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Synthesis of chiral Mn(III)-meso-tetrakis-[2.2]-*p*-cyclophanyl-porphyrin: a new catalyst for enantioselective epoxidation

Stefano Banfi, Amedea Manfredi, Fernando Montanari, Gianluca Pozzi, Silvio Quici *

Centro CNR and Dipartimento di Chimica Organica Industriale dell'Università, Via C. Golgi 19, 20133 Milano, Italy

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Abstract

The synthesis of Mn(III)-complexes of new chiral porphyrins **1a** and **1b** prepared by condensation of enantiomerically pure [2.2]-*p*-cyclophane-4-carbaldehyde and pyrrole are described. These compounds were used as catalysts in epoxidation reactions of prochiral alkenes, carried out in the presence of aqueous NaOCl at pH = 10.0 as oxygen donor and small amounts of 4-tert-butylpyridine as axial ligand, in CH_2Cl_2/H_2O two-phase conditions at 0°C. Results indicate a satisfactory catalytic efficiency (up to 700 overall turnovers), with enantiomeric excesses in the range 22–31%.

Keywords: Chiral complexes; Manganese; Porphyrin; Asymmetric oxidation catalysts; Enantioselectivity; Epoxidation; NaOCl epoxidation; [2.2]-*p*-Cyclophane-4-carbaldehyde resolution

1. Introduction

The preparation of optically active compounds by stereoselective syntheses is an important goal of organic chemistry, mostly when the reactions can be performed in a catalytic fashion by using chiral catalysts [1]. In this sense, one of the most challenging problems is the stereocontrolled formation of a carbon–oxygen bond by direct oxidation of unfunctionalized hydrocarbon substrates, carried out with appropriate chiral catalysts featuring high enantioselectivity together with a high catalytic efficiency [2]. Up to now the most effective catalysts for enantioselective epoxidation of unfunctionalized olefins are chiral Mn(III)–salen complexes [3]. Enantiomeric excesses (ee's) of more than 90% have been obtained in the epoxidation of *cis*-disubstituted alkenes by using aqueous NaOCl as oxidant [4]. The main drawback of Mn–salen catalysts is their poor chemical stability under the oxidation conditions, the maximum number of overall catalytic cycles reported being less than 40.

It is well known that metallo-porphyrins are efficient catalysts for alkane hydroxylation and alkene epoxidation in terms of catalytic activity and mildness of reaction conditions [5], for these reasons chiral Mn- or Fe-porphyrins have been widely investigated as asymmetric oxidation catalysts since the first report by Groves and Myers in 1983 [6]. Up to now several classes of

* Corresponding author.

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chiral metallo-porphyrins have been designed and synthesized [2], and their catalytic activity has been tested with a variety of substrates and reaction conditions [7].

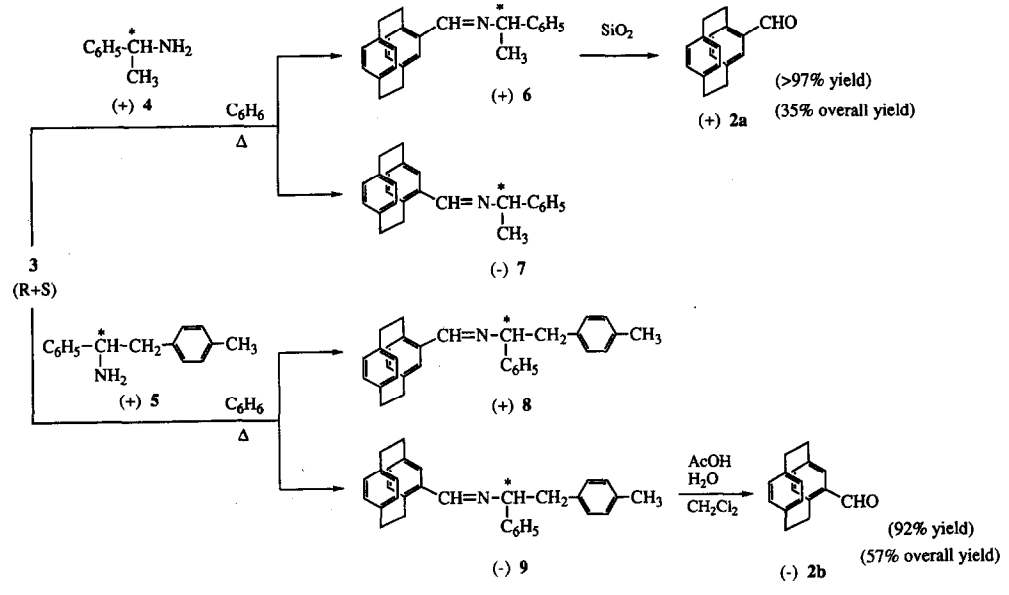
In the present paper we report the synthesis of new optically active Mn(III)-*meso*-tetrakis-[2.2]-*p*-cyclophanylporphyrins **1a–b** and the study of their catalytic activity in epoxidation reactions of prochiral alkenes by using aqueous NaOCl as oxygen donor.

