

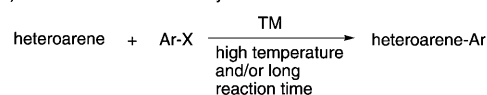
## Copper-Catalyzed Oxidative Arylation of Heteroarenes under Mild Conditions Using Dioxygen as the Sole Oxidant

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Arylation of heteroarene has been intensively studied over the past few years because aryl-substituted aromatic heterocycles are known to exhibit interesting biological activities and are also useful as electronic materials. Numerous methods have been reported to successfully construct this motif by transition-metal-catalyzed cross-coupling and most of them required expensive transition-metal catalysts such as Rh and Pd.<sup>[1,2]</sup> It is ideal to replace these catalysts by cheap metals. In 2007, Daugulis and co-workers first reported a copper-catalyzed cross-coupling of heteroarenes and aryl iodide under high temperature.<sup>[3a]</sup> You and co-workers modified a prior reported method by using aryl bromide as the electrophile; however, the reaction needed to be kept at high temperature for at least for one day.<sup>[3b]</sup> Very recently, Miura and Itami reported the Ni-catalyzed cross-coupling between heteroarenes and aryl halide, respectively. Their protocols also suffered from harsh conditions; for example, high temperatures and long reaction times.<sup>[3c,d]</sup> Therefore, finding a more practical and efficient method to achieve this aim remains a challenge.

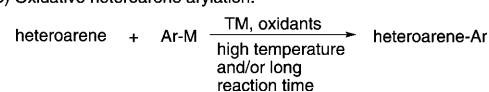
Like the traditional transition-metal-catalyzed cross-coupling reactions, previously reported catalytic methods for arylation of heteroarenes normally worked between heteroarene nucleophiles and aryl halide electrophiles (Scheme 1, A). Recently, remarkable progress has been made in oxidative cross-coupling.<sup>[4]</sup> Unlike the traditional cross-coupling reactions, the oxidative cross-coupling needs two nucleophilic partners in the reaction and the transformation includes three steps: a two-stage transmetalation to high-valent metal catalyst, reductive elimination, then reoxidation of the catalyst to high valency by the external oxidant. The termi-

A) Traditional heteroarene arylation:



TM = transition metal  
X = halogen, pseudo-halogen, COOH, etc.

B) Oxidative heteroarene arylation:



Scheme 1. Two pathways for the arylation of heteroarene.

nal oxidant that serves in oxidative cross-coupling always involves metal salts, organohalide, or benzoquinone, and so on. Replacement of these oxidants by dioxygen is more practical and more economical since this oxidant is very cheap and produces no environmentally hazardous byproduct.<sup>[5]</sup> The C-2 position of azole or thiazole is easily deprotonated under basic conditions. It may serve as a nucleophile and cross-couple with another nucleophile under oxidative coupling conditions (Scheme 1, B). Recently, Su and coworkers reported the Cu-catalyzed oxidative amination of azoles and thiazoles by using O<sub>2</sub> as the oxidant.<sup>[6]</sup> Only a few examples have been reported on oxidative arylation of azoles and thiazoles.<sup>[7]</sup> Miura and co-workers developed an oxidative arylation and alkenylation of heteroarenes including azole and thiazole with organosilicon reagents by a nickel catalyst.<sup>[8]</sup> You reported a Pd-catalyzed oxidative cross-coupling reaction between heteroarenes and aryl boronic acid.<sup>[9]</sup> Both of them require metal salts and/or benzoquinone as oxidant. Very recently, Pd<sup>[10]</sup> and Ni-catalyzed<sup>[11]</sup> oxidative arylation of azoles and thiazoles with aryl boronic acid by using dioxygen as oxidant have been achieved. The reactions also proceeded under high temperature and/or for a long reaction time. All above mentioned drawbacks have made the prior methods less attractive. In our study, we found that CuCl could very efficiently catalyze the oxidative cross-coupling between heteroarenes and arylboronic esters with good yields and selectivities. This reaction was complete in only minutes under mild conditions by using dioxygen as the sole oxidant.

