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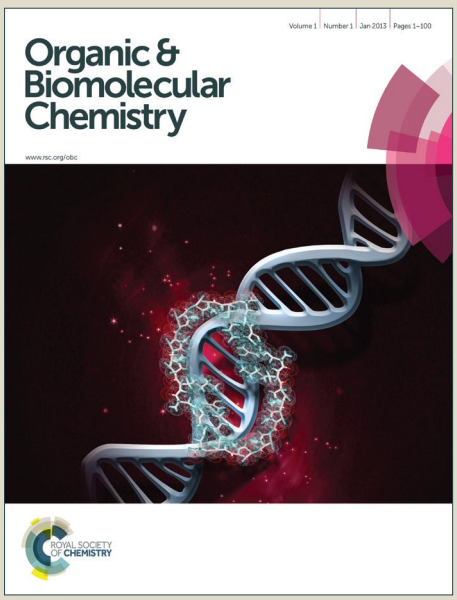

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Copper-Catalysed Oxidative Amination of Quinoxalin-2(1*H*)-ones with Aliphatic Amines

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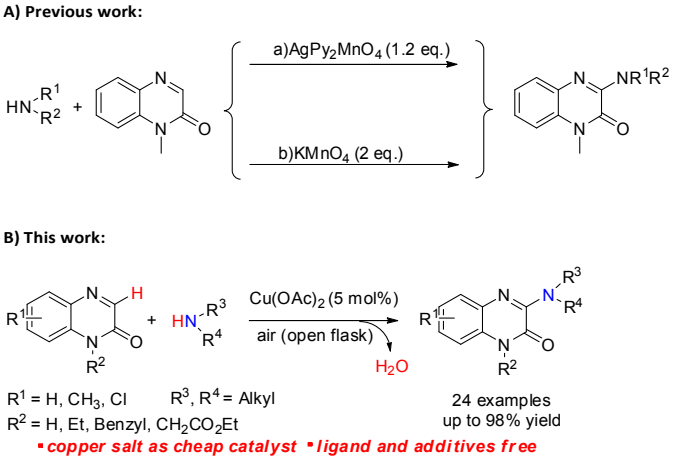
A novel, efficient and practical method for copper-catalysed oxidative C-3 amination of quinoxalin-2(1*H*)-ones with primary or secondary amines as the nitrogen sources has been developed. A wide variety of 3-aminoquinoxalin-2(1*H*)-ones were prepared in up to 98% yield with good functional group tolerance for 24 examples. This synthetic strategy features atom economy, concise steps, easy operation, and mild reaction conditions.

Quinoxalin-2(1*H*)-ones have attracted considerable attention since they are endowed with significant biological activities and outstanding chemical properties. They have been extensively investigated in organic syntheses, materials chemistry and pharmaceuticals.[1] In particular, 3-aminoquinoxalin-2(1*H*)-one as an important pharmacophore has appeared in numerous bioactive compounds, such as glycogen phosphorylase inhibitors, antimicrobial and anticancer agents.[2] Conventional, synthesis of 3-aminoquinoxalin-2(1*H*)-ones has involved the construction of the heterocycle rings or functionalization of already existing quinoxalin-2(1*H*)-ones via nucleophilic substitution of a halo or other leaving groups.[3] These transformations require prefunctionalized substrates and usually rely on multistep process, and suffer from poor atomic economy. Transition-metal-catalysed selective functionalization of C-H bond to build C-N bond are of great interest in terms of short step and highly atomic economy.[4-7] Impressive achievements have been recently made.[8] The novel metal, such as rhodium,[9] ruthenium,[10] and palladium[11] are usually used as a catalyst. The high cost and toxicity of heavy metal as catalyst has stimulated efforts to achieve cheaper metals, such as copper, promoted C-N bond forming processes due to their cost effectiveness, availability and low toxicity.[12] The pioneering work on Cu-catalysed 2-phenylpyridine with sulfonamide was reported by Yu.[13] Subsequently, Mori and co-workers[14] detailed the use of copper as the preferred catalyst for the direct amination of benzothiazole. Similarly, Schreiber[15], Li[16], and Duan[17] groups also reported their facile, practical method for copper-catalysed direct oxidative C-H amination. However, stoichiometric and environmental unfriendly additives, such as oxidant, ligand, base, acid were required. Moreover, and the high copper catalyst loadings (10-25 mol %) was necessary.[4b, 7b, 15-17, 18] Recently, we developed an efficient one-pot strategy for the direct amination of quinoline *N*-oxides *via* copper-catalysed dehydrogenative C-N coupling under ligand, additives, base, and external oxidant free conditions.[19]

