Pergamon

Tetrahedron, Vol. 53, No. 33, pp. 11277-11296, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00730-8

Synthesis and Catalytic Reactivity of Sterically and Electronically Modified D_4-Symmetric Metallotetraarylporphyrins

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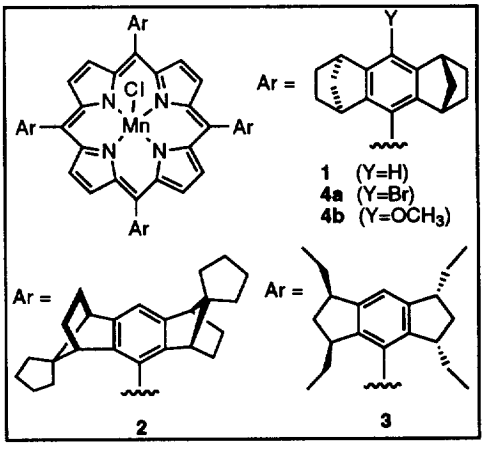
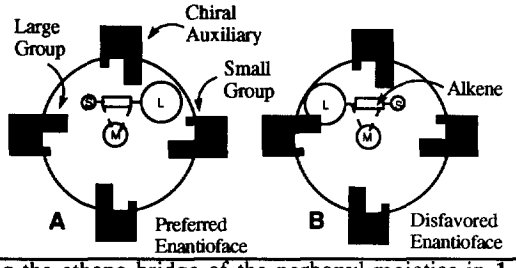
Abstract: Two new sterically-modified and two electronically-modified D_4-symmetrical tetraarylporphyrin ligands have been prepared and the catalytic activity of their manganese complexes in epoxidations of aryl-substituted alkenes studied. Moderate reactivity changes were observed in catalytic epoxdiations with these electronically varied tetraaarylporphyrin complexes, the methoxy derivative giving slightly improved selectivity (83% e.e. with cis-ß-methylstyrene). © 1997 Elsevier Science Ltd.

Since Groves published the first application of synthetic chiral metallotetraphenylporphyrins in catalytic asymmetric epoxidations of unfunctionalized alkenes in 1983,[1] the synthesis and application of new chiral metallotetraphenylporphyrins in catalytic asymmetric epoxidations of unfunctionalized alkenes have received considerable attention.[2] We reported that the first published D_4-symmetric metallotetraphenylporphyrin **1** gave up to 76% e.e. in the epoxidation of cis-β-methylstyrene and up to 6,800 turnovers and 56% e.e. within 24 h in the epoxidation of styrene.[3] In an effort to modify the reactivity of metalloporphyrin **1**, we are engaged in the preparation of derivatives of **1** and report here the synthesis and catalytic epoxidation results of sterically modified D4-symmetric[4] metalloporphyrin complexes **2** and **3** and complexes **4a** and **4b** which contain electronically modified arenes.



From the epoxidation results obtained with complex **1**, we postulated the sterically-based model in Figure 1 to explain the observed enantioselectivity. In this model the larger substituent on the alkene preferentially approaches the metal near the smaller substituent on the chiral auxiliary. By preparing

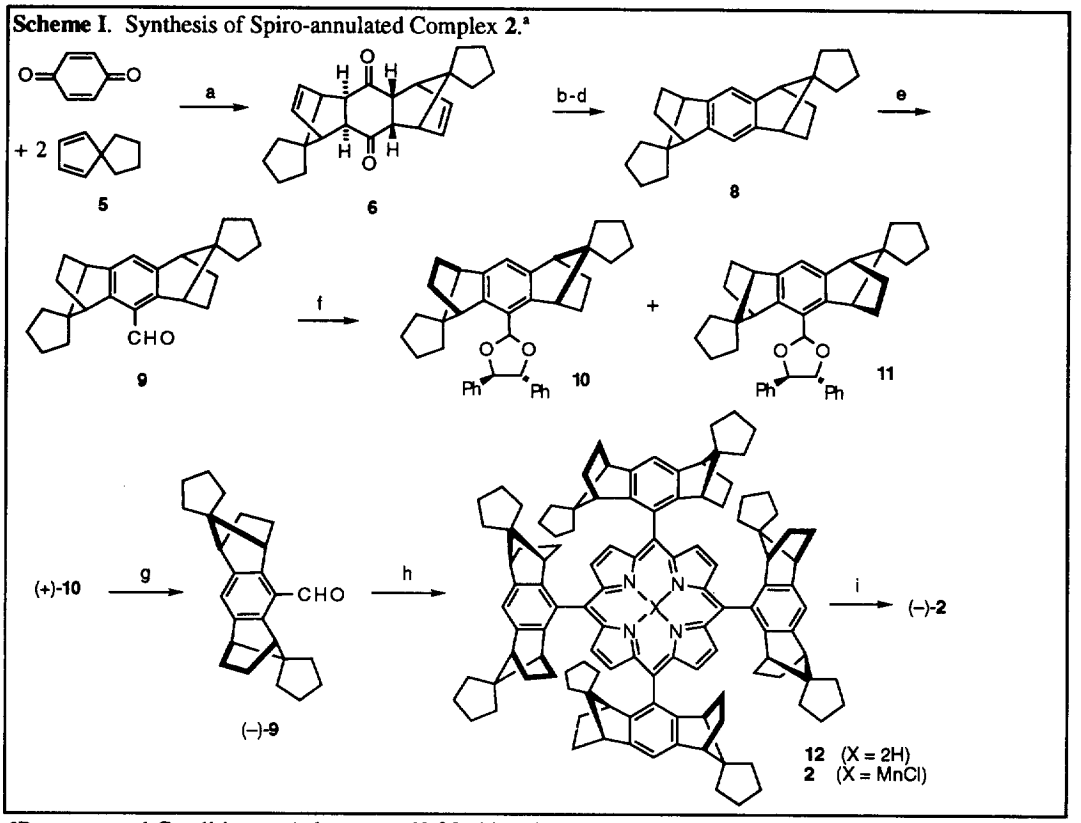
Figure 1. Model for Epoxidation with D_4-Symmetrical Metallotetraphenylporphyrins



modified catalysts with sterically modified groups on the arenes we hoped to alter the shape and selectivity of the catalyst. Increasing the substitution on the postulated small methano-bridge as in the "spiro-annulated" complex **2** was expected to decrease selectivity, but aid our understanding of these catalysts' shape-reactivity relationships. By opening the ethano-bridge of the norbonyl moieties in **1** we could prepare the "ring-opened" catalyst **3** which we expected to have a larger steric differentiation between small and large groups in our catalyst. Based on the observed perturbation of enantioselectivity of electronically modified chiral manganese salen complexes,[5] we determined the sensitivity of para-substitution on selectivity using complexes **4**.

Preparation of Spiro-Annulated Complex 2. By starting with spiro-pentane annulated cyclopentadiene[6] and generally following our original synthetic approach[3] we prepared the modified tetraphenylporphyrin chloromanganese complex **2** as shown in Scheme I. The initial Diels-Alder reaction with substituted cyclopentadiene **5** in place of cyclopentadiene required a longer reaction time at higher temperature, but we isolated diketone **6** in good yield. The desired C_2-symmetrical relationship between the two substituted norbonyl groups annulated on the center ring is already nicely established in this initial reaction. The formation of the bis(tosyl hydrazone) of **6** was successful which enabled a Shapiro-type elimination[7] and DDQ oxidation[8] sequence to give arene diene **7**. Attempts to form the hydrazone after hydrogenation of diketone **6** failed, presumably due to the greater steric hindrance in the hydrogenated diketone. Arene **8** was obtained after hydrogenation of the norbornene double bonds. Formylation of **8** gave racemic C_2-symmetric benzaldehyde **9** which was converted into diastereomeric ketals **10** and **11** following our earlier procedure.[3] These diastereomers were separable by recrystallization of isomer **10** which was isolated in 33% (out of a maximum of 50% in the resolution). Through X-ray crystallographic analysis of crystalline ketal **10**, we were able to assign the absolute configuration of resolved aldehyde (–)-**9** which was liberated upon acidic deketalization of **10**. In the deketalization, a high yield of (*R,R*)-hydrobenzoin was recovered enabling the resolving agent to be recycled. The condensation of (–)-**9** with pyrrole in the presence of BF_3-Et_2O,[9] followed by p-chloranil oxidation then triethylamine quenching provided a good yield (28%) of the modified tetraarylporphyrin **12**. As in our earlier example, the use of C_2-symmetrical chiral benzaldehyde (–)-**9** allowed only the formation of a single tetraphenylporphyrin isomer whose NMR spectra exhibited D_4-symmetry. Manganese chloride was introduced as before[3,10] to give good quantitites of metallotetraphenylporphyrin (–)-**2** in 92% yield. The identification of the green paramagnetic complex **2** was based on its mass spectrum (FAB) m/z 1629 (M^+ - Cl + 1); 1628 (M^+ - Cl) and the shift of UV absorption band (λ_{max}) between porphyrin **12** (λ_{max} = 412 nm) and its manganese(III) complex **2** (λ_{max} = 478 nm).

Scheme I. Synthesis of Spiro-annulated Complex **2**.[a]



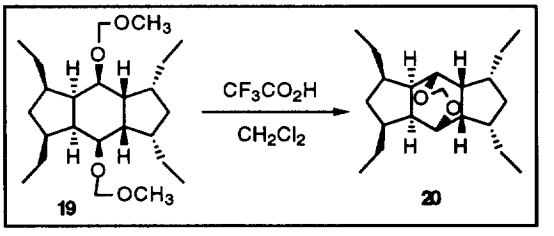
[a]Reagents and Conditions: a) benzene, 60 °C, 20 h, 88%; b) p-TsNHNH$_2$, CH_3CN, AcOH, 90 °C, 2 h; c) n-BuLi, THF, rt, 16 h; DDQ, 40 °C, 16 h, 70%; d) 1 atm H_2, 5% Pd/C, benzene, 23 °C, 15 h, 97%; e) Cl_2CHOCH_3 (1.5 equiv), $TiCl_4$ (2.0 equiv), CH_2Cl_2, -15 °C, 2 h, 93%; f) (R,R)-hydrobenzoin (1.2 equiv), PPTS (cat), benzene, 80 °C, 12 h, 86% mixture of diast.; pure **10** 35%; g) 1:4 3% H_2SO_4:THF, 70 °C, 2 h, 97%; h) pyrrole (1.0 equiv), BF_3-Et_2O (0.3 equiv), $CHCl_3$ 23 °C, 1.5 h; p-Chloranil (0.75 equiv), Et_3N (0.33 equiv), 60 °C, 1 h, 40%; i) $MnCl_2$-$4H_2O$ (10 equiv), DMF, 152 °C, 6 h; 1 N HCl extraction, 92%.

