A novel supported Katsuki-type (salen)Mn complex for asymmetric epoxidation†

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We have successfully prepared an unsymmetrical analogue of a Katsuki-type salen ligand having a hydroxyalkyl group at the 6-position of just one of the binaphthyl units in the ligand, and also several Mn(III) complexes; these complexes have been attached to a polymer by an ester link and such polymer catalysts have been shown to be highly enantioselective and recoverable catalysts for the epoxidation of 1,2-dihydronaphthalene.

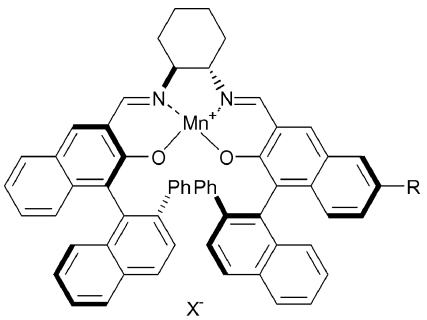
Introduction

Enantioselective epoxidation using chiral (salen)Mn(III) complexes has become a useful preparative method in organic synthesis.[1,2] Several suitable chiral (salen)Mn complexes have been developed, particularly by Jacobsen,[1] Katsuki,[2] and co-workers. The chiral (salen)Mn complexes have been found to be effective catalysts for asymmetric epoxidation of alkenes with high levels of enantioselectivity over a wide range of substrates.[1,2] However, such homogeneous catalysts are not easily recovered for reuse or recycle. By contrast, heterogeneous catalysts offer easy separation from products and facile recovery for recycling.

Recently, there have been many studies of the immobilisation of analogues of Jacobsen-type homogeneous catalysts such as [*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine]-Mn(III) chloride onto solid supports, including organic polymers,[3–9] a polysiloxane,[10] zeolites,[11,12] a clay,[13] silica gel,[14] MCM-41[15–17] and activated carbons.[18]

Thus far, the most effective methods have used organic polymer supports. Unfortunately, such immobilization has often caused significant decreases in the enantioselectivity the catalysts display.[5] For a successful polymer-supported catalyst that is stable, does not leach, can be recovered and gives high enantioselectivity, the catalytic moiety should be covalently bound to the polymer by a single point of attachment and with a suitable spacer group. We recently gave a preliminary account of the synthesis of such a complex.[19] We now report the full details of that work.

As our target complex for attachment to a polymer we chose **1**, an analogue of the Katsuki complex **2**, rather than a Jacobsen-type complex, for the following reasons: i) no supported Katsuki-type complexes have previously been prepared; ii) Katsuki-type complexes give higher enantioselectivities for epoxidation of certain types of alkenes;[2a] iii) Katsuki-type complexes are bulky and less prone to oxidative dimerisation reactions;[20] iv) the ligand may be more stable to decomposition; v) the hydroxyalkyl group would allow attachment to several different kinds of support, both organic and inorganic.



1a R = $CH_2CH_2CH_2OH$, X = AcO
1b R = $CH_2CH_2CH_2OH$, X = PF_6
1c R = $CH_2CH_2CH_2OH$, X = CF_3SO_3
2 R = H, X = PF_6

Results and discussion

General approach

The synthetic approach to **1** required the coupling of the known compound **3**, which we prepared by the literature route,[21] with 1,2-cyclohexanediamine (**4**), followed by coupling of the intermediate (**5**) with the novel compound **6** (Scheme 1). The synthetic route to **6** is described in Scheme 2.

Synthesis of substituted salicylaldehyde derivative 6. Bromine was introduced after one of the OH groups of the binaphthol had been replaced by phenyl, when the two naphthalene rings would have very different reactivities, so that formation of a selectively substituted compound was possible. Compound **11** was easily obtained in an almost quantitative yield from **10** by this approach.

Conversion of **11** into **12** by a Heck reaction,[22] followed by successive reductions of the double bond and the ester group, was straightforward. Compound **11** was converted into **12** (96% yield, 90% purity by ^{1}H NMR) with methyl acrylate in the presence of palladium acetate, tri(*o*-tolyl)phosphine, and anhydrous sodium acetate in *N*,*N*-dimethylformamide (DMF) at 130 °C. The NMR spectrum showed the presence of a large coupling constant

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† Electronic supplementary information (ESI) available: Details of the instrumentation and materials used and experimental details for the previously reported compounds **9**, **10**, **17**, **18**, **3**, **23**, **24** and **22**. See DOI: 10.1039/b517611p

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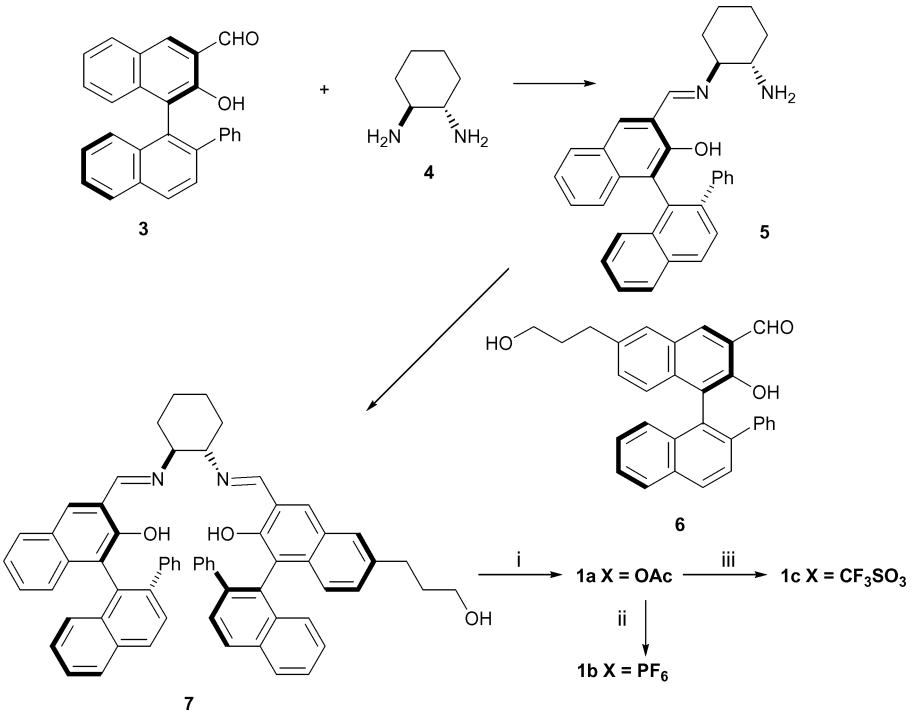
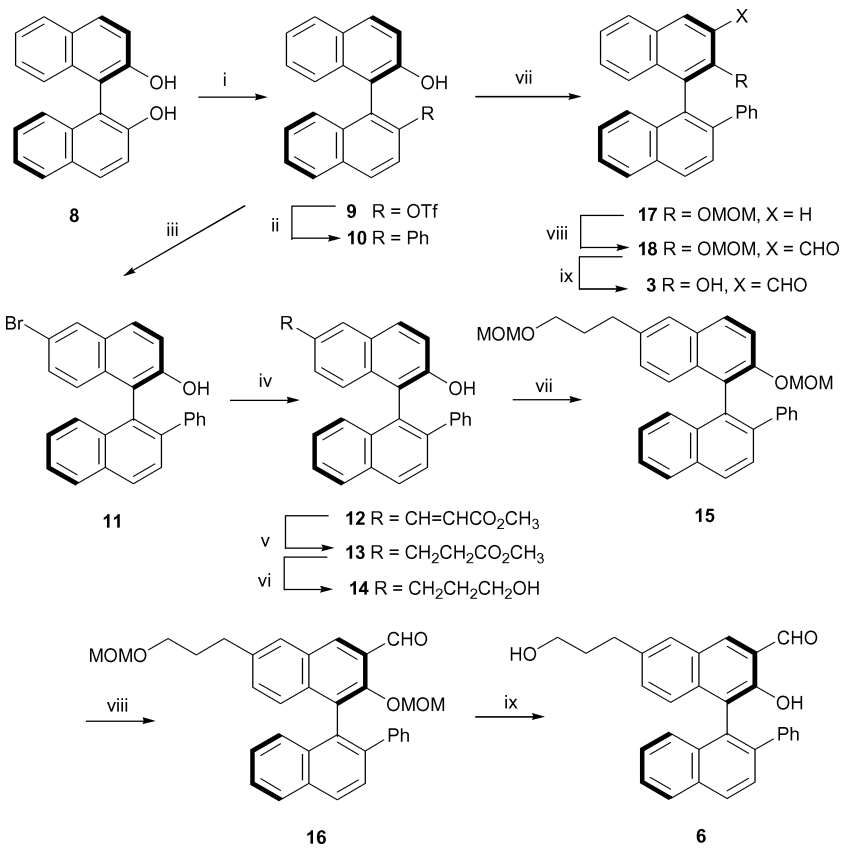


Scheme 1 *Reagents*: i) $Mn(OAc)_2{\cdot}4H_2O$, air; ii) $NaPF_6$; iii) $(CF_3SO_2)_2O$.



