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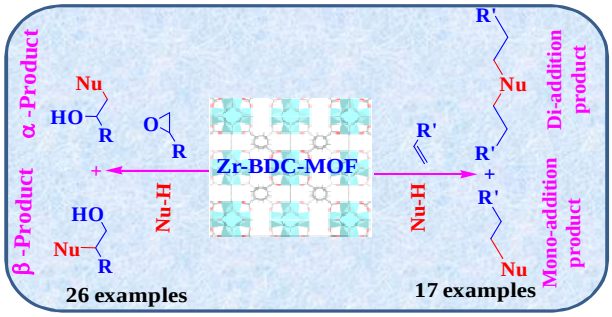
Graphical Abstract

Nucleophilic addition of amines, alcohols, and thiophenol with epoxide/olefin using highly efficient zirconium metal organic framework heterogeneous catalyst

Poonam Rani and Rajendra Srivastava*



Zr based MOF exhibited excellent activity in the ring opening of epoxides/nucleophilic addition of activated olefins with wide range of nucleophiles.

Nucleophilic addition of amines, alcohols, and thiophenol with epoxide/olefin using highly efficient zirconium metal organic framework heterogeneous catalyst

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Abstract

Zirconium metal–organic framework catalyst was synthesized and investigated in the ring opening of epoxides with nucleophiles such as amines, alcohols, and thiophenol. For comparative study, Cu and Zn metal-organic framework catalysts were prepared. Zirconium based porous metal–organic framework catalyst was characterized by powder X-ray diffraction, nitrogen adsorption, scanning electron microscopy, thermo gravimetric analysis, and Fourier transform infrared spectroscopic techniques. Application of these catalysts was also investigated in the nucleophilic addition of amines/thiophenol with activated olefins. Among the catalysts investigated in this study, zirconium metal–organic framework catalyst exhibited the highest activity in these reactions. In this study, the systematic assessment of the catalytic activity of zirconium metal–organic framework for wide range of aromatic and heterocyclic compounds is shown under one umbrella. Catalysts can be easily recovered and reused with negligible loss in the catalytic activity.

Keywords: Metal-organic framework, Zirconium, Heterogeneous catalyst, Regioselective synthesis, Nucleophilic addition, Ring opening.

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1. Introduction

Metal–organic frameworks (MOFs) (also known as porous coordination polymer (PCPs)) are a class of porous material that drew significant attention of scientists.[1-3] MOFs are constituted by transition metal ions or clusters of metal ion occupying nodal positions in a crystalline framework that are held in place by bi or multipodal rigid organic linkers. The crystal structure defines empty spaces in the range of nanometer scales that can be accessed from the exterior of the particle allowing the mass transfer in and out of the MOF crystallites. The advantage of MOFs over other porous solids is that the crystalline frameworks can be predicted sometimes based on the geometry of the metal clusters and the linkers. Furthermore, MOFs exhibited large surface area and porosity compared to other related micro- and mesoporous materials. Different inorganic nodes and organic linkers provide opportunity for the synthesis of wide range of MOFs.[4-8] Due to the extended 3-D ordered porous structure, novel properties can be imparted in MOFs.[9] Significant attention has been made for the synthesis of MOFs and find their applications in the selective adsorption/storage of gas molecules, photo catalysis, and biomedicine.[4-11] From last few years, scientists are exploring the possibility of using MOFs in the fine chemical synthesis, especially with respect to develop real industrial processes based on MOFs.[12, 13] Considering the high market value of fine chemicals and the mild reaction condition requirements, MOFs appear to be very promising catalysts in this sector. We have shown that Cu(I)-MOF catalyst exhibited higher activity than Cu(I) clusters.[14]

Amines, alcohols, amino alcohols, amino esters, and structurally similar compounds are important fine-chemicals. Ring-opening of epoxides and nucleophilic addition of activated olefins with wide range of nucleophiles are fundamental synthetic approaches to prepare these synthetic intermediates. Several homogeneous acid catalysts such as metal halides, metal triflates, ionic liquids, and sulfamic acid have been reported to catalyze these transformations.[15-18] However, many of these methods suffer from several disadvantages such as poor regioselectivity, long reaction time, high temperature, use of stoichiometric amount of catalyst, and the use of expensive reagents or catalysts. Hence, there is need to develop more efficient and reusable solid acid catalysts that are active at low temperatures and avoid the use of solvent. Very recently, we have shown that nanocrystalline zirconosilicate exhibited astonishing activity in the ring opening of epoxide with amines/alcohols and hydroamination reactions.[19, 20] The high activity was possible due to isomorphous substitution of Zr in the MFI framework. We were

interested to show that the high activity was due to tetrahedral Zr and not due to MFI framework. Therefore, we were interested to prepare Zr based MOF materials. It may be noted that $ZrOCl_2$ is also known for its Lewis acidity.[21] Recently, a few reports based on synthesis and catalytic investigation of Zr containing MOF have appeared in the literature.[22-25]

In this study, Zr based MOF was synthesized and investigated in the ring opening of epoxides/nucleophilic addition of activated olefins with wide range of nucleophiles. For comparative studies, Cu and Zn based MOF were also prepared. To the best of our knowledge, this is the first report that involves the systematic assessment of the catalytic activity of zirconium metal–organic framework for wide range of aromatic and heterocyclic amines under one umbrella.

2. Experimental

2.1. Synthesis of MOFs

Zr metal-organic framework (here after represented as Zr-BDC-MOF ($C_{48}H_{28}O_{32}Zr_6$) was prepared by following the reported procedure with little modification.[25] For comparative study, Zn-BDC-MOF ($C_{24}H_{12}O_{13}Zn_4$), Zn-BTC-MOF ($C_{18}H_{30}O_{24}Zn_3$), Zn-MeIMI-MOF ($C_8H_{10}N_4Zn$), and Cu-BTC-MOF ($C_{18}H_6O_{12}Cu_3$) were prepared by following the reported procedure.[26-29] Details of the synthesis of MOFs investigated in this study are provided in supporting information.