2. Results and discussion

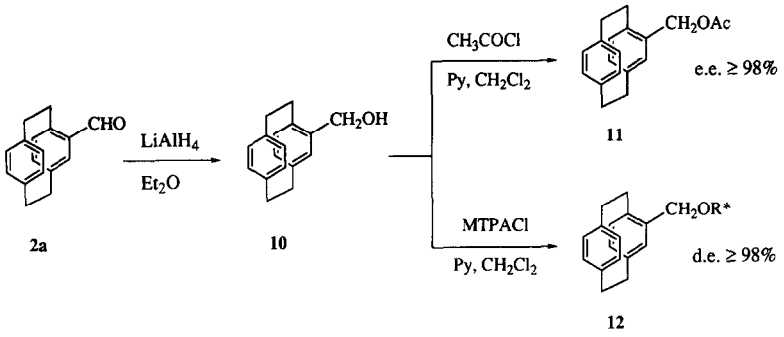
The synthesis of chiral porphyrins can be, in principle, achieved by following two general routes: (i) by covalently linking a chiral residue on a preformed porphyrin, or (ii) by direct condensation of enantiomerically pure aldehydes with pyrrole. The latter procedure is more straightforward and usually gives better results in terms of yields and chemical stability of the resulting porphyrin. For this purpose the starting aldehyde should feature: (i) high chemical and optical stability; (ii) relevant steric hindrance which promotes good chemical stability of the resulting metallo-porphyrin and an increased diastereoselectivity. Interesting examples are the porphyrin based on optically pure (*R*)-binaphthaldehyde reported by Kodadek and O'Malley [8], and that obtained from the resolved 1,2,3,4,5,6,7,8-octahydro-1:4,5:8-dimethanoanthracene-9-carboxaldehyde reported by Halterman and Jan [9].

Because compounds with planar chirality, such those derived from [2.2]-*p*-cyclophane, are very stable towards light, oxidation, acids, bases, and relatively high temperatures [10], we decided to use enantiomerically pure (*R*) or (*S*)-[2.2]-*p*-cyclophane-4-carbaldehydes, **2a** and **2b** respectively, as starting materials in the preparation of chiral porphyrins **1a** and **1b**.

Racemic *meso*-tetrakis-[2.2]-*p*-cyclophanylporphyrin has already been synthesized by Czuchajowski et al. [11], and its electronic structure and electrochemical behaviour have also been thoroughly investigated [12]. It must be noted that substitution of the *meso* positions of the porphyrin ring with four *p*-cyclophanyl groups allows the formation of a great number of stereoisomers which differs for the (*R*) or (*S*) configuration and by the orientation of the re-



Scheme 1. Resolution of racemic [2.2]-*p*-cyclophane-4-carbaldehyde.