Scheme 2 *Reagents*: i) Tf_2NPh, 2,4,6-collidine, DMAP, CH_2Cl_2, reflux, 24 h; ii) PhMgBr, $NiCl_2$(dppe), Et_2O, reflux, 2 h; iii) Br_2; iv) methyl acrylate, $Pd(OAc)_2$, P(*o*-tol)$_3$, CH_3COONa, DMF, 130 °C; v) Mg–CH_3OH; vi) $LiAlH_4$–ether; vii) i-Pr_2NEt, CH_3OCH_2Cl, CH_2Cl_2; viii) *t*-BuLi, THF, −78 °C, 3 h, then DMF, 20 °C, 1 h; ix) Me_3SiBr, CH_2Cl_2.

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(J_{trans} = 16 Hz) for the vinylic hydrogens indicating that the *trans* form was present as the major component. The *cis* form was also present to a small extent (J_{cis} = 12 Hz). There was no need to separate the two isomers as the mixture could be used directly for the subsequent steps. Reduction of **12** using magnesium in methanol[23] gave **13** in 61% yield after purification by column chromatography. Reduction of **13** using lithium aluminium hydride[24] gave **14** in 70% yield after crystallization from chloroform.

Protection of the two hydroxyl groups of **14** as MOM ethers was curiously difficult, **15** being obtained in only 60% yield, along with 40% of monoprotected (in the side chain) product, even with a large excess of MOMCl, although it was easy to protect the OH group of **10** with only a modest excess of reagent. However, compound **15** was purified by column chromatography on alumina and its structure was confirmed by the ^{1}H NMR spectrum, which showed a singlet CH_2 signal at 4.62 ppm for the MOM group in the side chain at C-6, and two doublets at 4.73 ppm and 4.87 ppm for the diastereotopic hydrogens of the methylene part of the MOM group at C-2.

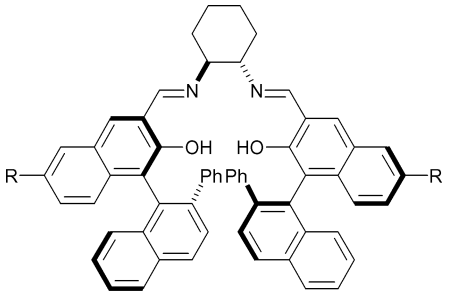
Compound **15** was next converted into **16** by *ortho*-metallation–formylation. Treatment of **15** with *tert*-butyllithium and then *N*,*N*-dimethylformamide afforded aldehyde **16** in 60% yield and recovered **15** in 40% yield under the standard conditions used by Katsuki *et al*.[21] Removal of the protecting groups with trimethylsilyl bromide gave **6** (92%), after a long reaction time under the standard conditions used by Katsuki *et al*.[21]

Synthesis of the unsymmetrical salen ligand 7 and its Mn complexes. There are claims in the literature for the high yield synthesis of simple unsymmetrical salen ligands by the sequential addition of two different aldehydes to cyclohexane-1,2-diamine.[25] However, these claims have been challenged.[26] We attempted the synthesis of the half-salen ligand **5** by reaction of a 1 : 1 mixture of **3** and **4** in chloroform, according to the literature method,[25] but the reaction product contained three components, the mono-imine (**5**), the bis-imine ligand (**19a**) and the cyclohexanediamine (**4**), according to ^{1}H NMR, and it proved difficult to obtain pure **5** from the mixture. The problem appeared to involve conversion of the mono-imine **5** into a mixture of **4** and **19a**.

Recent reports have indicated that half-salen ligands can be purified as salts,[27] but these reports appeared after our experiments.

Bis-imine ligands are known to be more stable than mono-imines.[26] Therefore, in order to avoid losing **5** through equilibration, **3** was reacted with two equivalents of **4** and the proportion of **5** : **19a** was estimated by the ^{1}H NMR spectrum to be 3 : 1. Compound **6** (molar amount equal to that of **5** present in the mixture) was added and the mixture was stirred for 3 h at room temperature. Column chromatography of the product mixture on silica in the presence of excess cyclohexanediamine produced pure samples of the three bis-imines: **19a**, **7** and **19b**. The yield of **7** was *ca.* 80% based on the amount of **6** used, while the yield of **19b** was *ca.* 20%. The symmetrical compounds **19a** and **19b** could be recycled by decomposing them in 4% HCl to give back the salicylaldehydes **3** and **6**, respectively.

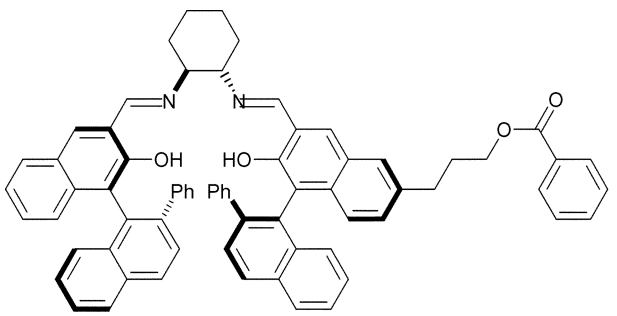
Salen ligand **7** was successfully converted into its manganese complexes, **1a–c**, which were more stable and could be purified by chromatography without any problem.



19a R = H
19b R = $CH_2CH_2CH_2OH$

Synthesis of polymer-model derivatives of compounds related to 1. Our initial intention was to attach the chiral salen ligand or its Mn complex *via* an ether linkage to a polystyrene resin. However, all of our attempts to link a model hydroxyalkyl compound **14** to benzyl chloride, iodide or triflate resulted in problems that would be difficult to handle with a polymeric substrate. Therefore, we decided to investigate instead the coupling of the ligand and/or complex *via* an ester link.

Ligand **7** was stirred with benzoyl chloride and triethylamine at room temperature for 24 h, at which time TLC indicated the presence of a new component. Purification of a small aliquot of the product by column chromatography on silica gel in the presence of cyclohexanediamine gave **7** and **20** in a weight ratio of about 2 : 1. The rest of the reaction mixture was heated to reflux for an additional 24 h. After purification by column chromatography, **7** and **20** were then obtained in a weight ratio of *ca.* 1 : 3, with no detectable decomposition of the ligand.



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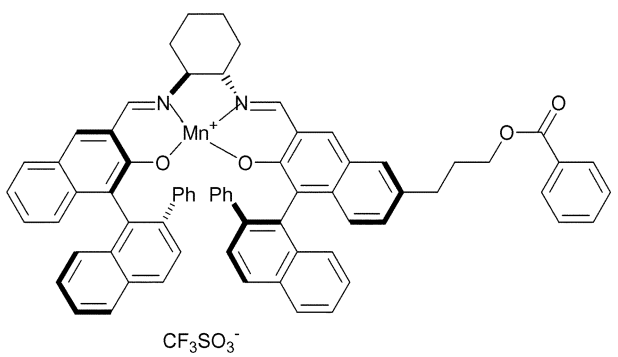

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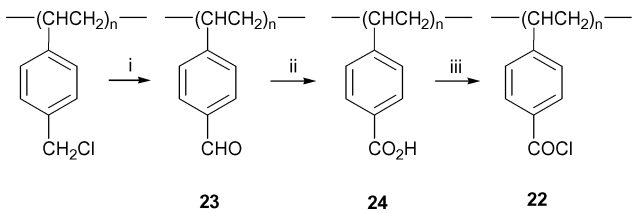
Treatment of complex **1c** with benzoyl chloride and triethylamine under reflux for 48 h gave a 72% yield of the corresponding

benzoate **21** and 5% of recovered **1c**. Negative ion electrospray mass spectrometry showed that the benzoate retained a triflate anion. The FT-IR spectrum showed a characteristic imine group at 1602 cm^{-1} and a new absorption at 1715 cm^{-1} corresponding to an ester group (see ESI†). In view of the success with benzoylation of both **7** and **1c**, the next step was to synthesise the polystyrenecarbonyl chloride.

Synthesis of polystyrenecarbonyl chloride (22). Synthesis of **22** was achieved from Merrifield's resin (Scheme 3).[28–31] Formylpolystyrene (**23**) was prepared by the oxidation of chloromethylated polystyrene using DMSO–$NaHCO_3$ according to a literature procedure.[28] The IR spectrum of the polymer-supported aldehyde showed that the –CH_2Cl vibration band at 1266 cm^{-1} in Merrifield's resin had been replaced by a new strong band at 1699 cm^{-1}, assigned to a carbonyl group. There was also an aldehydic C–H absorption around 2720 cm^{-1}.

Carboxypolystyrene (**24**) was prepared by a Baeyer–Williger type oxidation of **23** with *m*-chloroperoxybenzoic acid (*m*-CPBA) in 1,2-dimethoxyethane (DME).[29] The IR spectrum of **24** showed an intense absorption at 1701 cm^{-1} with a shoulder at 1730 cm^{-1}, corresponding to H-bonded and free carbonyl groups. There was also a very broad hydroxyl absorption at 3457 cm^{-1}. Acid–base titration[30] of resin **24** demonstrated that the functional yield of carboxyl groups was around 70% of that expected from the assumed concentration of chloride groups in the original Merrifield resin.

