Rational Synthesis of β-Substituted Chlorin Building Blocks

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Chlorins bearing synthetic handles at specific sites about the perimeter of the macrocycle constitute valuable building blocks. We previously developed methodology for preparing meso-substituted chlorin building blocks and now present methodology for preparing several complementary β-substituted chlorin building blocks. The chlorins bear one or two β substituents, one meso substituent, a geminal dimethyl group to lock in the chlorin hydrogenation level, and no flanking meso and β substituents. The synthesis involves convergent joining of an Eastern half and a Western half. New routes have been developed to two β-substituted bromo-dipyrromethane monocarbinols (Eastern halves). A new β-substituted Western half was prepared following the method for preparing an unsubstituted Western half (3,3-dimethyl-2,3-dihydrodipyrrin). Chlorin formation is achieved by a two-flask process of acid-catalyzed condensation followed by metal-mediated oxidative cyclization. β-Substituted chlorins have been prepared in 18−24% yield bearing a 4-iodophenyl group at the 8-position, a 4-iodophenyl group or a 4-[2-(trimethylsilyl)ethynyl]phenyl group at the 12-position, and a 4-iodophenyl group and a 4-[2-(trimethylsilyl)ethynyl]phenyl group at diametrically opposed β-positions (2, 12). The latter building block makes possible the stepwise construction of linear multi-chlorin architectures. The chlorins exhibit typical absorption and fluorescence spectra. A systematic shift in the absorption maximum (637−655 nm for the free base chlorins, 606−628 nm for the zinc chlorins) and intensity of the chlorin Q_y band (ε up to 79 000 M^{-1} cm^{-1}) is observed depending on the location of the substituents. The characteristic spectral features and location of substituents in defined positions make these chlorins well suited for a variety of applications in biomimetic and materials chemistry.

Introduction

The tetrapyrrole family encompasses not only the porphyrins but also a diverse collection of hydroporphyrins including the chlorophylls.[1] The fundamental chromophore of the chlorophylls is a chlorin, which differs from a porphyrin in having one pyrrole ring reduced at the β-positions. The reduced ring alters the symmetry of the conjugated system, eliciting distinct electronic properties including a strong absorption band in the red region. In porphyrin chemistry, the availability of porphyrin building blocks has enabled the construction of a wide variety of biomimetic model systems and molecular materials. However, the absence of suitable chlorin building blocks has resulted in the common use of porphyrins as surrogates for chlorins.

We recently described the synthesis of meso-substituted chlorin building blocks.[2] The condensation of a dihydrodipyrrin (Western half, **1**) with a bromodipyrromethane-monocarbinol (Eastern half, **2-OH**) affords a dihydrobilene-*a*, which upon metal-mediated oxidative cyclization affords the corresponding chlorin (Scheme 1). The chlorins bear substituents at two meso-positions, a geminal dimethyl group to lock in the chlorin hydrogenation level, and no flanking meso and β substituents that could cause ruffling of the macrocycle. The choice of meso substituents was a natural one, given the utility of meso-substituted porphyrin building blocks[3] and the versatile chemistry established for preparing meso-substituted dipyrromethanes.[4] The latter are readily functionalized,[5] have enabled the rational synthesis of porphyrins bearing up to four different meso substituents,[6] and were conveniently exploited as key components in the synthesis of the meso-substituted chlorins.[2] An alternative approach to chlorins that bear a geminal dimethyl lock, avoid flanking meso and β substituents, and can be used in model systems has involved reaction of a tripyrrole complex with a pyrrole functionalized for subsequent elaboration.[7]

Chlorin building blocks with substituents at the β-positions are of equal interest to those with substituents at the meso-positions. Our motivations for preparing β-substituted chlorin building blocks were 2-fold. (1) We sought to be able to probe systematically the effects of attaching linkers at different positions about the perimeter of the chlorin macrocycle. In our work with multi-porphyrin arrays, we have found that the extent of through-bond electronic communication (excited-state energy transfer,

(1) (a) *Chlorophylls*; Scheer, H., Ed.; CRC Press: Boca Raton, FL, 1991. (b) *The Chlorophylls*; Vernon, L. P., Seely, G. R., Eds.; Academic Press: New York, 1966.

(2) Strachan, J. P.; O'Shea, D. F.; Balasubramanian, T.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 3160−3172.

(3) Lindsey, J. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 1, pp 45−118.

(4) Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391−1396.

(5) Rao, P. D.; Littler, B. J.; Geier, G. R., III; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 1084−1092.

(6) Rao, P. D.; Dhanalekshmi, S.; Littler, B. J.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7323−7344.

(7) (a) Montforts, F.-P.; Kutzki, O. *Angew. Chem., Int. Ed.* **2000**, *39*, 599−601. (b) Abel, Y.; Montforts, F.-P. *Tetrahedron Lett.* **1997**, *38*, 1745−1748. (c) Schmidt, W.; Montforts, F.-P. *Synlett* **1997**, 903−904.

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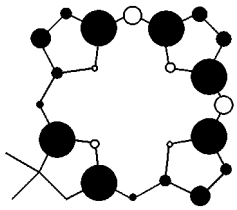
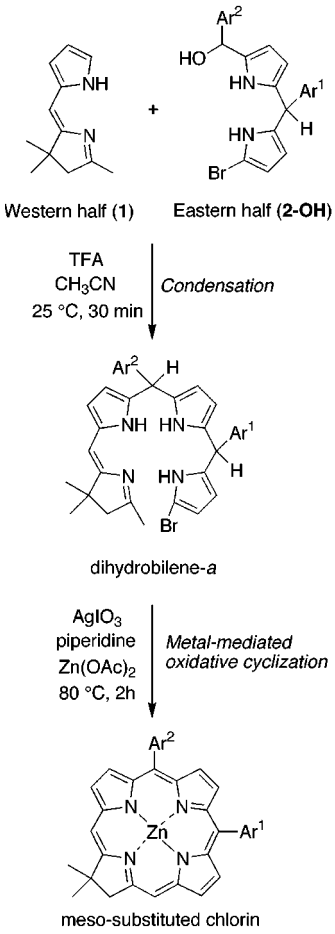
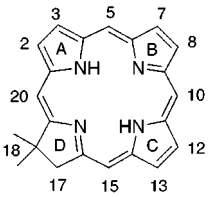


Figure 1. Highest occupied molecular orbital (a_2) of the chlorin.

Scheme 1



ground-state hole hopping) between porphyrins depends on the electron density in the frontier orbitals at the site of linker attachment.[8] All chlorins that have been examined exhibit an a_2 HOMO, which has electron density at all meso-positions and all nonreduced β-positions albeit in differing amounts at the various positions (Figure 1).[9,10] Chlorins differ from porphyrins in that the HOMO and HOMO-1 have substantial energetic separations.[11] Very limited efforts have been made to probe the effects of linker attachment site in hydroporphyrins on through-bond electronic communication[12] (as opposed to orientation-dependent through-space interactions that differ due to the distinct X and Y electronic transitions in hydroporphyrins). (2) We sought to be able to prepare linear multi-chlorin arrays analogous to our linear multi-porphyrin arrays,[13] which requires the availability of a building block bearing two substituents positioned at diametrically opposite sides of the macrocycle. The most suitable sites of di-substitution in this regard include the 2/12-, 3/13-, 5/15- and 10/20-positions. The β-positions (2/12, 3/13) are preferred over the meso-positions (5/15, 10/20), as the 15- and 20-positions flank the reduced ring and may result in unwanted steric congestion.



In this paper, we present the synthesis of β-substituted chlorin building blocks. Two new Eastern halves have been constructed in which each bears one β substituent and one (nonflanking) meso substituent, and one new Western half has been prepared that bears one β substituent. These new precursors have been used in conjunction with the prior Western half (**1**) to yield three new chlorins each bearing one β and one meso substituent. A chlorin bearing one meso substituent and substituents at the 2- and 12-positions also has been prepared. Such building blocks have heretofore not been available and in conjunction with the meso-substituted chlorins should enable a variety of fundamental studies, including investigation of the effects of site of linker connection on electronic communication in various chlorin-based architectures.

Results and Discussion

1. Synthesis of Chlorin Precursors. Eastern Halves. The synthesis of the β-substituted Eastern half begins in the same manner as our prior synthesis of β-substituted dipyrromethanes[14] but employs a number of significant improvements (Scheme 2). The iodophenyl-substituted pyrrole (**3**) is readily prepared from 4-iodobenzaldehyde, monoethyl malonate, and tosylmethylisocyanide. The ethoxycarbonyl group was removed by treatment with NaOH in ethylene glycol at 160 °C to give the 3-(4-iodophenyl)pyrrole (**4**) in 91% yield as pale brown crystals. This single-step decarboxylation[15] is more convenient than the two-step transformation on similar pyrrole compounds.[16] Vilsmeier−Haack formylation of **4** yielded a mixture of two regioisomers (~6:1 ratio) which were readily distinguished by ^{1}H NMR spectroscopy (see the Experimental Section). The major isomer, which gave appropriate peaks in the ^{1}H NMR spectrum similar to

(8) (a) Strachan, J. P.; Gentemann, S.; Seth, J.; Kalsbeck, W. A.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1997**, *119*, 11191−11201. (b) Yang, S. I.; Seth, J.; Balasubramanian, T.; Kim, D.; Lindsey, J. S.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1999**, *121*, 4008−4018.

(9) Fajer, J.; Davis, M. S. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 197−256.

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(12) Mössler, H.; Wittenberg, M.; Niethammer, D.; Mudrassagam, R. K.; Kurreck, H.; Huber, M. *Magn. Reson. Chem.* **2000**, *38*, 67−84.

(13) (a) Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759−9760. (b) Wagner, R. W.; Ciringh, Y.; Clausen, P. C.; Lindsey, J. S. *Chem. Mater.* **1999**, *11*, 2974−2983. (c) Lammi, R. K.; Ambroise, A.; Balasubramanian, T.; Wagner, R. W.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 7579−7591.

(14) Balasubramanian, T.; Lindsey, J. S. *Tetrahedron* **1999**, *55*, 6771−6784.

(15) Sessler, J. L.; Mozaffari, A.; Johnson, M. R. *Org. Synth.* **1991**, *70*, 68−78.

