Electronic supplementary information for

Vanadyl *β*-tetrabromoporphyrin: Synthesis, crystal structure and its use as an efficient and selective catalyst for olefin epoxidation in aqueous medium

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Table S1. UV-Visible spectral data of **1** in CH_2Cl_2 at 298 K.

Compound	B Band(s),nm (ε in $Ltmol^{-1}cm^{-1}$)	Q band(s), nm (ε in $Ltmol^{-1}cm^{-1}$)
$VOTPPBr_4$ (**1**)	435 (1.94×10^5)	560 (1.94×10^4), 604 (6.32×10^3).

Table S2. Electrochemical redox data[a] of **1** in triple distilled DCM containing 0.1 M $TBAPF_6$ as the supporting electrolyte at 298 K.

Porphyrin	Oxidation (V)		Reduction (V)	
	$P^{I+/II+}$	$P^{0/I+}$	$P^{0/-}$	$P^{I-/II-}$
1	1.46	1.28	-0.84	-1.06

[a]*vs.*Ag/AgCl reference electrode, Pt working and Pt wire auxiliary electrode.

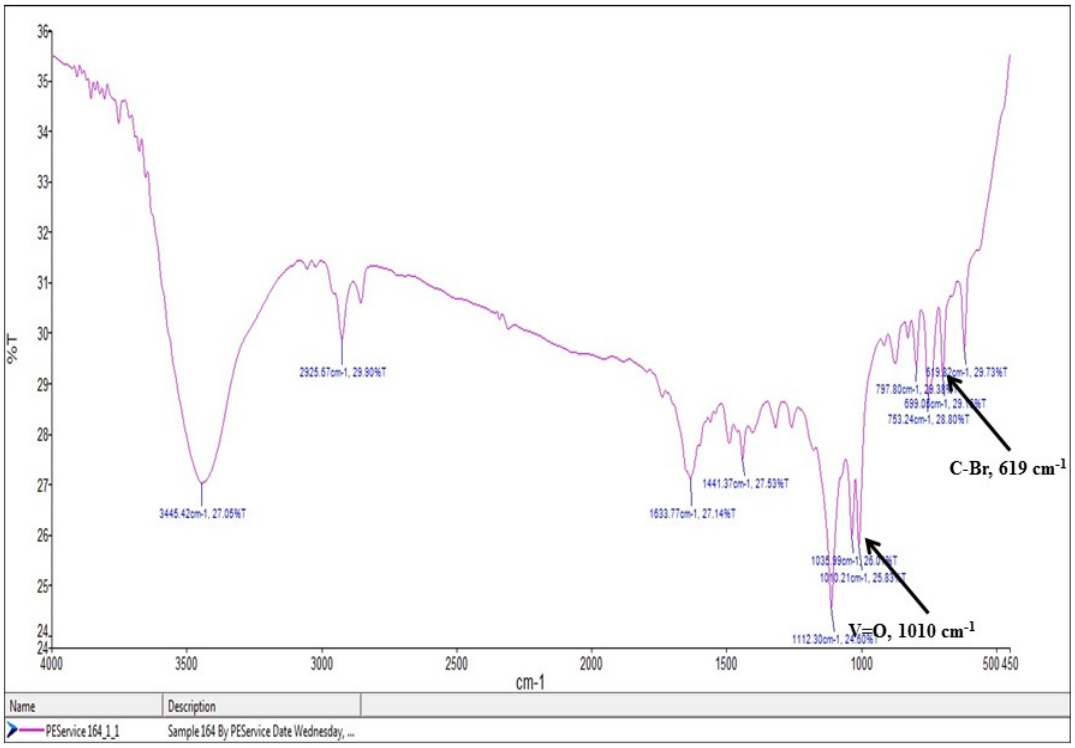
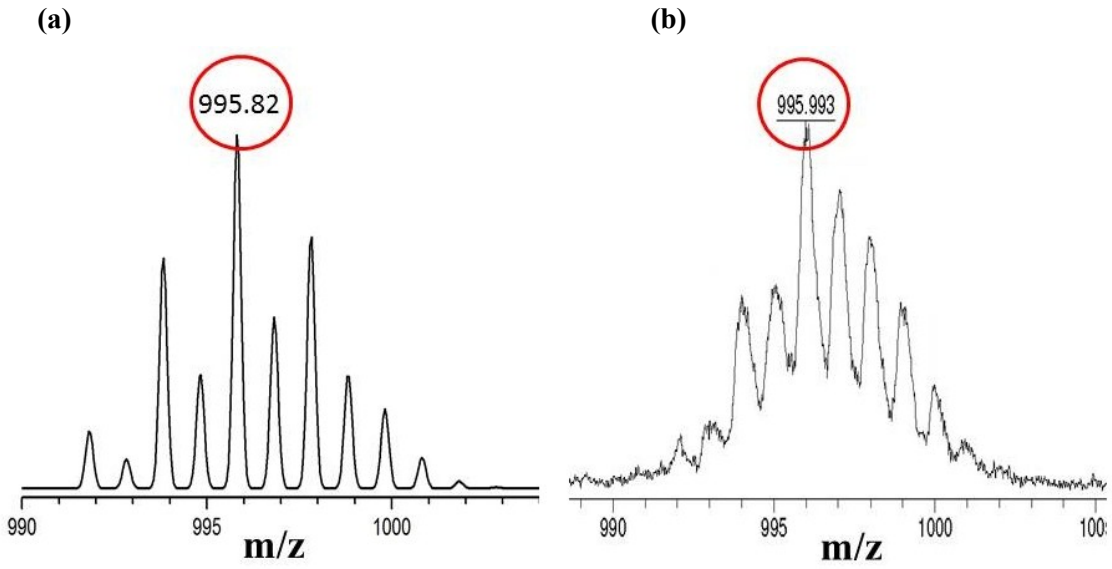


