Pergamon

Tetrahedron: Asymmetry, Vol. 7, No. 8, pp. 2293-2302, 1996

0957-4166/96 $15.00 + 0.00

PII: S0957-4166(96)00284-4

Heterogeneous Asymmetric Epoxidation of Unfunctionalized Olefins Catalyzed by Polymer-Bound (Salen)manganese Complexes

Filippo Minutolo†‡, Dario Pini†, Antonella Petri†, Piero Salvadori†*

†C.N.R. Centro Studi Macromolecole Stereoordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, I-56126 Pisa, Italy

‡Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56127 Pisa, Italy

Abstract: The synthesis of three different polymer-bound chiral Mn-salen complexes (Poly-**1**, -**2a**, -**2b**) is reported, along with their application as recyclable catalysts in heterogeneous asymmetric epoxidation with *m*CPBA/NMO of several unfunctionalized olefins. The introduction of a spacing group between the polymeric chain and the metal centre (Poly-**2a** and -**2b**) considerably increased the enantioselectivity of the process.

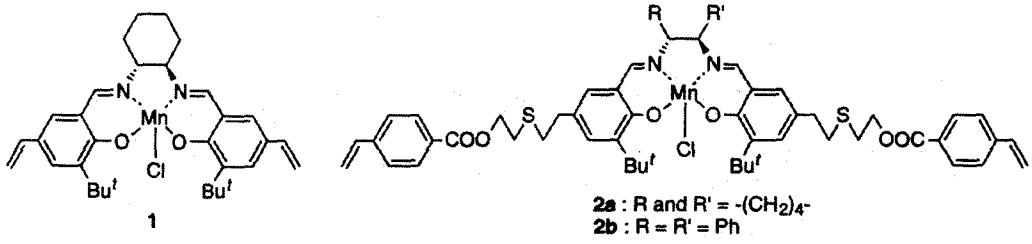
Epoxides constitute versatile synthetic intermediates, as they can be readily transformed into a large variety of useful functional groups by means of regioselective ring opening reactions. Hence, asymmetric olefin epoxidation stands as one of the most powerful strategies for the synthesis of enantiomerically enriched compounds. Sharpless asymmetric epoxidation proved to be highly effective with allylic alcohols.[1] In recent years, catalytic enantioselective epoxidation of unfunctionalized olefins has attracted a great deal of attention. Amongst the various catalysts developed so far, chiral Mn(III)-salen complexes proved to be extremely efficient in the catalysis of this outstanding reaction.[2] Besides their remarkable generality (high ee's are attainable with most unfunctionalized olefins), such manganese complexes can be easily prepared[3] and preserve their catalytic activity with a large number of terminal oxidants.[4]

To date, in spite of the increasing interest towards this reaction, only a few papers[5,6] have appeared dealing with performing asymmetric epoxidation with recyclable polymer-bound Mn-salen catalysts. Besides the easy recovery and reuse of such insoluble heterogeneous catalysts, a greater stability may be expected with respect to their soluble homogeneous counterpart. In fact, in the presence of an external oxygen source, Mn(III)-salen complexes can undergo dimerization to inactive μ-oxo manganese(IV) species,[7] with a progressive depletion of their overall catalytic activity. When the metal complex is anchored to a polymer support, there is a lower local concentration, therefore its spatial distribution along the chain would reduce the extent of the dimerization process, leading to longer-life catalysts.

We have recently reported[6] on our preliminary results attained with a new polymeric catalyst (Poly-**1**), containing chiral Mn-salen **1** (Figure 1) bound to a styrene-divinylbenzene matrix. In the presence of *m*-chloroperbenzoic acid and *N*-methylmorpholine-*N*-oxide,[4c,8] such polymeric catalyst gave extremely fast and efficient reactions with promising ee's. We now wish to report the application of two new polymeric catalysts

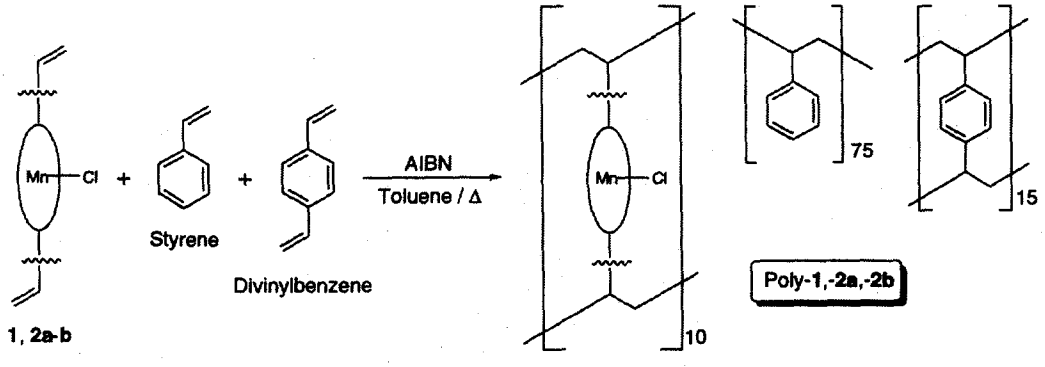
(Poly-**2a** and -**2b**), containing a spacing group between the polymeric chain and the active metal site, and compare their performances with the "not-spaced" catalyst Poly-**1**.

Figure 1.



Enantiopure Mn(III)-salen complexes **1**, **2a** and **2b** (Figure 1), all of them bearing styrene-type vinyl groups, were submitted to radical copolymerization with styrene and divinylbenzene in the presence of AIBN (Figure 2). The reaction was carried out in oxygen-free toluene at 100°C, and the monomeric ratio in the reaction mixture was 10:75:15 for the Mn-salen, styrene, and divinylbenzene, respectively.[9]

Figure 2.

