Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron
Tetrahedron 63 (2007) 12454–12464

Synthesis of hydroporphyrins based on comparative studies of palladium-catalyzed and non-catalyzed approaches

Natalia N. Sergeeva, Yasser M. Shaker, Eimear M. Finnigan, Thomas McCabe and Mathias O. Senge*

School of Chemistry, SFI Tetrapyrrole Laboratory, Trinity College Dublin, Dublin 2, Ireland

Received 1 June 2007; revised 4 September 2007; accepted 13 September 2007
Available online 22 September 2007

Abstract—Hydroporphyrins have been synthesized using both Pd-catalyzed and non-catalyzed approaches. Comparative studies of the reaction of tetrasubstituted porphyrins with organolithium reagents in the presence of and without palladium catalysts showed that depending on reagents, the catalyst structure and reactivity of the corresponding porphyrins, chlorins (β-hydroporphyrins) and/or porphodimethenes (*meso* hydroporphyrins) of 5,10-type can be prepared in reasonable yields. In the absence of Pd catalysts, the formation of chlorins is predominant in the reactions with aliphatic RLi while porphodimethenes are the main products in reactions with PhLi. The use of a palladium catalyst resulted in the formation of both types of hydroporphyrins and the selective formation of either β-mono- or disubstituted chlorins. Of special interest was the reaction of octaethylporphyrin. Here, reaction with *t*-BuLi in the presence of $Pd(PPh_3)_4$/CuI proceeded with complete regioselectivity for 5,10-porphodimethenes.

1. Introduction

Porphyrins and their derivatives attract considerable attention due to their numerous applications in medicinal chemistry, optics, and material science. Chlorins and porphodimethenes are hydroporphyrins and play an important role in nature. Chlorins, which are related to natural pigments such as chlorophylls,[1] are part of natural photosynthetic systems and have been utilized as photosensitizers in photodynamic therapy (PDT).[1] They are characterized by having sp^3-hybridized β-positions. Calixpyrrole-type systems are isomeric type of hydroporphyrins;[2] here the carbon atoms in the *meso* positions are sp^3-hybridized, effectively interrupting the aromatic conjugation pathway. General interest in designing and studying calixpyrroles is due to their unique structural features, which give rise to specific conformations[3–5] and result in potential applications in anion binding and recognition.[6]

Many reports that describe the synthesis and reactivity of hydroporphyrins have appeared. Besides chlorins, special attention has been given in the past to porphodimethenes (calix-type systems that contain two sp^3- and sp^2-hybridizied *meso* carbon atoms each).[7] Syntheses of porphodimethenes (PDM) include Buchler's classic reductive alkylation to yield 5,15-porphodimethenes[8] and unselective condensations with low yields[9] for the preparation of calix-type systems with non-hydrogen atom residues at the sp^3-hybridized *meso* centers.[2]

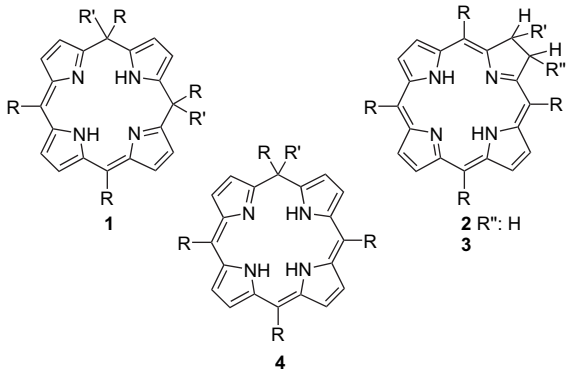
The synthesis of chlorins is typically based on three alternate strategies. These are total synthesis, modification of natural chlorins, and the derivatization of porphyrins, mostly through β−β-addition reactions.[10–13] The field of hydroporphyrin chemistry is rapidly expanding but most practical applications in medicine or materials science require simple and straightforward syntheses. In addition, most synthetic strategies target either *meso* hydroporphyrins (e.g., PDMs) or β-hydroporphyrins (chlorins). Here, we describe a methodology that allows access to either class of hydroporphyrin from the same porphyrin precursors through the use of organolithium reagents.

2. Results and discussion

In an initial study, we reported that tetrasubstituted porphyrins can undergo addition reactions with *t*-BuLi in the presence of palladium catalysts.[14] Depending on the catalyst structure and reactivity of the corresponding porphyrins, chlorins and/or porphodimethenes could be prepared. As this type of Pd-catalysis had not been previously examined, we have systematically studied the influence of Pd catalysts to develop a suitable synthetic route to the target materials **1**–**3**.

Keywords: Porphodimethenes; Chlorins; Porphyrins; Palladium catalysts; Organolithium reagents.
* Corresponding author. Tel.: +353 1 896 8537; fax: +353 1 896 8536; e-mail: sengem@tcd.ie

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.09.030

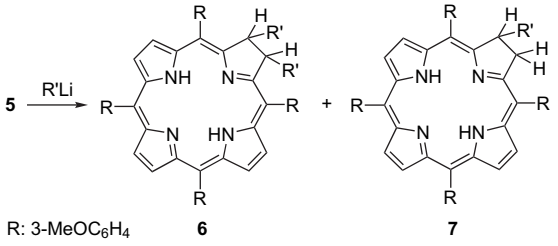


It is known that the reaction of porphyrins with RLi (e.g., R=alkyl or aryl) is an attractive synthetic method for the introduction of different residues into the *meso* position of unactivated porphyrins.[15–18] However, this method can also be applied to *meso* tetrasubstituted porphyrins with free β-positions. The first example of the non-catalyzed reaction of porphyrins with RLi followed by formation of hydroporphyrins **1**–**4** was reported by Callot's group in 1998. Depending on the free base porphyrin structure, phlorins **4** (phlorins are cyclic tetrapyrrole systems with one sp^3-hybridized *meso* center and three NH groups), chlorins **2**,**3**, and/or porphodimethenes **1** can be formed in these reactions.[15,16,19–21] Despite the potential utility of this method further progress was hampered by very low yields (1–5%) and non-regioselectivity in the formation of chlorins and porphodimethenes.

To understand the potential role of catalysts in these types of transformations, we decided to investigate the reaction behavior more closely and started with a re-examination of the non-catalyzed approach, i.e., standard reactions of porphyrins with organolithium nucleophiles.

2.1. Non-catalyzed approach

Starting from 5,10,15,20-tetrakis(3-methoxyphenyl)porphyrin **5**, we investigated the reaction with different aliphatic lithium reagents (RLi). Surprisingly, formation of either porphodimethenes or phlorins was not observed, this reaction resulted only in the formation of β-di- (**6**) and β-monosubstituted (**7**) chlorins (Scheme 1, Table 1).



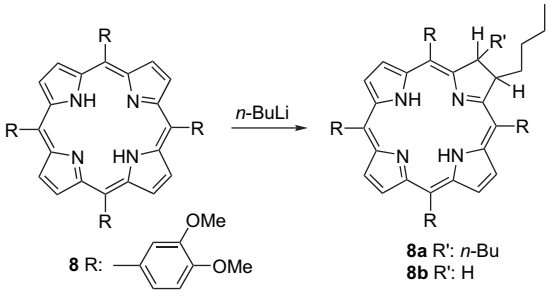
Scheme 1. Reaction of porphyrin **5** with R′Li.

Moreover, the sterically hindered *t*-BuLi reagent showed a slightly different reactivity towards **5**. Here, only the monoalkylated product **7d** was formed as the major product (7%). Reactions with other alkyl lithium reagents (*n*-Bu, *n*-Hex, and *sec*-Bu lithium) gave mixtures of the two chlorins in combined yields of up to 42% (Table 1).

Table 1. Reaction of **5** with RLi—method A

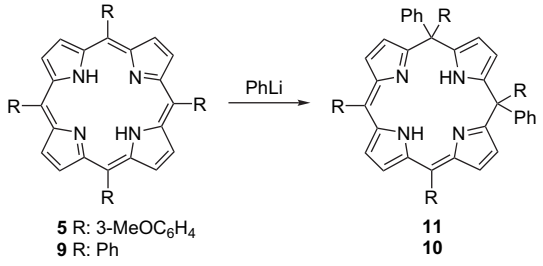
R′Li	Yield, % (**6**)	Yield, % (**7**)
n-BuLi	14 (**6a**)	17 (**7a**)
n-HexLi	20 (**6b**)	22 (**7b**)
sec-BuLi	18 (**6c**)	8.5 (**7c**)
t-BuLi	<2 (**6d**)	7 (**7d**)

Next, we turned our attention to the slightly more sterically demanding 5,10,15,20-tetrakis(3,4-dimethoxyphenyl)porphyrins **8**. Reaction with *n*-BuLi resulted in the formation of the di- and monosubstituted chlorins **8a** and **8b** in 7% and 9% yield, respectively (Scheme 2). Here, the steric effects of the aryl residues along with the lower solubility of the starting material account for the low yield.



Scheme 2. Reaction of **8** with *n*-BuLi.

Different results were obtained when PhLi was used as a reagent. Indeed, when 5,10,15,20-tetraphenylporphyrin (H_2TPP) **9** was treated with PhLi, two different products were formed of which only the major product could be isolated in 40% yield and was identified as 5,10-porphodimethene **10**. Moreover, in contrast to the observations made with alkyl lithium reagents, reaction of porphyrin **5** with PhLi also gave PDM **11** as the sole product in 18% yield (Scheme 3).



Scheme 3. Non-catalyzed reaction of **5** and **9** with PhLi.

The 'reduction' of the 5 and 10 *meso* positions of the porphyrin core to give the porphodimethenes effectively breaks the aromaticity of the parent porphyrin. This of course will crucially affect the 3D structure as well as the physical properties. An analysis of the structures based on ^{1}H NMR for compounds **10** and **11** showed four doublets for the β-H of the pyrrole rings in the area of 5.5–6.6 ppm with J_{HH} coupling constants ranging from ~2.3 to ~4.7 Hz. In addition, the signals of the NH protons are now shifted downfield, appearing at 10–13 ppm, as opposed to being upfield (at −3.5 ppm) for 'aromatic porphyrins'. Together with a comparison of published data,[21] the spectroscopic results clearly

identify compounds **10** and **11** to have the structure of a 5,10-porphodimethene.

2.2. Pd-catalyzed method

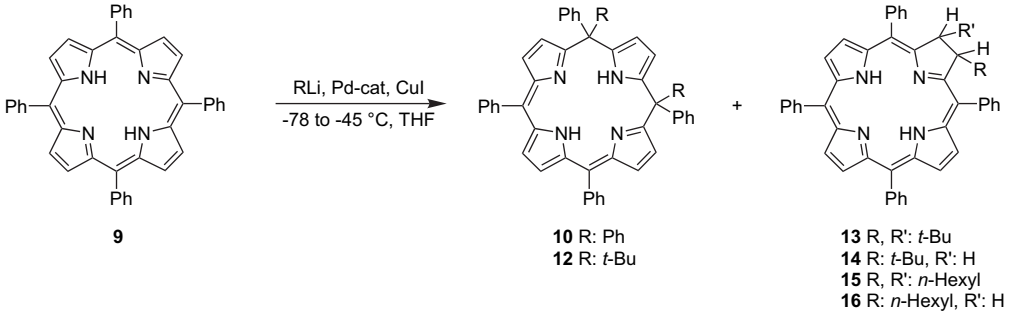
Having in hand these preliminary results on the reactivity and behavior of the tetrasubstituted porphyrins with RLi, we turned our attention back to the palladium-catalyzed approach. Initially, we started with the tetra arylsubstituted porphyrins **5** and **9** as model compounds. This served to allow for rapid characterization of the different products formed and comparison of the results from the non-catalyzed reactions. When porphyrin **5** was reacted with *t*-BuLi in the presence of $Pd(PPh_3)_4$ at low temperatures, the monosubstituted chlorin **7d** (8%) and the disubstituted chlorin **6d** (7%) were formed in low yields. This is probably a result of the lower solubility and the slightly deactivating effect of the methoxyphenyl groups of the starting porphyrin. Also, the use of $Pd_2(dba)_3\cdot CHCl_3$ increased the yields of compounds **6d** and **7d** to 26% each. This is in contrast to the non-catalyzed reaction of porphyrin **5** with *t*-BuLi where the disubstituted chlorin **6d** was formed as the major product. Treatment of porphyrin **5** with PhLi in the presence of $Pd(PPh_3)_4$ at 60 °C gave 5,10-PDM **11** in 14% yield. Here, no difference in the yield or the reaction behavior of porphyrin **5** compared to the non-catalyzed approach was found.

