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Meso Bromination and Derivatization of Synthetic Bacteriochlorins

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Abstract

The ability to prepare and tailor synthetic analogues of native bacteriochlorophylls enables diverse applications. A *de novo* route entails dimerization of a dihydrodipyrrin-acetal to afford the corresponding 5-methoxy and/or 5-unsubstituted bacteriochlorin, wherein each pyrroline ring contains a gem-dimethyl group to ensure stability toward adventitious dehydrogenation. The presence of a 5-methoxy group facilitates bromination at the distal meso-(15-) position. While bromination of 5-unsubstituted bacteriochlorins typically affords a mixture of brominated products, here the presence of two substitution patterns (2,12-dicarboethoxy, 2,12-diacetyl) has been found to facilitate selective meso-bromination in the absence of the methoxy substituent. The introduction of a single meso-bromine atom in a bacteriochlorin opens opportunities for Pd-mediated derivatization, which include (1) preparation of four ethynylphenyl building blocks (and two benchmark bacteriochlorins) with long-wavelength absorption band tuned across 725–757 nm, for use in preparation of multichromophore arrays; (2) installation of a bioconjugatable group to free base bacteriochlorins or a copper bacteriochlorin, the latter for possible use in photoacoustic imaging; and (3) installation of an *S*-acetylthio group for surface attachment. Altogether, 25 new bacteriochlorins are described including 5 meso-bromobacteriochlorin intermediates and 12 target bacteriochlorins.

Introduction

A common challenge in tetrapyrrole chemistry concerns tailoring the environment of the macrocycle for a given application without altering the intrinsic features of the chromophore. Examples range from installing features for attachment to surfaces, creating a protein-like environment for studies in catalysis, and equipping the macrocycle with water-solubilization and bioconjugatable groups for use in physiological milieu. Synthetic strategies to meet these molecular design challenges can be categorized into two camps – the installation of groups in precursors that are used to create the macrocycle, and derivatization of an intact macrocycle. The existence of few routes for forming bacteriochlorin macrocycles compels focus on methods for macrocycle derivatization.

In the preceding paper,[1] we described the synthesis of a wide variety of bacteriochlorins, including those that are equipped with bromine atoms at the β-pyrrole positions. The latter could be subjected to Pd-mediated coupling reactions (Sonogashira,[2,3] Stille,[4] Suzuki[5]) to install desired peripheral groups. The bacteriochlorins contain a gem-dimethyl group in each pyrroline ring to block adventitious dehydrogenation leading to the less saturated macrocycles, chlorins and porphyrins. In this paper, we describe the bromination of intact gem-dimethyl-substituted bacteriochlorin macrocycles at a single meso-position and subsequent derivatization via Pd-mediated coupling reactions. A challenge to this approach is that meso-bromination can be achieved only in the presence of selected substituent patterns. Altogether, 5 new meso-brominated bacteriochlorins are reported, and 11 target bacteriochlorins have been prepared by elaboration of these or known meso-brominated bacteriochlorins for use as building blocks for surface attachment, bioconjugation, and elaboration into multichromophore arrays.

Results and Discussion

meso-Bromination of bacteriochlorins – literature precedents

Several routes have been developed for the synthesis of bacteriochlorins.[6-12] The present route to gem-dimethyl-substituted bacteriochlorins relies on the self-condensation of a dihydrodipyrrin-acetal[1,13-17] or dihydrodipyrrin-carboxaldehyde,[1,18] in which case the substituents on the two pyrroles of the bacteriochlorin are identical. Hence, the selective bromination of a single meso-position of bacteriochlorins is attractive in providing a site for installation of a single substituent via Pd-mediated coupling reactions. The following literature precedents bear on this topic (Scheme 1).

(A) Treatment of 8,8,18,18-tetramethylbacteriochlorin (**BC-1**), which possesses four open meso-positions (two hindered due to the flanking gem-dimethyl substituent, two unhindered) and four open β-pyrrole positions, with NBS in THF afforded a complex mixture of products.[14]

(B) Similarly, the 2,12-di-*p*-tolylbacteriochlorin **BC-2** afforded four brominated products, the 3-bromo, 5-bromo, 3,13-dibromo, and 5,13-dibromo species.[19]

(C) The analogous 2,12-di-*p*-tolylbacteriochlorin bearing a 5-methoxy group (**BC-3**) under the same conditions smoothly afforded the 15-brominated product (**BrBC-3**).[19]

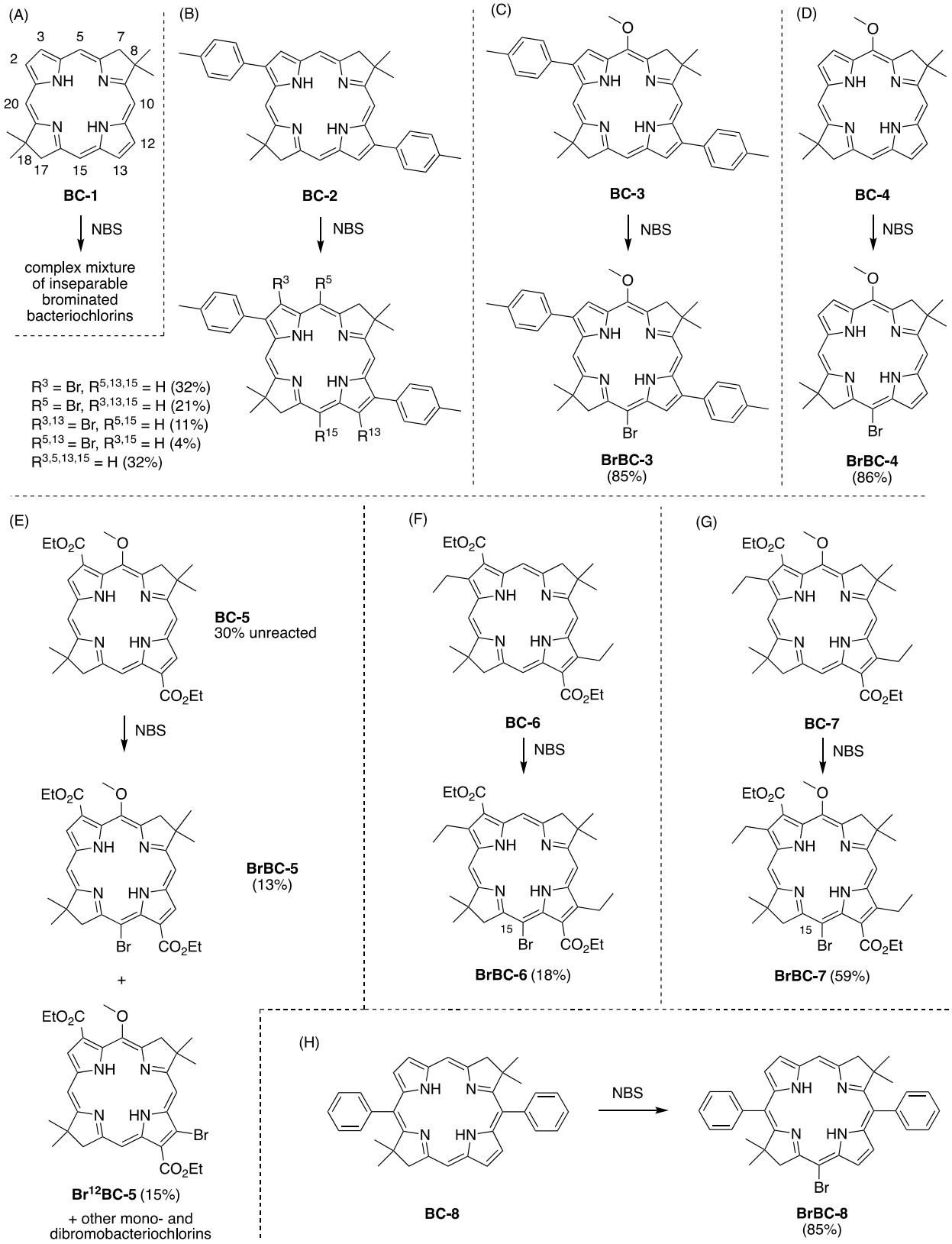
(D) The 5-methoxy analogue lacking any β-pyrrole substituents (**BC-4**) gave the 15-bromo product (**BrBC-4**) in 85% yield.[14]

(E) The 5-methoxybacteriochlorin bearing 3,13-diester substituents (**BC-5**), however, afforded a mixture of brominated products.[14]

(F) The 2,12-diethyl-3,13-diester-bacteriochlorin **BC-6**, which lacks a 5-methoxy group but contains all β-pyrrole positions blocked, gave the 15-brominated product **BrBC-6** albeit in poor yield.[20]

(G) The 5-methoxy-2,12-diethyl-3,13-diester-bacteriochlorin **BC-7** gave the 15-brominated product **BrBC-7** in far better yield (59% versus 18% for **BC-6** giving **BrBC-6**).[14]

(H) The 10,20-diphenylbacteriochlorin **BC-8** selectively afforded the 15-bromobacteriochlorin **BrBC-8** in 85% yield.[16]

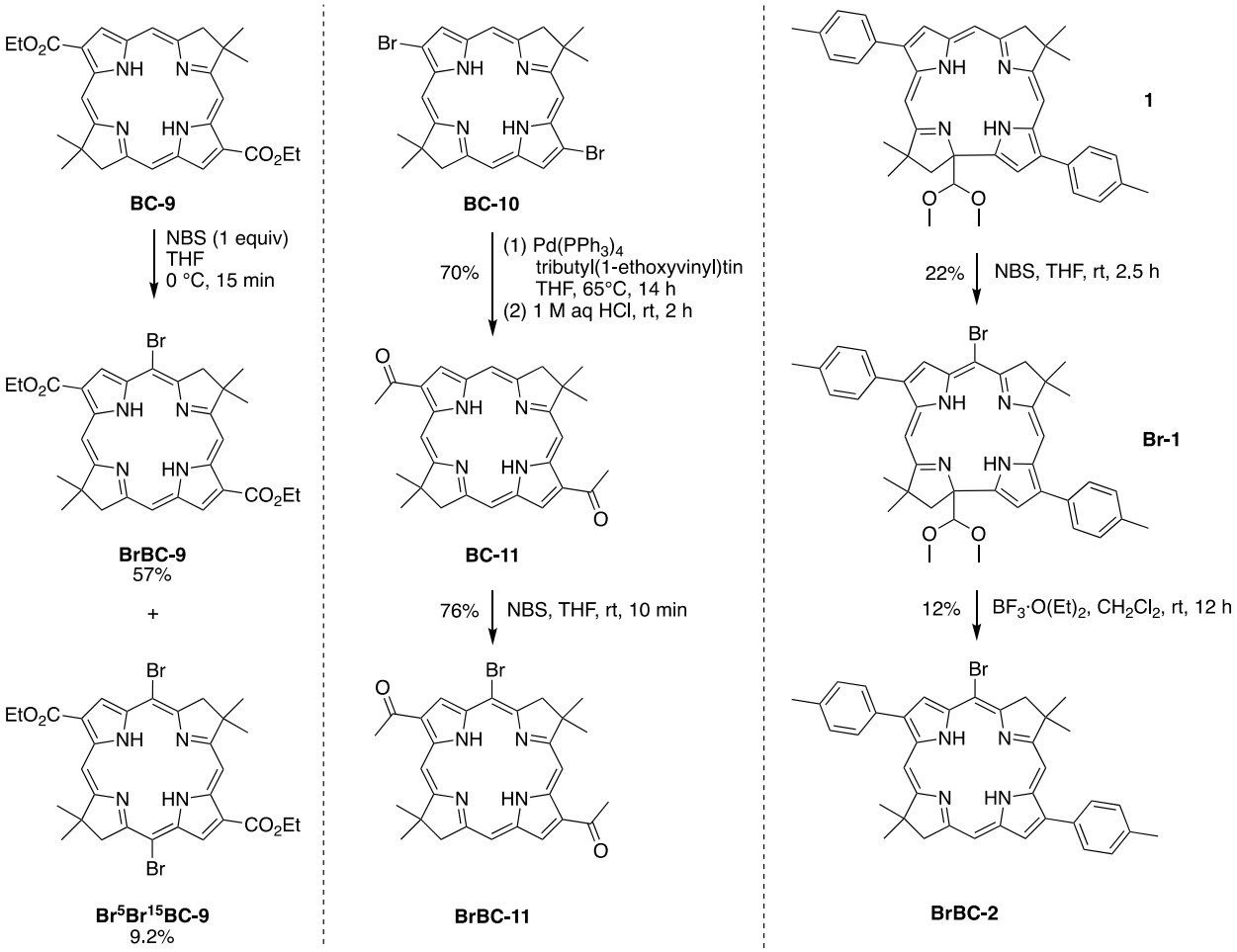


Scheme 1. Literature precedents for bacteriochlorin bromination (1 equiv of NBS).

