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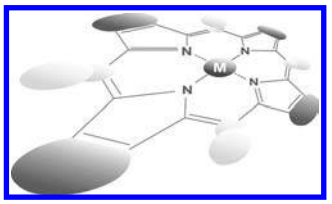

Towards the synthesis of substituted porphyrins by a pyridyl group bearing a reactive functionality

Maya El Ojaimi, Benoit Habermeyer, Claude P. Gros[◊] and Jean-Michel Barbe*[◊]

ICMUB UMR 5260, Université de Bourgogne, 9 avenue Alain Savary, BP 47870, 21078 Dijon Cedex, France

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ABSTRACT: Pyridyl-substituted porphyrins bearing a reactive functionality were prepared *via* Suzuki cross-coupling reactions and resulted in very good yields. These compounds are precursors of new porphyrin architectures able to coordinate two metals: one in the porphyrin core and the second around the pyridyl moiety. During the coupling reactions, a higher reactivity of a chloro picolyl group was evidenced compared to a bromo function on the same reacting molecule.

KEYWORDS: A_3B-porphyrins, pyridyl substituted porphyrins, Suzuki coupling, *meso*-functionalization.

INTRODUCTION

Although porphyrins and their structural variants have been extensively studied by organic chemists, less attention has been devoted during the last decades to the synthesis of unsymmetrical porphyrins functionalized by a reactive group [1–12]. The lack of effective synthesis for this type of compound may be one of the main reasons. On the other hand, there has been an increasing demand for unsymmetrical substituted porphyrins, *i.e.* chiral or amphiphilic porphyrins for various applications in porphyrin-based biomimetic systems, biological studies, catalysis, optics, molecular materials etc. [13–16] and despite a high demand, many applications are currently hampered due to their synthetic inaccessibility. Multistep syntheses are possible for selected types of substituents but still suffer in too many cases from acid-catalyzed scrambling, making them too cumbersome for large-scale synthesis or industrial use.

In the particular case of *meso*-pyridyl substituted porphyrins, the main problem stems from acid-catalyzed protocols which lead to the protonation of the pyridine ring by the acid catalyst, thus inducing deactivation of the catalyst and also precipitation of the pyridinium salt [5]. Lindsey and co-workers developed a step-by-step approach for the synthesis of porphyrins bearing from two to four *meso*-pyridyl groups [17]. It consists of the basic condensation of 1-acyldipyrromethanes in the presence of magnesium bromide. This pathway allows for easy access to *trans*-A_2B_2 and *trans*-A_2-porphyrins [17]. However, mono-*meso*-pyridyl substituted porphyrins are still difficult to obtain.

Here, we show that substituted porphyrins by a pyridyl group bearing a reactive functionality (Chart 1) can be easily prepared in good yields by Suzuki coupling starting from a A_3B-porphyrin. The pyridine nucleus is an ubiquitous structural motif in catalysis, supramolecular chemistry, and medicinal chemistry (…) [18–21]. The search for efficient routes toward pyridine-containing chiral structures is the key to the development of new catalysts for a wide range of enantioselective transformations. Our goal here is to introduce a reactive group on the pyridyl ring in order to further functionalize the molecule by a ligand allowing coordination of a second metal. Indeed, it occurs to us that incorporation of one pyridyl group bearing a reactive functionality at the *meso*-position of the porphyrin macrocycle should offer an efficient entry into novel molecular architectures (*e.g.* new flexible dyads, Scheme 1) by providing a third coordination site. This third metalation site should afford the means by which the flexibility of the tweezer can be modulated and should allow, at the same time, for the introduction of a new factor to the physical studies (*e.g.* closing and opening of the binding pocket).

[◊]SPP full member in good standing

*Correspondence to: Jean-Michel Barbe, email: Jean-Michel.Barbe@u-bourgogne.fr, fax: +33 (0)3 80 39 61 17

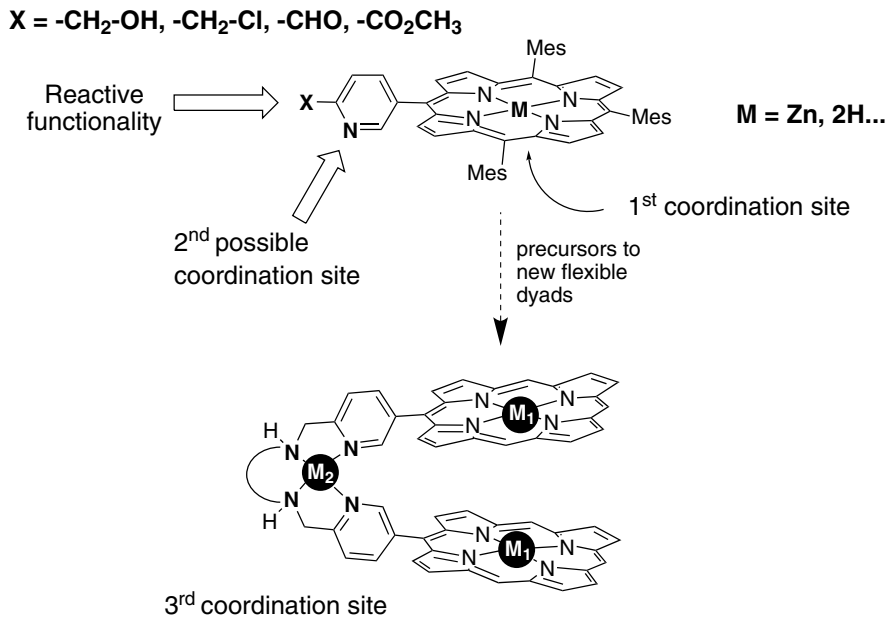
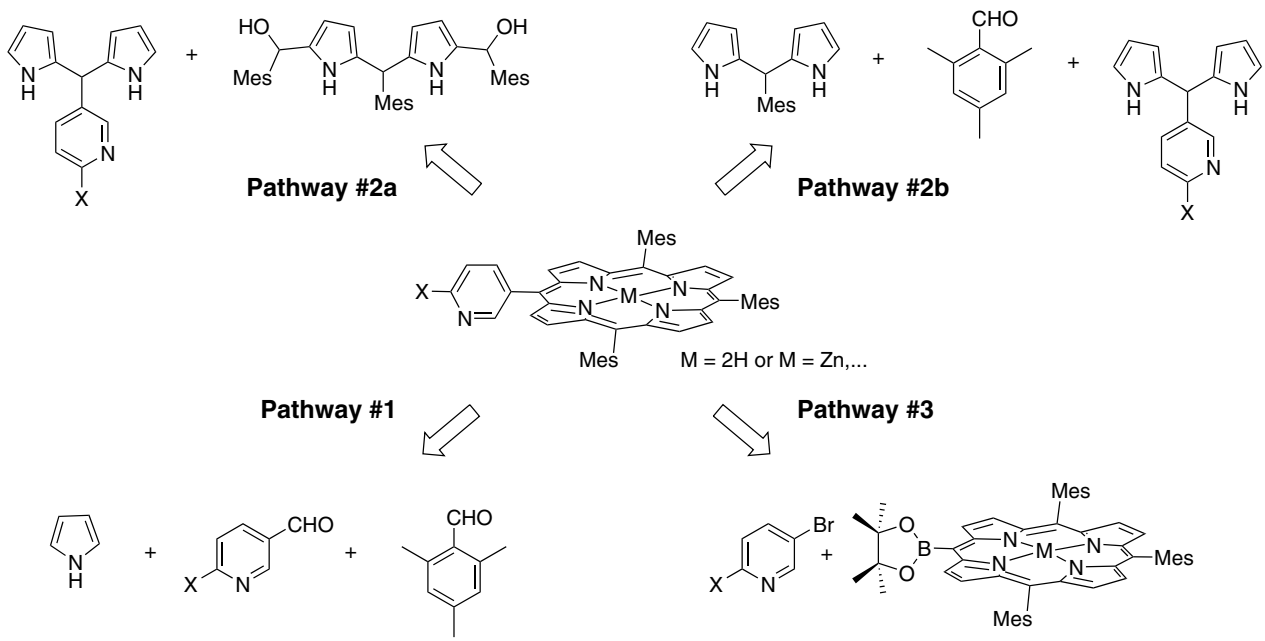


Chart 1. Substituted porphyrin by a pyridyl group bearing a reactive functionality. Possible access to new flexible dyads allowing three-metal coordination



Scheme 1. Different synthetic routes to access the unsymmetrical A_3B type porphyrin

RESULTS AND DISCUSSION

The structures of the studied functionalized porphyrins are described in Chart 2.

Different synthetic routes can be considered in order to access the unsymmetrical A_3B type porphyrins. Four of them are presented in Scheme 1.

The synthesis of the less symmetric A_3B-substituted porphyrin requires the establishment of two types of *meso*-carbon: one bearing the pyridyl substituent and the other an aryl group (*e.g.* mesityl). A variation of the well-known acid-catalyzed synthesis of TPP-like porphyrins (*e.g.* involving pyrrole and two different aldehydes) would, unfortunately, lead to a mixture of six isomers (from A_4-type to B_4-type through A_3B, A_2B_2, AB_3 substitutions, as statistically expected, see pathway 1 in Scheme 1) [22]. Such a mixed condensation reaction often requires laborious and lengthy chromatographic separation that affords only small quantities of the desired porphyrin. Therefore, this approach was not further considered.

