Tetrahedron Vol. 47, No. 41, pp. 8687-8700, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

THE SYNTHESIS OF A PORPHYRIN WITH A HYDROCARBON ENCAPSULATED FACE

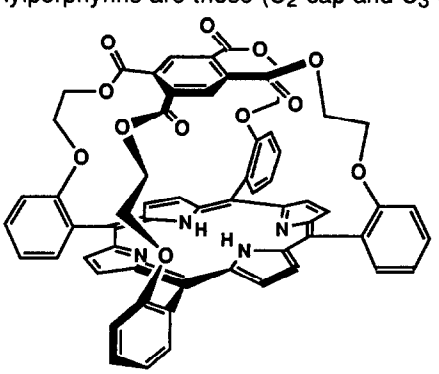
Wayne F.K. Schnatter, Örn Almarsson and Thomas C. Bruice*.

Department of Chemistry
University of California at Santa Barbara
Santa Barbara, CA 93106

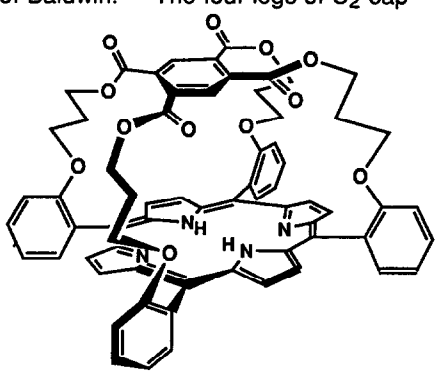
(*Received in USA* 4 *September* 1991)

Abstract. The uniquely hydrocarbon-like capped porphyrin ($C_{70}H_{68}N_4$), **1l**, has been successfully prepared by a high dilution reaction of pyrrole with tetrakis-1,2,4,5-[pentyl-5`-(2``-formylphenyl)]-benzene **1h** in the presence of boron trifluoride etherate. The aldehyde **1h** was prepared by four simultaneous Wittig condensations of a phosphonium salt, **1e**, with 1,2,4,5-tetraformylbenzene, followed by reduction of the double bonds with Raney nickel and deprotection with perchloric acid.

Introduction: We are in the process of synthesizing molecules that will be studied as catalysts for oxidation reactions. As a part of one such molecule we require a tetraphenylporphyrin {(TPP)H_2} that carries an inert cap. The structural requirement for a capped (TPP)H_2 is a central structure covalently linked to the four phenyl rings of (TPP)H_2 by four legs. The prototypical capped tetraphenylporphyrins are those (C_2-cap and C_3-cap) of Baldwin.[1] The four legs of C_2-cap



C_2-cap



C_3-cap

and C_3-cap are anchored to the phenyl rings of (TPP)H_2 through *ortho*-ether linkages and the capped structure is held together by four ester linkages. Recently, Ibers et al. published the syntheses and crystallographic structures of novel four atom benzenecapped TPP's. The caps are, as in the case of Baldwin's caps, attached through ether and ester linkages.[2] Iron tetraphenyl porphyrins whose *meso*-phenyl moities are substituted in the *ortho*-positions by alkyl-O substituents are quite susceptible to destructive oxidation[3] and ester linkages are susceptible to hydrolysis.

The aforementioned structures are, therefore, susceptible to destructive oxidation and hydrolysis. Much the same can be said of another capped $(TPP)H_2$ synthesized by Lindsey.[4] A completely hydrocarbon capped TPP would be much more resistant to oxidative and hydrolytic decomposition.

Results and Discussion. The completely hydrocarbon capped $(TPP)H_2$ (**1l**) of Scheme I was chosen as the target porphyrin. The energy minimized[5] structure **1l** (Figure 1) is essentially free of strain and eclipsing interactions. An effort at synthesis of the smaller congener **2l** (Scheme II) is described.

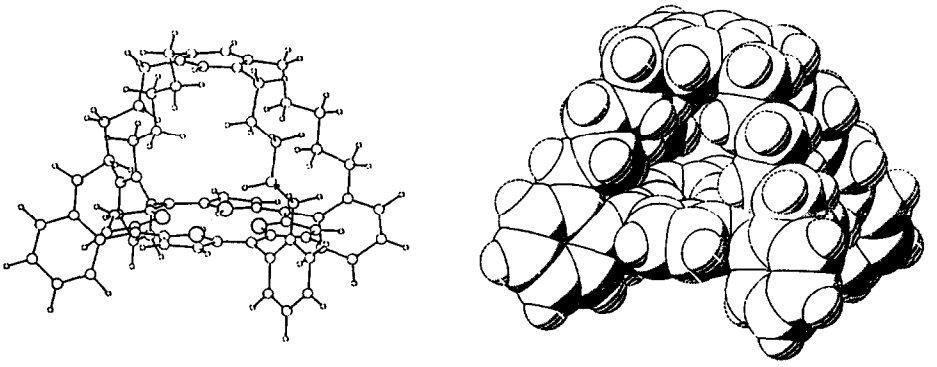
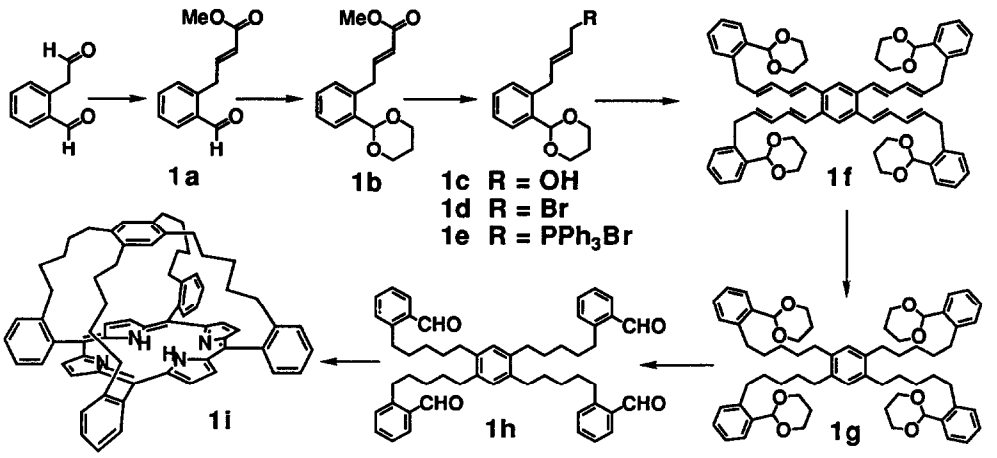


Figure 1. "Ball and stick" and CPK stereoviews of an extensively minimized structure of **1l** (see ref. 5).

A simple retrosynthetic disconnection of a porphyrin involves an aldehyde and pyrrole.[6] Application of this retrosynthetic operation to **1l** reduces the syntheses to the preparations of the tetraaldehyde **1h** (Scheme I). We elected to use the Wittig condensation of tetra-1,2,4,5-formylbenzene[7] with the phosphorous ylide of phosphonium salt **1e**. Ozonation of indene, by literature procedures[8] , afforded homophthalaldehyde which was immediately allowed to react with methyl triphenylphosphoranylidene acetate at -80 °C to provide the α,β unsaturated ester **1a** in 80% yield as a colorless oil. Although the geometric isomers were easily separated, reduction of the double bond in a later step made this unnecessary. Protection of the aldehyde function of **1a,** using propane-1,3-diol with toluenesulfonic acid as catalyst, provided **1b** (97% yield). Reduction of **1b** with two equivalents of DIBAL-H provided the allylic alcohol **1c** in 83% yield. Conversion of **1c** to the allylic bromide **1d** was achieved in 71% yield using carbon tetrabromide/triphenyl phosphine in the presence of collidine.[9] In the absence of collidine, **1d** was not obtained. The phosphonium salt **1e** was obtained in 89% yield by treatment of **1d** with triphenylphosphine in benzene[10] The crucial carbon-carbon bond forming reaction, condensation of **1e** with 1,2,4,5-tetraformylbenzene[7], proceeded under mild conditions to afford the highly fluorescent **1f** as a mixture of geometric isomers. Purification of this compound proved wasteful, and therefore it was directly reduced with hydrogen in the presence of Raney Nickel to give a 56% yield of the desired tetraacetal **1g**. Hydrolysis of **1g** with perchloric acid in wet THF gave the tetraaldehyde **1h** in 60% yield. Application of Baldwin's propionic acid procedure failed to provide detectable amounts of the

desired capped porphyrin as did a boron trifluoride catalyzed condensation according to the procedure of Lindsey (10^{-2} M). At higher dilution (7.5×10^{-5} M) the Lindsey conditions gave **1i** in 6 % yield.

