Synthesis, Self-Assembling Properties and Incorporation of Carbohydrate-Substituted Porphyrins into Cell Membrane Models

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Abstract: A general and very efficient synthesis of new carbohydrate-substituted porphyrins is described. Reaction of porphyrin **6** with different glycosyl imidates **7a–g** leads to the formation of carbohydrate-substituted porphyrins **9a–g** in good yield. Subsequent demetallation and removal of the carbohydrate protection groups leads to the metal-free compounds **11a–g**. In aqueous solution, compounds **11a–g** tend to form defined water-soluble aggregates in a self-assembling process. In methanol/water mixtures the aggregation process depends upon the configuration of the anomeric carbon in the carbohydrate moiety. The porphyrinic aggregates are characterized by strong exciton splitting in the Soret absorption spectrum and a red shift for all absorption bands. Interaction of the porphyrinic aggregates with phosphatidylethanolamine and DMPC liposomes leads to very efficient incorporation of mainly monomeric porphyrins **11a–g** into the liposomes, as was indicated by very large binding constants. At low liposome concentrations noncovalent porphyrin dimers were detected.

Keywords: aggregation · antitumor agents · carbohydrates · porphyrinoids · vesicles

Introduction

The development of new porphyrinic photosensitizers for photodynamic therapy (PDT) of cancer is one of the most important and interesting fields of modern porphyrin chemistry today.[1] PDT is based upon the selective accumulation of a photosensitizer in tumour tissue and on the production of singlet oxygen by irradiation of the sensitizer-enriched tumour with visible light. Thus formation of cytotoxic singlet oxygen directly in tumour cells causes cell death and often total tumour necrosis. Although the exact mechanism of sensitizer uptake by tumour cells is still unknown, there is evidence that hydrophobic and amphiphilic porphyrinic compounds associate strongly with plasma lipoproteins and may be incorporated into tumour cells through receptor-mediated endocytosis of low-density lipoproteins (LDL), since cancer cells contain high levels of LDL receptors.[2] Furthermore, amphiphilic porphyrinic sensitizers may also be more efficiently incorporated into cell membranes. As was shown recently by Shulok et al.,[3] incorporation of photosensitizers into plasma membranes leads to a high quantum yield of cell deactivation. Therefore, owing to possible enhanced selectivity to tumour cells and tumour cell destruction, hydrophobic and amphiphilic porphyrins or chlorins may be exceptionally good candidates for use in PDT. However, hydrophobic and amphiphilic porphyrins tend to aggregate in aqueous solution. Aggregation significantly alters the photochemical and biochemical properties of these compounds and leads to a decrease in uptake by cells and in singlet oxygen production.[4] Therefore a number of carbohydrate-substituted porphyrins have been synthesized recently, because these compounds show enhanced water solubility owing to the hydrophilic carbohydrate moiety.[5] Notably, porphyrinic compounds bearing one or two carbohydrate substituents gave promising results, most probably because of their amphiphilic nature. These compounds were often synthesized by reaction of a carbohydrate-substituted benzaldehyde with pyrrole and another benzaldehyde derivative under Lindsay conditions.[6] Unfortunately, the reaction leads to a mixture of different carbohydrate-substituted porphyrins bearing one to four carbohydrate moieties, and laborious multistep chromatographic separation is often necessary to obtain pure products.

An interesting alternative for the synthesis of carbohydrate-substituted porphyrins is the modification of simple porphyrins. It has been reported already that natural and artificial porphyrinic systems can be converted to the carbohydrate-substituted compounds in good yield. Franck et al. synthesized bis-galactosyl and glycosyl-substituted isohematoporphyrin derivatives starting from isohematoporphyrin dimethyl ester.[7] We were able to synthesize several galactosyl-substituted tetraphenylporphyrin derivatives in good yield by a transesterification procedure,[8] and Krausz[9] showed that it is possible to convert hydroxy-substituted porphyrinic compounds to carbohydrate-substituted porphyr-

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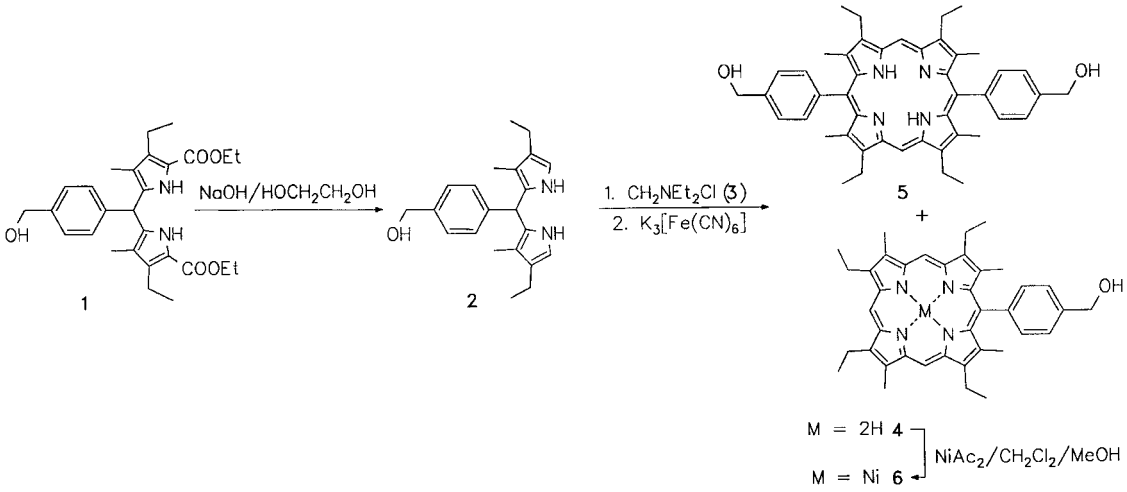


Scheme 1. Synthesis of porphyrins **4** and **6**.

ins with a spacer group between the porphyrin and the carbohydrate moiety.

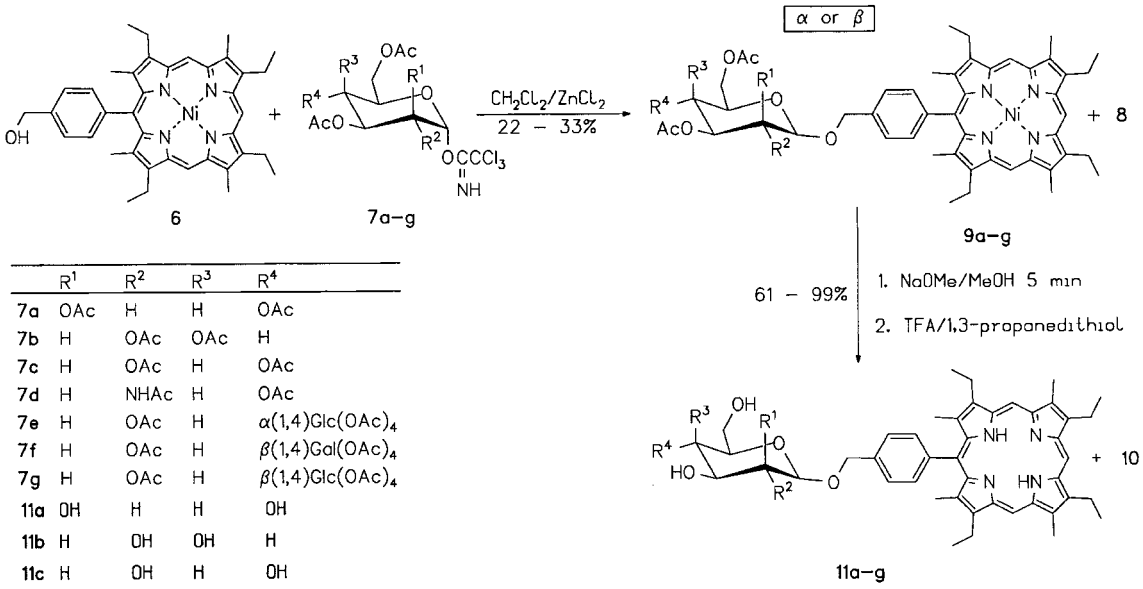
In connection with our research program on the synthesis and investigation of porphyrins for use in PDT, we report here a convenient synthetic procedure for the synthesis of carbohydrate-substituted porphyrins with strong amphiphilic character. The synthesized compounds exhibit very interesting properties with regard to cell uptake and PDT.

Results and Discussion

Synthesis: It is well-known that glycosyl imidates are very potent glycosyl donors that react readily with different hydroxy compounds such as alcohols, carboxylic acids and phenols.[10] We therefore attempted the reaction of different α-glycosyl imidates with hydroxy-substituted porphyrins to obtain carbohydrate-substituted porphyrins. Starting compound **4** was synthesized by reaction of the dipyrromethane **2** with iminium ion **3** in dichloromethane as described in the literature (Scheme 1).[11] By means of this procedure compound **4** was easily synthesized in multigram quantities, and only a diaryl-substituted compound **5** and etioporphyrin IV were obtained as side products in low yield. The porphyrins were separated by column chromatography on silica gel. Metallation of **4** with nickel acetate was performed by means of standard procedures.[12] The nickel complex **6** reacted with different glycosyl imidates **7a–g** at room temperature in dichloromethane with $ZnCl_2$ as catalyst. After one hour, the corresponding ortho esters **8** were isolated as the main reaction products and only minor amounts of compounds **9a–g** were obtained (Scheme 2). Nevertheless, if the reaction time was extended to 24 hours, the glycosylated porphyrins **9a–g** were obtained in 24–30% yield. Besides some unreacted starting material, the porphyrinic acetate **10** was isolated as the only side product in this reaction. Both compounds were most probably formed by acid-catalysed fragmentation of the ortho ester **8**. Compound **10** can be used to regenerate porphyrin **6** by a simple saponification reaction. The obtained carbohydrate-substituted porphyrins **9a–g** were purified by column chromatography on silica gel with dichloromethane as eluent. The acetal groups were removed by treatment with sodium methanolate in methanol[13] and demetallation was performed with propanedithiol/TFA[14] to give an overall yield of 61–99%. The porphyrinic compounds **11a–g** were purified by chromatography on silica gel with dichloromethane/methanol (2/1) as eluent. As expected, compounds **9b–g** and **11b–g** were obtained in the β-configuration, as indicated by NMR spectroscopy. Owing to the strong neighbouring group effect of the axial 2-acetoxy group, the mannosyl derivatives **9a** and **11a** were formed in the α-configuration. It is noteworthy that under the reaction conditions already described compound **4** yields only a mixture of more than 10 different, mainly nonporphyrinic compounds, as was indicated by TLC analysis and UV/Vis spectroscopy. No attempts were made to isolate these products. Therefore it is absolutely necessary to use the nickel complex **6** as starting material for the glycosylating procedure.

Abstract in German: *Es wird eine effiziente Synthesemethode für neuartige Kohlenhydrat-substituierte Porphyrine beschrieben. Das Porphyrin **6** reagiert in guter Ausbeute mit den Glycosylimidaten **7a–g** zu den Kohlenhydrat-substituierten Porphyrinen **9a–g**. Anschließende Demetallierung und Abspaltung der Kohlenhydratschutzgruppen führt zu den metallfreien Verbindungen **11a–g**. In wäßriger Lösung bilden die Verbindungen **11a–g** definierte Strukturen in einem Selbstorganisationsprozeß aus. Der Aggregationsprozeß hängt dabei in Methanol/Wasser von der Konfiguration des anomeren Kohlenstoffatoms der Kohlenhydratgruppe ab. Charakteristisch für die Porphyrinaggregate ist eine starke Aufspaltung der Soret-Bande sowie eine Rotverschiebung aller Absorptionsbanden. Die Wechselwirkung der Porphyrinaggregate mit Phosphatidylethanolamin- und DMPC-Liposomen führt zu einem sehr effizienten Einbau der Porphyrine **11a–g** in Form von Monomeren in die Liposome, was durch sehr hohe Bindungskonstanten belegt wird. Bei niedrigen Liposomkonzentrationen konnten außerdem nichtkovalente Porphyrindimere nachgewiesen werden.*

0947-6539/99/0502-0588 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 2



	R^1	R^2	R^3	R^4
7a	OAc	H	H	OAc
7b	H	OAc	OAc	H
7c	H	OAc	H	OAc
7d	H	NHAc	H	OAc
7e	H	OAc	H	α(1,4)Glc(OAc)$_4$
7f	H	OAc	H	β(1,4)Gal(OAc)$_4$
7g	H	OAc	H	β(1,4)Glc(OAc)$_4$
11a	OH	H	H	OH
11b	H	OH	OH	H
11c	H	OH	H	OH
11d	H	NHAc	H	OH
11e	H	OH	H	α(1,4)Glc
11f	H	OH	H	β(1,4)Gal
11g	H	OH	H	β(1,4)Glc

Scheme 2. Synthetic route to carbohydrate-substituted porphyrins **9a–g** and **11a–g**.

Characterization: All new compounds were fully characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, mass spectrometry and microanalysis and were found to be analytically pure as indicated by HPLC analysis. Nevertheless, all porphyrinic compounds showed significant aggregation in organic solvents at a concentration above 10^{-3} M, indicated in the NMR spectra by a broadening of all peaks and a splitting of the methyl and ethyl resonances. This effect was less significant if TFA was added to the solution. Assignments of the resonances to individual protons in the 500 MHz NMR spectra are based on COSY and HMQC spectra. Furthermore, the substitution pattern at the porphyrin periphery was proved by NOE experiments. The resonance of the C-1 proton of the glycosyl moieties in compounds **9b–g** appears as a well-resolved doublet ($J = 7.88–8.24$ Hz) between $\delta = 4.65$ and 4.83 in $CDCl_3$. For compounds **11b–g** this doublet ($J = 7.02–9.12$ Hz) was found between $\delta = 5.15$ and 5.37 in [D_5]pyridine. These findings indicate a β-configuration of the anomeric carbon of the carbohydrate moieties. In contrast with this, the resonance of the C-1 proton in compounds **9a** and **11a** appears as a doublet ($J = 2.39$ Hz) at $\delta = 5.13$ in $CDCl_3$ and 5.67 ($J = 6.34$ Hz) in [D_5]pyridine, respectively. This is in accordance with an α-configuration for this carbon atom.

Spectroscopic properties: The carbohydrate-substituted porphyrins **11a–g** were soluble in pure methanol or dichloromethane/methanol (1/1) and exhibit strong Soret absorptions at 399 and 402 nm ($\varepsilon = 1.2 \times 10^5 \pm 2000$ M^{-1}cm^{-1}), respectively. In addition, four Q bands were detected at 505, 540, 575 and 629 nm. The half-width of the Soret band in dichloromethane/methanol was 45 ± 5 nm. Thus the Soret band is significantly broadened and less intense than that produced by the original porphyrin **4** ($\lambda = 403$ nm, fwhm: 32 nm, $\varepsilon = 1.58 \times 10^5$ M^{-1}cm^{-1}) or the fully acetylated compounds **9a–g** (fwhm: 30 ± 5 nm, $\varepsilon = 2.2 \times 10^5$ M^{-1}cm^{-1}). Also, the Soret absorption of all-carbohydrate-substituted compounds has a more asymmetric shape than the Soret absorption of **4** or **9a–g**. Both findings indicate some degree of porphyrin aggregation or dimerization in this solvent. In micellar CHAPS (3-([3-cholamidopropyl]dimethylammonio)-1-propanesulfonate) or SDS (sodium dodecylsulfate) solutions, the electronic spectra of all compounds have very similar properties and are comparable with those obtained in dichloromethane/methanol. In the fluorescence spectra in dichloromethane/methanol or micellar solution, two emission peaks were detected at 630 and 695 nm and the excitation spectra detected at 630 nm were comparable with the absorption spectra.

