

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

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Supporting Information

Experimental details

Chemicals

All chemicals used in the study were of AR grade and used as received without further purification. $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ and HNO_3 were purchased from Loba Chemie, Mumbai, India. $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ (98 %), trimesic acid (95 %), 1, 4-benzenedicarboxylic acid (98 %) were obtained from Sigma-Aldrich, India. 2-Methyl imidazole was purchased from Spectrochem Pvt. Ltd., Mumbai, India. Dimethyl formamide (DMF) and ethanol were obtained from SD Fine Chem. Ltd., Mumbai. HCl (35%) and organic solvents used in this study were obtained from Merck India Pvt. Ltd. All other chemicals required for catalytic investigations were purchased from Sigma-Aldrich, India.

Catalyst preparation

Zr metal-organic framework (here after represented as Zr-BDC-MOF) was prepared by following the reported procedure with little modification.²⁵ In a typical synthesis, a mixture of $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ (3.22 g, 10 mmol), 1, 4-benzenedicarboxylic acid (H_2BDC) (1.6 g, 10 mmol), and 50 ml of DMF was taken in round bottom flask, which was fitted with reflux condenser. Reaction mixture was stirred for 10 min at ambient condition. 1.6 ml of HCl (19.2 mmol) was added to the reaction mixture at ambient condition. Upon addition of HCl, the reaction mixture turned white. Temperature of the reaction mixture was elevated to 150 °C using oil-bath and the reaction was continued for 24 h under open air atmosphere. The resultant white solid was filtered and washed with DMF. Product was dried in an oven at 100 °C for 12 h. Dried product was again taken in 50 mL of DMF and stirred overnight at ambient condition to remove any unreacted H_2BDC . Product was filtered and dried at 100 °C for 2 h. Finally, the obtained product was taken in 20 mL of methanol and stirred overnight at ambient condition. Product was filtered and again taken in fresh methanol. This methanol treatment process was performed thrice to remove most of the DMF from the product. Finally the product was dried in oven at 100 °C for 12 h. For comparative study, other MOF such as Zn-BDC-MOF, Zn-BTC-MOF, Zn-MeIMI-MOF, and Cu-BTC-MOF were prepared by following the reported procedure.²⁶⁻²⁹

Zn-BDC-MOF was prepared according to reported method.²⁶ A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.744 g, 2.5 mmol) and H_2BDC (0.083 g, 0.5 mmol) were dissolved in 75 mL of DMF at ambient condition and then the reaction mixture was sealed and heated at 120 °C for 24 h. The resultant white crystalline solid was filtered, washed with DMF, and then dried in vacuum.

Zn-BTC-MOF was prepared according to reported method.²⁷ $\text{Zn}(\text{II})$ acetate 3yclised3 (0.361 g, 1.65 mmol) and trimesic acid (0.20 g, 0.95 mmol) were dissolved in 15 mL of water. Reaction mixture was transferred to Teflon lined stainless steel autoclave and placed in a programmable furnace. The mixture was heated to 140 °C with a rate of 5 °C/min and held at that temperature for 24 h. Furness was then cooled at 0.1 °C/min to 120 °C and held at this temperature for 5 h, followed by further cooling at the same rate to 100 °C, and then held at this temperature for another 5 h. The resulting needle-like colorless large crystals were filtered, washed with deionized water & ethanol, and then dried in vacuum.

Zn-MeIMI-MOF was synthesized according to reported procedure.²⁸ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (350 mg, 1.17 mmol) and 2-methylimidazole (200 mg, 2.43 mmol) were taken in 15 mL of DMF. Catalytic amount (three drops) of HNO_3 was added and the reaction mixture was sonicated for 30 minutes. The reaction mixture was heated at 120 °C for 24 h. The resulting white crystalline solid was filtered, washed with DMF, and then dried in vacuum.

Cu-BTC-MOF was prepared by the following reported procedure.²⁹ First, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (2.6 g, 10.7 mmol) was dissolved in 30 mL of H_2O . In a separate flask, trimesic acid (0.68 g, 3.2 mmol) was dissolved in 30 mL of EtOH. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution was slowly added to the trimesic acid solution with stirring at ambient temperature. The solution turned turbid due to the precipitation. DMF (2 mL) was added to the reaction mixture and then it was transferred to an Teflon lined stainless steel autoclave, which was heated at 80 °C for 20 h. Autoclave was cooled to room temperature, the resulting blue precipitate was filtered, washed with H_2O and EtOH, and then dried in vacuum.

