Northern–Southern Route to Synthetic Bacteriochlorins

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S 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: Pdmediated 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 ($\varepsilon \sim 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) longwavelength absorption band located in the NIR region of \sim 750–800 nm², 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 we¹²⁻²⁰ and others²¹⁻²⁵ 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 CH₂Cl₂ containing trimethylsilyl triflate (TMSOTf) and 2,6-di-tertbutylpyridine (2,6-DTBP),¹⁴ or in CH₃CN¹² containing BF₃. $O(Et)_2$] 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-position¹⁹ and entities (e.g., carbonyl, aryl, ethynyl) that can be introduced at the 15-position via Pd-mediated coupling of the 5-alkoxy-15bromobacteriochlorin (Chart 2, panel A). Examples include BC-1¹³ 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 Mesosubstituted bacteriochlorins can of course be prepared by reduction of (or addition to) the corresponding porphyrin, but the approach generally does not afford the stabilizing gemdialkyl 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-(1,1dimethoxymethyl)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 2and 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 Chart 2. Known Bacteriochlorins (panels A, B) and New Target Bacteriochlorins (panel C)

(A) representative gem-dimethyl, meso-substituted bacteriochlorins:



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

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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 5position 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-carboxylate¹⁴ 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 conditions³⁵ gave



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

1,3-relationship

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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 NH₄OAc/NEt₃. Dihydrodipyrrin 5aa contains the gem-dimethyl group at the 2-position, by contrast with the 3position of dihydrodipyrrins employed in the E-W route to bacteriochlorins. Treatment of 5aa with SeO₂ and HC(OMe)₃ following a reported procedure¹⁷ 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 formation³⁴ 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 CH2Cl2 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 bacteriochlorin¹⁴ (which corresponds to the 10-position in the N-S route). Application of the reaction conditions of TMSOTf/2,6-DTBP in CH₂Cl₂ 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-

Scheme 5. Distinct Outcomes for Two Routes to Bacteriochlorins



iso) with identical pyrrole substituents (but positioninterchanged versus that for **6aa** and **6ba**) gave the 5methoxybacteriochlorin 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 5substituted 2,2-dimethylpent-4-ynoic acids $2\mathbf{b}-\mathbf{e}$. 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 could be largely overcome with a higher reaction temperature (Scheme 7). In this manner, six lactone-pyrroles were





Table 1. Synthesis of Meso-Substituted Bacteriochlorins

obtained in yields of 38-73% (denoted "**3xy**" where "x" derives from the pyrrole and "y" from the particular pentynoic acid). Subsequent TiCp₂Me₂ 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 SeO₂ and treatment with trimethyl orthoformate in acid. Each dihydrodipyrrin-acetal contains a meso-substituent and one or two β -pyrrole substituent(s).

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, dihydrodipyrrinacetal 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 compound⁴⁶ prepared here by a new procedure) and obtained the corresponding *tert*-butyl 5-

		EtO ₂ C - H	N= CH(OMe) ₂	TMSOTf 2,6-DTBP CH ₂ Cl ₂ , rt 15–18 h			
		6xy			bacteriochlorin		
entry	compd 6xy	Х	R	R ¹⁰	bacteriochlorin	yield (%)	$\lambda_{abs'} Q_y (nm)$
1	6bb	Et	Н	Н	7bb-HBC	35	753
2	6bc	<i>p</i> -tolyl	Н	Н	7bc-HBC	38	759
		<i>p</i> -tolyl	Н	OMe	7bc-MeOBC	9.1	748
3	6ac	<i>p</i> -tolyl	Et	Н	7ac-HBC	33	757
4	6cc	<i>p</i> -tolyl	Ph	Н	7cc-HBC	32	760
5	6cd	Me	Ph	Н	7cd-HBC	29	755
6	6be	1-naphthyl	Н	Н	7be-HBC	3.4	759
		1-naphthyl	Н	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 coworkers³⁵) 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 dihydrodipyrrins³³ 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 SeO₂ 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 SeO₂ followed immediately by TMSOTf/2,6-DTBP in CH₂Cl₂ gave a small amount (3.0 mg, 5.8%) of the desired 10-unsubstituted bacteriochlorin (**7da-HBC**), while SeO₂ treatment of **5dc-DC** directly gave an

