Oxazolidin-2-one-Promoted CuI-Catalyzed Amidation of Aryl Halides and Cyclization of *o*-Halobenzanilides

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Abstract: Oxazolidin-2-one was found to be a versatile and efficient ligand for the CuI-catalyzed amidation of aryl halides and the cyclization of *ortho*-halobenzanilides. Notably, the less active halides could also be applied successfully in the synthesis of benzoxazoles and benzothiazoles.

Key words: amidation, cyclizations, catalysis, ligand, coupling

The formation of C–N bond is of great importance in the preparation of intermediates and target molecules in the chemical, pharmaceutical, and materials industries.[1] Despite significant improvements in the palladium-catalyzed N-arylation of amines, some limitations still exist that prevent these reactions from being employed to their full potential.[2] For examples, substantial structural variations cannot be accommodated and certain functional groups are found to be incompatible in some cases,[3] the sterically hindered phosphine ligands are not easily available, and the palladium reagents have limited applications due to their high cost and air sensitivity. Copper-catalyzed Ullmann reaction and the related Goldberg reaction were applied as alternative C–N bond-forming methodologies.[4] Unfortunately, these methods also suffer from relatively limited scope of substrates, high reaction temperature (up to 210 °C), and the requirement of stoichiometric amounts of copper reagents.

In recent years, the use of ligands to facilitate the copper-catalyzed N-arylation of nucleophiles with aryl halides is one of the active research areas in the formation of functionalized nitrogen-containing structures. Several groups have disclosed the use of different ligands, including amino acids,[5] diamines,[6] diimines,[7] aminoarenethiolate,[8] phosphines,[9] 2-aminopyrimidine-4,6-diol,[10] hydroxyquinoline,[11] (*S*)-pyrrolidinylmethylimidazoles,[12] 4,7-dimethoxy-1,10-phenanthroline,[13] 2-oxocyclohexanecarboxylate,[14] benzotriazole,[15] and 1,1,1-tri(hydroxymethyl)ethane.[16] However, the high cost and/or tedious preparation of some ligands used in these important protocols are the major drawbacks. Hence, it is still essential to search for other new, less costly and versatile ligands for this copper-catalyzed protocol.

In our latest work we turned our attention to the synthesis of O–O type ligands and their use in copper-catalyzed C–N coupling reactions.[17] To extend the application of our ligands, we tested the commonly used oxazolidin-2-one as a C–N coupling partner. To our delight, the reactions afforded satisfactory results. In 2003, Buchwald reported the copper-catalyzed amidation of halides.[18] We noted from the work that the access to a molecule containing the oxazolidin-2-one unit is more efficient than others. Related works also documented that the five-membered lactams, used as C–N coupling substrates, displayed greater efficiency than the four-, and six-membered lactams.[3a] From these valuable clues, we speculated that oxazolidin-2-one has the possibility to be applied as a potential ligand. Through the systematic and rational design of oxazolidin-2-one-based structures, a series of derivatives was synthesized (Figure 1).

Initially, we tested the coupling reaction of pyrrolidin-2-one (**1a**) with 1-bromo-4-methoxybenzene (**2a**) in the presence of different copper salts and ligands, as well as bases. Employing the trial and error approach, we were pleased to find that the reaction of **1a** with **2a** in DMSO at 120 °C for 24 hours in the presence of CuI (10 mol%), L^1 (20 mol%), and MeONa (1.5 equiv) occurred smoothly to give the coupling product 1-(4-methoxyphenyl)pyrrolidin-2-one (**3a**) in good yield (78%, Table 1, entry 1).

The following details were noteworthy. First, not all ligands could be employed for the reaction. For examples, L^3 and L^4 could not be applied as promoters in our catalysis system (Table 1, entries 3 and 4), while the sterically more hindered ligands L^5, L^6, and L^7 afforded **3a** in lower

