Palladium-Catalyzed Direct Arylation of Indoles with Arylsulfonyl Hydrazides

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Supporting Information

Table of Contents

General Information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 FT spectrometer at 400 MHz and 100 MHz, respectively, with tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). ESI-MS data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software. Melting points were uncorrected.

1c-l were prepared according to the literature procedure.[1] Chemicals were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros and Alfa Aesar, and used as received.

Preparation of Arylsulfonyl Hydrazides

Hydrazine monohydrate (500 mg, 10.0 mmol) was added dropwise to a solution of an arylsulfonyl chloride (4.0 mmol) in tetrahyrdofuran (20 mL) under nitrogen at 0 °C. During the addition the mixture became brown and a white precipitate of hydrazine hydrochloride was deposited. The mixture was stirred at 0 °C for 30 min, added ethyl acetate (1200 mL), and washed with saturated brine (3 x 20 mL). The organic layer was dried over sodium sulfate, filtered, and added slowly to stirred hexane (25 mL) over 5 min. After being stirred for 10 min, the mixture was filtered, and the collected solid was dried in vacuum. The yields for the formation of arylsulfonyl hydrazides range from 66% to 90%.

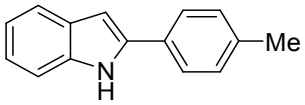
General Procedure for The Direct Arylation of Indoles with Arylsulfonyl Hydrazides

To a solution of indole **1** (0.20 mmol) in dimethyl sulfoxide (1.0 mL) under oxygen (1 atm) at room temperature were added arylsulfonyl hydrazide **2** (0.24 mmol), TfOH (36.0 mg, 0.24mmol) and $Pd(OAc)_2$ (2.2 mg, 0.010 mmol). The mixture was stirred at 70 ^{o}C for 20 h, cooled to room temperature, and directly purified by preparative thin layer chromatography on silica gel, developing with petroleum ether/ethyl acetate (100:1 to 20:1), to give compound **3**.

Procedure for The Control Reaction

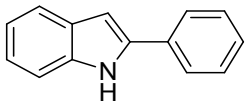
To a solution of indole **1a** (23.4 mg, 0.20 mmol) in dimethyl sulfoxide (1.0 mL) under oxygen (1 atm) at room temperature were added *p*-tolenesulfonyl hydrazide **2a** (44.6 mg, 0.24 mmol), TEMPO (31.2 mg, 0.20 mmol), TfOH (36.0 mg, 0.24 mmol) and $Pd(OAc)_2$ (2.2 mg, 0.010 mmol). The mixture was stirred at 70 ^{o}C for 20 h, cooled to room temperature, and directly purified by preparative thin layer chromatography on silica gel, developing with petroleum ether/ethyl acetate (100:1), to give compound **3aa** in 86% yield.

Analytical Data for The Products Shown in Tables 2 and 3



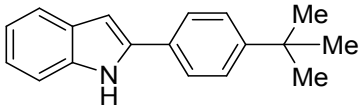
3aa

3aa,[2] white solid, m.p. 214-216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, br, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 1H), 7.23-7.08 (m, 4H), 6.82 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 138.1, 137.7, 136.7, 129.7, 129.6, 129.4, 125.1, 122.1, 120.6, 120.2, 110.9, 99.4, 21.3.



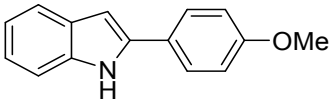
3ab

3ab, [2] white solid, m.p. 186-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, br, 1H), 7.68-7.62 (m, 3H), 7.45-7.41 (m, 3H), 7.34-7.29 (m, 1H), 7.23-7.17 (m, 2H), 6.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 137.9, 136.8, 132.4, 129.3, 129.0, 127.7, 125.2, 122.4, 120.7, 120.3, 110.9, 100.0.



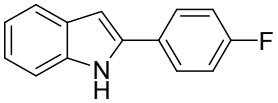
3ac

3ac, white solid, m.p. 251-253 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, br, 1H), 7.63-7.55 (m, 3H), 7.46 (d, J = 7.6 Hz, 2H), 7.39 (d, J = 8.0 Hz, 1H), 7.20-7.15 (m, 1H), 7.13-7.09 (m, 1H), 6.79 (s, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 150.9, 136.7, 129.6, 129.4, 126.0, 124.9, 122.1, 120.5, 120.2, 110.8, 99.5, 34.7, 31.3; HRMS (EI) calcd for $C_{18}H_{19}N$ (M) 249.1517, found 249.1530.



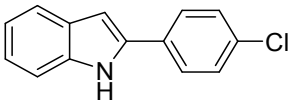
3ad

3ad, [2] white solid, m.p. 225-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, br, 1H), 7.61 (d, J = 8.0 Hz, 3H), 7.38 (d, J = 7.6 Hz, 1H), 7.18-7.08 (m, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.71 (s, 1H), 3.86 (s. 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.3, 137.8, 136.6, 129.3, 128.5, 126.4, 125.1, 121.8, 120.3, 120.1, 114.4, 110.6, 98.7, 55.3.



3ae

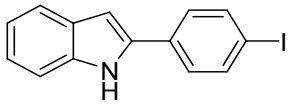
3ae, [2] white solid, m.p. 185-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, br, 1H), 7.66-7.57 (m, 3H), 7.37 (d, J = 8.4 Hz, 1H), 7.21-7.09 (m, 1H), 7.24-7.01 (m, 3H), 6.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.4 (d, J = 246 Hz), 137.0, 129.2, 126.9 (d, J = 8.1), 122.4, 120.4, 116.0 (d, J = 21.7), 110.9, 99.9.



3af

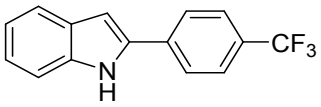
3af, [2] white solid, m.p. 204-205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, br, 1H), 7.63-7.54 (m, 3H), 7.40-7.30 (m, 3H), 7.24-7.12 (m, 2H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 136.9, 136.7, 133.4, 130.9, 129.2, 126.3, 122.7, 120.8, 120.5, 110.9,

100.5.



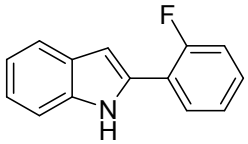
3ag

3ag, [2] white solid, m.p. 220-222 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, br, 1H), 7.74 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 8.0 Hz, 3H), 7.20-7.19 (m, 1H), 7.14-7.08 (m, 1H), 6.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 139.5, 137.5, 136.5, 130.8, 128.8, 127.6, 123.2, 121.1, 119.5, 111.7, 102.1.



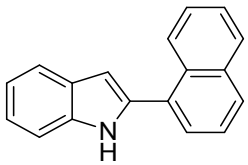
3ah

3ah, [2] white solid, m.p. 240-241 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, br, 1H), 7.78-7.64 (m, 5H), 7.43 (d, J = 8.4 Hz, 1H), 7.25-7.22 (m, 1H), 7.17-7.12 (m, 1H), 6.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 138.6, 136.5, 131.7, 130.8, 128.8, 127.5, 123.3, 121.1, 119.5, 118.4, 111.7, 102.3.



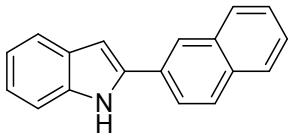
3ai

3ai, [2] white solid, m.p. 208-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, br, 1H), 7.83-7.77 (m, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.8 Hz, 1H), 7.32-7.11 (m, 5H), 6.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.3(d, J = 245 Hz), 136.6, 132.6, 128.9, 128.8, 128.1, 128.0, 124.8, 122.7, 120.7, 120.2, 116.5(d, J = 23 Hz),111.0, 101.6.



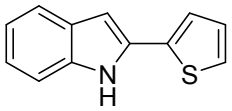
3aj

3aj, [2] white solid, m.p. 199-201 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33-8.30 (m, 2H), 7.93-7.87 (m, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.2 Hz, 1H), 7.55-7.51 (m, 3H), 7.44 (d, J = 8.0 Hz, 1H), 7.25-7.16 (m, 2H), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 136.7, 136.4, 133.9, 131.5, 128.9, 128.6, 128.5, 127.2, 126.7, 126.2, 125.7, 125.4, 122.2, 120.6, 120.2, 110.9, 103.7; HRMS (EI) calcd for $C_{18}H_{13}N$ (M) 243.1048, found 243.1039.



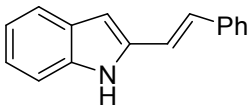
3ak

3ak, [2] white solid, m.p. 195-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, br, 1H), 8.00 (s, 1H), 7.88-7.77 (m, 4H), 7.65 (d, J = 7.6 Hz, 1H), 7.52-7.38 (m, 3H), 7.22-7.11 (m, 2H), 6.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 137.8, 137.0, 133.6, 132.8, 129.7, 129.3, 128.7, 128.0, 127.8, 126.7, 126.1, 123.8, 123.0, 122.5, 120.7, 120.3, 110.9, 100.7; HRMS (EI) calcd for $C_{18}H_{13}N$ (M) 243.1048, found 243.1056.



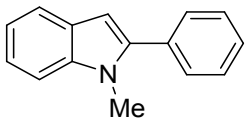
3al

3al,[3] white solid, m.p. 153–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, br, 1H), 7.80–7.73 (m, 1H), 7.44–7.40 (m, 1H), 7.39–7.35 (m, 1H), 7.26–7.13 (m, 3H), 7.12–7.087 (m, 1H), 6.90–6.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 137.9, 136.2, 129.8, 129.2, 128.5, 127.3, 127.2, 123.0, 120.8, 119.5, 111.5, 106.8



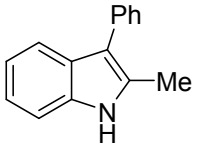
3am

3am, white solid, m.p. 181–183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, br, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 7.6 Hz, 2H), 7.40-7.34 (m, 3H), 7.29-7.26 (m, 1H), 7.21-7.17 (m, 1H), 7.15-7.08 (m, 2H), 6.91 (d, J = 16.4 Hz, 1H), 6.62 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 140.8, 136.6, 133.1, 131.5, 130.2, 128.7, 128.3, 125.8, 125.5, 123.5, 121.4, 119.3, 111.8, 100.3; HRMS (EI) calcd for $C_{16}H_{13}N$ (M) 219.1048, found 219.1041.



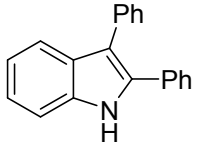
3bb

3bb, [2] white solid, m.p. 99-100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.6 Hz, 1H), 7.52-7.33 (m, 6H), 7.25-7.11 (m, 2H), 6.56 (s, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.5, 138.3, 132.8, 129.4, 128.5,,127.9, 127.8, 121.6, 120.5, 119.8, 109.6, 101.6, 31.1.



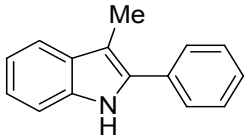
3cb'

3cb', [2] white solid, m.p. 113–115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, br, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.21–7.07 (m, 4H), 7.06–6.97 (m, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 139.3, 135.4, 130.3, 128.7, 125.5, 124.5, 122.2, 120.7, 119.0, 110.6, 99.3, 12.1.



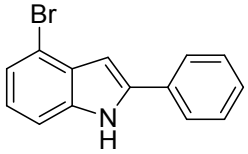
3db'

3db',[2] colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, br, 1H), 7.75–7.70 (m, 2H), 7.62 (d, J = 7.6 Hz, 1H), 7.43–6.98 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 139.3, 135.9, 131.5, 131.2, 128.9, 128.8, 128.7, 128.2, 125.6, 124.7, 123.4, 121.2, 120.0, 111.2.



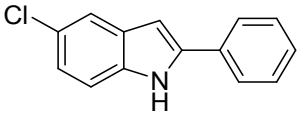
3eb

3eb, [4] white solid, m.p. 93-95 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, br, 1H), 7.61-7.56 (m, 2H), 7.52-7.44 (m, 3H), 7.43-7.43 (m, 2H), 7.22-7.12 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 135.8, 134.0, 130.0,128.8, 128.6, 127.7, 127.3, 122.3, 119.5, 119.0, 110.7, 108.7, 9.6.



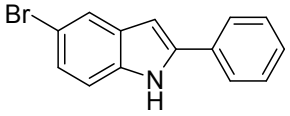
3fb

3fb, [4] white solid, m.p. 160-162 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, br, 1H), 7.72 (d, J = 7.2 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.52-7.27 (m, 5H), 7.18 (d, J = 7.6 Hz, 1H), 7.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 139.3, 135.4, 130.3, 128.7, 125.5, 124.5, 122.2, 120.7, 119.0, 110.6, 99.3.



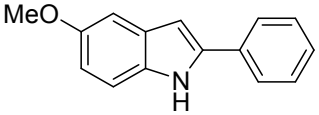
3gb

3gb, [4] white solid, m.p. 181-183 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, br, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.42 (d, J = 7.6 Hz, 2H), 7.34-7.20 (m, 4H), 7.18-7.15 (m, 1H), 6.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 139.1, 135.4, 131.7, 129.1, 128.1, 127.3, 125.4, 125.1, 123.0, 113.4, 112.4, 99.4.



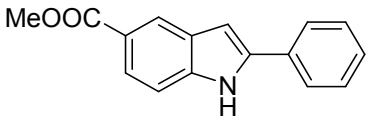
3hb

3hb, [4] white solid, m.p. 187-189 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, br, 1H), 7.65-7.11 (m, 7H), 7.10-7.05 (m, 1H), 6.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 139.7, 137.5, 135.0, 129.8, 128.6, 125.7, 124.6, 122.5, 120.5, 119.7, 109.7, 100.5.



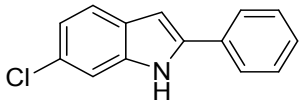
3ib

3ib, [4] white solid, m.p. 160-162 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, br, 1H), 7.62 (d, J = 7.2 Hz, 2H), 7.44-7.39 (m, 2H), 7.32-7.23 (m, 2H), 7.08 (s, 1H), 6.85 (d, J = 8.8 Hz, 1H), 6.75 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):154.5, 138.6, 132.4, 132.0, 129.7, 129.3, 129.0, 127.7, 125.1, 112.6, 111.7, 102.3, 99.8, 55.9.



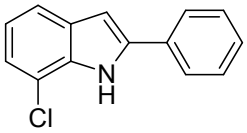
3jb

3jb, [4] white solid, m.p. 183-184 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, br, 1H), 8.32 (s, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.40-7.31 (m, 4H), 7.25-7.20 (m, 1H), 6.82 (s, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 167.2, 138.4, 137.4, 130.7, 128.1, 127.2, 124.2, 122.7, 122.5, 122.4, 120.9, 109.6, 99.9, 50.9.



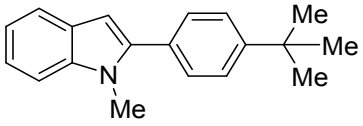
3kb

3kb, [4] white solid, m.p. 171-173 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, br, 1H), 7.65 (d, J = 7.2 Hz, 2H), 7.59 (s, 1H), 7.50-7.43 (m, 2H), 7.36-7.25 (m, 2H), 7.14 (d, J = 8.4 Hz, 1H), 6.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 139.3, 135.1, 131.9, 130.3, 129.1, 128.1, 125.9, 125.2, 122.6, 120.0, 111.9, 99.6.



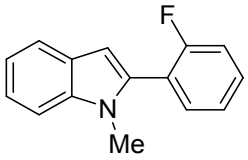
3lb

3lb, white solid, m.p. 145–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, br, 1H), 7.52–7.44 (m, 2H), 7.42 (d, J = 1.6 Hz, 1H), 7.20–7.02 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 136.8, 131.1, 129.1, 128.8, 127.7, 126.0, 125.0, 121.7, 120.6, 111.6, 103.5; HRMS (ESI) calcd for $C_{14}H_{10}ClN$ (M) 227.0502, found 227.0520.



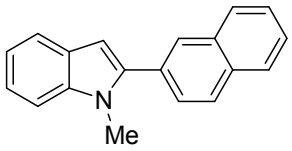
3bc

3bc, white solid, m.p. 112–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 7.6 Hz, 1H), 7.49-7.42 (m, 4H), 7.33 (d, J = 8.0 Hz, 1H), 7.24-7.10 (m, 2H), 6.54 (s, 1H), 3.72 (s, 3H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$):150.8, 141.6, 138.2, 129.9, 129.0, 125.4, 121.4, 120.3, 119.7, 109.5, 101.3, 34.6, 31.3, 31.1; HRMS (EI) calcd for $C_{19}H_{21}N$ (M) 263.1674, found 263.1661.



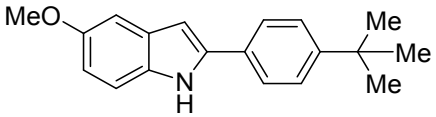
3bi

3bi, [4] white solid, m.p. 119-121°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.6 Hz, 1H), 7.48-7.36 (m, 3H), 7.28-7.12 (m, 4H), 6.58 (s, 1H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.1 (d, J = 246.7 Hz), 138.0, 135.4, 132.5, 132.4, 127.8, 130.3 (d, J = 8.0 Hz), 124.3, 121.9, 120.6, 119.8, 115.9 (d, J = 21.9 Hz), 109.6, 102.8, 30.9.



3bk

3bk, white solid, m.p. 158-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.92-7.85 (m, 3H), 7.67-7.60 (m, 2H), 7.52-7.49 (m, 2H), 7.37 (d, J = 7.6 Hz, 1H), 7.28-7.24 (m, 1H), 7.19-7.13 (m, 1H), 6.66 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.5, 138.5, 133.2, 132.7, 130.2, 128.3, 128.1, 128.0, 127.7, 127.2, 126.5, 126.4, 121.8, 120.5, 119.9, 109.6, 102.1, 31.3; HRMS (EI) calcd for $C_{19}H_{15}N$ (M) 257.1204, found 257.1217.

