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Synthesis and Catalytic Reactivity of D_4-Symmetric Dinorbornabenzene-Derived Metallotetraarylporphyrins

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Abstract: The condensation of the resolved C_2-symmetric benzaldehyde, 1,2,3,4,5,6,7,8-octahydro-1:4,5:8-dimethanoanthracene-9-carboxyaldehyde, with pyrrole produced the first chiral tetraarylporphyrin **1** exhibiting D_4-symmetry. The resolved benzaldehyde was synthesized in seven steps from *p*-benzoquinone and cyclopentadiene and included a resolution via diastereomeric ketals. A manganese chloride complex of porphyrin **1** was used as a catalyst for the asymmetric epoxidation of aromatic substituted alkenes in the presence of *excess* sodium hypochlorite in up to 7,200 turnovers and up to 76% e.e and >90% yield. © 1997 Elsevier Science Ltd.

In an effort to develop efficient catalysts for a variety of enantioselective bond formations we have investigated the use of metallotetraarylporphyrin complexes containing C_2-symmetric aryl groups. While several enantioselective catalysts are highly efficient for reactions involving substrates containing additional coordinating functional groups,[1] highly enantioselective bond formations involving unfunctionalized substrates have been the exception rather than the rule. One successful catalytic system for these difficult substrates is the chiral manganese salen system which catalyzes epoxidations of simple alkenes in greater than 90% enantioselectivity.[2] A limitation of these Schiff-base containing catalysts is their oxidative degradation results in generally limited catalyst turnovers. A potentially more robust class of enantioselective catalysts is based on derivatized chiral metallotetraarylporphyrins.[3] Although chiral porphyrins are generally more difficult to synthesize than chiral salen complexes, the greater stability of metalloporphyrins in most oxidation reactions may result in high enough catalyst turnover[4] to justify their synthesis if they also exhibit excellent selectivity.

The chirality in earlier metallotetraarylporphyrins stems from mono-substituted arenes and problems with isomer separation occur in their synthesis.[3,4] A drawback with some of these known metallotetraphenylporphyrins is that their enantioselectivity decreases during the reaction (possibly due to isomerization, oxidation of the ligand, or hydrolysis of ester linkages in the chiral auxiliaries). Maximum enantioselectivity is often only obtained when the ratio of alkene to oxidant is 10:1, resulting in a maximum

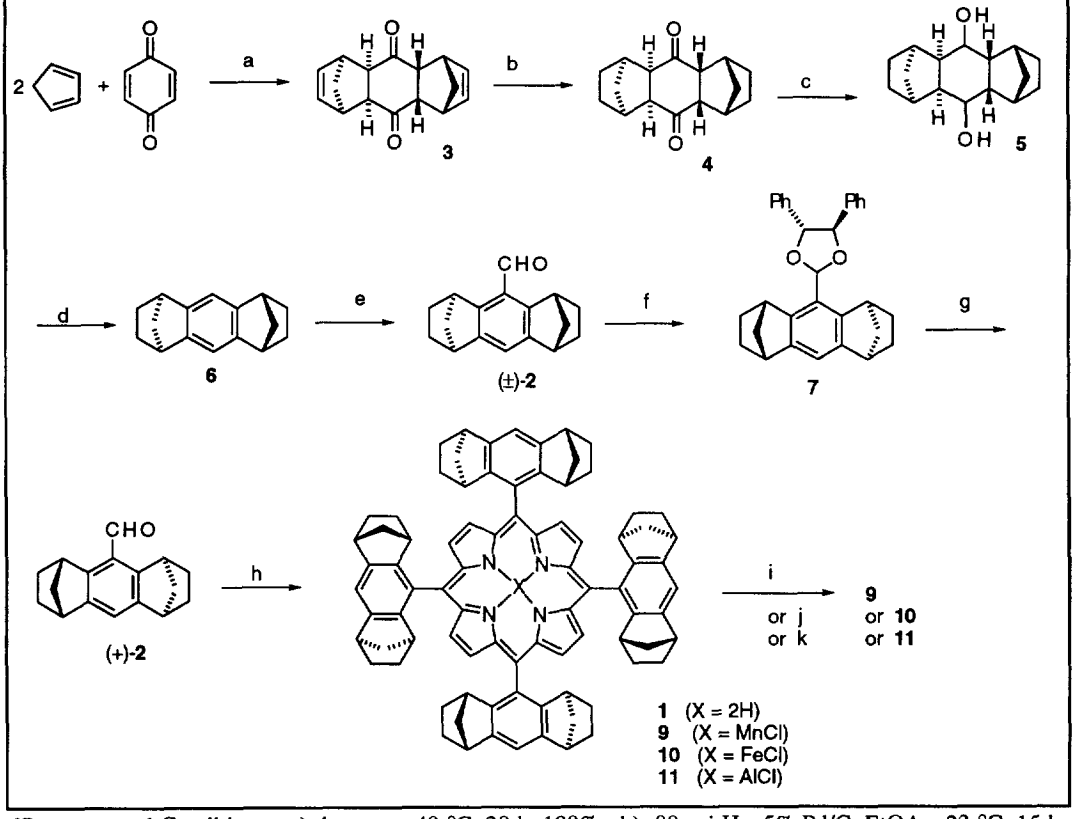
conversion of 10% of the starting alkene.[5] A review of metallotetraphenylporphyrin synthesis and catalytic oxidations has appeared.[3a] To circumvent prior limitations in the synthesis and stability of chiral tetraarylporphyrins, we concentrated on two concepts in designing our tetraarylporphyrin ligand **1**: 1) the aryl groups should be C_2-symmetric, leading to D_4-symmetric porphyrin ligands, and 2) the substituents on the arenes should be aliphatic with as much oxidative and hydrolytic stability as possible. Since our initial report of the synthesis and application of the first D_4-symmetric tetraarylporphyrin ligand **1**,[6] a D_4-symmetrical camphor-derived complex has been reported.[7] We report herein details of the synthesis and applications of catalysts derived from tetraarylporphyrin ligand **1**. These complexes are highly active, stable and moderately stereoselective catalysts for the epoxidation of aryl-substituted alkenes,[6] oxidation of sulfides,[8] and oxidation of benzylic methylenes, but are relatively poor catalysts for the Diels-Alder cycloaddition.

The key feature in our preparation of chiral tetraphenylporphyrin **1** was the development of an efficient synthesis of the C_2-symmetric benzaldehyde **2** which contains two norbornane groups fused to the central benzene ring (Scheme I). The desired C_2-symmetric stereochemical relationship between the two norbornane moieties was established in a known double Diels-Alder reaction between benzoquinone and cyclopentadiene. Isomerically pure diketone **3** was produced by the sequential Diels-Alder addition of cyclopentadiene to opposite faces of benzoquinone.[9] Catalytic hydrogenation of **3** as a slurry in ethyl acetate in a Parr reactor over Pd/C gave an intermediate diketone **4** which could be reduced as a slurry in methanol by sodium borohydride. After diluting the reaction mixture with water, insoluble diol **5** could be isolated in high yield by filtration. No purification of the nearly quantitatively-formed intermediates leading up to **5** was needed. Diol **5** was dehydrated and air-oxidized by stirring a warm solution of **5** in 85% phosphoric acid open to the air for 40 h to produce arene **6** which was isolated by extracting the diluted acid with petroleum ether.[10] In addition to signals arising from the desired product, the ^{1}H NMR spectrum of crude arene **6** exhibited large signals between 1-2 ppm, presumably due to cation-rearrangement products. Alternate dehydrations were examined (concentrated sulfuric acid, glacial acetic acid/iodine) but were found to be less effective. Arene **6** was readily purified by two recrystallizations from 95% ethanol (40% overall yield from benzoquinone). Friedel-Crafts formylation[11] of **6** with dichloromethyl methyl ether produced the desired racemic C_2-symmetric benzaldehyde **2**. Racemic benzaldehyde **2** was converted in high yield to a mixture of diastereomeric ketals[12] using readily available (*R,R*)-hydrobenzoin.[13] The less polar of the two diastereomers, ketal **7**, was crystalline and could be readily obtained in pure form by recrystallization from hot hexanes. The second diastereomeric ketal **8** could be isolated in pure form from the mother liquor by column chromatography. The solid state structure of ketal **7** was determined by X-ray diffraction. Based on the known configuration of the (*R,R*)-hydrobenzoin, the absolute stereochemistry of crystalline diastereomer **7** was established and is as shown in Scheme I. Acidic removal of the ketal protecting group provided resolved benzaldehyde (+)-(1*S*,4*R*,5*R*,8*S*)-**2** in high yield[14] with an 85% recovery of unisomerized (*R,R*)-hydrobenzoin. Condensation of benzaldehyde (+)-**2** with pyrrole in the presence of BF_3-Et_2O,[15] followed by subsequent addition of triethylamine[16] and chloranil oxidation afforded a 55% yield of the chiral tetraphenylporphyrin (+)-**1**. The addition of triethylamine between the condensation and oxidation steps increased the yield of tetraarylporphyrin from around 30% to 55%. Tetraarylporphyrin (+)-**1** exhibited D_4-

symmetry in the ^{1}H NMR spectrum. In addition to the expected Soret band at 423 nm, **1** exhibited a second band at 454 nm presumably due to complexation of the porphyrin by trace acid.

