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Use of Acylhydrazine- and Acylhydrazone-Type Ligands to Promote CuI-Catalyzed C–N Cross-Coupling Reactions of Aryl Bromides with N-Heterocycles

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A series of ten acylhydrazine- and acylhydrazone-type ligands were designed and synthesized. Their electronic and steric properties were easily modified and tuned by varying the substituents in the vicinity of the acylhydrazine and acylhydrazone units. The effect of ligands on the catalytic activity of Ullmann reactions was assessed by using a combination of these ligands with CuI. The catalytic system is very efficient for the C–N coupling reaction of azoles with aryl and heteroaryl bromides.

Introduction

N-Arylazoles are an important class of compounds that are used throughout material and life science industries.[1–6] A number of these compounds have been reported to serve as common building blocks of natural products and medical agents,[2] precursors of N-heterocyclic carbenes (NHCs),[3] and ionic liquids,[4] ligands of coordination polymers,[5] and transition-metal catalysis.[6] The most straightforward and efficient synthetic methods involve transition-metal-catalyzed C–N cross-coupling reactions of heterocycles with aryl halides.[7–9] Among them, the copper-catalyzed Ullmann-type coupling reactions are particularly attractive, because they often allow the use of low-cost starting materials and readily available copper complexes.[8–16] However, the initial protocols required harsh conditions, such as high temperatures, stoichiometric amounts of the copper reagents, and strong alkoxide bases.[17] Recent advances revealed that a judicious combination of certain ligands and copper reagents enables the reaction to be efficiently performed under milder conditions. It has been generally thought that ligands increase the solubility of copper salts and prevent their aggregation in the reaction process, while the ligands also enhance the reactivity by increasing the electronic density on the catalytic species.[11–16] Therefore, the flexible design and synthesis of ligands with an appropriate nature is crucial for the synthesis of *N*-arylazoles by copper-catalyzed Ullmann reaction.

Various types of ligands have been introduced to promote copper-catalyzed Ullmann-type *N*-arylation reactions.[10–16] Most notable ligands are bidentate N,O,[11–13] N,N,[14,15] or O,O[16] compounds. The high catalytic activity attained in these systems can most likely be ascribed to the formation of chelating Cu^{I} species. In addition, the activity, selectivity, and stability of the catalytic system can be modified and tuned by varying the steric and electronic properties of the ligands as well as their coordinating ability with metal ions. For example, Buchwald and co-workers have revealed that the activity and selectivity of various Cu-catalyzed Ullmann reactions can be controlled by changing the type, number, and position of substituents in the phenanthroline backbone.[14] Although many ligands have been reported,[9–14] the rapid assembly and flexible modification of structurally diverse ligand systems by simple synthetic methods are still important for the development of effective catalysts for the widespread applications of coupling reactions.

In our previous study, we synthesized a series of functionalized azolium-based ionic liquids[18,19] and energetic salts.[20] Their physical properties can be easily tuned by varying the substituents in the heterocycles. This strategy was also applied to Pd(NHC)-catalyzed cross-coupling reactions,[19] in which the catalytic activity and selectivity were optimized through ligand modification. As a continuation of our study on the design and synthesis of heterocyclic ligands for application in materials science and catalysis, we are interested in copper-catalyzed Ullmann reactions. Among the various bidentate ligands used in the cross-coupling reactions, chelating N,O compounds, such as 8-hydroxyquinoline[11] and amino acids,[12] are efficient li-

