

Asymmetric Epoxidation Catalysed by an Iron 'binap Capped' Porphyrin

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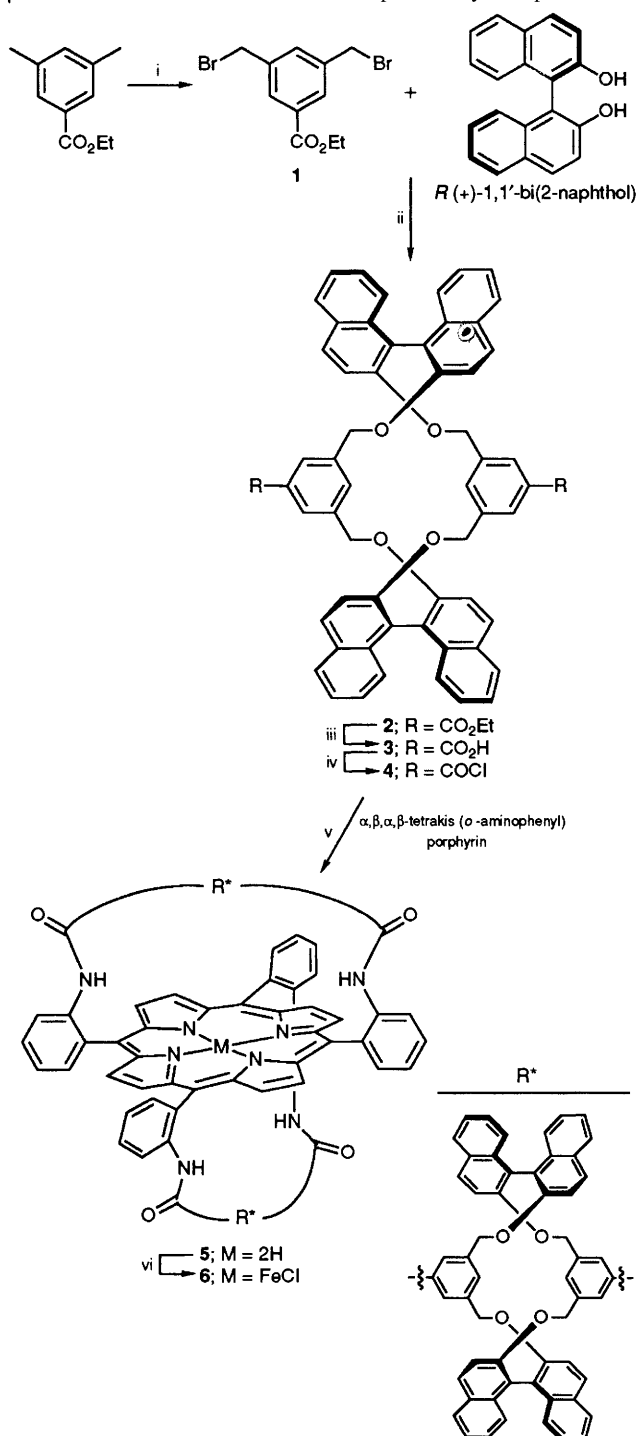
A new chiral metalloporphyrin (iron 'binap capped' porphyrin) has been synthesized and used to catalyse the asymmetric epoxidation of various unsubstituted aromatic olefins; [binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl].

Inspired by the stereoselective oxidations mediated by cytochrome P-450 enzymes,¹ synthetic chiral metalloporphyrins have been developed as catalysts for the asymmetric epoxidation of unfunctionalized olefins.² Typical enantiomeric excesses (e.e.s) range from 14 to 76%, although up to 89% e.e. has been achieved for an electron deficient olefin in a chiral metalloporphyrin system.^{2g} Metal complexes of chiral Schiff base ligands also catalyse the epoxidation of various unfunctionalized olefins with a high degree of enantioselectivity (>90% e.e. in some cases), although low catalyst turnovers (generally less than 40 turnovers) are reported with these systems due to catalyst degradation.³ Because metalloporphyrins are generally more stable to oxidative decomposition than Schiff base metal complexes (up to 3000 turnovers have been reported in a chiral metalloporphyrin system^{2c}), it is worth-

while to pursue new strategies for developing efficient chiral metalloporphyrin catalysts. Herein we report the synthesis and catalytic activity of a new chiral metalloporphyrin.