2.2. Procedure for catalytic reactions

2.4.1. Ring opening of epoxides with amines/alcohols

Epoxide (1.0 mmol) and amine (1.0 mmol) were reacted in the presence of required amount of catalyst at 50 °C for a desired period of time. Progress of the reaction was monitored by Gas-chromatograph (GC, Younglin YL6100) and products were identified by GC-MS (Shimadzu, QP2010 Ultra). Products were also characterized by using various spectroscopic tools that matched well with the reported literature.[30-33]

For the ring opening of epoxides with alcohols/thiols, epoxide (1.0 mmol) and alcohol (epoxide/alcohol = 1:25) were reacted using desired amount of the catalyst at 70 °C for 2 h. Progress of the reaction was monitored by GC as well as by NMR. Products were characterized by using various spectroscopic tools that matched well with the reported literature.[34]

2.4.2. Nucelophilic addition of amines/thiol with activated olefins

Olefin (2.1 mmol) and amine/thiol (2.0 mmol) were reacted using required amount of the catalyst at 80 °C for a desired period of time. Progress of the reaction was monitored by GC. The products were dissolved by adding a small amount of toluene to the reaction mixture and then analyzed by GC. Products were characterized by using various spectroscopic tools that matched well with the reported literature.[35]

To investigate the reusability of the catalyst, catalyst was recovered from the reaction mixture by centrifugation. Recovered catalyst was washed several times with ethyl acetate and dried in vacuum oven at 100 °C and then used in next cycle.

3. Results and discussion

Powder XRD patterns of various catalysts prepared in this study are shown in Fig. 1. XRD pattern of Zr-BDC-MOF (Fig. 1a) matched well with the XRD pattern of UIO-66 reported in the literature, which was prepared by using 1, 4-benzenedicarboxylic acid in DMF medium.[25] For comparative study, Zn and Cu based MOFs were prepared. A wide range of Zn based MOFs are known in the literature. In this study, three different Zn based MOFs were prepared. Three different organic building units such as 1, 4-benzenedicarboxylic acid, trimesic acid, and 2-methylimidazole were chosen to prepare Zn based MOFs, which are represented as Zn-BDC-MOF, Zn-BTC-MOF, and Zn-MeIMI-MOF, respectively. XRD patterns of Zn-BDC-MOF, Zn-BTC-MOF, and Zn-MeIMI-MOF matched well with the reported XRD pattern of MOF-5,[26] $Zn_3(BTC)_2.12H_2O$,[27] and ZIF-8,[36] respectively (Fig. 1b). Furthermore, XRD pattern of Cu-BTC-MOF matched well with the XRD pattern of HKUST-1 (Fig. 1a).[37] Catalytic activity data show that (discussed in the following section) among the catalysts investigated in this study, Zr-BDC-MOF exhibited the highest activity; therefore, detailed characterization was made for this material.

The N_2-adsorption study shows that Zr-BDC-MOF exhibited a typical type-IV isotherm similar to that of mesoporous materials (Fig. 2a). The distinct increase of N_2 adsorption in the region 0.6-0.9 can be attributed to a capillary condensation in the intercrystalline mesoporous void space. Mesopores show a pore size distribution in the range of 1.5–9 nm with peak maxima at 4.8 nm. Total surface area, external surface area, and total pore volume of Zr-BDC-MOF obtained from the N_2-adsorption study were found to be 1021 m^2/g, 380 m^2/g, and 1.08 cm^3/g,

respectively. Irregular crystal morphology was observed in the SEM images of Zr-BDC-MOF (Fig. S1a).

Three characteristic weight losses can be observed from TGA profile of Zr-BDC-MOF (Fig. 2b). First, the removal of physisorbed H_2O molecules between 25 °C and 100 °C, the second weight loss between 100 °C and 300 °C is attributable to removal of H_2O and other solvent molecules occluded in MOF framework, and third weight loss between 300 °C and 580 °C corresponds to the degradation of the framework to produce ZrO_2. FT-IR investigations confirm the presence of carboxylate groups (-O-C-O-) at 1390 and 1580 cm^{-1} (Fig. S1b). This observation confirmed that 1, 4-benzenedicarboxalate moiety is present in Zr-BDC-MOF. Furthermore, a wide band at 3400 cm^{-1} corresponds to the water molecules trapped within the pores.

Ring-opening of epoxide with amine leads to the formation of two isomerized products, α-amino alcohol and β-amino alcohol (Scheme 1a). Under our reaction condition, negligible amount of product was obtained in the absence of catalyst (Table 1). Initial aim was to find the best MOF catalyst for the ring opening of epoxide with amine. Under the reaction condition given in Table 1, among the MOF catalysts investigated in the study, Zr-BDC-MOF exhibited the best catalytic activity. $ZrOCl_2$ was also found to be active but its activity was much lower than Zr-BDC-MOF. Therefore, in order to optimize the reaction condition, Zr-BDC-MOF was chosen (Table S1). Influence of reaction parameters such as catalyst amount, temperature, and solvent was evaluated. Detail of optimization study is provided in supporting information. Study show that 0.005 mmol of catalyst for 1 mmol of reactant at 50 °C in neat condition was found to be the optimized reaction condition.

Having optimized the reaction condition, applicability of Zr-BDC-MOF was investigated in the synthesis of wide range of amino alcohols by varying the epoxides and amines. A wide range of amino alcohols was produced with good regioselectivity from styrene oxide and different amines (Table 2). A wide variety of epoxides can be converted to amino alcohols using this protocol. Among the epoxides investigated, epichlorohydrin and styrene oxide afforded better product yield when compared to propylene oxide (Table 2). The order of reactivity was found as: epichlorohydrin> styrene oxide> propylene oxide. This order of reactivity is consistent with the literature report.[19] Aromatic amines, aliphatic amines, and heterocyclic amines can be converted to amino alcohols. In the case of aromatic amines, aniline afforded high conversion

with excellent regioselectivity for β-amino alcohols. *Para*-substituted anilines were reacted to styrene oxide to afford β-amino alcohols in good yield. In general, electron donating substituent afforded good product yield than electron withdrawing substituent. Not only aromatic amines, aliphatic amines also produced amino alcohols (Table 2). Comparatively, less epoxide conversion was obtained, when aliphatic amines were reacted for 10 minutes. Product yield was improved by increasing the reaction time. It was interesting to note that, when aliphatic amines were reacted, α-amino alcohols were obtained in high selectivity (Table 2). Similarly, with heterocyclic compounds such as imidazole, piperidine, and pyrrole, longer reaction time was required to obtain good product yield. In contrast to aromatic amines, reaction with heterocyclic amines produced α-amino alcohol in high selectivity.

