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A *trans*-AB-Bacteriochlorin Building Block

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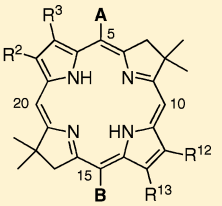
Supporting Information

ABSTRACT: Synthetic bacteriochlorins are of interest for fundamental studies in photochemistry because of their strong absorption in the near-infrared spectral region and close similarity with natural bacteriochlorophylls. A de novo route to 5-methoxybacteriochlorins entails self-condensation of a dihydrodipyrrin−acetal, which in turn is prepared from a 2-(2-nitroethyl)pyrrole species and an α,β-unsaturated ketone−acetal (e.g., 1,1-dimethoxy-4-methylpent-3-en-2-one). Here, four new results are reported concerning the synthesis of substituted bacteriochlorins. First, a new, scalable route to 1,1-dimethoxy-4-methylpent-3-en-2-one removes a significant previous impediment to the overall route. Second, the new route was employed to gain access to new α,β-unsaturated ketones and corresponding dihydrodipyrrins bearing alternative substituents in place of the dimethoxy unit. Third, a dihydrodipyrrin bearing a 1,3-dioxolan-2-yl moiety afforded the bacteriochlorin (30% yield) containing a 2-hydroxyethoxy substituent at the 5-position. Fourth, subsequent bromination proceeded regioselectively at the 15-position to give a *trans*-(5,15)-AB-bacteriochlorin building block. The linear 5,15-substitution pattern is attractive for a number of molecular designs. The results taken together afford deeper understanding of the scope and limitations of the de novo route and also advance the capabilities for tailoring synthetic bacteriochlorins.



a *trans*-**AB**-bacteriochlorin

INTRODUCTION

A longstanding theme in tetrapyrrole chemistry has been the de novo synthesis of building blocks for use in studies encompassing the broad fields of biomimetic chemistry, materials science, and clinical medicine. Porphyrins with up to four distinct meso-substituents are readily available.[1,2] The chemistry of chlorins is less developed, but chlorin macrocycles with substituents at designated meso- and β-pyrrole sites have been prepared.[3,4] For bacteriochlorins, synthetic access is under active development. Bacteriochlorins are of considerable interest owing to their strong absorption in the near-infrared spectral region, which is attractive for solar energy applications, low-energy photochemistry, and deep-tissue light-mediated medical therapies.[5,6] Realizing the scientific potential of bacteriochlorins has been largely crimped, however, by the limited means for synthesis of stable, tailorable bacteriochlorin building blocks.[7]

Distinct methods for the synthesis of bacteriochlorins entail semisynthesis procedures beginning with bacteriochlorophyll *a*,[8−14] hydrogenation[15,16] of (or addition to)[4,17−22] synthetic porphyrins and chlorins, and de novo routes.[5,23−28] Each has strengths and limitations. Representative building blocks available via such methods are shown in Chart 1. Derivatization of bacteriochlorophyll *a* to form the imide ring stabilizes the macrocycle and provides a convenient handle at the *N*-imide site for derivatization (entry I).[29] Still, few other sites are available given the nearly full complement of β-substituents. *meso*-Tetraarylbacteriochlorins (entry II) are readily synthesized, yet the presence of four identical substituents may limit the accessible architectures. Two variants on this approach include (i) a strategy by Brückner to achieve wavelength tunability[30] and (ii) a strategy by Boyle wherein *trans*-AB-porphyrins undergo vicinal dihydroxylation to afford the corresponding *trans*-AB-bacteriochlorin building blocks (albeit composed of a mixture of diastereomers, entry III).[31]

A rational, de novo route to synthetic bacteriochlorins[25,28] that we have been developing affords the following features: (1) resiliency of the macrocycles toward dehydrogenation upon routine handling by virtue of a geminal-dimethyl group in each reduced ring;[25] (2) a relatively concise (8-step) synthesis;[27,28] (3) characteristic bacteriochlorin absorption and photophysical features;[6,32] and (4) ability to introduce a variety of β-pyrrole substituents.[5,26,28] The synthetic route employs the acid-mediated, room-temperature self-condensation of a dihydrodipyrrin−acetal (Scheme 1). The use of TMSOTf in the presence of 2,6-di-*tert*-butylpyridine (2,6-DTBP) results in the formation of the 5-methoxybacteriochlorin in 8.4−63% yield, depending on the nature of the β-pyrrolic substituents.[28] The 5-methoxybacteriochlorin **BC-1** undergoes regioselective electrophilic bromination at the 15-position,[33] enabling further derivatization at this site via diverse palladium-coupling processes.[29,33] In contrast, bromination of the 5-unsubstituted bacteriochlorin **BC-2** (available via $BF_3{\cdot}OEt_2$ or other catalysis)[28] results in a mixture of mono- and dibromobacteriochlorins.[33]

While the de novo method has provided access to a larger palette of substituted bacteriochlorins versus those via semisynthesis or porphyrin/chlorin reductive transformations, numerous limitations have persisted: (1) the substituents at the 2- and 12-positions are identical with each other (R), as are those at the 3- and 13-position (R′) and (2) the 5-position has heretofore been occupied either by −H or $-OCH_3$. Accordingly, access to *trans*-AB-bacteriochlorins akin to those

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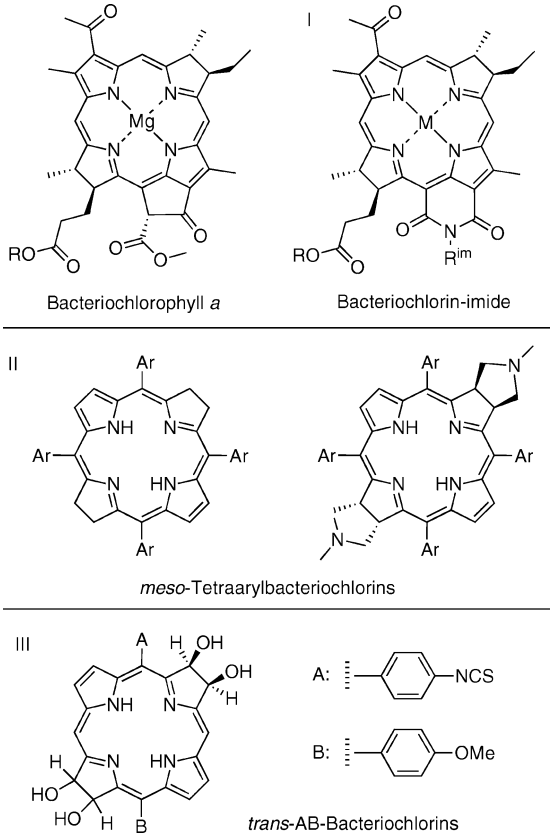
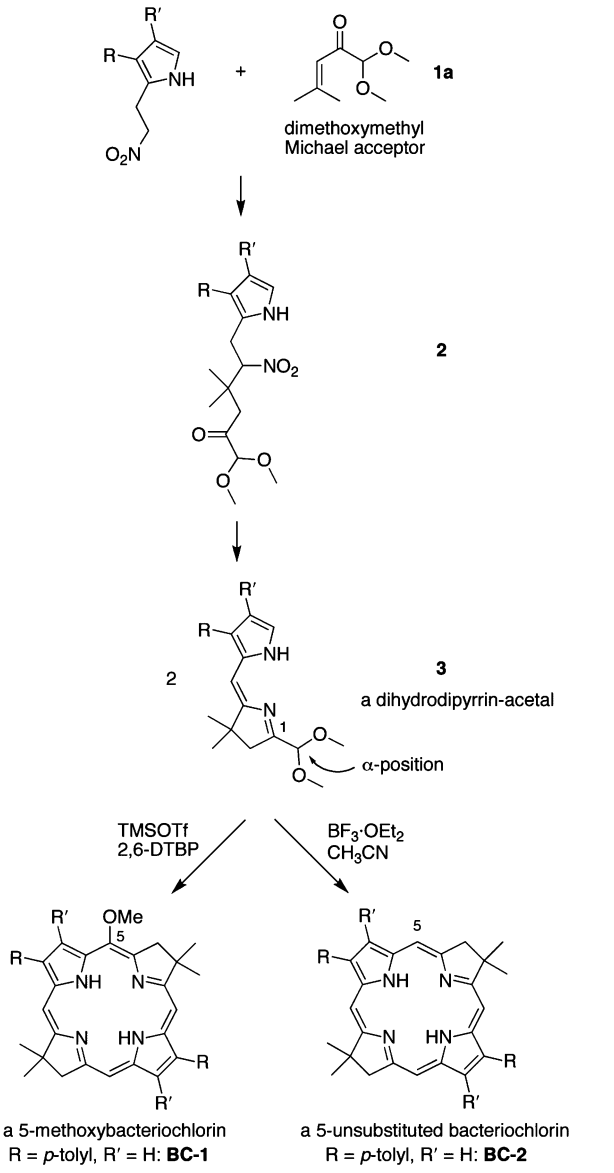
Chart 1. Bacteriochlorophyll *a* and Bacteriochlorin Building Blocks



Scheme 1. De Novo Route to Bacteriochlorins



of Boyle has not been available. A linear pattern of meso-AB-substituents is attractive for the design of diverse molecular architectures.

