Supporting information for

Pd/Cu-Cocatalyzed Regioselective Arylation of Thiazole Derivatives at 2-Position under Ligand-Free Conditions

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\begin{center}
\begin{tikzpicture}
\node at (0,0) {\text{N}};
\node at (1,0) {\text{S}};
\node at (2,0) {\text{N}};
\node at (3,0) {\text{R}1};
\node at (3,-1) {\text{N}};
\node at (3,-2) {\text{S}};
\node at (3,-3) {\text{R}1};
\end{tikzpicture}
\end{center}

\\text{+}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\text{I}};
\node at (1,0) {\text{R}1};
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\text{Pd(OAc)}_2, \text{Cu(TFA)}_2};
\node at (1,0) {\text{t-BuOLi}};
\node at (2,0) {\text{DMF, 130\textdegree C}};
\end{tikzpicture}
\end{center}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\text{N}};
\node at (1,0) {\text{S}};
\node at (2,0) {\text{R}1};
\node at (3,0) {\text{N}};
\node at (3,-1) {\text{S}};
\node at (3,-2) {\text{R}1};
\end{tikzpicture}
\end{center}

1. Experimental \hspace{1cm} 2

2. Characterization Data \hspace{1cm} 2

3. NMR Spectra of All Products \hspace{1cm} 5
1 Experimental

1.1 General
All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are identified by appropriate technique such as $^1$H NMR, $^{13}$C NMR and compared with previously reported data. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. $^1$H NMR and $^{13}$C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in CDCl$_3$, respectively, and chemical shifts are reported in ppm. GC analyses are performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m $\times$ 320 $\mu$m $\times$ 0.25 $\mu$m, carrier gas: H$_2$, FID detection. Mass spectra are taken on a Thermo Scientific ISQ LT GC-MS instrument in the electron ionization (EI) mode. Elemental analyses are performed on a Yanagimoto MT3CHN recorder.

1.2 Experimental Procedure
General Procedure for the Arylation of Thiazole Derivatives: A mixture of 4-methylthiazole (1.0 mmol), iodobenzene (1.0 mmol), Pd(OAc)$_2$ (0.01 mmol), Cu(TFA)$_2$ (0.2 mmol) and t-BuOLi (2.0 mmol) in DMF (3.0 mL) was stirred at 130°C for 3 h. After the completion of the reaction, the mixture was cooled to 25°C and then EtOAc and H$_2$O were added to it. The organic layer was separated and washed with brine, dried over Na$_2$SO$_4$. The volatiles were removed under vacuum to afford the crude product, and analyzed by GC. The crude product was purified by column chromatography on silica gel and eluted with EtOAc/hexanes (10/90) to afford the desired pure product.

2. Characterization Data

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\textbf{4-methyl-2-phenylthiazole (3a)}^{11}: ^1\text{H NMR (500 MHz, CDCl}_3\text{)} \delta 7.93 (dd, J = 7.9, 1.5 Hz, 2H), 7.46 – 7.38 (m, 3H), 6.87 (d, J = 0.8 Hz, 1H), 2.51 (s, 3H). ^{13}\text{C NMR (125 MHz, CDCl}_3\text{)} \delta 166.73 (s), 152.71 (s), 130.17 (s), 128.93 (s), 127.93 (s), 125.54 (s), 112.48 (s), 16.23 (s).
\]
4-methyl-2-o-tolylthiazole (3b)

$\mathrm{^{1}H\text{ NMR (500 MHz, CDCl}_{3}\delta 7.69 (dd, J = 7.5, 1.1 Hz, 1H), 7.32 – 7.25 (m, 3H), 6.94 (dd, J = 1.9, 0.9 Hz, 1H), 2.57 (s, 3H), 2.53 (d, J = 1.0 Hz, 3H).}}$

$\mathrm{^{13}C\text{ NMR (125 MHz, CDCl}_{3}\delta 167.09 (s), 153.13 (s), 136.65 (s), 133.41 (s), 131.39 (s), 130.01 (s), 129.31 (s), 126.10 (s), 114.14 (s), 21.38 (s), 17.39 (s).}}$

$\mathrm{MS (EI) m/z: 189 [M^+].}}$

$\mathrm{Anal. Calcd for C_{11}H_{11}NS: C, 69.80; H, 5.86, N, 7.40. Found: C, 69.85; H, 5.89; N, 7.36.}}$

4-methyl-2-m-tolylthiazole (3c)

$\mathrm{^{1}H\text{ NMR (500 MHz, CDCl}_{3}\delta 7.78 (s, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 6.86 (s, 1H), 2.51 (d, J = 0.8 Hz, 3H), 2.41 (s, 3H).}}$

$\mathrm{^{13}C\text{ NMR (125 MHz, CDCl}_{3}\delta 167.97 (s), 153.83 (s), 138.78 (s), 133.79 (s), 130.72 (s), 128.88 (s), 127.04 (s), 113.39 (s), 21.43 (s), 17.41 (s).}}$

$\mathrm{MS (EI) m/z: 189 [M^+].}}$ Anal. Calcd for C_{11}H_{11}NS: C, 69.80; H, 5.86, N, 7.40. Found: C, 69.85; H, 5.89; N, 7.36.

