D_2-Symmetric Chiroporphyrins Derived from (1*R*)-*cis*-Hemicaronaldehydic Acid: Preparation and Spectral Characterization

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Keywords: Porphyrins / Chiral auxiliaries / Macrocycles / Pyrethroids

Esters, *N*,*N*-disubstituted amides, and a *N*-acylurea derived from the enantiopure industrial intermediate (1*R*)-*cis*-hemicaronaldehydic acid (or biocartol) are convenient synthons for the preparation of a series of chiroporphyrins by condensation with pyrrole. These chiral *meso*-tetracyclopropylporphyrins are obtained exclusively as the D_2-symmetric α,β,α,β atropisomer, generally in low to moderate yields (2–20%), and in the urea case in excellent yield (60%). Hydrolysis of the urea substituents affords a chiroporphyrin with mono-*N*-substituted amide groups. ^{1}H-NMR spectroscopy indicates that the ester, amide, and urea stereogenic groups sit on the porphyrin close to the metal binding site and restrict substrate or ligand access along a C_2-symmetric groove. This structural feature of chiroporphyrins and of their metal complexes is of high potential interest in asymmetric catalysis and chiral recognition.

Introduction

During the last decade extensive work has been devoted to the development of efficient catalytic methods for the enantioselective epoxidation of non functionalized alkenes. Apart from recent work on dioxirane-mediated epoxidation,[1,2] most studies deal with chiral transition metal complexes as catalysts, especially metalloporphyrins[3] and metallosalens.[4] The latter catalysts provide excellent enantiomeric excesses (*ee*) in enantioselective epoxidation of substituted aromatic alkenes, and they are considered for industrial applications. However their turnover numbers are low due to the oxidative degradation of the salen ligands. Thus, chiral metalloporphyrins remain good candidates as catalysts for enantioselective epoxidation due to their stability towards oxidation, as illustrated by some recent papers.[5,6]

When we started our own investigations, most of the porphyrin complexes designed as epoxidation catalysts were derived from the *meso*-tetraphenylporphyrin moiety by attaching elaborated chiral substituents on *ortho* position on the phenyl groups before or after porphyrin ring formation. This type of construction necessarily places the potentially stereogenic elements at a distance from the reactive metal center. Inasmuch as close proximity of these groups is believed to be beneficial to the asymmetric induction, we have looked for alternative synthetic strategies using easily available chiral aldehydes of natural or industrial origin as synthons. Our goal was to find an aldehyde synthon which could place chiral groups near the center of the porphyrin ring, and at the same time provide substituent flexibility. These requirements have been fulfilled by (1*R*)-*cis*-hemicaronaldehydic acid, an enantiomerically pure cyclopropylaldehyde (also known under the name biocartol) which is an intermediate in the Roussel–Uclaf process for the production of pyrethroid insecticides.[7] Our investigations have revealed that biocartol *methyl* ester can be condensed with pyrrole to afford a prototypic chiral porphyrin which is obtained exclusively as the α,β,α,β atropisomer, and that we have called tetra*methyl*chiroporphyrin.[8] We describe here the preparation and characterization of a series of D_2-symmetric analogs, or *chiroporphyrins*, derived from various other esters and amides of biocartol, and from an urea derivative. Metal complexes of these chiroporphyrins have been shown to be useful as catalysts in enantioselective epoxidation and aziridination,[6,9] as hosts in chiral recognition of alcohols and β-amino alcohols,[10,11] and as chiral NMR shift reagent for amines.[12]

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Results and Discussion

Syntheses of Chiroporphyrins 2a–l

The chiral synthons **1a–k** were synthesized in three steps starting from biocartol.[13,14] The (1*R*,3*S*) configuration of biocartol is retained in esters and amides **1a–k** and no epimerization was seen by NMR. Urea **1l** was obtained by condensation of biocartol with *N*,*N'*-dicyclohexylcarbodiimide (DCC) in DMF in the presence of triethylamine.[15] An alternative one-step preparation of the methyl ester **1a** by methylation of the sodium salt of biocartol was also worked out,[16] and it is described in the Experimental Section.

The chiroporphyrins were prepared using the classical Lindsey conditions[17] for the synthesis of *meso*-tetraalkylporphyrins, i.e. condensation of pyrrole (1 equiv.) with the chiral aldehyde **1a–l** (1 equiv.) in dichloromethane in the presence of trifluoroacetic acid (TFA, 1 equiv.), followed by in situ oxidation of the intermediate porphyrinogen by 2,3-

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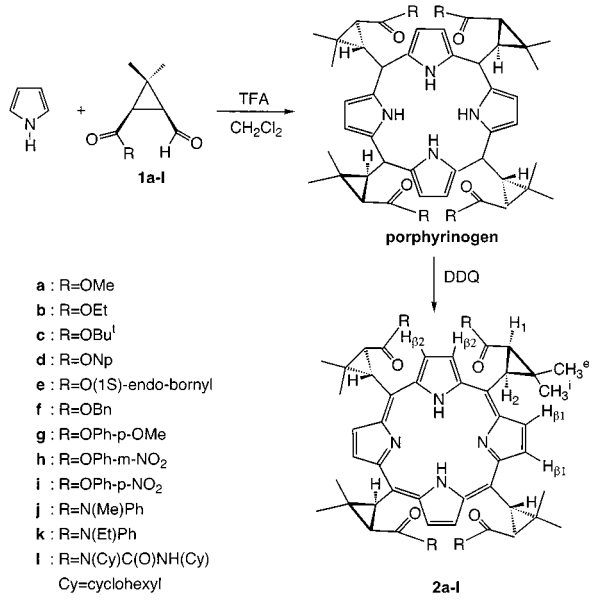
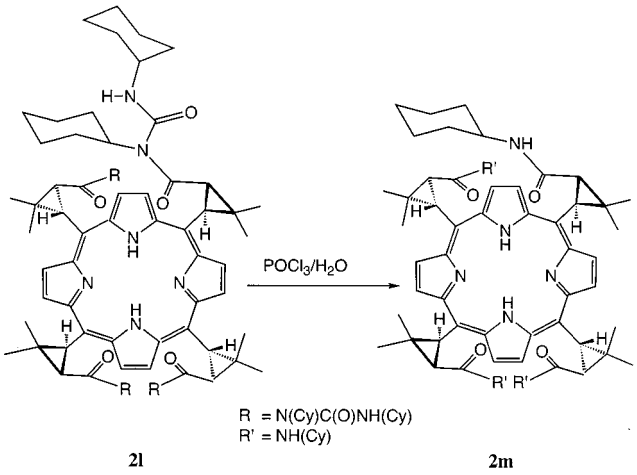