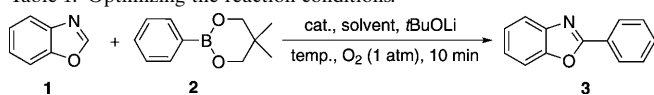
We initiated our investigation by using Pd as the catalyst and dioxygen as the oxidant (Table 1, entry 1). Under variant conditions, only low yields were obtained (details are shown in the Supporting Information).<sup>[12]</sup> We then switched

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Table 1. Optimizing the reaction conditions.<sup>[a]</sup>



Entry	Cat.	Solvent	T [°C]	Yield [%] <sup>[b]</sup>
1	Pd(OAc) <sub>2</sub>	DMF	40	0
2	CuI	DMF	40	83
3	CuCl <sub>2</sub>	DMF	40	85
4	Cu <sub>2</sub> O	DMF	40	trace
5	Cu	DMF	40	33
6	CuCl	DMF	40	93
7	CuCl	DMF	23	67
8	CuCl	dioxane	40	72
9	CuCl	<i>t</i> BuOH	40	45
10	CuCl	Toluene	40	0
11 <sup>[c]</sup>	CuCl	DMF	40	47
12 <sup>[d]</sup>	CuCl	DMF	40	32
13 <sup>[e]</sup>	CuCl	DMF	40	0

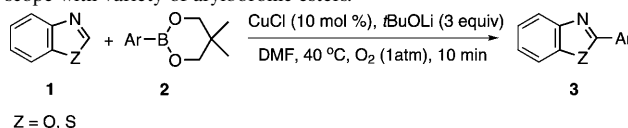
[a] All reactions were carried out by using **1** (0.4 mmol), compound **2** (1.5 equiv), *t*BuOLi (3 equiv), catalyst (10 mol %), and solvent (2 mL). [b] Isolated product yields. [c] *t*BuONa (3 equiv) was used as the base. [d] The corresponding boronic acid was used instead of **2**. [e] Reaction was carried out under argon atmosphere.

onic acid was used instead of the corresponding ester, the yield sharply declined (Table 1, entry 12). A control reaction was carried out by replacing the reaction atmosphere with argon; this resulted in the reaction being completely shut down and it revealed that the dioxygen was crucial to this transformation (Table 1, entry 13). It is known that copper can very efficiently catalyze heteroarene homocoupling under aerobic conditions.<sup>[13]</sup> However, our system has shown excellent selectivity for the cross-coupling of heteroarene and arylboronic ester. Only trace amounts (<2%) of benzoxazole homocoupling product was observed under the optimal conditions (Table 1, entry 6).

We first investigated the substrate scope with respect to arylboronic esters by using benzoxazole and benzothiazole as coupling partners under the optimal conditions. As shown in Table 2, uniformly high yields are obtained with a variety of arylboronic esters. Electron-deficient or electron-rich as well as heteroaryl boronic ester all provide high yields. It is worth mentioning that when 4-chlorophenylboronic ester is used as substrate, the reaction shows a very good selectivity for reacting at boronic ester side and keeps the chlorine side untouched (Table 2, entries 11 and 19). This gives the prod-

the catalyst to copper salts. To our delight, the copper catalyst was very active in the reaction. At 40 °C, under O<sub>2</sub> atmosphere, and with CuI (10 mol %) as the catalyst, the reaction was complete within 10 minutes and gave the desired arylation product in 83% yield (Table 1, entry 2). CuCl<sub>2</sub> provided a slightly higher yield whereas Cu<sub>2</sub>O only led to the formation of a trace amount of product (Table 1, entries 3 and 4). Copper powder exhibited low catalytic activity and only 33% yield was obtained (Table 1, entry 5). Under the same conditions, by using CuCl as the catalyst, the cross-coupling product was isolated in 93% yield (Table 1, entry 6). The reaction also proceeded under room temperature to give the product in moderate yield (Table 1, entry 7). The yield heavily relied on the choice of solvent; dioxane or *tert*-butanol (*t*BuOH) only provided moderate yield whereas toluene gave no arylation product (Table 1, entries 8–10). *t*BuOLi was superior to *t*BuONa in our test (Table 1, entry 11). When bor-

