A Unique Binaphthyl Strapped Iron–Porphyrin Catalyst for the Enantioselective Epoxidation of Terminal Olefins

Eric Rose,*[a] Qi-Zhi Ren,[b] and Bruno Andrioletti[a]

Abstract: A new chiral binaphthyl-strapped iron–porphyrin **4b** that exhibits unprecedented catalytic activity toward the enantioselective epoxidation of terminal olefins was synthesized. Typical enantiomeric excesses (*ee*) of 90% were measured with a maximum of 97% for the epoxidation of styrene, whereas the turnover numbers (TON) averaged 16000.

Keywords: asymmetric synthesis · chirality · epoxidation · iron · porphyrinoids

Introduction

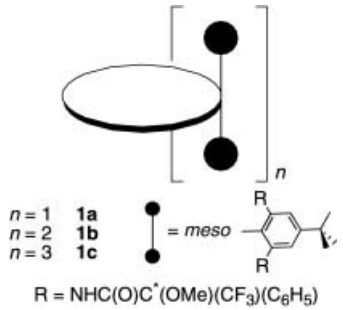
Asymmetric synthesis is a promising field in modern synthetic organic chemistry. During the past decades, dramatic improvements have been reported in catalytic asymmetric hydrogenation,[1] epoxidation of alkenes[2] and allylic alcohols,[3] and dihydroxylation[4] and cyclopropanation of prochiral olefins.[5] Nevertheless, the development of new tools is still crucial, particularly in the case of the enantioselective catalytic epoxidation of terminal olefins where significant improvement is still necessary from both a practical and mechanistic point of view.[6] Indeed, with regard to green and sustainable chemistry, chiral epoxides are becoming increasingly important as synthetic intermediates and in the development of new drugs. Metallosalens represent an important class of catalysts that are capable of efficiently epoxidizing terminal olefins.[2f,g] However, they suffer from two major drawbacks: first, although metallosalens are highly efficient for the epoxidation of *cis*-di-, tri-, and some tetrasubstituted olefins, they require temperatures as low as −78°C for the epoxidation of monosubstituted olefins such as styrene which are difficult to epoxidize.[2h] Second, the epoxidations generally proceed with low turnover numbers (TON).

On the other hand, metalloporphyrins have proven to be robust catalysts for oxidative processes but the enantioselectivities observed for the asymmetric epoxidation of terminal olefins have often remained below expectations.[7]

Results and Discussion

In 1998, we reported the synthesis of a new family of chiral porphyrin-based catalysts **1** bearing Mosher pickets (Scheme 1).[8] During the course of this study, we found that fine-tuning of the steric bulk of the strap dramatically influences the *ee* values.

Thus, we demonstrated that the most crowded systems **1b** and **1c** induced the lowest enantioselectivities, whereas the less bulky analogue **1a** afforded the best *ee* value. Thus, it appeared that providing more access to the catalytic center increased the selectivity of the epoxidation reaction. These results and those obtained with the binap-strapped porphyrin **3b** ($n=0$, Scheme 2)[9] prompted us to prepare the so-called "homologated" catalyst **4b** ($n=1$) whose strap differs



Scheme 1. Structures of the Mosher porphyrins".

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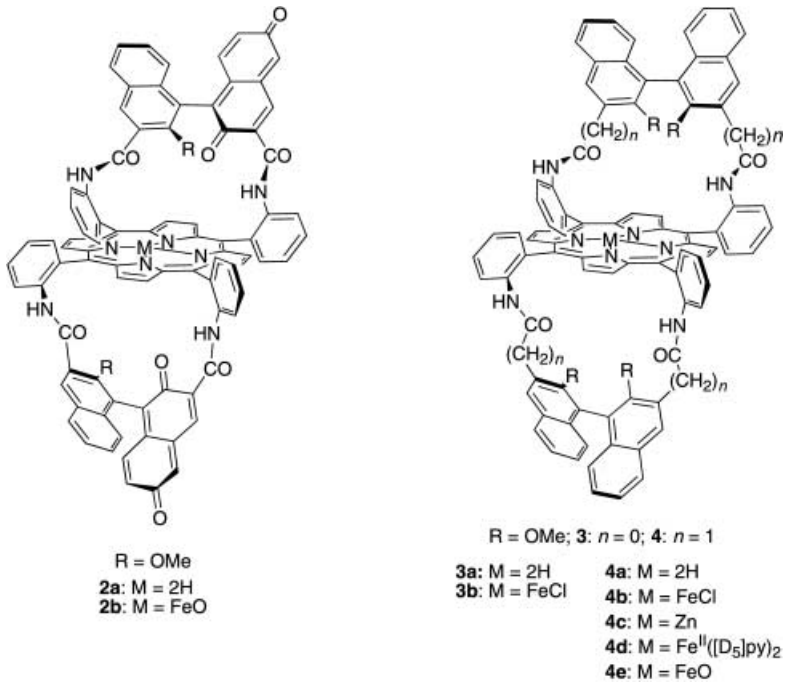
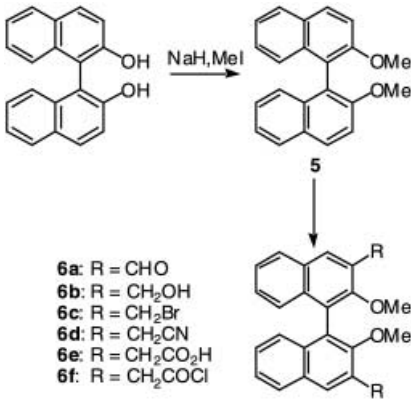


