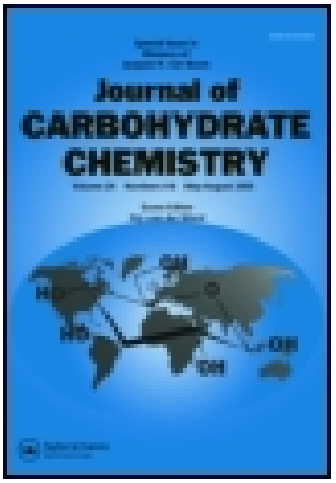

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Synthesis of Glycoconjugated Phthalonitriles for New Phthalocyanine-Based Photosensitizers

Göran Crucius[a], Michael Hanack[a] & Thomas Ziegler[a]
[a] Institute of Organic Chemistry, University of Tuebingen,, Tübingen, 72076, Germany
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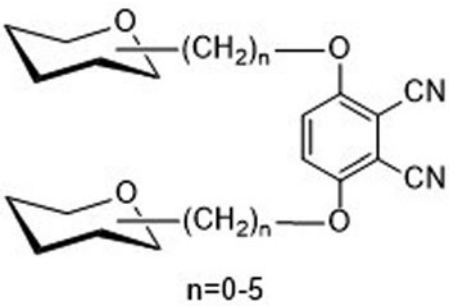
Institute of Organic Chemistry, University of Tuebingen, Auf der Morgenstelle 18 72076, Tübingen, Germany

GRAPHICAL ABSTRACT



Excellent photophysical and photochemical properties completed by magnificent take-up rates in malignant tissues attracted a great deal of interest to the application of glycosylated and glycoconjugated phthalocyanines in photodynamic therapy. In this study we describe the concise synthesis and full characterization of 16 differently 3,6-bisglycoconjugated phthalonitriles **3**, **5**, **6**, **8**, and **48**–**59,** which are precursors for a new generation of photosensitizers, namely, nonperipheral glycoconjugated phthalocyanines. The first example for the synthesis of a nonperipheral glycoconjugated zinc phthalocyanine **60** from phthalonitrile **48** is also presented in this work.

Keywords Glycoconjugated phthalonitrile; Photosensitizer; Carbohydrate tosylate; Hydroquinone; Zinc phthalocyanine

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Address correspondence to Thomas Ziegler, Institute of Organic Chemistry, University of Tuebingen, Auf der Morgenstelle 18, 72076, Tuebingen, Germany. E-mail: thomas.ziegler@uni-tuebingen.de

INTRODUCTION

Nowadays, photodynamic therapy (PDT) is a well-accepted method for the treatment of age-related macular degeneration, for some forms of cancer including skin and early lung cancer, and for antiviral and antibacterial applications.[1–3] The efficacy of PDT is based on the interaction of three components: photosensitizer, light, and molecular oxygen. After intravenous injection and accumulation of the photosensitizer in the malignant tissue, the phototherapeutic effect is activated by irradiation with light to generate highly reactive singlet oxygen from readily available triplet oxygen in the cells. These reactive oxygen species evoke a toxic response in the malignant tissue, ending, ultimately, in cell death.[4–6] Due to their absorbance in the red region of the visible spectrum, high stability during light exposure, and longer triplet-state lifetimes, phthalocyanines, especially their metalated diamagnetic complexes (MPc's, M = Zn, Al, etc.), turned out to be potential candidates for use in photodynamic processes.[4,7] However, one considerable problem of phthalocyanine-based photosensitizers (PSs) is the poor solubility of their hydrophobic skeleton in physiological media. Therefore, scientific attention has been focused on the development of water-soluble PSs.[8–13] The combination of the hydrophobic macrocycles with hydrophilic carbohydrate moieties has attracted a great deal of attention, mainly due to the fact that several carbohydrates have a specific recognition for cancer cells.[14–16] In addition, these carbohydrate residues enhance the solvation properties of the photosensitizer to ensure more effective photocytotoxic activity.[17–28]

In previous studies we have synthesized and fully characterized a series of peripheral glycosylated and glycoconjugated zinc (II) phthalocyanines bearing galactose, glucose, mannose, maltose, or cellobiose residues at the macrocyclic skeleton. Connection of the glycosides with the aromatic system was carried out via an oxygen or sulfur atom at C-1 or C-6 of the appropriated carbohydrate using nucleophilic aromatic displacement reactions at the phthalonitrile stages.[29–35] The achieved glycosylated and glycoconjugated zinc phthalocyanine species with excellent solubility in water, absorption maxima beyond 700 nm, and high triplet quantum yields ranging from 0.68 to 0.88 fulfilled the basic requirements for the successful application in PDT.[36,37]

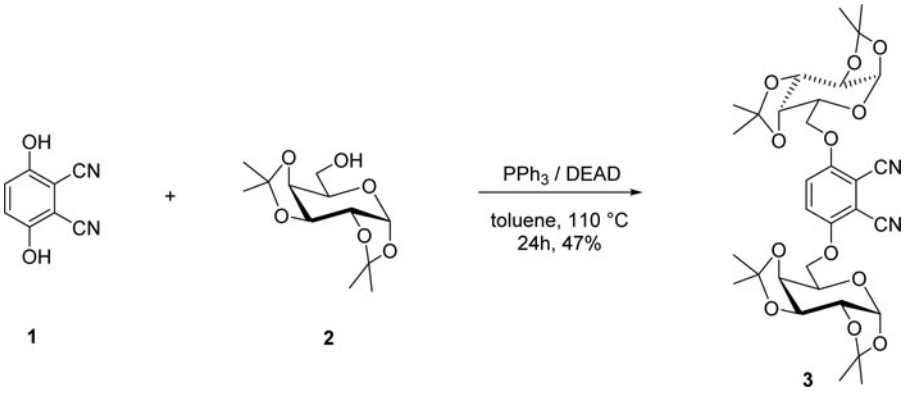
Herein, we present the synthesis and full characterization of 3,6-bisglycosylated and 3,6-bisglycoconjugated phthalonitriles, which are necessary starting materials for the formation of new nonperipheral glycosylated and glycoconjugated phthalocyanines.

RESULTS AND DISCUSSION

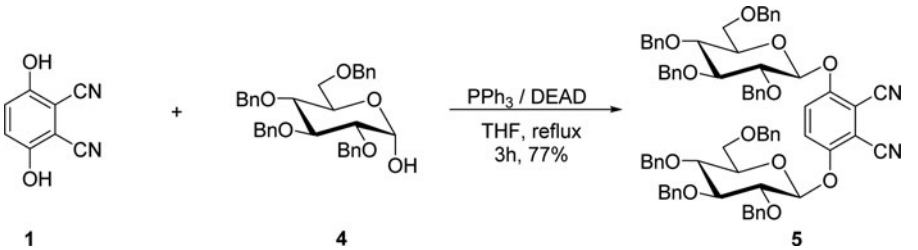
As mentioned before, the concept of nucleophilic aromatic displacement reaction was successfully applied for the synthesis of monoglycosylated

phthalonitriles—position three or four of the aromatic dinitrile is substituted by one sugar residue—as well as for the 4,5-bisglycosylated and the 3,4,5,6-tetraglycoconjugated phthalonitriles.[13,29–35] Additionally, we could show that 3,6-bisglycoconjugated phthalonitriles also have been accessible by nucleophilic aromatic displacement of two fluorine atoms or triflyl groups via a carbohydrate anion. Although the target structures were obtained, we developed a new and much more simple and efficient route for 3,6-bisglycosylated phthalonitriles using reaction conditions described by Oyo Mitsunobu for the formation of ethers starting from primary and secondary alcohols.[39]

Therefore, 2,3-dicyanohydroquinone (**1**) was reacted with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**2**) in toluene using Ph_3P and diethyl azodicarboxylate (DEAD) as reagents to afford 3,6-bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)phthalonitrile (**3**) in a 47% yield (Sch. 1). Driven by the successful formation of glycoconjugate **3**, hydroquinone **1** was also treated with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (**4**) under similar reaction conditions to give 3,6-bis(2,3,4,6-tetra-*O*-benzyl-β-D-gluco-1-yl)phthalonitrile (**5**) in a yield of 77% within 3 h (Sch. 2). No α-anomer of **5** could be detected.



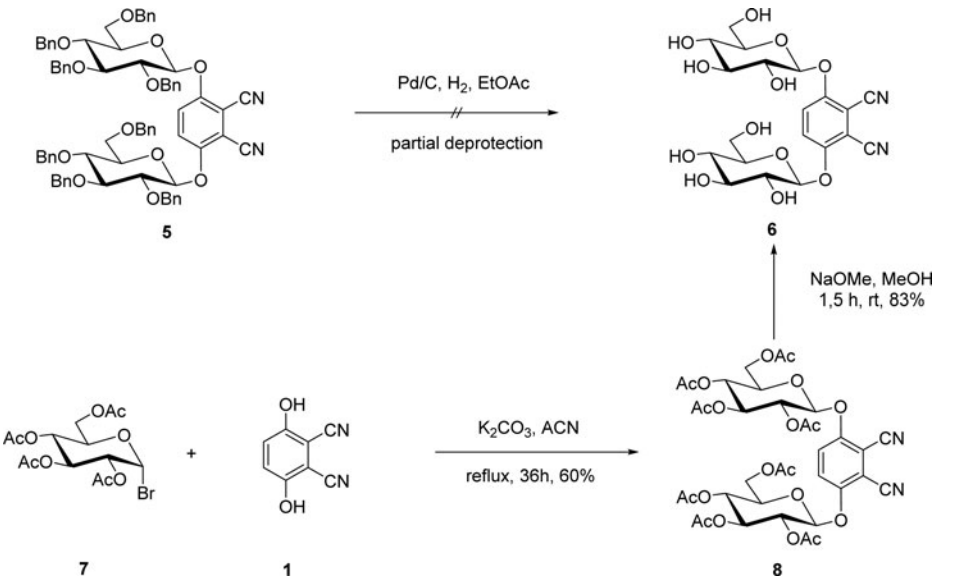
Scheme 1: Formation of glycoconjugate **3** catalyzed by Ph_3Ph and DEAD.



Scheme 2: Formation of bisglycoside **5** catalyzed by PPh_3 and DEAD.

Both phthalonitriles **3** and **5** were easily accessible from simple precursors like hydroquinone **1** and the corresponding carbohydrates **2** or **4**, protected by base-abiding groups to ensure stability during the subsequent transformation process of the metal phthalocyanine (MPc) under basic conditions, and serve as useful examples for the powerful application of DEAD and Ph_3P in the synthesis of ortho bis-substituted sugar dinitriles.

Taking into account that cleavage of benzyl groups at the phthalocyanine stage would become a challenging task,[31] we treated compound **5** with Pd/C under an atmosphere of hydrogen to yield 3,6-bis-(β-D-glucopyranosyl)-phthalonitrile (**6**) (Sch. 3). Although reaction conditions were diversified in terms of solvent and amount of Pd/C and so forth, incomplete cleavage of the benzyl protecting groups of sugar nitrile **5** occurred. However, **6** was synthesized following another strategy. Hydroquinone (**1**), 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**7**), and potassium carbonate were refluxed in dry acetonitrile (ACN) for 36 h to give 3,6-bis-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl phthalonitrile (**8**) in a yield of 60%. Subsequent deprotection of **8** under Zemplén conditions yielded 83% of dinitrile **6** (Sch. 3). To the best of our knowledge, compounds **5**, **6,** and **8** are the first examples for 3,6-disubstituted glyconitriles in which the carbohydrate moieties were anomerically linked to the aromatic system. All analytical data were in full agreement with the expected results. Configurational aspects were determined by using mono- and multidimensional NMR spectroscopy. Due to the evaluated coupling constants of the ^{1}H-^{1}H- and ^{1}H-^{13}C-signals, we assigned an all β-configuration



Scheme 3: Synthesis of dinitrile **6**.

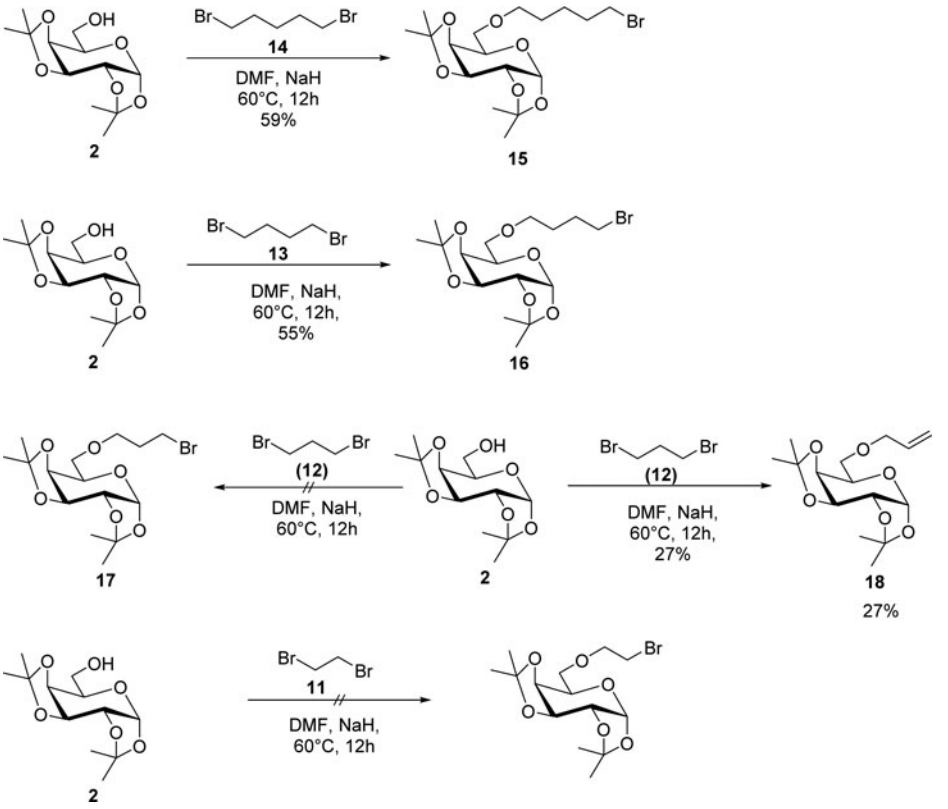
to compounds **5** and **8**. Although the synthesis of the corresponding zinc phthalocyanines is not a part of the present work, we can state that these new 3,6-bisglycosylated phthalonitriles will be potential precursors for new glycophotosensitizers with excellent photophysical properties.

Consequently, we were also focused on systems with the same substitution pattern but, as an additional aspect, with spacers between the aromatic and the carbohydrate moiety. Alkyl chains like ethyl, propyl, butyl, and pentyl seemed to be the best choice for the spacer part because three advantages could be expected. First, electron-donating alkyl chains would result in a bathochromic shift of the absorption maxima in the zinc macrocycle. Second, due to a lower steric hindrance, formation of the zinc phthalocyanine should be favored. Finally, spacers should create a more bulky atmosphere around the macrocycle, resulting in a lower aggregation behavior, which in turn is a basic requirement for the successful application in PDT.

To acknowledge our assumption, we first had to consider the synthesis of the appropriated carbohydrates. Special attention was paid to two main requirements. On the one hand, the sugars had to be protected with base-abiding groups that endure the harsh reaction conditions during the formation of phthalocyanines. On the other hand, protecting groups had to be labile enough to be cleaved at the macrocyclic stage. Additionally, the spacer had to carry a leaving group that is suitable for a subsequent nucleophilic substitution reaction with hydroquinone (**1**) and potassium carbonate to form the corresponding 3,6-bisglycoconjugated phthalonitriles. Therefore, D-galactose **2** (Sch. 4), D-glucose **10** (Sch. 5), and D-mannose **9** (Sch. 6), all of which were protected with isopropylidene acetals, were reacted with alkyl bromides 1,2-dibromoethane (**11**), 1,3-dibromopropane (**12**), 1,4-dibromobutane (**13**), and 1,5-dibromopentane (**14**).

Treatment of pyranose **2** with halogen bromides **13** or **14** in dry DMF catalyzed by sodium hydride yielded 6-*O*-(5-bromopentyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**15**, 59%) and 6-*O*-(4-bromobutyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**16**, 55%), respectively. Introducing 3-bromopropyl and 2-bromoethyl moieties at galactoside **2** with alkyl dibromides **11** and **12** was not successful. Instead of the target compound 6-*O*-(3-bromopropyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**17**), 6-*O*-allyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**18**) was isolated in a 27% yield from the reaction of carbohydrate **2**, 1,3-dibromopropane (**12**)**,** and sodium hydride in dry DMF (Sch. 4). Due to the electronic effect and steric hindrance of 1,2-dibromoethane (**11**), no substitution products with galactopyranose **2** were obtained. 1,2:3,4-di-*O*-Isopropylidene-α-D-galactopyranose (**2**) was recovered quantitatively after workup (Sch. 4).