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 (**'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 ¹H NMR spectroscopy, ¹³C 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 singlecrystal 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 hydrogenbonding³⁵ (in CDCl₃) typically causes a chemical shift of at least 10.5 ppm; in the absence of such hydrogen-bonding, the chemical shift is $\sim 8-9$ ppm.³⁴ Such evidence was supported by single-crystal X-ray structures of a Z-dihydrodipyrrin and an Edihydrodipyrrin determined by Jacobi and co-workers.³⁴ Here, in each case, the dihydrodipyrrins (5xy) and dihydrodipyrrinacetals (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_{ν} band.

all β -pyrrole positions (carboethoxy, phenyl) and two mesopositions (*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-halfmaximum (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 2formylpyrrole) 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. ¹H NMR (300 MHz) and ¹³C NMR (75 MHz) spectra were collected at room temperature in CDCl₃ unless noted otherwise. Silica gel (40 μ m 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-carboethoxy-pyrrole (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

bacteriochlorins were present, upon TLC analysis [silica, hexanes/ ethyl acetate (20:1)], the 10-unsubstituted bacteriochlorin or 10methoxybacteriochlorin typically exhibit an $R_{\rm f}$ 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 ¹H 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 10unsubstituted bacteriochlorin.

4-Carboethoxy-3-ethyl-2-iodopyrrole (1a). A stirred solution of 3carboethoxy-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 (Na₂SO₄) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (6:1)] afforded a white solid (2.26 g, 77%): mp 95–96 °C; ¹H 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); ¹³C 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 C₉H₁₃NO₂I 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 (Na₂SO₄) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a yellow solid (1.59 g, 60%): mp 86–88 °C; ¹H 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); ¹³C 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 C₇H₉INO₂ 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 (Na₂SO₄) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (5:1)] afforded a white solid (4.33 g, 55%): mp 121–122 °C; ¹H 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); ¹³C 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 C₁₃H₁₃NO₂I 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 (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; ¹H 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); ¹³C 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 C₉H₁₃BrNO₂ 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 NH₄Cl solution. The organic layer was extracted with diethyl ether. The combined organic extract was dried (Na₂SO₄) 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 CH₂Cl₂. The organic fraction was dried (Na₂SO₄) and concentrated to afford a colorless oil that was used without further purification (4.85 g, 63%): ¹H 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); ¹³C 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 C₉H₁₅O₂ 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 Et₃N (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(PPh₃)₄Cl₂ (150 mg, 0.208 mmol), and PPh₃ (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, CH₂Cl₂ (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 CH₂Cl₂. The organic extract was dried (Na₂SO₄) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (2:1)] afforded a white solid (2.73 g, 72%): mp 183–185 °C; ¹H NMR δ 1.38 (s, 6H), 2.34 (s, 6H), 2.69 (s, 3H), 7.08–7.31 (m, 4H); ¹³C 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 C₁₄H₁₇O₂ 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 Et₃N was added to a Schlenk flask and treated with 1-iodonaphthalene (12.7 g, 50.1 mmol), CuI (272 mg, 1.50 mmol), Pd(PPh₃)₄Cl₂ (355 mg, 0.500 mmol), and PPh₃ (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 CH₂Cl₂ 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 CH₂Cl₂. The organic extract was dried (Na₂SO₄) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a white solid (7.64 g, 60%): mp 153-155 °C; ¹H NMR δ 1.47 (s, 6H), 2.88 (s, 6H), 7.46–7.84 (m, 6H), 8.33 (d, J = 8.4 Hz, 1H); $^{13}\mathrm{C}$ 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 C₁₇H₁₇O₂ 253.1223; found 253.1219.