To achieve a *trans*-AB substituent pattern in bacteriochlorins, we considered that alternative dihydrodipyrrin units could be employed in the self-condensation. Because the acetal carbon of the dihydrodipyrrin−acetal (i.e., the α-carbon at the 1-position) forms the 5- and 15- carbons of the bacteriochlorin, alternative substituents at the "acetal" α-carbon in lieu of the methoxy group could be conveyed to the bacteriochlorin 5-position. The 15-position would then be accessible for bromination and subsequent substitution processes. This analysis is consistent with our current conceptualization of the mechanism of formation of the 5-methoxybacteriochlorin (Scheme 2). Treatment of the dihydrodipyrrin−acetal with TMSOTf affords an oxocarbenium ion and eliminates one molecule of methanol (as the trimethylsilyl ether); the oxocarbenium ion serves as the electrophile for attack by the pyrrole of the other dihydrodipyrrin−acetal. Repetition of this process eliminates a second molecule of methanol and affords the 5,15-dimethoxy-5,15-dihydrobacteriochlorin. Elimination of the third molecule of methanol results in the aromatic bacteriochlorin macrocycle containing the 5-methoxy substituent.[25]

Here, we report the synthesis of a handful of dihydrodipyrrins (containing diverse substituents at the 1-position) and investigate their conversion to bacteriochlorins. The synthesis of the dihydrodipyrrins was facilitated by the development of a new route to the α,β-unsaturated ketone−acetal **1a** (the Michael acceptor in formation of the dihydrodipyrrin−acetal), which also is reported herein. Among four new dihydrodipyrrins, one was found to afford the corresponding bacteriochlorin, which contains a 5-(2-hydroxyethoxy) substituent. Bromination of the 5-(2-hydroxyethoxy)-bacteriochlorin proceeded smoothly at the 15-position, affording the bacteriochlorin with reactive functional groups in a *trans*-AB architecture.

RESULTS AND DISCUSSION

Synthesis of New Michael Acceptors. *Reconnaissance.* The first reported synthesis of Michael acceptor **1a** was carried out in 56% yield when 2 mmol of mesityl oxide was treated with 10 mol % of diphenyl diselenide and excess ammonium peroxydisulfate in methanol (Scheme 3).[34] A subsequent scaled-up procedure (160-mmol scale) afforded **1a** in 29% yield.[25] Significant drawbacks to the synthesis of **1a** remain: (i) the use of expensive and toxic diphenyl diselenide; (ii) difficult purification including distillation followed by extensive chromatography, and (iii) relatively low yield. Moreover, the method has limited scope for introduction of substituents other than the dimethoxymethyl unit, which gives rise to the 5-methoxy substituent in the bacteriochlorin. Here, a

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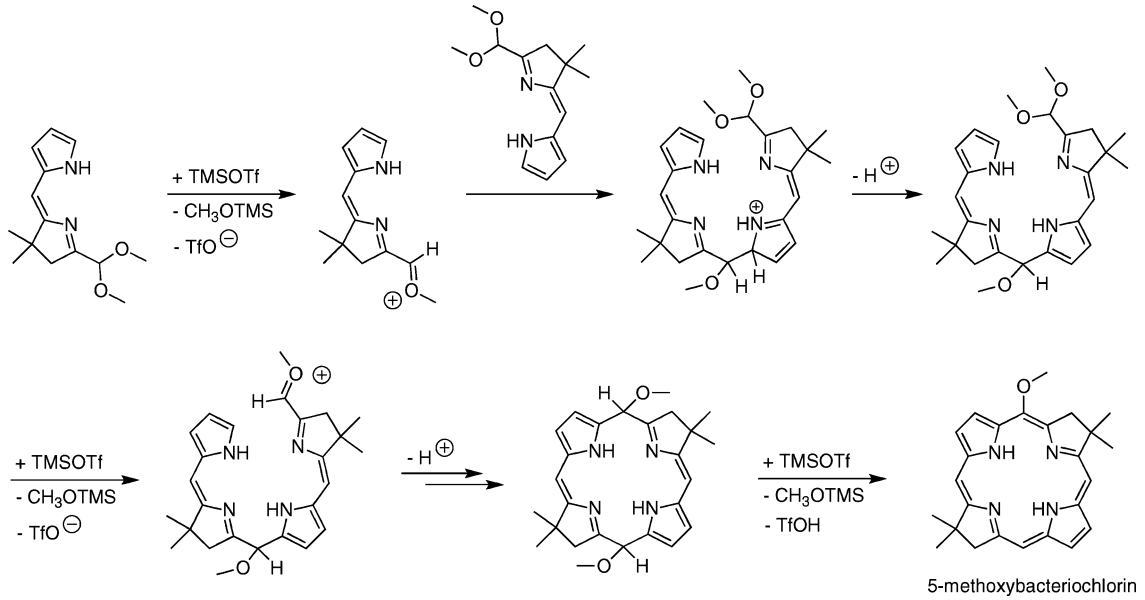
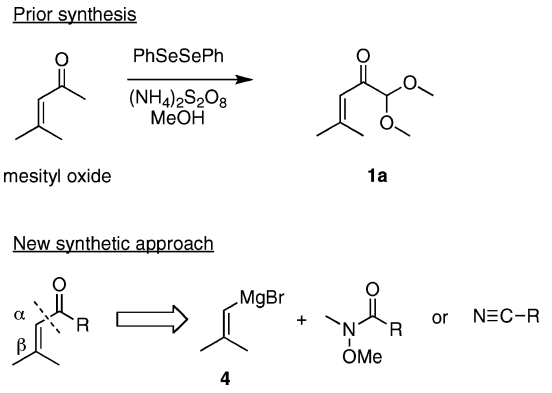
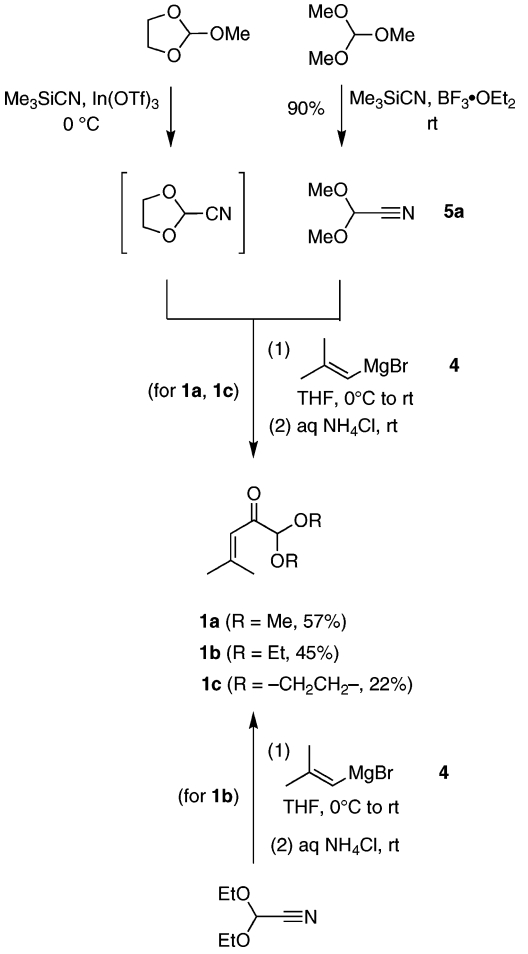
Scheme 2. Key Steps in the Formation of 5-Methoxybacteriochlorin



Scheme 3. Prior and Envisaged Routes to Michael Acceptors



Scheme 4. New Scalable Synthesis of Michael Acceptors via a Nitrile Intermediate



scalable and more versatile synthesis of Michael acceptors was envisaged to entail reaction of 2-methyl-1-propenylmagnesium bromide (**4**) with an acetal-containing nitrile or Weinreb amide (*N*-methoxy-*N*-methylamide; Scheme 3). To our knowledge, preparation of *α,β*-unsaturated ketones by reaction of a nitrile and a vinyl Grignard reagent has not been reported previously. Our attempts to prepare the 1,1-dialkoxy-*α,β*-unsaturated ketones via the Weinreb amide method were not successful (see the Supporting Information); however, we did prepare such compounds via the nitrile method. The *α,β*-unsaturated ketones bearing a single alkoxy group or other substituents examined herein were prepared via the Weinreb amide method (vide infra).