However, a different reactivity was observed for H_2TPP. Porphyrin **9** smoothly reacted with *t*-BuLi in the presence of $Pd(PPh_3)_4$ and CuI to give 5,10-porphodimethene (PDM) **12** and chlorins **13** and **14** in 16%, 27%, and 16% yields, respectively (Scheme 4, Table 2). For comparison, Callot and Krattinger reported the isolation of porphodimethene **12** and the disubstituted chlorin **13** in yields of 5% and 1%, respectively, in the same reaction without the catalyst.[19]

An interesting extension of this research concerned the use of sterically unhindered reagents in the reaction with H_2TPP. While *n*-BuLi, in the absence of catalysts, results in the formation of the respective phlorin and the monosubstituted chlorin,[19] quite a different reactivity was found in the presence of the catalysts. Depending on the type of catalyst, reaction of **9** with *n*-hexyl lithium gave either the dialkyl substituted chlorin **15** (25%) or the monosubstituted chlorin **16** (29%) as the respective sole products (Table 2). However, treatment of the free base **9** with PhLi in the presence of $Pd(PPh_3)_4$ resulted in the formation of 5,10-PDM **10** in 26% yield, which is lower than in the non-catalyzed reaction, where compound **10** was obtained in 40% yield. Attempts to increase the yield of the corresponding PDM by using similar conditions for the reaction of TPP and PhLi with a different catalyst, namely $Pd_2(dba)_3\cdot CHCl_3$ were unsatisfactory. The reactions resulted only in the formation of inseparable mixtures.

Next, we turned our attention to the reactivity of the *meso* tetraalkyl porphyrins **17**–**19**. The non-catalyzed approach was unsuccessful; here complete decomposition of the porphyrins was observed. Initial studies on their reaction with *n*-BuLi in the presence of catalysts yielded complex mixtures. Similar results were observed, when **17** or **18** was treated with 20 equiv of *t*-BuLi in the presence of $Pd(PPh_3)_4$ and CuI. In contrast, reaction of **17** with only 5 equiv of *t*-BuLi and $Pd_2(dba)_3\cdot CHCl_3$ resulted in the formation of PDM **20** and the 2-substituted chlorin **22** in 16% and 17% yield, respectively (Scheme 5, Table 3).

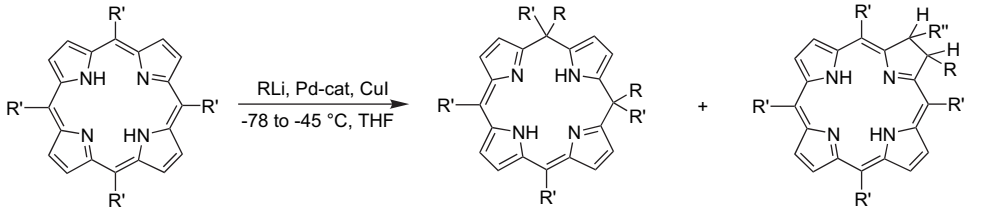
In order to improve the yields, we again tested other catalysts and found that $Pd_2(dba)_3$ allowed the preparation of **22** in 43% yield. This was accompanied by a slight reduction in the yield of PDM **20** (12%). So far, other *meso* alkylporphyrins gave significantly lower yields of the porphodimethene (Scheme 5). A different reactivity was observed in the case of porphyrin **19**. Reaction of **19** with *t*-BuLi resulted only in the formation of both types of chlorins. The yields of either the dialkylated chlorin **23a** or the monoalkylated chlorin **23b** could be slightly increased by varying the palladium catalyst. However, reaction of **19** with the less



Scheme 4. The reaction of porphyrin **9** with RLi in the presence of Pd catalysts.

Table 2. Reaction of TPP with RLi in the presence of Pd catalysts—method B

T (°C), RLi	Catalyst	PDM **1**, %	Chlorin type **2**, %	Chlorin type **3**, %
−78, *t*-BuLi	$Pd(PPh_3)_4$	16 (**12**)	16 (**14**)	27 (**13**)
−60, *t*-BuLi	$Pd_2(dba)_3\cdot CHCl_3$	21 (**12**)	22 (**14**)	20 (**13**)
−60, *n*-HexylLi	$Pd_2(dba)_3\cdot CHCl_3$	—	—	25 (**15**)
−80, *n*-HexylLi	$Pd(PPh_3)_4$	—	29 (**16**)	—
+52, PhLi	$Pd(PPh_3)_4$	26 (**10**)	—	—



17 R': *i*-Bu
18 R': *n*-Hexyl
19 R':1-Ethylpropyl

20 R': *i*-Bu; R: *t*-Bu
21 R': *n*-Hexyl; R: *t*-Bu

22 R': *i*-Bu; R: H; R'': *t*-Bu
23a R': 1-Ethylpropyl; R, R'': *t*-Bu
23b R': 1-Ethylpropyl; R: *t*-Bu; R'': H
24 R': 1-Ethylpropyl; R, R'': *n*-Hexyl

Scheme 5. The reaction of tetraalkyl porphyrins with RLi.

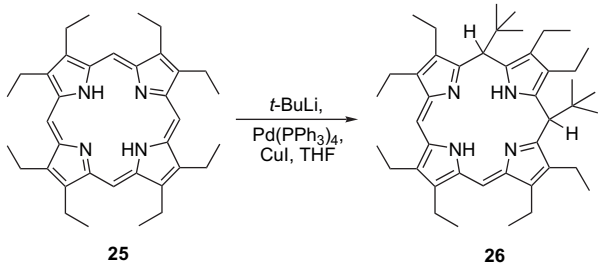
Table 3. Reaction of tetraalkyl porphyrins **17**–**19** with RLi—method B

Porphyrin	*T* (°C), RLi	Catalyst	PDM **1**, %	Chlorin type **2**, %	Chlorin type **3**, %
17	−60, *t*-BuLi	$Pd_2(dba)_3 \cdot CHCl_3$	16 (**20**)	17 (**22**)	—
17	−60, *t*-BuLi	$Pd_3(dba)_2$	12 (**20**)	43 (**22**)	—
18	−60, *t*-BuLi	$Pd_2(dba)_3 \cdot CHCl_3$	6 (**21**)	—	—
18	−60, *t*-BuLi	$Pd_2(dba)_3$	10 (**21**)	—	—
19	−60, *t*-BuLi	$Pd_2(dba)_3$	—	31 (**23b**)	10 (**23a**)
19	−60, *t*-BuLi	$Pd_2(dba)_3 \cdot CHCl_3$	—	10 (**23b**)	21 (**23a**)
19	−60, *n*-HexLi	$Pd(PPh_3)_4$	—	—	14 (**24**)

sterically hindered *n*-HexLi yielded only the disubstituted chlorin **24** in lower yield. Reaction of porphyrin **19** with PhLi led to the formation of a chlorin-type product (<6%, not shown). The lower reactivity of **19** compared to **17** could be a result of macrocyclic distortion caused by bulky substituents along with electronic effects.

Lastly, we turned our attention to the reactivity and reaction behavior of β-alkyl substituted porphyrins. As *meso* hydroporphyrins derived thereof are more closely related to the naturally occurring pigments they have some relevance to the biosynthesis of porphyrins.[3] Earlier reports showed that 2,3,7,8,12,13,17,18-octaethylporphyrin (H_2OEP, **25**) can be transformed into air-stable porphodimethenes. For example, the activated 2,3,7,8,12,13,17,18-octaethylporphyrin nickel complex reacts with *n*-BuLi in the presence of *n*-BuI and provides 5,15-porphodimethene in almost quantitative yield.[22]

However, applying the newly developed procedure to this porphyrin, a quite different reactivity was observed. Treatment of H_2OEP with *t*-BuLi in the presence of $Pd(PPh_3)_4$ and CuI surprisingly resulted in the formation of only one regioisomer **26** in an excellent yield of 73% (Scheme 6). According to spectroscopic investigations, some features



25 **26**

Scheme 6. The reaction of H_2OEP with *t*-BuLi.

of which will be discussed below, this compound was identified as 5,10-porphodimethene. In all earlier reactions of OEP derivatives with RLi in the absence of catalysts this type of compounds was never observed. Invariably, formation of 5,15-PDM was observed.[16,18,22] This shows the significant influence of palladium catalysts on this type of reactions.

2.3. Spectroscopic and structural analysis of the hydroporphyrins

The spectroscopic analysis of 5,10-PDM complexes requires a special comment. The first fully characterized example of a *meso* tetrasubstituted 5,10-PDM was given by Krattinger and Callot.[20] They showed that 5,10-PDM can be envisaged to consist of two parts: a 5,10-tripyrrolic unit and an isolated pyrrole ring linked via two *meso* sp^3-C atoms and identified the *t*-Bu groups to be in *anti* diaxial geometry.[23]

Interesting conclusions can be drawn from the 5,10-PDM series (**10**–**12**, **20**, and **21**) derived from *meso* tetrasubstituted porphyrins (**5**, **9**, **17**, and **18**). According to the ^{1}H NMR spectra, the chemical shifts of the β-hydrogen atoms in this series (δ, ppm **10** (5.46, 6.03, 6.15, 6.60), **11** (5.51, 6.08, 6.15, 6.64), **12** (5.23, 5.61, 6.13, 6.45), **20** (5.94, 6.68, 6.81, 7.26), **21** (6.02, 6.72, 6.88, 7.34)) vary in a regular fashion, with a decrease in shielding in the order **21**>**20**>**11**>**10**>**12**. This fact indicates that 5,10-PDMs **20** and **21**, with more flexible *meso* alkyl chains, have a less deformed macrocycle than the corresponding aryl derivatives **10**–**12**.

