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A copper-catalyzed cascade reaction of *o*-bromoarylisothiocyanates with isocyanides leading to benzo[*d*]imidazo[5,1-*b*]thiazoles under ligand-free conditions†

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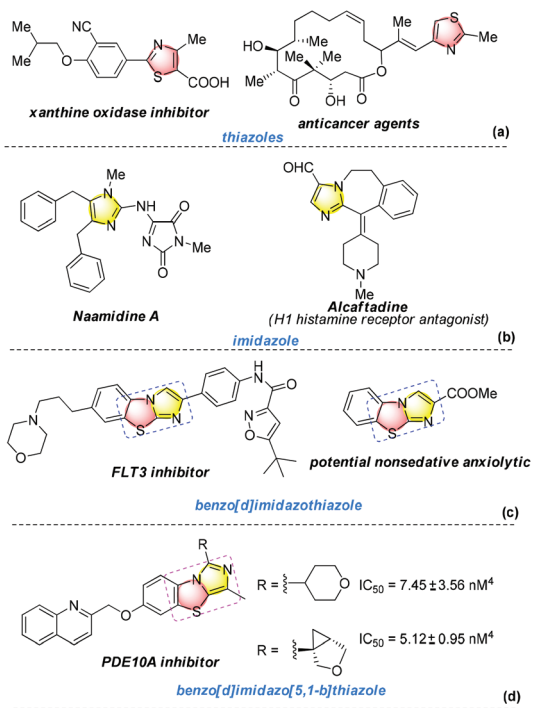
A convenient and efficient copper-catalyzed domino method has been initially developed for the synthesis of benzo[*d*]imidazo[5,1-*b*]thiazole derivatives *via* the reactions of readily available substituted *o*-bromoarylisothiocyanates with isocyanides under ligand-free conditions. This chemistry involves intermolecular [3 + 2] cycloaddition and intramolecular Ullmann-type C–S bond formation.

Seeking mild and efficient methods for the C–S bond formation is of fundamental and immense importance in organic chemistry because sulfur-containing frameworks exhibit important functions in organic transformations, and they are also widely used in pharmaceutical, agrochemical, and materials chemistry.[1] Thiazoles are an important class of sulfur-containing heterocycles possessing various excellent biological and medicinal activities. For example, they can be used as xanthine oxidase inhibitors,[2] antibiotics,[3] and anticancer agents[4] (Scheme 1a). On the other hand, imidazole is a key core scaffold that also occurs in natural products, drugs, and advanced materials[5] (Scheme 1b). The combined structure of thiazole and imidazole frameworks, the benzo[*d*]imidazothiazole ring system (Scheme 1c), has attracted much attention for its application in the FLT3 inhibitor (phase II clinical trials)[6] and potential nonsedative anxiolytics,[7] so that some efficient methods for its synthesis can be developed.[8] Moreover, the isomer of benzo[*d*]imidazo[5,1-*b*]thiazole (Scheme 1d) has recently been found as a core scaffold in phosphodiesterase 10A (PDE10A) inhibitors.[9] Surprisingly, few synthetic approaches for its formation have been reported.[9,10] In 2013, Gharat *et al.* reported a four-step method for the construction of benzo[*d*]imidazo[5,1-*b*]thiazole skeleton using C2-aminoalkylated benzothiazoles as key intermediates.[9] Very recently, Zhu and co-workers developed an efficient copper-promoted cycloaddition of benzothiazoles with isocyanides leading to benzo[*d*]imidazo[5,1-*b*]thiazoles at room temperature.[10]



Scheme 1 Bioactive molecules containing thiazole and imidazole frameworks.

However, several challenges remain in terms of starting materials and synthesis conditions. It is still highly desirable to develop new strategies to prepare functionalized benzo[*d*]-imidazo[5,1-*b*]thiazole frameworks by utilizing inexpensive substrates and proceed under mild conditions.

