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Porphyrins with exocyclic rings. Part 23: Synthesis of porphyrins with large exocyclic rings—cyclohexadeca[*b*]pyrroles and porphyrins therefrom ☆

Timothy D. Lash,* Thomas G. Marron and Jolie A. Bastian

Department of Chemistry, Illinois State University, Normal, IL 61790-4160, USA

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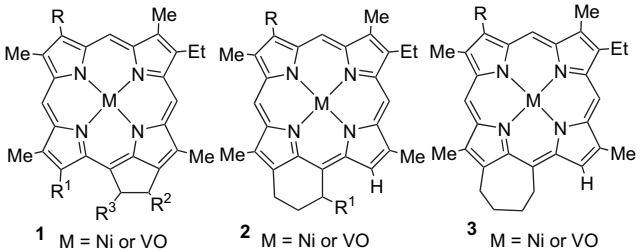
Abstract—Knorr-type condensation of cyclododecanone, cyclopentadecanone, and cyclohexadecanone with phenylhydrazones derived from acetoacetate esters in the presence of zinc dust at elevated temperatures gave the corresponding large ring cycloalka[*b*]pyrroles in excellent yields. A cyclohexadeca[*b*]pyrrole was reacted with lead tetraacetate to give an acetate derivative, and this condensed with α-unsubstituted pyrroles in the presence of *p*-toluenesulfonic acid in acetic acid to give a series of related dipyrrolic structures. Hydrogenolysis of the benzyl ester protective groups, followed by '2+2' condensations with dipyrrylmethane dialdehydes, gave unusual cycloalkanoporphyrins with 16-membered exocyclic rings. When an alkyl group is situated next to the carbocyclic ring, proton NMR spectroscopy indicates that the conformational mobility of the carbocyclic unit is severely restricted.

1. Introduction

Naturally Occurring Cycloalkanoporphyrins:



1 M = Ni or VO; R = H, Me or Et; R^1 = H, Me, Et or Pr; R^2,R^3 = H or Me

2 M = Ni or VO; R = H, Me or Et; R^1 = Me or CH_2OH

3 M = Ni or VO; R = H, Me or Et

Cycloalkanoporphyrins (CAPs; e.g., **1**–**3**) are commonly found in metalated form in organic-rich sediments such as oil shales and petroleum.[1,2] These geoporphyrins are primarily derived from the photosynthetic pigments of algae and bacteria, and can provide insights into the geological origins of sedimentary materials.[3] In addition, petroporphyrin mixtures can be used as chemical markers in petroleum exploration[4] and have been investigated for environmental applications in monitoring the origins of oil spills.[5] We have previously explored the syntheses of natural petroporphyrins and related 'type II' isomers starting from cyclic ketones.[6,7] Knorr-type condensations of oximes or phenylhydrazones with cyclohexanone, cycloheptanone, or cyclooctanone afford the related cycloalka[*b*]pyrroles **4** in good yields,[8–10] and these can be taken onto dipyrrolic intermediates **5** that represent the southern half of the CAP structures (Scheme 1).[9–11] Following the removal of the ester protective groups, the dipyrroles can be condensed with dipyrrylmethane dialdehydes **6** in the presence of an acid catalyst to give, following the addition of zinc acetate and air oxidation, the corresponding unnatural type II porphyrins **7**.[9–12] These porphyrins have proven to be useful model compounds in their own right,[13,14] but more stepwise routes have been developed for the synthesis of the less symmetrical naturally occurring petroporphyrins.[15] However, MacDonald-type '2+2' route to CAPs is very versatile and has been applied to the synthesis of porphyrins with *gem*-dimethylpropano subunits[16] and porphyrins with five-membered exocyclic rings.[11,12] As these straightforward procedures allow access to diverse CAP structures, the synthesis of more complex systems using the same type of methodology was considered a worthwhile goal. Given the many applications for porphyrin based materials, ranging from catalysis[17] to supramolecular assemblies,[18] molecular electronics,[19] and molecular scale data storage,[20] the formation of more complex CAP systems offers the potential to generate new types

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* Corresponding author. Tel.: +1 309 438 8554; fax: +1 309 438 5538; e-mail: tdlash@ilstu.edu

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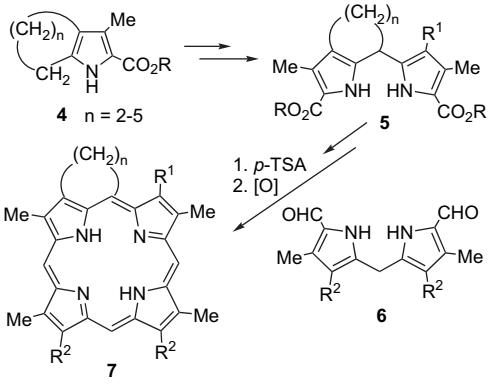
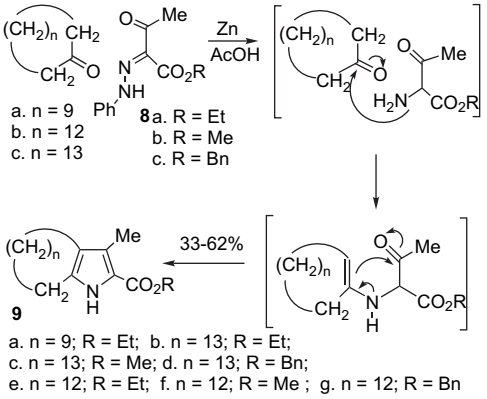
of porphyrin building blocks. For instance, porphyrins linked via this type of carbocyclic unit could act as linkers that enforce specific angle and distance connectivities between porphyrin within a larger assembly. In order to explore the potential of this methodology, porphyrins with large exocyclic rings were targeted for synthesis. The ability to form CAPs of this type would demonstrate that far more complex linkages can be introduced starting from simple ketone precursors.



Scheme 1.