Similarly, a higher distortion was expected for **12**, derived from H_2TPP, with two bulky *t*-Bu-residues compared to **10** and **11**. The chemical shifts for the proton signals of **10** and **11** are almost identical. This is most likely related to structural changes and the degree of steric interactions between neighboring groups attached to *meso* sp^3-carbon

atoms rather than inductive effects of the *meso* substituents alone. Hence, deformation of the 5,10-PDM macrocycle increases in the order **21**<**20**<**11**<**10**<**12** and decreases with respect to the overall aromatic character of the systems. Of course without detailed solid state structural data for these complexes, a precise explanation is difficult. However, this rationale is consistent with results previously reported by Buchler et al. for his series of 5,15-porphodimethenes.[4,24]

Compound **26** derived from H_2OEP with ethyl groups in the β-positions represents a more complex example of a 5,10-PDM. The structural features of **26** were analyzed by comparing it with previous data reported for 5,15-PDMs of H_2OEP. According to the results published by Buchler et al.[4] in 1987, 5,15-PDMs exist in two different conformeric forms: *syn*-axial '*aa*'[25a] as the major configuration (5–58%) and '*dd*'[25b] (2–8%) as the minor conformer. Spectroscopic studies for the series (*syn*-axial '*aa*') have shown that the 5,15-PDM skeleton is far from planar and displays a folding at the *meso* sp^3-hybridyzed carbon atoms and studies of the *syn*-5,15-PDM complexes have confirmed a high symmetry in the system. In the ^{1}H NMR spectra only two sets of signals appear for the corresponding β-CH_2 and β-CH_3 of the ethyl groups. Also, one set of signals is observed for the enantiotopic protons H5,15 at the *meso* sp^3-carbon atoms. The atoms H10 and H20 are enantiotopic in all the configurations too. A strong tautomeric effect of the NHs results in the appearance of one broad signal. The corresponding '*dd*' isomer of 5,15-PDM with two *t*-Bu groups derived from OEP shows two sets of signals for the enantiotopic protons H5,15 (at sp^3-C) and H10,20 (at sp^2-C), however, β-CH_2 (2.56 ppm) and β-CH_3 (1.17 ppm) appear as multiplets.[4]

Compound **26** should display a different symmetry for the 5,10-PDM macrocycle than the corresponding 5,15-PDM analog. This should result in significant differences in the physical data. The ^{1}H NMR spectrum of compound **26** also shows the presence of only two singlets at 3.86 and 6.58 ppm, which belong to an enantiotopic protons H5,10 (at sp^3-C) and H15,20 (at sp^2-C), respectively. An important spectroscopic feature for compound **26** is the presence of four triplets for the β-CH_3 diastereotopic groups at 1.11, 1.16, 1.17, and 1.25 ppm. Additionally, two sets of quartets from four diastereotopic β-CH_2 groups and two remaining groups with dq multiplicity of geminal β-CH_2 protons coupling are observed. Two singlets at 10.92 and 13.06 ppm are found for the corresponding NH protons. More detailed analysis based on HMBC and NOE experiments for compound **26** also confirms the 5,10-PDM structure.

For chlorin **13**, we were able to grow crystals suitable for single crystal X-ray crystallographic analysis. While the data set has some limitations it clearly shows the product to be the di-β-substituted chlorin (Fig. 1). The structure clearly shows the *anti* orientation of the two *tert*-butyl groups in line with the earlier observations on related systems[16a,21] and exhibits the typical zig–zag conformation of the reduced pyrrole ring.[26] The macrocycle shows moderate degrees of distortion with a Δ24 of 0.13 Å for the 24 macrocycle atoms. As expected, the largest deviations from the least-squares plane are observed in the vicinity of the reduced ring and clearly mimic the steric strain imposed on the macrocycle by the bulky *tert*-butyl groups.[27]

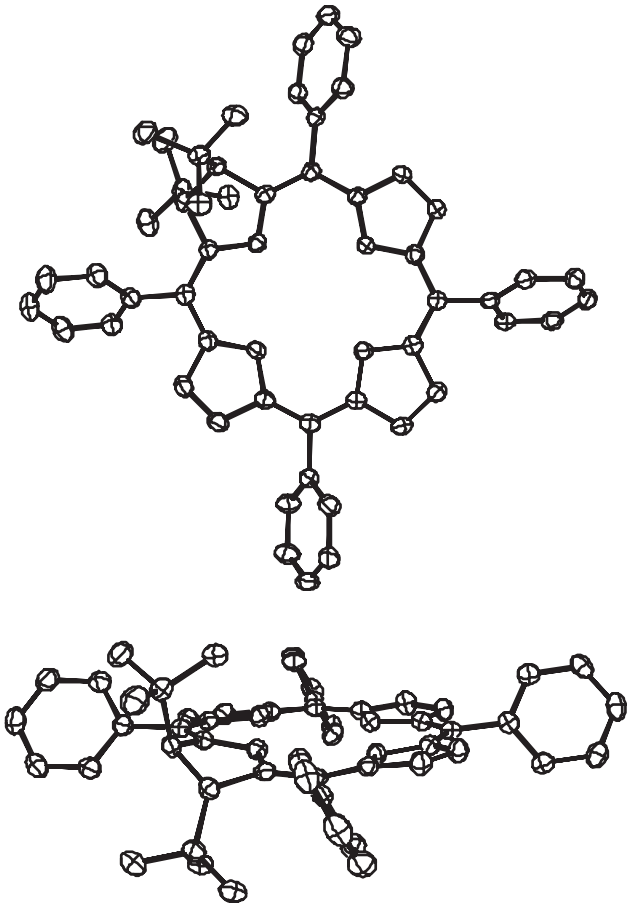


Figure 1. Top and side views of the molecular structure of **13** in the crystal. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are drawn for 50% occupancy.

2.4. Conclusions

Predominantly, the formation of either chlorins in the reaction with aliphatic RLi or porphodimethenes in the reactions with PhLi was observed using the non-catalyzed approach. The use of a palladium catalyst resulted in the synthesis of both types of hydroporphyrins and the selective formation of either type of chlorin. The yields of hydroporphyrins can be significantly increased by applying Pd-catalyzed methodology. Considerable improvement has been achieved by the reaction of R^{alk}Li with TPP in the presence of Pd catalysts. Moreover, the tetraalkyl substituted porphyrins can also undergo chemical transformation with RLi in the presence of Pd catalysts generating hydroporphyrins. Without a catalyst these reactions generally led to decomposition of the corresponding porphyrins. Of special interest was the reaction of H_2OEP with *t*-BuLi in the presence of $Pd(PPh_3)_4$/CuI as complete regioselectivity for 5,10-PDM was achieved. Interestingly, there was a reduction in the yield of hydroporphyrin **26** when this reaction was carried out without CuI. The role of CuI still remains unclear, but additional experiments have shown the significance of it, as without it an increase in the number of side reactions was observed. Mechanistically the reaction of RLi/Pd catalyst with a porphyrin could represent a type of nucleophilic addition reaction. Depending on the structure of the catalysts, the lithium reagents and the substituents on the porphyrin,

different regioselectivities could be achieved. However, in some cases, formation of both types of hydroporphyrins was observed. This may be explained on the basis of the affinity of the palladium catalysts to the π-electron moiety in general, which results in the activation of any double bonds bearing a substrate. We surmise the first step of the nucleophilic addition to be activation by a double bond in the porphyrin macrocycle, followed by addition of RLi (or complex intermediates containing RLi–Pd catalyst–CuI).

3. Experimental

3.1. General information

^{1}H NMR spectra were recorded on a Bruker DPX 400 (400 MHz for ^{1}H NMR) and/or Bruker AV 600 (600 MHz for ^{1}H NMR and 100.6 MHz for ^{13}C NMR). Chemical shifts are reported in (ppm) referenced to tetramethylsilane set at 0.00 ppm. HRMS spectra were measured on Micromass/Waters Corp. USA liquid chromatography time-of-flight spectrometer equipped with ES source. Low-resolution mass spectra were recorded on Micromass/Waters Corp. USA Quattro micro™ LC–MS/MS. UV–vis measurements were performed on Shimadzu MultiSpec-1501. Melting points were acquired on Stuart SMP10 melting point apparatus and are uncorrected. Thin layer chromatography (TLC) was performed on silica gel $60F_{254}$ (Merck) precoated aluminum sheets. Flash chromatography was carried out using Fluka Silica Gel 60 (230–400 mesh). Anhydrous THF distilled over sodium/benzophenone was used. All commercial chemicals and organolithium reagents were supplied by Aldrich and used without further purification. Other conditions were as described earlier.[28] Analytical data for compounds **12** and **13** agree with those reported in the literature.[21]

3.2. General procedures

3.2.1. Method A: non-catalyzed approach. To a solution of porphyrin (0.13 mmol) in anhydrous THF (30 mL) at −80 °C under argon, RLi (0.75 mmol for *n*-BuLi, *sec*-BuLi, and *t*-BuLi; 1.2 mmol for *n*-HexLi) was added. The mixture was warmed to rt and stirred for another 3 h (TLC control). The reaction was quenched with a mixture of water (2 mL) and THF (3 mL) and stirring was continued for 20 min. A solution of DDQ (13 mmol) in THF (50 mL) was added and the reaction mixture was stirred for 1 h at rt. The reaction mixture was filtered through silica gel and the organic solvents were removed under vacuum. The residue was purified by column chromatography on silica gel.

3.2.2. Method B: Pd-catalyzed approach. To a solution of porphyrin (0.13 mmol), CuI (4.7 mg, 0.0195 mmol), and Pd catalyst (0.013 mmol) in anhydrous THF (50 mL) at −60 °C under argon RLi was added. The reaction mixture was stirred at the same temperature (TLC control) and quenched with saturated aqueous solution of NH_4Cl (1 mL). The mixture was filtered through silica gel (eluent: *n*-hexane) and the solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel.

For reactions of porphyrins **5** and **9**, 2.6 mmol of RLi was used. Reduced amounts of RLi were used for the reaction of tetraalkyl porphyrins, *t*-BuLi (0.65 mmol) for **17** and **18**, *t*-BuLi and *n*-HexLi (1.3 mmol) for **19**. The crude products were purified as described above (method B). Addition of PhLi (1.8 mmol) was performed at rt and the reaction mixture was refluxed at 70 °C; further work up followed the procedure above (method A or B).

3.3. Syntheses

3.3.1. 2,3-Dibutyl-5,10,15,20-tetrakis(3-methoxyphenyl)-chlorin (6a). Compound **6a** was isolated from the reaction of **5** with *n*-BuLi using method A. Column chromatography on silica gel with EtOAc/*n*-hexane (1:6 v/v) yielded three fractions. The first fraction consisted of **6a** (15.4 mg, 0.018 mmol, 14%, as a purple solid), the second fraction was identified as **7a** (17.5 mg, 0.022 mmol, 17%, as purple crystals), and the third fraction contained porphyrin **5**. Analytical data for **6a**: mp 245 °C. [Found: C, 79.5; H, 6.5; N, 6.3. $C_{56}H_{56}N_4O_4$ requires: C, 79.22; H, 6.65; N, 6.60%.] R_f (EtOAc/*n*-hexane, 1:6 v/v, silica) 0.56; δ_H (400 MHz, $CDCl_3$) −1.44 (s, 2H, N*H*), 0.80 (t, *J* 7.5 Hz, 6H, $CH_2(CH_2)_2CH_3$), 1.22 (m, 8H, $CH_2(CH_2)_2CH_3$), 1.69 (m, 4H, $CH_2(CH_2)_2CH_3$), 4.00 (m, 12H, OCH_3), 4.42 (m, 2H, C*H*n-Bu), 7.28 (m, 6H, H_{Ph}), 7.62 (m, 8H, H_{Ph}), 7.86 (m, 2H, H_{Ph}), 8.24 (m, 2H, βH), 8.50 (s, 2H, βH), 8.65 (m, 2H, βH); δ_C NMR (100.6 MHz, $CDCl_3$) 13.6, 22.1, 26.2 (m), 28.3 (m), 31.0 (m), 33.9, 45.3, 51.5, 55.0, 113.0, 119.2, 123.3, 125.3, 126.5, 127.1, 127.4, 127.6, 128.2, 131.5, 134.6, 140.6, 143.0, 151.8, 157.5, 158.0, 158.5, 168.6; MS (EI, 80 eV), *m*/*z* (%): 848 (14) [M$^+$], 818 (100) [M$^+$−2(CH$_3$)], 792 (80) [M$^+$−C$_4$H$_9$+H], 735 (56) [M$^+$−2(C$_4$H$_9$)+H], 611 (16) [M$^+$−2(C$_4$H$_9$)+H−4(OCH$_3$)]; HRMS [$C_{56}H_{56}N_4O_4$]: calcd for [M+H$^+$] 849.4301, found 849.4308; UV–vis (CH_2Cl_2): λ_{max} (log ε) 420 (5.19), 454 (4.17), 519 (4.08), 519 (4.08), 547 (3.93), 652 (4.32).

