

Supporting Information

Pd-catalyzed C3-selective Arylation of Pyridines with Phenyl Tosylates

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Table of Contents

I General Consideration	S 2
II Representative Procedure	S 2
III Characterization Data for Selected Compounds	S 2- S 36

General Consideration:

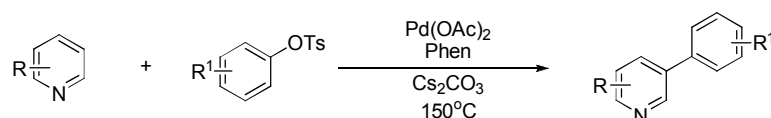
All solvents and reagents were purchased from the suppliers and used after further dried. ^1H NMR and ^{13}C NMR were recorded in CDCl_3 at room temperature on the spectrometer (400 MHz ^1H , 100 MHz ^{13}C). The chemical-shifts scale is based on internal TMS. Data for ^1H NMR and ^{13}C NMR are reported as follows: chemical shift (δppm), multiplicity, integration, and coupling constant (Hz). All reactions were carried out under dry nitrogen atmosphere.

Table 1 Reaction condition optimization^a

Entry	PdX_2 (mol %)	Base (equiv)	Ligand (mol%)	Temp ($^\circ\text{C}$)	Yield (%) ^b
1	$\text{Pd}(\text{OAc})_2$ (5)	Cs_2CO_3 (3)	Phen (15)	140	21
2	$\text{Pd}(\text{OAc})_2$ (10)	Cs_2CO_3 (3)	Phen (15)	140	32
3	$\text{Pd}(\text{OAc})_2$ (10)	Cs_2CO_3 (3)	Phen (30)	140	38
4	$\text{Pd}(\text{OAc})_2$ (10)	Cs_2CO_3 (3)	Phen (30)	150	63
5	$\text{Pd}(\text{OAc})_2$ (15)	Cs_2CO_3 (3)	Phen (30)	150	56
6	$\text{Pd}(\text{OAc})_2$ (10)	Cs_2CO_3 (3)	Phen (30)	160	52
7	PdCl_2 (10)	Cs_2CO_3 (3)	Phen (30)	150	50
8	$\text{Pd}(\text{TFA})_2$ (10)	Cs_2CO_3 (3)	Phen (30)	150	15
9	$\text{Pd}(\text{OAc})_2$ (10)	K_3CO_3 (3)	Phen (30)	150	41
10	$\text{Pd}(\text{OAc})_2$ (10)	K_3PO_4 (3)	Phen (30)	150	42
11	$\text{Pd}(\text{OAc})_2$ (10)	Cs_2CO_3 (3)	Phen (30)	150	5 ^c
12	$\text{Pd}(\text{OAc})_2$ (10)	Cs_2CO_3 (3)	Phen (30)	150	41 ^d
13	—	Cs_2CO_3 (3)	Phen (30)	150	0

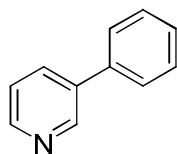
^a Reaction conditions: pyridine (3.0 mL) and **2a** (0.5 mmol) were stirred with 3 equiv of base in the presence of Pd-catalyst and ligand at desired temperature in a sealed tube under N_2 for 48 h. ^b Isolated yields. ^c Pyridine (0.24 mL, 3.0 mmol) with DMF (1 mL) was used. ^d Pyridine (2.0 mL, 25 mmol) with DMF (1 mL) was used.

1. General Procedure:

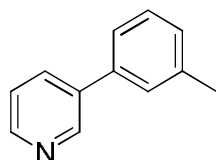


General Procedure for Pd(II)-catalyzed C-3 Arylation of Pyridine Derivatives:

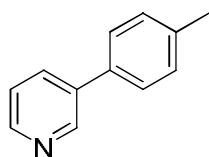
To a 15 mL sealed tube were added $\text{Pd}(\text{OAc})_2$ (11.2 mg, 0.05 mmol), 1,10-phenanthroline (27 mg, 0.3 mmol), Cs_2CO_3 (489 mg, 1.5 mmol), aryl tosylate (0.5 mmol) and pyridine derivative (3.0 mL). The tube was capped and stirred under N_2 at 150°C for 48 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through a short pad of Celite, washed with EtOAc, and concentrated in *vacuo*. The resulting residue was purified by flash column chromatography using hexanes:EtOAc (3:1 to 1:1, depending on different substrates) as the eluent. Known compounds are characterized by ^1H NMR, ^{13}C NMR and their comparison to literature values. Unknown compounds are characterized by ^1H NMR, ^{13}C NMR and HRMS.



