Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

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

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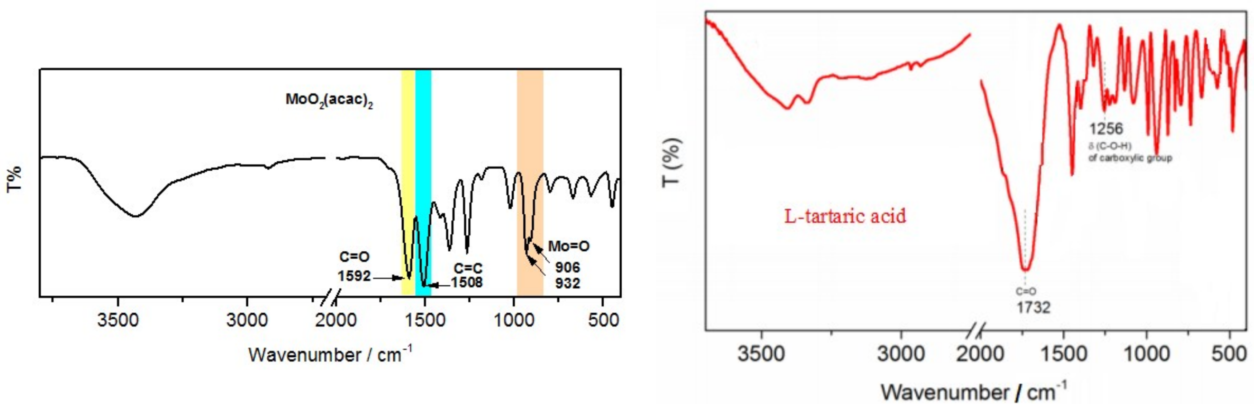
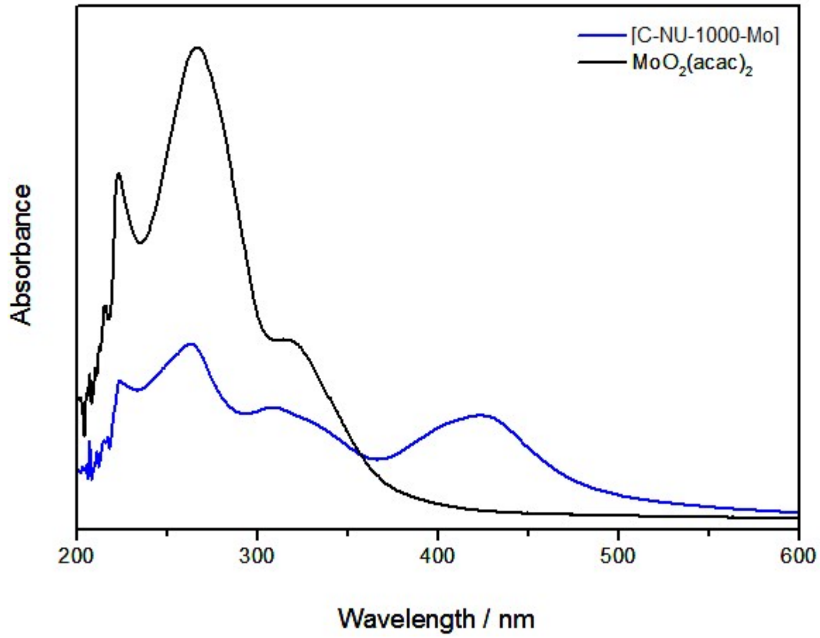
S1. FT-IR of *cis*-$MoO_2(acac)_2$ and L-tartaric acid. [1]



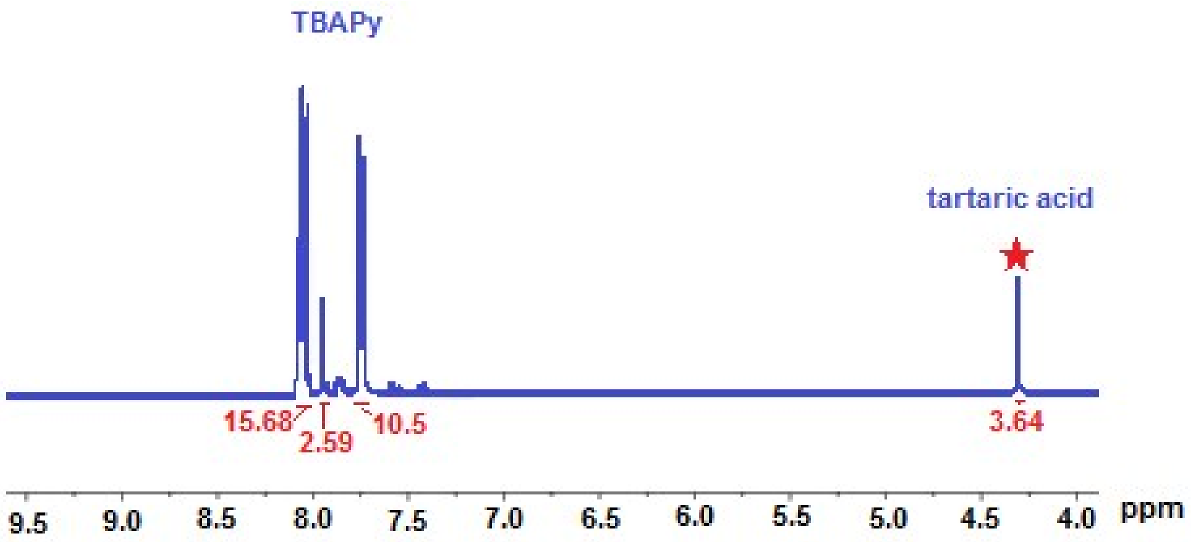
(906 and 932 cm^{-1}, $Mo{=}O_{sy}$ and $Mo{=}O_{asy}$, respectively).