As already mentioned, the ready aggregation of amphiphilic porphyrins in aqueous solution significantly alters their biophysical properties. We have shown recently that amphiphilic carbohydrate-substituted porphyrins can be stimulated to form closed vesicles in a self-assembling process.[15] These porphyrinic vesicles were characterized by strong exciton splitting of the Soret absorption band.[15] We therefore tried to stimulate a self-assembling process for the newly synthesized compounds **11a–g**. The porphyrinic compounds **11a–g** were added to a micellar solution of CHAPS in phosphate-buffered saline solution (PBS) at pH 7 and incubated for 24 hours. Then the surfactant was removed by dialysis and the dialysed solution was treated with ultrasound to promote the formation of self-assembling structures. By means of this procedure clear solutions of porphyrinic aggregates were formed for all compounds. The solutions were stable in the dark and no significant precipitation was observed even after five months. The electronic spectra of these solutions exhibited strong exciton splitting of the Soret

Table 1. Absorption spectra of porphyrin aggregates **11a–g** in PBS solution at pH 7.

	Soret 1		Soret 2		Q3		Q2		Q1	
Compound	λ [nm]	ε [$M^{-1}cm^{-1}$]	λ [nm]	ε [$M^{-1}cm^{-1}$]	λ [nm]	ε [$M^{-1}cm^{-1}$]	λ [nm]	ε [$M^{-1}cm^{-1}$]	λ [nm]	ε [$M^{-1}cm^{-1}$]
11a	362	1.7×10^4	445	2.3×10^4	521	1.5×10^4	576	9.8×10^3	530	7.5×10^3
11b	365	1.6×10^4	450	2.0×10^4	524	1.4×10^4	578	1.2×10^4	630	9.7×10^3
11c	362	1.3×10^4	445	1.6×10^4	522	1.0×10^4	575	7.0×10^3	630	4.6×10^3
11d	360	2.6×10^4	448	3.6×10^4	522	1.7×10^4	575	9.5×10^3	628	4.0×10^3
11e	359	1.0×10^4	445	1.3×10^4	521	8.2×10^3	575	5.2×10^3	628	2.9×10^3
11f	358	2.8×10^4	442	3.9×10^4	521	2.1×10^4	575	1.2×10^4	628	8.3×10^3
11g	360	2.2×10^4	445	3.0×10^4	522	1.9×10^4	582	1.2×10^4	626	8.3×10^3

band at $5525\pm40\ cm^{-1}$ with peaks centred at 360 ± 3 and 448 ± 3 nm (Table 1) and three red-shifted Q bands compared with the spectra obtained in dichloromethane/methanol (Figure 1). The relative intensities of the two Soret peaks

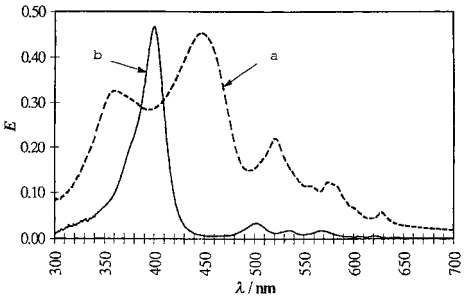


Figure 1. Electronic spectra of compound **11d** in PBS buffer (a) and dichloromethane/methanol (b). Porphyrin concentration 0.4×10^{-5} M. Curve a is enhanced by a factor of 7.35. E = absorbance

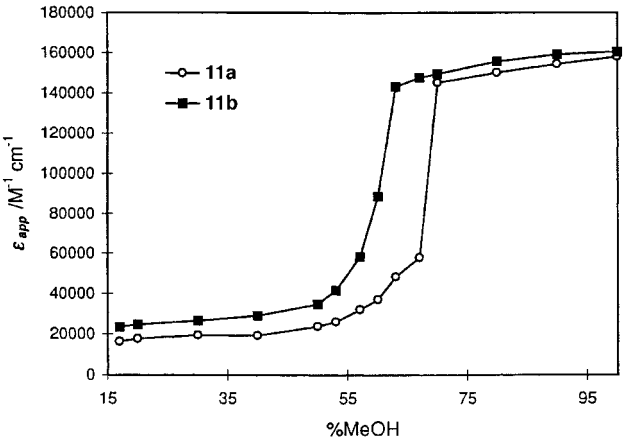


Figure 2. Aggregation curve of mannose derivative **11a** and galactose derivative **11b** ($c=1.8\times10^{-5}$ M) in methanol/water mixtures. Data are corrected for density changes. ε_{app} = apparent extinction coefficient.

depend only slightly upon the carbohydrate moiety. For all compounds the red-shifted peak is the most prominent one (Soret 1/Soret $2=1/1.36\pm0.09$) and the intensity of both Soret peaks is lowered by a factor of 3.5–4.5 compared with the peaks obtained in dichloromethane/methanol. Also, the blue shift of the Soret absorption (2770–3160 cm^{-1}) is always larger than the red shift (2420–2570 cm^{-1}). As Fuhrhop has already pointed out[16] this observation is only in accordance with a combination of edge-to-edge and cofacial interaction of the chromophores. It is important to note that both Soret absorptions have approximately the same half-width of $5200\pm200\ cm^{-1}$, indicating that both absorptions are due to only one type of porphyrin aggregate.[16] We also investigated the aggregation behaviour of the synthesized compounds in methanol/water and ethanol/water mixtures. As the proportion of water in the methanol/water mixtures was increased, a strong reduction in intensity and a red shift of all absorption bands was observed. For compounds **11b–g** aggregation occurs at a methanol concentration of less than 58–60% (Figure 2). For compound **11a** aggregation was significant at a somewhat higher methanol concentration of 67–69%. For mixtures containing less than 60% and 69% methanol, respectively, a splitting of the Soret absorption was observed for all compounds (Figure 3). Furthermore, two isosbestic points were detected at 358 and 415 nm. For ethanol/water mixtures the same behaviour was observed. Here aggregation occurs at 45% ethanol concentrations for compounds **11b–g** and at 55% ethanol concentrations for compound **11a**. These

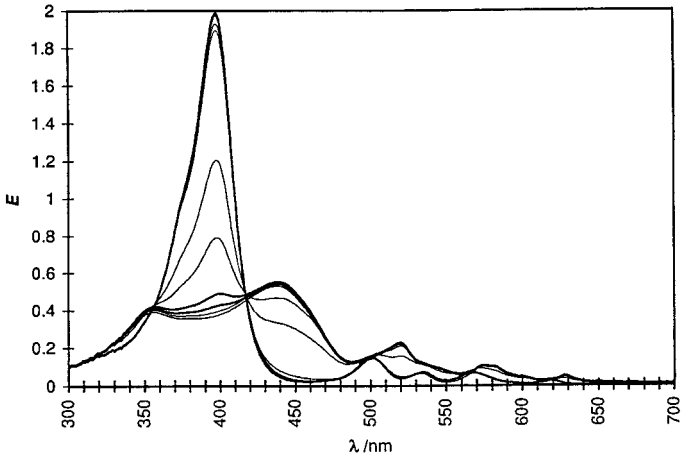


Figure 3. UV/Vis spectra of compound **11a** ($c=1.9\times10^{-5}$ M) in methanol/water mixtures. Uppermost curve: 100% methanol. Lowermost curve: 17% methanol.

observations clearly indicate that the aggregation is a controlled self-assembling process and that an aggregation process leading to a mixture of different types of aggregate can be ruled out. It is important to note that this process is not affected by the nature of the carbohydrate moieties in compounds **11b–g** and aggregation at a different methanol or ethanol concentration was only observed for compound **11a**. Therefore the self-assembling process depends upon the configuration of the anomeric carbon atom.

0947-6539/99/0502-0590 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 2

Interaction with cell membrane models: The use of liposomes as models of cell membranes is of considerable interest for investigations concerning the influence of several physicochemical and photobiological factors that are important for the uptake and incorporation of photosensitizers by cells.[17] In order to investigate the uptake of the synthesized porphyrinic aggregates by cell membrane models, we incubated the porphyrinic solutions (porphyrin concentration 2.5 $\mu g\,mL^{-1}$) with phosphatidylethanolamine (PE) liposomes obtained from *Escherichia coli* total lipid extract or dimyristoylphosphatidylcholine (DMPC) liposomes for 24 hours. The liposome concentration was varied between 5 $\mu g\,mL^{-1}$ and 300 $\mu g\,mL^{-1}$. Incorporation of the porphyrins into the liposomes was studied by fluorescence spectroscopy. The fluorescence spectra obtained were characterized by emissions at 630 and 690 nm which are due to porphyrin monomer fluorescence (Figure 4). In addition, a less intense emission

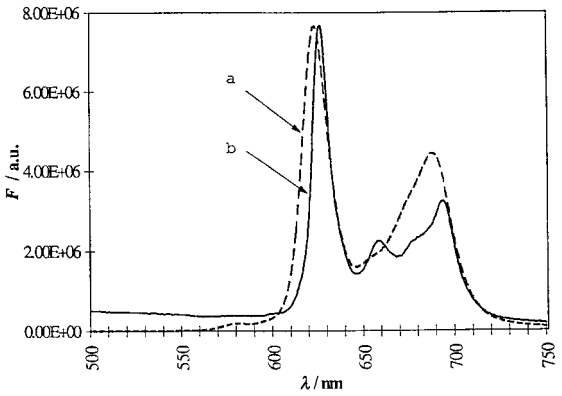


Figure 4. Fluorescence spectra of compound **11d** ($c = 1.0 \times 10^{-6}$ M) in dichloromethane/methanol (a) and PE liposomes (b). PE concentration 100 $\mu g\,mL^{-1}$. Curve b is enhanced by a factor of 4.

band was observed at 650–660 nm. The relative intensity of this emission compared with those at 630 nm and 690 nm decreased with increasing liposome concentration. The excitation spectra registered at 630 and 690 nm were almost identical to the absorption spectra obtained for the compounds in dichloromethane/methanol. The excitation spectra registered at 650 or 660 nm had a slightly broadened (fwhm: 35 ± 5 nm) and slightly red-shifted (3 nm) Soret band compared with those registered at 630 or 690 nm. We therefore conclude that the fluorescence observed at 650–660 nm is due to the formation of noncovalent porphyrin dimers incorporated into the liposome membrane, especially at low lipid concentration. Thus dimerization is accompanied by a red shift in fluorescence of 490 cm^{-1} and a decrease in fluorescence intensity.

The assumption of dimer formation is further strengthened by another experiment. After extraction of the PBS solution with dichloromethane, only emissions at 630 and 690 nm were detected in the organic phase. Furthermore, after addition of CHAPS, which is known to lead to complete monomerization of porphyrinic dimers and oligomers, a dramatic decrease in intensity of the 650 nm emission was observed (Figure 5). Therefore a covalently bound dimer or photobleaching products[18] formed from the porphyrins can be excluded as

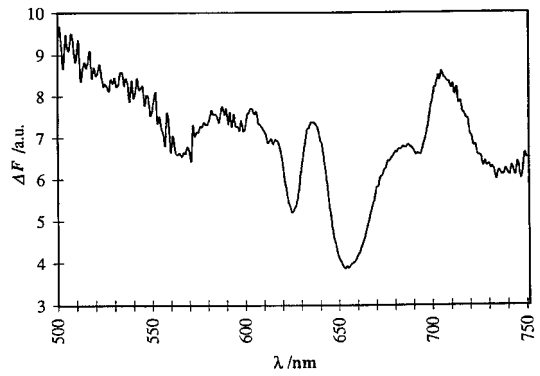


Figure 5. Fluorescence difference spectrum of compound **11a** in PE liposomes before and after addition of 100 mg CHAPS to the PE solution.

the origin of the 650 nm emission. The existence of strongly fluorescing dimers is in contrast with other porphyrins, where dimer fluorescence is known to be strongly quenched.[19] Nevertheless, it has been shown recently that sapphyrin dimers also show strong fluorescence in polar solvents and liposomes.[20] This is most probably due to a different mode of aggregation involving solvent-bridged dimers that makes radiationless deactivation of the excited states less likely.[21] Because the porphyrinic aggregates exhibit no or virtually no fluorescence, the incorporation of porphyrinic monomers into liposomes leads to a strong increase in fluorescence intensity (Figure 6).

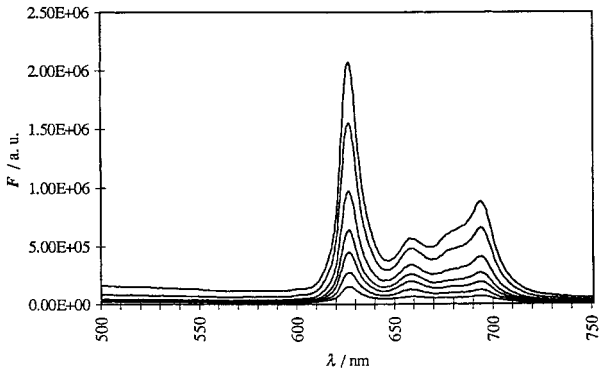


Figure 6. Fluorescence spectra of compound **11d** in PE liposomes. Porphyrin concentration: 2.5 $\mu g\,mL^{-1}$, PE concentration 5 $\mu g\,mL^{-1}$ (lower curve) to 200 $\mu g\,mL^{-1}$ (upper curve).

Association of liposomes and porphyrinic monomers: Equation (1) was used for calculating an analytical binding constant.[22]

$$1/F_O = 1/(K_B\, F_\infty\, [C_L]) + 1/F_\infty \quad (1)$$

Here, F_0 is the observed fluorescence intensity of the sensitizer in the presence of liposomes, F_∞ is the fluorescence intensity for complete association and $[C_L]$ is the liposome concentration expressed in $mg\,mL^{-1}$. From a linear regression analysis of a plot of $1/F_O$ against $1/[C_L]$, the binding constant K_B and F_∞ were calculated. Excellent correlations were obtained for all compounds investigated (Figure 7). The synthesized compounds exhibit very different analytical bind-

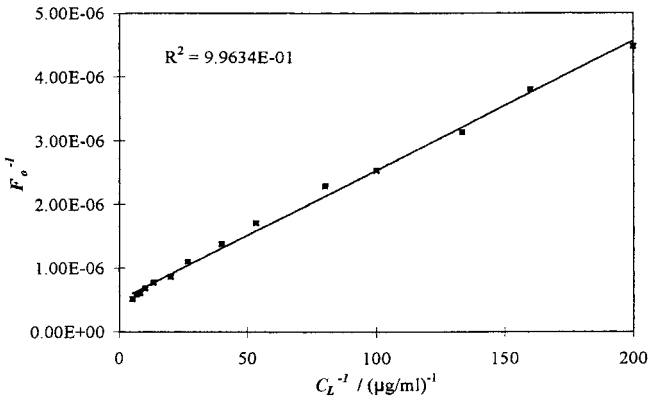


Figure 7. Plot of $1/F_O$ vs $1/C_L$ for compound **11d** in PE liposome solution.

ing constants for the two different types of liposomes examined (Table 2) and these results can be generalized according to the type of liposome used. The binding constant estimated for DMPC liposomes is always lower than that observed for the same porphyrin system with PE liposomes

Table 2. Analytical binding constants of synthesized porphyrins **11a–g** vs. liposomes.