tert-Butyl 2,2-Dimethyl-5-(pentafluorophenyl)pent-4-ynoate ('Bu-2f). A solution of tert-butyl isobutyrate (4.33 g, 30.1 mmol) in anhydrous THF (30 mL) at $-78\ ^\circ C$ 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 NH₄Cl solution. The organic layer was extracted with diethyl ether. The combined organic extract was dried (Na₂SO₄), concentrated, and transferred to a Schlenk flask. Then Et₃N (24 mL), iodopentafluorobenzene (8.82 g, 30.0 mmol), CuI (67 mg, 0.346 mmol), Pd(PPh₃)₄Cl₂ (90 mg, 0.125 mmol), and PPh₃ (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, CH₂Cl₂ (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%): ¹H NMR δ 1.30 (s, 6H), 1.45 (s, 9H), 2.70 (s, 2H); ¹³C 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

a solution of 1a (1.48 g, 5.05 mmol), 2a (1.26 g, 10.1 mmol), and BnNEt₃Cl (1.15 g, 5.05 mmol) in dry acetonitrile (20 mL) and Et₃N (5.0 mL) was added to a Schlenk flask and deaerated by three freeze–pump–thaw cycles. A sample of Pd(PPh₃)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 CH₂Cl₂ and water were added. The organic layer was dried (Na₂SO₄) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a clear yellow solid (1.22 g, 87%): mp 128–129 °C; ¹H 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); ¹³C 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 C₁₆H₂₂NO₄ 292.1543; found 292.1539.

4-*Carboethoxy*-(*E*)-2-[(4,4-*dimethyl*-5-oxodihydrofuran-2(3*H*)ylidene)methyl]pyrrole (**3ba**). Following the procedure for **3aa**, **1b** (1.32 g, 5.00 mmol), **2a** (1.26 g, 10.1 mmol), and BnNEt₃Cl (1.14 g, 5.00 mmol) in dry acetonitrile (30 mL) and Et₃N (6 mL) were treated with Pd(PPh₃)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; ¹H 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); ¹³C 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 C₁₄H₁₈NO₄ 264.1230; found 264.1227.

4-*Carboethoxy-(E)-2-[1-(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)propy]pyrrole* (**3bb**). Following the procedure for **3aa**, **1b** (1.35 g, 5.10 mmol), **2b** (2.36 g, 15.3 mmol), and BnNEt₃Cl (1.16 g, 5.06 mmol) in dry acetonitrile (20 mL) and Et₃N (5.0 mL) were treated with Pd(PPh₃)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; ¹H 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); ¹³C 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 C₁₆H₂₂NO₄ 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 BnNEt₃Cl (894 mg, 3.94 mmol) in dry acetonitrile (20 mL) and Et₃N (5.0 mL) were treated with Pd(PPh₃)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; ¹H 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); ¹³C 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 C₂₁H₂₄NO₄ 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 BnNEt₃Cl (590 mg, 2.59 mmol) in dry DMF (12 mL) and Et₃N (3 mL) were treated with Pd(PPh₃)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; ¹H 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); ¹³C 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 C₂₃H₂₈NO₄ 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 BnNEt₃Cl (346 mg, 1.52 mmol) in dry DMF (12 mL) and Et₃N (3 mL) were treated with Pd(PPh₃)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; ¹H 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); ¹³C 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 C₂₇H₂₈NO₄ 430.2013; found 430.2015.

4-*Carboethoxy*-(*E*)-2-(1-(4,4-*dimethyl*-5-*oxodihydrofuran*-2(3*H*)*ylidene)ethyl*)-3-*phenylpyrrole* (**3cd**). Following the procedure for **3aa**, **1c** (810 mg, 2.38 mmol), **2d** (665 mg, 4.75 mmol), and BnNEt₃Cl (542 mg, 2.38 mmol) in dry DMF (16 mL) and Et₃N (4 mL) were treated with Pd(PPh₃)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; ¹H 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); ¹³C 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 C₂₁H₂₄NO₄ 354.1700; found 354.1701.

4-*Carboethoxy*-(*E*)-2-[(4,4-*dimethyl*-5-oxodihydrofuran-2(3*H*)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 BnNEt₃Cl (1.14 mg, 5.00 mmol) in dry acetonitrile (20 mL) and Et₃N (5.0 mL) were treated with Pd(PPh₃)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; ¹H 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); ¹³C 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 C₂₄H₂₄NO₄ 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 BnNEt₃Cl (456 mg, 2.00 mmol) in dry acetonitrile (15 mL) and Et₃N (5.0 mL) were treated with Pd(PPh₃)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; ¹H 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); ¹³C 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 C₂₃H₂₇NO₄Na 404.1832; found 404.1824.