Synthesis of Michael Acceptors via Nitrile Method. Treatment of trimethyl orthoformate with an equimolar amount of trimethylsilyl cyanide in the presence of 10 mol % of $BF_3{\cdot}OEt_2$ afforded dimethoxyacetonitrile (**5a**).[35,36] The reaction was carried out at 255-mmol scale (11-fold larger than the literature procedure[35]). Reaction of **5a** with 1.2 molar equiv of Grignard reagent **4** at room temperature for 2.5 h followed by hydrolysis with saturated aqueous NH_4Cl afforded **1a** as the major product (Scheme 4). The two-step synthesis was carried out with streamlined workup procedures: distillation at atmospheric pressure gave **5a** in 90% yield (>90% purity), whereas distillation at reduced pressure gave **1a** in 57% yield (16.5 g, 90% purity). The formation of **1a** is accompanied by trace quantities of multiple products that could not be fully separated by distillation; on the other hand, when

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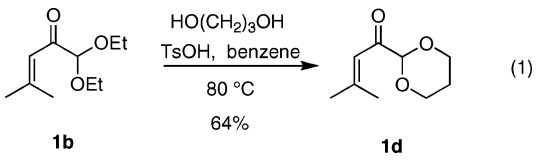
column chromatography [silica, hexanes/ethyl acetate] was employed, **1a** was obtained in high purity yet only 29% yield. The two-step synthesis of **1a** also uses little solvent. The conversion of trimethyl orthoformate to **5a** is solvent-free, and the conversion of **5a** to **1a** employs 2-methyl-1-propenylmagnesium bromide (**4**, available commercially as a 0.5 M solution in THF) and no other solvent. In this regard, both reactions are carried out at the highest possible concentration, an approach commensurate with the objective of preparing multigram quantities of the valuable intermediate **1a**. Although the yield of this transformation is not high, the nitrile method overcomes the limitations of the prior synthesis with diphenyl diselenide and, moreover, can be employed to prepare α,β-unsaturated ketones with diverse functionalities at the methyl site.

The new route established for **1a** was extended to two other Michael acceptors. First, commercially available diethoxyacetonitrile afforded diethoxymethyl Michael acceptor **1b** in 45% yield (Scheme 4). Second, treatment of 2-methoxy-1,3-dioxolane with 1 molar equiv of trimethylsilyl cyanide in the presence of a catalytic amount of $In(OTf)_3$ for 1 h at 0 °C afforded 1,3-dioxolane-2-carbonitrile. (An exploratory survey showed $BF_3{\cdot}OEt_2$, $InCl_3$, and $Yb(OTf)_3$ to give additional byproduct as observed upon ^1H NMR analysis of crude samples.) The ^1H NMR spectrum of the crude 1,3-dioxolane-2-carbonitrile was consistent with literature data.[37] The dioxolane–nitrile was found to be unstable and, for this reason, was used directly in the next step. Treatment of the crude nitrile with **4** afforded **1c** in 22% overall yield. Compound **1c** was found to be very unstable in air but could be stored in a degassed ether solution at −20 °C for several months without decomposition.

Transacetalization of diethoxyacetal **1b** with 1,3-propanediol in benzene/TsOH afforded 1,3-dioxane **1d** in 64% yield (eq 1).



1b **1d** (1)

This apparently simple approach could not be generalized: attempted transacetalization of **1b** with ethylene glycol afforded a chromatographically inseparable mixture of **1c** and an unidentified byproduct (see the Supporting Information).

Synthesis of New Michael Acceptors via Weinreb Amides. Treatment of α-methoxyacetic acid (**6e**) with 1,1′-carbonyldiimidazole (CDI) and *N,O*-dimethylhydroxylamine hydrochloride followed by **4** afforded methoxymethyl Michael acceptor **1e** in 22% yield (Table 1). The reaction of known phenoxymethyl Weinreb amide **7f** (prepared from phenoxyacetic acid (**6f**) and *N,O*-dimethylhydroxylamine hydrochloride with CDI)[38] with 1.1 molar equiv of **4** afforded phenoxymethyl Michael acceptor **1f** in nearly quantitative yield. Similarly, treatment of α-methoxyphenylacetic acid (**6g**) with CDI followed by triethylamine and *N,O*-dimethylhydroxylamine hydrochloride afforded amide **7g** in 58% yield. (The S-enantiomer of **7g** is described in the literature but without characterization data.[39]) The reaction of **7g** with 1.1 molar equiv of **4** afforded α-methoxybenzyl Michael acceptor **1g** in 87% yield.

A general procedure was followed to convert an ester to a Weinreb amide.[40] Thus, treatment of ethyl 1,3-dithiolane-2-carboxylate (**6h**) and 2.5 molar equiv of *N,O*-dimethylhydroxylamine hydrochloride in THF with 5 molar equiv of isopropylmagnesium chloride at −78 °C afforded **7h** in 49% yield. Compound **7h** was prepared previously in three steps from glyoxylic acid in 47% overall yield.[41] The reaction of Weinreb amide **7h** with 1.1 molar equiv of **4** afforded Michael acceptor **1h** in 77% yield (Table 1).

Synthesis of New Dihydrodipyrrins. Following a general approach to the synthesis of dihydrodipyrrins,[28] nitroethylpyrrole **8**[28] was treated with 1.1–2.4 molar equiv of a Michael acceptor (**1c–h**) in the presence of 3 molar equiv of DBU at room temperature to afford the corresponding hexanone (**2c–h**). The results are summarized in Table 2. The yields obtained with the benchmark compounds for the series **1a** → **2a** → **3a** are provided for comparison (Table 2, entry 1).[28] The $TiCl_3$-mediated reductive cyclization of **2c–f** afforded dihydrodipyrrins **3c–f** (Table 2, entries 2–5); however, analogous reaction of **2g** or **2h** did not afford the corresponding dihydrodipyrrin, yet all starting material was consumed (Table 2, entries 6 and 7). The crude **3g** decomposed immediately after the reaction workup. The reaction with **2h** afforded unidentified products.

Self-Condensation Study. The self-condensation conditions (5 equiv of TMSOTf and 20 equiv of 2,6-DTBP in CH_2Cl_2) employed previously for dihydrodipyrrin–acetals bearing a 1-(dimethoxymethyl) unit and diverse β-pyrrole substituents[28] were recently modified to use a lesser amount of reagents (4 equiv of TMSOTf and 8 equiv of 2,6-DTBP).[42] The latter conditions were applied with dihydrodipyrrins **3c–f**. The crude reaction mixtures (neutralized with saturated aqueous $NaHCO_3$ and washed with water) were analyzed for the presence of bacteriochlorin macrocycles by TLC, laser-desorption mass spectrometry (LD-MS), and UV–vis spectroscopy. The results are shown in Table 2. For comparison, dihydrodipyrrin–acetal **3a** affords bacteriochlorin **BC-1** (Table 2, entry 1). Dihydrodipyrrin–dioxolane **3c** also successfully afforded a bacteriochlorin (Table 2, entry 2; vide infra), whereas dihydrodipyrrin–dioxane **3d** resulted in partial decomposition and no bacteriochlorin (Table 2, entry 3). Dihydrodipyrrin **3e**, bearing a methoxymethyl group, gave only a small LD-MS peak corresponding to a tetradehydrocorrin[25,43] macrocycle, but the product was not isolated (Table 2, entry 4). Dihydrodipyrrin **3f**, bearing a phenoxymethyl group, gave decomposition with no starting material or macrocycle observed (Table 2, entry 5).

Synthesis of *trans*-AB-Bacteriochlorin Building Block. The success of dihydrodipyrrin **3c** in the survey reaction prompted scale-up to fully characterize the resulting bacteriochlorin. Thus, the self-condensation of dihydrodipyrrin **3c** (0.76 mmol) in the presence of 4 molar equiv of TMSOTf and 8 molar equiv of 2,6-DTBP in CH_2Cl_2 afforded bacteriochlorin **BC-3** in 30% yield; no other macrocycles were observed by TLC and LD-MS analyses. Consistent with the mechanistic picture shown in Scheme 2, bacteriochlorin **BC-3** contained a 2-(trimethylsilyloxy)ethoxy group at the 5-position (Scheme 5). Treatment with 1.5 molar equiv of TBAF at room temperature under argon cleaved the TMS group and afforded the 5-(2-hydroxyethoxy)bacteriochlorin **BC-4** in 83% yield.