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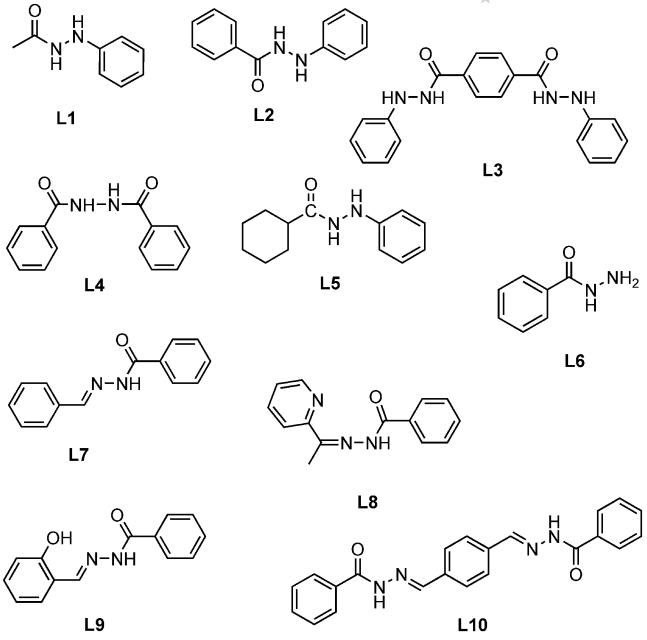
gands for copper-catalyzed *N*-arylation of azoles with aryl halides because of the synergetic effect of the nitrogen and oxygen coordination atoms. The transformation between hindered and functionalized azoles and aryl halides was achieved in good to excellent yields.

It is known that acylhydrazine and acylhydrazone derivatives possess high affinity and selectivity to metal ions,[21–23] and some insight into their binding and chelating ability to copper has also been explored.[22,23] A broad variety of substituents could also be introduced to the backbone units, which gives an opportunity to flexibly adjust their properties and coordinating ability to metal ions by varying the substituents. Although acylhydrazine- and acylhydrazone-type ligands have been extensively used in coordination chemistry,[21–23] they are seldom chosen as ligands in catalysis. The success of N,O-ligands in Cu-catalyzed C–N formation reactions prompted us to examine whether these types of ligands could be useful for the *N*-arylation of azoles with aryl halides, especially with inexpensive aryl and heteroaryl bromides. Herein, we report a copper-catalyzed Ullamnn reaction of aryl bromides promoted by acylhydrazine- and acylhydrazone-type ligands.



Scheme 1. Acylhydrazine- and acylhydrazone-type ligands used in this work.

Results and Discussion

As mentioned above, ligands play an important role in the success of Cu-catalyzed *N*-arylation of aryl halides and azoles. To test the catalytic performance and select the most efficient acylhydrazine- or acylhydrazone-type ligand, the coupling reaction of 4-bromoacetophenone and imidazole was chosen as a model reaction by using ligands **1**–**10** (Scheme 1) in the presence of CuI and Cs_2CO_3 in dimethyl sulfoxide (DMSO). As shown in Figure 1, *N*-(4-acetylphenyl)imidazole was obtained in moderate to excellent yields. The difference in their yields most likely resulted from steric and electronic variations of the substituents in the acylhydrazine or acylhydrazone unit. Use of ligands **L2**, **L6**, **L7**, and **L9** resulted in higher conversion of the 4-bromoacetophenone for this transformation compared with **L1** and **L5**, which revealed that the benzohydrazide group helped the corresponding acylhydrazine to be an effective ligand. Ligand **L2** displayed the best activity among the ligands tested, giving a 94% GC yield. The ligands that formed two chelating rings with copper(I), such as **L3**, **L8**–**10**, were less efficient than **L2**, which formed one chelating ring with copper(I); this can probably be ascribed to the strong coordinating ability of the former to copper(I), because the catalytically active species involves the simultaneous coordination of both nitrogen and oxygen atoms to the copper(I) atom.[8,23]

To determine the most suitable reaction conditions for the *N*-arylation of imidazole, the catalytic system was examined by using different copper sources, bases, solvents, and catalyst loading; the results are listed in Table 1. It was found that the copper source is important for effective catalysis; CuI was the most reactive, and the respective combination of CuBr, $CuSO_4 \cdot 5H_2O$, and Cu with either **L2** or

