Chiral Atropisomeric Metalloporphyrins in the Enantioselective Styrene Epoxidation

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A new series of porphyrins has been synthesised, incorporating four identical chiral binaphthyl derivatives in the *meso*-positions. Owing to a hindered rotation around the bond between the naphthyl and the porphyrin, four atropisomers are generated, which were fully separated by preparative TLC and thoroughly characterised. The free bases were metallated with iron(III) and manganese(III) and the resulting complexes were used as catalytic precursors in styrene epoxidation. The reactions show chemoselectivity and enantioselectivity, depending on the stereochemistry of the metalloporphyrin. It is demonstrated that highest efficiency is performed by the αααββ isomer, showing C_2 symmetry.

Introduction

In nature there is a wide variety of metalloenzymes[1] in which the active site is constituted by a metalloporphyrin moiety. Cytochromes P-450[2] belong to a particularly wide enzymatic family able to carry out regio- and stereoselective oxidation processes. Since 1979, the use of synthetic metalloporphyrins as mimics for cytochrome P-450[3] has been a very active area of research. In fact a large number of publications have appeared on the use of synthetic metalloporphyrins as catalytic precursors in olefin epoxidation,[4] cyclopropanation,[5] unactivated C–H bond hydroxylation[6] and sulfoxidation.[7]

Chiral porphyrins are often synthesised with the aim of forming catalytic precursors active in enantioselective reactions by introducing groups endowed with suitable stereogenic elements. The distribution of these chiral groups about the porphyrin plane is likely to influence both the activity and enantioselectivity of the catalyst. Unfortunately, to quote Kodadek,[4e] "the lack of methodical studies on structurally similar porphyrins with systematically varied shapes under comparable reaction conditions continues to hinder the design of effective catalysts." To this end, we undertook an investigation on a "chiral wall" porphyrin, similar to the one studied by Kodadek,[8] based on the condensation of pyrrole with an optically pure binaphthyl aldehyde. We synthesized a novel chiral macrocycle, the *meso*-tetrakis[(a*S*)-2′-methoxy-1,1′-binaphth-2-yl]porphyrin [T(OMe)BNPH$_2$, (**2**)] in which a methoxy group is introduced into the 2′ position of each binaphthyl moiety. Such a substituent provides a useful NMR spectroscopic probe for the differentiation of the porphyrin system: Furthermore it is expected to activate the naphthalene rings towards π-π interactions during the enantioselective catalytic process. In full analogy with similar systems, four atropisomers are produced in the reaction mixture. Their complete separation was achieved by preparative TLC. This made it possible to characterise spectroscopically the four ligands and the corresponding chloro-iron(III) complex of each atropisomer and, in one case, a chloro-manganese(III) complex.

The iron(III) and manganese(III) derivatives were tested as enantioselective catalytic precursors in the epoxidation of styrene by iodosobenzene – a reference reaction with a single substrate and primary oxidant. The results of these assays show that there are significant differences in yield, and chemo- and stereoselectivity among the four stereoisomers, which can be related to their structures. A comparison of the performances of the individual stereoisomers as catalysts leads to the conclusion that the αααββ C_2 isomer is the most efficient. This is in agreement with a recent report by Collman.[9]

It should also be mentioned that, besides their application in synthetic chemistry, porphyrins have also recently received renewed attention because of their peculiarities as chromophores. They have been introduced as selective probes in complex molecules, providing a sensitive means of investigating stereochemistry through exciton-coupling analysis.[10] Thus, the electronic and CD spectra will also be discussed.

Results and Discussion

Free Ligands

Synthesis

The necessary, enantiopure (a*S*)-2′-methoxy-1,1′-binaphthyl-2-carboxyaldehyde (**1**) was prepared following the procedure reported by Miyano:[11] the pure diastereoisomeric binaphthylic menthol ester was reduced to the alcohol by

