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An Effective Strategy in the Creating of Asymmetric MOFs for Chirality Induction: Chiral Zr-based MOF in Enantioselective Epoxidation

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Abstract

Recently the construction of chiral MOFs (CMOFs) as a challenge is very difficult and complex. For the first time, we synthesized a chiral Zr-based MOF with L-tartaric acid by solvent assisted ligand incorporation (SALI). We showed that a CMOF can be postsynthetically generated by the simple method: incorporated chiral carboxylic groups on the achiral NU-1000. The post-synthesized chiral NU-1000 was used as an asymmetric support for producing a chiral catalyst with molybdenum catalytic active centers as Lewis acid sites. Enantioselective epoxidation of various prochiral alkens to epoxids by using [C-NU-1000-Mo] is comparable to the other asymmetric homogeneous and heterogeneous catalysts along with high enantiomeric excess and selectivity to epoxide (up to 100%). The CMOF could be reused in the styrene oxidation after five cycles without substantial deterioration in the CMOF crystallinity or catalytic performance after five cycles.

***Keywords*:** Olefin epoxidation, Enantioselective catalysis, tert-Butyl hydroperoxide, NU-1000, L-Tartaric acid, $MoO_2(acac)_2$.

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† *Electronic supplementary information (ESI) available: FT-IR of cis-$MoO_2(acac)_2$ and L-tartaric acid, UV–Vis spectra, ^{1}H NMR, ICP analysis, N_2 adsorption and BJH pore size distribution data, BET plots, Structural properties of NU-1000 (N) and chiral catalyst [C-NU-1000-Mo], TGA, PXRD and FT-IR of the used catalyst, Chiral GC chromatograms, Table of enantioselective epoxidation examples of the styrene by various asymmetric heterogeneous catalysts.*

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Introduction

The progress of Metal-Organic Frameworks (MOFs) as a family of porous materials with ideal designing, useful properties and different potential applications is very impressive.[1a,9a] The tunability of MOFs composition such as organic linkers, metal nodes and even functional groups not only creates new structures with different features but also it can affect on MOFs capability especially catalytic activity.[1b,2] Diverse MOFs were reported as heterogeneous catalysts or supports for heterogenization of the homogeneous catalysts.[2h,i] Using the chiral synthetic catalysts for the asymmetric catalysis has advanced extraordinarily from twenty-five years ago until today. Recently, the preparing of CMOFs (Chiral Metal-Organic Frameworks) has been developed due to their asymmetric applications.[3] The primitive investigations on homochiral MOFs applications especially catalytic abilities have been further done in time range 2002 to 2013 and they are more widely being continued. The chirality is an attractive phenomenon, a fundamental property in asymmetric materials structures that its description is a remarkable subject.[4] The CMOFs could be created by using various methods that the selection of one of them with suitable performance is important because their preparing is limited to the some kinds of reactions. There are three main ways for synthesizing of CMOFs that the chiral species can be existed or not in these procedures. Although, the studies showed that the optical activity in achiral crystals was a scarce event.[5,6] When there are no chiral agents, MOFs framework topology can induce chirality though poor.[7,8] The synthesizing of CMOFs has elaborations, but the effective method is the using of chiral component as BINOL and chiral M-salen derivatives, the enantiopure 2,2′-dihydroxy-1,1′-biphenyl in homochiral biphenol-based MOF, DUT-67 as an 8-connected zirconium with L-proline with catalytic performance and the synthesis of a simple chiral catalyst, UiO-66 by using L-proline as modulator, for the aldol reaction.[9] In the present

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work, the construction of chiral Zr-MOF happened with the incorporation of L-tartaric acid to Zr-nodes by using SALI method. Several examples about the incorporation of different compounds by SALI have been reported such as carboxylate, phosphonate, and dye molecules with different applications. Recently, Zhou et al. investigated the functionalization of PCN-700 as a flexible Zr-MOF with a wide range of linear organic dicarboxylate ligands, too. Even, the functionalization of nodes in zirconium-based MOFs has been performed in solution phase with various metal centers by using different methods, such as Au(I), Ir(I), Cu(II), Co(II) and V(V).[10]

NU-1000 as a Zr-MOF was our selection due to its properties such as tetratopic organic linker, pores size and high surface area that after chiralization, it decreased. We achieved to a novel CMOF (Chiral NU-1000) without any hardness with SALI method that it is implicated in collaborating of Zr-OH2 and Zr-OH in chiralization of the Zr-nodes by using chiral carboxylic acid (CFG = carboxylic-acid-containing functional group). Then, $MoO_2(acac)_2$ as a catalytic active site was immobilized on chiral NU-1000 as chiral support. The metalation of chiral NU-1000 was done for enantioselective epoxidation of olefins because epoxides are intermediates or starting materials for generation of chiral key organic compounds with industrial applications.[11] Regardless of reports, no work has been presented similar to ours: the SALI-CFG with the interaction of L-tartaric acid as an chiral organic precursor with base species in NU-1000. The successful immobilization route of the $MoO_2(acac)_2$ onto chiral modified NU-1000 with the used conditions has been displayed in Scheme 1. In used catalytic system, TBHP was chosen as a smooth and green oxidant that the obtained results are presented as follows.[12]

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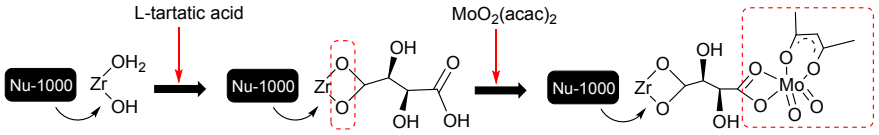
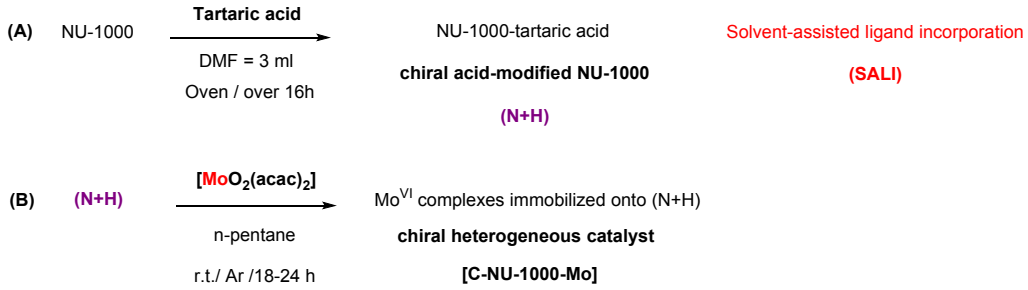


Interaction between **$Mo^{(VI)}$** and decorated **NU-1000** with **tartaric acid**



Scheme 1. The preparation steps of (N+H) and [C-NU-1000-Mo] catalyst with the used conditions.