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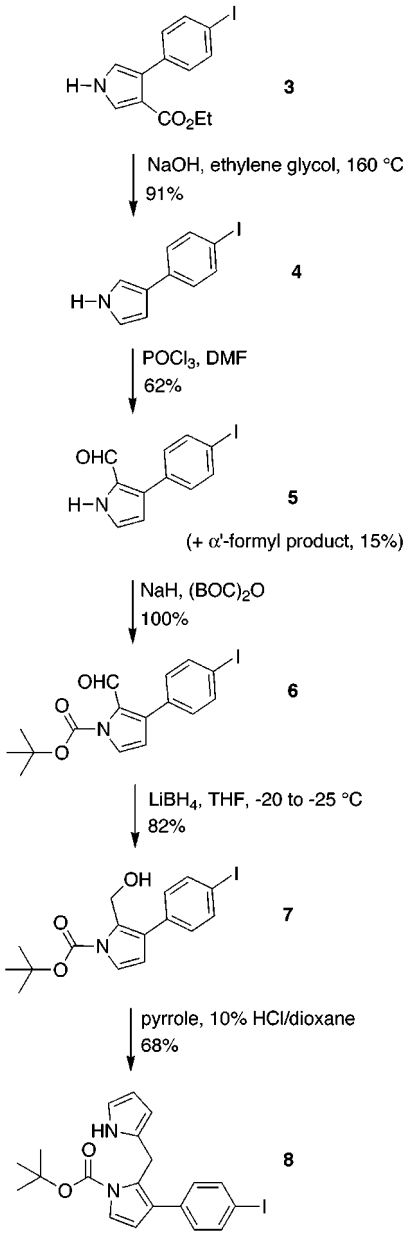
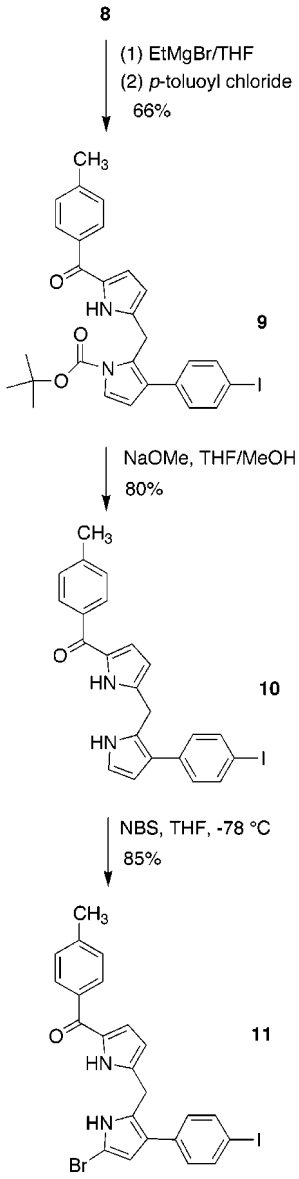
Scheme 2



those of 3-phenylpyrrole-2-carboxaldehyde,[17] was the desired compound (**5**) and was obtained in pure form by recrystallization in 62% yield. (The minor isomer was the α′-formylated product, 2-formyl-4-(4-iodophenyl)pyrrole.) Protection of the pyrrolic nitrogen with the *tert*-butyloxycarbonyl (BOC) group[18] gave pyrrole **6** in quantitative yield. Reduction to alcohol **7** was achieved with $LiBH_4$ at low temperature (longer reaction time or higher temperature led to the over-reduced, deprotected compound 2-methyl-3-(4-iodophenyl)pyrrole). Treatment of **7** with excess pyrrole under acidic conditions furnished the β-substituted, monoprotected dipyrromethane **8** in 68% yield. Excess pyrrole is necessary to minimize the formation of the tripyrromethane, while protection of the pyrrolic nitrogen is necessary to avoid self-condensation and allow the subsequent selective monoacylation. This approach afforded the β-substituted dipyrromethane as

Scheme 3



a single regioisomer, in contrast to our earlier methodology which gave a mixture of two regioisomers.[14]

We have developed methods for acylation of 5-substituted dipyrromethanes that involve formation of the pyrrolic Grignard reagent followed by treatment with an acid chloride. Our early work was performed in THF,[19] but more recent studies have revealed toluene to be a superior solvent.[6] In this case, the BOC-protected dipyrromethane was retained for selective monoacylation of the α-position in the unprotected pyrrole unit. Treatment of **8** with 2.5 equiv of EtMgBr in THF followed by *p*-toluoyl chloride afforded the monoacylated dipyrromethane **9** in 66% yield (Scheme 3). However, a similar reaction in toluene led to a mixture of the mono-acylated product, deprotected compound, and some unidentified impurities. A control experiment involving treatment of **8** with a slight excess of EtMgBr at 0 °C in THF for 1 h and the usual workup afforded the starting material in quantitative yield, thus revealing that the BOC group is stable to the acylation conditions. Removal of the BOC

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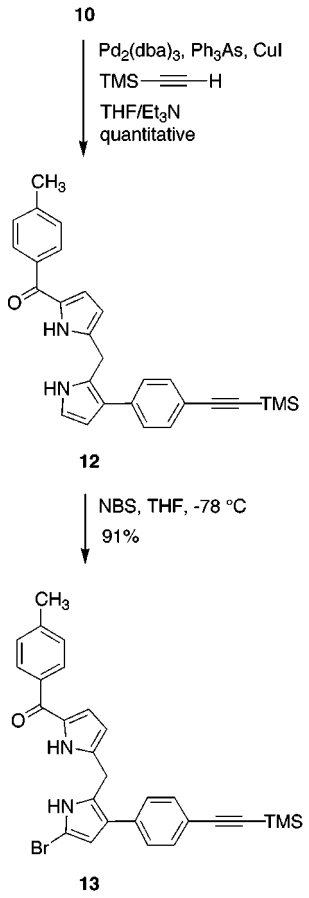
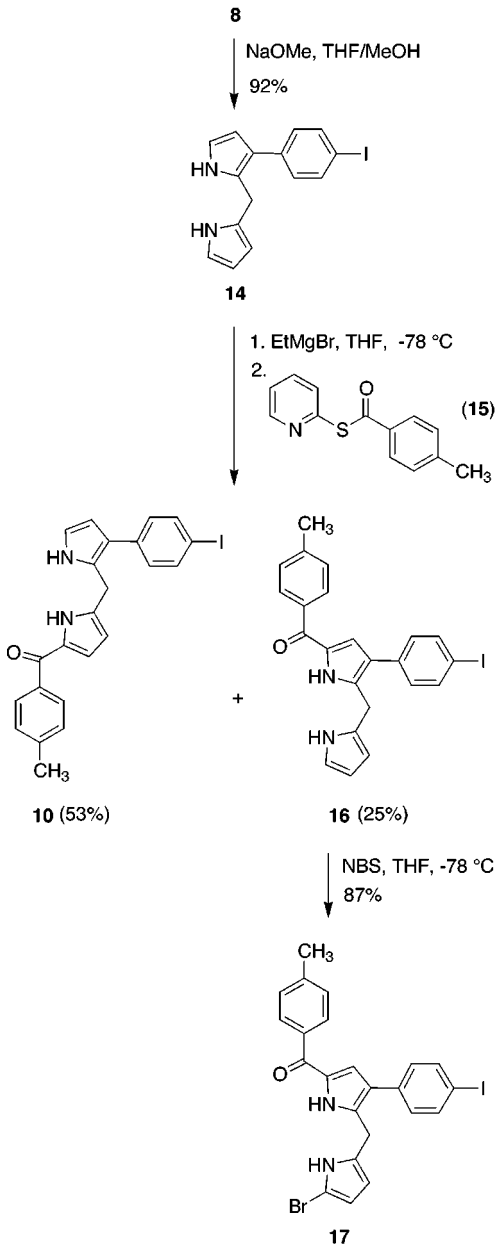
Scheme 4



Scheme 5



group under standard conditions[20] gave **10**. Electrophilic bromination of **10** with NBS (1 equiv) in THF at −78 °C following our earlier method[2] (excess NBS led to a considerable amount of a dibromo compound) afforded **11**.

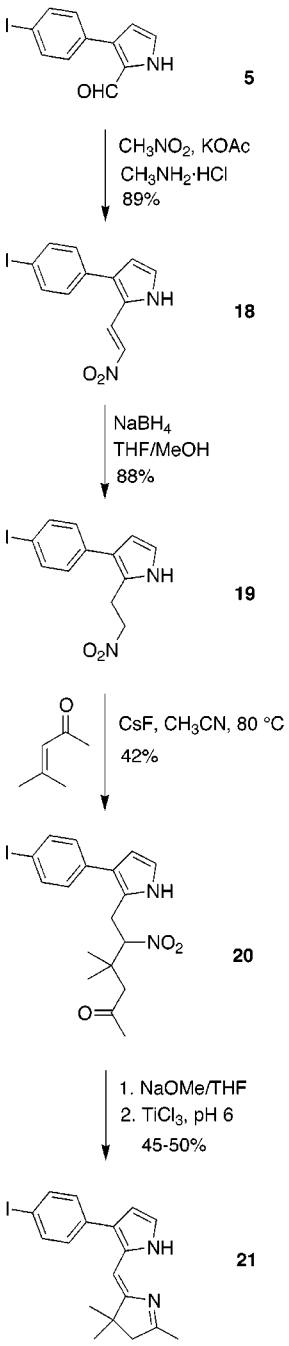
A second β-substituted dipyrromethane was prepared by Sonogashira coupling[21] of iodophenyl-substituted dipyrromethane **10** with trimethylsilylacetylene. In this manner, the trimethylsilylethynyl dipyrromethane **12** was obtained in quantitative yield (Scheme 4). Reaction of **12** with NBS at −78 °C furnished the corresponding bromodipyrromethane **13** in 91% yield.

