Syntheses of Glycoclusters Containing a Phosphocholine Residue Related to a Glycosphingolipid from the Earthworm *Pheretima hilgendorfi*

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Three types of glycoclusters related to an amphoteric glycosphingolipid found in the earthworm *Pheretima hilgendorfi* were synthesized. The glycoclusters were prepared from a common precursor and a simple approach for the rational design of a glycocluster was developed.

Key words glycocluster; amphoteric glycosphingolipid; *Pheretima hilgendorfi*; phosphocholine

In our continuing studies to investigate the relationship between the structure and biological function of glycolipids from invertebrate animal species that do not have gangliosides, we have synthesized glycolipids found in various protostomia phyla.[1—12] These compounds may serve as ganglioside mimics. Sugita *et al.* reported[13] the neogala series of glycosphingolipids, whose structures contain a β-D-Gal*p*-(1→6)-β-D-Gal*p*-core and phosphocholine residue, found in the earthworm *Pheretima* (*P.*) *hilgendorfi*, and we previously synthesized two phosphocholine (PC) glycolipid analogues containing octyl residues in place of ceramide, PC(→6)-β-D-Gal*p*-1→Oct and PC(→6)-β-D-Gal*p*-(1→6)-β-D-Gal*p*-1→Oct to investigate the biological function of zwitterionic oligosaccharides.[6] In later studies it was found that the disaccharide PC(→6)-β-D-Gal*p*-1→Oct has immunomodulatory functions leading to induced production of interleukin (IL)-12 and tumor necrosis factor (TNF)α by macrophages and dentritic cells and others.[14] In a previous paper,[12] we reported on the total synthesis of two phosphocholine (PC) glycosphingolipids, PC(→6)-β-D-Gal*p*-(1→6)-β-D-Gal*p*-1→Cer and PC(→6)-β-D-Gal*p*-(1→6)-β-D-Gal*p*-(1→6)-β-D-Gal*p*-1→Cer and other related analogues, in order to investigate another immunomodulatory functions of zwitterionic oligosaccharides. In addition, we also examined the potential of these newly synthesized glycosphingolipids and analogues to enhance production of IL-8 in TNFα-stimulated granulocytic HL-60 cells. Our results demonstrated that the phosphocholine and ceramide groups are potent enhancers of IL-8 production in TNFα-stimulated granulocytic HL-60 cells.

It is known that oligosaccharide chains generally interact with their protein receptors in a multivalent fashion to overcome the inherently low affinity of monovalent carbohydrate–protein interactions. Therefore, the construction of a clustered glycoconjugates is an important subject in glycoscience.[15,16] For this reason, we developed a new synthetic method of glycoclusters containing a sugar unit and ω-amino acid.[17] Here we report on the synthesis of three types of glycoclusters **A**, **B** and **C** (Fig. 1). Phenyl core cluster **A** was chosen as a model cluster due to the high reactivity and rigidity of the trifunctional trimesic acid scaffold.[18] Glycodendrons **B** and **C** were selected based on increased flexibility and variation in the number of attached amphoteric disaccharide units. 4-Aminobutanoic acid (GABA) was used as a flexible linker unit due to expected proteolytic stability[19] and commercial availability.

Results and Discussion

Synthesis of Disaccharide Units 6 and 9 In order to synthesize the glycoclusters access to the disaccharide units **6** and **9** was required (Chart 1). Monosaccharide derivative **3** was obtained by condensation of phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-β-D-galactopyranoside (**1**), prepared by silylation and benzoylation of phenylthio-β-D-galactopyranoside,[20] with the spacer **2** in the presence of *N*-iodosuccinimide (NIS) and trifluoromethanesulfonic acid (TfOH) in CH_2Cl_2 in 79% yield.[21,22] The anomeric proton of the galactose unit appeared as a doublet at δ 4.72 (d, J=7.9 Hz). Selective removal of the *tert*-butyldiphenylsilyl (TBDPS) group in **3** with tetrabutylammonium fluoride (TBAF) gave disaccharide acceptor **4**, which was subjected to glycosylation with thioglycosyl donor **1** in the presence of NIS/TfOH to afford the desired disaccharide **5** in 89% yield. The β-glycosidic linkage was assigned on the basis of homonuclear coupling constants (H-1′, δ=4.80 ppm, $J_{H1',H2'}$=7.9 Hz). Selective removal of the Troc-protecting group from **5** by Zn–AcOH gave the primary amine **6**. On the other hand, removal of the TBDPS group was achieved by treatment of **5** with TBAF to give **7**. Phosphorylation with phosphoryl chloride followed by exposure of the resulting dichloroester to choline tosylate yielded choline derivative **8**. Deblocking of the Troc group from **8** with Zn–AcOH produced the primary amine **9**.

Synthesis of Phenyl-Core Glycocluster A Two methods were studied for the synthesis of glycocluster **A** (Chart 2). Initially, we attempted to install the PC group at the end of the synthesis after cluster formation. Trimesoyl chloride was selected as the core for the synthesis of the phenyl-core cluster. *N*-Acylation of trimesoyl chloride with amine **6** in the presence of triethylamine afforded the trivalent oligosaccharide **10** in 56% yield. Removal of the TBDPS group using TBAF afforded alcohol **11** in 73% yield. Phosphorylation of alcohol **11** was carried out by a multi-step procedure using a phosphorodiamidite method.[23,24] Initially, **11** reacted with 2-cyanoethyl *N*,*N*,*N*′,*N*′-tetraisopropylphosphorodiamidite followed by exposure to choline tosylate. The obtained crude product was oxidized *in situ* by *m*-chloroperbenzoic acid (*m*CPBA) and the cyanoethyl protecting group was removed using aqueous ammonia in methanol. Chromatographic purification of the final product afforded 6-*O*-phosphocholine disaccharide **12** in a low yield (9%). To improve the yield of **12** we also studied phosphorylation of **11** with phosphoryl

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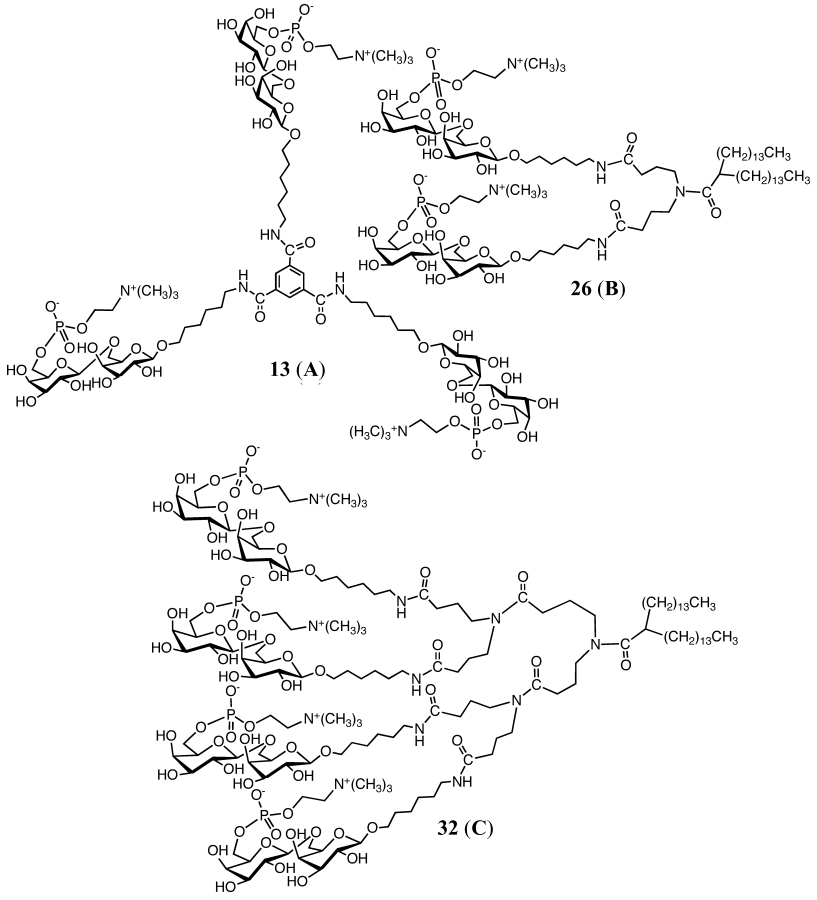
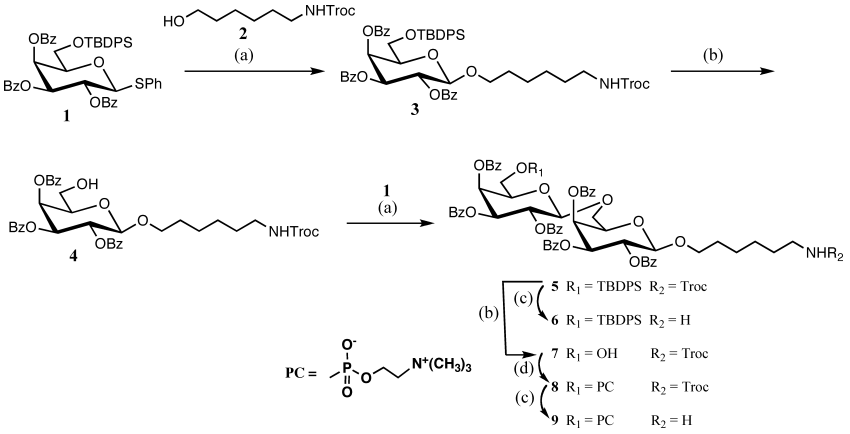


Fig. 1. Target Compounds



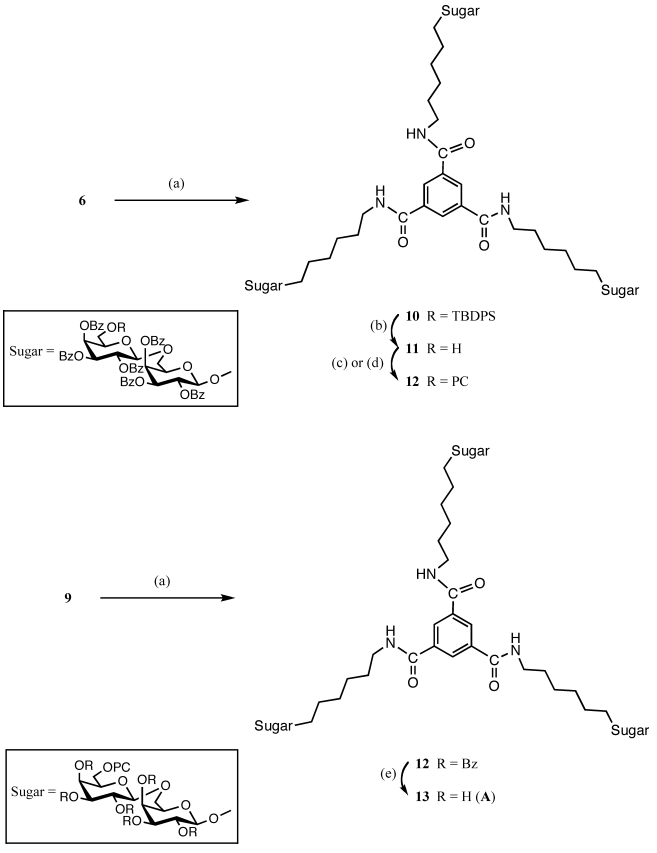
Reagents: (a) NIS, TfOH, CH_2Cl_2, MS 4 Å, **3**: 79%; **5**: 89%; (b) TBAF, AcOH, THF; **4**: 87%; **7**: 81%; (c) Zn, AcOH; **6**: quant.; **9**: quant.; (d) (i) $POCl_3$, Et_3N, MS 3 Å, CH_2Cl_2, (ii) choline tosylate, pyr., (iii) H_2O; 69% (three steps).

