

# Copper-Catalyzed Oxidative Amination of Benzoxazoles via C–H and C–N Bond Activation: A New Strategy for Using Tertiary Amines as Nitrogen Group Sources

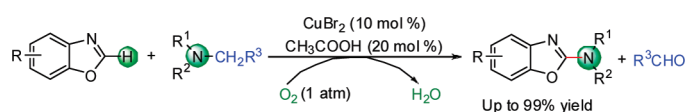
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## ABSTRACT



An efficient and conceptually new method for oxidative amination of azoles with tertiary amines via copper-catalyzed C–H and C–N bond activation has been developed. This protocol can be performed in the absence of external base and only requires atmospheric oxygen as oxidant. The catalyst system is very simple and efficient, which opens a new way for using tertiary amines as nitrogen group sources for C–N bond formation reactions.

The transition-metal-catalyzed selective C–N bond formation reaction through C–H bond activation is an efficient method to facilitate the construction of complex amines.<sup>1</sup> With respect to the nitrogen group sources, primary amines, secondary amines, chloroamines, and amides have been successfully installed into the corresponding substrates via C–H activation.<sup>2</sup> Despite that remarkable success has been achieved, to the best of our knowledge, tertiary amines used as amino group sources for a direct amination reaction via C–H and C–N bond activation have never been reported. This limitation is probably due to difficulty in the cleavage of the C–N bond as compared to other C–X bonds.<sup>3</sup> Herein, we report on a new and efficient procedure for aerobic

oxidative amination of azoles with tertiary amines as nitrogen sources, which were catalyzed by a copper catalyst through the cleavage of two C–H bonds and one C–N bond under external-base-free conditions.

Given the importance of the azole motif in biological medicinal chemistry and material chemistry, the direct C–H functionalization of azole rings is of great interest.<sup>4,5</sup> Among

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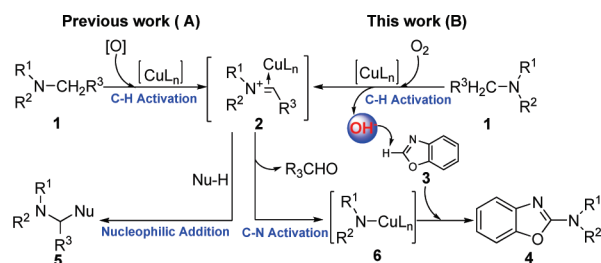
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the many types of C–H functionalization of azoles documented, the direct C–H amination of azoles pioneered by Mori,<sup>6a</sup> Schreiber,<sup>6b</sup> Chang,<sup>6c</sup> and others<sup>21,m</sup> provided a rapid and straightforward access to the heteroaryl amines. However, all of the aforementioned methods inherently suffer from harsh conditions such as high reaction temperature and use of a stoichiometric amount of expensive organometallic reagents and metal oxidant and a large amount of strong base or acid. Therefore, further development for direct C–H amination would be highly desired. The iminium-type intermediate **2** was first reported by Murahashi and has become one of the most useful active species for related transformations.<sup>7</sup> Li and co-workers developed the copper-catalyzed cross-dehydrogenative coupling (CDC) of tertiary amines with alkynes, active methylene, and nitromethane (Scheme 1, A) by using this strategy.<sup>8</sup> These elegant studies have prompted us to envisage that, in the presence of dioxygen–copper systems,<sup>9</sup> the iminium-type species **2** would be generated from tertiary amine via C–H bond cleavage. The reactive intermediate **2** might undergo C–N bond cleavage via hydrolysis to produce the copper amide

**Scheme 1.** Proposed New Strategy for Oxidative Amination



**6**,<sup>10</sup> which would react with azole **3** quickly. Thus the directed C–H amination of azoles with tertiary amines would be expected under the mild conditions (Scheme 1, B).

To test our hypothesis, the copper-catalyzed aerobic oxidative C–H amination of benzoxazole **3a** with Et<sub>3</sub>N **1a** as a nitrogen source was selected as a benchmark reaction. As shown in Table 1, use of CuCl<sub>2</sub> as a catalyst under 1 atm