4-methyl-2-p-tolylthiazole (3d)

$\mathrm{^{1}H\text{ NMR (500 MHz, CDCl}_{3}\delta 7.78 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 6.78 (d, J = 0.7 Hz, 1H), 2.45 (d, J = 0.7 Hz, 3H), 2.34 (s, 3H).}}$

$\mathrm{^{13}C\text{ NMR (125 MHz, CDCl}_{3}\delta 167.92 (s), 153.73 (s), 140.08 (s), 131.28 (s), 129.66 (s), 126.49 (s), 113.03 (s), 21.49 (s), 17.39 (s).}}$

2-(4-methoxyphenyl)-4-methylthiazole (3e)

$\mathrm{^{1}H\text{ NMR (500 MHz, CDCl}_{3}\delta 7.82 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.75 (s, 1H), 3.80 (s, 3H), 2.44 (s, 3H).}}$

$\mathrm{^{13}C\text{ NMR (126 MHz, CDCl}_{3}\delta 167.64 (s), 161.10 (s), 153.57 (s), 128.04 (s), 114.32 (s), 112.55 (s), 55.49 (s), 17.36 (s).}}$

$\mathrm{MS (EI) m/z: 205 [M^+].}}$ Anal. Calcd for C_{11}H_{11}NO_{2}S: C, 64.36; H, 5.40, N, 6.82. Found: C, 64.32; H, 5.43; N, 6.80.

4-methyl-2-(4-nitrophenyl)thiazole (3f)

$\mathrm{^{1}H\text{ NMR (500 MHz, CDCl}_{3}\delta 8.30 – 8.21 (m, 2H), 8.12 – 8.02 (m, 2H), 7.01 (s, 1H), 2.51 (s, 3H).}}$

$\mathrm{^{13}C\text{ NMR (125 MHz, CDCl}_{3}\delta 164.48 (s), 155.19 (s), 148.34 (s), 139.35 (s), 127.07 (s), 124.40 (s), 115.89 (s), 17.32 (s).}}$

$\mathrm{MS (EI) m/z: 220 [M^+].}}$ Anal. Calcd for C_{10}H_{8}N_{2}O_{2}S: C, 54.53; H, 3.66, N, 12.72. Found: C, 54.55; H, 3.70; N, 12.68.

2-(4-chlorophenyl)-4-methylthiazole (3g)

$\mathrm{^{1}H\text{ NMR (500 MHz, CDCl}_{3}\delta 7.94 – 7.88 (m, 2H), 7.14 – 7.08 (m, 2H), 6.85 (d, J = 0.9 Hz, 1H), 2.50 (d, J = 0.9 Hz, 3H).}}$

$\mathrm{^{13}C\text{ NMR (125 MHz, CDCl}_{3}\delta 166.49 (s), 164.82 (s), 162.83 (s), 153.98 (s), 130.26 (s), 128.47 (s), 116.13 (s), 115.95 (s), 113.52 (s), 17.34 (s).}}$

1,4-bis(4-methylthiazol-2-yl)benzene (3h)

$\mathrm{^{1}H\text{ NMR (500 MHz,}}$
CDCl$_3$ δ 7.95 (s, 4H), 6.86 (s, 2H), 2.48 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 166.77 (s), 154.27 (s), 134.92 (s), 126.99 (s), 114.03 (s), 17.36 (s). MS (EI) m/z: 272 [M$^+$]. Anal. Calcd for C$_{14}$H$_{12}$N$_2$S$_2$: C, 61.73; H, 4.44; N, 10.28. Found: C, 61.77; H, 4.50; N, 10.25.

2-phenylbenzo[d]thiazole (8a)[5]: $^1$H NMR (500 MHz, CDCl$_3$) δ 8.13 – 8.07 (m, 3H), 7.90 (d, $J$ = 8.0 Hz, 1H), 7.53 – 7.47 (m, 4H), 7.41 – 7.37 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 168.19 (s), 154.27 (s), 135.19 (s), 133.75 (s), 131.08 (s), 129.14 (s), 127.69 (s), 126.43 (s), 125.31 (s), 123.36 (s), 121.74 (s).

2-o-tolylbenzo[d]thiazole (8b)[5]: $^1$H NMR (500 MHz, CDCl$_3$) δ 8.08 (ddd, $J$ = 8.2, 1.0, 0.6 Hz, 1H), 7.90 (ddd, $J$ = 7.9, 1.1, 0.6 Hz, 1H), 7.84 (dd, $J$ = 7.9, 1.1 Hz, 1H), 7.73 (dd, $J$ = 7.9, 1.1 Hz, 1H), 7.48 (ddd, $J$ = 8.3, 1.2 Hz, 1H), 7.40 – 7.26 (m, 4H), 2.64 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 168.13 (s), 153.93 (s), 137.38 (s), 135.73 (s), 133.21 (s), 131.68 (s), 130.68 (s), 130.14 (s), 126.25 (s), 125.22 (s), 123.51 (s), 121.50 (s), 21.50 (s).

