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Syntheses of Novel Substituted Porphyrins by the Mercuration and Palladium/Olefin Methodology

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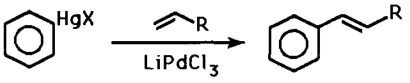
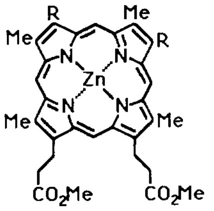
The palladium(II)-catalyzed carbon–carbon coupling reaction (Heck reaction) has been used to perform the 2,4-disubstitution of zinc(II) 2,4-bismercurated deuteroporphyrin IX dimethyl ester 2 with a variety of unsaturated side chains, to give protoporphyrin IX dimethyl ester derivatives that are terminally substituted on the vinyl groups. While aliphatic olefins have been shown to become coupled to deuteroporphyrin IX dimethyl ester in reasonable yield, more efficient coupling is observed with styrenes, particularly electron-deficient ones. Vinylferrocene has also been coupled to deuteroporphyrin, providing access to a variety of differentially metalated deuteroporphyrins. An alternate method for synthesis of styrylporphyrins and chlorins from vinylporphyrins (or vinylchlorins) and arylmercurials is also developed.

Introduction

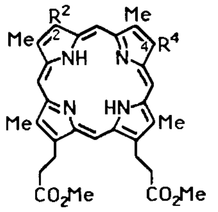
Mercurated aryl systems have been shown to undergo a myriad of transformations.[1] The most notable of these was discovered by Heck[2,3] and involves transmetalation of the arylmercurial with lithium chloropalladate in the presence of an olefin, generating the coupled aryl–olefin compound (Scheme I). The mercuration and transmetalation steps are relatively mild and normally accommodate a wide variety of functional groups.

Scheme I. Palladium/Olefin Methodology for Substitution of Arylmercurials



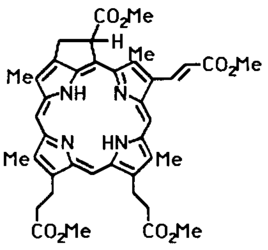


1 R = H
2 R = HgCl
29 R = $CH{=}CH_2$



3 $R^2 = R^4 = CH{=}CH_2$
4 $R^2 = R^4 = CH{=}CHCO_2Me$
5 $R^2 = CH{=}CH_2$; $R^4 = CH_2CH_2CO_2Me$
6 $R^2 = CH{=}CHCO_2Me$; $R^4 = CH_2CH_2CO_2Me$
16 $R^2 = R^4 = CH{=}CHCO_2Bu^t$
17 $R^2 = R^4 = CH_2CH{=}CH_2$
18 $R^2 = R^4 = CH_2\underset{Me}{C}{=}CH_2$
19 $R^2 = R^4 = CH{=}CHCH_2OPh$

This powerful methodology has recently found application as a means of functionalizing mercurated porphyrins.[4,5] Thus, zinc(II) deuteroporphyrin IX dimethyl ester (1) can be mercurated by using an excess of mercury(II) acetate in tetrahydrofuran. After formation of the chloride salt, the bismercurated deuteroporphyrin 2 was isolated and the site of the mercury(II) atoms was established by using both acid-catalyzed deuterolysis and reduction with $NaBD_4$. Protoporphyrin IX dimethyl ester (3) could be formed only with difficulty by reaction of 2 with ethylene followed by demetalation, but methyl acrylate added readily to the 2- and 4-positions, forming the bis(acrylate) porphyrin 4 in 37% yield. Coproporphyrin III tetramethyl ester (4, $R^2 = R^4 = CH_2CH_2CO_2Me$) was obtained from 4 by near-quantitative catalytic reduction of the acrylate side chains. Other naturally occurring type III porphyrins bearing three-carbon side chains (propionate and acrylate) were readily accessible; harderoporphyrin trimethyl ester (5) and the so-called S-411 porphyrin tetramethyl ester (6) were also synthesized by using routes that depended upon mercuration of the porphyrin periphery. In addition to isolating the bis(acrylate) deuteroporphyrin product 4, two "monoacrylate" byproducts were also obtained when mercuration was carried out with a large excess of mercury(II) acetate.[4,5] These were characterized as the two isomers 7 and 8, and this methodology was exploited to prepare the petroporphyrin deoxophylloerythroetioporphyrin (9) and deoxyophylloerythrin methyl ester (10).[6] Methods for synthesis of regioselectively methyl deuteriated hemes[7] have also been



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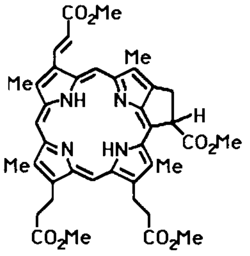

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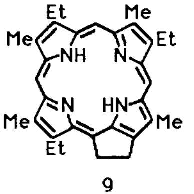

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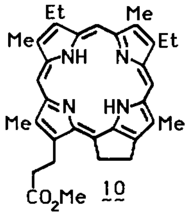

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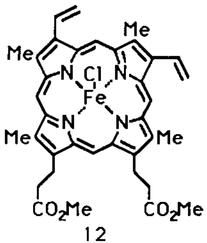

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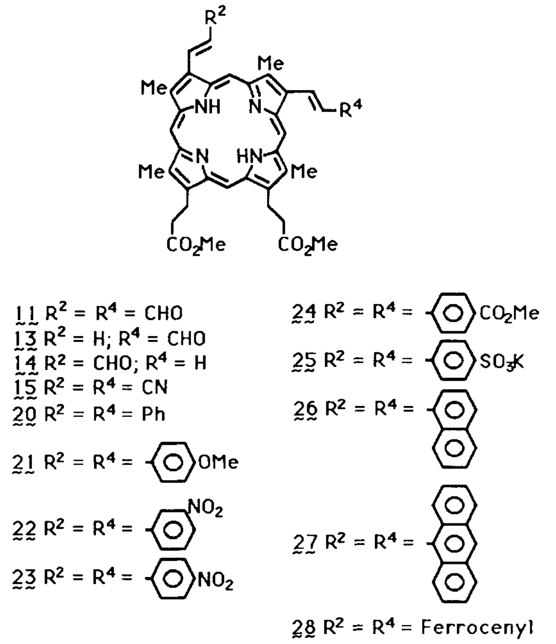
developed which utilize porphyrin acrylates obtained from the corresponding mercurated porphyrin. Finally, we have recently employed mercurated porphyrins for synthesis of the corresponding bromo- or iodoporphyrins in the deuteroporphyrin series.[8]