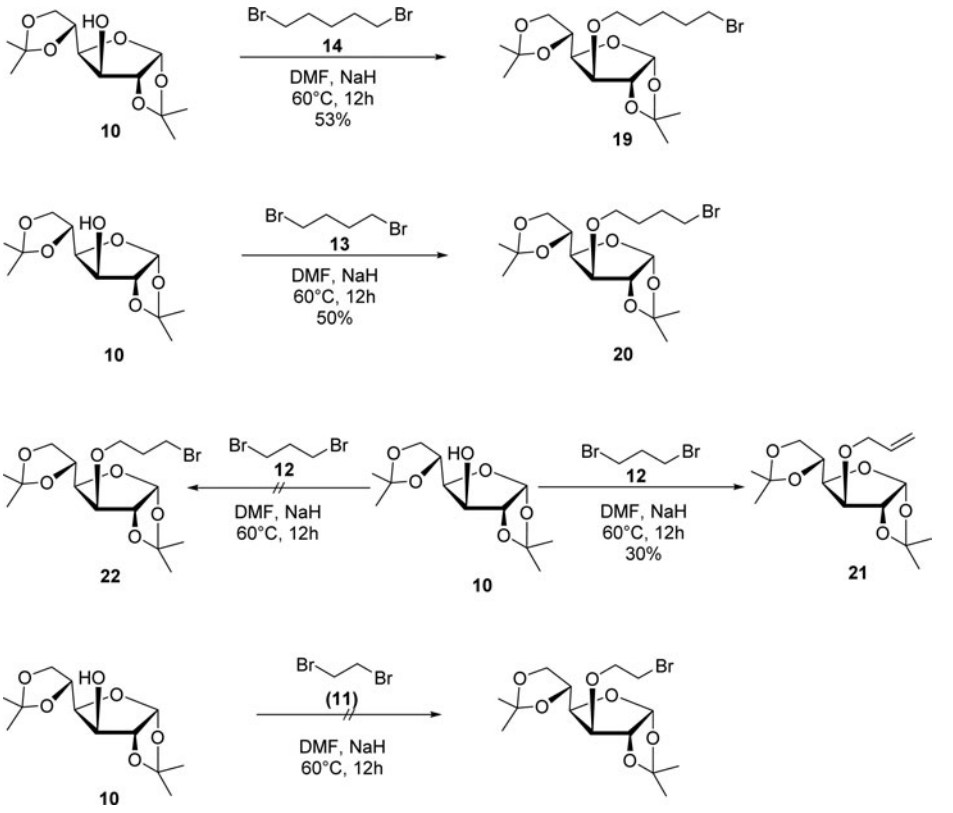
Likewise, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**10**) was treated with alkyl bromides **11**, **12**, **13**, and **14** in dry DMF using NaH as base (Sch. 5). 3-*O*-(5-Bromopentyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose



Scheme 4: Introduction of spacers to **2** to prepare **15**, **16**, and **18**.

(**19**) and 3-*O*-(4-bromobutyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**20**) as well as an elimination product 3-*O*-allyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**21**) were obtained in yields of 53%, 50%, and 30%, respectively. As previously mentioned for compound **17**, 3-*O*-(2-bromoethyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**22**) was not accessible either by nucleophilic substitution of 1,2-dibromoethane with an anion of glycoside **10**.

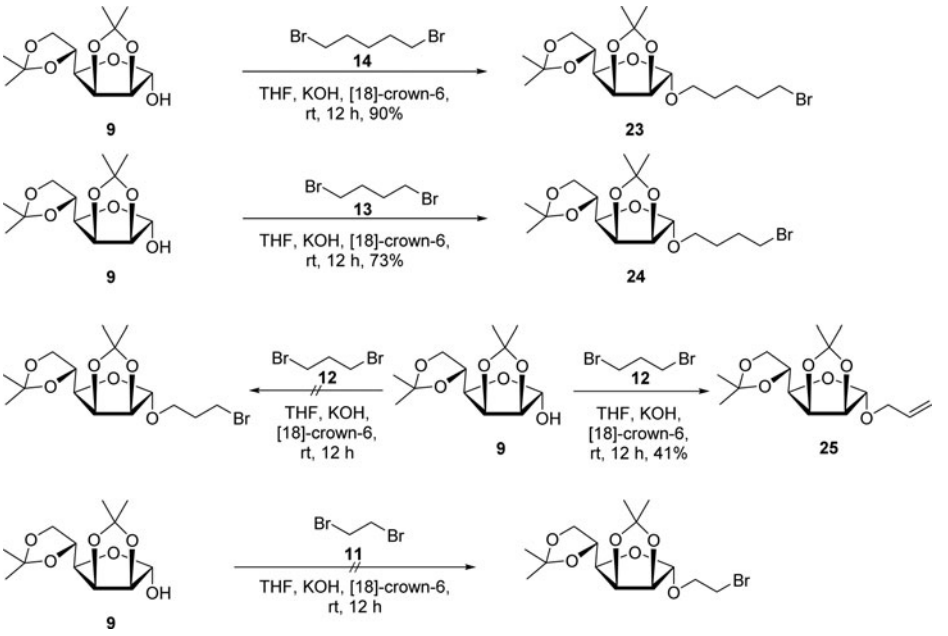
1-*O*-(5-Bromopentyl)-2,3:5,6-di-*O*-isopropylidene-α-D-galactopyranose (**23**), 1-*O*-(4-bromobutyl)-2,3:5,6-di-*O*-isopropylidene-α-D-galactopyranose (**24**), and 1-*O*-allyl-2,3:5,6-di-*O*-isopropylidene-α-D-galactopyranose (**25**) were synthesized from mannoside (**9**) and alkyl bromides **11**, **12,** or **13** using a phase transfer system of THF/water (99.5/0.5; v/v), 18-crown-6 ether, and KOH at ambient temperature (Sch. 6). Compounds **23**, **24**, and **25** were obtained in 90%, 73%, and 41% yields, respectively, after chromatographic purification. As previously described for sugar derivatives **2** and **10**, no reaction between 1,2-dibromoethane (**11**) and 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose



Scheme 5: Introduction of 5-bromopentyl, 4-bromobutyl, and allyl spacers to **10**.

(**9**) was detected, but **9** was recovered from the reaction mixture after standard workup.

Recapitulating, only compounds **15**, **19**, and **23** with 5-bromopentyl spacer as well as **16**, **20,** and **24** with 4-bromobutyl spacer were accessible by nucleophilic substitution of 1,5-dibromopentane (**14**) or 1,4 dibromobutane (**13**) using the anions of galactopyranose **2**, glucopyranose **10**, and mannofuranose **9**. Consequently, we chose another system that gave us access to both pentyl and butyl derivatives of **2**, **9**, and **10** and additionally the opportunity to synthesize propyl- and ethyl-prolonged sugars as well. Alkyl bistosylates, which are widely used in synthetic organic chemistry, such as the synthesis of crown ethers,[43] acetals,[44] and macrocycles,[45] seemed to be promising starting materials. 1,5-Pentanediyl bistosylate (**26**), 1,4-butanediyl bistosylate (**27**), 1,3-propanediyl bistosylate (**28**), and 1,2-ethanediyl bistosylate (**29**) were obtained by reactions of the corresponding diols with *p*-toluenesulfonyl chloride in dry pyridine.[44] Subsequently, all four alkyl spacers of different lengths were successfully introduced to galactose **2**, mannofuranose **9**, and glucofuranoside **10**

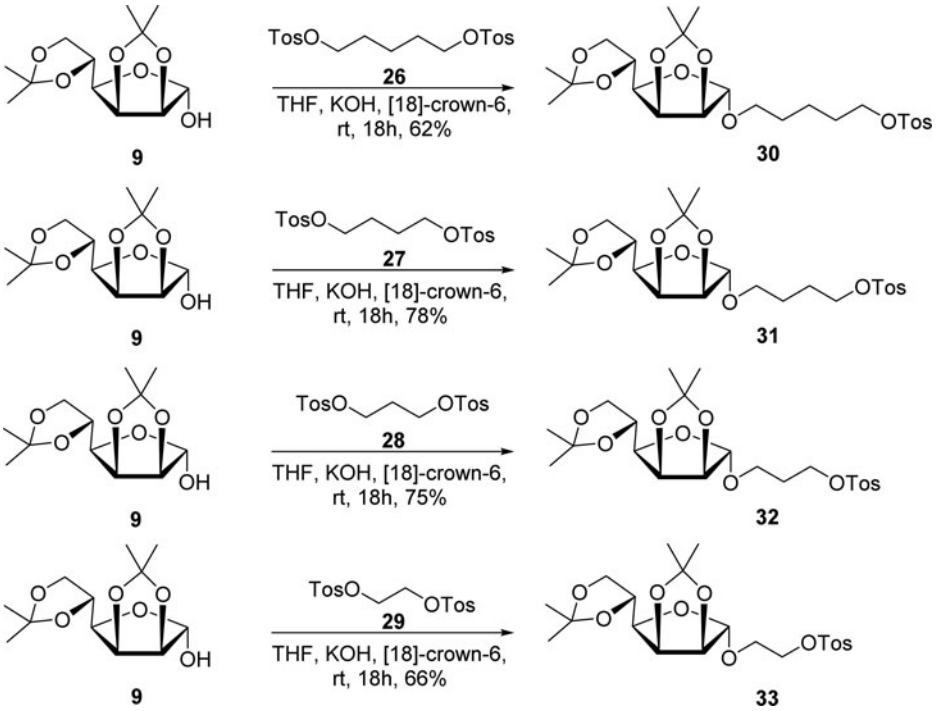


Scheme 6: Synthesis of compounds **23**, **24,** and **25**.

using bistosylates **26**–**29** as starting materials. As shown in Scheme 7, mannosides **30**–**33** were obtained in 62% to 78% yields. Reaction conditions were similar to those described for the transformation of **9** with halogen bromides **11–14**. Contrary to dibromides **11** and **12**, tosylates **28** and **29** granted access to ethyl- and propyl-modified mannosides **32** and **33**.

Similarly, glycosides **34**, **35**, **38**, and **39** were obtained from treatment of galactose **2** and glucose **10** with tosylates **26** and **27** in dry DMF after addition of sodium hydride followed by smooth heating (Sch. 8 and 9). In addition, compounds **36**, **37**, **40**, and **41** were prepared using a phase transfer system of benzene, benzyltriethylammonium chloride, and aqueous potassium hydroxide, which was established previously for nucleophilic substitution of tosylates by nucleophiles.[47] Although the isolated yields were moderate for **40** and **41** (30% to 38%) and low for **36** and **37** (15% to 16%), alkyl tosylates **28** and **29** granted access to both ethyl and propyl prolonged derivates of **2** and **10** (Sch. 8 and 9).

Moreover, because of the low yields for tosylates **36** and **37**, we developed a multistep synthesis to enhance quantities of the given target structures (Sch. 10). Therefore, galactose **2** was reacted with 2-benzyloxyethyl tosylate (**42**) or 3-benzyloxypropyl tosylate (**43**) to form benzyloxides **44** and **45**, respectively. Subsequent reduction of **44** and **45** yielded alcohols **46** and **47,** which were finally tosylated using *p*-toluenesulfonyl chloride and DABCO in



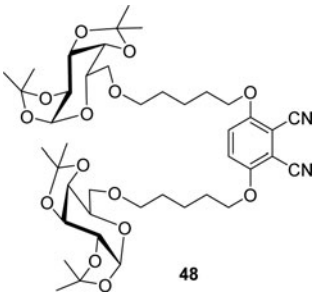
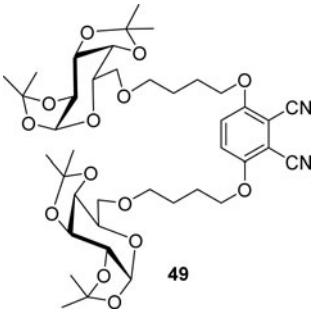
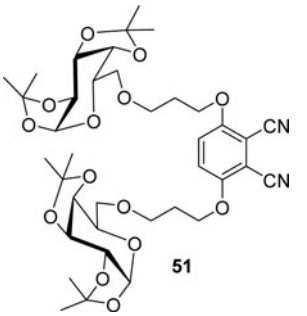
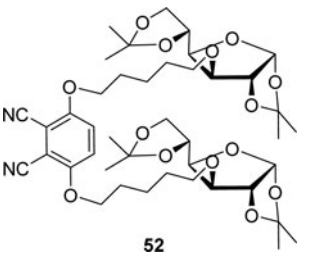
Scheme 7: Synthesis of mannose derivatives **30–33**.

dry ethyl acetate. With these additional synthetic steps, product quantities increased and overall yields of 55% for **36** and 34% for **37** were obtained.

With the prepared carbohydrate bromides as well as carbohydrate tosylates available, we were able to synthesize a set of 3,6-bisglycoconjugated phthalonitriles, which became essential starting materials for new nonperipheral glycoconjugated phthalocyanines. The general procedure for the nucleophilic substitution reaction of bromo-functionalized glycosides **15**, **16**, **19**, **20**, **23**, and **24** or for tosylates **30–41** with hydroquinone **1** in dry DMF under basic conditions is depicted in Scheme 11. Reaction times, yields, and chemical structures of the formed 3,6-bisglycoconjugated phthalonitriles **48–59** are summarized in Table 1. Both carbohydrate bromides and carbohydrate tosylates were suitable precursors for the formation of glycoconjugated phthalonitriles, in which dicyanohydroquinone 3- and 6-positions were substituted by sugar moieties.

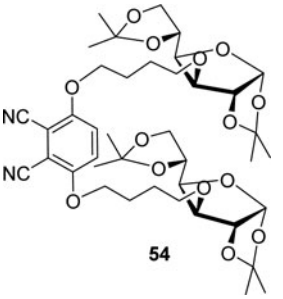
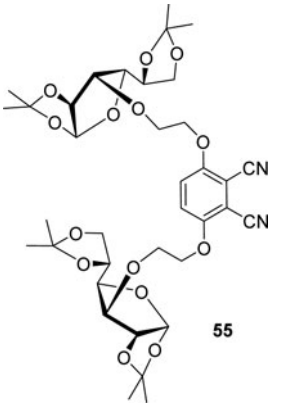
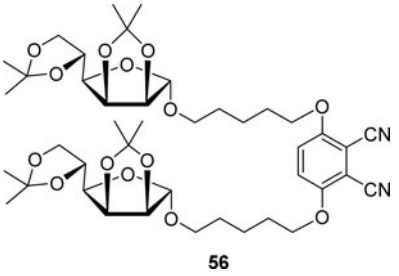
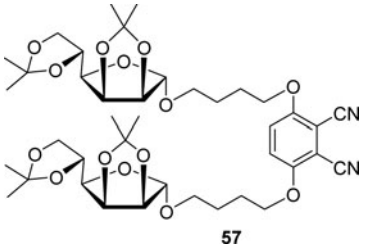
The bromide precursors **15**, **16**, **19**, **20**, **23**, and **24** tended to be more reactive than their corresponding tosylates **30–41**. This finding could be ascribed to a higher leaving tendency of bromide ions in nucleophilic reactions in comparison to tosylates. With the exception of compound **55** (38%), target compounds

Table 1: Time, yields, and product structures of reactions listed in Scheme 11

Sugar Component	Reaction Time	Product	Yield
15 or **34**	18 h	 **48**	91% or 76%
16 or **35**	18 h	 **49**	70% or 57%
36	18 h	 **51**	91%
37	24 h	51	78%
19 or **38**	18 h	 **52**	57% or 53%

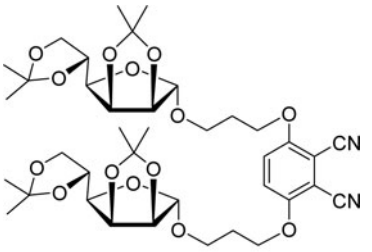
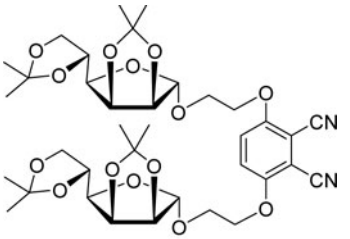
(Continued on next page)

Table 1: Time, yields, and product structures of reactions listed in Scheme 11 (Continued)

Sugar Component	Reaction Time	Product	Yield
20 or **39**	18 h	 **54**	85% or 59%
40	18 h	54	56%
41	36 h	 **55**	36%
23 or **30**	18 h	 **56**	79% or 76%
24 or **31**	18 h	 **57**	65% or 62%

(Continued on next page)

Table 1: Time, yields, and product structures of reactions listed in Scheme 11 (Continued)

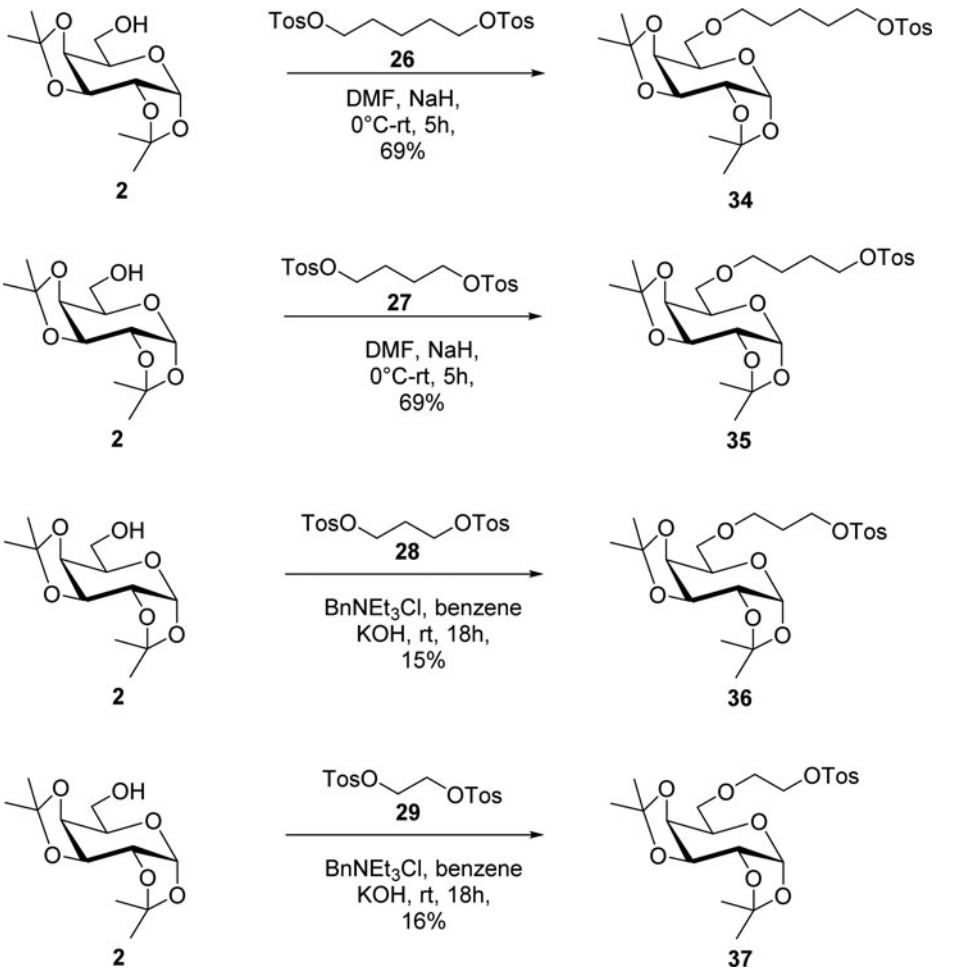
Sugar Component	Reaction Time	Product	Yield
32	18 h	 **58**	63%
33	36 h	 **59**	80%

48–**54** and **56**–**59** were obtained in good to excellent yields (53% to 91%). All synthesized compounds were fully characterized by spectroscopic techniques and elemental analysis, respectively. Analytical data were in agreement with the expected results.