Scheme I

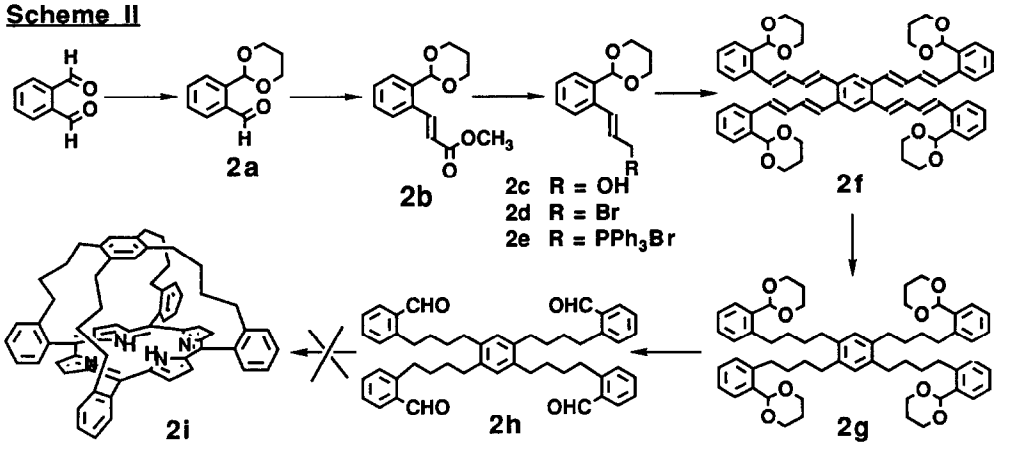


Characterization of {5,10,15,20[α,α',α'',α'''-duryl(tetrakis-*o*-butylphenyl)] porphyrin 1i. The high resolution mass spectrum of **1i** was determined by laser desorption mass spectrometry. A molecular weight of 964.59 and molecular formula of $C_{70}H_{68}N_4$ was established. Proton NMR exhibited the resonances expected for a capped porphyrin, i.e., β-pyrrole resonances at 8.57 and 8.56 ppm, indicative of C_{2v} symmetry and a broad N-H resonance at -2.79 ppm. Aromatic resonances typical for an *ortho*-disubstituted aromatic ring and a singlet at 5.52 ppm (capping benzene protons) were observed, but the spectrum in the aliphatic region is rather complicated. Signals are upfield shifted due to the magnetic anisotropy of the porphyrin ring. Inspection of the minimized structure in figure 1 reveals that two hydrogens on the same carbon atom should in most cases be in different environments, which explains the large number of peaks in the area of the spectrum between 2.4 and -0.3 ppm. All of the aliphatic resonances were broad, presumably due to slow interchange of conformations on the NMR time scale. At present, however, we cannot rule out the possibility that a guest be trapped inside the cavity under the cap, which could also be responsible for line broadening and upfield shifting of the resonances. Carbon 13 NMR aided in the identification of the five side chain methylenes (see Experimental). UV/visible spectrophotometry established the structure of a free base 5,10,15,20-tetraphenylporphyrin. As anticipated for a compound with a molecular formula of $C_{70}H_{68}N_4$, **1i** is soluble in petroleum ether, a most unusual characteristic for a tetraphenylporphyrin.

The synthesis of the more strained 2i, which is a tetrakis-(tetramethylene) homolog of the capped porphyrin **1i**, was attempted. The preparation of the precursor, tetraaldehyde **2h**, was straightforward as shown in Scheme II. Phthalic dialdehyde can be singly protected as the 1,3-

dioxane derivative **2a**. When one equivalent of propane-1,3-diol was used and the reaction monitored by ^1H NMR, azeotropic removal of water provided a mixture of **2a** contaminated with the starting dialdehyde. Since the two compounds exhibited coincidental R_f values, it was not possible to assess the progress of the reaction with TLC, nor was the purification of the product trivial. In most cases the impure material was used in the next reaction and the necessary purification effected at that time. Typically 84% yield of the desired monoprotected compound **2a** was obtained. Condensation of the latter with methyl triphenylphosphoranylidene acetate resulted in 65-95% yield of the cinnamate ester **2b**. The ester was reduced to the alcohol **2c** in 88% yield with two equivalents of DIBAL-H. Repetition of the bromination protocol (carbon tetrabromide/ triphenylphosphine/collidine) afforded the bromide **2d** in 58% yield. The phosphonium salt **2e** was obtained upon the combination of the **2d** with triphenylphosphine in benzene as before (95% yield). Condensation of the ylide of **2e** with tetra-1,2,4,5-formylbenzene proceeded readily to produce the desired tetradiene **2f**, again as a mixture of geometric isomers. Reduction to the tetraacetal **2g** after filtration through a short column of silica provided pure **2g** in an overall yield of 40%.

Scheme II



Hydrolysis of the dioxanes with perchloric acid in aqueous THF provided the tetraaldehyde **2h** in 47% yield. All approaches to produce the desired porphyrin provided high (~30%) yield of material posessing a Soret band. However, upon purification, no fraction exhibited spectral data consistent with the structure of a monomeric capped porphyrin; instead, it was apparent that mixtures of isomeric porphyrin dimers, trimers, etc. was obtained. It would appear that porphyrin **2i** is not attainable by use of either the Baldwin or high dilution Lindsey procedures for porphyrin synthesis.

Experimental Section

Melting points were obtained on a Laboratory Devices Mel-Temp. Benzene, pyrrole, boron trifluoride etherate, dichloromethane, and amines were distilled from calcium hydride.

Tetrahydrofuran was distilled from a continuous still of potassium benzophenone ketyl. Chloroform used for porphyrin preparations was distilled from anhydrous potassium carbonate. Phthalic dialdehyde was obtained from Lancaster Synthesis. Propane 1,3 diol was obtained from Fisher Scientific. Indene was purified by filtration through silica gel. Carbon tetrabromide was purified by sublimation at high vacuum (0.01 Torr) into a cold trap (-78 ^{o}C). Other reagents were purchased from Aldrich Chemical Co. Column chromatography was generally carried out according to the flash column method developed by Still.[11] Florisil (100-200 Mesh) was used as an adsorbent for loading chromatography columns. Silica gel column chromatography columns were run with Davisil Grade 633 Type 60A silica gel (200- 425 mesh) obtained through Fisher Scientific. Alumina column chromatography was carried out with neutral alumina (average particle size 150 μ) obtained from Aldrich Chemical Co. Filter column chromatography[12] was carried out using EM Reagents' Silica Gel GF-254 (particle size: 10-40 μ; 13% $CaSO_4$ as a binder). Thin layer plate chromatography was carried out using thin layer plates backed with glass (E. Merck Item: 5713 for alumina and 5715 for silica). ^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) were obtained on a General Electric GN-500 spectrometer and are reported in parts per million relative to TMS. IR spectra were recorded on a Perkin-Elmer 1330 infrared spectrophotometer and are reported in wavenumbers using a standard sample of polystyrene as a reference. Solution cell spectra were obtained using sealed precision pathlength cells in the solvent indicated (usual concentration 40 mg/ mL). Mass Spectra were obtained using electron impact (EI) or fast atom bombardment (FAB). High resolution mass spectra were obtained using PFK as a reference compound. Laser desorption mass spectrometry on the capped porphyrin **(1i)** was performed at the University of California, Riverside. Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tennessee. UV/Vis spectra were obtained on a Perkin-Elmer model 553 Spectrophotometer.