Leznoff *et al.* have reported conversion of carboxypolystyrene (**24**) into its acid chloride by treatment with thionyl chloride in benzene.[31] Application of this procedure gave a polymer-supported acid chloride. The IR spectrum showed that the C=O bands at 1730 cm^{-1} and 1701 cm^{-1} in carboxypolystyrene had been replaced by a new broad absorption band at 1700–1780 cm^{-1}, which was assigned to a –COCl group. Hydrolysis and analysis of the liberated HCl (*ca.* 1.17 mmol g^{-1} Cl) indicated that 86% of the carboxyl groups in **24** had been converted into carbonyl chloride groups in **22**.

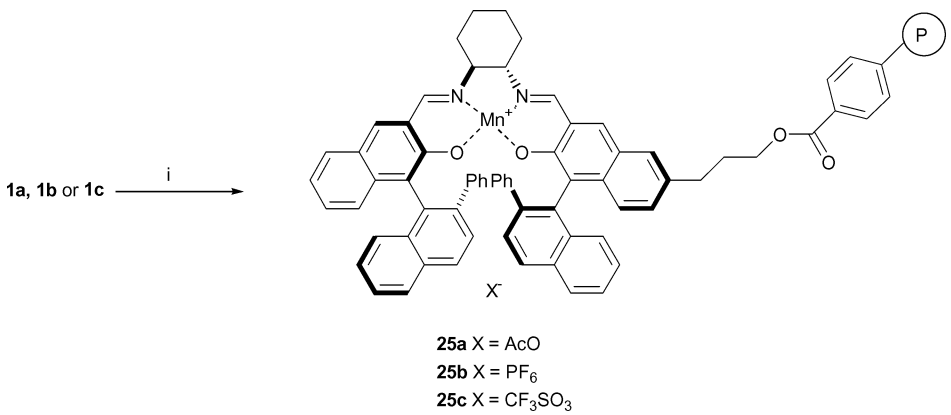


Scheme 3 *Reagents*: i) DMSO, $NaHCO_3$, 155 °C, 6 h; ii) *m*-$ClC_6H_4CO_3H$, DME, reflux, 24 h; iii) $SOCl_2$, benzene, reflux, 20 h.

Attachment of unsymmetrical chiral (salen)Mn(III) complexes 1 to polystyrenecarbonyl chloride (22). The acid chloride resin (**22**) was treated with various samples of unsymmetrical (salen)Mn complexes **1** as shown in Scheme 4. **Polymer A** was obtained directly from **1a** and had the structure **25a**. **Polymer B** was obtained from **1c**, but the initial polymer triflate salt **25c** was converted into the hexafluorophosphate by treatment with $NaPF_6$. Thus, **polymer B** had the structure **25b**. **Polymer C** was also **25b**, but obtained directly from **1b**. The polymers obtained were characterised by their infrared spectra. The spectra showed that the broad –COCl absorption band at 1700–1780 cm^{-1} in polymer **22** had been replaced by an ester absorption band at *ca.* 1721 cm^{-1} in all three polymer samples. Also, the absorption signals at *ca.* 1602 cm^{-1} were broader and more intense than that of polymer **22**, attributed to the additional presence of the stretching vibration of the –C=N– group.

Each resin was estimated by determination of its Mn concentration by atomic absorption spectroscopy (AAS). A sample of the polymer was calcined at 550 °C to produce an ash, which was treated with a mixture of hydrochloric and nitric acids (3 : 1), heated to dryness and then dissolved in distilled water and diluted to an appropriate volume. AAS of the solution was compared with a calibration curve to give the amount of Mn present. These analyses indicated that the polymers contained around 0.096 mmol g^{-1} (**polymer A**, **25a**), 0.12 mmol g^{-1} (**polymer B**, **25b**) and 0.24 mmol g^{-1} (**polymer C**, **25b**), which correspond to about 18%, 23% and 45%, respectively, of the amount expected for 100% incorporation of the salen complex.

Asymmetric epoxidation using the polymer-supported unsymmetrical chiral (salen)Mn(III) complexes. The catalytic activity and selectivity of the immobilised chiral (salen)Mn complexes were tested in the epoxidation of 1,2-dihydronaphthalene (**26**) using sodium hypochlorite (NaOCl) as the oxidant and 4-phenylpyridine *N*-oxide (4-PPNO) as the activator (Scheme 5). The conditions for these reactions were analogous to those used by Katsuki *et al.* for related homogeneous catalysts.[32] Analogues **2** and **1b** were also tested. The results are reported in Table 1.



Scheme 4 *Reagents*: i) polystyrenecarbonyl chloride, excess Et_3N, CH_2Cl_2, reflux.

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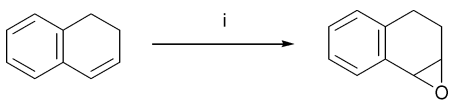
Table 1 Asymmetric epoxidation of 1,2-dihydronaphthalene (**26**) using (salen)Mn complexes[a]

No	Catalyst	Number of uses	Catalyst mg	Catalyst mol%	Alkene/mmol	Time/h	Yield (%)[b]	Ee[c] (%)
1	**2**		10	0.04	0.2	7.5	100	≥94
2	**1b**		10	0.04	0.2	6.5	100	≥94
3	**Polymer A**	1st	83	0.032	0.16	72	68	—
4	**Polymer A**	2nd	72	0.028	0.14	72	40	*ca.* 90
5	**Polymer B**	1st	87	0.042	0.21	48	40	*ca.* 94
6	**Polymer B**	2nd	73	0.036	0.18	48	42	*ca.* 94
7	**Polymer B**	3rd	28	0.014	0.07	72	26	*ca.* 93
8	**Polymer B**	4th	17	0.008	0.04	142	40	*ca.* 93
9	**Polymer C**	1st	78	0.018	0.18	24	37	*ca.* 94
10	**Polymer C**	2nd	70	0.017	0.17	24	30	*ca.* 94
11	**Polymer C**	3rd	42	0.010	0.10	48	70	*ca.* 94
12	**Polymer C**	4th	36	0.009	0.09	48	38	*ca.* 93
13	**Polymer C**	5th	27	0.006	0.06	48[d]	70[d]	*ca.* 90
14	**Polymer C**	6th	20	0.005	0.05	48[d]	50[d]	*ca.* 90

[a] Reactions were carried out using 1,2-dihydronaphthalene (1 eq.), catalyst (as indicated) in dichloromethane (2.5 ml for homogeneous reactions, 4 ml for heterogeneous) in the presence of 4-PPNO (0.25 eq.), using NaOCl (5 eq.) as the terminal oxidant, at 0 °C. [b] The yield of epoxide was determined by gas chromatography (GC) using hexadecane as an internal standard. The estimated error limits are ±5%. [c] The enantiomeric excess was determined by the integration of peak areas in ^{1}H NMR spectra using the chiral shift reagent Eu(hfc)$_3$ and the absolute configuration of the resultant epoxide, according to Katsuki *et al.*, should be 1*S*,2*R*.[32] [d] For these reactions the amount of solvent was reduced to 2 ml (from 4 ml).



26 **27**

Scheme 5 *Reagents*: i) catalyst, NaOCl, 4-PPNO.

The first experiment using **polymer A** (the lowest loaded polymer) showed that its activity was lower than that of its homogeneous analogues **1b** and **2**. After 72 h the yield of epoxide was still only about 68% according to GC. The product was lost during evaporation of solvent, so the ee could not be measured.

In that first run with **polymer A**, the quantity of polymer used was 83 mg, but it was difficult to recover all of the polymer after the reaction, primarily because of electrostatic attraction of the powder to the glass vessel and losses during filtration. Therefore, only 72 mg were used in the repeat experiment. To ensure that the stoichiometry remained the same, the quantities of substrate, oxidant and donor ligand were also scaled down proportionately, but the quantity of solvent was not altered, so the concentrations were less, which could account for the lower rate of reaction than in the first use. However, the enantiomeric excess was about 90%, more or less the same as that reported by Katsuki *et al.* (91% ee).[32]

Polymer B differed from **polymer A** in its loading (0.12 mmol Mn g^{-1}) and in its anion (PF_6^- rather than AcO^-), but its activity was comparable. The enantioselectivity observed with this complex was excellent, similar to that produced by the homogeneous analogues **1b** and **2**. Furthermore, reuse of the polymer resulted in a yield and enantioselectivity that were similar to those obtained during the first use. The polymer was recovered and reused again and then again for a fourth time. Each time the amount of polymer available was less, because of sampling for analyses or physical losses, and since the amount of solvent was the same the reactions were slower. However, measurement of the ee of the product recovered at the end of each run suggested that there was only a very small loss of enantioselectivity, if any, in sequential runs.

A similar trend was observed in the first four runs with **polymer C**, the polymer with the highest loading. For the fifth use of the polymer a smaller reaction vessel and a reduced amount of solvent were used. The reaction then became faster. The sixth use was slower than the fifth because of the lower concentrations, but still not as slow as the fourth run had been in the larger reaction flask and with more solvent. (The size of the flask is important because some of the polymer tends to collect on the walls of the vessel above the solvent during stirring, and is not then in contact with the solution. In a larger vessel the amount that is out of contact becomes more significant.)

