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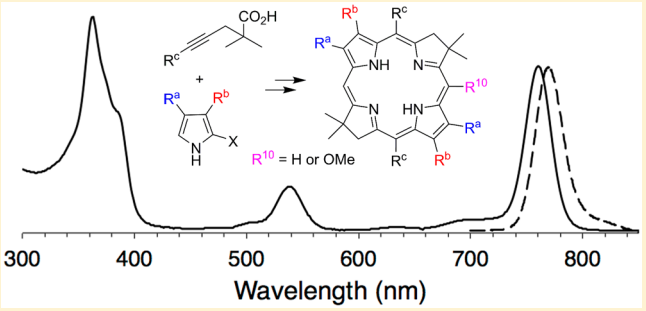
Northern−Southern Route to Synthetic Bacteriochlorins

Yizhou Liu and Jonathan S. Lindsey*

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8294, United States

Supporting Information

ABSTRACT: A new route to bacteriochlorins via Northern−Southern (N-S) self-condensation of a dihydrodipyrrin−acetal complements a prior Eastern−Western (E-W) route. Each bacteriochlorin was prepared in five steps from an α-halopyrrole and a 2,2-dimethylpent-4-ynoic acid. The first three steps follow Jacobi's synthesis of dihydrodipyrrins: Pd-mediated coupling to form a lactone−pyrrole, Petasis reagent treatment for methenylation, and Paal−Knorr type ring closure to form the 1,2,2-trimethyl-substituted dihydrodipyrrin. Subsequent steps entail conversion of the 1-methyl group to the 1-(dimethoxymethyl) unit and acid-catalyzed self-condensation of the resulting dihydrodipyrrin−acetal. The essential differences between the N-S and E-W routes lie in (1) the location of the *gem*-dimethyl group (with respect to the 1-acetal unit) at the 2- versus 3-position in the dihydrodipyrrin−acetals, respectively, (2) the method of synthesis of the dihydrodipyrrins, and consequently (3) access to diverse substituted bacteriochlorins including those with substituents at the meso-positions. Ten new bacteriochlorins bearing 0−6 total aryl, alkyl, and carboethoxy substituents at the β-pyrrole and/or meso-positions have been prepared, with yields of macrocycle formation of up to 39%. Four single-crystal X-ray structures (two intermediates, two bacteriochlorins) were determined. The bacteriochlorins exhibit characteristic bacteriochlorophyll-like absorption spectra, including a Q_y band in the region 713−760 nm.



INTRODUCTION

Bacteriochlorophylls are Nature's chosen chromophores for the near-infrared (NIR) spectral region and constitute the core light-harvesting pigments of anoxygenic phototrophic bacteria.[1] Bacteriochlorophylls, exemplified by bacteriochlorophyll *a* (Chart 1), feature a strong ($\varepsilon \sim 10^5$ M^{-1} cm^{-1}) long-wavelength absorption band located in the NIR region of ∼750−800 nm,[2] which enables capture of energy distinct from that of other tetrapyrrole macrocycles. The core chromophore of a bacteriochlorophyll is a bacteriochlorin, which contains alternating pyrrole and pyrroline units. Syntheses of bacteriochlorins enable photochemical studies, particularly in the comparatively less explored NIR spectral region.

The chief synthetic routes to bacteriochlorins entail (1) semisynthesis beginning with bacteriochlorophylls,[3,4] (2) reduction of or cycloaddition with porphyrins,[5,6] and (3) de novo syntheses. The de novo syntheses to date include the total synthesis of tolyporphin A as the diacetate (R = Ac, Chart 1) by Kishi and co-workers,[7−11] and a synthesis of non-natural bacteriochlorins that we[12−20] and others[21−25] have been developing. The latter route is shown in Scheme 1. The synthesis begins by conversion of a pyrrole-2-carboxaldehyde **A** to the corresponding 2-(2-nitroethyl)pyrrole **B**, which undergoes Michael addition with enone−acetal **C**; subsequent McMurry-like ring closure of the nitrohexanone **D** affords the dihydrodipyrrin−acetal **E**.[12] A recent alternative pathway employs the enone **C-Me** (mesityl oxide) and proceeds via analogues **D-Me** and **E-Me** to give **E**.[17,20] Self-condensation of the dihydrodipyrrin−acetal **E** at room temperature [in CH_2Cl_2 containing trimethylsilyl triflate (TMSOTf) and 2,6-di-*tert*-butylpyridine (2,6-DTBP),[14] or in CH_3CN[12] containing $BF_3{\cdot}O(Et)_2$] affords the bacteriochlorin. Each pyrroline ring is stabilized by the presence of a geminal dimethyl group, which blocks adventitious dehydrogenation of the corresponding bacteriochlorin (leading to the chlorin and porphyrin).

The synthesis shown in Scheme 1 has proved quite versatile for incorporation of diverse β-pyrrole substituents but is limited for the introduction of substituents at the meso- and the β-pyrroline positions. To date, the meso-substituents include alkoxy (methoxy, 2-hydroxyethoxy) at the 5-position[19] and entities (e.g., carbonyl, aryl, ethynyl) that can be introduced at the 15-position via Pd-mediated coupling of the 5-alkoxy-15-bromobacteriochlorin (Chart 2, panel A). Examples include **BC-1**[13] and **BC-2**.[15] Attempts to install *gem*-dialkyl groups other than *gem*-dimethyl at the 8,18-positions were successful only with a "spiro-piperidine" unit (**BC-3**); the very narrow scope stemmed from difficulties in the Michael addition with enone analogues of **C** and **C-Me** (Scheme 1).[17] Meso-substituted bacteriochlorins can of course be prepared by reduction of (or addition to) the corresponding porphyrin, but the approach generally does not afford the stabilizing *gem*-dialkyl feature and typically gives rise to positional isomers when diverse patterns of substituents are present. Representa-

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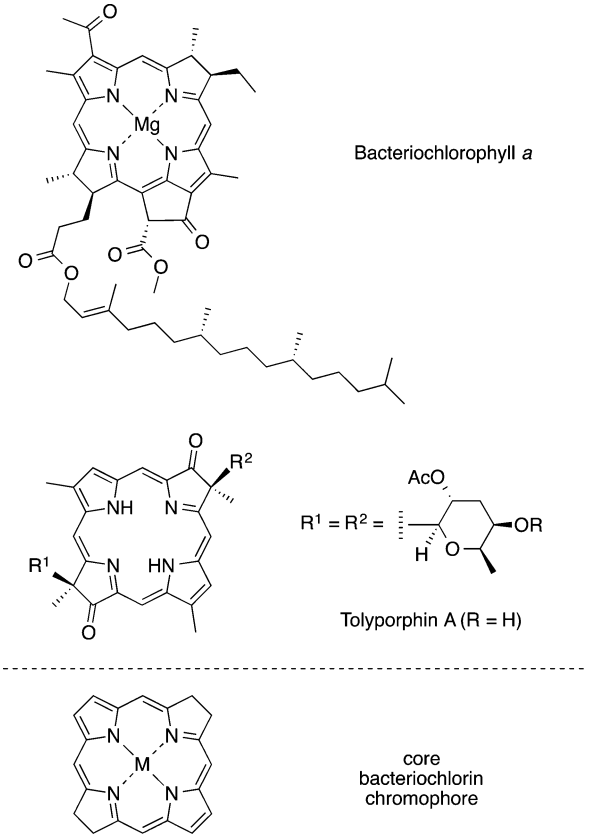
Chart 1. Naturally Occurring Bacteriochlorins (top) and the Core Chromophore (bottom)



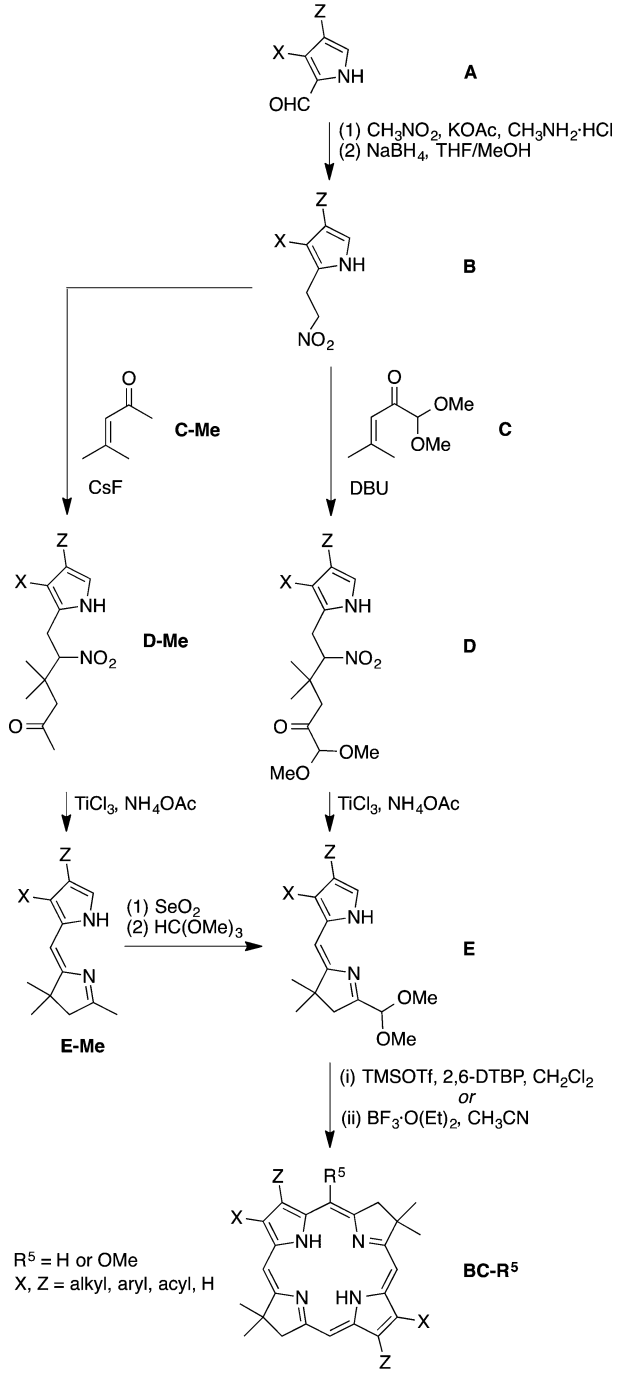
tive examples include *meso*-tetraphenylbacteriochlorin[26,27] and a novel set of *trans*-AB-bacteriochlorins prepared by Boyle,[28,29] as shown in Chart 2, panel B. Representative substituent patterns for synthetic bacteriochlorins that are not yet accessible are illustrated in Chart 2, panel C.

In this paper, we describe a new route to dihydrodipyrrin−acetals. The route affords 2,2-dimethyl-substituted 1-(1,1-dimethoxymethyl)dihydrodipyrrins whereas the prior E-W route afforded 3,3-dimethyl-substituted 1-(1,1-dimethoxymethyl)dihydrodipyrrins. We then examine the synthesis of a variety of bacteriochlorins that contain substituent patterns encompassing the β-pyrrole and meso-positions. The synthesis of bacteriochlorins bearing substituents in the pyrroline moiety other than *gem*-dimethyl (i.e., L = alkyl or aryl, not Me; Chart 2), which also have been largely inaccessible, will be reported elsewhere.

RESULTS AND DICUSSION

Reconnaissance with Jacobi. The pattern of substituents that can be introduced to a bacteriochlorin in a de novo synthesis depends in large part on methods for preparing the corresponding dihydrodipyrrin (or other precursors). In contemplating a new route to bacteriochlorins that complements the existing approach (Scheme 1), we were struck by the powerful chemistry of Jacobi and co-workers,[30−40] who developed methodology[30−32,34,40] supporting a new route to dihydrodipyrrins[33,35−37] with application of the latter to the synthesis of chlorins[33,36,37] (Scheme 2). For extension to bacteriochlorin chemistry, there are two notable features of the Jacobi route: (1) the starting reactants, a pent-4-ynoic acid (**J1**) and an iodopyrrole (**J2**), are joined via a Pd-coupling reaction

Scheme 1. De Novo Route to *gem*-Dimethyl-Stabilized Bacteriochlorins



to give a lactone−pyrrole (**J3**),[32,33,35] a precursor via ene−lactone−pyrrole (**J4**) to the dihydrodipyrrin (**J5**);[35] (2) the corresponding dihydrodipyrrin−carboxaldehyde (**J6**) has the *gem*-dimethyl group and carboxaldehyde at the respective 2- and 1-positions of the pyrroline unit. In contrast, the dihydrodipyrrin−acetal employed in the existing (E-W) route to bacteriochlorins has the *gem*-dimethyl group and acetal moiety at the 3- and 1-positions, respectively (Scheme 1). The route to the dihydrodipyrrin−acetal for the E-W synthesis has a distant antecedent in a route first demonstrated by Battersby and co-workers for the preparation of dihydrodipyrrin precursors to chlorins.[41]

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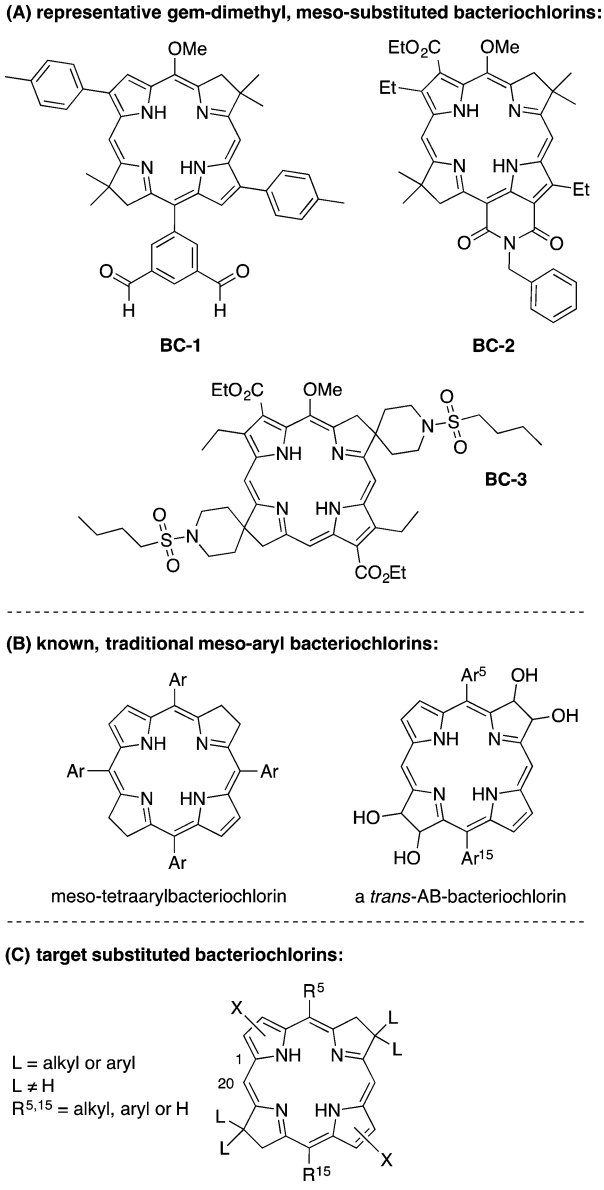
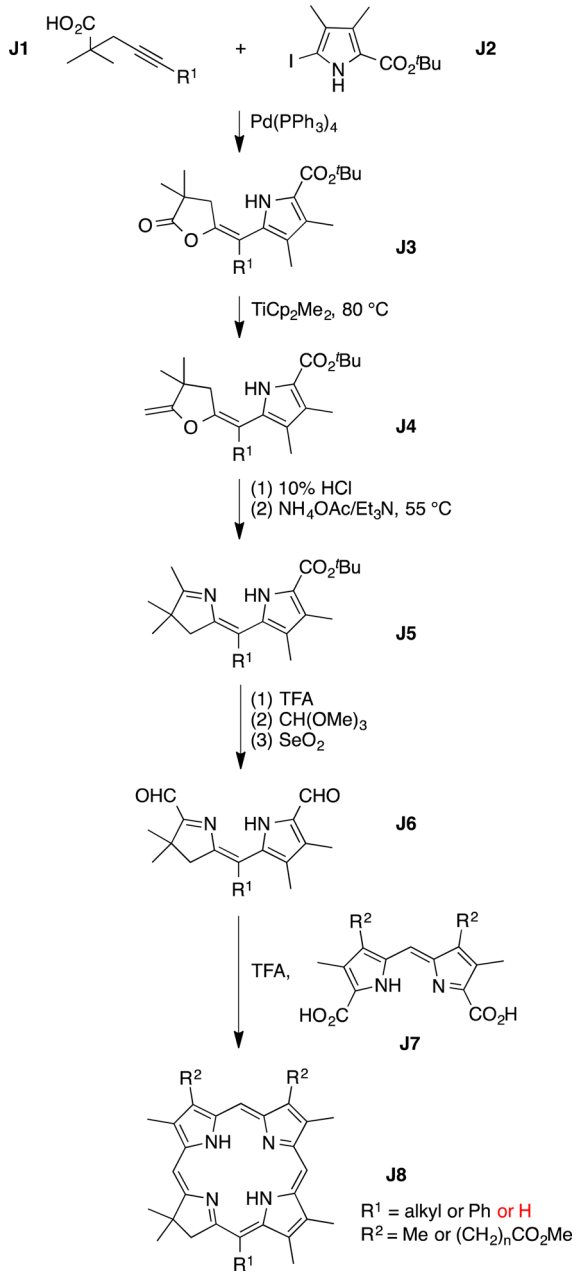
Chart 2. Known Bacteriochlorins (panels A, B) and New Target Bacteriochlorins (panel C)



Scheme 2. One of Jacobi's Chlorin Syntheses[36]



Jacobi and co-workers exploited the route shown in Scheme 2 (and variants thereof) for the preparation[33,36,37] and examination[38,39] of a family of *gem*-dimethyl-substituted chlorins bearing a variety of meso-substituents (H, Me, phenyl, and long chain-substituted alkyl). While a milestone in dihydrodipyrrin and chlorin chemistry, the methodology has remained undervalued given that (1) no macrocycles other than chlorins have been prepared, (2) no β-pyrrole substituents other than methyl have been employed in the dihydrodipyrrin (chlorin Southern half), and (3) no β-pyrroline substituents other than *gem*-dimethyl have been incorporated. We sought to adopt features of the Jacobi synthesis of dihydrodipyrrin precursors to chlorins for use in bacteriochlorin syntheses.

