Carbosilane Dendrimers Bearing Globotriaoses: Construction of a Series of Carbosilane Dendrimers Bearing Globotriaoses†

Koji Matsuoka,*,‡ Mikiko Terabatake,‡ Yasuaki Esumi,§ Ken Hatano,‡ Daiyo Terunuma,‡ and Hiroyoshi Kuzuhara‡

Department of Functional Materials Science, Faculty of Engineering, Saitama University, Sakura, Saitama 338-8570, Japan, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-0198, Japan

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To enhance biological activities on the basis of the sugar cluster effect, a series of carbosilane dendrimers as core scaffolds for the construction of glycodendrimers was systematically synthesized from appropriate chlorosilanes by a combination of alkenylation and hydrosylation reactions. Those carbosilane dendrimers having terminal C═C double bonds underwent general hydroboration reactions to give corresponding primary polyols. Further transformations of the alcohols were then performed by mesylation followed by a displacement with NaBr to provide corresponding dendrimers with 4 to 36 bromine atoms at each terminal end. Assembly of trisaccharide moieties of globotriaosyl ceramide using alkyl halide-type carbosilane dendrimers as the core frame was conducted in liquid ammonia by a one-pot reaction involving selective removal of a benzyl group under the Birch reduction condition and subsequent S_N2 reaction to yield a series of carbosilane dendrimers having appropriate numbers of trisaccharide moieties. These dendrimers have unique shapes and adequate numbers of terminal trisaccharide moieties. Some of the dendrimers showed unique biological activity against Stxs, which were produced by pathogenic *Escherichia coli* O157:H7.

Introduction

The sugar clustering effect, first reported by Lee,[1] is a significant phenomenon for enhancing a weak binding affinity between a carbohydrate and sugar-binding proteins. Plenty of effort has gone into elucidating such interactions using neoglycoproteins as well as neoglycoconjugates, which are artificial compounds derived from natural carbohydrates and other substances.[2] Lectins are a family of sugar-binding proteins and generally have more than two sugar-binding sites.[3] Therefore, lectins are suitable model ligands for investigation of the sugar clustering effect.[4] Shiga toxins (Stxs) are produced by enterohemorrhagic *E. coli* O157:H7[5] and belong to a bacterial AB_5 toxin family in which the A subunit has strong toxigenic activity and B subunits are composed of 5 B subunit monomers through a noncovalent bond and have lectin activity.[6] Since a monomeric B subunit has 3 carbohydrate binding sites, the total number of carbohydrate binding sites of the toxin is 15.[7] The binding site of the B subunit specifically recognizes a trisaccharide moiety of a globotriaosyl ceramide (Gb_3; Galα1→4Galβ1→4Glcβ1→Cer).[8] Therefore, to effectively neutralize the toxin activity, synthetic receptors having various numbers of globotriaosyl moieties for neutralization of Stxs have been prepared and shown biological activity.[9] Successful syntheses and biological activities have been reported; however, no therapeutic reagent having complete neutralization potency for Stxs in vivo is available. Our synthetic approach to create a toxin blocker has been reported,[10] and the toxin blocker has been shown to have effective biological activity.[11] The carbosilane dendrimer seemed to be an attractive substance for manufacturing a therapeutic reagent, because the carbosilane dendrimer has various advantages such as (1) simplicity of the synthetic process to extend the generation, (2) accessibility to a polymer with adequate molecular weight and adequate number of terminal functions, (3) neutral nature in contrast to polyamine-type dendrimers, (4) chemical and biochemical stability and (5) biological inertness.[12] Furthermore, synthesis of a series of carbosilane dendrimers functionalized with globotriaosyl moieties would give us information on the structure−activity relationship (SAR) of carbosilane dendrimers having globotriaosyl moieties against Stxs. In our previous work, we prepared carbosilane dendrimers having a fan shape in which the terminal ends are uniformly functionalized with three **1** and nine **2** globotriaosyl moieties. Those dendrimers were referred to as SUPER TWIG-Fan(0)3 and SUPER TWIG-Fan(1)9 (Figure 1). In this paper, we describe in detail the systematic synthesis of a series of carbosilane dendrimers having attractive molecular shapes (ball-shape and dumbbell-shape) and the introduction of an appropriate number of globotriaosyl residues into the carbosilane dendrimers to afford corresponding dendrimers uniformly functionalized with carbohydrate moieties **3**−**8**.

Results and Discussion

To develop a series of carbosilane dendrimers with appropriate numbers of trisaccharidic residues, the synthesis of carbosilane dendrimers used for the core frame to support the sugar moiety is first described. Results of incorporation of a globotriaosyl moiety into the carbosilane dendrimers are then presented.

Systematic Synthesis of Ball-Shaped Dendrimers. The synthetic route to obtain a series of ball-shaped dendrimers is summarized in Scheme 1. A known tetraallylsilane **9**[12] was a

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* To whom correspondence should be addressed. E-mail: koji@fms.saitama-u.ac.jp. Fax: +81−48−858−3099.

‡ Saitama University.

§ RIKEN.