Preparation of Ring-Opened Complex 3. The preparation of the key benzaldehyde **23** needed for the synthesis of ring-opened complex **3** could be envisioned by an oxidative cleavage of the olefinic moieties in the known compound **13** followed by appropriate refunctionalization, aromatization and formylation (Scheme II). An alternative approach was aromatization of the central ring followed by oxidative cleavage, but the ensuing benzylic aldehydes were too prone to epimerization for this route to be pursued. In practice, the two hydroxyl groups in **13** were protected as methoxymethyl ether by reacting **13** with dimethoxymethane in an acid catalyzed acetal exchange reaction in 99% yield.[11] Attempts at a one-step conversion of **14** to tetraaldehyde **16** through ozonolysis gave rise to multiple products but a two step cis-dihydroxylation/oxidative cleavage was successful. Treatment of diene **14** with catalytic osmium tetraoxide[12] in the presence of excess aqueous 4-methylmorpholine-*N*-oxide (NMO) produced a single isomer of very water soluble tetraol **15** which could be isolated in 87% yield by continuous methylene

chloride extraction. Tetraol **15** was oxidatively cleaved with $NaIO_4$ in a 3:1 mixture of ethyl acetate and water at room temperature for 7 minutes to afford a mixture of the crude product.[13] Longer reaction times led to epimerization of the product. In the ^1H NMR spectrum of the crude product signals arising from the desired tetraaldehyde **17** were observed along with signals indicating the presence of a bridging hydrate side product **16**.[14] Water was azeotropically removed from a refluxing methylene chloride solution of the crude product mixture through a molecular sieve filled Soxhlet thimble to afford **17** in 88% yield. The symmetry evident in the ^{13}C and ^1H NMR spectra of **17** indicated a lack of epimerization in this two-step oxidative cleavage.

The Wittig reaction of **17** was conducted with pre-mixed methyltriphenylphosphonium bromide and *t*-BuOK at low temperature to hinder epimerization.[15] After removing the triphenylphosphine oxide through precipitation and filtration of the supernatant through a silica gel plug, the crude tetraolefin was purified by chromatography to afforded pure tetraene **18** in 55% yield. When the Wittig olefination was attempted at higher temperatures, epimerization was observed. Several methods for the catalytic hydrogenation of tetraene **18** were investigated including the use of Pd/C, PtO_2 and Rh/Al_2O_3 as catalysts with various solvents, hydrogen pressures and temperatures. In each of these cases, significant amounts of epimerized tetraethyl compounds were formed, presumably through an initial migration of one or more of the terminal alkenes followed by non-selective hydrogenation of the trisubstituted alkenes. Since each molecule has four sites for isomerization and since the epimerized products were inseparable this problem was significant. Fortunately, a diimide reduction through treatment of tetraene **18** with hydrazine hydrate/$CuSO_4$-$5H_2O$ in CH_3CH_2OH at room temperature was found to cleanly form the desired tetraethyl complex **19** in 52% yield.[16] Interestingly, the NMR spectra of **19** did not exhibit the expected symmetry due to unsymmetrical conformational preferences, but this compound was nicely crystalline and its structure was confirmed by X-ray crystallography.

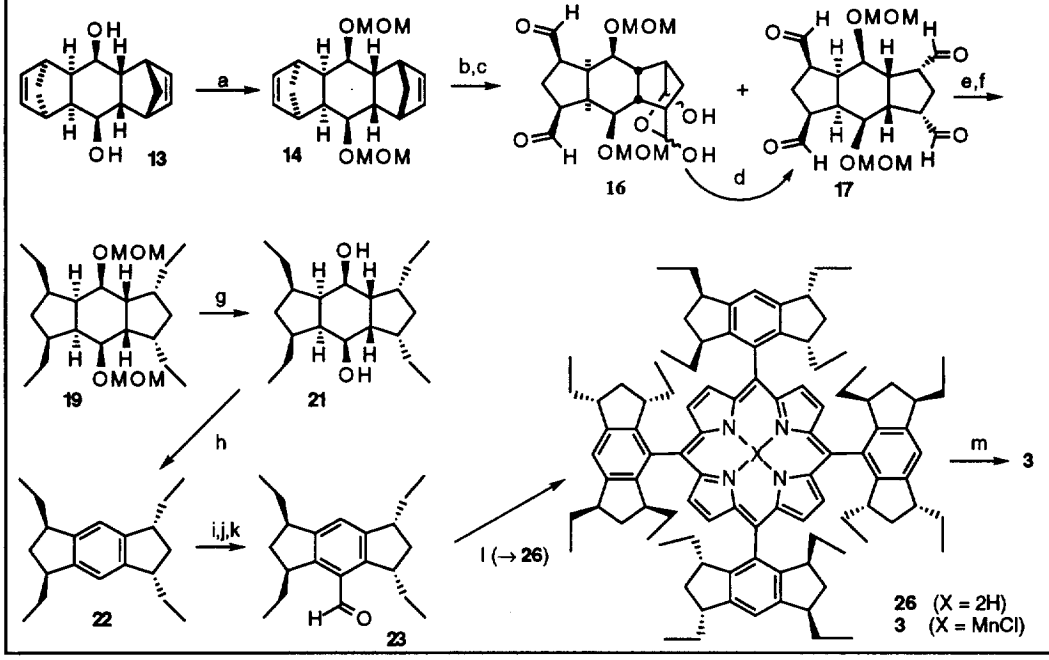
Attempted removal of methoxymethyl protecting group from **19** using a catalytic amount of CF_3CO_2H in methylene chloride, or acetic acid at 118 °C, or cat. HCl/THF/H_2O at 70 °C, or 2N HCl at 100 °C, or 85% H_3PO_4 at 105 °C all afforded the cyclic acetal **20** as the major product.[17] Cyclic acetal **20** was resistant to further acidic cleavage. When the deprotection of **19** was attempted under harsher acidic conditions (85% H_3PO_4 overnight at 125 °C) the removal of the methoxymethyl groups and the dehydration did take place, but these conditions led to an inseparable mixture of epimerized arenes.



A two step deprotection of **19** was successful through the use of trifluoroacetic anhydride and acetic acid in CH_2Cl_2 followed by potassium carbonate in refluxing methanol to provide **21** in 72% yield after column chromatography.[18] Since the direct dehydration of **19** using 85% H_3PO_4 overnight at 110 °C,[19] led to a mixture of epimerized arenes, a two step less-acidic route was successfully employed. Treatment of diol **21** with *p*-toluenesulfonyl chloride in pyridine at room temperature overnight and then at 55 °C for two days

afforded a crude mixture of diene (major) and arene (minor). This crude product mixture was directly treated with *p*-chloranil without to yield after chromatography arene **22** in 49% yield.

Scheme II Synthesis of "Ring-Opened" Tetraphenylporphyrin Complex **3**.[a]



[a]Reagents and Conditions: a) dimethoxymethane, p-TsOH, CH_2Cl_2, 40 °C, 5 d, 99%; b) OsO_4, NMO, acetone-water, 23 °C, 10 d, 87%; c) $NaIO_4$, EtOAc-water, rt, 7 min; d) CH_2Cl_2, 40 °C, mol. sieves, 15 h, 88%; e) Ph_3PCH_3Br, t-BuOK; -78 °C, THF 4 h, 55%; f) H_2NNH_2-H_2O, $CuSO_4$, EtOH, air, 24 h, 52%; g) AcOH, $(CF_3CO)_2O$, 23 °C, 6 h; h) p-TsCl, DMAP, pyridine, 23 °C, 16 h, 45 °C, 2 d; p-chloranil, benzene, 70 °C, 16 h, 49%; i) Cl_2CHOCH_3, $TiCl_4$, CH_2Cl_2, -78 °C, 2 h, 70%; j) (R,R)-hydrobenzoin, PPTS, benzene, 70 °C, 12 h; pure **24** 40%; k) 1:4 3% H_2SO_4:THF, 70 °C, 2 h, 89%; l) pyrrole (1.0 equiv), BF_3-Et_2O (0.3 equiv), $CHCl_3$ 23 °C, 1.5 h; p-Chloranil (0.75 equiv), Et_3N (0.33 equiv), 60 °C, 1 h, 5%; m) $MnCl_2$-$4H_2O$ (10 equiv), DMF, 152 °C, 6 h; 1 N HCl extraction, 92%.

When the formylation of arene **22** with $CHCl_2OCH_3/TiCl_4$ was conducted under the usual conditions[20] at -25 °C or -10 °C a mixture of aldehydes was observed–again presumably due to some epimerization of the benzylic positions. By lowering the temperature of formylation to -78 °C benzaldehyde **23** was obtained in 70% yield after purification.

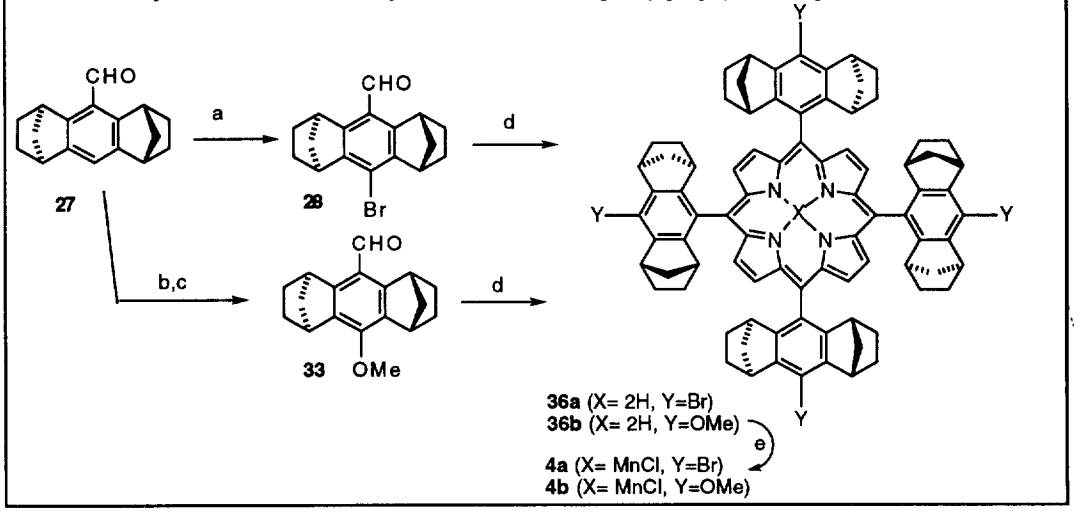
The racemic C_2-symmetric aldehyde **23** was resolved through the formation of diastereomeric ketals with (*R,R*)-hydrobenzoin and a catalytic amount of PPTs in refluxing benzene.[4] Recrystallization of the diastereomeric mixture afforded crystalline ketal **24** in 40% (based on maximum 50% yield for each diastereomeric acetal). The final mother liquor contained the second diastereomer **25** with 42% yield (based on maximum 50% yield). The configuration of these ketals was not determined. Acidic deketalization of

the crystalline ketal **24** followed by column chromatography afforded enantiomerically pure aldehyde (–)-**23** in 76% yield and a 89% recovery of unisomerized (*R,R*)-hydrobenzoin.