Chart 1

chloride and the resulting dichloroester was immediately converted to the phosphocholine derivative **12** using choline tosylate in 58% yield.[25] In the second method we studied cluster formation after incorporation of the PC-group. This was achieved by coupling of phosphocholine containing disaccharide **9** with trimesoyl chloride to afford **12** in 71% yield. Finally, removal of the benzoyl groups in **12** under Zemplén conditions, followed by column chromatography (Sephadex LH-20), furnished the target phenyl-core glycocluster **A** (**13**).

Synthesis of Glycodendrons B and C We selected amino diacid **20** as a new core unit for the preparation of glycodendrons **B** and **C**. Compound **20** required access to two building blocks 3-(benzyloxycarbonyl)-1-propanol (**14**) and 4-(4-nitro-benzenesulfonylamino)-butanoic acid benzyl ester (**16**). Benzyl ester **14** was prepared by basic hydrolysis of 4-butyrolactone using aq. NaOH followed by esterfication using benzyl bromide and tetrabutylammonium bromide in acetone in 85% yield. The second building block **16** was prepared from GABA in a two step procedure. At first, GABA was converted into benzylester under acidic conditions followed by protection of the amino group *p*-nitrobenzenesul-

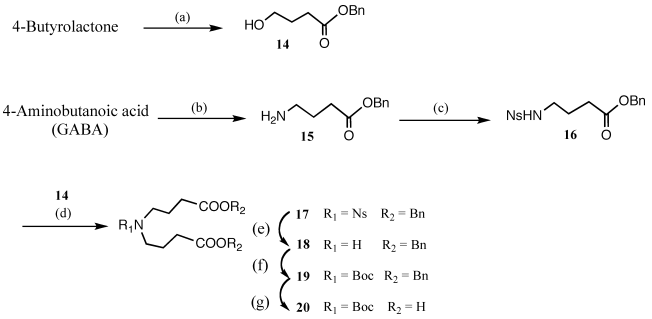
fonyl (*p*NBS) chloride to give **16**. The two building blocks **16** with **14** were coupled using Mitsunobu conditions[26] to produce **17**. Deblocking of the *p*NBS group with PhSH and K_2CO_3 in *N*,*N*-dimethylformamide (DMF)[27] followed by carbamoylation with di-*tert*-butyl dicarbonate ($(Boc)_2O$) afforded benzyl ester **19**. Finally, basic hydrolysis of ester **19** gave dicarboxylic acid derivative **20** (Chart 3).



Reagents: (a) trimesoyl chloride, Et_3N, CH_2Cl_2, **10**: 56%, **12**: 71%; (b) TBAF, AcOH, THF, 73%; (c) (i) 2-cyanoethyl-*N*,*N*,*N*′,*N*′-tetraisopropylphosphorodiamidide, 1*H*-tetrazole, CH_2Cl_2, MS 3 Å, (ii) 1*H*-tetrazole, choline tosylate, (iii) *m*CPBA, MeOH, (iv) aq. NH_3; 9% (four steps); (d) (i) $POCl_3$, Et_3N, MS 3 Å, CH_2Cl_2, (ii) choline tosylate, pyr., (iii) H_2O, 58% (three steps); (e) NaOMe, MeOH, 79%.

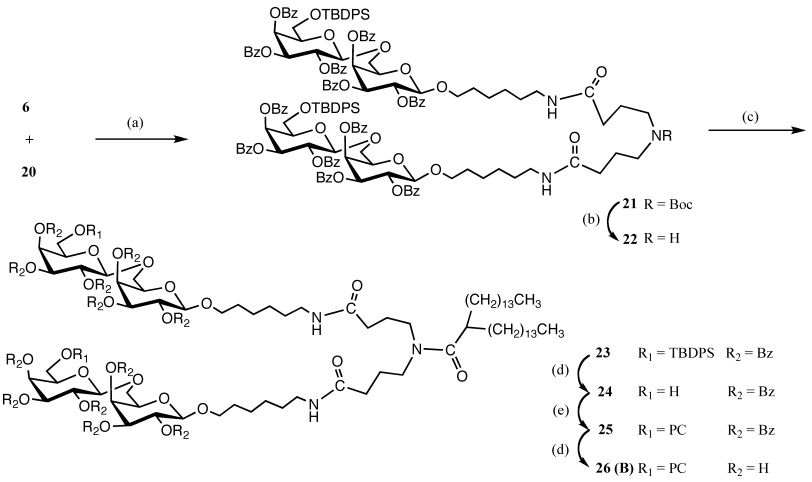
Chart 2

Next, we examined the outcome of the condensation of the core unit **20** with the PC-containing disaccharide unit **9**. However, coupling of **20** with **9** in the presence of diethylcyanophosphate (DEPC) and Et_3N was not successful (data not shown). Fortunately, coupling of **20** with sugar unit **6** in the presence DEPC and Et_3N was successful to produce desired divalent derivative **21** in 73% yield. The *tert*-butoxycarbonyl (Boc) group of **21** was removed under acidic conditions using 50% CF_3CO_2H in CH_2Cl_2 and the generated secondary amino group was acylated using 2-(tetradecyl)hexadecanoic acid and *N*-[3-(dimethylamino)propyl]-*N*′-ethylcarbodiimide hydrochloride (EDC) to give **23** in 87% yield. Deblocking of the *tert*-butyldiphenylsilyl (TBDPS) group was achieved by treatment of **23** with TBAF to produce **24** in 52% yield. Phosphorylation of **24** was peformed with phosphoryl chloride, and the resulting dichloroester was immediately converted to the phosphocholine derivative **25** by exposure to choline tosylate. Finally, de-*O*-benzoylation of **25** afforded symmetric glycodendron **26** (**B**) (Chart 4). Similarly, glycodendron **32** (**C**) was prepared by coupling of building blocks **20** with **22** to produce the desired tetramer derivative **27** in quantitative yield. Deblocking was performed as described above for dimer dendron **26** affording unprotected glycodendron **32** (**C**) (Chart 5). All of the glycoclusters described in this paper were purified by column chromatogra-



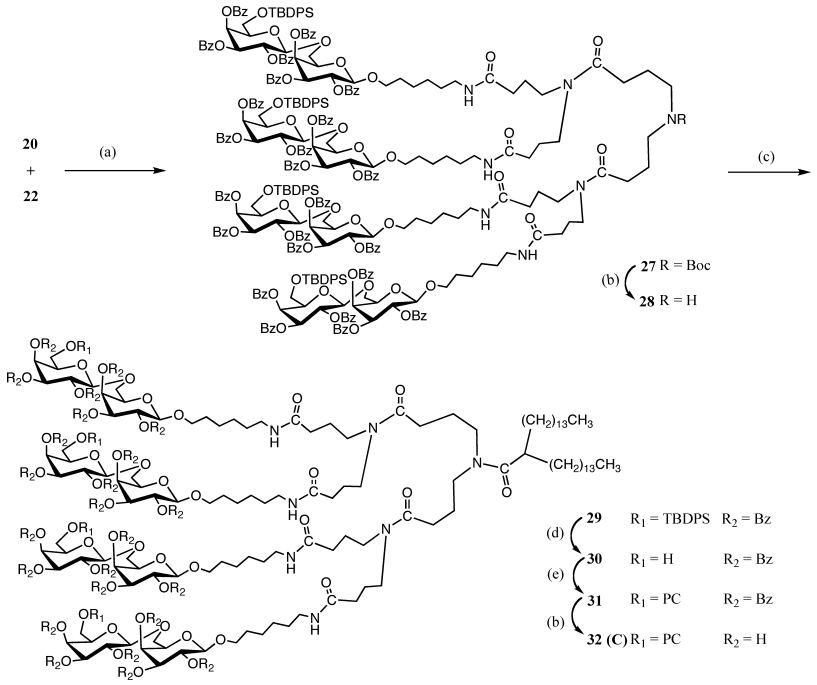
Reagents: (a) (i) NaOH, H_2O, (ii) BnBr, Bu_4NBr, acetone, 85%; (b) BnOH, TsOH, toluene, 98%; (c) *p*NsCl, Et_3N, CH_2Cl_2, 88%; (d) Ph_3P, DEAD, CH_2Cl_2, 78%; (e) PhSH, K_2CO_3, MeCN, 93%; (f) $(Boc)_2O$, Et_3N, CH_2Cl_2, 61%; (g) NaOH, H_2O, dioxane, quant.

Chart 3



Reagents: (a) DEPC, Et_3N, DMF, 73%; (b) TFA, CH_2Cl_2, 75%; (c) 2-(tetradecyl) hexadecanoic acid, EDC, DMAP, CH_2Cl_2, 87%; (d) TBAF, AcOH, THF, 52%; (e) (i) $POCl_3$, Et_3N, MS 3 Å, CH_2Cl_2, (ii) choline tosylate, pyr., (iii) H_2O, 54% (three steps); (f) NaOMe, MeOH. 84%.

Chart 4



Reagents: (a) DEPC, Et_3N, DMF, 99%; (b) TFA, CH_2Cl_2, 94%; (c) 2-(tetradecyl) hexadecanoic acid, EDC, DMAP, CH_2Cl_2, 90%; (d) TBAF, AcOH, THF, 85%; (e) (i) $POCl_3$, Et_3N, MS 3 Å, CH_2Cl_2, (ii) choline tosylate, pyr., (iii) H_2O, 21% (three steps); (f) NaOMe, MeOH, 80%.

Chart 5

phy on silica gel or Sephadex (LH 20). The solubilities of all final compounds (**A**, **B**, **C**) containing phosphocholine were excellent in methanol and in a mixture of 1 : 1 methanol–water. The purified final compounds were characterized by commonly available techniques, such as ^{1}H- and ^{13}C-NMR spectroscopy and time of flight mass spectrometry.

