(Carbowax 20 M, 100 °C for 10 min and then at 5°/min to 130 °C). Cycloheptanone (9.26 min) was used as an internal standard. The ratio of cycloheptene oxide to methylenecyclohexene oxide was 4.5:1. Similar oxidation of these olefins by mCPBA produced equal amounts of both epoxides.

Reaction of Iodosylbenzene with (+)-Limonene Catalyzed by FeTMPCl and FeTTPCl. Iodosylbenzene (0.117 g, 0.530 mmol) was added to a solution of (+)-limonene (0.50 mL, 3.09 mmol) and FeTTPCl (0.04 g, 0.053 mmol) in methylene chloride (5 mL). Analysis of GLPC (Carbowax 20 M, 110 °C) showed that the two epoxides were formed in a ratio of 19:1. Capillary GLPC (30 m SP-2250) showed the major peak to be a 1.15:1 mixture of the diastereomeric 1,2-oxides (larger peak eluted first). The 7,8-oxides were formed in equal amounts. The total yield of epoxides was 78% based on iodosylbenzene.

This reaction was repeated for FeTMPCl, and the total yield of epoxides was 69%. With mCPBA the ratio of 1,2-oxides to 7,8-oxides was 10:1.

Acknowledgment. Financial support of this research by the National Institutes of Health (Grant GM 25923) and the National Science Foundation (Grant CHE-81-06064) is gratefully acknowledged. The National Science Foundation provided funds for the purchase of an NMR spectrometer.

Registry No. FeTPPCl, 16456-81-8; FeTTPCl, 52155-50-7; FeTNPCl, 86456-39-5; FeTPPPCl, 86456-38-4; FeTMPC, 77439-21-5; FePPIX-DME, 15741-03-4; *cis*-CDT oxide, 42539-84-4; *trans*-CDT oxide, 40702-89-4; cyclohexene, 110-83-8; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *cis*-cyclododecene, 1129-89-1; *trans*-cyclododecene, 1486-75-5; *trans,trans,cis*-1,5,9-cyclododecatriene, 706-31-0; methylenecyclohexane, 1192-37-6; cycloheptene, 628-92-2; (+)-limonene, 5989-27-5; 2-norbornene, 498-66-8; cyclooctene, 931-88-4; 1,3-cyclohexadiene, 592-57-4; 2-cyclohexen-1-one, 930-68-7; iodosylbenzene, 536-80-1; 1,3-cyclohexadiene oxide, 6705-51-7; cyclooctene oxide, 286-62-4; *exo*-norbornene oxide, 3146-39-2; cyclohexene oxide, 286-20-4; *cis*-2,3-diphenyloxirane, 1689-71-0; *cis*-cyclododecene oxide, 1502-29-0; *trans*-cyclododecene oxide, 4683-60-7; (+)-limonene oxide (isomer 1), 4680-24-4; (+)-limonene oxide (isomer 2), 6909-30-4; (+)-limonene oxide (isomer 3), 28098-67-1; (+)-limonene oxide (isomer 4), 28098-68-2.

Catalytic Asymmetric Epoxidations with Chiral Iron Porphyrins

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Abstract: Iron porphyrins have been modified to include optically active functionalities at the meso positions. Asymmetric epoxidations of prochiral olefins with these chiral iron porphyrins and iodosyl compounds have been investigated. Thus, 5α,10β,15α,20β-tetrakis(*o*-(*R*)-hydratropamidophenyl)porphyrin ($H_2T(\alpha,\beta,\alpha,\beta$-Hyd)PP) and 5α,10β,15α,20β-tetrakis(*o*-[(*S*)-2′-carboxymethyl-1,1′-binaphthyl-2-carboxamido]phenyl)porphyrin ($H_2T(\alpha,\beta,\alpha,\beta$-Binap)PP) were synthesized by the condensation of optically active acid chlorides with 5α,10β,15α,20β-tetrakis(*o*-aminophenyl)porphyrin. Subsequent insertion of iron into $H_2T(\alpha,\beta,\alpha,\beta$-Hyd)PP and $H_2T(\alpha,\beta,\alpha,\beta$-Binap)PP gave Fe$T(\alpha,\beta,\alpha,\beta$-Hyd)PPCl and Fe$T(\alpha,\beta,\alpha,\beta$-Binap)PPCl, respectively. Employing Fe$T(\alpha,\beta,\alpha,\beta$-Hyd)PPCl and iodosylbenzene, styrene was oxidized to (*R*)-(+)-styrene oxide in 31% ee. Similarly, Fe$T(\alpha,\beta,\alpha,\beta$-Binap)PPCl and iodosylmesitylene gave (*R*)-(+)-styrene oxide in 48% ee. Various substituted styrenes and aliphatic olefins were epoxidized with enantiomeric excesses varying between 0% for 1-methylcyclohexene oxide and 51% for *p*-chlorostyrene oxide.

Asymmetric syntheses have been the focus of considerable recent attention. Among the most interesting approaches to this general problem is the use of chiral catalysts capable of catalytic asymmetric induction. Impressive results have been achieved in the case of catalytic asymmetric reductions,[1] such as the Monsanto process for the production of L-DOPA from prochiral starting materials.[2]

By contrast, asymmetric epoxidation reactions have received little attention. Monoperoxycamphoric acid has been reported to epoxidize simple olefins such as styrene with a 7.8% enantiomeric excess (ee).[3] The highest degrees of asymmetric epoxidation of olefins without coordinating functional groups, in the range of 5–35% ee, have been reported recently by Mimoun with a chiral peroxomolybdenum(VI) reagent.[4] Significant asymmetric inductions (25% ee) were observed by Wynberg et al. for the epoxidation of α,β-unsaturated ketones with basic hydrogen peroxide in the presence of a chiral phase-transfer catalyst.[5]

The first major advances in catalytic asymmetric epoxidation were reported by Sharpless[6] and Yamada,[7] who used chiral vanadium and molybdenum catalysts for the epoxidation of allylic alcohols by alkyl hydroperoxides. Very recently Sharpless has reported an improved, titanium tartarate catalytic system which gave spectacular enantiomeric excesses, greater than 95%, for a wide variety of allylic alcohols.[8] Molybdenum(VI)-catalyzed asymmetric oxidations give much lower optical yields (10–14%).[9]

Whole cell studies with *Corynebacterium equi* have been reported[10] in which 1-hexadecene was converted to (*R*)-(+)-1,2-epoxyhexadecane in 41% yield and 100% optical yield. Likewise, significant asymmetric induction for 1-octene epoxidation (80%) has been observed by May with the ω-hydroxylating system of *P. oleovorans*.[11]

