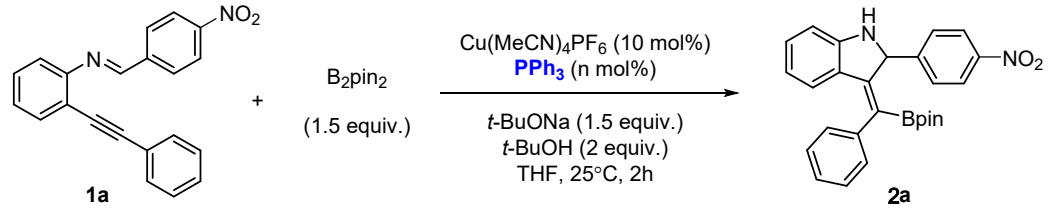


^{13}C NMR Spectra of **3d** (100 MHz, $CDCl_3$)



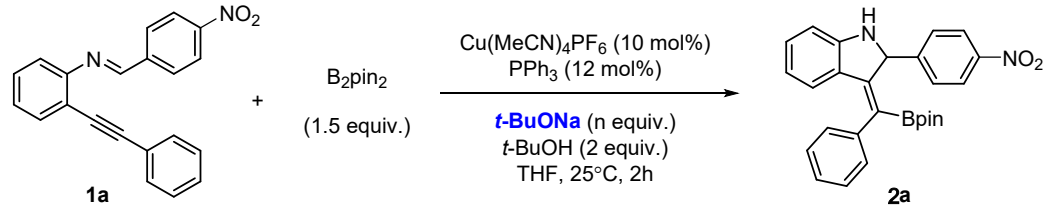
5. Control Experiments

A)



entry	PPh_3	results
1	PPh_3 (20 mol%)	81% yield
2	PPh_3 (30 mol%)	70% yield

B)



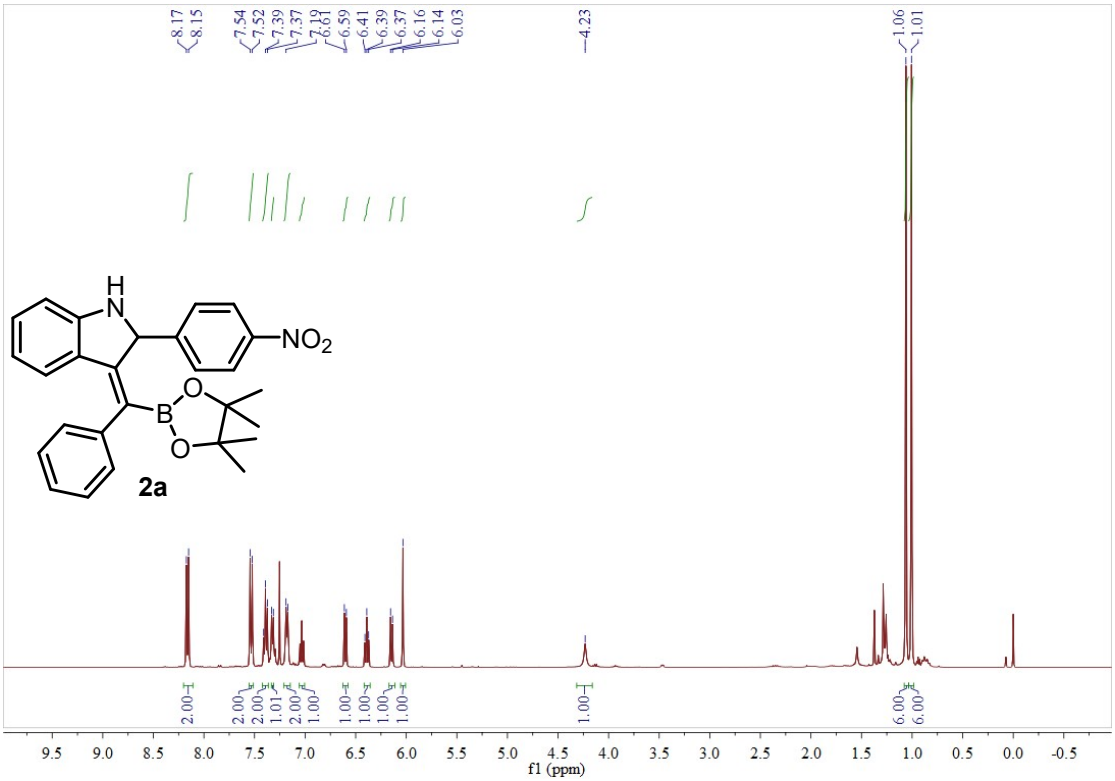
entry	*t*-BuONa	results
1	1.0 equiv.	62% yield
2	0.5 equiv.	34% yield
3	0.2 equiv.	16% yield

A) In an argon atmosphere, **1a** (0.1 mmol, 45.4 mg) was added to a solution of B_2pin_2 (0.15 mmol, 38 mg), $Cu(MeCN)_4PF_6$ (0.01 mmol, 4 mg), PPh_3 (n mol%), *t*-BuONa (0.15 mmol, 15 mg), *t*-BuOH (0.2 mmol, 19 μL) in THF (2 mL). After the reaction was stirred at room temperature for 2 h, the reaction solution was filtered, and concentrated *in vacuo*. The residue was analyzed by ^1H NMR using CH_2Br_2 as the internal standard.

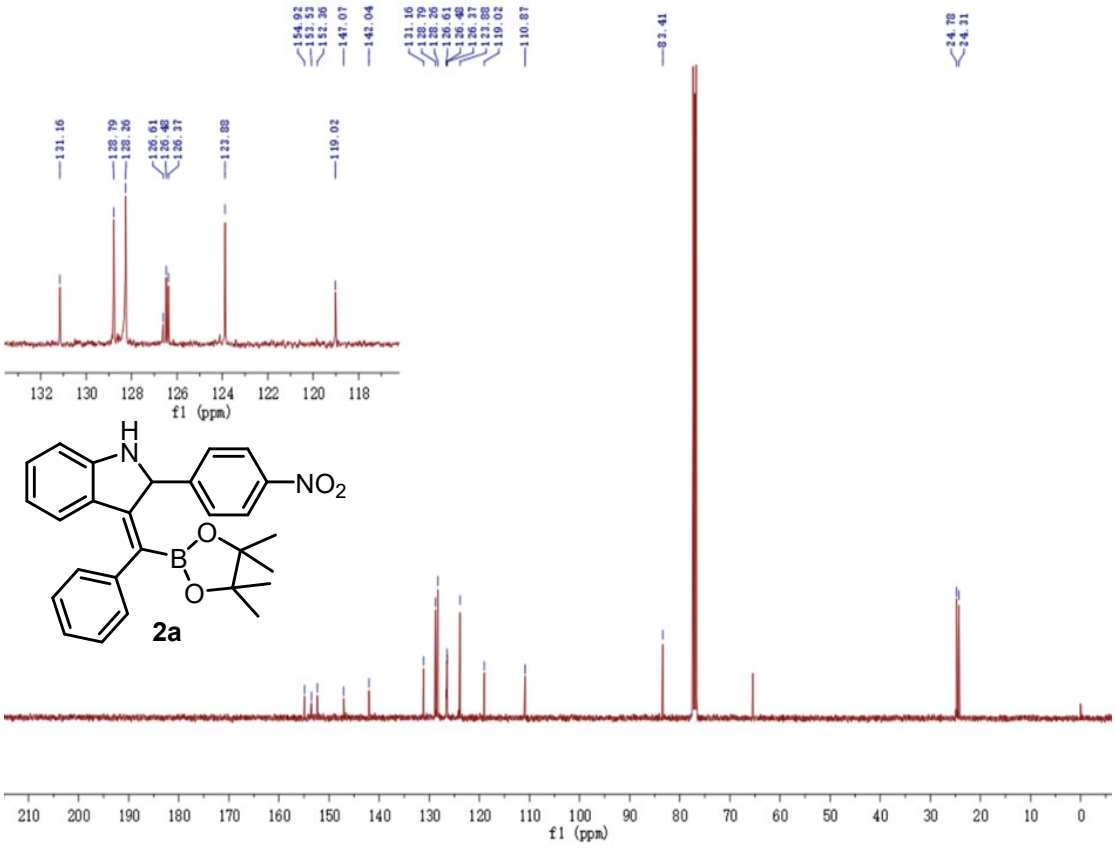
B) In an argon atmosphere, **1a** (0.1 mmol, 45.4 mg) was added to a solution of B_2pin_2 (0.15 mmol, 38 mg), $Cu(MeCN)_4PF_6$ (0.01 mmol, 4 mg), PPh_3 (0.012 mmol, 3 mg), *t*-BuONa (n equiv.), *t*-BuOH (0.2 mmol, 19 μL) in THF (2 mL). After the reaction was stirred at room temperature for 2 h, the reaction solution was filtered, and concentrated *in vacuo*. The residue was analyzed by ^1H NMR using CH_2Br_2 as the internal standard.

6. NMR Spectra of Products

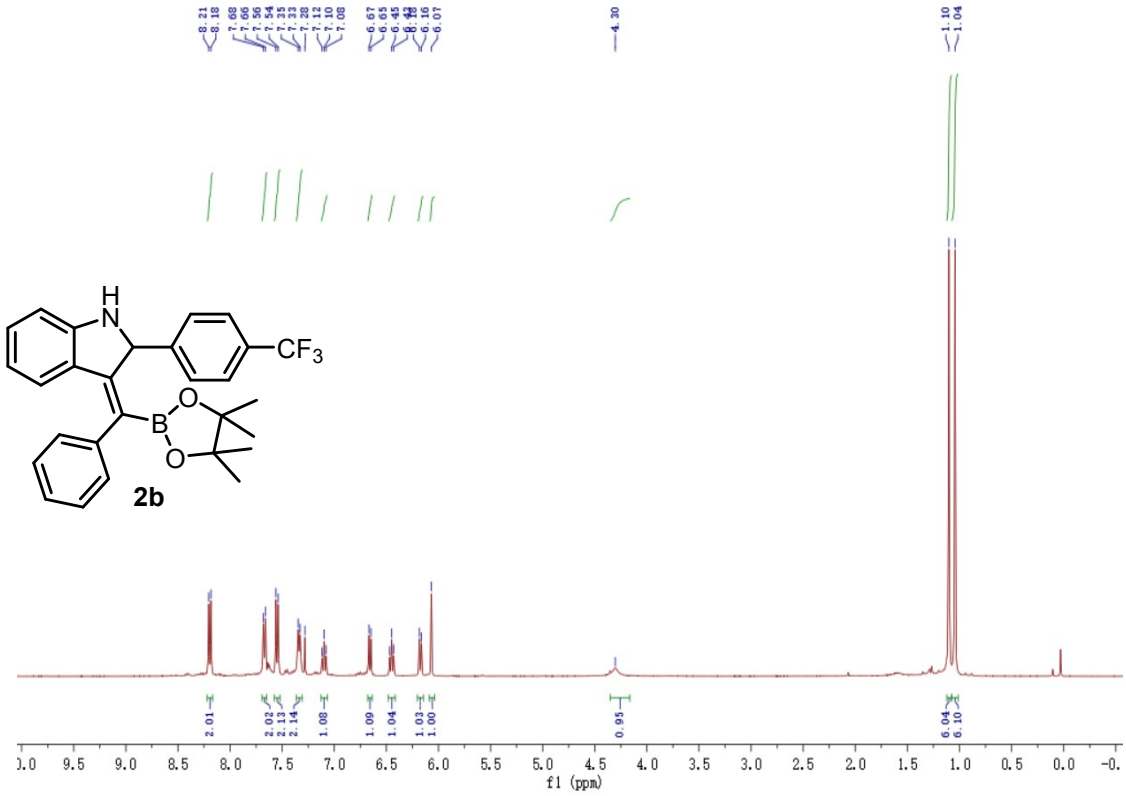
^{1}H NMR Spectra of **2a** (400 MHz, $CDCl_3$)



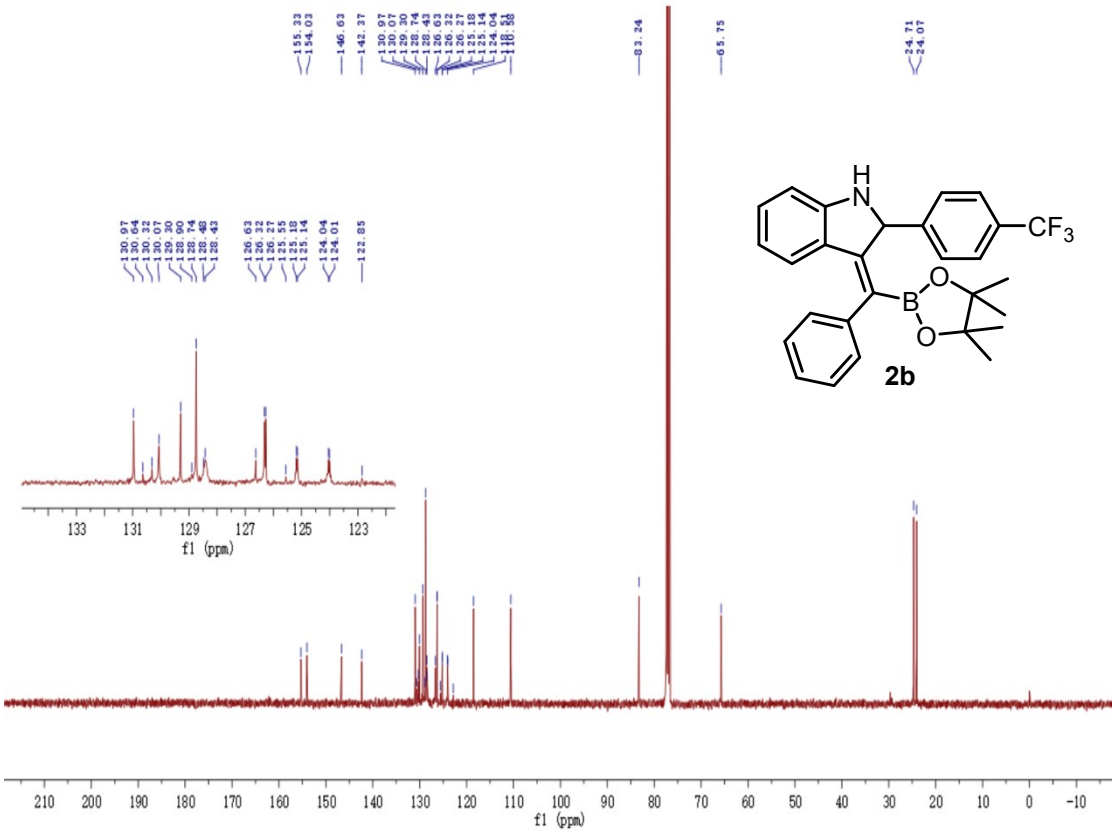
^{13}C NMR Spectra of **2a** (100 MHz, $CDCl_3$)



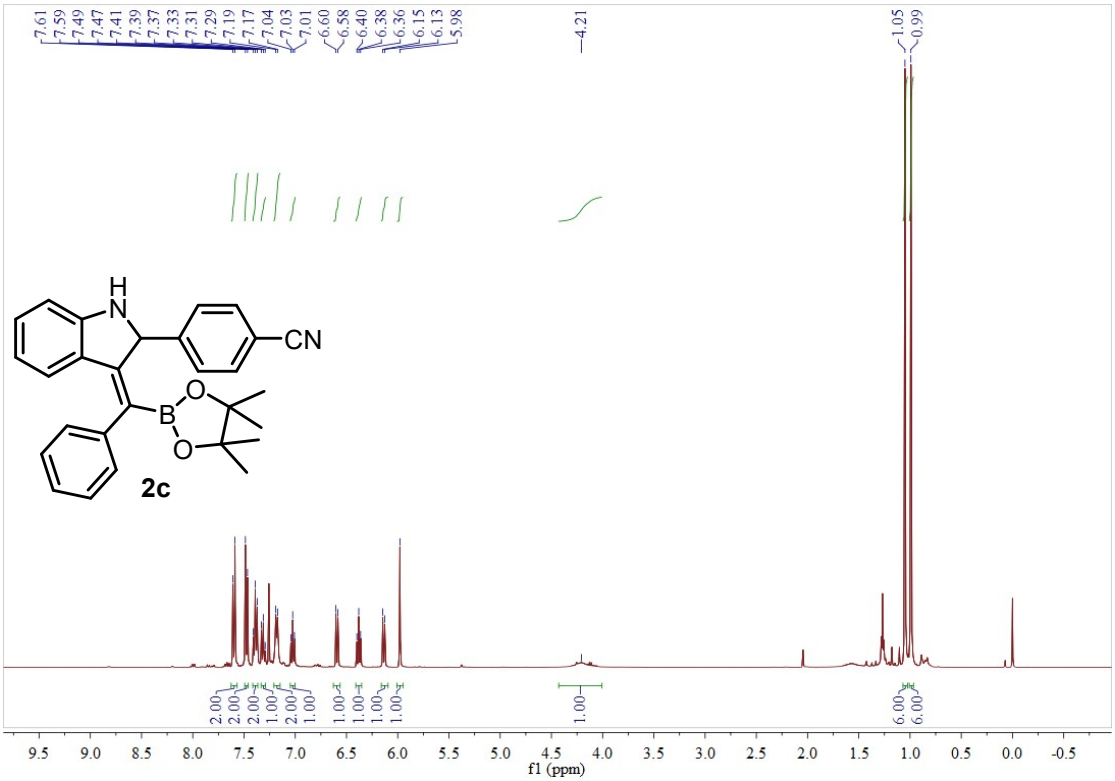
^{1}H NMR Spectra of **2b** (400 MHz, $CDCl_3$)



