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Liquid crystalline salen manganese(III) complexes. Mesomorphic and catalytic behaviour[†]

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Several salen manganese(III) complexes displaying stable columnar mesophases in a wide range of temperatures have been synthesized. In condensed phases the molecules are assembled into dimers through intermolecular manganese–oxygen interactions and the columnar structure of the mesophases consist of the stacking of supramolecular discs formed by the association of two or three dimers, depending on the number and location of alkoxy chains in the complex. The catalytic activity of the complexes in solution has been studied, and they behave as efficient homogeneous catalysts in the epoxidation of styrene with iodosylbenzene as oxidant.

Introduction

Metal complexes that give rise to liquid crystal phases (metallomesogens) have been systematically investigated in the past decades and constitute nowadays a classic field in the area of materials science.1 Many studies have been carried out showing that metallomesogens can display physical properties such as thermochromism,² nonlinear optical behaviour,³ magnetism,⁴ luminescence,⁵ or photosensitivity in the mesophase,⁶ which make them interesting candidates for various applications. Many metals and oxidation states of the periodic table have been used to prepare metallomesogens, but the number of liquid crystals based on manganese(III) is limited to tris(diketonate) derivatives,⁷ tetraphenylporphyrin compounds,⁸ and a family of calamitic bidentate Schiff base derivatives $[MnCl(L)_2]$ (L = N-alkyl[4-(4-decyloxybenzoyloxy)]salicylaldiminato) that display smectic and/or nematic mesophases.9 Tetradentate Schiff bases (salentype ligands) have been also used as ligands to produce interesting liquid-crystalline transition metal complexes,¹⁰ and also complexes that are efficient catalysts for a wide variety of processes,^{11,12} including epoxidation of alkenes in different conditions.^{13,14} Enantioselective epoxidation of unfunctionalized olefins using chiral Mn(III)-salen complexes have been also reported.¹⁵

Discotic liquid crystals producing columnar mesophases are interesting in the design of materials that can display interesting electronic properties, for instance high charge carrier mobility along the columnar stacks.¹⁶ Liquid crystalline salen manganese(III) complexes affording columnar mesophases have not yet been reported. We report here the synthesis of hemidiscotic- and polycatenar-like metallomesogens based on salenmanganese(III) complexes, namely dodecacatenars bearing dodecyl or chiral dimethyloctyl chains. In addition, similar salen manganese complexes with the dialkoxy-o-phenylenediamine ligand, which would more properly be considered as discotic, have also been obtained. Both types of complexes display columnar mesophases formed by self-assembling of dimer aggregates, and are efficient homogeneous catalysts in epoxidation of styrene.

Results and discussion

Synthesis and characterization

The synthesis of the ligands and their complexes is shown in Scheme 1. The Schiff bases, H_2L^n , were synthesized by condensation of 3-formyl-4-hydroxyphenyl-3,4,5-tris(dodecyloxy)benzoate or 3-formyl-4-hydroxyphenyl-3,4,5-tris[(*S*)-3,7-dimethylocty-loxy]benzoate with the appropriate diamine. The manganese complexes [MnXLⁿ] (X = Cl, Br) were prepared by refluxing a solution of the corresponding diimine with manganese(II) acetate in ethanol under aerobic conditions, as reported for similar complexes.¹⁷ They were isolated as brown waxy solids. Enantiomerically pure complexes were obtained introducing a chiral element either in the starting diamine ([MnClL³] and [MnClL⁷]) or in a chain of the starting acid (R^b in [MnClL⁵]).

C, H, N analyses for the complexes, yields, and relevant IR data are given in the supplementary information.† The IR spectra of the metal complexes display the characteristic v(C=N) band from the imine groups in the range 1603–1629 cm⁻¹ at higher wavenumbers than for the free ligand, as a consequence of coordination.¹⁸ The UV-Vis spectra show two or three broad bands in the range 244–480 nm, as reported for related manganese complexes.^{18,19}

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Scheme 1 Synthesis of manganese(III) complexes [MnXLⁿ]. The chiral complexes are indicated by (*).

Mesomorphic behaviour

All the manganese compounds prepared are thermotropic liquid crystals and display columnar mesophases, as could have been expected due to the large number of peripheral divergent chains. The mesophases were studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and small angle X-ray scattering (SAXS). The optical, thermal and thermodynamic data are collected in Table 1.

