Supporting Information for

One-step highly selective borylation/Suzuki cross-coupling of two distinct aryl bromides in pure water

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1. Experiment Details

1) General Methods

A GC-MS analysis was carried out using GCMS–QP2010 Ultra (SHIMADZU) provided with Agilent HP-5MS capillary column. All reagents were obtained from Sigma-Aldrich Chemical Co. or Alfa Aesar. $^1$H-NMR spectra were recorded on a Bruker Avance DPX 400 (400 MHz) spectrometer at 400 MHz using CDCl$_3$ as the solvent. The chemical shifts are reported in $\delta$ (ppm) values. Coupling constants are reported in hertz (Hz). The following abbreviations are used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. $^{13}$C-NMR spectra were recorded on a Bruker Avance DPX 400 (400 MHz) spectrometer at 100 MHz using CDCl$_3$ as the solvent. Elemental analyses were obtained on an Elementar Vario EI. All compounds were characterized by $^1$H-NMR, $^{13}$C-NMR and melting point determination (for solids); melting points were uncorrected.

2) General procedures

(1) Procedure for biaryls (1a-l)

Na$_2$PdCl$_4$ (2.9 mg, 1.0 mol%), PCy$_3$HBF$_4$ (14.7 mg, 4.0 mol%) and 2.5 ml H$_2$O in 25 ml round-bottom flask equipped with condenser and magnetic stirring were preheated at 60 $^\circ$C for 0.5h. Then, two bromides (1.0 mmol each), B$_2$(OH)$_4$ (108 mg, 1.2 mmol), NaOH (100 mg, 2.5 mmol) and SDS (28.8 mg, 10.0 mol%) were added. The resulting reaction mixture was stirred and heated at 100 $^\circ$C until the coupling reaction reached completion (monitoring by GC-MS). After extracted with EtOAc (3 x 15 mL), dried over Na$_2$SO$_4$, and concentrated in vacuo, the product was obtained by purification with silica gel flash chromatography.

(2) Procedure for the homo-coupling of PhBr or 4-BrPhCOCH$_3$ (Table 1, entry 11 or 12)

Na$_2$PdCl$_4$ (2.9 mg, 1.0 mol%), PCy$_3$HBF$_4$ (14.7 mg, 4.0 mol%) and 2.5 ml H$_2$O in 25 ml round-bottom flask equipped with condenser and magnetic stirring were preheated at 60 $^\circ$C for 0.5h. Then,
PhBr (314 mg, 2.0 mmol) or 4-BrPhCOCH₃ (398 mg, 2.0 mmol), B₂(OH)₄ (108 mg, 1.2 mmol), NaOH (100 mg, 2.5 mmol) and SDS (28.8 mg, 10.0 mol%) were added. The resulting reaction mixture was stirred and heated at 100 °C for 12 h. However, the reaction did not occur (monitored by GC-MS).

(3) Procedure for heterobiaryls (2a-k, 3a and 3b)

Na₂PdCl₄ (5.8 mg, 2.0 mol%), PCy₃HBF₄ (29.4 mg, 8.0 mol%) and 2.5 ml H₂O in 25 ml round-bottom flask equipped with condenser and magnetic stirring were preheated at 60 °C for 0.5 h. Then, two bromides (1.0 mmol each), B₂(OH)₄ (108 mg, 1.2 mmol), NaOH (100 mg, 2.5 mmol) and SDS (28.8 mg, 10.0 mol%) were added. The resulting reaction mixture was stirred and heated at 100 °C until the coupling reaction reached completion (monitored by GC). After extracted with EtOAc (3 x 15 mL), dried over Na₂SO₄, and concentrated in vacuo, the product was obtained by purification with silica gel flash chromatography.