Synthesis of Vinyl-Extended Derivatives of Protoporphyrin IX

Encouraged by the ease by which acrylate side chains could be attached to various mercurated porphyrins, we decided to investigate the feasibility of appending other unsaturated organic substrates. Heck[9] first reported the palladium-catalyzed coupling of acrolein to phenylmercuric acetate in 1971. This novel coupling reaction gave an 85% yield of only the *trans*-phenylacrolein product. Bis(3-oxopropenyl)deuteroporphyrin IX dimethyl ester (11) was accidentally synthesized by Nichol[10] during an attempt to formylate the meso positions of protohemin dimethyl ester (12) by standard Vilsmeier formylation ($POCl_3$/dimethylformamide). Nichol managed to obtain an 18% yield of bis(3-oxopropenyl)deuteroporphyrin IX dimethyl ester (11) and a 7% yield of a mixture of the (3-oxopropenyl)deuteroporphyrin IX isomers 13 and 14. It was estimated that the cis:trans ratio for the acrolein side chains was ~1:2. Our coupling of acrolein to zinc(II) 2,4-bis(chloromercurio)deuteroporphyrin IX dimethyl ester (2) was far more efficient and resulted in only one stereoisomer. Instead of using dimethyl sulfoxide as previously described,[4,5] we dissolved the mercurated porphyrin in a 1:1 mixture of acetonitrile/dimethylformamide in the presence of a trace of triethylamine. To this was added the acrolein (50:1 molar ratio of acrolein/mercurated site), and the mixture was stirred at 50 °C before addition of a preformed solution of $LiPdCl_3$ (5:1 molar ratio of $PdCl_2$/mercurated site; 2:1 molar ratio of LiCl to $PdCl_2$) in acetonitrile. Within 5 min, the red solution had turned green, and silica gel TLC indicated the presence of a mobile green compound. This general protocol was followed throughout our study. Removal of the zinc with trifluoroacetic acid afforded between 35% and 38% yield of the desired 2,4-bis(3-oxopropenyl)deuteroporphyrin IX dimethyl ester (11). The yields are in line with those achieved for the bis(acrylate) porphyrin 4 (38%). Only the bis(acrolein) product was isolated, and ^1H NMR spectroscopy clearly showed that only the trans isomer was formed. The optical spectrum is red-shifted by an average of 4 nm from that of the bis(acrylate) 4.



The coupling of acrylonitrile to phenylmercuric acetate has also been described by Heck.[9] However, whereas Heck observed that methyl acrylate and acrolein both gave excellent yields (~85%) of coupled product, acrylonitrile not only gave poor yield but also formed both stereoisomers (cis/trans, 17:26). We performed the coupling with zinc(II) 2,4-bis(chloromercurio)deuteroporphyrin IX dimethyl ester (2) in the same manner as described above and isolated the bis(2-cyanovinyl)deuteroporphyrin product 15 in 30% yield. The optical characteristics are consistent with the product isolated, but aggregation was a persistent problem which hampered the interpretation of ^1H NMR spectra. The coupling of acrylamide to pyrrolo[2,3-*d*]pyrimidines has been described by Bergstrom et al.,[11] albeit in low yield (7%). We too experienced poor results in the coupling of acrylamide to zinc(II) 2,4-bis(chloromercurio)deuteroporphyrin IX dimethyl ester (2). Porphyrin 2 was also coupled with *tert*-butyl acrylate, to give the acid-sensitive bis(acrylate) 16, which was therefore fully characterized as the zinc(II) chelate.

A variety of allyl substrates have also been coupled to arylmercurials. Again, Heck[12] described the coupling of a homologous series of allyl chlorides to phenylmercuric chloride. To assess feasibility, we chose two of these, namely, allyl chloride and 2-methyl-3-chloropropene. In each case, coupling of the substrate to the mercurated porphyrin occurred in good yield: 59% for allyl chloride and 48% for 2-methyl-3-chloropropene. Both the zinc(II) di-2-propenyldeuteroporphyrin IX dimethyl ester (17) and zinc(II) bis(2-methyl-2-propenyl)deuteroporphyrin IX dimethyl ester (18) were sensitive to acid; therefore, characterization was carried out on the zinc(II) chelates.

Allyl alcohol did not provide the corresponding dipropenyl porphyrin 17. Bergstrom[13] has demonstrated that coupling of allyl alcohol to a mercurated nucleotide gave the propene side chain. However, in our hands, we were only able to produce a complex mixture of porphyrinic products after coupling allyl alcohol to zinc(II) 2,4-bis(chloromercurio)deuteroporphyrin IX dimethyl ester. Although Heck[9] reported the coupling of allyl nitrile to arylmercurials without the loss of the nitrile moiety, as with allyl alcohol, only complex mixtures resulted from the attempted coupling of allyl nitrile to the mercurated porphyrin 2. We were more fortunate in coupling allyl phenyl ether to zinc(II) 2,4-bis(chloromercurio)deuteroporphyrin IX dimethyl ester and isolated a 21% yield of zinc(II) bis(3-phenoxypropenyl)deuteroporphyrin IX dimethyl ester (19).

One of Hecks's earlier publications[2] dealt with the facile coupling of styrene to arylmercurials. Utilizing the same protocol developed for the open-chain olefins described above, we were able to prepare distyryldeuteroporphyrin IX dimethyl ester (20) in 44% yield. This nonoptimized yield is substantially better than for any open-chain olefin we have utilized. The optical spectrum is consistent with a porphyrin bearing two, moderately electron-withdrawing,

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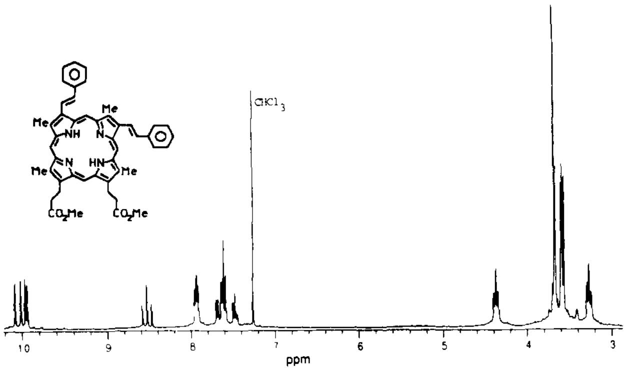

Figure 1. Proton NMR spectrum, at 300 MHz in $CDCl_3$, of 2,4-distyryldeuteroporphyrin IX dimethyl ester (**20**).

side chains (λ_{max} 408, 512, 550, 580, 638 nm), and the ^1H NMR spectrum clearly shows the presence of two styrene side chains (Figure 1). This particular reaction opened up a wide range of other possibilities. In essence, any derivative of styrene can be appended to deuteroporphyrin (or any mercurated porphyrin) by altering the location and identity of substituents on the benzene ring. Moreover, solubility properties of the porphryin can be adjusted and enhanced merely by utilizing appropriately substituted styrenes. And, with Stille's[14] recent discovery that aryl bromides can be converted into the corresponding arylethylenes by treatment with tri-*n*-butylethenylstannane, virtually any styrene derivative that is not commercially available may be prepared. We decided that this reaction warranted further exploration and attempted the coupling of a variety of readily available styrene derivatives.