3.3.2. 2-Butyl-5,10,15,20-tetrakis(3-methoxyphenyl)-chlorin (7a). Compound **6a** was isolated from the reaction of **5** with *n*-BuLi using method A as described above. Analytical data for **7a**: mp 233 °C; R_f (EtOAc/*n*-hexane, 1:6 v/v, silica) 0.70; δ_H (400 MHz, $CDCl_3$) −1.49 (br, 2H, N*H*), 0.61 (m, 3H, $(CH_2)_3CH_3$), 1.06 (m, 2H, $(CH_2)_2CH_2CH_3$), 1.66 (m, 2H, $CH_2CH_2CH_2CH_3$), 1.88 (m, 2H, $CH_2(CH_2)_2CH_3$), 4.03 (m, 13H, OCH_3, C*H*n-Bu), 4.50 (m, 1H, CH_2CHn-Bu), 4.78 (m, 1H, CH_2CHn-Bu), 7.28 (m, 4H, H_{Ph}), 7.63 (m, 12H, H_{Ph}), 8.31 (m, 2H, βH), 8.51 (s, 2H, βH), 8.66 (m, 2H, βH); δ_C (100.6 MHz, $CDCl_3$) 13.4, 21.7, 27.5, 34.6, 42.2, 44.6, 55.1, 111.6, 112.2, 112.6, 113.1, 116.8, 117.5, 117.8, 118.1, 119.3, 119.9, 121.6, 121.9, 123.2 (br), 124.5, 124.8, 125.0, 126.5 (br), 127.1 (br), 127.5 (br), 128.2, 128.4, 128.6, 131.4, 131.6, 131.9, 140.0, 140.6, 142.9, 143.0, 144.1, 151.7, 152.0, 154.6, 157.5 (br), 158.0, 158.5, 158.8, 165.0, 169.8; MS (EI, 80 eV), *m*/*z* (%): 792 (100) [M$^+$], 735 (51) [M$^+$−C$_4$H$_9$]; HRMS [$C_{52}H_{48}N_4O_4$]: calcd for [M+H$^+$] 793.3742, found 793.3747; UV–vis (CH_2Cl_2): λ_{max} (log ε) 421 (5.2), 486 (3.8), 519 (4.1), 547 (3.9), 598 (3.8), 656 (4.4).

3.3.3. 2,3-Dihexyl-5,10,15,20-tetrakis(3-methoxyphenyl)-chlorin (6b). Compound **6b** was isolated from the reaction of **5** with *n*-HexLi using method A. Column chromatography on silica gel with EtOAc/*n*-hexane (1:6 v/v) gave three fractions. The first fraction consisted of **6b** (23.5 mg,

0.026 mmol, 20%, as a purple solid), the second fraction was identified as **7b** (23.5 mg, 0.029 mmol, 22%, as purple crystals), and the third one contained porphyrin **5**. Analytical data for **6b**: mp 242 °C; R_f (EtOAc/*n*-hexane, 1:6 v/v, silica) 0.71; δ_H (400 MHz, $CDCl_3$) −1.44 (s, 2H, N*H*), 0.65 (t, *J* 8 Hz, 6H, $(CH_2)_5CH_3$), 1.16 (m, 8H, $(CH_2)_2(CH_2)_2CH_3$), 1.54 (m, 4H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.94 (m, 4H, $CH_2CH_2(CH_2)_3CH_3$), 3.19 (m, 4H, $CH_2(CH_2)_4CH_3$), 3.97 (m, 12H, OCH_3), 4.38 (m, 2H, C*H*n-Hex), 7.27 (m, 6H, H_{Ph}), 7.56 (m, 4H, H_{Ph}), 7.68 (m, 4H, H_{Ph}), 7.84 (m, 2H, H_{Ph}), 8.22 (m, 2H, βH), 8.46 (s, 2H, βH), 8.61 (m, 2H, βH); δ_C (100.6 MHz, $CDCl_3$) 13.4, 21.7, 21.8, 22.1, 28.3, 33.6, 51.5, 52.6, 55.0, 113.0, 119.2, 121.6, 123.3, 125.2, 126.5, 127.0, 131.5, 134.6, 140.6, 143.0, 151.8, 157.5, 158.0, 158.4, 168.5; MS (EI, 80 eV), *m*/*z* (%): 903 (34) [M^+−H], 847 (100) [$M^+-C_4H_9$], 818 (22) [$M^+-C_6H_{13}$–H], 791 (40) [$M^+-2(C_4H_9)$+H], 733 (13) [$M^+-2(C_6H_{13})$–H]; HRMS [$C_{60}H_{64}N_4O_4$]: calcd for [M+H^+] 905.4990, found 905.5019; UV–vis (CH_2Cl_2): λ_{max} (log ε) 448 (5.3), 556 (3.7), 606 (4.0), 652 (4.5).

3.3.4. 2-Hexyl-5,10,15,20-tetrakis(3-methoxyphenyl)-chlorin (7b). Compound **7b** was synthesized as described for **6b**. Analytical data for **7b**: mp 220 °C; R_f(CH_2Cl_2/*n*-hexane, 1:2 v/v, silica) 0.32; δ_H (400 MHz, $CDCl_3$) −1.48 (s, 2H, N*H*), 0.75 (t, *J* 7.3 Hz, 3H, $(CH_2)_5CH_3$), 1.07 (m, 4H, $(CH_2)_3(CH_2)_2CH_3$), 1.30 (m, 2H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.43 (m, 2H, $CH_2CH_2(CH_2)_3CH_3$), 1.65 (m, 2H, $CH_2(CH_2)_4CH_3$), 4.00 (m, 13H, OCH_3, C*H*n-Hex), 4.42 (m, 1H, CH_2CH*n*-Hex), 4.74 (m, 1H, CH_2CH*n*-Hex), 7.29 (m, 4H, H_{Ph}), 7.62 (m, 12H, H_{Ph}), 8.27 (m, 2H, βH), 8.48 (s, 2H, βH), 8.64 (m, 2H, βH); δ_C (100.6 MHz, $CDCl_3$) 13.5, 22.5 (m), 25.3 (m), 28.3, 30.9, 34.9 (m), 42.2 (m), 44.5, 55.0 (m), 111.7, 112.2, 112.6 (m), 113.0 (m), 117.5, 117.8, 118.2, 119.3, 119.9, 121.6, 121.9, 123.2, 124.5, 124.8, 125.0, 126.5 (m), 127.1 (m), 127.5 (m), 128.2, 128.4, 128.6, 131.4, 131.6, 134.5, 134.7, 140.1, 140.6, 142.9, 143.0, 143.1, 144.1, 151.7, 152.0, 157.6, 158.0, 158.6, 158.8, 164.9, 169.8; MS (EI, 80 eV), *m*/*z* (%): 820 (100) [M^+], 735 (51) [$M^+-C_6H_{13}$]; HRMS (ES^+) [$C_{54}H_{52}N_4O_4$]: calcd for [M+H^+] 821.4054, found 821.4045; UV–vis (CH_2Cl_2): λ_{max} (log ε) 451 (5.2), 557 (3.6), 605 (3.9), 656 (4.4).

3.3.5. 2,3-Di(*sec*-butyl)-5,10,15,20-tetrakis(3-methoxyphenyl)chlorin (6c). Compound **6c** was isolated from the reaction of **5** with *sec*-BuLi using method A. Column chromatography on silica gel with EtOAc/*n*-hexane (1:3 v/v) yielded three fractions. The first fraction consisted of **6c** (19.8 mg, 0.023 mmol, 18%, as a purple solid), the second fraction was identified as **7c** (8.8 mg, 0.011 mmol, 8.5%, as purple crystals), and the third one contained porphyrin **5**. Analytical data for **6c**: mp 245 °C. [Found: C, 79.4; H, 6.7; N, 6.5. $C_{56}H_{56}N_4O_4$ requires: C, 79.22; H, 6.65; N, 6.60%.] R_f (EtOAc/*n*-hexane, 1:3 v/v, silica) 0.59; ^{1}H NMR (400 MHz, $CDCl_3$) −1.50 (s, 2H, N*H*), 0.20 (m, 6H, CH_3), 0.68 (m, 3H, CH_3), 0.95 (m, 3H, CH_3), 1.29 (m, 2H, $CH(CH_3)(CH_2CH_3)$), 1.41 (m, 2H, $CH(CH_3)(CH_2CH_3)$), 1.99 (m, 2H, $CH(CH_3)(CH_2CH_3)$), 3.90 (m, 12H, OCH_3), 4.53 (m, 2H, C*H*sec-Bu), 7.28 (m, 4H, H_{Ph}), 7.90 (m, 12H, H_{Ph}), 8.27 (m, 2H, βH), 8.48 (s, 2H, βH), 8.62 (m, 2H, βH); δ_C (100.6 MHz, $CDCl_3$) 11.5 (br), 14.2 (br), 17.4 (br), 27.1, 27.4, 38.7, 49.7, 53.2, 55.1, 113.1, 117.3, 119.2, 119.3, 121.5, 123.5, 126.5, 127.1, 127.4, 127.5, 128.2, 131.4, 136.4, 140.9, 142.9, 143.3, 151.8, 157.6, 158.5, 168.6; MS (EI, 80 eV), *m*/*z* (%): 847 (92) [M^+−H], 791 (100) [$M^+-C_4H_9$], 734 (68) [$M^+-2(C_4H_9)$], 424 (17) [M^{2+}]; HRMS [$C_{56}H_{56}N_4O_4$]: calcd for [M+H^+] 849.4301, found 849.4311; UV–vis (CH_2Cl_2): λ_{max} (log ε) 446 (5.2), 552 (4.1), 595 (4.1), 656 (4.5).

3.3.6. 2-(*sec*-Butyl)-5,10,15,20-tetrakis(3-methoxyphenyl)chlorin (7c). Compound **7c** was synthesized as described for **6c**. Analytical data for **7c**: mp 228 °C; R_f (EtOAc/*n*-hexane, 1:3 v/v, silica) 0.66; δ_H (400 MHz, $CDCl_3$) −1.47 (s, 2H, N*H*), 0.65 (m, 3H, CH_3), 0.87 (m, 3H, CH_3), 1.27 (m, 2H, $CH(CH_3)(CH_2CH_3)$), 1.94 (m, 1H, $CH(CH_3)(CH_2CH_3)$), 4.01 (m, 13H, OCH_3, C*H*sec-Bu), 4.22 (m, 1H, CH_2CH*sec*-Bu), 4.98 (m, 1H, CH_2CH*sec*-Bu), 7.28 (m, 4H, H_{Ph}), 7.63 (m, 12H, H_{Ph}), 8.24 (m, 2H, βH), 8.48 (s, 2H, βH), 8.65 (m, 2H, βH); δ_C (100.6 MHz, $CDCl_3$) 13.3, 18.7, 24.5, 28.6, 30.3, 33.9, 55.3, 111.1, 112.5, 113.0, 117.4, 118.1, 119.3, 123.2, 124.4, 126.4, 127.0, 127.5, 131.3, 131.6, 134.5, 134.6, 140.1, 140.6, 142.9, 143.0, 143.1, 151.7, 157.5, 165.7, 173.6; MS (EI, 80 eV), *m*/*z* (%): 792 (28) [M^+], 735 (10) [$M^+-C_4H_9$]; HRMS [$C_{52}H_{48}N_4O_4$]: calcd for [M+H^+] 793.3742, found 793.3732; UV–vis (CH_2Cl_2): λ_{max} (log ε) 449 (5.2), 556 (3.6), 559 (3.9), 656 (4.4).