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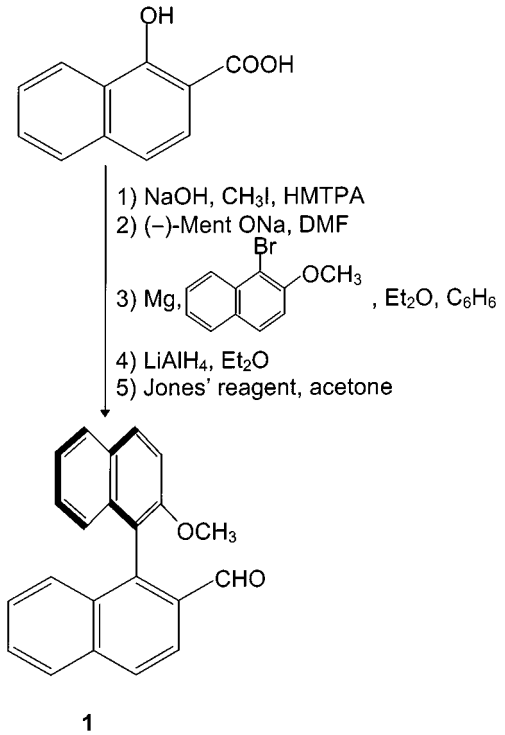
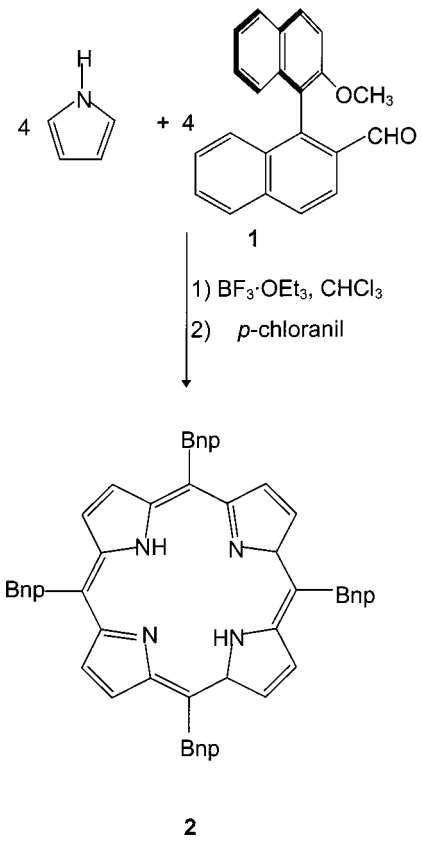
$LiAlH_4$ and then oxidised to the aldehyde by Jones' reagent[12] (Scheme 1).



Scheme 1. Synthesis of the chiral binaphthyl aldehyde



Scheme 2. Synthesis of the porphyrin; *Bnp* represents a 2′-methoxy-1,1′-binaphth-2-yl group

The preparation of **2** was accomplished following the protocol developed by Lindsey et al. (Scheme 2).[13] Some difficulties have been encountered during the cyclisation reaction, probably due to the steric hindrance of the bulky binaphthyl moiety and to the presence of the methoxy group which can act as a Lewis base towards the acid catalyst.

The reaction parameters were extensively varied in order to optimise the porphyrin yield. Higher yields were obtained when the same reagent concentration as reported by Lindsey[13] was used and the cyclization reaction was carried out by stirring for 48 h in the presence of $BF_3{\cdot}OEt_2$. We postulated that part of the catalyst was consumed by coordination to the methoxylic oxygen, lowering its effective concentration in the reaction mixture. Indeed, increasing the concentration of $BF_3{\cdot}OEt_2$ improved the porphyrin yield by up to 10%. The reaction progress was monitored by TLC on small portions previously oxidised by *p*-chloranil and treated with NEt_3. The final aromatisation step was carried out in situ with *p*-chloranil, the solution was stirred for about 24 h at room temperature in order to prevent thermal degradation, which makes the purification steps difficult. The crude product was purified by column chromatography (alumina, dichloromethane/heptane; silica gel, dichloromethane/cyclohexane). Porphyrin **2** was obtained in a satisfactory 10% yield.

Separation of the Atropisomeric Mixture

The cyclisation of pyrrole and the *ortho*-substituted aromatic aldehyde led to the formation of four atropisomeric porphyrins (Figure 1), which were successfully separated by preparative TLC (silica gel, CH_2Cl_2/heptane). The first three bands showed the typical red porphyrin colour, whereas the final band was green. Following isolation, we evaluated the ratios among the four chromatographic fractions as I:II:III:IV = 2.5:50:12.5:35.

The assignment of the molecular structure to each chromatographic fraction was obtained by the analysis of the NMR spectra in the region of the β-pyrrolic protons and by simple preliminary symmetry considerations with reference to the structures depicted in Figure 1. The ^1H NMR spectra of each chromatographic fraction in $CDCl_3$ solution revealed:

– fraction I: two doublets with $J = 4.5$ Hz; this pattern is only compatible with the isomer 5α,10α,15α,20α (symmetry C_4);

– fraction II: eight doublets indicating that it belongs to the least symmetric isomer, 5α,10α,15α,20β (symmetry C_1);

– fraction III: a single resonance and two doublets, atropisomer 5α,10α,15β,20β (symmetry C_2);

– fraction IV: two singlets, atropisomer 5α,10β,15α,20β (symmetry D_2).