Results and Discussion

Characterization of [C-NU-1000-Mo]

In this work, the Molybdenyl (VI) acetylacetonate was loaded onto chiral functionalized NU-1000 with tartaric acid that the probable interaction has been shown in Scheme 1. NU-1000 as a robust metal-organic framework showed great activity as a support for attachment of the chiral acids. Then, the immobilization of metal active site onto modified NU-1000 was performed due to the high and accessible ample hydroxyl and carboxyl functional groups of C-NU-1000. The asymmetric tartaric acid ligands created a chiral position close to Mo-complexes as catalytic centers. The resulted [C-NU-1000-Mo] indicated high activity as a chiral recyclable heterogeneous catalyst for the enantioselective epoxidation of several olefins. The most simple method for the investigation of the produced structures is FT-IR. The notable peaks were observed in FT-IR spectra of NU-1000 (N), functionalized NU-1000 (N+H) and catalyst [C-NU-1000-Mo] (Fig. 1). The appeared peaks from 2859 cm^{-1} to around 3500 cm^{-1} are

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characteristic of C-H stretching and O-H bonds, respectively. The benzene ring C=C bonds were appeared in 1535 cm^{-1}. The supported *cis*-MoO_2 (Mo=O) was confirmed with the existence of the strong new doublet bands in 910 and 933 cm^{-1}.[13] The weak peak at 1718 cm^{-1} is related to ν(C=O) vibrations of L-tartaric acid COOH and 1417 cm^{-1} is consistent with $\nu_s(CO_2^-)$ vibration of the present carboxylate group/O-H deformation.[14] The existence of 1718 and 1417 cm^{-1} peaks indicates that the used chiral acid is bound to NU-1000 due to the deprotonation carboxylate.[15]

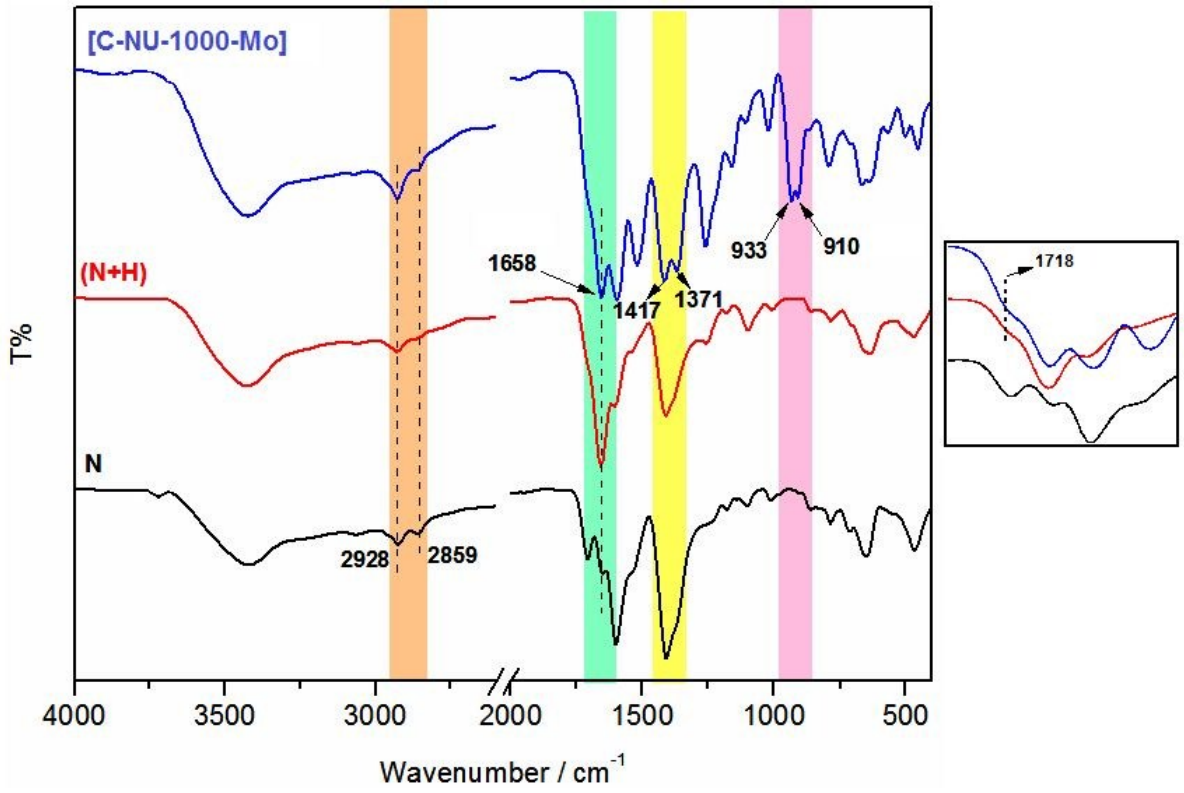

Fig. 1 FT-IR spectra of NU-1000 (N), NU-1000+L-tartaric acid (N+H) and [C-NU-1000-Mo].

In the molybdenum complexes with different ligands and solvents, separate UV-Vis spectra were seen. Undoubtedly, electronic transitions in catalyst depend on the type of the used ligands and nature of the metals.[16] UV-Vis spectra of dispersed [C-NU-1000-Mo] by using an ultrasound and $MoO_2(acac)_2$ were studied in DCE (Figure S2).