3.3.7. 2,3-Di(*tert*-butyl)-5,10,15,20-tetrakis(3-methoxyphenyl)chlorin (6d). Reaction of **5** with *t*-BuLi in the presence of $Pd_2(dba)_3\cdot CHCl_3$ and CuI resulted in the formation of **6d** and **7d**. Column chromatography on silica gel with CH_2Cl_2/*n*-hexane (1:3 v/v) gave three fractions. The first fraction consisted of **6d** (28.7 mg, 0.034 mmol, 26%, as a brown solid), the second fraction was identified as **7d** (26.8 mg, 0.034 mmol, 26%, as a dark brown crystals), and the third one contained porphyrin **5**. Analytical data for **6d**: mp>250 °C; R_f (CH_2Cl_2/*n*-hexane, 1:3 v/v, silica) 0.25; δ_H (400 MHz, $CDCl_3$) −0.59 (br, 2H, N*H*), 0.63 (s, 9H, $C(CH_3)_3$), 0.66 (s, 9H, $C(CH_3)_3$), 3.86 (m, 6H, OCH_3), 4.08 (m, 6H, OCH_3), 5.09 (d, *J* 6.4 Hz, 2H, C*H*t-Bu), 6.98 (m, 2H, H_{Ph}), 7.21 (m, 2H, H_{Ph}), 7.31 (m, 2H, H_{Ph}), 7.43 (m, 4H, H_{Ph}), 7.72 (m, 2H, H_{Ph}), 8.02 (m, 2H, H_{Ph}), 8.15 (m, 2H, H_{Ph}), 8.36 (m, 2H, βH), 8.46 (s, 2H, β-H), 8.58 (s, 2H, βH); δ_C (100.6 MHz, $CDCl_3$) 28.4, 37.0, 55.0, 55.1, 59.3, 111.6 (d), 111.7 (d), 112.1, 112.6, 112.8, 113.1, 117.0, 118.9, 119.4, 123.7, 124.4, 125.0, 125.1, 126.3, 127.1, 127.2, 127.7, 131.4, 131.6, 134.5, 141.6, 144.9, 145.0, 151.4, 157.5, 157.7, 158.2, 164.8; HRMS (ES^+) [$C_{56}H_{56}N_4O_4$]: calcd for [M+H^+] 849.4366, found 849.4363; UV–vis (CH_2Cl_2): λ_{max} (log ε) [381] (4.6), 426 (5.2), 526 (4.2), 558 (4.2), 611 (4.0), 668 (4.45).

3.3.8. 2-(*tert*-Butyl)-5,10,15,20-tetrakis(3-methoxyphenyl)chlorin (7d). Compound **7d** was synthesized as described for **6d**. Analytical data for **7d**: mp 241 °C; R_f (CH_2Cl_2/*n*-hexane, 1:2 v/v, silica) 0.25; δ_H (400 MHz, $CDCl_3$) −1.13 (s, 2H, N*H*), 0.30 (s, 9H, $C(CH_3)_3$), 3.99 (m, 13H, OCH_3, C*H*t-Bu), 4.45 (m, 1H, CH_2CH*t*-Bu), 4.69 (m, 1H, CH_2CH*t*-Bu), 7.29 (m, 5H, H_{Ph}), 7.81 (m, 11H, H_{Ph}), 8.28 (m, 2H, βH), 8.46 (s, 2H, βH), 8.61 (m, 2H, βH); δ_C (100.6 MHz, $CDCl_3$) 27.9, 34.2, 42.5, 55.1, 55.2, 110.2, 111.9, 112.7, 113.1 119.1, 119.4, 120.3, 122.8, 123.5, 126.4, 126.5, 126.7, 126.9, 127.1, 127.2, 127.7,

129.8, 131.2, 131.8, 131.9, 134.4, 134.8, 140.1, 142.3, 142.7, 143.0, 143.9, 151.4, 152.5, 157.6; HRMS [$C_{52}H_{48}N_4O_4$]: calcd for [M+H$^+$] 793.3742, found 793.3739; UV–vis (CH_2Cl_2): λ_{max}(log ε) 418 (5.1), 486 (4.4), 581 (4.0), 656 (4.2).

3.3.9. 2,3-Dibutyl-5,10,15,20-tetrakis(3,4-dimethoxyphenyl)chlorin (8a).[29] Compound **8a** was isolated from the reaction of **8** with *n*-BuLi using method A. Column chromatography on silica gel with EtOAc/*n*-hexane (1:6 v/v) yielded three fractions. The first fraction consisted of **8a** (8.8 mg, 0.009 mmol, 7%, as a brown solid), the second fraction was identified as **8b** (8.3 mg, 0.012 mmol, 9%, as brown crystals), and the third fraction contained porphyrin **8**. Analytical data for **8a**: mp 247 °C. [Found: C, 79.8; H, 6.6; N, 6.4. $C_{60}H_{60}N_4O_4$ requires: C, 79.97; H, 6.71; N, 6.22%.] R_f (EtOAc/*n*-hexane, 1:6 v/v, silica) 0.80; δ_H (300 MHz, $CDCl_3$) −1.43 (s, 2H, N*H*), 0.97 (t, *J* 7.5 Hz, 6H, $(CH_2)_3CH_3$), 1.25 (m, 8H, $CH_2(CH_2)_4CH_3$), 1.82 (m, 4H, $CH_2(CH_2)_2CH_3$), 4.14 (m, 24H, OC*H*$_3$), 4.72 (m, 2H, C*H*n-Bu), 6.92–7.80 (m, 12H, H_{Ph}), 8.27 (m, 2H, βH), 8.51 (s, 2H, βH), 8.66 (m, 2H, βH); δ_C NMR (100.6 MHz, $CDCl_3$) 13.6, 22.2, 26.3 (m), 28.4 (m), 31.2 (m), 33.9, 45.4, 51.4, 55.1, 113.1, 118.9, 122.9, 125.2, 126.4, 127.3 (br), 128.2, 131.4, 134.8, 140.5, 142.9, 151.9 (br), 157.5, 158.1, 158.4, 168.4; HRMS [$C_{56}H_{56}N_4O_4$]: calcd for [M+H$^+$] 901.4615, found 901.4622; UV–vis (CH_2Cl_2): λ_{max} (log ε) 4.60 (5.2), 556 (3.9), 598 (4.1), 656 (4.5).

3.3.10. 2-Butyl-5,10,15,20-tetrakis(3,4-dimethoxyphenyl)chlorin (8b).[29] Compound **8b** was obtained from the reaction yielding **8a**. Analytical data for **8b**: mp 233 °C. [Found: C, 79.5; H, 6.4; N, 6.7. $C_{56}H_{55}N_4O_4$ requires: C, 79.31; H, 6.54; N, 6.61%.] R_f (EtOAc/*n*-hexane, 1:6 v/v, silica) 0.70; δ_H (300 MHz, $CDCl_3$) −1.41 (s, 2H, N*H*), 0.58 (t, *J* 7.5 Hz, 3H, $CH_2(CH_2)_2CH_3$), 1.20 (m, 2H, $(CH_2)_2CH_2CH_3$), 1.65 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.20 (m, 2H, $CH_2(CH_2)_2CH_3$), 3.92 (m, 25H, OC*H*$_3$, C*H*n-Bu), 4.38 (m, 1H, C*H*$_2$CHn-Bu), 4.71 (m, 1H, C*H*$_2$CHn-Bu), 7.22 (m, 4H, H_{Ph}), 7.76 (m, 8H, H_{Ph}), 8.30 (m, 2H, βH), 8.50 (s, 2H, βH), 8.65 (m, 2H, βH); δ_C (100.6 MHz, $CDCl_3$) 13.4, 21.7, 27.6, 34.6, 42.2, 44.6, 55.1, 111.7, 113.1, 116.7, 117.5 (br), 118.1, 119.4 (br), 121.8 (br), 123.2 (br), 124.8 (br), 126.5 (br), 127.1 (br), 127.5 (br), 128.3, 128.5, 131.4, 131.6, 131.9, 140.0, 140.6, 142.9 (br), 144.1, 151.7, 152.0, 154.6, 157.5 (br), 158.0, 158.5, 158.8, 165.0, 169.7; HRMS [$C_{56}H_{55}N_4O_4$]: calcd for [M+H$^+$] 848.4233, found 848.4238; UV–vis (CH_2Cl_2): λ_{max} (log ε) 425 (5.2), 485 (4.4), 523 (4.3), 551 (4.2), 593 (4.1), 655 (4.6).

3.3.11. 5,5′,10,10′,15,20-Hexaphenylporphyrin (10). Compound **10** was isolated from the reaction of **9** with PhLi and purified by column chromatography on silica gel with EtOAc/*n*-hexane (1:8 v/v) to give 39.9 mg (0.052 mmol, 40%) for method A and 26 mg (0.034 mmol, 26%) for method B using $Pd(PPh_3)_4$ as dark violet product. Analytical data for **10**: mp 215 °C; R_f (EtOAc/*n*-hexane, 1:8 v/v, silica) 0.59; δ_H (400 MHz, $CDCl_3$) 5.46 (d, *J* 2.5 Hz, 2H, βH), 6.03 (d, *J* 2.5 Hz, 2H, βH), 6.15 (d, *J* 4.6 Hz, 2H, βH), 6.60 (d, *J* 4.6 Hz, 2H, βH), 7.06 (m, 8H, H_{Ph}•), 7.24 (m, 12H, H_{Ph}•), 7.42 (m, 10H, H_{Ph}•), 10.51 (s, 1H, N*H*), 12.59 (s, 1H, N*H*); δ_C (100.6 MHz, $CDCl_3$) 58.3, 109.5, 122.2, 126.2, 127.0, 127.2, 127.9, 129.0, 129.2, 130.2, 134.1, 134.8, 136.1, 137.1, 137.8, 138.7, 145.3, 151.3, 180.0; HRMS (ES$^+$) [$C_{56}H_{40}N_4$]: calcd for [M+H$^+$] 769.3331, found 769.3328; UV–vis (CH_2Cl_2): λ_{max} (log ε) 339 (4.8), 357 (4.8), 417 (4.4), 528 (4.6), 564 (4.6), 655 (3.9), 731 (3.6).

