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# One-pot synthesis of amides *via* the oxidative amidation of aldehydes and amines catalyzed by a copper-MOF†

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An efficient method for the oxidative amidation of aldehydes with primary aromatic and aliphatic amines has been developed for the synthesis of a wide variety of amides using inexpensive  $\text{Cu}_2(\text{BDC})_2\text{DABCO}$  (Cu-metal–organic framework [MOF]) as a recyclable heterogeneous catalyst, and *N*-chlorosuccinimide and aqueous *tert*-butyl hydroperoxide as oxidants in acetonitrile. This amidation reaction is operationally straightforward and provides secondary amides in good yields in most cases, utilizing inexpensive and readily available reagents under mild conditions.

## Introduction

Amide-bond formation is one of the most important organic reactions, and is essential in the synthesis of pharmaceuticals, natural products and polymers such as peptides, bortezomib (an anticancer drug) and nylon 66, for example.<sup>1</sup> Indeed, more than 25% of drugs contain at least one amide group.<sup>2</sup> Routine amide synthesis from amines and carboxylic acids involves the use of coupling agents including carbodiimides, carbonyldiimidazole, hydroxybenzotriazoles and 2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (TBTU), for example.<sup>3</sup> Alternatively, amides are often produced from the reaction of an amine with activated carboxylic acid derivatives.<sup>4</sup> These methods have several drawbacks, such as poor atom efficiency, use of hazardous and expensive reagents and generation of waste products leading to environmental problems. To address these challenges, novel routes to amide-bond formation have been developed over recent years, including the Staudinger reaction,<sup>5</sup> an acid-promoted Schmidt reaction that forms an amide from an alkyl azide and a ketone,<sup>6</sup> catalytic acylation of amines with carboxylic acid,<sup>7</sup> aerobic oxidative coupling of alcohols and amines,<sup>8</sup> hydroamination of alkynes,<sup>9</sup> amino carbonylation of haloarenes<sup>10</sup> and oxidative amidation of aldehydes.<sup>11–21</sup> Among these, oxidative amidation of aldehydes is synthetically useful, as not only are both starting materials readily available, but the process is atomically economical and environmentally benign.

Oxidative amidation of aldehydes with amines was first reported by Nakagawa and co-workers<sup>11</sup> using stoichiometric amounts of nickel peroxide. Subsequently, several research

groups have developed new methods for the direct conversion of amides from aldehydes using iodine,<sup>12</sup> *N*-bromosuccinimide (NBS),<sup>13</sup> manganese oxide<sup>14</sup> and *tert*-butylhydroperoxide (TBHP)<sup>16</sup> as oxidizing agents. In addition, catalytic methods using copper,<sup>22</sup> copper/silver,<sup>18</sup> transition metals (Pd, Rh and Ru)<sup>19</sup> and lanthanides<sup>20</sup> have also been reported. These pioneering works provide efficient and environmentally advantageous methods for amide formation. However, in some cases, the reactions require hazardous and expensive dual catalysts, and in most cases, separation of homogenous catalysts such as  $\text{CuSO}_4$  and  $\text{Cu}(\text{OAc})_2$  is problematic and the catalysts are not recyclable.<sup>22b,c</sup> Hence, the search for a less costly, greener, heterogeneous and simpler catalyst system remains a challenge.

As part of our ongoing work to develop metal–organic frameworks (MOFs) as efficient heterogeneous, green and recyclable catalysts in organic synthesis,<sup>23</sup> we report herein the improved oxidative amidation of aldehydes **1** with a primary amine **2** for the synthesis of secondary amides **3**, using inexpensive and a readily available Cu-MOF,  $\text{Cu}_2(\text{BDC})_2\text{DABCO}$ , as the recyclable catalyst, and *N*-chlorosuccinimide (NCS) and *tert*-butyl hydroperoxide (TBHP) as the oxidants (Scheme 1).