2-m-tolylbenzo[d]thiazole (8c)[5]: $^1$H NMR (500 MHz, CDCl$_3$) δ 8.04 (d, $J$ = 8.1 Hz, 1H), 7.90 (s, 1H), 7.84 (dd, $J$ = 12.4, 8.0 Hz, 2H), 7.45 (t, $J$ = 7.6 Hz, 1H), 7.34 (t, $J$ = 7.6 Hz, 2H), 7.26 (d, $J$ = 7.5 Hz, 1H), 2.41 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 168.51 (s), 154.14 (s), 139.00 (s), 135.10 (s), 133.56 (s), 131.98 (s), 129.06 (s), 128.12 (s), 126.44 (s), 125.13 (d, $J$ = 34.7 Hz), 123.26 (s), 121.74 (s), 21.49 (s).

2-p-tolylbenzo[d]thiazole (8d)[5]: $^1$H NMR (500 MHz, CDCl$_3$) δ 8.04 (d, $J$ = 8.2 Hz, 1H), 7.95 (d, $J$ = 8.0 Hz, 2H), 7.83 (d, $J$ = 8.0 Hz, 1H), 7.44 (t, $J$ = 7.7 Hz, 1H), 7.32 (t, $J$ = 7.6 Hz, 2H), 7.26 (d, $J$ = 7.5 Hz, 1H), 2.41 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 168.33 (s), 154.33 (s), 141.49 (s), 135.10 (s), 129.82 (s), 127.61 (s), 126.35 (s), 125.11 (s), 121.68 (s), 21.63 (s).

2-(4-methoxyphenyl)benzo[d]thiazole (8e)[6]: $^1$H NMR (500 MHz, CDCl$_3$) δ 8.01 (dd, $J$ = 8.5, 3.3 Hz, 3H), 7.86 (d, $J$ = 7.9 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.36 – 7.32 (m, 1H), 7.01 – 6.96 (m, 2H), 3.87 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 167.99 (s), 162.05 (s), 154.30 (s), 134.95 (s), 129.24 (s), 128.16 (s), 126.43 (d, $J$ = 25.2 Hz), 124.92 (s), 122.93 (s), 121.62 (s), 114.49 (s), 55.59 (s).

2-(4-nitrophenyl)benzo[d]thiazole (8f)[7]: $^1$H NMR (500 MHz, CDCl$_3$) δ 8.34 (d, $J$ = 8.8 Hz, 2H), 8.25 (d, $J$ = 8.8 Hz, 2H), 8.11 (d, $J$ = 8.1 Hz, 1H), 7.94 (d, $J$ = 8.0 Hz, 1H), 7.54 (t, $J$ = 7.4 Hz, 1H), 7.45 (t, $J$ = 7.4 Hz, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 164.95 (s), 154.20 (s), 149.13 (s), 139.28 (s), 135.59 (s), 128.35 (s), 127.04 (s), 126.34 (s), 124.24 (d, $J$ = 49.7 Hz), 124.01 – 123.62 (m), 121.96 (s).
2-(4-chlorophenyl)benzo[d]thiazole (8g)\[7\]: \( ^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.13 – 7.98 (m, 3H), 7.85 (d, \( J = 8.0 \text{ Hz} \), 1H), 7.54 – 7.43 (m, 1H), 7.41 – 7.31 (m, 1H), 7.14 (t, \( J = 8.6 \text{ Hz} \), 2H). \( ^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 166.78 (s), 165.53 (s), 163.52 (s), 154.19 (s), 135.15 (s), 130.03 (s), 129.58 (s), 126.50 (s), 125.33 (s), 123.29 (s), 121.70 (s), 116.31 (s), 116.14 (s).

[1] John, Oliver; Org. Lett. 2007, 9, 4009-4012

Copies of products \( ^1\)H NMR and \( ^{13}\)C NMR

\( ^1\)H NMR spectrum (500 MHz, CDCl\(_3\)) of 3a
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3a

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3b
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of $3b$  

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of $3c$
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3c

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3d
\( ^{13}\text{C} \) NMR spectrum (125 MHz, CDCl\(_3\)) of 3d

\( ^{1}\text{H} \) NMR spectrum (500 MHz, CDCl\(_3\)) of 3e
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3e

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3f
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3f

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3g
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3g

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 3h
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 3h

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 8a
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 8a

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 8b
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 8b

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 8c
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 8c

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 8d
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 8d

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 8e
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 8e

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 8f
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 8f

$^1$H NMR spectrum (500 MHz, CDCl$_3$) of 8g
$^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of 8g

MS 3c