X-Ray Structural Studies of Highly Enantioselective Mn(salen) Epoxidation Catalysts

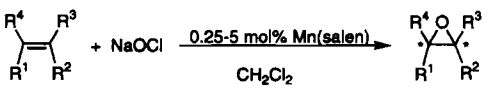
Paul J. Pospisil, Douglas H. Carsten, and Eric N. Jacobsen*

Abstract: The relationship between catalyst structure and enantioselectivity in the asymmetric epoxidation of unfunctionalized olefins by a series of chiral Mn(salen) complexes (**1**–**10**) was examined. The X-ray structures of 5-coordinate complexes **5**, **8**, of 6-coordinate **9** ([6,6′ = -*t*Bu; 4,4′ = -*t*Bu]$^+$$ClO_4^-$), and **10** (6,6′ = -*t*Bu; 4,4′ = -Br) were determined. Catalysts **1**–**9** were derived from (*R,R*)-1,2-diaminocyclohexane and catalyst **10** from (*S,S*)-1,2-diphenylethylenediamine. Catalysts **1**–**9** differ in the stereoelectronic substitution of the *ortho* (6,6′) and *para* (4,4′) positions of the salicylidene moiety. A comparison between structures **5**, **8**, and **9** reveals that the ligand geometry around the metal center and the chiral diimine backbone remains remarkably constant in both five- and six-coordinate cyclohexanediamine-derived complexes; in contrast, the salicylidene regions of the complexes display a wide range of conformations. The asymmetric epoxidation of indene and 6-cyano-2,2-dimethylchromene with NaOCl catalyzed by complexes **1**–**10** was effected. Systematically increasing the steric bulk on the *ortho* and then the *para* position in the order **1** (6,6′ = -H; 4,4′ = -H), **2** (6,6′ = -CH_3; 4,4′ = -CH_3), **3** (6,6′ = -*t*Bu; 4,4′ = -H), **4** (6,6′ = -*t*Bu; 4,4′ = -CH_3), **5** (6,6′ = -*t*Bu; 4,4′ = -*t*Bu), and **6** (6,6′ = -*t*Bu; 4,4′ = -trityl), and electronically modifying the *para* substituents in **7** (6,6′ = -*t*Bu; 4,4′ = -OMe) and **8** (6,6′ = -*t*Bu; 4,4′ = -OTIPS) resulted in enhanced enantioselectivities of the desired epoxides. The conformational variations observed in the solid state are likely to reflect accessible solution conformations and may help explain the high levels of stereoinduction obtained with these catalysts in the asymmetric epoxidation of unfunctionalized olefins.

Keywords
asymmetric epoxidations · catalysis · manganese complexes · structure elucidation

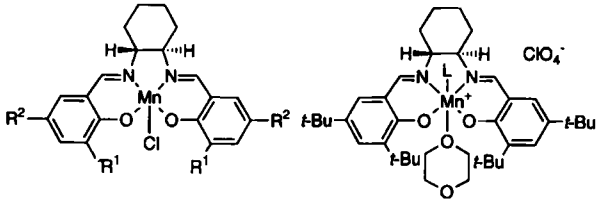
Introduction

Chiral (salen)Mn complexes (e.g., **1**–**10**; salen = *N,N′*-bis(salicylidene)ethylenediamine) have been developed recently as synthetically useful catalysts for the asymmetric epoxidation of unfunctionalized olefins.[1] For example, conjugated aryl, vinyl, or alkynyl-substituted alkenes can be induced to undergo epoxidation with good-to-excellent enantioselectivities (80–99%) under appropriate conditions (Scheme 1). Reactions carried out in two-phase systems employing NaOCl as the oxidant and 0.25–5 mol% of catalysts such as **5** have been applied in a range of laboratory and commercial-scale syntheses.[2] An anhydrous oxidation protocol consisting of *m*-chloroperbenzoic acid and *N*-methylmorpholine *N*-oxide has also been developed, allowing epoxidations to be carried out at reduced temperatures and often resulting in higher enantioselectivities.[3]



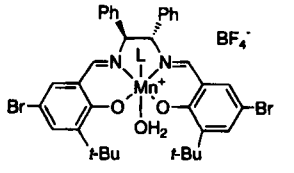
Scheme 1. R^1 = aryl, alkynyl, alkenyl (conjugating group); R^2 = R^3 = R^4 = H, alkyl, aryl, CO_2R.

The synthetic accessibility of these catalysts from readily available and inexpensive precursors constitutes one of their most vital and attractive features. The salen ligand system is easily constructed in a convergent manner from diamines and salicylaldehyde derivatives, and optimal selectivities for a given substrate can be achieved by modulating the catalyst's steric and electronic properties.[4] Thus, catalyst **8**, which bears sterically



1: R^1 = -H R^2 = -H
2: R^1 = -CH_3 R^2 = -CH_3
3: R^1 = -*t*-Bu R^2 = -H
4: R^1 = -*t*-Bu R^2 = -CH_3
5: R^1 = -*t*-Bu R^2 = -*t*-Bu
6: R^1 = -*t*-Bu R^2 = -(C)Ph_3
7: R^1 = -*t*-Bu R^2 = -OCH_3
8: R^1 = -*t*-Bu R^2 = *i*-Pr_3SiO

9



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L= H_2O

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demanding electron-donating substituents, is optimal for the epoxidation of dienes[5] and trisubstituted olefins,[6] whereas the highest enantioselectivities for terminal olefins have been attained with catalysts such as **10**, which bear a diphenyldiamine backbone.[3] A general pattern is less evident in the case of tetrasubstituted olefins, with unhindered catalysts such as **1** affording highest *ee*'s in certain cases, while the very hindered catalyst **8** is most effective in others.[7]

In order to gain insight into the transition structure geometry in oxygen atom transfer reactions and to effect the design of improved catalysts by a rational approach, it is clearly of interest to elucidate the elements of ligand structure responsible for high stereoinduction. However, the reactive intermediates in these (salen)Mn-catalyzed epoxidations have not yet been isolated,[8] so information about ligand conformation in the directly relevant complexes remains elusive. Still, available mechanistic data point to the intermediacy of discrete, highly reactive Mn^{V} oxo species.[8–11] Such intermediates may contain either 5- or 6-coordinate manganese, with the oxo ligand residing on an apical site relative to the salen system. Given that the general bonding characteristics of salen ligands are likely to be similar in both Mn^{III} and Mn^{V} complexes,[12] we have undertaken the structural characterization of several stable Mn^{III} derivatives in order to evaluate the range of ligand conformations available to these complexes. In this paper we describe the X-ray crystal structures of complexes **5**, **8**, **9**, and **10**, four highly enantioselective (salen)Mn^{III} epoxidation catalysts.[13, 14] The basis for stereoinduction in epoxidations with these catalysts is addressed through comparison of their solid-state structures, and by analysis of enantioselectivity data obtained with catalysts **1**–**10**.