In our continuing effort to develop green formation of C-N bond, we embarked on the development of copper-catalysed oxidative amination reaction of quinoxalin-2(1*H*)-ones. To the best of our knowledge, only one report on the C-H amination of quinoxalin-2(1H)-ones has been described by Gulevskaya's group,[20] in which excessive $AgPy_2MnO_4$ (1.2 eq) or $KMnO_4$ (2.0 eq) was used as an oxidant (Scheme 1A). There are some challenges with this approach, including usage of excessive oxidant and low efficiency (15%-68%). The protocol to various



Scheme 1 Amination of Quinoxalin-2(1H)-ones.

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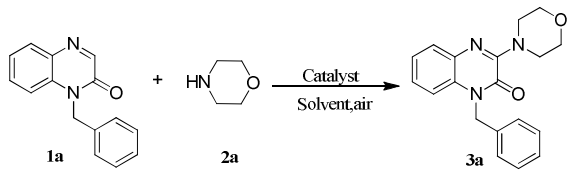
Table 1 Optimization of Reaction Parameters for Copper-Catalysed Amination of 1-Benzylquinoxalin-2(1*H*)-one (1a) with Morpholine (2a) [a]



Entry	Catalyst	Solvent	T(ºC)	Yield[f] (%)
1	$CuCl_2$ (10%)	DMSO	120	85
2	$CuBr_2$ (10%)	DMSO	120	83
3	CuCl (10%)	DMSO	120	93
4	CuBr (10%)	DMSO	120	66
5	CuI (10%)	DMSO	120	71
6	$Cu(OAc)_2$ (10%)	DMSO	120	98
7	$Cu(OAc)_2$ (10%)	DMF	120	48
8	$Cu(OAc)_2$ (10%)	Toluene	120	65
9	$Cu(OAc)_2$ (10%)	NMP	120	94
10	$Cu(OAc)_2$ (10%)	1,4-dioxane	120	42
11	$Cu(OAc)_2$ (10%)	DMSO	100	98
12	$Cu(OAc)_2$ (10%)	DMSO	90	90
13	$Cu(OAc)_2$ (5%)	DMSO	100	98
14	$Cu(OAc)_2$ (3%)	DMSO	100	89
15[b]	$Cu(OAc)_2$ (5%)	DMSO	100	90
16[c]	$Cu(OAc)_2$ (5%)	DMSO	100	83
17[d]	$Cu(OAc)_2$ (5%)	DMSO	100	98
18[e]	$Cu(OAc)_2$ (5%)	DMSO	100	21
19		DMSO	100	NR

[a]Reaction conditions: 1a (0.2 mmol), 2a (0.6 mmol), catalyst (10 mol%), solvent (2 mL), under air, 12h. [b]2a (2.5 equiv). [c]2a (2 equiv). [d]O_2 balloon. [e]N_2 balloon. [f]isolated yields based on 1a.

3-aminoquinoxalin-2(1H)-ones described herein employed parent amines as substrates with 5 mol% Cu loading and under ligand, base, acid and external oxidant free conditions, which featured being cheap, environment friend, practical and highly efficient (Scheme 1B).