Condensation of **23** with pyrrole was conducted in CH_2Cl_2 in the presence of BF_3-OEt_2 for 2 h, followed by oxidation of the resultant tetraphenylporphyrinogen with *p*-chloranil then neutralization with triethylamine and chromatography afforded the pure porphyrin **26** (UV: λ_{max} 424 nm) in 5% isolated yield.[9] Manganese chloride was introduced by heating **26** with $MnBr_2$ in DMF overnight, followed by treatment with HCl to give the green manganese-porphyrin complex **3** (UV: λ_{max} 481 nm) in 92% yield.[10]

Electronically-Differentiated Tetraphenylporphyrin Complexes 4a and 4b. Although studies implicating the importance of electronic and steric effects on the stability and reactivity of metallotetraphenylporphyrins have been published, those studies were not able to address systematic changes on only the remote para position.[21] Since our key substituted benzaldehyde **27** has only the para position open, we were in a favorable synthetic position to undertake such a systematic study. We have prepared two new metallotetraphenylporphyrins **4a** and **4b** according to the reactions shown in Scheme II. Bromination[22] of racemic benzaldehyde **27** gave racemic bromoaldehyde **28** which was resolved using (*R,R*)-hydrobenzoin as before to give a mixture of diastereomeric acetals **29** and **30**. A pure crystalline diastereomer was obtained and converted to (–)-**28**. When a sample of aldehyde (+)-**27** of known configuration was brominated, (+)-**28** was obtained–enabling its assignment of absolute configuration. The resolved aldehdye (–)-**28** was condensed with pyrrole as before[3] to yield tetra(bromoaryl)porphyrin (–)-**36a**. Porphyrin **36a** was metalated to the manganese chloride complex (–)-**4a** in good yield.

Scheme III. Synthesis of Electronically-Differentiated Tetraphenylporphyrin Complexes **4a-b**.[a]



[a]Reagents and Conditions: a) Br_2, Fe, CCl_4, 23 °C, 24 h; 81%; b) $NaNO_2$, CF_3COOH, AcOH, 23 °C, 24 h, 89%; c) (i) MeOH, H_2O, $NaHCO_3$, 23 °C, 96 h; (ii) 2 N NaOH, dimethyl sulfate, THF, 80 °C, 24 h, 81%; d) (i) (R,R)-hydrobenzoin (1.2 equiv), PPTS (cat), benzene, 80 °C, 12 h; separation; (ii) 1:4 3% H_2SO_4:THF, 70 °C, 2 h; (iii) pyrrole (1.0 equiv), BF_3-Et_2O (0.3 equiv), $CHCl_3$ 23 °C, 1.5 h; p-Chloranil (0.75 equiv), Et_3N (0.33 equiv), 60 °C, 1 h; e) $MnCl_2$-$4H_2O$ (10 equiv), DMF, 152 °C, 6 h; 1 N HCl extraction.

In an effort to synthesize a nitro derivative of racemic benzaldehyde **27** according to standard aromatic nitration procedures,[23] we isolated instead a p-acetoxybenzaldehyde **31** which was hydrolyzed to the racemic phenol **32**. Phenol **32** was methylated to give p-methoxybenzaldehyde **33**. The ether **33** was resolved through diastereomic acetals **34** and **35** of (*R,R*)-hydrobenzoin to give (–)-**33**. This oxygenated derivative (–)-**33** were converted as before to tetraphenylporphyrin ligand (–)-**36b** which was metalated to the manganese chloride complex (–)-**3b** in good yield. The absolute configuration of methoxy-substituted complex **4b** was not determined, but was assigned based on its facial selectivity in epoxidation reactions (*vide infra*). Due to the number and modest yield of the steps used to convert **27** into **33**, it was more efficient to oxidize larger quantities of racemic **27** and then resolve the oxygenated benzaldehyde.

Catalytic Asymmetric Epoxidations. Following the same catalytic epoxidation reaction conditions previously employed for "spiro-annulated" complex **1** (200:1 substrate to **2** in the presence of excess NaOCl)[3] the spirocyclopentane-modified complex **2** did prove to be an active catalyst. Styrene (1 h, 5% e.e.), cis-ß-methylstyrene (4 h, 6% e.e.) and dihydronaphthalene (1 h, 7% e.e.) were all cleanly converted to their corresponding epoxides as stated. When a 2000:1 ratio of styrene to **2** was examined, the epoxidation was complete within 3 h and the enantiomeric excess of the product was the same. When catalyst **2** was recovered from an epoxidation run and was used in fresh epoxidation, its reaction rate and enantioselectivity were identical as above. The small enantioselectivities observed (each case still favored the same relative enantioface as with catalyst **1**)[3] support our concept that the methano bridge was functioning as the "small" group in the initial epoxidations using **2**; by making it larger, enantioselectivity was greatly diminished.

Catalytic asymmetric epoxidations using "ring-opened" complex **3** were carried out using the same conditions employed for complex **2**. 1,2-Dihydronaphthalene and cis-β-methylstyrene were studied. Unfortunately, no desired epoxides were obtained and the starting olefins were recovered. It seemed that the ethyl groups completely blocked the metal center and consequently hindered the formation of epoxides. From the ^{1}H NMR spectrum of **12** one set of ethyl groups displayed peaks at 1.58 ppm (CH_2), 1.31 ppm (CH_2), and 1.10 ppm (CH_3) and the other set of ethyl groups displayed peaks at 0.10 ppm (CH_2), - 0.28 ppm (CH_2), and - 0.39 ppm (CH_3). The large upfield shift between these two sets of ethyl groups suggests that one set of ethyl groups is over the porphyrin ring and that the steric hindrance provided by these ethyl groups is large enough to hinder the approach of the alkene to the active site of the catalyst.

Our results using complexes **4a** and **4b** in catalytic epoxidations show modest electronic effects. The bromo-derivative **4a** reacted very similarly to the parent complex **1**, giving complete conversion to epoxide in about 1 h with a somewhat diminished enantioselectivity (values for catalyst **1** in parentheses): 40% (52%) e.e. for styrene, 50% (56%) e.e. for 1,2-dihydronaphthalene, 73% (76%) e.e. for cis-β-methylstyrene. The bromo-porphyrin derivative **4a** could be reisolated and reused in additional epoxidations. Epoxidations with methoxy-derivative **4b** gave in two cases gave higher enantioselectivity and were very fast, in the case of 1,2-dihydronaphthalene going to 90% conversion in 5 min. The enantioselectivities obtained were (values for catalyst **1** in parentheses): 40% (52%) e.e. for styrene, 68% (56%) e.e. for 1,2-dihydronaphthalene, 83% (76%) e.e. for cis-β-methylstyrene). The methoxy-porphyrin derivative **4b** could not be reisolated after the epoxidation and was suspected to have been oxidized. In each case, the use of (–)-

4a or (–)-**4b** gave opposite absolute configurations of epoxides as were produced with (+)-**1**.[3] Assuming that the selectivity of the epoxidation using the methoxy-derivative **4b** vs **4a** is not inverted, we assigned the (–)-**4b** enantiomer to have the same absolute configuration as bromo-derivative **4a** whose configuration was assigned through a chemical correlation.

Conclusions. While the ability of the "spiro-annulated" dimethanoanthrancene-based tetraarylporphyrinmanganese complex **2** to effect stereoselective asymmetric epoxidations is limited, the facile access to this ligand should enable its application in other metalloporphyrin catalyzed reactions. The unreactivity of the "ring-opened" tetraethylhydrindane-based tetraarylporphyrin complex **3** gives an indication of the upper level of steric incumbrance that can be tolerated in a reactive D_4-symmetrical tetraarylporphyrin complex. Moderate reactivity changes were observed with the electronically varied tetraaarylporphyrin complexes **4a** and **4b**.

Experimental Section

General. Standard experimental methods published for our laboratory were followed.[24] NMR spectra were acquired at 300 MHz for ^{1}H and 75 MHz for ^{13}C in $CDCl_3$. Solvent concentration was done by rotary evaporation. Thin layer chromatography Rf values are for SiO_2 plates (EM Silica gel 60, 0.2 mm).

(1*S,4*R**,5*R**,8*S**)-1,4,4a,5,8,8a,9a,10a-octahydro-11,12-di(spirocyclopentane)-1,4:5,8-dimethanoanthracen-9,10-dione (6).** A solution of benzoquinone (10.71 g, 99.1 mmol) and spiro[4,4]nona-1,3-diene (**5**) [6] (30.9 g, 257 mmol) in benzene (80 mL) was heated under reflux overnight under nitrogen. The cooled mixture was concentrated and the residue crystallized from boiling benzene to give **3** (30.2 g, 88%) as a white solid: Rf 0.48 (CH_2Cl_2); mp 204 - 205 °C; ^{1}H NMR δ 6.12 (s, 4 H), 2.90 (s, 8 H), 1.51 (dd, 4 H, J = 6.5, 6.5 Hz), 1.49 - 1.38 (m, 8 H), 1.30 (dd, 4 H, J = 7.0, 7.0 Hz); ^{13}C NMR δ 213.5, 137.2, 69.4, 56.0, 53.3, 32.2, 30.9, 25.8, 25.2; IR (film) 2955, 2858, 1673 cm^{-1}; MS (EI, 70 eV) m/z (relative intensity) 348 (M^+, 0.7%), 320 (0.2), 228 (3.7), 120 (13); HRMS (EI, 70 eV) m/z M^+ calcd for $C_{24}H_{28}O_2$ 348.2089, found 348.2078.

Di(tosylhydrazone) of 6. To a mixture of **6** (8.66 g, 24.88 mmol) and *p*-toluenesulfonhydrazide (12.05 g, 64.69 mmol) was added acetonitrile (20 mL) and glacial acetic acid (25 mL). The mixture was heated at 90 °C for 2 h then cooled to 4 °C for 2 h. The precipitated dihydrazone was collected by filtration and washed with acetic acid (3 x 30 mL) and ice water (3 x 50 mL) and dried under high vacuum to give crude dihydrazone (15.0 g) as a yellow solid which was used in the following reaction without further purification. Crude ^{1}H NMR spectrum: δ 7.86 (m, 4 H), 7.32 (m, 4 H), 6.13 (m, 2 H), 6.02 (s, 1 H), 5.79 (m, 1 H), 5.24 (bs, 2 H), 3.10 - 2.56 (m, 8 H), 2.43 (m, 6 H), 1.50 - 1.19 (m, 16 H).

