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A Strategy for the Targeting of Photosensitizers. Synthesis, Characterization, and Photobiological Property of Porphyrins Bearing Glycodendrimeric Moieties

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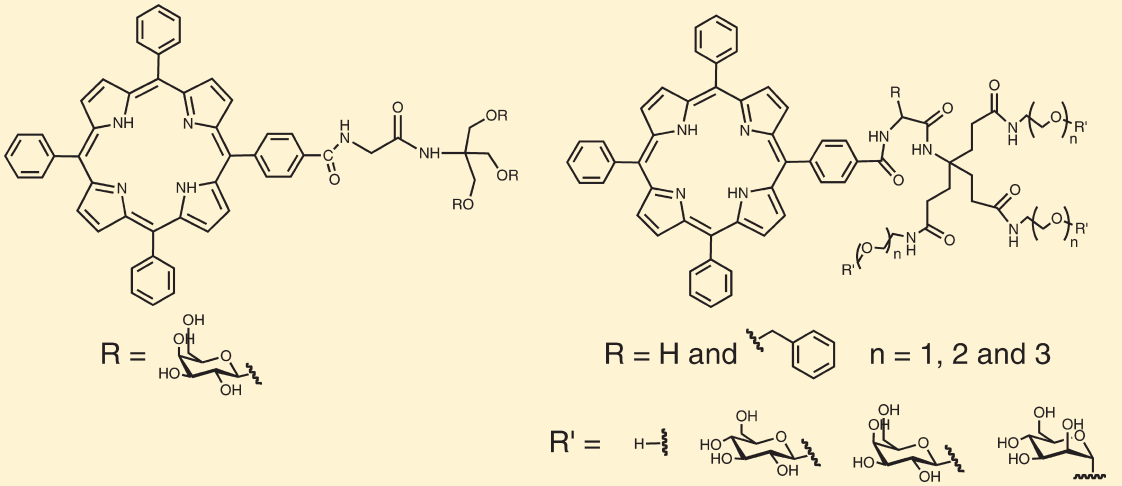
Supporting Information

ABSTRACT:



This paper describes the conception, synthesis, and characterization of new tetrapyrrolic chromophores bearing glycodendrimeric moieties inducing a potential increase of tumor targeting by a cluster effect. Two families of monoglycodendrimeric photosensitizers bearing three glycosyl units were designed, prepared with an acceptable overall efficiency and characterized by NMR, UV−visible, and fluorescence spectroscopies. The polarity and log *P* were evaluated by HPLC and the stir-flask method, respectively. The in vitro photoefficiency against two human tumor cell lines was assessed. The presence of the glycodendrimeric group does not appear to increase the tumor in vitro targeting.

INTRODUCTION

The incorporation of carbohydrates on tetrapyrrolic macrocyclic cores usable in photodynamic therapy (PDT) continues to be pursued vigorously by a number of research teams, particularly during these last two years.[1−3] In recent years, several articles and reviews describing the utility of porphyrin-based compounds in photodynamic therapy were published.[4−6] In our laboratory, efforts have been focused on the preparation and in vitro evaluation of the phototoxicity of a broad series of neutral glycoconjugated tetrapyrrolic macrocycles as potential photosensitizing agents for photodynamic therapy.[7−9] In these systems, glycoconjugation modifies the amphiphilicity of macrocycles and can favor their interactions with the tumor cell membrane.[10] Concerning this latter property, indications are that glycosylation provides the possibility for specific interactions of the conjugate with membrane lectin-type receptors. These receptors are overexpressed in certain malignant cells.[11,12] Thus glycoconjugation can be a potentially effective strategy for targeting photosensitizers toward tumor cells. In the last ten years, we have explored the effects of the number, the position, and the nature of *O*- or *S*-glycoconjugated moieties on the in vitro photoactivity. Generally, it has been shown that amphiphilic triglycoconjugated sensitizers are more phototoxic than either the parent tetrapyrrolic or the symmetrical tetraglycoconjugated derivatives.[13] Recently, we have shown that the presence of a diethylene glycol linking a monosaccharide as α-mannose or α-galactose to the macrocycle optimizes the in vitro[14] and in vivo[15] photoactivity.

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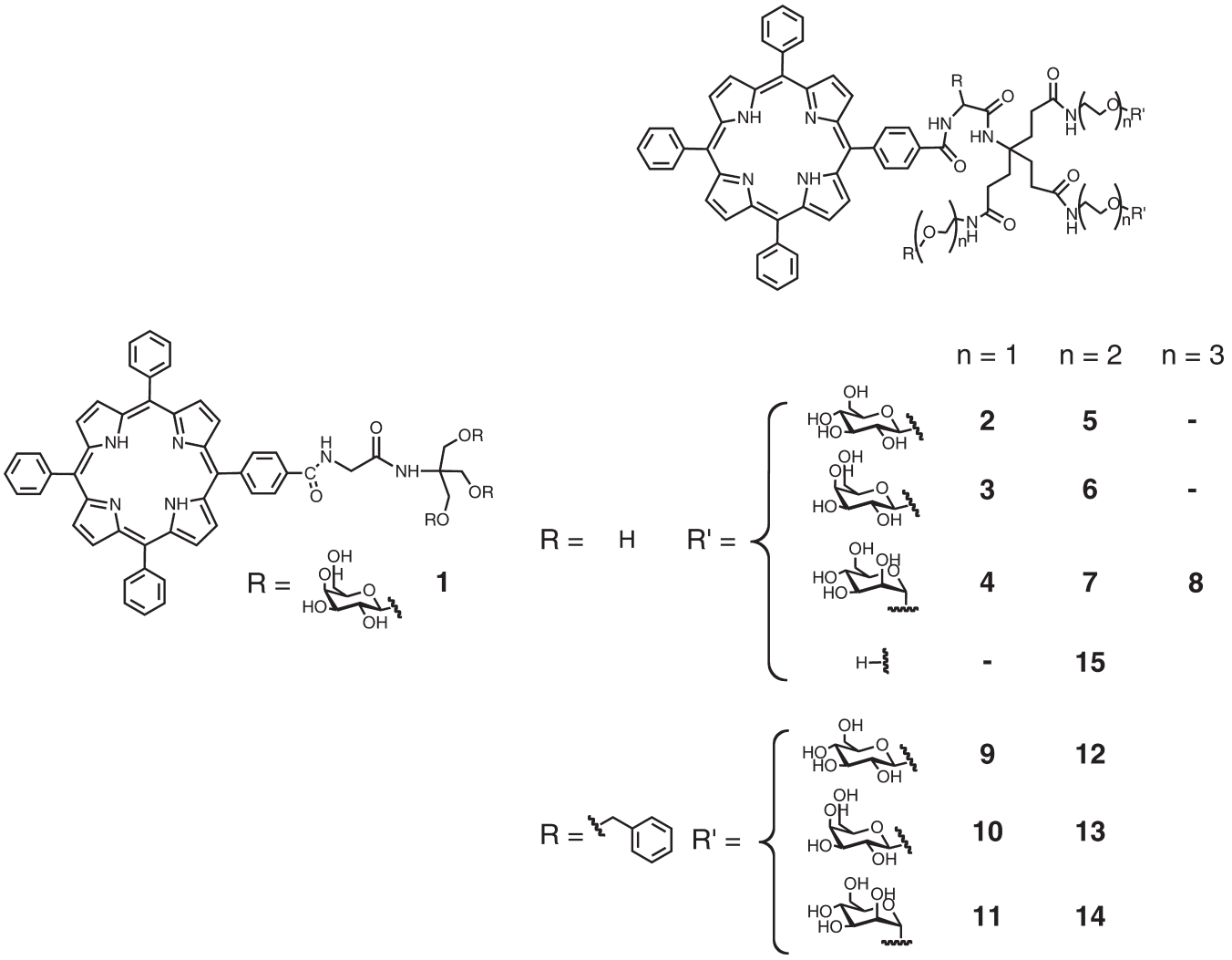

Figure 1. Structures of dendrimeric and glycodendrimeric porphyrins.

The photodynamic efficiency of a photosensitizer was determined by its cellular uptake and accurate subcellular localization in tumor cells. The identification of transport mechanisms through the biological membrane was a crux. This transport could be steered by the action of a membrane receptor such as lectin or by an active mechanism. It would be advantageous to use one of these mechanisms for the optimization of tumor targeting of photosensitizers. In this context, the use of glycodendrimeric groups as recognition motifs of lectin is very exciting. It has been widely accepted that carbohydrate−protein interactions play a crucial role in a large number of biological processes, such as pathogenic infections, receptor-mediated endocytosis, inflammation, and metastasis.[16−18] Carbohydrates receptors implied in carbohydrate−protein interactions are multisubunit and multivalent proteins with many important biological functions.[19−23] Since most proteins possess multiple carbohydrate-recognition domains and typically exist as oligomeric structures, this limitation is often overcome through multivalency.[24] Due to the weak nature, in the millimolar range, of interactions between single specific carbohydrate and receptor protein subunits, nature uses cluster carbohydrates in order to obtain biologically meaningful affinities for the receptors. The cluster effect appears when multivalent carbohydrates interact with more than one receptor-binding site simultaneously and cooperatively, resulting in better cellular recognition. Several methods of carbohydrate clustering have been described, including the attachment of carbohydrates to natural scaffolds, synthetic polymers, synthetic glycopeptides, or simple oligomerization through organic linkers.[25,26] Among them, dendritic structures or glycodendrimers are emerging as the ligand for carbohydrate-binding proteins.[27,28] Due to rapid advances in this area, promising potential medicinal applications appeared during the past decade, including treatment of cancers (renal cell carcinoma, melanoma, breast cancer, eradication of metastasis).[29−32] Recently, Ballardini et al. described the synthesis and photophysical properties of two dendrimer macrocycles, incorporating tetrasubstituted porphyrin units as core and, in one case, four benzyloylated or deprotected β-D-glucopyranosyl and in an other case, twelve acetylated-β-D-glucopyranosyl or β-D-glucopyranosyl residues at the peripheries of the tetrapyrrolic macrocycle.[33] These unprotected tetrasubstituted molecules are symmetric and highly water-soluble but no in vitro photoefficiency was described. In another approach, Matsuo et al. described the synthesis of glycosylated myoglobin by a reconstitutional method as an

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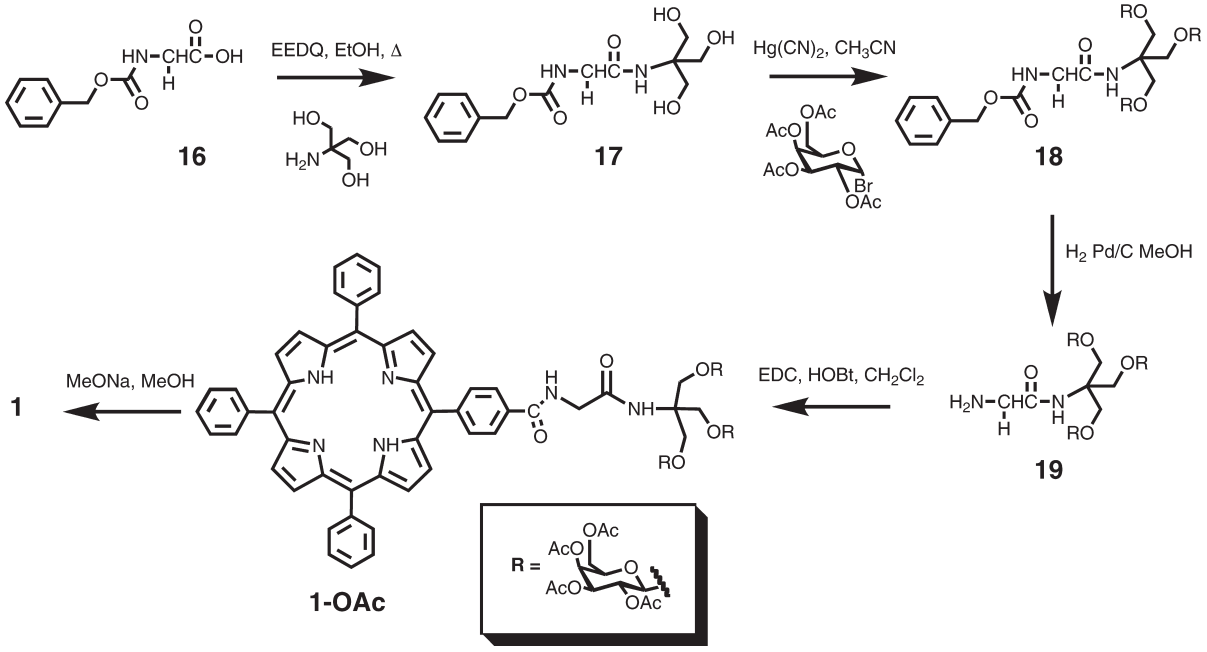
Scheme 1. Synthesis of Glycodendrimeric Porphyrin 1



artificial prosthetic group inserted into sperm whale apomyoglobin to afford a β-galactosylated myoglobin.[34]

We had shown that an amphiphilic structure of the glycoconjugated photosensitizers induced a best photocytotoxicity in vitro.[13] In the aim to increase this photoefficiency, we designed two new families of glycoconjugated photosensitizers **1** and **2**−**15** bearing only one glycodendrimer moiety, with variable length for the spacer linking carbohydrate, various sugars, and two different amino acids (Figure 1). In two recent articles, we have described the specific interactions of two glycodendrimeric porphyrins with concanavalin A, a protein recognizing α-mannosyl groups.[35,36]

RESULTS AND DISCUSSION

In this paper, we report the synthesis and characterization of two families of glycodendrimeric *meso*-tetraarylporphyrins **1**−**15** (Figure 1). The first one (compound **1**) presents a relative steric hindrance in the surrounding of glycoside moieties reducing the mobility of sugars. In the second one (compounds **2**−**15**), the presence of $-CH_2CH_2CONH-(CH_2CH_2O)-$, $-CH_2CH_2-CONH-(CH_2CH_2O)_2-$, or $-CH_2CH_2CONH-(CH_2CH_2O)_3-$ linkers between amino acid (glycyl or L-phenylalanyl) and glycoside parts reduces steric constraints between sugars and induces some variable flexibility of the sugars. The presence of an amino acid could lead to a modification of the hydrophobic part of the photosensitizer, which could change its cellular penetration or its anchorage in the lipid membrane of the targeted cancer cell.

Synthesis. Precursor **19** of the glycodendrimeric photosensitizer **1**, shown in Scheme 1, was prepared by the method described by Polidori et al. in 23% total yield from *N*-Z-glycine.[37] Compound **19** was condensed by using a mixture of EDC-HOBt as coupling agents in dry methylene chloride, with *meso*-5-(4-benzoic acid)-10,15,20-triphenylporphyrin to give porphyrin **1-OAc** in 49% yield. Porphyrin **1** was obtained quantitatively by Zemplen's transesterification.[38]

Glycodendrimers **26**−**28** and **31**−**32** (Schemes 2 and 3) were synthesized from di-*tert*-butyl 4-[2-(*tert*-butoxycarbonyl)ethyl]-4-aminoheptane-dicarboxylate **20**. This last compound was condensed with *N*-Z-glycine or *N*-Z-L-phenylalanine by a modified protocol described by Suda et al.,[39] using HOAt/WSCI−HCl as peptidic coupling agents, and giving quantitatively protected compounds **21-Gly** and **21-Phen**. Deprotection of compounds **21** by a mixture of trifluoroacetic acid/methylene chloride (1/2, v/v) gives compounds **22-Gly** and **22-Phen** with very good yields (92% and 97%, respectively). Condensation of peracetyl-glycosyl mono-, di-, or triethylene glycol amine[40−43] with dendrons **22-Gly** and **22-Phen**, in dry dimethylformamide, in the presence of HATU and DIPEA as coupling agents, gives Z-glycyl and Z-L-phenylalanyl glycodendrimers **23**−**25** and **29**−**30** in 31−84% and 32−90% yield ranges, respectively. Catalytic reduction by H_2/Pd−C allows the cleavage of the benzyloxycarbonyl protecting group and the quantitative formation of aminoglycodendrimers **26**−**28** and **31**−**32**.

Analogous nonglycosylated dendron **37** (Scheme 4) was prepared from diethylene glycol monochlorohydrin, which was protected by an acetyl group (94% yield). Protected compound **33** was transformed to azide derivative **34** (95% yield) by NaN_3 in DMSO and was then reduced by H_2/Pd to amine **35** (88% yield). This last one reacted with glycyl dendrons **22-Gly** in the presence of HATU and DIPEA in dry dimethylformamide to give dendrimer **36** in 73% yield, which was deprotected by hydrogenation to give dendrimer **37** (87%).

meso-5-(4-Benzoic acid)-10,15,20-triphenylporphyrin was condensed by using a mixture of EDC−HOBt as coupling agents in dry methylene chloride, with amino glycodendrons **26**−**28**, **31**−**32**, and **37** to give glycodendrimeric porphyrins **2-OAc**−**15-OAc** in the 40% yield range (Scheme 5). Deprotected glycodendrimeric porphyrins **2**−**15** (Scheme 5) were obtained quantitatively by Zemplen's transesterification.[38]

Characterization. ^1H and ^{13}C NMR spectroscopies, UV−visible, fluorescence, elemental analysis, ESI, and MALDI-TOF

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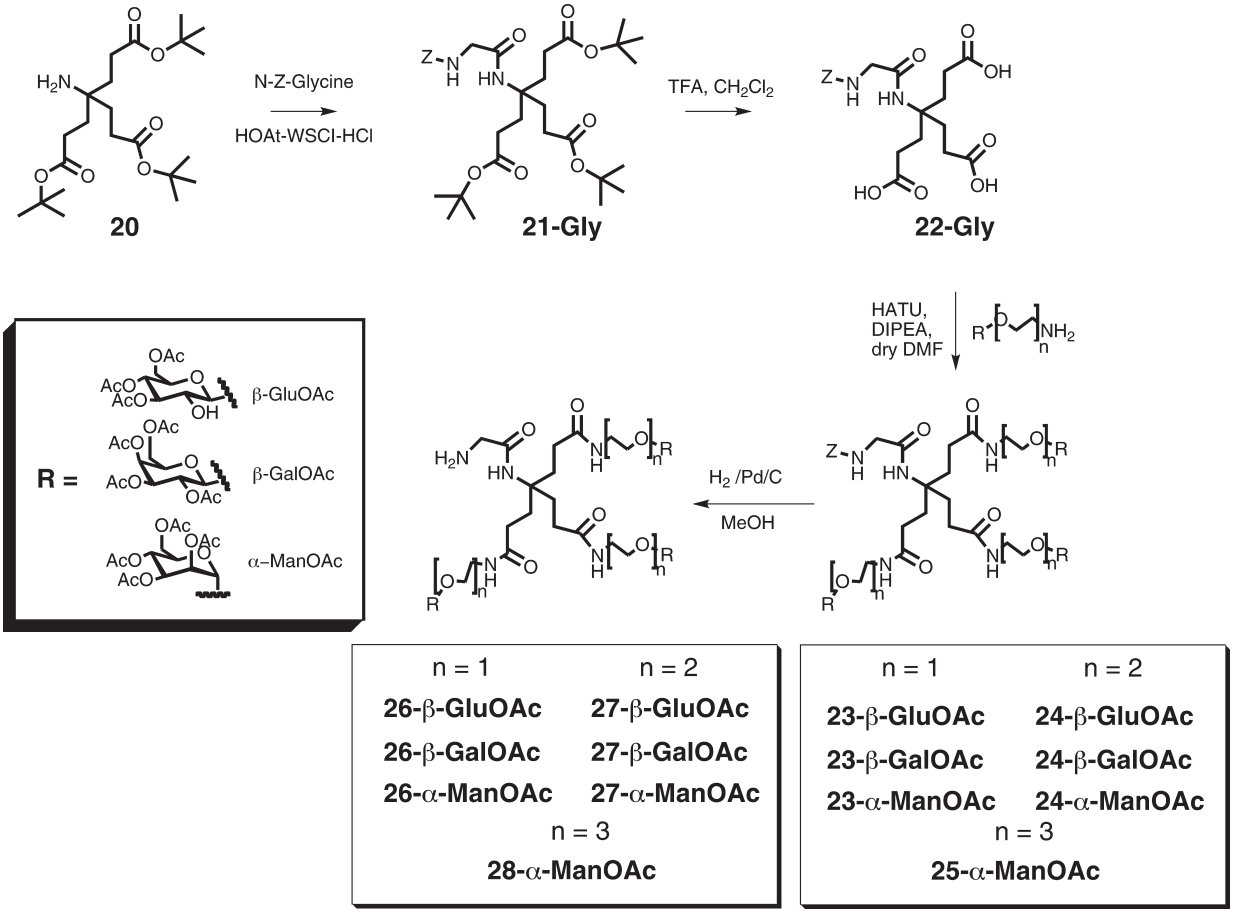
Scheme 2. Preparation of Glycyl-Glycodendrimers



mass spectrometries characterized all precursor molecules and final photosensitizers. The polarity of final deprotected porphyrins was assessed by HPLC analysis.

^{1}H and ^{13}C NMR. ^{1}H and ^{13}C NMR (300 and 75.3 MHz), homonuclear correlation (COSY), and heteronuclear multiple coherence (HMQC) spectra were obtained for all precursor dendrons and glycodendrimeric porphyrins in $CDCl_3$ and pyridine-d_5 solutions. The NMR spectra of these molecules are mainly governed by the symmetry of the tetrapyrrolic macrocycle and by the nature of the sugar part. The overall appearance of the ^{1}H and ^{13}C NMR spectra for protected glycoconjugated macrocyclic compounds **1-OAc**−**14-OAc** was very similar to that for the *p*-glycoconjugated porphyrins previously studied.[13,35] For illustration, the ^{1}H NMR spectrum of compound **2-OAc** (Supportong information) is composed of five main groups of resonance: the pyrrolic protons appearing near 8.85 ppm as one singlet (6 H) and one doublet (2 H), the phenyl protons as complex signals between 8.31 and 7.75 ppm, the sugar protons between 5.18 and 3.66 ppm, and protective acetyl group protons between 2.16 and 1.97 ppm. This results show that the ring current of the tetrapyrrolic macrocycle does not affect the glycodendrimer moieties. The absence of the deshielding effects is consistent with a conformation of compounds in which the dendrimers are located in the same plan as the porphyrin ring. The NH pyrrolic proton resonance appears as a broad singlet at −2.8 ppm. The integrations were in agreement with the fixation of one glycodendrimeric part bearing three sugar groups. Moreover, the anomeric proton resonance of the glycosyl group appears as a well-defined doublet with J = 8−9 Hz (characteristic of a β anomeric configuration) for glucosyl and galactosyl derivatives (**1-OAc, 2-OAc, 2, 3-OAc, 3, 5-OAc, 5, 6-OAc, 6, 9-OAc, 9, 10-OAc, 10, 12-OAc, 12, 13-OAc, 13, 19, 23-*β*-GluOAc, 23-*β*-GalOAc, 24-*β*-GluOAc, 24-*β*-GalOAc, 26-*β*-GluOAc, 26-*β*-GalOAc, 27-*β*-GluOAc, 27-*β*-GalOAc, 29-*β*-GluOAc, 29-*β*-GalOAc, 30-*β*-GluOAc, 30-*β*-GalOAc, 31-*β*-GluOAc,** and **31-*β*-GalOAc**) and as a narrow doublet with $J \leq 2$ Hz or a singlet (α anomeric configuration), for the mannosylated analogues (**4-OAc, 4, 7-OAc, 7, 8-OAc, 8, 11-OAc, 11, 14-OAc, 14, 23-α-ManOAc, 24-α-ManOAc, 25-α-ManOAc, 26-α-ManOAc, 27-α-ManOAc, 28-α-ManOAc, 29-α-ManOAc, 30-α-ManOAc,** and **31-α-ManOAc**).

Mass Spectroscopy. Compounds **1**−**15** were characterized by matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF). For all glycodendrimeric porphyrins, one peak was observed in the positive ion MALDI-TOF corresponding to the protonated porphyrin macrocycle (MH^+), with two small additional peaks $(MNa)^+$ and $(MK)^+$.