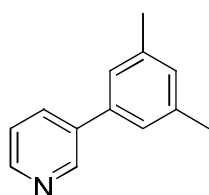
3-Phenylpyridine (3a)^[1]: Yield: 63%; Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.77 (s, 1H), 8.52 (d, *J* = 4.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.30 (dd, *J* = 4.0 Hz, 8.0 Hz, 1H).; ¹³C NMR (CDCl₃, 100 MHz) δ 147.5, 147.3, 136.9, 135.7, 133.3, 128.1, 127.1, 126.2, 122.5; **MS**: *m/z* C₁₁H₉N 155 (M⁺);



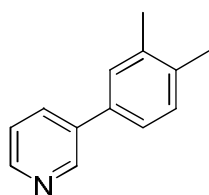
3-(*m*-Tolyl)pyridine (3b)^[2]: Yield: 55%; Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.75 (s, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.24 (m, 4H), 7.14 (d, *J* = 4.0 Hz, 1H), 2.35 (s, 3H).; ¹³C NMR (CDCl₃, 100 MHz) δ 147.3, 147.3, 137.7, 136.8, 135.7, 133.3, 127.9, 127.8, 126.9, 123.2, 122.5, 20.5; **MS**: *m/z* C₁₂H₁₁N 169 (M⁺);



3-(*p*-Tolyl)pyridine (3c)^[3]: Yield: 59%; Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.77 (s, 1H), 8.50 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.28 (dd, *J* = 4.0 Hz, 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ 148.2, 138.1, 135.0, 134.2, 129.8, 127.0, 123.6, 21.2; **MS**: *m/z* C₁₂H₁₁N 169 (M⁺);

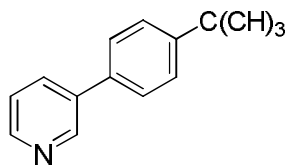


3-(3,5-Dimethylphenyl)pyridine (3d)^[4]: Yield: 67%; White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.74 (s, 1H), 8.48 (d, *J* = 4.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.25 (dd, *J* = 4.0 Hz, 8.0 Hz, 1H), 7.10 (s, 2H), 6.96 (s, 1H), 2.30 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 147.4, 147.3, 137.6, 136.8, 135.9, 133.3, 128.7, 124.0, 122.4, 20.3; **MS**: *m/z* C₁₃H₁₃N 183 (M⁺);

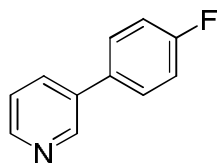


3-(3,4-Dimethylphenyl)pyridine (3e): Yield: 61%; White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.75 (s, 1H), 8.48 (d, *J* = 4.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.28–7.24 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 1H), 2.26 (s, 3H), 2.24 (s, 3H); ¹³C

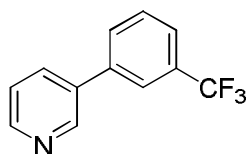
NMR (CDCl₃, 100 MHz) δ 147.2, 147.1, 136.3, 135.7, 135.6, 134.3, 133.1, 129.3, 127.3, 123.4, 122.4, 18.9, 18.5; **HRMS**: m/z calcd for C₁₃H₁₃N (M⁺): 183.1048, found: 183.1052;



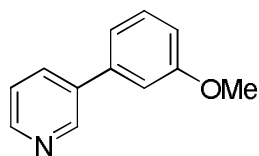
3-(4-Tert-Butylphenyl)pyridine (3f)^[5]: Yield: 41%; White solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.85 (s, J = 1.6 Hz, 1H), 8.57 (d, J = 4.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.55–7.49 (m, 4H), 7.34 (dd, J = 4.4 Hz, 8.0 Hz, 1H), 1.37 (s, 9H); **¹³C NMR** (CDCl₃, 100 MHz) δ 151.2, 148.2, 148.2, 136.5, 134.9, 134.2, 126.8, 126.0, 123.5, 34.6, 31.3; **MS**: m/z C₁₅H₁₇N 211 (M⁺);