We also sought to prepare a dipyrromethane bearing a substituent at a different β site using the same BOC-protected dipyrromethane **8**, reversing the order of acylation and deprotection that led to **10**. Thus, deprotection of **8** with NaOMe/MeOH afforded the β-substituted dipyrromethane **14** (Scheme 5). We recently devised a procedure for the selective mono-acylation of meso-substituted dipyrromethanes using EtMgBr and an *S*-pyridyl substituted benzothioate.[5] Application of this monoacylation method to **14** resulted in a mixture of two regioisomers (**10**, **16**). Our attempts to obtain **16** as the major product by varying the experimental conditions were unsuccessful. Separation of the two regioisomers was difficult and required extensive flash column chromatography. The minor isomer **16** was obtained in 25% yield. Treatment of **16** with 1 equivalent of NBS in THF at −78 °C yielded **17** in 87% yield as a yellow solid. All β-substituted 1-bromodipyrromethanes (**11**, **13**, **17**) are somewhat unstable (as are 2-halopyrroles in general[17]) but remain intact for a few weeks upon storage at 0 °C under argon.

A β-Substituted Western Half. We previously developed the synthesis of a Western half lacking any β-substituents except for the geminal dimethyl group (**1**).[2] Pyrrolecarboxaldehyde **5**, available in multigram quantities, provided a convenient starting point for the synthesis of a new Western half bearing a synthetic handle at a β-position. A β-substituted Western half in conjunction with the β-substituted Eastern half would enable the synthesis of chlorin building blocks bearing two β substituents positioned at opposite sides of the macrocycle. Application of the reaction conditions used to obtain 2-(2-nitrovinyl)pyrrole from 2-formylpyrrole[2] to the reaction of **5** resulted largely in recovery of starting material. After a limited study, we found that treatment of **5** with KOAc and a slight excess of methylamine hydrochloride in

(20) Hasan, I.; Marinelli, E. R.; Lin, L.-C. C.; Fowler, F. W.; Levy, A. B. *J. Org. Chem.* **1981**, *46*, 157−164.
(21) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470.

Scheme 6

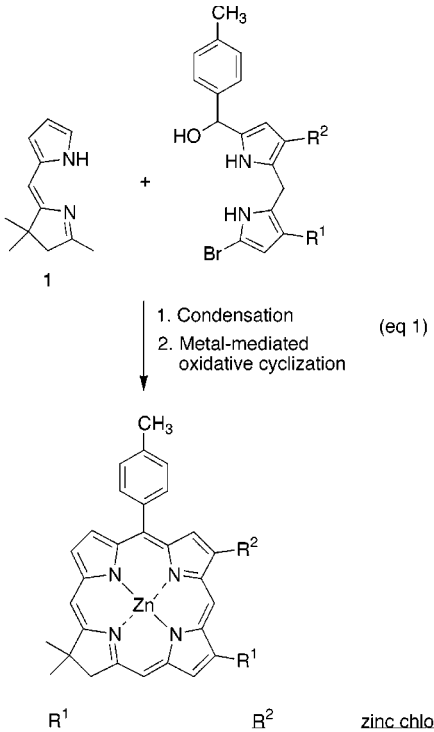


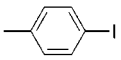
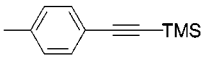
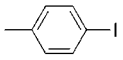
nitromethane (instead of methanol) as solvent at room temperature for 2 h (instead of 16 h) yielded the desired aldol-condensation product **18** in 89% yield (Scheme 6). It is noteworthy that a longer reaction time led to the formation of the Michael addition product of nitromethane at the nitrovinyl group in **18**, forming 2-(1,3-dinitro-2-propyl)-3-(4-iodophenyl)pyrrole in ~30% yield, a side reaction for which there is precedent.[22] $NaBH_4$ reduction of **18** gave **19**, which underwent Michael addition with mesityl oxide to give the nitro-hexanone product **20**, the precursor to the β-substituted Western half. The Michael addition was fast compared to that forming the β-unsubstituted counterpart (precursor to **1**), but the yield was slightly lower (42% vs 65%). Treatment of **20** with NaOMe followed by a buffered $TiCl_3$ solution yielded the β-substituted Western half **21** in 45−50% yield as a light green solid. The yield of the β-substituted Western half is greater than that of the unsubstituted analogue **1** (45−50% vs 25−30%), the stability is enhanced, and handling is facilitated (**21** has mp = 141−142 °C; **1** is an oil).

Proof of Structure. To confirm the substitution patterns, an X-ray structure was sought for one of the key precursors. Compound **19** afforded good crystals, and the X-ray structure confirmed the expected 2-alkyl-3-aryl substitution pattern. The data are included in the Supporting Information. This structure confirms the substitution pattern of the formylated pyrrole precursor **5**, in turn establishing the substitution pattern in the series of compounds **6**−**14** and **18**−**21**. These compounds include the β-substituted Eastern half precursors **11** and **13** and the β-substituted Western half **21**. The monoacylation of **14** was not regiospecific and afforded two α-acylated isomers: **10** and **16**. The assigned structures of **10** and **16** were confirmed by independent synthesis from **5** (Scheme 3) and 2D-NMR (see the Supporting Information), respectively. The minor isomer **16** serves as the Eastern half precursor **17**. These studies confirm the assigned substitution patterns of the dipyrromethane derivatives that serve as the Eastern and Western halves. The reaction of an Eastern half and a Western half yielding the chlorin proceeds in a regiospecific manner. Thus, the respective substitution patterns of the Eastern and Western halves are carried over to the chlorin product.

2. Chlorin Formation. Our prior synthesis of chlorins involved the following steps: (1) formation of the bromodipyrromethane-monocarbinol (**2-OH**, Eastern half) by reduction of the carbonyl group in the Eastern half precursor, (2) acid-catalyzed condensation of the Eastern half and Western half (**1**) to obtain the dihydrobilene-*a*, and (3) metal-mediated oxidative cyclization to give the chlorin.[2] All three steps are done in succession on the same day. This same procedure was employed herein except that the workup conditions are different due to the labile nature of the β-substituted Eastern half precursors (**11**, **13**, **17**) and corresponding β-substituted Eastern halves. In a typical reaction, **11** was treated with $NaBH_4$ in THF/MeOH (4:1) at room temperature under argon. Upon the disappearance of starting material (TLC analysis), the reaction mixture was worked up and the carbinol **11-OH** was treated with 1.2 equiv of **1** at room temperature in CH_3CN containing 10−11 mM TFA (see the Experimental Section). After 25−30 min, the resulting dihydrobilene-*a* was obtained by quenching the reaction mixture with aqueous $NaHCO_3$ followed by workup in CH_2Cl_2. Anhydrous toluene and 15 molar equiv each of $AgIO_3$, $Zn(OAc)_2$, and piperidine were added, and the mixture was heated at 80 °C for ~2.5 h. The reaction mixture slowly changed from red to green, indicating the formation of chlorin. Filtration of the reaction mixture through a pad of silica followed by column chromatography afforded the chlorin **Zn-22** in >90% purity. Precipitation with CH_2Cl_2/hexanes furnished pure chlorin (**Zn-22**) in 18% yield (eq 1). Similar treatment of **1** and Eastern half **13-OH** or **17-OH** gave the zinc chlorin **Zn-23** or **Zn-24** in 22% or 24% yield, respectively.

(22) Niazimbetova, Z. I.; Evans, D. H.; Liable-Sands, L. M.; Rheingold, A. L. *J. Electrochem. Soc.* **2000**, *147*, 256−259.



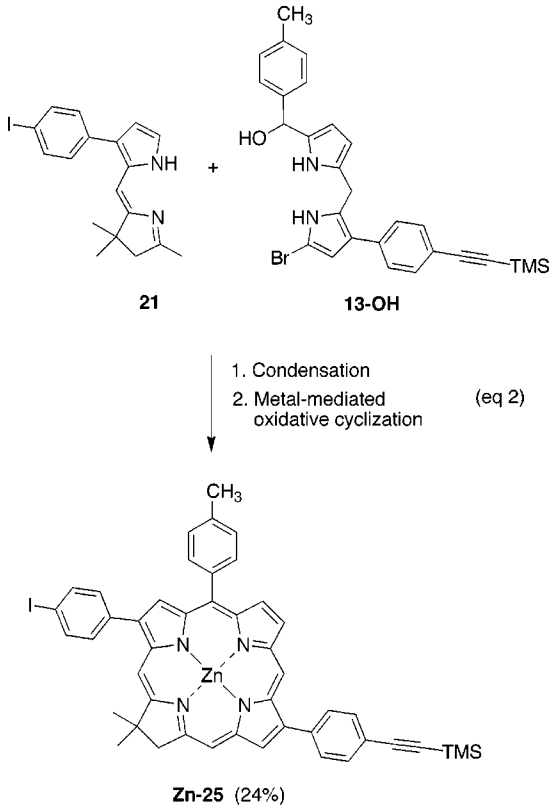
Eastern half	R^1	R^2	zinc chlorin
11-OH		H	**Zn-22** (18%)
13-OH		H	**Zn-23** (22%)
17-OH	H		**Zn-24** (24%)

The chlorins **Zn22** - **Zn24** each bear one β substituent. To prepare a chlorin bearing two β substituents, **13-OH** and Western half **21** were reacted to give zinc chlorin **Zn-25** in 24% yield (eq 2). This chlorin has an iodophenyl group and an ethynylphenyl group at β-positions on opposite sides of the macrocycle. Porphyrins bearing iodophenyl and ethynylphenyl groups in a related trans orientation (5,15-positions) have been employed in the stepwise synthesis of linear multi-porphyrin arrays.[13] Analogous linear multi-chlorin arrays should be attainable with **Zn-25**.

In each of these chlorin-forming reactions only one chlorin product was obtained, indicating the absence of scrambling during the course of the reaction. This methodology is quite general and the yields of 18−24% obtained with the three β-substituted Eastern halves (**11-OH**, **13-OH**, **17-OH**) and the Western halves (**1**, **21**) are noticeably superior to the ~10% obtained with the meso-substituted Eastern halves (**2-OH**) and Western half (**1**).

The Zn-chlorins were demetalated to give the corresponding free base chlorins by treatment with TFA in CH_2Cl_2. In most cases the crude product was pure enough for analysis while in other cases the free base chlorin was further purified by a short silica column.