Compound	Binding constant $[mg\,mL^{-1}]^{-1}$	
	E. coli liposomes	DMPC liposomes
11a	53.8 ± 9.5	38.7 ± 8.2
11b	132.6 ± 10.0	27.9 ± 8.9
11c	64.8 ± 9.5	43.2 ± 0.9
11d	90.0 ± 15.6	41.3 ± 5.8
11e	50.1 ± 10.0	55.2 ± 9.9
11f	161.8 ± 8.3	46.3 ± 6.8
11g	186.7 ± 20.5	65.9 ± 10.0

from *E. coli* lipid extract. In addition, all binding constants are greater than those reported for the binding of hematoporphyrin to PE liposomes.[23] Although the difference between the binding constants for binding to DMPC liposomes is relatively small, huge differences were found for the binding to PE liposomes. It is well-known that PE liposomes undergo a phase transition between the L_α and the inverse hexagonal phase (H_{II}) depending upon pH, temperature and additives.[24] It has been shown already that PE liposomes tend to exist in the inverse hexagonal phase at pH 7.[24] A bilayer composed of H_{II}-forming lipids like PE has different properties concerning thickness, permeability and deformability than a vesicle formed by other lipids.[24] Therefore, the rates of rotation and lateral self-diffusion are different, and it has also been shown that the membranes of lipid vesicles formed from PE have large elastic moduli.[25] Swelling of the inverted H_{II} phase causes the interfacial area per molecule to increase.[24] An increased interfacial area will lead to greater binding constants for hydrophobic or amphiphilic compounds. Therefore we believe that the large values estimated for the binding constants of porphyrins **11a–g** are due to a phase transition of PE liposomes to an inverse H_{II} phase. Nevertheless, this is only an assumption and more detailed investigations are necessary to clarify the unusally strong binding of the carbohydrate-substituted compounds to liposomes prepared from *E. coli* lipid extract.

Conclusion

We have synthesized several new carbohydrate-substituted porphyrins that show very interesting properties regarding PDT. The compounds were incorporated very efficiently into cell membrane models, mainly as monomers. The estimated binding constants were much greater than those reported for hematoporphyrin. All compounds formed stable aggregates in a self-assembling process in aqueous solution. Furthermore, these aggregates did not show any significant precipitation even after several months. Work is under way in our laboratories to elucidate the structure of the aggregates by means of electron microscopy and the interaction of the synthesized compounds with different lipoproteins.

Experimental Section

General: Melting points were determined with a Büchi 510 apparatus and are uncorrected. Column chromatography was carried out with silica gel 60, mesh size 0.060–0.2 mm, without fluorescence indicator (Merck). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or [D_5]pyridine on a Bruker DRX 500 MHz spectrometer. Chemical shift values are reported in ppm with TMS as an internal standard. The following abbreviations were used for the assignment of hydrogen and carbon atoms in the NMR spectra: Por for porphyrin, Mal for maltose, Glc for glucose, Gal for galactose, GlcNAc for *N*-acetylglucosamine, Man for mannose, Cel for cellobiose, Lac for lactose. IR spectra were recorded on a Shimadzu IR 435 spectrometer. UV/Vis spectra were measured on a Kontron Uvikon 860 spectrometer. Fluorescence spectra were recorded on a computer-controlled Spex Fluoromax 1 spectrofluorometer. FAB mass spectra were obtained with a VG-Analytical VG70:250E spectrometer. FAB-MS spectra were run in the positive ion mode. 3-Nitrobenzylalcohol was used as the matrix for FAB measurements. Laser-desorption mass spectrometry was carried out with a Leybold LAMMA 500 laser microprobe mass analyser and MALDI-TOF spectra were measured with a Fransen Bruker Analytik Reflex II spectrometer, both at at the Forschungsinstitut Borstel. Pulse sonification measurements were made with a Bandelin Sonoplus HD 200 sonicator fitted with a TT 13 Pt-sonotrode. *E. coli* total lipid extract (PE, Sigma, type IX) was purified by acetone/water extraction as described in the literature.[26] L-α-Dimyristoylphosphatidyl choline (DMPC) was purchased from Sigma (P6392, 99 + %) and used without further purification. Glycosylimidates were prepared according to a procedure given in the literature.[27]

Liposome preparation: *E. coli* lipid or DMPC (50 mg) and CHAPS (100 mg) were added to PBS solution (2 mL) at pH 7. After 24 hours the suspension was dialysed five times in a 0.5–3 mL Slide-A-Lyser-cassette (Pierce) at room temperature against a 1000-fold volume of PBS solution. The solution was removed from the cassette and diluted to 10 mL with PBS solution. The liposome stock solutions were stored in liquid nitrogen until use. Before use the solutions were carefully and slowly warmed to room temperature and subjected to sonar pulses (30% pulse, 40% intensity). From this stock solution aliquots were taken for incubation with porphyrin aggregates.

Formation of porphyrinic aggregates: Porphyrins **11a–g** (1 mg) and CHAPS (100 mg) were separately dissolved in 10 mL PBS solution (containing 0.155 M NaCl) at pH 7 and stirred for 24 h at 40 °C. The solution was passed through a 400 nm filter incorporated within a LiposoFast-Basic system (Milsch Equipment). Then the solution was dialysed 8 times in a 3–15 mL Slide-A-Lyser cassette (Pierce) against a 500-fold volume of PBS solution. The porphyrinic solution was removed from the cassette and diluted to 100 mL with PBS solution. Then the solution was subjected to sonar pulses (50% pulse, 40% intensity) until a clear solution was obtained.

Measurement of analytical binding constants: The binding affinity of the carbohydrate-substituted porphyrins **11a–g** for liposomes was quantified by estimating an analytical binding constant. For these measurements the

0947-6539/99/0502-0592 $ 17.50+.50/0 *Chem. Eur. J.* **1999**, *5*, No. 2

liposome concentration was varied between 5 $\mu g\,mL^{-1}$ and 300 $\mu g\,mL^{-1}$ by means of aliquots of the liposome stock solution described. Incubation of the liposome solution with the porphyrinic aggregates in PBS buffer was performed in the dark for 24 hours. The initial porphyrin concentration in the aggregate solutions was 10 $\mu g\,mL^{-1}$. This solution (500 µL) was diluted with liposome stock solution and PBS solution to a total volume of 2 mL, and then incubated at 37 °C, that is above the gel-to-liquid transition temperature of the lipids (23 °C for DMPC).[28] Because phosphatidylethanolamine liposomes prepared from *E. coli* lipid extract are formed from a mixture of different compounds that differ in the acyl chain composition, a distinct transition temperature cannot be given. Nevertheless, it is most likely that the transition temperature is much lower than 35 °C. At least three different, independent measurements with different liposome stock solutions were made for calculating the binding constants.

(4-Hydroxymethylphenyl)-bis(5-ethoxycarbonyl-4-ethyl-3-methyl-2-pyrryl)methane (**1**): 4-Hydroxymethylbenzaldehyde (7.88 g, 58.3 mmol) and 2-ethoxycarbonyl-3-ethyl-4-methylpyrrole (21.14 g, 116.7 mmol) were dissolved in ethanol (80 % 50 mL). Then concentrated H_2SO_4 (4 mL) was added and the reaction mixture was stirred for 24 h at room temperature. Then CH_2Cl_2 (400 mL) was added and the solution washed with water, saturated $NaHCO_3$ solution and water. The organic layer was separated and dried (Na_2SO_4), and the solvent was removed in vacuo. The crude product was separated by chromatography on a silica gel column (4 × 40 cm) with CH_2Cl_2 as eluent. Yield 24.19 g (89 %); m.p. 69–72 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 1.10$ (t, $J = 7.46$ Hz, 6H, $-CH_2-CH_3$), 1.26 (t, $J = 7.10$ Hz, 6H, $CO_2-CH_2-CH_3$), 1.82 (s, 6H, $-CH_3$), 2.52 (br s, 1H, Ar$-CH_2OH$), 2.73 (q, $J = 7.46$ Hz, 4H, $-CH_2-CH_3$), 4.18 (q, $J = 7.10$ Hz, 4H, $CO_2-CH_2-CH_3$), 4.59 (s, 2H, $-CH_2OH$), 5.53 (s, 1H, $CH(Pyr)_2$), 7.04 (d, $J = 8.07$ Hz, 2H, Aryl), 7.24 (d, $J = 8.07$ Hz, 2H, Aryl), 8.76 (br s, 2H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): $\delta = 8.42$ (q, $-CH_2-CH_3$), 14.20 (q, $-CH_3$), 14.91 (q, $-CO_2-CH_2-CH_3$), 18.33 (t, $-CH_2-CH_3$), 40.36 (d, Aryl$-CH(pyr)_2$), 59.63 (t, $-CO_2-CH_2-CH_3$), 64.46 (t, Aryl$-CH_2-$OH), 116.94 (s, C-5), 117.10 (s, C-3), 127.22 (d, Aryl C-2, C-6), 128.11 (d, Aryl C-3, C-5), 131.88 (s, C-2), 134.07 (s, C-4), 138.35 (s, Aryl C-1), 139.97 (s, Aryl C-4), 161.50 (s, $CO_2-CH_2-CH_3$); MS (70 eV): *m*/*z* (%) = 480 [M^+] (90), 435 [$M^+ - C_2H_5O$] (10), 407 [$M^+ - C_3H_5O_2$] (25), 327 (20), 300 [M^+ – pyrrole] (100), 268 (35), 254 (25), 181 (10), 91 [$C_7H_7^+$] (25), 88 (10), 69 (15); IR (KBr): $\tilde{\nu} = 3422$ (O–H), 3315 (N–H), 2956 (C–H), 1657 (C=O), 1434, 1237, 1144, 1087, 1013, 961, 770 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) ($\lg \varepsilon$) = 226 (4.15), 282 (4.55); $C_{28}H_{36}N_2O_5$ (480.60): calcd C 69.98, H 7.55, N 5.83; found C 69.53, H 7.45, N 5.74.

4-(Hydroxymethylphenyl)-bis(4-ethyl-3-methyl-2-pyrryl)methane (**2**): Sodium hydroxide (20.0 g, 500 mmol) and **1** (16.8 g, 35 mmol) were dissolved in ethylene glycol (190 mL). The mixture was refluxed for 20 mins, then cooled to room temperature and poured into water (500 mL). The precipitated product was collected by filtration, dissolved in diethyl ether and washed with brine and water. The organic layer was separated and dried (Na_2SO_4). The solvent was evaporated and the residue was used without further purification for the synthesis of porphyrin **3**. Yield 10.78 g (92 %); m.p. 142–144 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 1.20$ (t, 6H, $J = 7.50$ Hz, $-CH_2-CH_3$), 1.82 (s, 6H, $-CH_3$), 2.45 (q, 4H, $J = 7.50$ Hz, CH_2-CH_3), 4.64 (s, 2H, $-CH_2-$OH), 5.51 (s, 1H, Aryl$-CH(pyr)_2$), 6.37 (d, 2H, $J = 2.36$ Hz, pyr–CH), 7.14 (d, 2H, $J = 8.04$ Hz, Aryl), 7.29 (d, 2H, $J = 8.04$ Hz, Aryl), 7.37 (br s, 2H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): $\delta = 8.78$, 8.79 (2q, $-CH_2-CH_3$), 14.05 (q, $-CH_3$), 18.60 (t, $-CH_2-CH_3$), 40.59 (d, Aryl$-CH(pyr)_2$), 64.89 (t, CH_2-OH), 111.94 (d, C-5), 113.50 (s, C-3), 125.91 (s, C-4), 127.30 (d, Aryl C-3, C-5), 127.48 (s, C-2), 128.46 (d, Aryl C-2, C-6), 138.92 (s, Aryl C-4), 141.36 (s, Aryl C-1); IR (KBr): $\tilde{\nu} = 3369$ (N–H), 2948 (C–H), 1683, 1448, 1029 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) ($\lg \varepsilon$) = 229 (4.127); $C_{22}H_{28}N_2O$ (336.47): calcd C 78.53, H 8.39, N 8.32; found C 76.18, H 8.07, N 7.99.

5-(*p*-Hydroxymethylphenyl)-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin (**4**): *N,N*-Diethylmethylene ammonium chloride **3** (2.17 g, 17.8 mmol) and **1** (6.00 g, 17.8 mmol) were dissolved in 500 mL MeOH/CH_2Cl_2 (1/1). Then $K_3[Fe(CN)_6]$ (10 g) was added. The reaction mixture was stirred and refluxed for 2 h. Then potassium phosphate buffer (pH 6.5, 4 mL) was added and the mixture was refluxed further for 4 h. Then the mixture was cooled to room temperature and CH_2Cl_2 (300 mL) was added. The solution was washed with water (3 × 200 mL) and dried (Na_2SO_4). Silica gel (50 g) was added and the solvent was evaporated. The residue was dried in vacuo and separated by chromatography with a silica gel column (4 × 60 cm) and CH_2Cl_2 as eluent. Three porphyrinic fractions were collected: Fraction 1: etioporphyrin IV: yield 132 mg (2.9 %).

Fraction 2: porphyrin **4**: yield 787 mg (15.1 %); m.p. > 290 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = -3.2$ (br s, 2H, NH), 1.26 (s, 1H, Aryl$-CH_2-$OH), 1.76 (t, $J = 7.6$ Hz, 6H, Por$-CH_2-CH_3$), 1.88 (t, $J = 7.6$ Hz, 6H, Por$-CH_2-CH_3$), 2.46 (s, 6H, Por$-CH_3$), 3.64 (s, 6H, Por$-CH_3$), 3.96–4.12 (m, 8H, Por$-CH_2-CH_3$), 5.03 (s, 2H, Aryl$-CH_2-$OH), 7.70 (d, $J = 8.3$ Hz, 2H, Aryl), 8.05 (d, $J = 8.3$ Hz, 2H, Aryl), 9.96 (s, 1H, H-15), 10.16 (s, 2H, H-10, H-20); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): $\delta = 11.62$ (q, Por$-CH_3$), 14.68 (q, Por$-CH_3$), 17.58 (q, Por$-CH_2-CH_3$), 17.64 (q, Por$-CH_2-CH_3$), 19.83 (t, Por$-CH_2-CH_3$), 19.92 (t, Por$-CH_2-CH_3$), 65.45 (t, Aryl$-CH_2-$OH), 95.27 (d, Por-15), 96.41 (d, Por-10, Por-20), 117.99 (s, Por), 126.00 (d, Aryl), 133.16 (d, Aryl), 134.52 (s, Por), 135.69 (s, Por), 136.13 (s, Aryl), 141.02 (s, Aryl), 41.65 (s, Por), 141.75 (s, Por), 141.81 (s, Por), 142.09 (s, Por), 142.72 (s, Por), 144.18 (s, Por); MS (MALDI-TOF): *m*/*z* (%): 586 [M^++1] (100); IR (KBr): $\tilde{\nu} = 3396$ (O–H), 3255 (N–H), 2948 (C–H), 1703, 1599, 1438, 1366, 1252, 1050, 824, 736, 671 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) ($\lg \varepsilon$) = 403 (5.199), 502 (4.117), 536 (3.775), 570 (3.754), 622 (3.269); $C_{39}H_{44}N_4O \cdot H_2O$ (602.82): calcd C 77.71, H 7.69, N 9.29; found C 78.28, H 7.82, N 8.55.