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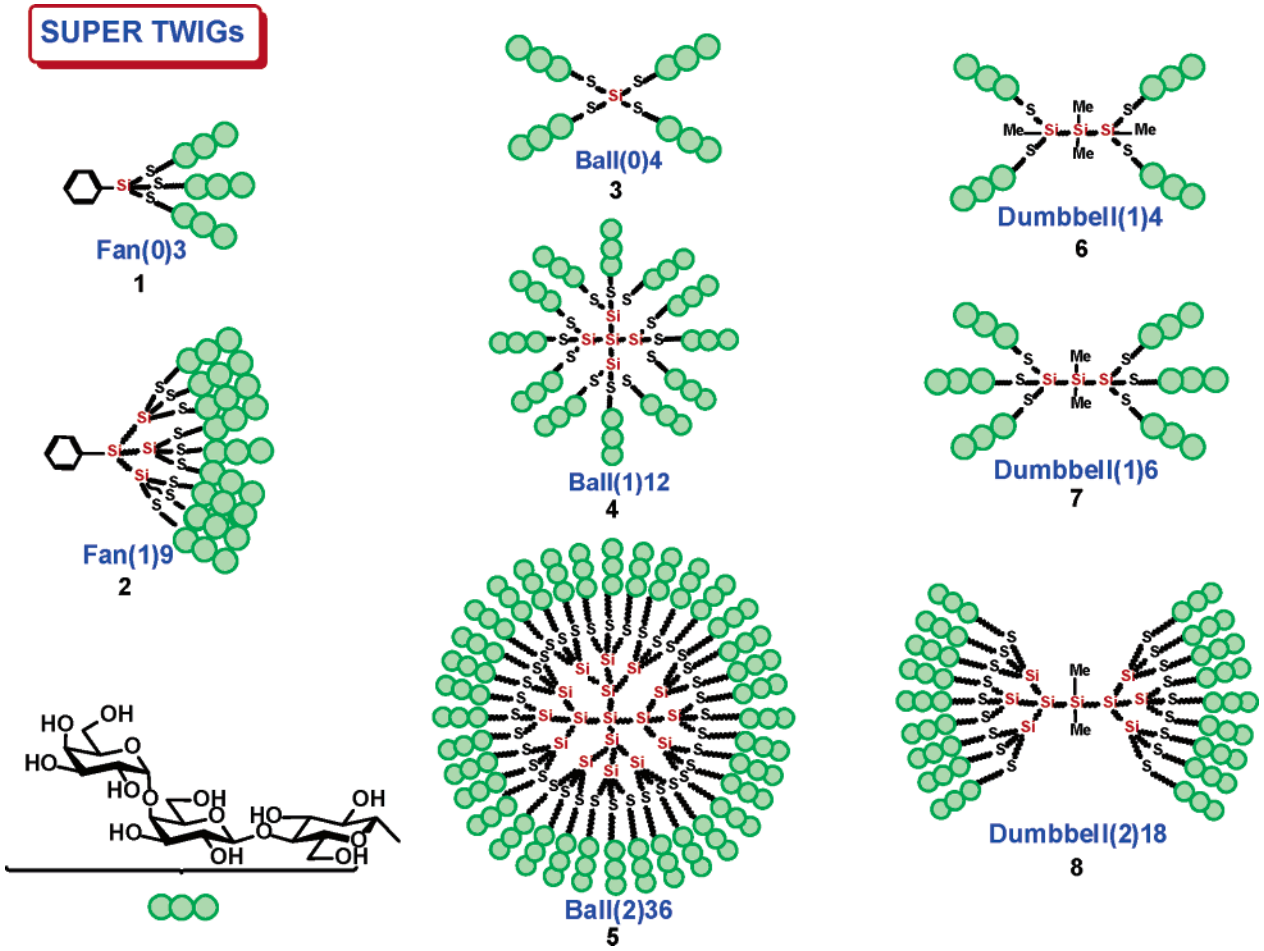
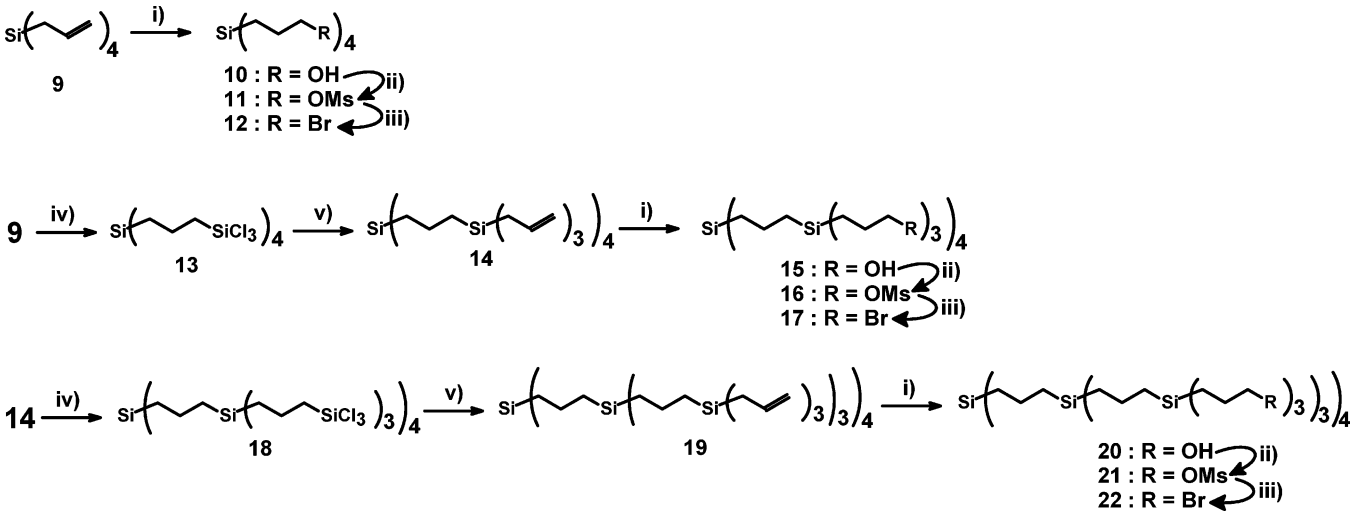


Figure 1. A series of carbosilane dendrimers uniformly functionalized with trisaccharide moieties of globotriaosy ceramide.