2. Results and discussion

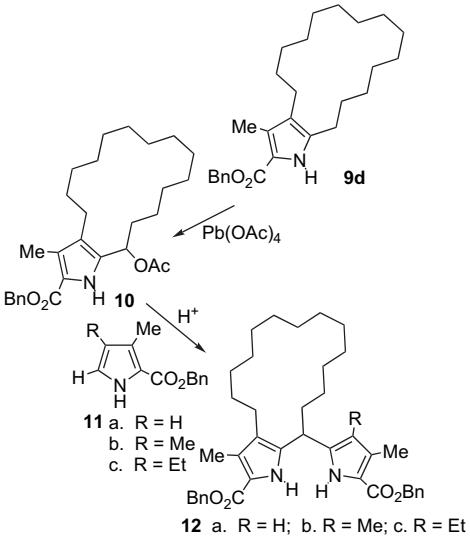
In our previous studies, we prepared cycloalka[*b*]pyrroles using a variant on Knorr pyrrole condensation.[6,21] In this chemistry, an aminoketone is generated in situ by reducing an oxime or phenylhydrazone with zinc dust in acetic acid and this condenses with the cyclic ketone to give the required porphyrin. Although oximes are more commonly used in Knorr syntheses,[21] phenylhydrazones give superior yields in some cases.[8–10,22] Phenylhydrazones **8** are easily prepared by reacting benzenediazonium chloride with esters of acetoacetic acid,[8,23] while oximes can be generated by nitrosation of the same starting materials.[6] In most Knorr-type reactions, the chemistry is initiated at ca. 70–80 °C, and the zinc metal reductant and aminoketone precursor are added simultaneously to the ketone in acetic acid while maintaining the temperature at 80–100 °C.[24] For cyclic ketones with six- to eight-membered rings, slightly higher temperatures were employed but yields plummeted if the reaction temperature was allowed to get too high.[8–10] With these concerns in mind, the same chemistry was attempted using inexpensive cyclododecanone and phenylhydrazone **8a** derived from ethyl acetoacetate (Scheme 2). Under conventional conditions, no pyrrolic products could be detected and most of the cyclic ketones could be recovered. However, if the reaction was conducted at the boiling point of acetic acid, trace amounts of the desired pyrrole product could be detected by NMR spectroscopy. Although the initial results were unexpected, they nonetheless suggested that still higher temperatures might facilitate pyrrole formation. Propionic acid was selected as the solvent due to its higher boiling point. Following further investigations, the best results were obtained using relatively dilute conditions with 3.0 g of sodium acetate for every 10 mL of propionic acid. Temperatures were maintained as high as possible during the initial phases of the chemistry (typically 145–150 °C), and following precipitation in ice/water and recrystallization from ethanol, pure cyclododeca[*b*]pyrrole **9a** was obtained in 33–37% yield.



Scheme 2.

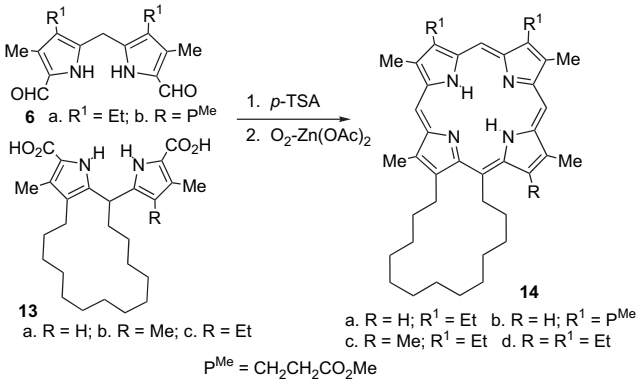
The success of this pilot study encouraged us to investigate the use of even large rings. Cyclopentadecanone is readily available, and 8-cyclohexadecenone is also reasonably inexpensive and accessible. The latter compound is easily hydrogenated over 10% Pd/C to give cyclohexadecanone in quantitative yields. The 16- and 15-membered ring ketones were reacted with phenylhydrazones **8a–c** under the conditions developed for cyclododecanone (Scheme 2), and the related cycloalka[*b*]pyrroles **9b–g** were isolated in excellent yields (40–68%). All six of these pyrroles were fully characterized and were obtained as white crystals or powders.[25]

In order to access the viability of synthesizing porphyrins with large exocyclic rings, cyclohexadeca[*b*]pyrrole **9d** was reacted with lead tetraacetate in 1:1 v/v acetic acid/dichloromethane to give the 17-acetoxy derivative **10** (Scheme 3). The acetate was subsequently reacted with α-unsubstituted pyrroles **11a–c** to give the novel dipyrroles **12a–c** in 52–71% yield. These reactions proceeded without any complications, although the NMR spectra were complex due to



Scheme 3.

the presence of a chiral center and the large number of chemically similar methylene subunits. The bridging CH unit in the β-unsubstituted product **12a** was observed as a triplet at 4.0 ppm, while the β-substituted dipyrroles showed this resonance further downfield at 4.19 ppm. Hydrogenolysis of the benzyl ester protective groups was easily accomplished over 10% Pd/C and the resulting dicarboxylic acids **13a–c** were then used to synthesize porphyrins with 16-membered exocyclic rings (Scheme 4).



Scheme 4.

Using MacDonald '2+2' methodology,[26] dipyrrole **13a** was reacted with dipyrrylmethane **6a** or **6b** in the presence of *p*-toluenesulfonic acid (Scheme 4). Following the addition of excess zinc acetate, the reaction mixture was allowed to air oxidize for 2 days. These mild conditions have been used to prepare porphyrins with five-, six-, seven- or eight-membered exocyclic rings previously.[8–12] However, the conformation of the intermediates can be a significant factor in the efficiency of these cyclizations[10] and the effect of large rings on these reactions was not known. In the event, good yields of the porphyrin products **14a** and **14b** could be isolated following chromatography and recrystallization from chloroform/methanol. In addition, similar results were obtained when dipyrroles **13b** and **13c** were reacted with **6a** under the same conditions. Porphyrins **14a–d** were fully characterized by UV–vis, proton NMR and carbon-13 NMR spectroscopies, mass spectrometry, and combustion analysis. Porphyrins gave the expected phyllo-type UV–vis spectra[27] in chloroform with Soret bands at 407–408 nm. Addition of TFA generated the corresponding dications **14**H_2^{2+} where Soret band shifts to 414–416 nm for **14a** and **14b**, and 417–418 nm for **14c** and **14d**. The slightly larger bathochromic shifts observed for the two porphyrins **14c**,**d** with alkyl groups next to the carbocyclic ring may be due to the steric crowding leading to a minor distortion to the chromophore (see below).

