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Efficient Copper-Catalyzed Ullmann Reaction of Aryl Bromides with Imidazoles in Water Promoted by a pH-Responsive Ligand

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A series of 1,10-phenanthroline derivatives were used as supporting ligands for copper-catalyzed Ullmann reaction in neat water. The catalytic system based on 4,7-dihydroxy-1,10-phenanthroline has demonstrated the promising catalytic performances for aryl bromides. The catalytic system was applicable to a wide scope of substrates, high catalytic activity and selectivity were observed for the reactions of electron-deficient, electron-rich, and heterocyclic aryl bromides with imidazoles containing different steric hindrance. The superior promoting effect of 4,7-dihydroxy-1,10-phenanthroline is attributed to its water solubility under the basic conditions.

Introduction

Transition-metal catalyzed cross-coupling reaction is an efficient and versatile tool in organic synthesis for the connection of two fragments through C–C or C–N formation.[1,2] Among them, Ullmann-type coupling reactions are particularly attractive because they often allow the usage of low-cost starting materials and readily available copper complexes.[3–7] However, the initial protocols required harsh conditions, such as high temperatures and stoichiometric proportion of copper reagents.[3] Recent approaches, which are involved in the judicial combination of organic ligands and copper ions, enable the reactions to be efficiently performed under the milder conditions.[4–7] Various types of ligands have been developed to facilitate the copper-catalyzed N-arylation of azoles with aryl halides. The use of the ligands not only increases the solubility of copper salts in reaction media and prevents their aggregation in the reaction process, but also enhances the reaction rate by varying the electronic and steric characters of the catalytic species.[5,6] Some elegant concepts for homogenous[4–6] and heterogeneous[7] protocols were developed based on the strategies, but these reactions were generally operated in volatile organic solvents or the mixed H_2O/organic solvents.

Organic reactions in water are of highly practical value because most wastes per mass unit produced in chemical industry have resulted from organic solvents.[8] Although the reaction rate in water may be slower than those in organic solvents, water is regarded as an environmentally benign and cheap medium, in which the unique reactivity is often observed.[9] Furthermore, the use of water-soluble catalytic systems may help simplify separation, recovery, and recycling of the catalysts.[10] Obviously, smooth implementation of the catalytic reactions in water requires the catalysts to be water-soluble. It is a common method to make metal complexes water-soluble by attaching ionic groups, such as sulfonate,[11] carboxylate,[12] and ammonium[13] to hydrophobic ligands. The majority of studies for transition-metal-catalyzed cross-coupling reactions in water have been concentrated on expensive palladium catalysts. In contrast, little progress has been reported for copper-catalyzed coupling reactions of aryl halide and azoles in neat water.[14]

During the investigation of Cu-catalyzed Ullmann-type cross-coupling reactions, it was noted that high catalytic activity was usually achieved in the Cu/bidentate N,N-[5a,6,15] and N,O-systems,[16] owing to the formation of stable copper-chelating species in catalytic reactions. Moreover, the steric and electronic properties of the bidentate ligands, which dictate activity, selectivity, and stability of the catalysts, could be modified by variation of the substituents in organic ligands. Among bidentate ligands, 1,10-phenanthroline and its derivatives[6] are one type of promising ligands for copper-catalyzed N-arylation of imidazoles with aryl halides owing to their strong electron-donating ability and ready availability (Scheme 1). However, the catalytic reactions were performed in organic solvents, and the hydrophobicity of these organic ligands limited their application in water. In our continuous effort to develop catalytic protocols in neat water,[17] we are interested in 4,7-dihydroxy-1,10-phenanthroline (**L1**), which is water-soluble under basic conditions; this provides a possibility for the development of copper-catalyzed organic reactions in neat water. Herein, we report a simple and efficient catalytic system for Ullmann

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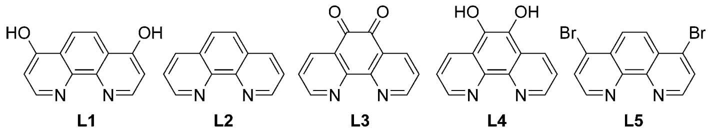


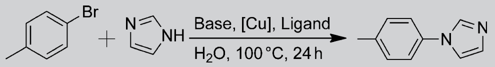
Scheme 1. 1,10-Phenanthroline and its derivatives employed in this work.

cross-coupling coupling reactions of aryl bromides with imidazoles promoted by **L1** under mild conditions in neat water.

