Carbosilane Dendrimers Bearing Globotriaoses: Syntheses of Globotrioasyl Derivative and Introduction into Carbosilane Dendrimers†

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As an application of a one-pot reaction involving Birch reduction and subsequent S_N2 reaction in liquid ammonia, synthetic assembly of trisaccharidic moieties of globotriaosyl ceramide onto carbosilane dendrimers was accomplished using tris(3-bromopropyl)phenylsilane and tris[tris(3-bromopropyl)silylpropyl]phenylsilane as the core scaffolds. The common globotriaosyl derivative having benzylsulfide functionality at the terminal of the aglycon was efficiently prepared from D-galactose and D-lactose as starting materials. The glycosyl donor derived from galactose and the glycosyl acceptor derived from lactose were condensed in the presence of silver triflate as the best promoter to provide corresponding trisaccharide with newly formed α-1−4 linkages in 90% yield. Fully benzylated protection of the trisaccharide was deprotected under the Birch reduction condition followed by acetylation to give an acetate in which alkene was converted into benzyl sulfide by radical addition of α-toluenethiol in high yields. On the other hand, carbosilane dendrimers were prepared from appropriate chlorosilanes as starting materials by a combination of hydrosylation followed by alkenylation. The terminal C═C double bonds of the carbosilanes were converted into corresponding alcohols by means of the usual hydroboration reaction, and the alcohols underwent further chemical manipulation to give carbosilane dendrimers with peripheral bromine atoms.

Introduction

In a number of glycolipids located on the surfaces of kidney glomerular endothelial cells, globotriaosyl ceramide (Gb_3; Galα1→4Galβ1→4Glcβ1→Cer) is the major glycolipid and is known to be a host receptor for Shiga toxins (Stx1 and Stx2),[2] which are produced by pathogenic *Escherichia coli* O157: H7.[3] Stxs belong to bacterial AB_5 toxin families and are classified into Stx1 and Stx2, which are closely related subgroups.[4] The toxic A subunit has RNA N-glycosidase activity, and the lectin-like B subunit has three carbohydrate-binding domains.[5] Since each Stx has five B subunits in a molecule through noncovalent bonds, the B subunit pentamer has a total of 15 binding sites for the globotriaosyl epitopes in the holotoxin.[6] Various artificial receptors for both Stxs for neutralizing the toxicities have been synthesized and have been shown to have significant biological activities.[7−13] Armstrong et al.[7] developed Synsorb-Pk as a toxin absorbent, which has Gb_3 trisaccharide units (globotriaose) covalently coupled to Chromosorb P, and Synsorb-Pk showed higher neutralization potency for Stx1 than Stx2 in cytotoxic assays. Synsorb-Pk was also tested in a clinical study in Canada and Japan, but the results were inconclusive.[8] Nishida and Kobayashi et al.[9] reported a water-soluble polymeric toxin neutralizer in which the globotriaose moieties branched from the linear polymer backbone and showed high affinity for Stx1. Kitov et al.[10] described a multivalent-type compound, referred to as "Starfish", which is composed of one glucose as the core scaffold and ten globotriaosyl moieties as epitopes for multi-binding sites of Stx1B. Paton et al.[11] developed genetically controlled nonpathogenic *E. coli* strains in which the cell surfaces display globotriaosyl epitopes and showed efficient neutralization potency for Stxs. We have also reported as a communication a series of dendrimers[12] and polymers,[13] both having globotriaosyl epitopes that showed effective protection from both toxins. Although those synthetic receptors have extremely high activities against Stxs, no therapeutic reagent as a neutralizer for Stxs is available. Because of the molecular complexity of Stxs as ligands and neutralizers as receptors, we selected dendrimers[14] as simple and well-defined compounds for the toxin blocker. Carbosilane dendrimers, well-known dendrimers, have been developed and found to have a wide variety of unique characteristics, including (1) simplicity of the synthetic process to extend the generation,[15] (2) accessibility to a polymer with definite molecular weight and definite number of terminal functional groups, which depend on the generation of the dendrimers, (3) neutral nature in contrast to the other dendrimers,[16] and (4) biological inertness. Because of such advantages, we have recently reported a series of carbosilane dendrimers, named "Glyco-silicon Functional Materials",[17] and syntheses and biological evaluations of some dendrimers having globotriaosyl moieties have also been reported as a communication.[12] In this paper, we describe the synthesis of a dendritic core frame using carbosilanes, the trisaccharide moiety of Gb_3 and its chemical modifications, and the assembly of those compounds by a one-pot reaction in liquid ammonia to provide a new class of glycoclusters **1** and **2** (Figure 1), where globotriaosyl epitopes at each terminal end function as multivalent bioactive carbohydrate epitopes.

† Glyco-Silicon Functional Materials, part 7. For part 6, see ref 1.

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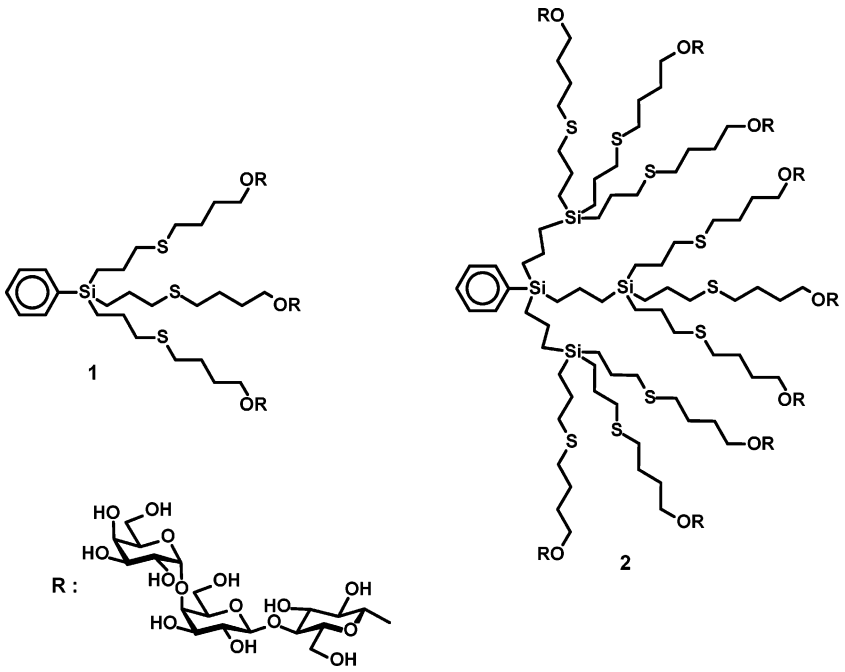
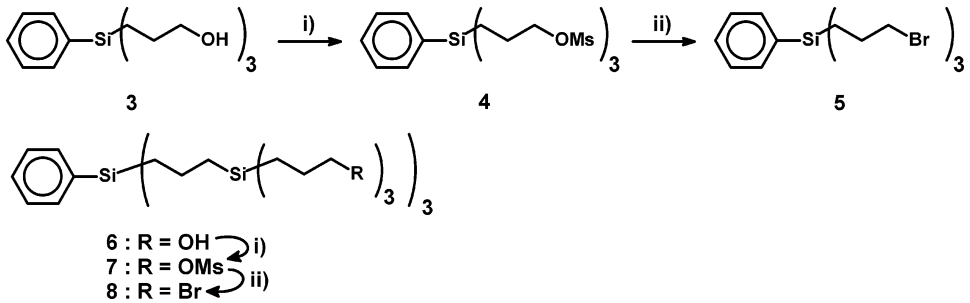


Figure 1. Carbosilane dendrimers uniformly functionalized with globotriaosyl epitopes at each terminal end.

Scheme 1[a]



[a] Reagents and conditions: (i) MsCl, Pyr, 0 °C for **4**, −20 °C for **7**; (ii) NaBr, DMF, 80 °C.

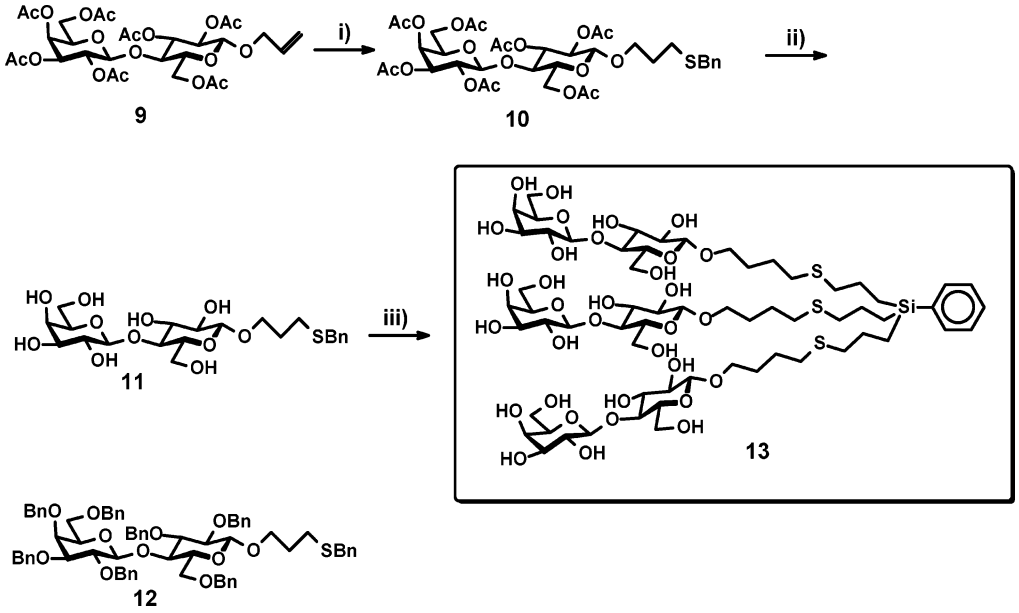
Results and Discussion

The key step of our synthetic plan for construction of a novel class of glycodendrimers was the final coupling reaction between sugar parts and carbosilane core scaffolds. Since multivalent-type compounds such as dendrimers have multiple reaction points, the coupling reaction between a functional molecule such as a bioactive sugar moiety and the multivalent scaffold needed high efficiency to produce new linkages without unreacted branches. Hence, the highly efficient method for sulfide formation by Williamson's ether synthesis prompted us to utilize the coupling reaction to obtain sulfide linkage-type glycodendrimers. Therefore, benzylsulfide derivative of globotriaose as the precursor for the coupling reaction was constructed starting from a D-galactose and a D-lactose. On the other hand, preparation of alkyl halide-type core frames has been accomplished by means of van der Made's strategy[15] followed by the usual chemical modification.

