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Synthesis, Characterization and Reactions of Enantiomerically Pure 'Winged' Spirane Porphyrazines

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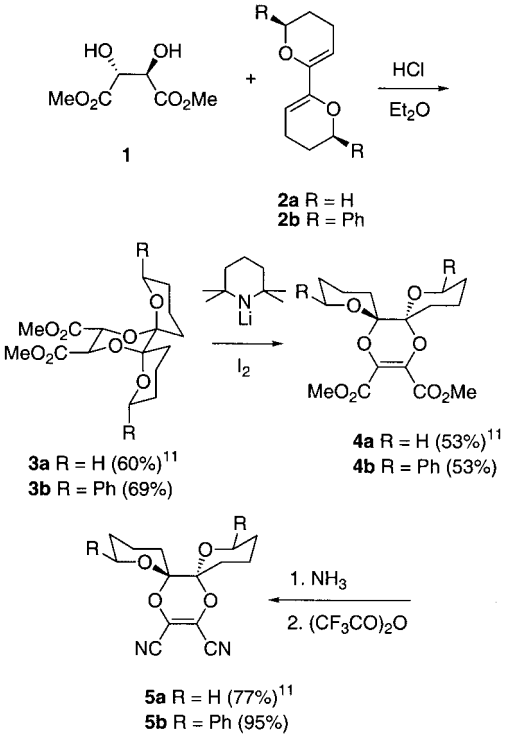
Abstract—A series of enantiomerically pure porphyrazineoctaol derivatives have been prepared from L-(+)-dimethyl tartrate via conversion into the corresponding dispoke protected dihydroxymaleonitrile, Linstead macrocyclization and transmetallation. The derived chloromanganese(III) complexes catalyzed the epoxidation of styrene with sodium hypochlorite as the oxygen atom source but with modest enantioselectivities (<25%).

Porphyrinic macrocycles are the subject of great interest in areas such as catalysis,[1] photodynamic therapy,[2] and in the fabrication of molecular electronic[3] or magnetic devices.[4] Our efforts in this area utilize the tetraazaporphyrin (porphyrazine, pz) ligand, and we have published extensively on the synthesis of diverse porphyrazines bearing 2, 4, 6 and 8 thio-[5–7] or amino[8] groups as peripheral macrocyclic ring substituents. More recently we described the first synthesis of porphyrazinoctaol derivatives in enantiomerically pure form via a simple, reliable strategy based on the Ley dispoke protection procedure.[9] Indeed, the development of oxidation reactions in which chiral metalloporphyrins are used as catalysts has received increased attention over the past two decades.[10] Herein we report full experimental data on the synthesis of porphyrazineoctaols **6a**, **6b**, **7a**, **7b**, **8a** and **8b** and a study of the epoxidation of styrene using the chloromanganese(III) complexes **8a** and **8b** as catalysts and sodium hypochlorite as the oxygen atom source.

Results and Discussion

The two chiral 2,3-dihydroxymaleonitrile precursors **5a**[11] and **5b**, employed in this study, were synthesized starting from dimethyl tartrate and using a Ley dispoke protection strategy.[12–14] Thus, reaction of excess L-(+)-dimethyl tartrate (**1**) with both 3,3′,4,4′-tetrahydro-6,6′-bi-2*H*-pyran (**2a**)[12] and (2*R*,2′*R*) 2,2′-diphenyl-3,3′,4,4′-tetrahydro-6,6′-bi-2*H*-pyran (**2b**)[13] in diethyl ether in the presence of hydrogen chloride[14] gave the dispiroketals **3a** and **3b** in 60 and 69% yield, respectively (Scheme 1). In consequence of the double anomeric effect, only one diastereoisomer of each **3a** and **3b** was formed under conditions of thermodynamic control.[15] In addition, the chirality inherent in the tartrate controlled the spirane stereochemistry and resulted



Scheme 1.

Keywords: porphyrins and analogs; complexes; epoxidation; asymmetric induction.