Fraction 3: 5,15-bis(4-hydroxymethylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**5**): yield 172 mg (2.8 %); m.p. > 265 °C; ^{1}H NMR (500 MHz, $CDCl_3$/[D_6]DMSO, 300 K): $\delta = -2.58$ (br s, 2H, NH), 1.73 (t, $J = 7.53$ Hz, 12H, $-CH_2CH_3$), 2.45 (s, 12H, $-CH_3$), 3.98 (q, $J = 7.53$ Hz, 8H, $-CH_2CH_3$), 4.91 (d, $J = 5.72$ Hz, 4H, $-CH_2OH$), 5.42 (m, $-$OH), 7.71 (d, $J = 7.70$ Hz, 4H, Aryl), 7.93 (d, $J = 7.70$ Hz, 4H, Aryl), 10.18 (s, 2H, H-10, H-20); ^{13}C NMR ($CDCl_3$, 125 MHz, 300 K): $\delta = 13.98$ (s, CH_3), 17.31 (q, CH_2CH_3), 19.18 (t, CH_2CH_3), 62.94 (t, CH_2OH), 95.71 (d, Por-10, Por-20), 117.79 (s, Por), 125.31 (d, Aryl), 131.91 (d, Aryl), 135.63 (s, Aryl), 139.29 (s, Por), 140.14 (s, Aryl), 142.73 (s, Por), 144.25 (s, Por), 144.54 (s, Por); MS (FAB): *m*/*z* (%): 691 [M^++1] (25); IR (KBr): $\tilde{\nu} = 3399$ (O–H), 2945 (C–H), 1686, 1607, 1437, 1371, 1050, 760 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) ($\lg \varepsilon$) = 407 (5.11), 505 (4.00), 539 (3.62), 571 (3.67), 613 (2.97) nm; $C_{46}H_{50}N_4O_2 \cdot 3H_2O$ (744.97): calcd C 74.16, H 7.58, N 7.52; found C 74.22, H 6.93, N 7.48.

5-(*p*-Hydroxymethylphenyl)-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin-Ni^{II} (**6**): Porphyrin **4** (200 mg, 0.34 mmol) and [Ni($CH_3COO)_2$] (1 g, 5.66 mmol) were dissolved in CH_2Cl_2/MeOH (1/1, 100 mL) and subjected to ultrasonic pulses for 15 h in an ultrasound cleaning bath (50 W). The mixture was poured into water (50 mL) and the organic layer was separated and dried (Na_2SO_4). The solvent was evaporated and the residue components separated by chromatography on a silica gel column (4 × 60 cm) with CH_2Cl_2/MeOH (98/2) as eluent. Recrystallization from dichloromethane/methanol gave purple crystals of **6** (200 mg, 91 %). M.p. 224–226 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 1.65–1.70$ (m, 6H, Por$-CH_2-CH_3$), 1.75–1.80 (m, 6H, Por$-CH_2-CH_3$), 1.93 (t, 1H, $J = 5.95$ Hz, Aryl$-CH_2OH$), 2.28, 2.31 (2s, 6H, Por$-CH_3$), 3.43, 3.45 (2s, 6H, Por$-CH_3$), 3.77–3.82 (m, 4H, Por$-CH_2CH_3$), 3.86–3.91 (m, 4H, Por$-CH_2CH_3$), 5.01 (d, 2H, $J = 5.70$ Hz, Aryl$-CH_2OH$), 7.60–7.64 (m, 2H, Aryl), 7.85–7.93 (m, 2H, Aryl), 9.56 (s, 1H, Por–H-15), 9.63 (s, 2H, Por–H-10, H-20); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): $\delta = 11.20$ (q, Por$-CH_3$), 15.22 (q, Por$-CH_3$), 17.15 (q, Por$-CH_2CH_3$), 17.32 (q, Por$-CH_2CH_3$), 17.34 (q, Por$-CH_3$), 19.50 (t, Por$-CH_2CH_3$), 19.57 (t, Por$-CH_2CH_3$), 65.26 (t, Aryl$-CH_2OH$), 95.4 (d, Por-15), 96.07 (d, Por-10), 96.19 (d, Por-20), 117.22 (s, Por), 125.70 (d, Aryl), 132.96 (d, Aryl), 136.23 (s, Aryl), 136.29 (s, Por), 138.10 (s, Por), 138.12 (s, Por), 139.07 (s, Por), 139.10 (s, Por), 139.11 (s, Por), 139.52 (s, Por), 139.72 (s, Por) 140.62 (s, Por), 140.65 (s, Por), 140.72 (s, Por), 140.79 (s, Por), 140.85 (s, Por), 140.91 (s, Por), 141.03 (s, Aryl), 141.702 (s, Por), 143.45 (s, Por), 143.51 (s, Por), 144.97 (s, Por); MS (FAB): *m*/*z* (%): 641.8 [M^++2]; IR (KBr): $\tilde{\nu} = 3388$ (O–H), 2947 (C–H), 1446, 1360, 1267, 1214, 1159, 1051, 976, 820, 778, 700 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) ($\lg \varepsilon$) = 397 (5.304), 520 (4.076), 555 (4.456); $C_{39}H_{42}N_4O$-ni $\cdot H_2O$ (659.47): calcd C 71.03, H 6.73, N 8.49, Ni 8.90; found C 70.53, H 7.14, N 8.57.

General procedure for the synthesis of porphyrins 9 a–g: In a 10 mL round-bottom flask porphyrin **6** (200 mg, 0.31 mmol) and the corresponding carbohydrate trichloroacetimidate **7** (1.22 mmol) were dissolved in CH_2Cl_2 (5 mL). Then molecular sieves 4Å (200 mg) were added and the suspension stirred for 10 min. Then $ZnCl_2 \cdot Et_2O$ (0.25 mL, 0.48 mmol) was added and the reaction mixture stirred at room temperature for 24 h. The mixture was poured into CH_2Cl_2 (200 mL) and washed with water (3 × 100 mL). The organic layer was separated and dried (Na_2SO_4). The solvent was removed

and the residue components separated by chromatography on a silica gel column (30 × 2 cm). Two porphyrinic fractions were collected. The first one was porphyrin acetate **10**, the second unreacted starting material **6**. Then the eluent was gradually changed from pure CH_2Cl_2 to CH_2Cl_2/MeOH (7/3) and a third fraction, the carbohydrate-substituted porphyrin was collected. Analytically pure compounds were obtained by TLC on silica plates with CH_2Cl_2/MeOH (99/1 – 95/5) as eluent.

5-[4-(2,3,4,6-Tetra-*O*-acetyl-α-D-manopyranos-1-oxy)benzyl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin-Ni^{II} (**9a**): According to the general procedure 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranotrichloroacetimidate (**7a**, 800 mg, 1.62 mmol) and **6** (200 mg, 0.312 mmol) were allowed to react to yield **9a** (88 mg, 29 %). M.p. 108 – 110 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 1.65 - 1.71$ (m, 6H, Por−CH_2−CH_3), 1.74 – 1.79 (m, 6H, Por−CH_2−CH_3), 2.08 (s, 3H, Man−CO_2−CH_3), 2.13 (s, 3H, Man−CO_2−CH_3), 2.21 (s, 3H, Man−CO_2−CH_3), 2.26 (s, 6H, Por−CH_3), 2.30 (s, 3H, Man−CO_2−CH_3), 3.43 (s, 6H, Por−CH_3), 3.77 – 3.82 (m, 4H, Por−CH_2−CH_3), 3.86 – 3.91 (m, 4H, Por−CH_2−CH_3), 4.26 (m, 1H, $J_{4/5} = 9.86$ Hz, $J_{5/6a} = 2.28$ Hz, $J_{5/6b} = 5.23$ Hz, Man-5), 4.27 (m, 1H, $J_{5/6a} = 2.28$ Hz, $J_{6a/6b} = 12.31$ Hz, Man-6a) 4.45 (dd, 1H, $J_{5/6b} = 5.23$ Hz, $J_{6a/6b} = 12.31$ Hz, Man-6b), 4.86 (d, 1H, $J = 11.88$ Hz, Aryl−CH_2−), 5.08 (d, 1H, $J = 11.88$ Hz, Aryl−CH_2−), 5.13 (d, 1H, $J_{1/2} = 2.39$ Hz, Man-1), 5.45 (t, 1H, $J_{3/4} = 10.06$ Hz, $J_{4/5} = 9.86$ Hz, Man-4), 5.48 (m, 1H, $J_{1/2} = 2.39$ Hz, $J_{2/3} = 3.69$ Hz, Man-2), 5.59 (dd, 1H, $J_{3/4} = 10.06$ Hz, $J_{2/3} = 3.69$ Hz, Man-3), 7.61 (d, 2H, $J = 7.93$ Hz, Aryl), 7.93 (d, 2H, $J = 7.93$ Hz, Aryl), 9.57 (s, 1H, Por-15), 9.61 (s, 2H, Por-10, Por-20); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): $\delta = 11.16$ (q, Por−CH_3), 15.27 (q, Por−CH_3), 17.14 (q, Por−CH_2−CH_3), 17.32 (q, Por−CH_2−CH_3), 19.51 (t, Por−CH_2−CH_3), 19.56 (t, Por−CH_2−CH_3), 20.62 (q, Man−CO_2−CH_3), 20.69 (q, Man−CO_2−CH_3), 20.81 (q, Man−CO_2−CH_3), 62.46 (t, Man-6), 66.18 (d, Man-4), 68.77 (d, Man-5), 69.11 (d, Man-3), 69.34 (t, Aryl−CH_2−), 69.63 (d, Man-2), 95.43 (d, Por-15), 96.21 (d, Por-10, Por-20), 96.60 (d, Man-1), 116.93 (s, Por), 126.52, 126.89 (d, Aryl), 133.07 (d, Aryl), 135.98 (s, Por), 136.26 (s, Por), 136.31 (s, Aryl), 138.00 (s, Por), 138.38 (s, Por), 139.09 (s, Por), 139.11 (s, Por), 139.40 (s, Por), 139.45 (s, Por), 139.74 (s, Por), 140.63 (s, Por), 140.82 (s, Por), 140.86 (s, Aryl), 141.48 (s, Por), 141.74 (s, Por), 143.47 (s, Por), 143.52 (s, Por), 145.01 (s, Por), 145.02 (s, Por), 169.65 (s, Man−CO_2−CH_3), 169.86 (s, Man−CO_2−CH_3), 170.57 (s, Man−CO_2−CH_3); MS (FAB): *m*/*z* (%): 971 [M^++1, ^{58}Ni] (100); IR (KBr): $\tilde{\nu} =$ 3407, 2948 (C−H), 1749 (C=O), 1620 (Aryl), 1440, 1364, 1210, 1129, 1040, 975 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) ($\lg \varepsilon$) = 397 (5.325), 520 (4.111), 555 (4.378); $C_{53}H_{60}N_4O_{10}Ni$ (971.75): calcd C 65.51, H 6.22, N 5.76; found C 65.84, H 6.40, N 5.80.

5-[4-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranos-1-oxy)benzyl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin-Ni^{II} (**9b**): According to the general procedure 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranotrichloroimidate (**7b**, 320 mg, 0.65 mmol) and **6** (100 mg, 0.156 mmol) were allowed to react to yield **9b** (44.8 mg, 30 %). M.p. 135 – 138 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 1.70 - 1.74$ (m, 6H, Por−CH_2−CH_3), 1.79 – 1.83 (m, 6H, Por−CH_2−CH_3), 2.11 (s, 3H, Gal−CO_2−CH_3), 2.15 (s, 3H, Gal−CO_2−CH_3), 2.18 (s, 3H, Gal−CO_2−CH_3), 2.29 (s, 3H, Gal−CO_2−CH_3), 2.35 (s, 6H, Por−CH_3), 3.45 (s, 6H, Por−CH_3), 3.82 – 3.86 (m, 4H, Por−CH_2−CH_3), 3.90 – 3.92 (m, 4H, Por−CH_2−CH_3), 3.99 (m, 1H, $J_{4/5} = 1.86$ Hz, $J_{5/6a} = 7.90$ Hz, $J_{5/6b} = 5.20$ Hz, Gal-5), 4.29 (m, 1H, $J_{5/6} = 7.90$ Hz, $J_{6a/6b} = 11.33$ Hz, Gal-6a), 4.33 (m, 1H, $J_{5/6b} = 5.20$ Hz, $J_{6a/6b} = 11.33$ Hz, Gal-6b), 4.71 (d, 1H, $J_{1/2} = 7.97$ Hz, Gal-1), 4.92 (d, 1H, $J = 12.39$ Hz, Aryl−CH_2−), 5.15 (dd, 1H, $J_{2/3} = 10.76$ Hz, $J_{3/4} = 3.58$ Hz, Gal-3), 5.23 (d, 1H, $J = 12.39$ Hz, Aryl−CH_2−), 5.49 (dd, 1H, $J_{1/2} = 7.97$ Hz, $J_{2/3} = 10.76$ Hz, Gal-2), 5.54 (dd, 1H, $J_{3/4} = 3.58$ Hz, $J_{4/5} = 1.86$ Hz, Gal-4), 7.61 (d, 2H, $J = 7.79$ Hz, Aryl), 7.91 (d, 2H, $J = 7.79$ Hz, Aryl), 9.61 (s, 1H, Por-15), 9.66 (s, 2H, Por-10, Por-20); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): $\delta = 11.23$ (q, Por−CH_3), 15.27 (q, Por−CH_3), 17.24 (q, Por−CH_2−CH_3), 17.36 (q, Por−CH_2−CH_3), 19.55 (t, Por−CH_2−CH_3), 19.59 (t, Por−CH_2−CH_3), 20.56 (q, Gal−CO_2−CH_3), 20.61 (q, Gal−CO_2−CH_3), 20.63 (q, Gal−CO_2−CH_3), 20.75 (q, Gal−CO_2−CH_3), 61.26 (t, Gal-6), 67.00 (d, Gal-4), 68.83 (d, Gal-2), 70.50 (t, Aryl−CH_2−), 70.70 (d, Gal-5), 70.97 (d, Gal-3), 95.49 (d, Por-15), 96.28 (d, Por-10, Por-20), 99.75 (d, Gal-1), 117.03 (s, Por), 126.20 (d, Aryl), 126.58 (d, Aryl), 132.93 (d, Aryl), 136.38 (s, Aryl), 136.58 (s, Por), 137.96 (s, Por), 138.47 (s, Por), 139.14 (s, Por), 139.45 (s, Por), 139.79 (s, Por), 140.69 (s, Por), 140.72 (s, Por), 140.89 (s, Por), 140.92 (s, Aryl), 141.27 (s, Por), 141.53 (s, Por), 141.78 (s, Por), 143.53 (s, Por), 143.58 (s, Por), 145.11 (s, Por), 169.39 (s, Gal−CO_2−CH_3), 170.14 (s, Gal−CO_2−CH_3), 170.24 (s, Gal−CO_2−CH_3), 170.32 (s, Gal−CO_2−CH_3); MS (FAB): *m*/*z* (%): 972 [M^++2, ^{58}Ni] (100); IR (KBr): $\tilde{\nu} = 3411$, 2950 (C−H), 1750 (C=O), 1624 (Aryl), 439, 1364, 1218, 1046 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) ($\lg \varepsilon$) = 397 (5.265), 519 (3.924), 555 (4.261); $C_{53}H_{60}N_4O_{10}Ni$ (971.75): calcd C 65.51, H 6.22, N 5.76; found C 65.23, H 6.35, N 4.92.