(1*S,4*R**,5*R**,8*S**)-1,4,5,8-Tetrahydro-11,12-di(spirocyclopentane)-1,4:5,8-dimethanoanthracene (7).** To a solution of the crude di(tosylhydrazone) of **6** (5.0 g, 7.31 mmol) in THF (100 mL) was added dropwise *n*-butyllithium (1.15 M; 64 mL, 73.1 mmol) at -20 °C under nitrogen. The

mixture was stirred overnight at rt then the reaction was quenched by slow addition of water. The mixture was concentrated and the residue dissolved in benzene (100 mL), washed with water and brine, dried over $MgSO_4$, and concentrated. Filtration through a short plug of silica gel (5:95 benzene-petroleum ether) gave a crude diene product (1.85 g, 80%) which was directly oxidized. A mixture of the crude diene product (3.22 g, 10.20 mmol) and DDQ (3.47 g, 15.30 mmol) in benzene (40 mL) was heated under nitrogen at 40 °C overnight. The cooled mixture was concentrated and the residue filtered through a short plug of silica gel (2:98 benzene-petroleum ether) to give arene **7** (2.79 g, 87%) as a white solid: mp 190 - 191 °C; R_f 0.74 (2:8 CH_2Cl_2-petroleum ether); ^{1}H NMR δ 6.95 (s, 2 H), 6.70 (dd, 4 H, J = 2.0, 2.0 Hz), 3.32 (dd, 4 H, J = 2.0, 2.0 Hz), 1.68 (dd, 4 H, J = 7.0, 7.0 Hz), 1.53 - 1.35 (m, 8 H), 1.13 (dd, 4 H, J = 7.0, 7.0 Hz); ^{13}C NMR δ 148.2, 142.9, 117.0, 91.8, 58.9, 33.8, 33.5, 25.3, 25.2; IR (film) 2953, 2861, 1446, 884, 791 cm^{-1}; MS (EI, 70 eV) m/z (relative intensity) 314 (M^+, 100%), 245 (41), 217 (55), 202 (55); HRMS (EI, 70 eV) m/z M^+ calcd for $C_{24}H_{26}$ 314.2034, found 314.2029.

(1*S,4*R**,5*R**,8*S**)-1,2,3,4,5,6,7,8-Octahydro-11,12-di(spirocyclopentane)-1,4:5,8-dimethanoanthracene (8).** A mixture of diene-arene **7** (2.53 g, 18.05 mmol), benzene (30 mL), and 5% Pd/C (300 mg) was stirred at rt under 1 atm of hydrogen overnight. The mixture was filtered through Celite and the filtrate was concentrated to give arene **8** (2.48 g, 97%) as a white solid: mp 174 - 175 °C. ^{1}H NMR δ 6.82 (s, 2 H), 2.68 (d, 4 H, J = 2.0 Hz), 1.92 - 1.88 (m, 4 H), 1.60 - 1.53 (m, 4 H), 1.48 - 1.38 (m, 8 H), 1.17 (dd, 4 H, J = 7.5, 7.5 Hz), 1.08 - 1.03 (m, 4 H); ^{13}C NMR δ 145.7, 114.5, 68.3, 51.7, 32.6, 31.9, 26.9, 26.1, 25.7; IR (film) 871, 1323, 2862, 2943 cm^{-1}; MS (EI, 70 eV) m/z (relative intensity) 318 (M^+, 58%), 249 (100), 167 (78); HRMS (EI, 70 eV) m/z M^+ calcd for $C_{24}H_{30}$ 318.2347, found 318.2347.

(1*S,4*R**,5*R**,8*S**)-1,2,3,4,5,6,7,8-octahydro-11,12-di(spirocyclopentane)-1,4:5,8-dimethanoanthracene-9-carboxaldehyde (9).** To a mixture of arene **8** (2.48 g, 7.81 mmol) and $TiCl_4$ (2.96 g, 15.62 mmol) in CH_2Cl_2 (120 mL) at -15 °C under nitrogen was added over 20 min $CHCl_2OCH_3$ (1.34 g, 11.71 mmol). After stirring at -15 °C for 2 h the mixture was poured into ice-water. The organic 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 racemic aldehyde **9** (2.5 g, 93%) as a white solid: R_f 0.31 (1:1 benzene-petroleum ether); mp 137 - 138 °C. ^{1}H NMR δ 10.33 (s, 1 H), 7.09 (s, 1 H), 3.50 (d, 2 H, J = 3.0 Hz), 2.75 (d, 2 H, J = 2.5 Hz), 2.05 - 1.90 (m, 4 H), 1.64 - 1.38 (m, 12 H), 1.16 - 1.02 (m, 8 H); ^{13}C NMR δ 192.5, 147.9, 147.3, 124.0, 120.5, 68.5, 51.1, 51.1, 49.2, 32.5, 31.7, 26.4, 26.0, 25.7; IR (film) 2947, 2864, 2726; 1689 cm^{-1}; MS (EI, 70 eV) m/z (relative intensity) 346 (M^+, 100%), 259 (50), 179 (56), 165 (65); HRMS (EI, 70 eV) m/z M^+ calcd for $C_{25}H_{30}O$ 346.2297, found 346.2267.

Diastereomeric acetals 10 and 11. A solution of the racemic aldehyde **9** (2.5g, 7.23 mmol), (*R,R*)-hydrobenzoin (3.87 g, 18.06 mmol), and pyridinium p-toluenesulfonate (PPTS) (50 mg, 0.20 mmol) in benzene (50 mL) was refluxed under nitrogen through a Soxhlet extractor filled with 4 Å molecular sieves for 18 h. The reaction mixture was washed with saturated $NaHCO_3$, H_2O, and brine, dried ($MgSO_4$), and

concentrated to afford a mixture of diastereomeric acetals and trace of excess (R,R)-hydrobenzoin which were separated by chromatography (SiO_2, 3:7 benzene-petroleum ether). The diastereomeric acetals (oily foam; 3.39 g, 86%) were crystallized from boiling hexane (5 mL) and one drop of benzene. The first crystallization afforded 1.14 g of crystalline **10** as a white solid, mp 193 - 194 °C, $[\alpha]_D^{23}$ +33.9 (c 1.02, $CHCl_3$). Overall three recrystallizations yielded pure crystalline **10** (1.35 g, 35% yield). After the last recrystallization removal of the solvent in the mother liquid portion afforded the liquid diastereomer **11** in a 9:1 ratio of **11**:**10** (1.43 g, 37% yield), ($[\alpha]_D^{23}$ +32.1 (c 1.0, benzene). Based on the known configuration of (*R,R*)-stilbene diol the absolute configuration of the crystalline diastereomer **10** was assigned by X-ray crystallography.

Data for (+)-**10**: ^{1}H NMR δ 7.41 - 7.30 (m, 10 H), 6.94 (s, 1 H), 6.57 (s, 1 H), 4.93 (s, 2 H), 3.28 (d, 2 H, J = 2.0 Hz), 2.75 (d, 2 H, J = 2.0 Hz), 1.95 (dd, 2 H, J = 10.0, 3.5 Hz), 1.89 (dd, 2 H, J = 10.0, 3.5 Hz), 1.67 - 1.44 (m, 12 H), 1.41 - 1.17 (m, 6 H), 1.08 (dd, 2H, J = 8.5, 8.5 Hz); ^{13}C NMR δ 146.5, 144.5, 139.5, 136.9, 128.6, 128.5, 128.3, 128.0, 126.6, 126.6, 123.4, 115.9, 103.7, 87.3, 84.9, 68.0, 51.7, 50.0, 32.7, 32.0, 26.9, 26.3, 26.3, 25.9; IR (film) 2949, 1107, 698 cm^{-1}; MS (EI 12 eV) m/z (relative intensity) 542 (M+, 90%), 436 (99), 345 (100), 328 (59), 277 (59), 179 (43).

Data for (+)-**11**: ^{1}H NMR δ 7.38 - 7.28 (m, 10 H), 6.94 (s, 1 H), 6.54 (s, 1 H), 4.93 (s, 2 H), 3.29 (d, 2 H, J = 3.0 Hz), 2.75 (d, 2 H, J = 2.5 Hz), 2.09 - 1.91 (m, 4H), 1.63 - 1.10 (m, 20 H); ^{13}C NMR δ 146.7, 144.7, 139.6, 136.9, 128.6 (2 signals), 128.3, 128.0, 126.9, 126.5, 123.2, 115.9, 103.8, 87.8, 85.2, 68.2, 51.7, 50.1, 32.7, 32.0, 27.0, 26.6, 26.2, 25.8; IR (film) 2951, 1109, 698 cm^{-1}; MS (EI 70 eV) m/z (relative intensity) 542 (M+, 73%), 436 (87), 345 (100), 277 (58), 105 (48).

(+)-(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-11,12-di(spirocyclopentane)-1,4:5,8-dimethanoanthracene-9-carboxaldehyde ((+)-9). Cystalline acetal (+)-**10** (1.13 g, 2.08 mmol) was heated at 70 °C for 2 h in 1:4 3% H_2SO_4:THF (43 mL). The reaction mixture was cooled to rt and extracted with EtOAc (3 x 50 mL). The combined organic portions were washed with H_2O and brine, dried ($MgSO_4$) and concentrated to give a mixture of enantiomeric pure aldehyde (+)-**9** and (*R,R*)-hydrobenzoin. The enantiomerically pure aldehyde (+)-**9** was isolated by chromatography (SiO_2, 1:1 benzene-petroleum ether) then (*R,R*)-hydrobenzoin (0.4 g, 90%) was recovered using ethyl acetate to give (+)-**9** (0.70 g, 97%) as a white solid. $[\alpha]_D^{23}$ +34.5 (c 1.0, $CHCl_3$). The ^{1}H and ^{13}C NMR spectra of (+)-**9** were identical to the racemic mixture.

(–)-5,10,15,20-Tetrakis-[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-11,12-di(spirocyclopentane)-1,4:5,8-dimethano anthracene-9-yl]porphyrin ((–)-12). To a solution of (+)-**9** (242 mg, 0.70 mmol) and pyrrole (49 μL, 0.7 mmol) in $CHCl_3$ (15 mL) at rt under nitrogen was added BF_3-etherate (32.8 mg, 0.23 mmol). The reaction solution was stirred at rt for 1 h excluding light when p-chloranil (128 mg, 0.53 mmol) was added and heated at 61 °C for 1 h. The reaction mixture then was cooled to rt, neutralized with Et_3N (0.26 mL, 1.87 mmol) and concentrated to dryness. The dry powder was purified by chromatography (Al_2O_3, 10% CH_2Cl_2/petroleum ether) to afford (–)-**12** (110 mg, 40%) as a red solid: R_f 0.79 (1:9 CH_2Cl_2-petroleum

ether); mp >300 °C, $[\alpha]_D^{23}$ -230 (c 0.22, CH_2Cl_2). ^1H NMR δ 8.63 (s, 8 H), 7.29 (s, 4 H), 3.00 (d, 8 H, J = 3.0 Hz), 2.06 (d, 8 H, J = 3.0 Hz), 1.99 - 1.92 (m, 8 H), 1.68 - 1.55 (m, 16 H), 1.51 - 1.03 (m, 64 H), 0.89 - 0.81 (m, 8 H), -2.66 (s, 2 H); ^{13}C NMR δ 147.7, 144.5, 130.4 (br, 2 C's), 129.7, 116.6, 114.7, 68.7, 52.3, 49.6, 32.9, 31.5, 27.2, 26.0, 25.4, 25.2; IR (film) 3316, 2950, 2869, 804 cm^{-1}; MS (FAB, 3-nitrobenzyl alcohol) m/z (relative intensity) 1575.5 (M^+ + H, 3%), 246 (41), 155 (42), 137 (100); UV ($CHCl_3$) λ_{max} 412 nm (ε = 113,889 $cm^{-1}M^{-1}$).