The efficiency of coupling was directly dependent on the nature of the styrene derivative. A 43% yield of bis(*p*-methoxystyryl)deuteroporphyrin IX dimethyl ester (**21**) was obtained [similar to the 44% yield of distyryldeuteroporphyrin IX dimethyl ester (**20**)] upon coupling of *p*-methoxystyrene with zinc(II) 2,4-bis(chloromercurio)deuteroporphyrin IX dimethyl ester. The absorbance maxima (λ_{max} 410, 514, 552, 580, 638 nm) are essentially the same as those of the distyryldeuteroporphyrin **20** in spite of the presence of electron-donating substituents. It was not possible to isolate product in attempts to couple *p*-hydroxystyrene to zinc(II) 2,4-bis(chloromercurio)deuteroporphyrin IX dimethyl ester, mainly because workup caused polymerization of residual *p*-hydroxystyrene, which trapped the porphyrin, leaving the solvent nearly colorless. Although not pursued, the obvious solution is temporary protection of the phenolic OH, followed by deprotection after demetalation is complete, but this may also be further developed for synthesis of polymer-supported porphyrins. Having an electron-withdrawing, nitro, substituent at the meta position increased the coupling yield by almost 50% (to 62% yield), and the optical spectrum (λ_{max} 416, 516, 556, 582, 638 nm) of the resultant bis(*m*-nitrostyryl)deuteroporphyrin IX dimethyl ester (**22**) was red-shifted from that of the distyryldeuteroporphyrin **20**. With the nitro group at the para position, the yield of porphyrin was increased by another 30% (to 79% yield) and the absorbance maxima (λ_{max} 412, 518, 556, 582, 642 nm) of the bis(*p*-nitrostyryl)deuteroporphyrin IX **23** were shifted even further to the red.

Difficulty was experienced during our first attempt at joining *p*-carboxystyrene to the mercurated porphyrin **2**. Silica gel TLC clearly indicated that a green product had formed, but isolation of the dicarboxylic acid was difficult. Although the product was only moderately soluble in water at neutral pH, care had to be taken during demetalation and subsequent treatment with base to prevent loss of the porphyrin. Moreover, purification by normal column chromatography was impossible. This obstacle was circumvented by converting the carboxylic acid of *p*-carboxystyrene into the methyl ester by treatment with diazomethane. The bis(*p*-carbomethoxystyryl)deuteroporphyrin IX dimethyl ester (**24**) was easily isolated in 57% yield; the optical spectrum (λ_{max} 418, 518, 556, 580, 640 nm) and ^1H NMR spectrum are consistent with the disubstituted product.

Unfortunately, problems in isolation were not easily solved after coupling of the potassium salt of *p*-vinylbenzenesulfonic acid to zinc(II) 2,4-bis(chloromercurio)deuteroporphyrin IX dimethyl ester (**2**). Coupling was clearly occurring, as evidenced by the deep green color that developed soon after mixing of the reactants, but it was impossible to keep the bis(*p*-sulfonylstyryl)deuteroporphyrin IX dimethyl ester (**25**) from dissolving in water. While this is a useful property for some porphyrins, it made it very difficult to remove undesired water-soluble byproducts from the reaction mixture. Lowering the pH to protonate the sulfonate groups only protonated the porphyrin nucleus. It was equally difficult to prepare a protected derivative of *p*-vinylsulfonic acid to be used in the coupling reaction. As a precursor to the sulfonamide, we attempted to convert the sulfonate to the sulfonyl chloride with PCl_5, but upon workup, residual acid always caused polymerization to occur.

These first experiments demonstrated that inductive effects governed the efficiency of coupling styrene derivatives to mercurated porphyrins. We were curious to know if steric effects might also play a role. When 1-vinylnaphthalene was used, a 52% yield of bis(naphthalenylvinyl)deuteroporphyrin IX dimethyl ester (**26**) was isolated. Clearly, the extra ring was not a hindrance; in fact, the second unsaturated ring caused a 20% improvement in yield as compared to the distyryldeuteroporphyrin IX **20**. There was also a moderate red shift of the optical spectrum (λ_{max} 416, 514, 552, 582, 640 nm) of **26** from that of distyryldeuteroporphyrin IX **20**. The attempted coupling of 9-vinylanthracene suffered from what can be reasonably interpreted as a steric effect. We were able to isolate the bis(anthracenyl-9-vinyl)deuteroporphyrin IX dimethyl ester (**27**), but in only 17% yield. The optical spectrum (λ_{max} 414, 510, 546, 578, 634 nm) is very similar to that of the distyryl (**20**) and bis(naphthyl) (**26**) porphyrins, but it exhibited a moderate blue shift in comparison, which may be a result of poor π overlap caused by twisting of the anthracene side chains.

We were not as successful coupling heterocycles to mercurated deuteroporphyrins as we had been with styrene. Kasahara et al.[15] reported the direct coupling of benzofuran to various arylmercurials without the usual vinyl linkage; the unsaturated linkage is provided by the 2-position in the five-membered ring of benzofuran. Whereas Kasahara reported yields in excess of 70%, in our hands with porphyrins the reaction failed completely. This is likely due to severe steric congestion at the β-pyrrolic positions.

Vinylferrocene was readily attached to zinc(II) 2,4-bis(chloromercurio)deuteroporphyrin IX dimethyl ester in 26% yield. The optical spectrum (λ_{max} 406, 504, 554, 572,

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(15) Kasahara, A.; Izumi, T.; Yodono, M.; Saito, R.; Takeda, T.; Sugawara, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1220.

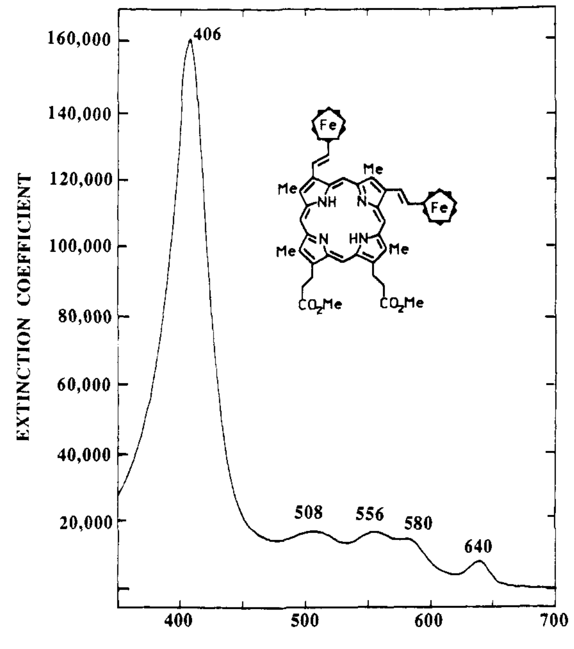


Figure 2. Optical spectrum, in CH_2Cl_2, of 2,4-bis(ferrocenylvinyl)deuteroporphyrin IX dimethyl ester (**28**).