Electronic Spectra. All protected glycodendrimeric porphyrins (**1-OAc**−**15-OAc**) were dissolved in methylene chloride and all free ones (**1**−**15**) in a mixture of methanol−pyridine (24/1, v/v). Electronic spectra of all protected compounds (**1-OAc**−**15-OAc**) are very similar to those of known free base *meso*-5,10,15,20-tetraphenylporphyrin with a Soret band near 420 nm and four less intense Q bands near 520, 550, 595, and 645 nm. The spectra of deprotected compounds (**1**−**15**) presented a small blue shift due to the

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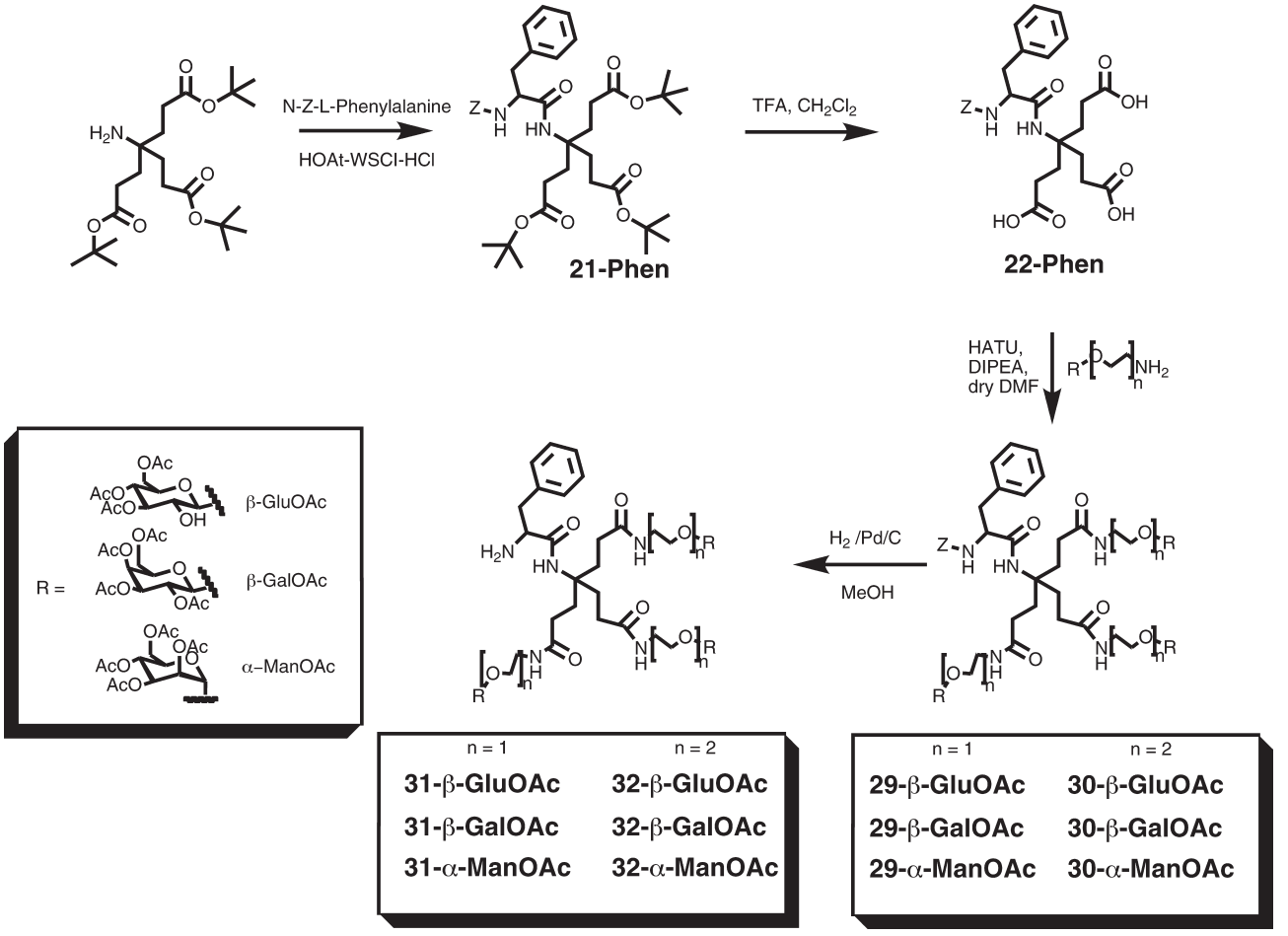
Scheme 3. Preparation of L-Phenylalanyl-Glycodendrimers



solvent, compared to their protected analogues, with a Soret band near 414 nm and four less intense Q bands near 513, 546, 589, and 645 nm. As expected, the presence of the glycodendron part on the *meso*-5-(4-benzoic acid)-10,15,20-triphenylporphyrin does not alter the UV−visible spectra of the chromophore systems. These spectral features show that the glycodendrimeric porphyrins were monomeric in methylene chloride and in a mixture of methanol−pyridine, at this concentration range.

Fluorescence Data. The corrected emission and excitation fluorescence spectra of compounds **1**−**15** (Supporting Information) in a mixture of MeOH/pyridine (24/1, v/v) are very similar to those of known free base *meso*-5,10,15,20-tetraphenylporphyrin with two emission bands at 650 and 715 nm but with a variable intensity ratio $I_{650/715nm}$ between 0.80 and 1.46.

HPLC and Polarity. The polarity of the final porphyrins **1**−**15** was checked by HPLC with a reverse phase column Waters X Terra MS C18. In the first approximation, the retention time (Rt) reflects the inverse of the polarity of the molecules. Compounds **2**−**15** may be categorized by increasing retention time (Table 1), in three families: Rt between 13.51 and 13.74 min for compounds **2**−**8** for which the glycodendrimeric group is linked to macrocycle by a glycine, 15.18 and 15.75 min for compounds **9**−**14** linked by a L-phenylalanine, and 18.49 min for nonglycoconjugated dendrimer **15**. These results show that only the amino acid group, leading to a modification of the hydrophobic part of the photosensitizer, regulates the polarity of the system. On the other hand, the partition coefficient (log *P*, Table 1) values of compounds **2**−**14**, obtained experimentally by the stir-flask method,[44] are near and included between −0.54 and −0.98 but do not reflect retention time. A positive versus negative log *P* value reflects preferential solubility in 2-octanol versus PBS solution, respectively. These values are characteristic of weakly hydrophilic compounds for **2**−**14** and lipophilic for **15**. The nature of the monosaccharide *β*-glucose, *β*-galactose, and α-mannose does not change noticeably the log *P* of the compounds.

Cellular Phototoxicity. Phototoxicity of the photosensitizers **1**−**15** was determined in HT 29 and Y79 cell lines by cell survival fraction measurements after incubation during 24 h and exposure to >540 nm light with a fluence of 2 J/cm^2. Toxicity in darkness was found to be negligible in all cases, with a survival fraction close to 100% (>10 μM, 24 h incubation). Photoefficiency of compounds **1**−**15** is presented in Table 2.

Compounds **1** and **13** are not cytotoxic and phototoxic. Among the results obtained with the glycodendrimer porphyrins, compounds **2**, **4**, and **6** have the highest LD_{50} (2.5 to 2.7 μM) for HT29 cells and compound **6** has an LD_{50} of 3 μM, being the best for Y79 cells. Compared with the value

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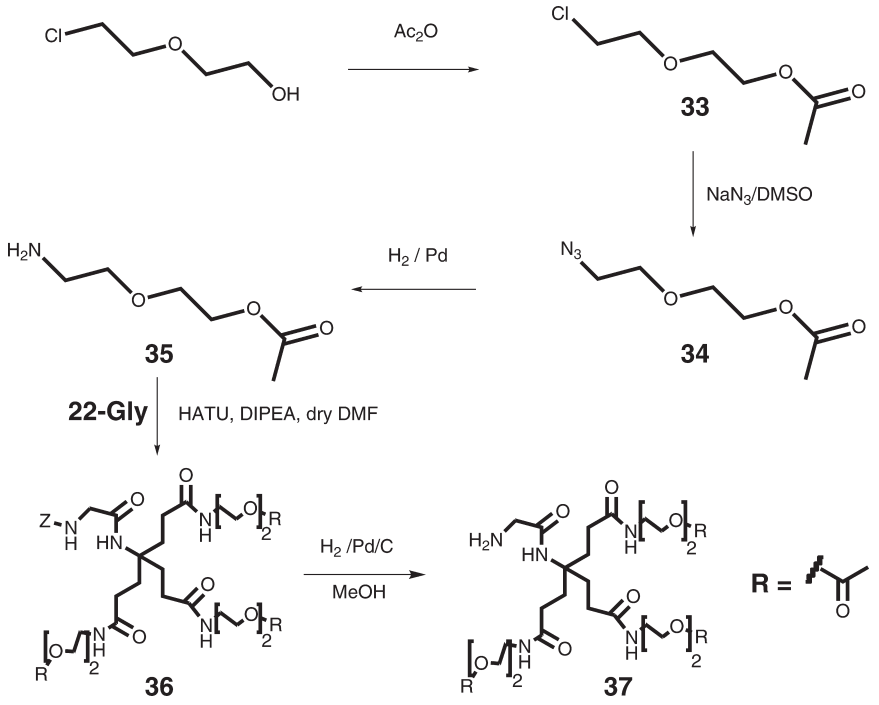
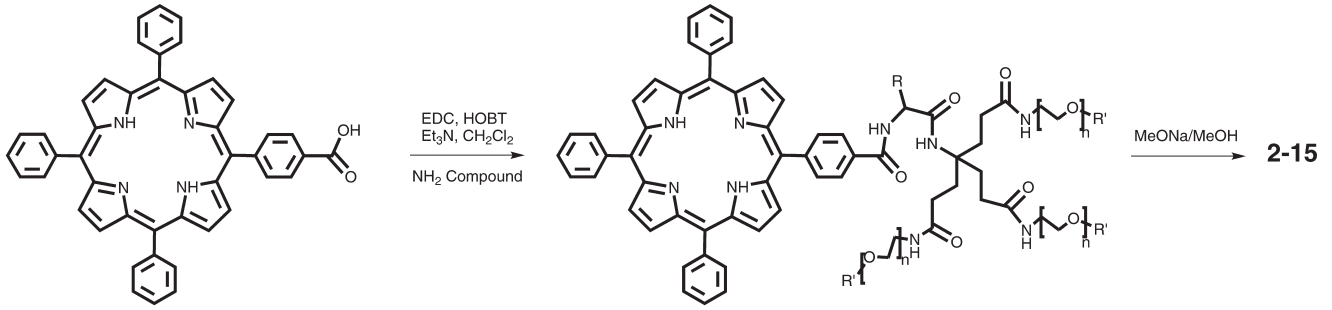
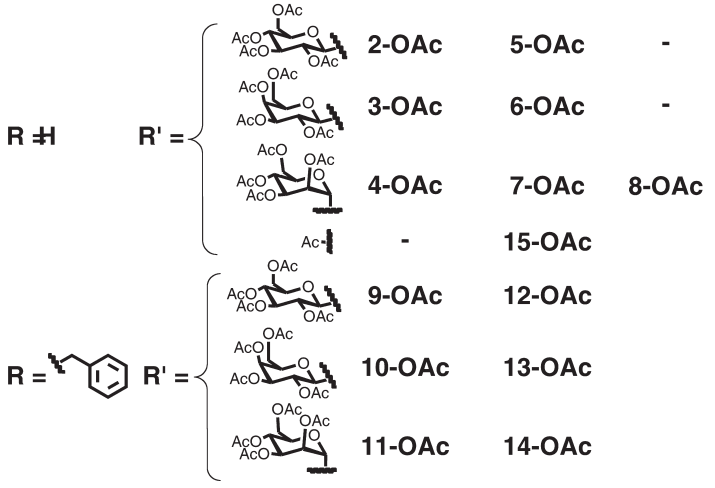
Scheme 4. Synthesis of Protected Diethyleneglycol Dendron



Scheme 5. Synthesis of Glycodendrimeric Porphyrins 2−15



NH_2 Compound	
26–β-GluOAc	31-β-GluOAc
26-β-GalOAc	31-β-GalOAc
26-α-ManOAc	31-α-ManOAc
27-β-GluOAc	32-β-GluOAc
27-β-GalOAc	32-β-GalOAc
27-α-ManOAc	32-α-ManOAc
28-α-ManOAc	37



of LD_{50} of TPP(*p*-DEG-O-α-ManOH)$_3$ used as reference,[13] porphyrins **2**−**14** are 6 times less phototoxic on HT29 and 10 times less phototoxic on Y79.

The analysis of the in vitro results obtained for both HT29 and Y79 cell lines does not bring to light a link between the nature of the sugar linked to the porphyrin and the type of membrane

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Table 1. Observed Retention Time (Rt) in HPLC Analysis on Waters X Terra MS C18 5μm, 3.9 × 150 mm Column and Log $P_{2\text{-octanol/PBS}}$ Measured at 20°C

compd	Rt (min)	log $P \pm 0.3$
TPP	nd	nd
1	nd	0.25
2	13.51	−0.54
3	13.56	−0.66
4	13.79	−0.66
5	13.55	−0.76
6	13.61	−0.87
7	13.73	−0.65
8	13.74	−0.94
9	15.20	−0.73
10	15.21	−0.67
11	15.75	−0.62
12	15.18	−0.98
13	15.19	−0.91
14	15.54	−0.31
15	18.49	1.6

Table 2. Dose of Porphyrin Derivatives (μM) Necessary To Observe 50% of Cell Survival (LD50) after Incubation (24 h) and Exposure to >540 nm Light at a Fluence of 2 J/cm^2

	LD_{50} ($\pm$1) μM	
compd	HT29	Y79
1	>10	>10
2	2.7	3.7
3	3	5
4	2.7	3.7
5	5	>10
6	2.5	3
7	5	5.6
8	5	5.2
9	4.5	5
10	4	5
11	3.7	5.2
12	6	>10
13	>10	>10
14	4.4	6
15	4.9	5.8
TPP-(*p*-Deg-O-α-ManOH)$_3$	0.43[14]	0.35[14]

receptor overexpressed in malignant cells although the carbohydrate−lectin recognition has been demonstrated on a model of the cell membrane.[35,36]

CONCLUSIONS

In this work, new glycodendrimeric porphyrins **1**−**15** bearing three glycosyls linked on a dendrimeric motif have been designed, synthesized, and characterized. We showed that it is possible to prepare two types of glycodendrimer porphyrins with an acceptable overall efficiency. In the first family, the macrocyclic chromophore is linked with a constrained galactodendrimer and in the other one, the chromophore is linked with miscellaneous flexible glycyl or L-phenylalanyl glycodendrons. The asymmetric structure of these new glycoconjugated porphyrins provides an amphiphilic character useful for drug administration (hydrophilicity) and transport through the organism. In spite of a specific affinity of mannodendrimeric photosensitizer **7** for lectin as Concanavalin A in a model of cellular membrane of retinoblastoma cell being demonstrated and the sugar groups of the glycoconjugated dendrimeric porphyrins favoring their nonspecific interaction with membranes,[35,36] the measured in vitro phototoxicities of derivatives **2**−**14** do not reflect these interactions.

EXPERIMENTAL SECTION

Synthesis and physical characterization of compounds **21-Gly**, **22-Gly**, **23-α-ManOAc**, **24 α-ManOAc**, **26-α-ManOAc**, **27-α-ManOAc**, **4-OAc**, **7-OAc**, **4**, and **7** were described in ref 35.

5-{*p*-*N*-[Tris(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyloxy) methyl]-*N*$^\alpha$-glycinamidophenyl}-10,15,20-triphenylporphyrin, 1-OAc: *meso*-5-(4-Benzoic acid)-10,15,20-tetraphenylporphyrin (75 mg, 11.4 × 10^{-2} mmol), compound **19** (267 mg, 22.8 × 10^{-2} mmol), HOBt (23 mg, 17.1 × 10^{-2} mmol), EDC (33 mg, 17.1 × 10^{-2} mmol), and Et_3N (75 μL) were dissolved in dry methylene chloride (25 mL) under argon. The solution was stirred at room temperature for 1 h. The reaction was followed up by analytical thin layer chromatography (silica gel, methylene chloride/acetone, 5/1, v/v). The crude mixture was washed with water, diluted aqueous chlorhydric acid, water, aqueous sodium bicarbonate, and water and dried over sodium sulfate then filtered and concentrated under vacuum. Title compound **1-OAc** was purified by preparative thin layer chromatography (silica gel, methylene chloride/acetone, 4/1, v/v, R_f 0.75). Pure product was obtained by crystallization from a mixture of methylene chloride/heptane as a red powder (110 mg, yield 49%). Anal. ($C_{93}H_{96}N_6O_{32}$), H_2O calcd: C 61.11, H 5.40, N 4.60. Found: C 61.22, H 5.11, N 4.48. UV−vis spectrum in CH_2Cl_2: λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 418 (423.6), 515 (18.2), 549.5 (9.7), 590 (7.7), 645 (6.4). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.87 (d, 2H, J = 4.8 Hz, $HC_{2,8}$ pyrrole), 8.85 (s, 4H, $HC_{12,13,17,18}$ pyrrole), 8.79 (d, 2H, J = 4.8 Hz, $HC_{3,7}$ pyrrole), 8.32 (d, 4H, J = 8.4 Hz, *o*-carboxyphenyl), 8.27 (d, 4H, J = 8.4 Hz, *m*-carboxyphenyl), 8.21 (d, 6H, J = 6.2 Hz, *o*-phenyl), 7.75 (m, 9H, *m*- and *p*-phenyl), 7.43 (t, 1H, J = 4.8 Hz, $NHCH_2$), 6.39 (s, 1H, NH-tris), 5.43 (d, 3H, J = 2.8 Hz, HC_4), 5.20 (dd, 3H, J = 7.7 and 10.5 Hz, HC_2), 5.08 (dd, 3H, J = 3.4 and 10.5 Hz, HC_3), 4.50 (d, 3H, J = 7.7 Hz, HC_1), 4.38 (dd, 1H, J = 5.4 and 16.9 Hz, CH_{2a} glycine), 4.29 (m, 3H, H_aC_6), 4.24 (d, 3H, $CH_{2a}NH$), 4.22 (m, 1H, CH_{2b} glycine), 4.16 (m, 3H, H_bC_6), 3.99 (t, 3H, J = 6.6 Hz, HC_5), 3.88 (d, 3H, J = 10.2 Hz, CH_{2b}-NH), 2.19 (s, 9H, CH_3CO), 2.14 (s, 9H, CH_3CO), 2.11 (s, 9H, CH_3CO), 2.0 (s, 9H, CH_3CO), −2.78 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 170.8 ($COCH_3$), 170.6 ($COCH_3$), 170.4 ($COCH_3$), 169.9 ($COCH_3$), 169.3 (glycine-CO), 167.8 (phenyl-CO), 146.2 (C_1 carboxyphenyl), 142.4 (C_1, phenyl), 135 (*o*-carboxyphenyl), 134.9 (*o*-phenyl), 131.6 (C pyrrole), 128.1 (*p*-carboxyphenyl and *p*-phenyl), 127.1 (*m*-carboxyphenyl), 125.9 (*m*-phenyl), 120.9 (*meso* C_{15}), 120.7 (*meso* $C_{10,20}$), 118.9 (*meso* C_5), 101.8 (C_1), 71.3 (C_5), 70.9 (C_3), 69.5 (C_2), 68.7 (CH_2-tris), 67.4 (C_4), 61.5 (C_6), 59.7 (C-NH), 43 (CH_2NH), 21.2 (CH_3CO), 21.1 (CH_3CO), 21 (CH_3CO), 20.9 (CH_3CO).

Compound 21-Phen: *N*-*Z*-L-Phenylalanine (3.917 g, 13.1 mmol), 1-hydroxy-7-azabenzotriazole (HOAt, 1.774 g, 13.1 mmol), and WSCI-HCl (2.519 g, 13.1 mmol) were dissolved in dry methylene chloride (60 mL) and **20** (4.53 g, 10.9 mmol) in dry methylene chloride (2 mL) was added. The reaction solution was stirred at room temperature for 36 h under argon. The reaction was quenched by addition of 10% aqueous citric acid (25 mL). The aqueous layer was extracted with methylene chloride. The organic layer was washed with water, saturated aqueous sodium bicarbonate, and water, and then dried over sodium sulfate, filtered, and concentrated under vacuum. The title compound

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was obtained as a white powder (yield 99%) and used without purification. MS calcd for $C_{39}H_{56}N_2O_9$ (MNa^+) 719.4, found 719.3. Anal. ($C_{39}H_{56}N_2O_9$), H_2O calcd: C 65.52, H 8.18, N 3.92. Found: C 65.80, H 8.00, N 3.96. Melting point 94 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.34 (m, 5H, benzyloxycarbonyl), 7.22 (m, 5H, phenylalanine), 6.10 (broad t, 1H, NH-C), 5.32 (d, 1H, NH phenylalanine), 5.09 (s, 2H, CH_2 benzyloxycarbonyl), 4.28 (dd, 1H, HC phenylalanine), 3.03 (m, 2H, CH_2 phenylalanine), 2.05 [t, 6H, $(CH_2)_3$-C)], 1.84 (t, 6H, CH_2COO-*t*-Bu), 1.43 (s, 27H, CH_3 *t*-Bu). ^{13}C NMR ($CDCl_3$): δ (ppm) 172.7 (CO dend), 169.9 (CO phenylalanine), 155.8 (CO benzyloxycarbonyl), 136.5 (C_1 benzyloxycarbonyl), 136.2 (C_1 phenylalanine), 129.3 (*o*-phenylalanine), 128.7 (*p*-phenylalanine), 128.5 (*m*-phenylalanine), 128.14 (*o*-benzyloxycarbonyl), 128.06 (*p*-benzyloxycarbonyl), 127 (*m*-benzyloxycarbonyl), 80.6 [C-$(CH_3)_3$], 67 (CH_2 benzyloxycarbonyl), 57.6 (C-NH), 56.6 (CH phenylalanine), 38.4 (CH_2 phenylalanine), 29.9 (CH_2CO), 29.5 [$(CH_2)_3$-C], 28 (CH_3 *t*-Bu).

Compound 22-Phen: **21-Phen** (3.331 g, 4.78 mmol) was dissolved in methylene chloride (120 mL) and trifluoroacetic acid (60 mL) and stirred 1 h at room temperature. The solution was concentrated under vacuum. Crude product was diluted in methylene chloride, then extracted with aqueous sodium hydroxide (5%). The aqueous phase was washed with methylene chloride (twice) and acidified by chlorhydric acid. The white precipitate was filtered, washed with water, and dried under vacuum. Pure title compound was obtained as white crystals and used without other purification (yield 97%). Melting point 171 °C (pasty). MS calcd for $C_{27}H_{32}N_2O_9$ (ES^+) 529.1, found 529.1, and calcd (ES^-) 527.2, found 527.1. Anal. ($C_{27}H_{32}N_2O_9$) calcd: C 61.35, H 6.10, N 5.30. Found: C 61.75, H 6.34, N 5.28. ^{1}H NMR (MeOD-d_4): δ (ppm) 7.29 (m, 5H, benzyloxycarbonyl), 7.24 (m, 5H, phenylalanine), 5.04 (d, 2H, CH_2 benzyloxycarbonyl), 4.29 (t, 1H, J = 7.6 Hz, HC phenylalanine), 2.99 (dd, 1H, J = 7.4 and 13.5 Hz, CH_{2a} phenylalanine), 2.85 (dd, 1H, J = 7.9 and 13.4 Hz, CH_{2b} phenylalanine), 2.12 (m, 6H, CH_2COO), 1.91 [m, 6H, $(CH_2)_3$-C)]. ^{13}C NMR (MeOD-d_4): δ (ppm) 177.1 (COOH), 173.4 (CO phenylalanine), 158.2 (CO benzyloxycarbonyl), 138.4 (C_1 benzyloxycarbonyl), 138.2 (C_1 phenylalanine), 130.5 (*o*-phenylalanine), 129.6 (*p*-phenylalanine), 129.5 (*m*-phenylalanine), 129 (*o*-benzyloxycarbonyl), 128.9 (*p*-benzyloxycarbonyl), 127.9 (*m*-benzyloxycarbonyl), 67.7 (CH_2 benzyloxycarbonyl), 58.7 (C-NH), 58.4 (CH phenylalanine), 39 (CH_2 phenylalanine), 30.6 [$(CH_2)_3$-C], 29.1 (CH_2COOH).

General Procedure for the Preparation of Compounds 23−25 and 29−30. All operations were identical with those described for the synthesis of compound **23-*β*-GluOAc**. A representative example is described below.

