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FULL PAPER

A novel copper framework with amino tridentate N-donor ligand as heterogeneous catalyst for ring opening of epoxides

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A novel metal–organic framework (MOF) $[Cu_3L(2,6\text{-}NDC)_2]\cdot 0.5DMF$ (**MOF-Cu-1**) was synthesized by solvothermal reaction of copper nitrate trihydrate with 2,6-naphthalenedicarboxylic acid (2,6-H_2NDC) and amino tridentate N-donor containing ligand of N^1-(4-(1*H*-imidazol-1-yl)benzyl)-N^1-(2-aminoethyl)ethane-1,2-diamine (L). **MOF-Cu-1** is a three-dimensional (3D) framework with one-dimensional (1D) channels. Because of the high stability of the framework and the existence of amino functional groups, **MOF-Cu-1** presents excellent heterogeneous catalytic activity for ring-opening reaction of epoxides by amines and reusability for four cycles with negligible loss of efficiency.

KEYWORDS

amino tridentate N-donor ligand, epoxides, heterogeneous catalyst, metal–organic framework, ring-opening reaction

1 | INTRODUCTION

Epoxides are common organic molecules with wide range of synthetic applications as intermediates in pharmaceutical and agrochemical industries.[1] The classical ring opening approach of epoxides involves heating of epoxides with large excess of amines at elevated temperature and works less well with poor nucleophilic amines, indicating that it is necessary to develop efficient catalysts for the ring opening reaction of epoxides.[2] Some homogeneous catalysts, including metal salts and acid, have already been applied.[3–5] However, with the rise of environmental awareness, heterogeneous catalysis has attracted extensive attention owing to the effective

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combination of the precise active sites of organometallic complexes and feasible recycling utilization.[6–10]

Metal–organic frameworks (MOFs) have been reported to present excellent performance in numerous cases of heterogeneous catalytic organic reactions resulting from their unique porous framework structures.[11–17] Among them, the instances of utilizing chelating effect to design and synthesize novel stable heterogeneous MOFs catalysts are particularly interested. It has been successfully verified that MOFs equipped with amino tridentate N-donors are able to withstand harsh heating and pressure conditions in our previously reported works.[18–20] In this work, to further explore the universality of this conception, we designed, solvothermally synthesized and characterized a novel crystalline MOF catalyst **MOF-Cu-1**, by utilizing $Cu(NO_3)_2{\cdot}3H_2O$, 2,6-naphthalenedicarboxylic acid (2,6-H_2NDC) and an amino tridentate N-donor containing ligand, namely N^1-(4-(1*H*-imidazol-1-yl)benzyl)-N^1-(2-aminoethyl)ethane-1,2-diamine (L) (Scheme 1). The combination of ligand L with copper salt possesses strong chelating effect comparing with the previously applied metal ions of Zn(II) and Cd(II).[18–21] Moreover, **MOF-Cu-1** shows preeminent chemical stability in varied solvent, and the heterogeneous catalytic activity was further examined for the ring-opening reactions of epoxides by different amines.

2 | EXPERIMENTAL

2.1 | Materials and characterization

All commercially available chemicals and solvents are of reagent grade and were used as received without further purification. Ligand L was prepared according to the previously reported procedures.[19] Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer with Cu Kα ($\lambda = 1.5418$ Å) radiation. Thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo (TGA/DSC1) thermal analyser with a heating rate of 10°C min^{-1} under a nitrogen atmosphere from room temperature to 800°C. Fourier Transform Infrared-Attenuated Total internal Reflectance (FTIR-ATR) spectra was measured on an infrared spectrophotometer (Bruker Tensor II) equipped with a diamond ATR module in the range of 400–4000 cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on Bruker-DRX (500 and 125 MHz, respectively) instruments internally referenced to TMS ($SiMe_4$) or chloroform signals. Elemental analyses for C, H and N were performed using an Elementar Vario MICRO. EPR spectrum was obtained on a Bruker EMX plus-6/1 variable temperature X-band apparatus in the solid state at 90 K.

2.2 | Synthesis of $[Cu_3L(2,6\text{-}NDC)_2]{\cdot}0.5DMF$ (MOF-Cu-1)