In order to understand the reason for the difference in the selectivity obtained with different kind of amines, basicity (nucleophilicity) of amines can be taken in account (Table 2). In general, aliphatic amines exhibit more basicity when compared to aromatic amines. Catalytic activity data show that aromatic amines (weak base) produced high selectivity for β-amino alcohols, whereas aliphatic amines (strong base) produced high selectivity for α-amino alcohols. Based on this correlation, mechanism for the ring opening of epoxide with amine is proposed (Scheme 2). Zr-BDC-MOF is an acid catalyst, and the acid base interaction is quite logical between amine reactant and acid sites of the catalyst. Strong base (for example, aliphatic amines) would have affinity for the preferential interaction with acid sites of the catalyst and produced intermediate A, which then attacks the least hindered carbon of epoxide by following the SN^2 mechanism to produce α-amino alcohol. In the presence of weak base (aromatic amines), first epoxide gets activated by the acid sites and ring opening of the epoxide would takes place to form stable carbocation (B). Weak amines are susceptible to attack on the stable carbocation formed by the epoxide to form β-amino alcohols.

To investigate the role of other nucleophile in the ring opening reaction, aliphatic alcohols, phenols, and thiophenol were investigated. MOF catalyzed the reaction to give mainly β-alkoxy alcohol. In addition to β-alkoxy alcohol, small amount of α-alkoxy alcohol was also observed (Scheme 1a). Influence of the reaction parameters such as reaction temperature, amount of catalyst, and epoxide/alcohol ratio was investigated and the results are summarized in Table S2. Study reveals that high catalytic activity was observed when epoxide/alcohol ratio was 1:25. In this manuscript, only comparative catalytic activities of ring opening of styrene oxide with

methanol are summarized over various catalysts investigated in this study (Table S2). Similar to ring opening of epoxide with amines, in this reaction also, Zr-BDC-MOF exhibited the highest activity. A wide range of aliphatic alcohols were successfully investigated to form β-alkoxy alcohol (Table 3). Reactivity of alcohols varies by varying the alkyl chain length of alcohols. With increase in the alkyl chain length, reactivity of aliphatic alcohols decreased (Table 3). This decrease in the activity is related to the decrease in the nucleophilicity of the alcohol with increase in the alkyl chain length. Such phenomenon is consistent with the literature report in which alcohols with different chain lengths were reacted with propylene carbonate.[38] Reactivity of aliphatic alcohol was low when compared to aliphatic amines (Compare Table 2 and Table 3). Reactivity of phenol was found to be more when compared to aliphatic alcohols (Table 3). However, it may be noted that in this case, selectivity of desired β-alkoxy alcohol was low. Several un-identified products were obtained during the GC-MS analysis. The reactivity of nitro phenol was found to be low when compared to phenol (Table 3), which confirms that electron withdrawing substituent's retard the reaction rate. When thiophenol was reacted with styrene oxide in 1:25 molar ratio, large amount of diphenyl disulfide was obtained. Reaction profile at different time intervals with styrene oxide:thiophenol, 1:25 and 1:1 molar ratio are shown in Fig. S2. In contrast to alcohols, in this case, 1:1 molar ratio of the reactants was found to be the best to obtain the desired product in high selectivity. Furthermore, reactivity and product formation in the ring opening of epoxide with substrates bearing two reactive nucleophilic groups were also investigated. Just for illustration, in this study, *o*-amino thiophenol, *o*-amino phenol and *p*-amino phenol were chosen (Table S3). Detail of this investigation is provided in the supporting information.

Similar to nucleophilic ring-opening of epoxide, nucleophilic addition of amines/thiophenol with activated olefins was investigated. The conjugate addition of amines/phenols/thiophenol and olefins was investigated over various catalysts prepared in this study (Table S4). MOF catalyzed the reaction to give mainly anti-Markovnikov adduct (anti-adduct), N-[2-(methoxycarbonyl) ethyl]aniline. In addition to main product; N, N'-bis[2-(methoxycarbonyl)ethyl]aniline was detected as a side product. The side product was formed by the double addition of methyl acrylate to aniline (Scheme 1b). To optimize the reaction condition for the conjugate addition of olefin with nucleophiles, methyl acrylate and aniline were chosen as representative olefin and nucleophile, respectively (Table S4). Among the catalysts investigated

in the study, Zr-BDC-MOF exhibited the highest activity (Table S4). This observation confirmed that, Zr incorporation in the MOF is ideally suited for this reaction. Having found the optimized reaction condition, applicability of Zr-BDC-MOF was investigated in the synthesis of wide range of amino esters. A range of amino esters was produced with high selectivity by the reaction of methyl acrylate and different amines (Table 4). Reaction was more facile when aliphatic amines were reacted when compared to aromatic amines (Table 4). It may further be noted that heterocyclic amines required significantly less time (5 min) when compared to aniline (12 h), which show that heterocyclic amines are highly reactive for the conjugate addition with methyl acrylate. The reactivity of nucleophiles can be correlated with the relative basicity of amines. A systematic increase in the activity was observed with increase in the relative basicity of amines. With increase in the relative basicity, the reaction became facile. For example, aniline and its derivative having low basicity required longer reaction time (12 h), whereas aliphatic amines with high basicity reacted very fast and produced good yield of the addition product in very less time. Not only amines determine the reactivity but it also depends on the reactivity of olefins (Table 4). For example: significantly less (9 %) product yield was obtained when acrylonitrile was reacted with aniline when compared to methyl acrylate (product yield = 61 %). Similarly, 1.5 h was required when acrylonitrile was reacted with imidazole when compared to methyl acrylate (time required = 5 minutes). Methyl vinyl ketone reactivity was also found to be less when compared to methyl acrylate (Table 4). Conjugate addition proceeds well even without catalyst when strong base such as butylamine, piperidine, and benzylamine were used. Amine conversions were in the range of 50-55% for these amines in the absence of catalyst under the optimized reaction condition given in Table 4. However, it is noteworthy to mention that the reaction do not proceed well (1 % aniline conversion) without catalyst when aniline was reacted with methyl acrylate.