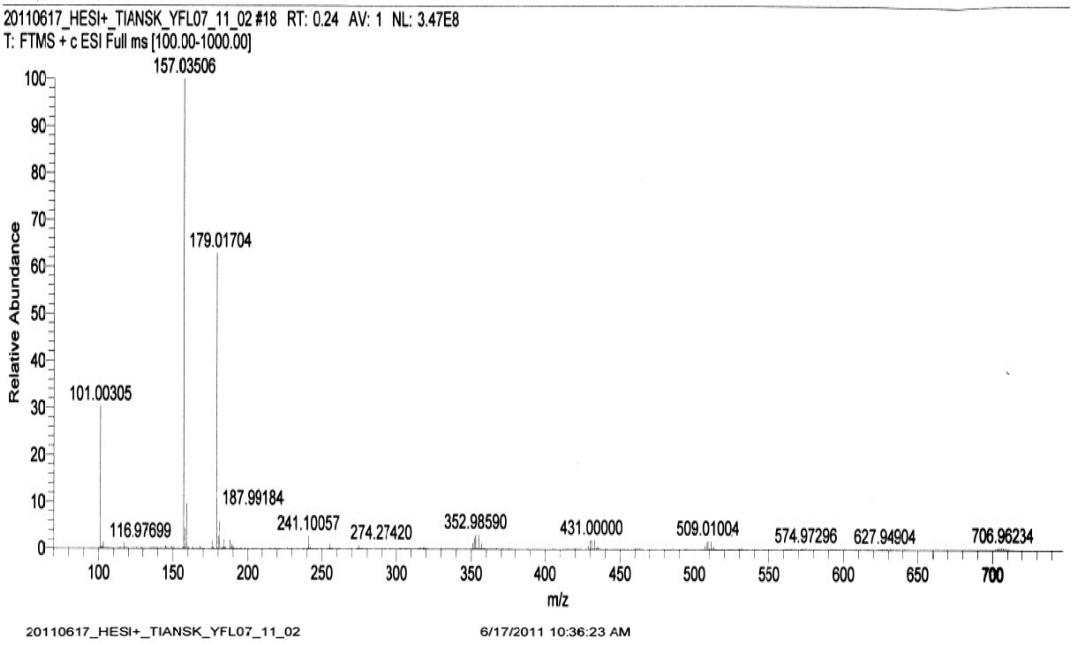


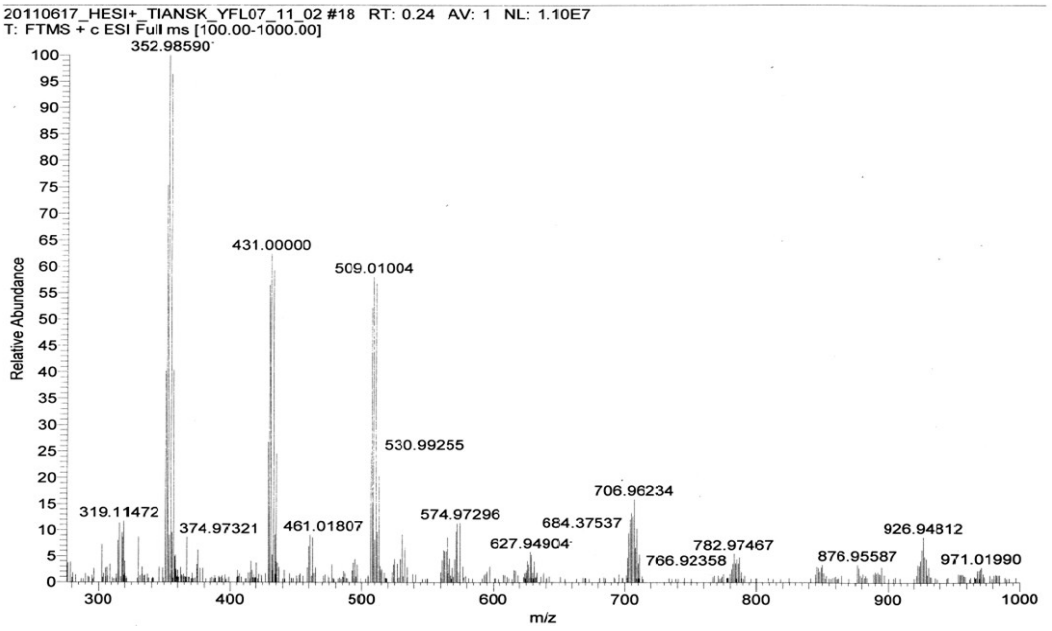
3ic

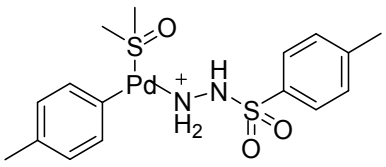
3ic, white solid, m.p. 248-250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, br, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.8 Hz, 1H), 7.08 (s, 1H), 6.83 (d, J = 8.8 Hz, 1H), 6.70 (s, 1H), 3.84 (s, 3H), 1.34 (s, 9H) ; ^{13}C NMR (100 MHz, $CDCl_3$): 154.4, 150.7, 138.7, 131.9, 129.8, 129.6, 125.9, 124.8, 112.3, 111.6, 102.2, 99.3, 55.8, 34.6, 31.2; HRMS (EI) calcd for $C_{19}H_{21}NO$ (M) 279.1263, found 279.1269.

ESI-MS Analysis of the mixture of p-toluenesulfonyl hydrazide (1a) and $Pd(OAc)_2$ in DMSO

To a solution of sulfonyl hydrazide **2a** (37.3 mg, 0.20 mmol) in DMSO (1.0 mL) were added $Pd(OAc)_2$ (2.2 mg, 0.010 mmol). The resulting mixture was stirred at 70 °C for 10 minutes. The mixture was cooled to room temperature, and subjected to ESI-MS (positive mode) spectroscopic analysis at room temperature. Copied below is the ESI-MS spectrum we obtained.

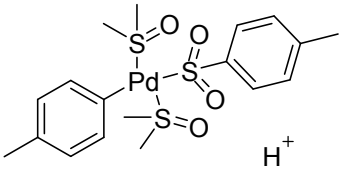






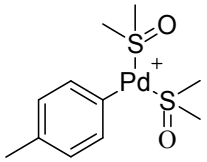
10a

10a: HRMS (ESI) calcd for $C_{16}H_{23}N_2O_3PdS_2^+$ (M) 461.01794, found 461.01807.



(**11a** + H)$^+$

(11a+H)$^+$: HRMS (ESI) calcd for $C_{18}H_{27}O_4PdS_3^+$ $(M+H)^+$ 509.01008, found 509.01004.

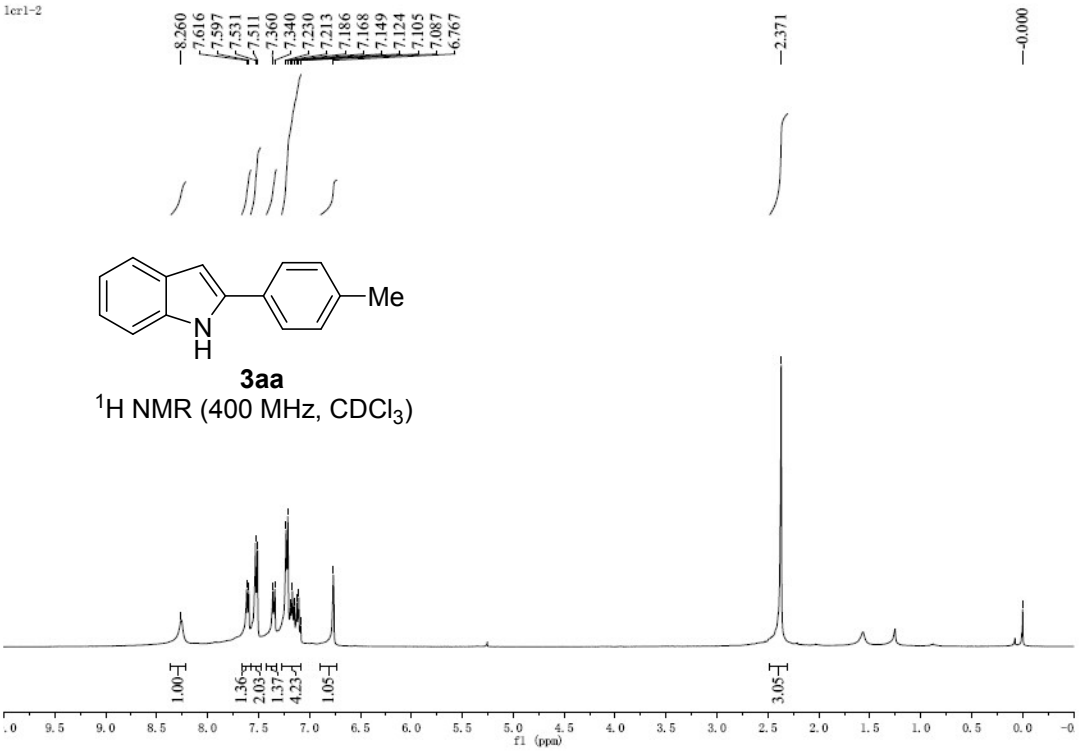


12a

12a: HRMS (ESI) calcd for $C_{11}H_{19}O_2PdS_2^+$ (M) 352.98558, found 352.98590.

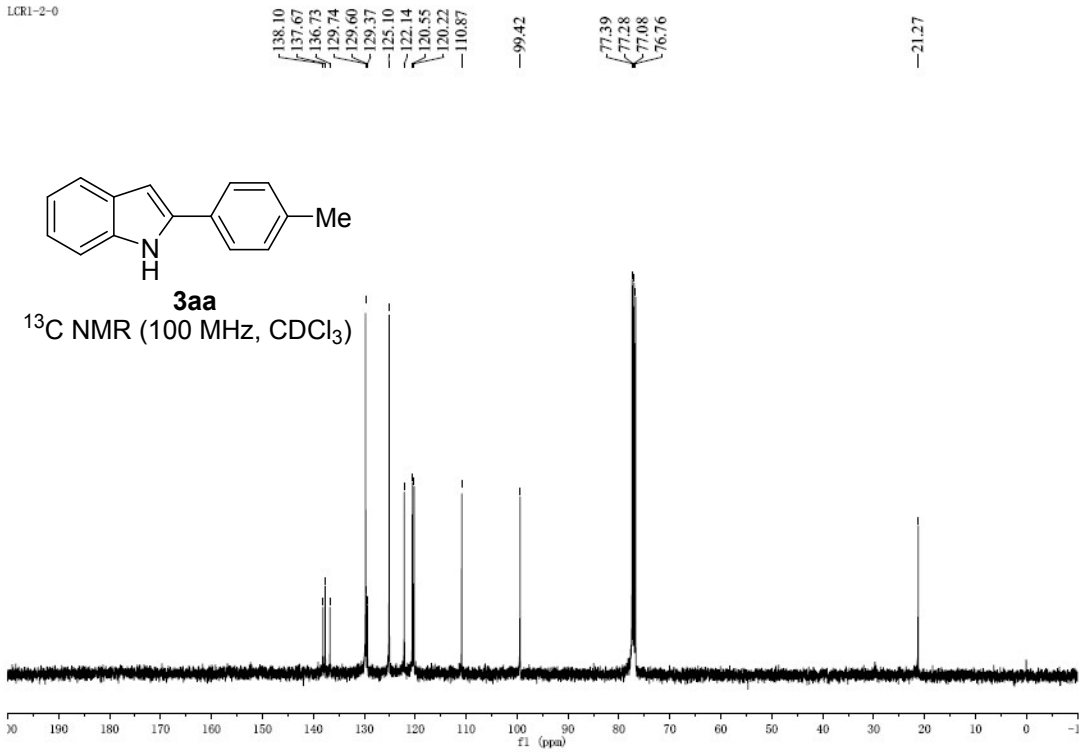
References

1. A. G. Myers, B. Zheng and M. Movassaghi, *J. Org. Chem.* 1997, **62**, 7507.
2. S. D. Yang, C. L. Sun, Z. Fang, B. J. Li, Y. Z. Li and Z. J. Shi, *Angew. Chem. Int. Ed.* 2008, **47**, 1473.
3. G. A. Kraus and H. T. Guo, *Org. Lett*, 2008, **10**, 3061.
4. S. Isiam and I. Larrosa, *Chem. Eur. J.* 2013, **19**, 15093.



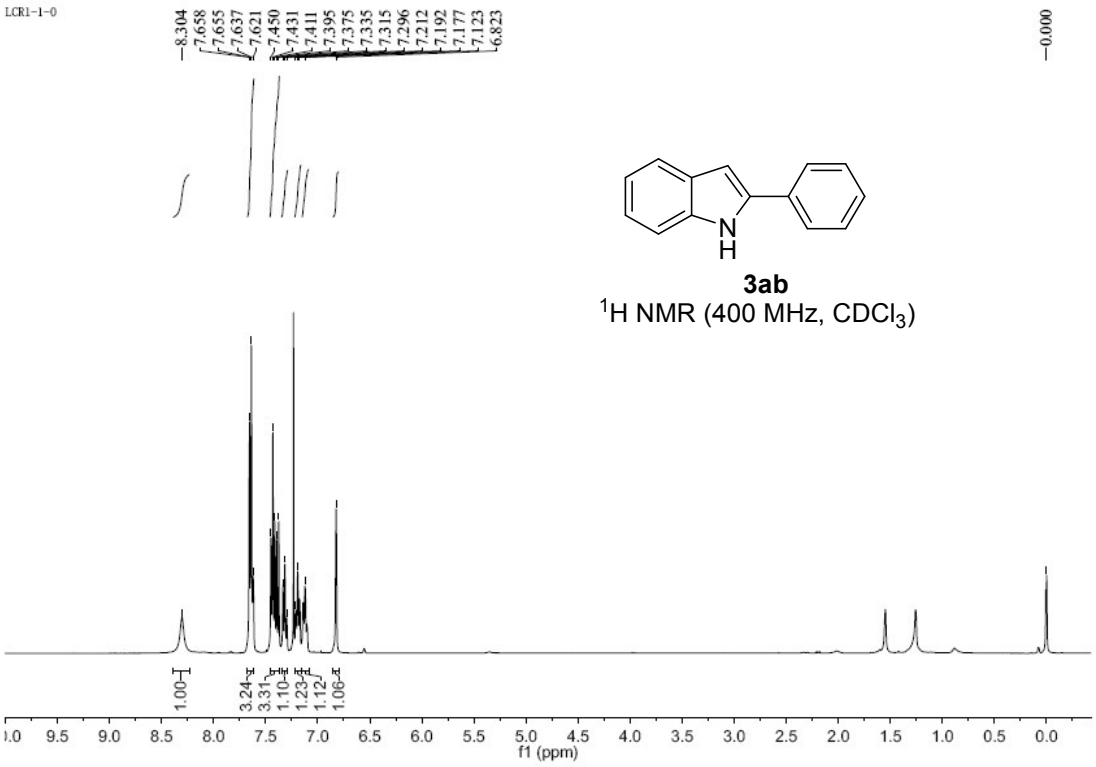
3aa

^{1}H NMR (400 MHz, $CDCl_3$)



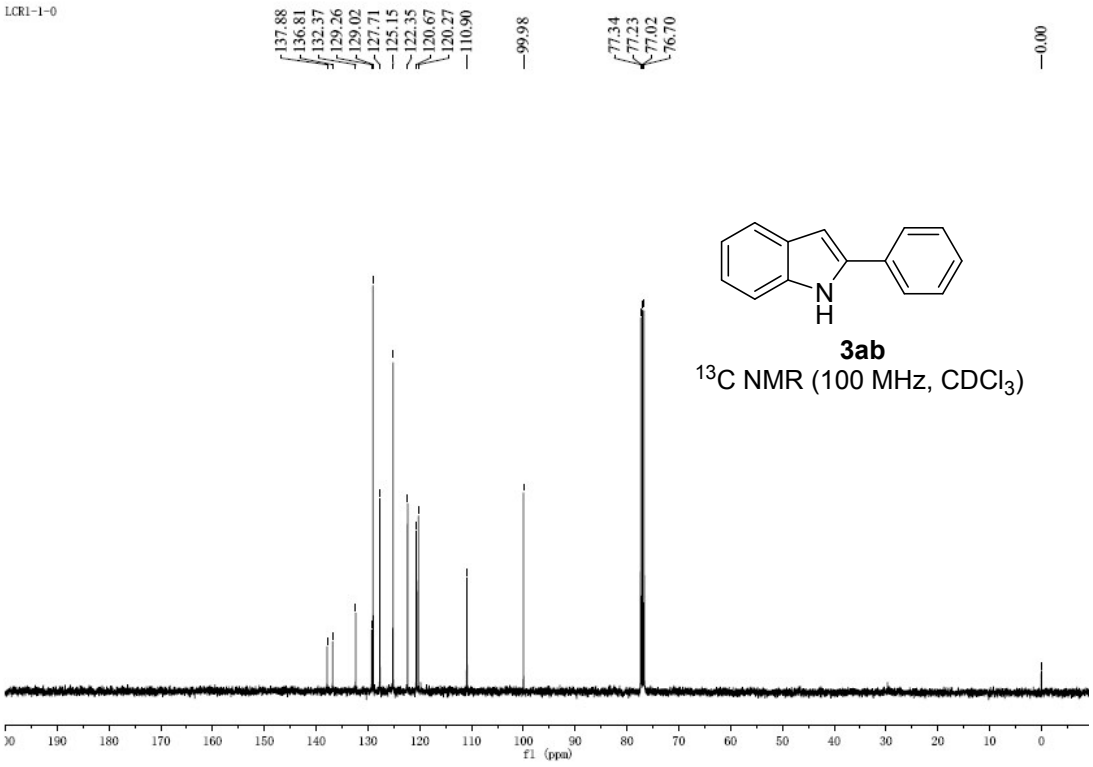
3aa

^{13}C NMR (100 MHz, $CDCl_3$)



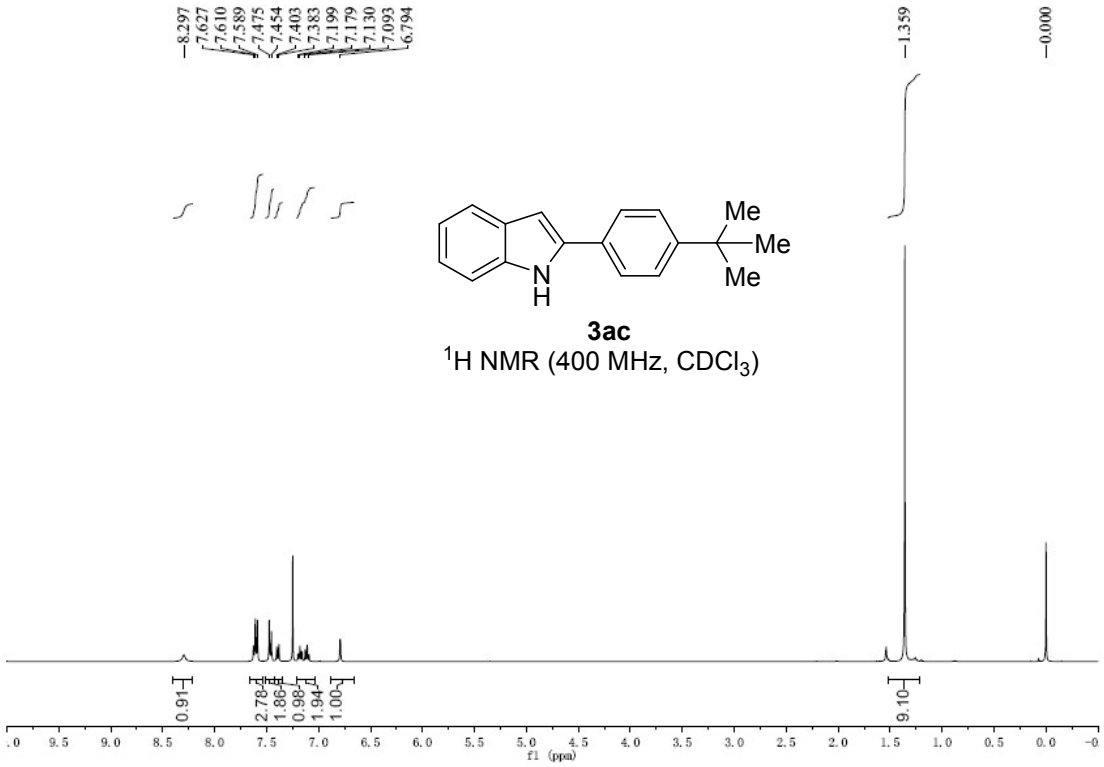
3ab

^{1}H NMR (400 MHz, $CDCl_3$)



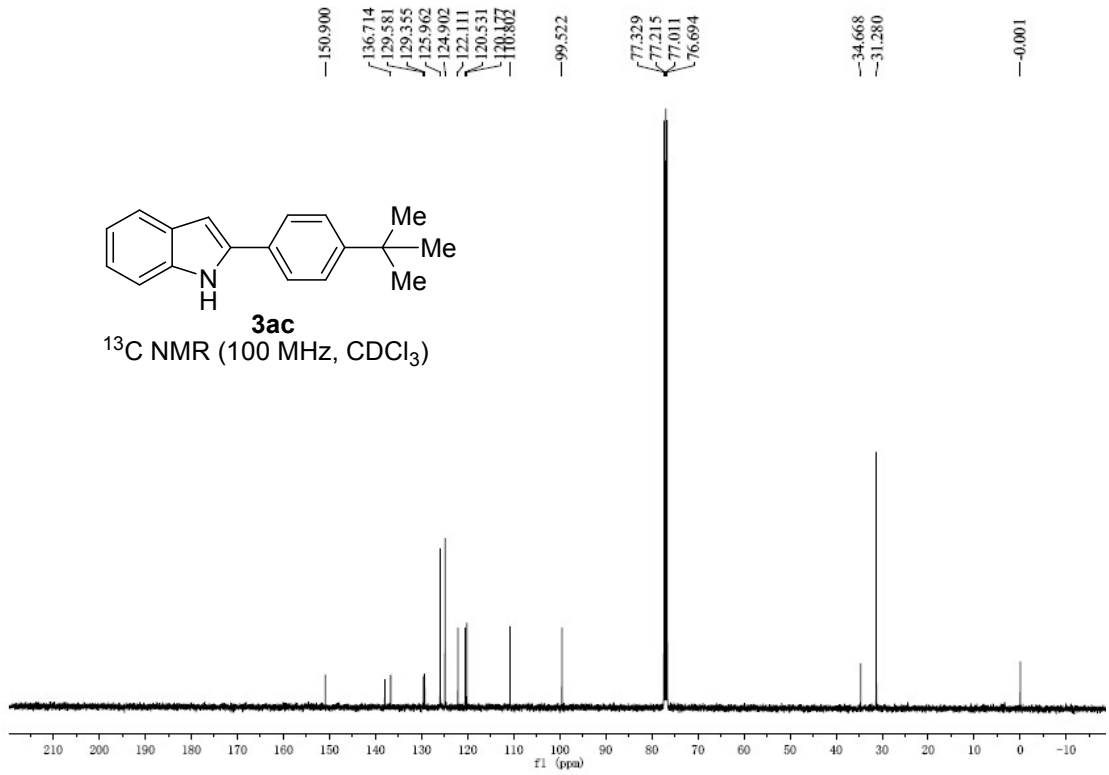
3ab

^{13}C NMR (100 MHz, $CDCl_3$)