Compound 23-*β*-GluOAc: **22-Gly**[35] (0.100 g, 0.228 mmol) and 2-aminoethoxy-*O*-2′,3′,4′,6′-tetraacetyl-*β*-D-glucopyranose (0.267 g, 0.684 mmol) were dissolved in dry free amine DMF (20 mL) under argon. HATU (0.260 g, 0.684 mmol) and diisopropyl ethyl amine (1 mL) were added. The solution was stirred overnight at room temperature. Crude product was obtained after concentration under vacuum and diluted in methylene chloride. The organic phase was washed successively with water, aqueous HCl (10%), water, aqueous NaOH (5%), and water then dried over sodium sulfate, filtered, and concentrated. Pure title compound was obtained after crystallization from a mixture of methyl chloride/ether as yellow crystals and used without other purification (0.185 g, 52% yield). Anal. ($C_{68}H_{95}N_5O_{36}$), $3H_2O$ calcd: C 50.65, H 6.31, N 4.34. Found: C 50.35, H 6.22, N 4.52. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.35 (m, 5H, benzyloxycarbonyl), 6.73 (broad t, 3H, NH-CH_2), 5.21 (t, 3H, J = 9.4 Hz, HC_3), 5.11 (s, 2H, CH_2 benzyloxycarbonyl), 5.07 (t, 3H, J = 9.5 Hz, HC_4), 4.96 (t, 3H, HC_2), 4.53 (d, 3H, J = 7.9 Hz, HC_1), 4.25 (dd, 3H, J = 4.4 and 12.2 Hz, H_aC_6), 4.15 (m, 3H, H_bC_6), 3.74 (m, 11H, CH_2-O-glucosyl, CH_2 glycine and HC_5), 3.41 (m, 6H, CH_2-NH), 2.17 [m, 6H, $(CH_2)_3$-C], 2.08 (s, 9H, CH_3CO), 2.03 (s, 9H, CH_3CO), 2.02 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO), 1.99 (m, 6H, CH_2CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.4 (CO dend), 170.7 ($COCH_3$), 170.1 ($COCH_3$), 169.6 (CO glycine), 169.5 ($COCH_3$), 169.3 ($COCH_3$), 156.9 (CO benzyloxycarbonyl), 136.3 (C_1 benzyloxycarbonyl), 128.4 (*o*-benzyloxycarbonyl), 128 (*p*-benzyloxycarbonyl), 127.8 (*m*-benzyloxycarbonyl), 100.7 (C_1), 72.5 (C_3), 71.7 (C_5), 71.1 (C_2), 68.4 (CH_2-O-glucosyl), 68.2 (C_4), 66.8 (CH_2 benzyloxycarbonyl), 61.7 (C_6), 58 (C-NH), 44.7 (CH_2 glycine), 39.2 (CH_2-NH), 30.7 (CH_2CO), 30.4 [$(CH_2)_3$-C], 20.6 ($2CH_3CO$), 20.45 ($2CH_3CO$).

Compound 23-*β*-GalOAc: The title compound was prepared as **23-*β*-GluOAc** from 2-aminoethoxy-*O*-2′,3′,4′,6′-tetraacetyl-*β*-D-galactopyranose and **22-Gly**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/ether as a beige powder (yield 34%). MS calcd for $C_{68}H_{96}N_5O_{36}$ (MH^+) 1559.58, found 1559.10. Anal. ($C_{68}H_{95}N_5O_{36}$), $3H_2O$ calcd: C 50.65, H 6.31, N 4.34. Found: C 50.8, H 6.15, N 4.45. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.35 (m, 5H, benzyloxycarbonyl), 6.49 (broad t, 3H, CH_2-NH), 5.39 (d, 3H, J = 2.5 Hz, HC_4), 5.16 (dd, 3H, J = 7.9 and 10.4 Hz, HC_2), 5.13 (s, 2H, CH_2 benzyloxycarbonyl), 5.04 (dd, 3H, J = 3.2 and 10.4 Hz, HC_3), 4.48 (d, 3H, J = 7.8 Hz, HC_1), 4.14 (m, 6H, J = 6.4 Hz, HC_6), 3.95 (m, 3H, J = 6.4 Hz, HC_5), 3.84 (m, 3H, CH_{2a}-O-galactosyl), 3.75 (d, 2H, J = 5 Hz, CH_2 glycine), 3.67 (m, 3H, CH_{2b}-O-galactosyl), 3.40 (d, 6H, J = 4.9 Hz, CH_2-NH), 2.16 [m, 6H, $(CH_2)_3$-C], 2.15 (s, 9H, CH_3CO), 2.13 (m, 6H, CH_2CO), 2.07 (s, 9H, CH_3CO), 2.05 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.1 (CO dend), 170.5 ($COCH_3$), 170.2 ($COCH_3$), 170.1 ($COCH_3$), 169.75 ($COCH_3$), 168.7 (CO glycine), 156.9 (CO benzyloxycarbonyl), 136.3 (C_1 benzyloxycarbonyl), 128.5 (*o*-benzyloxycarbonyl), 128.2 (*p*-benzyloxycarbonyl), 127.9 (*m*-benzyloxycarbonyl), 101.3 (C_1), 70.71 (C_5), 70.69 (C_3), 68.9 (C_2), 68.7 (CH_2-O-galactosyl), 67 (CH_2 benzyloxycarbonyl), 66.95 (C_4), 61.3 (C_6), 58 (C-NH), 44.9 (CH_2 glycine), 39.4 (CH_2-NH), 31 (CH_2CO), 30.7 [$(CH_2)_3$-C], 20.8 (CH_3CO), 20.7 (CH_3CO), 20.6 (CH_3CO), 20.55 (CH_3CO).

Compound 24-*β*-GluOAc: The title compond was prepared as **23-*β*-GluOAc** from 2-aminoethoxyethoxy-*O*-2′,3′,4′,6′-tetraacetyl-*β*-D-glucopyranose and **22-Gly**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as a beige powder (yield 31%). MS calcd for $C_{74}H_{107}N_5O_{39}Na$ (MNa^+) 1712.65, found 1713.0. Anal. ($C_{74}H_{107}N_5O_{39}$), $4H_2O$ calcd: C 50.42, H 6.58, N 3.97. Found: C 50.31, H 6.17, N 4.04. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.33 (m, 5H, benzyloxycarbonyl), 6.46 (broad t, 3H, NH-CH_2), 5.75 (broad s, 1H, NH glycine), 5.24 (t, 3H, J = 9.4 Hz, HC_3), 5.13 (s, 2H, CH_2 benzyloxycarbonyl), 5.09 (t, 3H, J = 9.4 Hz, HC_4), 4.99 (dd, 3H, J = 7.9 and 9.3 Hz, HC_2), 4.61 (d, 3H, J = 7.8 Hz, HC_1), 4.24 (dd, 3H, J = 4.4 and 12.3 Hz, H_aC_6), 4.11 (m, 3H, H_bC_6), 3.93 (m, 3H, CH_{2a}-O-glucosyl), 3.78 (m, 2H, CH_2 glycine), 3.70 (m, 6H, HC_5 and CH_{2b}-O-glucosyl), 3.60 (m, 6H, CH_2O), 3.49 (m, 6H, CH_2O), 3.4 (m, 3H, CH_{2a}-NH), 3.33 (m, 3H, CH_{2b}-NH), 2.21 [m, 6H, $(CH_2)_3$-C], 2.08 (s, 9H, CH_3CO), 2.05 (m, 6H, CH_2CO), 2.04 (s, 9H, CH_3CO), 2.02 (s, 9H, CH_3CO), 2.00 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.2 (CO dend), 170.7 ($COCH_3$), 170.4 ($COCH_3$), 169.6 ($COCH_3$), 169.4 ($COCH_3$), 168.7 (CO glycine), 157 (CO benzyloxycarbonyl), 136.3 (C_1 benzyloxycarbonyl), 128.5 (*o*-benzyloxycarbonyl), 128.1 (*p*-benzyloxycarbonyl), 127.9 (*m*-benzyloxycarbonyl), 100.8 (C_1), 72.6 (C_3), 71.7 (C_5), 71.3 (C_2), 69.9 (CH_2O), 69.85 (CH_2O), 68.9 (CH_2-O-glucosyl), 68.4 (C_4), 66.9 (CH_2 benzyloxycarbonyl), 61.9 (C_6), 58.2 (C-NH), 44.8 (CH_2 glycine), 39.1 (CH_2-NH), 30.8 (CH_2CO), 30.6 [$(CH_2)_3$-C], 20.7 ($2CH_3CO$), 20.6 ($2CH_3CO$).

Compound 24-*β*-GalOAc: The title compound was prepared as **23-*β*-GluOAc** from 2-aminoethoxyethoxy-*O*-2′,3′,4′,6′-tetraacetyl-*β*-D-galactopyranose and **22-Gly**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as a beige powder (yield 47%). MS calcd for $C_{74}H_{108}N_5O_{39}$ (MH^+) 1690.65 and (MNa^+) 1712.65, found 1690.9 and 1712.8. Anal.

($C_{74}H_{107}N_5O_{39}$), $3H_2O$ calcd: C 50.94, H 6.51, N 4.01. Found: 50.78, H 6.28, N 4.42. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.33 (m, 5H, benzyloxycarbonyl), 6.46 (broad t, 3H, CH_2-NH), 5.72 (broad s, 1H, NH-C), 5.39 (dd, 3H, J = 3.3 Hz, HC_4), 5.19 (dd, 3H, J = 7.8 and 10.4 Hz, HC_2), 5.13 (s, 2H, CH_2 benzyloxycarbonyl), 5.06 (dd, 3H, J = 3.3 and 10.4 Hz, HC_3), 4.58 (d, 3H, J = 7.8 Hz, HC_1), 4.14 (m, 6H, HC_6), 3.94 (m, 6H, HC_5 and CH_{2a}-O-galactosyl), 3.79 (m, 2H, CH_2 glycine), 3.71 (m, 3H, CH_{2b}-O-galactosyl), 3.60 (m, 6H, CH_2O), 3.50 (m, 6H, CH_2O), 3.42 (m, 3H, CH_{2a}-NH), 3.33 (m, 3H, CH_{2b}-NH), 2.22 [m, 6H, $(CH_2)_3$-C], 2.15 (s, 9H, CH_3CO), 2.06 (m, 6H, CH_2CO), 2.06 (s, 9H, CH_3CO), 2.04 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.1 (CO dend), 170.4 ($COCH_3$), 170.2 (2 $COCH_3$), 169.8 ($COCH_3$), 168.6 (CO glycine), 157 (CO benzyloxycarbonyl), 136.2 (C_1 benzyloxycarbonyl), 128.5 (*o*-benzyloxycarbonyl), 128.2 (*p*-benzyloxycarbonyl), 127.9 (*m*-benzyloxycarbonyl), 101.3 (C_1), 70.8 (C_3), 70.6 (C_5), 70 (CH_2O), 69.8 (CH_2O), 68.92 (CH_2-O-galactosyl), 68.88 (C_2), 66.9 (C_4), 66.8 (CH_2 benzyloxycarbonyl), 61.2 (C_6), 58.2 (C-NH), 44.8 (CH_2 glycine), 39.3 (CH_2-NH), 30.9 (CH_2CO), 30.7 [$(CH_2)_3$-C], 20.8 (CH_3CO), 20.7 (CH_3CO), 20.65 (CH_3CO), 20.6 (CH_3CO).

Compound 25-α-ManOAc: The title compound was prepared as **23-*β*-GluOAc** from 2-aminoethoxyethoxyethoxy-*O*-2′,3′,4′,6′-tetraacetyl-α-D-mannopyranose and **22-Gly**. Pure title compound was obtained as paste and used without other purification (yield 84%). Anal. ($C_{80}H_{119}N_5O_{42}$), H_2O calcd: C 52.20, H 6.63, N 3.80. Found: C 51.95, H 6.85, N 4.03. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.35 (m, 5H, benzyloxycarbonyl), 6.67 (broad t, 3H, NH), 6.25 (broad s, 1H, NH), 5.85 (broad t, 1H, J = 5.5 Hz, NH glycine), 5.30 (m, 6H, CH_2), 5.27 (m, 12H, CH_2), 4.88 (s, 3H, HC_1), 4.28 (dd, 3H, J = 4.6 and 12 Hz, H_aC_6), 4.10 (d, 3H, J = 12 Hz, H_bC_6), 4.07 (m, 3H, HC_5), 3.81 (m, 6H, CH_2), 3.75 (d, 2H, CH_2 glycine), 3.68 (m, 6H, CH_2), 3.65 (m, 24H, CH_2), 3.41 (m, 6H, CH_2), 2.20 (m, 12H, CH_2), 2.15 (s, 9H, CH_3CO), 2.10 (s, 9H, CH_3CO), 2.04 (s, 9H, CH_3CO), 2 (m, 12H, CH_2), 1.99 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.6 (CO dend), 171.1 ($COCH_3$), 170.5 ($COCH_3$), 170.4 ($COCH_3$), 170.1 ($COCH_3$), 169.1 (CO glycine), 157.1 (CO), 136.8 (C_1 benzyloxycarbonyl), 128.9 (*o*-benzyloxycarbonyl), 128.5 (*p*-benzyloxycarbonyl), 128.4 (*m*-benzyloxycarbonyl), 98.1 (C_1), 71 (CH_2), 70.6 (CH_2), 70.3 (CH_2), 70.2 (CH_2), 69.5 ($C_{2,3,4}$), 68.8 (C_5), 67.7 (CH_2), 67.4 (CH_2 benzyloxycarbonyl), 66.5 ($C_{2,3,4}$), 62.8 (C_6), 58.7 (C-NH), 45.4 (CH_2 glycine), 39.7 (CH_2), 31.5 (CH_2), 31.1 (CH_2), 21.31 [$(CH_2)_3$-C], 21.27 [$(CH_2)_3$-C], 21.1 [$(CH_2)_3$C].

General Procedure for the Preparation of Compounds 26−28-α-ManOAc and 31−32. All operations were identical with those described for the synthesis of compound **26-*β*-GluOAc**. A representative example is described below.

Compound 26-*β*-GluOAc: 23-*β*-GluOAc (0.5 g, 1 equiv, 0.32 mmol) and palladium on activated carbon (Pd/C 10%, 270 mg) were dissolved in methanol (200 mL). The solution was stirred under hydrogen atmosphere (3 bar) at room temperature for 24 h. The suspension was filtered over Celite and concentrated under vacuum. Pure title compound was obtained as beige crystals and used without purification (yield 85%). MS calcd for $C_{60}H_{90}N_5O_{34}$ (MH^+) 1424.54, found 1424.30. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.21 (t, 3H, J = 9.4 Hz, HC_3), 5.08 (t, 3H, J = 9.4 Hz, HC_4), 4.97 (m, 3H, HC_2), 4.54 (m, 3H, HC_1), 4.25 (m, 3H, H_aC_6), 4.16 (m, 3H, H_bC_6), 3.71 (m, 9H, HC_5 and CH_2-O-glucosyl), 3.38 (m, 6H, CH_2-NH), 2.20 [m, 6H, $(CH_2)_3$-C], 2.09 (s, 9H, CH_3CO), 2.06 (s, 9H, CH_3CO), 2.04 (m, 6H, CH_2CO), 2.03 (s, 9H, CH_3CO), 2.01 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.7 (CO dend), 170.7 ($COCH_3$), 170.2 ($COCH_3$), 169.7 ($COCH_3$), 169.4 ($COCH_3$), 100.7 (C_1), 72.6 (C_3), 71.8 (C_5), 71.3 (C_2), 68.9 (CH_2-O-glucosyl), 68.3 (C_4), 61.9 (C_6), 58.4 (C-NH), 42.3 (CH_2 glycine), 39.3 (CH_2-NH), 30.6 [CH_2CO and $(CH_2)_3$-C], 20.7 ($2CH_3CO$), 20.6 ($2CH_3CO$).

Compound 26-*β*-GalOAc: The title compound was prepared as **26-*β*-GluOAc** from **23-*β*-GalOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as yellow crystals (yield 70%). MS calcd for $C_{60}H_{90}N_5O_{34}$ (MH^+) 1424.54, found 1424.90. Anal. ($C_{60}H_{89}N_5O_{34}$), $4H_2O$ calcd: C 48.16, H 6.53, N 4.68. Found: C 48.16, H 6.08, N 4.90. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.39 (d, 3H, J = 2.7 Hz, HC_4), 5.15 (m, 3H, J = 7.7 Hz, HC_2), 5.05 (m, 3H, J = 10.4 Hz, HC_3), 4.52 (d, 3H, J = 7.7 Hz, HC_1), 4.15 (m, 6H, HC_6), 3.97 (m, 3H, HC_5), 3.96 (m, 2H, CH_2 glycine), 3.85 (m, 3H, CH_{2a}-O-galactosyl), 3.68 (m, 3H, CH_{2b}-O-galactosyl), 3.40 (d, 6H, CH_2-NH), 2.17 (s, 9H, CH_3CO), 2.16 [m, 6H, $(CH_2)_3$-C], 2.08 (s, 9H, CH_3CO), 2.05 (s, 9H, CH_3CO), 2.00 (m, 6H, CH_2CO), 1.99 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 170.5 ($COCH_3$), 170.2 ($COCH_3$), 170 ($COCH_3$), 169.8 ($COCH_3$), 168.6 (CO glycine), 101.2 (C_1), 70.7 (C_3 and C_5), 68.8 (C_2), 68.5 (CH_2-O-galactosyl), 67 (C_4), 61.2 (C_6), 57.7 (C-NH), 45 (CH_2 glycine), 39.4 (CH_2-NH), 30.9 (CH_2CO), 30.5 [$(CH_2)_3$-C], 20.8 (CH_3CO), 20.7 (CH_3CO), 20.6 (CH_3CO), 20.5 (CH_3CO).

Compound 27-*β*-GluOAc: The title compound was prepared as **26-*β*-GluOAc** from **24-*β*-GluOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as colorless crystals (yield 82%). MS calcd for $C_{66}H_{102}N_5O_{37}$ (MH^+) 1556.62 and (MNa^+) 1578.62, found 1556.8 and 1578.8. Anal. ($C_{66}H_{101}N_5O_{37}$), $10H_2O$ calcd: C 45.63, H 6.97, N 4.32. Found: C 45.99, H 6.29, N 4.37. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.23 (t, 3H, J = 9.6 Hz, HC_3), 5.09 (t, 3H, J = 9.4 Hz, HC_4), 4.99 (t, 3H, HC_2), 4.61 (d, 3H, J = 7.8 Hz, HC_1), 4.27 (dd, 3H, J = 4.4 and 12.3 Hz, H_aC_6), 4.14 (m, 3H, H_bC_6), 3.96 (m, 3H, CH_{2a}-O-glucosyl), 3.72 (m, 3H, HC_5), 3.67 (m, 3H, CH_{2b}-O-glucosyl), 3.61 (m, 6H, CH_2O), 3.51 (m, 6H, CH_2O), 3.38 (m, 6H, CH_2-NH), 2.19 [m, 6H, $(CH_2)_3$-C], 2.09 (s, 9H, CH_3CO), 2.06 (m, 6H, CH_2CO), 2.05 (s, 9H, CH_3CO), 2.03 (s, 9H, CH_3CO), 2.01 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.2 (CO dend), 170.6 ($COCH_3$), 170.2 ($COCH_3$), 169.5 ($COCH_3$), 169.4 ($COCH_3$), 100.7 (C_1), 72.6 (C_3), 71.7 (C_5), 71.2 (C_2), 69.7 (2 CH_2O), 68.9 (CH_2-O-glucosyl), 68.3 (C_4), 61.8 (C_6), 57.8 (C-NH), 39.1 (CH_2-NH), 30.8 (CH_2-CO), 30.5 [$(CH_2)_3$-C], 20.6 (2 CH_3CO), 20.5 (2 CH_3CO).

Compound 27-*β*-GalOAc: The title compound was prepared as **26-*β*-GluOAc** from **24-*β*-GalOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as a beige powder (yield 79%). MS calcd for $C_{66}H_{102}N_5O_{37}$ (MH^+) 1556.62, found 1556.9. Anal. ($C_{66}H_{101}N_5O_{37}$), $6H_2O$ calcd: C 47.58, H 6.59, N 4.62. Found: C 47.79, H 6.21, N 4.32. ^{1}H NMR ($CDCl_3$): δ (ppm) 6.88 (broad s, 1H, NH-C), 5.39 (d, 3H, J = 2.8 Hz, HC_4), 5.18 (m, 3H, HC_2), 5.05 (dd, 3H, J = 2.8 and 10.2 Hz, HC_3), 4.57 (d, 3H, J = 7.7 Hz, HC_1), 4.14 (m, 6H, HC_6), 3.96 (m, 6H, HC_5 and CH_{2b}-O-galactosyl), 3.96 (m, 2H, CH_2 glycine), 3.71 (m, 3H, CH_{2a}-O-galactosyl), 3.61 (m, 6H, CH_2O), 3.5 (m, 6H, CH_2O), 3.38 (m, 6H, CH_2-NH), 2.23 [m, 6H, $(CH_2)_3$-C], 2.15 (s, 9H, CH_3CO), 2.06 (s, 9H, CH_3CO), 2.05 (s, 9H, CH_3CO), 2.05 (m, 6H, CH_2CO), 1.99 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.1 (CO dend), 170.4 ($COCH_3$), 170.2 ($COCH_3$), 170.1 ($COCH_3$), 169.7 ($COCH_3$), 168.5 (CO glycine), 101.3 (C_1), 70.74 (C_3), 70.68 (C_5), 69.8 ($2CH_2O$), 68.9 (CH_2-O-galactosyl), 68.85 (C_2), 67 (C_4), 61.2 (C_6), 57.9 (C-NH), 45 (CH_2 glycine), 39.1 (CH_2-NH), 30.7 (CH_2CO), 30.5 [$(CH_2)_3$-C], 20.8 (CH_3CO), 20.7 ($2CH_3CO$), 20.6 (CH_3CO).

Compound 28-α-ManOAc: The title compound was prepared as **26-*β*-GluOAc** from **25-α-ManOAc**. Pure title compound was obtained after drying under vacuum as a brown powder and used without other purification (yield 94%). Anal. not obtained. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.29 (m, 9H, $HC_{2,3,4}$), 4.86 (s, 3H, HC_1), 4.26 (m, 3H), 4.10 (m, 6H, HC_5 and H_bC_6), 3.68 (m, 8H, CH_2-O-mannosyl and CH_2), 3.46 (m, 6H), 2.33 (m, 6H, CH_2), 2.16 (s, 9H, CH_3CO), 2.09 (s, 9H, CH_3CO), 2.05 (s, 9H, CH_3CO), 2.00 (m, 11H, CH_2 and CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 171.7 ($COCH_3$), 171.3 ($COCH_3$), 171.2

($COCH_3$), 171 ($COCH_3$), 170.7 ($COCH_3$), 166.2 (CO glycine), 142.8 (C-SO_3H), 141.2 (*p*-phenyl), 129.8 (*m*-phenyl), 126.7 (*o*-phenyl), 98.5 (C_1), 71.5 ($C_{2,3,4}$), 71.3 ($C_{2,3,4}$), 70.8 ($C_{2,3,4}$), 68.1 (C_5), 66.9 (C-O-mannosyl), 63.3 (C6), 43.6 (CH_2-glycine), 40.9 (C-NH), 22.2 (CH_3-phenyl), 21.8 (CH_3), 21.6 (CH_3).