The optical textures observed with a polarizing microscope for [MnClLⁿ] (n = 1-5) and for [MnBrL⁴], upon cooling from the isotropic liquid, providing a short stay in the isotropic liquid or in its vicinity to avoid extensive decomposition, are compatible with hexagonal columnar mesophases and display linear birefringent defects, large areas of uniform extinction, and fan domains (Fig. 1).²⁰ However, for [MnClLⁿ] (n = 6, 7) only a weak birefringence

 $\label{eq:Table 1} \begin{array}{l} \textbf{Table 1} & \textbf{Optical, thermal and thermodynamic data of the salen-Mn complexes} \end{array}$

Compound	Transition ^a	Temperature ^{<i>b</i>} (°C)	$\Delta H^{b} (\mathrm{kJ}\mathrm{mol}^{-1})$
MnClL ¹	$Cr \rightarrow Cr'$	55	0.6
	$Cr' \rightarrow Col_h$	84 ^d	6.9
	$\operatorname{Col}_{h} \to \operatorname{I}(\operatorname{dec})$	180 ^c	
MnClL ²	$Cr \rightarrow Col_h$	71 ^d	3.3
	$\operatorname{Col}_{h} \to \operatorname{I}(\operatorname{dec})$	170^{c}	
MnClL ³	$Cr \rightarrow Col_h$	80^{d}	6.2
	$\operatorname{Col}_{h} \to \operatorname{I}(\operatorname{dec})$	170^{c}	
MnClL ⁴	$Cr \rightarrow Cr'$	48	3.8
	$Cr \rightarrow Col_{h}$	68 ^d	3.1
	$\operatorname{Col}_{h} \to \operatorname{I}(\operatorname{dec})$	190 ^c	
MnBrL ⁴	$Cr \rightarrow Col_{h}$	77 ^d	17.6
	$\operatorname{Col}_{h} \to \operatorname{I}(\operatorname{dec})$	170^{c}	
MnClL ⁵	$\operatorname{Col}_{h} \to \operatorname{I}(\operatorname{dec})$	190 ^e	
MnClL ⁶	$Cr \rightarrow Col_r$	75 ^d	8.3
	$\operatorname{Col}_r \to \operatorname{I}(\operatorname{dec})$	190 ^c	
MnClL ⁷	$\operatorname{Col}_{h} \to \operatorname{I}(\operatorname{dec})$	150 ^c	

^{*a*} Cr, crystal; Col_h, columnar hexagonal; Col_r, columnar rectangular; I, isotropic liquid. ^{*b*} Data from the first heating scans. ^{*c*} Optical microscopy data. ^{*d*} The transitions are very broad and data refer to the peak temperature.



Fig. 1 Polarized optical microscopic texture (\times 100) observed for [MnClL²] at 150 °C, upon cooling from the isotropic liquid. The microphotography was taken in the cooling cycle of a sample that had been quickly heated to isotropic liquid (175 °C) in order to minimize decomposition.

could be observed upon mechanical shear, precluding mesophase assignment.

All the compounds show wide mesophase temperature ranges (*ca.* 100 °C). In general the mesophases freeze at low temperatures, but the exact moment of the fluid-to-solid transition is difficult to detect, whether optically or thermally (no peak is detected by DSC either), suggesting that the material is frozen retaining the order of the mesophase (since this is not a long range order we will refer to it as a glass liquid crystal state). All the compounds undergo some decomposition upon reaching the clearing point to the isotropic state (about 170–190 °C), possibly due to the high temperature at which this clearing happens. However, samples in the glass state free of decomposition can be obtained from the mesophases avoiding to heat close to the melting point.

It is noticeable that the melting enthalpy of [MnBrL⁴] is significantly larger than that of [MnClL⁴] in spite of the fact that it is out of the question that they produce the same kind of phase (see later). This could be due in part to differences in the starting



Fig. 2 Successive photographs of the evolution of a contact experiment showing the miscibility of the hexagonal columnar mesophase of [MnClL⁴] and that of [MnClL³]. (a) Separated mesophases at 125 °C on heating; (b) Contact preparation at 125 °C on heating; (c) Contact preparation at 130 °C on cooling from the isotropic liquid.

crystalline phase, and also the effect of changing the polarizability and dipolar moment of the molecule upon changing the halide ligand.

