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Article Title: **Regioselective reduction of 5-aryl-10,15,20-tris(pyridyl) porphyrin to 5-aryl-10,15,20-tris(pyridyl)dihydroporphyrin (chlorin)**

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Regioselective reduction of 5-aryl-10,15,20-tris(pyridyl) porphyrin to 5-aryl-10,15,20-tris(pyridyl)dihydroporphyrin (chlorin)

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ABSTRACT:

Dihydroporphyrins or chlorins differ from porphyrins only by saturation of a peripheral double bond of the macrocycle. However, this small structural difference lead to significant increase of the absorption band at approximately 650 nm, which make them very interesting candidates for photodynamic therapy applications. The reduction of porphyrin bearing two, three or four pyridyl substituents with tin(II) chloride has been developed for the synthesis of dihydroporphyrins in yields of 15–73%. The reduction of 5-(aryl)-10,15,20-tris(2 or 4-pyridyl)porphyrin with tin(II) chloride dihydrate demonstrated good regioselectivity. Porphyrin with one *meso*-aryl substituted with one electron-donating groups (EDG) gave 5-aryl-10,15,20-tris(2- or 4-pyridyl)-17,18-dihydroporphyrins in 17-72% yield. Porphyrin with one *meso*-aryl substituted with one electron-withdrawing groups (EWG) gave 5-aryl-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrins or 5-aryl-10,15,20-tris(4-pyridyl)-7,8-dihydroporphyrins in 15-21% yield and isobacteriochlorin. We have also proved the possibility to functionalize these compounds to design new regioisomerically pure photosensitizers.

KEYWORDS: Chlorins, Porphyrins, Reduction, Synthesis

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INTRODUCTION

Photodynamic therapy (PDT) is an alternative and a non-invasive cancer treatment requiring the simultaneous presence of three elements: photosensitive molecule, light source and molecular oxygen. The most used photosensitizers in PDT are porphyrins and their derivatives such as chlorins. Chlorins (dihydroporphyrins) differ from porphyrins only by saturation of a peripheral β,β'-pyrrolic double bond of the macrocycle. However, this small structural difference leads to significant changes in the absorption spectrum. Chlorins exhibit a strong absorption band in the violet-blue region (~380−450 nm), the B band whose molar extinction coefficient (ε) varies between 50000-400000 $M^{-1}.cm^{-1}$ and a moderately strong band in the red region (~600−700 nm), the Qy band, whose molar extinction coefficient (ε) varies between 30000-100000 $M^{-1}.cm^{-1}$[1]. The enhancement of the absorption intensity in the red region (in optical transparency window of biological tissues) makes them better candidates for photodynamic therapy than their porphyrin analogues. Among different PDT photosensitizers, several chlorins were clinically approved as cancer treatments. These include, Foscan® (meso-tetra-(m-hydroxyphenyl)chlorin, temoporfin, mTHPC; Biolitec AG)[2], Visudyne® (verteporfin, benzoporphyrin derivative monoacid ring A, BPD-MA; Novartis Pharmaceuticals)[3], Laserphyrin® (talaporfin sodium monoaspartyl chlorin(e6); Meiji Seika Pharma Co., Ltd.)[4]... In addition, great efforts of chlorins functionalization were made to improve PDT efficiency [5, 6].

5,10,15,20-Tetrakis(1-methylpyridinium-4-yl) porphyrin tosylate is also of great interest and have been reported to inhibit cervical cancer growth significantly with no apparent side effect [7]. In order to increase the absorption in the red and to graft latter by covalent bond a group inducing selectivity toward tumor cells, we are interested by the synthesis of non-symmetric 5-aryl-10,15,20-trispyridylchlorin. These chlorins could be classically prepared by reduction of the corresponding unsymmetrical porphyrin using diimide generated in situ from p-toluenesulfonhydrazide[8]. This method leads, in a first-step, to the formation of bacteriochlorins, which can be oxidized subsequently with *o*-chloranil to chlorins. This two-step process affords regioisomeric non-separable chlorins mixtures. This method is however the most used to date [9-11]. Some examples of regioselective synthesis have been proposed in recent years[12] but there is to our knowledge not direct dihydrogenation of porphyrins in one regioselective step.

Stannous chloride in an acidic medium is known since longtime to reduce aryl nitro compounds in aryl amine[13,14] It has been used for decades to prepare *meso*-tetraarylporphyrins bearing aminophenyl groups starting from corresponding nitroarylporphyrins[15]. In 1981, Zimmer *et al.* have developed a simple and rapid detection test of tin(II) using 5,10,15,20-Tetrakis(1-methylpyridinium-4-yl) porphyrin tosylate. This protocol involved the reduction of the porphyrin in the presence of acidic Sn(II) solutions to dihydroporphyrin, producing a red color change[16]. Moreover *meso* substitution with pyridyl groups has long been known to affect the porphyrin reduction potential[17]. In 2013, Kumar *et al.* reported the obtention of the 5-(4-aminophenyl)–10,15,20–tris(4-pyridyl)porphyrin from 5-(4-nitrophenyl)–10,15,20–tripyridylporphyrin in 70% yield [18]. However, by reproducing the experiment, the major product was not the expected porphyrin, but the corresponding 5-(4-aminophenyl)–

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10,15,20–tripyridylchlorin. In connection with our research program on the synthesis of new photosensitizers for photodynamic therapy application[19-24], and very interested by these unexpected results, we decide to explore this reaction and these limits. So, we report, in the present paper full experimental data concerning the synthesis and characterization (^{1}H, ^{13}C NMR, MS spectrometry, and absorption spectroscopy) of some aminophenyl trispyridylchlorin derivatives.

RESULTS AND DISCUSSION

Synthesis of porphyrins with pyridyls meso-substituents

Different porphyrins bearing pyridyls and aryls substituents were prepared by a propionic acid-mediated condensation developed by Adler-Longo *et al.* and adapted by Little *et al*.[25, 26]. This statistical approach leads to four different porphyrins in a non-negligible amount (Scheme 1). After chromatographic separations, the asymmetric A_3B porphyrins **2**–**10** and cis-A_2B_2 porphyrins **11-15** were isolated in yields of 3%-6% and 2%-6%, respectively. Porphyrins **3-16** were characterized by ^{1}H and ^{13}C NMR spectroscopy, and ESI-HRMS spectrometry (see Experimental Section and Supporting Information). <Scheme 1>

Reaction of 5-(4-nitrophenyl)-10,15,20-tris(4-pyridyl)porphyrin (2) with Tin(II) chloride

Synthesis of 5-(4-aminophenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (17)

Firstly, the reduction of 5-(4-nitrophenyl)-10,15,20-tris(4-pyridyl)porphyrin (**2**) was investigated. The porphyrin **2** in 6N HCl solution was treated with tin(II) chloride dihydrate and the resulting solution was stirred for two hours at 65 °C. After neutralization by addition of sodium bicarbonate, the mixture was extracted with dichloromethane. Porphyrin and chlorin are then separated by repeating preparative thin-layer chromatography. The chlorin **17** has been isolated with 73% yield. The mass spectrum showed the appropriate parent ion peak at 635.27 ($M+H^+$). The UV-vis spectrum of **17** is characteristic of metal-free chlorins. Interestingly, the ^{1}H NMR spectrum showed the presence of a single regioisomer. This result suggested that in these reaction conditions the reduction of porphyrin **17** is regioselective. The product displayed only one singlet at 4.12 ppm characteristic of the reduced β-pyrrolic protons, six doublets (δ 8.12, 8.15, 8.32, 8.52, 8.55 and 8.72) in the β-proton region and one singlet at -1.35 ppm corresponding to the internal pyrrolic NH protons. The structural elucidation of obtained regioisomer was achieved by means of 2D-NOESY NMR experiments (Figure 1). NOESY cross peaks indicated through-space interactions between the reduced β-pyrrolic protons (H_{17}/H_{18} 4.12 ppm) and the four *ortho* pyridyl protons in *meso* position 15 and 20 (H_f 7.83 ppm). Additional cross peaks, between H_3 (8.72 ppm) and the two *ortho* aryl protons (H_b 7.84) and H_7 (8.55 ppm) and the same two *ortho* aryl protons (H_b 7.84) can be observed. On the basis of these analyzes, we assumed that the reduction takes place preferentially on a pyrrole located between two pyridyl groups (Scheme 2). Further interpretation of the 2D spectra allowed assignment of each proton. The ^{13}C NMR spectrum (Figure 2) was also fully assigned with the help of two-dimensional NMR experiments (HSQC and HMBC). The ^{13}C NMR spectrum of chlorin **17** showed well defined signals for α and β carbons in comparison with porphyrin **2**. In the

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reduced macrocycle of the chlorin, the effect of NH tautomerism seemed smaller. We supposed that the activation barrier for the NH tautomerism is larger than that of porphyrin. <Scheme 2> <Figure 1> <Figure 2>

Examination of the influence of the reactions parameters

In order to rapidly evaluate the influence of experimental condition parameters, we investigated a design of experiment according to L_9 orthogonal array of the Taguchi method. This approach allowed us to conduct only nine experiments instead of 3^4 (81) using the simple factorial design[27]. The selected factors and their levels were listed in SI Table1. Yields of the chlorin **17** and 5-(4-aminophenyl)-10,15,20-tris(4-pyridyl)porphyrin (**2NH$_2$**) were studied as a function of four factors, temperature (35-100 °C), reaction time (2-18h), HCl concentration (4-8 M) and equivalent number of tin(II) chloride (0.5-3) at three levels each. Yields were determined by ^{1}H NMR analysis of crude using 3-methoxybenzaldehyde as an internal standard. Structure of Taguchi's orthogonal array design and yields of the chlorin **17** and porphyrin **2NH$_2$** were listed in SI Table2 and graphically represented in the Figure 3. These results show a clear influence of the different parameters in the reduction reaction of porphyrin to chlorin. A lower temperature than 35° C does not seem sufficient while a higher temperature than 100 ° C affects the yield of chlorin as well as porphyrin. A long reaction time leads to an increase in the amount of porphyrin **2NH$_2$**, which can be explained by a reoxidation of chlorin to the original porphyrin over time. A hydrochloric acid concentration of 6N promotes the reduction of porphyrin to chlorin. Finally, an increase in the amount of tin(II) chloride makes it possible to increase the yield of chlorin. However, the usable quantity of the latter is limited by complication of the extraction step. <Figure 3>

Influence of the number of pyridyls groups and electron-donating or -withdrawing nature of the others substituents

Secondly, we sought to determine whether the presence of one or more electron-donating or electron-withdrawing groups on *meso*-aryl position, the number of pyridyls groups and their relative position influenced the yields and the regioselectivity of the reduction. The results were presented in the Table 1. The low yields of **20** could be explained by difficult chromatographic separation between porphyrin **5** and chlorin. The presence of electron-withdrawing *meso*-substituents led to a decrease in the synthesis of chlorin yield. Chlorins **22** and **23** were obtained in 21% and 16% yield respectively. This decrease in chlorin amount was accompanied by the appearance of another compound in a significant amount. The UV-visible absorption spectrum allowed to identify these compounds as isobacteriochlorins (Figure 4)[28]. <Figure 4>

For all chlorins **18-23** the parent ions $[M+H]^+$ can be seen in ESI–MS spectra. The NMR spectra confirm the obtention of one single chlorin. Examination of the 2D ^{1}H-^{13}C- HMBC spectrum of compounds **18-22** showed correlation between the singlet of the four β-pyrrolic protons of the hydrogenated pyrrole unit at 4.1-4.2 ppm and the two signal for the *meso*-carbon C_{15} and C_{20} atoms. These results allowed us to conclude on the formation of the 5-aryl-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin. In the case of the compound **23**, the 2D ^{1}H-^{13}C HMBC spectrum showed correlation between the apparent singlet of the four β-pyrrolic protons of the hydrogenated pyrrole unit at 4.23 ppm and the two signals for the *meso*-carbon C_5 and C_{10} atoms. In addition, β-pyrrolic protons H_{17} and

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H_{18} appeared as a singlet whereas the inner NH protons were split into two broad singlets. These data suggested that the reduction taked place preferentially on a pyrrole located between a pyridyl group and the pentafluorophenyl group to give 5-pentafluorophenyl-10,15,20-tris(4-pyridyl)-7,8-dihydroporphyrin **23**.

