



Removable bidentate directing group assisted-recyclable metal–organic frameworks-catalyzed direct oxidative amination of sp^2 C–H bonds



Nga T.T. Tran, Quan H. Tran, Thanh Truong*

Department of Chemical Engineering, HCMC University of Technology, VNU-HCM, 268 Ly Thuong Kiet, District 10, Ho Chi Minh City, Viet Nam

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ABSTRACT

Several Cu-MOFs were showed to be efficient heterogeneous catalysts for *ortho*-amination of benzoic acid derivative C–H bonds by N–H amines using 8-aminoquinoline as bidentate directing group. The optimal reaction conditions involve the use of Cu-MOFs (25%), *N*-methylmorpholine oxide (NMO) as an oxidant, secondary or primary amine coupling partner, DMF, DMA, or NMP solvent at 90–100 °C. Furthermore, the Cu-MOFs catalyst could be facilely isolated from the reaction mixture and reused several times without remarkable degradation in catalytic reactivity. Contribution from homogeneous leached active copper species, if any, is negligible. To the best of our knowledge, C–H activation reactions using bidentate directing groups, which are increasingly gaining importance, under heterogeneous catalytic systems were not previously mentioned in the literature.

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1. Introduction

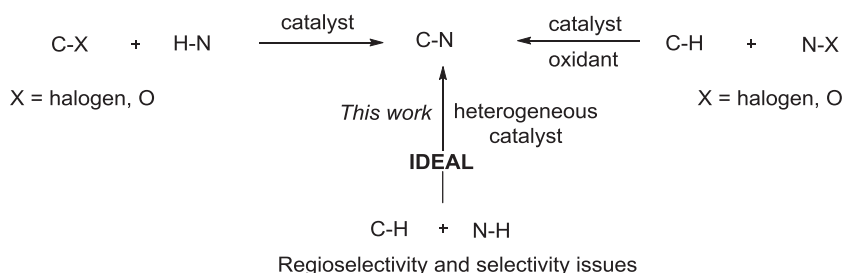
Transition metal-catalyzed carbon–nitrogen coupling reactions have offered widespread applications in the synthesis of many valuable substrates including pharmaceutical compounds, functional materials, and organic sensors [1–3]. Pre-functionalization of starting materials either in the aminated substrates or in the amines is required when conventional methods are employed either in homogeneous or heterogeneous manners [4,5]. Consequently, this adds up more chemical steps in the synthetic sequences which can significantly lengthen the procedures. From synthetic point of views, the direct coupling reactions from C–H and N–H are highly desired (Scheme 1) [6–8]. Since organic molecules often contain a wide range of chemically similar C–H bonds, selective transformations for non-activated C–H bonds are generally difficult to achieve [9,10]. Several approaches have been employed to address this challenge, the most common involves the use of directing groups, which bind to the metal center and bring catalysts to the proximal C–H bonds. Over last several years, a wide variety of functional groups have been evaluated as directing groups in the transformation of C–H bonds [11,12]. Homogeneous palladium, iridium, and ruthenium based catalysts have been employed for ligand-assisted direct amination of C–H bonds of [13–15]. Recently, reactivity enabled by cheap and abundant copper catalysts has attracted great interest. In particular, the first

copper-mediated directed amination of C–H arene bonds was described by Yu group [16]. However, stoichiometric amount of copper is required and only 2-phenylpyridine derivatives were active [17–19]. Recently, with the use of 8-aminoquinoline (8-AQ) directing group [20,21], Daugulis has firstly reported that *ortho*-amination of sp^2 C–H bonds is possible under copper catalysis [22]. The utilization of an inexpensive copper catalyst and removable directing group allows for a favorable comparison with previous direct amination methodologies. Thus, the heterogeneous catalytic system for this transformation should be targeted for practical chemical industry as well as simplifying the product purification [23,24].

Metal–organic frameworks (MOFs) have recently emerged as an incredible class of crystalline porous materials with potential applications in different fields [25–28]. Although the utilization of MOFs in catalysis is a young research area, many MOFs have been investigated as heterogeneous catalysts or catalyst supports for a variety of organic transformations [29–32]. Recently, the use of MOFs and other heterogeneous systems with transition metal clusters for organic transformations, especially C–H functionalization reactions have increasingly gained attention [33,34]. With respect to MOFs catalysis, Sanford and Swartzers have pioneered using Pd-MOFs for arylation of naphthalene by arene C–H bonds [34a]. Bipyridyl-containing metal–organic frameworks of palladium and iridium were demonstrated as efficient catalysts for borylation of aromatic C–H bonds [34b]. However, regioisomers were obtained in many cases where steric effect is not predominant. Our group has described the deprotonative arylation of

