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Original article

# A sulfonate-based Cu(I) metal-organic framework as a highly efficient and reusable catalyst for the synthesis of propargylamines under solvent-free conditions

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A new highly efficient and reusable Cu(I)-MOF has been developed for the synthesis of propargylamine compounds via the three-components reaction of secondary amines, alkynes, and aromatic aldehydes under solvent-free conditions. The desired propargylamines were obtained in good to excellent yields with a low catalyst loading. The catalyst may be recovered and reused for up to 5 cycles without major loss of activity. This protocol has the advantages of excellent yields, low catalyst loading, and catalyst recyclability.

## 1. Introduction

Propargylamine is an important motif that can be found in many natural products and therapeutic drugs [1–4]. They are also key intermediates for the preparation of many nitrogen-containing natural products and biologically active compounds, such as β-lactams [5] and oxotremorine [6] analogues. Because of their importance, many synthetic methods have been developed [7]; however, the most convenient preparation method for propargylamines is the catalytic three-component reaction involving the coupling of an aldehyde, an amine, and a terminal alkyne, which is known as an $A^3$ coupling reaction in the literature [8,9]. Nevertheless, most of the reported $A^3$ coupling catalysts used for the synthesis of propargylamines are homogeneous and have some serious drawbacks, such as the difficulty in the separation and subsequent reuse of the expensive catalysts and the indispensable use of organic solvents [10,11]. New heterogeneous catalysts with greater reusability, efficiency, and ease of synthesis are constantly sought out of environmental concerns. In recent years, micro/mesoporous materials have been extensively studied for their high internal surface area where the hybrid solids composed of organic struts and inorganic pore/channel catalytic sites lead to improved efficiency [12,13]. Metal–organic frameworks (MOFs) are crystalline nodes and have emerged as a novel class of porous materials [14,15]. Thanks to their catalysis friendly features such as large surface areas, porosity, and tunable and functionalizable pore walls, MOFs have proven to be more advantageous than traditional organic and inorganic porous materials in heterogeneous catalysis. Not surprisingly, several MOF-based catalysts, such as Pd/Zn-MOF [16], $Cu(2\text{-pymo})_2$ [17], and post-modified MOF-supported Cu(I) catalysts [18], have been used as the heterogeneous catalysts in the $A^3$ coupling reaction for the synthesis of propargylamines and demonstrated high stability and catalytic activity. Nonetheless, organic solvents are required for these catalytic systems, which is not green according to the green chemistry principles [19]. Recent studies indicate MOFs could be used as green heterogeneous catalysts in water or under solvent-free condition [20–22]. However, to our knowledge, there is no report on a MOF-catalyzed system that operates under solvent-free conditions for this $A^3$ coupling reaction.

As a small subgroup of MOFs, cationic MOFs occur when the positive charges on the metal ions outnumber the negative charges

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on the organic linkers [23]. Extra anions are necessary to balance the charge due to the net positive charge on the frameworks. Among cationic MOFs, sulfonate-based MOFs have been proven to be efficient heterogeneous catalysts due to their strong Lewis acidity as a result of the weak interactions between the sulfonate templates and the cationic metal-organic frameworks. Accordingly, Oliver and coworkers reported the first application of sulfonate-based MOFs as the catalyst for the ketal formation reaction [24]. Our groups are interested in developing novel MOFs for the applications in chiral separations and organic reactions [25,26]. Previously, we reported that sulfonate-based Zn- and Cd-MOFs are highly efficient catalysts for the Biginelli reaction [27] and for the synthesis of multi-functional pyridine derivatives [28] under mild conditions. Deng group has also reported that a sulfonate cadmium coordination polymer can be used to promote the epoxide ring-opening reaction of epoxides and amines [29]. Recently, a copper-exchanged USY zeolite has been reported as the catalyst for the production of propargylamine under solvent-free conditions [30] and a Ag(I)-exchanged K10 montmorillonite clay has been used as heterogeneous catalyst for the synthesis of propargylamine in water [31]. These two materials are both ion-exchangeable and show high Lewis acidity. On the basis of these findings, we speculated that Cu(I)-MOFs containing cationic framework and flexible anionic sulfonate template may also be highly efficient catalysts for the $A^3$ coupling reaction used for the synthesis of propargylamines due to their strong Lewis acidity and structural flexibility and robustness. Herein we report the synthesis, characterization of a new sulfonate-based Cu(I)-MOF and its application as a heterogeneous catalyst in the synthesis of propargylamines under solvent-free conditions.