It may be noted that when ethanol and phenol were reacted with methyl acrylate, no reaction took place. To further confirm this observation, *p*-amino phenol was reacted with methyl acrylate. In this case, the addition product was obtained only due to the nucleophilic addition of $-NH_2$ group with methyl acrylate (Table 4). Furthermore, reactivity and product formation in the nucleophilic addition of substrates bearing two reactive nucleophilic groups with methyl acrylate were also investigated. Just for illustration, in this study, *o*-amino

thiophenol, *o*-phenyl diammine, and *p*-phenyl diammine were chosen (Table S5). Detail of this investigation is provided in the supporting information.

In contrast to ring opening of epoxide, activation of nucleophile is an important step in the conjugate addition of nucleophiles with activated olefins (Scheme 3). The amine is activated on the acid sites in the first step. Amine is adsorbed on the acid site of MOF to form intermediate (C) by acid-base interaction, followed by Michael addition of olefins to give the intermediate (D). The intermediate (D), then, releases the desired anti-adduct (mono-addition product) to regenerate acid sites of the catalyst. Further, addition of olefins to the intermediate (E) affords side product (di-addition product) with regeneration of active catalyst. Let's assume that olefin is adsorbed at the acid site of catalyst, which is followed by the formation of corresponding cation. In this mechanism, unfortunately, nucleophilic attack of amine occurs preferentially to the α-carbon of olefin to give Markovnikov adduct. But this second possibility is ruled out in this study, because no Markovnikov adduct was formed. Since MOF catalyst is an acid catalyst, therefore, the adsorption of amine on acid sites of MOF by the acid-base interaction is more appropriate than that of olefin to yield carbocation.

Catalyst was found to be stable and recyclable. Recycling experiments were conducted to establish the stability of the catalyst (Fig. S3). For the recycling study, at the end of reaction, 3 mL of ethyl acetate was added and catalyst was separated by centrifugation. Thereafter, it was washed with another 3 mL of ethyl acetate, dried in vacuum oven at 100 °C for 4 h and then used in next cycle. Recycling experiments confirm that no significant change in the activity was observed even after three recycles. Textural characterizations using XRD and surface area analysis confirmed that the catalyst is stable. Surface area of the recycled catalyst was found to be 986 m^2/g.

4. Conclusion

Zirconium and copper based MOFs were prepared using 1, 4-benzenedicarboxylic acid and trimesic acid based organic building units, respectively. For comparative study, three different Zn based MOF catalysts were prepared using three different organic building units, 1, 4-benzenedicarboxylic acid, trimesic acid, and 2-methylimidazole. These MOFs were successfully used as heterogeneous catalyst in the nucleophilic ring opening of epoxide with amines, alcohols and thiphenols and nucleophilic addition of activated olefins with

amines/thiophenol. Among the MOF catalysts investigated in this study, Zr-BDC-MOF exhibited the highest activity in these reactions. Wide range of aromatic/aliphatic/heterocyclic amino alcohols, alkoxy alcohols, amino esters, and structurally similar compounds was successfully prepared using this synthesis protocols. Basicity of amines influenced the reactivity and regioselectivity of the products. Furthermore, the catalyst was easily separated from the reaction mixture and recycled with negligible loss in the activity. Following are some note worthy features of this catalytic process: (1) simple and mild synthetic route, (2) involves heterogeneous MOF catalyst, which is easily separable and recyclable, (3) solvent-less catalytic process, and (4) follows the green chemistry principles.

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Supporting information details

Details of MOFs synthesis, instrument used for the characterization, some part of characterization results, optimization of reaction condition for ring opening of epoxide with amine, details for the ring opening of epoxide with substrates bearing two reactive nucleophilic groups, details of nucleophilic addition of substrates bearing two reactive nucleophilic groups with methyl acrylate, and details of recyclability studies are provided.

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Figure, Scheme and Table caption

Figure caption:

Fig. 1. Powder X-ray diffraction patterns of (a) Zr-BDC-MOF and Cu-BDC-MOF, and (b) Zn-BDC-MOF, Zn-BTC-MOF and Zn-MeIMI-MOF.

Fig. 2. (a) N_2-adsorption isotherm (Inset shows pore size distribution) and (b) Thermo gravimetric analysis of Zr-BDC-MOF.

Scheme caption:

Scheme 1. (a) Ring-opening of epoxide with nucleophiles and (b) conjugate addition of olefins with nucleophiles.

Scheme 2. Proposed mechanism for the ring opening of epoxides with nucleophiles using MOFs.

Scheme 3. Proposed mechanism for the nucleophilic addition of olefins with nucleophiles using MOFs.

Table caption:

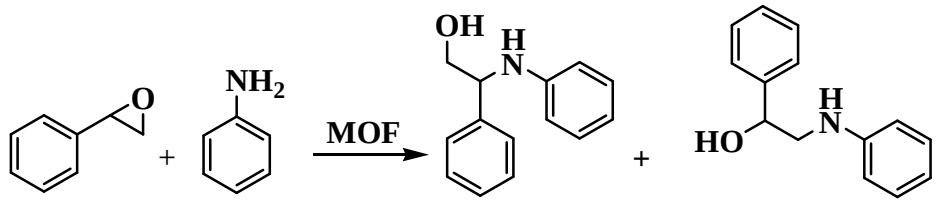
Table 1. Ring opening of styrene oxide with aniline over various MOFs investigated in this study.

Table 2. Ring opening of epoxides with wide range of amines over Zr-BDC-MOF.

Table 3. Ring opening of styrene oxide with wide range of alcohols/phenols/thiophenol over Zr-BDC-MOF.

Table 4. Nucleophilic addition of different olefins with wide range of nucleophiles over Zr-BDC-MOF.

Table 1. Ring opening of styrene oxide with aniline over various MOFs investigated in this study.

