# Metal–Organic Frameworks

# A Copper-Based Metal–Organic Framework Acts as a Bifunctional Catalyst for the Homocoupling of Arylboronic Acids and Epoxidation of Olefins

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**Abstract:** A copper(I)-based metal–organic framework  $(\{[Cu_2Br_2(pypz)]_n \cdot nH_2O\}$  (Cu—Br–MOF) [pypz = bis[3,5-dimethyl-4-(4'-pyridyl)pyrazol-1-yl] methane] has been synthesized by using an elongated and flexible bridging ligand. The structure analysis reveals that each pypz ligand acts as a tritopic ligand connected to two  $Cu_2Br_2$  dimeric units, forming a one-dimensional zig–zag chain, and these chains further connected by a  $Cu_2Br_2$  unit, give a two-dimensional framework on the *bc*-plane. In the  $Cu_2Br_2$  dimeric unit, the copper ions are four coordinated, thereby possessing a tetrahedral geometry; this proves to be an excellent heterogeneous catalyst for the aerobic homocoupling of arylboronic acids under mild reaction conditions. This method requires only 3 mol% of catalyst and it does not require any base or oxidant—compared to other conventional (Cu, Pd, Fe, and Au) catalysts—for the transformation of arylboronic acids in very good yields (98%). The shape and size selectivity of the catalyst in the homocoupling was investigated. The use of the catalyst was further extended to the epoxidation of olefins. Moreover, the catalyst can be easily separated by simple filtration and reused efficiently up to 5 cycles without major loss of reactivity.

# Introduction

Biaryls are an important class of organic compounds that occur in many natural products and they have a wide variety of applications in drugs, agrochemicals, dyes, semi-conductors, and asymmetric synthesis.<sup>[1]</sup> Several synthetic methods (such as palladium (Pd<sup>II</sup>)-catalyzed Suzuki reactions,<sup>[2a]</sup> modified Ullmann reaction,<sup>[2b]</sup> Hiyama-Kumada reaction,<sup>[2c]</sup> and the other metal catalysts such as Au,<sup>[3a]</sup> Cr,<sup>[3b]</sup> Rh,<sup>[3c]</sup> and V<sup>[3d]</sup>) have been developed so far for the construction of biaryl derivatives. In particular, the Pd<sup>II</sup>-catalyzed homocoupling of boronic acids has been extensively studied.<sup>[4]</sup> Apart from the homocoupling reactions, olefin epoxidation is a highly important oxidation reaction, because the resultant epoxides are extensively used in the manufacture of epoxy resins,<sup>[5]</sup> paints,<sup>[6]</sup> and surfactants.<sup>[7]</sup> Various methods have been developed for the epoxidation of olefins, amongst these are catalysts composed of metals such as V<sup>[8]</sup>, Mn<sup>[9]</sup>, Fe<sup>[10]</sup>, Co<sup>[11]</sup>, and Cu<sup>[12]</sup> and so forth.

However, most of the reported metal-catalyzed homocoupling reactions and epoxidations of olefins are homogeneous and have major limitations such as 1) difficulty in separation,<sup>[4a,8a]</sup> 2) large amounts of oxidants are needed to subsequent

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reuse of the expensive catalysts,<sup>[4b]</sup> 3) indispensability of additives such as stabilizing ligands and bases,<sup>[4c]</sup> and the 4) need of high temperatures.<sup>[4d, 11a]</sup>

Thus, the development of a robust, easily recoverable, and recyclable heterogeneous catalyst is needed to overcome such limitations. Recently, metal–organic frameworks (MOFs) have emerged as versatile materials in the field of heterogeneous catalysis owing to their poor solubility in common solvents and secondly tunable and uniform pore size.<sup>[13]</sup> One of the most common approaches for the synthesis of catalytic MOFs is to create an unsaturated metal coordination environment as catalytically active sites.<sup>[14]</sup> This method is more synthetically challenging, but when the MOF is obtained, the handling and recycling of the catalyst was significantly easier.

