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Direct Arylation of Benzothiazoles and Benzoxazoles with Aryl Boronic Acids

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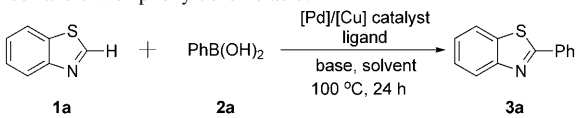
Aryl-substituted benzothiazoles and benzoxazoles are an important class of heterocyclic compound and have shown a wide range of biological activities, such as antitumor, antiviral, and antimicrobial activities.[1–3] In addition, these compounds have become essential building blocks for the synthesis of conjugated functional materials, such as industrial dyes and plant growth regulators.[4] The conventional methods for the synthesis of these compounds typically involve either the metal-catalyzed intramolecular cyclization of thioformanilides or the cross-coupling of carboxylic acids with 2-aminophenol (or 2-aminothiophenol) in the presence of the Lawesson reagent.[5,6] Alternatively, aryl-substituted benzothiazoles and benzoxazoles can be prepared by direct arylation of heterocycles through metal-catalyzed C–H bond activation with aryl halides.[7,8]

We have recently demonstrated that benzothiazole compounds can be obtained by a decarboxylative C–S cross-coupling of 2-nitrobenzoic acid with benzyl thiol, under relatively harsh conditions.[9] More recently, we have shown that the cross-coupling of nitro-substituted aryl halides with benzyl thiol can also afford aryl-substituted benzothiazole derivatives in moderate yield.[10] As part of our ongoing effort to synthesize aryl-substituted benzothiazoles and benzoxazoles, we describe herein a novel synthetic pathway that involves direct C–H bond functionalization of benzothiazole and benzoxazole precursors by using arylboronic acids and transition-metal catalysts under aerobic conditions. It should be noted that You et al. have recently reported the direct arylation of azoles through metal-catalyzed C–H bond functionalization with aryl boronic acids.[11]

The reaction of benzothiazole (**1a**) with phenylboronic acid (**2a**) was selected as a prototype reaction. Selected results from our experiments are summarized in Table 1. We observed that the reactions involving monometallic systems, such as $Pd(OAc)_2$ (10 mol%) or $Cu(OAc)_2$ (50 mol%), resulted in low conversions (Table 1, entries 1 and 2). Encouragingly, the reaction performed in DMSO at 100°C in the presence of a Pd/Cu cocatalyst (10:20 mol%) with 2,2′-bipyridine (bipy; 30 mol%) as the ligand afforded phenylbenzothiazole (**3a**) in 45% yield (Table, entry 3). After a screening of reaction conditions and bases, the optimum conditions for the direct arylation reaction were identified to be a combination of a Pd/Cu cocatalyst (5:10 mol%) and phenanthroline (phen; 30 mol%) as the ligand with inexpensive K_3PO_4 as the base (Table 1, entry 13). The reaction

Table 1. Screening of the reaction condition for the direct arylation of benzothiazole with phenylboronic acid.[a]



1a **2a** **3a**

Entry	$Pd(OAc)_2$ [mol%]	$Cu(OAc)_2$ [mol%]	Ligand [mol%]	Base	Solvent	Yield of **3a** [%][b]
1	10	0	–	K_3PO_4	DMSO	8
2	0	50	–	K_3PO_4	DMSO	<5
3	10	20	bipy (30)	K_3PO_4	DMSO	45
4	10	20	bipy (30)	K_3PO_4	DMF	15
5	10	20	bipy (30)	K_3PO_4	NMP	20
6	10	20	bipy (30)	K_3PO_4	dioxane	<5
7	10	20	bipy (30)	–	DMSO	<2
8	10	20	bipy (30)	KO*t*Bu	DMSO	<5
9	10	20	bipy (30)	K_2CO_3	DMSO	10
10	10	20	bipy (30)	Na_2CO_3	DMSO	<2
11	10	20	bipy (30)	Cs_2CO_3	DMSO	20
12	5	10	bipy (30)	K_3PO_4	DMSO	41
13	5	10	phen (30)	K_3PO_4	DMSO	89 (85)
14	2	10	phen (30)	K_3PO_4	DMSO	42
15	5	5	phen (30)	K_3PO_4	DMSO	30
16	5	10	phen (10)	K_3PO_4	DMSO	50

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1 mmol), base (1.5 mmol), solvent (3 mL), 100°C, 24 h; bipy: 2,2′-bipyridine; phen: 1,10-phenanthroline. [b] GC yield. The yield of isolated product is shown in parenthesis.