5-(tert-Butoxycarbonyl)-(*E*)-2-[(4,4-dimethyl-5-oxodihydrofuran-2(3*H*)-ylidene)methyl]pyrrole (**3da**). Following the procedure for **3aa**, **1d** (975 mg, 3.96 mmol), **2a** (1.25 g, 9.90 mmol), and BnNEt₃Cl (903 mg, 3.96 mmol) in dry acetonitrile (21 mL) and Et₃N (7.0 mL) were treated with Pd(PPh₃)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; ¹H 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); ¹³C 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 C₁₆H₂₁NO₄Na 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 CH₂Cl₂ were added. The organic layer was separated, dried (Na₂SO₄), and concentrated. Column chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a white solid (492 mg, 82%): mp 102–104 °C; ¹H 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); ¹³C 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 (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), K₂CO₃ (550 mg, 3.96 mmol), Pd(PPh₃)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 CH₂Cl₂ were added. The organic layer was separated, dried (Na₂SO₄), and concentrated. Column chromatography [silica, hexanes/ethyl acetate (5:1)] afforded a white solid (434 mg, 90%): mp 113–115 °C; ¹H 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, SH), 8.98 (s, 1H); ¹³C 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 C₂₂H₂₆NO₄ 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 TiCp₂Cl₂ (3.045 g, 12.37 mmol) in toluene (33 mL) was treated dropwise with LiMe solution (1.6 M, 17 mL in Et₂O, 27 mmol) at 0 °C under an argon atmosphere. After 1 h at 0 °C, saturated aqueous NH₄Cl solution was added. The organic layer was washed (water and brine), dried (Na2SO4), and filtered. The filtrate (now \sim 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 TiCp₂Cl₂ (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), NaHCO₃ (130 mg), and water (31 μ L) 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; ¹H 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); ¹³C 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 C₁₇H₂₄NO₃ 290.1751; found 290.1742.