3. Spectral Properties of the Chlorins. ^{1}H NMR Spectra. The NMR spectral information available for chlorins has been obtained largely from naturally occurring chlorins, which bear alkyl groups at most or all of the β-positions. The synthetic chlorins prepared herein and previously[2] are sparsely substituted. Examination by ^{1}H NMR spectroscopy confirms the expected substitution patterns and provides valuable information. In **22**, the two NH protons appear as broad peaks at δ −2.15 and −1.85 ppm; a downfield signal at δ 9.84 ppm is assigned to the meso proton H_{10}. The reduced ring exhibits a singlet at δ 2.07 ppm (geminal dimethyl groups) and another singlet at δ 4.64 ppm (ring CH_2), as also observed in the meso-substituted chlorins. Other characteristic features include an AB quartet at δ 8.85 ppm (β-pyrrole protons of ring A), two doublets at δ 8.64 and 8.90 ppm (β-pyrrole protons of ring B), and singlets at δ 8.91 (for 2H) and 8.99 ppm (H_{15}, H_{20}, and the one β-pyrrole proton (H_{13}) of ring C). The significant changes for the β-substituted **Zn-22** are the absence of signals corresponding to NH protons, and slight upfield shifts of the geminal dimethyl group (δ 2.01 ppm), ring methylene protons (δ 4.48 ppm) and all of the meso and β-pyrrole protons. Similar trends were observed for free base chlorin **23** and zinc chlorin **Zn-23**.



The ^{1}H NMR spectrum of chlorin **24** is slightly different due to the difference in the substitution pattern at the perimeter of the molecule. Distinctive features in addition to the different chemical shifts of the two NH protons include the singlet at δ 8.64 ppm (the one β-pyrrole proton, H_7, of ring B) and the downfield signal at δ 9.17 ppm as a doublet (one of the β-pyrrole protons of ring C). The ^{1}H NMR spectrum of chlorin **25** is more simple. The β-pyrrole protons of ring B appear as two doublets at δ 8.62 and 8.88 ppm, and the AB quartet corresponding to the β-pyrrole protons of ring A in chlorins **22**−**24** is absent. The remaining meso protons (H_{10}, H_{15}, H_{20}) and β-pyrrole protons (H_3, H_{13}) resonate as five singlets. **Zn-25** showed a similar pattern except for the slight upfield shift of the peaks due to the meso and β protons.

A distinctive feature of the chlorins is that the β-pyrrole protons of ring B resonate slightly upfield compared to the other pyrrole protons. This indicates that the β-pyrrole double bond of ring B does not participate as

Table 1. Absorption Spectral Properties of Chlorins[a]

chlorins	λ_{max} (nm), B	λ_{max} (nm), Q_y	B/Q_y intensity ratio
24	409	637	4.3
22	414	643	3.0
23	416	645	3.1
25	422	655	2.6
pheophytin *a*[b]	408	667	2.1
pheophytin *b*[b]	434	655	5.1
Zn-24	415	606	4.3
Zn-22	411	615	3.6
Zn-23	412	617	3.5
Zn-25	417	628	2.6
chlorophyll *a*[b]	430	662	1.3
chlorophyll *b*[b]	455	644	2.8

[a] In toluene at room temperature. [b] In diethyl ether.[23]

fully in the 18π electron ring current of the chlorin macrocycle, as expected based on resonance considerations.

Absorption Spectra. Each of the free base chlorins (**22**−**25**) exhibits an intense B (Soret) band and a characteristic strong Q_y band. The B band in each case exhibited a short-wavelength shoulder of significant intensity, resulting in a fwhm ranging from 32 to 35 nm for **22**−**25**. A similar spectral feature was observed for the previous set of meso-substituted free base chlorins.[2] The B band underwent a slight redshift with substitution located at position 8 (**24**), 12 (**22**, **23**), or 2 and 12 (**25**). Significant differences in Q_y absorption maximum and absorption intensity occurred depending on the site of substitution of the chlorin. The Q_y absorption maximum ranged from 637 to 655 nm and paralleled the redshift of the B band. In addition, a hyperchromic effect of the Q_y band was observed accompanying the bathochromic shift. Although the accurate determination of molar absorption coefficients can be difficult especially with handling small samples, the ratio of the Q_y and B bands provides a relative measure of the changing band intensities. The B/Q_y band ratio ranges from 4.3 (**24**) to 2.6 (**25**). These data are listed in Table 1. It is noteworthy that the chlorins with an iodophenyl or ethynylphenyl group at the 12-position exhibited nearly identical absorption spectra. For comparison, the meso-substituted free base chlorins exhibited absorption maxima at 411−414 nm and 640−644 nm.[2]

Each of the zinc chlorins (**Zn-22**−**Zn25**) exhibits an intense B band and a characteristic strong Q_y band. The B band in each case was sharp (fwhm 18−21 nm) with only a very weak short-wavelength shoulder. The Q_y band underwent a redshift from 606 to 628 nm as the substituent location was changed from 8 (**Zn-24**) to 12 (**Zn-22**, **Zn-23**) to 2 and 12 (**Zn-25**). A concomitant increase in intensity of the Q_y band also was observed, as displayed in Figure 2. In all of the chlorins examined, a slight redshift in the B band was accompanied by a more pronounced redshift in the Q_y band. The only discrepancy in this trend occurred in comparing **Zn-24** and **Zn-22** (or **Zn-23**). The former has the shortest wavelength Q_y band (606 nm) among the group but a B band at 415 nm, compared with 615 and 411 nm for that of the latter. For comparison, the meso-substituted zinc chlorins exhibited absorption maxima at 412 and 608 nm.[2]

The spectral changes observed in the synthetic chlorin building blocks have parallels in the spectra of naturally occurring chlorins. Chlorophyll *a* and chlorophyll *b* exhibit pronounced differences in ratio of the B and Q_y band intensities as well as differences in absorption maxima. Similar features are observed in the free base derivatives (pheophytin *a* and pheophytin *b*). Such spectral differences stem from replacement of a methyl group with a formyl group at a single location.[23] The ability to tune the long wavelength absorption maximum of synthetic chlorin building blocks may enable the construction of efficient chlorin-based light-harvesting and energy-cascade systems.[24]

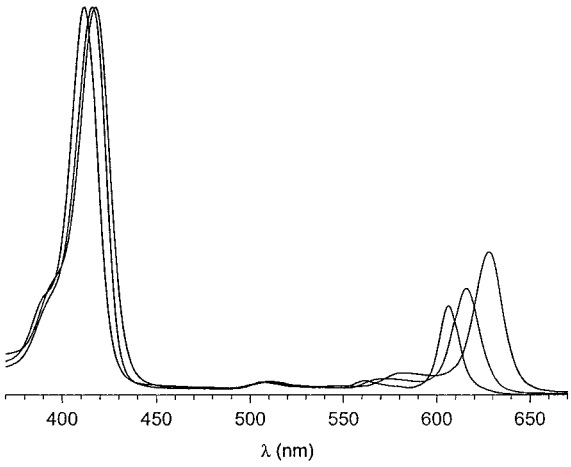
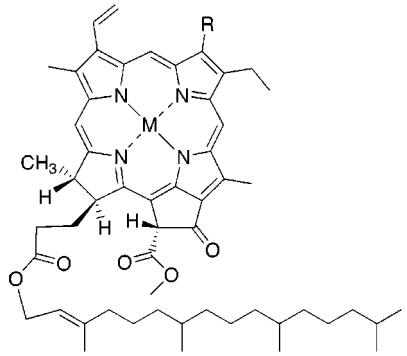


Figure 2. Absorption spectra in toluene at room temperature of three zinc chlorins (normalized at the B band). The Q_y bands differ significantly in absorption maximum (607 nm, **Zn-24**; 616 nm **Zn-22**; 629 nm, **Zn-25**) and intensity due to the position of the substituents at the perimeter of the macrocycle. Each chlorin bears one *p*-tolyl group (5-position). The other substituents are present at the 8-position (**Zn-24**), 12-position (**Zn-22**), or 2- and 12-positions (**Zn-25**).



Fluorescence Spectra and Yields. Similar to the meso-substituted chlorins, the free base chlorins **22**−**24** exhibit a characteristic sharp fluorescence band at 640 nm and a weaker emission in the region 660−720 nm. In each case the latter emission exhibited two discernible maxima at approximately 680 and 710 nm. The emission spectrum of free base chlorin **25** was shifted to 660 and 726 nm. The Zn chlorins **Zn-22** and **Zn-23** each exhibit a sharp fluorescence band at around 620 nm and a weak band at 676 nm, whereas the emission of **Zn-24** appears

(23) Smith, J. H. C.; Benitez, A. In *Modern Methods of Plant Analysis*; Paech, K., Tracey, M. V., Eds.; Springer-Verlag: Berlin 1955; Vol. IV, pp 142−196.

at 609 and 661 nm. The emission spectrum of **Zn-25** (635, 691 nm) is more red-shifted as observed in free base **25**. The fluorescence quantum yields were determined for those chlorins lacking iodophenyl substituents (which exhibit decreased yields due to the heavy atom effect). The fluorescence quantum yield of free base chlorin **23** was 0.25, while that of **Zn-23** was 0.11. These values are in line with those of other naturally occurring or synthetic chlorins.[2]

Conclusions

The synthesis of chlorins described herein provides the following features: (1) control over the location of the reduced ring, (2) locking in of the chlorin hydrogenation level through use of a geminal dimethyl group, (3) location of synthetic handles at designated sites at the perimeter of the macrocycle, and (4) a single chlorin product thereby facilitating purification. The ability to incorporate substituents at distinct locations (2, 5, 8, 10, or 12) about the chlorin perimeter opens a number of opportunities. With different substitution patterns, the Q_y absorption band can be tuned over the range 637−655 nm for free base chlorins and 606−628 nm for zinc chlorins, facilitating coverage of the solar spectrum. The chlorin bearing synthetic handles at the 2- and 12-positions (**25**) should enable the incorporation of chlorin building blocks into linear architectures. The availability of a family of synthetic chlorins bearing diverse substituents at defined locations should facilitate the systematic study of substituent effects and broaden the scope of chlorin-containing model systems.

Experimental Section

General Methods. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained in $CDCl_3$ unless noted otherwise. Absorption spectra (Cary 3, 0.25 nm data intervals) and fluorescence spectra (Spex FluoroMax, 1 nm data intervals) were collected routinely. Chlorins were analyzed in neat form by laser desorption mass spectrometry (LD-MS) in the absence of a matrix.[25] Pyrrole was distilled at atmospheric pressure from CaH_2. Melting points are uncorrected. Reagents and starting materials were obtained from Aldrich. Spectral parameters including molar absorption coefficients and fluorescence quantum yields (Φ_f) were determined as previously described.[2]

Chromatography. Preparative chromatography was performed using silica (Baker) or alumina (Fisher A540, 80−200 mesh) and eluants based on hexanes admixed with ethyl acetate or CH_2Cl_2.