In this study, we have developed a copper(I)-based 2D MOF, namely,  $\{[Cu_2Br_2(pypz)]_n \cdot nH_2O\}$  (Cu-Br-MOF) [pypz=bis[3,5-dimethyl-4-(4'-pyridyl)pyrazol-1-yl] methane] by using a flexible pypz bridging ligand (Scheme 1). In Cu-Br-MOF, the copper ions are four coordinated and have a tetrahedral geometry, and this proves to act as a heterogeneous catalyst for the aerobic homocoupling of arylboronic acids and the epoxidation of olefins.



Scheme 1. Ligand used in preparation of Cu-Br-MOF.

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Aerobic homocoupling of arylboronic acids, which can also be promoted by a copper MOF, has been previously reported.<sup>[15]</sup> However, an advantage of our MOF over other existing systems is that it transforms arylboronic acids into their corresponding homo-biarlys with a low catalyst loading (3 mol%) in shorter reaction times (3 h). In addition, the optimal catalyst Cu-Br-MOF was further used in the epoxidation of olefins<sup>[16]</sup> with low catalyst loadings. Moreover, the adsorption abilities of the material towards selective  $CO_2$  sorption applications were also investigated.

# **Results and Discussion**

### Structural Description of Cu-Br-MOF

Single-crystal structural analysis reveals that Cu-Br-MOF crystallizes in tetragonal system with the space group P42/mbc and the asymmetric unit contains two different Cu<sup>1</sup> ions, two bromides (Br<sup>-</sup>), half pypz ligand, and one lattice H<sub>2</sub>O molecule (see Figure S1 in the Supporting Information). The molecular structure of Cu-Br-MOF can be best described as if it consists of two crystallographically different dibromo-bridged dimeric Cu<sub>2</sub>Br<sub>2</sub> cores, Cu<sub>2</sub>Br<sub>2</sub>(1) and Cu<sub>2</sub>Br<sub>2</sub>(2) (Figure 1a). In the



**Figure 1.** (a) Bridging mode of pypz ligand with Cu<sup>1</sup> center, (b) Illustration of 2D framework with rhomboid-shaped channels along the *a*-axis. Color code: carbon (gray), nitrogen (blue), bromine (green), and copper (cyan).

 $Cu_2Br_2(1)$  dimeric unit, the  $Cu^1$  centre adopts a distorted tetrahedral geometry by the contribution of two different bromide anions and two pyrazolyl nitrogen atoms from one pypz ligand in a chelating fashion ( $t_4 = 0.93$ ) (see Figures S2 and S3 in the Supporting Information). In the  $Cu_2Br_2(2)$  dimeric unit, the  $Cu^1$  centre is four coordinated by two pyridyl nitrogen atoms from two different pypz ligands and the remaining two positions are occupied by two different bromide anions and

this affords a distorted tetrahedral geometry around the metal centre ( $t_4 = 0.88$ ) (see Figure S4 in the Supporting Information).

It was found that each pypz acts as a tritopic ligand connected to two crystallographically different  $Cu_2Br_2$  dimeric units and forms a 1D zig–zag chain along the *b*-axis (Figure 1 a and Figure S5 in the Supporting Information). These 1D chains are further connected by a  $Cu_2Br_2$  unit to give a 2D framework with a rhomboid-shaped channels along with *a*-axis with the cross-section of 17.186(4)×13.799(1) Å<sup>2</sup> (considering the distances between two Cu<sup>1</sup> centers bridged by pypz ligands) (Figure 1b, Figure 2 and Figures S6–S7 in the Supporting Informa-



**Figure 2.** Connolly surface of Cu-Br-MOF along the *b*-axis (inner surfaces: blue; outer surfaces: gray).

tion). The existence of large rhomboid channels along with the bent shaped spacer facilitates interweaving of one 2D nets to generate a 2-fold interwoven 2D network (Figure 2 and Figure S8 in the Supporting Information). These channels are occupied by guest water molecules and are stabilized by hydrogen bonding interactions (O3w-H1A···Br2 = 2.44 Å; C14-H14A···O3w = 2.485 Å) with bromide anion and  $-CH_3$  of pyrazole ligand (see Figure S9 in the Supporting Information). PLATON analysis reveals that Cu-Br-MOF has a pore-accessible void volume of 216.5 Å<sup>3</sup> out of 4635.1 Å<sup>3</sup>, which represents 4.7% per unit cell volume.

