Iodobenzene-Promoted Pd-Catalysed ortho-Directed C–H Activation: The Synthesis of Benzothiazoles via Intramolecular Coupling

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Abstract  
A series of 2-aminobenzothiazoles were synthesized by a palladium-catalysed oxidative coupling with good yields (62–89%). Iodobenzene was found to be effective as an additive in this intramolecular C–S bond-formation reaction. The directing thiourea group attached to the aryl ring is essential for the activation of the ortho C–H bond.

Key words palladium, iodobenzene, C–H activation, synthesis, aminobenzothiazole

Benzothiazole derivatives represent an extensive group of heterocyclic compounds, several of which have already found application in the medical sphere as antitumor agents with selective growth inhibitory properties against human cancer cell lines and in agriculture as plant growth regulators (PGR).  

The model reaction we chose was the intermolecular oxidative coupling between 1,1-dimethyl-3-phenylthiourea and iodobenzene. Gratifyingly, the intermolecular cross-coupling product was not detected, and the intramolecular cyclisation product (2-aminobenzothiazole) was furnished with a satisfactory yield of 81% (Scheme 1). The oxidative coupling product could not be obtained when no iodobenzene was present. Much less (23%) intramolecular cyclisation product was formed when the reaction was performed under nitrogen, revealing that atmospheric oxygen was the oxidant, and that iodobenzene was a necessary additive.

Encouraged by these results, we began to optimise the reaction conditions. First, a broad screening of copper and palladium catalysts revealed that copper salts were ineffective (Table 1, entries 1–3), but palladium catalysts, for example, PdBr2, PdCl2, Pd(OAc)2 could catalyse the model reaction to give the cyclisation products with 64%, 69% and 81% isolated yields, respectively (Table 1, entries 5, 4 and 8). Various other additives, for example, pyridine, ethyldiisopropylamine, KF, CsF and LiCl (Table 1, entries 18–22) that might promote the model reaction were screened, but results showed that these additives were less active than iodobenzene in promoting the intramolecular cyclisation. The additive loading was also investigated, with the optimal additive loading being found to be 0.5 equiv, with 1.0 or 1.5 equiv not improving the yield significantly, and a lower loading (0.1 equiv relative to thiourea) resulted in the yield reducing to 65%.

Substituted iodobenzenes proved to be less reactive than iodobenzene (Table 1, entries 8, 16 and 17). A range of bases, such as NaH, CH3ONa, NaOH, KOR-Bu, Cs2CO3, K2CO3, Na2CO3 and NEt3 was surveyed and K2CO3 was found to be the most suitable base for this reaction (Table 1, entries 8–15). Solvent and temperature studies showed that DMSO was the best solvent (Table 1, entries 8, 23–25) and 100 °C was the optimal temperature (Table 1, entries 8, 26–28). Under the optimal reaction conditions, various substituted N-arylthioureas (1a–p) underwent cyclisation smoothly, providing the corresponding 2-aminobenzothiazoles (2a–p) in good yields. Substrate scope experiments revealed that arylthioureas bearing electron-withdrawing groups at the para- (1b–h), meta- (1l) and ortho- (1j, 1k) positions cyclised well, giving 73–89% isolated yields (Table 2, entries...
2–8, 9, 10–11). However, electron-donating p-MeO (1l), p-Me (1m) substituents on the N-arylthiourea slowed the reaction and decreased the yields (Table 2, entries 12, 13). Presumably due to steric hindrance from the bulky alkylated amino group, the cyclisation yields of 2a, 2n and 2o decreased in turn, and substrate 1o and 1p, which bear two butyl groups on the nitrogen (Table 2, entries 15, 16), afforded the products in moderate yields (63% for 1o, 62% for 1p).

Table 1 Optimization of Model Reaction Conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Additive</th>
<th>Base</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
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<td>1</td>
<td>Cu(OAc)₂</td>
<td>Phil</td>
<td>K₂CO₃</td>
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<td>CuO</td>
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<td>0</td>
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</tr>
<tr>
<td>6</td>
<td>Pd(dba)₃</td>
<td>Phil</td>
<td>K₂CO₃</td>
<td>DMSO</td>
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<td>54</td>
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<td>7</td>
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<td>DMSO</td>
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<td>54</td>
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<td>8</td>
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<td>KBt·Bu</td>
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<td>Pd(OAc)₂</td>
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<td>Cs₂CO₃</td>
<td>DMSO</td>
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<td>56</td>
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</table>

* Reaction conditions: 1a (1.0 mmol), catalyst (10% mmol), additive (0.5 equiv), base (1.0 equiv), O₂ (air), DMSO (2 mL) for 4–6 h.