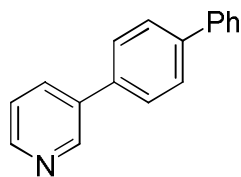
3-(4-Fluorophenyl)pyridine (3g)^[6]: Yield: 46%; Colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.73 (s, 1H), 8.52 (d, J = 4.0 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.47 (dd, J = 5.2 Hz, 8.0 Hz, 2H), 7.29 (dd, J = 4.8 Hz, 8.0 Hz, 1H), 7.10 (t, J = 8.0 Hz, 2H). **¹³C NMR** (CDCl₃, 100 MHz) δ 161.87 (J = 246 Hz), 147.5, 147.1, 134.7, 133.2, 127.8, 127.8, 122.6, 115.1 (J = 22 Hz), **MS**: m/z C₁₁H₈NF 173 (M⁺);



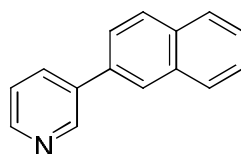
3-(3-(Trifluoromethyl)phenyl)pyridine (3h)^[7]: Yield: 32%; Colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.78 (s, 1H), 8.58 (d, J = 4.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.54 (t, J = 8.0 Hz, 1H), 7.35 (dd, J = 4.0, 8.0 Hz, 1H); **¹³C NMR** (CDCl₃, 100 MHz) δ 148.1, 147.1, 137.6, 134.3, 133.6, 130.7, 130.3, 129.4, 128.6, 123.8, 123.0, 122.8; **MS**: m/z C₁₂H₈NF₃ 223 (M⁺);



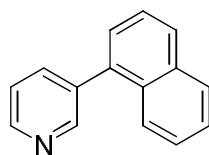
3-(3-Methoxyphenyl)pyridine (3i)^[8]: Yield: 48%; Colorless oil. **¹H NMR** (400 MHz, CDCl₃) δ 8.77 (s, 1H), 8.51 (d, J = 4.4 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.33–7.26 (m, 2H), 7.08 (d, J = 8.0 Hz, 1H), 7.02 (s, 1H), 6.87 (d, J = 8.0 Hz, 1H), 3.79 (s, 3H); **¹³C NMR** (CDCl₃, 100 MHz) δ 159.1, 147.6, 147.3, 138.3, 135.5, 133.4, 129.1, 122.5, 118.6, 112.4, 111.9, 54.3; **HRMS**: m/z calcd for C₂₁H₁₅N 185 (M⁺);



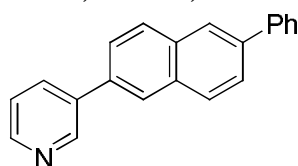
3-([1,1'-Biphenyl]-4-yl)pyridine (3j)^[9]: Yield: 57%; White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.83 (s, 1H), 8.54 (d, *J* = 4.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.56 (m, 6H), 7.41 – 7.34 (m, 2H), 7.32 – 7.28 (m, 2H). ¹³C NMR (CDCl₃, 100 MHz) δ 147.5, 147.2, 140.0, 139.3, 135.6, 135.1, 133.2, 127.9, 126.8, 126.6, 126.5, 126.0, 122.6; **MS**: *m/z* C₁₇H₁₃N 231 (M⁺);



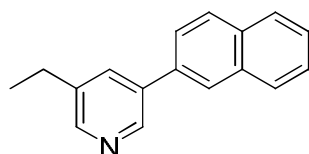
3-(Naphthalen-2-yl)pyridine (3k)^[10]: Yield: 60%; White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.97 (d, *J* = 2.0 Hz, 1H), 8.62 (dd, *J* = 1.2 Hz, 4.8 Hz, 1H), 8.03 (s, 1H), 8.00 – 7.86 (m, 4H), 7.69 (dd, *J* = 1.6 Hz, 8.4 Hz, 1H), 7.53–7.50 (m, 2H), 7.39 (dd, *J* = 4.8 Hz, 7.6 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 148.5, 148.5, 136.5, 135.1, 134.5, 133.5, 132.8, 128.9, 128.2, 127.7, 126.6, 126.4, 126.1, 125.0, 123.6; **MS**: *m/z* C₁₅H₁₁N 205 (M⁺);



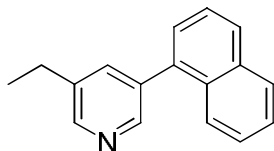
3-(Naphthalen-1-yl)pyridine (3l)^[11]: Yield: 52%; White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.75 (d, *J* = 1.6 Hz, 1H), 8.67 (dd, *J* = 1.6 Hz, 4.4 Hz, 1H), 7.91 (t, *J* = 7.2 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.55–7.40 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz) δ 150.5, 148.5, 137.3, 136.3, 136.2, 133.7, 131.4, 128.5, 128.4, 127.3, 126.5, 126.0, 125.3, 125.2, 123.1; **MS**: *m/z* C₁₅H₁₁N 205 (M⁺);