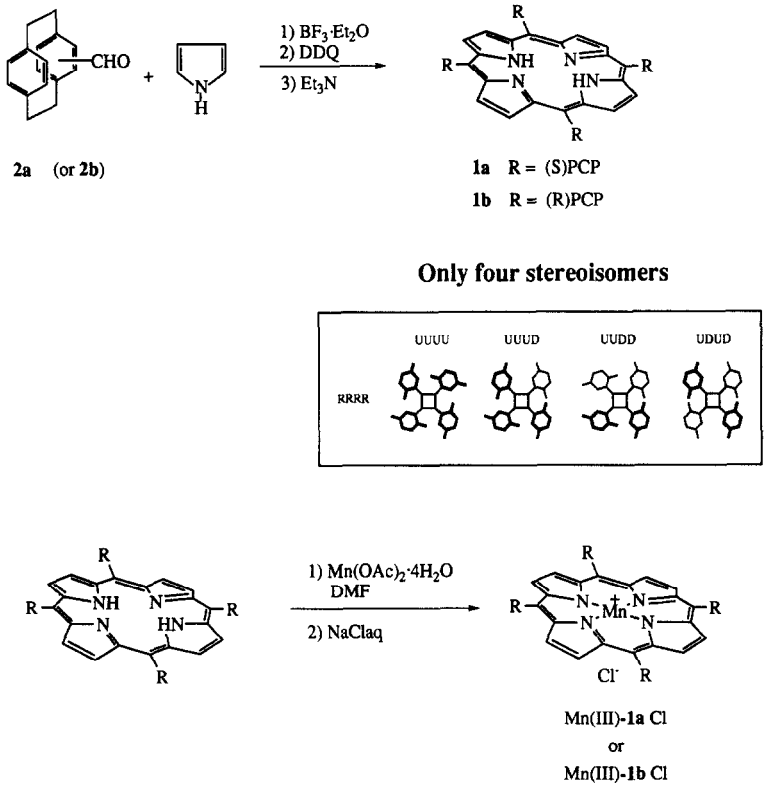


Scheme 2. Control of aldehyde enantiomeric purity.

maining benzene ring of the p-cyclophanyl group, up (U) or down (D) with respect to the porphyrin plane [13].

The racemic aldehyde **3** has been prepared by formylation of [2.2]-*p*-cyclophane according to Rieche's procedure [14]. Resolution of **3** was initially attempted by an enzymatic method, which is the only one reported in the literature, by using *Saccharomyces cerevisiae* [15]. However, this procedure appeared to us quite tedious mainly because of the very difficult separation of the product from the culture medium. Furthermore, the isolated products showed enantiomeric excesses somewhat lower than those reported by the Authors.

We then decided to use chemical resolution



Scheme 3. Synthesis of optically active Mn(III)-*meso*-tetrakis-[2.2]-*p*-cyclophanylporphyrins.