Experimental details for the synthetic procedures of Scheme I.

Preparation of methyl [4-(2`-formyl)phenyl]-2-butenoate (1a). To a toluene (60 mL) solution of homophthalaldehyde (8.72 g; 58.9 mmol) at -80^{o}C was added methyl triphenyl-phosphoranylidene acetate (15.0 g; 45.0 mmol) in 60 ml acetonitrile:toluene (1:3). The crude mixture was adsorbed onto Florisil and purified via column chromatography on silica (10 % ethyl acetate: hexanes) to provide **1a** as a colorless oil (7.35 g; 80 % yield; 85% E isomer, however both E and Z proved suitable for the reactions which follow). ^{1}H NMR ($CDCl_3$, 500 MHz) δ10.07 (s, 1H, CHO), 7.77 (dd, J = 6.5, 2.5 Hz, 1 H, H at C-3), 7.48 (td, J = 7.5, 1.5 Hz, 1 H, H at C-4), 7.40 (ddd, J = 8.0, 7.5, 1.5 Hz, 1 H, H at C-5), 7.20 (d, J = 8.0 Hz, 1 H, H at C-6), 7.08 (dt, J = 15.6, 6. 5 Hz,1 H, H at C-2 of butene), 5.66 (dt, J = 15.6, 1.7 Hz, 1 H, H at C-3 of butene), 3.91 (dd, J = 6.5, 1.7 Hz, 2 H, H's at C-1 of butene), 3.65 (s, 3 H, ester methyl), ^{13}C NMR ($CDCl_3$, 125 MHz) δ 192.5 (CHO), 166.7 (C=O, ester), 147.1 (C-2 of butene), 139.6 (4^{o} aromatic carbon), 134.1, 133.8, 131.4, 127.7, 122.1 (alkene and aromatic C-H's), 51.5 (ester methyl), 35.3 (C-1 of butene); IR (NaCl plates) 1720 (CHO), 1690 (ester), 1650 (C=C) cm^{-1}; MS (70 ev) *m/z* (rel abund) 204 (M^+, 2), 172 (M^+- OCH_2, 39), 144 (M^+- $C_4H_{10}O_2H$, 100), 115 (M^+- $C_4H_{10}O_2$ + HC=O, 67); HRMS calcd for $C_{12}H_{12}O_3$: M^+ = 204.0786. Found: 204.0759

Preparation of methyl [4-(2`-(2``-(1``,3``-dioxanyl)))phenyl]-2-butenoate (1b). To a benzene (100 mL) solution of **1a** (7.25g; 35.5 mmol) and propane-1,3-diol (2.69 mL; 2.84 g; 37.3 g) was added p-toluenesulfonic acid monohydrate (19.0 mg; 0.10 mmol). The solution was heated at reflux in a flask fitted with a Dean-Stark trap and condenser. Analysis of aliquots by ^{1}H NMR revealed the completion of reaction within three hours. The reaction was quenched with the addition of triethylamine (0.5 mL). The benzene solution was then evaporated directly onto Florisil and column chromatography (silica, 10 % ethyl acetate: hexanes) provided **1b** (9.04 g; 97%) as a *colorless solid* (*mp.* 55-57 ^{o}C). ^{1}H NMR ($CDCl_3$, *500 MHz*) δ 7.56 (dd, J = 7.0, 2.0 Hz, 1 H, H aromatic), 7.25 (m, 2 H, aromatic H), 7.12 (m, 2 H, aromatic and H at C-2 of butene), 5.75 (d, J = 16.0, 1 H, H at C-3 of butene), 5.52 (s, 1 H, H at C-2 of dioxane), 4.22 (dd, J = 11.5, 5.0 Hz, 2 H, H^e at C-4 and C-6 of dioxane)[13], 3.91 (td, J = 11.5 Hz, 1.5 Hz, 2 H, H^a at C-4 and C-6 of dioxane), 3.67 (s, 3 H, ester methyl), 3.66 (m, 2 H, H at C-1 of alkene), 2.18 (m, 1 H, H^a at C-5 of dioxane), 1.40 (dd, J = 4.0, 1.0 Hz, 1 H, H^e at C-5 of dioxane); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166 9 (C=O, ester), 148.0 (C-3 of alkene), 136.5 (4^o aromatic carbon), 135.5, 130.1, 129.1, 127.0, 121.8 (alkene and aromatic C-H's), 100.4 (C-2 of dioxane), 67.5 (C-4 and C-6 of dioxane), 51.4 (ester methyl), 35.2 (C-1 of alkene), 25.7 (C-5 of dioxane); IR (CCl_4) 2980 (aromatic C-H), 2850 (aliphatic C-H), 1755 (ester), 1655 (C=C-C=O), 1100 (C-O) cm^{-1}; MS (70 ev) *m/z* (rel abund) 262 (M^+, 4.5), 203 (M^+- C_3H_6O, 30), 186 (M^+- $C_3H_7O_2$, 67), 176 (M^+- C=C-C=O(OCH_3, 90), 144 (M^+- C_3H_6O + $COOCH_3$, 100); HRMS calcd for $C_{15}H_{18}O_4$: M^+ = 262.1205. Found: 262.1199.

Preparation of [2`-(2``-(1``,3``-dioxanyl))phenyl]but-2-enol (1c). To a toluene (340 mL) solution of **1b** (9.04g; 34.33 mmol) at -78^{o}C was added diisobutylaluminum hydride (72.1 mL of a 1 M hexane solution) dropwise. After 2 h the reaction mixture was allowed to warm to 25^{o}C and the reaction was quenched with methanol (2 mL) and aqueous sodium potassium tartrate (100 mL of a saturated solution). The mixture was transferred to a separatory funnel and the organic layer separated. The aqueous layer was extracted with two portions of ethyl acetate (100 mL). The organic layers were combined and dried over magnesium sulfate. Column chromatography on silica (43% ethyl acetate: hexanes) provided pure **1c** yield (6.67 g; 83%) ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (dd, J = 7.5, 1.5 Hz, 1 H, H at C-5), 7.24 (m, 2 H, aromatic H), 7.13(m, 1 H, aromatic H), 5.78(dt, J = 16.0, 7.0 Hz, 1 H, H at C-3 of butene), 5.59 (s, 1 H, H at C-2 of dioxane), 5.59 (m, 1 H, H at C-2 of butene), 4.21 (dd, J = 11.0, 5.0 Hz, 2 H, H^e at C-4 and C-6 of dioxane), 3.97 (m, 2 H, H at C-4 of butene), 3.92 (td, J = 6.0, 2.0 Hz, 2 H, H^a at C-4 and C-6 of dioxane), 3.47 (d, J = 6.5 Hz, 2 H, H at C-1 of butene), 2.18 (m, 1 H, H^a at C-5 of dioxane), 1.39 (dd, J = 14.0, 1.0 Hz, 1 H, H^e at C-5 of dioxane); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.6, 136.3 (4^o Carbons of aromatic ring), 131.3, 130.3, 129.8, 129.0, 126.5, 126.4 (alkene and aromatic C-H's), 100.0 (C-2 of dioxane), 67.5 (C-4 and C-6 of dioxane), 63.2 (C-4 of alkene), 35.2 (C-1 of alkene), 25.7 (C-5 of alkene) IR (NaCl plates) 3400 (br, OH), 2980 (aromatic C-H), 2860, 1100 (C-O), cm^{-1}; MS (70 ev) *m/z* (rel abund) 234 (M^+, 0.81), 176 (M^+- C_3H_5O, 36), 158 (M^+- $C_4H_7O_2$, 25), 145 (M^+- hydroxybutene side chain, 28), 128 (M^+- $C_4H_7O_2$ + H_2O, 100); HRMS calcd for $C_{14}H_{18}O_3$: M^+ = 234.1256. Found: 234.1232.