Scheme 1. One-pot, two-step synthesis of chiroporphyrins **2a–l**



Scheme 2. Access to chiroporphyrin **2m** with mono-*N*-substituted amide groups

dichloro-5,6-dicyano-1,4-benzoquinone (Scheme 1). Lindsey et al.[17] reported a beneficial effect of dilution and a 26% yield of *meso*-tetrapentylporphyrin with a 10^{-3} M concentration of the reactants. Nevertheless in their general procedure for *meso*-tetraalkylporphyrins, they recommended a 10^{-2} M concentration for convenience. Following their experimental conditions we obtained porphyrins **2a–l** in yields varying from from 2% for **2b** to 60% for **2l**. The lower yields were obtained for alcohol esters of biocartol. Tetramethylchiroporphyrin **2a**[8] (also called H_2TMCP) and its metal complexes were needed in large amounts to screen their potential in enantiocontrol,[6,9–12] so its yield was optimized to 20% using a 10^{-3} M concentration of reactants and a longer reaction time for porphyrinogen formation. Chiroporphyrin **2l** was obtained in a surprisingly excellent yield (60%), which has been accounted for by the presence of complementary intramolecular hydrogen-bonding interactions between *N*-acylurea substituents which direct the cyclisation of the tetrapyrrolic intermediate.[15]

Preparation of Porphyrin 2m

Chiroporphyrins **2j** and **2k** possess *N*,*N*-disubstituted *meso* substituents derived from disubstituted biocartol amides **1j** and **1k**. As we have reported earlier, access to chiroporphyrins from *N*-monosubstituted biocartol amides by the Lindsey method is prevented since the latter exist in a cyclic form in which the aldehyde function is masked.[14] This difficulty was circumvented by controlled hydrolysis of **2l** which afforded the desired chiroporphyrin with mono-*N*-substituted amide substituents. It has been reported that treatment of acylureas of general formula $RCON(C_6H_{11})$-$CONHC_6H_{11}$ with phosphorus oxychloride in benzene and then with water leads to the corresponding *N*-cyclohexylacylamides $RCONHC_6H_{11}$.[18] This reaction applied to **2l** afforded the tetra-*N*-cyclohexylchiroporphyrin **2m** in 60% yield (Scheme 2).

α,β,α,β Conformation of Porphyrins 2a–m

Each of the synthons **1a–l** affords only one porphyrin product, as indicated by the presence of a single spot in TLC (Soret band near 430 nm) and highly symmetric NMR signatures (vide infra).[19] The ^{1}H-NMR spectra of porphyrins **2a–m** at room temperature show two singlets in the 9 ppm region for the β pyrrolic protons; likewise, their ^{13}C spectra show two pairs of peaks for Cα and Cβ (Figure 1 and Figure 2). This indicates that the *meso* groups are not freely rotating at room temperature and that each of the chiroporphyrins **2a–m** is present as the D_2-symmetric α,β,α,β atropisomer (Scheme 3). The *cis* configuration of the starting chiral synthons **1a–l** is retained in the chiroporphyrins, as indicated by the characteristic NMR signature of protons H_1 and H_2 as two doublets at ca. 2.7 and ca. 4.8 ppm with a coupling constant J_{cis} = 8.8 Hz; this value would be J_{trans} = 5.6 Hz for the *trans* configuration.[20]

Our experience with *ortho*-substituted tetraphenylporphyrins had led us to anticipate that all four atropisomers would form in the synthesis of a given chiroporphyrin, and that tedious chromatographic separation of the desired α,β,α,β would be required. Thus the finding that a single α,β,α,β atropisomer product is formed for each of the compounds **2a–m** was indeed a very pleasant surprise. Among several possible determinants which may contribute to the atroposelective character of this reaction, we favor the following factors after examination of molecular models of the intermediate porphyrinogen. Steric exclusion apparently disfavours the cyclisation of linear tetrapyrroles having *cis* cyclopropyl substituents on neighbouring *meso* carbons, which therefore will lead to tars upon further polymeris-

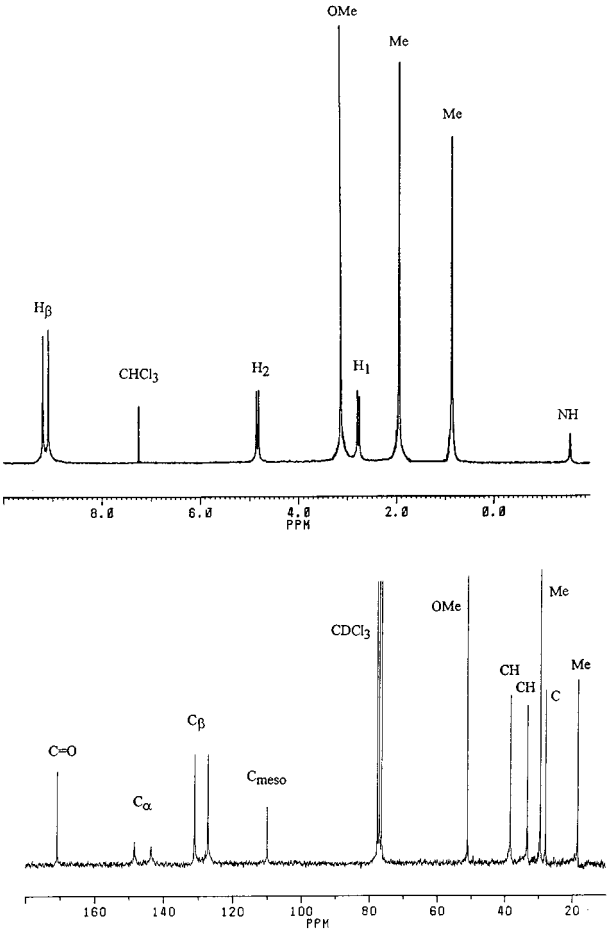


Figure 1. ^{1}H (top) and ^{13}C (bottom) NMR spectra of tetramethylchiroporphyrin **2a**