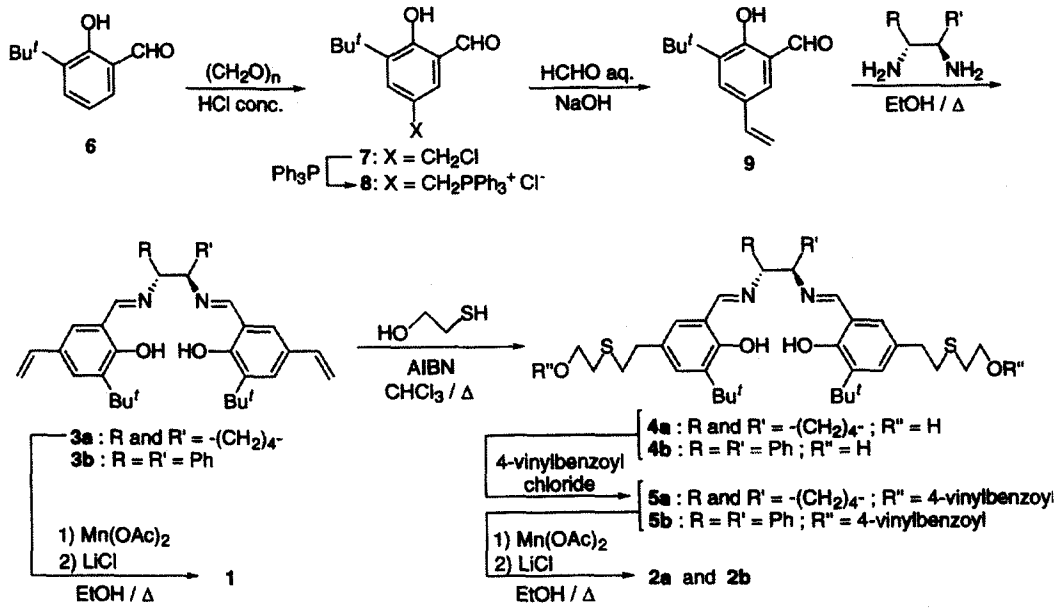


The monomeric compositions of the terpolymers obtained turned out to be essentially identical to the initial monomeric mixture, as confirmed by elemental analyses. This is consistent with comparable polymerization rates for all the monomers, due to the fact that all the double bonds involved in the copolymerization process are styrene-type ones. In order to ensure that no free monomers could interfere in the catalysis, the terpolymers were extracted before use in a Soxhlet device with acetonitrile for at least 48h, until no soluble Mn-salen complexes were detectable by UV in the solvent.

The chiral monomers **1**, **2a**, and **2b** were obtained by the synthetic sequence shown in Scheme 1. 3-*tert*-Butyl-2-hydroxybenzaldehyde **6** (Ref. 4a) was converted to **7** by classical chloromethylation methods.[14] The phosphonium salt **8** was readily obtained treating **7** with triphenylphosphine in refluxing benzene. Subsequent Wittig reaction with formalin in strongly basic condition (12.5M NaOH)[14] yielded the vinyl-substituted salicylaldehyde **9**. The chiral salen ligands **3a-b** were easily formed upon refluxing **9** in ethanol with (-)-

(*1R,2R*)-1,2-diaminocyclohexane and (+)-(*R,R*)-1,2-diphenylethylenediamine, respectively.[4b] Treatment of **3a** with $Mn(OAc)_2$ in refluxing ethanol yielded the chiral complex **1**, which was then used for the preparation of the "not spaced" polymeric catalyst Poly-**1**.

Scheme 1.



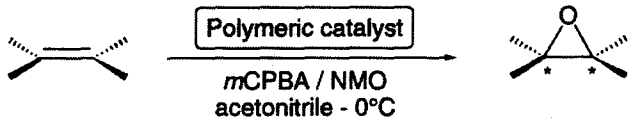
The introduction of a spacing portion on the vinylic groups of ligands **3a-b** was performed by radical *contra*-Markovnikov addition of 2-mercaptoethanol to the styrene-type double bonds,[15] to give intermediates **4a-b**, followed by acylation of the free OH groups with 4-vinylbenzoyl chloride.[16] The acylated ligands **5a-b** were treated with $Mn(OAc)_2$ to obtain complexes **2a-b**, which were then copolymerized as described earlier, yielding the "spaced" polymeric catalysts Poly-**2a** and -**2b**. All these polymers displayed a macroreticular behaviour under reaction conditions (see below).

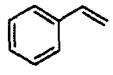
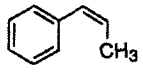
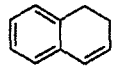
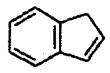
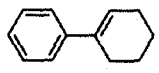
Catalytic epoxidations were carried out employing a combination of *m*-chloroperbenzoic acid and *N*-methylmorpholine-*N*-oxide,[4c,8] as the oxidant system, in acetonitrile at 0°C.[10] Iodosylbenzene (PhIO) was also known to be a potentially good oxygen source,[4a] but in our case it took quite a long time (>24 h) to achieve acceptable conversions. Moreover, the formation of $PhIO_2$, a disproportionation product derived from PhIO, severely complicated the recovery of the polymeric catalyst. In fact, this side product proved to be insoluble in all the solvents tried, therefore it was not possible to completely clean the polymer after its use. On the other hand, with the *m*CPBA / NMO system, epoxidations were very rapid (15-60 min) and the recovery of the clean catalyst was extremely handy. Amongst several solvent tried, CH_3CN gave the best combination in terms of reactivity and insolubility of our polymeric catalysts. Up to five recycles in these conditions, all the polymers Poly-**1**, -**2a**, and **2b** showed practically unmodified catalytic efficiencies, proving to be more resistant to inactivation with respect to their homogeneous counterpart. The sulfur atom, present in

the spacing group, was not oxidized under reaction conditions, as verified by IR analyses of the polymeric catalysts, after their recovery from the reaction mixture.