Synthesis of Carbosilane Dendrimers as Core Scaffolds. The synthetic scheme is summarized in Scheme 1. The triol **3** was prepared from commercially available trichlorophenyl silane and allyl Grignard reagent followed by hydroboration.[18] A leaving group for halide replacement was introduced by a two-step procedure. Thus, a usual mesylation of **3** gave syrupy **4** in quantitative yield. The substitution reaction of **4** was accomplished by means of sodium bromide in DMF to afford corresponding core scaffold **5** having three bromide atoms at each branching end. The structure of the tribromides **5** was elucidated by a combination of NMR, IR, and elemental analyses. Our next target compound was carbosilane dendrimer **8** having nine bromine atoms at each ω-position. Thus, the polyol **6** was prepared according to a previously reported method,[18] and **6** was treated in same manner as that described for the preparation of **5** to give pure **8** in good yield.

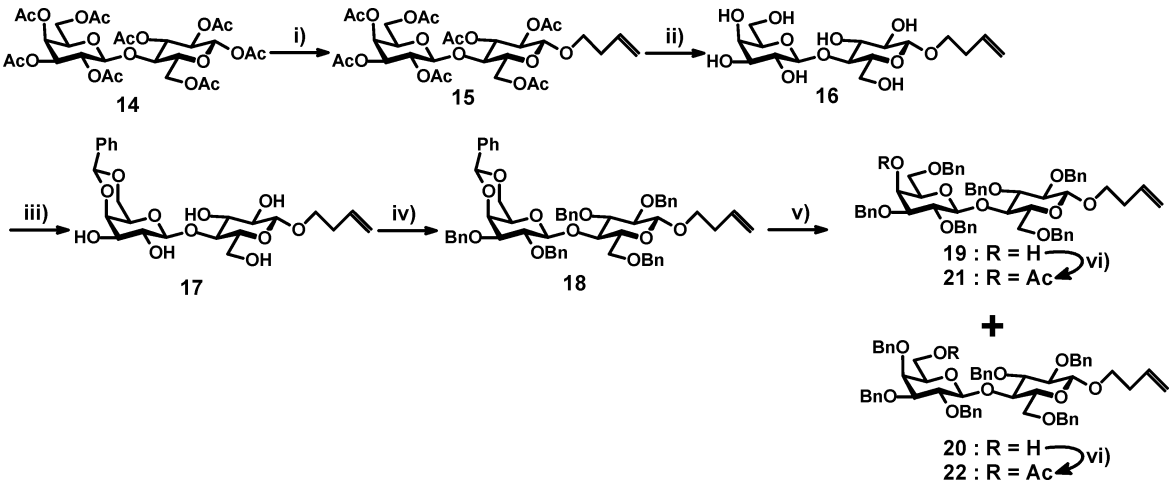
Synthetic Assembly of Lactose as a Saccharidic Model Using a Trivalent-Type Carbosilane Compound as a Core. Given the success in preparation of multivalent-type core scaffolds, we turned our attention to the establishment of complete introduction of sugars into core scaffolds to provide uniformly functionalized dendrimers. We used a lactose derivative as a simple model of a saccharide moiety for establishment of the coupling reaction. The known allyl β-lactoside **9**[19] was quantitatively converted into its benzylsulfide derivative **10** by means of radical addition reaction of α-toluenethiol with anti-Markovnikov orientation (see Scheme 2).[20] The removal of protection of **9** proceeded completely in methanolic sodium methoxide to yield the corresponding crystalline **11** in quantitative yield. Usual benzylation of **11** afforded **12** as a fully protected carbohydrate derivative, which was used for the next coupling reaction as a model for the direct conversion into a free sugar moiety with in situ generation. Thus, the coupling reaction was conducted by using **5** and **12** under a typical Birch reduction condition, in which the reaction included a combina-

Scheme 2[a]



[a] Reagents and conditions: (i) α-toluenethiol, AIBN, 1,4-dioxane, 50 → 80 °C; (ii) NaOMe, MeOH, rt; (iii) Na, liquid NH_3, −33 °C, then, NH_4Cl, **5**.

Scheme 3[a]

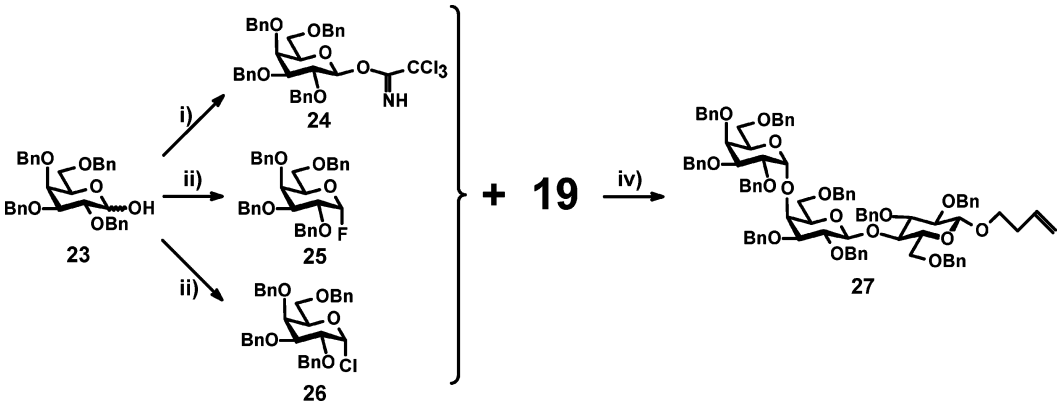


[a] Reagents and conditions: (i) 3-buten-1-ol, BF_3-OEt_2, CH_2Cl_2, 0 °C; (ii) NaOMe, MeOH, rt; (iii) α,α-dimethoxytoluene, CSA, DMF, 60 °C, under reduced pressure; (iv) BnBr, NaH, DMF, 0 °C; (v) BH_3-NMe_3, $AlCl_3$, MS4Å, THF, rt; (vi) Ac_2O-Pyr, rt.

tion of deprotection of all benzyl groups and the subsequent S_N2 reaction by thiolate anion generated from **12**. Consequently, a large excess of sodium metal and ammonium chloride (NH_4Cl) as a neutralizing agent had to be used, and purification of the resulting mixture was unfortunately unsuccessful. In contrast to such a complicated condition, unprotected benzyl sulfide **11** was selected for simple and easy handling for the coupling reaction. Birch reduction of **11** followed by dropwise addition of a solution of bromide **5** in THF−MeOH gave a syrupy residue after removal of liquid ammonia, which was purified by using gel filtration to afford the corresponding white powdery **13** in 80.2% yield after lyophilization. The results of ^1H NMR indicated complete introduction of three lactose moieties into the core scaffold. It was found that the use of an appropriate amount of sodium for introduction of the sugar moieties into a multivalent-type compound promises satisfactory coupling results.

Synthesis of Trisaccharidic Derivative of Gb_3. Results of synthetic studies of the trisaccharide moiety of Gb3 have been reported by a large number of groups in recent years.[21] Among the many synthetic routes, construction of trisaccharide by a glycosidation reaction between a D-galactosyl moiety and a D-lactosyl moiety producing α-1→4 linkage was selected for our synthetic plan, since it was a simple and feasible route for our objective. The synthetic scheme for lactosyl donor **19** having 4-OH is summarized in Scheme 3. The starting *β*-acetate **14** underwent glycosidation with 3-buten-1-ol (*n*-butenyl alcohol) in the presence of boron trifluoride diethyl ether complex (BF_3-OEt_2) to give *β*-acetate **15** in 59.9% yield, and **15** was subsequently deacetylated in the usual manner to yield **16** (96.9%). Conversion of the polyol **16** into the corresponding monoalcohol **19** was carried out in three steps. Thus, benzylidenation of **16** to protect 4′- and 6′-hydroxyl groups was first conducted by a typical procedure, giving **17**, in which the remaining hydroxyl groups were all benzylated to provide fully protected **18** in 65.0% yield (two steps). The selective ring-opening reaction of the benzylidene acetal of **18** under a reductive cleavage condition[22] by means of a combination of borane trimethylamine complex (BH_3-NMe_3) and $AlCl_3$ in absolute THF proceeded smoothly to give corresponding alcohol **19** with 4′-OH in 82.0% yield, accompanied by **20** having 6′-OH in 13.0% yield after silica gel chromatographic separation.

Scheme 4[a]



[a] Reagents and conditions: (i) ref 23; (ii) ref 24; (iii) $SOCl_2$−DMF, 1,2-dichloroethane, 0 °C; (iv) Table 1.

Table 1.

donor	donor (equiv)	activator	activator (equiv)	temp (°C)	MS4Å	solvent	time (h)	yield[a] (%)
24	2.0	$BF_3{\bullet}OEt_2$	0.5	25	W	Et_2O	3.5	24
24	2.0	$BF_3{\bullet}OEt_2$	0.25	25	W/O	Et_2O	21	62
24	3.0	$BF_3{\bullet}OEt_2$	0.3	25	W/O	Et_2O	5	62
25	3.0	AgOTf−$SnCl_4$	4.0	0	W	Et_2O	23	<10
26	3.0	AgOTf	3.6	−30	W	$Cl(CH_2)_2Cl$	3.5	52
26	2.0	AgOTf	3.0	−20	W	Et_2O	3	90

[a] After isolation.

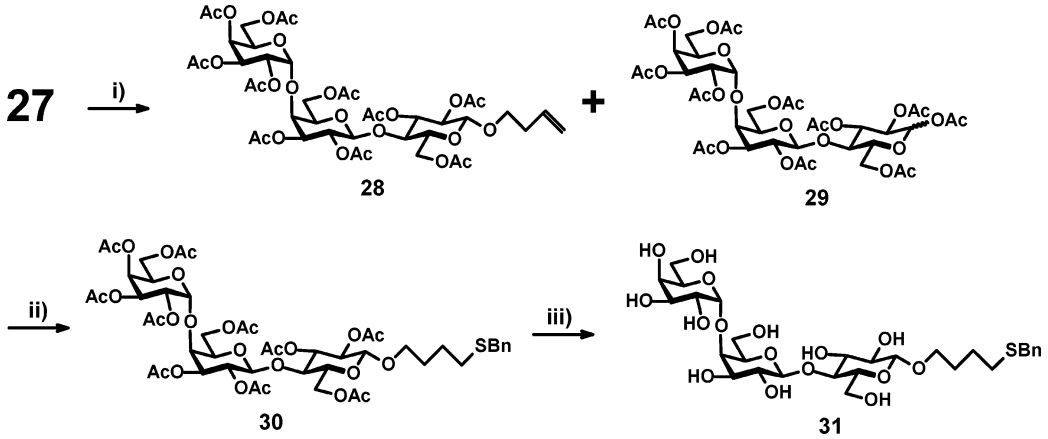
Each structure, as well as the position of the hydroxyl groups in **19** and **20**, was determined by the results of ^{1}H NMR of **21** and **22**, in which hydroxyl groups were each acetylated in the usual way.