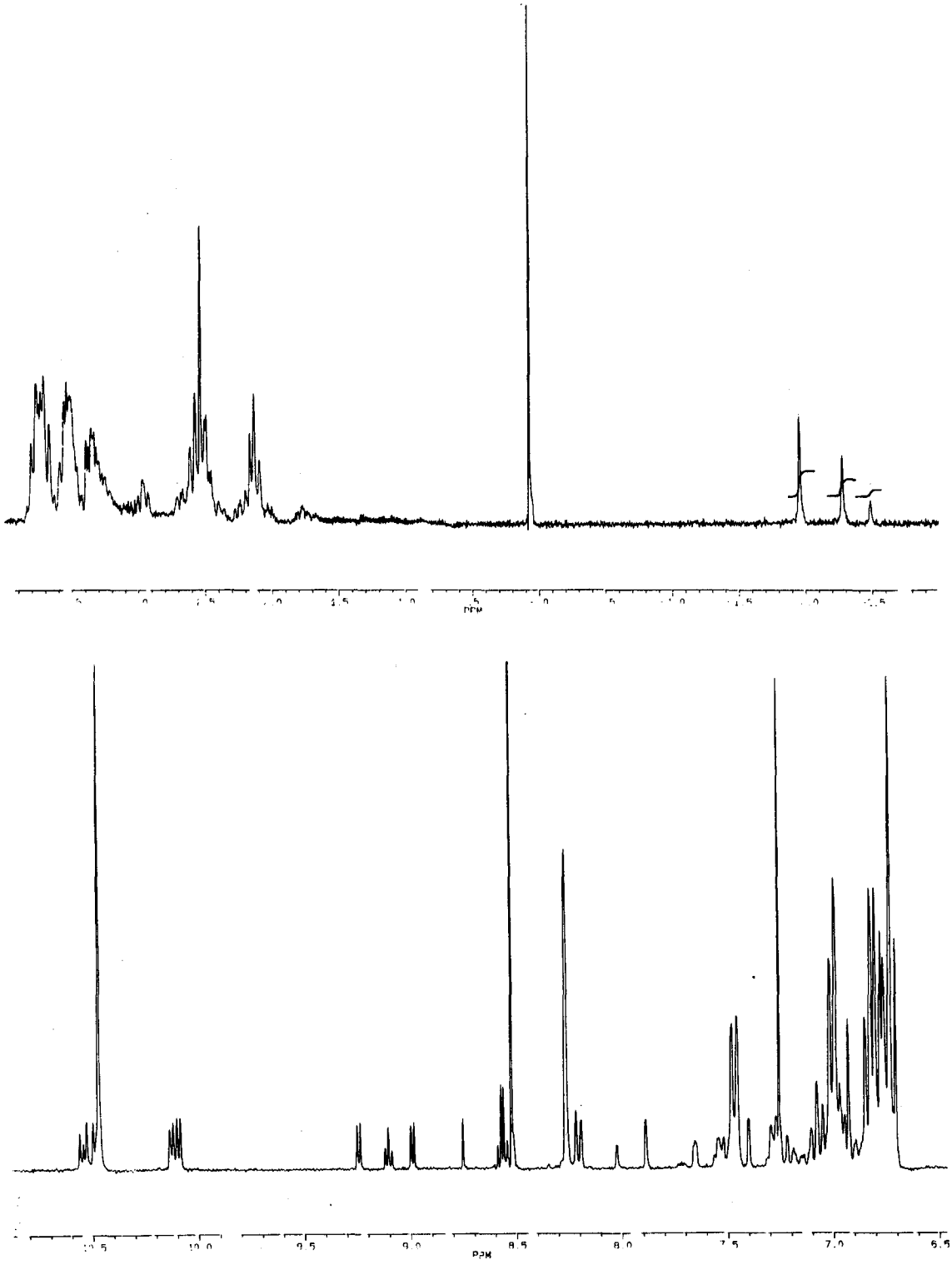


Fig. 1. Aliphatic and aromatic regions of the ^{1}H NMR (300 MHz) spectrum of **1a**.

through diastereoisomeric Schiff bases **6,7** and **8,9** obtained from **3** with enantiomerically pure amines **4** and **5**, respectively. Two crystallizations from *n*-hexane afforded pure **6** and **9** (diastereoisomeric excess (de) $\geq 98\%$ by 300 MHz ^{1}H NMR) in 36% and 62% yields, respectively. Hydrolysis of **6** and **9** afforded enantiomerically pure **2a** and **2b** in almost quantitative yields (Scheme 1)

A similar procedure was recently reported by Y.N. Belokon et al. for the resolution of racemic 2-formyl-3-hydroxy-[2.2]-*p*-cyclophane [16].

The enantiomeric purity of **2a** and **2b** was unambiguously confirmed according to Scheme 2. Aldehyde **2a**, $[\alpha]_{546} = +244°$ cm^2 g^{-1} (c = 1.0, $CHCl_3$), was reduced with $LiAlH_4$ in Et_2O to the corresponding alcohol **10**, $[\alpha]_{546} = +83.6°$ cm^2 g^{-1} ($c = 0.5$, $CHCl_3$), ee $> 96\%$, which was reacted either with CH_3COCl in CH_2Cl_2 and pyridine to afford the acetate **11** or with (−)(*R*)-α-methoxy-α-(trifluoromethyl)-phenylacetyl chloride (MTPACl) thus giving the corresponding Mosher's ester **12** [17]. Analysis of **12** by ^{1}H NMR, as well as that of **11** in the presence of europium(III) tris-3-(trifluoromethylhydroxymethylene)-camphorate [Eu(tfc)$_3$], showed an optical purity $\geq 98\%$ instead of the 77% calculated from the $[\alpha]_{546}$ value reported for the aldehyde obtained through enzymatic resolution [15].

Condensation of **2a** or **2b** with pyrrole in the presence of $BF_3 \cdot Et_2O$ in $CHCl_3$ as solvent under Lindsey's conditions [18], afforded, after oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), (*S*)- or (*R*)-*p*-cyclophanylporphyrin, (*S*)(PCP)P **1a** or (*R*)(PCP)P **1b**, respectively, as a mixture of stereoisomers. However, since the starting aldehyde is enantiomerically pure, the number of stereoisomers is reduced to the four possible atropoisomers (UUUU, UUUD, UUDD, UDUD) as shown in Scheme 3.

Unfortunately all the attempts to isolate a pure atropoisomer (i.e. flash column chromatography, gravity column chromatography and medium pressure liquid chromatography (MPLC) by using SiO_2, Florisil, neutral Al_2O_3 as stationary phases), failed. We also used, many times, the procedure reported for the separation of atropoisomers of racemic [2.2]-*p*-cyclophanyl porphyrin [19], without any success.