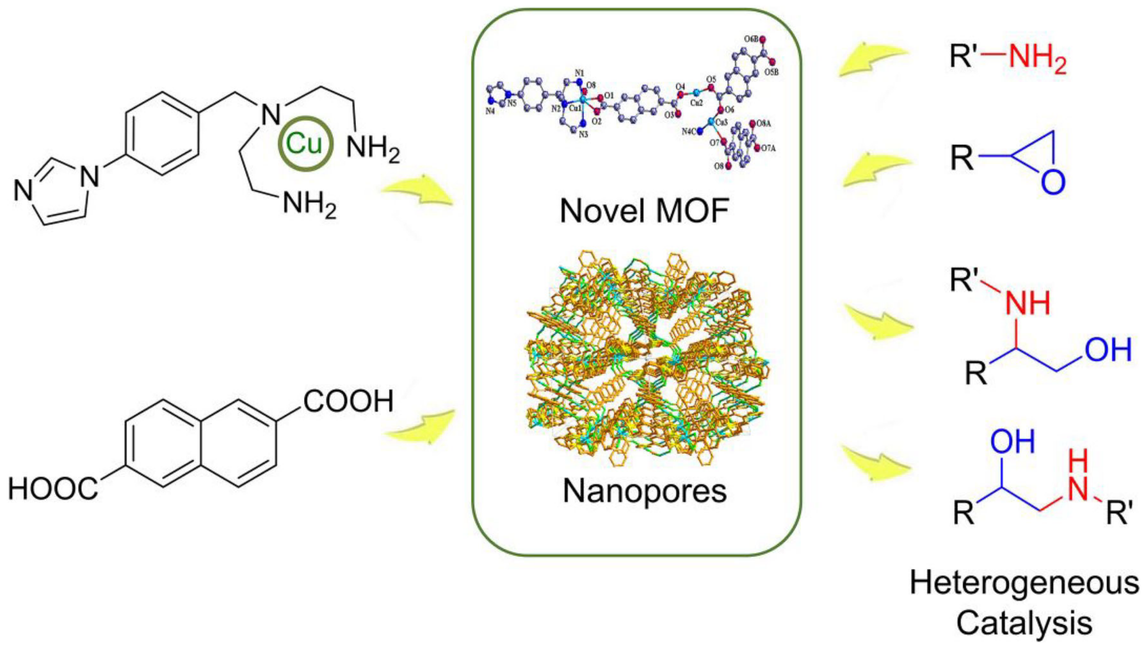
A mixture of 2,6-H_2NDC (17.4 mg, 0.08 mmol), L (20.76 mg, 0.08 mmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (48.6 mg, 0.2 mmol) in *N*,*N*-dimethylformamide (DMF)/methanol mixed solvent (8 ml, v/v = 3/1) was sealed in a 15-ml Teflon-lined reactor and heated for 72 h at 110°C under autogenous pressure. After cooling down to room temperature at a rate of 0.05°C per minute, blue block crystals were isolated in 52% yield. FTIR-ATR (Figure S1): 3175 (w), 1668 (w), 1610 (s), 1558 (vs), 1497 (m), 1391 (vs), 1346 (vs), 1192 (m), 1133 (w), 1056 (m), 920 (m), 885 (m), 779 (vs), 650 (m), 560 (m), 522 (s), 470 (vs) cm^{-1}. Elemental analysis calcd. for $C_{39.5}H_{36.5}Cu_3N_{5.5}O_{8.5}$: C, 51.86; H, 4.02; N, 8.42%; found C, 51.81; H, 4.25; N, 7.63%. EPR (Figure S2): $g \approx 2.05642$ at 90 K.

2.3 | Catalytic reaction procedure

As a typical reaction, styrene oxide (0.1 mmol) and benzylamine (0.1 mmol) were placed in a reaction vessel containing **MOF-Cu-1** (1.5 mg, 1.7 mol%). Then, this mixture was magnetically stirred under solvent-free conditions at 25°C for 4 h. Next, dichloromethane was added as a diluent solvent to separate the products from the solid catalyst by centrifugation. The final target products were isolated from the supernatant by column chromatography with silica gel (CH_2Cl_2/*n*-hexane = 2:1). Identification of the products was implemented by ^1H and ^{13}C NMR techniques. After the end of the reaction, the catalyst was refreshed by washing with dichloromethane (3 × 5 ml) and dried in air. The recovered catalyst was consecutively reused in the next cycle with fresh substrates. Each cycle followed the same procedure for catalyst recycling.

2.4 | X-ray crystallography

Crystallographic data for **MOF-Cu-1** were collected on a Bruker Smart Apex II CCD single-crystal X-ray diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 193 (2) K using the ω-scan technique. The integration of the diffraction data and intensity corrections for Lorentz and polarization effects were carried out using the SAINT program.[22] Semi-empirical absorption corrections were applied using SADABS program.[23] The structure was solved by direct methods with SHELXT-2014, expanded by subsequent Fourier-difference synthesis, and all the nonhydrogen atoms were



SCHEME 1 Schematic diagram of the formation of **MOF-Cu-1**, crystal structure and its application in heterogeneous catalysis

refined anisotropically on F^2 using the full-matrix least-squares technique and the SHELXL-2018 crystallographic software package.[24,25] The free solvent molecules in the unit cell have been taken into account with the SQUEEZE option of the PLATON program.[26] Hydrogen atoms were introduced at the calculated positions. The SHELX was interfaced with SHELXLE GUI for most of the refinement steps.[27] The final chemical formula of **MOF-Cu-1** was calculated based on volume/count electron analysis and the TG data of as-synthesized crystal (Figure S3). The reported refinement is of the guest-free structure obtained by the SQUEEZE routine, and the result was attached to the CIF file. The details of crystal parameters, data collection and refinements are listed in Table 1, and the selected bond lengths and angles are given in Table S1.

3 | RESULTS AND DISCUSSION

3.1 | Crystal structure description

Single crystal X-ray diffraction (XRD) analysis reveals that **MOF-Cu-1** crystallizes in triclinic *P*-1 space group (Table 1). As shown in Figure S1, the FTIR shows that there are no vibration bands between 1680 and 1760 cm^{-1}, implying the complete deprotonation of 2,6-H_2NDC to give NDC^{2-} in **MOF-Cu-1**. The asymmetric unit of **MOF-Cu-1** contains three copper atoms, one L and two NDC^{2-} ligands (Figure 1a). Cu$_1$ is

TABLE 1 The crystallographic data of **MOF-Cu-1**

	MOF-Cu-1
Empirical formula	$C_{39.50}H_{36.50}Cu_3N_{5.50}O_{8.50}$
Formula weight	914.86
Temperature (K)	193 (2)
Crystal system	Triclinic
Space group	*P*-1
a (Å)	11.844 (2)
b (Å)	12.748 (2)
c (Å)	14.126 (2)
α (°)	97.571 (2)
β (°)	92.395 (3)
γ (°)	112.918 (3)
V (Å^3)	1937.1 (6)
Z	2
D_c (g cm^{-3})	1.568
F (000)	934
θ range (°)	1.462–27.497
Reflections collected	17,423
Unique data	8701
Goodness-of-fit	1.035
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0493
$wR_2{}^b$ ($I > 2\sigma(I)$)	0.1411