Figure S1. FT-IR spectrum of $VOTPPBr_4$ (**1**) using KBr pellets.



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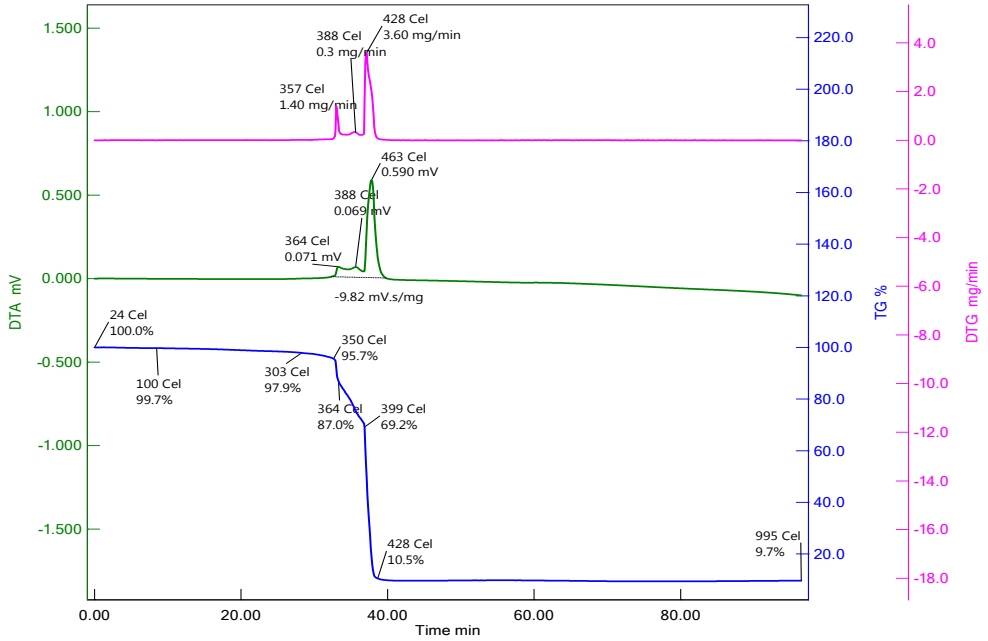

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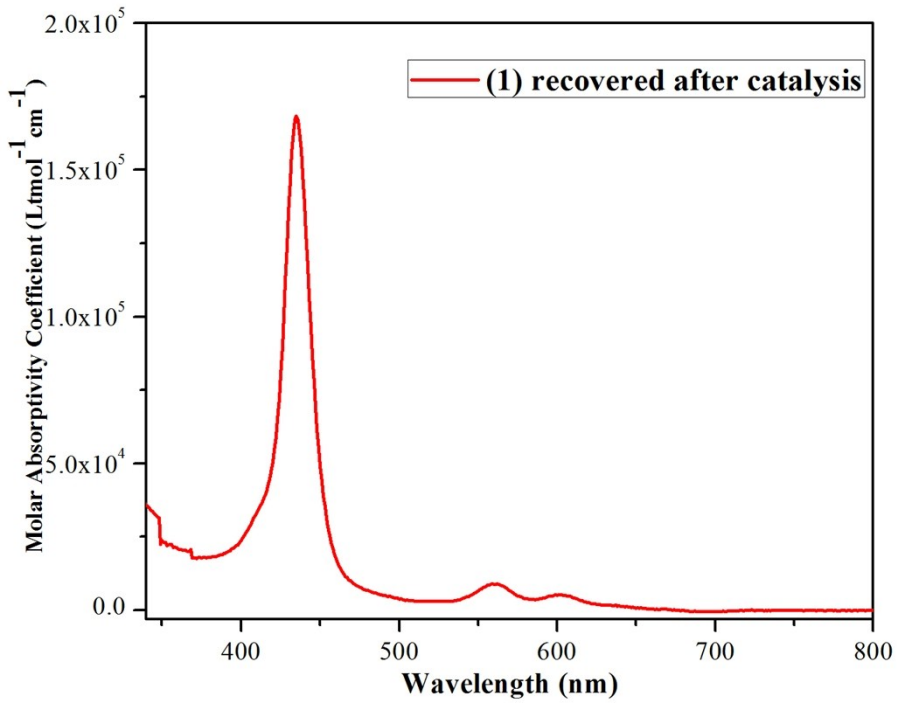


Figure S4. UV-Visible spectrum of recovered catalyst **1** in CH_2Cl_2 at 298 K showing its reversible nature.