Compound 29-*β*-GluOAc: The title compound was prepared as **23-*β*-GluOAc** from **22-Phen** and 2-aminoethoxy-*O*-2′,3′,4′,6′-tetraacetyl-*β*-D-glucopyranose tosylate. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as a yellow orange powder (yield 90%). MS calcd for $C_{75}H_{101}N_5O_{36}Na$ (MNa^+) 1670.62, found 1670.7. Anal. ($C_{75}H_{101}N_5O_{36}$), $4H_2O$ calcd: C 52.35, H 6.39, N 4.07. Found: C 52.18, H 6.01, N 4.09. ^{1}H NMR ($CDCl_3$): *δ* (ppm) 7.33 (m, 5H, benzyloxycarbonyl), 7.25 (m, 5H, phenylalanine), 6.37 (broad t, 3H, CH_2-NH), 5.18 (dd, 3H, *J* = 9.5 Hz, HC_3), 5.08 (d, 3H, HC_4), 5.07 (s, 2H, CH_2 benzyloxycarbonyl), 4.99 (dd, 3H, *J* = 9.3 Hz, HC_2), 4.51 (d, 3H, *J* = 7.8 Hz, HC_1), 4.31 (m, 1H, HC phenylalanine), 4.25 (dd, 3H, *J* = 4.5 and 12.2 Hz, H_aC_6), 4.14 (dd, 3H, *J* = 2.0 and 12.3 Hz, H_bC_6), 3.82 (m, 3H, CH_{2a}-O-glucosyl), 3.70 (m, 3H, HC_5), 3.69 (m, 3H, CH_{2b}-O-glucosyl), 3.37 (d, 6H, *J* = 5.2 Hz, CH_2-NH), 3.06 (m, 1H, CH_{2a}-phenylalanine), 2.95 (m, 1H, CH_{2b}-phenylalanine), 2.15 [m, 6H, $(CH_2)_3$-C], 2.07 (s, 9H, CH_3CO), 2.05 (s, 9H, CH_3CO), 2.02 (s, 9H, CH_3CO), 2.00 (s, 9H, CH_3CO), 1.98 (m, 6H, CH_2CO). ^{13}C NMR ($CDCl_3$): *δ* (ppm) 173 (CO dend), 170.7 ($COCH_3$), 170.5 (CO phenylalanine), 170.1 ($COCH_3$), 169.5 ($COCH_3$), 169.4 ($COCH_3$), 155.9 (CO benzyloxycarbonyl), 136.6 (C_1 benzyloxycarbonyl), 136.3 (C_1 phenylalanine), 129.4 (*o*-phenylalanine), 128.6 (*p*-phenylalanine), 128.5 (*m*-phenylalanine), 128.1 (*o*-benzyloxycarbonyl), 127.9 (*p*-benzyloxycarbonyl), 126.9 (*m*-benzyloxycarbonyl), 100.8 (C_1), 72.6 (C_3), 71.8 (C_5), 71.2 (C_2), 68.8 (CH_2-O-glucosyl), 68.3 (C_4), 66.8 (CH_2 benzyloxycarbonyl), 61.8 (C_6), 58.1 (C-NH), 57 (CH phenylalanine), 39.3 (CH_2-NH), 38.3 (CH_2 phenylalanine), 30.7 (CH_2CO), 30.4 [$(CH_2)_3$-C]), 20.7 (2 CH_3CO), 20.6 (2 CH_3CO).

Compound 29-*β*-GalOAc: The title compound was prepared as **23-*β*-GluOAc** from **22-Phen** and 2-aminoethoxy-*O*-2′,3′,4′,6′-tetraacetyl-*β*-D-galactopyranose. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as a beige powder (yield 46%). MS calcd for $C_{75}H_{101}N_5O_{36}Na$ (MNa^+) 1670.62, found 1670.7. Anal. ($C_{75}H_{101}N_5O_{36}$), $5H_2O$ calcd: C 51.81, H 6.43, N 4.03. Found: C 51.80; H 6.04; N 4.58. ^{1}H NMR ($CDCl_3$): *δ* (ppm) 7.33 (m, 5H, benzyloxycarbonyl), 7.24 (m, 5H, phenylalanine), 6.23 (broad t, 3H, CH_2-NH), 5.39 (d, 3H, *J* = 2.8 Hz, HC_4), 5.19 (dd, 3H, *J* = 7.8 and 10.3 Hz, HC_2), 5.09 (s, 2H, CH_2 benzyloxycarbonyl), 5.04 (dd, 3H, *J* = 3.3 and 10.4 Hz, HC_3), 4.51 (d, 3H, *J* = 7.8 Hz, HC_1), 4.30 (m, 1H, HC phenylalanine), 4.16 (m, 6H, HC_6), 3.94 (m, 3H, HC_5), 3.83 (m, 3H, CH_{2a}-O-galactosyl), 3.67 (m, 3H, CH_{2b}-O-galactosyl), 3.39 (d, 6H, *J* = 5.6 Hz, CH_2-NH), 3.00 (s, 2H, CH_2-phenylalanine), 2.16 [m, 6H, $(CH_2)_3$-C], 2.12 (s, 9H, CH_3CO), 2.06 (s, 9H, CH_3CO), 2.04 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO), 1.99 (m, 6H, CH_2CO). ^{13}C NMR ($CDCl_3$): *δ* (ppm) 173 (CO dend), 170.5 (CO phenylalanine), 170.4 ($COCH_3$), 170.1 ($COCH_3$), 170 ($COCH_3$), 169.7 ($COCH_3$), 156.4 (CO benzyloxycarbonyl), 136.6 (C_1 benzyloxycarbonyl), 136.3 (C_1 phenylalanine), 129.4 (*o*-phenylalanine), 128.6 (*p*-phenylalanine), 128.5 (*m*-phenylalanine), 128,1 (*o*-benzyloxycarbonyl), 127.8 (*p*-benzyloxycarbonyl), 127 (*m*-benzyloxycarbonyl), 101.3 (C_1), 70.7 (C_5 and C_3), 68.8 (C_2), 68.7 (CH_2-O-galactosyl), 67 (C_4), 66.8 (CH_2 benzyloxycarbonyl), 61.3 (C_6), 58 (C-NH), 57 (CH phenylalanine), 39.3 (CH_2-NH), 38.2 (CH_2 phenylalanine), 30.7 (CH_2CO), 30.4 [$(CH_2)_3$-C], 20.8 (CH_3CO), 20.6 (CH_3CO), 20.6 (CH_3CO), 20.5 (CH_3CO).

Compound 29-α-ManOAc: The title compound was prepared as **23-*β*-GluOAc** from **22-Phen** and 2-aminoethoxy-*O*-2′,3′,4′,6′-tetraacetyl-α-D-mannopyranose. Pure title compound was obtained as a yellow powder and used without purification (yield 90%). MS calcd for $C_{75}H_{101}N_5O_{36}Na$ (MNa^+) 1670.62, found 1670.7. Anal. ($C_{75}H_{101}N_5O_{36}$), $3H_2O$ calcd: C 52.91, H 6.33, N 4.11. Found: C 53.15; H 6.19; N 4.33. ^{1}H NMR ($CDCl_3$): *δ* (ppm) 7.32 (m, 5H, benzyloxycarbonyl), 7.24 (m, 5H, phenylalanine), 6.65 (broad t, 3H, CH_2-NH), 5.37 (dd, 3H, *J* = 3.2 and 10 Hz, HC_3), 5.30 (m, 3H, HC_2), 5.27 (m, 3H, HC_4), 5.07 (s, 2H, CH_2 benzyloxycarbonyl), 4.83 (d, 3H, *J* = 1.1 Hz, HC_1), 4.31 (m, 1H, HC phenylalanine), 4.28 (dd, 3H, *J* = 5.7 and 12.3 Hz, H_aC_6), 4.14 (dd, 3H, *J* = 2.0 and 12.2 Hz, H_bC_6), 4.03 (m, 3H, HC_5), 3.75 (m, 3H, CH_{2a}-O-mannosyl), 3.51 (m, 6H, CH_2NH), 3.34 (m, 3H, CH_{2b}-O-mannosyl), 3.03 (dd, 1H, *J* = 7 Hz, CH_{2a}-phenylalanine), 2.96 (m, 1H, *J* = 6.8 Hz, CH_{2b}-phenylalanine), 2.17 [m, 6H, $(CH_2)_3$-C], 2.15 (s, 9H, CH_3CO), 2.10 (s, 9H, CH_3CO), 2.05 (m, 6H, CH_2CO), 2.03 (s, 9H, CH_3CO), 1.97 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): *δ* (ppm) 173.5 (CO dend), 170.9 (CO phenylalanine), 170.7 ($COCH_3$), 170.2 ($COCH_3$), 170.1 ($COCH_3$), 169.7 ($COCH_3$), 156.2 (CO benzyloxycarbonyl), 136.7 (C_1 benzyloxycarbonyl), 136.3 (C_1 phenylalanine), 129.3 (*o*-phenylalanine), 128.5 (*p*-phenylalanine), 128.5 (*m*-phenylalanine), 128.1 (*o*-benzyloxycarbonyl), 127.8 (*p*-benzyloxycarbonyl), 126.9 (*m*-benzyloxycarbonyl), 97.6 (C_1), 69.4 (C_3), 69.1 (C_2), 68.6 (C_5), 67.1 (CH_2 benzyloxyarbonyl), 66.8 (CH_2-O-mannosyl), 66 (C_4), 62.4 (C_6), 58.5 (C-NH), 57 (CH phenylalanine), 38.8 (CH_2-NH), 38 (CH_2 phenylalanine), 31.2 (CH_2CO), 30.6 [$(CH_2)_3$-C], 20.8 (2 CH_3CO), 20.7 (2 CH_3CO).

Compound 30-*β*-GluOAc: The title compound was prepared as **23-*β*-GluOAc** from **22-Phen** and 2-aminoethoxyethoxy-*O*-2′,3′,4′,6′-tetraacetyl-*β*-D-glucopyranose. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as beige crystals (yield 32%). MS calcd for $C_{81}H_{113}N_5O_{39}Na$ (MNa^+) 1802.7, found 1802.8. Anal. ($C_{81}H_{113}N_5O_{39}$), $3H_2O$ calcd: C 53.03, H 6.54, N 3.82. Found: C 52.87, H 6.32, N 4.18. ^{1}H NMR ($CDCl_3$): *δ* (ppm) 7.33 (m, 5H, benzyloxycarbonyl), 7.25 (m, 5H, phenylalanine), 6.35 (broad t, 3H, CH_2-NH), 5.54 (m, 1H, NH-C), 5.48 (m, 1H, NH phenylalanine), 5.26 (t, 3H, *J* = 9.5 Hz, HC_3), 5.09 (m, 5H, HC_4 and CH_2 benzyloxycarbonyl), 5.0 (dd, 3H, *J* = 7.9 and 9.5 Hz, HC_2), 4.62 (d, 3H, *J* = 7.9 Hz, HC_1), 4.34 (m, 1H, HC phenylalanine), 4.24 (dd, 3H, *J* = 4.5 and 12.3 Hz, H_aC_6), 4.11 (m, 3H, H_bC_6), 3.94 (m, 3H, CH_{2a}-O-glucosyl), 3.70 (m, 6H, CH_{2b}-O-glucosyl and HC_5), 3.61 (m, 6H, CH_2O), 3.49 (m, 6H, CH_2O), 3.4 (m, 3H, CH_{2a}-NH), 3.3 (m, 3H, CH_{2b}-NH), 3.02 (m, 2H, CH_2-phenylalanine), 2.07 (s, 9H, CH_3CO), 2.06 (m, 6H, [$(CH_2)_3$-C]), 2.04 (s, 9H, CH_3CO), 2.02 (s, 9H, CH_3CO), 2.01 (s, 9H, CH_3CO), 1.91 (m, 6H, CH_2CO). ^{13}C NMR ($CDCl_3$): *δ* (ppm) 173.1 (CO dend), 170.7 ($COCH_3$), 170.4 (CO phenylalanine), 169.5 ($2COCH_3$), 169.4 ($COCH_3$), 156 (CO benzyloxycarbonyl), 136.5 (C_1 phenylalanine), 136.2 (C_1 benzyloxycarbonyl), 129.3 (*o*-phenylalanine), 128.7 (*p*-phenylalanine), 128.6 (*m*-phenylalanine), 128.2 (*o*-benzyloxycarbonyl), 127.7 (*p*-benzyloxycarbonyl), 127 (*m*-benzyloxycarbonyl), 100.8 (C_1), 72.6 (C_3), 71.7 (C_5), 71.2 (C_2), 70.1 (CH_2O), 69.9 (CH_2O), 68.9 (CH_2-O-glucosyl), 68.4 (C_4), 66.8 (CH_2 benzyloxycarbonyl), 61.9 (C_6), 58.1 (C-NH), 56.8 (CH phenylalanine), 39.2 (CH_2-NH), 38.2 (CH_2 phenylalanine), 30.6 (CH_2CO), 30.5 [$(CH_2)_3$-C], 20.7 (2 CH_3CO), 20.6 (2 CH_3CO).

Compound 30-*β*-GalOAc: The title compound was prepared as **23-*β*-GluOAc** from **22-Phen** and 2-aminoethoxyethoxy-*O*-2′,3′,4′,6′-tetraacetyl-*β*-D-galactopyranose. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as an orange powder (yield 61%). MS calcd for $C_{81}H_{113}N_5O_{39}Na$ (MNa^+) 1802.7, found 1802.8. Anal. ($C_{81}H_{113}N_5O_{39}$), $2H_2O$ calcd: C 53.55, H 6.49, N 3.85. Found: C 53.77, H 6.34, N 4.25. ^{1}H NMR ($CDCl_3$): *δ* (ppm) 7.33 (m, 5H, benzyloxycarbonyl), 7.25 (m, 5H, phenylalanine), 6.44 (broad t, 3H, CH_2-NH), 5.50 (m, 3H, NH phenylalanine), 5.38 (d, 3H, *J* = 3.0 Hz, HC_4), 5.21 (dd, 3H, *J* = 7.8 and 10.4 Hz, HC_2), 5.09 (m, 5H, CH_2 benzyloxycarbonyl and HC_3), 4.64 (d, 3H, *J* = 7.8 Hz, HC_1), 4.36 (m, 1H, HC phenylalanine), 4.11 (m, 6H, HC_6), 3.94 (m, 6H, HC_5 and CH_{2a}-O-galactosyl), 3.74 (m, 3H, CH_{2b}-O-galactosyl), 3.61 (m, 6H,

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CH_2O), 3.48 (m, 9H, CH_2O and CH_{2a}-NH), 3.26 (m, 3H, CH_{2b}-NH), 3.03 (m, 2H, CH_2-phenylalanine), 2.14 (s, 9H, CH_3CO), 2.13 [m, 6H, $(CH_2)_3$-C], 2.05 (s, 9H, CH_3CO), 2.00 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO), 1.94 (m, 6H, CH_2CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 172.9 (CO dend), 171 (CO phenylalanine), 170.4 ($COCH_3$), 170.3 ($COCH_3$), 170.2 ($COCH_3$), 169.6 ($COCH_3$), 156.5 (CO benzyloxycarbonyl), 136.6 (C_1 benzyloxycarbonyl), 136.3 (C_1 phenylalanine), 129.3 (*o*-phenylalanine), 128.7 (*p*-phenylalanine), 128.5 (*m*-phenylalanine), 128.3 (*o*-benzyloxycarbonyl), 127.7 (*p*-benzyloxycarbonyl), 127.1 (*m*-benzyloxycarbonyl), 101.3 (C_1), 70.9 (C_3), 70.6 (C_5), 70.3 (CH_2O), 70 (CH_2O), 68.9 (C_2), 68.7 (CH_2-O-galactosyl), 67.1 (C_4), 67 (CH_2 benzyloxycarbonyl), 61.4 (C_6), 58.7 (C-NH), 57.4 (CH phenylalanine), 39.2 (CH_2-NH), 38.3 (CH_2 phenylalanine), 30.6 (CH_2CO), 30.5 [$(CH_2)_3$-C], 20.8 (CH_3CO), 20.65 (CH_3CO), 20.63 (2 CH_3CO).

Compound 30-α-ManOAc: The title compound was prepared as **23-*β*-GluOAc** from **22-Phen** and 2-aminoethoxyethoxy-*O*-2′,3′,4′,6′-tetraacetyl-α-D-mannopyranose. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as a beige powder (yield 56%). MS calcd for $C_{81}H_{114}N_5O_{39}$ (MH^+) 1780.7 and calcd for $C_{81}H_{113}N_5O_{39}Na$ (MNa^+) 1802.7, found 1780.9 and 1802.8. Anal. ($C_{81}H_{113}N_5O_{39}$), $4H_2O$ calcd: C 52.51, H 6.58, N 3.70. Found: C 52.42, H 6.21, N 4.11. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.30 (m, 5H, benzyloxycarbonyl), 7.25 (m, 5H, phenylalanine), 6.45 (broad t, 3H, NH-CH_2), 5.29 (m, 9H, HC_2, HC_3 and HC_4), 5.06 (s, 2H, CH_2 benzyloxycarbonyl), 4.88 (s, 3H, HC_1), 4.31 (m, 1H, HC phenylalanine), 4.25 (dd, 3H, J = 5 and 12.2 Hz, H_aC_6), 4.12 (dd, 3H, J = 12 Hz, H_bC_6), 4.03 (m, 3H, HC_5), 3.77 (m, 3H, CH_{2a}-O-mannosyl), 3.67 (m, 3H, CH_{2b}-O-mannosyl), 3.61 (m, 6H, CH_2O), 3.5 (m, 6H, CH_2O), 3.38 (m, 6H, CH_2-NH), 3.03 (m, 2H, CH_2-phenylalanine), 2.15 (s, 9H, CH_3CO), 2.09 (s, 9H, CH_3CO), 2.06 [m, 6H, $(CH_2)_3$-C], 2.04 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO), 1.97 (m, 6H, CH_2CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.3 (CO dend), 170.9 (CO phenylalanine), 170.8 ($COCH_3$), 170.2 ($COCH_3$), 170.1 ($COCH_3$), 169.8 ($COCH_3$), 156 (CO benzyloxycarbonyl), 136.6 (C_1 benzyloxycarbonyl), 136.3 (C_1 phenylalanine), 129.4 (*o*-phenylalanine), 128.5 (*p*-phenylalanine), 128.5 (*m*-phenylalanine), 128.1 (*o*-benzyloxycarbonyl), 127.9 (*p*-benzyloxycarbonyl), 126.9 (*m*-benzyloxycarbonyl), 97.6 (C_1), 69.95 (CH_2O), 69.8 (CH_2O), 69.6 (C_3), 68.9 (C_2), 68.4 (C_5), 66.9 (CH_2-O-mannosyl), 66.1 (C_4), 65.9 (CH_2 benzyloxycarbonyl), 62.4 (C_6), 58 (C-NH), 56.9 (CH phenylalanine), 39.3 (CH_2-NH), 38.5 (CH_2 phenylalanine), 30.5 [CH_2CO and $(CH_2)_3$-C], 20.9 (CH_3CO), 20.7 (CH_3CO), 20.7 (2 CH_3CO).

Compound 31-*β*-GluOAc: The title compound was prepared as **26-*β*-GluOAc** from **29-*β*-GluOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as beige crystals (yield 70%). MS calcd for $C_{67}H_{96}N_5O_{34}$ (MH^+) 1514.59, found 1514.7. Anal. ($C_{67}H_{95}N_5O_{34}$), $4H_2O$ calcd: C 50.72, H 6.54, N 4.41. Found: C 50.47, H 6.21, N 4.54. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.3 (m, 5H, phenylalanine), 5.22 (dd, 3H, J = 9.4 Hz, HC_3), 5.07 (dd, 3H, J = 9.4 Hz, HC_4), 4.97 (dd, 3H, J = 9.4 Hz, HC_2), 4.54 (d, 3H, J = 7.8 Hz, HC_1), 4.27 (dd, 3H, J = 4.6 and 12.3 Hz, H_aC_6), 4.15 (dd, 3H, J = 12.2 Hz, H_bC_6), 3.39 (d, 6H, J = 4.2 Hz, CH_2-NH), 2.17 [m, 6H, $(CH_2)_3$-C], 2.08 (s, 9H, CH_3CO), 2.07 (m, 6H, CH_2CO), 2.06 (s, 9H, CH_3CO), 2.03 (s, 9H, CH_3CO), 2.00 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.2 (CO dend), 172.3 (CO phenylalanine), 170.7 ($COCH_3$), 170.2 ($COCH_3$), 169.6 ($COCH_3$), 169.4 ($COCH_3$), 137 (C_1 phenylalanine), 129.5 (*o*-phenylalanine), 128.8 (*p*-phenylalanine), 128.4 (*m*-phenylalanine), 100.8 (C_1), 72.6 (C_3), 71.8 (C_5), 71.3 (C_2), 68.7 (CH_2-O-glucosyl), 68.3 (C_4), 61.8 (C_6), 58.4 (C-NH), 39.3 (CH_2-NH), 30.8 (CH_2CO), 30.5 [$(CH_2)_3$-C], 20.7 (2 CH_3CO), 20.6 (2 CH_3CO).

Compound 31-*β*-GalOAc: The title compound was prepared as **26-*β*-GluOAc** from **29-*β*-GalOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as beige crystals (yield 63%). MS calcd for $C_{67}H_{95}N_5O_{34}Na$ (MNa^+) 1536.59, found 1536.6. Anal. ($C_{67}H_{95}N_5O_{34}$), $4H_2O$ calcd: C 50.72, H 6.54, N 4.41. Found: C 50.60, H 6.65, N 4.20. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.29 (m, 5H, phenylalanine), 5.39 (d, 3H, J = 2.6 Hz, HC_4), 5.16 (dd, 3H, J = 7.8 and 10.3 Hz, HC_2), 5.02 (dd, 3H, J = 2.5 and 10.2 Hz, HC_3), 4.51 (d, 3H, J = 7.8 Hz, HC_1), 4.28 (m, 1H, HC phenylalanine), 4.15 (m, 6H, HC_6), 3.94 (m, 3H, HC_5), 3.85 (m, 3H, CH_{2a}-O-galactosyl), 3.67 (m, 3H, CH_{2b}-O-galactosyl), 3.41 (d, 6H, CH_2-NH), 3.15 (m, 2H, CH_2-phenylalanine), 2.14 (s, 9H, CH_3CO), 2.12 [m, 6H, $(CH_2)_3$-C], 2.07 (s, 9H, CH_3CO), 2.05 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO), 1.99 (m, 6H, CH_2CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 172.9 (CO dend), 172 (CO phenylalanine), 170.4 ($COCH_3$), 170.2 ($COCH_3$), 170 ($COCH_3$), 169.8 ($COCH_3$), 138 (C_1 phenylalanine), 129.9 (*o*-phenylalanine), 129.4 (*p*-phenylalanine), 128.7 (*m*-phenylalanine), 101.3 (C_1), 70.8 (C_5), 70.7 (C_3), 68.9 (C_2), 68.8 (CH_2-O-galactosyl), 67 (C_4), 61.3 (C_6), 58.8 (C-NH), 57.1 (CH phenylalanine), 39.3 (CH_2-NH), 38.4 (CH_2 phenylalanine), 30.8 (CH_2CO), 30.6 [$(CH_2)_3$-C], 20.8 (CH_3CO), 20.7 (CH_3CO), 20.6 (2 CH_3CO), 20.55 (2 CH_3CO).

Compound 31-α-ManOAc: The title compound was prepared as **26-*β*-GluOAc** from **29-α-ManOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as yellow crystals (yield 97%). MS calcd for $C_{67}H_{96}N_5O_{34}$ (MH^+) 1514.6, found 1514.7. Anal. ($C_{67}H_{95}N_5O_{34}$), $2H_2O$ calcd: C 51.90, H 6.44, N 4.52. Found: C 51.4, H 6.00, N 4.39. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.29 (m, 5H, phenylalanine), 5.30 (m, 9H, HC_2, HC_3 and HC_4), 4.84 (d, 3H, J = 1.1 Hz, HC_1), 4.26 (dd, 3H, J = 5.4 and 12.3 Hz, H_aC_6), 4.13 (dd, 3H, J = 1.8 and 12 Hz, H_bC_6), 4.0 (m, 3H, HC_5), 3.76 (m, 3H, CH_{2a}-O-mannosyl), 3.67 (dd, 1H, J = 6.7 Hz, HC phenylalanine), 3.52 (m, 6H, CH_{2b}-O-mannosyl and CH_{2a}-NH), 3.38 (m, 3H, CH_{2b}-NH), 3.14 (m, 1H, CH_{2a}-phenylalanine), 3.07 (m, 1H, CH_{2b}-phenylalanine), 2.16 [m, 6H, $(CH_2)_3$-C], 2.15 (s, 9H, CH_3CO), 2.10 (s, 9H, CH_3CO), 2.04 (s, 9H, CH_3CO), 2.03 (m, 6H, CH_2CO), 1.98 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.5 (CO dend), 170.7 ($COCH_3$), 170.6 (CO phenylalanine), 170.2 ($COCH_3$), 170.1 ($COCH_3$), 169.7 ($COCH_3$), 136.9 (C_1 phenylalanine), 129.5 (*o*-phenylalanine), 128.7 (*p*-phenylalanine), 127.1 (*m*-phenylalanine), 97.5 (C_1), 69.3 (C_2), 69.2 (C_3), 68.6 (C_5), 66.9 (CH_2-O-mannosyl), 65.9 (C_4), 62.4 (C_6), 58.3 (C-NH), 53.7 (CH phenylalanine), 42 (CH_2 phenylalanine), 38.8 (CH_2-NH), 31.1 (CH_2CO), 30.5 [$(CH_2)_3$-C], 20.8 (2 CH_3CO), 20.6 (2 CH_3CO).