Preparation of [2`-(2``-(1``,3``-dioxanyl))phenyl]but-2-enyl bromide (1d). To a solution of **1c** (6.6 g ; 28.2 mmol), freshly sublimed carbon tetrabromide (10.77 g; 32.5 mmol) and anhydrous collidine (4.3 mL; 3.9 g; 32.5 mmol) in dry dichloromethane (135 mL) at -20°C was added solid triphenylphosphine (10.83 g; 41.3 mL). The reaction was complete within 20 min as demonstrated by thin layer chromatographic analysis (silica 5 % and 50 % ethyl acetate in hexanes), and was quenched with the addition of methanol (2 mL). The solvent was removed and the crude mixture purified by column chromatography with silica (10% ethyl acetate: hexanes) to provide **1d** as a colorless oil. (5.93 g; 71%yield).^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.60 (dd, J = 7.5, 1.5 Hz, 1 H, H at C-6), 7.25 (m, 2 H, H at C-4 and C-5), 7.12(dd,J = 7.5, 1.5 Hz, 1 H, H at C-3),5.92(dt, J = 15.0, 6.5 Hz, 1 H, H at C-3 of butene), 5.71 (m, 1 H, H at C-2 of butene), 5.56 (s, 1 H, H at C-2 of dioxane), 4.24 (dd, J = 11.5, 5.0 Hz, 2 H, H^e at C-4 and C-6 of dioxane), 3.96 (m, 4 H, H at C-4 of butene and H^a at C-4 and C-6 of dioxane), 3.53 (d, J = 6.5 Hz, 2 H, H at C-1 of butene), 2.22 (m, 1 H, H^a at C-5 of dioxane), 1.42 (d, J = 13.5, 1 H, H at C-5 of dioxane) ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.5, 134.9 (4° Carbons of aromatic ring), 129.8, 129.0, 127.4, 126.7, 126.5, 126.4 (alkene and aromatic C-H's), 100.0 (C-2 of dioxane), 67.6 (C-4 and C-6 of dioxane), 35.2 (C-4 of alkene), 33.2 (C-1 of alkene), 25.8 (C-5 of dioxane) IR 2985, 2860 (aromatic C-H), 1100 (C-O) cm^{-1}; MS (70 ev) *m/z* (rel abund) 297 (M^+ -, 0.5), 217 (M^+- Br, 86), 159 (M^+- C_3H_7O and Br, 37), 143 (M^+- $C_3H_7O_2$ and Br, 53), 131 (M^+- 1,3 dioxane and Br, 100); HRMS calcd for $C_{14}H_{16}BrO_2$: M^+ - H = 297.0317. Found: 297.0340.

Preparation of [2`-(2``-(1``,3``-dioxanyl))phenyl]but-2-enyl triphenylphosphonium bromide (1e). Freshly prepared **1d** (5.81 g; 19.57 mmol) was dissolved in benzene (50 mL) and a solution of triphenylphosphine (5.13 g; 19.57 mmol) in benzene (10 mL) added. A white precipitate commenced forming after 45 min. The solution was stirred for 48 h and the white precipitate collected on a medium porosity frit and washed with anhydrous hexanes to give **1e** (mp 195-197 °C, 10.949 g; 89 % yield). ^{1}H NMR (CD_3OD, 500 MHz) δ 6.92-7.84 (m, 19 H, aromatic H of phosphine phenyls and 3,4,5 and 6), 5.90 (m,1 H, H at C-3 of butene), 5.49 (s, 1 H, H at C-2 of dioxane), 5.38 (m,1 H, H at C-2 of butene), 4.26 (dd, J = 14.5, 7.5 Hz, 2 H, H at C-4 of butene), 3.91 (dd, J = 11.0, 5.0 Hz, H^e at C-4 and C-6 of dioxane), 3.78 (td, J = 12.0, 2.0 Hz, 2 H, H^a at C-4 and C-6 of dioxane), 3.48 (d, J = 6.0 Hz, 2 H, H at C-1 of butene), 2.05 (m, 1 H, H^a at C-5 of dioxane), 1.36 (d, J = 13.5, 1 H, H^e at C-5 of dioxane); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.2, 141.1 (4° Carbons of aromatic ring), 137.0, 136.4, 133.7, 130.0, 129.7, 128.6, 126.6, 125.9, 118.5, 117.8 (alkene and aromatic C-H's), 100.4 (C-2 of dioxane), 66.9 (C-4 and C-6 of dioxane), 63.2 (C-4 of alkene), 34.9 (C-1 of alkene), 25.5 (C-5 of alkene); MS (FAB) *m/z* (*m*-nitrobenzyl alcohol matrix) 480 (M^+- Br) Calcd 479.58.

Preparation of tetrakis-1,2,4,5-[penta-1`,3`-dienyl-5`-(2``-(1``,3``-dioxanyl)) phenyl]benzene (1f). To a suspension of **1e** (9.8 g; 17.52 mL), potassium carbonate (2.66 g; 19.25 mmol) [pulverized in a mortar and heated gently in a bunsen burner flame], 18-crown-6

(231.5 mg; 0.876 mmol) in anhydrous THF (70 mL) was heated at reflux. Tetra-1,2,4,5-formylbenzene[7] (570 mg; 3.0 mmol) was added in 5 portions over 1 h. The yellow suspension turned green after an additional hour. The mixture was poured into a separatory funnel and washed with water. The organic phase was separated and set aside. The aqueous phase was extracted twice with ethyl acetate (100 mL). The combined organic phases were dried over magnesium sulfate. The crude mixture was evaporated onto Florisil and immediately subjected to column chromatography (silica gel; 20-30% ethyl acetates; hexanes). **1f** was obtained as an unstable yellow-green amorphous solid (mp 84-90 °C; 2.43 g; 56 % yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.60-7.15 (m, 18 H, aromatic H), 6.80-5.80 (m, 16 H, olefinic H), 5.56 (s, 4 H, H at C-2 of dioxane), 4.15 (m, 8 H, H^e at C-4 and C-6 of dioxanes), 3.84 (m, 8 H, H^a at C-4 and C-6 of dioxanes), 3.55 (m, 8 H, H at C-1 of pentadienyls), 2.13 (m, 4 H, H^a at C-5 of dioxanes), 1.30 (m, 4 H, H^e at C-5 of dioxanes); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.6,136.9, 135.9, 135.0, 130.8, 130.6, 129.9, 129.7, 129.0, 128.9, 127.7, 127.3, 126.5, 126.4, 126.3 (alkene and aromatic C-H's), 100.0 (C-2 of dioxanes), 67.4 (C-4 and C-6 of dioxanes), 35.8 (C-1 of pentadienyls), 25.7 (C-5 of pentadienyls); IR ($CHCl_3$) 1265, 700 cm^{-1}; .MS (FAB) *m/z* (*m*-nitrobenzyl alcohol as matrix) 991 (M^+) Calcd 991.29.

