Supplementary Information

for

Palladium-Catalyzed Oxidative C–H/C–H Cross-Coupling of Benzothiazoles with Thiophenes and Thiazoles

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General information

Analytical thin layer chromatography (TLC) was HSGF 254 (0.15–0.2 mm thickness, Yantai Huiyou Company, China). Column chromatography was carried out on silica gel (200–300 mesh). NMR spectra were recorded at Varian Mercury-300 spectrometer, Varian Mercury-400 spectrometer and Varian Mercury-500 spectrometers (300 MHz or 400 MHz for $^1$H NMR, 100 MHz or 125 MHz for $^{13}$C NMR). Tetramethylsilane (TMS) was used as internal standard. Chemical shifts were reported in parts per million (ppm, δ). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), heptet (hept), multiplet (m) and broad (br). Low- and high-resolution mass spectra (LRMS and HRMS) were recorded on a Finnigan/MAT-95 (EI), Finnigan LCQ/DECA and Micromass Ultra Q-TOF (ESI) spectrometer. LC-MS was performed on an Agilent 1200-6110 instrument. Melting points (m.p.) were measured by Büchi 510 melting point apparatus and were uncorrected.

Optimization of reaction conditions

Table S1 Screening of Oxidants.$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidant</th>
<th>Time (h)</th>
<th>Yield$^b$ (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>Cu(OAc)$_2$</td>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td>2</td>
<td>CuBr$_2$</td>
<td>20</td>
<td>Trace</td>
</tr>
<tr>
<td>3</td>
<td>CuCl$_2$</td>
<td>20</td>
<td>Trace</td>
</tr>
<tr>
<td>4</td>
<td>Cu(OTf)$_2$</td>
<td>20</td>
<td>Trace</td>
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<tr>
<td>5</td>
<td>AgOAc</td>
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<td>18</td>
</tr>
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<td>6</td>
<td>AgTFA</td>
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<td>6</td>
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<tr>
<td>7</td>
<td>Ag$_2$CO$_3$</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>8</td>
<td>Ag$_2$SO$_4$</td>
<td>20</td>
<td>Trace</td>
</tr>
<tr>
<td>9</td>
<td>Ag$_2$O</td>
<td>20</td>
<td>13</td>
</tr>
<tr>
<td>10</td>
<td>AgNO$_3$</td>
<td>12</td>
<td>28</td>
</tr>
<tr>
<td>11$^c$</td>
<td>AgNO$_3$</td>
<td>12</td>
<td>27</td>
</tr>
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<td>12</td>
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<tr>
<td>13</td>
<td>BQ</td>
<td>20</td>
<td>Trace</td>
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$^a$ 1a (1.0 mmol, 1.0 equiv), 2a (4.0 mmol, 4.0 equiv), DMA (3.0 mL), all of reagents were mixed and stirred at r.t. for 5 minutes, then the sealed tubes were screw capped and heated at 110°C.
°C for indicated time. b Yield Determined by ¹H NMR analysis of the crude product using dimethyl terephthalate as an internal standard. c The reaction was carried out under N₂ atmosphere.

**Table S2 Screening of Ligands.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Time (h)</th>
<th>Yieldb (%)</th>
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<td>1</td>
<td>–</td>
<td>12</td>
<td>28</td>
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<tr>
<td>2</td>
<td>AcOH</td>
<td>12</td>
<td>29</td>
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<tr>
<td>3</td>
<td>PivOH</td>
<td>10</td>
<td>36</td>
</tr>
<tr>
<td>4</td>
<td>Me-Gly-OH</td>
<td>5</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>(Me)₂-Gly-OH</td>
<td>5</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>Pro-OH</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>Boc-Me-Ala-OH</td>
<td>2</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>PhCO₂H</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>9</td>
<td>ρNO₂-PhCO₂H</td>
<td>10</td>
<td>12</td>
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<tr>
<td>10</td>
<td>Bipy</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>11</td>
<td>Phen</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>12</td>
<td>Phen (15 mol%), Boc-Me-Ala-OH (15 mol%)</td>
<td>4</td>
<td>41</td>
</tr>
<tr>
<td>13</td>
<td>Phen (15 mol%), PivOH (15 mol%)</td>
<td>4</td>
<td>40</td>
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</table>

a 1a (1.0 mmol, 1.0 equiv), 2a (4.0 mmol, 4.0 equiv), DMA (3.0 mL), all of reagents were mixed and stirred at r.t. for 5 minutes, then the sealed tubes were screw capped and heated at 110 °C until 1a disappeared. b Determined by ¹H NMR analysis of the crude product using dimethyl terephthalate as an internal standard.

**Table S3 Screening of Solvents.**

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<th>Entry</th>
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<th>Time (h)</th>
<th>Yieldb (%)</th>
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<td>DMA</td>
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<td>50</td>
</tr>
<tr>
<td>2</td>
<td>DMF</td>
<td>10</td>
<td>31</td>
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<tr>
<td>3</td>
<td>NMP</td>
<td>10</td>
<td>27</td>
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<tr>
<td>4</td>
<td>DMSO</td>
<td>10</td>
<td>69(63)c</td>
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<tr>
<td>5</td>
<td>Dioxane</td>
<td>10</td>
<td>27</td>
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<tr>
<td>6</td>
<td>EtAc</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>DME</td>
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<td>12</td>
</tr>
<tr>
<td>8</td>
<td>nBuOH</td>
<td>10</td>
<td>21</td>
</tr>
</tbody>
</table>

a 1a (1.0 mmol, 1.0 equiv), 2a (4.0 mmol, 4.0 equiv), solvent (3.0 mL), all of reagents were mixed and stirred at r.t. for 5 minutes, then the sealed tubes were screw capped and heated at 110 °C until 1a disappeared. b Determined by ¹H NMR analysis of the crude product using dimethyl terephthalate as an internal standard.
terephthalate as an internal standard. The isolated yield was given in parentheses.