Solvents. THF was distilled from sodium benzophenone ketyl. CH_3CN (Fisher certified A. C. S.) was distilled from CaH_2 and stored over powdered molecular sieves. Nitromethane was stored over $CaCl_2$. CH_2Cl_2 was distilled from CaH_2. Dry methanol was prepared as described.[2] Other solvents were used as received.

Compounds **1**,[2] **3**,[14] and **15**[5] were prepared according to literature procedures.

3-(4-Iodophenyl)pyrrole (4). Following a standard procedure,[15] a mixture of 3-ethoxycarbonyl-4-(4-iodophenyl)pyrrole (7.20 g, 21.1 mmol) and ethylene glycol (55 mL) in a 100-mL Claisen flask was flushed with argon for 10 min, and then powdered NaOH (2.2 g, 55 mmol) was added. The flask was placed in an oil bath at 120 °C and the oil bath temperature was raised to 160 °C. After 2.5 h, the flask was cooled to room temperature and 10% aqueous NaCl (100 mL) was added. The aqueous layer was extracted with CH_2Cl_2. The organic layers were collected, washed with 10% aqueous NaCl, dried (Na_2SO_4), and concentrated. The product was recrystallized in ethanol affording light brown crystals (5.18 g, 91%): mp 164−165 °C; ^{1}H NMR δ 6.51 (m, 1H), 6.83 (m, 1H), 7.08 (s, 1H), 7.27 (d, J = 8.7 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 8.35 (br, 1H); ^{13}C NMR δ 89.9, 106.3, 114.7, 119.1, 123.8, 127.0, 135.2, 137.5; EI-MS obsd 268.9702, calcd 268.9702. Anal. Calcd for $C_{10}H_8IN$: C, 44.6; H, 3.0; N, 5.2. Found: C, 44.7; H, 3.0; N, 5.1. The synthesis starting from 4-iodobenzaldehyde (35 g), monoethyl malonate, and tosylmethyl isocyanide has been performed with linear scale-up of the established procedures, affording 21.5 g of **4**.

2-Formyl-3-(4-iodophenyl)pyrrole (5). A solution of **4** (5.15 g, 19.1 mmol) in DMF (6.1 mL) and CH_2Cl_2 (140 mL) under argon was cooled to 0 °C and then $POCl_3$ (2.11 mL, 22.6 mmol) was added dropwise. After 1 h, the flask was warmed to room temperature and stirred overnight. The reaction was quenched at 0 °C with 2.5 M NaOH (100 mL). The mixture was poured into water (500 mL), extracted with CH_2Cl_2, and the combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. ^{1}H NMR spectroscopy showed two regioisomers in ∼6:1 ratio. [The minor isomer exhibited signals at δ 7.21 and 7.39 ppm, compared with signals at δ 6.42 and 7.14 ppm for the major isomer. The most downfield signal (7.39 ppm) is assigned to the proton adjacent to a formyl group, which occurs in the 2-formyl-4-aryl substituted pyrrole. The chemical shift of the pyrrole peaks for the major isomer were similar to those reported for 3-phenylpyrrole-2-carboxaldehyde.[17]] Recrystallization from ethyl acetate afforded an orange solid corresponding to the major isomer (2.25 g). The mother liquor was concentrated and purified by flash column chromatography [silica, hexanes/ethyl acetate (3:1)]. The first fraction corresponded to the major aldehyde (1.25 g). The total yield of the title compound was 3.50 g (62%): mp 153−154 °C; ^{1}H NMR δ 6.42 (m, 1H), 7.14 (m, 1H), 7.22 (m, 2H), 7.76 (m, 2H), 9.59 (s, 1H), 10.72 (br, 1H); ^{13}C NMR δ 93.5, 104.3, 111.4, 125.8, 128.6, 130.8, 133.1, 137.8, 179.4; FAB-MS obsd 296.9663, calcd 296.9651. Anal. Calcd for $C_{10}H_8INO$: C, 44.5; H, 2.7; N, 4.7. Found: C, 44.4; H, 2.7; N, 4.6.

***N-tert*-Butoxycarbonyl-2-formyl-3-(4-iodophenyl)pyrrole (6).** Following a standard procedure,[18] a sample of NaH (70 mg, 1.8 mmol, 60% dispersion in mineral oil) in a round-bottomed flask under argon was washed twice with anhydrous pentane (∼5 mL). Anhydrous THF (14 mL) was added followed by **5** (400 mg, 1.35 mmol). After stirring for 30 min at room temperature, di-*tert*-butyl dicarbonate (325 mg, 1.5 mmol) was added, and stirring was continued for another 2 h. The reaction was quenched with 50% saturated aqueous NH_4Cl (50 mL). The mixture was extracted with ether. The combined organic layers were washed with brine, dried (Na_2SO_4), and filtered [silica, hexanes/ethyl acetate (4:1)] to yield a viscous oil (535 mg, quantitative): ^{1}H NMR δ 1.64 (s, 9H), 6.33 (d, J = 3.0 Hz, 1H), 7.30 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 3.0 Hz, 1H), 7.72 (d, J = 8.1 Hz, 2H), 10.22 (s, 1H); ^{13}C NMR δ 27.7, 85.8, 94.2, 113.2, 126.7, 128.5, 131.3, 132.8, 137.0, 137.4, 148.3, 181.6; FAB-MS obsd 397.0176, calcd 397.0175 ($C_{16}H_{16}INO_3$).

***N-tert*-Butoxycarbonyl-2-hydroxymethyl-3-(4-iodophenyl)pyrrole (7).** A solution of **6** (400 mg, 1.0 mmol) in anhydrous THF (12 mL) under argon was cooled to −20 to −25 °C and $LiBH_4$ (55 mg, 2.5 mmol) was added in portions. The reaction was monitored by TLC [silica, hexanes/ethyl acetate (4:1)], and when no starting material was detected (∼25 min), the reaction was quenched with cold water (30 mL). The aqueous layer was extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), concentrated, and purified by flash column chromatography [silica, hexanes/ethyl acetate containing 1% Et_3N (3:1)] yielding a gum (330 mg, 82%): ^{1}H NMR δ 1.62 (s, 9H), 3.61 (br, 1H), 4.66 (d, J = 7.2 Hz, 2H), 6.25 (d, J = 3.6 Hz, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 3.6 Hz, 1H), 7.71 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 27.8, 55.3, 84.7, 92.4,

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(25) (a) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93−99. (b) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 283−291.

111.2, 121.3, 127.9, 130.0, 130.4, 134.1, 137.5, 149.8; FAB-MS obsd 399.0336, calcd 399.0331 ($C_{16}H_{18}INO_3$).

3-(4-Iodophenyl)-10-*N*-(*tert*-butoxycarbonyl)dipyrromethane (8). A solution of **7** (1.2 g, 3.0 mmol) and pyrrole (3.36 mL, 48 mmol) in 1,4-dioxane (36 mL) at room temperature was treated with 10% aqueous HCl (6.0 mL). The reaction was monitored by TLC [silica, hexanes/ethyl acetate (4:1)]. After 4 h, saturated aqueous $NaHCO_3$ (50 mL) and water (50 mL) were added and the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, dried (Na_2SO_4), concentrated, and purified by flash column chromatography [silica, hexanes/ethyl acetate (4:1)]. A nonpolar product was isolated in minor amount (uncharacterized). The desired product was obtained as a pale brown solid (920 mg, 68% yield): mp 128−129 °C; ^{1}H NMR δ 1.57 (s, 9H), 4.18 (s, 2H), 5.87 (br, 1H), 6.10 (m, 1H), 6.22 (d, J = 3.0 Hz, 1H), 6.64 (m, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 3.6 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 8.78 (br, 1H); ^{13}C NMR δ 24.6, 27.8, 84.3, 92.1, 105.8, 107.9, 111.6, 116.3, 121.0, 126.8, 128.5, 130.4, 130.8, 135.0, 137.4, 150.0; FAB-MS obsd 448.0659, calcd 448.0648. Anal. Calcd for $C_{20}H_{21}IN_2O_2$: C, 53.6; H, 4.7; N, 6.3. Found: C, 54.1; H, 4.9; N, 5.9.

3-(4-Iodophenyl)-9-(4-methylbenzoyl)-10-*N*-(*tert*-butoxycarbonyl)dipyrromethane (9). A solution of **8** (448 mg, 1.0 mmol) in anhydrous THF (15 mL) under argon at 0 °C was treated slowly with EtMgBr (1 M in THF, 2.5 mL, 2.5 mmol). The mixture was stirred for 30 min at 0 °C. Then, *p*-toluoyl chloride (200 μL, 1.5 mmol) was added slowly and stirring was continued for 1 h at 0 °C. The reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. The product was purified by flash column chromatography [silica, hexanes/ethyl acetate (4:1)], affording a pale white solid (375 mg, 66%): mp 120−121 °C; (due to possible rotamers the ^{1}H NMR and ^{13}C NMR spectra are not very clean) ^{1}H NMR δ 1.56 (s, 9H), 2.42 (s, 3H), 4.29 (s, 2H), 5.95 (m, 1H), 6.26 (m, 1H), 6.76 (m, 1H), 7.09 (m, 2H), 7.25 (m, 2H), 7.31 (m, 1H), 7.71 (d, J = 8.7 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 9.95 (br, 1H); ^{13}C NMR δ 25.2, 27.8, 31.7, 84.8, 92.3, 109.3, 111.5, 119.6, 121.5, 125.8, 126.3, 128.9, 129.0, 130.2, 130.6, 134.7, 135.8, 137.5, 138.6, 142.0, 149.7, 183.8. Anal. Calcd for $C_{28}H_{27}IN_2O_3$: C, 59.4; H, 4.8; N, 5.0. Found: C, 59.4; H, 4.6; N, 5.1.