Compound 32-*β*-GluOAc: The title compound was prepared as **26-*β*-GluOAc** from **30-*β*-GluOAc**. Pure title compound was obtained as beige crystals and used without purification (yield 97%). MS calcd for $C_{73}H_{108}N_5O_{37}$ (MH^+) 1646.66, found 1646.8. Anal. ($C_{73}H_{107}N_5O_{37}$), $4H_2O$ calcd: C 51.01, H 6.74, N 4.07. Found: C 50.91, H 6.69, N 4.29. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.25 (m, 5H, phenylalanine), 6.44 (broad t, 3H, NH-CH_2), 5.23 (t, 3H, J = 9.4 Hz, HC_3), 5.09 (t, 3H, J = 9.4 Hz, HC_4), 4.99 (t, 3H, J = 8 Hz, HC_2), 4.59 (d, 3H, J = 7.8 Hz, HC_1), 4.26 (dd, 3H, J = 4.4 and 12.3 Hz, H_aC_6), 4.14 (dd, 3H, J = 1.6 and 12 Hz, H_bC_6), 3.96 (m, 3H, CH_{2a}-O-glucosyl), 3.70 (m, 6H, HC_5 and CH_{2b}-O-glucosyl), 3.61 (m, 7H, CH_2O and CH phenylalanine), 3.5 (m, 6H, CH_2O), 3.37 (m, 6H, CH_2-NH), 3.14 (m, 1H, CH_{2a} phenylalanine), 2.75 (m, 1H, CH_{2b} phenylalanine), 2.14 [m, 6H, $(CH_2)_3$-C], 2.08 (s, 9H, CH_3CO), 2.06 (m, 6H, CH_2CO), 2.04 (s, 9H, CH_3CO), 2.02 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173 (CO dend), 170.7 ($COCH_3$), 170.2 ($COCH_3$), 169.8 (CO phenylalanine), 169.6 ($COCH_3$), 169.4 ($COCH_3$), 137 (C_1 phenylalanine), 129.4 (*o*-phenylalanine), 128.7 (*p*-phenylalanine), 126.8 (*m*-phenylalanine), 100.8 (C_1), 72.6 (C_3), 71.8 (C_5), 71.3 (C_2), 69.8 (2 CH_2O), 69 (CH_2-O-glucosyl), 68.3 (C_4), 61.8 (C_6), 57.6 (C-NH), 57 (CH phenylalanine), 40.9 (CH_2 phenylalanine), 39.2 (CH_2-NH), 30.9 (CH_2CO), 30.6 [$(CH_2)_3$-C], 20.7 (2 CH_3CO), 20.6 (2 CH_3CO).

Compound 32-*β*-GalOAc: The title compound was prepared as **26-*β*-GluOAc** from **30-*β*-GalOAc**. Pure title compound was obtained

after crystallization from a mixture of methylene chloride/diethyl ether as beige crystals (yield 89%). MS calcd for $C_{73}H_{108}N_5O_{37}$ (MH^+) 1646.66, calcd for $C_{73}H_{107}N_5O_{37}Na$ (MNa^+) 1668.6, found 1646.8 and 1668.8. Anal. ($C_{73}H_{107}N_5O_{37}$), $5H_2O$ calcd: C 50.48, H 6.79, N 4.03. Found: C 50.73, H 6.33, N 4.59. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.27 (m, 5H, phenylalanine), 6.51 (broad t, 3H, NH-CH_2), 5.39 (d, 3H, J = 2.7 Hz, HC_4), 5.19 (dd, 3H, J = 7.8 and 10.2 Hz, HC_2), 5.06 (m, 3H, HC_3), 4.58 (d, 3H, HC_1), 4.26 (m, 1H, HC phenylalanine), 4.14 (m, 6H, HC_6), 3.96 (m, 6H, HC_5 and CH_{2a}-O-galactosyl), 3.71 (m, 3H, CH_{2b}-O-galactosyl), 3.62 (m, 6H, CH_2O), 3.52 (m, 6H, CH_2O), 3.39 (m, 6H, CH_2-NH), 3.14 (m, 2H, CH_2-phenylalanine), 2.14 (s, 9H, CH_3CO), 2.13 [m, 6H, $(CH_2)_3$-C], 2.05 (s, 9H, CH_3CO), 2.04 (s, 9H, CH_3CO), 1.98 (s, 9H, CH_3CO), 1.98 (m, 6H, CH_2CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173 (CO dend), 172.96 (CO phenylalanine), 170.2 ($COCH_3$), 170 ($2COCH_3$), 169.5 ($COCH_3$), 136.9 (C_1 phenylalanine), 129.3 (*o*-phenylalanine), 128.5 (*p*-phenylalanine), 126.7 (*m*-phenylalanine), 101.1 (C_1), 70.6 (C_3), 70.4 (C_5), 69.7 (CH_2O), 69.6 (CH_2O), 68.7 (CH_2-O-galactosyl), 68.7 (C_2), 66.9 (C_4), 61.1 (C_6), 57.7 (C-NH), 56.4 (CH phenylalanine), 40.3 (CH_2 phenylalanine), 39 (CH_2-NH), 30.7 (CH_2CO), 30.3 [$(CH_2)_3$-C], 20.6 (CH_3CO), 20.5 (2 CH_3CO), 20.4 (CH_3CO).

Compound 32-α-ManOAc: The title compound was prepared as **26-β-GluOAc** from **30-α-ManOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/diethyl ether as yellow crystals (yield 88%). MS calcd for $C_{73}H_{107}N_5O_{37}$ (MH^+) 1646.66, found 1647.0. Anal. ($C_{73}H_{107}N_5O_{37}$), $6H_2O$ calcd: C 49.97, H 6.84, N 3.99. Found: C 49.71, H 6.50, N 4.11. ^{1}H NMR ($CDCl_3$): δ (ppm) 7.3 (m, 5H, phenylalanine), 6.53 (broad t, 3H, NH-CH_2), 5.30 (m, 9H, HC_2, HC_3 and HC_4), 4.91 (d, 3H, J = 1.1 Hz, HC_1), 4.27 (dd, 3H, J = 5 and 12.2 Hz, H_aC_6), 4.11 (m, 3H, H_bC_6), 4.04 (m, 3H, HC_5), 3.78 (m, 3H, CH_{2a}-O-mannosyl), 3.68 (m, 3H, CH_{2b}-O-mannosyl), 3.63 (m, 6H, CH_2O), 3.51 (m, 6H, CH_2O), 3.39 (m, 6H, CH_2-NH), 3.16 (m, 2H, CH_2-phenylalanine), 2.16 [m, 6H, $(CH_2)_3$-C], 2.15 (s, 9H, CH_3CO), 2.10 (s, 9H, CH_3CO), 2.06 (m, 6H, CH_2CO), 2.05 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 173 (CO dend), 171.1 (CO phenylalanine), 170.8 ($COCH_3$), 170.2 ($COCH_3$), 170 ($COCH_3$), 169.8 ($COCH_3$), 138 (C_1 phenylalanine), 129.5 (*o*-phenylalanine), 128.7 (*p*-phenylalanine), 126.8 (*m*-phenylalanine), 97.6 (C_1), 70 (CH_2O), 69.9 (CH_2O), 69.6 (C_3), 68.9 (C_2), 68.4 (C_5), 67.1 (CH_2-O-mannosyl), 66.1 (C_4), 62.5 (C_6), 58 (C-NH), 57 (CH phenylalanine), 40.9 (CH_2 phenylalanine), 39.2 (CH_2-NH), 30.8 (CH_2CO), 30.5 [$(CH_2)_3$-C], 20.9 (CH_3CO), 20.7 (CH_3CO), 20.7 (2 CH_3CO).

2-(2-Chloroethoxy)ethyl ethanoate, 33: Diethylene glycol monochlorohydrin (2.50 g, 20 mmol) and acetic anhydride (2.1 mL, 22 mmol) were stirred at room temperature overnight. Progress of the reaction was followed by ^{1}H RMN spectroscopy. The crude mixture was dissolved in methylene chloride (30 mL), then washed with water, aqueous sodium bicarbonate solution, and water. The organic phase was dried over sodium sulfate, filtered, and concentrated under vacuum. The title compound **34** was used without purification (3.13 gr, yield 94%). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.26 (t, 2H, J = 4.7 Hz, CH_2OAc), 3.79 (t, 2H, J = 6.3 Hz, CH_2O), 3.74 (t, 2H, J = 4.7 Hz, CH_2O), 3.65 (t, 2H, J = 5.9 Hz, CH_2Cl), 2.11 (s, 3H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 171.3 ($COCH_3$), 71.6 (CH_2O), 69.5 (CH_2O), 63.7 (CH_2OAc), 42.9 (CH_2Cl), 21.4 (CH_3).

2-(2-Azidoethoxy)ethyl ethanoate, 34: Compound **33** (3.130 g, 18.8 mmol) and sodium azide (4.9 g, 75 mmol) were stirred in dimethyl sulfoxide (25 mL) under argon at 100 °C for 1 h 30 min. The solution was diluted in methylene chloride (100 mL) and washed twice with saturated aqueous sodium chloride solution (100 mL). The organic phase was dried over sodium sulfate, filtered, and concentrated under vacuum. The title compound was used without purification (3.09 g, yield 95%). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.26 (t, 2H, J = 4.7 Hz, CH_2OAc), 3.73 (t, 2H, J = 4.7 Hz, CH_2O), 3.70 (t, 2H, J = 5 Hz, CH_2O), 3.41 (t, 2H, J = 5 Hz, CH_2N_3), 2.11 (s, 3H, CH_3CO). ^{13}C NMR ($CDCl_3$): δ (ppm) 171.4 ($COCH_3$), 70.4 (CH_2O), 69.5 (CH_2O), 63.8 (CH_2OAc), 51 (CH_2N_3), 21.4 (CH_3).

2-(2-Aminoethoxy)ethyl ethanoate, tosylate salt, 35: Azido compound **34** (3.09 g, 18 mmol) and *p*-toluenesulfonic acid (3.52 g, 18 mmol) were dissolved in ethyl acetate (100 mL). Palladium (10%) under carbon (0.6 g) was added. The mixture was stirred under hydrogen atmosphere (5 bar) overnight at room temperature. The suspension was filtered over Celite, which was washed with ethanol. The crude solution was concentrated under vacuum. The title compound was obtained as a colorless oil. Ether (100 mL) was added and the title compound was crystallized as a hygroscopic white powder (5.02 g, yield 88%). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.77 (d, 5H, J = 8.1 Hz, CH tosylate and NH_3^+), 7.19 (d, 2H, J = 8 Hz, CH tosylate), 4.10 (t, 2H, J = 4.7 Hz, CH_2OAc), 3.62 (t, 2H, J = 5.1 Hz, CH_2O), 3.56 (t, 2H, J = 4.7 Hz, CH_2O), 3.09 (t, 2H, J = 5.1 Hz, CH_2O), 2.38 (s, 3H, CH_3), 2.02 (s, 3H, CH_3CO).

4-(*Z*-*N*-2-Aminoethanamido)-N^1,N^7-bis[2-(2-hydroxyethoxy)ethyl]-4-{3-[2-(2-hydroxyethoxy)ethylamino]-3-oxopropyl}heptanediamide, 36: The title compound was prepared as **23-β-GluOAc** from **35** (0.220 g, 0.5 mmol) and **22-Gly** (0.479 g, 1.5 mmol). The crude title compound was dried under vacuum and used without purification (0.282 g, yield 73%). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.37 (m, 5H, benzyloxycarbonyl), 7.24 (broad s, 1H, NH), 6.32 (broad t, 3H, NH), 5.62 (broad t, 1H, J = 5.4 Hz, NH), 5.15 (s, 2H, CH_2 benzyloxycarbonyl), 4.24 (t, 6H, J = 4.7 Hz, CH_2-OAc), 3.78 (d, 2H, J = 5.7 Hz, CH_2 glycine), 3.67 (t, 6H, J = 4.7 Hz, CH_2), 3.55 (t, 6H, J = 5.1 Hz, CH_2-O), 3.42 (dt, 6H, J = 5.1 Hz, CH_2), 2.22 (t, 6H, J = 7.2 Hz, CH_2-O), 2.10 (s, 9H, CH_3CO), 2.04 (t, 6H, J = 7.5 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.3 (CO dend), 171.1 ($COCH_3$), 168.7 (CO glycine), 156.7 (CO-benzyloxycarbonyl), 136 (C_1 Z-phenyl), 128.1 (*o*-benzyloxycarbonyl), 127.8 (*p*-benzyloxycarbonyl), 127.5 (*m*-benzyloxycarbonyl), 69.3 (C−O), 68.5 (C−O), 66.7 (C-benzyloxycarbonyl), 63 (C-O-acetyl), 58.2 (C-NH), 44.6 (C glycine), 38.9 (C-NH), 30.7 [$(CH_2)_3$-C], 30.4 (C-CO), 20.6 (CH_3CO).

4-(2-Aminoethanamido)-N^1,N^7-bis[2-(2-hydroxyethoxy)ethyl]-4-{3-[2-(2-hydroxyethoxy)ethylamino]-3-oxopropyl}heptanediamide, 37. The title compound was prepared as **26-β-GluOAc** from **36** (0.282 g, 0.34 mmol). The title compound was used without purification (0.206 g, yield 87%). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.65 (broad s, 1H, NH), 7.31 (broad s, 3H, NH), 4.20 (t, 6H, J = 4.3 Hz, CH_2-OAc), 3.64 (t, 6H, J = 4.3 Hz, CH_2), 3.52 (broad t, 6H, CH_2-O), 3.36 (broad s, 6H, CH_2), 2.20 (t, 6H, J = 7.2 Hz, CH_2-CO), 2.08 (s, 9H, CH_3CO), 1.99 (t, 6H, J = 7.5 Hz, CH_2).

General Procedure for the Preparation of Compounds 2-OAc−15-OAc. All operations were identical with those described for the synthesis of compound **2-OAc**. A representative example is described below.

Porphyrin 2-OAc: Compound **26-β-GluOAc** (200 mg, 0.14 mmol) was added after 5 min to a solution of *meso*-5-(4-benzoic acid)-10,15,20-tetraphenylporphyrin (46 mg, 7×10^{-5} mol) containing HOBt (14.6 mg, 0.105 mmol), EDC (20 mg, 0.105 mmol), and Et_3N (45 μL) in dry methylene chloride (20 mL) under argon. The solution was stirred overnight under argon at room temperature. The crude mixture was washed with aqueous chlorhydric acid (10%), water, aqueous sodium hydrogenocarbonate (10%), and water then dried over sodium sulfate, filtered, and concentrated under vacuum. Pure title compound was obtained by preparative thin layer chromatography (silica gel, methylene chloride/methanol, 100/5, v/v) and crystallization from a mixture of methylene chloride/*n*-heptane as a red powder, (47 mg, yield 33%). Anal. ($C_{105}H_{117}N_9O_{35}$), $6H_2O$ calcd: C 58.52, H 6.01, N 5.96. Found: C 58.36, H 5.90, N 5.74. UV−vis spectrum in CH_2Cl_2: λ_{max}, nm (ε, $L \cdot mmol^{-1} \cdot cm^{-1}$) 417.5 (403.7), 515.5 (16), 549 (6.9), 590 (4.7), 645 (3.4). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.86 (s, 6H,

$HC_{2,8,12,13,17,18}$ pyrrole), 8.81 (d, 2H, J = 4.5 Hz, $HC_{3,7}$ pyrrole), 8.31 (m, 4H, *m*- and *o*-carboxyphenyl), 8.20 (m, 6H, *o*-phenyl), 7.91 (broad t, 1H, J = 5.2 Hz, NH-glycine), 7.75 (m, 9H, *m*- and *p*-phenyl), 7.44 (s, 1H, NH-C), 6.92 (broad t, 3H, NH-CH_2), 5.18 (t, 3H, J = 9.4 Hz, HC_3), 5.05 (t, 3H, J = 9.5 Hz, HC_4), 4.98 (dd, 3H, J = 8 and 9.3 Hz, HC_2), 4.50 (d, 3H, J = 8 Hz, HC_1), 4.21 (dd, 2H, HC glycine), 4.21 (dd, 3H, J = 4.5 and 12.2 Hz, H_aC_6), 4.09 (m, 3H, H_bC_6), 3.85 (m, 3H, CH_{2a}-O-glucosyl), 3.66 (m, 6H, HC_5 and CH_{2b}-O-glucosyl), 3.44 (m, 6H, CH_2NH), 2.30 (m, 6H, CH_2CO), 2.16 [m, 6H, $(CH_2)_3$-C], 2.07 (s, 9H, CH_3CO), 2.05 (s, 9H, CH_3CO), 1.98 (s, 9H, CH_3CO), 1.97 (s, 9H, CH_3CO), −2.79 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.7 (CO dend), 170.7 ($COCH_3$), 170.1 ($COCH_3$), 169.7 ($COCH_3$), 169.4 ($COCH_3$), 168.2 (CO glycine), 167.8 (CO phenyl), 145.8 (C_1 carboxyphenyl), 141.9 (C_1 phenyl), 134.5 (*o*-carboxyphenyl), 134.5 (*o*-phenyl), 132.7 (*p*-carboxyphenyl), 131.2 (C pyrrole), 127.7 (*p*-phenyl), 126.7 (*m*-phenyl), 125.7 (*m*-carboxyphenyl), 120.4 (*meso*-C_{15}), 120.3 (*meso*-$C_{10,20}$), 118.5 (*meso*-C_5), 100.7 (C_1), 72.6 (C_3), 71.8 (C_5), 71.2 (C_2), 68.7 (CH_2-O-glucosyl), 68.2 (C_4), 61.8 (C_6), 58.3 (C-NH), 44.3 (CH_2 glycine), 39.4 (CH_2-NH), 30.9 [$(CH_2)_3$-C], 30.7 ($COCH_2$), 20.7 (2 CH_3CO), 20.5 (2 CH_3CO).

Porphyrin 3-OAc: The title compound was prepared as **2-OAc** from **26-β-GalOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/*n*-heptane as a red powder (yield 55%). Anal. ($C_{105}H_{117}N_9O_{35}$), 11H_2O calcd: C 55.72, H 6.19, N 5.57. Found: C 55.94, H 6.65, N 5.24. UV−vis spectrum in CH_2Cl_2: $\lambda_{max.}$, nm (ε, L·mmol^{-1}·cm^{-1}) 418 (477.9), 515.5 (19.8), 550 (9.4), 590 (6.8), 645.4 (5.4). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.80 (d, 2H, J = 4.8 Hz, $HC_{3,7}$ pyrrole), 8.31 (s, 4H, *m*- and *o*-carboxyphenyl), 8.21 (d, 6H, J = 4.7 Hz, *o*-phenyl), 7.74 (m, 9H, *m*- and *p*-phenyl), 6.71 (broad t, 3H, J = 5.4 Hz, NH-CH_2), 5.38 (d, 3H, J = 2.9 Hz, HC_4), 5.18 (dd, 3H, J = 7.8 and 10.4 Hz, HC_2), 5.06 (dd, 3H, J = 3.3 and 10.4 Hz, HC_3), 4.52 (d, 3H, J = 7.8 Hz, HC_1), 4.22 (d, 2H, CH_2 glycine), 4.12 (m, 6H, J = 6.6 and 11.2 Hz, HC_6), 3.96 (m, 3H, J = 6.6 Hz, HC_5), 3.88 (m, 3H, CH_{2a}-O-galactosyl), 3.70 (m, 3H, CH_{2b}-O-galactosyl), 3.45 (d, 6H, CH_2NH), 2.33 (m, 6H, CH_2CO), 2.14 [m, 6H, $(CH_2)_3$-C], 2.12 (s, 9H, CH_3CO), 2.09 (s, 9H, CH_3CO), 2.02 (s, 9H, CH_3CO), 1.96 (s, 9H, CH_3CO), −2.79 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.3 (CO dend), 170.5 ($COCH_3$), 170.1 ($COCH_3$), 170 ($COCH_3$), 169.8 ($COCH_3$), 168.7 (CO glycine), 168 (CO phenyl), 146 (C_1 carboxyphenyl), 142 (C_1 phenyl), 134.6 (*o*-carboxyphenyl), 134.5 (*o*-phenyl), 132.8 (*p*-carboxyphenyl), 131.3 (C pyrrole), 127.7 (*p*-phenyl), 126.7 (*m*-phenyl), 125.7 (*m*-carboxyphenyl), 120.6 (*meso*-C_{15}), 120.3 (*meso*-$C_{10,20}$), 118.4 (*meso*-C_5), 101.3 (C_1), 70.7 (C_3 and C_5), 68.9 (C_2), 68.7 (CH_2-O-galactosyl), 66.9 (C_4), 61.3 (C_6), 58.3 (C-NH), 44.5 (CH_2 glycine), 39.5 (CH_2-NH), 31.1 [$(CH_2)_3$-C], 30.8 ($COCH_2$), 20.9 (CH_3CO), 20.7 (CH_3CO), 20.6 (CH_3CO), 20.5 (CH_3CO).

Porphyrin 5-OAc: The title compound was prepared as **2-OAc** from **27-β-GluOAc.** Pure title compound was obtained after crystallization from a mixture of methylene chloride/*n*-heptane as a red powder (yield 41%). UV−vis spectrum in CH_2Cl_2: λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 417.5 (419.7), 514.5 (16.9), 549 (7.4), 590 (5.1), 645.5 (3.7). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.86 (s, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.79 (d, 2H, J = 4.4 Hz, $HC_{3,7}$ pyrrole), 8.31 (m, 4H, *m*- and *o*-carboxyphenyl), 8.19 (m, 6H, *o*-phenyl), 7.75 (m, 9H, *m*- and *p*-phenyl), 7.49 (broad s, 1H, NH-C), 6.71 (broad t, 3H, NH-CH_2), 5.28 (t, 3H, J = 9.6 Hz, HC_3), 5.08 (t, 3H, J = 9.5 Hz, HC_4), 5.0 (dd, 3H, J = 7.9 and 9.5 Hz, HC_2), 4.67 (d, 3H, J = 7.5 Hz, HC_1), 4.24 (m, 2H, CH_2 glycine), 4.21 (m, 3H, H_aC_6), 4.09 (m, 3H, H_bC_6), 3.93 (m, 3H, CH_{2a}-O-glucosyl), 3.76 (m, 3H, CH_{2b}-O-glucosyl), 3.60 (m, 9H, HC_5 and CH_2O), 3.53 (m, 9H, CH_2O and CH_{2a}-NH), 3.35 (m, 3H, CH_{2b}-NH), 2.36 [m, 6H, $(CH_2)_3$-C], 2.16 (m, 6H, CH_2CO), 2.06 (s, 9H, CH_3CO), 2.02 (s, 9H, CH_3CO), 2.01 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO), −2.8 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.4 (CO-dend), 170.6 ($COCH_3$), 170.4 ($COCH_3$), 169.6 ($COCH_3$), 169.3 ($COCH_3$), 169 (CO glycine), 168.1 (CO phenyl), 146 (C_1 carboxyphenyl), 141.8 (C_1 phenyl), 134.6 (*o*-carboxyphenyl), 134.4 (*o*-phenyl), 132.5 (*p*-carboxyphenyl), 131 (C pyrrole), 127.7 (*p*-phenyl), 126.6 (*m*-phenyl), 125.7 (*m*-carboxyphenyl), 120.5 (*meso*-C_{15}), 120.3 (*meso*-$C_{10,20}$), 118.3 (*meso*-C_5), 100.7 (C_1), 72.7 (C_3), 71.6 (C_5), 71.2 (C_2), 70.1 (CH_2O), 70 (CH_2O), 68.8 (CH_2-O-glucosyl), 68.4 (C_4), 61.8 (C_6), 58.5 (C-NH), 44.5 (CH_2 glycine), 39.3 (CH_2-NH), 30.6 [$(CH_2)_3$-C and $COCH_2$], 20.7 (2 CH_3CO), 20.6 (CH_3CO), 20.5 (CH_3CO).