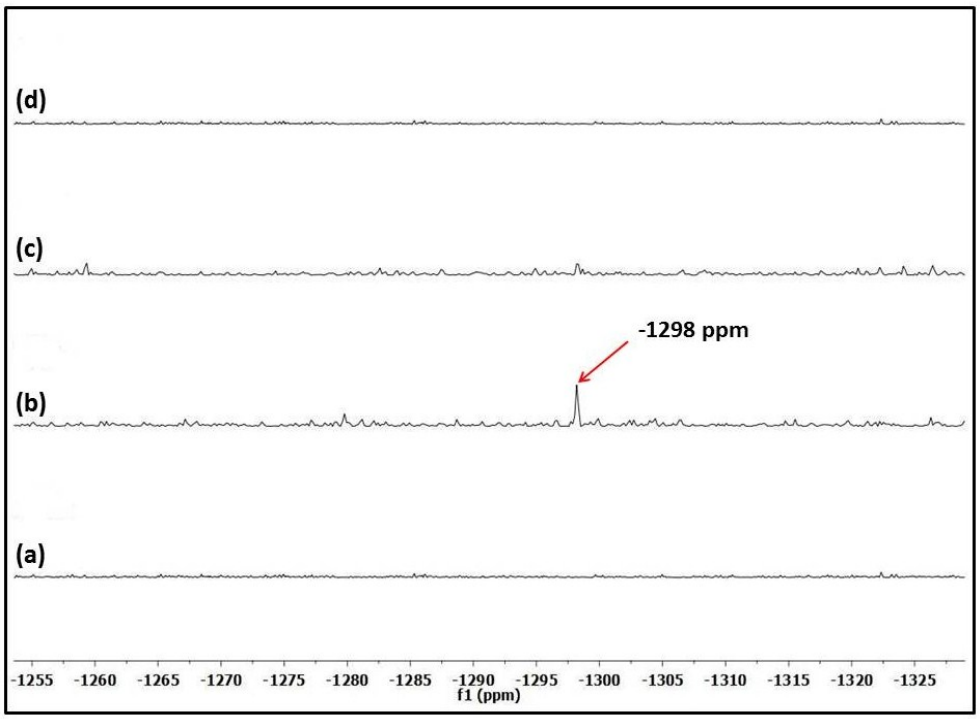
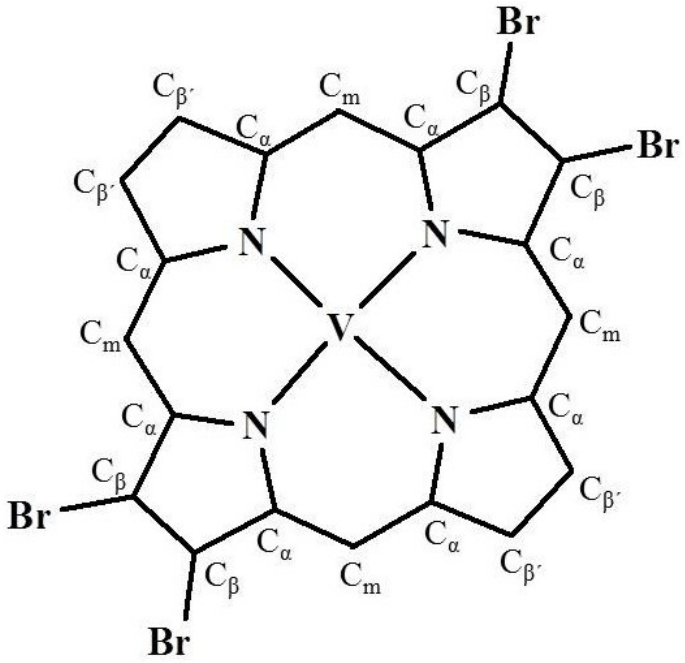


Figure S5. ^{51}V-NMR recorded in DMSO-d_6 for (a) porphyrin **1** (b) oxidoperoxido species $[VO(O_2)TPPBr_4]^-$ generated from **1** in presence of H_2O_2 and $NaHCO_3$ (c) on adding small amount of cyclohexene and (d) on adding excess amount of cyclohexene.

Table S3. Selected average bond lengths and bond angles for $VOTPPBr_4$ (**1**) calculated on the basis of DFT optimized geometry using LANL2DZ basis set.