Preparation of tetrakis-1,2,4,5-[pentyl-5`-(2``-(1``,3``-dioxanyl))phenyl]benzene (1g). A Parr pressure bottle was charged with an ethyl acetate (25 mL) solution of triethylamine (1.0 mL) and **1f** (2.59 g; 3.6 mL) and Raney nickel (thrice washed with 100 mL each of water; ethanol and then ethyl acetate). The mixture was hydrogenated with the Parr hydrogenation apparatus at 50 psig. Each hour aliquots were removed and analyzed by ^{1}H NMR. After each assay, fresh catalyst was added. Upon completion of the reaction the solution was filtered through a Celite pad to remove the catalyst. Column chromatography (silica, 25-35% ethyl acetate:hexanes) provided pure **1g** as a colorless solid (mp 62-65 °C, 2.63 g, 100% yield) as a colorless solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.63 (dd, J = 7.0, 1.5 Hz, 4 H, H at C-3), 7.24 (m, 8 H, H at C-4 and C-5), 7.17 (dd, J = 7.0, 1.5 Hz, 4 H, H at C-6), 6.95 (s, 2 H, H at C-3 and C-6 of central benzene), 3.97 (td, J = 12.0, 2.5 Hz, 8 H, H^a at C-4 and C-6 of dioxanes), 2.75 (t, J = 8.0 Hz, 8 H, H at C-5 of pentyl chains), 2.60 (t, J = 8.0 Hz, 8 H, H at C-1 of pentyl chains), 2.24 (m, 4 H, H^a at C-5 of dioxanes), 1.67 (overlapping peaks, J = 8.0 Hz, 16 H, H at C-2 and C-4 of pentyl chains), 1.52 (q, J = 8.0, 8 H, H at C-3 of pentyl chains), 1.40 (d, J = 13.5 Hz, 4 H, H^e at C-5 of dioxanes); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.1, 137.6 (4° C of aromatic rings), 136.2 (4° C of central benzene), 129.9, 129.4, 128.7, 126.2, 125.9 (aromatic C-H's), 99.8 (C-2 of dioxanes), 67.5 (C-4 and C-6 of dioxanes), 32.4 (C-5 and C-1 of pentyl chains), 31.5, 31.4 (C-2 and C-4 of pentyl chains), 29.9 (C-3 of pentyl chains), 25.7 (C-5 of dioxanes); IR (CCl_4) 2925 (aromatic C-H), 2850 (aliphatic C-H), 1110 (C-O) cm^{-1}; MS (FAB) *m/z* (*m*-nitrobenzyl alcohol as matrix) 1007 (M^+) Calcd 1007.42. Anal. Calcd for $C_{66}H_{86}O_8$: C, 78.69; H, 8.60. Found: C, 78.39; H, 8.12.

Preparation of tetrakis-1,2,4,5-[pentyl-5`-(2``-formylphenyl]benzene (1h). To a solution of **1g** (500 mg; 0.496 mmol) and 2,4 dinitrobenzaldehyde (389 mg; 1.98 mmol) in 10% aqueous THF (25 mL) was added concentrated perchloric acid (0.10 mL). The reaction was stirred

at 25 °C for 72 h. The solution was then poured into a separatory funnel containing ethyl acetate (100 mL) and 5% aqueous sodium bicarbonate (25 mL). The organic layer was separated and the aqueous layer twice extracted with ethyl acetate (50 mL). The combined organic solution was dried over anhydrous magnesium sulfate and then purified by column chromatography on neutral alumina (0-20% ethyl acetate: hexanes). Chromatography on silica (0-15% ethyl acetate: hexanes) provided pure **1h** as a colorless solid (mp 76-77 °C; 282 mg, 60% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.25 (s, 4 H, CHO), 7.82 (d, J = 7.5 Hz, 4 H, H at C-3 of aromatic rings), 7.47 (t, J = 7.5 Hz, 4 H, H at C-4 of aromatic rings), 7.33 (d, J = 7.0 Hz, 4 H, H at C-5),7.25 (d, J = 7.5 Hz, 4 H, H at C-6 of aromatic rings), 6.91 (s, 2 H, H at C-3 and C-6 of central benzene), 3.03 (t, J = 8.0 Hz, 8 H, H at C-5 of pentyl chains), 2.56 (t, J = 7.5 Hz, 8 H, H at C-1 of pentyl chains), 1.67 (t, J = 8.0 Hz, 8 H, H at C-4 of pentyl chains), 1.62 (qn, J = 7.5 Hz, 8 H, C-2 of pentyl chains), 1.50 (qn, J = 7.5, 8 H, H at C-3 of pentyl chains); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 192.0 (CHO), 145.4, 137.3 (4° C of aromatic rings), 129.8 (4° C of central benzene), 133.5, 133.4, 131.4, 130.8, 126.2 (aromatic C-H's), 32.3, 32.1, 31.1, 29.5 (C of pentyl chains); IR (CCl_4) 2930, 2860 (aliphatic C-H), 1700 (CHO) cm^{-1}; MS (FAB) *m/z* (*m*-nitrobenzyl alcohol as matrix) 775 (M^+) Calcd 775.09.

Preparation of 5,10,15,20-[α,α`,α``,α```-duryl(tetrakis-*o*-butyl phenyl)] porphyrin (1i). A chloroform solution (1600 mL) containing freshly distilled pyrrole (29 μL; 0.45 mmol) and tetraaldehyde **1h** (80.0 mg; 0.103 mmol) was treated with boron trifluoride etherate (60 μL of 2.0 M solution in chloroform). The mixture was stirred at 25°C for 20 h; dichlorodicyano-quinone (DDQ) (40 mg; 0.18 mmol) was added and the mixture was stirred at ambient temperature under a stream of air on a water bath overnight to remove some of the solvent. The solvent was evaporated to a small volume (approx. 20 ml) and transferred to a 100 ml round bottom flask. 30 ml of toluene was added and the resulting solution was refluxed for 10 hours. The solvent was removed *in vacuo*, and the residue was treated with 20 μl of triethylamine and applied as a highly concentrated solution in chloroform to a silica gel column (40% chloroform/ hexanes, 0.5% in triethylamine). Further purification of the fastest fraction (R_f 0.4) was achieved by medium pressure chromatography on a Lobar column (LiChroprep Si 60; size A) to afford **1i** as a purple solid (6.0 mg; 6 % yield, mp >300°C). UV/Vis λ_{max} (log ε): 402 (sh), 418 (5.52), 513 (4.74), 545 (4.37), 589 (4.38), 645 (4.21)o. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.57 and 8.56 (two s, 4 H each, β-pyrrole C-H), 7.88 (d, J = 7.5 Hz, 4 H, H at C-3), 7.68 (t, J = 7.5 Hz, 4 H, H at C-4 of aromatic rings), 7.63 (d, J = 7.5 Hz, 4 H, H at C-6 of aromatic rings), 7.45 (t, J = 7.5 Hz, 4 H, H at C-5 of aromatic rings), 5.52 (s, 2H, H of capping benzene), 2.4 - -0.3 (40 H, pentyl chain methylenes), -2.79 (broad s, 2 H, pyrrole N-H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.8, 141.0, 135.7, 134.3, 130.2, 129.3, 128.4, and 123.9 (aromatic C), 118.2 (meso-C), 34.2, 32.6, 32.0, 30.5, and 29.3 (pentyl chain C); MS (Laser Desorption) Calcd. for $C_{70}H_{68}N_4$, 964.54; Found (M^+).964.59; 965.59 ($M+H^+$); 987.58 ($M+Na^+$) ; 1003.56 ($M+K^+$).

Experimental details for the synthetic procedures of Scheme II.