The proton NMR data for the new porphyrins in $CDCl_3$ showed that the large exocyclic ring did not significantly affect the diatropic character for the macrocycle, and the *meso*-protons were observed at typical downfield values in the range of 9.78–10.06 ppm. The β-pyrrolic proton in **14a** or **14b** was also evident at 9.24 ppm, while the internal NHs gave upfield resonances between −2.8 and −3.2 ppm. The carbocyclic ring for the β-unsubstituted porphyrins **14a** and **14b** gave a series of five 2H multiplets between 1.8 and 2.6 ppm, a 4H multiplet at 1.7–1.8 ppm, and a 10H multiplet near 1.5 ppm, while the *meso*-CH_2 gave a 2H multiplet at nearly 5.0 ppm and the β-methylene gave a 2H multiplet near 4.0 ppm. These data essentially fall into the expected region for substituents attached to a porphyrin ring system, and indicate that the carbocyclic ring does not significantly fold back over the π-system. The equivalent signals for the fully β-substituted porphyrins **14c** and **14d** showed significant differences, and the resonances for the methylene units not directly connected to the porphyrin system did not extend beyond 2.3 ppm. In addition, at 25 °C the *meso*-CH_2 unit gave rise to two separate 1H resonances at 4.9 and 5.2 ppm indicating that steric crowding from the β-substituent introduces a significant restriction to the conformational mobility of the 16-membered ring. However, these broadened resonances coalesced as the temperature was raised to 50 °C (Fig. 1). Addition of a drop of TFA to the NMR tubes gave the related dications **14**H_2^{2+} and the resulting NMR spectra were also well resolved and confirmed the diatropic character. The four internal NHs gave rise to four well separated resonances in these spectra, indicating that there must be significant differences in their chemical environment. The carbocyclic ring protons also showed significantly different shifts, and in particular the *meso*-CH_2 unit for **14c**H_2^{2+} and **14d**H_2^{2+} no longer showed the presence of diastereotopic protons. The *meso*-protons for the dications of **14a** and **14b** showed a downfield shift of 0.4–0.5 ppm, affording three resonances between 10.3 and 10.6 ppm; however, the β-pyrrolic proton shifted upfield by ca. 0.2 ppm to give singlets at 9.09 and 9.07 ppm, respectively. Porphyrin dications generally show an increased diatropic ring current,[28] but any assessment of the diatropic character must take into account the associated positive charges. The latter effect should result in some deshielding, even though the β-proton is shifted upfield. The *meso*-protons for **14c**H_2^{2+} and **14d**H_2^{2+} are deshielded compared to the free base forms, but the effect is smaller than the one observed for **14a**H_2^{2+} and **14b**H_2^{2+} resulting in shifts of only 0.2–0.3 ppm with three 1H singlets showing up between 10.05 and 10.25 ppm. The alkyl substituents on the porphyrin macrocycle can give a good indication of the ring current without significant perturbation by the dicationic character.[29] For **14a**H_2^{2+} and **14b**H_2^{2+}, the methyl resonances fell into the range of 3.43–3.61 ppm compared to value of 3.57–3.72 for the free base porphyrins. The upfield shifts for **14c**H_2^{2+} and **14d**H_2^{2+} were even more significant, giving a series of singlets in the range of 3.28–3.49 compared to 3.59–3.62 in the free base compounds. Taken together, these data indicate that the diatropicity is reduced in the dications, particularly in the cases of **14c** and **14d**, and this is probably due to the relief of steric interactions that are exacerbated by the presence of four hydrogen atoms in the macrocyclic cavity. Distortion of the porphyrin nucleus appears to reduce the crowding between the ring and the adjacent alkyl substituent in **14c** and **14d**, thereby allowing increased mobility to the carbocyclic unit. Carbon-13 NMR data for porphyrins **14a–d** in TFA/$CDCl_3$ showed the three unsubstituted *meso*-carbons at typical values[30] between 94.7 and 98.9 ppm, while the substituted *meso*-carbon was observed near 126 ppm.

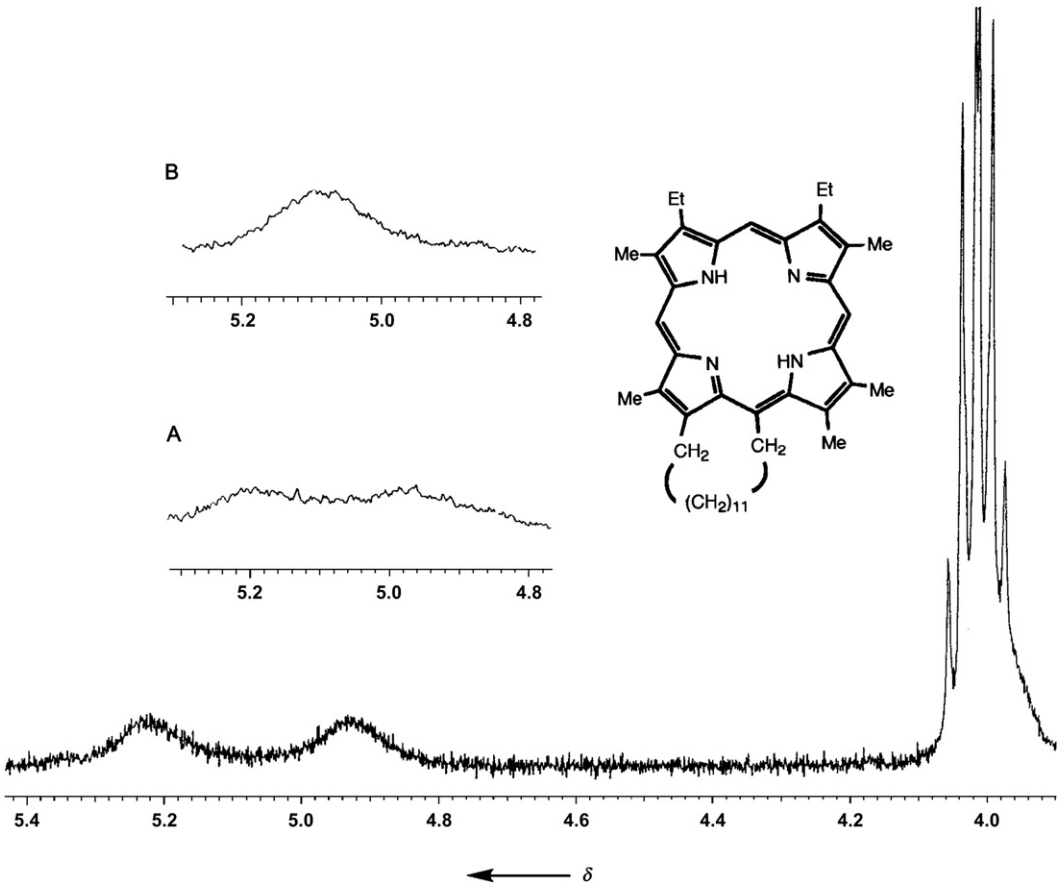


Figure 1. Partial 400 MHz proton NMR spectrum of *meso*-β-tridecanoporphyrin **14c** in $CDCl_3$ at 25 °C showing two broad resonances for the diastereotopic *meso*-CH_2 unit. Inset A: spectrum at 35 °C; inset B: spectrum at 50 °C showing coalescence of the methylene resonances.

3. Conclusions

A series of pyrroles fused to large carbocyclic rings are easily prepared from cyclic ketones using Knorr-type chemistry. A cyclohexadeca[*b*]pyrrole prepared by this methodology was used to prepare dipyrrolic intermediates that incorporate the fused carbocyclic ring. Following deprotection of the benzyl esters, these dipyrroles reacted with dipyrrylmethane dialdehydes under MacDonald '2+2' conditions to afford novel porphyrins with tridecano-bridges. The fused 16-membered rings appear to cause minor distortion to the porphyrin macrocycle due to steric crowding and this effect was exacerbated by a proximal alkyl substituent. Nevertheless, these results indicate that cycloalka[*b*]-pyrroles can be used to synthesize complex porphyrin systems.

4. Experimental

4.1. General

Ethyl acetoacetate, methyl acetoacetate, 8-cyclohexadecenone, cyclopentadecanone, cyclododecanone, lead tetraacetate, triethylamine, and *p*-toluenesulfonic acid were purchased from Aldrich or Acros, and were used without further purification. Benzyl acetoacetate was purchased from TCI America. Chromatography was performed using grade III neutral alumina (6 mL H_2O for 100 g grade I alumina) or 70–230 mesh silica gel; grade III silica was prepared by shaking 100 g SiO_2 with 10 mL of water. Melting points were determined in open capillary tubes on a Mel-Temp apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer 1600 Series FT-IR Spectrometer and only selected absorptions (in reciprocal centimeters) are listed, while UV–vis absorption spectra were run on a Beckmann DU-40 spectrophotometer or a Varian Cary Spectrophotometer. Proton and carbon-13 NMR data were obtained on Varian Gemini 300 or 400 MHz FT-NMR Spectrometers. Mass spectral determinations were conducted at the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana-Champaign. Elemental analyses were obtained from Micro-Analysis, Inc., Wilmington, DE 19808, or the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois.