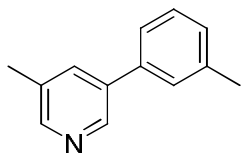
3-(6-Phenylnaphthalen-2-yl)pyridine (3m): Yield: 60%; White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.99 (d, *J* = 1.6 Hz, 1H), 8.62 (dd, *J* = 1.2 Hz, 4.8 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 8.01 – 7.81 (m, 3H), 7.78 (dd, *J* = 1.6 Hz, 4.4 Hz, 1H), 7.75–7.14 (m, 3H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.41–7.38 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 148.5, 140.8, 139.1, 136.5, 135.1, 134.5, 133.1, 132.7, 129.2, 128.9, 128.7, 127.5, 127.4, 126.3, 125.9, 125.5, 125.4, 123.6; **HRMS**: *m/z* calcd for C₂₁H₁₅N (M⁺): 281.1204, found: 281.1207;



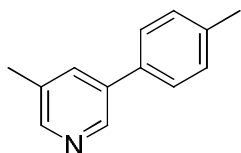
3-Ethyl-5-(Naphthalen-2-yl)pyridine (3n): Yield: 52%; White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.80 (d, $J = 2.0$ Hz, 1H), 8.48 (d, $J = 2.0$ Hz, 1H), 8.04 (s, 1H), 7.96 (s, 1H), 7.94–7.87 (m, 2H), 7.82 (s, 1H), 7.71 (dd, $J = 2.0$ Hz, 8.4 Hz, 1H), 7.54–7.51 (m, 3H), 2.75 (q, $J = 7.6$ Hz, 2H), 8.48 (t, $J = 7.6$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 148.3, 146.0, 139.2, 136.2, 135.3, 134.0, 133.5, 132.8, 128.8, 128.2, 127.7, 126.5, 126.3, 126.2, 125.1, 26.1, 15.4; **HRMS:** m/z calcd for $\text{C}_{17}\text{H}_{15}\text{N}$ (M^+): 233.1204, found: 233.1206;



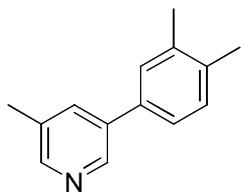
3-Ethyl-5-(Naphthalen-1-yl)pyridine (3o): Yield: 51%; White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.49 (s, 1H), 8.45 (s, 1H), 7.81 (t, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 1H), 7.55 (s, 1H), 7.46–7.31 (m, 4H), 2.66 (q, $J = 7.6$ Hz, 2H), 8.48 (t, $J = 7.6$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 148.2, 148.0, 138.8, 136.8, 136.6, 136.0, 133.8, 131.6, 128.5, 128.4, 127.4, 126.5, 126.1, 125.4, 26.1, 15.4; **HRMS:** m/z calcd for $\text{C}_{17}\text{H}_{15}\text{N}$ (M^+): 233.1204, found: 233.1209;



3-(*m*-Tolyl)pyridine (3p): Yield: 54%; White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.57 (s, 1H), 8.34 (s, 1H), 7.59 (s, 1H), 7.31–7.28 (m, 3H), 7.14 (d, $J = 4.0$ Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 147.8, 144.5, 137.7, 136.9, 135.2, 134.0, 131.9, 127.9, 127.7, 126.9, 123.2, 20.5, 17.5; **HRMS:** m/z calcd for $\text{C}_{13}\text{H}_{13}\text{N}$ (M^+): 183.1048, found: 183.1055;

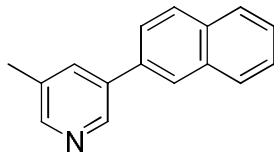


3-(*p*-Tolyl)pyridine (3q): Yield: 50%; White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.57 (s, 1H), 8.33 (s, 1H), 7.59 (s, 1H), 7.40 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 4.0$ Hz, 2H), 2.33 (s, 3H), 2.32 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 148.7, 145.4, 137.9, 135.0, 134.8, 129.8, 127.0, 21.2, 18.5; **HRMS:** m/z calcd for $\text{C}_{13}\text{H}_{13}\text{N}$ (M^+): 183.1048, found: 183.1058;