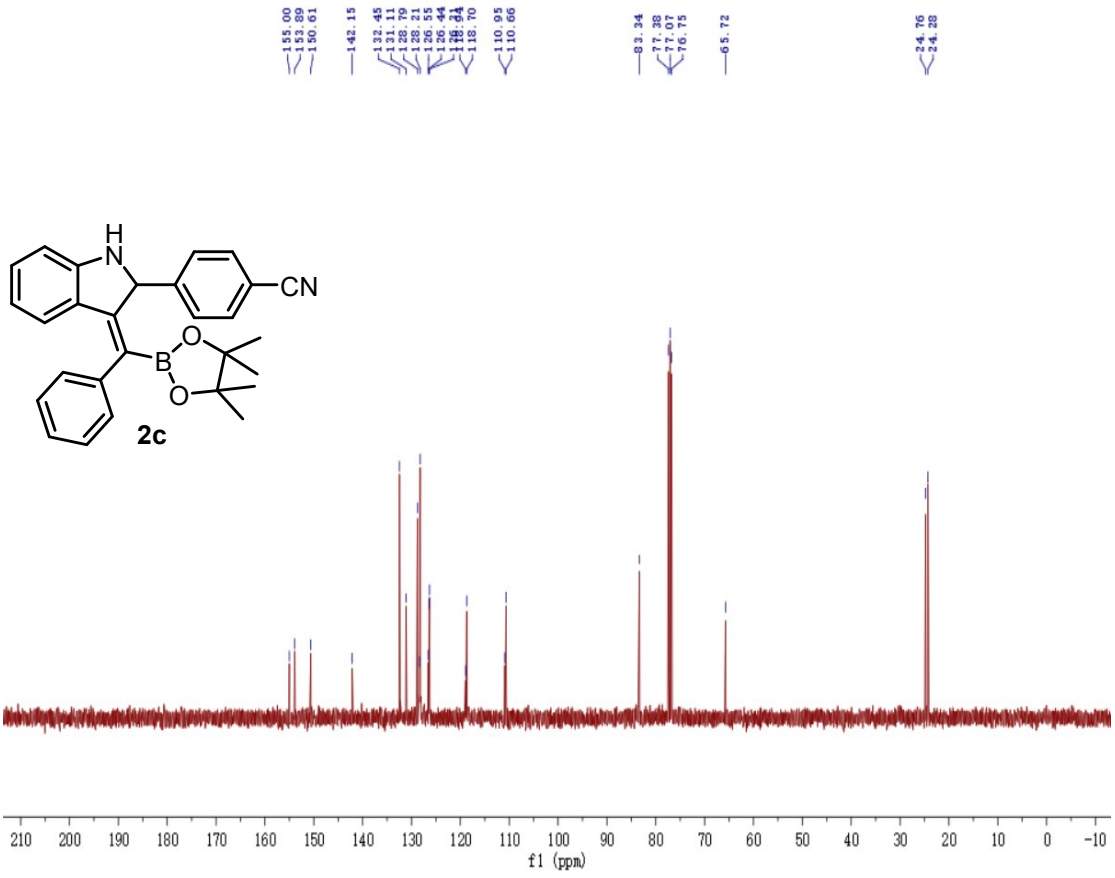
^{13}C NMR Spectra of **2b** (100 MHz, $CDCl_3$)



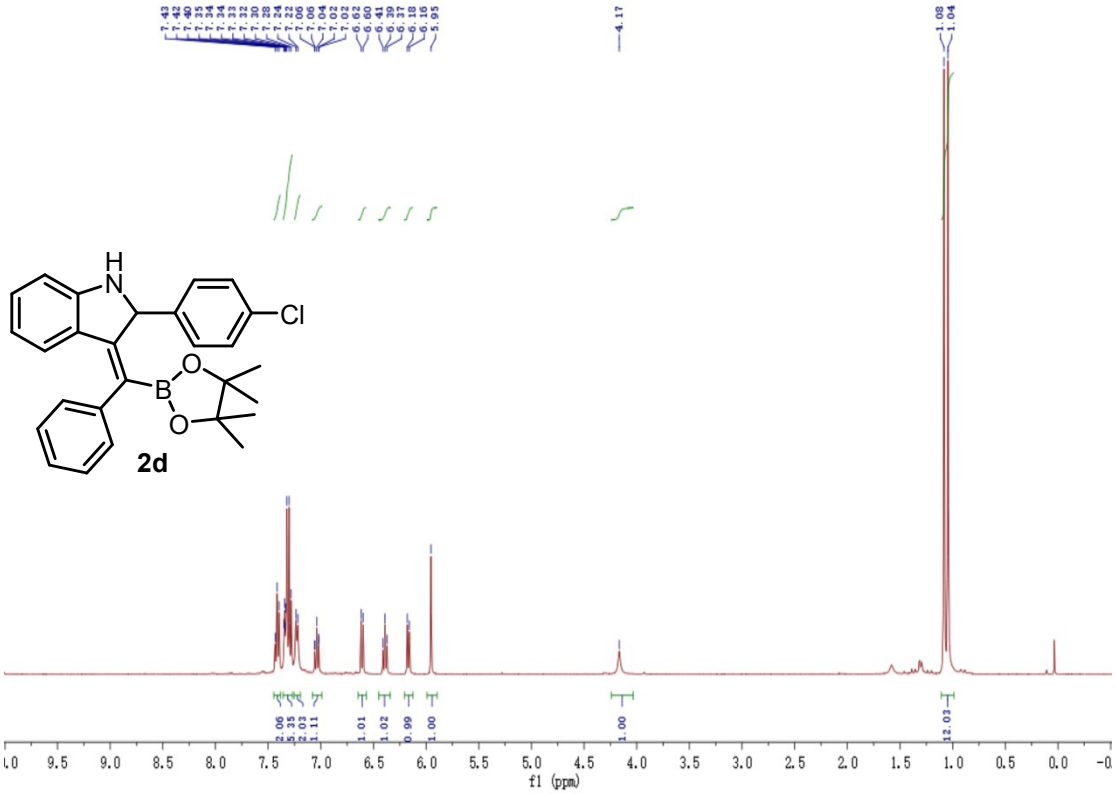
^{1}H NMR Spectra of **2c** (400 MHz, $CDCl_3$)



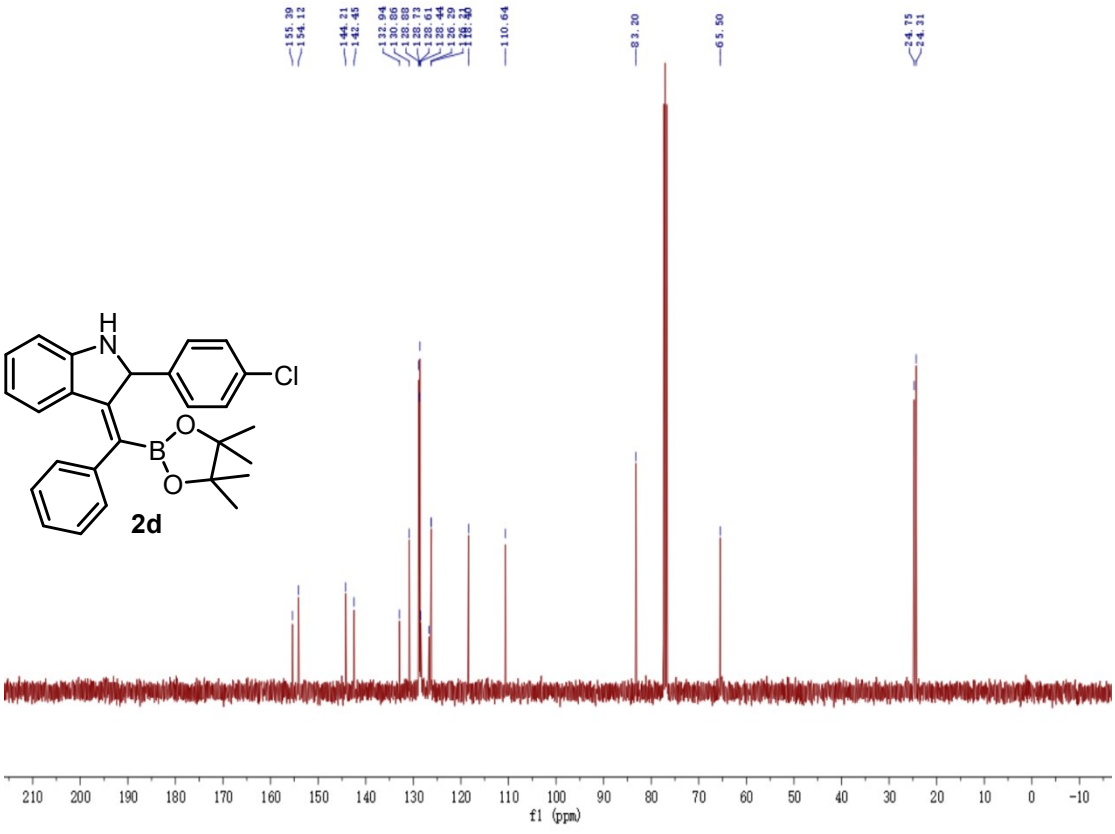
^{13}C NMR Spectra of **2c** (100 MHz, $CDCl_3$)



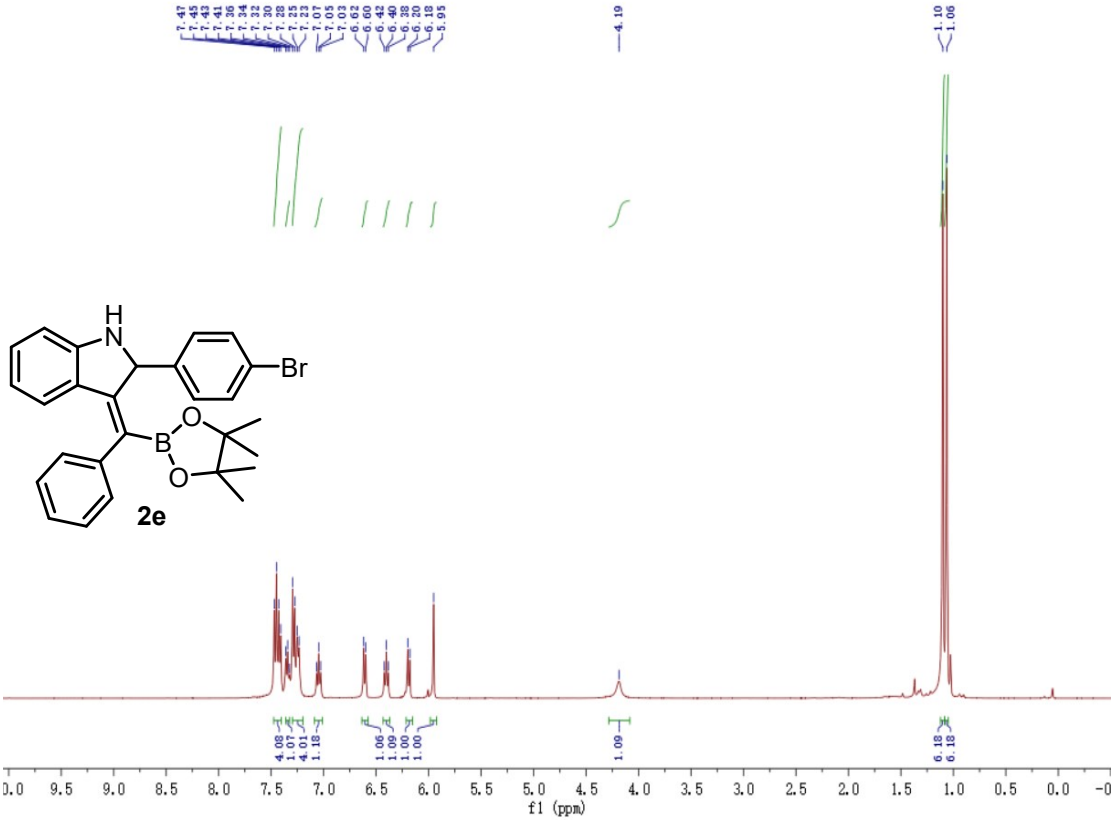
^{1}H NMR Spectra of **2d** (400 MHz, $CDCl_3$)



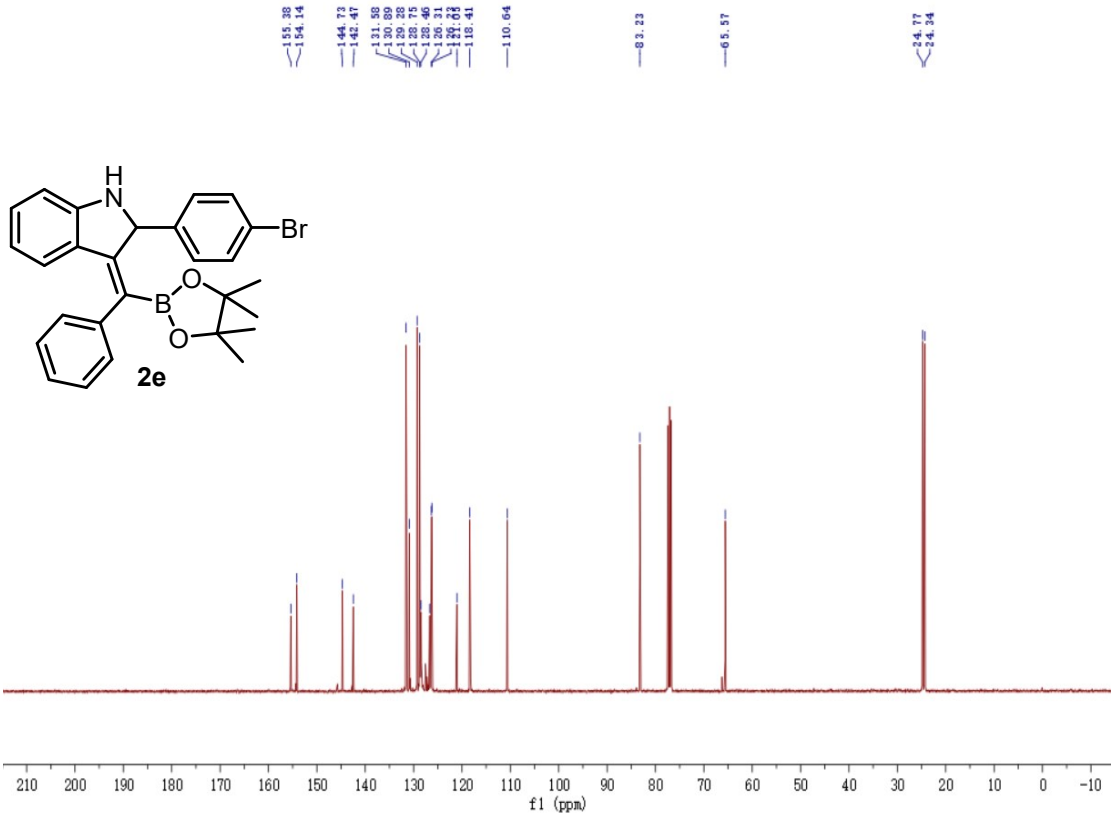
^{13}C NMR Spectra of **2d** (100 MHz, $CDCl_3$)



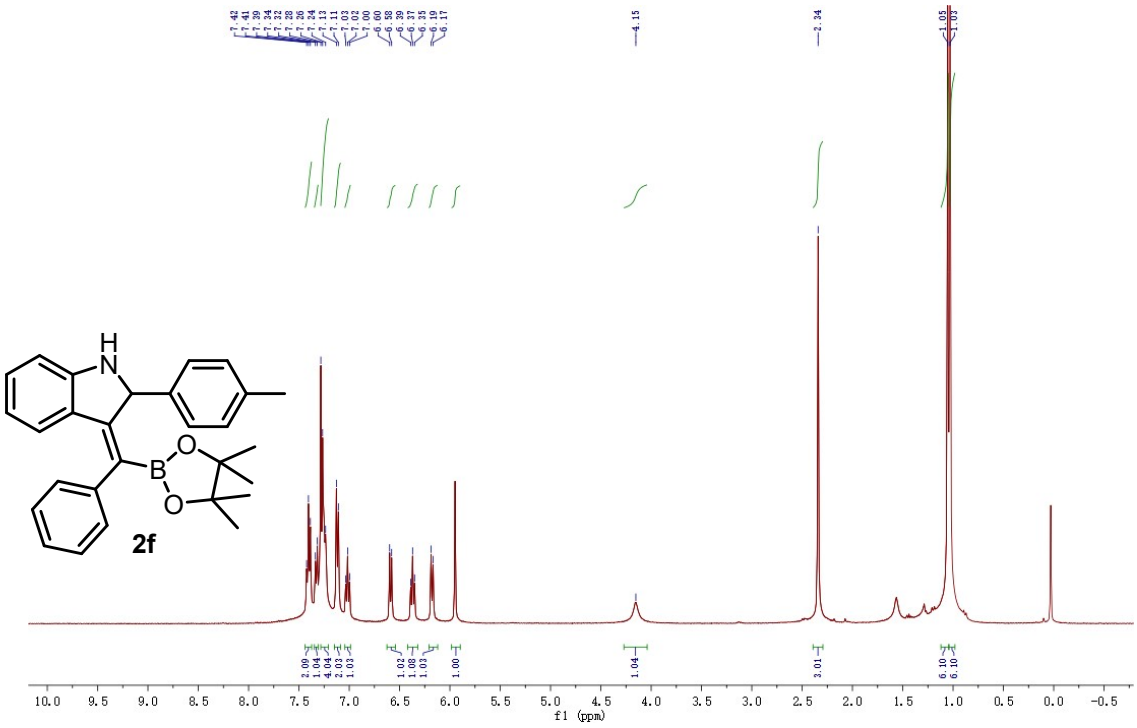
^{1}H NMR Spectra of **2e** (400 MHz, $CDCl_3$)