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The assignment of π-π^*, n-π^* and LMCT transitions is consistent with Mo-complex from 200 to 500 nm. In comparison to the neat complex spectrum (222, 267, 318 nm) with [C-NU-1000-Mo] (218, 263, 307, 423 nm), the tangible decreasing of the absorption bands and a little blue shift were seen that they could prove the immobilization Mo-complex onto NU-1000 (Fig S2).[17]

ICP determined the amount of Mo loading in the present catalyst, too (S3). ^{1}H NMR was another technique that confirmed the tartaric acid incorporation in the catalyst structure. Digested [C-NU-1000-Mo] with D_2SO_4 was analyzed in deuterated DMSO. The obtained spectrum exhibited the situation of the protons in 1,3,6,8-tetrakis(p-benzoic-acid)pyrene (TBAPy) and L-tartaric acid that appeared about 4.1 ppm and 7.5 to 8.3 ppm, respectively (Fig. S3). According to the obtained data, the extent of incorporated CFG on per node was estimated (2.8 chelating L-tartrates (T): 6 zirconiums: 0.5 molybdenum = T: Zr: Mo ratio). PXRD patterns of constructed samples are shown in Fig. 2.[10b] The XRD showed that NU-1000 maintained crystallinity after functionalization and metalation (SALI process/immobilization of Mo-complex). Peaks intensity decreased in carboxylic acid-functionalized NU-1000 and [C-NU-1000-Mo] that is logical due to crystallinity reduction. These relative changes confirm that the functionalization of NU-1000 nodes has occurred. The XRD pattern of experimental NU-1000 matches with its simulation.[10b]

In Figure 3, FE-SEM of NU-1000 and [C-NU-1000-Mo] has been shown. The images indicated that NU-1000 as a support maintained its cylinder structure during synthesis processes of [C-NU-1000-Mo], with the length of about 1.30 μm. So, it is concluded that tartaric acid and molybdenum-complex loading had not remarkably impressed on morphology NU-1000 framework.

For the porosity determination of the synthesized new porous materials, BET analysis is required as a useful method to confirm SALI-CFG and [C-NU-1000-Mo] porosity. With the comparing of

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the obtained data, such as decreasing of the surface area and pore volume during the catalyst synthesis, it can be found that the adding the tartaric acid to NU-1000 and immobilization of the $MoO_2(acac)_2$ have happened well, as expected.[10b] The further details have been summarized in Figure S4 and Table S1.

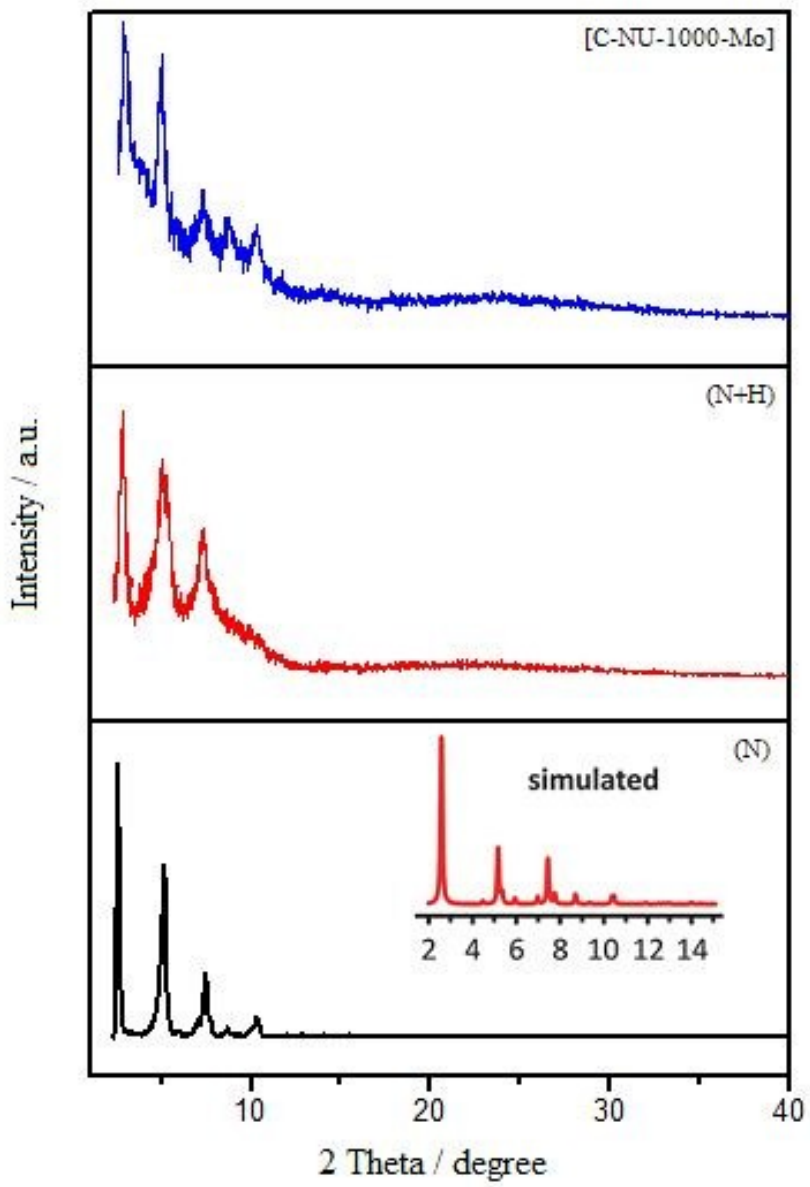

Fig. 2 The experimental XRD patterns of NU-1000 (N) (experimental (black) and simulated (red)), NU-1000+tartaric acid (N+H) and [C-NU-1000-Mo].

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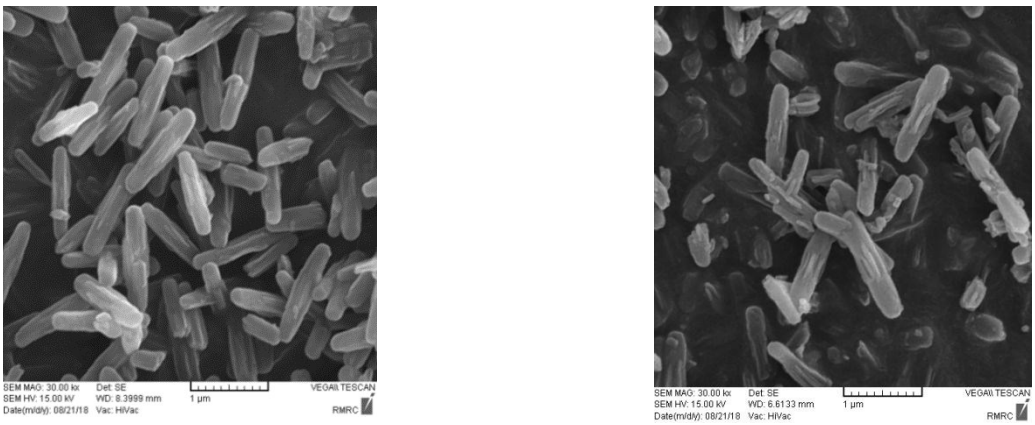

(a) (b)

Fig. 3 FE-SEM images of a) NU-1000 (N) and b) [C-NU-1000-Mo].