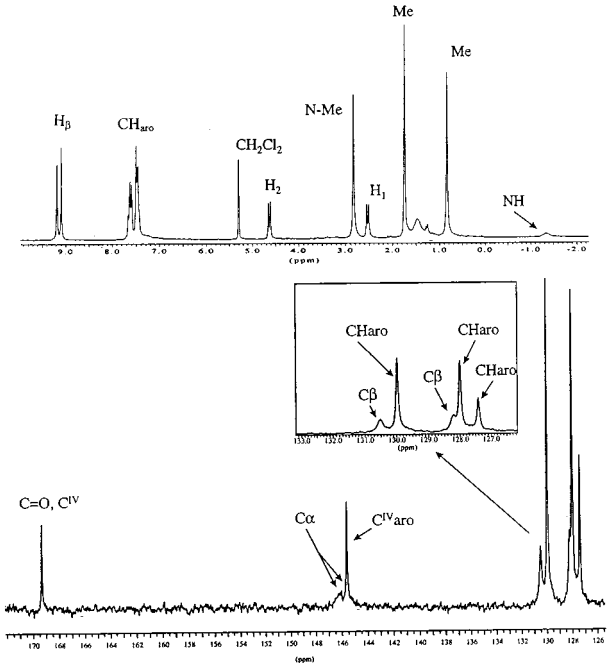
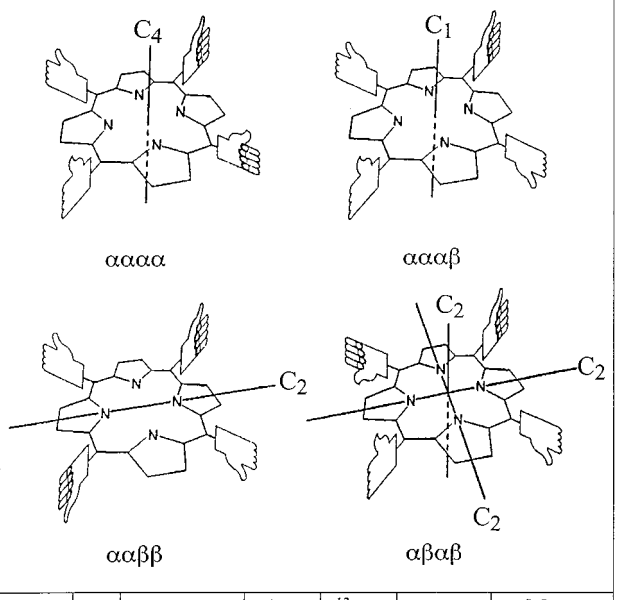


Figure 2. ^{1}H (top) and ^{13}C (bottom) NMR spectra of tetra-*N*-methyl-*N*-phenylchiroporphyrin **2j**

Symmetries and NMR mutiplicities of chiroporphyrin atropisomers



		H_β pyrr.	$^{13}C_\alpha$ pyrr.	$^{13}C_\beta$ pyrr.	$^{13}C_{meso}$	Meso substituents
αααα	C_4	2 d	2 s	2 s	1 s	1 type
ααβ	C_1	8 d	8 s	8 s	4 s	4 types
ααββ	C_2	2d and 2 s	4 s	4 s	2 s	2 types
αβαβ	D_2	2 s	2 s	2 s	1 s	1 type

s=singlet, d=doublet

Scheme 3. Symmetry elements and NMR of chiroporphyrins; homochiral substitutents are depicted as left hands

ation. On the other hand, an α,β,α,β substituted linear tetrapyrrole is preorganised for cyclisation by weak C–H···O hydrogen bonding between opposite *meso* substituents, leading to facile porphyrinogen cyclisation as shown in Figure 3 for tetramethylchiroporphyrinogen. Similar arguments have been used to explain the high yield synthesis of **2l**.[15]

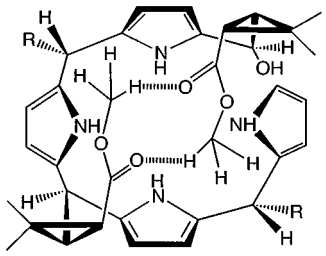


Figure 3. Conformation of an α,β,α,β substituted tetrapyrrole intermediate, preorganised by weak C–H···O hydrogen bonds between methyl ester substituents, which leads to facile cyclisation to the porphyrinogen. For the sake of clarity, only the H-bonding pattern on the top face is shown, and each of the two *meso* substituents on the bottom face is abbreviated as R

UV/Visible Spectroscopy

In Table 1 are collected the wavelengths of absorption maxima for the Soret and Q bands of chiroporphyrins **2a–m**, and those of H_2TPP (*meso*-tetraphenylporphyrin),

Table 1. Wavelengths (nm) of the absorption band maxima of chiroporphyrins **2a–2m** in dichloromethane

Compound	Soret	Q bands			
2a	428	528	565	605	663
2b	428	528	565	605	663
2c	428	528	565	605	662
2d	428	536	565	605	660
2e	430	530	567	605	664
2f	428	528	565	605	663
2g	431	529	567	608	666
2h	428	537	565	605	665
2i	431	536	565	605	670
2j	432	532	563	609	663
2k	434	533	564	610	663
2l	434	534	574	608	662
2m	432	532	569	608	667
H_2TPP[a]	417	515	552	594	650
H_2TCHP[a]	422	525	562	603	660
H_2TiPrP[b]	420	522	557	602	658
H_2T*t*BuP[b]	446	552	596	628	691

[a] Ref.[21] – [b] Ref.[22]

H_2TCHP (*meso*-tetracyclohexylporphyrin),[21] H_2TiPrP (*meso*-tetra-isopropylporphyrin) and H_2T*t*BuP (*meso*-tetra-*tert*-butylporphyrin)[22] are included for comparison. The small red shift of the Soret (10–17 nm) and Q bands of the chiroporphyrins relative to H_2TPP can be explained by the non planar distortion of the porphyrin induced by the steric bulk of the *meso* substituents.[23] The red shift is larger for the chiroporphyrins derived from amides (15–17 nm) than for those derived from esters (11–14 nm). However it is smaller than that observed for the highly distorted H_2T*t*BuP (29 nm) which exhibits anomalous porphyrinic properties.[22]

^{1}H NMR Spectroscopy

In Table 2 the ^{1}H-NMR chemical shifts of the pyrrole NH and β protons for chiroporphyrins **2a–m** are listed and compared to those of porphine, H_2TMP (*meso*-tetramesitylporphyrin), H_2TiPrP, and H_2T*t*BuP. Due to the aromatic ring current, the resonance of the β pyrrolic protons of porphine (δ = 9.74) are shifted to lower field by about 4 ppm relative to those of pyrrole, whereas its inner NH protons (δ = –3.76) are shifted to higher field by about 11 ppm. For chiroporphyrins **2a–m** the resonances of the NH protons (δ = –1.66 to –1.15) are also upfield shifted, but to a lower extent consistent with their less planar porphyrin ring and reduced ring current. Furthermore these shifts are correlated to the molecular volume of the R substituent[6] and are larger for the amides. The largest shift (2.61 ppm between **2m** and porphine) remains small compared to the 11 ppm difference between porphine and pyrrole. Thus the aromaticity of the chiroporphyrin is not strongly affected, as confirmed by the small red shift observed in UV-visible spectroscopy.