The ee values (Table 1) became progressively less reliable (because the spectra were noisier) for the smaller scale reactions, as the amount of available product became less. From the results it appeared that the initial enantioselectivity with **polymer C** was ≥94%, comparable to that obtained with the free complexes **2** and **1a**. It appeared that there might be a small drop in selectivity with successive re-uses of the polymer, but the ee was still at least 88% by the sixth use of the polymer. In view of the greater uncertainties for the reactions run with smaller quantities of polymer, it is even possible that there was no genuine reduction in ee at all.

AAS measurements of **polymers A**, **B** and **C** after completion of the full sequence of uses showed that all three polymers possessed a slightly increased Mn proportion, 0.10 mmol g^{-1} for **A**, 0.13 mmol g^{-1} for **B**, and 0.26 mmol g^{-1} for **C**, consistent with anion-exchange to the lighter anion chloride, but not with loss of complex from the polymers. The IR spectra of the recovered **polymers A**, **B** and **C** after use in the full set of reactions recorded in Table 1 were recorded. The broad absorption band at 840 cm^{-1} in **polymers B** and **C**, assigned to the PF_6^- anion, had disappeared after several reuses. Other changes in the spectra of the recovered polymers **B** and **C** may suggest some hydrolysis of residual acyl chloride groups to give carboxylic acid groups. It did not seem likely that there had been significant cleavage of the ester groups linking the catalyst units to the polymers in view of the retention of Mn. Further evidence for this was sought by subjecting a model polymer to similar conditions.

A model polymer was synthesised from 3-phenylpropanol and polystyrenecarbonyl chloride (**22**). This polymer was treated with NaOCl for 4 days under conditions similar to those used in the epoxidation reactions. There was little evidence for the presence of 3-phenylpropanol, suggesting that the ester link is stable to these conditions.

A further experiment was carried out to examine the stability of the homogeneous catalyst **2**. An epoxidation reaction was carried out using ten times the concentrations of substrate, 4-PPNO and NaOCl for the same amount of catalyst. After the reaction, the catalyst was recovered by column chromatography. The FT-IR spectrum showed major bands that were very similar to those of the original catalyst, but with additional bands due to 4-PPNO. The ee of the epoxide was also the same as in previous reactions, so again there seemed to be little to suggest significant decomposition of the catalyst.

In conclusion, therefore, we believe the salen unit of complexes **25** is relatively stable and the ester group linking it to the polymer remains largely intact during the epoxidation reactions. Therefore, the goal of producing a stable, recoverable, enantioselective catalyst has been achieved.

Conclusions

Compound **7**, a new monosubstituted analogue of Katsuki's chiral salen ligand **2**, has been successfully synthesised and converted into its Mn complexes, **1**. Several complexes were attached to a polymer *via* an ester link using polystyrenecarbonyl chloride. All three samples were tested in epoxidation reactions with 1,2-dihydronaphthalene using sodium hypochlorite as the oxidant and all were shown to be effective catalysts, giving high ee values. The reactions were much slower than with homogeneous analogues, in part a result of the more dilute conditions used in order to allow swelling of the polymer and stirring of the mixture, and in part due to the lower mobility of compounds within a polymer matrix.

All of the samples were recovered and re-used several times, resulting in the polymers' spending many days overall in contact with the basic reaction solutions. In all cases, the catalysts still gave high enantioselectivities even after six reuses in the case of **polymer C**.

This is the first demonstration of the successful use of a polymer-supported Katsuki complex. By having just a single point of attachment to the polymer at a part of the ligand remote from the catalytic centre, possibilities for complications arising from multiple reacting species or from interference by the polymeric support at the active site were minimized. Indeed, the enantioselectivities of the supported catalysts were undiminished. The drop in rate of reaction in comparison to homogeneous counterparts is not surprising, because it is expected that the accessibility of the active sites would be diminished.

Katsuki *et al.* have developed a new (salen)Mn complex having a monocarboxylate group on the ethylenediamine moiety as a very efficient catalyst for the asymmetric epoxidation of 2,2-dimethylchromene derivatives.[2c,33] This complex exhibits a high turnover number (up to 9200) and enantioselectivity (up to 99% ee). It is also stable enough to be used over a 10 day period and can be recovered by chromatography. Such a complex may be an even better candidate for immobilisation.

Experimental

Details of the instrumentation used and sources and methods of purification of materials are reported in the ESI†.

Preparations of known compounds by literature procedures are reported in the ESI†. Only the preparations of novel compounds are reported here.

Synthesis of (*R*)-6-bromo-2-hydroxy-2′-phenyl-1,1′-binaphthyl (11). A solution of **10** (7.75 g, 22.4 mmol) in dichloromethane (300 ml) was cooled to −78 °C in a cardice–acetone bath. A solution of bromine (4.30 g, 1.40 ml, 26.9 mmol) in dichloromethane (200 ml) was added dropwise. The mixture was stirred at −78 °C for 1 h, allowed to warm to room temperature and then stirred for a further 15 h to give an orange solution. The solution was evaporated *in vacuo* to give a viscous orange gum. Purification by flash column chromatography (SiO_2, dichloromethane) gave a cream solid product (9.14 g, 96% yield); $[\alpha]_D^{20}$ +43.16 (*c* 2.88, $CHCl_3$), mp 80–82 °C.

δ_H($CDCl_3$) 4.94 (s, 1 H, OH), 6.95 (d, $J = 9$ Hz, 1 H), 7.05–7.09 (m, 3 H), 7.11–7.13 (m, 2 H), 7.14 (d, $J = 9$ Hz, 1 H), 7.24 (d, $J = 8.5$ Hz, 1 H), 7.25 (dd, $J = 2$, 9 Hz, 1 H), 7.33 (dd, $J = 7$, 8.5 Hz, 1 H), 7.52 (dd, $J = 7$, 8 Hz, 1 H), 7.66 (d, $J = 9$ Hz, 1 H), 7.69 (d, $J = 8.5$ Hz, 1H), 7.91 (d, $J = 2$ Hz, 1 H), 7.97 (d, $J = 8$ Hz, 1 H) and 8.07 (d, $J = 8.5$ Hz, 1 H); δ_C($CDCl_3$) 117.0, 118.0, 118.3, 126.0, 126.5, 126.8, 127.1, 127.3, 3 × 127.8, 128.3, 2 × 128.5, 128.6, 128.9, 129.6, 129.7, 129.8, 130.0, 132.6, 132.9, 133.2, 140.6, 141.6 and 151.4; *m/z* (EI) 426 (M^+ ^{81}Br, 100%) and 424 (M^+ ^{79}Br, 100); *m/z* (CI) 444 ($M + NH_4^+$ ^{81}Br, 100%), 442 ($M^+ + NH_4^+$ ^{79}Br, 100) and 364 (70) (found: M^+ ^{79}Br, 424.0463. Calc. for $C_{26}H_{17}O^{79}Br$, 424.0463) (found: C, 72.87; H, 3.88. Calc. for $C_{26}H_{17}OBr$, C, 73.42; H, 4.03%).

Synthesis of (*R*)-methyl-3-(2-hydroxy-2′-phenyl-1,1′-binaphthyl-6-yl)acrylate (12). To a mixture of **11** (11.9 g, 28.0 mmol), anhydrous sodium acetate (2.76 g, 33.6 mmol), palladium acetate (63 mg, 0.28 mmol) and tris(*o*-tolyl)phosphine (341 mg, 1.12 mmol) in dry DMF (80 ml) under nitrogen was added methyl acrylate (2.89 g, 3.1 ml, 33.6 mmol) and the mixture was heated at 150 °C (oil bath) for 4 h. After the reaction was completed, it was quenched with water (150 ml) and extracted with ether (150 ml). The extract was washed with water (2 × 60 ml), dried over $MgSO_4$ and concentrated *in vacuo* to give a cream solid product (11.44 g, 95% yield).

δ_H($CDCl_3$) 3.80 (s, 3 H), 5.02 (s, 1 H, OH), 6.42 (d, $J_{trans} = 16$ Hz, 1 H), 7.09–7.14 (m, 6 H), 7.16 (d, $J = 9$ Hz, 1 H), 7.27 (d, $J = 8.5$ Hz, 1 H), 7.34 (dd, $J = 7$, 8.5 Hz, 1 H), 7.39 (dd $J = 9$ Hz, 1 H), 7.52 (dd, $J = 7$, 8.1 Hz, 1 H), 7.72 (d, $J = 8.5$ Hz, 1 H), 7.78 (d, $J_{trans} = 16$ Hz, 1 H), 7.79 (d, $J = 9$ Hz, 1 H), 7.86 (s, 1 H), 7.99 (d, $J = 8$ Hz, 1 H) and 8.05 (d, $J = 8.5$ Hz, 1 H); δ_C($CDCl_3$) 51.7, 116.7, 118.0, 118.2, 124.3, 125.7, 126.0, 126.5, 127.1, 2 × 127.3, 127.8, 128.3, 128.4, 3 × 128.5, 128.6, 129.3, 129.6, 130.3, 130.6, 133.0, 133.2, 135.1, 140.6, 141.6, 145.0, 152.4 and 167.4; *m/z* (EI) 430 (M^+, 100%), 204 (45) and 77 (25); *m/z* (CI) 448 ($M^+ + NH_4$, 5%) and 431 (MH^+, 100) (found: M^+, 430.1556. Calc. for $C_{30}H_{22}O_3$, 430.1569) (found: C, 83.74; H, 5.12. Calc. for $C_{30}H_{22}O_3$, C, 83.70; H, 5.15%).