The self-condensation of the dihydrodipyrrin−acetals in the existing and new routes to bacteriochlorins are shown in Scheme 3. With regards to the positions of the pyrroline substituents, the prior route entails an E-W joining whereas the new route entails a N-S joining. In the E-W route, the self-condensation and subsequent aromatization of the macrocycle result in elimination of three molecules of methanol, leaving one methoxy substituent.[16] Under some conditions and with some reactants, the methoxy group is lost upon macrocyclization.[12,14] If present, the methoxy group is at the 5-position in the E-W route versus the 10-position in the N-S route.

Synthesis of Meso-Unsubstituted Bacteriochlorins. The exploration of the N-S route began with 2-iodopyrrole **1a** and alkynoic acid **2a** (Scheme 4). The alkynoic acid **2a** contains a terminal alkyne, which ultimately gives rise to a meso-unsubstituted bacteriochlorin. The 2-iodopyrrole **1a** was obtained by iodination of ethyl 4-ethyl-pyrrole-3-carboxylate[14] with 1 equiv of NIS in DMF at room temperature. The presence of the carboethoxy group in the pyrrole affords stabilization versus that of pyrroles lacking electron-withdrawing groups (vide infra). The Pd-mediated coupling of **1a** and **2a** under Jacobi's original reaction conditions[33] gave

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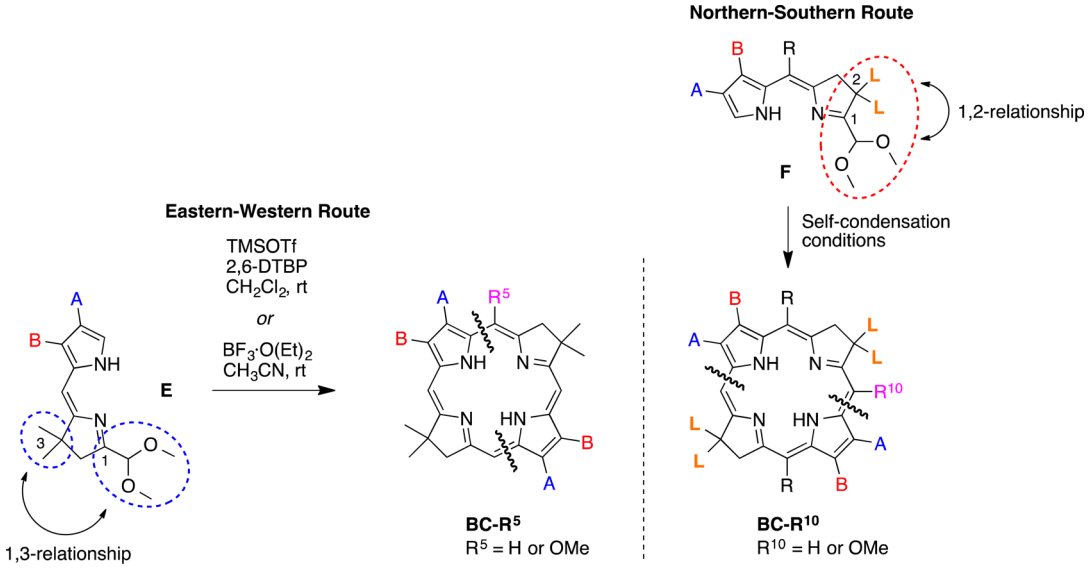
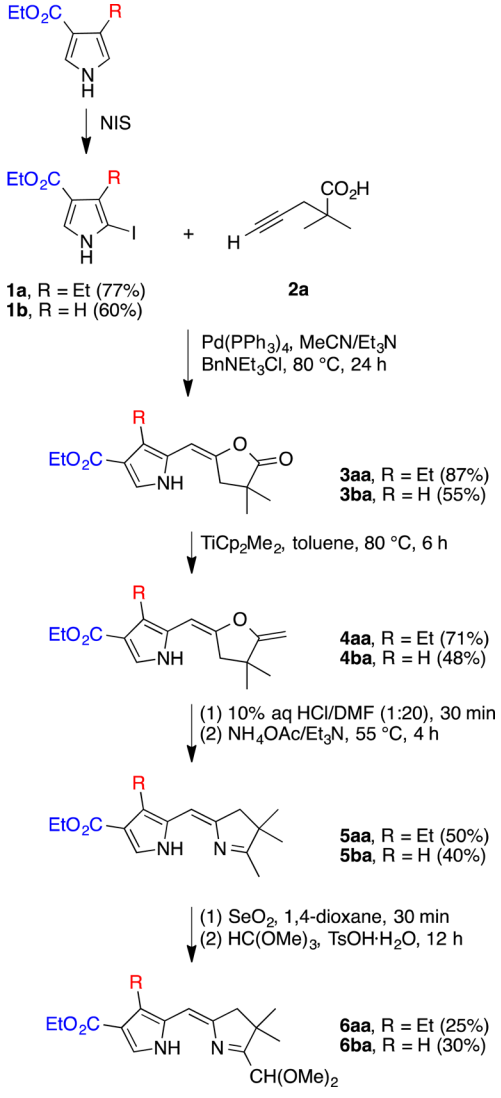
Scheme 3. Eastern–Western versus Northern–Southern Route



Scheme 4. Synthesis of 2,2-Dimethyldihydrodipyrrins Lacking Meso-Substituents



lactone–pyrrole **3aa** in 61% yield, and the use of excess **2a** (2 equiv) improved the yield to 87%.

Treatment of lactone–pyrrole **3aa** with the Petasis reagent gave the corresponding ene–lactone–pyrrole **4aa** in 71% yield. The latter was easily hydrolyzed under acidic conditions and converted to dihydrodipyrrin **5aa** via a Paal–Knorr type reaction with NH_4OAc/NEt_3. Dihydrodipyrrin **5aa** contains the *gem*-dimethyl group at the 2-position, by contrast with the 3-position of dihydrodipyrrins employed in the E-W route to bacteriochlorins. Treatment of **5aa** with SeO_2 and $HC(OMe)_3$ following a reported procedure[17] caused transformation of the 1-methyl group to the corresponding dimethyl acetal, affording dihydrodipyrrin–acetal **6aa**. Application of the same series of reactions with the homologous iodopyrrole **1b** led to dihydrodipyrrin–acetal **6ba**, which has only one *β*-pyrrole substituent. We note that ene–lactone–pyrroles **4aa** and **4ba** were each isolated exclusively as the *E*-isomer, whereas the dihydrodipyrrins (**5aa**, **5ba**, **6aa**, **6ba**) were each isolated exclusively as the *Z*-isomer (vide infra). Such isomers comport with observations by Jacobi and co-workers, who attributed the *E*-configuration of the ene–lactone–pyrroles to kinetically controlled formation[34] but the *Z*-configuration of the dihydrodipyrrins (analogues of **5aa** and **5ba**) to stabilization by intramolecular hydrogen-bonding.[35]

The dihydrodipyrrin–acetals **6aa** and **6ba** were treated to the acid-catalysis conditions established for the self-condensation of numerous 3,3-dimethyldihydrodipyrrin–acetals.[14] The standard conditions entail TMSOTf and 2,6-DTBP in CH_2Cl_2 at room temperature, which with 3,3-dimethyldihydrodipyrrin–acetals in the E-W route afford the 5-methoxybacteriochlorin to the invariable exclusion of any 5-unsubstituted bacteriochlorin[14] (which corresponds to the 10-position in the N-S route). Application of the reaction conditions of TMSOTf/2,6-DTBP in CH_2Cl_2 at room temperature to dihydrodipyrrin–acetal **6aa** gave 10-unsubstituted bacteriochlorin **7aa-HBC** in 39% yield, with no detected 10-methoxybacteriochlorin **7aa-MeOBC** (Scheme 5, top). Similarly, reaction of dihydrodipyrrin–acetal **6ba** gave 10-unsubstituted bacteriochlorin **7ba-HBC** in 6.0% yield, again with no 10-methoxybacteriochlorin **7ba-MeOBC**. The absence of the *meso*-methoxy group was unexpected given that the 3,3-dimethyldihydrodipyrrin–acetals (**6aa-iso**, **6ba-**

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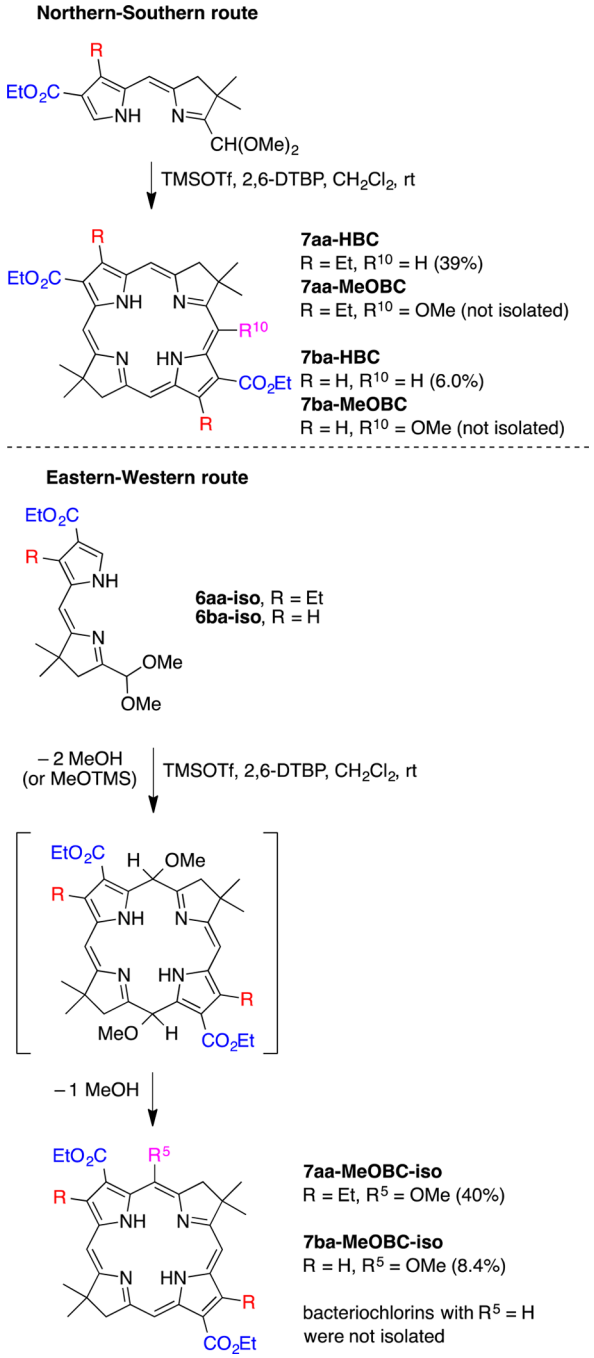
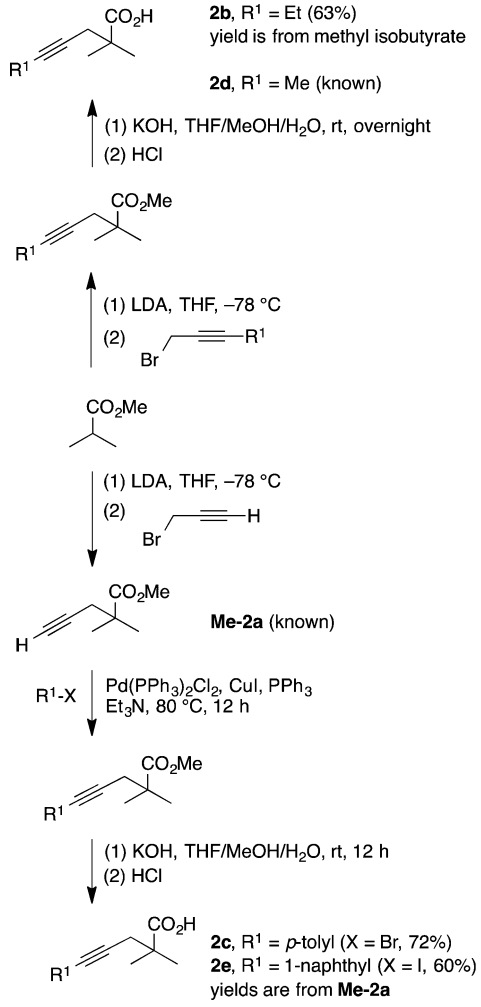
Scheme 5. Distinct Outcomes for Two Routes to Bacteriochlorins



iso) with identical pyrrole substituents (but position-interchanged versus that for **6aa** and **6ba**) gave the 5-methoxybacteriochlorin in yields of 40% and 8.4%, respectively (Scheme 5, bottom).[14] It is tempting to attribute this disparate behavior to the steric hindrance from the position changes of the geminal dimethyl groups, yet the process by which the methoxy group is lost remains unclear.

Meso-Disubstituted Bacteriochlorins from Meso-Substituted Dihydrodipyrrins. The synthesis of meso-substituted bacteriochlorins began with 5-substituted 2,2-dimethylpent-4-ynoic acids, where the 5-substituent is destined to become the bacteriochlorin meso-substituent. The 5-substituted 2,2-dimethylpent-4-ynoic acids **2b–e** were prepared following a reported procedure for known or similar compounds:[32,35] (1) alkyl substituents (methyl, ethyl) were introduced as the 1-alkyl-substituted propargyl bromide upon reaction with methyl isobutyrate; (2) aryl substituents (*p*-tolyl, 1-naphthyl) were installed via Sonogashira coupling of the aryl iodide and methyl 2,2-dimethylpent-4-ynoic acid (**Me-2a**) (Scheme 6). In each case, the resulting methyl ester was

Scheme 6. Alkynoic Acid Precursors for Meso-Substituted Bacteriochlorins



saponified to give the free acid, where the substituents include alkyl (methyl, **2d**; ethyl, **2b**) and aryl (*p*-tolyl, **2c**; 1-naphthyl, **2e**) groups.

Three pyrroles were prepared for use with the set of 5-substituted 2,2-dimethylpent-4-ynoic acids **2b–e**. Each pyrrole[14,42] bears a 4-carboethoxy group and varies in the nature of the 3-substituent. The 2-iodo group was installed upon treatment with NIS to give the pyrroles **1a** (4 substituent = Et), **1b** (H), and **1c** (Ph). Various combinations of the substituted pentynoic acids and halopyrroles were then explored. The same Pd-coupling conditions employed in Scheme 4 worked well with diverse acid precursors for pyrrole **1b**, which only has one *β*-substituent; by contrast, pyrrole **1a** and **1c** with **2b** or **2c** gave the meso-substituted lactone in trace quantities (detected by electrospray ionization mass spectrometry but not isolated). This difficulty may stem from steric hindrance between the *β*-pyrrole and meso-substituents but

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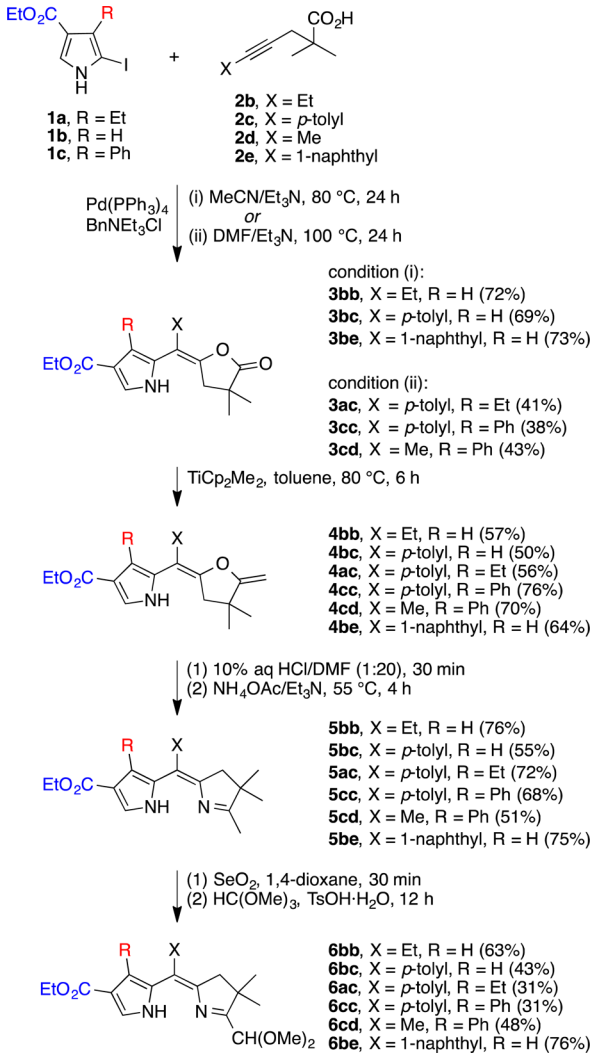
could be largely overcome with a higher reaction temperature (Scheme 7). In this manner, six lactone−pyrroles were obtained in yields of 38−73% (denoted "**3xy**" where "x" derives from the pyrrole and "y" from the particular pentynoic acid). Subsequent $TiCp_2Me_2$ treatment afforded ene−lactone−pyrroles **4xy**, which upon Paal−Knorr type reaction gave six dihydrodipyrrins **5xy** bearing various meso- and β-substituents. The dihydrodipyrrins **5xy** were converted to the corresponding dihydrodipyrrin−acetals **6xy** upon oxidation with SeO_2 and treatment with trimethyl orthoformate in acid. Each dihydrodipyrrin−acetal contains a meso-substituent and one or two β-pyrrole substituent(s).