Results and Discussion

To test the catalytic performances of **L1**-supported copper species and optimize reaction conditions, as shown in Table 1, the cross-coupling reaction of 4-bromotoluene and imidazole was initially performed by using 20 mol% **L1**, 10 mol% CuI in the presence of tetrabutylammonium bromide (TBAB) and Cs_2CO_3 at 100 °C in neat water; *N*-(4-tolyl)imidazole was obtained in 90% GC yield after 24 h (entry 1). However, if 1,10-phenanthroline and its derivatives (**L2**–**L5**) were used as supporting ligands, only trace amount of the target product was detected under the same conditions (entries 2–5). The water insolubility of **L2**–**L5** under the reaction conditions was responsible for their poor catalytic activity in water. **L1** is also insoluble in water, but it can dissolve in water after deprotonation of two hydroxyl groups in the presence of base (Figure 1), which results in high catalytic activity in the cross-coupling reaction. Although **L4** also contains two hydroxyl groups, **L4** is water-insoluble under basic conditions. It is not surprising that no product was observed in the absence of the supporting ligand (entry 6). If the molar ratio of **L1** to CuI was decreased from 2 to 1, the GC yield sharply decreased to 34% (entry 7). To determine the most suitable reaction conditions for N-arylation of imidazole, the catalytic system was examined by using different copper sources, bases, and additives. It was found that CuBr, $CuCl_2$, Cu_2O, and CuO were considerably inferior to CuI, and the target product was obtained in moderate yields (entries 9–12), CuCl was less efficient and only gave 35% GC yield under similar conditions (entry 8). It was known that phase-transfer catalysts may favor a better contact between the substrates and the aqueous catalytic species, and may accelerate the reaction rate in aqueous solution. The absence of TBAB resulted in 41% GC yield (entry 13). Sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) were also used as phase-transfer catalysts. The reaction was promoted by them, but SDS and SDBS were less effective than TBAB and *N*-(4-tolyl)imidazole was formed in 83% and 67% GC yields, respectively (entries 14 and 15). Bu_4NOH was usually employed as both base and phase-transfer catalyst, but the presence of 25% aqueous Bu_4NOH resulted in a 48% GC yield (entry 16), which was slightly higher than that in the absence of TBAB. Among the bases tested, K_3PO_4 was found to be the most effective, an almost quantitative yield was achieved (entry 20), whereas Cs_2CO_3, K_2CO_3, NaOH, and NEt_3 were slightly less effective and gave moderate to excellent GC yields under the same conditions (entries 1, 17–19). If copper loading was decreased to 1%, an 18% GC yield was obtained under the same conditions (entry 21). Wang et al. reported a 90% GC yield in the cross-coupling reaction of 4-bromotoluene and imidazole by using 1 mol% CuI as the copper source and 2 mol% 6,7-dihydroquinolin-8(5H)-one oxime as the supporting ligand, but the reaction was operated at 120 °C for 48 h.[14g]

Table 1. Screening reaction conditions for N-arylation of imidazole with 4-bromotoluene.[a]



Entry	Cu source	Ligand	Base	Additive	Yield [%][b]
1	CuI	**L1**	Cs_2CO_3	TBAB	90 (82)
2	CuI	**L2**	Cs_2CO_3	TBAB	<1
3	CuI	**L3**	Cs_2CO_3	TBAB	<1
4	CuI	**L4**	Cs_2CO_3	TBAB	<1
5	CuI	**L5**	Cs_2CO_3	TBAB	<1
6	CuI	–	Cs_2CO_3	TBAB	<1
7[c]	CuI	**L1**	Cs_2CO_3	TBAB	34
8	CuCl	**L1**	Cs_2CO_3	TBAB	35
9	CuBr	**L1**	Cs_2CO_3	TBAB	75
10	$CuCl_2$	**L1**	Cs_2CO_3	TBAB	75
11[d]	Cu_2O	**L1**	Cs_2CO_3	TBAB	59
12	CuO	**L1**	Cs_2CO_3	TBAB	66
13	CuI	**L1**	Cs_2CO_3	–	41
14	CuI	**L1**	Cs_2CO_3	SDS	83
15	CuI	**L1**	Cs_2CO_3	SDBS	67
16[e]	CuI	**L1**	Bu_4NOH	–	48
17	CuI	**L1**	NaOH	TBAB	67
18	CuI	**L1**	Net_3	TBAB	71
19	CuI	**L1**	K_2CO_3	TBAB	85
20	CuI	**L1**	K_3PO_4	TBAB	99 (95)
21	CuI	**L1**	K_3PO_4	TBAB	18

[a] Reaction conditions: 4-bromotoluene (0.50 mmol), imidazole (0.60 mmol), base (1.00 mmol), Cu source (0.05 mmol), ligand (0.10 mmol), additive (0.25 mmol), H_2O (2.0 mL), 100 °C, under N_2, 24 h; [b] GC yields, isolated yields are given in parentheses; [c] The molar of CuI-to-L ratio was 1:1; [d] An amount of 0.025 mmol Cu_2O was used; [e] 25% aqueous Bu_4NOH solution (1.05 mL) was used as the base; [f] An amount of 0.005 mmol CuI was used.