4-*Carboethoxy*-(*E*)-2-[(4,4-*dimethyl*-5-*methylenedihydrofuran*-2(3*H*)-ylidene)*methyl*]*pyrrole* (4ba). Following the procedure for 4aa, the filtrate containing the Petasis reagent [prepared from TiCp₂Cl₂ (2.13 g, 8.68 mmol) in toluene (23 mL) and LiMe solution (1.6 M, 12 mL in Et₂O, 19 mmol)] was treated with lactone–pyrrole 3ab (480 mg, 1.83 mmol) and additional TiCp₂Cl₂ (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; ¹H 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), 6.31 (s, 1H), 7.31 (m, 1H), 8.85 (s, 1H); ¹³C 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 C₁₅H₂₀NO₃ 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 TiCp₂Cl₂ (4.25 g, 17.3 mmol) in toluene (40 mL) and LiMe solution (1.6 M, 24 mL in Et₂O, 38 mmol)] was treated with lactone–pyrrole **3bb** (1.06 g, 3.63 mmol) and additional TiCp₂Cl₂ (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; ¹H 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); ¹³C 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 TiCp₂Cl₂ (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 TiCp₂Cl₂ (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; ¹H 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); ¹³C 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 TiCp₂Cl₂ (1.16 g, 4.74 mmol) in toluene (13 mL) and LiMe solution (1.6 M, 7.0 mL in Et₂O, 11 mmol)] was treated with lactone-pyrrole 3ac (380 mg, 1.00 mmol) and additional TiCp₂Cl₂ (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; ¹H 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); $^{13}\mathrm{C}$ 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 TiCp₂Cl₂ (512 mg, 2.08 mmol) in toluene (33 mL) and LiMe solution (1.6 M, 17 mL in Et₂O, 27 mmol)] was treated with lactone– pyrrole 3cc (185 mg, 0.431 mmol) and additional TiCp₂Cl₂ (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; ¹H 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); ¹³C 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 C₂₈H₃₀NO₃ 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 TiCp₂Cl₂ (588 mg, 2.39 mmol) in toluene (9.0 mL) and LiMe solution (1.6 M, 3.5 mL in Et₂O, 5.6 mmol)] was treated with lactone–pyrrole 3cd (178 mg, 0.504 mmol) and additional TiCp₂Cl₂ (7.0 mg). The standard reaction and workup including chromatog-raphy [silica, hexanes/ethyl acetate (5:1)] afforded a yellow solid (124 mg, 70%): mp 119–121 °C; ¹H 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* = 3.0 Hz, 1H), 8.35 (s, 1H); ¹³C 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 C₂₂H₂₆NO₃ 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 additional TiCp₂Cl₂ (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; ¹H 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, 2 H); ¹³C 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 C₂₅H₂₆NO₃ 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 TiCp₂Cl₂ (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 TiCp₂Cl₂ (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; ¹H 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); ¹³C 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 C₄₈H₅₇N₂O₆ 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 TiCp₂Cl₂ (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 TiCp₂Cl₂ (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; ¹H 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); ¹³C 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 C₁₇H₂₄NO₃ 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 CH₂Cl₂ (5.0 mL) at room temperature for 2 h. Aqueous saturated NaHCO₃ solution (100 mL) was added, and the resulting mixture was extracted with CH₂Cl₂ (100 mL). The organic layer was dried (Na₂SO₄) and concentrated. The resulting crude decarboxylated compound was directly treated with the Petasis reagent [prepared from $\tilde{Ti}Cp_2Cl_2$ (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 TiCp₂Cl₂ (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; ¹H NMR δ 1.28 (s, 6H), 2.77 (s, 2H), 4.02 (d, J = 2.4 Hz, 1H), 4.40 (d, I = 2.4 Hz, 1H), 5.93 (d, I = 1.8 Hz, 1H), 5.99 (s, 1H), 6.25 (t, I = 1.8 Hz, 1H), 5.99 (s, 100 H), 6.25 (t, I = 1.8 Hz, 100 Hz)2.7 Hz, 1H), 6.72-6.75 (m, 1H), 7.96 (s, 1H); ¹³C 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 C₁₂H₁₆NO 190.1226; found 190.1222.

(E)-2-[(4,4-Dimethyl-5-methylenedihydrofuran-2(3H)-ylidene)(ptolyl)methyl]pyrrole (4dc-DC). A sample of 3dc (608 mg, 1.60 mmol) was treated with TFA (5.0 mL) in CH₂Cl₂ (5.0 mL) at room temperature for 2 h. Aqueous saturated NaHCO₃ solution (100 mL) was added, and the resulting mixture was extracted with CH₂Cl₂ (100 mL). The organic layer was dried (Na₂SO₄) and concentrated. The resulting crude decarboxylated compound was directly treated with the Petasis reagent [prepared from TiCp₂Cl₂ (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 TiCp₂Cl₂ (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), NaHCO₃ (65 mg) and water (1.6 μ L) were added. The resulting solution was kept at 40 $^{\circ}$ 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 KH₂PO₄ 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; ¹H 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, I = 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); ¹³C 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, NH₄OAc (1.31 g, 17.1 mmol) and Et₃N (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 KH₂PO₄ 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; ¹H 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); ¹³C 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 C₁₅H₂₁N₂O₂ 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 NH₄OAc (3.20 g, 41.6 mmol) and Et₃N (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; ¹H 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); ¹³C 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 C₁₇H₂₅N₂O₂ 289.1910; found 289.1916.