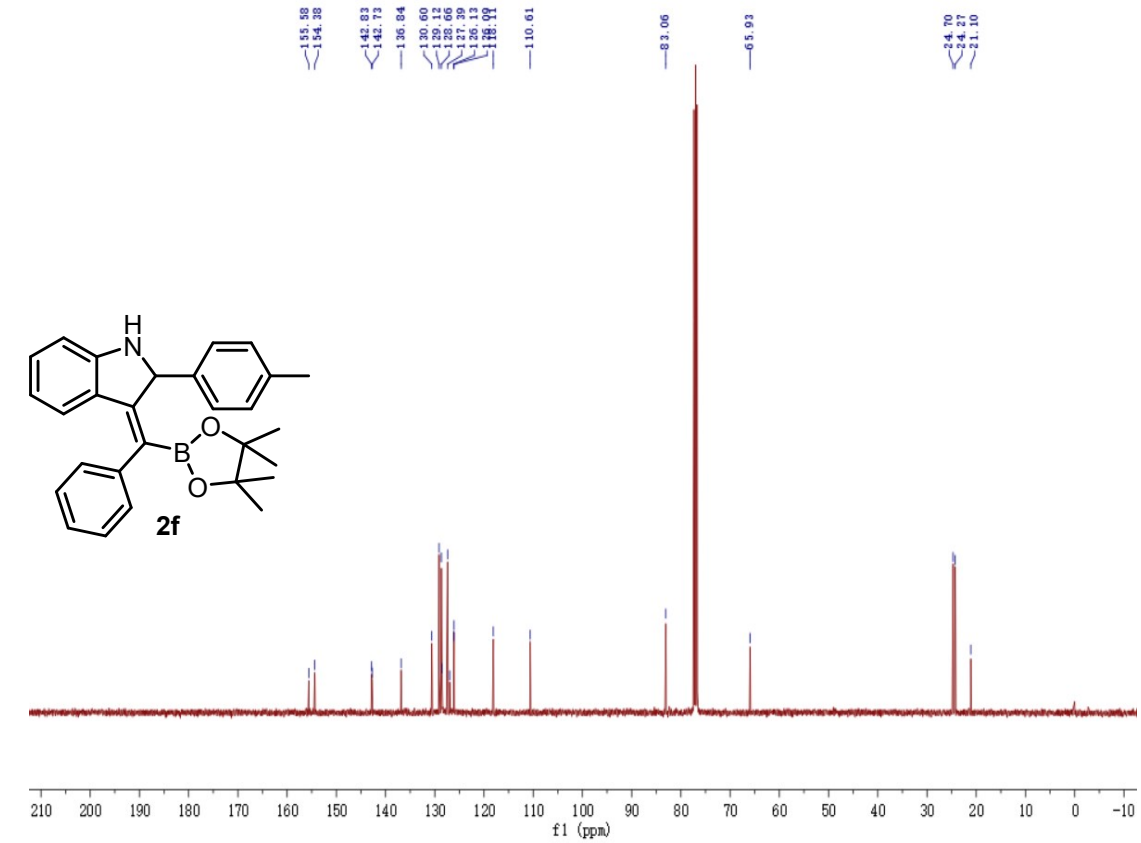
^{13}C NMR Spectra of **2e** (100 MHz, $CDCl_3$)



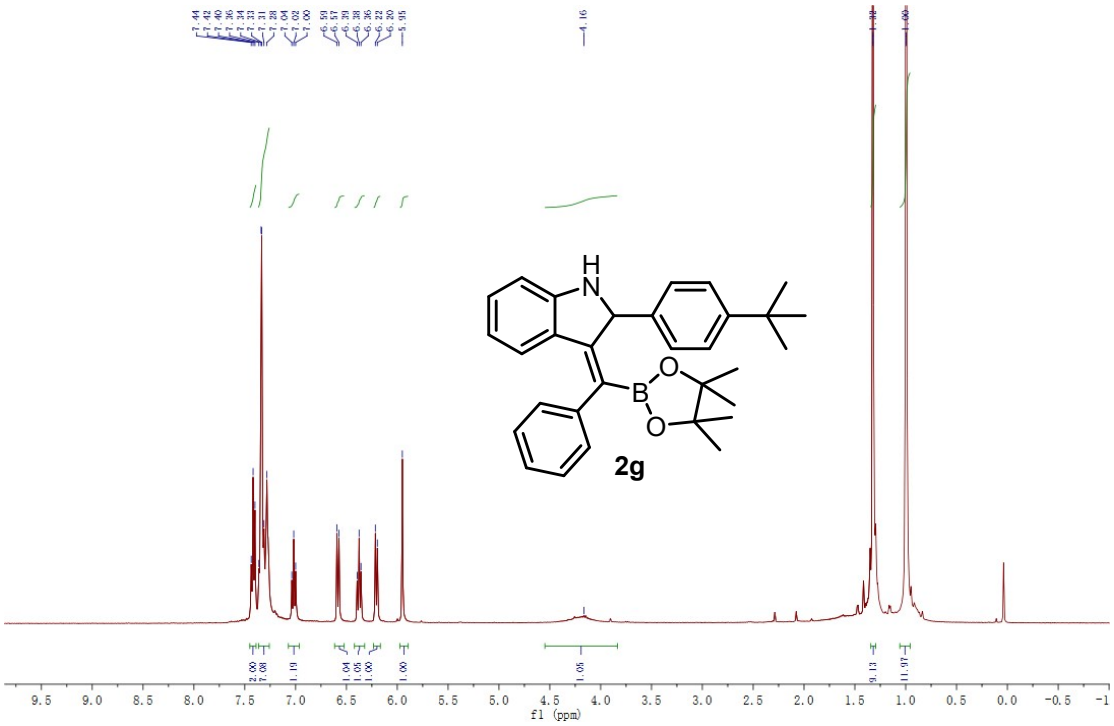
^{1}H NMR Spectra of **2f** (400 MHz, $CDCl_3$)



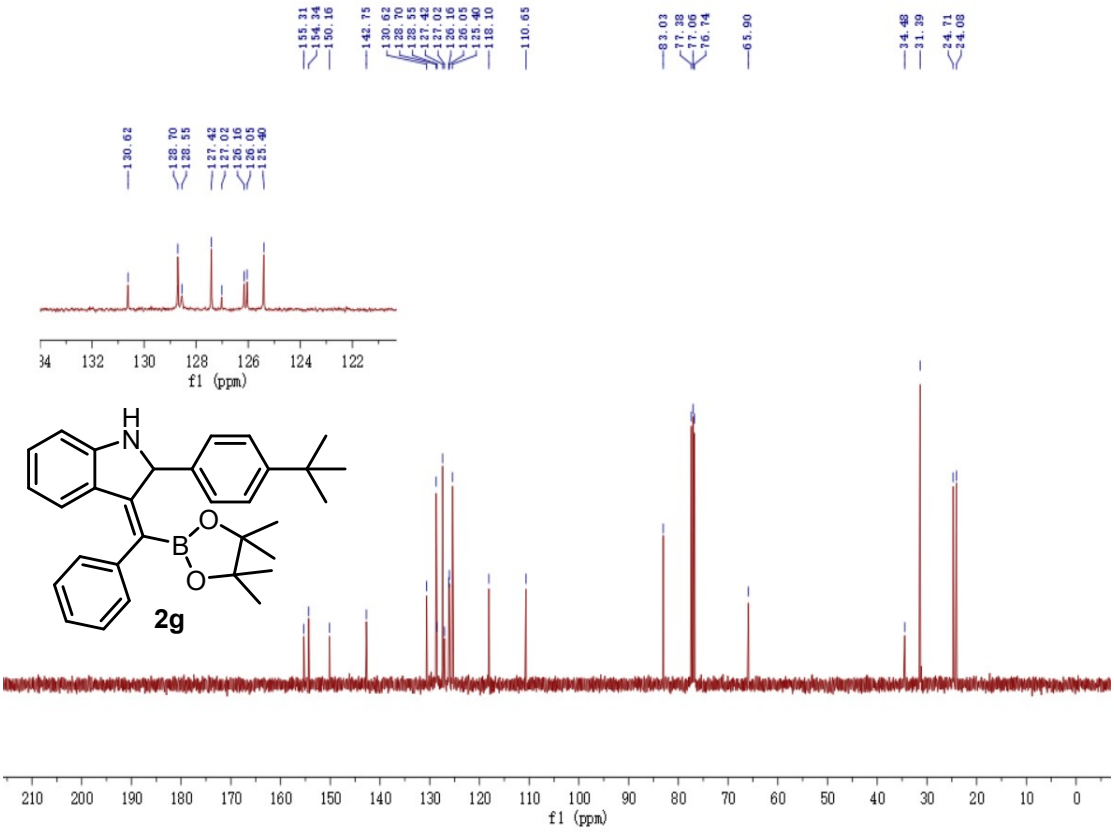
^{13}C NMR Spectra of **2f** (100 MHz, $CDCl_3$)



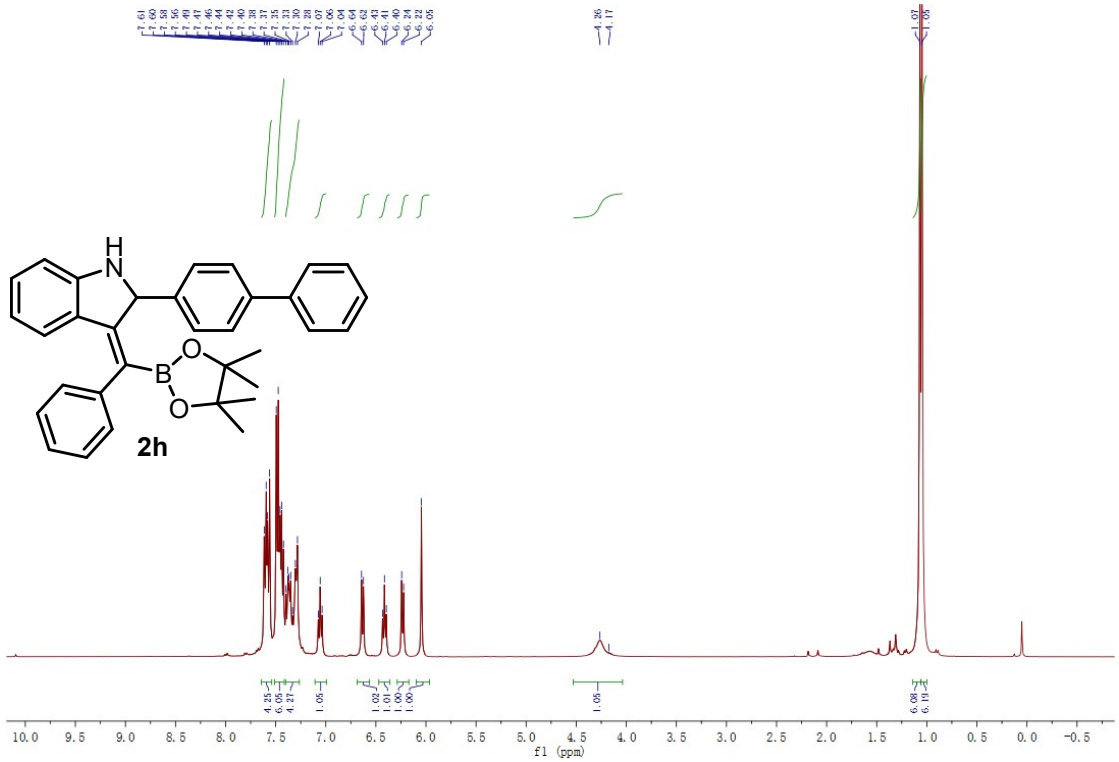
^{1}H NMR Spectra of **2g** (400 MHz, $CDCl_3$)



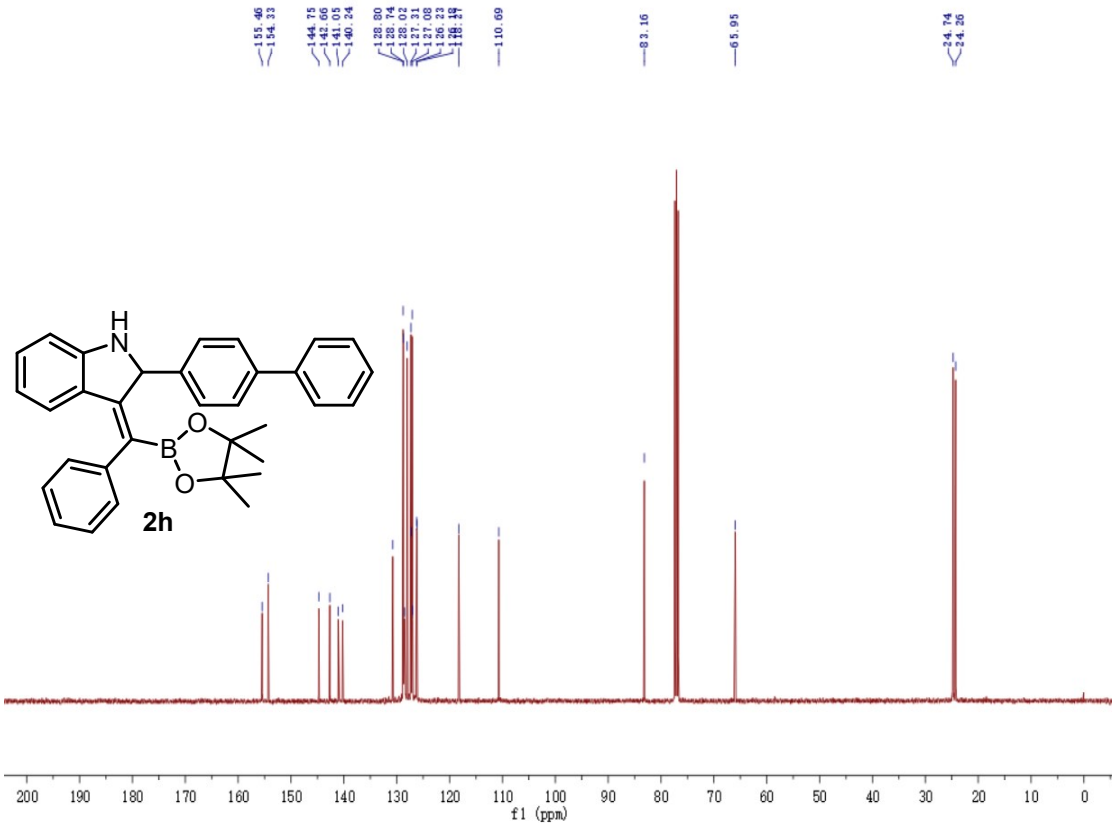
^{13}C NMR Spectra of **2g** (100 MHz, $CDCl_3$)



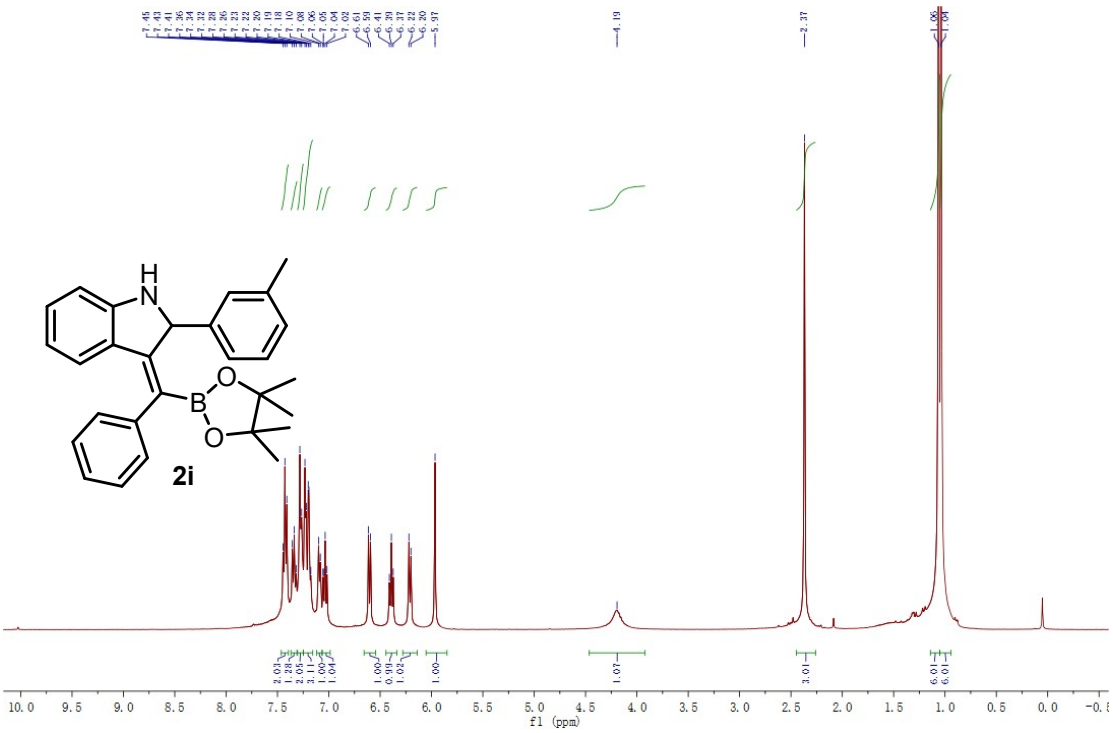
^{1}H NMR Spectra of **2h** (400 MHz, $CDCl_3$)



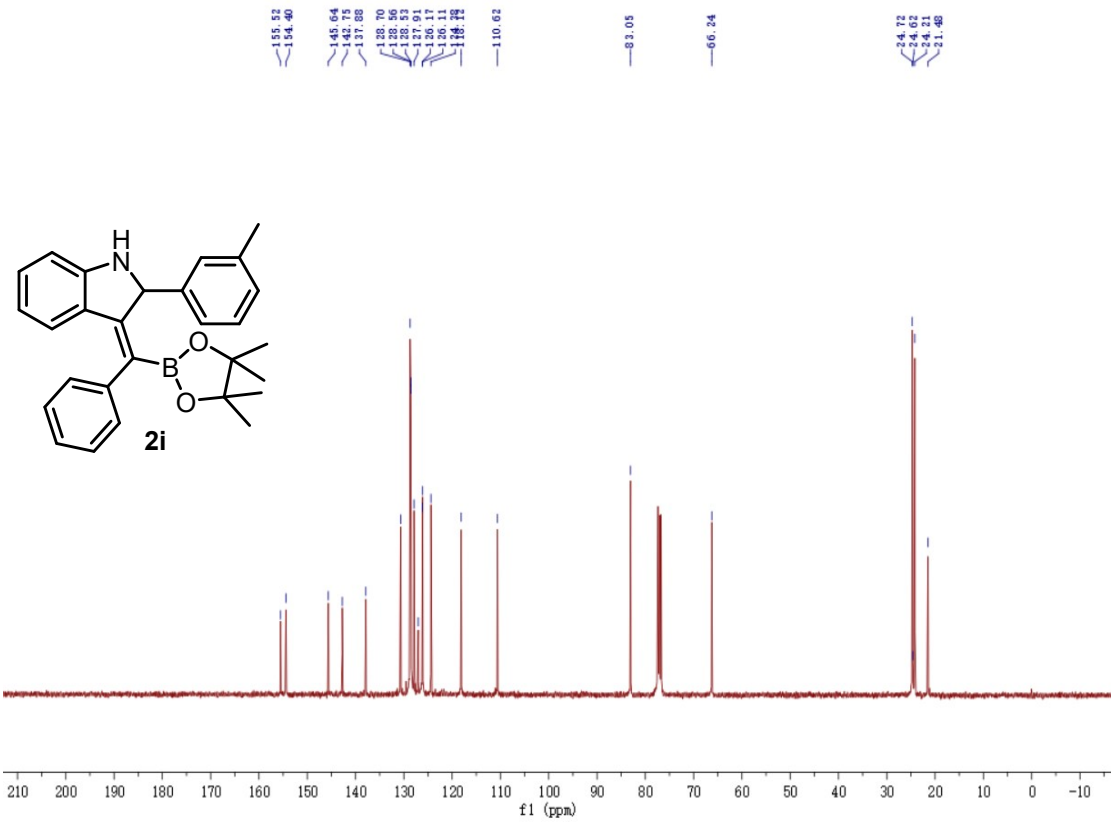
^{13}C NMR Spectra of **2h** (100 MHz, $CDCl_3$)