We initiated our investigation with the reaction of 1-benzyl-quinoxalin-2(1H)-one (**1a**) with morpholine (**2a**, 3equiv) in the presence of the $CuCl_2$ (10 mol%) as a model reaction to identify the optimal reaction conditions. By surveying various reaction parameters, such as catalyst, solvent and reaction temperature, the key results were shown in Table 1. Several copper salts (10 mol% based on **1a**), such as $CuCl_2$, $CuBr_2$, CuCl, CuBr, CuI, and $Cu(OAc)_2$, were tested in DMSO at 120°C (Table 1, entries 1-6). When $Cu(OAc)_2$ was employed as catalyst, the yield reached to 98% (Table 1, entry 6). Further investigating the solvent effect (DMF, toluene, NMP, 1, 4-dioxane) (Table 1, entry 6 vs entries 7-10). DMSO was found to be the best reaction medium, giving the highest yield (Table 1, entry 6). By lowering the reaction temperature to 90°C, the yield reduced to 90%, and 100°C was found to be the optimal reaction temperature for this reaction (Table 1, entries 11 and 12). Encouraged by these preliminary results, we subsequently tried to reduce the loading of catalyst. 5 mol% of $Cu(OAc)_2$ gave the similar yield as 10 mol% of catalyst loading (entry13). When the amount of $Cu(OAc)_2$ was decreased to 3 mol% from 10mol%, the yield reduced to 89% (entry 14). Then, we tried to change the ratio of **1a** and **2a** to 1:2.5/2, the yield decreased to 90% and 83%, respectively (Table 1, entries 15 and 16). The desired product was not observed in the absence of $Cu(OAc)_2$, and the product was only obtained in 21% yield under N_2 atmosphere (Table 1, entries 17-19), perhaps because DMSO worked as a weak oxidation to regenerate the active Cu(II) species (See "control experiment" in supporting information). After screening the catalysts, solvents, reaction temperatures and ratio of the substrates, the optimal reaction conditions were identified as follows: 1 equiv of **1a**, 3 equiv of **2a**, 5 mol% of $Cu(OAc)_2$ as the catalyst, DMSO as the solvent, and the temperature was 100°C under air.

With the optimal reaction conditions established, we investigated the substrates scope of this reaction (Scheme 2). Most quinoxalin-2(1*H*)-ones tested could furnish the corresponding products with morpholine in good to excellent yields under the optimal reaction conditions. *N*-Benzyl, *N*-ethyl and *N*-2-ethoxy-2-oxoethyl quinoxalin-2(1*H*)-ones could proceed smoothly and afford the corresponding products in excellent yields (Scheme 2, **3a**-**3d**). Parent quinoxalin-2(1*H*)-one and benzo[g]-quinoxalin-2(1*H*)-one also worked well and provided the desired product **3e** and **3f** in 97% and 77% yields, respectively. Electron-donating and electron-withdrawing groups in quinoxalin-2(1*H*)-one did not significantly influence on this transformation. For instance, 6,7-dimethylquinoxalin-2(1*H*)-one and 6,7-dicloroquinoxalin-2(1*H*)-one provided the desired products in 97% and 92% yields (Scheme 2, **3g**, **3h**). Their N-benzyl substituted derivatives gave 78% and 77% yields, respectively (Scheme 2, **3i**, **3j**).

We next investigated the generality of amines with 1-benzylquinoxalin-2(1*H*)-one under the optimal reaction conditions. As shown in Scheme 2, morpholine, piperidine, and pyrrolidine could afford the corresponding aminated products **3a**, **3k** and **3l** in good to excellent yields (73%-98%). This catalytic system was not effective with diethylamine and 2-methylpiperidine, maybe due to the steric hindrance. Various primary aliphatic amines proceeded smoothly to deliver the target compounds in up to 98% yields. Propylamine, isopropylamine, and butylamine gave the products **3m**-**3o** in yields of 91%, 97% and 98%, respectively, by increasing the reaction time to 24h. Cyclohexylamine afforded the product **3p** in 48% yield. Benzylamine could be employed as a suitable substrate for this conversion to smoothly provide the corresponding products **3q** in 86% yield. The steric