Scheme 2. Structures of porphyrins **2**–**4**.

from that of **3b** ($n=0$) by only two CH_2 groups. Two guidelines directed our choice: First, we decided to retain the C_2-symmetrical "binap-strapped" porphyrins that already proved to be efficient for the epoxidation of terminal olefins.[7n,9] Indeed, this approach allowed us to isolate styrene oxides with good enantiomeric excesses even after high TON. As has been suggested by others, it appears that the presence of two rigid "binap-walls" efficiently directs the approach of the olefin toward the metal center, induces a good transfer of asymmetry and inhibits the oxidative degradation of the catalyst as well as the formation of an unreactive μ-oxo dimer.[7b,d] In addition, C_2-symmetrical porphyrins are easily prepared from the readily available $\alpha^2\beta^2$-tetrakis-(*o*-aminophenyl)porphyrin. Second, considering the results of the Mosher series,[8] we decided to "homologate" the binap handle ($n=1$) which should move the proximal methoxy groups away from the metal center. The displacement of the methoxy groups, while offering an easier access of the olefin to the metal center, should prevent the observed oxidation of the methoxy–naphthyl moiety to the corresponding naphthoquinone **2b** (Scheme 2).

Preparation of the catalyst **4b** was achieved by condensing the chiral diacid chloride **6f** with αααβ-tetrakis(*o*-aminophenyl)porphyrin (αααβ-*o*-TAPP)[11] in the presence of a stoichiometric amount of *N*,*N*-diethylaniline. The diacid chloride **6f** was readily prepared from *R*-(+)-1,1′-binaphthol in an overall yield of 43% (Scheme 3). In the first step, the commercially available *R*-(+)-1,1′-binaphthol was quantitatively methylated by using NaH/MeI. The resulting diether **5** was then formylated with *n*BuLi/DMF in 71% yield. Subsequently, dialdehyde **6a** was quantitatively reduced to the corresponding diol **6b**, converted to the dibromide **6c** with PBr_3 according to Naruta's procedure,[7c] and then treated with NaCN. The resulting dicyano derivative **6d** was isolated in 84% yield and conveniently converted into the diacid **6e** by using aqueous sodium hydroxide at 100°C in 90% yield. It is worth noting that a more straightforward homologation sequence such as the Arndt–Eistert[10] method was not reproducible in our hands. A high dilution reaction involving a stoichiometric amount of freshly prepared diacid chloride **6f** and αααβ-*o*-TAPP[11] in THF in the presence of *N*,*N*-diethylaniline afforded the free base binap-strapped porphyrin **4a** in 31% reproducible yield. Finally, the desired catalyst **4b** was quantitatively prepared by refluxing the free base porphyrin **4a** with an excess of $FeBr_2$ in acetic acid before oxidation in air and washing with dilute hydrochloric acid. It is worth noting that metalation of **4a** was complete under these conditions, whereas no complexation of the free base porphyrin **3a** could be effected under similar conditions, thus confirming the idea that **4a** offered an easier access to the active site than **3a**.



Scheme 3. Synthesis of compounds **5**, **6a**–**6f**.

Preliminary catalytic measurements revealed that complex **4b** displayed remarkable activity toward the enantioselective epoxidation of terminal olefins (Table 1).

In a typical reaction, one equivalent of catalyst **4b** was allowed to react with 100 equivalents of iodosylbenzene and 1000 equivalents of olefin in CH_2Cl_2 at −5°C. Under these conditions, styrene was readily converted to styrene oxide in 97% *ee* (entry 1). Similarly, electron-deficient olefins such as pentafluoro- (entry 2), fluoro- (entry 3), chloro- (entries 4 and 6) and nitrostyrenes (entry 5) were efficiently epoxidized in about 90% *ee*. We also tested the efficiency of the epoxidation using smaller amounts of the catalyst (Table 1). Thus, we showed that a ratio catalyst/oxidant/olefin: 1/1000/

Table 1. Asymmetric epoxidation of styrene derivatives catalyzed by **4b**.