As a short outline of our ongoing work, Scheme 12 depicts the synthesis of one nonperipheral glycoconjugated zinc phthalocyanine **61**, which was obtained from cross-condensation of phthalonitrile (**60**), sugar derivative **48**, and zinc bromide in 2-dimethylaminoethanol (DMAE) at 100°C. The deep green macrocycle was isolated in a 16% yield after chromatographic purification and showed excellent photophysical properties, that is, absorption maxima beyond 700 nm. The syntheses and photophysical properties of other nonperipheral octaglycosylated zinc phthalocyanines will be published elsewhere.

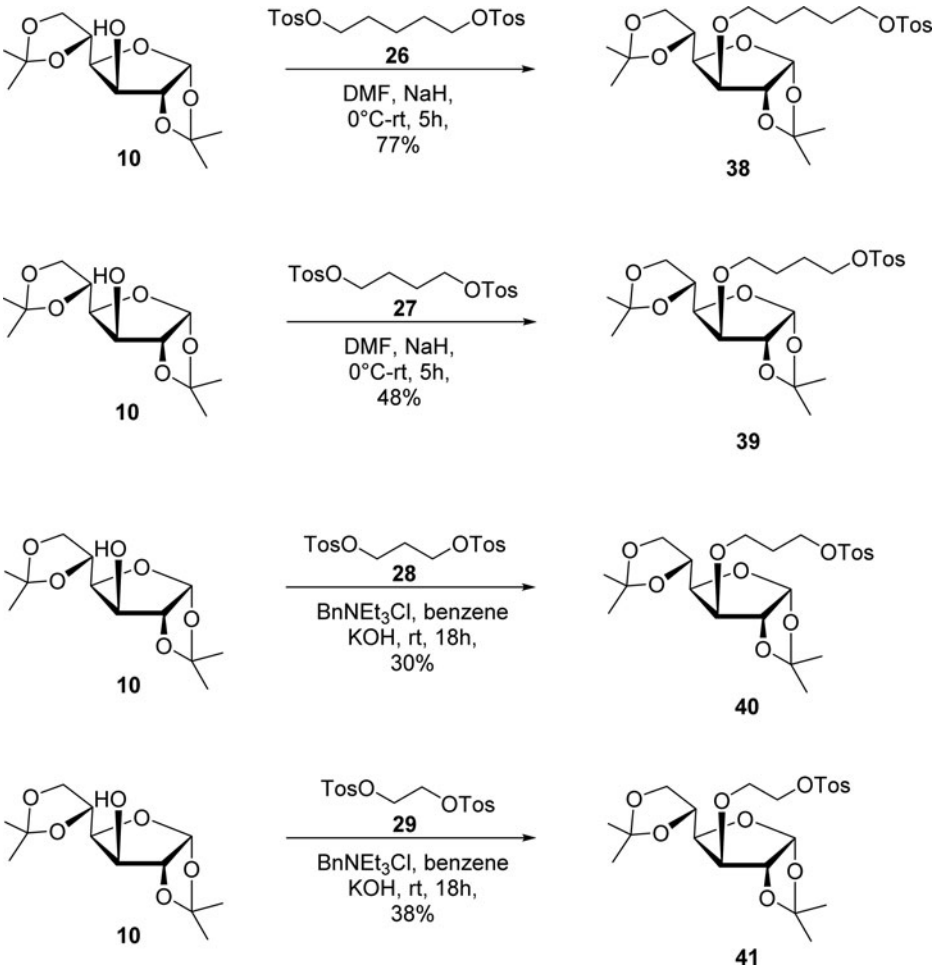
Summary

In this report, we summarized the recent progress that we made on the synthesis of new water-soluble phthalocyanine-based photosensitizers for the application in photodynamic therapy. In the first part of this work, we presented the synthesis of four unknown 3,6-bisglycosylated phthalonitriles 3, 5,



Scheme 8: Synthesis of galactose tosylates **34–37** starting from **2**.

and 6, which were obtained from dicyanohydroquinone (1) and sugars 2, 4, and 7. Additionally, starting from protected sugars 2, 9, and 10, we subsequently synthesized a set of new spacer-prolonged sugar bromides and tosylates 15, 16, 19, 20, 23, 24, and 30–41. Treatment of these bromides and tosylates with hydroquinone yielded phthalonitriles 48–59, which are the starting materials for the preparation of new nonperipheral substituted sugar phthalocyanines with good photophysical properties and solubility in physiological media. Moreover, the first nonperipheral glycoconjugated zinc phthalocyanine 61 was prepared from 48 via cross-condensation with phthalonitrile and zinc bromide as the metal source.

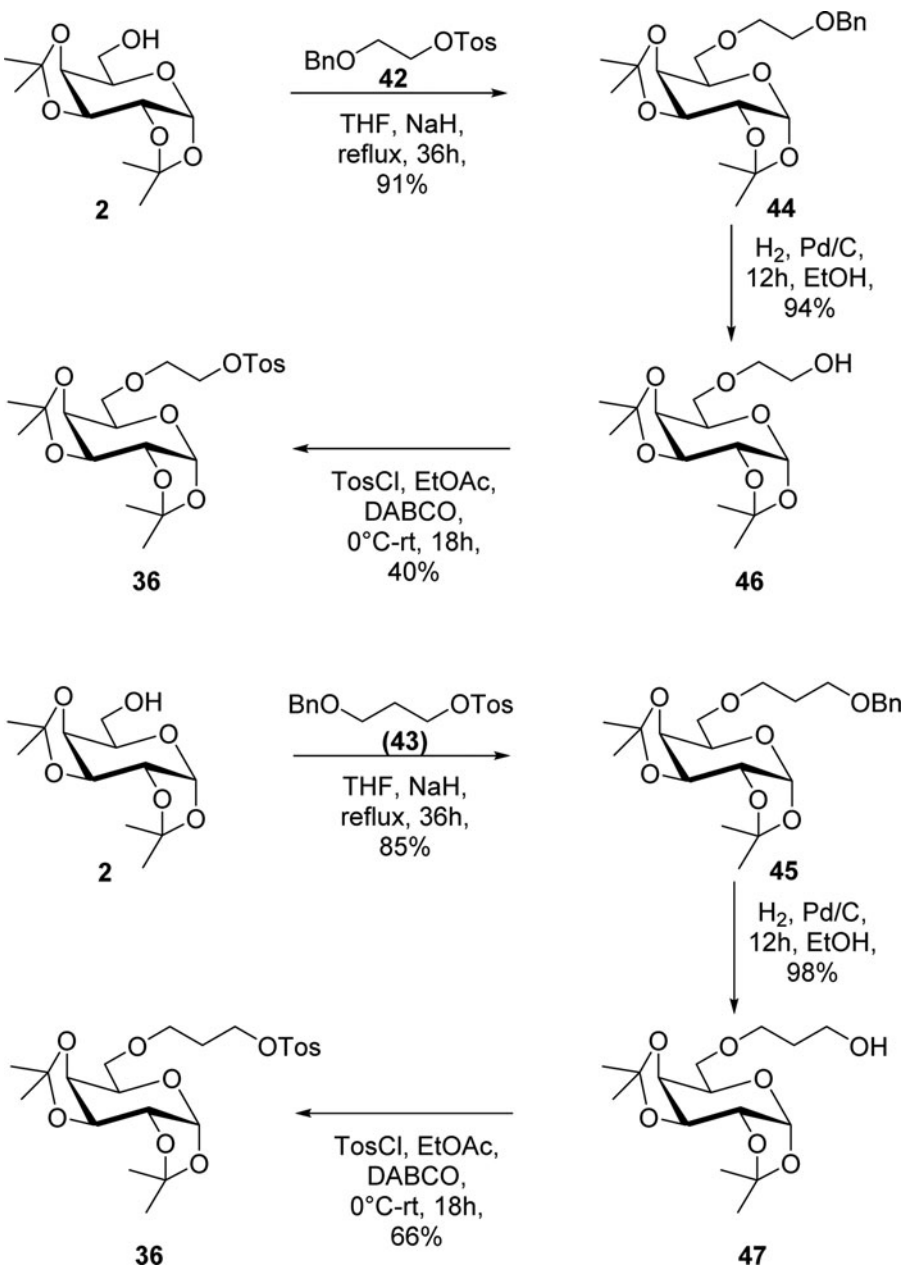


Scheme 9: Reaction of glucose **10** and tosylates **26**–**29**.

EXPERIMENTAL

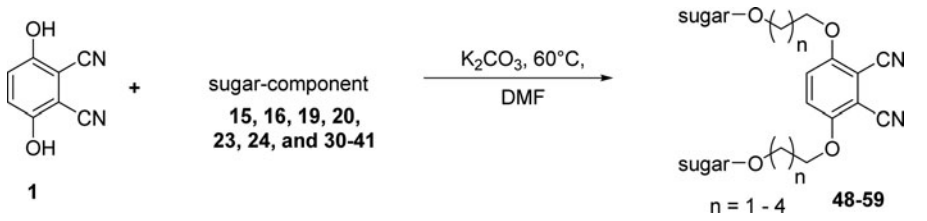
General Methods

Starting materials and reagents were purchased from ABCR GmbH (1,5-dibromopentane, 1,4-dibromobutane, 1,3-dibromopropane, 1,2-dibromoethane) and were of the highest purity available. DMF was distilled from phosphorous pentoxide. All solvents were stored over molecular sieve 3Å under an atmosphere of nitrogen until used. Silica gel 60 (particle size 0.04–0.063 mm) was used for column chromatography. NMR spectra were recorded on a Bruker Avance 400. UV-vis spectra were recorded on a Perkin Elmer Lambda 25 using a 1-cm quartz cell. Melting points were determined with a Büchi Melting Point

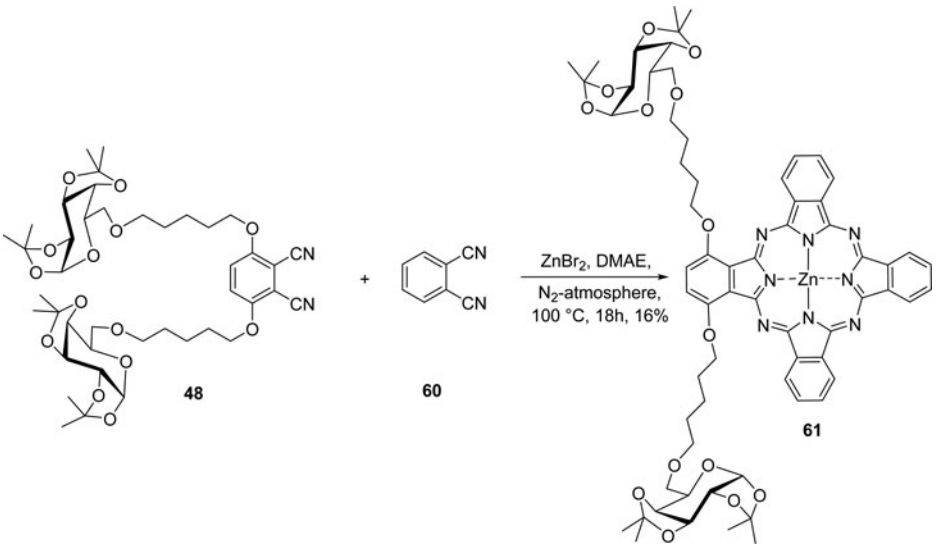


Scheme 10: Multistep synthesis of **46** and **47**.

M-560. Elemental analyses were performed on a HEKAtech Euro EA Analyzer. FT-ICR-MS spectra were recorded on a Bruker Daltonic Apex 2. ESI-TOF spectra were determined with a Bruker Daltonics Maxis G4.



Scheme 11: Reaction of modified sugars **15**, **16**, **19**, **20**, **23, 24,** and **30**–**41** with **1** in dry DMF.



Scheme 12: Synthesis of zinc phthalocyanine 61.

General procedure GP1: introduction of bromoalkyl chains using NaH

A suspension of 1.00 eq. of the protected sugar in dry DMF was cooled to 0°C under an atmosphere of nitrogen. Next, 1.30 eq. of sodium hydride was added to the suspension and cooling was removed. The mixture was stirred for an additional hour at rt before 5.00 eq. of the corresponding dibromide was added in one portion. The mixture was stirred for 12 h at 60°C. Next, the mixture was cooled to rt, diluted with water, and extracted with three portions of DCM. The combined organic layers were dried over $MgSO_4$ and the solvents were removed under reduced pressure. The crude product was purified by column chromatography.

General procedure GP2: introduction of bromoalkyl/tosylalkyl chains using KOH and [18]-crown-6 in THF

A solution of 1.00 eq. of saccharide, 4.00 eq. potassium hydroxide, and 0.01 eq. [18]-crown-6 ether in THF/water (99.5/0.5; v/v) was stirred for 1 h at rt.

Next, 5.00 eq. of the corresponding dibromide or bistosylate were added at once and stirring was continued for 24 to 72 h. The mixture was neutralized with saturated aqueous ammonium chloride and extracted several times with DCM, and the combined organic layers were dried over $MgSO_4$. The solvents were evaporated under reduced pressure and the residue was purified by column chromatography.

General procedure GP3: introduction of tosyl-spacers using DMF and sodium hybrid

A solution of 1.00 eq. of saccharide in dry DMF was cooled to 0°C under an atmosphere of nitrogen. Next, 1.20 eq. of sodium hydride was added to the solution and stirring was continued for 60 min. Next, 4.00 eq. of bistosylate was added to the mixture and stirring was continued for an additional 4 h at rt. The reaction was quenched by addition of a saturated aqueous solution of ammonium chloride and extracted with three portions of DCM, and the combined organic layers were dried over sodium sulfate. After evaporation of the solvents, the residue was purified by column chromatography.

General procedure GP4: introduction of tosyl-spacers using benzene and benzyl triethylammonium chloride

To a solution of 1.00 eq. of saccharide in benzene was added at rt 5.00 eq. of sodium hydroxide (50% in water) as well as 100 mg of benzyl triethylammonium chloride. The suspension was stirred for an additional hour before 4.00 eq. of tosylate was added at once and stirring was continued for 18 h. The solution was neutralized with a saturated aqueous solution of ammonium chloride and the aqueous phase was extracted three times using DCM. The combined organic layers were dried over magnesium sulfate, the solvents were removed under reduced pressure, and the residue was purified by column chromatography.

General procedure GP5: synthesis of 3,6-bisglycoconjugated phthalonitriles

A solution of 1.00 eq. 2,3-dicyanohydroquinone, 12.00 eq. potassium carbonate, and 2.20 eq. saccharide was suspended in dry DMF and heated to 60°C. Stirring was continued for 18 to 36 h at 60°C. The mixture was cooled to rt, water was added, and the phases were separated. The aqueous phase was extracted several times with DCM. The combined organic layers were dried upon magnesium sulfate and the solvent was evaporated under reduced pressure. The residue was purified using column chromatography.

3,6-Bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranos-6-yl)-phthalonitrile (3)

A solution of 27.40 mL (60 mmol) DEAD (40% in toluene) was added dropwise over a period of 5 min to a suspension of 3.20 g (20 mmol) 2,3-dicyanohydroquinone[40] and 15.70 g (60 mmol) PPh_3 in 180 mL of dry toluene. The mixture was stirred at rt until all solids were dissolved. Next, 15.60 g (60 mmol) 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose dissolved in dry toluene was added to the deeply red solution and the mixture was heated to 110°C for 24 h. The solution was cooled to rt and the solvent was evaporated under reduced pressure. The viscous oily residue was purified by column chromatography using a mixture of chloroform and methanol (250:1). Compound **3** was obtained by crystallization from acetone. Colorless solid (5.90 g, 47%); m.p. 180–182°C (acetone); $[\alpha]_D^{20} = -98.8$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 2 H, Ar-*H*), 5.52 (d, $J_{1,2} = 5.1$ Hz, 2 H, *H*-1), 4.67 (dd, $J_{3,4} = 7.8$ Hz, 2 H, *H*-3), 4.42 (d, $J_{4,5} = 8$ Hz, 2 H, *H*-4), 4.35 (dd, $J_{2,3} = 2.3$ Hz, 2 H, *H*-2), 4.26–4.18 (m, 6 H, *H*-5, *H*-6a, *H*-6b), 1.54, 1.43, 1.34, 1.33 (4s, 12H, -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 155.2 (2 C, Ar-*C*), 119.2 (2 C, Ar-*C*), 112.8 (2 C, Ar-*C*), 109.5 (2 C, 2 × -*C*$(CH_3)_2$), 109.0 (2 C, 2 × -*C*$(CH_3)_2$), 105.5 (2 C, 2 × -*C*N), 96.2 (2 C, *C*-1), 70.6 (2 C, *C*-2),* 70.5 (2 C, *C*-4),* 70.5 (2 C, *C*-3),* 68.8 (2 C, *C*-6), 66.3 (2 C, *C*-5), 26.2, 26.1, 25.0, 24.4 (8 C, 8 × -*C*H_3); IR (Neat) $\tilde{\nu}_{max}$ 2988, 2938, 2232, 1579, 1488, 1454, 1385, 1214, 1009, 920, 810, 514 cm^{-1}; Anal. calcd. for $C_{32}H_{40}N_2O_{12}$: C 59.62; H 6.25; N 4.35; Found: C 59.52; H 6.41; N 4.11.