Metalation of 1. Three metal complexes of tetraarylporphyrin **1** were prepared. The manganese (III) chloride complex (+)-**9** was produced by heating a purple solution of (+)-**1** with $MnCl_2$-$4H_2O$ in DMF for 6 h, followed by treatment with HCl in air.[17] Purification by alumina chromatography using methylene chloride to elute any unreacted ligand and then 5:95 methanol:methylene chloride gave green chloromanganese complex **9** in 82% yield. Paramagnetic complex (+)-**9** was determined to be dextrorotatory and was characterized based on its UV and mass spectroscopic data. Whereas the porphyrin ligand (+)-**1** exhibited a Soret band at 423 nm (ε = 94,000 cm^{-1} M^{-1}), chloromanganese complex (+)-**9**

Scheme I



[a]Reagents and Conditions: a) benzene, 40 °C, 20 h, 100%; b) 80 psi H_2, 5% Pd/C, EtOAc, 23 °C, 15 h, 96%; c) $NaBH_4$, MeOH, 0 to 23 °C, 2 h, 95%; d) 85% H_3PO_4 open to air, 110 °C, 14 h, 57% (recryst from 95% EtOH); e) Cl_2CHOCH_3 (1.5 equiv), $TiCl_4$ (2.0 equiv), CH_2Cl_2, -15 °C, 2 h, 87%; f) (R,R)-hydrobenzoin (1.2 equiv), PPTS (cat), benzene, 80 °C, 12 h, 89% mixture of diast.; pure **7** 45%; g) 1:4 3% H_2SO_4:THF, 65 °C, 2 h, 100%; h) pyrrole (1.0 equiv), BF_3-Et_2O (0.3 equiv), $CHCl_3$ 23 °C, 1.5 h; Et_3N (0.33 equiv); p-Chloranil (0.75 equiv), 60 °C, 1 h, 55% **1**; i) $MnCl_2$-$4H_2O$ (10 equiv), DMF, 152 °C, 6 h; 1 N HCl extraction, 82% **9**; j) $FeCl_2$-$4H_2O$ (10 equiv), DMF, 152 °C, 24 h; 1 N HCl extraction, 59% **10**. k) Et_2AlCl (1.2 equiv), CH_2Cl_2, rt, 6 h; 83% **11**.

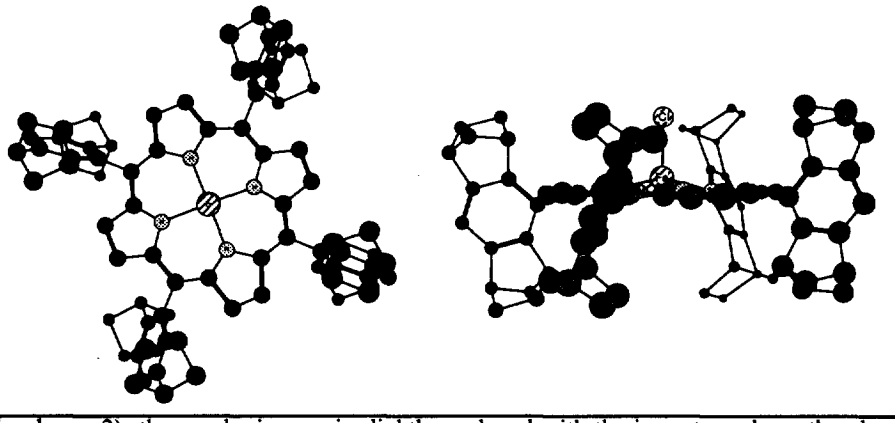
had an absorption maximum at 481 nm (ε = 81,400 cm^{-1} M^{-1}) and lacked the absorptions present in the free ligand. The mass spectrum also exhibited a strong ion corresponding to the manganese chloride molecular weight.

The iron (III) complex (+)-**10** was similarly prepared by heating (+)-**1** with $FeCl_2$-$4H_2O$ in DMF[18] for 30 h, followed by treatment with aqueous HCl in air. Purification by column chromatography (alumina, chloroform followed by 5:95 methanol:chloroform) gave the purple-brown chloroiron complex (+)-**10** in 65% yield. In addition to the new UV absorption of 380 nm (ε = 27,000 cm^{-1} M^{-1}) and 422 nm (ε = 50,000 cm^{-1} M^{-1}) providing evidence for the structure of (+)-**10**, we obtained the solid state structure of (+)-**10** by X-ray diffraction (see below).

The aluminum chloride complex (+)-**11** was prepared by stirring ligand (+)-**1** in the presence of diethylaluminum chloride[19] in methylene chloride at room temperature for 6 h. The aluminum complex was isolated by adding hexane to the reaction mixture to precipitate the desired complex in 83% yield. Whereas the iron and manganese complexes were paramagnetic and gave only very broad, uncharacterized signals in their NMR spectra, both the ^1H and ^{13}C NMR spectra of diamagnetic (+)-**11** were obtained. These spectra supported the C_4-symmetric formulation of (+)-**11**. For example, two different pyrrolic hydrogens were observed at 8.96 and 8.91 ppm. The presence of four different bridgehead hydrogen signals supports the chloride-induced inequivalence of the top and bottom faces of the metalloporphyrin.

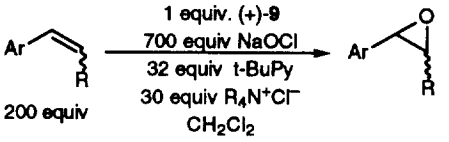
X-Ray Structure of (+)-10. Crystals suitable for X-ray diffraction were obtained by the slow evaporation of a solution of (+)-**10** in hexane. The solid state structure of the iron complex (+)-**10** of porphyrin (+)-**1** was determined by X-ray crystallography and two views of the structure are given in Figure 2.[20] Of particular interest: 1) the phenyl rings are nearly perpendicular (ca. 75°) to the porphyrin plane and are twisted in a propeller type arrangement with the methano-bridge of the norbornyl group nearer the

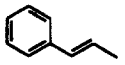
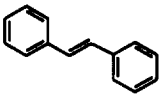
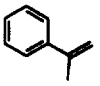
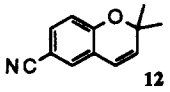
Figure 2. Two Views of the Crystal Structure of Iron Chloride Complex (+)-**10**.



porphyrin plane; 2) the porphyrin core is slightly puckered with the iron atom above the plane of the ligand; and 3) the sterically dissimilar portions of the chiral auxiliary (ethano vs methano-bridges) are somewhat remote from the metal, giving seemingly open access to the metal.

Table I. Asymmetric Epoxidation of Aromatic Alkenes[a]



Substrate	Time[b]	Yield[c]	e.e.[d]	Absolute Config.[e]
	1 h	90	52	S-(–)
	1 h	97	56	1R,2S-(+)
	1 h	98	41	1R,2S-(–)
	4 h	91(cis)	76 (cis)	1R,2S-(–)
		(+ 7% trans)	34 (trans)	1S,2S
	8 h	40[f]	4	1R,2R-(+)
	8 h	73[f]	10	1S,2S-(–)
	1 h	98	6	R-(+)
 **12**	3 h	72	65	

[a]Reactions were run at 20 °C typically with 0.5 mmol alkene, 2.5 mL Clorox™ bleach, 2 mL CH_2Cl_2, 0.0025 mmol (+)-**9**, 0.075 mmol 4-*tert*-butylpyridine, 0.075 mmol n-$C_{14}H_{29}(CH_3)_2(PhCH_2)NCl$ - $2H_2O$. [b]Time for complete consumption of alkene, except entry 5. [c]Isolated yield of epoxide after filtration through silica gel. [d]Determined by Chrompak cyclodextrin chiral capillary GC column and by ^1H NMR spectroscopy in the presence of Eu(hfc)$_3$. [e]Assigned by comparison of polarimetry measurements with literature. [f]Percent conversion after 8 h.