Table 2 Control experiments for the PhI-promoted synthesis of benzothiazole

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Additive</th>
<th>Base</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
</tr>
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<td>11</td>
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<td>Phil</td>
<td>CH₃ONA</td>
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<td>13</td>
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<td>Phil</td>
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</tr>
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<td>69</td>
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<td>1-iodo-4-nitrobenzene</td>
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<td>trace</td>
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<td>K₂CO₃</td>
<td>DMSO</td>
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<td>trace</td>
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<td>22</td>
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<td>LiCl</td>
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<td>23</td>
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<td>K₂CO₃</td>
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<td>25</td>
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<td>trace</td>
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<tr>
<td>27</td>
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<td>Phil</td>
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<td>K₂CO₃</td>
<td>DMSO</td>
<td>80</td>
<td>44</td>
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</table>

* Reaction conditions: 1a (1.0 mmol), catalyst (10% mmol), additive (0.5 equiv), base (1.0 equiv), O₂ (air), DMSO (2 mL) for 4–6 h.

* Isolated yield.
Table 2  Iodobenzene-Promoted Pd-Catalysed Synthesis of Benzothiazoles via an Intramolecular Coupling\textsuperscript{a}

\[
\begin{array}{cccc}
\text{Entry} & \text{Substrate} & \text{Product} & \text{Time (h)} & \text{Yield (%)} \\
1 & 1a & 2a & 4.0 & 81 \\
2 & 1b & 2b & 4.0 & 77 \\
3 & 1c & 2c & 4.0 & 76 \\
4 & 1d & 2d & 4.0 & 74 \\
5 & 1e & 2e & 4.0 & 83 \\
6 & 1f & 2f & 4.0 & 75 \\
7 & 1g & 2g & 4.0 & 87 \\
8 & 1h & 2h & 4.0 & 73 \\
9 & 1i & 2i & 4.0 & 76 \\
10 & 1j & 2j & 4.0 & 74 \\
\end{array}
\]

\[\text{Pd(OAc)}_2 \text{ (10 mol%), PhI (0.5 equiv), K}_2\text{CO}_3 \text{ (1.0 equiv), O}_2 \text{ (air), DMSO, 100 °C, 4–6 h}\]

\[\text{R}^1 \text{N} \text{H} \text{S} \text{R}^2 \xrightarrow{\text{Pd(OAc)}_2 \text{ (10 mol%), PhI (0.5 equiv), K}_2\text{CO}_3 \text{ (1.0 equiv), O}_2 \text{ (air), DMSO, 100 °C, 4–6 h}} \text{R}^1 \text{N} \text{H} \text{S} \text{R}^2 \]

\[\text{R}^1 \text{N} \text{H} \text{S} \text{R}^2 \]

\[\text{R}^1 \text{N} \text{H} \text{S} \text{R}^2 \]

\[\text{R}^1 \text{N} \text{H} \text{S} \text{R}^2 \]

\[\text{R}^1 \text{N} \text{H} \text{S} \text{R}^2 \]
In summary, we have presented an iodobenzene-promoted Pd-catalysed synthesis of benzothiazoles via an intramolecular coupling. A series of 2-aminobenzothiazoles was synthesised by a palladium-catalysed oxidative coupling in good yields (62–89%). Iodobenzene was found to be an effective additive in this intramolecular C–S bond-formation reaction. A directing group (thiourea) attached to the aryl ring is essential for activation of the ortho C–H. This protocol is experimentally simple and shows broad substrate scope, affording the 2-aminobenzothiazoles, and could be attractive in the fields of medicinal chemistry and materials science.

All reactions were carried out in dried glassware with septa. All starting materials were purchased from commercial suppliers. DMSO was dried over molecular sieves. Yields refer to isolated compounds estimated to be >95% pure as determined by ¹H NMR and capillary GC analysis.

**Typical Procedure for the Preparation of 2-Aminobenzothiazoles in the Presence of Iodobenzene and Palladium Diacetate**

1,1-Dimethyl-3-phenylthiourea (1.0 mmol), Pd(OAc)₂ (10% mmol), K₂CO₃ (1.0 mmol), iodobenzene (0.5 mmol) were placed in a dried tube equipped with a septum and magnetic stirrer bar, and DMSO (2 mL) was then added. The mixture was stirred at 100 °C and the reaction was followed by TLC until the starting material was consumed (ca. 4–6 h). The reaction was cooled to r.t., quenched with sat. NH₄Cl solution (5 mL) and then extracted with EtOAc (10 mL). The organic extract was dried over anhydrous Na₂SO₄, filtered and evaporated under vacuum. The residue was purified by flash column chromatography with a solvent system as described below to afford the desired product.
N,N-Dimethylbenzo[d]thiazol-2-amine (Table 2, entry 1, 2a)
The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1:3) to give the target compound 2a (144 mg, 81%) as a dark-yellow solid; mp 82–84 °C.