The elution order with which the four porphyrins were separated is therefore: 1) α,α,α,α; 2) α,α,α,β; 3) α,α,β,β; 4) α,β,α,β. Owing to the differences in the systems considered, it is not surprising that the elution order is different from that reported by Collman.[14]

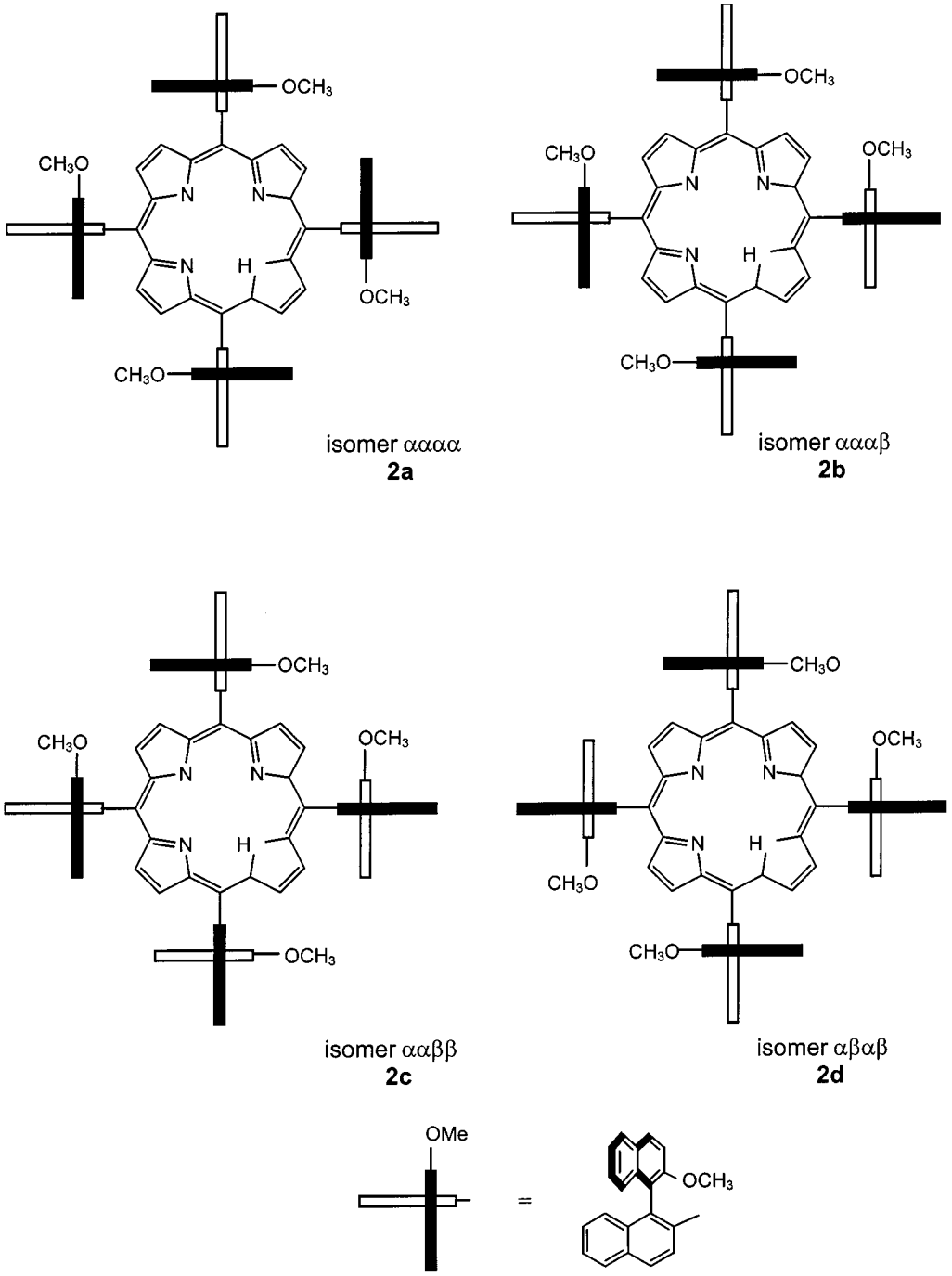


Figure 1. A schematic representation of the four atropisomers **2a–d**

Metalloporphyrins

The complexation of the free base porphyrins by iron and manganese was accomplished by classical methods starting from the corresponding metal carbonyls in toluene at 55 °C.[15] After chromatographic separation (alumina, CH_2Cl_2/MeOH, 90:10), the complexes were treated with dilute HCl affording the chloro iron porphyrins, **3a–d,** in good yields. Each complex was characterised by UV/Vis, CD, IR and MS spectroscopy.

Starting from the free base **2d**, the Mn^{III} complex **4** was prepared by the same route. It is analogous to Kodadek′s "chiral wall" porphyrin,[8] the only difference being the presence of the OMe group on the naphthyl fragments.

Spectroscopic Characterisation

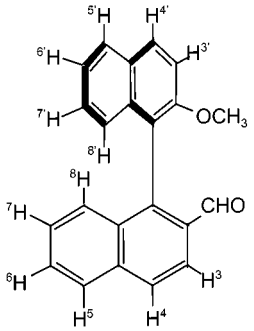
NMR Spectroscopy

The molecular symmetry of **2d** and **2a** allowed us to assign the chemical shifts of each aromatic hydrogen by means of DQF-COSY, Table 1. It is remarkable that the strong ring current of the macrocycle induces large shifts of protons lying above or on the side of the porphyrin plane with respect to the parent aldehyde, **1**.