*Signals could be reversed.

3,6-Bis(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)phthalonitrile (5)

A solution of 1.00 mL (2.20 mmol) DEAD (40% in toluene) was added dropwise over a period of 5 min to a suspension of 0.16 g (1.00 mmol) 2,3-dicyanohydroquinone[40] and 0.58 g (2.20 mmol) PPh_3 in 30 mL of dry THF and the mixture was stirred for 10 min at rt. Next, 1.19 g (2.20 mmol) 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose dissolved in 10 mL of dry THF was added to the deeply red solution and the mixture was heated under reflux for 3 h. The solution was cooled to rt and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography using a mixture of toluene and acetone (25:1). Compound **5** was obtained by recrystallization from ethanol/acetone as colorless needles (0.93 g, 77%); m.p. 138–140°C (ethanol/acetone); $[\alpha]_D^{20} = -58.4$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.40 (m, 4 H, Ar-*H*), 7.36–7.26 (m, 32 H, Ar-*H*), 7.22–7.19 (m, 6H, Ar-*H*), 5.16 (d, 2 H, -CH_2Ph), 5.02 (d, 2 H, -CH_2Ph), 4.99 (d, $J_{1,2} = 7.3$ Hz, 2 H,

H-1), 4.91–4.85 (m, 6 H, -CH_2Ph), 4.59–4.47 (m, 6 H, -CH_2Ph), 3.85 (dd, $J_{2,3}$ = 8.8 Hz, 2 H, *H*-2), 3.79–3.74 (m, 4 H, *H*-3, *H*-6a), 3.70–3.61 (m, 6 H, *H*-4, *H*-5, *H*-6b); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 154.2, 138.2, 137.9, 137.7, 137.7, 128.5, 128.5, 128.4, 128.3, 128.0, 128.0, 127.9, 127.8, 127.7, 121.0, 112.8 (54 C, Ar-*C*), 105.8 (2 C, -*C*N), 101.2 (2 C, *C*-1), 84.3 (2 C, *C*-3), 81.4 (2 C, *C*-2), 77.3 (2 C, *C*-4), 75.8 (2 C, -*C*H_2-), 75.5 (2 C, *C*-5), 75.4 (2 C, -*C*H_2-), 75.2 (2 C, -*C*H_2-), 73.5 (2 C, -*C*H_2-), 68.7 (2 C, *C*-6); IR (Neat) $\tilde{\nu}_{max}$ 3089, 3062, 3030, 2867, 2230, 1497, 1482, 1453, 1363, 1274, 1209, 1071, 1027, 813, 736 cm^{-1}; Anal. calcd. for $C_{76}H_{72}N_2O_{12}$: C 75.73; H 6.02; N 2.32; Found: C 75.92; H 6.00; N 2.30.

3,6-Bis-(β-D-glucopyranosyl)-phthalonitrile (6)

A solution of sodium methanolate in methanol (5.4 M, 150 μL) was added at rt to a suspension of 8.41 g (10.25 mmol) of compound **8** in 100 mL methanol. Stirring at rt was continued until TLC showed the complete disappearance of the starting material. Dowex H^+ ion exchange resin was added and subsequently removed by filtration. Methanol was removed under reduced pressure to yield an amorphous solid (4.11 g, 83%); $[\alpha]_D^{20}$ = –34.7 (c 0.5, MeOH); ^{1}H NMR (400 MHz, MeOH-d_4): δ 7.64 (s, 2 H, Ar-*H*), 5.10 (d, $J_{1,2}$ = 7.6 Hz, 2 H, *H*-1), 3.88 (dd, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 12.0 Hz, 2 H, *H*-6a), 3.68 (dd, $J_{5,6b}$ = 5.8 Hz, 2 H, *H*-6b), 3.55–3.37 (m, 8 H, *H*-2, *H*-3, *H*-4, *H*-5); ^{13}C NMR (100.6 MHz, MeOH-d_4): δ = 156.0, 123.8, 114.1 (6 C, Ar-*C*), 106.6 (2 C, -*C*N), 102.5 (2 C, *C*-1), 78.7 (2 C, *C*-3),* 78.2 (2 C, *C*-2),* 74.7 (2 C, *C*-4),* 71.2 (2 C, *C*-5),* 62.6 (2 C, *C*-6); IR (Neat) $\tilde{\nu}_{max}$ 3385, 2917, 2242, 1638, 1582, 1485, 1403, 1281, 1076, 924, 890, 825, 753, 703 cm^{-1}; Anal. calcd. for $C_{20}H_{24}N_2O_{12}$: C 49.59; H 4.99; N 5.78; Found: C 49.23; H 5.76; N 5.43.

*Signals could be reversed.

3,6,-Bis-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)phthalonitrile (8)

A suspension of 3.14 g (21.20 mmol) of 2,3-dicyanohydroquinone,[40] 18.20 g (44.60 mmol) 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranososyl bromide **(7),** and 17.28 g (125.20 mmol) K_2CO_3 in 200 mL of dry acetonitrile was heated under reflux for 36 h. The yellow suspension was cooled to rt, filtered, and concentrated. The filter cake was washed with acetonitrile and the combined solvents were concentrated under reduced pressure. Chromatography of the residue on silica gel using a mixture of *n*-hexane and ethyl acetate (1:1, v/v) and subsequent crystallization from methanol yielded **8** as a colorless solid (10.40 g, 60%); m.p. 216°C; $[\alpha]_D^{20}$ = –75.7 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (s, 2 H, Ar-*H*), 5.30–5.23 (m, 4 H, *H*-2, *H*-3), 5.19–5.14 (m, 2 H, *H*-4), 5.06–5.04 (m, 2 H, *H*-1), 4.28–4.20 (m, 4 H, *H*-6_a, *H*-6_b), 3.85–3.81 (m, 2 H, *H*-5), 2.11, 2.08, 2.04, 2.02 (4s, 24 H, 8 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$):

δ 170.5, 170.2, 169.5, 169.4 (8 C, -O*C*OCH$_3$), 154.6, 124.9, 111.7 (6 C, Ar-*C*), 108.5 (2 C, -*C*N), 100.6 (2 C, *C*-1), 72.7 (2 C, *C*-5), 72.7 (2 C, *C*-3),* 70.4 (2 C, *C*-2),* 67.9 (2 C, *C*-4), 61.5 (2 C, *C*-6), 20.8, 20.7, 20.6 (8 C, -COCH$_3$); IR (Neat) $\tilde{\nu}_{max}$ 3455, 2240, 1758, 1637, 1481, 1432, 1379, 1236, 1074, 1039, 904 cm^{-1}; Anal. calcd. for $C_{36}H_{40}N_2O_{20}$: C 52.68; H 4.91; N 3.41; Found: C 52.82; H 4.90; N 3.26.

*Signals could be reversed.

6-*O*-(5-Bromopentyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (15)

Pursuant to general procedure GP1, 1.40 g (5.38 mmol) of saccharide **2**, 168 mg (7.00 mmol) sodium hydride, and 3.64 mL (27.00 mmol) 1,5-dibromopentane **(14)** in 60 mL of dry DMF and chromatographic purification on silica gel using a mixture of toluene/acetone (30:1) gave compound **15** as a colorless oil (1.26 g, 59%). Analytical data were in accordance with the literature.[41]

6-*O*-(4-Bromobutyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (16)

Pursuant to general procedure GP1, 2.80 g (10.76 mmol) of saccharide **2**, 336 mg (13.99 mmol) sodium hydride, and 6.40 mL (54.00 mmol) 1,4-dibromobutane **(13)** in 60 mL of dry DMF and chromatographic purification on silica gel using a mixture of toluene/acetone (30:1) gave compound **16** as a colorless oil (3.34 g, 55%). Analytical data were in accordance with the literature.[41]

6-*O*-Allyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (18)

Pursuant to general procedure GP1, 2.80 g (10.76 mmol) of saccharide **2**, 337 mg (14.04 mmol) sodium hydride, and 5.48 mL (54.00 mmol) 1,3-dibromopropane **(12)** in 60 mL of dry DMF and chromatographic purification on silica gel using a mixture of toluene/acetone (30:1) gave compound **18** as a colorless oil (0.89 g, 27%). Analytical data were in accordance with the literature.[42]

3-*O*-(5-Bromopentyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (19)

Pursuant to general procedure GP1, 5.20 g (20.00 mmol) of saccharide **10**, 624 mg (26.00 mmol) sodium hydride, and 13.47 mL (100.00 mmol) 1,5-dibromopentane **(14)** in 75 mL of dry DMF and chromatographic purification on silica gel using a mixture of toluene/acetone (30:1) gave compound **19** as a

colorless oil (4.33 g, 53%). Analytical data were in accordance with the literature.[41]

3-*O*-(4-Bromobutyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (20)

Pursuant to general procedure GP1, 5.20 g (20.00 mmol) of saccharide **10**, 624 mg (26.00 mol) sodium hydride, and 11.81 mL (100.00 mmol) 1,4-dibromobutane **(13)** in 75 mL of dry DMF and chromatographic purification on silica gel using a mixture of toluene/acetone (30:1) gave compound **20** as a colorless oil (3.93 g, 50%). Analytical data were in accordance with the literature.[41]

3-*O*-Allyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (21)

Pursuant to general procedure GP1, 1.72 g (6.62 mmol) of saccharide **10**, 206 mg (8.60 mol) sodium hydride, and 3.36 mL (33.10 mmol) 1,3-dibromopropane **(12)** in 50 mL of dry DMF and chromatographic purification on silica gel using a mixture of toluene/acetone (30:1) gave compound **21** as a colorless oil (0.58 g, 30%). Analytical data were in accordance with the literature.[41]

1-*O*-(5-Bromopentyl)-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (23)

Pursuant to general procedure GP2, 7.00 g (26.92 mmol) of saccharide **9**, 6.03 g (107.30 mmol) potassium hydroxide, 72 mg (0.27 mmol) [18]-crown-6 ether, and 18.00 mL (134.50 mmol) 1,5-dibromopentane **(15)** in 250 mL THF/water (99.5:0.5; v:v) and chromatographic purification on silica gel using a mixture of *n*-hexane/ethyl acetate (7:1) gave compound **23** as a colorless oil (9.90 g, 90%); $[\alpha]_D^{20} = +35.6$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.97 (s, 1 H, *H*-1), 4.78 (dd, 1 H, $J_{3,4} = 3.7$ Hz, *H*-3), 4.58 (d, 1 H, $J_{2,3} = 6.1$ Hz, *H*-2), 4.43–4.38 (m, 1 H, *H*-5), 4.11 (dd, 1 H, $J = 8.6$ Hz, 6.3 Hz, *H*-6_a), 4.03 (dd, 1 H, $J = 8.6$ Hz, 4.4 Hz, *H*-6_b), 3.92 (dd, 1 H, $J_{4,5} = 7.8$ Hz, *H*-4), 3.66–3.60 (m, 1 H, H_a -OCH_2-), 3.43–3.36 (m, 3 H, H_b -OCH_2-, -CH_2Br-), 1.91–1.84 (m, 2 H, -CH_2-), 1.63–1.55 (m, 2 H, -CH_2-), 1.52–1.48 (m, 2 H, -CH_2-), 1.47, 1.46, 1.38, 1.32 (4s, 12 H, 4 × – -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 112.6, 109.2 (2 C, -*C*(CH_3)$_2$), 106.3 (1 C, *C*-1), 85.0 (1 C, *C*-2), 80.2 (1 C, *C*-4), 79.5 (1 C, *C*-3), 73.1 (1 C, *C*-5), 67.1 (1 C, -O*C*H_2-), 66.9 (1 C, *C*-6), 33.6, 32.4, 28.53, 24.8 (4 C, 4 × -*C*H_2-), 26.9, 25.9, 25.2, 24.5 (4 C, 4 × -*C*H_3); MS (FAB): m/z 409 $[M+H]^+$, 393 $[M\text{-}CH_3]^+$, $[M\text{-}C_{12}H_{19}O_6]^+$; Anal. calcd. for $C_{17}H_{29}BrO_6$: C 49.88; H 7.14; Found: C 49.79; H 7.12.

1-*O*-(4-Bromobutyl)-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (24)

Pursuant to general procedure GP2, 5.20 g (20.00 mmol) of saccharide **9**, 4.48 g (80.00 mmol) potassium hydroxide, 53 mg (0.20 mmol) [18]-crown-6 ether, and 11.80 mL (100.00 mmol) 1,4-dibromobutane **(13)** in 250 mL THF/water (99.5:0.5; v:v) and chromatographic purification on silica gel using a mixture of *n*-hexane/ethyl acetate (7:1) gave compound **24** as a colorless oil (5.75 g, 73%); $[\alpha]_D^{20} = +39.5$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.97 (s, 1 H, *H*-1), 4.79 (dd, 1 H, $J_{3,4} = 3.5$ Hz, *H*-3), 4.58 (d, 1 H, $J_{2,3} = 5.8$ Hz, *H*-2), 4.43–4.38 (m, 1 H, *H*-5), 4.11 (dd, 1 H, $J =$ 8.6 Hz, 6.3 Hz, *H*-6$_a$), 4.03 (dd, 1 H, $J = 8.6$ Hz, 4.5 Hz, *H*-6$_b$), 3.92 (dd, 1 H, $J_{4,5} = 7.6$ Hz, *H*-4), 3.69–3.63 (m, 1 H, H_a -OCH_2-), 3.45–3.38 (m, 3 H, H_b -OCH_2-, -C*H*$_2$Br-), 1.96–1.89 (m, 2 H, -C*H*$_2$-), 1.74–1.68 (m, 2 H, -C*H*$_2$-), 1.47, 1.46, 1.38, 1.33 (4s, 12 H, 4 × -C*H*$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 112.6, 109.2 (2 C, 2 × -*C*$(CH_3)_2$), 106.3 (1 C, *C*-1), 85.1 (1 C, *C*-2), 80.3 (1 C, *C*-4), 79.5 (1 C, *C*-3), 73.1 (1 C, *C*-5), 66.9 (1 C, *C*-6), 66.4 (1 C, -O*C*H_2-), 33.4, 29.5, 28.0 (3 C, 3 × -*C*H_2-), 26.9, 25.9, 25.1, 24.1 (4 C, 4 × -*C*H_3); MS (FAB): m/z 395 $[M+H]^+$, 379 $[M\text{-}CH_3]^+$; Anal. calcd. for $C_{16}H_{27}BrO_6$: C 48.62; H 6.88; Found: C 48.48; H 6.83.

1-*O*-Allyl-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (25)

Pursuant to general procedure GP2, 1.30 g (5.00 mmol) of saccharide **9**, 1.12 g (20.00 mmol) potassium hydroxide, 13 mg (0.05 mmol) [18]-crown-6 ether, and 2.54 mL (25.00 mmol) 1,3-dibromopropane **(12)** in 50 mL THF/water (99.5:0.5; v:v) and chromatographic purification on silica gel using a mixture of *n*-hexane/ethyl acetate (7:1) gave compound **25** as an oily residue (0.62 g, 41%). Analytical data were in accordance with literature.[48]

1-*O*-[(5-*p*-Toluenesulfonyl)-pentan-1-yl]-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (30)

Pursuant to general procedure GP2, 4.30 g (16.52 mmol) of **9**, 13.63 g (33.04 mmol) 1,5-bis(*p*-toluenesulfonyl)pentane **(26)**, 3.70 g (66.08 mmol) KOH, and 45 mg (0.17 mmol) 18-crown-6 ether in 150 mL THF and chromatographic purification on silica gel (toluene/acetone 25:1) gave **30** as a colorless oil (5.16 g, 62%); $[\alpha]_D^{20} = +27.8$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2 H, Ar-*H*), 7.35 (d, 2 H, Ar-*H*), 4.94 (s, 1 H, *H*-1), 4.77 (dd, 1 H, $J_{3,4} =$ 3,5 Hz, *H*-3), 4.56 (d, 1 H, $J_{2,3} = 5.8$ Hz, *H*-2), 4.40 (ddd, 1 H, $J_{5,6a} = 6.2$ Hz, $J_{5,6b} = 4.4$ Hz, *H*-5), 4.12–4.09 (m, 1 H, *H*-6a), 4.04–4.00 (m, 3 H, *H*-6b, -C*H*$_2$-), 3.90 (dd, 1 H, $J_{4,5} = 7.6$ Hz, *H*-4), 3.61–3.55 (m, 1 H, -C*H*$_2$-), 3.35–3.29 (m, 1 H, -C*H*$_2$-), 2.46 (s, 3 H, Ar-C*H*$_3$), 1.70–1.63 (m, 2 H, -C*H*$_2$-), 1.54–1.47 (m, 2 H, -C*H*$_2$-), 1.47, 1.45 (2s, 6 H, 2 × -C*H*$_3$), 1.40–1.34 (m, 2 H, -C*H*$_2$-), 1.38, 1.33 (2s,

6 H, 2 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.7, 133.1, 129.8, 127.9 (6 C, Ar-*C*), 112.6, 109.2 (2 C, 2 × -*C*(CH_3)$_2$), 106.3 (1 C, *C*-1), 85.0 (1 C, *C*-2), 80.2 (1 C, *C*-4), 79.5 (1 C, *C*-2), 73.1 (1 C, *C*-5), 70.4 (1 C, -*C*H_2-), 66.9, 66.9 (2 C, *C*-6, -*C*H_2-), 28.7, 28.6 (2 C, 2 × -*C*H_2-), 26.9, 25.9, 25.1, 24.5 (4 C, 4 × -*C*H_3), 22.1 (1 C, -*C*H_2-), 21.6 (1 C, Ar-*C*H_3); MS (FAB): m/z 523 $[M+Na]^+$, 485 $[M-CH_3]^+$; ESI-TOF-MS $[M+Na]^+$ calcd. for $C_{24}H_{36}NaO_9S$: 523.19722; Found: 523.19811.