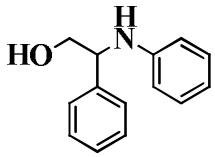
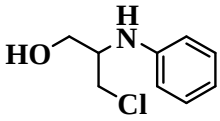
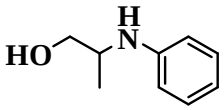
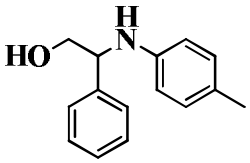
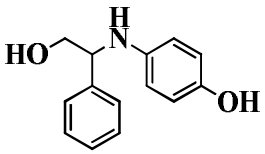
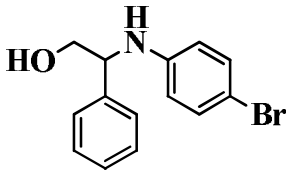
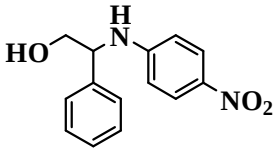


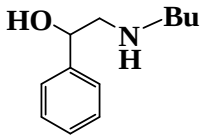
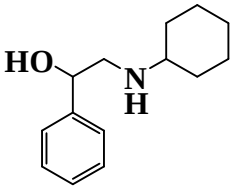
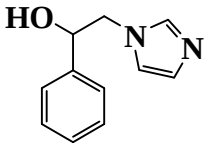
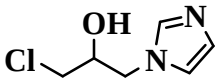
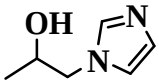
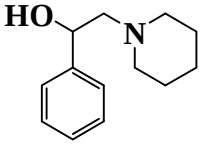
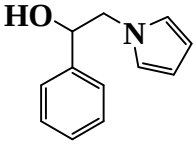
β-Amino alcohol **α-Amino alcohol**

Catalyst	Styrene oxide conversion (%)	Amino alcohol selectivity (β:α)	TOF (h^{-1})
None	<1	-	-
$ZrOCl_2$	10.5	94 : 06	121
Zr-BDC-MOF	80.7	93 : 07	968
Zn-BDC-MOF	3.4	87 : 13	41
Zn-BTC-MOF	1.7	86: 14	21
Zn-MeIMI-MOF	<1	-	-
Cu-BTC-MOF	5.2	87 : 13	63

Reaction condition: Catalyst (0.005 mmol), styrene oxide (1.0 mmol), aniline (1.0 mmol), reaction temperature (50 °C), time (10 min).
TOF (h^{-1}) = Turnover frequency [moles of epoxide converted per mole of active metal per hour]

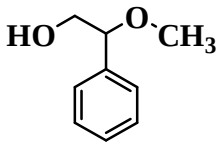
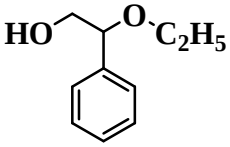
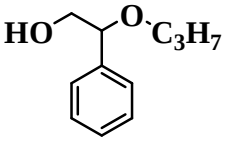
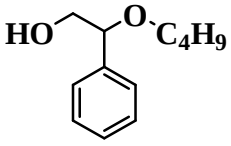
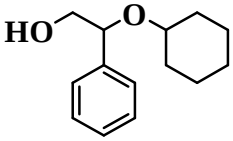
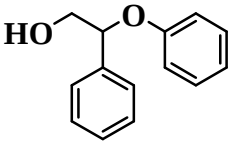
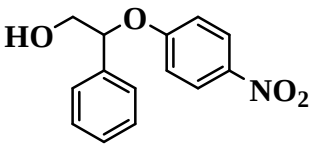
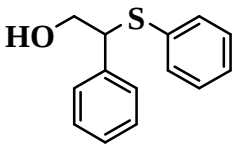
Table 2. Ring opening of epoxides with wide range of amines over Zr-BDC-MOF.

E. No.	Epoxide	Amine	Time	Selective Amino alcohol	Epoxide Conv. (%)	Amino alcohol selectivity β : α
1	Styrene oxide	Aniline	10 min		80.7	93 : 07
2	Epichlorohydrine	Aniline	10 min		91.4	90 : 10
3	Propylene oxide	Aniline	10 min		73.6	88 : 12
4	Styrene oxide	p-Toluidine	10 min		70.2	91 : 09
5	Styrene oxide	p-Amino phenol	10 min		17.6	98 : 02
6	Styrene oxide	p-Bromo aniline	10 min		54.1	96 : 04
7	Styrene oxide	p-Nitro aniline	10 min		5.2	100 : 0

8	Styrene oxide	Butyl amine	2 h		40.3	14 : 86
9	Styrene oxide	Cyclohexylamine	2 h		28.6	16 : 84
10	Styrene oxide	Imidazole	2 h		90.2	02 : 98
11	Epichlorohydrine	Imidazole	2 h		90.5	00 : 100
12	Propylene oxide	Imidazole	2 h		60.1	00 : 100
13	Styrene oxide	Piperidine	1 h		85.2	00 : 100
14	Styrene oxide	Pyrrole	1 h		80.3	5 : 95

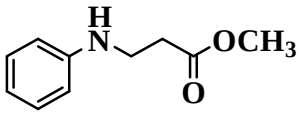
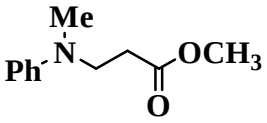
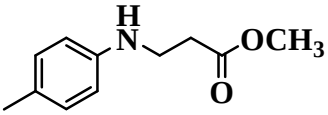
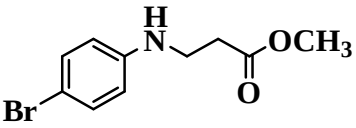
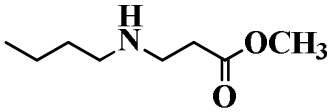
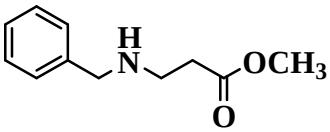
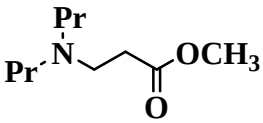
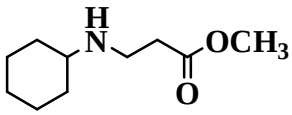
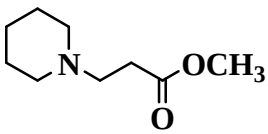
Reaction condition: Zr-BDC-MOF (0.005 mmol), epoxide (1.0 mmol), amine (1.0 mmol), reaction temperature (50 °C).