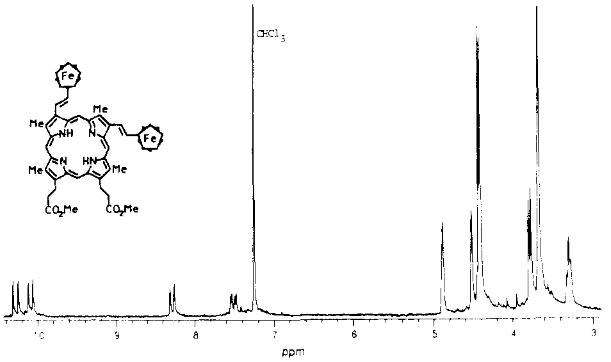


Figure 3. Proton NMR spectrum, at 300 MHz in $CDCl_3$, of 2,4-bis(ferrocenylvinyl)deuteroporphyrin IX dimethyl ester (**28**).

638 nm) of the bis(ferrocenylvinyl)deuteroporphyrin IX dimethyl ester (**28**) exhibited an unusual profile (Figure 2), and the absorbance maxima were similar to those of the distyryldeuteroporphyrin IX **20**. The ^{1}H NMR spectrum (Figure 3) unequivocally showed the presence of two ferrocenylvinyl substituents. With the commercial availability of a variety of metallocenes, the synthesis of a host of differentially metalated porphyrins is possible.

A viable alternate route to attachment of vinyl compounds to mercurated porphyrins would involve the coupling of porphyrins possessing unsaturated substituents with various arylmercurials. If mercurated deuteroporphyrin IX can be linked to styrene, it should be possible to link phenylmercurials to protoporphyrins IX. This idea was addressed by treating zinc(II) protoporphyrin IX dimethyl ester (**29**) with phenylmercuric chloride. To a solution of porphyrin and phenylmercuric chloride (1:10 molar ratio) in dimethylformamide at 50 °C was added a preformed solution of $LiPdCl_3$ (2:1 molar ratio of $PdCl_2$ to phenylmercuric chloride; 1:2 molar ratio of $PdCl_2$ to LiCl) in acetonitrile. The solution became green after ~10 min, and silica gel TLC showed one green spot running faster than starting material. The optical and ^{1}H NMR spectra of the main product following aqueous workup, demetalation, and chromatography were identical with those of the distyryldeuteroporphyrin IX **20**. The yield (60%) was also better than that obtained from mercurated deuteroporphyrin IX and styrene. A multitude of possibilities now became apparent; literally any aryl system that can be mercurated can now potentially be coupled to protoporphyrin IX. Larock[16] lists hundreds of benzene systems (phenols, halides, nitrates, alkoxylates, anilines, acetanilides, ethers, etc.), polynuclear arenes (naphthalenes, azulenes, biphenyls, etc.), and heterocycles (furans, thiophenes, indoles, purines, etc.) that can be mercurated, and the possibilities of coupled porphyrin systems seem limitless.

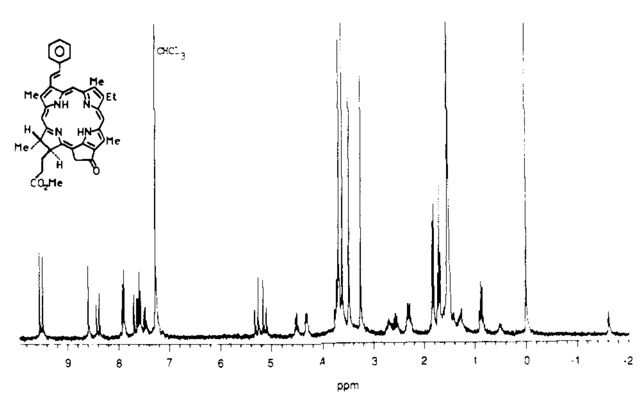
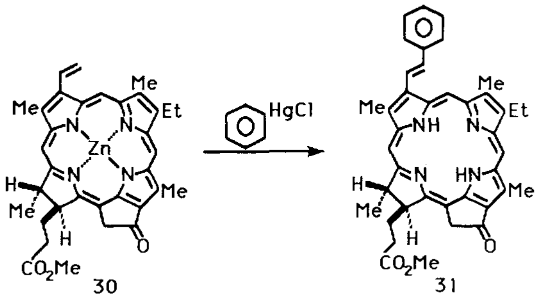


Figure 4. Proton NMR spectrum, at 300 MHz in $CDCl_3$, of methyl 2-styryl-2-devinylpyropheophorbide a (**31**).

In addition to porphyrins, we found that chlorins could also be converted into the corresponding styrene derivatives upon treatment with phenylmercuric chloride. Using the same general protocol as that developed for protoporphyrin IX, we treated zinc(II) methyl pyropheophorbide a (**30**) with phenylmercuric chloride and $LiPdCl_3$ at 60 °C in methylformamide/acetonitrile for 3 h. Silica gel TLC indicated that a significant quantity of a more mobile blue-green compound began to form after 20 min. Following demetalation, chromatography, and crystallization, methyl 2-styryl-2-devinylpyropheophorbide a (**31**) was isolated in 30% yield. ^{1}H NMR spectroscopy (Figure 4) and the red-shifted absorbance maxima (λ_{max} 416, 512, 542, 616, 674 nm) relative to methyl pyropheophorbide a are consistent with a moderately electron withdrawing benzene ring in conjugation with the chlorin macrocycle. It appears that the same wide-ranging applicability that applies to vinylporphyrins applies also to vinylchlorins.



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Conclusions

Various substituted olefins can be attached to mercurated porphyrins by using the Heck palladium-exchange reaction, and this allows fine-tuning of the optical spectra of protoporphyrin IX derivatives, as well as attachment of a variety of potentially interesting substituents to

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[16] Reference 1, pp 60–97.

porphyrin macrocycles. Electron-deficient acrylates and styrenes cause the Soret and satellite absorption bands to undergo a red shift. Arylmercurials can be efficiently coupled to vinylporphyrins and vinylchlorins to give basically similar molecules, thus extending the applicability of the reaction sequences discussed.

Experimental Section

General. Melting points are uncorrected and were measured on a Thomas/Bristoline hot stage. Electronic absorption spectra were measured on a Hewlett-Packard 8450A spectrophotometer, using solutions in dichloromethane. Mass spectra were obtained on a VG Analytical ZAB-HS instrument (70 eV, EI, mass reference perfluorokerosene; FAB, 8 keV Xe^0, dithiothreitol/dithioerythritol matrix). Proton NMR spectra (^{1}H NMR) were obtained (in $CDCl_3$ unless stated otherwise) at 300 MHz (GE QE300) with chemical shifts reported in parts per million relative to chloroform (7.258 ppm) as internal standard. Elemental analyses were performed at the Microchemical Analysis Laboratory, University of California, Berkeley. Reactions were usually carried out in the dark (aluminum foil) under nitrogen and were monitored by using thin-layer chromatography (TLC) on commercially available Eastman-Kodak 13181 (100-μm thick) silica sheets. Gravity and flash column chromatography employed either Merck neutral alumina (70–230 mesh) or Merck silica gel 60. The alumina was usually deactivated with 6% water (Brockmann grade III) before use.

