CuI nanoparticles Catalyzed Synthesis of Tetracyclic Heterocycles
benzo[e]benzo[4,5]imidazo[1,2-c][1,3]thiazin-6-imine by S_N_Ar-Type C-S, C-N Bond Formation with isothiocyanatobenzenes and Benzimidazoles

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1. Crystal data of 3b

<table>
<thead>
<tr>
<th>Compound</th>
<th>3b</th>
</tr>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>C21 H15 N3 S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>341.42</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C12/c1</td>
</tr>
<tr>
<td>T(K)</td>
<td>299</td>
</tr>
<tr>
<td>A (Å)</td>
<td>1.54184</td>
</tr>
<tr>
<td>A (Å)</td>
<td>23.3793(3)</td>
</tr>
<tr>
<td>B (Å)</td>
<td>7.23290(10)</td>
</tr>
<tr>
<td>C (Å)</td>
<td>19.5343(3)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>92.6530(10)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>3299.71(8)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>D_{calc} (mg/m³)</td>
<td>1.375</td>
</tr>
<tr>
<td>F(000)</td>
<td>1424</td>
</tr>
<tr>
<td>Crystal size (mm³)</td>
<td>0.4 x 0.2 x 0.2</td>
</tr>
<tr>
<td>θ range for data collection (deg.)</td>
<td>3.785 to 66.565</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>2882 / 0 / 226</td>
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<tr>
<td>Goodness-of-fit on F²</td>
<td>1.094</td>
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<tr>
<td>Final R₁/wR₂ indices [I&gt;2σ(I)]</td>
<td>0.0471 / 0.1295</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>0.0500</td>
</tr>
<tr>
<td>Largest diff. peak and hole(A⁻³)</td>
<td>0.199 and -0.491</td>
</tr>
</tbody>
</table>

Figure S1. ORTEP plot of 3b showing thermal ellipsoids at the 50% probability level
2. General Procedures

General Procedure for the Preparation of Substituted 2-(2-Halophenyl)-1H-benzo[d]imidazoles (1)

To a flask were added substituted 1,2-diaminobenzene (1.08 g, 10 mmol), 2-halobenzoic acid (10 mmol) and PPA (20 g), and the reaction mixture was heated at 170 °C in an oil bath for 7 h. After the reaction was complete, the reaction mixture was slowly poured into ice water, and the resulting mixture was basified with solid NaOH and NaHCO₃. Once the solution had reached pH 8-10, the precipitate was isolated by filtration, washed with cold water and recrystallized from hot aqueous ethanol. The solid was then dried to afford the corresponding 2-(2-halophenyl)-1H-benzo[d]imidazole.

2-(2-iodophenyl)-1H-benzo[d]imidazole

\[ \begin{array}{c}
\text{I} \\
\text{N} \end{array} \begin{array}{c}
\text{H} \\
\text{N} \\
\text{I} \\
\text{N} \\
\text{H} \\
\text{N} \end{array} \]

1H NMR (600 MHz, dmsso) δ 12.70 (s, 1H), 8.06 (dd, J = 8.0, 1.0 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.55 (ddd, J = 10.8, 8.5, 4.5 Hz, 2H), 7.30 – 7.19 (m, 3H).
13C NMR (151 MHz, dmsso) δ 152.54, 143.15, 139.61, 136.55, 134.32, 131.31, 131.16, 128.09, 122.51, 121.48, 119.10, 111.44, 97.34.

2-(2-iodophenyl)-1H-benzo[d]imidazole

\[ \begin{array}{c}
\text{I} \\
\text{N} \end{array} \begin{array}{c}
\text{N} \\
\text{H} \\
\text{Br} \\
\text{N} \\
\text{H} \\
\text{N} \end{array} \]

1H NMR (600 MHz, dmsso) δ 12.73 (s, 1H), 7.82 (dd, J = 8.1, 1.1 Hz, 1H), 7.77 (dd, J = 7.6, 1.7 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.49 – 7.44 (m, 1H), 7.24 (dt, J = 15.1, 6.7 Hz, 2H).
13C NMR (151 MHz, dmsso) δ 150.38, 143.15, 139.61, 136.55, 134.32, 132.38, 132.22, 131.32, 127.75, 122.62, 121.56, 121.51, 119.08, 111.54.