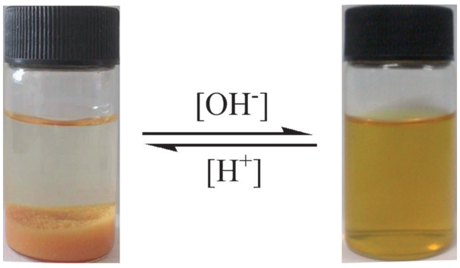
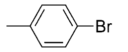
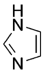
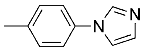
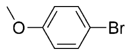
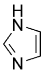
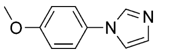
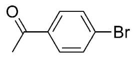
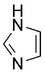
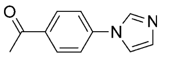
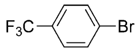
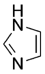
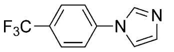
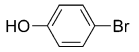
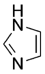
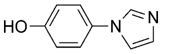
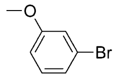
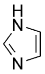
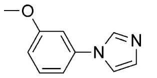
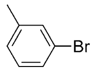
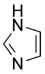
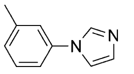
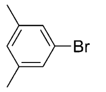
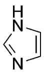
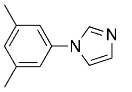
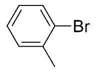
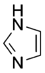
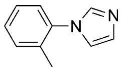
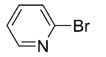
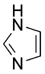
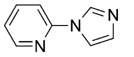
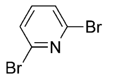
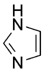
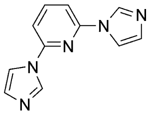
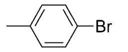
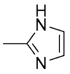
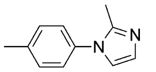
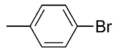
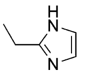
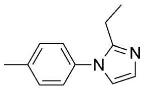
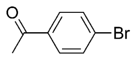
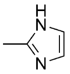
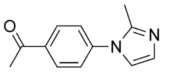
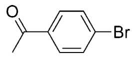
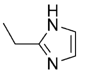
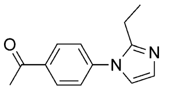
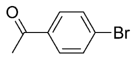
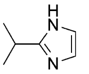
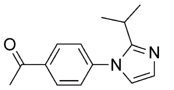
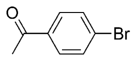
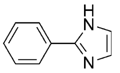
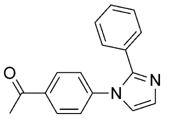
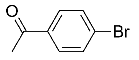
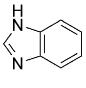
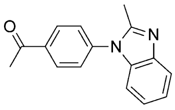
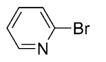
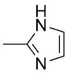
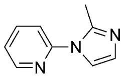
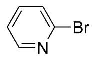
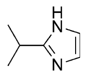
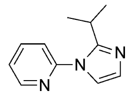


Figure 1. The pH-responsive behavior of **L1**.

The scope and generality of aryl bromides were then investigated under the optimized reaction conditions. As shown in Table 2, the effect of varying aryl bromides was explored by using imidazole as the nucleophile (entries 1–11). The *para*-substituted electron-rich and electron-deficient aryl bromides

Table 2. N-Arylation of imidazoles with aryl bromides catalyzed by CuI/**L1** in water.[a]

Entry	Ar-X	Nucleophile	Product	Yield[b] [%]
1				99 (95)
2				99 (93)
3				99 (93)
4				95
5				97 (94)
6				93
7				95 (88)
8				73
9				27
10				99 (80)
11[c]				99
12				93
13				72
14				99 (87)
15				99 (84)
16				99 (87)
17				79
18				99 (97)
19				99 (94)
20				99 (93)

[a] Reaction conditions: aryl bromides (0.50 mmol), N-nucleophile (0.60 mmol), K_3PO_4 (1.00 mmol), CuI (0.05 mmol), **L1** (0.10 mmol), TBAB (0.25 mmol), H_2O (2.0 mL), 100 °C, N_2; [b] GC yields, isolated yields are given in parentheses; [c] An amount of 0.25 mmol 2,6-dibromopyridine was used.

afforded the desirable products in almost quantitative yields (entries 1–5). A variety of functional groups, such as acetyl, ether, trifluoromethyl, and hydroxyl, were tolerated well in the catalytic system, In addition, the electronic nature in *para*-positioned substituents of aryl bromides did not seem to affect the cross-coupling reaction.