Scheme 7. Preparation of Meso-Substituted Dihydrodipyrrin−Acetals

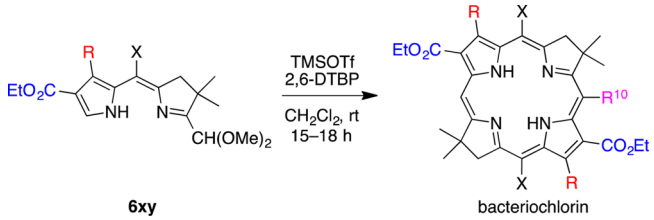


Each meso-substituted dihydrodipyrrin−acetal was treated to the standard acid-catalyzed conditions for self-condensation. The results are shown in Table 1. The 10-unsubstituted bacteriochlorin was obtained in yields ranging from 3.4% to 38%. In two cases, the 10-methoxybacteriochlorins also were observed and isolated. The 10-methoxybacteriochlorins derived from dihydrodipyrrin−acetals (**6bc** and **6be**) that lack a β-pyrrole substituent flanking the meso-aryl substituent. For the *p*-tolyl meso-substituent, the total yield of bacteriochlorins was 47% (9.1% and 38% with and without the 10-methoxy group). For the 1-naphthyl meso-substituent, the total yield of bacteriochlorins was 24% (21% and 3.4% with and without the 10-methoxy group). On the other hand, dihydrodipyrrin−acetal **6bb**, which contains a *meso*-ethyl substituent and no flanking β-pyrrole substituent, did not give a 10-methoxybacteriochlorin in detectable quantity as determined by TLC analysis.

Limitations in Scope of Bacteriochlorin β-Pyrrolic Substituents. All of the bacteriochlorins shown in Table 1 have a carboethoxy group at the β-pyrrole position. We explored several approaches to access bacteriochlorins lacking carboethoxy groups, with very limited success. The chief challenge stems in working around the beneficial role of the carboethoxy group in stabilizing electron-rich intermediates. Four major findings are shown in Scheme 8.

(1) We first examined use of a stabilizing *tert*-butyl ester at the α-pyrrolic position of the bacteriochlorin precursors, to be liberated at later stages of the synthesis. Halogenation of a pyrrole-2-carboxylate often affords complicated mixtures,[43,44] yet Trost and Dong recently prepared methyl 5-bromopyrrole-2-carboxylate via bromination of methyl pyrrole-2-carboxylate.[45] We applied the same procedure to *tert*-butyl pyrrole-2-carboxylate **8** (a known compound[46] prepared here by a new procedure) and obtained the corresponding *tert*-butyl 5-

Table 1. Synthesis of Meso-Substituted Bacteriochlorins



6xy bacteriochlorin

entry	compd **6xy**	X	R	R^{10}	bacteriochlorin	yield (%)	λ_{abs}, Q_y (nm)
1	**6bb**	Et	H	H	**7bb-HBC**	35	753
2	**6bc**	*p*-tolyl	H	H	**7bc-HBC**	38	759
		p-tolyl	H	OMe	**7bc-MeOBC**	9.1	748
3	**6ac**	*p*-tolyl	Et	H	**7ac-HBC**	33	757
4	**6cc**	*p*-tolyl	Ph	H	**7cc-HBC**	32	760
5	**6cd**	Me	Ph	H	**7cd-HBC**	29	755
6	**6be**	1-naphthyl	H	H	**7be-HBC**	3.4	759
		1-naphthyl	H	OMe	**7be-MeOBC**	21	748

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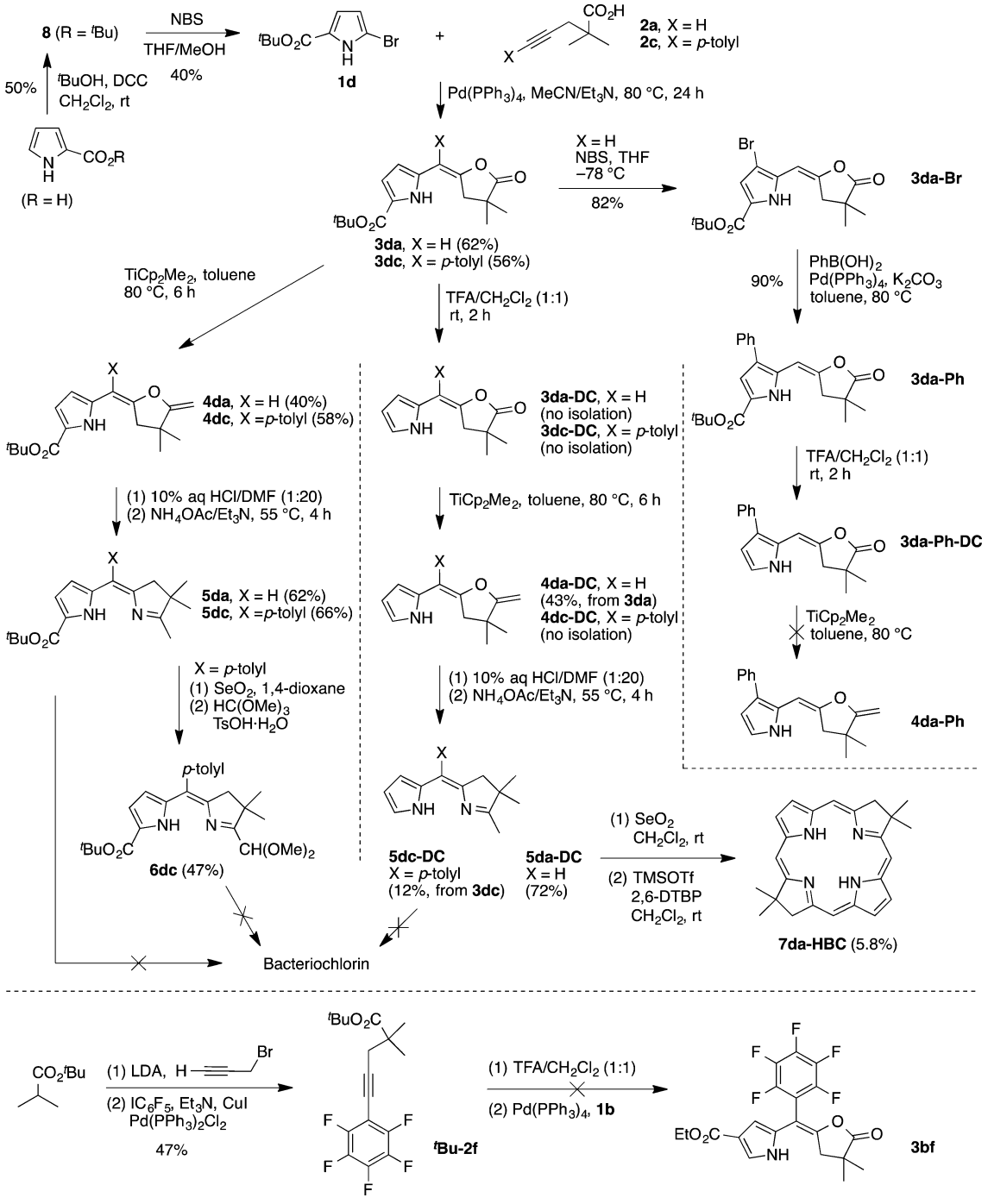
Scheme 8. Exploratory Syntheses of Bacteriochlorins Lacking Ester Substituents



bromopyrrole-2-carboxylate **1d**, albeit in modest yield. With pyrrole **1d** in hand, lactone−pyrroles **3da** and **3dc** were prepared following the procedures described above. Conversion to the corresponding dihydrodipyrrins **5da** and **5dc** proceeded smoothly (Scheme 8, left column). Attempts to remove the *tert*-butyl ester of **5da** and **5dc** under various conditions (e.g., neat TFA and other conditions explored by Jacobi and co-workers[35]) resulted in extensive decomposition. Conversion of **5dc** to the dihydrodipyrrin−acetal **6dc** was readily accomplished, but attempts to achieve in situ removal of the *tert*-butyl ester with subsequent self-condensation did not afford any bacteriochlorin. The difficult decarboxylation of dihydrodipyrrins[33] may stem from competitive protonation of the pyrroline nitrogen atom and deactivation of the π-system.

(2) Removal of *tert*-butyl esters at an earlier stage in the synthesis gave lactone−pyrroles **3da-DC** and **3dc-DC**, which were converted to the dihydrodipyrrins **5da-DC** and **5dc-DC**, respectively (Scheme 8, middle column). Upon treatment to SeO_2 conditions, neither of the expected dihydrodipyrrin−carboxaldehydes was sufficiently stable to be isolated or further converted to the dihydrodipyrrin−acetals (not shown). Treatment of **5da-DC** with SeO_2 followed immediately by TMSOTf/2,6-DTBP in CH_2Cl_2 gave a small amount (3.0 mg, 5.8%) of the desired 10-unsubstituted bacteriochlorin (**7da-HBC**), while SeO_2 treatment of **5dc-DC** directly gave an

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uncharacterized blue precipitate. The fully unsubstituted bacteriochlorin **7da-HBC** has been prepared previously by hydrodebromination of a 3,13-dibromobacteriochlorin.[47]

(3) We also attempted to incorporate β-aryl substituents on the bacteriochlorin. Thus, bromination of the lactone−pyrrole **3da** gave **3da-Br**, which upon Suzuki coupling gave **3da-Ph** in good yield. Removal of the *tert*-butyl ester with TFA gave the decarboxylated lactone−pyrrole **3da-Ph-DC**, which quickly decomposed under Petasis reagent treatment (Scheme 8, right column). Thus, the introduction of an aryl substituent at a β-pyrrole position did not afford sufficient improvement in stability.

(4) Finally, a pentafluorophenyl-substituted pentynoic ester (**^{t}Bu-2f**) was prepared by the propargylation of *tert*-butyl isobutyrate followed by a Sonogashira coupling reaction (Scheme 8, bottom panel). The subsequent Pd-coupling reaction with the iodopyrrole **1b**, however, did not provide any of the desired product **3bf**.

While several results described above offer a glimmer of possibility, at present the scope of the N-S route is best restricted to bacteriochlorins that bear a carboxylic ester substituent at a β-pyrrole position. The utility of other electron-withdrawing groups to impart stability remains to be determined.

Characterization. All new compounds, as well as known compounds synthesized via new pathways, were characterized by ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, and electrospray ionization mass spectrometry. Single-crystal X-ray structures were obtained for lactone−pyrroles **3ac** and **3da** as well as bacteriochlorins **7bb-HBC** and **7bc-HBC** (see Supporting Information). The X-ray structure of **3ac** and **3da** indicated a trans-conformation of the β-pyrrole- and meso-substituents, which minimizes steric interactions. The validity of the N-S self-condensation was confirmed by the X-ray structure determination of bacteriochlorins **7bb-HBC** and **7bc-HBC**.

Four types of bis-heterocycles prepared herein include an alkene joining the two heterocycles: the lactone−pyrrole (**3xy**), ene−lactone−pyrrole (**4xy**), 1-methyldihydrodipyrrin (**5xy**), and dihydrodipyrrin−acetal (**6xy**). The issue of the stereochemistry about the bridging alkene for these four types of structures has been studied by Jacobi and co-workers.[34,35] The *E*-configuration of lactone−pyrroles (analogues of **3**) was confirmed by NOE experiments,[34] consistent with the expected mechanism and kinetically controlled reaction.[34] Two single-crystal X-ray structure determinations (**3da** and **3ac**) obtained here also support this conclusion; the other lactone−pyrroles prepared herein are provisionally assigned as *E*-isomers. The ene−lactone−pyrroles (**4xy**) were prepared by treatment of lactone−pyrroles (**3xy**) with the Petasis reagent, for which the bridging alkene stereochemistry is expected to be preserved. The diagnostic feature for identification of the stereochemistry of dihydrodipyrrins (**5xy** and **6xy**) is given by the ^{1}H NMR chemical shift of the NH proton, as intramolecular hydrogen-bonding[35] (in $CDCl_3$) typically causes a chemical shift of at least 10.5 ppm; in the absence of such hydrogen-bonding, the chemical shift is ∼8−9 ppm.[34] Such evidence was supported by single-crystal X-ray structures of a *Z*-dihydrodipyrrin and an *E*-dihydrodipyrrin determined by Jacobi and co-workers.[34] Here, in each case, the dihydrodipyrrins (**5xy**) and dihydrodipyrrin−acetals (**6xy**) gave an NH proton resonance consistent with the *Z*-isomer.

The absorption spectra of all bacteriochlorins were obtained and exhibited features characteristic of known synthetic and natural bacteriochlorins.[2] The spectra include strong bands in the near-ultraviolet region and a strong band in the NIR region. The meso-disubstituted bacteriochlorins have a Q_y band in the NIR at 748−760 nm (Table 1). The absorption and fluorescence spectra of bacteriochlorin **7cc-HBC** are shown in Figure 1. Bacteriochlorin **7cc-HBC** contains substituents at

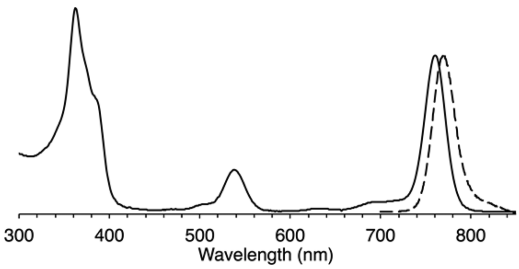

Figure 1. Absorption (solid line) and fluorescence (dashed line) spectra of meso-disubstituted bacteriochlorin **7cc-HBC** in CH_2Cl_2 at room temperature, normalized at the Q_y band.

all β-pyrrole positions (carboethoxy, phenyl) and two meso-positions (*p*-tolyl). The presence of the six substituents about the perimeter of the macrocycle, in addition to the two *gem*-dimethyl groups, does not impart significant conformational distortion, at least as measured by the sharpness of the Q_y absorption or emission band, which exhibits a full-width-at-half-maximum (fwhm) of 27 or 28 nm, respectively.

■ CONCLUSIONS

A new pathway to synthetic bacteriochlorins has been developed by melding Jacobi's dihydrodipyrrin synthesis and the E-W bacteriochlorin synthesis. This new N-S pathway complements the E-W synthesis by providing access to substitution patterns that previously were inaccessible, including *meso*-dialkyl, *meso*-diaryl, and meso-trisubstituted bacteriochlorins. Building the requisite dihydrodipyrrin−acetal requires four steps in both the E-W route (from the 2-formylpyrrole) and in the N-S route (from the 2-iodopyrrole). The bacteriochlorins prepared in this work have 6, 5, 4, 2, and 0 total aryl, alkyl, carboethoxy, and/or methoxy substituents at the β- and/or meso-positions. As with previously reported natural or synthetic bacteriochlorins, the new bacteriochlorins exhibit strong characteristic absorption in the near-infrared (NIR) spectral region, a feature that enables potential applications in fundamental studies as well as in artificial photosynthesis and photomedicine.

■ EXPERIMENTAL SECTION

General Methods. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were collected at room temperature in $CDCl_3$ unless noted otherwise. Silica gel (40 μm average particle size) was used for column chromatography. All solvents were reagent grade and were used as received unless noted otherwise. THF was freshly distilled from sodium/benzophenone ketyl. Electrospray ionization mass spectrometry data are reported for the molecular ion, protonated molecular ion, or sodium-cationized molecular ion. Commercial compounds were used as received. Pyrroles 4-ethyl-3-carboethoxypyrrole (**1a** precursor),[14] 3-carboethoxypyrrole (**1b** precursor),[14] and 3-carboethoxy-4-phenylpyrrole (**1c** precursor)[42] were prepared following literature procedures.