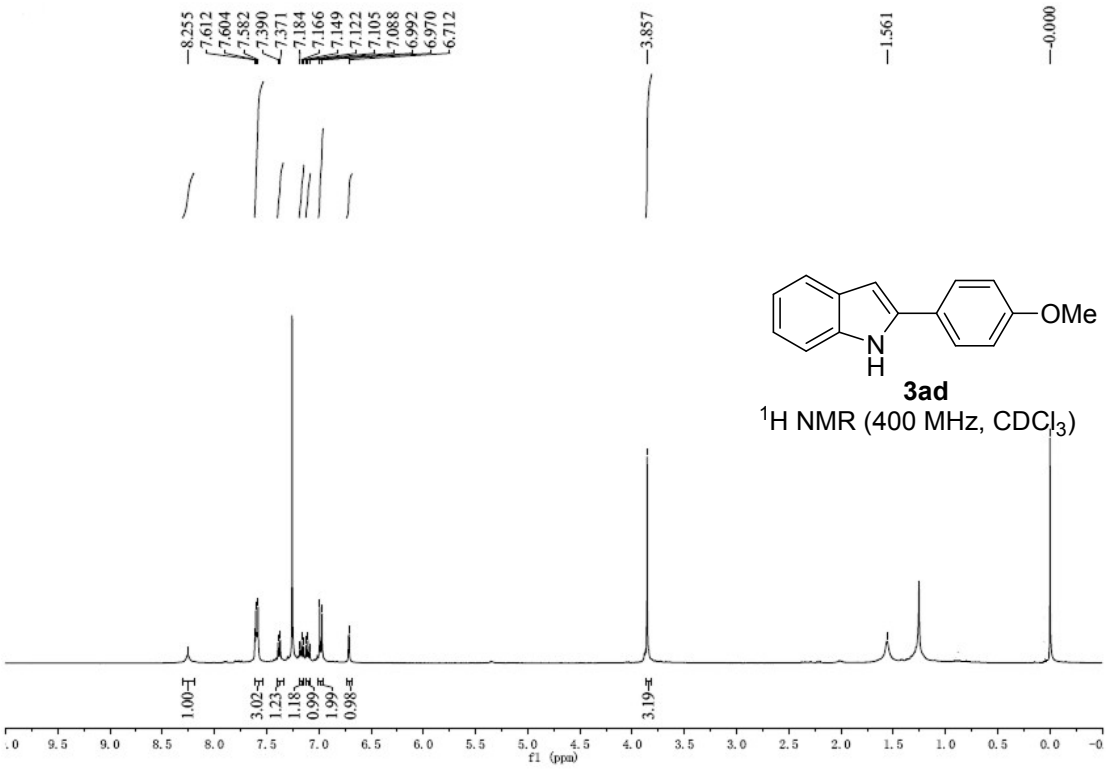
3ac

^{1}H NMR (400 MHz, $CDCl_3$)



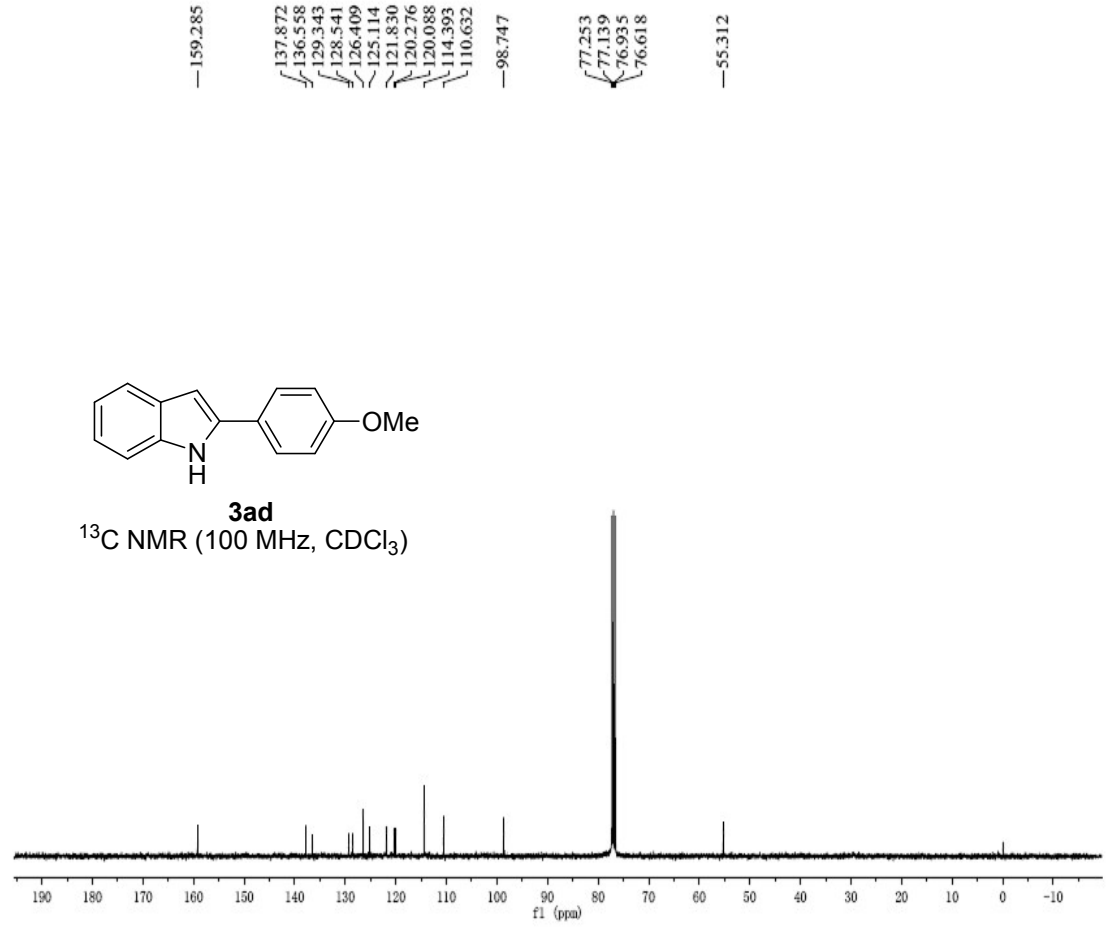
3ac

^{13}C NMR (100 MHz, $CDCl_3$)



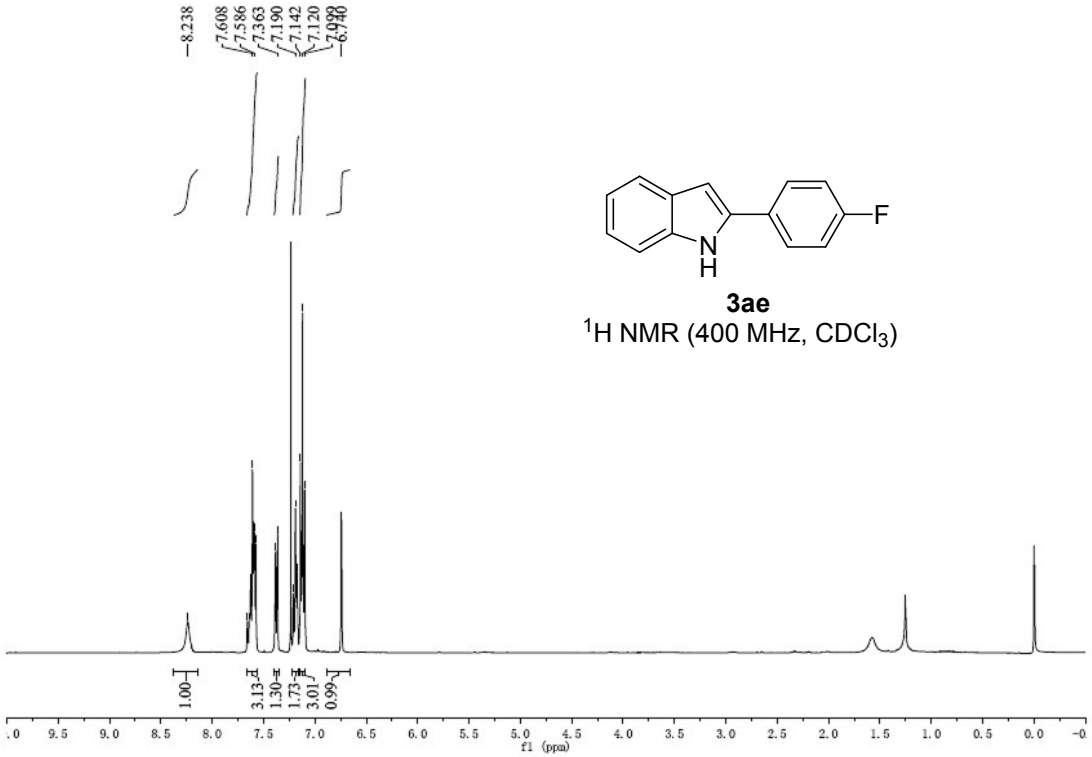
3ad

^{1}H NMR (400 MHz, $CDCl_3$)



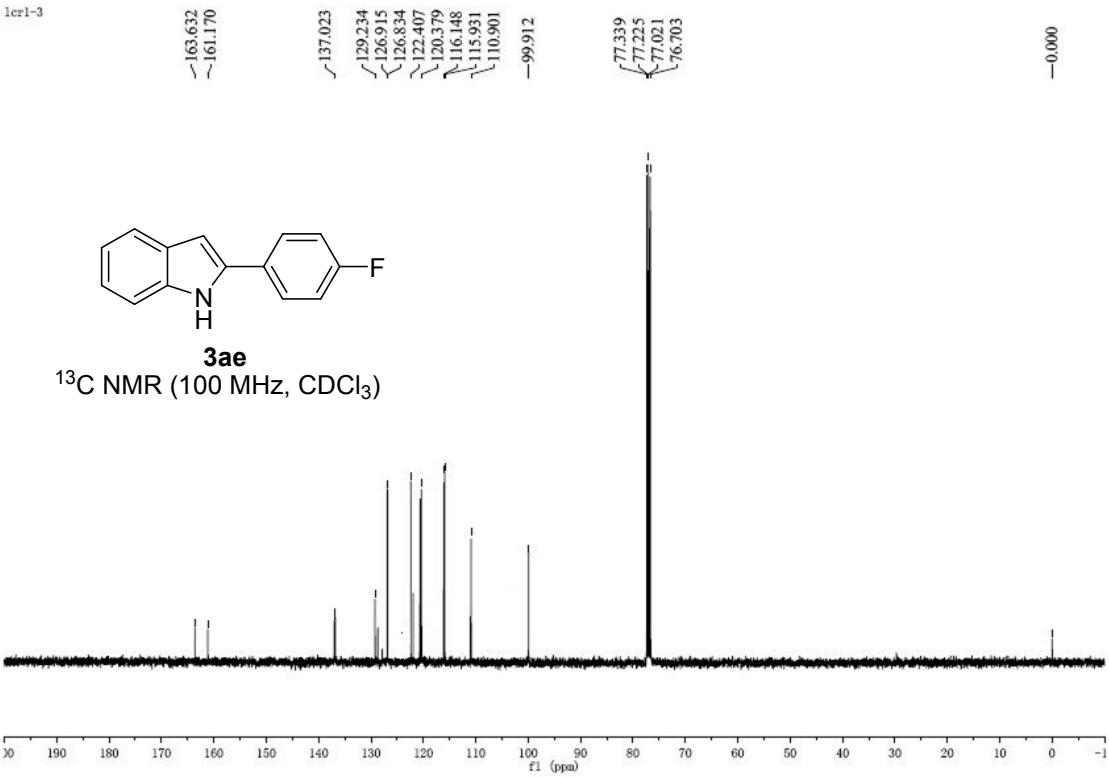
3ad

^{13}C NMR (100 MHz, $CDCl_3$)



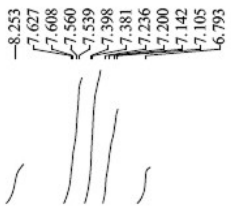
3ae

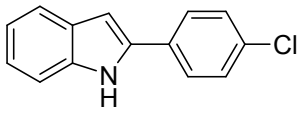
^{1}H NMR (400 MHz, $CDCl_3$)



3ae

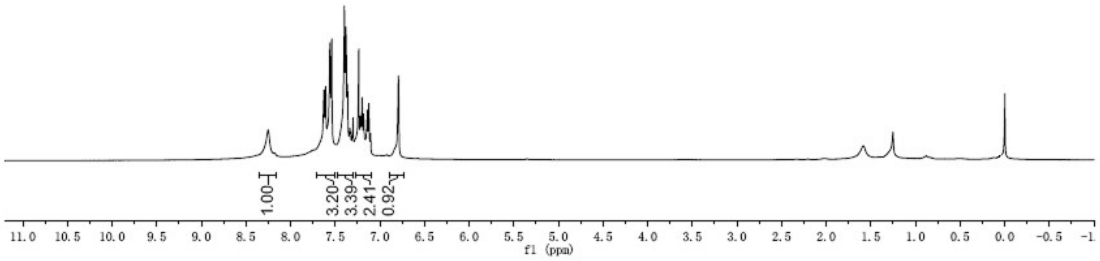
^{13}C NMR (100 MHz, $CDCl_3$)

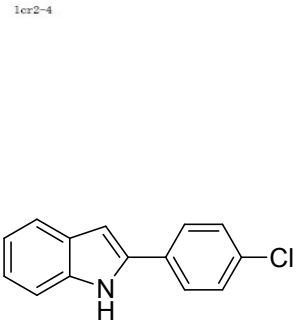




3af

^{1}H NMR (400 MHz, $CDCl_3$)





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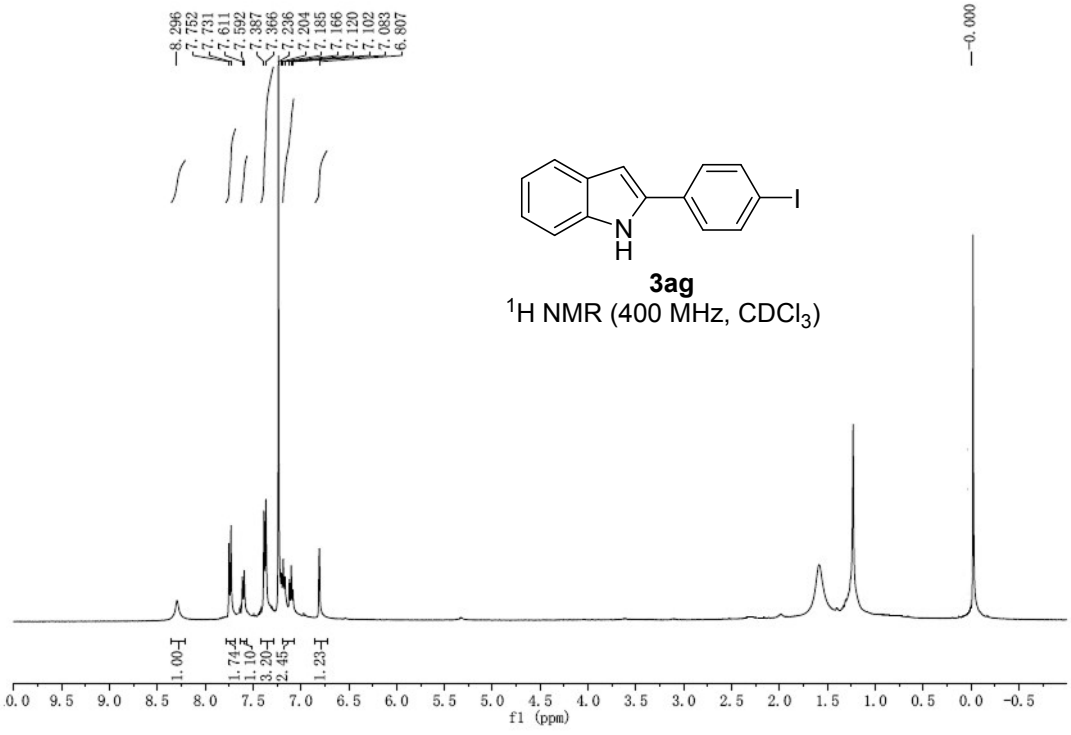
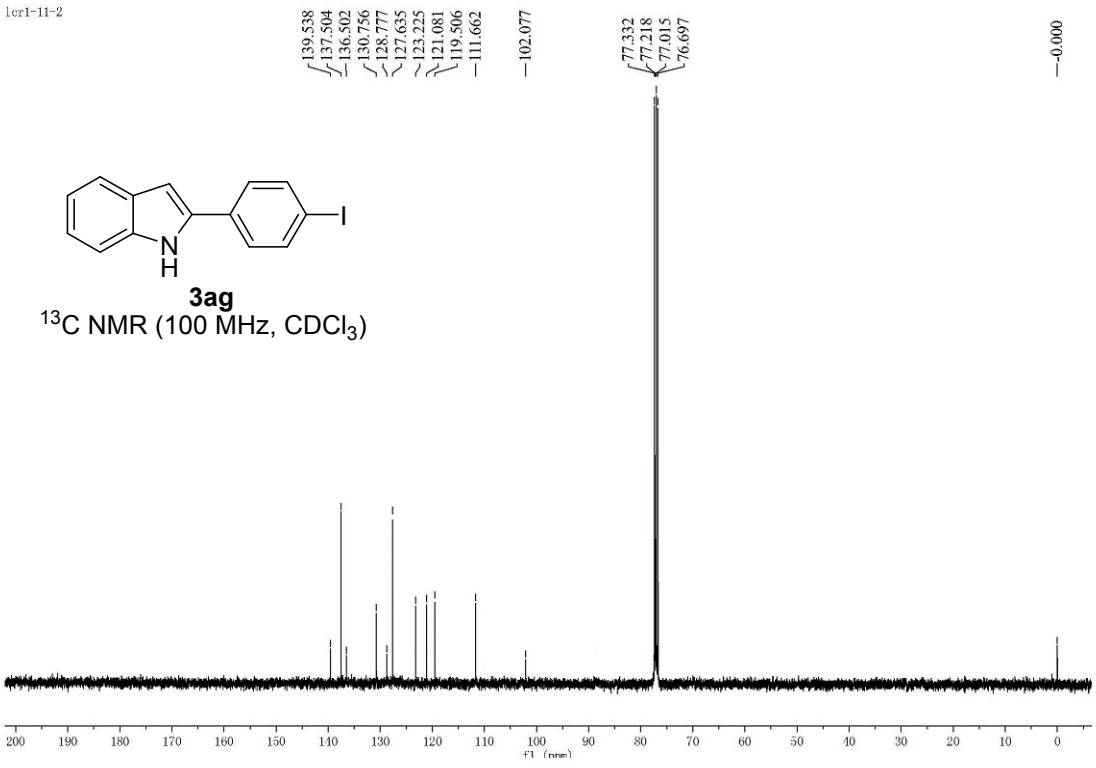
^{13}C NMR (100 MHz, $CDCl_3$)



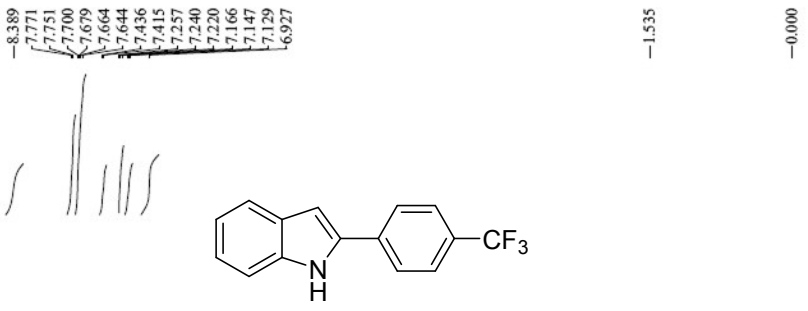
3ag

^{1}H NMR (400 MHz, $CDCl_3$)