Catalyst characterization

X-ray diffraction (XRD) patterns were recorded in the 2θ range of $5\text{--}60^\circ$ with a scan speed of $2^\circ/\text{min}$ on a PANalytical X'PERT PRO diffractometer, using Cu $K\alpha$ radiation ($\lambda=0.1542\text{ nm}$, 40 kV, 40 mA) and a proportional counter detector. Nitrogen adsorption measurements were performed at 77 K by Quantachrome Instruments, Autosorb-IQ volumetric adsorption analyzer. Sample was out-gassed at $150\text{ }^\circ\text{C}$ for 3 h in the degas port of the adsorption apparatus. The specific surface area was calculated from the adsorption data points obtained at P/P_0 between 0.05–0.3 using the Brunauer-Emmett-Teller (BET) equation. The pore diameter was estimated using the Barret–Joyner–Halenda (BJH) method. Scanning electron microscopy (SEM) measurements were carried out on a JEOL JSM-6610LV to investigate the morphology of the materials. Fourier transform infrared (FTIR) spectra were recorded on a Bruker spectrophotometer in the region $400\text{--}4000\text{ cm}^{-1}$ (spectral resolution = 4 cm^{-1} ; number of scans = 100). Samples were prepared in the form of KBr pellets (1 wt %). Thermo gravimetric analysis (TGA) was performed in the range of $25\text{--}600\text{ }^\circ\text{C}$ on a TGA/DSC 1 STAR^e SYSTEM from Mettler Toledo, Switzerland, with temperature increments of $10\text{ }^\circ\text{C}/\text{min}$ in O_2 atmosphere.

Results and Discussion

Optimization of reaction condition for ring opening of epoxide with amine.

To optimize the reaction condition, styrene oxide and aniline were chosen as representative epoxide and amine, respectively. As the temperature increased from $30\text{ }^\circ\text{C}$ to $70\text{ }^\circ\text{C}$, the conversion of styrene oxide was increased from 50 mol % to 96 mol % (Table S1). It is interesting to note that, unlike the conventional process, the ring opening of styrene oxide occurs even at ambient temperature ($30\text{ }^\circ\text{C}$) with good yields and selectivity for β -amino alcohol. However, to obtain good product yield, $50\text{ }^\circ\text{C}$ was chosen as optimum reaction temperature. The amount of catalyst also influenced the conversion of styrene oxide. As the catalyst amount was increased, the epoxide conversion was also increased (Table S1). To obtain good yield, 0.005 mmol of catalyst with respect to 1 mmol of reactant was chosen. At the end, influence of solvent on the catalytic activity was studied. Zr-BDC-MOF exhibited the highest activity when the reaction was performed in the absence of solvent. Low epoxide conversion was obtained, when

reaction was performed in polar aprotic solvent than nonpolar solvents (Table S1). This activity difference can be correlated with adsorption of solvent molecule on the catalytic active sites. Solvent molecules, especially polar solvent molecules could block the active sites due to the competitive adsorption of reactant and solvent molecules. This competitive adsorption creates hindrance for the reactant molecules to reach active sites; therefore, in the presence of solvent, catalytic activity was decreased.

Ring opening of epoxide with substrates bearing two reactive nucleophilic groups

When styrene oxide was reacted with *o*-amino thiophenol, four products were observed (Table S3). In the beginning, large amount of product based on the nucleophilic addition of amine group with styrene oxide was obtained. It may be noted that the reactivity of aniline was found to be much higher than thiophenol, therefore -NH_2 addition product was formed selectively in less time. With further increase in the reaction time, selectivity for -NH_2 addition products was decreased and selectivity for -SH addition products were increased (Table S3). However, in this case of *o*-amino phenol and *p*-amino phenols, only -NH_2 nucleophilic addition products were observed and no -OH addition product due to phenolic group was obtained. It may be noted that the nucleophilic ring opening of styrene oxide with phenol took place efficiently when they were reacted in 1:25 ratio at 70 °C (Table 3).