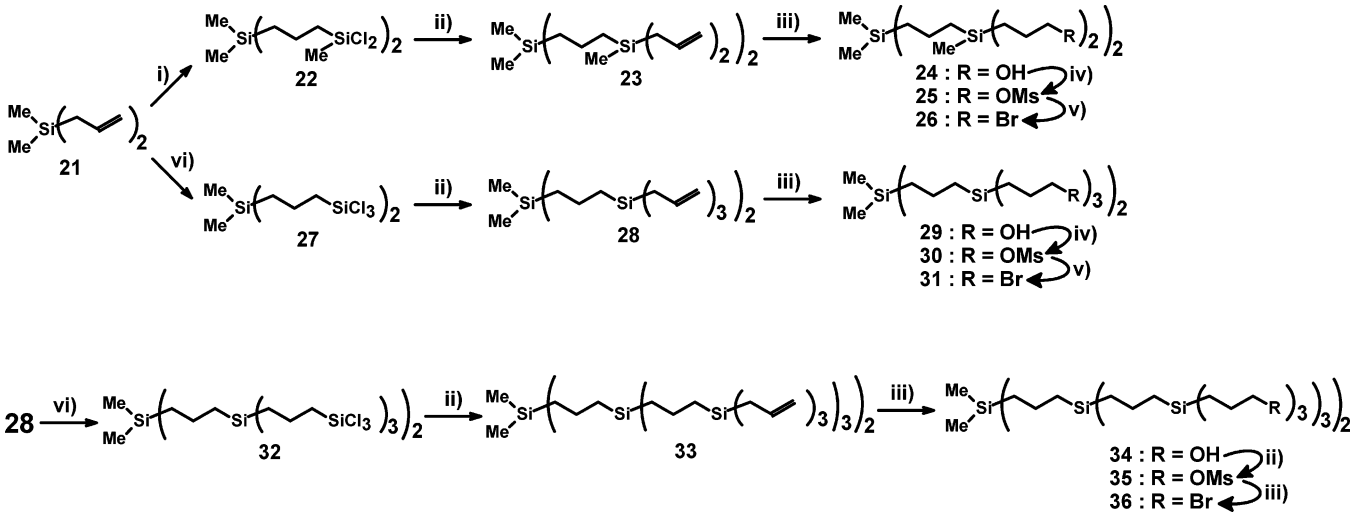
Scheme 1[a]



[a] Reagents and conditions: (i) ref 14 for **10** and **20**, cyclohexyl brane, then $NaOH-H_2O_2$, 0 °C; (ii) MsCl, Pyr, 0 °C for **11**, −40 °C for **16** and **21**; (iii) NaBr, DMF, 80 °C; (iv) Speier's catalyst, $HSiCl_3$; (v) $CH_2{=}CH_2CH_2MgBr$, absolute ether.

common intermediate for the synthesis of ball-shaped dendrimers. Thus, alkene **9** was converted into alcohols by the method previously reported[13] to give tetraol **10**, which was further modified via mesylate **11** to afford corresponding alkyl bromide **12** with four bromine atoms at each terminal end. Chemical elongation of the carbosilane dendrimer **9** was accomplished by a two-step reaction. Thus, hydrosylation of trichlorosilane to the alkene **9** in the presence of Speier's catalyst[12] was carried out to yield corresponding chloride **13**, which was treated with a suitable amount of allylmagnesium bromide to provide **14** with twelve alkenyl functional groups.[14] The terminal double bonds of the alkene **14** were efficiently converted into primary alcohols by the hydroboration reaction involving anti-Markovnikov fashion to give crystalline **15** in good yield. The treatment of the alcohol **15** with methane sulfonyl chloride quantitatively gave mesylate **16**, which underwent an S_N2 replacement using a large amount of sodium bromide to afford dendritic bromide **17** with twelve terminal ends. Hydrosylation

Scheme 2[a]



[a] Reagents and conditions: (i) Speier's catalyst, $HSiMeCl_2$; (ii) $CH_2{=}CH_2CH_2MgBr$, absolute ether; (iii) cyclohexyl brane then $NaOH-H_2O_2$, 0 °C; (vi) MsCl, Pyr, −40 °C; (v) NaBr, DMF, 80 °C; (iv) Speier's catalyst, $HSiCl_3$.

and alkenylation of the dendritic alkene **14** were performed similarly to those for **9** and **14** to give **19** via mesylate **18** as an intermediate of this reaction sequence. The alkene **19** was converted into known alcohol **20**,[14] which was converted into corresponding bromide **22** in a similar way.

Systematic Synthesis of Dumbbell-Shaped Dendrimers. Since a series of ball-shaped dendrimers was successfully prepared, our attention was then focused on the synthesis of a series of dumbbell-shaped dendrimers. The synthetic pathway for the construction of carbosilane dendrimers having dumbbell shapes is summarized in Scheme 2. The basic strategy for the preparation of dumbbell-shaped dendrimers was similar to that for ball-shaped dendrimers. Thus, a commercially available diallyldimethylsilane **23** was treated with dichloromethylsilane in the presence of a platinum catalyst to give chlorosilane **24** in quantitative yield after removal of unreacted reagent and solvent. Grignard reaction of **24** and allylmagnesium bromide gave alkenyl silane **25** in moderate yield. Tetraallyl functions were completely transformed into primary alcohols by the hydroboration reaction to afford **26** in good yield. A mesylation of the hydroxyl groups of **26** proceeded smoothly to give mesylate **27**, which was used for the next step without chromatographic purification. Bromo anion substitution to **27** gave alkyl bromide **28** in high yield. On the other hand, hexabromide **33** was similarly synthesized from **23** as the same starting material. The reaction of hydrosylation to **23** using trichlorosilane instead of dichloromethylsilane proceeded similarly as described for **24** to give hexachlorosilane **29**, which was treated with Grignard reagent to give hexaallyl silane **30** in good yield. The addition of a borane to the alkene **30** followed by oxidative treatment gave alcohol **31**, which was converted into bromide **33** through mesylate **32**.