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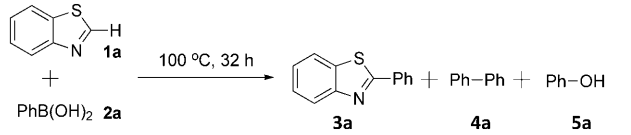
also proceeds at lower loadings of the Pd/Cu cocatalyst or the ligand, but with a substantial decrease in the reaction yields (Table 1, entries 14–16).

To gain a better understanding of the reaction mechanism, we carried out a series of reactions under the same reaction conditions, but under different atmospheres. Interestingly, the reaction resulted in a much lower yield of product **3a** under a nitrogen atmosphere than under aerobic conditions (Table 2, entries 1 and 2). However, the reaction performed under a pure oxygen atmosphere only afforded **3a** in 17% yield (Table 2, entry 3). Under these conditions, the predominant byproducts are biphenyl (16%) and phenol (48%), as determined by gas chromatography (see Supporting Information, Figure S2). These results indicate that oxygen accelerates the cross-coupling reactions; however, with high concentrations of oxygen, the oxidative hydroxylation of phenylboronic acid dominates the reaction.[12]

Table 2. The influence of the atmosphere on the yield of **3a**.[a]



Entry	Atmosphere	Yield [%][b]		
		3a	**4a**	**5a**
1	nitrogen	24	12	2
2	air	89	8	3
3	oxygen	17	16	48

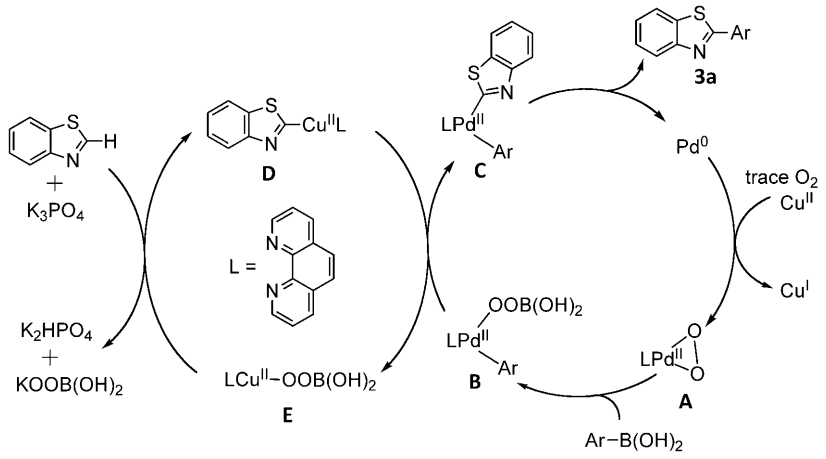
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1 mmol), $Pd(OAc)_2$ (5.0 mol%), $Cu(OAc)_2$ (10 mol%), 1,10-phenanthroline (30 mol%), K_3PO_4 (1.5 mmol), DMSO (3 mL), 100 °C, 24 h. [b] GC yield.

On the basis of these experimental data, a plausible catalytic mechanism was proposed (see Scheme 1) for the oxygen-promoted direct arylation of benzothiazole. The reaction first proceeds by deprotonation of benzothiazole, followed by transmetalation with organometallic copper complex **E** to give the corresponding heteroaryl copper intermediate (**D**).[13,8h] Subsequently, heteroaryl copper intermediate **D** reacts with palladium species **B** to form the corresponding diaryl palladium intermediate (**C**).[13] Upon reductive elimination, the desired cross-coupling product **3a** is formed. Trace molecular oxygen, in the presence of Cu^{II}, oxidizes the resulting Pd^0 to peroxopalladium complex **A**,[14] which reacts with aryl boronic acid to regenerate palladium species **B**. At high oxygen concentrations, the oxidative hydroxylation of aryl boronic acid competes with the transmetalation between species **B** and **D**, resulting in an increase in byproduct formation.