Nucleophilic addition of substrates bearing two reactive nucleophilic groups with methyl acrylate

Reactivity and product formation in the nucleophilic addition of substrates bearing two reactive nucleophilic groups with methyl acrylate were investigated. Just for illustration, in this study, *o*-amino thiophenol, *o*-phenyl diammine, and *p*-phenyl diammine were chosen (Table S5). In the case of *o*-amino thiophenol, with in 2 h, almost quantitative amount of -SH addition product was obtained (Table S5). It may be noted that the reactivity of thiophenol was found to be much higher than aniline therefore, -SH addition product was formed selectively in less time. When *o*-phenyldiammine was reacted with methyl acrylate, in addition to mono-addition products, one additional cyclized product was obtained (Table S5). This cyclized product was formed due to the removal of methanol from the mono-addition product (Table S5). To confirm, whether this cyclized product was formed due to the *o*- NH_2 substituent, *p*-phenyldiammine was reacted with

methyl acrylate. As anticipated, in this case, only mono-addition products were obtained ([Table S5](#)).

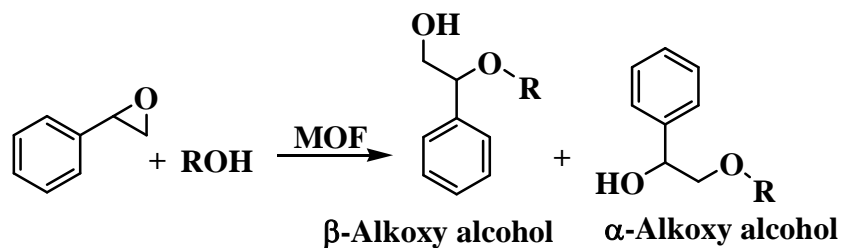
Table S1. Optimization of reaction condition in the ring opening of styrene oxide with aniline over Zr-BDC-MOF.

Temperature (°C)	Catalyst amount (mmol)	Solvent	Styrene oxide conversion (%)	Amino alcohol selectivity (β : α)	TOF (h^{-1})
30	0.005	None	50.4	91 : 09	605
50	0.005	None	80.7	95 : 05	968
70	0.005	None	96.2	93 : 07	1153
50	0.0025	None	52.7	90 : 10	1264
50	0.0075	None	99.6	95 : 05	797
50	0.005	Toluene	70.2	94 : 06	842
50	0.005	CH ₂ Cl ₂	56.7	92 : 08	680
50	0.005	CHCl ₃	57.0	92 : 08	684
50	0.005	CH ₃ CN	55.4	90 : 10	664

Reaction condition: Styrene oxide (1.0 mmol), aniline (1.0 mmol), reaction time (10 min).

TOF (h^{-1}) = Turnover frequency [moles of epoxide converted per mole of active Zr per hour]

Table S2. Optimization of reaction condition in the ring opening of styrene oxide with methanol over various catalysts investigated in this study.

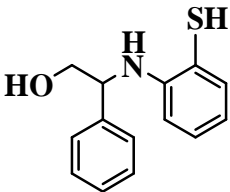
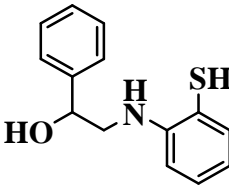
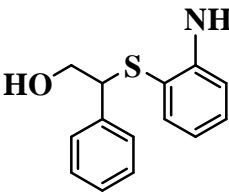
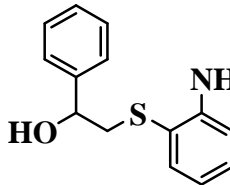
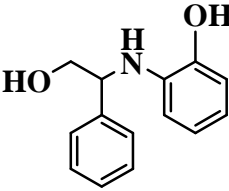
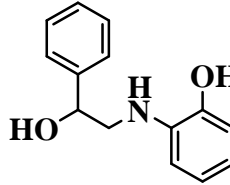
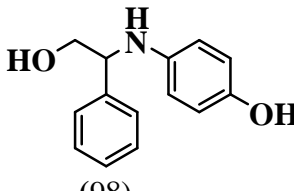
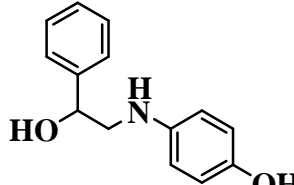