(4) Procedure for the double-coupled product (4a)

Na₂PdCl₄ (5.8 mg, 2.0 mol%), PCy₃HBF₄ (14.7 mg, 8.0 mol%) and 2.5 ml H₂O in 25 ml round-bottom flask equipped with condenser and magnetic stirring were preheated at 60 °C for 0.5 h before 3,5-dibromopyridine and o-CH₃C₆H₄Br (1.0 mmol each), B₂(OH)₄ (108 mg, 1.2 mmol), NaOH (100 mg, 2.5 mmol) and SDS (28.8 mg, 10.0 mol%) were added and heated at 100 °C for 12 h. Then, 1.0 mmol of 3-bromothiophene, 1.2 mmol B₂(OH)₄ and 2.5 mmol NaOH were added and heated for another 12 h at 100 °C. After extracted with EtOAc (3 x 15 mL), dried over Na₂SO₄, and concentrated in vacuo, the product was obtained by purification with silica gel flash chromatography.

3) Further Details on the cross-coupling selectivity of this method

To illustrate the cross-coupling selectivity of this method, the reaction mixture of entry 5 and the pure compounds of Ph-Ph and CH₃CO-Ph-Ph-COCH₃ were determined by GC-MS, the resulting data were as follows:
As seen from Fig. S1, no homo-coupling reactions occurred in this Na₂PdCl₄-B₂(OH)₄-H₂O system because neither Ph-Ph (Fig. S2, tᵣ = 15.17 min) nor CH₃COPh-PhCOCH₃ (Fig. S3, tᵣ = 25.67 min) could be detected in the reaction mixture of entry 5; the 4-BrPhCOCH₃ substrate was slightly reduced
into PhCOCH\textsubscript{3} (Fig. S1, \textit{t}_R = 9.46 min); the PCy\textsubscript{3} ligand (liberated from PCy\textsubscript{3}HBF\textsubscript{4}) is slightly air-sensitive and prone to oxidation into Cy\textsubscript{2}PH(OH)\textsubscript{2} (Fig. S1, \textit{t}_R = 28.63 min) and Cy\textsubscript{3}P=O (Fig. S1, \textit{t}_R = 30.17 min). The further explanation for the complete cross-selectivity of this method is as follows:

Although ArBr can be well homo-coupled in PEG4000 at 120 °C to form an Ar-Ar product,\textsuperscript{[1]} the reaction temperature of 100 °C in water in this study obviously did not lead to the homo-coupling of PhBr or 4-BrPhCOCH\textsubscript{3}. Instead, such reaction conditions proved to be optimal for the highly efficient and selective borylation of electron-rich PhBr into the highly reactive intermediate PhB(OH)\textsubscript{2} for the Suzuki coupling of electron-deficient 4-BrPhCOCH\textsubscript{3}. Due to the absence of O\textsubscript{2}-mediated oxidation as reported by Jung,\textsuperscript{[2]} this transient intermediate (which was undetectable by GC-MS) could not be oxidatively dimerized to produce the Ph-Ph product.

4) Characterization data

4-Acetyl biphenyl\textsuperscript{[3]} (1a)

\[
\begin{array}{c}
\text{\textbullet - } \text{\textbullet - } \text{COCH}_3 \\
\end{array}
\]
White solid, m.p. 119.8-120.3 °C (lit. 119-120 °C). \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} 8.04 (d, \textit{J} = 8.3 Hz, 2H), 7.70 (d, \textit{J} = 8.3 Hz, 2H), 7.64 (d, \textit{J} = 7.4 Hz, 2H), 7.50-7.46 (m, 2H), 7.43-7.39 (m, 1H), 2.65 (s, 3H). \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}): \textit{\delta} 197.63, 145.63, 139.71, 135.67, 128.79, 128.76, 128.07, 127.11, 127.07, 26.53.

