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Synthesis of New Macrocyclic Chiral Manganese(III) Schiff Bases as Catalysts for Asymmetric Epoxidation

Alexandre Martinez, Catherine Hemmert,* Christophe Loup, Guillaume Barré, and Bernard Meunier*

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse cedex 4, France

hemmert@lcc-toulouse.fr, bmeunier@lcc-toulouse.fr

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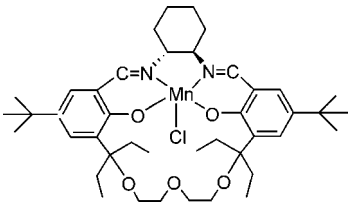

We describe a general synthetic strategy for the preparation of a series of macrocyclic chiral manganese(III) salen complexes. The developed reaction pathway allows the modulation of the different key groups, namely, the chiral diimine, the bulky substituents in positions 3 and 3′, and the linker used in the macrocyclization of the Schiff base. The different complexes presented here illustrate these readily available structural variations. The catalytic properties of the catalysts (5 mol %) were improved for the asymmetric epoxidation of 2,2′-dimethylchromene with NaOCl or H_2O_2 as oxygen atom donor. A large range of enantiomeric excesses was obtained (ee values from 30% to 96%), depending on the features and the stability of the complexes. The most efficient catalyst, in terms of stereoinduction (ee value = 96%), contains a diiminocyclohexyl moiety, ethyl groups in positions 3 and 3′, and a short polyether junction arm.

Introduction

Cytochrome P-450 enzymes represent a class of biological oxidation catalysts able to perform enantioselective epoxidation of prochiral olefins.[1,2] Synthetic metalloporphyrins[3,4] have been developed for enantioselective epoxidation, and in the same way, metallosalens,[4−9] since Schiff bases and porphyrin ligands have common features such as planar structures and electronic properties. Optically active metallosalens are among the widely used catalysts for asymmetric synthesis. This is mainly due to their facile preparation, the easy construction of a highly asymmetric coordination sphere, and their versatile catalytic activity, depending on the nature of the metal chelated by the salen ligands. At about the same time, Jacobsen[10] and Katsuki[11] have reported the use of chiral manganese(III)-salen catalysts in asymmetric epoxidations. The Jacobsen−Katsuki reaction is universally recognized as one of the most useful and widely applicable methods for the epoxidation of unfunctionalized olefins, and Jacobsen's catalyst (Figure 1) is now commercially available. Enantiomerically pure epoxides are key intermediates in organic chemistry because they can undergo stereospecific ring-opening reactions, giving rise to a wide range of biologically and pharmaceutically active compounds.[5−7,12] During the past 15 years, many different chiral manganense-salen catalysts have been reported for homogeneous or supported asymmetric

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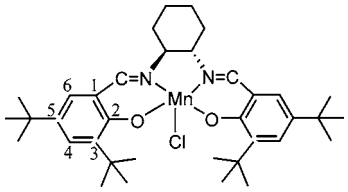

FIGURE 1. Jacobsen's catalyst.

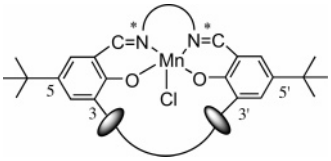

FIGURE 2. Design of the macrocyclic chiral Mn(III)-salen.

epoxidation.[5,6,13−17] However, the design of new salen ligands is still an active domaine because their structural, conformational, and electronic properties strongly influence the tuning of the catalytic activity of these metallosalen complexes.

In the present work, we describe the preparation of a series of original chiral macrocyclic manganese-salen complexes, where each building block of the salen molecule, i.e., bulky substituents, bridging linker, and chiral diimine, can be easily tuned (Figure 2). The catalytic activity of these new chiral complexes was evaluated in the asymmetric epoxidation of 2,2′-dimethylchromene with sodium hypochlorite or hydrogen peroxide as oxygen atom donors.

Results and Discussion

The scaffold of these macrocyclic salen complexes contains a linker between the 3 and 3′ positions, a chiral diimine, and bulky substituents in the "south part" of the ligand, in positions 3, 3′ and 5, 5′, to induce the approach of the olefin by the "north face" in the vicinity of the chiral diimine. The ligands retain a C_2 symmetry to have the same stereoinduction on both faces of the catalyst.

The macrocyclization of the Schiff bases was generated by introducing a symmetrical junction arm in the 3 and 3′ positions. Reinhoudt et al. have previously reported macrocyclic achiral Schiff bases containing aliphatic polyether linkers.[18] However, such a strategy has not been employed for chiral Mn(III)-salen catalysts. The macrocyclization of the ligand is expected to increase the stability of the corresponding complexes in asymmetric catalysis due to the macrocyclic effect. We have previously prepared a first generation of macrocyclic chiral Mn(III)-salen catalysts (one example is depicted in Figure 3).[19] The synthesis of this first generation of chiral macrocyclic complexes was convenient and was realized in three steps, starting from 4-*tert*-butylcatechol. Unfortunately, the enantiomeric excess values obtained in the asymmetric epoxidation of *cis*-disubstituted olefins were modest for these catalysts; the highest ee value was 74% with 2,2′-dimethylchromene as

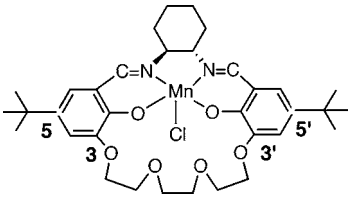

FIGURE 3. Macrocyclized Schiff base catalyst of first generation.

substrate and iodosylbenzene as oxidant. This result was probably due to the absence of bulky substituents in the close proximity of positions 3 and 3′. Moreover, the presence of two oxygen atoms on the aromatic entities of the ligand, making an electron-rich easily oxidable ligand, could explain the fragility of the complexes under oxidative conditions.

This prompted us to develop a new and more elaborated synthetic strategy. The synthetic pathway for the synthesis of one representative complex of the second generation (complex **7**) is illustrated in Scheme 1 and involves seven steps. The aromatic electrophilic substitution (compound **1**) was already described in the literature.[20] In the next step, the protection of the phenol function (compound **2**) was necessary for the further introduction of the bridging linker leading to compound **4**, thus avoiding the formation of undesired intracyclic byproduct. The choice of this group, allyl in our case,[21] was important because the deprotection conditions have to be mild. First attempts involving a methoxymethyl as protecting group were disappointing. All the experimental methods reported in the literature for the deprotection of this group[22−27] were unsuccessful (HBr 6 M, MeOH, rt; BF_3/Et_2O, MeOH, rt; BBr_3, CH_2Cl_2, −78 °C; Ph_3CBF_4, rt; LiCl, collidine, 160 °C; AcOH 0.2 M, MeOH, reflux) and led either to the deprotected starting material **1** or to complicated unseparable mixtures. Compound **3** was obtained, after a metal−halogen exchange, by the addition of a ketone, acetone in this case.[28] This is the key step in the preparation of these macrocyclic chiral salen ligands, since it corresponds to the insertion of the bulky substituents in positions 3 and 3′ of the final complex. The introduction of the junction arm was performed by a Williamson reaction.[18] The formylation step required the presence of TMEDA to obtain the dialdehyde **5**.[20] The deprotection of the phenol group was achieved under mild conditions at room temperature, [29] and the reaction was highly chimioselective since no cleavage of the ether bond of the linker was observed. Finally, the template synthesis of complex **7** was achieved by mixing stoechiometric amounts of the dialdehyde **6**, the chiral diamine, and manganese(II) diacetate. An air oxidation, followed by NaCl treatment to introduce a chloro axial ligand, produced complex **7**.