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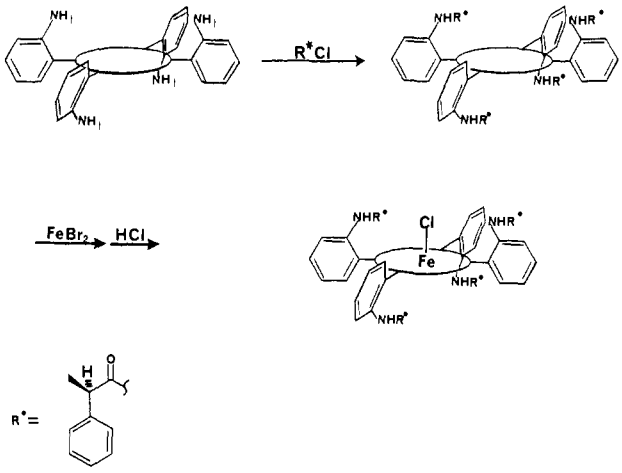
Scheme I



The discovery of iron porphyrin catalyzed epoxidation and hydroxylation using iodosylarenes[12,13] as oxidants has suggested that a suitably substituted, chiral, metalloporphyrin could catalyze asymmetric hydroxylation and epoxidation. We describe here chiral epoxidations catalyzed by two such iron–porphyrin complexes in which significant asymmetric induction results from nonbonded interactions.

Results and Discussion

Synthesis of Chiral Porphyrinates. In connection with model studies dealing with the binding of molecular oxygen to ferrous porphyrinates, Collman et al.[14] have described the synthesis of $5\alpha,10\alpha,15\alpha,20\alpha$-tetrakis(*o*-pivalamidophenyl)porphyrin (H_2TpivPP) from $5\alpha,10\alpha,15\alpha,20\alpha$-tetrakis(*o*-aminophenyl)-porphyrin (H_2TAPP, **1**). The isolation of the other three rotational atropisomers of H_2TAPP was also described in this work. Modification of the amino appendages of **1** provides a convenient approach to a chiral porphyrin. For the purposes of catalytic asymmetric epoxidation, it was decided that $\alpha,\beta,\alpha,\beta$-$H_2$TAPP (**2**) offered the most potential. Appending chiral moieties to this atropisomer would provide an iron–porphyrin molecule with two topologically identical faces. At the same time such a derivative would not be expected to be so bulky as to preclude the approach of substrates and iodosylarenes.

The chiral appendage chosen for modification of $\alpha,\beta,\alpha,\beta$-$H_2$TAPP had to meet several criteria; it should be relatively accessible in an optically pure form, the chiral site should be sufficiently close to the iron locus at which oxidation is to take place, it must allow facile reaction with the amino groups, and it should be relatively inert to oxidation. With these points in mind, 2-phenylpropionic acid (hydratropic acid) was the initial choice. According to the procedure of Pettersson,[15] formation of the (−)-α-methylbenzylamine salt of racemic 2-phenylpropionic acid and subsequent recrystallization gave (*R*)-(−)-2-phenylpropionic acid of high optical purity. This material was conveniently converted to (*R*)-2-phenylpropanoyl chloride which was found to be 97% optically pure.

Synthesis of the chiral porphyrin was achieved by stirring (*R*)-2-phenylpropanoyl chloride and $\alpha,\beta,\alpha,\beta$-$H_2$TAPP (**2**) in methylene chloride at room temperature (Scheme I). This procedure gave a high yield of $5\alpha,10\beta,15\alpha,20\beta$-tetrakis(*o*-(*R*)-hydratropamidophenyl)porphyrin (H_2T($\alpha,\beta,\alpha,\beta$-Hyd)PP, **3**). The ^{1}H NMR spectrum of **3** was completely consistent with the expected structure, displaying a doublet for the methyl and a quartet for the methine protons of the hydratropamido substituents,. The external, or β-pyrrole hydrogens, appeared as two singlets at δ 8.65 and 8.48 at room temperature. This is in contrast to generally reported lone singlet for the β-pyrrole hydrogens of 5,10,15,20-tetraphenylprophyrins, a result of the rapid tautomerism of the internal N–H protons.[16]

H_2T($\alpha,\beta,\alpha,\beta$-Hyd)PP (**3**) was metalated at room temperature by treatment with anhydrous ferrous bromide in tetrahydrofuran to give chloro[$5\alpha,10\beta,15\alpha,20\beta$-tetrakis(*o*-(*R*)-hydratropamidophenyl)porphyrinato]iron(III) (FeT($\alpha,\beta,\alpha,\beta$-Hyd)PPCl, **4**) after chromatography on alumina and treatment with dilute hydrochloric acid. The $\alpha,\alpha,\beta,\beta$,-antropisomer **5** and the $\alpha,\alpha,\alpha,\alpha$-$\mu$-oxo dimer **6** were prepared in a similar manner.

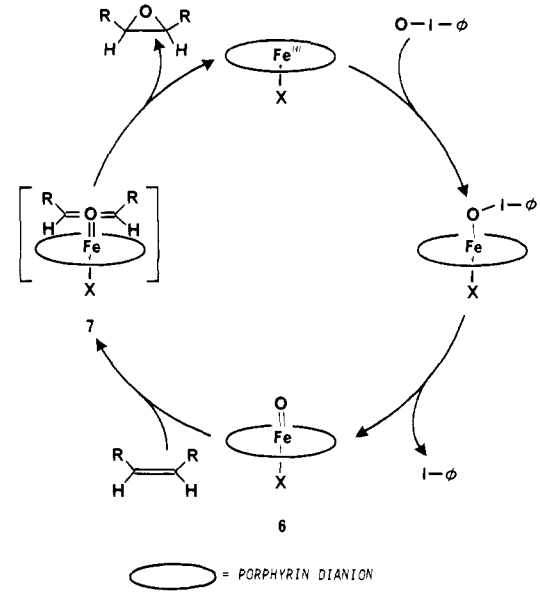
Chiral Epoxidation with FeT($\alpha,\beta,\alpha,\beta$-Hyd)PPCl, 3. Results for the epoxidation of some representative olefins by FeT($\alpha,\beta,\alpha,\beta$-Hyd)PPCl and iodosylbenzene are presented in Table I. Yields were determined by GLPC and the configuration of the predominant enantiomer was determined by polarimetry. The optical purity of the isolated epoxides was analyzed by reduction to secondary alcohols by lithium aluminum hydride[17] and conversion to a mixture of stereoisomeric esters with (*R*)-2-phenylpropanoyl chloride (eq 1). These esters were separated readily by GLPC.