3-(4-Iodophenyl)-9-(4-methylbenzoyl)dipyrromethane (10). Following a standard method for the deprotection of BOC-protected pyrroles,[20] a solution of **9** (328 mg, 0.58 mmol) in anhydrous THF (4 mL) under argon at room temperature was treated with methanolic NaOMe (0.7 mL of the supernatant from the mixture prepared from 200 mg of NaOMe and 1.0 mL of MeOH). After 25 min, the reaction was quenched with a mixture of hexanes and water (20 mL, 1:1). The mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. Purification by flash column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a pale brown solid (216 mg, 80%): mp 185−186 °C; ^{1}H NMR δ 2.43 (s, 3H), 4.17 (s, 2H), 6.15 (m, 1H), 6.24 (m, 1H), 6.56 (m, 1H), 6.85 (m, 1H), 7.17 (m, 2H), 7.28 (m, 2H), 7.69 (m, 2H), 7.77 (d, J = 7.8 Hz, 2H), 9.43 (br, 1H), 10.88 (br, 1H); ^{13}C NMR δ 21.6, 25.2, 90.6, 108.6, 110.3, 117.4, 121.1, 122.3, 123.9, 129.0, 129.1, 130.0, 130.7, 135.5, 136.2, 137.4, 139.4, 142.6, 185.2; FAB-MS obsd 466.0561, calcd 466.0542. Anal. Calcd for $C_{23}H_{19}IN_2O$: C, 59.2; H, 4.1; N, 6.0. Found: C, 59.3; H, 4.2; N, 5.9.

1-Bromo-3-(4-iodophenyl)-9-(4-methylbenzoyl)dipyrromethane (11). Following our earlier procedure,[2] a solution of **10** (120 mg, 0.26 mmol) in anhydrous THF (6 mL) was cooled to −78 °C under argon. Recrystallized NBS (46 mg, 0.26 mmol) was added and the reaction mixture was stirred for 1 h (−78 °C). Then the mixture was quenched with a mixture of hexanes and water (20 mL, 1:1) and allowed to warm to 0 °C. The aqueous portion was extracted with reagent-grade ether and the combined organic layers were dried over K_2CO_3. The solvent was evaporated under vacuum at room temperature. Purification by flash column chromatography [silica, hexanes/ether (2:1)] afforded a yellow solid (120 mg, 85%). The bromodipyrromethane is unstable but can be stored for several weeks at 0 °C: mp 160 °C dec; ^{1}H NMR δ 2.44 (s, 3H), 4.09 (s, 2H), 6.12 (d, J = 3.0 Hz, 1H), 6.16 (m, 1H), 6.89 (m, 1H), 7.14 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 10.33 (br, 1H), 11.59 (br, 1H); ^{13}C NMR δ 21.6, 24.9, 91.1, 97.9, 110.2, 110.5, 122.8, 123.5, 125.4, 129.2, 130.2, 130.0, 130.8, 135.2, 135.4, 137.5, 139.9, 142.8, 186.1; FAB-MS obsd 543.9642, calcd 543.9647. Anal. Calcd for $C_{23}H_{18}BrIN_2O$: C, 50.7; H, 3.3; N, 5.1. Found: C, 51.3; H, 3.5; N, 5.2.

3-[4-[2-(Trimethylsilyl)ethynyl]phenyl]-9-(4-methylbenzoyl)dipyrromethane (12). Samples of **10** (279 mg, 0.599 mmol), $Pd_2(dba)_3$ (42 mg, 0.046 mmol), Ph_3As (113 mg, 0.369 mmol), and CuI (9 mg, 0.047 mmol) were added to a 25-mL Schlenk flask. The flask was evacuated and purged with argon three times. Then deaerated anhydrous THF/triethylamine (6 mL, 1:1) was added followed by trimethylsilylacetylene (127 μL, 0.90 mmol). The flask was sealed and immersed in an oil bath (37 °C), and the mixture was stirred overnight. Then CH_2Cl_2 (20 mL) was added, and the mixture was filtered through a pad of Celite, washed several times with CH_2Cl_2, and concentrated. The residue was purified by flash column chromatography [silica, hexanes/ethyl acetate (3:1)] to afford a yellow solid (262 mg, quantitative): mp 126−127 °C; ^{1}H NMR δ 0.26 (s, 9H), 2.43 (s, 3H), 4.19 (s, 2H), 6.16 (m, 1H), 6.28 (m, 1H), 6.55 (m, 1H), 6.85 (m, 1H), 7.28 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 9.51 (br, 1H), 10.96 (br, 1H); ^{13}C NMR δ 0.0, 21.5, 25.3, 105.4, 108.6, 110.3, 117.4, 119.9, 121.5, 122.3, 124.1, 127.6, 129.0, 129.1, 130.7, 132.0, 135.5, 137.0, 139.5, 142.6, 185.2; FAB-MS obsd 436.1972, calcd 436.1971. Anal. Calcd for $C_{28}H_{28}N_2OSi$: C, 77.0; H, 6.5; N, 6.4. Found: C, 76.3; H, 6.3; N, 6.3.

1-Bromo-3-[4-[2-(trimethylsilyl)ethynyl]phenyl]-9-(4-methylbenzoyl)dipyrromethane (13). Following the procedure for the synthesis of **11**, treatment of **12** (150 mg, 0.34 mmol) with NBS (60 mg, 0.34 mmol) afforded a pale yellow solid (160 mg, 91%): mp 140 °C dec; ^{1}H NMR δ 0.26 (s, 9H), 2.44 (s, 3H), 4.12 (s, 2H), 6.17 (m, 2H), 6.89 (m, 1H), 7.31 (m, 4H), 7.50 (d, J = 9.0 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 10.16 (br, 1H), 11.42 (br, 1H); ^{13}C NMR δ 0.0, 21.5, 25.0, 94.1, 97.9, 105.2, 110.3, 110.5, 120.4, 123.3, 125.5, 127.7, 129.2, 130.7, 132.1, 135.4, 135.9, 139.7, 142.8, 185.9; FAB-MS obsd 514.1079, calcd 514.1076. Anal. Calcd for $C_{28}H_{27}BrN_2OSi$: C, 65.2; H, 5.3; N, 5.4. Found: C, 65.1; H, 5.2; N, 5.3.

3-(4-Iodophenyl)dipyrromethane (14). Following the deprotection procedure used to prepare **10**, a sample of **8** (225 mg, 0.50 mmol) in anhydrous THF (4 mL) under argon at room temperature was treated with methanolic NaOMe (0.6 mL of the supernatant of the mixture prepared from 200 mg of NaOMe and 1.0 mL of MeOH). After 15 min, the reaction was quenched with hexanes and water (14 mL, 1:1). The resulting mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. The residue was passed through a filtration column to yield a light brown solid (160 mg, 92%). Analytical data are in accord with the literature.[14]

3-(4-Iodophenyl)-1-(4-methylbenzoyl)dipyrromethane (16). Following a general monoacylation procedure for unprotected dipyrromethanes,[5] EtMgBr (1 M solution in THF, 2.2 mL, 2.2 mmol) was added to a solution of **14** (385 mg, 1.1 mmol) in anhydrous THF (14 mL). After the mixture was stirred for 10 min, the flask was cooled to −78 °C and a solution of pyridyl thioester **15** (255 mg, 1.1 mmol) in anhydrous THF (3 mL) was added slowly. After a few min, the cooling bath was removed and stirring was continued for 1 h. Then saturated aqueous NH_4Cl and water were added, and the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. TLC analysis [silica, hexanes/ethyl acetate (3:1)] showed two components with R_f = 0.34 (minor) and R_f = 0.29 (major). The two regioisomers formed were purified by two successive flash columns [silica, hexanes/ethyl acetate (3:1)], affording the minor isomer **16** (130 mg, 25%) and the major isomer **10** (270 mg, 53%). The identity of **10** was verified by

independent synthesis (vide supra). Data for **16**: mp 190 °C dec; ^{1}H NMR δ 2.43 (s, 3H), 4.15 (s, 2H), 6.05 (m, 1H), 6.13 (m, 1H), 6.58 (m, 1H), 6.94 (m, 1H), 7.19 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.7 Hz, 2H), 7.78 (d, J = 8.1 Hz, 2H), 9.17 (br, 1H), 10.83 (br, 1H); ^{13}C NMR δ 21.6, 25.2, 91.8, 106.8, 108.3, 117.8, 121.1, 124.3, 127.2, 129.1, 129.2, 129.7, 130.2, 134.6, 135.4, 136.3, 137.6, 142.9, 185.4; FAB-MS obsd 466.0573, calcd 466.0542. Anal. Calcd for $C_{23}H_{19}IN_2O$: C, 59.2; H, 4.1; N, 6.0. Found: C, 59.1; H, 4.2; N, 5.8.

9-Bromo-3-(4-iodophenyl)-1-(4-methylbenzoyl)dipyrromethane (17). Following the procedure for the synthesis of **11**, treatment of **16** (186 mg, 0.400 mmol) with NBS (72 mg, 0.40 mmol) gave a pale yellow solid (189 mg, 87%): mp 140 °C dec; ^{1}H NMR δ 2.43 (s, 3H), 4.08 (s, 2H), 5.94 (m, 1H), 6.00 (m, 1H), 6.96 (d, J = 2.1 Hz, 1H), 7.18 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 9.80 (br, 1H), 11.53 (br, 1H); ^{13}C NMR was attempted in $CDCl_3$ but the compound decomposed upon lengthy data acquisition; FAB-MS obsd 543.9628, calcd 543.9647. Anal. Calcd for $C_{23}H_{18}BrIN_2O$: C, 50.7; H, 3.3; N, 5.1. Found: C, 51.2; H, 3.4; N, 5.0.

2-(*trans*-2-Nitrovinyl)-3-(4-iodophenyl)pyrrole (18). A mixture of **5** (1.485 g, 5.00 mmol), KOAc (492 mg, 5.01 mmol), methylamine hydrochloride (402 mg, 5.95 mmol), and nitromethane (45 mL) was stirred at room temperature under argon. The mixture slowly yielded an orange-red precipitate. After stirring for 2 h, TLC showed the appearance of a new component and the disappearance of **5**. (A longer reaction time (10 h) led to formation of the Michael addition product, 2-(1,3-dinitro-2-propyl)-3-(4-iodophenyl)pyrrole, in ~30% yield.) The reaction was quenched with brine and extracted with ethyl acetate, and the organic layers were dried (Na_2SO_4) and concentrated. The residue was treated with hot ethyl acetate and filtered. The filtrate was concentrated and dissolved in hot CH_2Cl_2, followed by precipitation upon adding cold hexanes, affording an orange solid (1.52 g, 89%): mp 217−218 °C dec; ^{1}H NMR (acetone-d_6) δ 6.54 (m, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.33 (m, 1H), 7.80 (d, J = 13.5 Hz, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.97 (d, J = 13.4 Hz, 1H), 11.2 (br, 1H); ^{13}C NMR (acetone-d_6) δ 93.4, 112.5, 121.3, 127.1, 127.2, 128.4, 131.8, 132.8, 135.4, 138.9; FAB-MS obsd 339.9720, calcd 339.9709; λ_{abs} (toluene) 395 nm. Anal. Calcd for $C_{12}H_9IN_2O_2$: C, 42.4; H, 2.7; N, 8.2. Found: C, 41.8; H, 2.6; N, 7.9.