Results

X-ray Structural Studies: The crystal structures of four chiral (salen)Mn^{III} complexes were determined. ORTEP representations of structures **5** and **8**–**10** are provided in Figure 1. Compounds **5** and **9** correspond, respectively, to 5- and 6-coordinate Mn^{III} complexes of the commercially available di-*tert*-butylsalicylaldehyde-derived ligand.[4a] Complex **8** is 5-coordinate and representative of Mn(salen) catalysts bearing electron-donating substituents at the 4,4′ positions. Finally, complex **10** is a 6-coordinate example of a diphenylethylenediamine-derived complex. All catalyst structures were found to be monomeric and to display no significant distortions due to intermolecular contacts.[15] In the 6-coordinate structures, the complexes adopt pseudooctahedral geometries wherein the cationic Mn center resides within the basal ligand plane and bears two donor ligands coordinated to the apical positions. The structures of the 5-coordinate (salen)MnCl complexes **5** and **8** display a square-

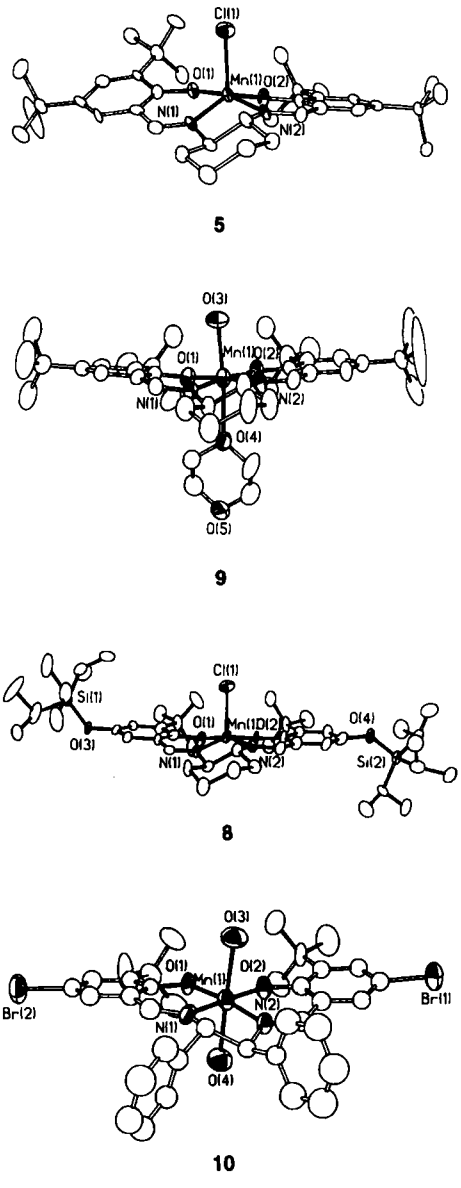


Fig. 1. ORTEP drawings of catalysts **5** and **8**–**10**.

Table 1. Crystal data for compounds **5** and **8**–**10**.

	5	**9**	**8**	**10**
formula	$C_{36}H_{52}N_2O_2ClMn$	$C_{48.5}H_{72.5}N_2O_{11}ClMn$	$C_{46}H_{76}N_2O_4Si_2ClMn$	$C_{45}H_{46}BN_2O_2F_4Br_2Mn$
fw	635.16	950.0	867.66	983.43
space group	*P*1	*C*2	*P*1	$P4_32_12$
a, Å	10.677(2)	39.827(6)	12.547(3)	16.428(5)
b, Å	12.841(2)	9.521(1)	14.685(2)	16.428(5)
c, Å	14.751(3)	28.696(5)	14.828(2)	34.422(15)
α, °	64.88	90	75.55	90
β, °	88.99	109.49(1)	72.24	90
γ, °	71.86	90	73.71	90
V, Å^3	1724.6(5)	10258(3)	2456.9(8)	9290(6)
Z	2	8	2	8
D (calcd), g cm^{-3}	1.223	1.230	1.173	1.402
μ, mm^{-1}	0.493	0.366	0.412	2.062
T, °C	−100	−100	−100	25
R(*F*)	0.053	0.068	0.054	0.0676

pyramidal geometry, with the manganese centers located only slightly above the basal plane (0.12–0.2 Å). Thus, the ligand geometry in the immediate vicinity of the metal center varies remarkably little from 5- to 6-coordinate complexes. The crystal data for the above structures is summarized in Table 1. Table 2 lists the bond lengths and angles around the metal center in each complex.

Table 2. Selected bond lengths [Å] and angles [°] of structures **5** and **8–10**.

	5	**9**	**8**	**10**
$Mn-N_1$	2.003	1.960	1.993	1.956
$Mn-N_2$	1.957	1.986	1.970	1.991
$Mn-O_1$	1.848	1.869	1.891	1.860
$Mn-O_2$	1.872	1.862	1.876	1.858
Mn–Cl	2.360	–	2.367	–
$Mn-O_3$	–	2.223	–	2.274
$Mn-O_4$	–	2.450	–	2.331
N_1-Mn-O_2	167.1	173.5	154.3	172.4
O_1-Mn-N_2	147.0	171.9	161.5	172.8
N_1-Mn-Cl	103.8	–	103.3	–
N_2-Mn-Cl	94.5	–	94.7	–
O_1-Mn-Cl	97.9	–	154.3	–
O_2-Mn-Cl	108.5	–	161.5	–

A superposition of the structures of catalysts **5**, **8**, and **9** reveals a remarkable degree of conformational variability in the salen ligand structures (Fig. 2). The 1,2-cyclohexanediamine

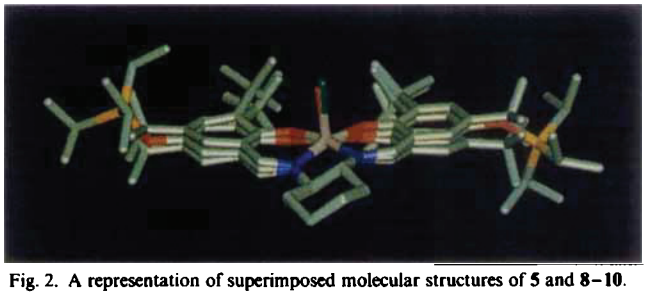


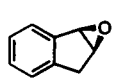
Fig. 2. A representation of superimposed molecular structures of **5** and **8–10**.

backbone and the axial ligands of the three structures were matched as common elements.[16] Whereas the cyclohexanediamine units and the coordination around the metal center are found to correspond almost perfectly in the three structures, substantial variation in the orientation of the bulky alkyl-substituted phenols is evident. Thus, the dihedral angles between the planes of the phenols in each complex range from 0.99 to 19.98°.

Structure-Enantioselectivity Studies: Enantioselectivities in the epoxidation of two *cis*-1,2-disubstituted model alkenes were determined with catalysts **1–10** (Table 3). Complexes **1–9**, derived from 1,2-diaminocyclohexane and differing in the identity of the 4,4′ and 6,6′ substituents of the salicylidene moiety, were selected in order to evaluate the effect of steric and electronic tuning on catalyst enantioselectivity. Epoxidation reactions were carried out at 0 °C with NaOCl (2 equiv) as the terminal oxidant, 10 mol% of 4-phenylpyridine *N*-oxide as a promoter, and 2 mol% of the appropriate (salen)Mn complex as catalyst.

In general, the olefin conversion and epoxide yields were good to excellent. The epoxidation of indene[3b, 17] and 6-cyano-2,2-dimethylchromene[2a] with catalyst **1**, bearing no substituents on the salicylidene moiety, yielded the desired epoxides **11** in

Table 3. Epoxidation of indene and 6-cyano-2,2-dimethylchromene with catalysts **1–10** to give **11** and **12**, respectively [a,b].



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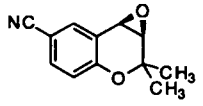

12

Entry	Catalysts	*ee*(**11**), % [c,d]	*ee*(**12**), % [c,d]
1	(*R,R*)-**1**	44 (1*R*,2*S*)	50 (3*R*,4*R*)
2	(*R,R*)-**2**	37 (1*R*,2*S*)	37 (3*R*,4*R*)
3	(*R,R*)-**3**	82 (1*R*,2*S*)	91 (3*R*,4*R*)
4	(*R,R*)-**4**	81 (1*R*,2*S*)	91 (3*R*,4*R*)
5	(*R,R*)-**5**	86 (1*R*,2*S*)	96 (3*R*,4*R*)
6	(*R,R*)-**6**	85 (1*R*,2*S*)	98 (3*R*,4*R*)
7	(*R,R*)-**7**	86 (1*R*,2*S*)	98 (3*R*,4*R*)
8	(*R,R*)-**8**	85 (1*R*,2*S*)	98 (3*R*,4*R*)
9	(*R,R*)-**9**	86 (1*R*,2*S*)	98 (3*R*,4*R*)
10	(*S,S*)-**10**	73 (1*S*,2*R*)	96 (3*S*,4*S*)

[a] Epoxidations were performed at 0 °C in CH_2Cl_2 with 2 mol% Mn(salen) catalysts **1–10**, 10 mol% 4-phenylpyridine *N*-oxide and 2 equiv of buffered, aqueous NaOCl (5%, pH = 11.3). [b] Conversions and epoxide yields were measured by GC and quantified vs. dodecane as the internal standard. [c] Enantiomeric excess (*ee*) was measured by HPLC (Chiralcel-OB) for indene oxide and GC for 6-cyano-2,2-dimethylchromene oxide (Cyclodex B). [d] Assignment of absolute stereochemistry for indene oxide [17] and 6-cyano-2,2-dimethylchromene oxide [2a].