Bond Lengths (Å)		Bond Angles (°)	
N-C_α	1.401	N-C_α-C_m	124.985
C_α-C_β	1.454	N-C_α-C_β	108.48
C_α-$C_{\beta'}$	1.452	N-C_α-$C_{\beta'}$	109.47
C_β-C_β	1.379	C_β-C_α-C_m	126.99
$C_{\beta'}$-$C_{\beta'}$	1.372	$C_{\beta'}$-C_α-C_m	124.91
C_α-C_m	1.411	C_α-C_β-C_β	107.61
M-N	2.077	C_α-$C_{\beta'}$-$C_{\beta'}$	107.33
ΔC_β	0.855	C_α-N-C_α	106.725
$\Delta C_{\beta'}$	0.725	M-N-C_α	124.58
Δ24	0.383	N-M-N	152.145
ΔC_α	0.291		
ΔC_m	0.065		
ΔN	0.071		
ΔM	0.538		
V=O	1.379		

Table S4. Crystal structure data of μ-oxo dimer of $VOTPPBr_4$ (**1**).

	1
Empirical formula	$C_{88}H_{48}Br_8N_8OV_2$
Formula wt.	1974.42
Crystal system	Monoclinic
Space group	P 2/c
a (Å)	29.844 (9)
b (Å)	13.822 (4)
c (Å)	19.654 (7)
α (˚)	90
β (˚)	107.719 (3)
γ (˚)	90
Volume ($Å^3$)	7723 (4)
Z	8
D_{cald} (mg/m^3)	1.698
λ (Å)	0.71073
T (K)	100
No. of total reflns.	5465
No. of indepnt. reflns.	3875
R	4.75
R_w	11.44
CCDC No.	1880991

Table S5. Selected average bond lengths and bond angles for μ-oxo dimer of $VOTPPBr_4$ (**1**) obtained from single crystal XRD studies.

	1
Bond Length (Å)	
$N\text{-}C_\alpha$	1.378
$C_\alpha\text{-}C_\beta$	1.439
$C_\alpha\text{-}C_{\beta'}$	1.454
$C_\beta\text{-}C_\beta$	1.356
$C_{\beta'}\text{-}C_{\beta'}$	1.342
$C_\alpha\text{-}C_m$	1.402
M-N	2.082
ΔC_β	0.663
$\Delta C_{\beta'}$	0.535
Δ24	0.3236
ΔC_α	0.214
ΔC_m	0.243
ΔN	0.070
ΔM	0.538
V-V	3.534
V=O	1.769
Bond Angle (°)	
$N\text{-}C_\alpha\text{-}C_m$	124.671
$N\text{-}C_\alpha\text{-}C_\beta$	109.172
$N\text{-}C_\alpha\text{-}C_{\beta'}$	109.402
$C_\beta\text{-}C_\alpha\text{-}C_m$	127.145
$C_{\beta'}\text{-}C_\alpha\text{-}C_m$	124.700
$C_\alpha\text{-}C_\beta\text{-}C_\beta$	107.380
$C_\alpha\text{-}C_{\beta'}\text{-}C_{\beta'}$	107.265
$C_\alpha\text{-}N\text{-}C_\alpha$	106.607
$M\text{-}N\text{-}C_\alpha$	124.691
N-M-N	152.290
Mean dihedral angle Relative to Mean Plane (°)	
meso-Ph	60.31, 54.79
Pyrrole	14.185, 19.925

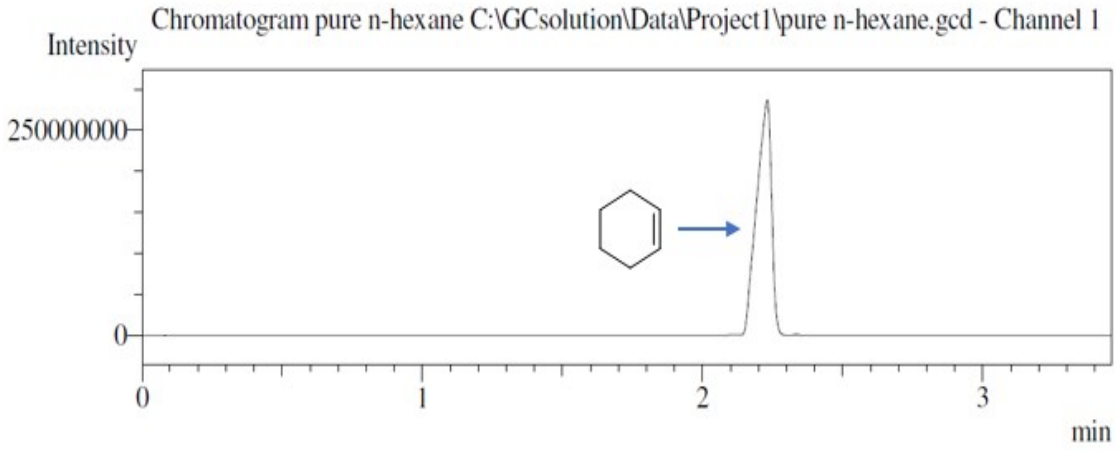
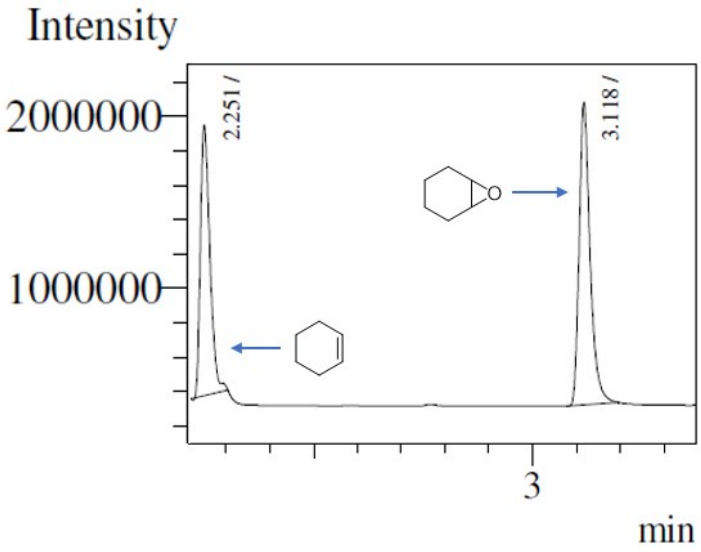