1-*O*-[(4-*p*-Toluenesulfonyl)-butan-1-yl]-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (31)

Pursuant to general procedure GP2, 5.40 g (20.00 mmol) of **9**, 15.92 g (40.00 mmol) 1,4-bis(*p*-toluenesulfonyl)butane **(27)**, 4.48 g (80.00 mmol) KOH, and 45 mg (0.17 mmol) 18-crown-6 ether in 150 mL THF and chromatographic purification on silica gel (toluene/acetone 25:1) gave **31** as a colorless oil (7.56 g, 78%); $[\alpha]_D^{20} = +30.2$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2 H, Ar-*H*), 7.36 (d, 2 H, Ar-*H*), 4.92 (s, 1 H, *H*-1), 4.75 (dd, 1 H, $J_{3,4} = 3.5$ Hz, *H*-3), 4.53 (d, 1 H, $J_{2,3} = 5.8$ Hz, *H*-2), 4.39 (ddd, 1 H, $J_{5,6a} = 6.3$ Hz, $J_{5,6b} = 4.3$ Hz, *H*-5), 4.12–4.10 (m, 1 H, *H*-6a), 4.05 (t, 2 H, -CH_2-), 4.02–3.99 (m, 1 H, *H*-6b), 3.88 (dd, 1 H, $J_{4,5} = 7.6$ Hz, *H*-4), 3.62–3.57 (m, 1 H, -CH_2-), 3.35–3.29 (m, 1 H, -CH_2-), 2.46 (s, 3 H, Ar-CH_3), 1.75–1.68 (m, 2 H, -CH_2-), 1.62–1.57 (m, 2 H, -CH_2-), 1.46, 1.45, 1.38, 1.32 (4s, 12 H, 4 × -CH_3); ^{13}C-NMR (100.6 MHz, $CDCl_3$): δ 144.7, 133.1, 129.8, 127.9 (6 C, Ar-*C*), 112.6, 109.2 (2 C, 2 × -*C*(CH_3)$_2$), 106.3 (1 C, *C*-1), 85.0 (1 C, *C*-2), 80.3 (1 C, *C*-4), 79.5 (1 C, *C*-3), 73.1 (1 C, *C*-5), 70.1 (1 C, -*C*H_2-), 66.9 (1 C, *C*-6), 66.4 (1 C, -*C*H_2-), 26.9, 25.9 (2 C, 2 × -*C*H_3), 25.8, 25.4 (2 C, 2 × -*C*H_2-), 25.1, 24.5 (2 C, 2 × -*C*H_3), 21.6 (1 C, Ar-*C*H_3); MS (FAB): m/z 471 $[M-CH_3]^+$; ESI-TOF-MS $[M+Na]^+$ calcd. for $C_{23}H_{34}NaO_9S$: 509.18227; Found: 509.18157.

1-*O*-[(3-*p*-Toluenesulfonyl)-propan-1-yl]-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (32)

Pursuant to general procedure GP2, 1.46 g (5.63 mmol) of **9**, 10.80 g (28.13 mmol) 1,3-bis(*p*-toluenesulfonyl)propane **(28)**, 1.26 g (22.50 mmol) KOH, and 16 mg (0.06 mmol) 18-crown-6 ether in 80 mL THF and chromatographic purification on silica gel (toluene/acetone 25:1) and crystallization from ethanol gave **32** as colorless crystals (2.00 g, 75%); mp 96–97°C (EtOH); $[\alpha]_D^{20} = +21.6$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2 H, *H*-aromat.), 7.36 (d, 2 H, Ar-*H*), 4.82 (s, 1 H, *H*-1), 4.73 (dd, 1 H, $J_{3,4} = 3.5$ Hz, *H*-3), 4.44 (d, 1 H, $J_{2,3} = 5.8$ Hz, *H*-2), 4.39–4.35 (m, 1 H, $J_{5,6a} = 4.6$ Hz, $J_{5,6b} = 8.8$ Hz, *H*-5), 4.13–4.08 (m, 3 H, *H*-6a, -CH_2-), 4.01 (dd, 1 H, *H*-6b), 3.86 (dd, 1 H, $J_{4,5} = 7.6$ Hz, *H*-4), 3.66–3.62 (m, 1 H, -CH_2-), 3.39–3.33 (m, 1 H, -CH_2-), 2.46 (s, 3 H, Ar-*C*H_3), 1.95–1.83 (m, 2 H, -CH_2-), 1.46, 1.45, 1.38, 1.32 (4s, 12 H, 4 ×

-C(CH_3)$_2$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.8, 133.0, 129.8, 127.9 (6 C, Ar-*C*), 112.6, 109.2 (2 C, 2 × -*C*(CH_3)$_2$), 106.3 (1 C, *C*-1), 84.9 (1 C, *C*-2), 80.4 (1 C, *C*-4), 79.4 (1 C, *C*-3), 73.1 (1 C, *C*-5), 67.2 (1 C, *C*-6),* 66.9 (1 C, -*C*H_2-),* 62.7 (1 C, -*C*H_2-), 28.9 (1 C, -*C*H_2-), 26.8, 25.9, 25.2, 24.5 (4 C, 4 × -C(*C*H_3)$_2$), 21.6 (1 C, -*C*H_3); MS (FAB): m/z 473 $[M+H]^+$, 457 $[M\text{-}CH_3]^+$; Anal. calcd. for $C_{22}H_{32}O_9S$: C 55.92; H 6.83; S 6.79; Found: C 56.24; H 6.81; S 6.80.

*Signals could be reversed.

1-*O*-[(2-*p*-Toluenesulfonyl)-ethan-1-yl]-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (33)

Pursuant to general procedure GP2, 5.39 g (20.72 mmol) of **9**, 23.00 g (62.16 mmol) 1,3-bis(*p*-toluenesulfonyl)propane **(29)**, 4.64 g (82.88 mmol) KOH, and 55 mg (0.21 mmol) 18-crown-6 ether in 200 mL THF and chromatographic purification on silica gel (toluene/acetone 25:1) gave **33** as an amorphous solid (6.31 g, 66%); $[\alpha]_D^{20} = +41.1$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2 H, Ar-*H*), 7.35 (d, 2 H, Ar-*H*), 4.90 (s, 1 H, *H*-1), 4.71 (dd, 1 H, $J_{3,4} = 3.8$ Hz, *H*-3), 4.47 (d, 1 H, $J_{2,3} = 5.8$ Hz, *H*-2), 4.36 (ddd, 1 H, $J_{5,6a} = 4.6$ Hz, $J_{5,6b} = 6.3$ Hz, *H*-5), 4.21–4.11 (m, 2 H, -CH_2-), 4.09 (dd, 1 H, *H*-6a), 3.98 (dd, 1 H, *H*-6b), 3.87 (dd, 1 H, $J_{4,5} = 7.6$ Hz, *H*–4), 3.78–3.73 (m, 1 H, -CH_2-), 3.62–3.57 (m, 1 H, -CH_2-), 2.46 (s, 3 H, Ar-CH_3), 1.44, 1.38, 1.31 (3s, 12 H, 4 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.8, 133.1, 129.8, 127.9 (6 C, Ar-*C*), 112.6, 109.2 (2 C, 2 × -*C*(CH_3)$_2$), 106.3 (1 C, *C*-1), 84.8 (1 C, *C*-2), 80.5 (1 C, *C*-4), 79.3 (1 C, *C*-3), 73.0 (1 C, *C*-5), 68.7 (1 C, -*C*H_2-), 66.8 (1 C, *C*-6), 64.6 (1 C, -*C*H_2-), 26.8, 25.8, 25.2, 24.5 (4 C, 4 × -*C*H_3), 21.6 (1 C, Ar-*C*H_3); MS (FAB): m/z 481 $[M+Na]^+$, 443 $[M\text{-}CH_3]^+$; ESI-TOF-MS $[M+Na]^+$ calcd. for $C_{21}H_{30}NaO_9S$: 481.15093; Found: 481.15027.

6-*O*-[5-(*p*-Toluenesulfonyl)-pentan-1-yl]-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (34)

Pursuant to general procedure GP3, 2.60 g (10.00 mmol) **2**, 288 mg (12.00 mmol) sodium hydride, and 16.50 g (40.00 mmol) 1,5-bis(*p*-toluenesulfonyl)pentane **(26)** and chromatographic purification on silica gel (toluene/acetone 25:1) gave **34** as colorless oil (3.43 g, 69%); $[\alpha]_D^{20} = -42.2$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 2 H, $J = 8.3$ Hz, Ar-*H*), 7.35 (d, 2 H, $J = 8.6$ Hz, Ar-*H*), 5.53 (d, 1 H, $J_{1,2} = 5.1$ Hz, *H*-1), 4.59 (dd, 1 H, $J_{3,4} = 8.1$ Hz, *H*-3), 4.30 (dd, 1 H, $J_{2,3} = 2.3$ Hz, *H*-2), 4.23 (dd, 1 H, $J_{4,5} = 1.8$ Hz, *H*-4), 4.02 (t, 2 H, $J_{6a,6b} = 6.6$ Hz, *H*-6a, *H*-6b), 3.95–3.92 (m, 1 H, *H*-5), 3.62–3.52 (m, 2 H, -CH_2-), 3.49–3.38 (m, 2 H, -CH_2-), 2.45 (s, 3 H, Ar-CH_3), 1.70–1.63 (m, 2 H, -CH_2-), 1.56–1.49 (m, 5 H, -CH_2-, -CH_3), 1.44 (s, 3 H, -CH_3), 1.41–1.36 (m, 2 H, -CH_2-), 1.34, 1.33 (2s, 6 H, 2 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.6, 133.2, 129.8, 127.9 (6 C, Ar-*C*), 109.2, 108.5 (2 C, 2 × -*C*(CH_3)$_2$), 96.3

(1 C, *C*-1), 71.2 (1 C, *C*-4), 70.9 (1 C, -*C*H_2-), 70.6 (1 C, *C*-3),* 70.6 (1 C, *C*-2),* 70.5 (1 C, -*C*H_2-), 69.4 (1 C, *C*-6), 66.7 (1 C, *C*-5), 28.8 (1 C, -*C*H_2-), 28.6 (1 C, -*C*H_2-), 26.1, 26.0, 24.9, 24.4 (4 C, 4 × -*C*H_3), 22.0 (1 C, -*C*H_2-), 21.6 (1 C, Ar-*C*H_3); MS (FAB): m/z 523 $[M+Na]^+$, 501 $[M+H]^+$, 485 $[M\text{-}CH_3]^+$; FT-ICR-MS $[M+Na]^+$ calcd. for $C_{24}H_{36}NaO_9S$: 523.19722; Found: 523.19712.

*Signals could be reversed.

6-*O*-[4-(*p*-Toluenesulfonyl)-butan-1-yl]-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (35)

Pursuant to general procedure GP3, 2.60 g (10.00 mmol) **2**, 288 mg (12.00 mmol) sodium hydride, and 15.94 g (40.00 mmol) 1,4-bis(*p*-toluenesulfonyl)butane **(27)** and chromatographic purification on silica gel (toluene/acetone 20:1) gave **35** as colorless oil (3.36 g, 69%); $[\alpha]_D^{20} = -44.5$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 2 H, Ar-*H*), 7.35 (d, 2 H, Ar-*H*), 5.52 (d, 1 H, $J_{1,2} = 5.1$ Hz, *H*-1), 4.60 (dd, 1 H, $J_{3,4} = 7.8$ Hz, *H*-3), 4.30 (dd, 1 H, $J_{2,3} = 2.3$ Hz, *H*-2), 4.22 (dd, 1 H, $J_{4,5} = 1.8$ Hz, *H*-4), 4.06 (t, 2 H, $J = 6.3$ Hz, -CH_2-), 3.94–3.90 (m, 1 H, *H*-5), 3.60–3.52 (m, 2 H, *H*-6a, *H*-6b), 3.48–3.40 (m, 2 H, -CH_2-), 2.45 (s, 3 H, Ar-CH_3), 1.78–1.70 (m, 2 H, -CH_2-), 1.63–1.58 (m, 2 H, -CH_2-), 1.53, 1.44, 1.33 (3 s, 12 H, 4 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.6, 133.2, 129.8, 127.5 (6 C, Ar-*C*), 109.2, 108.5 (2 C, 2 × -*C*$(CH_3)_2$), 96.3 (1 C, *C*-1), 71.1 (1 C, *C*-4), 70.6 (1 C, *C*-3), 70.5 (1 C, *C*-2), 70.4, 70.2 (2 C, 2 × -*C*H_2-), 69.4 (1 C, *C*-6), 66.7 (1 C, *C*-5), 26.0, 25.9 (2 C, 2 × -*C*H_3), 25.7, 25.5 (2 C, 2 × -*C*H_2-), 24.9, 24.4 (2 C, 2 × -*C*H_3), 21.6 (1 C, Ar-*C*H_3); MS (FAB): m/z 509 $[M+Na]^+$, 471 $[M\text{-}CH_3]^+$; FT-ICR-MS $[M+Na]^+$ calcd. for $C_{23}H_{34}NaO_9S$: 509.18157; Found: 509.18185.

6-*O*-[3-(*p*-Toluenesulfonyl)-propan-1-yl]-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (36)

Method 1: Pursuant to general procedure GP4, 2.60 g (10.00 mmol) **2**, 2.00 g (50.00 mmol) sodium hydroxide (50% in water), and 15.36 g (40.00 mmol) 1,3-bis(*p*-toluenesulfonyl)-propane **(28)** and chromatographic purification (toluene/acetone 25:1) on silica gel gave **36** (0.70 g, 15%) as colorless oil.

Method 2: To a solution of 4.20 g (13.20 mmol) **47** and 2.95 g (26.42 mmol) DABCO in 100 mL of ethyl acetate was added 3.77 g (19.81 mmol) *p*-toluenesulfonyl chloride at 0°C, and the mixture was stirred for 1 h at 0°C and for 18 h at rt. The organic layer was washed with 5% aqueous HCl, saturated aqueous sodium bicarbonate, and water. After drying over magnesium sulfate, the solvent was removed under reduced pressure and the residue was purified by column chromatography (toluene/acetone 25:1) on silica gel (4.12 g, 66%); $[\alpha]_D^{20} = -43.1$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 2 H,

J = 8.3 Hz, Ar-*H*), 7.34 (d, 2 H, J = 8.1 Hz, Ar-*H*), 5.51 (d, 1 H, $J_{1,2}$ = 5.1 Hz, *H*-1), 4.58 (dd, 1 H, $J_{3,4}$ = 7.8 Hz, *H*-3), 4.30 (dd, 1 H, $J_{2,3}$ = 2.3 Hz, *H*-2), 4.18 (dd, 1 H, $J_{4,5}$ = 1.8 Hz, *H*-4), 4.12–4.16 (m, 2 H, -CH_2-), 3.87–3.91 (m, 1 H, *H*-5), 3.47–3.55 (m, 4 H, *H*-6a, *H*-6b, -CH_2-), 2.45 (s, 3 H, Ar-CH_3), 1.88–1.94 (m, 2 H, -CH_2-), 1.53, 1.44, 1.33 (3s, 12 H, 4 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.6, 133.2, 129.8, 127.9 (6 C, Ar-*C*), 109.2, 108.5 (2 C, 2 × -*C*$(CH_3)_2$), 96.3 (1 C, *C*-1), 71.1 (1 C, *C*-4), 70.6 (1 C, *C*-3), 70.5 (1 C, *C*-2), 69.6 (1 C, *C*-6),* 67.8 (1 C, -*C*H_2-), 66.7 (1 C, -*C*H_2-),* 66.6 (1 C, *C*-3), 29.2 (1 C, -*C*H_2-), 26.0, 25.9, 24.9, 24.4 (4 C, 4 × -*C*H_3), 21.6 (1 C, Ar-*C*H_3); MS (FAB): m/z 473 $[M+H]^+$, 457 $[M\text{-}CH_3]^+$, 185 $[M\text{-}C_{14}H_{23}O_6]$; FT-ICR-MS $[M+Na]^+$ calcd. for $C_{22}H_{32}NaO_9S$: 495.16592; Found: 495.16543.

*Signals could be reversed.

6-*O*-[2-(*p*-Toluenesulfonyl)-ethan-1-yl]-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (37)

Method 1: Pursuant to general procedure GP4, 5.20 g (20.00 mmol) **2**, 4.00 g (100.00 mmol) sodium hydroxide (50% in water), and 29.60 g (80.00 mmol) 1,2-bis(*p*-toluenesulfonyl)-ethane **(29)** and chromatographic purification (toluene/acetone 25:1) on silica gel gave 37 (1.50 g, 16%) as a colorless oil.

Method 2: Treatment of a solution of 3.84 g (12.63 mmol) **46** and 2.87 g (25.63 mmol) DABCO in 100 mL ethyl acetate with 3.61 g (18.95 mmol) *p*-toluenesulfonyl chloride and workup as described for the preparation of **36** (method2) gave **37** (2.30 g, 40%) as a colorless oil; $[\alpha]_D^{20}$ = –47.4 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2 H, Ar-*H*), 7.35 (d, 2 H, Ar-*H*), 5.51 (d, 1 H, $J_{1,2}$ = 5.1 Hz, *H*-1), 4.58 (dd, 1 H, $J_{3,4}$ = 8.0 Hz, *H*-3), 4.31 (dd, 1 H, $J_{2,3}$ = 2.5 Hz, *H*-2), 4.18 (dd, 1 H, $J_{4,5}$ = 1.8 Hz, *H*-4), 4.16 (t, 2 H, -CH_2-), 3.93–3.90 (m, 1 H, *H*-5), 3.76–3.62 (m, 3 H, *H*-6a, -CH_2-), 3.58–3.53 (m, 1 H, *H*-6b), 2.45 (s, 3 H, Ar-CH_3), 1.54, 1.43, 1.33 (3s, 12 H, 4 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.7, 133.0, 129.8, 128.0 (6 C, Ar-*C*), 109.2, 108.6 (2 C, -*C*$(CH_3)_2$), 96.3 (1 C, *C*-1), 71.0 (1 C, *C*-4), 70.6 (1 C, *C*-3), 70.5 (1 C, *C*-2), 70.1 (1 C, *C*-6), 69.1, 68.7 (2 C, 2 × -*C*H_2-), 66.9 (1 C, *C*-6), 26.0, 25.9, 24.9, 24.4 (4 C, 4 × -CH_3), 21.6 (1 C, Ar-*C*H_3); MS (FAB): m/z 481.1 $[M+Na]^+$, 459.1 $[M+H]^+$; FT-ICR-MS $[M+Na]^+$ calcd. for $C_{21}H_{30}NaO_9S$: 481.15046; Found: 481.15027.