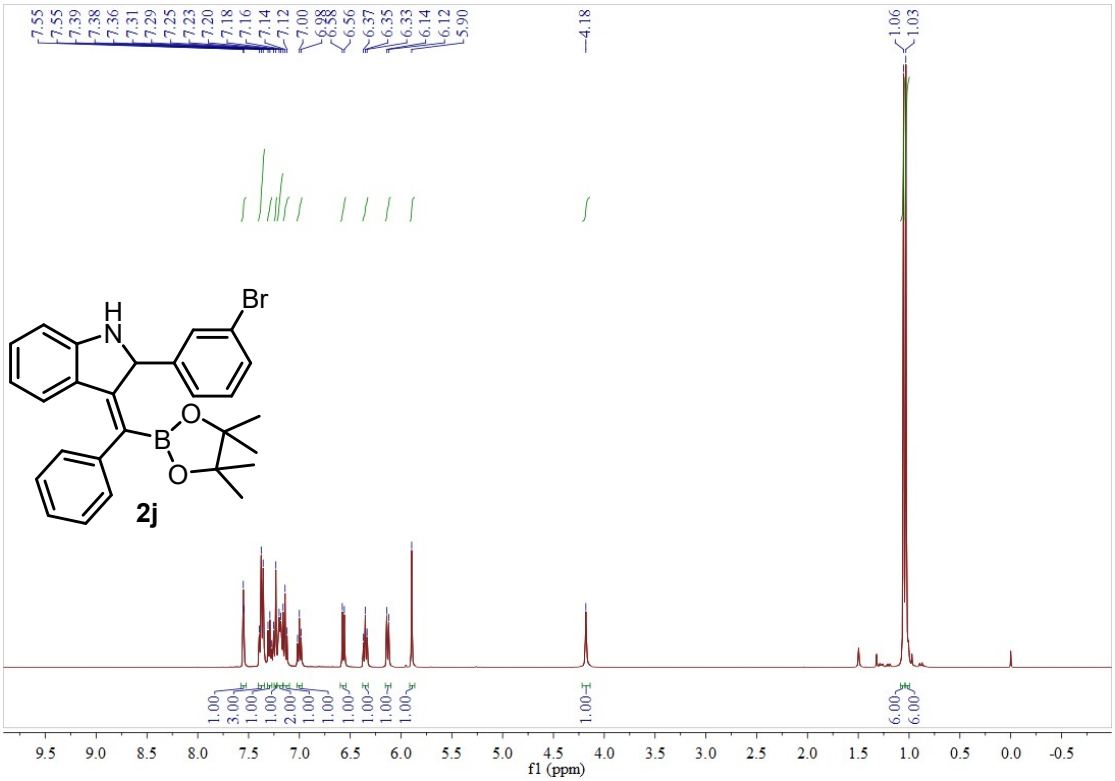
^{1}H NMR Spectra of **2i** (400 MHz, $CDCl_3$)



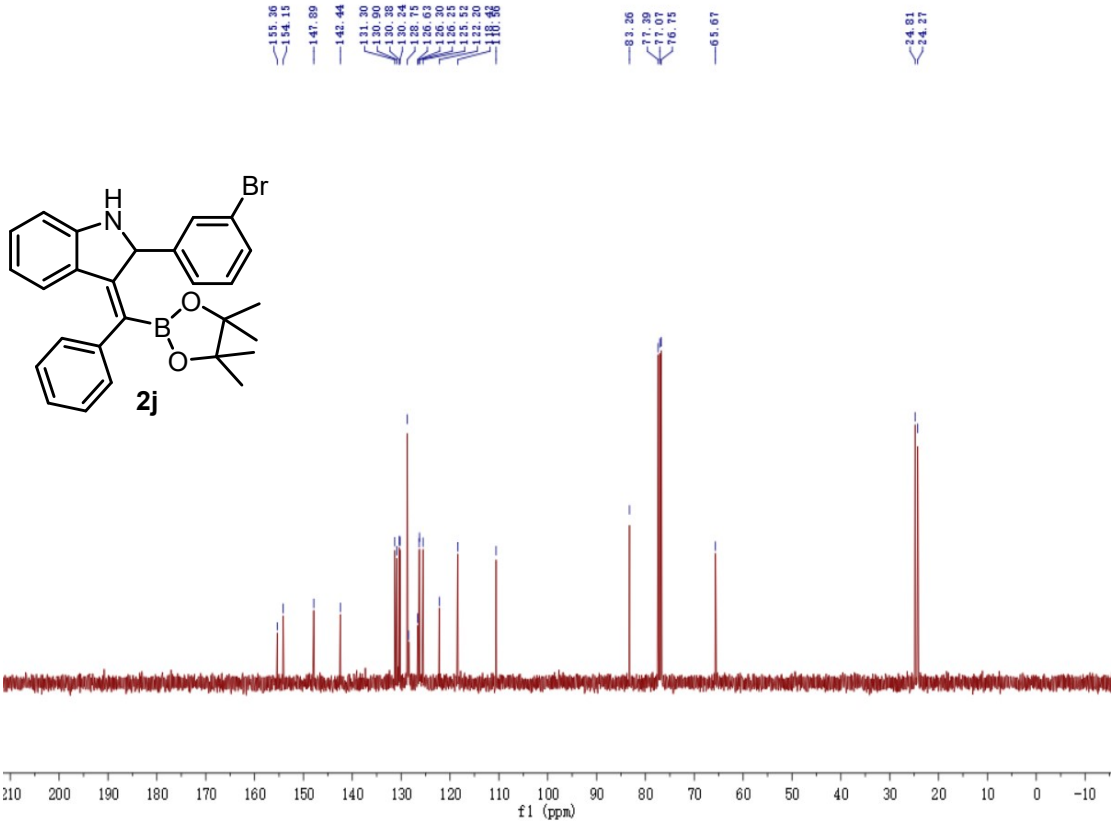
^{13}C NMR Spectra of **2i** (100 MHz, $CDCl_3$)



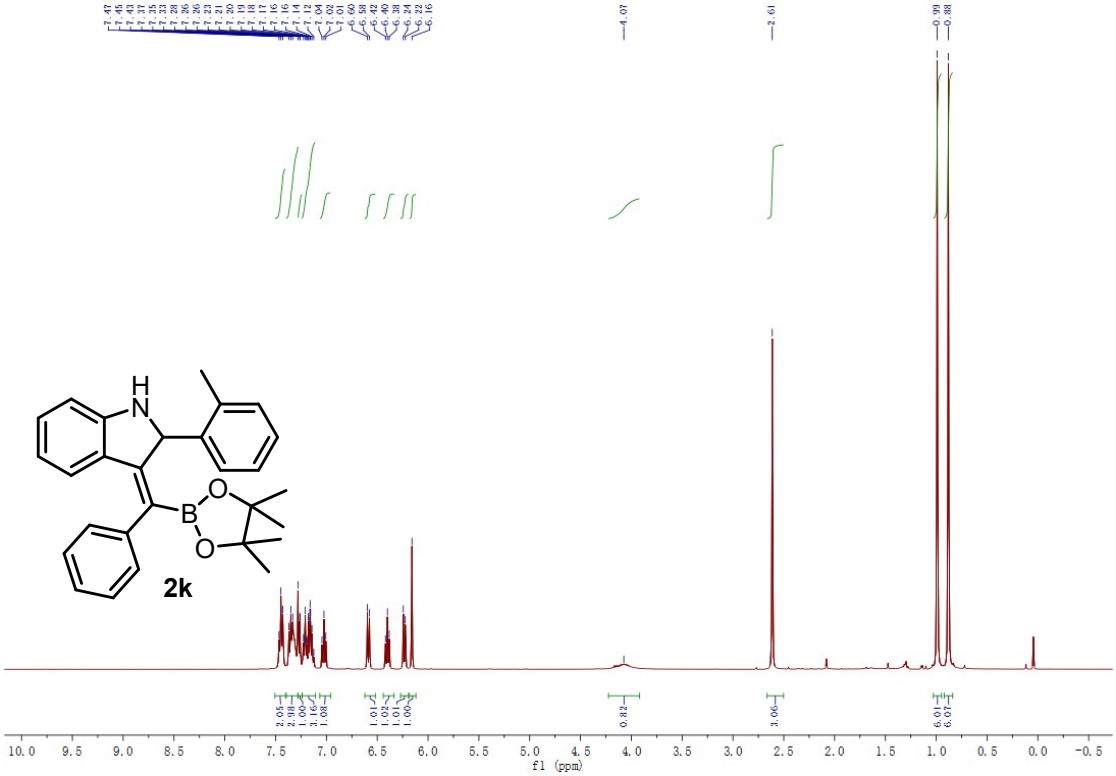
^{1}H NMR Spectra of **2j** (400 MHz, $CDCl_3$)



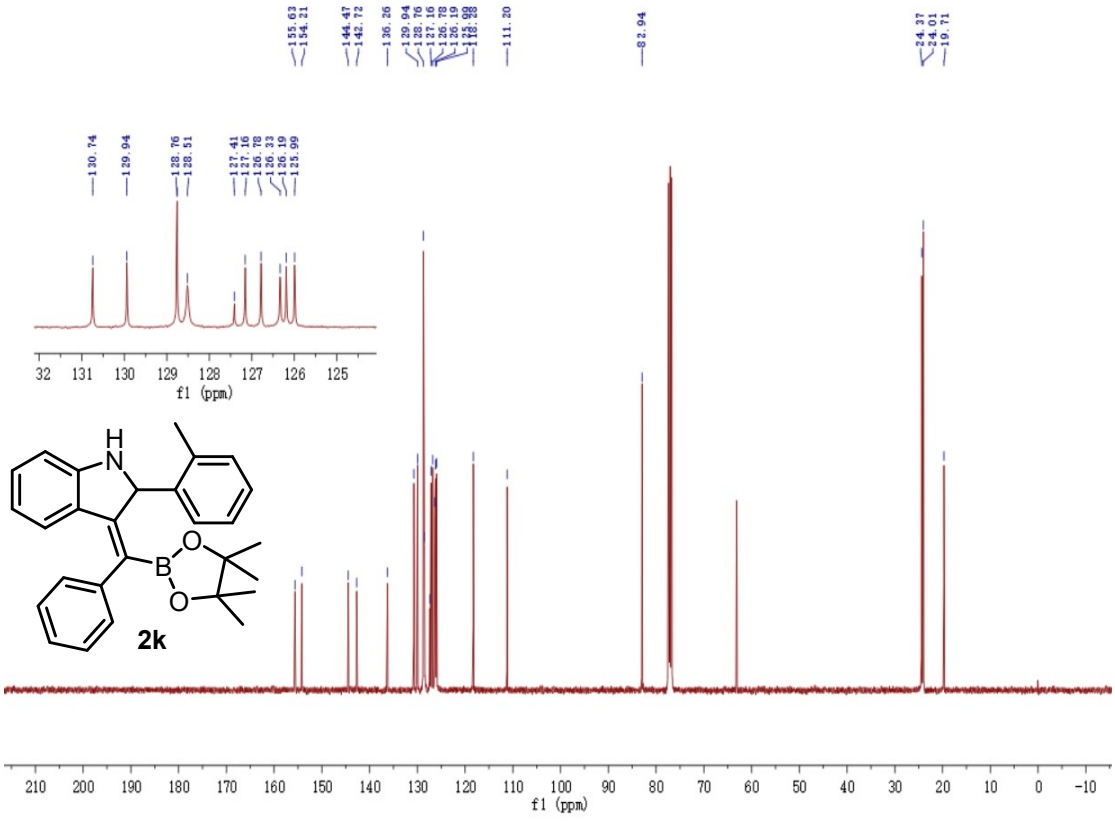
^{13}C NMR Spectra of **2j** (100 MHz, $CDCl_3$)



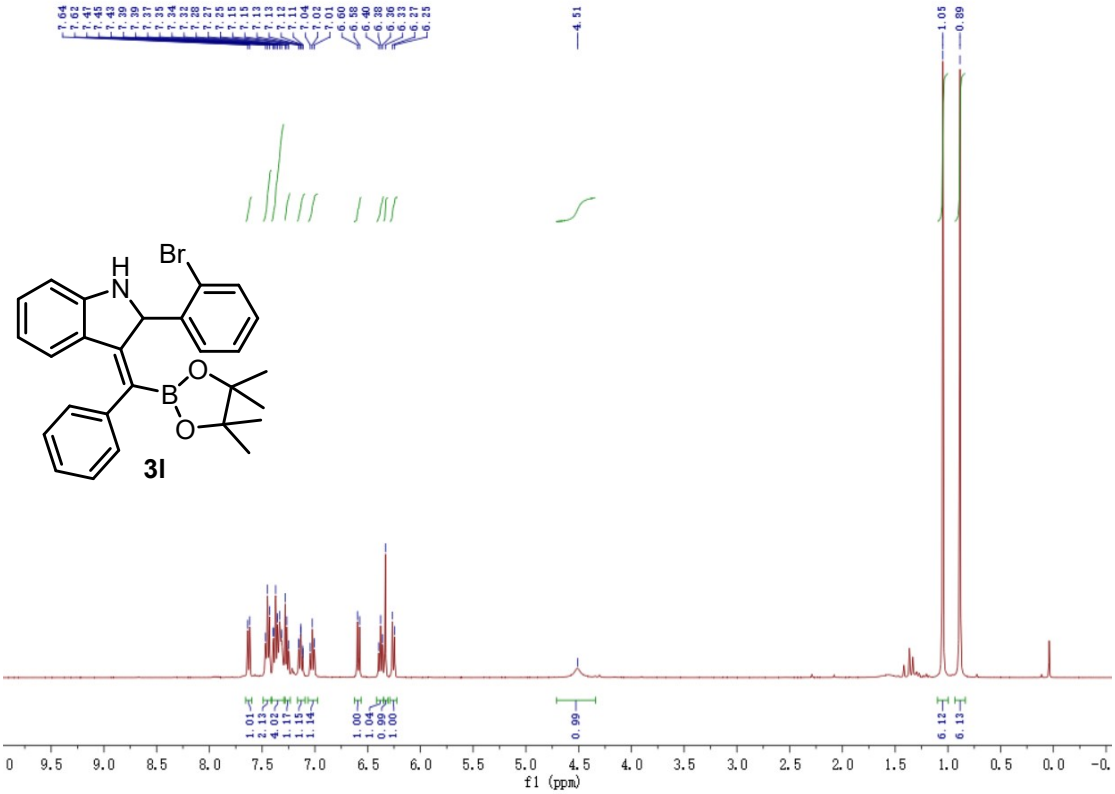
^{1}H NMR Spectra of **2k** (400 MHz, $CDCl_3$)



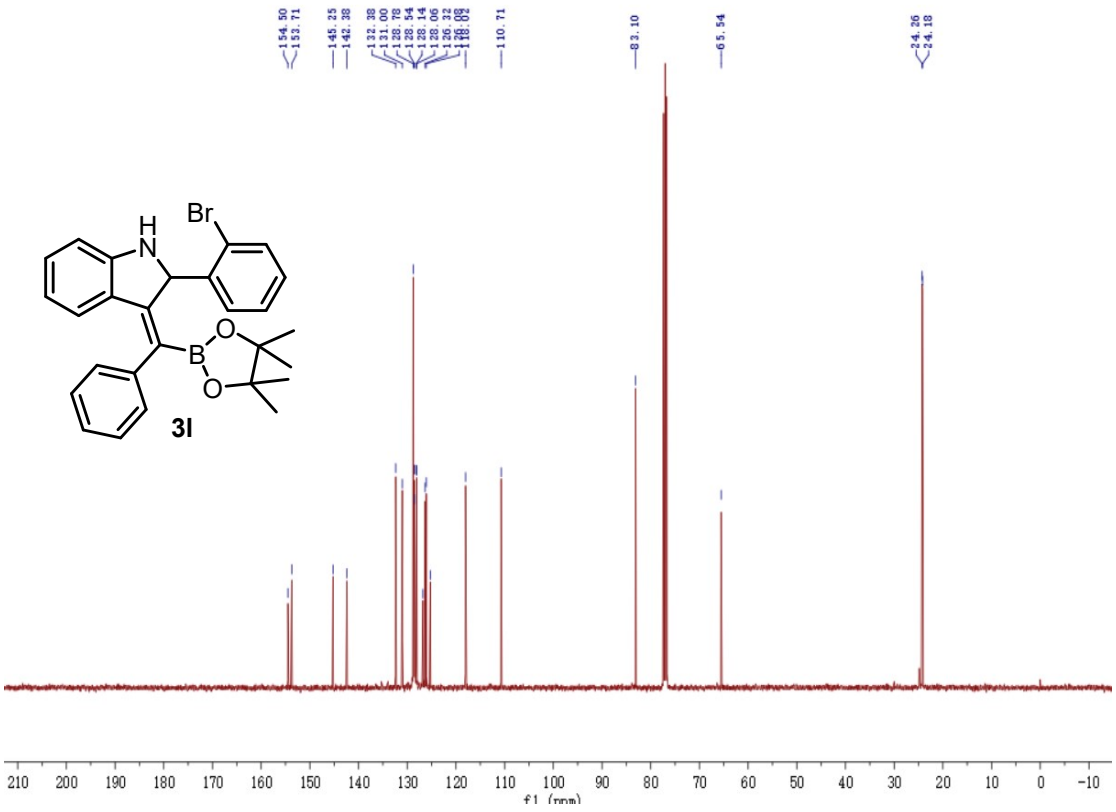
^{13}C NMR Spectra of **2k** (100 MHz, $CDCl_3$)