Synthesis of (*R*)-methyl-3-(2-hydroxy-2′-phenyl-1,1′-binaphthyl-6-yl)propanoate (13). To magnesium turnings (9.27 g, 381 mmol,

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pre-dried in an oven at 120 °C) in dry methanol (300 ml) under nitrogen was added a solution of **12** (3.90 g, 9.07 mmol) in dry THF (60 ml), and the mixture was heated to 80 °C (oil bath) for 3.5 h, by which time the reaction was complete. The mixture was cooled to room temperature and 3 M HCl was added carefully until the excess magnesium dissolved. The mixture was then extracted with ether (800 ml), and the extract was washed with brine (2 × 200 ml), dried over $MgSO_4$ and concentrated *in vacuo* to give a cream powder (3.49 g, 89% yield). Purification by column chromatography (SiO_2, toluene–ether 5 : 1) gave a cream solid (2.08 g, 61%); $[\alpha]_D^{20}$ +34.12 (*c* 2.70, $CHCl_3$), mp 66–68 °C.

δ_H($CDCl_3$) 2.65 (t, J = 8 Hz, 2 H), 3.01 (t, J = 8 Hz, 2 H), 3.61 (s, 3 H), 4.91 (bs, 1 H, OH), 7.00 (d, J = 9 Hz, 1 H), 7.03–7.06 (m, 4 H), 7.10 (d, J = 9 Hz, 1 H), 7.12–7.16 (m, 2 H), 7.28–7.31 (m, 2 H), 7.50 (dd, J = 6, 8 Hz, 1 H), 7.55 (bs, 1 H), 7.68 (d, J = 9 Hz, 1 H), 7.70 (d, J = 8.5 Hz, 1 H), 7.96 (d, J = 8 Hz, 1 H) and 8.05 (d, J = 8.5 Hz, 1 H); δ_C($CDCl_3$) 30.7, 35.5, 51.6, 117.3, 117.6, 125.2, 126.3, 126.4, 126.6, 126.9, 127.1, 2 × 127.6, 127.7, 128.1, 128.2, 2 × 128.6, 128.8, 129.0, 129.3, 129.4, 132.8, 133.1, 133.2, 135.1, 140.8, 141.5, 150.7 and 173.5; *m/z* (EI) 432 (M^+, 100%) and 359 (70); *m/z* (CI) 450 (M + NH_4^+, 100%) (found: M^+, 432.1722. Calc. for $C_{30}H_{24}O_3$, 432.1725) (found: C, 83.47; H, 5.71. Calc. for $C_{30}H_{24}O_3$, C, 83.31; H, 5.59%).

Synthesis of (*R*)-2-hydroxy-6-(3-hydroxypropyl)-2′-phenyl-1,1′-binaphthyl (14). $LiAlH_4$ (1.07 g, 28.3 mmol) in dry THF (150 ml) was stirred for 10 min at room temperature. A solution of **13** (6.30 g, 14.6 mmol) in dry THF (150 ml) was added over a period of 5 min and then the mixture was refluxed gently for 20 min. A colourless gelatinous precipitate appeared immediately. When the reaction was completed, ethyl acetate (100 ml) was added to destroy the excess $LiAlH_4$, followed by hydrochloric acid (3 M, 30 ml). The mixture was extracted with ethyl acetate (300 ml) and the extract was washed with water (2 × 100 ml), dried over $MgSO_4$ and concentrated *in vacuo* to give a cream solid. Crystallisation from chloroform gave a white powder (4.24 g, 72% yield); $[\alpha]_D^{20}$ +54.21 (*c* 2.87, $CHCl_3$), mp 162–164 °C.

δ_H($CDCl_3$) 1.25 (s, 1 H, OH), 1.91 (m, 2 H), 2.76 (t, J = 8 Hz, 2 H), 3.65 (t, J = 6 Hz, 2 H), 4.88 (s, 1 H, OH), 7.00 (d, J = 8.5 Hz, 1 H), 7.02–7.07 (m, 4 H), 7.10 (d, J = 8.9 Hz, 1 H), 7.12–7.15 (m, 2 H), 7.29–7.33 (m, 2 H), 7.50 (dd, J = 5.5, 8 Hz, 1 H), 7.55 (bs, 1 H), 7.68 (d, J = 9 Hz, 1 H), 7.69 (d, J = 8.5 Hz, 1 H), 7.96 (d, J = 8 Hz, 1 H) and 8.07 (d, J = 8.5 Hz, 1 H); δ_C($CDCl_3$) 31.8, 33.9, 62.4, 117.2, 117.6, 125.1, 2 × 126.4, 126.6, 126.9, 127.1, 2 × 127.7, 127.9, 128.2, 128.5, 2 × 128.6, 128.7, 128.8, 129.2, 129.3, 132.7, 133.2, 136.4, 140.8, 141.5 and 150.5; *m/z* (EI) 404 (M^+, 100%), 360 (35) and 359 (70); *m/z* (CI) 422 (M + NH_4^+, 100%) (found: M^+, 404.1784. Calc. for $C_{29}H_{24}O_2$, 404.1776) (found: C, 86.30; H, 5.66. Calc. for $C_{29}H_{24}O_2$, C, 86.11; H, 5.98%).

Synthesis of (*R*)-2-(methoxymethoxy)-6-[3-(methoxymethoxy)-propyl]-2′-phenyl-1,1′-binaphthyl (15). To a solution of **14** (3.82 g, 9.46 mmol) in a mixture of dry dichloromethane (120 ml) and dry THF (15 ml) under nitrogen was added *N*,*N*-diisopropylethylamine (13.65 g, 17.0 ml, 94.6 mmol) and chloromethyl methyl ether (9.88 g, 7.2 ml, 94.6 mmol). The mixture was stirred for 24 h at room temperature, quenched with water (160 ml), and extracted with dichloromethane (30 ml). The extract was washed with water (2 × 80 ml), dried over $MgSO_4$ and concentrated *in vacuo.* Purification by column chromatography on neutral alumina (elution with hexane–ether 5 : 4) gave **15** as a cream viscous product (2.79 g, 60% yield); $[\alpha]_D^{20}$ +60.14 (*c* 0.69, $CHCl_3$).

δ_H($CDCl_3$) 1.95 (m, 2 H), 2.78 (t, J = 8 Hz, 2 H), 3.08 (s, 3 H), 3.35 (s, 3 H), 3.54 (t, J = 6 Hz, 2 H), 4.62 (s, 2 H), 4.73 (d, J = 7 Hz, 1 H), 4.87 (d, J = 7 Hz, 1 H), 7.00–7.06 (m, 5 H), 7.10–7.15 (m, 2 H), 7.22–7.26 (m, 2 H), 7.39 (d, J = 9 Hz, 1 H), 7.43 (m, 1 H), 7.57 (bs, 1 H), 7.66 (d, J = 8.5 Hz, 1 H), 7.73 (d, J = 9 Hz, 1 H), 7.93 (d, J = 8 Hz, 1 H) and 8.00 (d, J = 8.5 Hz, 1 H); δ_C($CDCl_3$) 31.0, 32.2, 55.2, 55.6, 67.1, 95.2, 96.4, 116.4, 122.9, 125.6, 125.8, 126.2, 126.4, 126.5, 126.8, 2 × 127.3, 127.9, 2 × 128.0, 128.2, 2 × 128.8, 128.9, 129.5, 131.9, 132.7, 132.9, 133.1, 137.1, 139.9, 142.0 and 152.4; *m/z* (EI) 492 (M^+, 30%) and 45 (100); *m/z* (CI) 510 (M + NH_4^+, 100%) and 60 (100) (found: M^+, 492.2306. Calc. for $C_{33}H_{32}O_4$, 492.2301).

Synthesis of (*R*)-3-formyl-2-(methoxymethoxy)-6-[3-(methoxy-methoxy)propyl]-2′-phenyl-1,1′-binaphthyl (16). To a solution of **15** (2.02 g, 4.11 mmol) in dry THF (50 ml) at −78 °C under nitrogen was added a solution of *tert*-butyllithium (1.7 M in pentane, 2.90 ml, 4.93 mmol) by syringe and the mixture was stirred for 3 h at −78 °C. *N*,*N*-Dimethylformamide (901 mg, 0.95 ml, 12.3 mmol) was added and the reaction mixture was allowed to warm to room temperature and stirred for 2 h, then quenched with aqueous NH_4Cl (100 ml), and extracted with ethyl acetate (300 ml). The extract was washed with aqueous $NaHCO_3$ (100 ml) and brine (2 × 100 ml), dried over Na_2SO_4 and concentrated *in vacuo* to give a viscous product. Purification by column chromatography on neutral alumina gave recovered **15** (elution with hexane–ether 5 : 5) as a viscous product (808 mg, 40%) and then **16** (methanol) as a viscous product (1.28 g, 60% yield); $[\alpha]_D^{20}$ +9.96 (*c* 1.17, $CHCl_3$).