Since preparation of the glycosyl acceptor had been achieved, our attention was next directed to the preparation of glycosyl donors. To explore the best result in glycosidation between glycosyl donors and the glycosyl acceptor **19**, a few known glycosyl donors (**24**,[23] **25**,[24] and **26**;[25] Scheme 4) were selected and prepared from a common intermediate **23**.[26] For the synthesis of chloride **26**, it was found that the method of Ogawa et al.[27] with slight modification gave quantitative conversion of hemiacetal **23**. The glycosidation was carried out by means of those glycosyl donors with usual glycosidation protocols, and the results are summarized in Table 1. The chloride showed excellent stereoselectivity as well as yield for constructing a galactosyl α-1→4 lactose trisaccharide moiety, and the best result for the preparation of trisaccharide **27** in the glycosidation was 90.0%. The anomeric configuration of the newly formed α-glycosidic linkage in **27** was confirmed by the results of both ^{1}H and ^{13}C NMR. As for making a galactosyl α-1→4 lactose structure in this situation, we found that a combination of glycosyl chloride, silver triflate (AgOTf) as the promoter, and absolute ether as the solvent, namely, the traditional Koenigs−Knorr method,[28] was extremely effective.

Although the completely benzylated compound **27** had a terminal double bond, we had to deprotect all of the benzyl groups without affecting the C═C double bond at the aglycon. Use of Birch reduction condition is one of the suitable methods for such a purpose. Thus, removal of the benzyl group of **27** was conducted by Na−liquid NH_3-mediated reaction, giving polyol, which was temporarily protected by the acetyl group to give fully protected compound **28** in 53.8% yield (two steps; Scheme 5). In this reductive condition, the lack of a part of the *n*-butenyl group as the aglycon was confirmed, and the isolated yield of **29** was 22.5%, in which the anomeric ratio of the acetate was determined by the results of ^{1}H NMR to be α/β = 1:3. Radical addition of α-toluenethiol into the butenyl moiety of **28** in the presence of AIBN gave benzylthioether **30** in 92.5% yield. Removal of the ester function by the usual transesterification proceeded smoothly to provide **31** in quantitative yield, which was regarded as a precursor for introduction into carbosilane dendrimers.

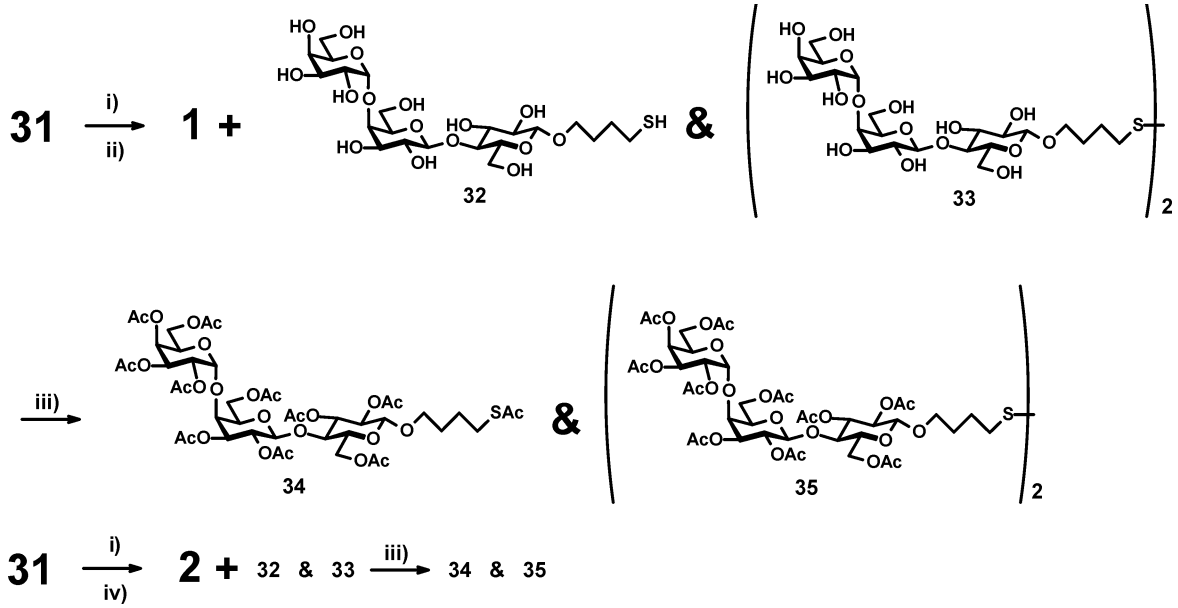
Synthesis of Carbosilane Dendrimers Having Three or Nine Globotriaosyl Moieties. We have demonstrated a model reaction to produce sulfide linkage by using trivalent bromide **5** and benzyl sulfide **11** derived from D-lactose. The condensation reaction included removal of the S-benzyl group and a subsequent coupling reaction by the thiolate anion in a one-pot manner using liquid ammonia as the solvent. Thus, removal of the benzyl group of **31** under the Birch reduction condition was performed in liquid ammonia in the presence of an appropriate amount of Na metal at boiling temperature, giving the corresponding thiolate anion, which was successively treated with brominated carbosilane **5** after neutralization of the excess of Na with NH_4Cl. Removal of ammonia gave the resulting raw products, which were purified by gel filtration to afford white powdery **1** carrying three globotriaosyl residues in 87.6% yield based on **31**. In the stage of purification, it was found that a mixture of thiol **32** and disulfide **33** was also isolated after eluting **31**. To confirm the structures of those byproducts, the mixture was acetylated to remove undesired inorganic salts by usual extraction, and the acetates were separated by silica gel chromatography to give thioacetate **34** in 9.7% yield based on charged **31** and disulfide **35** in 4.8% yield based on charged **31**, respectively. The results of ^{1}H NMR and mass spectroscopic analysis of each acetate supported those structures. Assembly of **31** using **8** was also performed in liquid ammonia in the same way as that for the preparation of **1**, giving **2** with nine globotriaosyl residues in 36.5% yield, which showed a corresponding molecular ion peak (*m*/*z*) at 6019.7. The byproducts in the preparation of **2** were also isolated, thioacetate **34** in 20.1% yield based on charged **31** and disulfide **35** in 15.9% yield based on charged **31**, respectively (Scheme 6).

Scheme 5[a]



[a] Reagents and conditions: (i) Na, liquid NH_3, −78 °C, then, NH_4Cl, then, Ac_2O−Pyr, rt; (ii) α-toluenethiol, AIBN, 1,4-dioxane, 50 → 80 °C; (iii) NaOMe, MeOH, rt.

Scheme 6[a]



[a] Reagents and conditions: (i) Na, liquid NH_3, −35 °C; (ii) NH_4Cl, then **5**; (iii) Ac_2O−Pyr, rt; (iv) NH_4Cl, then **8**.

In conclusion, the synthesis of Gb_3 trisaccharide derivative has been efficiently accomplished by a simple synthetic strategy, and the derivative was then uniformly incorporated into carbosilane dendrimers to afford a novel class of glycoclusters in good yields. Evaluation of the carbosilane dendrimers having Gb_3 saccharide moieties by several biological assay protocols was performed not only in vitro but also in vivo, and the results showed interesting biological responses against both Stxs. Some of the results regarding biological activities of the synthetic receptors prepared in this study have been published,[12b] and further details of the results about the biological activities have been published elswhere.[12c]

Experimental Section

Materials and Methods. Unless otherwise stated, all commercially available solvents and reagents were used without further purification. Pyridine (Pyr), *N*,*N*-dimethylformamide (DMF), and 1,4-dioxane were stored over molecular sieves (MS4Å), and methanol (MeOH) was stored over MS3Å before use. Tetrahydrofuran (THF) was distilled from the sodium benzophenone ketyl solution just before use. Melting points were measured with a Laboratory Devices MELTEMP II apparatus and were uncorrected. The optical rotations were determined with a JASCO DIP-1000 digital polarimeter. The IR spectra were obtained using a JASCO FT/IR-300E spectrophotometer. The ^1H NMR spectra were recorded at 400 MHz spectrometer with a Bruker AM-400 or at 200 MHz with a Varian Gemini-2000 spectrometer in chloroform-*d*, deuterium oxide, or methyl-d_3 alcohol-*d*. The ^{13}C NMR spectra were recorded at 50.3 or 100.6 MHz using the same instruments. Tetramethylsilane (TMS), $CHCl_3$ (7.26 ppm for ^1H or 77.0 ppm for ^{13}C), and MeOD (3.3 ppm for ^1H or 49.0 ppm for ^{13}C) were used as internal standards. Ring-proton assignments in NMR were made by first-order analysis of the spectra and were supported by the results of homonuclear decoupling experiments. Elemental analyses were performed with a Fisons EA1108 on samples extensively dried at 50−60 °C over phosphorus pentoxide for 4−5 h. Fast atom bombardment mass (FAB MS) spectra were recorded with a JEOL JMS−HX110 spectrometer. Reactions were monitored by thin-layer chromatography (TLC) on a precoated plate of silica gel $60F_{254}$ (layer thickness, 0.25 mm; E. Merck, Darmmstadt, Germany). For detection of the intermediates, TLC sheets were dipped with (a) a solution of 85:10:5 (v/v/v) MeOH−*p*-anisaldehyde−concentrated sulfuric acid and heated for a few minutes (for carbohydrate), (b) an aqueous solution of 5 wt % potassium permanganate and heated similarly (for C=C double bond), or (c) an ethanolic solution of 7% phosphomolybdic acid and heated similarly

(for organic compound). Column chromatography was performed on silica gel (Silica Gel 60; 63−200 μm, E. Merck). Flush column chromatography was performed on silica gel (Silica Gel 60, spherical neutral; 40−100 μm, E. Merck). All extractions were concentrated below 45 °C under diminished pressure.

Tris[3-(methylsulfonyloxy)propyl]phenylsilane (4). To a solution of known tris(3-hydroxypropyl)phenylsilane **3**[18] (0.88 g, 3.12 mmol) in pyridine (10 mL) was added methanesulfonyl chloride (1.1 mL, 14.0 mmol) at 0 °C under nitrogen atmosphere, and the mixture was stirred at 0 °C for 50 min. When TLC indicated complete conversion of **3**, water (1.0 mL) was added to the mixture. The mixture was extracted with $CHCl_3$ and partitioned. The organic solution was successively washed with 1 M aq H_2SO_4, saturated aqueous $NaHCO_3$, and brine, dried over anhydrous $MgSO_4$, filtered, and evaporated to give **4** as colorless syrup in quantitative yield, which was directly used for the next step without further purification: R_f 0.53 [1:2 (v/v) toluene−ethyl acetate]; IR (neat) 3645 (ν_{C-H}), 2940 (ν_{C-H}), 1428 (ν_{Si-C}), 1352 ($\nu_{O=S=O}$), 1172 ($\nu_{O=S=O}$), 1111 (δ_{C-H}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 0.92 (m, 6H, $3SiCH_2$), 1.76 (m, 6H, $3CH_2$), 3.00 (s, 9H, 3Me), 4.18 (t, 6H, J = 6.5 Hz, CH_2O), 7.4 (m, 5H, Ph); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) 7.65 ($SiCH_2$), 23.68 (CH_2), 37.38 (Me), 71.96 (CH_2O), 128.30 (Ph), and 133.86 (Ph).