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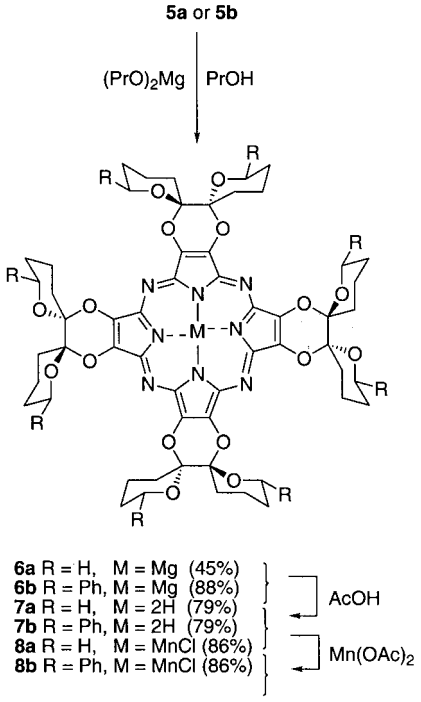

Scheme 2.

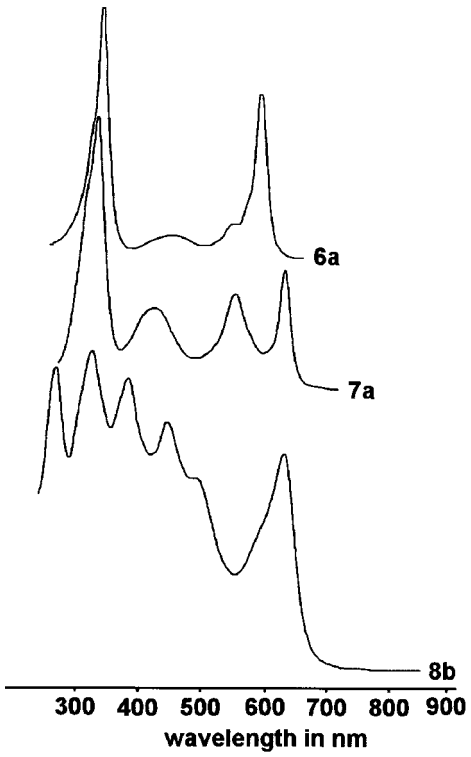

Figure 1. UV–Vis spectra of porphyrazines **6a**, **7a** and **8b** in $CHCl_3$.

in products in which the methoxycarbonyl moieties are equatorial. Monoiodination of **3a** and **3b**, via reaction of the corresponding enolates with iodine, followed by dehydroiodination in situ afforded the chiral alkenes **4a** and **4b** (53%). Amide formation using saturated ammonia solutions (in methanol for **4a** or in a 2:1 mixture of methanol/tetrahydrofuran in which **4b** is more soluble) and dehydration with trifluoroacetic anhydride proceeded smoothly to give dinitriles **5a** and **5b** in 77 and 95% overall yields (Scheme 1). Subsequent Linstead[16] macrocyclization of **5a** and **5b** using magnesium propoxide in propanol provided the magnesium porphyrazines **6a** and **6b** in 45 and 88% yield, respectively (Scheme 2). Demetallation was cleanly achieved without epimerization at the spirane centers by reaction with glacial acetic acid, thus providing macrocycles **7a** and **7b** (79%). The structure of the D_2-symmetric, enantiomerically pure porphyrazine **7a** was confirmed by X-ray analysis.[9] Remetallation of the corresponding free base porphyrazines **7a** and **7b** with manganese(II) acetate in the presence of potassium hydroxide and air, followed by exchange of the axial ligand during workup, gave the requisite manganese(III) chloride derivatives **8a** and **8b** in high yield (86%) (Scheme 2).