X-Ray diffraction experiments

Temperature-dependent X-ray diffraction experiments were systematically carried out in order to unambiguously identify the nature of the mesophase. The X-ray patterns of the MnCIL⁴, MnBrL⁴ and MnClL⁵ complexes, recorded between 50 °C and 120 °C, exhibited three sharp and intense small angle diffraction peaks with a reciprocal d spacing in a 1: $\sqrt{3}$: $\sqrt{4}$ ratio. In addition, a strong and diffuse halo at 4.5 Å was observed (Fig. 3). These features are unambiguously assigned to the (10), (11) and (20) reflections of a columnar phase with a hexagonal lattice and to the liquid-like order of the molten alkoxy chains, respectively, in agreement with the POM observations. The other complexes of the same series ([MnClLⁿ], $X = Cl, L^n = L^1, L^2, L^3$), except [MnCIL⁷] displayed the same textures, and similar diffraction patterns, although only one maximum was observed, suggesting hexagonal columnar packing. The hexagonal columnar nature of the mesophases of [MnXLⁿ] ($X = Cl, L^n = L^1, L^2, L^3$) was further supported by their miscibility with [MnClL⁴] (Fig. 2). In contrast, [MnClL⁷] was not miscible with [MnClL⁴]. This result did not allow us to identify the type of mesophase unambiguously. Finally, for [MnClL⁶], X-ray diffraction revealed two sharp small-angle reflections, indicating the formation of a columnar rectangular phase. The absence of additional higher order reflections considerably limits absolute mesophase assignment, although, the centred c2mm planar symmetry will be considered thereafter as the highest symmetry allowed, with a possible two sets of lattice parameters (a = 79.0/83.2 and b = 44.9/48.9 Å at 150 °C), which cannot be discriminated. Structural data from X-ray diffraction experiments are collected in Table 2.

As for other related polycatenar metallomesogens,²¹ the supramolecular organisation of the Mn complexes into columnar mesophases results in the present case from the increasing volume of the terminal chains not being accommodated by an increasing tilt of the molecular core (in a layer structure configuration), and thus limiting long-range lateral molecular ordering (breaking of the layers). Consequently, molecules will tend to self-associate into discrete molecular aggregates to form the basic unit of the supramolecular columnar stack. Furthermore, as far as the present systems are concerned, the structure of related compounds in the solid state consists of dimers formed by manganese–oxygen



Fig. 3 XRD pattern of [MnClL⁵] recorded at 100 °C.

interactions (Fig. 4).^{22,23} Consistent with this, the mass spectrum of **[MnClL¹]** shows the parent peak (1667.103 [M⁺]) corresponding to a dimeric aggregate. Consequently we suggest as a basic structural model that the dimer is likely preserved in the mesophase, and thus will constitute the elementary molecular entity, whose mean thickness is approximately in the range of 10 to 13 Å, depending on the substituents and the diamine bridge (Fig. 5).



Fig. 4 Dimeric structure of salen-Mn complexes formed *via* manganese–oxygen interactions.

Provided that this correct periodicity along the column, *h*, is known, the effective number of molecules or molecular equivalents (*N*) can be determined by the relationship between the columnar cross-section area (*S*) and the molecular volume (V_{mol}), according to the geometric relationship $hS = NV_{mol}$ (note that for *h* arbitrarily chosen to be equal to unity, the number of molecular equivalents is given per unit length *i.e.* per Å, and is appreciated as a linear density).²⁴ If the average thickness of the dimeric structure is considered as being of the same magnitude order of the main periodicity along the column, arbitrarily considered as 10 Å \leq