Noteworthy, the reaction between 4-bromophenol and imidazole selectively gave rise to 1-(4-hydroxyphenyl)-1*H*-imidazole in a 94% isolated yield regardless of the hydroxyl groups in the supporting ligand (entry 5), moreover, no formation of diaryl ether was observed, suggesting good chemoselectivity of the catalytic system in neat water. The cross-coupling reactions between imidazole and *meta*-substituted aryl bromides, such as 3-bromoanisole and 3-bromotoulene, were also smoothly carried out, 1-(3-methoxyphenyl)-1*H*-imidazole and 1-*m*-tolyl-1*H*-imidazole were obtained in 93% and 95% GC yields, respectively (entries 6 and 7). Interestingly, N-arylation reaction between imidazole and 5-bromo-*m*-xylene gave the target product in a 73% GC yield (entry 8). In comparison, if 2-bromotoluene was used as the substrate, 1-*o*-tolyl-1*H*-imidazole was produced in a 27% GC yield (entry 9), which was much lower than the yields if 3- or 4-bromotoluene was used, attributed to the steric effect of the methyl group. The catalytic system was also applied to N-arylation reactions of nitrogen-containing heteroaryl bromides with imidazole. The coupling reactions of imidazole with 2-bromopyridine and 2,6-dibromopyridine gave the corresponding *N*-arylimidazoles in almost quantitative yields (entries 10 and 11). These products are potentially good candidates for the preparation of N-heterocyclic carbene compounds, and their palladium(II) complexes have shown the excellent activities in many organic transformations.[12a,18] Thus, this catalytic system provides a valuable route for the preparation of functionalized N-heterocyclic carbene precursors.

The excellent catalytic performances of the catalytic system encouraged us to further examine N-arylation reactions between imidazole derivatives and aryl bromides. Aryl bromides with electron-withdrawing groups, such as 4-bromoacetophenone, were efficiently coupled with the sterically hindered nucleophiles, such as 2-methyl-, 2-ethyl-, and 2-isopropylimidazole, the corresponding products were obtained in almost quantitative yields (entries 14–16). However, the cross-coupling reaction of 4-bromotoluene with 2-methyl- and 2-ethylimidazole gave the resulting products in 93 and 72% GC yields, respectively (entries 12 and 13). Interestingly, the N-arylation reaction of 2-phenylimidazole and benzimidazole with 4-bromoacetophenone generated the desirable products in 79 and 99% GC yields, respectively (entries 17 and 18). 2-Bromopyridine was also successfully arylated with 2-methylimidazole and 2-ethylimidazole and gave rise to the target products in almost quantitative yields (entries 19 and 20).

Conclusions

We have developed an efficient protocol for Cu-catalyzed Ullmann cross-coupling reactions of a variety of imidazoles with aryl bromides, in which the catalytic system was promoted by 4,7-dihydroxy-1,10-phenanthroline in neat water. 4,7-Dihydroxy-1,10-phenanthroline is insoluble in water, but it can dissolve in water under basic conditions, resulting in superior catalytic performances in N-arylation reactions of imidazoles with aryl bromides. However, no catalytic activity was observed if water-insoluble 1,10-phenathroline and its derivatives were used as supporting ligands under the same conditions. This study further extends the scope of copper-catalyzed Ullmann cross-coupling reactions in water, and provides a new route for the development of highly efficient catalytic systems. Further investigation to broaden the scope of this catalytic system to other reactions is currently on progress.

Experimental Section

L1,[6b] **L3**,[19] **L4**,[19] **L5**[20] were synthesized according to literature methods, the others chemicals were purchased from commercial suppliers and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III NMR spectrometer at 400 and 100 MHz, respectively, by using deuterated $CDCl_3$ as locking solvent except otherwise indicated. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-5, 30 m×0.25 μm) by using a flame ionization detector.

General procedures for N-arylation of imidazoles with aryl bromides

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with CuI (0.05 mmol), organic ligands (0.1 mmol), K_3PO_4 (1.0 mmol), TBAB (0.25 mmol), imidazole (0.6 mmol), and aryl bromide (0.5 mmol). For solid aryl bromides, the tube was evacuated and back-filled with nitrogen, and this procedure was repeated three times; for liquid aryl bromides, the reaction components were added after removal of air. Then, water (2.0 mL) was added at RT under a stream of nitrogen and the tube was sealed and stirred in a preheated oil bath (100 °C). After 24 h, the mixture was cooled with icy water, the product was extracted with ethyl acetate (3× 5 mL). The combined organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude products were purified by flash column chromatography on silica gel to afford the desired product. The identity of the products was confirmed by comparison with literature spectroscopic data.

Acknowledgements

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Keywords: chelates · copper · cross-coupling · homogeneous catalysis · green chemistry

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