Porphyrin 6-OAc: The title compound was prepared as **2-OAc** from **27-β-GalOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/*n*-heptane as a red powder (yield 59%). UV−vis spectrum in CH_2Cl_2: $\lambda_{max.}$, nm (ε, L·mmol^{-1}·cm^{-1}) 417.5 (413.6), 515 (16.5), 549.5 (7.2), 590 (4.9), 644.5 (3.5). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.81 (d, 2H, J = 4.7 Hz, $HC_{3,7}$ pyrrole), 8.39 (m, 2H, *m*-carboxyphenyl), 8.32 (d, 2H, *o*-carboxyphenyl), 8.18 (m, 6H, *o*-phenyl), 7.73 (m, 9H, *m*- and *p*-phenyl), 7.41 (broad s, 1H, NH-C), 6.88 (broad t, 3H, NH-CH_2), 5.39 (d, 3H, J = 2.8 Hz, HC_4), 5.22 (dd, 3H, J = 7.5 and 10.4 Hz, HC_2), 5.14 (dd, 3H, J = 2.8 and 10.4 Hz, HC_3), 4.69 (d, 3H, J = 7.5 Hz, HC_1), 4.32 (m, 2H, CH_2 glycine), 4.13 (m, 6H, HC_6), 3.94 (m, 6H, HC_5 and CH_{2a}-O-galactosyl), 3.73 (m, 3H, CH_{2b}-O-galactosyl), 3.6 (m, 6H, CH_2O), 3.48 (m, 9H, CH_2O and CH_{2a}NH), 3.4 (m, 3H, CH_{2b}NH), 2.36 [m, 6H, $(CH_2)_3$-C], 2.16 (m, 6H, CH_2CO), 2.14 (s, 9H, CH_3CO), 2.06 (s, 9H, CH_3CO), 2.01 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO), −2.78 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.2 (CO dend), 170.4 ($COCH_3$), 170.25 ($COCH_3$), 170.22 ($COCH_3$), 169.7 ($COCH_3$), 169.1 (CO glycine), 168.1 (CO phenyl), 146.1 (C_1 carboxyphenyl), 141.8 (C_1 phenyl), 134.6 (*o*-carboxyphenyl), 134.4 (*o*-phenyl), 132.3 (*p*-carboxyphenyl), 131.2 (C pyrrole), 127.7 (*p*-phenyl), 126.6 (*m*-phenyl), 125.7 (*m*-carboxyphenyl), 120.5 (*meso*-C_{15}), 120.2 (*meso*-$C_{10,20}$), 118.2 (*meso*-C_5), 101.2 (C_1), 70.8 (C_3), 70.5 (C_5), 70.2 (CH_2O), 69.9 (CH_2O), 68.8 (C_2), 68.7 (CH_2-O-galactosyl), 67 (C_4), 61.3 (C_6), 58.5 (C-NH), 44.5 (CH_2 glycine), 39.3 (CH_2-NH), 30.7 [$(CH_2)_3$-C and $COCH_2$], 20.8 (2 CH_3CO), 20.6 (2 CH_3CO).

Porphyrin 8-OAc: The title compound was prepared as **2-OAc** from **28-α-ManOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/*n*-heptane as a red powder (yield 42%). UV−vis spectrum in CH_2Cl_2: $\lambda_{max.}$, nm (ε, L·mmol^{-1}·cm^{-1}) 417.5 (381.6), 515.5 (14.9), 549 (6.5), 590 (4.4), 645 (3.1). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.81 (d, 2H, J = 4.7 Hz, $HC_{3,7}$ pyrrole), 8.32 (s, 4H, *m*- and *o*-carboxyphenyl), 8.21 (m, 6H, *o*-phenyl), 8.06 (broad, 1H, NH glycine), 7.74 (m, 9H, *m*- and *p*-phenyl), 7.42 (broad s, 1H, NH), 7.32 (t, 3H, J = 5.3 Hz, NH-CH_2), 5.35 (t, 3H, J = 3.1 and 10.1 Hz, HC_3), 5.30 (t, 3H, J = 10 Hz, HC_4), 5.26 (m, 3H, HC_2), 4.87 (d, 3H, J = 1.2 Hz, HC_1), 4.27 (dd, 3H, J = 5.1 and 12.4 Hz, H_aC_6), 4.25 (d, 2H, HC glycine), 4.10 (dd, 3H, J = 2.2 and 12.3 Hz, H_bC_6), 4.05 (m, 3H, HC_5), 3.80 (m, 3H, CH_{2a}-O-mannosyl), 3.63 (m, 24H, CH_2), 3.46 (m, 6H, CH_2NH), 2.34 (m, 6H, CH_2CO), 2.15 [m, 6H, $(CH_2)_3$-C], 2.14 (s, 9H, CH_3CO), 2.08 (s, 9H, CH_3CO), 2.03 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO), −2.78 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.8 (CO dend), 170.8 ($COCH_3$), 170.03 ($COCH_3$), 170.02 ($COCH_3$), 169.6 ($COCH_3$), 169.1 (CO glycine), 168.1 (CO phenyl), 145.7 (C_1 carboxyphenyl), 141,9 (C_1 phenyl), 134.5 (*o*-carboxyphenyl), 134.4 (*o*-phenyl), 132.8 (*p*-carboxyphenyl), 131 (C and $C_{2,8,12,13,17,18}$ pyrrole), 127.7 (*p*-phenyl), 126.6 (*m*-phenyl), 125.7 (*o*-carboxyphenyl), 120.4 (*meso*-C_{15}), 120.2 (*meso*-$C_{10,20}$), 118.5 (*meso*-C_5), 97.6 (C_1), 70.5 (CH_2-O), 70.1 (CH_2-O), 69.8 (CH_2-O), 69.7 (CH_2-O), 69.4 (C_2), 69.1 (C_3), 68.3 (C_5), 67.2 (CH_2-O-glucosyl), 65.9 (C_4), 62.3 (C_6), 58.1 (C-NH), 44.3 (CH_2 glycine), 39.3 (CH_2-NH), 30.8 [$(CH_2)_3$-C], 30.6 ($COCH_2$), 20.8 (CH_3CO), 20.7 (CH_3CO), 20.6 (CH_3CO).

Porphyrin 9-OAc: The title compound was prepared as **2-OAc** from **31-β-GluOAc**. Pure title compound was obtained after

crystallization from a mixture of methylene chloride/*n*-heptane as a red powder (yield 35%). Anal. ($C_{112}H_{123}N_9O_{35}$), $7H_2O$ calcd: C 59.97, H 6.05, N 5.53. Found: C 59.20, H 5.52, N 5.06. UV−vis spectrum in CH_2Cl_2: λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 418 (471.2), 515.5 (19.2), 550 (9.2), 590 (6.6), 645.5 (5.2). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.79 (d, 2H, J = 4.3 Hz, $HC_{3,7}$ pyrrole), 8.30 (d, 4H, J = 8 Hz, *m*- and *o*-carboxyphenyl), 8.20 (d, 6H, J = 5.7 Hz, *o*-phenyl), 7.77 (m, 9H, *m*- and *p*-phenyl), 7.41 (m, 5H, phenylalanine), 6.44 (broad t, 3H, NH-CH_2), 5.19 (dd, 3H, J = 9.4 Hz, HC_3), 5.06 (dd, 3H, J = 9.6 Hz, HC_4), 5.0 (dd, 3H, J = 9.4 Hz, HC_2), 4.94 (d, 1H, J = 7.0 Hz, HC phenylalanine), 4.52 (d, 3H, J = 7.8 Hz, HC_1), 4.20 (dd, 3H, J = 4.6 and 12.2 Hz, H_aC_6), 4.11 (dd, 3H, J = 10.8 Hz, H_bC_6), 3.85 (m, 3H, CH_{2a}-O-glucosyl), 3.7 (m, 3H, HC_5), 3.68 (m, 3H, CH_{2b}-O-glucosyl), 3.43 (d, 6H, J = 4.4 Hz, CH_2NH), 3.32 (d, 2H, J = 6.7 Hz, CH_2 phenylalanine), 2.16 [m, 6H, $(CH_2)_3$-C], 2.05 (s, 9H, CH_3CO), 2.02 (s, 9H, CH_3CO), 2.01 (m, 6H, CH_2CO), 1.98 (s, 9H, CH_3CO), 1.96 (s, 9 H, CH_3CO), −2.79 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.2 (CO dend), 170.7 ($COCH_3$), 170.6 (CO phenylalanine), 170.1 ($COCH_3$), 169.6 ($COCH_3$), 169.4 ($COCH_3$), 167.6 (CO phenyl), 145.9 (C_1 carboxyphenyl), 142 (C_1 phenyl), 136.8 (C_1 phenylalanine), 134.7 (*o*-carboxyphenyl), 134.5 (*o*-phenyl), 133 (*p*-carboxyphenyl), 132.2 (*p*-phenyl), 131.5 (C pyrrole), 129.6 (*o*-phenylalanine), 128.8 (*p*-phenylalanine), 127.8 (*m*-phenylalanine), 126.7 (*m*-phenyl), 125.6 (*m*-carboxyphenyl), 120.5 (*meso*-C_{15}), 120.4 (*meso*-$C_{10,20}$), 118.4 (*meso*-C_5), 100.8 (C_1), 72.6 (C_3), 71.8 (C_5), 71.3 (C_2), 68.8 (CH_2-O-glucosyl), 68.3 (C_4), 61.8 (C_6), 58.4 (C-NH), 56 (CH phenylalanine), 39.4 (CH_2-NH), 38.2 (CH_2 phenylalanine), 30.9 [$(CH_2)_3$-C], 30.6 ($COCH_2$), 20.74 (CH_3CO), 20.71 (CH_3CO), 20.5 (2 CH_3CO).

Porphyrin 10-OAc: The title compound was prepared as **2-OAc** from **31-*β*-GalOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/*n*-heptane as a red powder (yield 62%). Anal. ($C_{112}H_{123}N_9O_{35}$), $3H_2O$ calcd: C 60.89, H 5.89, N 5.71. Found: C 60.91, H 5.69, N 5.25. UV−vis spectrum in CH_2Cl_2: λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 418 (491.2), 515.5 (19.9), 550 (9.7), 590 (6.9), 645.5 (5.4). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.80 (d, 2H, J = 4.5 Hz, $HC_{3,7}$ pyrrole), 8.31 (s, 4H, *m*- and *o*-carboxyphenyl), 8.20 (m, 6H, *o*-phenyl), 7.76 (m, 9H, *m*- and *p*-phenyl), 7.45 (m, 5H, phenylalanine), 6.44 (broad t, 3H, J = 5.1 Hz, NH-CH_2), 5.36 (d, 3H, J = 2.7 Hz, HC_4), 5.20 (dd, 3H, J = 7.8 and 10.4 Hz, HC_2), 5.03 (dd, 3H, J = 3.3 and 10.4 Hz, HC_3), 4.94 (d, 1H, J = 6.7 Hz, HC phenylalanine), 4.51 (d, 3H, J = 7.8 Hz, HC_1), 4.15 (m, 3H, J = 6.6 and 12.2 Hz, H_aC_6), 4.09 (m, 3H, J = 6.6 and 12.2 Hz, H_bC_6), 3.92 (m, 3H, J = 6.6 Hz, HC_5), 3.88 (m, 3H, CH_{2a}-O-galactosyl), 3.71 (m, 3H, CH_{2b}-O-galactosyl), 3.45 (d, 6H, J = 5 Hz, CH_2NH), 3.31 (m, 2H, CH_2 phenylalanine), 2.17 [m, 6H, $(CH_2)_3$-C], 2.17 (s, 9H, CH_3CO), 2.06 (s, 9H, CH_3CO), 2.05 (s, 9H, CH_3CO), 2.01 (m, 6H, CH_2CO), 1.99 (s, 9H, CH_3CO), −2.79 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.2 (CO dend), 170.6 (CO phenylalanine), 170.4 ($COCH_3$), 170.1 (2 $COCH_3$), 169.8 ($COCH_3$), 167.5 (CO phenyl), 146 (C_1 carboxyphenyl), 142 (C_1 phenyl), 136.8 (C_1 phenylalanine), 134.7 (*o*-carboxyphenyl), 134.5 (*o*-phenyl), 132.8 (*p*-carboxyphenyl), 132.3 (*p*-phenyl), 131 (C pyrrole), 129.6 (*o*-phenylalanine), 128.8 (*p*-phenylalanine), 127.8 (*m*-phenylalanine), 126.7 (*m*-phenyl), 125.6 (*m*-carboxyphenyl), 120.5 (*meso*-C_{15}), 120.3 (*meso*-$C_{10,20}$), 118.3 (*meso*-C_5), 101.3 (C_1), 70.7 (C_3 and C_5), 68.8 (C_2), 68.8 (CH_2-O-galactosyl), 67 (C_4), 61.3 (C_6), 58.4 (C-NH), 56.1 (CH phenylalanine), 39.4 (CH_2-NH), 38.2 (CH_2 phenylalanine), 30.8 [$(CH_2)_3$-C], 30.6 ($COCH_2$), 20.9 (CH_3CO), 20.65 (CH_3CO), 20.55 (2 CH_3CO).

Porphyrin 11-OAc: The title compound was prepared as **2-OAc** from **31-α-ManOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/*n*-heptane as a red powder (yield 79%). Anal. ($C_{112}H_{123}N_9O_{35}$), $10H_2O$ calcd: C 57.6, H 6.17, N 5.40. Found: C 57.77, H 5.78, N 5.21. UV−vis spectrum in CH_2Cl_2: λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 417.5 (390), 515 (15.1), 549.5 (7.1), 589.5 (4.5), 644.5 (3.2). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.75 (d, 2H, J = 4.8 Hz, $HC_{3,7}$ pyrrole), 8.29 (d, 4H, J = 8.1 Hz, *m*- and *o*-carboxyphenyl), 8.22 (m, 6H, *o*-phenyl), 7.77 (m, 9H, *m*- and *p*-phenyl), 7.42 (m, 5H, phenylalanine), 6.98 (broad t, 3H, NH-CH_2), 5.45 (dd, 3H, J = 3.4 and 10 Hz, HC_3), 5.34 (dd, 3H, J = 1.5 and 3.3 Hz, HC_2), 5.27 (m, 3H, J = 10 Hz, HC_4), 4.87 (d, 3H, J = 0.8 Hz, HC_1), 4.82 (m, 1H, HC phenylalanine), 4.25 (dd, 3H, J = 5.4 and 12.2 Hz, H_aC_6), 4.14 (m, 3H, H_bC_6), 4.07 (m, 3H, HC_5), 3.8 (m, 3H, CH_{2a}-O-mannosyl), 3.55 (m, 6H, CH_{2b}-O-mannosyl and $CH_{2a}NH$), 3.43 (m, 3H, $CH_{2b}NH$), 3.24 (m, 2H, CH_2 phenylalanine), 2.22 (m, 6H, CH_2CO), 2.12 [m, 6H, $(CH_2)_3$-C], 2.12 (s, 9H, CH_3CO), 2.09 (s, 9H, CH_3CO), 2.00 (s, 9H, CH_3CO), 1.99 (s, 9H, CH_3CO), −2.79 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.7 (CO dend), 171 (CO phenylalanine), 170.8 ($COCH_3$), 170.3 ($COCH_3$), 170.2 ($COCH_3$), 169.7 ($COCH_3$), 168.2 (CO phenyl), 146 (C_1 carboxyphenyl), 141.9 (C_1 phenyl), 136.9 (C_1 phenylalanine), 134.6 (*o*-carboxyphenyl), 134.5 (*o*-phenyl), 132.7 (*p*-carboxyphenyl), 132.2 (*p*-phenyl), 131.2 (C pyrrole), 129.3 (*o*-phenylalanine), 128.7 (*p*-phenylalanine), 127.7 (*m*-phenylalanine), 126.7 (*m*-phenyl), 125.7 (*m*-carboxyphenyl), 120.5 (*meso*-C_{15}), 120.2 (*meso*-$C_{10,20}$), 118.4 (*meso*-C_5), 97.7 (C_1), 69.5 (C_2), 69.2 (C_3), 68.6 (C_5), 67.1 (CH_2-O-mannosyl), 66 (C_4), 62.4 (C_6), 58.8 (C-NH), 56.6 (CH phenylalanine), 38.9 (CH_2-NH), 37.9 (CH_2 phenylalanine), 31.4 [$(CH_2)_3$-C], 30.7 ($COCH_2$), 20.9 (CH_3CO), 20.74 (CH_3CO), 20.67 (CH_3CO), 20.63 (CH_3CO).

Porphyrin 12-OAc: The title compound was prepared as **2-OAc** from **32-*β*-GluOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/*n*-heptane as a red powder (yield 39%). UV−vis spectrum in CH_2Cl_2: λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 417.5 (392.6), 515 (15.5), 550 (6.8), 589.5 (4.6), 645 (3.3). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.78 (d, 2H, J = 4.3 Hz, $HC_{3,7}$ pyrrole), 8.29 (m, 4H, *m*- and *o*-carboxyphenyl), 8.21 (d, 6H, *o*-phenyl), 7.75 (m, 9H, *m*- and *p*-phenyl), 7.41 (m, 5H, phenylalanine), 6.57 (broad t, 3H, NH-CH_2), 5.31 (t, 3H, J = 9.5 Hz, HC_3), 5.08 (m, 3H, HC_4), 5.0 (m, 3H, HC_2), 4.97 (m, 1H, HC phenylalanine), 4.69 (d, 3H, J = 7.7 Hz, HC_1), 4.19 (dd, 3H, J = 4.4 and 12.2 Hz, H_aC_6), 4.05 (m, 3H, J = 12.2 Hz, H_bC_6), 3.93 (m, 3H, CH_{2a}-O-glucosyl), 3.73 (m, 3H, CH_{2b}-O-glucosyl), 3.64 (m, 9H, HC_5 and CH_2O), 3.50 (m, 9H, CH_2O and CH_{2a}-NH), 3.33 (m, 5H, CH_{2b}-NH and CH_2 phenylalanine), 2.16 [m, 6H, $(CH_2)_3$-C], 2.06 (m, 6H, CH_2CO), 2.05 (s, 9H, CH_3CO), 2.01 (s, 18H, CH_3CO), 1.99 (s, 9H, CH_3CO), −2.8 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.2 (CO dend), 171 (CO phenylalanine), 170.7 ($COCH_3$), 170.6 ($COCH_3$), 169.6 ($COCH_3$), 169.3 ($COCH_3$), 167.7 (CO phenyl), 146 (C_1 carboxyphenyl), 141.9 (C_1 phenyl), 136.6 (C_1 phenylalanine), 134.7 (*o*-carboxyphenyl), 134.5 (*o*-phenyl), 133 (*p*-carboxyphenyl), 131.3 (C pyrrole), 129.5 (*o*-phenylalanine), 128.9 (*p*-phenylalanine), 127.8 (*m*-phenylalanine), 126.7 (*m*-phenyl and *p*-phenyl), 125.7 (*m*-carboxyphenyl), 120.7 (*meso*-C_{15}), 120.4 (*meso*-$C_{10,20}$), 118.1 (*meso*-C_5), 100.8 (C_1), 72.7 (C_3), 71.7 (C_5), 71.3 (C_2), 70.3 (CH_2O), 70.1 (CH_2O), 68.8 (CH_2-O-glucosyl), 68.4 (C_4), 61.8 (C_6), 58.5 (C-NH), 56 (CH phenylalanine), 39.3 (CH_2-NH), 38.2 (CH_2 phenylalanine), 30.3 [$(CH_2)_3$-C and $COCH_2$], 20.7 (2 CH_3CO), 20.63 (CH_3CO), 20.61 (CH_3CO).

Porphyrin 13-OAc: The title compound was prepared as **2-OAc** from **32-*β*-GalOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/*n*-heptane as a red powder (yield 54%). Anal. ($C_{118}H_{135}N_9O_{38}$), $16H_2O$ calcd: C 55.03, H 6.54, N 4.89. Found: C 55.07, H 5.49, N 4.9. UV−vis spectrum in CH_2Cl_2: λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 418 (402), 515 (15.9), 550.5 (6.9), 590 (4.7), 645 (3.4). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.76 (m, 2H, $HC_{3,7}$ pyrrole), 8.29 (m, 4H, *m*- and *o*-carboxyphenyl), 8.22 (m, 6H, *o*-phenyl), 7.76 (m, 9H, *m*- and *p*-phenyl), 7.42 (m, 5H, phenylalanine), 6.70 (broad t, 3H, NH-CH_2), 5.38 (d, 3H, HC_4), 5.22 (m, 6H, HC_2 and HC_3), 4.96 (m, 1H, HC

phenylalanine), 4.77 (d, 3H, J = 7.4 Hz, HC_1), 4.10 (m, 6H, HC_6), 3.94 (m, 6H, HC_5 and CH_{2a}-O-galactosyl), 3.80 (m, 3H, CH_{2b}-O-galactosyl), 3.52 (m, 9H, $CH_{2a}NH$ and CH_2O), 3.31 (m, 5H, CH_2 phenylalanine and $CH_{2b}NH$), 2.13 (s, 9H, CH_3CO), 2.07 (s, 9H, CH_3CO), 2.07 [m, 6H, $(CH_2)_3$-C], 2.02 (s, 9H, CH_3CO), 2.00 (m, 6H, CH_2CO), 1.96 (s, 9H, CH_3CO), −2.79 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.1 (CO dend), 171 (CO phenylalanine), 170.7 ($COCH_3$), 170.3 (2 $COCH_3$), 169.7 ($COCH_3$), 168 (CO phenyl), 146 (C_1 carboxyphenyl), 141.9 (C_1 phenyl), 136.6 (C_1 phenylalanine), 134.6 (*o*-carboxyphenyl), 134.4 (*o*-phenyl), 132.2 (*p*-carboxyphenyl), 132 (*p*-phenyl), 131.4 (C pyrrole), 129.4 (*o*-phenylalanine), 128.9 (*p*-phenylalanine), 127.7 (*m*-phenylalanine), 126.6 (*m*-phenyl), 125.6 (*m*-carboxyphenyl), 121 (*meso*-C_{15}), 120.4 (*meso*-$C_{10,20}$), 118 (*meso*-C_5), 101.3 (C_1), 71 (C_3), 70.6 (C_5), 70.1 (2 CH_2O), 68.9 (C_2), 68.6 (CH_2-O-galactosyl), 67.2 (C_4), 61.5 (C_6), 58.6 (C-NH), 56.9 (CH phenylalanine), 39.3 (CH_2-NH), 38.1 (CH_2 phenylalanine), 30.5 [$(CH_2)_3$-C], 30.2 ($COCH_2$), 20.9 (CH_3CO), 20.64 (CH_3CO), 20.63 (2 CH_3CO).

Porphyrin 14-OAc: The title compound was prepared as **2-OAc** from **32-α-ManOAc**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/*n*-heptane as a red powder (yield 30%). UV−vis spectrum in CH_2Cl_2: $\lambda_{max.}$, nm (ε, L·mmol^{-1}·cm^{-1}) 417.5 (358), 515 (14.3), 550 (6.2), 590.5 (4.3), 643 (3.1). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.85 (s, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.79 (d, 2H, J = 4.7 Hz, $HC_{3,7}$ pyrrole), 8.28 (d, 2H, J = 8.0 Hz, *o*-carboxyphenyl), 8.21 (m, 8H, *o*-phenyl and *m*-carboxyphenyl), 7.75 (m, 9H, *m*- and *p*-phenyl), 7.37 (m, 5H, phenylalanine), 7.30 (broad s, 1H, NH phenylalanine), 6.68 (broad t, 3H, NH-CH_2), 5.36 (m, 3H, HC_3), 5.28 (m, 6H, HC_4 and HC_2), 4.91 (m, 4H, HC_1 and CH phenylalanine), 4.26 (dd, 3H, J = 5 and 12.2 Hz, H_aC_6), 4.11 (dd, 3H, J = 2 and 12.3 Hz, H_bC_6), 4.05 (m, 3H, HC_5), 3.77 (m, 3H, CH_{2a}-O-mannosyl), 3.64 (m, 9H, CH_{2b}-O-mannosyl and CH_2O), 3.56 (m, 6H, CH_2O), 3.45 (m, 6H, CH_2-NH), 3.29 (m, 2H, CH_2 phenylalanine), 2.20 [m, 6H, $(CH_2)_3$-C], 2.13 (s, 9H, CH_3CO), 2.08 (m, 6H, CH_2CO), 2.07 (s, 9H, CH_3CO), 2.02 (s, 9H, CH_3CO), 1.98 (s, 9H, CH_3CO), −2.78 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.4 (CO dend), 170.7 ($COCH_3$), 170.6 (CO phenylalanine), 170.2 ($COCH_3$), 170 ($COCH_3$), 169.7 ($COCH_3$), 167.5 (CO phenyl), 145.8 (C_1 carboxyphenyl), 142 (C_1 phenyl), 136.8 (C_1 phenylalanine), 134.53 (*o*-carboxyphenyl), 134.47 (*o*-phenyl), 133.1 (*p*-carboxyphenyl), 131.1 (C pyrrole), 129.5 (*o*-phenylalanine), 128.7 (*p*-phenylalanine), 127.7 (*p*-phenyl and *m*-phenylalanine), 126.66 (*m*-phenyl), 125.6 (*m*-carboxyphenyl), 120.6 (*meso*-C_{15}), 120.3 (*meso*-$C_{10,20}$), 118.5 (*meso*-C_5), 97.5 (C_1), 70 (CH_2O), 69.8 (CH_2O), 69.6 (C_3), 69 (C_2), 68.3 (C_5), 67 (CH_2-O-mannosyl), 66.1 (C_4), 62.4 (C_6), 58.3 (C-NH), 56.1 (CH phenylalanine), 39.4 (CH_2-NH), 38.3 (CH_2 phenylalanine), 30.9 [$(CH_2)_3$-C], 30.6 ($COCH_2$), 20.9 (CH_3CO), 20.69 (CH_3CO), 20.67 (2 CH_3CO).