44% *ee* and **12** in 50% *ee*, respectively. Sterically increasing the substituents on either the *ortho* (6,6′) or the *para* (4,4′) positions of the ligand from hydrogen (**1** or **3**), to methyl (**2** or **4**), to *tert*-butyl (**5**) resulted in correspondingly increased enantioselectivities. However, enantioselectivities in the epoxidation reactions were found to plateau for catalysts having substituents larger than *tert*-butyl groups on either position. Strong evidence has been provided previously that the high enantioselectivities observed in epoxidations with methoxy-substituted complexes (e.g. **7**) are due to electronic modulation of the catalyst's reactivity rather than to steric effects.

Discussion

The high enantioselectivities observed in epoxidations with diaminocyclohexane-derived (salen)Mn catalysts has been rationalized according to models involving side-on approach of olefin to the oxo ligand from the direction of the diimine bridge (Fig. 3).[2d, 18–20]

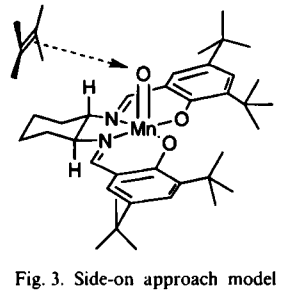

Fig. 3. Side-on approach model for olefin epoxidation with cyclohexanediamine-derived (salen)Mn catalysts.

The structure–enantioselectivity studies summarized in Table 3 are consistent with the notion that, by sterically blocking trajectories of the substrate to the catalyst other than over the chiral diamine backbone, the enantioselectivity of epoxidation is enhanced. Thus, catalyst **1**, which bears no substituents on the salicylidene, effects epoxidation of indene and 6-cyano-2,2-dimethylchromene with only moderate *ee*'s. Competing, unselective pathways involving the approach of the substrate to the metal oxo center over the salicyledene moiety are presumably responsible for the overall lower levels of stereoinduction.

Ligand substituents larger than *tert*-butyl lead, in the absence of additional electronic contributions, to negligible enhancement in enantioselectivities in the corresponding epoxidation

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reactions (e.g., catalysts **5** vs. **6**). It thus appears that the *tert*-butyl is large enough to block side-on approaches other than those over the diimine backbone. The highest observed enantioselectivities, in this case 86% *ee* for indene oxide and 98% *ee* for 6-cyano-2,2-dimethylchromene oxide, may thus reflect the extent to which the diimine bridge biases the substrate approach to the metal oxo center to yield one enantiomer over the other in the absence of competing approaches over other parts of the catalyst.

The solid-state data suggest an explanation for why the *tert*-butyl substituent can so effectively block these competing approaches. Although a precise correspondence between the solid-state and solution structures of these complexes cannot be assumed, it is likely that the range of conformations observed in the solid state reflects a similar degree of flexibility for these ligands in solution. In this context, the greatest variation observed between conformations of similar ligands is in the salicyledene moieties; this indicates that a ligand twisting motion centered around a rigid cyclohexane diimine–metal core is energetically accessible. The effect of this motion might be to enhance the steric properties of the *ortho* and *para* substituents, as suggested in Figure 2. The exaggerated steric influence of these substituents is also evident upon examination of superimposed space-filling models of the corresponding putative Mn^{V} oxo derivatives corresponding to catalysts **5**, **8**, and **9** (Fig. 4). A Mn–O bond length of 1.66 Å was employed in the structures.[21, 22]

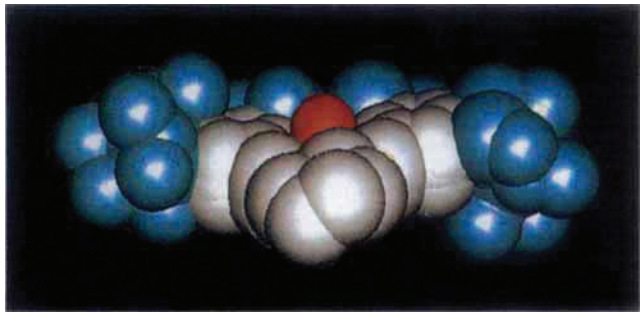

Fig. 4. Superimposed space-filling model of the putative Mn^{V}(salen) oxo intermediate derived from complexes **5** and **8–10**. The solid-state ligand conformations of the Mn^{III}(salen) derivatives were employed, and the manganese–oxygen distance was set to 1.66 Å. This corresponds to an average of reported Mn–O triple bond (1.58 Å) and Mn–O single bond (1.743 Å) lengths (see refs. [20–21]). The basal ligand plane containing the metal, the cyclohexane diimine group, and the salicylide aromatic groups are colored in gray, the bulky ligand substituents are shown in blue, and the oxo ligand is in red.

If the ligand twisting motion proposed above is rapid on the timescale of oxygen-atom transfer, then the reactive intermediate presented to an olefin in epoxidation reactions might indeed be approximated by the structure in Figure 4. The diimine bridge conserves its conformation, and it appears small. As a result, a side-on trajectory for olefin approach to these hindered catalysts is sterically tenable only if it occurs over the diimine bridge. The conformational flexibility of the ligand system may thus play an important role in determining the facial selectivity of olefin oxidation by rendering unselective, competing pathways to the oxo less accessible.

Conclusions

One of the greatest puzzles associated with the (salen)Mn-catalyzed asymmetric epoxidation reaction is that ligands that appear to be almost completely flat can impart such high levels of enantioselectivity with a wide range of substrates. Although the present work does not provide a complete answer to this question, it suggests that the catalysts may in fact be quite flexible conformationally, all within a conserved square planar coordination sphere for the ligand. In this context, we propose that the high degree of stereochemical communication between catalyst and substrate is attributable to the occurrence of a single approach, or a limited range of approaches, of the olefin within a conserved dissymmetric environment consisting of the diimine bridge and the metal oxo moiety.

Experimental Procedure

General Methods: Analytical-thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Flash chromatography was carried out on E. Merck 43–60 μ (230–400 mesh) silica gel. Gas chromatographic (GC) analyses were performed on Hewlett Packard 5890 Series II instruments equipped with FID detectors and Hewlett Packard HP-5 capillary columns. Chiral GC separations were performed using the commercially available Cyclodex-B (30 m × 0.25 mm i.d. × 0.25 μm film; J & W Scientific) capillary column. High-pressure liquid chromatography (HPLC) was performed on a Spectra Physics instrument equipped with a P100 isocratic pump and a UV-100 variable wavelength detector. Enantiomer ratios measured by HPLC were determined with the commercially available columns Chiralcel-OB (Daicel Chemical Industries, Exton, PA). Low resolution EI GC/MS analyses were performed on a Hewlett Packard 5970 Mass Selective Detector coupled to a Hewlett Packard 5890 GC. Melting points were determined by means of a Mel-Temp apparatus and are uncorrected. Karl Fisher titrations were performed on a Photovolt Aquatest CMA titrator and are correct to within $\pm 2.75 \times 10^{-3}$%.