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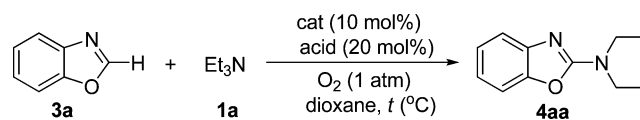
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**Table 1.** Optimization of the Reaction Conditions<sup>a</sup>



entry	catalyst	acid (20 mol %)	t (°C)	yield (%) <sup>b</sup>
1	CuCl <sub>2</sub>	none	80	29
2	CuBr	none	80	23
3	CuBr <sub>2</sub>	none	80	34
4	Cu(OAc) <sub>2</sub>	none	80	<1
5	CuBr <sub>2</sub>	CH <sub>3</sub> CO <sub>2</sub> H	80	55
6	CuBr <sub>2</sub>	HCO <sub>2</sub> H	80	49
7	CuBr <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H	80	52
8	CuBr <sub>2</sub>	(4-MeO)C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	80	49
9	CuBr <sub>2</sub>	(4-Me)C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	80	45
10	CuBr <sub>2</sub>	2-OHC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	80	31
11 <sup>c</sup>	CuBr <sub>2</sub>	CH <sub>3</sub> COOH	80	84
12	CuBr <sub>2</sub>	CH <sub>3</sub> COOH	100	81
13	CuBr <sub>2</sub>	CH <sub>3</sub> COOH	120	89
14 <sup>d</sup>	CuBr <sub>2</sub>	CH <sub>3</sub> COOH	120	70
15 <sup>e</sup>	CuBr <sub>2</sub>	CH <sub>3</sub> COOH	120	0
16	–	CH <sub>3</sub> COOH	120	0

<sup>a</sup> General conditions: **3a** (0.5 mmol), Et<sub>3</sub>N (1.0 mmol), 1,4-dioxane (1.0 mL), O<sub>2</sub> (1 atm), 16 h. <sup>b</sup> Isolated yield. <sup>c</sup> CuBr<sub>2</sub> (15 mol %). <sup>d</sup> CuBr<sub>2</sub> (5 mol %). <sup>e</sup> In the Ar atmosphere.

of O<sub>2</sub> at 80 °C yielded the desired amine **4aa** in 29% yield (Table 1, entry 1) and no dimer of benzoxazole was observed, which indicated that the desired C–H amination involving C–H and C–N bond cleavage was indeed possible albeit in low yield. Other copper sources, including CuBr, CuBr<sub>2</sub>, and Cu(OAc)<sub>2</sub>, were also tested, and the results demonstrated that CuBr<sub>2</sub> was the best choice (Table 1, entries 1–4). Other commonly used metal salts such as Ag(I) salts, Pd(OAc)<sub>2</sub>,

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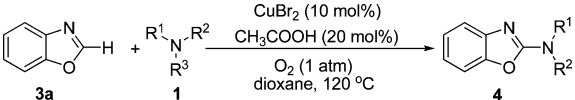
and Ni(II) salts proved to be either less effective or totally ineffective (see Supporting Information). The addition of 20 mol % CH<sub>3</sub>COOH greatly improved the reaction efficacy, and **4aa** was obtained in 55% yield (Table 1, entry 5). Other acids such as HCOOH, C<sub>6</sub>H<sub>5</sub>COOH, and salicylic acid were less effective than CH<sub>3</sub>COOH (Table 1, entries 6–10). Increasing the catalyst loading (from 10 mol % to 15 mol %) or temperature (from 80 to 120 °C) could enhance the reaction efficacy. High yields up to 84% with 15 mol % CuBr<sub>2</sub> as a catalyst at 80 °C and 89% yield with 10 mol % catalyst loading at 120 °C were obtained, respectively. The catalyst loading could be decreased to 5 mol % and still provide good yields at high temperature. In addition, in the absence of a copper source or in the presence of O<sub>2</sub>-free conditions, no aminated product was observed under the same reaction conditions (Table 1, entries 15 and 16).

Under the optimized conditions, the scope of this oxidative C–H amination reaction was investigated with a variety of tertiary amines. As shown in Table 2, almost all alkyl tertiary

suggesting that α-H is essential for the C–H amination under these conditions. In addition to simple alkyl amines, the unsaturated triallyl amine **1h** also participated in the oxidative C–H amination reaction to give the corresponding *N,N*-diallyl benzoxazole **4ah** (Table 2, entry 8). The bulky diisopropylethyl amine **1i** containing two kinds of α-H afforded two types of products, **4ai** and **4ai'**, in an almost 1:1 ratio, which indicated that the sterically less hindered alkyl group is much more facile for cleavage. Similarly, two kinds of aminated products, **4aa** and **4aj**, were obtained in the reaction of *N*-benzyl-*N*-ethylethanamine **1j**, where the C–N bond cleavage took place at the two cleavable C–N bonds, respectively. However, the morpholine derived tertiary amines **1k** and **1l** reacted exclusively at their exocyclic C–N bond to give cyclic amine **4ak** (Table 2, entries 11 and 12). The same regioselectivity was also observed in the reaction of benzoxazole with **1m** to exclusively cleave the exocyclic C–N bond giving the valuable **4am** in high yield (Table 2, entry 13). Whereas the reaction had been performed at 120 °C to rapidly obtain a cleaner process, it was found that a 15% mol amount of CuBr<sub>2</sub> at 80 °C was sufficient to provide the desired product in almost the same yields.