(The strong band at 1732 cm^{-1} is related to ν(C=O) vibrations of L-tartaric acid).

S2. UV–Vis absorption spectra of the $MoO_2(acac)_2$ and dispersed [C-NU-1000-Mo] in DCE.



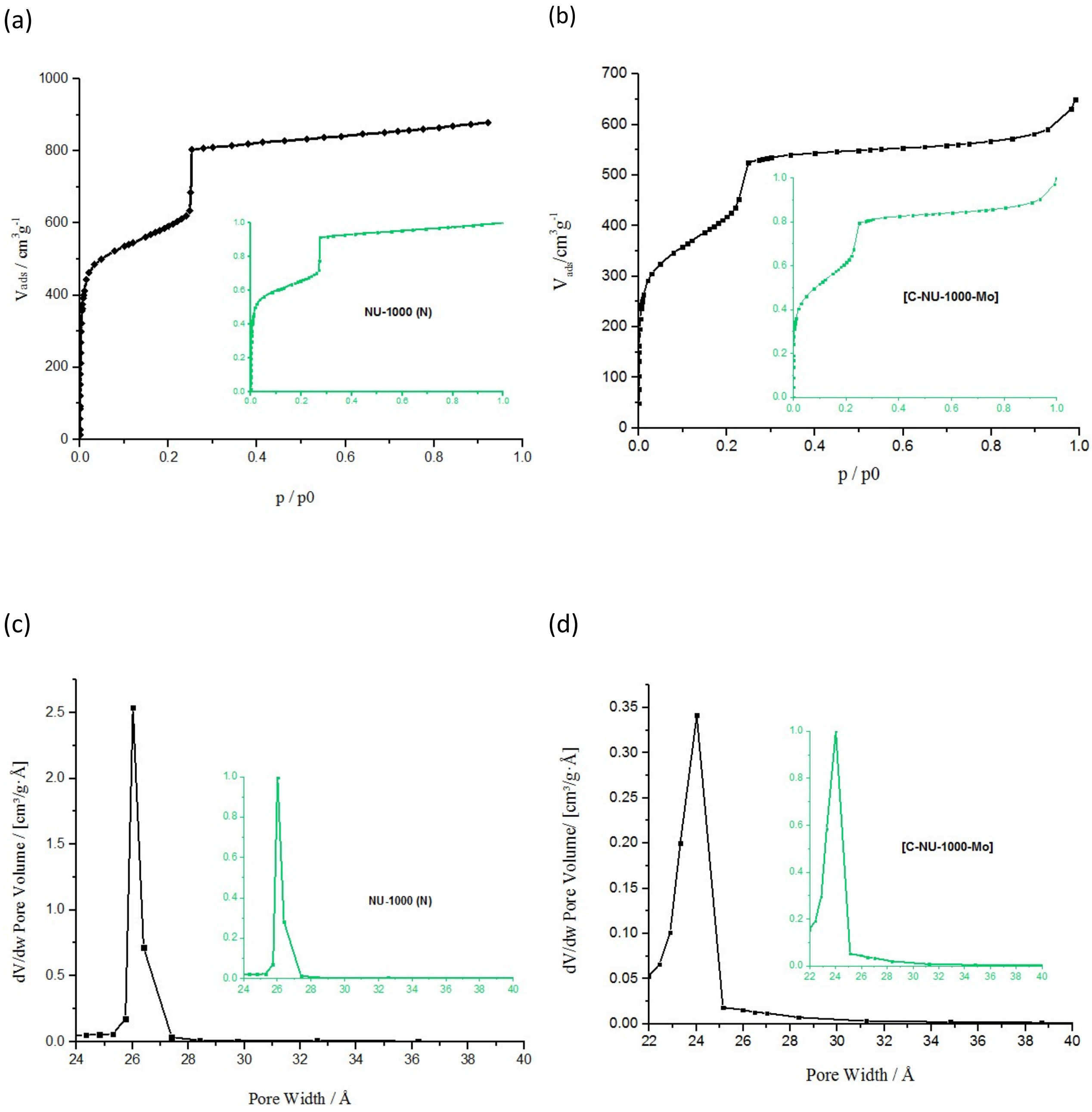
S3. ^{1}H NMR of NU-1000-tartaric acid (N+H) (SALI-CFG). [2,3]