Table 1. Chemical shifts ($CDCl_3$, 300 MHz) for the aromatic protons of the binaphthyl aldehyde, **1** and for porphyrins **2a** and **2d**

Proton δ (ppm)	H^3	H^4	H^5	H^6	H^7	H^8	$H^{3'}$	$H^{4'}$	$H^{5'}$	$H^{6'}$	$H^{7'}$	$H^{8'}$
1	8.16	7.99	7.94	7.56	7.29	7.33	7.43	8.04	7.88	7.32	7.21	6.95
2a	7.81	8.06	8.19	7.66	7.39	7.23	6.20	7.28	7.55	7.20	7.41	7.76
2d	8.32	8.23	8.22	7.63	7.35	7.24	6.22	6.83	7.06	7.87	7.03	7.48

The conformations of **1** and **2d**, with the numbering shown in Scheme 3 were investigated using ^1H transient (NOESY) and stationary-state nuclear Overhauser effects. On saturating the methoxyl protons of **1**, one can observe an enhancement of the aldehyde hydrogen resonance. No detectable effect can be seen between the two *peri* protons H^8 and $H^{8'}$ either in **1** or in **2d**. These results, confirmed by NOESY, lead to the conclusion that the dihedral angle between the two aromatic planes is rather large ($\theta \approx 90°$).



Scheme 3. Numbering of the protons of the binaphthyl

In **2d**, the two nonequivalent types of pyrrolic protons give a transient enhancement, one at the $-OCH_3$ group, the other at $H^{8'}$. This means that in order to accommodate the bulky methoxyl group leaning into the porphyrin plane, the binaphthyl axis must bend, thus pushing $H^{8'}$ towards the pyrrole (Figure 2).

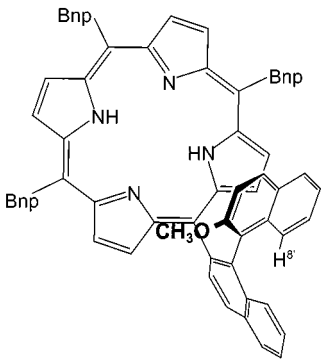


Figure 2. Preferential orientation of the binaphthyl axis with respect to the porphyrin

Electronic Spectra

The electronic absorption spectra of compounds **2a–d** were recorded between 200 and 700 nm in THF as the solvent (Figure 3, top). In all four cases they can be divided into two ranges: a) Between 200 and 350 nm, where the absorptions due to the binaphthyl moiety are present. The $\pi \rightarrow \pi^*$ transitions of the naphthalene chromophore mainly contribute in this range, around 230, 280 and 335 nm. The first two are electronically allowed (they are assigned to the ^1B and ^1L_a transitions and are polarised along the long and the short naphthalene axes, respectively[16]) and thus they give rise to very intense bands (ε values up to 3×10^4 dm^2 mol^{-1} and 5×10^3 dm^2 mol^{-1}, respectively); b) The range 400–700 nm, where the excitations localised on the porphyrin moiety occur. These absorptions show the typical porphyrin pattern: a strong band is present at about 430–435 nm ($\varepsilon = 2 \times 10^4$ dm^2 mol^{-1}, Soret B band)[17] and a series of four bands, named Q bands or IV, III, II, I, moving from shorter to longer wavelengths. The pattern of the Q bands is similar for the four atropisomers, suggesting that the spatial arrangement of the substituents around the macrocycle plane does not significantly affect the energy levels of the porphyrin chromophore. Owing to smaller intensity differences compound **2d** is green while the others are violet.

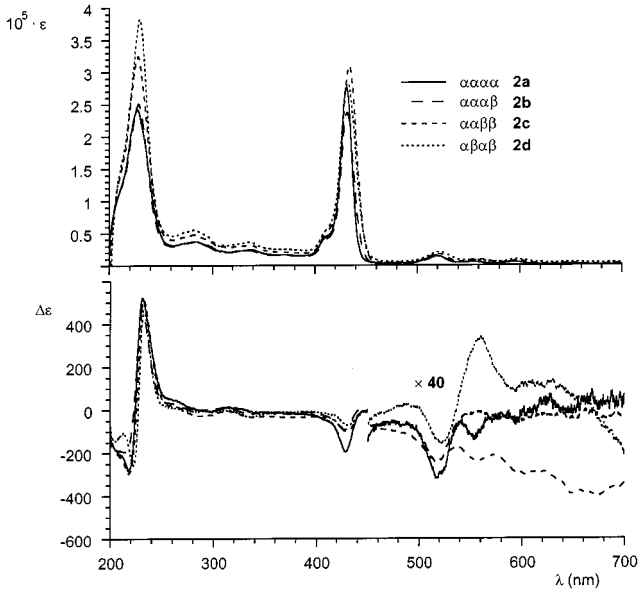


Figure 3. Absorption (top) and CD (bottom) spectra of the four atropisomers **2a–d**

Circular Dichroism Spectra

The atropisomers were characterised by circular dichroism (Figure 3, bottom). We analysed THF solutions in the wavelength ranges 200–500 nm and 450–700 nm, as depicted in Figure 3. From 200 to 500 nm the overall spectral pattern of the four compounds is very similar reflecting the results of UV/Vis spectroscopy. An intense exciton couplet is present at about 225 nm due to the coupling of the two naphthyl ^1B_b transitions. The Soret band has a negative Cotton effect. In the spectral region from 450 to 700 nm the IV band is quite evident while the other Q bands are less intense.