Several typical unfunctionalized olefins were submitted to heterogeneous epoxidation, and the results are given in Table 1.

Table 1. Heterogeneous Epoxidations of Unfunctionalized Olefins with *m*CPBA/NMO catalyzed by Polymeric Catalysts Poly-**1**, -**2a**, -**2b**.[a]



Entry	Substrate	Catalyst	Time (min)	Conversion (%)	Yield (%)[b]	Ee (%)
1[c]		Poly-**1**	30	96	99	14[d]
2		Poly-**2a**	15	98	94	16[d]
3		Poly-**2b**	15	99	86	26[d]
4[c]		Poly-**1**	60	78	96[e]	41[d,h]
5		Poly-**2a**	30	92	97[f]	62[d,h]
6		Poly-**2b**	30	99	93[g]	56[d,h]
7		Poly-**1**	30	95	48	10[i]
8		Poly-**2a**	30	99	40	21[i]
9		Poly-**2b**	30	98	49	37[i]
10		Poly-**1**	30	91	96	27[i]
11		Poly-**2a**	30	99	97	60[i]
12		Poly-**2b**	30	99	96	46[i]
13		Poly-**1**	30	67	39	21[j]
14		Poly-**2a**	30	79	25	38[j]
15		Poly-**2b**	30	99	46	42[j]

[a] See General Procedure in the Experimental Section. [b] Yields were determined by capillary GC, by integration of product peaks against an internal quantitative standard (*n*-dodecane or naphthalene), correcting for response factors and for the extent of olefin conversion. [c] See Ref. 6. [d] Ee's determined by chiral GC (see Experimental Section); major enantiomers: (*R*)-styrene oxide and (*1R,2S*)-β-methylstyrene oxide, determined by the comparison of the elution order with the authentic samples prepared under Jacobsen's conditions using (*R,R*)-catalyst (refs. 4a and 11). [e-g] *cis:trans* epoxide ratio = [e] 73:27; [f] 85:15; [g] 91:9. [h] Ee's are referred to *cis* epoxide. [i] Ee's were determined by HPLC on a Daicel CHIRALCEL OB column (Hex/IPA 90:10). [j] Ee's were determined by HPLC on a Daicel CHIRALCEL OJ column (Hex/IPA 90:10).

All the polymeric catalysts showed excellent catalytic activities with three substrates: styrene (entries 1-3), *cis*-β-methylstyrene (entries 4-6) and indene (entries 10-12). In fact, within short reaction times, high degrees of conversion were reached, together with a remarkable chemoselectivity towards the epoxidation reaction. However, epoxidations of the other two substrates, dihydronaphthalene (entries 7-9) and 1-phenylcyclohexene (entries 13-15), gave rise to the formation of considerable amounts of side products. In the case of dihydronaphthalene, the main side products were identified as naphthalene and α-tetralone, which globally constituted 50% of transformed olefin.

As already observed,[5,6] in heterogeneous catalytic epoxidation ee's are lower with respect to the analogous homogeneous reaction. This fact may be explained on the basis of steric reasons due to the proximity of the macromolecular system, whose microenviromental effects may strongly influence the enantioselection operated by the chiral Mn-salen. Anyway, a constant trend in the data of Table 1 is that polymers containing a spacing group between the active metal center and the polymeric chain, such as Poly-**2a** and -**2b**, always attained better ee's than the "not spaced" Poly-**1**. This means that when the catalytically active metal centre is farther from the polymeric chain, the influence of the surrounding polymeric chain is remarkably reduced, rendering the environment around the chiral complex even more similar to the homogeneous systems.

On the other hand, the influence of the chiral diimine bridge can not be simply rationalized. With certain substrates, such as *cis*-β-methylstyrene (entry 5) and indene (entry 11), the catalyst containing the 1,2-diiminocyclohexane moiety (Poly-**2a**) attained the best ee's (62 and 60%, respectively), while Poly-**2b**, containing a 1,2-diphenylethilenediimino portion, was the best catalyst for the other three olefins (entries 3, 9, and 15).

In conclusion, we note that these polymer-bound Mn(III)salen complexes constitute a promising class of heterogeneous catalysts in asymmetric epoxidation of unfunctionalized olefins. They usually show good catalytic activities and can be easily recycled in oxidant systems composed by *m*CPBA/NMO in acetonitrile. The introduction of a spacing group in this kind of polymeric catalyst notably improved their enantioselectivity levels, reaching very interesting values with some substrates. To the best of our knowledge such ee's are the highest ever reached with a polymeric catalyst in the heterogeneous asymmetric epoxidation of all the olefins dealt with in this paper.