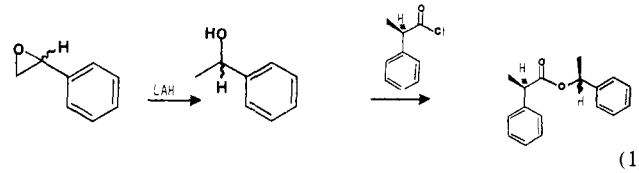
Table I. Catalytic Asymmetric Epoxidation with Fe($\alpha,\beta,\alpha,\beta$-Hyd)PPCl (3)

substrate	yield,[a] %	configuratn	ee, %
styrene	65[b]	(*R*)-(+)	31
with Fe($\alpha,\alpha,\beta,\beta$-Hyd)PPCl			0
with Fe($\alpha,\alpha,\alpha,\alpha$-HydPP)$_2$O			0
cis-β-methylstyrene	77	(1*R*,2*S*)-(−)	10
trans-β-methylstyrene	62	(1*R*,2*R*)-(+)	16
1-octene	16		9
with Fe($\alpha,\alpha,\beta,\beta$-Hyd)PPCl			0

[a] Based on iodosylbenzene consumed. [b] Phenylacetaldehyde produced in 16% yield.

Scheme II





(1)

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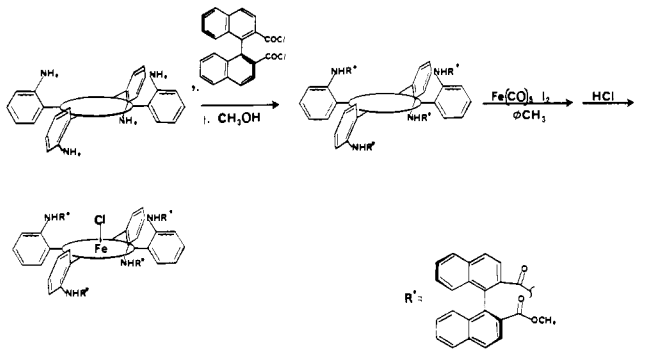
Scheme III

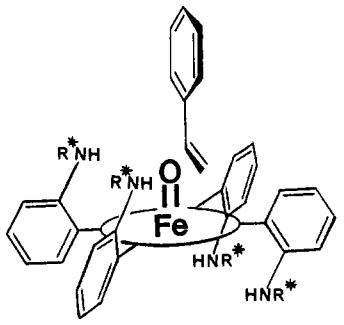


The epoxidation of styrene produced a 31% enantiomeric excess of the (*R*)-(+)-enantiomer of styrene oxide. This value corresponds to a $\Delta\Delta G^{\ddagger}$ of 0.34 kcal/mol between the diastereomeric transition states for oxygen atom transfer from the chiral porphyrin to the *si* and *re* faces of the styrene. By contrast, Fe($\alpha,\alpha,\beta,\beta$-Hyd)PPCl and [Fe($\alpha,\alpha,\alpha,\alpha$-Hyd)PP]$_2$O which produced similar yields of styrene oxide gave racemic products.

As we have reported elsewhere,[18] the mechanism of this porphyrin-catalyzed oxygen-transfer reaction involves a reactive iron–oxo intermediate, **6** (Scheme II). Proton NMR and Mössbauer measurements at low temperature indicate the presence of a new oxidized iron species and free iodobenzene.[19]

Cis olefins are more reactive than trans olefins torward porphyrin-catalyzed epoxidation by iodosylbenzene.[12,18] The degree of this selectivity has been shown to be sensitive to relatively small changes in the steric environment of the porphyrin. On this basis, an approach of the olefin to the oxoiron group from the side and parallel to the plane of the porphyrin ring as in **7** is indicated.

The opposite corner arrangement of the $\alpha,\beta,\alpha,\beta$-atropisomer chiral appendages apparently does not allow approach of the olefin to the oxoiron intermediate without chiral interactions at the periphery. The least hindered approach to the $\alpha,\alpha,\beta,\beta$ catalyst would be expected to be from the side opposite the chiral groups (**8**). Since negligible interactions between the approaching olefin and the chiral center are expected for such a geometry, the racemic product is understandable in these terms.



8

The lack of any asymmetric induction with the μ-oxo dimer (FeT-α-HydPP)$_2$O suggests that the oxo bridge is labile under the reaction conditions and that oxygen transfer was taking place at the unhindered and achiral β-face of this catalyst.

Comparison of the results obtained for styrene with those of *cis*- and *trans*-β-methylstyrene indicated that approach to the *re* face of the styrene double bond was preferred in each case. The decrease in asymmetric induction upon methyl substitution must be due to interference with the *re* face preference of the ((*R*)-hydratropamidophenyl)porphyrin **3**. Inspection of space-filling models does not reveal an obvious preference for the mode of approach of styrene depicted in **7**, not a surprising result in light of the small energy differences involved.

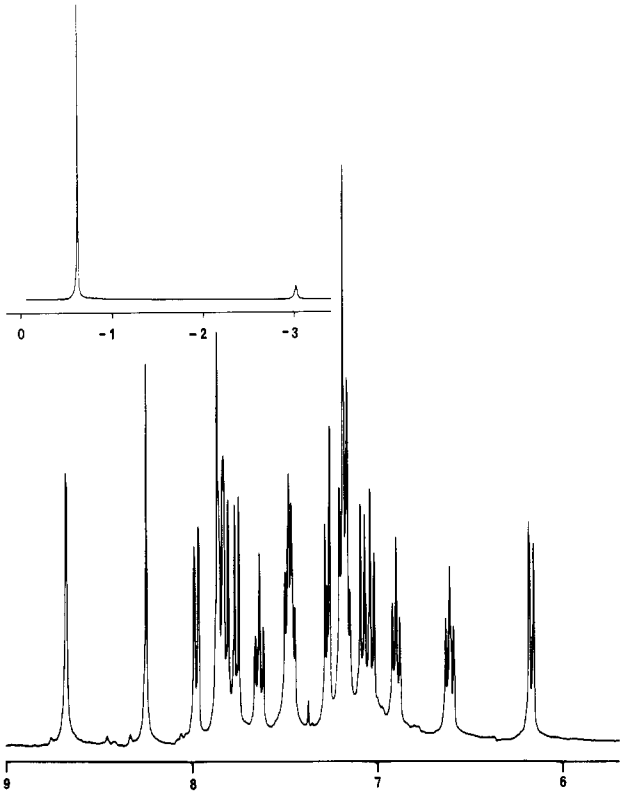


Figure 1. Proton NMR spectrum at 350 MHz of H$_2$T($\alpha,\beta,\alpha,\beta$-Binap)PP, **9**, in $CDCl_3$ at room temperature; units are δ relative to tetramethylsilane.