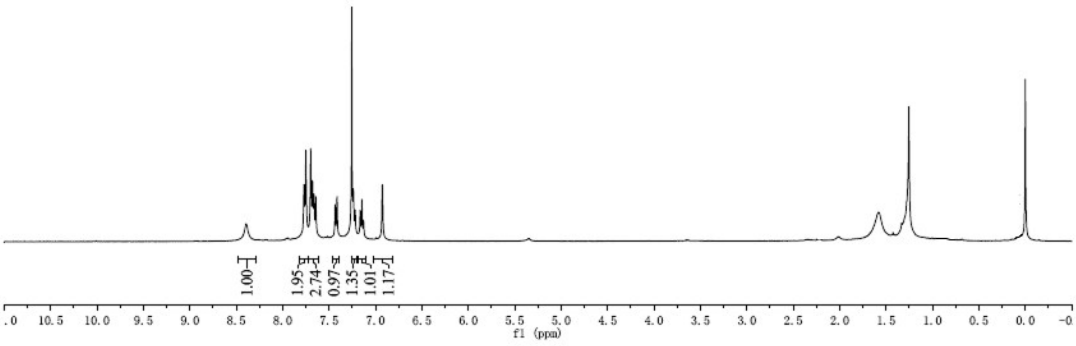
3ag

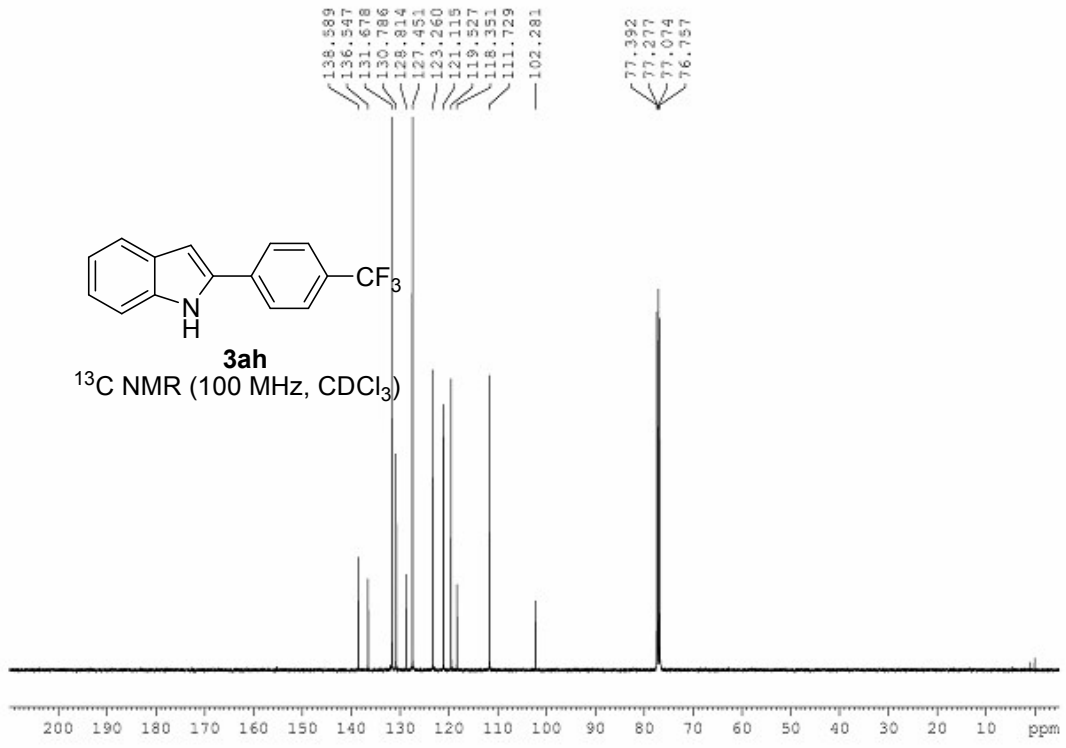
^{13}C NMR (100 MHz, $CDCl_3$)



3ah

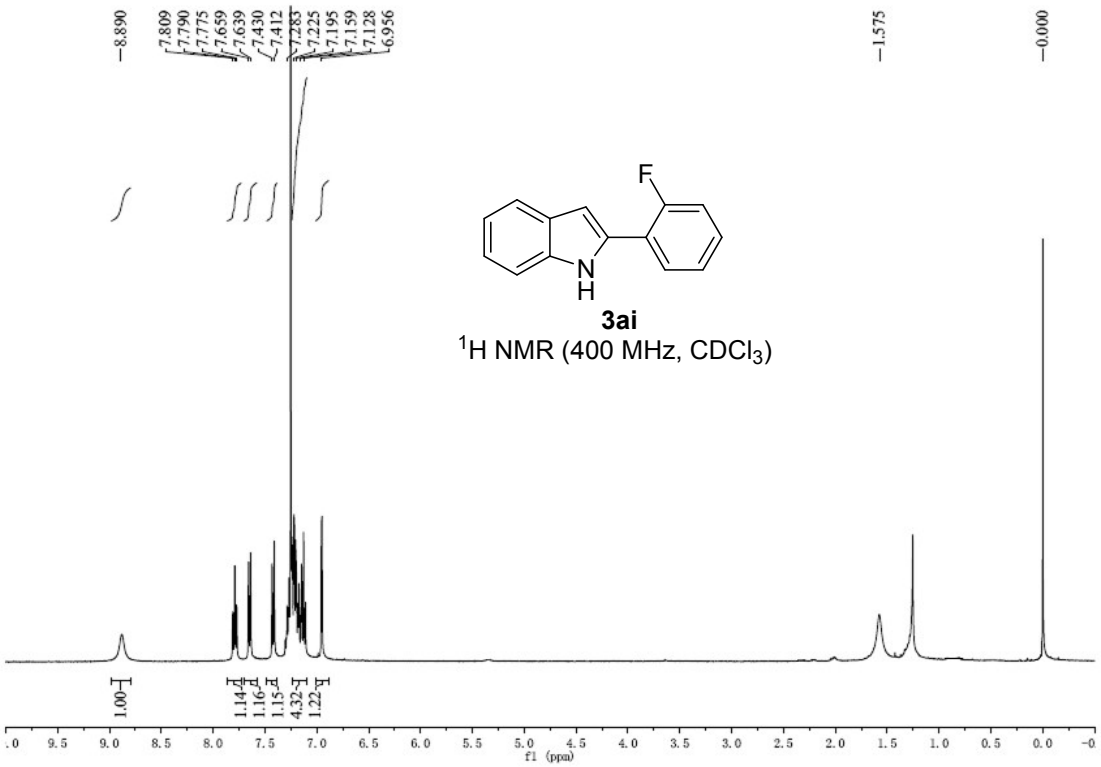
^{1}H NMR (400 MHz, $CDCl_3$)





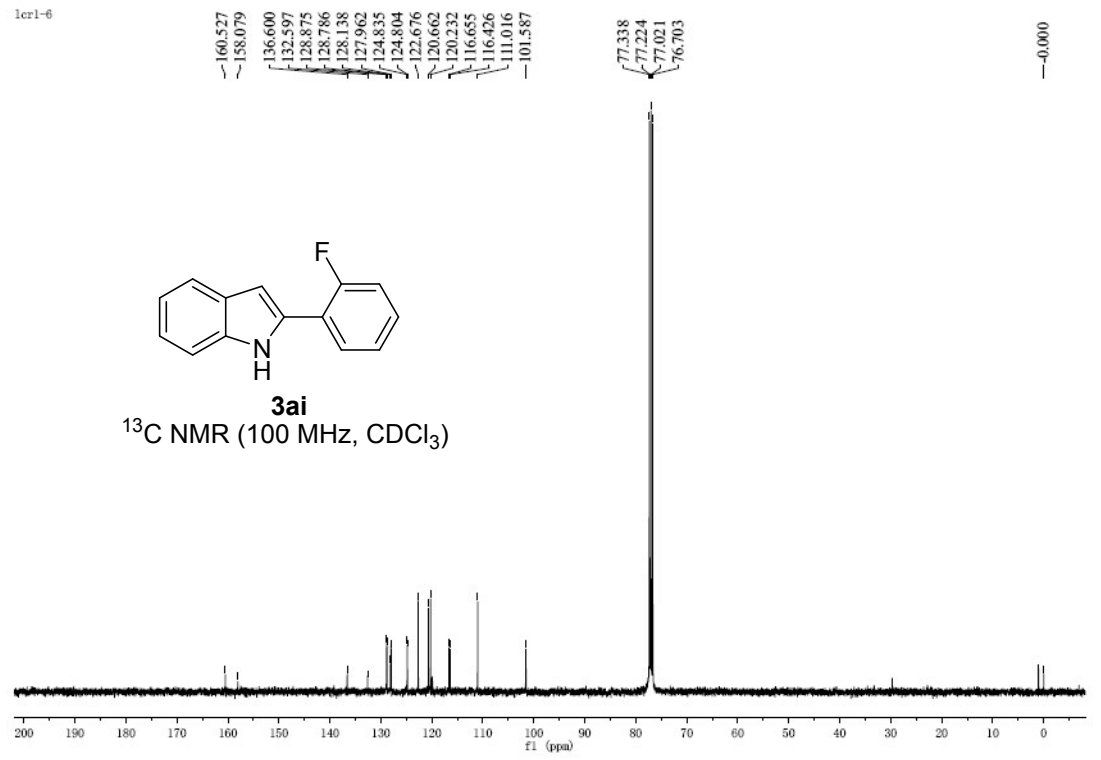
3ah

^{13}C NMR (100 MHz, $CDCl_3$)



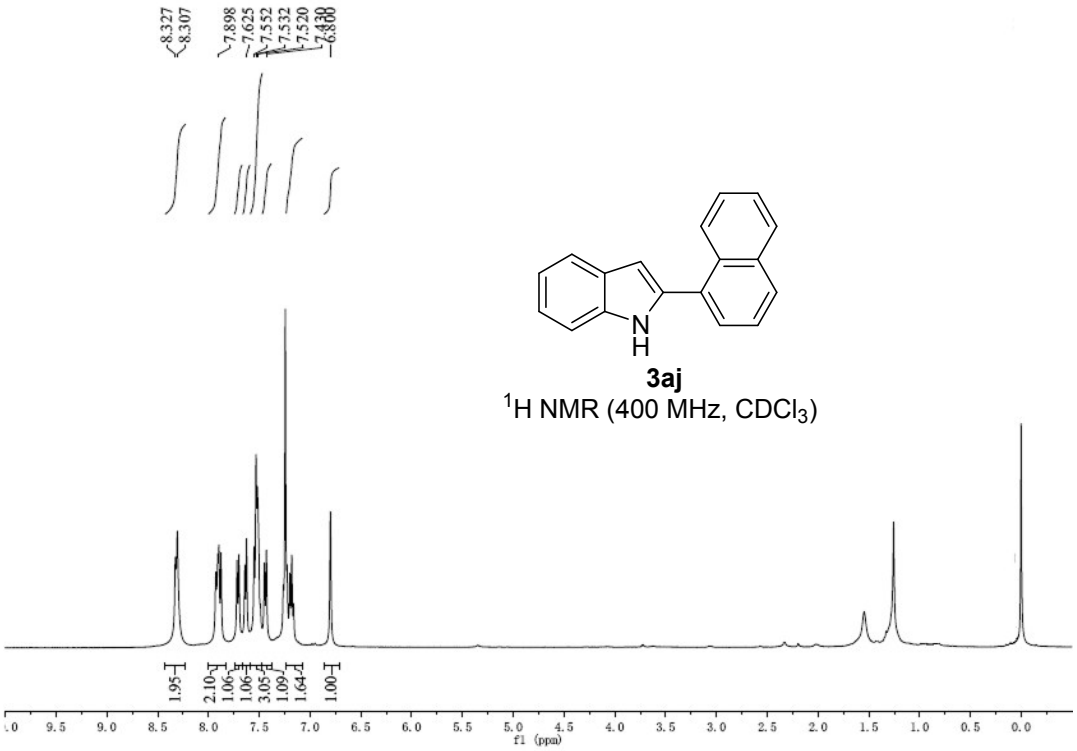
3ai

^{1}H NMR (400 MHz, $CDCl_3$)



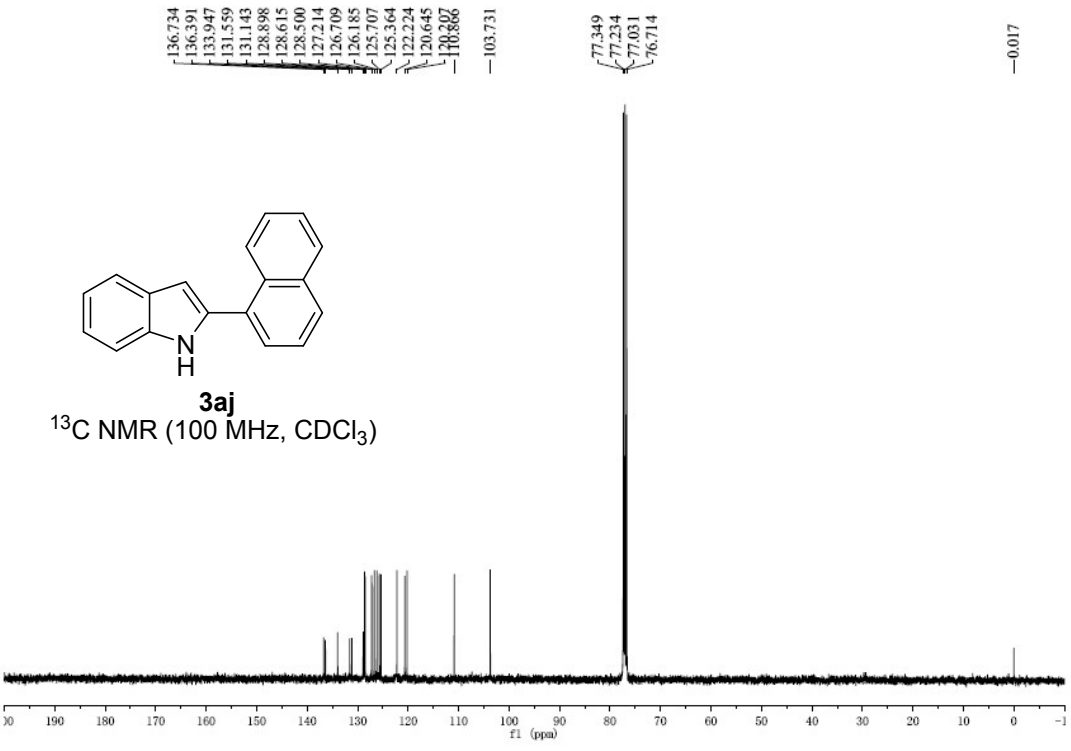
3ai

^{13}C NMR (100 MHz, $CDCl_3$)



3aj

^{1}H NMR (400 MHz, $CDCl_3$)



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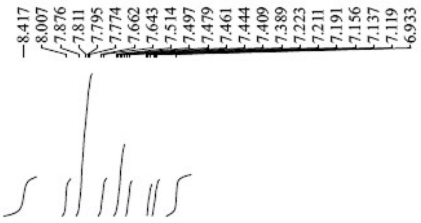
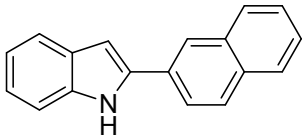
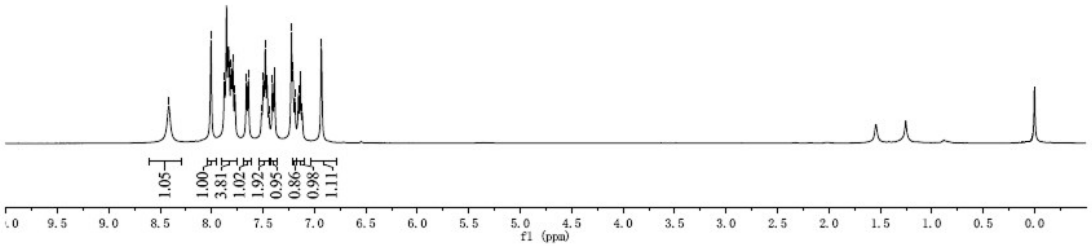
^{13}C NMR (100 MHz, $CDCl_3$)

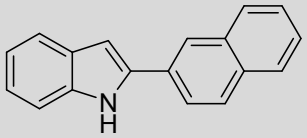




3ak

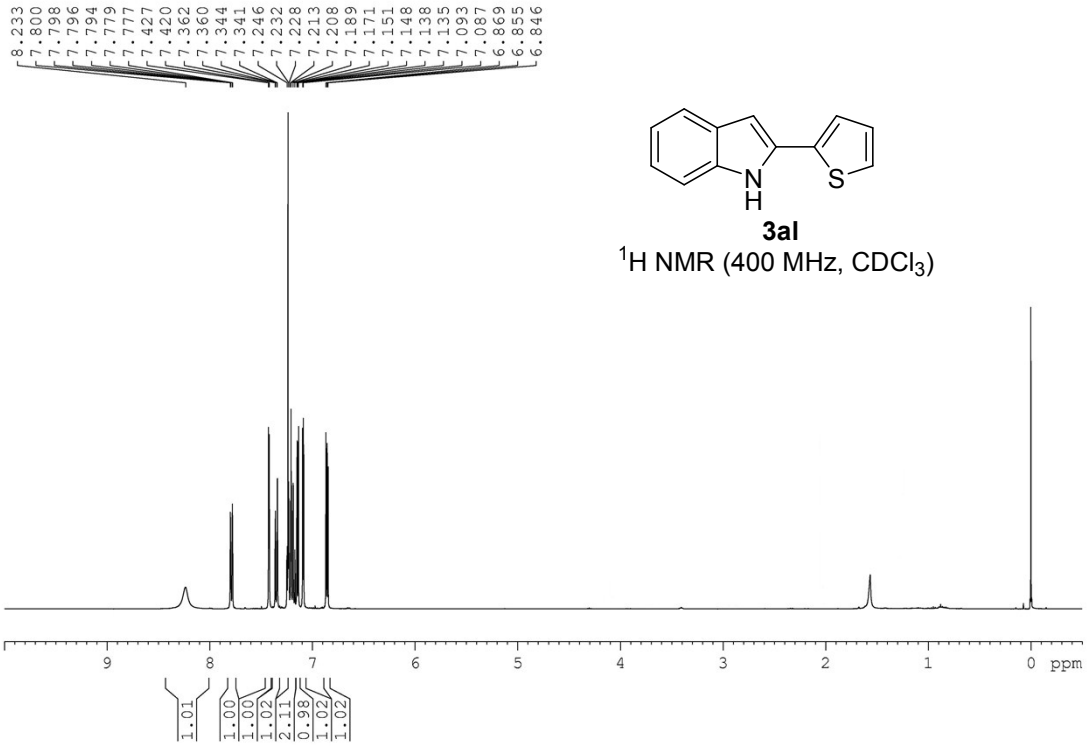
^{1}H NMR (400 MHz, $CDCl_3$)