Experimental Section

Melting points were measured with a Kofler hot-stage apparatus and were uncorrected. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded in $CDCl_3$ with a Varian Gemini 200 spectrometer using tetramethylsilane as internal standard. Mass spectra were carried out by electron impact on a VG 70-70E spectrometer, or by ion spray on a Perkin Elmer Sciex API III. Optical rotations were measured on a JASCO Dip 360 automatic polarimeter. Analytical TLC was performed on 0.2 mm silica gel plate Merck 60 F-254 and flash chromatography[12] was carried out with silica gel Merck 60 (230-400 mesh). Conversions and yields of catalytic epoxidations were determined by GC (FI detector) on a SGE BP1 column (25m X 0.53 mm i.d., 1.0 μm film) using an internal quantitative standard (*n*-dodecane or naphthalene). Enantiomeric excesses were determined by capillary GC using a commercial chiral column (SGE Cydex-B column, 25m X 0.33 mm i.d., 0.25 μm film), or by HPLC using chiral columns Daicel CHIRALCEL OB and CHIRALCEL OJ. 4-Vinylbenzoyl chloride was prepared from commercially available 4-vinylbenzoic acid (Fluka) according to a literature procedure.[13] Styrene and Divinylbenzene were distilled and stored under nitrogen. $CHCl_3$ was washed with conc. H_2SO_4, dried over $CaCl_2$, distilled over P_2O_5, and stored under nitrogen. Toluene was distilled over sodium, stored under nitrogen, and degassed immediately prior to use by the "freezing-pump" technique.

3-*tert*-Butyl-5-(chloromethyl)-2-hydroxybenzaldehyde 7. 13.4 g (0.075 mol) of 3-*tert*-butyl-2-hydroxybenzaldehyde **6**[4a] were treated with 5.0 g of paraformaldehyde in 50 ml of conc. HCl.[14] After 48 h of

stirring at r.t. the reaction mixture was repeatedly extracted with Et_2O. The organic phases were washed with saturated aqueous $NaHCO_3$, brine, and then dried over Na_2SO_4. Evaporation of the solvent afforded **7** as a viscous oil (16.4 g, 96% yield): IR (KBr) 2960, 2913, 2869, 1652, 1618, 1438, 1268, 1233, 1211, 1161, 978, 773, 694 cm^{-1}; ^1H NMR δ 1.42 (s, 9H), 4.58 (s, 2H), 7.43 (d, J = 2.2 Hz, 1H), 7.52 (d, J = 2.2 Hz, 1H), 9.86 (s, 1H), 11.85 (s, 1H); ^{13}C NMR δ 29.05, 34.89, 45.80, 120.29, 128.23, 131.68, 134.46, 139.10, 161.21, 196.65; MS (EI) *m/z* 226 (M^+, 43), 211 (100), 191 (46). Anal. Calcd for $C_{12}H_{15}O_2Cl$: C, 63.58; H, 6.67; Cl, 15.64. Found: C, 63.42; H, 6.78; Cl, 15.31.

3-*tert*-Butyl-5-formyl-4-hydroxybenzyl(triphenylphosphonium) Chloride 8. To a solution of benzyl chloride **7** (15.9 g, 0.070 mol) in benzene (150 ml) were added 18.3 g (0.070 mol) of triphenylphosphine, and the mixture was heated under reflux for 1 h.[14] After cooling down the solution at r.t., the product precipited and was filtered off, washed with Et_2O and dried under vacuum, giving 30.9 g (90% yield) of **8** as a white powder: m.p. 214-215°C; IR (KBr) 3056, 2991, 2956, 2868, 2775, 1640, 1438, 1325, 1112, 997, 742, 691, 518, 505, 496 cm^{-1}; ^1H NMR δ 1.11 (s, 9H), 5.65 (d, J = 13.9 Hz, 2H), 6.92 (d, J = 1.8 Hz, 1H), 7.34 (d, J = 1.8 Hz, 1H), 7.56-7.84 (m, 15H), 9.65 (s, 1H), 11.77 (s,1H); ^{13}C NMR δ 28.90, 34.67, 117.19, 118.89, 128.28, 130.01, 130.25, 134.35, 134.54, 134.85, 135.51, 136.91, 197.31; ion spray MS *m/z* 454 $(M\text{-}Cl)^+$; ion spray MS-MS *m/z* 454 (12), 326 (8), 300 (27), 172 (17), 155 (100), 146 (48). Anal. Calcd for $C_{30}H_{30}O_2PCl$: C, 73.69; H, 6.18; Cl, 7.25. Found: C, 73.73; H, 6.28; Cl, 6.99.

3-*tert*-Butyl-2-hydroxy-5-vinylbenzaldehyde 9. To a vigorously stirred suspension of the phosphonium salt **8** (24.6 g, 0.050 mol) in 170 ml of 40% aqueous formaldehyde, was dropwise added a solution of 12.5M NaOH (55 ml), keeping the reaction temperature below 40°C.[14] After 2 h at r.t., the alkaline mixture was cooled with ice and neutralized with 6N HCl. At pH ≈ 7, the aqueous phase was extracted with benzene. Evaporation of the solvent afforded a semisolid which was firstly purified by flash chromatography (petroleum ether/acetone 2:1), and then distilled under vacuum (107°C, 0.1 mmHg). The oily product of distillation solified at r.t. giving **9** as light yellow crystals (5.87 g, 57% yield): m.p. 43-44°C; IR (KBr) 3068, 2951, 2874, 2744, 1655, 1440, 1406, 1324, 1158, 898, 727 cm^{-1}; ^1H NMR δ 1.43 (s, 9H), 5.21 (d, J = 11.0 Hz, 1H), 5.65 (d, J = 17.6 Hz, 1H), 6.67 (dd, J = 17.6, 11.0 Hz, 1H), 7.40 (d, J = 2.2 Hz, 1H), 7.60 (d, J = 2.2 Hz, 1H), 9.87 (s, 1H), 11.79 (s, 1H); ^{13}C NMR δ 29.17, 34.91, 112.54, 120.46, 128.97, 129.44, 131.79, 135.57, 138.49, 160.95, 197.12; MS (EI) *m/z* 204 (M^+, 68), 189 (100), 161 (22). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.47; H, 7.84.