Also, for determining of the thermal stability, thermogravimetric analysis of [C-NU-1000-Mo] was done in the temperature range 25-600 °C (Fig. S5). At first, the decreased mass was 4.05% to about 110°C that was related to the existence of the adsorbed water.[17a,18] In the second and probably the third changing, decomposition of the incorporated tartaric acids has been happened.[19] It seems that from the end of the third step to the last stage, the weight loss is related to the ligands of Mo-complex.[20] So, it can be resulted that the catalyst thermal stability correlates to the employed materials nature.[10b] Base on the studies, such chiral MOF as Lewis-acid catalyst could act as an asymmetric catalyst with effective catalytic site for various olefins epoxidation. So, we searched the effects of $MoO_2(acac)_2$ and NU-1000-tartaric acid in the present reactions.

The Catalytic Activity of [C-NU-1000-Mo] in the Enantioselective Epoxidation Reactions

For investigation of [C-NU-1000-Mo] performance in asymmetric epoxidation of olefins, the styrene and TBHP were chosen as a model substrate and green oxidant, respectively. In the

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absence of [C-NU-1000-Mo], as control experiment, no significant result was obtained so the existence of catalyst was necessary (Table 1, entry 1). The proceeding of the reaction was investigated in the different temperatures as one of the most important factors in the control reactions. In the low temperatures, the reactions were not completed (40°C with conv. 54%, 60°C with conv. 75%) and approximately 70% ee were detected (not shown in Table 1), therefore the optimized temperature was raised until 80°C. As regards the solvent influences on the reaction conversion and selectivity of product,[21] so the solvent effect was investigated: *1,2-Dichloroethane (DCE)*, *methanol (MeOH), ethyl acetate (EtOAc)* and *acetonitrile (ACN)* (entries 3-6). Among these solvents, *DCE* was favorable solvent to complete the reaction that details have been demonstrated in Table 1 (entry 3). The other solvents have coordinating behavior to the metal site that cause the reaction rate to decrease but DCE has not striking coordinating property (Table 1, entries 4-6).[22] MeOH as a polar protic solvent with high donating power was the worst solvent in our experiments because it prevented the activity of catalyst.[23] The polar solvents have negative effect on catalyst performance because they decrease the hydroperoxo-metal species as essential factor in olefin oxidation. The epoxidation proceeded slowly in the presence of NU-1000 and NU-1000+tartaric acid with conversion less than 15% and 10%, respectively (not shown in Table 1). At the end, in comparison to [C-NU-1000-Mo] as a heterogeneous catalyst, $MoO_2(acac)_2$ as a homogeneous catalyst was used for styrene oxidation, too (0.044 mmol/2h), although no chiral agent in reaction mixture was existed (Table 1, entry 2). The primary experiments for determination of the optimized conditions revealed catalyst stability, enough extent of catalytic centers and chirality induction (full conversion, high degree to the wonderful enantioselectivities). To elucidate of chiral catalyst performance,

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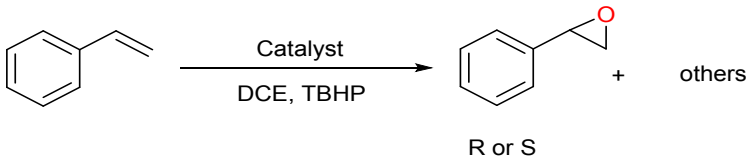
enantioselective oxygenation of some of the terminal linear and aromatic olefins was studied in the identical conditions (Table 2).

Table 1 The determination of the various parameters on the liquid phase oxidation of styrene with TBHP for the optimizing of the reaction condition.[a]



Entry	Catalyst/time	Solvent	Conv.(%) [b]	Sel (%)[b]	Ee (%)[c]
1	None/5h	1,2-Dichloroethane	<8	<25	
2	$MoO_2(acac)_2$/2h	1,2-Dichloroethane	100	<80	
3	**[C-NU-1000]/5h**	***1,2-Dichloroethane***	**100**	**86**	**95**
4	[C-NU-1000]/5h	***Methanol***	*N.R.*		
5	[C-NU-1000]/5h	***Ethyl acetate***	<40	<70	52
6	[C-NU-1000]/5h	***Acetonitrile***	<50	<60	68

[a] Reaction conditions: Catalyst 50.0 mg (0.044 mmol Mo), the molar ratio of styrene:TBHP = 0.5, solvent 5 mL, 80 °C, 5h. [b] Conversions and yields were determined by GC-FID. [c] Ee investigated by GC on a chiral SGE-CYDEX-B capillary column. TBHP, 70 wt. % in H_2O. N.R.= No Reaction.

Enantioselective epoxidation of *trans*-stilbene to *trans*-stilbene epoxide, with conversion and selectivity 100%, generated two enantiomers with 90% yield to (R,R)-*trans* stilbene, 80% ee and 68.18 h^{-1} TOF after 10 min (Table 2, entry 1). The calculated TOF at an enantiomeric excess level of 80% was the promising result.[24] There are the different results in *trans*-stilbene oxidation by using the various catalysts with TOFs of 20.6 and 19.7 h^{-1} after 9h like multi-wall carbon nanotubes supported molybdenyl acetylacetonate.[25] In the *trans*-stilbene epoxidation, the different by-products can be obtained for example, diol or benzaldehyde, but we did not have

