

Asymmetric epoxidation of unfunctionalized olefins catalyzed by Mn(salen) axially immobilized onto insoluble polymers

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Abstract—Chiral Mn(salen) complexes axially immobilized onto insoluble polymers by phenoxy group or phenyl sulfonic group afford comparable or even higher enantioselectivities than homogeneous Mn(salen) catalysts for the asymmetric epoxidation of various unfunctionalized olefins. These heterogeneous Mn(salen) catalysts are relatively stable and can be recycled in the asymmetric epoxidation.

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1. Introduction

Chiral Mn^{III}(salen) complexes are excellent catalysts for the asymmetric epoxidation of unfunctionalized olefins.¹ Heterogenization of Mn(salen) complexes has received great attention in recent years² due to the inherent advantages of easy separation and recycling of catalysts, purification of products and better handling properties.³ More importantly, the immobilization of Mn(salen) complexes also effectively restrains the formation of inactive μ -oxo-Mn(IV) dimers by isolating the catalytic sites.⁴ Various inorganic supports, such as mesoporous materials,⁵ carbon materials,⁶ clay compounds⁷ and inorganic membranes,⁸ have been used to immobilize chiral Mn(salen) complexes. These heterogeneous catalysts usually display activities and enantioselectivities for the asymmetric epoxidation of unfunctionalized olefins.

In addition to these inorganic supports, organic supports are also widely used for the heterogenization of Mn(salen).^{2b,9} Mn(salen) complexes, attached to a soluble polymer, such as PEG-OMe, can be precipitated out using a suitable solvent after reaction.¹⁰ Mn(salen) complexes with perfluorinated alkyl chains¹¹ can be recycled by simple phase separation. Functionalized Mn(salen) complexes were also copolymerized¹² or self-polymerized¹³ to form cross-linked insoluble polymers, which

always result in poor ee values when compared to the homogeneous catalysts due to the unhelpful steric restriction in the polymer microenvironment.^{4b} Another alternative approach is to graft Mn(salen) complexes onto insoluble polymer resins^{10a,14} or onto dendrimers.¹⁵ According to the grafting criteria that Sherrington et al.^{4b} have proposed, most of the polymer-supported Mn(salen) catalysts reported in the literature were grafted from salen ligands via a long flexible linkage, which usually gives comparable ee values to the homogeneous catalysts. However, immobilizing Mn(salen) catalysts onto insoluble polymers through the axial direction has rarely been reported.¹⁶ Almost no examples have been reported in the literature, where the enantioselectivity can be greatly enhanced by polymer-immobilized Mn(salen) catalysts in comparison to the homogeneous catalysts for the asymmetric epoxidation of unfunctionalized olefins.

We have recently reported that chiral Mn(salen) complexes axially immobilized onto mesoporous materials via a phenoxy group^{5a} or a phenyl sulfonic group¹⁷ show high stability and much higher ee values for the asymmetric epoxidation of unfunctionalized olefins. Herein, these grafting methods were further extended to the immobilization of chiral Mn(salen) complexes onto insoluble polystyrene resins, which are much easier to handle and recycle. It was found that the Mn(salen) catalysts axially grafted onto insoluble polymers show comparable and even higher enantioselectivities than the homogeneous catalysts for the asymmetric epoxidation of unfunctional olefins. The

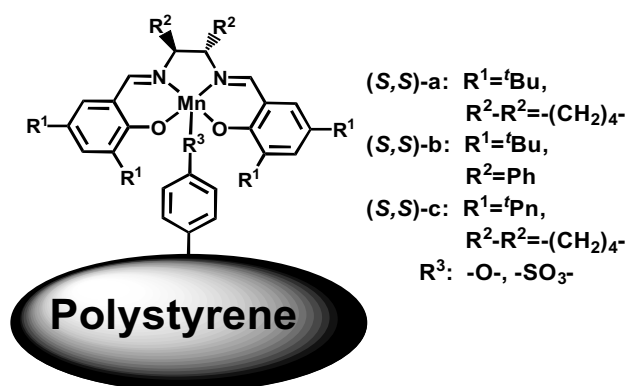
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polymer-immobilized Mn(salen) catalysts are stable and can be recycled at least two or three times in the asymmetric epoxidation.