(–)-Chloro{5,10,15,20-Tetrakis-[(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-11,12-di(spirocyclopentane)-1,4:5,8-dimethano anthracene-9-yl]porphyrinato}manganese ((–)-2). A solution of porphyrin (–)-**12** (80 mg, 0.05 mmol) and $MnCl_2$-$4H_2O$ (173 mg, 0.875 mmol) in DMF (6 mL) was heated under reflux for 8 h. After cooling, the solution was poured into a flask containing an ice-cold saturated NaCl solution (10 mL) and extracted by CH_2Cl_2 (3 x 15 mL). The combined (green) organic portion was washed with 5% HCl solution (3 x 15 mL) and brine, dried ($MgSO_4$), and concentrated. The crude product was purified by chromatography (Al_2O_3, CH_2Cl_2 to elute any unreacted porphyrin, then 5:95 MeOH:CH_2Cl_2) to yield (–)-**2** as a green solid (76 mg, 92%). mp >300 °C, $[\alpha]_D^{23}$ -7400 (c 0.027, CH_2Cl_2). IR (film) 805, 1108, 2869, 2950 cm^{-1}; UV ($CHCl_3$) λ_{max} 478 nm (ε = 96,528 $cm^{-1}M^{-1}$); MS (FAB, 3-nitrobenzyl alcohol) m/z (relative intensity) 1629 (M^+ - Cl + H, 100%), 1628 (M^+ - Cl, 93); HRMS m/z (M^+ - Cl+ H) calcd for $C_{116}H_{125}N_4Mn^+$ 1628.9285, found 1628.9282.

(1*S,1a*S**,4*R**,4a*R**,5*R**,5a*R**,8*S**,8a*S**)-1,4,4a,5,8,8a,9a,10a-Octahydro-cis-9,10-bis(methoxymethoxy)-1,4:5,8-dimethanoanthracene (14).** A mixture of diol **13** (70.0 g, 0.29 mol), dimethoxymethane (480 mL, 5.42 mol), *p*-toluenesulfonic acid (12 g, 0.06 mmol), and dry CH_2Cl_2 (1.1 L) were refluxed under nitrogen through a Soxhlet filled with 3 Å molecular sieves for 5 d. The cooled reaction mixture was washed with saturated aqueous sodium bicarbonate (3 x 300 mL), water (3 x 300 mL), and brine (300 mL), and concentrated to give **14** (95.1 g, 99%), which was used in the following reaction without further purification. Compound **14** was a 9:1 mixture of cis and trans isomers. For analytical purposes, a sample of the pure cis-isomer was obtained by Kugelrohr distillation at 160 °C (0.35mm) to give cis-**14** as a pale yellow solid, mp 64 - 65 °C. Data for cis-**14** : ^1H NMR δ 6.13 (s, 4 H), 4.73 (d, 2 H, J = 7.0 Hz), 4.54 (d, 2 H, J = 7.0 Hz), 3.39 (s, 6 H), 3.14 - 3.03 (m, 2 H), 2.88 (s, 2 H), 2.83 (s, 2 H), 2.63 (d, 2 H, J = 2.0 Hz), 1.88 - 1.76 (m, 2 H), 1.44 (d, 1 H, J = 8.0 Hz), 1.43 (d, 1 H, J = 8.0 Hz), 1.25 (d, 1 H, J = 8.0 Hz), 1.10 (d, 1 H, J = 8.0 Hz); ^{13}C NMR δ 135.8, 133.5, 94.9, 76.4, 55.4, 52.6, 48.9, 45.3, 45.0, 44.2, 42.9; IR (film) 2937, 1146, 1098, 1033, 916 cm^{-1}; MS (EI, 70 eV) m/z (relative intensity) 332 (M+, 3%), 270 (21), 225 (45) 143 (55), 107 (100).

(1*S,1a*S**,2*S**,3*R**,4*R**,4a*R**,5*R**,5a*R**,6*R**,7*S**,8*S**,8a*S**)-Perhydro-cis-9,10-bis(methoxymethoxy)-1,4:5,8-dimethano-2,3,6,7-tetrahydroxy-anthracene (15).** A mixture of **14** (208.6 g, 0.63 mol), NMO (613 g, 60 wt. % solution in water, 3.14 mol), OsO_4 (1.0 g, 3.93 mmol), and 8:1 acetone-

water (900 mL) was stirred at rt for 10 d. Solid $NaHSO_3$-$Na_2S_2O_5$ (60 g) was added and the mixture was stirred for 2 h at rt, concentrated and extracted with CH_2Cl_2 using a continuous extractor for 7 d to give **15** (218.5 g, 87%) as a white solid; mp 150 - 151 °C. ^{1}H NMR δ 4.75 (d, 2 H, J = 7.0 Hz), 4.57 (d, 2 H, J = 7.0 Hz), 4.41 (s, 2 H), 4.09 (s, 2 H), 3.80-3.74 (m, 2 H), 3.41 (s, 6 H), 2.52 (m, 4 H), 2.40 (s, 2 H), 2.33 (s, 4 H), 2.20 - 2.16 (m, 2 H), 1.95 - 1.89 (m, 2 H), 1.19 - 1.14 (m, 2 H); ^{13}C NMR δ 94.7, 70.8, 70.2, 69.3, 55.8, 48.1, 46.8, 42.2, 39.4, 34.3, 33.4; IR (film) 3300, 2912, 1011 cm^{-1}; MS (FAB, 3-nitrobenzyl alcohol) m/z (relative intensity) 423 (M^+ + Na, 100), 277 (41), 259 (78), 241 (27), 217 (44) 199 (35), 176 (73).

(1*S,1a*R**,3*R**,3a*S**,5*R**,5a*S**,7*S**,7a*R**)-Perhydro-cis-4,8-bis(methoxymethoxy)-*s*-indacene-1,3,5,7-tetracarboxaldehyde (17).** To a suspension of **15** (26.14 g, 65.35 mmol; finely ground) in ethyl acetate (312 mL) and H_2O (78 mL) was added the powdered $NaIO_4$ (36.34 g, 167 mmol). The slurry was stirred under air at rt for 7 min and then was filtered. The solid was rinsed with 3.5:6.5 CH_3OH-EtOAc (150 mL) and the filtrate was diluted with H_2O (60 mL) and extracted with 3.5:6.5 CH_3OH-EtOAc (3 x 120 mL). The combined extracts were washed with brine (2 x 40 mL), dried over $MgSO_4$, and concentrated to give a product mixture which contained the desired tetraaldehyde **17** and the bridging hydrate **16**. To this product mixture was added CH_2Cl_2 (200 mL) and it was refluxed overnight under nitrogen through a Soxhlet thimble containing 4 Å molecular sieves. The cooled mixture was dried in vacuo to give **17** (22.8 g, 88%) as a pale yellow solid. ^{1}H NMR δ 9.94 (s, 2 H), 9.77 (s, 2 H), 4.50 (d, 2 H, J = 7.0 Hz), 4.43 (d, 2 H, J = 7.0 Hz), 3.70 (bs, 2 H), 3.32 (s, 6 H), 3.01 - 2.62 (m, 8 H), 2.01 - 1.81 (m, 2 H), 1.78 - 1.69 (m, 2 H); ^{13}C NMR δ 202.1, 201.1, 97.9, 73.5, 56.9, 53.2, 52.5, 45.8, 43.9, 25.9, 21.4; IR (film) 2947, 2741, 1712, 1148, 1025 cm^{-1}; MS (CI, NH_3) m/z (relative intensity) 414 (M^+ + NH_4, 100), 335 (68), 308 (56), 280 (40), 259 (39), 159 (34), 149 (41), 124 (54), 108 (77).

(1*R,1a*S**,3*S**,3a*R**,5*S**,5a*R**,7*R**,7a*S**)-Perhydro-1,3,5,7-tetravinyl-cis-4,8-bis(methoxymethoxy)-*s*-indacene (18).** THF (1.5 L) was added to a solid mixture of potassium t-butoxide (34.3 g, 305.5 mmol) and methyltriphenylphosphonium bromide (119.0 g, 333.3 mmol) at rt under nitrogen. After 2 h, the yellow mixture was cooled to -78 °C and tetraaldehyde **17** (22.0 g, 55.55 mmol) in THF (200 mL) was added via cannula. After 4 h, the mixture was allowed to warm to rt and stirred overnight. The solution was concentrated to dryness. The residue was dissolved in a minimum amount of CH_2Cl_2 and an equal amount of hexanes was added and the mixture kept at 0 °C overnight to precipated most of the triphenylphosphine oxide. After filtration and concentration of the filtrate, pure **18** could be obtained by crystallization from boiling CH_3CH_2OH (11.8 g, 55%) or by chromatography (SiO_2, 2:8 CH_2Cl_2/hexanes) as a white solid; mp 58-59 °C. R_f 0.23 (100% CH_2Cl_2). ^{1}H NMR δ 6.25 - 6.13 (m, 2H), 5.93 - 5.82 (m, 2H), 4.97 - 4.85 (m, 8H), 4.63 (d, 2H, J = 7.0 Hz), 4.57 (d, 2H, J = 7.0 Hz), 3.52 (dd, 2H, J = 5.5, 5.5 Hz), 3.39 (s, 6H), 2.83 - 2.64 (m, 4H), 2.61 - 2.53 (m, 2H), 2.42 - 2.34 (m, 2H), 2.08 - 1.94 (m, 2H), 1.75 (dt, 1H, J = 13.0, 9.0 Hz), 1.50 (dt, 1H, J = 13.5, 10.0 Hz); ^{13}C NMR δ 142.0, 141.7, 113.2, 112.9, 98.0, 76.1, 56.4, 46.6, 45.9, 45.9, 44.6, 38.1, 34.0; IR (film) 3072, 2934, 1146, 1100, 1039, 909 cm^{-1}; MS (CI, NH_3) m/z (relative intensity) 389 (M^+ + H, 4%), 357 (3), 327 (16), 295 (48), 265 (100); HRMS (FAB, 3-nitrobenzyl alcohol) calcd for $(M + H)^+$ 389.2692, found 389.2722.

(1*S,1a*S**,3*R**,3a*R**,5*R**,5a*R**,7*S**,7a*S**)-Perhydro-1,3,5,7-tetraethyl-cis-4,8-bis(methoxymethoxy)-*s*-indacene (19).** To a mixture of **18** (3.14 g, 8.09 mmol) in EtOH (60 mL) was added copper(II) sulfate pentahydrate (2.5 g) and hydrazine hydrate (24 mL). Air was bubbled through the reaction mixture with vigorous stirring for 24 h. The flow of air was stopped and the mixture was filtered through Celite. The filtrate was concentrated and the residue was partitioned between water (40 mL) and ether (4 x 30 mL). The combined extracts were washed with 10% HCl (3 x 30 mL), water (3 x 30 mL), and brine (30 mL), dried over $MgSO_4$, and concentrated to give crude **19** (2.58 g) which was purified by chromatography (SiO_2, 3:97 ether-petroleum ether) to give **19** (1.68 g, 52%) as a white solid, mp 74 °C. The ^1H NMR spectrum of **19** displayed no symmetry and most peaks were broad except for the methoxy peak. A crystal of **19** was grown by crystallization from CH_3CH_2OH and the structure of **19** was confirmed by X-ray crystallography. R_f 0.55 (5:95 ether-petroleum ether); ^1H NMR δ 4.72 - 4.61 (m, 4H), 3.61 (m, 2H), 3.37 (m, 6H), 2.50 - 2.20 (bs, 3H), 2.16 - 2.06 (m, 2H), 2.02 - 1.70 (m, 8H), 1.69 - 1.40 (bs, 4H), 1.31 - 1.21 (m, 2H), 1.20 - 1.02 (br, 1H), 0.93 - 0.75 (m, 12H); MS (CI, NH_3) m/z (relative intensity) 397 (M^+ + H, 1%), 335 (8), 303 (25), 273 (100).

