Proline-Modified Porphyrin Catalysts for Enantioselective Epoxidations: Design, Synthesis, and Reactivity

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The syntheses of various strapped and 'picket-fence' chiral porphyrins are described, and their reactivities towards the enantioselective epoxidation of alkenes are reported. Four L-proline residues provide the chirality for the various *meso*-substituted catalysts, which differ by either the spatial arrangement of the stereogenic centers or the nature and length of the straps. The resulting bridged structures possess four amide linkages in each strap, leading to highly rigid molecules with well-defined geometries whereas the strapped Fe catalysts gave rise to only moderate enantioselectivities, the C_2-symmetrical ones being superior to the D_2-symmetrical compounds. The D_2-symmetrical 'picket-fence' porphyrins were as selective as their strapped counterparts.

1. Introduction. – In recent years, much effort has been put into the development of catalysts for enantioselective transformations of nonchiral molecules into chiral products [1]. This synthetic methodology provides potential building blocks for the synthesis of biologically active molecules. One such process relies on epoxidation, since epoxides are key industrial intermediates, and chiral epoxides are of particular importance for the synthesis of drugs and natural products [2]. In most cases, chiral transition-metal complexes are being used as epoxidation catalysts, especially manganese(III) salens [3] and metalloporphyrins [4]. The former provide excellent enantiomeric excess (ee) in enantioselective epoxidations of substituted aromatic alkenes, and they are considered for industrial applications [5]. However, their turnover numbers are low due to the oxidative degradation of the ligand itself. In contrast, owing to their stability towards oxidation, chiral metalloporphyrins are good candidates for catalysts of enantioselective epoxidation, but, with a few recent exceptions [6], the enantioselectivities achieved have been moderate. Therefore, the design and synthesis of chiral porphyrins continues to be an active area of research.

So far, two general approaches have been employed. The first involves so-called chiral 'picket-fence' porphyrins, and, since the original paper by *Groves* and *Myers* [7], these compounds have been thoroughly studied by the groups of *Halterman* and *Jan* [8], *Kodadek* and co-workers [9], *Momenteau* and co-workers [10], and *Salvadori* and *Guilard* and co-workers [11]. In the second method, chirality is introduced *via* straps. The first chiral strapped porphyrin was reported by *Mansuy* and co-workers [12], and this approach has been extensively elaborated by the groups of *Collman et al.* [13], *Groves* and *Viski* [14], *Rose* and co-workers [15], *Naruta et al.* [16], *Gross* and *Ini* [17],

Inoue and co-workers [18], and *Che* and co-workers [19]. Despite numerous advances, the specific features (sterics, conformation, electronic properties, rigidity, *etc.*) of the chiral ligand are far from being completely understood with respect to enantioselectivity.

Our own investigations prompted us to invent and develop several new types of chiral porphyrins, bearing either straps [20] or pickets [21], but always elaborated with the same chiral motif, namely L-proline. We have chosen this particular amino acid because of its cyclic structure, which does not allow the rotation of the lateral chain. Here, we report the synthesis of three series of strapped porphyrins, the preparation of four different 'picket-fence' porphyrins, as well as the activities of their Fe complexes towards the epoxidation of two different olefins.

2. Results and Discussion. – 2.1. *Synthesis of Porphyrins* **1**–**13**. The initially targeted D_2-symmetric compounds **1**–**6** were obtained from the atropisomer $\alpha\beta\alpha\beta$-**7** (*Scheme*) [22]. The latter was obtained by fourfold coupling of Boc-L-proline[1]) with 5,10,15,20-tetra(2-aminophenyl)porphyrin (**8**) by means of mixed-anhydride activation (ClCOO(i-Bu), THF, $-20°$) of the amino acid followed by coupling (*N*-methylpiperidine, THF, r.t.). Thereby, a large excess (100 equiv.) of Boc-L-Proline was required [20]. The chiral integrity of the amino acid was retained during the coupling reaction [15b]. The protective group was easily removed upon exposure to CF_3CO_2H/CH_2Cl_2 1:10 at room temperature, which gave rise to $\alpha\beta\alpha\beta$-**7b**. The latter was immediately reacted, to avoid rapid degradation upon neutralization, with the desired diacyl dichloride in THF/Et_3N under high-dilution conditions (8×10^{-4} M) and slow addition of the reagents to minimize the formation of polymeric products. The resulting doubly bridged porphyrins **1**–**6** were obtained in 10–70% yield, depending on the linker used. It is worth noting that **1** was obtained in an unexpectedly high yield of 70%. However, its lower homolog ($X=CH_2$) could not be isolated.

The same synthetic procedure was applied to obtain two other groups of strapped porphyrins. Indeed, the bis-strapped porphyrins **9**–**12** and **13** could be obtained from $\alpha\alpha\beta\beta$- and $\alpha\alpha\alpha\alpha$-**7a**, respectively. In contrast to the first two series of compounds, **13** represents a porphyrin with only one functionalized face, whereas **1**–**6** and **9**–**12** contain *two* enantiogenic sides.

2.2. *Structural Aspects.* To determine the conformations of the new porphyrins in solution, we compared most of their ^{1}H-NMR spectra. Whereas these spectra are not very informative in the cases of the four 'picket-fence' porphyrins **7a**, with broadened signals presumably due to the rotation of the Boc group, ^{1}H-NMR spectroscopy was a particularly useful technique to probe both the conformations of the straps and the overall symmetry in the case of the rigid bis-strapped porphyrins. Usually, the porphyrin NH resonances can be used as a probe to evaluate the macrocycle distortion, as illustrated with chiroporphyrins [23]. However, for our own compounds, considering the very different influence that aromatic rings within the straps may have on the internal NH H-atoms, we decided not to take them into account. Obviously, the bridging 1,4-disubstituted Ph ring in **5** can shield these two protons when parallel to the

[1]) Boc = (*tert*-butoxy)carbonyl.

porphyrin core, whereas the opposite effect is expected in the case of **6** or **12**, which contain 1,3-disubstituted, *perpendicular* Ph rings.

The usual ^{1}H-NMR pattern observed for the aromatic rings in *meso*-position consists of two *doublets* and two *triplets*, with a *J* value of *ca.* 7.5 Hz, and gives rise to cross-peaks in 2D-correlated spectra. The second observation to be made concerns the pattern of the pyrrole H-atoms in β-position, which appear as two *singlets* that integrate for four atoms each. Indeed, due to symmetry, as has already been shown [15b], these β-resonances of the porphyrin bear witness to the chirality of the proline residues. This observation holds true for all of the bis-strapped porphyrins described herein, with the exception of Zn-**1** (*Fig. 1,a*). In this particular case, the β-resonances appeared as eight *doublets*, with a *J* value of 4.7 Hz, indicating that the porphyrin is no longer symmetrical. This result was consistent with the crystal structure of Zn-**1**, as will be discussed below. Furthermore, for compounds **1**–**6**, the ^{1}H-NMR resonances of the linker experienced a significant upfield shift, as expected for H-atoms above the porphyrin macrocycle. For example, in the case of **4**, the δ(H) value of the fumaryl H-atoms was 2.68, whereas it is 6.84, in diethyl fumarate.

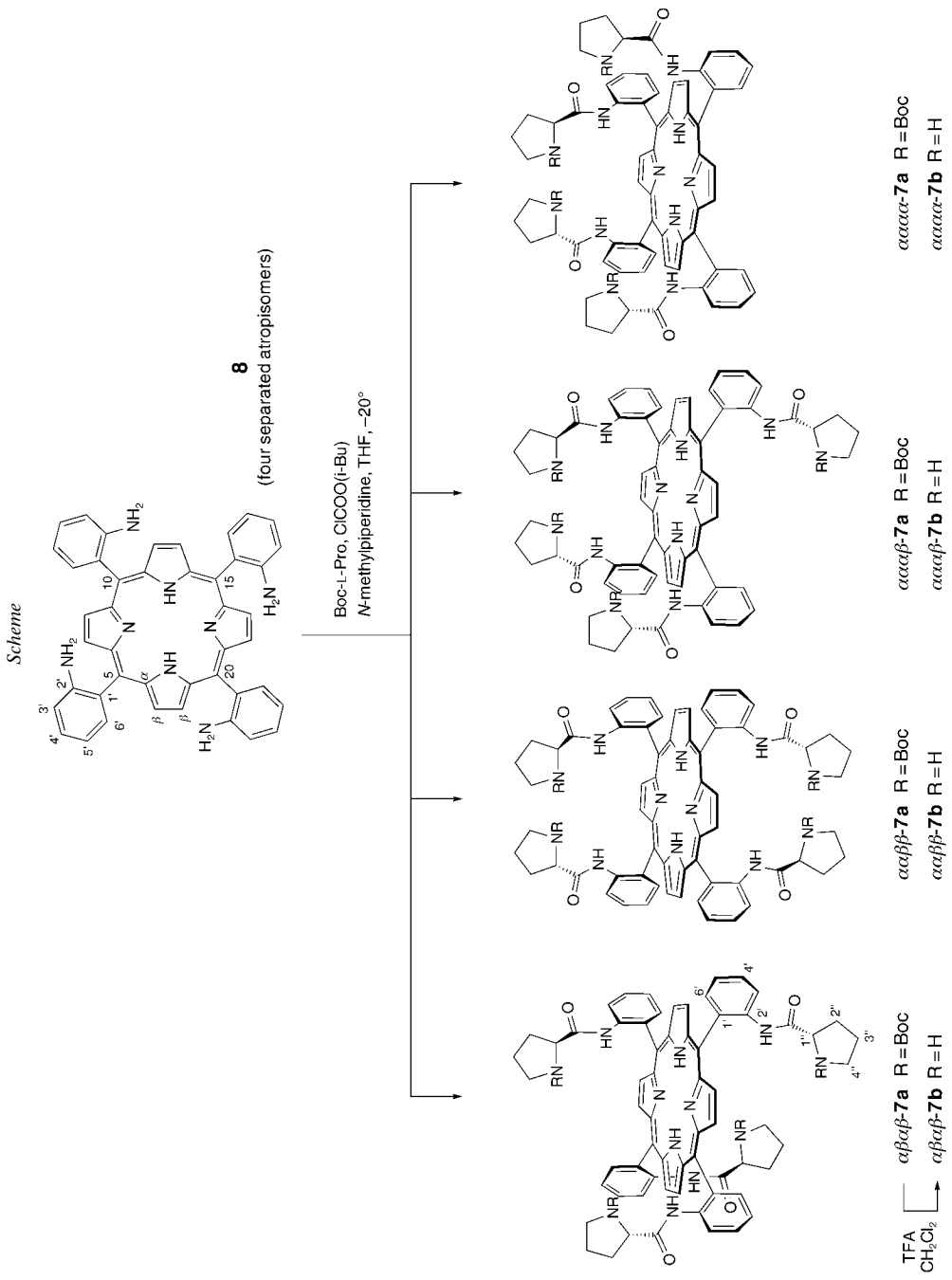
Among compounds **1**–**6**, which gave rise to characteristic NMR spectra with sharp signals, the porphyrins **1** and its zinc(II) analogue Zn-**1** were most intriguing. The incorporation of Zn^{2+} was achieved upon exposure to $(AcO)_2Zn$ in refluxing DMF/2,6-lutidine. The difficult access to the porphyrin core and the deformation of the complex may rationalize the high temperature required for metallation. Single crystals suitable for X-ray structure determination (see below) were obtained by slow evaporation of a solution of Zn-**1** in a mixture of toluene/MeCN 1:1 at room temperature [20].