Next, the scope of this reaction was investigated with respect to azole under the same conditions as those shown in Table 2. Some representative results are summarized in Scheme 2. The reactions of 6-, 4-, and 5-methylbenzoxazoles

**Table 2.** Substrate Scope of Amines<sup>a</sup>

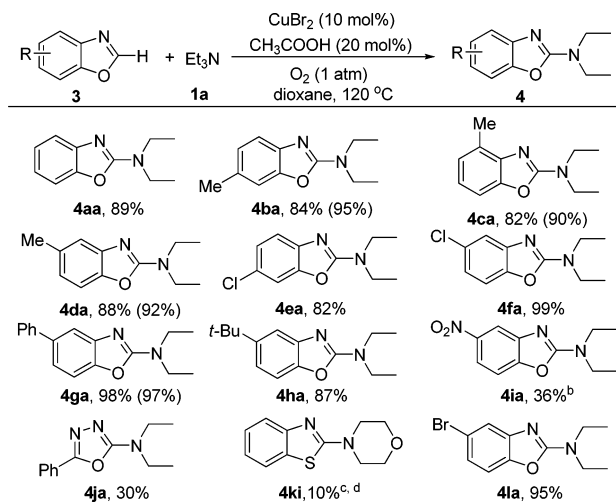


entry	amine	product	yield (%) <sup>b</sup>
1	<b>1a</b> R = Et	<b>4aa</b>	89
2	<b>1b</b> R = <i>n</i> -Pr	<b>4ab</b>	92
3	<b>1c</b> R = <i>n</i> -Bu	<b>4ac</b>	82
4	<b>1d</b> R = <i>i</i> -Bu	<b>4ad</b>	78
5	<b>1e</b> R = Oct	<b>4ae</b>	82
6 <sup>c</sup>	<b>1f</b> R = Bn	<b>4af</b>	54
7	<b>1g</b> R = Ph	<b>4ag</b>	0
8	<b>1h</b> R = allyl	<b>4ah</b>	32
9	<b>1i</b>	<b>4ai</b>	20
		<b>4ai'</b>	20
10	<b>1j</b>	<b>4aa</b>	59
		<b>4aj</b>	34
11	<b>1k</b>	<b>4ak</b>	25
12	<b>1l</b>	<b>4ak</b>	74
13	<b>1m</b>	<b>4am</b>	82

<sup>a</sup> The reaction conditions: **3a** (0.5 mmol), **1** (1.0 mmol), CuBr<sub>2</sub> (10 mol %), CH<sub>3</sub>COOH (20 mol %), in 1,4-dioxane (1 mL) under 1 atm of O<sub>2</sub>, 120 °C, 16 h. <sup>b</sup> Isolated yield. <sup>c</sup> CuBr<sub>2</sub> (15 mol %), 80 °C.

amines **1a–1f**, bearing α-H adjacent to the nitrogen atom, provided the desired products **4aa–4af** in 54–92% yield (Table 2, entries 1–6). No product formation was observed with triphenylamine **1g** as an amino group source, in which no C–H bond α to the nitrogen atom is contained, thus

**Scheme 2.** Substrate Scope of Azoles<sup>a</sup>



<sup>a</sup> (a) The reaction conditions: **3** (0.5 mmol), **1** (1.0 mmol), CuBr<sub>2</sub> (10 mol %), CH<sub>3</sub>COOH (20 mol %), in 1,4-dioxane (1 mL) under 1 atm of O<sub>2</sub>, 120 °C, 16 h; isolated yield; the data in parentheses are obtained at 80 °C with 15 mol % CuBr<sub>2</sub> in 30 h. (b) 100 mol % CuBr<sub>2</sub> was used. (c) With **2i** as amine source. (d) With 20 mol % PhCOOH as an additive.