The ^{1}H NMR of **1a** (or **1b**) showed the presence of three singlets in the N–H pyrrole region corresponding to three, out of the four possible, atropoisomers namely: UUUD (s, −1.96 ppm), UUDD (s, −2.28 ppm) and UDUD (s, −2.50 ppm) in 4: 2.5: 1 ratio respectively (Fig. 1). In fact, it is known that the number of N–H pyrrole resonances defines the number of atropoisomers, while the chemical shifts are diagnostic for their identification, the range of these resonances being limited, at lower and higher field, by the UUUU and the UDUD isomer [20]. The statistical ratio for UUUU:UUUD:UUDD:UDUD is 1:4:2:1, respectively [19], and even though this ratio is not direct structural evidence, we can reasonably exclude that the singlet at −1.96 ppm is that of the UUUU isomer.

Accordingly, our feeling is that the claimed separation of the UUUD and the UUDD classes of atropoisomers in the case of racemic [2.2]-*p*-cyclophanylporphyrin is not complete since the ^{1}H NMR, reported by the authors, still shows at least two resonances for the N–H pyrrole protons [19].

Unfortunately the aromatic region of the ^{1}H NMR spectrum of **1a** (or **1b**) is quite complicate and, at the moment, we are not able to assign unambiguously the peaks to the respective atropoisomer. Indeed, when the rotation of the *meso*-aryl groups is slow on the NMR time scale, each atropoisomer gives rise to distinct signals for *ortho*, *meta* and *para* hydrogens in the aromatic region of the ^{1}H NMR spectrum [21]. A thorough NMR investigation to assign all resonances of the aromatic hydrogens of **1a** and **1b** is under way.

In order to gain preliminary insight into the catalytic efficiency of the metallo-complexes of **1a** and **1b**, we prepared the corresponding Mn(III)-**1a**Cl and Mn(III)-**1b**Cl, by treatment

with $Mn(OAc)_2 \cdot 4H_2O$ in DMF at reflux for 2 h and subsequent exchange of the CH_3COO^- anion with Cl^- (see Experimental) (Scheme 3).

The catalytic activity of Mn(III)-**1a**Cl has been investigated in epoxidation of prochiral alkenes by using aqueous NaOCl at pH 10.0 as oxygen donor (OD) in a CH_2Cl_2/H_2O two phase system at 0°C and in the presence of 4-*tert*-butylpyridine as axial ligand (L)[22]. The results are reported in Table 1.

These results indicate that the catalytic efficiency depends on the substrate, in fact conjugated olefins such as styrene, 4-chlorostyrene and 2-methylstyrene afforded satisfactory overall turnovers (entries 1–3) whereas non-conjugated ones, like allylbenzene (entry 4), are not reactive at all. As expected for metalloporphyrins catalyzed olefin epoxidation, only *Z* alkenes are converted while *E* isomers are unreactive, due to steric constraints (entries 6 and 7).

The obtained ee values are in the range 22%–31%, indicating only a moderate enantioselectivity, but they are comparable with the average values reported in the literature for analogous catalytic systems.

We are currently trying to separate pure atropoisomers of **1a** and **1b** to see how reactivity and enantioselectivity depend on atropoisomer purity.

3. Experimental

3.1. General methods

^1H NMR spectra were recorded on a Bruker AC 300 MHz spectrometer in $CDCl_3$ as solvent. UV–Vis spectra were obtained with a Lambda 6 Perkin Elmer spectrophotometer. GC analyses were performed on a Varian model 3700 flame-ionization gas chromatograph (20 × 0.125 in. OV-101-5% on CHP 100–125 mesh column). FAB-MS mass spectra were obtained on an Analytical VG 7070 EQ instrument. Optical rotatory powers were measured on a Perkin Elmer 241 polarimeter. Melting points were determined with a Büchi 535 apparatus and are uncorrected. The pH of aqueous NaOCl solutions was measured with an Orion model SA 250 pH meter with pH electrode model 91-02. Epoxidations were carried out in a vessel thermostatted at 0 ± 0.05°C by a Haake F3 cryostat.