8-Carboethoxy-2,3-dihydro-1,2,2-trimethyl-5-p-tolyldipyrrin (**5bc**). Following the procedure for **Saa**, **4bc** (451 mg, 1.28 mmol) in DMF (20 mL) was treated with 1 M HCl (1.0 mL) and then NH₄OAc (1.97 g, 25.6 mmol) and Et₃N (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; ¹H 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); ¹³C 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 C₂₂H₂₇N₂O₂ 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 NH₄OAc (546 mg, 7.12 mmol) and Et₃N (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; ¹H 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); ¹³C NMR δ 14.7, 15.9, 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 C₂₄H₃₁N₂O₂ 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 NH₄OAc (700 mg, 9.13 mmol) and Et₃N (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); ¹³C 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 C₂₈H₃₁N₂O₂ 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 NH₄OAc (524 mg, 6.85 mmol) and Et₃N (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); ¹³C 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 C₂₂H₂₇N₂O₂ 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 NH₄OAc (4.77 g, 46.4 mmol) and Et₃N (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); ¹³C 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 C₂₅H₂₇N₂O₂ 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 NH₄OAc (1.62 g, 21.2 mmol) and Et₃N (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); ¹³C 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 C₂₄H₃₁N₂O₂ 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 NH₄OAc (0.957 g, 12.5 mmol) and Et₃N (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); ¹³C 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 C₁₇H₂₅N₂O₂ 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 NH₄OAc (0.87 g, 11.3 mmol) and Et₃N (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); ¹³C 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 (ESITOF) *m*/*z*: [M + H]⁺ calcd for C₁₂H₁₇N₂ 189.1386; found 189.1384.

2,3-Dihydro-1,2,2-trimethyl-5-p-tolyldipyrrin (**5dc-DC**). Following the procedure for **Saa**, **4dc-DC** (unpurified, prepared from 608 mg of **3dc**) in DMF (20 mL) was treated with 1 M HCl (1.0 mL) and then NH₄OAc (1.47 g, 19.2 mmol) and Et₃N (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); ¹³C 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 C₁₉H₂₃N₂ 279.1856; found 279.1855.

8-Carboethoxy-7-ethyl-2.3-dihydro-1-(1.1-dimethoxymethyl)-*2,2-dimethyldipyrrin (6aa*). Following a general procedure,¹ solution of 5aa (245 mg, 0.851 mmol) in 1,4-dioxane (15 mL) was treated with SeO₂ (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·H₂O (48 mg, 0.25 mmol). After 12 h with stirring at room temperature, the reaction mixture was quenched by the addition of saturated aqueous NaHCO₃ solution and then extracted with ethyl acetate. The organic layer was dried (Na₂SO₄) 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); ¹³C 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 **Saa**, **Sba** (109 mg, 0.42 mmol) in 1,4-dioxane (10 mL) was oxidized with SeO₂ (139 mg, 1.25 mmol) and then converted to the acetal by treatment with TsOH-H₂O (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); ¹³C 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 C₁₇H₂₅N₂O₄ 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 SeO₂ (527 mg, 4.75 mmol) and then converted to the acetal by treatment with TsOH·H₂O (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, 2H), 5.11 (s, 1H), 6.62 (s, 1H), 7.46 (dd, *J* = 2.9, 1.5 Hz, 1H), 11.67 (s, 1H); ¹³C 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 C₁₉H₂₉N₂O₄ 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 Saa, Sbc (247 mg, 0.706 mmol) in 1,4-dioxane (15 mL) was oxidized with SeO₂ (235 mg, 2.12 mmol) and then converted to the acetal by treatment with TsOH·H₂O (40 mg, 0.21 mmol) in HC(OMe)₃ (10 mL). The standard reaction and workup including chromatography [silica, hexanes/ethyl acetate (2:1)] afforded a brown oil (122 mg, 43%): ¹H 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); ¹³C 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 (ESITOF) *m/z*: [M + H]⁺ calcd for C₂₄H₃₁N₂O₄ 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 **Saa**, **Sac** (64 mg, 0.17 mmol) in 1,4-dioxane (10 mL) was oxidized with SeO₂ (56 mg, 0.51 mmol) and then converted to the acetal by treatment with TsOH·H₂O (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%): ¹H 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); ¹³C 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 C₂₆H₃₅N₂O₄ 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 **Saa**, **Scc** (85 mg, 0.20 mmol) in 1,4-dioxane (10 mL) was oxidized with SeO₂ (66 mg, 0.60 mmol) and then converted to the acetal by treatment with TsOH·H₂O (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%): ¹H 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); ¹³C 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 C₃₀H₃₅N₂O₄ 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 Saa, Scd (48 mg, 0.14 mmol) in 1,4-dioxane (10 mL) was oxidized with SeO₂ (44 mg, 0.40 mmol) and then converted to the acetal by treatment with TsOH·H₂O (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%): ¹H 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, SH), 7.51 (d, *J* = 3.3 Hz, 1H), 12.02 (br, 1H); ¹³C 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 C₂₄H₃₁N₂O₄ 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 **Saa**, **Sbe** (668 mg, 1.73 mmol) in 1,4-dioxane (25 mL) was oxidized with SeO₂ (576 mg, 5.19 mmol) and then converted to the acetal by treatment with TsOH·H₂O (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%): ¹H 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); ¹³C 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 C₂₇H₃₁N₂O₄ 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 Saa, Sdc (150 mg, 0.397 mmol) in 1,4-dioxane (10 mL) was oxidized with SeO₂ (132 mg, 1.19 mmol) and then converted to the acetal by treatment with TsOH·H₂O (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; ¹H 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); ¹³C 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 (ESITOF) m/z: [M + H]⁺ calcd for C₂₆H₃₅N₂O₄ 439.2591; found 439.2607.