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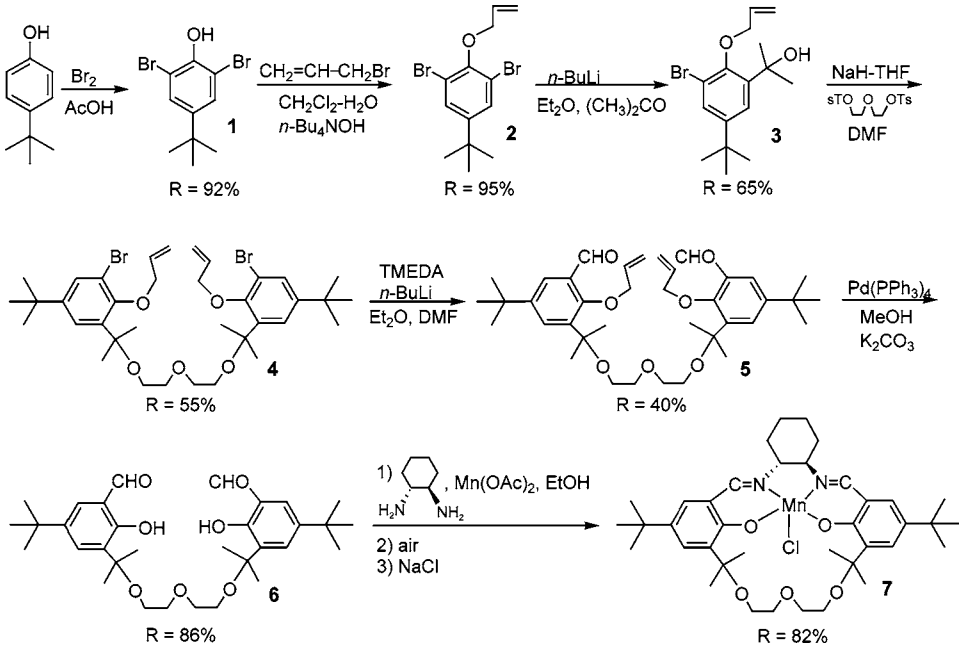
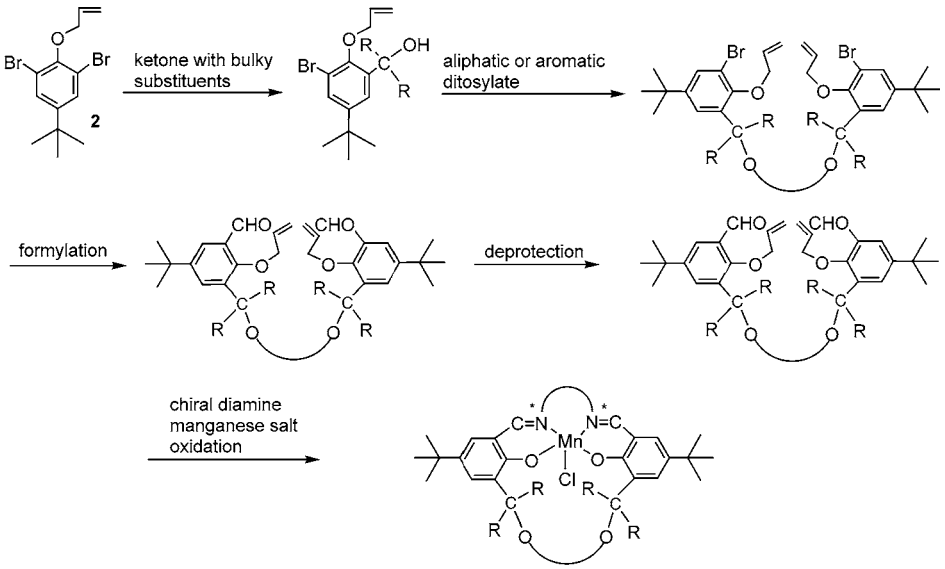
SCHEME 1. Synthesis of Complex 7

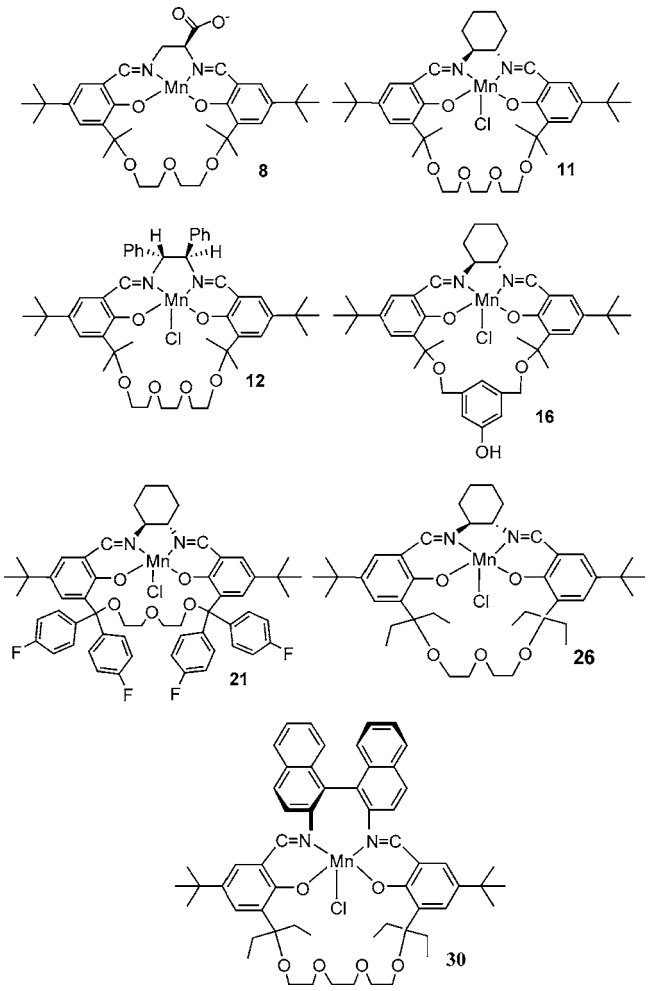


SCHEME 2. General Synthetic Pathway Allowing Modulation of the Different Building Blocks of These Macrocyclic Schiff Base Complexes



Complex	Ketone $(R_2)C=O$	Ditosylate	Diamine
8	R = CH_3	diethylene glycol ditosylate	(*S*)-2,3-diaminopropionic acid
11	R = CH_3	triethylene glycol ditosylate	(1*S*,2*S*)-(+)-1,2-diaminocyclohexane
12	R = CH_3	triethylene glycol ditosylate	(1*R*,2*R*)-(-)-diphenylethylenediamine
16	R = CH_3	5-allyloxy-1,3-benzenedimethyl ditosylate	(1*S*,2*S*)-(+)-1,2-diaminocyclohexane
21	R = C_6H_5F	diethylene glycol ditosylate	(1*S*,2*S*)-(+)-1,2-diaminocyclohexane
26	R = CH_2CH_3	diethylene glycol ditosylate	(1*S*,2*S*)-(+)-1,2-diaminocyclohexane
30	R = CH_2CH_3	triethylene glycol ditosylate	(*S*)-(-)-1,1'-binaphthyl-2,2'-diamine

SCHEME 3. Complexes 8, 11, 12, 16, 21, 26, and 30



This general strategy is original because it made it possible to modulate the different building blocks of the molecule, namely, the ketone with bulky substituents, the ditosylate containing the junction arm, and the chiral diamine (Scheme 2), and thus gives rise to a new family of chiral macrocyclic salen complexes (Scheme 3). For example, bulky substituents such as methyl (complexes **8**, **11**, **12**, and **16**), ethyl (complexes **26** and **30**) or halogenated aryl (complex **21**, Scheme 3) can be introduced. In the same way, simple polyether linkers of different lengths (see complexes **8** and **11** for example, Scheme 3) can be employed for homogeneous catalysis. A functionalized linker can also be included (complex **16**, Scheme 3) in order to have the possibility of grafting the corresponding catalyst on solid supports such as silica or dendrimers. Katsuki et al. have reported a metallosalen catalyst having a carboxylate group on the ethylene diimine moiety.[30] This catalyst associated with iodosylbenzene as oxidant was found to be efficient for the asymmetric epoxidation of 2,2′-chromene derivatives (ee values up to 99%) with a very high turnover number of 9200. The high catalytic activity of this complex was partly explained by the fact that it does not require any additional axial ligand, generally used in excess, and thus it possesses a free axial coordination site. This prompted us to synthesize complex **8** (Scheme 3), starting from (*S*)-2,3-diaminopropionic acid hydrogen chloride instead of the most common (1*S*,2*S*)-(+)-1,2-diaminocyclohexane, to study the influence of the carboxylate group in asymmetric epoxidation reactions. Complex **8** involved a ligand without a C_2 symmetry. Finally, three different chiral C_2-symmetric amines (namely, (1*R*,2*R*)-(−)-1,2-diaminocyclohexane or (1*S*,2*S*)-(+)-1,2-diaminocyclohexane, (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine, and (*S*)-(−)-1,1′-binaphthyl-2,2′-diamine) have been used in the template synthesis of these chiral macrocyclic manganese(III) Schiff bases (complexes **11**, **12**, and **30** for example, Scheme 3). These three complexes differed in terms of size and rigidity, and one can expect to observe different behaviors in catalytic reactions.