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

five-coordinated by three nitrogen atoms (N1, N2 and N3) from the amino tridentate N-donor of L and two oxygen ones from two different NDC^{2-}. Cu_3 is three-coordinated by one nitrogen from imidazole group of L and two oxygen atoms from two different NDC^{2-} with T-shaped coordination geometry, whereas Cu_2 has linear $[CuO_2]$ coordination environment. The T-shaped and linear coordination geometries together with consideration of charge balance of the framework imply that Cu_2 and Cu_3 are monovalent Cu(I) rather than Cu(II). It means that Cu(II) was partially reduced to Cu(I) during the formation of **MOF-Cu-1**, which is speculated to arise from the reducing ability of DMF.[28,29] The presence of one Cu(II) was ensured by EPR spectral measurements. As shown in Figure S2, the typical spectral shape and position ($g \approx 2.05642$) at 90 K confirmed the d^9 configuration of Cu(II).[30–32] In turn, each L and NDC^{2-} ligand links two Cu atoms. Such arrangement produces a three-dimensional (3D) framework with different channels (Figure S4), which is beneficial for mass transferring during the catalytic reactions. For example, there are channels with size of 3.73 × 21.79 Å from the view along *a* axis (Figure 1b). Two 3D nets mutually interpenetrate each other to result in formation of a twofold interpenetrated structure (Figure 1b), which could be well recognized as a kind of self-complementation to stabilize the framework.[19] After the free solvent molecules were removed, the void volume is approximately 387 $Å^3$ per 1937.1 $Å^3$ unit cell (20.0% of the total crystal volume). To better understand the nature of this intricate architecture, topological analysis was performed.[33] Cu_1 can be considered as a three-connected node, WHEREAS Cu_2 and Cu_3 are combined together as a four-connected node. Accordingly, a three-nodal 3D net with a rare reported Schläfli symbol of $\{4^2 \cdot 6^3 \cdot 8\}\{4^2 \cdot 6\}_2\{4^6 \cdot 6^{16} \cdot 8^5 \cdot 10\}$ is generated (Figure 1c).

3.2 | PXRD and thermal analysis

PXRD pattern of as-synthesized **MOF-Cu-1** was obtained at room temperature. The positions of characteristic