4-Phenylphenol\textsuperscript{[4]} (1b)

\[
\begin{array}{c}
\text{HO} - \text{\textbullet - } \text{\textbullet -} \\
\end{array}
\]
White solid, m.p. 163.6-164.7 °C (lit. 164-166 °C). \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} 7.55 (t, \textit{J} = 8.3 Hz, 2H), 7.49 (q, \textit{J} = 11.3 Hz, 2H), 7.44-7.40 (m, 2H), 7.33-7.21 (m, 1H), 6.91 (d, \textit{J} = 8.6 Hz, 2H), 4.81 (s, br, 1H). \textsuperscript{13}C-NMR (100 MHz, CDCl\textsubscript{3}): \textit{\delta} 154.86 140.57, 133.86, 128.57, 128.24, 126.56, 115.46.

3-Phenylbenzoic acid\textsuperscript{[5]} (1c)

\[
\begin{array}{c}
\text{\textbullet - } \text{\textbullet - } \text{COOH} \\
\end{array}
\]
White solid, m.p. 164.9-167.2 °C (lit.164-169 °C). \textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \textit{\delta} 8.38 (s, 1H), 8.12
(d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 8.4 Hz, 2H), 7.59-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.42-7.39 (m, 1H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 171.66, 141.48, 139.77, 132.28, 129.62, 128.85, 128.81, 128.78, 128.70, 127.69, 127.02.

**Biphenyl-4-carboxaldehyde**$^{[6]}$ (1d)

![Biphenyl-4-carboxaldehyde](attachment:image)

Colorless oil. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 10.07 (s, 1H), 7.95 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.65 (t, J = 3.8 Hz, 1H), 7.51-7.48 (m, 2H), 7.45-7.41 (m, 1H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 191.84, 147.04, 139.54, 135.01, 130.14, 128.87, 128.33, 127.54, 127.22.

**4'-Methoxy-[1,1'-biphenyl]-3-ol**$^{[7]}$ (1e)

![4'-Methoxy-[1,1'-biphenyl]-3-ol](attachment:image)

White solid, m.p. 90.2-90.7 (lit. 91 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.51 (q, J = 8.8 Hz, 2H), 7.31-7.27 (m, 1H), 7.14 (d, J = 7.7 Hz, 1H), 7.03 (t, J = 3.8 Hz, 1H), 6.97 (t, J = 8.7 Hz, 2H), 6.78 (q, J = 10.1 Hz, 1H), 4.85 (s, br, 1H), 3.86 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 159.03, 155.64, 142.41, 133.10, 129.82, 127.98, 119.19, 114.04, 113.48, 113.45, 55.23.

**4-(2-Methoxyphenyl)benzonitrile**$^{[8]}$ (1f)

![4-(2-Methoxyphenyl)benzonitrile](attachment:image)

White solid, m.p. 71.8-72.9 °C (lit. 72-74 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.70-7.63 (m, 4H), 7.41-7.37 (m, 1H), 7.33-7.29 (m, 1H), 7.08-6.97 (m, 2H), 3.80 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 156.14, 143.22, 131.61, 130.47, 130.08, 129.78, 128.44, 120.90, 119.04, 111.16, 110.24, 55.38.

**2-(4-Tolyl)benzonitrile**$^{[9]}$ (1g)

![2-(4-Tolyl)benzonitrile](attachment:image)

White solid, m.p. 49.1-49.3 °C (lit. 49-50 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.76 (q, J = 8.6 Hz, 1H), 7.65-7.61 (m, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.1 Hz, 2H), 7.44-7.40 (m, 1H), 7.31 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 145.38, 138.54, 135.11, 133.56, 132.62,
2-(2-Methoxyphenyl)benzoic acid\[^{[10]}\] (1h)

![Structure of 2-(2-Methoxyphenyl)benzoic acid](image)

White solid, m.p. 160.1-161.7 °C (lit. 160-162 °C). \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta\ 7.94\ (q, J = 8.7\ Hz, 1H), 7.60-7.56\ (m, 1H), 7.43-7.39\ (m, 1H), 7.35-7.31\ (m, 2H), 7.26\ (q, J = 9.0\ Hz, 1H), 7.06-7.02\ (m, 1H), 6.88\ (d, J = 8.2\ Hz, 1H), 3.71\ (s, 3H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\ 173.48, 155.94, 138.91, 132.15, 131.37, 130.46, 129.96, 129.67, 129.64, 128.89, 126.98, 120.71, 110.34, 54.86.