Catalyst	Temperature (°C)	Catalyst amount (mmol)	Styrene oxide conv. (%)	Alkoxy alcohol selectivity $\beta : \alpha$	TOF (h^{-1})
None	70	0.005	<1	-	
Zr-BDC-MOF	70	0.005	75.2	95 : 05	75
Zn-BDC-MOF	70	0.005	8.4	94 : 06	8
Zn-BTC-MOF	70	0.005	52.3	100 : 00	52
Zn-MeIMI-MOF	70	0.005	2.6	85 : 15	2
Cu-BTC-MOF	70	0.005	5.5	95 : 05	5
Zr-BDC-MOF	30	0.005	18.1	97 : 03	18
Zr-BDC-MOF	50	0.005	51.3	97 : 03	51
Zr-BDC-MOF	80	0.005	86.4	93 : 07	86
Zr-BDC-MOF	70	0.0025	52.3	96 : 04	104
Zr-BDC-MOF	70	0.0075	93.6	97 : 03	62

Reaction condition: Styrene oxide (1.0 mmol), methanol (25 mmol), reaction time (2 h).

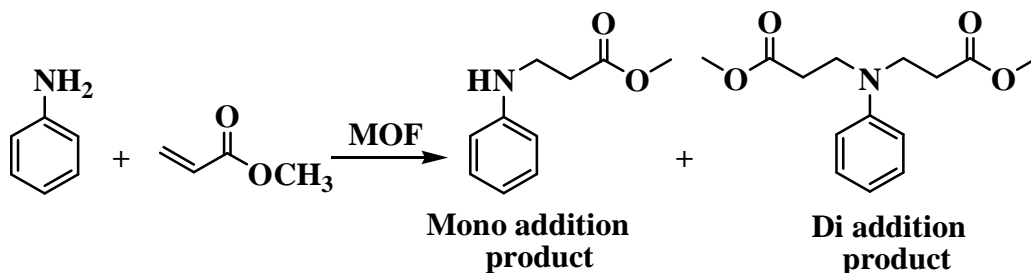
TOF (h^{-1}) = Turnover frequency [moles of epoxide converted per mole of active metal per hour]

Table S3. Ring opening of styrene oxide with nucleophiles bearing two nucleophilic sites over Zr-BDC-MOF.

Reactant	Time	Styrene oxide conv. %	Product distribution (selectivity)			
<i>o</i> -Amino thiophenol						
	10 min	73.5	(88)	(02)	(07)	(03)
	2 h	95	(65)	(05)	(20)	(15)
<i>o</i> -Amino phenol						
	10 min	21	(99)	(01)		
	2 h	80	(99)	(01)		
<i>p</i> -Amino phenol						
	10 min	17	(98)	(02)		
	2 h	75	(98)	(02)		

Reaction condition: Zr-BDC-MOF (0.005 mmol), styrene oxide (1.0 mmol), reactant (1.0 mmol), reaction temperature (50 °C).

Table S4. Optimization of reaction condition for the nucleophilic addition of methyl acrylate with aniline by different MOF investigated in this study.

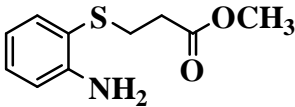
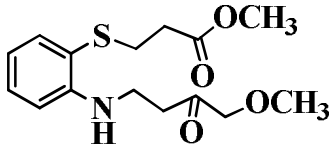
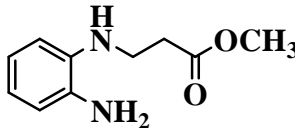
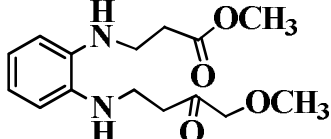
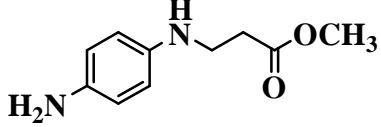
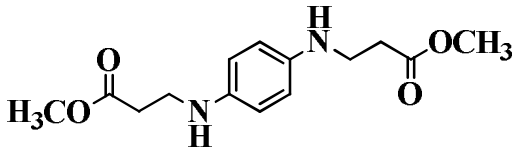