The assay reduction of AB_3 porphyrin carrying only one pyridyl group and *trans*-A_2B_2-porphyrin **16** did not work. By contrast, under the conditions used, the porphyrins *cis*-A_2B_2 **11-15** could be reduced to corresponding chlorin. However, the analysis of the proton NMR spectrum revealed the presence of a regioisomeric mixture for the chlorins **24**, **25** and **27** in a ratio of 7:3, 6:5, 5.5:4.5 respectively. The structural elucidation of the two obtained regioisomers in the reaction of porphyrin **11** with tin(II) chloride dihydrate was achieved by means of 2D-NOESY NMR experiments. NOESY cross peaks indicated through-space interactions between the four reduced β-pyrrolic protons (H_{17}/H_{18} 4.12 ppm) and the four *ortho* pyridyl protons in *meso* position 15 and 20 (H_f 7.81 ppm). Additional cross peaks, between the two β-protons singlet at 8.43 ppm and the two *ortho* aryl protons (H_b 7.81) can be observed. On the basis of these analysis, we assumed that the main regioisomer is the 5,10-(4-methoxyphenyl)-15,20-tris(4-pyridyl)-17,18-dihydroporphyrin. The multiplication of the signals in the ^{1}H NMR spectrum for the second regioisomers suggested a weaker symmetry compound: 5,10-(4-methoxyphenyl)-15,20-tris(4-pyridyl)-2,3-dihydroporphyrin. The chlorins **26** and **28** were isolated as a single regioisomer. In the case of **26**, regioisomerism could be explained by a steric hindrance of the methoxy group present at the *ortho*-position of aryl substituents which could prevent the approach of tin(II) chloride. The 2D ^{1}H-^{13}C HMBC spectrum of **28** showed correlation between the singlet of the four β-pyrrolic protons of the hydrogenated pyrrole unit at 4.26 ppm and the two signals for the *meso*-carbon C_5 and C_{10} atoms. These data suggested that the reduction taked place preferentially on a pyrrole located between the pentafluorophenyl substituents to give 5,10-bis(pentafluorophenyl)-15,20-bis(4-pyridyl)-7,8-dihydroporphyrin **28**. Moreover, in the ^{1}H NMR spectrum of **28**, the presence of the isobacteriochlorin **29** can be observed (Figure S67). <Table 1>

A_4-type porphyrins have also been tested. The A_4 porphyrin **1** have shown interesting results. The UV-Visible spectrum of crude product showed an absorption band at 745 nm which is characteristic of bacteriochlorin. ^{1}H NMR spectrum (Figure 5) revealed the presence of four different compounds. The starting porphyrin **1**, the chlorin **30**, the bacteriochlorin **31** and the iso-bacteriochlorin **32** were estimated to constitute 29%, 18%, 6% and 47% respectively of the mixture. Chlorin **30** was isolated in 15% and characterized by NMR, HRMS and UV/Vis spectroscopy. <Figure 5>

These results clearly highlight the importance of electron-withdrawing groups on porphyrin to allow reduction of macrocycle to dihydroporphyrin in the presence of tin(II) chloride. Electron-withdrawing *meso*-substituents on porphyrin are known to decrease the potential needed to reduce porphyrin[17]. It would appear that reduction was achieved at the pyrrole unit which is presumably more electron-deficient than the others. The presence of more than three electron-withdrawing *meso*-substituents led to the formation of isobacteriochlorins. Electronic influences on the reactivity of porphyrin β-pyrrolic positions have already been put forward[29-31]. Cavaleiro *et al.* have obtained by catalytic hydrogenation of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin with H_2/10% Pd/C corresponding isobacteriochlorin[32].

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Examination of the influence of the position of the nitrogen atom in pyridyls substituents

Pyridyl substituents play also a crucial role in this reduction reaction. To further understand the mechanism of this reaction, the reactions with porphyrins **9** and **10** were investigated. The reaction with the porphyrin **9** led to 5-(4-aminophenyl)-10,15,20-tris(3-pyridyl)porphyrin (**9NH$_2$**) in nearly quantitative yield, whereas with the porphyrin **10**, 5-(4-aminophenyl)-10,15,20-tris(2-pyridyl)chlorin (**33**) was obtained in 54% yield. Reduction potentials of *meso*-pyridyl substituted porphyrins are similar whatever the relative position of the nitrogen atom in the pyridyl ring[17]. Therefore, the low reduction potential alone of these porphyrins cannot suffice to explain these results and the mechanism shown in Scheme 3 was proposed. By addition of hydrogen chloride pyridyl substituents and the core of the porphyrins are protonated. In the first step of the reaction, tin(II) chloride provided one electron which was taken up by the porphyrin to form the corresponding radical anion. This intermediate state could be stabilized by delocalization of the negative charge to the pyridinium nitrogen atom. The following possible steps were a second electron transfer and two additional protonations by the hydrochloric acid to form the chlorin. <Scheme 3>

Functionalization of 5-(4-aminophenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (17)

These chlorins could be used as precursors for the design of new photosensitizers for anticancer and antimicrobial photodynamic therapy. The amino group of the chlorin **17** could be easily functionalized (Scheme 4). It was converted into azide using the Sandmeyer reaction by treatment with sodium nitrite and sodium azide in water to give chlorin **34** in 26% yield. Chlorin **17** was also acylated with glutaric anhydride to give chlorin **35** in 77% yield. Chlorins **34** and **35** may be later covalently bound to tumor-targeting agents by copper-catalyzed azide-alkyne cycloaddition[33] and esterification[34], respectively. <Scheme 4>

From chlorin **17**, we have designed and prepared a water soluble chlorin with a triphenylphosphonium group with the aim to obtain a new mitochondria-targeted photosensitizer (Scheme 5). In a first step, (3-carboxypropyl)triphenylphosphonium bromide was activated with ethylchloroformate in presence of trimethylamine followed by the addition of chlorin **17**. The compound **36** was obtained in 48% yield. The *N*-methylation of **36** with an excess of methyl iodide in DMF gave the cationic desired compound in 60% yield. The structure of **37** was confirmed by NMR spectroscopy (Figure S86 and S87). <**Scheme 5**> In order to evaluate the oxidative stability of the chlorin **37**, an aqueous solution was analysed by UV-Vis at different time intervals over a 72h period (Figure S88). Very little changes were observed, only a slight decrease in the overall absorption spectrum which could be attributed to a little aggregation in water.

EXPERIMENTAL

Materials

All reagents, solvents and chemicals were purchased from Sigma-Aldrich, VWR, Acros, Fisher chemical, Carlo Erba and Alfa Aesar. Triethoxysilane (TEOS) and pyrrole were distilled under reduced pressure before use.

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Analytical thin layer chromatography (TLC) were performed on Silica plates (Kieselgel 60 F254, thickness 0.2 mm, Merck) and revealed by direct observation. Purifications by column chromatography were carried out using silica gel 60 (Merck, 0.015-0.040 mm). The porphyrins to be purified are solubilized in a minimum of solvent and fixed on Florisil® (VWR, 60-100 mesh). Purifications by thin-layer chromatography were carried out on 2 mm silica gel plates (Merck, 60 P F254).

5,10,15,20-tetrakis(4-pyridyl)porphyrin **1** and 5-(4-nitrophenyl)–10,15,20–tris(4-pyridyl)porphyrin **2** were prepared according to the literature[18].

Analytical methods

NMR spectra were recorded on a Ascend^{TM}500 Bruker NMR spectrometer. All compounds are calibrated to tetramethylsilane. Quaternary carbons at the α-position of the N atoms of the free base porphyrin have long relaxation time, which result in very broad signals that could not be detected. UV–vis spectra were recorded on a double beam spectrophotometer AnalytikaJena SPECORD 210, using 10 mm quartz cells. High resolution electrospray ionization mass spectra (HR ESI-MS) were performed on a Bruker Q-TOF maXis mass spectrometer, coupled to an Ultimate 3000 RSLC chain (Dionex); by the ICOA/CBM (FR2708) platform (Orleans University).

General procedure for the preparation of porphyrins

Arylaldehyde (1 equiv.) and pyridinecarboxaldehyde (3 equiv.) were added to a round bottom flask containing propionic acid at 110 °C. Pyrrole (4 equiv.) was then added dropwise and the reaction mixture refluxed for 4 h. After cooling down to room temperature, propionic acid was removed by distillation under reduced pressure. The crude brown solid was adsorbed over Florisil® and purified by repeated column chromatography with chloroform/methanol, where it was possible to isolate the two porphyrins A_3B and Cis-A_2B_2.

A_3B porphyrins

5-(4-methoxyphenyl)-10,15,20-tris(4-pyridyl)porphyrin (3). Purple solid (140 mg, 3% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm -2.85 (s, 2H, NH), 4.10 (s, 3H, OCH_3), 7.30 (d, *J*=8.5 Hz, 2H, H_c), 8.11 (d, *J*=8.5 Hz, 2H, H_b), 8.15 (d, *J*=5.6 Hz, 6H, H_f), 8.81 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.84 (s, 4H, $H_{\beta\text{-pyrrolic}}$), 8.96 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 9.04 (m, 6H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 55.6 (1C, OCH_3), 112.5 (2C, C_b), 116.9 (1C, C_{15}), 117.4 (2C, C_{10} C_{20}), 121.7 (1C, C_5), 129.3 (6C, C_f), 131.0 (6C, $C_{\beta\text{-pyrrolic}}$), 132.4 (2C, $C_{\beta\text{-pyrrolic}}$), 133.8 (1C, C_a), 135.6 (2C, C_c), 148.38 (4C, C_g), 148.42 (2C, C_g), 149.97 (1C, $C_{e'}$), 150.04 (2C, C_e), 159.7 (1C, C_d) Quaternary carbons at the α-position are missing. ESI-HR *m/z*: calcd.exact mass for $C_{42}H_{30}N_7O$: 648.2506 $[M+H]^+$, found: 648.2501 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 418 (5.60), 515 (4.29), 550 (3.86), 591 (3.79), 646 (3.54).

5-(3-methoxyphenyl)-10,15,20-tris(4-pyridyl)porphyrin (4). Purple solid (264.3 mg, 5.6% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm -2.89 (s, 2H, NH), 3.99 (s, 3H, OCH_3), 7.36 (ddd, J_3=8.4 Hz, J_5=0.8 Hz, 1H, H_d), 7.66 (t, J_3=7.9 Hz, 1H, H_c), 7.76 (dd, J_4=1.6 Hz, J_5=0.8 Hz, 1H, $H_{b'}$), 7.80 (d, *J*=7.4 Hz, 1H, H_b), 8.13 (m, 6H, H_f), 8.79 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.83 (s, 4H, $H_{\beta\text{-pyrrolic}}$), 8.96 (m, 8H, $H_{\beta\text{-pyrrolic}}$ / H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 55.5 (1C, OCH_3), 113.7 (1C, C_d), 117.1 (1C, C_{15}), 117.4 (2C, C_{10} C_{20}), 120.7 (1C, $C_{b'}$), 121.4 (1C, C_5), 127.65

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(1C, C_b), 127.70 (1C, C_c), 129.3 (6C, C_f), 131.1 (8C, $C_{\beta\text{-pyrrolic}}$), 142.8 (1C, C_a), 148.28 (4C, C_g), 148.31 (2C, $C_{g'}$), 149.99 (1C, $C_{e'}$), 150.02 (2C, C_e), 158.1 (1C, $C_{c'}$) Quaternary carbons at the α-position are missing. ESI-HR *m/z*: calcd.exact mass for $C_{42}H_{30}N_7O$: 648.2506 $[M+H]^+$, found: 648.2499 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 417 (5.63), 513 (4.26), 548 (3.76), 589 (3.75), 644 (3.41).

5-(2-methoxyphenyl)-10,15,20-tris(4-pyridyl)porphyrin (**5)**. Purple solid (149.2 mg, 4.6% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -2.83 (s, 2H, NH), 3.61 (s, 3H, OCH_3), 7.36 (m, *2*H, H_c $H_{c'}$), 7.80 (dt, J_3=8.0 Hz, J_4=1.6 Hz, 1H, H_d), 7.99 (dd, J_3=7.3 Hz, J_4=1.5 Hz, 1H, H_b), 8.14 (m, 6H, H_f), 8.78 (d, *J*=4.7 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.83 (s, 4H, $H_{\beta\text{-pyrrolic}}$), 8.87 (d, *J*=4.7 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 9.03 (m, 6H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 55.8 (1C, OCH_3), 111.0 (1C, C_c), 117.1 (1C, C_{15}), 117.2 (2C, C_{10} C_{20}), 117.7 (1C, C_5), 119.6 (1C, $C_{c'}$), 129.3 (6C, C_f), 130.2 (1C, C_d), 130.3 (1C, C_a), 131.0 (6C, $C_{\beta\text{-pyrrolic}}$), 132.0 (2C, $C_{\beta\text{-pyrrolic}}$), 135.5 (1C, C_b), 148.34 (4C, C_g), 148.37 (2C, $C_{g'}$), 150.1 (3C, C_e), 159.3 (1C, $C_{b'}$) Quaternary carbons at the α-position are missing. ESI-HR *m/z*: calcd.exact mass for $C_{42}H_{30}N_7O$: 648.2506 $[M+H]^+$, found: 648.2508 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 417 (5.63), 513 (4.28), 547 (3.73), 589 (3.75), 644 (3.37).

5-(phenyl)-10,15,20-tris(4-pyridyl)porphyrin (**6)**. Purple solid (502 mg, 5.6% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -2.87 (s, 2H, NH), 7.79 (m, *3*H, H_c $H_{c'}$ H_d), 8.16 (d, J_3=5.8 Hz, 6H, H_f), 8.20 (m, 2H, H_b $H_{b'}$), 8.82 (d, J_3=4.7 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.85 (s, 4H, $H_{\beta\text{-pyrrolic}}$), 8.92 (d, *J*=4.7 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 9.05 (m, 6H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 117.1 (1C, C_{15}), 117.4 (2C, C_{10} C_{20}), 121.7 (1C, C_5), 126.9 (2C, C_c), 128.1 (1C, C_d), 129.4 (6C, C_f), 131.2 (8C, $C_{\beta\text{-pyrrolic}}$), 134.5 (2C, C_b), 141.5 (1C, C_a), 148.40 (4C, C_g), 148.43 (2C, $C_{g'}$), 149.97 (1C, $C_{e'}$), 150.01 (2C, C_e) Quaternary carbons at the β and α-position are missing. ESI-HR *m/z*: calcd.exact mass for $C_{41}H_{27}N_7$: 618.2406 $[M+H]^+$, found: 618.2400 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 417 (5.59), 514 (4.22), 548 (3.72), 589 (3.69), 649 (3.60).

5-(4-Iodophenyl)-10,15,20-tris(4-pyridyl)porphyrin (7). Purple solid (207 mg, 5.3% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -2.90 (s, 2H, NH), 7.92 (d, J_3=8.1 Hz, 2H, H_c), 8.10 (d, J_3=8.1 Hz, 2H, H_b), 8.15 (d, J_3=5.3 Hz, 6H, H_f), 8.83 (d, J_3=4.7 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.85 (s, 4H, $H_{\beta\text{-pyrrolic}}$), 8.90 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.15 (d, J_3=5.3 Hz, 6H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 94.6 (1C, C_d), 117.3 (1C, C_{15}), 117.6 (2C, C_{10} C_{20}), 120.0 (1C, C_5), 129.3 (6C, C_f), 131.2 (8C, $C_{\beta\text{-pyrrolic}}$), 136.1 (4C, C_b C_c), 141.1 (1C, C_a), 148.4 (6C, C_g), 149.88 (1C, $C_{e'}$), 149.90 (2C, C_e) Quaternary carbons at the α-position are missing. ESI-HR *m/z*: calcd.exact mass for $C_{41}H_{27}IN_7$: 744.1367 $[M+H]^+$, found: 744.1359 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 417 (5.58), 513 (4.25), 548 (3.79), 589 (3.76), 644 (3.44).