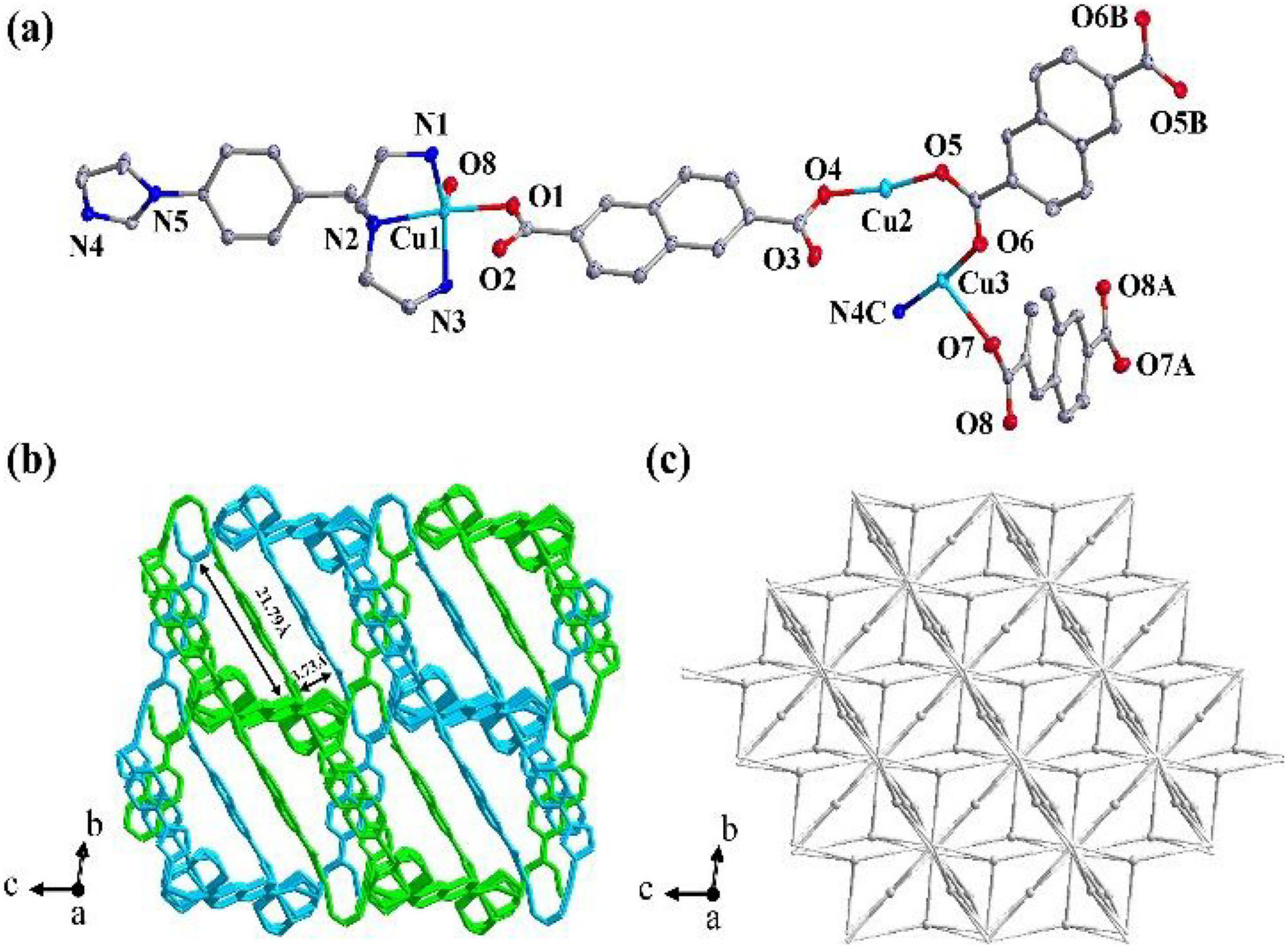


FIGURE 1 (a) The coordination environment of Cu(II) and Cu(I) in **MOF-Cu-1** with ellipsoids drawn at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. (b) The interpenetrating framework and channels of **MOF-Cu-1** in the view along a axis. (c) Topology of **MOF-Cu-1** peaks are matched well with the simulated ones created by single crystal data (Figure S5), manifesting the phase purity of the synthesized sample. The simulated PXRD of **MOF-Cu-1** in Figure S5 has a low-angle peak that appears of lower intensity in the experimental pattern, which may result from the different crystal orientation between the abundant crystal powders and a single crystal.[34] Thermogravimetric analysis (TGA) was performed under N_2 atmosphere to test the thermal stability of the framework. As illustrated in Figure S3, the TG data of **MOF-Cu-1** exhibited gradual weight loss of 3.5 w% before 225°C, which corresponds to the loss of free solvent DMF molecules (calcd. 3.9%). The following weight loss was found to start from 225°C representing the collapse of the framework, which was verified by the phenomenon of turning to brown lump after heating to 240°C. In order to prove the solvent molecules in the pores, **MOF-Cu-1** was heated to 225°C and kept for 5 h in a nitrogen atmosphere for the solvent removal. The TG data of the obtained sample indicates that the solvent molecules has been cleaned up and the existence of DMF in as-synthesized **MOF-Cu-1** is verified by the disappearance of the characteristic peak of 1493 cm^{-1} in the FTIR-ATR spectrum after heating (Figure S6).[35,36] In addition, the residue at 800°C for the sample after solvent removal is approximately 26% corresponding to the CuO (calcd. 27%).

3.3 | Chemical stability

The chemical stability of **MOF-Cu-1** was ascertained by treating it in air with varied common solvent for 48 h. PXRD patterns were tested for the dried samples. To our delight, **MOF-Cu-1** shows outstanding stability in these solvents without variation of XRD patterns (Figure 2). The results point out that the chemical stability of **MOF-Cu-1** offers great potential for gratifying heterogeneous catalysis. Besides, the interpenetrating structure formed by solvothermal reaction may also strengthen the stability of **MOF-Cu-1**.[37]

3.4 | Catalytic properties

The catalytic performance of **MOF-Cu-1** was examined by conducting amination of epoxides. For finding out the optimal experimental conditions, styrene oxide and benzylamine were selected as representative substrates, as their product 2-(benzylamino)-2-phenylethanol (abbreviated as BAPE) is a significant intermediate for the synthesis of imines and oxazolidine derivatives, which are critical to produce biological organic compounds containing hetero-nitrogen atom (Scheme 2).[38–40] The analysis of the resulted products was carried out by ^1H NMR using CH_2Br_2 as an internal standard. Furthermore, these experiments clearly suggest that **MOF-Cu-1** can effectively promote the reaction and afford BAPE as the major product.

3.4.1 | Reaction solvent

Various solvents with different polarity such as acetonitrile, ethyl acetate (EA), tetrahydrofuran (THF), dichloromethane (DCM), hexane and DMF were chosen

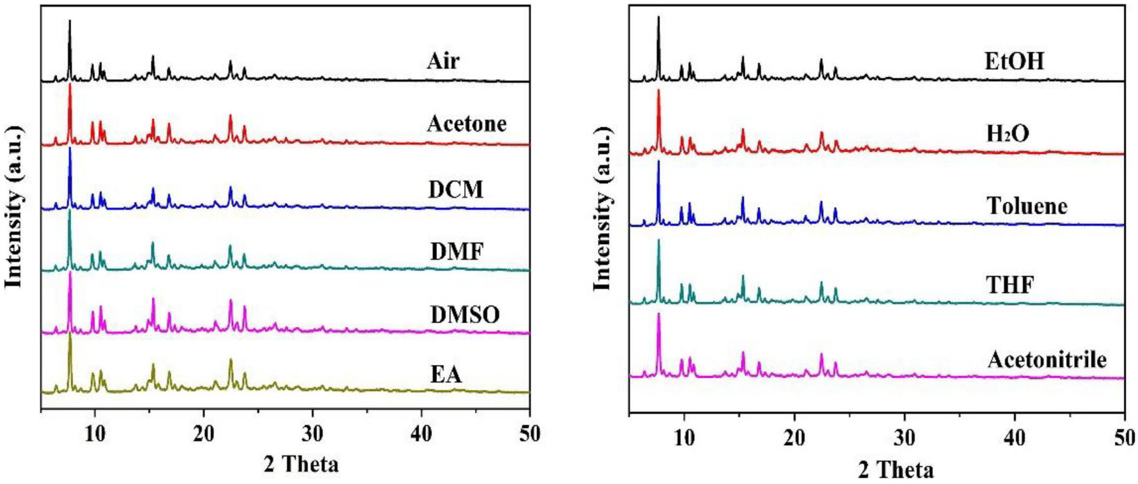


FIGURE 2 Powder X-ray diffraction (PXRD) patterns of **MOF-Cu-1** after preserving for 48 h under different conditions: air, acetone, dichloromethane (DCM), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethyl acetate (EA), ethanol (EtOH), water (H_2O), toluene, tetrahydrofuran (THF) and acetonitrile

and the ring-opening reactions between styrene oxide and benzylamine exhibited not detectable to moderate yield of 56% after stirring for 5 h at 25°C (Table 2, entries 1–6). Particularly, under solvent-free conditions, the ring-opening reaction gratifyingly afforded a good yield up to 98% (Table 2, entry 7) under the identical conditions. With the comprehensive consideration of high efficiency and eco-friendly and environmentally friendly chemistry, the following experiments were all performed under solvent-free conditions.