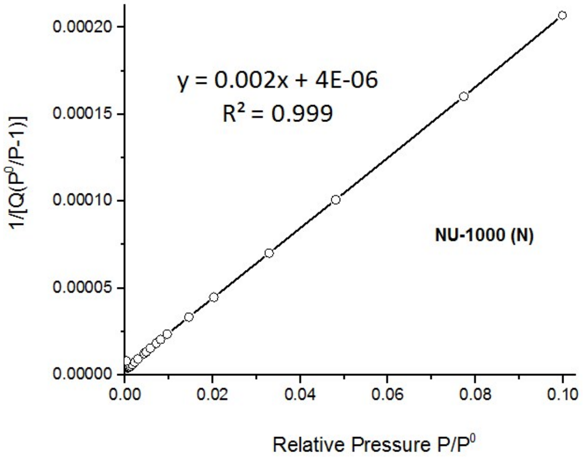
ICP analysis:

Destroying of catalyst was performed in the concentrated acid solution (2 mL) under reflux for over 2h. After digestion, the solution sample was made with deionized water for ICP analysis to determine the percentage of Mo loading on chiral NU-1000: 0.044 mmol/0.05g cat.

S4. N_2 adsorption isotherms of: a) NU-1000(N) and b) [C-NU-1000-Mo]; BJH pore size distribution data: c) NU-1000(N) and d) [C-NU-1000-Mo] (as recorded (black) and normalized (green); BET plots: e) NU-1000 and f) [C-NU-1000-Mo].



(e)



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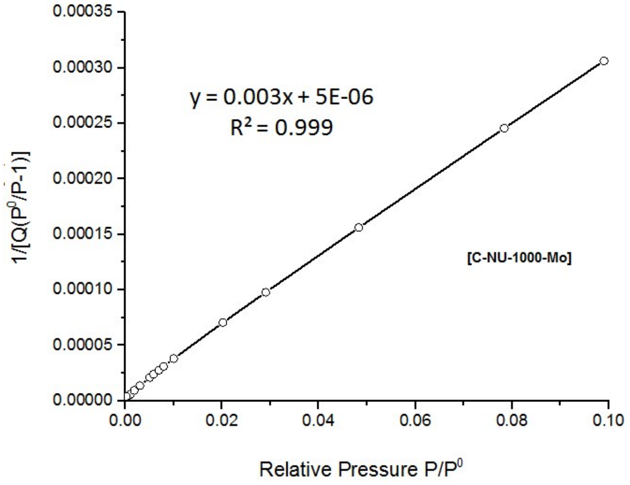


Table S1 Structural properties of NU-1000 (N)[4], fresh and used [C-NU-1000-Mo]

Compound	$S_{BET}{}^{a,c}$	$V_{tot}{}^{b}$	$D_{av}{}^{d}$
NU-1000 (N)	2100	1.40	29.00
Fresh-[C-NU-1000-Mo]	1412	0.97	27.48
Used-[C-NU-1000-Mo]	1043	0.64	24.67

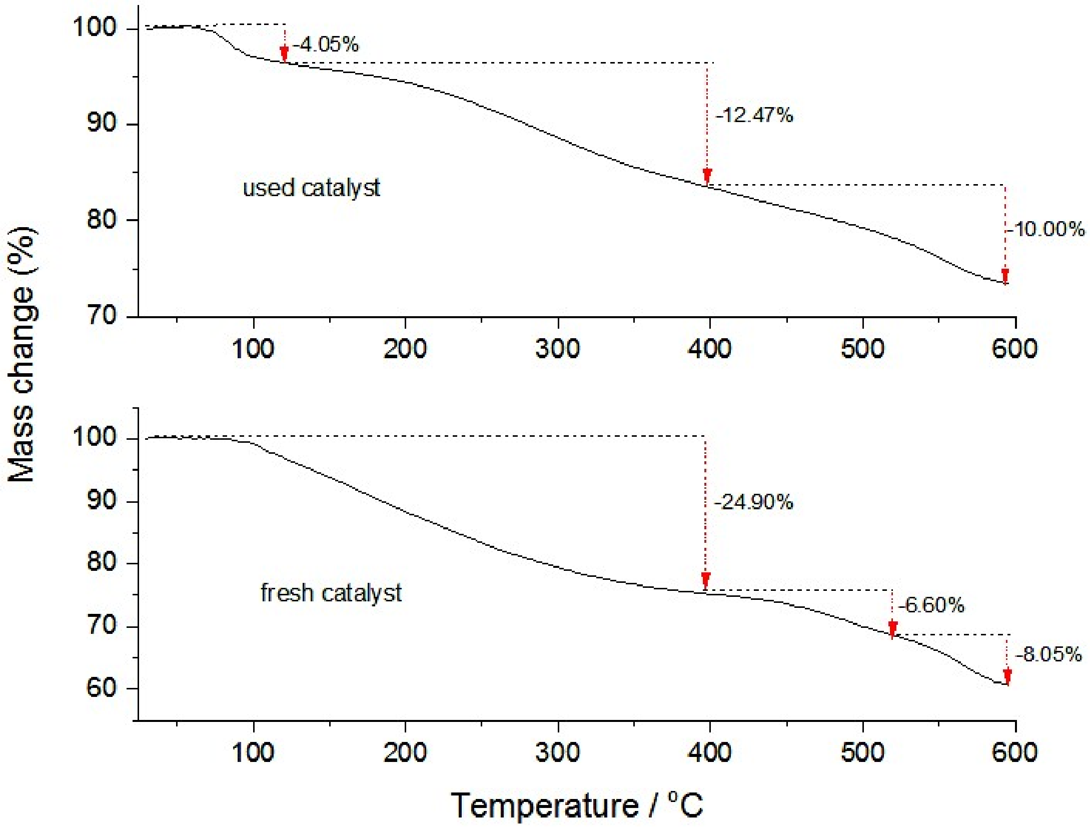
[a] The unit of the surface = m^2g^{-1}. The volume unit = cm^3g^{-1}. Surface area calculated from BET analysis at $p/p^0 = 0.099$