5-(pentafluorophenyl)-10,15,20-tris(4-pyridyl)porphyrin (8). Purple solid (426.1 mg, 6.0% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -2.88 (s, 2H, NH), 8.16 (m, 6H, H_f), 8.86 (m, 6H, $H_{\beta\text{-pyrrolic}}$), 8.92 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 9.06 (d, J_3=5.7 Hz, 6H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 101.8 (1C, C_5), 118.1 (2C, C_{10} C_{20}), 118.9 (1C, C_{15}), 129.24 (2C, C_f), 129.29 (4C, C_f), 131.3 (8C, $C_{\beta\text{-pyrrolic}}$), 148.47 (2C, C_g), 148.51 (4C, C_g), 149.51 (2C, C_e), 149.63 (1C, $C_{e'}$) In ^{13}C NMR Quaternary carbons at the α-position and pentafluorophenyl signals were not observed due to C-F coupling. ESI-HR *m/z*: calcd.exact mass for $C_{41}H_{23}F_5N_7$: 708.1930 $[M+H]^+$, found: 708.1923 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 415 (5.59), 511 (4.30), 544 (3.63), 586 (3.79), 642 (3.20).

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10-(4-nitrophenyl)-5,15,20-tris(3-pyridyl)porphyrin (9). Purple solid (175 mg, 2.8% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -2.81 (s, 2H, NH), 7.77 (dd, *J*=5.7 Hz, *J*=6.0 Hz, 3H, H_g), 8.39 (d, *J*=7.2 Hz, 2H, H_c), 8.53 (d, *J*=6.2 Hz, 3H, H_h), 8.64 (d, *J*=8.1 Hz, 2H, H_b), 8.81 (d, *J*=4.1 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.87 (m, 6H, $H_{\beta\text{-pyrrolic}}$), 9.07 (d, *J*=4.3 Hz, 3H, H_f), 9.45 (m, 3H, $H_{f'}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 116.9 (2C, C_{10} C_{20}), 117.0 (1C, C_{15}), 117.9 (1C, C_5), 122.0 (2C, C_b), 122.1 (3C, C_g), 131.6 (8C, $C_{\beta\text{-pyrrolic}}$), 135.1 (2C, C_c), 137.6 (1C, C_a), 140.9 (3C, C_h), 147.9 (1C, C_e), 148.6 (2C, C_e), 149.4 (3C, C_f), 153.6 (3C, $C_{f'}$) Quaternary carbons at the α-position are missing. ESI-HR *m/z*: calcd.exact mass for $C_{41}H_{27}N_8O_2$: 663.2251 $[M+H]^+$, found: 663.2247 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 417 (5.58), 516 (4.27), 550 (3.90), 590 (3.76), 646 (3.54).

10-(4-nitrophenyl)-5,15,20-tris(2-pyridyl)porphyrin (10). Purple solid (102 mg, 2.6% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -2.80 (s, 2H, NH), 7.71 (dd, *J*=5.1 Hz, *J*=6.6 Hz, 3H, H_g), 8.08 (m, 3H, H_h), 8.21 (d, *J*=7.6 Hz, 3H, $H_{g'}$), 8.36 (d, *J*=7.7 Hz, 2H, H_c), 8.61 (d, *J*=8.6 Hz, 2H, H_b), 8.76 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.87 (s, 6H, $H_{\beta\text{-pyrrolic}}$), 9.13 (d, *J*=4.5 Hz, 3H, H_f). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 117.6 (1C, C_5), 119.1 (1C, C_{15}), 119.2 (2C, C_{10} C_{20}), 121.8 (2C, C_c), 122.5 (1C, C_f), 122.6 (2C, C_f), 130.37 (2C, C_h), 130.42 (1C, C_h), 134.9 (3C, $C_{f'}$), 135.2 (2C, C_b), 147.8 (1C, C_a), 148.67 (1C, C_g), 148.70 (2C, C_g), 149.0 (1C, C_d), 160.38 (2C, C_e), 160.40 (1C, C_e) Quaternary carbons at the α-position are missing. ESI-HR *m/z*: calcd.exact mass for $C_{41}H_{27}N_8O_2$: 663.2251 $[M+H]^+$, found: 650.2247 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 417 (5.49), 514 (4.25), 549 (3.81), 589 (3.80), 644 (3.43).

A_2B_2 porphyrins

5,10-bis(4-methoxyphenyl)-15,20-bis(4-pyridyl)porphyrin (11). Purple solid (142.2 mg, 2.9% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm -2.78 (s, 2H, NH), 4.01 (s, 6H, OCH_3), 7.22 (d, J=8.6 Hz, 4H, H_c), 8.06 (d, J=8.5 Hz, 4H, H_b), 8.09 (d, J=6.0 Hz, 4H, H_f), 8.76 (d, J=4.8 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.79 (s, 2H, $H_{\beta\text{-pyrrolic}}$), 8.88 (s, 2H, $H_{\beta\text{-pyrrolic}}$), 8.91 (d, J=4.8 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.96 (d, J=5.7 Hz, 4H, H_g). ESI-HR m/z: calcd.exact mass for $C_{44}H_{33}N_6O_2$: 677.2660 $[M+H]^+$, found: 677.2654 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 420 (5.47), 517 (4.09), 552 (3.78), 591 (3.60), 647 (3.48).

5,10-bis(3-methoxyphenyl)-15,20-bis(4-pyridyl)porphyrin (12). Purple solid (108.3 mg, 2.2% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm -2.83 (s, 2H, NH), 3.97 (s, 6H, OCH_3), 7.32 (dd, J_3=8.3 Hz, J_5=2.2 Hz, 2H, H_d), 7.62 (t, J_3=7.9 Hz, 2H, H_c), 7.79 (m, J_4=1.6 Hz, J_5=0.8 Hz, 4H, H_b), 8.14 (d, J_3=5.6 Hz, 4H, H_f), 8.79 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.83 (s, 2H, $H_{\beta\text{-pyrrolic}}$), 8.92 (s, 2H, $H_{\beta\text{-pyrrolic}}$), 8.95 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 9.00 (d, J_3=5.5 Hz, 4H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 55.5 (2C, OCH_3), 113.7 (2C, C_d), 116.7 (2C, C_{15} C_{20}), 120.6 (2C, $C_{b'}$), 121.0 (2C, C_5 C_{10}), 127.60 (2C, C_b), 127.64 (2C, C_c), 129.4 (4C, C_f), 130.7 (4C, $C_{\beta\text{-pyrrolic}}$), 131.7 (4C, $C_{\beta\text{-pyrrolic}}$), 143.0 (2C, C_a), 148.3 (4C, C_g), 150.2 (2C, C_e), 158.0 (2C, $C_{c'}$) Quaternary carbons at the α-position are missing. ESI-HR *m/z*: calcd.exact mass for $C_{44}H_{33}N_6O2$: 677.2660 $[M+H]^+$, found: 677.2653 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 418 (5.66), 514 (4.31), 549 (3.82), 589 (3.80), 644 (3.49).

5,10-bis(2-methoxyphenyl)-15,20-bis(4-pyridyl)porphyrin (13). Purple solid (47.8 mg, 2.9% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -2.76 (s, 2H, NH), 3.58 (s, 3H, OCH_3), 3.60 (s, 3H, OCH_3), 7.34 (m, 4H, H_c $H_{c'}$), 7.77 (dt, J_3=8.0 Hz, J_4=1.6 Hz, 2H, H_d), 7.96 (dd, J_3=7.2 Hz, J_4=1.6 Hz, 1H, H_b), 8.00 (dd, J_3=7.3 Hz, J_4=1.6 Hz, 1H,

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H_b), 8.14 (m, 4H, H_f), 8.75 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.78 (s, 2H, $H_{\beta\text{-pyrrolic}}$), 8.79 (s, 2H, $H_{\beta\text{-pyrrolic}}$), 8.82 (d, *J*=4.3 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 9.01 (m, 4H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 55.8 (2C, OCH_3), 111.0 (2C, C_c), 116.42 (1C, C_{15}), 116.45 (1C, $C_{20,}$), 117.0 (2C, C_5 C_{10}), 119.50, 119.52 (2C, $C_{c'}$), 129.4 (4C, C_f), 130.1 (2C, C_d), 130.56, 130.58 (2C, C_a), 131.5 (8C, $C_{\beta\text{-pyrrolic}}$), 135.52, 135.60 (2C, C_b), 148.25 (4C, C_g), 150.4 (2C, C_e), 159.34, 159.41 (2C, $C_{b'}$) Quaternary carbons at the β and α-position are missing. ESI-HR *m/z*: calcd.exact mass for $C_{44}H_{33}N_6O_2$: 677.2660$[M+H]^+$, found: 648.2649 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 419 (5.42), 517 (4.13), 546 (3.66), 596 (3.64), 652 (3.34).

5,10-bis(4-Iodophenyl)-15,20-bis(4-pyridyl)porphyrin (14). Purple solid (123 mg, 5.7% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -2.90 (s, 2H, NH), 7.92 (d, J_3=8.1 Hz, 4H, H_c), 8.10 (d, J_3=8.1 Hz, 4H, H_b), 8.13 (d, J_3=5.2 Hz, 4H, H_f), 8.79 (d, J_3=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.81 (s, 2H, $H_{\beta\text{-pyrrolic}}$), 8.86 (s, 2H, $H_{\beta\text{-pyrrolic}}$), 8.90 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.95 (m, 4H, H_g). ESI-HR *m/z*: calcd.exact mass for $C_{42}H_{27}I_2N_6$: 869.0381 $[M+H]^+$, found: 869.0378 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 418 (5.63), 514 (4.27), 549 (3.85), 590 (3.74), 650 (3.62).

5,10-bis(pentafluorophenyl)-15,20-bis(4-pyridyl)porphyrin (15). Purple solid (160.4 mg, 4.0% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -2.86 (s, 2H, NH), 8.16 (d, *J*=5.8 Hz, 4H, H_f), 8.35 (m, 4H, $H_{\beta\text{-pyrrolic}}$), 8.91 (m, 4H, $H_{\beta\text{-pyrrolic}}$), 9.07 (d, J_3=5.7 Hz, 4H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 102.2 (2C, C_5 C_{10}), 119.2 (2C, C_{15} C_{20}), 129.2 (4C, C_f), 131.3 (8C, $C_{\beta\text{-pyrrolic}}$), 148.5 (4C, C_g), 149.4 (2C, C_e) In ^{13}C NMR Quaternary carbons at the α-position and pentafluorophenyl signals were not observed due to C-F coupling. ESI-HR *m/z*: calcd.exact mass for $C_{42}H_{19}F_{10}N_6$: 797.1506 $[M+H]^+$, found: 797.1490 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 414 (5.56), 510 (4.30), 541 (3.50), 585 (3.78), 652 (3.12).

5,15-bis(4-methoxyphenyl)-10,20-bis(4-pyridyl)porphyrin (16). Purple solid (77.8 mg, 1.6% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm -2.82 (s, 2H, NH), 4.10 (s, 6H, OCH_3), 7.30 (d, *J*=8.5 Hz, 4H, H_c), 8.11 (d, *J*=8.5 Hz, 4H, H_b), 8.16 (d, *J*=5.4 Hz, 4H, H_f), 8.80 (d, *J*=4.5 Hz, 4H, $H_{\beta\text{-pyrrolic}}$), 8.93 (d, *J*=4.4 Hz, 4H, $H_{\beta\text{-pyrrolic}}$), 9.03 (d, *J*=4.9 Hz, 4H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 55.6 (2C, OCH_3), 112.3 (4C, C_b), 116.4 (2C, C_{10} and C_{20}), 121.3 (2C, C_5 and C_{15}), 129.4 (4C, C_f), 130.6, 131.7 (8C, $C_{\beta\text{-pyrrolic}}$), 134.1 (2C, C_a), 135.6 (4C, C_c), 148.3 (4C, C_g), 150.3 (2C, C_e), 159.6 (2C, C_d) Quaternary carbons at the α-position are missing. ESI-HR *m/z*: calcd.exact mass for $C_{44}H_{33}N_6O_2$: 677.2660 $[M+H]^+$, found: 677.2656 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 420 (5.57), 517 (4.19), 552 (3.88), 592 (3.69), 648 (3.58).

General procedure for the reduction of tripyridylporphyrin

To a solution of 5-aryl-10,15,20-trispyridylporphyrin (1.0 equiv.) in 6N HCl was added stannous chloride (1.5 equiv.) and heated at 65 °C for 2 h. After cooling down to room temperature, it was then basified with solid sodium carbonate to pH ~ 8 and extracted with dichloromethane (3 × 50 mL). The solvent was evaporated under vaccum.