Conclusions

In summary, an efficient synthetic procedure for glycoclusters **13** (**A**), **26** (**B**) and **32** (**C**) containing a phosphocholine residue related to glycosphingolipids from the earthworm *Pheretima hilgendorfi* has been developed. It is expected that these glycocluster will induce enhanced immune responses when compared to their monovalent counterparts.

Experimental

General Methods Optical rotations were measured with a Jasco P-1020 digital polarimeter. ^{1}H- and ^{13}C-NMR spectra were recorded with a JMN A500 FT NMR spectrometer with Me_4Si as the internal standard for solutions in $CDCl_3$ CD_3OD. Matrix assisted laser desorption/ionization-time of flight (MALDI-TOF)-MS was recorded on a Perseptive Voyager RP mass spectrometer. High-resolution mass spectra were recorded on a JEOL JMS-700 under FAB conditions. TLC was performed on Silica Gel 60 F254 (E. Merck) with detection by quenching of UV fluorescence and by charring with 10% H_2SO_4. Column chromatography was carried out on Silica Gel 60 (E. Merck).

6-*N*-(2,2,2-Trichloroethoxycarbonyl)aminohexyl 2,3,4-Tri-*O*-benzoyl-6-*O*-(*tert*-butyldiohenylsilyl)-β-D-galactopyranoside (3) A solution of compound **1** (2.0 g, 2.4 mmol) and **2** (1.4 g, 4.9 mmol) containing activated MS 4 Å (2.0 g) in dry CH_2Cl_2 (10 ml) was stirred under an atmosphere of argon for 2 h at room temperature. After cooling to 0 °C, successively NIS (1.1 mg, 4.9 mmol) and TfOH (112 μl, 1.3 mmol) were added and stirring was continued at 0 °C for 30 min, then neutralized with Et_3N. The reaction mixture was filtered, and the filtrate was washed with aqueous sodium thiosulfate, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography (toluene : acetone = 6 : 1) as the eluent to give **3** (1.9 g, 79%). $[\alpha]_D^{24}$ +90.3 (c=1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.04—7.09 (15H, m, 3Ph), 6.04 (1H, d, $J_{3,4}$=2.4 Hz, H-4), 5.70 (1H dd, $J_{1,2}$=7.9 Hz, $J_{2,3}$=10.4 Hz, H-2), 5.62 (1H, dd , H-3), 4.81 (1H, br s, NH), 4.72 (1H, d, H-1), 4.72—4.68 (2H, m, $COOCH_2CCl_3$), 4.06 (1H, t, $J_{5,6}$=7.3 Hz, H-5), 3.93—3.89 (1H, m, CH_2CH_2O), 3.83 (2H, d, H-6), 3.50—3.46 (1H, m, CH_2CH_2O), 3.04—3.00 (2H, m, CH_2NH), 1.55—1.04 (8H, m, CH_2×4), 1.00 (9H, s, *t*-Bu); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 165.6, 165.4, 165.2, 154.4, 135.5, 135.4, 133.2, 133.1, 132.5, 130.0, 129.8, 129.73, 29.66, 129.6, 129.5, 129.0, 128.5, 128.3, 128.2, 127.7, 127.6, 101.6, 74.4, 73.7, 71.9, 70.1, 70.0, 67.9, 61.3, 41.0, 29.4, 29.1, 26.6, 26.1, 25.4, 19.0; MALDI-TOF-MS: Calcd for $C_{52}H_{56}Cl_{13}NNaO_{11}Si$: m/z 1026. Found: 1026.8 $[M+Na]^+$.

6-*N*-(2,2,2-Trichloroethoxycarbonyl)aminohexyl 2,3,4-Tri-*O*-benzoy-β-D-galactopyranoside (4) A solution of **3** (1.0 g, 0.99 mmol) and acetic acid (0.2 ml, 3.0 mmol) in THF (2.5 ml) was treated with 1 M TBAF in THF (2.0 ml, 2.0 mmol) at room temperature and then was stirred for 12 h. After concentration, the residue was added to the water, extracted with $CHCl_3$, and the organic layer was proceeded as usual. The product was purified by silica gel column chromatography (toluene : acetone = 4 : 1) as eluent to give **4** (667 mg, 87%). MALDI-TOF-MS: Calcd for $C_{36}H_{38}Cl_{13}NNaO_{11}$: m/z 788. Found: 788.9 $[M+Na]^+$.

6-*N*-(2,2,2-Trichloroethoxycarbonyl)aminohexyl 2,3,4-Tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoy-β-D-galactopyranoside (5) A solution of compound **1** (2.2 g, 2.6 mmol) and **4** (1.7 g, 2.2 mmol) containing activated MS 4 Å (1.7 g) in dry CH_2Cl_2 (9.0 ml) was stirred under an atmosphere of argon for 2 h at room temperature. After cooling to 0 °C, successively NIS (0.74 g, 3.3 mmol) and TfOH (39.0 μl, 0.44 mmol) were added and stirring was continued at 0 °C for 30 min, then neutralized with Et_3N. The reaction mixture was filtered, and the filtrate was washed with aqueous sodium thiosulfate, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography (toluene : acetone = 10 : 1) as the eluent to give **5** (2.9 g, 89%). $[\alpha]_D^{24}$ +93.0 (c=1.4, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.05—7.04 (40H, m, 8Ph), 6.00 (1H, d, $J_{3',4'}$=3.7 Hz, H-4′), 5.81 (1H, d, $J_{3,4}$=3.7 Hz, H-4), 5.68—5.63 (2H, m, H-2, 2′), 5.66 (1H, dd , $J_{2',3'}$=10.4 Hz, H-3′), 5.48 (1H, dd, $J_{2,3}$=10.4 Hz, H-3), 4.80 (1H, d, $J_{1',2'}$=7.9 Hz, H-1′), 4.73—4.68 (2H, m, $COOCH_2CCl_3$), 4.57 (1H, d, $J_{1,2}$=7.9 Hz, H-1), 4.09—4.06 (2H, m, H-5′, 6′a), 3.97 (1H, t, $J_{5,6}$=7.3 Hz, H-5), 3.80 (1H, dd, $J_{5,6'b}$=5.5 Hz, $J_{6'a,6'b}$=11.6 Hz, H-6′b), 3.63—3.58 (3H, m, H-6a, 6b, CH_2CH_2O), 3.22—3.17 (1H, m, CH_2CH_2O), 3.02—2.98 (2H, dd, CH_2NH), 1.34—0.95 (8H, m, CH_2×4) 0.92 (9H, s, *t*-Bu); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 165.6, 165.4, 165.3, 165.1, 135.5, 133.4, 133.2, 130.0, 129.9, 129.8, 129.74, 129.69, 129.66, 129.5, 129.0, 128.5, 128.4, 128.3, 128.2, 127.7, 127.5, 101.5, 101.1,

74.4, 73.2, 71.9, 71.6, 70.1, 69.9, 69.8, 68.6, 67.8, 67.6, 60.8, 41.0, 29.4, 29.0, 26.5, 26.1, 25.4, 18.9; MALDI-TOF-MS: Calcd for $C_{79}H_{78}Cl_3NNaO_{19}Si$: *m/z* 1500.4. Found: 1500.7 $[M+Na]^+$.

6-Aminohexyl 2,3,4-Tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoy-β-D-galactopyranoside (6) To a solution of **5** (936 mg, 0.63 mmol) in acetic acid (5 ml) was added zinc powder (2.0 g). The reaction mixture was stirred at 50 °C for 2 h. After completion of the reaction, the mixture was filtered off and washed with $CHCl_3$. The filtrate was concentrated and purified by silica gel column chromatography (chloroform : methanol=8 : 1) to give **6** (827 mg, quant.). $[\alpha]_D^{24}$ +93.0 (c=1.4, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.05—7.04 (40H, m, 8Ph), 6.00 (1H, d, $J_{3,4}$=3.7 Hz, H-4), 5.81 (1H, d, $J_{3',4'}$=3.1 Hz, H-4′), 5.69—5.63 (2H, m, H-2, 2′), 5.58 (1H, dd, H-3′), 5.48 (1H, dd, H-3), 4.80 (2H, br s, $J_{1',2'}$=7.9 Hz, NH, H-1′) 4.73—4.68 (2H, m, $COOCH_2CCl_3$), 4.57 (1H, d, $J_{1,2}$=7.9 Hz, H-1), 4.09—4.06 (2H, m, H-5′, 6′a), 3.97 (1H, t, H-5), 3.80 (1H, dd, H-6′b), 3.63—3.58 (3H, m, H-6, O–CH_2), 3.22—3.17 (1H, m, O–CH_2), 3.02—2.98 (2H, m, N–CH_2), 1.33—0.92 (8H, m, alkyl); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 165.6, 165.4, 165.3, 165.1, 135.5, 133.9, 135.35, 133.2, 133.1, 132.6, 130.0, 129.9, 129.8, 129.74, 129.69, 129.66, 129.5, 129.0, 128.5, 128.4, 128.3, 128.2, 127.7, 127.5, 101.5 (C-1), 101.1 (C-1′), 74.4, 73.6, 73.2, 71.9, 71.6, 70.1, 69.9, 69.8, 68.6, 67.8, 67.6, 60.8, 41.0, 29.4, 29.0, 26.5, 26.1, 25.4, 18.9; MALDI-TOF-MS: Calcd for $C_{76}H_{77}NNaO_{17}Si$: *m/z*. 1327.5. Found: 1327.7 $[M+Na]^+$.

6-*N*-(2,2,2-Trichloroethoxycarbonyl)aminohexyl 2,3,4-Tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoy-β-D-galactopyranoside (7) A solution of **5** (2.4 g, 1.59 mmol) and acetic acid (0.27 ml, 4.77 mmol) in THF (8.0 ml) was treated with 1 M TBAF in THF (3.2 ml, 3.2 mmol) at room temperature and then was stirred for 12 h. After concentration, the residue was added to the water, extracted with $CHCl_3$, and the organic layer was proceeded as usual. The product was purified by silica gel column chromatography (toluene : acetone=6 : 1) as eluent to give **7** (1.6 g, 81%). $[\alpha]_D^{24}$ +121.0 (c=1.0, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.12—7.14 (30H, m, 6Ph), 5.93 (1H, d, $J_{3',4'}$=3.7 Hz, H-4′), 5.83—5.78 (2H, m, H-2′, 4), 5.69 (1H, dd, $J_{1,2}$=7.1 Hz, $J_{2,3}$=10.4 Hz, H-2), 5.57—5.52 (2H, m , H-3, 3′), 4.89 (1H. t, NH), 4.85 (1H, d, $J_{1',2'}$=7.9 Hz, H-1′), 4.73—4.68 (2H, m, $COOCH_2CCl_3$), 4.64 (1H, d, H-1), 4.16—4.10 (2H, m, H-5′, 6′a), 3.95 (1H, t, $J_{5,6}$=6.7 Hz, H-5), 3.89 (1H, dd, $J_{5,6'b}$=6.1 Hz, $J_{6'a,6'b}$=9.8 Hz, H-6′b), 3.71—3.65 (2H, m, H-6a, $CH_2C\underline{H}_2O$), 3.50—3.49 (1H, br, H-6b), 3.22—3.16 (1H, m, CH_2CH_2O), 3.02 (2H, q, CH_2NH), 1.40—1.10 (8H, m, $CH_2\times$4). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 166.5, 165.54, 165.46, 165.2, 165.1, 154.4, 137.8, 137.7, 133.5, 133.3, 133.2, 133.1, 130.1, 129.9, 129.7, 129.4, 129.3, 129.02, 128.97, 128.8, 128.74, 128.66, 128.6, 128.5, 128.33, 128.25, 128.2, 127.9, 125.2, 101.5, 101.3, 95.7, 74.4, 73.0, 71.7, 71.6, 70.0, 69.9, 69.81, 68.77, 68.6, 68.1, 60.5, 41.0, 29.3, 29.0, 26.1, 25.4, 21.4; MALDI-TOF-MS: Calcd for $C_{63}H_{60}Cl_3NNaO_{19}$: *m/z* 1262.3. Found: 1262.1 $[M+Na]^+$.