[b] Total pore volume (V_{tot}) calculated at $p/p^0 = 0.98$

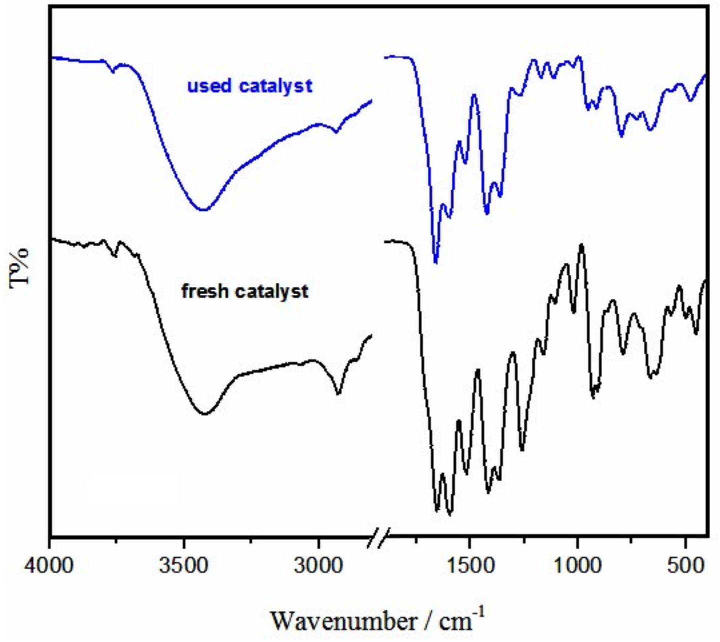
[c] For determining of the micropore volume (V_{micro}) and surface area, t-plot was used. (Harkins and Jura equation)

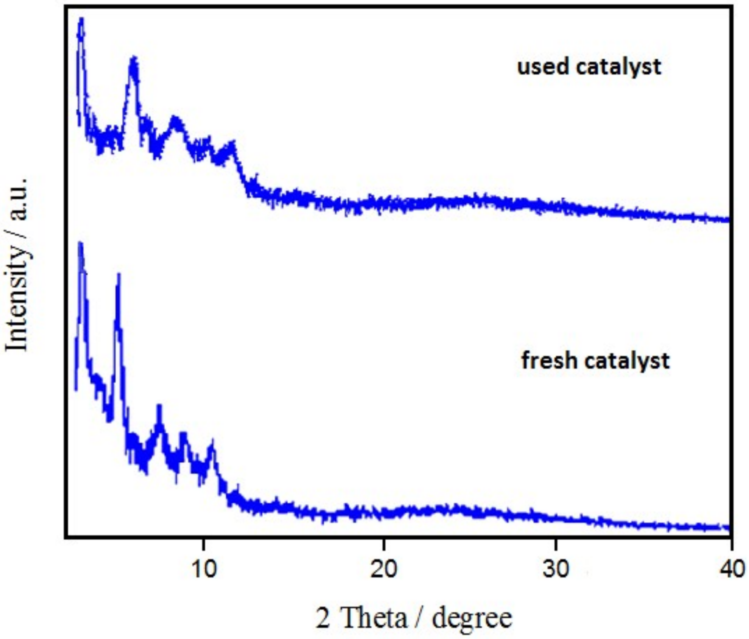
[d] The unit of the average pore diameter = Å. It was calculated from BJH analysis.

S5. Thermogravimetric analysis of the fresh and used catalyst.