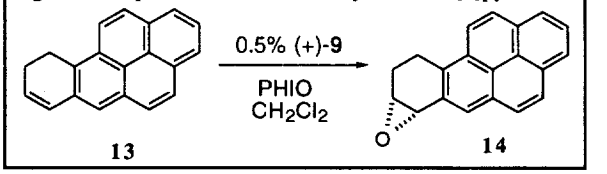
Epoxidations with 9 and 10. Epoxidation reactions of several aromatic-substituted alkenes under Meunier-Collman conditions[21] using of 0.5 mol % of chiral manganese catalyst (+)-**9**, excess sodium hypochlorite, a phase transfer catalyst, an axial 4-*t*-butylpyridine ligand in methylene chloride were studied and the results are shown in Table I. The enantioselectivities were determined either by resolution on a

chiral gas chromatography column or by obtaining the ^{1}H NMR spectra in the presence of a chiral lanthanide shift reagent. The absolute configurations were assigned by comparison of polarimetry data.[22] In the cases where the alkene was terminal, 1,1-disubstituted or cis-disubstituted the epoxidations were complete within 4 h. After filtration of the crude reaction mixture through a plug of silica gel the epoxides were isolated in high yields. In each case an excess of oxidant was used to insure complete conversion of the alkenes to epoxides. The monosubstituted and cis-disubstituted arylalkenes gave good enantioselectivity. The stereocenter at the benzylic position shows that styrene was oxidized from the opposite prochiral face than the cis-disubstituted alkenes. Epoxidation of trans-alkenes was markedly slower, not going to completion even after 8 h and gave much lower enantioselectivity.

The metalloporphyrin complex could be recovered after each of these reactions by eluting the silica gel plug used in the isolation of the epoxides with MeOH/CH_2Cl_2 and partitioning the eluent between methylene chloride and aqueous hydrochloric acid. The material obtained from the organic phase exhibited spectral characteristics identical to those of the original complex (+)-**9** and gave identical results when used in subsequent asymmetric epoxidation reactions.

Due to interest in synthesizing enantiomerically pure BPDE-derivatives,[23] we have examined the catalytic epoxidation of 9,10-dihydrobenzo[a]pyrene (**13**) using catalyst (+)-**9**. In the presence of bleach, dihydroarene **13** was decomposed whether in or out of the presence of our metalloporphyrin catalyst (+)-**9**. The use of iodosylbenzene in the presence of 0.5% of (+)-**9** effected the clean, but slow (66% conversion at 13 h) catalytic epoxidation of dihydroarene **13** into dihydroepoxide **14** in 56% enantioselectivity with no observable side-products (Figure 3).

Figure 3. Epoxidation of 9,10-dihydrobenzo[a]pyrene.



We have examined the ability of manganese complex (+)-**9** to undergo a high number of catalytic epoxidation turnovers. The epoxidation of styrene in the presence of 0.05 mol % of (+)-**9** (2,000 turnovers) under the phase-transfer conditions used in Table I was complete within 3 h with the same chemical yield and enantioselectivity as the reaction using 0.5 mol % catalyst (200 turnovers). The enantiomeric purity of the styrene oxide product was monitered every hour during the 2,000 turnovers and was found to be constant throughout the reaction. By omitting the phase transfer catalyst,[24] and using 100 equivalents of the axial *t*-butylpyridine ligand we have been able to acheive 5,000 turnovers in 24 h in the complete epoxidation of styrene to give a high yield of isolated epoxide with the same enantioselectivity as in our prior reactions. When 10,000 equivalents of styrene along with 100 equivalents of *t*-butylpyridine were exposed to excess bleach and (+)-**9**, we observed 6,800 turnovers after 24 h and 7,200 after 36 h. Very limited activity was observed after 36 h. The enantioselectivity of these epoxidations was the same as under our standard 200:1 reactions.

We also examined the catalytic epoxidation of aliphatic alkenes under our standard conditions ((+)-**9**:alkene:*t*-butylpyridine:PTC of 1:200:30:32 in excess NaOCl and methylene chloride). 1-Octene underwent 70% conversion in 8 h to a mixture of products that included about 50% (by GC internal

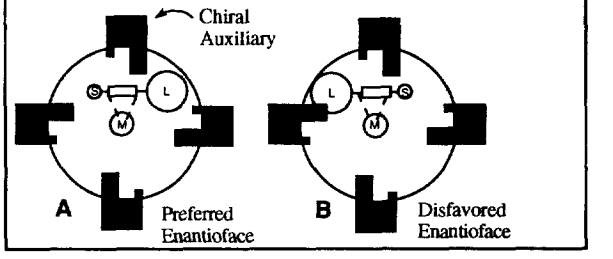
standard) of the corresponding epoxide whose enantiomeric purity was determined to be 26% e.e. Vinylcyclohexane underwent 43% conversion to a mixture of products that included about 50% of the epoxide in 28% e.e. In each case some diol product was detected and chlorinated side-products were suspected but not characterized.[24]

Epoxidations using the iron chloride complex (+)-**10** were also examined under the conditions of excess NaOCl and 30 equivalents of 4-*t*-butylpyridine in the presence of 200 equivalents of alkene and 1 equivalent of (+)-**10**. In the epoxidation of styrene, the reaction was slower than with the manganese complex, going to completion after 3 h to give a 70% yield of the epoxide but in only 8% e.e. The epoxidation of cis-β-methylstyrene gave after 3 h a 60% yield of epoxide in 75% e.e. The amount of trans-epoxide formed with this iron catalyst was the same as using the manganese catalyst.

The catalytic epoxidation results obtained with a manganese complex of the D_4-symmetric porphyrin (+)-**9** are encouraging in that inexpensive commercial bleach can be used as the oxidant, very high (200 to 7,200) rapid turnovers are possible, complete conversion of aryl-substituted alkenes to epoxides are seen with most substrates and the catalyst can be recycled.

Rationalization of Results. From the known absolute configuation of the epoxides produced in the catalyzed reactions, we know which face of the alkene is undergoing oxidation. The X-ray structure of the ketal **7** enabled us to determine the absolute configuration of the tetraarylporphyrin complex. From the examination of models, we can formulate the cartoon model in Figure 4 to rationalize our observed stereoselectivity. In this model, the larger, ethano-bridges in the norbornane chiral auxiliaries are represented by a larger block, the methano-bridge by a smaller one. The observed selectivity would be produced through complex **A**, in which the 1,2-disubsitituted alkene approaches the active site with the carbon-carbon double bond parallel to the porphyrin plane with the larger group on the alkene projecting toward the smaller group at the end of the channel. In the case of styrene, the alkene apparantly approaches with the carbon-carbon double bond perpendicular with the methylene group down and the phenyl group again pointing toward the smaller group at the end of the channel. This analysis would account for the reversal of facial selectivity between the disubstituted alkenes and styrene.

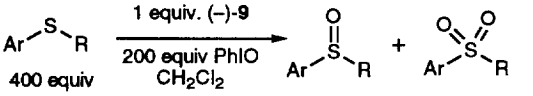
Figure 4. Rationalization of Observed Enantioselectivity.