## 2. Experimental

### 2.1. General

The crystallographic measurement of the Cu(I)-MOF was collected at 98(2) K on a Rigaku X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda$ = 0.71073 Å) with Saturn 724 CCD detector. Powder X-ray diffraction (PXRD) patterns were recorded by a RigakuUltima IV diffractometer operated at 40 kV and 44 mA with a scan rate of 1.0 deg/min. $^1$H NMR and $^{13}$C NMR spectra were obtained using a Varian Mercury 300 MHz spectrometer at room temperature. Tetramethylsilane (TMS) and deuterated solvents (CDCl$_3$, $\delta$ 77.0; DMSO-d$_6$, $\delta$ 39.5) were used as internal standards in $^1$H NMR and $^{13}$C NMR experiments, respectively.

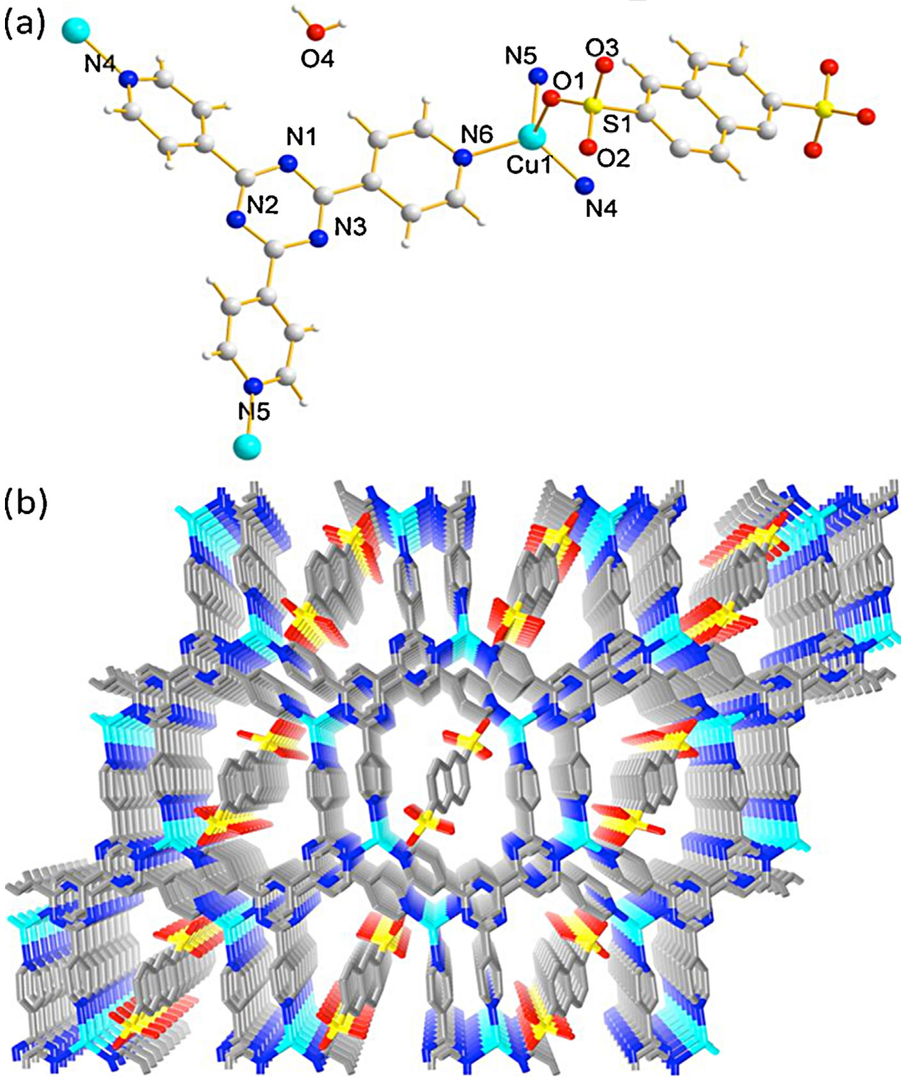

**Fig. 1.** (a) Coordination environment of Cu(I) ion in Cu(I)-MOF and (b) crystallographic a-projection of Cu(I)-MOF (copper: cyan; carbon: gray; sulfur: yellow; oxygen: red; nitrogen: blue, hydrogen atoms are omitted for clarity purpose). (For interpretation of reference to color in this figure legend, the reader is referred to the web version of this article.)