Representative electronic absorption spectra of compounds **6a**, **7a** and **8b** are shown in Fig. 1. Porphyrazine **6a** exhibits a Q-band at 599 nm, a less intense band at 455 nm, and a band in the Soret region at 347 nm. In agreement with other peripherally heterosubstituted (*S*, *N*) porphyrazines,[5,8] we tentatively assigned the peak at 455 nm to the $n-\pi^*$ transition from the lone-pairs on the peripheral oxygen atoms into a π^* ring orbital. In contrast, the demetallated product **7a** exhibits a split Q-band having Q_x and Q_y absorbances at 554 and 632 nm, respectively. The splitting reflects the change in symmetry ($D_{4h} \rightarrow D_{2h}$) and can be rationalized by Gouterman's four-orbital model.[17] In addition, the Soret band and the $n-\pi^*$ transition are blue-shifted to 338 and 427 nm, respectively. Insertion of the Mn(III) into the porphyrazine causes striking changes in the electronic absorption spectrum, which are not amenable to simple interpretation. Although **8b** exhibits similar bands to those of the Mg-derivative **6a** in the Soret and Q regions, additional transitions which we tentatively assigned to LMCT (Ligand to Metal Charge Transfer) absorbances of the type a_{2u} (ring)$\rightarrow e_g$, as suggested in analogous porphyrin spectra,[17,18] are observed.

In order to examine the enantioselective catalytic activity of the chiral manganese(III) chloride complexes **8a** and **8b**, epoxidations of styrene were carried out in buffered aqueous sodium hypochlorite solutions (pH 10.5) since epoxidation rates have been reported to be satisfactorily high and concomitant olefin chlorination low under these conditions for related porphyrin analogs.[19] Epoxidation of styrene in the presence of both trioctylmethylammonium chloride, as phase transfer catalyst, and porphyrazine **8a** (3 mol %) gave styrene oxide (82%, GC-MS). The enantiomeric excess (ee) of the isolated styrene oxide (39%) was shown to be 12% by proton NMR spectroscopy in the presence of the chiral shift reagent $Eu(hfc)_3$.[20] In the case of metalloporphyrin catalysts, addition of small amounts of nitrogen centered ligands have often been found to give better chemical yields and/or enantioselectivities.[21] However, no improved yields or enantioselectivities were observed for the **8a**-catalyzed reactions in the presence of pyridine. On the other hand, epoxidation catalyzed by the more bulky chloromanganese(III) porphyrazine **8b** gave styrene oxide (63% isolated yield, 25% ee).

The synthesis of a new family of chiral porphyrazineoctaol

derivatives has been achieved successfully. Whilst the chloromanganese(III) porphyrazines **8a** and **8b** were active as catalysts for the epoxidation of styrene, the enantioselectivities were too low to be of significance. However, the use of the dispoke protection is to be commended for the concise preparation of porphyrazinediols and related electron rich porphyrazine systems. Further aspects of the chemistry of such porphyrazines will be reported in due course.

Experimental

All reactions were conducted in oven or flame dried glassware. Reaction temperatures reported refer to external bath temperatures. Hexanes refers to the petroleum fraction bp 40–60°C. Solvents were distilled prior to use: THF and Et_2O (from Na/Ph_2CO); CH_2Cl_2 (from CaH_2); DMF [predried over BaO, distilled from alumina (activity I)]; propanol (from Mg); pyridine (from Zn). All other reagents were used as commercially supplied. Dinitrile **5a** was prepared from diester **1** via the dispiroketals **3a** and **4a** as reported elsewhere.[11] TLC was carried out on E. Merck precoated silica gel 60 F_{254} plates; compounds were visualized using UV radiation (254 nm). Chromatography refers to flash chromatography on E. Merck silica gel 60, 40–60 μm (eluants are given in parentheses).