Bacteriochlorins with a 5-methoxy group undergo smooth and selective bromination at the 15-position, whereas bacteriochlorins lacking a 5-methoxy group typically afford a mixture of bromobacteriochlorins.[28,33] To examine whether the hydroxyethoxy group directed selective bromination, bacteriochlorin **BC-4** was treated with 1 molar equiv of NBS at room

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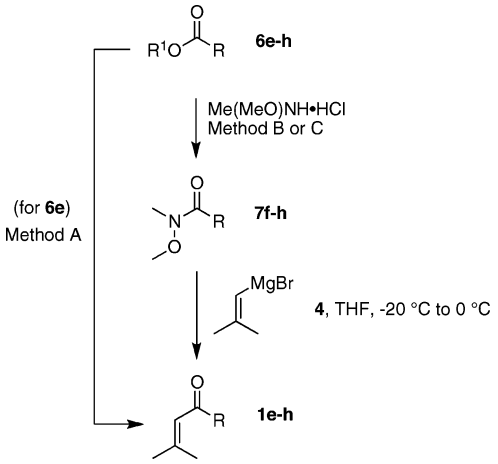
Table 1. Synthesis of Michael Acceptors via Weinreb Amides



Entry	R	Acid derivative	Weinreb amide	Method	Yield, %	1	Yield, %
1		**6e** (R^1 = H)	n/a	A[a]	n/a	**1e**	22
2		**6f** (R^1 = H)	**7f**	B[b]	91	**1f**	97
3		**6g** (R^1 = H)	**7g**	B[b]	58	**1g**	87
4		**6h** (R^1 = Et)	**7h**	C[c]	49	**1h**	77

[a]Method A: (1) CDI, CH_2Cl_2, 0 °C to rt; (2) Me(MeO)NH·HCl, Et_3N, CH_2Cl_2, 0 °C to rt; (3) **4**, THF, −20 to 0 °C. [b]Method B: (1) CDI, CH_2Cl_2, 0 °C to rt; (2) Me(MeO)NH·HCl, Et_3N, CH_2Cl_2, 0 °C to rt. [c]Method C: (1) Me(MeO)NH·HCl; (2) *i*-PrMgCl, THF, −78 °C.

temperature. The resulting bacteriochlorin (**BC-5**) was obtained in 64% yield and contained a bromine atom at the 15-position (established by NOESY). When TMS-protected bacteriochlorin **BC-3** was treated with 1 molar equiv of NBS, bacteriochlorin **BC-5** was obtained as well in 65% yield, indicating that NBS acted both as a deprotecting and brominating agent. Bacteriochlorin **BC-5** contains two reactive functional groups at opposing meso positions. Analogues of **BC-5** that bear diverse *β*-pyrrole substituents and the same *trans*-AB substituents are expected to afford valuable building blocks.

Outlook. A scalable synthesis was developed to gain access to *α*,*β*-unsaturated ketones for use as Michael acceptors in the preparation of bacteriochlorins. One method employed the reaction of a nitrile and vinyl Grignard reagent. This new approach and that with Weinreb amides afforded diverse substituents in place of the dimethoxymethyl unit. Upon screening of four new dihydrodipyrrins that bear distinct electrophilic centers, the dihydrodipyrrin bearing a 1,3-dioxolan-2-yl group (**3c**) was found to afford the corresponding 5-(2-hydroxyethoxy)bacteriochlorin (**BC-4**). Consistent with the mechanism of 5-methoxybacteriochlorin formation, the condensation of two molecules of a dihydrodipyrrin bearing a 1,3-dioxolan-2-yl group is accompanied by formal release of three alcohol units, yet here the first two are integral to an ethylene glycol molecule, whereas the third moiety is the terminus of the hydroxyethoxy unit anchored at the 5-position of the bacteriochlorin. Previously, the only type of 1-substituent in a dihydrodipyrrin that afforded a bacteriochlorin was a dimethoxymethyl unit (e.g., **3a**).[25,28] The resulting bacteriochlorin **BC-4** and its 15-brominated derivative (**BC-5**) are expected to be valuable building blocks, given the orthogonality and linear arrangement of the functional groups disposed at the 5- and 15-positions. The singular success with the new dihydrodipyrrin−acetal highlights the exacting structural features of the dihydrodipyrrin electrophilic site for successful self-condensation.

EXPERIMENTAL SECTION

General Methods. ^{1}H NMR (300 MHz) and ^{13}C NMR (100 MHz) spectra were collected at room temperature in $CDCl_3$ unless noted otherwise. Absorption spectra were obtained in toluene at room temperature unless noted otherwise. Electrospray ionization mass spectrometry [HRMS (ESI)] data are reported for the molecular ion or cationized molecular ion. Laser-desorption mass spectrometry was performed without a matrix. All commercially available materials (including **4**, **6e**−**h**) were used as received. Noncommercially available compounds **5a** (11-fold larger scale),[35,36] **7f**,[38] and **8**[28] were prepared as described in the literature; in each case, the identity and purity were established by ^{1}H NMR spectroscopy.

1,1-Dimethoxy-4-methyl-3-penten-2-one (1a). Dimethoxyacetonitrile (**5a**, 18.7 g, 185 mmol) in a 1 L round-bottom flask equipped with a stirring bar and a 500 mL addition funnel (all oven-dried) was treated under argon with **4** (445 mL, 222 mmol, 0.5 M in THF) over 30 min at 0 °C, followed by stirring for 2 h at room temperature. The bright yellow-orange solution was treated with saturated aqueous NH_4Cl (500 mL), and the reaction mixture was

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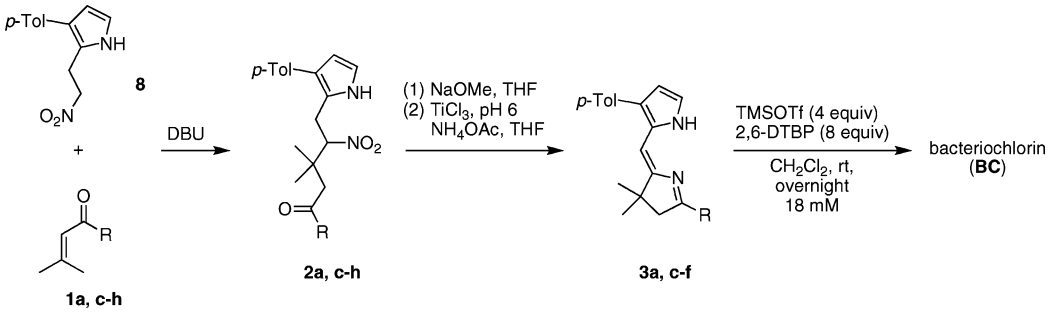
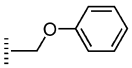
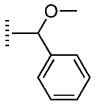
Table 2. Synthesis and Self-Condensation of Dihydrodipyrrins



Entry	1	R	2	Yield, %	3	Yield, %	BC, yield, %
1	**1a**[a]		**2a**	63	**3a**	54	**BC-1**,[b] 40.7 %
2	**1c**		**2c**	54	**3c**	31	**BC-3**, 30%
3	**1d**		**2d**	35	**3d**	18	0[c]
4	**1e**		**2e**	70	**3e**	22	0[d]
5	**1f**		**2f**	60	**3f**	37	0[c]
6	**1g**		**2g**	63	**3g**	0	n/a
7	**1h**		**2h**	36	**3h**	0	n/a

[a]Ref 28. [b]Ref 42. [c]Unreacted starting material and decomposition observed. [d]Decomposition.

vigorously stirred for 2 h. ^{1}H NMR spectroscopy indicated the completion of hydrolysis (disappearance of peaks at 5.89 ppm and 4.61 ppm (imine) and appearance of peaks at 6.34 ppm and 4.49 ppm). The aqueous phase was extracted with Et_2O (3 × 350 mL), and each organic extract was washed (brine). The combined organic extract was dried (Na_2SO_4) and concentrated to an orange liquid. Bulb-to-bulb distillation (95 °C/0.05 mmHg) afforded a yellow liquid (16.5 g, 57%, 90% purity). When the procedure was repeated on the same scale, but the crude product was purified by column chromatography [silica, EtOAc/hexanes (5:1)], the title compound was obtained in 29% yield. The characterization values (^{1}H NMR spectrum) were consistent with those in the literature.[25,34] IR (neat) 3518, 2937, 2834, 1699, 1620, 1445, 1381, 1192, 1106, 1073, 988, 846 cm^{-1}.

1,1-Diethoxy-4-methyl-3-penten-2-one (1b). A sample of diethoxyacetonitrile (5.00 g, 38.7 mmol) was subjected to the procedure described for **1a**. Chromatography [silica, EtOAc/hexanes (1:9)] afforded a yellow liquid (3.27 g, 45%): ^{1}H NMR δ 1.25 (t, J = 7.4 Hz, 6H), 1.95 (s, 3H), 2.20 (s, 3H), 3.52−3.74 (m, 4H), 4.58 (s, 1H), 6.40−6.42 (m, 1H); ^{13}C NMR δ 15.4, 21.5, 28.4, 63.2, 103.3, 119.2, 160.1, 194.9. HRMS (ESI). Calcd for $C_{10}H_{18}O_3Na$ $(M + Na)^+$: 209.1148. Found: 209.1148. IR (neat) 2976, 2880, 1697, 1620, 1444, 1380, 1317, 1235, 1104, 1060, 986, 845 cm^{-1}.