6-*N*-(2,2,2-Trichloroethoxycarbonyl)aminohexyl 2,3,4-Tri-*O*-benzoyl-6-*O*-phosphorylcoline-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoy-β-D-galactopyranoside (8) To a solution of **7** (200 mg, 0.15 mmol) and MS 3 Å (200 mg) in dry CH_2Cl_2 (3.0 ml) was added phosphoryl chloride (15.7 μl, 0.17 mmol) and triethylamine (64 μl, 0.46 mmol) at −10 °C under Ar. The solution was stirred for 1.5 h at the room temperature. To this were added pyridine (3 ml) and then choline tosylate (84.3 mg, 0.31 mmol) at 0 °C. This solution was stirred for 10 h at room temperature, and were added H_2O (1 ml) and stirred for 1 h at the same temperature. After that, the solution was filtered and concentrated. The product was purified by Iatrobeads column chromatography ($CHCl_3$: MeOH : H_2O=8 : 5 : 1) as eluent to give **8** (147 mg, 69%). $[\alpha]_D^{24}$ +85.4 (c=3.7, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.06—7.08 (30H, m, 6Ph), 5.93 (1H, d, $J_{3,4}$=2.4 Hz, H-4), 5.81 (1H, d, $J_{3',4'}$=3.2 Hz, H-4′), 5.70 (1H, dd, $J_{1',2'}$=7.9 Hz, $J_{2',3'}$=9.8 Hz, H-2′), 5.66 (1H, dd, $J_{2,3}$=10.4 Hz, H-2), 5.51—5.48 (2H, m, H-3, 3), 4.99 (1H, t, NH) 4.94 (1H, d, H-1′), 4.73—4.67 (2H, m, $COOCH_2CCl_3$), 4.62 (1H, d, $J_{1,2}$= 7.9 Hz, H-1), 4.35 (1H, br, H-6′a) 4.17—4.03 (5H, m, H-5, 6′b, 6a, $POC\underline{H}_2CH_2$), 3.84—3.54 (5H, m, H-5, 6b, $POCH_2C\underline{H}_2$, $CH_2C\underline{H}_2O$), 3.28—3.26 (1H, m, $CH_2C\underline{H}_2O$), 3.18 (9H, s, $N(CH_3)_3$), 3.02—2.97 (2H, m, $C\underline{H}_2NH$), 1.31—1.05 (8H, m, $CH_2\times$4); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 165.7, 165.4, 165.3, 165.1, 154.4, 143.5, 139.3, 133.4, 133.2, 133.1, 129.9, 129.8, 129.6, 129.5, 129.4, 129.2, 129.1, 129.0, 128.8, 128.6, 128.5, 128.3, 128.1, 125.8, 101.2, 100.8, 74.3, 72.8, 72.4, 71.7, 69.9, 69.6, 69.5, 68.7, 68.0, 67.6, 66.0, 61.9, 59.2, 54.1, 45.7, 40.9, 29.3, 28.9, 26.0, 25.3, 21.1, 8.48; MALDI-TOF-MS: Calcd for $C_{68}H_{73}Cl_3N_2O_{22}P$: *m/z* 1404. Found: 1404 $[M+H]^+$.

6-Aminohexyl 2,3,4-Tri-*O*-benzoyl-6-*O*-phosphorylcoline-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoy-β-D-galactopyranoside (9) To a solution of **8** (311 mg, 0.22 mmol) in acetic acid (5 ml) was added zinc powder (750 mg). The reaction mixture was stirred at 50 °C for 2 h. After completion of the reaction, the mixture was filtered off and washed with $CHCl_3$. The filtrate was concentrated and purified by Sephadex LH-20 column chromatography in MeOH to give **9** (285 mg, quant.). $[\alpha]_D^{24}$ +38.7 (c=4.5, MeOH). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.94—7.10 (30H, m, 6Ph), 5.86 (1H, d, $J_{3,4}$=3.1 Hz, H-4), 5.77 (1H, d, $J_{3',4'}$=3.1 Hz, H-4′), 5.63 (1H, dd, $J_{1',2'}$=7.9 Hz, $J_{2',3'}$=10.4 Hz, H-2′), 5.57—5.48 (3H, m, H-2, 3, 3′), 4.95 (1H, d, H-1′), 4.68 (1H, d, $J_{1,2}$=7.9 Hz, H-1), 4.23—4.12 (4H, m, H-5, 6′a, $POCH_2CH_2$), 4.05 (1H, t, $J_{5',6'a}$=4.9 Hz, $J_{5',6'b}$=10.4 Hz, H-5′), 3.93 (1H, br, H-6a), 3.81 (1H, dd, $J_{6'a,6'b}$=9.7 Hz, H-6′b), 3.59—3.49 (3H, m, $POC\underline{H}_2$-CH_2, $CH_2C\underline{H}_2O$), 3.29—3.26 (1H, m, $CH_2C\underline{H}_2O$), 3.09 (9H, s, $N(CH_3)_3$), 2.61 (2H, t, $C\underline{H}_2NH$), 1.31—1.07 (8H, m, $CH_2\times$4), 0.92 (9H, s, *t*-Bu). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 165.3, 165.1, 165.01, 164.96, 164.93, 133.05, 132.98, 132.8, 132.7, 129.12, 129.08, 128.9, 128.8, 128.7, 128.61, 128.56, 128.5, 128.4, 128.2, 128.1, 128.02, 127.95, 127.8, 127.64, 127.57, 100.5, 100.1, 71.9, 71.6, 71.2, 69.6, 69.3, 69.0, 68.2, 67.3, 66.8, 65.6, 61.8, 58.5, 56.6, 53.2, 48.2, 38.7, 28.4, 26.7, 25.3, 24.7, 16.9; MALDI-TOF-MS: Calcd for $C_{65}H_{72}N_2O_{20}P$: *m/z* 1231. Found : 1231 $[M+H]^+$.

***N*,*N*′,*N*″-Tri-{6-[2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoy-β-D-galactopyranoslyoxy]-hexyl}-1,3,5-benzenetriamide (10)** To a solution of **6** (830 mg, 0.63 mmol) in CH_2Cl_2 (5 ml) were added triethylamine (0.12 ml, 0.85 mmol) and trimesoyl chloride (35.0 mg, 0.13 mmol). The mixture was stirred for 15 min at room temperature. After completion of the reaction, the mixture was concentrated. The product was purified by silica gel column chromatography (toluene : acetone=6 : 1) as eluent to give **10** (306 mg, 56%). $[\alpha]_D^{24}$ +71.4 (c=6.9, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.32 (3H, S, Ph), 8.27—7.04 (120H, m, 24Ph), 6.34 (3H, t, NH), 6.02 (3H, d, $J_{3,4}$=3.7 Hz, H-4), 5.82 (3H, d, $J_{3',4'}$=3.7 Hz, H-4′), 5.69—5.63 (6H, m, H-2, 2′), 5.59 (3H, dd, $J_{2',3'}$=10.4 Hz, H-3′), 5.50 (3H, dd, $J_{2,3}$=10.4 Hz, H-3), 4.81 (3H, d, $J_{1',2'}$=7.9 Hz, H-1′), 4.59 (3H, d, $J_{1,2}$=7.9 Hz, H-1), 4.09—4.07 (6H, m, H-5′, 6′a), 3.98 (3H, t, $J_{5,6}$=7.3 Hz, H-5), 3.80 (3H, dd, $J_{5',6b'}$=9.1 Hz, $J_{6'a,6'b}$=11.6 Hz, H-6′b), 3.63—3.58 (6H, m, H-6, CH_2CH_2O), 3.24—3.17 (9H, m, CH_2CH_2O, CH_2NH), 1.34—0.96 (24H, m, $CH_2\times$12), 0.92 (27H, s, *t*-Bu); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 165.6, 165.4, 165.1, 135.5, 133.37, 133.35, 133.1, 132.7, 132.5, 130.0, 129.9, 129.8, 129.71, 129.68, 129.6, 129.5, 129.0, 128.5, 128.4, 128.3, 128.2, 127.7, 127.5, 101.4, 101.1, 73.6, 73.1, 71.9, 71.6, 70.1, 69.9, 69.8, 68.6, 67.8, 67.6, 60.7, 40.1, 29.2, 29.0, 26.5, 26.4, 25.5, 18.8; MALDI-TOF-MS: Calcd for $C_{237}H_{231}N_3NaO_{54}Si_3$: *m/z* 4089. Found: 4091 $[M+Na]^+$.

***N*,*N*′,*N*″-Tri-{6-[2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoy-β-D-galactopyranoslyoxy]hexyl}-1,3,5-benzenetriamide (11)** Compound **11** was prepared from **10** (256 mg) as described for preparation of **4**, yielding 154 mg (73%). $[\alpha]_D^{24}$ +122.3 (c=0.5, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.33 (3H, s, Ph), 8.25—7.14 (90H, m, 18Ph), 6.66 (3H, t, NH), 5.91 (3H, d, $J_{3',4'}$=3.7 Hz, H-4′), 5.81—5.78 (6H, m, H-4, 2′), 5.69 (3H, dd, $J_{1,2}$=7.9 Hz, $J_{2,3}$=10.4 Hz, H-2), 5.58—5.51 (6H, m, H-3, 3′), 4.90 (3H, d, $J_{1',2'}$=7.9 Hz, H-1′), 4.64 (3H, d, H-1), 4.15—4.09 (6H, m, H-5′, 6′a), 4.00 (3H, t, $J_{5,6}$=6.7 Hz, H-5), 3.92 (3H, dd, $J_{5',6b'}$=6.7 Hz, $J_{6'a,6'b}$=11.0 Hz, H-6′a), 3.78—3.66 (6H, m, H-6b, CH_2CH_2O), 3.65—3.33 (6H, m, H-6a, CH_2CH_2O), 2.99 (3H, t, OH), 1.40—1.16 (24H, m, $CH_2\times$12); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 166.54, 165.6, 165.5, 165.2, 135.1, 130.1, 129.9, 129.7, 129.4, 129.3, 129.04, 128.99, 128.8, 128.7, 128.6, 128.5, 128.4, 128.34, 128.26, 128.2, 125.3, 101.4, 101.3, 74.0, 73.2, 71.8, 71.7, 70.0, 69.9, 69.7, 68.8, 68.7, 68.0, 60.5, 40.1, 29.2, 29.0, 26.3, 25.4; MALDI-TOF-MS: Calcd for $C_{189}H_{177}N_3NaO_{54}$: *m/z* 3375. Found: 3377 $[M+Na]^+$.