2,12-Dicarboethoxy-3,13-diethyl-8,8,18,18-tetramethylbacterio*chlorin (7aa-HBC*). Following a general procedure,¹⁴ a solution of 6aa (47 mg, 0.14 mmol) in anhydrous CH₂Cl₂ (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 CH₂Cl₂ and washed with saturated aqueous NaHCO3. The organic layer was dried (Na₃SO₄) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a dark green solid (15 mg, 39%): ¹H 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); ¹³C 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 (CH₂Cl₂).

2,12-Dicarboethoxy-8,8,18,18-tetramethylbacteriochlorin (**7ba-HBC**). Following a general procedure,¹⁴ a solution of **6ba** (27 mg, 84 μ mol) in anhydrous CH₂Cl₂ (5.0 mL) was treated with 2,6-DTBP (385 μ L, 1.68 mmol) followed by TMSOTf (79 μ L, 0.42 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 24 h and then diluted with CH₂Cl₂ and washed with saturated aqueous NaHCO₃. The organic layer was dried (Na₂SO₄) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (5:1)] afforded a dark green solid (1.3 mg, 6.0%): ¹H 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); ¹³C 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 C₃₀H₃₅N₄O₄ 515.2653; found 515.2658. λ_{abs} 351, 377, 521, 752 nm (CH₂Cl₂).

2,12-Dicarboethoxy-5,15-diethyl-8,8,18,18-tetramethylbacterio*chlorin* (**7bb-HBC**). Following a general procedure,¹⁴ a solution of **6bb** (100. mg, 0.287 mmol) in anhydrous CH₂Cl₂ (15 mL) was treated with 2,6-DTBP (1.10 g, 5.75 mmol) followed by TMSOTf (262 μ L, 1.44 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 15 h and then diluted with CH₂Cl₂ and washed with saturated aqueous NaHCO₃. 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%): ¹H 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); ¹³C 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 (CH₂Cl₂).