4.2. Synthetic procedures

4.2.1. Cyclohexadecanone. A solution of 8-cyclohexadecenone (20.0 g) in acetone (150 mL) was shaken with 10% palladium/charcoal (200 mg) under a hydrogen atmosphere at room temperature and 30 psi for 90 min. The catalyst was removed by suction filtration and the solvent evaporated under reduced pressure to give the cyclic ketone (20.0 g, quantitative) as colorless crystals, mp 63–64 °C (lit. mp 56 °C,[31a] 62–63.5 °C,[31b] 60 °C[31c]); IR (Nujol mull): $\nu_{C=O}$

1714 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.26–1.31 (22H, m), 1.63 (4H, quintet, J=6.8 Hz), 2.40 (4H, t, J=6.6 Hz); ^{13}C NMR ($CDCl_3$): δ 23.7, 28.8 (3), 27.2, 27.4, 27.9, 42.2, 212.5.

4.2.2. Ethyl 3-methylcyclohexadeca[*b*]pyrrole-2-carboxylate (9a). A mixture of cyclohexadecanonone (3.00 g, 12.6 mmol), sodium acetate (18.0 g), and propionic acid (60 mL) was placed in a 500 mL Erlenmeyer flask and heated to 140 °C on an oil bath. A solution of phenylhydrazone **8a**[8,23] (3.14 g, 13.4 mmol) in propionic acid (60 mL) was added to the mixture while simultaneously adding zinc dust (10 g) in small portions over a period of 1 h, maintaining the temperature of the reaction above 150 °C. Once the addition was complete, the mixture was stirred for 1 h at 120–140 °C. The mixture was cooled to 70 °C and poured into ice/water (600 mL). The precipitate was filtered, washed with water, and recrystallized from ethanol to give the title compound (2.78 g, 8.01 mmol, 63%) as white crystals, mp 139–140 °C; IR (Nujol mull): ν 3297 (s, NH str.), 1657 (s, C=O str.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.25–1.32 (8H, m), 1.32–1.45 (14H, m), 1.34 (3H, t, J=7 Hz), 1.55–1.60 (2H, m), 2.27 (3H, s), 2.35 (2H, t, J=7.4 Hz), 2.52 (2H, t, J=8 Hz), 4.29 (2H, q, J=7.2 Hz), 8.59 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 10.9, 14.8, 24.6, 25.6 (2), 26.4, 26.5, 26.6, 26.7, 27.0, 27.7, 27.9, 28.0, 28.1, 29.4, 30.5, 59.8, 117.3, 122.3, 127.1, 134.5, 162.0. Anal. Calcd for $C_{22}H_{37}NO_2$: C, 76.03; H, 10.73; N, 4.03. Found: C, 75.75; H, 11.13; N, 4.28.

4.2.3. Ethyl 3-methylcyclododeca[*b*]pyrrole-2-carboxylate (9b). Cyclododecanone (9.10 g, 50.0 mmol) and phenylhydrazone **8a**[8,23] (11.70 g, 50.0 mmol) were reacted under the foregoing conditions. Recrystallization from ethanol gave cyclododeca[*b*]pyrrole (5.46 g, 18.7 mmol, 37%) as white crystals, mp 156–157 °C; IR (Nujol mull): ν 3301 (s, NH str.), 1657 (s, C=O str.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.21–1.28 (2H, m), 1.31–1.39 (6H, m), 1.35 (3H, t, J=7 Hz), 1.40–1.48 (4H, m), 1.56–1.63 (2H, m), 1.66–1.74 (2H, m), 2.28 (3H, s), 2.41 (2H, t, J=7.2 Hz), 2.55 (2H, t, J=7.4 Hz), 4.29 (2H, q, J=7.2 Hz), 8.60 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 11.1, 14.8, 21.4, 22.6, 22.8, 23.2, 24.4, 25.3, 25.4, 27.8, 28.2, 59.8, 117.8, 122.4, 127.2, 134.9, 162.0. Anal. Calcd for $C_{18}H_{29}NO_2$: C, 74.18; H, 10.03; N, 4.81. Found: C, 74.18; H, 10.26; N, 5.01.

4.2.4. Methyl 3-methylcyclohexadeca[*b*]pyrrole-2-carboxylate (9c). Cyclohexadecanone (3.00 g, 12.6 mmol) and phenylhydrazone **8b**[8] (2.77 g, 12.6 mmol) were reacted under the foregoing conditions. Recrystallization from ethanol gave cyclohexadeca[*b*]pyrrole (2.59 g, 7.77 mmol, 62%) as white crystals, mp 141–142 °C; IR (Nujol mull): ν 3310 (s, NH str.), 1668 (s, C=O str.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.2–1.5 (22H, m), 1.50–1.63 (2H, m), 2.27 (3H, s), 2.35 (2H, t, J=7 Hz), 2.52 (2H, t, J=8 Hz), 3.82 (3H, s), 8.83 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 10.8, 24.6, 25.5, 26.3, 26.4, 26.6, 26.7, 26.9, 27.7, 27.9, 28.0, 28.1, 29.4, 30.5, 51.0, 117.0, 122.3, 127.2, 134.8, 162.5. Anal. Calcd for $C_{21}H_{35}NO_2$: C, 75.63; H, 10.58; N, 4.20. Found: C, 75.88; H, 10.35; N, 4.23.

4.2.5. Benzyl 3-methylcyclohexadeca[*b*]pyrrole-2-carboxylate (9d). Cyclohexadecanone (3.02 g, 12.7 mmol) and phenylhydrazone **8c**[9c,23e] (3.85 g, 13.0 mmol) were reacted under the foregoing conditions. Recrystallization from hexanes gave benzyl ester (2.05 g, 5.03 mmol, 40%) as white crystals, mp 171–171.5 °C; IR (Nujol mull): ν 3294 (NH str.), 1661 (C=O str.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.2–1.45 (22H, m), 1.5–1.65 (2H, m), 2.27 (3H, s), 2.34 (2H, t, J=7 Hz), 2.50 (2H, t, J=7 Hz), 5.28 (2H, s), 7.3–7.45 (5H, m), 8.56 (1H, s); ^{13}C NMR ($CDCl_3$): δ 11.0, 24.6, 25.7, 26.4, 26.6, 26.7, 26.8, 27.0, 27.7, 27.9, 28.1, 29.4, 30.2, 65.6, 116.9, 122.5, 127.7, 128.2, 128.3, 128.7, 134.9, 137.0, 161.6. Anal. Calcd for $C_{27}H_{39}NO_2$: C, 79.17; H, 9.60; N, 3.42. Found: C, 78.68; H, 9.82; N, 3.69.