***N*,*N*′,*N*″-Tri-{6-[2,3,4-tri-*O*-benzoyl-6-*O*-phosphorylcoline-β-D-galactopyranosyl-(1→6)-2,3,4-tri-*O*-benzoy-β-D-galactopyranoslyoxy]hexyl}-1,3,5-benzenetriamide (12)** **A**: method (c); To a solution of **11** (74 mg, 31 μmol) and MS 3 Å (150 mg) in dry CH_2Cl_2 (2.0 ml) was added 2-cyanoethyl-*N*,*N*,*N*′,*N*′-tetraisopropylphosphorodiamidite (61 μl, 0.19 mmol) at room temperature under Ar. The solution was stirred for 0.5 h at the room temperature. To this were added 1*H*-tetrazole (27 mg, 0.39 mmol) and then choline tosylate (142 mg, 0.52 mmol) at room temperature. This solution was stirred for 4 h at room temperature, and was added MeOH (2 ml) and *m*CPBA (27 mg, 0.16 mmol) and stirred for 1 h at the same temperature. After that, the mixture was added 30% aq. NH_3 (2 ml) and stirred for 1 h at room temperature. The solution was filtered through a pad of Celite and concentrated. The product was purified by Iatrobeads column chromatography ($CHCl_3$: MeOH : H_2O=8 : 5 : 1) as eluent to give **12** (10 mg, 9%). **B**: method (d); To a solution of **11** (73 mg, 30 μmol) and MS 3 Å (73 mg) in dry CH_2Cl_2 (2 ml) was added phosphoryl chloride (14.9 μl, 0.10 mmol) and triethylamine (38 μl, 0.27 mmol) at −10 °C under Ar. The solution was stirred

for 1 h at the room temperature. To this were added pyridine (2 ml) and then choline tosylate (50.1 mg, 0.18 mmol) at 0 °C. This solution was stirred for 10 h at room temperature, and were added H_2O (1 ml) and stirred for 1 h at the same temperature. After that, the solution was filtered and concentrated. The product was purified by Iatrobeads column chromatography ($CHCl_3$: MeOH : H_2O=8 : 5 : 1) as eluent to give **12** (67.3 mg, 58%). **C**: To a solution of **9** (239 mg, 0.19 mmol) in CH_2Cl_2 (2 ml) were added triethylamine (56.8 μl, 0.40 mmol) and trimesoyl chloride (8.6 mg, 0.32 mmol). The mixture was stirred for 15 min at room temperature. After completion of the reaction, the mixture was concentrated. The product was purified by Iatrobeads column chromatography ($CHCl_3$: MeOH : H_2O=8 : 5 : 1) as eluent to give **12** (88.4 mg, 71 %). $[\alpha]_D^{24}$ +89.5 (c=2.2, MeOH); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.63 (3H, s, Ph), 8.33—7.11 (90H, m, 18Ph), 5.95 (3H, d, $J_{3,4}$=3.1 Hz, H-4), 5.89 (3H, d, $J_{3',4'}$=1.8 Hz, H-4′), 5.72 (3H, dd, $J_{1',2'}$=7.9 Hz, $J_{2',3'}$=10.4 Hz, H-2′), 5.66—5.64 (9H, m, H-2, 3, 3′), 5.06 (3H, d, H-1′), 4.81 (3H, d, $J_{1,2}$=7.9 Hz, H-1), 4.36—4.30 (6H, m, H-5′, 6′a), 4.22 (6H, br dd, $POCH_2CH_2$), 4.16 (3H, t, $J_{5,6a}$=4.9 Hz, $J_{5,6b}$=10.4 Hz, H-5), 4.01 (3H, br dd, H-6′a), 3.91—3.82 (6H, m, H-6b, 6), 3.66—3.62 (3H, m, CH_2CH_2O), 3.59—3.62 (6H, m, $POCH_2CH_2$), 3.34—3.32 (3H, m, CH_2CH_2O), 3.25—3.22 (6H, m, $NHCH_2$), 3.18 (18H, s, $N(CH_3)_3$), 1.41—1.16 (24H, m, CH_2×12); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 211.6, 168.1, 166.9, 166.8, 166.7, 166.5, 149.8, 145.9, 136.5, 134.5, 134.3, 130.7, 130.4, 130.4, 130.33, 130.29, 129.91, 129.86, 129.7, 129.6, 129.5, 129.3, 129.2, 129.1, 119.5, 102.0, 101.7, 78.9, 78.7, 78.43, 73.4, 73.3, 72.9, 71.4, 73.3, 72.9, 71.4, 71.1, 70.6, 69.9, 69.1, 68.6, 67.9, 67.9, 67.3., 63.6, 60.1, 54.7, 49.5, 48.5, 47.7, 40.9, 30.03, 29.97, 27.4, 26.4, 9.16; MALDI-TOF-MS: Calcd for $C_{204}H_{214}N_6O_{63}P_3$: m/z 3847. Found: 3853 $[M+H]^+$.

***N*,*N*′,*N*″-Tri-{6-[6-*O*-phosphorylcoline-*β*-D-galactopyranosyl-(1→6)-*β*-D-galactopyranosyloxy]hexyl}-1,3,5-benzenetriamide (13; A)** To a solution of **12** (81.1 mg, 23 μmol) in MeOH (3.0 ml) was added NaOMe (15 mg) at room temperature and the mixture was stirred for 10 h, then neutralized with Amberlite IR 120 [H^+]. The mixture was filtered off and concentrated. The product was purified by Sephadex LH-20 column chromatography in MeOH : H_2O (1 : 1) to give **13** (36.0 mg, 79%). $[\alpha]_D^{24}$ −8.9 (c=0.9, MeOH : H_2O=1 : 1); ^{1}H-NMR (500 MHz, CD_3OD) δ: 8.29 (s, 3H, Ph), 4.41 (d, 3H, $J_{1',2'}$=7.9 Hz, H-1′), 4.32 (d, 3H, $J_{1,2}$=7.9 Hz, H-1); ^{13}C-NMR (125 MHz, CD_3OD) δ: 169.1, 136.4, 129.6, 104.6, 104.1, 74.83, 74.75, 74.1, 74.0, 72.0, 71.9, 69.8, 69.5, 67.2, 65.5, 60.5, 55.0, 49.9, 41.1, 30.0, 29.7, 27.3, 26.1; MALDI-TOF-MS: Calcd for $C_{78}H_{141}N_6NaO_{45}P_3$: m/z 1997. Found: 1996 $[M+H]^+$.

3-(Benzyloxycarbonyl)-1-propanol (14) To a solution of 4-butyrolactone (5.1 g, 59.2 mmol) in H_2O (59 ml) was added NaOH (2.4 g, 59.2 mmol) at 70 °C and the mixture was stirred for 24 h. Toluene was added and evaporated. To a suspension of the residue in acetone (60 ml) was added tetrabutylammoniumbromide (955 mg, 2.96 mmol), BnBr (8.46 ml, 71.1 mmol). The reaction mixture was refluxed for 24 h, and then concentrated. The reaction mixture was extracted with ethyl acetate. The extract was washed with 1 M $NaHSO_4$, $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. The product was purified on silica gel column chromatography (hexane : ethyl acetate=5 : 1) to give **14** (9.8 g, 85%). ^{1}H-NMR (500MHz, $CDCl_3$) δ: 7.31—7.23 (5H, m, Ph), 5.06 (2H, s, benzyl methylene), 3.69 (1H, br, –OH) 3.56 (2H, t, HO–$\underline{CH_2}$), 2.41 (2H, t, $\underline{CH_2}$–CO), 1.85—1.79 (2H, m, CH_2–$\underline{CH_2}$–CH_2); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 173.0, 135.5, 127.9, 127.74, 127.67, 127.5, 127.4, 65.5, 60.7, 30.1, 27.1; MALDI-TOF-MS: Calcd for $C_{11}H_{15}O_3$: m/z 195. Found: 195 $[M+Na]^+$.

4-Aminobutanoic Acid Benzyl Ester (15) To a solution of 4-aminobutanoic acid (5.2 g, 50 mmol), BnOH (25 ml, 0.24 mol) and TsOH (11 g, 60 mmol) in toluene (50 ml) was refluxed for 5 h. After the reaction, the residue was crestallized from hexane and was recrestallized from ethyl acetate/hexane to give **15** (17.9 g, 98%).

4-(4-Nitro-benzenesulfonylamino)-butanoic Acid Benzyl Ester (16) To a solution of **15** (7.0 g, 19 mmol) in dry CH_2Cl_2 (70 ml) were added *p*-nitrobenzenesulfonyl chloride (4.7 g, 21 mmol) and Et_3N (7 ml, 48 mmol), and the mixture was stirred for 18 h at 0 °C. After the reaction, the residue was successively washed with water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 10 : 1 toluene–acetone as eluent to give **16** (6.7 g, 88%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.32 and 8.01 (4H, each d, Ns), 7.38—7.32 (5H, m, Ph), 5.24, (1H, t, NH) 5.10 (2H, s, benzyl methylene), 3.07 (2H, q, NH–$\underline{CH_2}$), 2.42 (2H, t, $\underline{CH_2}$–CO), 1.86—1.81 (2H, m, CH_2–$\underline{CH_2}$–CH_2); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 173.0, 150.0, 145.9, 135.5, 128.6, 128.4, 124.4, 66.7, 42.7, 31.2, 24.6; MALDI-TOF-MS: Calcd For $C_{17}H_{18}N_2NaO_6S$: m/z 401.1. Found: 401.1$[M+Na]^+$.