**Table S4** Screening of Bases.

<table>
<thead>
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<th>Entry</th>
<th>Base</th>
<th>Time (h)</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>–</td>
<td>10</td>
<td>69</td>
</tr>
<tr>
<td>2&lt;sup&gt;c&lt;/sup&gt;</td>
<td>–</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>NaOAc</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>Na₂CO₃</td>
<td>10</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>K₂CO₃</td>
<td>10</td>
<td>33</td>
</tr>
<tr>
<td>6</td>
<td>KF</td>
<td>10</td>
<td>37</td>
</tr>
<tr>
<td>7</td>
<td>Na₃PO₄·3H₂O</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

<sup>a</sup> 1a (1.0 mmol, 1.0 equiv), 2a (4.0 mmol, 4.0 equiv), DMSO (3.0 mL), all of reagents were mixed and stirred at r.t. for 5 minutes, then the sealed tubes were screw capped and heated at 110 °C until 1a disappeared. <sup>b</sup> Determined by ¹H NMR analysis of the crude product using dimethyl terephthalate as an internal standard. <sup>c</sup> TEMPO (30 mol%) was added.

**Table S5** Screening of loadings of reagents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reagent</th>
<th>Loading</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)₂</td>
<td>5 mol%</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)₂</td>
<td>2.5 mol%</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>Pd(OAc)₂</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Phen</td>
<td>1.0 equiv</td>
<td>42</td>
</tr>
</tbody>
</table>

<sup>a</sup> 1a (1.0 mmol, 1.0 equiv), 2a (4.0 mmol, 4.0 equiv), DMSO (3.0 mL), all of reagents were mixed and stirred at r.t. for 5 minutes, then the sealed tubes were screw capped and heated at 110 °C for 10 h. <sup>b</sup> Determined by ¹H NMR analysis of the crude product using dimethyl terephthalate as an internal standard.

**General procedure for cross-dehydrogenative coupling of benzothiazoles with thiophenes and thiazoles**

To a septum capped 25 mL of sealed tube were added Pd(OAc)₂ (10 mol%), AgNO₃ (2.0 equiv)
and 1,10-Phenanthroline hydrate (30 mol%) under air, followed by DMSO (3.0 mL) with stirring. Benzothiazoles 1 (1.0 mmol, 1.0 equiv) and thiophenes/thiazoles 2 (4.0 equiv) were then added subsequently. The sealed tube was screw capped and heated to 110 °C. After being stirred for 10 h, the reaction mixture was cooled to room temperature, diluted with 20 mL of CH$_2$Cl$_2$, filtered through a celite pad, washed with 80 mL of CH$_2$Cl$_2$. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (PE/EA) to provide the desired product.

2-(5-Methylthiophen-2-yl)benzo[d]thiazole 1: As a pale brown powder (PE:EA = 40:1 v:v); m.p. 95–97 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 (ddd, $J$ = 8.2, 1.2, 0.6 Hz, 1 H), 7.83 (ddd, $J$ = 8.0, 1.3, 0.6 Hz, 1 H), 7.48–7.42 (m, 2 H), 7.34 (ddd, $J$ = 8.0, 7.3, 1.2 Hz, 1 H), 6.80 (dq, $J$ = 3.4, 1.1 Hz, 1 H), 2.56 (d, $J$ = 1.0 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.59, 153.66, 144.68, 134.79, 134.46, 128.84, 126.43, 126.27, 124.92, 122.70, 121.33, 15.67; HRMS (EI): m/z Calcd. For C$_{12}$H$_9$NS$_2$ [M]$^+$: 231.0176; Found: 231.0149.

2-(5-Ethylthiophen-2-yl)benzo[d]thiazole: As brown oil which solidified at room temperature (PE:EA = 40:1 v:v); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.00 (ddd, $J$ = 8.2, 1.2, 0.6 Hz, 1 H), 7.82 (ddd, $J$ = 7.9, 1.3, 0.6 Hz, 1 H), 7.50–7.41 (m, 2 H), 7.34 (ddd, $J$ = 7.9, 7.3, 1.2 Hz, 1 H), 6.82 (dt, $J$ = 3.7, 1.0 Hz, 1 H), 2.91 (qd, $J$ = 7.5, 0.8 Hz, 2 H), 1.36 (t, $J$ = 7.5 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.69, 153.67, 152.37, 134.49, 134.40, 128.67, 126.27, 124.91, 124.62, 122.69, 121.34, 23.77, 15.69; HRMS (EI): m/z Calcd. For C$_{13}$H$_{11}$NS$_2$ [M]$^+$: 245.0333; Found: 245.0325.

2-(5-Chlorothiophen-2-yl)benzo[d]thiazole 2: As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 103–105 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.00 (ddd, $J$ = 8.2, 1.2, 0.6 Hz, 1 H), 7.82 (ddd, $J$ = 7.9, 1.3, 0.6 Hz, 1 H), 7.48–7.42 (m, 2 H), 7.43–7.32 (m, 2 H), 6.96 (d, $J$ = 4.0 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.28, 153.41, 135.79, 134.43, 134.38, 127.62, 127.19, 126.52, 125.40, 122.96, 121.44; HRMS (EI): m/z Calcd. For C$_{11}$H$_6$ClNS$_2$ [M]$^+$: 250.9630; Found: 250.9621.