1H NMR (400 MHz, CDCl3); δ = 7.6 (t, J = 7.6 Hz, 2 H), 7.33 (t, J = 8.0 Hz, 1 H), 7.10 (t, J = 7.6 Hz, 1 H), 3.23 (s, 6 H).

13C NMR (100 MHz, CDCl3); δ = 168.77, 153.08, 131.01, 125.98, 120.96, 120.66, 110.72, 40.22.

HRMS (ESI): m/z calcld for C19H19N2S; 283.9983; found: 283.9976.

d – thiazol-2-amine (Table 2, entry 2, 2b)
The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1:1) to give the target compound 2b (198 mg, 77%) as a pale-yellow syrup.

1H NMR (400 MHz, CDCl3); δ = 7.63 (s, 1 H), 7.36–7.31 (m, 2 H), 3.54–3.51 (m, 4 H), 1.24 (t, J = 7.2 Hz, 3 H).  
13C NMR (100 MHz, CDCl3); δ = 171.10, 147.23, 138.66, 135.14, 125.34, 123.13, 119.58, 119.04, 45.46, 14.07.

HRMS (ESI): m/z calcld for C19H19N2S; 224.0488; found: 224.0475.

6-Bromo-N,N-dimethylbenzo[d]thiazol-2-amine (Table 2, entry 3, 2c)
The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1:1) to give the target compound 2c (169 mg, 76%) as a bright-yellow solid; mp 209–211 °C.

1H NMR (400 MHz, CDCl3); δ = 7.79 (s, 1 H), 7.47 (s, 2 H), 3.30 (s, 6 H).

13C NMR (100 MHz, CDCl3); δ = 170.97, 156.53, 131.63, 130.03, 124.75, 119.73, 118.76, 103.15.

HRMS (ESI): m/z calcld for C19H17BrN2S; 326.9732; found: 326.9720.

6-Fluoro-N,N-dimethylbenzo[d]thiazol-2-amine (Table 2, entry 6, 2f)
The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1:3) to give the target compound 2f (147 mg, 75%) as a white solid; mp 118–120 °C.

1H NMR (400 MHz, CDCl3); δ = 7.98 (d, J = 8.4 Hz, 1 H), 7.74 (d, J = 7.6 Hz, 1 H), 7.02 (d, J = 8.0 Hz, 1 H), 3.24 (s, 6 H).

13C NMR (100 MHz, CDCl3); δ = 171.10, 147.23, 138.66, 135.14, 125.34, 123.13, 119.58, 119.04, 45.46, 14.07.

HRMS (ESI): m/z calcld for C19H17F2N2S; 283.9976; found: 283.9970.

4-Nitro-N,N-dimethylbenzo[d]thiazol-2-amine (Table 2, entry 9, 2i)
The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1:3) to give the target compound 2i (188 mg, 73%) as a white solid; mp 116–118 °C.

1H NMR (400 MHz, CDCl3); δ = 7.62 (s, 1 H), 7.32 (d, J = 8.4 Hz, 1 H), 7.06 (d, J = 8.4 Hz, 1 H), 3.08 (s, 6 H).

13C NMR (100 MHz, CDCl3); δ = 169.56, 154.61, 129.97, 123.55, 121.61, 119.41, 40.16.

HRMS (ESI): m/z calcld for C19H17F2N2S; 326.9732; found: 326.9720.

4-Bromo-N,N-dimethylbenzo[d]thiazol-2-amine (Table 2, entry 10, 2j)
The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1:3) to give the target compound 2j (166 mg, 74%) as a brown solid; mp 199–201 °C.

1H NMR (400 MHz, CDCl3); δ = 7.98 (d, J = 8.4 Hz, 1 H), 7.74 (d, J = 7.6 Hz, 1 H), 7.02 (t, J = 8.0 Hz, 1 H), 3.24 (s, 6 H).

13C NMR (100 MHz, CDCl3); δ = 171.10, 147.23, 138.66, 135.14, 125.80, 122.49, 119.42, 40.29.

HRMS (ESI): m/z calcld for C19H17F2N2S; 283.9976; found: 283.9970.
4-Chloro-NN-dimethylbenzothiazol-2-amine (Table 2, entry 11, 2k)
The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1:3) to give the target compound 2k (188 mg, 89%) as a white solid; mp 95–96 °C.