Further experimentation has shown that various substituted aryl boronic acids allow the direct arylation of benzothiazole **1a** under the optimum reaction conditions (Table 3). Both electron-rich and electron-poor aryl boronic acids were successfully converted to the corresponding cross-coupling products in moderate to good yields. The treatment of a heteroaryl boronic acid with **1a** also gave the corresponding product in moderate yield (Table 3, entry 10). Remarkably, chloro-substituted aryl boronic acid readily underwent direct arylation with **1a** to generate the desired chloro-substituted benzothiazole (**3i**) in 62% yield (Table 3, entry 8). This functional-group tolerance should allow further derivatization of compound **3i** through cross-coupling reactions such as the Suzuki–Miyaura and Heck reactions.

In another set of experiments, we carried out the direct arylation of benzoxazole (**1b**) with various substituted aryl boronic acids (Table 4). Similar to the arylation of **1a**, various substituted aryl boronic acids successfully reacted with **1b** to afford the corresponding aryl-substituted benzoxazoles under the optimum reaction conditions.

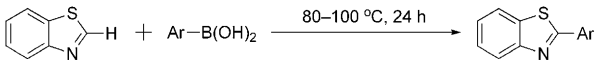
Although the groups of Daugulis and Miura have reported the direct arylation of benzothiazoles with aryl halides,[15] our method, reported herein, eliminates the use of aryl halide precursors and proceeds under milder conditions. More recently, Itami's group[16] has also reported an interesting nickel-catalyzed direct arylation of azole compounds with aryl halides and triflates, but the reactions with benzoxazole resulted in a substantial reduction in yield. In our reactions, benzoxazole can be efficiently and selectively arylated at the 2-position by electronically and structurally diverse boronic acids.



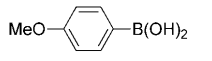
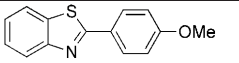
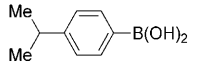
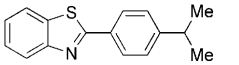
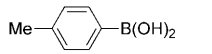
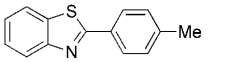
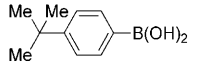
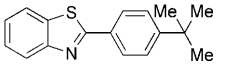
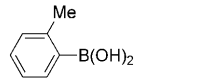
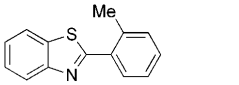
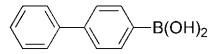
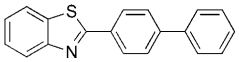
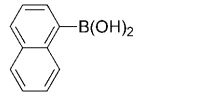
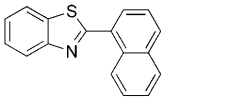
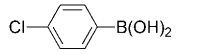
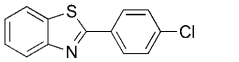
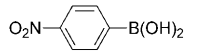
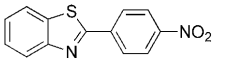
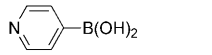
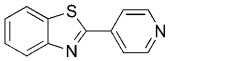
Scheme 1. The proposed mechanism for the arylation of benzothiazole through C–H activation.

To evaluate the suitability of the reaction for further scaleup, we prepared phenylbenzothiazole in DMSO (15 mL) by treating benzothiazole **1a** (5.0 mmol) with phenylboronic acid **2a** (10.0 mmol) in the presence of the Pd/Cu cocatalyst (0.25:0.5 mmol), 1,10-phenanthroline (1.5 mmol) and a large excess of K_3PO_4 (15.0 equiv) for 32 h at 100 °C under aerobic conditions (Scheme 2). The re-

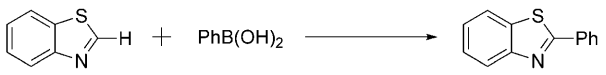
Table 3. The direct arylation of benzothiazole **1a** with various aryl boronic acids **2b–k**.[a]



1a **2b-k** **3b-k**

Entry	$ArB(OH)_2$ **2**	Product **3**		Yield [%][b]
1		**2b**		**3b** 72
2		**2c**		**3c** 88
3		**2d**		**3d** 86
4		**2e**		**3e** 80
5		**2f**		**3f** 57
6[c]		**2g**		**3g** 55
7[c]		**2h**		**3h** 60
8		**2i**		**3i** 62
9		**2j**		**3j** 58
10		**2k**		**3k** 59

[a] Reaction conditions: **1a** (0.5 mmol), **2** (1 mmol), $Pd(OAc)_2$ (5.0 mol%), $Cu(OAc)_2$ (10 mol%), 1,10-phenanthroline (30 mol%), and K_3PO_4 (1.5 mmol) in DMSO at 100°C (oil bath temperature) under aerobic conditions. [b] Yields of isolated products are the average of at least two experiments. [c] These reactions were conducted at 80°C (oil bath temperature).