δ_H($CDCl_3$) 1.90 (m, 2 H), 2.76 (t, J = 7 Hz, 2 H), 2.78 (s, 3 H), 3.29 (s, 3 H), 3.49 (t, J = 7 Hz, 2 H), 4.32 (d, J = 6 Hz, 1 H), 4.50 (d, J = 6 Hz, 1 H), 4.55 (s, 2 H), 6.89–7.07 (m, 5 H), 7.11–7.18 (m, 3 H), 7.23 (dd, J = 7, 8.5 Hz, 1 H), 7.40 (dd, J = 7, 8 Hz, 1 H), 7.59 (d, J = 9 Hz, 1 H), 7.68 (bs, 1 H), 7.88 (d, J = 8 Hz, 1 H), 7.96 (d, J = 9 Hz, 1 H), 8.27 (s, 1 H) and 10.24 (s, 1 H); δ_C($CDCl_3$) 30.9, 32.2, 55.2, 56.8, 66.9, 96.5, 99.7, 125.9, 126.5, 126.7, 2 × 126.8, 2 × 127.5, 128.1, 128.5, 2 × 128.6, 2 × 128.7, 128.8, 129.1, 129.7, 130.4, 130.8, 130.9, 132.7, 133.2, 136.2, 139.4, 140.8, 141.5, 152.7 and 191.1; *m/z* (EI) 520 (M^+, 55%), 476 (25), 326 (50), 215 (40) and 77 (100); *m/z* (CI) 538 (M + NH_4^+, 10%), 446 (30), 445 (100) and 58 (100) (found: M^+, 520.2255. Calc. for $C_{34}H_{32}O_5$, 520.2250) (found: C, 78.76; H, 6.14. Calc. for $C_{34}H_{32}O_5$: C, 78.44; H, 6.20%).

Synthesis of (*R*)-3-formyl-2-hydroxy-6-(3-hydroxypropyl)-2′-phenyl-1,1′-binaphthyl (6). To a solution of **16** (400 mg, 0.77 mmol) in dry dichloromethane (10 ml) containing 4 Å molecular sieves (2.51 g) under nitrogen was added bromotrimethylsilane (1.0 ml, 7.70 mmol). The mixture was stirred for 1 h at room temperature. It was then quenched with aqueous $NaHCO_3$ (40 ml) and stirred for 4 h until the solvent became clear, and then extracted with dichloromethane (50 ml). The extract was washed with water (30 ml) and brine (30 ml), dried over $MgSO_4$ and concentrated *in vacuo* to give a yellow product. Purification by column chromatography (SiO_2, hexane–ether, 1.5 : 5) gave **6** as a yellow solid (306 mg, 92% yield); $[\alpha]_D^{20}$ −23.60 (*c* 0.79, $CHCl_3$), mp 88–90 °C.

δ_H($CDCl_3$) 1.36 (s, OH, 1 H), 1.83 (m, 2 H), 2.69 (t, J = 8 Hz, 2 H), 3.59 (t, J = 6 Hz, 2 H), 6.94–6.98 (m, 4 H), 7.09 (d, J = 9 Hz,

1 H), 7.10–7.16 (m, 2 H), 7.17 (d, $J = 9$ Hz, 1 H), 7.22 (dd, $J = 7$, 8 Hz, 1 H), 7.40 (dd, $J = 7$, 8 Hz, 1 H), 7.55 (bs, 1 H), 7.57 (d, $J = 8.5$ Hz, 1 H), 7.89 (d, $J = 8$ Hz, 1 H), 7.96 (d, $J = 8.5$ Hz, 1 H), 8.00 (s, 1 H), 9.99 (s, 1 H) and 10.31 (s, 1 H, OH); δ_C($CDCl_3$) 31.6, 33.6, 62.1, 121.1, 121.5, 125.5, 125.8, 126.1, 126.5, 126.6, 127.3, 2 × 127.4, 127.9, 128.2, 128.3, 128.5, 2 × 128.6, 129.9, 131.9, 132.6, 132.9, 136.3, 137.3, 137.5, 140.6, 141.8, 153.1 and 196.9; *m/z* (EI) 432 (M^+, 100%), 387 (30), 326 (40), 77 (30) and 41 (30); (CI) 450 ($M + NH_4^+$, 20%), 433 (40), 58 (70) and 44 (100) (found: M^+, 432.1720. Calc. for $C_{30}H_{24}O_3$, 432.1725).

Synthesis of the unsymmetrical chiral salen ligand, *N*-[(*R*)-(2-hydroxy-2′-phenyl-1,1′-binaphthyl-3-ylmethylene)]-*N*′-[(*R*)-2-hydroxy-6-(3-hydroxypropyl)-2′-phenyl-1,1′-binaphthyl-3-ylmethylene]-1*S*,2*S*-cyclohexanediamine (7). A sample (200 mg) of the crude product from the above reaction, containing compound **5** (*ca.* 126 mg, 0.27 mmol) and **19a** (*ca.* 74 mg, 0.09 mmol), was dissolved in a mixture of methanol (10 ml) and dichloromethane (10 ml). Compound **6** (130 mg, 0.30 mmol) was added and the reaction mixture was stirred for 3 h at room temperature. The solvent was removed *in vacuo* to give a yellow powder, 330 mg. Purification by column chromatography (SiO_2, hexane–ether 1 : 5 then methanol) gave compound **19a** (100 mg), compound **7** (200 mg, 75% yield based on **6**, 84% based on **5**), and compound **19b** (30 mg).

Alternative procedure for synthesis of the unsymmetrical chiral salen ligand (7). To a solution of (1*S*,2*S*)-diaminocyclohexane (**4**, 44.2 mg, 0.39 mmol) in dichloromethane (25 ml) containing 4 Å molecular sieves (500 mg) at room temperature under nitrogen was added a solution of **3** (140.6 mg, 0.38 mmol) in dichloromethane (15 ml) dropwise over 1 h by means of a dropping funnel. After the addition was completed, the mixture was stirred for an additional 1 h. A solution of **6** (162.4 mg, 0.38 mmol) in dichloromethane (10 ml) was added and the reaction mixture was stirred for 24 h at room temperature and then filtered. The filtrate was concentrated *in vacuo* to give a yellow powder, 310 mg. The product was purified by column chromatography on silica gel (elution with pet. 40–60°–ether 1 : 5, then methanol). The product mixture was not soluble in pet. 40–60°–ether, so it was first dissolved in dichloromethane, one equivalent of **4** (0.38 mmol) was added, then silica (5 mg), and the solvent was removed. The dry silica was added to the top of a pre-prepared silica column, which was then eluted with pet. 40–60°–ether (1 : 5) then methanol. Evaporation of the appropriate fractions gave **19a** (109 mg, 35% yield; mp 300 °C), **7** (134 mg, 40% yield; mp 154 °C) and **19b** (66 mg, 19% yield; mp 200–202 °C).

***N*,*N*′-Bis[(*R*)-(2-hydroxy-2′-phenyl-1,1′-binaphthyl-3-ylmethylene)]-1*S*,2*S*-cyclohexanediamine (19a).** δ_H($CDCl_3$) 1.34 (m, 2 H), 1.66 (m, 2 H), 1.78 (m, 2 H), 1.93 (m, 2 H), 3.17 (m, 2 H), 6.01 (t, $J = 7$ Hz, 2 H), 6.21 (app. t, $J = 7$ Hz, 4 H), 6.87 (d, $J = 8.5$ Hz, 2 H), 6.90 (m, 2 H, H_7), 7.01–7.10 (m, 5 H), 7.13–7.17 (m, 3 H), 7.21 (m, 2 H), 7.26–7.30 (m, 4 H), 7.37 (dd, $J = 7$, 8 Hz, 2 H), 7.57 (d, $J = 8.5$ Hz, 2 H), 7.87 (d, $J = 8$ Hz, 2 H), 7.94 (d, $J = 8.5$ Hz, 2 H), 8.17 (s, 2 H) and 13.10 (s, 2 H, 2 OH); δ_C($CDCl_3$) 24.1, 32.5, 73.2, 119.8, 120.0, 123.1, 124.6, 125.7, 126.3, 126.4, 126.5, 127.1, 2 × 127.3, 128.0, 4 × 128.1, 128.3, 128.6, 131.2, 132.9, 133.0, 133.4, 134.7, 140.3, 141.8, 154.9 and 165.2; *m/z* (FAB) 827 (MH^+, 72%) and 149 (100) (found: MH^+, 827.3626. Calc. for $C_{60}H_{47}O_2N_2$, 827.3637); ν_{max}/cm^{-1} (KBr) 3359 (broad, O–H), 2927, 2856 and 1631 (C=N).