5-(4-aminophenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (17). The crude product mixture was purified using preparative thin-layer chromatography (TLC) plates (CH_2Cl_2/MeOH, 97:3) to afford chlorin **17** (140.3 mg, 0.221 mmol) in 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.35 (s, 2H, NH), 3.44 (bs, 2H, NH_2), 4.13 (s, 4H, H_{17} H_{18}), 6.96 (d, *J*=8.1 Hz, 2H, H_c), 7.83 (m, 6H, H_f, H_b), 8.03 (bs, 2H, $H_{f'}$), 8.12 (d, *J*=4.8 Hz, 1H, H_2), 8.15 (d,

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J=4.8 Hz, 1H, $H_{12/13}$), 8.32 (d, *J*=4.5 Hz, 1H, H_8), 8.52 (d, *J*=4.8 Hz, 1H, $H_{12/13}$), 8.55 (d, *J*=4.45 Hz, 1H, H_7), 8.72 (d, *J*=4.8 Hz, 1H, H_3), 9.01 (m, 6H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 35.6 (1C, C_{17}/C_{18}), 35.8 (1C, C_{17}/C_{18}), 109.4 (1C, C_{20}), 109.7 (1C, C_{15}), 113.6 (2C, C_b), 119.9 (1C, C_{10}), 122.8 (1C, C_2), 123.2 (1C, C_{12}/C_{13}), 125.0 (1C, C_5), 127.8 (4C, C_f), 127.9 (1C, C_{12}/C_{13}), 129.0 (2C, $C_{f'}$), 129.3 (1C, C_3), 131.4 (1C, C_8), 131.5 (1C, C_d), 133.2 (1C, C_7), 134.0 (1C, C_{11}), 135.0 (2C, C_c), 136.0 (1C, C_4), 139.81, 139.77 (2C, C_{14}, C_1), 146.3 (1C, C_a), 148.1 (2C, $C_{g'}$), 149.6 (4C, C_g), 150.1 (1C, C_e), 151.0 (1C, C_e), 151.1 (1C, C_e), 151.3 (1C, C_9), 153.8 (1C, C_6), 165.8 (1C, C_{19}), 166.4 (1C, C_{16}). ESI-HR *m/z*: calcd.exact mass for $C_{41}H_{31}N_8$: 635.2666 $[M+H]^+$, found: 635.2661 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 420 (5.11), 518 (4.04), 548 (3.90), 598 (3.67), 653 (4.27).

5-(4-methoxyphenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (18). The crude product mixture was partially purified using preparative TLC plates (CH_2Cl_2/MeOH, 97:3) to afford a mixture of chlorin **18** and starting porphyrin **3** in a ratio 83:17 (28 mg). The chlorin **18** (0,036 mmol) was obtained in 46% yield. Yields and ratio of compounds were determined using the integrals of the signals of pyridyl protons in 1H NMR spectrum. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.40 (s, 2H, NH), 4.06 (s, 3H, OCH_3), 4.16 (s, 4H, H_{17} H_{18}), 7.23 (d, *J*=8.6 Hz, 2H, H_c), 7.82 (d, *J*=5.8 Hz, 4H, H_f), 7.99 (d, *J*=5.8 Hz, 2H, H_b), 8.03 (d, *J*=5.8 Hz, 2H, $H_{f'}$), 8.14 (d, *J*=4.9 Hz, 1H, H_2), 8.17 (d, *J*=4.9 Hz, 1H, $H_{12/13}$), 8.35 (d, *J*=4.5 Hz, 1H, H_8), 8.49 (d, *J*=4.8 Hz, 1H, $H_{12/13}$), 8.55 (d, *J*=4.9 Hz, 1H, H_7), 8.67 (d, *J*=4.9 Hz, 1H, H_3), 8.96 (m, 6H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 35.7 (1C, C_{17}/C_{18}), 35.8 (1C, C_{17}/C_{18}), 55.6 (1C, OCH_3), 109.6 (1C, C_{20}), 109.8 (1C, C_{15}), 112.4 (2C, C_b), 120.0 (1C, C_{10}), 123.0 (1C, C_2), 123.3 (1C, C_{12}/C_{13}), 124.1 (1C, C_5), 127.4 (4C, C_f), 127.9 (1C, C_{12}/C_{13}), 128.7 (2C, $C_{f'}$), 129.2 (1C, C_3), 131.6 (1C, C_8), 133.1 (1C, C_7), 133.8 (1C, C_a), 134.1 (1C, C_{11}), 134.9 (2C, C_c), 135.9 (1C, C_4), 139.8, 139.9 (2C, C_{14}, C_1), 148.4 (2C, $C_{g'}$), 149.79, 149.81 (4C, C_g), 150.0 (1C, C_e), 151.0 (1C, C_e), 151.1 (1C, C_e), 151.5 (1C, C_9), 153.6 (1C, C_6), 159.6 (1C, C_d), 166.1 (1C, C_{19}), 166.5 (1C, C_{16}). ESI-HR *m/z*: calcd.exact mass for $C_{42}H_{32}N_7O$: 650.2663 $[M+H]^+$, found: 650.2660 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max} 420, 517, 546, 599, 653 nm.

5-(3-methoxyphenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (19). The crude product mixture was partially purified using preparative TLC plates (CH_2Cl_2/MeOH, 97:3) to afford a mixture of chlorin **19** and starting porphyrin **4** in a ratio 78:22 (7.3 mg, 0.011 mmol). The chlorin **19** was obtained in 34% yield. Yields and ratio of compounds were determined using the integrals of the signals of pyridyl protons in 1H NMR spectrum. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.43 (s, 2H, NH), 3.96 (s, 3H, OCH_3), 4.18 (s, 4H, H_{17} H_{18}), 7.29 (dd, J_3=8.2 Hz, J_4=2.6 Hz, 1H, H_d), 7.60 (t, J_3=7.9 Hz, 1H, H_c), 7.64 (bs, 1H, $H_{b'}$), 7.68 (d, *J*=7.6 Hz, 1H, H_b), 7.89 (m, 4H, H_f), 8.09 (d, *J*=5.2 Hz, 2H, $H_{f'}$), 8.14 (d, *J*=4.9 Hz, 1H, H_2), 8.18 (d, *J*=4.9 Hz, 1H, $H_{12/13}$), 8.34 (d, *J*=4.6 Hz, 1H, H_8), 8.51 (d, *J*=4.5 Hz, 1H, $H_{12/13}$), 8.55 (d, *J*=4.7 Hz, 1H, H_7), 8.70 (d, *J*=4.7 Hz, 1H, H_3), 9.00 (m, 6H, H_g). ESI-HR *m/z*: calcd.exact mass for $C_{42}H_{32}N_7O$: 650.2663 $[M+H]^+$, found: 650.2653 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max} 417, 515, 544, 596, 653 nm.

5-(2-methoxyphenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (20). The crude product mixture was purified using preparative TLC plates (CH_2Cl_2/MeOH, 97:3) to afford chlorin **20** (9.0 mg, 0.014 mmol) in 18% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.43 (s, 1H, NH), -1.41 (s, 1H, NH), 3.61 (s, 3H, OCH_3), 4.16 (s, 4H, H_{17} H_{18}), 7.30 (m, 2H, H_c $H_{c'}$), 7.73 (dt, J_3=8.0 Hz, J_4=1.5 Hz, 1H, H_d), 7.82 (m, 4H, H_f), 7.87 (d, J_3=8.3 Hz, 1H,

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H_b), 8.03 (m, 2H, $H_{f'}$), 8.13 (d, *J*=4.8 Hz, 1H, H_2), 8.15 (d, *J*=4.8 Hz, 1H, $H_{12/13}$), 8.33 (d, *J*=4.4 Hz, 1H, H_8), 8.41 (d, *J*=4.5 Hz, 1H, $H_{12/13}$), 8.53 (d, *J*=4.8 Hz, 1H, H_7), 8.58 (d, *J*=4.8 Hz, 1H, H_3), 8.96 (m, 6H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 35.73 (1C, C_{17}/C_{18}), 35.77 (1C, C_{17}/C_{18}), 55.8 (1C, OCH_3), 109.66 (1C, C_{20}), 109.69 (1C, C_{15}), 110.9 (1C, C_c), 119.6 (1C, $C_{c'}$),119.9 (1C, C_{10}), 120.1 (1C, C_5), 123.0 (1C, C_2), 123.2 (1C, C_{12}/C_{13}), 127.5 (4C, C_f), 127.6 (1C, C_{12}/C_{13}), 128.7 (2C, $C_{f'}$), 128.8 (1C, C_3), 130.0 (1C, C_d), 130.2 (1C, C_a), 131.8 (1C, C_8), 133.7 (1C, C_7), 134.0 (1C, C_{11}), 134.9 (1C, C_b), 135.8 (1C, C_4), 139.5, 139.9 (2C, C_{14}, C_1), 148.2 (2C, C_g), 149.69 (2C, C_g), 149.73 (2C, C_g), 150.1 (1C, C_e), 151.2 (2C, C_e), 151.3 (1C, C_9), 153.7 (1C, C_6), 159.1 (1C, $C_{b'}$), 165.9 (1C, C_{19}), 166.2 (1C, C_{16}). ESI-HR *m/z*: calcd.exact mass for $C_{42}H_{32}N_7O$: 650.2663 $[M+H]^+$, found: 650.2658 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 418 (4.95), 515 (3.86), 543 (3.63), 600 (3.88), 654 (4.21).

5-(phenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (21). The crude product mixture was partially purified using preparative TLC plates (CH_2Cl_2/MeOH, 97:3) to afford a mixture of chlorin **21** and starting porphyrin **6** in a ratio 80:20 (25 mg). The chlorin **21** (0.040 mmol) was obtained in 34% yield. Yields and ratio of compounds were determined using the integrals of the signals of pyridyl protons in 1H NMR spectrum. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.44 (s, 2H, NH), 4.17 (s, 4H, H_{17} H_{18}), 7.71 (m, 3H, H_c $H_{c'}$ H_d), 7.83 (d, J_3=5.8 Hz, 4H, H_f), 8.83 (d, J_3=5.8 Hz, 2H, $H_{f'}$), 8.08 (m, 2H, H_b $H_{b'}$), 8.15 (d, *J*=4.6 Hz, 1H, H_2), 8.18 (d, *J*=4.9 Hz, 1H, $H_{12/13}$), 8.35 (d, *J*=4.6 Hz, 1H, H_8), 8.45 (d, *J*=4.5 Hz, 1H, $H_{12/13}$), 8.55 (d, *J*=4.8 Hz, 1H, H_7), 8.63 (d, *J*=4.8 Hz, 1H, H_3), 8.96 (m, 6H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 35.75 (1C, C_{17}/C_{18}), 35.82 (1C, C_{17}/C_{18}), 109.73 (1C, C_{20}), 109.86 (1C, C_{15}), 120.0 (1C, C_{10}), 123.1 (1C, C_2), 123.3 (1C, C_{12}/C_{13}), 124.2 (1C, C_5), 126.9 (2C, C_c $C_{c'}$), 127.4 (4C, C_f), 127.96 (1C, C_7), 127.98 (1C, C_d), 128.7 (2C, $C_{f'}$), 129.1 (1C, C_3), 129.4 (1C, C_a), 131.7 (1C, C_8), 133.1 (1C, C_{12}/C_{13}), 133.8 (2C, C_b $C_{b'}$), 134.2 (1C, C_{11}), 135.6 (1C, C_4), 139.8, 139.9 (2C, C_{14}, C_1), 148.3 (2C, C_g), 149.78 (2C, C_g), 149.80 (2C, C_g), 150.0 (1C, C_e), 151.0 (1C, C_e), 151.1 (1C, C_e), 151.5 (1C, C_9), 153.2 (1C, C_6), 166.2 (1C, C_{19}), 166.4 (1C, C_{16}). ESI-HR *m/z*: calcd.exact mass for $C_{41}H_{30}N_7$: 620.2557 $[M+H]^+$, found: 620.2554 $[M+H]^+$. UV-vis (CH_2Cl_2) λ_{max} 417, 516, 544, 599, 653 nm.

5-(4-Iodophenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (22). The crude product mixture was purified using preparative TLC plates (CH_2Cl_2/MeOH, 97:3) to afford chlorin **22** (21.6 mg, 0.040 mmol) in 21% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.49 (s, 2H, NH), 4.18 (s, 4H, H_{17} H_{18}), 7.80 (d, J_3=8.0 Hz, 2H, H_c), 7.83 (d, J_3=4.9 Hz, 4H, H_f), 8.03 (m, 4H, $H_{f'}$, H_b), 8.17 (d, *J*=4.8 Hz, 1H, H_2), 8.19 (d, *J*=4.8 Hz, 1H, $H_{12/13}$), 8.37 (d, *J*=4.4 Hz, 1H, H_8), 8.43 (d, *J*=4.4 Hz, 1H, $H_{12/13}$), 8.56 (d, *J*=4.7 Hz, 1H, H_7), 8.61 (d, *J*=4.8 Hz, 1H, H_3), 8.98 (m, 6H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 35.78 (1C, C_{17}/C_{18}), 35.83 (1C, C_{17}/C_{18}), 94.3 (1C, C_d), 109.93 (1C, C_{20}), 110.01 (1C, C_{15}), 120.1 (1C, C_{10}), 122.5 (1C, C_5), 123.3 (1C, C_2), 123.5 (1C, C_{12}/C_{13}), 127.4 (4C, C_f), 128.1 (1C, C_7), 128.68 (2C, $C_{f'}$), 128.75 (1C, C_3), 131.9 (1C, C_8), 132.7 (1C, C_{12}/C_{13}), 134.3 (1C, C_{11}), 135.1 (1C, C_4), 135.4 (2C, C_c $C_{c'}$), 136.0 (2C, C_b $C_{b'}$), 139.87, 139.91 (2C, C_{14}, C_1), 141.0 (1C, C_a), 148.3 (2C, C_g), 149.8 (4C, C_g), 149.9 (1C, C_e), 150.91 (1C, C_e), 150.97 (1C, C_e), 151.6 (1C, C_9), 152.6 (1C, C_6), 166.4 (1C, C_{19}), 166.6 (1C, C_{16}). ESI-HR *m/z*: calcd.exact mass for $C_{41}H_{29}IN_7$: 746.1524 $[M+H]^+$, found: 746.1522 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 418 (5.19), 516 (4.08), 544 (3.87), 599 (3.63), 653 (4.42).