1-(1,3-Dioxolan-2-yl)-3-methyl-2-buten-1-one (1c). A solution of 2-methoxy-1,3-dioxolane (5.00 mL, 53.7 mmol) and trimethylsilyl cyanide (7.16 mL, 53.7 mmol) in CH_2Cl_2 (107 mL) at 0 °C was treated under argon with $In(OTf)_3$ (377 mg, 0.671 mmol). After stirring for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. After extraction, the organic phase was washed (water), dried (Na_2SO_4), and concentrated. The characterization values (^{1}H NMR, ^{13}C NMR) of the crude 1,3-dioxolane-2-carbonitrile were consistent with reported values.[37] A solution of the crude 1,3-dioxolane-2-carbonitrile in THF (10 mL) at −20 °C under argon was treated dropwise with **4** (107.4 mL, 53.7 mmol, 0.5 M in THF). After stirring for 1 h at −10 °C, saturated aqueous NH_4Cl (150 mL) was added, and the reaction mixture was stirred vigorously for 1 h at room temperature. The reaction mixture was extracted with Et_2O (3 × 150 mL). The combined organic extract was washed (water, brine), dried, and concentrated. Column chromatography [silica, hexanes/EtOAc (5:1)] afforded a pale yellow liquid (1.80 g, 22%). The title

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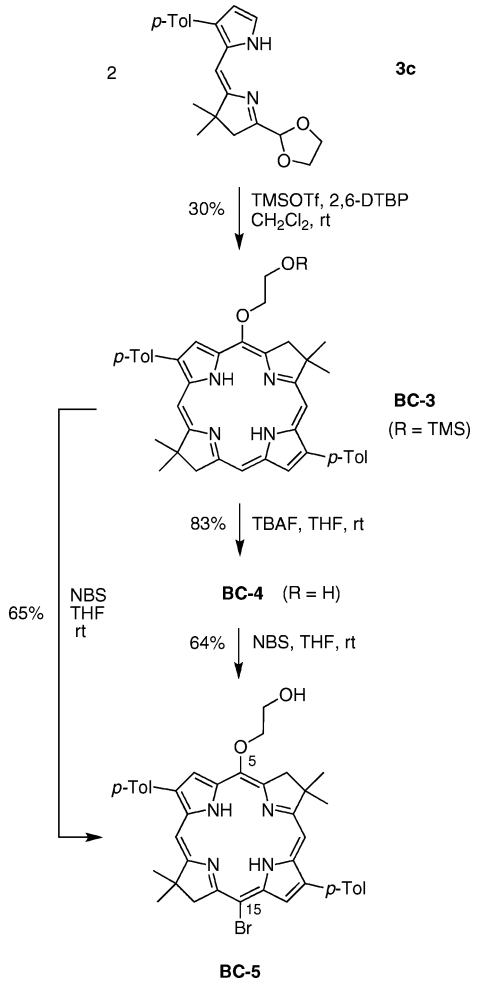
Scheme 5. Synthesis of a *trans*-AB-Bacteriochlorin



compound was found to be unstable in air even as a neat liquid but could be stored without decomposition in a degassed solution of Et_2O (~0.4 M) for 2 months at −20 °C. Data for the title compound: ^1H NMR δ 1.96 (s, 3H), 2.20 (s, 3H), 3.96−4.09 (m, 4H), 5.05 (s, 1H), 6.29−6.30 (m, 1H); ^{13}C NMR δ 21.6, 28.5, 65.8, 102.7, 118.8, 161.2, 194.5. HRMS (ESI). Calcd for $C_8H_{12}O_3Na$ $(M + Na)^+$: 179.0679. Found: 179.0678. IR (neat) 3525, 2978, 2893, 1697, 1618, 1445, 1380, 1236, 1162, 1101, 1033, 841 cm^{-1}.

1-(1,3-Dioxan-2-yl)-3-methyl-2-buten-1-one (1d). A solution of **1b** (1.06 g, 5.69 mmol) and 1,3-propanediol (0.600 mL, 8.30 mmol) in benzene (11.5 mL) was treated with *p*-toluenesulfonic acid (542 mg, 2.85 mmol) at 80 °C for 4.5 h. Saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with Et_2O. The organic extract was washed (water), dried (Na_2SO_4), concentrated to a brown liquid, and chromatographed [silica, hexanes/EtOAc (5:1)] to afford a yellow liquid (620 mg, 64%, ≥95% purity): ^1H NMR δ 1.40−1.45 (m, 1H), 1.96 (s, 3H), 2.20 (s, 3H), 2.12−2.25 (m, 1H), 3.83−3.92 (m, 2H), 4.20−4.26 (m, 2H), 4.79 (s, 1H), 6.40−6.42 (m, 1H); ^{13}C NMR δ 21.7, 25.9, 28.5, 67.3, 101.4, 119.0, 161.2, 192.1. HRMS (ESI). Calcd for $C_9H_{14}O_3Na$ $(M + Na)^+$: 193.0835. Found: 193.0833. IR (neat) 3480, 2975, 2863, 1726, 1618, 1446, 1380, 1240, 1149, 1103, 1034 cm^{-1}.

1-Methoxy-4-methyl-3-penten-2-one (1e). According to a reported procedure[38] with some modifications, a solution of α-methoxyacetic acid (**6e**, 1.17 g, 13.0 mmol) in anhydrous CH_2Cl_2 (20 mL) was treated portionwise with 1,1′-carbonyldiimidazole (2.54 g, 15.7 mmol) at 0 °C under argon. The reaction mixture was stirred for 30 min at room temperature, treated with triethylamine (2.18 mL, 15.7 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (1.53 g, 15.6 mmol) at 0 °C, and stirred overnight at room temperature under argon. Saturated aqueous NH_4Cl was added. The organic phase was washed with water, dried (Na_2SO_4), and concentrated to a transparent oil. The crude amide at −20 °C under argon was treated dropwise with **4** (28.7 mL, 14.4 mmol, 0.5 M in THF). The reaction mixture was stirred for 2 h under argon at 0 °C, upon which a white precipitate was formed. The mixture was diluted with Et_2O and treated with saturated aqueous NH_4Cl. The ethereal extract was washed (water, brine), dried (Na_2SO_4), concentrated, and chromatographed [silica, hexanes/EtOAc (3:1)] to afford an orange liquid (360 mg, 22%): ^1H NMR δ 1.93 (s, 3H), 2.20 (s, 3H), 3.43 (s, 3H), 4.01 (s, 2H), 6.19−6.20 (m, 1H); ^{13}C NMR δ 21.4, 28.2, 59.4, 78.5, 119.6, 158.3, 159.9, 197.9. HRMS (ESI). Calcd for $C_7H_{12}O_2Na$ $(M + Na)^+$: 151.0730. Found: 151.0731. IR (neat) 3451, 2979, 2935, 2825, 1699, 1618, 1447, 1379, 1227, 1200, 1109, 1038, 986, 934, 815 cm^{-1}.

4-Methyl-1-phenoxy-3-penten-2-one (1f). A solution of amide **7f** (508 mg, 2.60 mmol) in THF (5.1 mL) at −20 °C under argon was treated dropwise with **4** (5.70 mL, 2.85 mmol, 0.5 M in THF). The reaction mixture was stirred for 2 h under argon at 0 °C, upon which a white precipitate formed. The mixture was diluted with Et_2O and treated with saturated aqueous NH_4Cl. The ethereal extract was washed (water, brine), dried (Na_2SO_4), and concentrated to a slightly yellow oil (480 mg, 97%) of sufficient purity to not require further purification: ^1H NMR δ 1.95 (s, 3H), 2.23 (s, 3H), 4.56 (s, 2H), 6.35−6.37 (m, 1H), 6.88 (m, 2H), 6.91−7.00 (m, 1H), 7.27−7.32 (m, 2H); ^{13}C NMR δ 21.6, 28.4, 73.4, 114.8, 119.4, 121.7, 129.8, 159.9, 196.4. HRMS (ESI). Calcd for $C_{12}H_{14}O_2Na$ $(M + Na)^+$: 213.0892. Found: 213.0886. IR (neat) 3520, 3041, 2911, 1702, 1686, 1600, 1495, 1436, 1379, 1211, 1152, 1121, 1031, 844, 754 cm^{-1}.