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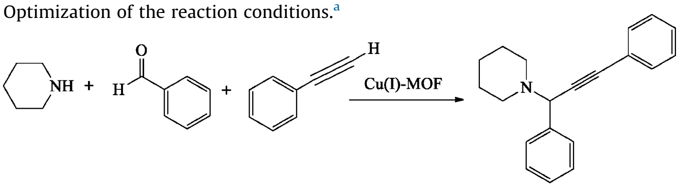
**Table 1**
Optimization of the reaction conditions.[a]



**1a** **2a** **3a** **4a**

| Entry | Catalyst (mol %) | Temp (°C) | Time (h) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | 10.0 | 80 | 14 | 90 |
| 2 | 0 | 80 | 14 | 0 |
| 3 | 10.0 | 60 | 20 | 85 |
| 4 | 10.0 | 40 | 28 | 49 |
| 5 | 10.0 | rt | 24 | 0 |
| 6 | 5.0 | 80 | 18 | 91 |
| 7 | 2.5 | 80 | 24 | 90 |
| 8 | 1.0 | 80 | 48 | 64 |

[a] Unless otherwise specified, all reactions were carried out with **1a** (0.50 mmol), **2a** (0.50 mmol), **3a** (0.50 mmol), and the Cu(I)-MOF catalyst (amount specified in the table) under neat conditions.
[b] Yield of the isolated product after column chromatography.

### *2.2. Synthesis of the Cu(I)-MOF*

$Cu(OAc)_2 \cdot 2H_2O$ (0.036 g, 0.2 mmol), 2,4,6-tri(4-pyridyl)-1,3,5-triazine (TPT) (0.062 g, 0.2 mmol), and 2,6-naphthalenendisulfonic acid disodium salt (NSA) (0.032 g, 0.1 mmol) were dissolved in 10 mL deionized water and were heated at 170 °C for 4 days under autogenous pressure, followed by slow cooling at a rate of 10 °C/min to room temperature. Dark red block crystals were isolated after filtration and washed by D.I. water three times (yield: 0.072 g, 74% based on $Cu(OAc)_2 \cdot 2H_2O$).

### *2.3. General procedure for the three-component reaction*

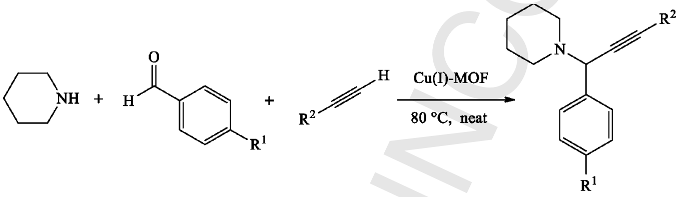
In a sample vial, to a mixture of piperidine (42.5 mg, 0.50 mmol), benzaldehyde (53.1 mg, 0.50 mmol), and phenylacetylene (51.1 mg, 0.50 mmol) was added the Cu(I)-MOF catalyst (6.7 mg, 0.0125 mmol, 2.5 mol%). The mixture was then stirred at 80 °C for the time given in the tables. After completion of the reaction (monitored by TLC), $CH_2Cl_2$ (2 mL) was added and the mixture was centrifuged to recover the catalyst. The crude product obtained after removing the solvent under reduced pressure was purified by column chromatography. Before reuse, the recovered catalyst was washed with $CH_2Cl_2$ (5 mL) and activated by heating at 50 °C under vacuum for 2 h.

## 3. Results and discussion

### *3.1. Crystal structure of the Cu(I)-MOF*

Single crystal structure reveals that the Cu(I)-MOF crystallizes in triclinic space group P-1 and every Cu center is coordinated by with three nitrogen atoms from TPT ligands and one oxygen from a NSA ligand in a tetrahedral coordination geometry (Fig. 1a). There exists a guest water molecule in the lattice. The interactions between the sulfonate ligand and Cu(I) ion [Cu–O distance is 2.370(2)Å] is relatively weak, which renders the Cu(I) site readily accessible as Lewis acid for potential heterogeneous catalysis. The Cu(I) ions are linked by TPT and NSA ligands into 2D frameworks, which are further stabilized by π–π stacking along a axis (Fig. 1b). However, due to condensed packing, Cu(I)-MOF does not show any pores in 3D structure, and no permanent porosity has been established.

**Table 2**
Three-component synthesis of propargylamines using piperidine catalyzed by the Cu(I)-MOF.[a]



**1a** **2** **3** **4**

| Entry | $R^1$ | $R^2$ | Time (h) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | H | Ph | 24 | 90 |
| 2 | H | $2\text{-}BrC_6H_4$ | 24 | 83 |
| 3 | H | $4\text{-}MeOC_6H_4$ | 26 | 87 |
| 4 | H | $2\text{-}CF_3C_6H_4$ | 27 | 85 |
| 5 | Cl | Ph | 24 | 89 |
| 6 | Br | Ph | 24 | 88 |
| 7 | Me | Ph | 24 | 88 |

[a] All reactions were carried out with **1a** (0.50 mmol), **2** (0.50 mmol), and **3** (0.50 mmol) and the MOF catalyst (0.0125 mmol, 2.5 mol %) under neat conditions at 80 °C.
[b] Yield of the isolated product after column chromatography.

