



Supporting Information

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Palladium-Catalyzed Direct Arylation of Aryl (Herero)Arenes with Aryl Boronic Acids

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General. All the reactions were carried out under dry oxygen atmosphere. CH₃COOH was used without further purification. Pd(OAc)₂ was purchased from Alfa Aesar Chemical. ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) were registered on Varian 300M spectrometers with CDCl₃ and acetone-d₆ as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ¹H spectrum as 0.00 ppm and CDCl₃ resonance in the ¹³C spectrum as 77.0 ppm. All coupling constants (*J* values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 200-300 mesh. IR, GC, MS, and HRMS were performed by the State-authorized Analytical Center at Peking University.

General procedures for arylation of mesitylene:

Mesitylene **1a** (120.0 mg, 1.0 mmol, 2.0 equiv), phenyl boronic acid **2a** (61 mg, 0.5 mmol, 1.0 equiv), Cu(OAc)₂ (91.0 mg, 0.5 mmol, 1.0 equiv and Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.05 equiv) were added to a Schlenk tube. After the addition of CF₃COOH (5.0 mL) by syringe, the reaction solution was degassed twice and refilled with O₂ (1.0 atm). The reaction mixture was further stirred for 48 h at room temperature. CF₃COOH was distilled under reduced pressure and recovered. The residue was dissolved in CH₂Cl₂ (50 mL) and washed with aqueous NaHCO₃ (2 x 30 mL). The organic layer was dried over MgSO₄. The desired product **3aa** was detected by GC with the use of *n*-dodecane as an internal standard.

General procedures for 2-arylation of 1-methylindole **1b**:

1-Methylindole **1b** (65.5 mg, 0.5 mmol, 1.0 equiv), phenyl boronic acid **2a** (91.5 mg, 0.75 mmol, 1.5 equiv) and Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.05 equiv) were added to a Schlenk tube. After AcOH (5.0 mL) was added by syringe, the resulting solution was degassed twice and refilled with O₂ (1.0 atm.). The mixture was stirred for 6-8 h at room temperature. AcOH was distilled under reduced pressure and recovered, and the residue was dissolved in CH₂Cl₂ (50 mL) and washed with aqueous NaHCO₃ (2 x 30 mL). The organic layer was dried over MgSO₄. After the removal of the solvent, the product **3ba** was purified in 77% yield by flash chromatography on silica gel (hexanes/dichloromethane = 10:1 as an eluent).

Reaction Condition Screening for Arylation of Mesitylene **1a**.

Table 1. Direct Arylation of mesitylene (**1a**) with phenyl boronic acid (**2a**).^a

Reaction scheme: Mesitylene (**1a**) + Phenyl boronic acid (**2a**) $\xrightarrow[\text{Solvent, rt, 48 h}]{\text{Pd, oxidant}}$ 2-phenylmesitylene (**3aa**)

entry	Pd (mol%)	oxidant (equiv)	solvent	GC yield (%) ^b
1	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (1.0)/O ₂	toluene	< 5
2	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (1.0)/O ₂	DMF	< 5
3	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (1.0)/O ₂	CH ₂ Cl ₂	< 5
4	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (1.0)/O ₂	HOAc	< 5
5	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (1.0)/O ₂	TFA	83
6	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (1.0)	TFA	48
7	Pd(OAc) ₂ (5.0)	Cu(OTf) ₂ (1.0)/O ₂	TFA	12
8	Pd(OAc) ₂ (5.0)	BQ (1.0)	TFA	15
9	Pd(OAc) ₂ (5.0)	TBHP (1.0)	TFA	15
10	Pd(OAc) ₂ (5.0)	oxone (1.0)	TFA	42
11	Pd(OAc) ₂ (5.0)	Cu(OTf) ₂ (0.2)/O ₂	TFA	30
12	Pd(OAc) ₂ (5.0)	O ₂ (1 atm)	TFA	20
13	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (1.0)/O ₂	TFA/CH ₂ Cl ₂	68
14	PdCl ₂ (5.0)	Cu(OAc) ₂ (1.0)/O ₂	TFA	10
15	Pd(PPh) ₃ Cl ₂ (5.0)	Cu(OAc) ₂ (1.0)/O ₂	TFA	19
16	Pd(PhCN) ₂ Cl ₂ (5.0)	Cu(OAc) ₂ (1.0)/O ₂	TFA	18
17	Pd(OTFA) ₂ (5.0)	Cu(OAc) ₂ (1.0)/O ₂	TFA	13
18	Pd(dba) ₂ (5.0)	Cu(OAc) ₂ (1.0)/O ₂	TFA	< 5

^a All the reactions were carried out in the scale of 1.0 mmol of **1a** and 0.5 mmol **2a**.

^b Yield were determined by GC with the *n*-dodecane as an internal standard.

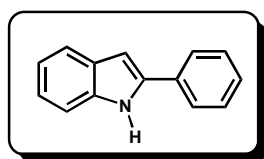
Reaction Condition Screening for Arylation of N-Methylindole 1b.