(*R,R*)-*N,N'*-Bis(3-*tert*-butyl-5-vinylsalicylidene)-1,2-cyclohexanediamine 3a. 1.23 g (6.00 mmol) of aldehyde **9** were dissolved in 10 ml of hot ethanol. A solution of (-)-(*1R,2R*)-1,2-diaminocyclohexane (0.34 g, 3.0 mmol) in 5 ml of ethanol was then added. The resulting solution was heated under reflux for 30 min.[4b] After partial removal of the solvent, the solution was slowly cooled to r.t., and the product **3a** was obtained as deep yellow crystals (1.33 g, 91%): m.p. 70-71°C; $[\alpha]_D^{25}$ = -326 (*c* 0.51, EtOH); IR (KBr) 2937, 2861, 1627, 1444, 1271, 1208, 1158, 884, 774 cm^{-1}; ^1H NMR δ 1.41 (s, 18H), 1.6-2.0 (m, 8H), 3.2-3.3 (m, 2H), 5.04 (d, J = 11.3 Hz, 2H), 5.49 (d, J = 16.9 Hz, 2H), 6.55 (dd, J = 17.0, 11.3 Hz, 2H), 7.02 (d, J = 2.1 Hz, 2H), 7.31 (d, J = 2.1 Hz, 2H), 8.25 (s, 2H); ^{13}C NMR δ 24.23, 29.28, 32.94, 34.75, 72.32, 110.81, 118.36, 127.23, 127.51, 127.57, 136.33, 137.11, 159.82, 165.33; ion spray MS *m/z* 487 $(M+H)^+$; ion spray MS-MS *m/z* 487 (81), 390 (28), 284 (100), 204 (73). Anal. Calcd for $C_{32}H_{42}N_2O_2$: C, 78.97; H, 8.70; N, 5.76. Found: C, 78.87; H, 8.78; N, 5.73.

[(*R,R*)-*N,N'*-Bis(3-*tert*-butyl-5-vinylsalicylidene)-1,2-cyclohexanediaminato(2-)]manganese(III) Chloride 1. To a solution of **3a** (985 mg, 2.02 mmol) in hot ethanol (20 ml), was added a solution of $Mn(OAc)_2 \cdot 4H_2O$ (1.24 g, 5.06 mmol) in ethanol (10 ml), and the resulting mixture was heated under reflux for 1 h. After addition of 260 mg of LiCl (6.12 mmol) to the mixture, it was refluxed for additional 30 min.[4b] The solvent was then evaporated under vacuum and the residue was dissolved in CH_2Cl_2. The organic phase was washed with water, and dried over Na_2SO_4. Evaporation of the solvent afforded the complex **1** as a dark brown solid (910 mg, 78% yield): m.p. 358°C (dec.); $[\alpha]_D^{25}$= -416 (*c* 0.013, EtOH); IR (KBr) 2940, 2862, 1610, 1538, 1313, 821, 566 cm^{-1}; ion spray MS *m/z* 539 $(M\text{-}Cl)^+$; ion spray MS-MS *m/z* 539 (55), 524 (100), 508 (22), 468 (30). Anal. Calcd for $C_{32}H_{40}N_2O_2MnCl$: C, 66.84; H, 7.01; N, 4.87; Cl, 6.16. Found: C, 67.06; H, 7.12; N, 4.78; Cl, 5.95.

(*R,R*)-*N,N'*-Bis{3-*tert*-butyl-5-[2-(hydroxyethylthio)ethyl]salicylidene}-1,2-cyclohexanediamine 4a. 1.19 g (2.44 mmol) of Schiff base **3a**, 173 mg of AIBN and 3.0 g (39 mmol) of 2-mercaptoethanol were dissolved under argon in 12 ml of oxygen-free $CHCl_3$.[15] The solution was heated to 80°C for 20 h. The solvent was evaporated. The recovered residue was repeatedly extracted with pentane to remove unreacted 2-mercaptoethanol, and then purified by flash chromatography ($CHCl_3/CH_3OH$ 9:1), yielding 1.32 g (84% yield) of **4a** as a yellow foam: $[\alpha]_D^{25}$= -237 (*c* 0.23, EtOH); IR (KBr) 2946, 2860, 1629, 1441, 1384, 1267, 1047, 773 cm^{-1}; ^1H NMR δ 1.40 (s, 18H), 1.6-2.0 (m, 8H), 2.2-2.5 (b, 2H), 2.6-2.7 (m, 8H), 2.68 (t, *J* = 5.9 Hz, 4H), 3.26-3.34 (m, 2H), 3.67 (t, *J* = 5.9 Hz, 4H), 6.81 (d, *J* = 2.2 Hz, 2H), 7.06 (d, *J* = 2.2 Hz, 2H), 8.24 (s, 2H); ^{13}C NMR δ 24.19, 29.27, 32.98, 33.27, 34.65, 35.30, 35.59, 60.18, 72.23, 118.27, 129.02, 129.10, 129.50, 137.09, 158.76, 165.29; ion spray MS *m/z* 643 $(M+H)^+$; ion spray MS-MS *m/z* 643 (26), 587 (14), 509 (14), 451 (11), 362 (65), 301 (51), 204 (100). Anal. Calcd for $C_{36}H_{54}N_2O_4S_2$: C, 67.25; H, 8.47; N, 4.36. Found: C, 67.12; H, 8.58; N, 4.41.