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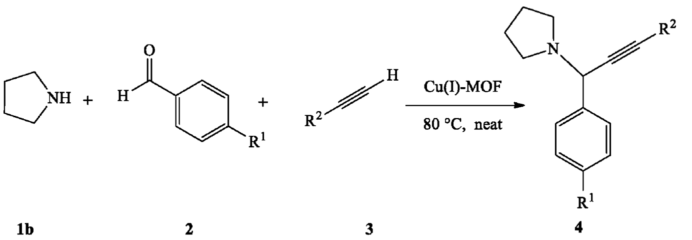
**Table 3**

Three-component synthesis of propargylamines using pyrrolidine catalyzed by the Cu(I)-MOF.[a]



| Entry | $R^1$ | $R^2$ | Time (h) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | H | Ph | 24 | 89 |
| 2[c] | H | 4-$MeOC_6H_4$ | 26 | 58 |
| 3 | $CH_3$ | Ph | 26 | 86 |
| 4 | Cl | Ph | 24 | 62 |
| 5 | MeO | Ph | 24 | 59 |

[a] Unless otherwise indicated, all reactions were carried out with **1b** (0.50 mmol), **2** (0.50 mmol), and **3** (0.50 mmol) and the MOF catalyst (0.0125 mmol, 2.5 mol%) under neat conditions at 80 °C.

[b] Yield of the isolated product after column chromatography.

[c] With a catalyst loading of 10 mol %.

### 3.2. *Optimization of model reaction*

Using piperidine (**1a**), benzaldehyde (**2a**), and phenylacetylene (**3a**) as the model substrates, we first examined the catalytic activity of the Cu(I)-MOF in the three-component reaction. The reaction was attempted under neat conditions in order to avoid the use of any organic solvent [18]. The results are summarized in Table 1. As the data in Table 1 show, when 10 mol % of the Cu(I)-MOF was applied at 80 °C under neat conditions, the desired propargylamine **4a** was formed in a high yield (90%) after 14 h (entry 1). The catalytic activity of the Cu(I)-MOF for this reactions was unequivocally established by conducting a control reaction in the absence of the catalyst: No formation product **4a** was observed without the MOF catalyst under otherwise identical reaction conditions (Table 1, entry 2). When the reaction temperature was decreased, a significant loss of the catalytic activity was observed, as is evident from the longer reaction times and lower product yields (entries 3 and 4). In addition, when the reaction was performed at room temperature, there was no observable conversion of the substrates (entry 5). Nevertheless, the catalyst loading can be reduced (entries 6 and 7) and the reaction proceeds well even with a catalyst loading of only 2.5 mol %, without affect the product yield, although the reaction time is slightly longer (entry 7). However, further reducing the catalyst loading to 1.0 mol% led to a much slower reaction and the product yield dropped significantly to 64% (entry 8).

### 3.3. *Scope of the $A^3$ coupling reaction*

With the optimized reaction conditions at hand, we then evaluated the scope of this reaction. The results are summarized in Table 2. As shown by the data in Table 2, besides phenylacetylene, 2-bromophenylacetylene also underwent the coupling reaction smoothly to yield the corresponding propargylamine in good yield (83%, entry 2). Similarly, high yields were obtained for phenylacetylenes with an electron-donating group (4-MeO) or an electron-withdrawing group (2-$CF_3$) on the phenyl ring (entries 3 and 4). Substituted benzaldehydes are also good substrates for this coupling reaction. High product yields were obtained when 4-halo-substituted benzaldehydes were reacted with phenylacetylene and piperidine (entries 5 and 6). When 4-methylbenzaldehyde was used, the corresponding propargylamine was obtained in 88% yield (entry 7).