Table 2. Direct Arylation of N-methylindole (**1b**) with phenyl boronic acid (**2a**).^a

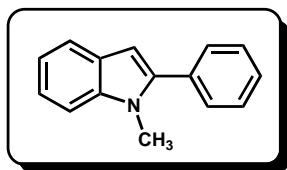
entry	Pd (mol%)	oxidant (equiv)	solvent	GC yield (%) ^b
1 ^c	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (2.0)	CH ₂ Cl ₂	64
2 ^c	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (2.0)	CH ₃ CN	43
3 ^c	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (2.0)	DMF	27
4 ^c	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (2.0)	dioxane	58
5 ^c	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (2.0)	toluene	31
6 ^c	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (2.0)	HOAc	76
7 ^c	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (2.5)	HOAc	89 (74)
8	Pd(OAc) ₂ (5.0)	BQ (1.0)	HOAc	66
9	Pd(OAc) ₂ (5.0)	TBHP (1.0)	HOAc	79
10	Pd(OAc) ₂ (5.0)	oxone (1.0)	HOAc	47
11	Pd(OAc) ₂ (5.0)	Cu(OAc) ₂ (0.2)/O ₂	HOAc	96
12	Pd(OAc) ₂ (5.0)	O ₂ (1 atm)	HOAc	94 (77)
13	PdCl ₂ (5.0)	O ₂ (1 atm)	HOAc	45
14	Pd(PPh) ₃ Cl ₂ (5.0)	O ₂ (1 atm)	HOAc	52
15	Pd(PhCN) ₂ Cl ₂ (5.0)	O ₂ (1 atm)	HOAc	49
16	Pd(OTFA) ₂ (5.0)	O ₂ (1 atm)	HOAc	92
17	Pd(dba) ₂ (5.0)	O ₂ (1 atm)	HOAc	38
18	Pd(OAc) ₂ (1.0)	O ₂ (1 atm)	HOAc	58

^a All the reactions were carried out in the scale of 0.5 mmol of **1b** and 1.0 mmol of **2a**. ^b Yields were determined by GC with the use of with the *n*-dodecane as an internal standard. Isolated yields were reported in parathesis

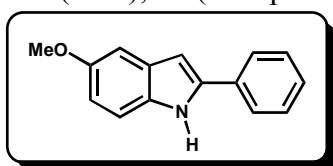
^c These reactions were carried out at 60 °C.



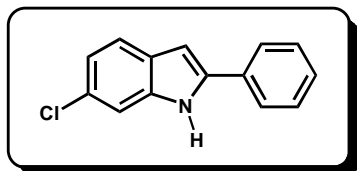
2-Phenyl-1H-indole (11a):¹ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 10 h. product **11a** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0801 g (83%). ¹H NMR (300 MHz, CDCl₃): 8.32 (s, 1 H), 7.69 (d, *J* = 8.4 Hz, 2 H), 7.52 (d, *J* = 7.8 Hz, 1 H), 7.49-7.41 (m, 4 H), 7.33-7.14 (m, 2 H), 6.87-6.6 (m, 1 H). ¹³C NMR (75 MHz, CDCl₃): 137.8, 136.7, 132.3, 129.2, 129.0, 127.7, 125.1, 122.3, 120.6, 120.2, 110.9, 99.9. *m/z* (EI) 193 (M⁺, 100%), 165 (32%); IR (KBr plate, CDCl₃) ν 3444, 1457, 742, 689.



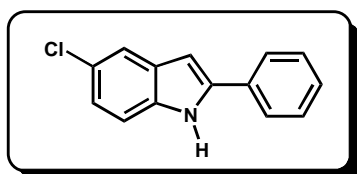
1-Methyl-2-phenyl-1H-indole (3ba):² Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 6-8 h. product **3ba** was obtained after silica gel chromatography (10:1 hexanes: dichloromethane), yield 0.0797 g (77%). ¹H NMR (300 MHz, CDCl₃): 7.64 (d, *J* = 7.9 Hz, 1H), 7.51-7.34 (m, 6H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 6.56 (s, 1H), 3.68 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 141.5, 138.3, 132.8, 129.3, 128.4, 127.9, 127.9, 127.8, 121.6, 120.4, 119.8, 109.6, 101.6, 31.1. *m/z* (EI) 207 (M⁺, 100%), 169 (18%); IR (KBr plate, CDCl₃) ν 3055, 2923, 1468, 749, 702.



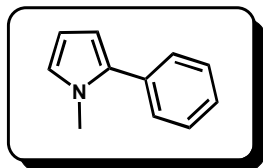
5-Methoxy-2-phenyl-1H-indole (1ma):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 10 h. product **1ma** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0814 g (73%). ¹H NMR (300 MHz, CDCl₃): 8.22 (s, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.43-7.24 (m, 4H), 7.08 (s, 1H), 6.85 (d, *J* = 8.1, 1H), 6.74 (s, 1H), 3.85 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 154.4, 152.0, 138.5, 129.7, 128.1, 127.7, 125.0, 112.6, 111.6, 102.2, 99.8, 55.8. *m/z* (EI) 223 (M⁺, 100%), 199 (22%); IR (KBr plate, CDCl₃) ν 3424, 1476, 1215, 1150, 763, 737.



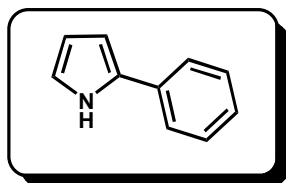
6-Chloro-2-phenyl-1H-indole (1na):⁴ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 20 h. product **1na** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0601 g (53%). ¹H NMR (300 MHz, acetone-d₆): 10.85 (s, 1H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.47-7.35 (m, 2H), 7.34-7.29 (m, 1H), 7.04 (d, *J* = 10.5 Hz, 1H), 6.90 (s, 1H). ¹³C NMR (75 MHz, acetone-d₆): 139.6, 138.3, 132.7, 129.4, 128.5, 128.2, 127.5, 125.6, 121.9, 120.6, 111.4, 99.6. *m/z* (EI) 229 (M⁺, 33%), 227 (M⁺, 100%), 203 (37%); IR (KBr plate, acetone-d₆) ν 3433, 1450, 1346, 1063, 815, 787, 688.