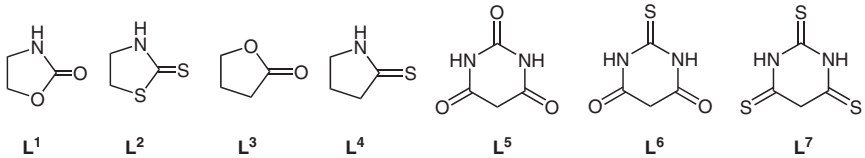

Figure 1

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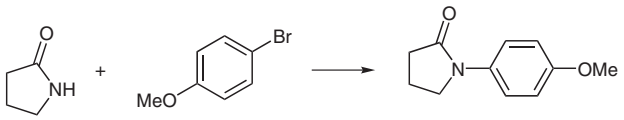
Table 1 Copper-Catalyzed Amidation of 1-Bromo-4-methoxybenzene (**2a**) with Pyrrolidin-2-one (**1a**)[a]



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

Entry	Ligand	[Cu]	Base	Solvent	Yield (%)[b]
1	L^1	CuI	MeONa	DMSO	78
2	L^2	CuI	MeONa	DMSO	71
3	L^3	CuI	MeONa	DMSO	–[c]
4	L^4	CuI	MeONa	DMSO	–[c]
5	L^5	CuI	MeONa	DMSO	25
6	L^6	CuI	MeONa	DMSO	24
7	L^7	CuI	MeONa	DMSO	28
8	L^1	CuI	MeONa	DMF	46
9	L^1	CuI	MeONa	toluene	45
10	L^1	CuI	MeONa	DMF–H_2O[d]	61
11	L^1	CuBr	MeONa	DMSO	63
12	L^1	$CuCl_2$	MeONa	DMSO	55
13	L^1	CuI	K_2CO_3	DMSO	67
14	L^1	CuI	Cs_2CO_3	DMSO	46

[a] Reaction conditions: **1a** (1.5 mmol), **2a** (1.5 mmol), base (2.3 mmol), [Cu] (10 mol%), ligand (20 mol%), solvent (2 mL), 120 °C.
[b] GC yield.
[c] No reaction was detected.
[d] DMF (2 mL) and H_2O (0.1 mL) as solvent.

yields (Table 1, entries 5–7). The best results were obtained only when the ligands contained O or S atom located in the lactam ring (Table 1, entries 1 and 2). Presumably, both L^1 and L^2 acted as tridentate O-, N-, and S-donor ligands that might be more effective in stabilizing or solubilizing the copper complex.[16] In our case, ligand L^1 was preferred due to its easy preparation and lower molecular weight. Secondly, the nature of solvent had noticeable influence on the reaction. The polar solvent DMSO was more favorable than others (yield 78%, Table 1, entry 1). Thirdly, with regard to the efficiency of the base in the amidation reaction, MeONa was found to be highly effective (Table 1, entry 1). Finally, various copper salts such as CuI, CuBr, $CuCl_2$ all afforded **3a** in average to good yields (Table 1, entries 1, 11 and 12).

The optimized reaction conditions, L^1 (20 mol%), CuI (10 mol%), amide (1.5 mmol), halide (1.5 mmol), MeONa (1.5 equiv, 2.3 mmol), in DMSO (2 mL) at 120 °C for 24 hours, were applied to the amidation of a number of functionalized halides. As can be seen from Table 2, a wide range of representative amides, including the cyclic amides and arylides, could be arylated to give the desired product in good to excellent yields. 2-Bromopyridine (**2d**) even displayed greater efficiency than iodobenzene (entry 4 vs. entry 2). As reported previously in the copper-catalyzed N-arylation reactions, certain groups at the *ortho* position of aryl halides had the ability to coordinate to copper and promoted the Ullmann-type reaction.[10] In our reactions, we also found that the nitrogen atom in 2-bromopyridine possessed the ability to promote the coupling reactions (Table 2, entries 4, 7, and 17). Interestingly, while pyrrolidin-2-one (**1a**) was an effective partner in all cases (Table 2, entries 1–4), the analogous piperidin-2-one (**1g**, n = 1) and azepan-2-one (**1g**, n = 2) were not reactive (Table 2, entry 18), presumably due to their increased steric hindrance and different pK_a values in DMSO.[3a,18,19]

As for the amides **1b**–**1e**, the N-arylation reactions were conducted successfully in good to excellent yields (Table 2, entries 5–15). Higher chemoselectivity was found for 2-iodochlorobenzene, and only the iodide function was displaced in the reaction (Table 2, entries 13–15). Competitive hydrolysis of the acetyl group in the products **3j**–**3m** led to low yields of the products in the presence of MeONa (Table 2, entries 10–13). Such problems could be circumvented when K_2CO_3 was used as an alternative, and the product yields were enhanced (Table 2, entries 10–13). For substrate **1f**, the reaction provided N-arylation products, and no O-arylation products were found (Table 2, entries 16 and 17).[20] It was also noted that a small amount of water did not have any effect on the reaction (Table 2, entry 16).