3-*O*-[5-(*p*-Toluenesulfonyl)propan-1-yl]-1,2:3,4-di-*O*-isopropylidene-α-D-glucofuranose (38)

Pursuant to general procedure GP3, 2.60 g (10.00 mmol) **10**, 288 mg (12.00 mmol) sodium hydride, and 16.50 g (40.00 mmol) 1,5-bis(*p*-toluenesulfonyl)-pentane **(26)** and chromatographic purification on silica gel (toluene/acetone 30:1) gave **38** as viscous oil (3.76 g, 77%); $[\alpha]_D^{20}$ = –20.1 (c

1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 2 H, Ar-*H*), 7.35 (d, 2 H, Ar-*H*), 5.86 (d, 1 H, $J_{1,2} = 3.5$ Hz, *H*-1), 4.50 (d, 1 H, *H*-2), 4.28–4.23 (m, 1 H, *H*-5), 4.09 (dd, 1 H, $J_{4,5} = 7.8$ Hz, *H*-4), 4.07–3.96 (m, 4 H, *H*-6a, *H*-6b, -CH_2-), 3.83 (d, 1 H, $J_{3,4} = 2.8$ Hz, *H*-3), 3.60–3.46 (m, 2 H, -CH_2-), 2.46 (m, 3 H, Ar-CH_3), 1.71–1.64 (m, 2 H, -CH_2-), 1.57–1.50 (m, 5 H, -CH_2-, -CH_3), 1.44–1.38 (m, 5 H, -CH_2-, -CH_3), 1.33 (s, 6 H, 2 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.7, 133.1, 129.8, 127.9 (6 C, Ar-*C*), 111.7, 108.9 (2 C, 2 × -*C*$(CH_3)_2$), 105.2 (1 C, *C*-1), 82.5 (1 C, *C*-2), 82.1 (1 C, *C*-3), 81.1 (1 C, *C*-4), 72.4 (1 C, *C*-5), 70.4, 70.1 (2 C, 2 × -*C*H_2-), 67.3 (1C, *C*-6), 29.0, 28.6 (2 C, 2 × -*C*H_2-), 26.8, 26.7, 26.2, 25.4 (4 C, 4 × -*C*H_3), 22.0 (1 C, -*C*H_2-), 21.6 (1 C, Ar-*C*H_3); MS (FAB): m/z 523.1 $[M+Na]^+$, 485.1 $[M-CH_3]^+$; FT-ICR-MS $[M+Na]^+$ calcd. for $C_{24}H_{36}NaO_9S$: 523.19722; Found: 523.19708.

3-*O*-[4-(*p*-Toluenesulfonyl)butan-1-yl]-1,2:3,4-di-*O*-isopropylidene-α-D-glucofuranose (39)

Pursuant to general procedure GP3, 5.20 g (20.00 mmol) **10**, 576 mg (24.00 mmol) sodium hydride, and 31.88 g (80.00 mmol) 1,4-bis(*p*-toluenesulfonyl)-butane **(27)** and chromatographic purification on silica gel (toluene/acetone 30:1) gave **39** as viscous oil (4.68 g, 48%); $[\alpha]_D^{20} = -21.3$ (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, 2 H, Ar-*H*), 7.36 (d, 2 H, Ar-*H*), 5.84 (d, 1 H, $J_{1,2} = 3.5$ Hz, *H*-1), 4.50 (d, 1 H, *H*-2), 4.25–4.20 (m, 1 H, *H*-5), 4.08–4.04 (m, 4 H, *H*-4, *H*-6a, -CH_2-), 3.98–3.95 (m, 1 H, *H*-6b), 3.80 (d, 1 H, $J_{3,4} = 3.0$ Hz, *H*-3), 3.62–3.57 (m, 1 H, -CH_2-), 3.51–3.46 (m, 1 H, -CH_2-), 2.46 (s, 3 H, -CH_3), 1.80–1.72 (m, 2 H, -CH_2-), 1.64–1.57 (m, 2 H, -CH_2-), 1.50, 1.41, 1.32 (3s, 12 H, 4 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.7, 133.1, 129.8, 127.9 (6 C, Ar-*C*), 111.8, 109.0 (2 C, -*C*$(CH_3)_2$), 105.2 (1 C, *C*-1), 82.4 (1 C, *C*-2), 82.1 (1 C, *C*-3), 81.1 (1 C, *C*-4), 72.3 (1 C, *C*-5), 70.2, 69.4 (2 C, 2 × -*C*H_2-), 67.4 (1 C, *C*-6), 26.8 (2 C, 2 × -*C*H_3), 26.2 (1 C, -*C*H_3), 25.7 (2 C, -*C*H_2-), 25.3 (1 C, -*C*H_3), 21.6 (1 C, Ar-*C*H_3); MS (FAB): m/z 509.1 $[M+Na]^+$,487.2 $[M+H]^+$ 471.1 $[M-CH_3]^+$; FT-ICR-MS $[M+Na]^+$ calcd. for $C_{23}H_{34}NaO_9S$: 509.18112; Found: 509.18157.

3-*O*-[3-(*p*-Toluenesulfonyl-)propan-1-yl]-1,2:3,4-di-*O*-isopropylidene-α-D-glucofuranose (40)

Pursuant to general procedure GP4, 5.20 g (20.00 mmol) **10**, 4.00 g (100.00 mmol) sodium hydroxide (50% in water), and 30.72 g (80.00 mmol) 1,3-bis(*p*-toluenesulfonyl)-propane **(28)** and chromatographic purification (toluene/acetone 25:1) on silica gel gave **40** as colorless oil (2.82 g, 30%); $[\alpha]_D^{20} = -26.9$ (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2 H, Ar-*H*), 7.36 (d, 2 H, Ar-*H*), 5.80 (d, 1 H, $J_{1,2} = 3.5$ Hz, *H*-1), 4.48 (d, 1 H, *H*-2), 4.21–4.02 (m, 5 H, -CH_2-, *H*-4, *H*-5, *H*-6a), 3.97–3.94 (m, 1 H, *H*-6b), 3.81 (d, 1 H, $J_{3,4} =$

3.0 Hz, *H*-3), 3.72–3.67 (m, 1 H, -CH_2-), 3.60–3.55 (m, 1 H, -CH_2-), 2.46 (s, 3 H, Ar-CH_3), 1.49, 1.41, 1.32 (3s, 12 H, 4 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.8, 133.1, 129.9, 127.9 (6 C, Ar-*C*), 111.8, 109.0 (2 C, 2 × -*C*(CH_3)$_2$), 105.2 (1 C, *C*-1), 82.3 (1 C, *C*-3),* 83.2 (1 C, *C*-2),* 81.1 (1 C, *C*-4), 72.3 (1 C, *C*-5), 67.3 (1 C, -*C*H_2-), 67.2 (1 C, *C*-6), 65.6 (1 C, -*C*H_2-), 29.2 (1 C, -*C*H_2-), 26.8, 26.8, 26.2, 25.3 (4 C, 4 × -*C*H_3), 21.6 (1 C, Ar-*C*H_3); MS (FAB): m/z 495.2 $[M+Na]^+$, 473.1 $[M+H]^+$ 457.1 $[M-CH_3]^+$; FT-ICR-MS $[M+Na]^+$ calcd. for $C_{22}H_{32}NaO_9S$: 495.16592; Found: 495.16591.

*Signals could be reversed.

3-*O*-[2-(*p*-Toluenesulfonyl)-ethan-1-yl]-1,2:3,4-di-*O*-isopropylidene-α-D-glucofuranose (41)

Pursuant to general procedure GP4, 2.60 g (10.00 mmol) **10**, 2.00 g (50.00 mmol) sodium hydroxide (50% in water), and 14.80 g (40.00 mmol) 1,2-bis(*p*-toluenesulfonyl)-ethane **(29)** and chromatographic purification (toluene/acetone 20:1) on silica gel gave **41** as colorless oil (1.76 g, 38%); $[\alpha]_D^{20}$ = –18.3 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, 2 H, Ar-*H*), 7.35 (d, 2 H, Ar-*H*), 5.80 (d, 1 H, $J_{1,2}$ = 3.8 Hz, *H*-1), 4.45 (d, 1 H, *H*-2), 4.18–4.14 (m, 3 H, *H*-5, -CH_2-), 4.05 (dd, 1 H, $J_{4,5}$ = 8.1 Hz, *H*-4), 4.03 (dd, 1 H, $J_{5,6a}$ = 6.3 Hz, *H*-6a), 3.94 (dd, 1 H, $J_{5,6b}$ = 5.6 Hz, *H*-6b), 3.86 (d, 1 H, $J_{3,4}$ = 3.0 Hz, *H*-3), 3.82–3.79 (m, 2 H, -CH_2-), 2.46 (s, 3 H, Ar-CH_3), 1.49, 1.40, 1.32, 1.31 (4s, 12 H, 4 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 144.9, 132.9, 129.8, 127.9 (6 C, Ar-*C*), 111.9, 109.0 (2 C, 2 × -*C*(CH_3)$_2$), 105.2 (1 C, *C*-1), 82.8 (1 C, *C*-3), 82.6 (1 C, *C*-2), 81.0 (1 C, *C*-4), 72.3 (1 C, *C*-5), 68.9, 68.3 (2 C, -*C*H_2-), 67.3 (1 C, *C*-6), 26.8, 26.2, 25.3 (4 C, 4 × -*C*H_3), 21.6 (1 C, Ar-*C*H_3); MS (FAB): m/z 481.1 $[M+Na]^+$, 459.1 $[M+H]^+$ 443.0 $[M-CH_3]^+$; FT-ICR-MS $[M+Na]^+$ calcd. for $C_{21}H_{30}NaO_9S$: 481.15062; Found: 481.15027.

6-*O*-(2-Benzyloxyethyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (44)

A suspension of 5.28 g (20.30 mmol) of **2** and 461 mg (19.20 mmol) sodium hydride in 130 mL of dry THF was stirred for 1 h at 60°C. Next, 7.45 g (24.40 mmol) 2-benzyloxyethyl-*p*-toluenesulfonate **(42)** dissolved in 25 mL of dry THF was added and the mixture refluxed for 36 h under an atmosphere of nitrogen. After cooling to rt, water was added. The aqueous phase was extracted several times with DCM and the combined organic phases were dried over magnesium sulfate and concentrated. Chromatographic purification of the residue on silica gel (toluene/acetone 30:1) gave **44** as a colorless oil (7.26 g, 91%); $[\alpha]_D^{20}$ = –52.7 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.26 (m, 5 H, Ar-*H*), 5.54 (d, 1 H, $J_{1,2}$ = 5.1 Hz, *H*-1), 4.60 (dd, 1 H, $J_{3,4}$ = 7.8 Hz, *H*-3), 4.58 (s, 2 H, -CH_2-Ph), 4.31 (dd, 1 H, $J_{2,3}$ = 2,4 Hz, *H*-2), 4.27 (dd, 1 H, $J_{4,5}$

= 1,9 Hz, *H*-4), 4.02 (ddd, 1 H, $J_{5,6a}$ = 6.3 Hz, $J_{5,6b}$ = 12.4 Hz, *H*-5), 3.77–3.63 (m, 6 H, 2 × -C*H*$_2$-, *H*-6a, *H*-6b), 1.55, 1.45, 1.34 (3s, 12 H, 4 × -C*H*$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 138.3, 128.3, 127.7 (6 C, Ar-*C*), 127.5 (1 C, Ar-*C*), 109.2, 108.5 (2 C, -*C*$(CH_3)_2$), 96.3 (1 C, *C*-1), 73.1 (1 C, -*C*H$_2$-Ph), 71.1 (1 C, *C*-4), 70.8 (1 C, *C*-2),* 70.6 (1 C, *C*-3)*, 70.5 (1 C, *C*-6),** 69.5 (1 C, -*C*H$_2$-),** 69.3 (1 C, -*C*H$_2$-),** 66.8 (1 C, *C*-5), 26.1, 26.0, 24.9, 24.4 (4 C, 4 × -C(*C*H$_3$)$_2$); MS (FAB): m/z 417.0 $[M+Na]^+$, 395.0 $[M+H]^+$, 379.1 $[M\text{-}CH_3]^+$; Anal. calcd. for $C_{21}H_{30}O_7$: C 63.94; H 7.67; Found: C 64.25; H 7.68.

*,** Signals could be reversed.

6-*O*-(3-Benzyloxypropyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (45)

Treatment of 1.68 g (6.46 mmol) of **2**, 171 mg (7.10 mmol) sodium hydride, and 3.10 g (9.68 mmol) 3-(benzyloxypropyl)-*p*-toluenesulfonate **(43)** in THF as described for the preparation of **44** gave **45** as a colorless oil (2.24 g, 85%); $[\alpha]_D^{20}$ = –49.5 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.28 (m, 5 H, Ar-*H*), 5.55 (d, 1 H, $J_{1,2}$ = 5.0 Hz, *H*-1), 4.60 (dd, 1 H, $J_{3,4}$ = 7.9 Hz, *H*-3), 4.51 (s, 2 H, -C*H*$_2$-Ph), 4.31 (dd, 1 H, $J_{2,3}$ = 2,4 Hz, *H*-2), 4.25 (dd, 1 H, $J_{4,5}$ = 1.9 Hz, *H*-4), 3.96 (ddd, $J_{5,6a}$ = 6.3 Hz, $J_{5,6b}$ 12.5 Hz, *H*-5), 3.67–3.56 (m, 6 H, *H*-6a, *H*-6b, 2 × -C*H*$_2$-), 1.91 (m, 2 H, -C*H*$_2$-), 1.54, 1.45, 1.34 (3s, 12 H, 4 × -C*H*$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 138.6, 128.3, 127.6, 127.5 (6 C, Ar-*C*), 109.2, 108.5 (2 C, -*C*$(CH_3)_2$), 96.3 (1 C, *C*-1), 72.9 (1 C, -*C*H$_2$Ph), 71.1 (1 C, *C*-4), 70.6 (1 C, *C*-2),* 70.6 (1 C, *C*-3),* 69.4 (1 C, -*C*H$_2$-),** 68.3 (1 C, -*C*H$_2$-),** 67.3 (1 C, *C*-6),** 66.6 (1 C, *C*-5), 30.1 (1 C, -*C*H$_2$-), 26.1, 26.0, 24.9, 24.4 (4 C, 4 × -*C*H$_3$); MS (FAB): m/z 431.0 $[M+Na]^+$, 409.0 $[M+H]^+$, 301.0 $[M\text{-}C_7H_7O]^+$; Anal. calcd. for $C_{22}H_{32}O_7$: C 64.69; H 7.90; Found: C 64.81; H 8.24.

*,**Signals could be reversed.

6-*O*-(2-Hydroxyethyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (46)

A suspension of 4.70 g (11.92 mmol) of **44** and a catalytic amount of palladium on charcoal in 100 mL of ethanol was stirred under an atmosphere of hydrogen for 12 h. The catalyst was filtered off and the solution concentrated to give **46** as a colorless oil (3.40 g, 94%); $[\alpha]_D^{20}$ = –72.9 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.55 (d, 1 H, $J_{1,2}$ = 5.1 Hz, *H*-1), 4.63 (dd, 1 H, $J_{3,4}$ = 7.8 Hz, *H*-3), 4.33 (dd, 1 H, $J_{2,3}$ = 2.5 Hz, *H*-2), 4.29 (dd, 1 H, $J_{4,5}$ = 2.0 Hz, *H*-4), 4.02–3.98 (m, 1 H, *H*-5), 3.75–3.64 (m, 5 H, *H*-6a, 2 × -C*H*$_2$-), 3.62–3.57 (m, 1 H, *H*-6b), 2.44 (s, 1 H, -O*H*), 1.55, 1.46, 1.35, 1.34 (4s, 12 H, 4 × -C*H*$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 109.4, 108.7 (2 C, 2 × -*C*$(CH_3)_2$), 96.3 (1 C, *C*-1), 72.4 (1 C, *C*-6), 71.2 (1 C, *C*-4), 70.6 (1 C, *C*-2)*, 70.4 (1 C, *C*-3)*, 69.3 (1 C, -*C*H$_2$-), 66.6 (1 C, *C*-5), 61.4 (1 C, -*C*H$_2$-), 26.0, 25.9, 24.9, 24.5 (4 C, 4 × -*C*H$_3$);

MS (FAB): m/z 327.0 $[M+Na]^+$, 305.0 $[M+H]^+$, 289.0 $[M\text{-}CH_3]^+$; Anal. calcd. for $C_{14}H_{24}O_7$: C 55.25; H 7.95; Found: C 55.54; H 8.20.

*Signals could be reversed.