Tris(3-bromopropyl)phenylsilane (5). A mixture of mesylate **4** (1.13 g, 2.19 mmol) and NaBr (3.38 g, 32.8 mmol) in DMF (15 mL) was stirred for 1 h at 80 °C under nitrogen atmosphere. After removal of DMF by evaporation, ethyl acetate and water were added to the residue, and the mixture was partitioned. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Silica gel chromatography of the residue with 10:1 (v/v) *n*-hexane−ethyl acetate gave pure **5** (0.90 g, 87.4%) as colorless syrup: R_f 0.54 [10:1 (v/v) *n*-hexane−ethyl acetate]; IR (neat) 2929 (ν_{C-H}), 1427 (ν_{Si-C}), 1238 (ν_{C-Br}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 0.96 (m, 6H, $3SiCH_2$), 1.86 (m, 6H, $3CH_2$), 3.39 (t, 6H, J = 6.8 Hz, $3CH_2Br$), 7.4 (m, 5H, Ph); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) 11.31 ($SiCH_2$), 27.39 (CH_2), 36.87 (CH_2Br), 128.15, 129.53, 133.85, and 134.90 (Ph).

Anal. Calcd for $C_{15}H_{23}Br_3Si_1$: C, 38.24; H, 4.92. Found: C, 38.64; H, 4.90.

Tris[tris(3-methylsulfonyloxypropyl)silylpropyl]phenylsilane (7). Methanesulfonyl chloride (0.41 mL, 5.26 mmol) was added dropwise to a solution of tris[tris(3-hydroxypropyl)silylpropyl]phenylsilane **6**[18] (165 mg, 0.195 mmol) in pyridine (5 mL) at −20 °C under nitrogen atmosphere with stirring, and the stirring was continued for 3 h at −20 °C. To the mixture was added water (2 mL) and $CHCl_3$ (10 mL), and the mixture was partitioned. The organic solution was successively washed with 1 M aq H_2SO_4, saturated aqueous $NaHCO_3$, and brine, dried over anhydrous $MgSO_4$, filtered, and evaporated to give pure **7** (279 mg, 92.4%) as colorless syrup, which was directly used for the next step without further purification: R_f 0.40 [5:4:1 (v/v/v) $CHCl_3$−ethyl acetate−MeOH]; IR (neat) 3628 (ν_{C-H}), 2916 (ν_{C-H}), 1417 (ν_{Si-C}), 1347 ($\nu_{O=S=O}$), 1170 ($\nu_{O=S=O}$), 1109 (δ_{C-H}) cm^{-1}.

Tris[tris(3-bromopropyl)silylpropyl]phenylsilane (8). Mesylate **7** (279 mg, 0.195 mmol) was treated with NaBr (0.90 g, 8.76 mmol) in DMF (10 mL) at 80 °C under nitrogen atmosphere for 3 h. The reaction mixture was evaporated to dryness, and the residue was diluted with toluene and water. The organic layer was partitioned, dried over anhydrous $MgSO_4$, filter, and concentrated in vacuo. The residual syrup was purified by silica gel chromatography with 20:1 then 15:1 (v/v) *n*-hexane−ethyl acetate as the eluent to give **8** (152 mg, 59.8%) as colorless syrup: R_f 0.23 [10:1 (v/v) *n*-hexane−ethyl acetate]; IR (neat) 2916 (ν_{C-H}), 1429 (ν_{Si-C}), 1238 (ν_{C-Br}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 0.63 (m, 24H, $12SiCH_2$), 0.87 [m, 6H, $3SiCH_2$ (G0)], 1.34 [m, 6H, $3CH_2$ (G0)], 1.78 [m, 18H, $9CH_2$ (G1)], 3.36 (t, 18H, J = 6.8 Hz, $9CH_2Br$), 7.4 (m, 5H, Ph); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) 11.39 [$SiCH_2$ (G1)], 16.84 [CH_2 (G0)], 17.27 [CH_2 (G0)], 18.30 [CH_2 (G0)], 27.63 [CH_2 (G1)], 37.04 (CH_2Br), 127.88 (Ph), 129.01 (Ph), 133.98 (Ph), and 137.07 (Ph).

Anal. Calcd for $C_{42}H_{77}Br_9Si_4$: C, 35.69; H, 5.49. Found: C, 36.03; H, 5.53.

3-Benzylmercaptopropyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (10). To a solution of known glycoside **9**[19] (1.54 g, 2.27 mmol) and α-toluenethiol (4.0 mL, 34.1 mmol) in 1,4-dioxane (12 mL) was added 2,2′-azobisisobutyronitrile (AIBN; 75 mg, 0.46 mmol) at 50 °C under argon atmosphere, and the solution was stirred at 80 °C for 3 h. After adding cyclohexene, the reaction mixture was evaporated in vacuo. The resultant liquid was chromatographed on silica gel with 3:1 (v/v) toluene−ethyl acetate as the eluent to afford **10** (1.45 g, 79.7%) as amorphous solids: R_f 0.61 [1:1 (v/v) toluene−ethyl acetate]; $[\alpha]_D^{22}$ −9.0° (*c* 0.33, $CHCl_3$); IR (KBr) 2939 (ν_{C-H}), 1753 ($\nu_{C=O}$), 1057 (ν_{C-O-C}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 1.81 (m 2H, CH_2), 1.96, 2.00, 2.04, 2.04, 2.06, 2.10, and 2.15 (each s, 21H, $7COCH_3$), 2.45 (t, 2H, J = 7.1 Hz, CH_2S), 3.57 (m, 1H, H-5), 3.68 (s, 2H, CH_2Ph), 3.71 (m, 2H, OCH_2), 3.78 (t, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 3.87 (m, 1H, H-5′), 4.15−4.25 (m, 3H, H-6a, −6′a, and −6′b), 4.43 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.48 (m, 1H, H-6b), 4.48 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1′), 4.87 (dd, 1H, $J_{2,3}$ = 9.4 Hz, H-2), 4.95 (dd, 1H, $J_{3',4'}$ = 3.4 Hz, H-3′), 5.11 (dd, 1H, $J_{2',3'}$ = 10.3 Hz, H-2′), 5.18 (t, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 5.34 (d, 1H, $J_{4',5'}$ = ∼0 Hz, H-4′), 7.3 (m, 5H, Ph).

Anal. Calcd for $C_{36}H_{48}O_{18}S_1$: C, 53.99; H, 6.04. Found: C, 54.30; H, 6.14.

3-Benzylmercaptopropyl *O*-(β-D-Galactopyranosyl)−(1→4)-β-D-glucopyranoside (11). To a solution of **10** (1.16 g, 1.45 mmol) in MeOH (30 mL) was added NaOMe (55 mg, 1.01 mmol), and the mixture was stirred for 6 h at room temperature under argon atmosphere. Dowex 50W X-8(H^+) resin was added to neutralize the solution, and the suspension was filtered and evaporated to yield **11** (675 mg, 92.0%) as white crystals: mp 136−138 °C; R_f 0.68 [65:25:4 (v/v/v) $CHCl_3$−MeOH−water]; IR (KBr) 3425 (ν_{O-H}), 2920 (ν_{C-H}), 1066 (ν_{C-O-C}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 1.77 (m, 2H, CH_2), 2.46 (t, 2H, J = 7.2 Hz, CH_2S), 3.64 (s, 2H, CH_2Ph), 4.32 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.39 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1′).

Anal. Calcd for $C_{22}H_{34}O_{11}S_1 \cdot 0.5H_2O$: C, 51.25; H, 6.84. Found: C, 51.19; H, 6.78.

Carbosilane Compound Carrying Three D-Lactose Moieties (13). To a stirred solution of **11** (239 mg, 0.471 mmol) in liquid NH_3 (ca. 50 mL) was added Na (110 mg, 4.78 mmol) at −35 °C, and the mixture was stirred for 30 min. The stirred mixture was treated with NH_4Cl (227 mg, 4.24 mmol) for 30 min, and then, a solution of tris(3-bromopropyl)phenylsilane **5** (37 mg, 78.5 μmol) in MeOH−THF (2 mL) was added dropwise to the mixture. The reaction mixture was stirred overnight and then evaporated to dryness. The residue was passed repeatedly through Sephadex G-25 (2.5 i.d. × 42 cm) with 5% aq AcOH as an eluent to give pure **13** (93 mg, 80.2%) as white powder after lyophilization: R_f 0.37 [50:25:3 (v/v/v) $CHCl_3$−MeOH−water]; ^1H NMR δ (400 MHz, D_2O) 1.48 (m, 6H, $3CH_2$), 1.71 (m, 6H, $3CH_2$), 4.16 (d, 3H, $J_{1,2}$ = 7.9 Hz, H-1), 4.19 (d, 3H, $J_{1',2'}$ = 7.6 Hz, H-1′), 7.4 (m, 5H, Ph).

***n*-Butenyl *O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (15).** To a stirred solution of D-lactosyl β-acetate **14** (50.0 g, 73.7 mmol) and 3-buten-1-ol (31.7 mL, 0.369 mol) in CH_2Cl_2 (368 mL) was dropwise added BF_3-OEt_2 (90.9 mL, 0.737 mol) at 0 °C under nitrogen atmosphere, and the stirring was continued for 4 h at 0 °C. The reaction mixture was poured into ice-cold water, followed by partition. The organic solution was washed successively with water, saturated aqueous $NaHCO_3$, and brine, dried over anhydrous $MgSO_4$, filtered, and evaporated in vacuo. The residual syrup was subjected to a column of silica gel (5 L) with 2:1 (v/v) toluene−ethyl acetate as the eluent to afford **15** (30.5 g, 59.9%) as fluffy solids: R_f 0.51 [1:1 (v/v) toluene−ethyl acetate]; $[\alpha]_D^{25}$ −14.8° (*c* 1.19, $CHCl_3$); IR (KBr) 2982 (ν_{C-H}), 1760 ($\nu_{C=O}$), 1643 ($\nu_{C=C}$), 1238 (ν_{C-O}), 1056 (ν_{C-O-C}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 1.97, 2.03, 2.05, 2.05, 2.06, 2.12, and 2.15 (each s, 21H, $7COCH_3$), 2.32 (m, 2H, CH_2), 3.61 (ddd, 1H, $J_{5,6a}$ = 5.0 Hz and $J_{5,6b}$ = 1.9 Hz, H-5), 3.70 (m,

2H, OCH_2), 3.80 (t, 1H, $J_{4,5}$ = 9.8 Hz, H-4), 3.88 (t, 1H, $J_{5',6'a} = J_{5',6'b}$ = 6.7 Hz, H-5′), 4.3 (m, 3H, H-6a, −6′a, and −6′b), 4.48 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.48 (m, 1H, H-6b), 4.49 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.89 (dd, 1H, $J_{2,3}$ = 9.5 Hz, H-2), 4.96 (dd, 1H, $J_{3',4'}$ = 3.4 Hz, H-3′), 5.1 (m, 2H, $=CH_2$), 5.11 (dd, 1H, $J_{2',3'}$ = 10.4 Hz, H-2′), 5.20 (t, 1H, $J_{3,4}$ = 9.3 Hz, H-3), 5.34 (d, 1H, $J_{4',5'}$ = ∼0 Hz, H-4′), 5.76 (m, 1H, CH=).