In the ^{1}H-NMR spectrum of **1**, the most striking observation concerns both the signal pattern and chemical shifts of the CH_2 succinyl moieties, which appeared as two *multiplets* at δ(H) -0.45 and -4.00 (*Fig. 1,b*). The 2D heteronuclear HMQC spectrum (not shown) indicated that the two CH_2 C-atoms appear as only one signal at δ(C) 24.5 in the decoupled spectrum (*Fig. 1,c*). The observed difference in chemical shift ($\Delta\delta$(H) = 3.5 ppm) between the two CH_2 signals indicates that two H-atoms are directed towards the center of the porphyrin, whereas the other two protrude from the cavity. This analysis was confirmed by the X-ray crystal structure of Zn-**1** shown in *Fig. 2*. Therefore, the 2D-HMQC fingerprint is explained by the fact that each C-atom bears two diastereotopic H-atoms, yielding *two* cross-peaks for the single C-atom signal. Moreover, this situation is a perfect illustration of the conformational information that can be obtained through the study of this type of structure in solution.

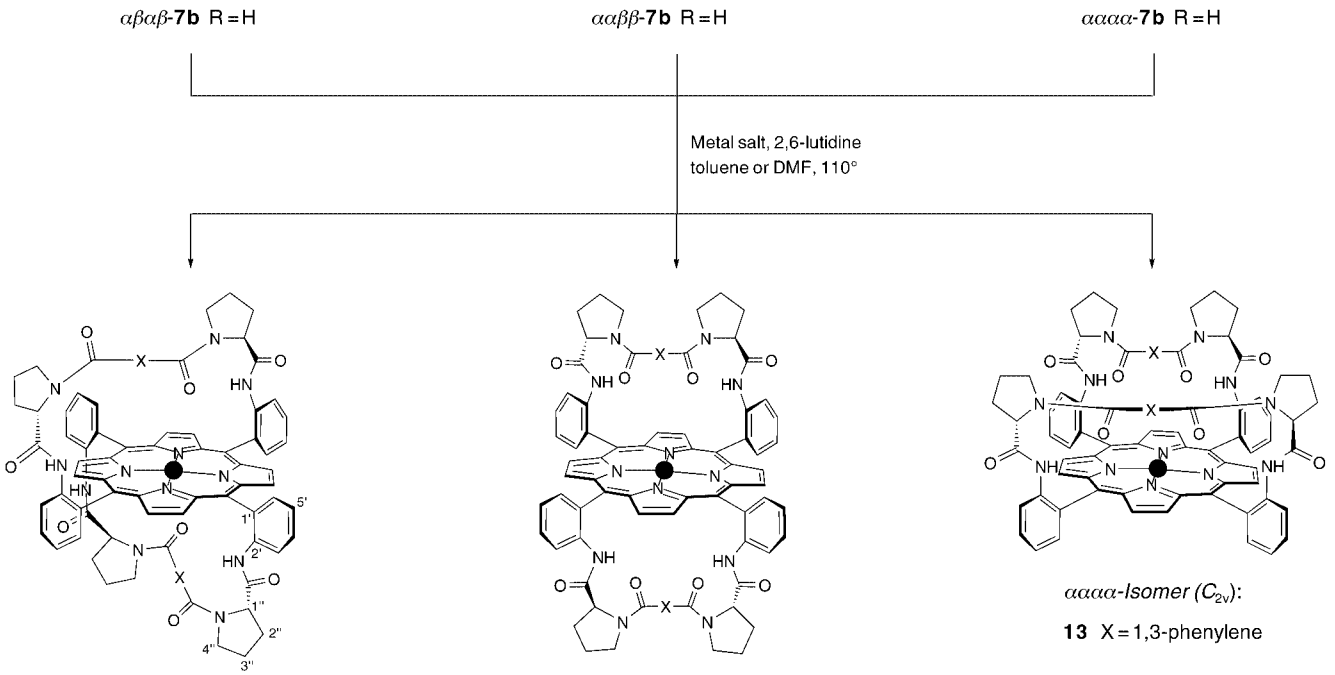
The second important remark concerns the ^{1}H-NMR spectra of **1** relative to Zn-**1**. Here, one would expect quite similar signatures, with the absence of the internal NH signal as the only major difference for the Zn complex. However, not only are the two straps in **1** *vs.* Zn-**1** magnetically different, the symmetry differs as well. In fact, as mentioned above and as revealed by signals for each β-H-atom, Zn-**1** has 'no' symmetry at all (C_1)! Therefore, its crystal structure (*Fig. 2*) appears to be maintained in solution. We also inserted Ni^{2+}, which is known to form square-planar complexes with porphyrins [24], to obtain an X-ray crystal structure of Ni-**1** with no internal coordination, but these attempts were unsuccessful.

In the case of compounds **9**–**12**, for which no crystal structures were available, we compared the ^{1}H-NMR spectra of, *e.g.*, **10** and **2** [25]. In the case of **2**, three *multiplets*

Scheme


8
(four separated atropisomers)
Boc-L-Pro, ClCOO(i-Bu)
N-methylpiperidine, THF, –20°
αααα-7a R=Boc
αααα-7b R=H
ααββ-7a R=Boc
ααββ-7b R=H
αααβ-7a R=Boc
αααβ-7b R=H
αβαβ-7a R=Boc
αβαβ-7b R=H
TFA
CH2Cl2

Scheme (cont.)



αβαβ-Isomer (D_2):

1 X = $(CH_2)_2$
2 X = $(CH_2)_3$
3 X = $(CH_2)_4$
4 X = (*E*)-CH=CH
5 X = 1,4-phenylene
6 X = 1,3-phenylene

ααββ-Isomer (C_2):

9 X = $(CH_2)_2$
10 X = $(CH_2)_3$
11 X = $(CH_2)_4$
12 X = 1,3-phenylene

αααα-Isomer (C_{2v}):

13 X = 1,3-phenylene

Boc = *tert*-butoxycarbonyl

● H_2 (metal-free form) or metal center: Zn, Ni, Fe; axial ligands have been omitted for clarity (see the *Table*)

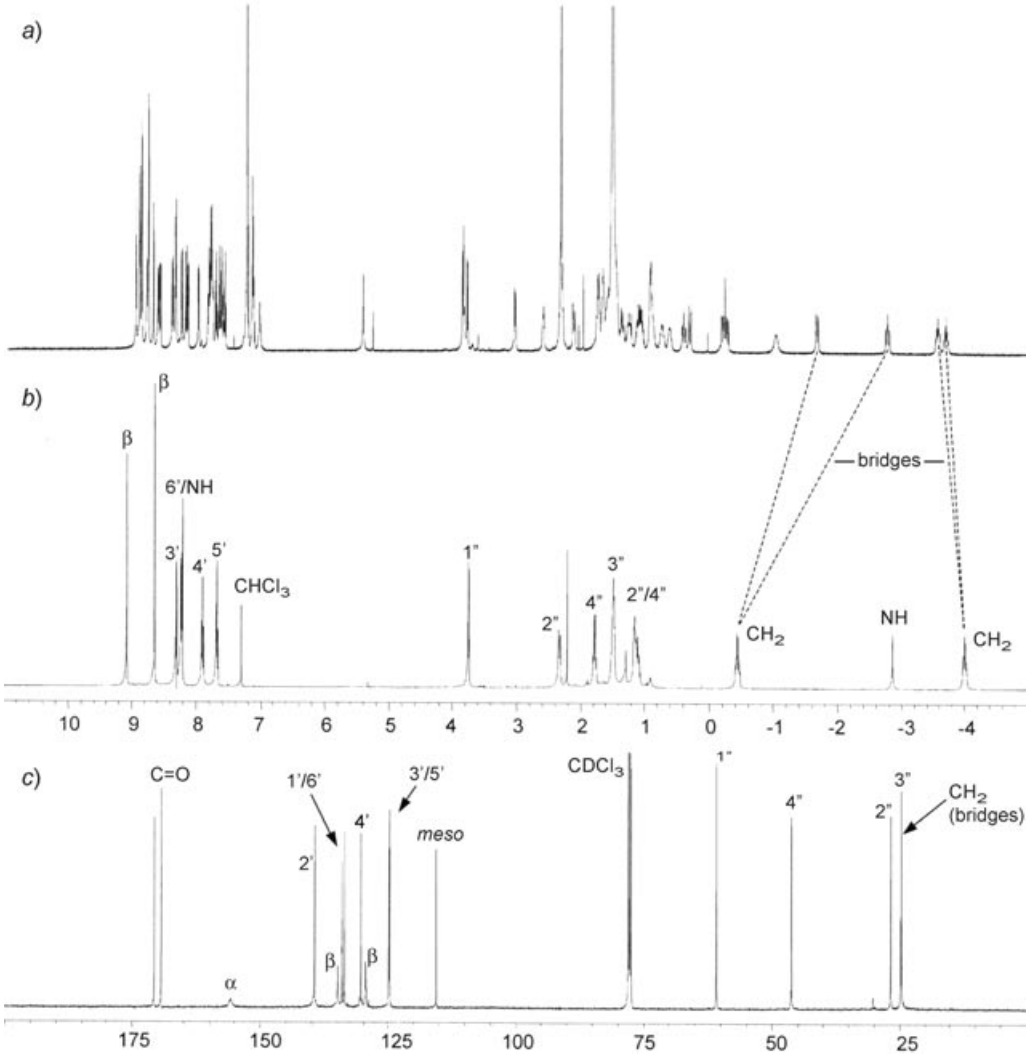


Fig. 1. *500-MHz ^{1}H-NMR Spectra of* a) *αβαβ*-Zn-**1** *and* b) *metal-free αβαβ*-**1**; *and* c) *125-MHz ^{13}C-NMR spectrum of metal-free αβαβ*-**1**. Solvent: $CDCl_3$, 27°. For atom numbering, see the *Scheme*.

appeared between δ(H) 0 and -3.5, which were attributed unambiguously to the three CH_2 groups of the glutaryl residues. For the corresponding *ααββ* atropisomer **10**, one would expect these signals to be more downfield-shifted, as the straps do not span the central porphyrin core. However, they were as shielded as in **2**, which seems to indicate that the bridges lie close to the porphyrin plane in both cases. Additionally, we have shown [25] that molecular mechanics (MM^+ force field; HyperChem software) predicts the conformations of such restricted straps and their distance to the porphyrin plane reasonably well. For instance, the central glutaryl CH_2 C-atom is evaluated to be 3.35 Å

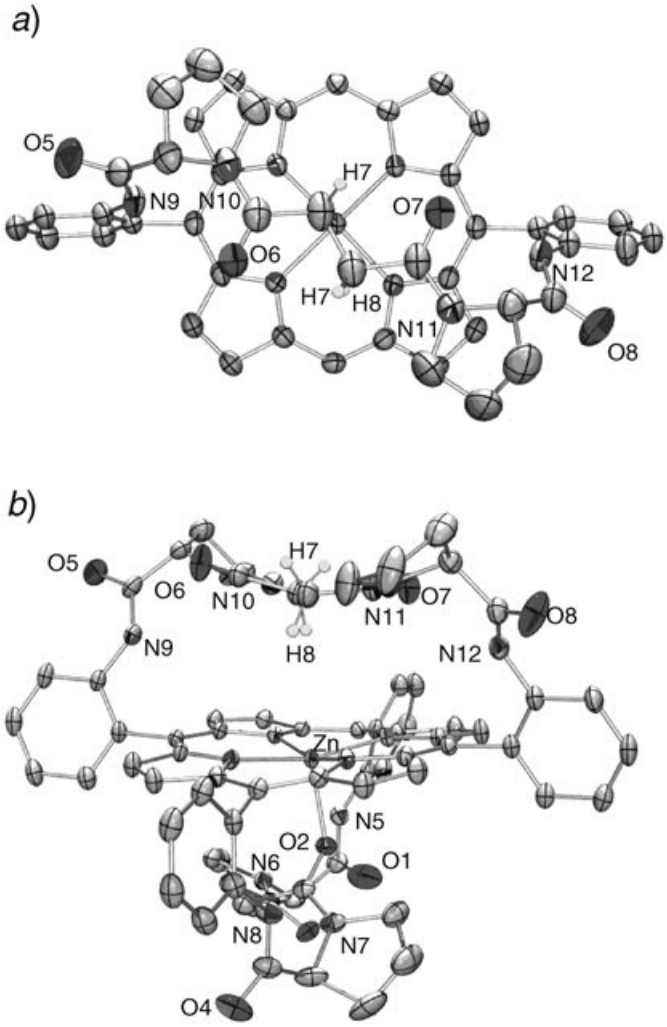


Fig. 2. *ORTEP Representation of the crystal structure of αβαβ*-Zn-**1** *viewed from top* (*a*) *and from the side* (*b*). In the top view, the coordinated strap has been omitted for clarity.

away from the plane of the porphyrin in **10** (*Fig. 3*), whereas it is 3.99 Å away in **2** (*Fig. 4,e*). In agreement with these evaluations, the most-shielded CH_2 atoms in **2** and **10** are observed at $\delta(H) -3.24$ and -3.88, respectively, confirming that the straps of **10** are actually bent over the porphyrin, as indicated by molecular mechanics.