(*R,R*)-*N,N'*-Bis{3-*tert*-butyl-5-{2-[2-(4-vinylbenzoyloxy)ethylthio]ethyl}salicylidene}-1,2-cyclohexanediamine 5a. A solution containing 0.86 g (5.2 mmol) of freshly distilled 4-vinylbenzoyl chloride in $CHCl_3$ (3 ml) was slowly added under argon atmosphere to a pre-cooled (0°C) solution of **4a** (1.19 g, 1.85 mmol) and triethylamine (0.6 g, 5.9 mmol) in $CHCl_3$ (22 ml).[16] The mixture was stirred at 0°C for 18 h, then was diluted with 25 ml of $CHCl_3$. The organic phase was washed with saturated aqueous $NaHCO_3$, brine, and then dried over anhydrous Na_2SO_4. Evaporation of the solvent afforded an oily residue, which was purified by flash chromatography ($CHCl_3$), yielding 1.04 g (62% yield) of **5a** as a yellow glass: $[\alpha]_D^{25}$= -214 (*c* 0.42, EtOH); IR (KBr) 2934, 2859, 1715, 1629, 1608, 1442, 1384, 1271, 1178, 1103, 860, 781, 712 cm^{-1}; ^1H NMR δ 1.38 (s, 18H), 1.6-2.0 (m, 8H), 2.75 (s, 8H), 2.86 (t, *J* = 6.9 Hz, 4H), 3.23-3.27 (m, 2H), 4.44 (t, *J* = 6.9 Hz, 4H), 5.39 (d, *J* = 10.9 Hz, 2H), 5.87 (d, *J* = 17.6 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 2H), 6.79 (d, *J* = 2.2 Hz, 2H), 7.06 (d, *J* = 2.2 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 4H), 7.98 (d, *J* = 8.4 Hz, 4H), 8.21 (s, 2H); ^{13}C NMR δ 24.26, 29.32, 30.63, 33.07, 34.05, 34.71, 35.62, 64.13, 72.31, 116.58, 118.34, 126.12, 129.12, 129.17, 129.61, 129.95, 131.12, 135.97, 137.14, 142.02, 158.80, 165.35, 166.05; ion spray MS *m/z* 903 $(M+H)^+$; ion spray MS-MS *m/z* 903 (24), 695 (18), 635 (33), 487 (21), 284 (43), 204 (21), 175 (100). Anal. Calcd for $C_{54}H_{66}N_2O_6S_2$: C, 71.81; H, 7.37; N, 3.10. Found: C, 71.66; H, 7.32; N, 3.00.

{(*R,R*)-*N,N'*-Bis{3-*tert*-butyl-5-{2-[2-(4-vinylbenzoyloxy)ethylthio]ethyl}salicylidene}-1,2-cyclohexanediaminato(2-)}manganese(III) Chloride 2a. 340 mg (0.376 mmol) of **5a** were treated with 231 mg of $Mn(OAc)_2 \cdot 4H_2O$ and 48 mg of LiCl in ethanol, following the same procedure described earlier for the preparation of complex **1**, affording 336 mg (90% yield) of **2a** as a brown solid: m.p. 72-73°C; $[\alpha]_D^{25}$= -267 (*c*

0.015, EtOH); IR (KBr) 2943, 2863, 1711, 1611, 1542, 1385, 1271, 1178, 1104, 781, 567 cm^{-1}; ion spray MS *m/z* 955 $(M-Cl)^+$; ion spray MS-MS *m/z* 955 (28), 586 (19), 558 (49), 538 (52), 526 (100), 485 (69), 405 (17). Anal. Calcd for $C_{54}H_{64}N_2O_6S_2MnCl$: C, 65.41; H, 6.51; N, 2.82; Cl, 3.58. Found: C, 65.34; H, 6.60; N, 2.88; Cl, 3.29.

(*R,R*)-*N,N'*-Bis(3-*tert*-butyl-5-vinylsalicylidene)-1,2-diphenyl-1,2-ethanediamine 3b. 613 mg (3.00 mmol) of aldehyde **9** were treated with 319 mg (1.50 mmol) of (+)-(*R,R*)-1,2-diphenylethylenediamine in ethanol, following the same procedure described earlier for the preparation of ligand **3a**, affording 842 mg (96% yield) of **3b** as deep yellow crystals: m.p. 79-80°C; $[\alpha]_D^{25}$= -90 (*c* 0.29, EtOH); IR (KBr) 3084, 3062, 3030, 3001, 2956, 2911, 2867, 1625, 1443, 1270. 1208, 1154, 986, 884, 772, 698 cm^{-1}; ^1H NMR δ 1.42 (s, 18H), 4.72 (s, 2H), 5.05 (d, *J* = 10.9 Hz, 2H), 5.49 (d, *J* = 17.5 Hz, 2H), 6.55 (dd, *J* = 17.6, 10.9 Hz, 2H), 7.02 (d, *J* = 2.1 Hz, 2H), 7.17-7.26 (m, 10H), 7.33 (d, *J* = 2.1 Hz, 2H), 8.35 (s, 2H); ^{13}C NMR δ 29.25, 34.81, 80.02, 110.87, 118.27, 127.51, 127.60, 127.85, 127.96, 128.36, 136.27, 137.27, 139.28, 160.17, 166.86; ion spray MS *m/z* 585 $(M+H)^+$; ion spray MS-MS *m/z* 585 (11), 420 (72), 338 (100), 293 (79), 232 (67), 191 (72), 152 (88). Anal. Calcd for $C_{40}H_{44}N_2O_2$: C, 82.15; H, 7.58; N, 4.79. Found: C, 82.23; H, 7.67; N, 4.73.