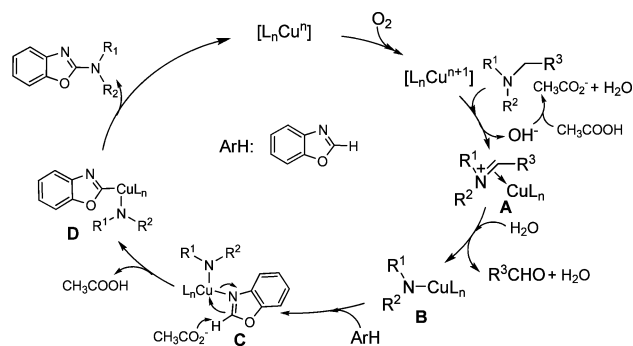
with Et<sub>3</sub>N took place smoothly to furnish the desired amines **4ba**, **4ca**, and **4da**, which were isolated in 82–88% yield, and no significant rate difference was observed. Furthermore, the sterically more demanding product **4ha** was also obtained in 87% yield. These results suggest that this reaction is not sensitive to the steric hindrance in the benzene ring of azole. The chloro and bromo group could survive the reaction

conditions to give the corresponding functionalized amine products such as **4ea**, **4fa**, and **4la** in excellent yield (up to 99% yield). The 5-arylated benzoxazole derivative could be used in this oxidative C–H amination reaction to give the functionalized product **4ga** in almost quantitative yield. However, in the case of 5-nitro-substituted benzoxazole, although the expected oxidative C–H amination product **4ia** could be obtained in 36% yield, stoichiometric CuBr<sub>2</sub> was required. In contrast to benzoxazoles, 2-phenyl-1,3,4-oxadiazole afforded the corresponding amine **4ja** in 30% yield, while benzothiazole afforded the desired product **4ki** in 10% yield, the lower reactivity of these substrates observed here is probably due to their weaker acidity.

To gain some insight into the mechanism of the present C–H amination process, we first conducted the reaction on gram scale with **3a** and **11** as reactants which afforded the desired aminated product **4ak** in 75% yield and inherently together with the benzaldehyde in 87% yield (based on **3a**, see Supporting Information). The concomitant isolation of benzaldehyde in amounts a little more than that of the desired amination product **4ak** might indicate that C–N bond cleavage most likely takes place prior to the new C–N bond formation step.<sup>3a</sup> Radical scavengers, such as TEMPO and 1,1-diphenylethylene, were employed in the standard reaction, and the desired product **4aa** was still obtained in 62% and 81% yields, respectively (see Supporting Information). This result suggested that a free radical process is not a requirement for the present reaction. To investigate the origin of the aldehyde and the transformation of the resected H atoms from the tertiary amine and azole, an isotopic labeling experiment with <sup>18</sup>O<sub>2</sub> was conducted. The results demonstrated clearly that the resected H atoms transformed into water and the oxygen of aldehyde was from molecular O<sub>2</sub>. Further isotopic labeling experiments with <sup>18</sup>O<sub>2</sub> and H<sub>2</sub><sup>18</sup>O suggested the oxygen of aldehyde directly originated from water and the produced water of the reaction participated in the C–N bond cleavage event for hydrolysis of the iminium-type intermediate. The kinetic isotope effects (KIEs) for both coupling partners were determined for investigation in which one of the C–H bond cleavage processes was involved in the rate-limiting step (see Supporting Information). An intermolecular competition reaction between 5-methylbenzoxazole and 2-deuterated-5-methylbenzoxazole showed a KIE of 1.4, suggesting that C–H cleavage of the azole is not involved in the rate-limiting step. However, the primary KIE of 2.7 was observed for 4-benzylmorpholine, which indicated that C–H cleavage of the tertiary amines is significant with respect to the rate-limiting step.

On the basis of the results that we obtained here and previously,<sup>10</sup> a plausible mechanism for the present process is proposed as shown in Scheme 3. Initially, the copper catalyst is oxidized by oxygen to form [LnCu<sup>n+1</sup>] composed

**Scheme 3.** Proposed Reaction Pathway for the Cu-Catalyzed Oxidative C–H Amination



of the copper salt and molecular oxygen.<sup>9</sup> The high Lewis acidic copper species coordinates to the tertiary amine and reacts with it to give the iminium-type intermediate **A** by elimination of water which was assisted by CH<sub>3</sub>COOH. Iminium-type intermediate **A** is then hydrolyzed to be converted into the key intermediate **B** by elimination of aldehyde.<sup>9</sup> **B** would coordinate to azole to yield **C**, and its subsequent deprotonation/rearrangement would afford **D** and regenerate CH<sub>3</sub>COOH followed by reductive elimination to form the desired product and regenerate the copper catalyst to complete the catalytic cycle. The results of KIE experiment indicate that the C–N bond cleavage is slow, which is beneficial to form a reactive copper amide **B**.<sup>11</sup>

In summary, we have established an efficient and conceptually new strategy for oxidative C–H and C–N bond activation, which provides a new method for C–H amination of azoles with tertiary amines as nitrogen group sources. This reaction can be performed in the absence of an external base under mild conditions and only requires atmospheric oxygen as an oxidant. The success of the present studies not only provides a powerful method for the construction of new C–H amination reactions but also suggests a new strategy for C–N bond activation.

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**Supporting Information Available:** Experimental details and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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