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them. It is resulted that (1) usually the mixture of *cis:trans*-stilbene epoxide ratio is observed but in this work, stereoselectivity was 100% to trans epoxide, and (2) *trans*-stilbene kept its structure and was not destroyed and deformed.[26] In the styrene epoxidation, full conversion, 86% epoxide selectivity and ee 95% were obtained after 5 h at 80 °C with TOF 9.09 h^{-1}. 84% epoxide selectivity related to the styrene oxide (S) as a major product. The catalytic activity of [C-NU-1000-Mo] could be improved in comparision to the other heterogeneous catalysts as UiO-66-NH_2-SA-Mo (7.54h^{-1}) and MoO_2(acac)-SiIm (3.8h^{-1}).[27] Benzaldehyde (BA) and 2-phenylacetaldehyde (PAA) were identified as minor products, too. The formation of BA can happen during the catalytic process via two methods: TBHP attack as a nucleophile on styrene epoxide or C-C bond cleavage in attached C=C to phenyl ring, directly.[28] The 2-phenylacetaldehyde is also afforded with small percentage due to partial rearrangement of styrene epoxide.[11c] In addition to mentioned products, tert-butyl benzoate, benzoic acid and *t*BuOH can be formed as adducts.[29] In supporting information, some examples of enantioselective epoxidation of styrene have been shown with different chiral heterogeneous catalysts. These results strongly indicated that present catalytic system was very effective in contrast to the others, from the point of enantiomeric excess. The selectivities and enantiomeric excesses rely on the substantial effects of NU-1000 and amount of L-tartaric acid. In the following, the examples of styrene derivatives oxidation and obtained conclusions were depicted in Table 2 (entry 3 to 6). In the epoxidation of α-methyl styrene (AMS) and *trans*-β-methyl styrene (TBMS), the conversions reached as high as 100% and 97%, separately (entry 3 and 4). Our result in the oxidation of AMS showed TOF 11.36 h^{-1} that was good result versus the other findings.[27b] Probably, the steric effects of alkyl group around double bond affect on the epoxide

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and enantioselectivity values of AMS and TBMS than styrene.[30] And the difference in the reaction completion time is related to their reactivity.

Table 2 Asymmetric epoxidation of different olefins with [C-NU-1000-Mo] in the presence of TBHP.[a]

Entry	Substrate	Conv.(%) / Sel.(%) [b]/Time (h)	Ee (%) [c]	TON [d]	TOF (h^{-1}) [e]
1	*trans*-stilbene	100/100/10 min	80 (R,R)	11.36	68.18
2	Styrene	100/86/5 h	95 (S)	45.45	9.09
3	α-methyl styrene	100/83/4h	83 (S)	45.45	11.36
4	*trans*-β-methyl styrene	97/ 85/4h	86 (R,R)	44.09	11.02
5	4-chloro styrene	88/75/7h	85 (S)	40.00	5.71
6	4-methyl styrene	100/80/4h	88 (S)	45.45	11.36
7	1-Phenyl-1-cyclohexene	80/100/8h	89 (R,R)	36.36	4.54
8	1-Octene	72/100/8h	100 (R or S)	32.72	4.09
9	1-Decene	68/100/8h	97 (R)	30.90	3.86

[a] Reaction conditions: [C-NU-1000-Mo] 50.0 mg (0.044 mmol Mo), substrates 2.0 mmol (*trans*-stilbene 0.5 mmol), TBHP 4 mmol, DCE 5 mL, 80 °C. [b] Conversion and epoxide selectivity were determined by GC-FID. [c] The enantiomeric excess (ee) values were determined by chiral-GC. *R*-(+)-limonene was used for the determining of the enantiomeric configuration of the major isomer. [d] TON (total turnover number) = (moles of products)/(per mole of catalyst.[e] Value of TOF (turnover frequency) = TON (turnover number)/(reaction time). Products were confirmed by ^{1}H NMR.

Surely, the existence of the large channels in this mesoporous catalyst can strongly affect on the substrate diffusion and oxidation rate. The examined functionalized styrenes were 4-chloro styrene and 4-methyl styrene that were oxidized with conversion 88% and 100%, respectively (Table 2, entries 5 and 6). The electronic effect of Cl- and Me- groups on the reaction rate is clear and cannot be ignored. It was found that in the epoxidation of styrene and its derivatives, apart from benzaldehyde, as an inseparable by-product, phenylacetaldehyde were rarely generated. Sometimes, acetophenone and benzoic acid based on catalytic conditions can be

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produced.[31] [C-NU-1000-Mo] indicated good catalytic performance in the proceeding of the 1-Phenyl-1-cyclohexene epoxidation (conv%:80%) with great enantioselectivity to epoxide (ee%:89%(R,R)) (Table 2, entry 7), so the enantiomers were measured in unequal amounts. Two aliphatic hydrocarbons were also investigated, 1-octene and 1-decene that were oxidized to epoxides in 72% and 68% conversions, separately (Table 2, entries 8 and 9). In both of them, high epoxide selectivity was seen (100%) after 8h. Apparently, the conversion of linear olefins can be selective to epoxide products with a specific catalytic system.[31] These findings show the presence of the steric hindrance and low electronic density.[32] Since, 1-decene is longer than 1-octene (shorter α-olefin) in term of the length, so there is steric effect in it, certainly.[33] Table 3 presents the carbon balance in some of olefin oxidations. The percent of carbon in initial and final time of reaction has been indicated. The interesting point was that the double bonds in used olefins were undergone highly chemoselectivity to chiral epoxide. Truly, more effect of starting tartaric acid stereochemistry is observed on enantiomeric excess of formed products.[34] Therefore, [C-NU-1000-Mo] demonstrated an ideal chiral platform due to physical and chemical features. Previously, the epoxidation mechanism by Mo center as Lewis acid was reported. Briefly, with immobilizing of the $MoO_2(acac)_2$ onto NU-1000-tartaric acid, acetylacetone ligand (Hacac) is lost.[35] During TBHP attack to molybdenum, the proton of terminal O atom in TBHP is transferred to one oxygen atom in Mo=O terminal bond and then the alkyl peroxo-Mo intermediate is generated. So, TBHP anion is coordinated to Mo(VI)-catalyst with high lewis acidity that is a key factor in oxidation reactions. If there are free zirconium nodes, their OH_2 groups can react with ^{t}BuOOH, and then node-^{t}BuO will be created.[36] About the chirality induction mechanism, it can be said that the olefins with pro-S face or R-face can approach to the catalytic active site. When the olefin approaches to the catalytic center, the chirality induction

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happens by H-bond interaction between the olefin (H atom on double bond) and tartrate (OH group). Herein, two generated intermediates in chirality induction have been shown (Fig. 4, a and b). For example, in the enantioselective epoxidation of 1-decene, the proposed transition state is (a). Similar intermediate has been suggested in the asymmetry epoxidation of olefins in the presence of chiral amines. [37]