Bacteriochlorin Mixtures. The presence of 10-unsubstituted bacteriochlorins and 10-methoxybacteriochlorins was assessed by TLC and UV−vis spectroscopy analysis of the crude mixtures from the self-condensation reactions. For the two cases herein where both types of

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bacteriochlorins were present, upon TLC analysis [silica, hexanes/ethyl acetate (20:1)], the 10-unsubstituted bacteriochlorin or 10-methoxybacteriochlorin typically exhibit an R_f value of 0.40−0.60 or <0.15, respectively. The 10-methoxybacteriochlorin also exhibits a hypsochromically shifted Q_y band and a bathochromically shifted Q_x band compared to those of the 10-unsubstituted bacteriochlorin. Upon purification and ^{1}H NMR analysis, the 10-methoxybacteriochlorin shows two distinguishable peaks upfield of tetramethylsilane for the characteristic N−H signals versus only one such peak for the 10-unsubstituted bacteriochlorin.

*4-Carboethoxy-3-ethyl-2-iodopyrrole (**1a**).* A stirred solution of 3-carboethoxy-4-ethylpyrrole (1.67 g, 10.0 mmol) in dry DMF (50 mL) at 0 °C was treated with NIS (2.25 g, 10.0 mmol) in batches. After 1 h, ethyl acetate (100 mL) was added. The mixture was washed with water and brine. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (6:1)] afforded a white solid (2.26 g, 77%): mp 95−96 °C; ^{1}H NMR δ 1.11 (t, J = 7.2 Hz, 3H), 1.33 (t, J = 6.9 Hz, 3H), 2.67 (q, J = 7.2 Hz, 2H), 4.27 (q, J = 6.9 Hz, 2H), 7.47 (d, J = 2.7 Hz, 1H), 8.36 (s, 1H); ^{13}C NMR δ 14.8, 15.1, 21.1, 60.3, 67.8, 115.5, 128.7, 132.9 165.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{13}NO_2I$ 293.9987; found 293.9980.

*4-Carboethoxy-2-iodopyrrole (**1b**).* A stirred solution of 3-carboethoxypyrrole (1.39 g, 10.0 mmol) in dry DMF (50 mL) at 0 °C was treated with NIS (2.25 g, 10.0 mmol) in batches. After 1 h, ethyl acetate (100 mL) was added. The mixture was washed with water and brine. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a yellow solid (1.59 g, 60%): mp 86−88 °C; ^{1}H NMR δ 1.33 (t, J = 6.9 Hz, 3H), 4.29 (q, J = 6.9 Hz, 2H), 6.78 (dd, J = 1.7, 2.8 Hz, 1 H), 7.42 (dd, J = 1.7, 2.8 Hz, 1H), 9.72 (br, 1H); ^{13}C NMR δ 14.7, 60.7, 64.1, 119.0, 119.2, 127.9, 164.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_7H_9INO_2$ 265.9674; found 265.9683.

*4-Carboethoxy-2-iodo-3-phenylpyrrole (**1c**).* A stirred solution of 3-carboethoxy-4-phenylpyrrole (4.99 g, 23.2 mmol) in dry DMF (115 mL) at 0 °C was treated with NIS (5.22 g, 23.2 mmol) in batches. After 1 h, ethyl acetate (200 mL) was added. The mixture was washed with water and brine. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (5:1)] afforded a white solid (4.33 g, 55%): mp 121−122 °C; ^{1}H NMR δ 1.14 (t, J = 7.2 Hz, 3H), 4.15 (q, J = 7.2 Hz, 2H), 7.25−7.36 (m, 5H), 7.56 (d, J = 3.3 Hz, 1H), 8.62 (s, 1H); ^{13}C NMR δ 14.3, 60.1, 68.8, 116.3, 127.4, 127.9, 128.4, 130.7, 131.7, 134.9, 163.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{13}NO_2I$ 341.9987; found 341.9983.

*2-(tert-Butoxycarbonyl)-5-bromopyrrole (**1d**).* Following a procedure for the preparation of a similar compound,[45] a solution of **8** (670 mg, 4.01 mmol) in THF (40 mL) and MeOH (20 mL) was treated with NBS (89 mg, 0.50 mmol) at 0 °C. After 30 min, another portion of NBS (89 mg, 0.50 mmol) was added. After 30 min, another portion of NBS (89 mg, 0.50 mmol) was added. After 30 min, another portion of NBS (89 mg, 0.50 mmol) was added. After 30 min, another portion of NBS (178 mg, 1.00 mmol) was added. After 30 min, the last portion of NBS (178 mg, 1.00 mmol) was added. After 2 h, the reaction solution was concentrated. Column chromatography [silica, hexanes/diethyl ether (20:1)] afforded a white solid (396 mg, 40%): mp 95−96 °C; ^{1}H NMR δ 1.21 (s, 9H), 6.22 (dd, J = 3.0, 3.2 Hz, 1H), 6.73 (dd, J = 3.0, 3.2 Hz, 1H), 9.37 (br, 1H); ^{13}C NMR δ 28.6, 81.7, 104.2, 112.7, 116.4, 125.8, 159.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{13}BrNO_2$ 246.0125; found 246.0117.

*2,2-Dimethylhept-4-ynoic Acid (**2b**).* A solution of methyl isobutyrate (4.54 g, 50.0 mmol) in anhydrous THF (50 mL) at −78 °C under argon was treated with LDA solution (2.0 M, 25 mL in THF/heptane/ethylbenzene, 50 mmol). After 30 min, 1-bromopent-2-yne (7.35 g, 50.0 mmol) was added dropwise, and the reaction mixture was allowed to warm to room temperature. After 1 h at room temperature, the reaction was quenched by the addition of saturated aqueous NH_4Cl solution. The organic layer was extracted with diethyl ether. The combined organic extract was dried (Na_2SO_4) and concentrated. To the resulting oil were added KOH (8.4 g, 150 mmol), water (10 mL), MeOH (10 mL), and THF (30 mL), and the mixture was stirred overnight under argon. Afterward, 6 M HCl solution was added until the reaction mixture exhibited pH = 1. The resulting mixture was extracted with CH_2Cl_2. The organic fraction was dried (Na_2SO_4) and concentrated to afford a colorless oil that was used without further purification (4.85 g, 63%): ^{1}H NMR δ 1.11 (t, J = 6.8 Hz, 3H), 1.27 (s, 6H), 2.15 (qd, J = 2.4 Hz, J = 7.2 Hz, 2H), 2.40 (t, J = 2.4 Hz, 2H); ^{13}C NMR δ 12.6, 14.4, 24.5, 29.9, 42.5, 75.8, 84.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{15}O_2$ 155.1066; found 155.1071.

*2,2-Dimethyl-5-(p-tolyl)pent-4-ynoic Acid (**2c**).* A solution of methyl 2,2-dimethylpent-4-ynoate (2.50 g, 17.8 mmol) in Et_3N (40 mL) was added to a Schlenk flask and treated with 4-bromotoluene (3.03g, 17.8 mmol), CuI (110 mg, 0.576 mmol), $Pd(PPh_3)_4Cl_2$ (150 mg, 0.208 mmol), and PPh_3 (206 mg, 0.801 mmol). The resulting mixture was deaerated by three freeze−pump−thaw cycles and then kept at 80 °C for 12 h. Upon cooling to rt, CH_2Cl_2 (150 mL) was added, and the reaction mixture was filtered through Celite. The filtrate was concentrated to dryness and sequentially treated with KOH (2.35 g, 42.0 mmol), water (10 mL), MeOH (10 mL), and THF (30 mL) under argon. After 12 h, 6 M HCl was added until the reaction mixture exhibited pH = 1. The organic layer was then extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (2:1)] afforded a white solid (2.73 g, 72%): mp 183−185 °C; ^{1}H NMR δ 1.38 (s, 6H), 2.34 (s, 6H), 2.69 (s, 3H), 7.08−7.31 (m, 4H); ^{13}C NMR δ 21.7, 24.6, 30.5, 42.6, 83.2, 85.7, 120.7, 129.2, 131.7, 138.0, 183.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{17}O_2$ 217.1223; found 217.1217.

*2,2-Dimethyl-5-(1-naphthyl)pent-4-ynoic Acid (**2e**).* A solution of methyl 2,2-dimethylpent-4-ynoate (7.01 g, 50.1 mmol) in Et_3N was added to a Schlenk flask and treated with 1-iodonaphthalene (12.7 g, 50.1 mmol), CuI (272 mg, 1.50 mmol), $Pd(PPh_3)_4Cl_2$ (355 mg, 0.500 mmol), and PPh_3 (525 mg, 2.00 mmol). The resulting mixture was deaerated by three freeze−pump−thaw cycles and then kept at 80 °C for 12 h. Upon cooling to room temperature, 200 mL of CH_2Cl_2 was added, whereupon the reaction mixture was filtered through Celite. The filtrate was concentrated to dryness and sequentially treated with KOH (8.40 g, 150 mmol), water (30 mL), MeOH (30 mL), and THF (90 mL) under argon. After 12 h, 6 M HCl was added until the reaction mixture exhibited pH = 1. The organic layer was then extracted with CH_2Cl_2. The organic extract was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a white solid (7.64 g, 60%): mp 153−155 °C; ^{1}H NMR δ 1.47 (s, 6H), 2.88 (s, 6H), 7.46−7.84 (m, 6H), 8.33 (d, J = 8.4 Hz, 1H); ^{13}C NMR δ 24.8, 30.9, 42.8, 81.2, 91.5, 121.5, 125.4, 126.4, 126.5, 126.8, 128.4, 128.5, 130.5, 133.4, 133.7, 183.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}O_2$ 253.1223; found 253.1219.

*tert-Butyl 2,2-Dimethyl-5-(pentafluorophenyl)pent-4-ynoate (^{t}Bu-**2f**).* A solution of *tert*-butyl isobutyrate (4.33 g, 30.1 mmol) in anhydrous THF (30 mL) at −78 °C under argon was treated with LDA solution (2.0 M, 15 mL in THF/heptane/ethylbenzene, 30 mmol). After 30 min, propargyl bromide (4.41 g, 30.0 mmol) was added dropwise, and the reaction mixture was allowed to warm to room temperature. After 1 h at room temperature, the reaction was quenched by the addition of saturated aqueous NH_4Cl solution. The organic layer was extracted with diethyl ether. The combined organic extract was dried (Na_2SO_4), concentrated, and transferred to a Schlenk flask. Then Et_3N (24 mL), iodopentafluorobenzene (8.82 g, 30.0 mmol), CuI (67 mg, 0.346 mmol), $Pd(PPh_3)_4Cl_2$ (90 mg, 0.125 mmol), and PPh_3 (124 mg, 0.481 mmol) were added to the flask. The resulting mixture was deaerated by three freeze−pump−thaw cycles and then kept at 80 °C for 12 h. Upon cooling to room temperature, CH_2Cl_2 (100 mL) was added, and the reaction mixture was filtered through Celite. The filtrate was concentrated. Column chromatography [silica, hexanes/ethyl acetate (20:1)] afforded a colorless oil (4.91g, 47%): ^{1}H NMR δ 1.30 (s, 6H), 1.45 (s, 9H), 2.70 (s, 2H); ^{13}C NMR δ 24.7, 27.8, 30.8, 42.7, 80.6, 100.92, 100.97, 175.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{17}H_{17}F_5O_2Na$ 371.1041; found 371.1039.

*4-Carboethoxy-(E)-3-ethyl-2-{[4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene]methyl}pyrrole (**3aa**).* Following a general procedure,[35]

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a solution of **1a** (1.48 g, 5.05 mmol), **2a** (1.26 g, 10.1 mmol), and $BnNEt_3Cl$ (1.15 g, 5.05 mmol) in dry acetonitrile (20 mL) and Et_3N (5.0 mL) was added to a Schlenk flask and deaerated by three freeze−pump−thaw cycles. A sample of $Pd(PPh_3)_4$ (293 mg, 0.253 mmol) was then added, and the resulting mixture was further deaerated. The reaction mixture was kept at 80 °C for 24 h and allowed to cool to room temperature, and then CH_2Cl_2 and water were added. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a clear yellow solid (1.22 g, 87%): mp 128−129 °C; ^{1}H NMR δ 1.12 (t, J = 7.2 Hz, 3H), 1.31−1.36 (m, 9H), 2.72 (q, J = 7.2 Hz, 2H), 2.91 (d, J = 2.1 Hz, 2H), 4.27 (q, J = 6.9 Hz, 2H), 6.22 (s, 1H), 7.39 (d, J = 3.3 Hz, 1H), 8.58 (s, 1H); ^{13}C NMR δ 14.7, 16.0, 18.4, 24.9, 40.2, 40.5, 60.1, 97.8, 115.5, 123.6, 125.0, 127.1, 147.2, 175.8, 179.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{22}NO_4$ 292.1543; found 292.1539.

*4-Carboethoxy-(E)-2-[(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)methyl]pyrrole (**3ba**).* Following the procedure for **3aa**, **1b** (1.32 g, 5.00 mmol), **2a** (1.26 g, 10.1 mmol), and $BnNEt_3Cl$ (1.14 g, 5.00 mmol) in dry acetonitrile (30 mL) and Et_3N (6 mL) were treated with $Pd(PPh_3)_4$ (375 mg, 0.325 mmol). The standard workup and chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a clear yellow solid (727 mg, 55%): mp 110−111 °C; ^{1}H NMR δ 1.35−1.38 (m, 9H), 2.93 (d, J = 2.4 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 6.18 (dd, J = 1.5, 2.4 Hz, 1H), 6.39 (s, 1H), 7.39 (dd, J = 1.5, 1.8 Hz, 1H), 9.44 (s, 1H); ^{13}C NMR δ 14.7, 25.5, 40.2, 40.7, 60.2, 97.9, 107.0, 117.7, 123.7, 127.8, 148.3, 165.5, 180.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{18}NO_4$ 264.1230; found 264.1227.

*4-Carboethoxy-(E)-2-[1-(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)propyl]pyrrole (**3bb**).* Following the procedure for **3aa**, **1b** (1.35 g, 5.10 mmol), **2b** (2.36 g, 15.3 mmol), and $BnNEt_3Cl$ (1.16 g, 5.06 mmol) in dry acetonitrile (20 mL) and Et_3N (5.0 mL) were treated with $Pd(PPh_3)_4$ (383 mg, 0.332 mmol). The standard workup and chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a light yellow solid (1.06 g, 72%): mp 121−122 °C; ^{1}H NMR δ 1.04 (t, J = 7.4 Hz, 3H), 1.31−1.38 (m, 9H), 2.52 (q, J = 7.4 Hz, 2H), 2.88 (s, 2H), 4.30 (q, J = 7.2 Hz, 2H), 6.44 (s, 1H), 7.42 (s, 1H), 8.76 (s, 1H); ^{13}C NMR δ 13.7, 14.7, 22.3, 25.3, 40.3, 41.3, 60.2, 108.7, 111.7, 117.4, 123.4, 129.8, 143.7, 165.2, 180.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{22}NO_4$ 292.1543; found 292.1538.

*4-Carboethoxy-(E)-2-[(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)(p-tolyl)methyl]pyrrole (**3bc**).* Following the procedure for **3aa**, **1b** (1.05 g, 3.96 mmol), **2c** (1.70 g, 7.87 mmol), and $BnNEt_3Cl$ (894 mg, 3.94 mmol) in dry acetonitrile (20 mL) and Et_3N (5.0 mL) were treated with $Pd(PPh_3)_4$ (296 mg, 0.296 mmol). The standard workup and chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a yellow solid (960 mg, 69%): mp 117−119 °C; ^{1}H NMR δ 1.33−1.37 (m, 9H), 2.36 (s, 3H), 3.06 (s, 2H), 4.30 (q, J = 7.1 Hz, 2H), 6.56 (dd, J = 2.6, 1.5 Hz, 1H), 7.18 (s, 4H), 7.32 (dd, J = 3.2, 1.5 Hz, 1H), 8.10 (s, 1H); ^{13}C NMR δ 14.8, 21.5, 25.4, 40.2, 42.0, 60.1, 109.2, 111.1, 117.5, 123.4, 129.6, 129.8, 129.9, 132.3, 138.0, 145.0, 165.1, 179.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{24}NO_4$ 354.1700; found 354.1696.

*4-Carboethoxy-3-ethyl-2-[(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)(p-tolyl)methyl]pyrrole (**3ac**).* Following the procedure for **3aa**, **1a** (760 mg, 2.59 mmol), **2c** (1.12 g, 5.19 mmol), and $BnNEt_3Cl$ (590 mg, 2.59 mmol) in dry DMF (12 mL) and Et_3N (3 mL) were treated with $Pd(PPh_3)_4$ (194 mg, 0.168 mmol). The standard workup and chromatography [silica, hexanes/ethyl acetate (2:1)] afforded a clear white solid (405 mg, 41%): mp 131−133 °C; ^{1}H NMR δ 1.09 (t, J = 7.2 Hz, 3H), 1.31−1.36 (m, 9H), 2.31 (s, 3H), 2.56 (q, J = 7.2 Hz, 2H), 2.66 (s, 2H), 4.27 (q, J = 6.9 Hz, 2H), 7.07−7.31 (m, 4H), 7.40 (d, J = 3.3 Hz, 1H), 8.16 (s, 1H); ^{13}C NMR δ 14.7, 15.6, 18.9, 21.4, 25.0, 39.7, 41.9, 59.8, 109.3, 114.9, 124.8, 126.0, 126.4, 128.7, 129.1, 133.4, 137.3, 147.2, 165.4, 180.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{28}NO_4$ 382.2013; found 382.2005.