Anal. Calcd for $C_{30}H_{42}O_{18}$: C, 52.17; H, 6.13. Found: C, 52.03; H, 6.10.

***n*-Butenyl *O*-(*β*-D-Galactopyranosyl)-(1→4)-*β*-D-glucopyranoside (16).** NaOMe (0.76 g, 14.2 mmol) was added to a solution of acetate **15** (13.97 g, 20.2 mmol) in MeOH (150 mL) at room temperature, and the solution was stirred for 26 h. To the solution was added Dowex 50W X-8 (H^+) resin for neutralization of the solution. The suspension was filtered, and the filtrate was concentrated in vacuo to yield **16** (7.77 g, 96.9%) as white amorphous solids: R_f 0.48 [65:25:4 (v/v/v) $CHCl_3$−MeOH−H_2O]; $[\alpha]_D^{28}$ −11.5° (*c* 1.33, MeOH); IR (KBr) 3410 (ν_{O-H}), 2918 (ν_{C-H}), 1645 ($\nu_{C=C}$), 1065 (ν_{C-O-C}) cm^{-1}; ^1H NMR δ (400 MHz, D_2O) 2.35 (q, 2H, J = 6.7 Hz, CH_2), 3.26 (dd, 1H, $J_{2,3}$ = 9.0 Hz, H-2), 3.49 (dd, 1H, $J_{2',3'}$ = 9.8 Hz, H-2′), 4.40 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.45 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 5.1 (m, 2H, $=CH_2$), 5.74 (m, 1H, CH=); ^{13}C NMR δ (100.6 MHz, D_2O) 33.40 (CH_2), 60.20 (C-6), 61.14 (C-6′), 68.66 (C-4′), 69.68 (OCH_2), 71.07 (C-2′), 72.64 (C-3′), 72.90 (C-2), 74.52 (C-3), 74.88 (C-5), 75.46 (C-5′), 78.48 (C-4), 102.13 (C-1), 103.04 (C-1′), 116.94 ($=CH_2$), 135.40 (CH=).

Anal. Calcd for $C_{16}H_{28}O_{11}\cdot 0.2H_2O$: C, 48.05; H, 7.15. Found: C, 47.99; H, 7.12.

***n*-Butenyl *O*-(4,6-*O*-Benzylidene-*β*-D-galactopyranosyl)-(1→4)-*β*-D-glucopyranoside (17).** To a solution of alcohol **16** (9.25 g, 23.3 mmol) and α,α-dimethoxytoluene (5.25 mL, 35.0 mmol) in DMF (50 mL) was added CSA (0.54 g, 2.33 mmol) at room temperature, and the solution was heated for 2 h at ca. 60 °C while removing the liberated MeOH under reduced pressure. After cooling to room temperature, the reaction mixture was neutralized with Et_3N (0.65 mL, 4.67 mmol) and evaporated in vacuo. The residual syrup was treated with toluene to give crude **17** (13.14 g) as amorphous solids, which was used for next step without further purification. An analytical sample was purified by silica gel chromatography with 5:1 (v/v) $CHCl_3$−MeOH as the eluent to give pure **17** as white crystals: mp 227−229 °C; R_f 0.56 [4:1 (v/v) $CHCl_3$−MeOH]; $[\alpha]_D^{29}$ −36.8° (*c* 1.01, MeOH); IR (KBr) 3410 (ν_{O-H}), 2878 (ν_{C-H}), 1646 ($\nu_{C=C}$), 1066 (ν_{C-O-C}) cm^{-1}; ^1H NMR δ (200 MHz, DMSO-d_6) 4.20 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.36 (d, 1H, $J_{1',2'}$ = 7.2 Hz, H-1′), 5.54 (s, 1H, C*H*Ph), 7.4 (m, 5H, Ph).

Anal. Calcd for $C_{23}H_{32}O_{11}$: C, 57.02; H, 6.66. Found: C, 56.80; H, 6.65.

***n*-Butenyl *O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-*β*-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (18).** To a suspension of NaH (50%, 11.20 g, 0.233 mol, washed with hexane) in DMF (170 mL) was dropwise added alcohol **17** (13.14 g, ca. 23.3 mmol) in DMF (50 mL) at 0 °C, and the mixture was stirred for 20 min. Benzyl bromide (27.8 mL, 0.233 mol) was added dropwise to the mixture at 0 °C, and the whole mixture was stirred overnight at room temperature. To the mixture was added MeOH (18.9 mL, 0.467 mol) at 0 °C, and the mixture was evaporated and poured into ice-cold water. The whole mixture was extracted with $CHCl_3$, washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residual syrup was chromatographed on silica gel with 5:1−1:1 (v/v) *n*-hexane−ethyl acetate as the eluent to yield pure **18** as a syrup (65.0% in two steps), which was crystallized itself to afford white crystals: mp 128−129 °C; R_f 0.45 [2:1 (v/v) *n*-hexane−ethyl acetate]; $[\alpha]_D^{22}$ +13.4° (*c* 1.01, $CHCl_3$); IR (KBr) 2867 (ν_{C-H}), 1642 ($\nu_{C=C}$), 1497 (δ_{C-H}), 1453 (δ_{C-H}), 1096 (ν_{C-O-C}), 732 (δ_{C-H}), 696 (δ_{C-H}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 2.42 (m, 2H, CH_2), 2.92 (s, 1H, H-5′), 3.89 (dd, 1H, $J_{2',3'}$ = 10.9 Hz and $J_{3',4'}$ = 4.1 Hz, H-3′), 4.34 (d, 1H, J_{gem} = 12.1 Hz, CH_aPh), 4.41 (d, 1H, $J_{1,2}$ = 7.8 Hz, H-1), 4.47 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.56 (d, 1H, J_{gem} = 12.1 Hz, CH_bPh), 4.72 (s, 2H, CH_2Ph), 4.73 (d, 1H, J_{gem} = 11.2 Hz, CH_aPh), 4.76 (d, 1H, J_{gem} = 10.7 Hz, CH_aPh), 4.80 (d, 1H, J_{gem} = 10.9 Hz, CH_aPh), 4.85 (d, 1H, J_{gem} = 11.2 Hz, CH_bPh), 4.93 (d, 1H, J_{gem} = 10.9 Hz, CH_bPh), 5.09 (m, 2H, $=CH_2$), 5.19 (d, 1H, J_{gem} = 10.7 Hz, CH_bPh), 5.46 (s, 1H, C*H*Ph), 5.86 (m, 1H, CH=), 7.4 (m, 30H, 6Ph); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) 34.11 (CH_2), 66.25, 68.24, 68.85, 69.15, 71.51, 72.89, 73.55, 74.85, 75.03, 75.14, 75.65, 77.56, 78.74, 79.60, 81.72, 82.92, 101.23 (*C*HPh, benzylidene), 102.77 (C-1), 103.59 (C-1′), 116.51 ($=CH_2$), 134.98 (CH=).

Anal. Calcd for $C_{58}H_{62}O_{11}$: C, 74.50; H, 6.68. Found: C, 74.45; H, 6.68.

***n*-Butenyl *O*-(2,3,6-Tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (19) and *n*-Butenyl *O*-(2,3,4-Tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (20).** Benzylidene **18** (5.61 g, 6.00 mmol) and BH_3−Me_3N complex (3.16 g, 42.0 mmol) was stirred in THF (56 mL) at room temperature in the presence of MS4Å for 30 min. To the mixture was portionwise added $AlCl_3$ (5.60 g, 42.0 mmol) with vigorous stirring at room temperature, and the stirring was continued for 1 h. After cooling to ca. 0 °C, $CHCl_3$ was added to the mixture, and the suspension was filtered through a pad of Celite. The filtrate was washed with ice-cold 1 M aq H_2SO_4, followed by partitioning. The organic solution was washed successively with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, filtered, and evaporated in vacuo. The residual syrup was purified by using a column of silica gel with 3:1−1:1 (v/v) *n*-hexane−ethyl acetate as the eluent to give **19** (4.61 g, 82.0%) as crystals and **20** (0.76 g, 13.5%) as a syrup. **19**: mp 100−101 °C; R_f 0.59 [2:1 (v/v) *n*-hexane−ethyl acetate]; $[\alpha]_D^{24}$ +20.3° (*c* 1.03, $CHCl_3$); IR (KBr) 3481 (ν_{O-H}), 2871 (ν_{C-H}), 1641 ($\nu_{C=C}$), 1497 (δ_{C-H}), 1454 (δ_{C-H}), 1070 (ν_{C-O-C}) 736 (δ_{C-H}), 697 (δ_{C-H}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 2.40 (m, 2H, CH_2), 3.31 (br t, 1H, H-5′), 3.37 (m, 1H, H-5), 3.39 (t, 1H, $J_{2,3}$ = 9.1 Hz, H-2), 3.46 (dd, 1H, $J_{5',6'a}$ = 5.3 Hz, H-6′a), 3.54 (dd, 1H, $J_{3',4'}$ = 3.6 Hz, H-3′), 3.56 (t, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 3.58 (dd, 1H, $J_{2',3'}$ = 9.2 Hz, H-2′), 3.65 (dd, 1H, $J_{5',6'b}$ = 7.2 Hz and $J_{6'a,6'b}$ = 9.6 Hz, H-6′b), 3.67 (m, 2H, OCH_2), 3.71 (dd, 1H, $J_{5,6a}$ = ∼1 Hz, H-6a), 3.79 (dd, 1H, $J_{5,6b}$ = 4.3 Hz and $J_{6a,6b}$ = 10.9 Hz, H-6b), 3.95 (t, 1H, $J_{4,5}$ = 9.4 Hz, H-4), 4.01 (br d, 1H, $J_{3',4'}$ = 3.6 Hz, H-4′), 4.38 (d, 1H, J_{gem} = 12.1 Hz, CH_aPh), 4.38 (d, 1H, $J_{1,2}$ = 7.4 Hz, H-1), 4.41 (d, 1H, J_{gem} = 11.5 Hz, CH_aPh), 4.42 (d, 1H, $J_{1',2'}$ = 7.6 Hz, H-1′), 4.44 (d, 1H, J_{gem} = 11.5 Hz, CH_bPh), 4.54 (d, 1H, J_{gem} = 12.1 Hz, CH_bPh), 4.65 (d, 1H, J_{gem} = 11.7 Hz, CH_aPh), 4.69 (d, 1H, J_{gem} = 10.9 Hz, CH_aPh), 4.71 (d, 1H, J_{gem} = 11.7 Hz, CH_bPh), 4.76 (s, 2H, CH_2Ph), 4.76 (d, 1H, J_{gem} = 10.8 Hz, CH_aPh), 4.89 (d, 1H, J_{gem} = 10.9 Hz, CH_bPh), 4.96 (d, 1H, J_{gem} = 10.8 Hz, CH_bPh), 5.08 (m, 2H, $=CH_2$), 5.85 (m, 1H, CH=), 7.3 (m, 30H, 6Ph); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) 34.10 (CH_2), 66.07, 68.18, 68.38, 69.09, 71.90, 72.70, 73.02, 73.39, 74.78, 75.01, 75.13, 75.20, 76.49, 79.29, 81.02, 81.63, 82.73, 102.43 (C-1), 103.55 (C-1′), 116.49 ($=CH_2$), 134.99 (CH=).