4.2.6. Ethyl 3-methylcyclopentadeca[*b*]pyrrole-2-carboxylate (9e). Cyclopentadecanone (1.00 g, 4.46 mmol) and phenylhydrazone **8a**[8,23] (1.10 g, 4.62 mmol) were reacted under the foregoing conditions. Recrystallization from ethanol gave cyclopentadeca[*b*]pyrrole (0.742 g, 2.23 mmol, 50%) as white crystals, mp 139.5–140 °C; IR (Nujol mull): ν 3306 (NH str.), 1665 (C=O str.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.25–1.50 (20H, m), 1.35 (3H, triplet overlapping with previous multiplet), 1.58–1.67 (2H, m), 2.27 (3H, s), 2.34 (2H, t, J=7.5 Hz), 2.52 (2H, t, J=8 Hz), 4.30 (2H, q, J=7.2 Hz), 8.85 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 10.7, 14.8, 24.2, 25.6, 25.9, 26.1, 26.2, 26.3, 27.0, 27.1, 27.3, 27.5, 27.7, 28.6, 29.8, 59.7, 117.0, 122.2, 127.2, 134.7, 162.1. Anal. Calcd for $C_{21}H_{35}NO_2$: C, 75.63; H, 10.58; N, 4.20. Found: C, 76.09; H, 10.12; N, 4.37.

4.2.7. Methyl 3-methylcyclopentadeca[*b*]pyrrole-2-carboxylate (9f). Cyclopentadecanone (1.00 g, 4.46 mmol) and phenylhydrazone **8b**[8] (1.11 g, 5.04 mmol) were reacted under the foregoing conditions. Recrystallization from ethanol gave pyrrole ester (0.97 g, 3.04 mmol, 68%) as white crystals, mp 150–150.5 °C; IR (Nujol): ν 3310 (s, NH str.), 1665 (s, C=O str.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.25–1.50 (20H, m), 1.58–1.67 (2H, m), 2.27 (3H, s), 2.34 (2H, t, J=7.5 Hz), 2.52 (2H, t, J=8 Hz), 3.82 (3H, s), 8.74 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 10.7, 24.2, 25.6, 25.9, 26.0, 26.2, 26.3, 27.0, 27.1, 27.3, 27.4, 27.7, 28.6, 29.7, 51.0, 116.7, 122.3, 127.4, 134.8, 162.4. Anal. Calcd for $C_{20}H_{33}NO_2$: C, 75.19; H, 10.31; N, 4.38. Found: C, 75.61; H, 10.23; N, 4.16.

4.2.8. Benzyl 3-methylcyclopentadeca[*b*]pyrrole-2-carboxylate (9g). Cyclopentadecanone (1.00 g, 4.46 mmol) and phenylhydrazone **8c**[9c,23e] (1.34 g, 4.53 mmol) were reacted as previously. Recrystallization from ethanol gave **9g** (0.758 g, 1.92 mmol, 43%) as white crystals, mp 157.5–158 °C IR (Nujol): ν 3307 (s, NH str.), 1669 (s, C=O str.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.25–1.50 (20H, m), 1.58–1.67 (2H, m), 2.30 (3H, s), 2.35 (2H, t, J=7 Hz), 2.52 (2H, t, J=8 Hz), 5.31 (2H, s), 7.32–7.45 (5H, m), 8.73 (1H, s); ^{13}C NMR ($CDCl_3$): δ 10.9, 24.2, 25.6, 25.9, 26.1, 26.2, 26.4, 27.0, 27.1, 27.3, 27.4, 27.7, 28.3, 29.7, 65.6, 116.6, 122.5, 127.8, 128.2, 128.3, 128.7, 135.0, 137.0, 161.6. Anal. Calcd for $C_{26}H_{37}NO_2$: C, 78.94; H, 9.43; N, 3.54. Found: C, 78.92; H, 9.37; N, 3.24.

4.2.9. Benzyl 17-acetoxy-3-methylcyclohexadeca[*b*]pyrrole-2-carboxylate (10). In an oven dried 1 L round bottom flask fitted with a calcium chloride drying tube, benzyl 3-methylcyclohexadeca[*b*]pyrrole-2-carboxylate (**9d**, 5.00 g, 12.2 mmol) was placed in a mixture of dichloromethane

(330 mL) and glacial acetic acid (330 mL). Lead tetraacetate (95%, 5.68 g, 12.2 mmol) was added over several minutes. After stirring overnight, the mixture was poured into water (200 mL). The organic phase was washed with saturated sodium bicarbonate solution, then with water, dried over sodium sulfate, filtered, and evaporated under reduced pressure. The residue was recrystallized with petroleum ether (60–80°) to yield the acetoxy pyrrole as white crystals (4.766 g, 10.2 mmol, 84%), mp 85.5–86.5 °C; IR (Nujol mull): ν 3319 (NH str.), 1736 (acetoxy C=O str.), 1668 (pyrrole ester C=O str.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.1–1.55 (22H, m), 1.72–1.95 (2H, m), 2.00 (3H, s), 2.26 (3H, s), 2.46–2.53 (2H, m), 5.32 (2H, s), 5.84 (1H, dd, J=6.0, 8.2 Hz), 7.3–7.44 (5H, m), 8.91 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 10.8, 21.2, 24.3, 24.4, 25.3, 26.3, 26.5, 26.9, 27.6, 28.0, 28.2, 30.6, 34.4, 65.9, 68.0, 118.8, 124.0, 126.9, 128.3, 128.7, 131.9, 136.6, 161.8, 170.2. Anal. Calcd for $C_{29}H_{41}NO_4$: C, 74.48; H, 8.84; N, 2.99. Found: C, 74.37; H, 8.59; N, 3.00.

4.2.10. Benzyl 17-(5-benzyloxycarbonyl-3-methyl-2-pyrrolyl)-3-methylcyclohexadeca[*b*]pyrrole-2-carboxylate (12a). Acetoxycyclohexadeca[*b*]pyrrole **10** (2.16 g, 4.62 mmol) and benzyl 3-methylpyrrole-2-carboxylate[32] (**11a**, 1.00 g, 4.65 mmol) were dissolved in glacial acetic acid (40 mL). *p*-Toluenesulfonic acid (100 mg) was added immediately, and the mixture was stirred overnight at room temperature. The solution was poured over an ice/water slurry (500 mL) and allowed to stand for 1 h. The precipitate was filtered and recrystallized from hexanes to give the title dipyrrole as white crystals (1.53 g, 2.46 mmol, 53%), mp 173.5–174 °C; IR (Nujol mull): ν 3349 (NH str.), 3301 (NH str.), 1693 (C=O str.), 1635 (C=O str.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.1–1.5 (22H, m), 1.83–2.05 (2H, m), 2.24 (3H, s), 2.28 (3H, s), 2.3–2.5 (2H, m), 4.00 (1H, t, J=7.4 Hz), 5.21–5.23 (4H, m), 5.92 (1H, d, J=2.4 Hz), 7.23–7.36 (10H, m), 9.07 (1H, br s), 9.16 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 11.2, 13.4, 24.6, 25.4, 25.6, 26.2, 26.6, 26.7, 26.9, 28.0, 28.2, 30.6, 34.0, 36.2, 65.89, 65.94, 110.6, 118.1, 118.5, 122.8, 127.6, 128.2, 128.7, 129.4, 134.4, 136.6, 136.7, 137.7, 161.8, 162.0. Anal. Calcd for $C_{40}H_{50}N_2O_4$: C, 77.14; H, 8.09; N, 4.50. Found: C, 76.73; H, 8.25; N, 4.60.

