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ScienceDirect
Tetrahedron 63 (2007) 3840–3849
Tetrahedron

Sparsely substituted chlorins as core constructs in chlorophyll analogue chemistry. Part 2: Derivatization

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Received 24 November 2006; revised 7 February 2007; accepted 9 February 2007
Available online 22 February 2007

Abstract—Stable chlorins bearing few or no substituents have been subjected to a variety of reactions including demetalation, magnesium insertion, oxochlorin formation, and bromination followed by Suzuki coupling. The kinetics of deuteration also have been determined for two oxochlorins and a series of chlorins bearing 0, 1, 2, or 3 meso-aryl substituents.

1. Introduction

The preceding paper describes the synthesis of chlorins bearing no meso substituents or a single meso substituent at the 5- or 10-position.[1] The chlorins are stable toward adventitious dehydrogenation owing to the presence of a geminal dimethyl moiety in the reduced, pyrroline ring. The availability of stable chlorins bearing few or no meso substituents opens the door to a series of fundamental studies of reactivity as well as spectroscopic characterization. Studies on these sparsely substituted chlorins may serve as benchmarks for comparison with the naturally occurring chlorophylls, which bear a full complement of β-substituents. The sparsely substituted chlorins also provide minimalist scaffolds for chemistry aimed at mimicking chlorophylls. The presence of the geminal dimethyl group in the pyrroline ring renders these new synthetic chlorins more synthetically malleable than the existing model synthetic chlorins including *meso*-tetraphenylchlorin,[2] octaethylchlorin,[3] and chlorin.[4,5]

In this paper, we describe the examination of sparsely substituted synthetic chlorins in studies of fundamental reactivity. These studies include measuring the kinetics of deuteration for chlorins that bear 0, 1, 2, or 3 meso substituents and no β-substituents, and assessing the regioselectivity of bromination in a series of chlorins that bear 0 or 1 meso substituents. Selected bromo-chlorins have been subjected to Suzuki coupling reactions. Other reactions carried out include demetalation of zinc chlorins to give free-base chlorins, metalation of a free-base chlorin to give the magnesium chlorin, and oxochlorin formation. Altogether 14 new chlorins have been prepared. The subsequent paper describes the spectroscopic properties of a number of chlorins prepared herein.[6]

2. Results and discussion

The shorthand nomenclature for the chlorins described herein employs the following abbreviations with superscripts to denote substituents and their positions: B (3,5-di-*tert*-butylphenyl), P (phenyl), M (mesityl), and T (*p*-tolyl). The chlorins examined include those bearing no meso substituents (**ZnC**);[1,7] one meso substituent ((**ZnC-B^5**),[1] (**ZnC-T^5**),[1] (**ZnC-M^{10}**),[7] and (**ZnC-P^{10}**)[1]); two meso substituents (**H$_2$C-T^{5}M^{10}** and **ZnC-T^{5}M^{10}**);[8,9] and three meso substituents (**H$_2$C-T^{5}M^{10}P^{15}** and **ZnC-T^{5}M^{10}P^{15}**).[10] One oxochlorin (**Oxo-H$_2$C-T^{5}M^{10}**) also was examined.[11]

2.1. Reactivity of chlorins

(1) *Stability.* All of the synthetic chlorins prepared herein were stable upon routine handling under aerobic conditions, including use of procedures such as chromatography, recrystallization, and standing in solution on the open benchtop. The ready synthesis, purification, and stability of the chlorins enabled the studies of reactivity described in the following sections.

(2) *Oxochlorin formation*. Oxochlorins have more positive oxidation potentials compared with chlorins.[11,12] To gain information regarding spectral properties, the chlorins **ZnC-B^5** and **ZnC** were converted to their corresponding oxochlorins using an established procedure.[11] Accordingly, **ZnC-B^5** or **ZnC** was heated in the presence of basic alumina followed by oxidation with DDQ, giving **Oxo-ZnC-B^5** or **Oxo-ZnC** in 47 or 56% yield, respectively (Scheme 1).

Keywords: Chlorin; Deuteration; Bromination; Metalation.
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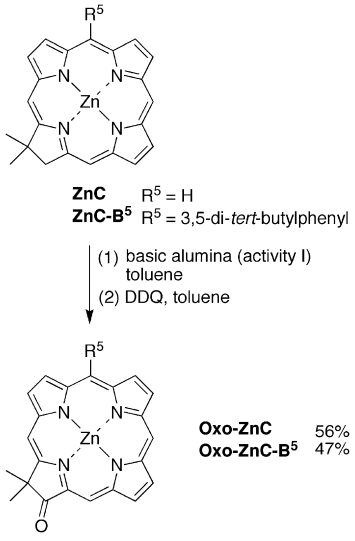
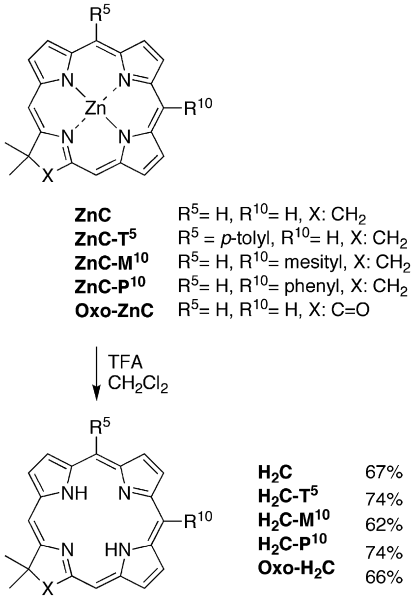
0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.02.076



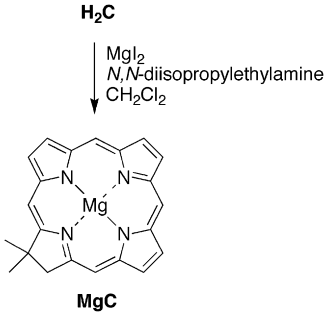
Scheme 1.

(3) *Demetalation*. Free-base chlorins are valuable compounds and also serve as precursors to diverse metallochlorins. In this regard, the availability of zinc chlorins from the chlorin synthesis is particularly attractive given the facile demetalation of the zinc chelates in the presence of weak acidic conditions. Thus, treatment of each member of a series of zinc chlorins and a zinc oxochlorin (**ZnC**, **ZnC-T^5**, **ZnC-M^{10}**, **ZnC-P^{10}**, and **Oxo-ZnC**) with TFA in CH_2Cl_2 afforded the corresponding free base species (**H$_2$C**, **H$_2$C-T^5**, **H$_2$C-M^{10}**, **H$_2$C-P^{10}**, and **Oxo-H$_2$C**) in good yield (Scheme 2). By contrast, the direct synthesis of other metallochlorins (e.g., Cu(II), Pd(II), and ClIn(III))[1] is attractive only if these are the ultimate metallochlorin targets, given that such tetrapyrrole coordination complexes require severe conditions for demetalation (e.g., concentrated sulfuric acid).[13]



Scheme 2.