Formaldehyde acetal 20. To a solution of **19** (238 mg, 0.6 mmol) in CH_2Cl_2 (15 mL) was added trifluoroacetic acid (20 μL, 0.26 mmol) under nitrogen. The mixture was refluxed overnight then the cooled mixture was washed with saturated $NaHCO_3$ (3 x 5 mL), water (3 x 5 mL), and brine (5 mL), dried over $MgSO_4$, and concentrated to give crude **20** (175 mg). After chromatography (SiO_2, CH_2Cl_2) **20** (88 mg) was obtained as a colorless oil. R_f 0.46 (CH_2Cl_2); ^1H NMR δ 4.95 (d, 1 H, J = 7.0 Hz), 4.63 (d, 1 H, J = 7.0 Hz) 4.24 (s, 2 H), 2.61 - 2.52 (m, 2 H), 2.02 - 1.93 (m, 4 H), 1.79 - 1.44 (m, 10 H), 1.39 - 1.23 (m, 4 H), 0.94 (dd, 6 H, J = 7.5, 7.5 Hz), 0.93 (dd, 6 H, J = 7.0, 7.0 Hz); ^{13}C NMR d 85.3, 73.9, 45.7, 44.8, 42.7, 40.7, 37.9, 36.3, 23.4, 22.1, 14.1, 13.9; IR (film) 2956, 2868, 1462, 1165, 1087 1029 cm^{-1}; MS (EI, 12 eV) m/z (relative intensity) 320 (M^+, 33), 272 (100), 243 (60); (FAB, 3-nitrobenzyl alcohol) m/z 319 (M^+ - H, 8%), 273 (100), 123 (64); HRMS (FAB, 3-nitrobenzyl alcohol) m/z (M^+ - H) calcd for $C_{20}H_{35}O_2$ 319.2637, found 319.2638.

(1*S,1a*S**,3*R**,3a*R**,5*R**,5a*R**,7*S**,7a*S**)-Perhydro-1,3,5,7-tetraethyl-*s*-indacene-cis-4,8-diol (21).** Glacial acetic acid (6.32 mL, 105 mmol) was added to a 0 °C solution of **19** (6.95 g, 17.54 mmol) and trifluoroacetic acid (14.86 mL, 105.2 mmol) in CH_2Cl_2 (180 mL). The solution was stirred for 6 h at rt then washed with saturated $NaHCO_3$, H_2O, and brine. The solvent was removed and to the residue (8.6 g) was added MeOH (150 mL) and K_2CO_3 (24.2 g, 175 mmol). This mixture was refluxed overnight under nitrogen. The cooled mixture was diluted with H_2O (100 mL), neutralized by 30% HCl, and then extracted with ethyl acetate (4 x 250 mL). The combined extracts were washed with H_2O (2 x 150 mL) and brine (150 mL), dried over $MgSO_4$, and concentrated. The crude product was purified by chromatography (SiO_2, CH_2Cl_2) to give **21** (3.89 g, 72%) as a white solid, mp 163-164 °C. R_f 0.32 (5:95 ethyl acetate-CH_2Cl_2); ^1H NMR δ 4.19 (bs, 2 H), 3.96 (s, 2 H), 2.48 (m, 2 H), 2.02 (bs, 2 H), 1.82 - 1.62 (m, 10 H), 1.58 - 1.45 (m, 2H), 1.29 - 1.16 (m, 2H), 1.10 - 0.73 (m, 14H); ^{13}C NMR δ 67.7, 45.8, 45.7, 44.7, 41.4, 38.9, 36.5, 23.8, 22.4, 14.3, 13.9; IR

(film) 3144, 2928, 1457, 994 cm^{-1}; MS (EI, 70 eV) m/z (relative intensity) 308 (M^+, 1%), 290 (4), 272 (13), 154 (100), 95 (90).

(1*R,3*S**,5*S**,7*R**)-1,2,3,5,6,7-hexahydro-1,3,5,7-tetraethyl-*s*-indacene (22):** *p*-Toluenesulfonyl chloride (7.08 g, 37.14 mmol) and catalytic amount of DMAP (10 mg) were added to a solution of **21** (2.86 g, 9.29 mmol) in anhydrous pyridine (15 mL) at rt under nitrogen. This mixture was stirred at rt overnight then at 45 °C for 2 d. The solution was poured into ice-water (20 mL) and extracted with ether (3 x 20 mL). The combined extracts were washed with 10% H_2SO_4 (3 x 20 mL), H_2O, and brine, dried over $MgSO_4$, and concentrated to give a mixture of presumably dienes and crude **22** (2.3 g) to which was added p-chloranil (2.49 g, 10.15 mmol) and anhydrous benzene (30 mL). This mixture was refluxed overnight then was cooled and concentrated. After chromatography (SiO_2, petroleum ether) **22** (1.2 g, 49% from **21**) was obtained as a white solid, mp 106 - 107 °C. R_f 0.57 (100% petroleum ether). ^1H NMR δ 7.00 (s, 2 H), 2.93 - 2.83 (m, 4 H), 2.49 (dt, 2 H, J = 12.0, 7.0 Hz), 2.12 - 1.99 (m, 4 H), 1.44 - 1.29 (m, 4 H), 1.15 (dt, 2 H, J = 12.0, 10.0 Hz), 1.01 (dd, 12 H, J = 7.5, 7.5 Hz); ^{13}C NMR δ 146.0, 117.9, 44.8, 39.2, 27.8, 12.1; MS (EI, 70 eV) m/z (relative intensity) 270 (M^+, 13%), 241 (100), 185(10), 157 (8); IR (film) 2951, 2920, 2849, 1465, 871 cm^{-1}.

(1*R,3*S**,5*S**,7*R**)-1,2,3,5,6,7-hexahydro-1,3,5,7-tetraethyl-*s*-indacene-4-carboxaldehyde (23).** To a solution of arene **22** (470 mg, 1.74 mmol) and $TiCl_4$ (477 μL, 4.35 mmol) in CH_2Cl_2 (4 mL) at -78 °C under nitrogen was added dropwise $CHCl_2OCH_3$ (315 μL, 3.48 mmol). The mixture was stirred at -78 °C for 2 h then was poured into ice-water. The organic layer was washed with saturated $NaHCO_3$ (2 x 2 mL), H_2O (3 x 2 mL), and brine, dried ($MgSO_4$), and concentrated. The crude product was purified by chromatography (SiO_2, 0-15% CH_2Cl_2-petroleum ether) to give racemic aldehyde **23** (363 mg, 70%) as a white solid, mp 137 °C. R_f 0.33 (25:75 CH_2Cl_2-petroleum ether). ^1H NMR δ 10.37 (s, 1 H), 7.24 (s, 1 H), 3.59 - 3.50 (m, 2 H), 2.95 - 2.87 (m, 2 H), 2.38 (ddd, J = 13.5, 9.0, 9.0 Hz), 1.82 - 1.64 (m, 6H), 1.55 - 1.40 (m, 2H), 1.36 - 1.21 (m, 2H), 1.04 (dd, 6 H, J = 7.5, 7.5 Hz), 1.00 (dd, 6H, J= 7.5, 7.5 Hz); ^{13}C NMR δ 192.4, 149.2, 147.9, 126.0, 125.9, 45.1, 44.6, 34.3, 31.7, 31.1, 31.0, 12.9; IR (film) 2957, 2865, 1683 cm^{-1}; MS (EI, 70 eV) m/z (relative intensity) 298 (M^+, 54%), 269 (100), 251 (23), 185 (27), 29 (60).

Diastereomeric acetals 24 and 25. A solution of the racemic aldehyde **23** (224 mg, 0.75 mmol), (*R,R*)-hydrobenzoin (644 mg, 3.00 mmol), and PPTs (20.0 mg, 0.080 mmol) were subjected to the conditions used in the formation of diastereomeric acetals of **9**. The crude mixture of acetals was purified by chromatography (SiO_2, 3:7 CH_2Cl_2-petroleum ether) and the resulting oily foam was subjected to crytallization from boiling hexane (1.5 mL) and one drop of benzene. Overall three to four recrystallizations yielded pure crystalline (+)-**24** as a white solid (150 mg, 40%), mp 174 °C. After the last recrystallization, the mother liquid portion afforded the liquid diastereomer (+)-**25** with the ratio of liquid acetal:crystalline acetal ≥ 10:1 (156.0 mg, 42%). The absolute configurations of (+)-**24** and (+)-**25** were not determined.

Data for crystalline acetal (+)-**24**: $[\alpha]_D^{23}$ + 17.8 (c 1.0, benzene); ^1H NMR δ 7.39 - 7.28 (m, 10 H), 7.14 (s, 1 H), 6.59 (s, 1 H), 4.98 (d, 1 H, J = 8.5 Hz), 4.94 (d, 1 H, J = 8.5 Hz), 3.44 - 3.37 (m, 2 H), 2.95 - 2.87 (m, 2 H), 2.38 - 2.15 (m, 4 H), 1.85 - 1.74 (m, 4 H), 1.64 - 1.51 (m, 2 H), 1.49 - 1.34 (m, 2 H), 1.09 (dd,

6 H, J = 7.5, 7.5 Hz), 1.04 (dd, 6 H, J = 7.5, 7.5 Hz); ^{13}C NMR δ 147.4, 146.1, 139.7, 136.0, 128.6, 128.5, 127.9, 127.3, 126.8, 126.2, 122.2, 122.3, 103.7, 87.8, 84.3, 45.6, 45.4, 33.7, 31.5, 31.4, 13.4, 13.2; MS (EI, 70 eV) m/z (relative intensity) 494 (M^+, 2%), 297 (100), 269 (34), 167 (27).

Data for liquid acetal (+)-**25**: $[\alpha]_D^{23}$ + 98.4 (c 0.5, benzene); ^{1}H NMR δ 7.39 - 7.25 (m, 10 H), 7.12 (s, 1 H), 6.52 (s, 1 H), 4.93 (d, 1 H, J = 8.0 Hz), 4.88 (d, 1 H, J = 8.0 Hz), 3.42 - 3.36 (m, 2 H), 2.94 - 2.86 (m, 2 H), 2.40 - 2.30 (m, 2 H), 2.14 - 2.02 (m, 2 H), 1.87 - 1.70 (m, 4 H), 1.61 - 1.46 (m, 2 H), 1.39 - 1.22 (m, 2 H), 1.07 (dd, 6 H, J = 7.5, 7.5 Hz), 1.00 (dd, 6 H, J = 7.5, 7.5 Hz); ^{13}C NMR δ 147.5, 146.1, 139.5, 136.4, 128.6, 128.5, 128.0, 127.3, 127.0, 126.2, 122.4, 103.6, 87.2, 83.8, 45.7, 45.5, 33.6, 31.4, 13.49, 13.4; IR (film) 2956, 1456, 1110, 1008 cm^{-1}; MS (EI, 70 eV) m/z (relative intensity) 494 (M^+, 2%), 297 (100), 269 (39), 167 (22), 105 (29).