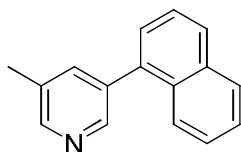


3-Methyl-5-(3,4-Dimethylphenyl)pyridine (3r): Yield: 56%; White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.56 (s, 1H), 8.31 (s, 1H), 7.57 (s, 1H), 7.27 (s, 1H), 7.23 (d, $J = 7.6$ Hz, 1H), 7.14 (d, $J = 7.6$ Hz, 1H), 2.31 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 147.6, 144.4, 136.2, 135.5, 135.2, 134.5,

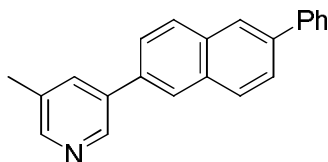
133.7, 131.8, 129.3, 127.3, 123.5, 18.9, 18.4, 17.4; **HRMS**: m/z calcd for C₁₄H₁₅N (M⁺):197.1204, found: 197.1214;



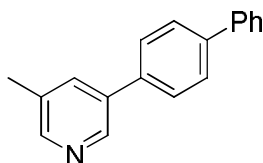
3-Methyl-5-(Naphthalen-2-yl)pyridine (3s): Yield: 46%; White solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.77 (d, *J* = 2.0 Hz, 1H), 8.45 (d, *J* = 1.2 Hz, 1H), 8.02 (d, *J* = 1.2 Hz, 1H), 7.94 (s, 1H), 7.92–7.86 (m, 2H), 7.79 (d, *J* = 0.8 Hz, 1H), 7.69 (dd, *J* = 2.0 Hz, 8.4 Hz 1H), 7.52–7.50 (m, 2H), 2.42 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 149.0, 145.7, 136.0, 135.2, 135.2, 133.5, 133.0, 132.8, 128.7, 128.2, 127.6, 126.5, 126.3, 126.0, 125.1, 18.5; **HRMS**: m/z calcd for C₁₆H₁₃N (M⁺):219.1048, found: 219.1053;



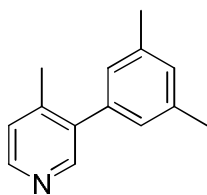
3-Methyl-5-(Naphthalen-1-yl)pyridine (3t): Yield: 47%; White solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.56 (s, 1H), 8.52 (s, 1H), 7.90 (t, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.62 (s, 1H), 7.55–7.43 (m, 3H), 7.39 (dd, *J* = 0.8 Hz, 7.2 Hz 1H), 2.42 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 149.0, 147.7, 137.8, 136.4, 135.8, 133.7, 132.6, 131.5, 128.4, 128.3, 127.2, 126.4, 126.0, 125.3, 125.3, 18.4; **HRMS**: m/z calcd for C₁₆H₁₃N (M⁺):219.1048, found: 219.1042;



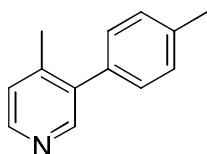
3-Methyl-5-(6-Naphthalen-2-yl)pyridine (3u): Yield: 49%; White solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.79 (d, *J* = 1.6 Hz, 1H), 8.45 (s, 1H), 8.06–8.03 (m, 2H), 7.99–7.80 (m, 2H), 7.79–7.70 (m, 5H), 7.51–7.47 (m, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 2.43 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 149.0, 145.7, 140.8, 139.0, 136.0, 135.2, 135.1, 133.1, 132.7, 129.1, 128.9, 128.7, 127.5, 127.3, 126.2, 125.8, 125.5, 18.5; **HRMS**: m/z calcd for C₂₂H₁₇N (M⁺):295.1361, found: 295.1371;



3-Methyl-5-([1,1'-Biphenyl]-4-yl)pyridine (3v): Yield: 53%; White solid. **¹H NMR** (400 MHz, CDCl₃) δ 8.63 (s, 1H), 8.36 (s, 1H), 7.64–7.55 (m, 7H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 2.33 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 148.0, 144.4, 139.8, 139.4, 135.7, 134.6, 133.8, 132.0, 127.8, 126.7, 126.5, 126.5, 126.0, 17.5; **HRMS**: m/z calcd for C₁₈H₁₅N (M⁺): 245.1024, found: 245.1034;