*4-Carboethoxy-2-[(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)(p-tolyl)methyl]-3-phenylpyrrole (**3cc**).* Following the procedure for **3aa**, **1c** (520 mg, 1.53 mmol), **2c** (658 mg, 3.05 mmol), and $BnNEt_3Cl$ (346 mg, 1.52 mmol) in dry DMF (12 mL) and Et_3N (3 mL) were treated with $Pd(PPh_3)_4$ (114 mg, 0.099 mmol). The standard workup and chromatography [silica, hexanes/ethyl acetate (2:1)] afforded a white solid (250 mg, 38%): mp 137−139 °C; ^{1}H NMR δ 0.90 (s, 6H), 1.23 (t, J = 7.2 Hz, 3H), 2.19 (s, 2H), 2.35 (s, 3H), 4.23 (q, J = 7.2 Hz, 2H), 7.15−7.41 (m, 9H), 7.51 (d, J = 2.7 Hz, 1H), 8.22 (s, 1H); ^{13}C NMR δ 14.5, 21.4, 24.5, 39.4, 41.3, 59.9, 114.5, 125.3, 125.7, 127.0, 127.3, 127.9, 128.2, 129.1, 129.4, 129.6, 130.0, 133.8, 134.7, 137.5, 147.2, 164.9, 180.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{28}NO_4$ 430.2013; found 430.2015.

*4-Carboethoxy-(E)-2-(1-(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)ethyl)-3-phenylpyrrole (**3cd**).* Following the procedure for **3aa**, **1c** (810 mg, 2.38 mmol), **2d** (665 mg, 4.75 mmol), and $BnNEt_3Cl$ (542 mg, 2.38 mmol) in dry DMF (16 mL) and Et_3N (4 mL) were treated with $Pd(PPh_3)_4$ (178 mg, 0.155 mmol). The standard workup and chromatography [silica, hexanes/ethyl acetate (2:1)] afforded a white solid (362 mg, 43%): mp 125−127 °C; ^{1}H NMR δ 0.95 (s, 6H), 1.25 (t, J = 7.2 Hz, 3H), 1.98 (s, 3H), 2.05 (s, 2H), 4.19 (q, J = 7.2 Hz, 2H), 7.18−7.34 (m, 5H), 7.47 (s, 1H), 8.41 (s, 1H); ^{13}C NMR δ 14.8, 16.8, 24.6, 40.0, 59.8, 103.7, 118.4, 124.8, 126.8, 128.0, 129.5, 130.3, 134.9, 146.7, 180.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{21}H_{24}NO_4$ 354.1700; found 354.1701.

*4-Carboethoxy-(E)-2-[(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)(1-naphthyl)methyl]pyrrole (**3be**).* Following the procedure for **3aa**, **1b** (1.33 g, 5.02 mmol), **2e** (2.52 g, 10.0 mmol), and $BnNEt_3Cl$ (1.14 mg, 5.00 mmol) in dry acetonitrile (20 mL) and Et_3N (5.0 mL) were treated with $Pd(PPh_3)_4$ (375 mg, 0.325 mmol). The standard workup and chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a yellow solid (1.42 g, 73%): mp 137−139 °C; ^{1}H NMR δ 1.31−1.41 (m, 9H), 3.25 (s, 2H), 4.26 (q, J = 7.2 Hz, 2H), 6.64 (dd, J = 2.7, 1.5 Hz, 1H), 7.15 (dd, J = 2.7, 1.5 Hz, 1H), 7.39−7.89 (m, 8H); ^{13}C NMR δ 14.7, 24.8, 25.5, 40.3, 41.9, 60.2, 107.4, 109.6, 110.0, 117.8, 123.3, 125.2, 125.9, 126.4, 126.9, 128.5, 128.8, 129.2, 130.1, 131.9, 132.1, 134.3, 145.6, 165.1, 179.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{24}NO_4$ 390.1700; found 390.1704.

*5-(tert-Butoxycarbonyl)-(E)-2-[(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)(p-tolyl)methyl]pyrrole (**3dc**).* Following the procedure for **3aa**, **1d** (493 mg, 2.01 mmol), **2c** (645 mg, 3.00 mmol), and $BnNEt_3Cl$ (456 mg, 2.00 mmol) in dry acetonitrile (15 mL) and Et_3N (5.0 mL) were treated with $Pd(PPh_3)_4$ (150 mg, 0.130 mmol). The standard workup and chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a yellow solid (426 mg, 56%): mp 117−119 °C; ^{1}H NMR δ 1.37 (s, 6H), 1.52 (s, 9H), 2.37 (s, 3H), 3.03 (s, 2H), 6.14−6.17 (m, 1H), 6.82−6.84 (m, 1H), 7.18 (s, 4H), 8.52 (s, 1H); ^{13}C NMR δ 21.5, 25.1, 25.3, 28.5, 28.6, 40.2, 42.0, 81.1, 110.4, 111.7, 115.4, 124.2, 128.3, 129.4, 129.58, 129.65, 132.2, 133.4, 138.0, 145.7, 160.8, 179.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{23}H_{27}NO_4Na$ 404.1832; found 404.1824.

*5-(tert-Butoxycarbonyl)-(E)-2-[(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)methyl]pyrrole (**3da**).* Following the procedure for **3aa**, **1d** (975 mg, 3.96 mmol), **2a** (1.25 g, 9.90 mmol), and $BnNEt_3Cl$ (903 mg, 3.96 mmol) in dry acetonitrile (21 mL) and Et_3N (7.0 mL) were treated with $Pd(PPh_3)_4$ (309 mg, 0.258 mmol). The standard workup and chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a yellow solid (711 mg, 62%): mp 96−98 °C; ^{1}H NMR δ 1.35 (s, 6H), 1.58 (s, 9H), 2.95 (s, 2H), 6.03−6.06 (m, 1H), 6.31−6.32 (m, 1H), 6.83−6.85 (m, 1H), 9.73 (s, 1H); ^{13}C NMR δ 25.6, 28.6, 40.1, 40.8, 81.4, 98.3, 108.4, 116.5, 123.9, 131.4, 149.6, 161.2, 179.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{21}NO_4Na$ 314.1363; found 314.1350.

*5-(tert-Butoxycarbonyl)-3-bromo-(E)-2-[(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)methyl]pyrrole (**3da-Br**).* A solution of **3da** (470 mg, 1.62 mmol) in THF (15 mL) was treated with NBS (287 mg, 1.62 mmol) at −78 °C for 15 min. Water and CH_2Cl_2 were added. The organic layer was separated, dried (Na_2SO_4), and concentrated. Column chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a white solid (492 mg, 82%): mp 102−104 °C; ^{1}H NMR δ 1.36 (s, 6H), 1.56 (s, 9H), 2.95 (d, J = 2.4 Hz, 2H), 6.23 (t, J = 2.4 Hz, 1H), 6.81 (d, J = 2.7 Hz, 1H), 8.91 (s, 1H); ^{13}C NMR δ 25.4, 28.5, 40.2, 40.6, 82.1, 96.5, 99.3, 117.4, 124.5, 128.7, 150.1, 160.2, 179.1; HRMS

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(ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{21}BrNO_4$ 370.0649; found 370.0650.

*5-(tert-Butoxycarbonyl)-(E)-2-[(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)methyl]-3-phenylpyrrole (**3da-Ph**).* A solution of **3da-Br** (490 mg, 1.32 mmol), K_2CO_3 (550 mg, 3.96 mmol), $Pd(PPh_3)_4$ (76 mg, 0.066 mmol), and phenylboronic acid (323 mg, 2.64 mmol) in toluene (20 mL) was added to a Schlenk flask and deaerated by three freeze−pump−thaw cycles. The reaction mixture was kept at 80 °C for 16 h. After cooling to room temperature, water and CH_2Cl_2 were added. The organic layer was separated, dried (Na_2SO_4), and concentrated. Column chromatography [silica, hexanes/ethyl acetate (5:1)] afforded a white solid (434 mg, 90%): mp 113−115 °C; ^{1}H NMR δ 1.26 (s, 6H), 1.56 (s, 9H), 2.71 (d, J = 2.1 Hz, 2H), 6.34 (s, 1H), 6.94 (d, J = 2.7 Hz, 1H), 7.37−7.41 (m, 5H), 8.98 (s, 1H); ^{13}C NMR δ 25.3, 28.6, 40.2, 40.4, 81.6, 97.7, 115.3, 124.4, 126.2, 126.8, 128.3, 128.9, 135.4, 149.9, 161.1, 179.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{26}NO_4$ 368.1856; found 368.1862.

*4-Carboethoxy-(E)-3-ethyl-2-[(4,4-dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)methyl]pyrrole (**4aa**).* Following a standard procedure for formation and reaction of the Petasis reagent,[35] a solution of $TiCp_2Cl_2$ (3.045 g, 12.37 mmol) in toluene (33 mL) was treated dropwise with LiMe solution (1.6 M, 17 mL in Et_2O, 27 mmol) at 0 °C under an argon atmosphere. After 1 h at 0 °C, saturated aqueous NH_4Cl solution was added. The organic layer was washed (water and brine), dried (Na_2SO_4), and filtered. The filtrate (now ∼30−40 mL owing to solvent losses in handling) contained the Petasis reagent. The filtrate in its entirety was treated with lactone−pyrrole **3aa** (760 mg, 2.61 mmol) and additional $TiCp_2Cl_2$ (39 mg). The solution was heated to 80 °C in the dark for 6 h under argon. Afterward, the resulting mixture was allowed to cool to room temperature whereupon MeOH (3.1 mL), $NaHCO_3$ (130 mg), and water (31 μL) were added. The mixture was kept at 40 °C for 12 h with stirring and then filtered through Celite. The filtrate was concentrated. Column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a clear orange solid (536 mg, 71%): mp 101−102 °C; ^{1}H NMR δ 1.11 (t, J = 7.2 Hz, 3H), 1.24 (s, 6H), 1.33 (t, J = 6.9 Hz, 3H), 2.62 (s, 2H), 2.75 (q, J = 7.2 Hz, 2H), 4.01 (d, J = 2.4 Hz, 1H), 4.26 (q, J = 6.9 Hz, 2H), 4.40 (d, J = 2.4 Hz, 1H), 5.91 (s, 1H), 7.35 (d, J = 3.3 Hz, 1H), 8.19 (s, 1H); ^{13}C NMR δ 14.3, 16.1, 18.4, 27.9, 40.5, 42.2, 59.5, 80.8, 92.1, 115.1, 123.8, 125.1, 153.4, 165.8, 169.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{24}NO_3$ 290.1751; found 290.1742.

*4-Carboethoxy-(E)-2-[(4,4-dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)methyl]pyrrole (**4ba**).* Following the procedure for **4aa**, the filtrate containing the Petasis reagent [prepared from $TiCp_2Cl_2$ (2.13 g, 8.68 mmol) in toluene (23 mL) and LiMe solution (1.6 M, 12 mL in Et_2O, 19 mmol)] was treated with lactone−pyrrole **3ab** (480 mg, 1.83 mmol) and additional $TiCp_2Cl_2$ (27 mg). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a yellow solid (231 mg, 48%): mp 99−101 °C; ^{1}H NMR δ 1.25 (s, 6H), 1.34 (t, J = 7.2 Hz, 3H), 2.68 (d, J = 1.8 Hz, 2H), 4.00 (d, J = 2.4 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 4.37 (d, J = 2.4 Hz, 1H), 5.85 (t, J = 1.5 Hz, 1H), 6.31 (s, 1H), 7.31 (m, 1H), 8.85 (s, 1H); ^{13}C NMR δ 14.7, 28.1, 40.3, 42.7, 60.1, 92.5, 105.6, 117.5, 122.8, 129.8, 154.9, 165.6, 169.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{20}NO_3$ 262.1438; found 262.1429.

*4-Carboethoxy-(E)-2-[1-(4,4-dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)propyl]pyrrole (**4bb**).* Following the procedure for **4aa**, the filtrate containing the Petasis reagent [prepared from $TiCp_2Cl_2$ (4.25 g, 17.3 mmol) in toluene (40 mL) and LiMe solution (1.6 M, 24 mL in Et_2O, 38 mmol)] was treated with lactone−pyrrole **3bb** (1.06 g, 3.63 mmol) and additional $TiCp_2Cl_2$ (56 mg). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a brown solid (601 mg, 57%): mp 106−108 °C; ^{1}H NMR δ 1.04 (t, J = 7.4 Hz, 3H), 1.21 (s, 6H), 1.34 (t, J = 7.2 Hz, 3H), 2.48 (q, J = 7.2 Hz, 2H), 2.62 (s, 2H), 3.98 (d, J = 2.2 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 4.38 (d, J = 2.2 Hz, 1H), 6.37 (s, 1H), 7.36 (dd, J = 3, 1.7 Hz, 1H), 8.34 (s, 1H); ^{13}C NMR δ 13.9, 14.9, 22.2, 27.9, 40.1, 43.0, 60.1, 80.4, 106.3, 107.5, 117.6, 122.5, 132.4, 150.0, 165.1, 170.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{24}NO_3$ 290.1751; found 290.1748.

*4-Carboethoxy-(E)-2-[(4,4-dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)(p-tolyl)methyl]pyrrole (**4bc**).* Following the procedure for **4aa**, the filtrate containing the Petasis reagent [prepared from $TiCp_2Cl_2$ (2.99 g, 12.1 mmol) in toluene (30 mL) and LiMe solution (1.6 M, 17 mL in THF/heptane/ethylbenzene, 27 mmol)] was treated with lactone−pyrrole **3bc** (904 mg, 2.56 mmol) and additional $TiCp_2Cl_2$ (39 mg). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a yellow solid (451 mg, 50%): mp 107−108 °C; ^{1}H NMR δ 1.27 (s, 6H), 1.35 (t, J = 7.2 Hz, 3H), 2.35 (s, 3H), 2.79 (s, 2H), 4.00 (d, J = 2.2 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 4.35 (d, J = 2.2 Hz, 1H), 6.48 (dd, J = 2.6, 1.5 Hz, 1H), 7.14−7.24 (m, 4H), 7.36 (dd, J = 3.0, 1.5 Hz, 1H), 8.04 (s, 1H); ^{13}C NMR δ 14.7, 21.5, 27.8, 40.1, 44.2, 60.0, 81.4, 105.8, 108.5, 117.1, 122.7, 129.3, 129.8, 131.9, 133.8, 136.9, 151.8, 165.3, 170.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{26}NO_3$ 352.1907; found 352.1914.

*4-Carboethoxy-3-ethyl-2-[(4,4-dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)(p-tolyl)methyl]pyrrole (**4ac**).* Following the procedure for **4aa**, the filtrate containing the Petasis reagent [prepared from $TiCp_2Cl_2$ (1.16 g, 4.74 mmol) in toluene (13 mL) and LiMe solution (1.6 M, 7.0 mL in Et_2O, 11 mmol)] was treated with lactone−pyrrole **3ac** (380 mg, 1.00 mmol) and additional $TiCp_2Cl_2$ (15 mg). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a yellow solid (212 mg, 56%): mp 123−125 °C; ^{1}H NMR δ 1.09 (t, J = 7.2 Hz, 3H), 1.22 (s, 6H), 1.35 (t, J = 6.9 Hz, 3H), 2.31 (s, 3H), 2.43 (s, 2H), 2.60 (q, J = 7.2 Hz, 2H), 4.06 (d, J = 2.1 Hz, 1H), 4.26 (q, J = 6.9 Hz, 2H), 4.50 (d, J = 2.1 Hz, 1H), 7.07−7.30 (m, 4H), 7.39 (d, J = 3.3 Hz, 1H), 7.90 (s, 1H); ^{13}C NMR δ 14.7, 15.6, 18.8, 21.3, 27.5, 39.4, 44.4, 59.6, 81.9, 103.5, 114.7, 124.0, 125.9, 128.1, 128.2, 129.0, 134.8, 135.9, 154.1, 165.5, 170.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{30}NO_3$ 380.2220; found 380.2214.

*4-Carboethoxy-2-[(4,4-dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)(p-tolyl)methyl]-3-phenylpyrrole (**4cc**).* Following the procedure for **4aa**, the filtrate containing the Petasis reagent [prepared from $TiCp_2Cl_2$ (512 mg, 2.08 mmol) in toluene (33 mL) and LiMe solution (1.6 M, 17 mL in Et_2O, 27 mmol)] was treated with lactone−pyrrole **3cc** (185 mg, 0.431 mmol) and additional $TiCp_2Cl_2$ (4 mg). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a yellow solid (140 mg, 76%): mp 123−125 °C; ^{1}H NMR δ 0.84 (s, 6H), 1.23 (t, J = 6.9 Hz, 3H), 2.00 (s, 2H), 2.33 (s, 3H), 3.90 (d, J = 2.7 Hz, 1H), 4.23 (q, J = 6.9 Hz, 2H), 4.36 (d, J = 2.7 Hz, 1H), 7.13−7.43 (m, 9H), 7.48 (d, J = 3.3 Hz, 1H), 8.10 (s, 1H); ^{13}C NMR δ 14.5, 21.3, 27.0, 38.9, 43.8, 59.7, 81.4, 102.7, 114.4, 124.8, 126.6, 127.9, 128.6, 129.1, 129.4, 130.1, 134.9, 135.2, 136.2, 154.1, 164.9, 170.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{30}NO_3$ 428.2220; found 428.2216.