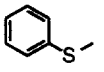
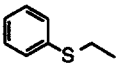
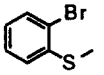
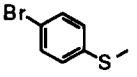
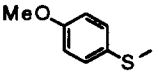
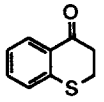


Sulfide Oxidations. We examined the manganese complex (–)-**9** as a catalyst for the enantioselective oxidation of aryl alkyl sulfides to sulfoxides[25] in the presence of iodosylbenzene.[8] The reactions were run under the conditions of (–)-**9**:iodosylbenzene:sulfide of 1:200:400 in methylene chloride at room temperature. A mixture of (–)-**9** in methylene chloride was added to iodosylbenzene under an atmosphere of nitrogen. Within two minutes the catalyst turned from a dark green color to an orange brown color and the sulfide was then added. The reaction was judged complete when the solution changed from an orange

brown of the presumed oxo species back to the original green color of (–)-**9** upon depletion of the iodosylbenzene. In all cases, the sulfide oxidation was complete within two hours. Yields were based on gas chromatographic analysis of the crude reaction mixture using decane as the internal standard and by examination of the ^{1}H NMR spectrum of the crude mixture, which could be recorded unperturbed, even with the presence of small amounts of paramagnetic metalloporphyrin. In addition to the desired sulfoxides, small amounts of sulfone, formed by overoxidation, were detected. In most cases, the yield of the sulfoxides was greater than 90%, the single exception being ethyl phenyl sulfoxide (82%) which formed the largest amount of sulfone (7.5%). The enantioselectivities were determined either by resolution on a chiral β-cyclodextrin capillary gas chromatography column, or by obtaining the ^{1}H NMR spectrum in the presence of either Eu(hfc)$_3$ as a chiral shift reagent or the chiral solvating reagent (*R*)-(+)-1,1'-binaphth-2,2'-diol.[26] The absolute configurations were assigned based on the findings of Toda and co-workers that the higher magnetic-field methyl signals of aryl methyl sulfoxides can be assigned to those of the (*R*)-isomers in the presence of (*R*)-(+)-1,1'-binaphth-2,2'-diol.[26] The rotation of purified sulfoxides was also determined. The yield of the sulfoxides and the sulfoxide/sulfone ratio were very good and the enantioselectivity ranged from 40% e.e. (*p*-methoxyphenyl methyl sulfide) to 68% e.e. (o-bromophenyl methyl sulfide). These selectivities

Table II Results of the catalytic asymmetric sulfoxidation reactions using (–)-**9**



substrate	config.	e.e.	yield	sulfoxide/ sulfone
	R-(+)	55	93	44:1
	R-(+)	42	82	13:1
	R-(+)	68	99	>95:1
	R-(+)	59	98	34:1
	R-(+)	40	99	44:1
	(–)	47	99	>95:1

are comparable to previously reported metalloporphyrin-catalyzed sulfide oxidations.[3c,25] The results are shown in Table II. The manganese tetraphenylporphyrin catalyst (–)-**9** could be recovered at the end of the reaction through alumina chromatography. After an extraction with 10% HCl, the recovered catalyst could be used again under our standard conditions to give identical results as those obtained with freshly prepared catalyst.

Several alternative conditions for the enantioselective sulfoxidation were studied, using thioanisole as the substrate. When the oxidation was carried out with a 1:1 ratio of sulfide to iodosylbenzene, rather than the 2:1 ratio used in the standard conditions, the enantioselectivities remained unchanged, but the ratio of sulfone formed increased substantially, from 44:1 to 9:1. With a 10:1 ratio of sulfide to iodosylbenzene, no sulfone could be detected. Increasing the catalyst to oxidant to thioanisole levels to 1:1875:3750 led to complete consumption of the oxidant within 12 hours, with a lower enantioselectivity of 40% and a lower sulfoxide to sulfone ratio of 8:1. When 4-*tert*-butylpyridine (10 equivalents based on manganese) was used as an axial ligand, a decrease in the enantioselectivity to 34% e.e. was observed in a much more rapid reaction (20 minutes). Performing the reaction at 0 °C did not appreciably increase the enantioselectivity, but the ratio of sulfone formed increased from 44:1 to 24:1.

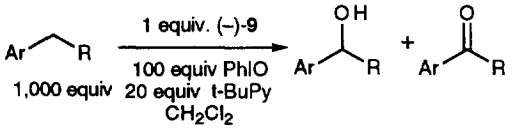
A kinetic resolution of a racemic mixture of methyl phenyl sulfoxide was attempted using 0.5 equivalents of iodosylbenzene in the presence of 0.5 mole % of (–)-**9**. After 7 hours, the oxidant was consumed. Although the ^{1}H NMR spectrum of the resulting mixture indicated the expected 1:1 ratio of methyl phenyl sulfoxide and methyl phenyl sulfone, the sulfoxide was found to be racemic.

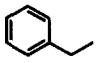
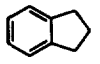
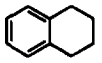
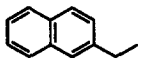
Methylene Oxidations. The enantioselective oxidation of benzylic methylene groups to secondary benzylic alcohols is known to be catalyzed by metallotetraphenylporphyrin complexes.[3c] Our D_4-symmetric manganese tetraphenylporphyrin (–)-**9** was examined as a catalyst for the asymmetric oxidation of benzylic methylene groups in the presence of iodosylbenzene. The reactions were run under the conditions of (–)-**9**:*t*-butylpyridine:iodosyl-benzene:benzylic methylene substrate in a ratio of 1:20:100:1000 in degassed methylene chloride at room temperature. The manganese catalyst in degassed methylene chloride was added to iodosylbenzene under an atmosphere of nitrogen. Within two minutes the catalyst turned from dark green to orange brown and the benzylic methylene substrate was then added. The reaction was judged complete by a color change from an orange brown of the presumed oxo species back to the original green color of manganese tetraphenylporphyrin (–)-**9**. The reaction times ranged from 20 minutes to 16 hours. Yields were based on gas chromatographic analysis of the crude mixture using decane as an internal standard. The enantioselectivities were determined either by resolution on a chiral β-cyclodextrin capillary gas chromatography column, or by obtaining the ^{1}H NMR spectrum of the purified alcohol in the presence of Eu(hfc)$_3$ as a chiral shift reagent. The rotations of the purified alcohols were recorded in methylene chloride. In addition to the desired alcohols, moderate to large amounts of ketone were also detected. Poor to moderate yields of the alcohols were found, ranging from 24 to 50%. These low yields can be attributed to the large amounts of ketone present in several cases. The enantiomeric purities of these alcohols ranged from 9 to 53% e.e. The results of these reactions are shown in Table III. When the oxidation was run without 4-*tert*-butylpyridine, the reaction times were markedly lengthened. For example, with

ethylbenzene the time was increased from 16 h to 47 h when no axial ligand was used. The enantioselectivities of these slower reactions were unchanged.

The manganese tetraphenylporphyron catalyst (–)-**9** could be recovered at the completion of each reaction. After extracting with 10% HCl and column chromatography, the recovered catalyst could be reused to give results identical to the oxidations run using freshly prepared catalysts.

Table III: Results of the catalytic asymmetric hydroxylation reactions using (–)-**9**

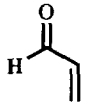
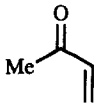
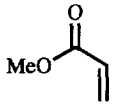
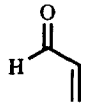
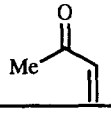


Substrate	time	config.	e.e.	yield	alcohol/ketone
	16 h	(+)	9	27	1:1
	20 min	(–)	53	50	5:1
	40 min	(–)	44	39	3:1
	14 h	(–)	40	24	2:1

Diels-Alder Catalysis. Based on a report that an aluminum tetraphenylporphyrin complex could catalyze Diels-Alder cycloadditions,[27] we examined the ability of aluminum chloride complex (+)-**11** to catalyze the cycloaddition reactions. We employed the conditions of (+)-**11**:dienophile:diene of 1:100:100 in methylene chloride at room temperature using either isoprene or cyclopentadiene as the diene and acrolein, methyl vinyl ketone or methyl acrylate as the dieneophile. Kodadek reported that no uncatalyzed reaction occurs under these conditions with isoprene, and minimal (0 - 16%) uncatalyzed reaction occurs with cyclopentadiene.[27] The reactions were monitored by gas chromatography and the yields of the endo Diels-Alder adducts were based on analysis of the crude reaction mixtures after 24 h at room temperature using decane as the internal standard. The enantioselectivities were determined directly by resolution on a chiral ß-cyclodextrin capillary gas chromatography column or by obtaining the ^1H NMR spectrum in the presence of a chiral shift reagent. Reduction of the Diels-Alder adducts to primary alcohols enabled an additional method for the determination of enantiomeric purity through the use of Mosher ester derivatives.[28] Optical rotations were recorded in methylene chloride for the purified endo products. The results of our reactions are summarized in Table IV.