Preparation of 2-(2-formylphenyl)-1,3-dioxane (2a). To a benzene solution (150 mL) of phthalic dialdehyde (6.71 g; 50.0 mmol) and propane-1,3-diol (3.6 mL; 3.8 g; 50.0 mmol) in a round

bottom flask fitted with a condenser and Dean-Stark receiver was added *p*-toluenesulfonic acid monohydrate (95.0 mg; 0.50 mmol). The solution was heated at reflux and water removed as an azeotrope with benzene. After 1-3 h the reaction was complete as verified by ^{1}H NMR analysis of an aliquot. The reaction was quenched by the addition of triethylamine (ca. 500 μL) and the mixture adsorbed onto Florisil. Column chromatography on silica gel (15 % ethyl acetate: hexanes) provided a colorless oil (9.2 g which consisted of a 5:1 mixture of the desired compound contaminated with phthalic dialdehyde). This mixture was suitable for the subsequent transformations in this series, however further flash chromatography of small portions on a 300 fold mass ratio of compound to silica gel (10% ethyl acetate: hexanes) provided pure **2a** (8.07 g; 84 % yield) as a colorless oil.[14] ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.489 (s, 1 H, aldehyde H),7.91 (dd, J = 7.5, 1.0 Hz, 1 H, H at C-3), 7.64 (d, J = 7.0 Hz, 1 H, H at C-6), 7.57 (td, J = 7.5, 1.0 Hz,1 H, H at C-5), 7.48 (t, J =7.0, 1 H, H at C-4), 5.97 (s, 1 H, H at C-2 of dioxane), 4.23 (dd, J = 11.0, 5.0 Hz, 2 H, H^e at C-4 and C-6 of dioxane), 4.02 (td, J = 12.0, 5.0 Hz, H^a at C-at C-4 and C-6 of dioxane), 2.19 (m, 1 H, H^a at C-5 of dioxane),1.43 (dd, J = 4.0, 1.0 Hz, 1 H, H^e at C-5 of dioxane),^{13}C NMR ($CDCl_3$, 125 MHz) δ 192.3 (aldehyde C=O), 162.8 (C-2), 139.7 (C-1), 133.5, 129.6, 129.2, 127.3 (aromatic CH), 100.1 (C-2 of dioxane), 67.6 (C-4 and C-6 of dioxane), 25.7 (C-5 of dioxane); IR (NaCl plates) 2980 (aromatic C-H), 1690 (C=O aldehyde) cm^{-1}; MS (70 ev) *m/z* (rel abund) 192 (M^+, 6), 149 (M^+ - C_3H_7, 13), 133 (M^+- C_3H_7O, 100), 105 (M^+ - 1,3-dioxane, 55); HRMS calcd for $C_{11}H_{12}O_3$: M^+ = 192.0786. Found: 192.0780.

Preparation of 2[2-(3-carboxy-2-propenyl)phenyl]-1,3-dioxane, methyl ester (2b). To a benzene solution (0.3 M) of **2a** was added solid methyl triphenylphosphoranylidene acetate (1 equivalent). The solution was stirred at room temperature until ^{1}H NMR analysis of an aliquot revealed consumption of the aldehyde. Florisil was added and the solvent removed. Filter column chromatography was performed to facilitate removal of triphenylphosphine oxide. The crude product which could be used in the next reaction without deleterious consequences was purified by flash column chromatography (silica, 12% ethyl acetate: hexanes) to afford colorless oils: (yields vary from 65-95 % based on the amount of **2a** in the starting material, the E isomer (data given) predominated (ca. 85%) in both cases. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.22 (d, J = 16.0 Hz, 1 H, H at C-1 of alkene), 7.60 (d, J = 7.5 Hz, 1 H, H at C-3), 7.56 (d, J = 7.5 Hz, 1 H, H at C-6), 7.37 (t, J = 7.5 Hz, 1 H, H at C-4 or C-5), 7.30 (t , J =7.5 Hz, 1 H, H at C-5 or C-4), 6.34 (d, J = 16.0 Hz, 1 H, H at C-2 of alkene), 5.68 (s, 1 H, H at C-2 of dioxane), 4.26 (dd, J = 11.0, 5. 0 Hz, 2 H, H^e at C-4 and C-6 of dioxane), 3.99 (td, J = 12.5, 2.0 Hz, 2 H, H^a at C-4 and C-6 of dioxane), 3.79 (s, 3 H, ester methyl), 2.25 (m, 1 H, H^aat C-5 of dioxane), 1.44 (dd, J = 12.0, 1.0 Hz, H^e at C-5 of dioxane), ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.4 (ester C=O), 142.5 (C-1 of alkene), 137.1, 132.8 (4^o aromatic carbons), 129.9, 129.2, 127.0, 126.7, 119.4 (aromatic C-H and H at C-2 of alkene), 100.3 (C-2 of dioxane), 67.6 (C-4 and C-6 of dioxane), 51.7 (ester methyl), 25.7 (C-5 of dioxane); IR (NaCl plates) 2980 (aromatic C-H), 2860, 1720 (C=O ester), 1630 (C=C ester) cm^{-1}; MS (70 ev) *m/z* (rel abund) 248 (M^+, 16), 233 (M^+- Me, 5), 217 (M^+ - OMe, 8), 189 (M^+-CO(OMe), 69), 161 (M^+- 1,3 dioxane, 32),

131 (M^+- 1,3 dioxane and OMe, 100); HRMS calcd for $C_{14}H_{16}O_4$: M^+ =248.1049. Found: 248.1034.

Preparation of 2-[2-(3-hydroxy-2-propenyl)phenyl]-1,3,dioxane (2c). To a toluene solution (20 mL) of **2c** (1.10 g; 4.19 mmol) at -60 °C was added dropwise diisobutyl aluminum hydride (8.38 mL of a 1.0 M solution in hexanes). After 1 h the solution was allowed to warm to room temperature and then cooled to 0 °C. Methanol (2 mL) and aqueous potassium sodium tartrate (100 mL of a 0.3M solution) were added sequentially. The mixture was allowed to warm to room temperature and stirred for at least six hours. The mixture was then transferred to a separatory funnel and the organic layer separated. The aqueous layer was extracted with two portions (25 mL) of ethyl acetate which were combined with the organic layer. The solution was dried with anhydrous magnesium sulfate and adsorbed onto Florisil and then purified by column chromatography (silica, 35 to 45 % ethyl acetate: hexanes) to provide **2c** (0.814 g; 88% yield) as a colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (dd, J = 6.5, 1.5 Hz, 1 H, H at C-6), 7.44 (dd, J = 7.5, 2.0 Hz, 1 H, H at C-3), 7.29, 7.23 (overlapping d, 2 H, H at C-4 and C-5), 6.98 (d, J = 15.5 Hz, 1 H, H at C-1 of alkene), 6.22 (dt, J = 15.5, 5. 5 Hz,1 H, H at C-2 of alkene), 5.64 (s, 1 H, H at C-2 of dioxane), 4.29, 4.22 (overlapping m, 4 H, H^e's at C-4 and at C-6 of dioxane and C-3 of alkene), 3.96 (td, J = 12.0, 2.0 Hz, 2 H, H^a at C-4 and C-6 of dioxane), 2.22 (m, 1 H, H^a at C-5 of dioxane), 1.89 (br s, 1 H, OH), 1.42 (dd, J = 11.5, 1.5 Hz, 1 H, H^e at C-5 of dioxane); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.3, 135.0 (4^o aromatic carbons), 130.9, 129.0, 127.8, 127.6, 126.2 (alkene and aromatic C-H's), 100.2 (C-2 of dioxane), 67.5 (C-4 and C-6 of dioxane), 63.9 (C-3 of dioxane), IR (NaCl plates) 3400 (br O-H), 2980 (aromatic C-H), 2860 (aliphatic C-H), 1100, 1000 (C-O) cm^{-1}; MS (70 ev) *m/z* (rel abund) 220 (M^+, 29), 203 (M^+- OH, 6), 189 (M^+- CH_2OH, 100), 133 (M^+- 1,3 dioxane, 19), HRMS calcd for $C_{13}H_{16}O_3$: M^+ = 220.1099. Found: 220.1074.