4-[Benzyloxycarbonylpropyl-(4-nitro-benzenesulfonyl)-amino]-butanoic Acid Benzyl Ester (17) To a solution of **16** (3.0 g, 7.9 mmol) and **14** (2.0 g, 10 mmol) in dry CH_2Cl_2 (30 ml) was added Ph_3P (2.7 g, 10 mmol) and 40% DEAD in toluene (4.7 ml, 10 mmol) at 0 °C, and the solution was stirred for 3 h at same temperature. The mixture was washed with water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 20 : 1 toluene–acetone as eluent to give **17** (3.5 g, 78%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.24 and 7.91 (4H, each d, Ns), 7.33—7.23 (10H, m, Ph), 5.10 (4H, s, benzyl methylene), 3.19 (4H, t, NH–$\underline{CH_2}$×2), 2.37 (4H, t, $\underline{CH_2}$–CO×2), 1.88—1.82 (4H, m, CH_2–$\underline{CH_2}$–CH_2×2); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 172.1, 149.6, 145.2, 135.6, 128.8, 128.3, 128.0, 124.1, 66.1, 64.0, 47.4, 30.5, 23.4; MALDI-TOF-MS: Calcd for $C_{28}H_{30}N_2NaO_8S$: m/z 577. Found: 577 $[M+Na]^+$.

4-(Benzyloxycarbonylpropyl-amino)-butanoic Acid Benzyl Ester (18) To a solution of **17** (1.1 g, 1.9 mmol) in CH_3CN (10 ml) was added K_2CO_3 (790 mg, 5.8 mmol) and PhSH (790 μl, 7.7 mmol), and the mixture was stirred for 2 h at room temperature. After concentration, the residue was diluted with $CHCl_3$, washed with 5% HCl, aq. $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 30 : 1 $CHCl_3$–MeOH as eluent to give **18** (638 mg, 93%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.36—7.29 (10H, m, 2Ph), 5.09 (4H, s, benzyl methylene), 3.00 (4H, t, NH–$\underline{CH_2}$×2), 2.50 (4H, t, $\underline{CH_2}$–CO×2), 2.20—2.14 (4H, m, CH_2–$\underline{CH_2}$–CH_2×2); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 172.0, 135.6, 128.6, 128.3, 66.5, 46.6, 31.0, 21.0; MALDI-TOF-MS: Calcd for $C_{22}H_{27}NNaO_4$: m/z 392.2. Found: 392.4 $[M+Na]^+$.

4-(Benzyloxycarbonylpropyl-*tert*-butoxycarbonyl-amino)-butanoic Acid Benzyl Ester (19) To a solution of **18** (513 mg, 1.3 mmol) in CH_2Cl_2 (30 ml) was added $(Boc)_2O$ (352 μl, 1.5 mmol) and Et_3N (582 μl, 4.2 mmol), and the mixture was stirred for 18 h at room temperature. The mixture was diluted with $CHCl_3$, washed with water, dried ($MgSO_4$), and concentrated. The product was purified by silica gel column chromatography using 20 : 1 toluene–acetone as eluent to give **19** (400 mg, 61.2%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.37—7.30 (10H, m, 2Ph), 5.11 (4H, s, benzyl methylene), 3.19 (4H, br, NH–$\underline{CH_2}$×2), 2.33 (4H, t, $\underline{CH_2}$–CO×2), 1.86—1.81 (4H, m, CH_2–$\underline{CH_2}$–CH_2×2), 1.43 (9H, s, *t*-butyl); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 172.8, 155.5, 135.9, 128.5, 128.2, 79.5, 66.2, 46.2, 31.4, 28.4, 28.4, 23.8, 23.4; MALDI-TOF-MS: Calcd for $C_{27}H_{35}NNaO_6$: m/z 492. Found: 492 $[M+Na]^+$.

4-(*tert*-Butoxycarbonyl-carbonylpropyl-amino)-butanoic Acid (20) To a solution of **19** (400 mg, 0.85 mmol) in 1,4-dioxane–H_2O (2 : 1, 6 ml) was added aq NaOH (2.0 ml), and the mixture was stirred for 5 h at room temperature. The mixture was diluted with EtOAc, washed with water, dried ($MgSO_4$), and concentrated to give **20** (245 mg, quant.). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 11.1 (2H, br s, COO$\underline{H}$), 3.25 (4H, br, NH–$\underline{CH_2}$×2), 2.36 (4H, t, $\underline{CH_2}$–CO×2), 1.88—1.83 (4H, m, CH_2–$\underline{CH_2}$–CH_2×2), 1.42 (9H, s, *t*-butyl); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 178.6, 171.3, 80.0, 60.4, 46.1, 31.1, 28.2, 23.3, 23.1, 14.0; MALDI-TOF-MS: Calcd for $C_{13}H_{23}NNaO_6$: m/z 312. Found: 312 $[M+Na]^+$.

Glycocluster 21 To a solution of core unit **20** (44 mg, 0.15 mmol) and sugar unit **6** (500 mg, 0.38 mmol) in DMF (4.0 ml) were added triethylamine (85 μl, 0.61 mmol) and DEPC (91 μl, 0.61 mmol). The reaction mixture was stirred for 18 h at room temperature. After completion of the reaction, the mixture was extracted with $CHCl_3$, washed with water, dried ($MgSO_4$), and concentrated. The product was purified on silica gel column chromatography ($CHCl_3$: MeOH=10 : 1) to give **21** (413 mg, 73%). $[\alpha]_D^{25}$ +90.1 (c=4.2, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.06—7.03 (80H, m, 16Ph), 6.03 (2H, d, $J_{3',4'}$=3.7 Hz, H-4′), 5.84 (2H, d, $J_{3,4}$=3.1 Hz, H-4), 5.71—5.59 (6H, m, H-2,2′, H-3′), 5.50 (2H, dd, H-3), 4.82 (2H, d, $J_{1',2'}$=7.9 Hz, H-1′), 4.59 (2H, d, $J_{1,2}$=7.9 Hz, H-1), 4.14—4.06 (4H, m, H-5′, H-6′a), 3.99 (2H, t, H-5) 3.84—3.80 (2H, m, H-6′b), 3.66—3.61 (6H, m, H-6, O–C$\underline{H_2}$), 3.22 (6H, br, O–$\underline{CH_2}$, 2N$\underline{CH_2}$), 3.08—3.03 (4H, m, NH$\underline{CH_2}$), 2.12 (4H, br, NHCO$\underline{CH_2}$), 1.83—1.77 (4H, m, 2NHCOCH$_2$$\underline{CH_2}$$CH_2$N), 1.34—0.91 (43H, m, 3*t*-butyl, alkyl); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 165.5, 165.3, 165.23, 165.16, 165.1, 165.0, 156.1, 137.7, 135.4, 135.3, 133.23, 133.15, 133.03, 132.98, 132.6, 132.4, 129.9, 129.8, 129.7, 129.59, 129.56, 129.5, 129.4, 129.3, 129.0, 128.9, 128.8, 128.4, 128.3, 128.2, 128.1, 127.6, 127.4, 125.2, 101.3, 101.0, 79.6, 73.5, 73.0, 71.8, 71.6, 70.0, 69.84, 69.78, 68.5, 67.6, 67.5, 63.51, 63.46, 60.6, 53.8, 45.9, 39.3, 33.4, 29.1, 29.0, 28.9, 28.3, 26.5, 26.3, 25.4, 24.5, 23.1, 21.3, 18.7, 16.03, 15.98; MALDI-TOF-MS: Calcd for $C_{165}H_{173}N_3NaO_{38}Si_2$: m/z 2883.1. Found: 2885.0 $[M+Na]^+$.

Glycocluster 22 To a solution of **21** (374 mg, 0.13 mmol) in CH_2Cl_2 (2.0 ml) was added trifluoroacetic acid (400 μl). The reaction mixture was stirred for 1 h at room temperature. After completion of the reaction, the mixture was concentrated and purified on silica gel column chromatography (chloroform : methanol=10 : 1) to give **22** (273 mg, 75%). $[\alpha]_D^{25}$ +97.6 (c=1.24, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.08—7.02 (80H, m, 16Ph),

6.28 (1H, br s, $CH_2\underline{NH}CH_2$), 6.01 (2H, d, $J_{3',4'}$=3.7 Hz, H-4′), 5.82 (2H, d, $J_{3,4}$=3.1 Hz, H-4), 5.69—5.57 (6H, m, H-2,2′, H-3′), 5.49 (2H, dd, H-3), 4.81 (2H, d, $J_{1',2'}$=7.9 Hz, H-1′), 4.59 (2H, d, $J_{1,2}$=8.0 Hz, H-1), 4.09—4.07 (4H, m, H-5′, H-6′a), 3.98 (2H, t, H-5), 3.82—3.80 (2H, m, H-6′b), 3.62—3.59 (6H, m, H-6, O–$\underline{CH_2}$), 3.06—2.83 (2H, m, O–C$\underline{H_2}$), 2.82—2.33 (4H, m, CONH$\underline{CH_2}$), 2.30 (4H, t, $\underline{CH_2}NH\underline{CH_2}$), 1.90 (4H, t, NHCO$\underline{CH_2}$), 1.92—1.89 (4H, m, $NHCOCH_2\underline{CH_2}CH_2N$), 1.26—0.88 (34H, m, 2*t*-butyl, alkyl); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 172.4, 165.6, 165.4, 165.3, 165.2, 165.1, 135.5, 135.4, 133.3, 133.2, 133.13, 133.08, 132.7, 132.5, 130.0, 129.8, 129.74, 129.68, 129.63, 129.56, 129.5, 129.4, 129.1, 129.0, 128.9, 128.5, 128.4, 128.2, 127.7, 127.5, 101.4, 101.1, 73.6, 73.1, 71.8, 71.6, 70.1, 69.94, 69.88, 68.6, 67.7, 67.6, 60.6, 48.1, 39.5, 34.0, 29.1, 26.5, 25.5, 23.5, 18.8; MALDI-TOF-MS: Calcd for $C_{160}H_{165}N_3NaO_{36}Si_2$: *m/z* 2783.1. Found: 2785.4 $[M+Na]^+$.