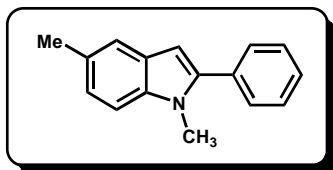
5-Chloro-2-phenyl-1H-indole (10a):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 20 h. product **10a** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0692 g (61%). ¹H NMR (300 MHz, acetone-d₆): 10.85 (s, 1H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.47-7.35 (m, 2H), 7.34-7.29 (m, 1H), 7.04 (d, *J* = 10.5 Hz, 1H), 6.90 (s, 1H). ¹³C NMR (75 MHz, acetone-d₆): 139.6, 138.3, 132.7, 129.4, 128.5, 128.2, 127.5, 125.6, 121.9, 120.6, 111.4, 99.6. *m/z* (EI) 229 (M⁺, 33%), 227 (M⁺, 100%), 203 (37%); IR (KBr plate, acetone-d₆) ν 3350, 1700, 1247, 762, 692.



1-Methyl-2-phenyl-1H-pyrrole (1ja): Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 8 h. product **1ja** was obtained after silica gel chromatography (10:1 hexanes: dichloromethane), yield 0.0307 g (43%). ¹H NMR (300 MHz, acetone-d₆): 7.37-7.50 (m, 4H), 7.27-7.34 (m, 1H), 6.72 (t, *J* = 2.0 Hz, 1H), 6.19-6.26 (m, 2H), 2.88 (s, 3H). ¹³C NMR (75 MHz, acetone-d₆): 134.5, 133.3, 128.5, 128.2, 126.6, 123.6, 108.6, 107.7, 34.9. *m/z* (EI) 143 (M⁺, 100%), 128 (21%); IR (KBr plate, acetone-d₆) ν 3062, 1478, 1308, 741, 698.

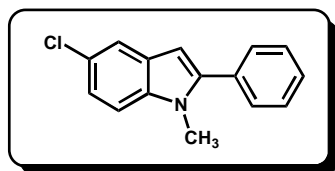


2-Phenyl-1H-pyrrole (1ka): Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 6 h. product **1ka** was obtained after silica gel chromatography (40:10 hexanes: dichloromethane), yield 0.0358 g (56%). ¹H NMR (300 MHz, acetone-d₆): 10.62 (s, 1H), 7.51-7.54 (m, 2H), 7.39-7.45 (m, 2H), 7.21-7.29 (m, 1H), 6.90-6.92 (m, 1H), 6.58-6.60 (m, 1H), 6.36 (d, *J* = 3.6, 1H). ¹³C NMR (75 MHz, acetone-d₆): 133.2, 132.5, 133.2, 132.5, 129.3, 126.6, 124.3, 119.3, 110.5, 106.4. *m/z* (EI) 129 (M⁺, 100%), 54 (13%); IR (KBr plate, acetone-d₆) ν 3434, 3391, 1465, 1033, 904, 757, 719, 605.

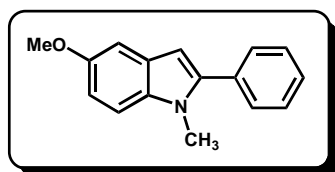


1,5-Dimethyl-2-phenyl-1H-indole (1pa):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 8 h. product **1pa** was obtained after silica gel chromatography (10:1

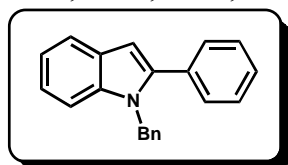
hexanes:dichloromethane), yield 0.0762 g (69%). ^1H NMR (300 MHz, CDCl_3): 7.48-7.34 (m, 6H), 7.21 (d, $J = 8.4$ Hz, 1H), 7.06 (d, $J = 2.1$ Hz, 1H), 6.46 (s, 1H), 3.68 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 141.5, 136.8, 132.9, 130.5, 129.2, 129.0, 128.4, 128.2, 127.6, 123.2, 120.1, 109.3, 101.2, 30.2, 21.4; m/z (EI) 221 (M^+ , 100%), 204 (12%); IR (KBr plate, CDCl_3) ν 3026, 2914, 1478, 1183, 795, 761, 695. Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{N}$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.79; H, 6.81; N, 6.23.



5-Chloro-1-methyl-2-phenyl-1H-indole (10a): Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % $\text{Pd}(\text{OAc})_2$ scale at room temperature for 16 h. product **10a** was obtained after silica gel chromatography (10:1 hexanes: dichloromethane), yield 0.0735 g (61%). ^1H NMR (300 MHz, CDCl_3): 7.64 (d, $J = 2.4$ Hz, 1H), 7.54-7.47 (m, 5H), 7.29-7.21 (m, 3H), 6.54 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3): 142.8, 136.7, 132.2, 130.0, 129.2, 128.8, 128.5, 128.1, 125.4, 121.7, 120.1, 110.5, 101.1, 31.2. m/z (EI) 241 (M^+ , 100%), 205 (31%); IR (KBr plate, CDCl_3) ν 3058, 1470, 1277, 1065, 765, 698. Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{NOCl}$: C, 74.53; H, 5.00; N, 5.79. Found: C, 74.49; H, 4.91; N, 5.68.