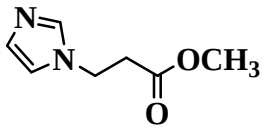
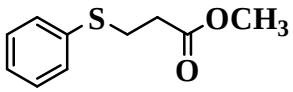
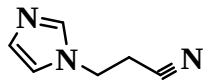
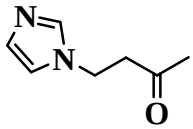
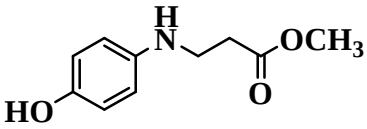
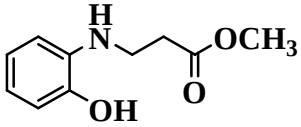
Table 3. Ring opening of styrene oxide with wide range of alcohols/phenols/thiophenol over Zr-BDC-MOF.

E. No.	Alcohol	Time	Selective Alkoxy alcohol	Styrene oxide Conv. (%)	Product selectivity β : α
1	Methanol	2 h		75.2	95 : 05
2	Ethanol	2 h		56.4	89 : 11
3	1- Propanol	2 h		42.1	93 : 07
4	1-Butanol	2 h		20.6	87 : 13
5	Cyclohexanol	2 h		31.2	93 : 07
6	Phenol	1/2 h		94.1	66 : 0 (34)[a]
8	*p*-Nitrophenol	1 h		40.2	70 : 0 (30)[a]
9	Thiophenol[b]	1/2 h		79.8	62 : 35 (3 % diphenyl disulfide)

Reaction condition: Zr-BDC-MOF (0.005 mmol), styrene oxide (1.0 mmol), alcohol (25 mmol), reaction temperature (70 °C). [a] Un-identified products. [b] Styrene oxide:thiophenol = 1:1

Table 4. Nucleophilic addition of different olefins with wide range of nucleophiles over Zr-BDC-MOF.

E. No.	Epoxide	Nucleophile	Selective product	Time	Nucleophile Conversion (%)	Product selectivity Mono : Di %
1	Methyl acrylate	Aniline		12 h	61.3	97 : 03
2	Methyl acrylate	N-methyl aniline		12 h	53.5	98 : 02
3	Methyl acrylate	p-Toluidine		12 h	66.4	96 : 04
4	Methyl acrylate	p-bromo aniline		12 h	20.5	100 : 0
5	Methyl acrylate	Butyl amine		0.5 h	99.6	82 : 18
5	Methyl acrylate	Benzyl amine		0.5 h	96.4	92: 08
6	Methyl acrylate	Dipropylamine		0.5 h	90.4	100 : 0
7	Methyl acrylate	Cyclohexylamine		0.5 h	98.1	95 : 05
8	Methyl acrylate	Piperidine		5 min	98.8	100 : 00

9	Methyl acrylate	Imidazole		5 min	92.0	100 : 0
10	Methyl acrylate	Thiophenol		2 h	86	98 : 0 (2 % diphenyl disulfide)
11	Acrylonitrile	Imidazole		1.5 h	92.3	100 : 0
12	Methyl vinyl ketone	Imidazole		1.5 h	95.3	76 : 0 (24)[a]
13.	Methyl acrylate	4-Amino phenol		12 h	81.0	79 : 21
14.	Methyl acrylate	2-Amino phenol		12 h	96.0	55 : 45

Reaction condition: Catalyst (0.01 mmol), olefin (2.1 mmol), nucleophile (2 mmol), reaction temperature (80 °C). [a] Un-identified products.

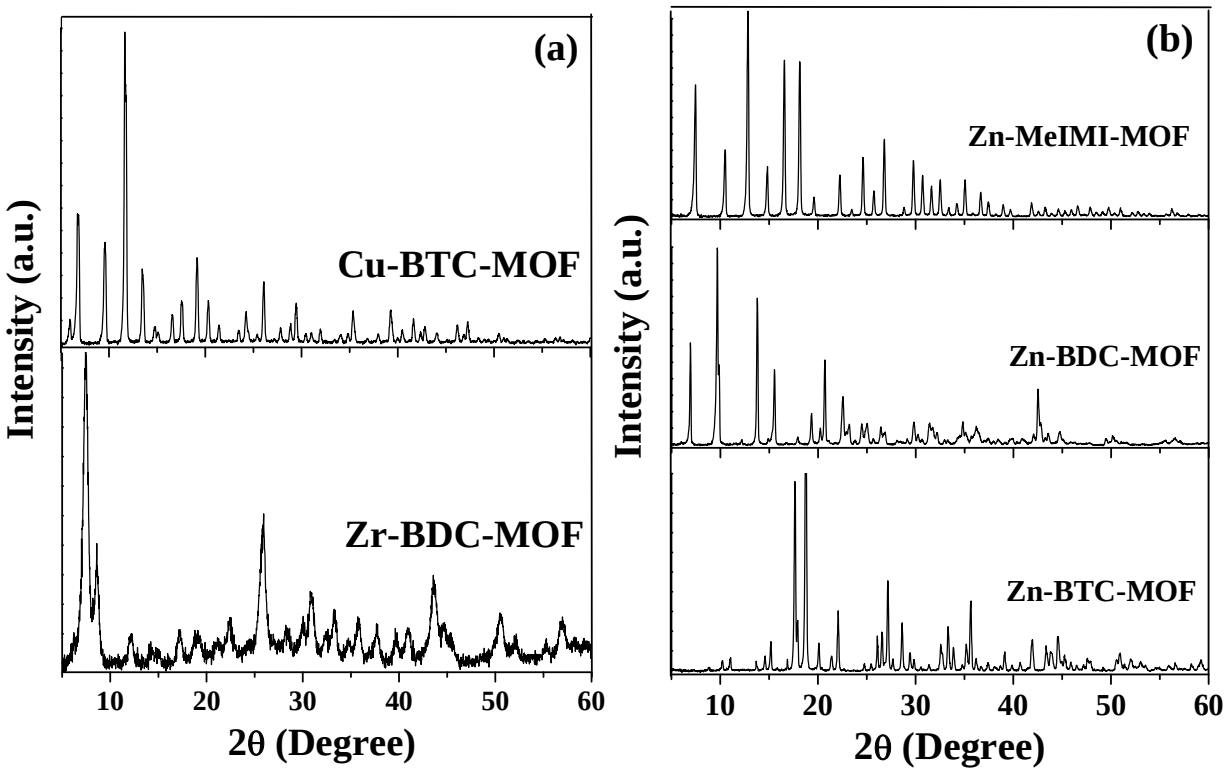


Fig. 1. Powder X-ray diffraction patterns of (a) Zr-BDC-MOF and Cu-BDC-MOF, and (b) Zn-BDC-MOF, Zn-BTC-MOF and Zn-MeIMI-MOF.