2-(2-Nitroethyl)-3-(4-iodophenyl)pyrrole (19). Following the procedure for a β-unsubstituted pyrrole,[2] a sample of **18** (1.36 g, 4.00 mmol) was dissolved in anhydrous THF/MeOH (40 mL, 9:1) under argon at 0 °C. $NaBH_4$ (605 mg, 16.0 mmol) was added in portions and stirring was continued for 1 h at 0 °C. Then the mixture was stirred for 2 h at room temperature. The reaction mixture was neutralized with acetic acid (pH = 7), water (50 mL) was then added, and the mixture was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried (Na_2SO_4), and concentrated. Purification by passage through a short column [silica, hexanes/ethyl acetate (3:1)] gave a pale white solid (1.2 g, 88%): mp 88−89 °C; ^{1}H NMR δ 3.41 (t, J = 6.6 Hz, 2H), 4.52 (t, J = 6.6 Hz, 2H), 6.26 (s, 1H), 6.74 (s, 1H), 7.07 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.1 Hz, 2H), 8.33 (br, 1H); ^{13}C NMR δ 24.0, 75.0, 91.1, 109.3, 117.8, 122.1, 122.2, 129.8, 135.7, 137.7; FAB-MS obsd 341.9877, calcd 341.9865. Anal. Calcd for $C_{12}H_{11}IN_2O_2$: C, 42.1; H, 3.2; N, 8.2. Found: C, 42.3; H, 3.3; N, 8.1.

1-[3-(4-Iodophenyl)pyrro-2-yl]-2-nitro-3,3-dimethyl-5-hexanone (20). Following the procedure for a β-unsubstituted pyrrole,[2] a mixture of **19** (1.03 g, 3.0 mmol), CsF (2.28 g, 15.0 mmol), and mesityl oxide (1.72 mL, 15.0 mmol) in anhydrous acetonitrile (22.5 mL) was heated at 80 °C for 2.5 h to 3 h. The mixture turned dark red. TLC analysis confirmed the absence of starting material. The solvent was evaporated under vacuum. The residue was taken up in ethyl acetate and filtered through a pad of silica using ethyl acetate as eluant. The solvent was evaporated under vacuum and the product was purified by a gravity column [alumina, hexanes/ethyl acetate (2:1)] followed by recrystallization (CH_2Cl_2/hexanes) to afford brown crystals (550 mg, 42%): mp 124−125 °C; ^{1}H NMR δ 1.08 (s, 3H), 1.19 (s, 3H), 2.11 (s, 3H), 2.37 (d, J = 17.4 Hz, 1H), 2.56 (d, J = 17.4 Hz, 1H), 3.15 (m, 1H), 3.39 (m, 1H), 5.20 (m, 1H), 6.21 (m, 1H), 6.68 (m, 1H), 7.10 (m, 2H), 7.70 (m, 2H), 8.22 (br, 1H); ^{13}C NMR δ 23.9, 24.2, 24.8, 31.6, 36.8, 51.2, 91.1, 94.2, 109.1, 117.8, 122.2, 122.4, 130.1, 135.9, 137.5, 206.7; FAB-MS obsd 440.0605, calcd 440.0597. Anal. Calcd for $C_{18}H_{21}IN_2O_3$: C, 49.1; H, 4.8; N, 6.4. Found: C, 49.1; H, 4.7; N, 6.3.

1,3,3-Trimethyl-7-(4-iodophenyl)-2,3-dihydrodipyrrin (21). Following the procedure for a β-unsubstituted pyrrole,[2] a solution of **20** (220 mg, 0.50 mmol) in anhydrous THF (5.0 mL) under argon was treated with NaOMe (135 mg, 2.5 mmol), and the mixture was stirred for 1 h at room temperature (first flask). In a second flask, $TiCl_3$ (8.6 wt % $TiCl_3$ in 28 wt % HCl, 3.8 mL, 2.1 mmol, 4.2 mol equivalent) and H_2O (20 mL) were combined, NH_4OAc (~15 g) was added to buffer the solution to pH 6.0, and then THF (5 mL) was added. The nitronate anion of **20** formed in the first flask was transferred via cannula to the buffered $TiCl_3$ solution in the second flask. Additional THF (3 mL) was added to the nitronate anion flask, and the resulting supernatant was also transferred to the buffered $TiCl_3$ solution. The resulting mixture was stirred at room temperature for 6 h under argon. Then the mixture was extracted with ethyl acetate and the combined organic layers were washed with saturated aqueous $NaHCO_3$, water, and brine, and then dried ($MgSO_4$). The solvent was removed under reduced pressure at room temperature. The crude product was passed through a short column [alumina, hexanes/ethyl acetate (2:1)] to afford a light green solid (80 mg, 45%). A second preparation at the same scale gave 92 mg (50%): mp 140−142 °C; ^{1}H NMR δ 1.18 (s, 6H), 2.22 (s, 3H), 2.52 (s, 2H), 5.89 (s, 1H), 6.26 (m, 1H), 6.85 (m, 1H), 7.19 (m, 2H), 7.69 (m, 2H), 11.09 (br, 1H); ^{13}C NMR δ 20.7, 29.1, 29.7, 41.2, 53.7, 90.3, 102.3, 108.6, 118.5, 122.2, 127.5, 130.4, 136.8, 137.4, 161.9, 177.2; FAB-MS obsd 390.0595, calcd 390.0593 ($C_{18}H_{19}IN_2$); λ_{abs} (toluene) 352 nm.

General Procedure for Chlorin Formation: Zn(II)-17,-18-Dihydro-18,18-dimethyl-5-(4-methylphenyl)-12-(4-iodophenyl)porphyrin (Zn-22). Following a general procedure,[2] to a solution of **11** (110 mg, 0.20 mmol) in 7.5 mL of anhydrous THF/MeOH (4:1) at room temperature was added excess $NaBH_4$ (100 mg, 2.6 mmol) in small portions. The reaction was monitored by TLC [alumina, hexanes/ethyl acetate (3:1)] and upon completion the mixture was quenched with cold water (~10 mL) and then extracted with distilled CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with brine (50 mL), dried (K_2CO_3) for 2−3 min, and concentrated in vacuo at room temperature to leave the resulting carbinol **11-OH** in ~1−2 mL of CH_2Cl_2. A sample of **1** (45 mg, 0.24 mmol) was dissolved in a few milliliters of anhydrous CH_3CN and combined with **11-OH**, then additional anhydrous CH_3CN was added to give a total of 22 mL CH_3CN (total volume assuming solvent additivity is 23−24 mL). The solution was stirred at room temperature under argon and TFA (20 μL, 0.26 mmol, ~11 mM) was added. The reaction was monitored by TLC [alumina, hexanes/ethyl acetate (3:1)], which after 25−30 min showed the disappearance of **11-OH** and the appearance of a bright spot just below that of **1**. The reaction mixture was quenched with 10% aqueous $NaHCO_3$ and extracted with distilled CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with water and brine, dried (Na_2SO_4), and the solvent was removed in vacuo at room temperature. The residue was dissolved in anhydrous toluene (14 mL) under argon, then $AgIO_3$ (848 mg, 3.0 mmol), piperidine (300 μL, 3.0 mmol) and $Zn(OAc)_2$ (550 mg, 3.0 mmol) were added. The resulting mixture was heated at 80 °C for 2.5 h. The reaction was monitored by TLC [silica, hexanes/CH_2Cl_2, (1:1); showing a single green spot)] and absorption spectroscopy (bands at ~410 nm and ~610 nm). The change of the reaction mixture from red to green indicated the formation of chlorin. The reaction mixture was cooled to room temperature then passed through a short column (silica, CH_2Cl_2). The major fraction was concentrated and again chromatographed [silica, hexanes/CH_2Cl_2 (2:1 then 1:1)]. The greenish blue solid obtained was dissolved in a minimum of CH_2Cl_2 and precipitated by adding hexanes, affording a greenish blue solid (25

mg, 18%): ^{1}H NMR δ 2.01 (s, 6H), 2.67 (s, 3H), 4.48 (s, 2H), 7.50 (d, J = 7.2 Hz, 2H), 7.91 (d, J = 7.2 Hz, 2H), 7.95 (d, J = 8.1 Hz, 2H), 8.09 (d, J = 8.1 Hz, 2H), 8.51 (d, J = 4.2 Hz, 1H), 8.67 (m, 5H), 8.78 (d, J = 4.2 Hz, 1H), 9.56 (s, 1H); LD-MS obsd 693.78; FAB-MS obsd 694.0580, calcd 694.0572 ($C_{35}H_{27}IN_4Zn$); λ_{abs} (toluene)/nm 411 (log ε = 5.33, fwhm = 18 nm), 616 (4.76); λ_{em} 619, 674 nm.

Notes about Chlorin Formation. (1) The complete reduction of the carbonyl in the Eastern half precursor to the corresponding carbinol sometimes requires additional $NaBH_4$. The reduction must be complete prior to performing the chlorin-forming reaction. (2) Upon workup of the Eastern half, the organic layers were dried in K_2CO_3 (the carbinol decomposes quickly upon drying over Na_2SO_4 or $MgSO_4$). Upon solvent removal, the solution was not taken to dryness because the Eastern half decomposes more rapidly upon removal of the solvent. (3) The Eastern half upon workup, and the condensation solution giving the dihydrobilene-*a*, generally were either yellow or light red; these solutions led to chlorins in good yield. In some instances, further darkening was observed, in which case the chlorin was obtained in low yield. (4) The uncertainty in the volume of solvent accompanying the Eastern half upon workup (typically ∼1−2 mL for the scales employed herein) leads to ∼5% uncertainty in the concentrations of the components and reagents in condensation giving the dihydrobilene-*a*. The [TFA] was ∼11 mM for the syntheses of **Zn22** and **Zn24**; ∼10 mM for **Zn23** and **Zn25**.