Zinc(II) 2,4-Bis(chloromercurio)deuteroporphyrin IX Dimethyl Ester (2). This compound was prepared in yields varying between 85% and 100% by the method previously described in detail.[4,5]

2,4-Bis(3-oxopropenyl)deuteroporphyrin IX Dimethyl Ester (11). The foregoing porphyrin **2** (100 mg, 0.094 mmol, 1 equiv), acrolein (630 μL, 9.4 mmol, 100 equiv), and triethylamine (0.1 mL) in dry dimethylformamide (5 mL) and acetonitrile (5 mL) were stirred under a nitrogen atmosphere at 50 °C for 5 min before the addition of $LiPdCl_3$ in acetonitrile dropwise over a period of 2 min. The palladium catalyst was preprepared by refluxing LiCl (74 mg, 1.8 mmol, 20 equiv) and $PdCl_2$ (181 mg, 1.0 mmol, 10 equiv) in acetonitrile (5 mL) for 1 h under nitrogen. The green mixture was stirred at this temperature for an additional 60 min. The mixture was cooled to room temperature before filtering of the solution through a bed of Celite to remove Pd^0 and rinsing of the Celite with dichloromethane. The organic layer was washed four times with water and twice with brine and finally dried over Na_2SO_4. The solvent was removed under vacuum, and the porphyrin residue was taken up in dichloromethane (10 mL) and treated with trifluoroacetic acid (1 mL) to demetalate the porphyrin. The mixture was poured onto ice water, diluted with dichloromethane, and neutralized with Na_2CO_3. The organic layer was washed four times with water and twice with brine, dried over Na_2SO_4, and evaporated to dryness. The green residue was chromatographed on a 3 × 40 cm alumina (Brockmann grade III) column, and the title compound eluted as the most mobile band with 2% methanol in dichloromethane. The appropriate eluates were combined and evaporated, to give the title compound (21.5 mg, 35%) following crystallization from dichloromethane/petroleum ether; mp 140–150 °C. ^{1}H NMR ($CDCl_3$): δ −4.19 (s, 2 H, NH), 2.97 (s, 3 H, ring CH_3), 3.25, 3.28 (each t, 2 H, $CH_2CH_2CO_2CH_3$), 3.35, 3.42, 3.52 (each s, 3 H, ring CH_3), 3.69 (s, 6 H, OCH_3), 4.31, 4.34 (each t, 2 H, $CH_2CH_2CO_2CH_3$), 6.98 (m, 2 H, 2 × CH=CHCHO), 8.28 (d, J_{HH} = 16.2 Hz, 1 H, CH=CHCHO), 8.44 (d, J_{HH} = 16.2 Hz, 1 H, CH=CHCHO), 9.02, 9.43, 9.68, 9.91 (each s, 1 H, meso-*H*), 9.93 (d, J_{HH} = 7.5 Hz, 1 H, CH=CHCHO), 10.00 (d, J_{HH} = 7.5 Hz, 1 H, CH=CHCHO). UV–vis (CH_2Cl_2): λ_{max} (nm) 434 (ϵ 106 000), 520 (13 700), 560 (13 200), 590 (8700), 646 (6000). LR mass spectrum: *m/e* 647 (42). HR mass spectrum: $C_{38}H_{38}N_4O_6$ requires 646.2791, found 646.2793.

Using the general method described above, we prepared the following compounds from the zinc(II) bis(chloromercurio)deuteroporphyrin **2**.

2,4-Bis(2-cyanovinyl)deuteroporphyrin IX dimethyl ester (15): 30% yield from acrylonitrile; mp 176–180 °C. ^{1}H NMR ($CDCl_3$): δ −3.74 (br s, 2 H, NH), 3.28, 3.31 (each t, 2 H, $CH_2CH_2CO_2CH_3$), 3.34, 3.55 (each s, 3 H, ring CH_3), 3.63 (s, 6 H, ring CH_3), 3.67 (s, 6 H, OCH_3), 4.37, 4.40 (each t, 2 H, $CH_2CH_2CO_2CH_3$), 6.28, 6.34 (each d, J_{HH} = 17.0 and 16.8 Hz, respectively, 1 H, 2 × CH=CHCN), 8.73, 8.75 (each d, J_{HH} = 16.8 and 17.0 Hz, respectively 1 H, CH=CHCN), 9.54, 9.68, 9.99, 10.06 (each s, 1 H, meso-*H*). UV–vis (CH_2Cl_2): λ_{max} (nm) 426 (ϵ 106 800), 516 (13 200), 554 (11 700), 584 (7300), 642 (5500). LR mass spectrum: *m/e* 640 (100). HR mass spectrum: $C_{38}H_{36}N_6O_4$ requires 640.2798, found 640.2737.

Zinc(II) 2,4-bis[2-(*tert*-butoxycarbonyl)vinyl]deuteroporphyrin IX dimethyl ester (16): 40% yield from *tert*-butyl acrylate. This porphyrin is unstable to trifluoroacetic acid, and therefore demetalation was avoided; mp 196–200 °C. ^{1}H NMR ($CDCl_3$ + pyridine-d_5): δ 1.74 (s, 18 H, *t*-Bu), 3.26 (m, 4 H, $CH_2CH_2CO_2CH_3$), 3.61 (s, 6 H, OCH_3), 3.63, 3.64, 3.83, 3.84 (each s, 3 H, ring CH_3), 4.38 (m, 4 H, $CH_2CH_2CO_2CH_3$), 7.07, 7.08 (each d, J_{HH} = 16.2 and 15.9 Hz, respectively, 1 H, CH=$CHCO_2$-*t*-Bu), 9.42, 9.45 (each d, J_{HH} = 15.9 and 16.2 Hz, 1 H, CH=$CHCO_2$-*t*-Bu), 9.92, 10.10, 10.15, 10.31 (each s, 1 H, meso-*H*). UV–vis (CH_2Cl_2): λ_{max} (nm) 416 (ϵ 190 200), 544 (14 200), 586 (24 800). LR mass spectrum (EI): *m/e* 852 (35), 796 (18), 740 (42). HR mass spectrum: $C_{46}H_{52}N_4O_8Zn$ requires 852.3077, found 852.3039. Anal. Calcd for $C_{46}H_{52}N_4O_8Zn{\cdot}H_2O$: C, 63.34; H, 6.24; N, 6.42. Found: C, 63.20; H, 6.09; N, 6.72.