4-bromo-4'-methoxybiphenyl\[^{[11]}\] (1i)

![Structure of 4-bromo-4'-methoxybiphenyl](image)

White solid, m.p. 144.5-145.6 °C (lit. 143-144 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\ 7.53\ (d, J = 8.5\ Hz, 2H), 7.49\ (d, J = 8.8\ Hz, 2H), 7.42\ (d, J = 8.4\ Hz, 2H), 6.98\ (d, J = 8.7\ Hz, 2H), 3.86\ (s, 3H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\ 159.23, 139.56, 132.31, 131.62, 128.14, 127.82, 120.62, 114.15, 55.20.

1-(4-(Naphthalen-1-yl)phenyl)ethanone\[^{[12]}\] (1j)

![Structure of 1-(4-(Naphthalen-1-yl)phenyl)ethanone](image)

White solid, m.p. 102.7-103.6 °C (lit.103-104 °C). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\ 8.10\ (d, J = 8.2\ Hz, 2H), 7.94-7.90\ (m, 2H), 7.85\ (d, J = 8.4\ Hz, 1H), 7.62\ (d, J = 8.2\ Hz, 2H), 7.57-7.50\ (m, 2H), 7.48-7.43\ (m, 2H), 2.69\ (s, 3H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta\ 197.70, 145.63, 138.85, 135.82, 133.62, 131.03, 130.16, 128.26, 128.21, 126.77, 126.22, 125.84, 125.40, 125.18, 26.57.

4-(naphthalen-2-yl)benzoic acid\[^{[13]}\] (1k)

![Structure of 4-(naphthalen-2-yl)benzoic acid](image)

White solid, m.p. 209.1-210.8 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\ 8.26\ (d, J = 8.0\ Hz, 2H), 7.99\ (d, J = 8.3\ Hz, 1H), 7.95-7.91\ (m, 2H), 7.87\ (d, J = 8.4\ Hz, 1H), 7.64\ (d, J = 8.1\ Hz, 2H), 7.58-7.47\ (m,
$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 171.59, 146.41, 138.80, 133.61, 131.75, 131.55, 130.99, 130.12, 130.09, 128.25, 126.81, 126.27, 125.86, 125.39, 125.18.

5-(3-Methoxyphenyl)-2, 3-dihydro-1H-inden-1-one[$^{14}$] (II)

White solid, m.p. 103.7-104.6 °C (lit. 103-104 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.81 (d, $J = 8.0$ Hz, 1H), 7.67 (s, 1H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.39 (t, $J = 15.9$ Hz, 1H), 7.21 (d, $J = 7.7$ Hz, 1H), 7.15 (d, $J = 1.9$ Hz, 1H), 6.96 (q, $J = 10.4$ Hz, 1H), 3.88 (s, 3H), 3.20 (t, $J = 11.6$ Hz, 2H), 2.74 (t, $J = 12.0$ Hz, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 206.48, 159.85, 155.67, 147.39, 141.54, 135.94, 129.83, 126.66, 125.06, 123.89, 119.78, 113.51, 113.05, 55.21, 36.36, 25.71.

1-(4-(Thiophen-2-yl)phenyl)ethanone[$^{15}$] (2a)

White solid, m.p. 103.7-104.6 °C (lit. 103-104 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 3.6$ Hz, 1H), 7.38 (d, $J = 5.1$ Hz, 1H), 7.13 (q, $J = 8.6$ Hz, 1H), 2.62 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 197.19, 142.77, 138.61, 135.56, 128.95, 128.21, 126.31, 125.50, 124.45, 26.43.

