Selective Synthesis of \(N\)-H and \(N\)-Aryl Benzotriazoles by the [3+2] Annulation of Sodium Azide with Arynes

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Supporting Information

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1. Optimization Studies for the \( N \)-H Benzotriazole Synthesis

*Variation of \( \text{NaN}_3 \) stoichiometry:*

\[
\begin{array}{ccc}
\text{entry} & \text{NaN}_3 \text{ (equiv)} & \text{F\textsuperscript{-} Source (equiv)} & \text{yield of } 2a^a \\
1 & 2 & \text{CsF (2), 18-crown-6 (2)} & 45\% \\
2 & 3 & \text{CsF (2), 18-crown-6 (2)} & 51\% \\
3 & 4 & \text{CsF (2), 18-crown-6 (2)} & 59\% \\
4^b & 4 & \text{CsF (5), 18-crown-6 (5)} & 64\%
\end{array}
\]

Reaction condition: 1a (0.5 mmol), \( \text{NaN}_3 \), CsF, 18-crown-6, MeCN (2.0 mL), 70 °C for 12 h. \(^a\) Yields of the isolated product is given. \(^b\) Reaction was performed in 3 mL CH\textsubscript{3}CN

*Variation of Temperature:*

\[
\begin{array}{ccc}
\text{entry} & \text{temperature (°C)} & \text{yield of } 2a^a \\
1 & 0 \text{ °C} & <5\% \\
2 & \text{rt (25 °C)} & 32\% \\
3 & 60 \text{ °C} & 39\% \\
4 & 70 \text{ °C} & 45\% \\
5 & 80 \text{ °C} & 41\%
\end{array}
\]

Reaction condition: 1a (0.5 mmol), \( \text{NaN}_3 \) (2 equiv), CsF (2 equiv), 18-crown-6 (2 equiv), MeCN (2.0 mL) for 12 h. \(^a\) Yields of the isolated product is given.

*Solvent Screening:*
### 2. Optimization Studies for the N-Aryl Benzotriazole Synthesis

<table>
<thead>
<tr>
<th>entry</th>
<th>variation of the standard conditions</th>
<th>yield of 3a (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>1.5 equiv of 1a</td>
<td>18</td>
</tr>
<tr>
<td>3&lt;sup&gt;c&lt;/sup&gt;</td>
<td>CsF instead of KF/18-crown-6</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>TBAF instead of KF/18-crown-6</td>
<td>53</td>
</tr>
<tr>
<td>5</td>
<td>60 °C instead of 25 °C</td>
<td>47</td>
</tr>
<tr>
<td>6</td>
<td>0 °C instead of 25 °C</td>
<td>39</td>
</tr>
<tr>
<td>7&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Open-flask reaction</td>
<td>86</td>
</tr>
<tr>
<td>8</td>
<td>1,4-Dioxane instead of THF</td>
<td>67</td>
</tr>
<tr>
<td>9</td>
<td>2.0 equiv water added</td>
<td>82</td>
</tr>
</tbody>
</table>

<sup>a</sup> Standard conditions: 1a (0.625 mmol), NaN₃ (0.25 mmol), KF (5.0 equiv), 18-crown-6 (5.0 equiv), THF (1.0 mL), 25 °C for 12 h. <sup>b</sup> Yields of the isolated product is given. <sup>c</sup> Reaction was performed in CH₃CN. <sup>d</sup> Reaction performed in open air using commercial KF, 18-crown-6, and NaN₃.
3. Mechanistic Experiments

*Deuterium Labeling Experiment:*

![Chemical Structure](image)

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the KF (0.073 g, 1.25 mmol) and 18-crown-6 (0.330 g, 1.25 mmol) in a glove-box. Then NaN₃ (0.016 g, 0.25 mmol) and D₂O (0.004 g, 4 μL, 0.25 mmol) was added outside the glove-box under nitrogen atmosphere followed by addition of THF (1 mL). To the stirring solution, aryne precursor 1a (0.186 g, 152 μL, 0.625 mmol) was added and reaction mixture was allowed to stir at rt for 12 h. After 12 h the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet. ether) on silica gel to afford the 3a-D in 76% yield with 80% D incorporation at the 2-position.