## **PXRD and Thermal Stabilities**

To check the phase purity of the bulk materials, a powder Xray diffraction (PXRD) experiment was carried out on Cu-Br-MOF. All major peaks in the experimental PXRD matched well with the simulated pattern, indicating equitable crystalline phase purity of the Cu-Br-MOF (see Figure S10 in the Supporting Information). Thermo gravimetric analysis (TGA) analysis of Cu-Br MOF shows a gradual weight loss of approximately

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3 wt% (calcd. 2.5 wt%) in the temperature range of 90–140 °C, which corresponds to the loss of one guest water molecule from the framework and the dehydrated framework was found to be stable up to 340 °C (see Figure S11 in the Supporting Information). The desolvated phase of Cu-Br-MOF was obtained by heating the sample for 12 h at 90 °C under reduced pressure. The PXRD pattern of the desolvated framework matches well with the as-synthesized compound; this indicates the stability of the framework after removal of guest molecules (see Figure S12 in the Supporting Information)

#### **Adsorption Studies**

To examine the porous nature of the compound, adsorption studies with N<sub>2</sub> at 77 K and CO<sub>2</sub> at 195 K were carried out. The desolvated framework of Cu-Br-MOF shows a diminished uptake for N<sub>2</sub>, with an amount of 18 cm<sup>3</sup>g<sup>-1</sup>. On the basis of the N<sub>2</sub> adsorption isotherm, the Brunauer–Emmett–Teller (BET) surface area of Cu-Br-MOF is found to be 36 m<sup>2</sup>g<sup>-1</sup>. However, Cu-Br-MOF adsorbs a significant amount of CO<sub>2</sub> with the uptake amount of 55.25 cm<sup>3</sup>g<sup>-1</sup> at 1 bar pressure (Figure 3).



Figure 3. Gas adsorption isotherms of Cu-Br-MOF at low temperature,  $N_{\rm 2}$  at 77 K and CO  $_{\rm 2}$  at 195 K.

The similar sorption behavior was also observed in some well-known MOFs such as  $\{[Ni(bpe)_2(N(CN)_2)](N(CN)_2)(5H_2O)\}_{n'}^{[17a]}$  $[Cu(tba)_2]n^{[17b]}$   $\{[Zn(C_{10}H_2O_8)_{0.5}(C_{10}S_2N_2H_8)]\cdot 5H_2O]\}_n^{[17c]}$  (bpe = 1,2-bis(4-pyridyl)ethane,  $N(CN)_2$  = dicyanamide), tba = 4-(1*H*-1,2,4-triazol-1-yl)benzoate) and others.<sup>[13i,17d,e,18d]</sup>

Furthermore, to check the structural stability of the framework after adsorption of  $N_2$ , the adsorbed compound was subjected to PXRD analysis. The PXRD pattern of the  $N_2$  adsorbed sample matched well with those of the as-synthesized sample (see Figure S12 in the Supporting Information). This clearly indicates that the framework remains intact after  $N_2$  adsorption.

## Catalytic Activity of Cu-Br-MOF in the Homocoupling of Arylboronic Acids

Previous studies have shown that coordinatively unsaturated copper sites in the MOF can show interesting catalytic activities.<sup>[18]</sup> When phenyl boronic acid (2 mmol) was added to *N*,*N*-

dimethylformamide (DMF; 2 mL) in the presence of activated Cu-Br-MOF (3 mol%) at room temperature and stirred for 3 h, the yield of the homocoupling product was 98%. However, no product was isolated in the absence of Cu-Br-MOF under the same reaction conditions even after stirring for a long time (ca. 24 h).