3.3.12. 5,10,15,20-Tetrakis(3-methoxyphenyl)-5,10-diphenylporphyrin (11). Compound **11** was isolated from the reaction of **5** with PhLi and purified by column chromatography on silica gel with EtOAc/*n*-hexane (1:3 v/v) to give 21 mg (0.023 mmol, 18%) using method A and 16.2 mg (0.018 mmol, 14%) with method B using $Pd(PPh_3)_4$ and CuI, as dark violet product. Analytical data for **11**: mp 232 °C; R_f (*n*-hexane/EtOAc, 3:1 v/v, silica) 0.61; δ_H (400 MHz, $CDCl_3$) 3.71 (m, 6H, OC*H*$_3$), 3.84 (s, 6H, OC*H*$_3$), 5.51 (m, 2H, βH), 6.08 (m, 2H, βH), 6.15 (m, 2H, βH), 6.64 (d, *J* 4.6 Hz, 2H, βH), 6.64 (m, 6H, βH, H_{Ph}), 6.79 (m, 2H, H_{Ph}•), 7.02 (m, 11H, H_{Ph}•), 7.19 (m, 9H, H_{Ph}), 10.57 (s, 1H, N*H*), 12.57 (s, 1H, N*H*); δ_C (100.6 MHz, $CDCl_3$) 54.7, 54.9, 109.7, 111.5, 113.6, 115.3, 115.8, 121.9, 122.9, 128.0, 129.0, 129.1, 134.7; HRMS (ES$^+$) [$C_{60}H_{49}N_4O_4$]: calcd for [M+H$^+$] 889.3754, found 889.3772; UV–vis (CH_2Cl_2): λ_{max} (log ε) 328 (4.1), 353 (4.1), 419 (4.0), 453 (3.6), 532 (4.0), 566 (4.0).

3.3.13. 2-(*tert*-Butyl)-5,10,15,20-tetraphenylchlorin (14). Compound **14** was formed in the reaction of **9** with *t*-BuLi in the presence of $Pd(PPh_3)_4$ and CuI, purified by column chromatography on silica gel eluting with CH_2Cl_2/*n*-hexane (1:2 v/v) and isolated as the third fraction to yield 19.2 mg (0.029 mmol, 22%) of a brown solid. Analytical data for **14**: mp>250 °C; R_f (CH_2Cl_2/*n*-hexane, 1:2 v/v, silica) 0.30; δ_H (400 MHz, $CDCl_3$) −1.06 (br, 2H, N*H*), 0.29 (s, 9H, C(C*H*$_3$)$_3$), 4.08 (m, 1H, C*H*$_2$CH*t*-Bu), 4.48 (m, 1H, C*H*$_2$CH*t*-Bu), 4.69 (m, 1H, C*Ht*-Bu), 7.71 (m, 12H, H_{Ph}), 7.88 (m, 2H, H_{Ph}), 7.99 (m, 2H, H_{Ph}), 8.24 (m, 2H, βH), 8.26 (m, 2H, H_{Ph}), 8.39 (m, 2H, H_{Ph}), 8.44 (br, 2H, βH), 8.56 (m, βH); δ_C (100.6 MHz, $CDCl_3$) 26.8, 36.7, 41.6, 53.9, 110.4, 115.1, 121.3, 122.8, 123.4, 123.5, 126.2, 126.3, 126.6, 126.7, 127.05, 127.1, 127.2, 127.25, 127.3, 127.6 (m), 131.2 (m), 131.8 (m), 133.5 (m), 134.0, 134.2, 134.6, 134.9, 136.9, 140.3, 140.4, 141.7, 141.9, 142.6, 142.7, 151.5, 152.6, 164.6, 166.7; HRMS (ES$^+$) [$C_{48}H_{40}N_4$]: calcd for [M+H$^+$] 673.3331, found 673.3347; UV–vis (CH_2Cl_2): λ_{max} (log ε) [376] (4.2), 413 (4.7), 423 (4.8), 525 (3.9), 553 (3.8), 604 (3.7), 659 (4.1).

3.3.14. 2,3-Dihexyl-5,10,15,20-tetraphenylchlorin (15). Compound **15** was formed in the reaction of **9** with *n*-HexLi in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ and CuI. Purification by column chromatography on silica gel with CH_2Cl_2/*n*-hexane (1:3 v/v) gave a first fraction that contained 25.5 mg (0.0325 mmol, 25%) of a brown solid. Analytical data for **15**: mp>250 °C; R_f (CH_2Cl_2/*n*-hexane, 1:3 v/v, silica) 0.50; δ_H (400 MHz, $CDCl_3$) −1.41 (br, 2H, N*H*), 0.87 (m, 6H, C*H*$_3$), 0.91 (m, 4H, C*H*$_2$), 1.06 (m, 4H, C*H*$_2$), 1.18 (m, 4H, C*H*$_2$), 1.61 (m, 8H, C*H*$_2$), 4.37 (m, 2H, C*H*n-Hex), 7.77 (m, 14H, H_{Ph}), 7.97 (m, 2H, H_{Ph}), 8.1 (m, 2H, H_{Ph}), 8.20 (m, 2H, βH), 8.29 (m, 2H, H_{Ph}), 8.45 (m, 2H, βH), 8.50 (m, 2H, βH); δ_C (100.6 MHz, $CDCl_3$) 13.5, 22.0, 26.1, 28.2, 31.0, 33.6, 51.3, 112.4, 121.9, 123.2, 126.2, 126.7, 126.9, 127.1, 127.2, 127.3, 132.3, 133.4 (m), 133.6, 134.7, 140.7, 141.7, 141.9, 151.9, 168.7; HRMS (ES$^+$)

[$C_{56}H_{56}N_4$]: calcd for [M+H$^+$] 785.4583, found 785.4583; UV–vis (CH_2Cl_2): λ_{max} (log ε) [371] (4.7), 409 (5.15), 420 (5.3), 519 (4.4), 548 (4.3), 598 (4.2), 652 (4.5).

3.3.15. 2-Hexyl-5,10,15,20-tetraphenylchlorin (16). Compound **16** was formed in the reaction of **9** with *n*-HexLi in the presence of $Pd(PPh_3)_4$ and CuI. Purification by column chromatography on silica gel with CH_2Cl_2/*n*-hexane (1:3 v/v) gave the title compound as the first fraction (26.4 mg, 0.038 mmol, 29%, a brown solid). Analytical data for **16**: mp 241 °C; R_f (CH_2Cl_2/*n*-hexane, 1:3 v/v, silica) 0.45; δ_H (400 MHz, $CDCl_3$) −1.47 (br, 2H, N*H*), 0.77 (t, *J* 7.5 Hz, 3H, CH_3), 0.94 (m, 3H, CH_2), 1.09 (m, 3H, CH_2), 1.43 (m, 2H, CH_2), 1.62 (m, 2H, CH_2), 3.94 (d, *J* 17.0 Hz, 1H, CH_2CH*n*-Hex), 4.49 (dd, *J* 9.4, 17.0 Hz, 1H, CH_2CH*n*-Hex), 4.70 (m, 1H, C*H*n-Hex), 7.72 (m, 14H, H_{Ph}), 8.06 (m, 2H, H_{Ph}), 8.16 (m, 2H, H_{Ph}), 8.24 (m, 2H, βH), 8.27 (m, 2H, H_{Ph}), 8.47 (s, 2H, βH), 8.62 (m, 2H, βH); δ_C (100.6 MHz, $CDCl_3$) 13.5, 22.0, 25.3, 28.2, 30.9, 34.7, 42.3, 44.5, 111.85, 112.4, 121.9, 122.2, 123.16, 123.18, 126.3, 126.7, 127.0, 127.1, 127.3, 127.4, 127.48, 127.52, 127.6, 131.4, 131.6, 131.7, 132.05, 132.1, 133.3, 133.4, 133.5, 133.6, 134.2, 134.7, 134.8, 140.2, 140.8, 141.6, 141.7, 141.8, 142.8, 151.9, 152.1, 165.0, 170.0; HRMS (ES$^+$) [$C_{50}H_{44}N_4$]: calcd for [M+H$^+$] 701.3644, found 701.3635; UV–vis (CH_2Cl_2): λ_{max} (log ε) [371] (3.2), 409 (3.7), 420 (3.9), 519 (3.0), 547 (2.9), 598 (2.8), 651 (3.2).

3.3.16. 5,10-Di(*tert*-butyl)-5,10,15,20-tetra-*iso*-butylporphyrin (20). Compound **20** was formed in the reaction of **17** with *t*-BuLi in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ and CuI. Purification by column chromatography on silica gel with EtOAc/*n*-hexane (1:40 v/v) gave the title compound as the first fraction (13.5 mg, 0.021 mmol, 16%, red crystals). Analytical data for **20**: mp 179 °C. [Found: C, 81.7; H, 9.8; N, 8.8. $C_{44}H_{64}N_4$ requires: C, 81.43; H, 9.94; N, 8.63%.] R_f (EtOAc/*n*-hexane, 1:40 v/v, silica) 0.25; δ_H (400 MHz, CD_2Cl_2) 0.73 (d, *J* 6.6 Hz, 6H, CH_2CHCH_3), 0.80 (s, 18H, $C(CH_3)_3$), 0.93 (d, *J* 6.6 Hz, 6H, CH_2CHCH_3), 1.02 (d, *J* 6.6 Hz, 12H, CH_2CHCH_3), 1.97 (m, 2H, CH_2CHCH_3), 2.08 (m, 2H, CH_2CHCH_3), 2.16 (m, 4H, CH_2CHCH_3), 2.80 (d, *J* 7.1 Hz, 4H, CH_2CHCH_3), 5.94 (d, *J* 2.6 Hz, 2H, βH), 6.69 (d, *J* 4.9 Hz, 2H, βH), 6.81 (d, *J* 2.6 Hz, 2H, βH), 7.26 (d, *J* 4.9 Hz, 2H, βH), 11.28 (br, 1H, N*H*), 12.68 (br, 1H, N*H*); δ_C (100.6 MHz, CD_2Cl_2): 22.8, 23.0, 23.8, 24.9, 26.5, 26.8, 31.3, 40.2, 41.0, 41.3, 52.0, 107.2, 117.4, 129.8, 129.5, 129.9, 134.3, 137.5, 151.6, 179.0; HRMS (ES$^+$) [$C_{44}H_{64}N_4$]: calcd for [M+H$^+$] 649.5209, found 649.5223; UV–vis (CH_2Cl_2): λ_{max} (log ε) 316 (4.5), 348 (4.5), 508 (4.1), 706 (3.8).

3.3.17. 5,10-Di(*tert*-butyl)-5,10,15,20-tetrahexylporphyrin (21). Compound **21** was formed in the reaction of **18** with *t*-BuLi in the presence of $Pd_2(dba)_3$ and CuI and was purified by column chromatography on silica gel with CH_2Cl_2/*n*-hexane (1:1 v/v). The first fraction yielded 10 mg (0.013 mmol, 10%) of red crystals. Analytical data for **21**: mp 195 °C (decomp.); R_f (CH_2Cl_2/*n*-hexane, 1:1 v/v, silica) 0.45; δ_H (400 MHz, $CDCl_3$) 0.86−1.43 (m, 52H, $C(CH_3)_3$, $CH_2CH_2(CH_2)_3CH_3$), 1.74 (m, 8H, $CH_2(CH_2)_2(CH_2)_2CH_3$), 2.23 (m, 6H, $(CH_2)_2(CH_2)_3CH_3$), 2.91 (m, 4H, $CH_2(CH_2)_4CH_3$), 6.02 (d, *J* 1.7 Hz, 2H, βH), 6.73 (d, *J* 5.0 Hz, 2H, βH), 6.88 (d, *J* 1.7 Hz, 2H, βH), 7.35 (d, *J* 5.0 Hz, 2H, βH), 10.49 (br, 1H, N*H*), 11.92 (br, 1H, N*H*); δ_C (100.6 MHz, $CDCl_3$) 13.6 (m), 22.2 (m), 22.4 (m), 26.0, 27.6, 28.3, 29.3 (m), 30.1, 31.2, 31.3, 32.8, 33.0, 33.2, 39.5, 53.0, 108.1, 117.7, 128.6, 130.4, 130.9, 135.2, 137.1, 150.1, 178.1; HRMS (ES$^+$) [$C_{52}H_{80}N_4$]: calcd for [M+H$^+$] 761.6383, found 760.6392; UV–vis (CH_2Cl_2): λ_{max} (log ε) 290 (3.7), 306 (3.3), 342 (1.6), 386 (2.4), 403 (2.3).