This conclusion is corroborated by the chemical shifts of the singlet pair for the β pyrrolic protons, which are not

Table 2. ^{1}H-NMR data (δ values) in $CDCl_3$ for chiroporphyrins **2a–2m** and the starting biocartol derivatives **1a–1m**[a]

	δ_{NH}'	δ_H pyrrolic	δH^1 ($\Delta\delta H_1$)	δH^2	δMe^{C2} ($\Delta\delta$Me)	δ_{Others} ($\Delta\delta$)
2a	–1.66	9.17–9.18	2.69 (+0.56)	4.75	0.79; 1.87 (–0.46, +0.34)	3.07 (–0.64) (OMe)
2b	–1.60	9.07–9.19	2.71 (+0.62)	4.78	0.82; 1.92 (–0.48, +0.40)	3.5 (–0.66) (OCH_2); 0.75 (–0.46) (Me)
2c	–1.58	9.06–9.27	2.61 (+0.60)	4.72	0.83; 1.92 (–0.38, +0.42)	0.44 (–0.98) (*t*Bu)
2d	–1.36	9.06–9.15	2.75 (+0.61)	4.83	0.77; 1.93 (–0.52, +0.39)	2.85, 3.18 (–0.94,–0.61) (OCH_2); 0.32 (–0.59) (*t*Bu)
2e	–1.27	9.03–9.17	2.71 (+0.63)	4.78	0.77; 1.92 (–0.45, +0.45)	4.1 (–0.75) (OCH_{exo}); –0.45, 0.41, 0.42 (ca. –1.2, –0.4, –0.4) (Me)
2f	–1.51	9.11–9.18	2.86 (+0.70)	4.86	0.87; 1.97 (–0.37, +0.44)	4.38, 4.48 (–0.74, –0.63) (OCH_2); 6.3, 6.47, 6.85 (ca. –0.8) (*o,m,p*-H_{aro})
2g	–1.45	9.10–9.45	2.95 (+0.60)	4.95	0.9; 2.05 (–0.40, +0.45)	3.55 (–0.15) (OMe); 6.45 (ca. –0.5) (mult H_{aro})
2h	–1.50	9.13–9.60	3.05 (+0.66)	5.16	0.88; 2.05 (–0.50, +0.42)	6.64, 7.06, 7.5, 7.73 (–0.82, ca. –0.5, ca. –0.5, –0.38) (H_{aro})
2i	–1.41	9.14–9.38	3.00 (+0.64)	5.05	0.88; 2.05 (–0.50, +0.42)	6.51, 7.77 (–0.78, –0.49) (H_{aro})
2j	–1.29	9.01–9.13	2.53 (+0.70)	4.58	0.95; 1.74 (+0.05, +0.20)	2.88 (–0.41) (NMe); 7.42–7.66 (ca. +0.22) (H_{aro})
2k	–1.21	9.01–9.15	2.38 (+0.64)	4.56	0.9; 1.72 (+0.06, +0.21)	3.37 (–0.2); 0.80 (–0.3) (NCH_2CH_3); 7.42–7.65 (+0.22) (H_{aro})
2l	–1.39	9.03–9.13	2.83 (+1.04)	4.77	0.86; 1.98 (–0.43, +0.53)	6.45 (–0.81) (NH), 3.56, 3.88 (–0.05, +0.02) (CHN), 0.87–1.81 (Cy)
2m	–1.15	9.06–9.21	2.44	4.62	0.72; 1.92	4.34 (NH); 3.13 (CHN); 0.81–1.30 (Cy)
porphine[b]	–3.76	9.74				
H_2TMP	–2.53	8.61				
H_2TiPrP[c]	–1.60	9.48		5.34		
H2T*t*BuP[c]	1.52	9.08				

[a] The numbers in parentheses show the difference Δδ between the chemical shifts of the relevant proton in the chiroporphyrin **2** and the corresponding biocartol derivative **1**. – [b] Ref.[25] – [c] Ref.[22]

very different from that of porphine (δ = 9.74). The chemical shift difference for each pair of singlets remains smaller than 0.21 ppm, except for chiroporphyrins **2g–i** for which the four β pyrrolic protons are subjected to the additional ring current of four phenyl rings. It has been possible to show by NOE-difference experiments on H_2TMCP **2a** that the singlet at lower field effectively belongs to the four $H_{\beta 2}$ protons neighbouring the four ester carbonyl groups.[24]

Our goal was to introduce stereogenic substituents close to the center of the porphyrin ring, and a comparison of corresponding chemical shifts between starting synthons and chiroporphyrins can be illustrative of the actual conformations (Table 2). The magnetic shielding resulting from the porphyrin ring current is positive for nuclei located inside and negative for nuclei located outside a doubly flared cylinder passing by the eight pyrrolic β-carbons.[25] The H^1 protons, with an average downfield shift of 0.65 ppm relative to the starting aldehyde, lie outside the nodal cylinder, and the methyl groups CH_3^s alike (downfield shift of ca. 0.4 ppm). On the other hand, the CH_3^i groups with a 0.4 ppm upfield shift are inside the cylinder. All the other protons belonging to the R groups show upfield shifts of 0.2 to 1.2 ppm. This suggests that the axial areas above and under the center of the porphyrins remain vacant and that the stereogenic groups sit on the porphyrin ring close to its periphery, thus restricting substrate or ligand access to the metal center along a C_2-symmetric groove in the corresponding catalysts. Such a dissymmetric environment is potentially very interesting for enantioselective catalysis.

Experimental Section

General Methods and Materials: Solvents and chemicals were used without purification unless indicated. Dichloromethane was stabilized either by ethanol (Carlo Erba Reagent, ACS for analysis, C_2H_5OH 0.2%) or 2-methyl-2-butene (SDS, "Purex pour analyses", 2-methyl-2-butene 0.002%). Pyrrole was purified by filtration on silica before use. Biocartol ester **1c** was a gift from Hoechst–Marion-Roussel. Esters **1a**,**b**,**d–i**[13] and amides **1j**,**k**[14] were prepared according to previously published procedures. Thin-layer chromatography was performed using Merck precoated silica plates 60F-254. Silica gel (230–400 mesh) and alumina (neutral, act. I) were used for column chromatography.