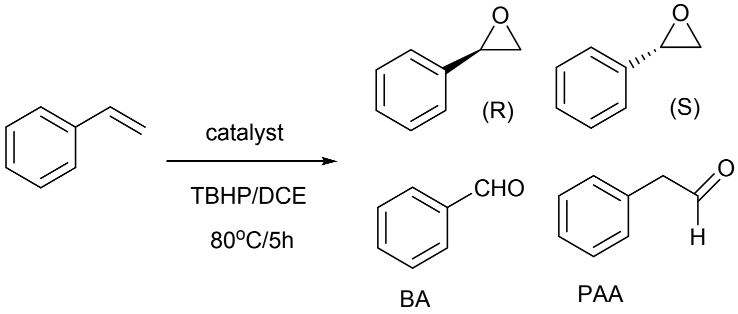


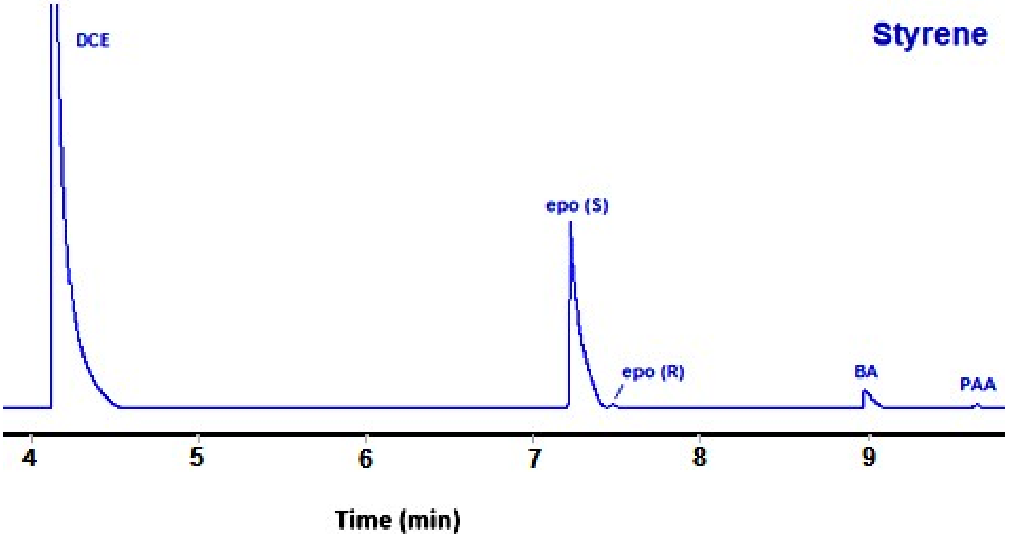
S6. FT-IR and PXRD of the used catalyst.





S7. Several chiral GC chromatograms of the asymmetric epoxidation of various olefins with recognizable products.

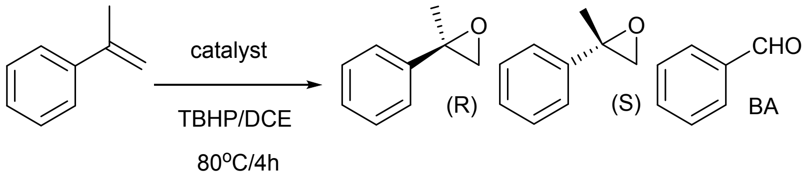


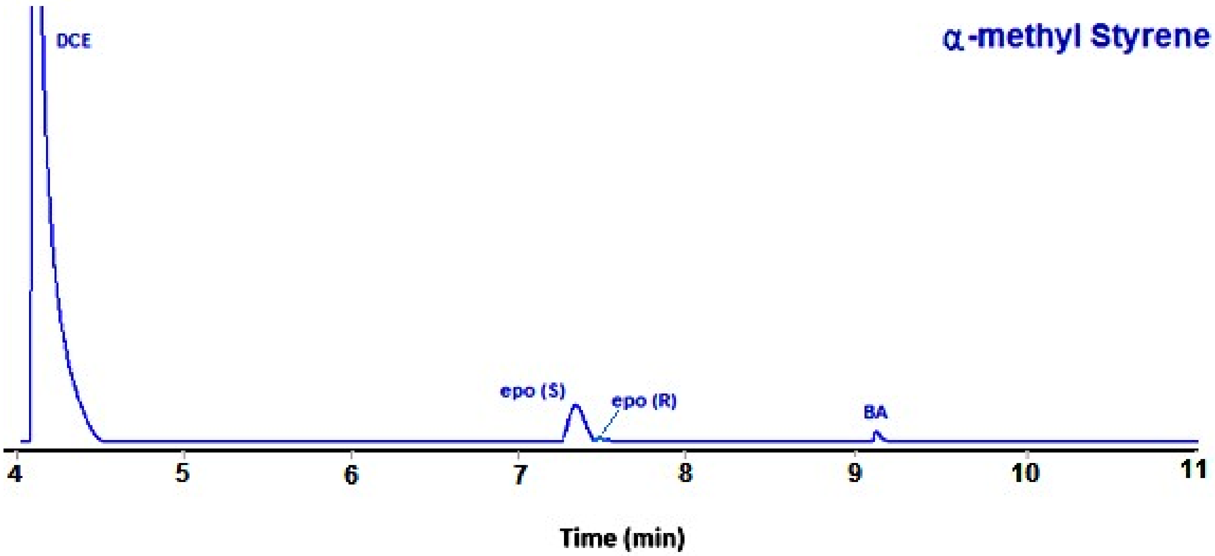


Integration Data

Parameter	DCE[a]	epo(S)[b]	epo(R)[b]	BA[c]	PAA[d]
Time(min)	4.21	7.36	7.45	9.01	9.76
Area(%)	91.30	8.4	0.2	1	0.4

[a] 1,2-Dichloroethane. [b] Styrene epoxide. [c] Benzaldehyde. [d] Phenylacetaldehyde.