2.3. *Synthesis and Catalytic Properties of Bridged Fe Porphyrins.* Insertion of Fe^{2+} into compounds **1**–**6** and **9**–**13** was carried out with $FeBr_2$ in refluxing toluene in the presence of 2,6-lutidine under exclusion of O_2 (glove box). Completion of the reaction was monitored by UV/VIS spectroscopy. This procedure failed when applied to porphyrin **5**, presumably for steric reasons. Thus, it was necessary to insert Fe into the

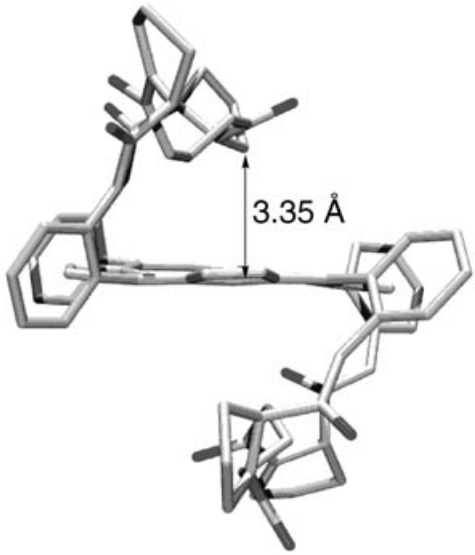


Fig. 3. *Molecular-mechanics model of* $\alpha\alpha\beta\beta$-**10** (stick representation)

less-hindered picket porphyrin $\alpha\beta\alpha\beta$-**7a** to avoid any possible atropisomerization, followed by the final strapping reaction.

Chloro derivatives were generated by shaking a CH_2Cl_2 solution of the Fe porphyrin with aqueous NaCl. The resulting Fe^{III}(Cl) porphyrins were characterized by MS and UV/VIS spectroscopy. The mass spectra of the complexes exhibited peaks corresponding to the chloro ligand. The $Fe^{III}Cl$ porphyrins were then used as asymmetric-epoxidation catalysts. For this purpose, iodosylbenzene (= phenyliodane oxide) was used as the single O-atom donor, and a substrate/oxidant/catalyst ratio of 1000/100/1 was maintained. All reactions were performed in O_2-free CH_2Cl_2 at room temperature for 30 min, before being quenched with 2% Ph_3P in CH_2Cl_2 to consume the excess iodosylbenzene. The enantiomeric excess (ee) was determined by GC, and the results for two different olefinic substrates are listed in the *Table*.

With respect to the 'picket-fence' porphyrins Fe(Cl)-**7a**, the following observations must be underlined: *1*) For both olefins, it is striking that the $\alpha\alpha\beta\beta$ isomer leads to the lowest ee value (4%). Surprisingly, the same atropisomer, but bearing binaphthyl residues in *meso*-positions, exhibited very high enantioselectivities [6b]. *2*) The $\alpha\beta\alpha\beta$ atropisomer of Fe(Cl)-**7a** gave rise to 34% ee in the case of dihydronaphthalene epoxidation, which is the highest value for such a compound reported to date. In previously published work [25] with the analogous, but strapped, porphyrin $\alpha\beta\alpha\beta$-Fe(Cl)-**6**, only 19% ee was obtained. *3*) For the $\alpha\alpha\alpha\alpha$ atropisomer Fe(X)-**13**, the enantiogenic face is sterically crowded, provided a bulky axial base is employed (X = 1-(*tert*-butyl-5-phenyl-1*H*-imidazole). Here, the best selectivity (ee 22%) among the four atropisomers was obtained with 4-chlorostyrene.

The choice of L-proline as a chirality-inducing moiety gives rise to a significant increase in ee in comparison with, *e.g.*, phenylalanine or related compounds [26]. In the

Table. *Enantiomeric Excess* (ee; in %) *for the Fe-Porphyrin-Catalyzed Epoxidation of Two Olefinic Substrates.* The ee values were determined by GC on a chiral column (see *Exper. Part*). Reaction conditions: catalyst (1 μmol), olefin (1 mmol), PhIO (0.1 mmol); in O_2-free CH_2Cl_2 (2 ml) at r.t. for 30 min.

Catalyst	4-Chlorostyrene	1,2-Dihydronaphthalene
$\alpha\beta\alpha\beta$-Fe(Cl)-**7a**	16.5	34
$\alpha\alpha\beta\beta$-Fe(Cl)-**7a**	4	9
$\alpha\alpha\alpha\beta$-Fe(Cl)-**7a**	10	14.5
$\alpha\alpha\alpha\alpha$-Fe(L)-**7a**[a])	22	10
$\alpha\beta\alpha\beta$-Fe(Cl)-**1**	1	0
$\alpha\beta\alpha\beta$-Fe(Cl)-**2**	7	4
$\alpha\beta\alpha\beta$-Fe(Cl)-**3**	3	1
$\alpha\beta\alpha\beta$-Fe(Cl)-**4**	2	2
$\alpha\beta\alpha\beta$-Fe(Cl)-**5**	18	3
$\alpha\beta\alpha\beta$-Fe(Cl)-**6**	5	19
$\alpha\alpha\beta\beta$-Fe(Cl)-**9**	26	3
$\alpha\alpha\beta\beta$-Fe(Cl)-**10**	20	8
$\alpha\alpha\beta\beta$-Fe(Cl)-**11**	31	26
$\alpha\alpha\beta\beta$-Fe(Cl)-**12**	28	14
$\alpha\alpha\alpha\alpha$-Fe(L)-**13**[a])	6	4

[a]) Axial ligand (L) = 1-(*tert*-butyl)-5-phenylimidazole (0.25 mmol).

latter, although ee values do not reach 10%, an inverted structure/activity relationship is found, depending on the number of pickets.

Interestingly, the $\alpha\alpha\alpha\beta$ conformation seems to be optimal with respect to the nature of the olefin. Indeed, $\alpha\alpha\alpha\beta$-Fe(Cl)-**7a** was the only catalyst that gave rise to similar ee values for the epoxidation of the two different olefins (*Table*). Unfortunately, this atropisomer is not readily available.

In the case of the different strapped catalysts, extremely low ee values (0–7%) were found for catalysts with aliphatic linkers. Obviously, these linkers are attached just above the Fe···O species generated by the action of iodosylbenzene on the Fe^{III} porphyrin, and are, thus, likely to be oxidized instead of the olefin. These low ee values are also to be compared with those reported by *Rose* and *Collman* [26] for 'blank picket' porphyrins, for which the ee varied inversely with the number of chiral pickets. The explanation advanced by the authors for their picket catalysts could also be valid for our strapped catalysts. The lowest ee value was obtained with $\alpha\beta\alpha\beta$-Fe(Cl)-**1**, which is sterically the most hindered among the six strapped $\alpha\beta\alpha\beta$ catalysts (*Fig. 4*, *d*). When, we compare the side views of $\alpha\beta\alpha\beta$-**1** and -**4** (*Fig. 4*, *d vs. 4*, *b*), and if the ee followed the lateral steric hindrance, the selectivity should be much lower in the case of the latter. Actually, however, the experimental ee values were almost the same. This means that either there is no relationship between this steric hindrance and enantioselectivity, or that it is not applicable in this case for other reasons, *e.g.*, oxidative degradation of the catalyst. The straps in catalysts **1**–**4** are so close to the metal center and so sensitive to oxidation that they are oxidized straight away. Thus, the ee could reflect the enantioselectivity of the resulting *mixture* of degraded compounds. This explanation is consistent with previous results [26], where it has been suggested that providing more access to the metal center could increase the selectivity.

Let us now compare the two catalysts $\alpha\beta\alpha\beta$-**5** and -**6**, based on 1,4- and 1,3-disubstituted aromatic spacers, respectively. The results of this 'precise' comparison are much more instructive, as the correlation between steric hindrance and enantioselectivity appears to be verified, but only for the styrene-based olefin. Actually, opposite trends are found when one compares the ee values obtained for the epoxidation of the styrene relative to the naphthalene. For $\alpha\beta\alpha\beta$-Fe(Cl)-**5**, which exhibits greater steric hindrance than $\alpha\beta\alpha\beta$-Fe(Cl)-**6**, the observed ee was 18% for 4-chlorostyrene, but only 3% for 1,2-dihydronaphthalene. Conversely, with catalyst **6**, the ee was 5% for 4-chlorostyrene, but 19% for 1,2-dihydronaphthalene. It appears that, with the terminal olefin (styrene), the steric hindrance is a pertinent parameter with a positive influence, whereas the effect is adverse for the disubstituted (*Z*)-olefin (dihydronaphthalene). This result, while difficult to anticipate *a priori*, can be rationalized considering two aspects. First, the olefin can not approach from the top of the catalyst [7], but only from the side, with its aromatic ring in a position parallel to the mean plane of the porphyrin (side approach) [27]. Second, it is striking that the aromatic rings of the straps in these two catalysts are in perpendicular positions, as shown in the computer models (*Fig. 4,a* and *4,c*; bottom strap). For catalyst **6**, the aromatic ring is in a position *perpendicular* to the mean plane of the porphyrin, whereas for porphyrin **5** it is *parallel* to that plane. In the case of **5**, the enantioselectivity is, thus, much better for 4-chlorostyrene, because the olefin can introduce its double bond just above the Fe···O center, and perpendicularly to the strap, with its aromatic ring avoiding the steric hindrance of the L-proline residues. In the case of 1,2-dihydronaphthalene, this approach is not possible and, therefore, its C(3)=C(4) bond remains parallel to the strap, with no real steric discrimination. Furthermore, in the case of **5**, the aromatic ring of the strap parallel to the porphyrin plane actually decreases the apparent hindrance of the L-proline residues. On the other hand, for catalyst **6** (*Fig. 4,a*; top strap), there is only a slight steric hindrance, mainly because the aromatic cycle remains in the plane of the strap. Apparently, this subtle difference is sufficient to discriminate the two different approaches of 1,2-dihydronaphthalene, but not at all in the case of 4-chlorostyrene.

The above comparison of two structurally closely related catalysts with respect to the recognition of two different types of olefins is a fine example of how subtle conformational changes can induce dramatic differences in enantioselectivity. It also demonstrates that there is a relationship between steric hindrance and enantioselectivity. Furthermore, our catalyst $\alpha\beta\alpha\beta$-Fe(Cl)-**5**, an L-proline analogue of *Rose*'s L-alanine bis-handle porphyrin [15a] and *Mansuy*'s L-phenylalanine catalyst [12b], must also be compared. In the L-phenylalanine series, an ee of 50% was reported for the epoxidation of 4-chlorostyrene, a value 2.5 times higher than obtained with **5**. This result, again, confirms that nonflexible structures, as found in L-proline, are not optimal for efficient enantioselectivity, and that L-phenylalanine, despite possible rotation of the Ph ring about the CH_2 group of the side chain, is a much better chiral inducer. This criterion has to be considered for further developments of catalysts based on L-proline.

Since 1995, we have been aware of a study concerning the four atropisomers of a chiral catalyst synthesized by the condensation of a BINAP-type[2]) aldehyde with pyrrole [28], leading to aromatic analogues of the well-known 'chiroporphyrins' [23]. It

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[2]) BINAP refers to 2,2′-(diphenylphosphino)[1,1′-binaphthalene].