Spectroscopy: UV-visible spectra were recorded on a Perkin–Elmer Lambda 9 instrument. Nuclear magnetic resonance spectra were obtained with Bruker AC 200, AM 300, and AM 400 instruments. Spectra are tabulated in the following order: chemical shift (δ values), multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, b = broad), coupling constant (*J*, Hz), number of protons, assignment [CH_{aro} (aromatic proton), Hβ (β-pyrrolic protons of chiroporphyrins)]. Mass spectra were determined on a VG ZAB2-SEQ instrument.

Synthetic Procedures

Alternative One-Step Procedure for the Synthesis of Methyl (1*R*,3*S*)-2,2-Dimethyl-3-formylcyclopropane-1-carboxylate (1a, biocartol methyl ester): A flask equipped with a magnetic stirring bar was charged with biocartol (5.0 g, 35.2 mmol) and dry THF (120 mL) under an argon atmosphere. The solution was cooled to 10 °C and sodium hydride (60% dispersion of in mineral oil, 1.42 g, 35.4 mmol) was slowly added under gentle argon flow. The reaction mixture was stirred for 30 minutes, and 4.7 mL (75.4 mmol, 2.1 equiv.) of methyl iodide and DMF (50 mL) were added. The reaction mixture was then warmed to room temperature and stirred for two more hours. Upon addition of diethyl ether (100 mL), sodium iodide precipitated and was filtered off. The mixture was washed by water (6 × 100 mL) and dried with Na_2SO_4. Column chromatography (silica gel, CH_2Cl_2) gave the pure product. Yield: 81%. NMR and IR spectra were identical to those previously described.[13]

Optimized Procedure for the Synthesis of *meso*-Tetrakis[(1*R*,3*S*)-1-methoxycarbonyl-2,2-dimethylcycloprop-3-yl]porphyrin (2a): A 2.5-L commercial brown bottle filled with CH_2Cl_2 (containing 0.2% ethanol), equipped with a gas inlet, and shielded from ambient light by aluminum foil, was purged for one hour with argon. The flask was further charged with 1.8 g of aldehyde ester **1a** (11.5 mmol) and 0.96 mL of pyrrole (13.8 mmol, 1.2 equiv.) under argon, followed 10 minutes later by the addition of 1.08 mL of TFA (14.0 mmol, 1.2 equiv.). The resulting mixture was magnetically stirred at room temperature under gentle argon flow for 5 days. At this time, the reaction mixture was divided in three 2.5-liter bottles which were completed to a total volume of 7.5 L with CH_2Cl_2. A 0.86 g sample of DDQ (3 × 3.8 mmol, 0.83 equiv.) was added to each of the bottles which were magnetically stirred at room temperature under argon for 4 hours. The content of the three flasks was evaporated to dryness. The residue was chromatographed on 300 g of alumina (neutral, act. I), eluted with CH_2Cl_2 containing rising percentages of ethyl acetate (0, 2, 4, 6, 10%) under UV-visible spectroscopic control. The initial impure fractions were discarded and 0.472 g of pure porphyrin **2a** was obtained (20% yield relative to **1a**). MS (EI, Fe complex generated in situ) *m*/*z*: found. 868.810 (M – 2 H + Fe), calcd. for $C_{48}H_{52}N_4O_8Fe$: 868.808; (FAB^+) *m*/*z*: 814. – UV/Vis (CH_2Cl_2) λ_{max}/nm (log ε) = 428 (5.56), 528 (4.15), 565 (2.65), 605 (3.71), 663 (3.18). – ^{1}H NMR (400 MHz, $CDCl_3$) δ = –1.66 (s, NH), 0.79 (s, 12 H, CH_3^i), 1.87 (s, 12 H, CH_3^s), 2.69 [d, 4 H, *J* = 8.9 Hz, CH-C(O)], 3.07 (s, 12 H, OCH_3), 4.75 [d, 4 H, *J* = 8.9 Hz, C*H*-CH-C(O)O], 9.07 (1s, 4 H, $H_{\beta 1}$), 9.18 (s, 4 H, $H_{\beta 2}$). – ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.2 (CH_3), 27.7 (C^{IV}), 29.3 (CH_3), 33.2 (CH), 38.3 (CH), 51.0 (OCH_3), 110.1 (C_{meso}), 127.2 (Cβ), 131.1 (Cβ), 143.7 (Cα), 148.6 (Cα), 170.9 [C(O)]

Typical Procedure for the Synthesis of Porphyrins 2b–l: 14 mmol of ester or amide **1b–l** (0.88 equiv.) and 1.1 mL of pyrrole (1 equiv.) were dissolved in 1.5 L of CH_2Cl_2 (stabilized with 0.2% ethanol) which was degassed with argon for 10 minutes. A 1.23 mL amount of TFA (1 equiv.) dissolved in 50 mL of CH_2Cl_2 was then added under argon. The resulting solution, kept under argon and sheltered from light, was stirred for 18 hours at 20 °C. A 3.63 g amount of DDQ (1 equiv.) was then added, an the mixture was stirred for three more hours. The solution was evaporated under vacuum and the residue diluted in CH_2Cl_2 (150 mL, stabilized with amylene).

Note: The presence of polymeric material and tar in the crude product leads to a tedious purification of the porphyrin. The procedure given thereafter can be modified as necessary.

The resulting suspension was filtered over celite (20 g) or sodium sulfate to remove the precipitated tars. The filtrate was passed successively through three glass frit Buchner funnels containing each 100 g of silica. Several 200 mL aliquots of CH_2Cl_2, and of CH_2Cl_2/AcOEt mixtures (up to 70:30) were used to elute the porphyrin (followed by UV-visible spectroscopy). These impure fractions were evaporated and the porphyrin further purified over silica plates with CH_2Cl_2 as eluent. Occasionnally at the end of the process the

free base porphyrin was obtained as a mixture with its zinc complex (presumably due to inorganic additives on silica plates). In that case the mixture was dissolved in CH_2Cl_2, washed with 0.2 N HCl (3 × 25 mL) and with a saturated aqueous $NaHCO_3$ solution (3 × 25 mL). After drying (Na_2SO_4) and solvent evaporation, the pure porphyrin was obtained in 2–15% yield.