At the onset of this study, phenylboronic acid was chosen as a model substrate to optimize the reaction conditions (solvent, base, and the amount of catalyst) and all the reactions were

Table 1. Effe	Table 1. Effect of solvents on the aerobic homocoupling reaction catalyzed by Cu-Br-MOF.				
Entry	Solvent	<i>t</i> [h]	Yield [%]		
1	DMF	3	98		
2	DMSO	3	60		
3	$DMF + H_2O$	3	65		
4	H <sub>2</sub> O	12	12		
5	EtOH	12	32		
6	MeOH	12	41		
7	Toluene	12	7		
8	Xylene	12	11		
9	DCM	12	Traces		
10	DCE	12	12		
11	1,4-dioxane	12	Traces		
12	THF	12	Traces		
13	CHCl₃	12	8		

performed at room temperature (Table 1). Interestingly, Cu-Br-MOF does not show any catalytic activity in non-polar solvents, namely, toluene, xylene, dichloromethane (DCM), 1,2-dichloro-ethane (DCE), 1,4-dioxane, tetrahydrofuran (THF), and chloro-form (CHCl<sub>3</sub>). However, in contrast, the products are formed in low-to-moderate yields in protic solvents such as EtOH, MeOH,  $H_2O$  with phenol as a side product. The obtained phenol side product might be due to the formation of the C–O bond through a peroxyboronate intermediate.

When the reaction was carried out in a DMF/water (1:1) mixture, biphenyl and phenol were formed in approximately 65% and 15% yield, respectively. Based on the above solvent screening, DMF was found to be the best choice among all the solvents to catalyze the reaction without any side products.

To determine the role of oxygen, the reactions were also carried out under nitrogen as well as in oxygen atmosphere. Interestingly, no product was obtained under an atmosphere of nitrogen, but the reaction was complete in 3 h under an atmosphere of oxygen with the yield of 98%, which is similar to the yield obtained in atmosphere. These results show that the dioxygen might be playing a vital role as an oxidant during the reaction.

The addition of a base can enhance the reaction efficiency for some catalytic systems<sup>[19]</sup> (see Table S1 in the Supporting Information). Consequently, we carried out the reaction in the presence of different bases such as NaOH, KOH, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NEt<sub>3</sub>, and cyclohexylamine. Surprisingly, these bases reduced the yield of the desired product. Additionally, to check the structural stability of the framework after addition of a base, the recovered compound was subjected to PXRD analysis and found to remain intact (see Figure S13 in the Supporting Information).

A screening of the catalyst loading revealed that the yield of product increases from 65 to 98% when the amount of catalyst increased from 1.0 to 3.0 mol%, respectively, but a further increase in the amount of the catalyst led to no change in the reaction yield (Table 2).

Table 2. Effect of catalyst loading on the aerobic homocoupling reactions.					
Entry	Amount of catalyst	Solvent	<i>t</i> [h]	Yield [%]	
1	1 mol %	DMF	3	65	
2	2 mol %	DMF	3	82	
3	3 mol %	DMF	3	98	
4	4 mol %	DMF	3	98	
5	5 mol%	DMF	3	98	

The homocoupling products were isolated in lower yields under the similar reaction conditions with other copper sources, for example, Cu(NO<sub>3</sub>)<sub>2</sub>·3 H<sub>2</sub>O (41%), CuCl ( $\approx$ 50%), CuBr ( $\approx$ 50%), and Cu(Ac)<sub>2</sub>·H<sub>2</sub>O ( $\approx$ 30%). This demonstrates that CuBr-MOF is much more efficient, as well as selective than the commercially available copper salts as the catalyst. The major advantage of this solid MOF is that it is easily separable from the reaction mixture by simple filtration.

Once the reaction conditions were optimized, the scope of this homocoupling reaction of aryl boronic acids was investigated and the results are summarized in Table 3. As is evident from the results, all meta- and para-substituted electron-rich boronic acids gave the biaryls in excellent yields. But moderate yields are observed with ortho-substituted arylboronic acids (Table 3, entries 4 and 8); this might be due to the steric hindrance caused by the ortho groups and also low-to-moderate yields were obtained for the coupling of electron-deficient and hetero arylboronic acids (Table 3, entries 10-12). To ascertain that the reaction occurred in the channel of Cu-Br-MOF, we carried out some homo coupling reactions for arylboronic acids with larger substrates. As shown in Table 4, the yield of the reaction steadily decreases with an increase in the size of the substrate (Table 4, entry 1-3), probably due to its large diameter that restricts access to the internal pores.