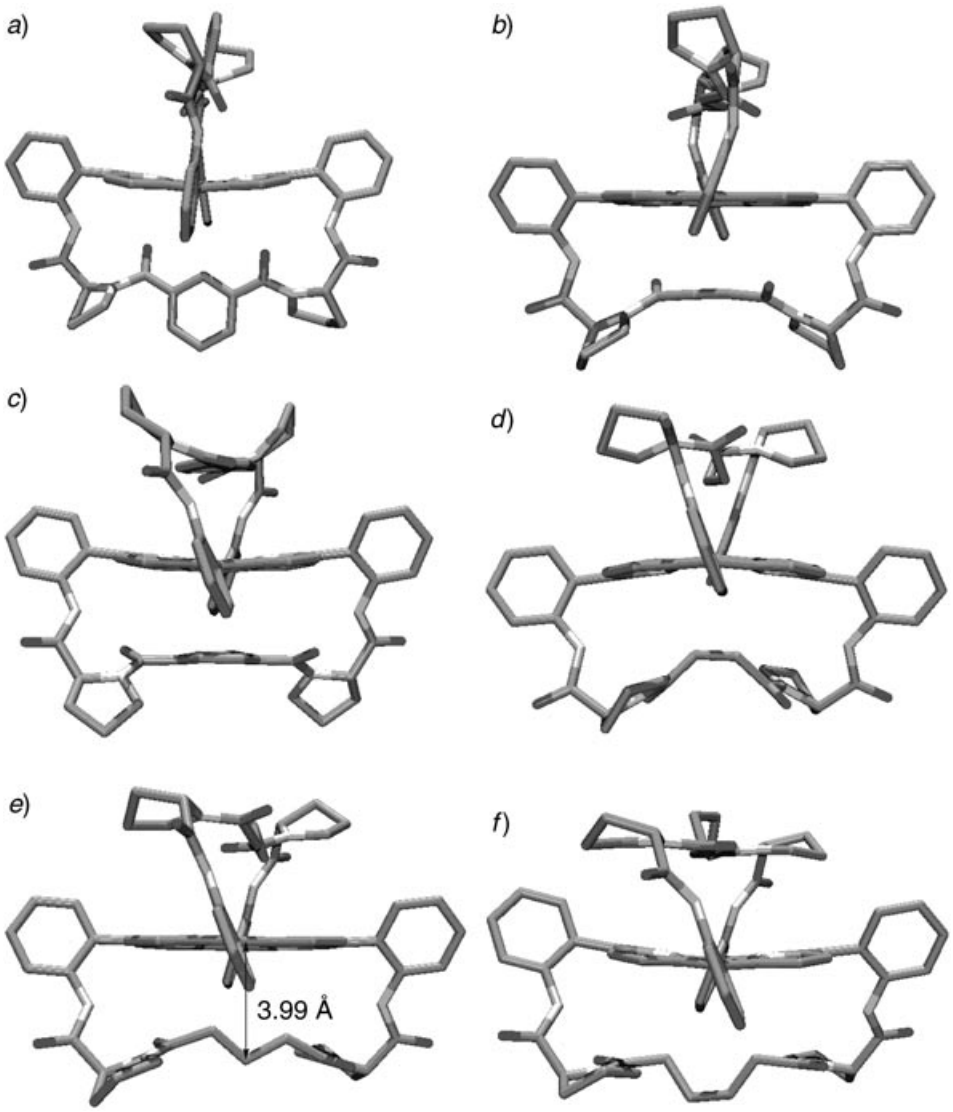

Fig. 4. *Molecular-mechanics models of the αβαβ-atropisomeric compounds* **6** (*a*), **4** (*b*), **5** (*c*), **1** (*d*), **2** (*e*), and **3** (*f*)

was shown in this report that the Fe complex of the $\alpha\alpha\beta\beta$ atropisomer was the most enantioselective catalyst among the four atropisomers for the epoxidation of styrene (59% ee *vs.* 7.5% for the $\alpha\beta\alpha\beta$ isomer). Later on, this result was published [11] and successfully generalized for a porphyrin bearing BINAP straps [6b]. This study led to our second series of strapped catalysts **9**–**12**, the respective analogues of **1**–**3** and **6** with $\alpha\alpha\beta\beta$ geometry. The results of the asymmetric epoxidation for the two olefins are interesting.

The most obvious difference is represented by the ee values themselves. Indeed, for the epoxidation of the terminal olefin, they are much higher than for the first series. Additionally, they are almost the same (*ca.* 30%) for the three catalysts **9**, **11**, and **12**. Certainly, our preliminary modelling results seem to indicate that the bending of the straps over the porphyrin center does not differ significantly when varying the length of the strap from one to three CH_2 groups. This could explain why the observed enantioselectivities are of the same order of magnitude in the case of 4-chlorostyrene as the substrate. On the other hand, for 1,2-dihydronaphthalene, the ee value obtained with $\alpha\alpha\beta\beta$-Fe(Cl)-**11** is significantly higher (26%) than with the other catalysts, but almost the same as for the terminal olefin (31%). This second observation can be rationalized by assuming that the structural feature in favor of olefin discrimination for the $\alpha\beta\alpha\beta$-family catalysts does not apply to the $\alpha\alpha\beta\beta$ family. Indeed, during a side approach, the crevasse, generated by bending of the straps over the porphyrin core, can accommodate both types of olefins, with a slightly better selectivity for the terminal one. The low ee values obtained with the Fe(Cl) complexes of **9** (3% ee) and **10** (8% ee) with respect to dihydronaphthalene can be the results of less-pronounced bending due to shorter straps compared to **11** or **12**. Hence, if the linker is long enough to allow the strap to bend over the metal center, the enantioselectivity should not be decreased by switching from the $\alpha\beta\alpha\beta$ to the $\alpha\alpha\beta\beta$ geometry. This phenomenon is observed only in the case of $\alpha\alpha\beta\beta$-Fe(Cl)-**11**, prepared with adipic acid dichloride.

Finally, in light of the results obtained with $\alpha\alpha\alpha\alpha$-Fe(Cl)-**7a** and -**13**, it is obvious that sterically congesting the center of the porphyrin decreases dramatically the enantioselectivity for both olefins. Additionally, in the case of the Fe complex **13**, this effect is emphasized by the finding that only one face of the catalyst is both enantiogenic and sterically hindered, which facilitates epoxidation at the other face.

3. Conclusions. – The combined results obtained from 'picket-fence' and strapped porphyrins containing L-proline residues show that the $\alpha\beta\alpha\beta$-strapped compounds are not very selective epoxidation catalysts, independent of the nature of the olefin, in contrast to analogous 'picket-fence' catalysts. For the $\alpha\alpha\beta\beta$ geometry, the opposite is true. This cannot be rationalized only by the possible mobility of the pickets, which should be at least equivalent in the $\alpha\beta\alpha\beta$ conformation. It must be noted that, despite the availability of several series of related chiral ligands and the confirmation of different trends, it still remains difficult to rationalize, from a general point of view, how porphyrin-based catalysts have to be designed to achieve high enantioselectivities in epoxidation reactions.

Experimental Part

General. Solvents (*ACS* for analysis) were purchased from *Carlo Erba*. THF was distilled over K metal. CH_2Cl_2 was used as received. Et_3N and *N*-methylpiperidine were distilled over CaH_2. The starting materials were purchased from *Acros* or *Aldrich*, and used without further purification. All reactions were performed under an Ar atmosphere and monitored by TLC (SiO_2; CH_2Cl_2/MeOH). Flash column chromatography (FC) was performed on silica gel (*Kieselgel 60 H*, 15 μm; *Merck*). The enantiomeric excess (ee) was determined by GC (see *Determination of Enantiomeric Excess* at the end of the *Exper. Part*). UV/VIS Spectra were recorded on a *Varian Cary-1E* spectrophotometer; λ in nm (ε in 1 mol^{-1} cm^{-1} $\times$ 10^{-3}). IR Spectra were recorded on a *Bruker IFS-66* spectrometer; in cm^{-1}. ^{1}H- (500.13 or 300.14 MHz) and ^{13}C-NMR (125.05 or 75.47 MHz) spectra

were recorded on *Bruker Avance DRX-500* or *-Avance-300* spectrometers at 300 K (unless otherwise stated); chemical shifts δ in ppm, coupling constants J in Hz. Mass spectra were recorded on an MS/MS *ZABSpec* TOF (time-of-flight) spectrometer at the University of Rennes I (C.R.M.P.O.); in m/z.

Typical Procedure (*TP1*) *for the Synthesis of Proline-Modified Porphyrins: α-5,15 :β-10,20-Tetrakis[({1-[(*tert*-butoxy)carbonyl]-*L*-prolyl}amino)phenyl]porphyrin* ($\alpha\beta\alpha\beta$-**7a**). *N*-[(*tert*-butoxy)carbonyl]-L-proline (Boc-Pro; 19.46 g, 90.4 mmol, 100 equiv.) was dissolved in anh. THF (120 ml) at $-20°$ under Ar atmosphere. *N*-methylpiperidine (16.5 ml, 135 mmol, 150 equiv.) followed by isobutylchloroformate (11.15 ml, 85.9 mmol, 95 equiv.) were added. Immediately, a white precipitate appeared. Then a cooled ($-20°$) soln. of $\alpha\beta\alpha\beta$-**8** (610 mg, 0.9 mmol) in THF (50 ml) was added to the mixture, which was stirred for 3 h at $-20°$ before being warmed to r.t. The mixture was filtered, and the precipitate was washed with Et_2O. The soln. was evaporated *in vacuo*, and the residue was subjected to FC (SiO_2; CH_2Cl_2/MeOH 98 :2): 1.15 g (85%) of $\alpha\beta\alpha\beta$-**8**. R_f (CH_2Cl_2/acetone 94 :6) 0.52. UV/VIS (CH_2Cl_2): 419 (357.2), 513 (22.3), 546 (5.2), 588 (6.3), 645 (1.9). IR (KBr): 3380 (NH), 1698 (CO). ^{1}H-NMR (500 MHz, $CDCl_3$)[3]): -2.58 (*s*, 2 NH); 0.35 (*m*, 12 H, Pro); 0.95 (*s*, 36 H, Boc); 1.28 (*s*, 8 H, Pro); 1.53 (*s*, 4 H, Pro); 3.56 (*s*, 4 H, Pro); 7.57 (*s*, 8 arom. H); 7.88 (*s*, 4 arom. H); 8.05 (*s*, 4 NHCO); 8.69 (*s*, 4 arom. H); 8.75 (*s*, 4 β-H); 8.78 (*s*, 4 β-H). ^{13}C-NMR (125 MHz, $CDCl_3$): 28.2; 30.7; 45.3; 46.4; 61.7; 79.5; 80.1; 115.3; 121.4; 122.3; 123.6; 130.4; 131.9; 132.0; 134.8; 138.7; 153.2; 154.6; 170.7; 171.3. FAB-MS: 1463.0 (M^+).

Typical Procedure (*TP2*) *for Boc Deprotection: α-5,15 :β-10,20-Tetrakis[[(*L*-prolyl)amino]phenyl]porphyrin* ($\alpha\beta\alpha\beta$-**7b**). Compound $\alpha\beta\alpha\beta$-**7a** (0.16 g, 0.11 mmol) was dissolved in CH_2Cl_2 (10 ml) under Ar gas, and F_3CCOOH (TFA; 1 ml) was added. After 30 min, the solvent was removed *in vacuo:* 0.11 g (quant.). R_f (CH_2Cl_2/MeOH 96 :4) 0.31. ^{1}H-NMR (500 MHz, $CDCl_3$, 300 K)[3]): -2.52 (*s*, 2 NH); 0.01 (*m*, 4 H–C(1″)); 0.3 (*s*, 4 NH); 0.47 (*m*, 4 H–C(4″)); 0.73 (*m*, 4 H–C(3″)); 1.12 (*m*, 4 H–C(4″)); 1.51 (*m*, 8 β-H); 3.16 (*t*, $J = 6.8$, 4 H–C(1″)); 7.54 (*td*, $J = 7.6$, 1.2, 4 H–C(5′)); 7.86 (*td*, $J = 7.5$, 1.5, 4 H–C(4′)); 7.99 (*dd*, $J = 7.6$, 1.5, 4 H–C(6′)); 8.76 (*s*, 4 β-H); 8.78 (*dd*, $J = 7.5$, 1.2, 4 H–C(3′)); 8.83 (*s*, 4 β-H); 9.47 (*s*, 4 NH). ^{13}C-NMR (125 MHz, $CDCl_3$, 300 K)[4]): 25.2 (CH_2(3″)); 30.5 (CH_2(2″)); 45.6 (CH_2(4″)); 60.5 (CH(1″)); 120.9 (C(3′)); 123.3 (C(5′)); 130.3 (C(4′)); 134.7 (C(6′)). FAB-MS: 1062.0 (M^+).