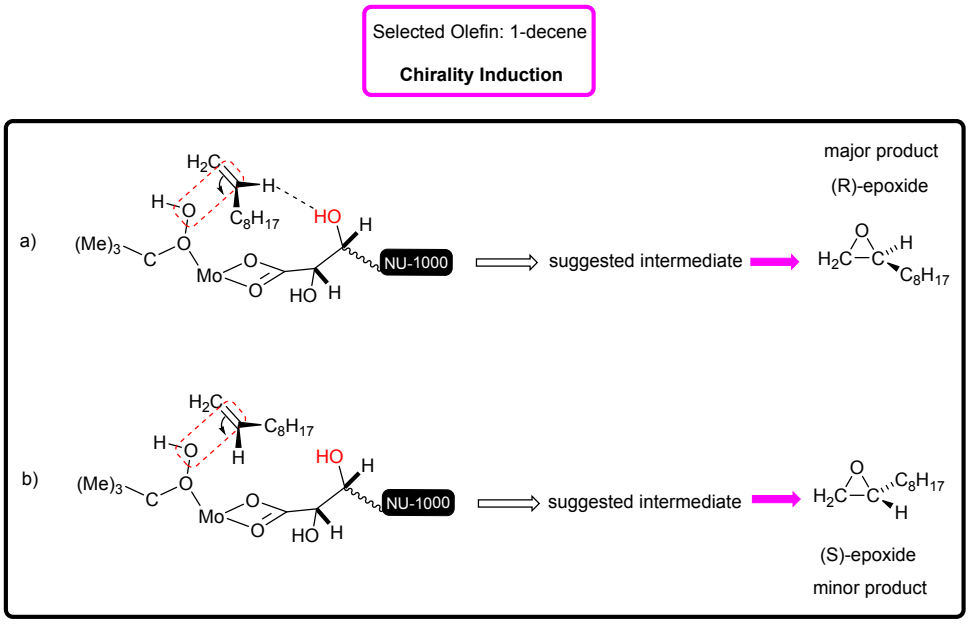

Fig. 4 The chirality induction mechanism (a) the closing of 1-decene through pro-S face and (b) pro-R face with suggested transition states.

Table 3 Carbon balance results of some of the oxidation reactions.

substrate	Carbon(%) in initial time	Carbon(%) in final time
Styrene/5h	92.26	0
Styrene epoxide	-	79.344
Benzaldehyde	-	9.226
Phenylacetaldehyde	-	3.690
1-Phenyl-1-cyclohexene/8h	91.08	18.216
1-Phenyl-1-cyclohexene epoxide	-	72.864
1-Octene/8h	85.63	23.977

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1-Octene epoxide	-	61.654

Recycling, Leaching and Hot Filtration Tests

Our heterogeneous catalyst could be easily separated from reaction mixture by filtration and repeatedly reused in the new styrene oxidation. To investigate the [C-NU-1000-Mo] stability, the oxidation of styrene as model substrate was performed under the same catalytic condition for 5 runs that no significant drop was not seen in conversion of each running (Conv%: 100%). It is important that the enantiosmeric excess and epoxide selectivity from 95 and 86% in fresh step changed to 92 and 85% in the fifth step, respectively. So, the considerable changes were not observed in the mentioned parameters in each of the recycle solutions (Fig. 5). FT-IR, XRD (Fig. S6), SEM, TGA (Fig. S5) and BET (Table S1) of the used catalyst were also investigated that the important changes in the catalyst structure were not observed rather than fresh catalyst. These techniques confirmed the retention of recovered [C-NU-1000-Mo] chemical stability, therefore, it had intact crystal structure. All of the solutions of the recycle reactions to the fifth stage were investigated by ICP analysis (Table 4). From fresh step Mo content was evaluated to the fifth stage that leaching of Mo ions was observed in the sixth step. In the Table 4, conversion, ee, epoxide selectivity and Mo concentration have been reported in each recycle.

Accordingly, the recycling experiment results displayed that [C-NU-1000-Mo] is a stable Zr-MOF. BET of recovered catalyst was studied after 5 cycles, as well. The S_{BET} from 1412 m^2g^{-1} in fresh catalyst decreased to 1043 m^2g^{-1} which most probably, aggregation has occurred. In the last recycle, decreasing of the V_{tot} and D_{av} was not significant to fresh catalyst (0.64 cm^3g^{-1} and 24.67 Å, respectively). Hot filtration test was also performed to show the catalyst positive effect in the

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epoxidation process of styrene. After 1h, the catalyst was separated from the reaction mixture and then the present solution was stirred for 4h. The reaction proceeding had not any appreciable increase in conversion (*ca*. 25%, Fig. 5(c)). So these observations corroborate the anchored Mo species on newly chiral Zr-MOF.