The findings shown in Scheme 1 indicate that the 5-methoxy group is a potent director of bromination at the distal (15) meso-position in some instances, as illustrated for cases C, D, and G.[14,19,20] The 5-methoxy group is not a panacea, however, as shown by case E where the presence of two carboethoxy groups results in a mixture of products. A larger body of bromination studies of gem-dimethyl-substituted chlorins, which contain only a single pyrroline ring,[21] highlight the pronounced steric effect of substituents on adjacent positions. For example, the gem-dimethyl group at the 8-position hinders electrophilic bromination at the adjacent meso-(10)-position. We surmised that the 13-ester substituent may similarly hinder the adjacent meso-(15)-position as shown in cases E and F. Accordingly, we turned our attention to the bromination of a 2,12-diester bacteriochlorin rather than a 3,13-diester (as in case E).

meso-Bromination of bacteriochlorins – new patterns for derivatization

Treatment of bacteriochlorin-2,12-diester **BC-9**[1] with NBS afforded the mono-meso-brominated bacteriochlorin **BrBC-9** in 57% yield along with a small amount (~9%) of 5,15-dibrominated bacteriochlorin **Br^{5}Br^{15}BC-9** (Scheme 2). The 2,12-dibromobacteriochlorin **BC-10**[1] was subjected to Stille coupling[4,22] with tributyl(1-ethoxyvinyl)tin[23] followed by acidic workup to give the corresponding 2,12-diacetylbacteriochlorin **BC-11**. Treatment of **BC-11** with NBS afforded the meso-bromo-bacteriochlorin **BrBC-11** in 76% yield. The selective meso-bromination of the two 2,12-dicarbonyl-substituted bacteriochlorins, each lacking a 5-methoxy group, likely stems from an unhindered meso-position and the deactivation of the carbonyl-substituted pyrrole unit.



Scheme 2. Synthesis of meso-brominated bacteriochlorins.

Characterization of the bromination process could be achieved by routine methods. The absorption, ^{1}H NMR, and ESI-MS spectra for the conversion of **BC-9** to **BrBC-9** are shown in Figure 1. The absorption spectra for the starting material and product are nearly identical in the strong near-ultraviolet (NUV) and near-infrared (NIR) regions, the B and Q_y bands, respectively; however, the green-region (Q_x) absorption band shifts considerably upon bromination. The shift is bathochromic, from 521 to 536 nm, and provides a convenient diagnostic for the bromination process. The ESI-MS data shows the characteristic doublet owing to the presence of ^{79}Br and ^{81}Br (nominal *m/z* = 592 and 594 for M^{-} versus 514 for the starting bacteriochlorin) in the product **BrBC-9**. The ^{1}H NMR spectrum of the starting bacteriochlorin shows 3 lines given the inherent

symmetry: 8.75 ppm for the ^{5}H and ^{15}H (meso-protons), 9.17 ppm for ^{3}H and ^{13}H (β-protons) and 9.70 ppm for ^{10}H and ^{20}H (meso-protons). Upon bromination, the signal from the ^{5}H is lost, yet the number of lines increases owing to the diminished symmetry of the macrocycle **BrBC-9**. The ^{15}H shifts slightly upfield; the ^{3}H, which is adjacent to the bromine atom, resonates downfield (9.41 ppm); while the distal ^{13}H is nearly unchanged at 9.15 ppm. The ^{10}H and ^{20}H, which also previously resonated as a singlet, are split into two singlets at 9.59 and 9.72 ppm.

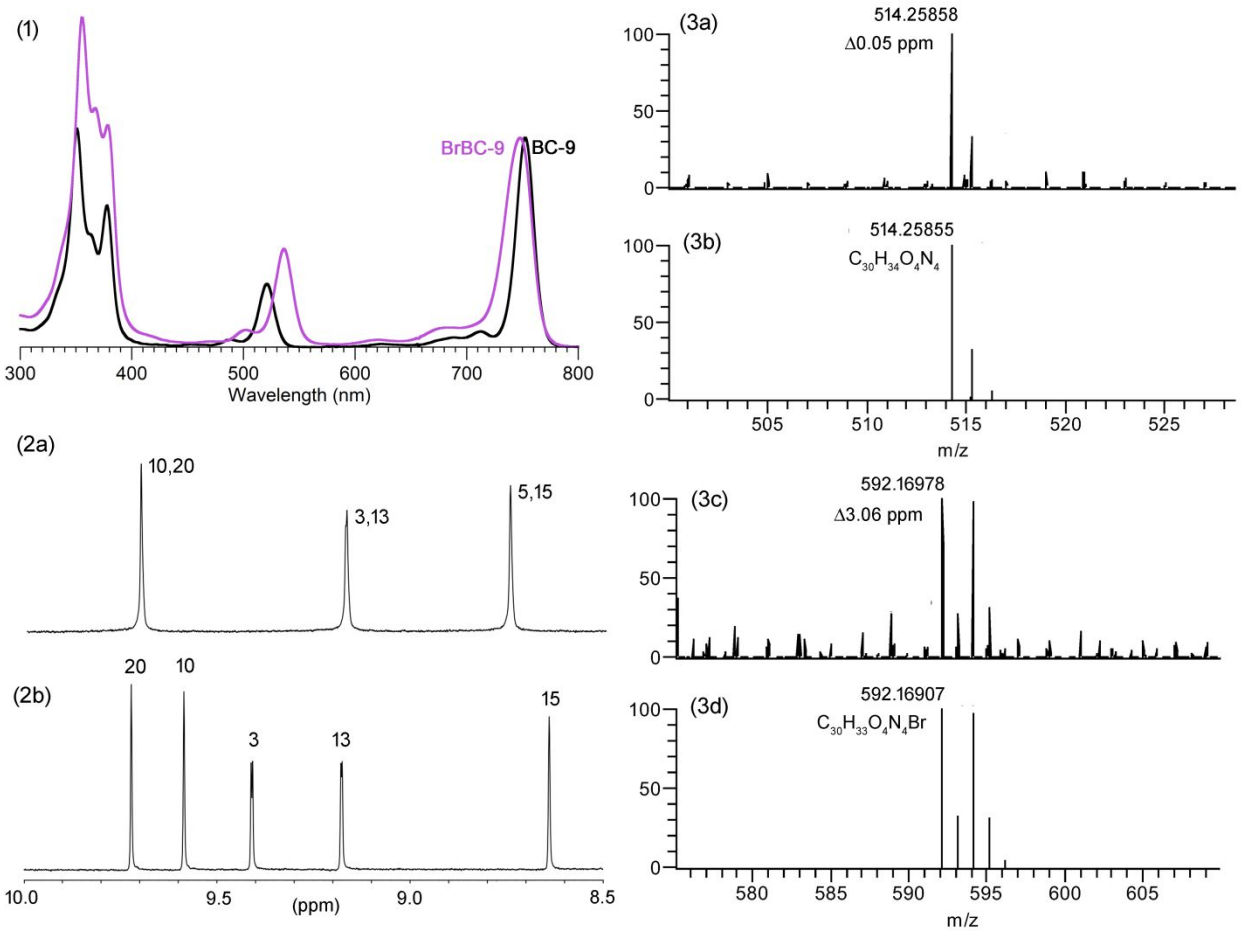


Figure 1. Characterization at room temperature of the conversion of **BC-9** to **BrBC-9**. Panel 1: Absorption spectra in CH_2Cl_2 normalized at the Q_y band. Panel 2: ^{1}H NMR data in $CDCl_3$ showing assigned protons for (a) **BC-9** and (b) **BrBC-9**. Panel 3: ESI-MS data in the negative-ion mode (a, **BC-9**; c, **BrBC-9**) and simulated data (b, **BC-9**; d, **BrBC-9**).

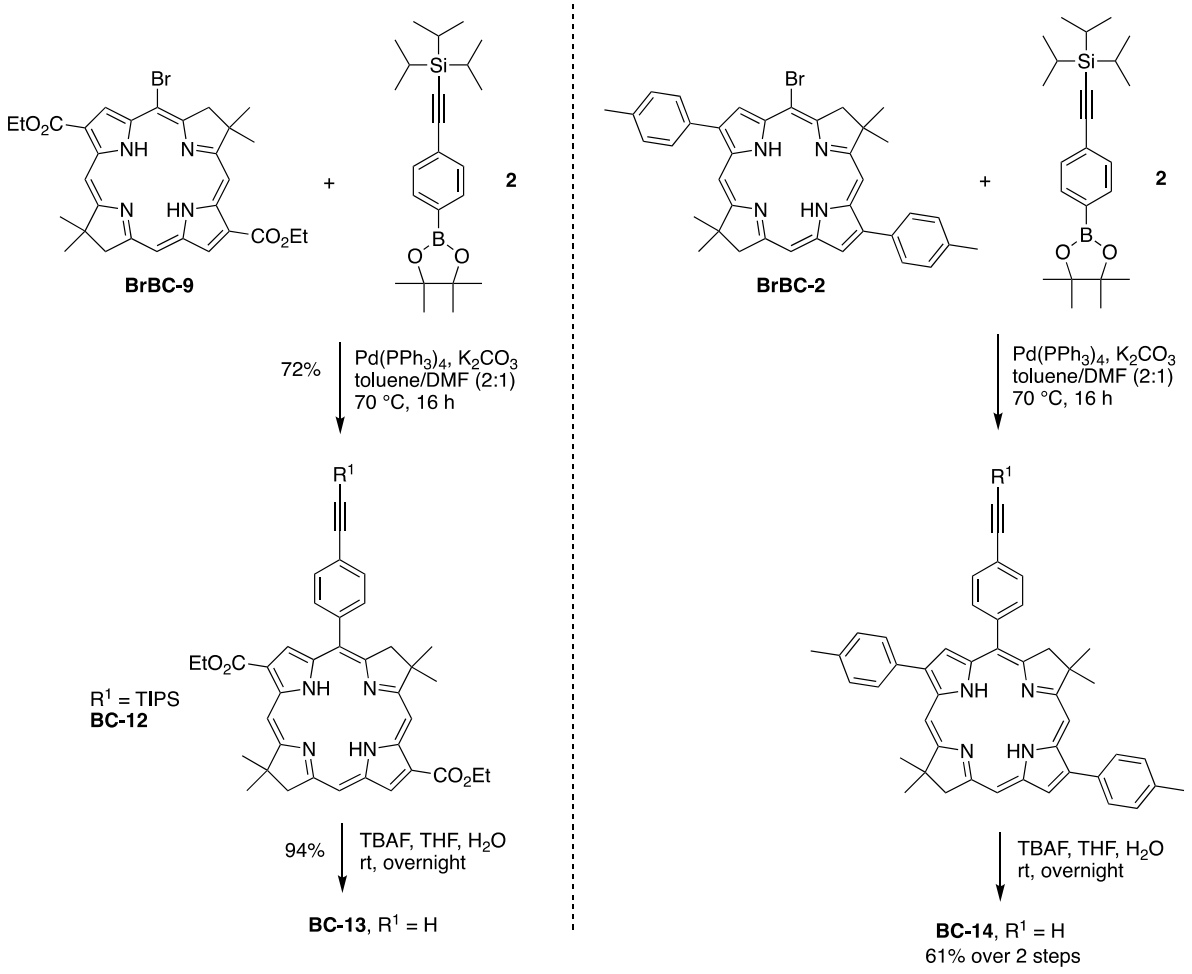
The condensation of a dihydrodipyrrin-acetal in CH_3CN containing $BF_3{\cdot}O(Et)_2$ affords a mixture of the 5-methoxybacteriochlorin, the 5-unsubstituted bacteriochlorin, and the

tetradehydrocorrin bearing an unreacted dimethyl acetal moiety at the A–D ring junction (**1**).[13] Mild acid catalysis with $Yb(OTf)_3$ instead of $BF_3{\cdot}O(Et)_2$ affords the tetradehydrocorrin selectively.[24] Such tetradehydrocorrins are known to undergo rearrangement upon acid catalysis stronger than $Yb(OTf)_3$ to form the bacteriochlorin.[24] Treatment of tetradehydrocorrin **1** with NBS afforded the brominated derivative **Br-1**, where the bromine is located at the meso-position distal to the A–D ring junction (Scheme 2).[24] Here, treatment of **Br-1** with $BF_3{\cdot}O(Et)_2$ gave the corresponding meso-brominated bacteriochlorin **BrBC-2**. The **BrBC-2** was previously identified in a complex mixture containing other bromobacteriochlorins as shown for case B in Scheme 1, but was not isolated in pure form. The overall transformation in Scheme 2 is attractive in providing access to the 5-bromobacteriochlorin lacking any methoxy group (**BrBC-2**), but the yields in the two steps are quite low.

Derivatization of meso-bromobacteriochlorins

Ethynylphenyl-containing bacteriochlorins. The synthesis of multichromophore arrays comprised of tetrapyrrole macrocycles has provided molecular architectures for studies of photosynthetic-like energy transduction. Most such studies have necessarily been carried out with porphyrins given the greater ease of synthesis and the earlier advent of synthetic methods. Arrays containing ≥ 2 bacteriochlorins have slowly begun to emerge.[25-34] A general synthetic requirement is the ability to install a single synthetic handle on the bacteriochlorin; a generally desirable molecular design feature is the ability to tune the long-wavelength absorption band over a defined range given that the position of the band sets an upper bound on the energy of resulting photochemical processes. For preparation of arrays, we sought bacteriochlorin building blocks bearing a 4-ethynylphenyl group at a meso-position.