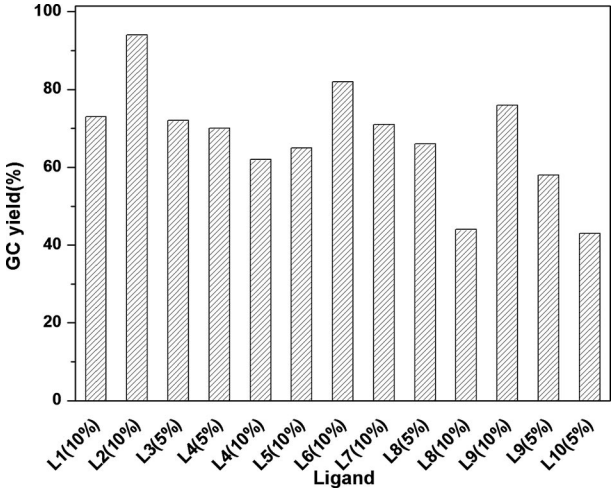
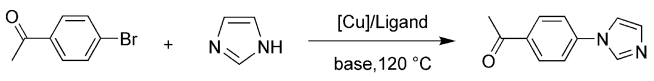


Figure 1. Ligand comparison in Cu-catalyzed *N*-arylation of imidazole with 4-bromoacetophenone. Reagents and conditions: 4-bromoacetophenone (1.0 mmol), imidazole (1.2 mmol), Cs_2CO_3 (2.0 mmol), CuI (0.05 mmol), ligand (0.05 or 0.10 mmol), DMSO (2 mL), 120 °C, 14 h.

L5 afforded *N*-(4-acetylphenyl)imidazole in moderate yields (Entries 1–7). Among them, **L5** gave higher GC yields than **L2** in all copper sources except CuI. Among the bases tested, Cs_2CO_3 was found to be the most efficient; catalysis by **L2** and **L5** using K_3PO_4 gave 64 and 80% yields, respectively (Entries 8 and 9); however, the use of K_2CO_3 and Et_3N were inefficient for the catalysis (Entries 10–12). Investigation of a variety of solvents revealed that the use of DMSO was superior to either *N*,*N*-dimethylformamide (DMF) (Entries 13–16) or toluene (Entries 17 and 18). No desirable product was detected when the coupling reaction was run in pure water (Entry 21) because of decomposition

of the ligand in water;[11f] however, trace amounts of water had no effect on the reaction. Further studies revealed that catalyst loading also had an important effect on the catalytic activity of the reaction system. An apparent decrease in catalytic activity was observed when the catalyst loading was decreased from 5 mol-% CuI and 10 mol-% **L2** to 2 mol-% CuI and 4 mol-% **L2** (Entry 19), whereas no difference was observed by doubling the amounts of CuI and **L2** (Entry 20).

Table 1. Cu/**L2**-catalyzed *N*-arylation of imidazole with 4-bromoacetophenone under different conditions.[a]

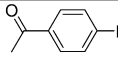
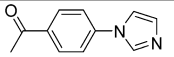
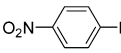
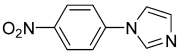
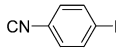
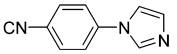
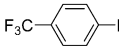
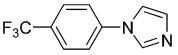
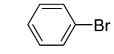
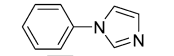
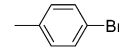
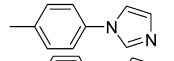
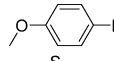
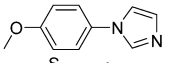
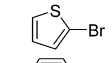
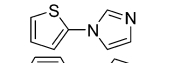
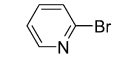
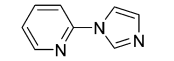
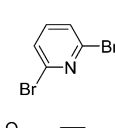
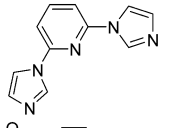
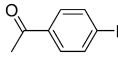
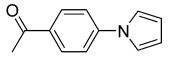
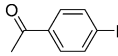
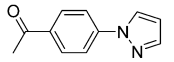
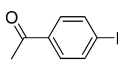
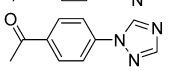