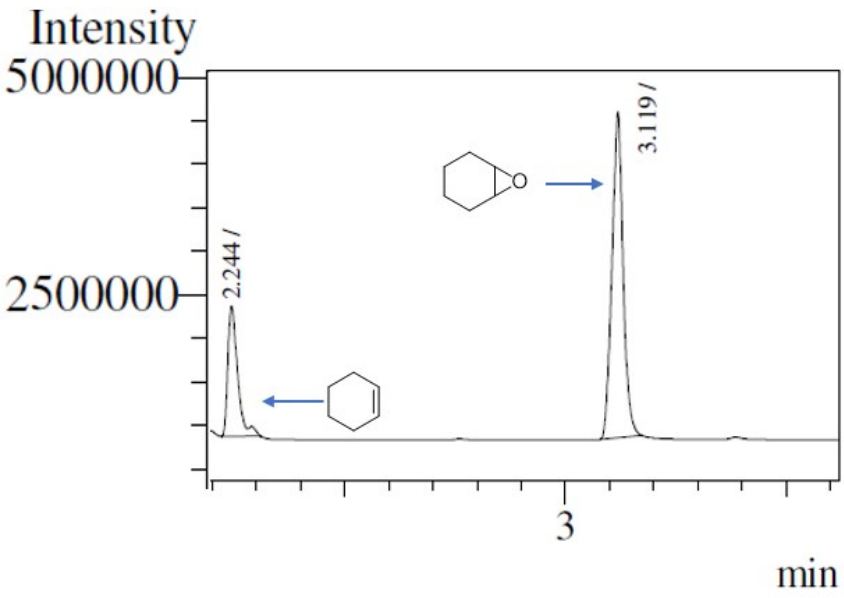
Figure S6. GC trace corresponding to pure cyclohexene (substrate) as observed in gas chromatography.



sample information - Channel 1

Name	Peak#	Ret.Time	Area	Area%
	1	2.251	2745024	43.6512
	2	3.118	3543522	56.3488
Total			6288546	100.0000

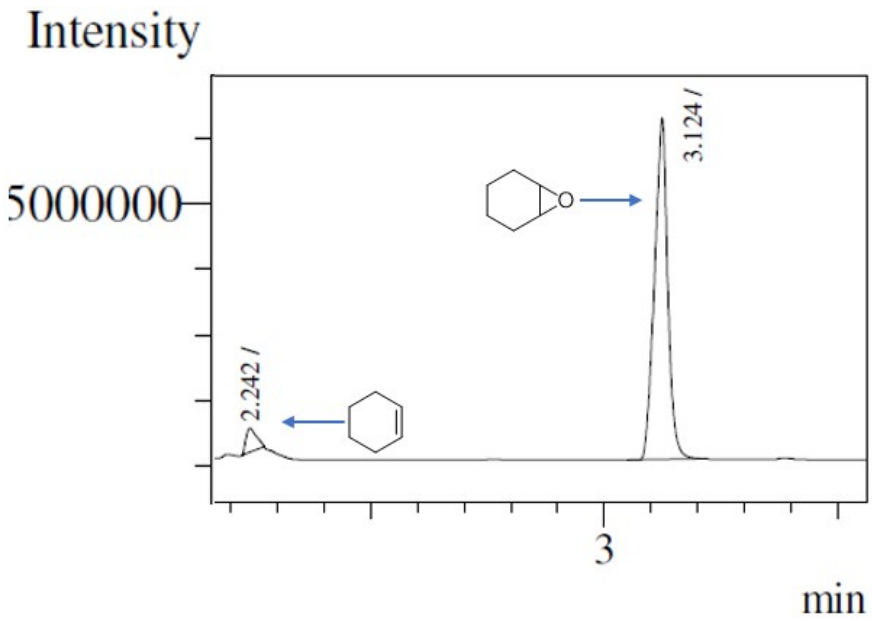
Figure S7. GC traces corresponding to cyclohexene (substrate) and cyclohexene epoxide (product) chromatograms showing their respective percentages after 10 min. of reaction time.