4.2.11. Benzyl 17-(5-benzyloxycarbonyl-3,4-dimethyl-2-pyrrolyl)-3-methylcyclohexadeca[*b*]pyrrole-2-carboxylate (12b). Acetoxycyclohexadeca[*b*]pyrrole **10** (1.00 g, 2.14 mmol) and benzyl 3,4-dimethylpyrrole-2-carboxylate[33] (**11b**, 0.515 g, 2.25 mmol) were reacted under the foregoing conditions. Recrystallization from hexanes gave the title dipyrrole as white crystals (0.963 g, 1.51 mmol, 71%), mp 125–126 °C; IR (Nujol mull): ν 3348 (NH str.), 1689 (C=O str.), 1651 (C=O str.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.15–1.55 (22H, m), 1.98 (3H, s), 2.0–2.2 (2H, m), 2.21 (3H, s), 2.23 (3H, s), 2.37–2.52 (2H, m), 4.19 (1H, t, J=7 Hz), 5.16–5.21 (4H, m), 7.15–7.30 (10H, m), 9.88 (1H, br s), 9.97 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 9.3, 11.2, 11.3, 24.6, 25.4, 25.6, 26.2, 26.7, 27.0, 27.7, 28.0, 28.3, 30.7, 33.1, 34.1, 66.0, 117.6, 117.8, 118.0, 122.3, 127.9, 128.1, 128.3, 128.6, 134.8, 135.4, 136.5, 162.3. Anal. Calcd for $C_{41}H_{52}N_2O_4$: C, 77.32; H, 8.23; N, 4.40. Found: C, 76.79; H, 8.21; N, 4.38.

4.2.12. Benzyl 17-(5-benzyloxycarbonyl-4-ethyl-3-methyl-2-pyrrolyl)-3-methylcyclohexadeca[*b*]pyrrole-2-carboxylate (12c). Prepared from **10** (0.961 g, 2.06 mmol) and benzyl 4-ethyl-3-methylpyrrole-2-carboxylate[33,34] (**11c**, 0.500 g, 2.06 mmol) by the procedure detailed for **12a**. Recrystallization from hexanes afforded the dipyrrole as white crystals (0.753 g, 1.16 mmol, 56%), mp 136.5–137.5 °C; IR (Nujol mull): ν 3357 (NH str.), 1686 (C=O str.), 1644 (C=O str.) cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.00 (3H, t, J=7 Hz), 1.15–1.6 (22H, m), 2.0–2.2 (2H, m), 2.24 (6H, s), 2.4–2.55 (4H, m), 4.19 (1H, t, J=7 Hz), 5.16–5.23 (4H, m), 7.20–7.30 (10H, m), 9.87 (1H, br s), 10.06 (1H, br s); ^{13}C NMR ($CDCl_3$): δ 11.0, 11.2, 15.8, 17.7, 24.6, 25.4, 25.5, 26.2, 26.6, 26.7, 26.9, 27.8, 28.1, 28.3, 30.7, 33.6, 34.0, 66.0, 66.1, 118.0, 122.2, 124.5, 127.8, 127.9, 128.1, 128.4, 128.6, 134.4, 135.4, 136.5, 162.2, 162.4. Anal. Calcd for $C_{42}H_{54}N_2O_4$: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.42; H, 8.38; N, 4.48.

4.2.13. (5-Carboxy-3-methyl-2-pyrrolyl)-3-methylcyclohexadeca[*b*]pyrrole-2-carboxylic acid (13a). Dibenzyl ester **12a** (502 mg, 0.807 mmol) was dissolved in methanol (200 mL) in a hydrogenation vessel. Triethylamine of 10 drops was added and the solution was purged with nitrogen. Palladium/charcoal (10%, 100 mg) was rinsed with a small amount of methanol, and the reaction vessel was shaken under an atmosphere of hydrogen (~40 psi) overnight. The catalyst was filtered off, and the solvent was evaporated under reduced pressure while maintaining the temperature below 40 °C. The residue was taken up in 5% ammonia solution, and the catalyst was washed with 5% ammonia to dissolve any remaining product. The combined aqueous solutions were cooled to 0 °C in a salt/ice bath and neutralized to litmus with glacial acetic acid. After standing at 0 °C for 1 h, the precipitate was filtered, washed with liberal amounts of water, and dried in vacuo. The product was isolated as pink crystals (326 mg, 0.738 mmol, 91%), mp 95 °C, dec; ^1H NMR ($CDCl_3$): δ 1.2–1.5 (22H, m), 1.64 (2H, quintet, J=6.8 Hz), 1.8–2.2 (2H, m), 2.25 (3H, s), 2.28 (3H, s), 2.4–2.5 (2H, m), 4.10 (1H, t, J=8 Hz), 5.92 (1H, s), 10.99 (1H, br s), 11.14 (1H, br s). Anal. Calcd for $C_{26}H_{38}N_2O_4$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.88; H, 9.01; N, 6.25.

4.2.14. (5-Carboxy-3,4-dimethyl-2-pyrrolyl)-3-methylcyclohexadeca[*b*]pyrrole-2-carboxylic acid (13b). Dicarboxylic acid was prepared from **12b** (500 mg, 0.79 mmol) with 10% palladium/charcoal (50 mg) as a catalyst as described above. The title compound was isolated as a pink solid (360 mg, 0.79 mmol, 100%), mp 118 °C, dec; ^1H NMR ($CDCl_3$): δ 1.1–1.6 (22H, m), 1.8–2.0 (2H, m), 2.02 (3H, s), 2.22 (3H, s), 2.25 (3H, s), 2.4–2.55 (2H, m), 4.18 (1H, br t), 11.2 (2H, br s).

4.2.15. (5-Carboxy-4-ethyl-3-methyl-2-pyrrolyl)-3-methylcyclohexadeca[*b*]pyrrole-2-carboxylic acid (13c). Dicarboxylic acid was prepared from **12c** (300 mg, 0.461 mmol) by the procedure described previously. The title dipyrrole was isolated as pink powder (196 mg, 0.417 mmol, 90%), mp 114 °C, dec; ^1H NMR ($CDCl_3$): δ 1.0–1.6 (22H, m), 1.9–2.1 (2H, m), 2.26 (6H, s), 2.4–2.6 (4H, m), 4.17 (1H, br t), 11.15 (1H, br s), 11.30 (1H, br s). Anal. Calcd for $C_{28}H_{42}N_2O_4 \cdot H_2O$: C, 68.82; H, 9.07; N, 5.73. Found: C, 69.12; H, 8.98; N, 6.08.