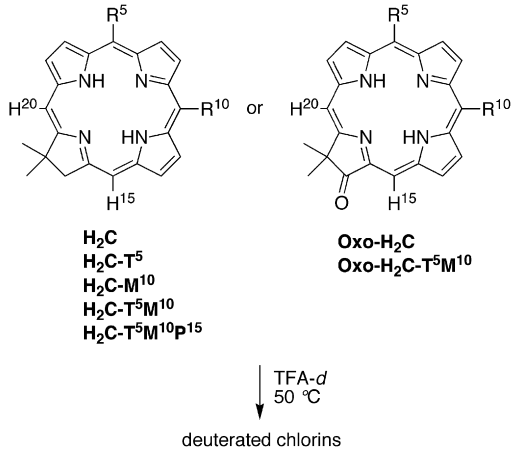
(4) *Metalation*. The treatment of **H$_2$C** to a mild method for magnesium insertion[14] (MgI_2 in CH_2Cl_2 containing *N*,*N*-diisopropylethylamine at room temperature) afforded the magnesium chelate **MgC**, a benchmark compound for comparison with chlorophylls (Scheme 3). **MgC** underwent partial demetalation upon chromatography on basic alumina, or on standing in CH_2Cl_2 solution, but was stable in toluene. Analysis of the isolated sample of **MgC** by ^{1}H NMR spectroscopy showed the presence of H_2O, THF, and **MgC** in ~12:1:2 ratio. Magnesium chlorins are often isolated as solids in conjunction with coordinative molecules.[14]



Scheme 3.

(5) *Deuteration*. Woodward first reported that chlorins possessing no meso substituents and a partial or full complement of β-substituents undergo deuteration preferentially at the meso sites (15- and 20-positions) flanking the pyrroline ring.[15] However, conclusions concerning relative reactivity were restricted to the four-meso sites owing to the presence of the blocking β-substituents. We recently examined the deuteration of chlorins bearing substituents only at the 5- and 10-positions and found that deuteration occurred preferentially at the 15- and 20-positions, but the presence of substituents at the 5- and 10-positions also limited the conclusions that could be drawn.[10] Here we carried out analogous studies using the free-base chlorin **H$_2$C** and free-base oxochlorin **Oxo-H$_2$C**, each of which has 10 sites potentially open to electrophilic aromatic substitution (six β-pyrrole and four meso sites).

Five chlorins (**H$_2$C**, **H$_2$C-T^5**, **H$_2$C-M^{10}**, **H$_2$C-T^{5}M^{10}**, and **H$_2$C-T^{5}M^{10}P^{15}**) and two oxochlorins (**Oxo-H$_2$C** and **Oxo-H$_2$C-T^{5}M^{10}**) were exposed to neat TFA-*d* at 50 °C, and the exchange progress was measured by ^{1}H NMR spectroscopy (Scheme 4). For example, dissolution of **H$_2$C** in neat TFA-*d*



Scheme 4.

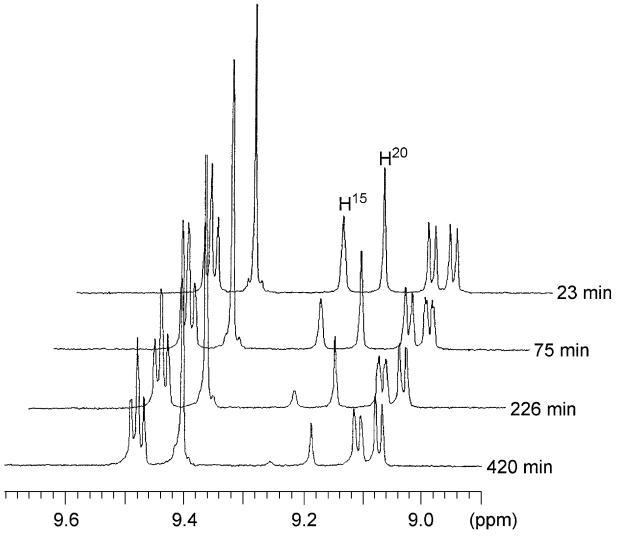


Figure 1. ^{1}H NMR spectra over time showing the deuteration of the 15- and 20-positions of chlorin **H_2C** in TFA-*d* at 50 °C.

at 50 °C resulted in a steady decrease over a few hours in the intensity of the resonances from H^{15} (9.26 ppm) and H^{20} (9.19 ppm) (Fig. 1). By contrast, the resonances from the 5, 10-, and all β-protons remained intact over the duration of the experiment (up to 24 h). No deuteration other than at the 15- or 20-positions was observed with the chlorin samples examined herein. Note that upon addition of TFA-*d* at room temperature, the pyrrolic NH protons of **H_2C** were immediately exchanged to form **D_2C** (observed by ^{1}H NMR spectroscopy), and the imino nitrogens also were deuterated (as observed by the absorption spectrum of the chlorin dication[6]).

The data obtained obeyed first-order rate expressions quite closely; thus, rate constants (k) and half-lives ($t_{1/2}$) were calculated. First-order rate plots of deuterium exchange of chlorins (**H_2C**, **H_2C-M^{10}**, and **H_2C-$T^5M^{10}P^{15}$**) and oxochlorins (**Oxo-H_2C** and **Oxo-H_2C-T^5M^{10}**) are illustrated in Figure 2. The deuterium exchange of each proton was monitored to at least 50% conversion (except for H^{15} of **Oxo-H_2C** or **Oxo-H_2C-T^5M^{10}**, which was deuterated up to 40% conversion). These data were used to determine the correlation coefficient R ($\geq$0.998 in each case).

Although the rate constants at the 15- and 20-positions for **H_2C-T^5** and **H_2C-T^5M^{10}** could not be calculated due to the overlapping resonances of H^{15} and H^{20}, the reactivity of **H_2C-T^5** and **H_2C-T^5M^{10}** could be compared with other chlorins by plotting the sum of the deuteration at both of 15- and 20-positions versus time (Fig. 3). The order of overall reactivity toward deuteration was **H_2C-$T^5M^{10}P^{15}$**>**H_2C-T^5M^{10}**>**H_2C**~**H_2C-T^5**~**H_2C-M^{10}**.

The pseudo-first-order rate constants for deuterium exchange at the 15- and 20-positions of chlorins and oxochlorins are summarized in Table 1. The rate constants for **H_2C-T^5** and **H_2C-T^5M^{10}** could not be calculated directly; accordingly, the range of minimum and maximum values for the rate constants was estimated from the time of 50 to 75% total conversion (both for the 15- and 20-positions) as described in the following procedure.

(i) When the overall exchange for the sum of the 15- and 20-positions reached 50%, at least 50% of the faster exchanging species (in this case H^{15}) should be already deuterated; thus, the maximum $t_{1/2}$ of H^{15} is obtained. The maximum value of $t_{1/2}$ gives the minimum value of the rate constant. For example, 50% of the sum of the 15- and 20-positions was deuterated at 138 min in **H_2C-T^5**, giving a maximum $t_{1/2}$ of 138 min for H^{15}; in turn, the rate constant for H^{15} should be $\geq 8.4\times10^{-5}$ s^{-1}.

(ii) When the exchange reached 75% for the sum of the 15- and 20-positions, at least 50% of the slower exchanging species (in this case H^{20}) should already be deuterated; thus, the maximum value for $t_{1/2}$ and the minimum value of the rate constant for H^{20} are obtained. For example, 75% of the sum of 15- and 20-positions was deuterated at 286 min in **H_2C-T^5**, giving a maximum $t_{1/2}$ of 286 min for H^{20}; in turn, the rate constant for H^{20} should be $\geq 4.0\times10^{-5}$ s^{-1}.

(iii) The maximum value of the rate constant for H^{15} can be calculated by considering the minimum contribution of deuteration of H^{20} at 75% of the overall exchange.

(iv) The maximum value of the rate constant for H^{20} can be calculated by considering the minimum contribution of H^{15} at 50% of the overall exchange.

Iteration of the process described above enabled the range of maximum and minimum rate constant values to be narrowed. For example, the rate constants of **H_2C-T^5** are close to those of **H_2C** and **H_2C-M^{10}** (as seen in Fig. 3); thus, k for the 15-position should be close to 12×10^{-5} s^{-1}, and k for the 20-position should be close to 5.6×10^{-5} s^{-1} (see Table 1).

The major findings from the kinetic study of deuteration are as follows.