***meso*-Tetrakis[(1*R*,3*S*)-1-ethoxycarbonyl-2,2-dimethylcycloprop-3-yl]porphyrin (2b):** Chiroporphyrin **2b** was obtained in 2% yield. – UV/Visible (CH_2Cl_2) λ_{max}/nm = 428, 528, 565, 605, 663. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = –1.6 (s, NH), 0.75 (t, 12 H, *J* = 7.05 Hz), 0.82 (s, 12 H, CH_3), 1.92 (s, 12 H, CH_3), 2.71 [d, 4 H, *J* = 8.8 Hz, CH-C(O)], 3.55 (m, 8 H, OCH_2), 4.78 [d, 4 H, *J* = 8.8 Hz, C*H*-CH-C(O)O], 9.07 (1s, 4 H, $H_{\beta1}$), 9.19 (s, 4 H, $H_{\beta2}$). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.7 (CH_3), 18.1 (CH_3), 27.5 (C^{IV}), 29.2 (CH_3), 33.2 (CH), 37.9 (CH), 59.5 (OCH_2), 110.0 (C_{meso}), 127.6 (Cβ pyr.), 130.9 (Cβ), 145.8 (Cα pyr.), 153.7 (Cα), 170.3 (C=O).

***meso*-Tetrakis[(1*R*,3*S*)-1-*tert*-butoxycarbonyl-2,2-dimethylcycloprop-3-yl]porphyrin (2c):** Chiroporphyrin **2c** was obtained in 5% yield. MS-FAB+ *m*/*z*: 983.2 [MH^+]. – UV/Vis (CH_2Cl_2) λ_{max}/nm 428, 528, 565, 605, 662. – ^{1}H NMR: δ = –1.58 (s, NH), 0.44 (s, 36 H, *t*Bu), 0.83 (s, 12 H, CH_3), 1.92 (s, 12 H, CH_3), 2.61 [d, 4 H, *J* = 8.8 Hz, CH-C(O)], 4.72 [d, 4 H, *J* = 8.8 Hz, C*H*-CH-C(O)O], 9.06 (1s, 4 H, $H_{\beta1}$), 9.27 (s, 4 H, $H_{\beta2}$). – ^{13}C NMR 50 MHz, $CDCl_3$, δ 18.4 (CH_3), 27.2 (CH_3 *t*Bu), 29.4 (CH_3), 30.7 (C^{IV} *t*Bu) 34.7 (CH), 37.7 (CH), 79.4 (C^{IV} *t*BuO), 110.4 (C_{meso}), 127.5 (Cβ pyr.), 131.1 (Cβ), 142.9 (Cα pyr.), 149.2 (Cα), 169.8 (C=O).

***meso*-Tetrakis[(1*R*,3*S*)-1-neopentoxycarbonyl-2,2-dimethylcycloprop-3-yl]porphyrin (2d):** Chiroporphyrin **2d** was obtained in 1.5% yield. MS-FAB$^+$ *m*/*z*: 1039.6 [MH^+]. – UV/Vis (CH_2Cl_2) λ_{max}/nm (log ε) = 428 (5.5), 536 (4), 565 (3.6), 605 (3.5), 660(3). – ^{1}H NMR (200 MHz, $CDCl_3$) δ = –1.36 (s, NH), 0.32 (s, 36 H, *t*Bu), 0.77 (s, 12 H, CH_3), 1.93 (s, 12 H, CH_3), 2.75 [d, 4 H, *J* = 8.8 Hz, CH-C(O)], 2.85 (d, 4 H, *J* = 10.5 Hz, OCH), 3.18 (d, 4 H, J 10.5 Hz, OCH), 4.83 [d, 4 H, *J* = 8.8 Hz, C*H*-CH-C(O)O], 9.06 and 9.15 (2s, 8 H, H_β).

***meso*-Tetrakis[(1*R*,3*S*)-1-(1(*S*)-*endo*-bornoxy)carbonyl-2,2-dimethylcycloprop-3-yl]porphyrin (2e):** Chiroporphyrin **2e** was obtained in 5% yield. MS-FAB$^+$ *m*/*z*: 1303.8 [MH^+]. – UV/Vis (CH_2Cl_2) λ_{max} / nm (log ε) = 376 (4.1), 430 (5.4), 530 (4), 567 (3.6), 605 (3.6), 664 (3). – ^{1}H NMR (200 MHz, $CDCl_3$) δ = –1.27 (s, NH), –0.45 (s, 12 H, bornyl CH_3), 0.41 (s, 12 H, bornyl CH_3), 0.42 (s, 12 H, bornyl CH_3), 0.77 (s, 12 H, CH_3), 1.92 (m, bornyl H), 1.92 (s, 12 H, CH_3), 2.71 [d, 4 H, *J* = 8.8 Hz, CH-C(O)], 4.10 (m, 4 H, bornyl OCH), 4.78 [d, 4 H, *J* = 8.8 Hz, C*H*-CH-C(O)O], 9.03 and 9.17 (2s, 8 H, H_β).

***meso*-Tetrakis[(1*R*,3*S*)-1-benzyloxycarbonyl-2,2-dimethylcycloprop-3-yl]porphyrin (2f):** Chiroporphyrin **2f** was obtained in 2% yield. – UV/Vis (CH_2Cl_2) λ_{max}/nm = 428, 528, 565, 605, 663. – ^{1}H NMR (300 MHz, $CDCl_3$) δ = –1.51 (s, NH), 0.87 (s, 12 H, CH_3), 1.97 (s, 12 H, CH_3), 2.86 [d, 4 H, *J* = 8.9 Hz, CH-C(O)O], 4.38 (d, 4 H, *J* = 12.2 Hz, benzylic OCH), 4.48 (d, 4 H, *J* = 12.2 Hz, OCH), 4.86 [d, 4 H, *J* = 8.8 Hz, C*H*-CH-C(O)O], 6.30 (d, 8 H, $CH_{aro\text{-}o}$, *J* = 7.6 Hz), 6.47 (t, 8 H, $CH_{aro\text{-}m}$, *J* = 7.6 Hz), 6.85 (t, 4 H, $CH_{aro\text{-}p}$, *J* = 7.3 Hz), 9.11(s, 4 H, H_β), 9.18 (s, 4 H, H_β). – ^{13}C NMR 75 MHz, $CDCl_3$ δ 18.2 (CH_3), 28.1 (C^{IV}), 29.2 (CH_3), 33.6 (CH), 38.4 (CH), 66.0 (OCH_2), 110.7 (C_{meso}), 127.9 (CH_{aro}), 128.0 (CH_{aro}), 128.1 (CH_{aro} et Cβ), 131.3 (Cβ), 136.0 (C^{IV}_{aro}), 144.7 (C_α), 147.8 (C_α), 170.6 (C=O).