Infrared spectra were recorded on a Mattson Galaxy Series FTIR 3000 spectrometer. Peaks are reported in cm^{-1} with the following relative intensities: s (strong, 67–100%), m (medium, 34–67%), w (weak, 0–34%). ^{1}H NMR spectra were recorded on General Electric QE-300, Bruker AM-500 or AM-400 spectrometers. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: $\delta = 7.26$). Multiplicities are represented as s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), or br (broadened). Coupling constants, *J*, are recorded in Hz. ^{13}C NMR spectra were recorded on Bruker AM-500 (125 MHz) or AM-400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: $\delta = 77.0$). Mass spectra were obtained on a JEOL AX-505 or SX-102 high-resolution magnetic sector mass spectrometer by the Harvard University Mass Spectrometry Laboratory. Elemental analyses were carried out in the Microanalysis Laboratory at the University of Illinois or at QTI, Whitehouse, NJ.

Materials: Petroleum ether, pentane, dioxane, and reagent-grade acetone were used as received from commercial sources. Benzene was distilled from its benzophenone/ketyl solution. CH_3CN and CH_2Cl_2 were distilled from CaH_2. Reagents were used as supplied by Aldrich, Janssen, and Lancaster. The following salicylaldehyde derivatives were prepared by previously reported procedures [4a]: 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 3-*tert*-butyl-2-hydroxy-5-methoxy-benzaldehyde, and 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde. The preparation of catalyst **5** is described elsewhere [4a].

Chloro-[(*R*,*R*)-2,2′-[[(1,2-cyclohexanediyl)bis(nitrilomethylidyne)]bis[phenolato]]-*N*,*N*′,*O*,*O*′]manganese(III) (1): This catalyst was prepared by the published procedure [23]. Brown powder, M.p. > 350 °C; IR (KBr): $\tilde{\nu} = 2945$ (w), 2935 (m), 2859 (m), 1611 (s), 1543 (s), 1467 (m), 1443 (m), 1309 (s), 1285 (m), 1202 (m), 908 (m), 814 (m), 752 (m), 628 (m), 504 (w) cm^{-1}; MS (FAB): 375.0905 [*M* − Cl]$^{+}$; Anal. calcd for $C_{20}H_{20}N_2O_2MnCl \cdot 3/4\,H_2O$ (410.059): C, 56.71; H, 5.12; N, 6.62, Mn, 12.97. Found: C, 56.80; H, 4.73; N, 6.56; Mn, 12.41.

(*R*,*R*)-2,2′-[(1,2-Cyclohexanediyl)bis(nitrilomethylidyne)]bis[4,6-dimethylphenol] (ligand of 2): The requisite salicylaldehyde derivative, 3,5-dimethyl-2-hydroxybenzaldehyde, was prepared by the published procedure [24]. The salicylaldehyde (0.500 g, 3.33 mmol) was dissolved in ethanol (25 mL), and (*R*,*R*)-1,2-diaminocyclohexane (0.190 g, 1.66 mmol, Aldrich, used as received) was added in one portion as a solution in ethanol (20 mL). The resulting yellow solution was heated to reflux for 2 h and then allowed to cool to room temperature. Dichloromethane (200 mL) was added, and the organic phase was washed with brine (100 mL) and dried over anhydrous Na_2SO_4. Solvent was removed by rotary evaporation to afford the salen ligand (0.571 g, 91%) as a yellow solid. M.p. = 91–92 °C; IR (KBr): $\tilde{\nu} = 2935$ (s), 2926 (s), 2859 (s), 1632 (s), 1602 (s), 1476 (s), 1445 (s), 1377 (m), 1269 (s), 1167 (m), 1096 (m), 806 (m), 784 (m), 751 (m), 572 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.68$ (s, 2H), 8.21 (s, 2H), 6.94 (s, 2H), 6.80 (s, 2H), 3.30–3.27 (m, 2H),

2.21 (s, 6H), 2.19 (s, 6H), 1.93–1.86 (m, 4H), 1.71–1.69 (m, 2H), 1.49–1.46 (m, 2H); ^{13}C NMR (106 MHz, $CDCl_3$): δ = 164.7, 156.9, 134.11, 129.1, 127.1, 125.4, 117.7, 72.7, 33.2, 24.2, 20.2, 15.3; MS (FAB): 379.2386 $[M+H]^+$, 378.2307 $[M]^+$; Anal. calcd for $C_{24}H_{30}N_2O_2$ (378.23): C, 76.13; H, 7.99. Found: C, 75.64; H, 8.02.

Chloro[(*R,R*)-2,2′-[(1,2-cyclohexanediyl)bis(nitrilomethylidyne)]bis[4,6-di-methylphenolato]]-*N,N′,O,O′*]manganese(III) (2): To a solution of the ligand (0.960 g, 2.54 mmol) in ethanol (40 mL) was added solid $Mn(OAc)_2 \cdot 4H_2O$ (0.653 g, 2.66 mmol), and the mixture was heated to reflux for 2.5 h. After cooling to room temperature, the mixture was treated with brine (100 mL) and stirred for 1 h. The mixture was then filtered, and the isolated brown solid was washed with several portions of H_2O and redissolved in benzene (50 mL). The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (gradient: CH_2Cl_2 to CH_2Cl_2/ethanol 9:1) to afford a brown solid (0.800 g, 68%). M. p. = 309–310 °C; IR (KBr): $\tilde{\nu}$ = 3010 (w), 2930 (m), 2859 (w), 1614 (s), 1548 (s), 1434 (m), 1383 (w), 1342 (m), 1310 (s), 1257 (m), 1174 (w), 1031 (w), 821 (s), 758 (m), 564 (m), 539 (m) cm^{-1}; MS (FAB): 431.1531 $[M-Cl]^+$; Anal. calcd for $C_{24}H_{28}N_2O_2MnCl$ (466.122): C, 61.79; H, 6.05; N, 6.01; Cl, 7.50; Mn, 11.79. Found: C, 61.13; H, 5.93; N, 5.85; Cl, 7.31; Mn, 11.25.

3-*tert*-Butyl-2-hydroxybenzaldehyde (salicylaldehyde precursor to **3**): A three-neck round-bottom flask equipped with a mechanical stirrer, addition funnel, and a reflux condenser connected to a nitrogen inlet was charged with 2,6-lutidine (4.60 mL, 78.1 mmol), 4-*tert*-butylphenol (9.81 g, 65.1 mmol), $SnCl_4$ (2.28 mL, 19.5 mmol), and toluene (200 mL). The resulting yellow heterogeneous mixture was stirred at room temperature under nitrogen for 10 min prior to the addition of paraformaldehyde (7.82 g, 260 mmol). The mixture was heated under reflux for 4 h, and the reaction progress was monitored by GC. The reaction mixture was allowed to cool to room temperature before the addition of water (200 mL) and ether (200 mL). The resulting emulsion was filtered through a pad of Celite before the layers were separated. The organic layer was washed with water (1 ×), brine (1 ×), dried over anhydrous Na_2SO_4, and then concentrated. Purification by flash chromatography (1:9 EtOAc/hexane) afforded the product as a light yellow oil (5.01 g, 64% yield). ^{1}H NMR ($CDCl_3$): δ = 1.42 (s, 9H), 6.94 (t, 1H, J = 7.7 Hz), 7.39 (dd, 1H, J = 1.4, 7.7 Hz), 7.52 (dd, 1H, J = 1.4, 7.7), 9.86 (s, 1H), 11.8 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 31.2, 34.0, 117.1, 119.9, 129.7, 134.6, 142.6, 159.4, 196.7.