In Table 1 are summarized the comparative catalytic activities of the various macrocyclic Schiff base complexes in the asymmetric epoxidation of three *cis*-disubstituted olefins, namely, 2,2′-dimethylchromene, *cis*-*β*-methylstyrene, and 1,2-dihydronaphthalene and sodium hypochlorite as oxygen atom donor (except for catalyst **8**). The epoxidations reactions were typically performed with a substrate/oxidant/catalyst molar ratio of 1/2/0.05 in a biphasic system, in the presence of an excess of 4-phenylpyridine-*N*-oxide (5 equiv with respect to the caralyst, except for catalyst **8**) at 0 °C. In the case of complex **8**, involving a carboxylate on the diethylene diimine moiety, no additional axial ligand was used and the reaction was conducted in an organic medium with the attractive hydrogen peroxide oxidant (3.4 equiv with respect to the substrate). As expected for these chiral macrocyclic metallosalen catalysts of second generation, the asymmetric induction is efficiently increased, giving rise to enantiomeric excesses up to 96% (Table 1, entry 6), when compared to those of the first series (ee = 74% with iodosylbenzene as oxidant).[19] This a general trend with the three substrates employed. Complex **7**, with methyl groups as bulky substituents, a short polyether bridging arm and a cyclohexyl diimine, gave a highly selective epoxidation reaction (entry 1, yield and selectivity of the epoxychromane derivative = 100%).[31] The best stereoinduction was achieved with the efficient catalyst **26**, analogous to complex **7** but bearing ethyl groups instead of methyl groups (entry 6, ee = 96%). Moreover, the asymmetric epoxidation proceeded more rapidly with catalyst **26** (30 min) than with the other complexes, whereas 2 h were required to obtain a complete conversion of the olefin. By lengthening the linker of the catalyst in order to study the influence of the flexibility of the macrocycle in the high-valent salen-Mn^V = O species, the selectivity in epoxide remained excellent (100%) but the ee value slightly decreased (entry 2, ee = 85%, catalyst **11**). In the same way, the presence of an aromatic linker gave similar results (entry 4, ee = 85%, catalyst **16**). In addition, catalyst **16** is interesting because the phenol group could act as an axial ligand while still keeping the C_2 symmetry for enantioselective epoxidation. This functionalized linker could also serve to graft the corresponding catalyst on a solid support for heterogeneous asymmetric catalysis. Introducing the bulkier diiminodiphenylethylene entity has not a strong influence on the enantioselectivity (entries 2 and 3 to be compared, ee = 83% and 85% for catalysts **11** and **12**, respectively). However, complex **30** containing the bulk and rigid diiminobinaphthyl backbone showed a poor catalytic activity (entry **7**), when compared to the cyclohexyl-based analogues. Surprisingly, catalyst **21** with bulky fluorinated aromatic groups in 3 and 3′ positions gave a significantly lower enantiomeric excess (ee value = 59%, entry 5, catalyst **21**).

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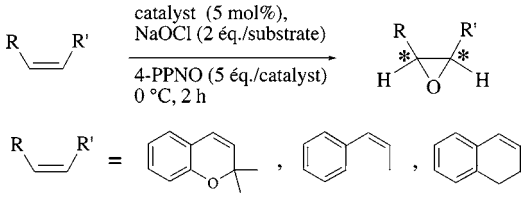
TABLE 1. Asymmetric Epoxidation of 2,2′-Dimethylchromene with Catalysts 7, 8, 11, 12, 16, 21, 26, and 30[e]



entry	catalyst	substrate	conversion(%)	yield (%)	selectivity (%)	ee[a] (%)
1[31]	**7**	2,2′-dimethylchromene	100	100	100	93
2	**11**	2,2′-dimethylchromene	100	100	100	85
3	**12**	2,2′-dimethylchromene	95	93	98	83
4	**16**	2,2′-dimethylchromene	100	80	80	85
5	**21**	2,2′-dimethylchromene	99	98	99	59
6[b]	**26**	2,2′-dimethylchromene	99	73	79	96
7	**30**	2,2′-dimethylchromene	5	3		
8	Jacobsen's catalyst	2,2′-dimethylchromene	100	87	87	96
9[c]	**7**	2,2′-dimethylchromene	80	63	79	84
10[c]	**8**	2,2′-dimethylchromene	39	36	92	30
11[31]*d*	**7**	*cis*-*β*-methylstyrene	67	51 (11)	76	73
12[d]	**11**	*cis*-*β*-methylstyrene	99	47 (25)	48	67
13[d]	**12**	*cis*-*β*-methylstyrene	92	42 (10)	46	74
14[d]	**16**	*cis*-*β*-methylstyrene	96	55 (18)	58	73
15[d]	**21**	*cis*-*β*-methylstyrene	14	5 (3)	36	39
16[d]	**26**	*cis*-*β*-methylstyrene	99	74 (25)	75	91
17	Jacobsen's catalyst	*cis*-*β*-methylstyrene	95	88 (7)	93	85
18[31]·*d*	**7**	1,2-dihydronaphthalene	80	55 (23)	69	60
19[d]	**8**	1,2-dihydronaphthalene	95	60 (11)	63	11
20[d]	**11**	1,2-dihydronaphthalene	63	22 (10)	35	57
21[d]	**12**	1,2-dihydronaphthalene	92	74 (13)	80	61
22[d]	**16**	1,2-dihydronaphthalene	100	56 (20)	56	57
23[d]	**21**	1,2-dihydronaphthalene	54	31 (10)	57	38
24[d]	**26**	1,2-dihydronaphthalene	100	64 (16)	64	78
25[d]	Jacobsen's catalyst	1,2-dihydronaphthalene	100	60 (25)	60	86

[a] ee values were determined by chiral GC; ee values are given for the major enantiomer. [b] After 30 min. [c] H_2O_2 (0.34 mmol) was used as oxidant instead of NaOCl. [d] Epoxide yield (naphthalene or *trans*-*β*-methylstyrene yield). [e] Reactions were carried out with substrate (0.1 mmol), catalyst (5 μmol), and NaOCl as oxidant (0.2 mmol) at 0 °C in the presence of 5 equiv of 4-PPNO with respect to the catalyst.

This unexpected result could be explained by the presence of these sterically hindered substituents that probably block the C_2 axis of the ligand by conformational constraints and create the possibility of having diastereomeric complexes. The less efficient catalyst was the unsymmetrical complex **8** with the carboxylate group on the diethylenediamine (entry 10 to be compared with entry 9 or entry 19 to be compared with entry 18). These two later results suggested that the C_2 symmetry of the ligand constitutes one of the key factors to have a good stereoinduction with these chiral macrocyclic metallosalen catalysts. To summarize these results, complexes **7** and **26** are the most efficient in terms of stereoinduction (entries 1 and 6, 11 and 16, and 18 and 24) for the asymmetric epoxidation of *cis*-disubstituted olefins and can be compared to the commercially available Jacobsen's catalyst (entries 8, 17, and 25).

Conclusion

In summary, we have developed a new family of macrocyclic chiral manganese(III) Schiff bases. The strategy consists of the macrocyclization of the ligand via the 3 and 3′ positions, to have efficient and robust catalysts in oxidative conditions. Enantiomeric excesses up to 96% have been obtained in the asymmetric epoxidation of 2,2′-dimethylchromene with NaOCl as oxidant, associated with a quantitative conversion of the olefin. Moreover, the same synthetic pathway allowed the modulation of the key groups of the molecule: the bulky substituents in the south part of the catalyst, which are necessary for a good orientation of the olefin and the bridging linker, which can be more or less flexible or functionalized for the fixation on a solid support.

Experimental Section

Synthesis of Ligands and Complexes. 1,3-Dibromo-5-(1,1-dimethylethyl)-2-(2-propen-1-yloxy)benzene (2). To a solution of **1** (3.82 g, 0.0124 mol) in 30 mL of CH_2Cl_2/H_2O (10/7 v/v) and 8.52 mL of a 40 wt % solution of nBu$_4$NOH in water was added an excess of allylbromide (13.4 mL, 0.062 mol) at room temperature. The reaction mixture was stirred vigorously for 24 h. Addition of 200 mL of NaOH 1 M was followed by extraction with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed with NaOH 1 M (100 mL) and water (2 × 200 mL), dried ($MgSO_4$), filtered, and concentrated. The crude product was dissolved in CH_2Cl_2 and the ammonium salt was precipitated by addition of Et_2O. After filtration, the liquid layer was dried under vacuum to give a colorless oil (4.1 g, 95%). ^{1}H NMR ($CDCl_3$): δ 1.3 ppm (s, 9H), 4.5 (m, 2H), 5.4−5.5 (m, 2H), 6.3 (m, 1H), 7.5 (s, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 31.2, 34.6, 73.9, 118.5, 133.2. $C_{13}H_{16}O_1Br_2$ (348): calcd C 44.86, H 4.63; found C 44.57, H 4.55. MS (EI): m/z = 348 [M], 333, 307, 267, 226, 147, 132, 91, 77, 57, 41.

2-[3-Bromo-5-(1,1-dimethylethyl)-2-(2-propen-1-yloxy)phenyl]-2-propanol (3). To a solution of **2** (6.05 g, 0.017 mol) in anhydrous diethyl ether (20 mL) under nitrogen at −78 °C was added dropwise *n*-BuLi (1.6 M, 13 mL, 0.0204 mol). After stirring for 1 h at −78 °C, acetone (1.65 mL, 0.0221 mol) in anhydrous Et_2O (10 mL) was added dropwise at −78 °C. The solution was allowed to warm

to room temperature and stirred for 1 h. Water (15 mL) was added to the solution at 5 °C. The mixture was extracted with ether (3 × 100 mL), and the combined organic layers were washed with water (2 × 100 mL) and dried over $MgSO_4$. The solvent was removed and the crude product was purified by column chromatography using hexane/ethyl acetate (9/1) as the eluent to give a colorless oil (3.7 g, 65%). ^{1}H NMR ($CDCl_3$): δ 1.3 ppm (s, 9H), 1.6 (s, 6H), 3.8 (s, 1H), 4.5 (m, 2H), 5.4−5.5 (m, 2H), 6.3 (m, 1H), 7.32 (d, J = 2.3 Hz, 1H) 7.44 (d, J = 2.3 Hz, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 31.2, 34.3, 73.2, 74.3, 117.2, 118.3, 122.9, 129.8, 133.0, 142.2, 148.2, 150.9. $C_{16}H_{23}O_2Br_1$ (328): calcd C 58.72, H 7.08; found C 58.49, H 7.09. MS (EI): m/z = 328 [M], 311, 270, 255, 91, 77, 43.