(1) 15- Versus 20-positions: The 15-position was ~3-times more reactive than the 20-position toward deuterium exchange in chlorins, versus the equivalent reactivity of the 15- and 20-positions in the symmetric **H_2OEC** (2,3,7,8,12,13,17,18-octaethylchlorin).[16,17] This difference stems from the steric effect of the geminal dimethyl group at the 18-position. On the other hand, the 15-position was ~3-times less reactive than the 20-position toward deuterium exchange in oxochlorins (**Oxo-H_2OEC**, **Oxo-H_2C**, and **Oxo-H_2C-T^5M^{10}**). In the case of the oxochlorins, steric and electronic effects of the oxo group at the 17-position should be considered together with the steric effects of geminal dimethyl group at the 18-position. The lesser reactivity of the 15-position in oxochlorins shows that the electron-withdrawing effect of the carbonyl group outweighs the steric effects of the 18-geminal dimethyl group. In summary, the order of reactivity toward deuterium exchange in the benchmark chlorin **H_2C** is 15>20>>all other meso and β-positions, and the order for the benchmark oxochlorin **Oxo-H_2C** is 20>15>>all other meso and β-positions.

(2) Chlorin versus oxochlorin: The comparisons were made where rate constants could be obtained (**H_2C** versus **Oxo-H_2C**, **H_2C-T^5M^{10}** versus **Oxo-H_2C-T^5M^{10}**). Introduction of the oxo group at the 17-position of **H_2C** to give

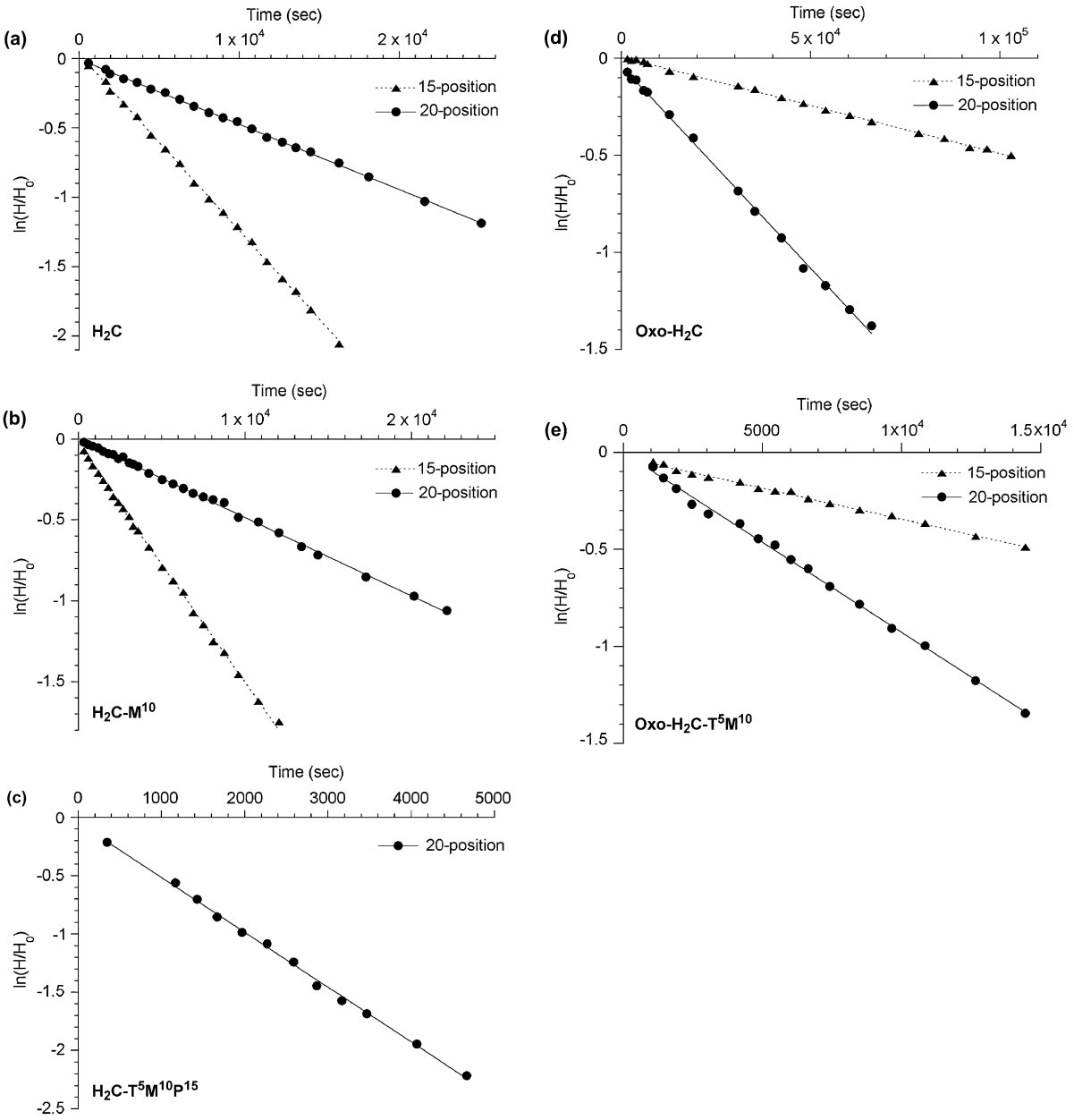


Figure 2. First-order rate plots for deuterium exchange. The rate constants and half-lives are listed in Table 1.

Oxo-H_2C rendered the 15-position ~20-times less reactive. Similar results were obtained from the comparison of **H_2C-T^5M^{10}** versus **Oxo-H_2C-T^5M^{10}**, where the 15-position was ~20-times less reactive in the latter versus the former.[10] The presence of the 17-oxo group suppresses reaction at the adjacent 15-position via steric factors and also electronically deactivates the chlorin macrocycle toward deuteration.

(3) Effects of meso-aryl substituents: The rate of exchange of the 15- and 20-positions depends largely on the number of meso-aryl substituents. The rate constants for **H_2C**, **H_2C-T^5**, and **H_2C-M^{10}** show almost identical values; thus, introduction of one aryl substituent has almost no effect regardless of steric bulk. The values of the rate constants increase ~5-fold (15-position) and ~2-fold (20-position) upon introduction of two aryl groups in chlorins (**H_2C-T^5M^{10}** versus **H_2C**). Similar effects are observed for oxochlorins, where the rate constants increase in value 6.4-fold (15-position) and 4.4-fold (20-position) upon introduction of two aryl groups (**Oxo-H_2C-T^5M^{10}** versus **Oxo-H_2C**). Introduction of three meso-aryl groups (**H_2C-$T^5M^{10}P^{15}$**) causes the value of the rate constant to increase 10-fold (20-position).