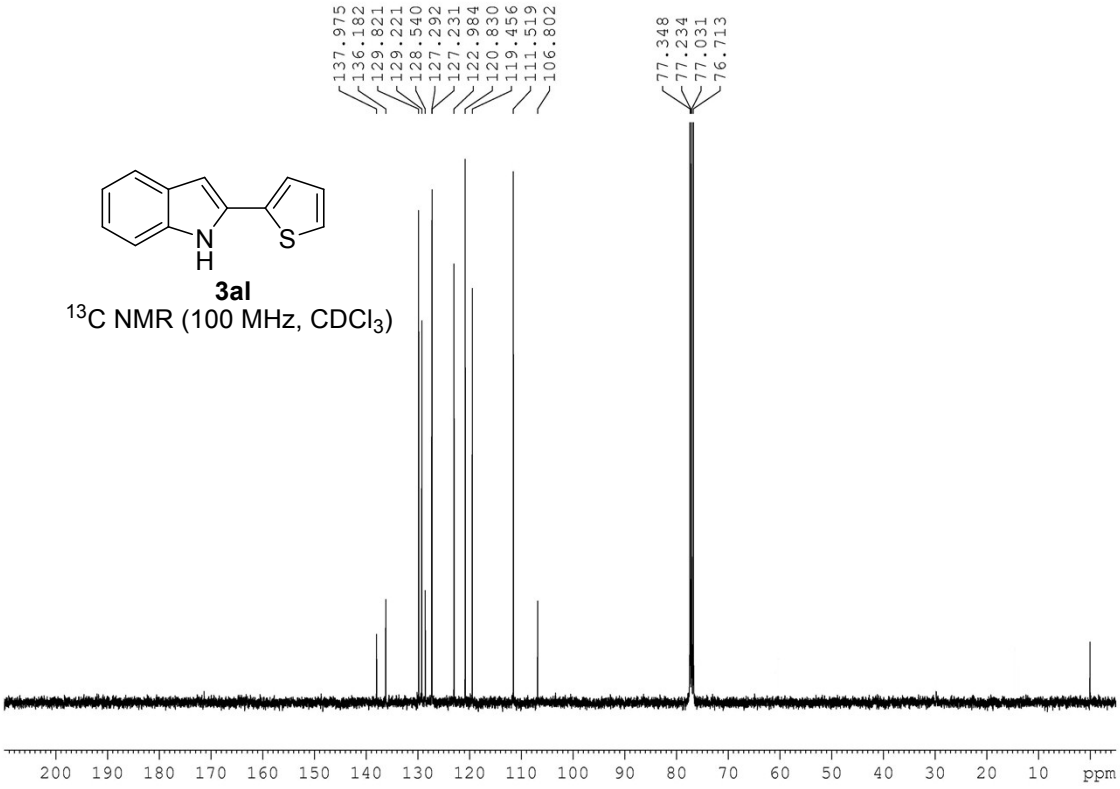
3ak

^{13}C NMR (100 MHz, $CDCl_3$)



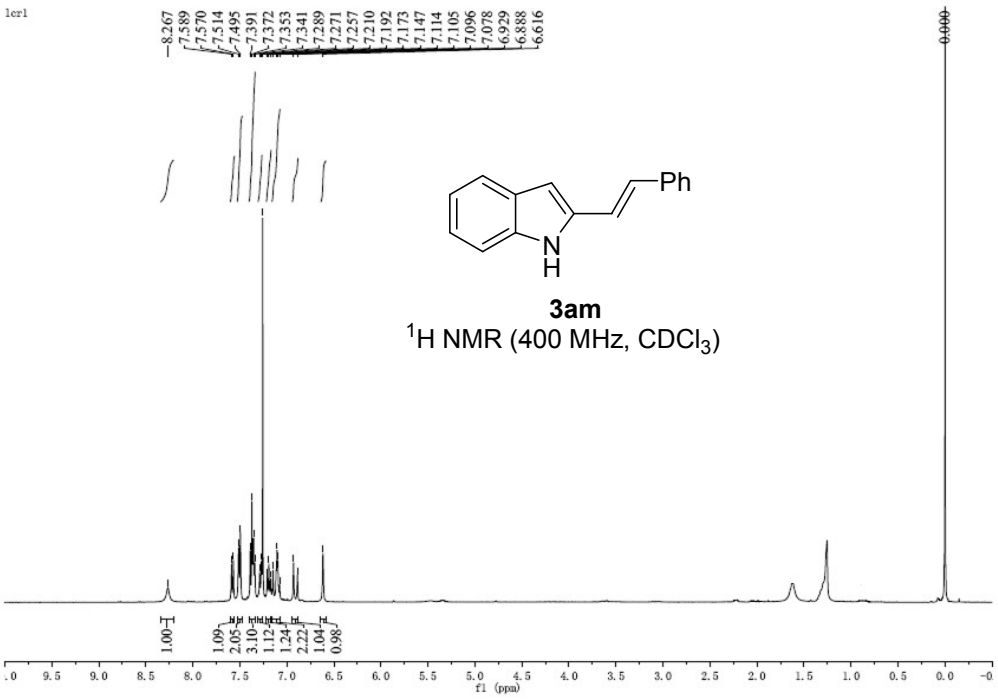
3al

^{1}H NMR (400 MHz, $CDCl_3$)



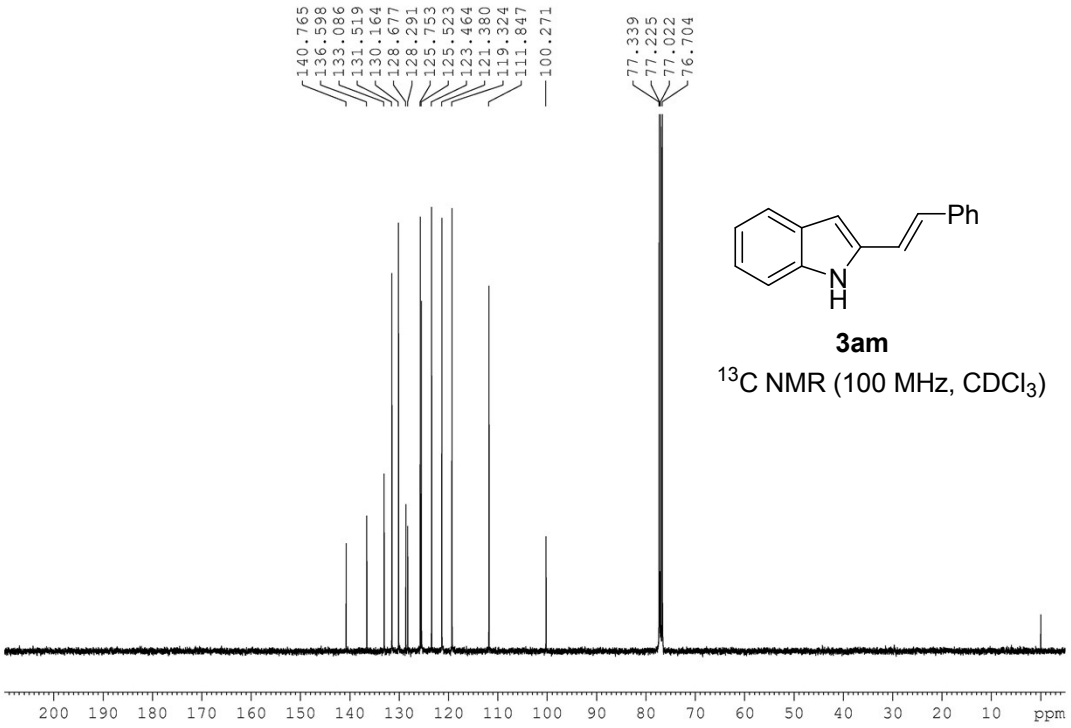
3al

^{13}C NMR (100 MHz, $CDCl_3$)



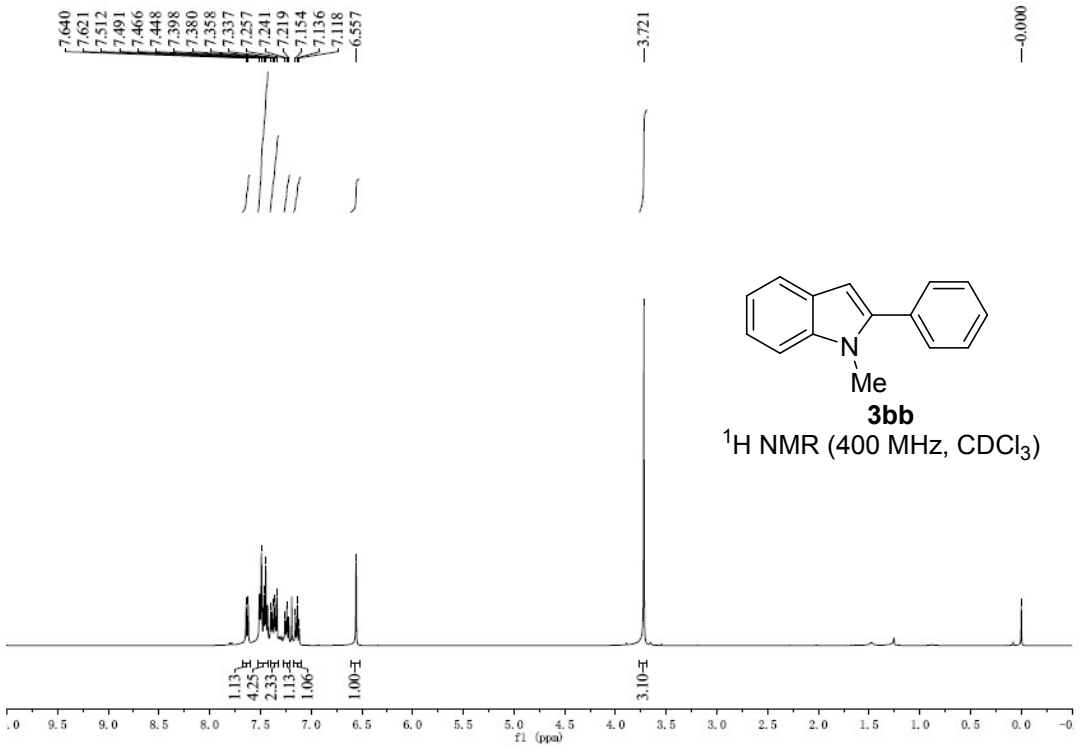
3am

^{1}H NMR (400 MHz, $CDCl_3$)



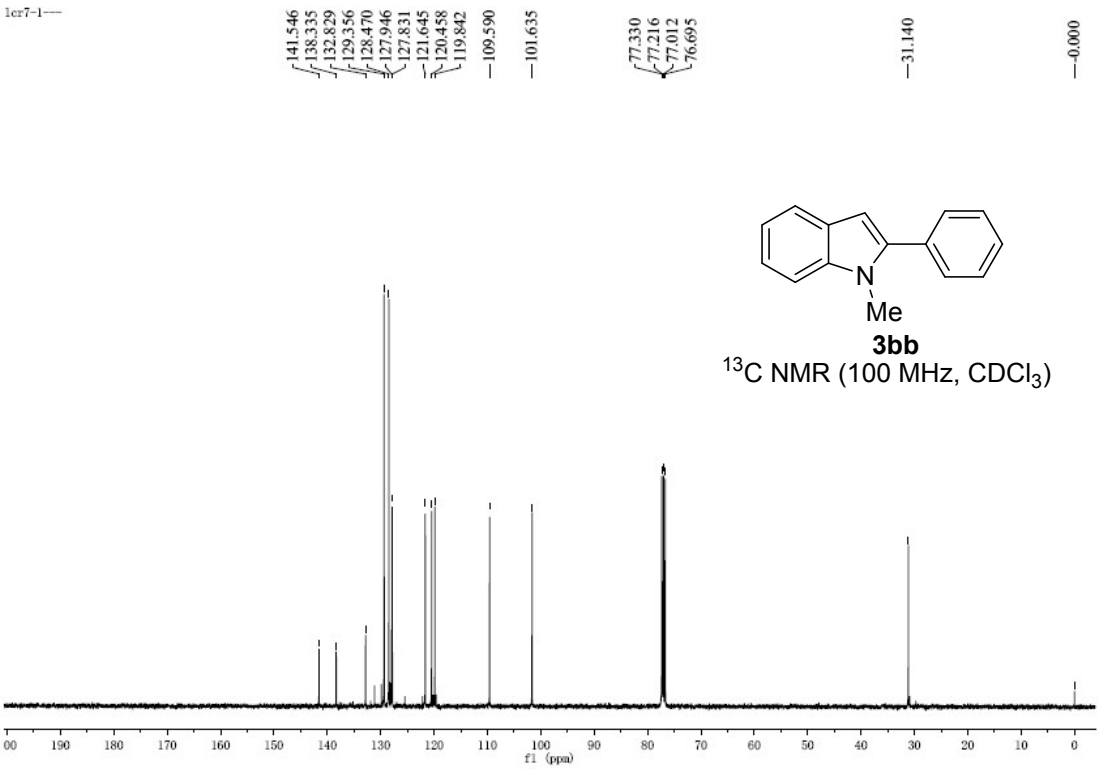
3am

^{13}C NMR (100 MHz, $CDCl_3$)



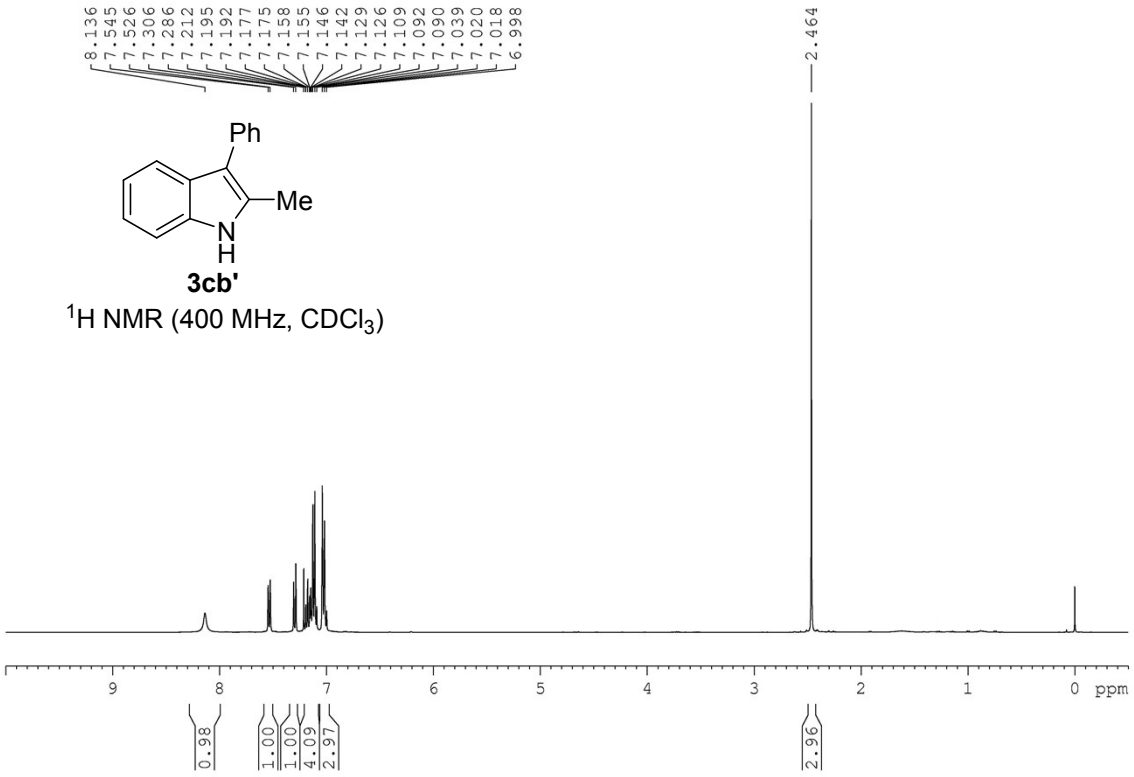
3bb

^{1}H NMR (400 MHz, $CDCl_3$)



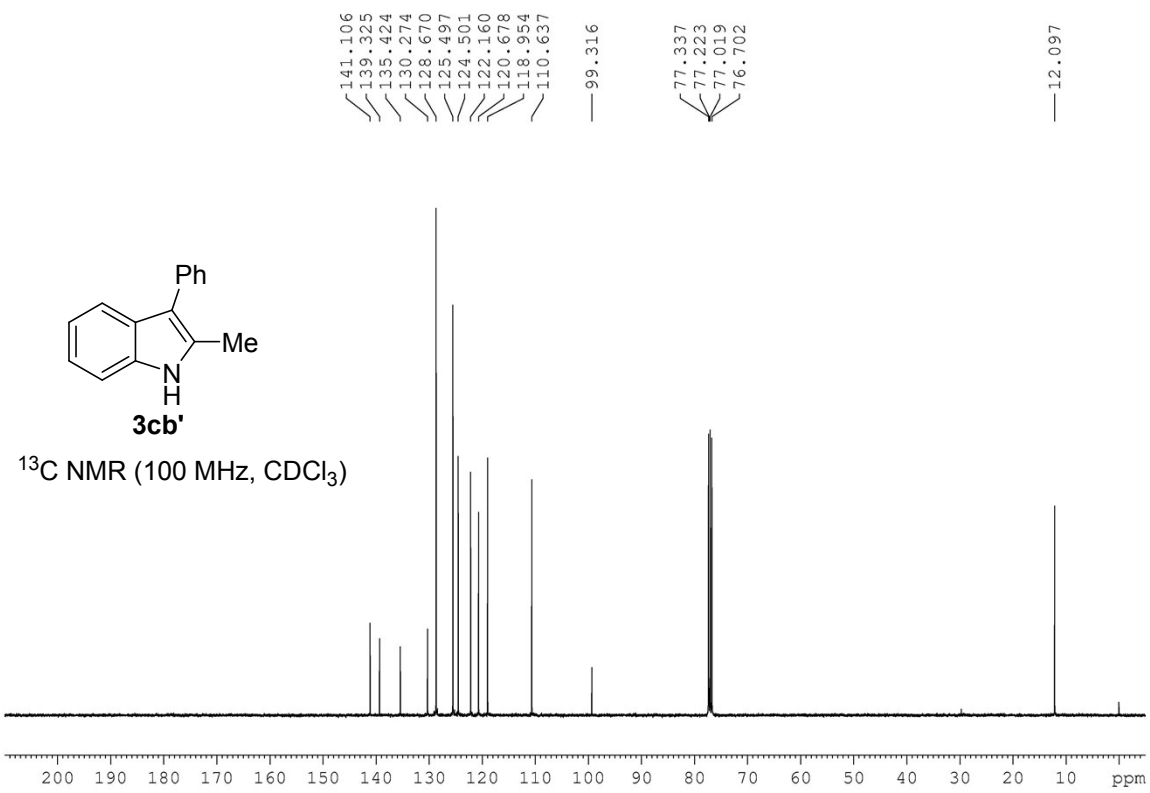
3bb

^{13}C NMR (100 MHz, $CDCl_3$)



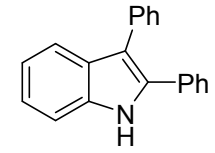
3cb'

^{1}H NMR (400 MHz, $CDCl_3$)



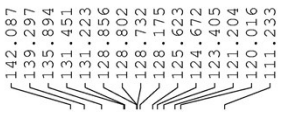
3cb'

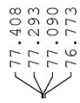
^{13}C NMR (100 MHz, $CDCl_3$)

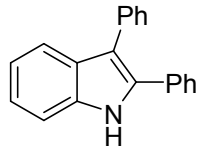


3db'

^{1}H NMR (400 MHz, $CDCl_3$)