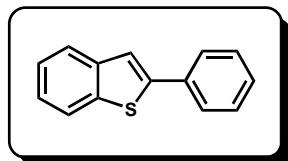


5-Methoxy-1-methyl-2-phenyl-1H-indole (1ra):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % $\text{Pd}(\text{OAc})_2$ scale at room temperature for 8 h. product **1ra** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.1019 g (86%). ^1H NMR (300 MHz, CDCl_3): 7.59-7.46 (m, 5H), 7.32 (d, $J = 9.3$ Hz, 1H), 7.19 (d, $J = 2.4$ Hz, 1H), 7.00 (d, $J = 11.4$, 1H), 6.58 (s, 1H), 3.94 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 154.3, 142.0, 133.7, 132.8, 129.2, 128.4, 128.1, 127.7, 111.8, 110.3, 102.1, 101.2, 55.8, 31.2. m/z (EI) 237 (M^+ , 100%), 222 (55%), 194 (67%); IR (KBr plate, CDCl_3) ν 3054, 2927, 1490, 1209, 1085, 752, 714.

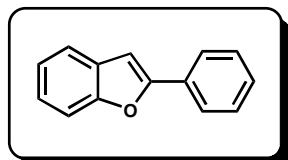


1-Benzyl-2-phenyl-1H-indole (1sa):⁴ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % $\text{Pd}(\text{OAc})_2$ scale at room temperature for 8 h. product **1sa** was obtained after silica gel chromatography (10:1 hexanes: dichloromethane), yield 0.1033 g (73%). ^1H NMR (300MHz, CDCl_3) δ 7.85 (d, $J = 4.2$ Hz, 1H), 7.62 (d, $J = 4.2$ Hz, 2H), 7.60 (m, 3H), 7.51-7.32 (m, 6H), 7.18 (d, $J =$

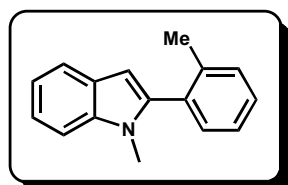
6.3 Hz, 2H), 6.84 (s, 1H), 5.50 (s, 2H), ; ^{13}C NMR (75 MHz, CDCl_3) δ 141.7, 138.1, 137.9, 132.6, 129.1, 128.7, 128.5, 128.2, 127.9, 127.1, 125.9, 121.9, 120.5, 110.5, 102.3, 47.6; m/z (EI) 283 (M^+ , 100%), 165 (9%), 91 (69%); IR (KBr plate, CDCl_3) 3060, 2924, 1461, 1346, 747, 697



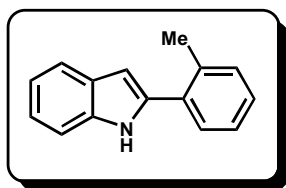
2-Phenyl-benzo[*b*]thiophene (1ha): Following the general procedures, the reaction was performed in a 0.5 mmol, 10 mol % $\text{Pd}(\text{OAc})_2$ and 0.5 mmol $\text{CF}_3\text{SO}_3\text{Na}$ scale at 100°C for 12 h. product **1ha** was obtained after silica gel chromatography (hexanes), yield 0.0714 g (68%). ^1H NMR (300 MHz, CDCl_3): 7.83 (d, J = 8.7 Hz, 2H), 7.55 - 7.39 (m, 4H), 7.35 - 7.21 (m, 3H), 6.98(s, 1H); ^{13}C NMR (75 MHz, CDCl_3): 155.9, 154.8, 130.4, 129.2, 128.8, 128.5, 124.9, 124.2, 122.9, 120.9, 111.1, 101.3; m/z (EI) 178 (M^+ , 100%), 134 (48%); IR (KBr plate, CDCl_3) ν 3021, 1463, 1109, 904, 755, 725, 605.



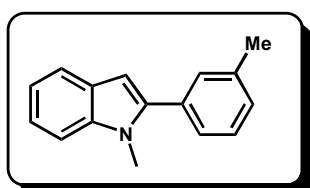
2-Phenyl-benzofuran (1ia): Following the general procedures, the reaction was performed in a 0.5 mmol, 5 mol % $\text{Pd}(\text{OAc})_2$ and 0.5 mmol NaOAc scale at 60°C for 8 h. product **1ia** was obtained after silica gel chromatography (hexanes), yield 0.0213-0.0563 g (22-58%). ^1H NMR (300 MHz, CDCl_3): 7.86 (d, J = 9.9 Hz, 2H), 7.59 - 7.42 (m, 4H), 7.37 - 7.22 (m, 3H), 7.02(s, 1H); ^{13}C NMR (75 MHz, CDCl_3): 155.9, 154.8, 130.4, 129.2, 128.8, 128.5, 124.9, 124.2, 122.9, 120.9, 111.1, 101.3; m/z (EI) 194 (M^+ , 100%), 165 (62%); IR (CHCl_3): 3020, 1615, 1510, 1492, 1109, 904, 755, 725, 605.



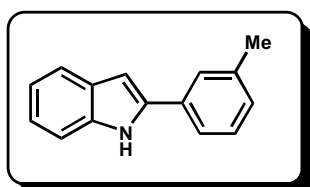
1-Methyl-2-o-tolyl-1H-indole (3bb):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % $\text{Pd}(\text{OAc})_2$ scale at room temperature for 8 h. product **3bb** was obtained after silica gel chromatography (10:1 hexanes: dichloromethane), yield 0.0966 g (87%). ^1H NMR (300 MHz, CDCl_3): 7.63 (d, J = 9.8 Hz, 1H), 7.37-7.14 (m, 7H), 6.55 (s, 1H), 3.75 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 141.7, 138.3, 138.1, 132.7, 130.1, 128.6, 128.3, 127.9, 126.4, 121.5, 120.4, 119.8, 109.5, 101.5, 31.3, 21.5. m/z (EI) 221 (M^+ , 100%), 206 (29%); IR (KBr plate, CDCl_3) ν 3052, 2935, 1463, 766, 749, 734.