(*R,R*)-*N,N'*-Bis{3-*tert*-butyl-5-[2-(hydroxyethylthio)ethyl]salicylidene}-1,2-diphenyl-1,2-ethanediamine 4b. 785 mg (1.34 mmol) of **3b** were treated with 1.78 g of 2-mercaptoethanol and 96 mg of AIBN in $CHCl_3$, following the same procedure described earlier for the preparation of compound **4a**, affording a semisolid. Further purification of the crude product by flash chromatography ($CHCl_3/CH_3OH$ 9:1) yielded 808 mg (81% yield) of compound **4b** as a yellow foam: $[\alpha]_D^{25}$= -52 (*c* 0.26, EtOH); IR (KBr) 3062, 3030, 2998, 2953, 2913, 2870, 1626, 1597, 1440, 1266, 1212, 1163, 1050, 774, 699 cm^{-1}; ^1H NMR δ 1.41 (s, 18H), 2.6-2.8 (m, 8H), 2.68 (t, *J* = 5.9 Hz, 4H), 3.67 (t, *J* = 5.9 Hz, 4H), 4.70 (s, 2H), 6.80 (d, *J* = 2.1 Hz, 2H), 7.07 (d, *J* = 2.1 Hz, 2H), 7.16-7.20 (m, 10H), 8.32 (s, 2H); ^{13}C NMR δ 29.32, 33.28, 34.76, 35.41, 35.66, 60.19, 80.05, 118.33, 127.52, 127.97, 128.31, 129.22, 129.44, 129.97, 137.25, 139.39, 158.78, 166.74; ion spray MS *m/z* 741 $(M+H)^+$; ion spray MS-MS *m/z* 741 (63), 636 (31), 453 (20), 371 (29), 223 (100). Anal. Calcd for $C_{44}H_{56}N_2O_4S_2$: C, 71.31; H, 7.62; N, 3.78. Found: C, 71.39; H, 7.70; N, 3.75.

(*R,R*)-*N,N'*-Bis{3-*tert*-butyl-5-{2-[2-(4-vinylbenzoyloxy)ethylthio]ethyl}salicylidene}-1,2-diphenyl-1,2-ethanediamine 5b. 700 mg (0.945 mmol) of ligand **4b** were treated with 0.46 g of triethylamine and 0.67 g of 4-vinylbenzoyl chloride in $CHCl_3$, following the same procedure described earlier for the preparation of ligand **5a**, affording a semisolid. Further purification of the crude product by flash chromatography ($CHCl_3$) yielded 604 mg (64% yield) of ligand **5b** as a yellow syrup: $[\alpha]_D^{25}$= -59 (*c* 0.25, EtOH); IR (KBr) 3030, 2954, 2913, 1716, 1626, 1607, 1440, 1384, 1271, 1218, 1178, 1103, 989, 859, 781, 712 cm^{-1}; ^1H NMR δ 1.40 (s, 18H), 2.74 (s, 8H), 2.84 (t, *J* = 6.9 Hz, 4H), 4.44 (t, *J* = 6.9 Hz, 4H), 4.69 (s, 2H), 5.37 (d, *J* = 10.8 Hz, 2H), 5.85 (d, *J* = 17.6 Hz, 2H), 6.73 (dd, *J* = 17.6, 10.8 Hz, 2H), 6.79 (d, *J* = 2.2 Hz, 2H), 7.08 (d, *J* = 2.2 Hz, 2H), 7.14-7.20 (m, 10H), 7.43 (d, *J* = 8.4 Hz, 4H), 7.97 (d, *J* = 8.4 Hz, 4H), 8.29 (s, 2H); ^{13}C NMR δ 29.31, 30.63, 34.02, 34.76, 35.62, 64.08, 80.03, 116.59, 118.31, 126.11, 127.50, 127.98, 128.29, 129.25, 129.45, 129.94, 130.01, 130.91, 135.96, 137.22, 139.45, 142.02, 158.76, 166.75; ion spray MS *m/z* 1001 $(M+H)^+$; ion spray MS-MS *m/z* 1001 (100), 908 (51), 703 (64), 435 (47), 335 (34). Anal. Calcd for $C_{62}H_{68}N_2O_6S_2$: C, 74.37; H, 6.84; N, 2.80. Found: C, 74.29; H, 6.91; N, 2.76.

{(*R,R*)-*N,N'*-Bis{3-*tert*-butyl-5-{2-[2-(4-vinylbenzoyloxy)ethylthio]ethyl}salicylidene}-1,2-diphenyl-1,2-ethanediaminato(2-)}manganese(III) Chloride 2b. 543 mg (0.542 mmol) of ligand **5b** were treated with 336 mg of $Mn(OAc)_2 \cdot 4H_2O$ and 70 mg of LiCl in ethanol, following the same procedure described earlier for

the preparation of complex **1**, affording 484 mg (82% yield) of complex **2b** as a brown solid: m.p. 79-80°C; $[\alpha]_D^{25}$= -164 (*c* 0.011, EtOH); IR (KBr) 3032, 3004, 2951, 2912, 1716, 1607, 1540, 1418, 1384, 1271, 1178, 1104, 860, 781, 714, 576, 563 cm^{-1}; ion spray MS *m/z* 1053 $(M\text{-}Cl)^+$; ion spray MS-MS *m/z* 1053 (100), 752 (10), 624 (22), 469 (17), 321 (11). Anal. Calcd for $C_{62}H_{66}N_2O_6S_2MnCl$: C, 68.34; H, 6.10; N, 2.57; Cl, 3.25. Found: C, 68.18; H, 6.21; N, 2.53; Cl, 3.10.

Preparation of polymeric catalyst. Typical procedure. 1.0 mmol of the Mn-salen (**1**, **2a**, or **2b**), 7.5 mmol of styrene and 1.5 mmol of 1,4-divinylbenzene were dissolved in 10 ml of oxygen-free toluene. 25 mg of 2,2'-azobis(isobutyronitrile) (AIBN) were added under argon, and the mixture was heated to 100°C for 24 h under vigorous stirring. After cooling, 50 ml of methanol were added and the resulting insoluble solid was centrifuged and collected. The polymer was then extracted for 48 h in a Soxhlet device with acetonitrile, until no complex molecules were detectable (UV) in the solvent, and finally dried under vacuum.