Zinc(II) 2,4-di-2-propenyldeuteroporphyrin IX dimethyl ester (17): 59% yield from allyl chloride. This porphyrin is unstable to trifluoroacetic acid, and therefore demetalation was avoided; mp 207–210 °C. ^{1}H NMR ($CDCl_3$): δ 3.09, 3.12 (each t, 2 H, $CH_2CH_2CO_2CH_3$), 3.29, 3.31, 3.38, 3.43 (each s, 3 H, ring CH_3), 3.65, 3.67 (each s, 3 H, OCH_3), 4.14, 4.20 (each t, 2 H, $CH_2CH_2CO_2CH_3$), 4.45, 4.58 (each d, J_{HH} = 6.0 Hz, 2 H, CH_2CH=CH_2), 5.10–5.31 (m, 4 H, CH_2CH=CH_2), 6.37–6.52 (m, 2 H, 2 × CH_2CH=CH_2), 9.30, 9.33, 9.37, 9.46 (each s, 1 H, meso-*H*). UV–vis (CH_2Cl_2): λ_{max} (nm) 400 (ϵ 345 000), 530 (24 300), 568 (30 900). LR mass spectrum: *m/e* 683 (100), 681 (66), 680 (93), 653 (14), 624 (10), 608 (20). HR mass spectrum (FAB): $C_{38}H_{40}N_4O_4Zn$ requires 681.2420 (M + 1), found 681.2431.

Zinc(II) 2,4-bis(2-methyl-2-propenyl)deuteroporphyrin IX dimethyl ester (18): 48% yield from 2-methyl-3-chloropropene. The product was unstable to trifluoroacetic acid, and therefore demetalation was avoided; mp 262–268 °C. ^{1}H NMR ($CDCl_3$): δ 1.95, 1.97 (each s, 3 H, $CH_2C(CH_3)$=CH_2), 3.19 (t, 4 H, $CH_2CH_2CO_2CH_3$), 3.40, 3.42, 3.49, 3.50 (each s, 3 H, ring CH_3), 3.66, 3.68 (each s, 3 H, OCH_3), 4.26, 4.29 (each t, 2 H, $CH_2CH_2CO_2CH_3$), 4.55, 4.61 [each s, 2 H, $CH_2C(CH_3)$=CH_2], 4.96–5.02 [m, 4 H, $CH_2C(CH_3)$=CH_2], 9.66 (s, 3 H, 3 × meso-H), 9.74 (s, 1 H, meso-*H*). UV–vis (CH_2Cl_2): λ_{max} (nm) 400 (ϵ 320 000), 532 (14 800), 568 (21 600). LR mass spectrum (FAB): *m/e* 711 (75), 710 (71), 709 (100), 708 (92), 707 (26), 680 (22). HR mass spectrum: $C_{40}H_{44}N_4O_4Zn$ requires 708.2654, found 708.2681.

Zinc(II) 2,4-bis(3-phenoxypropenyl)deuteroporphyrin IX dimethyl ester (19): 21% yield from allyl phenyl ether; mp 112–116 °C. ^{1}H NMR ($CDCl_3$): δ 3.11 (m, 4 H, $CH_2CH_2CO_2CH_3$), 3.33, 3.38, 3.40, 3.42 (each s, 3 H, ring CH_3), 3.64, 3.65 (each s, 3 H, OCH_3), 4.21 (m, 4 H, $CH_2CH_2CO_2CH_3$), 5.24 (m, 4 H, $PhOCH_2CH$=CH), 6.81–6.92 (m, 2 H, $PhOCH_2CH$=CH), 7.13 (m, 2 H, 2 × *p*-*H*Ph), 7.32 (m, 4 H, 4 × *o*-*H*Ph), 7.50 (m, 4 H, 4 × *m*-*H*Ph), 7.88, 8.04 (each d, J_{HH} = 16.2 Hz, 1 H, 2 × $PhOCH_2CH$=CH), 9.20, 9.29, 9.35, 9.40 (each s, 1 H, meso-*H*). UV–vis (CH_2Cl_2): λ_{max} (nm) 408 (ϵ 222 000), 538 (13 600), 576 (19 300). LR mass spectrum (FAB): *m/e* 866 (100), 863 (52). HR mass spectrum (FAB): $C_{50}H_{48}N_4O_6Zn$ requires 864.2865, found 864.2851.

2,4-Distyryldeuteroporphyrin IX Dimethyl Ester (20). Method A. *The title compound was prepared in 44% yield from* **2** *and styrene by the same general method described above for* porphyrin **11**. It was also prepared (method B) from zinc(II) protoporphyrin IX dimethyl ester (**29**) (95 mg), phenylmercuric chloride (516 mg), and triethylamine (0.1 mL), in dry dimethylformamide (10 mL) at 60 °C with $LiPdCl_3$ [from LiCl (177 mg) and $PdCl_2$ (341 mg) in acetonitrile (10 mL)]. After being stirred for 1 h, the mixture was worked up, with demetalation in the usual way, to give **20** (65 mg, 60%); mp 264–267 °C from dichloromethane/petroleum ether. ^{1}H NMR ($CDCl_3$): δ −3.80 (s, 2 H, NH), 3.27 (t, 4 H, $CH_2CH_2CO_2CH_3$), 3.56, 3.58, 3.59, 3.66 (each s, 3 H, ring CH_3), 3.67 (s, 6 H, OCH_3), 4.37 (t, 4 H,

$\mathrm{CH_2C}\mathit{H}_2\mathrm{CO_2CH_3}$), 7.47 [t, 2 H, 2 × CH=CH(*p*-*H*Ph)], 7.58–7.70 [m, 6 H, 2 × CH=CH(*m*-*H*Ph), 2 × CH=C*H*Ph], 7.92–7.96 [m, 6 H, 2 × CH=CH(*o*-*H*Ph)], 8.50 [d, J_{HH} = 16.5 Hz, 1 H, C*H*=CHPh], 8.56 [d, J_{HH} = 16.5 Hz, 1 H, C*H*=CHPh], 9.94, 9.96, 10.01, 10.08 (each s, 1 H, meso-*H*). UV–vis (CH_2Cl_2): λ_{max} (nm) 408 (ϵ 175 000), 512 (22 600), 550 (24 900), 580 (16 120), 638 (14 000). LR mass spectrum: *m/e* 742 (100), 683 (8), 669 (17). HR mass spectrum: $C_{48}H_{46}N_4O_4$ requires 742.3519, found 742.3523.