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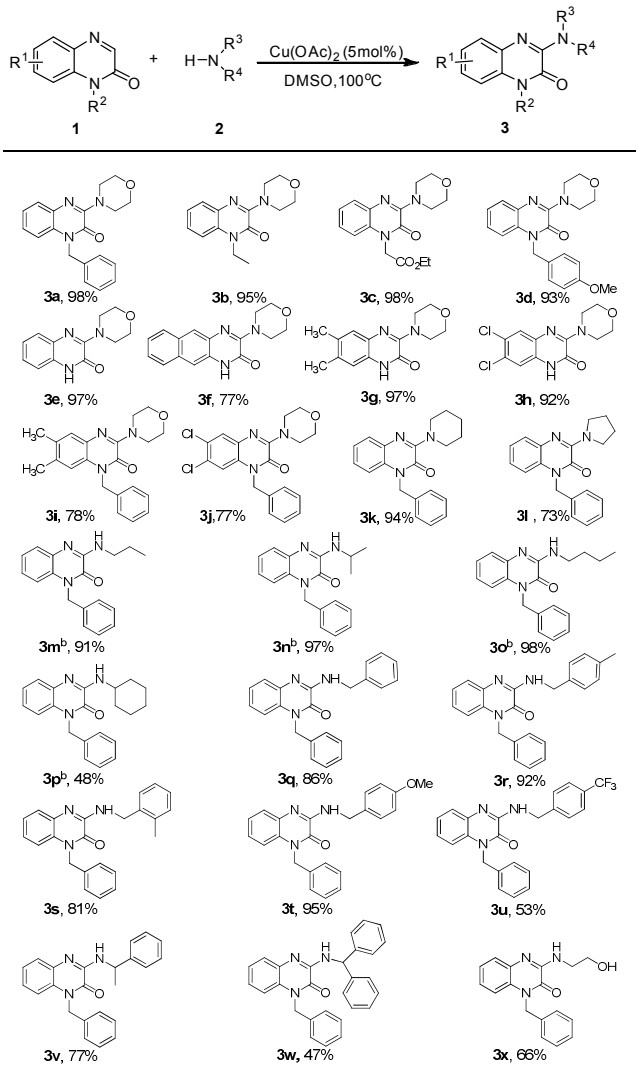
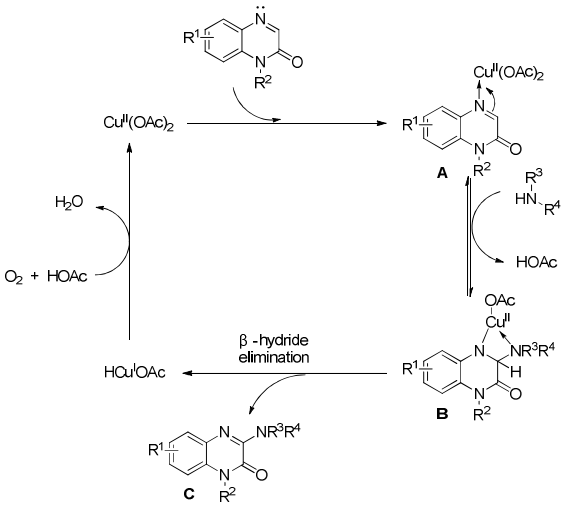
Scheme 2 Copper Catalysed C-H Amination of Quinoxalin-2(1*H*)-ones [a,b]



[a]Reaction conditions: **1** (0.2mmol), **2** (0.6mmol), $Cu(OAc)_2$ (5 mol%), DMSO (2 mL), 100°C, 12h under air. [b]24h.

hindrance in benzylamines slightly affected the reaction. *p*-Methylbenzylamine, *o*-methylbenzylamine, and *p*-methoxyl-benzylamine gave the desired products in 92%, 81%, and 95% yields, respectively (**3r**-**3t**). *p*-Triflloromethylbenzylamine gave the yield of 53% (**3u**). The *α*-methyl and *α*-phenyl benzylamine with large steric hindrance could afford the products **3v** and **3w** in 77% and 47% yields. It was noting that this catalytic system was also applied to amino alcohol. For example, ethanolamine successfully provided products **3x** in 66% yields. While no desired products were obtained for aromatic amines under the standard reaction conditions, perhaps due to the low nucleophilicity of N atom.

Based on the experimental results and literature,[4g,14,17,19,21] a plausible catalytic cycle was proposed and depicted in Scheme 3. Firstly, the Cu(II) coordinated to the imine of the quinoxalin-2(1*H*)-one and gave the species **A**. Then, the nucleophilic amine attacked to the activated imine and afforded σ^H-adduct



Scheme 3 Possible Mechanism for Copper-Catalysed Direct C-H Amination of Quinoxalin-2(1*H*)-one.

B, the balance between the electrophilicity of the **A** and σ^H-adduct **B** has to be favorable.[22a] Subsequent β-hydrogen elimination from σ^H-adduct **B** produces the target product **C** and regenerated the active copper(I) species, which was oxidized into active Cu(II) species for the next catalytic cycle.[22b]

In conclusion, we have successfully developed a novel and mild methodology for Cu-catalysed oxidative amination of quinoxalin-2(1*H*)-ones, which allow primary and secondary amines as the nitrogen reagents. Various 3-aminoquinoxalin-2(1*H*)-ones were afforded in moderate to excellent yields using molecular oxygen from air as a sole oxidant. This method provides one of the easy pathways for rapid synthesis of 3-aminoquinoxalin-2(1*H*)-ones and features being particularly cheap, efficient, atom-economic, and with great practical worth. The products are potentially useful in medicinal chemistry.

Acknowledgment

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