(2*R*,6*R*,7*R*,9*R*,14*R*,15*R*)-Dimethyl 2,9-diphenyl-1,8,13, 16-tetraoxadispiro-[5.0.5.4]hexadecane-14,15-dicarboxylate (3b). HCl was bubbled through L-(+)-dimethyl tartrate (13.0 g, 73.2 mmol) in Et_2O (390 mL) for 40 min at 0°C when diene **2b**[13] (5.18 g, 16.3 mmol) in THF (30 mL) was added and the mixture was allowed to warm up to 10°C over 5 h. The mixture was neutralized with 10% NaOH, extracted with EtOAc (3×100 mL) and the combined organic layers were washed with saturated $NaHCO_3$ (3×100 mL), H_2O (3×50 mL), brine (3×50 mL) and dried (Na_2SO_4). Rotary evaporation and chromatography (CH_2Cl_2/Et_2O 9/1) followed by recrystallization (EtOAc/CH_2Cl_2) afforded diester **3b** (6.0 g, 69%) as a white crystalline solid: mp 212°C; R_f 0.40 (Et_2O/hexanes 1/1); $[\alpha]_D^{25}=+51.2$ (c=0.66, $CHCl_3$); IR (neat) 1747, 1454, 1047 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.46–2.16 (m, 12H), 3.76 (s, 6H), 4.64 (s, 2H), 4.82 (dd, J=2.3, 11.6 Hz, 2H), 7.26–7.43 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.7, 27.9, 33.2, 52.4, 68.2, 72.4, 97.7, 125.9, 127.3, 128.3, 142.6, 168.7; MS (FAB) 497 ($M^{+\cdot}$); HRMS (CI) calcd for $C_{28}H_{36}NO_8$: $(M+NH_4)^+$ 514.2441, found: $(M+NH_4)^+$ 514.2435. Anal. Calcd for $C_{28}H_{32}O_8$: C, 67.71; H, 6.50. Found: C, 67.63; H, 6.48.

(2*R*,6*R*,7*R*,9*R*)-Dimethyl 2,9-diphenyl-1,8,13,16-tetraoxadispiro-[5.0.5.4]hexadec-14-ene-14,15-dicarboxylate (4b). Lithium 2,2,6,6-tetramethylpiperidide, prepared from 2,2,6,6-tetramethylpiperidine (2.39 mL, 14.2 mmol) in THF (6.0 mL) and *n*-BuLi in hexane (2.5 M; 5.49 mL), was added dropwise to diester **3b** (2.20 g, 4.43 mmol) in THF (15 mL) at −78°C over 20 min. After stirring at −78°C for 2 h, I_2 (1.35 g, 5.31 mmol) in THF (11 mL) was added and the mixture allowed to warm up to 20°C over 16 h. The solution was poured onto saturated NH_4Cl (50 mL) and extracted with Et_2O (3×50 mL). The combined organic layers were washed with saturated Na_2SO_3 (3×25 mL), H_2O (3×25 mL), brine (3×25 mL) and dried (Na_2SO_4). Rotary evaporation and chromatography (hexanes/CH_2Cl_2/EtOAc 22/10/1) followed by recrystallization (EtOAc/CH_2Cl_2/hexanes) afforded alkene **4b** (1.15 g, 53%) as a white crystalline solid: mp 184°C; R_f 0.45 (hexanes/CH_2Cl_2/EtOAc 22/10/1); $[\alpha]_D^{25}=-125.0$ (c= 0.28, $CHCl_3$); IR (neat) 1746, 1436, 1318, 1195, 1080, 970 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.59–1.70 (m, 2H), 1.83–2.05 (m, 6H), 2.20–2.33 (m, 4H), 3.82 (s, 6H), 4.97 (dd, J=1.7, 11.7 Hz, 2H), 7.28–7.37 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.7, 27.6, 32.7, 52.5, 73.3, 98.0, 125.9, 127.4, 128.2, 130.6, 142.6, 163.1; MS (FAB) 495 ($M^{+\cdot}$); HRMS (FAB) calcd for $C_{28}H_{31}O_8$: $(M+H)^+$ 495.2019, found: $(M+H)^+$ 495.2058. Anal. Calcd for $C_{28}H_{30}O_8$: C, 67.99; H, 6.12. Found: C, 67.87; H, 6.14.