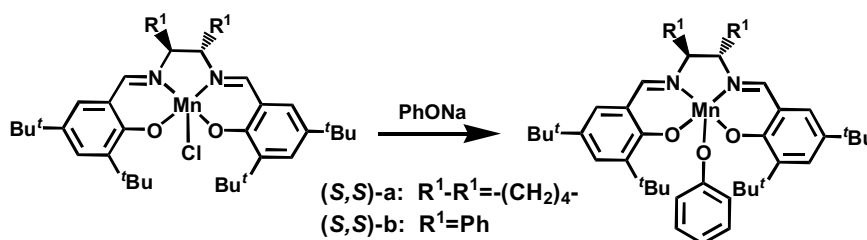
2. Results and discussion

2.1. Synthesis and characterization of catalysts

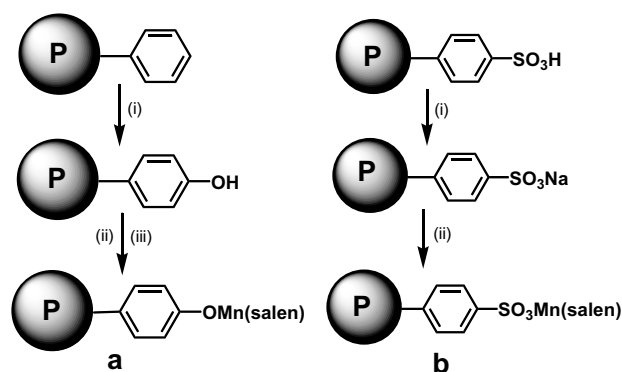
High cross-linked and insoluble polystyrene resin and polystyrene sulfonic acid resins were used as supports to immobilize chiral Mn(salen) complexes. Three Mn(salen)Cl complexes were synthesized and well characterized (Scheme 1).¹⁸ Mn(salen)OPh complexes were prepared by reaction of Mn(salen)Cl complexes with PhONa in refluxed ethanol (Scheme 2). The formed NaCl was detected by HNO₃–AgNO₃ solution. Elemental analysis results show that the ratios of the C/H/N of the synthesized Mn(salen)OPh complexes compare very well with the calculated results. According to the method reported previously,¹⁹ phenyl groups on the surface of the polystyrene resin were hydroxylated into phenoxy groups by H₂O₂ catalyzed by sulfuric acid and FeCl₃ in ethanol solution (Scheme 3a). After converting PS–PhOH into its sodium salt, Mn(salen) complexes can be readily anchored onto the polystyrene resin under reflux.^{5a} Polystyrene sulfonic acid resin was directly converted into its sodium salt, followed by anchoring Mn(salen) complexes through ion exchange (Scheme 3b).¹⁷ The heterogeneous Mn(salen) catalysts were thoroughly washed by ethanol and CH₂Cl₂ until no peaks could be detected from the UV–vis spectra of the filtrate (with CH₂Cl₂ as reference). The grafting



Scheme 1. A schematic description of heterogeneous chiral Mn(salen) catalysts axially immobilized onto polymers.



Scheme 2. Preparation of Mn(salen)OPh catalysts.



Scheme 3. Preparation of heterogeneous Mn(salen) catalysts immobilized by phenoxy group (a) and phenyl sulfonic group (b). Reagents and conditions: (a) (i) H₂O₂, H₂SO₄, FeCl₃·H₂O, EtOH, 50 °C, 20 h; (ii) NaOH, rt, 3 h; (iii) Mn(salen)Cl, EtOH, reflux 5 h. (b) (i) NaOH, rt, 3 h; (ii) Mn(salen)Cl, EtOH, reflux, 5 h.

proved unsuccessful in ethanol at room temperature. The formed chloride ion during the grafting procedure was analyzed by the titration with H⁺–AgNO₃ aqueous solution.