Two main syntheses are classically used to prepare A_3B-porphyrins, involving either an A_3-dipyrromethanedicarbinol and a B-dipyrromethane, or a A- and a

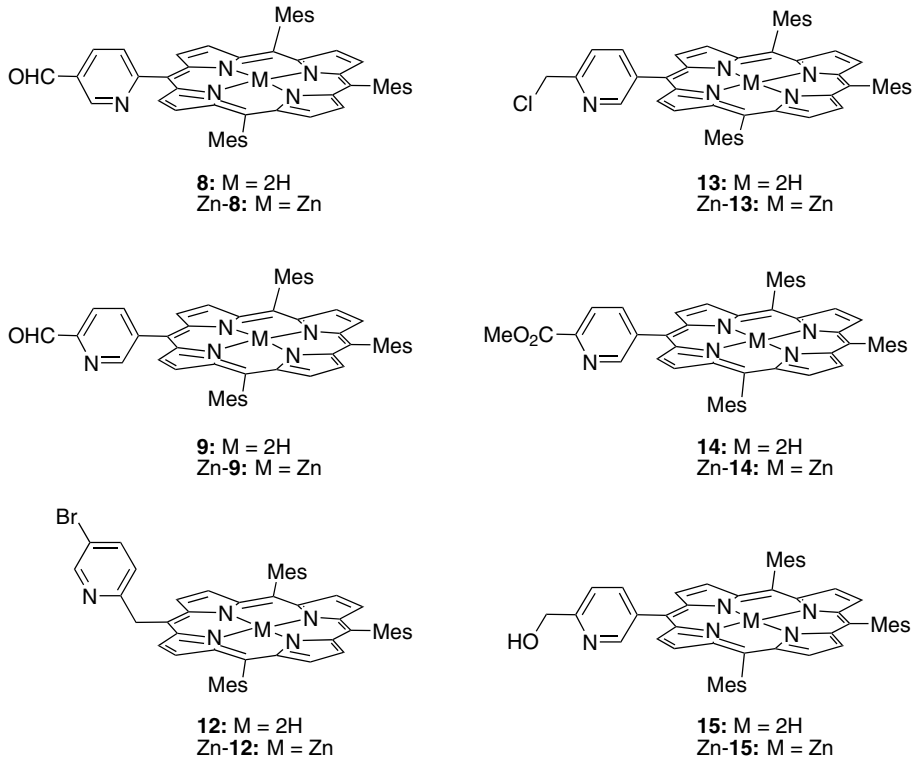


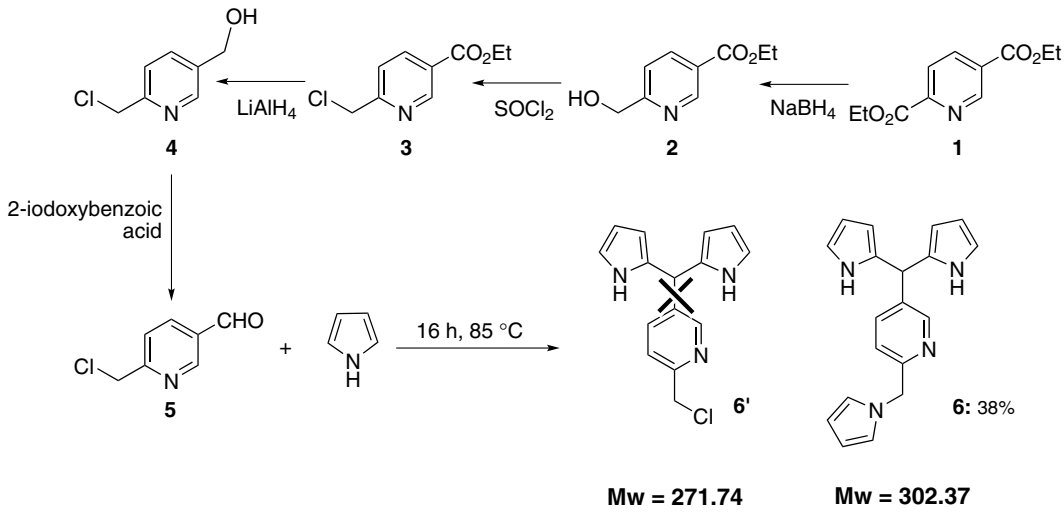
Chart 2. Structures of prepared compounds

B-dipyrromethane with an A-aldehyde (pathways 2a and 2b respectively, Scheme 1). Pathway 2a consists of the condensation of a dipyrrolic compound carrying the linking carbon in the form of a hydroxymesityl group with the α-free substituted pyridyldipyrromethane [23]. Pathway 2b, the acid-catalyzed condensation of two different dipyrromethanes with mesitylaldehyde, is a variation of the classical synthesis of 5,15-diphenylporphyrins. Pathway 2a, when compared to 2b, has the intrinsic disadvantage of requiring additional synthetic steps, and the hydroxymesityl derivatives, prepared generally by reduction of the parent carbonyl compounds, are known to be very sensitive. Finally, the synthesis of the pyridyl-substituted porphyrin can be pursued by a Suzuki coupling route (involving the preparation of a dioxaborolane-porphyrin) to avoid the obvious potential complications of condensation of pyrrole or dipyrromethane with the pyridyl aldehyde derivative [24–33]. However, this synthesis requires more reaction steps than the previous ones.

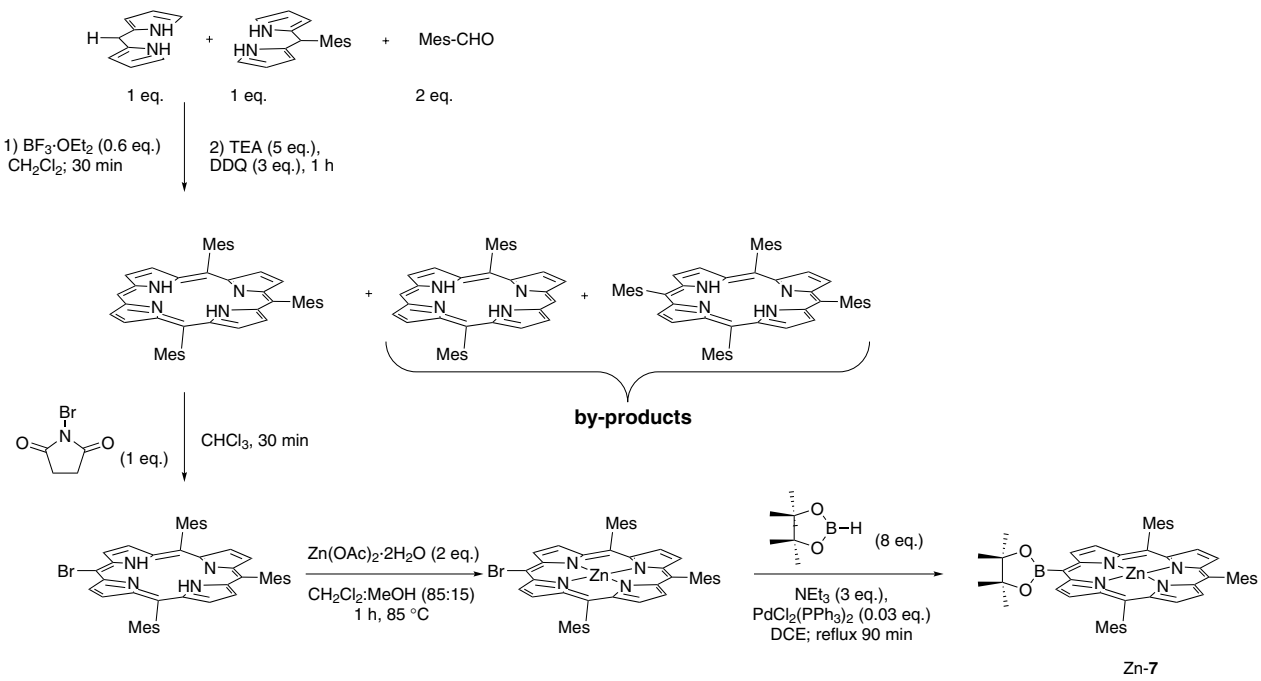
Pathways 2a and 2b both start with the preparation of a pyridyl dipyrromethane bearing a reactive functionality. This latter is generally synthesized in a one-step procedure from pyrrole [34–37] and, in our case, pyridine aldehyde. The key chloromethyl-pyrid-3-yl-carbaldehyde **5** of pathways 2a and 2b was prepared in a four-step procedure starting from the diethyl ester (Scheme 2). The synthetic route to 6-chloromethyl-pyrid-3-yl-carbaldehyde **5** began with reduction of diethyl pyridine-2,5-dicarboxylate **1** to ethyl 6-(hydroxy-methyl)-pyrid-3-yl-carboxylate **2** using sodium borohydride in 66% yield. The resulting hydroxy derivative **2** was further converted to the chloro by thionyl chloride to give **3** in 76% yield. Reduction of **3** with $LiAlH_4$ finally gave the (6-chloromethyl-pyrid-3-yl) methanol **4** (in 83% yield), which was further oxidized to aldehyde **5** in 92% using 2-iodoxybenzoic acid in dry dimethylsulfoxide at room temperature. The overall yield for this four-step procedure is more than 38%.

Our first attempts to prepare the (chloromethyl)pyridyldipyrromethane **6′** by a one-flask reaction of the pyridine aldehyde **5** with pyrrole in the absence of any solvent were unsuccessful (Scheme 2). The general procedure for the preparation of a dipyrromethane usually requires the presence of acid catalysts: TFA, HCl or mild Lewis acid (*i.e.* $BF_3{\cdot}OEt_2$, $InCl_3$, $MgBr_2$) [34–37]. The synthesis can also be performed by heating at high temperature in the absence of any acid but the yield is usually lower [23].