3.4.2 | Reaction time and heterogeneous catalysis

For further study, the next logical action was to investigate the influence of reaction time under the same conditions. The time-dependent yield profile for the ring-opening reaction of styrene oxide and benzylamine was provided in Figure 3 by observing in the yield of desired product BAPE as a function of reaction time. It was found that 4 h was the optimal selection as acting as the minimum time to complete the reaction (Figure 3a). For facilitating comparison, a control experiment without addition catalyst of **MOF-Cu-1** was performed (Figure 3c) and displayed negligible yield, which stresses the necessity of catalytic agent in the reaction between styrene oxide and benzylamine. In order to further validate whether the present catalytic method is inherently heterogeneous or not, the catalyst **MOF-Cu-1** was filtered out from the mixture after reacting for 2 h with the yield of 41%. Next, the reaction in the absence of catalyst was carried out for the remaining time (Figure 3b). The observed results suggested that the yield was almost a constant after eliminating **MOF-Cu-1** from the reaction vessel, which excluded the possibility of catalysing by species etched from the catalyst.

TABLE 2 Optimization of reaction solvent for the ring opening of styrene oxide by benzyl- amine employing **MOF-Cu-1** as heterogeneous catalyst

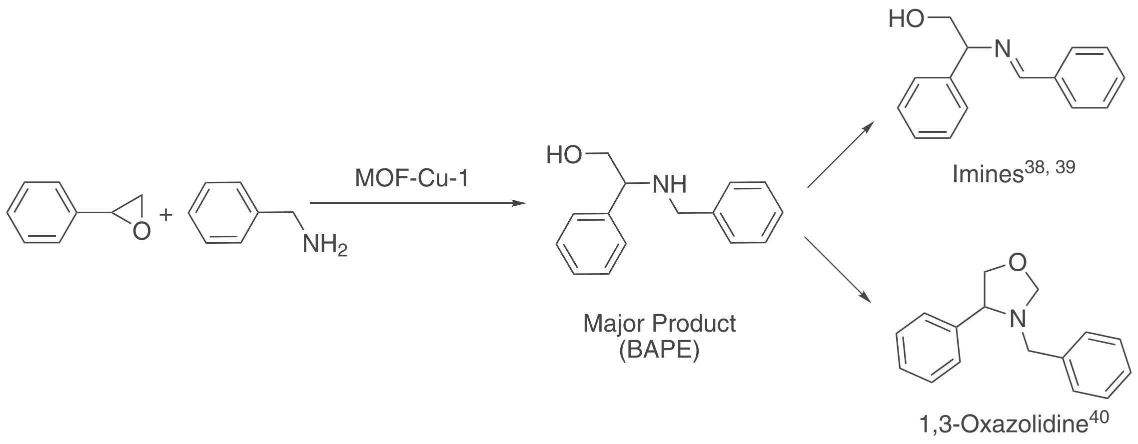
Entry	Solvent	Yield of product[a] (%)
1	Acetonitrile	16
2	EA	45
3	THF	41
4	DCM	56
5	Hexane	1
6	DMF	Not detectable
7	/	98

Note: Reaction conditions unless specified otherwise: styrene oxide (0.1 mmol), benzylamine (0.1 mmol), solvent (1 ml), catalyst **MOF-Cu-1** (1.5 mg), 25°C, 5 h.

[a] The yield was determined by ^{1}H NMR analysis of crude product using CH_2Br_2 as an internal standard.

3.4.3 | Recycling performance

The high stability of **MOF-Cu-1** in varied organic solvent has already mentioned above and then the stability in the optimal reaction conditions is further tested by stirring for 4 h at 25°C without the use of solvent. After completion of the first-time reaction, the catalyst was recovered by centrifuging, washing with dichloromethane and then drying in air. The recovered catalyst was used for the next round of reaction with fresh substrates under the identical conditions and showed almost consistent activity with a slight decrease in the yield of BAPE (Figure 4). The conversion decrease may be attributed to the loss of a small amount of catalyst in the recovering experiment.[9,41] In addition, the crystalline pattern of the catalyst after being used for four cycles was tested by PXRD analysis and revealed the identical XRD pattern with that of the original **MOF-Cu-1** (Figure 5), which indicated the



SCHEME 2 The reaction scheme for producing BAPE and the reported derivatives

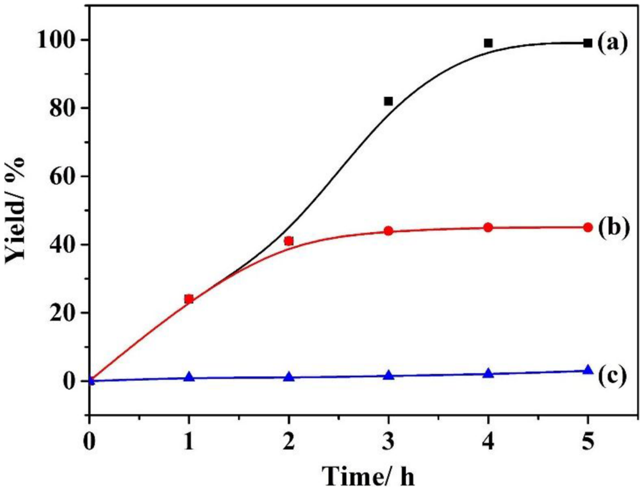


FIGURE 3 Time-yield plot for ring opening of styrene oxide by benzylamine using **MOF-Cu-1** as a heterogeneous catalyst: (a) with catalyst; (b) with filtering of the catalyst after reaction for 2 h; (c) without catalyst. Reaction conditions: styrene oxide (0.1 mmol), benzylamine (0.1 mmol), **MOF-Cu-1** (1.5 mg), 25°C, without solvent. The yield was determined by 1H NMR analysis of crude product using CH2Br2 as an internal standard