The research groups of Demir,<sup>[20a]</sup> Yamamoto,<sup>[20b]</sup> and Kaboudin<sup>[20c]</sup> examined the Cu-mediated homocoupling of arylboronic acids, and proposed a tentative mechanism for the transformation. However, at the present stage the mechanism of the reaction is not yet obvious. The following observations may be useful to speculate on the mechanism: (1) Copper in any oxidation state, Cu<sup>1</sup>, or Cu<sup>11</sup>, is catalytically active in the homocoupling reaction. (2) Dioxygen is essential for the reaction as an oxidant. Therefore, the Cu<sup>11</sup> state might be responsible for the homocoupling reactions. (3) The bridging halide ion plays an important role as Cu-Br-MOF. The effective transformation of arylboronic acids into their corresponding homo-biarlys using a low catalyst loading (3 mol%) in shorter reaction times (3 h)



over existing systems  $[(Cu_3(BTC)_2-MOF^{[15a]} \text{ or } Cu(BTC)-MOF)^{15b}]$  might be due to the easy replacement of the labile-coordinated Br<sup>-</sup> anion and give more catalytically active Cu<sup>1</sup> sites to enhance the reaction.

On the basis of these observations, a plausible reaction pathway is proposed, as shown in Scheme 2. During the homocoupling reaction, in the first step the  $Cu_2Br_2$  bridge might open up by the arylboronic acid. Double transmetallation of  $Cu^1$  with two molecules of arylboronic acid affords a Ar-Cu<sup>1</sup>-Ar, which undergoes air oxidation to yield a  $Cu^{11}$  intermediate, and this undergoes subsequent reductive elimination to the symmetrical biaryl compound.







Scheme 2. A possible mechanism for the homocoupling of arylboronic acids.

#### **Epoxidation of Olefins**

Encouraged by these preliminary results, the catalyst was further extended to the epoxidation of olefins, as it is one of the most important organic transformations and frequently used as intermediates in industry. The catalytic activity of Cu-Br-MOF towards selective epoxidation was evaluated, *trans*- $\beta$ -methylstyrene (0.5 mmol) and *tert*-butyl hydroperoxide (TBHP) were added to toluene (2 mL) in the presence of activated Cu-Br-MOF (1 mol%) at 353 K and stirred for 8 h. The corresponding product was obtained in high yield without any byproduct.

To confirm the role of catalyst, a blank reaction was performed under similar conditions with *trans*- $\beta$ -methylstyrene and TBHP as an oxidant. No products were isolated even after stirring for a long time ( $\approx$ 24 h).

To determine the role of TBHP, the reactions were carried out in the presence of 1 atm. molecular oxygen instead of TBHP. Using molecular oxygen as an oxidant prolonged the reaction time (48 h) and gave poor yields and selectivity of the product (28%), however, the reaction was completed within 8 h when TBHP was used as an oxidant and the product was obtained in 99% yield. Therefore, TBHP as an oxidant is crucial for the reaction.

To explore the versatility of Cu-Br-MOF, various alkenes were evaluated with different molecular dimensions. As shown in Table 5 (entries 1–4), substrates participated well in this epoxi-



dation reaction. Excellent yields ( $\approx$ 99%) were achieved within 8 h without any byproduct. Epoxidation of styrene gave a the product in moderate yield (64%; Table 5, entry 5) along with benzaldehyde as a byproduct (36%). Similarly, epoxidation of 2-vinylnaphthalene required a longer reaction time and gave poor yields (46%; Table 5, entry 6) and selectivity of the product along with  $\alpha$ -methyl-2-naphthalenemethanol (23%) and 2-acetonaphthone (27%) as byproducts.

A plausible reaction pathway is proposed as shown in Scheme 3. It can be predicted that the reaction proceeds



Scheme 3. A possible mechanism for the epoxidation of olefins.

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through formation of a copper-peroxo species using TBHP as an oxidant. Bhaumik et al.<sup>[21]</sup> have reported a similar reaction mechanism for epoxidation reactions of olefins over a Cu Schiff base complex immobilized on mesoporous silica. Therefore, a similar pathway is expected to be followed for the Cu-Br-MOF in the liquid phase partial oxidation reactions.