Anal. Calcd for $C_{58}H_{64}O_{11}$: C, 74.34; H, 6.88. Found: C, 74.51; H, 6.90.

20: R_f 0.32 [2:1 (v/v) *n*-hexane−ethyl acetate]; $[\alpha]_D^{25}$ +15.1° (*c* 1.03, $CHCl_3$); ^1H NMR δ (400 MHz, $CDCl_3$) 2.40 (m, 2H, CH_2), 3.15 (dd, 1H, $J_{5',6'a}$ = 4.7 Hz and $J_{5',6'b}$ = 7.2 Hz, H-5′), 3.88 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.2 Hz, H-4), 4.38 (d, 1H, J_{gem} = 12.2 Hz, CH_aPh), 4.40 (d, 1H, $J_{1,2}$ = 7.5 Hz, H-1), 4.42 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1′), 4.54 (d, 1H, J_{gem} = 12.2 Hz, CH_bPh), 4.56 (d, 1H, J_{gem} = 11.6 Hz, CH_aPh), 4.71 (d, 1H, J_{gem} = 11.6 Hz, CH_bPh), 4.72 (s, 2H, CH_2Ph), 4.73 (d, 1H, J_{gem} = 10.8 Hz, CH_aPh), 4.79 (s, 2H, CH_2Ph), 4.87 (d, 1H, J_{gem} = 8.8 Hz, CH_aPh), 4.92 (d, 1H, J_{gem} = 8.8 Hz, CH_bPh), 5.01 (d, 1H, J_{gem} = 10.8 Hz, CH_bPh), 5.08 (m, 2H, $=CH_2$), 5.84 (m, 1H, CH=), 7.3 (m, 30H, 6Ph); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) 34.13 (CH_2), 61.75 (C-1′), 69.10, 72.86, 73.06, 73.66, 74.35, 74.78, 74.90, 75.01, 75.13, 75.26, 75.48, 76.88, 79.82, 81.47, 82.56, 82.62, 102.78 (C-1), 103.54 (C-1′), 116.52 ($=CH_2$), 135.01 (CH=).

Anal. Calcd for $C_{58}H_{64}O_{11}$: C, 74.34; H, 6.88. Found: C, 74.34; H, 6.93.

Each monoalcohol **19** and **20** were acetylated by the usual way to afford corresponding monoacetates **21** with 4′-OAc and **22** with 6′-

OAc, respectively. **21**: R_f 0.44 [4:1 (v/v) *n*-hexane−ethyl acetate]; IR (neat) 2871 (ν_{C-H}), 1743 ($\nu_{C=O}$), 1496 (δ_{C-H}), 1456 (δ_{C-H}), 1093 (ν_{C-O-C}), 733 (δ_{C-H}), 698 (δ_{C-H}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 2.03 (s, 3H, $COCH_3$), 2.41 (m, 2H, CH_2), 3.58 (dd, 1H, $J_{5',6'b} = 7.0$ Hz and $J_{6'a,6'b} = 9.3$ Hz, H-6′b), 3.69 (dd, 1H, $J_{5,6a} = \sim 1$ Hz, H-6a), 3.77 (dd, $J_{5,6b} = 4.3$ Hz and $J_{6a,6b} = 10.9$ Hz, H-6b), 3.94 (t, 1H, $J_{3,4} = J_{4,5} = 9.3$ Hz, H-4), 4.25 (d, 1H, $J_{gem} = 12.0$ Hz, C*H*$_a$Ph), 4.36 (d, 1H, $J_{gem} = 12.1$ Hz, C*H*$_a$Ph), 4.38 (d, 1H, $J_{1,2} = 7.7$ Hz, H-1), 4.45 (d, 1H, $J_{1',2'} = 7.3$ Hz, H-1′), 4.47 (d, 2H, $J_{gem} = 11.0$ Hz, C*H*$_a$Ph and C*H*$_b$Ph), 4.54 (d, 1H, $J_{gem} = 12.1$ Hz, C*H*$_b$Ph), 4.69 (d, 1H, $J_{gem} = 11.0$ Hz, C*H*$_b$Ph), 4.69 (d, 1H, $J_{gem} = 12.4$ Hz, C*H*$_a$Ph), 4.75 (d, 1H, $J_{gem} = 10.6$ Hz, C*H*$_a$Ph), 4.76 (d, 1H, $J_{gem} = 11.0$ Hz, C*H*$_a$Ph), 4.77 (d, 1H, $J_{gem} = 12.4$ Hz, C*H*$_b$Ph), 4.89 (d, 1H, $J_{gem} = 11.0$ Hz, C*H*$_b$Ph), 4.96 (d, 1H, $J_{gem} = 10.6$ Hz, C*H*$_b$Ph), 5.08 (m, 2H, $=CH_2$), 5.45 (d, 1H, $J_{3',4'} = 2.9$ Hz, H-4′), 5.85 (m, 1H, CH=), 7.3 (m, 30H, 6Ph).

22: R_f 0.57 [2:1 (v/v) *n*-hexane−ethyl acetate]; IR (neat) 2871 (ν_{C-H}), 1745 ($\nu_{C=O}$), 1647 ($\nu_{C=C}$), 1496 (δ_{C-H}), 1454 (δ_{C-H}), 737 (δ_{C-H}), 698 (δ_{C-H}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 1.92 (s, 3 H, $COCH_3$), 2.40 (m, 2H, CH_2), 3.30 (t, 1H, $J_{5',6'} = 6.5$ Hz, H-5′), 3.80 (dd, 1H, $J_{5,6b} = 4.4$ Hz and $J_{6a,6b} = 10.9$ Hz, H-6b), 3.96 (t, 1H, $J_{3,4} = J_{4,5} = 9.4$ Hz, H-4), 4.38 (d, 1H, $J_{1,2} = 7.5$ Hz, H-1), 4.40 (d, 1H, $J_{gem} = 12.2$ Hz, C*H*$_a$Ph), 4.45 (d, 1H, $J_{1',2'} = 7.7$ Hz, H-1′), 4.56 (d, 1H, $J_{gem} = 12.2$ Hz, C*H*$_b$Ph), 4.57 (d, 1H, $J_{gem} = 11.5$ Hz, C*H*$_a$Ph), 4.70 (d, 1H, $J_{gem} = 11.0$ Hz, C*H*$_a$Ph), 4.73 (d, 1H, $J_{gem} = 10.7$ Hz, C*H*$_a$Ph), 4.74 (s, 1H, CH_2Ph), 4.75 (d, 1H, $J_{gem} = 11.5$ Hz, C*H*$_b$Ph), 4.79 (d, 1H, $J_{gem} = 11.2$ Hz, C*H*$_a$Ph), 4.89 (d, 1H, $J_{gem} = 11.0$ Hz, C*H*$_b$Ph), 4.97 (d, 1H, $J_{gem} = 11.2$ Hz, C*H*$_b$Ph), 4.99 (d, 1H, $J_{gem} = 10.7$ Hz, C*H*$_b$Ph), 5.07 (m, 2H, $=CH_2$), 5.85 (m, 1H, CH=), 7.3 (m, 30H, 6Ph).

2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl Chloride (26).[25] To a solution of hemiacetal **23**[26] (200 mg, 0.370 mmol) and DMF[27] (0.01 mL) in 1,2-dichloroethane (2 mL) was dropwise added thionyl chloride (0.054 mL, 0.74 mmol) at 0 °C under nitrogen atmosphere. After showing complete conversion of starting materials on TLC, the reaction mixture was evaporated in vacuo and coevaporated with toluene (3 times) to give pure **26** quantitatively: R_f 0.50 [4:1 (v/v) *n*-hexane−ethyl acetate]; IR (neat) 2913 (ν_{C-H}), 1496 (δ_{C-H}), 1454 (δ_{C-H}), 1059 (ν_{C-O-C}), 737 (δ_{C-H}), 698 (δ_{C-H}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 3.53 (d, 1H, $J_{5,6b} = 5.8$ Hz, H-6b), 3.53 (d, 1H, $J_{5,6a} = 7.0$ Hz, H-6a), 3.96 (dd, 1H, $J_{3,4} = 2.6$ Hz, H-3), 3.98 (d, 1H, $J_{4,5} = \sim 0$ Hz, H-4), 4.20 (dd, 1H, $J_{2,3} = 9.6$ Hz, H-2), 4.21 (t, 1H, H-5), 4.37 (d, 1H, $J_{gem} = 11.8$ Hz, C*H*$_a$Ph), 4.45 (d, 1H, $J_{gem} = 11.8$ Hz, C*H*$_b$Ph), 4.55 (d, 1H, $J_{gem} = 11.3$ Hz, C*H*$_a$Ph), 4.68 (d, 1H, $J_{gem} = 11.8$ Hz, C*H*$_a$Ph), 4.72 (d, 1H, $J_{gem} = 11.7$ Hz, C*H*$_a$Ph), 4.73 (d, 1H, $J_{gem} = 11.8$ Hz, C*H*$_b$Ph), 4.83 (d, 1H, $J_{gem} = 11.7$ Hz, C*H*$_b$Ph), 4.94 (d, 1H, $J_{gem} = 11.3$ Hz, C*H*$_b$Ph), 6.14 (d, 1H, $J_{1,2} = 3.8$ Hz, H-1), 7.2 (m, 20H, 4Ph); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) 67.84 (C-6), 72.27, 72.89, 73.23, 73.31, 74.25, 74.88, 76.10, 78.23, 94.85 (C-1), 103.59 (C-1′).