(*R,R*)-2,2′-[(1,2-Cyclohexanediyl)bis(nitrilomethylidyne)]bis[6-(1,1-dimethylethyl)-phenol] (ligand of **3**): To a solution of (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt (418 mg, 1.96 mmol) in 100 mL of EtOH and 5 mL of H_2O was added K_2CO_3 (543 mg, 3.93 mmol). The mixture heated at 70 °C for 10 min. To this solution was added 3-*tert*-butyl-2-hydroxy-5-benzaldehyde, and the resulting yellow mixture was heated at reflux for 30 min. The reaction was cooled to room temperature, and the volume reduced to approximately 50 mL. At that point, H_2O (200 mL) was added to induce the precipitation of the title compound. The yellow precipitate was redissolved in 120 mL of CH_2Cl_2 and washed with 100 mL of brine, 100 mL of distilled water, and dried over anhydrous Na_2SO_4. The drying agent was removed by filtration, and the salen ligand (553 mg, 65% yield) was isolated as a powder after removal of the solvent. IR (CH_2Cl_2): $\tilde{\nu}$ = 2955, 2941, 1630, 1608, 1440, 1360, 1200, 1145, 1084, 853 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.39–1.45 (m, 20H), 1.69–1.95 (m, 6H), 3.17–3.30 (m, 2H), 6.70 (t, J = 7.7 Hz, 2H) 6.98 (dd, J = 1.6, 1.7 Hz, 2H) 7.20 (dd, J = 1.5, 7.7 Hz, 2H) 8.26, (s, 2H). ^{13}C NMR ($CDCl_3$): δ = 24.2, 29.3, 33.1, 34.7, 72.3, 117.7, 118.5, 129.2, 129.8, 137.0, 160.3, 165.5. FAB-HRMS m/z: calcd $C_{28}H_{38}N_2O_2$ 434.2933, found 434.2921.

Chloro-(*R,R*)-[2,2′-[(1,2-cyclohexanediyl)bis(nitrilomethylidyne)]bis[6-(1,1-dimethylethyl)phenolato]]-*N,N′O,O′*]manganese(III) (3): A three-neck round-bottom flask equipped with a reflux condenser, addition funnel, and a septum was charged with the salen ligand (422 mg, 0.964 mmol) and 60 mL of EtOH. The mixture was heated to reflux, and a solution of $Mn(OAc)_2 \cdot 4H_2O$ (496 mg, 2.03 mmol) dissolved in 5 mL of H_2O was added, whereupon the solution immediately turned brown. After refluxing for 30 min, air was bubbled into the solution and reflux was continued for an additional 30 min. Brine (3 mL) was added and the mixture allowed to cool to room temperature. The solvents were removed under vacuum and then 100 mL of CH_2Cl_2 was added. The organic phase was washed with 100 mL of brine and 100 mL of H_2O, and dried over anhydrous Na_2SO_4. Removal of the drying agent followed by concentration of filtrate resulted in a brown powder which was chromatographed ($EtOH/CH_2Cl_2$) to afford the catalyst (410 mg, 87% yield) as a brown solid. M.p. 309.5–310.5 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 2950, 2867, 2360, 2341, 1616, 1594, 1547, 1417, 1391, 1328, 1308, 1292, 1148, 765, 761, 751 cm^{-1}. FAB-HRMS m/z: calcd $C_{28}H_{36}ClMnN_2O_2$ 487.2157 ($M-Cl^+$), found 487.2166 ($M-Cl^+$).

(*R,R*)-2,2′-[(1,2-Cyclohexanediyl)bis(nitrilomethylidyne)]bis[4-methyl-6-(1,1-dimethylethyl)phenol] (ligand of **4**): To a solution of (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt (2.77 g, 13.0 mmol) in water (15 mL) was added potassium carbonate (3.59 g, 26.0 mmol), and the mixture was stirred until dissolution was achieved. Ethanol (60 mL) was added, and 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde (5.00 g, 26.0 mmol) was added as a solid to the resulting solution. The yellow heterogeneous mixture was heated to reflux for 30 min and then allowed to cool to room temperature. The product was collected by filtration and washed with a small portion of 95% ethanol to afford 5.71 g (95% yield) of a fluffy yellow solid. M.p. 134–135 °C; ^{1}H NMR ($CDCl_3$): δ = 13.75 (s, 1H), 8.30 (s, 1H), 7.15 (s, 1H), 6.87 (s, 1H), 3.35 (m, 1H), 2.30 (s, 3H), 2.05–1.78 (m, 4H), 1.52 (s, 9H). ^{13}C NMR ($CDCl_3$): δ = 165.5, 157.9, 136.7, 130.2, 129.7, 126.3, 118.3, 72.3, 34.6, 33.0, 29.4, 24.3, 20.5. Anal. calcd for $C_{30}H_{42}N_2O_2$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.89; H, 9.16; N, 6.04.

Chloro-(*R,R*)-[[2,2′-[(1,2-cyclohexanediyl)bis(nitrilomethylidyne)]bis[4-methyl-6-(1,1-dimethylethyl)phenolato]]-*N,N′O,O′*]manganese(III) (4): A three-neck round-bottom flask equipped with a reflux condenser, addition funnel, and a septum was charged with the salen ligand (503 mg, 1.09 mmol) and 60 mL of EtOH. The mixture was heated at reflux for 10 min before the addition of a solution of $Mn(OAc)_2 \cdot 4H_2O$ (560 mg, 2.28 mmol) dissolved in 5 mL of water. The resulting brown solution was refluxed for 30 min. Reflux was continued for an additional 10 min while air was bubbled into the solution via a syringe. Brine (3 mL) was added to the solution and the mixture refluxed for an additional 30 min. After cooling to room temperature, the mixture was concentrated to remove the EtOH. Methylene chloride (100 mL) and brine (100 mL) were added, and the organic layer separated, washed with distilled water (100 mL), and dried over anhydrous Na_2SO_4. The drying agent was removed by filtration and the mother liquor concentrated to yield a brown solid. The crude catalyst was chromatographed (gradient eluent, CH_2Cl_2 to 10% $EtOH/CH_2Cl_2$) to afford the catalyst (519 mg, 87% yield). M.p. 311.3–312.0 °C. IR (solution): $\tilde{\nu}$ = 3146, 3110, 2949, 2396, 2390, 1614, 1558, 1542, 1431, 1390, 1341, 1307, 1292, 1268, 1207, 1030 cm^{-1}. FAB-HRMS m/z: calcd $C_{30}H_{40}ClMnN_2O_2$ 515.2470 ($M-Cl^+$), found 515.2480 ($M-Cl^+$).

2-Hydroxy-5-triphenylmethyl-3-*tert*-butylbenzaldehyde (salicylaldehyde precursor of **6**): The requisite phenol was prepared by the published procedure [25]. The salicylaldehyde derivative was prepared in 94% yield on a 16 mmol scale by adaptation of the published procedure [4a]. The product was recrystallized from methanol and isolated as a yellow solid, m. p. 189–190 °C; IR (KBr): $\tilde{\nu}$ = 3086 (w), 2991 (w), 2957 (m), 2956 (m), 2911 (m), 2867 (m), 1646 (s), 1492 (m), 1442 (m), 1202 (m), 776 (m), 763 (m), 751(s), 647 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.82 (s, 1H), 9.69 (s, 1H), 7.36–7.18 (m, 17H), 1.27 (s, 9H); ^{13}C NMR (106 MHz, $CDCl_3$): δ = 197.4, 159.6, 146.4, 138.0, 137.5, 133.0, 131.1, 131.0, 127.6, 127.3, 126.2, 119.5, 64.3, 34.9, 29.3; MS (FAB): 421.217 $[M+H]^+$, 420.209 $[M]^+$; Anal. calcd for $C_{30}H_{28}O_2$ C, 85.67; H, 6.72. Found: C, 85.04; H, 7.00.