1H NMR (400 MHz, CDCl3): δ = 7.41 (d, J = 8.0 Hz, 1 H), 7.26 (d, J = 8.0 Hz, 1 H), 6.90 (t, J = 7.6 Hz, 1 H), 3.12 (s, 6 H).

13C NMR (100 MHz, CDCl3): δ = 168.80, 150.21, 132.34, 126.18, 122.98, 121.18, 119.14, 40.15.

HRMS (ESI): m/z calcd for C13H14N2S: 233.0773; found: 233.0770.

6-Methoxy-NN-dimethylbenzothiazol-2-amine (Table 2, entry 12, 2l)
The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1:1) to give the target compound 2l (148 mg, 71%) as a pale-yellow solid; mp 90–92 °C.

1H NMR (400 MHz, CDCl3): δ = 7.43 (d, J = 8.8 Hz, 1 H), 7.09 (s, 1 H), 8.85 (d, J = 8.4 Hz, 1 H), 3.75 (s, 3 H), 3.10 (s, 6 H).

13C NMR (100 MHz, CDCl3): δ = 167.43, 154.66, 147.22, 131.86, 119.06, 113.49, 119.14, 105.23, 55.87, 40.21.

HRMS (ESI): m/z calcd for C13H14N2S: 206.0872; found: 208.0682.

N,N,6-Trimethylbenzothiazol-2-amine (Table 2, entry 13, 2m)
The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1:1) to give the target compound 2m (126 mg, 73%) as a red-brown solid; mp 96–98 °C.

1H NMR (400 MHz, CDCl3): δ = 7.43 (d, J = 8.0 Hz, 1 H), 7.09 (d, J = 4.0 Hz, 1 H), 6.85 (d, J = 8.8 Hz, 1 H), 3.76 (s, 3 H), 3.10 (s, 6 H).

13C NMR (100 MHz, CDCl3): δ = 168.25, 150.92, 147.22, 131.86, 127.11, 120.72, 118.34, 40.19, 21.21.


N,N-Diethylbenzothiazol-2-amine (Table 2, entry 14, 2n)
The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1:4) to give the target compound 2n (163 mg, 79%) as a pale-yellow syrup.

1H NMR (400 MHz, CDCl3): δ = 7.59 (t, J = 8.0 Hz, 2 H), 7.26 (t, J = 7.2 Hz, 1 H), 7.01 (t, J = 7.6 Hz, 1 H), 3.57–3.51 (m, 4 H), 1.26 (t, J = 7.2 Hz, 6 H).

13C NMR (100 MHz, CDCl3): δ = 167.30, 130.24, 125.93, 120.88, 120.56, 118.45, 45.54, 12.87.

HRMS (ESI): m/z calcd for C13H14N2S: 206.0878; found: 208.0885.

N,N-Dibutylbenzothiazol-2-amine (Table 2, entry 15, 2o)
The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1:10) to give the target compound 2o (165 mg, 63%) as a colourless viscous oil.

1H NMR (400 MHz, CDCl3): δ = 7.54 (t, J = 8.0 Hz, 2 H), 7.25 (t, J = 8.0 Hz, 1 H), 7.01 (t, J = 8.0 Hz, 1 H), 3.48 (t, J = 8.0 Hz, 4 H), 1.70–1.63 (m, 4 H), 1.42–1.33 (m, 4 H), 0.96 (t, J = 8.0 Hz, 6 H).

13C NMR (100 MHz, CDCl3): δ = 167.90, 153.06, 130.52, 125.82, 120.71, 120.47, 118.51, 51.05, 29.64, 20.15, 13.96.

HRMS (ESI): m/z calcd for C18H20N2S: 262.1504; found: 262.1497.

6-Methoxy-NN-dibutylbenzothiazol-2-amine (Table 2, entry 16, 2p)
The residue was purified by flash chromatography on silica gel (EtOAc/PE = 1:7) to give the target compound 2p (180 mg, 62%) as a pale-yellow syrup.

1H NMR (400 MHz, CDCl3): δ = 7.41 (d, J = 8.8 Hz, 1 H), 7.09 (s, 1 H), 6.84 (d, J = 9.2 Hz, 1 H), 3.76 (s, 3 H), 3.43 (t, J = 7.6 Hz, 4 H), 1.67–1.60 (m, 4 H), 1.38–1.32 (m, 4 H), 0.94 (t, J = 7.2 Hz, 6 H).

13C NMR (100 MHz, CDCl3): δ = 166.52, 154.50, 147.46, 131.50, 118.83, 113.19, 105.21, 55.88, 50.92, 26.69, 20.16, 13.96.

HRMS (ESI): m/z calcd for C18H22N2S: 292.1609; found: 292.1615.

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References