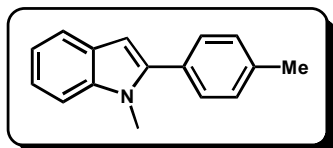
2-o-Tolyl-1H-indole (3lb):⁴ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 10 h. product **3lb** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0517 g (50%). ¹H NMR (300 MHz, acetone-d₆): 7.53 (d, *J* = 7.5 Hz, 1H), 7.22 (s, 1H), 7.15 (s, 1H), 7.05 (s, 1H), 6.88-6.78 (m, 3H), 6.41 (s, 1H), 5.89 (s, 1H), 3.60 (s, 3H). ¹³C NMR (75 MHz, acetone-d₆): 147.5, 141.2, 138.1, 127.8, 126.6, 123.1, 121.5, 120.3, 119.8, 109.7, 108.3, 101.2, 31.0. *m/z* (EI) 207 (M⁺, 100%), 155 (13%); IR (KBr plate, acetone-d₆) ν 3400, 1455, 1302, 797, 746, 720.



1-Methyl-2-m-tolyl-1H-indole (3bc):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 8 h. product **3bc** was obtained after silica gel chromatography (10:1 hexanes: dichloromethane), yield 0.0966 g (87%). ¹H NMR (300 MHz, CDCl₃): 7.61 (d, *J* = 7.5 Hz, 1H), 7.32-7.12 (m, 7H), 6.53 (s, 1H), 3.67 (s, 3H), 2.39 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 141.7, 138.3, 138.1, 132.7, 130.0, 128.6, 128.3, 127.9, 126.4, 121.5, 120.4, 119.7, 109.5, 101.5, 31.1, 21.4. *m/z* (EI) 221 (M⁺, 100%), 204 (20%); IR (KBr plate, CDCl₃) ν 3050, 1465, 1146, 776, 749, 701.

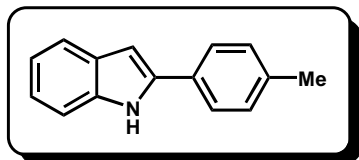


2-m-Tolyl-1H-indole (3lc):⁴ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 10 h. product **3lc** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0755 g (73%). ¹H NMR (300 MHz, acetone-d₆): 10.51 (s, 1H), 7.69-7.55 (m, 3H), 7.43 (d, *J* = 9.0 Hz, 1H), 7.16-7.00 (m, 3H), 6.87 (s, 1H), 2.35 (s, 3H). ¹³C NMR (75 MHz, acetone-d₆): 143.4, 143.2, 142.6, 137.8, 134.5, 133.9, 130.8, 127.3, 126.8, 125.3, 124.7, 116.2, 104.1, 25.7. *m/z* (EI) 207 (M⁺, 100%), 155 (16%); IR (KBr plate, acetone-d₆) ν 3431, 2921, 1607, 1303, 785, 747, 688.

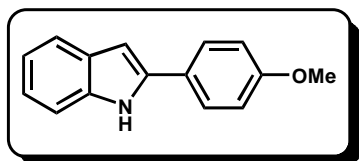


1-Methyl-2-p-tolyl-1H-indole (3bd):³ Following the general procedures, the reaction

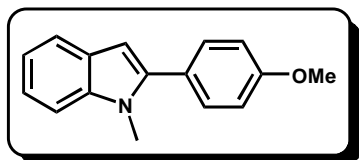
was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 8 h. product **3bd** was obtained after silica gel chromatography (10:1 hexanes: dichloromethane), yield 0.0718 g (65%). ¹H NMR (300 MHz, CDCl₃): 7.73 (d, *J* = 8.4 Hz, 1H), 7.51-7.43 (m, 3H), 7.38-7.31 (m, 3H), 7.25 (m, 1H), 6.64 (s, 1H), 3.81 (s, 3H), 2.51 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 141.6, 138.2, 137.7, 129.9, 129.2, 129.1, 127.9, 121.4, 120.3, 119.7, 109.5, 101.2, 31.0, 21.2. *m/z* (EI) 221 (M⁺, 100%), 204 (11%); IR (KBr plate, CDCl₃) ν 3054, 2913, 1465, 828, 773, 751.



2-p-Tolyl-1H-indole (3ld):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 10 h. product **3ld** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0797 g (77%). ¹H NMR (300 MHz, acetone-d₆): 10.56 (s, 1H), 7.71 (t, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.38-7.34 (m, 1H), 7.23 (d, *J* = 7.8, 1H), 7.08-7.03 (m, 2H), 7.00-6.95 (m, 1H), 6.80 (s, 1H), 2.29 (s, 3H). ¹³C NMR (75 MHz, acetone-d₆): 138.1, 137.1, 130.8, 130.2, 125.7, 122.3, 120.8, 120.2, 111.8, 99.2, 21.0. *m/z* (EI) 221 (M⁺, 100%), 169 (18%); IR (KBr plate, acetone-d₆) ν 3441, 1698, 1248, 904, 790, 748.

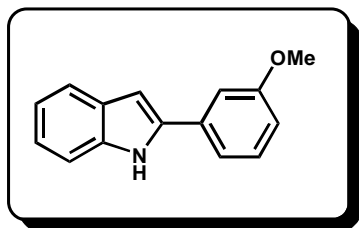


2-(4-Methoxy-phenyl)-1H-indole (3le):⁴ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 10 h. product **3le** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0591 g (53%). ¹H NMR (300 MHz, acetone-d₆): 10.55 (s, 1H), 7.85-7.77 (m, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 9.0, 1H), 7.01-6.97 (m, 4H), 6.76 (s, 1H), 3.86 (s, 3H). ¹³C NMR (75 MHz, acetone-d₆): 165.1, 143.8, 143.1, 135.2, 132.1, 131.1, 126.9, 125.5, 125.1, 120.0, 116.6, 103.5, 60.4. *m/z* (EI) 223 (M⁺, 100%), 109 (53%); IR (KBr plate, acetone-d₆) ν 3432, 1501, 1027, 834, 786, 748.