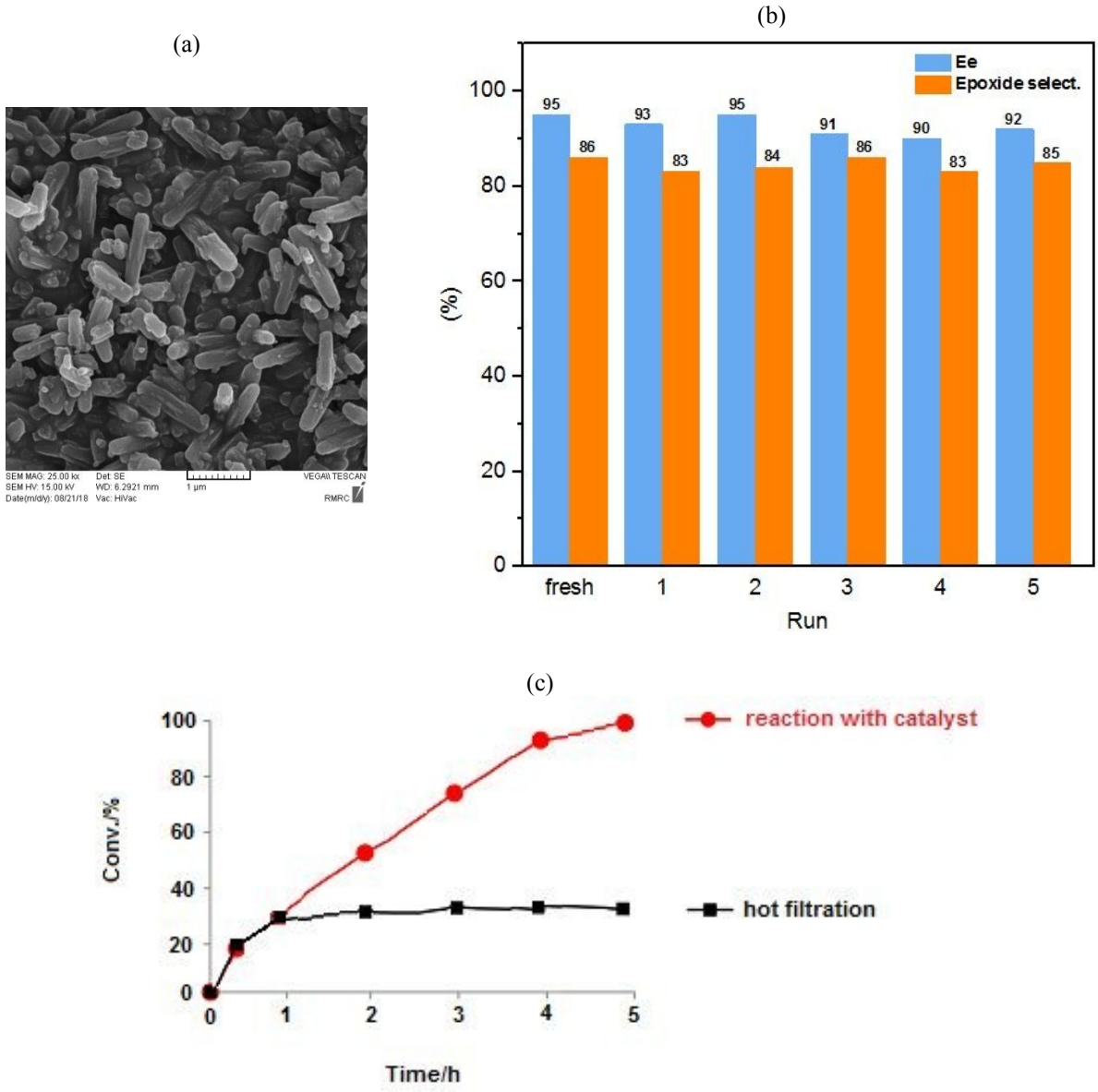

Fig. 5 The SEM image of the used catalyst in the fifth run. The obtained ee and epoxide selectivity by using the reusable [C-NU-1000-Mo] in the oxidation of styrene to five recycles. Hot filtration test was carried out at 80 °C. The epoxidation of styrene with catalyst (red) and after filtering the catalyst from reaction mixture after 1 h (black).

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Table 4. Recycling of [C-NU-1000-Mo] and leaching content of Mo in each recycle.[a]

Run	[C-NU-1000-Mo]			
	Conv.(%)	Ee(%)	Epoxide selectivity	Mo leached(%)[b]
Fresh	100	95	86	-0.055
1	100	93	83	-0.049
2	100	95	84	-0.034
3	100	91	86	-0.031
4	100	90	83	-0.031
5	100	92	85	-0.030

[a] The reaction condition is similar to Table 1 (optimized condition). [b] based on Mo concentration (ppm). Determined by ICP.

Conclusions

In summary, for the first time we presented a unique CMOF based on NU-1000 and chiral tartaric acid by using SALI route. Its preponderance was due to the simple designing with high density of the incorporated L-tartaric acid on the Zr_6 nodes and Mo-complex as Lewis acid site. We beleive that we have created a new incomplex CMOF with a facile strategy that it can be displaced with the other chiralization methods. Simplified designing is a ideal and noteworthy aspect in this chiral catalyst, which surely is not exaggerated. The participation of three components in this catalyst, NU-1000, tartaric acid and Mo-complex play essential role in enantioselective epoxidation. The asymmetric catalytic activity of [C-NU-1000-Mo] was assayed in the enantioselective epoxidation of the various prochiral alkenes to form the enantiomers of epoxides with excellent enantioselectivities. Tartaric acid with two chiral centers and appropriate orientation has significant effect on chirality induction to epoxides. [C-NU-1000-Mo] had the capable of the sensible discrimination of the R configuration or S configuration in epoxides, therefore, the racemic mixture (50:50) was not seen. In addition, [C-NU-1000-Mo] as a

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heterogeneous catalyst can be separated from the reaction mixture and reused without any considerable degradation.

Experimental Methods

Materials and Characterization

(2*R*,3*R*)-(+)-tartaric acid (L-(+)-tartaric acid), MoO_3, D_2SO_4, the various olefins, oxidant and the other reagents such as solvents were bought from different chemical companies. NU-1000 was successfully synthesized based on the previous report.[38] In this research different analytical techniques were employed such as GC-FID, ^{1}H NMR, UV-Vis, FT-IR, XRD, FE-SEM, BET, TGA and ICP.

Echrom GC A90 gas chromatography with flame-ionization detector (China) was employed (Agilent HP-5 capillary column, 30 m × 0.320 mm × 0.25 μm, temperature limits from 60 to 325 °C) for the oxidative reactions products. For determining of the enantiomeric excess (ee) a chiral column was used (Agilent CYCLODEX-B capillary column, 30 m × 0.25 mm × 0.25 μm, temperature limits from 50 to 230°C). ^{1}H-NMR spectra were investigated by using INOVA 500 MHz spectrometer. The UV-vis spectra were recorded by using a UV/VIS-Double Beam Spectrophotometer with RAYLEIGH model UV-2601. The Thermo Nicolet IR 100 FT-IR was used for studying of the generated compounds structures in the 4000-400 cm^{-1} region (Mid-infrared). The X-ray diffraction analysis was done by using X'Pert Pro-MPD powder diffractometer that has been made by Philips Company, Netherlands (tube: Co, λ=1.78897 Å, voltage: 40 kV, current: 40 mA). Scanning electron microscope (SEM, Tescan VEGA-II, voltage=15 KV) was consumed for studying of the synthesized materials morphology to final catalyst. The surfaces sorption was analyzed by using the Micrometrics TriStar II 3020 with N_2

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at 77 K. NETZSCH Thermal Analysis was used for investigation of the catalyst thermal behavior with this condition: the heating range from 25-600°C at 10 °C/min under N_2 atmosphere. Then, for determination of Mo amount in catalyst construction and recycle solutions, Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used with operating of a VISTA PRO-axial CCD spectrometer from Varian.