1-Methoxy-4-methyl-1-phenyl-3-penten-2-one (1g). Compound **7g** (585 mg, 2.80 mmol) was subjected to the procedure described for preparation of **1f**. Chromatography [silica, hexanes/EtOAc (5:1)] afforded the title compound (495 mg, 87%): ^1H NMR δ 1.87 (s, 3H), 2.14 (s, 3H), 3.39 (s, 3H), 4.64 (s, 1H), 6.27−6.28 (m, 1H), 7.32−7.38 (m, 5H); ^{13}C NMR δ 21.4, 28.3, 57.4, 89.7, 119.3, 127.1, 128.4, 128.8, 136.8, 159.4, 197.8. HRMS (ESI). Calcd for $C_{13}H_{16}O_2Na$ $(M + Na)^+$: 227.1043. Found: 227.1041. IR (neat) 2933, 2826, 1686, 1618, 1445, 1379, 1199, 1099, 989 cm^{-1}.

1-(1,3-Dithiolan-2-yl)-3-methyl-2-buten-1-one (1h). Compound **7h** (250 mg, 1.30 mmol) was subjected to the procedure described for preparation of **1f**. Chromatography [silica, hexanes/EtOAc (3:1)] afforded a yellow oil (189 mg, 77%): ^1H NMR δ 1.95 (s, 3H), 2.19 (s, 3H), 3.31−3.35 (m, 4H), 4.87 (s, 1H), 6.23−6.24 (m, 1H); ^{13}C NMR δ 21.4, 28.4, 39.2, 58.5, 120.3, 159.8, 193.3. HRMS (ESI). Calcd for $C_8H_{12}OS_2Na$ $(M + Na)^+$: 211.0222. Found: 211.0227. IR (neat) 3434, 2928, 1674, 1619, 1441, 1379, 1237, 1121, 1039 cm^{-1}.

1-(1,3-Dioxolan-2-yl)-3,3-dimethyl-4-nitro-5-(3-*p*-tolylpyrrol-2-yl)-1-pentanone (2c). Following a literature procedure,[28] a mixture of **1c** (1.56 g, 9.99 mmol) and **8** (950 mg, 4.13 mmol) was treated with DBU (2.54 mL, 13.1 mmol) at room temperature. When no starting material was observed upon TLC analysis (3 h in this case), the reaction mixture was diluted with EtOAc, and water was added. The combined organic extract was washed (brine), dried (Na_2SO_4), and concentrated to a brown oil. Column chromatography [silica, hexanes/EtOAc (3:1)] afforded a brown oil (861 mg, 54%): ^1H NMR δ 1.11 (s, 3H), 1.20 (s, 3H), 2.37 (s, 3H), 2.50 (d, J = 18.4 Hz, 1H), 2.71 (d, J = 18.4 Hz, 1H), 3.19 (dd, J = 2.6 Hz, J = 15.5 Hz, 1H), 3.40 (dd, J = 11.4 Hz, J = 15.5 Hz, 1H), 3.98−4.03 (m, 4H), 4.93 (s, 1H), 5.13 (dd, J = 2.6 Hz, J = 11.4 Hz, 1H), 6.23−6.24 (m, 1H), 6.67−6.69 (m, 1H), 7.18 (d, J = 8.8 Hz, 2H), 7.26 (d, J = 8.8 Hz, 2H), 8.07 (br, 1H); ^{13}C NMR δ 21.2, 23.9, 24.1, 25.3, 36.7, 44.4, 65.7, 94.9, 102.0, 109.4, 117.7, 121.8, 123.4, 128.2, 129.3, 133.5, 135.5, 204.1. HRMS (ESI). Calcd for $C_{21}H_{27}N_2O_5$ $(M + H)^+$: 387.1914. Found: 387.1906.

1-(1,3-Dioxan-2-yl)-3,3-dimethyl-4-nitro-5-(3-*p*-tolylpyrrol-2-yl)-1-pentanone (2d). Samples of **1d** (268 mg, 1.58 mmol), **8** (302 mg, 1.31 mmol) and DBU (0.765 mL, 3.93 mmol) were subjected (overnight) to the general procedure described for **2c**. Chromatography [silica, CH_2Cl_2/EtOAc (9:1)] afforded a brown solid (186 mg, 35%): mp 45 °C (dec.); ^1H NMR δ 1.11 (s, 3H), 1.19 (s, 3H), 1.40−1.44 (m, 1H), 2.07−2.21 (m, 1H), 2.37 (s, 3H), 2.60 (d, J

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= 18.8 Hz, 1H), 2.75 (d, J = 18.8 Hz, 1H), 3.20 (dd, J = 2.5 Hz, J = 15.6 Hz, 1H), 3.39 (dd, J = 11.7 Hz, J = 15.6 Hz, 1H), 3.79−3.88 (m, 2H), 4.17−4.23 (m, 2H), 4.68 (s, 1H), 5.16 (dd, J = 2.5 Hz, J = 11.7 Hz, 1H), 6.22−6.24 (m, 1H), 6.67−6.68 (m, 1H), 7.17−7.24 (m, 4H), 8.05−8.10 (br, 1H); ^{13}C NMR δ 21.4, 24.2, 24.3, 25.4, 25.8, 36.8, 45.1, 67.3, 95.1, 100.7, 109.6, 117.7, 122.1, 123.7, 128.4, 129.5, 133.6, 135.6, 201.0. HRMS (ESI). Calcd for $C_{22}H_{28}N_2O_5Na$ (M + Na)$^+$: 423.1890. Found: 423.1890.

1-Methoxy-4,4-dimethyl-5-nitro-6-[3-*p*-tolylpyrrol-2-yl]-2-hexanone (2e). Samples of **1e** (187 mg, 1.46 mmol), **8** (250 mg, 1.09 mmol) and DBU (0.636 mL, 3.27 mmol) were subjected (for 8 h) to the general procedure described for **2c**. Chromatography [silica, hexanes/EtOAc (3:1)] afforded a brown oil which solidified upon storage at 1 °C (274 mg, 70%): mp 103−104 °C (dec); ^{1}H NMR δ 1.09 (s, 3H), 1.20 (s, 3H), 2.36 (d, J = 17.6 Hz, 1H), 2.37 (s, 3H), 2.56 (d, J = 17.6 Hz, 1H), 3.22 (dd, J = 1.8 Hz, J = 15.8 Hz, 1H), 3.40 (s, 3H), 3.38 (dd, J = 9.9 Hz, J = 15.8 Hz, 1H), 3.90 (s, 2H), 5.14 (dd, J = 1.8 Hz, J = 9.9 Hz, 1H), 6.22−6.24 (m, 1H), 6.67−6.68 (m, 1H), 7.19 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 8.19 (br, 1H); ^{13}C NMR δ 21.3, 24.2, 24.5, 25.3, 37.0, 46.5, 59.5, 78.4, 95.0, 109.5, 117.7, 122.0, 123.7, 128.4, 129.4, 133.6, 135.7, 206.8. HRMS (ESI). Calcd for $C_{20}H_{26}N_2O_4Na$ (M + Na)$^+$: 381.1785. Found: 381.1782. Anal. Calcd for $C_{20}H_{26}N_2O_4$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.04; H, 7.25; N, 7.62.

4,4-Dimethyl-5-nitro-1-phenoxy-6-(3-*p*-tolylpyrrol-2-yl)-2-hexanone (2f). Samples of **1f** (256 mg, 1.35 mmol), **8** (250 mg, 1.09 mmol) and DBU (0.635 mL, 3.26 mmol) were subjected (overnight) to the general procedure described for **2c**. Chromatography (silica, CH_2Cl_2) afforded a brown oil (274 mg, 60%): ^{1}H NMR δ 1.10 (s, 3H), 1.21 (s, 3H), 2.34 (s, 3H), 2.50 (d, J = 18.2 Hz, 1H), 2.72 (d, J = 18.2 Hz, 1H), 3.23 (dd, J = 2.7 Hz, J = 15.6 Hz, 1H), 3.40 (dd, J = 11.4 Hz, J = 15.6 Hz, 1H), 4.43 (d, J = 3.6 Hz, 2H), 5.20 (dd, J = 2.7 Hz, J = 11.4 Hz, 1H), 6.23−6.24 (m, 1H), 6.69−6.67 (m, 1H), 6.86 (d, J = 8.8 Hz, 2H), 6.99−7.03 (m, 1H), 7.18−7.33 (m, 6H), 8.08 (br, 1H); ^{13}C NMR δ 21.3, 24.2, 24.5, 25.3, 37.0, 46.7, 73.3, 94.8, 109.5, 114.6, 117.7, 121.9, 122.1, 123.7, 128.4, 129.4, 129.9, 133.5, 135.7, 157.7, 205.6. HRMS (ESI). Calcd for $C_{25}H_{28}N_2O_4Na$ (M + Na)$^+$: 443.1941. Found: 443.1940.