Table 2. Arylation scope with variety of arylboronic esters.<sup>[a]</sup>



Entry	Product	Yield [%] <sup>[b]</sup>	Entry	Product	Yield [%] <sup>[b]</sup>
1		93	11		91
2		99	12		92
3		82	13		98
4		81	14		93
5		91	15		87
6		78	16		85
7		83	17		81
8		80	18		77
9		87	19		73
10		85			

[a] All reactions were carried out by using **1** (0.4 mmol), compound **2** (1.5 equiv), *t*BuOLi (3 equiv), and DMF (2 mL). [b] Isolated product yields.

Table 3. Arylation scope with respect to heteroarenes.<sup>[a]</sup>

Entry	Heteroarene	Product	Yield [%] <sup>[b]</sup>
1 <sup>[c]</sup>			90
2 <sup>[d]</sup>			75
3			98
4			92
5			85
6			80
7			88
8			85
9 <sup>[d]</sup>			82

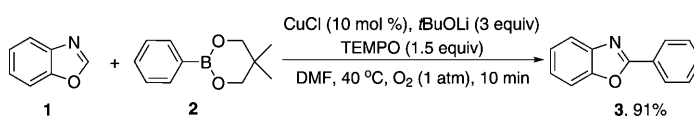
[a] All reactions were carried out by using **4** (0.4 mmol), compound **2** (1.5 equiv), *t*BuONa (3 equiv), and DMF (2 mL), except as noted. [b] Isolated product yields. [c] Reaction carried out at 60 °C. [d] 1,10-phenanthroline (15 mol %), *t*BuOLi (3 equiv), and DMF (4 mL) were used and the reaction carried out at 100 °C.

uct good opportunities for further transformations, such as transition-metal-catalyzed cross-coupling.

The scope of the reaction with respect to the heteroarenes is presented in Table 3. Although a higher temperature is needed, the reactions are still very efficient and are complete within 20 minutes in good yields and with good selectivities. With azole or substituted azole as the substrate, *t*BuONa was superior to *t*BuOLi (Table 2, entries 1, 3–8), whereas when thiazole or substituted thiazole is used as substrate *t*BuOLi gives a better yield (Table 2, entries 2 and 9). Azole can be monoarylated at 60 °C with very good selectivity. No diarylation product was observed in the system (Table 2, entry 1). Thiazole is normally diarylated by previously reported method.<sup>[3a]</sup> We found that by using 1,10-phenanthroline as ligand (15 mol %), the thiazole can be selectively monoarylated at C-2 position and only a trace amount (<2%) of diaryl product is obtained. When 5-phenylazole is used, electron-rich and electron-poor arylboronic esters all give good results (Table 2, entries 3–5). Azole with either an electron-withdrawing substituent or electron-donating substituent provides excellent conversion to the desired product (Table 2, entries 6–8). A appropriate ligand is important for

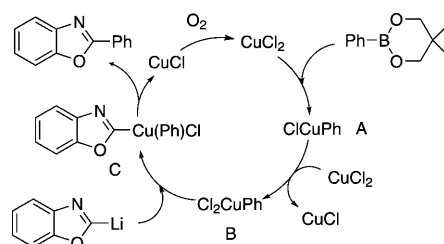
the arylation of aryl-substituted thiazole. When 1,10-phenanthroline (15 mol %) is added, 5-phenylthiazole is also active and couples with phenylboronic ester in 82 % yield (Table 2, entry 9).