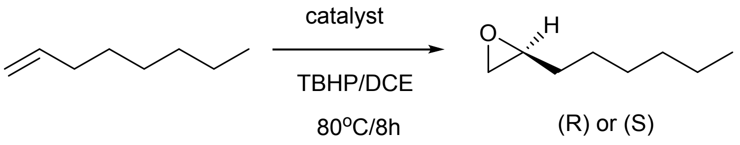


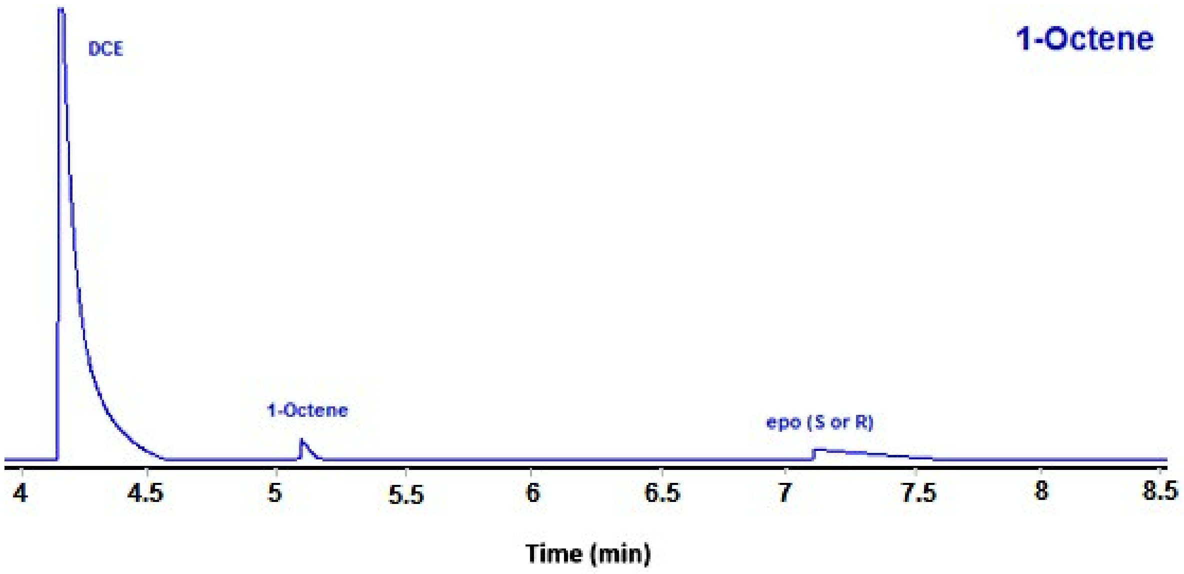


Integration Data

Parameter	DCE[a]	epo(S)[b]	epo(R)[b]	BA[c]
Time(min)	4.21	7.32	7.45	9.15
Area(%)	83.30	7.6	0.7	1.7

[a] 1,2-Dichloroethane. [b] α-methyl styrene epoxide. [c] Benzaldehyde.