***n*-Butenyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (27).** A suspension of an acceptor **19** (593 mg, 0.633 mmol), a donor **26** (706 mg, 1.26 mmol), and MS4Å (91 mg) in diethyl ether (20 mL) was stirred for 30 min at room temperature under argon atmosphere. To the suspension was added AgOTf (490 mg, 1.91 mmol) at −20 °C with vigorous stirring, and the stirring was maintained for 3 h at −20 °C. When TLC indicated the complete disappearance of the starting materials, $CHCl_3$ was added to the mixture. The reaction mixture was filtered through a pad of Celite, and the filtrate was successively washed with water, saturated aqueous $NaHCO_3$, and brine, dried over anhydrous $MgSO_4$, filtered, and evaporated in vacuo. Chromatographic purification of the residue on silica gel with 8:1 (v/v) *n*-hexane−ethyl acetate as the eluent gave trisaccharide **27** (832 mg, 90.0%) as colorless syrup: R_f 0.26 [4:1 (v/v) *n*-hexane−ethyl acetate]; $[\alpha]_D^{26}$ +35.3° (*c* 1.09, $CHCl_3$); IR (KBr) 2870 (ν_{C-H}), 1641 ($\nu_{C=C}$), 1496 (δ_{C-H}), 1454 (δ_{C-H}), 1095 (ν_{C-O-C}), 735 (δ_{C-H}), 697 (δ_{C-H}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 2.38 (m, 2H, CH_2), 3.20 (dd, 1H, J = 4.7 Hz and J = 8.4 Hz), 3.63 (dd, 1H, $J_{5',6'b} = 7.7$ Hz and $J_{6'a,6'b} = 9.9$ Hz, H-6′b), 3.71 (t, 1H, $J_{5,6a} = \sim 1$ Hz, H-6a), 3.81 (dd, 1H, $J_{5,6b} = 4.4$ Hz and $J_{6a,6b} = 10.9$ Hz, H-6b), 4.06 (dd, 1H, $J = 3.3$ Hz and $J = 10.1$ Hz), 4.47 (d, 1H, $J_{1,2} = 7.5$ Hz, H-1), 4.52 (d, 1H, $J_{1',2'} = 8.0$ Hz, H-1′), 5.04 (d, 1H, $J_{1'',2''} = 3.5$ Hz, H-1″), 5.06 (m, 2H, $=CH_2$), 5.83 (m, 1H, CH=), 7.2 (m, 50H, 10Ph); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) 34.20 (CH_2), 100.63 (C-1″), 102.86 (C-1), 103.60 (C-1′), 116.48 ($=CH_2$), 135.08 (CH=).

Anal. Calcd for $C_{92}H_{98}O_{16}$: C, 75.70; H, 6.77. Found: C, 75.41; H, 6.77.

***n*-Butenyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (28).** To a blue-colored mixture of Na (2.11 g, 91.8 mmol) in liquid NH_3 (ca. 100 mL) was dropwise added a solution of benzyl-protected trisaccharide **27** (3.35 g, 2.29 mmol) in 1,2-dimethoxyethane (30 mL) at −78 °C with vigorous stirring. After 10 min, NH_4Cl (4.91 g, 91.8 mmol) was added portionwise to the blue-colored mixture at −78 °C, and the stirring was continued overnight to remove NH_3 gas. Complete removal of liquid NH_3 was done under reduced pressure. The whole residue was acetylated in acetic anhydride (40 mL) and pyridine (40 mL) at room temperature for 18 h. The residue after evaporation was poured into ice-cold water and extracted with $CHCl_3$. The organic layer was successively washed with 1 M aq H_2SO_4, saturated aqueous $NaHCO_3$, and brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residual syrup was chromatographed on silica gel with 3:1−1:3 (v/v) toluene−ethyl acetate as the eluent to give pure **28** (1.21 g, 53.8%) as a colorless syrup, **27** (0.27 g, 8%) as the starting material, and colorless syrupy *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)−(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-galactopyranosyl)−(1→4)-1,2,3,6-tetra-*O*-acetyl-D-glucopyranose **29** (0.50 g, 22.5%) as a mixture of 1:3 (mol/mol) α-acetate−β-acetate, respectively. **28**: R_f 0.46 [1:2 (v/v) toluene−ethyl acetate]; $[\alpha]_D^{25}$ +38.3° (*c* 0.13, $CHCl_3$); IR (KBr) 2941 (ν_{C-H}), 1747 ($\nu_{C=O}$), 1057 (ν_{C-O-C}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 1.98, 2.03, 2.04, 2.06, 2.07, 2.07, 2.08, 2.08, 2.11, 2.13, (each s, 30H, 10$COCH_3$), 2.32 (q, 2H, $J = 5.7$ Hz, CH_2), 3.63 (ddd, 1H, $J_{5,6a} = 2.0$ Hz and $J_{5,6b} = 6.3$ Hz, H-5), 3.71 (m, 2H, OCH_2), 3.76 (t, 1H, $J_{5',6'a} = J_{5',6'b} = 6.6$ Hz, H-5′), 3.79 (t, 1H, $J_{4,5} = 9.8$ Hz, H-4), 4.01 (d, 1H, $J_{4',5'} = \sim 0$ Hz, H-4′), 4.15 (m, 4H, H-6a, −6′a, −6′b, and H-5″), 4.43 (dd, 1H, $J_{6a,6b} = 11.0$ Hz, H-6b), 4.45 (m, 2H, H-6″a and −6″b), 4.49 (d, 1H, $J_{1,2} = 7.9$ Hz, H-1), 4.52 (d, 1H, $J_{1',2'} = 7.7$ Hz, H-1′), 4.74 (dd, 1H, $J_{3',4'} = 2.4$ Hz, H-3′), 4.89 (dd, 1H, $J_{2,3} = 9.3$ Hz, H-2), 4.99 (d, 1H, $J_{1'',2''} = 3.6$ Hz, H-1″), 5.07 (m, 2H, $=CH_2$), 5.11 (dd, 1H, $J_{2',3'} = 10.8$ Hz, H-2′), 5.18 (dd, 1H, $J_{2'',3''} = 11.2$ Hz, H-2″), 5.20 (t, 1H, $J_{3,4} = 9.5$ Hz, H-3), 5.39 (dd, 1H, $J_{3'',4''} = 3.3$ Hz, H-3″), 5.59 (d, 1H, $J_{4'',5''} = \sim 0$ Hz, H-4″), 5.76 (m, 1H, CH=).

Anal. Calcd for $C_{42}H_{58}O_{26}$: C, 51.53; H, 5.97. Found: C, 51.66; H, 5.99.

29: R_f 0.38 [1:2 (v/v) toluene−ethyl acetate]; ^1H NMR δ (400 MHz, $CDCl_3$) 5.70 [d, $^3/_4$H, $J_{1,2} = 8.2$ Hz, H-1(β)], 4.52 [d, $^1/_3$H, $J_{1,2} = 3.7$ Hz, H-1(α)].

Anal. Calcd for $C_{40}H_{54}O_{27}$: C, 49.69; H, 5.63. Found: C, 49.88; H, 5.68.

4-Benzylmercaptobutyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (30). To a stirring solution of olefin **28** (604 mg, 0.617 mmol) and α-toluenethiol (1.45 mL, 12.3 mmol) in 1,4-dioxane (3 mL) at 50 °C was added AIBN (52 mg, 0.309 mmol) under nitrogen atmosphere. The reaction mixture was heated at 80 °C for 1.5 h. When TLC indicated the complete consumption of **28**, cyclohexene (1.25 mL, 12.3 mmol) was added to the mixture at room temperature. The reactant was concentrated and subjected to a column of silica gel with 1:0−1:1 (v/v) toluene−ethyl acetate as the eluent to yield **30** (630 mg, 92.5%) as a colorless syrup: R_f 0.52 [1:2 (v/v) toluene−ethyl acetate]; $[\alpha]_D^{26}$ +34.7° (*c* 0.59, $CHCl_3$); IR (KBr) 2941 (ν_{C-H}), 1747 ($\nu_{C=O}$), 1055 (ν_{C-O-C}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 1.70 (m, 4H, 2CH_2), 1.98, 2.03, 2.04, 2.06, 2.07, 2.07, 2.08, 2.08, 2.10, 2.13, (each s, 30H, 10$COCH_3$), 2.40 (t, 2H, $J = 6.8$ Hz, SCH_2CH_2), 3.6 (m, 2H, OCH_2), 3.62 (ddd, 1H, $J_{5,6a} = 3.2$ Hz and $J_{5,6b}$

= 6.2 Hz, H-5), 3.69 (s, 2H, SCH_2Ph), 3.78 (t, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 3.8 (m, 1H, H-5′), 4.01 (d, 1H, $J_{4',5'}$ = ∼0 Hz, H-4′), 4.1 (m, 4H, H-6a, −6′a, −6′b, and H-5″), 4.43 (dd, 1H, $J_{6a,6b}$ = 11.0 Hz, H-6b), 4.44 (d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.45 (m, 2H, H-6″a and −6″b), 4.51 (d, 1H, $J_{1',2'}$ = 7.7 Hz, H-1′), 4.73 (dd, 1H, $J_{3',4'}$ = 2.5 Hz, H-3′), 4.87 (dd, 1H, $J_{2,3}$ = 9.5 Hz, H-2), 4.99 (d, 1H, $J_{1'',2''}$ = 3.5 Hz, H-1″), 5.10 (dd, 1H, $J_{2',3'}$ = 10.8 Hz, H-2′), 5.18 (dd, 1H, $J_{2'',3''}$ = 11.0 Hz, H-2″), 5.19 (t, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 5.39 (dd, 1H, $J_{3'',4''}$ = 3.3 Hz, H-3″), 5.59 (d, 1H, $J_{4'',5''}$ = ∼0 Hz, H-4″), 7.3 (m, 5H, Ph).

Anal. Calcd for $C_{49}H_{60}O_{26}S_1$: C, 53.35; H, 6.03. Found: C, 53.40; H, 6.00.