(*R,R*)-2,2′-[(1,2-Cyclohexanediyl)bis(nitrilomethylidyne)]bis[4-methyl-6-(1,1,1-triphenylmethyl)phenol] (ligand of **6**): The salen ligand was prepared in 88% yield on a 2 mmol scale by adaptation of the published procedure [4a]. Yellow solid, m.p. 199–201 °C; IR (KBr): $\tilde{\nu}$ = 3088 (m), 3085 (m), 2956 (s), 2934 (s), 2861 (m), 1628 (s), 1595 (s), 1492 (s), 1484 (s), 1468 (s), 1369 (m), 1391 (m), 1279 (m), 1203 (m), 1085 (m), 874 (m), 766 (m), 750 (m), 702 (s), 635 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 11.18 (s, 2H), 8.17 (s, 2H), 7.37–7.15 (m, 30H), 7.10 (s, 2H), 6.90 (s, 2H), 3.32–3.28 (m, 2H), 1.71–1.63 (m, 2H), 1.55–1.46 (m, 2H), 1.23 (s, 18H); ^{13}C NMR (106 MHz, $CDCl_3$): δ = 165.6, 158.6, 146.9, 135.9, 133.6, 133.3, 131.3, 131.1, 131.0, 127.6, 127.4, 125.8, 117.4, 72.2, 64.4, 34.8, 33.3, 29.3, 24.2; MS (FAB): 919.520 $[M+H]^+$, 918.512 $[M]^+$; Anal. calcd for $C_{66}H_{66}N_2O_2$ (918.512): C, 86.23; H, 7.24. Found: C, 85.73.; H, 7.00.

Chloro-[(*R,R*)-2,2′-[(1,2-cyclohexanediyl)bis(nitrilomethylidyne)]bis[4-methyl-6-(1,1,1-triphenylmethyl)phenolato]]-*N,N′,O,O′*]manganese(III) (6): The manganese complex was prepared in 64% yield on a 0.5 mmol scale by adaptation of the published procedure [4a]. Brown solid, m.p. 325–326 °C; IR (KBr): $\tilde{\nu}$ = 3056 (w), 3029 (w), 2949 (m), 2867 (w), 1609 (s), 1534 (s), 1431 (m), 1314 (s), 1200 (m), 1189 (m), 870 (m), 711 (s), 702 (s), 573 (w) cm^{-1}; Anal. calcd for $C_{66}H_{70}N_2O_2MnCl$ (1012.45): C, 78.23; H, 6.87; N, 2.77; Cl, 3.45. Found: C, 78.43; H, 6.83; N, 2.93; Cl, 3.16.

(*R,R*)-2,2′-[(1,2-Cyclohexaneanediyl)bis(nitrilomethylidyne)]bis[4-methoxy-6-(1,1-dimethylethyl)phenol] (ligand of **7**): A 25 mL round-bottom flask was charged with (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt (0.125 g, 0.604 mmol), potassium carbonate (83.5 mg, 0.604 mmol), and H_2O (2 mL). The reaction mixture was heated to 60 °C for 10 min before the addition of 2-*tert*-butyl-4-methoxysalicylaldehyde (63 mg, 0.302 mmol) dissolved in 15 mL of EtOH. The solution turned yellow immediately and the mixture was heated to reflux for one additional hour. Volatiles were removed under vacuum and the resulting residue was dissolved in 20 mL of CH_2Cl_2 and 20 mL of H_2O. The organic layer was separated, washed with 20 mL of brine, and then dried over anhydrous Na_2SO_4. The drying agent was removed by filtration and the filtrate was concentrated. A solution of 10% EtOAc/hexane was added to the residue and the resulting solution was passed through a plug of SiO_2 (10% EtOAc/Hexane Rf = 0.44) and concentrated to give a fine yellow powder (0.440 g, 74% yield). M.p. 64–65 °C; IR (CH_2Cl_2): $\tilde{\nu}$ = 2941, 2864, 1633, 1599, 1451, 1432, 1415, 1331, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 1.20–1.41 (m, 20H), 3.26 (s, 2H), 3.66 (s, 6H), 6.46 (d, J = 3.0 Hz, 2H), 6.88 (d, J = 3.0 Hz, 2H), 8.21 (s, 2H), 13.5 (s, 2H). ^{13}C NMR ($CDCl_3$): δ = 24.4, 21.3, 33.2, 35.0, 55.7, 72.5, 111.4, 117.9, 118.3, 138.7, 151.2, 154.8, 165.5. FAB-HRMS m/z: calcd. for $C_{30}H_{42}N_2O_4$ 494.3145, found 494.3156.

Chloro-(*R,R*)-[[2,2′-[(1,2-cyclohexanediyl)bis(nitrilomethylidyne)] bis[4-methoxy-6-(1,1-dimethylethyl)phenolato]]-*N,N′O,O′*]manganese(III) (7): A three-neck round-bottom flask equipped with a reflux condenser, addition funnel, and a septum was

0947-6539/96/0208-0978 $ 15.00+.25/0 Chem. Eur. J. 1996, 2, No. 8

charged with the salen ligand (3.10 g, 6.26 mmol) and 100 mL of ethanol. The solution was heated to reflux as $Mn(OAc)_2 \cdot 4H_2O$ (3.84 g, 15.7 mmol) in 5 mL of H_2O was added slowly. The mixture turned brown. The solution was refluxed for 30 min before LiCl (0.80 g, 18.8 mmol) was added, and the mixture was then heated at reflux for an additional 30 min. Air was then bubbled into the solution, and reflux was continued for 30 min before the mixture was allowed to cool to room temperature. The solvents were removed under vacuum, and then 100 mL of CH_2Cl_2 was added. The solution was washed with 100 mL of brine and 100 mL of H_2O, and then dried over anhydrous Na_2SO_4. The drying agent was removed by filtration and the resulting filtrate was concentrated. The residue was chromatographed (5% EtOH/CH_2Cl_2) to afford the catalyst (2.87 g, 79% yield). M.p. 295.7–296.6 °C; IR (CH_2Cl_2): $\tilde{\nu}$ = 2949, 1618 1544, 1418, 1358, 1341, 1306, 1291, 1209, 1197, 1158, 1061, 821, 745, 734 cm^{-1}. FAB-HRMS *m/z*: calcd $C_{30}H_{40}ClMnN_2O_4$ 547.2369 (M − Cl^+), found 547.2359 (M − Cl^+).

2-*tert*-Butyl-4-triisopropylsiloxyphenol (phenol precursor to **8**): To a solution of *tert*-butylhydroquinone (5.00 g, 30.1 mmol) in CH_2Cl_2 (300 mL) was added imidazole (2.66 g, 39.1 mmol) and *N*,*N*-dimethylaminopyridine (DMAP) (1.84 g, 15.1 mmol). To the resulting solution was added triisopropyl chloride (6.96 g, 36.1 mmol) in 25 mL of CH_2Cl_2 in a dropwise manner, and the mixture was then stirred for 15 h at ambient temperature. The mixture was then filtered, and the solution was concentrated under vacuum. The residue was purified by flash chromatography (2:8 EtOAc/hexane) to yield the product as a clear liquid (8.49 g, 88% yield). B.p. 120 °C/0.2 mm Hg. IR (film): $\tilde{\nu}$ = 2947, 2894, 1607, 1498, 1463, 1221, 965 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.88 (s, 1H), 6.63–6.5 (m, 2H), 3.01 (s, 1H), 1.43 (s, 9H), 1.34–1.24 (m, 3H), 1.16 (dd, J = 7.2, 2.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.1, 148.7, 148.0, 137.2, 118.7, 117.2, 117.0, 38.9, 29.5, 17.9, 12.6; HRMS (FAB): calcd for $C_{19}H_{34}O_2Si$ 322.2328 $[M]^+$, found 322.2325.