## Experimental section

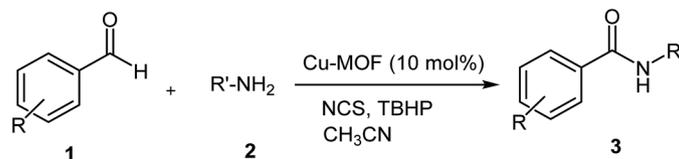
### Materials and methods

All chemicals were purchased from commercial sources and used without further purification.  $\text{Cu}_2(\text{BDC})_2(\text{DABCO})$  was synthesized according to our previously reported procedure.<sup>23a</sup> All reactions were monitored by thin-layer chromatography (TLC) using plates coated with Merck 60 HF254 silica under ultraviolet (UV) light. Infrared (IR) spectra were recorded using a Shimadzu 8400s Fourier-transform (FTIR) spectrometer. <sup>1</sup>H-nuclear magnetic resonance (NMR) and <sup>13</sup>C-NMR spectra were recorded using a BRUKER DRX 500-AVANCE FT-NMR instrument ( $\text{CDCl}_3$  solution) at 500 and 125 MHz, respectively.

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Scheme 1 Oxidative amidation of aldehydes with amine catalyzed by  $\text{Cu}_2(\text{BDC})_2\text{DABCO}$  (Cu-MOF).

Scanning electron microscope (SEM) images were captured with a ZEISS scanning electron microscope at 30 kV with gold coating.

### Synthesis of amides *via* the oxidation amidation of aldehydes and amines catalyzed by $\text{Cu}_2(\text{BDC})_2(\text{DABCO})$

To a solution of amine (1 mmol) in  $\text{CH}_3\text{CN}$  (5 ml), NCS was added (1 mmol) and the reaction mixture was stirred for 1 h at room temperature. Then, aldehyde (1 mmol),  $\text{Cu}_2(\text{BDC})_2\text{DABCO}$  (10% mol) and TBHP 70% (1 mmol) were added, and the reaction temperature was increased up to 65 °C and the reaction mixture was allowed to stir for 2 h. The reaction progress was monitored by TLC. After reaction completion, the catalyst was filtered and the filtrate was evaporated under reduced pressure, before the residue was purified using silica gel column chromatography (hexane/ethyl acetate [4 : 1]).

### Synthesis of *N*-benzylbenzamide (2 g scale)

To a solution of benzylamine (1.4 ml, 12.8 mmol) in  $\text{CH}_3\text{CN}$  (20 ml), NCS (1.71 g, 12.8 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. Then, benzaldehyde (1.3 ml, 12.8 mmol),  $\text{Cu}_2(\text{BDC})_2\text{DABCO}$  (10% mol) and TBHP 70% (1.76 ml, 12.8 mmol) were added, and the reaction temperature was increased up to 65 °C and the reaction mixture was allowed to stir for 2 h. The reaction progress was monitored by TLC. After reaction completion, the catalyst was filtered and the filtrate was evaporated under reduced pressure, before the residue was purified using silica gel column chromatography (hexane/ethyl acetate [4 : 1]) to yield 2.01 g of **3a** (74%).

### Selected spectral data

*N*-Benzylbenzamide, white solid; 160 mg, yield: 75%; mp: 104–106 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d,  $J = 7.1$  Hz, 2H), 7.48–7.51 (t,  $J = 7.1$  Hz, 1H), 7.41–7.44 (m, 2H), 7.32–7.36 (m, 4H), 7.26–7.31 (m, 1H), 6.44 (brs, 1H), 4.65 (d,  $J = 5.5$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.5, 138.2, 134.5, 131.7, 128.9, 128.7, 128.1, 127.7, 127.1, 44.2.