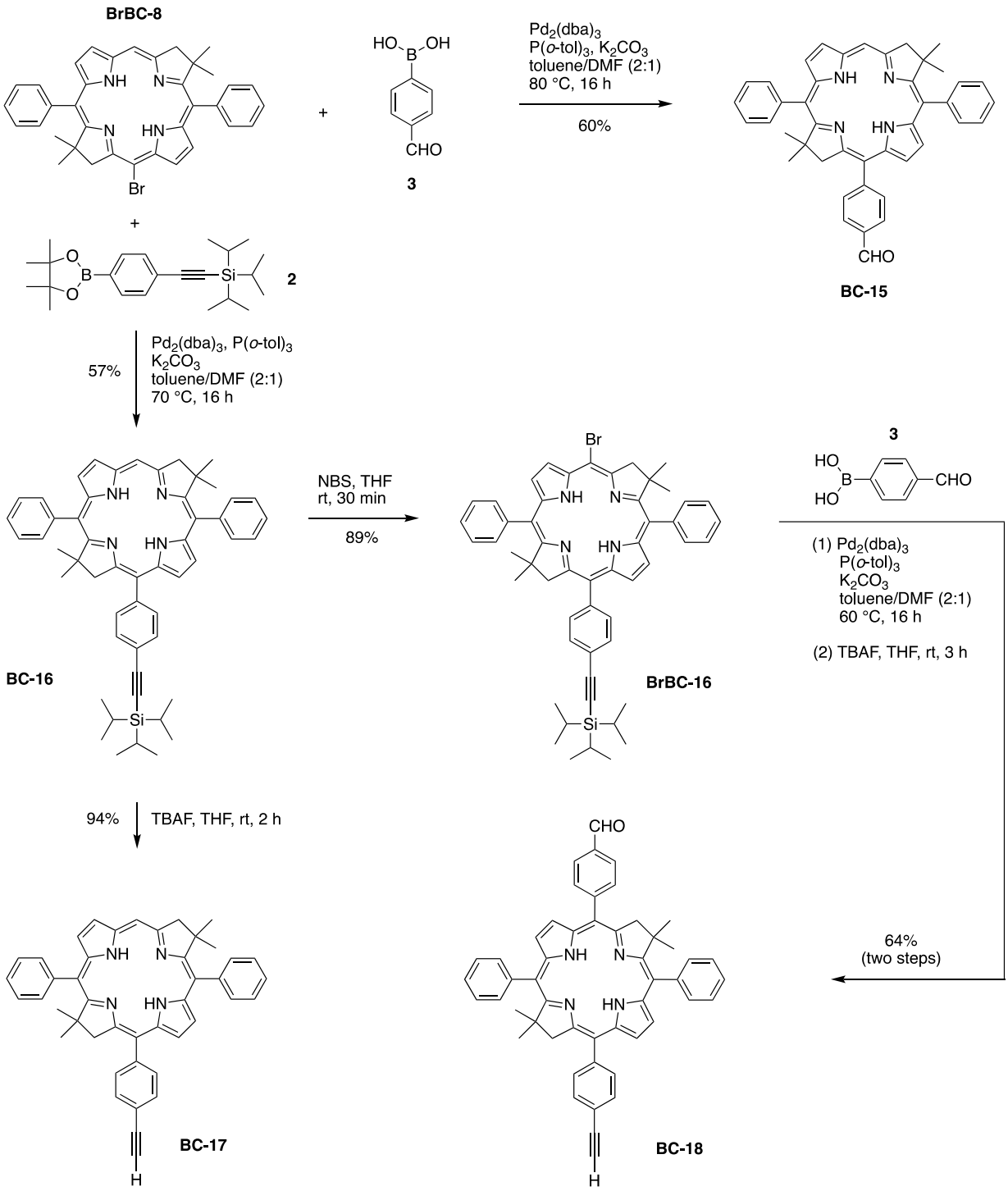
The 5-bromo-2,12-dicarboethoxybacteriochlorin **BrBC-9** and aryl building block **2** were subjected to a Suzuki coupling reaction. Compound **2** is equipped with a 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl group for Suzuki coupling[5] and a 2-(triisopropylsilyl)ethynyl group for subsequent Sonogashira coupling.[2,3] The synthesis of **2** has been reported three times.[35-37] The Suzuki reaction proceeded smoothly to afford the aryl-substituted bacteriochlorin-2,12-diester **BC-12** in 72% yield. Treatment with TBAF gave the corresponding ethynylphenyl-substituted **BC-13** in 94% yield. The analogous Suzuki reaction of the 5-bromo-2,12-di-*p*-tolylbacteriochlorin **BrBC-2** and **2** gave the corresponding triarylbacteriochlorin, which upon treatment with TBAF gave the desired ethynylphenyl-substituted bacteriochlorin **BC-14** in 61% yield over the two steps (Scheme 3).



Scheme 3. Synthesis of ethynylphenylbacteriochlorin building blocks.

A similar set of reactions was carried out starting with the 5-bromo-10,20-diphenylbacteriochlorin **BrBC-8**. First, Suzuki coupling of **BrBC-8** and 4-formylphenylboronic acid (**3**) gave A_2B-type bacteriochlorin-benzaldehyde **BC-15** in 60% yield. Second, Suzuki coupling[28] of **BrBC-8** and linker unit **2** gave the TIPS-protected ethynylphenyl-bacteriochlorin **BC-16**, which upon deprotection with TBAF afforded the target ethynylphenyl-bacteriochlorin **BC-17**. The TIPS-protected ethynylphenyl-bacteriochlorin **BC-16** was treated with NBS to afford bromination at the lone open meso-position, affording bromobacteriochlorin **BrBC-16** in 89% yield. Subsequent Suzuki coupling with 4-formylphenylboronic acid (**3**) followed by removal of the TIPS group with TBAF gave the tetra-meso-substituted building block **BC-18** (Scheme 4). The latter is an example of an A_2BC-bacteriochlorin and is equipped for orthogonal derivatization at the peripheral carboxaldehyde and ethynyl groups. Prior syntheses of bacteriochlorins[8-10] that bear a full complement of meso-substituents have relied on (1) hydrogenation of a porphyrin at the appropriate β-pyrrolic positions;[38,39] (2) cycloaddition of an organic reactant with the porphyrin at the β-pyrrolic positions;[7,9] (3) condensation of a dihydrodipyrrin-acetal bearing aryl groups at the meso site and the acetal carbon;[40] or (4) sequential bromination/Pd-coupling of the 10- and 20-positions of **BC-8**.[16,17]

The absorption spectra of the four ethynylphenyl-bacteriochlorins are shown in Figure 2. For studies of energy transfer, the position of the long-wavelength band is of paramount importance. The long-wavelength (Q_y) band of the four bacteriochlorins spans the following range: 725 nm (**BC-17**), 730 nm (**BC-18**), 741 nm (**BC-14**), and 757 nm (**BC-13**). The highest energy absorber contains two meso-phenyl groups whereas the lowest energy absorber is equipped with 2,12-dicarboethoxy substituents, with all compounds bearing two gem-dimethyl groups and the phenylethyne unit.



Scheme 4. Modification of 10,20-diphenylbacteriochlorins.

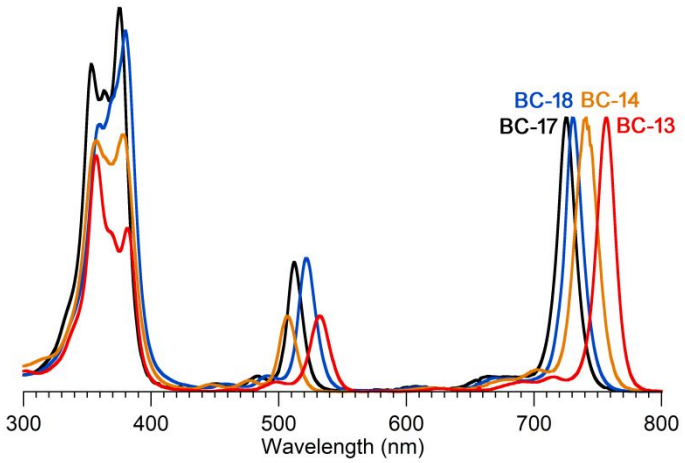
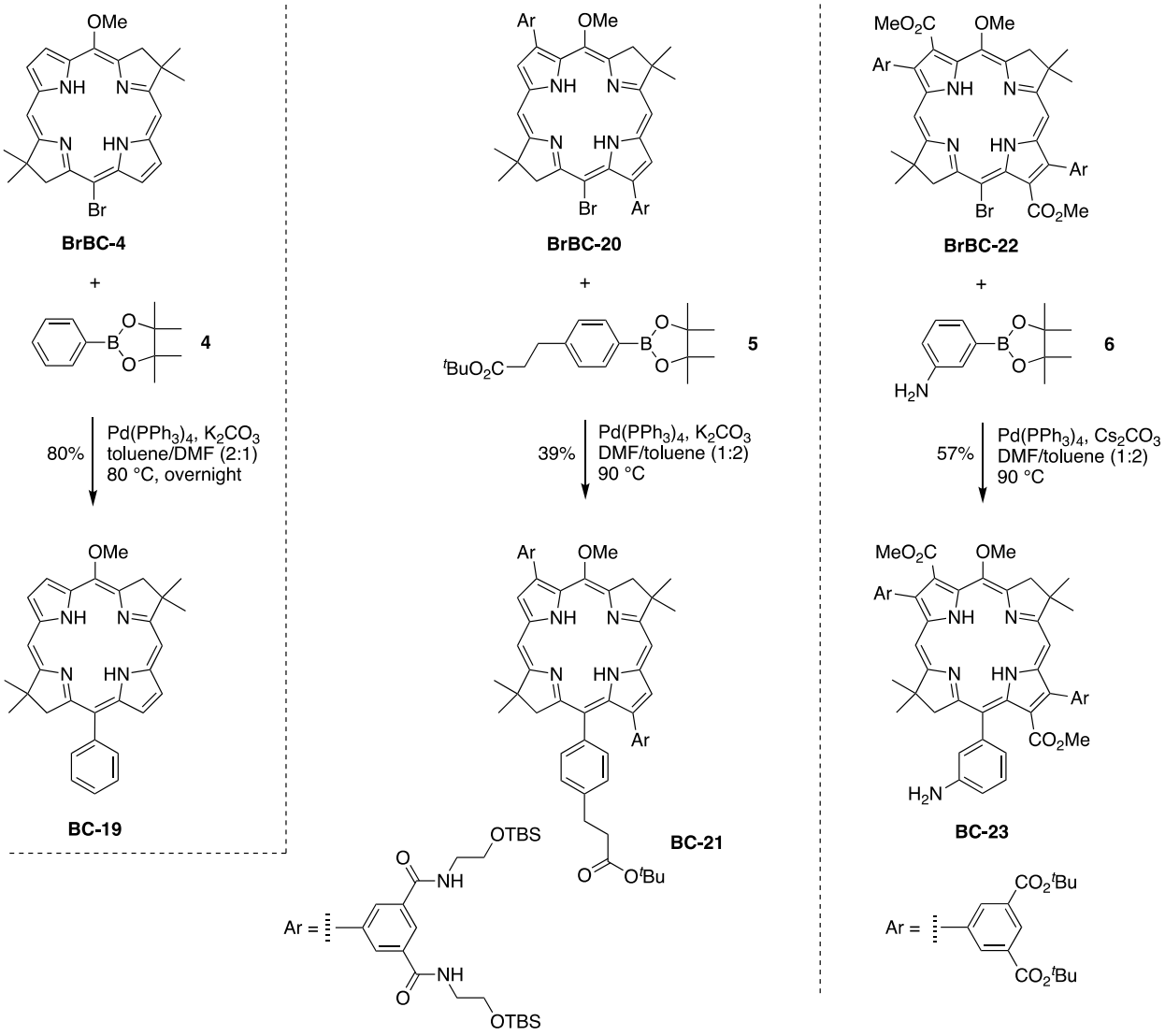


Figure 2. Absorption spectra (normalized at the Q_y band) of **BC-17** (black), **BC-18** (blue), **BC-14** (orange) and **BC-13** (red) in CH_2Cl_2 at room temperature.

Each bacteriochlorin shown in Schemes 3 and 4 is derived from a parent macrocycle that lacks a 5-methoxy group. The following derivatizations were carried out on 5-methoxy-15-bromobacteriochlorins. Sparsely substituted bacteriochlorins are valuable benchmarks in studies of the effects of substituents on spectral and physicochemical studies.[22] The bacteriochlorin **BrBC-4** is sparsely substituted, containing only the 5-methoxy-15-bromo substituents along with the two gem-dimethyl groups. Suzuki coupling[28] of **BrBC-4** with 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (**4**) gave the 5-methoxy-15-phenylbacteriochlorin **BC-19** in 80% yield (Scheme 5). A *p*-tolyl homologue is known.[28] In a similar manner, bacteriochlorin **BrBC-20**, which contains two 3,5-disubstituted aryl groups, was prepared by 15-bromination in 71% yield.[41] Suzuki coupling with borolane **5**[42] gave the amphiphilic bioconjugatable bacteriochlorin **BC-21** wherein the four hydroxy groups and the carboxylic acid are in protected form. Bacteriochlorin **BrBC-22**, which also contains two 3,5-disubstituted aryl groups, was prepared by 15-bromination in 42% yield.[42] Suzuki coupling with 4,4,5,5-tetramethyl-2-(3-aminophenyl)-1,3,2-dioxaborolane (**6**) gave the water-soluble bioconjugatable aminophenyl-bacteriochlorin **BC-23** wherein the four carboxylic acid groups are in protected form.



Scheme 5. Attachment of bioconjugatable handles and a reference compound (upper left).