## **Recyclability and Leaching Test**

The Cu-Br-MOF catalyst demonstrated excellent reusability for aerobic homocoupling of arylboronic acids and epoxidation of olefins. After the first reaction cycle, Cu-Br-MOF was recovered by simple filtration, washed thoroughly with DMF, and then dried in an oven at 100 °C. The recovered frameworks were subjected to PXRD analysis; this reveals that all major peaks are well matched with the as-synthesized sample and indicates structural stability of the framework (see Figures S14 and S15 in the Supporting Information) and can be reused at least for five subsequent cycles without any significant loss in catalytic activity (Figure 4a).



**Figure 4.** (a) The kinetic profiles in five consecutive reaction cycles employing Cu-Br-MOF as the catalyst. (b) The leaching test (filtration test) indicated no contribution from the homogeneous catalysis of the active species (A) in the presence of Cu-Br-MOF. (B) The catalyst filtration (after 1 h).

To ensure the structural stability and porosity of the framework, N<sub>2</sub> adsorption measurement was performed at 77 K on recovered Cu-Br-MOF after five reaction cycles (see Figure S16 in the Supporting Information). Remarkably, the recovered sample shows a similar uptake ( $\approx 16 \text{ cm}^3 \text{g}^{-1}$ ) of N<sub>2</sub> compared

with as-synthesized sample ( $\approx 18~cm^3\,g^{-1}$ ), and the BET surface area was found to be 30  $m^2\,g^{-1}$ .

Leaching is a common problem in heterogeneous catalysis, especially in C–C coupling reactions. The simplest and most effective test for leaching is in situ catalyst filtration and re-addition (Figure 4b). To ensure it, after 1 h of the reaction, Cu-Br-MOF was filtered out from the reaction mixture and the reaction was allowed to stir further without Cu-Br-MOF for 5 h and no further product was observed. Furthermore, the filtered Cu-Br-MOF was added to the above reaction mixture after 5 h of standing without it, and a sudden increase in the yield was observed after the addition of catalyst; this indicates that the copper(I)-based MOF in the reaction is heterogeneous in nature.

# Conclusions

In conclusion, a copper(I)-based 2D MOF was found to be an excellent heterogeneous catalyst for the homocoupling of arylboronic acids and epoxidation of olefins. The shape and size of the catalyst in the selectivity of the homocoupling was investigated. Furthermore, the catalyst can be easily separated by simple filtration and reused efficiently up to 5 cycles without major loss in reactivity. Ongoing research in our laboratory is aimed at developing new functionalized MOFs as catalysts for the C–C coupling reactions under progress.

# **Experimental Section**

## Materials

All the reagents and solvents for synthesis were purchased from commercial sources and used as supplied without further purification. CuCl, CuBr, 4-methylpyridine, hydrazine hydrate, dibromomethane, *tert*-butyl hydroperoxide (TBHP); all the olefins and arylboronic acid were obtained from the Sigma–Aldrich Chemical Co. India. Pypz ligand was obtained according to the literature procedure.<sup>[22]</sup>

#### **Physical Measurements**

Thermo gravimetric analysis (TGA) was recorded on a PerkinElmer TGA 4000 instrument. Elemental analysis was carried out on an Elementar vario Micro Cube Elemental Analyzer. PXRD patterns were measured on a PAnalytical Empyrian instrument by using  $Cu_{K\alpha}$  radiation.

### Single Crystal X-ray Diffraction

Single crystal data for Cu-Br-MOF was collected on a Bruker APEX II diffractometer equipped with a graphite monochromator and  $Mo_{\kappa\alpha}$  ( $\lambda = 0.71073$  Å, 296 K) radiation. Data collections were performed using  $\phi$  and  $\omega$  scan. Non-hydrogen atoms are located from the difference Fourier maps, were refined anisotropically by full-matrix least-squares on F<sup>2</sup>, using SHELXS-97.<sup>[23]</sup> All hydrogen atoms were included in the calculated positions and refined isotropically using a riding model. Determinations of the crystal system, orientation matrix, and cell dimensions were performed according to the established procedures. Lorentz polarization and multi-scan absorption correction were applied. All calculations were carried out