*4-Carboethoxy-(E)-2-(1-(4,4-dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)ethyl)-3-phenylpyrrole (**4cd**).* Following the procedure for **4aa**, the filtrate containing the Petasis reagent [prepared from $TiCp_2Cl_2$ (588 mg, 2.39 mmol) in toluene (9.0 mL) and LiMe solution (1.6 M, 3.5 mL in Et_2O, 5.6 mmol)] was treated with lactone−pyrrole **3cd** (178 mg, 0.504 mmol) and additional $TiCp_2Cl_2$ (7.0 mg). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (5:1)] afforded a yellow solid (124 mg, 70%): mp 119−121 °C; ^{1}H NMR δ 0.92 (s, 6H), 1.19 (t, J = 7.2 Hz, 3H), 1.87 (s, 3H), 1.93 (s, 2H), 3.87 (d, J = 2.1 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 4.29 (d, J = 2.1 Hz, 1H), 7.21−7.30 (m, 5H), 7.42 (d, J = 3.0 Hz, 1H), 8.35 (s, 1H); ^{13}C NMR δ 14.5, 16.2, 27.2, 39.9, 42.0, 59.7, 80.2, 98.1, 114.7, 122.8, 123.9, 126.4, 127.7, 130.4, 130.8, 135.2, 152.4, 165.1, 170.3; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{26}NO_3$ 352.1907; found 352.1911.

*4-Carboethoxy-(E)-2-[(4,4-dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)(1-naphthyl)methyl]pyrrole (**4be**).* Following the procedure for **4aa**, the filtrate containing the Petasis reagent [prepared from $TiCp_2Cl_2$ (4.48 g, 18.1 mmol) in toluene (40 mL) and LiMe solution (1.6 M, 23 mL in THF/heptane/ethylbenzene, 36 mmol)] was treated with lactone−pyrrole **3be** (1.41 g, 3.62 mmol) and

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additional $TiCp_2Cl_2$ (55 mg). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a white solid (903 mg, 64%): mp 134−136 °C; ^{1}H NMR δ 1.32−1.36 (m, 9H), 3.01 (s, 2H), 3.91 (d, J = 2.2 Hz, 1H), 4.13 (d, J = 2.2 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 6.55 (dd, J = 2.7, 1.5 Hz, 1H), 7.09 (dd, J = 2.7, 1.5 Hz, 1H), 7.38−7.52 (m, 4H), 7.70 (s, 1H), 7.86 (d, J = 1.5 Hz, 1H), 7.88 (d, J = 1.5 Hz, 2 H); ^{13}C NMR δ 14.6, 27.9, 40.2, 43.8, 59.8, 81.3, 104.0, 106.0, 117.2, 122.3, 125.7, 125.8, 126.0, 128.3, 128.4, 128.7, 132.1, 132.2, 133.5, 134.1, 151.9, 164.2, 169.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{26}NO_3$ 388.1907; found 388.1908.

*5-(tert-Butoxycarbonyl)-(E)-2-[(4,4-dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)(p-tolyl)methyl]pyrrole (**4dc**).* Following the procedure for **4aa**, the filtrate containing the Petasis reagent [prepared from $TiCp_2Cl_2$ (1.23 g, 4.93 mmol) in toluene (15 mL) and LiMe solution (1.6 M, 17 mL in THF/heptane/ethylbenzene, 27 mmol)] was treated with lactone−pyrrole **3dc** (396 mg, 1.04 mmol) and additional $TiCp_2Cl_2$ (18 mg). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a yellow solid (228 mg, 58%): mp 93−95 °C; ^{1}H NMR δ 1.28 (s, 6H), 1.53 (s, 9H), 2.37 (s, 3H), 2.77 (s, 2H), 4.00 (d, J = 2.1 Hz, 1H), 4.37 (d, J = 2.1 Hz, 1H), 6.08 (t, J = 2.9 Hz, 1H), 6.82 (t, J = 2.9 Hz, 1H), 7.15−7.26 (m, 4H), 8.43 (s, 1H); ^{13}C NMR δ 21.5, 27.8, 28.6, 40.2, 44.2, 80.8, 81.6, 106.5, 109.8, 115.4, 123.3, 129.4, 129.8, 133.6, 135.7, 137.0, 152.3, 160.9, 169.8; HRMS (ESI-TOF) m/z: [2 M - H]$^+$ calcd for $C_{48}H_{57}N_2O_6$ 757.4211; found 757.4195.

*5-(tert-Butoxycarbonyl)-(E)-2-[(4,4-dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)methyl]pyrrole (**4da**).* Following the procedure for **4aa**, the filtrate containing the Petasis reagent [prepared from $TiCp_2Cl_2$ (1.90 g, 7.60 mmol) in toluene (21 mL) and LiMe solution (1.6 M, 11 mL in THF/heptane/ethylbenzene, 18 mmol)] was treated with lactone−pyrrole **3da** (474 mg, 1.63 mmol) and additional $TiCp_2Cl_2$ (24 mg). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a yellow solid (189 mg, 40%): mp 90−92 °C; ^{1}H NMR δ 1.26 (s, 6H), 1.57 (s, 9H), 2.72 (s, 2H), 4.03 (d, J = 2.1 Hz, 1H), 4.41 (d, J = 2.1 Hz, 1H), 5.91 (s, 1H), 3.97 (t, J = 2.8 Hz, 1H), 6.81 (t, J = 2.8 Hz, 1H), 8.82 (s, 1H); ^{13}C NMR δ 28.1, 28.6, 40.3, 42.6, 79.9, 80.8, 92.5, 105.8, 113.1, 122.3, 129.5, 154.8, 164.9, 169.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{24}NO_3$ 290.1755; found 290.1752.

*(E)-5-[(4,4-Dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)-methyl]pyrrole (**4da-DC**).* A sample of **3da** (401 mg, 1.38 mmol) was treated with TFA (5.0 mL) in CH_2Cl_2 (5.0 mL) at room temperature for 2 h. Aqueous saturated $NaHCO_3$ solution (100 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (100 mL). The organic layer was dried (Na_2SO_4) and concentrated. The resulting crude decarboxylated compound was directly treated with the Petasis reagent [prepared from $TiCp_2Cl_2$ (1.90 g, 7.60 mmol) and LiMe solution (1.6 M, 11 mL in THF/heptane/ethylbenzene, 18 mmol) in toluene (21 mL)] and additional $TiCp_2Cl_2$ (24 mg). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (10:1)] afforded a yellow solid (112 mg, 43%): mp 75−77 °C; ^{1}H NMR δ 1.28 (s, 6H), 2.77 (s, 2H), 4.02 (d, J = 2.4 Hz, 1H), 4.40 (d, J = 2.4 Hz, 1H), 5.93 (d, J = 1.8 Hz, 1H), 5.99 (s, 1H), 6.25 (t, J = 2.7 Hz, 1H), 6.72−6.75 (m, 1H), 7.96 (s, 1H); ^{13}C NMR δ 28.2, 40.4, 42.6, 80.5, 93.5, 105.4, 109.8, 117.0, 128.6, 153.2, 169.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{16}NO$ 190.1226; found 190.1222.

*(E)-2-[(4,4-Dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)(p-tolyl)methyl]pyrrole (**4dc-DC**).* A sample of **3dc** (608 mg, 1.60 mmol) was treated with TFA (5.0 mL) in CH_2Cl_2 (5.0 mL) at room temperature for 2 h. Aqueous saturated $NaHCO_3$ solution (100 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (100 mL). The organic layer was dried (Na_2SO_4) and concentrated. The resulting crude decarboxylated compound was directly treated with the Petasis reagent [prepared from $TiCp_2Cl_2$ (1.81 g, 7.24 mmol) and LiMe solution (1.6 M, 11 mL in THF/heptane/ethylbenzene, 18 mmol) in toluene (21 mL)] and additional $TiCp_2Cl_2$ (24 mg). The resulting solution was heated to 80 °C in the dark for 6 h. Afterward, the resulting mixture was allowed to cool to room temperature whereupon MeOH (1.6 mL), $NaHCO_3$ (65 mg) and water (1.6 μL) were added. The resulting solution was kept at 40 °C for 12 h and then filtered through Celite. The filtrate was concentrated. The compound was directly subjected to the next step without purification or further characterization due to limited stability.

*8-Carboethoxy-7-ethyl-2,3-dihydro-1,2,2-trimethyldipyrrin (**5aa**).* Following a general procedure,[35] a solution of **4aa** (569 mg, 1.97 mmol) in DMF (20 mL) was treated with 1 M HCl (1.0 mL). After 30 min, NH_4OAc (3.03 g, 39.5 mmol) and Et_3N (5.4 mL, 40 mmol) were added, and the resulting mixture was stirred at 55 °C for 4 h. Then the reaction was quenched by the addition of saturated aqueous KH_2PO_4 solution. Ethyl acetate (100 mL) was added, and the organic layer was washed (water), dried, and concentrated. Column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a light yellow solid (281 mg, 50%): mp 117−119 °C; ^{1}H NMR δ 1.14−1.18 (m, 9H), 1.35 (t, J = 6.9 Hz, 3H), 2.08 (s, 3H), 2.62 (s, 2H), 2.79 (q, J = 7.2 Hz, 2H), 4.27 (q, J = 6.9 Hz, 2H), 5.93 (s, 1H), 7.39 (d, J = 3.3 Hz, 1H), 11.1 (br, 1H); ^{13}C NMR d 14.3, 15.9, 16.6, 18.3, 25.8, 44.3, 48.4, 58.9, 103.8, 113.9, 124.3, 124.6, 128.5, 149.2, 164.7, 186.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{25}N_2O_2$ 289.1910; found 289.1903.

*8-Carboethoxy-2,3-dihydro-1,2,2-trimethyldipyrrin (**5ba**).* Following a general procedure,[35] a solution of **4ba** (220 mg, 0.842 mmol) in DMF (10 mL) was treated with 1 M HCl (0.5 mL). After 30 min, NH_4OAc (1.31 g, 17.1 mmol) and Et_3N (2.2 mL, 17 mmol) were added, and the resulting mixture was stirred at 55 °C for 6 h. Then the reaction was quenched by the addition of saturated aqueous KH_2PO_4 solution. Ethyl acetate (100 mL) was added, and the organic layer was washed (water), dried, and concentrated. Column chromatography [silica, hexanes/ethyl acetate (8:1)] afforded a yellow solid (87 mg, 40%): mp 110−112 °C; ^{1}H NMR δ 1.16 (s, 6H), 1.33 (t, J = 7.2 Hz, 3H), 2.13 (s, 3H), 2.55 (d, J = 1.8, 2H), 4.27 (q, J = 7.2 Hz, 2H), 5.79 (s, 1H), 6.41 (t, J = 1.8 Hz, 1 H), 7.40 (m, 1H), 11.2 (br, 1H); ^{13}C NMR δ 14.8, 15.8, 25.9, 44.1, 48.6, 59.7, 105.8, 108.2, 116.5, 124.2, 132.2, 150.4, 165.6, 187.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{21}N_2O_2$ 261.1598; found 261.1595.

*8-Carboethoxy-5-ethyl-2,3-dihydro-1,2,2-trimethyldipyrrin (**5bb**).* Following the procedure for **5aa**, **4bb** (601 mg, 2.08 mmol) in DMF (20 mL) was treated with 1 M HCl (1.0 mL) and then NH_4OAc (3.20 g, 41.6 mmol) and Et_3N (5.7 mL, 42 mmol). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a light yellow solid (456 mg, 76%): mp 133−134 °C; ^{1}H NMR δ 1.11−1.19 (m, 9H), 1.35 (t, J = 7.2 Hz, 3H), 2.12 (s, 3H), 2.34 (q, J = 7.2 Hz, 2H), 2.56 (s, 2H), 4.28 (q, J = 7.2 Hz, 2H), 6.56 (s, 1H), 7.43 (d, J = 3.3 Hz, 1H), 11.86 (br, 1H); ^{13}C NMR δ 13.9, 14.8, 15.8, 24.2, 26.2, 42.8, 48.0, 59.8, 106.7, 106.8, 116.0, 119.6, 124.1, 124.2, 146.8, 185.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{25}N_2O_2$ 289.1910; found 289.1916.

*8-Carboethoxy-2,3-dihydro-1,2,2-trimethyl-5-p-tolyldipyrrin (**5bc**).* Following the procedure for **5aa**, **4bc** (451 mg, 1.28 mmol) in DMF (20 mL) was treated with 1 M HCl (1.0 mL) and then NH_4OAc (1.97 g, 25.6 mmol) and Et_3N (3.5 mL, 26 mmol). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a light yellow solid (247 mg, 55%): mp 114−116 °C; ^{1}H NMR δ 1.13 (s, 6H), 1.28 (t, J = 7.2 Hz, 3H), 2.17 (s, 3H), 2.37 (s, 2H), 2.40 (s, 3H), 4.22 (q, J = 7.2 Hz, 2H), 6.02(t, J = 1.9 Hz, 1H), 7.16−7.19 (m, 4H), 7.48 (dd, J = 3.0, 1.7 Hz, 1H), 11.85 (s, 1H); ^{13}C NMR δ 14.8, 15.9, 21.5, 25.9, 44.1, 48.2, 59.7, 109.6, 116.1, 120.4, 124.4, 129.3, 129.8, 135.0, 136.2, 137.0, 148.1, 165.6, 186.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{27}N_2O_2$ 351.2067; found 351.2076.

*8-Carboethoxy-7-ethyl-2,3-dihydro-1,2,2-trimethyl-5-p-tolyldipyrrin (**5ac**).* Following the procedure for **5aa**, **4ac** (135 mg, 0.356 mmol) in DMF (10 mL) was treated with 1 M HCl (0.5 mL) and then NH_4OAc (546 mg, 7.12 mmol) and Et_3N (1.0 mL, 7.2 mmol). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a light yellow solid (97 mg, 72%): mp 115−116 °C; ^{1}H NMR δ 0.74 (t, J = 7.2 Hz, 3H), 1.11 (s, 6H), 1.29 (t, J = 6.9 Hz, 3H), 2.00 (q, J = 6.9 Hz, 2H), 2.14 (s, 3H), 2.29 (s, 2H), 2.39 (s, 3H), 4.21 (q, J = 7.2 Hz, 2H), 7.12−7.16 (m, 4H), 7.46 (d, J = 3.3 Hz, 1H), 11.61 (br, 1H); ^{13}C NMR δ 14.7, 15.9,

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16.5, 17.8, 21.5, 25.9, 44.5, 47.9, 59.2, 114.5, 121.2, 124.8, 127.2, 129.1, 129.3, 129.6, 136.9, 137.1, 148.7, 165.6, 186.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{31}N_2O_2$ 379.2380; found 379.2381.

*8-Carboethoxy-2,3-dihydro-1,2,2-trimethyl-7-phenyl-5-p-tolyldipyrrin (**5cc**).* Following the procedure for **5aa**, **4cc** (130 mg, 0.304 mmol) in DMF (10 mL) was treated with 1 M HCl (0.5 mL) and then NH_4OAc (700 mg, 9.13 mmol) and Et_3N (1.2 mL, 9.2 mmol). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (5:1)] afforded a light yellow solid (88 mg, 68%): mp 117−119 °C; ^1H NMR δ 0.79 (s, 6H), 1.23 (t, J = 7.2 Hz, 3H), 1.86 (s, 2H), 1.96 (s, 3H), 2.33 (s, 3H), 4.20 (q, J = 7.2 Hz, 2H), 7.10−7.50 (m, 10H), 8.11 (s, 1H); ^{13}C NMR δ 14.5, 15.9, 21.4, 25.5, 44.6, 48.4, 59.7, 114.4, 117.8, 124.7, 124.8, 126.5, 127.9, 128.8, 130.0, 130.3, 131.3, 135.2, 136.6, 136.8, 154.9, 165.1, 189.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{31}N_2O_2$ 427.2380; found 427.2382.

*8-Carboethoxy-2,3-dihydro-1,2,2,5-tetramethyl-7-phenyldipyrrin (**5cd**).* Following the procedure for **5aa**, **4cd** (120 mg, 0.342 mmol) in DMF (10 mL) was treated with 1 M HCl (0.5 mL) and then NH_4OAc (524 mg, 6.85 mmol) and Et_3N (1.0 mL, 7.2 mmol). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a yellow solid (62 mg, 51%): mp 111−112 °C; ^1H NMR δ 1.06 (t, J = 7.2 Hz, 3H), 1.17 (s, 6H), 1.41 (s, 3H), 2.14 (s, 3H), 2.48 (s, 2H), 4.21 (q, J = 7.2 Hz, 2H), 7.28−7.29 (m, 5H), 7.48 (d, J = 3.3 Hz, 1H), 12.18 (br, 1H); ^{13}C NMR δ 14.3, 15.8, 18.1, 26.3, 43.8, 47.8, 59.2, 114.4, 115.6, 123.8, 123.9, 126.5, 127.2, 130.8, 131.1, 137.8, 148.0, 165.3, 185.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{27}N_2O_2$ 351.2067; found 351.2073.