(2*R*,6*R*,7*R*,9*R*)-2,9-Diphenyl-1,8,13,16-tetraoxadispiro-[5.0.5.4]hexadec-14-ene-14,15-dinitrile (5b). Diester **4b** (1.23 g, 2.48 mmol) in MeOH and THF (2/1; 40 mL) was saturated with NH_3 at 0°C and stirred at 20°C for 96 h. Rotary evaporation and chromatography (EtOAc) followed by recrystallization (CH_2Cl_2) afforded the corresponding diamide (1.2 g, 100%) as a white crystalline solid: mp 130–135°C; R_f 0 (Et_2O/hexanes 1/1); $[\alpha]_D^{25}=-110.0$ (c=0.22, $CHCl_3$); IR (neat) 3474, 3200, 1675, 1594, 1172, 1067, 971 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.56–1.68 (m, 2H), 1.63–2.08 (m, 6H), 2.16–2.30 (m, 4H), 4.82 (d, J=11.7 Hz, 2H), 7.25–7.36 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.0, 27.6, 33.0, 73.6, 97.1, 125.8, 127.5, 128.3, 132.3, 142.0, 146.4; MS (FAB) 465 ($M^{+\cdot}$); HRMS (FAB) calcd for $C_{26}H_{29}N_2O_6$: $(M+H)^+$ 465.2026, found: $(M+H)^+$ 465.2038. Trifluoroacetic anhydride (0.79 mL, 5.58 mmol) was added dropwise to the diamide in pyridine (30 mL) at −30°C over 30 min under N_2. The solution was allowed to warm up to 20°C over 2 h, when Et_2O (100 mL) was added. The mixture was neutralized with 3N HCl and extracted with EtOAc (3×50 mL). The combined organic layers were washed with H_2O (3×25 mL), and brine (3×25 mL) and dried (Na_2SO_4). Rotary evaporation and chromatography (hexanes/CH_2Cl_2/EtOAc 22/10/1) gave dinitrile **5b** (0.94 g, 95%) as a white solid: mp 215–218°C; R_f 0.65 (hexanes/CH_2Cl_2/EtOAc 22/10/1); $[\alpha]_D^{25}=-83.6$ (c=0.56, $CHCl_3$); IR (neat) 2230, 1633, 1256, 1218, 1089, 1044 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.63–1.70 (m, 2H), 1.84–2.30 (m, 10H), 4.81 (dd, J=2.4, 11.7 Hz, 2H), 7.27–7.44 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.2, 27.4, 32.6, 74.7, 100.0, 111.6, 121.5, 125.7, 128.0, 128.5, 140.9; MS (CI) 446 $(M+NH_4)^+$; HRMS (CI) calcd for $C_{26}H_{28}N_3O_4$: $(M+NH_4)^+$ 446.2080, found: $(M+NH_4)^+$ 446.2088. Anal. Calcd for $C_{26}H_{24}N_2O_4$: C, 72.87; H, 5.65; N, 6.54. Found: C, 72.35; H, 5.64; N, 6.39.

Mg-Pz (6a). A mixture of propanol (3 mL), Mg (5 mg, 0.04 mmol), and I_2 (one small crystal) was heated to reflux for 12 h under N_2. The suspension was cooled and dinitrile **5a**[11] (95 mg, 0.34 mmol) was added and the mixture further heated at reflux for 4 h. The deep blue suspension was allowed to cool, filtered (silica) and the solids washed with MeOH. Rotary evaporation and chromatography ($CHCl_3$; $CHCl_3$/MeOH 39/1) gave Mg-porphyrazine **6a** (44 mg, 45%) as a dark blue solid: mp >330°C; R_f 0.37

(CH_2Cl_2/MeOH 15/1); IR ($CHCl_3$) 1638, 1187, 1098, 973 cm^{-1}; UV–Vis ($CHCl_3$) λ_{max} (log ϵ) 347 (4.79), 455 (3.77), 551 (3.94), 599 (4.62) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.71–1.89 (m, 16H), 1.96–2.11 (m, 16H), 2.39–2.56 (m, 16H), 3.60–3.73 (m, 8H), 4.02–4.10 (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.4, 25.0, 28.9, 62.3, 99.3, 137.6, 146.4; MS (FAB) 1129 $(M+H)^+$.