Next pyrrolidine was used in the three-component coupling reaction under identical conditions. The results are summarized in Table 3. When benzaldehyde and phenylacetylene were used as the starting materials, the corresponding propargylamine was obtained in 89% yield (entry 1), which is similar to that of piperidine (Table 2, entry 1). However, unlike that of piperidine (Table 2, entry 3), 4-methoxyphenylacetylene is much less reactive and gave a much lower yield of the propargylamine (58%) even with a much higher catalyst loading (10 mol %, entry 2). On the other hand, 4-methylbenzaldehyde produced a good yield of the expected product (entry 3). However, 4-chloro- and 4-methoxy

**Table 4**

Catalyst recyclability study.[a]

$$\mathbf{1a} + \mathbf{2a} + \mathbf{3a} \xrightarrow[80\ ^\circ\mathrm{C},\ \mathrm{neat}]{\mathrm{Cu(I)\text{-}MOF}} \mathbf{4a}$$

| Entry | Cycle | Catalyst recovery (%) | Time (h) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | I | 96 | 14 | 91 |
| 2 | II | 96 | 22 | 82 |
| 3 | III | 96 | 15 | 88 |
| 4 | IV | 95 | 15 | 88 |
| 5 | V | 95 | 20 | 87 |

[a] Unless otherwise specified, all reactions were carried out with **1** (0.50 mmol), **2a** (0.50 mmol), and **3a** (0.50 mmol) and the MOF catalyst (0.0125 mmol, 2.5 mol%) under neat conditions at 80 °C.

[b] Yield of the isolated product after column chromatography.

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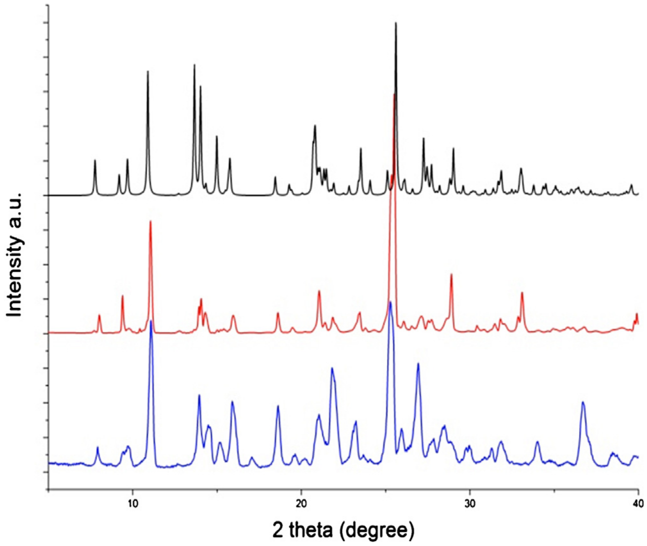

**Fig. 2.** PXRD of simulated Cu(I)-MOF (black), fresh Cu(I)-MOF (red) and Cu(I)-MOF after five times catalytic cycle (blue). (For interpretation of reference to color in this figure legend, the reader is referred to the web version of this article.)

groups on benzaldehyde resulted in much lower product yields (entries 4 and 5). Thus, the coupling reaction with pyrrolidine as the amine component is highly substrate-dependent.

### 3.4. Catalyst stability and recyclability

The major advantages of the MOF catalysts lie in the fact that they can be readily recovered after the reaction and reused due to their stability and heterogeneous nature.

To verify the stability of the catalyst under the experimental conditions, leaching experiment was performed by examining the $^1$H NMR of the supernatant of reaction mixture. No leaching of TPT or NSA ligand was observed in the supernatant. To further confirm that the catalysis is indeed heterogeneous, we filtered the reaction mixture after 5 h, and continued to monitor the progress of the reactions in the filtrate. No further catalytic reactions has been observed in the filtrated solution.

We also investigated the recyclability of this new Cu(I)-MOF using piperidine (**1a**), benzaldehyde (**2a**) and phenylacetylene (**3a**). The results are summarized in Table 4. In fact, the MOF catalyst could be easily recovered by centrifuging the reaction mixture after the reaction. The PXRD pattern indicates the crystal structures of Cu(I)-MOF maintained after the catalytic reactions (Fig. 2).

After washing the recovered MOF with $CH_2Cl_2$ (5 mL) to remove traces of the previous reaction mixture and drying it under vacuumed at 50 °C for 2 h, the MOF catalyst can be directly used in the next cycle. As the data in Table 4 show, the Cu(I)-MOF catalyst may be easily recovered and successfully reused for up to 5 cycles without any significant loss in the catalytic activity.

## 4. Conclusion

In summary, we have developed a new Cu(I)-MOF that is a highly efficient catalyst for the three-component synthesis of propargylamines under solvent-free conditions. The corresponding propargylamines were obtained in good to excellent yields, especially when piperidine was used as the amine component. Heterogeneity tests demonstrate the absence of leaching under the examined experimental conditions. The MOF catalyst can be readily recycled and reused without major loss of their activity for up to five cycles. This heterogeneous catalyst based on the Cu(I)-MOFs might lead to its practical applications on the production of propargylamine in an environmentally benign manner.

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