Supporting Information

Palladium(II)-Catalyzed oxidative ortho Arylation of 2-phenylpyridines

1. General information
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1. General information
   All the reagents were commercially available and used without any further purification. The solvents were dried before use. GC analyses were performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30m×320μm×0.25μm, carrier gas: N2, Injector: 300 °C, FID detection detector: initial temperature 80 °C, temperature program: 15 °C /min, final temperature 325 °C. H2 30mL/min, air 400mL/min, N2 25mL/min). GC-MS analyses were performed on an Agilent 7890A-5975C instrument (Column: DB-5 MS). 1H NMR was recorded on Bruker DRX 500 and tetramethylsilane (TMS) was used as a reference.

2. General Procedure for the Arylation of indoles
   A sealed tube was charged with 2-phenylpyridine (1; 68.0 mg, 0.44 mmol), phenylboronic acid (2.5 equiv), Cu(OTf)2 (0.2 equiv), TBHP (2 equiv), and Pd(OAc)2 (10 mol%) in acetonitrile (15 mL). The mixture was heated to 60 °C and stirred violently at this temperature for 24 h. After being cooled to room temperature, the mixture was filtered. The filtrate was evaporated under vacuum. Subsequently, the residue was purified by chromatography (silica gel, n-hexane:EtOAc, 10:1).

3. Product data
   All the known products were identified by comparison of their spectroscopic data with those of authentic samples. New products (3m, 3n, 3p) were characterized with 1H-NMR, 13C-NMR and Mass Spectrometry. Characterization datas are given as following.

   2-((1,1’-biphenyl)-2-yl)pyridine 3a
   1H NMR (500 MHz, CDCl3) δ 8.66 (d, J = 4.5 Hz, 1H), 7.70 (t, J = 4.3 Hz, 1H), 7.48-7.41 (m, 3H), 7.38 (td, J = 7.5, 1.4 Hz, 1H), 7.25-7.22 (m, 3H), 7.17-7.14 (m, 2H), 7.10 (dd, J = 6.6, 5.4 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 158.18, 157.28, 148.32, 140.33, 139.65, 138.31, 134.35, 129.52, 128.73, 127.60, 127.09, 126.69, 125.73, 124.49, 120.40; MS (EI+) m/z 231 [M]+.

   2-(3’-methyl-[1,1’-biphenyl]-2-yl)pyridine 3c
   1H NMR (500 MHz, CDCl3) δ 8.66 (d, J = 4.6 Hz, 1H), 7.77 – 7.68 (m, 1H), 7.53 – 7.40 (m, 4H), 7.13 (dd, J = 14.4, 7.0 Hz, 2H), 7.09 – 7.02 (m, 2H), 6.93 (d, J = 7.7 Hz, 2H), 2.28 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 158.23, 148.14, 140.18, 139.77,
2-(3'-nitro-[1,1'-biphenyl]-2-yl)pyridine 3d
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.60 (ddd, $J$ = 4.9, 1.8, 0.9 Hz, 1H), 8.13 – 8.07 (m, 2H), 7.73 – 7.68 (m, 1H), 7.57 – 7.50 (m, 3H), 7.50 – 7.47 (m, 1H), 7.45 – 7.41 (m, 1H), 7.41 – 7.36 (m, 1H), 7.16 (ddd, $J$ = 7.6, 4.9, 1.1 Hz, 1H), 7.04 (dt, $J$ = 7.9, 1.0 Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 157.60, 148.57, 147.13, 142.15, 138.72, 137.72, 137.20, 134.88, 134.83, 129.71, 129.36, 127.92, 127.83, 127.70, 124.05, 123.34, 120.86, 120.63, 76.29, 76.03, 75.78; MS (EI$^+$) $m/z$ 246 [M+H]$^+$. 

2-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine 3e
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.66 (d, $J$ = 4.2 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.51 – 7.38 (m, 4H), 7.26 – 7.20 (m, 2H), 7.16 (ddd, $J$ = 7.5, 4.9, 0.9 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.94 (d, $J$ = 7.9 Hz, 1H), 3.81 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 158.50, 157.55, 148.46, 139.21, 138.42, 134.22, 132.76, 129.78, 129.49, 129.44, 127.50, 126.30, 124.41, 120.27, 112.56, 54.21; MS (EI$^+$) $m/z$ 268 [M+H]$^+$. 

2-(4'-chloro-[1,1'-biphenyl]-2-yl)pyridine 3f
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.68 – 8.62 (m, 1H), 7.73 – 7.67 (m, 1H), 7.55 – 7.40 (m, 4H), 7.26 – 7.20 (m, 2H), 7.16 (ddd, $J$ = 7.5, 4.9, 0.9 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.94 (d, $J$ = 7.9 Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 158.08, 148.54, 138.89, 138.57, 138.39, 134.46, 131.85, 129.96, 129.59, 129.32, 127.62, 127.27, 126.95, 124.24, 120.50; MS (EI$^+$) $m/z$ 267 [M+H]$^+$. 