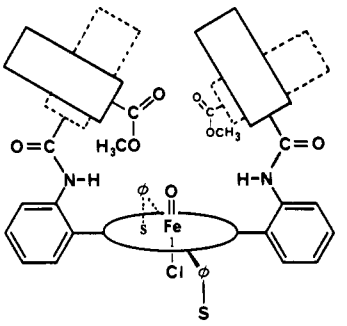


Figure 2. Idealized molecular geometry of oxidized FeT($\alpha,\beta,\alpha,\beta$-Binap)PPCl, **10**.

Chiral Epoxidation with the ([Binaphthylcarboxyamido]-phenyl)porphyrin FeT($\alpha,\beta,\alpha,\beta$-Binap)PPCl, 10. The binaphthyl group as a potential porphyrin appendage has the useful property of creating a relatively large and possibly rigid chiral cavity around the iron–porphyrin core of the catalyst.[20] To this end the diacid chloride[21] of 1,1′-binaphthyl-2,2′-dicarboxylic acid[22] was reacted with $\alpha,\beta,\alpha,\beta$-H$_2$TAPP (**2**) and then with methanol to produce 5α,10β,15α,20β-tetrakis(*o*[(*S*)-2′-carboxymethyl-1,1′-binaphthyl-2-carboxamido]phenyl)porphyrin (H$_2$T($\alpha,\beta,\alpha,\beta$-Binap)PP, **9** (Scheme III).

The ^{1}H NMR spectrum of **9** (Figure 1) was consistent with a single porphyrin with the symmetry expected for the $\alpha,\beta,\alpha,\beta$-atropisomer. The resonance of the methyl ester protons was observed at δ −0.72 relative to Me_4Si. This unusally high-field position is indicative of a conformation of the binaphthyl groups such that the methyl lies directly above the porphyrin ring. Such a conformation allows the larger end of the binaphthyl group to

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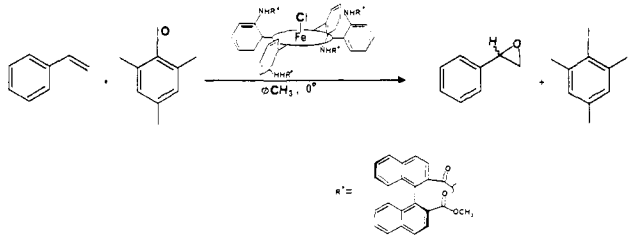
Table II. Catalytic Asymmetric Epoxidations with FeT($\alpha,\beta,\alpha,\beta$-Binap)PPCl[a] (10)

substrate	yield	epoxide/ aldehyde	configuratn	ee[b]
styrene	67	5	(R)-(+)	48
		5	(R)-(+)	41.4
p-chlorostyrene		12	(+)	50
	63[c]		(+)	51
p-methylstyrene	75.5	0.82	(+)	43.5
p-nitrostyrene		10	(+)	36
o-methylstyrene	58	1.34	(−)	15.6[d]
2-vinylnaphthalene		1.66	(+)	36
1-vinylnaphthalene		1.48	(−)	25[d]
trans-β-methylstyrene		*e*	(1*R*,2*R*)-(+)	7.2
1-octene	31[f]	*e*		20
1-methylcyclohexene		*e*		0[g]

[a] Reactions in toluene at 0 °C with iodosylmesitylene. [b] From integration of the *E* proton resonance of the epoxide. [c] At −23 °C; 7.5% *p*-chlorophenylacetaldehyde was also detected. [d] From integration of the *Z* proton resonance. [e] Small amounts of aldehyde were detected. [f] In methylene chloride with iodosylbenzene. [g] From integration of the methyl resonance.

Scheme IV



avoid contact with the porphyrin ring. As in the case of H_2T-($\alpha,\beta,\alpha,\beta$-Hyd)PP (**3**), the β-pyrrole hydrogens appeared at two singlets at δ 8.67 and 8.24.

Attempts to metalate $H_2T(\alpha,\beta,\alpha,\beta$-Binap)PP with ferrous bromide in THF were unsuccessful, presumably due to the hindered nature of this porphyrin. Reaction of **9** with iron pentacarbonyl and iodine[23] and subsequent chromatography on alumina led to an 84% yield of chloro[5α,10β,15α,20β-tetrakis(*o*-[(*S*)-2′-carboxymethyl-1,1′-binaphthyl-2-carboxamido]phenyl)-porphyrinato]iron(III) (FeT($\alpha,\beta,\alpha,\beta$-Binap)PPCl, **10**).

An idealized molecular diagram of the iron–oxo complex of FeT($\alpha,\beta,\alpha,\beta$-Binap)PPCl, **11**, is shown in Figure 2. Inspection of this diagram reveals that all approaches to the iron–oxo center are such that a substrate molecule will encounter a carbomethoxy group on the left and the edge of a naphthalene ring on the right.

Results of the epoxidation of various olefins with this catalyst and iodosylmesitylene in toluene are presented in Table II. The enhanced solubility of iodosylmesitylene in toluene allowed the reaction to proceed at a reasonable rate. Under these conditions reactions were complete after 12 h at 0 °C with 0.625% porphyrin catalyst, relative to iodosylmesitylene (Scheme IV). The formation of iodoxylmesitylene accounted for the remainder of the oxidant.

Optical yields for these reactions were conveniently measured with the chiral shift reagent tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III) [Eu(hfc)$_3$]. For most monosubstituted epoxides the ^{1}H NMR resonance due to the epoxide proton *E* to the substituent group was found to separate into two apparent triplets. The ratio of intensities of these peaks was taken as the ratio of enantiomeric epoxides. As expected, racemic epoxides showed a 1:1 ratio in each case. Data obtained in this manner for *p*-chlorostyrene and 2-vinylnaphthalene are shown in Figure 3.