As reported in the literature, acidic medium for heterocyclic aldehydes (specially 2-, 3- or 4-pyridinecarboxylate) is problematic [23]. The pyridylaldehyde **5** was dissolved in excess of pyrrole and heated at 85 °C for 8 h without any catalyst. The resulting dipyrromethane was then purified by filtration through a pad of silica, followed by recrystallization. ^{1}H NMR spectrum showed the disappearance of a peak at about 4.75 ppm (s, 2H, $-CH_2$-Cl) and the appearance of a singlet at 5.87 ppm. In addition, two new doublets at 6.26 and 6.82 ppm corresponding to a *N*-alkylated pyrrole ring were also observed. We concluded that the chloro-leaving group has been removed during the reaction, leading to an *N*-alkylated (pyrrolo)pyridyldipyrromethane **6**. ESI mass spectrometry confirmed the presence of the *N*-alkylated pyrrole (*m/z* = 303.17 $[M + H]^+$ and *m/z* = 325.15 $[M + Na]^+$).



Scheme 2. Tentative synthesis of a pyridyl dipyrromethane



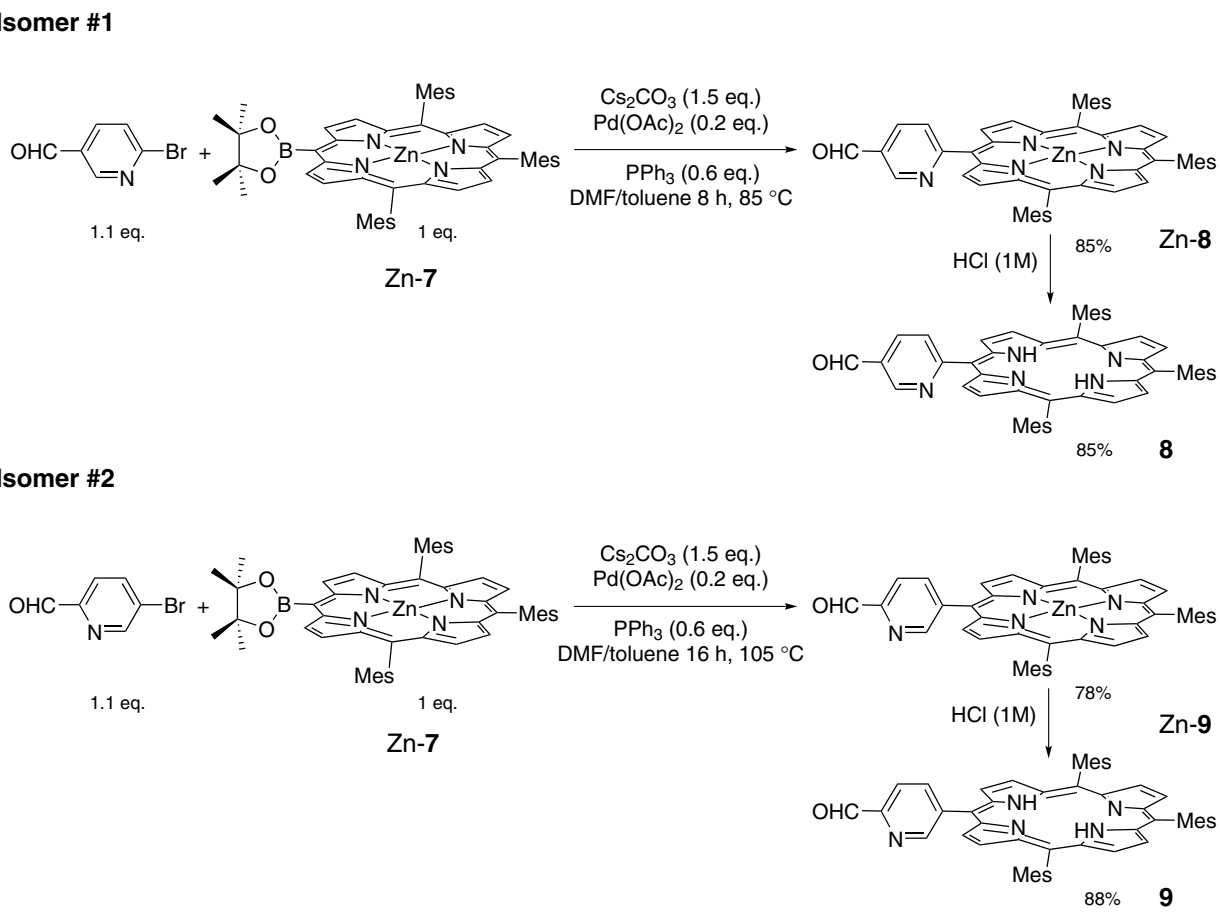
Scheme 3. Synthesis of the dioxaborolane-porphyrin Zn-**7**

The nucleophilic substitution of the chloro leaving group by a pyrrole ring clearly evidences the sensitivity of the *ortho*-position of the pyridyl group and its instability in acidic media. This unexpected result led us to focus on pathway 3 detailed in Scheme 3.

The synthetic pathway leading to the porphyrin precursor for the Suzuki coupling is shown in Scheme 3. Following the conditions described by Shultz *et al.* for the synthesis of the trimesityl-porphyrin [38], a mixture of three porphyrins was obtained. The resulting mixture was then used in the following steps without any purification. The bromination was carried out with a standard method by treatment of the mixture with *N*-bromosuccinimide (NBS) in chloroform at room temperature for 30 min. The bromo-porphyrins were further metalated with $Zn(OAc)_2{\cdot}2H_2O$ to give the zinc complexes, which were coupled with pinacolborane under $PdCl_2(PPh_3)_2$ catalysis to yield a mixture of boronate-porphyrins and tetramesityl porphyrin. The dioxaborolane-porphyrin **7**, previously described by Nocera *et al.* [25, 26], was then easily separated from the others by column chromatography affording Zn-**7** in 14% overall yield.

The functionalized porphyrin Zn-**8** was prepared in high yields (85%) by a Suzuki coupling reaction of porphyrin Zn-**7** and 6-bromo-pyridine-3-carbaldehyde using a catalytic amount of $Pd(OAc)_2$ and anhydrous Cs_2CO_3 in the presence of PPh_3 in a mixture of DMF/toluene at 85 °C for 8 h (Scheme 4) [31–33, 38, 39].

The same experimental conditions were applied for the preparation of Zn-**9**, starting from the dioxaborolane-porphyrin Zn-**7** and 5-bromo-pyridine-2-carbaldehyde but this reaction required heating up to 105 °C for a longer

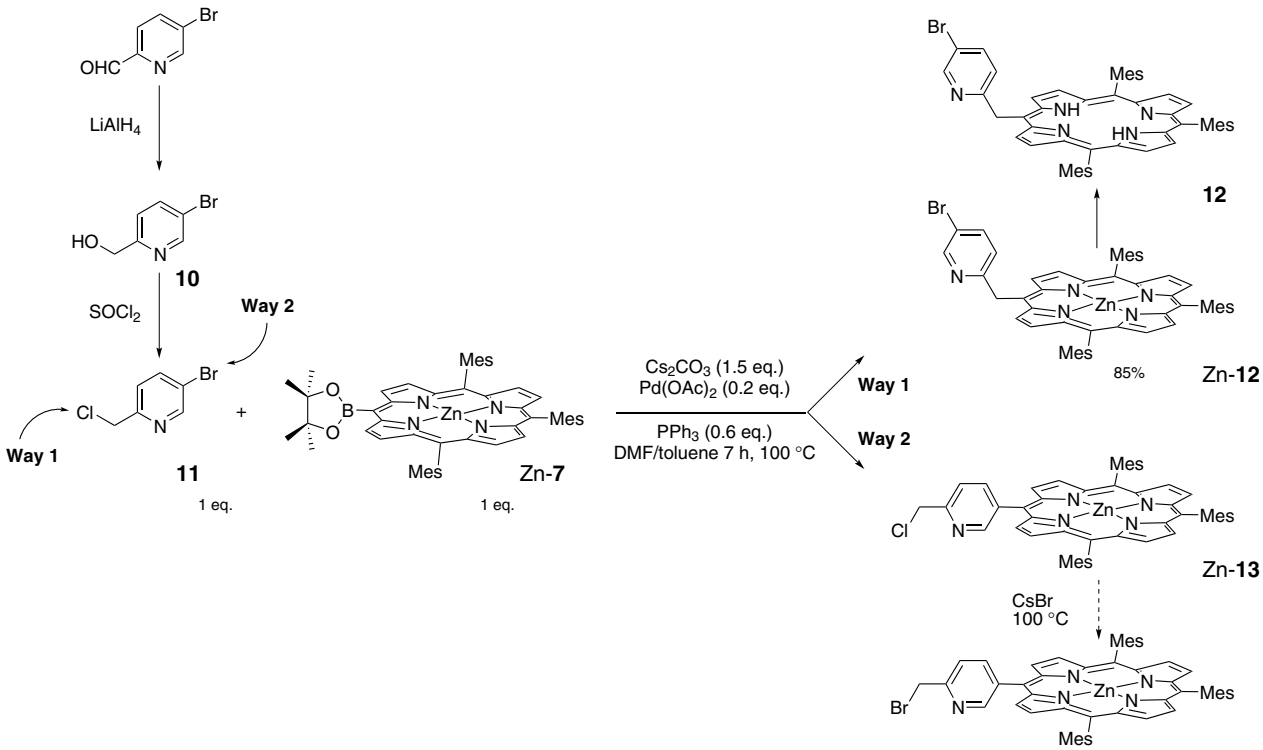


Scheme 4. Synthetic procedures for porphyrins **8** and **9**

time (16 h). In both cases, the coupling reactions were monitored by TLC and MALDI-TOF mass spectrometry. The higher reactivity observed during the preparation of Zn-**8** can be explained by the presence of the nitrogen atom at the *ortho*-position of the bromo-leaving group in the starting pyridine-carbaldehyde, which enhances the reactivity of the bromo group. Demetalation of the zinc porphyrins Zn-**8** and Zn-**9** using HCl 1 M at room temperature afforded the free-base derivatives, porphyrins **8** and **9**, in yields superior to 85%.