1,1′-[Oxybis(2,1-ethanediyloxy-2,2-propanediyl)]bis[3-bromo-5-(1,1-dimethylethyl)-2-(vinyloxy)benzene] (4). NaH (0.78 g, 20.34 mmol, 60% dispersion in oil) was washed with pentane (3 × 4 mL) and a solution of **3** (3.7 g, 11.3 mmol) in THF (15 mL) was then added dropwise under nitrogen. The reaction mixture was stirred for 3 h at room temperature. To the resulting suspension was added a solution of diethylene glycol ditosylate (2.86 g, 6.9 mmol) in anhydrous DMF (10 mL) in one portion and the mixture was stirred for 48 h. The reaction was quenched by addition of brine (100 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The organic layer was washed with H_2O (2 × 100 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography using hexane/ethyl acetate (96/4) as the eluent to obtain a colorless oil (2.3 g, 55%). ^{1}H NMR ($CDCl_3$): δ 1.26 ppm (s, 18 H), 1.62 (s, 6H), 3.43 (t, J = 5.5 Hz, 4H), 3.66 (t, J = 5.5 Hz, 4H), 4.48 (m, 4H), 5.24−5.48 (m, 4H), 6.10 (m, 2H), 7.43 (d, J = 2.9 Hz, 2H), 7.48 (d, J = 2.9 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 28.3, 31.3, 62.1, 71.0, 73.8, 77.5, 117.4, 118.4, 124.7, 129.7, 133.6, 139.7, 147.9, 151.3. $C_{36}H_{52}O_5Br_2$ (724.6): calcd C 59.67, H 7.23; found C 59.42, H 7.30. MS (DCI/NH_3): m/z = 742 [M + NH_4^+]$^+$.

3,3′-[Oxybis(2,1-ethanediyloxy-2,2-propanediyl)]bis[5-(1,1-dimethylethyl)-2-(vinyloxy)benzaldehyde] (5). To a well-stirred solution of **4** (1.6 g, 2.2 mmol) in anhydrous ether (5 mL) at −90 °C was added dropwise a mixture of TMEDA (330 mg, 2.9 mmol) and *n*-BuLi (1.6 M, 4 mL, 6.4 mmol) in anhydrous ether (5 mL) at −90 °C under nitrogen. The yellow solution was stirred at −90 °C for 1 h. Then a solution of anhydrous DMF (1.8 mL, 22.4 mmol) in diethyl ether (2 mL) was added at −90 °C under nitrogen. The mixture was allowed to warm to room temperature and stirred for an other hour. Water (5 mL) was slowly added to the solution at 5 °C. The mixture was extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic layers were washed with water (2 × 100 mL) and dried over $MgSO_4$. The solvent was removed and the crude product was purified by column chromatography using hexane/ethyl acetate (96/4) as the eluent to give a pale yellow oil (530 mg, 40%). ^{1}H NMR ($CDCl_3$): δ 1.29 ppm (s, 18H), 1.65 (s, 12H), 3.45 (t, J = 5.6 Hz, 4H), 3.68 (t, J = 5.6 Hz, 4H), 4.46 (m, 4H), 5.30−5.40 (m, 4H), 6.05 (m, 1H), 7.75 (d, J = 2.8 Hz, 2H) 7.83 (d, J = 2.8 Hz, 2H) 10.28 (s, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 28.1, 31.3, 34.66, 62.1, 70.8, 71.0, 78.9, 117.7, 125.0, 129.7, 131.9, 132.8, 139.2, 142.4, 149.2, 190.6. $C_{38}H_{54}O_7$ (622.85): calcd (+ H_2O) C 71.62, H 8.80; found C 71.56, H 9.21. MS (ES) m/z = 645 [M + Na^+].

3,3′-[Oxybis(2,1-ethanediyloxy-2,2-propanediyl)]bis[5-(1,1-dimethylethyl)-2-hydroxy-benzaldehyde] (6). To a solution of **5** (120 mg 0.193 mmol) in MeOH (3 mL) was added catalytic amounts of $Pd(PPh_3)_4$ (11.1 mg, 0.0098 mmol) under nitrogen. The slightly yellow solution was stirred for 5 min, and K_2CO_3 (160 mg, 1.16 mmol) was added. The reaction was completed within 2 h (monitored by TLC). The reaction mixture was concentrated in a vacuum and the residue was treated with water (20 mL). The aqueous solution was extracted with CH_2Cl_2 (3 × 20 mL) and dried over Na_2SO_4. The organic layer was concentrated in a vacuum and purified by column chromatography using CH_2Cl_2 as the eluent to give a pale yellow oil (90 mg, 86%). ^{1}H NMR ($CDCl_3$): δ 1.29 ppm (s, 18H), 1.64 (s, 12H), 3.54 (t, J = 5.0 Hz, 4H), 3.73 (t, J = 5.0 Hz, 4H), 7.50 (d, J = 2.4 Hz, 2H), 7.66 (d, J = 2.4 Hz, 2H), 10.07 (s, 2H), 10.66 (s, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 26.6, 31.3, 34.5, 62.1, 70.75, 78.0, 121.5, 127.1, 128.4, 131.8, 142.1, 157.5, 194.8. $C_{32}H_{46}O_7$ (542): calcd C 70.82, H 8.54; found C 70.46, H 8.62. MS (ES) m/z = 565.25 [M + Na^+].

Mn^{III}-Salen Complex 7. The compound **6** (80 mg, 0.148 mmol) was dissolved in 50 mL of EtOH under nitrogen. To the resulting solution was added successively (1*R*,2*R*)-(+)-1,2-diaminocyclohexane (17 mg, 0.148 mmol) and manganese(II) diacetate tetrahydrate (36.4 mg, 0.148 mmol). After stirring overnight, air was bubbled through the solution for 4 h. The reaction mixture was concentrated to 20 mL, treated with 20 mL of brine, and extracted with 2 × 50 mL of CH_2Cl_2. The organic layer was washed with 100 mL of H_2O and dried over Na_2SO_4. After evaporation of the solvent and drying under vacuum, 85 mg (82%) of complex **7** was obtained as a dark brown microcrystalline solid. $C_{38}H_{54}N_2O_5ClMn$ (709): calcd C 64.35, H 7.67, N 3.95, Mn 7.75, Cl 5.00; found C 64.66, H 7.61, N 3.54, Mn 7.75, Cl 5.39. MS (ES): m/z = 673.55 [M − Cl^-]$^+$. IR (KBr, cm^{-1}): 1631(C═N). UV−vis (CH_3OH): λ (ϵ) = 274 nm (14000 L mol^{-1} cm^{-1}), 290 (13210), 318 (8928), 354 (5714), 416 (4103). $[\alpha]^{20}_D$ = −0.0231 (589 nm, 0.039 g/dm^{-3} in CH_3OH, 10 cm path).

Mn^{III}-Salen Complex 8. Two equivalents of sodium hydroxide (18.8 mg, 0.47 mmol) in EtOH (10 mL) were added slowly to a suspension of **6** (107.8 mg, 0.24 mmol) and (*S*)-2,3-diaminopropionic acid hydrogen chloride (33.1 mg, 0.24 mmol) in EtOH (50 mL). After stirring for 2 h under nitrogen, $Mn(OAc)_2 \cdot 4H_2O$ (58.0 mg, 0.24 mmol) in EtOH (10 mL) was added to the mixture. After stirring overnight, air was bubbled through the solution for 4 h. The solvent was evaporated and the residue was dissolved in 50 mL of CH_2Cl_2. The organic layer was washed with 2 × 50 mL of H_2O and dried over Na_2SO_4. After evaporation of the solvent and drying under vacuum, 89 mg (57%) of complex **8** was obtained as a dark brown microcrystalline solid. $C_{35}H_{47}N_2O_7Mn$ (662.7): calcd (+ CH_2Cl_2 + MeOH) C 57.00, H 6.85, N 3.59, Mn 7.05; found C 57.34, H 7.03, N 3.63, Mn 6.61. MS (ES): m/z = 663.4 [M + H^+]$^+$, 685.4 [M +Na^+]$^+$, 701.3 [M + K^+]$^+$. IR (KBr, cm^{-1}): 1619 (C═N). UV−vis (CH_3OH): λ (ϵ) = 278 nm (16430 L mol^{-1} cm^{-1}), 290(15700), 324(11420), 352 (8200), 420 (5130). $[\alpha]^{20}_D$ = −0.0460 (589 nm, 0.050 g/dm^{-3} in CH_3OH, 10 cm path).