Entry[a]	Substrate	*ee* [%][b]	*ee* [%][c]	Best *ee* previously reported[d]	Yield [%][e]	Config.[f]
1	styrene	97	93	83[g]	96	*R*
2	pentafluorostyrene	96	94	88[g]	80	*R*
3	3-fluorostyrene	93	92	nd	87	*R*
4	3-chlorostyrene	88	87	90[g]	90	*R*
5	3-nitrostyrene	90	87	74[h]	84	*R*
6	4-chlorostyrene	84	81	70[i]	75	R

[a] The reactions were carried out in CH_2Cl_2 at −5 °C. Enantiomeric excesses were determined by GC with use of a Lipodex-E chiral capillary column (50 m × 0.25 mm). [b] Reaction conditions: catalyst **4b**/PhIO/olefin = 1:100:1000. [c] Reaction conditions: catalyst **4b**/PhIO/olefin = 1:1000:10000. [d] These results do not take into account the absolute configuration of the chiral carbon atom. [e] Yields are based on consumed PhIO. Results have been confirmed by integration of the peak of the epoxide versus the peak of an internal reference (1,2,4-trichlorobenzene). [f] Assigned by comparing the GC retention time with standard samples. [g] Best *ee* values were obtained by using **2b**.[9] Noticeably, *ee* values obtained with D_2-, D_4-, C_4-symmetrical porphyrins varied in a 20–69% range, depending on the number, the rigidity, and the nature of the substituents. [h] Interestingly, the best *ee* values were obtained by using the nonrigid tetralin derivative.[7f] [i] In this case the best *ee* values were obtained using the threitol porphyrins first prepared by Collman and coworkers and developed by Gross and co-workers later on.[7g,j]

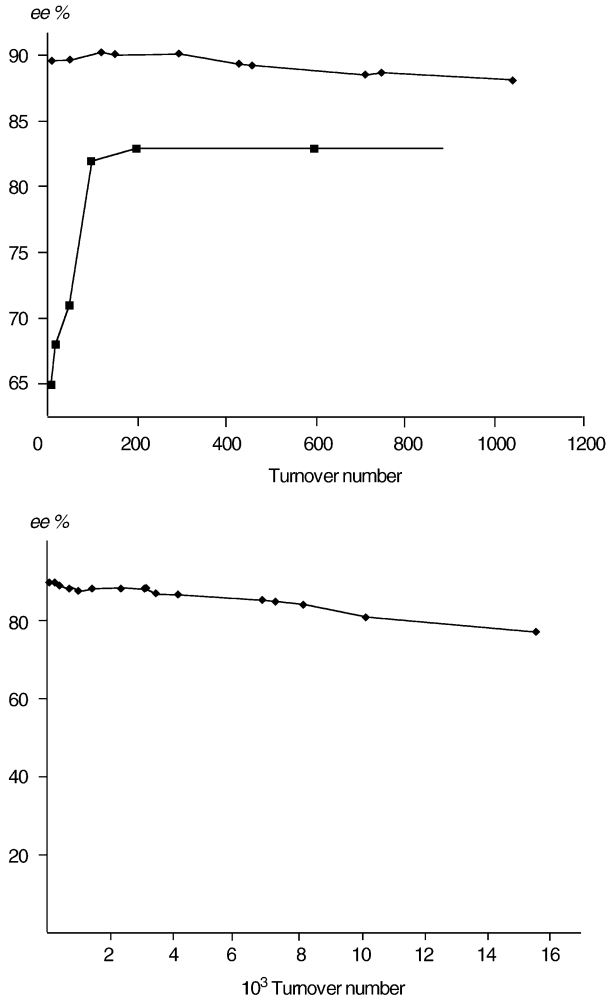


Figure 1. Change in *ee* with increasing turnover: comparison between **3b** (■)and **4b** (◆).

10000 afforded similar enantiomeric excesses for the olefins in this study. It is also worth noting that the chemical yields based on the consumed PhIO varied from about 85% in most cases but reached 96% in the case of styrene (Table 1, entry 1). In addition, very good enantioselectivities were maintained when the reactions were carried out at room temperature. Thus, epoxidation of styrene at room temperature afforded the desired epoxide in 94% *ee*! Furthermore, catalyst **4b** proved to be extremely robust. It could be reused for a second run without significant loss of enantioselectivity and the oxidation could be carried out in neat styrene with equally good enantiomeric excesses. Figure 1 shows the relationship between the enantiomeric excess and the TON. The graphs reveal that the enantiomeric excesses decrease very slowly: after 15 turnovers, the *ee* value is 90 %; from 15 to 4200 TON, the *ee* are still close to 90% and remain close to 80% even after 16000 TON. Another interesting feature concerns the turnover frequency (TOF) of the catalyst that reaches 2000 turnovers per hour at room temperature. Even after a high TON, no bleaching was observed, which underlines the robustness of the catalyst. Its stability was also corroborated by spectroscopic analyses of the catalyst recovered after epoxidation. In particular, ^{1}H and ^{13}C NMR spectra of the hexacoordinate iron complex **4d** obtained after reduction of the catalyst using $Na_2S_2O_4$ in the presence of deuterated pyridine revealed diamagnetic Fe^{II} ($S=0$) porphyrin spectra with no evidence of strap degradation. The presence of the methoxy signals at $\delta = 2.21$(6H) and 1.97(6H) ppm confirmed that no quinone formation had occurred (Table 2).