3.3.18. 5,10,15,20-Tetra(*iso*-butyl)-2-(*tert*-butyl)chlorin (22). Compound **22** was formed in the reaction of **17** with *t*-BuLi in the presence of $Pd_2(dba)_3$ and CuI. Purification by column chromatography on silica gel with EtOAc/*n*-hexane (1:40 v/v) gave **22** as the second fraction to yield 32.3 mg (0.055 mmol, 42%) of a brown solid. Analytical data for 22: mp>200 °C; R_f (EtOAc/*n*-hexane, 1:40 v/v, silica) 0.25; δ_H (600 MHz, CD_2Cl_2) −1.27 (br, 2H, N*H*), 0.55 (s, 9H, $C(CH_3)_3$), 1.11 (d, *J* 6.4 Hz, 3H, $CH_2CH(CH_3)_2$), 1.15 (d, *J* 6.4 Hz, 3H, $CH_2CH(CH_3)_2$), 1.19 (m, 9H, $CH_2CH(CH_3)_2$), 1.23 (d, *J* 7.0 Hz, 3H, $CH_2CH(CH_3)_2$), 1.26 (d, *J* 6.4 Hz, 3H, $CH_2CH(CH_3)_2$), 1.39 (d, *J* 7.0 Hz, 3H, $CH_2CH(CH_3)_2$), 2.51 (m, 2H, $CH_2CH(CH_3)_2$), 2.74 (m, 2H, $CH_2CH(CH_3)_2$), 4.01 (m, 1H, CH_2CH*t*-Bu), 4.23 (m, 2H, CH_2CH$(CH_3)_2$), 4.61 (m, 7H, CH_2CH*t*-Bu, CH_2CH$(CH_3)_2$), 4.81 (m, 1H, C*H*t-Bu), 8.98 (m, 2H, βH), 9.14 (m, 2H, βH), 9.28 (m, 2H, βH); δ_C (150.9 MHz, CD_2Cl_2): 20.9, 21.9, 22.5, 22.56, 22.6, 22.7, 22.8, 23.3, 26.2, 32.3, 34.6, 35.5, 35.6, 36.4, 39.5, 42.4, 42.8, 42.9, 44.2, 52.5, 106.7, 109.5, 118.5, 119.8, 120.5, 121.3, 124.6, 125.1, 128.6, 129.0, 133.9, 134.3, 139.1, 140.0, 151.4, 152.1, 164.8, 167.0; HRMS (ES$^+$) [$C_{40}H_{56}N_4$]: calcd for [M+H$^+$] 593.4570, found 593.4564; UV–vis (CH_2Cl_2): λ_{max} (log ε) [377] (4.2), 416 (5.0), 439 (4.9), 535 (4.1), 562 (4.1), 605 (3.9), 661 (4.2).

3.3.19. 2,3-Di(*tert*-butyl)-5,10,15,20-tetrakis(1-ethylpropyl)chlorin (23a). Compound **23a** was formed in the reaction of **19** with *t*-BuLi in the presence of $Pd_2(dba)_3 \cdot CHCl_3$ and CuI followed by column chromatography on silica gel with MeOH/*n*-hexane (1:80 v/v). The first fraction gave 19.2 mg (0.027 mmol, 21%) of a green-purple crystalline material. The second fraction contained 8.4 mg of **23b** (0.013 mmol, 10%). Analytical data for **23a**: mp 248 °C; R_f (MeOH/*n*-hexane, 1:80 v/v, silica) 0.45; δ_H (400 MHz, $CDCl_3$) 0.02 (br, 2H, N*H*), 0.84 (m, 27H, $CH(CH_2CH_3)_2$, $C(CH_3)_3$), 1.09 (t, *J* 7.5 Hz, 9H, $CH(CH_2CH_3)_2$), 1.29 (m, 2H, $CH(CH_2CH_3)_2$), 1.47 (m, 2H, $CH(CH_2CH_3)_2$), 1.60 (m, 2H, $CH(CH_2CH_3)_2$), 1.73 (t, *J* 7.5 Hz, 6H, $CH(CH_2CH_3)_2$), 2.35 (m, 3H, $CH(CH_2CH_3)_2$), 2.62 (br, 2H, $CH(CH_2CH_3)_2$), 2.91 (m, 3H, $CH(CH_2CH_3)_2$), 3.29 (m, 2H, $CH(CH_2CH_3)_2$), 3.83 (m, 2H, C*H*$(CH_2CH_3)_2$), 4.48 (m, 2H, C*H*$(CH_2CH_3)_2$), 4.68 (s, 2H, C*H*t-Bu), 8.75 (m, 2H, βH), 9.06 (br, 2H, βH), 9.10 (m, 2H, βH); δ_C (100.6 MHz, $CDCl_3$) 13.1, 13.8, 18.1, 28.4, 29.2, 33.2, 33.9, 34.0, 36.5, 47.6, 49.4, 60.3, 115.9, 123.0, 124.0, 125.1, 128.7, 133.2, 161.2; HRMS (ES$^+$) [$C_{48}H_{72}N_4$]: calcd for [M+H$^+$] 705.5818, found 705.5801; UV–vis (CH_2Cl_2): λ_{max} (log ε) 429 (4.1), 458 (3.8), 581 (3.1), 603 (3.2), 650 (3.2).

3.3.20. 2-(*tert*-Butyl)-5,10,15,20-tetrakis(1-ethylpropyl)chlorin (23b). Compound **23b** was formed in the reaction of **19** with *t*-BuLi in the presence of $Pd_2(dba)_3$ and CuI. Purification by column chromatography on silica gel with

MeOH/*n*-hexane (1:80 v/v) gave the title compound as the second fraction to yield 26.1 mg (0.04 mmol, 31%) as dark green crystals. The first fraction contained 9.2 mg of **23a** (0.013 mmol, 10%). Analytical data for **23b**: mp 199 °C; R_f (MeOH/*n*-hexane, 1:80 v/v, silica) 0.22; δ_H (400 MHz, $CDCl_3$) −0.07 (br, 2H, N*H*), 0.41 (s, 9H, C(CH_3)$_3$), 1.19 (m, 26H, CH(CH_2CH_3)$_2$), 1.94 (m, 1H, CH(CH_2-CH$_3$)$_2$), 2.23 (m, 2H, CH(CH_2CH$_3$)$_2$), 2.77 (m, 11H, CH(CH_2CH$_3$)$_2$), 3.69 (m, 1H, C*H*(CH$_2$CH$_3$)$_2$), 3.92 (m, 1H, C*H*(CH$_2$CH$_3$)$_2$), 4.53 (m, 5H, C*H*(CH$_2$CH$_3$)$_2$, CH_2C*H*t-Bu), 8.82 (m, 2H, βH), 9.11 (m, 4H, βH); δ_C (100.6 MHz, $CDCl_3$) 13.1, 13.5, 13.7, 13.8, 14.1, 26.8, 29.3, 30.1, 30.4, 32.5, 33.1, 35.3, 40.9, 47.5, 48.4, 49.4, 49.8, 54.0, 108.9, 114.5, 120.4 (br), 122.2 (br), 123.6 (br), 125.9, 128.6 (br), 133.2 (br), 138.5 (br), 162.8; HRMS (ES$^+$) [$C_{44}H_{65}N_4$]: calcd for [M+H$^+$] 649.5209, found 649.5217; UV–vis (CH_2Cl_2): λ_{max} (log ε) 424 (4.0), 538 (3.0), 562 (3.1), 608 (3.1), 662 (3.3).

3.3.21. 5,10,15,20-Tetrakis(1-ethylpropyl)-2,3-dihexyl)-chlorin (24). Compound **24** was formed in the reaction of **19** with *n*-HexLi in the presence of $Pd(PPh_3)_4$ and CuI. Column chromatography on silica gel eluting with EtOAc/*n*-hexane (1:20 v/v) gave 11.2 mg (0.015 mmol, 14%) of a purple solid. Analytical data for **24**: mp 190 °C (decomp.); R_f (EtOAc/*n*-hexane, 1:20 v/v, silica) 0.34; δ_H (400 MHz, $CDCl_3$) −0.41 (s, 2H, N*H*), 0.57 (t, *J* 7.3 Hz, 6H, CH_3), 0.91 (m, 12H, CH_3), 1.33 (m, 6H, CH_3), 1.55 (t, *J* 7.4 Hz, 6H, CH_3), 1.68 (m, 10H, CH_2), 2.19 (m, 8H, CH_2), 2.55 (m, 10H, CH_2), 2.95 (m, 8H, CH_2), 3.69 (m, 2H, C*H*(CH$_2$CH$_3$)$_2$), 4.54 (m, 4H, C*H*(CH$_2$CH$_3$)$_2$, CH(*n*-Hex)), 8.93 (m, 2H, βH), 9.13, (br, 2H, βH), 9.19 (m, 2H, βH); δ_C (100.6 MHz, $CDCl_3$) 13.3, 13.6, 22.2, 27.5, 28.8, 28.9, 29.3, 30.9, 31.4, 31.5, 32.2, 32.5, 47.3, 49.7, 51.4, 111.5, 121.4, 125.0, 129.1, 166.2; HRMS (ES$^+$) [$C_{52}H_{80}N_4$]: calcd for [M+H$^+$] 761.6422, found 761.6432; UV–vis (CH_2Cl_2): λ_{max} (log ε) 299 (3.6), 377 (3.5), 422 (4.1), 536 (3.1), 564 (3.1), 660 (3.2).

3.3.22. 5,10-Di(-*tert*-butyl)-2,3,7,8,12,13,17,18-octaethyl-5,10-dihydroporphyrin (26). To a solution of **25** (100 mg, 0.187 mmol), CuI (7.63 mg, 0.0281 mmol), and $Pd(PPh_3)_4$ (20.5 mg, 0.0168 mmol) in anhydrous THF (30 mL) was added *t*-BuLi (2.5 mL, 3.268 mmol, 1.5 M in pentane) at −70 °C under inert gas. The reaction mixture was stirred at the same temperature (TLC control) and quenched with a saturated solution of NH_4Cl (1 mL). The mixture was filtered through silica gel (eluent: hexane) and the solvents were removed under reduced pressure. The residue was purified by column chromatography to give 87 mg of a purple solid product (0.135 mmol, 72%): mp >250 °C; R_f (*n*-hexane) 0.57; δ_H (400 MHz, $CDCl_3$) 0.84 (br, 18H, C(CH_3)$_3$), 1.11 (t, *J* 7.6 Hz, 6H, CH$_2$CH_3), 1.16 (t, *J* 7.3 Hz, 6H, CH$_2$CH_3), 1.17 (t, *J* 7.6 Hz, 6H, CH$_2$CH_3), 1.25 (t, *J* 7.6 Hz, 6H,CH$_2$CH$_3$), 2.51 (m, 16H, CH_2CH$_3$), 3.86 (s, 2H, C*H*t-Bu), 6.58 (s, 2H, 15, 20-H), 10.92 (s, 1H, N*H*), 13.06 (s, 1H, N*H*); δ_C (150.9 MHz, $CDCl_3$) 14.4, 15.9, 16.4, 16.5, 17.0, 17.5, 17.9, 18.3, 28.0, 38.5, 44.2, 112.8, 118.8, 120.9, 131.6, 132.2, 138.9, 143.5, 150.0, 177.1; HRMS (ES$^+$) [$C_{44}H_{64}N_4$]: calcd for [M+H$^+$] 649.5210, found 649.5214; UV–vis (CH_2Cl_2): λ_{max} (log ε) 337 (4.7), 398 (4.8), 501 (4.3), 532 (4.4), 667 (4.4).