Preparation of 2-[2-(3-bromo-2-propenyl)phenyl]-1,3-dioxane(2d). To a solution of **2c** (5.0 g; 22.7 mmol), resublimed carbon tetrabromide (8.68 g; 26.17 mmol), and anhydrous collidine (3.47 mL; 3.18 g; 26.26 mmol) in anhydrous dichloromethane (100 mL) at -10 °C , was added solid triphenylphosphine (8.71 g; 33.21 mmol). The reaction appeared to proceed instantaneously as demonstrated by the formation of a deep red color upon the addition of excess triphenylphosphine- presumably a consequence of formation of dibromomethylene triphenylphosphine. Thin layer chromatographic analysis (Silica gel; 5 and 50 % ethyl acetate in hexanes) revealed that the starting material was consumed. Methanol (2 mL) was then added to quench the reaction. The solvent was removed and the organic material adsorbed onto Florisil. Column chromatography (silica, 0-10 % ethyl acetate: hexanes) provided pure **2d** (3.7 g; 58% yield) which was used immediately in the next reaction due to its instability. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (m, 1 H, aromatic H), 7.46 (m, 1 H, aromatic H), 7.28 (m, 2 H, aromatic H), 7.07 (d, J = 15.5 Hz, H at C-1 of alkene), 6.28 (d, J = 15.5 Hz,7.0 Hz, H at C-2 of alkene), 5.78 (m,1 H, alkene H), 5.62 (s, 1 H, H at C-2 of dioxane), 4.25 (dd, J = 11.5, 5.0 Hz, 2 H, H^e at C-4 and C-6 of dioxane), 4.16 (d, J = 7.0 Hz, 2 H, H at C-3 of alkene), 3.97 (td, J = 12.0 Hz, 1.5 Hz, 2 H, H^a at C-4 and C-6 of dioxane), 2.23 (m, 1 H, H^a at C-5 of dioxane), 1.40 (dd, J = 13.0, 1.5 Hz, 1 H, H^e at C-of dioxane); ^{13}C NMR ($CDCl_3$, 125

MHz) δ 135.7, 134.2 (4° Carbons of aromatic ring), 131.7, 129.0, 128.2, 127.4, 126.6, 126.5 (alkene and aromatic C-H's), 100.2 (C-2 of dioxane), 67.5 (C-4 and C-6 of dioxane), 33.6 (C-3 of alkene), 25.7 (C-5 of dioxane); IR (NaCl plates) 2950, 2850 (aromatic CH), 1105, 1095 (C-O) cm^{-1}; MS (70 ev) *m/z* (rel abund) 284 (M^+, 0.9) 282 (M^+, 0.9), 204 (M^+ - Br, 51), 163 (M^+- C_3H_7O and Br, 10), 145 (M^+- 1,3 dioxane and Br, 76), 115 (M^+ - C_3H_6O and C_4H_6Br, 100); HRMS calcd for $C_{13}H_{15}O_2Br$: M^+ = 282.0256. Found: 282.0255.

Preparation of [2-(-2-propenyl)phenyl]-1,3-dioxanyltriphenyl-phosphonium bromide (2e). Freshly purified **2d** (3.50 g; 12.36 mmol) was dissolved in benzene (12 mL). A solution of triphenylphosphine (3.23 g; 12.36 mmol) in benzene (18 mL) was added at 25 °C in one portion. Within 45 min a white precipitate began forming which was collected after 48 h onto a medium porosity sintered glass funnel and washed with five portions of benzene (ca. 3-5 mL). Residual solvent was removed under high vacuum to provide the desired phosphonium salt **2e** as a colorless solid (6.38 g; 95 % yield). ^1H NMR ($CDCl_3$, 500 MHz) δ 7.90-7.10 (m, 20 H, aromatic H and H at C-1 of propene), 5.95 (m, 1 H, H at C-3 of propene), 5.49 (s, 1 H, H at C-2 of dioxane), 4.59 (dd, 2H, J = 15.5, 7.5 Hz, 2 H, H at C-3 of propene), 4.06 (dd, J = 11.0 , 5.0 Hz, 2 H, H^e at C-4 and C-6 of dioxane), 3.90 (td, J = 12.0, 2.0 Hz, 2 H, H^a at C-4 and C-6 of dioxane), 2.06 (m, 1 H, H^a at C-5 of dioxane), 1.39 (d, J = 14.0 Hz, 1 H, H^e at C-5 of dioxane), ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.9, 136.8, 135.9 (4° Carbons of aromatic ring), 135.1, 133.8, 133.7, 130.3, 130.1, 128.7, 128.0, 127.9, 126.5, 125.7, 118.6, 117.9, 116.2, 116.1 (alkene and aromatic C-H's), 99.7 (C-2 of dioxane), 67.1 (C-4 and C-6 of dioxane), 47.9 (C-3 of alkene), 25.7 (C-5 of dioxane); MS (FAB) *m/z* (*m*-nitrobenzyl alcohol matrix) 466 (M^+- Br) Calcd 465.55.

Preparation of tetrakis-1,2,4,5-[buta-1,3-dienyl-4-[2(1,3-dioxanyl) phenyl]]benzene (2f). To a suspension of **2e** (6.27g; 11.5 mmol), anhydrous potassium carbonate (1.59 g; 11.5 mmol), and 18-crown-6 (0.152 g; 0.575 mmol) in anhydrous THF (100 mL) at reflux was added freshly prepared solid 1,2,4,5 tetraformylbenzene (0.475 g; 2.5 mmol) in 5 portions over 1.5 h. The yellow solution became muddy brown and was allowed to stir at reflux for 45 min after the last portion of tetraaldehyde had been added. The mixture was then cooled and the organic phase extracted with ethyl acetate and washed once with water and then dried over magnesium sulfate and concentrated onto Florisil. Column chromatography (silica, 35-45 % ethyl acetate, hexanes) provided **2f**, a yellow solid, (mp 95-101 °C, 1.73 g; 74 % yield) as a mixture of geometric isomers which was used in the next reaction without further purification. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.70-6.50 (m, 34 H, aromatic and alkene H), 5.65 (s, 4 H, H at C-2 of dioxane), 4.28 (m, 8 H, H^e at C-4 and C-6 of dioxane), 3.96 (m, 8 H, H^a at C-4 and C-6 of dioxane), 2.24 (m, 4 H, H^a at C-5 of dioxane), 1.43 (m, 4 H, H^e at C-5 of dioxane); IR ($CHCl_3$) 2860 (C-H), 1110 (C-O) cm^{-1}; MS (FAB) *m/z* (*m*-nitrobenzyl alcohol matrix) 934 (M^+) Calcd 934.44.