*α-5,10 :β-15,20-Tetrakis[({1-[(*tert*-butoxy)carbonyl]-*L*-prolyl}amino)phenyl]porphyrin* ($\alpha\alpha\beta\beta$-**7a**). Prepared according to *TP1:* 1.18 g (89%). R_f (CH_2Cl_2/acetone 94 :6) 0.48. UV/VIS (CH_2Cl_2): 419 (308.2), 513 (16.8), 546 (3.9), 587 (4.9), 642 (1.7). IR (KBr): 3383 (NH), 1698 (CO). ^{1}H-NMR (500 MHz, $CDCl_3$)[3]): -2.68 (*s*, 2 NH); -1.96 (*s*, 1 H, Pro); -1.63 (*m*, 1 H, Pro); -0.99 (*m*, 1 H, Pro); -0.44 (*m*, 2 H, Pro); -0.12 (*m*, 4 H, Pro); 0.63 (*m*, 4 H, Pro); 0.89 (*m*, 6 H, Pro); 1.17 (*m*, 36 H, Boc); 1.61 (*s*, 3 H, Pro); 2.66 (*m*, 2 H, Pro); 3.49 (*m*, 4 H, Pro); 7.18 (*s*, 2 H); 7.64 (*d*, $J = 7.0$, 2 H); 7.90 (*m*, 4 H); 8.00 (*d*, $J = 7.5$, 4 H); 8.10 (*s*, 2 H); 8.16 (*m*, 4 H); 8.61 (*d*, $J = 6.5$, 2 H); 8.71 (*s*, 2 H); 8.80 (*s*, 4 NHCO); 8.87 (*s*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 28.7; 28.9; 30.1; 43.9; 46.4; 59.5; 61.7; 114.5; 117.7; 120.6; 123.7; 124.6; 125.0; 127.3; 127.5; 130.2; 130.6; 131.8; 133.2; 134.0; 136.09; 139.1; 145.9; 152.9; 154.3; 170.5; 171.5. HR-LSI-MS: 1485.6994 ($[M + Na]^+$, $C_{84}H_{94}N_{12}NaO_{12}^+$; calc. 1485.7012).

*α-5,10,15 :β-20-Tetrakis[({1-[(*tert*-butoxy)carbonyl]-*L*-prolyl}amino)phenyl]porphyrin* ($\alpha\alpha\alpha\beta$-**7a**). Prepared according to *TP1:* 1.19 g (90%). R_f (CH_2Cl_2/acetone 94 :6) 0.37. UV/VIS (CH_2Cl_2): 419 (372.7), 513 (19.8), 547 (5.1), 588 (6.0), 644 (2.2). IR (KBr): 3382 (NH), 1698 (CO). ^{1}H-NMR (500 MHz, $CDCl_3$)[3]): -2.61 (*s*, 2 NH); -0.88 (*s*, 2 H, Pro); -0.75 (*s*, 2 H, Pro); 0.55 (*s*, 12 H, Pro); 1.13 (*s*, 8 H, Pro); 1.30 (*s*, 27 H, Boc); 1.45 (*s*, 9 H, Boc); 1.58 (*s*, 4 H, Pro); 3.53 (*s*, 4 H, Pro); 7.64 (*s*, 4 H); 7.89 (*s*, 4 H); 8.01 (*s*, 4 H); 8.31 (*s*, 2 H); 8.78 (*m*, 10 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 26.3; 28.0; 28.9; 30.1; 30.2; 40.9; 43.8; 45.8; 61.7; 79.8; 112.5; 114.4; 121.8; 123.7; 125.0; 130.4; 131.8; 133.6; 134.7; 138.9; 153.7; 154.5; 169.3; 170.5. HR-LSI-MS: 1485.7015 ($[M + Na]^+$, $C_{84}H_{94}N_{12}NaO_{12}^+$; calc. 1485.7012).

*α-5,10,15,20-Tetrakis[({1-[(*tert*-butoxy)carbonyl]-*L*-prolyl}amino)phenyl]porphyrin* ($\alpha\alpha\alpha\alpha$-**7a**). Prepared according to *TP1:* 1.05 g (79%). R_f (CH_2Cl_2/acetone 94 :6) 0.30. UV/VIS (CH_2Cl_2): 419 (443.1), 514 (20.1), 549 (5.6), 587 (6.3), 644 (4.4). IR (KBr): 3481 (NH), 1697 (CO). ^{1}H-NMR (500 MHz, $CDCl_3$)[3]): -2.63 (*s*, 2 NH); 0.47 (*m*, 2 H, Pro); 0.98 (*m*, 9 H, Pro); 1.49 (*m*, 9 H, Pro); 1.53 (*m*, 36 H, Boc); 3.01 (*m*, 2 H, Pro); 3.41 (*m*, 2 H, Pro); 3.80 (*m*, 4 H, Pro); 7.44 (*m*, 2 H); 7.54 (*m*, 2 H); 7.64 (*m*, 1 H); 7.84 (*m*, 1 H); 7.89 (*t*, $J = 7.5$, 2 H); 8.10 (*m*, 1 H); 8.21 (*m*, 1 H); 8.25 (*d*, $J = 7.5$, 2 H); 8.64 (*t*, $J = 7.5$, 2 H); 8.73 (*m*, 2 H); 8.77 (*d*, $J = 4.5$, 2 β-H); 8.79 (*d*, $J = 4.5$, 2 β-H); 8.83 (*m*, 2 H); 8.87 (*m*, 2 H); 9.01 (*d*, $J = 4.0$, 2 β-H); 9.05 (*d*, $J = 4.0$, 2 β-H). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.3; 21.5; 22.3; 23.2; 24.1; 28.9; 29.1; 29.7; 30.2; 30.7; 31.1; 43.9; 45.4; 46.7; 46.8; 59.4; 60.6;

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[3]) For atom numbering, see the *Scheme.*

[4]) Selected signals.

61.6; 79.5; 79.9; 81.0; 81.9; 82.4; 114.8; 115.1; 117.7; 118.1; 120.7; 120.9; 124.1; 124.7; 125.0; 127.9; 128.4; 129.7; 130.2; 130.6; 131.9; 134.7; 135.0; 135.4; 135.6; 135.8; 136.1; 136.5; 137.6; 137.8; 138.2; 153.7; 154.2; 154.5; 170.1; 170.2; 171.1; 172.2. HR-LSI-MS: 1485.7024 ($[M+Na]^+$, $C_{84}H_{94}N_{12}NaO_{12}^+$; calc. 1485.7012).

Typical Procedure (*TP3*) *for the Synthesis of Porphyrins* **1**–**6**. A freshly prepared soln. of *αβαβ*-**7a** (0.11 mmol) in THF (10 ml) and a soln. of the desired diacyl dichloride (space; 0.33 mmol, 3 equiv.) in THF (10 ml) were added *via* syringe pump over 5 h to a soln. of Et_3N (1.37 ml, 9.8 mmol, 90 equiv.) in THF (120 ml) at 0°. The mixture was stirred for 10 h. After evaporation of the solvent *in vacuo*, the crude product was purified by FC (SiO_2; CH_2Cl_2/MeOH).

Doubly Succinyl-Bridged, Metal-Free αβαβ-Porphyrin **1**. Prepared from succinyl dichloride (= butanedioyl dichloride) according to *TP3:* 94 mg (70%). R_f (CH_2Cl_2/MeOH 96:4) 0.54. UV/VIS (CH_2Cl_2): 421 (203.9), 516 (10.1), 548 (3.6), 588 (3.1), 644 (1.4). IR (KBr): 3484 (NH), 1691, 1625 (CO). ^{1}H-NMR (500 MHz, $CDCl_3$)[3]): −4.00 (*m*, 4 H, H_2C−C(O)N); −2.87 (*s*, 2 NH); −0.45 (*m*, 4 H, CH_2−C(O)N); 1.13 (*m*, 8 H, H−C(2″), H−C(4″)); 1.47 (*m*, 8 H, H−C(3″)); 1.76 (*q*, *J* = 8.8, 4 H, H−C(4″)); 2.32 (*d*, *J* = 8.8, 4 H, H−C(2″)); 3.74 (*d*, *J* = 8.0, 4 H, H−C(1″)); 7.66 (*td*, *J* = 7.5, 1.1, 4 H, H−C(5′)); 7.89 (*td*, *J* = 7.9, 1.2, 4 H, H−C(4′)); 8.20 (*s*, 4 NH); 8.23 (*dd*, *J* = 7.5, 1.2, 4 H, H−C(6′)); 8.30 (*dd*, *J* = 7.9, 1.1, 4 H, H−C(3′)); 8.64, 9.07 (2*s*, 2 × 4 *β*-H). ^{13}C-NMR (125 MHz, $CDCl_3$): 24.5 (2 H_2C−C(O)N); 24.7 (CH_2(3″)); 26.6 (CH_2(2″)); 46.1 (CH_2(4″)); 60.7 (CH(1″)); 115.4 (*meso*-C); 124.6 (C(5′)); 124.7 (C(3′)); 129.2 (*β*-C); 130.2 (C(4′)); 133.4 (C(6′)); 133.9 (C(1′)); 134.5 (*β*-C); 139.3 (C(2′)); 155.0 (*α*-C); 169.2, 170.6 (2 C=O). FAB-MS: 1226.9 ($[M+H]^+$). Anal. calc. for $C_{72}H_{66}N_{12}O_8 \cdot CH_2Cl_2$ (1312.3): C 66.81, H 5.22, N 12.81; found: C 66.38, H 5.40, N 12.16.

Doubly Glutaryl-Bridged, Metal-Free αβαβ-Porphyrin **2**. Prepared from glutaryl dichloride (= pentanedioyl dichloride) according to *TP3:* 37 mg (27%). R_f (CH_2Cl_2/MeOH 96:4) 0.60. UV/VIS (CH_2Cl_2): 421 (280.1), 516 (15.1), 549 (3.4), 588 (4.6), 643 (1.7). IR (KBr): 3477 (NH), 1691, 1631 (CO). ^{1}H-NMR (300 MHz, $CDCl_3$)[3]): −3.24 (*m*, 4 H, glutaryl); −2.67 (*s*, 2 NH); −1.60 (*m*, 4 H, glutaryl); −0.21 (*m*, 4 H, glutaryl); 1.29 (*m*, 8 H, Pro); 1.45 (*m*, 8 H, Pro); 1.95 (*m*, 4 H, Pro); 2.25 (*m*, 4 H, Pro); 3.90 (*d*, 4 H, *J* = 7.3, Pro); 7.58 (*t*, *J* = 7.3, 4 arom. H); 7.86 (*t*, *J* = 7.5, 4 arom. H); 8.09 (*m*, 4 arom. H, 4 *β*-H); 8.64 (*s*, 4 NHCO); 8.66 (*d*, *J* = 8.2, 4 arom. H); 8.95 (*s*, 4 *β*-H). ^{13}C-NMR (75 MHz, $CDCl_3$): 15.0; 24.6; 27.3; 31.4; 46.4; 60.6; 115.4; 122.4; 123.6; 129.3; 130.3; 131.9; 134.4; 139.3; 169.3; 169.6; 171.6. MALDI-TOF-MS: 1254.3 (M^+). Anal. calc. for $C_{74}H_{70}N_{12}O_8 \cdot MeOH \cdot CH_2Cl_2$ (1372.40): C 66.51, H 5.58, N 12.25; found: C 66.52, H 6.05, N 11.88.