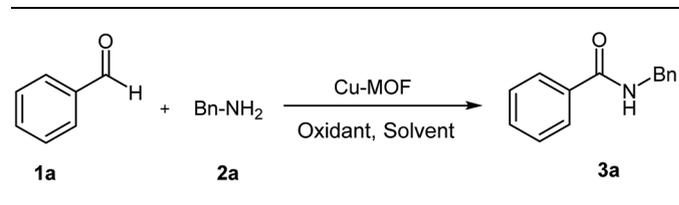
## Results and discussion

$\text{Cu}_2(\text{BDC})_2\text{DABCO}$  (Cu-MOF) catalysts were prepared and characterized using our previously reported method.<sup>23a</sup> First, a model reaction of benzaldehyde **1a** and benzyl amine in the presence of TBHP to form *N*-benzylbenzamide was chosen to identify the catalytic system. Different amounts of Cu-MOF were screened at room temperature under reflux conditions, but unfortunately, only a trace of product was observed (Table 1,

entries 1–4). In another attempt, benzylamine and NCS were first reacted together in acetonitrile at room temperature for 1 h followed by the addition of 5 mol% of the catalyst and stoichiometric amounts of benzaldehyde and TBHP (1.0 equiv.) at room temperature. In this case, we found that benzaldehyde was converted to *N*-benzylbenzamide, **3a**, in only 35% yield after 24 h (entry 5). Increasing the reaction temperature from 25 to 65 °C resulted in a significant increase in the yield of up to 75% after 2 h (entry 6). With 1 mol% catalyst loading, the yield of the amide decreased slightly to 60% (entry 7), while use of 10 mol% loading did not significantly affect the yield of the reaction (Table 1, entry 8).

The effect of the solvents was also investigated, and benzaldehyde and benzylamine were subjected to the same reaction conditions with two other solvents, dimethylformamide (DMF) and tetrahydrofuran (THF). It was found that acetonitrile was the best solvent for this reaction (entries 9–10), possibly due to the dependence of the proton-transfer-mediated electron transfer on the solvent type. The donor number of the solvent decreases in the order of DMF (26.6) > THF (20.0) >  $\text{CH}_3\text{CN}$  (14.8), and as a result, the yield of products increased

Table 1 Optimization of the reaction conditions for amide bond formation from aldehydes<sup>a</sup>

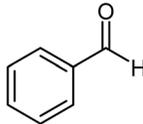
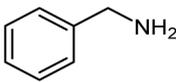
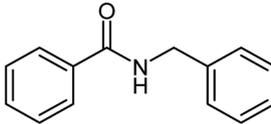
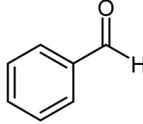
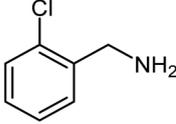
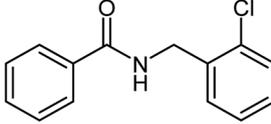
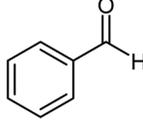
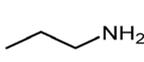
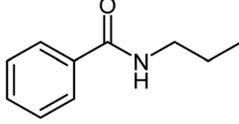
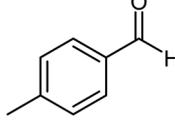
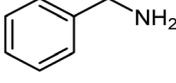
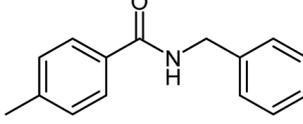
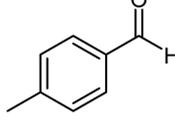
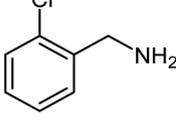
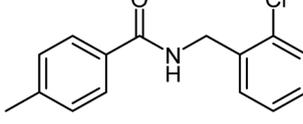
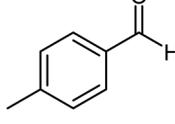
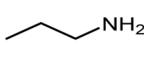
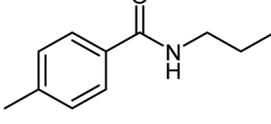
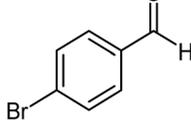
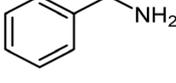
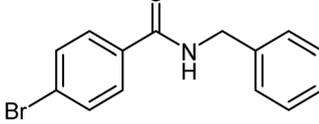
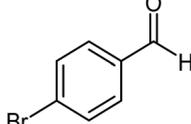
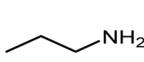
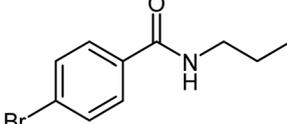
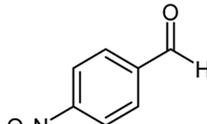
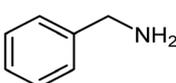
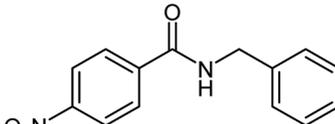
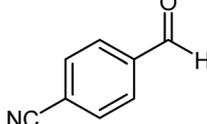
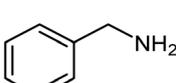
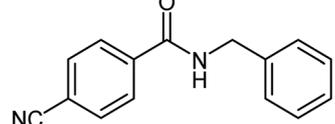