1-Methoxy-4,4-dimethyl-5-nitro-6-[3-*p*-tolylpyrrol-2-yl]-1-phenyl-2-hexanone (2g). Samples of **1g** (250 mg, 1.23 mmol), **8** (235 mg, 1.02 mmol) and DBU (0.600 mL, 3.06 mmol) were subjected (overnight) to the general procedure described for **2c**. Chromatography [silica, hexanes/EtOAc (5:1)] afforded a brown oil (280 mg, 63%, a mixture of diastereomers): ^{1}H NMR δ 0.96 (s, 3H), 0.97 (s, 3H), 1.04 (s, 3H), 1.09 (s, 3H), 2.36 (s, 3H), 2.37 (s, 3H), 2.40 (m, 2H), 2.56−2.62 (m, 1H), 2.69−2.75 (m, 1H), 3.09−3.12 (m 1H), 3.14−3.18 (m, 1H), 3.29−3.33 (m, 2H), 3.35 (s, 3H), 3.36 (s, 3H), 4.57 (s, 1H), 4.58 (s, 1H), 5.14−5.15 (m, 1H), 5.17−5.19 (m, 1H) 6.21−6.22 (m, 2H), 6.64−6.67 (m, 2H), 7.14−7.25 (m, 8H), 7.31−7.40 (m, 10H), 8.03 (br, 1H), 8.07 (br, 1H); ^{13}C NMR δ 21.23, 21.25, 23.95, 23.99, 24.04, 24.2, 25.3, 25.4, 36.8, 36.9, 45.1, 45.5, 57.35, 57.42, 89.7, 89.8, 95.0, 95.1, 109.4, 109.5, 117.65, 117.66, 121.96, 122.00, 123.5, 123.6, 127.2, 127.4, 128.25, 128.33, 128.89, 128.98, 129.01, 129.1, 129.3, 133.59, 133.61, 135.5, 135.6, 206.4, 206.7. HRMS (ESI). Calcd for $C_{26}H_{31}N_2O_4$ (M + H)$^+$: 435.2278. Found: 435.2275.

1-(1,3-Dithiolan-2-yl)-3,3-dimethyl-4-nitro-5-(3-*p*-tolylpyrrol-2-yl)-1-pentanone (2h). Samples of **1h** (180 mg, 0.958 mmol), **8** (200 mg, 0.869 mmol) and DBU (0.508 mL, 2.61 mmol) were subjected (for 3.5 h) to the general procedure described for **2c**. Chromatography [silica, hexanes/EtOAc (3:1)] afforded a brown oil (129 mg, 36%): ^{1}H NMR (400 MHz) δ 1.12 (s, 3H), 1.16 (s, 3H), 2.37 (s, 3H), 2.63 (d, J = 18.0 Hz, 1H), 2.76 (d, J = 18.0 Hz, 1H), 3.23 (dd, J = 2.8 Hz, J = 15.5 Hz, 1H), 3.25−3.32 (m, 4H), 3.38 (dd, J = 11.4 Hz, J = 15.5 Hz, 1H), 4.74 (s, 1H), 5.14 (dd, J = 2.8 Hz, J = 11.4 Hz, 1H), 6.22−6.23 (m, 1H), 6.66−6.68 (m, 1H), 7.18 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 8.12 (br, 1H); ^{13}C NMR δ 21.6, 24.4, 24.5, 25.7, 37.6, 39.4, 46.4, 58.6, 95.6, 109.9, 118.1, 122.3, 123.9, 128.6, 129.7, 133.9, 136.0, 202.1. HRMS (ESI). Calcd for $C_{21}H_{27}N_2O_3S_2$ (M + H)$^+$: 419.1453. Found: 419.1458.

1-(1,3-Dioxolan-2-yl)-2,3-dihydro-3,3-dimethyl-7-*p*-tolyldipyrrin (3c). Following a reported procedure,[28] in a first flask a solution of **2c** (940 mg, 2.43 mmol) in THF/MeOH (11.4 mL, 5:1) at 0 °C under argon was treated with NaOMe (395 mg, 7.32 mmol) for 40 min. In a second flask, $TiCl_3$ (20 wt % $TiCl_3$ in 3 wt % HCl, 9.30 mL, 14.7 mmol) in THF (9.5 mL) was treated with a solution of NH_4OAc (7.52 g, 97.7 mmol) in H_2O (6.0 mL) that had been bubbled with argon for 1 h. The solution from the first flask was transferred to the second flask. The resulting reaction mixture was stirred overnight under argon at room temperature. Ethyl acetate and water were added. The organic extract was washed (brine), dried (Na_2SO_4), concentrated, and chromatographed [alumina, hexanes/EtOAc (3:1)] to afford a yellow solid (255 mg, 31%): mp 185 °C (dec); ^{1}H NMR (400 MHz) δ 1.20 (s, 6H), 2.39 (s, 3H), 2.61 (s, 2H), 4.01−4.12 (m, 4H), 5.64 (s, 1H), 6.10 (s, 1H), 6.26−6.29 (m, 1H), 6.85−6.87 (m, 1H), 7.21 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 10.82 (br, 1H); ^{13}C NMR δ 21.3, 29.2, 40.7, 47.1, 66.0, 101.4, 106.6, 109.2, 119.4, 124.8, 126.8, 128.7, 129.4, 134.2, 135.4, 160.0, 173.4. HRMS (ESI). Calcd for $C_{21}H_{25}N_2O_2$ (M + H)$^+$: 337.1911. Found: 337.1911.

1-(1,3-Dioxan-2-yl)-2,3-dihydro-3,3-dimethyl-7-*p*-tolyldipyrrin (3d). A sample of **2d** (255 mg, 0.422 mmol) was subjected to the procedure described for preparation of **3c**. Chromatography [silica, hexanes/EtOAc (2:1)] afforded a light yellow solid (27 mg, 18%): mp 145 °C (dec); ^{1}H NMR (400 MHz) δ 1.18 (s, 6H), 1.44−1.47 (m, 1H), 2.17−2.23 (m, 1H), 2.38 (s, 3H), 2.67 (s, 2H), 3.92−3.98 (m, 2H), 4.21−4.24 (m, 2H), 5.39 (s, 1H), 6.10 (s, 1H), 6.26−6.28 (m, 1H), 6.85−6.87 (m, 1H), 7.21 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 8.3 Hz, 2H), 10.92 (br, 1H); ^{13}C NMR δ 21.4, 26.0, 29.3, 40.4, 48.0, 67.3, 99.9, 106.6, 109.1, 119.3, 124.6, 126.9, 128.7, 129.4, 134.3, 135.3, 160.2, 173.4. HRMS (ESI). Calcd for $C_{22}H_{27}N_2O_2$ (M + H)$^+$: 351.2067. Found: 351.2064.

2,3-Dihydro-1-(methoxymethyl)-3,3-dimethyl-7-*p*-tolyldipyrrin (3e). A sample of **2e** (150 mg, 0.419 mmol) was subjected to the procedure described for preparation of **3c**. Chromatography [alumina, hexanes/EtOAc (5:1)] afforded a brown solid (28 mg, 22%). (The title compound decomposed upon attempted column chromatography on silica gel.) Data for the title compound: mp 93−95 °C; ^{1}H NMR δ 1.20 (s, 6H), 2.39 (s, 3H), 2.61 (s, 2H), 3.44 (s, 3H), 4.33 (s, 2H), 6.06 (s, 1H), 6.27−6.30 (m, 1H), 6.85−6.87 (m, 1H), 7.21 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 10.90 (br, 1H); ^{13}C NMR δ 21.7, 29.7, 41.0, 50.6, 59.6, 73.3, 105.3, 109.5, 119.2, 124.5, 127.4, 129.0, 129.7, 134.7, 135.6, 160.8, 176.8. HRMS (ESI). Calcd for $C_{20}H_{25}N_2O$ (M + H)$^+$: 309.1961. Found: 309.1971.

2,3-Dihydro-3,3-dimethyl-1-(phenoxymethyl)-7-*p*-tolyldipyrrin (3f). A sample of **2f** (270 mg, 0.642 mmol) was subjected to the procedure described for preparation of **3c**. Chromatography [silica, CH_2Cl_2/hexanes (1:1)] afforded a light brown oil, which quickly turned dark brown (87.5 mg, 37%): ^{1}H NMR δ 1.18 (s, 6H), 2.39 (s, 3H), 2.66 (s, 2H), 4.97 (s, 2H), 6.07 (s, 1H), 6.28−6.30 (m, 1H), 6.82−6.84 (m, 1H), 6.94−6.98 (m, 3H), 7.20−7.23 (d, J = 7.7 Hz, 2H), 7.29−7.37 (m, 4H), 10.78 (br, 1H); ^{13}C NMR δ 21.4, 29.3, 40.8, 50.3, 68.3, 105.3, 109.3, 114.8, 119.1, 121.7, 122.7, 124.4, 128.7, 129.4, 129.9, 134.3, 135.4, 160.3, 175.4. HRMS (ESI). Calcd for $C_{25}H_{27}N_2O$ (M + H)$^+$: 371.2118. Found: 371.2105.