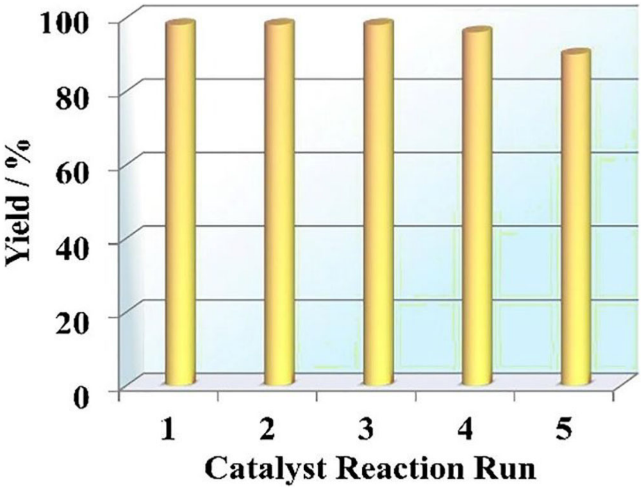


FIGURE 4 Circulation yields for the ring opening of styrene oxide by benzylamine using **MOF-Cu-1** as a catalyst

structural integrity during the reaction process. To sum up, these results indicate the excellent recyclable catalytic performance of **MOF-Cu-1** in this reaction.

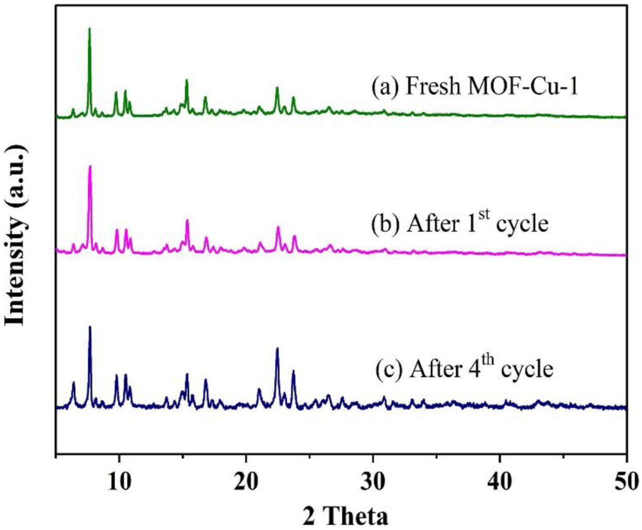
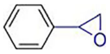
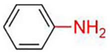
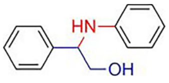
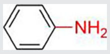
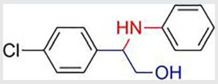
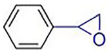
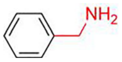
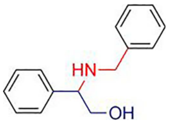
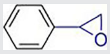
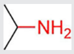
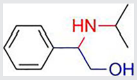
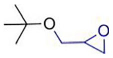
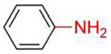
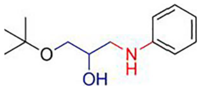
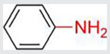
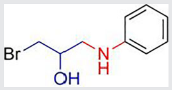
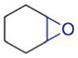
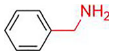
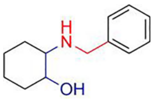


FIGURE 5 Comparison of the Powder X-ray diffraction (PXRD) patterns of fresh sample of **MOF-Cu-1** (a) with that of the sample recovered after the first (b) and fourth (c) cycles of catalysis

3.4.4 | Scope of substrates

In order to further explore the applicable scope of this catalytic reaction, multiple substrate combinations with different features including the aromatic epoxide with aniline, aromatic epoxide with alkylamine and alkyl epoxide with aniline, were subjected to react under the optimal conditions. As demonstrated in Table 3, great reaction yields were achieved ranging from 85% to 98% (Table 3, entries 1–7, Figures S7–S13), and especially, cyclohexene oxide provided a satisfactory yield of 85% with benzylamine (Table 3, entry 7). In addition to the excellent reactivity catalysed by **MOF-Cu-1**, the regioselectivity is apparently controlled by the substrate effect that the electronic property and steric hindrance of the oxirane ring play a major role in the regioisomer of reaction products.[42] The reaction between styrene oxide and aniline as well as 4-chlorostyreneoxide, respectively, obtained 97% and 98% yields (Table 3, entries 1 and 2) and the yields of the reactions between styrene oxides and benzylamine, isopropylamine are 98% and 86%, respectively (Table 3, entries 3 and 4). In the above situations, isomer A (Scheme 3) was detected as the main regioisomer that was dominated by the electronic effect.[43,44] It is supposed that the coordination between **MOF-Cu-1** and epoxide is conducive to form the carbocation at aromatic methyl position, which could be stabilized by p–π conjugation for reducing the transition state energy during the amino attack.[45] Isopropylamine is apparently less reactive, which may arise from the higher basicity of aliphatic amines resulting in the occupation of the uncoordinated catalytic site and the catalyst poisoning.[46–48] Furthermore, when aniline individually reacted with alkyl oxirane *tert*-butyl glycidyl ether and 1-bromo-2,3-epoxypropane (Table 3, entries 5 and 6), the yields were manifested as 96% and 90% and isomer B turned into the major product. It is probably because of the prior

TABLE 3 Ring opening of varied epoxide by aryl and alkyl amine substrates employing **MOF-Cu-1** as a heterogeneous catalyst

Entry	Epoxide	Amine	Major product	Major isomer	Yield (%)[a] (A: B)[b]
1				A	97 (97: trace)
2				A	98 (98: trace)
3				A	98 (98: trace)
4				A	86 (86: 3)
5				B	96 (trace: 96)
6				B	90 (5: 90)
7				-	85

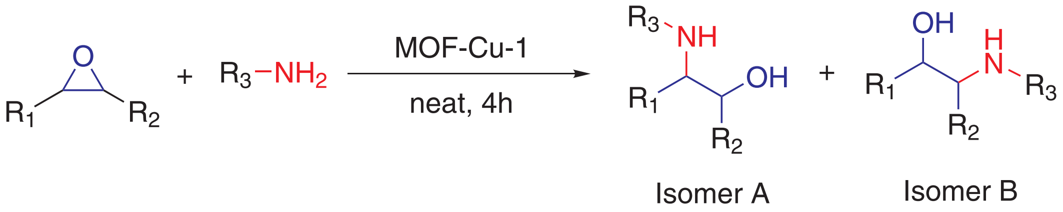
Note: Reaction conditions unless specified otherwise: epoxide (0.5 mmol), amine (0.5 mmol), **MOF-Cu-1** (7.5 mg, 0.026 mmol), 25°C, solvent free, stirred for 4 h.