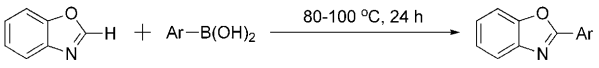
1a **2a** **3a**

Scheme 2. The scaled-up phenylation of benzothiazole **1a** (5 mmol) in the presence of **2a** (10 mmol), $Pd(OAc)_2$ (5 mol%), $Cu(OAc)_2$ (10 mol%), 1,10-phenanthroline (30 mol%), and K_3PO_4 (15 equiv) in DMSO at 100°C under aerobic conditions. Product **3a** was isolated in 80% yield.

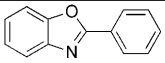
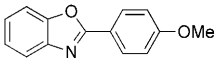
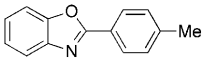
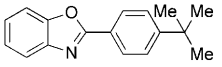
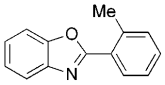
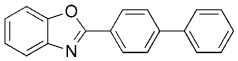
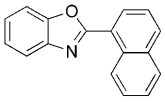
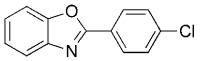
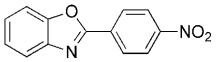
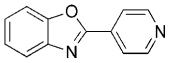
sulting mixture was isolated and purified to obtain the desired product **3a** in 80% yield.

In summary, we have presented a new transition-metal-catalyzed C–C bond-forming reaction between benzothiazoles or benzoxazoles and arylboronic acids. This transformation represents a simple way to carry out the arylation of benzothiazole or benzoxazole compounds, a task that otherwise requires several synthetic steps or harsh reaction conditions. Further studies aimed at obtaining a better understanding of the reaction mechanism and at expanding the substrate scope of the reaction are underway.

Table 4. The direct arylation of benzoxazole **1b** with various aryl boronic acids **2a–k**.[a]



1b **2** **3l-u**

Entry	$ArB(OH)_2$ **2**	Product **3**		Yield [%][b]
1	**2a**		**3l**	90
2	**2b**		**3m**	88
3	**2d**		**3n**	85
4	**2e**		**3o**	67
5	**2f**		**3p**	65
6[c]	**2g**		**3q**	75
7[c]	**2h**		**3r**	80
8	**2i**		**3s**	68
9	**2j**		**3t**	62
10	**2k**		**3u**	60

[a] Reaction conditions: **1b** (0.5 mmol), **2** (1 mmol), $Pd(OAc)_2$ (5.0 mol%), $Cu(OAc)_2$ (10 mol%), 1,10-phenanthroline (30 mol%), and K_3PO_4 (1.5 mmol) in DMSO at 100°C (oil bath temperature) under aerobic conditions. [b] Yields of isolated products are the average of at least two experiments. [c] These reactions were conducted at 80°C (oil bath temperature).

Experimental Section

Representative procedure for the Pd^{II}/Cu^{II}-catalyzed direct arylation of benzothiazoles:

*Synthesis of **3a** (Table 1, entry 13)*: $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), $Cu(OAc)_2$ (9.0 mg, 0.05 mmol), 1,10-phenanthroline (27 mg, 0.15 mmol), and K_3PO_4 (318.3 mg, 1.5 mmol) were added to a solution of DMSO (3 mL) charged with phenylboronic acid (1.0 mmol) and benzothiazole (0.5 mmol). The reaction was stirred at 100°C under aerobic conditions for 24 h. The resulting mixture was then cooled to room temperature and diluted with ethyl acetate (45 mL). The organic layer was collected, washed with water and brine, dried over magnesium sulfate, and filtered. The solvent was removed in vacuo and the remaining residue was purified by silica gel column chromatography (eluent: hexane/ethyl acetate, 9:1) to yield **3a** in 85% yield as a white solid.

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