3-*tert*-Butyl-2-hydroxy-5-triisopropylsiloxybenzaldehyde (salicylaldehyde precursor to **8**): The same procedure provided above for the synthesis of 3-*tert*-butyl-2-hydroxybenzaldehyde was followed using 7.00 g (19.2 mmol) of the appropriate phenol (2-*tert*-butyl-4-triisopropylsiloxyphenol) and all of the other reagents in the corresponding proportions. After addition of paraformaldehyde, the mixture was maintained at 90 °C for 6 h. Purification of the crude product was effected by flash chromatography (1:30 EtOAc/hexane) to afford 6.25 g (83%) of pure product. IR (film): $\tilde{\nu}$ = 2947, 1868, 1656, 1596, 1464, 1435, 1233, 1148, 1034, 1003, 882 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 9.78 (s, 1H), 7.14 (d, J = 2.9 Hz, 1H), 6.86 (d, J = 2.9 Hz, 1H), 1.28–1.22 (m, 3H), 1.15 (d, J = 7.2 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.6, 155.6, 139.4, 127.5, 127.4, 119.8, 34.7, 29.1, 17.8, 12.5; HRMS (FAB): calcd for $C_{20}H_{34}O_3Si$ 350.2277 $[M]^+$, found 350.2269.

(*S*,*S*)-2,2′-[(1,2-Cyclohexanediyl)bis(nitrilomethylidyne)]bis[4-triisopropylsiloxy-6-(1,1-dimethylethyl)]phenol (ligand for **8**): A 25 mL round-bottom flask was charged with (*R*,*R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt (1.51 g, 7.71 mmol), potassium carbonate (1.52 g, 11.4 mmol), H_2O (11 mL), and EtOH (25 mL). The reaction mixture was heated to 60 °C for 10 min before the addition of 2-*tert*-butyl-4-triisopropylsiloxysalicylaldehyde (4.30 g, 11.4 mmol) as a solution in EtOH (30 mL). The solution turned yellow immediately, and the mixture was heated to reflux for 30 min. The solvent was removed under vacuum, and the resulting residue was dissolved in CH_2Cl_2 (40 mL) and H_2O (40 mL). The organic layer was separated, washed with brine (40 mL), and then dried over anhydrous Na_2SO_4. The drying agent was removed by filtration, the filtrate concentrated, and the titled compound recrystallized from EtOH/H_2O (7.77 g, 73% yield). ^1H NMR ($CDCl_3$): δ = 1.04 (d, J = 5.2 Hz, 36H), 1.09–1.20 (m, 10H), 1.37 (s, 18H), 3.25–3.30 (m, 2H), 6.48 (d, J = 2.9, 2H), 6.85 (d, J = 2.9, 2H), 8.16 (s, 2H), 13.36 (bs, 2H); ^{13}C NMR ($CDCl_3$): δ = 13.4, 18.7, 25.0, 30.1, 33.8, 35.5, 73.1, 119.0, 119.6, 122.9, 138.7, 147.7, 155.3, 166.1; FAB-HRMS *m/z* calcd $C_{46}H_{78}N_2O_4Si_2$ 779.5578, found 779.5558.

Chloro-(*R*,*R*)-[[2,2′-[(1,2-cyclohexanediyl)bis(nitrilomethylidyne)]bis[4-triisopropylsiloxy-6-(1,1-dimethylethyl)phenolato]]-*N*,*N*′,*O*,*O*′]manganese(III) (**8**): A 500 mL round-bottom flask equipped with a reflux condenser, addition funnel, and a septum was charged with the salen ligand (3.00 g, 3.84 mmol) and EtOH (300 mL) and heated to reflux. A solution of $Mn(OAc)_2 \cdot H_2O$ (1.74 g, 7.10 mmol) in H_2O (10 mL) was added dropwise, and the resulting brown mixture was heated at reflux for 30 min. Air was bubbled via a syringe into the solution, and the mixture heated for an addition 30 min. Brine (10 mL) was then added, and the mixture refluxed for 30 min longer. The mixture was cooled to room temperature, and solvents were removed under vacuum. Methylene chloride (200 mL) and brine (100 mL) were added, and the organic layer was separated, washed with distilled water (200 mL), and dried over anhydrous Na_2SO_4. The drying agent was removed by filtration and the solution concentrated to yield a brown powder which was chromatographed (SiO_2, 5:95 EtOH/CH_2Cl_2) to afford the title compound (3.01 g, 91% yield). M.p. 300.1–300.8 °C. IR (CH_2Cl_2): $\tilde{\nu}$ = 2947, 2894, 2868, 1615, 1608, 1538, 1431, 1409, 1354, 1339, 1290, 1231 cm^{-1}; FAB-HRMS *m/z*: calcd $C_{46}H_{76}ClMnN_2O_4Si_2$ 831.4724 (M − Cl^+), found 831.4723 (M − Cl^+).

Perchloro-[(*R*,*R*)-2,2′-[(1,2-cyclohexanediyl)bis(nitrilomethylidyne)]bis[4,6-di-(1,1-dimethylethyl)phenolato]]-*N*,*N*′,*O*,*O*′]manganese(III) (**9**): To a solution of **5** (400 mg, 0.629 mmol, 1 equiv) in dry benzene (50 mL) was added a benzene solution of $AgClO_4$ (150 mg, 0.667 mmol, 1.05 equiv). The reaction mixture was stirred at room temperature for 12 h, filtered over a pad of diatomaceous earth, and evaporated to dryness under vacuum to yield 370 mg of a brown solid (84%). IR (KBr): $\tilde{\nu}$ = 3436–3400 (m, br), 2957 (s), 2908 (m), 2867(m), 1612 (s), 1536 (s), 1433 (m), 1341 (m), 1311 (m), 1251 (m), 1177 (m), 1107 (m), 1025 (m), 839 (m), 779 (w), 751 (m), 578 (m) cm^{-1}. Suitable crystals for X-ray diffraction were obtained under ambient conditions by slow vapor diffusion of benzene (10 mL) into a solution of **9** (15 mg) in dioxane (0.5–1 mL). The dioxane was not purified prior to usage and a Karl Fischer titration of it revealed the presence of 0.5% H_2O (w/w). *Caution: several metal perchlorates have been reported to detonate when shocked and the appropriate precautions are advisable. No incidents were experienced in handling this complex.*

(*S*,*S*)-2,2′-[(1,2-Diphenyl-1,2-ethanediyl)bis(nitrilomethylidyne)]bis[4-bromo-6-(1,1-dimethylethyl)phenol (ligand of **10**): To a stirred suspension of 5-bromo-3-*tert*-butyl-2-hydroxybenzaldehyde (2.50 g, 9.70 mmol) in ethanol (20 mL) was added a solution of (*S*,*S*)-diphenylethylenediamine (1.03 g, 4.85 mmol, Aldrich, used as received). The reaction mixture was heated to reflux for 1 h and then allowed to cool to room temperature. Product isolation was effected by inducing precipitation by addition of water (200 mL), filtration, and air-drying overnight. Product (3.25 g, 97%) was obtained as a yellow solid, m.p. 124–125 °C; IR (KBr): $\tilde{\nu}$ = 2960 (s), 2872 (s), 1629 (s), 1601 (s), 1483 (s), 1469 (s), 1452 (s), 1392 (s), 1303 (s), 1172 (s), 906 (s), 869 (s), 775 (s), 697 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.78 (s, 2H), 8.21 (s, 2H), 7.34 (d, J = 2.4 Hz, 2H), 7.24–7.16 (m, 10H), 7.05 (d, J = 2.5 Hz, 2H), 4.69 (s, 2H), 1.40 (s, 18H) ; ^{13}C NMR (106 MHz, $CDCl_3$): δ = 165.7, 159.2, 139.9, 138.7, 132.6, 131.8, 128.4, 127.9, 119.7, 109.9 80.0, 35.0, 29.0; Anal. calcd for $C_{36}H_{36}N_2O_2Br_2$ (688.47): C, 62.80; H, 5.27; N, 4.07; Br, 23.21. Found: C, 62.61; H, 5.40; N, 4.02; Br, 23.40.