Doubly Adipinyl-Bridged, Metal-Free αβαβ-Porphyrin **3**. Prepared from adipinyl dichloride (= hexanedioyl dichloride) according to *TP3:* 15 mg (11%). R_f (CH_2Cl_2/MeOH 96:4) 0.62. UV/VIS (CH_2Cl_2): 424 (288.5), 519 (15.2), 553 (3.9), 592 (4.7), 651 (2.2). IR (KBr): 3473 (NH), 1689, 1621 (CO). ^{1}H-NMR (300 MHz, $CDCl_3$3)[3]): −3.95 (*m*, 4 H, adipinyl); −2.52 (*m*, 4 adipinyl H, 2 NH); −1.79 (*m*, 4 H, adipinyl); −0.05 (*m*, 4 H, adipinyl); 1.42 (*m*, 4 H, Pro); 1.70 (*m*, 4 H, Pro); 1.88 (*m*, 4 H, Pro); 2.29 (*m*, 8 H, Pro); 2.58 (*m*, 4 H, Pro); 4.33 (*d*, 4 H, *J* = 7.3, Pro); 7.42 (*m*, 8 arom. H); 7.82 (*td*, *J* = 7.7, 2.1, 4 arom. H); 8.47 (*d*, *J* = 8.1, 4 arom. H); 8.67 (*s*, 4 *β*-H); 8.85 (*s*, 4 *β*-H); 9.69 (*s*, 4 NHCO). ^{13}C-NMR (75 MHz, $CDCl_3$): 19.9; 24.9; 26.4; 31.2; 46.6; 60.4; 115.8; 124.2; 124.7; 129.5; 129.9; 133.4; 134.0; 135.5; 137.7; 169.9; 172.1. HR-LSI-MS: 1283.5848 ($[M+H]^+$, $C_{76}H_{75}N_{12}O_8^+$; calc. 1283.5831).

*Doubly Fumaryl-Bridged, Metal-Free αβαβ-***4**. Prepared from fumaroyl dichloride (= (*E*)-but-2-enedioyl dichloride) according to *TP3:* 14 mg (10%). R_f (CH_2Cl_2/MeOH 96:4) 0.60. UV/VIS (CH_2Cl_2): 425 (172.3), 518 (7.2), 548 (1.4), 590 (2.7), 648 (1.6). IR (KBr): 3461 (NH), 1694, 1634 (CO). ^{1}H-NMR (500 MHz, $CDCl_3$)[3]): −3.00 (*s*, 2 NH); 1.04 (*m*, 8 H, Pro); 1.48 (*m*, 8 H, Pro); 1.83 (*d*, *J* = 6.8, 4 H, Pro); 2.33 (*dd*, *J* = 12.3, 4.5, 4 H, Pro); 2.68 (*s*, 4 H, 2 CH=CH); 3.71 (*d*, *J* = 7.3, 4 H−C(1″)); 7.64 (*td*, *J* = 7.6, 1.2, 4 H−C(5′)); 7.89 (*td*, *J* = 8.0, 1.4, 4 H−C(4′)); 8.18 (*dd*, *J* = 7.6, 1.4, 4 H−C(6′)); 8.22 (*dd*, *J* = 8.0, 1.2, 4 H−C(3′)); 8.53 (*s*, 4 *β*-H); 8.56 (*s*, 4 NH); 9.01 (*s*, 4 *β*-H). ^{13}C-NMR (125 MHz, $CDCl_3$)[1]): 24.6 (CH_2(3″)); 26.2 (CH_2(2″)); 46.4 (CH_2(4″)); 61.2 (CH(1″)); 115.0 (*meso*-C), 124.6 (C(5′)); 124.9 (C(3′)); 126.8 (2 CH=CH); 128.7 (*β*-C); 130.0 (C(4′)); 132.7 (C(6′)); 134.2 (*β*-C); 135.0, 139.7, 162.2, 168.7 (2 *C*=O). EI-MS: 1222.0 (M^+).

Doubly Terephthaloyl-Bridged, Metal-Free αβαβ-Porphyrin **5**. Prepared from terephthaloyl dichloride (= benzene-1,4-dicarbonyl dichloride) according to *TP3:* 57 mg (40%). R_f (CH_2Cl_2/MeOH 96:4) 0.70. UV/VIS (CH_2Cl_2): 419 (150.7), 514 (7.5), 547 (1.6), 582 (2.6), 637 (1.4). IR (KBr): 3482 (NH), 1691, 1650 (C=O). ^{1}H-NMR (500 MHz, $CDCl_3$)[3]): −3.15 (*s*, 2 NH); 1.40 (*m*, 4 H−C(3″)); 1.50 (*m*, 4 H−C(2″)); 1.67 (*m*, 4 H−C(2″), 4 H−C(3″)); 1.88 (*m*, 4 H−C(4″)); 2.35 (*m*, 4 H−C(4″)); 3.68 (*s*, terephthaloyl); 4.62 (*m*, 4 H−C(1″)); 7.48 (*td*, *J* = 7.3, 0.7, 4 H−C(5′)); 7.69 (*dd*, *J* = 7.3, 0.9, 4 H−C(6′)); 7.88 (*td*, *J* = 8.3, 0.9, 4 H−C(4′)); 8.53 (*s*, 4 NH); 8.73 (*s*, 4 *β*-H); 8.85 (*s*, 4 *β*-H); 8.86 (*dd*, *J* = 8.3, 0.7, 4 H−C(3′)). ^{13}C-NMR (125 MHz, $CDCl_3$)[3]): 28.2 (CH_2(3″)); 30.1 (CH_2(2″)); 49.6 (CH_2(4″)); 60.9 (CH(1″)); 115.2 (*meso*-C); 122.1 (C(3′)); 123.8 (C(5′)); 124.2 (terephthaloyl); 129.5 (*β*-C); 130.5 (C(4′)); 131.5; 134.3; 134.7 (*β*-C); 135.6 (C(6′)); 138.4, 169.6 (2 C=O). FAB-MS: 1323.9 ($[M+H]^+$).

Doubly Isophthaloyl-Bridged, Metal-Free αβαβ-Porphyrin **6**. Prepared from isophthaloyl dichloride (= benzene-1,3-dicarbonyl dichloride) according to *TP3:* 58 mg (40%). R_f (CH_2Cl_2/MeOH 96 :4) 0.62. UV/VIS (CH_2Cl_2): 421 (388), 517 (22), 548 (6), 590 (7), 653 (6). IR (KBr): 3499 (NH), 1693, 1623 (C=O). ^{1}H-NMR (500 MHz, $CDCl_3$)[3]): −3.91 (*s*, 2 NH); 1.37 (*m*, 4 H−C(3″)); 1.57 (*m*, 16 H, Pro); 2.22 (*m*, 4 H−C(4″)); 4.25 (*m*, 4 H−C(1″)); 4.52 (*s*, 2 H, isophthaloyl); 5.14 (*m*, 2 H, isophthaloyl); 5.22 (*m*, 4 H, isophthaloyl); 7.57 (*t*, *J* = 7.1, 4 H−C(5′)); 7.87 (*t*, *J* = 8.2, 4 H−C(4′)); 8.08 (*d*, *J* = 7.1, 4 H−C(6)); 8.17 (*s*, 4 NH); 8.57 (*s*, 4 *β*-H); 8.88 (*d*, *J* = 8.2, 4 H−C(3′)); 8.91 (*s*, 4 *β*-H). ^{13}C-NMR (125 MHz, $CDCl_3$)[3]): 25.4 (CH_2(3″)); 27.4 (CH_2(2″)); 49.3 (CH_2(4″)); 61.6 (CH(1″)); 114.8 (*meso*-C); 121.2 (C(3′)); 122.7 (isophthaloyl); 123.3 (C(5′)); 125.1 (isophthaloyl); 127.8 (isophthaloyl); 129.2 (*β*-C); 130.3 (C(4′)); 131.1; 131.4; 134.1 (*β*-C); 135.7 (C(6′)); 139.1; 167.1 (C=O); 169.4 (C=O). HR-LSI-MS: 1345.5027 ($[M+Na]^+$, $C_{80}H_{66}N_{12}NaO_8^+$; calc. 1345.5024). Anal. calc. for $C_{80}H_{66}N_{12}O_8 \cdot CHCl_3 \cdot CH_2Cl_2$: C 64.47, H 4.55, N 11.00; found: C 64.71, H 4.45, N 11.13.

Typical Procedure (*TP4*) *for the Synthesis of the Bridged, Metal-Free Porphyrins* **9**–**13**. These porphyrins were synthesized in analogy to *TP3* from *ααββ*- and *αααα*-**7b** for **9**–**12** and **13**, respectively, but with 2.4 instead of 3.0 equiv. of diacyl dichloride. The products were purified by FC (SiO_2; CH_2Cl_2/MeOH).

Doubly Succinyl-Bridged, Metal-Free ααββ-Porphyrin **9**. Prepared from succinyl dichloride (= butanedioyl dichloride) according to *TP4:* 57 mg (45%). R_f (CH_2Cl_2/MeOH 96 :4) 0.32. UV/VIS (CH_2Cl_2): 422 (265.2), 516 (14.4), 549 (3.5), 589 (4.9), 646 (1.2). IR (KBr): 3449 (NH), 1681 (C=O). ^{1}H-NMR (500 MHz, (D_5)pyridine, 383 K)[3]): −1.78 (*s*, 2 NH); −1.52 (*s*, 2 H); −0.19 (*s*, 2 H); 0.12 (*s*, 2 H); 0.92 (*s*, 2 H); 1.08 (*m*, 8 H); 1.28 (*m*, 2 H); 1.43 (*m*, 2 H); 1.58 (*m*, 2 H); 1.79 (*m*, 2 H); 2.12 (*m*, 2 H); 2.46 (*s*, 2 H); 2.70 (*m*, 2 H); 2.85 (*m*, 2 H); 3.91 (*m*, 2 H, Pro); 4.29 (*m*, 2 H, Pro); 7.43 (*t*, *J* = 7.5, 2 arom. H); 7.84 (*m*, 8 H); 8.04 (*d*, ^3J = 7.0, 2 arom. H); 8.34 (*s*, 2 H); 8.84 (*d*, *J* = 4.5, 2 *β*-H); 8.89 (*d*, *J* = 4.5, 2 *β*-H); 8.95 (*s*, 2 H); 9.04 (*m*, 4 H); 9.12 (*s*, 2 H); 9.63 (*s*, 2 H). ^{13}C-NMR (500 MHz, $CDCl_3$): 24.2; 25.1; 25.7; 26.2; 27.6; 28.7; 45.2; 46.9; 60.1; 61.1; 114.2; 117.0; 119.7; 121.3; 122.4; 123.7; 130.1; 130.4; 131.5; 133.5; 135.1; 136.8; 138.1; 140.0; 169.7; 170.7. FAB-MS: 1227.5 ($[M+H]^+$). Anal. calc. for $C_{72}H_{66}N_{12}O_8 \cdot H_2O \cdot CH_2Cl_2$ (1330.32): C 65.91, H 5.30, N 12.63; found: C 65.78, H 5.58, N 12.25.