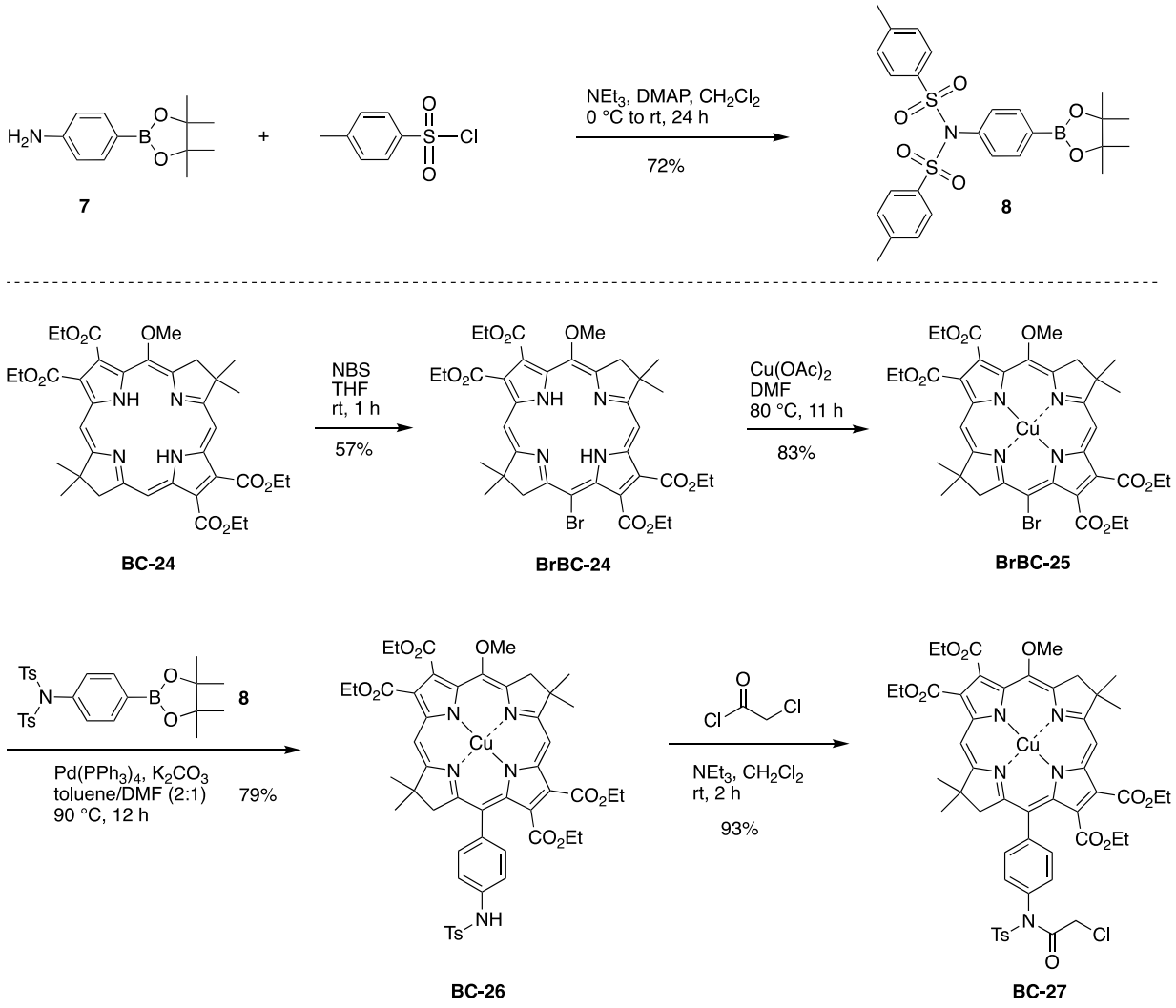
Bioconjugatable copper bacteriochlorin. Copper tetrapyrroles have been sought for multiple purposes. One pursuit concerns resonance Raman spectroscopy, given that copper tetrapyrroles are generally non-fluorescent.[43,44] A second pursuit concerns positron emission tomography (PET),[45,46] which can utilize the ^{64}Cu decay[47] ($t_{1/2}$ = 12.7 h, decay by β^+ (61%) and β^- (39%)). A third and more recent pursuit concerns photoacoustic imaging (PAI),[48-50] which relies on light activation and ultrasound detection. PAI can utilize intrinsic chromophores (e.g., hemoglobin, melanin, lipids)[48,51-56] or injected exogenous contrast agents (e.g., organic dyes,

nanoparticles, nanotubes, metallic agents).[57-66] Regardless, the rapid and full relaxation of the excited state to the ground state affords the desired acoustic signal. The penetration depth of visible light is limited due to absorption and scattering in biological tissues,[67] whereas NIR light is less susceptible in these regards and penetrates more deeply into soft tissue. Thus, exogenous contrast agents with strong NIR absorption are attractive for deep-tissue PAI imaging.[49,68] Metalation of a bacteriochlorin generally shifts the Q_y absorption to deeper in the NIR,[69] which is quite attractive for PAI.

As a prelude to studies of PET and/or PAI, we sought to construct a bioconjugatable copper bacteriochlorin. Copper tetrapyrroles are generally non-fluorescent owing to rapid excited-state relaxation under ambient conditions. The metalation of bacteriochlorins[70-72] depends strongly on the nature of the substituents, with more electron-withdrawing groups facilitating metalation. Thus, 2,3,12,13-tetracarboethoxybacteriochlorin **BC-24**[14] was successfully zincated with $Zn(OAc)_2 \cdot 2H_2O$ in DMF at 60−80 °C, whereas at the other extreme in the absence of any esters, treatment with a strong base (e.g., NaH or LDA) is required.[70] Treatment of bacteriochlorin **BC-24** with 1.0 equiv of NBS in THF gave the 15-bromobacteriochlorin counterpart **BrBC-24** in 57% yield. Subsequent treatment with $Cu(OAc)_2$ in DMF at 80 °C gave the copper bacteriochlorin **BrBC-25** in 83% yield. Attempted Suzuki coupling with 2-(4-aminophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**7**) was unsuccessful, hence **7** was treated with tosyl chloride in CH_2Cl_2 in an established procedure[73] to give the *N,N*-ditosyl 4-aminophenylborolane **8**. Ditosylamide **8** was characterized by single-crystal X-ray diffraction (see Electronic Supplementary Information). Ditosylamides are well known compounds; indeed, 21 single-crystal X-ray structures have been reported in the past 30 years (for leading references, see refences 74-76).

Suzuki coupling of copper bacteriochlorin **BrBC-25** with **8** afforded **BC-26**, which contains only one tosyl group. Attempted cleavage of the tosyl group caused decomposition of

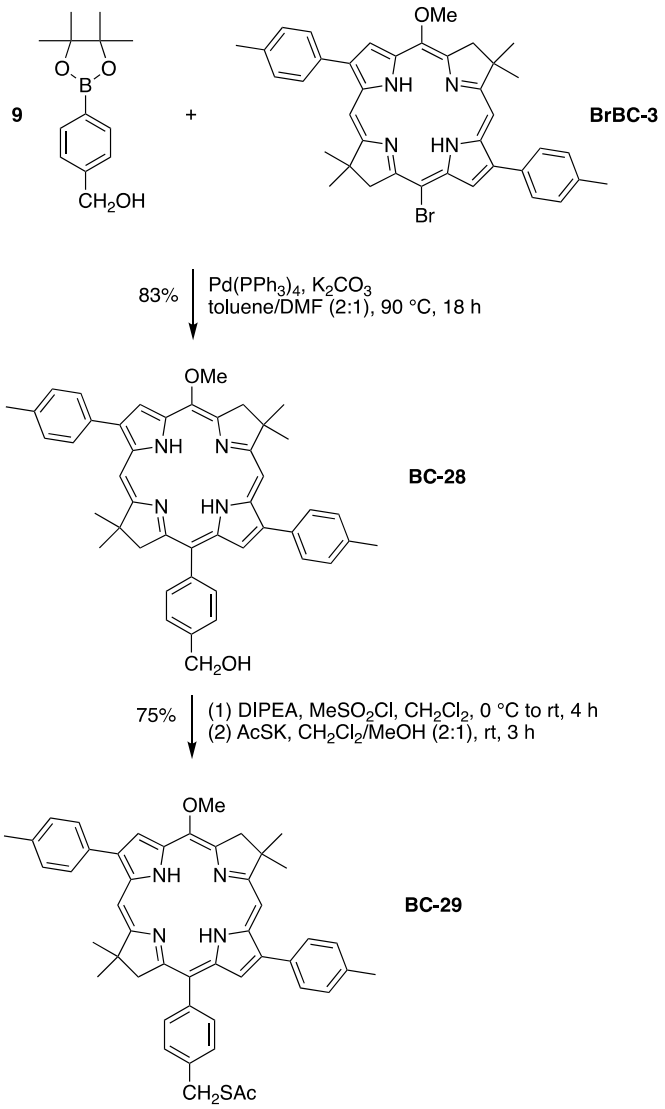
BC-26. Accordingly, the *N*-tosyl group was left intact, and treatment[77] of **BC-26** with chloroacetyl chloride in CH_2Cl_2 provided the *N*-chloroacetamido-substituted copper bacteriochlorin **BC-27** in 93% yield (Scheme 6).



Scheme 6. Synthesis of a bioconjugatable copper bacteriochlorin.

Bacteriochlorin equipped for surface attachment. The attachment of tetrapyrrole macrocycles to electroactive surfaces has enabled electrochemical interrogation and a variety of physicochemical studies.[78] The Suzuki coupling reaction of 15-bromobacteriochlorin **BrBC-3** and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl alcohol (**9**) previously gave the corresponding bacteriochlorin-benzyl alcohol **BC-28** in 22% yield (Scheme 7).[79] The

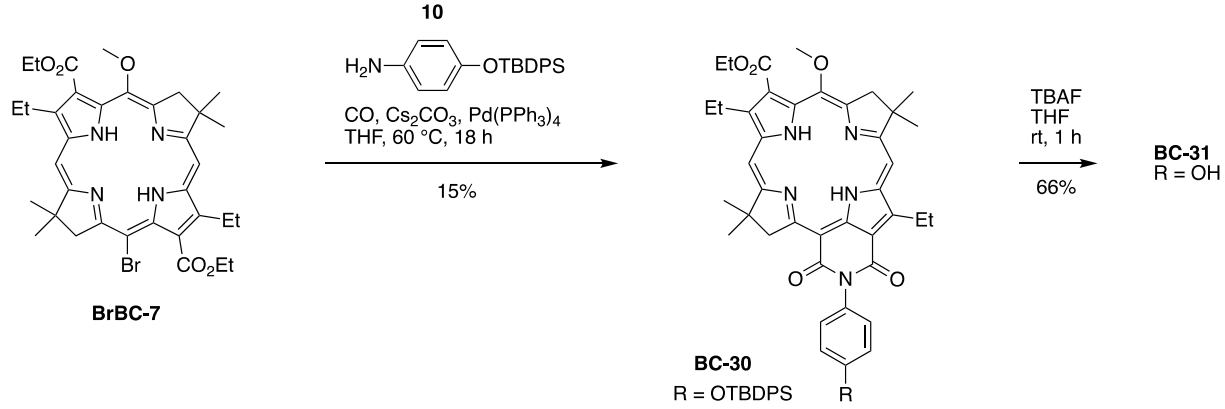
hydroxymethyl bacteriochlorin **BC-28** was attached to Si(100) and examined by cyclic voltammetry, FTIR, XPS, and ellipsometry.[79] An *S*-acetylthio-substituted analogue was sought, knowing that the *S*-acetyl protecting group is removed *in situ* upon contact with a gold surface.[80] Because the previous Suzuki coupling reaction proceeded in low yield (22%),[79] the reaction was repeated here with **BrBC-3** and **9**, affording **BC-29** in 83% yield. The higher yield (83% versus 22%) was obtained at approximately the same scale, affording 20 mg of **BC-28** rather than 6 mg. To introduce the *S*-acetylthio group, the alcohol in **BC-28** was transformed[81] to a sulfonate by reaction with methanesulfonyl chloride in the presence of diisopropylethylamine. The sulfonate intermediate was used directly without purification, and the substitution with potassium thioacetate afforded the desired target compound, **BC-29**, in 75% yield. The resulting **BC-29** was found to be stable upon storage in a dry environment.



Scheme 7. Synthesis of a surface-attachable bacteriochlorin.

Exploratory bacteriochlorinimide. Annulated rings that span the β,meso- or β,β-positions of bacteriochlorins and are equipped with conjugated moieties impart a bathochromic shift of the long-wavelength absorption band. The formation of annulated imides was first demonstrated by derivatization of native bacteriochlorophylls.[25] The Pd-mediated carbonylation of known[14] bacteriochlorin **BrBC-7** in the presence of 4-(*tert*-butyldiphenylsilyloxy)aniline (**10**)[82] afforded the meso,β-annulated bacteriochlorin **BC-30** (Scheme 8). Removal of the silyl protecting group gave **BC-31**, which bears a phenol substituent as a potent linker. The Q_y band of each annulated

bacteriochlorin (**BC-30** in toluene, **BC-31** in THF) appeared around 785 nm, to be compared with 739 nm for the parent 2,12-diethyl-3,13-dicarboethoxy-5-methoxybacteriochlorin.



Scheme 8. Synthesis of a phenol-substituted bacteriochlorinimide.