sample information - Channel 1

Name	Peak#	Ret.Time	Area	Area%
	1	2.244	2777533	26.1562
	2	3.119	7841476	73.8438
Total			10619009	100.0000

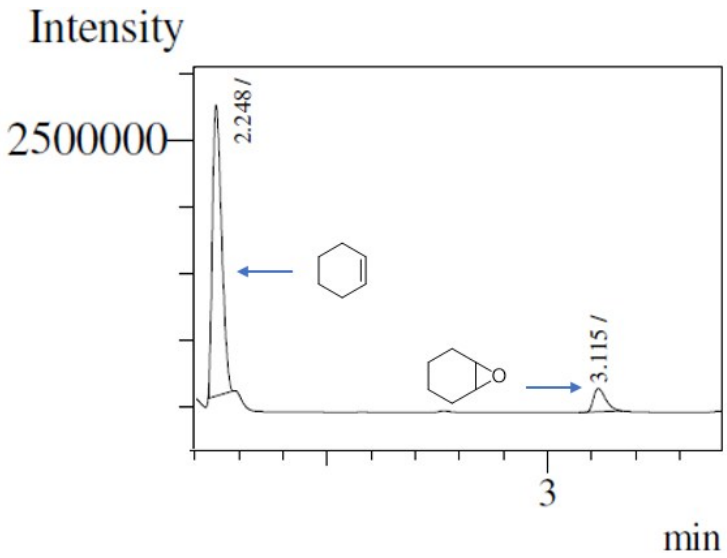
Figure S8. GC traces corresponding to cyclohexene (substrate) and cyclohexene epoxide (product) chromatograms showing their respective percentages after 20 min. of reaction time.



sample information - Channel 1

Name	Peak#	Ret.Time	Area	Area%
	1	2.242	655434	5.0729
	2	3.124	12264788	94.9271
Total			12920222	100.0000

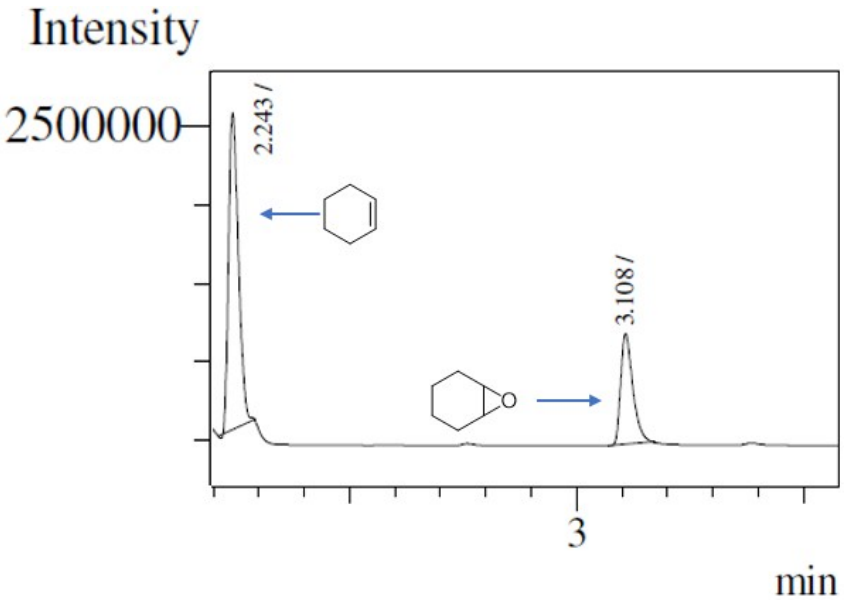
Figure S9. GC traces corresponding to cyclohexene (substrate) and cyclohexene epoxide (product) chromatograms showing their respective percentages after 30 min. of reaction time.



sample information - Channel 1

Name	Peak#	Ret.Time	Area	Area%
	1	2.248	3714525	90.4169
	2	3.115	393696	9.5831
Total			4108221	100.0000

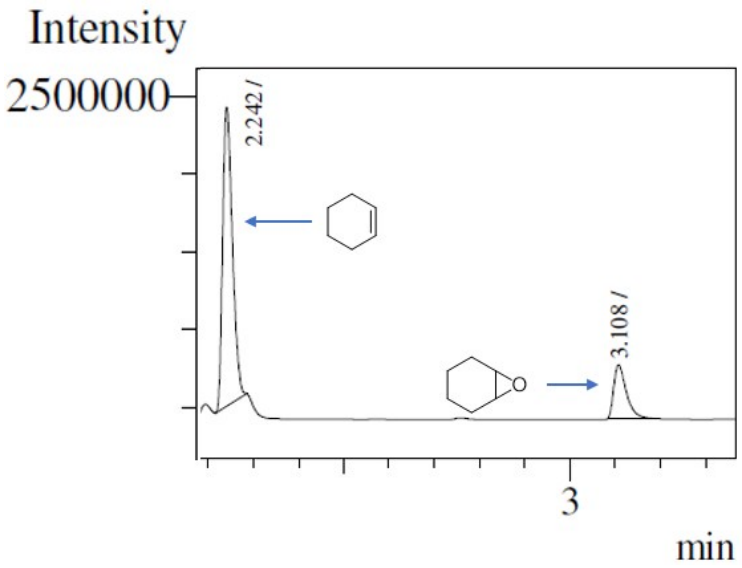
Figure S10. GC traces corresponding to cyclohexene (substrate) and cyclohexene epoxide (product) chromatograms showing their respective percentages after 30 min. of reaction time without catalyst (**1**) and without $NaHCO_3$.