We further tried the reactivity of 5-bromo-2-chloromethyl-pyridine **11** with porphyrin Zn-**7** using the same Suzuki coupling conditions (Scheme 5). The 5-bromo-2-chloromethyl-pyridine **11** was synthesized in two steps by reduction of the aldehyde function of bromopicolinaldehyde using $LiAlH_4$ in THF at 0 °C, followed by nucleophilic substitution of the hydroxy-leaving group by chloro using thionyl chloride in toluene. Unexpectedly, after 7 h at 80 °C, the MALDI-TOF mass spectrum did not exhibit the expected molecular peak at m/z = 852.84 corresponding to porphyrin Zn-**13** but a peak at m/z = 897.10 Daltons (way 2, Scheme 5). The isotopic distribution confirmed the presence of a zinc porphyrin bearing a bromine atom instead of the expected chloride. Based on different assumptions, two protocols (ways 1 and 2 in Scheme 5) can be considered to explain the observed MALDI-TOF mass spectrum: (i) the Suzuki coupling route could have occurred on the chloro-leaving group rather than the bromo one, or (ii) the bromine atoms released during the catalytic reaction could lead to a nucleophilic substitution of the chloro substituent.

A closer look at the ^{1}H NMR spectrum of the isolated porphyrin is informative (Fig. 1). The absence of any singlet in the 4–5 ppm range and the presence of a singlet at 6.59 ppm (2H) are in agreement with the structure of porphyrin **12**. Indeed, for comparison, the methylene groups of either the 2,6-dibromomethylpyridine or the 5-bromo-2-chloromethylpyridine compounds appear at δ = 4.70 ppm (s, 2H, -CH_2-Br) [40] and δ = 4.63 ppm (s, 2H, -CH_2-Cl) [40], respectively, whereas the methylene groups of tetrabenzylporphyrin appear at δ = 6.34 ppm (s, 8H, -CH_2-Ph) [41]. Therefore, only the formation of porphyrin **12** occurs in 90% yield using this synthetic procedure and unfortunately the target porphyrin Zn-**13** was present only as traces. It is also worthy to note on the MALDI-TOF spectrum of the reaction mixture the presence of a peak at m/z = 1541.48 daltons. This peak can be attributed to the formation of a dimer (Scheme 6) corresponding to the Suzuki coupling of the dioxaborolane-porphyrin Zn-**7** with the zinc bromopyridylporphyrin Zn-**12**. This dimer was not further characterized.



Scheme 5. Porphyrin Zn-**7** and Suzuki couplings

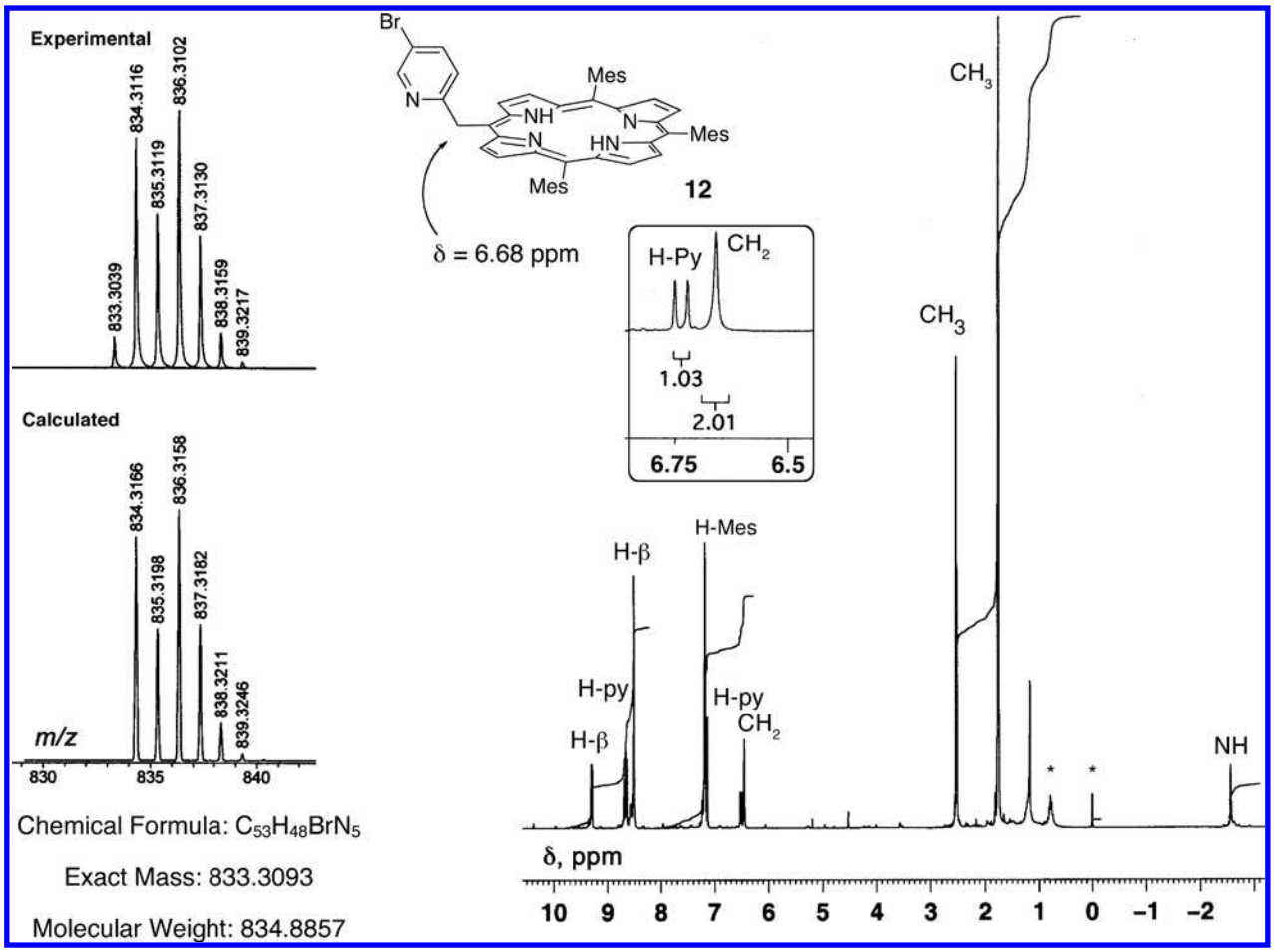
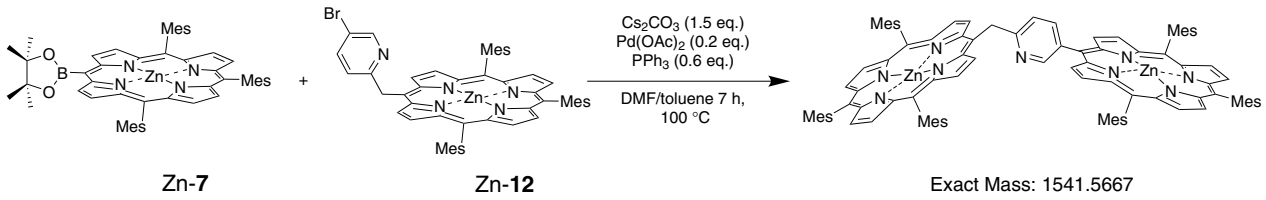
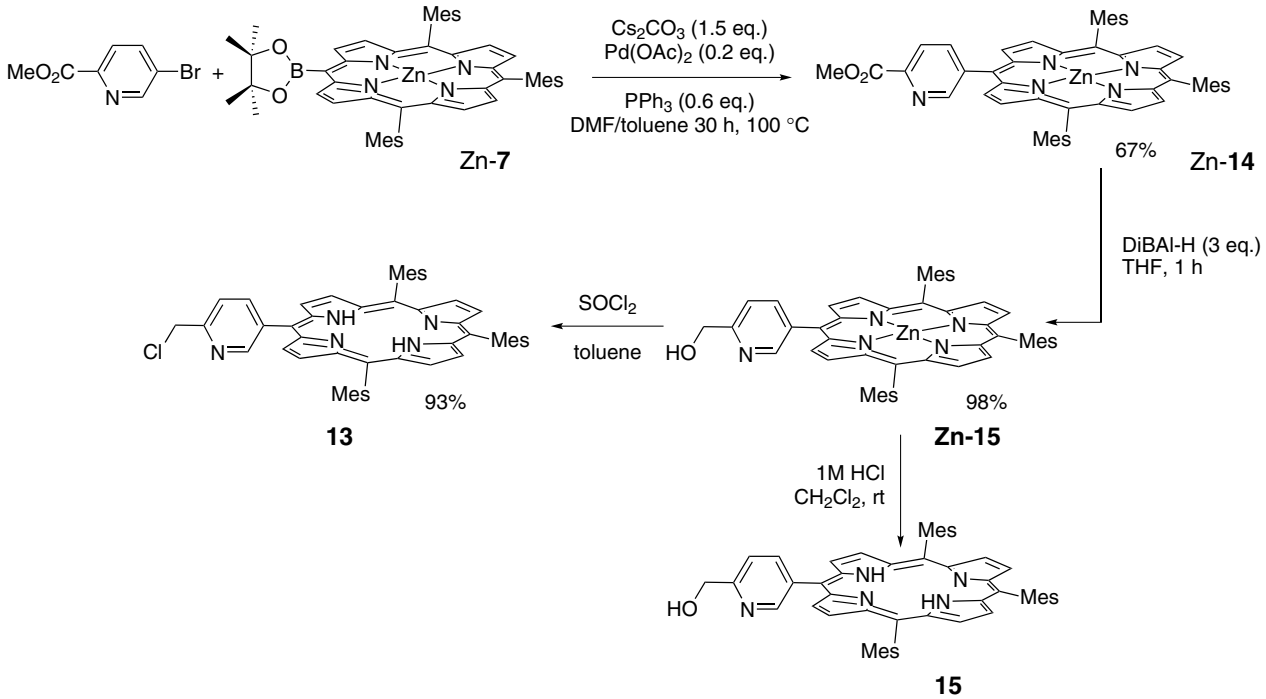