Outlook

Understanding how to tailor bacteriochlorin macrocycles is enabling for diverse applications in the photosciences. Two substitution patterns (2,12-dicarboethoxy, 2,12-diacetyl) have been identified that enable selective meso-bromination of bacteriochlorins that lack a 5-methoxy group. Explaining why the lone bromine atom goes to a particular position, and why the bromine doesn't go to many other positions, are opposite sides of the same coin. Concerning where the bromine doesn't go, one interpretation is that (1) two open meso-positions (10,20) are hindered toward substitution due to the flanking 8,8,18,18-tetramethyl groups and the 2,12-dicarbonyl groups; and (2) two open pyrrole β-positions (3,13) are deactivated toward substitution by the adjacent 2,12-dicarbonyl groups. Concerning where the bromine does go, one interpretation is that (3) the remaining two open meso positions (5,15) are unhindered and hence susceptible to electrophilic substitution; but only one site substitutes because (4) introduction of a single bromine atom partially deactivates the macrocycle toward subsequent bromination. While further studies, likely including computation, will be required to probe the interplay of steric and electronic factors, the ability to selectively install a bromine atom at one of six open sites in a sparsely substituted

bacteriochlorin macrocycle opens access to new molecular designs. Arrays comprised of multiple bacteriochlorins and other bacteriochlorin-containing constructs have largely been unexplored compared to studies with porphyrins even though bacteriochlorins provide far superior light-harvesting capacity particularly in the red and NIR regions. The preparation of bacteriochlorin building blocks described here broadens an avenue for pursuing such studies.

Experimental Section

General methods

^{1}H NMR and ^{13}C NMR spectra were collected at room temperature in $CDCl_3$ unless noted otherwise. THF was freshly distilled from sodium/benzophenone. All other solvents (anhydrous or reagent-grade) were employed as received from commercial suppliers. Electrospray ionization mass spectrometry (ESI-MS) data generally enable accurate mass measurements, were obtained in the positive-ion mode (unless noted otherwise) and are reported for the molecular ion or protonated molecular ion. Commercial compounds were used as received. NBS was recrystallized from water. $BF_3{\cdot}O(Et)_2$ was neat (8.1 M). Silica (40 μm average particle size) was used for column chromatography. Preparative-scale size-exclusion chromatography (SEC) was carried out using Bio-beads S-X1 (200–400 mesh) in toluene. Matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) was performed using the matrix α-cyano-4-hydroxycinnamic acid unless noted otherwise.

Non-commercial Compounds

Compounds 10-bromo-1*H*,22*H*,24*H*-7,8,17,18-tetradehydro-1-(1,1-dimethoxymethyl)-3,3,13,13-tetramethyl-7,17-di-*p*-tolylcorrin (**Br-1**),[24] 2-{4-[2-(triisopropylsilyl)ethynyl]phenyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**),[35-37] 2-[4-(2-(*tert*-butoxycarbonyl)ethyl)phenyl]-3,3,4,4-tetramethyl-1,3,2-dioxaborolane (**5**),[42] 4-(*tert*-butyldiphenylsilyloxy)aniline (**10**),[82] and several bacteriochlorins (**BrBC-3**,[19] **BrBC-4**,[265] **BrBC-7**,[14] **BrBC-8**,[16] **BrBC-20**,[41] **BrBC-22**,[42] and **BC-24**[14]) were prepared following literature procedures. Bacteriochlorins **BC-9** and **BC-10** were reported in the companion paper.[1]

Pd-coupling reactions with bacteriochlorins

Suzuki coupling reactions were generally carried out at small scale using a solution of bromobacteriochlorin (1 equiv), borolane (5–10 equiv), P(*o*-tol)$_3$ (2–5 equiv), $Pd_2(dba)_3$ (1–2.5 equiv), and K_2CO_3 (10–20 equiv) in toluene/DMF (1–5 mL, 2:1) at 80 °C under anaerobic conditions on a Schlenk line.[19] An alternative procedure employed a solution of bromobacteriochlorin (1 equiv), borolane (5–10 equiv), $(PPh_3)_4Pd$ (0.4–2.5 equiv), and K_2CO_3 (8–20 equiv) in toluene/DMF (1–5 mL, 2:1) at 80 °C under anaerobic conditions on a Schlenk line.[28,83] In general, variations within the stated ranges depended on the amount of bromobacteriochlorin used, with larger excesses employed with lesser quantities of bacteriochlorin to inhibit possible side reactions such as debromination.

Synthesis procedures

5-Bromo-8,8,18,18-tetramethyl-2,12-di-*p*-tolylbacteriochlorin (BrBC-2). A solution of **Br-1** (27 mg, 39 μmol) in anhydrous CH_2Cl_2 (7.6 mL) was treated with $BF_3{\cdot}O(Et)_2$ (25 μL, 0.20 mmol). The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was quenched by the addition of saturated aqueous $NaHCO_3$ solution and then extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), concentrated and purified by chromatography [silica, hexanes/CH_2Cl_2 (4:1 to 2:1)] to give a green solid (3.0 mg, 12%). ^{1}H NMR (700 MHz) δ −1.74 (s, 1H), −1.70 (s, 1H), 1.90 (s, 6H), 1.91 (s, 6H), 2.60 (s, 3H), 2.61 (s, 3H), 4.40 (s, 2H), 4.50 (s, 2H), 7.57 (d, J = 7.1 Hz, 2H), 7.58 (d, J = 7.1 Hz, 2H), 8.08 (d, J = 7.8 Hz, 2H), 8.11 (d, J = 7.8 Hz, 2H), 8.69 (d, J = 2.0 Hz, 1H), 8.70 (s, 1H), 8.73 (s, 1H), 8.80 (s, 1H), 9.04 (d, J = 2.3 Hz, 1H); ^{13}C{^{1}H} NMR (175 MHz) δ 21.40, 21.43, 31.0, 31.1, 45.7, 46.2, 51.8, 54.0, 95.7, 96.9, 98.5, 120.9, 121.8, 129.7, 129.8, 130.9, 131.2, 132.0, 132.9, 133.2, 133.9, 13.4,7 136.2, 137.0, 137.6, 138.1; ESI-MS obsd 628.2194, calcd 628.2196 [$(M)^+$, M = $C_{38}H_{37}BrN_4$]; λ_{abs} (CH_2Cl_2) 354, 376, 510, 737 nm.

5-Bromo-2,12-dicarboethoxy-8,8,18,18-tetramethylbacteriochlorin (BrBC-9). A solution of **BC-9** (15.0 mg, 29 μmol) in freshly distilled THF (15.0 mL) was cooled in an ice bath. The mixture was treated with 0.52 mL of NBS solution (5.1 mg, 29 μmol, from 56 mM freshly prepared THF stock solution pre-chilled at −20 °C) at 0 °C for 15 min. The reaction mixture was diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4), concentrated and purified by chromatography [silica, hexanes/CH_2Cl_2 (3:2) to CH_2Cl_2]. The first purple band was the dibromobacteriochlorin **Br^{5}Br^{15}BC-9** (1.8 mg, 9.2%) and the second purple band was the title compound (9.9 mg, 57%). Data for the title compound: ^{1}H NMR (600 MHz) δ −1.12 (s, 1H), −1.10 (s, 1H), 1.69 (t, J = 7.2 Hz, 3H), 1.70 (t, J = 7.2 Hz, 3H), 1.95 (s, 6H), 1.96 (s, 6H), 4.33 (s, 2H), 4.41 (s, 2H), 4.74 (q, J = 7.2 Hz, 2H), 4.75 (q, J = 7.2 Hz, 2H), 8.64 (s, 1H), 9.18 (d, J = 2.5 Hz, 1H), 9.41 (d, J = 2.9 Hz, 1H), 9.59 (s, 1H), 9.72 (s, 1H); ^{13}C{^{1}H} NMR (150 MHz) δ 14.7, 14.8, 31.10, 31.13, 45.7, 46.4, 51.5, 53.7, 60.8, 61.1, 97.6, 98.7, 100.4, 100.7, 120.6, 124.8, 125.0, 128.4, 131.2, 135.4, 136.9, 158.6, 163.0, 165.0, 165.7, 171.7, 175.5; ESI-MS obsd 592.1698, calcd 592.1691 [$(M)^-$, M = $C_{30}H_{33}BrN_4O_4$]; λ_{abs} (CH_2Cl_2) 355, 367, 379, 536, 749 nm.

Data for **5,15-Dibromo-2,12-dicarboethoxy-8,8,18,18-tetramethylbacteriochlorin (Br^{5}Br^{15}BC-9)**: ^{1}H NMR (600 MHz) δ −1.20 (s, 2H), 1.70 (t, J = 7.2 Hz, 6H), 1.96 (s, 12H), 4.41 (s, 4H), 4.76 (q, J = 7.2 Hz, 4H), 9.49 (d, J = 2.4 Hz, 2H), 9.74 (s, 2H); ^{13}C{^{1}H} NMR (150 MHz) δ 14.7, 31.3, 46.0, 53.9, 61.1, 99.2, 100.0, 123.2, 127.4, 133.1, 135.9, 161.4, 165.3, 173.8; ESI-MS obsd 670.0778, calcd 670.0785 [$(M + H)^+$, M = $C_{30}H_{32}Br_2N_4O_4$]; λ_{abs} (CH_2Cl_2) 359, 371, 380, 551, 755 nm.

2,12-Diacetyl-8,8,18,18-tetramethylbacteriochlorin (BC-11). Following a general procedure[22] with modification, a solution of **BC-10** (5.0 mg, 9.4 μmol) and tributyl(1-ethoxyvinyl)tin (15 μL, 44 μmol) in freshly distilled THF (3.0 mL) was deaerated by four freeze/pump/thaw cycles. A sample of $Pd(PPh_3)_4$ (7.5 mg, 6.5 μmol) was then added, and the resulting mixture was stirred for 14 h at 70 °C. Then the reaction mixture was treated with 1M aqueous HCl (5 mL) at room temperature for 2 h. The resulting mixture was poured into a saturated aqueous solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), concentrated and purified by chromatography [silica, CH_2Cl_2/ethyl acetate (1:0 to 30:1)]. The pink band was concentrated to dryness to afford a dark brown solid (3.0 mg, 70%): ^{1}H NMR (700 MHz) δ −1.21 (s, 2H), 1.96 (s, 12H), 3.17 (s, 6H), 4.36 (s, 4H), 8.71 (s, 2H), 9.03 (d, J = 2.1 Hz, 2H),

9.76 (s, 2H); $^{13}C\{^1H\}$ NMR (175 MHz) δ 30.8, 31.8, 46.2, 51.1, 98.5, 100.5, 125.4, 128.9, 129.4, 133.2, 135.5, 159.9, 173.4, 196.6; ESI-MS obsd 454.2362, calcd 454.2363 [$(M)^+$, M = $C_{28}H_{30}N_4O_2$]; λ_{abs} (CH_2Cl_2) 360, 390, 532, 768 nm.

2,12-Diacetyl-5-bromo-8,8,18,18-tetramethylbacteriochlorin (BrBC-11). A solution of **BC-11** (2.6 mg, 4.9 μmol) in freshly distilled THF (3.5 mL) was treated with 95 μL of NBS solution (0.95 mg, 5.3 μmol, from 56 mM freshly prepared THF stock solution) at room temperature for 20 min. The reaction mixture was diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4), concentrated and purified by chromatography [silica, CH_2Cl_2]. The second purple band was the title compound (2.0 mg, 76%): ^1H NMR (700 MHz) δ −0.90 (s, 1H), −0.81 (s, 1H), 1.937 (s, 6H), 1.944 (s, 6H), 3.16 (s, 3H), 3.17 (s, 3H), 4.30 (s, 2H), 4.38 (s, 2H), 8.61 (s, 1H), 9.03 (d, J = 2.0 Hz, 1H), 9.28 (d, J = 2.1 Hz, 1H), 9.63 (s, 1H), 9.78 (s, 1H); $^{13}C\{^1H\}$ NMR (175 MHz) δ 31.03, 31.05, 31.9, 45.8, 46.5, 51.5, 53.7, 98.9, 100.0, 100.4, 100.8, 124.5, 127.3, 128.2, 129.9, 131.1, 131.2, 134.9, 135.6, 136.6, 158.7, 163.1, 172.7, 176.5, 196.4, 196.9; ESI-MS obsd 532.1466, calcd 532.1468 [$(M)^+$, M = $C_{28}H_{29}BrN_4O_2$]; λ_{abs} (CH_2Cl_2) 364, 389, 546, 765 nm. A putative unknown bacteriochlorin was observed from the ^1H NMR spectrum, but may be present in lesser amount than shown in the ^1H NMR spectrum due to the poor solubility of the title compound. The product so-obtained could be used without further purification.