3,14-Bis[3-bromo-5-(1,1-dimethylethyl)-2-(2-propen-1-yloxy)-phenyl]-3,14-dimethyl-4,7,10,13-tetraoxahexadecane (9). Compound **9** was prepared as described for **4** starting from NaH (0.22 g, 5.5 mmol, 60% dispersion in oil) in THF (5 mL), **3** (1.2 g, 3.7 mmol) in THF (5 mL), and triethylene glycol ditosylate (0.924 g, 2.0 mmol) in DMF (5 mL).The crude product was purified by column chromatography using hexane/ethyl acetate (9/1) as the eluent to obtain a colorless oil (0.85 g, 55%). ^{1}H NMR ($CDCl_3$): δ 1.27 ppm (s, 18H), 1.62 (s, 12H), 3.43 (t, J = 5.4 Hz, 4H), 3.64 (t, J = 5.4 Hz, 4H), 3.65 (s, 4H) 4.46 (m, 2H), 5.45 (m, 4H), 5.30−5.40 (m, 4H), 6.05 (m, 2H), 7.75 (d, J = 2.8 Hz, 2H) 7.83 (d, J = 2.8 Hz, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 28.3, 31.3, 34.7, 62.1, 70.7, 70.9, 73.8, 77.4, 117.3, 118.3, 124.7, 129.7, 133.6, 139.8, 147.8, 151.3. $C_{38}H_{56}O_6Br_2$ (768.7): calcd C 59.38, H 7.34; found C 59.51, H 7.52. MS (DCI/NH_3) m/z = 786 [M + NH_4^+]$^+$.

3,3′-(1,1,12,12-Tetramethyl-2,5,8,11-tetraoxadodecane-1,12-diyl)bis[5-(1,1-dimethylethyl)-2-hydroxybenzaldehyde] (10). Compound **10** was prepared as described for **5** starting from **9** (0.7 g, 0.93 mmol), TMEDA (140 mg, 1.22 mmol), and *n*-BuLi (1.6 M, 1.5 mL, 2.4 mmol) in Et_2O (3 mL) and DMF (0.8 mL, 10.3 mmol) at −90 °C. The crude product was purified by column chromatography using hexane/ethyl acetate (9/1) as the eluent to give a pale yellow oil (230 mg) which was an inseparable mixture of deprotected and allyl protected compounds. This mixture (230 mg) was dissolved in MeOH (5 mL) and deprotected as described for compound **6** starting from $Pd(PPh_3)_4$ (16 mg, 0.014 mmol) and K_2CO_3 (230 mg, 1.66 mmol). The crude product was purified by column chromatography using pentane/ethyl acetate (9/1) as the

eluent to give a pale yellow oil (160 mg, 30%). ^{1}H NMR ($CDCl_3$): δ 1.30 ppm (s, 18H), 1.63 (s, 12H), 3.51 (t, J = 4.8 Hz, 4H), 3.70 (t, J = 4.8 Hz, 4H), 3,72 (s, 4H), 7.49 (d, J = 2.3 Hz, 2H), 7.65 (d, J = 2.3 Hz, 2H), 10.09 (s, 2H), 10.61 (s, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 26.6, 31.3, 34.1, 62.1, 70.7, 77.9, 121.6, 127.0, 131.8, 132.3, 142.1, 157.5, 194.7. $C_{34}H_{50}O_8$ (586): calcd (+ 0.4 CH_2Cl_2) C 66.56, H 8.25; found C 66.98, H 7.81. MS (DCI/NH_3) m/z = 604 [M + NH_4^+]$^+$.

Mn^{III}-Salen Complex 11. Complex **11** was synthesized as described above for complex **7**, starting from **9** (88.0 mg, 0.15 mmol) in 50 mL of EtOH, (1*S*,2*S*)-(+)-1,2-diaminocyclohexane (17.1 mg, 0.15 mmol), and $Mn(OAc)_2{\cdot}4H_2O$ (36.8 mg, 0.15 mmol). Yield: 90 mg, 80% as a dark brown microcrystalline solid. $C_{40}H_{58}N_2O_6ClMn$ (753.3): calcd (+ 0.4 CH_2Cl_2) C 63.78, H 7.76, N 3.72, Mn 6.98, Cl 4.51; found C 63.55, H 7.56, N 3.65, Mn 6.61, Cl 4.78. MS (ES): m/z = 717.5 [M − Cl$^-$]$^+$. IR (KBr, cm^{-1}): 1615 (C═N). UV−vis (CH_3OH): λ (ϵ) = 290 nm (19031 L mol^{-1} cm^{-1}), 318 (13379), 356 (8469), 412 (6124). [α]$^{20}_D$ = 0.0482 (589 nm, 0.108 g/dm^{-3} in CH_3OH, 10 cm path).

Mn^{III}-Salen Complex 12. The complex **12** was synthesized as described above, starting from **10** (47 mg, 0.08 mmol) in 20 mL of EtOH, (1*R*,2*R*)-(−)-1,2-diphenylethylenediamine (17 mg, 0.08 mmol), and $Mn(OAc)_2{\cdot}4H_2O$ (19.6 mg, 0.08 mmol). Yield: 63 mg, 67% as a dark brown powder. $C_{48}H_{60}N_2O_6ClMn$ (851.4): calcd C 67.72, H 7.10, N 3.29, Mn 6.46, Cl 4.16; found C 67.96, H 7.29, N 2.94, Mn 6.21, Cl 4.67. MS (ES): m/z = 815.5 [M − Cl$^-$]$^+$. IR (KBr, cm^{-1}): 1612 (C═N). UV−vis (CH_3OH): λ (ϵ) = 274 nm (16440 L mol^{-1} cm^{-1}), 290 (14126), 326 (10210), 356 (6625) 424 (4352). [α]$^{20}_D$ = −0.0237 (589 nm, 0.038 g/dm^{-3} in CH_3OH, 10 cm path).

1,1′-[[5-(Ethenyloxy)benzene-1,3-diyl]bis(methanediyloxy-2,2-propanediyl)]bis[3-bromo-5-(1,1-dimethylethyl)-2-(2-propen-1-yloxy)benzene] (13). Compound **13** was prepared as described for **4** starting from NaH (0.60 g, 15.0 mmol, 60% dispersion in oil) in THF (5 mL) and **3** (2.8 g, 8.54 mmol) in THF (5 mL). 5-Allyloxy-1,3-benzenedimethyl ditosylate (2.0 g, 3.98 mmol) in DMF (5 mL) was added in one portion and the mixture was stirred for 48 h. The crude product was purified by column chromatography using hexane/ethyl acetate (95/5) as the eluent to obtained a colorless oil (1.45 g, 42%). ^{1}H NMR ($CDCl_3$): δ 1.22 ppm (s, 18H), 1.70 (s, 12H), 4.31 (s, 4H), 4.48 (m, 4H), 4.52 (m, 2H), 5.23−5.47 (m, 6H), 6.08 (m, 3H), 6.86 (s, 2H), 6.89 (s, 1H), 7.45 (d, J = 2.3 Hz, 2H) 7.52 (d, J = 2.3 Hz, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 28.3, 31.2, 34.2, 64.5, 73.7, 77.4, 112.3, 117.2, 118.8, 118.9, 124.3, 129.8, 133.2, 133.3, 139.9, 141.1, 151.3, 158.8. $C_{43}H_{56}O_5Br_2$ (812.7): calcd C 63.55, H 6.95; found C 63.21, H 6.83. MS (DCI/NH_3) m/z = 830 [M + NH_4^+]$^+$.

3,3′-[[5-(Ethenyloxy)benzene-1,3-diyl]bis(methanediyloxy-2,2-propanediyl)]bis[5-(1,1-dimethylethyl)-2-(2-propen-1-yloxy)-benzaldehyde] (14). Compound **14** was prepared as described for **5** starting from **13** (0.32 g, 0.39 mmol), TMEDA (330 mg, 2.9 mmol), and *n*-BuLi (1.6 M, 0.75 mL, 1.2 mmol) in ether (5 mL) and DMF (0.25 mL, 3.25 mmol) at −90 °C. After workup, the solvent was removed to give a pale yellow oil (280 mg, 98%). ^{1}H NMR ($CDCl_3$): δ 1.29 ppm (s, 18H), 1.74 (s, 12H), 4.35 (s, 4H), 4.44 (m, 4H), 4.53 (m, 2H), 5.23−5.48 (m, 6H), 6.05 (m, 3H), 6 0.87 (s, 2H), 6.91 (s, 1H) 7.77 (d, J = 2.4 Hz, 2H) 7.86 (d, J = 2.4 Hz, 2H), 10.29 (s, 2 H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 28.4, 31.3, 34.7, 64.7, 68.8, 79.0, 112.3, 117.5, 117.7, 118.2, 125.2, 129.8, 131.8, 132.7, 133.3, 138.9, 140.7, 147.0, 190.7. $C_{45}H_{58}O_7$ (711): calcd (+ 0.4 CH_2Cl_2) C 73.23, H 7.96; found C 73.25, H 7.88.MS (DCI/NH_3) m/z = 728 [M + NH_4^+]$^+$.