No clear trend was evident upon changing the para substituent on the phenyl group. Competitive oxidations of these substrates have shown large differences in reactivity under these conditions

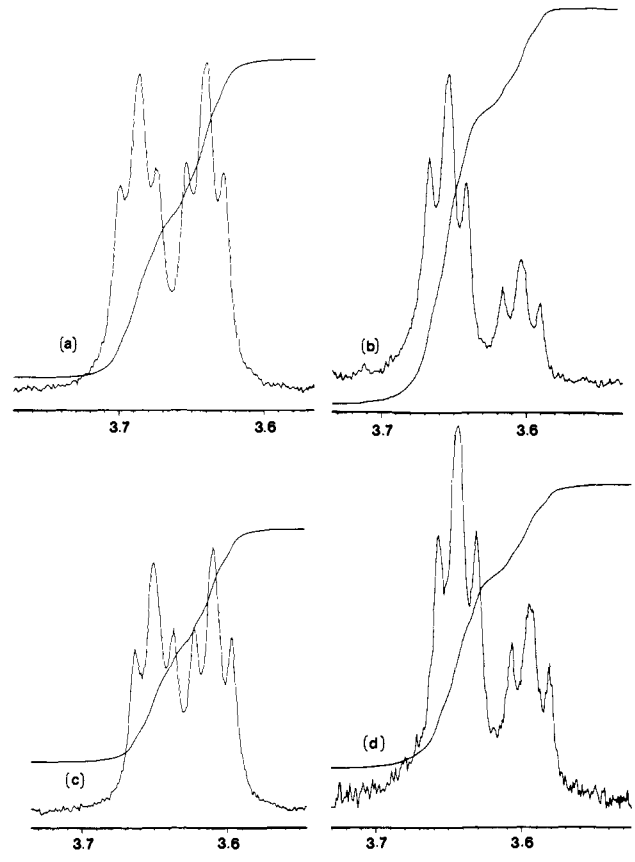


Figure 3. Eu(hfc)$_3$-shifted, proton NMR spectra at 350 MHz of chiral and racemic epoxides (units in δ relative to Me_4Si): (a) racemic *p*-chlorostyrene oxide; (b) chiral *p*-chlorostyrene oxide produced by **10**; (c) racemic 2-vinylnaphthalene oxide; (d) chiral 2-vinylnaphthalene oxide produced by **10**.

as expected for our electrophilic oxidant.[19b] Apparently, any changes in transition-state geometry upon varying the electronic properties of the substituent were too small to be reflected in diastereomeric, nonbonded interactions between the substrate and the chiral periphery of the catalyst.

Changes in the steric environment of the olefin had a pronounced effect on asymmetric induction. Substitution of either the phenyl group, as in *o*-methylstyrene and 1-vinylnaphthalene, or the double bond, as in *trans*-2-methylstyrene and 2-methylcyclohexene, resulted in significantly lower enantiomeric excesses. These changes are not as expected since increasing the size of substituent groups should have increased nonbonded interactions between the catalyst and the substrate. Inspection of space-filling models suggests that the degree of asymmetry around the double bond has decreased upon substitution and, accordingly, differences in the diastereomeric transition state energies for *si* and *re* approach may have also decreased.

As noted above, the stoichiometry of these reactions required the catalyst to undergo at least 100 catalytic cycles. When a sample of used catalyst (FeT($\alpha,\beta,\alpha,\beta$-Binap)PPCl) (**10**) was purified, reisolated, and committed to another oxidation of styrene, an enantiomeric excess of only 26.7% was observed. This decrease in asymmetric induction indicates that the catalyst has been altered in some way. By inference, enantiomeric excesses for the first few cycles of fresh catalyst may be larger than those reported in Table II.

The formation of aldehydes in these reactions is noteworthy. Control experiments have shown that negligible rearrangement of styrene oxide occurred under the reaction conditions although significant rearrangment did take place in the GC injector port. Accordingly, the rearrangement to form aldehydes must be competitive with epoxide formation. A reasonable interpretation, consistent with the enhanced epoxidation rates of styrenes with electron-releasing para substituents, is an unsymmetrical transition

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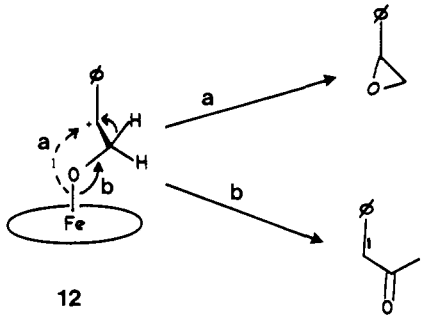
state such as **12** which can close to give epoxide (path a) or rearrange to give aldehyde (path b). This latter path is exactly



analogous to the celebrated NIH shift. The NIH shift has often been taken as evidence for an arene oxide precursor but, as the present example indicates, an oxy-substituted carbonium ion from any source would be expected to rearrange in this way.[24]

Significant catalytic asymmetric epoxidations have been demonstrated for a series of olefins that can only have nonbonded interactions with the catalyst. The asymmetric inductions observed confirm our earlier conclusion that an oxidized iron porphyrin is responsible for oxygen transfer from iodosylbenzene. The enantiometric excesses observed with these two chiral porphyrins appear to be limited by the conformational mobility of the chiral appendages and by the degradation of the catalyst.

Experimental Section

General Data. Gas chromatography was performed on Varian Instruments Model 1200 or 3700 using flame ionization detectors. GLPC integrations were measured by using a Hewlett-Packard 3380 A or Spectra Physics SP 4100 integrator recorders. Mass spectra were obtained on a Du Pont Instruments Dimaspec 321 GC/MS or a Finnegan Model 4021 GC/MS. NMR spectra were taken on a Varian T-60A, JEOL DS-100, or Brüker WM 360 NMR spectrometer. Chemical shifts are reported relative to Me_4Si. Infrared spectra were taken on a Beckman IR 4240 or Perkin-Elmer 457 instrument. Visible spectra were measured on a Varian Cary 219 spectrometer. Rotations were measured on a Jasco ORD/UV-5 optical rotatory dispersion recorder or a Perkin-Elmer 241 polarimeter as solutions in benzene.

Synthesis and Resolution of Chiral Appendages. (*R*)-2-Phenylpropanoyl Chloride (Hydratropoyl Chloride). The resolution of (*R*)-(−)-2-phenylpropionic acid was performed as described by Pettersson.[15] To 2.50 g (16.7 mmol) of (*R*)-(−)-2-phenylpropionic acid was added 2.96 mL (41.6 mmol) of thionyl chloride and several boiling stones to promote evolution of gas. The solution was allowed to stand for several hours. After removal of the boiling stones excess thionyl chloride was distilled away under aspirator pressure. The acid chloride was distilled (40–41 °C at 0.12 mm) to yield 4.43 g (6.3 mmol). No free acid was detectable by IR spectroscopy: IR (thin film) 3035 (sh), 2990 (sh), 1785 (s), 1600 (w), 1587 (w), 1495 (s), 1455 (sh), 910 (s), 710 (s) cm^{-1}.