Porphyrin 15-OAc: The title compound was prepared as **2-OAc** from **37**. Pure title compound was obtained after crystallization from a mixture of methylene chloride/*n*-heptane as a red powder (yield 86%). Anal. ($C_{75}H_{81}N_9O_{14}$), 3 H_2O calcd: C 64.97, H 6.32, N 9.09. Found: C 65.29, H 6.16, N 8.88. UV−vis spectrum in CH_2Cl_2: $\lambda_{max.}$, nm (ε, L·mmol^{-1}·cm^{-1}) 417.5 (436.9), 515 (17), 549.5 (7.4), 590 (5), 645 (3.5). ^{1}H NMR ($CDCl_3$): δ (ppm) 8.83 (s, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.79 (d, 2H, J = 4.8 Hz, $HC_{3,7}$ pyrrole), 8.30 (s, 3H, *m*- and *o*-carboxyphenyl), 8.20 (broad s, 1H, NH glycine), 8.16 (dd, 6H, J = 7.5 and 1.8 Hz, *o*-phenyl), 7.70 (m, 9H, *m*- and *p*-phenyl), 7.53 (broad, 1H, NH glycine), 7.10 (t, 3H, J = 5.1 Hz, NH), 4.23 (d, 2H, J = 5.1 Hz, CH_2 glycine), 4.20 (m, 6H, CH_2OAc), 3.62 (m, 6H, CH_2), 3.55 (m, 6H, CH_2), 3.43 (m, 6H, CH_2-NH), 2.36 (m, 6H, CH_2), 2.15 (m, 6H, CH_2), 2.03 (s, 9H, CH_3CO), −2.79 (s, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 173.8 (CO dend), 170.8 ($COCH_3$), 169.3 (CO glycine), 168.3 (CO phenyl), 146 (C_1 carboxyphenyl), 141.8 (C_1 phenyl), 134.6 (*o*-phenyl and *o*-carboxyphenyl and CO-phenyl), 131 (C pyrrole), 128 (*p*-phenyl), 126.4 (*m*-phenyl), 125.8 (*m*-carboxyphenyl), 120.3 (*meso*-$C_{10,15,20}$), 118.5 (*meso*-C_5), 69.5 (CH_2), 68.9 (CH_2), 63.4 (CH_2OAc), 58,1 (C-NH), 44.6 (CH_2 glycine), 39.4 (CH_2-NH), 30.9 (CH_2), 20.9 (CH_3CO).

General Procedure for the Preparation of Compounds 1−15. All operations were identical with those described for the synthesis of compound **1**. A representative example is described below.

5-{*p*-*N*-[Tris(*O*-*β*-D-galactopyranosyloxy)methyl]-*N*$^{\alpha}$-glycineamidophenyl}-10,15,20-triphenylporphyrin, 1: The peracetylated porphyrin **1-OAc** was dissolved (75 mg, 0.04 mmol) in dry methanol (10 mL) and dry methylene chloride (5 mL) then a solution of sodium methanolate in methanol (100 μL, 1 M) was added. The solution was stirred during 4 h at room temperature. IWT TMD-8 ion-exchange resin (400 mg) was added and the suspension was slowly stirred 30 min then filtered. The resin was washed with methanol and pyridine. The solution was concentrated under vacuum. The title compound **1** was obtained as a red powder and used without other purification (55 mg, yield 95%). MALTI-TOF calcd for $C_{69}H_{72}N_6O_{20}$ (MH^+) 1305.48, found 1305.49, calcd for (MNa^+) 1327.47, found 1327.51, calcd for (MK^+) 1343.44, found 1343.48. Anal. ($C_{69}H_{72}N_6O_{20}$) calcd: C 63.49, H 5.56, N 6.44. Found: C 63.85, H 5.23, N 6.05. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 414 (378.5), 513 (17), 547 (8.8), 588.5 (6.7), 644.5 (5.5). ^{1}H NMR (pyridine-d_5) δ (ppm) 9.68 (t, 1H, $NHCH_2$), 9.02 (m, 8H, pyrrole), 8.31 (d, 2H, *o*′-phenyl), 8.23 (d, 8H, C_{ortho} phenyl), 7.75 (2 t and 1 d, 19H, *m*- and *p*-phenyl), 7.00−6.25 (broad, 12H, OH), 4.94 (d, 9H, J = 7.5 Hz, HC_1 and CH_2O-Gal), 4.73 (d, 2H, CH_2NH), 4.62 (d, 3H, J = 4.6 Hz, HC_2), 4.53 (m, 6H, HC_4 and CH_2O-galactosyl), 4.43 (d, 6H, J = 4.6 Hz, H_aC_6 and H_bC_6), 4.15 (dd, 3H, J = 1.3 and 9 Hz, HC_3), 4.05 (t, 3H, J = 7.8 Hz, HC_5), −2.44 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 170.9 (CONH), 168.7 (CONH), 145.8 (C_1 carboxyphenyl), 142.9 (C_1 phenyl), 136.1, 135 (*o*-phenyl and *o*-carboxyphenyl), 132.2 (C pyrrole), 128.7 (*p*-phenyl), 127.7 (*m*-phenyl), 127.2 (*m*-carboxyphenyl), 121.4 (*meso*-C_{15}), 121.3 (*meso*-$C_{10,20}$), 120.2 (*meso*-C_5), 106.9 (C_1), 77.5 (C_5), 75.5 (C_3), 73.3 (C_2), 71 (C_4), 70.3 (CH_2O-galactosyl), 62.9 (C_6), 61.8 (C_{quat} tris), 45.2 (CH_2NH).

Porphyrin 2: The title compound was deprotected as in compound **1** from peracetylated porphyrin **2-OAc**. Product **2** was obtained as a red powder and used without other purification (yield 89%). HPLC Rt = 13.51 min. MALDI-TOF MS calcd for $C_{81}H_{94}N_9O_{23}$ (MH^+) 1560.64. Found: 1560.70. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 414 (286.1), 512.5 (11.9), 546.5 (5.3), 589 (3.6), 644 (2.6). ^{1}H NMR (pyridine-d_5): δ (ppm) 10.01 (m, 1H, NH glycine), 9.06 (d, 2H, J = 4.6 Hz, $HC_{3,7}$ pyrrole), 9.03 (m, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.76 (d, 2H, J = 7.4 Hz, *m*-carboxyphenyl), 8.62 (broad s, 3H, NH-CH_2), 8.40 (d, 2H, J = 7.7 Hz, *o*-carboxyphenyl), 8.36 (m, 6H, *o*-phenyl), 7.79 (m, 9H, *m*- and *p*-phenyl), 4.88 (d, 3H, J = 7.3 Hz, HC_1), 4.69 (m, 2H, CH_2 glycine), 4.57 (m, 3H, H_aC_6), 4.34 (m, 3H, H_bC_6), 4.23 (m, 9H, HC_3, HC_4 and CH_{2a}-O-glucosyl), 4.04 (m, 3H, HC_2), 3.97 (m, 6H, HC_5 and CH_{2b}-O-glucosyl), 3.76 (m, 6H, CH_2NH), 2.69 (m 6H, CH_2CO), 2.56 (m, 6H, [$(CH_2)_3$-C]), −2.44 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 173.9 (CO-den), 169.6 (CO glycine), 168.6 (CO phenyl), 145.2 (C_1 carboxyphenyl), 142.1 (C_1 phenyl), 134.8 (*o*-carboxyphenyl and *o*-phenyl), 134.1 (*p*-carboxyphenyl), 131.5 (C pyrrole), 128.1 (*p*-phenyl), 127.2 (*m*-phenyl), 126.7 (*m*-carboxyphenyl), 120.8 (*meso*-C_{15}), 120.6 (*meso*-$C_{10,20}$), 119.5 (*meso*-C_5), 104.7 (C_1), 78.2 (C_3 and C_5), 75 (C_2), 71.4 (C_4), 69.4 (CH_2-O-glucosyl), 62.5 (C_6), 58.7 (C-NH), 44.6 (CH_2 glycine), 40.1 (CH_2-NH), 31.3 [$(CH_2)_3$-C], 30.8 ($COCH_2$).

Porphyrin 3: The title compound was deprotected as in compound **1** from peracetylated porphyrin **3-OAc**. Pure product was obtained as a red powder and used without other purification (yield 92%). HPLC Rt = 13.56 min. MALDI-TOF MS calcd for $C_{81}H_{94}N_9O_{23}$ (MH^+) 1560.64, found 1560.57. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 414 (306.1), 512.5 (12.6), 547 (5.6), 588.5 (3.7), 645 (2.6). ^{1}H NMR (pyridine-d_5): δ (ppm) 9.97 (broad s, 1H, NH glycine), 9.08 (d, 2H, J = 4.3 Hz, $HC_{3,7}$ pyrrole), 9.03

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(s, 4H, $HC_{12,13,17,18}$ pyrrole), 8.76 (d, 2H, $HC_{2,8}$ pyrrole), 8.57 (m, 2H, *m*-carboxyphenyl), 8.37 (m, 8H, *o*-carboxyphenyl and *o*-phenyl), 7.80 (m, 9H, *m*- and *p*-phenyl), 7.12 (t, 3H, OH), 6.84 (t, 3H, OH), 6.62 (t, 3H, OH), 6.46 (t, 3H, OH), 4.8 (d, 3H, J = 7.4 Hz, HC_1), 4.64 (m, 2H, CH_2 glycine), 4.46 (m, 12H, $HC_{2,4,6}$), 4.18 (m, 6H, CH_{2a}-O-galactosyl and HC_3), 4.07 (m, 3H, HC_5), 3.99 (m, 3H, CH_{2b}-O-galactosyl), 3.72 (m, 6H, CH_2-NH), 2.62 [broad s, 6H, $(CH_2)_3$-C], 2.52 (broad s, 6H, CH_2-CO), −2.43 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 173.9 (CO-den), 169.7 (CO glycine), 168.6 (CO carboxyphenyl), 145.3 (C_1 carboxyphenyl), 142.3 (C_1 phenyl), 134.8 (*o*-phenyl and *o*-carboxyphenyl), 134.2 (*p*-carboxyphenyl), 131.7 (C pyrrole), 128.2 (*p*-phenyl), 127.7 (*m*-phenyl), 126.8 (*m*-carboxyphenyl), 120.9 (*meso*-C_{15}), 120.8 (*meso*-$C_{10,20}$), 119.7 (*meso*-C_5), 105.3 (C_1), 77 (C_5), 75.2 (C_3), 72.6 (C_2), 70.3 (C_4), 69.5 (CH_2-O-galactosyl), 62.4 (C_6), 58.8 (C-NH), 44.7 (CH_2 glycine), 40.4 (CH_2-NH), 31.5 [$(CH_2)_3$-C], 31 (CH_2CO).

Porphyrin 4:[35] The title compound was deprotected as in compound **1** from peracetylated porphyrin **4-OAc**. Product **4** was obtained as a red powder and used without other purification (yield 92%). HPLC Rt = 13.79 min. MALDI-TOF MS calcd for $C_{81}H_{94}N_9O_{23}$ (MH^+) 1560.64, found 1560.68. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 414 (274.4), 514.5 (12.2), 548 (5.3), 588.5 (3.6), 645.5 (2.4). ^{1}H NMR (pyridine-d_5): δ (ppm) 10 (broad s, 1H, NH glycine), 9.05 (m, 8H, HC pyrrole), 8.78 (s, 2H, *m*-carboxyphenyl), 8.73 (m, 1H, NH-CH_2), 8.42 (s, 2H, *o*-carboxyphenyl), 8.37 (m, 6H, *o*-phenyl), 7.81 (m, 9H, *m*- and *p*-phenyl), 6.97 (t, 3H, OH), 6.77 (t, 3H, OH), 6.70 (t, 3H, OH), 6.56 (t, 3H, OH), 5.41 (s, 3H, HC_1), 4.58 (d, 2H, CH_2 glycine), 4.58 (m, 12H, $HC_{2,3,4,6a}$), 4.39 (m, 6H, $HC_{5,6b}$), 4.12 (m, 3H, HC_{2a}-O-mannosyl), 3.80 (m, 3H, HC_{2b}-O-mannosyl), 3.74 (m, 6H, CH-NH), 2.71 (m, 6H, CH_2-CO), 2.60 [m, 6H, $(CH_2)_3$-C], −2.41 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 174 (CO-den), 169.9 (CO glycine), 168.6 (CO carboxyphenyl), 145.4 (C_1 carboxyphenyl), 142.4 (C_1 phenyl), 135 (*o*-phenyl and *o*-carboxyphenyl), 134.3 (*p*-carboxyphenyl), 131.7 (C pyrrole), 128.3 (*p*-phenyl), 127.3 (*m*-phenyl), 126.9 (*m*-carboxyphenyl), 120.9 (*meso*-$C_{10,15,20}$), 119.8 (*meso*-C_5), 101.8 (C_1), 75.5 (C_5), 72.8 ($C_{2,3,4}$), 72 ($C_{2,3,4}$), 69.1 ($C_{2,3,4}$), 67.1 (CH_2-O-mannosyl), 63.1 (C_6), 59 (C-NH), 44.9 (CH_2 glycine), 39.9 (C-NH), 31.7 [$(CH_2)_3$-C], 31.2 ($COCH_2$).

Porphyrin 5: The title compound was deprotected as in compound **1** from peracetylated porphyrin **5-OAc**. Product **5** was obtained as a red powder and used without other purification (yield 94%). HPLC Rt = 13.55 min. MALDI-TOF MS calcd for $C_{87}H_{106}N_9O_{26}$ (MH^+) 1692.72, found 1692.72. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 414 (298.5), 513 (12.4), 546 (5.5), 589 (3.7), 644.5 (2.7). ^{1}H NMR (pyridine-d_5): δ (ppm) 9.95 (broad s, 1H, NH glycine), 9.05 (d, 2H, J = 4.7 Hz, $HC_{3,7}$ pyrrole), 9.03 (m, 6H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.76 (d, 2H, J = 7.7 Hz, *m*-carboxyphenyl), 8.61 (broad t, 3H, NH-CH_2), 8.38 (m, 8H, *o*-phenyl and *o*-carboxyphenyl), 7.8 (m, 9H, *m*- and *p*-phenyl), 7.37 (t, 3H, OH), 7.16 (m, 6H, 2OH), 6.48 (t, 3H, OH), 4.91 (d, 3H, J = 7.3 Hz, HC_1), 4.63 (m, 2H, CH_2 glycine), 4.49 (m, 3H, H_aC_6), 4.32 (m, 3H, H_bC_6), 4.19 (m, 9H, HC_3, HC_4 and CH_{2a}-O-glucosyl), 4.02 (m, 3H, HC_2), 3.88 (m, 6H, HC_5 and CH_{2b}-O-glucosyl), 3.64 (m, 18H, CH_2NH and $2CH_2O$), 2.65 (m, 6H, CH_2CO), 2.58 [m, 6H, $(CH_2)_3$-C], −2.44 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 173.8 (CO-den), 168.6 (CO glycine), 168.4 (CO phenyl), 145.2 (C_1 carboxyphenyl), 142.2 (C_1 phenyl), 134.7 (*o*-phenyl and *o*-carboxyphenyl), 134.3 (*p*-carboxyphenyl), 131.4 (C pyrrole), 128.2 (*p*-phenyl), 127.2 (*m*-phenyl), 126.7 (*m*-carboxyphenyl), 120.9 (*meso*-C_{15}), 120.8 (*meso*-$C_{10,20}$), 119.6 (*meso*-C_5), 104.5 (C_1), 78.3 (C_3 and C_5), 74.9 (C_2), 71.3 (C_4), 70.3 (CH_2O), 70 (CH_2O), 69.8 (CH_2-O-glucosyl), 62.4 (C_6), 58.6 (C-NH), 44.7 (CH_2 glycine), 39.6 (CH_2-NH), 31.4 [$(CH_2)_3$-C], 30.8 ($COCH_2$).

Porphyrin 6: The title compound was deprotected as in compound **1** from peracetylated porphyrin **6-OAc**. Product **6** was obtained as a red powder and used without other purification (yield 94%). HPLC Rt = 13.51 min. MALDI-TOF MS calcd for $C_{87}H_{106}N_9O_{26}$ (MH^+) 1692.72, found 1692.73. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 414 (294.7), 512.5 (11.6), 548 (5.9), 590.5 (3.7), 643.5 (2.2). ^{1}H NMR (pyridine-d_5): δ (ppm) 9.92 (broad s, 1H, NH glycine), 9.07 (d, 2H, J = 4.7 Hz, $HC_{3,7}$ pyrrole), 9.03 (s, 4H, $HC_{12,13,17,18}$ pyrrole), 9.02 (d, 2H, J = 4.7 Hz, $HC_{2,8}$ pyrrole), 8.76 (d, 2H, *m*-carboxyphenyl), 8.59 (broad t, 3H, NH-CH_2), 8.39 (m, 2H, *o*-carboxyphenyl), 8.37 (m, 6H, *o*-phenyl), 7.80 (m, 9H, *m*- and *p*-phenyl), 7.20 (t, 3H, OH), 6.77 (t, 3H, OH), 6.54 (t, 3H, OH), 6.43 (t, 3H, OH), 4.82 (d, 3H, J = 7.6 Hz, HC_1), 4.64 (m, 2H, CH_2 glycine), 4.55 (m, 3H, HC_4), 4.45 (m, 9H, HC_2 and HC_6), 4.18 (m, 6H, HC_3 and CH_{2a}-O-galactosyl), 4.04 (m, 3H, HC_5), 3.90 (m, 3H, CH_{2b}-O-galactosyl), 3,64 (m, 18H, $2CH_2O$ and CH_2NH), 2.67 (m, 6H, CH_2CO), 2.57 [m, 6H, $(CH_2)_3$-C], −2.42 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 173.8 (CO-den), 169.6 (CO glycine), 168.3 (CO phenyl), 145.2 (C_1 carboxyphenyl), 142.2 (C_1 phenyl), 134.8 (*o*-phenyl and *o*-carboxyphenyl), 134.3 (*p*-carboxyphenyl), 131.6 (C pyrrole), 128.2 (*p*-phenyl), 127.2 (*m*-phenyl), 126.7 (*m*-carboxyphenyl), 120.9 (*meso*-C_{15}), 120.8 (*meso*-$C_{10,20}$), 119.6 (*meso*-C_5), 105.1 (C_1), 77 (C_5), 75.1 (C_3), 72.3 (C_2), 70.3 (CH_2O), 70.1 (C_4), 70 (CH_2O), 68.7 (CH_2-O-galactosyl), 62.2 (C_6), 58.7 (C-NH), 44.7 (CH_2 glycine), 39.6 (CH_2-NH), 31.3 [$(CH_2)_3$-C], 30.8 ($COCH_2$).

Porphyrin 7:[35] The title compound was deprotected as in compound **1** from peracetylated porphyrin **7-OAc**. Pure title compound was obtained as a red powder and used without other purification (yield 95%). HPLC Rt = 13.73 min. MALDI-TOF MS calcd for $C_{87}H_{106}N_9O_{26}$ (MH^+) 1692.71, found 1692.78. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 414 (347), 513 (14.2), 546.5 (6.4), 589 (4.3), 644.5 (3.1). ^{1}H NMR (pyridine-d_5): δ (ppm) 9.88 (t, 1H, J = 5.1 Hz, NH glycine), 9.08 (d, 2H, J = 4.4 Hz, $HC_{3,7}$), 9.03 (s, 6H, $HC_{12,13,17,18}$), 9.02 (d, 2H, $HC_{2,8}$), 8.76 (d, 2H, J = 8 Hz, *m*-carboxyphenyl), 8.64 (broad s, 1H, NH-CH_2), 8.58 (broad s, 3H, NH−CH_2), 8.40 (m, 6H, *o*-carboxyphenyl), 8.36 (m, 2H, *o*-phenyl), 7.80 (m, 9H, *m*- and *p*-phenyl), 5.39 (s, 3H, HC_1), 4.61 (m, 3H, CH_2), 4.55 (m, 12H, $C_{2,3,4,6}$), 4.36 (m, 6H, HC_5), 4.36 (d, 3H, J = 8.4 Hz, H_aC_6), 4.06 (m, 3H, CH_{2a}-O-mannosyl), 3.72 (m, 3H, CH_{2b}-O-mannosyl), 3.63 (m, 14H, CH_2), 2.70 [s, 6H, $(CH_2)_3$-C], 2.58 (broad s, 6H, CH_2CO), −2.44 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 173.9 (CO-den), 169.7 (CO glycine), 168.4 (CO-phenyl), 145.4 (C_1 carboxyphenyl), 142.4 (C_1 phenyl), 135 (*o*-carboxyphenyl and *o*-phenyl), 134.5 (*p*-carboxyphenyl), 131.8 (C pyrrole), 128.3 (*p*-phenyl), 127.4 (*m*-phenyl), 126.9 (*m*-carboxyphenyl), 121 (*meso*-C_{15}), 120.9 (*meso*-$C_{10,20}$), 119.8 (*meso*-C_5), 101.6 (C_1), 75.3 (C_5), 72.9 ($C_{2,3,4}$), 72 ($C_{2,3,4}$), 70.4 (CH_2-O-mannosyl), 70.2 (CH_2), 69.2 ($C_{2,3,4}$), 66.8 (CH_2-O-mannosyl), 63.3 (C_6), 58.8 (C-NH), 44.8 (CH_2 glycine), 40 (CH_2-NH), 31.5 [$(CH_2)_3$-C], 31 ($COCH_2$).

Porphyrin 8: The title compound was deprotected as in compound **1** from peracetylated porphyrin **8-OAc**. Pure title compound was obtained as a red powder powder and used without other purification (yield 94%). HPLC Rt = 13.74 min. MALDI-TOF MS calcd for $C_{93}H_{119}N_9O_{29}$ (MH^+) 1825.80, found 1825.82. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 414 (389.3), 513 (15.9), 546 (7.2), 589 (4.9), 645 (3.5). ^{1}H NMR (pyridine-d_5): δ (ppm) 9.97 (t, 1H, J = 5.2 Hz, NH glycine), 9.07 (d, 2H, J = 4.8 Hz, $HC_{3,7}$ pyrrole), 9.02 (s, 4H, $HC_{2,8,12,13,17,18}$ pyrrole), 8.75 (d, 2H, J = 8.1 Hz, *m*-carboxyphenyl), 8.64 (broad s, 1H, NH), 8.60 (broad t, 1H, NH-CH_2), 8.41 (d, 2H, J = 8.1 Hz, *o*-carboxyphenyl), 8.35 (m, 6H, *o*-phenyl), 7.79 (m, 6H, *m*- and *p*-phenyl), 6.97 (t, 6H, 2OH), 6.67 (t, 3H, OH), 6.27 (t, 3H, OH), 5.40 (d, 3H, J = 1.2 Hz, HC_1), 4.62 (m, 3H, $HC_{2,3,4,5}$), 4.60 (s, 2H, CH_2 glycine), 4.55 (m, 3H, H_aC_6), 4.55 (dd, 3H, J = 3.1 and 10.1 Hz, $HC_{2,3,4,5}$), 4.55 (d, 3H, J = 10 Hz, $HC_{2,3,4,5}$), 4.36 (d, 6H, J = 6 and 13.6 Hz, H_bC_6), 4.34 (m, 3H, $HC_{2,3,4,5}$), 4.05 (m, 3H, CH_{2a}-O-mannosyl), 3.72 (m, 3H, CH_{2b}-O-mannosyl), 3.64 (m, 18H, CH_2-NH and CH_2), 3.57 (m, 12H, CH_2-O),

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2.66 (m, 6H, CH_2-CO), 2.56 (m, 6H, $(CH_2)_3$-C), −2.43 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 173.8 (CO-den), 169.6 (CO glycine), 168.5 (CO carboxyphenyl), 145.4 (C_1 carboxyphenyl), 142.3 (C_1 phenyl), 135 (*o*-phenyl and *o*-carboxyphenyl), 134.6 (*p*-carboxyphenyl), 131.8 (C pyrrole), 128.4 (*p*-phenyl), 127.4 (*m*-phenyl), 126.9 (*m*-carboxyphenyl), 121.1 (*meso*-C_{15}), 121 (*meso*-$C_{10,20}$), 119.8 (*meso*-C_5), 101.8 (C_1), 75.3 ($C_{2,3,4,5}$), 73 ($C_{2,3,4,5}$), 72.2 ($C_{2,3,4,5}$), 70.8 (CH_2-O), 70.6 (CH_2-O), 70.4 (CH_2-O), 69.2 ($C_{2,3,4,5}$), 66.8 (CH_2-O-mannosyl), 63.2 (C_6), 58.8 (C-NH), 45 (CH_2 glycine), 40 (C-NH), 31.6 [$(CH_2)_3$-C], 31 ($COCH_2$).