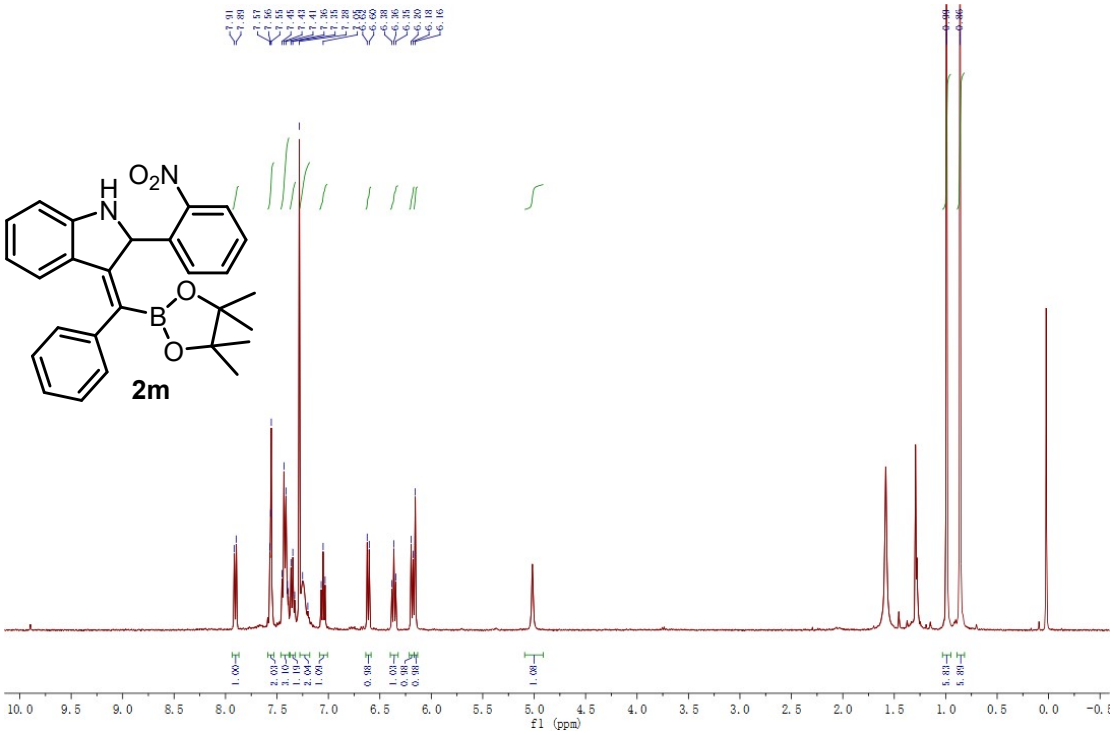
^{1}H NMR Spectra of **2l** (400 MHz, $CDCl_3$)



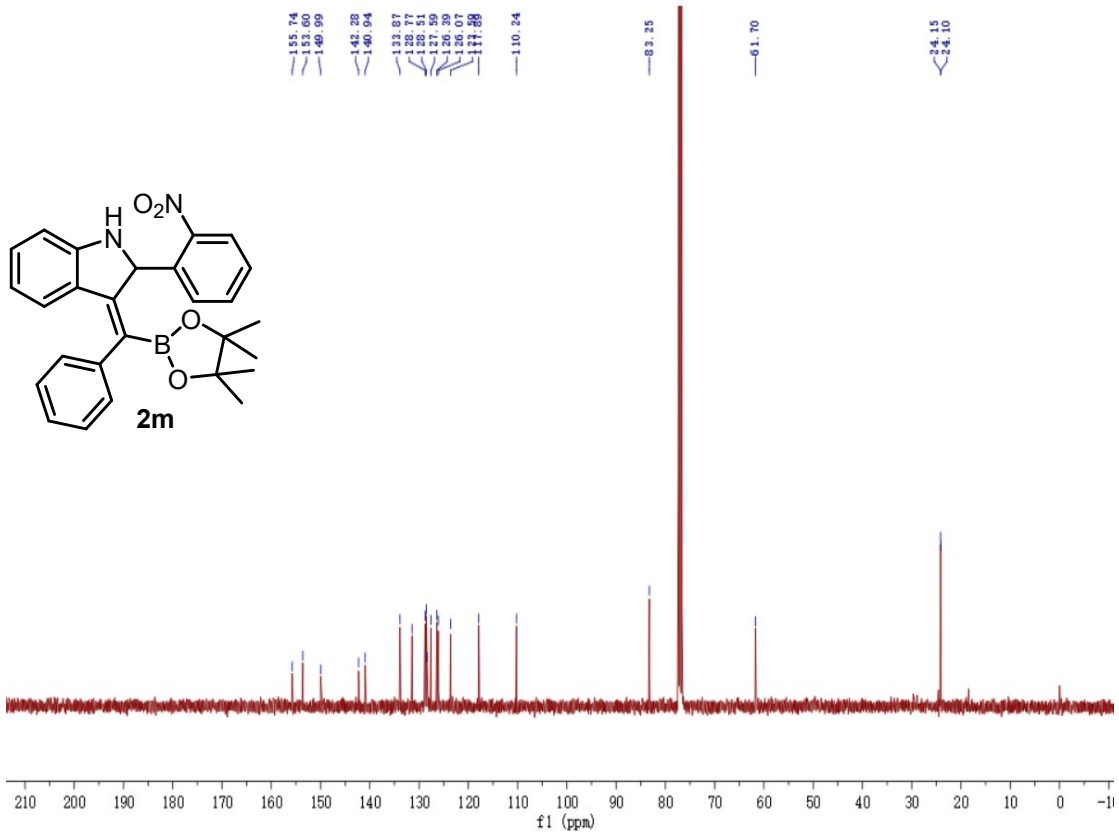
^{13}C NMR Spectra of **2l** (100 MHz, $CDCl_3$)



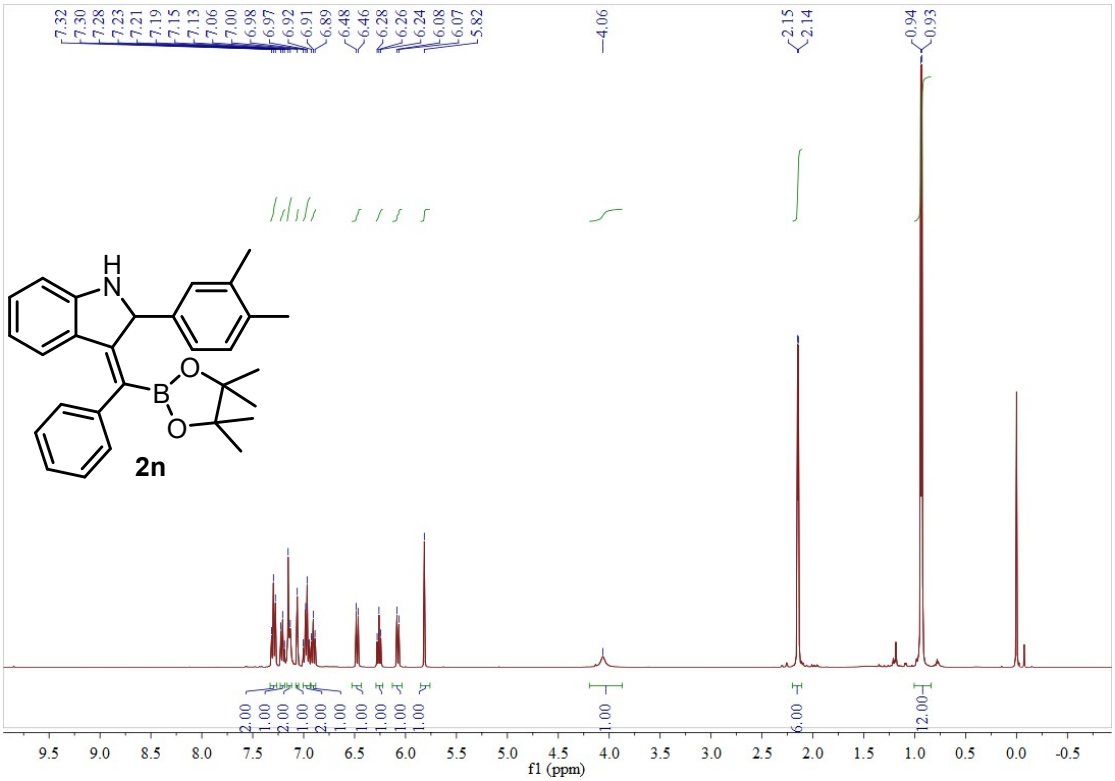
^{1}H NMR Spectra of **2m** (400 MHz, $CDCl_3$)



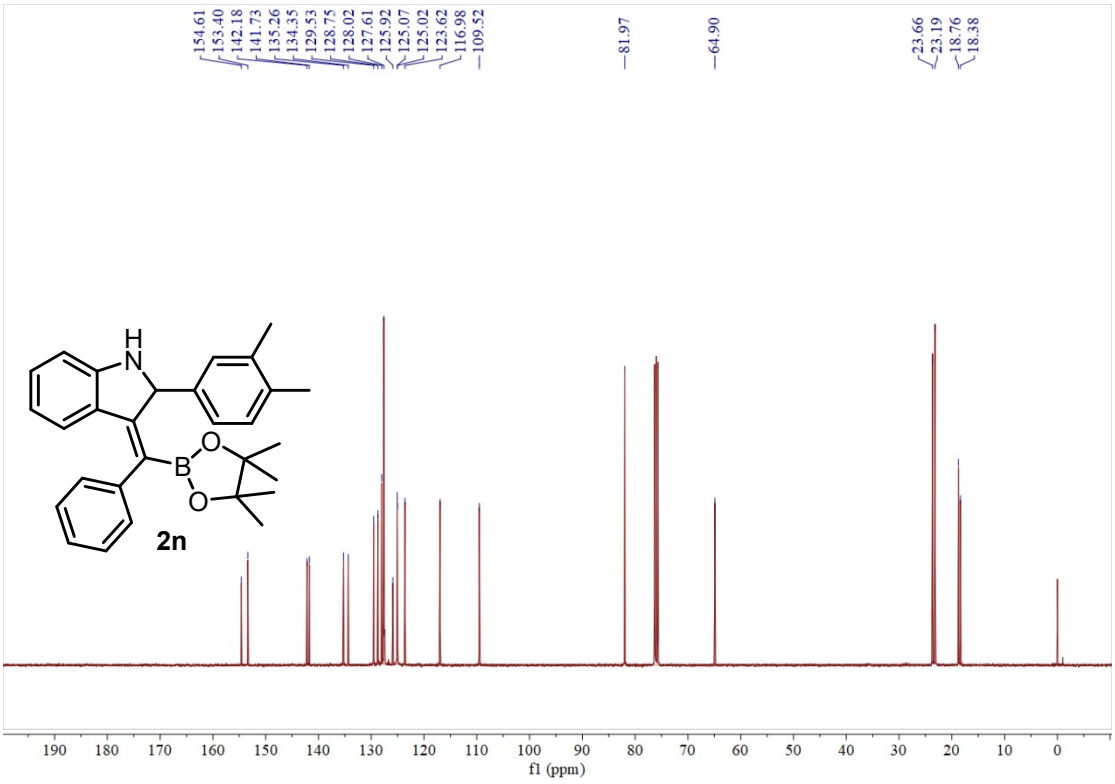
^{13}C NMR Spectra of **2m** (100 MHz, $CDCl_3$)



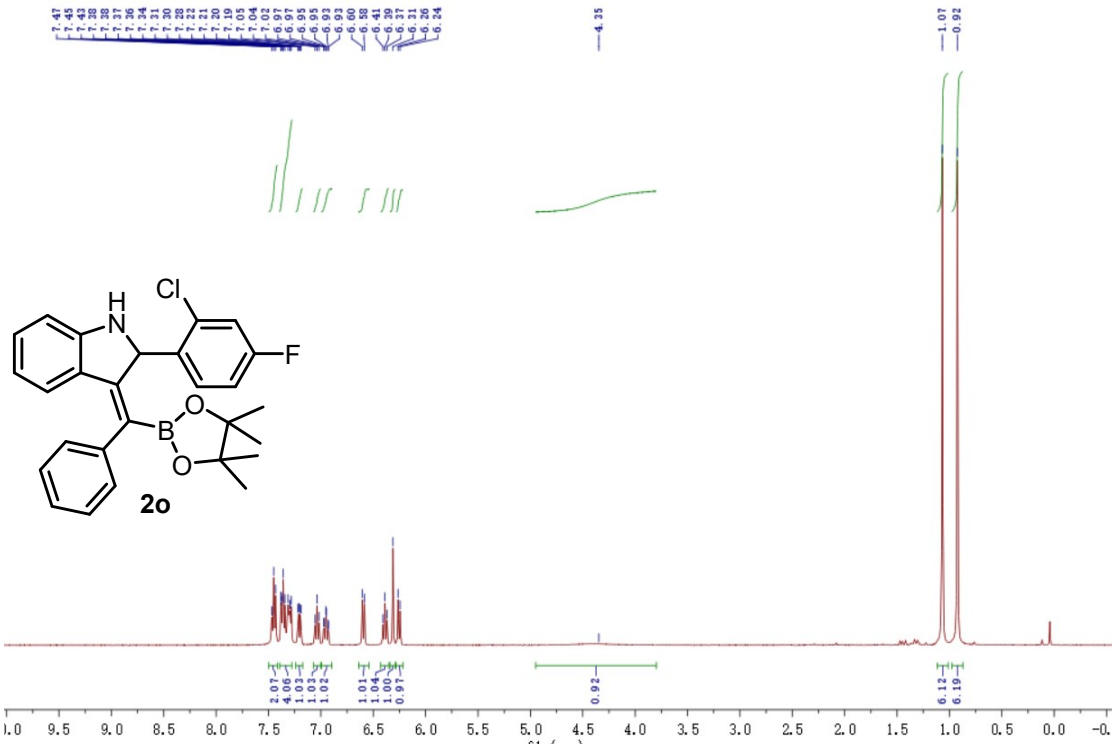
^{1}H NMR Spectra of **2n** (400 MHz, $CDCl_3$).



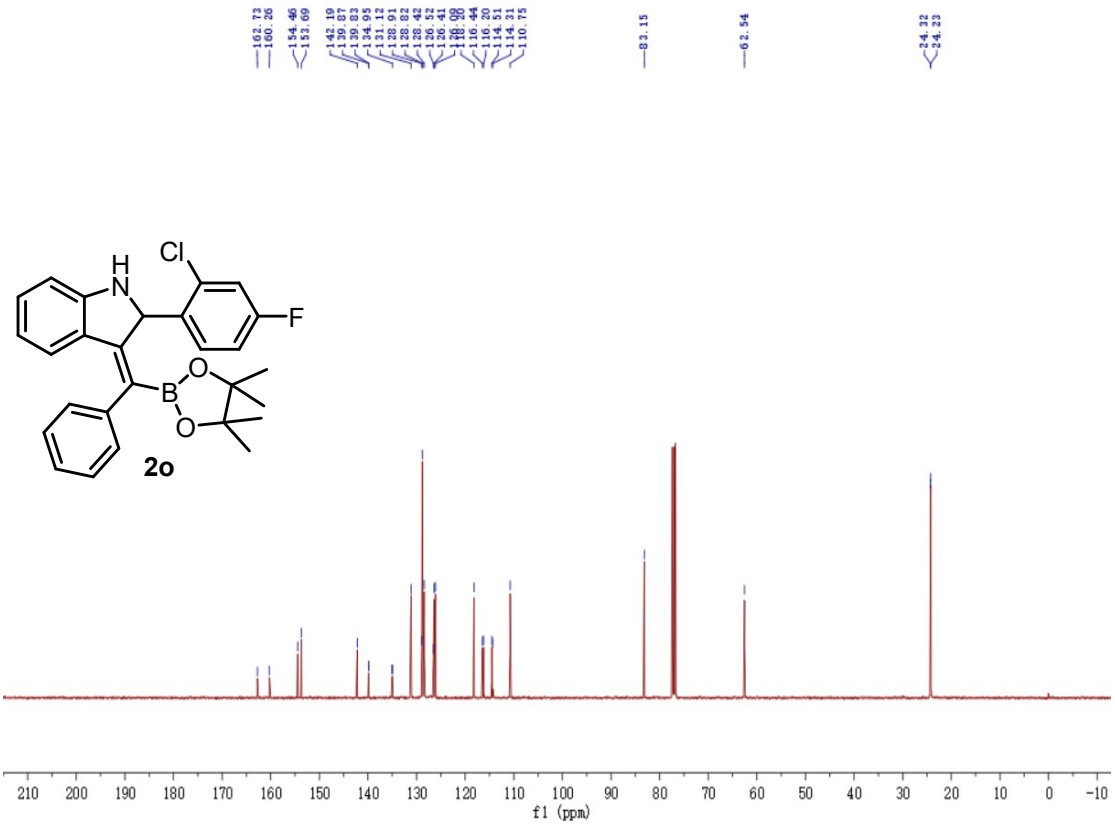
^{13}C NMR Spectra of **2n** (100 MHz, $CDCl_3$)



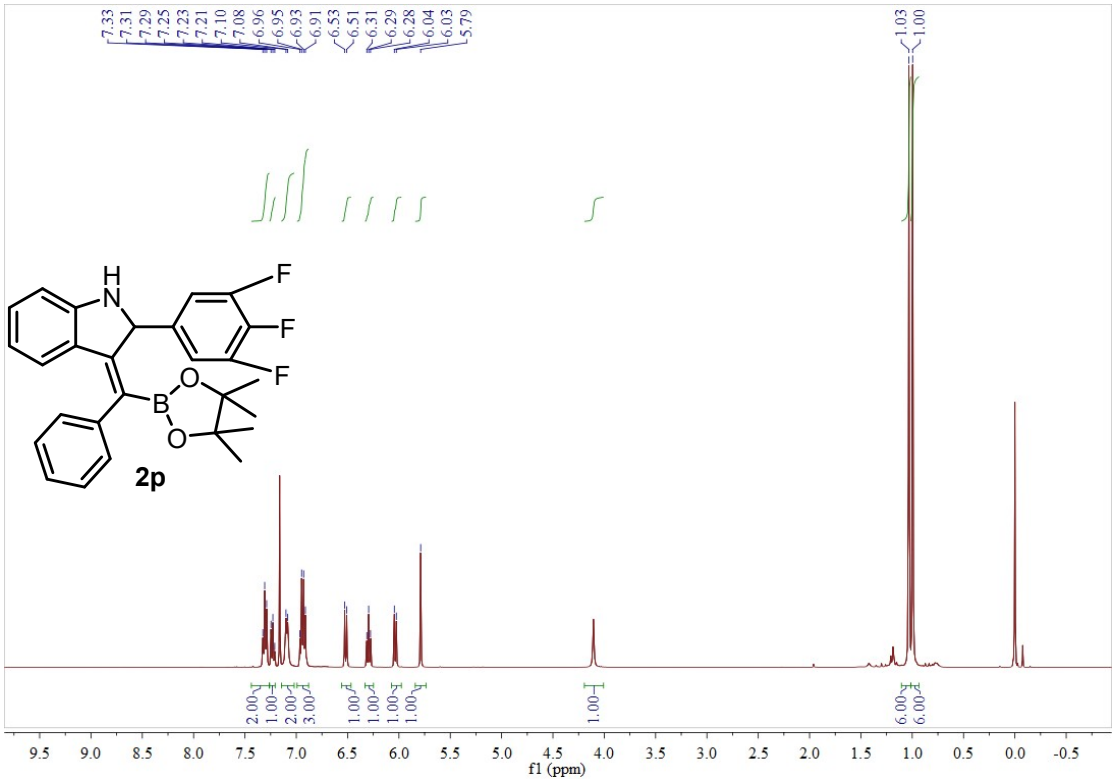
^{1}H NMR Spectra of **2o** (400 MHz, $CDCl_3$)