Preparation of the Materials

Synthesis of (N+H) with SALI method. NU-1000 (40.0 mg),[38] L-tartaric acid in the quantity of 10 times of mmole of the used zirconium (28.06 mg, 0.187 mmol) and DMF (3 mL) were added to a vial 6 mL. The vial with reaction mixture was heated at 80 ˚C over 16 h. IR and ^{1}H NMR spectra showed the presence of tartaric acid well.

Immobilization of $MoO_2(acac)_2$ onto (N+H), [C-NU-1000-Mo]. The functionalized NU-1000 (40.0 mg) and $MoO_2(acac)_2$[13] (21.72 mg, 0.066 mmol) were mixed in a Schlenk flask with n-pentane (~30 mL). The reaction mixture was stirred at room temperature for 18-24 h under Ar atmosphere. The resulting yellow sediment was filtered and dried in air. The amount of Mo loading in [C-NU-1000] was determined by ICP (0.88 mmol/g cat.).

Catalytic Asymmetric Epoxidation of Olefins. Several alkenes were used in catalytic oxidation reactions. Styrene as a model substrate (208.3 mg, 2 mmol), TBHP 70% (360.0 mg, 4 mmol), 1,2-dichloroethane (5 ml) and catalyst (50.0 mg) were refluxed under stirring. The progress of the enantioselective epoxidation of olefins was monitored by gas chromatography. At the end of an oxidative process, the used catalyst was separated from the reaction mixture. The obtained products were determined with ^{1}H NMR and GC analysis.

Reusable Solid Catalyst. For modifying of the high cost and difficult conditions specially in industrial processes, reusable heterogeneous catalysts have been considered. For checking of the

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reusing and stability of [C-NU-1000-Mo], it was examined in enantioselective epoxidation of styrene. After completing the reaction in per cycle, the catalyst was filtered, washed with acetonitrile and dried. Then, it was used for another new reaction with fresh styrene, TBHP and DCE. The ICP-OES was employed for determining of Mo leaching in filtrates. Until the fifth recycle, no Mo leaching was not detected. [C-NU-1000-Mo] was much more stable in five cycles under the first determined conditions. The reaction conversion of styrene was 100% per time. The significant decreasing in styrene oxide selectivity and ee after five cycles were not consecutively seen. The SEM, BET, TGA, FT-IR and XRD of [C-NU-1000-Mo] were employed for comparing of the used and fresh catalyst structure. Clear difference was not observed in the structure and morphology of catalyst in two mentioned cases.

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Conflicts of interest

There are no conflicts to declare.

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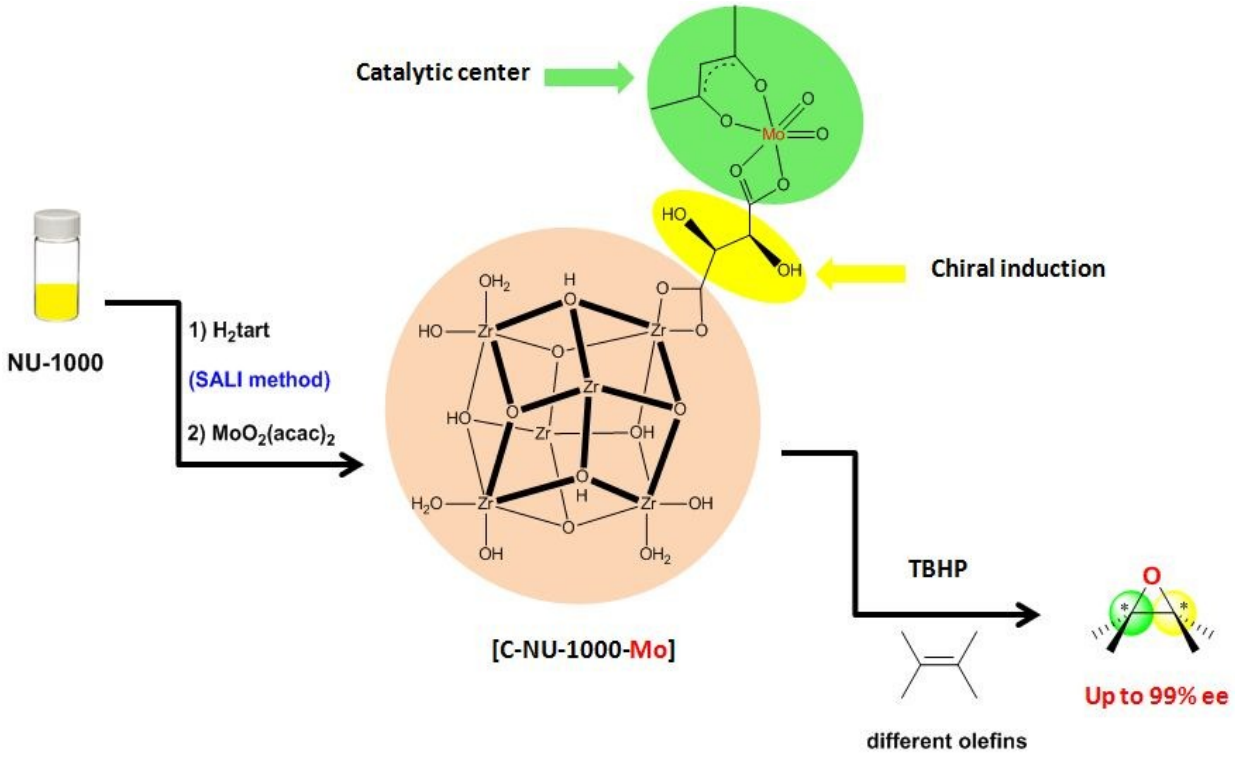
Graphical abstract



Highlights

1. A simple and rapid procedure for preparing of a chiral NU-1000 as a robust Zr-based MOF without complexity.
2. The functionalization of the NU-1000 by utilizing chiral L-(+)-tartaric acid via solvent-assisted linker incorporation: [C-NU-1000].
3. An easy method for preparation of an asymmetric oxidative catalyst: [C-NU-1000-Mo].
4. [C-NU-1000-Mo] as a wonderful chiral heterogeneous catalyst for enantioselective epoxidation of olefins: high epoxide selectivity, enantiomeric excess and conversion.
5. The catalyst could be reused without significant deactivation.