Alkenes and all the purchased reagents were of the highest purity commercially available and

Table 1
Asymmetric olefin epoxidation catalyzed by Mn(III)–**1a**Cl [a] in the presence of $NaOCl_{aq}$ [b]

Entry	Substrate S	Molar ratio (S/P)	Time (min)	Conversion [c] (%)	Yield [d] (%)	ee (%)
1	styrene	500	200	95	65	25 [e]
		1000	300	80	51	26 [e]
2	*p*-chlorostyrene	500	150	90	50	22 [f]
3	*o*-methylstyrene	500	300	65	31	31 [f]
4	allylbenzene	500	120	7	0	–
5	1,2-dihydronaphthalene	1000	200	95	73	22 [e]
6	*E*-β-methylstyrene	500	85	0	0	–
7	*E*-stilbene	500	60	0	0	–
8	1-methylcyclohexene	250	60	0	0	–

[a] The same results were obtained using Mn(III)–**1b**Cl, the epoxides having the opposite absolute configuration.
[b] L/P = 10, NaOCl/S = 3.
[c] Determined by GC.
[d] Based on the isolated epoxide.
[e] Determined by comparison of polarimetry measurements with literature values (see Ref. [23] for entries 1 and 2 and Ref. [24] for entry 5).
[f] Determined by ^1H-NMR in the presence of $Eu(hfc)_3$.

were used without further purification. Enantiomerically pure 1-phenyl-2-(4-tolyl)ethylamine **5** was prepared according to literature [25]. All the solvents were distilled over the appropriate drying agent just before use.

Satisfactory elemental analyses (± 0.4% for C, H and N) were obtained for all of the new compounds.

3.2. *[N-(1-Phenylethyl)]-4-[2.2]-p-cyclophanyl] methanimine (6)*

A solution of 2.36 g (10 mmol) of racemic [2.2]-*p*-cyclophane-4-carbaldehyde **3** and 1.21 g (10 mmol) of *R*(+)-phenylethylamine in 80 ml of benzene was refluxed under magnetic stirring. The course of the reaction was followed by ^{1}H NMR because the reaction product proved to be unstable under, either SiO_2 or Al_2O_3, thin layer chromatography (TLC). After 5 h the reaction was complete, the solvent was evaporated in vacuo and the crude product (mixture of diastereoisomers **6** and **7**) was crystallized from 60 ml of *n*-hexane affording a white solid. After filtration the solid was recrystallized from 35 ml of *n*-hexane giving 0.61 g (36%) of a white crystalline product, m.p. 139.5–141°C; $[\alpha]_D = +180°$ cm^2 g^{-1} ($c = 1.0$, $CHCl_3$), diastereoisomeric excess (de) ≥ 98% calculated by ^{1}H NMR considering the resonances at 1.67, 7.00 and 8.35 ppm; ^{1}H NMR ($CDCl_3$) δ = 1.67 (d, 3H, $J = 6.6$ Hz), 2.80–2.95 (m, 2H), 2.95–3.25 (m, 5H), 3.80–3.95 (m, 1H), 4.57 (q, 1H, $J = 6.6$ Hz), 6.29 (d, 1H, $J = 7.8$ Hz), 6.39 (d, 1H, $J = 7.8$ Hz),, 6.45–6.60 (m, 4H), 7.00 (s, 1H), 7.27 (t, 1H, $J = 6.5$ Hz), 7.40 (t, 1H, $J = 7.5$ Hz), 7.52 (t, 1H, $J = 7.5$ Hz), 8.35 (s, 1H).

3.3. *S(+)-[2.2]-p-Cyclophane-4-carbaldehyde (2a)*

This product was obtained by hydrolysis of **6** on SiO_2, thus column chromatography of 0.69 g (2.03 mmol) of **6** eluted with CH_2Cl_2 afforded 0.47 g (97%) of **2a**; m.p. = 158–161°C; $[\alpha]_{546} = +244°$ cm^2 g^{-1} ($c = 1$, $CHCl_3$), ee = ≥ 98%; ^{1}H NMR ($CDCl_3$) δ = 2.70–3.30 (m, 7H), 3.90–4.15 (m, 1H), 6.15–6.80 (m, 6H), 7.00 (s, 1H), 9.95 (s, 1H). The phenylethylamine residue remained absorbed on SiO_2.

3.4. *[N-[1-Phenyl-2-(4-methylphenyl)ethyl]]-4-[2.2]-p-cyclophanyl-methanimine (9)*