4-Benzylmercaptobutyl *O*-(α-D-Galactopyranosyl)-(1→4)-*O*-(*β*-D-galactopyranosyl)-(1→4)-*β*-D-glucopyranoside (31). NaOMe (28 mg, 0.52 mmol) was added to a stirring solution of acetate **30** (574 mg, 0.520 mmol) in MeOH (10 mL) at room temperature under nitrogen atmosphere. After 3.5 h at room temperature, the solution was neutralized by adding Dowex 50W X-8 (H^+) resin, and the suspension was filtered. The filtrate was evaporated to afford quantitative yield of **31** as hard colorless syrup: R_f 0.46 [50:25:3 (v/v/v) $CHCl_3$−MeOH−H_2O]; $[\alpha]_D^{27}$ +38.8° (*c* 1.02, MeOH); IR (KBr) 3400 (ν_{O-H}), 2926 (ν_{C-H}), 1075 (ν_{C-O-C}) cm^{-1}; ^{1}H NMR δ (400 MHz, D_2O) 1.46 (m, 4H, 2CH_2), 2.25 (br s, 2H, SC$H_2$$CH_2$), 4.29 (d, 1H, $J_{1,2}$ = 6.1 Hz, H-1), 4.46 (d, 1H, $J_{1',2'}$ = 6.7 Hz, H-1′), 4.91 (br s, 1H, H-1″), 7.1 (m, 5H, Ph); ^{13}C NMR δ (100.6 MHz, D_2O) 25.23 (CH_2), 28.42 (CH_2), 30.90 (CH_2), 35.69 (CH_2), 60.31, 60.49, 60.68, 68.67, 69.05, 69.23, 69.77, 70.95, 71.02, 72.36, 73.01, 74.61, 74.76, 75.49, 77.56, 78.70, 100.44 (C-1″), 102.31 (C-1), 103.35 (C-1′), 127.00 (Ph), 128.58 (Ph), 128.95 (Ph), 138.58 (Ph).

Anal. Calcd for $C_{29}H_{46}O_{16}S_1$·1.5H_2O: C, 49.07; H, 6.96. Found: C, 49.07; H, 6.84.

Carbosilane Compound Carrying Three Globotriaosyl Moieties (1). To a stirred solution of **31** (280 mg, 0.410 mmol) in liq NH_3 (ca. 30 mL) was added Na (94 mg, 4.10 mmol) at −35 °C, and the mixture was stirred for 25 min. The stirred mixture was treated with NH_4Cl (197 mg, 3.69 mmol) for 5 min, and then, a solution of dendrimer **5** (32 mg, 68.4 μmol) in 1,2-dimethoxyethane (2 mL) was added dropwise to the mixture. The reaction mixture was stirred overnight and then evaporated to dryness. The residue was diluted with 5% aq AcOH and purified by Sephadex G-25 with 5% aq AcOH as an eluent to give homogeneous **1** (120 mg, 87.6%) as white powder after lyophilization: R_f 0.26 [3:5:1 (v/v/v) $CHCl_3$−MeOH−H_2O]; IR (KBr) 3391 (ν_{O-H}), 2922 (ν_{C-H}), 1426 (ν_{Si-C}), 1075 (ν_{C-O-C}), 702 (ν_{Si-C}) cm^{-1}; ^{1}H NMR δ (400 MHz, D_2O) 0.83 (br s, 6H, 3$SiCH_2$), 1.6 (m, 18H, 9CH_2), 2.45 (br s, 12H, 6SC$H_2$$CH_2$), 4.31 (t, 3H, *J* = 6.3 Hz), 4.37 (d, 3H, $J_{1,2}$ = 7.1 Hz, H-1), 4.48 (d, 3H, $J_{1',2'}$ = 7.1 Hz, H-1′), 4.91 (d, 3H, $J_{1'',2''}$ = 3.3 Hz, H-1″), 7.3 (m, 5H, Ph); ^{13}C NMR δ (100.6 MHz, D_2O) 11.71 ($SiCH_2$), 24.05 (CH_2), 25.97 (CH_2), 28.71 (CH_2), 31.58 (CH_2), 35.55 (CH_2), 60.41, 60.55, 60.71, 68.72, 69.09, 69.29, 69.94, 71.04, 71.04, 72.39, 73.11, 74.68, 74.91, 75.58, 77.56, 78.72, 100.47 (C-1″), 102.44 (C-1), 103.40 (C-1′), 128.20 (Ph), 134.21 (Ph), 136.73 (Ph); FAB MS Calcd for [M + H^+]: 2005.75. Found: *m*/*z* 2005.64.

The gel filtration also gave a mixture of mercaptan **32** and disulfide **33**, which was acetylated by the usual way to afford thioacetate **34** (42 mg, 9.7% based on **31**) and **35** (20 mg, 4.8% based on **31**), respectively. **32**: R_f 0.55 [1:2 (v/v) toluene−ethyl acetate]; ^{1}H NMR δ (400 MHz, $CDCl_3$) 1.62 (m, 4H, 2CH_2), 1.98, 2.04, 2.04, 2.06, 2.06, 2.07, 2.07, 2.08, 2.11, 2.13, (each s, 30H, 10$COCH_3$), 2.32 (s, 3H, $SCOCH_3$), 2.86 (t, 2H, *J* = 6.5 Hz, SC$H_2$$CH_2$), 3.62 (ddd, 1H, $J_{5,6a}$ = 3.7 Hz and $J_{5,6b}$ = 6.2 Hz, H-5), 3.67 (m, 2H, OCH_2), 3.76 (t, 1H, $J_{5',6'a}$ = $J_{5',6'b}$ = 6.8 Hz, H-5′), 3.79 (t, 1H, $J_{4,5}$ = 9.7 Hz, H-4), 4.01 (d, 1H, $J_{4',5'}$ = ∼0 Hz, H-4′), 4.1 (m, 4H, H-6a, −6′a, −6′b, and H-5″), 4.43 (dd, 1H, $J_{6a,6b}$ = 11.0 Hz, H-6b), 4.46 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 4.47 (m, 2H, H-6″a and −6″b), 4.52 (d, 1H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.73 (dd, 1H, $J_{3',4'}$ = 2.2 Hz, H-3′), 4.87 (t, 1H, $J_{2,3}$ = 8.9 Hz, H-2), 4.98 (d, 1H, $J_{1'',2''}$ = 3.5 Hz, H-1″), 5.10 (dd, 1H, $J_{2',3'}$ = 10.7 Hz, H-2′), 5.19 (dd, 1H, $J_{2'',3''}$ = 11.0 Hz, H-2″), 5.20 (t, 1H, $J_{3,4}$ = 9.6 Hz, H-3), 5.39 (dd, 1H, $J_{3'',4''}$ = 3.2 Hz, H-3″), 5.58 (d, 1H, $J_{4'',5''}$ = ∼0 Hz, H-4″).

33: R_f 0.27 [1:2 (v/v) toluene−ethyl acetate]; ^{1}H NMR δ (400 MHz, $CDCl_3$) 1.67 (m, 8H, 4CH_2), 1.98, 2.04, 2.04, 2.06, 2.06, 2.07, 2.08, 2.08, 2.12, 2.13, (each s, 60H, 20$COCH_3$), 2.66 (t, 4H, *J* = 6.8 Hz, 2SC$H_2$$CH_2$), 3.62 (ddd, 2H, $J_{5,6a}$ = 3.2 Hz and $J_{5,6b}$ = 6.2 Hz, H-5), 3.67 (m, 4H, 2 OCH_2), 3.76 (t, 2H, $J_{5',6'a}$ = $J_{5',6'b}$ = 6.8 Hz, H-5′), 3.79 (t, 2H, $J_{4,5}$ = 9.7 Hz, H-4), 4.01 (d, 2H, $J_{4',5'}$ = ∼0 Hz, H-4′), 4.1 (m, 6H, H-6′a, −6′b, and H-5″), 4.14 (dd, 2H, $J_{6a,6b}$ = 11.0 Hz, H-6a), 4.43 (dd, 2H, H-6b), 4.47 (d, 2H, $J_{1,2}$ = 8.1 Hz, H-1), 4.48 (m, 4H, H-6″a and −6″b), 4.52 (d, 2H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.73 (dd, 2H, $J_{3',4'}$ = 2.5 Hz, H-3′), 4.88 (dd, 2H, $J_{2,3}$ = 9.2 Hz, H-2), 4.99 (d, 2H, $J_{1'',2''}$ = 3.6 Hz, H-1″), 5.10 (dd, 2H, $J_{2',3'}$ = 10.8 Hz, H-2′), 5.18 (dd, 2H, $J_{2'',3''}$ = 11.1 Hz, H-2″), 5.20 (t, 2H, $J_{3,4}$ = 9.5 Hz, H-3), 5.39 (dd, 2H, $J_{3'',4''}$ = 3.3 Hz, H-3″), 5.58 (d, 2H, $J_{4'',5''}$ = ∼0 Hz, H-4″); FAB MS Calcd for [M + H^+]: 2023.61. Found: *m*/*z* 2023.46.

Carbosilane Dendrimer Carrying Nine Globotriaosyl Moieties (2). A mixture of **31** (174 mg, 0.255 mmol), Na (59 mg, 2.55 mmol) in liq NH_3 (ca. 30 mL) was stirred for 25 min at −35 °C. After adding NH_4Cl (123 mg portionwise, 2.29 mmol), a dendrimer **8** (20 mg, 14.1 μmol) in 1,2-dimethoxyethane (2 mL) was injected dropwise to the stirred mixture, and the stirring was continued overnight and evaporated for removal of liq NH_3. Chromatographic purification by Sephadex G-25 eluting with 5% aq AcOH gave pure **2** (31 mg, 36.5%) as syrup, which was lyophilized from water to afford white powder of **2**: R_f 0.47 [7:14:6 (v/v/v) $CHCl_3$−MeOH−H_2O]; IR (KBr) 3393 (ν_{O-H}), 2915 (ν_{C-H}), 1419 (ν_{Si-C}), 1073 (ν_{C-O-C}), 707 (ν_{Si-C}) cm^{-1}; ^{1}H NMR δ (400 MHz, D_2O) 0.62 (br m, 30H, 15$SiCH_2$), 2.55 (br s, 36H, 18SC$H_2$$CH_2$), 4.41 (d, 9H, $J_{1,2}$ = 6.4 Hz, H-1), 4.48 (d, 9H, $J_{1',2'}$ = 7.0 Hz, H-1′), 4.91 (d, 9H, $J_{1'',2''}$ = 3.2 Hz, H-1″), 7.3 (br m, 5H, Ph); ^{13}C NMR δ (100.6 MHz, D_2O) 12.11 ($SiCH_2$; G1), 17.74 (CH_2; G0), 18.94 (CH_2; G0), 21.07 (CH_2; G0), 24.51 (CH_2), 26.12 (CH_2), 28.89 (CH_2), 31.84 (CH_2), 35.88 (CH_2), 60.42, 60.65, 60.77, 68.71, 69.05, 69.27, 69.51, 70.05, 71.14, 72.46, 73.26, 74.81, 75.01, 75.68, 77.60, 78.78, 100.55 (C-1″), 102.54 (C-1), 103.48 (C-1′); FAB MS Calcd for [M + H^+]: 6019.3. Found: *m*/*z* 6019.7.

The gel filtration also gave a mixture of mercaptan **32** and disulfide **33** after eluting **2**, which was acetylated by the usual way to afford thioacetate **34** (54 mg, 20.1% based on **31**) and **35** (41 mg, 15.9% based on **31**), respectively.

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