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5-(pentafluorophenyl)-10,15,20-tris(4-pyridyl)-7,8-dihydroporphyrin (23). The crude product mixture was purified using preparative TLC plates (AcOEt/$CHCl_3$, 1:1) to afford chlorin **23** (21.8 mg, 0.040 mmol) in 16% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.41 (s, 1H, NH), -1.34 (s, 1H, NH), 4.23 (s, 4H, H_7 H_8), 7.84 (d, J_3=4.9 Hz, 2H, $H_{f'}$), 8.03 (m, 4H, H_f), 8.21 (d, *J*=4.8 Hz, 1H, H_{13}), 8.25 (d, *J*=4.7 Hz, 1H, H_2), 8.39 (s, 2H, H_7 H_8), 8.59 (d, *J*=4.7 Hz, 1H, H_{12}), 8.64 (d, *J*=4.8 Hz, 1H, H_3), 8.99 (m, 6H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 35.35 (1C, C_7/C_8), 35.95 (1C, C_7/$_8$), 95.5 (1C, C_5), 110.5 (1C, C_{10}), 121.14, 121.24 (2C, C_{15} C_{20}), 122.4 (1C, C_2), 124.1 (1C, C_{13}), 127.5 (2C, $C_{f'}$), 128.8 (4C, C_f), 128.9 (1C, C_{12}), 129.2 (1C, C_3), 132.7 (2C, C_7/$_8$), 134.68, 134.80 (2C, C_{14} C_1), 140.11 (1C, C_{11}), 140.65 (1C, C_4), 148.66, 148.67 (4C, C_g), 149.7 (1C, C_e), 149.8 (1C, C_e), 150.2 (2C, $C_{g'}$), 150.7 (1C, C_e), 152.0, 152.1 (2C, C_{16} C_{19}), 167.81 (1C, C_9), 167.98 (1C, C_6). In ^{13}C NMR pentafluorophenyl signals were not observed due to C-F coupling. ESI-HR *m/z*: calcd.exact mass for $C_{41}H_{25}F_5N_7$: 710.2086 $[M+H]^+$, found: 710.2086 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 416 (5.23), 514 (4.12), 542 (3.74), 600 (3.67), 655 (4.43).

5,10-bis(4-methoxyphenyl)-15,20-bis(4-pyridyl)-17,18-dihydroporphyrin (24). The crude product mixture was purified using preparative TLC plates (CH_2Cl_2/MeOH, 95:5) to afford a regioisomeric mixture of 5,10-bis(4-methoxyphenyl)-15,20-bis(4-pyridyl)-17,18-dihydroporphyrin and 5,10-bis(4-methoxyphenyl)-15,20-bis(4-pyridyl)-12,13-dihydroporphyrin in a ratio 7:3 (22 mg, 0.032 mmol, 43%). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.26 (s, 2H, NH), 4.04 (s, 6H, OCH_3), 4.12 (s, 4H, H_{17} H_{18}), 7.21 (d, *J*=8.6 Hz, 4H, H_c), 7.81 (d, *J*=5.8 Hz, 4H, H_f), 7.99 (d, *J*=8.7 Hz, 4H, H_b), 8.09 (d, *J*=5.1 Hz, 2H, H_2 H_{13}), 8.43 (s, 2H, H_7 H_8), 8.62 (d, *J*=4.9 Hz, 2H, H_3 H_{12}), 8.93 (m, 4H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 35.6 (2C, C_{17}/C_{18}), 55.5 (2C, OCH_3), 109.0 (2C, C_{15} C_{20}), 112.3 (4C, C_b), 122.5 (2C, C_2 C_{13}), 123.8 (2C, C_5 C_{10}), 127.5 (4C, C_f), 128.9 (2C, C_3 C_{12}), 132.4 (2C, C_8, C_7), 134.1 (2C, C_a), 134.9 (4C, C_c), 135.5 (2C, C_4 C_{11}), 139.8 (2C, C_{14} C_1), 149.7 (4C, C_g), 151.3 (2C, C_e), 153.3 (2C, C_6 C_9), 159.5 (2C, C_d), 165.8 (2C, C_{16} C_{19}). ESI-HRMS *m/z*: calcd.exact mass for $C_{44}H_{35}N_6O_2$: 679.2816 $[M+H]^+$, found: 679.2808 $[M+H]^+$. UV-vis (CH_2Cl_2) λ_{max} 420, 519, 548, 598, 652 nm.

5,10-Bis(3-methoxyphenyl)-15,20-bis(4-pyridyl)-17,18-dihydroporphyrin (25). The crude product mixture was partially purified using preparative TLC plates (CH_2Cl_2/MeOH, 97:3) to afford a mixture (28 mg) of the both regioisomeric 5,10-bis(3-methoxyphenyl)-15,20-bis(4-pyridyl)-17,18-dihydroporphyrin and 5,10-bis(3-methoxyphenyl)-15,20-bis(4-pyridyl)-12,13-dihydroporphyrin in a ratio 6:4 and starting porphyrin **12** in a ratio 84:16. The chlorin **25** (0.027 mmol) was obtained in 36% yield. Yields and ratio of compounds were determined using the integrals of the signals of pyridyl protons in 1H NMR spectrum. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm -1.34 (s, 2H, NH), 3.94 (s, 6H, OCH_3), 4.15 (s, 4H, H_{17} H_{18}), 7.27 (dd, J_3=8.6 Hz, J_4=1.5 Hz, 2H, H_d), 7.58 (t, J_3=7.9 Hz, 2H, H_c), 7.67 (m, 4H, H_b), 7.83 (m, 4H, H_f), 8.11 (d, *J*=4.8 Hz, 2H, H_2 H_{13}), 8.45 (s, 2H, H_7 H_8), 8.65 (d, *J*=4.6 Hz, 2H, H_3 H_{12}), 8.96 (m, 4H, H_g). ESI-HRMS *m/z*: calcd.exact mass for $C_{44}H_{35}N_6O_2$: 679.2816 $[M+H]^+$, found: 679.2807 $[M+H]^+$. UV-vis (CH_2Cl_2) λ_{max} 418, 515, 545, 596, 652 nm.

5,10-Bis(2-methoxyphenyl)-15,20-bis(4-pyridyl)-17,18-dihydroporphyrin (26). The crude product mixture was purified using preparative TLC plates (CH_2Cl_2/MeOH, 95:5) to afford 5,10-bis(2-methoxyphenyl)-15,20-bis(4-pyridyl)-17,18-dihydroporphyrin (**26**) (11.5 mg, 0.017 mmol) in 48% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm -1.30 (s, 2H, NH), 3.59 (s, 3H, OCH_3), 3.61 (s, 3H, OCH_3), 3.94 (s, 6H, OCH_3), 4.13 (s, 4H, H_{17} H_{18}), 7.27 (m, 4H,

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H_c $H_{c'}$), 7.70 (dt, J_3=8.0 Hz, J_4=1.6 Hz, 2H, H_d), 7.82 (m, 4H, H_f), 7.85 (dd, J_3=7.5 Hz, J_4=1.7 Hz, 1H, H_b), 7.88 (dd, J_3=7.2 Hz, J_4=1.4 Hz, 1H, H_b), 8.07 (d, J=4.8 Hz, 2H, H_2 H_{13}), 8.33 (s, 2H, H_7 H_8), 8.52 (d, J=4.6 Hz, 2H, H_3 H_{12}), 8.94 (d, J=4.8 Hz, 4H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 35.6 (2C, C_{17}/C_{18}), 55.8 (2C, OCH_3), 109.05 109.07 (2C, C_{15} C_{20}), 110.9 (2C, C_b), 119.43, 119.46 (2C, $C_{c'}$), 119.7 (2C, C_2 C_{13}), 122.45, 122,47 (2C, C_5 C_{10}), 127.6 (4C, C_f), 128.17, 128.20 (2C, C_3 C_{12}), 129.8 (2C, C_d), 130.55, 130.57 (2C, C_a), 132.20, 132.22 (2C, C_8, C_7), 134.88, 134.95 (2C, C_c), 135.30, 135.31 (2C, C_4 C_{11}), 139.5 (2C, C_{14} C_1), 149.6 (4C, C_g), 151.5 (2C, C_e), 153.3 (2C, C_6 C_9), 159.14, 159,20 (2C, C_d), 165.3 (2C, C_{16} C_{19}). ESI-HRMS *m/z*: calcd.exact mass for $C_{44}H_{35}N_6O_2$: 679.2816 $[M+H]^+$, found: 679.2811 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 418 (4.94), 515 (3.89), 541 (3.71), 599 (3.45), 653 (4.23).

5,10-Bis(4-iodophenyl)-15,20-bis(4-pyridyl)-17,18-dihydroporphyrin (27). The crude product mixture was purified using preparative TLC plates (CH_2Cl_2/MeOH, 97:3) to afford a regioisomeric mixture of 5,10-bis(4-iodophenyl)-15,20-bis(4-pyridyl)-17,18-dihydroporphyrin and 5,10-bis(4-iodophenyl)-15,20-bis(4-pyridyl)-12,13-dihydroporphyrin in a ratio 55:45 (12.5 mg, 0.012 mmol, 45%). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.43 (s, 2H, NH), 4.16 (s, 4H, H_{17} H_{18}), 7.79 (d, J=8.0 Hz, 4H, H_c), 7.82 (m, 4H, H_f), 8.02 (d, J=8.1 Hz, 4H, H_b), 8.14 (d, J=4.6 Hz, 2H, H_2 H_{13}), 8.39 (s, 2H, H_7 H_8), 8.59 (d, J=4.6 Hz, 2H, H_3 H_{12}), 8.97 (m, 4H, H_g). ESI-HRMS *m/z*: calcd.exact mass for $C_{42}H_{29}I_2N_6$: 871.0538 $[M+H]^+$, found: 871.0535 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 419 (5.13), 517 (4.00), 545 (3.82), 599 (3.56), 653 (4.31).

5,10-bis(pentafluorophenyl)-15,20-bis(4-pyridyl)-7,8-dihydroporphyrin (28) and 5,10-bis(pentafluorophenyl)-15,20-bis(4-pyridyl)-2,3,7,8-tetrahydroporphyrin (29). The crude product mixture was purified using preparative TLC plates (CH_2Cl_2/Ethyl acetate 5/5) to afford a mixture (10.2 mg) of 5,10-bis(pentafluorophenyl)-15,20-bis(4-pyridyl)-7,8-dihydroporphyrin **28** (0.010 mmol, 9.6%) and 5,10-bis(pentafluorophenyl)-15,20-bis(4-pyridyl)-2,3,7,8-tetrahydroporphyrin **29** (0.003 mmol, 3.2%).

28: ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.21 (s, 2H, NH), 4.26 (s, 4H, H_7 H_8), 8.04 (d, J=5.0 Hz, 4H, H_f), 8.23 (d, J=4.7 Hz, 2H, H_2 H_{13}), 8.35 (s, 2H, H_{17} H_{18}), 8.62 (d, J=4.8 Hz, 2H, H_3 H_{12}), 8.97 (d, J=4.4 Hz, 4H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 35.0 (2C, C_7 C_8), 95.4 (2C, C_5 C_{10}), 121.7 (2C, C_{15} C_{20}), 122.4 (2C, C_2 C_{13}), 128.6 (4C, C_f), 129.40 (2C, C_3 C_{12}), 132.6 (2C, C_{17} C_{18}), 134.6 (2C, C_1 C_{14}), 140.5 (2C, C_4 C_{11}), 148.3 (4C, C_g), 149.5 (2C, C_e), 152.0 (2C, C_{16} C_{19}), 168.6 (2C, C_6 C_9). In ^{13}C NMR pentafluorophenyl signals were not observed due to C-F coupling. ESI-HRMS *m/z*: calcd.exact mass for $C_{42}H_{21}F_{10}N_6$: 799.1663 $[M+H]^+$, found: 799.1659 $[M+H]^+$.

29: ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm 3.35 (s, 4H, $H_{\beta\text{-pyrrolic}}$), 3.40 (s, 4H, $H_{\beta\text{-pyrrolic}}$), 6.87 (d, J=4.5 Hz, 1H, $H_{\beta\text{-pyrrolic}}$), 6.93 (d, J=4.4 Hz, 1H, $H_{\beta\text{-pyrrolic}}$), 7.35 (d, J=4.5 Hz, 1H, $H_{\beta\text{-pyrrolic}}$), 7.40 (d, J=4.5 Hz, 1H, $H_{\beta\text{-pyrrolic}}$), 7.55 (d, J=4.2 Hz, 2H, H_f), 7.70 (d, J=4.9 Hz, 2H, H_f), 8.80 (d, J=3.8 Hz, 4H, H_g). ESI-HRMS *m/z*: calcd.exact mass for $C_{42}H_{23}F_{10}N_6$: 801.1819 $[M+H]^+$, found: 801.1780 $[M+H]^+$.

5,10,15,20-tetra(4-pyridyl)-2,3-dihydroporphyrin (30), 5,10,15,20-tetra(4-pyridyl)-2,3,12,13-tetrahydroporphyrin (31) and 5,10,15,20-tetra(4-pyridyl)-2,3,17,18-tetrahydroporphyrin (32).

30: ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.56 (s, 2H, NH), 4.20 (s, 4H, H_2 H_3), 7.84 (d, J=5.7 Hz, 4H, H_f), 8.04 (d, J=5.7 Hz, 4H, H_f), 8.22 (d, J=4.7 Hz, 2H, H_7 H_{18}), 8.40 (s, 2H, H_{12} H_{13}), 8.59 (d, J=4.8 Hz, 2H, H_8 H_{17}), 8.97 (d,

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J=4.7 Hz, 4H, H_g), 8.98 (d, *J*=5.0 Hz, 4H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 35.9 (2C, C_2 C_3), 110.3 (4C, C_{meso}), 123.7 (2C, C_7 C_{18}), 127.4 (4C, C_f), 128.2 (2C, C_8 C_{17}), 128.7 (4C, C_f), 132.3 (2C, C_{12} C_{13}), 134.5 (2C, C_9 C_{16}), 139.9 (2C, C_6 C_{19}), 148.3 (4C, C_g), 149.80 (4C, C_g), 149.84 (2C, C_e), 150.8 (2C, C_e), 151.7 (2C, C_{11} C_{14}), 166.8 (2C, C_1 C_4). ESI-HRMS *m/z*: calcd.exact mass for $C_{40}H_{29}N_8$: 621.2510 $[M+H]^+$, found: 621.2501 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 417 (5.15), 516 (4.03), 543 (3.71), 599 (3.54), 654 (4.31).