A solution of 2.38 g (10.1 mmol) of racemic **3** and 2.33 g (11.1 mmol) of (+)-1-phenyl-2-(4-methylphenyl)-ethylamine **5** in 100 ml of benzene was refluxed, under magnetic stirring, in a Dean–Stark apparatus for 30 h. The course of the reaction was followed by ^{1}H NMR because the reaction product undergoes partial hydrolysis on TLC. The solvent was evaporated under vacuum and the residue (mixture of diastereoisomers **8** and **9**) was crystallized with 70 ml of *n*-hexane affording 1.83 g of a white solid, m.p. = 136–138.8°C; $[\alpha]_D = -183.7°$ cm^2 g^{-1} ($c = 1.0$, $CHCl_3$). This product was recrystallized with 60 ml of *n*-hexane giving 1.34 g (62%) of a crystalline solid, m.p. = 140.5–141.1°C; $[\alpha]_D = -198.5°$ cm^2 g^{-1} ($c = 1.0$, $CHCl_3$), de ≥ 98% calculated by ^{1}H NMR considering the resonances at 2.30 and 8.05 ppm; ^{1}H NMR ($CDCl_3$) δ = 2.30 (s, 3H), 2.65–2.80 (m, 2H), 2.95–3.15 (m, 5H), 3.28 (d, 2H, $J = 7.0$ Hz), 3.65–3.75 (m, 1H), 4.57 (t, 1H, $J = 7.0$ Hz), 5.98 (d, 1H, $J = 7.9$ Hz), 6.28 (d, 1H, $J = 7.9$ Hz), 6.40–6.55 (m, 4H), 6.95 (s, 1H), 7.02–7.10 (m, 4H), 7.27 (t, 1H, $J = 6.5$ Hz), 7.39 (t, 2H, $J = 7.5$ Hz), 7.55 (d, 2H, $J = 7.5$ Hz), 8.05 (s, 1H).

3.5. *R(-)[2.2]-p-Cyclophane-4-carbaldehyde (2b)*

A mixture of 1.25 g (2.8 mmol) of **9**, 0.7 ml of glacial acetic acid, 0.7 ml of H_2O and 50 ml of CH_2Cl_2 was magnetically stirred at RT for 24 h. The CH_2Cl_2 phase was separated, washed with 5% aqueous HCl (30 ml) and then with H_2O until it became colourless, and the solvent was evaporated. Purification of the crude by column chromatography (SiO_2, CH_2Cl_2) af-

forded 0.61 g (92%) of pure **2b** m.p. = 158–161°C; $[\alpha]_{546} = -245°$ cm^2 g^{-1} (c = 1.0, $CHCl_3$), ee ≥ 98%; ^{1}H NMR ($CDCl_3$) δ = 2.70–3.30 (m, 7H), 3.90–4.15 (m, 1H), 6.15–6.80 (m, 6H), 7.00 (s, 1H), 9.95 (s, 1H).

3.6. S(+) 4-Hydroxymethyl-[2.2]-p-cyclophane (10)

A solution of 50 mg of **2a** in 3 ml of Et_2O was slowly added to a stirred suspension of $LiAlH_4$ in 12 ml of Et_2O maintained under nitrogen atmosphere. The reaction mixture was stirred at RT for 90 min and then quenched by adding in the order: 6 μl of H_2O, 9 μl of 5% aqueous NaOH and 20 μl H_2O. The precipitate was filtered off and the solvent was evaporated to afford 50.4 mg (100%) of pure **10**, $[\alpha]_{546}$ = +83.6° cm^2 g^{-1} (c = 0.504, $CHCl_3$), ee = 96% (Lit.: [15]).

3.7. 4-Acetoxymethyl-S-(+)-[2.2]-p-cyclophane (11)

A solution of 17 mg (0.07 mmol) of **10**, 5.2 μl (0.07 mmol) of CH_3COCl and 6.3 μl (0.08 mmol) of pyridine was maintained at RT under magnetic stirring for 18 h. The reaction mixture was taken up, with 10 ml of CH_2Cl_2 and 5 ml of H_2O, in a separatory funnel, the organic phase was separated and washed with 5 ml of 5% aqueous HCl and 5 ml of H_2O, dried with $MgSO_4$ and the solvent evaporated. Purification by chromatography through a short column [SiO_2, Et_2O–Light petroleum = 1:1 (v/v)] afforded 19.5 mg (99%) of a solid, m.p. = 97–101°C; ^{1}H NMR ($CDCl_3$) δ = 2.10 (s, 3H), 2.80–3.40 (m, 8H), 4.84 (d, 1H, J = 12.5 Hz), 5.07 (d, 1H, J = 12.5 Hz), 6.35–6.60 (m, 7H); ee ≥ 98% ±2% by ^{1}H NMR in the presence of $Eu(tfc)_3$ as shift reagent.