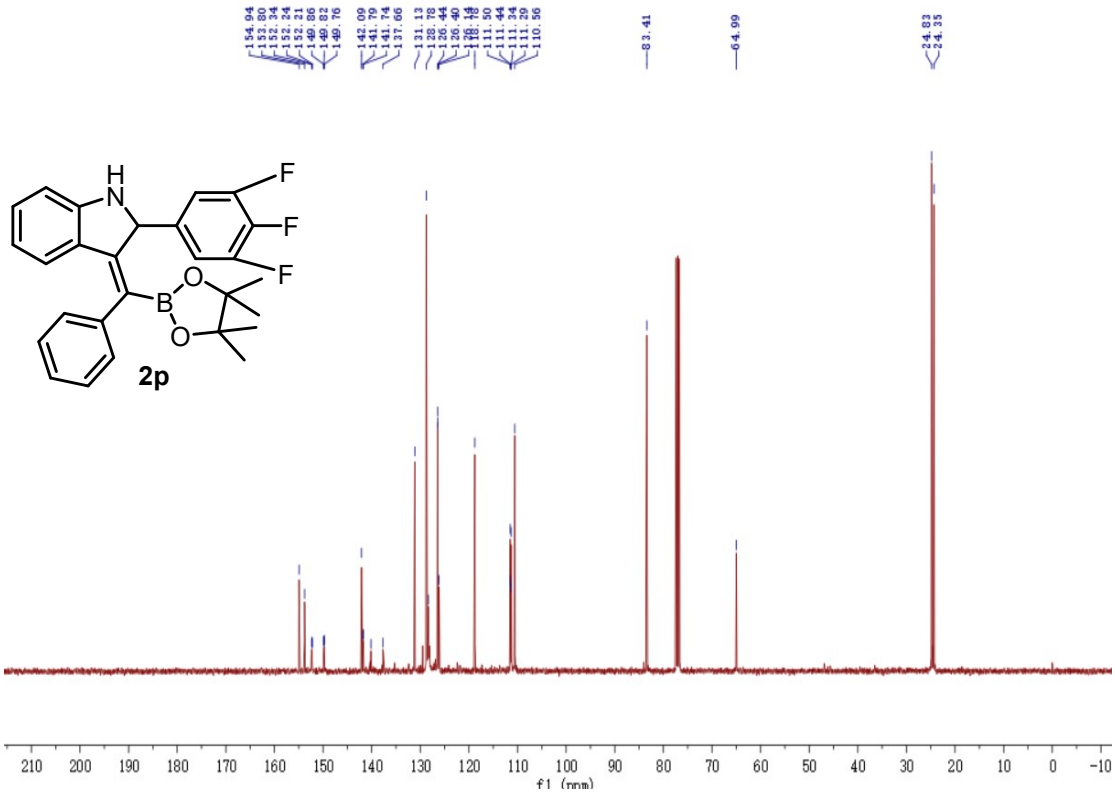
^{13}C NMR Spectra of **2o** (100 MHz, $CDCl_3$)



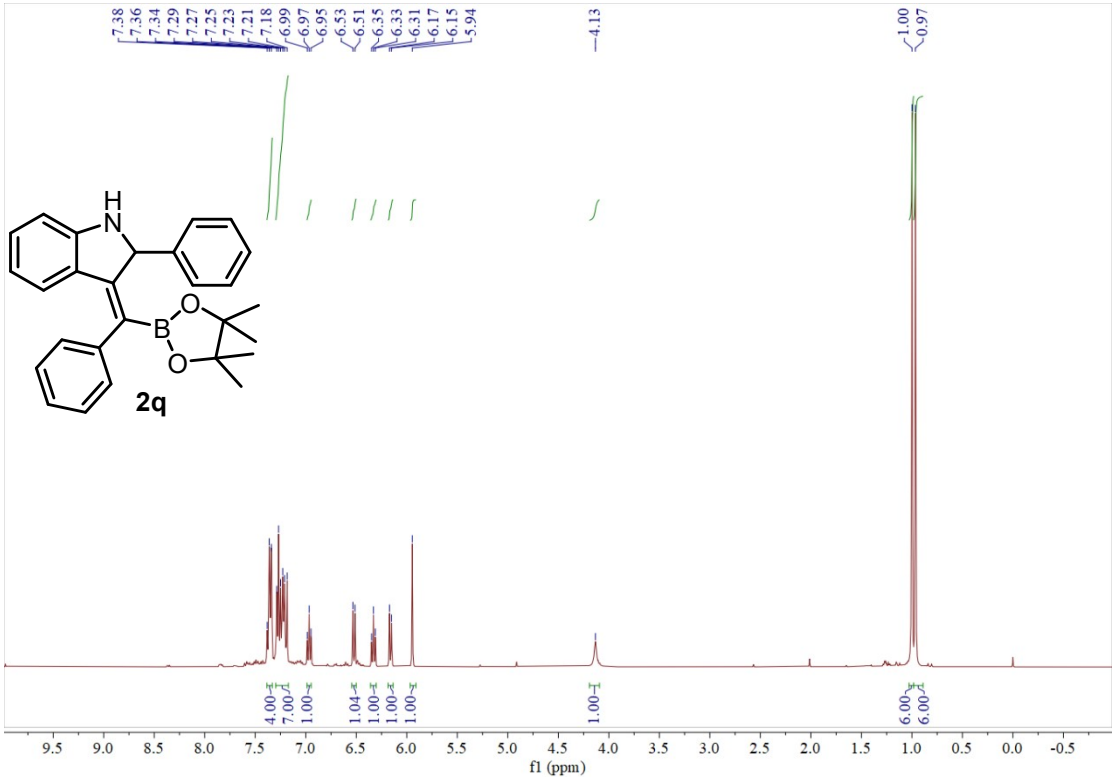
^{1}H NMR Spectra of **2p** (400 MHz, $CDCl_3$)



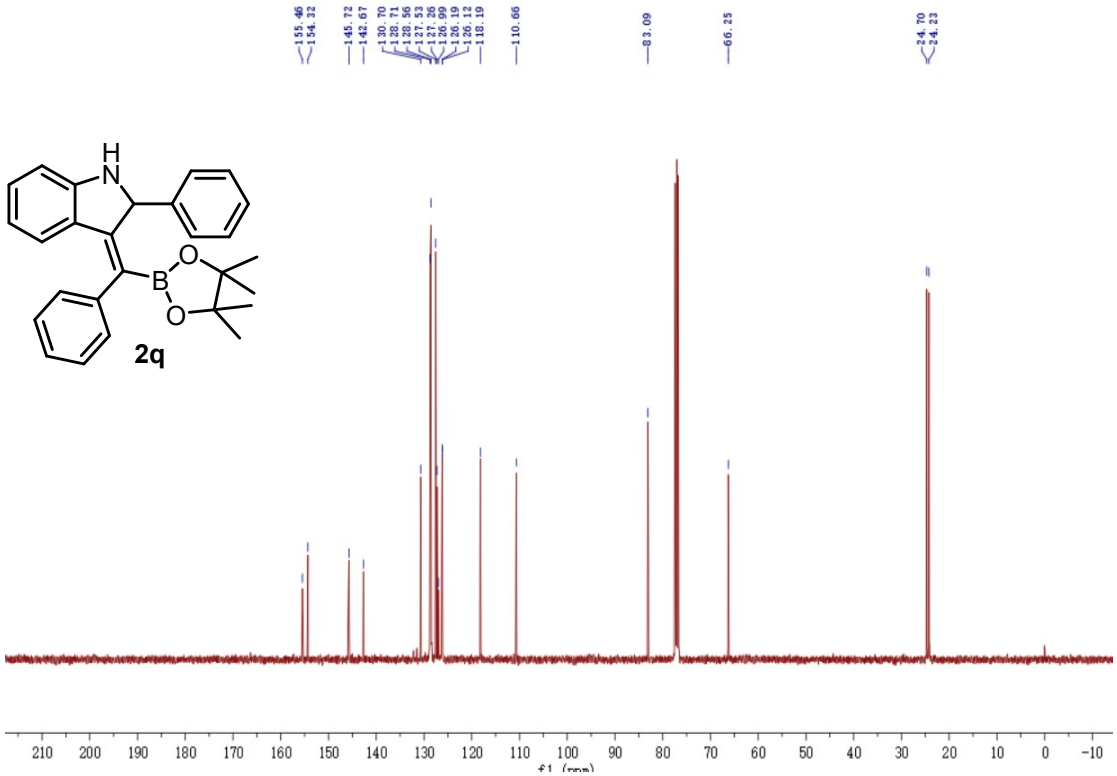
^{13}C NMR Spectra of **2p** (100 MHz, $CDCl_3$)



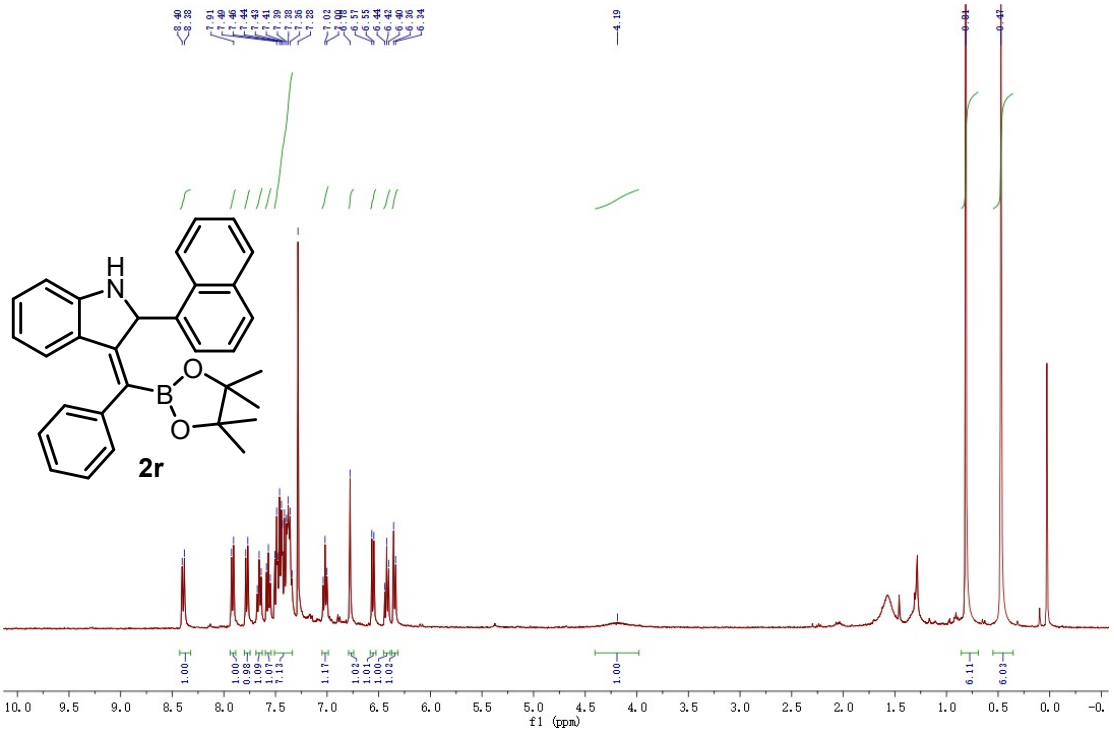
^{1}H NMR Spectra of **2q** (400 MHz, $CDCl_3$)



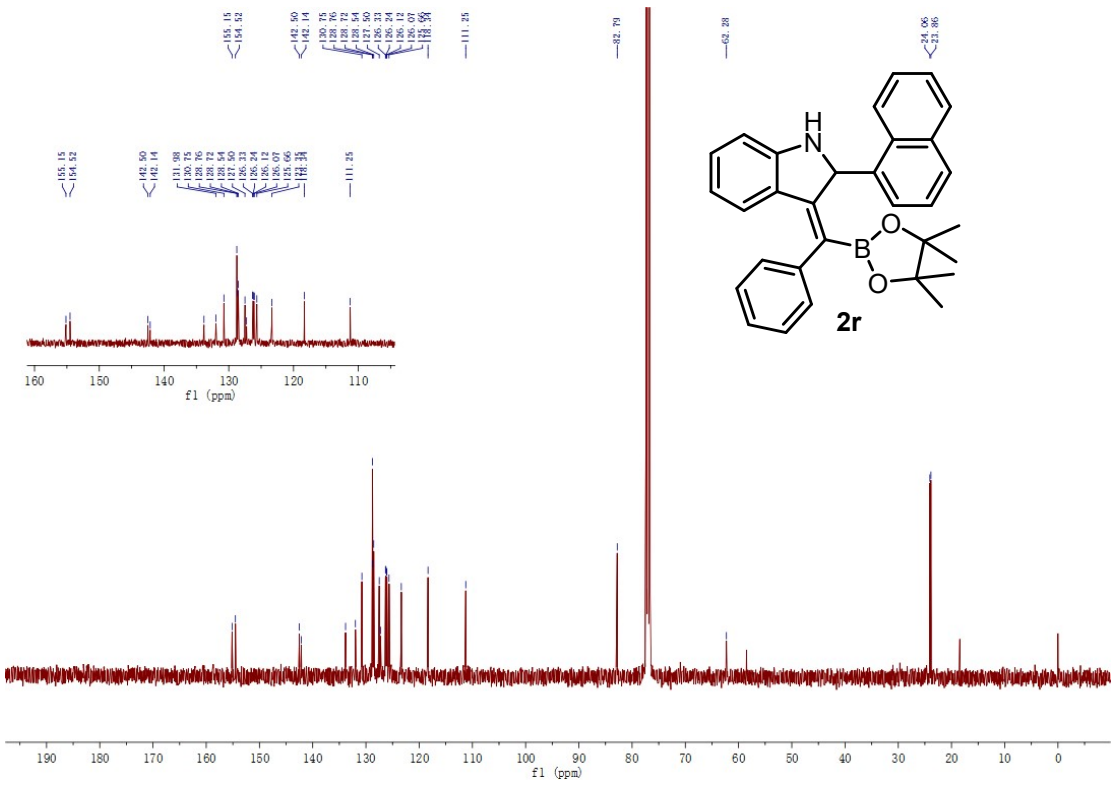
^{13}C NMR Spectra of **2q** (100 MHz, $CDCl_3$)



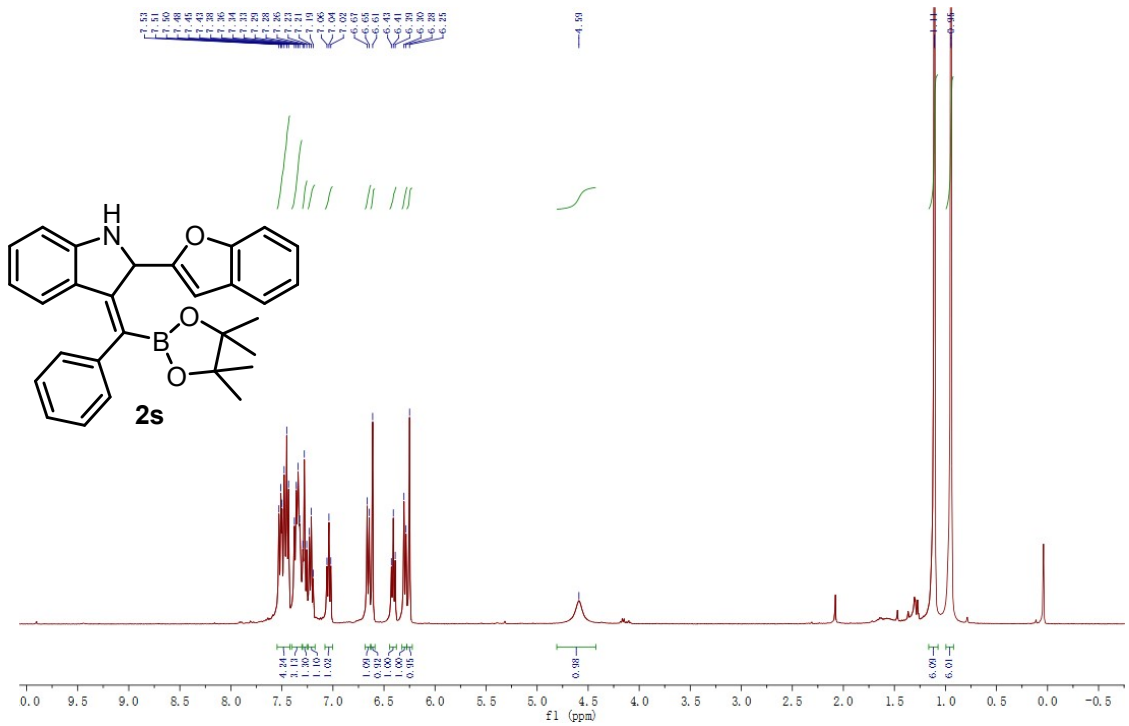
^{1}H NMR Spectra of **2r** (400 MHz, $CDCl_3$)