5-[4-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranos-1-oxy)benzyl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin-Ni^{II} (**9c**): According to the general procedure, 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranotrichloroacetimidate (**7c**, 250 mg, 0.510 mmol) and **6** (100 mg (0.156 mmol) were allowed to react to yield **9c** (44.5 mg, 30 %). M.p. > 260 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 1.67 - 1.72$ (m, 6H, Por−CH_2−CH_3), 1.76 – 1.81 (m, 6H, Por−CH_2−CH_3), 2.10 (s, 3H, Glc−CO_2−CH_3), 2.11 (s, 3H, Glc−CO_2−CH_3), 2.14 (s, 3H, Glc−CO_2−CH_3), 2.19 (s, 3H, Glc−CO_2−CH_3), 2.32, 2.33 (2s, 6H, Por−CH_3), 3.44, 3.45 (2s, 6H, Por−CH_3), 3.79 (m, 1H, $J_{4/5} = 10.21$ Hz, $J_{5/6a} = 2.48$ Hz, $J_{5/6b} = 4.73$ Hz, Glc-5), 3.80 – 3.84 (m, 4H, Por−CH_2−CH_3), 3.87 – 3.92 (m, 4H, Por−CH_2−CH_3), 4.25 (dd, 1H, $J_{5/6a} = 2.48$ Hz, $J_{6a/6b} = 12.41$ Hz, Glc-6a), 4.37 (dd, 1H $J_{5/6b} = 4.73$ Hz, $J_{6a/6b} = 12.41$ Hz, Glc-6b), 4.75 (d, 1H, $J_{1/2} = 7.98$ Hz, Glc-1), 4.90 (d, 2H, $J = 12.34$ Hz, Aryl−CH_2−), 5.19 (d, 2H, $J = 12.34$ Hz, Aryl−CH_2−), 5.22 (t, 1H, $J_{3/4} = 9.53$ Hz, $J_{4/5} = 10.21$ Hz, Glc-4), 5.24 (t, 1H, $J_{1/2} = 7.98$ Hz, $J_{2/3} = 9.60$ Hz, Glc-2), 5.30 (t, 1H, $J_{2/3} = 9.60$ Hz, $J_{3/4} = 9.53$ Hz, Glc-3), 7.56 (d, 2H, $J = 7.95$ Hz, Aryl), 7.89 (d, 2H, $J = 7.95$ Hz, Aryl), 9.55 (s, 1H, Por-15), 9.62 (s, 2H, Por-10, Por-20); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): $\delta = 11.27$ (q, Por−CH_3), 15.24 (q, Por−CH_3), 17.20 (q, Por−CH_2−CH_3), 17.36 (q, Por−CH_2−CH_3), 19.52 (t, Por−CH_2−CH_3), 19.57 (t, Por−CH_2−CH_3), 20.51 (q, Glc−CO_2−CH_3), 20.55 (q, Glc−CO_2−CH_3), 20.62 (q, Glc−CO_2−CH_3), 20.67 (q, Glc−CO_2−CH_3), 61.80 (t, Glc-6), 68.34 (d, Glc-2), 70.64 (t, Aryl−CH_2−), 71.24 (d, Glc-4), 71.81 (d, Glc-5), 72.82 (d, Glc-3), 95.47 (d, Por-15), 96.26 (d, Por-10, Por-20), 99.33 (d, Glc-1), 116.99 (s, Por), 126.54 (d, Aryl), 132.91 (d, Aryl), 136.31 (s, Por), 136.36 (s, Aryl), 136.52 (s, Por), 137.94 (s, Por), 137.96 (s, Por), 138.09 (s, Por), 138.45 (s, Por), 139.09 (s, Por), 139.12 (s, Por), 139.13 (s, Por), 139.19 (s, Por), 139.40 (s, Por), 139.43 (s, Por), 139.47 (s, Por), 139.77 (s, Por), 139.80 (s, Por), 142.00 (s, Aryl), 143.00 (s, Por), 169.10 (s, Glc−CO_2−CH_3), 169.20 (s, Glc−CO_2−CH_3), 170.10 (s, Glc−CO_2−CH_3), 170.20 (s, Glc−CO_2−CH_3); MS (FAB): *m*/*z* (%): 971 [M^++2, ^{58}Ni] (100); IR (KBr): $\tilde{\nu} = 3410$, 2950 (C−H), 1755 (C=O), 1362, 1219, 1034 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) ($\lg \varepsilon$) = 397 (5.379), 521 (4.172), 555 (4.431); $C_{53}H_{60}N_4O_{10}Ni$ (971.75): calcd C 65.50, H 6.22, N 5.76; found C 64.82, H 6.19, N 5.66.

5-[4-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-desoxy-β-D-glucopyranos-1-oxy)benzyl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin-Ni^{II} (**9d**): According to the general procedure given above, 2-acetamido-3,4,6-tri-*O*-acetyl-α-D-glucopyranotrichloroacetimidate (**7d**, 310 mg, 0.63 mmol) and **6** were allowed to react to give **9d** (31.9 mg, 22 %). M.p. 160 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): $\delta = 1.66 - 1.70$ (m, 6H, Por−CH_2−CH_3), 1.75 – 1.80 (m, 6H, Por−CH_2−CH_3), 1.96 (s, 3H, GlcNAc−CO_2−CH_3), 2.08, 2.09 (2s, 3H, GlcNAc−CO_2−CH_3), 2.10 (s, 3H, GlcNAc−CO_2−CH_3), 2.166, 2.170 (s, 3H, GlcNAc−CO_2−CH_3), 2.30, 2.31 (2s, 6H, Por−CH_3), 3.45 (s, 6H, Por−CH_3), 3.63 (m, 1H, $J_{4/5} = 10.05$ Hz, $J_{5/6a} = 3.12$ Hz, $J_{5/6b} = 4.55$ Hz, GlcNAc-5), 3.78 – 3.83 (m, 4H, Por−CH_2−CH_3), 3.87 – 3.91 (m, 4H, Por−CH_2−CH_3), 4.06 (m, 1H, $J_{1/2} = 8.24$ Hz, $J_{2/3} = 10.78$ Hz, $J_{2/NH} = 8.91$ Hz, GlcNAc-2), 4.20 (dd, 1H, $J_{5/6a} = 3.12$ Hz, $J_{6a/6b} = 12.34$ Hz, GlcNAc-6a), 4.34 (dd, 1H, $J_{5/6b} = 4.55$ Hz, $J_{6a/6b} = 12.34$ Hz, GlcNAc-6b), 4.65 (d, 1H, $J_{1/2} = 8.24$ Hz, GlcNAc-1), 4.70 (d, 1H, $J = 11.94$ Hz, Aryl−CH_2−), 5.06 (d, 1H, $J = 11.94$ Hz, Aryl−CH_2−), 5.17 (t, 1H, $J_{3/4} = 9.12$ Hz, $J_{4/5} = 10.05$ Hz, GlcNAc-4), 5.23 (t, 1H, $J_{2/3} = 10.78$ Hz, $J_{3/4} = 9.12$ Hz, GlcNAc-3), 5.39 (d, 1H, $J_{2/NH} = 8.91$ Hz, N*H*(Ac)), 7.51 (d, 2H, $J = 7.99$ Hz, Aryl), 7.91 (d, 2H, $J = 7.99$ Hz, Aryl), 9.58 (s, 1H, Por-15), 9.65 (s, 2H, Por-10, Por-20); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): $\delta = 11.21$ (q, Por−CH_3), 15.29 (q, Por−CH_3), 17.19 (q, Por−CH_2−CH_3), 17.33 (q, Por−CH_2−CH_3), 19.52 (t, Por−CH_2−CH_3), 19.56 (t, Por−CH_2−CH_3), 20.54 (q, GlcNAc−CO_2−CH_3), 20.58 (q, GlcNAc−CO_2−CH_3), 20.68 (q, GlcNAc−CO_2−CH_3), 23.18(q, GlcNAc−CO_2−CH_3), 54.44 (d, GlcNAc-2), 61.95 (t, GlcNAc-6), 68.40 (d, GlcNAc-4), 70.47 (t, −Aryl−CH_2−), 71.76 (d, GlcNAc-5), 72.31 (d, GlcNAc-3), 95.49 (d, Por-15), 96.28 (d, Por-10, Por-20), 99.69 (d, GlcNAc-1), 117.08 (s, Por), 126.41 (d, Aryl), 132.82 (d, Aryl), 136.32 (s, Aryl), 136.38 (s, Por), 136.86 (s, Por), 136.92 (s, Por), 137.93 (s, Por), 137.95 (s, Por), 139.11 (s, Por), 139.13 (s, Por), 139.45 (s, Por), 139.76 (s, Por), 140.66 (s, Por), 140.86 (s, Aryl), 140.89 (s, Por), 140.99 (s, Por), 141.274 (s, Por), 143.52 (s, Por), 143.57 (s, Por), 145.07 (s, Por), 169.27 (s, GlcNAc−CO_2−CH_3), 169.98 (s, GlcNAc−CO_2−CH_3), 170.64 (s, GlcNAc−CO_2−CH_3), 170.84 (s, GlcNAc−CO_2−CH_3); MS (FAB): *m*/*z* (%) = 971 [M^++2, ^{58}Ni] (100); IR (KBr): $\tilde{\nu} = 3412$, 2950 (C−H), 1744

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(C=O), 1629 (Aryl), 1438, 1364, 1232, 1039 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) ($\lg\varepsilon$) = 397 (5.338), 521 (4.095), 555 (4.379); $C_{53}H_{61}N_5O_9Ni$ (970.76): calcd C 65.58, H 6.33, N 7.21; found C 64.67, H 6.33, N 6.97.

5-[4-(2,3,6,8,9,10,12-*O*-Heptaacetyl-β-D-maltopyranos-1-oxy)-benzyl]-2,8,-13,17-tetraethyl-3,7,12,18-tetramethylporphyrin-Ni^{II} (9e): According to the general procedure, 2,3,6,8,9,10,12-hepta-*O*-acetyl-α-D-maltopyranotrichloroacetimidate (**7e**, 350 mg, 0.448 mmol) and **6** (100 mg, 0.156 mmol) were allowed to react to yield **9e** (52.3 mg, 27%). M. p. 147–150 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.65–1.69 (m, 6H, Por−CH_2−CH_3), 1.75–1.79 (m, 6H, Por−CH_2−CH_3), 2.06 (s, 3H, Mal−CO_2−CH_3), 2.08 (s, 3H, Mal−CO_2−CH_3), 2.09 (s, 3H, Mal−CO_2−CH_3), 2.11 (s, 3H, Mal−CO_2−CH_3), 2.13 (s, 3H, Mal−CO_2−CH_3), 2.16 (s, 3H, Mal−CO_2−CH_3), 2.25 (s, 3H, Mal−CO_2−CH_3), 2.31, 2.32 (2s, 6H, Por−CH_3), 3.43 (s, 6H, Por−CH_3), 3.42–3.44 (m, 4H, Por−CH_2−CH_3), 3.85–3.90 (m, 4H, Por−CH_2−CH_3), 3.84 (m, 1H, $J_{4/5}$ = 8.55 Hz, $J_{5/6a}$ = 3.80 Hz, $J_{5/6b}$ = 2.29 Hz, Mal-5) 4.06 (m, 1H $J_{4'/5'}$ = 9.84 Hz, $J_{5'/6'a}$ = 3.82 Hz, $J_{5'/6'b}$ = 2.28 Hz, Mal-5′), 4.13 (dd, 1H $J_{5'/6'b}$ = 2.28 Hz, $J_{6'a/6'b}$ = 12.44 Hz, Mal-6′b), 4.16 (t, 1H $J_{3/4}$ = 9.21 Hz, $J_{4/5}$ = 8.55 Hz, Mal-4), 4.33 (dd, 1H, $J_{5'/6'a}$ = 3.82 Hz, $J_{6'a/6'b}$ = 12.44 Hz, Mal-6′a), 4.38 (dd, 1H, $J_{5/6}$ = 3.80 Hz, $J_{6a/6b}$ = 12.17 Hz, Mal-6a), 4.64 (dd, 1H, $J_{5/6}$ = 2.29 Hz, $J_{6a/6b}$ = 12.17 Hz, Mal-6b), 4.83 (d, 1H, J = 7.88 Hz, Mal-1), 4.92 (d, 1H, J = 12.44 Hz, Aryl−CH_2−), 4.94 (dd, 1H, $J_{1'/2'}$ = 3.95 Hz, $J_{2'/3'}$ = 10.34 Hz, Mal-2′), 5.09 (dd, 1H, $J_{1/2}$ = 7.88 Hz, $J_{2/3}$ = 9.55 Hz, Mal-2), 5.13 (t, 1H, $J_{4'/5'}$ = 9.84 Hz, $J_{9/10}$ = 9.80 Hz, Mal-4′), 5.20 (d, 1H, J = 12.44 Hz, Aryl−CH_2−), 5.38 (t, 1H, $J_{3/4}$ = 9.21 Hz, $J_{2/3}$ = 9.55 Hz, Mal-3), 5.45 (t, 1H, $J_{3'/4'}$ = 9.80 Hz, $J_{2'/3'}$ = 10.34 Hz, Mal-3′), 5.51 (d, 1H, $J_{1'/2'}$ = 3.95 Hz, Mal-1′), 7.57 (d, 2H, J = 7.89 Hz, Aryl), 7.88 (d, 2H, J = 7.89 Hz, Aryl), 9.57 (s, 1H, Por-15), 9.62 (s, 2H, Por-10, Por-20); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 11.19 (q, Por−CH_3), 15.26 (q, Por−CH_3), 17.17 (q, Por−CH_2−CH_3), 17.30 (q, Por−CH_2−CH_3), 19.50 (t, Por−CH_2−CH_3), 19.55 (t, Por−CH_2−CH_3), 20.47 (q, Mal−CO_2−CH_3), 20.57 (q, Mal−CO_2−CH_3), 20.79 (q, Mal−CO_2−CH_3), 20.82 (q, Mal−CO_2−CH_3), 61.41 (t, Mal-6′), 62.77 (t, Mal-6), 67.93 (d, Mal-4′), 68.43 (d, Mal-5′), 69.24 (d, Mal-3′), 69.93 (d, Mal-2′), 70.63 (t, Aryl−CH_2−), 72.12 (d, Mal-2), 72.21 (d, Mal-5), 72.71 (d, Mal-4), 75.34 (d, Mal-3), 95.44 (d, Por-15), 95.50 (d, Mal-1′), 96.22 (d, Por-10, Por-20), 98.94 (d, Mal-1), 126.11, 126.50 (d, Aryl), 132.91 (d, Aryl), 136.27 (s, Por), 136.32 (s, Por), 136.53 (s, Aryl), 137.97 (s, Por), 138.88 (s, Por), 139.09 (s, Por), 139.42 (s, Por), 139.77 (s, Por), 140.63 (s, Por), 140.83 (s, Por), 141.50 (s, Por), 141.72 (s, Por), 143.48 (s, Por), 143.53 (s, Aryl), 145.05 (s, Por), 148.45 (s, Por), 169.30 (s, Mal−CO_2−CH_3), 169.57 (s, Mal−CO_2−CH_3), 169.84 (s, Mal−CO_2−CH_3), 170.10 (s, Mal−CO_2−CH_3), 170.42 (s, Mal−CO_2−CH_3); MS (FAB): m/z (%): 1258 [M^+, ^{58}Ni] (100), 1260 [M^+, ^{60}Ni] (40); IR (KBr): $\tilde{\nu}$ = 3410, 2950 (C−H), 1751 (C=O), 1624 (Aryl), 1364, 1227, 1032 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) ($\lg\varepsilon$) = 397 (5.408), 519 (4.110), 555 (4.426); $C_{65}H_{76}N_4O_{18}Ni$ (1260.08): calcd C 61.96, H 6.08, N 4.44; found C 61.51, H 6.08, N 4.40.