6-*O*-(3-Hydroxypropyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (47)

Treatment of 5.70 g (13.97 mmol) of **45** and a catalytic amount of palladium on charcoal in 100 mL ethanol under an atmosphere of hydrogen and workup as described for the preparation of **46** gave **47** as a colorless oil (4.35 g, 98%); $[\alpha]_D^{20} = -64.0$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.55 (d, 1 H, $J_{1,2}$ = 5.1 Hz, *H*-1), 4.60 (dd, 1 H, $J_{3,4}$ = 8.1 Hz, *H*-3), 4.32 (dd, 1 H, $J_{2,3}$ = 2.5 Hz, *H*-2), 4.23 (dd, 1 H, $J_{4,5}$ = 2.0 Hz, *H*-4), 3.97 (m, 1 H, *H*-5), 3.80–3.63 (m, 6 H, *H*-6a, *H*-6b, 2 × -CH_2-), 2.61 (t, 1 H, J = 5.8 Hz, -O*H*), 1.82 (m, 2 H, -CH_2-), 1.54, 1.45, 1.34, 1.33 (4s, 12 H, 4 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 109.4, 108.6 (2 C, 2 × -*C*$(CH_3)_2$), 96.3 (1 C, *C*-1), 71.2 (1 C, *C*-4), 70.7 (1 C, *C*-3), 70.5 (1 C, *C*-2), 70.1 (1 C, *C*-6),* 69.7 (1 C, -*C*H_2-),* 66.8 (1 C, *C*-5), 61.5 (1 C, -*C*H_2-), 31.9 (1 C, -*C*H_2-), 26.0, 25.9, 24.9, 24.4 (4 C, 4 × -*C*H_3); MS (FAB): m/z 319.0 $[M+H]^+$, 303.0 $[M\text{-}CH_3]^+$; FT-ICR-MS $[M+Na]^+$ calcd. for $C_{15}H_{26}NaO_7$: 341.15719; Found: 341.15707.

*Signals could be reversed.

3,6-Bis[1,2:3,4-di-*O*-isopropylidene-6-*O*-(5-oxypentan-1-yl)-α-D-galactopyranosyl]phthalonitrile (48)

Method 1: Pursuant to general procedure GP5, 0.41 g (2.56 mmol) dicyanohydroquinone **(1)**, 2.61 g (6.40 mmol) **15,** and 4.24 g (30.70 mmol) K_2CO_3 in 60 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 100:1) gave **48** as a colorless foam (1.90 g, 91%).

Method 2: Pursuant to general procedure GP5, 0.37 g (2.31 mmol) dicyanohydroquinone **(1)**, 2.89 g (5.78 mmol) **34,** and 3.83 g (27.72 mmol) K_2CO_3 in 60 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 100:1) gave **48** as a colorless foam (1.44 g, 76%); $[\alpha]_D^{20} = -47.4$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (s, 2 H, Ar-*H*), 5.54 (d, 2 H, $J_{1,2}$ = 5.1 Hz, *H*-1), 4.60 (dd, 2 H, $J_{3,4}$ = 7.8 Hz, *H*-3), 4.30 (dd, 2 H, $J_{2,3}$ = 2.5 Hz, *H*-2), 4.25 (dd, 2 H, $J_{4,5}$ = 1.8 Hz, *H*-4), 4.05 (t, 4 H, J = 6.3 Hz, -CH_2-), 3.98–3.94 (m, 2 H, *H*-5), 3.65–3.58 (m, 4 H, *H*-6a, *H*-6b), 3.55–3.47 (m, 4 H, -CH_2-), 1.89–1.83 (m, 4 H, -CH_2-), 1.59–1.50 (m, 4 H, -CH_2-), 1.53, 1.44, 1.34, 1.32 (4s, 24 H, -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.1, 118.4, 113.0 (6 C, Ar-*C*), 109.2, 108.5 (4 C, -*C*$(CH_3)_2$), 105.3 (2 C, -*C*N), 96.3 (2 C, *C*-1), 71.2 (2 C, *C*-4), 71.0 (2 C, -*C*H_2-), 70.6 (2 C, *C*-3),* 70.5 (2 C, *C*-2),* 70.0 (2 C, -*C*H_2-), 69.5 (2 C, *C*-6), 66.7 (2 C, *C*-5), 29.1 (2 C, -*C*H_2-), 28.6 (2 C, -*C*H_2-), 26.1, 26.0, 24.9,

24.4 (8 C, -*C*H_3), 22.4 (2 C, -*C*H_2-); MS (FAB): m/z 839.0 $[M+Na]^+$, 801.0 $[M-CH_3]^+$; Anal. calcd. for $C_{42}H_{60}N_2O_{14}$: C 61.75; H 7.40; N 3.43; Found: C 61.51; H 7.40; N 3.35.

*Signals could be reversed.

3,6-Bis[1,2:3,4-di-*O*-isopropylidene-6-*O*-(4-oxybutan-1-yl)-α-D-galactopyranosyl]phthalonitrile (49)

Method 1: Pursuant to general procedure GP5, 0.65 g (4.05 mmol) dicyanohydroquinone **(1)**, 3.19 g (8.10 mmol) **16,** and 6.71 g (48.62 mmol) K_2CO_3 in 60 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 100:1) gave **49** as a colorless foam (2.23 g, 70%).

Method 2: Pursuant to general procedure GP5, 0.45 g (2.83 mmol) dicyanohydroquinone **(1)**, 2.90 g (5.96 mmol) **35,** and 4.70 g (34.00 mmol) K_2CO_3 in 75 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 100:1) gave **49** as a colorless foam (1.27 g, 57%); $[\alpha]_D^{20} = -53.4$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (s, 2 H, Ar-*H*), 5.50 (d, 2 H, $J_{1,2} = 5.1$ Hz, *H*-1), 4.57 (dd, 2 H, $J_{3,4} = 8.1$ Hz, *H*-3), 4.28 (dd, 2 H, $J_{2,3} = 2.3$ Hz, *H*-2), 4.21 (dd, 2 H, $J_{4,5} = 1.8$ Hz, *H*-4), 4.07 (t, 4 H, 2 × -CH_2-), 3.96–3.92 (m, 2 H, *H*-5), 3.62–3.49 (m, 8 H, *H*-6a, *H*-6b, 2 × -CH_2-), 1.94–1.87 (m, 4H, 2 × -CH_2-), 1.78–1.72 (m, 4H, 2 × -CH_2-), 1.50, 1.42, 1.31, 1.30 (4s, 24 H, 8 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.2, 118.7, 113.2 (6 C, Ar-*C*), 109.3, 108.6 (4 C, 4 × -*C*$(CH_3)_2$), 105.2 (2 C, 2 × -*C*N), 96.4 (2 C, *C*-1), 71.3 (2 C, *C*-4), 70.7 (4 C, C-3, -*C*H_2-), 70.6 (2 C, *C*-2), 70.0 (2 C, -*C*H_2-), 69.7 (2 C, *C*-6), 66.9 (2 C, *C*-5), 26.2 (2 C, 2 × -*C*H_3), 26.1 (4 C, 4 × -*C*H_2-), 25.9, 25.1, 24.5 (6 C, 6 × -*C*H_3); IR (neat): $\tilde{\nu}$ 2989, 2937, 2232, 1576, 1491, 1468, 1383, 1283, 1257, 1213, 1070, 1000 cm^{-1}; MS (FAB): m/z 811.0 $[M+Na]^+$; FT-ICR-MS $[M+Na]^+$ calcd. for $C_{40}H_{56}N_2NaO_{14}$: 811.36237; Found: 811.36294.

3,6-Bis[1,2:3,4-di-*O*-isopropylidene-6-*O*-(3-oxypropan-1-yl)-α-D-galactopyranosyl]phthalonitrile (50)

Pursuant to general procedure GP5, 0.40 g (2.50 mmol) dicyanohydroquinone **(1)**, 2.60 g (5.51 mmol) **36,** and 4.14 g (30.00 mmol) K_2CO_3 in 100 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 100:1) gave **50** as a colorless foam (1.74 g, 91%); $[\alpha]_D^{20} = -56.8$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (s, 2 H, Ar-*H*), 5.53 (d, 2 H, $J_{1,2} = 5.1$ Hz, *H*-1), 4.60 (dd, 2 H, $J_{3,4} = 7.8$ Hz, *H*-3), 4.32 (dd, 2 H, $J_{2,3} = 2.3$ Hz, *H*-2), 4.21 (dd, 2 H, $J_{3,4} = 2.1$ Hz, *H*-4), 4.18 (t, 4 H, 2 × -CH_2-), 3.94–3.98 (m, 2H, *H*-5), 3.69 (t, 4 H, 2 × -CH_2-), 3.60–3.66 (m, 4 H, *H*-6a, *H*-6b), 2.10 (q, 4 H, 2 × -CH_2-), 1.51, 1.44, 1.33, 1.32 (4 s, 24 H, 8 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.2, 118.7, 113.0 (6 C, Ar-*C*), 109.3, 108.5 (4 C, 4 × -*C*$(CH_3)_2$), 105.2 (2 C, 2 × -*C*N), 96.4 (2 C, *C*-1), 71.2 (2 C, *C*-4), 70.7 (2 C, *C*-3), 70.5 (2 C, *C*-2), 69.8 (2 C,

C-6), 67.1 (2 C, 2 × -*C*H_2-), 67.0 (2 C, 2 × -*C*H_2-), 66.8 (2 C, *C*-3), 29.3 (2 C, 2 × -*C*H_2-), 26.1, 26.0, 25.0, 24.4 (8 C, 8 × -*C*H_3); IR (neat): $\tilde{\nu}$2988, 2934, 2232, 1576, 1491, 1465, 1383, 1282, 1212, 1070, 1003 cm^{-1}; MS (FAB): m/z 783.0 $[M+Na]^+$, 760.0 $[M]^+$, 745 $[M]^+$; Anal. calcd. for $C_{38}H_{52}N_2O_{14}$: C 59.99; H 6.89; N 3.68; Found: C 59.98; H 6.99; N 3.51.

3,6-Bis[1,2:3,4-di-*O*-isopropylidene-6-*O*-(2-oxyethan-1-yl)-α-D-galactopyranosyl]phthalonitrile (51)

Pursuant to general procedure GP5, 0.31 g (1.95 mmol) dicyanohydroquinone **(1)**, 2.04 g (5.51 mmol) **37,** and 3.23 g (23.40 mmol) K_2CO_3 in 50 mL of dry DMF and chromatographic purification on silica gel (*n*-hexane/ethyl acetate 2:3) gave **51** as a colorless foam (1.11 g, 78%); $[\alpha]_D^{20} = -57.3$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (s, 2 H, Ar-*H*), 5.53 (d, 2 H, $J_{1,2} = 5.1$ Hz, *H*-1), 4.61 (dd, 2 H, $J_{3,4} = 7.8$ Hz, *H*-3), 4.32 (dd, 2 H, $J_{2,3} = 2.3$ Hz, *H*-2), 4.27–4.24 (m, 6 H, *H*-4, -CH_2-), 4.00–3.97 (m, 2 H, *H*-5), 3.94–3.86 (m, 4 H, -CH_2-), 3.78–3.69 (m, 4 H, *H*-6a, *H*-6b), 1.52, 1.45, 134, 1.33 (4s, 24 H, 4 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.5, 119.6, 113.0 (6 C, Ar-*C*), 109.3, 108.6 (4 C, 4 × -*C*$(CH_3)_2$), 105.5 (2 C, -*C*N), 96.3 (2 C, *C*-1), 71.1 (2 C, *C*-4), 70.6 (2 C, *C*-3), 70.5 (4 C, *C*-2, *C*-6), 69.9, 69.5 (4 C, -*C*H_2-), 67.0 (2 C, *C*-5), 26.1, 26.0, 24.9, 24.4 (8 C, 8 × -*C*H_3); IR (neat): $\tilde{\nu}$2989, 2937, 2233, 1737, 1578, 1489, 1455, 1383, 1283, 1257, 1213, 1169, 1070, 1002, 892, 863 cm^{-1}; MS (FAB): m/z 755.0 $[M+Na]^+$, 717.0 $[M]^+$; Anal. calcd. for $C_{36}H_{48}N_2O_{14}$: C 59.01; H 6.60; N 3.82; Found: C 59.25; H 6.71; N 3.59.

3,6-Bis[1,2:5,6-di-*O*-isopropylidene-3-*O*-(5-oxypentan-1-yl)-α-D-glucofuranosyl]phthalonitrile (52)

Method 1: Pursuant to general procedure GP5, 0.73 g (4.55 mmol) dicyanohydroquinone **(1)**, 4.10 g (10.02 mmol) **19,** and 7.53 g (54.57 mmol) K_2CO_3 in 80 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 150:1) gave **52** as a colorless foam (2.10 g, 57%).

Method 2: Pursuant to general procedure GP5, 0.71 g (4.41 mmol) dicyanohydroquinone **(1)**, 4.72 g (9.71 mmol) **38,** and 7.30 g (52.92 mmol) K_2CO_3 in 100 mL of dry DMF and chromatographic purification on silica gel (*n*-hexane/ethyl acetate 1:1) gave **52** as a colorless foam (1.91 g, 53%); $[\alpha]_D^{20} = -25.9$ (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (s, 2 H, Ar-*H*), 5.88 (d, 2 H, $J_{1,2} = 3.8$ Hz, *H*-1), 4.54 (d, 2 H, *H*-2), 4.32–4.27 (m, 2 H, *H*-5), 4.12 (dd, 2 H, $J_{4,5} = 7.6$ Hz, *H*-4), 4.08–4.04 (m, 6 H, *H*-6a, -CH_2-), 4.00–3.97 (m, 2 H, *H*-6b), 3.68–3.54 (m, 4 H, -CH_2-), 1.90–1.83 (m, 4 H, -CH_2-), 1.67–1.62 (m, 4 H, -CH_2-), 1.61–1.55 (m, 4 H, -CH_2-), 1.50, 1.42, 1.34, 1.32 (4s, 24 H, 8 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.1, 118.3, 112.9 (6 C, Ar-*C*), 111.7, 108.9 (4 C, 4 × -*C*$(CH_3)_2$), 105.4 (2 C, 2 × -*C*N), 105.2 (2 C, *C*-1), 82.5 (2 C, *C*-2), 82.1

(2 C, *C*-3), 81.1 (2 C, *C*-4), 72.5 (2 C, *C*-5), 70.3, 70.0 (4 C, 4 × -*C*H_2-), 67.3 (2 C, *C*-6), 29.3, 28.7 (4 C, 4 × -*C*H_2-), 26.8, 26.8, 26.2, 25.4 (8 C, 8 × -*C*H_3), 22.5 (2 C, 2 × -*C*H_2-); IR (neat): $\tilde{\nu}$2988, 2938, 2231, 1576, 1491, 1468, 1436, 1383, 1283, 1217, 1074, 1020, 847 cm^{-1}; MS (FAB): m/z 839.0 $[M+Na]^+$, 801.0 $[M]^+$; Anal. calcd. for $C_{42}H_{60}N_2O_{14}$: C 61.75; H 7.40; N 3.43; Found: C 61.48; H 7.32; N 3.17.

3,6-Bis[1,2:5,6-di-*O*-isopropylidene-3-*O*-(4-oxybutan-1-yl)-α-D-glucofuranosyl]phthalonitrile (53)

Method 1: Pursuant to general procedure GP5, 0.73 g (4.55 mmol) dicyanohydroquinone **(1)**, 3.94 g (10.00 mmol) **20,** and 7.53 g (54.57 mmol) K_2CO_3 in 80 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 150:1) gave **53** as a colorless foam (3.05 g, 85%).

Method 2: Pursuant to general procedure GP5, 0.64 g (3.99 mmol) dicyanohydroquinone **(1)**, 4.27 g (8.79 mmol) **39,** and 6.61 g (48.92 mmol) K_2CO_3 in 100 mL of dry DMF and chromatographic purification on silica gel (*n*-hexane/ethyl acetate 1:1) gave **53** as a colorless foam (1.78 g, 59%); $[\alpha]_D^{20}$ = –19.2 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (s, 2 H, Ar-*H*), 5.86 (d, 2 H, $J_{1,2}$ = 3.8 Hz, *H*-1), 4.55 (d, 2H, *H*-2), 4.28 (m, 2 H, *H*-5), 4.11 (dd, 2 H, $J_{4,5}$ = 7.8 Hz, *H*-4), 4.09–4.05 (m, 6 H, *H*-6a, -CH_2-), 3.98 (dd, 2 H, $J_{5,6b}$ = 5.8 Hz, $J_{6a,6b}$ = 8.6 Hz, *H*-6b), 3.88 (d, 2 H, $J_{3,4}$ = 3,0 Hz, *H*-3), 3.74–3.69 (m, 2 H, -CH_2-), 3.62–3.57 (m, 2 H, -CH_2-), 1.97–1.90 (m, 4 H, -CH_2-), 1.82–1.75 (m, 4 H, -CH_2-), 1.50, 1.42, 1.33, 1.32 (4s, 24 H, 8 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.1 (2 C, Ar-*C*), 118.4 (2 C, Ar-*C*), 112.9 (2 C, Ar-*C*), 111.8, 108.9 (4 C, 4 × -*C*$(CH_3)_2$), 105.5 (2 C, 2 × -*C*N), 105.2 (2 C, *C*-1), 82.4 (2 C, *C*-2), 82.2 (2 C, *C*-3), 81.1 (2 C, *C*-4), 72.4 (2 C, *C*-5), 69.9 (2 C, -*C*H_2-),* 69.8 (2 C, *C*-6),* 67.3 (2 C, -*C*H_2-), 26.8, 26.8, 26.2 (6 C, 6 × -*C*H_3), 26.1, 25.8 (4 C, 4 × -*C*H_2-), 25.4 (2 C, 2 × -*C*H_3); IR (neat): $\tilde{\nu}$3106, 2982, 2947, 2879, 2230, 1573, 1492, 1465, 1372, 1287,1217, 1073, 1019 cm^{-1}; MS (FAB): m/z 811.0 $[M+Na]^+$, 773.0 $[M]^+$; Anal. calcd. for $C_{40}H_{56}N_2O_{14}$: C 60.90; H 7.16; N 3.55; Found: C 61.02; H 7.14; N 3.23.