(*R*)-2-Phenylpropanoyl chloride (25 μL) was allowed to react with excess 1-borneol (Aldrich Chemical Co.) and a few drops of pyridine in tetrahydrofuran. Analysis of the product diasteriomeric esters by GLPC (Carbowax 20 M, 30-m capillary, 175 °C) showed two peaks in a ratio of 3:97. The acid chloride was thus determined to be 97% optically pure.

(*S*)-(−)-1,1′-Binaphthyl-2,2′-dicarboxylic Acid. The synthesis, isolation, and resolution of (*S*)-(−)-1,1′-binaphthyl-2,2′-dicarboxylic acid have been reported by Hall and Turner[22] ($[\alpha]^{27}_{598}$ −111.4°, $[\alpha]^{27}_{546}$ −130.1°; reported $[\alpha]^{22}_{579}$ −108.6°, $[\alpha]^{22}_{546}$ −125.2°).

Diacid Chloride of 1,1′-Binaphthyl-2,2′-dicarboxylate (13). The diacid chloride **13** was prepared in small quantities according to the procedure of Mislow and Grasemann[21] (mp 177–178 °C; reported 173–177 °C). Yields could be improved by further extraction of the salts with carbon tetrachloride. Formation of the diacid chloride has been shown to proceed without racemization of the binaphthyl moiety.

Chiral Porphyrin Syntheses. 5α,10β,15α,20β-Tetrakis(*o*-(*R*)-hydratropamidophenyl)porphyrin ($H_2T(\alpha,\beta,\alpha,\beta$-Hyd)PP, 3). The procedure used was similar to that employed by Collman et al.[14] for the synthesis of 5α,10α,15α,20α-tetrakis(*o*-pivalamidophenyl)porphyrin. To 75 mL of dry (P_4O_{10}) methylene chloride was added 0.715 g (1.06 mmol) of 5α,10β,15α,20β-tetrakis(*o*-aminophenyl)porphyrin (H_2-α,β,α,β-TAPP, 2), 0.7 mL of pyridine, and 1.00 g (5.93 mmol) of (*R*)-(−)-2-phenylpropanoyl chloride (hydratropyl chloride). This solution was stirred for 2 h under nitrogen, and then 30 mL of 10% aqueous ammonium hydroxide was added and the solution stirred for an additional hour. The organic layer was separated and washed twice with water and once with saturated brine. Methylene chloride was removed and the material was chromatographed on silica gel (Woelm, activity I) with chloroform–ether (4:1) as the eluting solvent. Removal of solvent yielded 1.22 g (1.01 mmol) of product **3**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.76 (4 H, d, J = 8.0 Hz), 8.65 (4 H, s), 8.48 (4 H, s), 7.98 (4 H, d, J = 7.6 Hz), 7.88 (4 H, t, J = 8.0 Hz), 7.57 (4 H, t, J = 7.6 Hz), 6.81 (4 H, s), 5.69 (8 H, d, J = 7.3 Hz), 5.11 (8 H, d,d, J = 7.3, 7.0 Hz), 4.87 (4 H, t, J = 7.0 Hz), 2.73 (4 H, q, J = 7.3 Hz), 0.85 (12 H, d, J = 7.3 Hz), −3.01 (2 H, s); vis (CH_2Cl_2) λ_{max} 421 nm (ε 325 000 cm^{-1} m^{-1}), 482 (3300) 513 (19 600), 546 (4340), 588 (6120), 644 (1740). Anal. Calcd for $C_{80}H_{66}H_8O_4$: C, 79.84; H, 5.53; N, 9.31. Found: C, 79.62; H, 5.78; N, 9.06.

The α,α,β,β- and α,α,α,α-hydratropoyl derivatives were synthesized in an identical manner.

5α,10β,15α,20β-Tetrakis(*o*-[(*S*)-2′-carboxymethyl-1,1′-binaphthyl-2-carboxamido]phenyl)porphyrin ($H_2T(\alpha,\beta,\alpha,\beta$-Binap)PP, 9). To 100 mL of dry (P_4O_{10}) methylene chloride was added 1.00 g (1.48 mmol) of H_2-α,β,α,β-TAPP (**2**), 3.3 g (8.7 mmol) of the diacid chloride in 1,1′-binaphthyl-2,2′-dicarboxylate, and 3 mL of pyridine. This mixture was stirred under nitrogen for 3 h and 2 mL of methanol added. After 30 min, the reaction mixture was diluted to 300 mL with methylene chloride and extracted twice with water and once with saturated brine. Two major products of very similar R_f were observed. These two products were separated by silica gel (Woelm, activity I) chromatography using benzene–ether–ethyl acetate (94:4:2) as the eluting solvent mixture. Due to the difficultly of separation only 310 mg of the desired product was obtained in pure form. The major impurity of similar R_f has been tentatively identified by its NMR spectrum as the product derived by a single binaphthyl bridging between two porphyrins. The amount of product **9** obtained was sufficient for the studies designed: ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.67 (4 H, s), 8.24 (4 H, s), 7.97 (4 H, d, J = 8.4 Hz), 7.79–7.86 (16 H, m), 7.75 (4 H, d, J = 8.4 Hz), 7.62 (4 H, t, J = 8.0 Hz), 7.49–7.43 (8 H, m), 7.25 (4 H, d, J = 8.4 Hz), 7.14–7.19 (12 H, m), 7.07 (4 H, d, J = 8.4 Hz), 7.02 (4 H, d, J = 8.0 Hz), 6.87–6.91 (4 H, m), 6.58–6.62 (4 H, m), 6.15 (4 H, d, J = 8.4 Hz), −0.72 (12 H, s), −3.12 (2 H, s); IR ($CHCl_3$) 3320 (m), 3075 (m), 2960 (m), 1715 (s), 1680 (s), 1585 (sh), 1520 (s), 1450 (s), 1275 (s) cm^{-1}; vis (CH_2Cl_2) λ_{max} 423 nm (ε 252 000 cm^{-1} M^{-1}), 484 (3200), 515 (15 400), 547 (3970), 590 (5080), 645 (1620). Anal. Calcd for $C_{136}H_{90}N_8O_{12}$: C, 80.54; H, 4.47; N, 5.52. Found: C, 80.49; H, 4.47; N, 5.49.