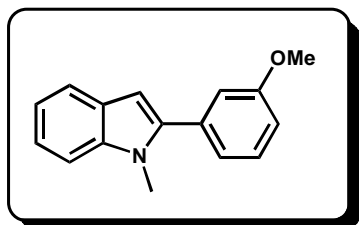


2-(4-Methoxy-phenyl)-1-methyl-1H-indole (3be):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 8 h. product **3be** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0995 g (84%). ¹H NMR (300 MHz, CDCl₃): 7.67 (d, *J* = 8.7 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 9.9 Hz, 1H), 7.22 (m, 1H), 7.04 (d, *J* = 11.7 Hz, 2H), 6.55 (s, 1H), 3.92 (s, 3H), 3.76 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 159.3, 141.3, 138.1, 130.5, 127.9, 125.1, 121.3,

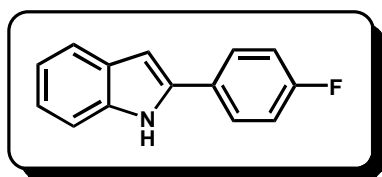
120.2, 119.7, 113.9, 109.5, 100.9, 55.2, 30.9. m/z (EI) 237 (M^+ , 100%), 222 (63%); IR (KBr plate, $CDCl_3$) ν 3050, 2924, 1496, 1466, 1245, 841, 786, 750.



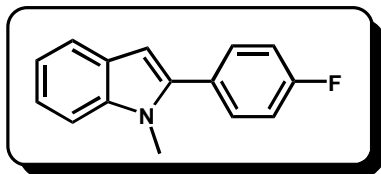
2-(3-Methoxy-phenyl)-1H-indole (3lf):⁴ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % $Pd(OAc)_2$ scale at room temperature for 10 h. product **3lf** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0669 g (60%). 1H NMR (300 MHz, $CDCl_3$): 8.23 (s, 1H), 7.61 (d, $J = 7.2$ Hz, 2H), 7.43-7.24 (m, 4H), 7.08 (s, 1H), 6.84 (d, $J = 8.4$ Hz, 1H), 6.74 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 154.4, 152.0, 138.6, 129.7, 128.9, 127.5, 125.0, 112.6, 111.6, 102.2, 99.8, 55.8. m/z (EI) 223 (M^+ , 100%), 109 (53%); IR (KBr plate, $CDCl_3$) ν 3432, 1501, 1027, 834, 786, 748.



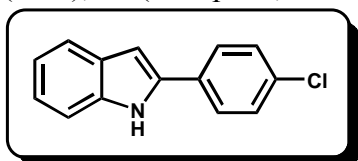
2-(3-Methoxy-phenyl)-1-methyl-1H-indole (3bf):⁴ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % $Pd(OAc)_2$ scale at room temperature for 8 h. product **3bf** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0995 g (84%). 1H NMR (300 MHz, $CDCl_3$): 7.68 (d, $J = 8.4$ Hz, 1H), 7.38-7.27 (m, 2H), 7.22 (d, $J = 8.2$ Hz, 1H), 7.19-7.09 (m, 2H), 6.99 (d, $J = 9.3$, 1H), 6.62 (s, 1H), 3.88 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 159.5, 141.3, 138.3, 134.1, 129.4, 127.8, 121.7, 120.4, 119.8, 115.0, 113.3, 109.6, 101.6, 55.3, 31.1. m/z (EI) 237 (M^+ , 100%), 194 (25%); IR (KBr plate, $CDCl_3$) ν 3050, 2924, 1496, 1466, 1245, 841, 786, 750.



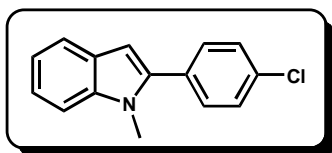
2-(4-Fluoro-phenyl)-1H-indole (3lg):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 10 mol % $Pd(OAc)_2$ scale at room temperature for 22 h. product **3lg** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0812 g (77%). 1H NMR (300 MHz, acetone- d_6): δ 10.58 (s, 1H), 7.89-7.84 (m, 1H), 7.56 (d, $J = 8.1$ Hz, 1H), 7.42 (d, $J = 10.2$ Hz, 1H), 7.24-7.01 (m, 3H), 6.84 (s, 1H). ^{13}C NMR (75 MHz, acetone- d_6): δ 164.3, 138.1, 129.9, 127.6, 127.5, 122.4, 120.8, 120.2, 116.3, 116.1, 111.7, 99.6. m/z (EI) 211 (M^+ , 100%), 169 (34%); IR (KBr plate, acetone- d_6) ν 3415, 1499, 1235, 837, 794, 756.