Since the preparation of alkyl bromides **28** and **33** as first-generation compounds was accomplished, we tried to prepare a second-generation dendrimer using alkene **30** as the key intermediate. Thus, hydrosylation of **30** using trichlorosilane gave corresponding chloride **34**, which was further treated with allylmagnesium bromide to afford alkenyl silane **35** with 18 functional terminal ends. Further chemical manipulation to obtain alkyl bromide **38** was performed on **35** by means of the same protocol as that used for the preparation of **33**. Thus, the alcohol **36** was derived from the alkene **35** and converted into corresponding mesylate **37**, in which mesyloxy groups were completely displaced by bromo atoms to yield carbosilane dendrimer **38**.

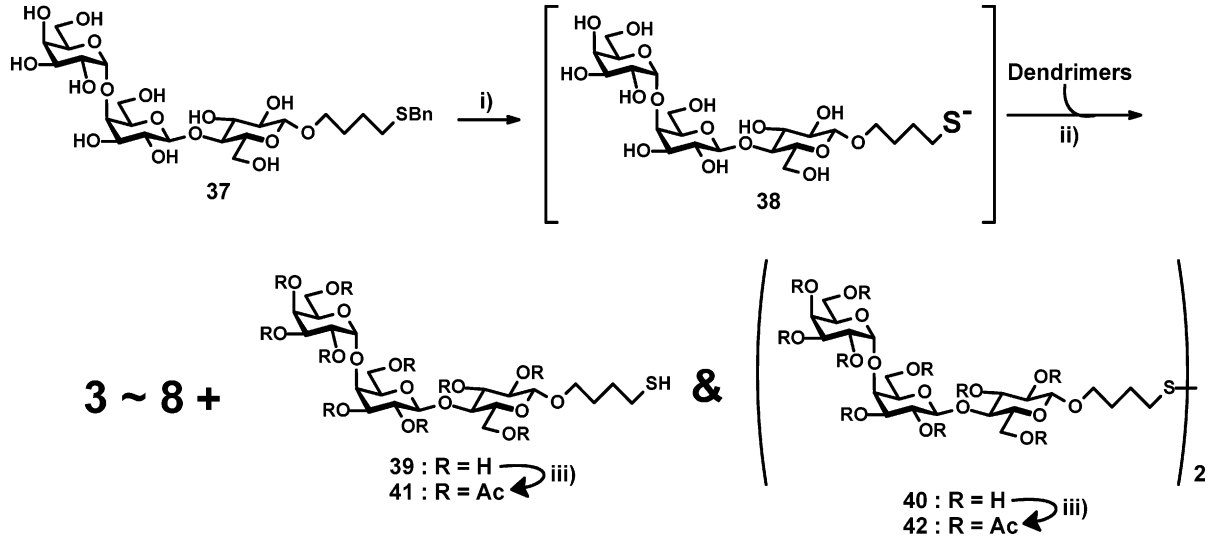
Assembly of Globotriaosyl Derivatives Using a Series of Carbosilane Dendrimer Scaffolds. Given the success of the preparation of a series of carbosilane dendrimer scaffolds having appropriate alkyl bromide functionalities, we next turned our attention to the coupling reaction of the dendrimer scaffolds and globotriaosyl derivative **39**.[15] The synthetic approach for construction of glycodendrimers **3**−**8** is shown in Scheme 3, where the thiol derivative **41** and the disulfide **42** are also shown as byproducts. Removal of benzyl group of sulfide **39** under the Birch reduction condition gave corresponding thiolate **40**, which was directly reacted with alkyl bromide-type dendrimers to afford carbosilane dendrimers having appropriate numbers of globotriaosyl moieties. The results of the one-pot coupling reaction are summarized in Table 1. Furthermore, in the coupling reaction, thiol **41** and the disulfide **42** were also obtained, and both globotriaosyl derivatives were converted into their complete acetate in the usual manner to provide **43** and **44**, respectively. The synthesis of fan-shaped dendrimers **1** and **2** was reported in detail previously.[15] The coupling reactions using carbosilane dendrimers having G0 and G1 proceeded effectively to give corresponding glycodendrimers with appropriate molecular ion peaks after purification by suitable gel filtration. When G2 carbosilane dendrimers **22** and **38** as the core frames were subjected to this reaction, a threefold greater amount of **39** was needed.

In conclusion, we have succeeded in the synthesis of a series of carbosilane dendrimers uniformly functionalized with globotriaosyl moieties. Biological responses using this library against Stxs have been reported elsewhere, and the result of the biological investigation suggested SARs in the generation and the shape of the carbosilane dendrimers were observed.[11a,d]

Experimental Section

Materials and Methods. Unless otherwise stated, all commercially available solvents and reagents were used without further purification. Pyridine, dimethylformamide (DMF), and 1,4-dioxane were stored over molecular sieves (MS4Å), and methanol (MeOH) was stored over MS3Å before use. Tetrahydrofuran (THF) was used after distillation in the presence of lithium aluminum hydride. Diallyldimethylsilane **23**, dichloromethylsilane, and trichlorosilane was purchased from Tokyo

Scheme 3[a]



[a] Reagents and conditions: (i) Na, liquid NH_3, −35 °C; (ii) NH_4Cl, then alkyl bromide-type dendrimers in $MeOCH_2CH_2OMe$.