Quite similar chemical shifts were observed for the Zn complex **4c** ($\delta = 2.64$ and 1.40 ppm, respectively, in deuterated pyridine). On the contrary, the ^{1}H NMR spectrum of the free base porphyrin **4a** in [D_5]pyridine revealed methoxy signals at $\delta = 2.37$ and 0.47 ppm, respectively. The significant chemical shift difference of the proximal methoxy groups can be explained by considering the repulsion between the metal-coordinated [D_5]pyridine and the strap. Thus, the steric hindrance ascribable to the axial ligand displaces the handle from the porphyrin center and moves it away from the corresponding strongly shielding anisotropic cone. Simi-

Table 2. ^{1}H and ^{13}C chemical shifts of selected signals.

Porphyrins	**3a**[a]	**4a**[a]	**4a**[b]	**4c**[a]	**4c**[b]	**4d**[b]	**4d**[b]Recovered
δ_H distal OMe (6H)	2.96	1.98	2.37	2.04	2.64	2.21	2.21
δ_H proximal OMe(6H)	−0.65	−0.51	0.47	1.97	1.40	1.97	1.97
δ_C distal OMe	nd	59.4	nd	61.0	nd	61.4	61.5
δ_C proximal OMe	nd	57.5	nd	60.0	nd	60.4	60.4

[a] NMR spectra were recorded at 25 °C in $CDCl_3$ or in deuterated pyridine. [b] Chemical shifts were calibrated by using residual solvent peaks as reference. nd = not determined.

larly, ^{13}C NMR data of the recovered catalyst **4d** clearly indicated the presence of the two methoxy groups at $\delta = 60.4$ and 61.5 ppm. Complementary UV/Vis spectroscopy and MALDI-TOF analyses confirmed again the integrity of the structure: *catalyst **4b** had not been degraded during the oxidative process.* This observation is in total contrast with other catalysts such as [Mn(salen)][2] or other porphyrinic systems including binap porphyrins which rapidly degrade.[12,13]

In addition to the remarkable stability and efficiency of **4b**, the analytical investigations revealed another unique feature of the catalyst. Indeed, while catalyst **3b**, or more precisely its derivative **2b** mainly afforded *S* epoxides, catalyst **4b** generated the opposite *R* enantiomers (Table 1). We tried to rationalize this surprising observation on the basis of molecular modeling. Preliminary molecular modeling of the free base porphyrins **2a** and **4a** revealed several interesting features that might explain the reverse enantioselectivity observed with the homologated catalyst **4b** (Figure 2).

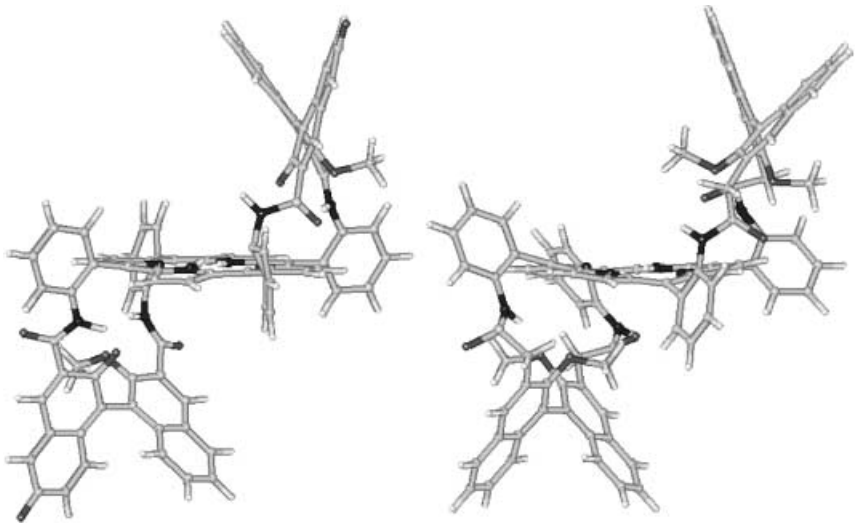


Figure 2. Lowest energy conformations for porphyrins **2a** (left) and **4a** (right).

The minimum-energy conformations of the free base porphyrins **2a** and **4a** were calculated by using a molecular mechanics conformation search method (Tripos force field in SYBYL computation).[14] In both cases, molecular modeling revealed slightly ruffled porphyrin planes.

It is noteworthy that the porphyrin plane deformation is more important when $n = 1$ (porphyrin **4a**) than when $n = 0$ (porphyrin **2a**). This is in agreement with what has been observed in the case of bridled porphyrins.[15] However, the major differences between the two structures concern the geometries of the binaphthyl cavities. In particular, it appears that the dihedral angles of the binaphthyl handles are different which may be explained by the absence of the proximal methoxy group for **2a** and a higher flexibility for **4a**. Thus, the dihedral angle between the two naphthyl moieties is 5° smaller in the case of **2a** than in the case of **4a** (60° versus 65°). This is also confirmed using classical CPK models of **2b** and **4e** that show that in both cases the approach of the olefin *operates on opposite faces* (Figure 3). In **2b**, the quinone structure may generate enough room to accommodate the approach of the substrate via the *Re* face, near the oxidized naphthalene ring. Such an approach induces the formation of the *S* epoxide. In the case of **4e**, the methoxy group of the homologated binaphthyl structure more likely prevents the *Re* face approach of the olefin on the proximal methoxy-naphthalene. Thus, it favors the *Si* face approach affording the *R* enantiomer.