31: ^{1}H NMR (500 MHz, $CDCl_3$/MeOD 9:1): δ_H,ppm 4.01 (s, 8H, $H_{\beta\text{-pyrrolic}}$), 7.82 (d, *J*=5.9 Hz, 8H, H_f), 7.95 (s, 4H, $H_{\beta\text{-pyrrolic}}$), 8.90 (d, *J*=5.9 Hz, 8H, H_g).

32: ^{1}H NMR (500 MHz, $CDCl_3$/MeOD 9:1): δ_H,ppm 3.32 (m, 8H, $H_{\beta\text{-pyrrolic}}$), 6.90 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 7.36 (d, *J*=4.4 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 7.48 (d, *J*=6.0 Hz, 2H, H_f), 7.58 (d, *J*=6.1 Hz, 4H, H_f), 7.74 (d, *J*=6.0 Hz, 2H, H_f), 8.77 (m, 8H, H_g). ESI-HRMS *m/z*: calcd.exact mass for $C_{40}H_{31}N_8$: 623.2666 $[M+H]^+$, found: 623.2664 $[M+H]^+$.

5-(4-aminophenyl)-10,15,20-tris(3-pyridyl)porphyrin (9NH$_2$). Purple solid (92 mg, 97% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -2.75 (s, 2H, NH), 3.98 (s, 2H, NH_2), 6.99 (d, *J*=8.3 Hz, 2H, H_c), 7.70 (dd, *J*=5.3 Hz, *J*=7.2 Hz, 3H, H_g), 7.95 (d, *J*=8.0 Hz, 2H, H_b), 8.50 (d, *J*=7.4 Hz, 3H, H_f), 8.79 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 8.84 (s, 4H, $H_{\beta\text{-pyrrolic}}$), 9.01 (d, *J*=4.6 Hz, 2H, $H_{\beta\text{-pyrrolic}}$), 9.03 (dd, *J*=4.9 Hz, *J*=1.2 Hz, 3H, H_h), 9.47 (s, 3H, $H_{f'}$). δ_C, ppm 113.6 (2C, C_b), 115.9 (1C, C_{15}), 116.4 (2C, C_{10} C_{20}), 122.2 (3C, C_g), 122.5 (1C, C_5), 131.1 (6C, $C_{\beta\text{-pyrrolic}}$), 131.8 (1C, C_a), 132.3 (2C, $C_{\beta\text{-pyrrolic}}$), 136.0 (2C, C_c), 138.0 (1C, C_e), 138.1 (2C, C_e), 141.1 (3C, C_f), 146.6 (1C, C_d), 149.3 (3C, C_h), 153.8 (3C, $C_{f'}$) Quaternary carbons at the α-position are missing. ESI-HR *m/z*: calcd.exact mass for $C_{41}H_{29}N_7$: 633.2510 $[M+H]^+$, found: 633.2507 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 420 (5.16), 518 (3.86), 555 (3.61), 593 (3.37), 650 (3.30).

5-(4-aminophenyl)-10,15,20-tris(2-pyridyl)-17,18-dihydroporphyrin (33). The crude product mixture was purified using preparative TLC plates (CH_2Cl_2/MeOH, 97:3) to afford chlorin **33** (51.5 mg, 0.081 mmol) in 54% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.27 (s, 2H, NH), 4.20 (bs, 6H, NH_2 H_{17} H_{18}), 6.98 (d, *J*=8.3 Hz, 2H, H_c), 7.57 (m, 2H, H_g), 7.62 (m, 1H, H_g), 7.87 (m, 4H, H_b $H_{g'}$), 8.01 (m, 3H, H_h), 8.11 (m, 2H, $H_{g'}$ H_2), 8.15 (d, *J*=4.9 Hz, 1H, $H_{12/13}$), 8.33 (d, *J*=4.5 Hz, 1H, H_8), 8.51 (d, *J*=4.5 Hz, 1H, H_7), 8.57 (d, *J*=4.9 Hz, 1H, $H_{12/13}$), 8.68 (d, *J*=4.8 Hz, 1H, H_3), 9.01 (m, 2H, H_f), 9.05 (d, *J*=4.8 Hz, 1H, H_f). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 34.8 (1C, C_{17}/C_{18}), 35.1 (1C, C_{17}/C_{18}), 111.1 (1C, C_{20}), 111.3 (1C, C_{15}), 113.5 (2C, C_b), 121.0 (1C, C_{10}), 122.2 (1C, C_2), 122.3 (3C, C_g), 123.1 (1C, C_{12}/C_{13}), 124.3 (1C, C_5), 127.89, 127.97, 128.04 (3C, $C_{g'}$ C_{12}/C_{13}), 128.7 (1C, C_3), 129.6, (1C, $C_{g'}$), 131.1 (1C, C_8), 132.2 (1C, C_d), 132.7 (1C, C_7), 134.7 (1C, C_{11}), 134.8 (1C, C_4), 135.1 (2C, C_c), 135.6 (1C, C_h), 136.0 (2C, C_h), 140.4, 140.6 (2C, C_{14}, C_1), 146.0 (1C, C_a), 148.5 (1C, C_f), 149.26, 149.28 (2C, C_f), 152.0 (1C, C_9), 153.1 (1C, C_6), 160.7 (1C, C_e), 161.5 (1C, C_e), 161.7 (1C, C_e), 166.9 (1C, C_{19}), 167.8 (1C, C_{16}). ESI-HR *m/z*: calcd.exact mass for $C_{41}H_{31}N_8$: 635.2666 $[M+H]^+$, found: 635.2660 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 422 (5.09), 518 (3.99), 548 (3.81), 598 (3.58), 653 (4.28).

Functionalization of 5-(4-aminophenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (17)

5-(4-azidophenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (34). 5-(4-aminophenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (**17**) (121.7 mg, 0.192 mmol) was dissolved in trifluoroacetic acid (1.2 mL) and

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cooled at 0 ˚C. A solution of sodium nitrite (27.5 mg, 0.40 mmol) in water (0.5 mL) was added dropwise. The mixture was stirred for 15 minutes at 0 ˚C before adding dropwise a solution of sodium azide (51.3 mg, 0.79 mmol) in water (0.5 mL). The reaction mixture was stirred at 0 ˚C for 1 hour. The mixture was diluted with water and neutralized with saturated sodium bicarbonate solution. The aqueous mixture was extracted three times with chloroform (3 x 20 mL), and the organic layer dried over magnesium sulfate. The solvent was removed under reduced pressure. The crude was purified by column chromatography (CH_2Cl_2/MeOH, 97:3) to afford chlorin **34** (33.3 mg, 0.050 mmol) in 26% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H,ppm -1.44 (s, 2H, NH), 4.17 (s, 4H, H_{17} H_{18}), 7.34 (d, *J*=8.0 Hz, 2H, H_c), 7.81 (m, 4H, $H_{f'}$), 8.03 (d, *J*=5.5 Hz, 2H, $H_{f'}$), 8.05 (d, *J*=8.5 Hz, 2H, H_b), 8.17 (d, *J*=5.0 Hz, 1H, H_2), 8.19 (d, *J*=5.0Hz, 1H, $H_{12/13}$), 8.36 (d, *J*=4.5 Hz, 1H, H_8), 8.44 (d, *J*=4.0 Hz, 1H, $H_{12/13}$), 8.56 (d, *J*=4.5 Hz, 1H, H_7), 8.62 (d, *J*=4.5 Hz, 1H, H_3), 8.96 (m, 6H, H_g). ESI-HR m/z: calcd.exact mass for $C_{41}H_{29}N_{10}$: 661.2571 $[M+H]^+$, found: 661.2572 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 418 (5.35), 518 (4.22), 543 (4.01), 599 (3.75), 653 (4.49).

Compound 35. 5-(4-aminophenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (**17**) (53.6 mg, 0.084 mmol) was dissolved in dry dichloromethane (7 mL). Glutaric anhydride (18 mg, 1.58 mmol) was added. The mixture was stirred for 20h at room temperature. The solvent was removed under reduced pressure. The crude product mixture was purified using preparative TLC plates (CH_2Cl_2/MeOH, 95:5) to afford chlorin **35** (49.2 mg, 0.065 mmol) in 77% yield. ^{1}H NMR (500 MHz, $CDCl_3$/MeOD 9:1): δ_H,ppm -1.43 (s, 2H, NH), 2.16 (quin, *J*=7.0 Hz, 2H, CH_2), 2.55 (t, *J*=6.9 Hz, 2H, CH_2), 2.60 (t, *J*=7.4 Hz, 2H, CH_2), 3.40 (m, 1H, NH), 4.16 (s, 4H, H_{17} H_{18}), 7.87 (d, *J*=4.6 Hz, 2H, H_f), 7.88 (d, *J*=4.5 Hz, 2H, H_f), 7.92 (d, *J*=8.2 Hz, 2H, H_c), 8.02 (d, *J*=8.2 Hz, 2H, H_b), 8.07 (d, *J*=5.7 Hz, 2H, $H_{f'}$), 8.13 (d, *J*=4.8 Hz, 1H, H_2), 8.17 (d, *J*=4.9 Hz, 1H, $H_{12/13}$), 8.32 (d, *J*=4.7 Hz, 1H, H_8), 8.49 (d, *J*=4.4 Hz, 1H, $H_{12/13}$), 8.54 (d, *J*=4.8 Hz, 1H, H_7), 8.68 (d, *J*=4.7 Hz, 1H, H_3), 8.93 (m, 6H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$/MeOD 9:1): δ_C, ppm 21.1 (1C, CH_2), 33.2 (1C, CH_2), 35.8 (1C, C_{17}/C_{18}), 35.9 (1C, C_{17}/C_{18}), 36.5 (1C, CH_2), 109.5 (1C, C_{20}), 109.7 (1C, C_{15}), 118.2 (2C, C_b), 119.8 (1C, C_{10}), 123.1 (1C, C_2), 123.4 (1C, C_{12}/C_{13}), 124.1 (1C, C_5), 127.8 (4C, C_f), 128.0 (1C, C_{12}/C_{13}), 129.0 (2C, $C_{f'}$), 129.3 (1C, C_3), 131.7 (1C, C_8), 133.2 (1C, C_7), 133.9 (1C, C_{11}), 134.4 (2C, C_c), 135.6 (1C, C_4), 136.9 (1C, C_d), 138.4 (1C, C_a), 139.64, 139.74 (2C, C_{14}, C_1), 147.66 (2C, $C_{g'}$), 149.10 (2C, C_g), 149.16 (2C, C_g), 150.9 (1C, C_e), 151.4 (1C, C_e), 151.8 (1C, C_e), 152.0 (1C, C_9), 153.4 (1C, C_6), 166.8 (1C, C_{19}), 166.5 (1C, C_{16}), 171.9 (1C, C=O), 176.2 (1C, C=O). ESI-HR m/z: calcd.exact mass for $C_{46}H_{37}N_8O_3$: 749.2983 $[M+H]^+$, found: 749.2979 $[M+H]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 419 (4.98), 517 (3.84), 545 (3.69), 599 (3.43), 653 (4.12).

Compound 36. A solution of (3-carboxypropyl)triphenylphosphonium bromide (202 mg, 0.471 mmol) in dichloromethane (5 mL) was cooled to 0 °C. Triethylamine (0.077 mL, 0.552 mmol) and ethylchloroformate (0.054 mL, 0.565 mmol) were added. The reaction mixture was stirred for 30 min and then transferred to a solution in another flask containing 5-(4-aminophenyl)-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrin (**17**) (45 mg, 0.071 mmol) dissolved in dichloromethane (5 mL) and triethylamine (0.077 mL, 0.552 mmol) at 0 °C. Stirring was continued for 1 h at the same temperature and allowed to reach at room temperature for another 1 h. After completion of the reaction, water (5 mL) was added into the reaction mixture and basified to pH ~ 8 with sodium

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carbonate and extracted with chloroform (3 × 25 mL). The solvent was evaporated and purified on a silica gel column chromatography (CH_2Cl_2/MeOH, 94:6) to produce compound **36** (35 mg, 0,034 mmol) in 48% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H, ppm -1.42 (s, 2H, NH), 2.21 (m, 2H, CH_2), 3.21 (m, 2H, CH_2CO), 3.82 (t, *J*=16.2 Hz, 2H, CH_2P), 4.16 (s, 4H, H_{17} H_{18}), 7.76 (m, 6H, H_{Ph}), 7.84 (m, 13H, H_{Ph} $H_{f'}$), 7.99 (d, J=8.2 Hz, 2H, H_b), 8.03 (d, J=4.8 Hz, 2H, H_f), 8.12 (d, J=4.6 Hz, 1H, H_2), 8.16 (d, J=4.5 Hz, 1H, $H_{12/13}$), 8.25 (d, J=8.4 Hz, 2H, H_c), 8.32 (d, J=4.4 Hz, 1H, H_8), 8.52 (d, J=4.6 Hz, 1H, H_7), 8.53 (d, J=5.1 Hz, 1H, $H_{12/13}$), 8.69 (d, J=4.8 Hz, 1H, H_3), 8.96 (m, 6H, H_g), 10.83 (s, 1H, NH). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C, ppm 19.8 (1C, CH_2), 22.0 (d, 1C, CH_2P), 35.71 (1C, C_{17}/C_{18}), 35.77 (1C, C_{17}/C_{18}), 37.2 (d, 1C, CH_2CO), 109.5 (1C, C_{20}), 109.7 (1C, C_{15}), 118.0 (d, 3C, C_{Ph}), 118.5 (2C, C_c), 119.8 (1C, C_{10}), 123.0 (1C, C_2), 123.1 (1C, C_{12}/C_{13}), 124.4 (1C, C_5), 127.5 (4C, $C_{f'}$), 127.8 (1C, C_{12}/C_{13}), 128.7 (2C, C_f), 129.4 (1C, C_3), 130.7, 130.8 (6C, C_{Ph}), 131.6 (1C, C_8), 133.3 (1C, C_7), 133.5, 133.6 (6C, C_{Ph}), 134.0 (1C, C_{11}), 134.2 (2C, C_b), 135.3 (3C, C_{Ph}), 135.8 (1C, C_4), 136.5 (1C, C_d), 139.0 (1C, C_a), 139.7, 139.9 (2C, C_{14}, C_1), 148.2 (2C, C_g), 149.66 (2C, $C_{g'}$), 149.70 (2C, $C_{g'}$), 150.2 (1C, C_e), 151.16 (1C, C_e), 151.24 (1C, C_e), 151.37 (1C, C_9), 153.5 (1C, C_6), 166.0 (1C, C_{19}), 166.3 (1C, C_{16}), 171.2 (1C, C=O). ESI-HR m/z: calcd.exact mass for $C_{63}H_{50}N_8OP$: 965.3840 $[M]^+$, found: 965.3833 $[M]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 420 (5.28), 517 (4.12), 545 (3.96), 599 (3.69), 653 (4.40).