Table 1. Results of Assembly of Globotoriaose Using Carbosilane Dendrimers

dendrimer	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
M_w (Da)	2006	6019	2563	7913	23 964	2763	4001	12 026
generation	G0	G1	G0	G1	G2	G1	G1	G2
end groups	3	9	4	12	36	4	6	18
charge ratio SBn/Br	2:1	2:1	2:1	2:1	3:1	2:1	2:1	3:1
gel used for purification	G-25	G-50	G-25	G-50	G-75 & −50	G-25	G-50	G-50 & −25
yield (%)	87.6	36.5	88.0	36.4	45.4	49.4	50.0	24.7
43[a] (%)	9.7	20.1	17.1	30.4	69.8	6.4	38.5	60.4
44[a] (%)	4.8	15.9	12.4	12.8	8.3	4.0	13.2	8.8

[a] Based on carbohydrate amount used for the one-pot reaction.

Kasei Co., Ltd. (Tokyo, Japan). 1 M allylmagnesium bromide in THF was purchased from Sigma-Aldrich Co. (Milwaukee, WI). 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 spectra (FAB MS) were recorded with a JEOL JMS−HX110 spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF-MS) were obtained using Perseptive Biosystems Voyager Elite 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 aq 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). Flash 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.

Tetrakis(3-bromopropyl)silane (12). A mixture of tetrakis[3-(methylsulfonyloxy)propyl]silane[13] **11** (432 mg, 0.749 mmol) and NaBr (1.54 g, 15.0 mmol) in DMF (5 mL) was stirred for 3 h at 80 °C under nitrogen atmosphere. After removal of DMF by evaporation, toluene and water were added to the residue, and the mixture was partitioned. The organic layer was successively washed with water, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Silica gel chromatography of the residue with 1:0−20:1 (v/v) *n*-hexane−ethyl acetate gave pure **12** (286 mg, 74.1%) as colorless syrup: R_f 0.49 [10:1 (v/v) *n*-hexane−ethyl acetate]; IR (neat) 2927 (ν_{C-H}), 1431 (ν_{Si-C}), 1238 (ν_{C-Br}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) 0.70 (m, 8H, $4SiCH_2$), 1.84 (m, 8H, $4SiCH_2CH_2$), 3.40 (t, 8H, J = 6.8 Hz, $4CH_2Br$); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) 11.15 ($SiCH_2$), 27.40 (CH_2), 36.80 (CH_2Br).

Tetrakis[tris(3-hydroxypropyl)silylpropyl]silane (15).[14] To a solution of 1 M BH_3−THF (33.7 mL) was added a solution of cyclohexene (3.42 mL, 33.7 mmol) in THF (10 mL) at 0 °C under argon atmosphere, and the reaction mixture was stirred for 1 h at 0 °C. Tetrakis(tetraallylsilylpropyl)silane **14**[12] (3.00 g, 3.74 mmol) was dropwise added to the mixture at 0 °C. The mixture was stirred for 3 h at room temperature, then at 0 °C. To the cooled mixture was added MeOH (6 mL), then 3 M aq NaOH (33.7 mL). After addition of 30% H_2O_2 (14 mL, 121 mmol), the reaction mixture was stirred at reflux temperature of THF (ca. 70 °C) for 1 h. The reaction mixture was washed with saturated aqueous NaCl. The aqueous solution was back-extracted with THF. The organic layer was combined and treated with $FeSO_4$ to remove peroxide. After removal of insoluble mass by a simple filtration, the filtrate was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residual syrup was diluted with 1:2 (v/v) mixture of THF−MeOH and purified by reprecipitation from EtOAc. Further purification was carried out by means of Sephadex LH-20 to provide pure polyol **15** (2.84 g, 74.6%), which crystallized itself: mp 83−84 °C; R_f 0.48 [50:25:3 (v/v/v) $CHCl_3$−MeOH−H_2O]; IR (KBr) 3337 (ν_{O-H}), 2910 (ν_{C-H}),

1418 (ν_{Si-C}), 720 (ν_{Si-C}) cm^{-1}; ^{1}H NMR δ (400 MHz, CD_3OD) 0.58 (m, 40H, 20$SiCH_2$), 1.39 [m, 8H, 4$SiCH_2CH_2$ (G0)], 1.54 [m, 24H, 12$SiCH_2CH_2$ (G1)], 3.49 (t, 24H, J = 6.7 Hz, 12CH_2OD); ^{13}C NMR δ (100.6 MHz, CD_3OD) 9.10 [$SiCH_2$ (G1)], 18.39 [CH_2 (G0)], 18.71 [CH_2 (G0)], 19.79 [CH_2 (G0)], 28.03 [$SiCH_2CH_2$ (G1)], 66.00 (CH_2OD).

Anal. Calcd for $C_{48}H_{108}O_{12}Si_5$: C, 56.64; H, 10.69. Found: C, 56.51; H, 10.85.

Tetrakis[tris(3-methylsulfonyloxypropyl)silylpropyl]silane (16). Methanesulfonyl chloride (0.35 mL, 4.53 mmol) was added dropwise to a solution of alcohol **15** (128 mg, 0.126 mmol) in pyridine (3 mL) at −40 °C under nitrogen atmosphere with stirring, and the stirring was continued for 2 h at −40 °C. To the mixture was added water (10 mL) and $CHCl_3$ (50 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 **16** (236 mg, 95.9%) as colorless syrup, which was directly used for the next step without further purification: R_f 0.42 [10:1 (v/v) $CHCl_3$−MeOH]; IR (neat) 2916 (ν_{C-H}), 1416 (ν_{Si-C}), 1337 ($\nu_{O=S=O}$), 1173 ($\nu_{O=S=O}$), 718 (ν_{Si-C}) cm^{-1}; ^{1}H NMR δ (400 MHz, $CDCl_3$) 0.63 (m, 40H, 20$SiCH_2$), 1.30 [m, 8H, 4$SiCH_2CH_2$ (G0)], 1.74 [m, 24H, 12$SiCH_2CH_2$ (G1)], 3.02 (s, 36H, 12CH_3), 4.18 (t, 24H, J = 6.5 Hz, 12CH_2OMs); ^{13}C NMR δ (100.6 MHz, CD_3OD) 7.51 [$SiCH_2$ (G1)], 16.76 [CH_2 (G0)], 17.34 [CH_2 (G0)], 18.28 [CH_2 (G0)], 23.73 [$SiCH_2CH_2$ (G1)], 37.20 (CH_3), 72.48 (CH_2OMs).