[a] The yields were calculated by using the isolated product.

[b] The selectivity was determined by ^{1}H NMR analysis of crude product using the major product as an internal standard.

steric effect, since the carbon atom with less substituted functional groups becomes much more vulnerable to be attacked by the nucleophilic amine owing to the disappearance of the arylmethyl carbocation.[49] The catalytic activity of our present **MOF-Cu-1** is compared with other previously reported works on the reaction of styrene oxide and benzylamine (Table S2). In terms of product yield, **MOF-Cu-1** ranks among the top and also performs well in reaction rate, generally manifesting excellent catalytic efficiency.

A possible mechanism is proposed for the aminolysis of epoxide with **MOF-Cu-1** as heterogeneous catalyst based on the structure of **MOF-Cu-1** and previous literature reports.[50] Besides the classical mechanism that the



SCHEME 3 Reaction scheme for the ring opening of epoxides by primary amine under neat conditions using **MOF-Cu-1** as a heterogeneous catalyst

coordinatively unsaturated metal centers serve as active sites (Scheme S1), the structure of **MOF-Cu-1** may also plays a significant role in promoting catalytic efficiency. As a matter of fact, the MOF is a porous framework without end capping, and the walls of the macro-intergranular pores are distributed with abundant uncoordinated copper site, carboxylate and amino groups. Compared with the majority of narrow internal pores, a unique channel effect is allowed to display for facilitating the diffusion and concentration of organic substrates, intermediate formation and approach to the active sites.[51] Furthermore, the interpenetrating structure of **MOF-Cu-1** itself may play a significant role in mass transferring.[52] As it is mentioned above, the integral bulky **MOF-Cu-1** heterogeneous solid catalyst is a functional porous structure that is beneficial to boost catalytic efficiency.

4 | CONCLUSIONS

In summary, a novel stable 3D MOF with coordinatively unsaturated metal sites and amino tridentate N-donor containing ligand L was successfully synthesized as a heterogeneous catalyst for epoxide ring-opening reactions by varied amines. The catalyst can be separated and reused for multicycles without significant yield loss or structural damage.

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AUTHOR CONTRIBUTIONS

Ziqing Huang: Conceptualization; formal analysis; investigation; methodology. **Zou-Hong Xu:** Investigation; methodology. **Xiao-Hui Liu:** Investigation; methodology. **Yue Zhao:** Investigation; methodology. **Peng Wang:** Investigation; methodology. **Zhi-Qiang Liu:** Investigation; methodology. **Wei-Yin Sun:** Conceptualization; funding acquisition; project administration; supervision.

CONFLICT OF INTEREST

All authors certify that they have no conflict of interest to declare.

SUPPORTING INFORMATION DATA

CCDC—2045503 contains the supplementary crystallographic data for this contribution. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or deposit@ccdc.ca.ac.uk).

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supporting information of this article.

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REFERENCES

[1] V. T. Kamble, N. S. Joshi, *Green Chem. Lett. Rev.* **2010**, *3*, 275.
[2] J. A. Deyrup, C. L. Moyer, *J. Org. Chem.* **1969**, *34*, 175.
[3] A. T. Placzek, J. L. Donelson, R. Trivedi, R. A. Gibbs, S. K. De, *Tetrahedron Lett.* **2005**, *46*, 9029.
[4] B. Pujala, S. Rana, A. K. Chakraborti, *J. Org. Chem.* **2011**, *76*, 8768.
[5] D. Li, J. Wang, S. Yu, S. Ye, W. Zou, H. Zhang, J. Chen, *Chem. Commun.* **2020**, *56*, 2256.
[6] F. L. Li, Q. Shao, X. Q. Huang, J. P. Lang, *Angew. Chem. Int. Ed.* **2018**, *57*, 1888.
[7] F. L. Li, P. T. Wang, X. Q. Huang, D. J. Young, H. F. Wang, P. Braunstein, J. P. Lang, *Angew. Chem. Int. Ed.* **2019**, *58*, 7051.