3.4. Crystal structure determination of 13

Growth and handling of crystals followed the concept developed by Hope.[30] Intensity data were collected at 123 K with a Bruker SMART Apex system complete with 3-circle goniometer and CCD detector utilizing Mo Kα radiation (λ=0.71073 Å). The intensities were corrected for Lorentz, polarization, and extinction effects. The structure was solved with Direct Methods using the SHELXTL PLUS program system[31a] and refined against $|F^2|$ with the program XL from SHELX-97 using all data.[31b] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generally placed into geometrically calculated positions and refined using a ridging model. The N–H hydrogen atoms were located in difference maps and refined using the standard riding model. Compound crystallized as a racemic mixture in the centrosymmetric space group *P*-1 and no determination of the absolute structure was possible. In addition, the crystals showed low high angle diffraction limiting the quality of the data set. Crystal data for **13**: $C_{52}H_{48}N_4$, M=728.94, triclinic, space group *P*-1, a=10.255(2), b=12.091(2), c=18.229(3) Å, α=70.791(3), β=86.584(4), γ=68.519(3)°, V=1981.4(6) Å^3, Z=2, T=130 K, μ (Mo Kα)=0.71073 cm^{-1}, 13 865 reflections measured, 5737 unique reflections measured (R_{int}=0.0283), 511 parameters, 4512 reflections with $I>2.0\sigma(I)$, refinement against $|F^2|$, $R1(I>2.0\sigma(I))$=0.0384, $wR2$ (all data)=0.1103, S=1.062, ρ_{max}=0.222. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-649147. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was generously supported by a Science Foundation Ireland Research Professorship grant (SFI 04/RP1/B482) and used facilities provided by the Centre of Chemical Synthesis and Chemical Biology funded by the HEA.

References and notes

1. (a) Scheer, H. *Chlorophylls*; CRC: Boca Raton, FL, 1991; (b) Balaban, T. S. *Acc. Chem. Res.* **2005**, *38*, 612–623; (c) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435–461; (d) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40–48; (e) Jasat, A.; Dolphin, D. *Chem. Rev.* **1997**, *97*, 2267–2340; (f) Ali, H.; van Lier, J. E. *Chem. Rev.* **1999**, *99*, 2379–2450; (g) Senge, M. O.; Wiehe, A.; Ryppa, C. *Chlorophylls and Bacteriochlorophylls: Biochemistry, Biophysics, Functions and Applications*; Grimm, B., Porra, R., Rüdiger, W., Scheer, H., Eds.; Advances in Photosynthesis and Respiration; Springer: Dordrecht, 2006; Vol. 25, pp 27–37.
2. (a) Sessler, J. L.; Gale, P. A. *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic: San Diego, CA, 2000; Vol. 6, pp 257–278; (b) Sessler, J. L.; Zimmerman, R. S.; Bucher, C.; Kral, V.; Andrioletti, B. *Pure Appl. Chem.* **2001**, *73*, 1041–1057.
3. Dwyer, P. N.; Buchler, J. W.; Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 2789–2795.

4. Botulinski, A.; Buchler, J. W.; Abbes, N. E.; Scheidt, W. R. *Liebigs Ann. Chem.* **1987**, 305–309.
5. (a) Senge, M. O.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1108–1109; (b) Senge, M. O.; Smith, K. M. *Z. Naturforsch.* **1993**, *48b*, 991–999.
6. (a) Sessler, J. L.; Camiolo, S.; Gale, P. A. *Coord. Chem. Rev.* **2003**, *240*, 17–55; (b) Custelcean, R.; Delmau, L. H.; Moyer, B. A.; Sessler, J. L.; Cho, W. S.; Gross, D.; Bates, G. W.; Brooks, S. J.; Light, M. E.; Gale, P. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2537–2542.
7. (a) Kral, V.; Sessler, J. L.; Zimmerman, R. S.; Seidel, D.; Lynch, V.; Andrioletti, B. *Angew. Chem., Int. Ed.* **2000**, *39*, 1055–1058; (b) Bucher, C.; Zimmerman, R. S.; Lynch, V.; Kral, V.; Sessler, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 2099–2100. Correction: *J. Am. Chem. Soc.* **2001**, *123*, 12744; (c) Harmjanz, M.; Scott, M. J. *Chem. Commun.* **2000**, 397–398; (d) Harmjanz, M.; Bozidarevic, I.; Scott, M. J. *Org. Lett.* **2001**, *3*, 2281–2284; (e) Harmjanz, M.; Gill, H. S.; Scott, M. J. *J. Org. Chem.* **2001**, *66*, 5374–5383.
8. Buchler, J. W.; Puppe, L. *Liebigs Ann. Chem.* **1970**, *740*, 142–163.
9. (a) Runge, S.; Senge, M. O. *Z. Naturforsch.* **1998**, *53b*, 1021–1030; (b) Senge, M. O.; Runge, S.; Speck, M.; Ruhlandt-Senge, K. *Tetrahedron* **2000**, *56*, 8927–8932.
10. (a) Smith, K. M. *Chlorophylls*; Sheer, H., Ed.; CRC: Boca Raton, FL, 1991; pp 115–143; (b) Montforts, F.-P.; Gerlach, B.; Hoper, F. *Chem. Rev.* **1994**, *94*, 327–347.
11. (a) Pavlov, V. Y.; Ponomarev, G. V. *Khim. Geterotsikl. Soedin.* **2004**, 483–519; *Chem. Heterocycl. Compd.* **2004**, *40*, 393–425; (b) Huber, V.; Katterle, M.; Lysetska, M.; Würthner, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 3147–3151; (c) Balaban, T. S.; Tamiaki, H. R.; Holzwarth, A. R. *Top. Curr. Chem.* **2005**, *258*, 1–38; (d) Kozyrev, A. N.; Chen, Y.; Goswami, L. N.; Tabaczynski, W. A.; Pandey, R. K. *J. Org. Chem.* **2006**, *71*, 1949–1960; (e) Sasaki, S.; Mizoguchi, T.; Tamiaki, H. *Tetrahedron* **2005**, *61*, 8041–8048.
12. (a) Montforts, F.-P.; Glasenapp-Breiling, M.; Kusch, D. *Houben–Weyl Methods of Organic Chemistry*; Schaumann, E., Ed.; Thieme: New York, NY, 1998; Vol. E9d, pp 614–635; (b) Jaquinoid, L.; Gros, C.; Khoury, R. G.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1996**, 2581–2582.
13. (a) Balaban, T. S.; Linke-Schaetzel, M.; Bhise, A. D.; Vanthuyne, N.; Roussel, C. *Eur. J. Org. Chem.* **2004**, 3919–3930; (b) McCarthy, J. R.; Jenkins, H. A.; Brückner, C. *Org. Lett.* **2003**, *5*, 19–22; (c) Galezowski, M.; Gryko, D. T. *J. Org. Chem.* **2006**, *71*, 5942–5950; (d) Silva, A. M. G.; Lacerda, P. S. S.; Tome, A. C.; Neves, M. G. P. M. S.; Silva, A. M. S.; Cavaleiro, J. A. S.; Makarova, E. A.; Lukyanets, E. A. *J. Org. Chem.* **2006**, *71*, 8352–8356; (e) Fouchet, J.; Jeandon, C.; Ruppert, R.; Callot, H. *Org. Lett.* **2005**, *7*, 5257–5260; (f) Taniguchi, M.; Ra, D.; Mo, G.; Balasubramanian, T.; Lindsey, J. S. *J. Org. Chem.* **2001**, *66*, 7342–7354.
14. Sergeeva, N. N.; Senge, M. O. *Tetrahedron Lett.* **2006**, *47*, 6169–6172.
15. Kalisch, W. W.; Senge, M. O. *Angew. Chem., Int. Ed.* **1998**, *37*, 1107–1109.
16. (a) Senge, M. O.; Kalisch, W. W.; Bischoff, I. *Chem.—Eur. J.* **2000**, *6*, 2721–2738; (b) Feng, X.; Bischoff, I.; Senge, M. O. *J. Org. Chem.* **2001**, *66*, 8693–8700.
17. (a) Ryppa, C.; Senge, M. O.; Hatscher, S. S.; Kleinpeter, E.; Wacker, P.; Schilde, U.; Wiehe, A. *Chem.—Eur. J.* **2005**, *11*, 3427–3442; (b) Shaker, Y. M.; Senge, M. O. *Heterocycles* **2005**, *65*, 2441–2450.
18. Senge, M. O. *Acc. Chem. Res.* **2005**, *38*, 733–743.
19. Krattinger, B.; Callot, H. J. *Tetrahedron Lett.* **1996**, *37*, 7699–7702.
20. Krattinger, B.; Callot, H. J. *Tetrahedron Lett.* **1998**, *39*, 1165–1168.
21. Krattinger, B.; Callot, H. J. *Eur. J. Org. Chem.* **1999**, *8*, 1857–1867.
22. Bischoff, I.; Feng, X.; Senge, M. O. *Tetrahedron* **2001**, *57*, 5573–5583.
23. Note that Buchler et al. observed a difference between the solid state and the solution conformation for the 5,15-PDM series derived from octaethylporphyrins, indicating a notable degree of conformational flexibility for such systems (conformer ratio in $CDCl_3$ *dd*:*ae*=4:1).[4]
24. Botulinski, A.; Buchler, J. W.; Wicholas, M. *Inorg. Chem.* **1987**, *26*, 1540–1543.
25. (a) The term *syn*-axial '*aa*' configuration for 5,15-PDM is used for the conformers where large substituents at *meso* sp^3-C atoms are displayed in axial positions to the folding axis of the porphyrin core and parallel to each other; (b) The keys '*dd*' are used to point out the 'diagonal' conformation of two groups if the porphodimethene core is planar. Then the two substituents at the 5- and 15-position can no longer be termed as axial or equatorial due to their intermediate positions.
26. Senge, M. O.; Hope, H.; Iakovides, P.; Smith, K. M. *Photochem. Photobiol.* **1993**, *58*, 748–752; Senge, M. O.; Smith, K. M. *Photochem. Photobiol.* **1994**, *60*, 139–142; Senge, M. O.; Ruhlandt-Senge, K.; Smith, K. M. *Z. Naturforsch.* **1995**, *50b*, 139–146.
27. Senge, M. O. *J. Photochem. Photobiol. B: Biol.* **1992**, *16*, 3–36; Senge, M. O. *Chem. Commun.* **2006**, 243–256.
28. Wiehe, A.; Shaker, Y. M.; Brandt, J. C.; Mebs, S.; Senge, M. O. *Tetrahedron* **2005**, *61*, 5535–5564.
29. The solubility of these compounds is rather poor and makes detailed ^{13}C spectroscopic analyses difficult.
30. Hope, H. *Prog. Inorg. Chem.* **1994**, *41*, 1–19.
31. (a) Sheldrick, G. M. *SHELXS-93, Program for the Solution of Crystal Structures*; Universität Göttingen: Göttingen, Germany, 1993; (b) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; Universität Göttingen: Göttingen, Germany, 1997.