*8-Carboethoxy-2,3-dihydro-1,2,2-trimethyl-5-(1-naphthyl)-dipyrrin (**5be**).* Following the procedure for **5aa**, **4be** (899 mg, 2.32 mmol) in DMF (50 mL) was treated with 1 M HCl (2.5 mL) and then NH_4OAc (4.77 g, 46.4 mmol) and Et_3N (6.7 mL, 46 mmol). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (5:1)] afforded a yellow solid (678 mg, 75%): mp 133−135 °C; ^1H NMR δ 1.07 (s, 3H), 1.11 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H), 2.00−2.26 (m, 5H), 4.18 (q, J = 7.2 Hz, 2H), 5.79 (t, J = 1.8 Hz, 1H), 7.36−7.54 (m, 5H), 7.82−7.91 (m, 3H), 11.95 (s, 1H); ^{13}C NMR δ 14.7, 16.0, 25.9, 26.0, 43.7, 48.3, 59.7, 109.6, 116.3, 118.1, 124.4, 125.7, 125.9, 126.0, 126.4, 127.8, 128.0, 128.6, 132.1, 134.1, 134.9, 136.4, 149.3, 165.5, 187.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{25}H_{27}N_2O_2$ 387.2067; found 387.2081.

*9-(tert-Butoxycarbonyl)-2,3-dihydro-1,2,2-trimethyl-5-p-tolyldipyrrin (**5dc**).* Following the procedure for **5aa**, **4dc** (228 mg, 0.602 mmol) in DMF (20 mL) was treated with 1 M HCl (1.0 mL) and then NH_4OAc (1.62 g, 21.2 mmol) and Et_3N (2.9 mL, 21 mmol). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a white solid (150 mg, 66%): mp 114−116 °C; ^1H NMR δ 1.13 (s, 6H), 1.58 (s, 9H), 2.19 (s, 3H), 2.38 (s, 5H), 5.63 (dd, J = 1.2, 2.4 Hz, 1H), 6.71 (dd, J = 1.2, 2.4 Hz, 1H), 7.14−7.21 (m, 4H), 12.0 (s, 1H); ^{13}C NMR δ 16.1, 21.5, 25.9, 28.7, 44.3, 48.3, 80.3, 110.8, 114.8, 120.2, 124.5, 129.3, 129.8, 136.1, 137.0, 137.4, 149.9, 160.9, 188.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{31}N_2O_2$ 379.2380; found 379.2381.

*9-(tert-Butoxycarbonyl)-2,3-dihydro-1,2,2-trimethyldipyrrin (**5da**).* Following the procedure for **5aa**, **4da** (181 mg, 0.626 mmol) in DMF (20 mL) was treated with 1 M HCl (1.0 mL) and then NH_4OAc (0.957 g, 12.5 mmol) and Et_3N (1.7 mL, 13 mmol). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a white solid (112 mg, 62%): mp 90−91 °C; ^1H NMR δ 1.25 (s, 6H), 1.55 (s, 9H), 2.14 (s, 3H), 2.55 (s, 2H), 5.80 (s, 1H), 6.01−6.02 (m, 1H), 6.75−6.77 (m, 1H), 11.3 (s, 1H); ^{13}C NMR δ 16.0, 23.8, 29.5, 44.7, 49.5, 80.2, 105.8, 109.7, 115.1, 124.3, 135.0, 152.2, 160.4, 188.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{25}N_2O_2$ 289.1910; found 289.1905.

*2,3-Dihydro-1,2,2-trimethyldipyrrin (**5da-DC**).* Following the procedure for **5aa**, **4da-DC** (107 mg, 0.566 mmol) in DMF (20 mL) was treated with 1 M HCl (0.2 mL; the acid dose was reduced due to substrate stability) and then NH_4OAc (0.87 g, 11.3 mmol) and Et_3N (1.6 mL, 12 mmol). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (10:1)] afforded a yellow solid (77 mg, 72%): mp 82−84 °C; ^1H NMR δ 1.17 (s, 6H), 2.12(s, 3H), 2.55 (s, 2H), 5.86 (s, 1H), 6.05 (s, 1H), 6.14 (q, J = 3.0 Hz, 1H), 6.81 (d, J = 1.5 Hz, 1H), 10.8 (s, 1H); ^{13}C NMR δ 15.8, 25.8, 44.3, 48.4, 106.5, 107.9, 108.4, 118.7, 131.3, 148.4, 186.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{17}N_2$ 189.1386; found 189.1384.

*2,3-Dihydro-1,2,2-trimethyl-5-p-tolyldipyrrin (**5dc-DC**).* Following the procedure for **5aa**, **4dc-DC** (unpurified, prepared from 608 mg of **3dc**) in DMF (20 mL) was treated with 1 M HCl (1.0 mL) and then NH_4OAc (1.47 g, 19.2 mmol) and Et_3N (2.6 mL, 19 mmol). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a white solid (57 mg, 12% overall from **3dc**): mp 103−105 °C; ^1H NMR δ 1.11 (s, 6H), 2.15 (s, 3H), 2.35 (s, 2H), 2.38 (s, 3H), 5.61−5.64 (m, 1H), 6.06−6.09 (m, 1H), 6.86−6.88 (m, 1H), 7.16−7.22 (m, 4H), 11.4 (s, 1H); ^{13}C NMR δ 15.8, 21.5, 25.9, 44.2, 48.1, 108.1, 109.2, 118.9, 121.2, 129.1, 129.9, 134.1, 136.4, 137.1, 146.3, 185.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{23}N_2$ 279.1856; found 279.1855.

*8-Carboethoxy-7-ethyl-2,3-dihydro-1-(1,1-dimethoxymethyl)-2,2-dimethyldipyrrin (**6aa**).* Following a general procedure,[17] a solution of **5aa** (245 mg, 0.851 mmol) in 1,4-dioxane (15 mL) was treated with SeO_2 (284 mg, 2.55 mmol). The reaction mixture was stirred at room temperature for 30 min. Ethyl acetate and water were then added. The organic layer was washed (brine), dried, and concentrated to dryness. The crude product was dissolved in $HC(OMe)_3$ (7.0 mL) and treated with $TsOH·H_2O$ (48 mg, 0.25 mmol). After 12 h with stirring at room temperature, the reaction mixture was quenched by the addition of saturated aqueous $NaHCO_3$ solution and then extracted with ethyl acetate. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a brown oil (74 mg, 25%): ^1H NMR δ 1.16 (t, J = 7.2 Hz, 3H), 1.27 (s, 6H), 1.33 (t, J = 6.9 Hz, 3H), 2.61 (s, 2H), 2.78 (q, J = 7.2 Hz, 2H), 3.44 (s, 6H), 4.28 (q, J = 6.9 Hz, 2H), 5.10 (s, 1H), 6.01 (s, 1H), 7.41 (d, J = 3.3 Hz, 1H), 10.96 (br, 1H); ^{13}C NMR δ 14.9, 16.2, 18.1, 26.2, 45.9, 48.1, 54.3, 59.7, 102.2, 106.1, 125.7, 126.4, 128.3, 148.3, 165.7, 181.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{29}N_2O_4$ 349.2122; found 349.2116.

*8-Carboethoxy-2,3-dihydro-1-(1,1-dimethoxymethyl)-2,2-dimethyldipyrrin (**6ba**).* Following the procedure for **5aa**, **5ba** (109 mg, 0.42 mmol) in 1,4-dioxane (10 mL) was oxidized with SeO_2 (139 mg, 1.25 mmol) and then converted to the acetal by treatment with $TsOH·H_2O$ (25 mg, 0.13 mmol) in $HC(OMe)_3$ (5.0 mL). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a yellow oil (41 mg, 30%): ^1H NMR δ 1.27 (s, 6H), 1.33 (t, J = 7.2 Hz, 3H), 2.59 (d, J = 1.5 Hz, 2H), 3.44 (s, 6H), 4.27 (q, J = 7.2 Hz, 2H), 5.10 (s, 1H), 5.95 (m, 1H), 6.47 (m, 1H), 7.42 (m, 1H), 10.99 (br, 1H); ^{13}C NMR δ 14.7, 26.1, 45.8, 48.4, 54.7, 59.8, 102.3, 108.9, 109.4, 116.6, 124.9, 131.8, 149.4, 165.4, 182.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{25}N_2O_4$ 321.1809; found 321.1797.

*8-Carboethoxy-5-ethyl-2,3-dihydro-1-(1,1-dimethoxymethyl)-2,2-dimethyldipyrrin (**6bb**).* Following the procedure for **5aa**, **5bb** (456 mg, 1.58 mmol) in 1,4-dioxane (20 mL) was oxidized with SeO_2 (527 mg, 4.75 mmol) and then converted to the acetal by treatment with $TsOH·H_2O$ (90 mg, 0.475 mmol) in $HC(OMe)_3$ (10 mL). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a brown solid (347 mg, 63%): mp 124−126 °C; ^1H NMR δ 1.15 (t, J = 7.2 Hz, 3H), 1.29 (s, 6H), 1.35 (t, J = 7.2 Hz, 3H), 2.37 (q, J = 7.2 Hz, 2H), 2.60 (s, 2H), 3.44 (s, 6H), 4.28 (q, J = 7.2 Hz, 2H), 5.11 (s, 1H), 6.62 (s, 1H), 7.46 (dd, J = 2.9, 1.5 Hz, 1H), 11.67 (s, 1H); ^{13}C NMR δ 13.8, 14.8, 24.4, 26.5, 44.5, 47.9, 54.5, 59.8, 102.2, 107.8, 116.1, 123.1, 124.9, 133.5, 146.0, 166.6, 179.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{29}N_2O_4$ 349.2122; found 349.2116.

*8-Carboethoxy-2,3-dihydro-1-(1,1-dimethoxymethyl)-2,2-dimethyl-5-p-tolyldipyrrin (**6bc**).* Following the procedure for **5aa**, **5bc** (247 mg, 0.706 mmol) in 1,4-dioxane (15 mL) was oxidized with SeO_2 (235 mg, 2.12 mmol) and then converted to the acetal by treatment with $TsOH·H_2O$ (40 mg, 0.21 mmol) in $HC(OMe)_3$ (10 mL). The standard reaction and workup including chromatography [silica,

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hexanes/ethyl acetate (2:1)] afforded a brown oil (122 mg, 43%): ^{1}H NMR δ 1.22 (s, 6H), 1.28 (t, J = 7.2 Hz, 3H), 2.40 (s, 5H), 3.48 (s, 6H), 4.22 (q, J = 7.2 Hz, 2H), 5.11 (s, 1H), 6.07 (s, 1H), 7.15−7.23 (m, 4H), 7.50 (dd, J = 2.9, 1.7 Hz, 1H), 11.65 (s, 1H); ^{13}C NMR δ 14.7, 21.5, 26.2, 45.8, 48.0, 54.6, 59.8, 102.2, 110.7, 116.3, 123.6, 125.1, 129.3, 129.5, 134.6, 135.8, 137.3, 147.2, 165.5, 181.4; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{24}H_{31}N_2O_4$ 411.2278; found 411.2268.

*8-Carboethoxy-7-ethyl-2,3-dihydro-1-(1,1-dimethoxymethyl)-2,2-dimethyl-5-p-tolyldipyrrin (**6ac**).* Following the procedure for **5aa**, **5ac** (64 mg, 0.17 mmol) in 1,4-dioxane (10 mL) was oxidized with SeO_2 (56 mg, 0.51 mmol) and then converted to the acetal by treatment with TsOH·H_2O (20 mg, 0.10 mmol) in $HC(OMe)_3$ (5.0 mL). After 1 h with stirring at room temperature, standard workup and chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a yellow oil (23 mg, 31%): ^{1}H NMR δ 0.75 (t, J = 7.2 Hz, 3H), 1.21 (s, 6H), 1.30 (t, J = 6.9 Hz, 3H), 2.01 (q, J = 7.2 Hz, 2H), 2.32 (s, 2H), 2.41 (s, 3H), 3.47 (s, 6H), 4.23 (q, J = 6.9 Hz, 2H), 5.12 (s, 1H), 7.06−7.18 (m, 4H), 7.51 (d, J = 3.3 Hz, 1H), 11.50 (br, 1H); ^{13}C NMR δ 14.7, 16.5, 17.9, 21.6, 21.9, 26.2, 46.2, 47.7, 54.7, 59.3, 102.4, 114.7, 124.3, 125.6, 128.3, 128.8, 129.4, 130.0, 136.8, 137.2, 147.8, 165.5, 181.1; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{26}H_{35}N_2O_4$ 439.2591; found 439.2587.

*8-Carboethoxy-2,3-dihydro-1-(1,1-dimethoxymethyl)-2,2-dimethyl-7-phenyl-5-p-tolyldipyrrin (**6cc**).* Following the procedure for **5aa**, **5cc** (85 mg, 0.20 mmol) in 1,4-dioxane (10 mL) was oxidized with SeO_2 (66 mg, 0.60 mmol) and then converted to the acetal by treatment with TsOH·H_2O (10 mg, 0.050 mmol) in $HC(OMe)_3$ (5.0 mL). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a brown oil (30 mg, 31%): ^{1}H NMR δ 1.04 (t, J = 7.2 Hz, 3H), 1.18 (s, 6H), 2.15 (s, 3H), 2.35 (s, 2H), 3.48 (s, 6H), 4.02 (q, J = 7.2 Hz, 2H), 5.12 (s, 1H), 6.62−6.90 (m, 9H), 7.58 (d, J = 3.3 Hz, 1H), 11.69 (s, 1H); ^{13}C NMR δ 14.3, 21.2, 26.2, 29.9, 46.4, 47.8, 54.7, 59.3, 102.3, 124.2, 124.8, 126.2, 126.4, 128.4, 129.8, 131.0, 135.0, 135.6, 136.3, 148.9, 165.1, 181.7; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{30}H_{35}N_2O_4$ 487.2591; found 487.2594.

*8-Carboethoxy-2,3-dihydro-1-(1,1-dimethoxymethyl)-2,2,5-trimethyl-7-phenyldipyrrin (**6cd**).* Following the procedure for **5aa**, **5cd** (48 mg, 0.14 mmol) in 1,4-dioxane (10 mL) was oxidized with SeO_2 (44 mg, 0.40 mmol) and then converted to the acetal by treatment with TsOH·H_2O (10 mg, 0.050 mmol) in $HC(OMe)_3$ (5.0 mL). After 1 h with stirring at room temperature, standard workup including chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a brown oil (27 mg, 48%): ^{1}H NMR δ 1.06 (t, J = 7.2 Hz, 3H), 1.27 (s, 6H), 1.45 (s, 3H), 2.52 (s, 2H), 3.45 (s, 6H), 4.04 (q, J = 7.2 Hz, 2H), 5.11 (s, 1H), 7.26−7.31 (m, 5H), 7.51 (d, J = 3.3 Hz, 1H), 12.02 (br, 1H); ^{13}C NMR δ 14.3, 18.4, 26.6, 45.5, 47.5, 54.5, 59.2, 102.2, 115.8, 118.1, 124.4, 124.9, 126.6, 127.3, 130.5, 131.0, 137.6, 147.2, 165.2, 179.6; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{24}H_{31}N_2O_4$ 411.2278; found 411.2283.

*8-Carboethoxy-2,3-dihydro-1-(1,1-dimethoxymethyl)-2,2-dimethyl-5-(1-naphthyl)dipyrrin (**6be**).* Following the procedure for **5aa**, **5be** (668 mg, 1.73 mmol) in 1,4-dioxane (25 mL) was oxidized with SeO_2 (576 mg, 5.19 mmol) and then converted to the acetal by treatment with TsOH·H_2O (99 mg, 0.52 mmol) in $HC(OMe)_3$ (30 mL). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (2:1)] afforded a yellow oil (591 mg, 76%): ^{1}H NMR δ 1.17−1.26 (m, 9H), 2.15 ($\Delta\delta_{AB}$ = 0.175, J = 17.1 Hz, 2H), 3.53 (s, 6H), 4.17 (q, J = 7.2 Hz, 2H), 5.21 (s, 1H), 5.86 (t, J = 1.8 Hz, 1H), 7.39−7.57 (m, 5H), 7.82−7.91 (m, 3H), 11.66 (s, 1H); ^{13}C NMR δ 14.7, 26.1, 26.3, 45.3, 48.1, 54.7, 54.9, 59.7, 102.2, 110.7, 116.4, 121.4, 125.2, 125.6, 125.9, 126.1, 126.5, 127.5, 128.2, 128.6, 131.8, 134.1, 134.5, 136.0, 148.5, 165.4, 182.2; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{27}H_{31}N_2O_4$ 447.2278; found 447.2290.

*9-(tert-Butoxycarbonyl)-2,3-dihydro-1-(1,1-dimethoxymethyl)-2,2-dimethyl-5-p-tolyldipyrrin (**6dc**).* Following the procedure for **5aa**, **5dc** (150 mg, 0.397 mmol) in 1,4-dioxane (10 mL) was oxidized with SeO_2 (132 mg, 1.19 mmol) and then converted to the acetal by treatment with TsOH·H_2O (23 mg, 0.12 mmol) in $HC(OMe)_3$ (5.0 mL). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (2:1)] afforded a brown solid (82 mg, 47%): mp 123−125 °C; ^{1}H NMR δ 1.23 (s, 6H), 1.59 (s, 9H), 2.39 (s, 3H), 2.41 (s, 2H), 3.50 (s, 6H), 5.16 (s, 1H), 5.67−5.69 (m, 1H), 6.71−6.74 (m, 1H), 7.14−7.21 (m, 4H), 11.70 (s, 1H); ^{13}C NMR δ 21.5, 26.3, 28.7, 46.1, 48.2, 54.9, 80.4, 103.1, 111.8, 114.9, 123.3, 125.2, 129.3, 129.6, 135.9, 136.8, 137.3, 149.0, 160.7, 182.3; HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{26}H_{35}N_2O_4$ 439.2591; found 439.2607.