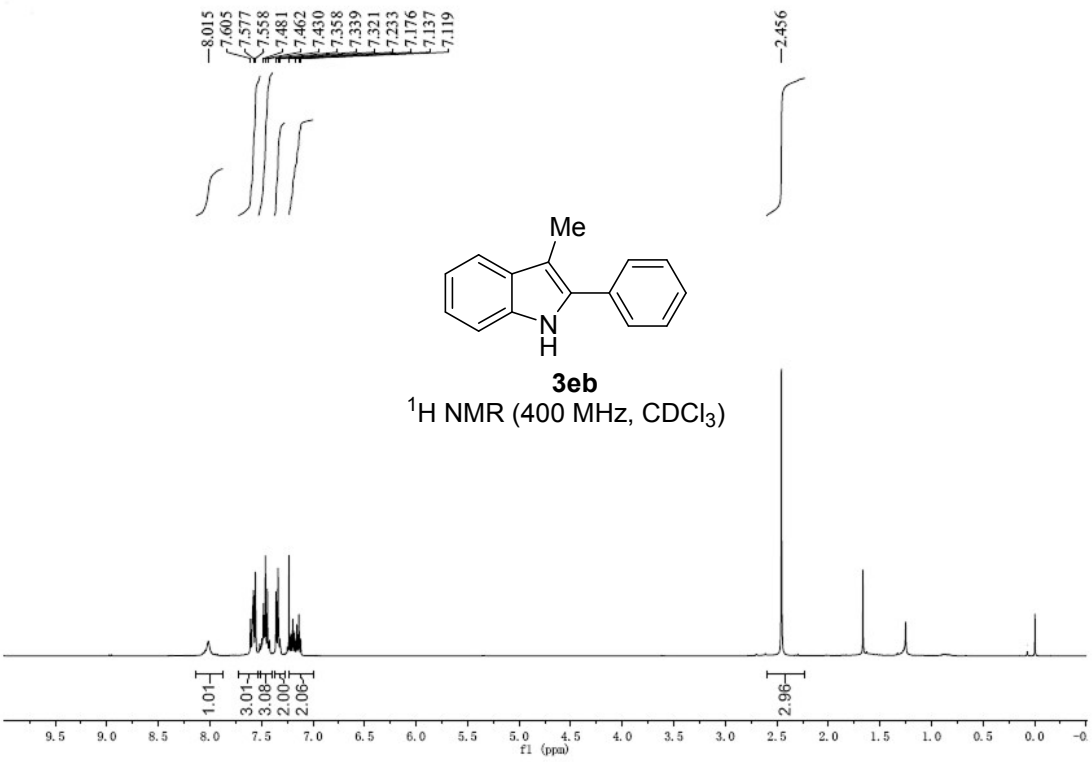






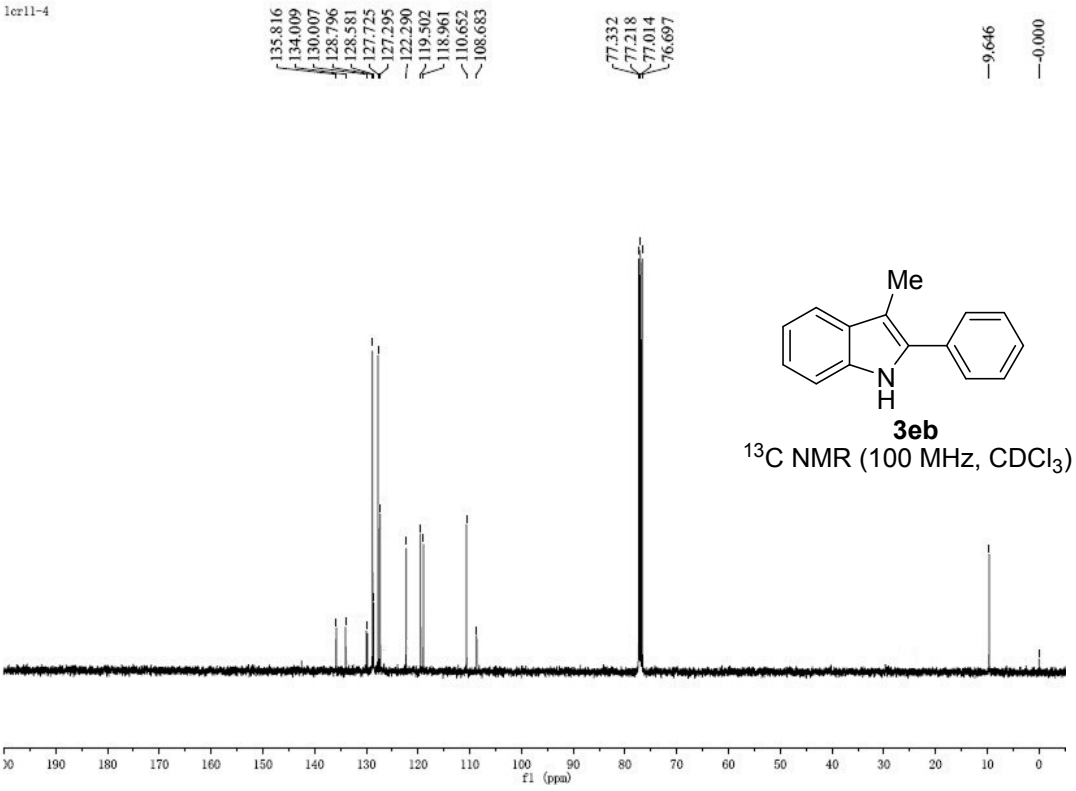
3db'

^{13}C NMR (100 MHz, $CDCl_3$)



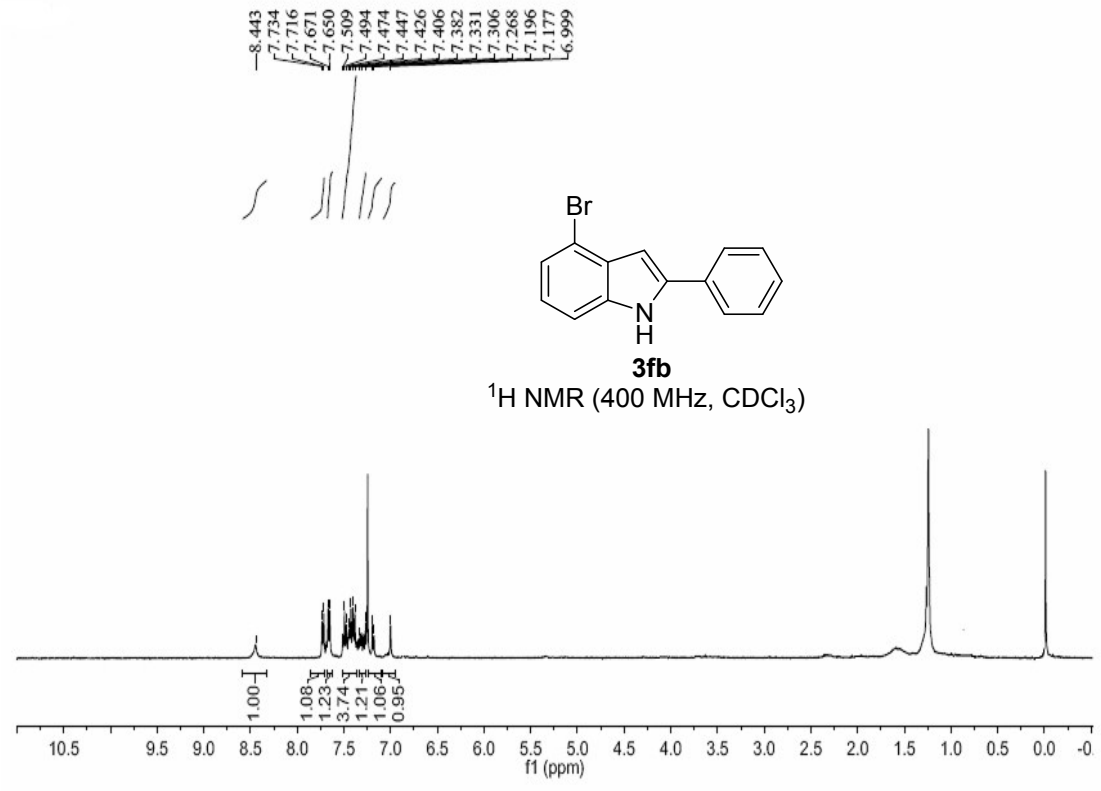
3eb

^{1}H NMR (400 MHz, $CDCl_3$)



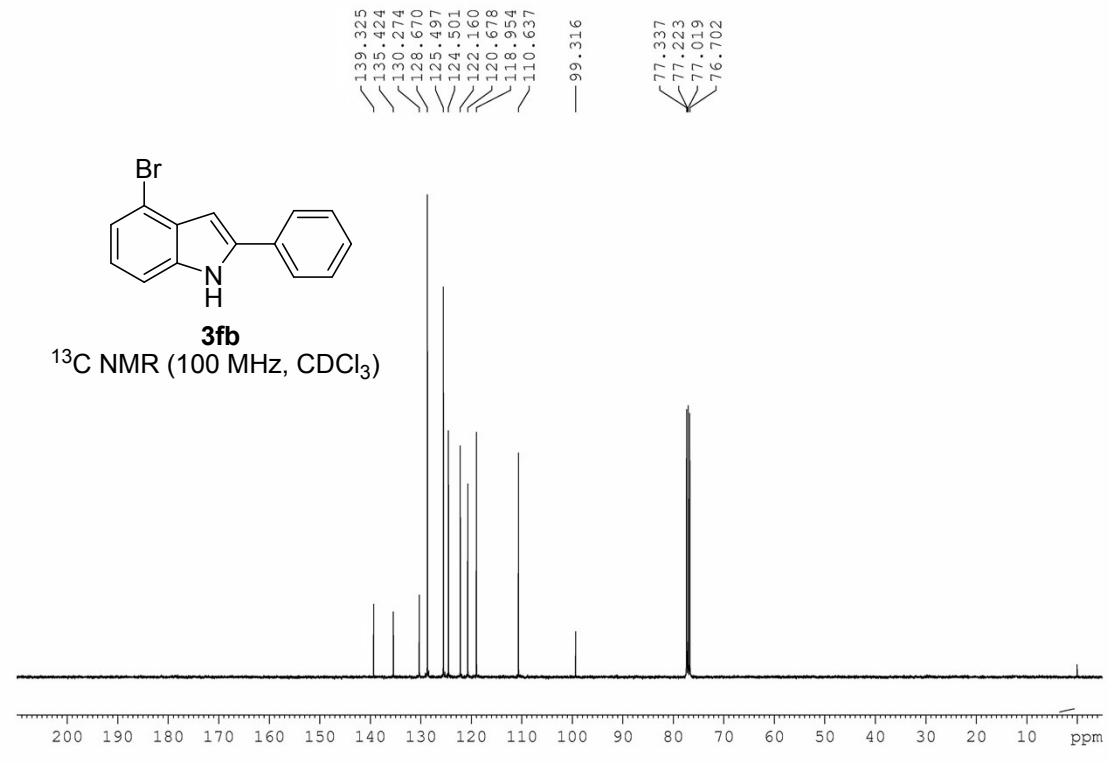
3eb

^{13}C NMR (100 MHz, $CDCl_3$)



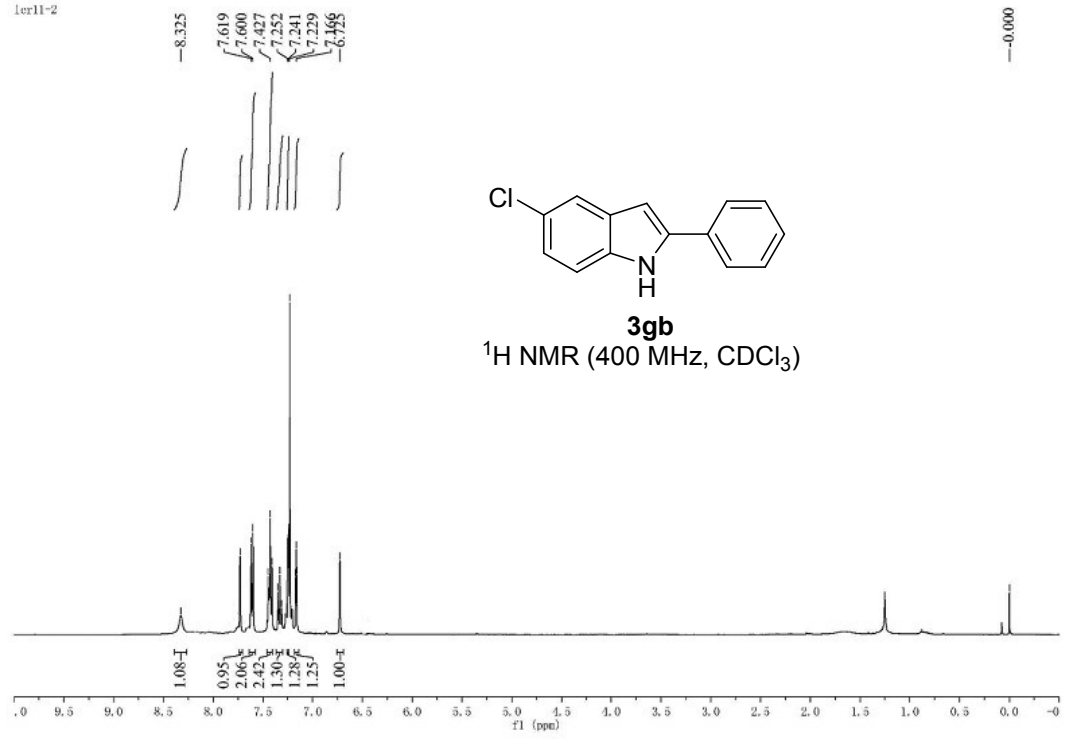
3fb

^{1}H NMR (400 MHz, $CDCl_3$)



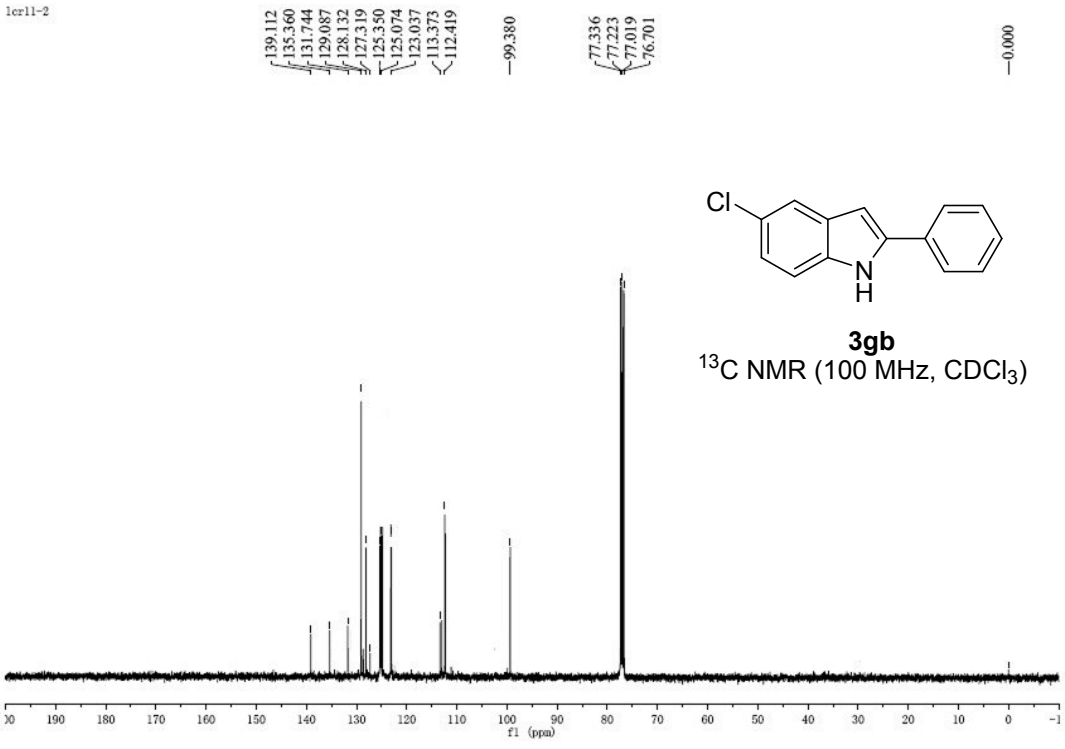
3fb

^{13}C NMR (100 MHz, $CDCl_3$)



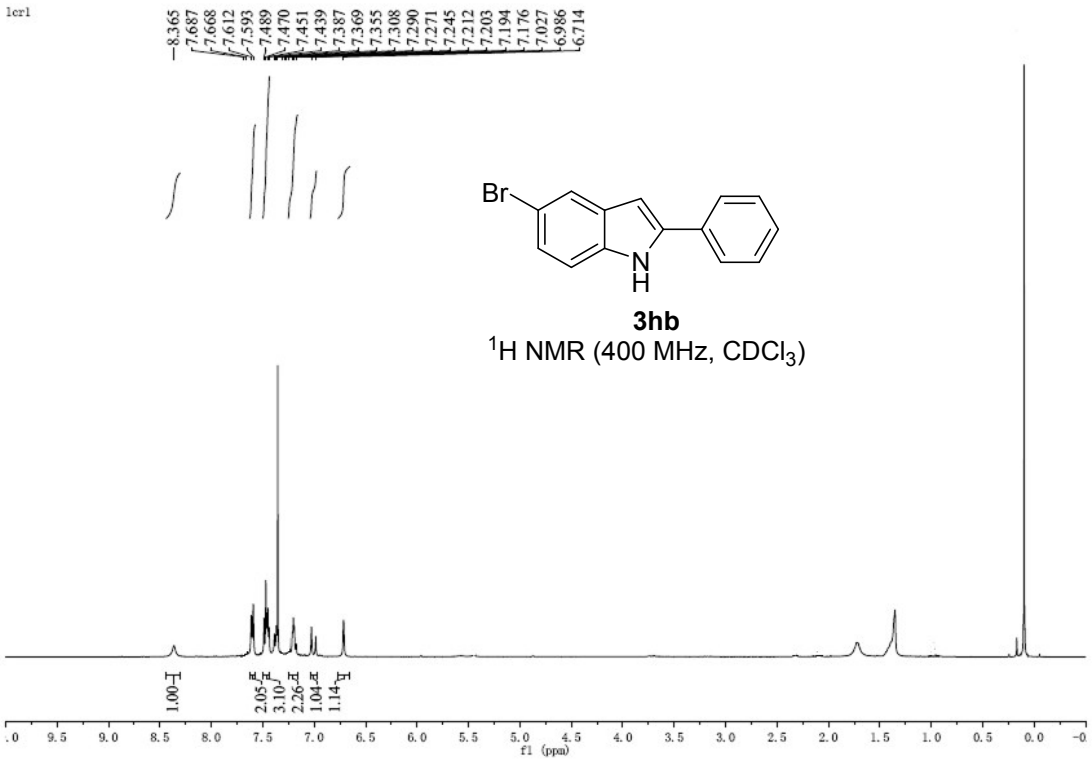
3gb

^{1}H NMR (400 MHz, $CDCl_3$)



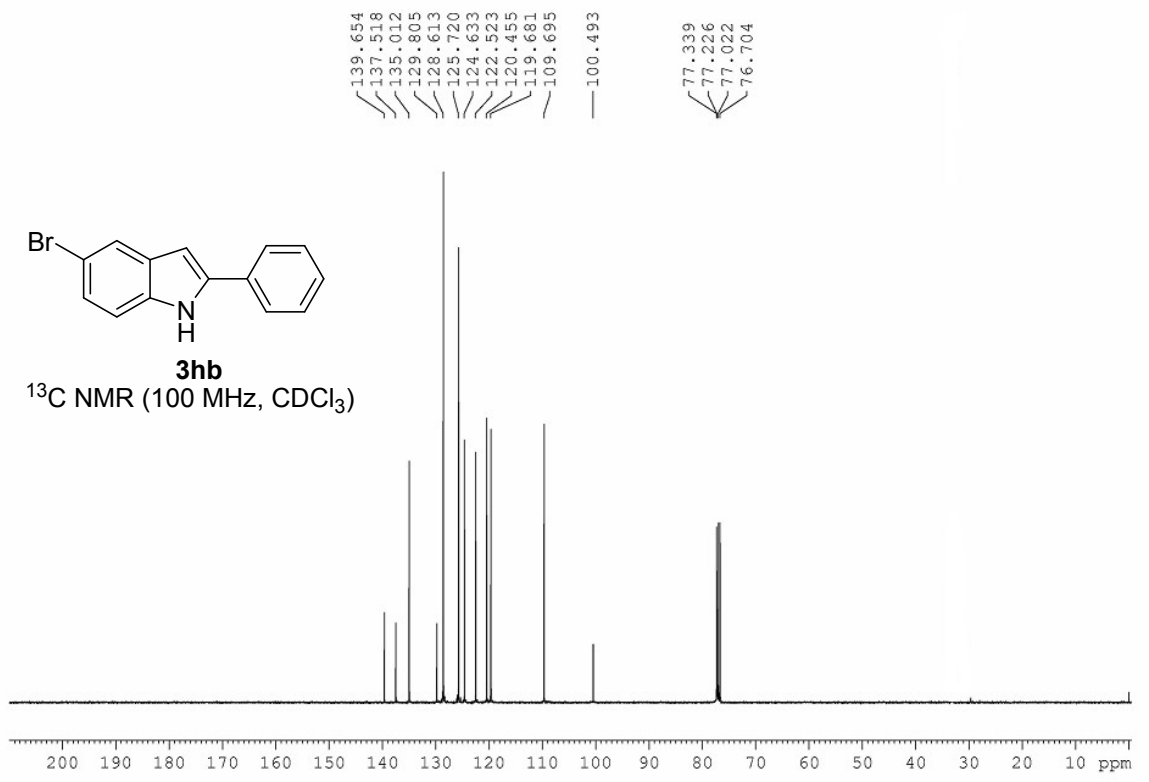
3gb

^{13}C NMR (100 MHz, $CDCl_3$)