2-(2-bromophenyl)-6-methyl-1H-benzo[d]imidazole

\[ \begin{array}{c}
\text{I} \\
\text{N} \end{array} \begin{array}{c}
\text{N} \\
\text{H} \\
\text{Br} \\
\text{N} \\
\text{H} \\
\text{N} \end{array} \]

1H NMR (600 MHz, dmsso) δ 12.55 (s, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.60 (d, J = 7.4 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.49 (s, 1H), 7.38 (s, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 2.44 (s, 3H).
13C NMR (151 MHz, dmsso) δ 166.18, 161.19, 160.49, 139.67, 136.66, 134.78, 131.31, 131.14, 130.01, 128.74, 128.14, 97.36, 21.33.

2-(2-bromophenyl)-6-methyl-1H-benzo[d]imidazole
**2-(2-bromophenyl)-3H-imidazo[4,5-b]pyridine**

$^1$H NMR (600 MHz, dmso) $\delta$ 12.58 (s, 1H), 7.81 (dd, $J = 8.0$, 0.7 Hz, 1H), 7.75 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.54 (td, $J = 7.5$, 0.9 Hz, 1H), 7.50 (d, $J = 2.1$ Hz, 1H), 7.45 (td, $J = 7.8$, 1.7 Hz, 1H), 7.39 (s, 1H), 7.06 (d, $J = 8.1$ Hz, 1H), 2.44 (s, 3H).

$^{13}$C NMR (151 MHz, dmso) $\delta$ 150.00, 133.35, 132.46, 132.17, 131.19, 127.72, 123.52, 121.47, 21.29.

**6-bromo-2-(2-iodophenyl)-1H-benzo[d]imidazole**

$^1$H NMR (600 MHz, dmso) $\delta$ 13.27 (s, 1H), 8.40 (d, $J = 4.1$ Hz, 1H), 8.06 (d, $J = 7.5$ Hz, 1H), 7.84 (d, $J = 7.9$ Hz, 1H), 7.76 (dd, $J = 7.5$, 1.0 Hz, 1H), 7.58 (dd, $J = 10.9$, 4.1 Hz, 1H), 7.50 (td, $J = 7.8$, 1.6 Hz, 1H), 7.29 (dd, $J = 8.0$, 4.7 Hz, 1H).

$^{13}$C NMR (151 MHz, dmso) $\delta$ 152.17, 143.99, 133.38, 132.20, 131.99, 131.73, 127.79, 121.63, 118.13.

**Preparation of Cul NPs**

The nanocatalyst was produced by ultrasonic irradiation using copper sulfate (CuSO$_4$) as the Cu source. First, CuSO$_4$ (1 mmol) was cleaned for 20 s in acetone under ultrasonic irradiation followed. The dried substrate was then slowly dipped into a solution of potassium iodide (1 mmol) in 40 mL of distilled water, and the mixture was sonicated for 30 min. When the reaction was complete, the obtained gray precipitate was isolated by filtration, washed with distilled water and dried to afford pure Cul NPs.

According to the diffraction data card (JCPDS, 75-0832); all the peaks can be perfectly indexed to the peak positions characteristic of Cul (Fig. S2).

Scanning electron microscopy (SEM) was used to confirm the size of the Cul nanoparticles, and the SEM micrograph is shown in Fig. S3. This figure illustrates that, the Cul NPs obtained under ultrasonic irradiation had diameters on the order of nanometers.
3. References


4. Copies of $^1$H and $^{13}$C NMR Spectra