*2,12-Dicarboethoxy-3,13-diethyl-8,8,18,18-tetramethylbacteriochlorin (**7aa-HBC**).* Following a general procedure,[14] a solution of **6aa** (47 mg, 0.14 mmol) in anhydrous CH_2Cl_2 (9.0 mL) was treated with 2,6-DTBP (735 μL, 3.2 mmol) followed by TMSOTf (150 μL, 0.80 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 15 h, and then diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a dark green solid (15 mg, 39%): ^{1}H NMR δ −1.46 (s, 2H), 1.25 (t, J = 7.2 Hz, 6H), 1.71−1.78 (m, 12H), 1.96 (s, 12H), 4.13 (q, J = 7.2 Hz, 4H), 4.40 (s, 4H), 4.79 (q, J = 6.9 Hz, 4H), 8.77 (s, 2H), 9.62 (s, 2H); ^{13}C NMR δ 14.9, 17.8, 20.8, 31.3, 46.4, 51.7, 61.0, 96.81, 96.89, 132.7, 135.8, 159.3, 166.6, 172.6; MALDI-MS obsd 570.8, calcd 570.3206 (M$^+$); HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{34}H_{43}N_4O_4$ 571.3279; found 571.3265. λ_{abs} 353, 383, 519, 758 nm (CH_2Cl_2).

*2,12-Dicarboethoxy-8,8,18,18-tetramethylbacteriochlorin (**7ba-HBC**).* Following a general procedure,[14] a solution of **6ba** (27 mg, 84 μmol) in anhydrous CH_2Cl_2 (5.0 mL) was treated with 2,6-DTBP (385 μL, 1.68 mmol) followed by TMSOTf (79 μL, 0.42 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 24 h and then diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (5:1)] afforded a dark green solid (1.3 mg, 6.0%): ^{1}H NMR δ −1.46 (s, 2H), 1.70 (t, J = 6.9 Hz, 6H), 1.98 (s, 12H), 4.38 (s, 4H), 4.75 (q, J = 6.9 Hz, 4H), 8.78 (s, 2H), 9.17 (s, 2H), 9.71(s, 2H); ^{13}C NMR δ 14.9, 31.2, 46.4, 51.4, 61.1, 97.6, 100.8, 125.9, 133.4, 136.2, 160.1; MALDI-MS obsd 514.7, calcd 514.2580 (M$^+$); HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{30}H_{35}N_4O_4$ 515.2653; found 515.2658. λ_{abs} 351, 377, 521, 752 nm (CH_2Cl_2).

*2,12-Dicarboethoxy-5,15-diethyl-8,8,18,18-tetramethylbacteriochlorin (**7bb-HBC**).* Following a general procedure,[14] a solution of **6bb** (100. mg, 0.287 mmol) in anhydrous CH_2Cl_2 (15 mL) was treated with 2,6-DTBP (1.10 g, 5.75 mmol) followed by TMSOTf (262 μL, 1.44 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 15 h and then diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a purple solid (29 mg, 35%): ^{1}H NMR δ −0.98 (s, 2H), 1.68−1.79 (m, 12H), 1.96 (s, 12H), 4.07 (q, J = 7.4 Hz, 4H), 4.24 (s, 4H), 4.77 (q, J = 7.0 Hz, 4H), 9.32 (d, J = 2.2 Hz, 2H), 9.74 (s, 2H); ^{13}C NMR δ 15.0, 18.7, 27.4, 31.5, 45.9, 49.5, 61.1, 97.3, 115.8, 122.3, 123.0, 134.2, 134.9, 160.4, 166.2, 171.2; MALDI-MS obsd 570.9, calcd 570.3206 (M$^+$); HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{34}H_{43}N_4O_4$ 571.3279; found 571.3268. λ_{abs} 361, 383, 548, 753 nm (CH_2Cl_2).

*2,12-Dicarboethoxy-8,8,18,18-tetramethyl-5,15-di-p-tolylbacteriochlorin (**7bc-HBC**).* Following a general procedure,[14] a solution of **6bc** (122 mg, 0.297 mmol) in anhydrous CH_2Cl_2 (15 mL) was treated with 2,6-DTBP (1.14 g, 5.95 mmol) followed by TMSOTf (270 μL, 1.50 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 15 h, diluted with CH_2Cl_2, and washed with saturated aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (4:1)] gave two bands (both purple). The first band [R_f = 0.53, TLC, silica, hexanes/ethyl acetate (20:1)] was isolated and concentrated to afford the title compound as a dark purple solid (39 mg, 38%). The second band [R_f = 0.15, TLC, silica, hexanes/ethyl acetate (20:1)] afforded bacteriochlorin **7bc-MeOBC** as a dark purple solid (9.8 mg, 9.1%). Data for the title compound: ^{1}H

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NMR δ −0.99 (s, 2H), 1.62 (t, J = 7.2 Hz, 6H), 1.88 (s, 12H), 2.65 (s, 6H), 3.96 (s, 4H), 4.68 (q, J = 7.2 Hz, 4H), 7.51 (d, J = 7.7 Hz, 4H), 7.72 (d, J = 7.7 Hz, 4H), 8.65 (s, 2H), 9.77 (s, 2H); ^{13}C NMR δ 15.0, 21.8, 31.3, 46.1, 51.3, 61.0, 98.1, 115.9, 122.2, 126.0, 129.0, 132.2, 135.0, 135.7, 137.5, 139.1, 160.7, 166.0, 172.5; MALDI-MS obsd 695.1, calcd 694.3514 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{44}H_{47}N_4O_4$ 695.3597; found 695.3583. λ_{abs} 360, 371, 382, 542, 759 nm (CH_2Cl_2). Data for 2,12-dicarboethoxy-10-methoxy-8,8,18,18-tetramethyl-5,15-di-*p*-tolylbacteriochlorin (**7bc-MeOBC**): ^{1}H NMR δ −0.91 (s, 1H), −0.81 (s, 1H), 1.49−1.62 (m, 6H), 1.84 (s, 6H), 1.96 (s, 6H), 2.61 (s, 4H), 2.63 (s, 4H), 3.86 (s, 3H), 3.88 (s, 3H), 4.04 (s, 3H), 4.57−4.88 (m, 4H), 7.45−7.69 (m, 4H), 8.09 (d, J = 2.2 Hz, 1H), 8.56 (d, J = 2.2 Hz, 1H), 9.55 (s, 1H); ^{13}C NMR δ 14.5, 14.9, 21.7, 29.3, 30.9, 46.1, 50.9, 61.0, 96.8, 116.2, 122.0, 125.0, 126.9, 128.9, 129.7, 131.9, 132.1, 134.2, 135.3, 136.5, 137.4, 137.5, 137.9, 139.1, 139.4, 159.2, 159.7, 165.8, 168.4, 173.1; MALDI-MS obsd 725.1, calcd 724.3625 (M^+); HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{45}H_{49}N_4O_5$ 725.3697; found 725.3692. λ_{abs} 379, 548, 748 nm (CH_2Cl_2).

*2,12-Dicarboethoxy-3,13-diethyl-8,8,18,18-tetramethyl-5,15-di-p-tolylbacteriochlorin (**7ac-HBC**).* Following a general procedure,[14] a solution of **6ac** (21 mg, 0.048 mmol) in anhydrous CH_2Cl_2 (5.0 mL) was treated with 2,6-DTBP (220 μL, 0.96 mmol) followed by TMSOTf (45 μL, 0.24 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 15 h and then diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (5:1)] afforded a purple solid (6.0 mg, 33%): ^{1}H NMR δ −0.54 (s, 2H), 1.15 (t, J = 7.2 Hz, 6H), 1.65 (t, J = 6.9 Hz, 6H), 1.82 (s, 12H), 2.63 (s, 6H), 3.08 (q, J = 7.2 Hz, 4H), 3.78 (s, 4H), 4.73 (q, J = 6.9 Hz, 4H), 7.55 (ABq, $\Delta\delta_{AB}$ = 0.19, J = 7.8 Hz, 8H), 9.51 (s, 2H); ^{13}C NMR δ 14.8, 17.9, 20.7, 21.8, 26.6, 31.3, 45.8, 51.7, 61.1, 86.8, 115.2, 122.4, 129.1, 131.6, 132.5, 134.1, 137.6, 139.5, 142.7, 161.2, 167.1, 170.1; MALDI-MS obsd 751.2, calcd 750.4140 (M^+); HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{48}H_{54}N_4O_4$ 750.4140; found 750.4142. λ_{abs} 361, 387, 534, 757 nm (CH_2Cl_2).

*2,12-Dicarboethoxy-8,8,18,18-tetramethyl-3,13-diphenyl-5,15-di-p-tolylbacteriochlorin (**7cc-HBC**).* Following a general procedure,[14] a solution of **6cc** (25 mg, 0.051 mmol) in anhydrous CH_2Cl_2 (5.0 mL) was treated with 2,6-DTBP (234 μL, 1.0 mmol) followed by TMSOTf (50 μL, 0.25 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 15 h, and then diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a dark purple solid (7.0 mg, 32%): ^{1}H NMR δ −0.31 (s, 2H), 1.05 (t, J = 7.2 Hz, 6H), 1.82 (s, 12H), 2.36 (s, 6H), 3.77 (s, 4H), 4.30 (q, J = 7.2 Hz, 4H), 6.89−7.20 (m, 18H), 9.52 (s, 2H); ^{13}C NMR δ 13.9, 31.2, 45.8, 51.7, 60.8, 88.4, 97.2, 116.3, 124.3, 125.4, 126.6, 128.3, 131.2, 132.5, 132.8, 133.4, 136.5, 137.4, 137.6, 138.7, 162.0, 166.7, 171.7, 183.8; MALDI-MS obsd 847.4, calcd 847.4218 [$(M + H)^+$]; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{56}H_{55}N_4O_4$ 847.4218; found 847.4191. λ_{abs} 363, 538, 760 nm (CH_2Cl_2).

*2,12-Dicarboethoxy-5,8,8,15,18,18-hexamethyl-3,13-diphenylbacteriochlorin (**7cd-HBC**).* Following a general procedure,[14] a solution of **6cd** (25 mg, 0.061 mmol) in anhydrous CH_2Cl_2 (9.0 mL) was treated with 2,6-DTBP (280 μL, 1.2 mmol) followed by TMSOTf (56 μL, 0.30 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 15 h, and then diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a dark purple solid (6.1 mg, 29%): ^{1}H NMR δ −0.19 (s, 2H), 1.15 (t, J = 6.9 Hz, 6H), 1.91 (s, 12H), 2.92 (s, 6H), 4.06 (s, 4H), 4.39 (q, J = 6.9 Hz, 4H), 7.57−7.72 (m, 10H), 9.62 (s, 2H); ^{13}C NMR δ 14.1, 21.0, 29.9, 31.6, 45.7, 51.0, 60.8, 96.7, 110.0, 123.3, 127.5, 128.0, 130.8, 132.9, 133.1, 137.7, 139.4, 161.9, 166.7, 170.3; MALDI-MS obsd 695.1, calcd 694.3514 (M^+); HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{44}H_{46}N_4O_4$ 694.3513; found 694.3514. λ_{abs} 365, 547, 755 nm (CH_2Cl_2).

*2,12-Dicarboethoxy-8,8,18,18-tetramethyl-5,15-bis(1-naphthyl)-bacteriochlorin (**7be-HBC**).* Following a general procedure,[14] a solution of **6be** (587 mg, 1.32 mmol) in anhydrous CH_2Cl_2 (72 mL) was treated with 2,6-DTBP (5.02 g, 26.3 mmol) followed by TMSOTf (1.46 g, 6.58 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 18 h, diluted with CH_2Cl_2, and washed with saturated aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (20:1)] gave two bands (both purple). The first band [R_f = 0.43, TLC, silica, hexanes/ethyl acetate (20:1)] was isolated and concentrated to afford the title compound as a dark purple solid (17 mg, 3.4%). The second band [R_f = 0.12, TLC, silica, hexanes/ethyl acetate (20:1)] afforded bacteriochlorin **7be-MeOBc** as a dark purple solid (110 mg, 21%). Data for the title compound: ^{1}H NMR δ −0.78 (s, 2H), 1.55 (t, J = 7.2 Hz, 6H), 1.78 (d, J = 3.0 Hz, 6H), 1.86 (d, J = 2.7 Hz, 6H), 3.58−3.88 (m, 4H), 4.57−4.64 (m, 4H), 7.19−7.23 (m, 4H), 7.52−7.55 (m, 2H), 7.81−8.22 (m, 8H), 8.48 (d, J = 1.2 Hz, 2H), 9.82 (s, 2H); ^{13}C NMR δ 14.9, 31.0, 31.3, 31.4, 46.2, 50.6, 61.1, 98.3, 113.4, 122.6, 125.6, 126.1, 126.2, 126.8, 128.7, 130.6, 130.7, 133.9, 134.5, 135.1, 135.9, 139.2, 161.3, 165.8, 172.94, 127.97; MALDI-MS obsd 767.2 calcd 766.3514 (M^+); HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{50}H_{46}N_4O_4$ 766.3514; found 766.3512. λ_{abs} 359, 383, 539, 759 nm (CH_2Cl_2). Data for 2,12-dicarboethoxy-10-methoxy-8,8,18,18-tetramethyl-5,15-bis(1-naphthyl)bacteriochlorin (**7be-MeOBC**): ^{1}H NMR δ −0.75 (s, 1H), −0.62 (s, 1H), 1.21−1.55 (m, 6H), 1.77−1.91 (m, 12H), 3.49−3.80 (m, 4H), 4.06 (s, 3H), 4.51−4.59 (m, 4H), 7.18−7.26 (m, 4H), 7.49−7.54 (m, 2H), 7.80−8.21 (m, 9H), 8.40 (t, J = 2.1 Hz, 1H), 9.59 (s, 1H); ^{13}C NMR δ 14.4, 14.8, 29.1, 29.3, 30.7, 30.9, 46.2, 47.1, 47.2, 50.2, 53.2, 61.0, 61.9, 68.1, 97.1, 112.8, 113.7, 121.6, 122.4, 125.2, 125.6, 126.1, 126.2, 126.6, 126.7, 127.0, 128.6, 128.7, 129.9, 130.5, 130.8, 132.4, 133.9, 134.3, 134.4, 135.4, 136.7, 138.0, 139.2, 139.5, 159.7, 160.4, 165.7, 166.2, 168.2, 173.4, 173.5; MALDI-MS obsd 797.2, calcd 796.3619 (M^+); $[M]^+$ calcd for $C_{51}H_{48}N_4O_5$ 796.3619; found 796.3615. λ_{abs} 364, 381, 547, 748 nm (CH_2Cl_2).

*8,8,18,18-Tetramethylbacteriochlorin (**7da-HBC**).* Compound **5da-DC** (53 mg, 0.28 mmol) in CH_2Cl_2 (15 mL) at room temperature under argon was treated with SeO_2 (67 mg, 0.60 mmol). After TLC analysis showed the disappearance of **5da-DC**, TMSOTf (282 μL, 1.55 mmol) and 2,6-DTBP (1.18 g, 6.16 mmol) were added immediately to the reaction mixture. The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 3 h and then diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (10:1)] afforded a dark green solid (3.0 mg, 5.8%): ^{1}H NMR δ −2.38 (s, 2H), 1.97(s, 12H), 4.46 (s, 4H), 8.71−8.77 (m, 6H), 8.83 (s, 2H); ^{13}C NMR δ 31.3, 46.2, 51.7, 96.7, 98.9, 121.9, 122.1, 135.5, 136.4, 157.8, 169.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{27}N_4$ 371.2230; found 371.2224. λ_{abs} 339, 364, 488, 713 nm (CH_2Cl_2). The characterization data match those obtained from an alternative route.[47]

*2-(tert-Butoxycarbonyl)pyrrole (**8**).* A solution of pyrrole-2-carboxylic acid (5.00 g, 45.0 mmol) in THF (120 mL) was treated with *tert*-butyl alcohol (60 mL) followed by DCC (13.9 g, 67.6 mmol) at 0 °C under an argon atmosphere. After 1 h, the reaction mixture was filtered. The filtrate was concentrated and chromatographed [silica, hexanes/ethyl acetate (10:1)] to afford a white solid (3.76 g, 50%): mp 91−93 °C; ^{1}H NMR δ 1.47 (s, 9H), 6.22−6.25 (m, 1H), 6.82−6.85 (m, 1H), 6.90−6.92 (m, 1H), 9.23 (br, 1H); ^{13}C NMR δ 28.6, 81.0, 110.4, 114.8, 122.1, 160.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{14}NO_2$ 168.1019; found 168.1017. The characterization data match those obtained from an alternative route.[46]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b10637.

Spectral data for all new compounds (PDF)
X-ray data for **3da** (CCDC 1505669) (CIF)

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X-ray data for **3ac** (CCDC 1505670) (CIF)
X-ray data for **7bb-HBC** (CCDC 1505671) (CIF)
X-ray data for **7bc-HBC** (CCDC 1505672) (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: jlindsey@ncsu.edu.

Notes

The authors declare the following competing financial interest(s): One coauthor (JSL) is co-founder of NIRvana Sciences Inc., to which the technology described in the present paper has been licensed. Substantial portions of the present paper were included in a patent application submitted in August 2016.

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