Compound 7. δ_H($CDCl_3$) 1.35 (m, 2 H), 1.50 (bs, 1 H, OH), 1.6–1.7 (m, 4 H), 1.78 (m, 2 H), 1.94 (m, 2 H), 2.45 (m, 2 H), 3.15 (m, 2H), 3.41 (m, 2 H), 6.02 (t, $J = 7$ Hz, 1 H), 6.06 (t, $J = 7$ Hz, 1 H), 6.20 (t, $J = 8$ Hz, 2 H), 6.28 (t, $J = 8$ Hz, 2 H), 6.79 (d, $J = 9$ Hz, 2 H), 6.82–6.93 (m, 4 H), 7.02 (m, 1 H), 7.07 (d, $J = 8$ Hz, 2 H), 7.10 (d, $J = 8$ Hz, 2 H), 7.15 (s, 1 H, CH=N), 7.16 (s, 1 H), 7.21 (m, 3 H), 7.28 (m, 2 H), 7.37 (m, 2 H), 7.56 (d, $J = 8$ Hz, 1 H), 7.57 (d, $J = 8$ Hz, 1 H), 7.86 (d, $J = 8$ Hz, 1 H), 7.87 (d, $J = 8$ Hz, 1 H), 7.93 (d, $J = 8$ Hz, 1 H), 7.94 (d, $J = 8$ Hz, 1 H), 8.14 (s, 2 H) and 13.00 (bs, 2 H, 2 OH); δ_C($CDCl_3$) 2 × 24.1, 31.4, 2 × 32.5, 33.5, 62.1, 2 × 73.2, 119.8, 119.9, 120.0, 122.9, 2 × 124.6, 125.5, 125.7, 126.2, 126.3, 2 × 126.4, 2 × 126.5, 2 × 127.0, 127.2, 4 × 127.4, 127.9, 128.0, 4 × 128.1, 4 × 128.2, 2 × 128.3, 128.6, 129.2, 2 × 131.3, 132.8, 2 × 132.9, 2 × 133.0, 133.3, 133.4, 134.6, 136.1, 2 × 140.3, 2 × 141.9, 154.4, 154.9, 165.3 and 165.4; *m/z* (FAB) 885 (MH^+, 30%), 884 (M^+, 13), 286 (58), 178.1 (54), 165.1 (80) and 153 (100) (found: M^+, 884.3961. Calc. for $C_{63}H_{52}O_3N_2$, 884.3978); ν_{max}/cm^{-1} (KBr) 3359 (broad, O–H), 2927, 2856 and 1631 (C=N).

***N*,*N*′-Bis[(*R*)-2-hydroxy-6-(3-hydroxypropyl)-2′-phenyl-1,1′-binaphthyl-3-ylmethylene]-1*S*,2*S*-cyclohexanediamine (19b).** δ_H($CDCl_3$) 1.38 (2 H, m), 1.5–1.6 (m, 4 H), 1.64 (m, 4 H), 1.80 (m, 2 H), 1.95 (m, 2 H), 2.47 (m, 4H), 3.19 (m, 2 H), 3.42 (m, 4 H), 6.00 (t, $J = 8$ Hz, 2 H), 6.22 (t, $J = 8$ Hz, 4 H), 6.78 (d, $J = 9$ Hz, 2 H), 6.87 (d, $J = 9$ Hz, 2 H), 6.89 (s, 2 H), 7.09 (m, 4 H), 7.21 (s, 2 H, 2 CH=N), 7.21–7.29 (m, 4 H), 7.38 (dd, $J = 7$, 8 Hz, 2 H), 7.57 (d, $J = 8.5$ Hz, 2 H), 7.88 (d, $J = 8$ Hz, 2 H), 7.95 (d, $J = 8.5$ Hz, 2 H), 8.19 (s, 2 H) and 13.00 (2 H, s, 2 OH); δ_C($CDCl_3$) 24.1, 31.4, 32.5, 33.6, 62.1, 73.3, 119.8, 124.6, 125.7, 126.2, 126.4, 126.5, 126.9, 127.2, 2 × 127.4, 2 × 128.1, 2 × 128.2, 128.3, 129.4, 131.3, 2 × 132.8, 2 × 132.9, 133.2, 136.1, 140.2, 141.9, 154.5 and 165.4; *m/z* (FAB) 965 ($M + Na^+$, 10%), 943 (MH^+, 100), 511 (28) and 107 (90) (found: MH^+, 943.4500. Calc. for $C_{66}H_{59}O_4N_2$, 943.4475); ν_{max}/cm^{-1} (KBr) 3359 (broad, O–H), 2927, 2856 and 1631 (C=N).

Synthesis of unsymmetrical complexes 1a and 1b. To a solution of **7** (348.8 mg, 0.394 mmol) in a mixture of ethanol (50 ml), acetonitrile (10 ml) and dichloromethane (10 ml) was added $Mn(OAc)_2{\cdot}4H_2O$ (126.0 mg, 0.514 mmol) and the mixture was stirred in air for 24 h at room temperature. The solution was concentrated *in vacuo* to give a dark brown mass (460 mg). The crude product was redissolved in dichloromethane and filtered. The filtrate was concentrated *in vacuo* to give a dark brown solid, **1a** (400 mg, *ca.* 108% of the theoretical yield).

Complex **1a** (93.6 mg, 0.094 mmol) was dissolved in acetonitrile and a solution of $NaPF_6$ (157.5 mg, 0.938 mmol) in a minimum of water (1 ml) was added. The mixture was stirred for 24 h at room temperature and then the solvent was removed *in vacuo.* The crude material was redissolved in dichloromethane and filtered. The filtrate was concentrated *in vacuo* and purified by column chromatography (SiO_2, CH_2Cl_2–MeOH 5 : 0.5) to give a dark brown product **1b** (77.0 mg, 76% yield).

Chiral (salen)Mn(III)OAc complex (1a). *m/z* (FAB) 937 ($[M - AcO]^+$, 100%) and 885 (30) (found: $[M - AcO]^+$, 937.3192. Calc. for $C_{63}H_{50}N_2O_3Mn$, 937.3202); *m/z* (ES^-) 59 ($CH_3CO_2^-$, 100%); ν_{max}/cm^{-1} 1608 (C=N).

Chiral (salen)Mn(III)PF_6 complex (1b). *m/z* (FAB) 938 ($[MH - PF_6]^+$, 85%), 937 ($[M - PF_6]^+$, 100), 885 (20), 215

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(60), 135 (73) and 107 (77) (found: $[M - PF_6]^+$, 937.3180. Calc. for $C_{63}H_{50}N_2O_3Mn$, 937.3202); *m/z* (ES^-) 145 (PF_6^-, 100%); ν_{max}/cm^{-1} 1608 (C=N).

Chiral (salen)Mn(III)PF_6 complex (2). The procedure was similar to that for complex **1b**. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2–MeOH 5 : 0.2) to give dark brown solid **2** (98% yield).

m/z (FAB) 880 ($[MH - PF_6]^+$, 85%), 879 ($[M - PF_6]^+$, 100), 827.5 (90), 374 (82) and 149 (57) (found: $[M - PF_6]^+$, 879.2762. Calc. for $C_{60}H_{44}N_2O_2Mn$, 879.2783); *m/z* (ES^-) 145 (PF_6^-, 100%); ν_{max}/cm^{-1} 1608 (C=N).

Mn complex of ligand 19b, chiral (salen)Mn(III)OAc complex. The procedure was similar to that for complex **1a**. The crude product was redissolved in dichloromethane and filtered. The solvent was concentrated *in vacuo* to give the complex (97% yield) as a dark brown solid.

m/z (FAB) 996 ($[MH - CH_3CO_2]^+$, 45%), 995 ($[M - CH_3CO_2]^+$, 100), 943 (20), 938 (5), 391 (35), 149 (65) and 107 (50) (found: $[MH - CH_3CO_2]^+$, 996.3698. Calc. for $C_{66}H_{57}N_2O_4Mn$, 996.3699); *m/z* (ES^-) 59 ($CH_3CO_2^-$, 100%); ν_{max}/cm^{-1} 1608 (C=N).

Synthesis of *N*-[(*R*)-(2-hydroxy-2′-phenyl-1,1′-binaphthyl-3-ylmethylene)]-*N*′-[(*R*)-2-hydroxy-6-(3-benzoyloxypropyl)-2′-phenyl-1,1′-binaphthyl-3-ylmethylene]-1*S*,2*S*-cyclohexanediamine (20). To a solution of ligand **7** (40.1 mg, 0.0453 mmol) in dry dichloromethane (5 ml) at 0 °C under argon was added triethylamine (3.0 ml of 0.023 M solution in dry dichloromethane, 0.069 mmol) under argon. A solution of benzoyl chloride (0.80 ml of 0.067 M solution in dry dichloromethane, 0.054 mmol) was slowly added and the mixture was stirred at 0 °C for 24 h. The reaction was monitored by TLC (SiO_2, hexane–ether 3 : 5; **7** R_f = 0.4), but showed no reaction. Therefore, the mixture was warmed to room temperature for an additional 24 h, at which time TLC indicated the presence of one new component at R_f = 0.6 and a spot at R_f = 0.2, which was nevertheless presumed to be the starting material, **7**. An aliquot of the solution (*ca.* 2 ml) was diluted to *ca.* 10 ml with dichloromethane, washed with saturated aqueous $NaHCO_3$ (10 ml) and brine (10 ml), and then dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a cream solid product, 10 mg. Purification by column chromatography (SiO_2, hexane–ether 3 : 5) gave **7** (5.9 mg) and **20** (3.2 mg).