Chiral Ferric Porphyrins. Chloro[5α,10β,15α,20β-tetrakis(*o*-(*R*)-hydratropamidophenyl)porphyrinato]iron(III) (FeT(α,β,α,β-Hyd)PPCl, 4). To 30 mL of dry (distilled from LAH), deoxygenated tetrahydrofuran was added 1.20 g (1.0 mmol) of $H_2T(\alpha,\beta,\alpha,\beta$-Hyd)PP, 1.5 g of anhydrous ferrous bromide,[25] and 0.4 mL of 2,6-lutidine. This reaction is most conveniently carried out in a glovebox due to the ease of oxidation of the ferrous salt. The mixture was allowed to stir for 4 h at room temperature and then exposed to air and allowed to stir for several hours more. Solvent was removed and the residue chromatographed on alumina (Woelm, basic, activity III) with chloroform as the eluent. The effluent was washed twice with 10% hydrochloric acid and filtered through sodium chloride. Solvent was removed to yield 1.22 g (944 μmol) of product: vis (CH_2Cl_2) λ_{max} 379 nm (ε 49 400 cm^{-1} M^{-1}), 419 (99 800), 509 (12 800), 579 (4020), 649 (37 500), 672 (3050). Anal. Calcd for $C_{80}H_{64}N_8O_4FeCl$: C, 74.33; H, 4.99; N, 8.67. Found: C, 73.99; H, 5.18; N, 8.58.

Chloro[5α,10α,15β,20β-tetrakis(*o*-(*R*)-hydratropamidophenyl)-porphyrinato]iron(III) (FeT(α,α,β,β-hyd)PPCl, 5). The procedure was identical with that used for the preparation of FeT(α,β,α,B-Hyd)PPCl (**4**) except that the α,α,β,β-atropisomer was substituted for α,β,α,β: vis (CH_2Cl_2) λ_{max} 379 nm (ε 46 000 cm^{-1} M^{-1}), 419 (88 300), 509 (12 400), 579 (4470), 649 (3830), 672 (3300). Anal. Calcd for $C_{80}H_{64}N_8O_4FeCl$: C, 74.33; H, 4.99; N, 8.67. Found: C, 74.11; H, 5.13; N, 8.49.

(μ-Oxo)bis([5α,10α,15α,20α-tetrakis(*o*-(*R*)-hydratropamidophenyl)-porphyrinato]iron(III)) ((FeT-α-HydPP)$_2$O, 6). The procedure used was identical with that used for the preparation of FeT(α,β,α,β-Hyd)PPCl (**4**) except that the α,α,α,α,-atropisomer was substituted for α,β,α,β. Effluent from the alumina column gave the μ-oxo dimer (i.e., no treatment with HCl): vis (CH_2Cl_2) λ_{max} 412 nm (ε 173 000 cm^{-1} M^{-1}), 568 (18 700), 605 (6270). Anal. Calcd for $C_{160}H_{128}N_{16}O_9Fe_2$: C, 75.94; H, 5.10; N, 8.86. Found: C, 75.70; H, 5.26; N, 8.82.

Chloro[5,10,15,20-tetra(α,β,α,β-*o*-[(*S*)-2′-carboxymethyl-1,1′-binaphthyl-2-carboxamido]phenyl)porphyrinato]iron(III) (FeT(α,β,α,β-Binap)PPCl, 10). The procedure used was a modification of that re-

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ported by Buchler and Lay for metalation of porphodimethenes.[23] A mixture of 150 mg (73.9 μmol) of $H_2T(\alpha,\beta,\alpha,\beta$-Binap)PP, 26 mg (102 μmol) of iodine, 595 mg (0.410 mL, 3.038 mmol) of iron pentacarbonyl, and 30 mL of dry (Na) degassed toluene were stirred for 3 h at 55 °C under nitrogen. The reaction mixture was then allowed to stir for several hours open to air and then chromatographed on alumina (Woelm, neutral, activity I) eluting first with methylene chloride to remove unreacted porphyrin and then with a methylene chloride–methanol (95:5) mixture to remove the metalated material. The effluent was diluted with methylene chloride and washed twice with 5% aqueous hydrochloric acid. The solution was dried by filtration through sodium chloride, and the solvent was removed to yield 131 mg (62.1 μmol) of product **10** (84%): vis (CH_2Cl_2) λ_{max} 422 nm (ϵ 116 000 cm^{-1} M^{-1}), 511 (12 200), 587 (4710), 647 (3900), 699 (2900). Anal. Calcd for $C_{136}H_{88}N_8O_{12}FeCl$: C, 77.14; H, 4.19; N, 5.29. Found: C, 76.42; H, 4.53; N, 5.11.

Epoxidations. Oxidation of Styrene by FeT($\alpha,\beta,\alpha,\beta$-Hyd)PPCl (4) and Iodosylbenzene. To 10 mL of methylene chloride was added 40.66 mg (31.45 μmol) of FeT($\alpha,\beta,\alpha,\beta$-Hyd)PPCl (**4**) and 0.30 mL (2.618 mmol) of freshly distilled styrene. The reaction mixture was cooled to −8 °C (ice–salt bath) under nitrogen. Over a period of 3 h 175 mg (795.4 μmol) of solid iodosylbenzene was added, maintaining the temperature at −5 ± 2 °C throughout. After the addition of all the iodosylbenzene, the reaction was allowed to stir for an additional 45 min. The chemical yield of oxidation was determined to be approximately 65% based on iodosylbenzene (an insoluble precipitate of iodoxybenzene was also formed) as determined by GLPC (Carbowax 20 M, 30-m capillary, 130 °C). In addition to expected iodobenzene (retention time of 4.90 min) and styrene oxide (retention time of 6.51 min), phenylacetaldehyde (retention time of 7.10 min) was also observed. This product was to some extent the result of rearrangement in the injector port (250 °C) as was determined by the injection of standard styrene oxide (Aldrich Chemical Co.). Oxidation products were isolated by column chromatography. After removal of the methylene chloride, the entire reaction mixture was deposited on a silica gel column as a pentane slurry. Iodobenzene and unreacted styrene were eluted with pentane (100 mL). Oxidation products (63 mg) were eluted with pentane–ether (85:15). The ^1H NMR spectrum indicated that the styrene oxide to phenylacetaldehyde ratio was 75:25. It was determined, by subjecting a portion of pure styrene oxide to the reaction conditions in the presence of the catalyst and the same work-up procedure, that the source of phenylacetaldehyde was not due to the workup. Polarimetric measurement of the oxidation product dissolved in benzene determined that (*R*)-(+)-styrene oxide[26] was formed in excess.