In conclusion, we have demonstrated that the C_2-symmetrical binaphthyl porphyrin **4b** constitutes an exceptional catalyst for the asymmetric epoxidation of styrene derivatives. Indeed, unprecedented enantiomeric excesses and very high TON were simultaneously obtained for the epoxidation of terminal olefins. A key role of the proximal methoxy group was proposed for explaining the reversed enantioselectivities observed with iron derivatives **3b** and **4b**. We suggested that the proximal methoxy group forces the approach of the *Si* face of the substrate for epoxidation by the oxoferryl active site. On the other hand, we exclude π–π stacking interactions as we have already demonstrated that **2b** is a remarkable catalyst for the epoxidation of non-aromatic *tert*-butyl- and trimethylsilyl ethylenes (82 and 90 % *ee* were respectively measured for the latter olefins). Thus, we were able to synthesize a novel oxidizing catalyst which can discriminate prochiral faces of simple olefins throughout weak nonbonding interactions. It appeared that the binaphthyl handle acts as a butterfly wing that could preferentially attract the *Re* or the *Si* face of the substrate and move it near the active site for the oxidation process. Work is in progress to investigate further the potential of catalyst **4b**. In particular, we are currently investigating the use of more environmentally friendly oxidants such as H_2O_2 or NaOCl. Applications of catalyst **4b** in reactions as different as chiral hydroxylation, and asymmetric cyclopropanation are also underway.

Experimental Section

General: Information: All reagents were used as supplied commercially unless otherwise noted. THF and diethyl ether were distilled from sodium under N_2 before use. **5**, **6a**–**6c**, αααββ-*o*-TAPP were prepared according to literature method.[7c,11] ^1H and ^{13}C NMR spectra were performed on a Bruker AC200, ARX400 or DRX500 spectrometers and referenced to the residual solvent signals. Infrared spectra were recorded on a Nicolet-Avatar 320 FT-IR. UV/Vis spectra were recorded on UVIKON 923 Spectrometer. MS/HRMS were obtained from the University of Lille on an Applied Biosystems Voyager DE-STR MALDI-TOF MS. Optical rotation data were measured on a Perkin Elmer Model 343 Polarimeter