Poly-**1.** (69% yield) IR (KBr) 3024, 2922, 2862, 1611, 1536, 1310, 819, 780, 699, 569 cm^{-1}. Anal. Calcd for $(C_{32}H_{40}N_2O_2MnCl)_{10}\cdot(C_8H_8)_{75}\cdot(C_{10}H_{10})_{15}$: C, 81.77; H, 8.66; N, 1.78. Found: C, 81.19; H, 8.06; N, 1.84.

Poly-**2a.** (83% yield) IR (KBr) 3024, 2920, 2859, 1716, 1610, 1540, 1270, 1102, 1018, 781, 700, 567, 542 cm^{-1}. Anal. Calcd for $(C_{54}H_{64}N_2O_6S_2MnCl)_{10}\cdot(C_8H_8)_{75}\cdot(C_{10}H_{10})_{15}$: C, 78.73; H, 7.12; N, 1.42. Found: C, 78.74; H, 7.57; N, 1.56.

Poly-**2b.** (78% yield) IR (KBr) 3082, 3058, 3025, 2919, 1718, 1606, 1540, 1270, 1102, 1018, 762, 700, 576, 550 cm^{-1}. Anal. Calcd for $(C_{62}H_{66}N_2O_6S_2MnCl)_{10}\cdot(C_8H_8)_{75}\cdot(C_{10}H_{10})_{15}$: C, 79.64; H, 6.88; N, 1.36. Found: C, 79.17; H, 7.13; N, 1.54.

General procedure for the epoxidation using polymeric catalysts. A solution containing 1.0 mmol of olefin and 5.0 mmol of NMO in acetonitrile (10 ml), precooled at 0°C, was treated with the polymeric catalyst (amount equivalent to 0.10 mmol of complex, 10mol%). *m*CPBA (2.0 mmol) was then added. Upon consumption of the olefin, the catalyst was filtered off and washed with Et_2O. The filtrate, diluted with Et_2O, was washed with 2N NaOH, water, and dried over Na_2SO_4. The crude product, obtained after evaporation under vacuum of the solvent, was purified by column chromatography on silica gel (Hex/Et_2O).

The recovered polymeric catalyst was thoroughly washed with acetonitrile and dried under vacuum. Its recovery was always ≥ 96%.

Acknowledgment. Financial support by Consiglio Nazionale delle Ricerche (C.N.R.), Progetto Strategico Tecnologie Chimiche Innovative, is gratefully acknowledged.

References and Notes

1. a) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974. b) For a recent review see: Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*, Ojima, I., Ed.; VCH: New York, 1993; Chapter 4.1.
2. a) Jacobsen, E. N. In *Catalytic Asymmetric Synthesis*, Ojima, I., Ed.; VCH: New York, 1993, Chapter 4.2. b) Jacobsen, E. N. In *Comprehensive Organometallic Chemistry II*, Abel, E. W.; Stone, F. G. A.; Wilkinson, G. eds.; Pergamon: New York, 1995, Vol. 12, Chapter 11.1. c) Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189.
3. Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X.; Zepp, C. M. *J. Org. Chem.* **1994**, *59*, 1939.

4. a) PhIO: Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801. b) NaOCl: Zhang, W.; Jacobsen, E. N. *J. Org. Chem.* **1991**, *56*, 2296. c) *m*CPBA: Palucki, M.; Pospisil, P. J.; Zhang, W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1994**, *116*, 9333. d) H_2O_2: Schwenkreis, T.; Berkessel, A. *Tetrahedron Lett.* **1993**, *34*, 4785. e) $NaIO_4$: Pietikäinen, P. *Tetrahedron Lett.* **1995**, *36*, 319. f) O_2/RCHO: Yamada, T.; Imagawa, K.; Nagata, T.; Mukaiyama, T. *Chem. Lett.* **1992**, 2231. g) Dimethyldioxirane: Adam, W.; Jekö, J.; Lévai, A.; Nemes, C.; Patonay, T.; Sebök, P. *Tetrahedron Lett.* **1995**, *36*, 3669.
5. De, B. B.; Lohray, B. B.; Sivaram, S.; Dhal, P. K. *Tetrahedron: Asymmetry* **1995**, 6, 2105.
6. Minutolo, F.; Pini, D.; Salvadori, P. *Tetrahedron Lett.* **1996**, *37*, 3375.
7. Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.
8. Palucki, M.; McCormick, G. J.; Jacobsen, E. N. *Tetrahedron Lett.* **1995**, *36*, 5457.
9. A lower concentration of the metal complex (5%) in the initial mixture, resulted in a sharp worsening of the catalytic properties of the final polymer: Minutolo, F. *Studies in Enantioselective Catalytic Oxidations of Hydrocarbons*, Ph.D. Thesis, Scuola Normale Superiore, Pisa (Italy) 1996 (in prep.).
10. As reported in refs. 4c and 6, the uncatalyzed reaction between *m*-CPBA and the olefinic substrate, leading to racemic epoxide, is completely shut down by the presence of an excess of NMO.
11. Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063.
12. Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
13. Ishizone, T.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 2895.
14. Wulff, G.; Akelah, A. *Makromol. Chem.* **1978**, *179*, 2647.
15. Inagaki, M.; Hiratake, J.; Yamamoto, Y.; Oda, J. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4121.
16. Pini, D.; Petri, A.; Salvadori, P. *Tetrahedron* **1994**, *50*, 11321.

(*Received in UK* 9 *May* 1996; *accepted* 13 *June* 1996)