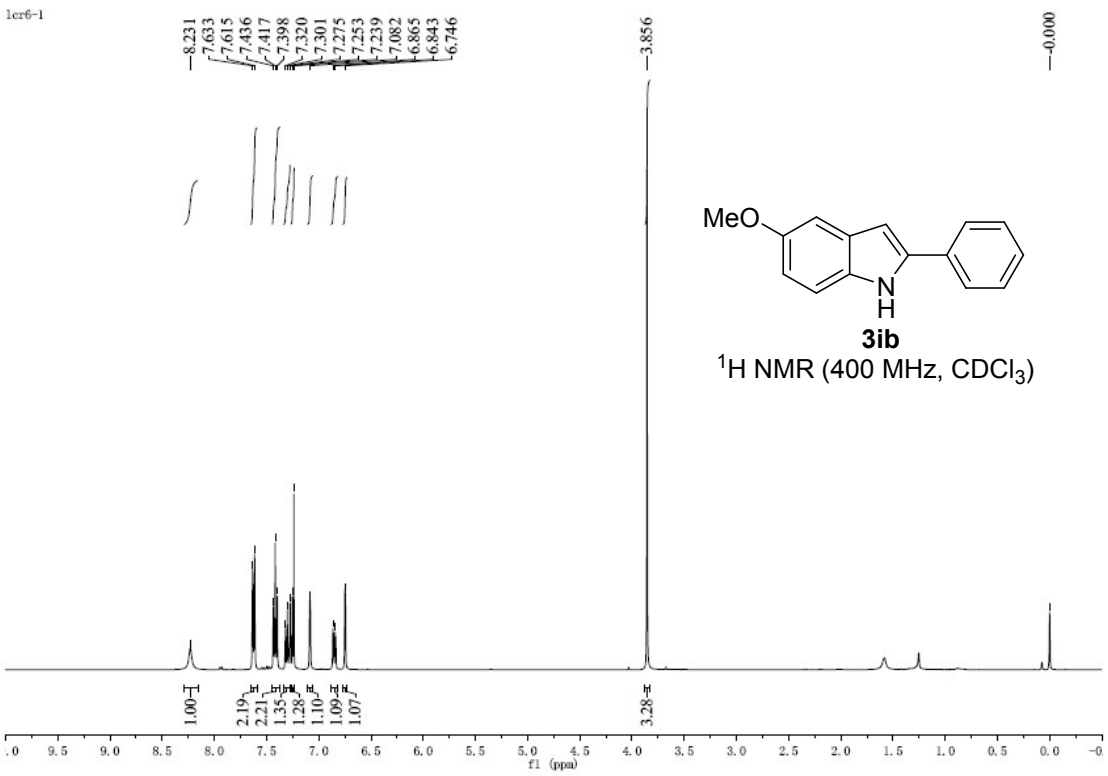
3hb

^{1}H NMR (400 MHz, $CDCl_3$)



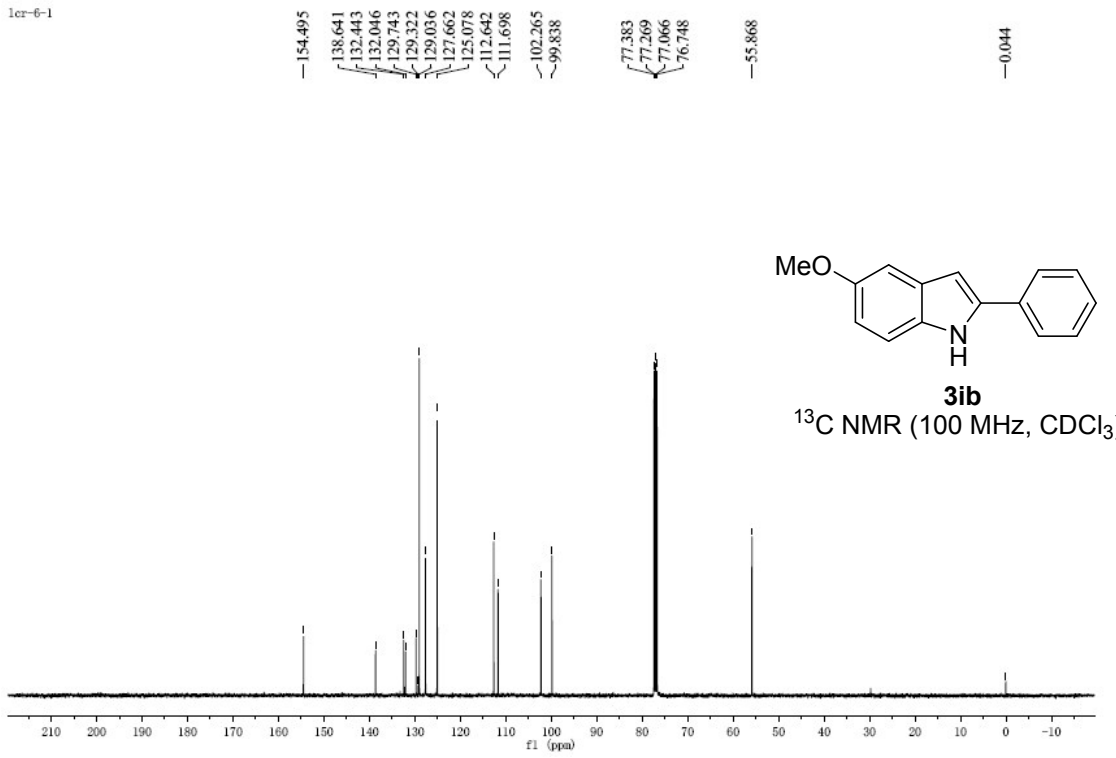
3hb

^{13}C NMR (100 MHz, $CDCl_3$)



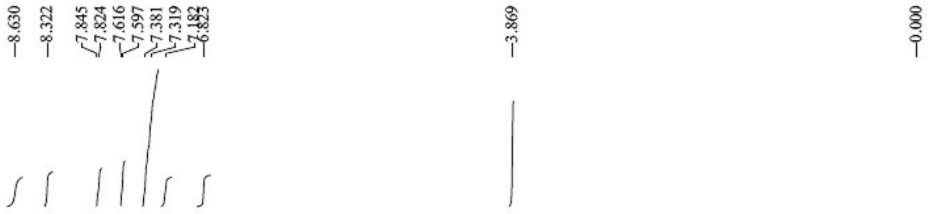
3ib

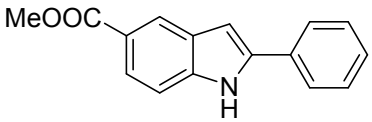
^{1}H NMR (400 MHz, $CDCl_3$)



3ib

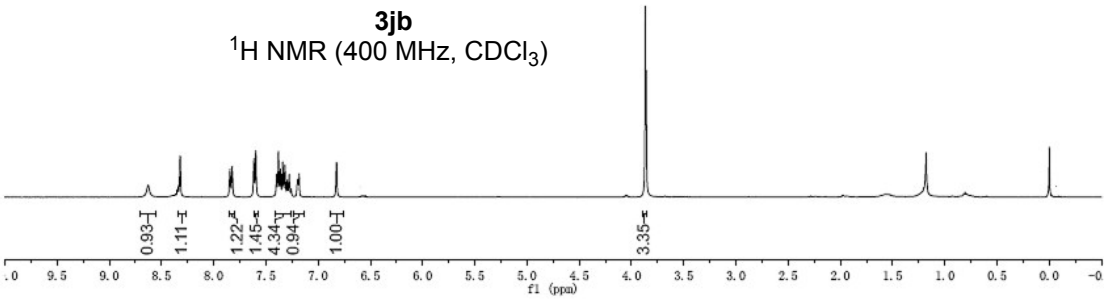
^{13}C NMR (100 MHz, $CDCl_3$)

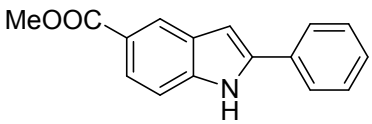




3jb

^{1}H NMR (400 MHz, $CDCl_3$)





3jb

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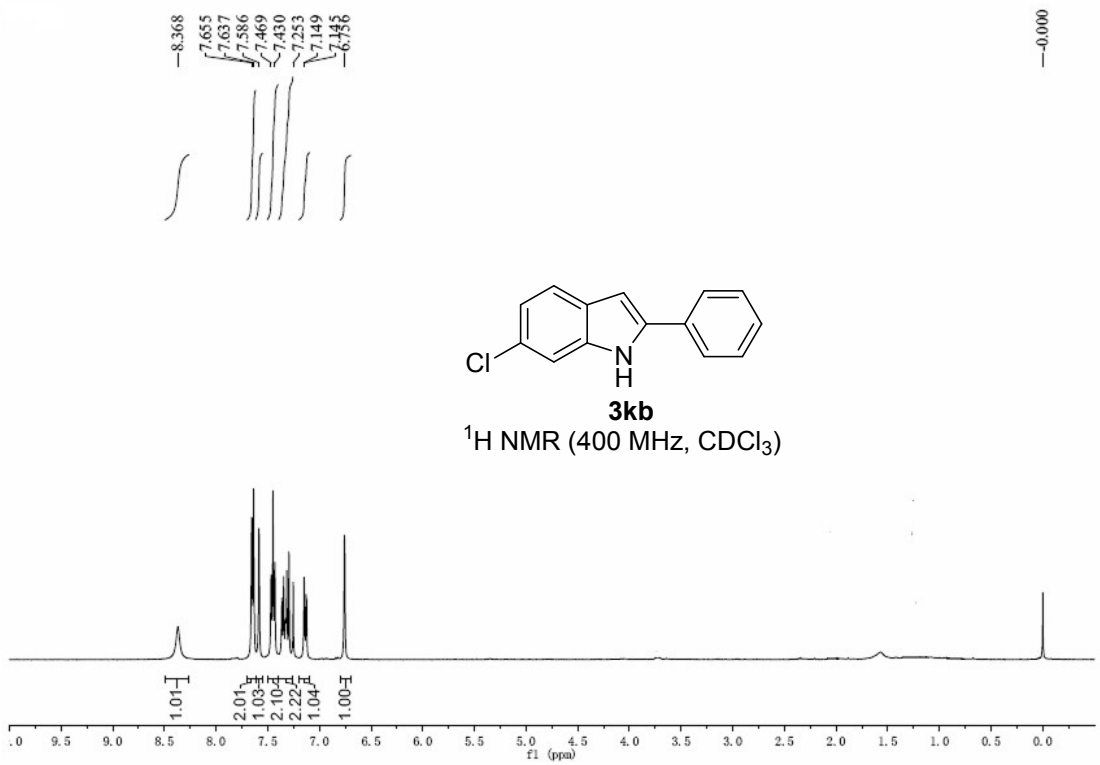
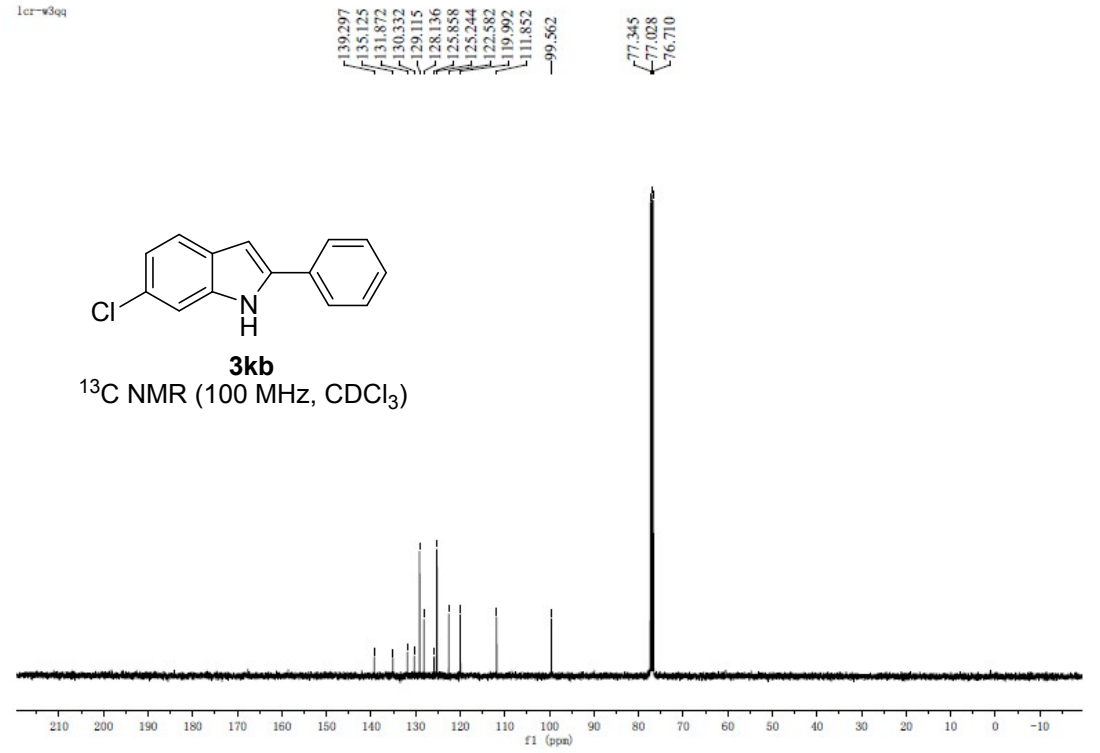


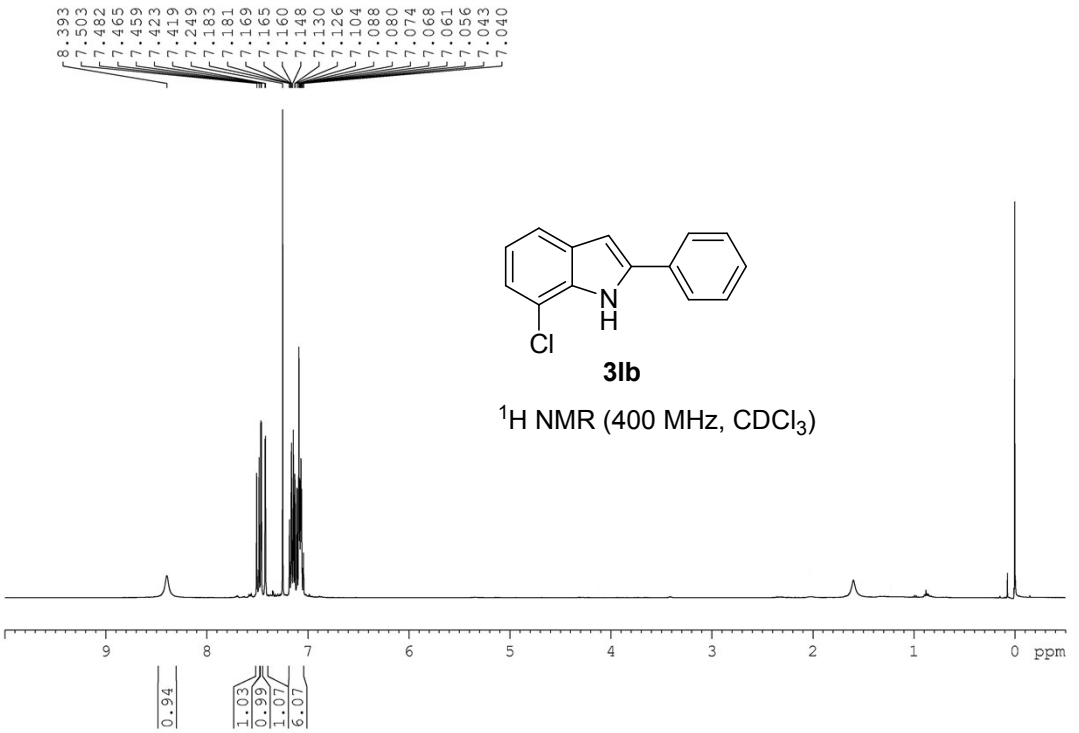
3kb

^{1}H NMR (400 MHz, $CDCl_3$)



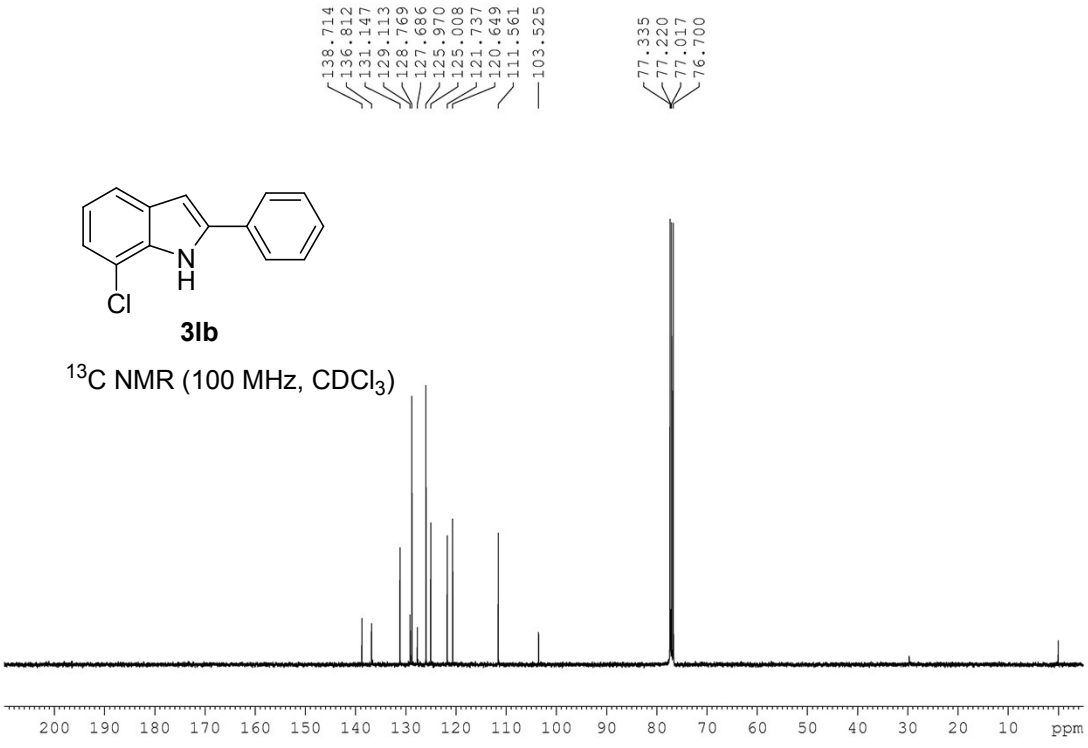
3kb

^{13}C NMR (100 MHz, $CDCl_3$)



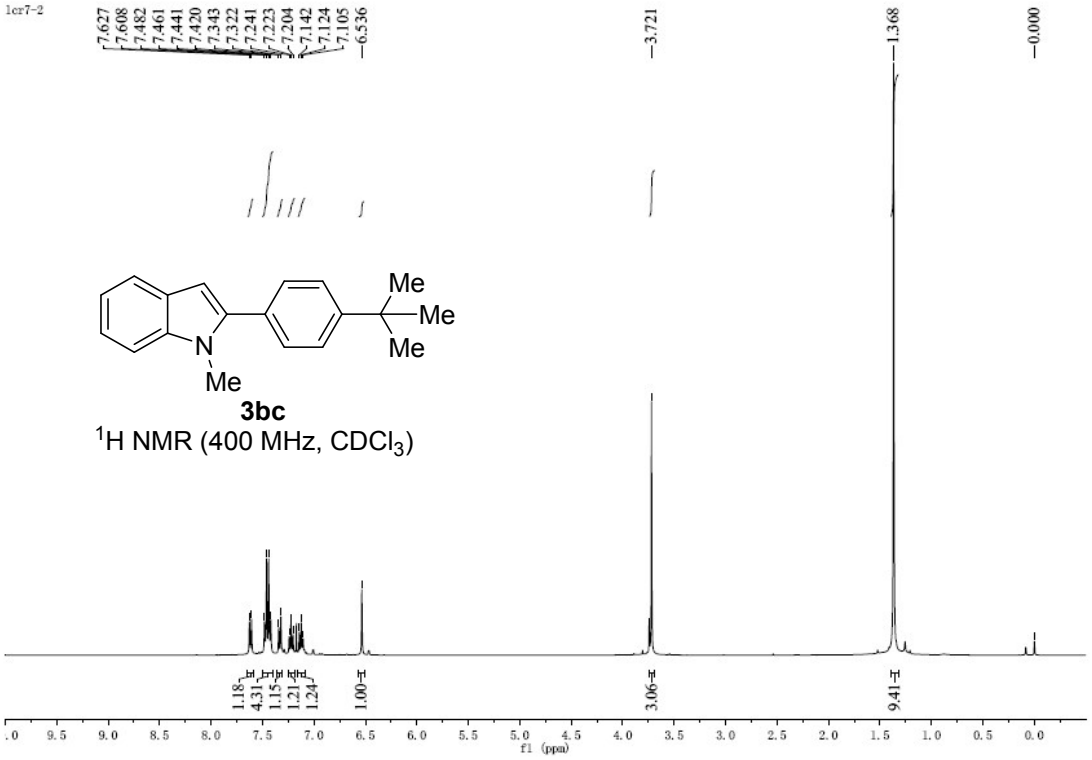
3Ib

^{1}H NMR (400 MHz, $CDCl_3$)