Compound 37. To a solution of compound **36** (16 mg, 0.015 mmol) in dry DMF (1.5 mL) was added methyl iodide (0.187 mL, 3.004 mmol). The reaction mixture was stirred for 24 h at 40 °C. The product was precipitated by addition of a large excess of diethyl ether. It was then filtered and washed well with diethyl ether to afford the chlorin derivative **37** as a brown solid (13 mg, 0.009 mmol) in 60% yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ_H, ppm -1.29 (s, 2H, NH), 1.96 (m, 2H, CH_2), 2.78 (m, 2H, CH_2CO), 3.73 (m, 2H, CH_2P), 4.28 (s, 4H, H_{17} H_{18}), 4.63 (s, 6H, H_{Me}), 4.66 (s, 3H, H_{Me}), 7.83 (m, 6H, H_{Ph}), 7.92 (m, 13H, H_{Ph} $H_{f'}$), 8.11 (d, J=8.5 Hz, 2H, H_b), 8.17 (d, J=8.2 Hz, 2H, H_c), 8.42 (s, 2H, $H_{12/13}$), 8.43 (d, J=5.2 Hz, 1H, H_8), 8.54 (d, J=5.9 Hz, 1H, H_2), 8.71 (d, J=5.2 Hz, 1H, H_7), 8.75 (m, 4H, H_f), 8.83 (d, J=6.5 Hz, 2H, H_f), 8.88 (d, J=5.9 Hz, 1H, H_3), 9.38 (m, 6H, H_g), 10.46 (s, 1H, NH). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C, ppm 18.1 (1C, CH_2), 20.1 (d, 1C, CH_2P), 35.58 (1C, C_{17}/C_{18}), 35.83 (1C, C_{17}/C_{18}), 36.1 (d, 1C, CH_2CO), 47.9 (3C, CH_3), 107.7 (1C, C_{20}), 107.9 (1C, C_{15}), 117.4 (1C, C_{10}), 117.7 (4C, C_c C_d C_5), 118.4 (d, 3C, C_{Ph}), 123.6 (1C, C_8), 124.3 (1C, C_2), 129.1 (1C, C_3), 129.8 (1C, C_7), 130.2, 130.3 (6C, C_{Ph}), 131.0 (4C, $C_{f'}$), 131.4 (2C, C_f), 131.8 (1C, C_{12}/C_{13}), 133.1 (1C, C_4), 133.3 (1C, C_{12}/C_{13}), 133.59, 133.67 (6C, C_{Ph}), 133.9 (2C, C_b), 135.0 (3C, C_{Ph}), 135.1 (1C, C_9), 139.0 (1C, C_6), 139.20 (1C, C_a), 139.29 (1C, C_1), 144.2 (2C, C_g), 145.4 (4C, C_g), 150,0, 152.8 (2C, C_{11} C_{14}), 156.5 (1C, C_e), 157.7 (1C, C_e), 157.9 (1C, C_e), 167.1 (1C, C_{19}), 168.0 (1C, C_{16}), 170.2 (1C, C=O). ESI-HR m/z: calcd.exact mass for $C_{66}H_{59}N_8OP$: 252.6132 $[M]^{4+}$, found: 252.6139 $[M]^{4+}$. UV-vis (MeOH): λ_{max}, nm (log ε) 426 (5.11), 518 (4.08), 550 (3.97), 607 (3.66), 661 (4.33). UV-vis (H_2O): λ_{max}, nm (log ε) 423 (4.47), 521 (3.34), 553 (3.2), 602 (2.93), 655 (3.54).

CONCLUSION

In summary, we have developed a one-step reduction method of porphyrins substituted with two, three or four 2- or 4-pyridyls to corresponding dihydroporphyrins. The reduction of 5-(aryl)-10,15,20-tris(2 or 4-pyridyl)porphyrin

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with tin(II) chloride dihydrate demonstrated good regioselectivity. Porphyrin with one *meso*-aryl substituted with electron-donating groups gave 5-aryl-10,15,20-tris(2- or 4-pyridyl)-17,18-dihydroporphyrins in 17-72% yield. Porphyrin with one *meso*-aryl substituted with electron-withdrawing groups gave 5-aryl-10,15,20-tris(4-pyridyl)-17,18-dihydroporphyrins or 5-aryl-10,15,20-tris(4-pyridyl)-7,8-dihydroporphyrins in 15-21% yield and isobacteriochlorin. It would seem that the reduction occurs on the more electron deficient pyrrole unit. We assumed that protonated 2- or 4-pyridyl substituents play an essential role in the reaction by stabilizing the reaction intermediate. We have also proved the possibility to functionalize these compounds to design new regioisomerically pure photosensitizers.

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Supporting Information:

Supplementary material is available via the Internet at http://www.u-bourgogne.fr/jpp/.

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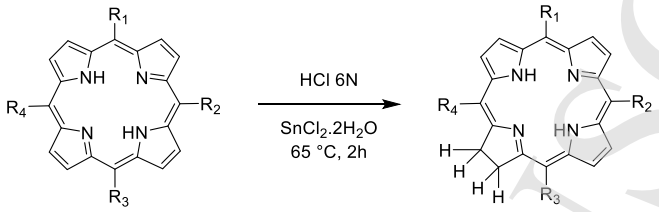
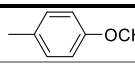
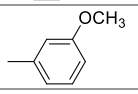
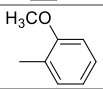
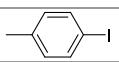
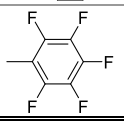
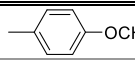
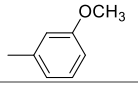
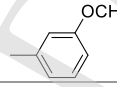
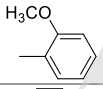
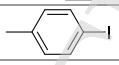
Table 1. Results from various porphyrin reduction using Tin(II) chloride. [a] Presence of a single regioisomer. [b] Presence of residual starting porphyrin. Yields were determined by ^{1}H NMR analysis of the partially purified reaction mixture. [c] Presence of two regioisomers. Regioisomeric ratio was calculated from the integrals of the β-pyrrolic protons. [d] Presence of isobacteriochlorin. Yields of chlorin were determined by ^{1}H NMR analysis.



Porphyrin		Substituents				Chlorin	yield
		R_1	R_2	R_3	R_4		
A_3B	**3**					**18**[a][b]	46%
	4					**19**[a][b]	34%
	5					**20**[a]	17%
	6					**21**[a][b]	34%
	7					**22**[a] [d]	21%
	8					**23**[a] [d]	16%
Cis-A_2B_2	**11**					**24**[b] [c]	43% 7:3 r.r.
	12					**25**[b] [c]	36% 6:4 r.r.
	13					**26**[a]	48%
	14					**27**[b]	45% 5.5:4.5 r.r.
	15					**28**[a][d]	10%
A_4	**1**					**30**	15%

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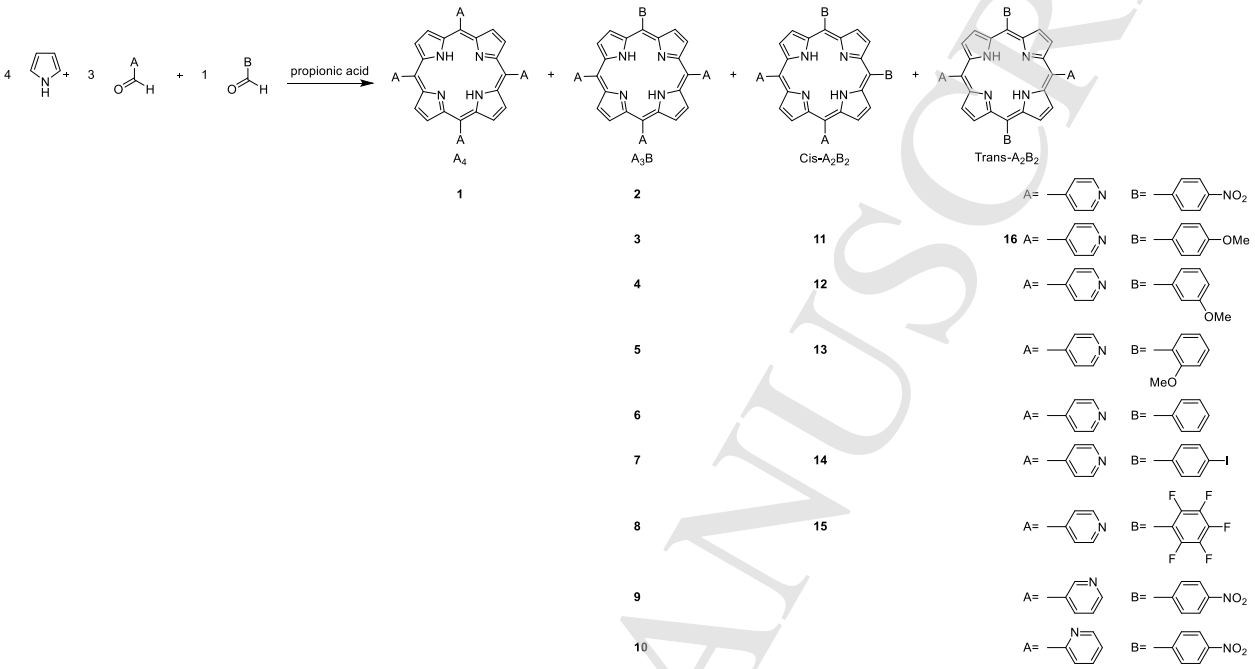

Scheme 1. Synthesis of porphyrins bearing pyridyls and aryls substituents

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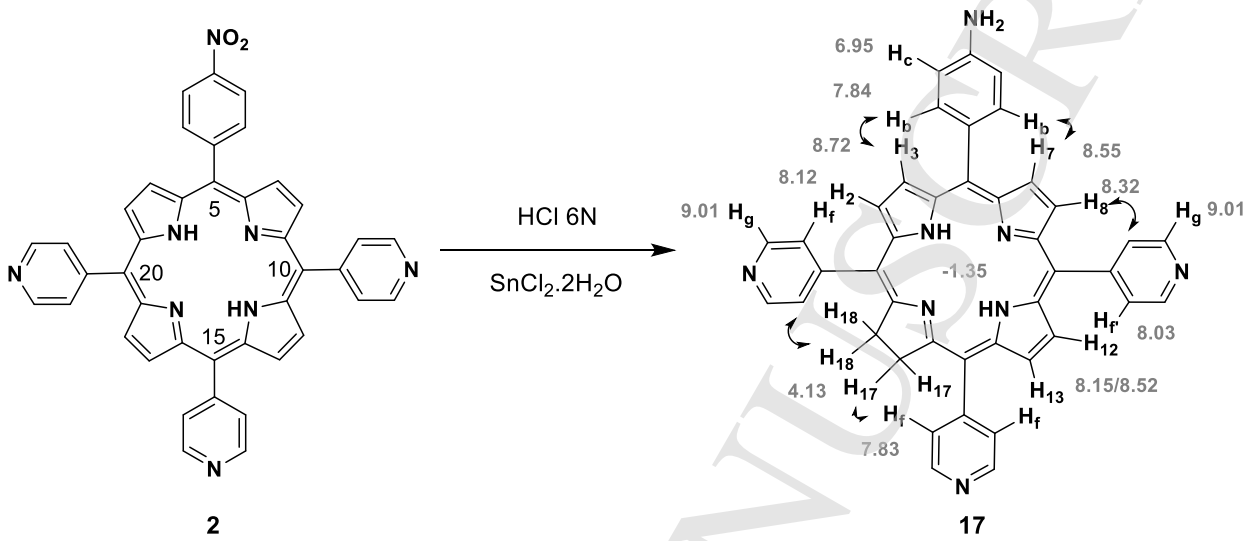

Scheme 2. Synthesis of chlorin **17** and assignments based on the results obtained from the 2D NOESY NMR studies in $CDCl_3$.