2-(5-Bromothiophen-2-yl)benzo[d]thiazole 3: As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 110–112 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.01 (ddd, $J$ = 8.1, 1.3, 0.6 Hz, 1 H), 7.85 (ddd, $J$ = 7.9, 1.4, 0.6 Hz, 1 H), 7.48...
(ddd, J = 8.3, 7.2, 1.4 Hz, 1 H), 7.41–7.33 (m, 2 H), 7.10 (d, J = 4.0 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.15, 153.45, 138.66, 134.44, 130.88, 128.43, 126.53, 125.43, 122.99, 121.45, 117.10; HRMS (EI): m/z Calcd. For C$_{11}$H$_6$BrNS$_2$ [M$^+$]: 294.9125; Found: 294.9124.

2-(5-Phenylthiophen-2-yl)benzo[d]thiazole$^1$: As a yellow powder (PE:EA: 80:1 v:v); m.p. 156–158 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.08–7.99 (m, 1 H), 7.90–7.80 (m, 1 H), 7.71–7.65 (m, 2 H), 7.62 (d, J = 4.0 Hz, 1 H), 7.52–7.32 (m, 6 H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.28, 153.71, 148.19, 136.09, 134.66, 133.52, 129.55, 129.12, 128.49, 126.49, 125.97, 125.22, 123.90, 122.90, 121.47; HRMS (EI): m/z Calcd. For C$_{17}$H$_{11}$NS$_2$ [M$^+$]: 293.0333; Found: 293.0038.

1-(5-(Benzo[d]thiazol-2-yl)thiophen-2-yl)ethanone$^4$: As a pale yellow powder (PE:EA: 30:1 v:v); m.p. 188–190 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.20–7.96 (m, 1 H), 7.93–7.86 (m, 1 H), 7.70 (d, J = 4.0 Hz, 1 H), 7.65 (d, J = 4.0 Hz, 1 H), 7.50–7.36 (m, 1 H), 2.61 (s, 3 H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 190.49, 160.05, 153.60, 146.01, 144.05, 135.12, 132.57, 128.47, 126.81, 125.97, 123.51, 121.62, 26.97; HRMS (EI): m/z Calcd. For C$_{13}$H$_9$NOS$_2$ [M$^+$]: 259.0126; Found: 259.0120.

5-(Benzo[d]thiazol-2-yl)thiophene-2-carbaldehyde$^4$: As a yellow powder (PE:EA: 10:1 v:v); m.p. 146–148 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 9.96 (s, 1 H), 8.08 (ddd, J = 8.1, 1.2, 0.6 Hz, 1 H), 7.88 (ddd, J = 8.0, 1.2, 0.6 Hz, 1 H), 7.76 (d, J = 4.0 Hz, 1 H), 7.70 (d, J = 4.0 Hz, 1 H), 7.52 (ddd, J = 8.3, 7.2, 1.3 Hz, 1 H), 7.43 (ddd, J = 8.3, 7.2, 1.3 Hz, 1 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 182.87, 159.65, 153.54, 145.48, 145.18, 136.19, 135.20, 128.41, 126.87, 126.13, 123.61, 121.61; HRMS (EI): m/z Calcd. For C$_{12}$H$_7$NOS$_2$ [M$^+$]: 244.9969; Found: 244.9961.

Methyl 5-(benzo[d]thiazol-2-yl)thiophene-2-carboxylate$^5$: As a pale yellow powder (PE:EA: 20:1 v:v); m.p. 162–164 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.06 (ddd, J = 8.2, 1.2, 0.6 Hz, 1 H), 7.88 (ddd, J = 8.0, 1.3, 0.6 Hz, 1 H), 7.79 (d, J = 4.0 Hz, 1 H), 7.61 (d, J = 4.0 Hz, 1 H), 7.51 (ddd, J = 8.2, 7.3, 1.3 Hz, 1 H), 7.41 (ddd, J = 8.3, 7.2, 1.2 Hz, 1 H), 3.93 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.18, 160.06, 153.52, 143.02, 135.72, 134.95, 133.75, 128.11, 126.69, 125.81, 123.38, 121.54, 52.46; HRMS (EI): m/z Calcd. For C$_{13}$H$_9$NO$_2$S$_2$ [M$^+$]: 275.0075; Found: 275.0066.

5-(Benzo[d]thiazol-2-yl)thiophene-2-carbonitrile$^1$: As a pale yellow powder (PE:EA: 80:1 v:v); m.p. 156–158 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.08–7.99 (m, 1 H), 7.90–7.80 (m, 1 H), 7.71–7.65 (m, 2 H), 7.62 (d, J = 4.0 Hz, 1 H), 7.52–7.32 (m, 6 H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.28, 153.71, 148.19, 136.09, 134.66, 133.52, 129.55, 129.12, 128.49, 126.49, 125.97, 125.22, 123.90, 122.90, 121.47; HRMS (EI): m/z Calcd. For C$_{11}$H$_6$BrNS$_2$ [M$^+$]: 294.9125; Found: 294.9124.

1-5-(Benzo[d]thiazol-2-yl)thiophen-2-yl)ethanone$^4$: As a pale yellow powder (PE:EA: 30:1 v:v); m.p. 188–190 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.08–7.99 (m, 1 H), 7.90–7.80 (m, 1 H), 7.71–7.65 (m, 2 H), 7.62 (d, J = 4.0 Hz, 1 H), 7.52–7.32 (m, 6 H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.28, 153.71, 148.19, 136.09, 134.66, 133.52, 129.55, 129.12, 128.49, 126.49, 125.97, 125.22, 123.92, 122.90, 121.47; HRMS (EI): m/z Calcd. For C$_{17}$H$_{11}$NS$_2$ [M$^+$]: 293.0333; Found: 293.0038.