Tetrakis[tris(3-bromopropyl)silylpropyl]silane (17). Mesylate **16** (163 mg, 83.4 μmol) was treated with NaBr (0.51 g, 5.00 mmol) in DMF (5 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 $MgSO_4$, filtered, and concentrated in vacuo. Chromatographic purification of the residual syrup by silica gel with 6:1 (v/v) *n*-hexane−ethyl acetate as the eluent to give **17** (101 mg, 68.2%) as colorless syrup: R_f 0.65 [4:1 (v/v) *n*-hexane−ethyl acetate]; IR (neat) 2910 (ν_{C-H}), 1431 (ν_{Si-C}), 1238 (ν_{C-Br}), 727 (ν_{Si-C}) cm^{-1}; ^{1}H NMR δ (400 MHz, $CDCl_3$) 0.64 (m, 40H, 20$SiCH_2$), 1.32 [m, 8H, 4 $SiCH_2$ (G0)], 1.84 [m, 24H, 12$SiCH_2CH_2$ (G1)], 3.40 (t, 24H, J = 6.8 Hz, 12CH_2Br); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) 11.40 [$SiCH_2$ (G1)], 17.08 [CH_2 (G0)], 17.41 [CH_2 (G0)], 18.35 [CH_2 (G0)], 27.65 [$SiCH_2CH_2$ (G1)], 37.10 (CH_2Br).

Anal. Calcd for $C_{48}H_{96}Br_{12}Si_5$: C, 32.53; H, 5.46. Found: C, 32.78; H, 5.47.

Tetrakis{tris[tris(3-methylsulfonyloxypropyl)silylpropyl]silylpropyl}silane (21). This compound was prepared from a known alcohol **20**[14] (2.60 g, 0.793 mmol) in a same manner as that described for **16** to give pure **21** (2.70 g, 55.7%) as colorless syrup: R_f 0.51 [10:1 (v/v) $CHCl_3$−MeOH]; IR (neat) 2914 (ν_{C-H}), 1415 (ν_{Si-C}), 1353 ($\nu_{O=S=O}$), 1173 ($\nu_{O=S=O}$) cm^{-1}; ^{1}H NMR δ (400 MHz, $CDCl_3$) 0.65 (m, 136H, 68$SiCH_2$), 1.29 [m, 32H, 8$SiCH_2CH_2$], 1.75 [m, 72H, 36$SiCH_2CH_2$ (G2)], 3.02 (s, 108H, 36CH_3), 4.17 (t, 72H, J = 6.6 Hz, 36CH_2OMs).

Tetrakis{tris[tris(3-bromopropyl)silylpropyl]silylpropyl}silane (22). Mesylate **21** (114 mg, 18.7 μmol) was treated in same manner as that described for **17** to give **22** (61 mg, 58.7%) as colorless syrup: R_f 0.66 [5:2 (v/v) *n*-hexane−ethyl acetate]; IR (neat) 2910 (ν_{C-H}), 1431 (ν_{Si-C}), 1238 (ν_{C-Br}) cm^{-1}; ^{1}H NMR δ (400 MHz, $CDCl_3$) 0.66 (m, 136H, 68$SiCH_2$), 1.30 [m, 32H, 16$SiCH_2$], 1.85 [m, 72H, 36$SiCH_2CH_2$ (G2)], 3.41 (t, 72H, J = 6.8 Hz, 36CH_2Br); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) 11.47 [$SiCH_2$ (G2)], 17.24 [CH_2 (G1)], 17.52 [CH_2 (G1)], 18.04 [CH_2 (G0)], 18.33 [CH_2 (G0)], 18.49 [CH_2 (G1)], 18.59 [CH_2 (G0)], 27.72 [$SiCH_2CH_2$ (G2)], 37.20 (CH_2Br).

Bis(diallylmethylsilylpropyl)dimethylsilane (25). To a solution of a commercially available diallyldimethylsilane **23** (2.40 mL, 12.5 mmol) in THF (5 mL) in the presence of Speier's catalyst[12] (H_2PtCl_6 in *i*-Pr−OH) was dropwise added a solution of methyldichlorosilane (5.3 mL, 50.0 mml) in THF (5 mL) at 0 °C. The solution was stirred overnight at room temperature, then evaporated to provide chloride **24**, which was dissolved in THF (10 mL). The solution was treated with 1 M allylmagnesium bromide (100 mL, 100 mmol) at 0 °C under nitrogen atmosphere, which was heated at 50 °C. 1 M aq HCl (50 mL) was added to the resulting solution at 0 °C. The organic phase was partitioned, washed with brine (twice), dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was subjected to a column of silica gel with *n*-hexane as the eluent to afford corresponding tetraallyl compound **25** (2.72 g, 55.4%) as colorless syrup: R_f 0.44 (*n*-hexane); IR (neat) 3077 (ν_{C-H}), 2913 (ν_{C-H}), 1630 ($\nu_{C=C}$),1419 (ν_{Si-C}), 1158 (δ_{C-H}) cm^{-1}; ^{1}H NMR δ (400 MHz, $CDCl_3$) −0.05 [s, 6H, 2Me (G0)], −0.01 [s, 6H, 2Me (G1)], 0.55 [m, 4H, 2$SiCH_2$ (G0)], 0.62 [m, 4H, 2$SiCH_2$ (G0)], 1.35 [m, 4H, 2$SiCH_2CH_2$ (G0)], 1.55 [d, 8H, J = 8.2 Hz, 4$SiCH_2$ (G1)], 4.86 (m, 8H, 4CH_2═), 5.78 (m, 4H, 4CH═); ^{13}C NMR δ (100.6 MHz, CD_3OD) −5.76 [Me (G1)], −3.26 [Me (G0)], 17.79 [CH_2 (G0)], 18.17 [CH_2 (G0)], 20.07 [CH_2 (G0)], 21.47 [$SiCH_2$ (G1)], 113.00 (CH_2═), 134.86 (CH═).