3,3′-[(5-Hydroxybenzene-1,3-diyl)bis(methanediyloxy-2,2-propanediyl)]bis[5-(1,1-dimethylethyl)-2-hydroxybenzaldehyde] (15). Compound **15** was prepared as described for **6** starting from **14** (280 mg, 0.385 mmol) in MeOH (6 mL), Pd (PPH_3)$_4$ (20.0 mg, 0.019 mmol), and K_2CO_3 (360 mg, 2.61 mmol). The crude product was purified by column chromatography using hexane/ethyl acetate (9/1) as the eluent to give a pale yellow oil (145 mg, 64%). ^{1}H NMR ($CDCl_3$): δ 1.26 ppm (s, 18H), 1.70 (s, 12H), 4.40 (s, 4H), 4.81 (s, 1H), 6.83 (s, 2H), 6.93 (s, 1H), 7.49 (d, J = 2.7 Hz, 2H), 7.73 (d, J = 2.7 Hz, 2H) 10.01 (s, 2H), 11.01 (s, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 26.8, 31.3, 34.2, 64.7, 78.3, 113.3, 118.1, 121.2, 128.0, 132.1, 132.4, 140.7, 142.2, 156.1, 157.5, 195.6. $C_{36}H_{46}O_7$ (590.76): calcd (+ 0.7 CH_2Cl_2) C 67.79, H 7.35; found C 67.90, H 7.26. MS (DCI/NH_3) m/z = 608 [M + NH_4^+]$^+$.

Mn^{III}-Salen Complex 16. Complex **16** was synthesized as described above for complex **7**, starting from **15** (130 mg, 0.22 mmol) in 50 mL of EtOH, (1*S*,2*S*)-(+)-1,2-diaminocyclohexane (25 mg, 0.22 mmol), and $Mn(OAc)_2{\cdot}4H_2O$ (53.9 mg, 0.22 mmol). Yield: 120 mg, 73% as a dark brown microcrystalline solid. $C_{42}H_{54}N_2O_5ClMn$ (757.3): calcd (+ 0.6 CH_2Cl_2) C 63.38, H 6.77, N 3.47, Mn 6.81, Cl 4.39; found C 63.01, H 6.7, N 3.35, Mn 6.89, Cl 4.77. MS (ES): m/z = 721.8 [M − Cl$^-$]$^+$. IR (KBr, cm^{-1}): 1615 (C═N). UV−vis (CH_3OH): λ (ϵ) = 278 nm (14663 L mol^{-1} cm^{-1}), 320 (8333), 358 (5292), 412 (3805). [α]$^{20}_D$ = 0.0275 (589 nm, 0.052 g/dm^{-3} in CH_3OH, 10 cm path).

[3-Bromo-5-(1,1-dimethylethyl)-2-(2-propen-1-yloxy)phenyl]-[bis(4-flurophenyl)]methanol (17). Compound **17** was prepared as described for **3** starting from **2** (2.00 g, 5.75 mmol) in Et_2O (8 mL), *n*-BuLi (1.6 M, 4.31 mL, 6.89 mmol), and 4,4′-difluorobenzophenone (2.51 g, 11.5 mmol) in anhydrous ether (30 mL) at −78 °C. The solvent was removed, the crude product was dissolved in 20 mL of CH_2Cl_2, hexane (60 mL) was added, and the flask was placed at −20 °C overnight. The supernatant was collected by filtration and the solvent was removed to give a pale yellow solid (2.51 g, 90%). ^{1}H NMR ($CDCl_3$): δ 1.11 ppm (s, 9H), 3.8 (m, 2H), 5.02−5.14 (m, 2H), 5.64−5.73 (m, 2H), 5.71 (s, 1H), 6.49 (d, J = 2.5 Hz, 1H), 7.02 (m, 4H), 7.24 (m, 4H), 7.48 (d, J = 2.5 Hz, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 31.0, 34.4, 73.7, 81.8, 114.5, 114.9, 117.4, 118.7, 127.0, 129.6, 129.7, 130.4, 132.3, 141.8, 151.4, 160.2, 164.1. $C_{26}H_{25}O_2Br_1F_2$ (487): calcd C 64.07, H 5.17; found C 64.24, H 4.71. MS (ES): m/z = 510 [M + Na^+]$^+$.

1,1′-(Oxybis{2,1-ethanediyloxy[bis(4-fluorophenyl)-methanediyl]})bis[3-bromo-5-(1,1-dimethylethyl)-2-(2-propen-1-yloxy)benzene] (18). Compound **18** was prepared as described for **4** starting from NaH (0.24 g, 6.2 mmol, 60% dispersion in oil) in THF (6 mL), **17** (2.0 g, 4.1 mmol) in THF (8 mL), and diethylene glycol ditosylate (0.85 g, 2.05 mmol) in DMF (8 mL).The crude product was purified by column chromatography using hexane/ethyl acetate (95/5) as the eluent to obtained a pale yellow solid (0.643 g, 30%). ^{1}H NMR ($CDCl_3$): δ 1.24 ppm (s, 18H), 3.10 (t, J = 4.9 Hz, 4H), 3.70 (t, J = 4.9 Hz, 4H), 3.92 (m, 4H), 4.88−4.99 (m, 4 H), 5.47−5.62 (m, 2H), 6.92 (m, 8H), 7.42 (m, 8H), 7.50 (d, J = 2.5 Hz, 2H), 7.70 (d, J = 2.5 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 31.2, 34.6, 63.4, 70.8, 72.29, 84.9, 114.4, 114.7, 116.7, 118.1, 126.2, 129.7, 129.9, 130.8, 133.3, 137.8, 138.9, 147.3, 159.7, 163.6. $C_{56}H_{56}O_5Br_2F_4$ (1044.87): calcd (+ 0.4 CH_2Cl_2) C 62.79, H 5.31; found C 62.98, H 5.30. MS (ES): m/z = 1068 [M + Na^+]$^+$.

3,3′-(Oxybis{2,1-ethanediyloxy[bis(4-fluorophenyl)-methanediyl]})bis[5-(1,1-dimethylethyl)-2-(2-propen-1-yloxy)-benzaldehyde] (19). Compound **19** was prepared as described for **5** starting from **18** (0.410 g, 0.39 mmol), TMEDA (0.1 mL), and *n*-BuLi (1.6 M, 1.0 mL, 1.2 mmol) in Et_2O (2.5 mL), and DMF (0.5 mL, 3.2 mmol) in Et_2O (2 mL). The crude product was dissolved in ethyl acetate/hexane (30 mL/30 mL) and the flask was placed at −20 °C overnight. The solid was collected and dried in a vacuum (338 mg, 92%). ^{1}H NMR ($CDCl_3$): δ 1.28 ppm (s, 18H), 3.13 (t, J = 5.1 Hz, 4H), 3.71 (t, J = 5.1 Hz, 4H), 3.89 (d, J = 5.2 Hz, 4H), 4.92−5.04 (m, 4H), 5.49 (m, 2H), 6.94 (m, 8H), 7.44 (m, 8H), 7.81 (d, J = 2.9 Hz, 2H), 8.08 (d, J = 2.9 Hz, 2H) 10.12 (s, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 31.2, 34.7, 63.3, 70.8, 77.2, 84.2, 114.5, 114.8, 117.1, 125.7, 129.8, 130.0, 132.5, 132.9, 137.0, 138.5, 158.2, 159.8, 163.7, 190.3. $C_{58}H_{58}O_7F_4$ (942): calcd (+ 0.2 CH_2Cl_2) C 72.81, H 6.13; found C 72.90, H 5.88. MS (ES) m/z = 965.5 [M + Na^+]$^+$, 981 [M + K^+]$^+$, 997.5 [M + MeOH + Na^+]$^+$, 1013.5 [M + MeOH + K^+]$^+$.

3,3′-(Oxybis{2,1-ethanediyloxy[bis(4-fluorophenyl)-methanediyl]})bis[5-(1,1-dimethylethyl)-2-hydroxybenzaldehyde] (20). Compound **20** was prepared as described for **6** starting from **19** (220 mg 0.234 mmol) in MeOH (5 mL), $Pd(PPH_3)_4$ (12.5 mg, 0.011 mmol), and K_2CO_3 (200 mg, 1.45 mmol). The crude product was purified by column chromatography using hexane/ethyl acetate (95/5) as the eluent to give a white solid (160 mg, 80%). ^{1}H NMR ($CDCl_3$): δ 1.27 ppm (s, 18H), 3.16 (t, J = 4.9 Hz, 4H), 3.71 (t, J = 4.9 *Hz*, 4H), 6.98 (m, 8H), 7.43 (m, 10H), 8.12 (d, J = 2.4 Hz, 2H,), 9.86 (s, 2H), 11.15 (s, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 31.2, 34.3, 63.2, 70.8, 84.5, 114.2, 114.6, 120.8, 129.2, 130.5, 130.6, 131.2, 133.1, 137.2, 156.7, 159.9, 163.9, 196.2. $C_{52}H_{50}O_7F_4$ (863): calcd (+ 0.7 CH_2Cl_2). C 68.62, H 5.62; found C 68.77, H 5.41. MS (DCI/NH_3) m/z = 880 $[M + NH_4^+]^+$.