2,4-Bis(*p*-methoxystyryl)deuteroporphyrin IX dimethyl ester (21): 43% yield from *p*-methoxystyrene; mp 252–255 °C. ^{1}H NMR ($CDCl_3$): δ −4.02 (s, 2 H, NH), 3.24 (t, 4 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO_2CH_3}$), 3.45, 3.50, 3.51, 3.53 (each s, 3 H, ring CH_3), 3.68 (s, 6 H, CO_2CH_3), 3.98 (s, 6 H, 2 × OCH_3), 4.33 (t, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CO_2CH_3}$), 7.13 [(m, 4 H, 2 × CH=CH(*Ph*-4-OCH_3)], 7.50 [d, J_{HH} = 16.2 Hz, 1 H, CH=C*H*(Ph-4-OCH_3)], 7.56 [d, J_{HH} = 16.2 Hz, 1 H, CH=C*H*(Ph-4-OCH_3)], 7.84 [m, 4 H, 2 × CH=CH(*Ph*-4-OCH_3)], 8.22 [d, J_{HH} = 16.2 Hz, 1 H, CH=C*H*(Ph-4-OCH_3)], 8.33 [d, J_{HH} = 16.2 Hz, 1 H, CH=C*H*(Ph-4-OCH_3)], 9.77, 9.80, 9.87, 9.95 (each s, 1 H, meso-*H*). UV–vis (CH_2Cl_2): λ_{max} (nm) 410 (ϵ 159 000), 512 (18 500), 552 (21 100), 582 (13 200), 638 (10 300). LR mass spectrum: *m/e* 803 (100), 788 (10), 772 (12), 745 (17), 730 (13). HR mass spectrum: $C_{50}H_{50}N_4O_6$ requires 802.3730, found 802.3746.

2,4-Bis(*m*-nitrostyryl)deuteroporphyrin IX dimethyl ester (22): 62% yield from *m*-nitrostyrene; mp 213–218 °C. ^{1}H NMR ($CDCl_3$ + trace of TFA-*d* for disaggregation): δ 3.15, 3.17 (each t, 2 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO_2CH_3}$), 3.64 (s, 9 H, 3 × ring CH_3), 3.70 (s, 3 H, ring CH_3), 3.79, 3.84 (each s, 3 H, OCH_3), 4.48, 4.51 (each t, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CO_2CH_3}$), 7.61, 7.67 [each d, J_{HH} = 16.2 Hz, 1 H, CH=C*H*(Ph-3-NO_2)], 7.79 [m, 2 H, 2 × CH=CH(5-*H*Ph-3-NO_2)], 8.19, 8.21 [each d, 1 H, CH=CH(6-*H*Ph-3-NO_2)], 8.37 [d, 2 H, 2 × CH=CH(4-*H*Ph-3-NO_2)], 8.63, 8.67 [each d, J_{HH} = 16.2 Hz, 1 H, C*H*=CH(Ph-3-NO_2)], 8.81, 8.83 [each s, 1 H, CH=CH(2-*H*Ph-3-NO_2)], 10.70, 10.71, 10.79, 10.93 (each s, 1 H, meso-H). UV–vis (CH_2Cl_2): λ_{max} (nm) 416 (ϵ 143 000), 516 (14 300), 556 (17 600), 580 (11 000), 638 (5830). LR mass spectrum (FAB): *m/e* 833 (100), 817 (45), 801 (27), 758 (36). HR mass spectrum: $C_{48}H_{44}N_6O_8$ requires 832.3221, found 832.3234. Anal. Calcd for $C_{48}H_{44}N_6O_8 \cdot H_2O$: C, 67.75; H, 5.45; N, 9.88. Found: C, 67.96; H, 5.11; N, 9.40.

2,4-Bis(*p*-nitrostyryl)deuteroporphyrin IX dimethyl ester (23): 79% yield from *p*-nitrostyrene; mp 206–212 °C. ^{1}H NMR ($CDCl_3$): δ 3.16, 3.18 (each t, 2 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO_2CH_3}$), 3.57, 3.58, 3.61, 3.67 (each s, 3 H, ring CH_3), 3.74, 3.80 (each s, 3 H, OCH_3), 4.41, 4.44 (each t, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CO_2CH_3}$), 7.58, 7.64 [each d, J_{HH} = 16.2 Hz, 1 H, CH=C*H*(Ph-*p*-NO_2)], 8.05, 8.06 [each d, J_{HH} = 9.0 Hz, 2 H, CH=CH(*o*-*H*Ph-*p*-NO_2)], 8.45, 8.46 [each d, J_{HH} = 9.0 Hz, 2 H, CH=CH(*m*-*H*Ph-*p*-NO_2)], 8.62, 8.65 [each d, J_{HH} = 16.2 Hz, 1 H, C*H*=CH(Ph-*p*-NO_2)], 10.56, 10.59, 10.66, 10.89 (each s, 1 H, meso-*H*). UV–vis (CH_2Cl_2): λ_{max} (nm) 420 (ϵ 88 600), 522 (12 500), 558 (16 000), 580 (11 000), 642 (6040). LR mass spectrum (FAB): *m/e* 833 (100), 803 (21), 760 (10). HR mass spectrum: $C_{48}H_{44}N_6O_8$ requires 832.3221, found 832.3234.

2,4-Bis(*p*-carbomethoxystyryl)deuteroporphyrin IX dimethyl ester (24): 57% yield from *p*-carbomethoxystyrene; mp 187–189 °C. ^{1}H NMR ($CDCl_3$ + trace of TFA-*d* for disaggregation): δ 3.15, 3.18 (each t, 2 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO_2CH_3}$), 3.60, 3.61, 3.615, 3.63 (each s, 3 H, ring CH_3), 3.68 (s, 6 H, OCH_3), 3.76, 3.81 (each s, 3 H, OCH_3), 4.45, 4.47 (each t, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CO_2CH_3}$), 7.60, 7.64 [each d, J_{HH} = 16.2 Hz, 1 H, CH=C*H*(Ph-*p*-CO_2CH_3)], 7.98, 8.00, 8.26, 8.27 [each d, J_{HH} = 8.4 Hz, 2 H, CH=CH(*Ph*-*p*-CO_2CH_3)], 8.59, 8.62 [each d, J_{HH} = 16.2 Hz, 1 H, C*H*=CH(Ph-*p*-CO_2CH_3)], 10.66 (s, 2 H, 2 × meso-*H*), 10.76, 10.93 (each s, 1 H, meso-H). UV–vis (CH_2Cl_2): λ_{max} (nm) 418 (ϵ 189 000), 520 (22 500), 554 (26 300), 580 (18 000), 640 (10 700). LR mass spectrum (FAB): *m/e* 859 (100), 845 (20), 828 (9), 801 (27), 786 (32). HR mass spectrum: $C_{52}H_{50}N_4O_8$ requires 858.3629, found 858.3623.