Anal. Calcd for $C_{22}H_{44}Si_3$: C, 67.26; H, 11.29. Found: C, 67.32; H, 11.35.

Bis[bis(3-hydroxypropyl)methylsilylpropyl]dimethylsilane (26). This compound was prepared from **25** (206 mg, 0.509 mmol) in a similar manner as that described for **15** to give pure **26** (157 mg, 66.5%) as colorless syrup: R_f 0.33 [7:1 (v/v) $CHCl_3$−MeOH]; IR (neat) 3337 (ν_{O-H}), 2912 (ν_{C-H}), 1415 (ν_{Si-C}) cm^{-1}; ^{1}H NMR δ (400 MHz, DMSO-d_6) −0.09 [s, 6H, 2Me (G1)], −0.08 [s, 6H, 2Me (G0)], 0.41 [m, 8H, 4$SiCH_2$], 0.53 [m, 8H, 4$SiCH_2$], 1.37 [m, 12H, 6$SiCH_2CH_2$], 3.30 [t, 8H, J = 6.6 Hz, 4CH_2O]; ^{13}C NMR δ (100.6 MHz, DMSO-d_6) −4.85 [Me (G1)], −2.83 [Me (G0)], 9.51 [$SiCH_2$ (G1)], 18.22 [2 CH_2 (G0)], 19.79 [CH_2 (G0)], 27.23 [$SiCH_2$ (G1)], 64.10 (CH_2O).

Anal. Calcd for $C_{22}H_{52}O_4Si_3$: C, 56.84; H, 11.27. Found: C, 56.58; H, 11.44.

Bis[bis(3-methylsulfonyloxypropyl)methylsilylpropyl]dimethylsilane (27). This compound was prepared from **26** (90 mg, 19.4 μmol) in a same manner as that described for **16** to give **27** (155 mg, 99%) as colorless syrup, which was directly used for the next step without further purification: R_f 0.62 [10:1 (v/v) $CHCl_3$−MeOH]; IR (neat) 2910 (ν_{C-H}), 1419 (ν_{Si-C}), 1361 ($\nu_{O=S=O}$), 1164 ($\nu_{O=S=O}$) cm^{-1}; ^{1}H NMR δ (400 MHz, $CDCl_3$) −0.10 [s, 6H, 2Me (G1)], −0.05 [s, 6H, 2Me (G0)], 0.52 [m, 16H, 8$SiCH_2$], 1.25 [m, 4H, 2$SiCH_2CH_2$ (G0)], 1.67 [m, 8H, 4$SiCH_2CH_2$ (G1)], 2.96 (s, 12H, 4CH_3), 4.11 [t, 8H, J = 6.7 Hz, 4CH_2O]; ^{13}C NMR δ (100.6 MHz, $CDCl_3$) −5.61 [Me (G1)], −3.39 [Me (G0)], 8.97 [$SiCH_2$ (G1)], 17.86 [CH_2 (G0)], 18.06 [CH_2 (G0)], 19.90 [CH_2 (G0)], 23.67 [$SiCH_2CH_2$ (G1)], 37.14 (CH_3), 72.28 (CH_2O).

Bis[bis(3-bromopropyl)methylsilylpropyl]dimethylsilane (28). This compound was prepared from a mesylate **27** (153 mg, 19.4 μmol) in the same manner as that described for **17** to give pure **28** (120 mg, 86.3%) as colorless syrup: R_f 0.50 [10:1 (v/v) *n*-hexane−ethyl acetate]; IR (neat) 2910 (ν_{C-H}), 1431 (ν_{Si-C}), 1238 (ν_{C-Br}), 710 (ν_{Si-C}) cm^{-1}; ^{1}H NMR δ (400 MHz, $CDCl_3$) −0.05 [s, 6H, 2Me], −0.02 [s, 6H, 2Me], 0.58 [m, 16H, 8$SiCH_2$], 1.31 [m, 4H, 2$SiCH_2CH_2$ (G0)], 1.81 [m, 8H, 4$SiCH_2CH_2$ (G1)], 3.38 [t, 8H, J = 7.0 Hz, 4CH_2O]; ^{13}C NMR δ (100.6 MHz, $CDCl_3$) −5.27 [Me (G1)], −3.22 [Me (G0)], 12.97 [$SiCH_2$ (G1)], 18.19 [CH_2 (G0)], 18.23 [CH_2 (G0)], 20.08 [CH_2 (G0)], 27.80 [$SiCH_2CH_2$ (G1)], 36.98 (CH_2Br).

Anal. Calcd for $C_{22}H_{48}Br_4Si_3$: C, 36.88; H, 6.75. Found: C, 36.96; H, 6.78.