sample information - Channel 1

Name	Peak#	Ret.Time	Area	Area%
	1	2.243	3622797	70.0237
	2	3.108	1550877	29.9763
Total			5173674	100.0000

Figure S11. GC traces corresponding to cyclohexene (substrate) and cyclohexene epoxide (product) chromatograms showing their respective percentages after 30 min. of reaction time without catalyst (**1**).



sample information - Channel 1

Name	Peak#	Ret.Time	Area	Area%
	1	2.242	3416842	81.2830
	2	3.108	786795	18.7170
Total			4203637	100.0000

Figure S12. GC traces corresponding to cyclohexene (substrate) and cyclohexene epoxide (product) chromatograms showing their respective percentages after 30 min. of reaction time without $NaHCO_3$.

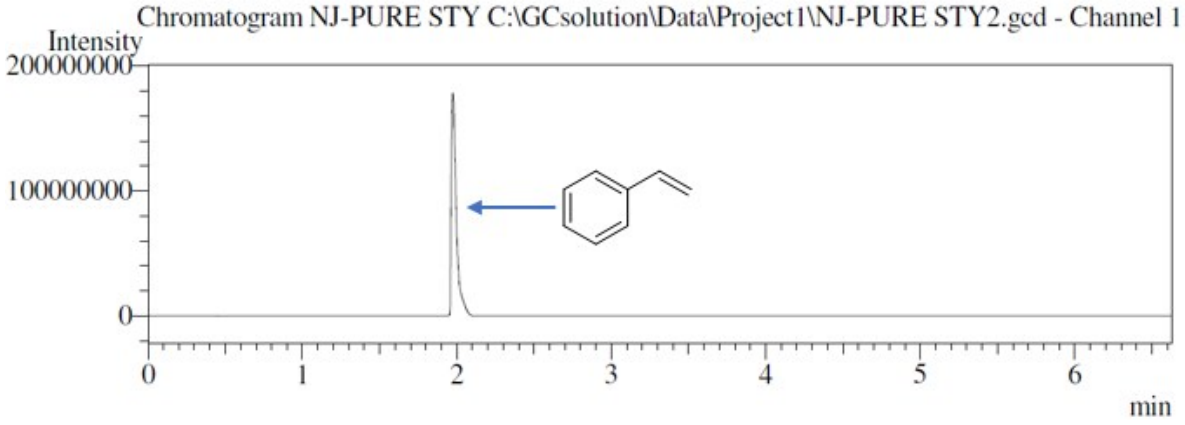
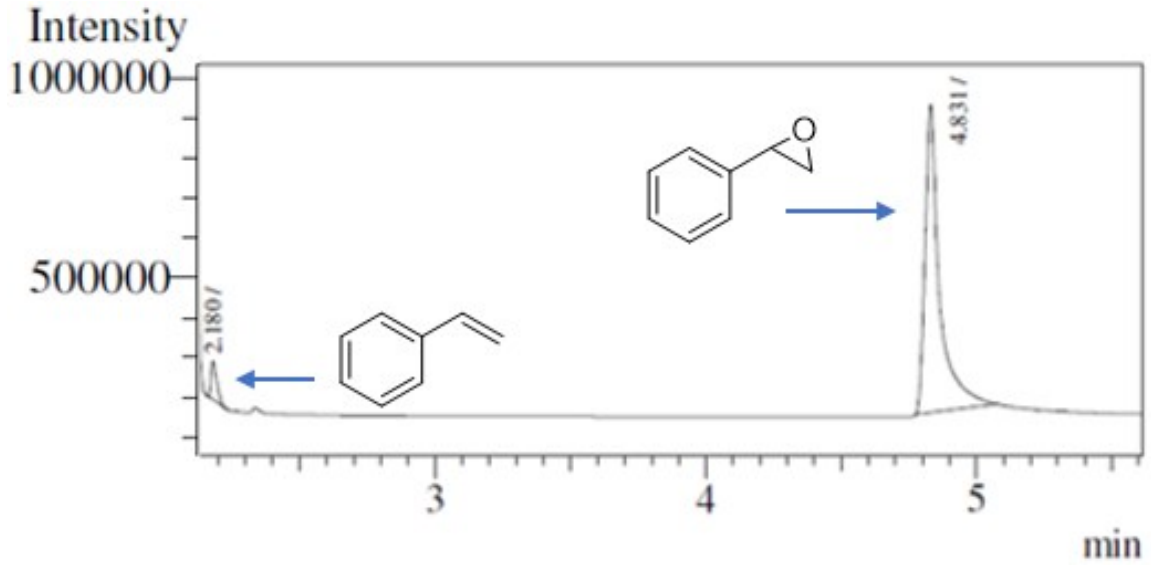