2,12-Dicarboethoxy-5-[4-(2-(triisopropylsilyl)ethynyl)phenyl]-8,8,18,18-tetramethylbacteriochlorin (BC-12). A solution of **BrBC-9** (4.4 mg, 7.4 μmol), **2** (11.5 mg, 29.9 μmol) and K_2CO_3 (12.9 mg, 93.3 μmol) in toluene/DMF (3.0 mL, 2:1) was deaerated by four freeze/pump/thaw cycles. A sample of $Pd(PPh_3)_4$ (9.2 mg, 8.0 μmol) was then added, and the resulting mixture was stirred 16 h at 70 °C. After allowing to cool to room temperature, CH_2Cl_2 and water were added. The organic layer was dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (1:1 to 0:1)]. The resulting crude product was further purified by one passage via SEC to afford a purple solid (4.1 mg, 72%): ^1H NMR (500 MHz) δ −1.30 (s, 1H), −1.21 (s, 1H), 1.24 (s, 18H), 1.62 (t, J = 7.2 Hz, 3H), 1.70 (t, J = 7.2 Hz, 3H), 1.87 (s, 6H), 1.97 (s, 6H), 3.91 (s, 2H), 4.37 (s, 2H), 4.68 (q, J = 7.2 Hz, 2H), 4.76 (q, J = 7.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H), 8.56 (d, J = 2.3 Hz, 1H), 8.70 (s, 1H), 9.18 (d, J = 2.1 Hz, 1H), 9.71 (s, 1H), 9.79 (s, 1H), the 2° proton of each TIPS group was not observed; $^{13}C\{^1H\}$ NMR (125 MHz) δ 11.4, 14.7, 14.8, 18.8, 31.0, 46.0, 46.2, 51.16, 51.21, 60.8, 61.0, 91.5, 97.5, 98.0, 100.4, 115.2, 121.4, 122.8, 123.1, 125.0, 126.3, 131.8, 131.9, 133.5, 134.1, 135.6, 136.1, 142.5, 161.1, 165.5, 165.7, 172.4, 173.3; ESI-MS obsd 770.4248, calcd 770.4222 [$(M)^-$, M = $C_{47}H_{58}N_4O_4Si$]; λ_{abs} (toluene) 357, 382, 533, 757 nm.

2,12-Dicarboethoxy-5-(4-ethynylphenyl)-8,8,18,18-tetramethylbacteriochlorin (BC-13). A solution of **BC-12** (3.0 mg, 3.9 μmol) in THF (3.0 mL) and water (30 μL) was treated overnight with TBAF/THF (1.0 M, 30 μL, 30 μmol) at room temperature. [The water was added because in an earlier trial, the reaction was not complete in 4 h.] Then CH_2Cl_2 and water were added. The organic layer was dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (1:1 to 0:1)] to afford a purple solid (2.2 mg, 94%): ^1H NMR (700 MHz) δ −1.29 (s, 1H), −1.20 (s, 1H), 1.62 (t, J = 7.2 Hz, 3H), 1.70 (t, J = 7.2 Hz, 3H), 1.88 (s, 6H), 1.97 (s, 6H), 3.28 (s, 1H), 3.91 (s, 2H), 4.37 (s, 2H), 4.68 (q, J = 7.2 Hz, 2H), 4.76 (q, J = 7.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 8.53 (d, J = 2.3 Hz, 1H), 8.71 (s, 1H), 9.19 (d, J = 2.1 Hz, 1H), 9.71 (s, 1H), 9.78 (s, 1H); $^{13}C\{^1H\}$ NMR (175 MHz) δ 14.70, 14.72, 30.9, 31.0, 46.0, 46.2, 51.1, 51.2, 60.8, 61.0, 83.7, 97.5, 98.0, 100.5, 115.0, 121.3, 121.4, 123.3, 124.8, 126.5, 131.9, 132.0, 133.4, 134.2, 135.5, 136.2, 143.0, 158.7, 161.2, 165.5, 165.7, 172.3, 173.4; ESI-MS obsd 615.2949, calcd 615.2966 [$(M+H)^+$, M = $C_{38}H_{38}N_4O_4$]; λ_{abs} (toluene) 357, 382, 533, 757 nm.

5-(4-Ethynylphenyl)-8,8,18,18-tetramethyl-2,12-di-*p*-tolylbacteriochlorin (BC-14). A solution of **BrBC-2** (3.0 mg, 4.8 μmol), **2** (10.5 mg, 27.3 μmol) and K_2CO_3 (7.3 mg, 53 μmol) in toluene/DMF (3.0 mL, 2:1) was deaerated by four freeze/pump/thaw cycles. A sample of $Pd(PPh_3)_4$ (7.3 mg, 6.3 μmol) was then added, and the resulting mixture was stirred for 14 h at 70 °C. After allowing to cool to room temperature, CH_2Cl_2 and water were added. The organic layer was dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (2:1 to 1:1)]. The resulting crude product was further purified by one passage via SEC to afford a green solid. The solid was dissolved in THF (2.0 mL) and treated with TBAF/THF (1.0 M, 10 μL, 10 μmol) at room temperature for 4 h. Then CH_2Cl_2 and water were added. The organic layer was dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (2:1 to 1:1)] to afford a green solid (1.9 mg, 61% over two steps): ^{1}H NMR (700 MHz) δ −1.83 (s, 1H), −1.74 (s, 1H), 1.83 (s, 6H), 1.92 (s, 6H), 2.56 (s, 3H), 2.61 (s, 3H), 3.25 (s, 1H), 4.00 (s, 2H), 4.44 (s, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 7.9 Hz, 2H), 7.58 (d, J = 8.1 Hz, 2H), 7.81, 7.85 (AB, J = 7.5 Hz, 4H), 8.00 (d, J = 7.6 Hz, 2H), 8.10–8.14 (m, 3H), 8.72 (s, 1H), 8.76 (s, 1H), 8.84 (s, 1H), 8.87 (s, 1H); ^{13}C{^{1}H} NMR (175 MHz) δ 21.36, 21.42, 30.9, 31.0, 46.0, 51.4, 51.5, 78.1, 83.9, 121.5, 126.9, 129.6, 129.8, 130.96, 131.04, 131.6, 132.2, 132.6, 136.7, 137.2, 140.5, 144.0; ESI-MS obsd 650.3398, calcd 650.3404 [$(M + H)^+$, M = $C_{46}H_{42}N_4$]; λ_{abs} (CH_2Cl_2) 355, 377, 505, 707, 741 nm.

5-(4-Formylphenyl)-8,8,18,18-tetramethyl-10,20-diphenylbacteriochlorin (BC-15). Following a general procedure[19] with modification, a solution of **BrBC-8** (0.80 mg, 1.3 μmol), **3** (1.5 mg, 10 μmol), P(*o*-tol)$_3$ (2.0 mg, 6.6 μmol) and K_2CO_3 (2.0 mg, 14 μmol) in toluene/DMF (900 μL, 2:1) was deaerated by four freeze/pump/thaw cycles. A sample of $Pd_2(dba)_3$ (1.3 mg, 1.4 μmol) was then added, and the resulting mixture was stirred for 15 h at 80 °C. The mixture was allowed to cool to room temperature, concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (1:1) to CH_2Cl_2] to afford a green solid (0.50 mg, 60%): ^{1}H NMR (700 MHz) δ −1.52 (s, 1H), −1.42 (s, 1H), 1.42 (s, 6H), 1.52 (s, 6H), 3.83 (s, 2H), 4.37 (s, 2H), 7.54–7.60 (m, 4H), 7.61–7.66 (m, 3H), 7.74–7.76 (m, 1H), 7.77–7.79 (m, 1H), 7.85–7.88 (m, 3H), 7.95–7.96 (m, 1H), 7.97 (d, J = 7.7 Hz, 2H), 8.15 (d, J = 7.7 Hz, 2H), 8.54 (dd, J = 4.6, 1.9 Hz, 1H), 8.76 (s, 1H), 10.26 (s, 1H); ^{13}C{^{1}H} NMR (175 MHz) δ 29.9, 30.1, 47.0, 47.3, 55.2, 55.4, 99.5, 113.4, 114.5, 115.8, 121.1, 121.5, 123.3, 124.1, 126.3, 126.4, 127.55, 127.64, 129.2, 132.7, 133.7, 133.8, 134.2, 135.3, 136.1, 137.9, 139.6, 140.7, 140.8, 151.3, 154.1, 158.2, 166.0, 168.2, 192.3; ESI-MS obsd 627.3115, calcd 627.3118 [$(M + H)^+$, M = $C_{43}H_{38}N_4O$]; λ_{abs} (CH_2Cl_2) 353, 374, 512, 725 nm.

5-[4-(2-(Triisopropylsilyl)ethynyl)phenyl]-8,8,18,18-tetramethyl-10,20-diphenylbacteriochlorin (BC-16). Following a general procedure[28] with modification, a solution of **BrBC-8** (5.8 mg, 9.6 μmol), **2** (9.1 mg, 24 μmol), P(*o*-tol)$_3$ (7.5 mg, 25 μmol) and K_2CO_3 (14.5 mg, 105 μmol) in toluene/DMF (4.5 mL, 2:1) was deaerated by four freeze/pump/thaw cycles. A sample of $Pd_2(dba)_3$ (9.7 mg, 11 μmol) was then added, and the resulting mixture was stirred for 16 h at 70 °C. After allowing to cool to room temperature, CH_2Cl_2 and water were added. The organic layer was dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (3:1)]. The resulting crude product was further purified by one passage via SEC to afford a green solid (4.3 mg, 57%): ^{1}H NMR (500 MHz) δ −1.57 (s, 1H), −1.53 (s, 1H), 1.21 (s, 18H), 1.41 (s, 6H), 1.52 (s, 6H), 3.49 (s, 3H), 3.86 (s, 2H), 4.36 (s, 2H), 7.53–7.66 (m, 6H), 7.68–7.78 (m, 5H), 7.83–7.91 (m, 5H), 7.94 (dd, J = 4.6, 1.8 Hz, 1H), 8.53 (dd, J = 4.6, 1.9 Hz, 1H), 8.73 (s, 1H); ^{13}C{^{1}H} NMR (175 MHz) δ 11.4, 18.8, 29.9, 30.1, 41.1, 50.9, 55.3, 55.4, 91.0, 99.4, 107.3, 114.1, 114.6, 115.5, 121.6, 121.8, 122.3, 123.7, 126.29, 126.34, 127.5, 127.6, 131.5, 131.9, 133.7, 133.8, 134.8, 135.8, 138.0, 139.2, 140.9, 141.0, 144.8, 155.1, 157.7, 166.1, 167.7; ESI-MS obsd 778.4427, calcd 778.4425 [$(M)^+$, M = $C_{53}H_{58}N_4Si$]; λ_{abs} (toluene) 355, 365, 377, 513, 725 nm.

15-Bromo-5-[4-(2-(triisopropylsilyl)ethynyl)phenyl]-8,8,18,18-tetramethyl-10,20-diphenylbacteriochlorin (BrBC-16). Following a reported procedure,[16] a solution of **BC-16** (5.6 mg, 7.3 μmol) in freshly distilled THF (6.0 mL) was treated with 0.26 mL of NBS solution (1.3 mg, 7.3 μmol, from 28 mM freshly prepared THF stock solution) at room temperature for 10 min. The resulting solution was poured into saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (2:1)] to give a purple solid (5.6 mg, 89%): ^{1}H NMR (700 MHz) δ −1.534 (s, 1H), −1.527 (s, 1H), 1.21 (s, 18H), 1.37 (s, 6H), 1.49 (s, 6H), 3.49 (s, 3H), 3.83 (s, 2H), 4.48 (s, 2H), 7.54–7.59 (m, 4H), 7.61–7.65 (m, 3H), 7.70, 7.74 (AB, ^2J = 8.0 Hz, 4H), 7.77 (dd, J = 4.6, 1.8 Hz, 1H), 7.82–7.86 (m, 4H), 7.92 (dd, J = 4.6, 1.8 Hz, 1H), 8.90 (dd, J = 4.6, 1.9 Hz, 1H); ^{13}C{^{1}H} NMR (175 MHz) δ 11.4, 14.1, 18.8, 30.0, 30.4, 46.5, 47.2, 55.7, 58.3, 91.3, 100.2, 107.1, 114.1, 115.4, 116.4, 122.5, 122.8, 123.0, 123.5, 124.2, 126.31, 126.34, 127.6, 127.7, 131.5, 131.8, 131.9, 133.4, 133.6, 133.9, 136.6, 138.1, 139.2, 140.6, 140.9, 143.8, 156.2, 158.4, 165.9, 169.2; ESI-MS obsd 857.3587, calcd 857.3609 [$(M + H)^+$, M = $C_{53}H_{57}BrN_4Si$]; λ_{abs} (CH_2Cl_2) 358, 379, 526, 729 nm.

5-(4-Ethynylphenyl)-8,8,18,18-tetramethyl-10,20-diphenylbacteriochlorin (BC-17). Following a general procedure[19] with modification, a solution of **BC-17** (2.4 mg, 3.1 μmol) in THF (2.0 mL) was treated with TBAF/THF (1.0 M, 10 μL, 10 μmol) at room temperature for 2 h. Then CH_2Cl_2 and water were added. The organic layer was dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (2:1)] to afford a green solid (1.8 mg, 94%): ^{1}H NMR (500 MHz) δ −1.56 (s, 1H), −1.52 (s, 1H), 1.42 (s, 6H), 1.52 (s, 6H), 3.22 (s, 1H), 3.85 (s, 2H), 4.36 (s, 2H), 7.53–7.66 (m, 6H), 7.72–7.79 (m, 1H), 7.75 (s, 4H), 7.81–7.91 (m, 5H), 7.94 (d, J = 3.0 Hz, 1H), 8.53 (d, J = 2.6 Hz, 1H), 8.75 (s, 1H); ^{13}C{^{1}H} NMR (125 MHz) δ 29.9, 30.1, 47.0, 47.1, 55.32, 55.34, 99.4, 113.9, 114.5, 115.5, 120.8, 121.56, 121.59, 122.9, 123.7, 126.28, 126.34, 127.5, 127.6, 131.5, 132.0, 133.7, 133.8, 134.7, 135.8, 138.0, 139.3, 140.8, 140.9, 145.3, 154.9, 157.8, 166.0, 167.8; ESI-MS obsd 622.3097, calcd 622.3099 [$(M)^+$, M = $C_{44}H_{38}N_4$]; λ_{abs} (CH_2Cl_2) 353, 363, 375, 512, 725 nm.