The rest of the reaction mixture was heated to reflux for an additional 24 h. The organic phase was then washed with saturated aqueous $NaHCO_3$ (10 ml) and brine (10 ml), and then dried over anhydrous $MgSO_4$. Evaporation of the solvent gave a cream solid product, 30 mg. Purification by column chromatography gave **7** (4.4 mg) and **20** (12.6 mg).

δ_H($CDCl_3$) 1.35–2.00 (m, 12 H), 3.15 (m, 2 H), 4.15 (m, 2 H), 6.09 (t, J = 7 Hz, 1 H), 6.14 (t, J = 7 Hz, 1 H), 6.25 (t, J = 8 Hz, 2 H), 6.36 (t, J = 8 Hz, 2 H), 6.77 (bs, 1 H), 6.82 (d, J = 9 Hz, 1 H), 6.85 (d, J = 9 Hz, 1 H), 6.90 (m, 2 H), 6.99–7.09 (m, 6 H), 7.13 (m, 2 H), 7.20–7.30 (m, 4 H), 7.33–7.43 (m, 4 H), 7.48 (m, 1 H), 7.56 (d, J = 8 Hz, 1 H), 7.57 (d, J = 8 Hz, 1 H), 7.88 (d, J = 8 Hz, 2 H), 7.95 (d, J = 8 Hz, 4 H), 8.10 (s, 1 H), 8.12 (s, 1 H), 12.97 (bs, 1 H, OH) and 13.06 (bs, 1 H, OH); *m/z* (FAB) 989 (MH^+, 53%), 988 (M^+, 57) and 827 (7) (found: MH^+, 989.4303. Calc. for $C_{70}H_{57}N_2O_4$, 989.4318); ν_{max}/cm^{-1} (thin film) 1718 (C=O) and 1632 (C=N).

Synthesis of {*N*-[(*R*)-(2-hydroxy-2′-phenyl-1,1′-binaphthyl-3-ylmethylene)]-*N*′-[(*R*)-2-hydroxy-6-(3-benzoyloxypropyl)-2′-phenyl-1,1′ - binaphthyl - 3 - ylmethylene] - 1*S*,2*S* - cyclohexanediamine} Mn(III) trifluoromethanesulfonate (21). To a solution of **1c** (46.6 mg, 0.0429 mmol) in dry dichloromethane (5 ml) at room temperature was added triethylamine (3.0 ml of a 0.071 M solution in dry dichloromethane, 0.21 mmol) under argon. A solution of benzoyl chloride (3.0 ml of a 0.069 M solution in dichloromethane, 0.21 mmol) was slowly added and the mixture was refluxed for 48 h. The mixture was quenched with saturated aqueous $NaHCO_3$ (10 ml), separated, and the organic layer was washed with brine (10 ml), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give a dark brown solid, 53.1 mg. Purification by column chromatography (SiO_2, DCM–MeOH 5 : 0.6) gave **21** (36.8 mg, 72% yield) and **1c** (2.2 mg, 5%).

m/z (FAB) 1041 ($[M - F_3CSO_3]^+$, 20%) and 989 (10) (found: $[M - F_3CSO_3]^+$, 1041.3450. Calc. for $C_{70}H_{54}N_2O_4Mn$, 1041.3464); *m/z* (ES^-) 149 ($F_3CSO_3^-$, 100%); ν_{max}/cm^{-1} (KBr) 1715 (C=O) and 1610 (C=N).

Attachment of the unsymmetrical complex 1a to polystyrenecarbonyl chloride. Complex **1a** (0.156 g, 0.157 mmol) in dichloromethane (5 ml) was treated with excess triethylamine (0.12 M solution in dry dichloromethane, 5.0 ml, 0.60 mmol) and the mixture was added to polystyrenecarbonyl chloride (0.125 g, 1.17 mmol g^{-1}, 0.146 mmol), swollen in dichloromethane (5 ml) for 1 h and the mixture was heated at reflux for 6 d. The resulting polymer was filtered, washed with CH_2Cl_2 (20 ml), H_2O (20 ml), THF (20 ml), THF–H_2O (1 : 1, 20 ml), H_2O (20 ml), CH_2Cl_2 (20 ml), and finally MeOH (20 ml). After being dried in a vacuum oven for 24 h, the resin (**polymer A**, **25a**, 0.0981 g) was obtained as a pale brown solid. AAS suggested that the polymer contained around 0.096 mmol g^{-1} Mn.

ν_{max}/cm^{-1} (KBr) 1721 (C=O) and 1602 (C=N).

Attachment of the unsymmetrical complex 1c to polystyrenecarbonyl chloride and subsequent ion-exchange. The procedure for the attachment of complex **1c** was similar to that for **1a** except that reflux was maintained for 2 d. After being dried in a vacuum oven for 24 h, polymer **25c** was obtained as a dark brown powder. AAS suggested that it contained around 0.12 mmol g^{-1} Mn.

The resin **25c** (0.103 g) was swollen in a mixture of dioxane (5 ml), ethanol (5 ml) and acetonitrile (5 ml) for 1 h, a solution of $NaPF_6$ (25.0 mg, 0.149 mmol) in a minimum of water (1 ml) was added and the mixture was stirred for 24 h at room temperature. The polymer was filtered off, washed with EtOH (20 ml), H_2O (20 ml), CH_2Cl_2 (20 ml), H_2O (20 ml), CH_2Cl_2 (20 ml) and finally MeOH (20 ml). After being dried in a vacuum oven (50 °C, 10 mmHg) for 24 h, **polymer B** (**25b**, 0.0922 g) was obtained as a dark brown solid.

Attachment of the unsymmetrical complex 1b to polystyrenecarbonyl chloride. The procedure for the attachment of complex **1b** was similar to that for **1a** except that reflux was maintained for 2 d. **Polymer C** (**25b**) was obtained as a dark brown solid. AAS suggested that the polymer contained around 0.24 mmol g^{-1} Mn.

General procedure for the epoxidation of 1,2-dihydronaphthalene (26) using free or polymer-supported unsymmetrical chiral (salen)Mn complexes

The procedure for the free complexes was as follows. To a solution of 1,2-dihydronaphthalene (**26**; 0.2 mmol), 4-PPNO (0.05 mmol) and hexadecane (0.2 mmol) as an internal standard in dichloromethane (2.5 ml) was added catalyst **1b** or **2** (0.02 mmol) and the mixture was cooled to 0 °C. A solution of NaOCl in phosphate buffer (1.0 ml, 0.588 M, 0.6 mmol) (pH = 11.4) was added. The two-phase system was stirred at 0 °C. The progress of the reaction was monitored by GC and the results are recorded in Table 1. After the reaction was completed, the layers were separated, the organic layer was washed with water (2 × 10 ml) and the aqueous layer was extracted with dichloromethane (2 × 10 ml). The organic extracts were combined with the original organic layer, dried over Na_2SO_4 and concentrated *in vacuo.* Purification by column chromatography (SiO_2, pet. 40–60 °C–ethyl acetate, 5 : 0–5 : 0.2) gave epoxide **27** as a cream oil.

δ_H($CDCl_3$) 1.65 (m, 1 H), 2.30 (m, 1 H), 2.44 (m, 1 H), 2.68 (m, 1 H), 3.62 (m, 1 H), 3.74 (d, J = 4 Hz, 1 H), 6.98 (d, J = 7 Hz, 1 H), 7.08–7.17 (m, 2 H) and 7.28 (d, J = 8 Hz, 1 H); δ_C($CDCl_3$) 21.8, 24.4, 52.7, 55.1, 126.1, 2 × 128.4, 129.5, 132.6 and 136.7.

The enantiomeric excess (ee) was determined by ^{1}H NMR spectroscopy using the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] (Eu(hfc)$_3$) in $CDCl_3$.

The procedure for use of the polymer-bound complexes was as follows. **Polymer A**, **B** or **C** (as indicated in Table 1) was swelled in dichloromethane (2 ml) for 1 h. A solution containing 1,2-dihydronaphthalene (1 eq.), 4-PPNO (0.25 eq.) and hexadecane as an internal standard in dichloromethane (2 ml) was added and the mixture was cooled to 0 °C. A solution of NaOCl in phosphate buffer (0.588 M, 5 eq., pH = 11.4) was added, the mixture was stirred at 0 °C and the progress of the reaction was monitored by GC. After the appropriate time the suspension was filtered and the residue was washed with CH_2Cl_2 (50 ml), H_2O (50 ml), CH_2Cl_2 (50 ml), and finally MeOH (50 ml). After being dried in a vacuum oven (50 °C, 10 mmHg) for 24 h the polymer was available for reuse. This procedure was repeated after each use of the polymer. The filtrate was collected and concentrated *in vacuo.* The residue was then treated in an identical manner to the product obtained from the reactions involving free complexes.

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