3,6-Bis[1,2:5,6-di-*O*-isopropylidene-3-*O*-(3-oxypropan-1-yl)-α-D-glucofuranosyl]phthalonitrile (54)

Pursuant to general procedure GP5, 0.37 g (2.30 mmol) dicyanohydroquinone **(1)**, 2.46 g (5.06 mmol) **40,** and 3.81 g (27.60 mmol) K_2CO_3 in 70 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 150:1) gave **54** as a colorless foam (0.98 g, 56%); $[\alpha]_D^{20}$ = –48.2 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (s, 2 H, Ar-*H*), 5.82 (d, 2 H, $J_{1,2}$ = 3.8 Hz, *H*-1), 4.57 (d, 2 H, *H*-2), 4.28–4.23 (m, 2 H, *H*-5), 4.17 (t, 4 H, -CH_2-), 4.09

(dd, 2 H, $J_{4,5}$ = 8.3 Hz, *H*-4), 4.07–4.04 (m, 2 H, *H*-6a), 4.00–3.97 (m, 2 H, *H*-6b), 3.92–3.87 (m, 4 H, *H*-3, -CH_2-), 3.75–3.70 (m, 2 H, -CH_2-), 2.16–2.05 (m, 4 H, -CH_2-), 1.50, 1.40, 1.32, 1.28 (4 s, 24 H, 4 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.1, 118.4, 112.8 (6 C, Ar-*C*), 111.9, 109.0 (2 C, 2 × -*C*(CH_3)$_2$), 105.5 (2 C, 2 × -*C*N), 105.2 (2 C, *C*-1), 82.2 (2 C, *C*-3),* 82.2 (2 C, *C*-2),* 81.0 (2 C, *C*-4), 72.4 (2 C, *C*-5), 67.4 (2 C, *C*-6), 66.6 (2 C, -*C*H_2-), 65.9 (2 C, -*C*H_2-), 29.2 (2 C, -*C*H_2-), 26.8, 26.8, 26.2, 25.4 (8 C, 8 × -*C*H_3); IR (neat): $\tilde{\nu}$2988, 2232, 1578, 1491, 1465, 1382, 1282, 1217, 1166, 1075, 887, 847, 735 cm^{-1}; MS (FAB): m/z 783.0 $[M+Na]^+$, 745.0 $[M]^+$; Anal. calcd. for $C_{38}H_{52}N_2O_{14}$: C 59.99; H 6.89; N 3.68; Found: C 60.35; H 6.99; N 3.62.

*Signals could be reversed.

3,6-Bis[1,2:5,6-di-*O*-isopropylidene-3-*O*-(2-oxypropan-1-yl)-α-D-glucofuranosyl]phthalonitrile (55)

Pursuant to general procedure GP5, 0.14 g (0.89 mmol) dicyanohydroquinone **(1)**, 0.90 g (1.97 mmol) **41,** and 1.48 g (10.70 mmol) K_2CO_3 in 35 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 100:1) gave **55** as a colorless foam (0.23 g, 36%); $[\alpha]_D^{20}$ = –51.5 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (s, 2 H, Ar-*H*), 5.89 (d, $J_{1,2}$ = 3.8 Hz, 2 H, *H*-1), 4.66 (d, 2 H, *H*-2), 4.32–4.28 (m, 2 H, *H*-5), 4.24–4.18 (m, 4 H, -CH_2-), 4.11–3.97 (m, 12 H, *H*-3, *H*-4, *H*-6a, *H*-6b, -CH_2-), 1.51, 1.42, 1.34, 1.32 (4 s, 24 H, 8 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.2, 118.5, 112.7 (6 C, Ar-*C*), 111.9, 109.1 (4 C, 4 × -*C*(CH_3)$_2$), 105.8 (2 C, 2 × -*C*N), 105.3 (2 C, *C*-1), 82.7 (2 C, *C*-2), 82.6 (2 C, *C*-3), 80.9 (2 C, *C*-4), 72.3 (2 C, *C*-5), 69.4 (2 C, -*C*H_2-), 68.5 (2 C, *C*-6), * 67.3 (2 C, -*C*H_2-), 26.9, 26.8, 26.1, 25.4 (8 C, 8 × -*C*H_3); IR (neat): $\tilde{\nu}$3442, 2989, 2938, 2233, 1580, 1490, 1455, 1383, 1284, 1217, 1166, 1137, 1072, 1018, 888, 846, 754 cm^{-1}; MS (FAB): m/z 755.0 $[M+Na]^+$, 717.0 $[M\text{-}CH_3]^+$; Anal. calcd. for $C_{36}H_{48}N_2O_{14}$: C 59.01; H 6.60; N 3.82; Found: C 59.10; H 6.61; N 3.73.

*Signals could be reversed.

3,6-Bis[1,2:5,6-di-*O*-isopropylidene-1-*O*-(5-oxypentan-1-yl)-α-D-mannofuranosyl]phthalonitrile (56)

Method 1: Pursuant to general procedure GP5, 0.48 g (3.00 mmol) dicyanohydroquinone **(1)**, 2.60 g (6.40 mmol) **23,** and 4.97 g (36.00 mmol) K_2CO_3 in 65 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 100:1) gave **56** as a viscous oil (1.94 g, 79%);

Method 2: Pursuant to general procedure GP5, 0.57 g (3.57 mmol) dicyanohydroquinone **(1)**, 3.88 g (7.76 mmol) **30,** and 5.86 g (42.49 mmol) K_2CO_3 in 80 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 100:1) gave **56** as a viscous oil (2.20 g, 76%); $[\alpha]_D^{20}$ = +35.7 (c

1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.14 (s, 2 H, Ar-*H*), 4.97 (s, 2 H, *H*-1), 4.79 (dd, 2 H, $J_{3,4} = 3.5$ Hz, *H*-3), 4.58 (d, 2 H, $J_{2,3} = 5.8$ Hz, *H*-2), 4.43–4.38 (m, 2 H, *H*-5), 4.13–4.02 (m, 8 H, 2 × -CH_2-, *H*-6a, *H*-6b), 3.93 (dd, 2 H, $J_{4,5} =$ 7.8 Hz, *H*-4), 3.69–3.63 (m, 2 H, -CH_2-), 3.44–3.38 (m, 2 H, -CH_2-), 1.89–1.82 (m, 4 H, -CH_2-), 1.67–1.59 (m, 4 H, -CH_2-), 1.59–1.51 (m, 4 H, -CH_2-), 1.46, 1.44, 1.37, 1.32 (4s, 24 H, -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.1, 118.3 (4 C, Ar-*C*), 112.9, 112.5 (4 C, -*C*(CH_3)$_2$), 109.1, 106.3 (4 C, Ar-*C*), 105.5 (2 C, -*C*N), 85.0 (2 C, *C*-1), 80.2 (2 C, *C*-4), 79.5 (2 C, *C*-3), 73.2 (2 C, *C*-5), 70.0 (2 C, -*C*H_2-), 67.0 (2 C, *C*-6),* 66.9 (2 C, -*C*H_2-),* 29.0, 28.6 (4 C, -*C*H_2-), 26.9, 25.9, 25.1, 24.5 (8 C, -*C*H_3), 22.5 (2 C, -*C*H_2); MS (FAB): m/z 839.0 $[M+Na]^+$, 801.0 $[M\text{-}CH_3]^+$; FT-ICR-MS $[M+Na]^+$ calcd. for $C_{42}H_{60}N_2NaO_{14}$: 839.39367; Found: 839.39304.

*Signals could be reversed.

3,6-Bis[1,2:5,6-di-*O*-isopropylidene-1-*O*-(4-oxybutan-1-yl)-α-D-mannofuranosyl]phthalonitrile (57)

Method 1: Pursuant to general procedure GP5, 0.73 g (4.55 mmol) dicyanohydroquinone **(1)**, 3.94 g (10.00 mmol) **24,** and 7.53 g (54.50 mmol) K_2CO_3 in 70 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 100:1) gave **57** as a viscous oil (2.32 g, 65%).

Method 2: Pursuant to general procedure GP5, 0.57 g (3.54 mmol) dicyanohydroquinone **(1)**, 3.79 g (7.79 mmol) **31,** and 5.86 g (42.49 mmol) K_2CO_3 in 80 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 100:1) gave **57** as a viscous oil (2.20 g, 76%); $[\alpha]_D^{20} = +37.2$ (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.16 (s, 2 H, Ar-*H*), 4.98 (s, 2 H, *H*-1), 4.78 (dd, 2 H, $J_{3,4} = 3.5$ Hz, *H*-3), 4.57 (d, 2 H, $J_{2,3} = 5.8$ Hz, *H*-2), 4.43–4.38 (m, 2 H, *H*-5), 4.13–4.01 (m, 8 H, *H*-6a, *H*-6b, 2 × -CH_2-), 3.92 (dd, 2 H, $J_{4,5} =$ 7.6 Hz, *H*-4), 3.73–3.67 (m, 2 H, -CH_2-), 3.48–3.42 (m, 2 H, -CH_2-), 1.94–1.87 (m, 4 H, -CH_2-), 1.80–1.74 (m, 4 H, -CH_2-), 1.47, 1.45, 1.38, 1.32 (4s, 24 H, 8 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.1, 118.4 (4 C, Ar-*C*), 112.9, 112.6 (4 C, 4 × -*C*(CH_3)$_2$), 109.2 (2 C, Ar-*C*), 106.3 (2 C, *C*-1), 105.5 (2 C, 2 × -*C*N), 85.0 (2 C, *C*-2), 80.3 (2 C, *C*-4), 79.5 (2 C, *C*-3), 73.1 (2 C, *C*-5), 69.7 (2 C, -*C*H_2-), 66.9 (2 C, *C*-6),* 66.6 (2 C, -*C*H_2-),* 26.9, 25.8 (4 C, 4 × -*C*H_3), 25.8, 25.7 (4 C, 4 × -*C*H_2-), 25.1, 24.5 (4 C, 4 × -*C*H_3); MS (FAB): m/z 811.0 $[M+Na]^+$, 773.0 $[M\text{-}CH_3]^+$; FT-ICR-MS $[M+Na]^+$ calcd. for $C_{40}H_{56}N_2NaO_{14}$: 811.36237; Found: 811.36177.

*Signals could be reversed.

3,6-Bis[1,2:5,6-di-*O*-isopropylidene-1-*O*-(3-oxypropan-1-yl)-α-D-mannofuranosyl]phthalonitrile (58)

Pursuant to general procedure GP5, 0.66 g (4.10 mmol) dicyanohydroquinone **(1)**, 4.07 g (8.61 mmol) **32,** and 6.80 g (49.20 mmol) K_2CO_3 in 80 mL of

dry and chromatographic purification on silica gel (chloroform/methanol 100:1) gave **58** as a colorless foam (1.98 g, 63%); $[\alpha]_D^{20} = +33.2$ (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (s, 2 H, Ar-*H*), 4.99 (s, 2 H, *H*-1), 4.77 (dd, 2 H, $J_{3,4} = 3.5$ Hz, *H*-3), 4.57 (d, 2 H, $J_{2,3} = 5.8$ Hz, *H*-2), 4.42–4.37 (ddd, 2 H, $J_{5,6a} = 6.2$ Hz, $J_{5,6b} = 4.3$ Hz, *H*-5), 4.14–4.09 (m, 6 H, *H*-6a, -CH_2-), 4.03 (dd, 2 H, $J_{6a,6b} = 8.8$ Hz, *H*-6b), 3.89–3.81 (m, 4 H, $J_{4,5} = 7.6$ Hz, *H*-4, -CH_2-), 3.65–3.59 (m, 2 H, -CH_2-), 2.13–2.07 (m, 4 H, -CH_2-), 1.46, 1.41, 1.37, 1.32 (4s, 24 H, 8 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.0, 118.3, 112.8 (6 C, Ar-*C*), 112.7, 109.1 (4 C, 4 × -*C*$(CH_3)_2$), 106.5 (2 C, *C*-1), 105.6 (2 C, 2 × -*C*N), 85.1 (2 C, *C*-2), 80.4 (2 C, *C*-4), 79.5 (2 C, *C*-3), 73.1 (2 C, *C*-5), 66.9 (4 C, *C*-6, -*C*H_2-), 29.0 (2 C, -*C*H_2-), 26.9, 25.9, 25.1, 24.6 (8 C, 8 × -*C*H_3); IR (neat): $\tilde{\nu}$2988, 2939, 2888, 2233, 1579, 1492, 1465, 1382, 1282, 1211, 1084, 848 cm^{-1}; MS (FAB): m/z 783.0 $[M+Na]^+$, 745.0 $[M\text{-}CH_3]^+$; Anal. calcd. for $C_{38}H_{52}N_2O_{14}$: C 59.99; H 6.89; N 3.68; Found: C 60.10; H 6.92; N 3.30.

3,6-Bis[1,2:5,6-di-O-isopropylidene-1-O-(2-oxyethan-1-yl)-α-D-mannofuranosyl]phthalonitrile (59)

Pursuant to general procedure GP5, 0.16 g (0.99 mmol) dicyanohydroquinone **(1)**, 1.00 g (2.18 mmol) **33,** and 1.66 g (12.00 mmol) K_2CO_3 in 50 mL of dry DMF and chromatographic purification on silica gel (chloroform/methanol 100:1) gave **59** as a colorless solid (0.58 g, 80%); $[\alpha]_D^{20} = +12.4$ (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (s, 2 H, Ar-*H*), 5.07 (s, 2 H, *H*-1), 4.79 (dd, 2 H, $J_{3,4} = 3.8$ Hz, *H*-3), 4.61 (d, 2 H, $J_{2,3} = 5.8$ Hz, *H*-2), 4.40 (ddd, 2 H, $J_{5,6a} = 6.3$ Hz, $J_{5,6b} = 11.6$ Hz, *H*-5), 4.27–4.19 (m, 4 H, -CH_2-), 4.09 (dd, 2 H, $J_{6a,6b} = 8.6$ Hz, *H*-6a), 4.00–3.95 (m, 6 H, $J_{4,5} = 4.6$ Hz, *H*-4, *H*-6b, -CH_2-), 3.87–3.81 (m, 2 H, -CH_2-), 1.47, 1.45, 1.37, 1.32 (4s, 24 H, 4 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 155.1, 118.9 (4 C, Ar-*C*), 112.8, 112.7 (4 C, 4 × -*C*$(CH_3)_2$), 109.2 (2 C, Ar-*C*), 106.7 (2 C, *C*-1), 106.2 (2 C, 2 × -*C*N), 85.0 (2 C, *C*-2), 80.5 (2 C, *C*-4), 79.4 (2 C, *C*-3), 73.1 (2 C, *C*-5), 69.3 (2 C, -*C*H_2-), 66.7 (2 C, *C*-6), 65.1 (2 C, -*C*H_2-), 26.9, 25.9, 25.1, 24.5 (8 C, 8 × -*C*H_3); IR (neat): $\tilde{\nu}$2991, 2940, 2885, 2229, 1740, 1579, 1382, 1065, 851, 821 cm^{-1}; MS (FAB): m/z 733.0 $[M+H]^+$, 717.0 $[M\text{-}CH_3]^+$; Anal. calcd. for $C_{36}H_{48}N_2O_{14}$: C 59.01; H 6.60; N 3.82; Found: C 59.22; H 6.66; N 3.76.

{1,4-Bis[1,2:3,4-di-O-isopropylidene-6-O-(5-oxypentan-1-yl)-α-D-galaktopyranosyl]-phthalocyaninato} zinc(II) (61)

A solution of 0.66 g (0.81 mmol) **48**, 1.97 g (8.74 mmol) zinc bromide, and 1.12 g (8.74 mmol) phthalonitrile (**60**) in 5 mL of freshly distilled DMAE was

prepared with smooth heating. The temperature was raised to 100°C and stirring was continued for 12 h under an atmosphere of nitrogen. Next, the reaction mixture was poured onto crushed ice, filtered, and washed with water. The collected solid was extracted in a Soxhlet apparatus with DCM. Concentration and chromatographic purification of the residue on silica gel using a mixture of toluene/acetone (20:1 → 5:1) gave **61** as a deep green solid (0.16 g, 16%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.26–9.24 (m, 4 H, Pc-H_α), 9.02 (m, 2 H, Pc-H_α), 8.16–8.08 (m, 6 H, Pc-H_β), 7.37 (s, 2 H, Pc-H_β), 5.44 (d, 2 H, $J_{1,2} = 5.1$ Hz, *H*-1), 4.56–4.48 (m, 6 H, $J_{3,4} = 5.8$ Hz, *H*-3, -CH_2-), 4.27 (dd, 2 H, $J_{2,3} = 2.0$ Hz, *H*-2), 4.18 (dd, 2 H, $J_{4,5} = 8.1$ Hz, *H*-4), 3.87–3.83 (m, 2 H, *H*-5), 3.63–3.56 (m, 6 H, -CH_2-, *H*-6a), 3.48–3.45 (m, 2 H, *H*-6b), 2.33–2.25 (m, 4 H, -CH_2-), 2.06–1.98 (m, 4 H, -CH_2-), 1.96–1.87 (m, 4 H, -CH_2-), 1.36, 1.31, 1.22, 1.21 (4s, 24 H, 4 × -CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 152.5, 150.0, 138.2, 137.9 (Pc-*C*), 108.2, 107.7 (4 C, 4 × -*C*(CH_3)$_2$, 95.6 (2 C, *C*-1), 70.7 (2 C, *C*-4), 70.5 (2 C, -*C*H_2-), 70.0 (2 C, *C*-3), 69.8 (2 C, *C*-2), 69.3 (2 C, *C*-6), 68.8 (2 C, -*C*H_2-), 66.3 (2 C, *C*-5), 29.5, 29.5 (4 C, -*C*H_2-), 25.9, 25.8, 24.8, 24.2 (8 C, 8 × -*C*H_3), 23.0 (2 C, -CH_2-); UV-VIS (DMSO): λ_{max} (log ε) 709 (5.20), 638 (4.48), 350 (4.77); FT-ICR-MS $[M+H]^+$ calcd. for $C_{66}H_{73}N_8O_{14}Zn$: 1265.45322; Found: 1265.45142.

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