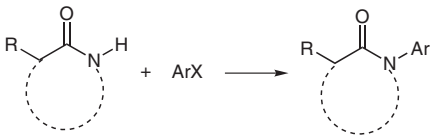
During our investigation on the amidation of 1-chloro-2-iodobenzene (Table 2, entries 14 and 15), further cyclization products, such as benzoxazoles and benzothiazoles, were observed when the temperature was elevated to 150 °C for longer reaction time. We recognized the utility of this protocol for the one-pot preparation of these heterocyclic products. However, the yields were low; it was possible that the intermediates **3n** and **3o** were easily hydrolyzed in the presence of NaOMe. Therefore we tested other bases for the cyclization reaction, and found that K_2CO_3 was more efficient than others.

Consequently, we employed this modified reaction conditions to effect the intramolecular cyclization of *o*-halobenzanilides and the results were detailed in Table 3. Generally, the desired products could be obtained from the cyclization reaction. For less active chlorides, higher temperature (up to 150 °C) and longer reaction time (72 h) were required in comparison with reactions involving bromides and iodides. As expected, cyclizations to benzothiazole occurred more readily than those to benzoxazoles. For example, *N*-(2-chlorophenyl)benzothioamide (**4b**) gave the cyclized product **5b** in 56% yield when the reaction was conducted at 140 °C for 30 hours (Table 3, entry 2). However, *N*-(2-chlorophenyl)benzamide (**4a**) only gave the benzoxazole analogue in 22% yield even the reaction was performed at 150 °C for three days (Table 3, entry 1). When we utilized the more reactive bromo- and iodo-substituted reactants, the cyclizations proceeded

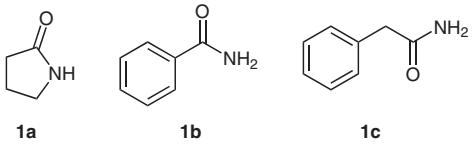
smoothly in good yields under milder reaction conditions. The rate of cyclization of the *ortho*-haloanilides followed the order I >Br >Cl, and was consistent with the generally accepted reaction mechanism.[17]

In summary, we have disclosed that oxazolidin-2-one could act as a versatile and efficient ligand for the CuI-catalyzed arylation of amides and the cyclization of *o*-halobenzanilides. The newly developed catalyst system was also applicable to the less active chloro-substituted substrates. We believe that the present catalyst system could provide an excellent complement to the Pd- or Cu-catalyzed methods that have already been utilized in a number of applications, and is of great importance to the research and development in the pharmaceutical industry.

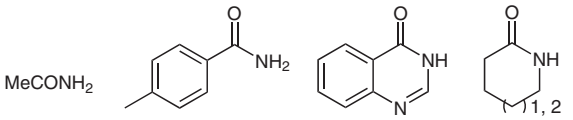
Table 2 N-Arylation of Amides[a]