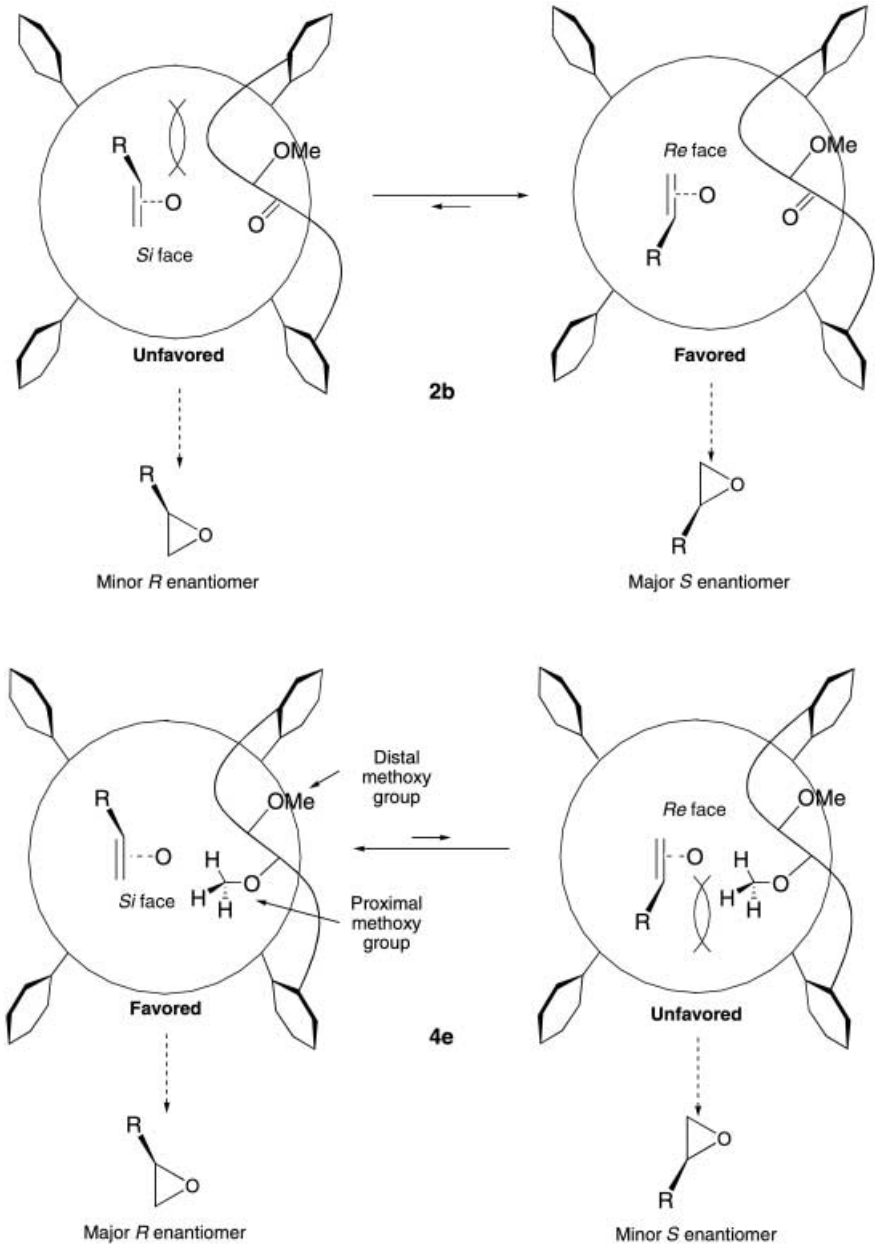


Figure 3. Proposed mechanism for the enantioselective epoxidation with catalysts **2b** and **4e**.

at 589 nm. GC analyses were performed on HRGC MEGA series 9000 chromatographs with flame ionization detector and using a QC3/PBX5 capillary column (25 m × 0.5 mm) and chiral capillary column Lipodex-E (50 m × 0.25 mm, id.; 0.125 μm thickness) respectively. Nitrogen was used as the carrier gas.

6d: A solution of **6c** (4.27 g, 8.53 mmol) and sodium cyanide (1.90 g, 38.8 mmol) in DMSO (20 mL) was stirred at 50 °C for 36 h. After the reaction was completed, the reaction mixture was poured into a water/dichloromethane (350 mL/350 mL) mixture and extracted. The organic phases were collected, dried over Na_2SO_4, filtered, and evaporated to dryness. The crude residue was purified by column chromatography on silica gel (SiO_2 15–40 μm, eluent CH_2Cl_2) to yield the pure dicyano derivative **6d** (2.83 g; 84 %).

^{1}H NMR (200.13 MHz, $CDCl_3$, 298 K): $\delta = 3.24$ (s, 6H; OCH_3), 4.00 (s, 4 H; CH_2Ph), 7.15 (d, $^3J(H,H) = 8.4$ Hz, 2H; ArH), 7.30 (t, $^3J(H,H) = 8.4$ Hz, 2H; ArH), 7.45 (t, $^3J(H,H) = 8.0$ Hz, 2H; ArH), 7.91 (d, $^3J(H,H) = 8.0$ Hz, 2H; ArH), 8.09 ppm (s, 2H; ArH); ^{13}C NMR (50 MHz, $CDCl_3$, 298 K): 27.5, 68.1, 125.2, 131.6, 132.8, 133.3, 135.0, 135.8, 136.9, 137.5, 138.1, 141.8, 153.0 ppm; EI/MS: *m/z*: 392.15 $[M + H]^+$; elemental analysis (%): calcd: C 79.57, H 5.14, N 7.14; found: C 79.46, H 5.20, N 7.13; $[\alpha]_D^{20} = -78.7$ ($c = 0.50$, THF).

6e: Compound **6d** (2.6 g, 6.63 mmol) was taken up in aqueous NaOH (8 M; 30 mL) and stirred at 100 °C for 24 h. The pale yellow precipitate that had formed during the reaction was filtered off under vacuum and taken up in ethyl acetate and water. The aqueous solution was acidified until pH 2, and extracted three times with AcOEt. The organic layers were combined, dried over $MgSO_4$, filtered, and evaporated to dryness to afford **6e** as a pale yellow powder (2.56 g; 90 %). ^{1}H NMR (200.13 MHz, $CDCl_3$, 298 K): $\delta = 3.23$ (s, 6H; OCH_3), 3.99 (d, $^2J(H,H) = 16.7$ Hz, 2H; CH_2Ph), 4.01 (d, $^2J(H,H) = 16.7$ Hz, 2H; CH_2Ph), 7.19 (d, $^3J(H,H) = 8.1$ Hz, 2H; ArH), 7.30 (t, $^3J(H,H) = 8.4$ Hz, 2H; ArH), 7.45 (t, $^3J(H,H) = 8.4$ Hz, 2H; ArH), 7.87 (d, $^3J(H,H) = 8.1$ Hz, 2H; ArH), 7.91 (s, 2H; ArH), 8.75 ppm (2H; large s, CO_2H); ^{13}C NMR (50 MHz, $CDCl_3$, 298 K): 36.9, 61.0, 125.8, 126.4, 127.3, 128.1, 130.7, 131.7, 132.9, 134.0, 154.1, 179.8 ppm; EI/MS: *m/z*: 430.08; elemental analysis (%): calcd: C 69.66, H 5.17; found: C 69.50, H 5.09; $[\alpha]_D^{20} = -24.3$ ($c = 0.50$, THF)

6f: Compound **6f** was freshly prepared by refluxing **6e** (213 mg, 0.495 mmol) in oxalyl chloride (5 mL) under stirring at 50 °C for 8 h under N_2. Excess of oxalyl chloride was then removed by using a water aspirator affording the crude diacid chloride as a pale yellow foam. The latter was used in the following reaction without any further purification.