The chemical yields of the Diels-Alder adducts are on the same order as those observed by Kodadek using an achiral aluminum tetraphenylporphyrin.[27] As in the previous study,[27] the cycloaddition between methyl acrylate and isoprene was not observed. The enantioselectivities varied from less than 5% up to 20% e.e. in the reaction of isoprene with acrolein. Although our observed enantioselectivities in this reaction are low, the fact that we do see asymmetric induction indicates that chiral aluminum tetraphenylporphyrin complex (+)-**11** can serve as a Lewis acid catalyst and that future, more suitably engineered metallotetraphenylporphyrin catalysts may provide higher levels of enantioselectivity.

Table IV. Diels-Alder Reactions in the Presence of (+)-**11**

Dienophile	Diene	Yield[a]	% e.e.	rotation
		85	10[b]	(+)
		70	10[c]	(+)
		30	<5[d]	(-)
		40	20[b]	(-)
		20	10[d]	(-)

[a]Yield of the endo adduct as determined by gas chromatrography. [b]Enantioselectivity determined by Mosher's ester of reduced product. [c]Enantioselectivity determined by ^{1}H NMR in presence of chiral shift reagent Eu(hfc)$_3$. [d]Enantioselectivity determined by ß-cyclodextrin chiral capillary gas chromatography.

Summary. Details for the synthesis of the first D_4-symmetrical tetraarylporphyrin ligand **1** are described along with procedures for the preparation of its chloromanganese, chloroiron and chloroaluminum complexes. A manganese derivative was highly active and gave good enantioselectivities in epoxidations of aryl-substituted alkenes in the presence of NaOCl. Benzylic methylenes and aryl alkyl sulfides were catalytically oxidized with good enantioselectivity in the presence of PhIO. An aluminum complex was marginally active as a catalyst for the Diels-Alder reaction.

Experimental Section[29]

General. General laboratory techniques were followed as reported in a recent article from our laboratory.[30] Unless otherwise noted, ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz and coupling constants are rounded to 0.5 Hz. Gas chromatography was performed with an achiral Hewlett-Packard fused silica capillary column (#19091J-102, 25 m X 0.20 mm i.d., 0.33 mm film) and a chiral Cyclodex-B capillary column (J & W Scientific, Folsom, CA. 95630, 30 m X 0.25 mm i.d., 0.25 μm film).

Preparation of 1,1a,2,3,4,4a,5,5a,6,7,8,8a-Dodecahydro-1:4,5:8-dimethanoanthracen-9,10-dione (4). A slurry of the known Diels-Alder adduct **3** (52.4 g, 254 mmol), 5% palladium on carbon (1.05 g), and ethyl acetate (200 mL) was stirred at room temperature under 600 psi of hydrogen for 18 h. After checking for completeness by ^{1}H NMR spectroscopy, the Pd/C was removed by filtration through a pad of silica gel and celite. The solubility of **4** in ethyl acetate is low and $CHCl_3$ was used to elute the solid product (2 x 50 mL). The combined organic portions were dried in vacuo to afford known **4** (50.0 g, 96%) as a white solid which was used directly in the following reaction. ^{1}H NMR δ 2.89 (s, 4 H), 2.83 (s, 4 H), 1.52 (m, 4 H), 1.43 (m, 4 H), 1.30 (m, 4 H).

Preparation of 1,1a,2,3,4,4a,5,5a,6,7,8,8a,9,10-Tetradecahydro-1:4,5:8-dimethanoanthracen-9,10-diol (5). Sodium borohydride (61 g, 1.61 mol) was added over a period of 40 min to a stirred slurry of diketone **4** (260 g, 1.08 mol) in methanol (1.5 L) at 0 °C. The reaction mixture was stirred under air at room temperature for 8 h. The reaction was quenched by slow addition of H_2O (350 mL) and the mixture was stirred at rt for 20 min. The solvent was concentrated to ca. 30% by rotary evaporation. The low solubility product was collected by filtration and washed by H_2O (2 x 150 mL). The residual H_2O was removed by high vacuum or by azeotropic distillation (Dean Stark trap with benzene) to afford **5** (250 g, 95%) as a white powder, mp 268 - 270 °C. Diol **5** is a mixture of cis (**5a**) and trans (**5b**) isomers (cis:trans = 9:1). Data for **5a:** ^{1}H NMR (DMSO-d_6) δ 4.20 (d, 2 H, J = 4.5 Hz), 3.74 (br s, 2 H), 2.37 (br s, 2 H), 2.26 (br s, 2 H), 2.22 (br s, 2 H), 2.15 (m, 2 H), 1.82 (d, 2 H, J = 8.0 Hz), 1.46 (d, 2 H, J = 8.0 Hz), 1.28 (br s, 6 H), 1.19 (d, 2 H, J = 9.0 Hz); ^{13}C NMR of **5a** (DMSO-d_6) δ 66.0, 44.5, 43.9, 41.2, 40.1, 39.4, 39.2, 25.2, 21.4; MS (EI, 70 eV) m/z (relative intensity) 248 (M^+, 6%), 230 (16), 212 (20), 179 (100), 163 (30), 161 (41), 146 (51), 123 (28), 95 (24), 79 (28), 77 (45).

Preparation of 1,2,3,4,5,6,7,8-Octahydro-1:4,5:8-dimethanoanthracene (6). Diol **5** (10.8 g, 50.9 mmol) and 85% H_3PO_4 (500 mL) were mixed in a 2 L round-bottomed flask which was open to the air and heated at 110° C for 16 h. The dark brown reaction mixture was cooled to room temperature and poured onto ice. After extracting the mixture by hexanes (3x 400 mL), the combined organic portion was washed with saturated $NaHCO_3$ solution (3x 100 mL), H_2O (3x 100 mL), and brine (1 x 100 mL). The organic layer

was dried ($MgSO_4$) and concentrated under reduced pressure to yield 8.5 g crude product. Two recrystallizations of the crude product from a minimum amount of hot 95% ethanol afforded pure desired arene **6** as white crystals (5.2 g, 57%), mp 155 - 156 °C. ^{1}H NMR δ 6.93 (s, 2 H), 3.25 (s, 4 H), 1.83 (m, 4 H), 1.69 (m, 2 H), 1.43 (dd, J = 1.5, 8.5 Hz, 2 H), 1.08 (m, 4 H); ^{13}C NMR δ 145.2, 113.4, 49.4, 43.7, 27.3; IR (KBr, pellet) 2981, 2956, 1444, 1330, 1286, 1102, 945, 898, 863, 840 cm^{-1}; MS (CI, 150 eV, NH_3) m/z 228 (M + NH_4^+, 15%), 211 (M + H^+, 69), 210 (M^+, 87), 183 (16), 182 (100), 154 (48); HRMS (CI, 150 eV, NH_3) mass calcd for M + H^+ 211.1487, found 211.1478.

Preparation of Racemic C_2-symmetric 1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethano anthracene-9-carboxaldehyde ((±)-2). Freshly distilled $TiCl_4$ (17.9 g, 95 mmol) was added to a cooled (-15°C) solution of arene **6** (10.00 g, 47.6 mmol) in CH_2Cl_2 (250 ml) under a nitrogen atmosphere. $CHCl_2OCH_3$ (8.21 g, 71.4 mmol) was added dropwise to the solution under stirring within 20 min. The mixture was stirred at 0 °C for another 2 h before it was allowed to come to rt and poured into ice-water. The CH_2Cl_2 layer was washed sequentially with saturated $NaHCO_3$ solution (2 x 60 mL), H_2O (3 x 50 mL), and brine, dried over anhydrous $MgSO_4$, and concentrated to give (±)-**2** (17.39 g, 87%) as a light yellow oil. The racemic aldehyde (±)-**2** was sufficiently pure for the following step. ^{1}H NMR δ 10.41 (s, 1 H), 7.16 (s, 1 H), 4.09 (br s, 2 H), 3.28 (d, 2 H, J = 2.0 Hz), 1.89 (m, 4 H), 1.69 (m, 2 H), 1.49 (d, 2 H, J = 9.0 Hz), 1.08 (m, 4 H); ^{13}C NMR δ 192.1, 147.3, 146.7, 122.7, 119.3, 49.1, 43.2, 41.1, 26.8, 26.4; IR (film) 2964, 2870, 2736, 1689, 1328, 1108 cm^{-1}. MS (EI, 70 eV) m/z (relative intensity) 238 (M^+, 46%), 210 (100), 182 (99), 153 (50); HRMS (EI, 70 eV) mass calcd for M^+ 238.1357, found 238.1359.