2-(4-methyl-[1,1'-biphenyl]-2-yl)pyridine 3h
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.65 (d, $J$ = 4.6 Hz, 1H), 7.54 (s, 1H), 7.42 – 7.33 (m, 2H), 7.30 (dd, $J$ = 7.8, 1.1 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.18 – 7.13 (m, 2H), 7.11 (m, 1H), 6.88 (d, $J$ = 7.9 Hz, 1H), 2.47 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 158.39, 148.39, 140.33, 138.26, 136.85, 136.43, 134.16, 130.08, 129.48, 128.75, 128.31, 127.03, 125.52, 124.50, 120.31, 76.31, 76.05, 75.80, 20.09; MS (EI$^+$) $m/z$ 245 [M+H]$^+$. 

2-(3-methyl-[1,1'-biphenyl]-2-yl)pyridine 3i
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.64 (d, $J$ = 4.8 Hz, 1H), 7.46 (td, $J$ = 7.7, 1.6 Hz, 1H), 7.38 (t, $J$ = 7.6 Hz, 1H), 7.30 (dd, $J$ = 15.3, 7.3 Hz, 2H), 7.18 – 7.06 (m, 6H), 6.90 (d, $J$ = 7.8 Hz, 1H), 2.21 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.81, 149.03, 141.89, 141.49, 139.53, 136.92, 135.93, 129.87, 129.63, 128.26, 128.81, 126.44, 125.86, 121.51, 77.51, 77.25, 77.00, 20.68; MS (EI$^+$) $m/z$ 245 [M+H]$^+$. 

4'-(trifluoromethyl)-1,1':2',1''-terphenyl 3j
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.67 (d, $J$ = 4.7 Hz, 1H), 7.76 (d, $J$ = 8.4 Hz, 1H), 7.44 (dd, $J$ = 7.7, 1.6 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.32 (s, 1H), 7.29 (s, 1H), 7.28 (s, 1H), 7.20 (d, $J$ = 2.9 Hz, 1H), 7.19 (s, 1H), 7.18 (d, $J$ = 1.8 Hz, 1H), 7.16 (d, $J$ = 3.5 Hz,
2-(5-chloro-[1,1'-biphenyl]-2-yl)pyridine 3k
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.65 (d, $J = 4.8$ Hz, 1H), 7.67 (d, $J = 8.9$ Hz, 1H), 7.46 (dd, $J = 6.2, 2.1$ Hz, 2H), 7.40 (d, $J = 1.7$ Hz, 1H), 7.27 – 7.25 (m, 2H), 7.19 – 7.08 (m, 4H), 6.86 (d, $J = 7.9$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 158.34, 149.72, 142.44, 140.30, 138.10, 135.56, 134.57, 132.12, 130.55, 128.45, 127.89, 127.47, 125.53, 121.83; MS (EI$^+$) $m/z$ 265 [M+H$^+$].

2-(5-methoxy-[1,1'-biphenyl]-2-yl)pyridine 3l
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.62 (ddd, $J = 4.9, 1.7, 0.9$ Hz, 1H), 7.68 (d, $J = 8.5$ Hz, 1H), 7.36 (td, $J = 7.7, 1.8$ Hz, 1H), 7.28 – 7.24 (m, 3H), 7.22 – 7.17 (m, 2H), 7.10 – 7.07 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 158.64, 157.93, 148.36, 141.00, 134.10, 131.27, 130.92, 128.64, 127.13, 125.90, 124.39, 119.95, 114.73, 112.31, 54.47; MS (EI$^+$) $m/z$ 268 [M+H$^+$].

2-([1,1'-biphenyl]-2-yl)-6-phenylpyridine 3m
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.84 – 7.80 (m, 3H), 7.57 (t, $J = 3.9$ Hz, 2H), 7.53 – 7.48 (m, 3H), 7.45 – 7.39 (m, 3H), 7.31 – 7.29 (m, 1H), 7.28 – 7.23 (m, 4H), 7.05 – 7.00 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 157.95, 155.79, 140.90, 139.98, 138.67, 138.56, 135.26, 129.72, 129.68, 128.76, 127.76, 127.55, 127.06, 126.59, 126.02, 125.58, 122.28, 117.06.; MS (EI$^+$) $m/z$ 308 [M+H$^+$].

2-(([1,1'-terphenyl]-2'-yl)-6-phenylpyridine 3n
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.93 (dd, $J = 9.7, 8.3$ Hz, 5H), 7.60 – 7.53 (m, 6H), 7.50 – 7.45 (m, 4H), 7.39 (d, $J = 2.5$ Hz, 2H), 7.36 (t, $J = 7.2$ Hz, 2H), 7.15 (d, $J = 2.5$ Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 155.95, 150.77, 147.31, 135.04, 127.73, 127.71, 127.01, 126.36, 125.47, 124.78, 123.20, 121.52, 119.70, 113.82, 110.93, 104.30; MS (EI$^+$) $m/z$ 384 [M+H$^+$].