5-(Benzo[d]thiazol-2-yl)thiophene-2-carbonitrile$^1$: As a pale yellow powder (PE:EA: 80:1 v:v); m.p. 156–158 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.08–7.99 (m, 1 H), 7.90–7.80 (m, 1 H), 7.71–7.65 (m, 2 H), 7.62 (d, J = 4.0 Hz, 1 H), 7.52–7.32 (m, 6 H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 161.28, 153.71, 148.19, 136.09, 134.66, 133.52, 129.55, 129.12, 128.49, 126.49, 125.97, 125.22, 123.92, 122.90, 121.47; HRMS (EI): m/z Calcd. For C$_{11}$H$_6$BrNS$_2$ [M$^+$]: 294.9125; Found: 294.9124.
powder (PE:EA = 30:1 v:v); m.p. 176–178 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.07 (ddd, \(J = 8.2, 1.3, 0.6\) Hz, 1 H), 7.90 (ddd, \(J = 7.9, 1.4, 0.7\) Hz, 1 H), 7.63 (d, \(J = 4.0\) Hz, 1 H), 7.59 (d, \(J = 4.0\) Hz, 1 H), 7.54 (ddd, \(J = 8.3, 7.2, 1.4\) Hz, 1 H), 7.45 (ddd, \(J = 7.9, 7.2, 1.3\) Hz, 1 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.64, 153.33, 143.79, 134.69, 127.44, 126.99, 123.59, 121.66, 113.67, 112.01; HRMS (EI): \(m/z\) Calcd. For C\(_{12}\)H\(_6\)N\(_2\)S\(_2\)[M]+: 241.9972; Found: 242.0001.

2-(Benzo[b]thiophen-2-yl)benzo[d]thiazole \(^6\): As a pale yellow powder (PE:EA = 100:1 v:v); m.p. 193–195 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.09 (ddd, \(J = 8.2, 1.2, 0.6\) Hz, 1 H), 7.95–7.73 (m, 4 H), 7.50 (td, \(J = 8.3, 7.7, 1.3\) Hz, 1 H), 7.45–7.33 (m, 3 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 161.48, 153.68, 140.82, 139.53, 137.14, 135.01, 126.58, 126.17, 125.63, 125.33, 125.00, 124.59, 123.34, 122.62, 121.54; HRMS (EI): \(m/z\) Calcd. For C\(_{15}\)H\(_9\)NS\(_2\)[M]+: 267.0176; Found: 267.0169.

Tert-butyl 2-(benzo[d]thiazol-2-yl)-6,7-dihydrothieno[3,2-c]pyridine-5(4H)-carboxylate: As yellow oil which solidified at room temperature (PE:EA = 10:1 v:v); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.99 (ddd, \(J = 8.2, 1.2, 0.6\) Hz, 1 H), 7.83 (ddd, \(J = 8.0, 1.3, 0.6\) Hz, 1 H), 7.46 (ddd, \(J = 8.3, 7.3, 1.3\) Hz, 1 H), 7.39–7.31 (m, 2 H), 4.52 (brs, 2 H), 3.76 (t, \(J = 5.5\) Hz, 2 H), 2.90 (t, \(J = 5.5\) Hz, 2 H), 1.50 (s, 9 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 161.26, 154.74, 153.62, 138.42, 134.76, 134.57, 133.38, 126.39, 125.13, 122.79, 121.41, 80.23, 44.12, 40.58, 28.47, 25.43; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 161.26, 154.74, 153.62, 137.95, 134.76, 134.57, 133.75, 126.39, 125.13, 122.79, 121.41, 80.23, 43.44, 41.80, 28.47, 25.31; HRMS (EI): \(m/z\) Calcd. For C\(_{19}\)H\(_{20}\)N\(_2\)O\(_2\)S\(_2\)[M]+: 372.0966; Found: 372.0965.

2-(2-Methylthiazol-5-yl)benzo[d]thiazole \(^7\): As a pale yellow powder (PE:EA = 20:1 v:v; m.p. 123–125 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.15 (s, 1 H), 8.02 (ddd, \(J = 8.0, 1.2, 0.6\) Hz, 1 H), 7.87 (ddd, \(J = 7.9, 1.3, 0.7\) Hz, 1 H), 7.49 (ddd, \(J = 8.2, 7.2, 1.3\) Hz, 1 H), 7.40 (ddd, \(J = 7.9, 7.2, 1.2\) Hz, 1 H), 2.79 (s, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.25, 158.37, 153.35, 142.78, 134.39, 132.60, 126.55, 125.59, 123.01, 121.49, 19.59; HRMS (EI): \(m/z\) Calcd. For C\(_{11}\)H\(_8\)N\(_2\)S\(_2\)[M]+: 232.0129; Found: 232.0121.

2-(2-Isobutylthiazol-5-yl)benzo[d]thiazole: As colorless oil which solidified at room temperature (PE:EA = 20:1 v:v); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.18 (s, 1 H), 8.02 (ddd, \(J = 8.2, 1.3, 0.7\) Hz, 1 H), 7.86 (ddd, \(J = 8.2, 1.3, 0.7\) Hz, 1 H), 7.49 (ddd, \(J = 8.2, 7.2, 1.3\) Hz, 1 H), 7.40 (ddd, \(J = 7.9, 7.2, 1.2\) Hz, 1 H), 2.79 (s, 3 H); HRMS (EI): \(m/z\) Calcd. For C\(_{11}\)H\(_8\)N\(_2\)S\(_2\)[M]+: 232.0129; Found: 232.0121.

\(^2\)-(3am)
7.9, 1.3, 0.6 Hz, 1 H), 7.48 (ddd, J = 8.3, 7.2, 1.3 Hz, 1 H), 7.39 (ddd, J = 8.3, 7.2, 1.3 Hz, 1 H), 2.93 (d, J = 7.2 Hz, 2 H), 2.17 (hept, J = 6.8 Hz, 1 H), 1.03 (d, J = 6.7 Hz, 6 H); 13C NMR (100 MHz, CDCl₃) δ 173.05, 169.31, 157.61, 152.92, 142.38, 134.12, 132.88, 126.26, 125.39, 122.74, 121.16, 69.39, 20.61, 20.34; HRMS (EI): m/z Calcd. For C₁₄H₁₄N₂S₂ [M]+: 274.0598; Found: 274.0604.