The polymer-supported Mn(salen) catalysts were well characterized by IR and UV–vis spectra. PS–Ph and PS–PhONa gave similar IR spectra (Fig. 1). The appearance of the characteristic band of Mn(salen) complexes at 1535 cm⁻¹ in the IR spectra of PS–PhOMn(salen)-b

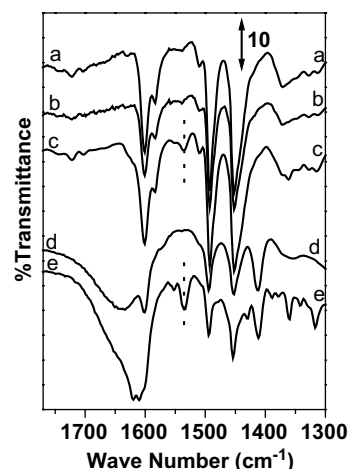


Figure 1. The FT-IR spectra of (a) polystyrene, that is, PS–Ph; (b) PS–PhONa; (c) PS–PhOMn(salen)-b; (d) PS–PhSO₃Na; and (e) PS–PhSO₃Mn(salen)-c.

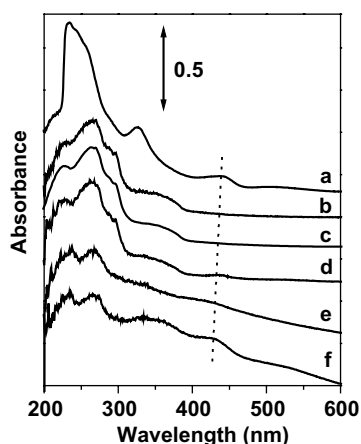


Figure 2. The UV-vis spectra of (a) Mn(salen-a)Cl; (b) polystyrene, that is, PS-Ph; (c) PS-PhONa; (d) PS-PhOMn(salen-a); (e) PS-PhSO₃Na; and (f) PS-PhSO₃Mn(salen-a).

and PS-PhSO₃Mn(salen-c) confirms the presence of the Mn(salen) on the polystyrene resins. The UV-vis spectra (Fig. 2) give further evidence for the successful grafting based on the fact that the characteristic peak of Mn(salen-a)Cl at 439 nm is, respectively, shifted to 435 nm for PS-PhOMn(salen-a) and 431 nm for PS-PhSO₃Mn(salen-a). The shifts of the characteristic band also show the presence of the interaction of the Mn(salen) complexes with polymer supports. The grafting amount of Mn(salen) for PS-PhOMn(salen) and PS-PhSO₃Mn(salen) catalysts are in the range of 2–5 and 10–20 μmol/g, respectively, detected by ICP-AES based on the Mn element.

2.2. Asymmetric catalytic epoxidation

Five typical substituted unfunctionalized olefins: a mono-substituted styrene, disubstituted 6-cyano-2,2-dimethylchromene, *cis*-β-methylstyrene and α-methylstyrene, and tri-substituted 1-phenylcyclohexene were tested against these heterogeneous catalysts for asymmetric epoxidation. All the heterogeneous catalysts used for the asymmetric epoxidation contain the same amount of active centres, 0.5–1.5 mol % Mn(salen) based on the amount of substrates. *n*-Nonane was used as the internal standard due to its stability, inertia and easy handling (bp 151 °C). The asymmetric epoxidations of styrene and other substrates were respectively at 0 and 20 °C. PPNO as the auxiliary was used for the asymmetric epoxidation of styrene, 6-cyano-2,2-dimethylchromene and 1-phenylcyclohexene. The solid catalysts were filtrated, washed thoroughly with distilled water, ethanol and CH₂Cl₂ and used for the next cycle. The reaction results are listed in Tables 1 and 2.