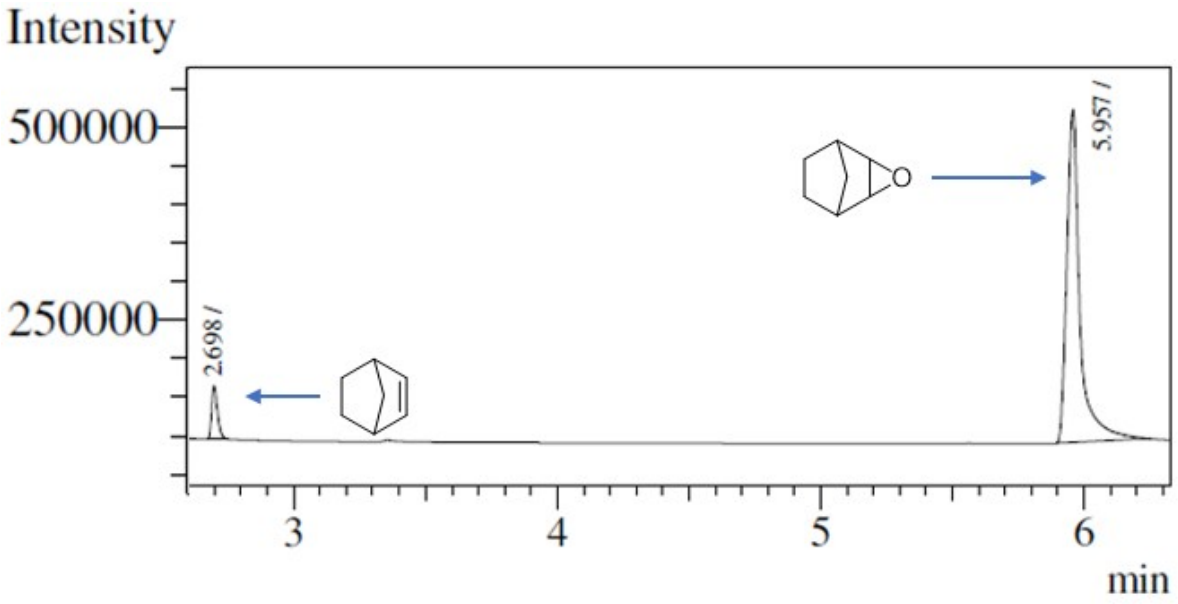
Figure S13. GC trace corresponding to pure styrene (substrate) as observed in gas chromatography.



sample information - Channel 1

Name	Peak#	Ret.Time	Area	Area%
	1	2.180	158744	4.4825
	2	4.831	3382678	95.5175
Total			3541422	100.0000

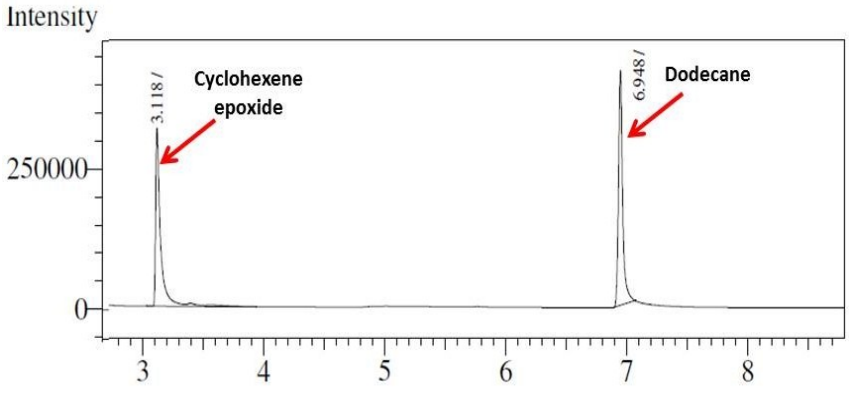
Figure S14. GC traces corresponding to styrene (substrate) and styrene epoxide (product) chromatograms showing their respective percentages after 30 min. of reaction time.



sample information - Channel 1

Name	Peak#	Ret.Time	Area	Area%
	1	2.698	124402	6.5446
	2	5.957	1776441	93.4554
Total			1900843	100.0000

Figure S15. GC traces corresponding to bicyclo[2.2.1]heptene (substrate) and bicyclo[2.2.1]heptene epoxide (product) chromatograms showing their respective percentages after 30 min. of reaction time.



sample information - Channel 1

Peak#	Ret.Time	Area	Area%
1	3.118	921469	48.1272
2	6.948	993184	51.8728
		1914653	100.0000

Figure S16. GC traces corresponding to cyclohexene epoxide (product) and dodecane (internal standard).