***meso*-Tetrakis[(1*R*,3*S*)-1-(*p*-methoxyphenoxycarbonyl)-2,2-dimethylcycloprop-3-yl]porphyrin (2g):** Chiroporphyrin **2g** was prepared in 7% yield. MS-FAB$^+$ *m*/*z*: 1183 [MH^+]. – UV/Vis (CH_2Cl_2) λ_{max}/nm (log ε) = 431 (5.47), 529 (4.11), 567 (3.64), 608 (3.59), 666 (2.95). ^{1}H NMR (200 MHz, $CDCl_3$) δ = –1.45 (s, NH), 0.9 (s, 12 H, CH_3), 2.05 (s, 12 H, CH_3), 2.95 [d, 4 H, *J* = 8.8 Hz, CH-C(O)], 3.55 (s, 12 H, OCH_3), 4.95 [d, 4 H, *J* = 8.8 Hz, C*H*-CH-C(O)O], 6.45 (m, 16 H, H_{aro}), 9.1 (s, 4 H, H_β), 9.45 (s, 4 H, H_β).

***meso*-Tetrakis[(1*R*,3*S*)-1-(*m*-nitrophenoxycarbonyl)-2,2-dimethylcycloprop-3-yl]porphyrin (2h):** Chiroporphyrin **2h** was obtained in 14% yield. MS-FAB$^+$ 1243 [MH^+]. – UV/Vis (CH_2Cl_2) λ_{max}/nm (log ε) = 428 (5.2), 537 (4), 565 (3.5), 605 (3.5), 665 (3.1). – ^{1}H NMR (200 MHz, $CDCl_3$) δ = –1.5 (s, NH), 0.88 (s, 12 H, CH_3), 2.05 (s, 12 H, CH_3), 3.05 (d, 4 H, *J* = 8.8 Hz, CH-C(O)), 5.16 (d, 4 H, *J* = 8.8 Hz, C*H*-CH-C(O)O), 6.64 (ddd, 4 H, CH_{aro}, *J* = 8.17, *J* = 2 and *J* = 1 Hz), 7.06 (dd, 4 H, CH_{aro}, *J* = 8.2, 2 and 1 Hz), 7.5 (dd, 4 H, CH_{aro}, *J* = 8.2 and 2 Hz), 7.73 (ddd, 4 H, CH_{aro}, *J* = 8.1, 2 and 1 Hz), 9.13 and 9.60 (2s, 8 H, H_β).

***meso*-Tetrakis[(1*R*,3*S*)-1-(*p*-nitrophenoxycarbonyl)-2,2-dimethylcycloprop-3-yl]porphyrin (2i):** Chiroporphyrin **2i** was obtained in 5.5% yield. Crystallization of the pure product was induced by slow addition of *n*-hexane to a concentrated dichloromethane solution of the crude product. UV/Vis (CH_2Cl_2) λ_{max} /nm (log ε) = 431 (5.5), 536 (4), 565 (3.6), 605 (3.6), 670 (3). – ^{1}H NMR (200 MHz, $CDCl_3$) δ = –1.41 (s, NH), 0.88 (s, 12 H, CH_3), 2.05 (s, 12 H, CH_3), 3.0 [d, 4 H, *J* = 8.8 Hz, CH-C(O)], 5.05 [d, 4 H, *J* = 8.8 Hz, C*H*-CH-C(O)O], 6.51 (d, 8 H, *J* = 8.6 Hz, CH_{aro}), 7.77 (d, 8 H, *J* = 8.6 Hz, CH_{aro}), 9.14 and 9.38 (2s, 8 H, H_β).

***meso*-Tetrakis[(1*R*,3*S*)-1(*N*-methyl-*N*-phenyl)carbamoyl-2,2-dimethylcycloprop-3-yl]porphyrin (2j):** Chiroporphyrin **2j** was obtained in 7% yield. MS-FAB$^+$ *m*/*z*: 1114 [$M^{\bullet+}$] [exact mass of MH^+ = 1115.5868 (Δ = 3.8 ppm); exact mass of $M^{\bullet+}$ = 1114.5602 (Δ = 21 ppm)]. – UV/Vis (CH_2Cl_2) λ_{max}/nm = 432, 532, 563, 609, 663. – ^{1}H NMR (400 MHz, $CDCl_3$) δ = –1.29 (br. s, 2 H, NH), 0.95 (s, 12 H, CH_3), 1.74 (s, 12 H, CH_3), 2.53 [d, *J* = 8.2 Hz, 4 H, C*H*-C(O)N], 2.88 (s, 12 H, N-CH_3), 4.58 [d, *J* = 8.2 Hz, 4 H, C*H*-CH-C(O)N], 7.42–7.66 (m, 20 H, CH_{aro}), 9.01 and 9.13 (2s, 8 H, H_β). – ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 18.0 (Me), 27.6 (C^{IV}), 28.6 (CH_3), 32.5 (CH), 37.1 (CH), 38.0 (N-CH_3), 111.3 (C^{IV} *meso*), 127.4 (CHaro), 128.0 (CHaro), 128.2 (Cβ), 130.0 (CHaro), 130.5 (Cβ), 145.6 (C^{IV} aro), 146.3 (b, Cα), 169.3 (C=O).

***meso*-Tetrakis[(1*R*,3*S*)-1(*N*-ethyl-*N*-phenyl)carbamoyl-2,2-dimethylcycloprop-3-yl]porphyrin (2k):** Chiroporphyrin **2k** was prepared in 6% yield using the "typical procedure". By adding Et_3N (1 equiv.) after reaction with DDQ, the yield rose to 12%. MS-FAB$^+$ *m*/*z*: 1171.7 [MH^+]. – UV/Vis (CH_2Cl_2) λ_{max}/nm = 434, 533, 564, 610, 633. – ^{1}H NMR (400 MHz, $CDCl_3$) δ = –1.21 (b, 2 H, NH), 0.80 (t, *J* = 6.8 Hz, 12 H, CH_3), 0.90 (s, 12 H, CH_3), 1.72 (s, 12 H, CH_3), 2.38 [d, *J* = 8.3 Hz, 4 H, C*H*-C(O)N], 3.37 (m, 8 H, N-CH_2), 4.56 [d, *J* = 8.3 Hz, 4 H, C*H*-CH-C(O)N], 7.42–7.65 (m, 20 H, CH_{aro}), 9.01 and 9.15 (2s, 8 H, H_β). – ^{13}C NMR (100 MHz, CD_2Cl_2) δ 12.7 (Me), 17.4 (Me), 26.8 (C^{IV}), 27.9 (CH_3), 32.2 (CH), 37.2 (CH), 43.2 (N-CH_2), 110.7 (C^{IV} *meso*), 126.9 (CHaro), 127.5 (Cβ), 128.4 (CHaro), 129.2 (CHaro), 130.0 (Cβ), 143.4 (C^{IV} aro), 144.4 (Cα), 146.1 (Cα), 168.0 (C=O, C^{IV}).