Doubly Glutaryl-Bridged, Metal-Free ααββ-Porphyrin **10**. Prepared from glutaryl dichloride (= pentanedioyl dichloride) according to *TP4:* 33 mg (24%). R_f (CH_2Cl_2/MeOH 96 :4) 0.35. UV/VIS (CH_2Cl_2): 424 (301.2), 518 (15.4), 551 (4.2), 591 (5.1), 646 (1.8). IR (KBr): 3467 (NH), 1690, 1625 (C=O). ^{1}H-NMR (300 MHz, $CDCl_3$)[3]): −3.88 (*m*, 2 H, glutaryl); −3.16 (*m*, 4 H, glutaryl); −2.72 (*s*, 2 NH); −0.63 (*m*, 6 H, glutaryl); 1.55 (*m*, 10 H, Pro); 1.93 (*m*, 4 H, Pro); 2.90 (*m*, 10 H, Pro); 4.16 (*m*, 4 H, Pro); 7.44 (*t*, *J* = 7.3, 2 arom. H); 7.56 (*t*, *J* = 7.3, 2 arom. H); 7.84 (*m*, 2 arom. H, 2 *β*-H); 7.92 (*d*, *J* = 7.6, 2 arom. H); 7.98 (*d*, *J* = 7.6, 2 arom. H); 8.25 (*d*, *J* = 8.2, 2 arom. H); 8.73 (*d*, *J* = 7.3, 4 arom. H); 8.79 (*s*, 4 NHCO); 8.87 (*m*, 4 *β*-H); 9.01 (*s*, 2 *β*-H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.6; 15.9; 20.2; 24.6; 24.7; 26.2; 26.4; 27.3; 28.8; 31.7; 33.3; 33.6; 46.1; 47.0; 60.2; 60.5; 60.9; 115.3; 116.0; 121.6; 123.0; 124.6; 125.8; 129.8; 129.9; 131.9; 134.5; 135.6; 136.6; 138.2; 138.6; 169.6; 170.2; 171.4; 172.1; 173.4; 177.6. HR-LSI-MS: 1255.5516 ($[M+H]^+$, $C_{74}H_{71}N_{12}O_8^+$; calc. 1255.5518).

Doubly Adipinyl-Bridged, Metal-Free ααββ-Porphyrin **11**. Prepared from adipinyl dichloride (= hexanedioyl dichloride) according to *TP4:* 22 mg (15%). R_f (CH_2Cl_2/MeOH 96 :4) 0.38. UV/VIS (CH_2Cl_2): 423 (170.3), 517 (9.6), 551 (2.8), 591 (2.9), 647 (0.9). IR (KBr): 3477 (NH), 1694, 1636 (C=O). ^{1}H-NMR (500 MHz, $CDCl_3$, 423 K): −2.49 (*m*, 6 H, adipinyl); −2.32 (*m*, 2 NH); −1.34 (*m*, 2 H, adipinyl); −0.55 (*m*, 4 H, adipinyl); 0.89 (*m*, 4 H, adipinyl); 1.21 (*m*, 4 H, Pro); 1.29 (*m*, 6 H, Pro); 1.59 (*m*, 6 H, Pro); 2.18 (*m*, 4 H, Pro); 2.29 (*m*, 4 H, Pro); 3.79 (*m*, 2 H, Pro); 3.92 (*m*, 2 H, Pro); 7.55 (*t*, *J* = 6.8, 2 arom. H); 7.63 (*t*, *J* = 7.3, 2 arom. H); 7.77 (*s*, 4 H); 7.85 (*q*, *J* = 8.2, 4 arom. H); 8.05 (*d*, *J* = 6.4, 2 arom. H); 8.32 (*s*, 4 H); 8.61 (*s*, 4 H); 8.69 (*s*, 2 H); 8.77 (*s*, 4 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 14.6; 20.5; 24.5; 24.7; 34.3; 46.5; 60.4; 60.7; 115.6; 123.5; 124.3; 124.5; 124.9; 130.1; 130.3; 130.8; 131.8; 132.4; 133.2; 133.9; 134.8; 135.0; 135.7; 136.1; 138.6; 138.8; 149.5; 172.5; 172.7. HR-LSI-MS: 1283.5835 ($[M+H]^+$, $C_{76}H_{75}N_{12}O_8^+$; calc. 1283.5831).

Doubly Isophthaloyl-Bridged, Metal-Free ααββ-Porphyrin **12**. Prepared from isophthaloyl dichloride (= benzene-1,3-dicarbonyl dichloride) according to *TP4:* 48 mg (29%). R_f (CH_2Cl_2/MeOH 96 :4) 0.45. UV/VIS (CH_2Cl_2): 419 (219.7), 513 (12.5), 546 (3.3), 588 (3.8), 644 (1.4). IR (KBr): 3412 (NH), 1684, 1639 (C=O). ^{1}H-NMR (500 MHz, (D_6)DMSO, 373 K): −3.30 (*s*, 2 NH); 0.89 (*m*, 2 H); 1.30 (*m*, 4 H); 1.42 (*m*, 2 H); 1.62 (*m*, 2 H); 1.80 (*m*, 6 H); 1.93 (*m*, 4 H); 2.51 (*m*, 4 H); 3.90 (*m*, 2 H); 4.10 (*m*, 4 H); 5.04 (*m*, 4 H); 5.70 (*m*, 2 H); 7.58 (*m*, 4 H); 7.86 (*m*, 8 H); 8.15 (*d*, *J* = 7.1, 4 H); 8.43 (*m*, 2 H); 8.51 (*d*, *J* = 7.7, 2 H); 8.55 (*s*, 2 H); 8.62 (*s*, 2 H); 8.67 (*s*, 4 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 22.9; 23.1; 25.5; 25.6; 25.7; 26.0; 26.6; 28.9; 29.5; 30.2; 33.5; 40.3; 40.4; 40.6; 48.1; 49.5; 49.4; 50.5; 51.2; 51.4; 61.2; 62.5; 62.8; 117.7; 119.9; 120.6; 121.3; 123.3; 123.6; 123.8; 124.4; 124.8; 125.0; 126.5; 127.0; 127.2; 127.8; 128.3; 129.9; 130.2; 130.7; 135.8; 136.5; 136.7; 136.9; 138.0; 139.0; 152.8; 154.3; 157.9; 169.1; 170.4; 171.4. HR-LSI-MS: 1345.5079 ($[M+Na]^+$, $C_{80}H_{66}N_{12}NaO_8^+$; calc. 1345.5024).

Doubly Isophthaloyl-Bridged, Metal-Free αααα-Porphyrin **13**. Prepared from isophthaloyl dichloride (= benzene-1,3-dicarbonyl dichloride) according to *TP4:* 27 mg (20%). R_f (CH_2Cl_2/MeOH 96:4) 0.33. UV/VIS (CH_2Cl_2): 421 (387.8); 517 (2.2); 548 (0.6); 590 (0.7); 653 (0.6). IR (KBr): 3460 (NH), 1741 (C=O). ^{1}H-NMR (500 MHz, $CDCl_3$)[3]): −2.50 (*s*, 2 NH); 1.71 (*m*, 16 H, Pro); 2.43 (*m*, 4 H, Pro); 3.37 (*m*, 2 H, Pro); 3.89 (*m*, 2 H, Pro); 4.07 (*d*, *J* = 7.4, 2 H, Pro); 4.28 (*dd*, *J* = 8.4, 2.6, 2 H, Pro); 6.50 (*s*, 2 H, isophthaloyl); 7.09 (*dd*, *J* = 7.5, 1.5, 2 arom. H); 7.13 (*dt*, *J* = 7.4, 1.5, 2 H, isophthaloyl); 7.33 (*td*, *J* = 7.5, 1.0, 2 arom. H); 7.38 (*td*, *J* 07.5, 1.0, 2 arom. H); 7.48 (*m*, 4 H, isophthaloyl); 7.77 (*td*, *J* = 8.0, 1.5, 2 arom. H); 7.89 (*m*, 4 arom. H); 8.10 (*s*, 2 *β*-H); 8.39 (*d*, *J* = 4.5, 2 *β*-H); 8.60 (*d*, *J* 04.5, 2 *β*-H); 8.71 (*s*, 4 NHCO); 7.82 (*d*, *J* = 8.5, 2 arom. H); 9.19 (*d*, *J* = 8.5, 2 arom. H); 9.49 (*s*, 2 *β*-H). ^{13}C-NMR (125 MHz, $CDCl_3$): 22.1; 23.1; 31.6; 46.4; 47.2; 61.2; 64.8; 113.1; 117.5; 118.9; 120.4; 122.1; 124.1; 126.2; 126.3; 128.9; 129.8; 130.1; 130.4; 130.7; 131.1; 131.7; 135.2; 135.8; 136.8; 138.4; 140.0; 169.1; 169.4; 169.5; 172.2. HR-LSI-MS: 1345.5019 ($[M + Na]^+$, $C_{80}H_{66}N_{12}NaO_8^+$; calc. 1345.5024).

Doubly Succinyl-Bridged Zink(II) Porphyrin αβαβ-Zn-**1**. To a soln. of metal-free *αβαβ*-**1** (50 g) in DMF (10 ml), 2,6-lutidine (=2,6-dimethylpyridine; 0.2 ml) and an excess of $Zn(OAc)_2$ were added, and the soln. was heated for 24 h at 110°. The solvent was removed *in vacuo*, and the resulting residue was dissolved in CH_2Cl_2, and washed with H_2O. The crude product was purified by FC (SiO_2; CH_2Cl_2/MeOH 95:5): 50 mg (95%). R_f (CH_2Cl_2/MeOH 96:4) 0.34. UV/VIS (CH_2Cl_2): 418 (144.9), 560 (5.9), 596 (1.2). IR (KBr): 3460 (NH), 1689, 1613 (C=O). ^{1}H-NMR (500 MHz, $CDCl_3$)[3]): −3.63 (*m*, 1 H, succinyl); −3.48 (*m*, 1 H, succinyl); −2.69 (*td*, *J* = 14.3, 3.9, 1 H, succinyl); −1.60 (*d*, *J* = 16.0, 1 H, succinyl); −0.17 (*m*, 2 H, succinyl); 0.38 (*td*, *J* = 17.2, 2.9, 1 H, succinyl); 0.47 (*td*, *J* = 14.1,3.9, 1 H, succinyl); 0.99 (*m*, 2 H, Pro); 1.17 (*m*, 2 H, Pro); 1.34 (*m*, 1 H, Pro); 1.43 (*m*, 1 H, Pro); 1.58 (*m*, 8 H, Pro); 1.72 (*m*, 2 H, Pro); 1.81 (*m*, 2 H, Pro); 2.19 (*m*, 1 H, Pro); 2.39 (*m*, 4 H, Pro); 2.67 (*m*, 1 H, Pro); 3.13 (*d*, *J* = 8.1, 1 H−C(1″)); 3.85 (*d*, *J* = 7.9, 1 H−C(1″)); 3.91 (*d*, *J* = 8.2, 2 H−C(1″)); 7.19 (*s*, 1 H); 7.27 (*m*, 2 H); 7.63 (*t*, *J* = 7.5, 1 H); 7.68 (*t*, *J* = 7.5, 1 H); 7.72 (*t*, *J* = 7.5, 1 H); 7.77 (*t*, *J* = 7.5, 1 H); 7.86 (*m*, 4 H); 8.05 (*d*, *J* = 7.3, 1 H); 8.21 (*d*, *J* = 7.3, 1 H); 8.25 (*d*, *J* = 8.2, 1 H); 8.31 (*d*, *J* = 8.2, 1 H); 8.40 (*d*, *J* = 7.6, 1 H); 8.45 (*d*, *J* = 8.5, 1 H); 8.64 (*d*, *J* = 7.2, 1 H); 8.68 (*d*, *J* = 7.2, 1 H); 8.75 (*d*, *J* = 4.7, 1 *β*-H); 8.82 (*d*, *J* = 4.9, 2 *β*-H); 8.85 (*s*, 1 H); 8.92 (*d*, *J* = 4.5, 1 *β*-H); 8.93 (*d*, *J* = 4.7, 1 *β*-H); 8.95 (*d*, *J* = 4.6, 1 *β*-H); 8.96 (*d*, *J* = 4.3, 1 *β*-H); 9.02 (*d*, *J* = 4.8, 1 *β*-H). ^{13}C-NMR (125 MHz, $CDCl_3$)[3]): 21.4 (succinyl); 24.2, 24.7, 24.9, 25.1 (4 Pro CH_2); 26.1 (succinyl); 26.4, 26.7, 30.1 (3 Pro CH_2); 30.6 (succinyl); 30.9 (succinyl); 43.7, 46.0, 47.2 (3 Pro CH_2); 60.4, 60.5, 60.6, 61.6 (4 CH(1″)); 112.4; 115.0, 116.4, 117.2 (3 *meso*-C); 118.9, 120.1 (*β*-C); 123.3; 123.9; 124.5; 124.7; 125.8; 129.6; 129.7; 130.2; 130.4; 130.8; 131.2; 131.3 (2 *β*-C); 131.9; 132.4, 132.7, 133.5, 133.6, 134.1 (5 *β*-C); 134.4; 134.5; 134.8; 134.9; 135.1; 138.5; 138.7; 139.2; 148.6; 148.8; 149.9; 150.7; 150.8; 151.0; 151.9; 167.3; 169.5; 169.6; 169.9; 170.3; 170.5; 170.7. HR-LSI-MS: 1311.4168 ($[M + Na]^+$, $C_{72}H_{64}N_{12}NaO_8Zn^+$; calc. 1311.4159). Anal. calc. for $C_{72}H_{64}N_{12}O_8Zn \cdot CH_2Cl_2$: C 63.73, H 4.84, N 12.22; found: C 63.78, H 5.25, N 11.79.