A detailed analysis of the CD spectra in terms of degenerate and nondegenerate exciton coupling is in progress.

Metalloporphyrins

The patterns of the UV/Vis (Figure 4, top) spectra for the four iron porphyrins are very similar indicating that, as already observed for the free porphyrins, the distortion of the porphyrin plane due to the relative geometry of the binaphthyl framework is almost negligible. The manganese porphyrin, as is usual for this metal, has additional weak bands at about 380 and 405 nm (ε = 4220 and 4019 dm^2 mol^{-1}, respectively), corresponding to the splitting of the B band.[18] The CD spectra (Figure 4, bottom) reveal that the couplet at about 230 nm is larger than for the free bases, at least for the αααβ and ααββ isomers. Moreover, the Soret band is hardly visible and again negative.

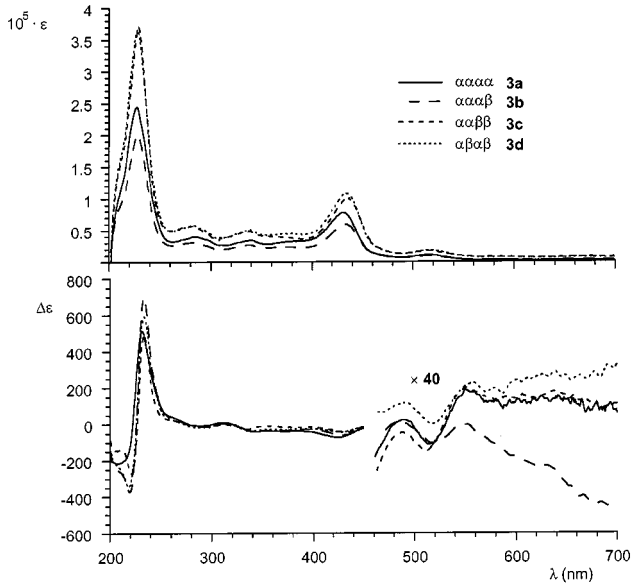
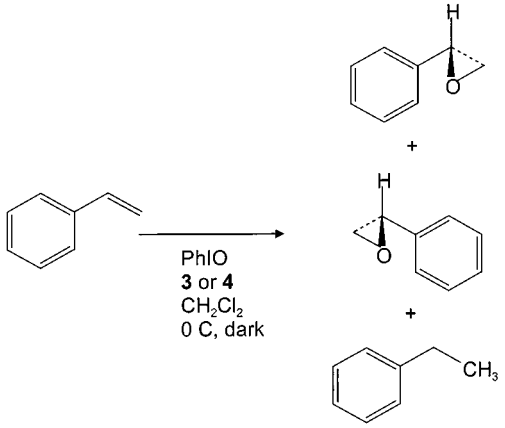


Figure 4. Absorption (top) and CD (bottom) spectra of the four atropisomeric chloro-iron porphyrins **3a–d**

Asymmetric Epoxidation of Styrene

The four iron(III) chloro complexes **3a–d** and the Mn derivative **4** have been tested as catalytic precursors in the asymmetric epoxidation of styrene, a typical substrate for these reactions. All the reactions were carried out following a standard procedure,[15] in which iodosylbenzene was used as a single oxygen-atom donor. Substrate, oxidant and catalyst were used in the ratio 1000:100:1 (1 mmol of olefin) and stirred in the dark at 0 °C in dichloromethane as the solvent for about 3 h (Scheme 4).

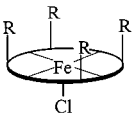
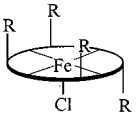
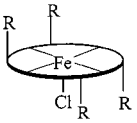
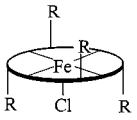
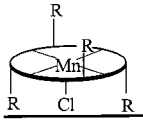
The reaction mixture contained naphthalene (0.05 mmol) as internal standard for the gas-chromatographic evaluation of the yields. A preliminary purification of the oxidation products through a short silica gel column (pentane/diethyl ether) was carried out prior to GC analysis. The enantiomeric excesses have been determined by GC using the chiral stationary phase Cydex-B [heptakis (2,3,6-tri-*O*-methyl)-β-cyclodextrin]. The absolute configuration of the products



Scheme 4. Reaction conditions for the catalytic epoxidation of styrene, to be compared with Table 2; in the last entry of Table 2, the Mn^{III} complex **4** was used instead

was determined by comparison of the GC retention time of an authentic sample of (*R*)-styrene oxide (Fluka). The results are collected in Table 2.