Fig. 1. HR-MS and ^{1}H NMR spectra of porphyrin **12**



Scheme 6. Formation of a dimer *via* Suzuki coupling



Scheme 7. Three-step procedure for the synthesis of porphyrin **13**

This latter result led us to investigate a new three-step procedure to synthesize porphyrin **13** (Scheme 7). Indeed, the other possibility to obtain the porphyrin **13** consists of the introduction of the chloromethyl functionality after the Suzuki coupling reaction. This was successfully performed by reacting methyl-5-bromopyridine-2-carboxylate with Zn-**7** under the same Suzuki reaction conditions as above (Scheme 7). Zn-**14** was obtained in 67% yield. The further reduction of the methyl ester group by DiBAl-H, followed by chlorination of the alcohol derivative (Zn-**15**), led to **13** in quantitative yield.

EXPERIMENTAL

Instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at the "*Plateforme d'Analyse Chimique et de Synthèse Moléculaire de l'Université de Bourgogne (PACSMUB)*"; chemical shifts are expressed in ppm relative to chloroform (7.26 ppm for ^{1}H and 77 ppm for ^{13}C). UV-visible spectra were recorded on a Varian Cary 1 spectrophotometer. Mass spectra and accurate mass measurements (HR-MS) were obtained on a Bruker Daltonics Ultraflex II spectrometer in the MALDI-TOF reflectron mode using dithranol as a matrix or on a Bruker micrOTOF-Q instrument in ESI mode. Accurate mass measurements (HR-MS MALDI-TOF) were carried out in the same conditions as before using PEG ion series as internal calibrant. Both measurements were made at *PACSMUB*. GC-MS analysis were carried out on a Thermo Trace GC-Ultra-DSQII instrument in EI ionization mode (using a Thermo TR-5MS non-polar column, 0.25 mm × 30 m length). The melting points were measured on a Büchi B-545 apparatus and are uncorrected.

Chemicals and reagents

Absolute dichloromethane (CH_2Cl_2) was obtained from Carlo Erba and used as received. Silica gel (Merck; 70–120 mm) and alumina (Merck; aluminum oxide 90 standardized) were used for column chromatography. Analytical thin-layer chromatography was performed using Merck 60 F254 silica gel (precoated sheets, 0.2 mm thick). Reactions were monitored by thin-layer chromatography, UV-visible spectroscopy, and MALDI-TOF

mass spectrometry. 5-mesityldipyrromethane was synthesized as already described [42]. 6-bromo-pyridine-3-carbaldehyde, 5-bromo-pyridine-2-carbaldehyde and methyl-5-bromopyridine-2-carboxylate are commercialy available and were used as received (Acros and Alfa Aesar). The pyridyl precursors **1**–**4** were described in the literature [43, 44].

Synthesis

Diethyl pyridine-2,5-dicarboxylate (1). To a suspension of 2,6-dipicolinic acid (60.0 g, 360 mmol, 1 eq.) in ethanol (500 mL) was slowly added thionyl chloride (200 mL, 2.75 mol, 7.6 eq.). The mixture was refluxed for 14 h. After all volatiles were removed under reduced pressure, the residue was dissolved in CH_2Cl_2, washed three times with saturated hydrogen carbonate solution, and then dried over magnesium sulfate. The title compound was isolated in almost quantitative yields (98.9%, 79.5 g, 356 mmol) as a slightly yellow solid compound; mp 46–47 °C. ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm 1.45 (t, 3H, $^3J_{H\text{-}H}$ = 7.1 Hz, CH_2-*CH_3*), 1.48 (t, 3H, $^3J_{H\text{-}H}$ = 7.1 Hz, CH_2-*CH_3*), 4.46 (q, 2H, $^3J_{H\text{-}H}$ = 7.1 Hz, *CH_2*-CH_3), 4.52 (q, 2H, $^3J_{H\text{-}H}$ = 7.1 Hz, *CH_2*-CH_3), 8.21 (dd, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz, $^5J_{H\text{-}H}$ = 0.8 Hz, H_{meta}-pyridine), 8.45 (dd, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz, $^4J_{H\text{-}H}$ = 2.1 Hz, H_{para}-pyridine), 9.33 (dd, 1H, $^4J_{H\text{-}H}$ = 2.1 Hz, $^5J_{H\text{-}H}$ = 0.8 Hz, H_{ortho}-pyridine). ^{13}C NMR (75 MHz; $CDCl_3$; 298 K): δ, ppm 14.2 (CH_2-*CH_3*), 14.3 (CH_2-*CH_3*), 61.9 (*CH_2*-CH_3), 62.4 (*CH_2*-CH_3), 124.6 (C_3-pyridine), 128.8 (C_5-pyridine), 138.2 (C_4-pyridine), 150.8 (C_2-pyridine), 151.1 (C_6-pyridine), 164.4 (CO), 164.5 (CO). GC-MS (EI, 70 eV): *m/z* (%) 222.9 (100) $[M]^{+\bullet}$, 223.08 calcd. for $C_{11}H_{13}NO_4$.

Ethyl 6-(hydroxy-methyl)-pyrid-3-yl-carboxylate (2). To a suspension of **1** (80.0 g, 360 mmol, 1 eq.) in ethanol (1000 mL) was added pellets of sodium borohydride (8.0 g, 210 mmol, 0.6 eq.) and the mixture was refluxed for 14 h. After all volatiles were removed under reduced pressure, the residue was dissolved in CH_2Cl_2, washed three times with saturated hydrogen carbonate solution, and then dried over magnesium sulfate. The compound was purified through alumina column chromatography using CH_2Cl_2/MeOH (50/50) as eluents. The title derivative was isolated in 66% yield (43.0 g, 237 mmol) as a yellow powder; mp 50–51 °C. ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm 1.41 (t, 3H, $^3J_{H\text{-}H}$ = 7.1 Hz, CH_2-*CH_3*), 2.85 (sl, 1H, OH), 4.41 (q, 2H, $^3J_{H\text{-}H}$ = 7.1 Hz, *CH_2*-CH_3), 4.82 (s, 2H, *CH_2*-OH), 7.39 (d, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz, H_{meta}-pyridine), 8.29 (dd, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz, $^4J_{H\text{-}H}$ = 2.1 Hz, H_{para}-pyridine), 9.14 (d, 1H, $^4J_{H\text{-}H}$ = 2.1 Hz, H_{ortho}-pyridine). ^{13}C NMR (75 MHz; $CDCl_3$; 298 K): δ, ppm 14.2 (CH_2-*CH_3*), 61.9 (*CH_2*-CH_3), 64.9 (*CH_2*-OH), 120.0 (C_5-pyridine), 124.9 (C_3-pyridine), 138.2 (C_4-pyridine), 149.9 (C_2-pyridine), 163.6 (C_6-pyridine), 165.1 (CO). GC-MS (EI, 70 eV): *m/z* (%) 178.8 (100), 181.07 calcd. for $C_9H_{11}NO_3$ (molecular peak not visible).

Ethyl 6-chloromethyl-pyrid-3-yl-carboxylate (3). To a solution of **2** (43.0 g, 237 mmol, 1 eq.) in toluene (500 mL) was slowly added thionyl chloride (52 mL, 716 mmol, 3 eq.). The suspension was stirred at room temperature for 3 h till complete dissolution. After all volatiles were removed under reduced pressure, the residue was dissolved in CH_2Cl_2 (100 mL), washed three times with saturated hydrogen carbonate solution (1000 mL), and then dried over magnesium sulfate. The compound was purified through alumina column chromatography using CH_2Cl_2 as eluent. The title compound was isolated in 76% yield (35.7 g, 180 mmol) as a yellow powder; mp 42–43 °C. ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm 1.40 (t, 3H, $^3J_{H\text{-}H}$ = 7.1 Hz, CH_2-*CH_3*), 4.41 (q, 2H, $^3J_{H\text{-}H}$ = 7.1 Hz, *CH_2*-CH_3), 4.71 (s, 2H, *CH_2*-Cl), 7.56 (d, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz, H_{meta}-pyridine), 8.32 (dd, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz, $^4J_{H\text{-}H}$ = 1.9 Hz, H_{para}-pyridine), 9.15 (d, 1H, $^4J_{H\text{-}H}$ = 1.9 Hz, H_{ortho}-pyridine). ^{13}C NMR (75 MHz; $CDCl_3$; 298 K): δ, ppm 14.2 (CH_2-*CH_3*), 46.1 (*CH_2*-Cl), 61.5 (*CH_2*-CH_3), 122.2 (C_5-pyridine), 125.6 (C_3-pyridine), 138.2 (C_4-pyridine), 150.5 (C_2-pyridine), 160.5 (C_6-pyridine), 164.9 (CO).