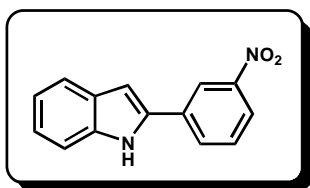
2-(4-Fluorophenyl)-1-methyl-1H-indole (3bg):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 16 h. product **3bg** was obtained after silica gel chromatography (10:1 hexanes: dichloromethane), yield 0.0922 g (82%). ¹H NMR (300 MHz, CDCl₃): 7.64 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.35-7.12 (m, 5H), 7.10 (d, *J* = 7.2, 1H), 6.48 (s, 1H), 3.78 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 136.6, 131.0, 128.6, 127.8, 121.8, 121.4, 120.7, 119.6, 115.4, 109.4, 100.8, 32.8. *m/z* (EI) 225 (M⁺, 100%), 183 (18%); IR (KBr plate, CDCl₃) ν 3061, 2925, 1495, 1219, 842, 787, 734.



2-(4-Chlorophenyl)-1H-indole (3lh):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 10 mol % Pd(OAc)₂ scale at room temperature for 22 h. product **3lh** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0874 g (77%). ¹H NMR (300 MHz, acetone-d₆): δ 11.59 (s, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.1, 1H), 7.00 (d, *J* = 7.8, 1H), 6.94 (d, *J* = 0.9 Hz, 1H). ¹³C NMR (75 MHz, acetone-d₆): δ 137.1, 136.3, 131.7, 131.4, 128.4, 126.8, 121.8, 120.2, 120.1, 119.4, 111.3, 99.2. *m/z* (EI) 227 (M⁺, 100%), 191 (22%); IR (KBr plate, acetone-d₆) ν 3443, 1701, 1246, 1095, 831, 793, 748.

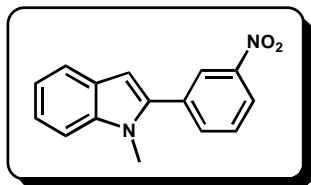


2-(4-Chlorophenyl)-1-methyl-1H-indole (3bh):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 12 h. product **3bh** was obtained after silica gel chromatography (10:1 hexanes: dichloromethane), yield 0.0819 g (68%). ¹H NMR (300 MHz, CDCl₃): 7.80-7.66 (m, 5H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.37 (m, 1H), 7.27 (d, *J* = 7.9, 1H), 6.71 (s, 1H), 3.81 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 139.8, 138.7, 136.3, 129.4, 127.8, 125.4, 122.3, 120.9, 120.2, 109.7, 102.8, 31.2. *m/z* (EI) 241 (M⁺, 100%), 205 (19%); IR (KBr plate, CDCl₃) ν 3058, 2923, 1323, 1109, 1067, 789, 732.

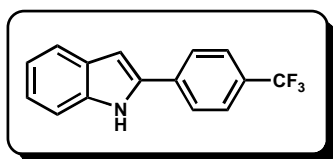


2-(3-Nitrophenyl)-1H-indole (3li):⁶ Following the general procedures, the reaction

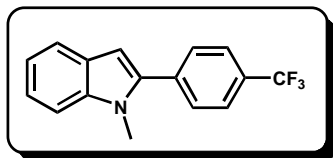
was performed in a 0.5 mmol and 10 mol % Pd(OAc)₂ scale at room temperature for 24 h. product **3li** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0976 g (82%). ¹H NMR (300 MHz, acetone-d₆): δ 10.53 (s, 1H), 8.35 (s, 1H), 8.21 (d, *J* = 9.0, 1H), 7.81 (d, *J* = 9.0, 1H), 7.66-7.58 (m, 2H), 7.38-7.16 (m, 4H), 6.65(s, 1H). ¹³C NMR (75 MHz, acetone-d₆): δ 148.3, 138.7, 134.9, 134.4, 129.5, 127.6, 123.6, 122.6, 120.8, 120.3, 109.8, 103.2. *m/z* (EI) 238 (M⁺, 100%), 192 (21%); IR (KBr plate, acetone-d₆) ν 3370, 1517, 1349, 794, 734.



1-Methyl-2-(3-nitro-phenyl)-1H-indole (3bi):⁶ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 16 h. product **3bi** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0794 g (63%). ¹H NMR (300 MHz, CDCl₃): δ 8.35 (s, 1H), 8.21 (d, *J* = 9.0, 1H), 7.81 (d, *J* = 9.0, 1H), 7.66-7.58 (m, 2H), 7.38-7.16 (m, 4H), 6.65(s, 1H), 3.76 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 148.3, 138.7, 134.9, 134.4, 129.5, 127.6, 123.6, 122.6, 120.8, 120.3, 109.8, 103.2, 31.3. *m/z* (EI) 252 (M⁺, 100%), 206 (18%); IR (KBr plate, CDCl₃) ν 2963, 2917, 1523, 1348, 738, 727.

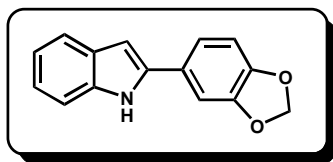


2-(4-Trifluoromethyl-phenyl)-1H-indole (3lj):⁴ Following the general procedures, the reaction was performed in a 0.5 mmol and 10 mol % Pd(OAc)₂ scale at room temperature for 22 h. product **3lj** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0770 g (59%). ¹H NMR (300MHz, acetone-d₆) δ 10.36(br, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.43-7.24 (m, 4H), 6.64 (s, 1H); ¹³C NMR (75 MHz, acetone-d₆) δ 140.2, 138.4, 133.9, 130.4, 128.7, 121.9, 120.5, 119.9, 109.6, 101.9; *m/z* (EI) 261 (M⁺, 100%), 199 (21%); IR (KBr plate, acetone-d₆) 3424, 1330, 1122, 1113, 842, 796, 756.