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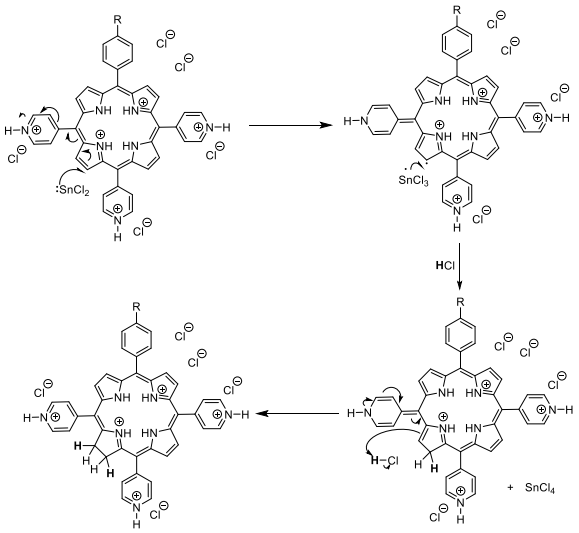

Scheme 3. Proposition of mechanistic pathway for the reduction of porphyrin

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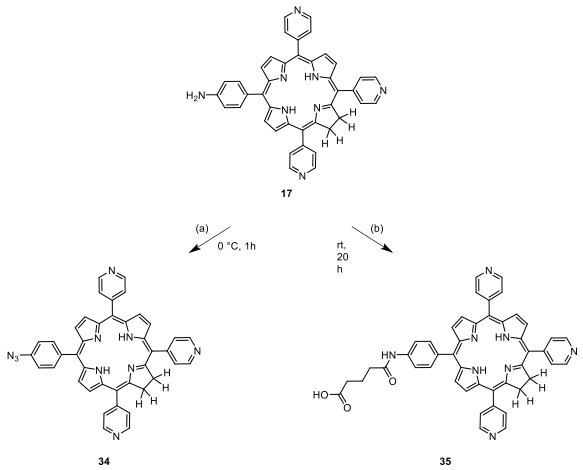

Scheme 4. Reagents and conditions: (a) TFA, $NaNO_2$, H_2O, NaN_3, H_2O; (b) glutaric anhydride, CH_2Cl_2

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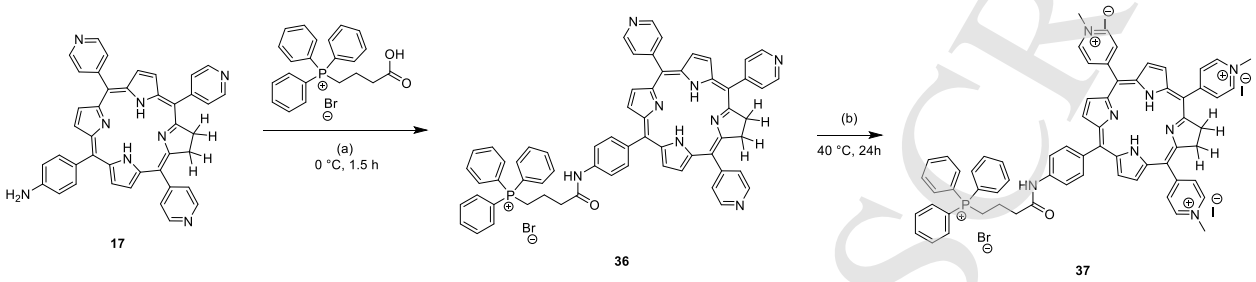

Scheme 5. Reagents and conditions: (a) ClCOOEt, TEA, CH_2Cl_2; (b) excess CH_3I, DMF

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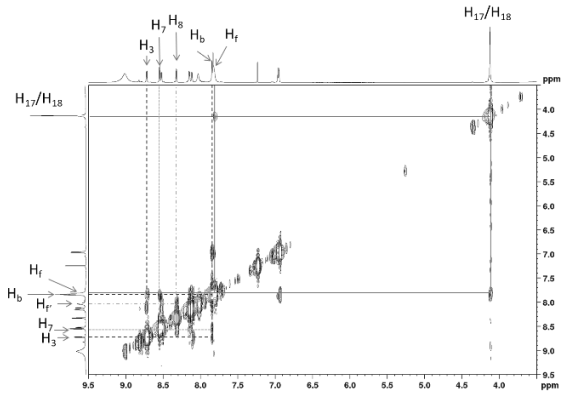

Figure 1. 2D NOESY NMR spectrum of compound **17** in $CDCl_3$

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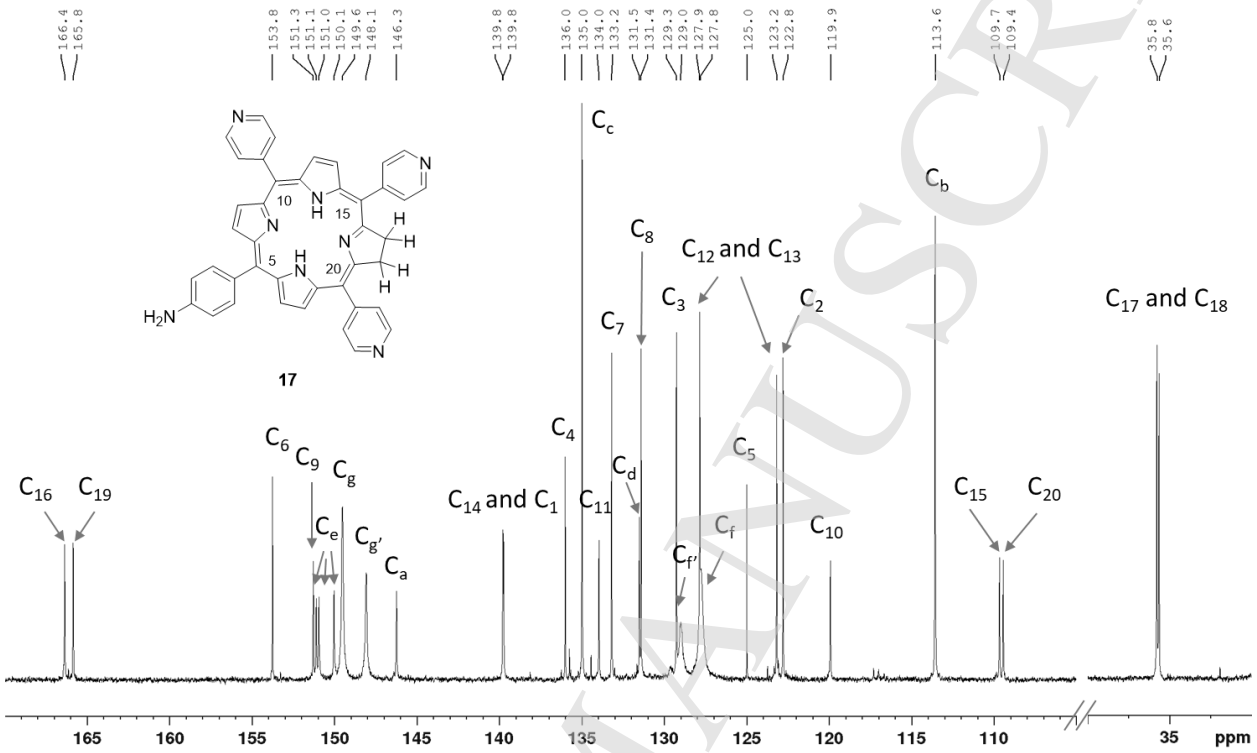

Figure 2. ^{13}C NMR spectrum of compound **17** in $CDCl_3$

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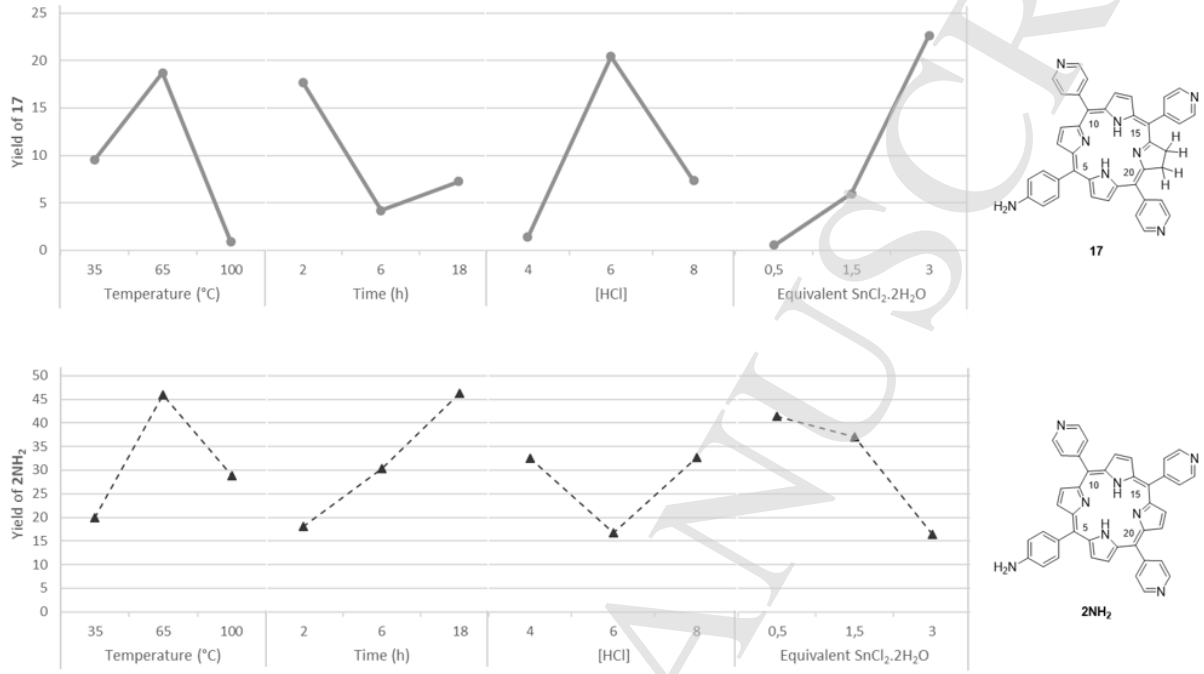

Figure 3. Average effect of temperature, reaction time, HCl concentration and $SnCl_2.2H_2O$ equivalent on yield of chlorin **17** and porphyrin **2**NH_2

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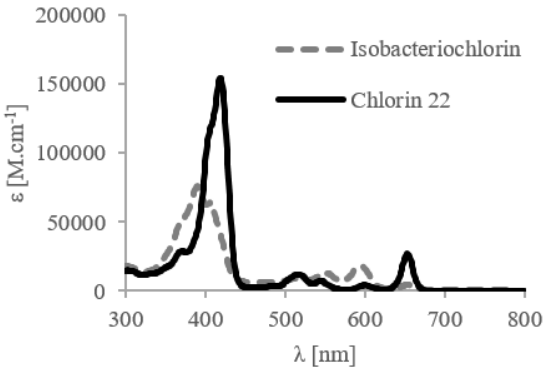

Figure 4. UV-Visible spectra of isobacteriochlorin and chlorin **22** in CH_2Cl_2

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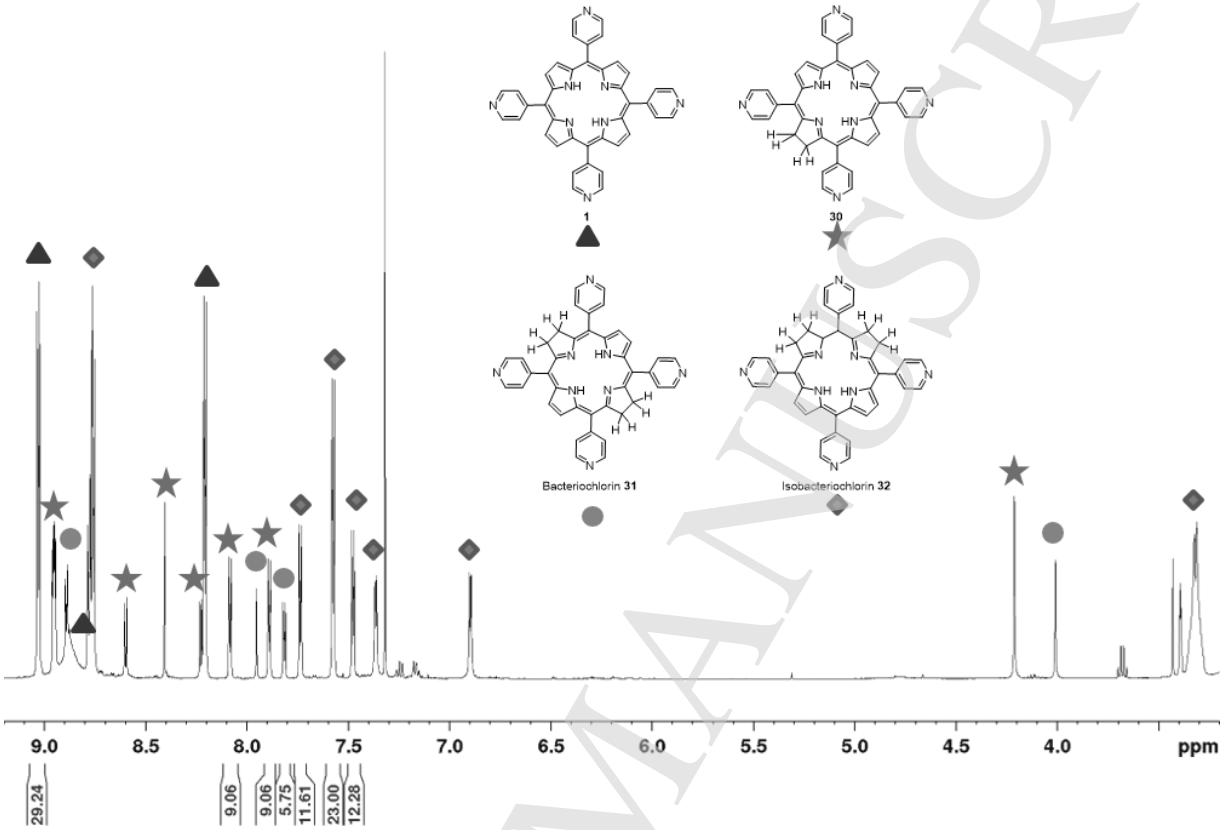

Figure 5. ^{1}H NMR spectrum in $CHCl_3$ of the crude product of the reaction of porphyrin **1** with $SnCl_2.2H_2O$.

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