Catalyst	Temperature (°C)	Catalyst amount (mmol)	Aniline conversion (%)	Product selectivity Mono : Di	TOF (h ⁻¹)
None	80	-	-	-	-
ZrOCl ₂	80	0.01	22.8	95 : 05	3.7
Zr-BDC-MOF	80	0.01	61.3	97 : 03	10.2
Zn-BDC-MOF	80	0.01	7.0	100 : 00	1.2
Zn-BTC-MOF	80	0.01	6.3	100 : 00	1.1
Zn-MeIM-MOF	80	0.01	3.5	100 : 00	0.5
Cu-BTC-MOF	80	0.01	2.4	100 : 00	0.4
Zr-BDC-MOF	30	0.01	7.4	100 : 00	1.2
Zr-BDC-MOF	50	0.01	32.2	98 : 02	5.4
Zr-BDC-MOF	100	0.01	77.6	95 : 05	12.9
Zr-BDC-MOF	80	0.005	40.3	98 : 02	13.4
Zr-BDC-MOF	80	0.015	86.7	96 : 04	9.6

Reaction condition: Methyl acrylate (2.1 mmol), aniline (2 mmol), reaction time (12 h).

TOF (h⁻¹) = Turnover frequency [moles of epoxide converted per mole of active metal per hour]

Table S5. Nucleophilic addition of methyl acrylate with nucleophiles bearing two nucleophilic sites over Zr-BDC-MOF.

Reactant	Time	Nucleophile conversion (%)	Product distribution (selectivity)	
<i>o</i> -Amino thiophenol	2 h	98	 (99)	 (01)
<i>o</i> -Phenylene diamine	12 h	62	 (76)	 (08)
<i>p</i> -Phenylene diamine	12 h	72	 (54)	 (46)

Reaction condition: Catalyst (0.01 mmol), methyl acrylate (2.1 mmol), nucleophile (2 mmol), reaction temperature (80 °C).

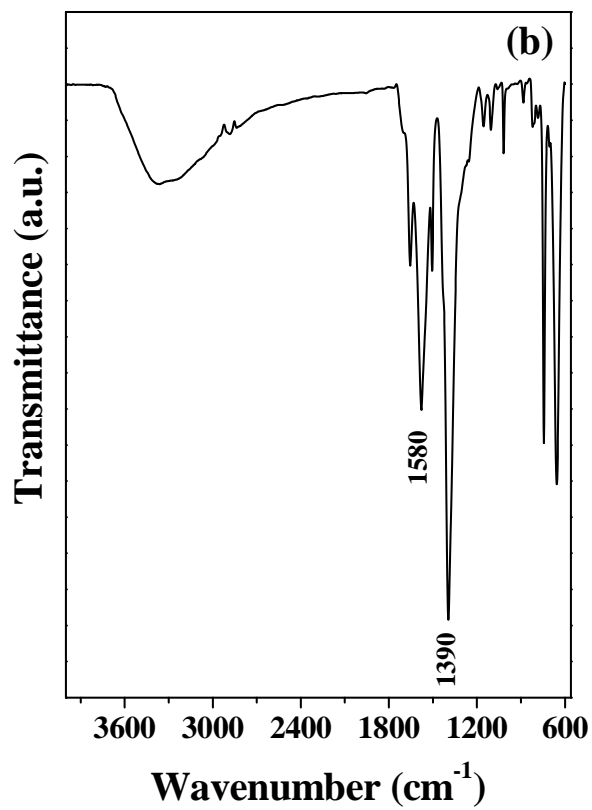
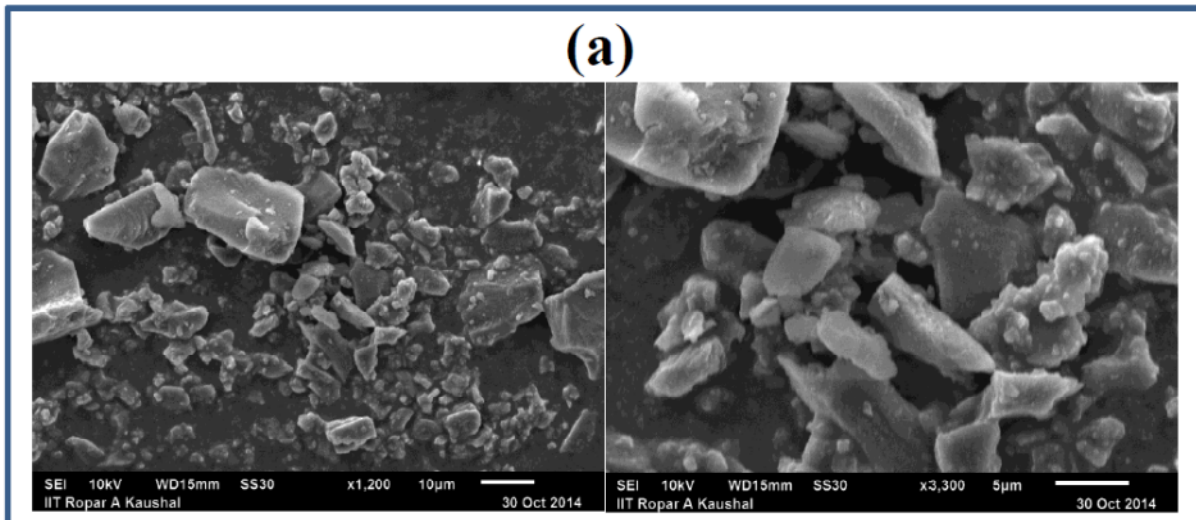