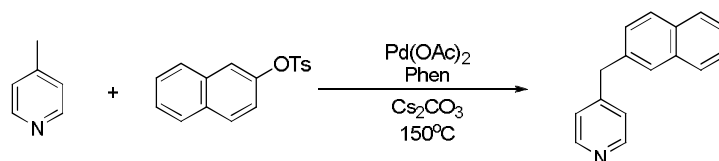


4-Methyl-3-(3,5-Dimethylphenyl)pyridine (3w): Yield: 61%; White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.33 (s, 2H), 7.09 (d, $J = 4.0$ Hz, 1H), 6.95 (s, 1H), 6.85 (s, 2H), 2.29 (s, 6H), 2.21 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 148.9, 147.0, 143.4, 136.9, 136.8, 128.1, 126.0, 124.0, 20.3, 18.8; **HRMS:** m/z calcd for $\text{C}_{14}\text{H}_{15}\text{N}$ (M^+):197.1204, found: 197.1031;



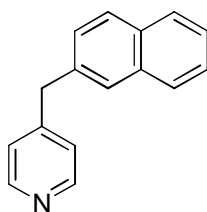
4-Methyl-3-(p-Tolyl)pyridine (3x): Yield: 53%; White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.35 (s, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 5.2$ Hz, 1H), 2.34 (s, 3H), 2.21 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) δ 149.0, 147.1, 143.5, 136.6, 136.3, 133.9, 128.1, 128.1, 124.1, 20.2, 18.8; **HRMS:** m/z calcd for $\text{C}_{13}\text{H}_{13}\text{N}$ (M^+):183.1048, found: 183.1056;

2. General Procedure:



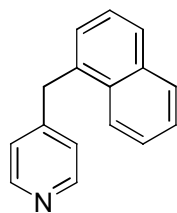
General Procedure for Pd(II)-catalyzed Arylation of Pyridine Derivatives:

To a 15-mL sealed tube were added $\text{Pd}(\text{OAc})_2$ (16.8 mg, 0.15 mmol), 1,10-phenanthroline (40.6 mg, 0.225 mmol), Cs_2CO_3 (489 mg, 1.5 mmol), Naphthyltosylates (0.5 mmol) and 4-methyl pyridine (3.0 mL). The tube was capped and stirred under N_2 at 150°C for 48 h. The reaction mixture was cooled to room temperature and diluted with EtOAc, filtered through a short pad of Celite, washed with EtOAc, and concentrated in *vacuo*. The resulting residue was purified by flash column chromatography using hexanes:EtOAc (3:1 to 1:1, depending on different substrates) as the eluent.

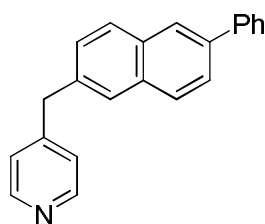


4-(naphthalen-2-ylmethyl)pyridine (3y): Yield: 51%; White solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.49 (d, $J = 6.0$ Hz, 2H), 7.82–7.76 (m, 3H), 7.62 (s, 1H), 7.49–7.43 (m, 2H), 7.25 (dd, $J = 2.0$ Hz, 8.0 Hz, 1H), 7.13 (d, $J = 6.0$ Hz, 2H), 4.11 (s, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 148.8, 135.3, 132.5, 131.2, 127.4, 126.7, 126.5, 126.5, 126.3, 125.2, 124.7, 123.2, 40.3; **HRMS:** m/z calcd for

$C_{16}H_{13}N$ (M^+): 219.1048, found: 219.1056;



4-(naphthalen-1-ylmethyl)pyridine (3z): Yield: 47%; White solid. 1H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 2H), 7.88–7.79 (m, 3H), 7.47–7.42 (m, 3H), 7.31 (d, J = 7.2 Hz, 1H), 7.08 (d, J = 5.2 Hz, 2H), 4.41 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 134.3, 133.9, 131.8, 128.8, 127.8, 127.7, 126.2, 125.8, 125.5, 123.9, 38.4; **HRMS:** m/z calcd for $C_{16}H_{13}N$ (M^+): 219.1048, found: 219.1056;



4-((6-phenylnaphthalen-2-yl)methyl)pyridine (3aa): Yield: 59%; White solid. 1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 6.0 Hz, 2H), 8.01 (s, 1H), 7.85–7.82 (m, 2H), 7.75–7.69 (m, 3H), 7.63 (s, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 8.0 Hz, 1H), 7.28 (dd, J = 2.0, 8.8 Hz, 1H), 7.13 (d, J = 6.0 Hz, 2H), 4.11 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 149.8, 140.9, 138.4, 136.4, 132.7, 132.4, 128.8, 128.7, 128.0, 127.7, 127.3, 127.2, 126.0, 125.5, 124.2, 41.3; **HRMS:** m/z calcd for $C_{22}H_{17}N$ (M^+): 295.1361, found: 295.1369;

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