1a–h **2a–g** **3a–r**



1a **1b** **1c**



1d **1e** **1f** **1g**

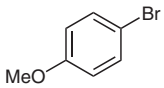
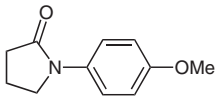
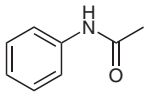
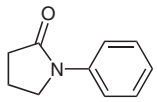
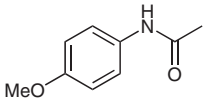
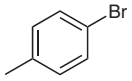
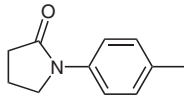
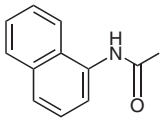
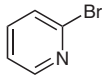
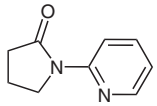
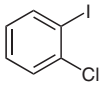
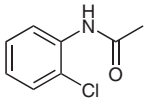
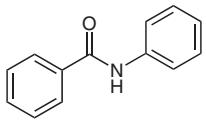
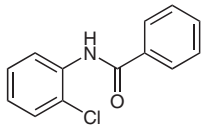
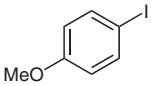
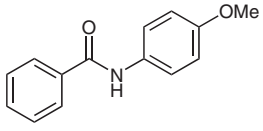
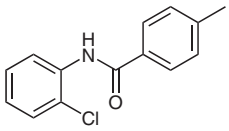
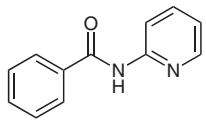
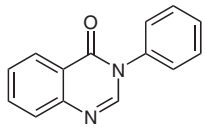
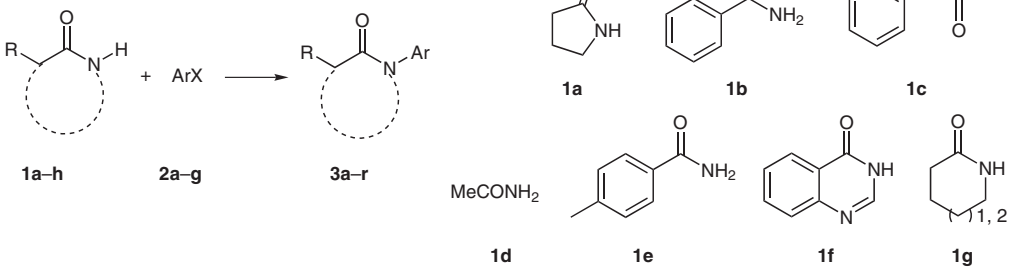
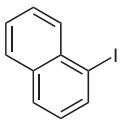
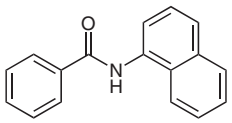
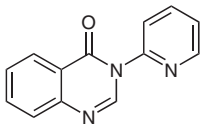
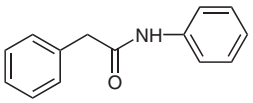
Entry	Amide	Halide	Product	Yield (%)[b]	Entry	Amide	Halide	Product	Yield (%)[b]
1	 **1a**	 **2a**	**3a**	74	10	**1d**	**2b**	 **3j**	42 88[c]
2	 **1a**	 **2b**	**3b**	85	11	**1d**	**2e**	 **3k**	32 80[c]
3	 **1a**	 **2c**	**3c**	76	12	**1d**	**2f**	 **3l**	45 76[c]
4	 **1a**	 **2d**	**3d**	89	13	**1d**	 **2g**	 **3m**	32 78[c]
5	**1b**	 **2b**	**3e**	70	14	**1b**	**2g**	 **3n**	86
6	 **1b**	 **2e**	**3f**	85	15	**1e**	**2g**	 **3o**	78
7	**1b**	 **2d**	**3g**	80	16	**1f**	**2b**	 **3p**	87 81[d]

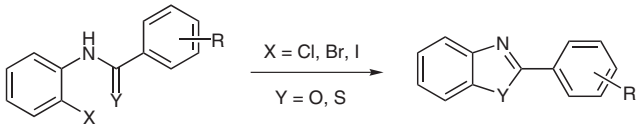
Table 2 N-Arylation of Amides[a] (continued)



Entry	Amide	Halide	Product	Yield (%)[b]	Entry	Amide	Halide	Product	Yield (%)[b]
8	 **1b**	 **2f**	**3h**	79	17	**1f**	**2d**	 **3q**	93
9	**1c**	 **2b**	**3i**	69	18	**1g**	**2b**	no reaction	

[a] Reaction conditions: L^1 (20 mol%), CuI (10 mol%), amide (1.5 mmol), halide (1.5 mmol), MeONa (1.5 equiv, 2.3 mmol), DMSO (2 mL), 120 °C, 24 h.
[b] Isolated yield.
[c] Reaction was performed with 2 equiv of K_2CO_3 instead.
[d] With DMSO (2 mL) and H_2O (0.1 mL) as solvent.