Fig. S1. (a) SEM and (b) FT-IR spectrum of Zr-BDC-MOF.

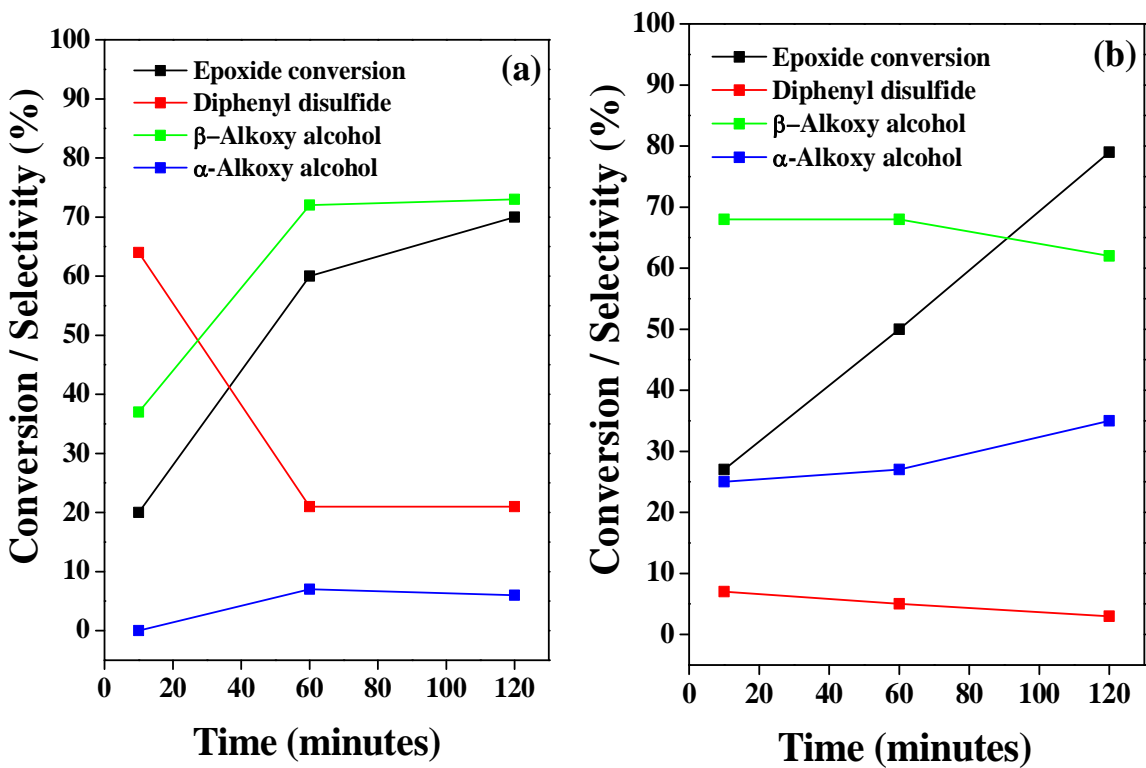


Fig. S2. Reaction profile obtained by the reaction of styrene and thiophenol in the molar ratio of (a) 1:25 (b) 1:1.