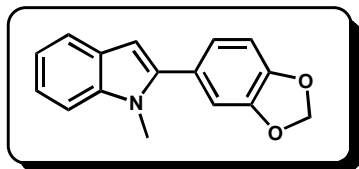


1-Methyl-2-(4-trifluoromethyl-phenyl)-1H-indole (3bj):² Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 16 h. product **3bj** was obtained after silica gel chromatography (10:1 hexanes: dichloromethane), yield 0.1076 g (78%). ¹H NMR (300MHz, CDCl₃) δ 7.73 (d, *J* = 8.9 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.43-7.24 (m, 4H), 6.64 (s, 1H), 3.80 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 140.2, 138.4, 133.9, 130.4, 128.7, 121.9, 120.5, 119.9, 109.6, 101.9, 31.1; *m/z* (EI) 275 (M⁺, 100%), 205

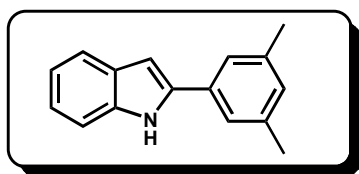
(24%); IR (KBr plate, CDCl_3) 3046, 2925, 1466, 1089, 834, 792, 736.



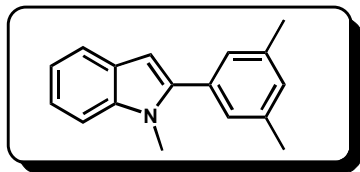
2-Benzo[1,3]dioxol-5-yl-1H-indole (3lk):⁵ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % $\text{Pd}(\text{OAc})_2$ scale at room temperature for 12 h. product **3lk** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0628 g (53%). ^1H NMR (300 MHz, acetone- d_6): 11.6 (s, 1 H), 7.87 (d, $J = 8.4$ Hz, 2 H), 7.52 (d, $J = 7.8$ Hz, 1 H), 7.41-7.49 (m, 3 H), 7.29-7.34 (m, 1 H), 7.09-7.14 (m, 1 H), 6.99-7.04 (m, 1 H), 6.91 (d, $J = 0.9$ Hz, 1 H). ^{13}C NMR (75 MHz, acetone- d_6): 147.6, 147.4, 141.2, 138.1, 127.8, 126.7, 123.2, 121.5, 119.8, 109.7, 109.5, 108.3, 101.3, 101.2. m/z (EI) 237 (M^+ , 100%), 178 (17%); IR (KBr plate, acetone- d_6) 3417, 2899, 1702, 1481, 1451, 1041, 789, 750.



2-Benzo[1,3]dioxol-5-yl-1-methyl-1H-indole (3bk):⁵ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % $\text{Pd}(\text{OAc})_2$ scale at room temperature for 16 h. product **3bk** was obtained after silica gel chromatography (5:1 hexanes: dichloromethane), yield 0.0778 g (62%). ^1H NMR (300 MHz, CDCl_3): 7.53 (d, $J = 7.8$ Hz, 1 H), 7.23 (m, 1 H), 7.15 (m, 1 H), 7.05 (m, 1 H), 6.88-6.79 (m, 3 H), 6.41 (s, 1 H), 5.89 (s, 2 H), 3.50 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3): 147.6, 147.4, 141.2, 138.1, 127.8, 126.7, 123.2, 121.5, 119.8, 109.7, 109.5, 108.3, 101.3, 101.2, 29.7. m/z (EI) 251 (M^+ , 100%), 192 (12%); IR (KBr plate, CDCl_3) 2955, 2923, 2853, 1475, 1232, 1039, 781, 750.



2-(3,5-Dimethyl-phenyl)-1H-indole (3ll):⁸ Following the general procedures, the reaction was performed in a 0.5 mmol and 10 mol % $\text{Pd}(\text{OAc})_2$ scale at room temperature for 10 h. product **3ll** was obtained after silica gel chromatography (4:1 hexanes: dichloromethane), yield 0.0685 g (62%). ^1H NMR (300 MHz, acetone- d_6) δ 8.35 (bs, 1 H), 7.73 (d, $J = 8.1$ Hz, 1 H), 7.46-7.20 (m, 5 H), 7.06 (s, 1 H), 6.90-6.87 (m, 1 H), 2.47 (s, 6 H); ^{13}C NMR (75 MHz, acetone- d_6): δ 138.6, 138.3, 136.8, 132.3, 129.6, 129.4, 123.1, 122.2, 120.7, 120.2, 111.0, 99.8, 21.5. m/z (EI) 221 (M^+ , 100%), 191 (38%); IR (KBr plate, acetone- d_6) ν 3402, 3049, 2918, 1607, 1457, 1311, 844, 797, 744. Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{N}$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.72; H, 6.84; N, 6.69.



2-(3,5-Dimethyl-phenyl)-1-methyl-1H-indole (3bl):³ Following the general procedures, the reaction was performed in a 0.5 mmol and 5 mol % Pd(OAc)₂ scale at room temperature for 8 h. product **3bl** was obtained after silica gel chromatography (10:1 hexanes: dichloromethane), yield 0.0587 g (50%). ¹H NMR (300 MHz, CDCl₃) δ 8.35 (bs, 1 H), 7.73 (d, *J* = 8.1 Hz, 1 H), 7.46-7.20 (m, 5 H), 7.06 (s, 1 H), 6.90-6.87 (m, 1 H), 2.47 (s, 6 H); ¹³C NMR (75 MHz, CDCl₃): δ 138.6, 138.3, 136.8, 132.3, 129.6, 129.4, 123.1, 122.2, 120.7, 120.2, 111.0, 99.8, 21.5. *m/z* (EI) 235 (M⁺, 100%), 197 (34%); IR (KBr plate, CDCl₃) ν3050, 1465, 1146, 776, 749, 701.

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