1-(5-(Benzo[d]thiazol-2-yl)thiazol-2-yl)ethyl acetate: As a pale yellow powder (PE:EA = 8:1 v:v); m.p. 108–109 °C; 1H NMR (300 MHz, CDCl₃) δ 8.22 (s, 1 H), 8.03 (ddd, J = 8.2, 1.2, 0.6 Hz, 1 H), 7.87 (ddd, J = 8.0, 1.3, 0.7 Hz, 1 H), 7.50 (ddd, J = 8.3, 7.3, 1.3 Hz, 1 H), 7.45 – 7.35 (m, 1 H), 6.18 (q, J = 6.6 Hz, 1 H), 2.18 (s, 3 H), 1.73 (d, J = 6.6 Hz, 3 H); 13C NMR (100 MHz, CDCl₃) δ 173.24, 158.10, 152.97, 142.35, 131.82, 126.14, 125.17, 122.60, 121.10, 42.22, 29.44, 21.85; HRMS (EI): m/z Calcd. For C₁₄H₁₂N₂O₂S₂ [M]+: 304.0340; Found: 304.0342.

5-(Benzo[d]thiazol-2-yl)furan-2-carbaldehyde: As a brown powder (PE:EA = 30:1 v:v); m.p. 180–182 °C; 1H NMR (300 MHz, CDCl₃) δ 9.79 (s, 1 H), 8.10 (ddd, J = 8.2, 1.3, 0.7 Hz, 1 H), 7.95 (ddd, J = 8.0, 1.3, 0.7 Hz, 1 H), 7.54 (dd, J = 8.2, 1.4 Hz, 1 H), 7.46 (dd, J = 8.0, 1.3 Hz, 1 H), 7.39 (d, J = 3.8 Hz, 1 H), 7.35 (d, J = 3.8 Hz, 1 H); 13C NMR (100 MHz, CDCl₃) δ 177.87, 155.84, 153.63, 153.15, 152.78, 152.78, 142.35, 142.00, 131.82, 126.14, 125.17, 122.60, 121.10, 42.22, 29.44, 21.85; HRMS (EI): m/z Calcd. For C₁₂H₇NO₂S [M]+: 229.0197; Found: 229.0193.

2-(5-Ethylthiophen-2-yl)-6-methoxybenzo[d]thiazole: As a brown powder (PE:EA = 20:1 v:v); m.p. 74–76 °C; 1H NMR (300 MHz, CDCl₃) δ 7.87 (d, J = 9.0 Hz, 1 H), 7.41 (d, J = 3.7 Hz, 1 H), 7.26 (dd, J = 8.2, 1.9 Hz, 1 H), 6.81 (dt, J = 3.7, 1.0 Hz, 1 H), 2.90 (qd, J = 7.5, 1.0 Hz, 2 H), 1.36 (t, J = 7.5 Hz, 3 H); 13C NMR (100 MHz, CDCl₃) δ 159.33, 157.55, 151.64, 148.15, 135.85, 134.55, 127.93, 124.47, 123.18, 115.30, 104.15, 55.75, 23.73, 15.70; HRMS (EI): m/z Calcd. For C₁₄H₁₃NOS₂ [M]+: 275.0439; Found: 275.0445.

2-(5-Ethylthiophen-2-yl)-6-methylbenzo[d]thiazole: As brown oil which solidified at room temperature (PE:EA = 40:1 v:v); 1H NMR (300 MHz, CDCl₃) δ 7.87 (d, J = 8.3 Hz, 1 H), 7.61 (dd, J = 1.8, 1.0 Hz, 1 H), 7.45 (d, J = 3.7 Hz, 1 H), 7.26 (dd, J = 8.2, 1.9 Hz, 1 H), 6.81 (dt, J = 3.7, 1.0 Hz, 1 H), 2.90
(qd, J = 7.6, 1.0 Hz, 2 H), 2.47 (s, 3 H), 1.36 (t, J = 7.5 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.69, 151.99, 151.75, 135.06, 134.64, 134.56, 128.28, 127.80, 124.52, 122.19, 121.13, 23.75, 21.50, 15.71; HRMS (EI): m/z Calcd. For C$_{14}$H$_{13}$NS$_2$ [M]$^+$: 259.0489; Found: 259.0486.

2-(5-Ethylthiophen-2-yl)-6-fluorobenzo[d]thiazole: As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 102–103 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.92 (dd, J = 9.0, 4.8 Hz, 1 H), 7.51 (dd, J = 8.1, 2.6 Hz, 1 H), 7.45 (d, J = 3.7 Hz, 1 H), 7.18 (td, J = 9.0, 2.6 Hz, 1 H), 6.82 (dt, J = 3.7, 1.0 Hz, 1 H), 2.91 (qd, J = 7.5, 1.0 Hz, 2 H), 1.36 (t, J = 7.5 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.39 (d, J = 3.4 Hz, C–CH–CH–CF), 160.26 (d, J = 246.0 Hz, C–F), 152.48, 150.27, 135.46 (d, J = 10.8 Hz, C–CH–CF), 134.04, 128.69, 124.64, 123.50 (d, J = 9.4 Hz, CH–CH–CF), 114.76 (d, J = 24.7 Hz, CH–CF), 107.66 (d, J = 26.8 Hz, CH–CF), 23.75, 15.67; HRMS (EI): m/z Calcd. For C$_{13}$H$_{10}$FNS$_2$ [M]$^+$: 263.0239; Found: 263.0241.