15-(4-Formylphenyl)-5-(4-ethynylphenyl)-8,8,18,18-tetramethyl-10,20-diphenylbacteriochlorin (BC-18). Following a general procedure[19] with modification, a solution of **BrBC-16** (5.7 mg, 6.6 μmol), **3** (11.8 mg, 78.7 μmol), P(o-tol)$_3$ (16.4 mg, 53.9 μmol) and K_2CO_3 (21.4 mg, 155 μmol) in toluene/DMF (4.5 mL, 2:1) was deaerated by five freeze/pump/thaw cycles. A sample of $Pd_2(dba)_3$ (14.0 mg, 15.3 μmol) was then added, and the resulting mixture was stirred for 15 h at 70 °C. After allowing to cool to room temperature, CH_2Cl_2 and water were added. The organic layer was dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (2:1 to 0:1)]. The resulting crude product was dissolved in THF (6.0 mL) and treated with TBAF/THF (1.0 M, 15 μL, 15 μmol) at room temperature for 3 h. Then CH_2Cl_2 and water were added. The organic layer was dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (2:1 to 0:1)]. The resulting crude with further purified by one passage via SEC to afford a brown-green solid (3.3 mg, 64%) which contained 4-formylphenylboronic acid (about 6.7% of the total mass, 25% in mole ratio) as the main impurity. The resulting product was used without further purification. The following NMR signals are listed for the bacteriochlorin: ^{1}H NMR (700 MHz) δ −1.52 (s, 1H), −1.49 (s, 1H), 1.40 (s, 12H), 3.23 (s, 1H), 3.85 (s, 2H), 3.87 (s, 2H), 7.53–7.63 (m, 7H), 7.76–7.77 (m, 3H), 7.79 (dd, J = 4.6, 2.0 Hz, 1H), 7.81 (dd, J = 4.8, 1.8 Hz, 1H), 7.83 (dd, J = 4.7, 2.0 Hz, 1H), 7.84–7.86 (m, 4H), 7.91 (dd, J = 4.8, 2.0 Hz, 1H), 7.98 (d, J = 7.8 Hz, 2H), 8.16 (d, J = 7.7 Hz, 2H), 10.26 (s, 1H); ^{13}C{^{1}H} NMR (175 MHz) δ 29.92, 29.97, 46.9, 47.1, 55.3, 55.5, 77.7, 83.7, 113.2, 114.0, 115.5, 115.9, 121.1, 121.6, 122.5, 122.8, 123.2, 126.0, 126.32, 126.35, 127.61, 127.64, 129.2, 129.5, 129.6, 129.9, 131.6, 132.0, 132.8, 133.70, 133.73, 135.1,

135.4, 135.8, 138.2, 138.7, 140.95, 140.98, 144.6, 150.8, 155.6, 156.9, 166.7, 167.2, 192.2; ESI-MS obsd 726.3347, calcd 726.3353 [$(M)^+$, M = $C_{51}H_{42}N_4O$]; λ_{abs} (toluene) 360, 380, 522, 730 nm.

5-Methoxy-15-phenyl-8,8,18,18-tetramethylbacteriochlorin (BC-19). Following a general procedure[28] with modification, samples of **BrBC-4** (11.0 mg, 22.9 μmol), **4** (11.3 mg, 55.4 μmol) and K_2CO_3 (25.0 mg, 181 μmol) were added to toluene/DMF (6.0 mL, 2:1) under argon in a Schlenk flask. The system was deaerated by three freeze/pump/thaw cycles. A sample of $Pd(PPh_3)_4$ (10.2 mg, 8.83 μmol) was then added, and the resulting mixture was stirred overnight at 80 °C. After allowing to cool to room temperature, CH_2Cl_2 and water were added. The organic layer was dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (2:1)] to afford a purple solid (8.7 mg, 80%): ^{1}H NMR (500 MHz) δ −2.18 (s, 1H), −1.93 (s, 1H), 1.87 (s, 6H), 1.97 (s, 6H), 4.03 (s, 2H), 4.41 (s, 2H), 4.50 (s, 3H), 7.62–7.70 (m, 3H), 7.83–7.86 (m, 2H), 8.16 (dd, J = 4.5, 1.9 Hz, 1H), 8.63 (dd, J = 4.6, 2.0 Hz, 1H), 8.67 (s, 1H), 8.68 (s, 1H), 8.70 (dd, J = 4.4, 2.0 Hz, 1H), 8.93 (dd, J = 4.4, 2.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz) δ 31.0, 31.2, 45.2, 45.8, 47.5, 51.7, 65.2, 97.0, 97.3, 113.2, 117.3, 120.7, 122.5, 122.9, 131.5, 132.2, 135.0, 135.5, 136.3, 137.3, 142.8, 153.3, 158.8, 168.6, 168.8; ESI-MS obsd 477.2650, calcd 477.2649 [$(M + H)^+$, M = $C_{31}H_{32}N_4O$]; λ_{abs} (CH_2Cl_2) 348, 358, 369, 507, 713 nm.

15-[4-(2-(*tert*-Butoxycarbonyl)ethyl)phenyl]-3,13-bis[3,5-bis(2-((*tert*-butyldimethylsilyl)oxy)ethylamidocarbonyl)phenyl]-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (BC-21). Following a general procedure,[83] samples of **BrBC-20** (35.0 mg, 24.4 μmol), **5** (40.5 mg, 121 μmol), $Pd(PPh_3)_4$ (11.3 mg, 9.70 μmol), K_2CO_3 (20.2 mg, 146 μmol) and toluene/DMF [2.40 mL (2:1), deaerated by bubbling with argon for 45 min] were added to a Schlenk flask and deaerated by three freeze/pump/thaw cycles. The reaction mixture was stirred at 90 °C for 16 h. The reaction mixture was allowed to cool to room temperature, concentrated to dryness, diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic layer was separated, dried (Na_2SO_4) and concentrated. Column chromatography [twice, silica, CH_2Cl_2/ethyl acetate (7:3 to 11:9)] afforded a green solid (15.0 mg, 39%): ^{1}H NMR (400 MHz) δ–1.55 (s, 1H), –1.19 (s, 1H), 0.086 (s, 12H), 0.093 (s, 12H), 0.871 (s, 18H), 0.879 (s, 18H), 1.50 (s, 9H), 1.85 (s, 6H), 1.99 (s, 6H), 2.55 (t, J = 5.4 Hz, 2H), 2.86 (t, J = 5.4 Hz, 2H), 3.63 (s, 3H), 3.69–3.73 (m, 8H), 3.85–3.91 (m, 10H), 4.37 (s, 2H), 6.68 (t, J = 3.6 Hz, 2H), 6.88 (t, J = 3.6 Hz, 2H), 7.01 (d, J = 5.7 Hz, 2H), 7.43 (d, J = 5.7 Hz, 2H), 7.82 (s, 2H), 8.05 (s, 1H), 8.44 (s, 1H), 8.65–8.66 (m, 3H), 8.72 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz) δ –5.03, –5.02, 18.54, 18.56, 26.2, 28.4, 30.9, 31.32, 31.36, 36.8, 42.6, 42.7, 45.2, 46.0, 47.8, 52.3, 62.1, 62.2, 63.4, 80.7, 97.4, 97.8, 113.7, 123.2, 123.3, 124.4, 127.1, 127.6, 128.0, 131.9, 132.6, 133.4, 133.8, 134.0, 134.1, 134.2, 134.8, 135.5, 136.1, 138.96, 139.00, 139.4, 139.8, 155.1, 161.2, 166.6, 167.1, 169.3, 169.4, 172.6; MALDI-MS (POPOP[84] matrix) obsd 1560.0945; ESI-MS obsd 803.4280, calcd 803.4282 [$(M + 2Na)^{2+}$, M = $C_{86}H_{128}N_8O_{11}Si_4$]; λ_{abs} (CH_2Cl_2) 367, 518, 731 nm.

15-(3-Aminophenyl)-2,12-bis[3,5-bis(*tert*-butoxycarbonyl)phenyl]-3,13-dicarbomethoxy-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (BC-23). Following a general procedure,[83] samples of **BrBC-22** (9.2 mg, 8.0 μmol), **6** (8.8 mg, 40 μmol), $Pd(PPh_3)_4$ (2.8 mg, 2.4 μmol), K_2CO_3 (13 mg, 96 μmol) and toluene/DMF [0.80 mL (2:1), deaerated by bubbling with argon for 45 min] were added to a Schlenk flask and deaerated by three freeze/pump/thaw cycles. The reaction mixture was stirred at 90 °C for 20 h. The reaction mixture was allowed to cool to room temperature, concentrated to dryness, diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic layer was separated, dried (Na_2SO_4) and concentrated. Column chromatography [twice, silica, CH_2Cl_2/ethyl acetate (47:3)] afforded a red solid (5.5 mg, 62%): ^{1}H NMR (300 MHz) δ–1.40 (s, 1H), –1.09 (s, 1H), 1.64 (s, 18H), 1.66 (s, 18H), 1.74 (s, 3H), 1.77 (s,

3H), 1.83 (s, 3H), 1.85 (s, 3H), 3.52 (s, 3H), 3.86 (s, 2H), 4.20 (s, 3H), 4.30 (s, 3H), 4.37 (s, 2H), 6.93 (d, J = 2.4 Hz, 1H), 7.10 (s, 2H), 7.41 (t, J = 2.4 Hz, 1H), 8.50 (s, 1H), 8.60 (s, 1H), 8.75 (d, J = 1.8 Hz, 2H), 8.86 (s, 1H), 8.88 (s, 1H), 8.90 (d, J = 1.8 Hz, 2H), the two amino protons were not observed; MALDI-MS (POPOP[84] matrix) obsd 1061.8424; ESI-MS MS obsd 1060.5585, calcd 1060.5591 [$(M + H)^+$, M = $C_{67}H_{77}N_5O_{13}$]; λ_{abs} (CH_2Cl_2) 374, 527, 742 nm.

15-Bromo-2,3,12,13-tetracarboethoxy-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (BrBC-24). Following a reported procedure[14] with some modification, a solution of **BC-24** (12 mg, 17 μmol) in THF (7 mL) was treated with NBS (3.1 mg, 17 μmol) at room temperature. The reaction was monitored by absorption spectroscopy. When the Q_x band shifted from 548 nm to 560 nm (~1 h), the reaction mixture was diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$ immediately. The organic layer was dried (Na_2SO_4), concentrated and purified by column chromatography [silica, CH_2Cl_2/ethyl acetate (4:1)] to afford a purple solid (8.3 mg, 57%): ^{1}H NMR (500 MHz, toluene-d_8) δ −0.89 (s, 1H), −0.64 (s, 1H), 1.56–1.53 (m, 6H), 1.68–1.65 (m, 6H), 1.98 (s, 6H), 1.99 (s, 6H), 4.18 (s, 2H), 4.30 (s, 3H), 4.38 (s, 2H), 4.69–4.62 (m, 4H), 4.96–4.89 (m, 4H), 10.15 (s, 1H), 10.31 (s, 1H); ^{13}C{^{1}H} NMR (175 MHz, toluene-d_8) δ 13.9, 13.99, 14.01, 14.1, 30.0, 30.5, 30.7, 45.50, 45.52, 47.2, 54.3, 60.83, 60.86, 61.4, 61.7, 64.0, 98.43, 98.46, 99.9, 119.9, 120.7, 130.47, 130.53, 133.1, 135.3, 159.0, 161.6, 163.7, 164.1, 166.7, 166.9, 170.3, 174.8; ESI-MS obsd 767.2280, calcd 767.2286 [$(M + H)^+$, M = $C_{37}H_{43}BrN_4O_9$]; λ_{abs} (CH_2Cl_2) 362, 371, 560, 757 nm.

Cu(II)-15-Bromo-2,3,12,13-tetracarboethoxy-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (BrBC-25). Following a reported procedure[70] with some modification, a solution of **BrBC-24** (5.0 mg, 6.5 μmol) in anhydrous DMF (1.6 mL) was treated with copper(II) acetate (59.0 mg, 0.325 mmol) under an argon atmosphere. The reaction mixture was stirred at 80 °C for 11 h. The mixture was allowed to cool to room temperature. The Q_y band had shifted from 757 nm to 787 nm in the absorption spectrum. The disappearance of fluorescence showed that the reaction was completed. The reaction mixture was washed with brine and water. The organic layer was dried (Na_2SO_4) and concentrated to afford a blue solid (4.5 mg, 83%): TLC analysis [silica, CH_2Cl_2/ethyl acetate (4:1)] showed only one spot. ESI-MS obsd 828.1412 calcd 828.1426 [$(M + H)^+$, M = $C_{37}H_{41}BrCuN_4O_9$]; λ_{abs} (toluene) 352, 388, 581, 787 nm.