2-(4-Methoxyphenyl)pyridine[$^{16}$] (2b)

White solid, m.p. 58.7-59.1 °C (lit. 53-55 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.66 (d, $J = 4.8$ Hz, 1H), 7.98-7.94 (m, 2H), 7.74-7.66 (m, 2H), 7.19-7.16 (m, 1H), 7.12-6.99 (m, 2H), 3.87 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 160.30, 156.93, 149.33, 136.54, 131.80, 128.01, 121.25, 119.67, 113.96, 55.17.

2-Methoxy-5-(thiophen-3-yl)pyridine[$^{17}$] (2c)
Colorless oil. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.42 (d, $J = 2.2$ Hz, 1H), 7.77 (q, $J = 10.9$ Hz, 1H), 7.41-7.37 (m, 2H), 7.32 (d, $J = 4.9$ Hz, 1H), 6.78 (d, $J = 8.6$ Hz, 1H), 3.97 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 163.11, 144.16, 138.66, 136.73, 126.51, 125.69, 125.10, 119.58, 110.71, 53.40.

[2,2'-Bithiophene]-5-carbaldehyde$^{[18]}$ (2d)

White solid, m.p. 120.1-120.3 °C (lit. 122-123 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 9.87 (s, 1H), 7.69 (d, $J = 3.9$ Hz, 1H), 7.58 (d, $J = 1.6$ Hz, 1H), 7.39 (q, $J = 7.9$ Hz, 1H), 7.35 (d, $J = 4.9$ Hz, 1H), 7.28 (d, $J = 3.9$ Hz, 1H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 182.58, 148.56, 141.41, 137.31, 134.34, 127.06, 125.79, 123.94, 122.54.

3-Bromo-5-(o-tolyl)pyridine$^{[19]}$ (2e)

Light yellow oil. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.67 (d, $J = 2.2$ Hz, 1H), 8.52 (d, $J = 2.2$ Hz, 1H), 7.82 (t, $J = 4.0$ Hz, 1H), 7.34-7.28 (m, 3H), 7.20 (d, $J = 7.2$ Hz, 1H), 2.28 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 148.91, 147.89, 138.86, 136.35, 135.35, 130.53, 129.62, 128.46, 126.05, 120.16, 20.13.

5-(Naphthalen-1-yl)thiophene-2-carbaldehyde$^{[20]}$ (2f)

Colorless solid, m.p. 55.4-56.1 °C (lit. 56.7-56.9 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 9.97 (s, 1H), 8.16 (t, $J = 9.4$ Hz, 1H), 7.94 (t, $J = 8.1$ Hz, 2H), 7.85 (d, $J = 3.8$ Hz, 1H), 7.61 (q, $J = 7.8$ Hz, 1H), 7.58-7.51 (m, 3H), 7.37 (d, $J = 3.8$ Hz, 1H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 182.81, 152.14, 143.38, 136.55, 133.68, 130.97, 130.93, 129.66, 128.52, 128.46, 128.21, 126.94, 126.28, 125.10, 124.94.

Ethyl 4-(thiophen-3-yl)benzoate$^{[21]}$ (2g)

S9
White solid, m.p. 85.3-85.7 °C (lit. 87 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.08 (q, $J = 8.5$ Hz, 2H), 7.66 (t, $J = 8.5$ Hz, 2H), 7.57 (q, $J = 4.1$ Hz, 1H), 7.45-7.41 (m, 2H), 4.42-4.37 (q, 2H), 1.43-1.40 (t, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 166.27, 141.07, 139.76, 130.01, 128.79, 126.51, 126.04, 125.99, 121.67, 60.79, 14.20.