Transition-metal-catalyzed cross-coupling reactions are useful tools in synthetic organic chemistry, since they provide

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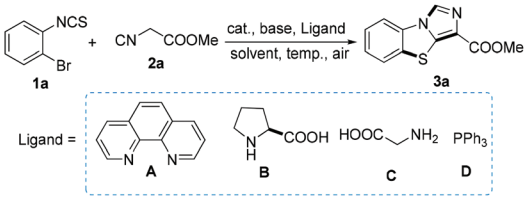
a convenient, and straightforward approach to valuable molecules from readily accessible starting materials under mild conditions.[11] In the past few years, with the renaissance of the Ullmann-type reactions, the copper-catalyzed cross-coupling reactions have been demonstrated to be versatile methods for the construction of C(sp^2)–X (X = N, O, C, S, P) bonds.[12] Although the chemistry of copper-catalyzed C–N, C–O and C–C bond formations has been well explored, methods available for the C–S bond coupling are rather limited due to the deactivation of the metal catalysts by the strong coordinating properties of sulfur.[13] As a consequence, there is continued interest to develop new synthetic methodologies for constructing sulfur-containing compounds *via* the copper-catalyzed Ullmann-type C–S bond formation.

Moreover, isocyanides are easily prepared from readily available chemical materials, which have been widely used as powerful and versatile C1 building blocks possessing nucleophilicity, electrophilicity, and isocyanide insertion properties.[14] In recent years, using isocyanides as the starting materials to construct N-heterocycles have caught considerable attention.[15] As a part of our continuous efforts for the synthesis of sulfur-containing organic compounds,[16] herein we wish to report a ligand-free inexpensive copper-catalyzed approach for the synthesis of benzo[*d*]imidazo[5,1-*b*]thiazoles which could possibly possess some important biological activities.

First, 1-bromo-2-isothiocyanatobenzene (**1a**) and methyl 2-isocyanoacetate (**2a**) were selected as the model substrates to optimize the reaction conditions including the catalysts, bases, ligands, reaction temperatures and solvents in an air atmosphere. As shown in Table 1, eight catalysts such as CuCl, CuBr, CuI, $CuCl_2$, $CuSO_4$, $Cu(OAc)_2$, $FeCl_3$, and $FeCl_2$ were investigated at 60 °C by using 2.0 equiv. of K_3PO_4 as the base in 2 mL DMSO, and $CuCl_2$ provided methyl benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate (**3a**) in 80% yield (Table 1, entries 1–8). Notably, the reaction did not proceed without the catalyst (Table 1, entry 9). Furthermore, we compared different bases (Table 1, compare entries 4, 10, 11, 12, and 13). It was found that K_3PO_4 was superior to the others (entry 1), where no target product **3a** was obtained in the absence of a base (entry 14). Moreover, we screened various solvents including DMSO, DMF, DCE, CH_3CN, EtOH, 1,4-dioxane, THF, and H_2O, and CH_3CN was found to be the best choice (Table 1, entry 4 *versus* entries 15–21). In addition, various temperatures were investigated (Table 1, entries 17, 22–24), and 60 °C was discovered to be more suitable for this transformation (Table 1, entry 17). Of note, elevating the reaction temperature did not enhance the yield (Table 1, entry 22). Furthermore, the effect of ligands was also investigated (entries 24–28), and no obvious increase of the yield was observed. After the optimization process for catalysts, bases, ligands, temperatures, and solvents, various benzo[*d*]imidazo[5,1-*b*]thiazole derivatives were synthesized under our standard conditions: 10 mol% $CuCl_2$ as the catalyst, 2 equiv. of K_3PO_4 as the base (relative to *o*-bromoarylisothiocyanates), and CH_3CN as the solvent, at 60 °C in an air atmosphere.

Table 1 Optimization of the conditions[a]