General Conditions for Demetalation, Given for 17,-18-Dihydro-18,18-dimethyl-5-(4-methylphenyl)-12-(4-iodophenyl)porphyrin (22). To a solution of **Zn-22** (10.0 mg, 14.4 μmol) in anhydrous CH_2Cl_2 (5 mL) was added TFA (58 μL, 0.75 mmol). After being stirred for 30 min at room temperature (monitoring by TLC and UV−vis spectroscopy), the reaction was quenched with 10% aqueous $NaHCO_3$ (20 mL). The mixture was extracted with CH_2Cl_2. The combined organic layers were washed with water, dried (Na_2SO_4), and concentrated. Further purification (if necessary) was achieved by chromatography on a short column [silica, hexanes/CH_2Cl_2 (1:1 then 1:2)] affording a green solid (8.0 mg, 88%): ^{1}H NMR δ −2.15 (br, 1H), −1.85 (br, 1H), 2.07 (s, 6H), 2.69 (s, 3H), 4.64 (s, 2H), 7.54 (d, J = 7.5 Hz, 2H), 8.04 (m, 4H), 8.16 (d, J = 8.1 Hz, 2H), 8.64 (d, J = 4.5 Hz, 1H), 8.85 (AB quartet, J = 4.5 Hz, 2H), 8.90 (m, 3H), 8.99 (s, 1H), 9.84 (s, 1H); LD-MS obsd 633.88; FAB-MS obsd 632.1434, calcd 632.1437 ($C_{35}H_{29}IN_4$); λ_{abs} (toluene)/nm 414 (log ε = 5.13, fwhm = 34 nm), 505 (4.12), 643 (4.65); λ_{em} 646, 682 nm.

Zn(II)-17,18-dihydro-18,18-dimethyl-5-(4-methylphenyl)-12-[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (Zn-23). Following the general procedure for chlorin formation, the condensation of **13-OH** [prepared from **13** (130 mg, 0.25 mmol)] and **1** (57 mg, 0.30 mmol) in a solution of CH_3CN/CH_2Cl_2 (25 mL + ∼1 mL) containing TFA (20 μL, 0.26 mmol, ∼10 mM) followed by the standard oxidative cyclization yielded a blue solid (36 mg, 22%): ^{1}H NMR δ 0.35 (s, 9H), 2.03 (s, 6H), 2.67 (s, 3H), 4.54 (s, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.96 (d, J = 7.5 Hz, 2H), 8.16 (d, J = 8.1 Hz, 2H), 8.53 (d, J = 4.5 Hz, 1H), 8.60 (s, 1H), 8.68 (m, 2H), 8.73 (d, J = 4.5 Hz, 1H), 8.75 (s, 1H), 8.80 (d, J = 4.5 Hz, 1H), 9.63 (s, 1H); LD-MS obsd 665.74; FAB-MS obsd 664.2007, calcd 664.2001; ($C_{40}H_{36}IN_4SiZn$); λ_{abs} (toluene)/nm 413 (log ε = 5.31, fwhm = 21 nm), 618 (4.77), λ_{em} 622, 676 nm (Φ_f = 0.11).

17,18-Dihydro-18,18-dimethyl-5-(4-methylphenyl)-12-[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (23). Following the general demetalation procedure, a sample of **Zn-23** (10 mg, 15 μmol) gave a green solid (8.0 mg, 89%): ^{1}H NMR δ −2.15 (br, 1H), −1.85 (br, 1H), 0.35 (s, 9H), 2.07 (s, 6H), 2.69 (s, 3H), 4.64 (s, 2H), 7.53 (d, J = 7.5 Hz, 2H), 7.91 (d, J = 8.1 Hz, 2H), 8.03 (d, J = 8.1 Hz, 2H), 8.27 (d, J = 8.1 Hz, 2H), 8.64 (d, J = 4.5 Hz, 1H), 8.84 (AB quartet, J = 4.5 Hz, 2H), 8.89 (m, 2H), 8.93 (s, 1H), 8.99 (s, 1H), 9.86 (s, 1H); LD-MS obsd 604.31; FAB-MS obsd 602.2880, calcd 602.2866 ($C_{40}H_{38}IN_4Si$); λ_{abs} (toluene)/nm 415 (log ε = 4.97, fwhm = 36 nm), 506 (3.96), 647 (4.49); λ_{em} 648, 685, 715 nm (Φ_f = 0.25).

Zn(II)-17,18-dihydro-18,18-dimethyl-5-(4-methylphenyl)-8-(4-iodophenyl)porphyrin (Zn-24). Following the general procedure for chlorin formation, the condensation of **17-OH** [prepared from **17** (110 mg, 0.20 mmol)] and **1** (45 mg, 0.24 mmol) in a solution of CH_3CN/CH_2Cl_2 (20 mL + ∼1 mL) containing TFA (18 μL, 0.23 mmol, ∼11 mM) followed by the standard oxidative cyclization yielded a blue solid (33 mg, 24%): ^{1}H NMR δ 2.03 (s, 6H), 2.67 (s, 3H), 4.51 (s, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.97 (d, J = 8.1 Hz, 2H), 8.02 (d, J = 8.1 Hz, 2H), 8.54 (s, 1H), 8.60 (s, 1H), 8.69 (m, 4H), 8.97 (d, J = 4.2 Hz, 1H), 9.61 (s, 1H); LD-MS obsd 696.39; FAB-MS obsd 694.0607, calcd 694.0572 ($C_{35}H_{27}IN_4Zn$); λ_{abs} (toluene)/nm 416 (log ε = 5.13, fwhm = 18 nm), 607 (4.49); λ_{em} 609, 661 nm.

17,18-Dihydro-18,18-dimethyl-5-(4-methylphenyl)-8-(4-iodophenyl)porphyrin (24). Following the general demetalation procedure, a sample of **Zn-24** (10 mg, 14 μmol) gave a green solid (7.5 mg, 83%): ^{1}H NMR δ −2.20 (br, 1H), −1.96 (br, 1H), 2.07 (s, 6H), 2.68 (s, 3H), 4.63 (s, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H), 8.03 (m, 4H), 8.64 (s, 1H), 8.85 (m, 3H), 8.91 (s, 1H), 8.99 (s, 1H), 9.17 (d, J = 4.5 Hz, 1H), 9.83 (s, 1H); LD-MS obsd 631.58; FAB-MS obsd 632.1454, calcd 632.1437 ($C_{35}H_{29}IN_4$); λ_{abs} (toluene)/nm 410 (log ε = 5.11, fwhm = 32 nm), 504 (4.01), 638 (4.48); λ_{em} 639, 679, 702 nm.

Zn(II)-17,18-dihydro-18,18-dimethyl-2-(4-iodophenyl)-5-(4-methylphenyl)-12-[4-[2-(trimethylsilyl)ethynyl]phenyl]porphyrin (Zn-25). Following the general procedure for chlorin formation, the condensation of **13-OH** [prepared from **13** (103 mg, 0.20 mmol)] and **21** (86 mg, 0.22 mmol) in a solution of CH_3CN/CH_2Cl_2 (20 mL + ∼1 mL) containing TFA (16 μL, 0.21 mmol, ∼10 mM) followed by the standard oxidative cyclization yielded a blue solid (42 mg, 24%): ^{1}H NMR δ 0.36 (s, 9H), 1.96 (s, 6H), 2.67 (s, 3H), 4.48 (s, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.82 (d, J = 8.7 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.97 (d, J = 8.1 Hz, 2H), 8.02 (d, J = 8.1 Hz, 2H), 8.13 (d, J = 7.8 Hz, 2H), 8.51 (d, J = 4.2 Hz, 1H), 8.63 (s, 1H), 8.67 (s, 1H), 8.70 (s, 2H), 8.78 (d, J = 4.2 Hz, 1H), 9.58 (s, 1H); LD-MS 866.34; FAB-MS obsd 866.1257, calcd 866.1280 ($C_{46}H_{39}IN_4SiZn$); λ_{abs} (toluene)/nm 417 (log ε = 5.32, fwhm = 21 nm), 629 (4.90); λ_{em} 635, 691 nm.

17,18-Dihydro-18,18-dimethyl-2-(4-iodophenyl)-5-(4-methylphenyl)-12-[4-[2-(trimethylsilyl)ethynyl]phenyl]-porphyrin (25). Following the general demetalation procedure, a sample of **Zn-25** (11.0 mg, 13.7 μmol) gave a green solid (8.0 mg, 78%): ^{1}H NMR δ −1.95 (br, 1H), −1.70 (br, 1H), 0.36 (s, 9H), 2.0 (s, 6H), 2.68 (s, 3H), 4.60 (s, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.91 (d, J = 8.1 Hz, 4H), 8.03 (d, J = 8.1 Hz, 2H), 8.07 (d, J = 8.1 Hz, 2H), 8.26 (d, J = 8.1 Hz, 2H), 8.62 (d, J = 4.2 Hz, 1H), 8.81 (s, 1H), 8.88 (d, J = 4.2 Hz, 1H), 8.91 (s, 1H), 8.95 (s, 1H), 8.96 (s, 1H), 9.84 (s, 1H); LD-MS 804.02; FAB-MS obsd 804.2157, calcd 804.2145 ($C_{46}H_{41}IN_4Si$); λ_{abs} (toluene)/nm 422 (log ε = 5.09, fwhm = 34 nm), 509 (4.08), 655 (4.68); λ_{em} 660, 726 nm.

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Supporting Information Available: ^{1}H NMR spectra for **6**, **7**, **10**, **16**, and **21**; ^{13}C NMR spectra for **6**, **7**, and **21**; 2D-NMR data for **16**; complete spectral data (absorption, fluorescence, ^{1}H NMR, LD-MS) for all chlorins (**22**−**25**, **Zn-22**−**Zn-25**); X-ray data for **19**; and a brief discussion of chlorin nomenclature. This material is available free of charge via the Internet at http://pubs.acs.org.

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