Table 2. Yields of styrene oxide and phenylacetaldehyde, and the enantiomeric excesses obtained in the oxidation reactions of styrene catalysed by complexes **3a–d** and **4**

Catalytic precursor		Styrene oxide (%)	Phenyl acetaldehyde (%)	e.e. (%)
	**3a**	44	6	21
	**3b**	40	10	39
	**3c**	47	8	57
	**3d**	35	12	48
	**4**	37	19	8

The following observations can be made:

1. The epoxide is produced in satisfactory (up to 47%) chemical yield. In all the runs, variable quantities of phenylacetaldehyde were produced (about 10%).

2. The enantiomeric excess, *ee*, is strongly dependent on the structure of the catalytic precursor, ranging from 21% with compound **2a** (αααα) to 57% with compound **2c** (ααββ). It can also be noticed that in this latter case the maximum *ee* is accompanied by the minimum amount of by-product. Compound **2c** is the "best" catalytic precursor

of this family. This may be attributed to greater ease of access to the metal ion for this isomer.[9]

3. The manganese derivative **4** is the analogue of Kodadek's catalyst.[7] It shows rather poor enantioselectivity.

4. In all the runs, the absolute configuration of the product was (*S*), suggesting that the stereochemical outcome of this reaction is primarily determined by the absolute configuration of the binaphthyl moiety rather than from the overall molecular arrangement. We hypothesise[] that when the olefin double bond approaches the active iron-oxo site from the prochiral *re* face, stabilising π-π electronic interactions between the styrene π system and the naphthyl ring bearing the methoxyl group are generated. Such an arrangement would lead to the (*S*) enantiomer. These interactions cannot take place when the oxo transfer is directed to *si* face; the formation of the (*R*) enantiomer is thus disfavoured.

Conclusions

We prepared and separated four atropisomeric "chiral wall" porphyrins in order to investigate the influence of the stereochemistry on a model enantioselective reaction. The catalytic precursors prepared perform satisfactorily as for chemical and optical yields and compare well with other similar catalysts. The separation of the four atropisomers achieved in the present work allows us to assess the role played by the overall molecular organisation upon activity and to draw interesting conclusions on the relation between activity and stereochemistry, in particular symmetry. The "best catalyst" is the system derived from the αααββ porphyrin. Probably a major role is played by steric effects: it is not surprising that the crowded αααα and the αααβ give rather poor results. Rationalising the lower yields obtained by the αβαβ isomer seems, however, more difficult.

Another important comparison is between Mn and Fe, the latter being much more suited. A spectroscopic characterisation of the four atropisomers of the porphyrin was performed. A full conformational analysis of these systems and account of the spectral results is in progress.

Experimental Section

General: ^{1}H NMR spectra were obtained in the indicated deuterated solvents on a Varian VXR 300 (300 MHz for ^{1}H) or on a Bruker DRX 500 (500 MHz for ^{1}H) spectrometers. Solution spectra in the UV/Vis region were recorded on a Varian Cary 1 instrument. Infrared measurements were carried out on a Bruker IFS 66v FT instrument as KBr or CsI disks. Mass spectra were recorded on a Kratos Concept 32S. Circular dichroism spectra were recorded on a Jasco J-600 Model dichrograph. GC analysis was performed on a Perkin–Elmer 8420 chromatograph with a flame ionisation detector and a DB1 capillary column, nitrogen was used as the carrier gas. Chiral GC analysis was carried out using a Perkin–Elmer Autosystem with flame ionisation detector using the chiral capillary column SGE-Cydex-B (25m × 0.32 mm), helium was used as the carrier gas.

***Meso*-tetrakis[2′-methoxy-(a*S*)-1,1′-binaphth-2-yl]porphyrin (2):** A three necked 3 L flask equipped with a reflux condenser and a nitrogen inlet port was charged with 1.8 L of deareated $CHCl_3$, 2′-methoxy-(a*S*)-1,1′-binaphth-2-aldehyde (**1**) (6 g, 19.2 mmol) and freshly distilled pyrrole (1.33 cm^3, 19.2 mmol). After the solution was purged with N_2 for 30 min, it was shielded from ambient light and 2.58 cm^3 of 48% $BF_3{\cdot}OEt_2$ was added with a syringe. The reaction mixture was stirred for 24 h and monitored by TLC of aliquots oxidised with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone). A further 2.58 cm^3 of 48% $BF_3{\cdot}OEt_2$ was added and the solution was stirred for 24 h. *p*-Chloranil (1.5 g, 6.10 mmol) was then introduced into the flask. The oxidation was allowed to proceed for 24 h at room temperature. The contents of the flask were then neutralised with NEt_3 until the colour changed from red to green and finally the solution was evaporated to dryness. The crude dry product was dissolved in a minimum quantity of CH_2Cl_2, loaded onto a neutral alumina chromatography column and eluted with a mixture of CH_2Cl_2/heptane (70:30). A second silica gel chromatography column (eluent CH_2Cl_2/cyclohexane, 55:45) allowed the recovery of the pure porphyrin mixture in a 10% yield. The atropisomers were separated by preparative TLC (silica gel, CH_2Cl_2/cyclohexane, 55:45).