2,4-Bis(naphthyl-1-vinyl)deuteroporphyrin IX dimethyl ester (26): 52% yield from 1-vinylnaphthalene; mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ 3.29 (t, 4 H, 2 × $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO_2CH_3}$), 3.63, 3.64 (each s, 3 H, ring CH_3), 3.67 (s, 6 H, ring CH_3), 3.77, 3.79 (each s, 3 H, OCH_3), 4.41 (t, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CO_2CH_3}$), 7.51–7.60 (m, 4 H, naphthyl-*H*), 7.86–8.09 (m, 8 H, 2 × CH=C*H*(naphthyl) and naphthyl-*H*), 8.22–8.24 (m, 4 H, naphthyl-*H*), 8.75, 8.77 (each d, J_{HH} = 16.5 Hz, 1 H, C*H*=CH(naphthyl), 10.04, 10.08, 10.24, 10.26 (each s, 1 H, meso *H*). UV–vis (CH_2Cl_2): λ_{max} (nm) 416 (ϵ 138 000), 514 (22 000), 554 (24 600), 582 (18 340), 640 (15 800). LR mass spectrum (FAB): *m/e* 843 (100), 784 (17), 770 (21). HR mass spectrum: $C_{56}H_{50}N_4O_4$ requires 842.3832, found 842.3835.

2,4-Bis(anthracenyl-9-vinyl)deuteroporphyrin IX dimethyl ester (27): 17% yield from 9-vinylanthracene; mp 145–149 °C. ^{1}H NMR ($CDCl_3$) (highly aggregated): δ −3.46 (s, 2 H, NH), 3.28 (m, 4 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO_2CH_3}$), 3.55, 3.56, 3.67, 3.69, (each s, 3 H, ring CH_3), 3.84, 3.94 (each s, 3 H, OCH_3), 4.40 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CO_2CH_3}$), 7.61 (m, 12 H, anthracene), 8.17 (m, 4 H, anthracene), 8.43 (m, 2 H, vinyl), 8.58, 8.60 (each s, 1 H, 10-H), 8.87 (m, 2 H, vinyl), 10.08, 10.20, 10.29, 10.42 (each s, 1 H, meso *H*). UV-vis (CH_2Cl_2): λ_{max} (nm) 414 (ϵ 142 000), 514 (21 800), 548 (21 300), 580 (17 700), 634 (13 000). LR mass spectrum (FAB): *m/e* 943 (100), 929 (43), 884 (16), 870 (15). A satisfactory HR mass measurement on the *m/e* 943 peak could not be obtained.

2,4-Bis(ferrocenylvinyl)deuteroporphyrin IX dimethyl ester (28): 26% yield from vinylferrocene; mp 126–134 °C. ^{1}H NMR ($CDCl_3$): δ −3.51 (s, 2 H, NH), 3.29 (t, 4 H, 2 × $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO_2CH_3}$), 3.67 (s, 12 H, 4 × ring CH_3), 3.76, 3.79 (each s, 3 H, OCH_3), ($\mathrm{C}\mathit{H}_2\mathrm{CH_2CO_2CH_3}$ obscured around 4.4 ppm), 4.41, 4.44 (each s, 5 H, distal ring of ferrocene), 4.52, 4.89 (each s, 4 H, 2 × *H*-proximal ring of ferrocene), 7.50, 7.52 [each d, J_{HH} = 16.2 Hz, 1 H, CH=C*H*(ferrocenyl)], 8.29 [d, J_{HH} = 16.2 Hz, 2 H, 2 × C*H*=CH(ferrocenyl)], 10.06, 10.12, 10.25, 10.31 (each s, 1 H, meso-*H*). UV–vis (CH_2Cl_2): λ_{max} (nm) 406 (ϵ 159 000), 508 (16 500), 556 (16 700), 580 (14 500), 640 (8340). LR mass spectrum (FAB): *m/e* 959 (100), 945 (7), 900 (5), 892 (12), 839 (20). Anal. Calcd for $C_{56}H_{54}Fe_2N_4O_4$: C, 70.16; H, 5.68; N, 5.84. Found: C, 69.95; H, 5.71; N, 5.79.

Methyl 2-Styryl-2-devinylpyropheophorbide a (31). This chlorin was prepared in 30% yield by method B as described above for the distyryldeuteroporphyrin IX **20**; mp 256–259 °C. ^{1}H NMR ($CDCl_3$): δ −1.62, 0.50 (each s, 1 H, NH), 1.71 (t, 3 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.82 (d, 3 H, 8-Me), 2.26–2.35 (m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CO_2CH_3}$), 2.50–2.58 (m, 2 H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CO_2CH_3}$), 3.25, 3.48, 3.61 (each s, 3 H, ring CH_3), 3.68 (s, 3 H, OCH_3), 3.70 (q, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 4.30 (m, 1 H, 7-H), 4.50 (m, 1 H, 8-H), 5.11, 5.27 (each d, J_{HH} = 19.8 Hz, 1 H, 10-H), 7.46 (t, J_{HH} = 7.5 Hz, 1 H, *p*-H), 7.58 (t, J_{HH} = 7.5 Hz, 2 H, *m*-H), 7.65 (d, J_{HH} = 16.2 Hz, 1 H, CH=C*H*Ph), 7.89 (d, J_{HH} = 7.5 Hz, 2 H, *o*-H), 8.39 (d, J_{HH} = 16.2 Hz, 1 H, C*H*=CHPh), 8.58, 9.47, 9.53 (each s, 1 H, meso-*H*). UV–vis (CH_2Cl_2): λ_{max} (nm) 418 (ϵ 119 000), 512 (16 600), 542 (14 800), 614 (13 100), 674 (50 200). LR mass spectrum (FAB): *m/e* 625 (100), 609 (11), 597 (9), 537 (24), 523 (22). HR mass spectrum (FAB): $C_{40}H_{40}N_4O_3$ requires 625.3179 (M + 1), found 625.3189. HR mass spectrum (EI): $C_{40}H_{40}N_4O_3$ requires 624.3100, found 624.3098.

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Registry No. **2**, 74822-31-4; **11**, 28712-42-7; **11** metalated, 124443-90-9; **15**, 124461-09-2; **16**, 124443-91-0; **17**, 124443-92-1; **18**, 124443-93-2; **19**, 124443-94-3; **20**, 124443-84-1; **21**, 124443-85-2; **22**, 124443-86-3; **23**, 124443-87-4; **24**, 124443-88-5; **26**, 124443-89-6; **27**, 124461-10-5; **28**, 124443-95-4; **29**, 15304-09-3; **31**, 124461-11-6; acrolein, 107-02-8; acrylonitrile, 107-13-1; *tert*-butyl acrylate, 1663-39-4; allyl chloride, 107-05-1; 2-methyl-3-chloropropene, 563-47-3; allyl phenyl ether, 1746-13-0; styrene, 100-42-5; *p*-methoxystyrene, 637-69-4; *m*-nitrostyrene, 586-39-0; *p*-nitrostyrene, 100-13-0; *p*-carbomethoxystyrene, 1076-96-6; 1-vinylnaphthalene, 826-74-4; 9-vinylanthracene, 2444-68-0; vinylferrocene, 1271-51-8.