(6-chloromethyl-pyrid-3-yl)methanol (4). To a solution of $LiAlH_4$ (204 mg, 5.4 mmol, 0.6 eq.) in dry tetrahydrofuran (40 mL) was added at 0 °C a solution of **3** (1.8 g, 9 mmol, 1 eq.) in dry tetrahydrofuran (30 mL). The mixture was stirred at that temperature for 1 h and then warmed to room temperature and quenched with water (5 mL). After evaporation of the solvent in vacuum, the residue was extracted with CH_2Cl_2, washed with water, dried over magnesium sulfate, and then filtered. The title compound was isolated in 83% yield (1.37 g, 7.56 mmol) as a yellow powder; mp 59–60 °C. ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm 2.12 (br. s, 1H, OH), 4.67 (s, 2H, *CH_2*-OH), 4.75 (s, 2H, *CH_2*-Cl), 7.47 (d, 1H, $^3J_{H\text{-}H}$ = 8 Hz, H_{meta}-pyridine), 7.76 (dd, 1H, $^3J_{H\text{-}H}$ = 8 Hz, $^4J_{H\text{-}H}$ = 2.2 Hz, H_{para}-pyridine), 8.53 (d, 1H, $^4J_{H\text{-}H}$ = 2.2 Hz, H_{ortho}-pyridine). ^{13}C NMR (75 MHz; $CDCl_3$; 298 K): δ, ppm 46.4 (*CH_2*-Cl), 62.3 (*CH_2*-OH), 122.7 (C_5-pyridine), 135.8 (C_3-pyridine), 138.7 (C_4-pyridine), 148.1 (C_2-pyridine), 155.8 (C_6-pyridine).

6-chloromethyl-pyrid-3-yl-carbaldehyde (5). To a solution of **4** (1.37 g, 7.56 mmol, 1 eq.) in dry dimethylsulfoxide (20 mL) was added 2-iodoxybenzoic acid (2.68 g, 9.56 mmol, 1.1 eq.). The mixture was stirred at room temperature for 2 h, and then quenched with addition of sodium hydrogen carbonate (0.1 M). After evaporation of the solvent in vacuum, the residue was extracted with CH_2Cl_2, dried over magnesium sulfate, and then filtered. The title compound was isolated in 92% yield (1.36 g, 8.79 mmol) as yellow oil; mp 52–53 °C. ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm 4.75 (s, 2H, *CH_2*-Cl), 7.68 (d, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz, H_{meta}-pyridine), 8.22 (dd, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz, $^4J_{H\text{-}H}$ = 2.0 Hz, H_{para}-pyridine), 9.03 (d, 1H, $^4J_{H\text{-}H}$ = 2.0 Hz, H_{ortho}-pyridine), 10.12 (s, 1H, CHO). ^{13}C NMR (75 MHz; $CDCl_3$; 298 K): δ, ppm 46.0 (*CH_2*-Cl), 123.7 (C_5-pyridine), 130.5 (C_3-pyridine), 135.9

(C_4-pyridine), 150.2 (C_2-pyridine), 160.3 (C_6-pyridine), 189.9 (CHO).

{[(2-methyl)-pyrrol-1-yl]-pyrid-5-yl}-2,2′-dipyrrylmethane (6). Under nitrogen and shielding from light, aldehyde **5** (1.69 g, 10.9 mmol) was mixed with pyrrole (20 mL), and the mixture was heated at 85 °C for 16 h. After cooling to room temperature and filtration, the excess pyrrole was evaporated *in vacuo* with slight heating on a rotary evaporator to yield a dark oil. The oil was taken up in minimal dichloromethane, washed three times with an aqueous solution of $NaHCO_3$ (100 mL), dried over magnesium sulfate, and then evaporated. The oil was dried overnight *in vacuo* at 55 °C to give the title compound in 38% yield (1.25 g, 4.14 mmol). ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm 5.45 (s, 1H, *CH*-pyridine), 5.87 (m, 2H, H-dipyrromethane), 6.02 (s, 2H, *CH_2*-pyrrole), 6.15 (m, 2H, H-dipyrromethane), 6.26 (2d, 2H, $^3J_{H\text{-}H}$ = 4.3 Hz, H-pyrrole), 6.71 (m, 2H, H-dipyrromethane), 6.82 (2d, 2H, $^3J_{H\text{-}H}$ = 4.3 Hz, H-pyrrole), 7.12 (d, 1H, $^3J_{H\text{-}H}$ = 8.0 Hz, H_{meta}-pyridine), 7.42 (dd, 1H, $^3J_{H\text{-}H}$ = 8.0 Hz, $^4J_{H\text{-}H}$ = 2.3 Hz, H_{para}-pyridine), 8.03 (sl, 2H, NH-dipyrromethane), 8.40 (d, 2H, $^4J_{H\text{-}H}$ = 2.3 Hz, H_{ortho}-pyridine). GC-MS (EI, 70 eV): *m/z* (%) 302.4 (48) $[M]^{+\bullet}$, 302.15 calcd. for $C_{19}H_{18}N_4$, 236.3 (29) [M - CH_2-pyrrole]$^+$ 145.1 (100) [M - (pyridine-CH_2-pyrrole)]$^+$, 302.15 calcd. for $C_{19}H_{18}N_4$. HR-MS (ESI): *m/z* 303.1717 [M + H]$^+$, 303.1610 calcd. for $C_{19}H_{19}N_4$, 325.1606 [M + Na]$^+$, 325.1429 calcd. for $C_{19}H_{18}N_4Na$.

5,10,15-trimesityl-20-(4′,4′,5′,5′-tetramethyl-[1′,3′,2′]dioxaborolan-2′-yl)-porphyrinatoZn(II)(Zn-7). Under nitrogen and shielding from light, the *meso*-unsubstituted dipyrromethane (1.33 g, 9 mmol, 1 eq.), mesityldipyrromethane (2.38 g, 9 mmol, 1 eq.) and mesitylaldehyde (2.67 g, 18 mmol, 2 eq.) were dissolved in dichloromethane (1800 mL). After 5 min, $BF_3{\cdot}OEt_2$ (0.66 µL, 5.4 mmol, 0.6 eq.) was added and the mixture was stirred at room temperature for 30 min. Triethylamine (6.3 mL, 45 mmol, 5 eq.) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, (DDQ, 6.13 g, 27 mmol, 3 eq.) were then added under stirring. After 1 h, the reaction mixture was concentrated, filtered over a pad of silica using dichloromethane as eluent, and then evaporated under reduced pressure. Following a general procedure, the residue was redissolved in chloroform (1000 mL) and an excess of N-bromosuccinimide (NBS, 386 mg) was added to the mixture. The mixture was stirred at room temperature for 30 min, concentrated and then filtered over a pad of silica using dichloromethane as eluent. A solution of the mixture of brominated and tetramesityl porphyrins in chloroform/MeOH was treated with $Zn(OAc)_2{\cdot}2H_2O$ (1.5 g) and the mixture was heated at 75 °C. The reaction was monitored by TLC, UV-visible and MALDI-TOF mass spectrometry. After 2 h, CH_2Cl_2 was added and the mixture was washed three times with water (300 mL), one time with $NaHCO_3$, and then dried over magnesium sulfate. The zinc porphyrins are finally dissolved under argon in anhydrous 1,2-dichloroethane (250 mL) and triethylamine (3.64 mL) was added. The mixture was treated with 4,4,5,5-tetramethyl-1,2,3-dioxaborolane (2.45 mL) in the presence of *trans*-dichlorobis(triphenylphosphine)palladium(II) (42 mg). After 1 h at 85 °C, the mixture was cooled to room temperature and the reaction was quenched with aqueous solution of KCl (30%). The mixture was then washed three times with water, dried over magnesium sulfate, and then the solvent was evaporated under reduced pressure. The residue obtained was chromatographed using CH_2Cl_2/heptane (first 50/50, then 70/30, and finally 90/10). Chromatography afforded mainly two products: the fast-moving zinc tetra-mesitylporphyrin and the slow-moving title compound. The second red band was collected, affording after evaporation of the solvent under reduced pressure 1.11 g of the title compound Zn-**7** (1.31 mmol, 14% yield); mp > 300 °C. ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm 1.81 (s, 12H, CH_3-pinacol), 1.85 (s, 18H, CH_3-mesityl), 2.64 (s, 9H, CH_3-mesityl), 7.27 (s, 6H, H_{meta}-mesityl), 8.68 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, $H_β$-porphyrin), 8.71 (d, 2H, $^3J_{H\text{-}H}$ = 4.6 Hz, $H_β$-porphyrin), 8.88 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, $H_β$-porphyrin), 9.81 (d, 2H, $^3J_{H\text{-}H}$ = 4.7 Hz, $H_β$-porphyrin). UV-vis (CH_2Cl_2): $λ_{max}$, nm (ε × 10^{-3} $M^{-1}.cm^{-1}$) 419 (453), 550 (13), 594 (2). MS (MALDI-TOF): *m/z* 852.32 $[M]^{+\bullet}$, 852.35 calcd. for $C_{53}H_{53}BN_4O_2Zn$. HR-MS (ESI): *m/z* 853.3600 [M + H]$^+$, 853.3631 calcd. for $C_{53}H_{54}BN_4O_2Zn$, 875.3430 [M + Na]$^+$, 875.3451 calcd. for $C_{53}H_{53}BN_4NaO_2Zn$ (in agreement with literature data [25, 26]).