Entry	Copper source (mol-%)	Ligand (mol-%)	Base	Solvent	Yield[b]
1	CuI (5)	**L2** (10)	Cs_2CO_3	DMSO	94%
2	CuBr (5)	**L2** (10)	Cs_2CO_3	DMSO	64%
3	$CuSO_4·5H_2O$ (5)	**L2** (10)	Cs_2CO_3	DMSO	61%
4	Cu (5)	**L2** (10)	Cs_2CO_3	DMSO	67%
5	CuI (5)	**L5** (10)	Cs_2CO_3	DMSO	65%
6	CuBr (5)	**L5** (10)	Cs_2CO_3	DMSO	75%
7	$CuSO_4·5$ (5)	**L5** (10)	Cs_2CO_3	DMSO	75%
8	CuI (5)	**L2** (10)	K_3PO_4	DMSO	64%
9	CuI (5)	**L5** (10)	K_3PO_4	DMSO	80%
10	CuI (5)	**L2** (10)	K_2CO_3	DMSO	46%
11	CuI (5)	**L5** (10)	K_2CO_3	DMSO	19%
12	CuI (5)	**L2** (10)	Et_3N	DMSO	8%
13	CuI (5)	**L2** (10)	Cs_2CO_3	DMF	52%
14	CuI (5)	**L5** (10)	Cs_2CO_3	DMF	41%
15	CuI (5)	**L2** (10)	K_3PO_4	DMF	28%
16	CuI (5)	**L5** (10)	K_3PO_4	DMF	40%
17	CuI (5)	**L2** (10)	Cs_2CO_3	toluene	11%
18	CuI (5)	**L5** (10)	Cs_2CO_3	toluene	10%
19	CuI (2)	**L2** (4)	Cs_2CO_3	DMSO	68%
20	CuI (10)	**L2** (20)	Cs_2CO_3	DMSO	95%
21	CuI (5)	**L2** (10)	Cs_2CO_3	H_2O	trace

[a] Reagents and conditions: 4-bromoacetophenone (1.0 mmol), imidazole (1.2 mmol), base (2 mmol) in the presence of copper and ligand in solvent (2 mL) at 120 °C for 14 h. [b] GC yield.

To further explore the catalytic efficiency of this system, a more versatile and practical method was applied to the coupling reactions between aryl bromides and azoles by using 10 mol-% CuI, 20 mol-% Ligand (**L2**), and 2.0 equiv. of Cs_2CO_3 in DMSO at 120 °C (Table 2). The effect of varying the aryl bromides used in the reaction was initially investigated by using imidazole as a substrate (Entries 1–7). The *N*-arylimidazoles were provided in good yields. In general, aryl bromides bearing electron-withdrawing groups, such as -$COCH_3$, -CN, and -NO_2, were more reactive than bromobenzene and aryl bromides bearing electron-donating groups, such as -Me and -OCH_3, which afforded the corresponding *N*-arylated imidazoles in lower yields, even with an extended reaction time of 48 h. For example, the reaction of *p*-bromonitrobenzene and imidazole proceeded with 91% isolated yield in 1 h (Entry 2), whereas the inactive 4-bromoanisole required more than 48 h reaction time to give the corresponding product in 60% isolated yield (Entry 7). These results are consistent with well-established trends observed for the Ullmann reaction. Unfortunately, this catalytic system is ineffective for chlorobenzene; with this reagent, only trace amounts of *N*-phenylimidazole were detected by GC analysis, even when the reaction time was prolonged to 48 h.

Table 2. Cu/**L2**-catalyzed *N*-arylation of azoles with aryl bromides and heteroaryl bromides.[a]

Entry	Aryl bromide	Azole	Product	*t* [h]	Yield[b]
1				14	91 %
2				1	91 %
3				5	87 %
4				8	78 %
5				43	89 %
6				48	68 %
7				48	60 %
8				24	67 %
9				24	91 %
10				24	90 %
11				24	75 %
12				24	87 %
13				24	72 %
14				24	75 %
15				24	95 %
16				24	92 %
17				24	94 %

[a] Reagents and conditions: aryl bromide (1.0 mmol), azole (1.2 mmol), Cs_2CO_3 (2 mmol), CuI (0.10 mmol), **L2** (0.20 mmol), DMSO (2 mL), 120 °C. [b] Isolated yield.