Table 3 Synthesis of Substituted Benzoxazoles and Benzothiazole[a]



4a–f **5a–f**

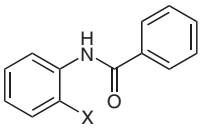
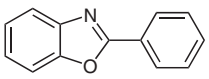
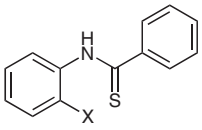
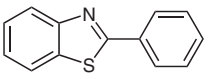
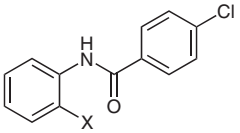
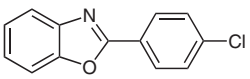
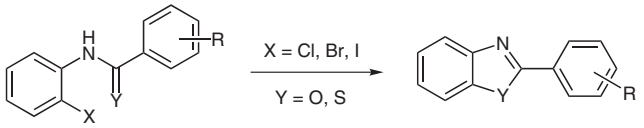
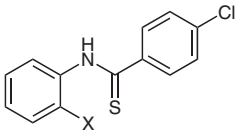
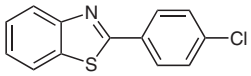
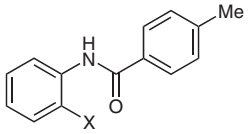
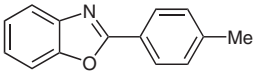
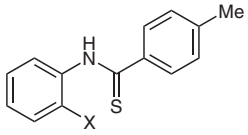
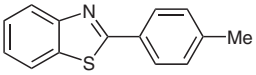
Entry	Reactant	Product	Conditions, Yield[b]
1	 **4a**	 **5a**	X = Cl, 150 °C, 72 h, 22% X = Br, 110 °C, 20 h, 67% X = I, 90 °C, 6 h, 83%
2	 **4b**	 **5b**	X = Cl, 140 °C, 30 h, 56% X = Br, 110 °C, 18 h, 77% X = I, 90 °C, 6 h, 83%
3	 **4c**	 **5c**	X = Br, 110 °C, 20 h, 64% X = I, 90 °C, 6 h, 88%

Table 3 Synthesis of Substituted Benzoxazoles and Benzothiazole[a] (continued)



4a–f **5a–f**

Entry	Reactant	Product	Conditions, Yield[b]
4	 **4d**	 **5d**	X = Cl, 140 °C, 30 h, 70% X = Br, 110 °C, 18 h, 84% X = I, 90 °C, 6 h, 83%
5	 **4e**	 **5e**	X = Br, 110 °C, 20 h, 62% X = I, 90 °C, 6 h, 80%
6	 **4f**	 **5f**	X = Cl, 140 °C, 30 h, 66% X = Br, 110 °C, 18 h, 83% X = I, 90 °C, 6 h, 87%

[a] Reaction conditions: L^1 (20 mol%), CuI (10 mol%), *ortho*-halobenzanilides (1.5 mmol), and K_2CO_3 (2 equiv) as base.
[b] Isolated yield.

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References and Notes

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(21) **General Procedure for the Coupling of Halides with Amides**: To a solution of MeONa (2.3 mmol) in DMSO (2 mL) were added CuI (29 mg, 0.15 mmol) and L^1 (26 mg, 0.3 mmol). After stirring the mixture at r.t. for 30 min, the halide (1.5 mmol) and the amide (1.5 mmol) were added to the flask, and the reaction mixture was stirred at 120 °C for 24 h. The mixture was cooled to r.t., H_2O (10 mL) was added, and the resulting suspension was extracted with EtOAc (4 × 10 mL). The extracted layer was dried over $MgSO_4$, then concentrated, and purified by column chromatography on silica gel to provide the desired products.
(22) **3-(Pyridin-2-yl)quinazolin-4(3*H*)-one (3q)**: bright yellow solid; mp 135–137 °C(uncorrected). IR (KBr): 3448, 2924, 1688, 1610, 1590, 1563, 1478, 1440, 1294, 1255, 774, 760 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.65–8.66 (d, *J* = 4.4 Hz, 1 H), 8.57 (s, 1 H), 8.22–8.24 (d, *J* = 8.0 Hz, 1 H), 8.06–8.08 (t, *J* = 7.2 Hz, 1 H), 7.83–7.91 (m, 2 H), 7.74–7.76 (d, *J* = 8.0 Hz, 1 H), 7.54–7.63 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 149.9, 149.6, 147.8, 146.1, 138.9, 135.4, 128.0, 127.8, 126.9, 124.6, 122.6, 122.1. LRMS (EI, 20 eV): *m*/*z* (%) = 223 (100) [M^+]. Anal. Calcd for $C_{13}H_9N_3O$: C, 69.95; H, 4.06; N, 18.82. Found: C, 69.46; H, 4.38; N, 18.65.