5-[4-(2,3,6,8,9,10,12-*O*-Heptaacetyl-β-D-lactopyranos-1-oxy)benzyl]-2,8,1-3,17-tetraethyl-3,7,12,18-tetramethylporphyrin-Ni^{II} (9f): According to the general procedure 2,3,6,8,9,10,12-hepta-*O*-acetyl-α-D-lactopyranotrichloroacetimidate (**7f**, 800 mg, 1.02 mmol) and **6** (200 mg, 0.312 mmol) were allowed to react to yield **9f** (128 mg, 33%). M.p. 147–149 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.62–1.68 (m, 6H, Por−CH_2−CH_3), 1.73–1.78 (m, 6H, Por−CH_2−CH_3), 2.00 (s, 3H, Lac−CO_2−CH_3), 2.10 (2s, 6H, Lac−CO_2CH_3), 2.11 (s, 3H, Lac−CO_2−CH_3), 2.12 (s, 3H, Lac−CO_2−CH_3), 2.19 (s, 3H, Lac−CO_2−CH_3), 2.21 (s, 3H, Lac−CO_2−CH_3), 2.28, 2.29 (2s, 6H, Por−CH_3), 3.42 (s, 6H, Por−CH_3), 3.73 (m, 1H, $J_{4/5}$ = 9.68 Hz, $J_{5/6a}$ = 5.00 Hz, $J_{5/6b}$ = 2.13 Hz, Lac-5), 3.76–3.81 (m, 4H, Por−CH_2−CH_3), 3.86–3.88 (m, 4H, Por−CH_2−CH_3), 3.92 (m, 1H, $J_{4'/5'}$ = 0.52 Hz, $J_{5'/6'a}$ = 6.94 Hz, $J_{5'/6'b}$ = 8.07 Hz, Lac-5′), 3.92 (t, 1H, $J_{3/4}$ = 9.08 Hz, $J_{4/5}$ = 9.68 Hz, Lac-4), 4.13 (dd, 1H, $J_{5'/6'b}$ = 8.07 Hz, $J_{6'a/6'b}$ = 11.20 Hz, Lac-6′b), 4.18 (dd, 1H, $J_{5'/6'a}$ = 6.94 Hz, $J_{6'a/6'b}$ = 11.20 Hz, Lac-6′a), 4.21 (dd, 1H, $J_{5/6a}$ = 5.00 Hz, $J_{6'a/6'b}$ = 12.04 Hz, Lac-6′a), 4.56 (d, 1H, $J_{1'/2'}$ = 7.76 Hz, Lac-1′), 4.63 (dd, 1H, $J_{5/6b}$ = 2.13 Hz, $J_{6b/6a}$ = 12.04 Hz, Lac-6b), 4.76 (d, 1H, $J_{1/2}$ = 8.05 Hz, Lac-1), 4.90 (d, 1H, J = 11.40 Hz, Aryl−CH_2−), 5.01 (dd, 1H, $J_{2'/3'}$ = 10.37 Hz, $J_{3'/4'}$ = 3.45 Hz, Lac-3′), 5.14 (t, 1H, $J_{1/2}$ = 8.05 Hz, $J_{2/3}$ = 9.67 Hz, Lac-2), 5.16 (d, 1H, J = 11.40 Hz, Aryl−CH_2−), 5.19 (t, 1H, $J_{1'/2'}$ = 7.76 Hz, $J_{2'/3'}$ = 10.37 Hz, Lac-2′), 5.30 (t, 1H, $J_{2/3}$ = 9.67 Hz, $J_{3/4}$ = 9.08 Hz, Lac-3), 5.39 (d, 1H, $J_{3'/4'}$ = 3.45 Hz, $J_{4'/5'}$ = 0.52 Hz, Lac-4′), 7.55 (d, 2H, J = 7.86 Hz, Aryl), 7.86 (d, 2H, J = 7.86 Hz, Aryl), 9.56 (s, 1H, Por-15), 9.60 (s, 2H, Por-10, Por-20); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 11.19 (q, Por−CH_3), 15.23 (q, Por−CH_3), 17.17 (q, Por−CH_2−CH_3), 17.30 (q, Por−CH_2−CH_3), 19.49 (t, Por−CH_2−CH_3), 19.55 (t, Por−CH_2−CH_3), 20.37 (q, Lac−CO_2−CH_3), 20.52 (q, Lac−CO_2−CH_3), 20.63 (q, Lac−CO_2−CH_3), 20.72 (q, Lac−CO_2−CH_3), 20.80 (q, Lac−CO_2−CH_3), 60.65 (t, Lac-6′), 61.90 (t, Lac-6), 66.469 (d, Lac-4′), 69.01 (d, Lac-2′), 70.51 (t, Aryl−CH_2−), 70.57 (d, Lac-3′), 70.88 (d, Lac-5′), 71.61 (d, Lac-2), 72.67 (d, Lac-5), 72.80 (d, Lac-2), 76.24 (d, Lac-4), 95.43 (d, Por-15), 96.21 (d, Por-10, Por-20), 98.92, 99.06 (d, Lac-1), 101.08 (d, Lac-1′), 126.52 (d, Aryl), 132.89 (d, Aryl), 136.27 (s, Por), 136.32 (s, Por), 136.48 (s, Aryl), 137.91 (s, Por), 137.93 (s, Por), 139.07 (s, Por), 139.38 (s, Por), 139.42 (s, Por), 139.72 (s, Por), 140.61 (s, Por), 140.81 (s, Por), 141.50 (s, Aryl), 141.70 (s, Por), 143.47 (s, Por), 143.53 (s, Por), 145.07 (s, Por), 168.97 (s, Lac−CO_2−CH_3), 169.56 (s, Lac−CO_2−CH_3), 169.65 (s, Lac−CO_2−CH_3), 169.93 (s, Lac−CO_2−CH_3), 170.01 (s, Lac−CO_2−CH_3), 170.22 (s, Lac−CO_2−CH_3), 170.28 (s, Lac−CO_2−CH_3); MS (MALDI-TOF): m/z (%): [M^++1, ^{60}Ni] (80); IR (KBr): $\tilde{\nu}$ = 3413, 2950 (C−H), 1750 (C=O), 1625, 1437, 1365, 1223, 1046 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) ($\lg\varepsilon$) = 397 (5.712), 519 (4.482), 555 (4.761); $C_{65}H_{76}N_4O_{18}Ni$ (1260.13): calcd C 61.96, H 6.08, N 4.44; found C 62.00, H 6.25, N 4.29.

5-[4-(2,3,6,8,9,10,12-*O*-Heptaacetyl-β-D-cellopyranos-1-oxy)benzyl]-2,8,1-3,17-tetraethyl-3,7,12,18-tetramethylporphyrin-Ni^{II} (9g): According to the general procedure 2,3,6,8,9,10,12-hepta-*O*-acetyl-α-D-cellobiotrichloroacetimidate (**7g**, 420 mg, 538 mmol) and **6** (100 mg, 0.156 mmol) were allowed to react to yield **9g** (42.9 mg, 22%). M.p. 153–157 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = 1.66–1.71 (m, 6H, Por−CH_2CH_3), 1.75–1.80 (m, 6H, Por−CH_2CH_3), 2.04 (s, 3H, Cel−CO_2CH_3), 2.07 (s, 3H, Cel−CO_2CH_3), 2.09 (s, 3H, Cel−CO_2CH_3), 2.11 (s, 3H, Cel−CO_2CH_3), 2.13 (s, 3H, Cel−CO_2CH_3), 2.15 (s, 3H, Cel−CO_2CH_3), 2.24 (s, 3H, Cel−CO_2CH_3), 2.31, 2.32 (2s, 6H, Por−CH_3), 3.43, 3.44 (2s, 6H, Por−CH_3), 3.64 (m, 1H, $J_{4'/5'}$ = 10.06 Hz, $J_{5'/6'a}$ = 2.21 Hz, $J_{5'/6'b}$ = 4.26 Hz, Cel-5′), 3.71 (m, 1H, $J_{5/4}$ = 9.15 Hz, $J_{5/6a}$ = 4.80 Hz, $J_{5/6b}$ = 2.04 Hz, Cel-5), 3.79–3.84 (m, 4H, Por−CH_2CH_3), 3.84 (t, 1H, $J_{4/3}$ = 8.88 Hz, $J_{4/5}$ = 9.15 Hz, Cel-4), 3.86–3.91 (m, 5H, Por−CH_2CH_3), 4.05 (dd, 1H, $J_{6'a/6'b}$ = 12.55 Hz, $J_{6'a/5'}$ = 2.21 Hz, Cel-6′a), 4.18 (dd, 1H, $J_{6a/6b}$ = 4.80 Hz, $J_{6a/5}$ = 12.06 Hz, Cel-6a), 4.41 (dd, 1H, $J_{6'b/5'}$ = 4.26 Hz, $J_{6'b/6'a}$ = 12.55 Hz, Cel-6′b), 4.53 (d, 1H, $J_{1'/2'}$ = 7.99 Hz, Cel-1′), 4.64 (dd, 1H, $J_{6b/6a}$ = 12.06 Hz, $J_{6/5}$ = 2.04 Hz, Cel-6b), 4.74 (d, 1H, $J_{1/2}$ = 8.25 Hz, Cel-1), 4.91 (d, 1H, J = 12.45 Hz, Aryl−CH_2−), 4.99 (dd, 1H, $J_{2'/1'}$ = 7.99 Hz, $J_{2/3'}$ = 9.78 Hz, Cel-2′), 5.12 (dd, 1H, $J_{4'/3'}$ = 13.74 Hz, $J_{4'/5'}$ = 10.06 Hz, Cel-4′), 5.14 (dd, 1H, $J_{2/1}$ = 8.25 Hz, $J_{2/3}$ = 9.83 Hz, Cel-2), 5.19 (dd, 1H, $J_{3/2'}$ = 9.78 Hz, $J_{3/4'}$ = 13.74 Hz, Cel-3′), 5.188 (d, 1H, J = 12.45 Hz, Aryl−CH_2−), 5.29 (t, 1H, $J_{3/2}$ = 9.83 Hz, $J_{3/4}$ = 8.88 Hz, Cel-3), 7.57 (d, 2H, J = 7.92 Hz, Aryl), 7.89 (d, 2H, J = 7.92 Hz, Aryl), 9.57 (s, 1H, Por-15), 9.64 (s, 2H, Por-10, Por-20); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 11.20 (q, Por−CH_3), 15.25 (q, Por−CH_3), 17.20 (q, Por−CH_2−CH_3), 17.32 (q, Por−CH_2−CH_3), 19.52 (t, Por−CH_2−CH_3), 19.56 (t, Por−CH_2−CH_3), 20.43 (q, Cel−CO_2−CH_3), 20.46 (q, Cel−CO_2−CH_3), 20.55 (q, Cel−CO_2−CH_3), 20.63 (q, Cel−CO_2−CH_3), 20.82 (q, Cel−CO_2−CH_3), 61.38 (t, Cel-6′), 61.79 (t, Cel-6), 67.64 (d, Cel-4′), 70.52 (t, Aryl−CH_2−), 70.61 (t, Aryl−CH_2−), 71.51 (d, Cel-3′), 71.53 (d, Cel-2′), 71.81 (d, Cel-5′), 72.49 (d, Cel-3), 72.74 (d, Cel-5), 72.85 (d, Cel-2), 76.47 (d, Cel-4), 95.46 (d, Por-15), 96.26 (d, Por-10, Por-20), 98.99 (d, Cel-1), 99.13 (d, Cel-1), 100.76 (d, Cel-1′), 116.96 (s, Por), 126.55 (d, Aryl), 132.92 (d, Aryl), 136.30 (s, Por), 136.37 (s, Por), 136.51 (s, Aryl), 137.95 (s, Por), 138.48 (s, Por), 139.10 (s, Por), 139.12 (s, Por), 139.41 (s, Por), 139.45 (s, Por), 139.75 (s, Por), 140.65 (s, Por), 140.85 (s, Por), 141.28 (s, Por), 141.53 (s, Aryl), 141.74 (s, Por), 143.50 (s, Por), 143.57 (s, Por), 145.11 (s, Por), 68.97 (q, Cel−CO_2−CH_3), 169.19 (q, Cel−CO_2−CH_3), 169.54 (q, Cel−CO_2−CH_3), 169.70 (q, Cel−CO_2−CH_3), 170.11 (q, Cel−CO_2−CH_3), 170.23 (q, Cel−CO_2−CH_3), 170.38 (q, Cel−CO_2−CH_3); MS (FAB): m/z (%): 1261 [M^++1, ^{60}Ni] (100); IR (KBr): $\tilde{\nu}$ = 2950 (C−H), 1752 (C=O), 1622, 1435, 1363, 1223, 1036 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) ($\lg\varepsilon$) = 397 (5.324), 520 (4.121), 555 (4.383); $C_{65}H_{76}N_4O_{18}Ni$ (1260.13): calcd C 61.96, H 6.08, N 4.44; found C 61.31, H 6.09, N 4.30.

General procedure for the synthesis of porphyrins 11a–g: In a 10 mL round-bottom flask the porphyrins **9** (100 mg) were dissolved separately in CH_2Cl_2/MeOH (1/1, 5 mL) at room temperature. Then sodium ethoxide solution (1 mL, 1M) was added and the mixture was stirred for 10 mins. Dichloromethane (100 mL) was added and the solution washed with water. The organic layer was separated and dried ($MgSO_4$), and the solvent removed in vacuo. The residue was poured into trifluoroacetic acid (5 mL) and 1,3-propanedithiol (0.25 mL) was added immediately. The mixture was stirred at room temperature for 5 mins, CH_2Cl_2 (5 mL) was added and the mixture was neutralized by addition of saturated $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted with

CH_2Cl_2/MeOH (2/1). The combined organic layers were dried ($MgSO_4$/Na_2CO_3) and the solvent was removed in vacuo. The residue was filtered through a plug of silica gel with CH_2Cl_2/MeOH (70/30) as solvent. The crude reaction product was purified by TLC on silica gel plates by means of CH_2Cl_2/MeOH eluent (10–25% MeOH). The products were extracted from the TLC plates with 100 mL CH_2Cl_2/MeOH (1/1). Then water was added and the solvent was very slowly evaporated until precipitation of the porphyrins occurred. The precipitated porphyrins were isolated by filtration, washed with cold MeOH (80%) and dried at room temperature in vacuo.