The polymer-immobilized Mn(salen) catalysts are active and enantioselective for the asymmetric epoxidation of various substituted olefins. 1-Phenylcyclohexene was quantitatively converted into its epoxide with 51.6% ee (without PPNO) and 83.6% ee (with PPNO) catalyzed by homogeneous Mn(salen-c)Cl catalyst (entries 1 and 2). Without PPNO, the heterogeneous PS-PhSO₃Mn(salen-c) catalyst gave 31.4% yield and nearly racemic epoxides. The addition of PPNO results in a conversion increase from 31.4% to 92.9% and ee values increased from 2.07% to 70.5% (entries 3 and 4). The increase in activity and the ee values might be due to the presence of the partial interaction between Mn(salen) and PPNO

Table 1. Asymmetric epoxidation of unfunctional olefins^a

Entry	Substrate	Catalyst	Cat. (mol %)	<i>t</i> (h)	Yield (%)	ee (%)	Config.
1		Mn(salen-c)Cl ^b	1.5	6	94.0	51.6	(<i>R,R</i>)
2		Mn(salen-c)Cl	1.5	6	94.3	83.6	(<i>R,R</i>)
3		PS-PhSO ₃ Mn(salen-c) ^b	0.5	24	31.4	2.07	(<i>R,R</i>)
4		PS-PhSO ₃ Mn(salen-c)	0.5	24	92.9	70.5	(<i>R,R</i>)
5		Mn(salen-a)Cl	1.5	6	100	90.0	(<i>S,S</i>)
6		PS-PhSO ₃ Mn(salen-a)	1.0	24	99.4	87.9	(<i>S,S</i>)
7		PS-PhSO ₃ Mn(salen-a) ^c	1.0	24	14.1	91.7	(<i>S,S</i>)
8		Mn(salen-c)Cl	1.5	6	100	89.3	(<i>S,S</i>)
9	PS-PhSO ₃ Mn(salen-c)	1.0	24	100	86.8	(<i>S,S</i>)	
10		Mn(salen-a)Cl	1.5	6	100	38.7	(<i>S</i>)
11		Mn(salen-a)OPh	1.5	6	100	37.2	(<i>S</i>)
12		PS-PhOMn(salen-a) ^d	0.5	24	81.4	41.1	(<i>S</i>)
13		Mn(salen-b)Cl	1.5	6	100	58.0	(<i>S</i>)
14		Mn(salen-b)Cl ^{b,e}	1.5	6	73.0	52.0	(<i>S</i>)
15		PS-PhOMn(salen-b) ^f	0.5	24	76.3	60.5	(<i>S</i>)
16		PS-PhOMn(salen-b) ^{b,g}	0.5	24	16.4	34.4	(<i>S</i>)

^a Reactions were performed in CH₂Cl₂ (3 mL) with olefins (1.0 mmol), *n*-nonane (internal standard, 1.0 mmol), PPNO (0.38 mmol), homogeneous (1.5 mol %) or heterogeneous Mn(salen) catalysts (0.5–1.0 mol %) and NaClO (pH 11.5, 0.55 M, 3.64 mL) at 20 °C for entries 1–6, 8–9 and at 0 °C for entries 7, 10–16.

^b Without PPNO.

^c Reaction at 0 °C.

^d Phenyl aldehyde and acetophenone as by-products, Sel% 94.2%.

^e Sel% 82.9%.

^f Sel% 95.3%.

^g Sel% 63.3%.

Table 2. Asymmetric epoxidation of unfunctional olefins^a

Entry	Catalyst	Cat. (mol %)	<i>t</i> (h)	Yield (%)	ee (%)
1	Mn(salen-b)Cl	1.5	6	25.3 ^c	25.3
2	PS-PhSO ₃ Mn(salen-b)	1.5	24	55.0 ^d 43.3 ^c 42.5 ^d	93.3 68.8 89.2
3	Mn(salen-a)Cl	1.5	6	100	55.0
4	PS-PhSO ₃ Mn(salen-a)	0.5	24	50.2	65.5
5	PS-PhOMn(salen-a)	0.5	24	30.6	74.0
6	Mn(salen-a)OPh	1.5	6	100	53.3
7	PS-PhOMn(salen-a) ^f	0.5	24	0.81	80.3
8	PS-PhSO ₃ Mn(salen-a)	1.5	24	87.3	65.2
9	Mn(salen-b)Cl	1.5	6	100	26.4
10	Mn(salen-b)OPh	1.5	6	100	23.6
11	PS-PhSO ₃ Mn(salen-b) (1st)	0.5	24	37.3	57.0
12	PS-PhSO ₃ Mn(salen-b) (2nd)	0.5	24	41.1	56.3
13	PS-PhOMn(salen-b) (1st)	0.5	24	36.3	76.9
14	PS-PhOMn(salen-b) (2nd)	0.5	24	40.5	75.3
15	PS-PhOMn(salen-b) (3rd)	0.5	24	35.7	76.0

^a Reactions were performed in CH₂Cl₂ (3 mL) with α -methylstyrene (1.0 mmol), *n*-nonane (internal standard, 1.0 mmol), homogeneous (1.5 mol %) or heterogeneous Mn(salen) catalysts (0.5 or 1.5 mol %) and NaClO (pH = 11.5, 0.55 M, 3.64 mL) at 20 °C.