2a: r_f = 0.287. – ^{1}H NMR ([D$_8$]THF): δ = –3.43 (s, 2 H, N*H*), 1.50 (s, 12 H, OC*H*$_3$), 6.20–8.19 (m, 48 H, binaphthyl H), 8.35 (d, 4 H, β-H), 8.69, (d, 4 H, β-H). – λ_{max}(THF) /nm (ε/dm^2 mol^{-1}): 228 (23299), 283 (3908), 338 (2357), 371 (1609), 431 (24610), 518 (1329), 554 (445), 592 (420), 649 (117). – CD (THF) /nm (Δε): 218 (–285.6), 231 (522.9), 260 (47.2), 298 (–8.8), 315 (11.9), 429 (–191.0), 519 (–7.8), 554 (–3.2), 594 (–1.3), 625 (1.1), 647 (–0.2), 666 (1.4), 678 (0.5). – IR: ν_{NH} = 3327 cm^{-1}. – FAB$^+$MS; *m*/*z*: 1440 [M·$^+$].

2b: r_f = 0.224. – ^{1}H NMR ([D$_8$]THF): δ = –3.46 (s, 2 H, N*H*), 1.75 (s, 4 H, OC*H*$_3$), 2.93 (s, 4 H, OC*H*$_3$), 3.04 (s, 4 H, OC*H*$_3$), 3.10 (s, 4 H, OC*H*$_3$), 6.10–8.54 (m, 48 H, binaphthyl H), 8.22 (d, 1 H, β-H), 8.25 (d, 1 H, β-H), 8.27 (d, 1 H, β-H), 8.48 (d, 1 H, β-H), 8.53 (d, 1 H, β-H), 8.71 (d, 1 H, β-H), 8.80 (d, 1 H, β-H), 8.85 (d, 1 H, β-H). – λ_{max}(THF) /nm (ε/dm^2 mol^{-1}): 229 (29772), 283 (4647), 337 (2833), 432 (28830), 519 (1590), 554 (542), 594 (500), 650 (152). – CD (THF) /nm (Δε): 215 (–194.7), 231 (465.8), 286 (–2.5), 312 (12.3), 336 (–17.7), 428 (–92.1), 518 (–6.11). – IR: ν_{NH} = 3323 cm^{-1}. – FAB$^+$MS; *m*/*z*: 1440 [M·$^+$].

2c: r_f = 0.142. – ^{1}H NMR ([D$_8$]THF): δ = –3.42 (s,2 H,N*H*), 2.54 (s, 12 H, OC*H*$_3$), 5.87–8.78 (m, 48 H, binaphthyl H), 8.57 (d, 2 H, β-H), 8.72 (d, 2 H, β-H), 8.82 (d, 4 H, β-H). – λ_{max}(THF) /nm (ε/dm^2 mol^{-1}): 228 (22377), 283 (4328), 337 (2719), 433 (25278), 521 (1420), 560 (722), 597 (493), 652 (158). – CD (THF) /nm (Δε): 216 (–296.5), 233 (512.4), 287 (–27.6), 339 (–33.1), 430 (–102.9), 518 (–5.9), 558 (–6.0), 602 (–7.7), 673 (–10.2). – IR: ν_{NH} = 3323 cm^{-1}. – FAB$^+$MS; *m*/*z*: 1440 [M·$^+$].

2d: r_f = 0.063. – ^{1}H NMR ([D$_8$]THF): δ = –3.56 (s,2 H,N*H*), 2.88 (s, 12 H, OC*H*$_3$), 6.22–8.32 (m, 48 H, binaphthyl H), 8.35 (s, 4 H, β-H), 8.73 (s, 4 H, β-H). – λ_{max}(THF) /nm (ε/dm^2 mol^{-1}): 229 (30313), 283 (5088), 371 (1911), 433 (20384), 522 (1413), 536 (2967), 559 (516), 597 (492), 653 (142). – CD (THF) /nm (Δε): 206 (–143.5), 223 (–255.7), 233 (453.0), 299 (–10.8), 309 (–1.7), 337 (–35.3), 429 (–72.9), 486 (0.23), 522 (–1.64), 560 (–3.5), 608 (81.3), 628 (1.37). – IR: ν_{NH} = 3323 cm^{-1}. – FAB$^+$MS; *m*/*z*: 1440 [M·$^+$].