Resolution of racemic C_2-symmetric benzaldehyde 2; Formation of (1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-carboxaldehyde (1*R*,2*R*)-diphenylethylene ketal ((+)-7) and (1*R* ,4 *S* ,5*S*,8*R*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-carboxaldehyde (1*R*,2*R*)-diphenylethylene ketal ((-)-8). To a well-stirred solution of racemic aldehyde (±)-**2** (13.27 g, 55.77 mmol) in dry benzene (700 mL) were added (*R,R*)-hydrobenzoin[13] (17.92 g, 83.65 mmol) and pyridinium *p*-toluenesulfonate (0.86 g, 3.4 mmol). The mixture was heated to reflux under nitrogen for 18 h, and water was removed azeotropically with a Soxhlet extractor filled with 4 Å molecular sieve pellets. After cooling the reaction mixture to rt, white crystalline hydrobenzoin formed in the reaction flask. The reaction mixture was filtered, and the filtrate was rinsed by benzene (1 x 50 mL). The combined benzene portion was washed with saturated $NaHCO_3$, H_2O, and brine, dried ($MgSO_4$), and concentrated to afford mixture of diastereomeric acetals **7** and **8** and trace of excess (*R,R*)-hydrobenzoin. Column chromatography on silica gel (3:7 CH_2Cl_2-petroleum ether) afforded the pure product as a diastereomeric mixture (89%). Recrystallization from hot hexane afforded 27% yield of (+)-**7** as a white solid, mp 157 - 159 °C; $[\alpha]_D^{23}$ +109.4 (c 1.0, $CHCl_3$). The mother liquid was concentrated and run a silica gel flash column (CH_2Cl_2:hexane = 2:8) to afford 18% yield of more (+)-**7** and 30% yield of (-)-**8** as an oil, $[\alpha]_D^{23}$ -31.8° (c 1.0, $CHCl_3$). The overall isolated yields of pure ketals were 45% for (+)-**7** and 30% for (-)-**8**.

(+)-**7**: ^{1}H NMR δ 7.42 - 7.32 (m, 10 H), 7.04 (s, 1 H), 6.66 (s, 1 H), 5.03 (d, 1 H, J = 8.0 Hz), 4.98 (d, 1 H, J = 8.0 Hz), 3.86 (s, 2 H), 3.31 (s, 2 H), 1.85 (m, 4H), 1.81 (m, 2 H), 1.51 (m, 2 H), 1.22 (m, 2 H), 1.11 (m, 2 H); ^{13}C NMR δ 146.1, 143.9, 139.4, 136.6, 128.6, 128.6, 128.4, 128.0, 126.8, 126.3, 121.9, 114.8,

103.4, 87.6, 84.6, 48.9, 43.6, 42.0, 27.3, 26.8; IR (KBr) 3006, 2959, 2921, 2872, 1496, 1456, 1450, 1327, 1151, 1123, 1101, 1080, 1034, 1026, 1004, 972, 862, 762, 750, 700 cm^{-1}; MS (CI, 150 eV, NH_3) m/z (relative intensity) 435 ($(M + H)^+$, 100%), 434 (M^+, 6), 328 (27), 256 (30), 239 (29); HRMS (CI, 150 eV, NH_3) mass calcd for (M^+ + H) 435.2324, found 435.2322.

(-)-8: ^1H NMR δ 7.41-7.32 (m, 10 H), 7.02 (s, 1H), 6.61 (s, 1H), 5.03 (d, 1H, J = 8.0 Hz), 4.96 (d, 1H, J = 8.0 Hz), 3.84 (d, 2H, J = 2.5 Hz), 3.29 (d, 2H, J = 2.5 Hz), 1.98-1.84 (m, 4H), 1.75 (m, 2H), 1.49 (m, 2H), 1.31 (m, 2H), 1.13 (m, 2H); ^{13}C NMR δ 146.1, 144.1, 139.2, 136.6, 128.5 (2C's), 128.4, 128.0, 126.9, 126.3, 121.7, 114.9, 103.4, 87.8, 85.1, 49.0, 43.7, 41.9, 27.3, 27.0; HRMS (CI, 150 eV, NH_3) mass calcd for (M^+ + H) 435.2324, found 435.2328.

(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-carboxaldehyde ((+)-2). A 4:1 mixture of THF and 3% H_2SO_4 (100 mL) was added to a 250 mL round-bottomed flask containing ketal (+)-**7** (1.81 g, 4.16 mmol). The reaction mixture was heated at 70 °C for 2 h and checked by TLC. The reaction mixture was cooled to room temperature and extracted with ethyl acetate (3 x 80 mL). The combined organic portions were washed with H_2O and brine, dried ($MgSO_4$) and concentrated to afford the mixture of enantiomeric pure aldehyde (+)-**2** and (*R,R*)-hydrobenzoin. The aldehyde (+)-**2** and hydrobenzoin were separated by column chromatography on silica gel (3:7 CH_2Cl_2-hexane; pure ethyl acetate). (*R,R*)-hydrobenzoin was recovered as 84% yield of unisomerized diol. The enanatiomerically pure aldehyde (+)-**2** was obtained with a yield of 100% as a white solid, mp 90 - 92 °C; $[\alpha]_D^{23}$ +212.7 (c 1.0, $CHCl_3$). The ^1H and ^{13}C NMR spectra of (+)-**2** are same as those of its racemic mixture (±)-**2**.

5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl]-porphyrin ((+)-1). A 1 L three neck round-bottomed flask fitted with reflux condensor was charged with $CHCl_3$ (250 mL, distilled from $CaSO_4$), resolved aldehyde (+)-**2** (0.632 g, 3.07 mmol) and freshly distilled pyrrole (213 μL, 3.07 mmol). After purging the solution with nitrogen for 5 min, freshly distilled BF_3-etherate (108 μL, 1.02 mmol) was added via syringe at room temperature. The reaction solution was stirred at rt for 1 h excluding light. At the end of 1 h, triethylamine (141 μL, 1.02 mmol) was added followed by p-chloranil (0.562 g, 2.30 mmol) was added in powder form and the reaction was gently refluxed (61°C) for 1 h. The reaction mixture then was cooled to rt, and evaporated to dryness. The dry powder was then placed on a alumina column. The column was eluted by 10% CH_2Cl_2 in hexane to afford (+)-**1** as a red solid (0.46 g, 55%), mp >330 °C; $[\alpha]_D^{23}$ +365 (c 1.92 x 10^{-3}, $CHCl_3$); ^1H NMR δ 8.72 (s, 8 H), 7.36 (s, 4 H), 3.56 (s, 8 H), 2.77 (s, 8 H), 2.00 (d, 8 H, J = 8.0 Hz), 1.85 (m, 8 H), 1.32 (m, 24 H), 1.05 (m, 8H), -2.56 (s, 2 H); ^{13}C NMR δ 148.0, 144.0, 129.6-130.2 (br, weak signals) 128.6, 116.2, 113.6, 49.3, 44.3, 42.4, 27.6, 26.8; UV ($CHCl_3$) λ_{max} 454 nm (ε = 170,000 cm^1 $\underline{M}^{-1}$), 423 (94,074); IR (KBr) 3442, 2958, 2920, 2868, 803 cm^{-1}; MS (FAB, p-nitrobenzyl alcohol) m/z (relative intensity) 1143 (M^+ + H), 19%), 1142 (M^+, 14), 307 (24), 289 (17), 155 (22), 154 (100), 152 (17).

Chloro-{5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl]porphyrinato}manganese (III) ((+)-9). Porphyrin (+)-**1** (100 mg, 0.0875 mmol) was dissolved in refluxing DMF (6 mL). After waiting for several minutes to allow the porphyrin to dissolve, $MnCl_2$-$4H_2O$ (173 mg, 0.875 mmol) was added to the solution. After refluxing for 8 h, the mixture

was allowed to cool to rt and then poured into a flask containing an ice-cold saturated NaCl solution (10 mL). The resulting green fine powder was extracted by CH_2Cl_2 (3 x 15 mL). The combined CH_2Cl_2 portion was washed with 5% HCl solution (3 x 15 mL) and brine, dried ($MgSO_4$), and concentrated to yield crude product which was a mixture of starting material and desired product. The crude product was chromatographed on aluminum oxide column using CH_2Cl_2 (porphyrin portion) and 5:95 MeOH: CH_2Cl_2 (metalloporphyrin portion) as eluents to yield 14 mg recovered starting material (+)-**1** and metalloprphyrin (+)-**9** (77 mg, 82% yield based on porphyrin consumed) as a green solid, mp > 330 °C. $[\alpha]_D^{23}$ +252.1 (c 3.57 x 10^{-3}, $CHCl_3$); MS (FAB, *p*-nitrobenzyl alcohol) m/z (relative intensity) 1196.7 (M^+ - Cl + 1, 3), 1195.7 (M^+ - Cl, 1); UV ($CHCl_3$) λ_{max} 481 nm (ε = 81,429 cm^{-1} $\underline{M}^{-1}$).