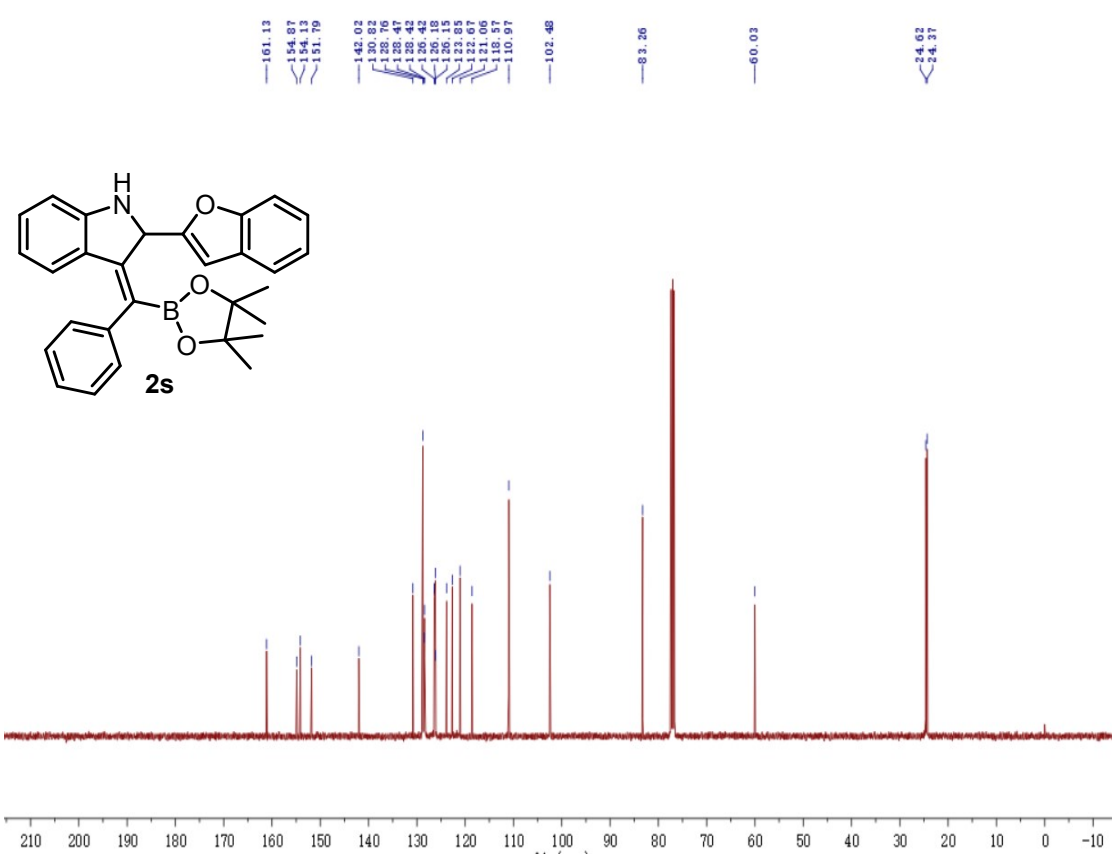
^{13}C NMR Spectra of **2r** (100 MHz, $CDCl_3$)



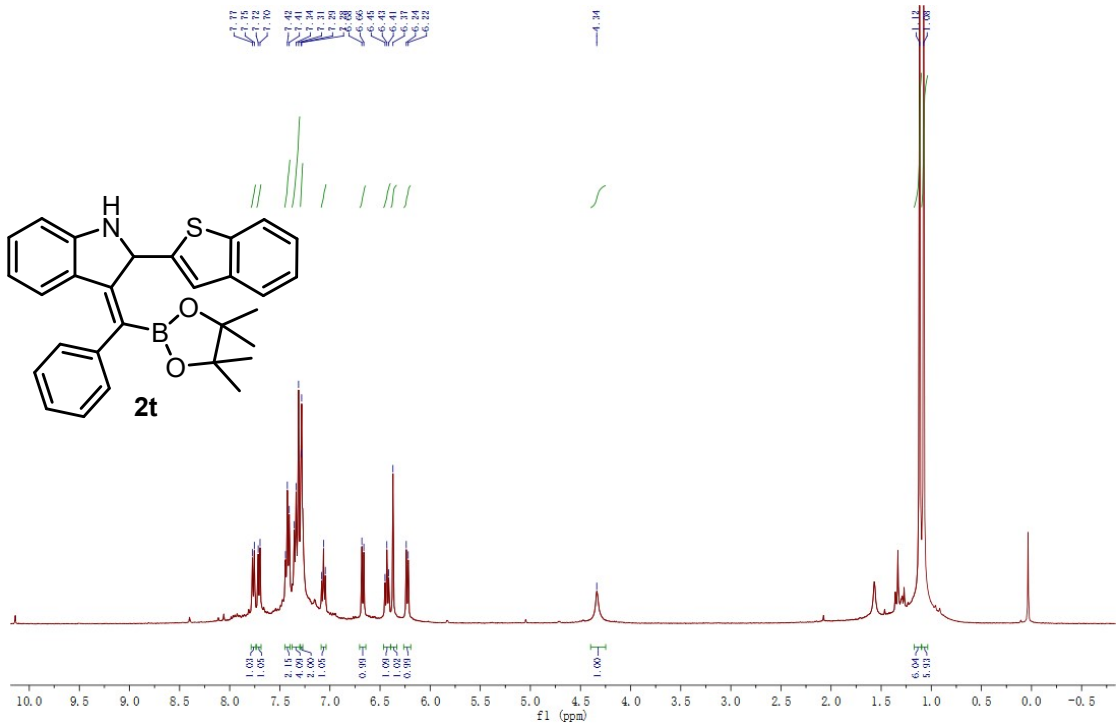
^{1}H NMR Spectra of **2s** (400 MHz, $CDCl_3$)



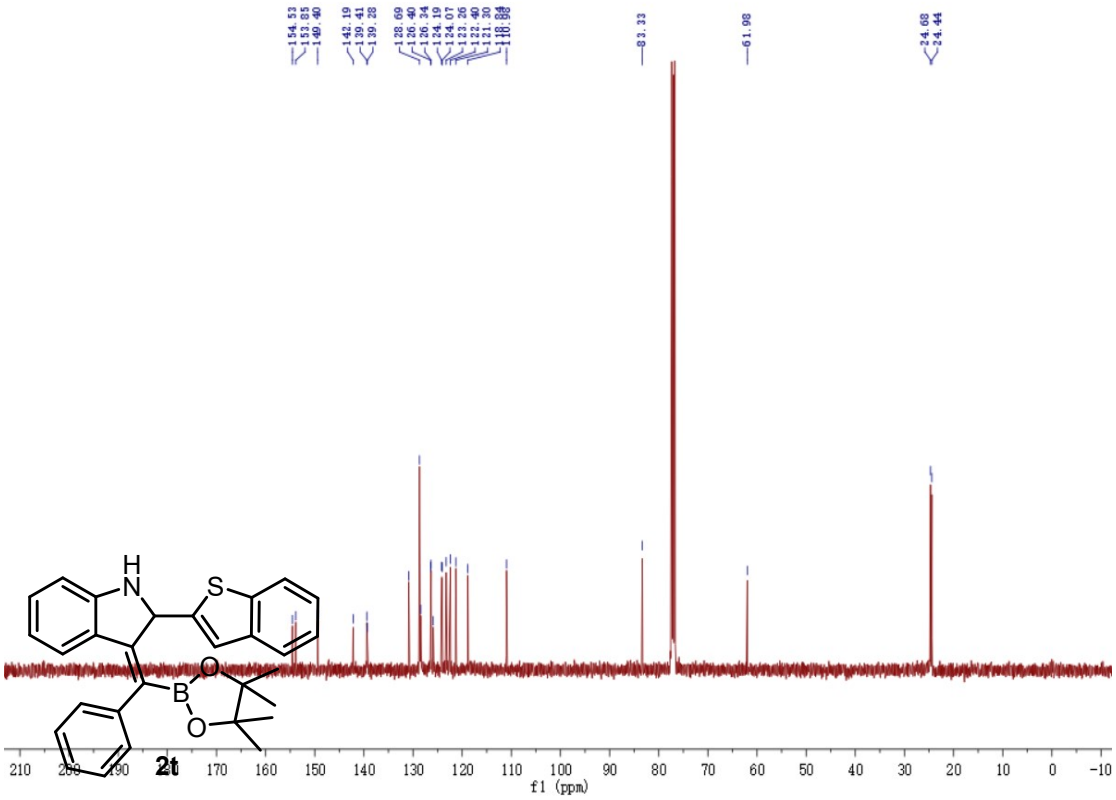
^{13}C NMR Spectra of **2s** (100 MHz, $CDCl_3$)



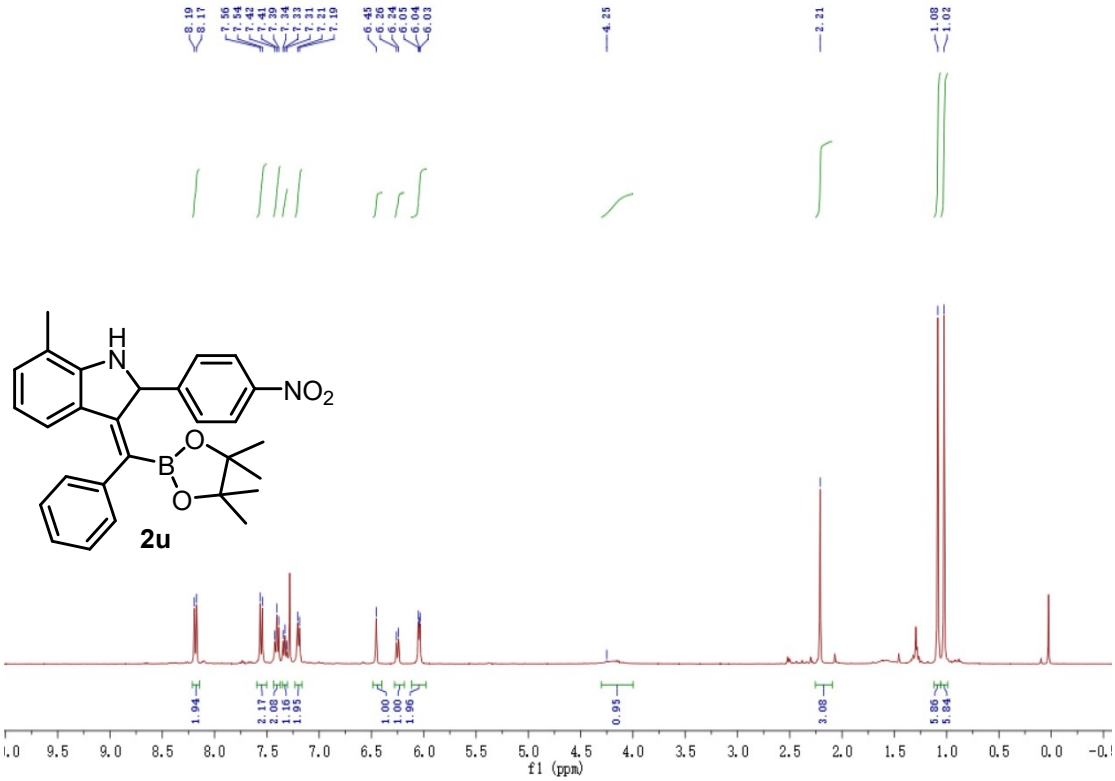
^{1}H NMR Spectra of **2t** (400 MHz, $CDCl_3$)



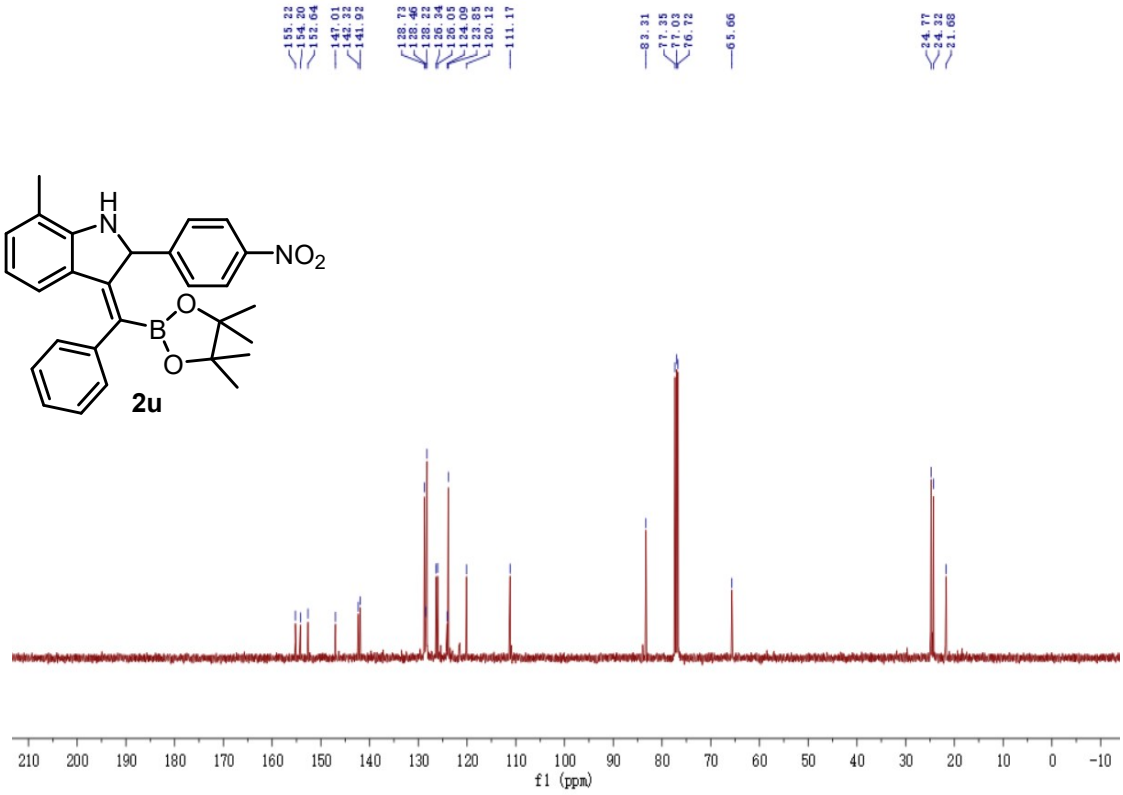
^{13}C NMR Spectra of **2t** (100 MHz, $CDCl_3$)



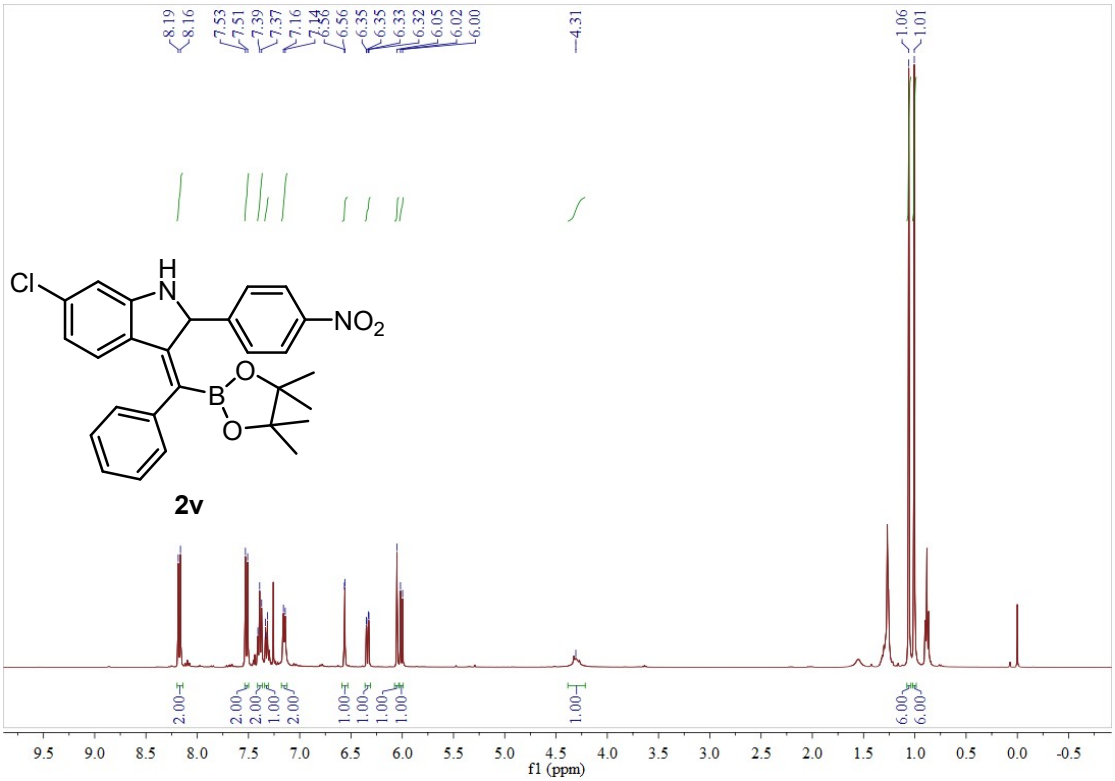
^{1}H NMR Spectra of **2u** (400 MHz, $CDCl_3$)



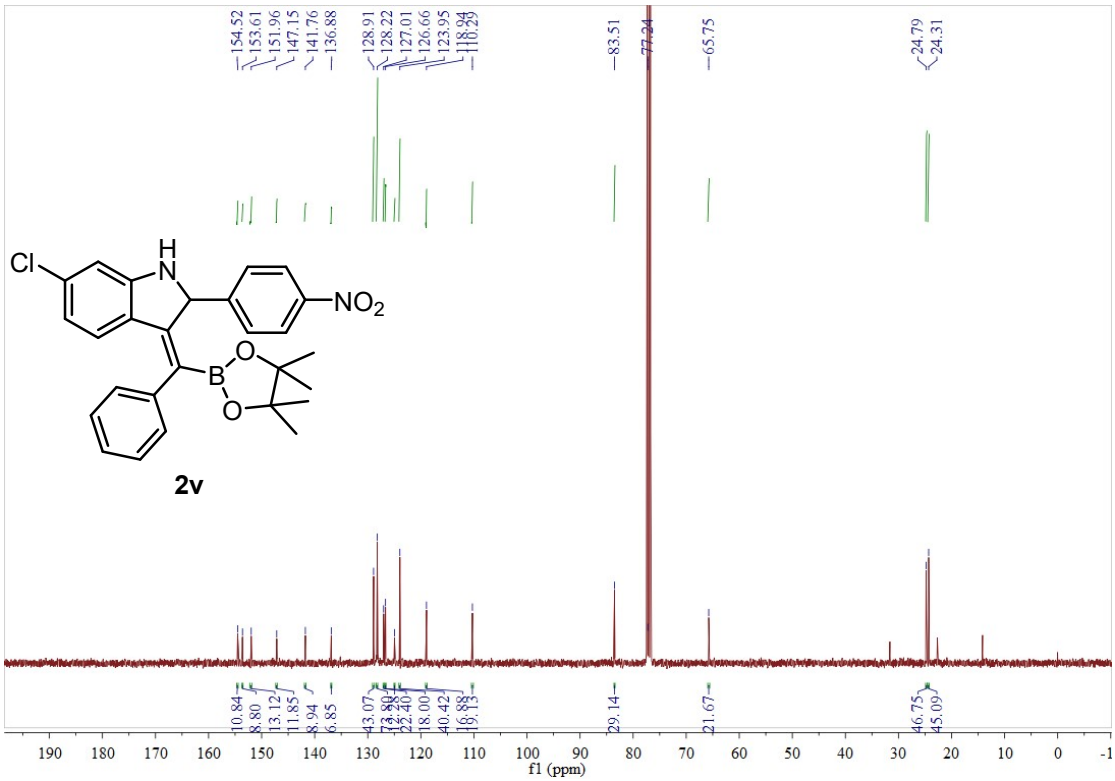
^{13}C NMR Spectra of **2u** (100 MHz, $CDCl_3$)