Understanding the origin of the increased rate of deuteration with increasing number of meso-aryl groups requires consideration of multiple factors. Relevant factors include the equilibrium between neutral chlorin and chlorin dication (obtained by dideuteration in the core of the macrocycle), ion pairing of deuterated chlorin species and the conjugate base of the acid, the conformational flexibility of the

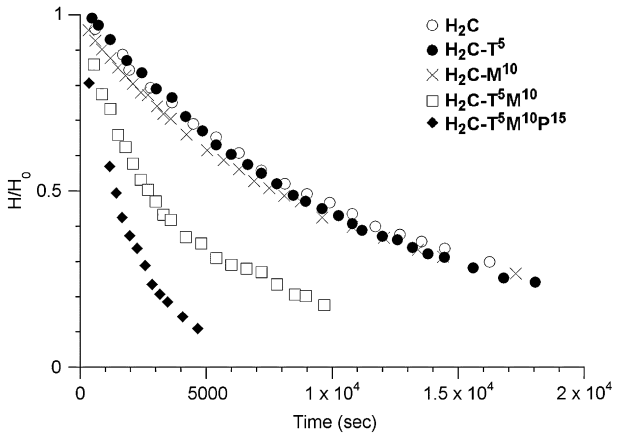
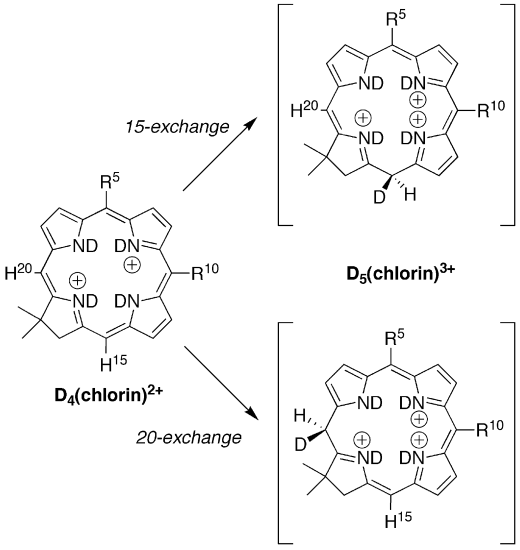


Figure 3. Comparison of the deuteration of chlorins (**H_2C**, **H_2C-T^5**, **H_2C-M^{10}**, **H_2C-T^5M^{10}**, and **H_2C-$T^5M^{10}P^{15}$**). The sum of the deuteration at both 15- and 20-positions is plotted as a function of time (sec).



Scheme 5.

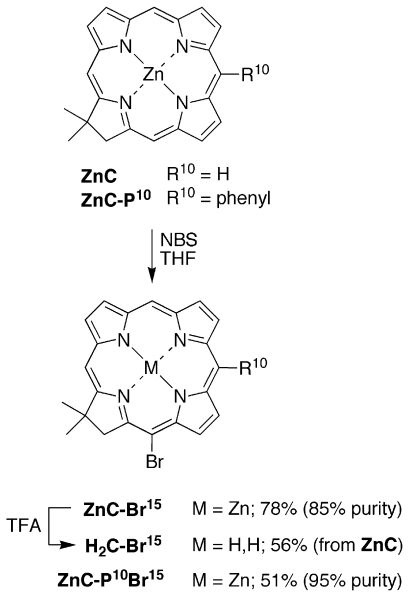
Table 1. Pseudo-first-order rate constants for deuterium exchange of chlorin meso-protons[a]

Compound	Rate constants k ($\times 10^{-5}$) in s^{-1} and ($t_{1/2}$ in min)	
	15-position	20-position
Chlorins		
H_2OEC[b]	5.7 (200)[c]	5.7 (200)[c]
H_2C	13 (91)	4.7 (250)
H_2C-T^5	10∼12[d]	5.6∼6.5[d]
H_2C-M^{10}	15 (74)	4.8 (240)
H_2C-T^5M^{10}	55∼53[d]	9.7∼10[d]
H_2C-$T^5M^{10}P^{15}$	n.a.	47 (23)
Oxochlorins		
Oxo-H_2OEC[e]	1.5 (780)[f]	4.8 (240)[f]
Oxo-H_2C	0.50 (2300)	2.1 (520)
Oxo-H_2C-T^5M^{10}[g]	3.2 (350)	9.3 (120)

[a] In TFA-*d* at 50 °C.
[b] The stereochemistry of **H_2OEC** (2,3,7,8,12,13,17,18-octaethylchlorin) is not clear.
[c] Ref. 16.
[d] Due to the overlap of the resonances from H^{15} and H^{20} in TFA-*d*, the rate constants could not be calculated directly (see text).
[e] 2,3,7,8,12,13,17,17-Octaethyl-18-oxochlorin.
[f] Ref. 17.
[g] See Ref. 10 for previous data.

macrocycle, the energy of the initial reactant, and the energy of the transition state. While the charge state of the species undergoing deuteration is not known, in neat TFA-*d* the chlorin dication is expected to be present in nearly quantitative amount, and hence is the likely precursor. The relevant electronic feature of the initial chlorin reactant is given by the chlorin HOMO, which shows larger lobes at the α-positions (which cannot be deuterated) and the β-pyrrolic positions versus the meso positions.[18–20] On the other hand, an intermediate near the transition state during the course of deuteration of a chlorin would be polyenic in character as illustrated in Scheme 5. A tentative interpretation for the increased rate of reaction owing to the meso-aryl groups is that the transition state is stabilized (by inductive and/or resonance effects) more so than the chlorin HOMO is destabilized. High-level calculations are required to gain insight into the origin of the regiospecificity of deuteration and the role of meso-aryl groups in accelerating the rate of deuteration.

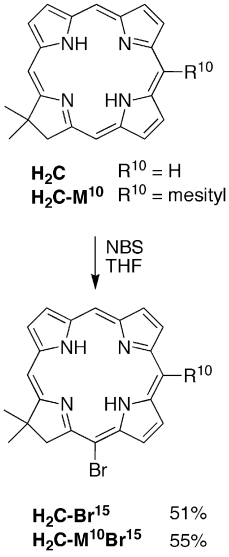
(6) *Halogenation*. Prior studies have shown that chlorins undergo electrophilic halogenation at the meso sites flanking the pyrroline ring.[10] Electrophilic bromination of **ZnC** was carried out using NBS in THF at room temperature (Scheme 6). The 15-bromochlorin **ZnC-Br^{15}** was obtained accompanied by a small amount of dibromochlorins, as indicated by LDMS analysis of the crude mixture. Substitution at the 15-position was confirmed upon ^{1}H NMR spectroscopy by (1) the disappearance of the resonance upon bromo substitution, and (2) the downfield shift of the resonance of the hydrogen positioned adjacent to the bromo atom (H^{13}, ca. 0.3 ppm).[6] Trace amounts of dibrominated products in the purified fraction were observed by LDMS and ^{1}H NMR spectroscopy.



Scheme 6.

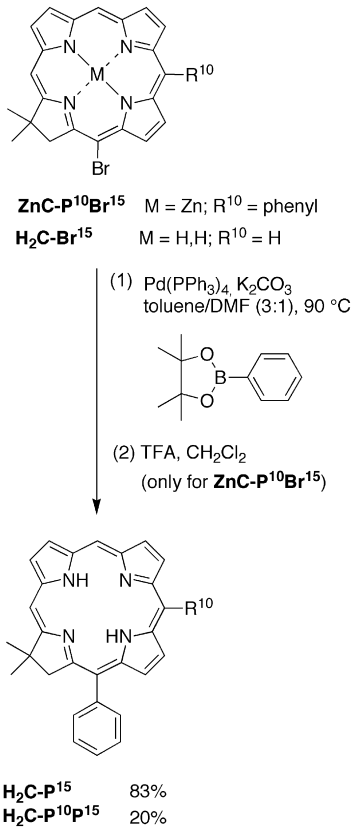
The purification of **ZnC-Br^{15}** proved to be difficult; therefore, we treated the crude reaction mixture to conditions for demetalation (TFA/CH_2Cl_2). Chromatographic separation of the free-base chlorin species proved easier than the corresponding zinc complexes. In this manner, **H_2C-Br^{15}** was obtained in 56% yield, together with **H_2C** (~5%) and one isolated (unidentified) dibromochlorin (~1%). Similar bromination of **ZnC-P^{10}** provided **ZnC-P^{10}Br^{15}** together with an unidentified (non-bromo) chlorin. Complete purification again was not achieved, and LDMS analysis of the isolated sample of **ZnC-P^{10}Br^{15}** (95% purity, 51% yield) revealed the presence of traces of dibromochlorins. The chromatographic retention of otherwise hydrophobic zinc chlorins is dominated by the polar apical site of the zinc chelated macrocycle. Accordingly, we turned to the bromination of free-base chlorins.