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Table 6. Crystallographic data for Cu-Br-MOF. <sup>[27]</sup>			
CCDC	1400148		
Formula	$C_{21}H_{24}Br_2Cu_2N_6O$		
Weight [g mol <sup>-1</sup> ]	663.36		
Crystal shape	Block		
Color	Green		
Size	$0.46 \times 0.34 \times 0.26$		
Crystal system	Tetragonal		
Space group	P4 <sub>2</sub> /mbc		
Cell length <i>a</i> [Å]	16.4226(8)		
Cell length b [Å]	16.4226(8)		
Cell length <i>c</i> [Å]	17.1859(12)		
Cell angle alpha [°]	90		
Cell angle beta [°]	90		
Cell angle gamma [°]	90		
Cell volume V [ų]	4635.07		
Cell formula units Z	8		
Temperature [K]	298(2)		
λ (Mo <sub>κα</sub> ) [Å]	0.71073		
$\mu \text{ [mm^{-1}]}$	5.310		
Dc [g cm <sup>-3</sup> ]	1.901		
Crystal_F_000	2624.0		
Measured reflections	2137		
Unique reflections	1782		
$R_1[l > 2\sigma(l)]^{[a]}$	0.0257		
$R_{w}[l > 2\sigma(l)]^{[b]}$	0.0598		
[a] $R_1 = \Sigma   F_o  -  F_c  /\Sigma  F_{or}  b] R_w = [\Sigma \{w(F_o^2 - F_c^2)^2\}/\Sigma \{w(F_o^2)^2\}]^{1/2}$ .			

using SHELXL 97,<sup>[24]</sup> PLATON 99,<sup>[25]</sup> and WinGXsystemVer-1.64.<sup>[26]</sup> Data collection and structure refinement parameters and crystallographic data in Table 6 and selected bond lengths and bond angles for Cu-Br-MOF are given in Table S3 in the Supporting Information.

#### **NMR Measurements**

<sup>1</sup>H NMR spectra were recorded on Bruker Avance III FT-NMR spectrometers at 400 MHz. Chemical shifts ( $\delta$ ) are reported in ppm relative to the residual solvent (CDCl<sub>3</sub>) signal ( $\delta$  = 7.26 for <sup>1</sup>H NMR). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

**Synthesis of Cu-Br-MOF**: A mixture containing CuBr (17.00 mg, 0.12 mmol), pypz (25 mg, 0.07 mmol) dissolved in DMF/H<sub>2</sub>O mixture (4:2 v/v), was placed in a pressure tube (15 mL). The tube was properly sealed and kept at 100 °C for 48 h. After cooling down to room temperature, green colored X-ray quality crystals of Cu-Br-MOF were obtained at the bottom of the tube. The crystals were washed with DMF. Elemental analysis: Calcd. C, 38.05 %, N, 12.66 %, H, 3.64 %, Found: C, 38.3 %, N, 12.8 %, H, 3.3 %.

Activation of Cu-Br-MOF: Activated MOF catalyst was obtained by heating the sample for 12 h at 90 °C under reduced pressure and the structural stability was confirmed by PXRD studies (see Figure S11 in the Supporting Information).

General experimental procedure for the Cu-Br-MOF catalyzed homocoupling reaction of arylboronic acid: Cu-Br-MOF (34 mg) and arylboronic acids (2 mmol) were dissolved in DMF (2 mL) under an atmosphere of air. After stirring at room temperature for 3 h, the mixture was diluted with ethyl acetate (10 mL) and then the catalyst removed by filtration, followed by evaporation of solvent under reduced pressure. The progression and yield of the reaction were monitored by using GCMS analysis. The resulting

crude product was finally purified by column chromatography on silica gel (100–200 mesh) with hexane/ethyl acetate (8:2, v/v) as eluting solvent to give the desired product in up to 98% yield. The recovered catalyst was thoroughly washed with DMF, and subsequently reused.

General experimental procedure for the Cu-Br-MOF catalyzed epoxidation of olefins: A solution of olefins (0.065 mL, 0.5 mmol), 5.0–6.0 M TBHP in decane (0.2 mL), and toluene (2 mL), was stirred at 363 K with Cu-Br-MOF (15 mg) in powder form. The progression and yield of the reaction were monitored by using GCMS analysis. The recovered catalyst was thoroughly washed with DMF, and subsequently reused.

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