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 CH₂Cl₂ (15 mL) was treated with 2,6-DTBP (1.14 g, 5.95 mmol) followed by TMSOTf (270 μ L, 1.50 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 15 h, diluted with CH₂Cl₂, and washed with saturated aqueous NaHCO₃. The organic layer was dried (Na₂SO₄) 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 7**bc-MeOBC** as a dark purple solid (9.8 mg, 9.1%). Data for the title compound: ¹H 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); ¹³C 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 (CH₂Cl₂). Data for 2,12-dicarboethoxy-10-methoxy-8,8,18,18tetramethyl-5,15-di-*p*-tolylbacteriochlorin (7bc-MeOBC): ¹H 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); ¹³C 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,¹ solution of 6ac (21 mg, 0.048 mmol) in anhydrous CH₂Cl₂ (5.0 mL) was treated with 2,6-DTBP (220 μ L, 0.96 mmol) followed by TMSOTf (45 μ L, 0.24 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 15 h and then diluted with CH₂Cl₂ and washed with saturated aqueous NaHCO₃. The organic layer was dried (Na₂SO₄) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (5:1)] afforded a purple solid (6.0 mg, 33%): ¹H 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); ¹³C 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-5,15di-p-tolylbacteriochlorin (7cc-HBC). Following a general procedure, a solution of 6cc (25 mg, 0.051 mmol) in anhydrous CH₂Cl₂ (5.0 mL) was treated with 2,6-DTBP (234 μ L, 1.0 mmol) followed by TMSOTf (50 μ L, 0.25 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 15 h, and then diluted with CH2Cl2 and washed with saturated aqueous NaHCO3. 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%): ¹H 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 C₅₆H₅₅N₄O₄ 847.4218; found 847.4191. λ_{abs} 363, 538, 760 nm (CH₂Cl₂).

2,12-Dicarboethoxy-5,8,8,15,18,18-hexamethyl-3,13-diphenylbacteriochlorin (7cd-HBC). Following a general procedure, solution of 6cd (25 mg, 0.061 mmol) in anhydrous CH2Cl2 (9.0 mL) was treated with 2,6-DTBP (280 µL, 1.2 mmol) followed by TMSOTf (56 μ L, 0.30 mmol). The reaction mixture was stirred under a nitrogen atmosphere at room temperature for 15 h, and then diluted with CH₂Cl₂ and washed with saturated aqueous NaHCO₃. The organic layer was dried (Na₂SO₄) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a dark purple solid (6.1 mg, 29%): ¹H 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); ¹³C 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 C₄₄H₄₆N₄O₄ 694.3513; found 694.3514. λ_{abs} 365, 547, 755 nm (CH₂Cl₂).

2,12-Dicarboethoxy-8,8,18,18-tetramethyl-5,15-bis(1-naphthyl)bacteriochlorin (7be-HBC). Following a general procedure,¹ solution of 6be (587 mg, 1.32 mmol) in anhydrous CH2Cl2 (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 CH₂Cl₂, and washed with saturated aqueous NaHCO₃. The organic layer was dried (Na₂SO₄) 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: ¹H 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, I = 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); ¹³C 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 C₅₀H₄₆N₄O₄ 766.3514; found 766.3512. λ_{abs} 359, 383, 539, 759 nm (CH₂Cl₂). Data for 2,12dicarboethoxy-10-methoxy-8,8,18,18-tetramethyl-5,15-bis(1naphthyl)bacteriochlorin (7be-MeOBC): ¹H 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 $C_{51}H_{48}N_{-4}O_5$ 796.3619; found 796.3615. λ_{abs} 364, 381, 547, 748 nm (CH₂Cl₂).

8,8,18,18-Tetramethylbacteriochlorin (7da-HBC). Compound Sda-DC (53 mg, 0.28 mmol) in CH₂Cl₂ (15 mL) at room temperature under argon was treated with SeO₂ (67 mg, 0.60 mmol). After TLC analysis showed the disappearance of Sda-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 CH₂Cl₂ and washed with saturated aqueous NaHCO₃. The organic layer was dried (Na₂SO₄) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (10:1)] afforded a dark green solid (3.0 mg, 5.8%): ¹H NMR δ –2.38 (s, 2H), 1.97(s, 12H), 4.46 (s, 4H), 8.71–8.77 (m, 6H), 8.83 (s, 2H); ¹³C 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 C₂₄H₂₇N₄ 371.2230; found 371.2224. λ_{abs} 339, 364, 488, 713 nm (CH₂Cl₂). The characterization data match those obtained from an alternative route.⁴⁷

2-(*tert-Butoxycarbonyl*)*pyrrole* (8). A solution of pyrrole-2carboxylic 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; ¹H 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); ¹³C NMR δ 28.6, 81.0, 110.4, 114.8, 122.1, 160.9; HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₉H₁₄NO₂ 168.1019; found 168.1017. The characterization data match those obtained from an alternative route.⁴⁶

ASSOCIATED CONTENT

S 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) 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)

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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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