Bromination of **H_2C** under the same conditions employed for **ZnC** provided **H_2C-Br^{15}** in 51% yield (with recovery of 27% of starting material) without detectable formation of any dibrominated chlorin (Scheme 7). Bromination of **H_2C-M^{10}** provided the corresponding 15-bromochlorin **H_2C-M^{10}Br^{15}** in 55% yield, together with an unidentified dibromochlorin (~5%).



Scheme 7.

(7) *Suzuki coupling*. The availability of regioselective bromination has been exploited in the synthesis of a variety of substituted chlorins.[10] Here, 15-bromination opens the door for further derivatization of sparsely substituted chlorins. Thus, Suzuki coupling of **ZnC-P^{10}Br^{15}** afforded the corresponding 10,15-diphenylchlorin **ZnC-P^{10}P^{15}**; however, ^{1}H NMR spectroscopy of the fraction containing the product revealed the presence of a significant amount of aromatic impurities. Demetalation of the partially purified **ZnC-P^{10}P^{15}** followed by column chromatography afforded the pure **H_2C-P^{10}P^{15}** in 20% yield. On the other hand, Suzuki coupling of **H_2C-Br^{15}** with 2-phenyl-1,3-dioxoborolane in the presence of $Pd(PPh_3)_4$ afforded **H_2C-P^{15}** in 83% yield (Scheme 8). In both cases the respective starting bromochlorin was quantitatively consumed, but the free-base chlorin product was more easily purified.



Scheme 8.

3. Conclusions

Reactivity studies on the unsubstituted chlorin **H_2C** showed that the positions flanking the pyrroline ring (15- and 20-positions) are most reactive (among four meso sites and six β-pyrrolic sites) toward deuteration in acidic media, with the 15-position reacting ~3-times faster than the 20-position. A single aryl group at the 5- or 10-position has little effect on the rate of deuteration, whereas the presence of two aryl groups (5- and 10-positions) increases the rate by ~5.5-fold. The 15-position of the free base or zinc chlorins also was the most reactive site in the macrocycle toward electrophilic bromination. The sequence of bromination and palladium-mediated coupling provided access to chlorins with substituents at the 15- or 10,15-position. Compared with prior minimalist or benchmark chlorins, the unsubstituted chlorin **H_2C** prepared herein and its metal chelates are more accessible, more stable, and therefore more amenable for diverse fundamental studies. The chlorins prepared herein also have been examined spectroscopically as described in the next paper in this series.[6]

4. Experimental section

4.1. General methods

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were collected at room temperature in $CDCl_3$ unless noted otherwise. Chlorins and oxochlorins were analyzed by laser desorption mass spectrometry without a matrix (LDMS).[9,21]

Fast atom bombardment mass spectrometry (FABMS) or electrospray ionization mass spectrometry (ESIMS) data is reported for the molecule ion or protonated molecule ion. Chromatography was performed with flash silica (80–200 mesh). NBS was recrystallized (H_2O). Absorption and fluorescence spectra were obtained in toluene at room temperature.

4.2. Solvents

THF was distilled over sodium metal and benzophenone as required. Toluene for coupling reactions was distilled from Na. DMF and CH_2Cl_2 were used as anhydrous grade. Toluene used in absorption and fluorescence studies was spectroscopic grade. All other solvents were used as received.

4.3. Deuterium exchange studies

The resonances of the meso- and β-protons of the chlorins exhibit significant shifts in $CDCl_3$ versus TFA-*d*. Prior to the deuteration study, the resonances from the four meso-protons and the six β-protons of **H_2C** were assigned by NOESY and HH COSY spectra (in $CDCl_3$ or in TFA-*d* at 25 °C). Note that no significant exchange occurred in TFA-*d* under these conditions during the course of these preliminary spectral measurements. Deuteration of chlorins and oxochlorins was examined using neat TFA-*d* in sealed NMR tubes at 50 °C (relaxation time=3 s).

An exemplary procedure is as follows: a sample of **H_2C** (3.4 mg, 10 μmol, 17 mM) was dissolved in TFA-*d* (600 μL, 780 equiv). The ^{1}H NMR spectrum was recorded at 50 °C over time, and the resonances of the aromatic region were integrated. The deuterium exchange processes were followed relative to the non-exchanging protons (H^7 and H^8 at 9.42 ppm). Pseudo-first-order rate constants were obtained by non-weighted least-squares fitting of the log of the intensity of the resonance versus the elapsed time.

4.4. Oxochlorin formation

4.4.1. Zn(II)-17,18-dihydro-18,18-dimethyl-17-oxoporphyrin (Oxo-ZnC). Following a general procedure,[11] a mixture of **ZnC** (39 mg, 0.097 mmol) and basic alumina (activity I, 3.58 g) in toluene (4.5 mL) was stirred for 7 h at 50 °C exposed to air. After standard workup, the residue was dissolved in toluene (44 mL). DDQ (44 mg, 0.19 mmol) was added. Standard workup and chromatography (silica, $CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH (19:1)) gave a bluish-green solid (25 mg, 56%): ^{1}H NMR δ 2.04 (s, 6H), 8.65–8.68 (m, 2H), 8.83–8.86 (m, 2H), 8.98–8.99 (m, 2H), 9.05–9.07 (m, 1H), 9.30 (s, 1H), 9.36 (s, 1H), 9.44 (s, 1H); ^{13}C NMR δ 23.3, 49.4, 94.5, 96.0, 106.9, 109.4, 129.0, 129.6, 129.9, 130.7, 132.2, 132.9, 142.7, 147.1, 147.4, 148.7, 149.1, 150.8, 153.5, 163.9, 208.7; LDMS obsd 415.5; FABMS obsd 416.0605, calcd 416.0616 ($C_{22}H_{16}N_4OZn$); λ_{abs} 412 (log ε= 5.19), 602 (4.65) nm; λ_{em} 605 nm.

4.4.2. Zn(II)-5-(3,5-di-*tert*-butylphenyl)-17,18-dihydro-18,18-dimethyl-17-oxoporphyrin (Oxo-ZnC-B^5). Following a general procedure,[11] a mixture of **ZnC-B^5** (32.0 mg, 0.0540 mmol) and basic alumina (activity I, 2.0 g) in 2.5 mL of toluene was stirred for 16 h at 60 °C exposed to air. After standard workup, the residue was dissolved in toluene (25 mL). DDQ (24.5 mg, 0.108 mmol) was added. Standard workup and chromatography (silica, CH_2Cl_2/ethyl acetate (5:1)) gave a bluish-purple solid (15.3 mg, 47%): ^{1}H NMR δ 1.54 (s, 18H), 2.03 (s, 6H), 7.79–7.81 (m, 1H), 7.99–8.01 (m, 2H), 8.75–8.78 (m, 1H), 8.93–8.95 (m, 2H), 8.97–8.99 (m, 1H), 9.01 (s, 1H), 9.03–9.05 (m, 1H), 9.05–9.07 (m, 1H), 9.47 (s, 1H), 9.77 (s, 1H); LDMS obsd 603.86; FABMS obsd 604.2200, calcd 604.2181 ($C_{36}H_{36}N_4OZn$); λ_{abs} 419 (log ε=5.39), 606 (4.77) nm; λ_{em} 608 nm.