Entry	Catalyst Cu-MOF (mol%)	Oxidant	Solvent	$T$ (°C)	Yield (%)
1	5	TBHP	$\text{CH}_3\text{CN}$	25	Trace
2	10	TBHP	$\text{CH}_3\text{CN}$	25	Trace
3	20	TBHP	$\text{CH}_3\text{CN}$	25	Trace
4	20	TBHP	$\text{CH}_3\text{CN}$	80	10
5	5	NCS/TBHP	$\text{CH}_3\text{CN}$	25	35
6	5	NCS/TBHP	$\text{CH}_3\text{CN}$	65	75
7	1	NCS/TBHP	$\text{CH}_3\text{CN}$	65	60
8	10	NCS/TBHP	$\text{CH}_3\text{CN}$	65	76
9	5	NCS/TBHP	DMF	80	51
10	5	NCS/TBHP	THF	65	62
11	5	NCS	$\text{CH}_3\text{CN}$	65	Trace
12	—	NCS/TBHP	$\text{CH}_3\text{CN}$	65	—

<sup>a</sup> Reaction conditions: benzaldehyde (1 mmol), benzylamine (1 mmol), oxidant (1.0 mmol), solvent (5 ml), time: 2 h.



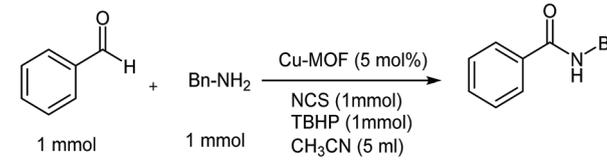
Table 2 Cu-MOF catalyzed synthesis of secondary amides from aldehydes and primary amines<sup>a</sup>

Entry	Aldehyde 1	Amine 2	Product 3	Yield (%)
1				75
2				72
3				70
4				74
5				69
6				68
7				76
8				72
9				74
10				72

<sup>a</sup> Reaction conditions: **1** (1.0 equiv.), **2** (1.0 equiv.), NCS (1.0 equiv.), TBHP (1.0 equiv.), Cu-MOF (10 mol%) in CH<sub>3</sub>CN (5 ml) at 65 °C for 2 h.



Table 3 Recovery and reuse of Cu-MOF in the oxidative amination of aldehyde



Run	1	2	3	4
Yield (%)	75	75	74	72

accordingly.<sup>24</sup> Control experiments (entries 11–12) revealed that an oxidant (TBHP; entry 11) and Cu-MOF catalyst (entry 12), are both necessary for amide bond formation.