^b (*S,R*)-*cis*-Epoxide, (*S,S*)-*trans*-epoxide.

^c *cis*-Epoxide.

^d *trans*-Epoxide.

^e (*S*)-Epoxide.

^f Reaction at 0 °C.

during the catalytic reaction. However, the ee value of 70.5% is still lower than the ee value of 83.6% for the homogeneous case. In fact the grafting of Mn(salen) from the salen ligand via a long linkage always gave comparable ee values to the homogenous catalysts,^{4b} because PPNO can readily coordinate with the central Mn atom. Herein, the axial immobilization of Mn(salen) complexes results in the unhelpful coordination of PPNO, leading to lower ee values than the homogeneous result.

The heterogeneous Mn(salen) catalysts also exhibit high activity and enantioselectivity for asymmetric epoxidation of a disubstituted cyclic olefin. 6-Cyano-2,2-dimethylchromene can be completely converted into its epoxide with 87.9% ee catalyzed by PS-PhSO₃Mn(salen-a), which is comparable to its homogeneous 90.0% ee value (entries 5 and 6). If the reaction temperature is decreased from room temperature to 0 °C, the yield of the epoxide is greatly reduced from 99.4% to 14.1% (entries 6 and 7). However, the ee value remains unchanged. The heterogeneous PS-PhSO₃Mn(salen-c) catalyst also gave a similar ee value to the homogeneous result for this epoxidation reaction (entries 8 and 9). It has been reported that (pyrrolidine salen) Mn complex bounded onto the polymer via a long flexible linkage to give 87% ee for this epoxidation reaction at 0 °C.^{14d} The axially immobilized Mn(salen) catalysts afford comparable ee values when the asymmetric epoxidation is carried out at room temperature (20 °C).

As for the asymmetric epoxidation of single-substituted styrene, polymer-immobilized Mn(salen) catalysts gives comparable or even higher ee values than the homogeneous Mn(salen) catalysts. Immobilized PS-PhOMn(salen-a) catalyst gave 41.1% ee for the asymmetric epoxidation of styrene; while the homogeneous Mn(salen-a)Cl and Mn(salen-a)OPh catalysts afford 38.7%

and 37.2% ee value, respectively (entries 10–12). Similarly, the 60.5% ee obtained for the PS-PhOMn(salen-b) catalyst is slightly higher than its corresponding homogeneous 58.0% ee value (entries 13 and 15). If without PPNO (entries 14 and 16), both the homogeneous and heterogeneous catalysts give poorer reaction results than those with PPNO. The addition of PPNO improves the activity, chemical selectivity and enantioselectivity of the heterogeneous catalyst for the asymmetric epoxidation of styrene (entries 15 and 16). It should be noted that heterogeneous Mn(salen) catalysts prepared by a co-polymerization method always result in poor^{12b,c} or slightly lower ee values^{15a} than homogeneous catalysts. Furthermore, immobilizing Mn(salen) onto some inorganic supports often results in a low selectivity of styrene epoxide with some phenyl aldehyde and acetophenone as by-products;²⁰ herein, the polymer-immobilized Mn(salen) catalysts can give chemical selectivities up to 95%.