Approximately 50 mg of the oxidation product was dissolved in 5 mL of tetrahydrofuran and 3.5 mL of 0.58 M lithium aluminum hydride in tetrahydrofuran. The mixture was allowed to stir for 45 min under nitrogen and then the excess reducing agent quenched by the dropwise addition of water. The entire mixture was then centrifuged and the solvent pipetted from the precipitated lithium salts. The salts were washed with tetrahydrofuran, and the centrifuging process was repeated. Removal of the tetrahydrofuran and analysis by GLPC revealed the formation of 1-phenylethanol (~72%) as well as 2-phenylethanol (~28%). The alcohols were diluted in 3 mL of dry tetrahydrofuran and several drops of pyridine added. To this mixture was added 150 μL of (*R*)-2-phenylpropanoyl chloride. The reaction was allowed to stir for at least 1 h, and the product diastereomeric esters were analyzed by GLPC (Carbowax 20 M, 30-m capillary, 190 °C). Three peaks were observed, the first (retention time of 20.42) and second (retention time of 22.82) of which coinjected with diastereomeric esters derived from reaction with inactive 1-phenylethanol (Aldrich Chemical Co.). The third peak (retention time of 31.0 min) coinjected with ester derived from 2-phenylethanol (Aldrich Chemical Co.). The ratio of the first two peaks indicated that a 31% ee had been achieved in the epoxidation reaction (after correcting for the fact that (*R*)-2-phenylpropanoyl chloride was 97% optically pure). The reaction and analysis of the other substrates in Table I were conducted in a manner identical with that used for styrene oxidation.

Oxidation of Styrene Catalyzed by FeT($\alpha,\alpha,\beta,\beta$-Hyd)PPCl (5) and (FeT-α-Hydpp)$_2$O (6). The reaction procedure was in all respects idetical with that used in the epoxidation of styrene by FeT($\alpha,\beta,\alpha,\beta$-Hyd)PPCl (**4**) and iodosylbenzene except FeT($\alpha,\alpha,\beta,\beta$-Hyd)PPCl (**5**) and (FeTα-HydPP)$_2$O (**6**) were employed. Analysis of the products in an identical manner revealed no asymmetric induction with either catalyst.

Epoxidation of Styrene by FeT($\alpha,\beta,\alpha,\beta$-Binap)PPCl (10) and Iodosylmesitylene. The epoxidation of styrene by FeT($\alpha,\beta,\alpha,\beta$-Binap)PPCl (**10**) and iodosylmesitylene was carried out in a manner similar to that described above for FeT($\alpha,\beta,\alpha,\beta$-Hyd)PPCl. Styrene oxide (retention time of 8.34 min) and phenylacetaldehyde (retention time of 8.74 min) were produced in 76% yield based on iodomesitylene (retention time of 19.50 min) as determined by GLPC (105 °C initial, 10 min, 3 °C/min, 135 °C final). Isolation of the oxidation products and qualitative polarimetric determination of rotation revealed that (*R*)-(+)-styrene oxide was produced in excess. ^1H NMR spectral analysis of the products showed a 4.85:1 ratio of styrene oxide to phenylacetaldehyde. The oxirane proton trans[27] to the phenyl ring showed a resonance at δ 3.15 (d,d, J = 5.6, 4.2 Hz) in chloroform-*d* which shifted in a downfield direction when treated with the chiral shift reagent Eu(hfc)$_3$ (tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III)). After the addition of several equivalents of shift reagent, this resonance had separated into two resonances of unequal intensity, the larger appearing at δ 4.42 (m) and the smaller at δ 4.31 (m). The integrated ratio of these peaks showed that a 40% ee had been achieved in the epoxidation reaction. The inactive styrene oxide also showed two resonances, these being of equal intensity.

This entire reaction sequence was repeated, except that the reaction temperature remained isothermal (0 °C). The same pattern was observed when the product epoxide was treated with chiral shift reagent and the resonances at δ 3.56 (m) and 3.60 (m) revealed a 41.4% ee.

Styrene was also epoxidized (0 °C) by using catalyst that had been recycled from earlier epoxidation reactions. In this case, asymmetric induction in the epoxidation reaction decreased to 26.7% ee.

Oxidations and analyses of the other substrates were carried out analogously except as noted in Table II.

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Registry No. 2, 68070-28-0; **3**, 86457-67-2; **4**, 86457-73-0; **5**, 86495-91-2; **6**, 86457-74-1; **9**, 86457-68-3; **10**, 86457-75-2; **13**, 86457-66-1; $H_2T(\alpha,\alpha,\beta,\beta$-Hyd)PP, 86495-89-8; $H_2T(\alpha,\alpha,\alpha,\alpha$-Hyd)PP, 86495-90-1; FeT($\alpha,\beta,\alpha,\beta$-Hyd)PPBr, 86495-92-3; iodosylbenzene, 536-80-1; *cis*-β-methylstyrene, 766-90-5; *trans*-β-methylstyrene, 873-66-5; styrene, 100-42-5; *p*-chlorostyrene, 1073-67-2; *p*-nitrostyrene, 100-13-0; *o*-methylstyrene, 611-15-4; 2-vinylnaphthalene, 827-54-3; 1-vinylnaphthalene, 826-74-4; 1-octene, 111-66-0; (*R*)-(+)-styrene oxide, 20780-53-4; (1*R*,2*S*)-(−)-β-methylstyrene oxide, 934-45-2; (1*R*,2*R*)-(+)-β-methylstyrene oxide, 14212-54-5; iodosyl mesitylene, 75851-49-9; 1-methylcyclohexene, 591-49-1; (+)-*p*-chlorostyrene oxide, 21019-51-2; (+)-*p*-methylstyrene oxide, 86457-69-4; (+)-*p*-nitrostyrene oxide, 78038-42-3; (−)-*o*-methylstyrene oxide, 86457-70-7; (+)-2-vinylnaphthalene oxide, 86457-71-8; (−)-1-vinylnaphthalene oxide, 86457-72-9; (*R*)-2-phenylpropanoyl chloride, 36240-11-6; (*R*)-(−)-2-phenylpropionic acid, 7782-26-5; (*S*)-(−)-1,1′-binaphthyl-2,2′-dicarboxylic acid, 18531-96-9; ferrous chloride, 7789-46-0.

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