Table 2	Structural	data	from	X-ray	diffraction	experimen
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Compound	Indexation					
T/°C	$d_{ m meas}$ /Å ^{<i>a</i>}	hk ^b	I ^c	$d_{\rm calc}/{ m \AA}^a$	Parameters ^{d,e}	
MnClL ¹	35.66	10	VS (sh)	35.66	a = 41.18 Å	
100	4.6		VS (br)	$h_{ m ch}$	$S = 1468 \text{ A}^2$ $V_{\text{mol}} = 2828 \text{ Å}^3$	
MnClL ²	35.83	10	VS (sh)	35.83	N = 6 for h = 11.56 A a = 41.37 Å	
	4.7		VS (br)	$h_{ m ch}$	$S = 1482 \text{ Å}^2$	
120					$V_{\rm mol} = 2917 {\rm \AA}^3$	
M CH 3	20.00	10		20.00	N = 6 for $h = 11.81$ A	
MnClL ³	38.09	10	VS (sh)	38.09	a = 43.98 A	
100	4.6		VS (br)	$h_{ m ch}$	$S = 16/5 A^2$	
100					$V_{\rm mol} = 291 / A^2$ N = 6 for h = 10.45 Å	
MnCII 4	30.81	10	VS (sh)	30.84	$N = 0.101 \ h = 10.43 \ \text{A}$	
MICIL	17.85	10	$V_{\rm S}(\rm sh)$	17.81	u = 55.01 A S = 1008 Å ²	
100	15.4	20	M(sh)	15.42	S = 1098 A $V = -3520 \text{ Å}^3$	
100	15.4	20	VS(br)	13.42 h	$V_{\rm mol} = 5520$ A N = 4 for $h = 12.81$ Å	
MnBrI ⁴	31.02	10	VS(01) VS(sh)	n_{ch}	n = 4101 n = 12.01 A a = 35.88 Å	
MIDIL	17.93	10	\mathbf{S} (sh)	17.94	u = 55.00 A S = 1115 Å ²	
100	15 57	20	M(sh)	15.53	$V = 3593 \text{ Å}^3$	
100	4.6	20	VS (br)	h.	N = 4 for $h = 12.90$ Å	
MnCIL ⁵	29.11	10	VS (sh)	29 05	a = 3355 Å	
MILCIE	16.81	11	M(sh)	16 77	$S = 975 \text{ Å}^2$	
100	14 47	20	W (br)	14 53	$V_{\rm max} = 3240 \text{ Å}^3$	
100	4.6		VS (br)	h.	N = 4 for $h = 13.3$ Å	
MnClL ⁶	41.6	11/20	VS (sh)	41.6	$a = 79 \text{ Å}; b = 48.9 \text{ Å}; S = 1933 \text{ Å}^2$	
	39.5	20/11	VS (br)	39.5	$a = 83.2 \text{ Å}; b = 44.9 \text{ Å}; S = 1867 \text{ Å}^2$	
150	4.5		. 2 (11)	$h_{\rm ch}$	$V_{\rm mol} = 2828 \text{ Å}^3$	
MpCII 7	40.55	10	VS (ch)	40.55	N = 8 for $h = 11.7 - 12.1$ A	
MICIL	40.55	10	VS(SII) VS(br)	40.55 h	u = 40.8 A S = 1899 Å ²	
100	т		v 5 (01)	<i>n</i> _{ch}	$V = 3104 \text{ Å}^3$	
100					N = 6 for 9.8 Å	
					N = 8 for $h = 13.0$ Å	
					n = 0.101 m = 15.071	

^{*a*} d_{meas} and d_{cule} stand for measured and calculated periodicity. ^{*b*} Miller indices, *hk*. ^{*c*} I corresponds to the intensity of the reflections (VS: very strong, M: medium; br and sh stand for broad and sharp); h_{ch} represents the molten chain short-range distance. ^{*d*} Phase parameters: Col_h, intercolumnar distance, $a = 2 \times [\Sigma d_{hk} \sqrt{(h^2 + k^2 + hk)}]/N_{hk} \sqrt{3}$; number of reflections, N_{hk} ; columnar cross-section of the hexagonal cell, $S = \frac{1}{2}a^2\sqrt{3}$; Col_r, $1/d_{hk} = \sqrt{((a/h)^2 + (b/k)^2)}$; columnar cross-section in the rectangular cell, $S = a \times b/2$; V_{mol} , molecular volume, is determined considering a density of 1 according to MW/(6.022.10^{23})(10^{-24}), where MW is the molecular weight. The repeating columnar unit *h* is related to the molecular volume and the cross-section columnar area by the relationship $N \times V_{\text{mol}}/S$, where *N* is the number of molecular equivalent per repeat unit (in this case, to maintain the density along the column constant, *N* must be an integer or half-integer). ^{*c*} The parameters given for MnClL⁷ have been calculated on the assumption that their mesophases were hexagonal columnar (see text).

 $h \le 13$ Å, the number of dimers ($N_{\rm D} = N/2$) constituting the supramolecular disc of all complexes can be determined. Recall, nevertheless, that no specific signs have been observed in the XRD patterns, due to the liquid-like order within the columns, but such an approximation is helpful in the understanding of the molecular packing.

The X-ray data of compounds [MnClLⁿ] ($L^n = L^1$, L^2 , L^3) are consistent with a disc formed by three pairs in order to fully pave the hexagonal net, whilst for the bulkier [MnXL⁴] (X = Br, Cl), and [MnClL⁵] the discs are made of two dimers (larger assemblies seem unfavourable because of the lateral chains) assembled backto-back. For the latter, the compounds have eight alkoxy chain per metal center surrounding the molecular core, and give rise to a dimer with a discotic shape, however not planar: these dimeric molecules could easily pack as two dimers in a complementary arrangement, so as to make a disk (Fig. 5).