After optimization of the model reaction, and in order to understand the substrate scope of this reaction, a wide range of aromatic aldehydes and the amine were reacted under the optimized reaction conditions (Table 2). Good yields of secondary amides were obtained in most cases (3a–g). Aldehydes with electron-donating or electron-withdrawing substituents achieved good to excellent yields of secondary amides (3k–p), indicating that the reaction is not sensitive to electronic effects. Benzyl and aliphatic amines (2a–g) were the most favored substrates, and provided good yields of the amide products.

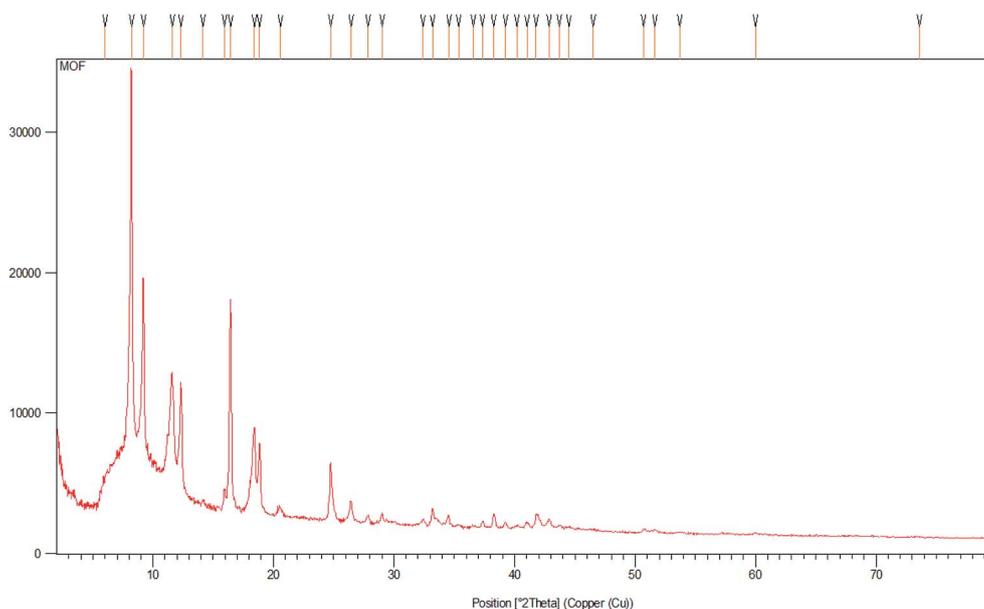
The catalyst Cu-MOF also exhibited good recyclability and stability. For instance, the catalyst was recovered by simple filtration, washed with methanol and dried in an oven, and could be reused four times (Table 3). The catalyst could also be stored for a long time under an air atmosphere without any significant loss of catalytic activity.

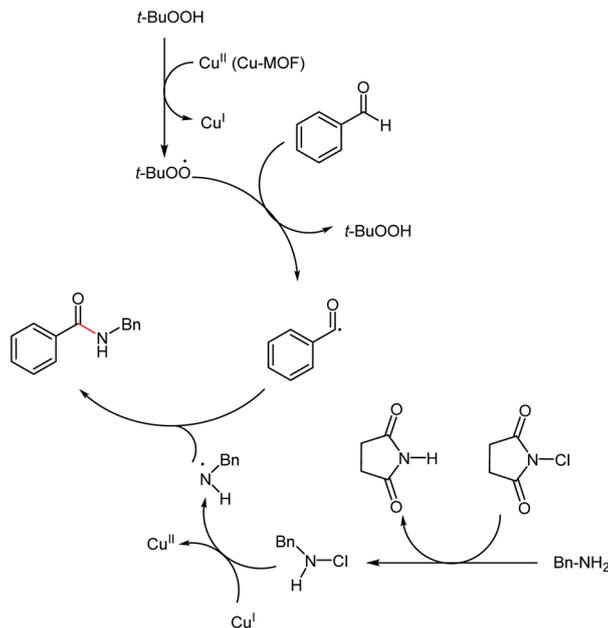
The X-ray diffraction (XRD) pattern of Cu<sub>2</sub>(BDC)<sub>2</sub>DABCO shows that the crystalline structure of Cu<sub>2</sub>(BDC)<sub>2</sub>DABCO is maintained after four runs (Fig. 1).<sup>23</sup>