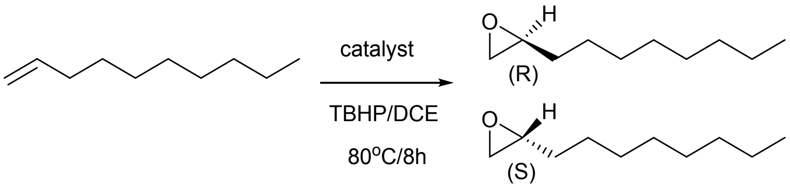


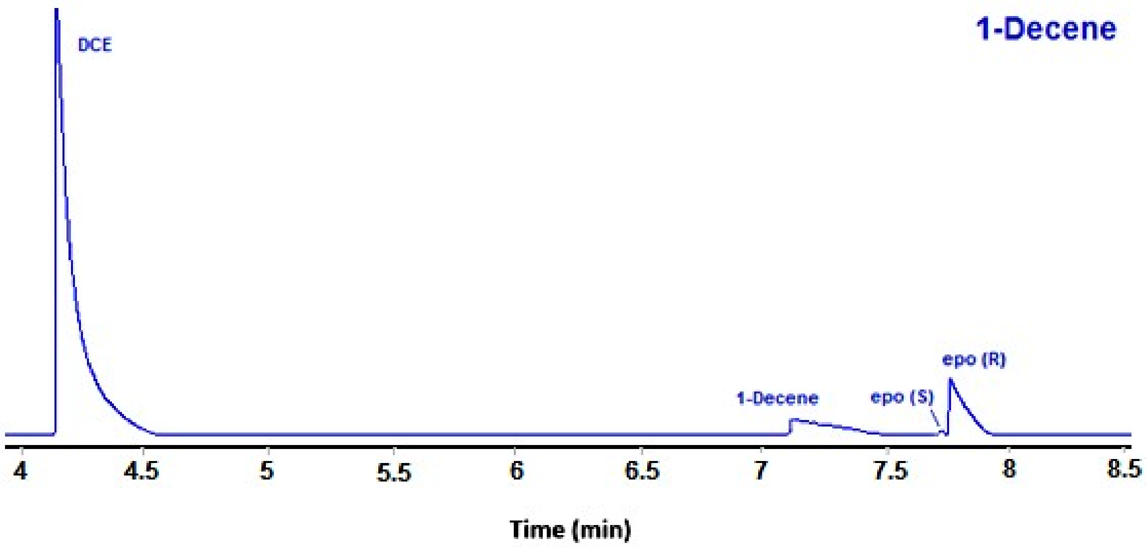


Integration Data

Parameter	DCE[a]	1-Octene	epo(S or R)[b]
Time(min)	4.23	5.21	7.22
Area(%)	80.32	2.70	7.00

[a] 1,2-Dichloroethane. [c] 1-Octene epoxide.

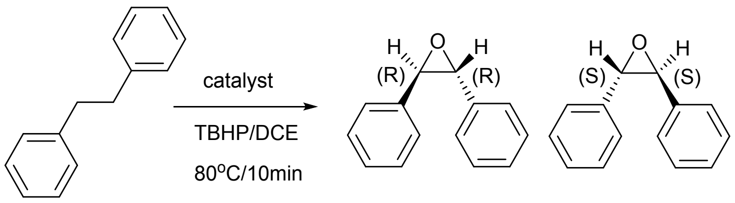


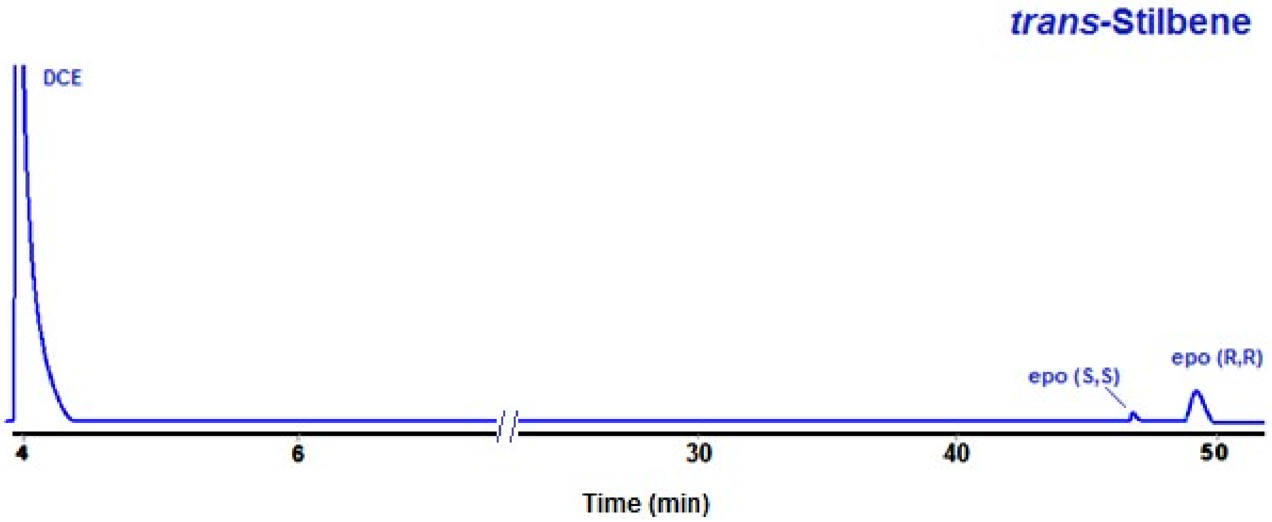


Integration Data

Parameter	DCE[a]	1-Decene	epo(S)[b]	epo(R)[b]
Time(min)	4.22	7.21	7.74	7.75
Area(%)	79.98	4.1	0.11	8.8

[a] 1,2-Dichloroethane. [b] 1-Decene epoxide.