4.5. Demetalation

4.5.1. 17,18-Dihydro-18,18-dimethylporphyrin (H_2C). Following a general procedure,[8,10] a solution of **ZnC** (15.0 mg, 0.0371 mmol) in anhydrous CH_2Cl_2 (13 mL) was treated with TFA (284 μL, 3.68 mmol). The mixture was stirred for 30 min at room temperature. The reaction mixture was quenched by addition of 10% aqueous $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2. The organic extract was washed with water, dried (Na_2SO_4), and filtered. The filtrate was concentrated. Purification on a short column (silica, CH_2Cl_2) afforded a green solid (8.5 mg, 67%): ^{1}H NMR δ −2.60 to −2.44 (br, 2H), 2.07 (s, 6H), 4.66 (s, 2H), 8.94 (d, *J*=4.4 Hz, 1H), 8.98 (s, 1H), 8.99 (d, *J*=4.4 Hz, 1H), 9.06–9.10 (m, 2H), 9.08 (s, 1H), 9.24 (d, *J*=4.4 Hz, 1H), 9.26 (d, *J*=4.4 Hz, 1H), 9.86 (s, 1H), 9.89 (s, 1H); ^{13}C NMR δ 31.5, 46.8, 52.2, 94.7, 96.7, 106.5, 106.9, 123.66, 123.72, 128.12, 128.20, 132.6, 132.8, 134.7, 135.0, 139.7, 140.5, 151.6, 151.9, 163.3, 174.9; LDMS obsd 339.7; FABMS obsd 340.1692, calcd 340.1688 ($C_{22}H_{20}N_4$); λ_{abs} 389 (log ε=5.20), 634 (4.82) nm; λ_{em} 636 nm.

4.5.2. 17,18-Dihydro-18,18-dimethyl-5-(4-methylphenyl)porphyrin (H_2C-T^5). Following a general procedure,[8,10] a solution of **ZnC-T^5** (98.7 mg, 0.200 mmol) in CH_2Cl_2 (100 mL) was treated with TFA (770 μL, 10.0 mmol). The mixture was stirred for 1 h at room temperature. The reaction mixture was washed with saturated aqueous $NaHCO_3$ (100 mL), dried (Na_2SO_4), filtered, and concentrated to dryness under reduced pressure. Chromatography (silica, hexanes/CH_2Cl_2 (2:1)) afforded a greenish purple solid (63.6 mg, 74%): ^{1}H NMR δ −2.34 to −2.24 (br, 1H), −2.00 to −1.90 (br, 1H), 2.05 (s, 6H), 2.68 (s, 3H), 4.61 (s, 2H), 7.53 (d, *J*=7.8 Hz, 2H), 8.04 (d, *J*=7.8 Hz, 2H), 8.67 (d, *J*=4.4 Hz, 1H), 8.84 (d, *J*=4.4 Hz, 1H), 8.87 (d, *J*=4.4 Hz, 1H), 8.89 (d, *J*=4.4 Hz, 1H), 8.91 (s, 1H), 8.95 (d, *J*=4.4 Hz, 1H), 8.98 (s, 1H), 9.21 (d, *J*=4.4 Hz, 1H), 9.82 (s, 1H); ^{13}C NMR δ 21.8, 31.5, 46.8, 52.0, 95.1, 96.4, 107.1, 122.3, 123.4, 123.6, 127.8, 128.55, 128.57, 132.4, 132.6, 134.3, 134.6, 135.4, 137.5, 139.1, 140.43, 140.46, 151.3, 152.8, 163.9, 174.5; LDMS obsd 429.9; FABMS obsd 430.2174, calcd 430.2157 ($C_{29}H_{26}N_4$); λ_{abs} 403, 637 nm; λ_{em} 639 nm.

4.5.3. 17,18-Dihydro-18,18-dimethyl-10-phenylporphyrin (H_2C-P^{10}). A solution of **ZnC-P^{10}** (10 mg, 0.021 mmol) in CH_2Cl_2 (7 mL) was treated with TFA (0.159 mL, 2.06 mmol) and stirred at room temperature for 1 h. The reaction mixture was neutralized with excess triethylamine (1 mL), and then concentrated. Chromatography (silica, hexanes/CH_2Cl_2 (1:2)) afforded a green solid (6.5 mg, 74%): ^{1}H NMR δ −2.35 to −2.28 (br, 1H),

−1.99 to −1.88 (br, 1H), 2.08 (s, 6H), 4.66 (s, 2H), 7.73–7.76 (m, 3H), 8.16–8.18 (m, 2H), 8.66 (d, *J*=4.4 Hz, 1H), 8.82–8.85 (m, 2H), 8.93 (s, 1H), 8.97 (d, *J*=4.4 Hz, 1H), 8.97 (d, *J*=4.4 Hz, 1H), 8.99 (d, *J*=4.4 Hz, 1H), 9.05 (s, 1H), 9.25 (d, *J*=4.4 Hz, 1H), 9.88 (s, 1H); ^{13}C NMR δ 31.4, 46.7, 52.2, 94.4, 97.1, 107.4, 121.7, 123.4, 123.7, 127.0, 127.8, 128.51, 128.52, 132.3, 132.5, 134.33, 134.37, 135.5, 139.7, 141.1, 141.9, 151.1, 152.8, 163.0, 175.5; LDMS obsd 416.0; FABMS obsd 416.2018, calcd 416.2001 ($C_{28}H_{24}N_4$); λ_{abs} 403, 637 nm.

4.5.4. 17,18-Dihydro-10-mesityl-18,18-dimethylporphyrin (H_2C-M[10]). As described for **H_2C**, a solution of **ZnC-M[10]** (39.0 mg, 0.0747 mmol) in anhydrous CH_2Cl_2 (26 mL) was demetalated by treatment with TFA (288 μL, 3.74 mmol). Standard workup including chromatography (silica, hexanes/CH_2Cl_2 9:1→3:1→1:1) afforded a green solid (21.0 mg, 62%): ^{1}H NMR δ −2.28 to −2.18 (br, 1H), −1.96 to −1.82 (br, 1H), 1.85 (s, 6H), 2.06 (s, 6H), 2.61 (s, 3H), 4.63 (s, 2H), 7.25 (s, 2H, overlapped to $CHCl_3$), 8.47 (d, *J*=4.4 Hz, 1H), 8.63 (d, *J*=4.4 Hz, 1H), 8.77 (d, *J*=4.4 Hz, 1H), 8.89 (s, 1H), 8.91 (d, *J*=4.4 Hz, 1H), 8.93 (d, *J*=4.4 Hz, 1H), 8.99 (s, 1H), 9.21 (d, *J*=4.4 Hz, 1H), 9.81 (s, 1H); ^{13}C NMR δ 21.61, 21.71, 31.5, 46.7, 52.2, 94.4, 96.8, 107.2, 120.1, 123.4, 123.4, 123.9, 127.4, 128.0, 128.3, 131.3, 133.0, 134.4, 134.9, 137.7, 138.1, 139.4, 139.8, 141.1, 151.3, 152.8, 163.0, 175.3; LDMS obsd 459.1; FABMS obsd 458.2449, calcd 458.2470 ($C_{31}H_{30}N_4$); λ_{abs} 395, 638 nm.

4.5.5. 17,18-Dihydro-18,18-dimethyl-17-oxoporphyrin (Oxo-H_2C). Following a general procedure,[8,10] a solution of **Oxo-ZnC** (34.0 mg, 0.0814 mmol) in CH_2Cl_2 (28 mL) was treated with TFA (316 μL, 4.10 mmol). Standard workup including chromatography (silica, hexanes/CH_2Cl_2 (1:1)→CH_2Cl_2) afforded a blue solid (19 mg, 66%): ^{1}H NMR δ −3.12 to −3.02 (br, 1H), −2.98 to −2.88 (br, 1H), 2.12 (s, 6H), 9.18 (d, *J*=4.4 Hz, 1H), 9.23 (d, *J*=4.4 Hz, 1H), 9.26 (d, *J*=4.4 Hz, 1H), 9.31 (d, *J*=4.4 Hz, 1H), 9.34 (d, *J*=4.4 Hz, 1H), 9.37–9.42 (m, 2H), 9.98 (s, 1H), 10.03 (s, 1H), 10.11 (s, 1H); ^{13}C NMR δ 24.1, 50.4, 95.7, 96.3, 105.8, 107.8, 126.3, 126.7, 127.9, 129.0, 134.0, 134.9, 135.8, 137.0, 137.6, 140.0, 146.7, 153.1, 154.4, 168.1, 210.6; LDMS obsd 353.9; FABMS obsd 354.1494, calcd 354.1481 ($C_{22}H_{18}N_4O$); λ_{abs} 401, 634 nm.