5-(5-formylpyrid-2-yl)-10,15,20-trimesitylporphinato-Zn(II) Zn-(8). Under argon and shielding from light, borolanyl porphyrin **7** (160 mg, 0.187 mmol, 1 eq.), 6-bromopyridine-3-carbaldehyde (38.1 mg, 0.206 mmol, 1.1 eq.) and Cs_2CO_3 (106.6 mg, 0.28 mmol, 1.5 eq.) were dissolved in a mixture of anhydrous DMF (12 mL) and distilled toluene (21 mL). $Pd(OAc)_2$ (8.4 mg, 0.037 mmol, 0.2 eq.). $P(Ph)_3$ (29.3 mg, 0.11 mmol, 0.6 eq.) were then added and the mixture was heated at 85 °C for 8 h. After cooling the mixture to room temperature, dichloromethane (150 mL) was added. The mixture was washed three times with $NaHCO_3$, dried over magnesium sulfate, and concentrated. The residue obtained was chromatographed on silica (CH_2Cl_2/MeOH first 100/0 then 98/2). The red-pink fraction was isolated and the solvent was removed under reduced pressure to give the title compound in 85% yield (132.2 mg, 0.159 mmol); mp > 300 °C. UV-vis (CH_2Cl_2): $λ_{max}$, nm (log ε) 425 (5.42), 555 (4.11), 600 (3.48). HR-MS (MALDI-TOF): *m/z* 831.2951 $[M]^{+\bullet}$, 831.2916 calcd. for $C_{53}H_{45}N_5OZn$.

5-(5-formylpyrid-2-yl)-10,15,20-trimesitylporphyrin (8). Shielding from light, a solution of the zinc porphyrin Zn-**8** (113.87 mg, 0.137 mmol) in dichloromethane (40 mL) was stirred vigorously with a 1 M HCl solution (40 mL). After separation of the two phases, the organic layer was washed two more times with HCl 1 M, then washed three times with water (3 × 50 mL), dried over magnesium sulfate, filtered and evaporated. The residue was purified by chromatography (silica,

dichloromethane/MeOH 98/2). The red fraction was collected and then evaporated to give the title compound in 85% yield (89.5 mg, 0.116 mmol); mp > 300 °C. ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm -2.49 (br. s, 2H, NH), 1.91 (s, 18H, CH_3-mesityl), 2.67 (s, 9H, CH_3-mesityl), 7.33 (s, 6H, H_{meta}-mesityl), 8.05 (s, 1H, H_{meta}-pyridine), 8.46 (s, 1H, H_{para}-pyridine), 8.73 (s, 4H, H_β-porphyrin), 8.82 (s, 4H, H_β-porphyrin), 9.67 (s, 1H, H_{ortho}-pyridine), 10.51 (s, 1H, aldehyde). UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 419 (5.34), 514 (3.84), 552 (3.84), 591 (3.84), 648 (3.70). MS (MALDI-TOF): *m/z* 770.34 $[M + H]^+$, 769.38 calcd. for $C_{53}H_{47}N_5O$. HR-MS (ESI): *m/z* 770.3858 $[M + H]^+$, 770.3859 calcd. for $C_{53}H_{48}N_5O$, 792.3679 $[M + Na]^+$, 792.3678 calcd. for $C_{53}H_{47}N_5NaO$.

5-(6-formylpyrid-3-yl)-10,15,20-trimesitylporphinato-Zn(II) Zn-(9). Porphyrin Zn-**9** was prepared in 78% (485 mg, 0.582 mmol) as a purple compound using the procedure described above for Zn-**8**, starting from 5-bromopyridine-2-carbaldehyde (138 mg, 0.755 mmol, 1.1 eq.), Cs_2CO_3 (424 mg, 1.12 mmol, 1.5 eq.), $Pd(OAc)_2$ (33.4 mg, 0.149 mmol, 0.2 eq.) and $P(Ph)_3$ (116.8 mg, 0.447 mmol, 0.6 eq.), the reaction mixture was heated at 105 °C for 16 h. mp > 300 °C. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 426 (5.39), 555 (4.08), 601 (3.40). HR-MS (MALDI-TOF): *m/z* 831.2897 $[M]^{+\bullet}$, 831.2916 calcd. for $C_{53}H_{45}N_5OZn$.

5-(6-formylpyrid-3-yl)-10,15,20-trimesitylporphyrin (9). Porphyrin **9** was prepared in 88% (394.19 mg, 0.512 mmol) as a purple compound using the procedure described above for **8**, starting from porphyrin Zn-**9** (485 mg, 0.582 mmol). mp > 300 °C. ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm -2.52 (br. s, 2H, NH), 1.87 (s, 18H, CH_3-mesityl), 2.64 (s, 9H, CH_3-mesityl), 7.31 (s, 6H, H_{meta}-mesityl), 8.43 (dd, 1H, $^3J_{H\text{-}H}$ = 7.9 Hz, $^5J_{H\text{-}H}$ = 0.8 Hz, H_{meta}-pyridine), 8.69 (d, 6H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β-porphyrin), 8.72 (dd, 1H, $^3J_{H\text{-}H}$ = 7.9 Hz, $^4J_{H\text{-}H}$ = 2.0 Hz, H_{para}-pyridine), 8.78 (d, 2H, $^3J_{H\text{-}H}$ = 4.8 Hz, H_β-porphyrin), 9.64 (dd, 1H, $^4J_{H\text{-}H}$ = 2.0 Hz, $^5J_{H\text{-}H}$ = 0.8 Hz, H_{ortho}-pyridine), 10.48 (s, 1H, aldehyde). UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 420 (5.32), 516 (3.95), 551 (3.30), 592 (3), 648 (3). MS (MALDI-TOF): *m/z* 770.41 $[M + H]^+$, 769.38 calcd. for $C_{53}H_{47}N_5O$. HR-MS (ESI): *m/z* 770.3927 $[M + H]^+$, 770.3859 calcd. for $C_{53}H_{48}N_5O$.

(5-bromo-pyrid-2-yl)methanol (10). This compound was prepared in 86% (864 mg, 4.62 mmol) using the procedure described for **4**, starting from 5-bromopicolinaldehyde (1.00 g, 5.37 mmol, 1 eq.) and $LiAlH_4$ (122 mg, 3.22 mmol, 0.6 eq.). mp 59–60 °C. ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm 4.72 (br. s, 1H, OH), 5.22 (s, 2H, CH_2-OH), 7.18 (d, 1H, $^3J_{H\text{-}H}$ = 8.3 Hz, H_{meta}-pyridine), 7.81 (dd, 1H, $^3J_{H\text{-}H}$ = 8.3 Hz, $^4J_{H\text{-}H}$ = 2.3 Hz, H_{para}-pyridine), 8.63 (d, 1H, $^4J_{H\text{-}H}$ = 2.3 Hz, H_{ortho}-pyridine). ^{13}C NMR (75 MHz; $CDCl_3$; 298 K): δ, ppm 63.9 (CH_2-OH), 121.7 (C_5-pyridine), 128.8 (C_3-pyridine), 139.3 (C_4-pyridine), 149.7 (C_6-pyridine), 151.1 (C_2-pyridine). GC-MS (EI, 70eV): *m/z* (%) 187.0 (9) $[M]^{+\bullet}$, 186.96 calcd. for C_6H_6BrNO, 156.0 (15) $[M - CH_2OH]^+$, 155.94 calcd. for C_5H_3BrN.

5-bromo-2-chloromethyl-pyridine (11). This compound, isolated as a liquid at room temperature, was prepared in 94% (890 mg, 4.34 mmol) using the procedure described for **3**, starting from **10** (864 mg, 4.62 mmol, 1 eq.) and thionyl chloride (1.0 mL, 13.86 mmol, 3 eq.). ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm 4.63 (s, 2H, CH_2-Cl), 7.38 (d, 1H, $^3J_{H\text{-}H}$ = 8.3 Hz, H_{meta}-pyridine), 7.85 (dd, 1H, $^3J_{H\text{-}H}$ = 8.3 Hz, $^4J_{H\text{-}H}$ = 2.4 Hz, H_{para}-pyridine), 8.63 (d, 1H, $^4J_{H\text{-}H}$ = 2.4 Hz, H_{ortho}-pyridine). ^{13}C NMR (75 MHz; $CDCl_3$; 298 K): δ, ppm 45.9 (CH_2-Cl), 120.1 (C_5-pyridine), 124.1 (C_3-pyridine), 139.7 (C_4-pyridine), 150.5 (C_6-pyridine), 155.2 (C_2-pyridine). GC-MS (EI, 70eV): *m/z* (%) 204.9 (38) $[M]^{+\bullet}$, 204.93 calcd. for C_6H_5BrClN, 169.9.0 (60) $[M - Cl]^+$, 169.96 calcd. for C_6H_5BrN.