The incorporation of the very bulky *tert*-butyl group at the C5and C5'-positions of the salicylidene ligand [MnClL⁷] produces a substantial increase in the hexagonal lattice parameter (a) and as a consequence, for the same columnar thickness, the number of dimers arranged side-by-side is increased in order to pave the larger surface area.

Finally, the case of [MnClL⁶], which is an isomer of [MnClL¹] with the benzoate substituent groups in C4 and C4' positions of the salicylidene ligand, deserves some comments: the bent polycatenar structure of [MnClL⁶] differs significantly from that of [MnClL¹] (Fig. 6), which has the benzoate substituents groups arranged straight along the molecular axis (C3 and C3' positions of salicylidene group). As for their homologous vanadyl complexes,^{21a} they possess similar thermal behaviour, but the symmetry of the mesophase is changed. The multipolar structure of these complexes is not so easy to analyze, but it looks reasonable that the bent structure should be more polar and with stronger core interactions, which should produce a more efficient molecular stacking.25 For a corresponding thickness along the column, again chosen arbitrarily for comparison sake, now four dimers are required to pave the surface area of the rectangular lattice, which is also in agreement with the important increase in the columnar



Fig. 5 Schematic molecular model for the mesophase structure of Mn complexes.



Fig. 6 Structural differences between [MnClL⁶] and [MnClL¹] complexes.

cross-section area (*ca*. 25%), from 1468 Å² for [MnClL¹] to *ca*. 1900 Å² for [MnClL⁶]. At this stage, and due to the limited information gained from X-ray diffraction, the exact details of the intimate supramolecular ordering within the columns cannot be proposed further.

Finally, insertion of chiral chains (**MnClL⁴** *versus* **MnClL⁵**) or chiral diamine (**MnClL²** *versus* **MnClL³**) in the various molecular structures has no or little effect on the thermal behaviour, and no sign of chiral phases was detected.

 Table 3
 Catalytic results in the epoxidation of styrene catalyzed by chiral catalysts, in acetonitrile and using iodosylbenzene as oxidant

Entry	Catalyst (3.4-mol%) (hexane solution)	Yield (%) ^a	ee (%) ^a
Blank	_	0	_
1	[MnClL ³]	68	2
2	[MnClL ⁵]	78	2
3	[MnClL ⁷]	89	11

^{*a*} Determined by GC on a LIPODEX-E chiral column. ee values are given for the major enantiomer (Rt = 11.4 min).

Catalytic behaviour

Salen-manganese(III) complexes are efficient catalysts in the oxidation of olefins to epoxides.²⁶ The catalytic activity of [**MnClL**²] was studied in the epoxidation of styrene with iodosylbenzene in acetonitrile (Scheme 2), under liquid–liquid biphasic conditions using a solution of the catalyst in hexane (which is immiscible with acetonitrile). The epoxidation of styrene proceeded in moderate yield (60% GC yield after 24 h) with a catalyst loading of 3.4 mol%. A blank test showed that no reaction occurs without catalyst under the same conditions.

The potential of the complexes for enantioselective epoxidations of alkenes under the same conditions, using chiral catalysts, was tested on [MnCIL³], [MnCIL⁵] and [MnCIL⁷]. The results are shown in Table 3. The three catalysts produced good yields but, unfortunately, no enantioselectivity was found for [MnCIL³] or [MnCIL⁵]. Even for [MnCIL⁷], which bears bulky *tert*-butyl substituents at C5- and C5'-positions of the salicylidene ligand (as usually required to induce enantioselectivity),²⁷⁻²⁹ only poor enantiomeric excess was observed (Table 3, entry 3). Similar yields and low enantioselectivities have been reported for catalytic epoxidations of styrene with related polymeric chiral Mn(III) complexes,³⁰ and for biphasic epoxidation of 1,2-dihydronaphthalene with iodosylbenzene in the presence of pyridine *N*-oxide and chiral(salen)manganese complexes bearing six perfluoroalkyl substituents.³¹

The induction of enantioselectivity in the epoxidation of unfunctionalized olefins highly depends on the proximity of the stereocenters to the active catalytic centre, thus one could expect higher enantioselectivity with [MnClL⁷] (as observed) and [MnClL³] (which is not observed). This difference in favour of the former might be associated to the presence in L⁷ of a bulky substituent, which was meant for this purpose as said before.