6-Chloro-2-(5-ethylthiophen-2-yl)benzo[d]thiazole: As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 138–142 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.88 (d, J = 8.7 Hz, 1 H), 7.79 (d, J = 2.1 Hz, 1 H), 7.47 (d, J = 3.7 Hz, 1 H), 7.40 (dd, J = 8.7, 2.1 Hz, 1 H), 6.83 (dt, J = 3.7, 1.0 Hz, 1 H), 2.91 (qd, J = 7.5, 1.0 Hz, 2 H), 1.36 (t, J = 7.5 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.10, 152.88, 152.24, 135.66, 133.91, 130.62, 128.99, 127.02, 124.72, 123.32, 120.93, 23.78, 15.65; HRMS (EI): m/z Calcd. For C$_{13}$H$_{10}$ClNS$_2$ [M]$^+$: 278.9943; Found: 278.9925.

6-Bromo-2-(5-ethylthiophen-2-yl)benzo[d]thiazole: As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 136–138 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.95 (d, J = 1.9 Hz, 1 H), 7.83 (d, J = 8.7 Hz, 1 H), 7.54 (dd, J = 8.7, 2.0 Hz, 1 H), 7.48 (d, J = 3.7 Hz, 1 H), 6.83 (dt, J = 3.8, 1.0 Hz, 1 H), 2.91 (qd, J = 7.5, 0.9 Hz, 2 H), 1.36 (t, J = 7.5 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.12, 152.99, 152.58, 136.12, 133.86, 129.75, 129.05, 124.75, 123.85, 123.32, 120.93, 23.78, 15.66; HRMS (EI): m/z Calcd. For C$_{13}$H$_{10}$BrNS$_2$ [M]$^+$: 322.9438; Found: 322.9440.

4,6-Dichloro-2-(5-ethylthiophen-2-yl)benzo[d]thiazole: As a brown powder (PE:EA = 40:1 v:v); m.p. 103–105 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.69 (d, J = 2.0 Hz, 1 H), 7.50 (d, J = 3.8 Hz, 1 H), 7.47 (d, J = 2.0 Hz, 1 H), 6.83 (dt, J = 3.7, 1.0 Hz, 1 H), 2.91 (qd, J = 7.7,
1.1 Hz, 2 H), 1.36 (t, $J = 7.5$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.66, 153.67, 149.54, 136.56, 133.55, 130.42, 129.51, 127.80, 126.97, 124.82, 119.53, 23.82, 15.64; HRMS (EI): $m/z$ Calcd. For C$_{13}$H$_9$Cl$_2$NS$_2$ [M]$^+$: 312.9553; Found: 312.9555.

2-(5-Ethylthiophen-2-yl)-6-phenylbenzo[d]thiazole: As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 126–128 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.10–8.01 (m, 2 H), 7.75–7.62 (m, 3 H), 7.54–7.44 (m, 3 H), 7.39 (t, $J = 7.3$ Hz, 1 H), 6.85 (dt, $J = 3.7$, 1.0 Hz, 1 H), 2.94 (dt, $J = 7.4$, 1.1 Hz, 2 H), 1.39 (t, $J = 7.5$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.84, 153.02, 152.49, 140.54, 138.33, 135.29, 134.43, 128.86, 128.70, 127.42, 127.28, 125.94, 124.66, 122.73, 119.60, 23.79, 15.70; HRMS (EI): $m/z$ Calcd. For C$_{19}$H$_{15}$NS$_2$ [M]$^+$: 321.0646; Found: 321.0645.

Ethyl 2-(5-ethylthiophen-2-yl)benzo[d]thiazole-6-carboxylate: As a pale yellow powder (PE:EA = 20:1 v:v); m.p. 122–124 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.55 (dd, $J = 1.7$, 0.6 Hz, 1 H), 8.13 (dd, $J = 8.6$, 1.7 Hz, 1 H), 7.99 (dd, $J = 8.6$, 0.6 Hz, 1 H), 7.54 (d, $J = 3.8$ Hz, 1 H), 6.85 (dt, $J = 3.7$, 1.0 Hz, 1 H), 4.42 (q, $J = 7.1$ Hz, 2 H), 2.92 (qd, $J = 7.4$, 0.8 Hz, 2 H), 1.43 (t, $J = 7.1$ Hz, 3 H), 1.37 (t, $J = 7.5$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.08, 164.85, 156.64, 153.54, 134.39, 133.97, 129.59, 127.59, 126.88, 124.89, 123.43, 122.17, 61.19, 23.81, 15.63, 14.34; HRMS (EI): $m/z$ Calcd. For C$_{16}$H$_{15}$NO$_2$S$_2$ [M]$^+$: 317.0544; Found: 317.0546.

2-(5-Ethylthiophen-2-yl)-6-(trifluoromethyl)benzo[d]thiazole: As a pale yellow powder (PE:EA = 40:1 v:v); m.p. 139–142 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.13–8.09 (m, 1 H), 8.05 (dd, $J = 8.8$, 1.0 Hz, 1 H), 7.71–7.65 (m, 1 H), 7.54 (d, $J = 3.7$ Hz, 1 H), 6.86 (dt, $J = 3.8$, 0.9 Hz, 1 H), 2.92 (qd, $J = 7.6$, 0.9 Hz, 2 H), 1.37 (t, $J = 7.6$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 164.53, 155.69, 153.67, 134.56, 133.69, 129.69, 126.87 (q, $J = 32.4$ Hz, C–CF$_3$), 123.90 (q, $J = 272.2$ Hz, C–F$_3$), 124.90, 123.31 (q, $J = 3.5$ Hz, CH–C–CF$_3$), 122.80, 118.95 (q, $J = 4.2$ Hz, CH–C–CF$_3$), 23.80, 15.61; HRMS (EI): $m/z$ Calcd. For C$_{14}$H$_{10}$F$_3$NS$_2$ [M]$^+$: 313.0207; Found: 313.0201.