4.6. Magnesium insertion

4.6.1. Mg(II)-17,18-dihydro-18,18-dimethylporphyrin (MgC). Following a general procedure,[14] a sample of **H_2C** (22.0 mg, 0.0646 mmol) in anhydrous CH_2Cl_2 (6.0 mL) was treated with diisopropylethylamine (0.440 mL, 2.53 mmol) and anhydrous MgI_2 (0.358 g, 1.29 mmol). The mixture was stirred at room temperature. After 1 h, the mixture was washed (water and brine), dried (K_2CO_3), and concentrated. The ^{1}H NMR spectrum (in C_6D_6) showed the presence of water and THF (12:1:2 of water/THF/**MgC**), which could not be removed under high vacuum. The title compound was obtained as a greenish-blue solid (18 mg). The following NMR data omit the signals from water and THF: ^{1}H NMR (THF-d_8) δ 2.05 (s, 6H), 4.59 (s, 2H), 8.57 (s, 1H), 8.61 (s, 1H), 8.63 (d, *J*=4.0 Hz, 1H), 8.67 (d, *J*=4.0 Hz, 1H), 8.85–8.87 (m, 2H), 8.97–8.99 (m, 2H), 8.56 (d, *J*=4.0 Hz, 2H); FABMS obsd 362.1393, calcd 362.1382 ($C_{22}H_{18}N_4Mg$); λ_{abs} 402 (log ε=5.35), 607 (4.65) nm; λ_{em} 611 nm. Note that the reported molar absorption coefficient has been corrected for the solvent of inclusion as observed by ^{1}H NMR spectroscopy.[6]

4.7. Bromination

4.7.1. Zn(II)-15-bromo-17,18-dihydro-18,18-dimethylporphyrin (ZnC-Br[15]). Following a general procedure,[10] a solution of **ZnC** (9.00 mg, 0.0223 mmol) in dry THF (11 mL) under argon was treated with NBS (3.97 mg, 0.0223 mmol). The mixture was stirred at room temperature for 30 min. CH_2Cl_2 (20 mL) was added. The mixture was washed with aqueous $NaHCO_3$. The organic extract was dried (Na_2SO_4) and filtered. The filtrate was concentrated. Purification on a short column (silica, hexanes/CH_2Cl_2 (1:1)) afforded a green solid (8.4 mg) that was ~85% pure: ^{1}H NMR (THF-d_8) δ 2.05 (s, 6H), 4.64 (s, 2H), 8.62 (s, 1H), 8.74 (d, *J*=4.4 Hz, 1H), 8.89 (d, *J*=4.4 Hz, 1H), 8.93 (d, *J*=4.4 Hz, 1H), 9.02–9.06 (m, 2H), 9.10 (d, *J*=4.4 Hz, 1H), 9.57 (s, 1H), 9.63 (s, 1H); LDMS obsd 479.9; ESIMS obsd 479.9913, calcd 479.9928 ($C_{22}H_{17}BrN_4Zn$); λ_{abs} 406, 607 nm.

4.7.2. 15-Bromo-17,18-dihydro-18,18-dimethylporphyrin (H_2C-Br[15]) by a bromination–demetalation procedure. Following a general procedure,[10] a solution of **ZnC** (81 mg, 0.20 mmol) in dry THF (100 mL) under argon was treated at room temperature with NBS (35 mg, 0.20 mmol). The resulting mixture was stirred for 45 min. Saturated aqueous $NaHCO_3$ solution was added (~50 mL). The resulting mixture was extracted with CH_2Cl_2. The organic extract was washed with brine, dried (Na_2SO_4), and concentrated. The resulting green-violet solid was dissolved in CH_2Cl_2 (70 mL) and treated with TFA (1.53 mL, 19.8 mmol). The resulting green solution was stirred at room temperature for 1.5 h, neutralized with excess triethylamine (2 mL), and concentrated. TLC analysis (silica, hexanes/CH_2Cl_2 (1:1)) revealed the presence of one large green spot and several minor spots. Column chromatography (silica, hexanes/CH_2Cl_2 (1:1)) provided an unidentified dibromochlorin (first fraction, violet, 1.3 mg), **H_2C-Br[15]** (second fraction, green, 47 mg, 56%), a discarded third fraction, and starting material (fourth fraction, green, 4.2 mg). Data for **H_2C-Br[15]**: ^{1}H NMR δ −2.61 (s, 1H), −2.43 (s, 1H), 2.02 (s, 6H), 4.64 (s, 2H), 8.86 (s, 1H), 8.92 (d, *J*=4.4 Hz, 1H), 8.94 (d, *J*=4.4 Hz, 1H), 8.98 (d, *J*=4.4 Hz, 1H), 9.12 (d, *J*=4.4 Hz, 1H), 9.14 (d, *J*=4.4 Hz, 1H), 9.22 (d, *J*=4.4 Hz, 1H), 9.70 (s, 1H), 9.75 (s, 1H); ^{13}C NMR δ 31.8, 46.6, 55.00, 95.2, 96.0, 106.2, 108.6, 124.2, 125.1, 128.2, 128.5, 132.5, 133.6, 134.3, 136.2, 138.3, 140.6, 151.2, 153.3, 162.4, 176.1; LDMS obsd 417.9; FABMS obsd 418.0797, calcd 418.0793 ($C_{22}H_{19}BrN_4$); λ_{abs} 396, 639 nm.

4.7.3. 15-Bromo-17,18-dihydro-18,18-dimethylporphyrin (H_2C-Br[15]) by bromination of H_2C. Following a general procedure,[10] a solution of **H_2C** (26 mg, 0.076 mmol) in dry THF (38 mL) was treated under argon at room temperature with NBS (13 mg, 0.076 mmol). The resulting mixture was stirred for 30 min. Saturated aqueous $NaHCO_3$ solution was added. The resulting mixture was extracted with CH_2Cl_2. The organic extract was washed with brine, dried (Na_2SO_4), and concentrated. Column

chromatography (silica, hexanes/CH_2Cl_2 (1:1)) afforded traces of an unidentified chlorin (first fraction, green, $<<1$ mg), **H_2C-Br^{15}** (second fraction, green, 16 mg, 51%), and unreacted starting material (third fraction, green, 7 mg). The characterization data (^{1}H NMR, LDMS, FABMS, and UV–vis) were consistent with those described previously.