(1*R*,3*S*,5*S*,7*R*)-1,2,3,5,6,7-Hexahydro-1,3,5,7-tetraethyl-*s*-indacene-4-carboxaldehyde (-) -23. The hydrolysis of crstalline acetal (+)-**24** (150 mg, 0.30 mmol) was carried out by using the same conditions (3% H_2SO_4:THF = 1:4, 6.25 mL) as those used in the formation of (+)-**9**. The crude product containing the mixture of enantiomeric pure aldehyde (-)-**23** and (*R,R*)-hydrobenzoin was separated by chromatography (SiO_2, 3:7 CH_2Cl_2-petroleum ether to elute (–)-**23** then ethyl acetate to elute (*R,R*)-hydrobenzoin) yield (*R,R*)-hydrobenzoin (58 mg, 89%) and (-)-**23** (68 mg, 97%) as a white solid; mp 137 °C, $[\alpha]_D^{23}$ - 154.5 (c 1.0, benzene). The ^{1}H and ^{13}C NMR spectra of (-)-**23** are same as racemic **23**.

5,10,15,20-Tetrakis[(1*R*,3*S*,5*S*,7*R*)-1,2,3,5,6,7-hexahydro-1,3,5'7-tetraethyl-*s*-indacene-4-yl]porphyrin (26). The condensation of (-)-**23** (86 mg, 0.29 mmol) with pyrrole (20 μL, 0.29 mmol) catalyzed by BF_3-etherate (13.5 mg, 0.10 mmol) was carried out as described for the formation of **12**. Porphyrin **26** (5.1 mg, 5%) was obtained as a red solid, mp > 250 °C. R_f 0.4 (5:95 CH_2Cl_2-petoleum ether); ^{1}H NMR δ 8.68 (s, 8 H), 7.38 (s, 4 H), 3.15 (m, 8 H), 2.98 (m, 8 H), 2.34 (ddd, 8 H, J = 13.0, 8.0, 8.0 Hz), 2.16 (m, 8 H), 1.58 (m, 8 H), 1.31 (m, 8 H), 1.10 (dd, 24 H, J = 7.5, 7.5 Hz), 0.10 (m, 8 H), -0.28 (m, 8 H), -0.39 (dd, 24 H, J = 7.00, 7.0 Hz), -2.50 (s, 2 H); ^{13}C NMR δ 163.2, 147.4, 145.9, 135.6, 118.7, 116.9, 45.9, 45.4, 36.5, 29.4, 27.3, 12.6, 11.0; IR (film) 2940, 2900, 2840 cm^{-1}; MS (FAB, 3-nitrobenzyl alcohol) m/z (relative intensity) 1384 (M^++ 1, 88%), 1383 (M^+, 100), 1368 (39); UV ($CHCl_3$) λ_{max} 424 nm (ε = 114,483 cm^{-1} M^{-1}).

Chloro-{5,10,15,20-tetrakis[(1*R*,3*S*,5*S*,7*R*)-1,2,3,5,6,7-hexahydro-1,3,5'7-tetraethyl-*s*-indacene-4-yl]porphyrinato}manganese (3). Porphyrin **26** (4.0 mg) was subjected to the metal insertion conditions as those used in the formation of **2**. Metalloporphyrin **3** was obtained as a green solid (3.9 mg, 92%). UV ($CHCl_3$) λ_{max} 481 nm (ε = 79,412 cm^{-1} M^{-1}); MS (FAB, 3-nitrobenzyl alcohol) m/z (relative intensity) 1436 (M^+ - Cl, 100%), 1422 (37).

(1*S,4*R**,5*R**,8*S**)-10-Bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-carboxaldehyde (28).** To a mixture of benzaldehyde **27** (1.70 g, 7.13 mmol), a small crystal of iodine and iron powder (5 mg) in CCl_4 (9 mL) was added Br_2 (1.14 g, 7.13 mmol) in CCl_4 (1 mL) at 0 °C under

nitrogen. After 24 h at rt, the mixture was extracted with 10% aqueous NaOH (50 mL) and water. The combined aqueous portion was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic portion washed with water, dried ($MgSO_4$) and concentrated to give **28** (1.85 g, 81%) as a brown solid; mp 240 - 245 °C. ^{1}H NMR δ 10.36 (s, 1 H), 4.18 (br s, 2 H), 3.54 (br s, 2 H), 1.93-2.08 (m, 4 H), 1.88 (d, 2 H, J = 9.0 Hz), 1.55 (d, 2 H, J = 9.0 Hz), 1.20-1.35 (m, 4 H); ^{13}C NMR δ 190.6, 149.0, 146.2, 128.6, 126.8, 48.5, 43.6, 42.3, 26.3, 25.7; IR (thin film) 2964, 1447, 1327, 995, cm^{-1}; MS (EI, 70ev) *m/z* 316 (M^+, 10%), 290 (23), 288 (25), 163 (77), 140 (25), 81 (100).

(*R,R*)-Hydrobenzoin Ketals of (1*S,4*R**,5*R**,8*S**)-10-Bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-carboxaldehyde (29 and 30).** A solution of racemic bromoaldehyde **28** (4.5 g, 14.2 mmol), PPTS (0.3 g), (*R,R*)-hydrobenzoin (5.0 g, 23.5 mmol) was refluxed through a Soxhlet thimble containing 4 Å molecular sieves under nitrogen for 20 h. The mixture was cooled to rt and washed with saturated $NaHCO_3$, water and brine, dried ($MgSO_4$) and concentrated to give a crude mixture of diastereomeric ketals **29** and **30**. Diagnostic ketal hydrogen ^{1}H NMR signals at 6.68 and 6.71 ppm for the two diastereomers. Recrystallization from hot hexane gave pure **29** which was the less polar compound by TLC (1.5 g, 20%), $[\alpha]_D^{25}$= -18 (c = 1.0 $CHCl_3$). ^{1}H NMR δ 7.30-7.37 (m, 10 H), 6.71 (s, 1 H), 4.95 (m, 2 H), 3.92 (s, 2 H), 3.55 (s, 2 H), 1.95-2.05 (m, 4 H), 1.46-1.53 (m, 2 H), 1.15-1.27 (m, 4 H); ^{13}C NMR δ 148.3, 147.1, 139.3, 136.6, 135.9, 128.5, 128.4, 128.0, 126.7, 126.3, 126.2, 117.5, 103.3, 87.7, 85.0, 60.9, 49.1, 48.7, 42.1, 40.3, 31.6, 27.1, 27.0, 22.6, 14.1; $[\alpha]_D^{25}$ -18.4° (c 1.0, $CHCl_3$); IR (thin film) 3020, 2980, 1555, 1442, 1140, 750 cm^{-1}; MS (EI, 70 ev).

(1*R*,4*S*,5*S*,8*R*)-10-Bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-carboxaldehyde ((–)-28). A solution of bromoketal **29** (0.94 g, 1.84 mmol) in 4:1 THF:30% H_2SO_4 (45 mL) was heated under reflux for 24 h. The cooled mixture was extracted with ethyl acetate (3 x 15 mL) and the combined organic portion was washed with water and brine, dried ($MgSO_4$) and concentrated. The crude product was chromatographed (SiO_2, 3:7 CH_2Cl_2:petroleum ether) to give resolved (–)-**28** (0.50 g, 85%) as a tan solid; mp 235-240 °C, $[\alpha]_D^{25}$= -46 (c = 1.0 $CHCl_3$). The NMR spectral data were identical to racemic **28**.

(1*S,4*R**,5*R**,8*S**)-10-Acetoxy-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-carboxaldehyde (31).** A solution of sodium nitrate (1.50 g, 18.0 mmol) in trifluoracetic acid (150 mL) was added to a solution of aldehyde **27** (4.0 g, 16.8 mmol) in acetic acid (100 mL) under nitrogen. The mixture was stirred at rt for 24 h then poured into ice water (200 mL) containing conc. H_2SO_4 (5 mL) and extracted with ethyl acetate (3 x 50 mL) The organic portion was washed with saturated $NaHCO_3$, water and brine, dried ($MgSO_4$) and concentrated to give **31** as a yellow solid (4.45 g, 89%); mp 95-100 °C. ^{1}H NMR δ 10.35 (s, 1 H), 4.12 (br s, 2 H), 3.29 (br s, 2 H), 2.35 (s, 3 H), 1.87-1.95 (m, 4 H), 1.72 (br d, 2 H, J = 9.0 Hz), 1.49 (d, 2 H, J = 9.0 Hz), 1.12-17 (m, 4 H); ^{13}C NMR δ 190.9, 168.6, 150.6, 141.9, 138.0, 121.4, 49.0, 41.7, 39.9, 26.4, 25.8, 20.7; IR (thin film) 2980, 1760, 1690, 1565, 1190, 1090 cm^{-1}, MS (EI, 70 eV) m/z 296 (M^+, 19), 254 (26), 226 (100), 198 (99), 141 (80), 115 (92).

(1*S,4*R**,5*R**,8*S**)-10-Hydroxy-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-carboxaldehyde (32).** A solution of aldehyde **31** (2.00 g, 6.75 mmol), methanol (4 mL), water (1 mL) and saturated $NaHCO_3$ (2 mL) was stirred at rt under nitrogen for 96 h. The mixture was acidified with 10% HCl (10 mL) and extracted with ethyl acetate. The organic portion was washed with water, dried ($MgSO_4$) and concentrated to give **32** (1.54 g, 90%) as a colorless oil. ^{1}H NMR δ 10.29 (s, 1 H), 5.27 (s, 1 H), 4.12 (s, 2 H), 3.48 (s, 2 H), 1.85-1.95 (m, 4 H), 1.68 (d, J = 9 Hz, 2 H), 1.49 (d, J = 9 Hz, 2 H), 1.10-1.20 (m, 4 H); ^{13}C NMR δ 190.4, 151.4, 147.5, 131.3, 117.7, 49.0, 41.7, 28.6, 26.4, 26.3; IR (thin film) 3385, 2952, 1653, 1536, 1214, 1111 cm^{-1}; MS (EI, 70 ev) 254 (M$^+$, 45%), 226 (92), 198 (100), 148 (84), 115 (20).