Reaction condition: Zr-BDC-MOF (0.005 mmol), styrene oxide (1.0 mmol), reaction temperature (70 °C).

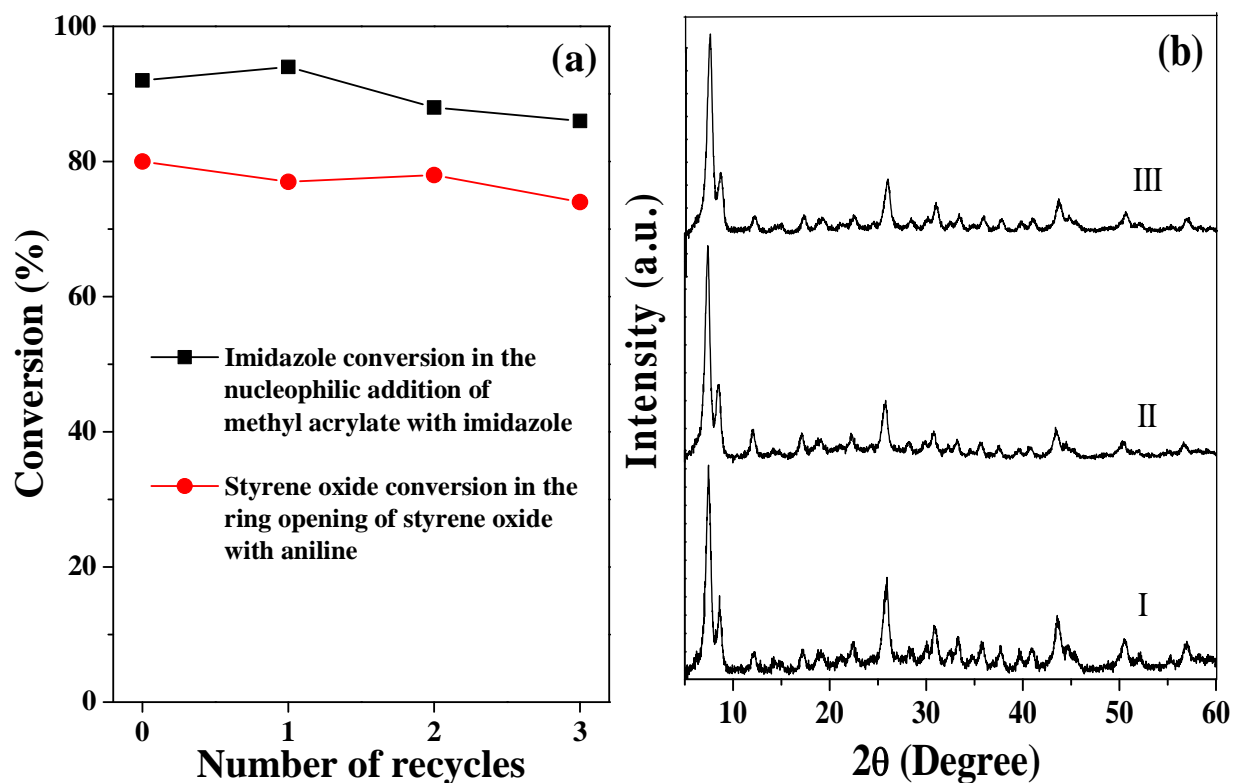


Fig. S3. (a) Reactant conversion vs number of cycles during the ring opening of styrene oxide with aniline and nucleophilic addition of imidazole with methyl acrylate. (b) XRD pattern of (I) fresh catalysts, (II) catalyst obtained after the three cycles in the ring opening of styrene oxide with aniline, and (III) catalyst obtained after the three cycles in the nucleophilic addition of imidazole with methyl acrylate.