5-[4-(α-D-Mannopyranos-1-oxy)-benzyl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin (11a): According to the general procedure, **9a** (89 mg, 0.09 mmol) was converted into **11a** (yield 65 mg, 95%). M.p. > 270 °C; ^{1}H NMR (500 MHz, [D$_5$]pyridine, 300 K): $\delta = -2.70$ (m, 2H, N*H*), 1.73–1.78 (m, 6H, Por–CH_2–CH_3), 1.82–1.89 (m, 6H, Por–CH_2–CH_3), 2.51 (s, 6H, Por–CH_3), 3.59 (s, 6H, Por–CH_3), 3.99–4.11 (m, 8H, Por–CH_2–CH_3), 4.52 (dd, 1H, $J_{5/6a} = 5.94$ Hz, $J_{6a/6b} = 11.60$ Hz, Man-6a), 4.57 (m, 1H, $J_{4/5} = 9.17$ Hz, $J_{5/6a} = 5.94$ Hz, $J_{5/6b} = 2.89$ Hz, Man-5), 4.70 (dd, 1H, $J_{5/6b} = 2.89$ Hz, $J_{6a/6b} = 11.60$ Hz, Man-6b) 4.75 (m, 1H, $J_{1/2} = 6.34$ Hz, $J_{2/3} = 4.11$ Hz, Man-2), 4.76 (m, 1H, $J_{3/4} = 9.67$ Hz, $J_{4/5} = 9.17$ Hz, Man-4), 4.77 (m, 1H, $J_{2/3} = 4.11$ Hz, $J_{3/4} = 9.67$ Hz, Man-3), 5.07 (d, 1H, $J = 12.32$ Hz, Aryl–CH_2–), 5.39 (d, 1H, $J = 12.32$ Hz, Aryl–CH_2–), 5.67 (d, 1H, $J_{1/2} = 6.34$ Hz, Man-1), 7.85 (d, 2H, $J = 7.76$ Hz, Aryl), 8.22 (d, 2H, $J = 7.76$ Hz, Aryl), 10.25 (m, 1H, Por-15), 10.41 (m, 2H, Por-10 and Por-20); ^{13}C NMR (125 MHz, [D$_5$]pyridine, 300 K): $\delta = 11.11$ (q, Por–*C*H$_3$), 14.55 (q, Por–*C*H$_3$), 17.50 (q, Por–CH_2–*C*H$_3$), 19.54 (t, Por–*C*H$_2$–CH_3), 19.68 (t, Por–*C*H$_2$–CH_3), 62.86 (t, Man-6), 68.26 (t, Aryl–*C*H$_2$–), 68.81, 71.86, 71.89, 72.85 (d, Man-2, Man-3, Man-4), 75.46 (d, Man-5), 95.56 (d, Por-15), 96.75 (d, Por-10 and Por-20), 100.41 (d, Man-1), 119.12 (s, Por), 127.19 (d, Aryl), 132.87 (d, Aryl), 135.71 (s, Por), 136.10 (s, Por), 136.37 (s, Por), 136.47 (s, Aryl), 138.63 (s, Por), 138.70 (s, Por), 141.45 (s, Por), 141.71 (s, Por), 141.96 (s, Por), 142.00 (s, Por), 143.16 (s, Aryl), 144.50 (s, Por), 144.54 (s, Por); MS (MALDI-TOF): *m*/*z* (%): 747.9 [M^++1] (100), 748.8 [M^++2] (40); IR (KBr): $\tilde{\nu} = 3400$ (N–H), 2950 (C–H), 1626 (Aryl), 1441, 1369, 1224, 1052, 968 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) (lg ε) = 399 (5.321), 501 (4.232), 535 (3.942), 570 (3.896), 619 (3.340); $C_{45}H_{54}N_4O_6$ (746.94): calcd C 72.36, H 7.29, N 7.50; found C 72.37, H 7.44, N 7.34.

5-[4-(β-D-Galactopyranos-1-oxy)-benzyl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin (11b): According to the general procedure **9b** (34 mg, 0.035 mmol) was converted into **11b** (yield 26 mg, 99%). M.p. > 270 °C; ^{1}H NMR (500 MHz, [D$_5$]pyridine, 300 K): $\delta = -2.68$ (m, 2H, N*H*), 1.74–1.80 (m, 6H, Por–CH_2–CH_3), 1.83–1.89 (m, 6H, Por–CH_2–CH_3), 2.55, 2.56 (2s, 6H, Por–CH_3), 3.59, 3.66 (2s, 6H, Por–CH_3), 4.02–4.12 (m, 8H, Por–CH_2–CH_3), 4.27 (m, 1H, $J_{4/5} = 2.29$ Hz, $J_{5/6a} = 5.43$ Hz, $J_{5/6b} = 6.71$ Hz, Gal-5), 4.35 (dd, 1H, $J_{2/3} = 9.55$ Hz, $J_{3/4} = 3.52$ Hz, Gal-3), 4.61 (dd, 1H, $J_{5/6a} = 5.43$ Hz, $J_{6a/6b} = 11.08$ Hz, Gal-6a), 4.65 (dd, 1H, $J_{5/6b} = 6.71$ Hz, $J_{6a/6b} = 11.08$ Hz, Gal-6b), 4.72 (dd, 1H, $J_{3/4} = 3.52$ Hz, $J_{4/5} = 2.29$ Hz, Gal-4), 4.76 (t, 1H, $J_{1/2} = 7.87$ Hz, $J_{2/3} = 9.55$ Hz, Gal-2), 5.17 (d, 1H, $J_{1/2} = 7.87$ Hz, Gal-1), 5.25 (d, 1H, $J = 11.76$ Hz, Aryl–CH_2–), 5.59 (d, 1H, $J = 11.76$ Hz, Aryl–CH_2–), 7.96 (d, 2H, $J = 7.96$ Hz, Aryl), 8.03 (d, 2H, $J = 7.96$ Hz, Aryl), 10.29 (s, 1H, Por-15), 10.46 (s, 2H, Por-10, Por-20); ^{13}C NMR (125 MHz, [D$_5$]pyridine, 300 K): $\delta = 11.39$ (q, Por–*C*H$_3$), 14.94 (q, Por–*C*H$_3$), 17.78 (q, Por–CH_2–*C*H$_3$), 17.83 (q, Por–CH_2–*C*H$_3$), 20.03 (t, Por–*C*H$_2$–CH_3), 20.05 (t, Por–*C*H$_2$–CH_3), 62.53 (t, Gal-6), 70.34 (d, Gal-2), 70.74 (t, Aryl–*C*H$_2$–), 72.66 (d, Gal-4), 75.51 (d, Gal-3), 77.29 (d, Gal-5), 95.93 (d, Por-15), 96.94 (d, Por-10 and Por-20), 104.71 (d, Gal-1), 119.79 (s, Por), 127.32 (d, Aryl), 133.03 (d, Aryl), 135.45 (s, Por), 135.64 (s, Por), 135.93 (s, Aryl), 136.50 (s, Por), 136.87 (s, Por), 139.40 (s, Por), 141.81 (s, Por), 142.34 (s, Por), 142.38 (s, Por), 143.42 (s, Aryl), 144.83 (s, Por), 144.87 (s, Por), 144.91 (s, Por); MS (MALDI-TOF): *m*/*z* (%): 747.2 [M^++1] (100), 748.2 [M^++2] (70); IR (KBr): $\tilde{\nu} = 3395$ (N–H), 2949 (C–H), 1627, 1441, 1364, 1050 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) (lg ε) = 399 (5.017), 500 (3.921), 534 (3.598), 570 (3.582), 619 (3.104); $C_{45}H_{54}N_4O_6$ (746.94): calcd C 72.36, H 7.29, N 7.50; found C 72.16, H 7.33, N 7.63.

5-[4-(β-D-Glucopyranos-1-oxy)-benzyl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin (11c): According to the general procedure **9c** (89 mg, 0.092 mmol) was converted into **11c** (yield 65 mg, 95%). M.p. 252–255 °C; ^{1}H NMR (500 MHz, [D$_5$]pyridine, 300 K): $\delta = -2.68$ (br, 2H, N*H*), 1.64–1.68 (m, 6H, Por–CH_2CH_3), 1.74–1.79 (m, 6H, Por–CH_2CH_3), 2.46 (s, 6H, Por–CH_3), 3.51 (s, 6H, Por–CH_3), 3.93–4.01 (m, 8H, Por–CH_2–CH_3), 4.05 (m, 1H, $J_{4/5} = 6.52$ Hz, $J_{5/6a} = 5.47$ Hz, $J_{5/6b} = 3.42$ Hz, Glc-5), 4.23 (dd, 1H, $J_{2/3} = 7.71$ Hz, $J_{3/4} = 4.32$ Hz, Glc-3), 4.32 (m, 1H, $J_{1/2} = 7.22$ Hz, $J_{2/3} = 7.71$ Hz, Glc-2), 4.33 (m, 1H, $J_{3/4} = 4.32$ Hz, $J_{4/5} = 6.52$ Hz) 4.46 (dd, 1H, $J_{5/6a} = 5.47$ Hz, $J_{6a/6b} = 11.38$ Hz, Glc-6a), 4.63 (dd, 1H, $J_{5/6b} = 3.42$ Hz, $J_{6a/6b} = 11.38$ Hz, Glc-6b), 5.14 (d, 1H, $J = 12.20$ Hz, Aryl–CH_2–), 5.15 (d, 1H, $J_{1/2} = 7.22$ Hz, Glc-1), 5.47 (d, 1H, $J = 12.20$ Hz, Aryl–CH_2–), 7.86 (d, 2H, $J = 7.86$ Hz, Aryl), 7.95 (d, 1H, $J = 7.86$ Hz, Aryl), 10.21 (s, 1H, Por-15), 10.36 (s, 2H, Por-10, Por-20); ^{13}C NMR (125 MHz, [D$_5$]pyridine, 300 K): $\delta = 12.56$ (q, Por–*C*H$_3$), 16.11 (q, Por–*C*H$_3$), 18.94 (q, Por–CH_2–CH_3), 18.98 (q, Por–CH_2–*C*H$_3$), 21.16 (t, Por–*C*H$_2$–CH_3), 21.19 (t, Por–*C*H$_2$–CH_3), 64.04 (t, Glc-6), 71.93 (t, Aryl–*C*H$_2$–), 72.89 (d, Glc-2), 76.53 (d, Glc-3), 79.901 (d, Glc-4), 80.00 (d, Glc-5), 97.25 (d, Por-15), 98.27 (d, Por-10, Por-20), 105.29 (d, Glc-1), 120.92 (s, Por), 128.43 (d, Aryl), 134.25 (d, Aryl), 136.18 (s, Por), 137.00 (s, Aryl), 137.11 (s, Por), 137.66 (s, Por), 137.90 (s, Por), 138.00 (s, Por), 140.46 (s, Por), 143.05 (s, Aryl), 143.54 (s, Por), 144.54 (s, Por), 144.58 (s, Por), 145.98 (s, Por), 146.03 (s, Por); MS (MALDI-TOF): *m*/*z* (%): 746.8 [M^++1] (95), 747.9 [M^++2] (100); IR (KBr): $\tilde{\nu} = 3405$ (N–H), 2950 (C–H), 1626, 1440, 1370, 1251, 1051, 1017 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) (lg ε) = 399 (5.284), 501 (4.169), 535 (3.862), 567 (3.839), 620 (3.313); $C_{45}H_{54}N_4O_6$ (746.94): calcd C 72.36, H 7.29, N 7.50; found C 72.10, H 7.66, N 7.39.

5-[4-(β-D-*N*-Acetyl-glucosaminopyranos-1-oxy)-benzyl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin (11d): According to the general procedure **9d** (44 mg, 0.046 mmol) was converted into **11d** (yield 24 mg, 68%). M.p. 248–250 °C; ^{1}H NMR (500 MHz, [D$_5$]pyridine, 300 K): $\delta = -2.66$ (br s, 1H, N*H*), 1.70–1.76 (m, 6H, Por–CH_2–CH_3), 1.81–1.86 (m, 6H, Por–CH_2–CH_3), 2.21 (s, 3H, Glc–NHCO–CH_3), 2.50 (s, 6H, Por–CH_3), 3.58 (s, 6H, Por–CH_3), 3.98–4.08 (m, 9H, $J_{4/5} = 9.91$ Hz, $J_{5/6a} = 5.57$ Hz, $J_{5/6b} = 2.26$ Hz, $J_{6a/6b} = 11.78$ Hz, GlcNAc-5, Por–CH_2–CH_3), 4.33 (t, 1H, $J_{3/4} = 7.78$ Hz, $J_{4/5} = 9.91$ Hz, GlcNAc-4), 4.47 (dd, 1H, $J_{5/6a} = 5.57$ Hz, $J_{6a/6b} = 11.78$ Hz, GlcNAc-6a), 4.54 (t, 1H, $J_{2/3} = 9.87$ Hz, $J_{3/4} = 7.78$ Hz, GlcNAc-3), 4.65 (dd, 1H, $J_{5/6b} = 2.26$ Hz, $J_{6a/6b} = 11.78$ Hz, GlcNAc-6b), 4.83 (m, 1H, $J_{1/2} = 9.17$ Hz, $J_{2/3} = 9.87$ Hz, $J_{2/NH} = 9.78$ Hz, GlcNAc-2), 5.37 (d, 1H, $J_{1/2} = 9.17$ Hz, GlcNAc-1), 5.39 (d, 1H, $J = 12.44$ Hz, Aryl–CH_2–), 5.50 (d, 1H, $J = 12.44$ Hz, Aryl–CH_2–), 7.93 (d, 2H, $J = 7.52$ Hz, Aryl), 8.03 (d, 2H, $J = 7.52$ Hz, Aryl), 9.16–9.20 (m, 1H, $J_{NH/2} = 9.78$ Hz, Glc–N*H*Ac), 10.26 (s, 1H, Por-15), 10.44 (s, 2H, Por-10, Por-20); ^{13}C NMR (125 MHz, [D$_5$]pyridine, 300 K): $\delta = 11.43$ (q, Por–*C*H$_3$), 14.95 (q, Por–*C*H$_3$), 17.87 (q, Por–CH_2–*C*H$_3$), 17.91 (q, Por–CH_2–*C*H$_3$), 19.90 (t, Por–*C*H$_2$–CH_3), 20.02 (t, Por–*C*H$_2$–CH_3), 23.61, 23.63 (q, –NH–CO–*C*H$_3$), 57.63 (d, GlcNAc-2), 62.84 (t, GlcNAc-6), 70.32 (t, –*C*H$_2$–Aryl), 72.54 (d, GlcNAc-4), 76.40 (d, GlcNAc-4), 78.87 (d, GlcNAc-5), 96.21 (d, Por-15), 97.13 (d, Por-10, Por-15), 102.13 (d, GlcNAc-1), 119.75 (s, Por), 127.00 (d, Aryl), 133.16 (d, Aryl), 135.24 (s, Por), 136.05 (s, Por), 136.15 (s, Por), 136.56 (s, Aryl), 136.92 (s, Por), 139.39 (s, Por), 139.47 (s, Por), 141.82 (s, Aryl), 142.41 (s, Por), 142.44 (s, Por), 143.47 (s, Por), 144.86 (s, Por), 144.91 (s, Por), 144.95 (s, Por), 171.19, 171.21 (s, –NH–*C*O–CH$_3$); MS (MALDI-TOF): *m*/*z* (%): 789.1 [M^++2] (40); IR (KBr): $\tilde{\nu} = 3394$ (N–H), 2949 (C–H), 1641, 1538, 1440, 1368, 1302, 1053, 733 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) (lg ε) = 399 (5.090), 500 (3.990), 535 (3.689), 570 (3.660), 619 (3.152); $C_{47}H_{57}N_5O_6$ (787.97): calcd C 71.64, H 7.29, N 8.88; found C 71.51, H 7.53, N 8.76.