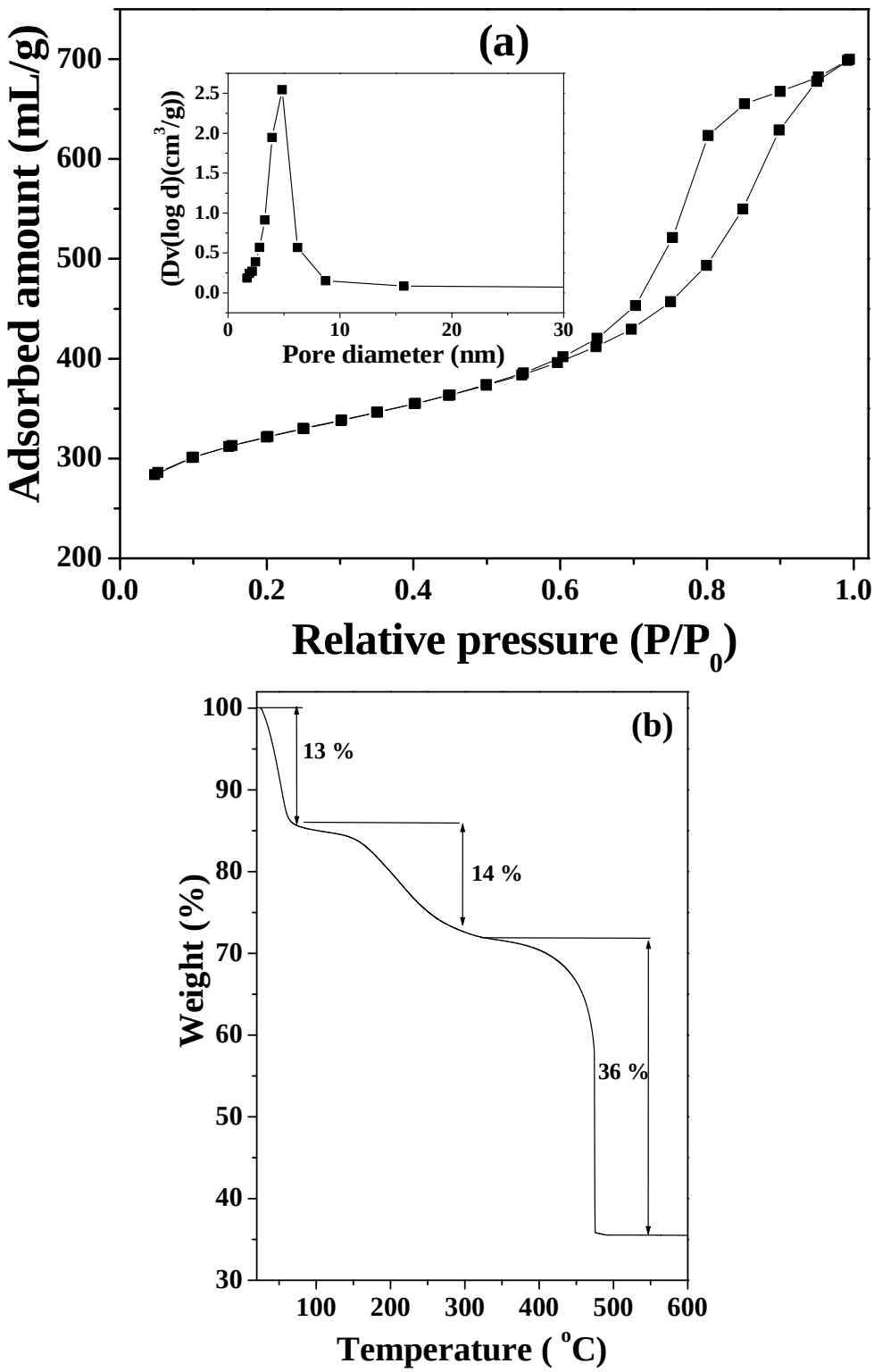
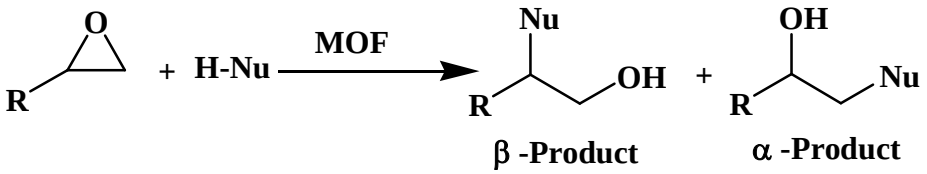
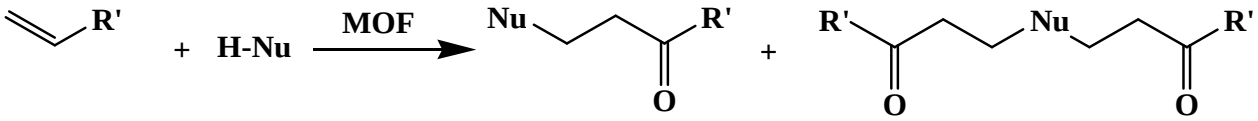


Fig. 2. (a) N_2-adsorption isotherm (Inset shows pore size distribution) and (b) Thermo gravimetric analysis of Zr-BDC-MOF.