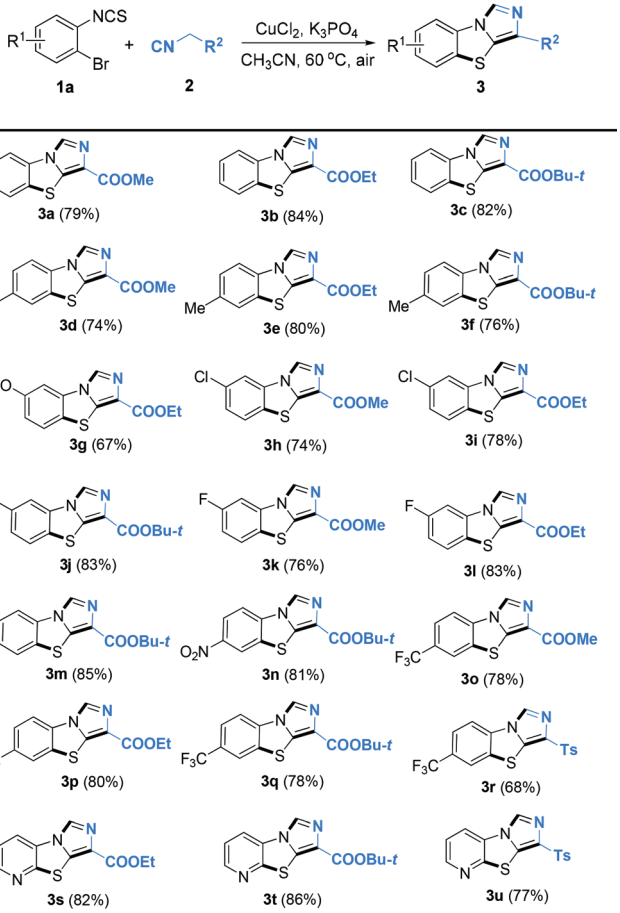


Entry	Cat.	Base	Solvent	Yield[b] [%]
1	CuCl	K_3PO_4	DMSO	75
2	CuBr	K_3PO_4	DMSO	71
3	CuI	K_3PO_4	DMSO	73
4	$CuCl_2$	K_3PO_4	DMSO	80
5	$CuSO_4$	K_3PO_4	DMSO	Trace
6	$Cu(OAc)_2$	K_3PO_4	DMSO	71
7	$FeCl_3$	K_3PO_4	DMSO	Trace
8	$FeCl_2$	K_3PO_4	DMSO	Trace
9	None	K_3PO_4	DMSO	0
10	$CuCl_2$	K_2CO_3	DMSO	76
11	$CuCl_2$	Cs_2CO_3	DMSO	77
12	$CuCl_2$	Na_2CO_3	DMSO	71
13	$CuCl_2$	$NaHCO_3$	DMSO	69
14	$CuCl_2$	None	DMSO	0
15	$CuCl_2$	K_3PO_4	DMF	28
16	$CuCl_2$	K_3PO_4	DCE	Trace
17	**$CuCl_2$**	**K_3PO_4**	**CH_3CN**	**84**
18	$CuCl_2$	K_3PO_4	EtOH	Trace
19	$CuCl_2$	K_3PO_4	1,4-Dioxane	79
20	$CuCl_2$	K_3PO_4	THF	73
21	$CuCl_2$	K_3PO_4	H_2O	68
22	$CuCl_2$	K_3PO_4	CH_3CN	83[c]
23	$CuCl_2$	K_3PO_4	CH_3CN	72[d]
24	$CuCl_2$	K_3PO_4	CH_3CN	39[e]
25	$CuCl_2$	K_3PO_4	CH_3CN	85[f]
26	$CuCl_2$	K_3PO_4	CH_3CN	84[g]
27	$CuCl_2$	K_3PO_4	CH_3CN	83[h]
28	$CuCl_2$	K_3PO_4	CH_3CN	80[i]

[a] Reaction conditions: 1-bromo-2-isothiocyanatobenzene (**1a**) (0.3 mmol), methyl 2-isocyanoacetate (**2a**) (0.6 mmol), catalyst (0.03 mmol), base (0.6 mmol), solvent (2 mL), and reaction time (18 h). [b] Isolated yield. [c] 70 °C. [d] 50 °C. [e] 25 °C. [f] Using **A** as the ligand. [g] Using **B** as the ligand. [h] Using **C** as the ligand. [i] Using **D** as the ligand.