More interestingly, Mn(salen) catalysts axially immobilized onto polymers show remarkably higher ee values than the homogeneous Mn(salen) catalysts for asymmetric epoxidation of disubstituted *cis*- β -methylstyrene and α -methylstyrene (Table 2). Homogeneous Mn(salen-b)Cl catalyst gave the *cis*-epoxide with 25.3% ee and the *trans*-epoxide with 93.3% ee (entry 1). The polymer-immobilized Mn(salen-b) catalyst results in the ee value of the *cis*-epoxide being increased from 25.3% to 68.8% (entry 2). The ee value of the *trans*-epoxide is comparable to that of the homogeneous catalyst. The immobilized catalyst also altered the *cis/trans* ratio of the epoxides, which increased from homogeneous 0.46 to heterogeneous 1.02. This is due to the rotation of the formed radical intermediate being partially restrained by the axial grafting mode and/or the rigid polymer support.

As for the asymmetric epoxidation of α -methylstyrene, the homogeneous Mn(salen-a)Cl catalyst gives a 55.0% ee value, while the PS-PhSO₃Mn(salen-a) catalyst gave a 65.5% ee value and the PS-PhOMn(salen-a) affords a further increased ee value of 74.0% (entries 3–5). However, the Mn(salen-a)OPh catalyst gives the similar ee value to that of Mn(salen-a)Cl (entries 3 and 6). However, decreasing the reaction temperature led to nearly no conversion of the olefin substrate (entry 7). Increasing the catalyst loading from 0.5 to 1.5 mol % resulted in a conversion increase from 50.2% to 87.3% with a constant ee value of 65% (entries 4 and 8). Homogeneous Mn(salen-b)Cl and Mn(salen-b)OPh catalysts respectively showed 26.4% and 23.6% ee for the asymmetric epoxidation of α -methylstyrene (entries 9 and 10). Immobilization of Mn(salen-b) onto polymers by a phenyl sulfonic group gives 57.0% ee and immobilization by a phenoxy group results in a further increased enantioselectivity of 76.9% (entries 11 and 13). Almost no examples have been observed in the literature for the great increase in ee (up to 50%) for the polymer-immobilized Mn(salen)-catalyzed asymmetric epoxidation. It should also be noted that grafting Mn(salen) complexes with a phenoxy group always affords higher ee values than those with a phenyl sulfonic group for the asymmetric epoxidation of α -methylstyrene. The addition of the modified supports, PS-PhONa or PS-PhSO₃Na, to the homogeneous Mn(salen-a)Cl catalytic systems exhibits the identical reaction results as those without the addition. This means that only immobilized Mn(salen) catalysts can give higher ee values.

To the best of our knowledge, the heterogeneous Mn(salen) catalysts prepared by the co-polymerization or grafting via a long flexible linkage always result in lower than or comparable ee values to the homogeneous catalysts for the asymmetric epoxidation of unfunctionalized olefins.^{4b,12,14d} Mn(salen) axially immobilized onto the polymer by pyridine coordination also show poor ee values (16–46%).¹¹ It has been reported that some inorganic support-immobilized Mn(salen) catalysts show higher ee values than homogeneous catalysts for the asymmetric epoxidation; the reason is due to the steric effect of supports.^{2d,e} Herein, for the rigid polymer-immobilized Mn(salen) catalysts, the polymer is not only used for the separation and stabilization of Mn(salen) complexes but also used as a big and rigid ligand axially coordinated to Mn(salen). Therefore, the axial grafting modes and the rigid polymer supports, as well as the restriction in the rotation of the radical intermediate, may be the main reasons for the increase in the ee values for the asymmetric epoxidation.

The heterogeneous Mn(salen) catalysts show comparable catalytic activities to the homogeneous Mn(salen) catalysts. For example, the TOF is, respectively, estimated to be 8 h⁻¹ for PS-PhSO₃Mn(salen-c) catalyst and 10 h⁻¹ for the homogeneous Mn(salen-c)Cl catalyst for the asymmetric epoxidation of 1-phenylcyclohexene. It is noteworthy that the polymer-immobilized Mn(salen) catalysts can be easily recycled. These heterogeneous catalysts are stable in terms of activity and

enantioselectivity when recycled at least two or three times for the asymmetric epoxidation of α -methylstyrene (Table 2, entries 9–13). The TON was estimated to be 225 (the sum of three cycles) for the heterogeneous PS-PhOMn(salen-b) catalyst, much higher than 67 for the homogeneous Mn(salen-b)Cl catalyst. It was reported that homogeneous Mn(salen) complexes are prone to oxidative degradation²¹ and dimerization to μ -oxo-Mn(IV) species,^{12a} which result in the deactivation of the catalytic species. Immobilization of Mn(salen) onto the polymer supports leads to site isolation and enhances the stability of the Mn(salen) complexes.