In summary, we have prepared metallomesogens based on salen-Mn(III) complexes, which display columnar mesophases in a wide range of temperatures, varying in the nature of the chains (dodecyl and dimethyloctyl), the nature of the diamine (ethenediamine, cyclohexene diamine, and dialkoxybenzene amine) and shape



catalyst = [MnCIL²] (3.4 mol %); Epoxide yield: 60 %

Scheme 2 Epoxidation of styrene with iodosylbenzene in acetonitrile, under liquid–liquid biphasic conditions, using a solution of the Mn catalyst in hexane.

(linear versus bent). These modifications hardly modify the overall mesomorphic behaviour of the samples. The columnar structures of the mesophases have been determined by X-ray diffraction experiments. The columnar structure consists of the staking of discs formed by either four or six molecules of the complexes, associated into dimers through intermolecular manganese–oxygen interactions, two or three (respectively) of these dimers in each disc. Their catalytic activity has been studied and they behave as efficient catalysts in the epoxidation of styrene with iodosylbenzene as oxidant.

Experimental section

Experimental conditions for the analytical, spectroscopic and diffraction studies were as reported elsewhere.³² Mass spectra were recorded on an MicroTOF, Bruker Daltonics. Analytical gas chromatography was performed on a Hewlett Packard 5890 Series II machine, equipped with a LIPODEX-E (25 m \times 0.25 mm \times 0.40 mm) capillary chiral column. The retention times were: for styrene: t = 2.2 min; for styrene epoxides: $t_1 = 9.7$ min, $t_2 = 11.4$ min. GC: isotherm at 90 °C. Literature methods were used to prepare iodosylbenzene,³³ *tert*-butyl-2,5-dihydroxybenzaldehyde,³⁴ 1,2-bis(dodecyloxy)-4,5-diaminobenzene,³⁵ and (S)-3,7-dimethyloctylbromide.³⁶

Synthesis of salen ligands (H₂L)

All salen-type ligands were synthesized similarly to that described for 4-hydroxy-3-[($\{2-[((E)-\{2-hydroxy-5-[(3,4,5-trido-decyloxybenzoyl) oxy] phenyl\}methylidene) amino] ethyl} imino) - methyl]phenyl 3,4,5-tris(dodecyloxy)benzoate (<math>H_2L^1$),³⁷ starting from 3-formyl-4-hydroxyphenyl-3,4,5-tris(dodecyloxy)benzoate, 4-formyl-5-hydroxyphenyl-3,4,5-tris(dodecyloxy)benzoate or 3-formyl-5-*tert*-butyl-4-hydroxyphenyl-3,4,5-tris[dodecyloxy] benzoate and the corresponding diamine. A typical procedure is as follows:

To a solution of 3-formyl-4-hydroxyphenyl-3,4,5-tris(dodecyloxy)benzoate (1.28 g, 1.61 mmol) in 100 mL of toluene was added the corresponding diamine (0.80 mmol) and 5 drops of glacial acetic acid. The mixture was refluxed for 3 h and water formed by the reaction was removed azeotropically using a Dean–Stark apparatus. Then the mixture was cooled to room temperature and the solvent was removed at reduced pressure. The crude product was purified by recrystallization from absolute ethanol and it was isolated as a yellow solid.

Preparation of salen-Mn(III) complexes (MnXLⁿ)

All the compounds were synthesized using a reported method.³⁸ Salen ligand (0.186 mmol) and manganese(II) acetate tetrahydrate (0.069 g, 0.28 mmol) were added to 20 mL of ethanol, and the mixture was refluxed for 3 h in air. Upon cooling, 3 mL of an aqueous saturated sodium chloride solution was added, and the mixture was extracted with dichloromethane (2×15 mL). The combined organic portions were then washed with 15 mL of water and dried over MgSO₄. The solvent was recrystallized in dichloromethane–ethanol.

General procedure for the epoxidation of styrene with iodosylbenzene as the oxidant

To a mixture thermostated at 25 $^{\circ}$ C, formed by the catalyst (0.036 mmol) dissolved in hexane (3 mL) and acetonitrile (5 mL), were added successively under nitrogen styrene (1 mmol) and iodosylbenzene (2 mmol). After stirring for 24 h, the hexane was evaporated under vacuum and the solid catalyst was removed by filtration. The resulting acetonitrile solution was analyzed by GC.

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