4.2.16. 3,5-Tridecano-13,17-diethyl-2,8,12,18-tetramethylporphyrin (14a). A solution of *p*-toluenesulfonic acid monohydrate (230 mg) in methanol (5 mL) was added to a stirred solution of **13a** (200 mg, 0.452 mmol) and 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrrylmethane-5,5′-dicarbaldehyde[9c] (**6a**, 124 mg, 0.433 mmol) in dichloromethane (50 mL) and methanol (5 mL). After few minutes, a deep red-orange solution was formed. The mixture was stirred at room temperature overnight in the dark, and a saturated solution of zinc acetate in methanol (4.5 mL) was then added. The resulting solution was allowed to stir in the dark for two more days at room temperature. The mixture was washed successively with water (100 mL), 5% hydrochloric acid solution (2×100 mL), 5% ammonia solution (100 mL), and water (100 mL). The organic solution was evaporated under reduced pressure, and the residue chromatographed on grade III alumina, eluting with dichloromethane. The colored fractions were evaporated under reduced pressure and further purified on a grade 3 silica gel column, eluting with toluene. The red band was collected and recrystallized from chloroform/methanol to give the title porphyrin as mauve crystals (61 mg, 0.101 mmol, 23%), mp 276 °C, dec; UV–vis (1% $Et_3N/CHCl_3$, free base): λ_{max} ($\log_{10}\varepsilon$) 407 (5.33), 505 (4.31), 540 (4.06), 574 (4.08), 627 (3.83) nm; UV–vis (1% TFA/$CHCl_3$, dication): λ_{max} ($\log_{10}\varepsilon$) 394 (infl, 4.89), 414 (5.57), 557 (4.35), 598 (infl, 4.02) nm; ^{1}H NMR ($CDCl_3$): δ −3.13 (2H, br s), 1.5–1.65 (10H, m), 1.70–1.81 (4H, m), 1.84 (3H, t), 1.86 (3H, t), 1.82–1.93 (2H, m), 2.21–2.29 (2H, m), 2.53–2.61 (2H, m), 3.57 (3H, s), 3.64 (3H, s), 3.66 (3H, s), 3.72 (3H, s), 3.96–4.02 (4H, m), 4.08 (2H, q, *J*=7.6 Hz), 4.95–4.99 (2H, m), 9.25 (1H, s), 9.86 (1H, s), 10.05 (1H, s), 10.06 (1H, s); ^{1}H NMR (TFA/$CDCl_3$): δ −3.91 (1H, s), −3.64 (1H, s), −3.48 (1H, s), −2.80 (1H, s), 1.48–1.64 (10H, m), 1.69 (3H, t, *J*=7.8 Hz), 1.74 (3H, t, *J*=7.8 Hz), 1.70–1.82 (4H, m), 1.89 (2H, quintet, *J*=7.0 Hz), 2.10 (2H, quintet, *J*=7.6 Hz), 2.27–2.35 (2H, m), 2.59–2.68 (2H, m), 3.44 (3H, s), 3.56 (3H, s), 3.59 (3H, s), 3.60 (3H, s), 3.64–3.69 (2H, m), 4.01–4.09 (4H, two overlapping quartets), 4.90–4.95 (2H, m), 9.09 (1H, s), 10.31 (1H, s), 10.44 (1H, s), 10.45 (1H, s); ^{13}C NMR (TFA/$CDCl_3$): δ 11.82, 11.84, 12.1, 14.0, 16.2, 16.3, 20.14, 20.16, 25.1, 26.1, 26.3, 26.7, 26.9, 27.1, 27.2, 28.9, 30.1, 311.5, 35.6, 39.1, 96.0, 98.4, 98.7, 124.2, 125.5, 138.2, 138.7, 138.8, 140.0, 140.1, 141.4, 141.5, 141.8, 141.9, 142.0, 143.1, 143.3, 144.0, 144.1, 144.3. HRMS (EI) calcd for $C_{41}H_{54}N_4$: 602.4348, found: 602.4349; HRMS (FAB) calcd for $C_{41}H_{54}N_4$+H: 603.4430, found: 603.4407. Anal. Calcd for $C_{41}H_{54}N_4\cdot 1/4H_2O$: C, 81.07; H, 9.04; N, 9.22. Found: C, 80.84; H, 9.00; N, 9.19.

4.2.17. 3,5-Tridecano-13,17-bis-(2-methoxycarbonylethyl)-2,8,12,18-tetramethylporphyrin (14b). Dipyrrole **13a** (100 mg, 0.226 mmol) was condensed with dialdehyde **6b**[35] (86 mg, 0.214 mmol) under the foregoing conditions. Recrystallization from chloroform/methanol gave porphyrin (35 mg, 0.049 mmol, 23%) as purple crystals, mp 248 °C, dec; UV–vis (1% $Et_3N/CHCl_3$, free base): λ_{max} ($\log_{10}\varepsilon$) 408 (5.36), 506 (4.30), 541 (4.01), 574 (4.04), 628 (3.74) nm; UV–vis (1% TFA/$CHCl_3$, dication): λ_{max} ($\log_{10}\varepsilon$) 396 (infl, 4.88), 416 (5.58), 559 (4.29), 598 (infl, 3.89) nm; ^{1}H NMR ($CDCl_3$): δ −3.18 (1H, s), −3.11 (1H, s), 1.5–1.64 (10H, m), 1.68–1.82 (4H, m), 1.88 (2H, quintet, *J*=7.6 Hz), 2.00 (2H, quintet, *J*=8 Hz), 2.19–2.27 (2H, m), 2.51–2.59 (2H, m), 3.24–3.30 (4H, two overlapping triplets), 3.59 (3H, s), 3.649 (3H, s), 3.654 (3H, s), 3.66 (3H, s), 3.67 (3H, s), 3.71 (3H, s), 3.96–4.01 (2H, m), 4.32 (2H, t, *J*=7.8 Hz), 4.41 (2H, t, *J*=7.8 Hz), 4.92–4.97 (2H, m), 9.24 (1H, s), 9.86 (1H, s), 10.05 (1H, s), 10.06 (1H, s); ^{1}H NMR (TFA/$CDCl_3$): δ −3.58 (1H, s), −3.32 (1H, s), −3.22 (1H, s), −2.55 (1H, s), 1.48–1.63 (10H, m), 1.69 (2H, quintet, *J*=7 Hz), 1.76 (2H, quintet, *J*=7 Hz), 1.89 (2H, quintet, *J*=7.0 Hz), 2.09 (2H, quintet, *J*=7.0 Hz), 2.27–2.35 (2H, m), 2.59–2.67 (2H, m), 3.10 (2H, t, *J*=7.8 Hz), 3.15 (2H, t, *J*=7.8 Hz), 3.43 (3H, s), 3.57 (3H, s), 3.59 (6H, s), 3.61 (6H, s), 3.63–3.68 (2H, m), 4.36–4.42 (4H, two overlapping triplets), 4.89–4.94 (2H, m), 9.07 (1H, s), 10.42 (1H, s), 10.43 (1H, s), 10.56 (1H, s); ^{13}C NMR (TFA/$CDCl_3$): δ 12.0, 12.2, 14.0, 21.7, 25.1, 26.1, 26.3, 26.7, 26.9, 27.1, 27.2, 28.8, 29.5, 30.1, 31.5, 35.54, 35.58, 39.1, 52.7, 96.9, 98.6, 98.9, 124.3, 125.5, 138.3, 139.5, 139.6, 139.7, 139.87, 139.95, 140.2, 141.1, 141.5, 141.7, 142.1, 142.3, 142.8, 143.0, 144.5, 175.0. HRMS (EI) calcd for $C_{45}H_{58}N_4O_4$: 718.4458, found: 718.4465. Anal. Calcd for $C_{45}H_{58}N_4O_4$: C, 75.17; H, 8.13; N, 7.79. Found: C, 75.02; H, 8.28; N, 7.82.