3.8. Mosher's ester (12)

A solution of 23.8 mg (0.1 mmol) of **2a**, 27.3 mg (0.11 mmol) of *R*(−)MTPACl and 8.9 μl (0.11 mmol) of pyridine in 3 ml of anhydrous CH_2Cl_2 was maintained at RT under magnetic stirring for 24 h. The solvent was evaporated and the residue was purified by preparative TLC eluting with CH_2Cl_2–light petroleum = 1:1 (v/v) affording 45 mg of pure **12**, ^{1}H NMR ($CDCl_3$) δ = 2.80–3.32 (m, 8H), 3.50 (s, 3H), 5.11 (d, 1H, J = 12.5 Hz), 5.25 (d, 1H, J = 12.5 Hz), 6.22–6.31 (m, 2H), 6.43–6.56 (m, 5H), 7.32–7.56 (m, 5H); ee ≥ 98% calculated by ^{1}H NMR on the doublets at 5.11 and 5.25 ppm.

3.9. meso-Tetrakis-4S-[2.2]-p-cyclophanyl-porphyrin (1a)

A solution of 0.47 g (1.97 mmol) of S(+)-[2.2]-*p*-cyclophane-4-carbaldehyde **2a**, 135 μl (1.97 mmol) of pyrrole and 160 μl (1.30 mmol) of $BF_3 \cdot Et_2O$, in 200 ml of $CHCl_3$, freshly distilled over K_2CO_3, under nitrogen atmosphere was equilibrated at RT in the dark for 17 h. After this time 0.35 g (1.5 mmol) of DDQ was added, the reaction mixture was magnetically stirred for 30 min. then treated with 0.5 ml of Et_3N and evaporated in vacuo. Purification by column chromatography (SiO_2, CH_2Cl_2) afforded 0.24 g (43%) of **1a** as a brownish violet solid, UV–Vis (CH_2Cl_2): λ 667 nm (log ε 3.81), 608 (3.71), 574 (4.23), 535 (4.10), Soret band 438 (5.56); MS-FAB(+) m/e 1135 ($M + H^+$).

3.10. meso-Tetrakis-4R-[2.2]-p-cyclophanyl-porphyrin (1b)

This porphyrin was prepared in 61% yield as reported for **1a** but using **2b** as starting aldehyde.

3.11. meso-Tetrakis-4S-[2.2]-p-cyclophanyl-porphyrin Mn(III) chloride complex Mn(III)-1aCl

A mixture of 0.12 g (0.1 mmol) of **1a** and 0.25 g (1.0 mmol) of $Mn(OAc)_2 \cdot 4H_2O$ in 20 ml of dimethylformamide was refluxed under

magnetic stirring for 2 h. The solvent was evaporated in vacuo, purification of the residue by column chromatography (SiO_2, CH_2Cl_2 and CH_2Cl_2:CH_3OH = 95:5 v/v as eluent) afforded 0.13 g of product. This product was dissolved in 100 ml of CH_2Cl_2 and treated with 20 ml of saturated NaCl aqueous solution in order to exchange the acetate for chloride anion. Evaporation of the solvent gave 0.12 g (95%) of a greenish powder; MS-FAB(+) *m/e* 1187 (M^+), UV–Vis (CH_2Cl_2): λ_{max} 490 nm (log ϵ 5.03).

3.12. *meso-Tetrakis-4R-[2.2]-p-cyclophanyl-porphyrin Mn(III) chloride complex Mn(III)-**1b**Cl*

This complex was prepared, starting from porphyrin **1b**, in 90% yield as reported for Mn(III)-**1a**Cl.

3.13. *Epoxidation reactions: general procedure*

Epoxidations were carried out in a 10 ml flask equipped with a Teflon-lined screw cap and a magnetic stirrer, thermostated at 0 ± 0.05°C with circulating ethanol. The reactor was charged with 1 mmol of the alkene, 1×10^{-3} mmol of **1a** (or **1b**), 1×10^{-3} mmol of 4-*tert*-butylpyridine in 2 ml of CH_2Cl_2 and 6 ml of a 0.5 M (3 mmol) of an aqueous solution of NaOCl at pH = 10.0. Reactions were followed by G.C analysis. When the conversion of the substrate was maximum, the reaction mixture was poured into 10 ml of H_2O and the flask was washed with 10 ml of CH_2Cl_2. The combined organic phase was washed twice with H_2O (10 ml) and dried over $MgSO_4$. The epoxide was purified by column chromatography on florisil and its purity was tested by GC and ^1H NMR. The enantiomeric excesses were evaluated by measuring the optical rotation and by ^1H NMR in the presence of chiral shift reagents. Results are reported in Table 1.

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