Chloro Iron(III)-5α,10α,15α,20α-tetrakis[2′-methoxy-(a*S*)-1,1′-binaphth-2-yl]porphyrin (3a): A solution of **2a** (39 mg, 0.027 mmol), $Fe(CO)_5$ (0.46 cm^3, 3.55 mmol) and I_2 (19.8 mg, 0.078 mmol) in 30 cm^3 of dry toluene, was heated at 50 °C and stirred for about 4 h

under nitrogen. The mixture was then cooled to room temperature under aerobic conditions and the solvent was evaporated at reduced pressure. The crude dry product was dissolved in CH_2Cl_2, washed with water and dried over Na_2SO_4. The ferric complex was recovered by column chromatography (alumina, eluent CH_2Cl_2/CH_3OH, 90:10), treated with HCl 10% and dried over Na_2SO_4. Compound **3a** was obtained as a precipitate from heptane in 55% yield.

3a: λ_{max}(THF) /nm (ε /dm^2 mol^{-1}): 224 (24370), 284 (4033), 339 (3480), 431 (7730), 516 (1073), 591 (254). – CD (THF) /nm ($\Delta\varepsilon$): 208 (–213.8), 231 (513.0), 288 (–7.5), 310 (9.0), 343 (–40.1), 424 (–73.0), 517 (–7.6), 620 (–10.9). – IR: ν_{Fe-Cl} = 358 cm^{-1}. – FAB$^+$MS; *m*/*z*: 1494 [M – Cl], 1529 [M$^{\cdot+}$].

Using the same experimental procedures compounds (**2b**), (**2c**) and (**2d**) were metallated with $Fe(CO)_5$ to obtain complexes (**3b**), (**3c**) and (**3d**), respectively.

3b: λ_{max}(THF) /nm (ε /dm^2 mol^{-1}): 229 (30644), 283 (6173), 337 (5066), 377 (4420), 434 (11051), 517 (1600), 589 (462), 660 (437). – CD (THF) /nm ($\Delta\varepsilon$): 219 (−371.1), 233 (698.3), 287 (–17.6), 315 (–39.6), 429 (–60.8), 515 (–7.8). – IR: ν_{Fe-Cl} = 363 cm^{-1}. – FAB$^+$MS; *m*/*z*: 1494 [M – Cl], 1529 [M$^{\cdot+}$].

3c: λ_{max}(THF) /nm (ε/dm^2 mol^{-1}): 228 (26212), 283 (5380), 337 (4278), 376 (3738), 434 (9870), 515 (1338), 590 (369), 659 (320). – CD (THF) /nm ($\Delta\varepsilon$): 219 (–342.3), 233 (593.0), 285 (–18.0), 310 (2.3), 340 (–36.5), 428 (–42.3), 517 (–8.6). – IR: ν_{Fe-Cl} = 363 cm^{-1}. – FAB$^+$MS; *m*/*z*: 1494 [M – Cl], 1529 [M$^{\cdot+}$].

3d: λ_{max}(THF) /nm (ε /dm^2 mol^{-1}): 229 (29683), 281 (5900), 337 (4608), 371 (3640), 435 (9513), 514 (1359), 584 (423), 657 (375). – CD (THF) /nm ($\Delta\varepsilon$): 207 (–146.7), 221 (269.4), 299 (–9.5), 335 (–27.1), 432 (–45.8), 517 (–5.0). – IR: ν_{Fe-Cl} = 363 cm^{-1}. – FAB$^+$MS; *m*/*z*: 1494 [M – Cl], 1529.

Chloro Manganese(III)-5α,10β,15α,20β-tetrakis[2′-methoxy-(a*S*)-1,1′-binaphth-2-yl]porphyrin (4): Compound **4** was prepared from the corresponding free base porphyrin (**2a**) and $Mn_2(CO)_{10}$, following the same protocol as above (yield 30%). λ_{max}(THF) /nm (ε / dm^2 mol^{-1}) 229 (30763), 282 (5838), 338 (4282), 380 (4220), 405 (4019), 428 (3058), 487 (10125), 591 (1108), 627 (893). – CD (THF) /nm ($\Delta\varepsilon$): 233 (384), 297 (–18.9), 333 (–31.9), 392 (–23.2), 483 (–44.9), 560 (1.7), 595 (–0.4), 607 (0.6), 622 (–1.9), 641 (0.1). – IR: ν_{Mn-Cl} = 351 cm^{-1}. – FAB$^+$MS; *m*/*z*: 1493 [M – Cl], 1528 [M$^{\cdot+}$].

Styrene Oxidations: All reactions were carried out following the same procedure. A solution of styrene (114 μL, 1 mmol), naphthalene (6 mg, 5×10^{-2} mmol) as GC internal standard and the catalytic precursor **3a–d** or **4** (2.5 mg, 1.6×10^{-3} mmol) in dry CH_2Cl_2 was stirred under nitrogen shielded from ambient light at 0 °C. To this solution iodosylbenzene[19] (22 mg, 0.1 mmol) was then added. The mixture was stirred for 3.5 h. Then the solvent was evaporated and the crude mixture, a brown oil, was passed through a short silica gel column (Et_2O/pentane, 20:80) to eliminate the catalyst and the remaining mixture was analysed by GC. The enantiomeric excesses were evaluated by GC using a Cydex B capillary column. The absolute configuration was assigned by comparison with an optically pure standard.

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