Mn^{III}-Salen Complex 21. Complex **21** was obtained as described above for complex **7**, from **20** (82 mg, 0.10 mmol) in 40 mL of EtOH, (1*S*,2*S*)-(+)-1,2-diaminocyclohexane (11.8 mg, 0.10 mmol), and $Mn(OAc)_2{\cdot}4H_2O$ (25.6 mg, 0.10 mmol). Yield: 85 mg, 83% as a dark brown microcrystalline solid. $C_{58}H_{58}N_2O_5F_4ClMn$ (1029.5): calcd (+ 0.2 CH_2Cl_2) C 66.8, H 5.63, N 2.68, Mn 5.26, Cl 3.40; found C 66.55, H 5.86, N 2.42, Mn 5.18, Cl 3.84. MS (ES): m/z = 993.75 $[M - Cl^-]^+$. IR (KBr, cm^{-1}): 1615 (C═N). UV−vis (CH_3OH): λ (ϵ) = 276 nm (19463 L mol^{-1} cm^{-1}), 330 (9743), 420 (4417). $[\alpha]^{20}_D$ = 0.0072 (589 nm, 0.056 g/dm^{-3} in CH_3OH, 10 cm path).

3-[3-Bromo-5-(1,1-dimethylethyl)-2-(2-propen-1-yloxy)phenyl]-3-pentanol (22). To a solution of **2** (32.51 g, 93.4 mmol) in anhydrous diethyl ether (82 mL) under nitrogen at −78 °C was added dropwise *n*-BuLi (1.6 M, 72 mL, 0.0112 mol). After stirring for 1 h at −78 °C, 3-pentanone (beforehand dried over molecular sieves 4Å, 12.83 mL, 121.4 mmol) in anhydrous Et_2O (10 mL) was added dropwise at −78 °C. The reaction mixture was stirred for 1 h and then allowed to warm to room temperature. H_2O (15 mL) was added to the solution at 5 °C. The mixture was extracted with ether (3 × 100 mL), and the combined organic layers were washed with H_2O (2 × 100 mL) and dried over Na_2SO_4. The solvent was removed and the crude product was purified by column chromatography using hexane/ethyl acetate (98/2) as the eluent to give a colorless oil (15.17 g, 45%). ^{1}H NMR ($CDCl_3$): δ 0.79 ppm (t, 6H), 1.27 (s, 9H), 1.73−1.97 (m, 4H), 4.22 (s, 1H), 4.57 (d, J = 5.5 Hz, 2H), 5.44 (dd, ^3J = 17 Hz, ^4J = 1.6 Hz, 2H), 5.51 (d, ^3J = 17 Hz, ^4J = 1.6 Hz, 2H), 6.12 (m, 1H), 7.16 (d, J = 2.0 Hz, 1H),7.43 (d, J = 2.0 Hz, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 8.2, 31.2, 34.4, 34.9, 74.7, 79.3, 117.5, 118.3, 125.0, 129.2, 132.9, 138.5, 147.9, 151.3. $C_{18}H_{27}O_2Br_1$ (354): calcd C 60.85, H 7.66; found C 60.86, H 7.60. SM (EI): m/z (%) = 354 [M].

1,1′-[Oxybis(2,1-ethanediyloxy-3,3-pentanediyl)]bis[3-bromo-5-(1,1-dimethylethyl)-2-(2-propen-1-yloxy)benzene] (23). Compound **23** was prepared as described for **4** starting from NaH (6.37 g, 159.3 mmol, 60% dispersion in oil, washed with 2 × 20 mL of pentane) in THF (50 mL) and **22** (12.85 g, 36.2 mmol) in THF (50 mL), and diethylene glycol ditosylate (7.50 g, 18.1 mmol) in DMF (26 mL) was added in one portion. The reaction was monitored by TLC and after 15 h, a subsequent portion of diethylene glycol ditosylate (2.7 g, 6.51 mmol) in DMF (5 mL) was added and stirred for 33 h. After workup, the crude product was dissolved in MeOH (250 mL) and the flask was placed at −20 °C overnight. The white solid was collected and dried in a vacuum (4.47 g, 32%). ^{1}H NMR ($CDCl_3$): δ 0.64 ppm (t, 12H), 1.27 (s, 18H), 2.00 (q, J = 7.3 Hz, 8H), 3.44 (t, J = 5.2 Hz, 4H), 3.83 (t, J = 5.2 Hz, 4H), 4.50 (d, J = 5.3 Hz, 4H), 5.28 (dd, ^3J = 10 Hz, ^4J = 1.0 Hz, 2H), 5.44 (dd, ^3J = 17 Hz, ^4J = 1.5 Hz, 2H), 6.05−6.21 (m, 2H), 7.43 (d, J = 2.4 Hz, 2H), 7.66 (d, J = 2.4 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 8.0, 27.5, 31.3, 34.5, 60.4, 71.3, 73.4, 81.9, 117.3, 117.4, 126.7, 129.7, 133.6, 137.6, 147.2, 150.6. $C_{40}H_{60}O_5Br_2$ (778.3): calcd C 61.54, H 7.75; found C 61.80, H 7.79. SM (FAB, MNBA): m/z (%) = 803 $[M + Na^+]^+$.

3,3′-[Oxybis(2,1-ethanediyloxy-3,3-pentanediyl)]bis[5-(1,1-dimethylethyl)-2-(2-propen-1-yloxy)benzaldehyde] (24). Compound **24** was prepared as described for **5** starting from **23** (1.0 g, 1.28 mmol), TMEDA (0.88 mL) and *n*-BuLi (1.6 M, 3.2 mL, 5.12 mmol) in Et_2O (3 mL) and DMF (0.99 mL, 12.8 mmol) in Et_2O (3 mL). The reaction was realized at −90 °C. The crude product was dissolved in ethyl acetate/hexane (30 mL/30 mL) and the flask was placed at −20 °C overnight. After filtration and drying, the crude product was directly used for the deprotection of the phenol function. ^{1}H NMR ($CDCl_3$): δ 0.62 ppm (t, 12H), 1.30 (s, 18 H), 1.90−2.10 (m, 8H), 3.45 (t, J = 5.5 Hz, 4H), 3.74 (t, J = 5.5 Hz, 4H), 3.76 (s, 4H), 4.41 (dd, ^3J = 3.7 Hz, ^4J = 1.5 Hz, 4H), 5.29 (dd, ^3J = 9.1 Hz, ^4J = 1.2 Hz, 2H), 5.49 (dd, ^3J = 9.1 Hz, ^3J = 1.2 Hz, 2H), 5.99−6.12 (m, 2H), 7.73 (d, J = 2.9 Hz, 2 H) 7.96 (d, J = 2.9 Hz, 2H) 10.26 (s, 2H).

3,3′-[Oxybis(2,1-ethanediyloxy-3,3-pentanediyl)]bis[5-(1,1-dimethylethyl)-2-hydroxybenzalde] (25). Compound **25** was prepared as described for **6** starting from **24** (530 mg 0.781 mmol) in MeOH (15 mL), $Pd(PPH_3)_4$ (45.0 mg, 0.391 mmol), and K_2CO_3 (647.4 mg, 4.68 mmol). The crude product was purified by column chromatography using hexane/ethyl acetate (96/4) as the eluent to give a white solid (707 mg, 80%). ^{1}H NMR ($CDCl_3$): δ 0.68 ppm (t, 12H), 1.29 ppm (s, 18H), 1.88−2.15 (m, 8H), 3.54 (t, J = 5.1 Hz, 4H), 3.84 (t, J = 4.7 Hz, 4H), 7.50 (d, J = 2.5 Hz), 2H), 7.67 (d, J = 2.5 Hz, 2H), 10.11 (s, 2H), 10.81 (s, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 7.7, 27.0, 31.2, 34.1, 60.3, 70.9, 83.5, 121.3, 126.4, 129.4, 133.7, 141.4, 157.5, 194.7. $C_{36}H_{54}O_7$ (598.8): calcd C 72.22, H 9.09; found C 71.93, H 9.37. SM (ES) m/z (%) = 621.8 [M + $Na^+]^+$, 637.8 [M + $K^+]^+$.