R = -Ph, $-CH_2Cl$, $-CH_3$ **Nu = Aromatic/aliphatic/heterocylic amines alcohol/phenol/thiophenol**

(1a)



R' = $-COOCH_3$, -CN, $-COCH_3$

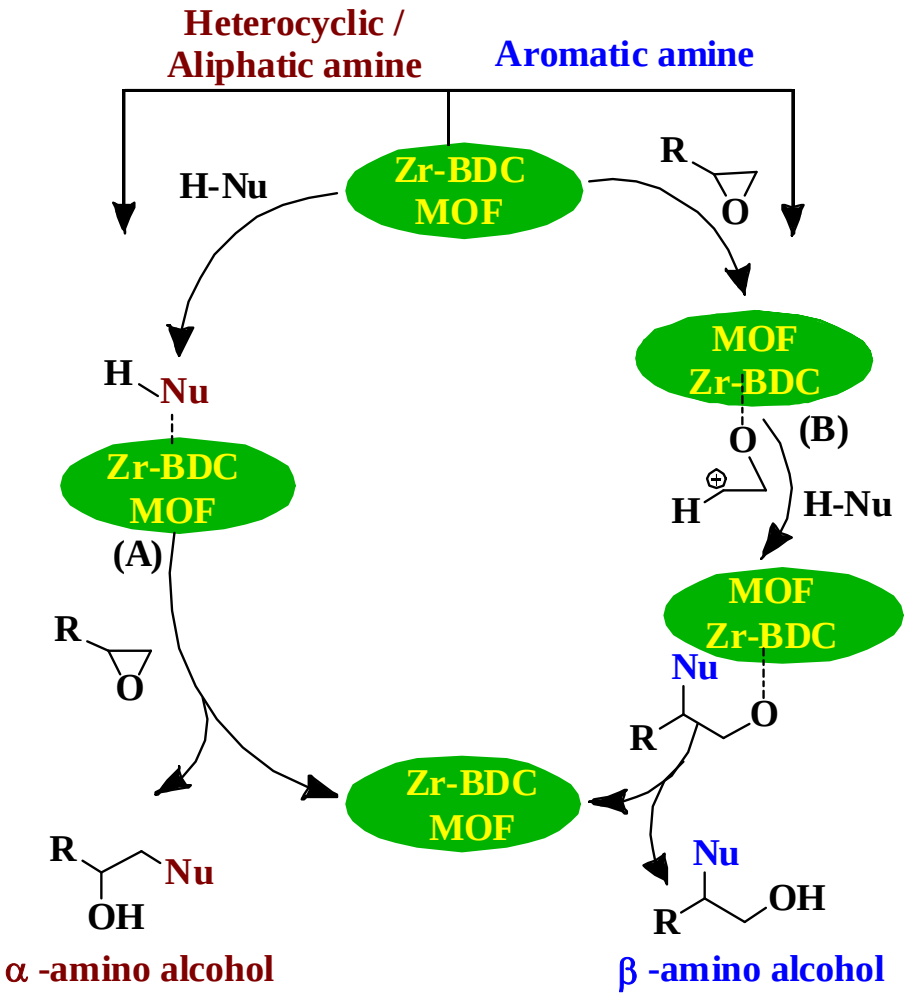
Mono-addition product

Di-addition product

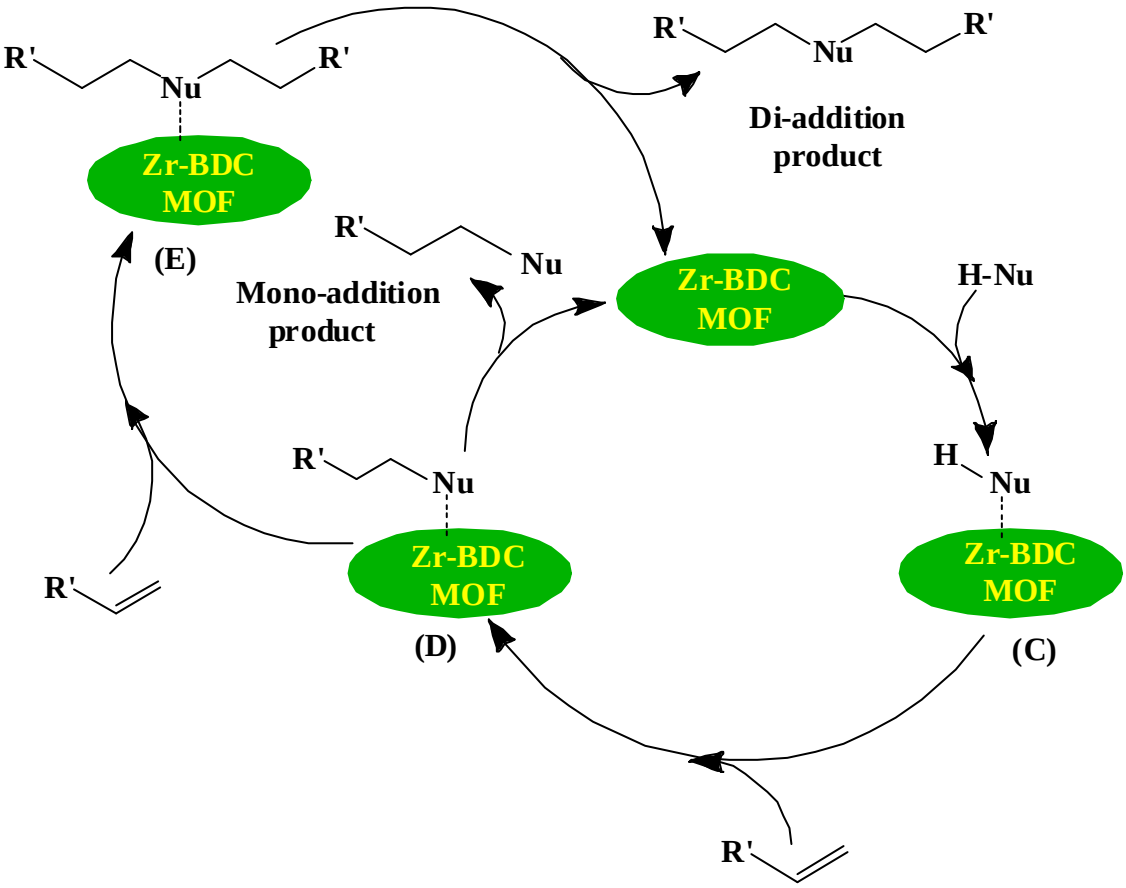
Nu = Aromatic/aliphatic/heterocylic amines alcohol/phenol/thiophenol

(1b)

Scheme 1. (a) Ring-opening of epoxide with nucleophiles.and (b) nucleophilic addition of olefins with nucleophiles.



Scheme 2. Proposed mechanism for the ring opening of epoxides with nucleophiles using MOFs.



Scheme 3. Proposed mechanism for the nucleophilic addition of olefins with nucleophiles using MOFs.