5-(5-bromo-picol-2-yl)-10,15,20-trimesitylporphinato-Zn(II) Zn-(12). Porphyrin Zn-**12** was prepared in 78% (284 mg, 0.317 mmol) as a purple compound using the procedure described for Zn-**8**, starting from 5-bromo-2-chloromethyl-pyridine **11** (86 mg, 0.42 mmol, 1 eq.), Cs_2CO_3 (239.5 mg, 0.63 mmol, 1.5 eq.), $Pd(OAc)_2$ (18.9 mg, 0.0084 mmol, 0.2 eq) and $P(Ph)_3$ (65.84 mg, 0.252 mmol, 0.6 eq.), the reaction mixture being heated at 80 °C for 7 h. mp > 300 °C. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 422 (5.35), 552 (4.04), 589 (3.40). HR-MS (MALDI-TOF): *m/z* 895.2176 $[M]^{+\bullet}$, 895.2228 calcd. for $C_{53}H_{46}BrN_5Zn$.

5-(5-bromo-picol-2-yl)-10,15,20-trimesitylporphyrin (12). Porphyrin **12** was prepared in 90% (238 mg, 0.285 mmol) as a purple compound using the procedure described for **8**, starting from porphyrin Zn-**12** (284 mg, 0.317 mmol). mp > 300 °C. ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm -2.44 (br. s, 2H, NH), 1.88 (s, 18H, CH_3-mesityl), 2.66 (s, 9H, CH_3-mesityl), 6.59 (s, 2H, CH_2-pyridine), 6.64 (d, 1H, $^3J_{H\text{-}H}$ = 8.5 Hz, H_{meta}-pyridine), 7.31 (s, 6H, H_{meta}-mesityl), 8.65 (d, 4H, $^3J_{H\text{-}H}$ = 4.9 Hz, H_β-porphyrin), 8.70 (dd, 1H, $^3J_{H\text{-}H}$ = 8.5 Hz, $^4J_{H\text{-}H}$ = 2.4 Hz, H_{para}-pyridine), 8.78 (d, 2H, $^3J_{H\text{-}H}$ = 4.9 Hz, H_β-porphyrin), 8.82 (d, 1H, $^4J_{H\text{-}H}$ = 2.4 Hz, H_{ortho}-pyridine), 9.42 (d, 2H, $^3J_{H\text{-}H}$ = 4.9 Hz, H_β-porphyrin). UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 418 (5.37), 516 (4.08), 549 (3.70), 593 (3.40), 650 (3.40). MS (MALDI-TOF): *m/z* 834.31 $[M + H]^+$, 833.31 calcd. for $C_{53}H_{48}BrN_5$. HR-MS (ESI): *m/z* 834.3166 $[M + H]^+$, 834.3171 calcd. for $C_{53}H_{49}BrN_5$.

5-(6-methylcarboxylate-pyrid-3-yl)-10,15,20-trimesitylporphinato-Zn(II) (Zn-14). Porphyrin Zn-**14** was prepared in 67% (202 mg, 0.235 mmol) as a purple compound using the procedure described for Zn-**8**, starting from methyl-5-bromopyridine-2-carboxylate (82 mg, 0.38 mmol, 1.1 eq.), Cs_2CO_3 (119 mg, 0.525 mmol, 1.5 eq.), $Pd(OAc)_2$ (15.7 mg, 0.007 mmol, 0.2 eq.) and $P(Ph)_3$ (54.8 mg, 0.21 mmol, 0.6 eq.), the reaction mixture being heated at 100 °C for 30 h. mp > 300 °C. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 422 (5.37), 553 (4.04), 593 (3.48). MS (MALDI-TOF): *m/z* 862.29 $[M + H]^+$, 861.30 calcd. for $C_{54}H_{47}N_5O_2Zn$. HR-MS (ESI): *m/z* 861.2992 $[M]^{+\bullet}$, 861.3021 calcd. for $C_{54}H_{47}N_5O_2Zn$, 884.2884 $[M + Na]^+$, 884.2919 calcd. for $C_{54}H_{47}N_5NaO_2Zn$.

5-(6-hydroxymethyl-pyrid-3-yl)-10,15,20-trimesitylporphinato-Zn(II) (Zn-15). Under nitrogen and shielding from light, a solution of porphyrin Zn-**14** (200 mg, 0.23 mmol, 1 eq.) in dry THF (25 mL) was treated with DiBAl-H (0.69 mL, 0.69 mmol, 3 eq.). After 1 h at room temperature (TLC analysis showed that the reaction was complete), the reaction was quenched with water (5 mL). The mixture was concentrated to dryness. The residue was dissolved in dichloromethane and washed with $NaHCO_3$ and then dried over magnesium sulfate. The residue obtained was chromatographed (silica, dichloromethane/MeOH 100/0 first, then 90/10), affording the title compound in 98% yield as a purple solid (188 mg, 0.225 mmol); mp > 300 °C. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 422 (5.46), 552 (4.11). MS (MALDI-TOF): *m/z* 834.29 $[M + H]^+$, 834.31 calcd. for $C_{53}H_{47}N_5OZn$. HR-MS (ESI): *m/z* 834.3088 $[M + H]^+$, 834.3150 calcd. for $C_{53}H_{48}N_5OZn$, 856.2922 $[M + Na]^+$, 856.2970 calcd. for $C_{53}H_{47}N_5NaOZn$.

5-(6-hydroxymethyl-pyrid-3-yl)-10,15,20-trimesitylporphyrin (15). Porphyrin **15** was prepared in 75% (130 mg, 0.168 mmol) as a purple compound using the procedure described for **8**, starting from porphyrin Zn-**15** (188 mg, 0.225 mmol). mp > 300 °C. ^1H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm -2.54 (br. s, 2H, NH), 1.87 (s, 18H, CH_3-mesityl), 2.65 (s, 9H, CH_3-mesityl), 4.41 (br. s, 1H, OH), 5.10 (s, 2H, CH_2-OH), 7.31 (s, 6H, H_{meta}-mesityl), 8.51 (d, 1H, $^3J_{H\text{-}H}$ = 8.0 Hz, H_{meta}-pyridine), 8.68 (d, 4H, $^3J_{H\text{-}H}$ = 4.9 Hz, H_β-porphyrin), 8.74 (m, 5H, H_β-porphyrin + H_{para}-pyridine), 9.30 (s, 1H, H_{ortho}-pyridine). UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 419 (5.57), 515 (4.20), 550 (3.78), 594 (3.70), 647 (3.48). MS (MALDI-TOF): *m/z* 772.36 $[M + H]^+$, 771.40 calcd. for $C_{53}H_{49}N_5O$. HR-MS (ESI): *m/z* 772.4010 $[M + H]^+$, 772.4015 calcd. for $C_{53}H_{50}N_5O$, 794.3779 $[M + Na]^+$, 794.3835 calcd. for $C_{53}H_{49}N_5NaO$.

5-(6-chloromethyl-pyrid-3-yl)-10,15,20-trimesitylporphyrin (13). Shielding from light, a solution of porphyrin **15** (125 mg, 0.15 mmol, 1 eq.) in toluene (15 mL) was reacted with thionyl chloride (0.4 mL). The reaction was monitored by TLC. After 2 h at room temperature, the reaction mixture was concentrated. The residue was dissolved in dichloromethane, washed three times with aqueous $NaHCO_3$, and then dried over magnesium sulfate. The crude product was chromatographed (silica, dichloromethane) to give the title compound as a purple powder in 93% yield (110 mg, 0.139 mmol); mp > 300 °C. ^1H NMR (300 MHz; $CDCl_3$; 298 K): δ, ppm -2.52 (br. s, 2H, NH), 1.89 (s, 18H, CH_3-mesityl), 2.65 (s, 9H, CH_3-mesityl), 5.09 (s, 2H, CH_2-Cl), 7.32 (s, 6H, H_{meta}-mesityl), 7.94 (d, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz, H_{meta}-pyridine), 8.57 (d, 1H, $^3J_{H\text{-}H}$ = 8.1 Hz, H_{para}-pyridine), 8.58 (d, 4H, $^3J_{H\text{-}H}$ = 4.9 Hz, H_β-porphyrin), 8.76 (d, 4H, $^3J_{H\text{-}H}$ = 4.9 Hz, H_β-porphyrin), 9.44 (s, 1H, H_{ortho}-pyridine). UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 418 (5.58), 515 (4.20), 548 (3.78), 591 (3.70), 646 (3.48). MS (MALDI-TOF): *m/z* 790.34 $[M + H]^+$, 790.3676 calcd. for $C_{53}H_{49}ClN_5$. HR-MS (ESI): *m/z* 790.3619 $[M + H]^+$, 790.3676 calcd. for $C_{53}H_{49}ClN_5$, 812.3422 $[M + Na]^+$, 812.3496 calcd. for $C_{53}H_{48}ClN_5Na$, 828.3174 $[M + K]^+$, 828.3235 calcd. for $C_{53}H_{48}ClKN_5$.

CONCLUSION

The desired porphyrins were obtained without statistical reactions and the approach described here should prove to be useful for the preparation of a broad variety of substituted porphyrins by a pyridyl group bearing different reactive functionalities. The functionalization of the pyridyl moiety by reactive groups allows for the preparation of new porphyrin ligands able to coordinate two metals in close proximity. Further work in this direction and towards more sophisticated structures (*e.g.* new flexible dyads allowing three-metal coordination) is under investigation by our group and will be published in a forthcoming paper.

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