Doubly Succinyl-Bridged Nickel(II) Porphyrin αβαβ-Ni-**1**. Prepared in analogy to *αβαβ*-Zn-**1**, but with $Ni(OAc)_2$. Yield: 30%. R_f (CH_2Cl_2/MeOH 96:4) 0.40. UV/VIS (CH_2Cl_2): 416 (165.9), 531 (11.2), 561 (1.8). IR (KBr): 3477 (NH), 1693 (CO), 1623 (C=O). ^{1}H-NMR (500 MHz, $CDCl_3$): −1.56 (*m*, 4 H, succinyl); 0.40 (*m*, 4 H, succinyl); 1.12 (*m*, 8 H, Pro); 1.21 (*m*, 8 H, Pro); 1.48 (*m*, 4 H, Pro); 2.34 (*m*, 4 H, Pro); 3.87 (*m*, 8 H, Pro); 3.90 (*d*, *J* = 7.9, 4 H, Pro); 7.62 (*d*, *J* = 7.3, 4 arom. H); 7.84 (*t*, *J* = 7.6, 4 arom. H); 8.11 (*m*, 4 arom. H, 4 NHCO); 8.27 (*d*, *J* = 8.2, 4 arom. H); 8.70 (*s*, 4 *β*-H); 8.94 (*s*, 4 *β*-H). ^{13}C-NMR (125 MHz, $CDCl_3$): 24.6; 26.4; 26.8; 46.2; 60.6; 115.7; 124.5; 124.9; 130.1; 132.3; 133.1; 133.3; 133.8; 138.3; 143.8; 144.8; 169.3; 170.8. MALDI-TOF MS: 1282.0 (M^+). Anal. calc. for $C_{72}H_{64}N_{12}NiO_8 \cdot CHCl_3 \cdot H_2O$: C 61.68, H 4.75, N 11.82; found: C 62.11, H 5.13, N 11.74.

Typical Procedure (*TP5*) *for the Fe Insertion into the 'Picket-Fence' Porphyrins of Type* **7b**. The initial metallation was performed in a glove box maintained at less than 1 ppm of molecular O_2. The selected atropisomer of **7b** (50 mg) was dissolved in THF (10 ml). Then, 2,6-lutidine (=2,6-dimethylpyridine) and an excess of $FeBr_2$ were added. The resulting soln. was heated at reflux until the reaction was complete (*ca.* 12 h), as indicated by UV/VIS analysis. Then, the metallated product was oxidized in air for 1 h, the solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2, which was washed with H_2O and brine. The crude product was purified by FC (SiO_2; CH_2Cl_2/MeOH 95:5) to afford the corresponding atropisomer of Fe(Cl)-**7b** in *ca.* 95% yield.

αβαβ-Fe(Cl)-**7b**. Prepared according to *TP5*. UV/VIS (CH_2Cl_2): 417 (66.1), 572 (3.7). IR (KBr): 3382 (NH), 1701 (C=O). HR-LSI-MS: 1116.4212 ($[M - 4\ Boc - Cl + 4\ H]^+$, $C_{64}H_{60}FeN_{12}O_4^+$; calc. 1116.4212).

ααββ-Fe(Cl)-**7b**. Prepared according to *TP5*. UV/VIS (CH_2Cl_2): 417 (102.1), 574 (6.1). IR (KBr): 3387 (NH), 1699 (C=O). FAB-MS: 1514.3 ($[M - Cl - 2\ H]^+$).

αααβ-Fe(Cl)-**7b**. Prepared according to *TP5*. UV/VIS (CH_2Cl_2): 418 (99.0), 575 (8.5). IR (KBr): 3383 (NH), 1699 (C=O). FAB-MS: 1515.6 ($[M - Cl - H]^+$).

αααα-Fe(Cl)-**7b**. Prepared according to *TP5*. UV/VIS (CH_2Cl_2):417 (67.8), 572 (6.5). IR (KBr): 3411 (NH), 1697 (C=O). FAB-MS: 1513.6 ($[M-Cl-3\,H]^+$).

Typical Procedure (*TP6*) *for the Fe Insertion into the Strapped Porphyrins* **1**–**6** *and* **9**–**13**. In a glove box containing less than 1 ppm of molecular O_2, the metal-free porphyrin (50 mg) was dissolved in toluene[5]) (20 ml). Then 2,6-lutidine (=2,6-dimethylpyridine; 0.2 ml) and an excess of $FeBr_2$ were added. The resulting soln. was heated at reflux until the reaction was complete (*ca.* 12 h), as indicated by UV/VIS analysis. Then, the crude product was oxidized in air for 1 h. The solvent was removed *in vacuo*, and the residue was dissolved in CH_2Cl_2, which was washed with brine. The product was chromatographed by FC (SiO_2; CH_2Cl_2/MeOH 95:5) to afford the corresponding Fe(Cl) complex in *ca.* 95% yield.

αβαβ-Fe(Cl)-**1**. Prepared according to *TP6*. UV/VIS (CH_2Cl_2): 426 (92.9), 583 (7.0). IR (KBr): 3459 (NH), 1692, 1650 (C=O). HR-LSI-MS: 1302.4224 ($[M-HCl+Na]^+$, $C_{72}H_{63}FeN_{12}NaO_8^+$; calc. 1302.4139).

αβαβ-Fe(Cl)-**2**. Prepared according to *TP6*. UV/VIS (CH_2Cl_2): 422 (58.2), 580 (4.4). IR (KBr): 3471 (NH), 1691, 1655 (C=O). MALDI-TOF-MS: 1308.1 ($[M-Cl]^+$). Anal. calc. for $C_{74}H_{68}ClFeN_{12}O_8\cdot 3$ MeOH (1440.83): C 64.19, H 5.60, N 11.67; found: C 64.20, H 5.31, N 10.44.

αβαβ-Fe(Cl)-**3**. Prepared according to *TP6*. UV/VIS (CH_2Cl_2): 422 (49.7), 580 (5.8). IR (KBr): 3415 (NH), 1692, 1620 (C=O). MALDI-TOF-MS: 1336.5 ($[M-Cl+H]^+$). Anal. calc. for $C_{76}H_{72}ClFeN_{12}O_8\cdot CH_2Cl_2\cdot CHCl_3\cdot$MeOH (1609.11): C 58.97, H 4.95, N 10.45; found: C 58.98, H 5.53, N 10.38.

αβαβ-Fe(Cl)-**4**. Prepared according to *TP6*. UV/VIS (CH_2Cl_2): 426 (69.9), 586 (4.8). IR (KBr): 3461 (NH), 1694, 1634 (C=O). HR-LSI-MS: 1330.4081 ($[M-HCl+CH_3OH+Na]^+$, $C_{73}H_{63}FeN_{12}NaO_9^+$; calc. 1330.4088).

αβαβ-Fe(Cl)-**5**. Prepared according to *TP6*. UV/VIS (CH_2Cl_2): 426 (48.9), 583 (5.8). IR (KBr): 473 (NH), 1692, 1637 (C=O). HR-LSI-MS: 1430.4477 ($[M-HCl+CH_3OH+Na]^+$, $C_{81}H_{67}FeN_{12}NaO_9^+$; calc. 1430.4404).

αβαβ-Fe(Cl)-**6**. Prepared according to *TP6*. UV/VIS (CH_2Cl_2): 422 (77.3), 584 (6.4). IR (KBr): 3499 (NH), 1693, 1630 (C=O). HR-LSI-MS: 1376.4318 ($[M-Cl]^+$, $C_{80}H_{64}FeN_{12}O_8^+$; calc. 1376.4319).

ααββ-Fe(Cl)-**9**. Prepared according to *TP6*. UV/VIS (CH_2Cl_2): 420 (7.6), 504 (1.1). IR (KBr): 3416 (NH), 1638 (C=O). FAB-MS: 1281.7 ($[M-Cl+H]^+$).

ααββ-Fe(Cl)-**10**. Prepared according to *TP6*. UV/VIS (CH_2Cl_2): 421 (9.6), 513 (1.4). IR (KBr): 3447 (NH), 1693, 1629 (C=O). MALDI-TOF-MS: 1307.5 ($[M-Cl]^+$).

ααββ-Fe(Cl)-**11**. Prepared according to *TP6*. UV/VIS (CH_2Cl_2): 421 (67.1), 579 (6.2). IR (KBr): 3415 (NH), 1695, 1636 (C=O). MALDI-TOF-MS: 1336.4 ($[M-Cl]^+$). Anal. calc. for $C_{76}H_{72}ClFeN_{12}O_8\cdot CH_2Cl_2\cdot CHCl_3$ (1577.07): C 59.40, H 4.79, N 10.66; found: C 59.28, H 4.95, N 10.52.

ααββ-Fe(Cl)-**12**. Prepared according to *TP6*. UV/VIS (CH_2Cl_2): 420 (36.1), 578 (2.6). IR (KBr): 3394 (NH), 1698 (C=O). FAB-MS: 1377.6 ($[M-Cl+H]^+$).

αααα-Fe(Cl)-**13**. Prepared according to *TP6*. UV/VIS (CH_2Cl_2): 422 (4.4), 509 (0.5). IR (KBr): 3417 (NH), 1698, 1617 (C=O). FAB-MS: 1378.6 ($[M-Cl+H]^+$).

General Procedure for Asymmetric Olefin Epoxidation. The catalyst (1 μmol) and the olefin[6]) (1 mmol) were dissolved in degassed CH_2Cl_2 (2 ml) in a *Schlenk* tube under N_2 atmosphere[7]). Under stirring, PhIO (0.1 mmol) was added in one portion, and the mixture was stirred at r.t. for 30 min. Then, the reaction was quenched with a 2% CH_2Cl_2 soln. of Ph_3P, concentrated *in vacuo*, and analyzed by gas chromatography (GC; see below).

Determination of Enantiomeric Excess. The crude residue from the epoxidation reaction (see above) was taken up in pentane, the mixture was filtered, and dodecane (10 μl) was added (GC standard). The enantiomeric excess (ee) was determined by gas chromatography (GC) on a *Chirasil-Dex CB* chiral-capillary column (25 m × 0.25 mm; *Chrompack*). The following analytical data were obtained: t_R 22.5 and 24.3 min, resp., for the two enantiomers of 4-chlorostyrene oxide (oven temp. 120°); and t_R 18.9 and 20.4 min for the two enantiomers of 1,2-dihydronaphtalene oxide (oven temp. 130°). For ee values obtained with the various porphyrin catalysts, see the *Table*.

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5) THF was used as solvent for the metallation of **5** (reduced reflux temperature).

6) 4-Chlorostyrene (=1-chloro-4-ethenylbenzene) or 1,2-dihydronaphthalene (see the *Table*).

7) In the case of the single-face-functionalized porphyrins *αααα*-**7a** and *αααα*-Fe(Cl)-**13**, 1-(*tert*-butyl)-5-phenyl-1*H*-imidazole (0.25 mmol) was additionally added as the axial base.

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