5-[4-(β-D-Maltopyranos-1-oxy)-benzyl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin (11e): According to the general procedure **9e** (105 mg, 0.083 mmol) was converted into **11e** (yield 56 mg, 74%). M.p. > 260 °C; ^{1}H NMR (500 MHz, [D$_5$]pyridine, 300 K): $\delta = -2.58$ (br s, 2H, N*H*), 1.71–1.77 (m, 6H, Por–CH_2–CH_3), 1.80–1.85 (m, 6H, Por–CH_2–CH_3), 2.53 (s, 6H, Por–CH_3), 3.56 (s, 6H, Por–CH_3), 3.95 (m, 1H, $J_{4/5} = 9.88$ Hz, $J_{5/6} = 3.86$ Hz, $J_{5/6b} = 3.97$ Hz, Mal-5), 4.00–4.07 (m, 8H, Por–CH_2–CH_3), 4.20 (m, 1H, $J_{2'/3'} = 9.27$ Hz, $J_{3'/4'} = 2.78$ Hz, Mal-3′), 4.24 (m, 1H, $J_{1'/2'} = 3.97$ Hz, $J_{2'/3'} = 9.27$ Hz, Mal-2′), 4.26 (m, 1H, $J_{1/2} = 7.70$ Hz, $J_{2/3} = 9.90$ Hz, Mal-2), 4.39 (dd, 1H, $J_{5'/6'a} = 3.72$ Hz, $J_{6'a/6'b} = 10.87$ Hz, Mal-6′a), 4.48 (m, 1H, $J_{2/3} = 9.90$ Hz, $J_{3/4} = 7.15$ Hz, Mal-3), 4.50 (m, 1H, $J_{3/4} = 7.15$ Hz, $J_{4/5} = 9.88$ Hz, Mal-4), 4.59 (m, 1H, $J_{4'/5'} = 11.04$ Hz, $J_{5'/6'a} = 3.72$ Hz, $J_{5'/6'b} = 2.45$ Hz, Mal-5′), 4.60 (m, 1H, $J_{5/6a} = 3.86$ Hz, $J_{6/6b} = 7.99$, Mal-6a), 4.62 (m, 1H, $J_{5/6b} = 3.97$ Hz, $J_{6a/6b} = 7.99$ Hz, Mal-6b), 4.65 (m, 1H, $J_{3'/4'} = 2.78$ Hz, $J_{4'/5'} = 11.04$ Hz, Mal-4′), 4.67 (m, 1H, $J_{5'/6'b} = 2.45$ Hz, $J_{6'a/6'b} = 10.87$ Hz, Mal-6′b), 5.12 (d, 1H, $J_{1/2} = 7.70$ Hz, Mal-1), 5.13 (d, 1H, $J = 12.35$ Hz, Aryl–CH_2–), 5.47 (d, 1H, $J = 12.35$ Hz, Aryl–CH_2–), 6.01 (d, 1H, $J_{1'/2'} = 3.97$ Hz, Mal-1′), 7.89 (d, 2H, $J = 7.05$ Hz, Aryl), 8.03 (d, 2H, $J = 7.05$ Hz, Aryl), 10.27 (s, 1H, Por-15), 10.43 (s, 1H, Por-10, Por-20); ^{13}C NMR (125 MHz, [D$_5$]pyridine, 300 K): $\delta = 11.04$ (q, Por–*C*H$_3$), 14.59 (q, Por–*C*H$_3$), 17.47 (q,

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Por−CH_2−CH_3), 17.54 (q, Por−CH_2−CH_3), 19.53 (t, Por−CH_2−CH_3), 19.68 (t, Por−CH_2−CH_3), 61.60 (t, Mal-6), 62.41 (t, Mal-6′), 70.51 (t, Aryl−CH_2−), 71.53 (d, Mal-3′), 74.14 (d, Mal-2′), 74.45 (d, Mal-2), 75.01 (d, Mal-4′), 75.15 (d, Mal-5′), 76.70 (d, Mal-5), 77.61 (d, Mal-4), 80.96 (d, Mal-3), 95.76 (d, Por-15), 96.77 (d, Por-10, Por-20), 102.85 (d, Mal-1), 103.69 (d, Mal-1′), 119.39 (s, Por), 126.89 (d, Aryl), 132.74 (d, Aryl), 136.15 (s, Aryl), 136.38 (s, Por), 136.48 (s, Por), 138.81 (s, Por), 141.56 (s, Por), 141.99 (s, Por), 142.04 (s, Por), 143.07 (s, Por), 144.49 (s, Aryl), 144.53 (s, Por), 144.57 (s, Por); MS (FAB): *m*/*z* (%): 909 [M^++1] (85), 932 [M^++23] (25); IR (KBr): $\tilde{\nu}$ = 3396 (N−H), 2949 (C−H), 1628, 1397, 1132, 1047, 1017 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) (lg ε) = 399 (5.159), 501 (3.999), 535 (3.609), 570 (3.589), 619 (3.169); $C_{51}H_{64}N_4O_{11}$ (909.08): calcd C 67.38, H 7.10, N 6.16; found C 67.16, H 7.62, N 5.86.

5-[4-(β-D-Lactopyranos-1-oxy)-benzyl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin (**11f**): According to the general procedure, **9f** (128 mg, 0.102 mmol) was converted into **11f** (yield 56 mg, 61%). M.p. > 270 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ = −2.65 (m, 2H, N*H*), 1.71–1.80 (m, 6H, Por−CH_2−CH_3), 1.83–1.90 (m, 6H, Por−CH_2−CH_3), 2.55 (s, 6H, Por−CH_3), 3.59 (s, 6H, Por−CH_3), 4.04–4.11 (m, 8H, Por−CH_2−CH_3 and 1H, $J_{4/5}$ = 11.27 Hz, $J_{5/6a}$ = 2.15 Hz, $J_{5/6b}$ = 4.35 Hz, Lac-5), 4.21 (m, 1H, $J_{2'/3'}$ = 9.07 Hz, $J_{3'/4'}$ = 6.65 Hz, Lac-3′), 4.213 (m, 1H, $J_{4'/5'}$ = 1.96 Hz, $J_{5'/6'a}$ = 5.29 Hz, $J_{5'/6'b}$ = 9.95 Hz, Lac-5′), 4.32 (t, 1H, $J_{1/2}$ = 7.02 Hz, $J_{2/3}$ = 9.79 Hz, Lac-2), 4.42 (m, 1H, $J_{2/3}$ = 9.79 Hz, $J_{3/4}$ = 5.55 Hz, Lac-3), 4.45 (m, 1H, $J_{5'/6'b}$ = 9.95 Hz, $J_{6'a/6'b}$ = 8.58 Hz, Lac-6′b), 4.46 (m, 1H, $J_{3/4}$ = 5.55 Hz, $J_{4/5}$ = 11.27 Hz, Lac-4), 4.53 (m, 1H, $J_{3'/4'}$ = 6.65 Hz, $J_{4'/5'}$ = 1.96 Hz, Lac-4′), 4.54 (m, 1H, $J_{5'/6'a}$ = 5.29 Hz, $J_{6'a/6'b}$ = 8.58 Hz, Lac-6′a), 4.62 (t, 1H, $J_{1/2'}$ = 7.83 Hz, $J_{2'/3'}$ = 9.07 Hz, Lac-2′), 4.66 (m, 1H, $J_{5/6a}$ = 2.15 Hz, $J_{6a/6b}$ = 9.73 Hz, Lac-6a), 4.68 (m, 1H, $J_{5/6b}$ = 4.35 Hz, $J_{6a/6b}$ = 9.73 Hz, Lac-6b), 5.16 (d, 1H, $J_{1'/2'}$ = 7.83 Hz, Lac-1′), 5.19 (d, 1H, $J_{1/2}$ = 7.02 Hz, Lac-1), 5.23 (d, 1H, J = 11.67 Hz, Aryl−CH_2−), 5.51 (d, 1H, J = 11.67 Hz, Aryl−CH_2−), 7.96 (d, 2H, J = 6.71 Hz, Aryl), 8.11 (d, 2H, J = 6.71 Hz, Aryl), 10.30 (s, 1H, Por-15), 10.47 (m, 2H, Por-10, Por-20); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ = 12.18 (q, Por−CH_3), 15.72 (q, Por−CH_3), 18.62 (q, Por−CH_2−CH_3), 18.69 (q, Por−CH_2−CH_3), 20.66 (t, Por−CH_2−CH_3), 20.82 (t, Por−CH_2−CH_3), 62.83 (t, Lac-6), 62.97 (t, Lac-6′), 70.85 (d, Lac-4′), 71.64 (t, Aryl−CH_2−), 73.29 (d, Lac-2′), 75.63 (d, Lac-2), 76.00 (d, Lac-3′), 77.52 (d, Lac-3), 77.61 (d, Lac-5), 78.07 (d, Lac-5′), 82.84 (d, Lac-4), 96.91 (d, Por-15), 97.90 (d, Por-10, Por-20), 104.59 (d, Lac-1′), 106.60 (d, Lac-1), 120.54 (s, Por), 128.06 (d, Aryl), 133.88 (d, Aryl), 137.30 (s, Aryl), 137.64 (s, Por), 139.96 (s, Por), 142.69 (s, Por), 143.14 (s, Por), 143.18 (s, Por), 144.19 (s, Por), 144.22 (s, Por), 145.63 (s, Aryl), 145.68 (s, Por), 145.72 (s, Por); MS (MALDI-TOF): *m*/*z* (%): 909.4 [M^++1] (100), 910.4 [M^++2] (80); IR (KBr): $\tilde{\nu}$ = 3393 (N−H), 2948 (C−H), 1626, 1442, 1367, 1049 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) (lg ε) = 399 (5.282), 501 (4.120), 535 (3.788), 570 (3.788), 620 (3.260); $C_{51}H_{64}N_4O_{11}$ (909.08): calcd C 67.38, H 7.09, N 6.16; found C 66.83, H 7.66, N 5.28.

5-[4-(β-D-Cellobiospyranos-1-oxy)-benzyl]-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin (**11g**): According to the general procedure **9g** (86 mg, 0.068 mmol) was converted into **11g** (yield 38 mg, 61%). M.p. > 270 °C; ^{1}H NMR (500 MHz, [D_5]pyridine, 300 K): δ = −2.60 (m, 2H, N*H*), 1.73–1.78 (m, 6H, Por−CH_2−CH_3), 1.83–1.88 (m, 6H, Por−CH_2−CH_3), 2.55 (s, 6H, Por−CH_3), 3.59, 3.61 (2s, 6H, Por−CH_3), 4.01–4.11 (m, 10H, Por−CH_2−CH_3, {$J_{4/5}$ = 9.71 Hz, $J_{5/6a}$ = 4.80 Hz, $J_{5/6b}$ = 2.86 Hz, Cel-5}, {$J_{4'/5'}$ = 10.23 Hz, $J_{5'/6'a}$ = 5.29 Hz, $J_{5'/6'b}$ = 2.49 Hz, Cel-5′}), 4.17 (t, 1H, $J_{1'/2'}$ = 7.81 Hz, $J_{2'/3'}$ = 9.81 Hz, Cel-2′), 4.25 (t, 1H, $J_{3'/4'}$ = 8.45 Hz, $J_{4'/5'}$ = 10.23 Hz, Cel-4′), 4.30 (t, 1H, $J_{1/2}$ = 7.64 Hz, $J_{2/3}$ = 9.56 Hz, Cel-2), 4.27 (t, 1H, $J_{2/3'}$ = 9.81 Hz, $J_{3'/4'}$ = 8.45 Hz), 4.37 (t, 1H, $J_{5'/6'a}$ = 5.29 Hz, $J_{6'a/6'b}$ = 11.20 Hz, Cel-6′a), 4.44 (t, 1H, $J_{2/3}$ = 9.56 Hz, $J_{3/4}$ = 8.38 Hz, Cel-3), 4.54 (t, 1H, $J_{3/4}$ = 8.38 Hz, $J_{4/5}$ = 9.71 Hz, Cel-4), 4.56 (dd, 1H, $J_{5'/6'b}$ = 2.49 Hz, $J_{6'b/6'a}$ = 11.20 Hz, Cel-6′b), 4.64 (dd, 1H, $J_{5/6b}$ = 2.86 Hz, $J_{6b/6a}$ = 11.94 Hz, Cel-6b), 4.72 (dd, 1H, $J_{5/6a}$ = 4.80 Hz, $J_{6a/6b}$ = 11.94 Hz, Cel-6a), 5.16 (d, 1H, $J_{1/2}$ = 7.64 Hz, Cel-1), 5.19 (d, 1H, J = 12.25 Hz, Aryl−CH_2−), 5.34 (d, 1H, $J_{1'/2'}$ = 7.81 Hz), 5.49 (d, 1H, J = 12.25 Hz, Aryl−CH_2−), 7.93 (d, 2H, J = 8.05 Hz, Aryl), 8.04 (d, 2H, J = 8.05 Hz, Aryl), 10.31 (s, 1H, Por-15), 10.47 (s, 2H, Por-10, Por-20); ^{13}C NMR (125 MHz, [D_5]pyridine, 300 K): δ = 11.44 (q, Por−CH_3), 14.98 (q, Por−CH_3), 17.86 (q, Por−CH_2−CH_3), 17.93 (q, Por−CH_2−CH_3), 19.93 (q, Por−CH_2−CH_3), 20.07 (q, Por−CH_2−CH_3), 61.93 (t, Cel-6′), 62.17 (t, Cel-6), 70.88 (t, Aryl−CH_2−), 71.41 (d, Cel-4′), 74.89 (d, Cel-3′, Cel-2′), 76.79 (d, Cel-3), 76.92 (d, Cel-5), 78.22 (d, Cel-2), 78.40 (d, Cel-5′), 80.71 (d, Cel-4), 97.01 (d, Por-15), 97.15 (d, Por-10, Por-20), 103.83 (d, Cel-1′), 104.94 (d, Cel-1), 119.77 (s, Por), 119.81 (s, Por), 127.28 (d, Aryl), 133.14 (d, Aryl), 135.08 (s, Por), 135.90 (s, Por), 136.00 (s, Aryl), 136.55 (s, Por), 136.77 (s, Por), 136.87 (s, Por), 139.18 (s, Por), 141.98 (s, Por), 142.39 (s, Por), 142.43 (s, Por), 143.47 (s, Aryl), 144.88 (s, Por), 144.92 (s, Por); MS (MALDI-TOF): *m*/*z* (%): 908.9 [M^++1] (100), 910.1 [M^++2] (80); IR (KBr): $\tilde{\nu}$ = 3404 (N−H), 2956 (C−H), 1626, 1463, 1393, 1225, 1053, 739 cm^{-1}; UV/Vis (CH_2Cl_2): λ (nm) (lg ε) = 399 (5.382), 501 (4.300), 534 (3.963), 570 (3.941), 619 (3.475); $C_{51}H_{64}N_4O_{11}$ (909.08): calcd C 67.38, H 7.09, N 6.16; found C 67.47, H 7.33, N 5.83.

Acknowledgments

The support of this research by the Deutsche Forschungsgemeinschaft (HO 1122/4-1) and the Fonds der Chemischen Industrie is gratefully acknowledged.

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Received: June 15, 1998 [F1209]

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