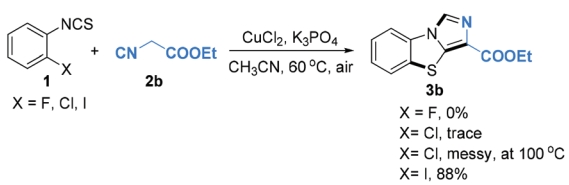
Under the optimized conditions, we next explored the substrate scope with different *o*-bromoarylisothiocyanates and isocyanides. The results are summarized in Table 2. We were pleased to find that various *o*-bromoarylisothiocyanate derivatives could be transferred into the benzo[*d*]imidazo[5,1-*b*]thiazoles in good to excellent yields. Electron-donating groups such as methyl, methoxy and electron-withdrawing groups such as fluoro-, chloro-, nitro, and trifluoromethyl groups were well-tolerated under the copper-catalyzed reaction conditions. To our delight, 2-bromo-3-isothiocyanatopyridine was also compatible under the standard conditions and the desired products were generated with good yield (**3s–3u**). Upon changing R^2 to tosyl (Ts), the reaction also occurred to give **3r** and **3u** in yields of 68% and 77%, respectively. The copper-catalyzed cascade reactions could tolerate some functional groups such as C–F bonds, C–Cl bonds, C–Br bonds, nitro, ester, and alkyl groups, which could be used for further transformations.

Table 2 Copper-catalyzed synthesis of benzo[*d*]imidazo[5,1-*b*]thiazoles from coupling *o*-bromoarylisothiocyanates with isocyanides[a,b,c]

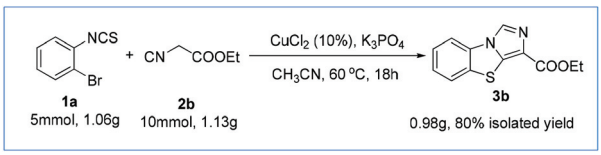


[a] Reaction conditions: substituted *o*-bromoarylisothiocyanates (0.3 mmol), isocyanides (0.6 mmol), $CuCl_2$ (0.03 mmol), K_3PO_4 (0.6 mmol), CH_3CN (2 mL). [b] Isolated yield. [c] Reaction time (18 h).

We also attempted cascade reactions of different *o*-haloarylisothiocyanates with ethyl 2-isocyanoacetate **2b** to synthesize **3b** under our standard catalytic conditions. Among the substituted *o*-haloarylisothiocyanates, *o*-iodoisothiocyanate showed higher reactivity than *o*-bromoarylisothiocyanate. However, *o*-fluoroarylisothiocyanate and *o*-chloroarylisothiocyanate are poor substrates, no desired products were obtained under the standard conditions, even though the reaction temperature was elevated to 100 °C (Scheme 2). Although *o*-bromoaryl-



Scheme 2 Investigation on the effect of different *o*-haloarylisothiocyanates for synthesis of **3b**.



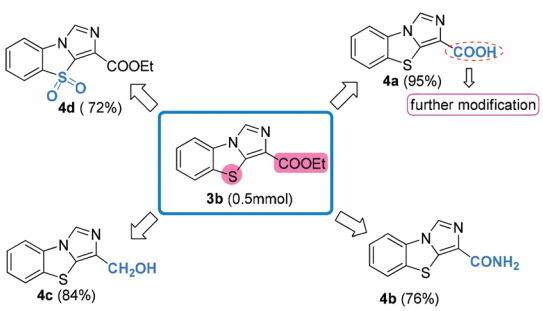
Scheme 3 Synthesis of **3b** on the gram scale.

isothiocyanates gave a slightly lower yield than *o*-iodoarylisothiocyanates, they are cheaper and of practical application.

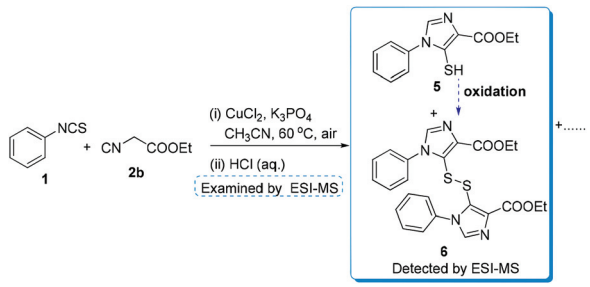
Further, we explored the synthetic applicability of the present method. The gram-scale reaction was performed between **1a** and **2b**, and the reaction afforded **3b** in 80% yield (Scheme 3). Therefore, this simple protocol could serve as an efficient and practical method for the synthesis of various benzo[*d*]imidazo[5,1-*b*]thiazole derivatives containing ester groups which could be easily transformed to other useful groups.