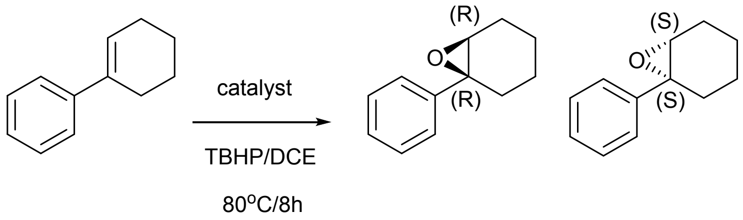


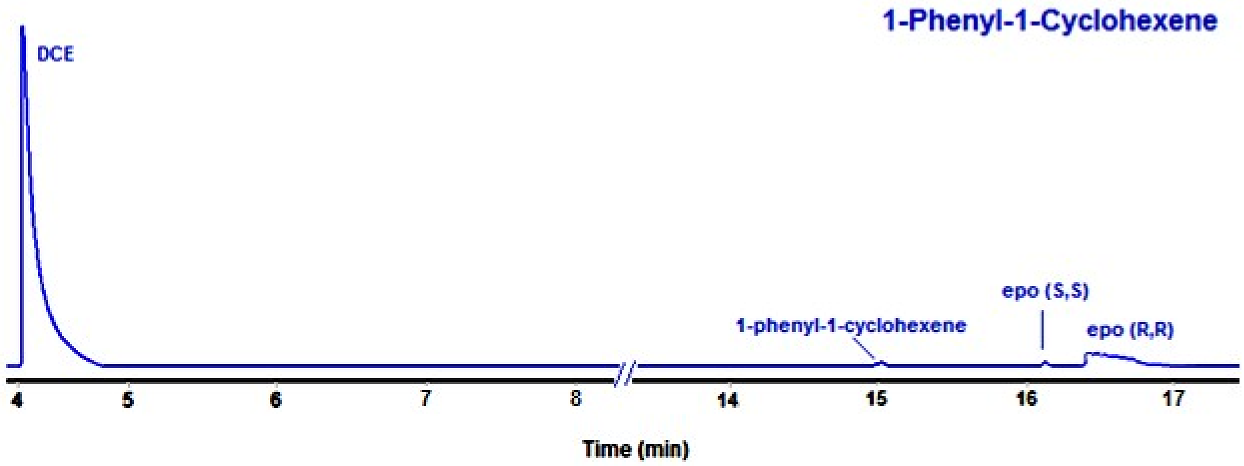


Integration Data

Parameter	DCE[a]	epo(S,S)[b]	epo(R,R)[b]
Time(min)	3.98	46.87	49.20
Area(%)	89.56	0.48	4.32

[a] 1,2-Dichloroethane. [b] *trans*-Stilbene epoxide.





Integration Data

Parameter	DCE[a]	1-Phenyl-1-cyclohexene	epo(S,S)[b]	epo(R,R)[b]
Time(min)	4.10	15.01	16.18	16.49
Area(%)	78.30	0.65	0.15	2.60

[a] 1,2-Dichloroethane. [b] 1-Phenyl-1-cyclohexene epoxide.

S8. Table S2 Table of enantioselective epoxidation examples of the styrene by various asymmetric heterogeneous catalysts.

The catalytic activity of [C-NU-1000-Mo] was compared to the other chiral heterogeneous catalysts with different acidic centers as catalytic active sites and supports. Herein, it has been attempted that the good data as conversion, enantiomeric excess and styrene oxide selectivity in the various catalytic systems to be reported. These findings showed that [C-NU-1000-Mo] with high amount of L-tartaric acid and $MoO_2(acac)_2$ in its surrounding has excellent ee with full conversion for 5h.

No.	Catalyst	Catalytic system	Conv. (%)	Ee. (%)	SO (%)[a]	Ref.
1	[C-NU-1000-Mo]	TBHP/DCE/5h	100	95	86	This work
2	ZPS-PVPA-(Mo-ligand) (R_1=H, R_2=H, C_n in ligand=0)	TBHP/DCE/6h	83	83	75	[5]
3	ZPS-PVPA-(Mo-ligand) (R_1=H, R_2=Me, C_n in ligand=0)	TBHP/DCE/6h	52	68	63	[5]
4	ZPS-PVPA-(Mo-ligand) (R_1=Me, R_2=H, C_n in ligand=0)	TBHP/DCE/6h	74	76	72	[5]
5	ZPS-PVPA-(Mo-ligand) (R_1=H, R_2=H, C_n in ligand=1)	TBHP/DCE/6h	85	85	76	[5]
6	DET-Ti-MCM_{550}	TBHP/MeCN/24h	68	55	44	[6]
7	DIPT-Ti-MCM_{550}	TBHP/MeCN/24h	59	62	46	[6]
8	ZPS-PVPA-R-(Mn-salen) R= -$O(CH_2)_6O$-	m-CPBA/CH_2Cl_2	91	72	90	[7]
9	ZPS-PVPA-R-(Mn-salen) R= -$O(CH_2)_6O$-	m-CPBA/NMO/ CH_2Cl_2	96	5.6	97	[7]
10	ZPS-PVPA-R-(Mn-salen) R= -$O(CH_2CH_2O)_4$-	m-CPBA/CH_2Cl_2	90	68	91	[7]
11	ZPS-PVPA-R-(Mn-salen) R= -$O(CH_2CH_2O)_4$-	m-CPBA/NMO/ CH_2Cl_2	95	4.8	96	[7]
12	PAMAM dendrimer (G1) in PPCC (chiral salen Mn(III))	m-CPBA/PyNO/ CH_2Cl_2/1h		38	99	[8]
13	PAMAM dendrimer (G2) in PPCC (chiral salen Mn(III))	m-CPBA/PyNO/ CH_2Cl_2/1h		28	96	[8]
14	PAMAM dendrimer (G3) in PPCC (chiral salen Mn(III))	m-CPBA/PyNO/ CH_2Cl_2/1h		19	97	[8]
15	GO-chiral Mn(III)	m-CPBA/DCM/6h	90	65	98	[9]
16	Fe_3O_4-[Mn(TPyP)tart]	O_2/IBA/MeCN/4h	100	89	67	[10]

[a] SO = Styrene oxide.

S9. References

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