Glycocluster 23 To a solution of **22** (273 mg, 99 μmol) and 2-(tetradecyl) hexadecanoic acid (113 mg, 0.24 mmol) in CH_2Cl_2 (2.0 ml) were added EDC (114 mg, 0.59 mmol) and DMAP (54 mg, 0.44 mmol). The reaction mixture was stirred for 18 h at room temperature. After completion of the reaction, the mixture was extracted with chloroform, washed with water, dried (Na_2SO_4), and concentrated. The product was purified on silica gel column chromatography (toluene : acetone=5 : 1) to give **23** (276 mg, 87.3%). $[\alpha]_D^{25}$ +76.6 (c=5.7, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.05—7.03 (80H, m, 16Ph), 6.01 (2H, $J_{3',4'}$=3.7 Hz, d, H-4′), 5.82 (2H, d, $J_{3,4}$=3.2 Hz, H-4), 5.69—5.63 (4H, m, H-2, 2′), 5.59 (2H, dd, H-3′), 5.51—5.47 (2H, m, H-3), 4.81 (2H, d, $J_{1',2'}$=7.9 Hz, H-1′), 4.59 (2H, d, $J_{1,2}$=7.9 Hz, H-1), 4.09—4.07 (4H, m, H-5′, H-6′a), 3.97 (2H, t, H-5) 3.82—3.78 (2H, m, H-6′b), 3.62—3.59 (6H, m, H-6, O–C$\underline{H_2}$), 3.36—3.30 (4H, m, $\underline{CH_2}N\underline{CH_2}$), 3.24—3.08 (2H, m, O–C$\underline{H_2}$), 3.08—3.00 (4H, m, CONH$\underline{CH_2}$), 2.61 (1H, br t, COCH), 2.16—2.14 (4H, m, NHCO$\underline{CH_2}$), 1.83 (4H, m, $NHCOCH_2\underline{CH_2}CH_2N$), 1.30—0.80 (92H, m, 2*t*-butyl, alkyl); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 171.1, 165.6, 165.4, 165.3, 165.24, 165.15, 165.1, 135.5, 135.4, 133.2, 133.1, 132.7, 132.5, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.1, 129.0, 128.9, 128.5, 128.4, 128.3, 128.2, 127.7, 127.5, 125.3, 101.4, 101.1, 73.6, 73.1, 73.0, 71.9, 71.6, 70.1, 70.0, 69.9, 68.6, 67.7, 67.6, 60.7, 47.3, 45.1, 41.6, 39.7, 39.4, 33.2, 32.9, 31.9, 30.0, 29.6, 29.5, 29.32, 29.285, 29.14, 29.08, 27.8, 26.5, 25.6, 25.5, 25.0, 24.1, 22.7, 18.8, 14.1; MALDI-TOF-MS: Calcd for $C_{190}H_{223}N_3NaO_{37}Si_2$: *m/z* 3217. Found: 3217 $[M+Na]^+$.

Glycocluster 24 Compound **24** was prepared from **23** (228 mg) as described for preparation of **4**, yielding 101 mg (52%). $[\alpha]_D^{25}$ +105.5 (c=0.7, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.11—7.02 (6H, m, 12Ph), 5.93 (2H, br d, H-4′), 5.82—5.78 (4H, m, H-2′, 4), 5.71—5.67 (2H, m, H-2), 5.56—5.52 (4H, m, H-3, 3′), 4.88 (2H, d, $J_{1',2'}$=7.3 Hz, H-1′), 4.64 (2H, d, $J_{1,2}$=7.3 Hz, H-1), 4.14—4.10 (4H, m, H-5′, H-6′a), 3.98—3.91 (4H, m, H-5, 6′b), 3.72—3.65 (4H, m, H-6a, O–C$\underline{H_2}$), 3.51—3.47 (2H, m, H-6b), 3.34 (6H, br, O–C$\underline{H_2}$, $\underline{CH_2}N\underline{CH_2}$), 3.07 (4H, br, CONH$\underline{CH_2}$), 2.64 (1H, br t, COCH), 2.16 (4H, br, NHCO$\underline{CH_2}$), 1.85 (4H, br, $NHCOCH_2\underline{CH_2}CH_2N$), 1.56—0.86 (74H, m, alkyl); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 171.3, 166.5, 165.5, 165.2, 133.6, 166.5, 165.2, 133.6, 133.5, 133.2, 133.1, 130.1, 129.9, 129.64, 129.59, 129.4, 129.3, 129.1, 128.8, 128.71, 128.67, 128.6, 128.5, 128.34, 128.29, 128.23, 128.15, 101.4, 101.3, 74.1, 73.1, 71.8, 70.0, 69.9, 68.7, 68.6, 67.9, 60.5, 47.2, 45.2, 41.5, 39.4, 33.2, 33.0, 31.8, 29.9, 29.6, 29.5, 29.3, 29.1, 27.7, 26.5, 25.5, 25.4, 25.1, 24.1, 22.6, 14.0; MALDI-TOF-MS: Calcd for $C_{158}H_{187}N_3NaO_{37}$: *m/z* 2741. Found: 2741 $[M+Na]^+$.

Glycocluster 25 Compound **25** was prepared from **24** (101 mg) as described for preparation of **8**, yielding 61 mg (54%). $[\alpha]_D^{25}$ +76.4 (c=1.0, MeOH); ^{1}H-NMR (500 MHz, CD_3OD) δ: 8.07—7.20 (60H, m, 12Ph), 5.93 (2H, d, $J_{3',4'}$=3.7 Hz, H-4′), 5.89 (2H, d, $J_{3,4}$=3.1 Hz, H-4), 5.73—5.60 (8H, m, H-2, 2′, 3, 3′), 5.10 (2H, d, $J_{1',2'}$=7.3 Hz, H-1′), 4.81 (2H, d, $J_{1,2}$=7.9 Hz, H-1), 4.35—4.33 (4H, m, H-5′, H-6′a), 4.26 (4H, br s, $POCH_2CH_2$), 4.17—4.14 (2H, m, H-5′), 3.97 (2H, br, H-6a), 3.89—3.81 (4H, m, H-6b, 6′b), 3.63—3.51 (6H, m, $POCH_2CH_2$, OCH_2), 3.37—3.33 (6H, m, O–C$\underline{H_2}$, $\underline{CH_2}N\underline{CH_2}$), 3.17 (18H, s, $N(CH_3)_3$), 3.00—2.95 (4H, m, $NHCH_2$), 2.66 (1H, br t, COCH), 2.17 (4H, t×2, $NCH_2C\underline{H_2}CH_2CO$), 1.88—1.78 (4H, m, $NCH_2CH_2C\underline{H_2}CO$), 1.54—0.83 (74H, m, alkyl); ^{13}C-NMR (125 MHz, CD_3OD) δ: 178.7, 175.0, 174.5, 167.1, 167.0, 166.9, 166.8, 166.7, 134.9, 134.8, 134.6, 134.5, 130.92, 130.89, 130.71, 130.65, 130.6, 130.5, 130.3, 130.2, 129.91, 129.87, 129.7, 129.6, 129.5, 129.4, 102.2, 73.6, 73.4, 73.3, 73.0, 71.7, 71.4, 70.7, 70.2, 69.4, 68.7, 64.1, 60.8, 54.7, 49.5, 49.3, 49.2, 49.12, 49.07, 48.9, 48.8, 48.73, 48.66, 48.5, 48.3, 47.0, 42.6, 40.4, 40.3, 34.5, 34.4, 33.7, 33.0, 31.0, 30.8, 30.7, 30.64, 30.57, 30.4, 30.3, 30.2, 28.7, 27.7, 27.6, 26.7, 25.2, 23.7, 14.5; MALDI-TOF-MS: Calcd for $C_{168}H_{212}N_5O_{43}P_2$: *m/z* 3049. Found: 3049 $[M+H]^+$.

Glycocluster 26 (B) Compound **26** was prepared from **25** (39 mg) as described for preparation of **13**, yielding 22 mg (84%). $[\alpha]_D^{25}$ −11.1 (c=0.3, MeOH); ^{1}H-NMR (500 MHz, CD_3OD) δ: 4.30 (2H, d, $J_{1',2'}$=7.9 Hz, H-1′), 4.21—4.17 (6H, m, H-1, $2POCH_2$), 3.07 (18H, s, $2N(CH_3)_3$); ^{13}C-NMR (125 MHz, CD_3OD) δ: 178.8, 175.2, 174.7, 105.2, 104.9, 75.4, 75.3, 75.0, 74.8, 74.7, 72.6, 72.4, 70.9, 70.04, 69.98, 69.25, 67.6, 66.1, 60.58, 6055, 54.8, 48.1, 47.0, 42.5, 40.5, 40.4, 34.4, 33.7, 33.0, 30.9, 30.7, 30.6, 30.5, 30.4, 30.3, 28.6, 27.9, 27.8, 26.8, 26.7, 25.1, 23.7, 14.5, 1.5; MALDI-TOF-MS: Calcd for $C_{84}H_{164}N_5O_{31}P_2$: *m/z* 1801. Found: 1801 $[M+H]^+$.

Glycocluster 27 Compound **27** was prepared from **20** (15 mg, 50 μmol) and **22** (346 mg, 0.13 mmol) as described for preparation of **21**, yielding 287 mg (99%). $[\alpha]_D^{25}$ +84.0 (c=3.2, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.98—6.95 (160H, m, 32Ph), 5.93 (4H, d, H-4′), 5.75 (4H, d, H-4), 5.61—5.54 (8H, m, H-2,2′), 5.51 (4H, dd, H-3′), 5.41 (4H, dd, H-3), 4.73 (4H, d, $J_{1',2'}$=7.3 Hz, H-1′), 4.51 (4H, d, $J_{1,2}$=7.9 Hz, H-1), 4.02—4.00 (8H, m, H-5′, H-6′a), 3.89 (4H, t, H-5), 3.73—3.70 (4H, m, H-6′b), 3.53—3.51 (12H, m, H-6, O–C$\underline{H_2}$), 3.25—3.12 (16H, m, O–C$\underline{H_2}$, $\underline{CH_2}N\underline{CH_2}$), 2.95—2.93 (8H, m, 4CONH$\underline{CH_2}$), 2.22—2.05 (12H, m, 6NHCO$\underline{CH_2}$), 1.85—1.78 (12H, m, $6NHCOCH_2\underline{CH_2}CH_2N$), 1.26—0.78 (78H, m, 5*t*-butyl, alkyl); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 171.3, 165.6, 165.4, 165.3, 165.24, 165.19, 165.1, 155.7, 135.5, 135.4, 133.31, 133.25, 133.1, 132.7, 132.5, 130.8, 130.0, 129.9, 129.8, 129.71, 129.66, 129.6, 129.5, 129.1, 129.0, 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 127.7, 127.5, 101.4, 101.1, 79.4, 73.6, 73.1, 73.0, 71.9, 71.6, 70.1, 69.9, 68.6, 68.1, 67.7, 67.6, 60.7, 39.7, 39.5, 38.7, 32.8, 31.9, 30.3, 30.0, 29.7, 29.3, 29.1, 28.9, 28.5, 26.5, 25.54, 25.46, 24.4, 23.9, 23.7, 22.9, 22.7, 18.8, 14.1, 10.9, 1.0; MALDI-TOF-MS: Calcd for $C_{333}H_{349}N_7NaO_{76}Si_4$: *m/z* 5796.2. Found: 5795.5 $[M+Na]^+$.