Cu(II)-15-(4-(tosylamino)phenyl)-2,3,12,13-tetracarboethoxy-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (BC-26). Following a reported procedure with some modification,[83] a mixture of **BrBC-25** (2.1 mg, 2.5 μmol), **8** (3.4 mg, 6.4 μmol), $Pd(PPh_3)_4$ (0.9 mg, 0.8 μmol) and K_2CO_3 (4.3 mg, 31 μmol) was placed in a Schlenk flask which was then pump-purged three times with argon. Anhydrous DMF and toluene were deaerated by bubbling argon for 0.5 h. Toluene/DMF (375 μL, 2:1) was added to the Schlenk flask under an argon atmosphere and the reaction mixture was deaerated by three freeze/pump/thaw cycles. The reaction mixture was stirred at 90 °C for 12 h. Then the mixture was allowed to cool to room temperature, diluted with CH_2Cl_2 and washed with aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4), concentrated and purified by one time of SEC (Bio-beads S-X1, 200–400 mesh, toluene) to afford a purple solid (2.0 mg, 79%): MALDI-MS obsd 994.615 $(M)^+$, calcd 994.275 [$(M)^+$, M = $C_{50}H_{53}CuN_5O_{11}S$]; ESI-MS obsd 994.2720, calcd 994.2753 [$(M)^+$, M = $C_{50}H_{53}CuN_5O_{11}S$]; λ_{abs} (toluene) 350, 388, 578, 788 nm.

Cu(II)-15-(4-(2-Chloro-*N*-tosylacetamido)phenyl)-2,3,12,13-tetracarboethoxy-5-methoxy-8,8,18,18-tetramethylbacteriochlorin (BC-27). Following a reported procedure,[77] a mixture of **BC-26** (1.9 mg, 1.9 μmol) and triethylamine (2.4 μL, 1.7 mg, 17 μmol) in anhydrous CH_2Cl_2 (35 μL) was treated with a solution composed of chloroacetyl chloride (0.90 μL, 1.3 mg,

12 μmol) and anhydrous CH_2Cl_2 (35 μL) under an argon atmosphere. The reaction mixture was stirred at room temperature until TLC analysis [silica, CH_2Cl_2/ethyl acetate (2:1)] showed disappearance of the starting material (~2 h). Then the mixture was diluted with CH_2Cl_2 and washed with aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4) and concentrated to give a purple solid (1.9 mg, 93%): MALDI-MS obsd 1069.984, calcd 1070.247 [$(M)^+$, M = $C_{52}H_{54}ClCuN_5O_{12}S$]; ESI-MS obsd 1071.25161 [$(M + H)^+$, M = $C_{52}H_{54}ClCuN_5O_{12}S$], calcd 1071.25470; λ_{abs} (toluene) 350, 388, 578, 788 nm.

15-[4-(Hydroxymethyl)phenyl]-5-methoxy-8,8,18,18-tetramethyl-2,12-di-*p*-tolylbacteriochlorin (BC-28). Following a Suzuki coupling procedure,[19] samples of **BrBC-3** (23.2 mg, 35.2 μmol), **9** (26.1 mg, 111 μmol) and K_2CO_3 (59.4 mg, 430 μmol) were placed into a 10 mL Schlenk flask and dissolved in toluene/DMF (4 mL, 2:1). The resulting mixture was deaerated by three freeze/pump/thaw cycles under argon. Then $Pd(PPh_3)_4$ (18.4 mg, 15.9 μmol) was added, and the reaction mixture was stirred at 90 °C for 18 h. The mixture was allowed to cool to room temperature and then diluted with CH_2Cl_2. The organic layer was washed (aqueous $NaHCO_3$), separated, dried (Na_2SO_4), and filtered. The filtrate was concentrated and chromatographed (silica, CH_2Cl_2) to afford a black green solid (20.0 mg, 83%): ^{1}H NMR (400 MHz) δ –1.86 (s, 1H), –1.61 (s, 1H), 1.82 (s, 6H), 1.91 (s, 6H), 2.56 (s, 3H), 2.61 (s, 3H), 4.00 (s, 2H), 4.40 (s, 2H), 4.51 (s, 3H), 4.98 (s, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.59 (d, J = 7.6 Hz, 2H), 7.68 (d, J = 7.7 Hz, 2H), 7.87 (d, J = 7.9 Hz, 2H), 7.99 (d, J = 8.0 Hz, 2H), 8.14–8.16 (m, 3H), 8.83 (d, J = 8.8 Hz, 2H), 8.96 (d, J = 9.0 Hz 1H); ^{13}C{^{1}H} NMR (100 MHz) δ 21.37, 21.41, 24.9, 30.9, 31.0, 45.4, 46.0, 47.4, 51.8, 65.1, 65.5, 95.8, 96.2, 112.7, 116.2, 121.0, 126.5, 129.6, 129.8, 130.3, 131.0, 131.1, 132.4, 133.1, 133.6, 133.98, 134.02, 134.6, 135.0, 135.1, 135.8, 136.4, 137.0, 137.1, 139.7, 142.4, 153.6, 158.9, 169.2, 169.5; MALDI-MS (POPOP[84] matrix) obsd 686.9, ESI-MS obsd 686.3599, calcd 686.3615 [$(M)^+$, M = $C_{46}H_{46}N_4O_2$]; λ_{abs} (CH_2Cl_2) 377, 487, 518, 736 nm.

15-[4-(*S*-Acetylthiomethyl)phenyl]-5-methoxy-8,8,-18,18-tetramethyl-2,12-di-*p*-tolylbacteriochlorin (BC-29). Following a general procedure[81] with modification, a solution of **BC-28** (11.6 mg, 16.9 μmol) in dichloromethane (2 mL) was treated with diisopropylethylamine (15 μL, 86 μmol) at 0 °C under argon followed by methanesulfonyl chloride (7.0 μL, 90 μmol). After stirring at room temperature for 2 h, diisopropylethylamine (15 μL) and methanesulfonyl chloride (7 μL) were added. The reaction mixture was stirred for another 2 h at room temperature. The mixture was diluted with CH_2Cl_2 and then washed (aqueous $NaHCO_3$), dried (Na_2SO_4) and concentrated. The resulting residue was dissolved in CH_2Cl_2/methanol (3 mL, 2:1) whereupon potassium thioacetate (18.1 mg, 159 μmol) was added at room temperature under argon. The solution was stirred for 3 h, then washed with water, dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/CH_2Cl_2 (2:1)] to afford a dark-green solid (9.4 mg, 75%): ^{1}H NMR (300 MHz) δ –1.87 (s, 1H), –1.62 (s, 1H), 1.81 (s, 6H), 1.91 (s, 6H), 2.48 (s, 3H), 2.52 (s, 2H), 2.56 (s, 3H), 2.61 (s, 3H), 3.99 (s, 2H), 4.40 (s, 2H), 4.51 (s, 3H), 7.51 (d, J = 7.5 Hz, 2H), 7.57–7.60 (m, 4H), 7.79 (d, J = 7.8 Hz, 2H), 7.98 (d, J = 8.0 Hz, 2H), 8.08 (s, 1H), 8.13 (s, 1H), 8.15 (s, 1H), 8.81 (d, J = 8.8 Hz, 2H), 8.95 (s, 1H); ^{13}C{^{1}H} NMR (175 MHz) δ 195.4, 169.5, 169.2, 158.9, 154.3, 153.6, 141.9, 137.2, 137.0, 136.5, 135.8, 135.0, 134.6, 134.07, 134.04, 133.7, 133.1, 132.5, 131.10, 131.05, 131.0, 130.3, 129.8, 129.8, 129.7, 129.6, 129.3, 128.3, 121.1, 116.2, 112.6, 96.3, 95.8, 65.1, 51.8, 47.4, 46.0, 45.4, 33.5, 31.00, 30.97, 30.95, 30.93, 30.5, 21.43, 21.39; MALDI-MS (POPOP[84] matrix) obsd 744.9, ESI-MS obsd 758.3261, calcd 758.3261 [$(M + Na)^+$, M = $C_{43}H_{38}N_4O$]; λ_{abs} (CH_2Cl_2) 377, 485, 519, 736 nm.

15²-*N*-(4-*tert*-Butyldiphenylsilyloxy)phenyl-3-carboethoxy-2,12-diethyl-5-methoxy-8,8,18,18-tetramethylbacteriochlorin-13,15-dicarboximide (BC-30). Following a reported

procedure,[20] a mixture of **BrBC-7** (20 mg, 30 μmol), **1** (52 mg, 0.15 mmol), $Pd(PPh_3)_4$ (34 mg, 30 μmol), and Cs_2CO_3 (30 mg, 90 μmol) was dried under high vacuum in a Schlenk flask for 1 h. The flask was filled with THF (5 mL), flushed with CO and then stirred at 60 °C for 16 h under a CO atmosphere. The reaction mixture was allowed to cool to room temperature, diluted with CH_2Cl_2 (30 mL), washed with water (30 mL) and brine (30 mL), and then dried, concentrated to dryness and chromatographed (silica, CH_2Cl_2) to afford a purple solid (4.0 mg, 15%): ^{1}H NMR (700 MHz, CD_2Cl_2) δ –0.71 (s, 1H), –0.10 (s, 1H), 1.54 (s, 9H), 1.59 (t, J = 7.2 Hz, 3H), 1.71 (t, J = 7.8 Hz, 3H), 1.74 (t, J = 7.7 Hz, 3H), 1.90 (s, 6H), 1.91 (s, 6H), 3.70 (q, J = 7.8 Hz, 2H), 4.11 (q, J = 7.7 Hz, 2H), 4.22 (s, 3H), 4.25 (d, J = 1.6 Hz, 2H), 4.63 (d, J = 1.8 Hz, 2H), 4.73 (q, J = 7.2 Hz, 2H), 7.35–7.51 (m, 10H), 7.67–7.72 (m, 4H), 8.40 (s, 1H), 8.67 (s, 1H); ^{13}C{^{1}H} NMR (175 MHz, CD_2Cl_2) δ 14.7, 17.1, 17.2, 20.1, 20.3, 26.6, 31.08, 31.12, 45.0, 46.8, 49.0, 52.8, 62.6, 65.0, 94.2, 94.4, 101.3, 109.6, 120.0, 120.5, 128.16, 128.19, 128.21, 128.38, 128.43, 179.9, 128.46, 128.49, 128.9, 129.1, 129.9, 130.1, 130.2, 130.3, 130.8, 130.95, 131.01, 131.7, 132.3, 135.0, 135.36, 135.40, 135.43, 135.86, 135.92, 136.7, 138.2, 139.1, 139.3, 139.9, 160.0, 161.5, 165.3, 167.6, 167.7, 170.1; ESI-MS obsd 926.4329, calcd 926.4318 [$(M - H)^-$, M = $C_{56}H_{61}N_5O_6Si$]; λ_{abs} (toluene) 368, 402, 548, 734, 787 nm.

15^2-*N*-(4-Hydroxyphenyl)-13-carboethoxy-2,12-diethyl-5-methoxy-8,8,18,18-tetramethylbacteriochlorin-13,15-dicarboximide (BC-31). A solution of **BC-30** (4.0 mg, 4.3 μmol) in THF (2 mL) was treated with TBAF solution (10 μL, 1.0 M in THF) at room temperature for 1.5 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL), washed with water (20 mL × 2) and brine (20 mL), dried, concentrated to dryness and purified by chromatography [silica, hexanes/CH_2Cl_2 (4:1 to 1:1) to afford a purple solid (2.0 mg, 66%): ^{1}H NMR (500 MHz) δ –0.71 (s, 1H), –0.09 (s, 1H), 1.59 (t, J = 7.2 Hz, 3H), 1.71 (t, J = 7.7 Hz, 3H), 1.74 (t, J = 6.8 Hz, 3H), 1.89 (s, 6H), 1.90 (s, 6H), 3.70 (q, J = 7.6 Hz, 2H), 4.11 (q, J = 7.7 Hz, 2H), 4.25 (s, 2H), 4.63 (s, 2H), 4.73 (q, J = 7.2 Hz, 2H), 7.37–7.45 (m, 2H), 7.63–7.75 (m, 2H), 8.40 (s, 1H), 8.67 (s, 1H); ESI-MS obsd 690.3271, calcd 690.3286 [$(M + H)^+$, M = $C_{40}H_{43}N_5O_6$]; λ_{abs} (THF) 350, 369, 404, 551, 787 nm.

4,4,5,5-Tetramethyl-2-(4-(*N*,*N*-ditosylamino)phenyl)-1,3,2-dioxaborolane (8). Following a reported procedure,[73] a solution of **7** (100 mg, 0.456 mmol), triethylamine (139 mg, 0.191 mL, 1.37 mmol), and 4-dimethylaminopyridine (11 mg, 0.091 mmol) in CH_2Cl_2 was treated with tosyl chloride (174 mg, 0.913 mmol) at 0 °C under an argon atmosphere. The reaction mixture was stirred at room temperature for 24 h. Then the mixture was concentrated and purified by column chromatography [silica, CH_2Cl_2/ethyl acetate (5:1)] to give a white solid (173 mg, 72%): mp: 200–202 °C; ^{1}H NMR (500 MHz) δ 7.82–7.77 (m, 6H), 7.32 (d, J = 8.1 Hz, 4H), 7.02 (d, J = 8.3 Hz, 2H), 2.47 (s, 6H), 1.34 (s, 12H); ^{13}C{^{1}H} NMR (125 MHz) δ 145.0, 136.8, 136.7, 135.5, 130.82, 129.6, 128.6, 84.2, 24.9, 21.7; ESI-MS obsd 528.1675, calcd 528.1680 [$(M + H)^+$, M = $C_{26}H_{30}BNO_6S_2$].

Electronic supplementary information (ESI) available. Single-crystal X-ray data. CCDC 2125372 (**8**), 2120236 (**BC-6**), 2120266 (**BC-7**), and 2120133 (**BC-8**).

Conflicts of interest

The authors declare no competing financial interests.

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