4a: A 500-L two-neck round-bottom flask equipped with a stir bar, a rubber septum, and a nitrogen inlet was charged with freshly distilled THF (150 mL). *N*,*N*-Diethylaniline (970 mg, 6.5 mmol) was added to the THF. Under N_2, in a separate flask a solution of αααββ-*o*-TAPP (508 mg, 0.76 mmol) in dry THF (20 mL) was prepared and transferred into two 10 mL syringes. Likewise, a solution of **6f** (705 mg, 1.51 mmol) in dry THF (10 mL) was transferred in a dry 10 mL syringe. A syringe pump was equipped with the three syringes. The porphyrin and the diacid chloride were simultaneously added over 3 h at 5 °C and the reaction mixture was allowed to stir at room temperature for an additional 12 h. THF was removed under reduced pressure and the residue was directly poured onto a column and the mixture was purified by column chromatography (SiO_2, 15–40 μm, eluent CH_2Cl_2). The expected bis-strapped porphyrin **4a** was eluted with a mixture CH_2Cl_2/MeOH: 99/1 as a purple band. Evaporation of the fractions containing the expected porphyrin afforded **4a** as purple powder (350 mg; 31 %). ^{1}H NMR (400.13 MHz, $CDCl_3$, 298 K): $\delta = -2.91$ (s, 2H; NH_{pyr}), −0.51 (s, 6H; OMe), 1.98 (s, 6H; OMe), 2.58 (d, $^2J(H,H) = 14.0$ Hz, 2H; CH_2Ph), 3.15 (d, $^2J(H,H) = 14.0$ Hz, 2H; CH_2Ph), 3.33 (d, $^2J(H,H) = 16.8$ Hz, 2H; CH_2Ph), 3.68 (d, $^2J(H,H) = 16.8$ Hz, 2H; CH_2Ph), 5.80 (d, $^3J(H,H) = 8.3$ Hz, 2H; ArH), 6.20 (d, $^3J(H,H) = 8.3$ Hz, 2H; ArH), 6.33 (t, $^3J(H,H) = 7.4$ Hz, 2H; ArH), 6.77 (t, $^3J(H,H) = 8.3$ Hz, 2H; ArH), 6.84 (t,

^3J(H,H) = 7.4 Hz, 2H; ArH), 7.02 (d, ^3J(H,H) = 8.4 Hz, 2H; ArH), 7.13 (t, ^3J(H,H) = 7.6 Hz, 2H; ArH), 7.21 (d, ^3J(H,H) = 8.0 Hz, 2H; ArH), 7.40 (s, 2H; ArH), 7.47 (t, ^3J(H,H) = 7.4 Hz, 2H; ArH), 7.57 (t, ^3J(H,H) = 7.4 Hz, 2H; ArH), 7.62 (d, ^3J(H,H) = 8.2 Hz, 2H; ArH), 7.80 (large s, 4H; NH), 7.82 (t, ^3J(H,H) = 8.2 Hz, 2H; ArH), 7.89 (t, ^3J(H,H) = 8.0 Hz, 2H; ArH), 8.15 (d, ^3J(H,H) = 6.9 Hz, 2H; ArH), 8.54 (d, ^3J(H,H) = 8.4 Hz, 2H; ArH), 8.59 (s, 2H; H_β), 8.65 (d, ^3J(H,H) = 5.1 Hz, 2H; H_β), 8.70 (s, 2H; H_β), 8.73 (d, ^3J(H,H) = 5.1 Hz, 2H; H_β), 8.85 ppm (d, ^3J(H,H) = 7.7 Hz, 2H; ArH); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): 38.7, 39.3, 57.5, 59.4, 112.6, 113.9, 120.4, 120.9, 121.9, 122.2, 122.6, 123.1, 123.4, 123.7, 124.1, 124.2, 125.3, 125.5, 126.5, 128.2, 128.9, 129.2, 129.3, 129.5, 131.3, 131.7, 133.2, 134.0, 136.8, 137.9, 151.5, 152.8, 168.3 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 424 (320000), 517 (18700), 552 (5820), 592 (5780), 649 nm (3420). MALDI-TOF HRMS: *m/z* calcd for $[C_{96}H_{70}N_8O_8 + H]^+$: 1463.5397, found: 1463.5343; elemental analysis (%): calcd (M + CH_2Cl_2): C 75.21, H 4.69, N 7.23; found: C 74.98, H 5.06, N 6.96.