2H-Pz (7a). AcOH (1 mL) and porphyrazine **6a** (36 mg, 0.032 mmol) was stirred at 20°C for 16 h, poured onto ice and water (10 mL) and the resulting suspension brought to pH 7 with 1 M NaOH. The precipitate was collected via vacuum filtration, washed with water and chromatographed ($CHCl_3$) to give porphyrazine **7a** (30 mg, 79%) as a blue solid: mp >300°C (decomp.); R_f 0.65 (CH_2Cl_2/Et_2O 4/1); IR ($CHCl_3$) 3313, 1662, 1619, 1216, 1185, 1103, 971, 894, 755 cm^{-1}; UV–Vis ($CHCl_3$) λ_{max} (log ϵ) 338 (4.20), 427 (3.68), 554 (3.75), 632 (3.83) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ −3.51 (br s, 2H), 1.77–1.90 (m, 16H), 2.09 (d, J=12.8 Hz, 8H), 2.21 (dd, J=13.2, 4.5 Hz, 8H), 2.62 (d, J=13.3 Hz, 8H) 2.76 (dd, J=12.0, 4.1 Hz, 8H), 3.72 (d, J=9.5 Hz, 8H), 4.27 (td, J=10.8, 4.7 Hz, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.3, 24.9, 28.9, 62.5, 100.1, 137.6, 143.3; MS (FAB) 1107 $(M+H)^+$; HRMS (FAB) calcd for $C_{56}H_{67}N_8O_{16}$: $(M+H)^+$ 1107.4675, found: $(M+H)^+$ 1107.4706. An X-ray crystallography determination for **7a** has already been reported,[9] CCDC-100184.

2H-Pz (7b). Propanol (15 mL), Mg (26.8 mg, 1.1 mmol) and I_2 (one small crystal) were heated to reflux for 12 h under N_2. The suspension was cooled and dinitrile **5b** (0.82 g, 1.92 mmol) was added and the mixture further heated at reflux for 24 h. The deep blue suspension was allowed to cool, filtered (Celite) and the solids washed with CH_2Cl_2. Rotary evaporation and chromatography (hexanes/CH_2Cl_2/EtOAc 22/10/1) gave Mg-porphyrazine **6b** (0.73 g, 88%) as a dark blue solid: R_f 0.30 (hexanes/CH_2Cl_2/EtOAc 22/10/1); IR (neat) 1638, 1212, 1095, 969 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.72–1.90 (m, 8H), 2.16–2.25 (m, 16H), 2.30–2.44 (m, 8H) 2.80–2.93 (m, 8H), 2.93–3.14 (m, 8H), 5.39 (br d, J=11.3 Hz, 8H), 7.02–7.17 (m, 40H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.0, 29.0, 33.5, 73.4, 100.5, 125.9, 127.0, 127.9, 137.9, 142.6, 146.3; MS (FAB) 1738 ($M^{+\cdot}$). Porphyrazine **6b** and AcOH (20 mL) in CH_2Cl_2 (20 mL) were stirred at 20°C for 72 h. The solution was diluted with Et_2O (50 mL), brought to pH 7.0–7.5 with 1 M NaOH and the organic layer was separated, washed with saturated NH_4Cl (3×30 mL), H_2O (3×30 mL), brine (3×25 mL) and dried (Na_2SO_4). Rotary evaporation and chromatography (hexanes/CH_2Cl_2/EtOAc 22/10/1) gave porphyrazine **7b** (0.46 g, 79%) as a blue solid: R_f 0.28 (hexanes/CH_2Cl_2/EtOAc 22/10/1); IR (neat) 3309, 1665, 1621, 1504, 1453, 1264, 1216, 1162, 1096, 1048, 987, 873, 732 cm^{-1}; UV–Vis ($CHCl_3$) λ_{max} (log ϵ) 338 (4.89), 429 (4.37), 553 (4.45), 632 (4.55) nm; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.80–1.97 (m, 8H), 2.19–2.27 (m, 16H), 2.32–2.47 (m, 8H), 2.84–2.93 (m, 8H), 2.96–3.10, (m, 8H), 5.38 (br d, J=10.5 Hz, 8H), 7.05–7.10 (m, 24H), 7.16–7.19 (m, 16H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.0, 28.9, 33.1, 73.7, 100.9, 126.1, 127.2, 128.0, 137.4, 142.1, 145.0; MS (FAB) 1718 $(M+2H)^+$. Anal. Calcd for $C_{104}H_{98}N_8O_{16}\cdot H_2O$: C, 72.03; H, 5.81; N, 6.46. Found: C, 71.93; H, 5.81; N, 6.25.