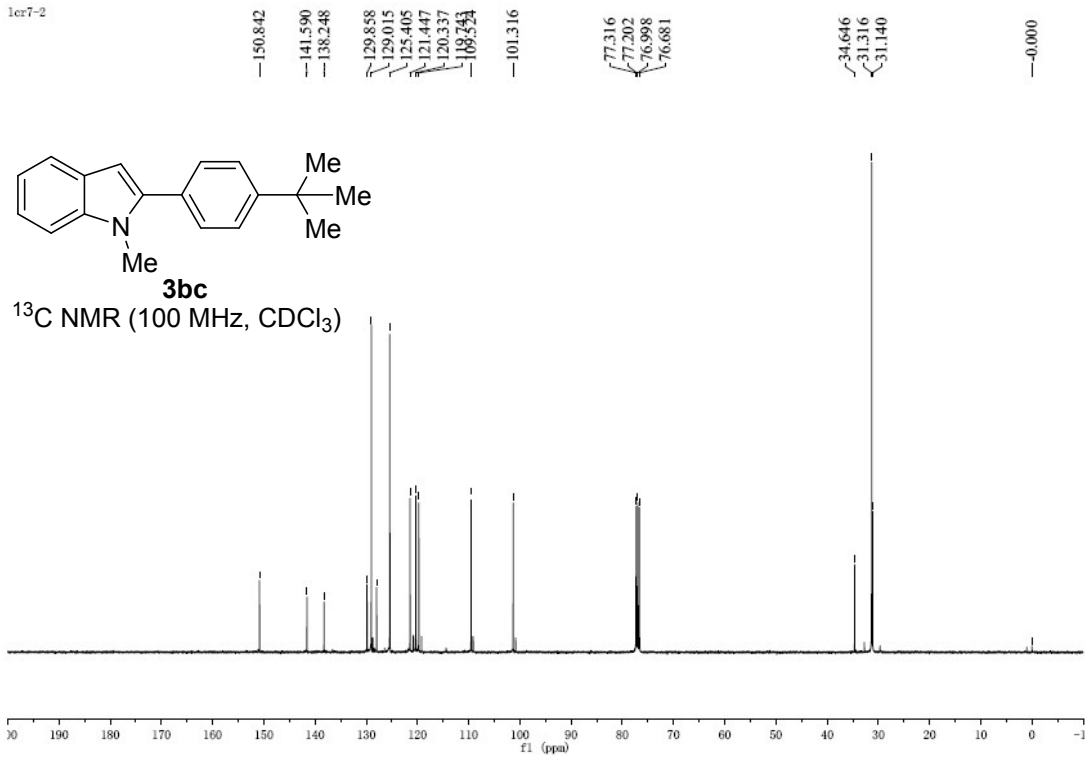
3Ib

^{13}C NMR (100 MHz, $CDCl_3$)



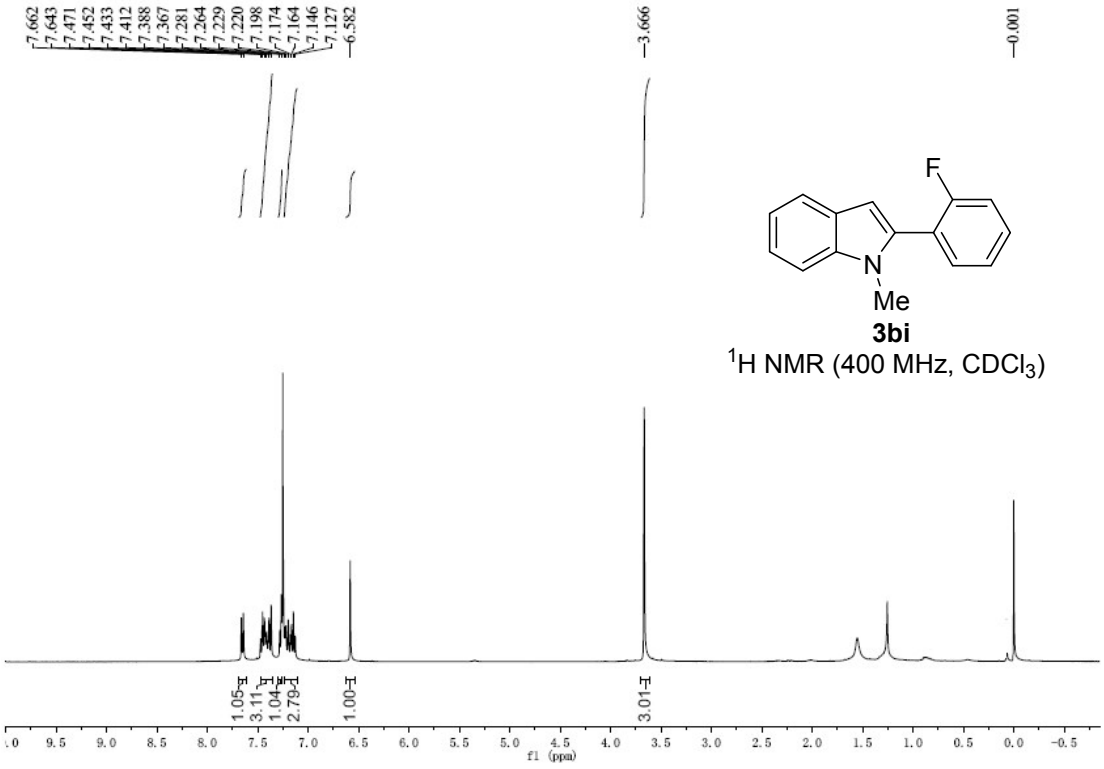
3bc

^{1}H NMR (400 MHz, $CDCl_3$)



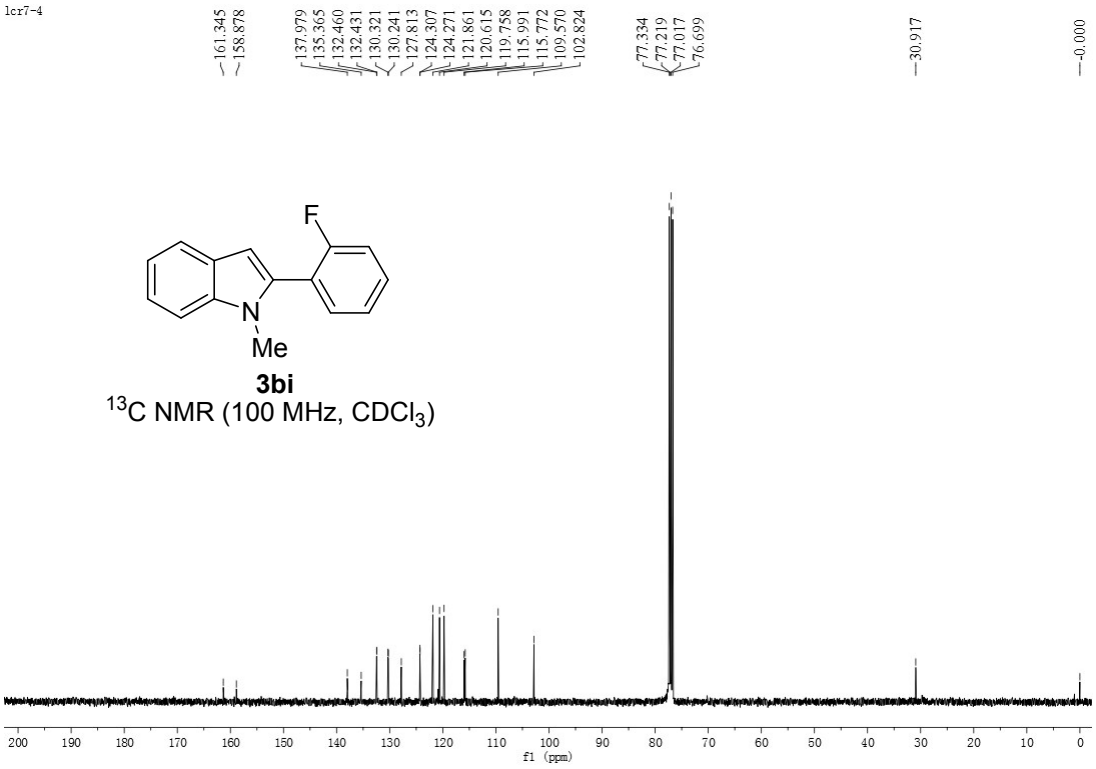
3bc

^{13}C NMR (100 MHz, $CDCl_3$)



3bi

^{1}H NMR (400 MHz, $CDCl_3$)



3bi

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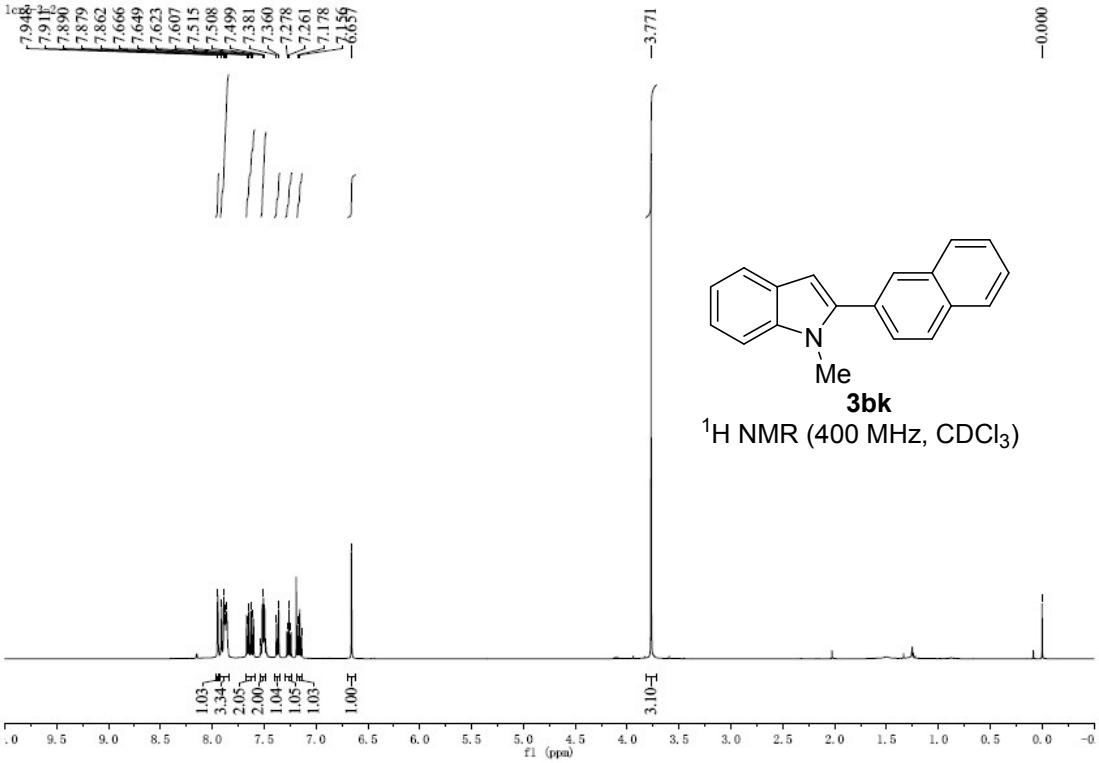
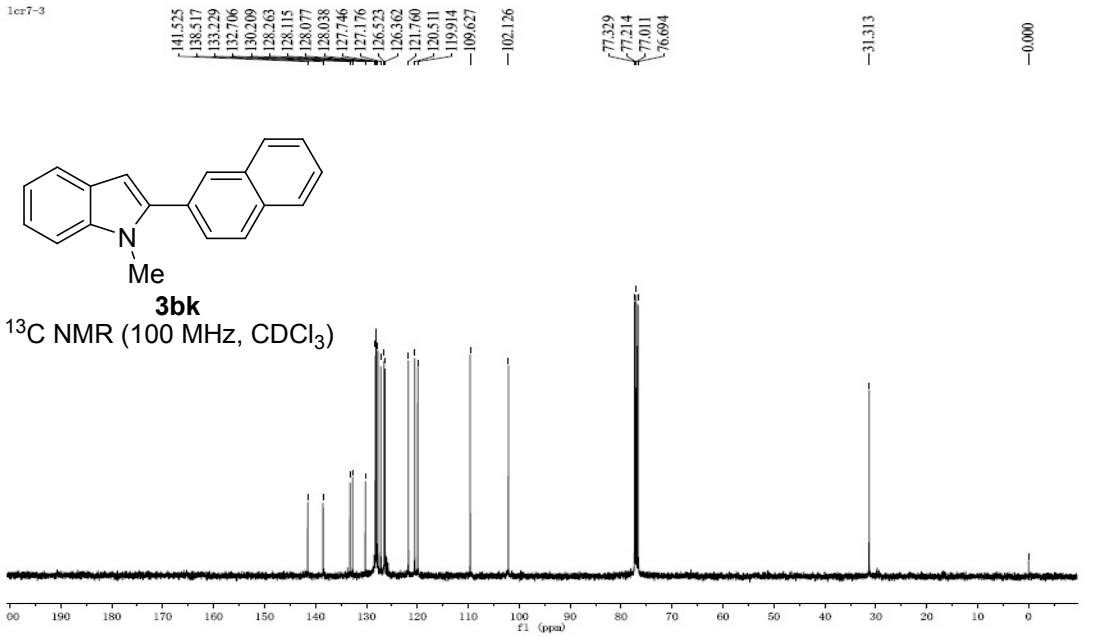


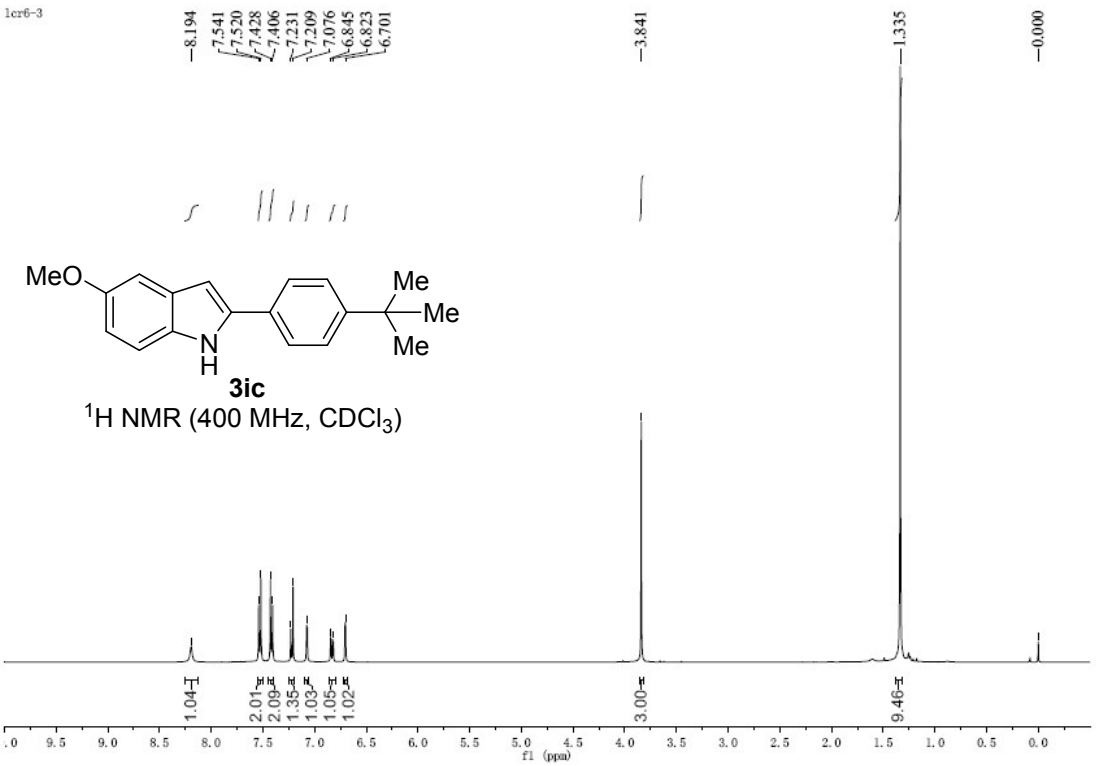
3bk

^{1}H NMR (400 MHz, $CDCl_3$)



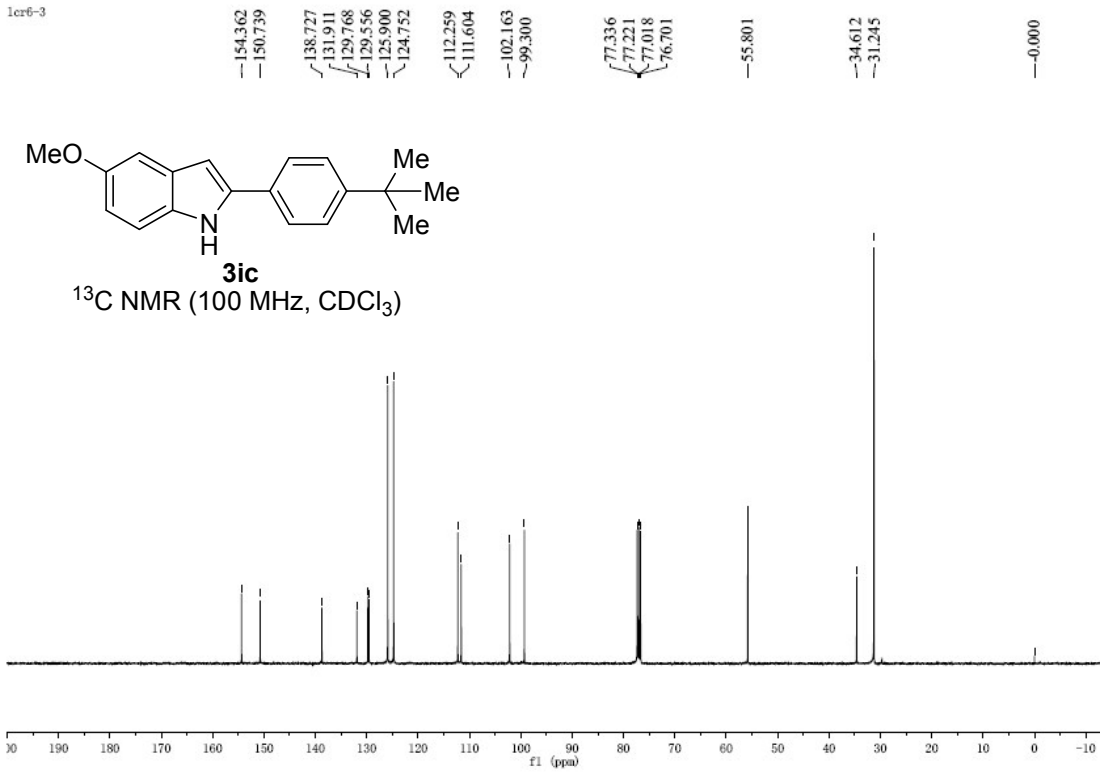
3bk

^{13}C NMR (100 MHz, $CDCl_3$)



3ic

^{1}H NMR (400 MHz, $CDCl_3$)



3ic

^{13}C NMR (100 MHz, $CDCl_3$)