Based on previously reported studies,<sup>25</sup> we considered a possible mechanism for this reaction, as shown in Scheme 2. Cu(II) oxidized TBHP in such a way that TBHP was transformed into a *tert*-butylperoxy radical and Cu(II) was also reduced to Cu(I). The *tert*-butylperoxy radical captured a hydrogen from benzaldehyde, thereby converting the aldehyde into a benzoyl radical, as reported by Xu *et al.*<sup>26</sup> With the redox reaction, the *N*-chloramine (resulting from the reaction of benzylamine and NCS) was transformed into an amino radical, as reported as reported by Minisci.<sup>21,22,27</sup> In the last step, the amino radical and the benzoyl radical were coupled to yield the corresponding amide products.

A comparison with other catalytic systems in the oxidative amidation of aldehydes and amines demonstrated that our present Cu-MOF catalyst system exhibits a better catalyst performance (Table 4).

The structures of all products were elucidated from their <sup>1</sup>H-NMR spectra and melting points, as described for *N*-

Fig. 1 XRD pattern of recycled Cu<sub>2</sub>(BDC)<sub>2</sub>DABCO.



Scheme 2 Proposed mechanism for the synthesis of amides catalyzed by Cu-MOF.

Table 4 Comparison of activity for different catalytic systems in the oxidative amidation of aldehydes

Entry	Catalyst	Reaction condition	Recyclable	Time	Yield	Ref. no.
1	CuBr (5 mol%)	NBS CH <sub>3</sub> CN/CCl <sub>4</sub> , 90 °C	No	15 h	87	13b
2	NHC/DBU (20 mol%)	HFIP as additive (1.5 equiv.), R-NH <sub>2</sub> (2.5 equiv.), THF	No	8 h	92	15
3	FeSO <sub>4</sub> ·7H <sub>2</sub> O (5 mol%)	TBHP, CaCO <sub>3</sub> , CH <sub>3</sub> CN, 60 °C	No	16 h	72	21
4	CuSO <sub>4</sub> ·5H <sub>2</sub> O	TBHP, K <sub>2</sub> CO <sub>3</sub> , CH <sub>3</sub> CN/H <sub>2</sub> O, 80 °C	No	4 h	63	22a
5	Cu(OAc) <sub>2</sub>	TBHP, CH <sub>3</sub> CN, reflux	No	4 h	74	22b
6	CuSO <sub>4</sub> ·5H <sub>2</sub> O (50 mol%)	TBHP, CH <sub>3</sub> CN, reflux	No	24 h	90	22c
7	Cu <sub>2</sub> (BDC) <sub>2</sub> DABCO (0.05 mol%)	TBHP, CH <sub>3</sub> CN, reflux	Yes	1 h	75	Present work

phenylbenzamide. The <sup>1</sup>H-NMR spectrum of diphenyl amine showed that the aromatic protons gave rise to multiplets in the region δ = 6.92–7.28 ppm, benzylic CH<sub>2</sub> at 4.64 ppm and N–H at 6.45 ppm.

## Conclusion

In conclusion, we have identified Cu-MOF as a green and recyclable heterogeneous catalyst for the efficient oxidative amidation of aldehydes with primary amines for the synthesis of secondary amides. A different range of amines and aldehydes are applicable in this reaction. Furthermore, this novel cost-effective amide formation reaction provides practical alternatives for the synthesis of amides under mild conditions. Further studies on the catalytic application MOFs are in progress and will be presented in the future.

## Conflicts of interest

There are no conflicts to declare.

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