4.7.4. Zn(II)-15-bromo-17,18-dihydro-18,18-dimethyl-10-phenylporphyrin (ZnC-P^{10}Br^{15}). Following a general procedure,[10] a solution of **ZnC-P^{10}** (48 mg, 0.10 mmol) in dry THF (50 mL) was treated under argon at room temperature with NBS (18 mg, 0.10 mmol). The resulting mixture was stirred for 30 min. Saturated aqueous $NaHCO_3$ solution was added. The resulting mixture was extracted with CH_2Cl_2. The organic extract was washed with brine, dried (Na_2SO_4), and concentrated. Column chromatography (silica, hexanes/CH_2Cl_2 (1:2)) afforded **ZnC-P^{10}Br^{15}** (first fraction, green, 28 mg, 51%). Further elution (CH_2Cl_2) afforded an unidentified chlorin (green, 4.2 mg). Data for **ZnC-P^{10}-Br^{15}**: ^{1}H NMR (THF-d_8) δ 2.53 (s, 6H), 4.63 (s, 2H), 7.66–7.72 (m, 3H), 8.04–8.07 (m, 2H), 8.39 (d, J=4.4 Hz, 1H), 8.52 (d, J=4.4 Hz, 1H), 8.59 (s, 1H), 8.73 (d, J=4.4 Hz, 1H), 8.77 (d, J=4.4 Hz, 1H), 9.01–903 (m, 2H), 9.52 (s, 1H); ^{13}C NMR δ 31.9, 45.8, 55.2, 95.0, 97.1, 109.4, 126.4, 127.4, 127.7, 128.3, 128.8, 129.1, 130.5, 133.4, 134.1, 134.7, 144.2, 146.8, 147.8, 148.5, 148.9, 152.8, 155.8, 158.1, 173.1; LDMS obsd 555.9; FABMS obsd 556.0225, calcd 556.0241 ($C_{28}H_{21}BrN_4Zn$); λ_{abs} 411, 610 nm.

4.7.5. 15-Bromo-17,18-dihydro-18,18-dimethyl-10-mesitylporphyrin (H$_2$C-M^{10}Br^{15}). Following a general procedure,[10] a solution of **H$_2$C-M^{10}** (23 mg, 0.050 mmol) in dry THF (25 mL) was treated under argon at room temperature with NBS (9 mg, 0.05 mmol). The resulting mixture was stirred for 30 min. Saturated aqueous $NaHCO_3$ solution was added. The resulting mixture was extracted with CH_2Cl_2. The organic extract was washed with brine, dried (Na_2SO_4), and concentrated. Column chromatography (silica, hexanes/CH_2Cl_2 (1:1)) afforded a dibrominated chlorin (first fraction, green, 1.5 mg) and **H$_2$C-M^{10}Br^{15}** (second fraction, green, 16 mg, 55%). Data for **H$_2$C-M^{10}Br^{15}**: ^{1}H NMR δ −2.01 (s, 1H), −1.93 (s, 1H), 1.83 (s, 6H), 1.98 (s, 6H), 2.60 (s, 3H). 4.66 (s, 2H), 7.24 (s, 2H), 8.43 (d, J=4.4 Hz, 1H), 8.59 (d, J=4.4 Hz, 1H), 8.80–8.82 (m, 2H), 8.89 (d, J=4.4 Hz, 1H), 9.14 (d, J=4.4 Hz, 2H), 9.68 (s, 1H); ^{13}C NMR δ 21.5, 21.7, 31.7, 46.5, 55.2, 95.0, 96.4, 106.6, 122.4, 124.4, 124.8, 127.5, 127.9, 128.8, 132.4, 132.8, 134.6, 136.0, 137.9, 138.2, 138.3, 139.2, 141.2, 152.3, 153.0, 162.3, 176.7; LDMS obsd 536.1; FABMS obsd 536.1587, calcd 536.1576 ($C_{31}H_{29}BrN_4$); λ_{abs} 403, 643 nm.

4.8. Suzuki reactions

4.8.1. 17,18-Dihydro-18,18-dimethyl-10,15-diphenylporphyrin (H$_2$C-P^{15}). Following a general procedure,[10] samples of **H$_2$C-Br^{15}** (42 mg, 0.10 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxoborolane (207 mg, 1.00 mmol), $Pd(PPh_3)_4$ (35 mg, 0.030 mmol), and K_2CO_3 (111 mg, 0.800 mmol) were weighed in a Schlenk flask. The flask was pump-purged with argon three times. A degassed mixture of toluene/DMF (3:1, 10 mL) was added. The resulting mixture was stirred at 90–95 °C for 20 h. The reaction mixture was diluted with CH_2Cl_2 and filtered. The filtrate was concentrated. Column chromatography (silica, hexanes/CH_2Cl_2 (1:3)) afforded a trace amount of putative **PdC-P^{15}** (first fraction, violet, <1 mg) and the title compound (second fraction, green, 35 mg, 83%). Data for **H$_2$C-P^{15}**: ^{1}H NMR δ −2.48 to −2.38 (br, 1H), −2.36 to −2.24 (br, 1H), 1.99 (s, 6H), 4.25 (s, 2H), 7.67–7.76 (m, 2H), 7.90–7.95 (m, 2H), 8.42 (d, J=4.4 Hz, 1H), 8.99 (s, 1H), 9.00 (d, J=4.4 Hz, 1H), 9.06–9.09 (m, 2H), 9.13 (d, J=4.4 Hz, 1H), 9.24 (d, J=4.4 Hz, 1H), 9.84 (s, 1H), 9.89 (s, 1H); ^{13}C NMR δ 31.6, 46.4, 52.3, 94.9, 106.2, 107.4, 112.2, 123.6, 124.2, 127.70, 127.83, 128.2 (two peaks are overlapped), 132.5, 132.7, 133.0, 134.5, 135.4, 140.2, 140.4, 143.0, 151.4, 152.3, 162.6, 174.7; LDMS obsd 415.9; FABMS obsd 416.1985, calcd 416.2001 ($C_{28}H_{24}N_4$); λ_{abs} 395, 638 nm.

4.8.2. 17,18-Dihydro-18,18-dimethyl-10,15-diphenylporphyrin (H$_2$C-P^{10}P^{15}). Following a general procedure,[10] samples of **ZnC-P^{10}Br^{15}** (24 mg, 0.043 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxoborolane (87 mg, 0.43 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol), and K_2CO_3 (47 mg, 34 mmol) were weighed in a Schlenk flask. The flask was pump-purged with argon three times. A degassed mixture of toluene/DMF (3:1, 4.3 mL) was added. The resulting mixture was stirred at 90–95 °C for 20 h. The reaction mixture was diluted with CH_2Cl_2 and filtered. The filtrate was concentrated. The crude mixture was chromatographed (silica, hexanes/CH_2Cl_2 (1:2)) to obtain a green solid, which was chromatographed further (silica, hexanes/CH_2Cl_2 (2:3)) to obtain a green solid (11 mg). The resulting crude **ZnC-P^{10}P^{15}** (contaminated with some aromatic impurities as shown by ^{1}H NMR spectroscopy) was dissolved in CH_2Cl_2 (15 mL). The solution was treated with TFA (0.57 mL, 7.4 mmol) and stirred at room temperature for 30 min. The reaction mixture was neutralized with excess triethylamine (1 mL) and concentrated. Chromatography (silica, hexanes/CH_2Cl_2 (1:1)) afforded a green solid (5 mg, 20%): ^{1}H NMR δ −2.20 to −2.12 (br, 1H), −2.05 to −1.90 (br, 1H), 1.98 (s, 6H), 4.20 (s, 2H), 7.68–7.72 (m, 6H), 7.89–7.91 (m, 2H), 8.11–8.14 (m, 2H), 8.25 (d, J=4.4 Hz, 1H), 8.61 (d, J=4.4 Hz, 1H), 8.64 (d, J=4.4 Hz, 1H), 8.92 (s, 1H), 8.95 (d, J=4.4 Hz, 1H), 8.96 (d, J=4.4 Hz, 1H), 9.23 (d, J=4.4 Hz, 1H), 9.81 (s, 1H); LDMS obsd 491.8; FABMS obsd 492.2300, calcd 492.2314 ($C_{34}H_{28}N_4$); λ_{abs} 408, 641 nm.

Acknowledgements

This work was supported by the NIH (GM36238). Mass spectra were obtained at the mass Spectrometry Laboratory for Biotechnology at North Carolina State University. Partial funding for the facility was obtained from the North Carolina Biotechnology Center and the NSF.

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