Mn^{III}-Salen Complex 26. Complex **26** was synthesized as described above for complex **7**, starting from **25** (80 mg, 0.0134 mmol) in 80 mL of EtOH, (1*S*,2*S*)-(+)-1,2-diaminocyclohexane (15.3 mg, 0.0134 mmol), and $Mn(OAc)_2{\cdot}4H_2O$ (32.8 mg, 0.0134 mmol). Yield: 87 mg, 85% as a dark brown microcrystalline solid. $C_{42}H_{62}N_2O_5ClMn$ (765.4): calcd (+ 1 EtOH +1 H_2O) C 63.72, H 8.51, N 3.38, Mn 6.62, Cl 4.27; found C 63.69, H 8.59, N 3.44, Mn 6.80, Cl 4.39. MS (ES): m/z = 730.4 $[M - Cl^-]^+$, 788.4 [M + $Na^+]^+$. IR (KBr, cm^{-1}): 1613 (C═N). UV−vis (CH_3OH): λ (ϵ) = 220 nm (40370 L mol^{-1} cm^{-1}), 244 (37400), 293 (14650), 327 (9500), 357 (6440), 409 (4010). $[\alpha]^{20}_D$ = 0.0250 (589 nm, 0.044 g/dm^{-3} in CH_3OH, 10 cm path).

3,14-Bis[3-bromo-5-(1,1-dimethylethyl)-2-(2-propen-1-yloxy)-phenyl]-3,14-diethyl-4,7,10,13-tetraoxahexadecane (27). Compound **27** was prepared as described for **4** starting from NaH (4.23 g, 105.6 mmol, 60% dispersion in oil, washed with 2 × 25 mL of pentane) in THF (35 mL) and **22** (8.53 g, 24.0 mmol) in THF (35 mL), and triethylene glycol ditosylate (5.5 g, 12.0 mmol) in DMF (20 mL) was added in one portion. The reaction was monitored by TLC and after 24 h, a subsequent portion of triethylene glycol ditosylate (4.4 g, 9.6 mmol) in DMF (15 mL) was added and stirred for 24 h. After workup, the crude product was purified by column chromatography using hexane/ethyl acetate (9/1) as the eluent to give a colorless oil (4.86 g, 49%). ^{1}H NMR ($CDCl_3$): δ 0.61 ppm (t, 12H), 1.26 (s, 18H), 1.88−2.07 (m, 8H), 3.42 (t, J = 5.4 Hz, 4H), 3.71 (t, J = 5.4 Hz, 4H), 3.73 (s, 4H), 4.49 (d, J = 5.3 Hz, 4H), 5.27 (dd, ^3J = 16 Hz, ^4J = 1.4 Hz, 2H), 5.43 (dd, ^3J = 16 Hz, ^4J = 1.4 Hz, 2H), 6.04−6.19 (m, 2H), 7.41 (d, J = 2.5 Hz, 2H), 7.59 (d, J = 2.5 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 8.0, 27.5, 31.3, 34.5, 60.3, 71.0, 71.1, 73.4, 82.0, 117.3, 117.4, 126.7, 129.3, 133.6, 137.6, 147.2, 150.6. $C_{42}H_{64}O_6Br_2$ (824.8): calcd C 61.16, H 7.81; found C 61.26, H 7.46. SM (EI): m/z (%) = 824 [M].

3,3′-(1,1,12,12-Tetraethyl-2,5,8,11-tetraoxadodecane-1,12-diyl)-bis[5-(1,1-dimethylethyl)-2-(2-propenyloxy)benzaldehyde] (28). Compound **28** was prepared as described for **5** starting from **27** (2.25 g, 2.73 mmol) in Et_2O (155 mL), TMEDA (1.9 mL, 12.5 mmol) and *n*-BuLi (1.6 M, 6.9 mL, 11.0 mmol) in Et_2O (6.5 mL), and DMF (2.12 mL, 27.3 mmol) in Et_2O (6.5 mL). The reaction was realized at −90 °C. After workup and drying, the crude product (colorless oil) was was directly used for the deprotection of the phenol function. ^{1}H NMR ($CDCl_3$): δ 0.62 ppm (t, 12H), 1.30 (s,

18H), 1.90−2.10 (m, 8H), 3.45 (t, J = 5.5 Hz, 4H), 3.74 (t, J = 5.5 Hz, 4H), 3.76 (s, 4H), 4.41 (dd, ^3J = 3.7 Hz, ^4J = 1.5 Hz), 5.29 (dd, ^3J = 9.1 Hz, ^4J = 1.2 Hz, 2H), 5.49 (dd, ^3J = 9.1 Hz, ^3J = 1.2 Hz, 2H), 5.99−6.12 (m, 2H), 7.73 (d, J = 2.9 Hz, 2H) 7.96 (d, J = 2.9 Hz, 2H) 10.26 (s, 2H).

3,3′-(1,1,12,12-Tetraethyl-2,5,8,11-tetraoxadodecane-1,12-diyl)-bis[5-(1,1-dimethylethyl)-2-hydroxybenzaldehyde] (29). Compound **29** was prepared as described for **6** starting from **28** (1.98 g 2.74 mmol) in MeOH (56 mL), $Pd(PPH_3)_4$ (158.2 mg, 0.137 mmol), and K_2CO_3 (2.27 g, 16.44 mmol). The crude product was purified by column chromatography using hexane/ethyl acetate (9/1) as the eluent to give a colorless oil (1.43 g, 81%). ^{1}H NMR ($CDCl_3$): δ 0.64 ppm (t, 12H), 1.28 ppm (s, 18H), 1.88−2.12 (m, 8H), 3.50 (t, J = 4.9 Hz, 4H), 3.75 (t, J = 4.9 Hz, 4H), 3.75 (s, 4H), 7.49 (d, J = 2.4 Hz, 2H), 7.66 (d, J = 2.4 Hz, 2H), 10.10 (s, 2H), 10.80 (s, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 7.7, 26.9, 31.2, 34.1, 60.2, 70.6, 71.0, 83.4, 121.3, 126.4, 129.5, 133.7, 141.5, 157.5, 194.7. $C_{38}H_{58}O_8$ (642.9): calcd C 71.00, H 9.09; found C 70.79, H 9.28. SM (ES) m/z (%) = 665.85 [M + Na^+]$^+$, 681.65 [M + K^+]$^+$.

Mn^{III}-Salen Complex 30. Complex **30** was synthesized as described above for complex **7**, starting from **29** (200 mg, 0.311 mmol) in 50 mL of EtOH, (*S*)-(−)-1,1′-binaphthyl-2,2′-diamine (88.5 mg, 0.311 mmol) and $Mn(OAc)_2 \cdot 4H_2O$ (114.5 mg, 0.467 mmol). The resulting solution was refluxed for 10 h. Yield: 120 mg, 40% as a dark brown microcrystalline solid. $C_{58}H_{68}N_2O_6ClMn$ (979.6): calcd C 71.12, H 7.00, N 2.86, Mn 5.61, Cl 3.62; found C 71.13, H 7.01, N 3.11, Mn 5.82, Cl 3.70. SM (ES): m/z = 975.85 [Mn^{III}SalenCl + H^+]$^+$, 989.85 [Mn^{III}Salen(EtOH) − Cl^-]$^+$. IR (KBr, cm^{-1}): 1610(C═N). UV−vis (CH_2Cl_2): λ (ϵ) = 233 nm (89400 L mol^{-1} cm^{-1}), 282 (49300), 327 (24400), 388 (15400). $[\alpha]^{20}_D$ = 0.0588 (589 nm, 0.080 g/dm^{-3} in CH_3OH, 10 cm path).

Catalytic Epoxidation Procedures. With NaOCl as Oxidant. A typical reaction mixture contained substrate (16 μL of 2,2′-dimethylchromene, 0.1 mmol) and internal standart (23.6 mg of 1,4-dibromobenzene, 0.1 mmol) in 0.5 mL of CH_2Cl_2, 5 μmol of the appropriate catalyst (0.5 mL of a 10 mM CH_2Cl_2 stock solution; catalyst/substrate ratio = 5%), and 4-phenylpyridine-*N*-oxide (4.3 mg, 25 μmol). After stirring at 0 °C for 10 min, 0.2 mmol NaOCl (0.4 mL of a 0.5 M solution in 0.16 mL of a 0.05 M aqueous Na_2HPO_4 solution, 2 equiv of oxidant with respect to the substrate) was added. After vigorous stirring for 2 h, the reaction was diluted with water (2 mL) and CH_2Cl_2 (2 mL). The layers were separated, the organic phase dried over Na_2SO_4, concentrated to ≈1 mL and analyzed by gas chromatography.

With Hydrogen Peroxide as Oxidant. The reaction mixture was prepared according to the procedure described above. After stirring at 0 °C for 10 min, 35% aqueous H_2O_2 (30 μL, 0.34 mmol, 3.4 equiv of oxidant with respect to the substrate) was added in four portions during 40 min. After stirring for 2 h, the reaction mixture was diluted with water (2 mL) and CH_2Cl_2 (2 mL). The filtrate was worked up as previously described and analyzed by chiral GC as described above.

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Supporting Information Available: Copies of ^{1}H NMR and proton-decoupled ^{13}C NMR spectra for compounds **6**, **10**, **15**, **20**, and **25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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