2-(5-Ethylthiophen-2-yl)-1-methyl-1H-benzo[d]imidazole: As brown oil which solidified at room temperature (PE:EA = 8:1 v:v); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.81–7.75 (m, 1 H), 7.39 (d, $J = 3.7$ Hz, 1 H), 7.37–7.32 (m, 1 H), 7.32–7.26 (m, 2 H), 6.88 (dt, $J = 3.7$, 0.8 Hz, 1 H), 3.98 (s, 3 H), 2.92 (qd, $J = 7.5$, 0.8 Hz, 2
H), 1.37 (t, J = 7.5 Hz, 3 H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 151.17, 148.17, 142.85, 136.51, 129.69, 127.78, 124.29, 122.59, 122.42, 119.53, 109.19, 31.58, 23.50, 15.80; HRMS (EI): \(m/z\) Calcd. For C\(_{14}\)H\(_{14}\)N\(_2\)S: [M]\(^+\): 242.0878; Found: 242.0885.

2-(5-Ethylthiophen-2-yl)benzo[d]oxazole: As brown oil which solidified at room temperature (PE:EA = 30:1 v:v); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, J = 3.7 Hz, 1 H), 7.72–7.68 (m, 1 H), 7.55–7.49 (m, 1 H), 7.34–7.29 (m, 2 H), 6.88 (d, J = 3.7 Hz, 1 H), 2.93 (q, J = 7.4 Hz, 2 H), 1.37 (t, J = 7.4 Hz, 3 H);

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 159.20, 153.43, 150.34, 142.08, 130.06, 126.61, 124.87, 124.71, 124.54, 119.56, 110.25, 23.71, 15.66; HRMS (EI): \(m/z\) Calcd. For C\(_{13}\)H\(_{11}\)NS: [M]\(^+\): 229.0561; Found: 229.0558.

2-(5-Ethylthiophen-2-yl)-4,5-dimethylthiazole: As brown oil which solidified at room temperature (PE:EA = 40:1 v:v); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.19 (d, J = 3.6 Hz, 1 H), 6.71 (dt, J = 3.6, 1.0 Hz, 1 H), 2.84 (qd, J = 7.5, 1.1 Hz, 2 H), 2.34 (s, 3 H), 2.32 (s, 3 H), 1.31 (t, J = 7.5 Hz, 3 H);

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 157.53, 149.36, 148.51, 134.96, 125.40, 125.06, 124.09, 23.60, 15.77, 14.69, 11.37. HRMS (EI): \(m/z\) Calcd. For C\(_{11}\)H\(_{13}\)NS\(_2\): [M]\(^+\): 223.0489; Found: 223.0480.

2-(2-Isobutylthiazol-5-yl)-6-methoxybenzo[d]thiazole: As pale yellow oil which solidified at room temperature (PE:EA = 15:1 v:v); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.10 (s, 1 H), 7.89 (d, J = 8.9 Hz, 1 H), 7.31 (d, J = 2.5 Hz, 1 H), 7.07 (dd, J = 9.0, 2.5 Hz, 1 H), 3.88 (s, 3 H), 2.92 (d, J = 7.2 Hz, 2 H), 2.16 (hept, J = 13.5, 6.8 Hz, 1 H), 1.03 (dd, J = 6.6, 0.7 Hz, 6 H);

\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 173.01, 158.01, 155.97, 147.90, 142.06, 135.88, 132.35, 123.50, 115.79, 104.03, 55.77, 42.60, 29.83, 22.25; HRMS (EI): \(m/z\) Calcd. For C\(_{15}\)H\(_{16}\)N\(_2\)S\(_2\): [M]\(^+\): 304.0704; Found: 304.0701.

6-Fluoro-2-(2-isobutylthiazol-5-yl)benzo[d]thiazole: As a pale yellow powder (PE:EA = 20:1 v:v); m.p. 68–69 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.15 (s, 1 H), 7.96 (dd, J = 9.0, 4.8 Hz, 1 H), 7.55 (dd, J = 8.0, 2.6 Hz, 1 H), 7.22 (td, J = 9.0, 2.6 Hz, 1 H), 2.93 (d, J = 7.2 Hz, 2 H), 2.17 (hept, J = 13.6, 6.8 Hz, 1 H), 1.03 (d, J = 6.6 Hz, 6 H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 173.01, 158.01, 155.97, 147.90, 142.06, 135.88, 132.35, 123.50, 115.79, 104.03, 55.77, 42.60, 29.83, 22.25; HRMS (EI): \(m/z\) Calcd. For C\(_{16}\)H\(_{18}\)FNS\(_2\): [M]\(^+\): 304.0704; Found: 304.0701.
C_{14}H_{13}FN_{2}S_{2}: [M]^+: 292.0504; Found: 292.0508.

6-Chloro-2-(2-isobutylthiazol-5-yl)benzo[d]thiazole: As a pale yellow powder (PE:EA = 20:1 v:v); m.p. 90–91 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.17 (s, 1 H), 7.92 (dd, J = 8.7, 0.5 Hz, 1 H), 7.84 (dd, J = 2.1, 0.5 Hz, 1 H), 7.45 (dd, J = 8.7, 2.1 Hz, 1 H), 2.94 (d, J = 7.2 Hz, 2 H), 2.17 (hept, J = 13.6, 6.7 Hz, 1 H), 1.04 (d, J = 6.6 Hz, 6 H); ¹³C NMR (125 MHz, CDCl₃) δ 174.00, 158.91, 151.92, 143.04, 135.57, 131.78, 131.41, 127.35, 121.09, 42.63, 29.83, 22.25; HRMS (EI): m/z Calcd. For C_{14}H_{13}ClN_{2}S_{2}: [M]^+: 308.0209; Found: 308.0204.