Chloro-(*S*,*S*)-[[2,2′-[1,2-diphenyl-1,2-ethanediyl)bis(nitrilomethylidyne)]-bis[4-bromo-6-(1,1-dimethylethyl)phenolato]]-*N*,*N*′,*O*,*O*′]manganese(III) (precursor to **10**): To a stirred suspension of the ligand (3.00 g, 4.36 mmol) in ethanol (180 mL) was added solid $Mn(OAc)_2 \cdot 4H_2O$ (2.14 g, 8.71 mmol), and the resulting mixture was heated to reflux for 30 min. After the reaction had been allowed to cool to room temperature, a 10% w/v aqueous solution of NaCl (60 mL) was added, and the resulting mixture was stirred for 30 min. Product precipitation was induced by the dropwise addition of water. The brown solid was isolated by filtration and washed with 30% ethanol to afford 4.2 g of crude material. Purification was effected by flash chromatography (CH_2Cl_2/ethanol 9:1) to provide 2.93 g (86%) of product. M.p. 325–26 °C; IR (KBr): $\tilde{\nu}$ = 2957 (m), 1619 (s), 1584 (s), 1530 (s), 1424 (s), 1403 (s), 1026 (w), 778 (m), 734 (s), 576 (m) cm^{-1}; Anal. calcd for $C_{36}H_{36}N_2O_2Br_2MnCl$ (776.84): C, 55.66; H, 4.41; N, 3.61; Br, 20.57; Cl, 4.56, Mn, 7.07. Found: C, 55.61; H, 4.48; N, 3.56; Br, 20.48; Cl, 4.51; Mn, 6.79.

Tetrafluoroboro-(*S*,*S*)-[[2,2′-[1,2-diphenyl-1,2-ethanediyl)bis(nitrilomethylidyne)]-bis[4-bromo-6-(1,1-dimethylethyl)phenolato]]-*N*,*N*′,*O*,*O*′]manganese(III) (**10**): To a solution of **5** (100 mg, 0.129 mmol, 1 equiv) in CH_3CN (40 mL) was added a solution of $AgBF_4$ (30 mg, 0.0.154 mmol, 1.2 equiv) in 10 mL CH_3CN. The reaction mixture stirred at room temperature for 24 h, filtered over a pad of diatomaceous earth and evaporated to dryness under vacuum. The solid was washed with distilled H_2O (60 mL) to remove the excess $AgBF_4$. The brown solid was filtered and air dried, and 70 mg were recovered (67%). M.p. 245–246 °C; IR (KBr): $\tilde{\nu}$ = 3484–3384 (m, br), 2956 (m), 2910 (m), 1611 (s), 1531 (s), 1425 (m), 1404 (m), 1299 (s), 1175 (s), 1026 (m), 779 (w), 735 (s), 687 (m), 576 (m) cm^{-1}.

Epoxidation Reactions—General: Authentic, racemic indene oxide and 6-cyano-2,2-dimethylchromene oxide were prepared using racemic Mn(salen) catalyst **5**. The pH of a solution of commercial household bleach (Clorox) was buffered to pH = 11.3 with 0.05 M Na_2HPO_4 and 1 M NaOH and then cooled to 0 °C (approx. 0.55 M in NaOCl). Conversions of olefin and epoxide yields were established by GC and quantified versus dodecane as the internal standard.

Epoxidation of indene: To magnetically stirred solutions of indene (30 mg, 0.257 mmol), dodecane (44 mg, 0.257 mmol), 4-phenylpyridine *N*-oxide (4-PPNO) (4.4 mg, 0.0257 mmol, 0.1 equiv) in CH_2Cl_2 cooled to 0 °C was added 100 μL of a 0.051 mM stock solution of Mn(salen) catalyst (2 mol%) (**1**–**10**). Cold, buffered NaOCl (1 mL, 0.55 mmol, 2.1 equiv) was added, and the reaction mixtures were stirred for 14 h at 0 °C. The reaction mixtures were passed through plugs of Celite with excess CH_2Cl_2 so as to remove the decomposed catalyst and 4-PPNO. Conversions were 40% for **1**, 57% for **2**, and 100% for **3**–**10**. Epoxide yields were 28% (**1**), 29% (**2**), and 67–85% (**3**–**10**). The *ee*'s were analyzed by HPLC (Chiralcel-OB, UV detector λ = 225 nm, hexane/EtOH (95:5), flow rate 1 mL min^{-1}).

Epoxidation of 6-cyano-2,2-dimethylchromene: To magnetically stirred solutions of 6-cyano-2,2-dimethylchromene (48 mg, 0.257 mmol), dodecane (44 mg, 0.257 mmol), 4-phenylpyridine *N*-oxide (4.4 mg, 0.0257 mmol, 0.1 equiv) in CH_2Cl_2 cooled to 0 °C was added 100 μL of a 0.051 mM stock solution of Mn(salen) catalyst (2 mol%)(**1**–**10**). Cold, buffered NaOCl (1 mL, 0.55 mmol, 2.1 equiv) was added, and the reaction mixtures were stirred for 14 h at 0 °C. The reaction mixtures were passed through plugs of silica with excess CH_2Cl_2. Conversions were 30% for **1** and 70–100% for **3**–**10**. Epoxide yields were 30% for **1** and 60–95% for **3**–**10**. The *ee*'s were analyzed by chiral GC (Cyclodex-B, 140 °C isothermal temperature).

X-ray analyses of complexes 5, 8–10 [26]: Structures **5**, **8**, **9** were acquired on a Siemens P4 diffractometer fitted with a Siemens low-temperature attachment ($Mo_{K\alpha}$ radiation, $2\theta_{max}$ 52°, absorption correction based upon ψ scans). The structure for **10** was acquired on a Siemens P3 diffractometer ($Mo_{K\alpha}$ radiation, $2\theta_{max}$ 45°, absorption correction based upon ψ scans). Structures **5**, **8–10** were solved by the heavy-atom method and refined anisotropically on F^2 (SHELXL-93 program, G. M. Sheldrick, University of Goettingen). H atoms were included by using a riding model.

For **5**: Single dark brown crystals appropriate for diffraction experiments were obtained by slow vapor diffusion of 15 mL of petroleum ether (b.p. 20–40 °C) into a solution of (*R,R*)-**5** (10 mg) in acetone (0.5–1 mL). Under ambient conditions crystals formed over two days. A brown needle (crystal dimensions 0.6 × 0.5 × 0.1 mm) was mounted on a glass fiber using epoxy resin. A total of 9368 intensities, all of which were independent, were collected. The final $wR(F^2)$ value was 0.134, with conventional $R(F)$ = 0.053, for 757 parameters and 3 restraints.

For **9**: A brown rectangular crystal of (*R,R*)-**9** (dimensions 0.4 × 0.6 × 0.4 mm) was mounted on a glass fiber using epoxy resin. A total of 18351 intensities, of which 18072 were independent, were collected. The final $wR(F^2)$ value was 0.1250, with $R(F)$ = 0.0608, for 1143 parameters using 9544 reflections.

For **8**: (*R,R*)-**8** crystallized from acetone/pentane by slow vapor diffusion over 5 days under ambient conditions. A brown rectangular crystal (dimensions 0.6 × 0.4 × 0.2 mm) was mounted on a glass fiber using epoxy resin. A total of 9647 intensities, of which 9615 were independent, were collected. The 32 nonindependent reflections were attributed to crystal defects. The final $wR(F^2)$ value was 0.1430, with conventional $R(F)$ = 0.0524, for 1007 parameters and 0 restraints.

For **10**: Crystals for X-ray diffraction were obtained under ambient conditions by slow evaporation of a solution of (*S,S*)-**10** (20 mg) in benzene (1 mL) in an NMR tube over two months. A brown rectangular crystal (dimensions 0.4 × 0.6 × 0.4 mm) was mounted on a glass fiber using epoxy resin. A total of 5215 intensities, of which 4813 were independent, were collected. The final $wR(F^2)$ value was 0.1192, with $R(F)$ = 0.0676, for 347 parameters using 2368 reflections.

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