MnCl-Pz (8a). $Mn(OAc)_2\cdot 4H_2O$ (50.6 mg, 0.21 mmol) and KOH (13.2 mg, 0.24 mmol) were added to porphyrazine **7a** (0.11 g, 0.10 mmol) in DMF (3 mL) and the mixture was heated at 100°C for 12 h. Brine (5 mL) was added, and the mixture extracted with Et_2O and CH_2Cl_2 (4/1, 3×30 mL). The combined organic layers were washed with H_2O (3×20 mL) and brine (3×20 mL) and dried (Na_2SO_4). Rotary evaporation and chromatography (CH_2Cl_2/Et_2O 9/1; 19/1) gave Mn-porphyrazine **8a** (106 mg, 86%) as a dark green solid: R_f 0.26 (CH_2Cl_2/MeOH 19/1); IR (KBr) 1631, 1222, 1104, 1053, 970, 918, 876 cm^{-1}; UV–Vis ($CHCl_3$) λ_{max} (log ϵ) 272 (4.43), 330 (4.44), 386 (4.38), 450 (4.32), 497 (4.23), 635 (4.22) nm; MS (FAB) 1159 $(M+H-Cl)^+$. Anal. Calcd for $C_{56}H_{64}ClMnN_8O_{16}$: C, 56.26; H, 5.40; N, 9.38. Found: C, 55.97; H, 5.17; N, 9.17.

MnCl-Pz (8b). The same reaction conditions as above, but at 120°C and 3 h, gave Mn-porphyrazine **8b** (0.45 g, 86%) after chromatography (CH_2Cl_2/EtOAc 9/1) as a dark green solid: R_f 0.16 (CH_2Cl_2/EtOAc 9/1); IR (neat) 2951, 1631, 1227, 1051, 936, 863 cm^{-1}; UV–Vis ($CHCl_3$) λ_{max} (log ϵ) 230 (4.32), 330 (4.45), 388 (4.41), 448 (4.34), 491 (4.23), 633 (4.28) nm; MS (FAB) 1768 $(M-H-Cl)^+$. Anal. Calcd for $C_{104}H_{96}ClMnN_8O_{16}.H_2O$: C, 68.55; H, 5.42; N, 6.15. Found: C, 68.58; H, 5.51; N, 6.05.

General procedure for the epoxidation of styrene with NaOCl

Aqueous Na_2HPO_4 (0.05 M; 60 mL) was added to aqueous NaOCl (1.6 M; 20 mL) and the pH adjusted to 10.5 with 3 M HCl. An aliquot (5 mL) of this solution was added to the porphyrazine catalyst (0.015 mmol), styrene (52 mg, 0.5 mmol), dodecane (42.6 mg, 0.25 mmol) as the internal standard, and trioctylmethylammonium chloride (101 mg, 0.5 mmol) in CH_2Cl_2 (2 mL) at 0°C and the mixture was allowed to warm up to 20°C. Aliquots were removed at intervals and the formation of the styrene oxide monitored by GC-MS. After stirring for 3 h, the mixture was extracted with Et_2O (3×20 mL) and the combined organic layers washed with H_2O (3×50 mL), brine (3×50 mL) and dried (Na_2SO_4). Rotary evaporation and chromatography (hexanes/Et_2O 19:1) gave styrene oxide of which the enantiomeric excess was determined by ^1H NMR spectroscopy in the presence of $Eu(hfc)_3$ as the chiral shift reagent.[20]

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