Preparation of tetrakis-1,2,4,5-[butyl-4-[2-(1,3-dioxanyl)phenyl]]-benzene (2g). A solution of crude **2f** (1.25 g; 1.34 mmol) in ethyl acetate (50 mL) with triethylamine (0.5 mL) was

placed in a Parr hydrogenation bottle with Raney nickel (washed thrice with 100mL portions of deionized distilled water, absolute ethanol and then ethylacetate. The system was purged and pressurized with hydrogen. At one hour intervals the reaction was stopped, an aliquot removed and ^{1}H NMR analysis used to assess the progress of the reaction. Additional catalyst was then added and the procedure resumed. This was continued until ^{1}H NMR analysis revealed the absence of double bonds. The catalyst was removed by filtration through a Celite pad which was washed exhaustively with ethyl acetate (500 mL). The filtrate was adsorbed onto Florisil and purified by column chromatography on silica gel (30-45 % ethyl acetate hexanes) to provide pure **2g** as a colorless oil (717 mg; 56 % yield) which solidified upon standing (mp 101-103 °C).^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.62 (d, J = 7.5 Hz, 4 H, H at C-3 of aromatic rings),7.26-7.17 (m, 12 H, H at C-4,5,6 of aromatic rings), 6.96 (s, 2 H, H at C-3 and C-6 of central benzene ring), 5.64 (s, 4 H, H at C-2 of dioxane), 4.23 (dd, J = 11.0, 4.5 Hz, 8 H, H^e at C-4 and C-6 of dioxane), 3.93 (td, J = 12.0, 1.0 Hz, 8 H, H^a at C-4 and C-6 of dioxane), 2.77 (t, J = 7.5 Hz, 8 H, H at C-4 of butane), 2.63 (t, J = 7.0 Hz, 8 H, H at C-1 of butane), 2.20 (m, 4 H, H^a at C-5 of dioxane), 1.71 (m, 16 H, H at C-2 and C-3 of butane), 1.38 (d, J = 14.0 Hz, 4 H, H^e at C-5 of dioxane); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.1, 137.6, 136.2 (4° Carbons of aromatic ring), 129.9, 129.4, 128.7, 126.3, 126.0 (aromatic C-H), 100.0 (C-2 of dioxane), 67.6 (C-4 and C-6 of dioxane), 32.8, 32.7 31.6, 31.5 (C-1,2,3,4 of butanes), 25.8 (C-5 of dioxane); IR (CCl_4) 2935 (aromatic C-H), 2850 (aliphatic C-H), 1110 (C-O) cm^{-1}; MS (FAB) *m/z* (*m*-nitrobenzyl alcohol matrix) 951 (M^+) Calcd 950.57.

Preparation of tetrakis-1,2,4,5-[butyl-4-(2-formylphenyl)]benzene (2h). A solution of **2g** (400 mg; 0.420 mmol) and 2,4 dinitrobenzaldehyde (330 mg; 1.68 mmol) in 10% aqueous THF (25 mL) was treated with 0.1 mL of concentrated perchloric acid and the reaction monitored by TLC (alumina 25% ethyl acetate: hexanes). After 72 h at 25 °C the solution was poured into a separatory funnel containing ethyl acetate (100 mL) and 5% aqueous sodium bicarbonate (25 mL). The organic layer was separated and the aqueous layer twice extracted with ethyl acetate (50 mL). The combined organic solution was dried over anhydrous magnesium sulfate and then purified by column chromatography on neutral alumina (0-20% ethyl acetate: hexanes). Chromatography on silica (0-20% ethyl acetate: hexanes) provided pure **2h** as a colorless solid (mp 90-91 °C; 143 mg; 47%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.23 (s, 4 H, CHO), 7.81 (dd, J = 7.5, 1.0 Hz, 4 H, H at C-3 of aromatic rings), 7.47 (td, J = 7.5, 1.0 Hz, 4 H, H at C-4 of aromatic rings), 7.33 (t, J = 7. 0 Hz, 4 H, H at C-5 of aromatic rings), 7.26 (d, J = 7.0 Hz, 4 H, H at C-6 of aromatic rings), 6.88 (s, 2 H, H at C-3 and C-6 of central benzene ring), 3.05 (t, J = 7.5 Hz, 8 H, H at C-4 of butane), 2.56 (t, J = 7.0 Hz, 8 H, H at C-1 of butane), 1.67 (m, 16 H, H at C-2 and C-3 of butane); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 192.2 (CHO), 145.3, 137.3, 129.8 (4° Carbons of aromatic ring), 133.5, 133.6, 131.5, 130.9, 126.3 (aromatic C-H), 32.3, 32.2 32.0, 31.0 (C-1,2,3,4 of butanes); MS (FAB) *m/z* (*m*-nitrobenzyl alcohol matrix) 719 (M^+) Calcd 718.99.

Acknowledgement: We express our gratitude to Protos Corporation of Emeryville California for a grant in support of this study.

Supplementary material: ^{1}H and ^{13}C NMR spectra for all compounds are available upon request from the senior author.

References

[1] Almog, J.; Baldwin, J. E.; Crossley, M. J.; Debernardis, John F.; Dyer, R. L.; Huff, J. R.; Peters, M. K.; *Tetrahedron*, **1981**, *37*, 3589. For reviews see: Morgan,B.; Dolphin, D. *Structure and Bonding* **1987**, *64*, 115 and Baldwin, J. E.; Perlmutter, P. *Top. Curr. Chem.* **1984**, *121*, 181. There is mention of a C-4 capped porphyrin, however the details of its preparation are not available see: Shimizu, M.; Basolo, F.; Vallejo, M. N.; Baldwin, J. E. *Inorganica Chim. Acta* **1984**, *91*, 247.

[2] Johnson, M. R., Seok, W. K., Ibers, J. A. *J.Am.Chem.Soc.* **1991**, *113*, 3998.

[3] Tetrakis-5,10,15,20-(*p*-methoxy)phenylporphinato iron(III) is destructively oxidized by weak oxidants such as *p*-cyano-N,N-dimethyl aniline N-oxide. R. W. Lee, T. C. Bruice, unpublished results.

[4] Lindsey, J.S., Mauzerall, D.C. *J.Am.Chem.Soc.* **1982**, *104*, 4498.

[5] **1i** was created with the molecular modelling program Quanta (version 2.1A, Polygen Corp.) and coordinates generated by the energy minimization programs steepest descents and adopted basis Newton-Raphson until the energy-change tolerance was less than 10^{-9} kcal/mole.(CHARMm, version 21.1.7, Polygen Corp.). Initial coordinates and parameters for the porphyrin ring of **1i** were obtained from the file PORPHYRINH.RTF supplied with Quanta and CHARMm. During minimization a distance-dependent dielectric constant and the CHARMm shift functions were used with nonbonded and hydrogen bonded interaction cutoff distances of 11.5 Å and 7.5 Å, respectively. The nonbonded and hydrogen bonded lists were updated every 5 steps. All computational analyses and graphics were carried out on a Silicon Graphics Iris 4D/220 GTX workstation.

[6] a) Rothemund, P., Menotti, A.R., *J.Am.Chem.Soc.*, **1941**, *63*, 267.
b) Lindsey, J. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828.

[7] Schrievers, T.; Brinker, U. H. *Synthesis* **1988**, 330.

[8] Garratt, P. J.; Vollhardt, K. P. C. *Synthesis* **1972**, 424.

[9] Castro, B. R. *Org. React.* **1983**, *29*, 1.

[10] It is crucial that an allylic bromide is used for this step. Before the synthesis of **1e** was undertaken, we prepared analogues (i.e. homoallyl bromide, bromide, iodide and triflate) which formed complex mixtures upon reaction with triphenylphosphine.

[11] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

[12] Yau, E. K.; Coward, J. K. *Aldrichimica Acta* **1988**, *21*, 106.

[13] Langer, E.; Lehner, H. *Monatshefte Chem.* **1976**, *107*, 1.

[14] This compound was also prepared by esterification of 2-carboxybenzaldehyde (Lancaster) with diazomethane followed by protection as the 1,3 dioxane. Reduction with DIBAL-H gave the aldehyde contaminated with large amounts of alcohol. Oxidation to the aldehyde **2a** was achieved with pyridinium chlorochromate. The overall yield of this sequence was less than 10%.