4,4',5,5'-Tetramethyl-2,2'-bithiazole: As a pale yellow powder (PE:EA = 40:1 v:v); ¹H NMR (300 MHz, CDCl₃) δ 2.39 (q, J = 0.8 Hz, 6 H), 2.36 (q, J = 0.7 Hz, 6 H); LRMS (ESI): m/z 225 [M+H]^+.

The H/D exchange experiment for 1a

To a solution of 1a (1.0 mmol, 1.0 equiv) in DMSO (2.0 mL), Pd(OAc)₂ (10 mol%) and D₂O (1.0 mL) was added, and the mixture was heated at 110 °C for 10 h. After cooling, the reaction solution was washed with saturated brine and extracted with ethyl acetate three times. The combined organic fractions were dried over anhydrous Na₂SO₄ and concentrated under vacuum to yield the crude product. 1a-[D₂] was detected by LC-MS, and the ratio of 1a and 1a-[D₂] was determined by ¹H NMR analysis of the crude product.
Copy of low-resolution mass spectrum (ESI) of 1a

Copy of low-resolution mass spectrum (ESI) of the crude product
Preparation of 2-deutero-benzothiazole (1a-[D$_1$])$^{10}$: A stirred solution of benzothiazole 1a (10 mmol) in dry THF (10 mL) under nitrogen was cooled to −78 °C and 12 mmol nBuLi in hexane was added dropwise. 2-Lithiobenzothiazole was immediately formed. This orange-colored anion solution was quickly quenched at −78 °C with CD$_3$OD (1.0 mL) after the addition of nBuLi. The suspension was extracted with water and ethyl acetate three times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and evaporated in vacuum. After purification by column chromatography on silica gel with petroleum ether /ethyl acetate (PE:EA = 20:1 v:v), the desired products were obtained in 95% yield as pale yellow oil; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.15 (ddd, $J$ = 7.9, 1.3, 0.7 Hz, 1 H), 7.97 (ddd, $J$ = 7.9, 1.4, 0.7 Hz, 1 H), 7.57−7.49 (m, 1 H), 7.48−7.41 (m, 1 H); MS (ESI): m/z 137 [M+H]$^+$. 

**Kinetic isotope experiments**
Preparation of 2-deutero-benzothiophene (2j-[D$_1$])$^{11}$: A stirred solution of benzothiophene 2j (10 mmol) in dry THF (10 mL) under nitrogen was cooled to −78 °C and 12 mmol nBuLi in hexane was added dropwise. CD$_3$OD (1.0 mL) was added to the reaction system after reacting for 1 h. The suspension was extracted with water extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and evaporated in vacuum. After purification by column chromatography on silica gel with petroleum ether /ethyl acetate (PE:EA = 20:1 v:v), the desired products were obtained in 97% yield as colorless oil which solidified at room temperature; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.92–7.79 (m, 2 H), 7.41–7.30 (m, 3 H); MS (EI): m/z 135 [M$^+$].

\[
\begin{align*}
\text{1a/1a-[D$_1$]} & \quad \text{2j} \\
& \xrightarrow{\text{Pd(OAc)$_2$ (10 mol\%), AgNO$_3$ (2.0 equiv), Phen (30 mol\%), DMSO, 110 °C, 8 h}} \quad \text{3aj} \quad K_H/K_D = 1.1
\end{align*}
\]

Two sets of reactions were carried out in a parallel manner. In each case benzothiophene 2j (4.0 mmol) was allowed to react with benzothiazole 1a (1.0 mmol) and 2-deuterio-benzothiazole 1a-[D$_1$] (1.0 mmol), respectively. The sealed tubes were screw capped and heated to 110 °C. After being stirred for 8 h, the reaction mixture was cooled to room temperature, diluted with 20 mL of CH$_2$Cl$_2$, filtered through a celite pad, washed with 80 mL of CH$_2$Cl$_2$. The combined organic extracts were concentrated. The yield of 3aj was determined by LC-MS.

\[
\begin{align*}
\text{1a} & \quad \text{2j/2j-[D$_1$]} \\
& \xrightarrow{\text{Pd(OAc)$_2$ (10 mol\%), AgNO$_3$ (2.0 equiv), Phen (30 mol\%), DMSO, 110 °C, 8 h}} \quad \text{3aj} \quad K_H/K_D = 3.0
\end{align*}
\]

Two sets of reactions were carried out in a parallel manner. In each case benzothiazole 1a (4.0 mmol) was allowed to react with benzothiophene 2j (1.0 mmol) and 2-deuterio-benzothiophene 2j-[D$_1$] (1.0 mmol), respectively. The sealed tubes were screw capped and heated to 110 °C. After being stirred for 8 h, the reaction mixture was cooled to room temperature, diluted with 20 mL of CH$_2$Cl$_2$, filtered through a celite pad, washed with 80 mL of CH$_2$Cl$_2$. The combined organic extracts were concentrated. The yield of 3aj was determined by LC-MS.

References

$^1$H NMR, $^{13}$C NMR and HSQC spectra

3aa
3ab
3ac

![NMR Spectra](image)

![Chemical Structure](image)
3ae

N
S
S

121.47
122.90
123.92
125.22
125.97
126.49
128.49
129.12
129.55
133.52
134.66
136.09
148.19
153.71
161.28

N
S
S

160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)
3ah
3ak

\[
\begin{align*}
N & \quad S \\
S & \quad N
\end{align*}
\]

\[
\begin{align*}
O & \quad C \\
C & \quad H \quad 3 \\
C & \quad H \quad 3 \\
C & \quad H \quad 3
\end{align*}
\]
3al
3am

![Chemical Structure](image)

![Chemical Structure](image)
3an
3ap
3bb
3cb
S38
3mb
3bm
$^3$em
4m