3. Conclusion

Chiral Mn(salen) complexes were axially immobilized onto different rigid polymers via a phenoxy group and phenyl sulfonic group. The polymer-immobilized Mn(salen) catalysts give comparable or even higher ee values than the homogeneous catalysts. These heterogeneous Mn(salen) catalysts are stable and can be recycled in the asymmetric epoxidation of unfunctional olefins.

4. Experimental

4.1. General

Polystyrene resin (cross-link: 15% DVB, 200–400 mesh) and polystyrene sulfonic acid resin (cross-link: 15% DVB, 200–400 mesh, 3.48 mmol/g sulfonic acid capacity) were used as supports. Racemic epoxides were synthesized and detected by GC-MS (GC6890-MS5973N). The reaction products were analyzed by GC-MS with yields (with *n*-nonane as internal standard) and ee values determined by gas chromatography (6890N, Agilent Co.) using a chiral column (HP19091G-B213, 30 m \times 0.32 mm \times 0.25 μ m, Agilent Co.). All IR spectra were collected on a Fourier transform infrared spectrometer (Nicolet Nexus 470). UV-vis spectra were recorded on a JASCO V-550 spectrometer.

4.2. Synthesis of Mn(salen)OPh

Three salen ligands and three Mn(salen)Cl complexes (Scheme 1) were synthesized and well-characterized according to the literature.¹⁸ Phenol (25 g, 0.265 mol, 1.11 equiv) as a solid was added to distilled water (10 mL) containing NaOH (9.54 g, 0.238 mol) with stirring. After reaction for 30 min at room temperature, the mixture was filtrated and washed thoroughly with toluene until no residual phenol could be detected by FeCl₃ characteristic reaction, and then washed by 3 \times 30 mL of ethanol. The white powder PhONa was obtained after drying at 80 °C for 8 h under a high vacuum (20.71 g, 75%) and stored under Ar.

Mn(salen-a or -b)Cl complex (0.256 mmol) and PhONa (35.9 mg, 0.309 mmol, 1.2 equiv) were added to ethanol (60 mL), and the mixture refluxed for 3 h at 80 °C (Scheme 2). After cooling to room temperature, ethanol

was removed. To this dark solid, 30 mL of CH_2Cl_2 was added, and the organic phase washed with 15 mL of distilled water. The water samples were detected by HNO_3 – AgNO_3 solution until no characteristic white floc was observed (needed about three times). Then the CH_2Cl_2 solution was washed with 10 mL of saturated NaCl solution and dried over anhydrous Na_2SO_4 . Removing CH_2Cl_2 gave brown-dark solid $\text{Mn}(\text{salen-a, or b})\text{OPh}$ complexes. $\text{Mn}(\text{salen-a})\text{OPh}$: IR (KBr, cm^{-1}): $\nu = 2955, 1612, 1535, 1477, 1312, 1253, 1175, 837$; Elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{57}\text{MnN}_2\text{O}_3$: C, 73.26; H, 8.28; N, 1.16. Found: C, 74.09; H, 8.37; N, 1.04. $\text{Mn}(\text{salen-b})\text{OPh}$: IR (KBr, cm^{-1}): $\nu = 2956, 1614, 1533, 1252, 1174, 836, 699$; Elemental analysis calcd (%) for $\text{C}_{50}\text{H}_{59}\text{MnN}_2\text{O}_3$: C, 75.95; H, 7.47; N, 1.01. Found: C, 76.81; H, 7.79; N, 1.30.