Chloro-{5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl]porphyrinato}iron (III) ((+)-10). Porphyrin (+)-**1** (0.238 g, 0.208 mmol) was dissolved in refluxing DMF (100 mL). After waiting for several minutes to allow the porphyrin to dissolve, $FeCl_2$-$4H_2O$ (0.414 g, 2.08 mmol) was added to the solution. After refluxing for 24 h, the solution was evaporated to dryness. The purple-brown residue was dissolved in $CHCl_3$ (5 mL) and concentrated HCl (1 mL) was added, the mixture shaken and the organic portion removed and concentrated. The crude product was chromatographed (Al_2O_3, 30% $CHCl_3$/pet ether) to yield first any recovered starting material (+)-**1** then metalloprphyrin (+)-**10** (152 mg, 59 % yield) as a purple-brown solid, mp > 330 °C. $[\alpha]_D^{23}$ +170° (c 3.3 x 10^{-3}, $CHCl_3$); MS (FAB, *p*-nitrobenzyl alcohol) m/z (relative intensity) 1197 (M^+ - Cl + 1, 3), 1196 (M^+ - Cl, 1); UV ($CHCl_3$) λ_{max} 380 nm (ε = 27,100 cm^{-1} $\underline{M}^{-1}$), 422 nm (ε = 50,000 cm^{-1} $\underline{M}^{-1}$), 510 nm (ε = 7,000 cm^{-1} $\underline{M}^{-1}$), 578 nm (ε = 1,800 cm^{-1} $\underline{M}^{-1}$), 696 nm (ε = 1,720 cm^{-1} $\underline{M}^{-1}$).

Chloro-{5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl]porphyrinato}aluminum (III) (+)-11. To the porphyrin (+)-**1** (0.144 g, 0.100 mmol) in deoxygenated methylene chloride (2 mL) was added diethyl aluminum chloride (1 M in hexane, 0.120 mL, 0.120 mmol). The reaction was stirred at 23 °C for 1 h. A second portion of diethyl aluminum chloride (0.050 mL, 0.050 mmol) was added. The mixture was stirred an additional 5 h. Deoxygenated hexane (10 mL) was added and the product was allowed to slowly recrystallize out under nitrogen. The crystals were filtered to give pure (+)-**11** as a purple solid (0.100 g, 83%). >260 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 5 Hz, 4 H), 8.91 (d, J = 5 Hz, 4 H), 7.33 (s, 4 H), 3.54 (bs, 4 H), 3.53 (bs, 4 H), 3.52 (bs, 4 H), 3.51 (bs, 4H). 2.74 - 1.80 (m, 16 H), 1.52 (bs, 8 H), 1.39 - 1.31 (m, 16 H), 1.05 - 1.02 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 148.0, 147.8, 146.8, 144.5, 144.1, 136.6, 131.9, 127.3, 116.9, 113.9, 49.4, 49.3, 44.3, 42.4, 42.3, 37.2, 27.6, 27.5, 27.0, 26.8; IR (KBr) 3500, 2940, 1605, 1440, 1285, 1250, 1060, 1010, 945, 860, 795, 750 cm^{-1}; MS (FAB, *p*-nitrobenzylalcohol) M^+-Cl 1167.6, $[\alpha]^{23}_D$ +36.0 (0.025, $CHCl_3$).

General Procedure for Asymmetric Epoxidation. NaOCl (0.7 M; 2.5 mL, 1.75 mmol) was added to a flask containing olefin (0.5 mmol, 1 equiv), (+)-**9** (3.0 mg, 0.0025 mmol, 0.005 equiv), 4-*tert*-butylpyridine (10.8 mg, 0.08 mmol, 0.16 equiv), n-$C_{14}H_{29}(CH_3)_2(PhCH_2)NCl$-$2H_2O$ (30.7 mg, 0.076 mmol, 0.15 equiv) and 2 mL CH_2Cl_2. The reaction mixture was stirred very vigorously at rt open to the air.

When the reaction was completed as evidenced by lack of starting material by TLC or GC analysis, the organic layer was separated from the aqueous layer by pipet. The aqueous layer was extracted by CH_2Cl_2 (1 mL). The combined organic portion was dried ($MgSO_4$) and passed through a short pipet silica gel column. The column was rinsed by CH_2Cl_2 (1 mL). The combined organic portions were concentrated to afford the desired enantiomerically enriched epoxide. The short pipet column was kept for the recovery of catalyst (see below).

Determination of Epoxide Enantiomeric Purity. The enantiomeric purity of all compounds was determined by integration of ^1H NMR spectra obtained in the presence of the chiral shift reagent $Eu(hfc)_3$. A solution of $Eu(hfc)_3$ in $CDCl_3$ was prepared in a glove box by dissolving $Eu(hfc)_3$ (0.13 mmol, 150 mg) in $CDCl_3$ (3 mL). The shift study was conducted by adding the $Eu(hfc)_3$ solution (10 μL portions) to the NMR tube containing the solution of enantiomerically enriched epoxide (about 10 -12 mg in $CDCl_3$ (1 mL) each time and acquiring a ^1H NMR spectrum. Usually after adding three or four portions of the $Eu(hfc)_3$ solution the desired separation of peaks could be reached. The ratio of the isomers was obtained from the electronic integration and checked by cut-and-weigh of the expanded peaks. In the case of styrene oxide, the enantiomeric purity could also be determined by separation of the crude reaction mixture on a Chrompak cyclodextrin chiral capillary GC column. The absolute configurations were assigned by isolating the pure epoxides by preparative thin layer chromatography and measuring the optical rotation and comparison of the sign of rotation with the literature values.

Recovery of Catalyst (+)-9. The pipet columns collected from the epoxidation runs were washed by 5:95 MeOH: CH_2Cl_2. The combined fractions were concentrated and the residue was dissolved in CH_2Cl_2 (10 mL) and shook with 20% HCl (3 x 5 mL). The organic portion was washed with brine (3 x 5 mL) and dried over $MgSO_4$ and concentrated. The resulting residue was purified by column chromatography (Al_2O_3, CH_2Cl_2 followed by 10% MeOH in CH_2Cl_2). The second portion from the column was concentrated to give pure recoverd catalyst (+)-**9** (around 85% recovery) which exhibited an identical UV spectrum as before.

High Turnover Epoxidation Experiments without Phase Transfer Catalyst. NaOCl (0.7 M; 250 mL, 175 mmol) was added to a flask containing styrene (5.72 mL, 50 mmol, 10,000 equiv), (+)-**9** (5.9 mg, 0.005 mmol, 1 equiv), 4-*tert*-butylpyridine (73 mg, 0.5 mmol, 100 equiv) and CH_2Cl_2 (20 mL). The reaction mixture was stirred very vigorously at rt open to the air. The reaction was monitored periodically by stopping the stirring, removing a small amount of the organic portion and analyzing it by GC. After 16 h, 6,200 turnovers were observed, after 24 h, 6,800 and after 36 h, 7,200 turnovers were recorded. The mixture was then extracted by CH_2Cl_2 (3 x 50 mL). The combined organic portion was dried ($MgSO_4$), concentrated and passed through a short pipet silica gel column. The yield and enantiomeric purity of the epoxide were determined by ^1H NMR spectroscopy of the epoxide/stryene mixture in the presence of $Eu(hfc)_3$ and were found to be 67% yield (based on weight of product mixture and mol fraction of epoxide in the mixture) and 56% e.e. When this experiment was run at the same concentrations, but with 200 equivalents of *t*-butylpyridine, the epoxidation was much slower, giving 2,400 turnovers in 24 h.