The synthesis of this chiral porphyrin is summarized in Scheme 1. Two chiral binap [binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl] groups are linked in a macrocyclic ether structure⁴ above each face of the porphyrin. In contrast to the 'basket handle'^{2b} and 'vaulted binaphthyl'^{2d} porphyrins, which have only one chiral group above each face of the porphyrin, **5** has two chiral groups above each face. Corey-Pauling-Koltun models suggest that the ether linkages force the binap groups into close proximity to the metal centre and result in a rigid chiral environment. The final coupling step in this synthesis proceeds in 24% yield. Elemental analysis, mass spectrometry, and the ¹H NMR spectrum of the porphyrin are

in agreement with the indicated structure 5.† The porphyrin has overall D_2 symmetry, leading to two sets of β -pyrrolic protons and four sets of diastereotopic methylene protons in



Scheme 1 Reagents and conditions: i, *N*-bromosuccinimide, cat. benzoyl peroxide, CCl_4 , reflux (32%); ii, Bu^tOK , THF, reflux (30%); iii, NaOH , $\text{EtOH-H}_2\text{O}$, reflux (96%); iv, SOCl_2 , cat. *N,N'*-dimethylformamide, reflux (95%); v, Et_3N , CH_2Cl_2 , $0^\circ\text{C} \sim \text{room temp.}$, then SiO_2 column ($\text{CH}_2\text{Cl}_2:\text{Et}_2\text{O}$, 10:1) (24%); vi, FeBr_2 , 2,6-lutidine, THF-toluene, reflux, washed with 10% HCl (90%)

† Selected spectroscopic data for 5 m/z (FAB) = 2332 ($\text{M} + \text{H}^+$) for $\text{C}_{160}\text{H}_{106}\text{N}_8\text{O}_{12}$. $^1\text{H NMR}$ (CDCl_3) δ 9.44 (s, 4H), 9.04 (s, 4H), 8.76 (d, J 8.2 Hz, 4H), 8.06 (d, J 7.5 Hz, 4H), 7.94 (m, 8H), 7.67 (d, J 7.6 Hz, 8H), 7.55 (t, J 7.5 Hz, 4H), 7.37–7.20 (m, 12H), 7.13–7.06 (m, 8H), 6.99 (t, J 7.5 Hz, 4H), 6.78 (m, 8H), 6.58 (d, J 8.5 Hz, 4H), 6.11 (s, 4H), 4.74 (s, 4H), 4.38 (d, J 12.1 Hz, 4H), 3.86 (d, J 12.1 Hz, 4H), 3.64 (d, J 8.7 Hz, 4H), 3.56 (s, 4H), 2.11 (d, J 12.1 Hz, 4H), 0.90 (d, J 12.1 Hz, 4H), -1.98 (s, 2H).

Table 1 Asymmetric epoxidation of aromatic olefins with 6

Substrate	Yield (%) ^a	E.e (%)	Configuration ^b
	62	48	$S(-)$
	64	50	$S(-)$
	39	56	(-)
	26	63	(-)
	59	29	$1S, 2R(+)$
	45	21	$1S, 2R(-)$

^a Yields are based on PhIO and were determined by GC analysis.
^b Assigned by comparison of polarimetry measurements with literature (ref. 2d, 2f).

the $^1\text{H NMR}$ spectrum. Iron was inserted by heating 5 with FeBr_2 in tetrahydrofuran (THF)-toluene for 6 h under N_2 , followed by air oxidation and extraction with aqueous HCl to give the iron(III) 'binap capped' porphyrin 6.‡

Results for asymmetric epoxidation of several mono- and di-substituted aromatic olefins catalysed by 6 are listed in Table 1.§ The e.e.s of the epoxides are comparable to the best obtained with other chiral porphyrin systems. For the styrene derivatives, it appears that electron-deficient olefins give higher e.e.s, although this trend is not as pronounced as that reported in the literature.^{2g} Epoxidation of 2-vinylnaphthalene gives good enantioselectivity (63% e.e.). Unlike most chiral porphyrin systems, the optical yields obtained from the epoxidation of *cis*-disubstituted aromatic olefins (*cis*- β -methylstyrene and 1,2-dihydronaphthalene) are lower than those obtained with terminal olefins. This may result from the smaller cavity in 6 compared with other chiral metalloporphyrins; thus, more sterically demanding disubstituted olefins might be forced to approach the reactive centre by another path.

Asymmetric epoxidation with related chiral binap porphyrin systems has been explored and will be the subject of subsequent publications. Investigations are also in progress to apply 6 to the asymmetric hydroxylation of alkanes.^{2d,5}

‡ 6, m/z (FAB) = 2421 ($\text{M} + \text{H}^+$) for $\text{C}_{160}\text{ClFeH}_{104}\text{N}_8\text{O}_{12}$.

§ General procedure of asymmetric olefin epoxidation. To deaerated CH_2Cl_2 (3 ml) was added 6 (1 μmol), nonane or dodecane (25 μl) as a GC standard, and olefin (3 mmol). The reaction mixture was stirred under N_2 and PhIO (110 μmol) was introduced. The epoxidation products were measured by GC over time intervals. Each aliquot was quenched with 2% PPh_3 in CH_2Cl_2 . At the end of the reaction, CH_2Cl_2 was removed under reduced pressure and the residue was loaded onto a fluorescent silica gel column (1 \times 10 cm, quartz column) prepared from a pentane slurry. PhI and unreacted olefins were eluted with pentane. Epoxides were eluted with 20% diethyl ether-pentane. The e.e.s of the epoxides were determined by a Cyclodex-B chiral capillary column.

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