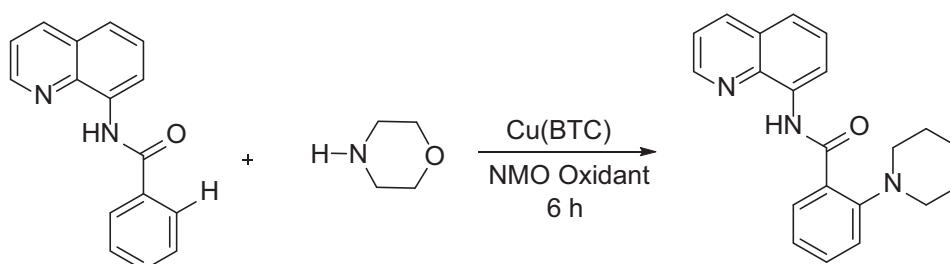
* Corresponding author.

E-mail address: tvthanh@hcmut.edu.vn (T. Truong).



Scheme 1. Methods for transition metal-catalyzed C–N bond formation.

Table 1
Reaction condition development.^a



Entry	Temperature (°C)	Amount of catalyst (%)	Solvent	Ratio	GC yield (%)
1	100	25	NMP	2	73
2	110	25	NMP	2	59
3	90	25	NMP	2	73 (65)
4	90	20	NMP	2	55
5	90	25	DMA	2	71
6	90	25	DMF	2	62
7	90	25	Dioxane	2	9
8	90	25	<i>p</i> -xylene	2	<2
9	90	25	NMP	1	66
10	90	25	NMP	3	71
11	90	25	NMP	0.5	44
12 ^b	90	25	NMP	2	81 (71)
13^c	90	25	NMP	2	99 (87)

Bold texts indicated the optimal conditions. These optimal conditions were further used in next studies.

^a Volume of solvent 5 mL, 1.0 mmol scale, 6 h. Conversion by GC analysis.

^b Reaction for 12 h.

^c With AgOAc (20%) additive. Numbers in parentheses indicate the isolated yields. Kinetic studies of entries were placed in Supporting Information.

Table 2
Effect of silver salt additives to reaction yields.

Entry	Additive	Oxidant (2 equiv.)	GC yield
1	AgOAc	NMO	99
2 ^a	AgOAc	NMO	92
3 ^b	AgOAc	NMO	95
4	Ag ₂ CO ₃	NMO	99
5	AgF	NMO	92
6	AgNO ₃	NMO	73
7	Silica-supported silver	NMO	94
8 ^c	AgOAc	–	14
9 ^d	AgOAc	–	23
10	O ₂	NMO	73

Reaction conditions: amide (0.5 mmol), amine (1 mmol), MOF-199 (25 mol%, 25.2 mg), AgOAc (25 mol%), NMO (2 equiv., 117 mg) in 5 mL NMP at 90 °C for 6 h.

^a 10 mol% AgOAc was used.

^b 50 mol% AgOAc was used.

^c 1 equiv. AgOAc was used.

^d 2 equiv. AgOAc was used.

variety of heterocycles using Cu-MOFs [35–37]. Despite the importance of ligand-assisted C–H activation reactions, especially in controlling regioselectivity, conditions using MOFs for these types of

reactions have not been reported in the literature. Herein, we present the amination of *ortho*-aromatic C–H bonds using bidentate 8-aminoquinoline directing group under Cu-MOF catalysis. Similar isolated yields were obtained as compared to reports using homogeneous catalysts. Additionally, catalysts were able to be recycled and reused several times by simple filtration or centrifugation without significant degradation in catalytic activity.

2. Experimental

All Cu-MOFs were synthesized according reported literature (See Supporting Information for details) [38–43]. In addition, procedures for making all *N*-arenoyl-8-aminoquinoline were obtained from previous studies and placed in Supporting Information [21,44].

In a typical procedure, a mixture of *N*-benzoyl-8-aminoquinoline (0.124 g, 0.5 mmol), morpholine (0.087 g, 1 mmol) and diphenyl ether (0.055 mL) as an internal standard in *N*-methyl-2-pyrrolidone (NMP, 5 mL) were added into 25-mL flask containing the predetermined amount of Cu-MOF catalyst and *N*-methylmorpholine oxide (NMO, 0.087 g, 1 mmol) as an oxidant. The catalyst

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