To further demonstrate the utility of the present method in synthesizing various benzo[*d*]imidazo[5,1-*b*]thiazole derivatives, the transformations of the ethyl benzo[*d*]imidazo[5,1-*b*]-thiazole-3-carboxylate **3b** obtained above were then investigated. To our satisfaction, benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylic acid **4a** was efficiently obtained by the hydrolysis of **3b** under mild basic conditions, which could be used for further modifications (Scheme 4). Furthermore, ammonolysis and reduction of **3b** led to amide **4b** and alcohol **4c** in 76% and 84% yield, respectively. Additionally, the sulfonyl product **4d** was directly synthesized in good yield from **3b** through oxidative reaction with *m*-chloroperbenzoic acid (*m*-CPBA). These representative transformations clearly demonstrate the versatilities of benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylates in organic chemistry.

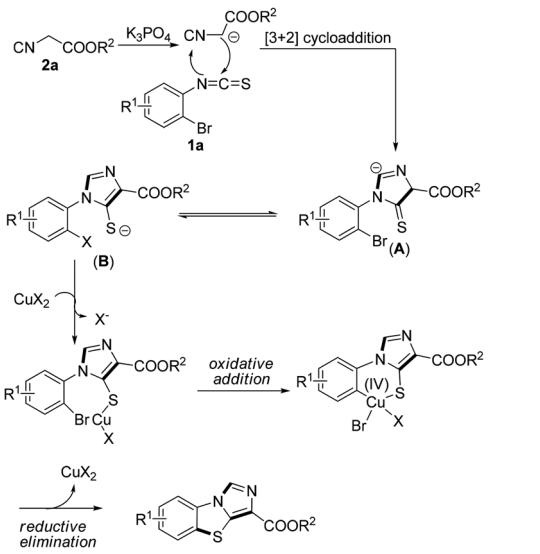
Upon treatment of isothiocyanatobenzene **1** with ethyl 2-isocyanoacetate **2b** under the standard conditions, the reaction detected by TLC was messy and no **3b** was detected. After acidifying the reaction mixture and examining it by ESI-MS, the intermediates **5** and **6** were found (see Fig. 1 in the ESI†). As shown in Scheme 5, the disulfide **6** might come from **5** under oxidative conditions.[17] These preliminary results indi-



Scheme 4 Further transformations of ethyl benzo[*d*]imidazo[5,1-*b*]thiazole-3-carboxylate.



Scheme 5 Investigations of the mechanism.



Scheme 6 A proposed mechanism for the direct transformation.

cated that **B** (see Scheme 6) might be the important intermediate in the present transformations.

Although many Cu(II)-catalyzed Ullmann-type reactions have been reported so far, the mechanism of these couplings remains rare. In 2009, Reddy and co-workers developed a nanocrystalline CuO-catalyzed coupling of aryl halides with diphenyl diselenide to form diaryl selenide, in which the proposed reaction mechanism was suggested to start from $Cu^{II}O$ and involve Cu(IV) intermediates.[18] In 2013, Zeng's group reported a $Cu(OAc)_2$-catalyzed C–S Ullmann cross coupling reaction of thiols with aryl halides. In this work, the proposed reaction mechanism also involves Cu(IV) intermediates.[19] Although the mechanism for the present transformation is not yet clear, on the basis of these preliminary results mentioned above together with the previous related literature,[17,20] a proposal mechanism would be herein presented (Scheme 6). Initially, the [3 + 2] cycloaddition of isocyanides **2** to *o*-bromoarylisothiocyanates **1a** produces the intermediate **A** in the presence of a base, which undergoes isomerization to give intermediate **B**. Subsequently, the intermediate **B** might proceed in the Ullmann-type pathway leading to the desired products **3**. Nevertheless, further investigations on more detailed mechanisms are still ongoing in our laboratory.

In conclusion, we have developed a general and highly efficient method for the synthesis of benzo[*d*]imidazo[5,1-*b*]-thiazole derivatives *via* copper-catalyzed cascade couplings of *o*-haloarylisothiocyanates with isocyanides under mild conditions. The present method shows simple, economical and practical advantages over the previous methods, holding great potential for wide applications in the synthesis of diverse benzo[*d*]imidazo[5,1-*b*]thiazoles with sulfur-containing frameworks in organic chemistry and medicinal chemistry.

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