2-(([1,1':3',1''-terphenyl]-2'-yl)-1H-indole 3p
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.11 (s, 1H), 7.52 (dd, $J = 6.6, 3.0$ Hz, 2H), 7.49 -7.42 (m, 2H), 7.35 (d, $J = 8.1$ Hz, 1H), 7.18 (m, 8H), 7.02 (d, $J = 8.1$ Hz, 1H), 6.95 (t, $J = 7.6$ Hz, 1H), 6.82 (t, $J = 7.4$ Hz, 1H), 6.74 (d, $J = 8.2$ Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 158.27, 136.17, 134.55, 128.75, 127.29, 126.77, 126.77, 126.52, 125.80, 124.43, 121.41, 120.60, 119.04, 118.23, 111.30, 109.71; MS (EI$^+$) $m/z$ 346 [M+H$^+$].

1-([1,1'-biphenyl]-2-yl)-1H-pyrazole 3q
$^1$H NMR (500 MHz, CDCl$_3$): $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.69 – 7.61 (m, 2H), 7.54 – 7.46 (m, 3H), 7.34 – 7.29 (m, 3H), 7.17 – 7.06 (m, 3H), 6.21 (t, $J = 2.1$ Hz, 1H);
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 139.26, 137.58, 135.73, 130.35, 130.03, 127.55, 127.45, 127.37, 127.27, 126.43, 125.58, 105.38. MS (EI$^+$) $m/z$ 221 [M+H]$^+$. 
4. NMR spectra

2-([1,1'-biphenyl]-2-yl)pyridine 3a $^1$H NMR

2-([1,1'-biphenyl]-2-yl)pyridine 3a $^{13}$C NMR
2-(3'-methyl-[1,1'-biphenyl]-2-yl)pyridine $3c$ $^1$H NMR

2-(3'-methyl-[1,1'-biphenyl]-2-yl)pyridine $3c$ $^{13}$C NMR
2-(3'-nitro-[1,1'-biphenyl]-2-yl)pyridine 3d $^1$H NMR

2-(3'-nitro-[1,1'-biphenyl]-2-yl)pyridine 3d $^{13}$C NMR
2-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine 3e $^1$H NMR

2-(4'-methoxy-[1,1'-biphenyl]-2-yl)pyridine 3e $^{13}$C NMR
2-(4'-chloro-[1,1'-biphenyl]-2-yl)pyridine 3f $^1$H NMR

2-(4'-chloro-[1,1'-biphenyl]-2-yl)pyridine 3f $^{13}$C NMR
2-(4-methyl-[1,1′-biphenyl]-2-yl)pyridine 3h $^1$H NMR

2-(4-methyl-[1,1′-biphenyl]-2-yl)pyridine 3h $^{13}$C NMR
2-(3-methyl-[1,1'-biphenyl]-2-yl)pyridine 3i $^1$H NMR

2-(3-methyl-[1,1'-biphenyl]-2-yl)pyridine 3i $^{13}$C NMR
$4'-(trifluoromethyl)-1,1':2',1''$-terphenyl 3j

$^1$H NMR

$4'-(trifluoromethyl)-1,1':2',1''$-terphenyl 3j

$^{13}$C NMR
2-(5-chloro-[1,1'-biphenyl]-2-yl)pyridine 3k $^1$H NMR

2-(5-chloro-[1,1'-biphenyl]-2-yl)pyridine 3k $^{13}$C NMR
2-(5-methoxy-[1,1'-biphenyl]-2-yl)pyridine 31 $^1$H NMR

$^1$H NMR spectrum showing peaks at various ppm values.

2-(5-methoxy-[1,1'-biphenyl]-2-yl)pyridine 31 $^{13}$C NMR

$^{13}$C NMR spectrum showing peaks at various ppm values.
2-([1,1′:3′,1″-terphenyl]-2′-yl)-6-phenylpyridine 3m $^1$H NMR

2-([1,1′:3′,1″-terphenyl]-2′-yl)-6-phenylpyridine 3m $^{13}$C NMR
2-[[1,1′:3′,1″-terphenyl]-2′-yl]-6-phenylpyridine 3n $^1$H NMR

2-[[1,1′:3′,1″-terphenyl]-2′-yl]-6-phenylpyridine 3n $^{13}$C NMR
2-([1,1':3',1''-terphenyl]-2'-yl)-1H-indole 3p $^{1}H$ NMR

2-([1,1':3',1''-terphenyl]-2'-yl)-1H-indole 3p $^{13}C$ NMR
$1-([1,1'-biphenyl]-2-yl)-1H-pyrazole \ 3q \ ^1H\ NMR$

$1-([1,1'-biphenyl]-2-yl)-1H-pyrazole \ 3q \ ^13C\ NMR$