4b: In a typical experiment, **4a** (10 mg, 7 μmol) and $FeBr_2$ (50 mg, 0.23 mmol) were added to glacial acetic acid (5 mL) and brought to reflux overnight under argon. After this reaction time, UV/Vis monitoring confirmed that the reaction had reached completion. Excess of acetic acid was then removed under vacuum, and the residue taken in CH_2Cl_2. The organic phases were washed with dilute HCl (1 M), dried over Na_2SO_4, filtered through a pad of NaCl, and evaporated to dryness to afford the chloro–iron complex **4b** as a brown powder in quantitative yield. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 418 (25730), 481 (3724), 575 (1996), 744 nm (602). MALDI-TOF HRMS: *m/z* calcd. for $[C_{96}H_{68}N_8O_8Fe]^+$: 1517.3707, found: 1517.4563.**4c**: A 50-mL round-bottom flask equipped with a stir bar was charged with **4a** (20 mg, 14 μmol), CH_2Cl_2 (5 mL), and AcONa (5 mg, 0.06 mmol) and was brought to reflux. When the reaction reached a gentle reflux, 1 mL of a saturated methanolic solution of $Zn(OAc)_2{\cdot}2H_2O$ (154 g/100 g: w/w) was added. Reflux was maintained for 1 h. TLC revealed that the reaction was not complete, so an additional 1 mL of a saturated solution of $Zn(OAc)_2{\cdot}2H_2O$ was added, and the reaction was stirred for another 1 h. After this reaction time, both UV/Vis spectroscopy and a TLC revealed that the reaction had reached completion. The reaction mixture was then diluted with CH_2Cl_2 and washed with water (3 times). After drying over Na_2SO_4, the organic phase was filtered and evaporated to dryness. The resulting purple powder was taken up in CH_2Cl_2 and purified by column chromatography (SiO_2 15–40 μm, eluent CH_2Cl_2/MeOH: 1/1) to afford the pure zinc complex **4c** in quantitative yield. ^{1}H NMR (200.13 MHz, $CDCl_3$, 298 K): δ = 1.99 (s, 6H; OMe), 2.10 (s, 6H; OMe), 2.59 (d, ^2J(H,H) = 14.0 Hz, 2H; CH_2Ph), 3.15 (d, ^2J(H,H) = 14.0 Hz, 2H; CH_2Ph), 3.33 (d, ^2J(H,H) = 16.0 Hz, 2H; CH_2Ph), 3.20 (d, ^2J(H,H) = 16.0 Hz, 2H; CH_2Ph),), 3.28 (d, ^2J(H,H) = 15.0 Hz, 2H; CH_2Ph),), 3.61 (d, ^2J(H,H) = 15.0 Hz, 2H; CH_2Ph), 5.63 (d, ^3J(H,H) = 8.0 Hz, 2H; ArH), 5.70 (d, ^3J(H,H) = 8.0 Hz, 2H; ArH), 6.28 (t, ^3J(H,H) = 8.4 Hz, 2H; ArH), 6.71 (s, 2H; ArH), 6.84 (t, ^3J(H,H) = 7.9 Hz, 2H; ArH), 7.12 (s, 2H; ArH), 7.17 (t, ^3J(H,H) = 7.4 Hz, 2H; ArH), 7.37 (t, ^3J(H,H) = 7.4 Hz, 2H; ArH), 7.53 (t, ^3J(H,H) = 7.4 Hz, 4H; ArH), 7.63 (t, ^3J(H,H) = 7.4 Hz, 4H; ArH), 7.79 (t, ^3J(H,H) = 8.2 Hz, 4H; ArH), 7.80 (t, ^3J(H,H) = 8.2 Hz, 4H; ArH), 7.85 (s, 2H; ArH), 8.01 (s, 2 H; ArH), 8.22 (d, ^3J(H,H) = 7.4 Hz, 2H; ArH), 8.74 (m, 8H; H_β), 8.94 ppm (s, 2H; ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): 29.8, 40.2, 41.0, 60.0, 61.0, 114.7, 116.0, 120.6, 122.0, 122.8, 122.9, 123.1, 123.2, 123.8, 124.2, 125.2, 125.3, 127.0, 127.5, 127.7, 127.8, 128.5, 129.3, 129.7, 130.3, 130.4, 131.2, 131.7, 132.0, 132.2, 132.7, 133.0, 134.8, 136.8, 138.3, 138.8, 149.4, 150.5, 150.6, 151.0, 153.3, 168.8, 169.9 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 428 (352670), 553 nm (19910).

General procedure for asymmetric olefin epoxidation:

Epoxidations were carried out using the following standard conditions: A mixture of the catalyst **4b** (1 μmol), olefin (1.0 mmol), and 1,2,4-trichlorobenzene (160 μmol, as an internal standard) in freshly distilled and degassed CH_2Cl_2 (2 mL) were stirred under N_2 in an ice-bath in a dry 1.5 cm diameter Schlenk tube. After addition of PhIO (100 μmol, 22 mg), aliquots were taken, purified by chromatography on a short silica-gel column and monitored by GC at appropriate intervals. Enantiomeric excesses were determinated by using Lipodex-E capillary chiral column (50 m × 0.25 mm, id.; 0.125 μm thickness). The retention times were compared to the retention times of standard racemates. The yield of he reactions was calculated based on the consumed PhIO on a QC3/PBX5 capillary column (25 m × 0.5 mm).

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