Porphyrin 9: The title compound was deprotected as in compound **1** from peracetylated porphyrin **9-OAc**. Pure title compound was obtained as a red powder and used without other purification (yield 88%). HPLC Rt = 15.20 min. MALDI-TOF MS calcd for $C_{88}H_{100}N_9O_{23}$ (MH^+) 1650.69, found 1650.75. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 414 (322.9), 513 (13.1), 547 (5.8), 588.5 (3.8), 644.5 (2.7). ^{1}H NMR (pyridine-d_5): δ (ppm) 9.82 (d, 1H, J = 7.68 Hz, NH phenylalanine), 9.06 (d, 2H, J = 4.7 Hz, $HC_{3,7}$ pyrrole), 9.03 (s, 4H, $HC_{12,13,17,18}$ pyrrole), 8.93 (d, 2H, J = 4.7 Hz, $HC_{2,8}$ pyrrole), 8.63 (d, 2H, J = 8.0 Hz, *m*-carboxyphenyl), 8.43 (broad t, 3H, NH-CH_2), 8.36 (m, 6H, *o*-phenyl), 8.34 (m, 2H, *o*-carboxyphenyl), 7.8 (m, 9H, *m*- and *p*-phenyl), 7.53 (d, 2H, J = 7.2 Hz, *o*-phenylalanine), 7.39 (t, 2H, *m*-phenylalanine), 7.26 (m, 1H, *p*-phenylalanine), 7.25 (m, 6H, 2OH), 7.17 (t, 3H, OH), 6.52 (t, 3H, OH), 5.56 (dd, 1H, J = 6.7 Hz, HC phenylalanine), 4.88 (d, 3H, J = 7.6 Hz, HC_1), 4.57 (m, 3H, H_aC_6), 4.34 (m, 3H, H_bC_6), 4.22 (m, 6H, HC_3 and HC_4), 4.17 (m, 3H, CH_{2a}-O-glucosyl), 4.05 (m, 3H, HC_2), 3.98 (m, 6H, HC_5 and CH_{2b}-O-glucosyl), 3.73 (m, 6H, CH_2NH), 3.63 (m, 1H, CH_{2a} phenylalanine), 3.51 (m, 1H, CH_{2b} phenylalanine), 2.57 [broad s, 6H, $(CH_2)_3$-C], 2.51 (broad s, 6H, CH_2CO), −2.44 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 173.7 (CO-den), 172.1 (CO phenylalanine), 168.7 (CO phenyl), 145.3 (C_1 carboxyphenyl), 142.3 (C_1 phenyl), 139.1 (C_1 phenylalanine), 134.9 (*o*-carboxyphenyl and *o*-phenyl), 134.7 (*p*-carboxyphenyl), 131.5 (C pyrrole), 129.9 (*o*-phenylalanine), 128.8 (*m*-phenylalanine), 128.2 (*m*- and *p*-phenyl), 127.2 (*p*-phenylalanine), 126.9 (*m*-carboxyphenyl), 121 (*meso*-C_{15}), 120.8 (*meso*-$C_{10,20}$), 119.6 (*meso*-C_5), 104.9 (C_1), 78.4 (C_3), 78.3 (C_5), 75.1 (C_2), 71.5 (C_4), 69.5 (CH_2-O-glucosyl), 62.6 (C_6), 59 (C-NH), 57.2 (CH phenylalanine), 40.3 (CH_2-NH), 38.5 (CH_2 phenylalanine), 31.5 [$(CH_2)_3$-C], 30.9 ($COCH_2$).

Porphyrin 10: The title compound was deprotected as in compound **1** from peracetylated porphyrin **10-OAc**. Pure product **10** (yield 92%) was obtained as a red powder and used without other purification. HPLC Rt = 15.21 min. MALDI-TOF MS calcd for $C_{88}H_{100}N_9O_{23}$ (MH^+) 1650.69, found 1650.67. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 414 (320.7), 513 (13), 546 (5.8), 589.5 (3.8), 644.5 (2.7). ^{1}H NMR (pyridine-d_5): δ (ppm) 9.81 (broad s, 1H, NH phenylalanine), 9.07 (d, 2H, J = 4.5 Hz, $HC_{3,7}$ pyrrole), 9.03 (s, 4H, $HC_{12,13,17,18}$ pyrrole), 8.93 (d, 2H, J = 4.6 Hz, $HC_{2,8}$ pyrrole), 8.64 (d, 2H, J = 7.9 Hz, *m*-carboxyphenyl), 8.42 (m, 3H, NH-CH_2), 8.36 (m, 6H, *o*-phenyl), 8.33 (m, 2H, *o*-carboxyphenyl), 7.80 (m, 9H, *m*- and *p*-phenyl), 7.54 (d, 2H, J = 6.9 Hz, *o*-phenylalanine), 7.39 (t, 2H, J = 7.4 Hz, *m*-phenylalanine), 7.32 (d, 1H, J = 6.9 Hz, *p*-phenylalanine), 7.05 (t, 3H, OH), 6.83 (t, 3H, OH), 6.59 (t, 3H, OH), 6.42 (3H, OH), 5.58 (dd, 1H, J = 7.3 Hz, HC phenylalanine), 4.79 (d, 3H, J = 7.6 Hz, HC_1), 4.44 (m, 12H, HC_2, HC_4 and HC_6), 4.17 (m, 6H, HC_3 and CH_{2a}-O-galactosyl), 4.06 (m, 3H, HC_5), 3.99 (m, 3H, CH_{2b}-O-galactosyl), 3.69 (m, 6H, CH_2NH), 3.61 (m, 1H, CH_{2a} phenylalanine), 3.51 (m, 1H, CH_{2b} phenylalanine), 2.53 [m, 12H, $(CH_2)_3$-C and CH_2CO], −2.44 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 173.9 (CO-den), 172.1 (CO phenylalanine), 168.6 (CO phenyl), 145.1 (C_1 carboxyphenyl), 142.2 (C_1 phenyl), 138.3 (C_1 phenylalanine), 134.8 (*o*-carboxyphenyl and *o*-phenyl), 134.3 (*p*-carboxyphenyl), 131.5 (C pyrrole), 129.8 (*o*-phenylalanine), 128.7 (*m*-phenylalanine), 128.1 (*m*- and *p*-phenyl), 127.2 (*p*-phenylalanine), 126.8 (*m*-carboxyphenyl), 120.8 (*meso*-C_{15}), 120.7 (*meso*-$C_{10,20}$), 119.6 (*meso*-C_5), 105.2 (C_1), 76.8 (C_5), 75 (C_3), 72.4 (C_2), 70 (C_4), 69.2 (CH_2-O-galactosyl), 62.3 (C_6), 58.8 (C-NH), 57 (CH phenylalanine), 40.2 (CH_2-NH), 38.5 (CH_2 phenylalanine), 31.3 [$(CH_2)_3$-C], 30.8 ($COCH_2$).

Porphyrin 11: The title compound was deprotected as in compound **1** from peracetylated porphyrin **11-OAc**. Pure title compound was obtained after drying as a red powder and used without other purification (yield 80%). HPLC Rt = 15.75 min. MALDI-TOF MS calcd for $C_{88}H_{100}N_9O_{23}$ (MH^+) 1650.69, found 1650.66. Anal. ($C_{88}H_{99}N_9O_{23}$), $8H_2O$ calcd: C 58.89, H 6.46, N 7.02. Found: C 58.75; H 6.22; N 6.87. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 414 (380.4), 512.5 (15.4), 547 (6.7), 588.5 (4.5), 644.5 (3). ^{1}H NMR (pyridine-d_5): δ (ppm) 9.78 (d, 1H, NH phenylalanine), 9.06 (d, 2H, J = 4.8 Hz, $HC_{3,7}$ pyrrole), 9.02 (s, 4H, $HC_{12,13,17,18}$ pyrrole), 8.98 (d, 2H, J = 4.8 Hz, $HC_{2,8}$ pyrrole), 8.63 (d, 2H, J = 8.2 Hz, *m*-carboxyphenyl), 8.52 (m, 3H, NH-CH_2), 8.36 (m, 6H, *o*-phenyl), 8.33 (m, 2H, *o*-carboxyphenyl), 7.79 (m, 9H, *m*- and *p*-phenyl), 7.51 (d, 2H, J = 7.0 Hz, *o*-phenylalanine), 7.37 (t, 2H, J = 7.6 Hz, *m*-phenylalanine), 7.29 (d, 1H, J = 7.3 Hz, *p*-phenylalanine), 6.91 (t, 3H, OH), 6.71 (t, 3H, OH), 6.64 (t, 3H, OH), 6.46 (t, 3H, OH), 5.49 (dd, 1H, J = 7.9 Hz, HC phenylalanine), 5.37 (m, 3H, HC_1), 4.56 (m, 12H, HC_2, HC_3, HC_4 and H_aC_6), 4.35 (m, 6H, HC_5 and H_bC_6), 4.08 (m, 3H, CH_{2a}-O-mannosyl), 3.80 [m, 3H, CH_{2b}-O-mannosyl), 3.71 (m, 6H, CH_2NH), 3.55 (m, 2H, CH_2 phenylalanine), 2.56 [m, 12H, CH_2CO and $(CH_2)_3$-C], −2.45 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 173.8 (CO-den), 172.2 (CO phenylalanine), 168.8 (CO phenyl), 145.2 (C_1 carboxyphenyl), 142.2 (C_1 phenyl), 138.3 (C_1 phenylalanine), 134.8 (*o*-carboxyphenyl), 134.7 (*o*-phenyl), 134.2 (*p*-carboxyphenyl), 131.7 (C pyrrole), 129.9 (*o*-phenylalanine), 128.8 (*m*-phenylalanine), 128.2 (*m*- and *p*-phenyl), 127.2 (*p*-phenylalanine), 126.9 (*m*-carboxyphenyl), 120.8 (*meso*-C_{15}), 120.7 (*meso*-$C_{10,20}$), 119.6 (*meso*-C_5), 101.6 (C_1), 75.3 (C_5), 72.7 (C_3), 71.9 (C_2), 69 (C_4), 67 (CH_2-O-mannosyl), 62.9 (C_6), 58.9 (C-NH), 57.4 (CH phenylalanine), 39.8 (CH_2-NH), 38.4 (CH_2 phenylalanine), 31.4 ($COCH_2$), 31 [$(CH_2)_3$-C].

Porphyrin 12: The title compound was deprotected as in compound **1** from peracetylated porphyrin **12-OAc**. Pure title compound was obtained after drying as a red powder and used without other purification (yield 96%). HPLC Rt = 15.18 min. MALDI-TOF MS calcd for $C_{94}H_{112}N_9O_{26}$ (MH^+) 1782.76, found 1782.77. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, L·mmol^{-1}·cm^{-1}) 414 (265), 513 (10.8), 546 (4.7), 589 (3.2), 644 (2.2). ^{1}H NMR (pyridine-d_5): δ (ppm) 9.81 (d, 1H, J = 7.4 Hz, NH phenylalanine), 9.07 (d, 2H, J = 4.7 Hz, $HC_{3,7}$ pyrrole), 9.03 (s, 4H, $HC_{12,13,17,18}$ pyrrole), 8.93 (d, 2H, J = 4.8 Hz, $HC_{2,8}$ pyrrole), 8.84 [broad s, 1H, NH-(C)], 8.60 (d, 2H, J = 7.9 Hz, *m*-carboxyphenyl), 8.50 (broad t, 3H, NH-CH_2), 8.33 (m, 8H, *o*-phenyl and *o*-carboxyphenyl), 7.8 (m, 9H, *m*- and *p*-phenyl), 7.56 (m, 2H, *o*-phenylalanine), 7.38 (m, 2H, *m*-phenylalanine), 7.35 (t, 3H, OH), 7.29 (m, 1H, *p*-phenylalanine), 7.18 (m, 6H, 2OH), 6.45 (t, 3H, OH), 5.57 (m, 1H, HC phenylalanine), 4.90 (d, 3H, J = 7.7 Hz, HC_1), 4.48 (m, 3H, H_aC_6), 4.34 (m, 3H, H_bC_6), 4.23 (m, 6H, HC_3 and HC_4), 4.16 (m, 3H, CH_{2a}-O-glucosyl), 4.01 (m, 3H, HC_2), 3.88 (m, 6H, HC_5 and CH_{2b}-O-glucosyl), 3.59 (m, 20H, CH_2NH, CH_2 phenylalanine and $2CH_2O$), 2.57 [m, 12H, $(CH_2)_3$-C and CH_2CO], −2.44 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 173.8 (CO-den), 172 (CO phenylalanine), 168.5 (CO phenyl), 145.2 (C_1 carboxyphenyl), 142.2 (C_1 phenyl), 138 (C_1 phenylalanine), 134.9 (*o*-phenyl), 134.7 (*o*-carboxyphenyl and *p*-carboxyphenyl), 131.5 (C pyrrole), 129.9 (*o*-phenylalanine), 128.7 (*m*-phenylalanine), 128.2 (*p*-phenyl), 127.3 (*m*-phenyl and *p*-phenylalanine), 126.9 (*m*-carboxyphenyl), 120.9 (*meso*-C_{15}), 120.8 (*meso*-$C_{10,20}$), 119.6 (*meso*-C_5), 104.6 (C_1), 78.4 (C_3 and C_5), 75 (C_2), 71.5 (C_4), 70.4 (CH_2O), 70.1 (CH_2O), 69.7 (CH_2-O-glucosyl), 62.5 (C_6), 58.8 (C-NH), 57.6 (CH phenylalanine), 39.7 (CH_2-NH), 38.5 (CH_2 phenylalanine), 31.3 [$(CH_2)_3$-C], 30.8 ($COCH_2$).

Porphyrin 13: The title compound was deprotected as in compound **1** from peracetylated porphyrin **13-OAc**. Pure title compound was obtained as a red powder and used without other purification (yield 98%). HPLC Rt = 15.19 min. MALDI-TOF MS calcd for $C_{94}H_{112}N_9O_{26}$ (MH^+) 1782.76, found 1782.75. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, $L \cdot mmol^{-1} \cdot cm^{-1}$) 414 (339.5), 512.5 (13.9), 546.5 (6.2), 588.5 (4.1), 644 (2.9). ^{1}H NMR (pyridine-d_5): δ (ppm) 9.81 (d, 1H, NH phenylalanine), 9.08 (d, 2H, J = 4.8 Hz, $HC_{3,7}$ pyrrole), 9.04 (s, 4H, $HC_{12,13,17,18}$ pyrrole), 8.96 (d, 2H, J = 4.8 Hz, $HC_{2,8}$ pyrrole), 8.85 [broad s, 1H, NH-(C)], 8.64 (d, 2H, J = 8.0 Hz, *m*-carboxyphenyl), 8.51 (broad t, 3H, NH-CH_2), 8.35 (m, 8H, *o*-phenyl and *o*-carboxyphenyl), 7.80 (m, 9H, *m*- and *p*-phenyl), 7.58 (m, 2H, *o*-phenylalanine), 7.38 (m, 2H, *m*-phenylalanine), 7.28 (m, 1H, *p*-phenylalanine), 7.21 (t, 3H, OH), 6.75 (t, 3H, OH), 6.54 (t, 3H, OH), 6.42 (t, 3H, OH), 5.60 (m, 1H, HC phenylalanine), 4.82 (d, 3H, J = 7.6 Hz, HC_1), 4.54 (m, 3H, HC_4), 4.46 (m, 9H, HC_2 and HC_6), 4.19 (m, 6H, HC_3 and CH_{2a}-O-galactosyl), 4.04 (m, 3H, HC_5), 3.91 (m, 3H, CH_{2b}-O-galactosyl), 3,67 (m, 20H, $2CH_2O$, CH_2NH and CH_2 phenylalanine), 2.63 [m, 12H, $(CH_2)_3$-C and CH_2CO], −2.42 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 173.8 (CO-den), 171.9 (CO phenylalanine), 168.4 (CO phenyl), 145.1 (C_1 carboxyphenyl), 142.2 (C_1 phenyl), 138.5 (C_1 phenylalanine), 134.7 (*o*-phenyl), 134.6 (*o*-carboxyphenyl), 134.5 (*p*-carboxyphenyl), 131.6 (C pyrrole), 129.8 (*o*-phenylalanine), 128.7 (*m*-phenylalanine), 128.2 (*p*-phenyl), 127.2 (*m*-phenyl and *p*-phenylalanine), 126.8 (*m*-carboxyphenyl), 120.9 (*meso*-C_{15}), 120.8 (*meso*-$C_{10,20}$), 119.6 (*meso*-C_5), 105.1 (C_1), 76.8 (C_5), 75.2 (C_3), 72.3 (C_2), 70.4 (CH_2O), 70.1 (C_4), 70 (CH_2O), 68.7 (CH_2-O-galactosyl), 62.2 (C_6), 58.7 (C-NH), 57.1 (CH phenylalanine), 39.7 (CH_2-NH), 38.6 (CH_2 phenylalanine), 31.4 [$(CH_2)_3$-C], 30.9 ($COCH_2$).

Porphyrin 14: The title compound was deprotected as in compound **1** from peracetylated porphyrin **14-OAc**. Pure title compound was obtained after drying as a red powder and used without other purification (yield 96%). HPLC Rt = 15.54 min. MALDI-TOF MS calcd for $C_{94}H_{112}N_9O_{26}$ (MH^+) 1782.76, found 1782.71. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, $L \cdot mmol^{-1} \cdot cm^{-1}$) 414 (220.7), 513 (10.1), 546 (4.7), 589 (3.2), 645 (2.4). ^{1}H NMR (pyridine-d_5): δ (ppm) 9.74 (m, 1H, NH phenylalanine), 9.07 (d, 2H, J = 4.7 Hz, $HC_{3,7}$ pyrrole), 9.03 (s, 4H, $HC_{12,13,17,18}$ pyrrole), 8.94 (d, 2H, J = 4.9 Hz, $HC_{2,8}$ pyrrole), 8.82 [m, 1H, NH-(C)], 8.60 (m, 2H, *m*-carboxyphenyl), 8.43 (m, 3H, NH-CH_2), 8.34 (m, 8H, *o*-phenyl and *o*-carboxyphenyl), 7.80 (m, 9H, *m*- and *p*-phenyl), 7.54 (m, 2H, *o*-phenylalanine), 7.37 (m, 2H, *m*-phenylalanine), 7.29 (m, 1H, *p*-phenylalanine), 5.55 (m, 1H, HC phenylalanine), 5.38 (m, 3H, HC_1), 4.56 (m, 12H, HC_2, HC_3, HC_4 and H_aC_6), 4.35 (m, 6H, HC_5 and H_bC_6), 4.06 (m, 3H, CH_{2a}-O-mannosyl), 3.76 (m, 3H, CH_{2b}-O-mannosyl), 3.58 (m, 20H, $2CH_2O$, CH_2NH and CH_2 phenylalanine), 2.56 [m, 12H, $(CH_2)_3$-C and CH_2CO], −2.44 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 173.7 (CO-den), 172 (CO phenylalanine), 168 (CO phenyl), 145.2 (C_1 carboxyphenyl), 142.3 (C_1 phenyl), 138.5 (C_1 phenylalanine), 134.8 (*o*-phenyl), 134.6 (*o*-carboxyphenyl and *p*-carboxyphenyl), 131.5 (C pyrrole), 129.9 (*o*-phenylalanine), 128.7 (*m*-phenylalanine), 128.2 (*p*-phenyl), 127.2 (*m*-phenyl and *p*-phenylalanine), 126.8 (*m*-carboxyphenyl), 120.9 (*meso*-C_{15}), 120.8 (*meso*-$C_{10,20}$), 119.9 (*meso*-C_5), 101.5 (C_1), 75.2 (C_5), 72.8 (C_3), 71.9 (C_2), 70.2 (CH_2O), 70.1 (CH_2O), 69.1 (C_4), 66.6 (CH_2-O-mannosyl), 63.2 (C_6), 58.8 (C-NH), 57.1 (CH phenylalanine), 39.9 (CH_2-NH), 38.6 (CH_2 phenylalanine), 31.1 [$(CH_2)_3$-C], 30.7 ($COCH_2$).

Porphyrin 15: The title compound was deprotected as in compound **1** from peracetylated porphyrin **15-OAc**. Product **15** was obtained as a red powder and used without other purification (yield 95%). HPLC Rt = 18.49 min. MALDI-TOF MS calcd for $C_{69}H_{76}N_9O_{11}$ (MH^+) 1206.56, found 1206.56. Anal. ($C_{69}H_{75}N_9O_{11}$), $2H_2O$ calcd: C 66.70, H 6.41, N 10.15. Found: C 66.38, H 6.13, N 10.03. UV−vis spectrum in MeOH/pyridine (24/1, v/v): λ_{max}, nm (ε, $L \cdot mmol^{-1} \cdot cm^{-1}$) 414 (441.4), 512.5 (17.7), 547 (7.8), 589.5 (5.2), 644.5 (3.6). ^{1}H NMR (pyridin-d_5): δ (ppm) 8.81 (d, 2H, J = 4.8 Hz, $HC_{3,7}$ pyrrole), 8.77 (d, 2H, J = 4.8 Hz, $HC_{2,8}$ pyrrole), 8.74 (s, 6H, $HC_{12,13,17,18}$ pyrrole), 8.71 (broad s, 1H, NH glycyl), 8.32 (d, 2H, J = 8.3 Hz, *m*-carboxyphenyl), 8.25 (d, 2H, J = 8.2 Hz, *o*-carboxyphenyl), 8.17 (dd, 2H, J = 1.7 and 7.8 Hz, *o*-phenyl), 8.07 (dd, 2H, J = 1.3 and 7.8 Hz, *o*-phenyl), 7.82 (broad t, 1H, J = 3 Hz, NH), 7.72 (m, 9H, *m*- and *p*-phenyl), 7.58 (m, 9H, *m*- and *p*-phenyl), 7.52 (broad t, 3H, NH), 4.78 (t, 3H, OH), 4.27 (d, 2H, J = 4.6 Hz, CH_2 glycine), 3.71 (m, 6H, CH_2OH), 3.54 (m, 12H, CH_2-O), 3.43 (m, 6H CH_2), 2.32 (m, 6H, CH_2-CO), 2.11 (m, 6H, CH_2-C), −2.83 (s, 2H, NH). ^{13}C NMR (pyridine-d_5): δ (ppm) 174.3 (CO-den), 169.9 (CO glycine), 168.8 (CO carboxyphenyl), 145.9 (C_1 carboxyphenyl), 142 (C_1 15-phenyl), 141.9 (C_1 10,20-phenyl), 134.6 (*o*-carboxyphenyl), 134.5 (15-*o*-phenyl), 134.4 (10,20-*o*-phenyl), 132.6 (*p*-carboxyphenyl), 131 (C pyrrole), 128.3 (*p*-phenyl), 127.6 (*p*-phenyl), 126.6 (*m*-phenyl), 125.9 (*m*-carboxyphenyl), 120.5 (*meso*-C_{15}), 120.3 (*meso*-$C_{10,20}$), 118.5 (*meso*-C_5), 75.5 (CH_2-O), 69.4 (CH_2-O), 61.5 (CH_2OH), 58.9 (C-NH), 44.5 (CH_2 glycine), 39.6 (C-NH), 31.1 [$(CH_2)_3$-C and $COCH_2$].

■ ASSOCIATED CONTENT

Supporting Information. General experimental information and ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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