***N*-Methoxy-*N*-methyl-2-methoxy-2-phenylacetamide (7g).** According to a reported procedure with some modifications,[38] a solution of **6g** (1.00 g, 6.02 mmol) in anhydrous CH_2Cl_2 (9.0 mL) at 0 °C under argon was treated portionwise with 1,1′-carbonyldiimidazole (1.27 g, 7.83 mmol). The reaction mixture was stirred for 40 min at room temperature, treated with triethylamine (1.2 mL, 8.6 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (826 mg, 8.43 mmol) at 0 °C, and stirred overnight at room temperature under argon. A sample of 1 M HCl (10 mL) was added. The organic extract was washed with water, dried (Na_2SO_4), and concentrated to give a transparent oil. Chromatography [silica, hexanes/EtOAc (1:1)] afforded a transparent oil (735 mg, 58%): ^{1}H NMR δ 3.17 (s, 3H), 3.39 (s, 3H), 3.42 (br, 3H), 5.12 (s, 1H), 7.32−7.39 (m, 3H), 7.44−7.46 (m, 2H); ^{13}C NMR δ 32.6, 57.4, 61.2, 81.0, 127.5, 128.4, 128.9, 136.7, 172.0. HRMS (ESI). Calcd for $C_{11}H_{15}NO_3Na$ (M + Na)$^+$: 232.0944. Found: 232.0952. IR (neat) 3504, 2938, 2823, 1675, 1455, 1385, 1197, 1176, 1111 cm^{-1}.

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***N*-Methoxy-*N*-methyl-1,3-dithiolane-2-carboxamide (7h).** Following a general procedure with modifications,[40] a vigorously stirred slurry of **6h** (1.50 mL, 10.5 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (2.57 g, 26.2 mmol) in THF (21 mL) at −78 °C under argon was treated dropwise with isopropylmagnesium bromide (52.5 mmol, 26.3 mL, 2 M in THF) over 40 min. The reaction mixture was stirred for 1 h at −78 °C under argon. Saturated aqueous NH_4Cl/H_2O (1:1) was added. The aqueous phase was extracted with ether (3 × 100 mL). The combined organic extract was washed (water, brine), dried (Na_2SO_4), concentrated, and chromatographed [silica, EtOAc/hexanes (2:1)] to afford a yellow oil that solidified upon storage at 1 °C (985 mg, 49%). The characterization values [^{1}H NMR, ^{13}C NMR, HRMS (ESI) spectra] were consistent with those for the title compound prepared via a different synthetic route.[41]

8,8,18,18-Tetramethyl-2,12-di-*p*-tolyl-5-[2-(trimethylsilyloxy)ethoxy]bacteriochlorin (BC-3). Following a general procedure,[42] a solution of **3c** (255 mg, 0.758 mmol) and 2,6-DTBP (1.36 mL, 6.06 mmol) in CH_2Cl_2 (42 mL) was treated with TMSOTf (0.55 mL, 3.0 mmol) at room temperature. The reaction mixture was stirred for 22 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 and saturated aqueous $NaHCO_3$. The organic phase was washed (water, brine), dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2/hexanes (1:1)] afforded a green solid (77 mg, 30%): mp 230−232 °C (dec.); ^{1}H NMR δ −1.92 (br, 1H), −1.80 (br, 1H), 0.34 (s, 9H), 1.89 (s, 6H), 1.91 (s, 6H), 2.61 (s, 6H), 4.32 (t, J = 4.4 Hz, 2H), 4.38 (s, 2H), 4.43 (s, 2H), 4.66 (t, J = 4.4 Hz, 2H), 7.56−7.58 (m, 4H), 8.08−8.15 (m, 4H), 8.68 (s, 2H), 8.78 (s, 1H), 8.81 (s, 1H), 9.07−9.08 (m, 1H); ^{13}C NMR δ 0.22, 21.6, 31.10, 31.16, 45.94, 46.18, 47.9, 51.9, 62.6, 76.8, 79.3, 95.7, 95.8, 97.8, 116.8, 121.0, 129.9, 130.0, 130.3, 131.1, 131.3, 133.2, 133.8, 134.1, 134.2, 134.4, 134.8, 135.6, 137.0, 137.2, 137.5, 153.4, 159.6, 169.6, 170.0; LD-MS obsd 681.8. HRMS (ESI). Calcd for $C_{43}H_{51}N_4O_2Si$ $(M + H)^+$: 683.3776. Found: 683.3762. λ_{abs} 355, 374, 512, 732 nm.

5-(2-Hydroxyethoxy)-8,8,18,18-tetramethyl-2,12-di-*p*-tolylbacteriochlorin (BC-4). A solution of **BC-3** (20 mg, 0.029 mmol) in THF (3.0 mL) was treated with TBAF (44 μL, 0.044 mmol, 1 M in THF) under argon at room temperature for 45 min. Water and CH_2Cl_2 were added. The organic extract was washed (brine), dried (Na_2SO_4), concentrated, and chromatographed (silica, CH_2Cl_2) to afford a green solid (15 mg, 83%): mp 208−210 °C (dec.); ^{1}H NMR δ −1.85 (br, 1H), −1.75 (br, 1H), 1.90 (s, 6H), 1.91 (s, 6H), 2.60 (s, 3H), 2.61 (s, 3H), 2.62−2.68 (m, 1H), 4.31−4.37 (m, 2H), 4.40 (s, 4H), 4.70 (t, J = 4.0 Hz, 2H), 7.55−7.59 (m, 4H), 8.08−8.12 (m, 4H), 8.67 (s, 2H), 8.77 (s, 1H), 8.80 (s, 1H), 8.94 (s, 1H); ^{13}C NMR δ 21.61, 21.64, 31.05, 31.20, 46.0, 46.3, 47.8, 52.1, 63.1, 78.9, 95.8, 96.0, 98.0, 116.0, 121.4, 129.8, 129.97, 130.03, 131.1, 131.3, 133.0, 133.6, 133.7, 134.2, 134.3, 135.3, 136.0, 137.1, 137.6, 137.7, 152.6, 160.1, 169.6, 170.3; LD-MS 610.0. HRMS (ESI). Calcd for $C_{40}H_{43}N_4O_2$ $(M + H)^+$: 611.3381. Found: 611.3365. λ_{abs} 355, 374, 511, 731 nm.

15-Bromo-5-(2-hydroxyethoxy)-8,8,18,18-tetramethyl-2,12-di-*p*-tolylbacteriochlorin (BC-5). A sample of **BC-4** (14 mg, 0.023 mmol) in THF (11.5 mL) was treated with NBS (0.23 mL, 0.023 mmol, 100 mM in THF) at room temperature. After stirring for 1 h, water and CH_2Cl_2 were added. The organic extract was washed (brine), dried (Na_2SO_4), and concentrated. Chromatography (silica, CH_2Cl_2) afforded a green solid (10 mg, 64%): mp 205−207 °C (dec.); ^{1}H NMR (400 MHz, THF-d_8) δ −2.01 (br, 1H), −1.82 (br, 1H), 1.90 (s, 12 H), 2.47 (s, 6H), 4.17−4.22 (m, 2H), 4.47 (s, 2H), 4.47−4.50 (m, 1H), 4.51 (s, 2H), 4.67 (t, J = 4.4 Hz, 2H), 7.55−7.59 (m, 4H), 8.06−8.11 (m, 4H), 8.77 (s, 1H), 8.82 (s, 1H), 8.98−8.99 (m, 1H), 9.04−9.05 (m, 1H); ^{13}C NMR (THF-d_8) δ 21.6, 31.3, 31.5, 46.4, 46.9, 49.0, 55.0, 62.9, 81.3, 96.4, 98.4, 119.5, 121.6, 129.1, 129.8, 130.67, 130.70, 132.0, 132.1, 133.1, 133.9, 134.0, 134.6, 134.8, 135.4, 135.8, 137.0, 137.6, 138.1, 138.3, 158.0, 158.7, 169.1, 172.9; LD-MS, 688.4. HRMS (ESI). Calcd for $C_{40}H_{41}BrN_4O_2Na$ $(M + Na)^+$: 711.2305. Found: 711.2297. λ_{abs} 362, 378, 524, 734 nm.

Conversion of BC-3 to BC-5. A sample of **BC-3** (73 mg, 0.11 mmol) in THF (53.5 mL) was treated with NBS (19 mg, 0.11 mmol) at room temperature. After stirring for 1 h at room temperature, water and CH_2Cl_2 were added. The organic phase was washed (brine), dried (Na_2SO_4), and concentrated. Chromatography (silica, CH_2Cl_2) afforded a green solid (48 mg, 65%). The characterization values (^{1}H NMR, LD-MS spectra) were consistent with those reported above.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Attempted syntheses and spectral data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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