6-(Thiophen-3-yl)quinolone$^{[22]}$ (2h)

White solid, m.p. 96.4-96.9 °C (lit. 94-98 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.93 (q, $J = 5.5$ Hz, 1H), 8.22 (d, $J = 9.0$ Hz, 2H), 8.00 (q, $J = 8.6$ Hz, 2H), 7.62 (q, $J = 3.8$ Hz, 1H), 7.52 (q, $J = 6.0$ Hz, 1H), 7.47-7.43 (m, 2H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 149.63, 146.80, 141.11, 136.51, 133.91, 129.32, 128.78, 128.50, 126.62, 126.14, 124.19, 121.39, 121.32.

3-(o-Tolyl)quinolone$^{[23]}$ (2i)

Light yellow oil. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.96 (d, $J = 2.0$ Hz, 1H), 8.19 (d, $J = 8.4$ Hz, 1H), 8.10 (s, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.74 (t, $J = 15.3$ Hz, 1H), 7.58 (t, $J = 15.0$ Hz, 1H), 7.37 (q, $J = 10.0$ Hz, 4H), 2.34 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 151.29, 146.79, 137.93, 135.68, 135.24, 134.68, 130.50, 130.05, 129.27, 129.08, 128.06, 127.73, 127.61, 126.78, 126.05, 20.34.

5-(4-Methoxyphenyl)-1-methyl-1H-indole$^{[24]}$ (2j)

White solid, m.p. 144.4-145.9 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J = 0.6$ Hz, 1H), 7.58 (d, $J = 8.6$ Hz, 2H), 7.46 (q, $J = 9.8$ Hz, 1H), 7.37 (d, $J = 8.5$ Hz, 1H), 7.08 (d, $J = 2.2$ Hz, 1H), 6.99 (d, $J =$
8.7 Hz, 2H), 6.53 (d, J = 2.5 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 158.25, 135.78, 135.11, 132.35, 129.26, 128.17, 127.58, 121.03, 118.74, 113.92, 109.23, 101.00, 55.2, 32.8.

2-(4-Methoxyphenyl)benzofuran$^{[25]}$ (2k)

White solid, m.p. 150.9-151.3 °C (lit. 150-151 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.77 (d, J = 8.2 Hz, 2H), 7.57 (t, J = 8.1 Hz, 1H), 7.52 (d, J = 7.9 Hz, 1H), 7.29-7.21 (m, 4H), 6.98 (s, 1H), 2.41 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 156.02, 154.60, 138.44, 129.33, 129.18, 127.58, 124.72, 123.83, 122.69, 120.58, 110.93, 100.39, 21.24.

5-Bromo-2-(p-tolyl)pyridine$^{[26]}$ (3a)

White solid, m.p. 108.2-109.2 °C (lit. 109-110 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.71 (d, J = 2.1 Hz, 1H), 7.87-7.82 (m, 3H), 7.60 (d, J = 8.4 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 2.41 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 155.77, 150.41, 139.25, 139.00, 135.28, 129.40, 126.46, 121.12, 118.70, 21.10.

5-Bromo-2-(thiophen-3-yl)pyridine$^{[27]}$ (3b)

White solid, m.p. 72.8-73.2 °C (lit. 73-74 °C). $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.45 (d, J = 2.3 Hz, 1H), 7.67-7.61 (m, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.41-7.37 (m, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 151.81, 150.45, 140.19, 139.06, 126.44, 125.85, 123.81, 121.17, 118.35.

3-(Thiophen-3-yl)-5-(o-tolyl)pyridine (4a)

Light yellow oil. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ 8.86 (s, 1H), 8.52 (s, 1H), 7.86 (d, J = 1.8 Hz, 1H), 7.57 (d, J = 1.6 Hz, 1H), 7.48-7.43 (m, 2H), 7.32 (d, J = 9.8 Hz, 2H), 7.29 (d, J = 8.7 Hz, 2H), 2.32 (s,
$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ 147.85, 145.52, 138.37, 137.63, 137.45, 135.47, 134.14, 130.92, 130.46, 129.68, 128.12, 126.95, 125.98, 125.75, 121.53, 20.23.

2. Reference


3. NMR Spectra