It is known that alkylborane could generate an alkyl radical by reacting with dioxygen.<sup>[14]</sup> Also, copper can catalyze terminal alkyne homocoupling reactions under a dioxygen atmosphere through a radical mechanism, for example, in Glaser coupling.<sup>[15]</sup> To gain insight into the reaction mechanism, a model reaction was carried out with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 1.5 equiv) as the additive under standard conditions (Scheme 2). The arylation prod-



Scheme 2. Arylation of benzoxazole with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as an additive.

uct was obtained with similar yield. So, the possibility of a radical pathway could be ruled out. The copper-catalyzed oxidative cross-coupling of arylboronic acid and heteroatom (N or O), which is called the Chan–Evans–Lam reaction, typically employ milder conditions than the analogous Ullmann and Buchwald–Hartwig reactions. The mechanism has been proved to involve a Cu<sup>I</sup> to Cu<sup>III</sup> pathway.<sup>[16]</sup> Combining the reported mechanisms for similar reactions<sup>[16]</sup> and our experimental observations, a preliminary reaction mechanism for CuCl-catalyzed cross-coupling reaction of benzoxazole with phenylboronic ester might be proposed, as shown in Scheme 3. CuCl is oxidized to CuCl<sub>2</sub> by molecular oxygen,



Scheme 3. Proposed reaction mechanism for CuCl-catalyzed cross-coupling reaction of benzoxazole with phenylboronic ester.

followed by a transmetalation from phenyl boronic ester to CuCl<sub>2</sub>, which forms an arylcopper(II) species A. A similar aryl copper(II) species was proposed as an intermediate in Cu-catalyzed oxidative coupling of arylboronic acids with nucleophiles.<sup>[16a]</sup> Recently, a well defined aryl copper(III) species was isolated by Stahl group and proved to be the key intermediate in the catalytic cycle for copper-catalyzed aerobic oxidative functionalization of arene C–H bond.<sup>[16b,c]</sup> In our system, we also propose that aryl copper(II) A is oxi-

dized to aryl copper(III) intermediate B by another equivalent of CuCl<sub>2</sub>. Subsequently, a second transmetalation gives intermediate C. Reductive elimination results the desired cross-coupling product in addition to the recycled catalyst. However, we could not completely rule out other possibilities such as a pathway involving a [η<sup>2</sup>-CuCl(O<sub>2</sub>)]-complex-mediated-process at this stage.<sup>[17]</sup>

In summary, we have discovered a novel copper-catalyzed oxidative heteroarene arylation reaction. Heteroarene compounds such as benzoxazole and benzothiazole were easily cross-coupled with arylboronic esters at 40 °C in minutes under an O<sub>2</sub> atmosphere. The mild reaction conditions and the use of O<sub>2</sub> as oxidant is a significant practical advantage. It is the first example of Cu-catalyzed cross-coupling of arylboronic acid derivatives with azoles and thiazoles using O<sub>2</sub> as sole oxidant under mild conditions.

## Experimental Section

**Representative procedure:** Synthesis of 2-phenylbenzoxazole:<sup>[3a]</sup> tBuOLi (96 mg, 1.2 mmol), CuCl (4 mg, 0.04 mmol), and DMF (2 mL) were added to a 25 mL Schlenk tube charged with dry oxygen. The mixture was stirred until the solid dissolved, after which benzoxazole (**1**, 48 mg, 0.4 mmol) and phenylboronic ester (**2**, 114 mg, 0.6 mmol) were added in order. The mixture was stirred at room temperature for 2 minutes, and then at 40 °C for 10 minutes. The reaction was quenched with water, extracted with ethyl acetate, dried over sodium sulphate and concentrated in vacuo. After column chromatography (2% ethyl acetate in petroleum ether), 73 mg (93%) of 2-phenylbenzoxazole (**3**) was obtained as a white solid. R<sub>f</sub>=0.32 (2% ethyl acetate in petroleum ether). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.34–7.37 (m, 2H), 7.52–7.54 (m, 3H), 7.57–7.60 (m, 1H), 7.78–7.80 (m, 1H), 8.25–8.28 ppm (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 110.7, 120.1, 124.8, 125.3, 127.2, 127.8 (2C), 129.0 (2C), 131.7, 142.0, 150.8, 163.2 ppm.

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**Keywords:** arylation • boronic ester • copper • cross-coupling • heterocycles

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