Sulfoxidation Reaction: General Procedure: To PhIO (0.110 g, 0.5 mmol) was added at 23 °C under an atmosphere of nitrogen chloromanganese porphyrin complex (-)-**9** (3.0 mg, 0.0025 mmol) in methylene chloride (0.47 mL). The reaction mixture was stirred for 2 min whereby there was a color change

from green to orange-brown and a mixture of decane (0.194 mL, 1.0 mmol), sulfide (1.0 mmol) and methylene chloride (0.2 mL) was added. An inital aliquot was analyzed by GC. The reaction was judged complete within 2 h, as evidenced by a color change back to green. The crude product mixture was analyzed by GC and by ^{1}H NMR spectroscopy. The identities of the sulfide, sulfoxide and sulfone components were deduced by comparison with authentic known materials. The GC conditions are listed below.

Achiral GC: (20 PSI helium) The data are listed as initial temperature °C (initial time in min) /rate in °C/min / final temperature °C (final time in min) followed by the retention times of each component. Thioanisole 125(5) / 5 / 145(3) decane 2.6; iodobenzene 3.3; sulfide 3.8; sulfoxide 9.0; sulfone 10.7. Ethyl phenyl sulfide 125(5) / 5 / 155(3) decane 2.6; iodobenzene 3.3; sulfide 4.5; sulfoxide 11.1; sulfone 12.8. 4-Methoxythioanisole 125(3) / 10 / 235(0) decane 2.7; iodobenzene 3.3; sulfide 7.0; sulfoxide 11.1; sulfone 11.8. 4-Bromothioanisole 125(3) / 10 / 235(10) decane 2.7; iodobenzene 3.3; sulfide 7.6; sulfoxide 11.0; sulfone 11.5. 2-Bromothioanisole 125(3) / 10 / 235(3) decane 2.7; iodobenzene 3.3; sulfide 7.9; sulfoxide 10.4. Thiochroman-4-one 125(3) / 10 / 250(3) decane 2.7; iodobenzene 3.3; sulfide 10.1; sulfoxide 13.5. The sulfoxide of 2-bromothioanisole could be separated using a chiral ß-cyclodextrin GC column at 160 °C isotherm, minor 40.995; major 41.664 min.

Sulfoxide Enantiomeric Purity Determination by ^{1}H NMR Spectroscopy in the Presence of (*R*)-(+)-1,1'-binaphth-2,2'-diol: The ^{1}H NMR spectra of 1:1 solutions of the crude product mixtures and (*R*)-1,1'-binaphth-2,2'-diol in $CDCl_3$ were recorded.[26] The ^{1}H NMR data are listed for the sulfoxide methyl group without the solvating reagent followed by the shifts of the enantiomeric methyl groups in the presence of the solvating reagent. Thioanisole from δ 2.69 ppm to minor 2.68 ppm; major 2.66 ppm. 4-Methoxythioanisole from δ 2.70 ppm to minor 2.67 ppm; major 2.65 ppm. 4-Bromothioanisole from δ 2.7 ppm to minor 2.69 ppm; major 2.68 ppm. 2-Bromothioanisole from δ 2.8 ppm to minor 2.79 ppm; major 2.77 ppm.

Sulfoxide Enantiomeric Purity Determination by ^{1}H NMR Spectroscopy in the Presence of Eu(hfc)$_3$: To purified (by prep TLC methylene chloride) thiochroman-4-one (0.06 M in $CDCl_3$) was added Eu(hfc)$_3$ (0.1 M in $CDCl_3$) in 2 µl portions to give at 0.200 equivalents a resolution of Δδ 0.08 ppm between the major and minor isomers.

General Hydroxylation Procedure: To PhIO (0.018 g, 0.081 mmol) was added chloromanganese porphyrin complex (-)-**9** (1.0 mg, 0.0008 mmol) in deoxygenated methylene chloride (0.47 mL). This mixture was stirred for 2 minutes and there was a color change from green to orange brown. To this mixture was added a standard solution containing decane (0.116 g, 0.813 mmol), alkane (0.813 mmol) and degassed methylene chloride (1.13 mL). An initial decane:alkane ratio was obtained by GC analysis. 4-*tert*-Butylpyridine (1.4 µL, 0.016 mmol) was added via syringe to the reaction mixture. The reaction was judged complete when the color changed back to green. The crude product mixture was analyzed by GC under the conditions listed below. The GC data are listed as for the sulfoxides.

Achiral GC: (20 psi unless otherwise noted) Ethyl benzene 90(12) at 15 PSI alkane 3.8; decane 6.7; iodobenzene 8.5; alcohol 9.6; ketone 10.0. Indane 110(5) / 20 / 185(10) decane 3.4; alkane 4.2;

iodobenzene 4.3; alcohol 7.6; ketone 8.3. 1,2,3,4-Tetrahydronaphthylene 125(5) / 10 / 175(1) decane 2.7, iodobenzene 3.3; alkane 5.0; ketone 8.7; alcohol 9.1. 2-Ethylnaphthylene 125(3.5) / 10 / 250(0) decane 2.7; iodobenzene 3.3; alkane 8.6; alcohol 11.4; ketone 11.6.

Chiral GC: Ethyl benzene 125(17) major 15.103, minor 15.500.

Alcohol Enantiomeric Purity Determination by ^{1}H NMR Spectroscopy in the Presence of Eu(tfc)$_3$: To purified (prep. SiO_2 TLC, methylene chloride) indanol (0.07 M in $CDCl_3$) was added Eu(hfc)$_3$ (0.1 M in $CDCl_3$) in 2 μL alliquots until 0.027 equivalents were added whereby a set of signals resolved to a $\Delta\delta$ of 0.15 ppm. To purified 1,2,3,4-tetrahydronaphthylen-1-ol (0.07 M, $CDCl_3$) was added Eu(hfc)$_3$ (0.1 M in $CDCl_3$) in 2 μL alliquots until 0.030 equivalents where added where the signal resolved to a $\Delta\delta$ of 0.06 ppm. To purified 2-(1-hydoxyethan-1-yl)naphthylene (0.03 M in $CDCl_3$) was added Eu(hfc)$_3$ (0.1 M in $CDCl_3$) in 2 μL alliquots until 0.009 equivalents was added where the signal resolved to a $\Delta\delta$ of 0.15 ppm.

General Diels-Alder Procedure: To (+)-**11** (12 mg, 0.010 mmol) in methylene chloride (1.1 mL) was added a standard solution of decane (0.097 mL, 0.5 mmol) and dienophile (1.0 mmol) in methylene chloride (2.0 mL). An initial decane:dienophile ratio was determined by GC analysis. The diene (1.0 mmol) was then added. The mixture was stirred for 24 h at rt except in the case of acrolein with dicyclopentadiene which was stirred 1 h. At the end of the reaction period the crude mixture was analyzed by GC. The GC conditions for the cycloadducts are given below. The data are recorded as for the sulfoxides.

Achiral GC: (15 psi) Acrolein with cyclopentadiene 40(3) / 25 / 210(0) dienophile 2.0; decane 7.9; product 8.1. Methyl vinyl ketone with cyclopentadiene 60(3) / 25 / 210(0) dienophile 2.3; decane 6.9; product 8.0. Methyl acrylate with cyclopentadiene 60(3) / 25 / 210(0) dienophile 2.5; decane 6.9; product 8.1. Acrolein with isoprene 40(3) / 25 / 210(0) dienophile 2.1; decane 7.9; product 8.4. Methyl vinyl ketone with isoprene 60(3) / 25 / 210(0) dienophile 2.3; decane 6.9; product 8.2.

Chiral GC: Methyl acrylate with cyclopentadiene 100(50) major 34.816; minor 35.400. Methyl vinyl ketone with isoprene 100(50) minor 39.767; major 40.170.

(-)-Mosher Ester: Acrolein with cyclopentadiene δ 5.94 and 5.89. Acrolein with isoprene δ 4.28 and 4.25, 4.20 and 4.17.

Eu(hfc)$_3$: To the purified product of the reaction between methyl vinyl ketone with cyclopentadiene (0.07 M in $CDCl_3$) was added 2 μl alliquots of Eu(hfc)$_3$ (0.1 M, $CDCl_3$) until 0.079 equivalents was added at which time a signal resolution of $\Delta\delta$ 0.04 ppm was found.

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29. ^{1}H and ^{13}C NMR spectra for porphyrin (+)-**1** and key intermediates in its synthesis can be found in the Supplementary Material in reference 6.

30. For general experimental methods and instrumentation details used in our laboratory see: Halterman, R. L.; Ramsey, T. M. *J. Organomet. Chem.* **1994**, *465*, 175.

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