(1*R*,3*S*)-*N*-(*N*'-cyclohexyl)carbamoyl-*N*-cyclohexyl-3-formyl-2,2-dimethylcyclopropane-1-carboxamide (1l): (1*R*)-*cis*-hemicaronaldehydic acid (7.1 g, 50 mmol), Et_3N (8.4 mL, 1.2 equiv.), and DCC (12.4 g, 60 mmol, 1.2 equiv.) were mixed and stirred in DMF (100 mL) for 12 hours. After addition of CH_2Cl_2 (25 mL), the reaction mixture was washed successively with an aqueous HCl (10%) solution (3 × 25 mL), with a saturated aqueous $NaHCO_3$ solution (3 × 25 mL) and with water (8 × 25 mL). The organic layer was dried with Na_2SO_4 and the solvent was removed in vacuo. The

residue was purified by silica gel chromatography. Elution with a CH_2Cl_2/AcOEt mixture (90:10) gave 8.6 g of **1l** (50% yield). NMR and IR spectra were identical to those previously described.[13]

***meso*-Tetrakis{(1*R*,3*S*)-1[*N*-(*N*'-cyclohexyl)carbamoyl-*N*-cyclohexyl]carbamoyl-2,2-dimethylcycloprop-3-yl}porphyrin (2l):** Chiroporphyrin **2l** was prepared in 34% yield using the "typical procedure". By adding Et_3N (1 equiv.) after reaction with DDQ, the yield rose to 60%. MS-FAB$^+$ *m/z*: 1583.8 [MH^+]. – UV/Vis (CH_2Cl_2) λ_{max}/nm = 434, 534, 574, 608, 662. – ^{1}H NMR (200 MHz, $CDCl_3$) δ = –1.39 (br. s, 2 H, NH) 0.86 (s, 12 H, CH_3), 0.87–1.81 (m, cyclohexyl), 1.98 (s, 12 H, CH_3), 2.83 [d, *J* = 8.3 Hz, 4 H, C*H*-C(O)N], 3.56 (m, 4 H, N-CH), 3.88 (m, 4 H, N-CH), 4.77 [d, *J* = 8.3 Hz, 4 H, C*H*-CH-C(O)N], 6.45 (br. s, 4 H, NH), 9.03 and 9.13 (2s, 8 H, H_β). – ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 18.1 (Me), 24.8 (CH_2), 25.5 (CH_2), 25.7 (CH_2), 26.6 (CH_2), 28.6 (C^{IV}), 29.5 (CH or CH_3), 29.9 (CH_2), 31.4 (CH_2), 31.7 (CH_2), 32.8 (2 CH_2), 34.1 (CH or CH_3), 39.1 (CH or CH_3), 49.6 (CH or CH_3), 53.6 (CH_2), 55.6 (CH or CH_3), 110.3 (C^{IV} *meso*), 127.7 (Cβ), 130.9 (Cβ), 143.9 (Cα), 147.9 (Cα), 154.8 (C=O), 170.8 (C=O).

***meso*-Tetrakis[(1*R*,3*S*)-1(*N*-cyclohexyl)carbamoyl-2,2-dimethylcycloprop-3-yl]porphyrin (2m):** Compound **2l** (100 mg) was dissolved in dry benzene (10 mL) under argon, $POCl_3$ (212 μL) was added, and the mixture was stirred for 5 days. Water (5 mL) was then added. After stirring for one more day, the reaction mixture was washed with a saturated aqueous $NaHCO_3$ solution (3 × 25 mL). The organic layer was dried with Na_2SO_4 and the solvent removed under vacuum. After TLC (CH_2Cl_2/MeOH: 96:4) of the residue, 40 mg of chiroporphyrin **2m** were obtained (yield 60%). MS-FAB$^+$ *m/z*: 1082.7 [$M^{\bullet+}$]. – UV/Vis ($CHCl_3$) λ_{max}/nm = 432, 532, 569, 608, 667. – ^{1}H NMR (200 MHz, $CDCl_3$) δ = –1.15 (b, 2 H, NH), 0.72 (s, 12 H, CH_3), 0.81–1.30 (m, cyclohexyl), 1.92 (s, 12 H, CH_3), 2.44 [d, *J* = 8.8 Hz, 4 H, C*H*-C(O)N], 3.13 (m, 4 H, N-CH), 4.34 (d, *J* = 7.3 Hz, 4 H, NH), 4.62 [d, *J* = 8.8 Hz, 4 H, C*H*-CH-C(O)N], 9.06 and 9.21 (2s, 8 H, H_β); ^{1}H NMR (200 MHz, CD_2Cl_2) δ = –1.27 (b, 2 H, NH), 0.75 (s, 12 H, CH_3), 0.68–1.30 (m, cyclohexyl), 1.93 (s, 12 H, CH_3), 2.38 [d, *J* = 9.1 Hz, 4 H, C*H*-C(O)N], 3.15 (m, 4 H, N-CH), 5.12 (d, *J* = 7.9 Hz, 4 H, NH), 4.71 [d, *J* = 8.5 Hz, 4 H, C*H*-CH-C(O)N], 9.14 and 9.22 (2s, 8 H, H_β). – ^{13}C NMR (50 MHz, CD_2Cl_2) δ 18.3, 24.5, 25.6, 26.6, 29.8, 30.1, 33.0, 35.6, 36.9, 47.5, 110.3 (C^{IV} *meso*), 129.9 (Cβ), 130.8 (Cβ), 146.1 (Cα), 146.8 (Cα), 168.9 (C=O).

Acknowledgments

We thank Dr. Jean Buendia of Hoechst–Marion Roussel for a generous supply of biocartol, Marc Veyrat for breaking new ground in the synthesis of **2a**, Patrick Dubourdeaux and Nathalie Gon for help with the syntheses, Colette Lebrun for providing the mass spectra.

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Received July 6, 1999
[O99435]