4.2.18. 3,5-Tridecano-13,17-diethyl-2,7,8,12,18-pentamethylporphyrin (14c). The title porphyrin was prepared from **13b** (100 mg, 0.219 mmol) and dipyrrylmethane dialdehyde **6a**[9c] (60 mg, 0.210 mmol) as described previously. Recrystallization from chloroform/methanol afforded the desired porphyrin as dark maroon crystals (42 mg, 0.068 mmol, 33%), mp 270 °C, dec; UV–vis (1% $Et_3N/CHCl_3$, free base): λ_{max} ($\log_{10}\varepsilon$) 407 (5.45), 507 (4.45), 540 (4.19), 575 (4.19), 627 (3.95) nm; UV–vis (1% TFA/$CHCl_3$, dication): λ_{max} ($\log_{10}\varepsilon$) 417 (5.66), 561 (4.46), 602 (4.15) nm; ^{1}H NMR ($CDCl_3$, 25 °C): δ −2.86 (2H, br s), 1.45–1.63 (10H, m), 1.65–1.71 (2H, m), 1.73–1.80 (2H, m), 1.81–1.86 (6H, two overlapping triplets), 1.8–2.0 (4H, m), 2.27 (2H, quintet, *J*=8 Hz), 3.59 (3H, s), 3.60 (3H, s), 3.61 (6H, s), 3.62 (3H, s), 3.96–4.06 (6H, m), 4.85–5.04 (1H, m), 5.14–5.32 (1H, m), 9.80 (1H, s), 10.05 (1H, s), 10.06 (1H, s); ^{1}H NMR (TFA/$CDCl_3$): δ −3.60 (1H, s), −3.53 (1H, s), −2.69 (1H, s), −2.57 (1H, s), 0.96–1.48 (12H, m), 1.67 (3H, t, *J*=7.6 Hz), 1.70 (3H, t, *J*=7.6 Hz), 1.73–1.83 (4H, m), 2.04 (2H, quintet, *J*=7.6 Hz), 2.15–2.24 (2H, m), 2.48–2.56 (2H, m), 3.28 (3H, s), 3.30 (3H, s), 3.32 (3H, s), 3.42–3.47 (2H, m), 3.488 (3H, s), 3.493 (3H, s), 3.97 (4H, q, *J*=7.7 Hz), 4.92–4.96 (2H, m), 10.08 (1H, s), 10.248 (1H, s), 10.253 (1H, s); ^{13}C NMR (TFA/$CDCl_3$): δ 11.7, 12.1, 12.2, 14.6, 16.18, 16.22, 20.0, 25.0, 26.0, 26.6, 26.7, 27.0, 28.8, 29.4, 29.9, 31.3, 33.8, 38.1, 94.8, 98.12, 98.15, 126.0, 133.3, 137.0, 138.6, 138.7, 141.0, 141.4, 141.5, 141.6, 142.4, 143.0, 143.5, 143.6, 143.75, 143.78. HRMS (FAB) calcd for $C_{42}H_{56}N_4$+H: 617.4587, found: 617.4570. Anal. Calcd for $C_{42}H_{56}N_4\cdot 1/4H_2O$: C, 81.18; H, 9.16; N, 9.01. Found: C, 81.00; H, 9.36; N, 9.00.

4.2.19. 3,5-Tridecano-7,13,17-diethyl-2,8,12,18-tetramethylporphyrin (14d). Porphyrin **14d** was prepared by the same procedure from **13c** (200 mg, 0.425 mmol) and dialdehyde **6a**[9c] (116 mg, 0.405 mmol). Recrystallization with chloroform/methanol yielded the title porphyrin as dark maroon crystals (75 mg, 0.12 mmol, 29%), mp 235 °C, dec; UV–vis (1% $Et_3N/CHCl_3$, free base): λ_{max} ($\log_{10}\varepsilon$) 408

(5.26), 507 (4.27), 541 (4.02), 576 (4.02), 628 (3.78) nm; UV–vis (1% TFA/$CHCl_3$, dication): λ_{max} ($\log_{10}\varepsilon$) 418 (5.46), 561 (4.27), 604 (3.99) nm; ^{1}H NMR ($CDCl_3$, 21 °C): δ −2.88 (1H, br s), −2.81 (1H, br s), 1.46–1.68 (12H, m), 1.75–1.85 (2H, m), 1.79 (3H, t, J=7.4 Hz), 1.84 (6H, t, J=7.6 Hz), 1.9–2.0 (4H, m), 2.27 (2H, quintet, J=8 Hz), 3.59 (3H, s), 3.60 (3H, s), 3.61 (6H, s), 3.95–4.07 (6H, m), 4.86–5.02 (1H, m), 5.04–5.17 (1H, m), 9.78 (1H, s), 10.04 (1H, s), 10.05 (1H, s); ^{1}H NMR (TFA/$CDCl_3$): δ −3.51 (2H, s), −2.57 (1H, s), −2.54 (1H, s), 1.37 (3H, t, J=7.4 Hz), 1.45–1.65 (12H, m), 1.65–1.71 (3H, two overlapping triplets), 1.72–1.82 (4H, m), 2.02 (2H, quintet, J=8 Hz), 2.13–2.21 (2H, m), 2.47–2.58 (2H, m), 3.29 (6H, s), 3.42–3.48 (2H, m), 3.476 (3H, s), 3.481 (3H, s), 3.63–3.71 (2H, m), 3.95 (4H, q, J=7.7 Hz), 4.87–4.92 (2H, m), 10.05 (1H, s), 10.22 (1H, s), 10.23 (1H, s); ^{13}C NMR (TFA/$CDCl_3$): δ 117, 11.8, 12.0, 15.5, 16.1, 20.0, 21.1, 24.7, 25.9, 26.4, 26.6, 26.9, 27.0, 28.8, 29.4, 29.8, 31.2, 33.6, 38.6, 94.7, 97.8, 98.3, 125.7, 136.1, 137.0, 138.7, 138.8, 141.1, 141.2, 141.6, 141.7, 142.2, 142.3, 143.6, 143.8. HRMS (FAB) calcd for $C_{43}H_{58}N_4$+H: 631.4744, found: 631.4760. Anal. Calcd for $C_{43}H_{58}N_4$: C, 81.85; H, 9.26; N, 8.88. Found: C, 81.74; H, 9.59; N, 8.93.

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