(1*S,4*R**,5*R**,8*S**)-10-Methoxy-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-carboxaldehyde (33).** To a solution of aldehyde **32** (1.00 g, 3.93 mmol) in THF (5 mL) and 2 N NaOH (10 mL) was added dimethyl sulfate (2.5 mL). After 5 min more 2 N NaOH (5 mL) was added the mixture was heated at 80 °C under nitrogen for 24 h. The cooled mixture was extracted by ether and the organic portion dried ($MgSO_4$) and concentrated to yield **33** (0.95 g, 90%) as a white waxy solid. ^{1}H NMR δ 10.29 (s, 1 H), 4.10 (s, 2 H), 3.98 (s, 3 H), 3.61 (s, 2 H), 1.85-1.95 (m, 4 H), 1.69 (d, J = 9 Hz, 2 H), 1.47 (d, J = 9 Hz, 2 H), 1.05-1.15 (m, 4 H); ^{13}C NMR δ 190.6, 151.4, 135.3, 128.5, 126.0, 60.2, 48.8, 41.3, 40.2, 26.7, 26.4; IR (thin film) 2980, 2756, 1675, 1560, 1310, 1105 cm^{-1}; MS (EI, 70 ev) m/z 268 (M$^+$, 43), 240 (96), 212 (100), 165 (25), 153 (34).

5,10,15,20-tetrakis[(1*R*,4*S*,5*S*,8*R*)-10-Bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl]porphyrin (36a). Bromoaldehyde (–)-**28** (0.20 g, 0.63 mmol) was dissolved in chloroform (30 mL) and pyrrole (044 μL, 0.63 mmol) was added at rt. Nitrogen was bubbled through the solution for 10 min then $BF_3.Et_2O$ (23 μL, 0.19 mmol) was added along with absolute ethanol (0.1 mL). The mixture was stirred at rt for 12 h under nitrogen excluding light. p-Chloranil (0.116 g, 0.47 mmol) was added and the mixture heated at 60 °C for 6 h. After cooling to rt, Et_3N (0.26 μL, 0.19 mmol) was added and the solution was concentrated and chromatographed (SiO_2, 30:70 $CHCl_3$:petroleum ether) to afford porphyrin **36a** (60 mg, 26% yield) as a red shiny powder: $[\alpha]_D^{25}$ -350°(c =2.0 x 10^{-3}, $CHCl_3$); mp. > 300 °C. ^{1}H NMR δ 8.72 (s, 8 H), 3.81 (s, 8 H), 2.81 (s, 8 H), 2.05 (d, J = 8.5 Hz, 8 H), 1.83-1.90 (m, 8 H), 1.20-1.50 (m, 16 H), 1.00-1.07 (m, 8 H), 0.80-0.90 (m, 8 H), -2.63 (s, 2H); ^{13}C NMR δ 149.8, 143.4, 131 (br), 127.6, 115.6, 110.8, 48.7, 44.6, 43.7, 29.7, 26.6, 26.3; IR (thin film) 3440, 3010, 2980, 1220, 1055 cm^{-1}; MS (FAB 3-nitrobenzyl alcohol) 1225 (14%), 1079 (1), 663 (2), 393 (7), 289 (25), 225 (41), 197 (100); UV λ_{max} 454 nm (ε = 135,600 cm^{-1} M^{-1}).

Chloro{5,10,15,20-tetrakis[((1*S*,4*R*,5*R*,8*S*)-10-Bromo-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl]porphyrinato}manganese (4a). Bromoporphyrin **36a** (75 mg, 0.051 mmol) was dissolved in hot DMF (5 mL) and $MnCl_2$–$4H_2O$ (85 mg, 0.51 mmol) was added to the solution which was stirred at 150 °C for 6 h. After cooling to rt, the solution was poured into a flask containing saturated aqueous NaCl (10 mL) at 0 °C. The resulting green solution was extracted with CH_2Cl_2 (3 x 5 mL) and the

combined organic layer was washed with 5% HCl (2 x 5 mL), brine and then dried ($MgSO_4$) and to give **4a** (71 mg, 99% yield) as green solid: $[\alpha]_D^{25}$ -420°(c = 1.7 x 10^{-3}, $CHCl_3$); mp > 300 °C. IR (thin film) 3000, 2935, 1250, 1205, 750 cm^{-1}; MS (FAB, 3-nitrobenzyl alcohol) 1507 (M^+– Cl, 16%), 1508 (M^++1 - Cl, 21), 1509 (M^++2 - Cl, 60), 1510 (M^++3 - Cl, 62), 1511 (M^++4 - Cl, 100), 1512 (M^++5 - Cl, 86), 1513 (M^++6 - Cl, 94), 1514 (M^++7 - Cl, 61), 1515 (M^++8 - Cl, 38), 1516 (M^++9 - Cl, 16), 625 (13), 581 (14), 537 (17), 338 (39); UV ($CHCl_3$) λ_{max} 480 nm (ε = 24,600 cm^{-1} M^{-1}).

(*R,R*)-Hydrobenzoin Ketals of (1*S,4*R**,5*R**,8*S**)-10-Methoxy-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-carboxaldehyde (34 and 35).** Following the procedure described for **28**, p-methoxybenzaldehdye **33** (1.0 g, 3.71 mmol) gave pure **34** as a white solid (9:1 hexane:CH_2Cl_2, 0.59 g, 34%): mp 87-89 °C, $[\alpha]_D^{25}$ = -40 (c = 1.0 $CHCl_3$). Diagnostic ^{1}H NMR ketal hydrogen signals for diastereomeric mixture of ketals **34** and **35**: 6.55 and 6.58 ppm. Spectral characteristics for crystalline diastereomer **34**: ^{1}H NMR δ 7.37-7.30 (m, 10 H), 6.55 (s, 1 H), 5.01 (d, J = 8 Hz, 1 H) 4.93 (d, J = 8 Hz, 1 H), 3.88 (s, 3 H), 3.83 (s, 2 H), 3.59 (s, 2 H), 1.95-2.05 (m, 4 H), 1.74 (d, J = 8 Hz, 2 H), 1.48 (d, J = 8 Hz, 2 H), 1.15-1.30 (m, 4 H), 1.124; ^{13}C NMR δ 147.1, 139.3, 136.6, 135.9, 128.6, 125.5 (2 C), 128.4, 127.9, 126.9, 126.3, 126.3, 103.3, 87.7, 85.0, 60.9, 48.7, 42.1, 40.3, 27.1, 27.0; IR (thin film) 3010, 2950, 1650, 1560, 1235, 1125; MS (EI, 70 eV) m/z 464 (M^+, 13), 358 (69), 329 (100), 302 (22), 239 (26), 179 (51), 165 (68), 152 (50), 105 (53); mp 85-90 °C.

(1*R*,4*S*,5*S*,8*R*)-10-Methoxy-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-carboxaldehyde ((–)-33). Following the procedure described for **29**, methoxy ketal **34** (1.00 g, 2.15 mmol) gave (–)-**33** (0.52 g, 90%) as a white waxy solid; $[\alpha]_D^{25}$= -38 (c = 1.0, $CHCl_3$).

5,10,15,20-tetrakis[(1*R*,4*S*,5*S*,8*R*)-10-Methoxy-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl]porphyrin (36b). In a round bottom flask, a solution of p-methoxybenzaldehyde (–)-**33** (100 mg, 0.37 mmol) in $CHCl_3$ (30 mL) was mixed with pyrrole, (26 μL, 0.37 mmol). Nitrogen was bubbled through the solution for 5 min and BF_3.Et_2O (14 μL, 0.11 mmol) was added. The mixture was stirred for 12 h at rt then p-chloranil (68 mg, 0.28 mmol) was added. The mixture was heated under reflux for 3 h and then allowed to cool to rt. Et_3N (16 μL, 0.11 mmol) was added and the solution was concentrated and chromatographed (SiO_2, 30:70 $CHCl_3$:petroleum ether) to give porphyrin **36b** (36 mg, 30%) as a red powder: mp > 300 °C; $[\alpha]_D^{25}$ -350° (c 2 x 10^{-3}, $CHCl_3$). ^{1}H NMR δ 8.73 (s, 8 H), 4.18 (s, 12 H), 3. 86 (s, 8 H), 2.75 (s, 8 H), 1.95-2.05 (m, 16 H), 1.25-1.505 (m, 16 H), 0.95-1.15 (m, 16 H), –2.48 (s, 2H); ^{13}C NMR δ 173.4, 150.5, 133.5, 128.3, 115.3, 60.5, 49.0, 42.6, 41.1, 29.7, 27.3, 26.8; IR (thin film), 3430, 3020, 1675, 1218, 755 cm^{-1}; MS (FAB, 3-nitrobenzyl alcohol) m/z 1263 (M^+, 6%), 1189 (10), 1147 (10), 1096 (11), 643 (10), 603 (10), 313 (53), 273 (88), 205 (100) 185 (88), 130 (89); UV ($CHCl_3$) λ_{max} 458 nm (ε = 133,900 cm^{-1} M^{-1}).

Chloro{5,10,15,20-tetrakis[(1*S*,4*R*,5*R*,8*S*)-10-Methoxy-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl]porphyrinato}manganese (4b). p-Methoxy-substituted porphyrin **36b** (100 mg, 0.079 mmol) was dissolved in hot DMF (60 mL) and $MnCl_2.4H_2O$ (120 mg, 0.72 mmol) was added. The mixture was then stirred under reflux for 6 h and worked up according to the previous procedure to give after chromatography (SiO_2, CH_2Cl_2) complex **4b** (80 mg, 75%) as a green solid; mp >300 °C; $[\alpha]_D^{25}$ -220 (c 1.8 x 10^{-3}, $CHCl_3$). UV λ_{max} 482 nm (ε = 58,500 $cm^{-1}M^{-1}$); MS (FAB) m/z 1315 (M^+- Cl, 100), 1316 (96), 1286 (12), 658 (7.3), 431 (9).

Standard Asymmetric Epoxidation Procedure. The epoxidations were run at 20 °C by combining under air, 0.5 mmol alkene, 2.5 mL Clorox™ bleach, 2 mL CH_2Cl_2, 0.0025 mmol **2**, 0.075 mmol 4-tert-butylpyridine, 0.075 mmol n-$C_{14}H_{29}(CH_3)_2(PhCH_2)N^+Cl^-$. The reaction mixture was stirred at rt and monitored by gas chromatography every hour. When the reaction was complete (after 1 h for styrene and dihydronaphthalene or 4 h for cis-ß-methylstyrene), the CH_2Cl_2 layer was separated from H_2O layer by pipet. The water 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 with CH_2Cl_2. The entire eluent was concentrated to afford the enantiomerically enriched epoxide in each case in >90% yield. Washing the pipet column by 5:95 MeOH: CH_2Cl_2 provided a green solution of the recovered catalyst which after washing with dilute HCl provided metalloporphyrin **2** by solvent removal. This reisolated compound exhibited an UV spectrum indistinguishable to the originally prepared complex **2** and gave indistinguishable results when reused in the asymmetric epoxidation reaction. The enantiomeric purity of all compounds was determined by integration of ^1H NMR spectra obtained in the presence of the chiral shift reagent $Eu(hfc)_3$.

Acknowledgement: We thank the American Cancer Society (Grant CN-6) and The Oklahoma Center for the Advancement of Science and Technology (HR2-036) for funding this research.

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4. We refer to complexes such as **2** as exhibiting D_4-symmetry since the "naked" metalloporphyrin complex (lacking chloride or other ligands) does possess this symmetry and operationally it behaves

like a D_4-symmetrical complex; only one oxo complex can form due to the homotopicity of the faces in the "naked" complex.

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(*Received in USA* 17 *April* 1997; *accepted* 17 *June* 1997)