4.3. Immobilizing Mn(salen) catalyst by phenoxy group

Polystyrene (short for PS, 5.4 g) was added to ethanol (180 mL) containing concentrated sulfuric acid (3.44 g) and catalyst $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (132 mg) and this suspension stirred for 30 min at 50°C .¹⁹ Then H_2O_2 (13.2 mL) was added to the mixture in four equal portions and the mixture stirred for an additional 20 h (Scheme 3a). The solid was filtrated and washed with ethanol and distilled water until neutrality to give PS–PhOH. To this resulting PS–PhOH powder, 180 mL of distilled water and 20 mL ethanol containing NaOH (216 mg) was added and this mixture stirred for 3 h at room temperature. The solid was filtrated and washed with distilled water until pH 7 to give PS–PhONa as white powder. A mixture of $\text{Mn}(\text{salen})\text{Cl}$ (1.0 mmol) and PS–PhONa (2.0 g) was added to ethanol (60 mL) and this suspension was stirred for 5 h under reflux. The mixture was then filtrated, washed thoroughly with ethanol and CH_2Cl_2 to produce PS–PhOMn(salen) as little yellow powder. The CH_2Cl_2 filtrate was detected by UV–vis until no peaks could be detected (with CH_2Cl_2 as reference).

4.4. Immobilizing Mn(salen) catalysts by phenyl sulfonic group

To this brown powder sulfonic acid modified polystyrene (short for PS– PhSO_3H , 2.87 g, 10 mmol H^+) was added distilled water (100 mL) containing NaOH (400 mg, 10 mmol) and this mixture stirred for 4 h at room temperature (Scheme 3b). The solid was filtrated and washed to neutral to produce PS– PhSO_3Na as a brown powder.¹⁷ The mixture of $\text{Mn}(\text{salen})\text{Cl}$ (1.0 mmol) and PS– PhSO_3Na (1.0 g) were added to ethanol (60 mL) and this suspension stirred for 5 h under reflux. After the solid was filtrated and washed thoroughly with ethanol and CH_2Cl_2 , PS– $\text{PhSO}_3\text{Mn}(\text{salen})$ was obtained as brown powder. The CH_2Cl_2 filtrate was analyzed by UV–vis until no peaks could be detected from the spectra (with CH_2Cl_2 as reference).

4.5. Characterization

The measurements of the IR spectra were performed on a Fourier transform infrared spectrometer (Nicolet Nexus 470) with a resolution of 4 cm^{-1} and 64 scans

in the region of $4000\text{--}400\text{ cm}^{-1}$. The samples of $\text{Mn}(\text{salen})\text{Cl}$, $\text{Mn}(\text{salen})\text{OPh}$ and polymer-immobilized $\text{Mn}(\text{salen})$ catalysts were prepared as KBr pellets and measured under ambient conditions (20°C). The UV–vis spectra were recorded on a JASCO V-550 spectrometer under ambient conditions (20°C) in the wavelength range of $190\text{--}800\text{ nm}$ with a band width of 5 nm. The solution of $\text{Mn}(\text{salen-a})\text{Cl}$ in CH_2Cl_2 with a concentration of about 1.0 mM was prepared and put into a 1 cm quartz cell for UV–vis adsorption with CH_2Cl_2 as reference. Diffuse reflectance UV–vis spectra of the solid polymer samples were recorded in the spectrophotometer with an integrating sphere using BaSO_4 as reference.

4.6. Asymmetric epoxidation reactions

The racemic epoxides samples were synthesized by epoxidation of the corresponding olefins with *m*-CPBA in CHCl_3 at 0°C and confirmed by GC–MS analysis. A typical epoxidation procedure is shown as follows. A solution of olefins (1 mmol) in CH_2Cl_2 (3 mL) containing *n*-nonane (internal standard, 1.0 mmol), PPNO (0.38 mmol, if necessary) and homogeneous (1.5 mol %) or heterogeneous catalysts (0.5–1.5 mol %, based on the Mn amount in the catalysts) was kept at either 0 or 20°C . NaClO aqueous solution (pH 11.5, 0.55 M, 3.64 mL) was added and this heterogeneous system was then stirred for either 6 h or 24 h. After reaction, the organic layer was concentrated and purified by flash chromatography to remove homogeneous catalysts or filtrated to remove heterogeneous catalysts. The yields and ee values of the epoxides were determined by GC. The solid catalysts were filtrated and washed thoroughly with distilled water and ethanol followed by dichloromethane and used for the next cycle.

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