Glycocluster 28 Compound **28** was prepared from **27** (287 mg, 50 mmol) as described for preparation of **22**, yielding 266 mg (94%). $[\alpha]_D^{25}$ +87.6 (c=1.9, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.97—6.95 (160H, m, Ar-H), 5.93 (4H, br s, H-4′), 5.75 (4H, br d, H-4), 5.61—5.52 (12H, m, H-2,2′,3′), 5.50—5.41 (4H, m, H-3), 4.23 (4H, d×2, $J_{1',2'}$=7.9 Hz, H-1′), 4.51 (4H, d, $J_{1,2}$=7.9 Hz, H-1), 4.02—4.00 (8H, m, H-5′, H-6′a), 3.90 (4H, t, H-5) 3.74—3.68 (4H, m, H-6′b), 3.57—3.52 (12H, m, H-6, O–C$\underline{H_2}$), 3.25—3.12 (16H, m, O–C$\underline{H_2}$, $\underline{CH_2}N\underline{CH_2}$) 2.92 (10H, m, CONH$\underline{CH_2}$, $\underline{CH_2}NH\underline{CH_2}$), 2.49 (4H, br, $CH_2NHCH_2CH_2\underline{CH_2}CO$) 2.07—2.03 (8H, m, $NHCO\underline{CH_2}CH_2CH_2NHCOCH_2$), 1.89—1.73 (12H, m, $6CONHCH_2\underline{CH_2}CH_2.CONH$) 1.18—0.63 (68H, m, 4*t*-butyl, alkyl); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 172.8, 172.2, 171.6, 165.6, 165.4, 165.3, 1652, 165.1, 135.5, 135.4, 133.33, 133.26, 133.1, 132.7, 132.5, 130.0, 129.9, 129.8, 129.71, 129.66, 129.6, 129.5, 129.1, 129.0, 128.9, 128.5, 128.4, 128.3, 128.2, 127.7, 127.5, 101.4, 101.1, 73.6, 73.0, 71.9, 71.6, 70.1, 69.9, 68.6, 67.7, 67.6, 60.7, 48.0, 47.3, 45.1, 39.4, 33.3, 32.6, 31.9, 30.8, 29.7, 29.3, 29.2, 29.1, 26., 25.5, 24.3, 23.6, 22.7, 18.8, 14.1, 1.0; MALDI-TOF-MS: Calcd for $C_{328}H_{341}N_7NaO_{74}Si_4$: *m/z* 5696. Found: 5696 $[M+Na]^+$.

Glycocluster 29 Compound **29** was prepared from **28** (344 mg) as described for preparation of **23**, yielding 331 mg (90%). $[\alpha]_D^{25}$ +86.2 (c=5.7, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.97—6.95 (160H, m, 32Ph), 5.93 (4H, d, H-4′), 5.75 (4H, d, H-4), 5.61—5.50 (12H, m, H-2,2′,3′), 5.41 (4H, dd, H-3), 4.73 (4H, d×2, $J_{1',2'}$=7.6 Hz, H-1′), 4.51 (4H, d, $J_{1,2}$=7.9 Hz, H-1), 4.02—4.00 (8H, m, H-5′, H-6′a), 3.89 (4H, t, H-5) 3.74—3.68 (4H, m, H-6′b), 3.57—3.52 (12H, m, H-6, O–C$\underline{H_2}$), 3.25—3.12 (16H, m, O–C$\underline{H_2}$, $\underline{CH_2}N\underline{CH_2}$), 2.95—2.92 (10H, m, CONH$\underline{CH_2}$, $\underline{CH_2}NH\underline{CH_2}$), 2.26—2.23 (4H, br, $CH_2NHCH_2CH_2C\underline{H_2}CO$), 2.05 (8H, br s, $NHCO\underline{CH_2}CH_2CH_2NCOCH_2$), 1.85—1.75 (12H, br s, $COCH_2\underline{CH_2}CH_2N$), 1.17—0.71 (126H, m, 4*t*-butyl, alkyl); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 176.5, 172.6, 172.3, 171.9, 171.4, 171.3, 167.8, 165.6, 165.4, 165.3, 165.24, 165.18, 165.1, 135.5, 135.4, 133.3, 133.1, 132.7, 132.5, 133.1, 132.5, 130.0, 129.9, 129.8, 129.71, 129.68, 129.61, 129.5, 129.4, 129.1, 129.0, 128.9, 128.5, 128.5, 128.4, 128.3, 128.2, 127.7, 127.5, 126.4, 101.5, 101.1, 77.4, 77.1, 76.8, 73.6, 73.0, 71.9, 71.6, 70.1, 69.9, 68.6, 67.6, 60.7, 47.4, 47.3, 47.2, 45.7, 45.1, 44.7, 41.4, 39.4, 33.3, 32.9, 32.7, 31.9, 30.9, 30.4, 30.1, 29.7, 29.6, 29.3, 29.2, 27.8, 26.5, 25.54, 25.47, 24.9, 24.4, 23.9, 23.6, 22.7, 18.8, 14.1; MALDI-TOF-MS: Calcd for $C_{358}H_{399}N_7NaO_{75}Si_4$: *m/z* 6131. Found: 6131 $[M+Na]^+$.

Glycocluster 30 Compound **30** was prepared from **29** (331 mg) as described for preparation of **24**, yielding 237 mg (85%). $[\alpha]_D^{25}$ +110.5 (c=2.6, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 8.10—7.20 (120H, m, 24Ph), 5.93 (4H, br s, H-4′), 5.82—5.78 (8H, m, H-2′, 4), 5.69 (4H, br t, H-2), 5.57—5.52 (8H, m, H-3,3′), 4.90 (4H, d, $J_{1',2'}$=7.9 Hz, H-1′), 4.65 (4H, d, $J_{1,2}$=7.9 Hz, H-1), 4.16—4.10 (8H, m, H-5′, H-6′a), 3.99—3.90 (8H, m, H-5, 6′b), 3.72—3.64 (8H, m, H-6a, O–C$\underline{H_2}$), 3.51—3.44 (4H, m, H-6b), 3.34—3.25 (16H, m, 4O–C$\underline{H_2}$, 4$\underline{CH_2}N\underline{CH_2}$), 3.05 (8H, br, CONH$\underline{CH_2}$), 2.62 (1H, br t, COCH), 2.35—2.32 (4H, m, $CH_2NHCH_2CH_2C\underline{H_2}CO$), 2.14 (8H, br, $NHCO\underline{CH_2}CH_2CH_2NHCOCH_2$), 1.84—1.75 (12H, br s, $COCH_2\underline{CH_2}CH_2NH$), 1.52—0.85 (90H, m, alkyl); ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 176.6, 172.8, 172.7, 172.5, 172.0, 171.7, 171.5, 166.5, 165.6, 165.5, 165.3, 133.7, 133.6,

133.3, 133.2, 130.1, 130.0, 129.73, 129.66, 129.5, 129.4, 129.2, 128.9, 128.8, 128.6, 128.44, 128.39, 128.33, 128.25, 127.8, 101.5, 101.3, 74.1, 73.2, 71.9, 71.8, 70.1, 70.0, 69.0, 68.73, 68.66, 67.9, 60.5, 47.4, 47.3, 45.1, 44.8, 41.5, 39.5, 33.3, 33.1, 32.8, 31.9, 30.5, 30.1, 29.72, 29.67, 29.6, 29.4, 29.2, 27.8, 26.5, 25.6, 25.5, 24.9, 24.6, 24.5, 23.9, 23.6, 22.7, 14.1; MALDI-TOF-MS: Calcd for $C_{294}H_{327}N_7O_{75}Na$: *m/z* 5178. Found: 5178 $[M+Na]^+$.

Glycocluster 31 Compound **31** was prepared from **30** (133 mg) as described for preparation of **8**, yielding 31 mg (21%). $[\alpha]_D^{25}$ +79.6 (c=0.8, MeOH); ^{1}H-NMR (500 MHz, CD_3OD) δ: 8.03—7.18 (120H, m, 24H), 5.94 (4H, d, H-4′), 5.88 (4H, d, H-4), 5.73—5.59 (16H, m, H-3, 3′, 2, 2′), 5.04 (4H, d, $J_{1',2'}$=6.7 Hz, H-1′), 4.82 (4H, d, $J_{1,2}$=7.9 Hz, H-1), 4.37—4.32 (8H, m, H-5, H-6′a), 4.20—4.14 (8H, m, PO–CH_2, H-5′), 4.00—3.95 (4H, m, H-6a), 3.88—3.77 (8H, m, H-6b, 6′b), 3.57 (12H, t, PO–CH_2, OCH_2), 3.38—3.30 (20H, m, 4O–$\underline{CH_2}$, 3$\underline{CH_2}$N$\underline{CH_2}$), 3.17 (36H, s, $N(CH_3)_3$), 2.96—2.95 (8H, m, CONH$\underline{CH_2}$), 2.61 (1H, br t, COCH), 2.42—2.33 (4H, m, CH_2NHCH$_2$CH$_2$C$\underline{H_2}$CO), 2.18—2.11 (8H, m, NHCO$\underline{CH_2}$CH$_2$CH$_2$NCOCH$_2$), 1.82—1.76 (12H, m, COCH$_2\underline{CH_2}$CH$_2$NH), 1.51—0.81 (90H, m, alkyl); ^{13}C-NMR (125 MHz, CD_3OD) δ: 181.2, 167.1, 167.0, 166.9, 166.8, 166.7, 134.9, 134.8, 134.63, 134.60, 134.56, 134.5, 130.9, 130.7, 130.63, 130.55, 130.5, 130.3, 130.2, 129.9, 129.7, 129.5, 102.2, 102.0, 73.6, 73.5, 73.3, 71.7, 71.5, 70.7, 70.3, 69.5, 68.9, 67.5, 67.4, 63.9, 60.5, 60.4, 54.7, 40.38, 40.35, 33.0, 31.0, 30.8, 30.7, 30.6, 30.43, 30.36, 30.3, 28.7, 27.7, 26.7, 23.7, 14.5; MALDI-TOF-MS: Calcd for $C_{314}H_{375}N_{11}O_{87}P_4Na$: *m/z* 5836. Found: 5836 $[M+Na]^+$.

Glycocluster 32 (C) Compound **32** was prepared from **31** (31 mg) as described for preparation of **13**, yielding 14 mg (80%). $[\alpha]_D^{25}$ −8.95 (c=0.4, MeOH); ^{1}H-NMR (500 MHz, CD_3OD) δ: 4.30 (4H, d, $J_{1',2'}$=7.9 Hz, H-1′), 4.21 (4H, d, $J_{1',2'}$=7.3 Hz, H-1), 4.16 (8H, br s, 4POCH$_2$), 3.06 (36H, s, 4N$(CH_3)_3$); ^{13}C-NMR (125 MHz, CD_3OD) δ: 178.7, 175.3, 175.2, 174.7, 174.6, 174.2, 105.3, 105.0, 75.40, 75.35, 75.1, 74.84, 74.75, 72.6, 72.4, 70.9, 70.1, 69.3, 67.6, 66.1, 60.61, 60.58, 54.8, 49.8, 49.6, 42.5, 40.5, 34.5, 34.4, 33.8, 33.6, 33.1, 31.4, 31.0, 30.8, 30.6, 30.5, 30.4, 28.7, 27.9, 26.8, 25.9, 25.1, 25.0, 24.7, 23.7, 14.5; MALDI-TOF-MS: Calcd for $C_{146}H_{280}N_{11}O_{63}P_4$: *m/z* 3319.8. Found: 3320.3 $[M+H]^+$.

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