[8] J. Y. Xue, C. Li, F. L. Li, H. W. Gu, P. Braunstein, J. P. Lang, *Nanoscale* **2020**, *12*, 4816.
[9] W. Hou, G. Wang, X. J. Wu, S. Y. Sun, C. Y. Zhao, W. S. Liu, F. X. Pan, *New J. Chem.* **2020**, *44*, 5019.
[10] N. Van Velthoven, M. Henrion, J. Dallenes, A. Krajnc, A. L. Bugaev, P. Liu, S. Bals, A. V. Soldatov, G. Mali, D. E. De Vos, *ACS Catal.* **2020**, *10*, 5077.
[11] A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov, F. Verpoort, *Chem. Soc. Rev.* **2015**, *44*, 6804.
[12] T. K. Pal, D. De, S. Senthilkumar, S. Neogi, P. K. Bharadwaj, *Inorg. Chem.* **2016**, *55*, 7835.
[13] L. Zhu, X. Q. Liu, H. L. Jiang, L. B. Sun, *Chem. Rev.* **2017**, *117*, 8129.
[14] A. K. Gupta, D. De, K. Tomar, P. K. Bharadwaj, *Dalton Trans.* **2018**, *47*, 1624.
[15] Y. S. Kang, Y. Lu, K. Chen, Y. Zhao, P. Wang, W. Y. Sun, *Coord. Chem. Rev.* **2019**, *378*, 262.
[16] B. Venu, V. Shirisha, B. Vishali, G. Naresh, R. Kishore, I. Sreedhar, A. Venugopa, *New J. Chem.* **2020**, *44*, 5972.
[17] A. Bavykina, N. Kolobov, I. S. Khan, J. A. Bau, A. Ramirez, J. Gascon, *Chem. Rev.* **2020**, *120*, 8468.
[18] D. Zhao, X. H. Liu, Z. Z. Shi, C. D. Zhu, Y. Zhao, P. Wang, W. Y. Sun, *Dalton Trans.* **2016**, *45*, 14184.
[19] D. Zhao, X. H. Liu, C. Zhu, Y. S. Kang, P. Wang, Z. Shi, Y. Lu, W. Y. Sun, *ChemCatChem* **2017**, *9*, 4598.
[20] D. Zhao, X. H. Liu, J. H. Guo, H. J. Xu, Y. Zhao, Y. Lu, W. Y. Sun, *Inorg. Chem.* **2018**, *57*, 2695.
[21] C. S. Chang, *J. Chem. Educ.* **1968**, *45*, 581.
[22] SAINT, *Program for Data Extraction and Reduction*, Bruker AXS, Inc, Madison, WI **2001**.
[23] G. M. Sheldrick, *SADABS, Program for Empirical Adsorption Correction of Area Detector Data*, University of Göttingen, Germany **2003**.
[24] G. M. Sheldrick, *SHELXS-2014, Program for the Crystal Structure Solution*, University of Göttingen, Germany **2014**.
[25] G. M. Sheldrick, *SHELXS-2018, Program for the Crystal Structure Refinement*, University of Göttingen, Germany **2018**.
[26] D. S. P. Van, A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, 194.
[27] C. B. Hüebschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Cryst.* **2011**, *44*, 1281.
[28] M. X. Liu, C. J. Li, *Angew. Chem. Int. Ed.* **2016**, *55*, 10806.
[29] P. Nunes, N. V. Nagy, E. C. B. A. Alegria, A. J. L. Pombeiro, I. Correia, *J. Mol. Struct.* **2014**, *1060*, 142.
[30] E. Walger, N. Marlin, F. Molton, G. Morthe, *Molecules* **2018**, *23*, 242.
[31] A. Kunishita, H. Ishimaru, S. Nakashima, T. Ogura, S. Itoh, *J. Am. Chem. Soc.* **2008**, *130*, 4244.
[32] M. Contel, P. R. Villuendas, J. Fernández-Gallardo, P. J. Alonso, J. M. Vincent, R. H. Fish, *Inorg. Chem.* **2005**, *44*, 9771.
[33] V. A. Blatov, *TOPOS, A Multipurpose Crystallochemical Analysis with the Program Package*, Samara State University, Russia **2009**.
[34] Y. Y. Liu, J. D. An, T. T. Wang, Y. Li, B. Ding, *Z. Anorg. Allg. Chem.* **2020**, *646*, 390.
[35] K. I. Hadjiivanov, D. A. Panayotov, M. Y. Mihaylov, E. Z. Ivanova, K. K. Chakarova, S. M. Andonova, N. L. Drenchev, *Chem. Rev.* **2021**, *121*, 1286.
[36] K. Vellingiri, J. E. Szulejko, P. Kumar, E. E. Kwon, K. H. Kim, A. Deep, D. W. Boukhvalov, R. J. C. Brown, *Sci. Rep.* **2016**, *6*, 27813.
[37] D. Tanaka, S. Kitagawa, *Chem. Mater.* **2008**, *20*, 922.
[38] H. Choi, M. P. Doyle, *Chem. Commun.* **2007**, *7*, 745.
[39] G. Jiang, J. Chen, J. S. Huang, C. M. Che, *Org. Lett.* **2009**, *11*, 4568.
[40] Y. Zhang, L. Huang, X. Li, L. Wang, H. Feng, *J. Org. Chem.* **2019**, *84*, 5046.
[41] B. Xu, P. Wang, M. Lv, D. Yuan, Y. Yao, *ChemCatChem* **2016**, *8*, 2466.
[42] C. Wang, L. Luo, H. Yamamoto, *Acc. Chem. Res.* **2016**, *49*, 193.
[43] D. Bhuyan, L. Saikia, D. K. Dutta, *Appl. Catal. A. Gen.* **2014**, *487*, 195.
[44] G. Negrón-Silva, C. X. Hernández-Reyes, D. Angeles-Beltrán, L. Lomas-Romero, E. González-Zamora, J. Méndez-Vivar, *Molecules* **2007**, *12*, 2515.
[45] H. Firouzabadi, N. Iranpoor, A. Khoshnood, *J. Mol. Catal. A: Chem.* **2007**, *274*, 109.
[46] C. Wang, H. Yamamoto, *Angew. Chem. Int. Ed.* **2015**, *54*, 8760.
[47] W. S. Li, H. Morrison, *Org. Lett.* **2000**, *2*, 2000.
[48] C. Wang, H. Yamamoto, *J. Am. Chem. Soc.* **2014**, *136*, 6888.
[49] A. Kamal, B. Rajendra Prasad, A. M. Reddy, M. N. A. Khan, *Cat. Com.* **2007**, *8*, 1876.
[50] E. N. Jacobsen, *Acc. Chem. Res.* **2000**, *33*, 421.
[51] H. Li, F. C. Meng, S. Y. Zhang, L. G. Wang, M. Li, W. N. Zhang, W. L. Zhang, Z. H. Yang, T. P. Wu, S. Lee, F. W. Huo, J. Lu, *Am. Ethnol.* **2020**, *59*, 2457.
[52] L. Liu, Z. Yao, Y. Ye, Q. Lin, S. Chen, Z. Zhang, S. Xiang, *Cryst. Growth Des.* **2018**, *18*, 3724.

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