The Cu/**L2** catalytic system was also applied to the coupling reactions of nitrogen- or sulfur-containing heteroaryl halides with imidazole under the standard conditions. Interestingly, the reactions with 2-bromothiophene (Entry 8), 2-bromopyridine (Entry 9), and 2,6-dibromopyridine (Entry 10) with imidazole produced 2-(1*H*-imidazol-1-yl)pyridine, 2,6-bis(1*H*-imidazol-1-yl)pyridine, and 2-(1*H*-imidazol-1-yl)thiophene in 67, 91, and 90% isolated yields, respectively. The former two products are potentially good candidates for the preparation of hemilabile[24] and pincer-type NHC compounds,[25] respectively, and their metal complexes have shown excellent activities in many organic

transformations. This procedure thus provides a valuable route for the preparation of functionalized NHC precursors.

The CuI/**L2** catalytic system is also applicable to the Ullmann coupling reactions of other N-heterocycles with 4-bromoacetophenone and 2-bromopyridine (Entries 11–17). The heterocycles, such as pyrrole (Entry 11), pyrazole (Entries 12 and 15), triazole (Entries 13 and 16), and benzimidazole (Entries 14 and 17) were found to be effective nucleophilic counterparts for the coupling process, and the respective *N*-arylated products were obtained in good to excellent yields. Clearly, the catalytic system is more suitable for heteroaryl bromides, because 2-bromopyridine is more reactive than 4-bromoacetophenone; this is very attractive for the synthesis of coordination ionic liquids and hemilabile NHCs.

Conclusions

We have demonstrated that *N*-arylated azoles can be easily prepared by the coupling reaction of aryl and heteroaryl bromides with NH-containing heterocycles by using a combination of CuI and acylhydrazine- or acylhydrazone-type ligands. The ligands are readily prepared from inexpensive starting materials, and their electronic and steric properties can easily be modified and tuned by varying the substituents in the acylhydrazine and acylhydrazone units. The substituents have a clear effect on the catalytic activity of the copper-catalyzed Ullmann reaction. The catalytic system shows broad scope and encompasses both N-containing azoles and aryl bromides, especially heteroaryl bromides, and gives good to excellent yields. Thus, this system can be widely used for the preparation of coordination ionic liquids, ligands of coordination polymers, as well as hemilabile and pincer NHCs.

Experimental Section

General: Ligands **L1**–**3**,[26a] **L4**,[26b] **L5**,[26a] **L6**,[26c] **L7**,[26d] **L8**,[26e] and **L9**–**10**[26f] were synthesized according to modified literature methods. All the reagents were purchased from commercial sources and used without further purification. All reactions were carried out in Schlenk tubes under nitrogen. DMSO, DMF, and toluene were distilled before use. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Biospin Avance III spectrometer at 400 and 100 MHz, respectively, by using $CDCl_3$ as a locking solvent except where otherwise indicated. Chemical shifts are reported in ppm relative to TMS.

Typical Procedure for the Ullmann Cross-Coupling Reactions: A Schlenk tube was charged with CuI (19 mg, 0.1 mmol), ligand (0.2 mmol), azole (1.2 mmol), aryl or heteroaryl halide (1.0 mmol), Cs_2CO_3 (652 mg, 2.0 mmol), and DMSO (2 mL) under nitrogen. The reaction mixture was stirred at 120 °C for the indicated period of time. After completion of the reaction, the mixture was cooled to room temperature and directly passed through a plug of Celite. The Celite was washed with ethyl acetate (3 × 5 mL), and the combined filtrates were washed with saturated brine (2 × 10 mL). The organic layer was dried with $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel to provide the desired products.

Supporting Information (see footnote on the first page of this article): Experimental procedures for the synthesis of **L1**–**10**, ^{1}H and ^{13}C NMR spectroscopic data of **L1**–**10** and the coupled products for the Ullmann reactions.

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