![NMR Spectra](image)
4. $^1$H and $^{13}$C NMR Spectra of all Products

$1H$-Benzo[d][1,2,3]triazole (2a)
5,6-Dimethyl-1H-benzo[d][1,2,3]triazole (2b)
1,5,6,7-Tetrahydroindeno[5,6-d][1,2,3]triazole (2d)
4,7-Dimethyl-1H-benzo[d][1,2,3]triazole (2e)

2e (known compound ref 4)
$\textit{IH-Naphtho[2,3-d][1,2,3]triazole (2f)}$

![Chemical structure of 1H-Naphtho[2,3-d][1,2,3]triazole (2f)](attachment:image)

![NMR spectrum of 1H-Naphtho[2,3-d][1,2,3]triazole (2f)](attachment:image)
1H-Phenanthro[9,10-d][1,2,3]triazole (2g)
1H-naphtho[1,2-d][1,2,3]triazole (2h)
6,7,8,9-Tetrahydro-1H-naphth[1,2-d][1,2,3]triazole (2i)
5-methyl-1\textit{H}-benzo[\textit{d}][1,2,3]triazole (2j)
5-Chloro-1H-benzo[d][1,2,3]triazole (2k)
5-fluoro-1H-benzo[d][1,2,3]triazole (2l)
1-Phenyl-1H-benzo[d][1,2,3]triazole (3a)
1-(3,4-Dimethylphenyl)-5,6-dimethyl-1H-benzo[d][1,2,3]triazole (3b)

![NMR spectrum of 1-(3,4-Dimethylphenyl)-5,6-dimethyl-1H-benzo[d][1,2,3]triazole (3b)](image)
1-(Benzo[d][1,3]dioxol-5-yl)-1H-[1,3]dioxolo[4',5':4,5]benzo[1,2-d][1,2,3]triazole (3c)
1-(2,3-Dihydro-1H-inden-5-yl)-1,5,6,7-tetrahydroindeno[5,6-d][1,2,3]triazole (3d)

S20
1-(2,5-Dimethylphenyl)-4,7-dimethyl-1H-benzo[d][1,2,3]triazole (3e)
1-(Naphthalen-2-yl)-1H-naphtho[2,3-d][1,2,3]triazole (3f)

![NMR spectrum of 1-(Naphthalen-2-yl)-1H-naphtho[2,3-d][1,2,3]triazole (3f)](image-url)
1-(Phenanthren-9-yl)-1H-phenanthro[9,10-d][1,2,3]triazole (3g)
1-(3,4-dimethylphenyl)-1H-benzo[d][1,2,3]triazole (3h)
1-(benzo[\textit{d}][1,3]dioxol-5-yl)-1\textit{H}-benzo[\textit{d}][1,2,3]triazole (3i)
1-(2,3-Dihydro-1H-inden-5-yl)-1H-benzo[d][1,2,3]triazole (3j)
1-(2,5-dimethylphenyl)-1H-benzo[d][1,2,3]triazole (3k)
1-(Naphthalen-2-yl)-1H-benzo[d][1,2,3]triazole (3l)

**Chemical Structure:**

![Chemical Structure Image]

**NMR Spectrogram:**

- **1H NMR:**
  - 7.4-8.2 ppm
- **13C NMR:**
  - 27.0-197.7 ppm

**Chemical Shifts:**

- 1H NMR:
  - 1H: 7.4-8.2 ppm
- 13C NMR:
  - 27.0-197.7 ppm

**S28**
1-(Phenanthren-9-yl)-1H-benzo[d][1,2,3]triazole (3m)
1-(3,4-Difluorophenyl)-1H-benzo[d][1,2,3]triazole (3n)
2-Phenyl-2H-benzo[d][1,2,3]triazole (4a)