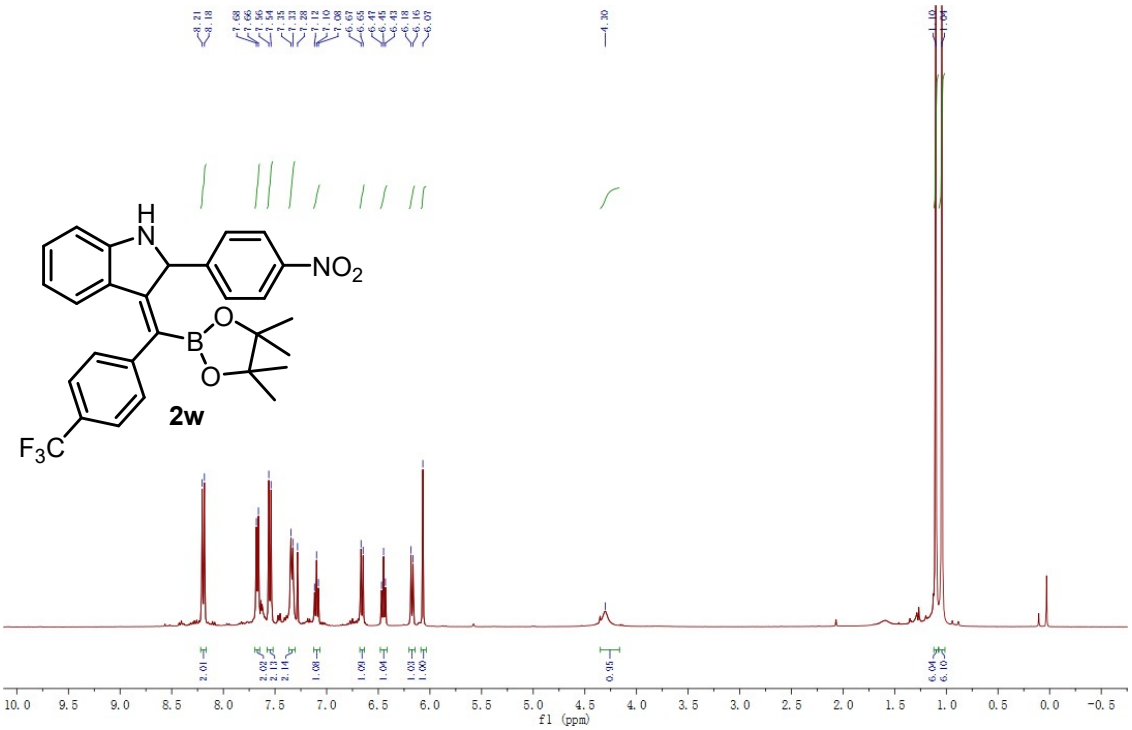
^{1}H NMR Spectra of **2v** (400 MHz, $CDCl_3$)



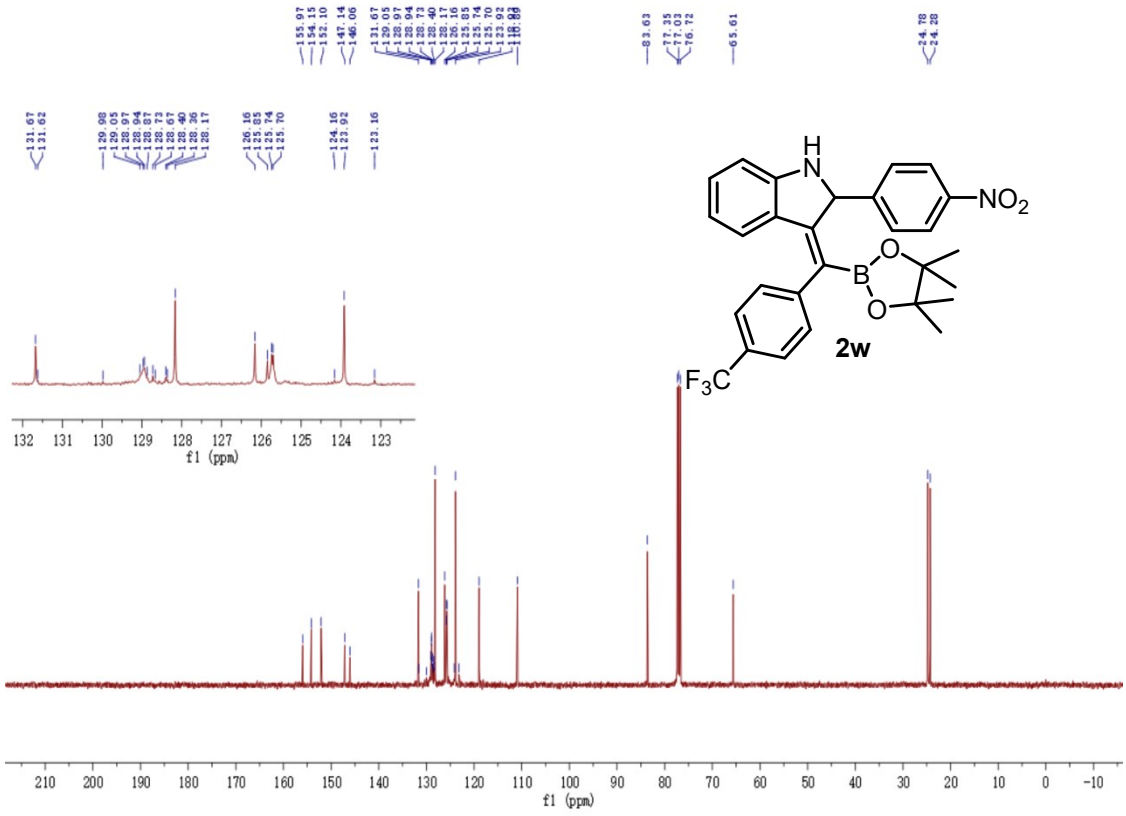
^{13}C NMR Spectra of **2v** (100 MHz, $CDCl_3$)



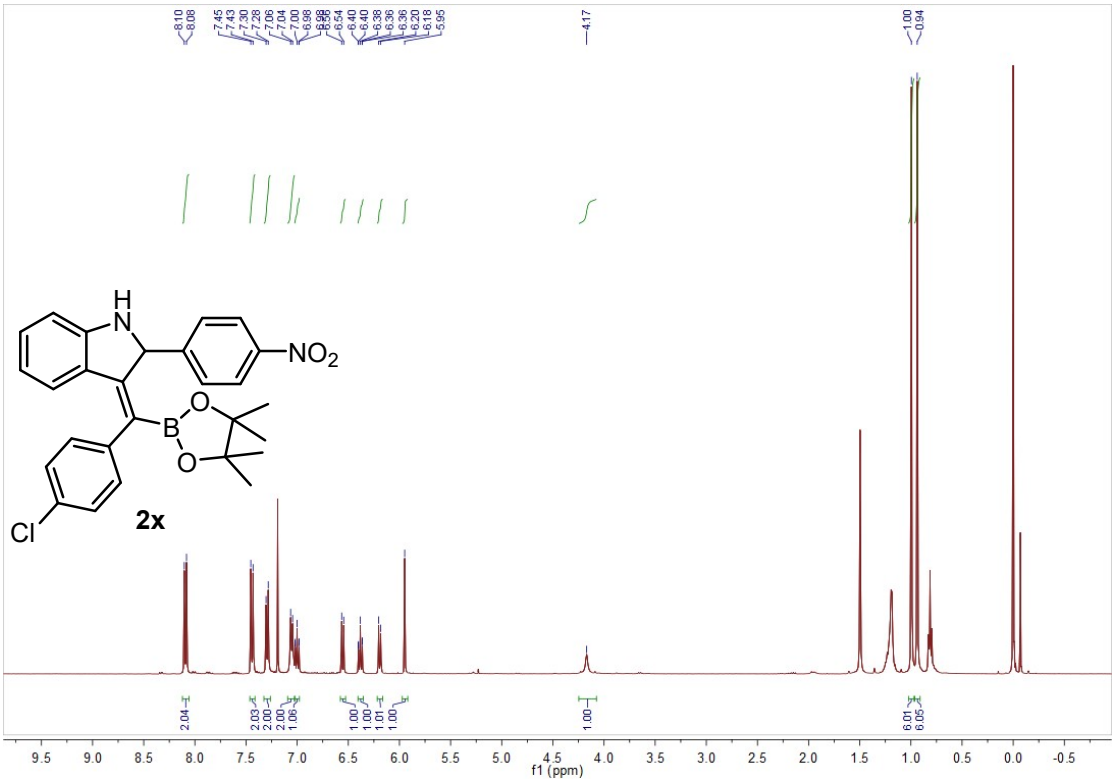
^{1}H NMR Spectra of **2w** (400 MHz, $CDCl_3$)

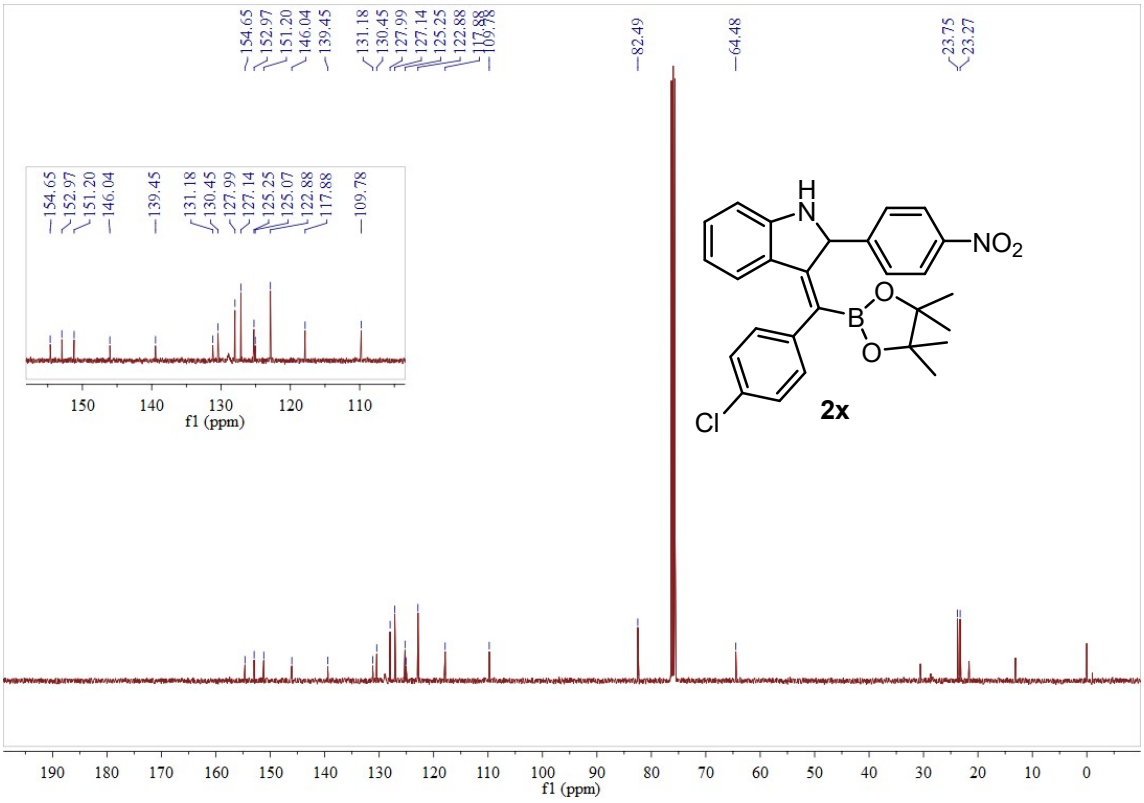


^{13}C NMR Spectra of **2w** (100 MHz, $CDCl_3$)



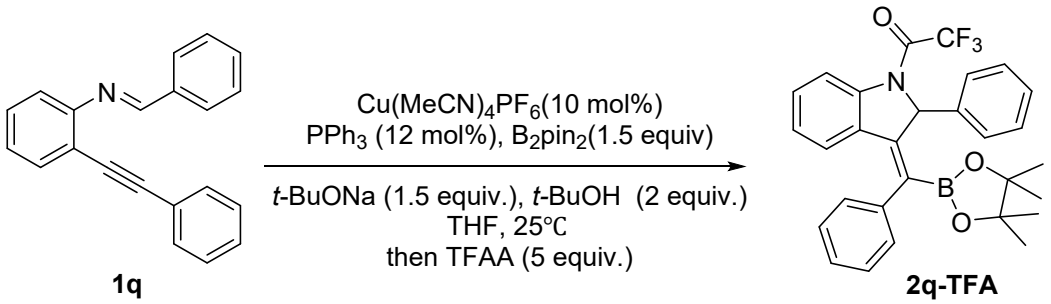
^{1}H NMR Spectra of **2x** (400 MHz, $CDCl_3$)





^{13}C NMR Spectra of **2x** (100 MHz, $CDCl_3$)

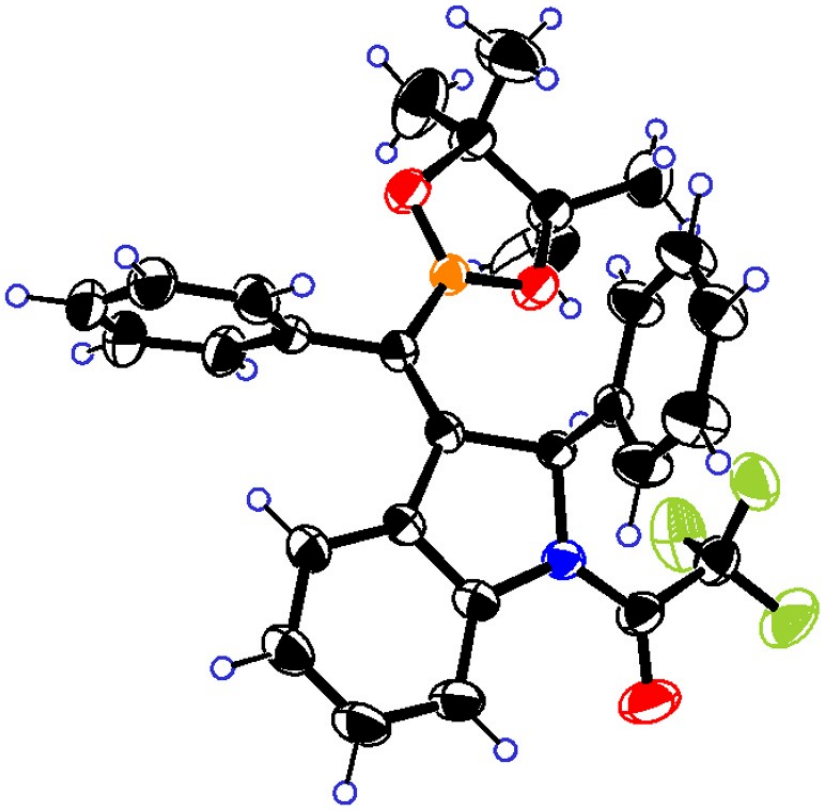
7. Single-crystal X-ray Diffraction Studies



1q **2q-TFA**

In an argon atmosphere, **1q** (0.1 mmol, 1.0 equiv.) was added to a solution of B_2pin_2 (0.15 mmol, 38 mg), $Cu(MeCN)_4PF_6$ (0.01 mmol, 4 mg), PPh_3 (0.012 mmol, 3 mg), *t*-BuONa (0.15 mmol, 15 mg), *t*-BuOH (0.2 mmol, 19 μL) in THF (2 mL). The reaction was stirred at room temperature and monitored by TLC. After the reaction was completed, trifluoroacetic anhydride (TFAA) (0.5 mmol, 69 μL) was added to the reaction system. After stirring at room temperature for 5 minutes, the resulting mixture was extract with EtOAc twice. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford **2q-TFA**.

The structure of **2q-TFA** was determined by the X-ray diffraction analysis of single crystal, which recrystallized from a mixed solution of CH_2Cl_2 and hexane. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre.



ORTEP of **2q-TFA** (CCDC: 2415602)
(Thermal probability ellipsoids shown at the 40% probability level)

Table S1 Crystal data and structure refinement for 2q-TFA.

Identification code	**2q-TFA**
Empirical formula	$C_{29}H_{27}BF_3NO_3$
Formula weight	505.32
Temperature/K	291.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.9881(4)
b/Å	13.1835(4)
c/Å	14.3886(4)
α/°	90
β/°	104.046(2)
γ/°	90
Volume/Å^3	2574.10(13)
Z	4
ρ_{calc}g/cm^3	1.304
μ/mm^{-1}	0.815
F(000)	1056.0
Crystal size/mm^3	0.3 × 0.22 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.908 to 136.558
Index ranges	$-16 \leq h \leq 16$, $-15 \leq k \leq 13$, $-17 \leq l \leq 16$
Reflections collected	34191

Independent reflections	4642 [R_{int} = 0.0829, R_{sigma} = 0.0532]
Data/restraints/parameters	4642/0/338
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0715, wR_2 = 0.1778
Final R indexes [all data]	R_1 = 0.0815, wR_2 = 0.1882
Largest diff. peak/hole / e $Å^{-3}$	0.43/-0.39

8. References

1. L. Ferrand, Y. Lyu, A. Rivera-Hernández, B. J. Fallon, M. Amatore, C. Aubert and M. Petit, *Synthesis*, 2017, **49**, 3895−3904.
2. W. Ming, X. Liu, A. Friedrich, J. Krebs and T. B. Marder, *Org. Lett.* 2020, **22**, 365−370.
3. S. Perrone, A. Salomone, A. Caroli, A. Falcicchio, C. Citti, G. Cannazza and L. Troisi, *Eur. J. Org. Chem.* 2014, **2014**, 5932−5938.