Bis(triallylsilylpropyl)dimethylsilane (30). This compound was prepared from **23** (1.00 g, 7.13 mmol) and trichlorosilane in a similar manner as that described for **25** to give pure **30** (2.47 g, 77.9%) as colorless syrup: R_f 0.46 (*n*-hexane); IR (neat) 3076 (ν_{C-H}), 2914 (ν_{C-H}), 1630 ($\nu_{C=C}$),1417 (ν_{Si-C}), 1159 (δ_{C-H}) cm^{-1}; ^{1}H NMR δ (400 MHz, $CDCl_3$) −0.05 (s, 6H, 2Me), 0.54 [m, 4H, 2$SiCH_2$ (G0)], 0.66 [m, 4H, 2$SiCH_2$ (G0)], 1.36 [m, 4H, 2$SiCH_2CH_2$ (G0)], 1.58 [m, 12H, 6$SiCH_2$ (G1)], 4.88 (m, 12H, 6 CH_2═), 5.79 (m, 12H, 6CH═); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) −3.29 (Me), 16.28 [CH_2 (G0)], 18.08 [CH_2 (G0)], 19.71 [$SiCH_2$ (G1)], 20.16 [CH_2 (G0)], 113.47 (CH_2═), 134.49 (CH═).

Bis[tris(3-hydroxypropyl)silylpropyl]dimethylsilane (31). This compound was prepared from **30** (1.00 g, 2.25 mmol) in a similar manner as that described for **15** to give pure **31** (750 mg, 60.5%) as colorless syrup: R_f 0.55 [4:1 (v/v) $CHCl_3$−MeOH]; IR (neat) 3306

(ν_{O-H}), 2923 (ν_{C-H}), 1414 (ν_{Si-C}), 746 (ν_{Si-C}) cm^{-1}; ^1H NMR δ (400 MHz, D_2O-CD_3OD) −0.08 (s, 6H, 2Me), 0.53 (m, 20H, $10SiCH_2$], 1.34 [m, 4H, $2SiCH_2CH_2$ (G0)], 1.50 [m, 4H, $6SiCH_2CH_2$ (G1)], 3.47 [t, 12H, J = 6.8 Hz, $6CH_2O$]; ^{13}C NMR δ (100.6 MHz, D_2O-CD_3OD) −2.28 (Me), 8.76 [$SiCH_2$ (G1)], 17.97 [CH_2 (G0)], 19.43 [CH_2 (G0)], 21.11 [CH_2 (G0)], 27.42 [$SiCH_2CH_2$ (G1)], 65.74 (CH_2O).

Anal. Calcd for $C_{26}H_{60}O_6Si_3$: C, 56.47; H, 10.94. Found: C, 56.21; H, 11.10.

Bis[tris(3-methylsulfonyloxypropyl)silylpropyl]dimethylsilane (32). This compound was prepared from a polyol **31** (711 mg, 1.29 mmol) in the same manner as that described for **16** to give **32** (1.35 g, 99%) as light yellow syrup, which was directly used for the next step without further purification: R_f 0.49 [10:4:1 (v/v/v) $CHCl_3$−EtOAc−MeOH]; IR (neat) 2910 (ν_{C-H}), 1419 (ν_{Si-C}), 1361 ($\nu_{O=S=O}$), 1164 ($\nu_{O=S=O}$) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) −0.10 [s, 6H, 2Me (G1)], −0.05 [s, 6H, 2Me (G0)], 0.52 [m, 16H, $8SiCH_2$], 1.25 [m, 4H, $2SiCH_2CH_2$ (G0)], 1.67 [m, 8H, $4SiCH_2CH_2$ (G1)], 2.96 (s, 12H, $4CH_3$), 4.11 [t, 8H, J = 6.7 Hz, $4CH_2O$]; ^{13}C NMR δ (100.6 MHz, $CDCl_3$) −5.61 [Me (G1)], −3.39 [Me (G0)], 8.97 [$SiCH_2$ (G1)], 17.86 [CH_2 (G0)], 18.06 [CH_2 (G0)], 19.90 [CH_2 (G0)], 23.67 [$SiCH_2CH_2$ (G1)], 37.14 (CH_3), 72.28 (CH_2O).

Bis[tris(3-bromopropyl)silylpropyl]dimethylsilane (33). This compound was prepared from a mesylate **32** (1.35 g, 1.29 mmol) in the same manner as that described for **17** to give pure **33** (767 mg, 64.2%) as colorless syrup: R_f 0.47 [10:1 (v/v) *n*-hexane−ethyl acetate]; IR (neat) 2910 (ν_{C-H}), 1430 (ν_{Si-C}), 1239 (ν_{C-Br}), 733 (ν_{Si-C}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) −0.04 (s, 6H, 2Me), 0.61 (m, 20H, $10SiCH_2$), 1.31 [m, 4H, $2SiCH_2CH_2$ (G0)], 1.82 [m, 12H, $6SiCH_2CH_2$ (G1)], 3.38 [t, 12H, J = 6.9 Hz, $6CH_2O$]; ^{13}C NMR δ (100.6 MHz, $CDCl_3$) −3.22 (Me), 11.40 [$SiCH_2$ (G1)], 16.75 [CH_2 (G0)], 18.21 [CH_2 (G0)], 20.17 [CH_2 (G0)], 27.64 [$SiCH_2CH_2$ (G1)], 37.00 (CH_2Br).

Anal. Calcd for $C_{26}H_{54}Br_6Si_3$: C, 33.56; H, 5.85. Found: C, 34.29; H, 6.00.

Bis[tris(triallylsilylpropyl)silylpropyl]dimethylsilane (35). This compound was prepared from **30** (1.65 g, 3.70 mmol) and trichlorosilane in a similar manner as that described for **25** to give pure **35** (1.36 g, 27.0%) as colorless syrup: R_f 0.83 [10:1 (v/v) *n*-hexane−ethyl acetate]; ^1H NMR δ (400 MHz, $CDCl_3$) −0.03 (s, 6H, 2Me), 0.56 [m, 20H, $10SiCH_2$ (G0 and G1)], 0.66 [m, 12H, $6SiCH_2$ (G1)], 1.34 [m, 16H, $SiCH_2CH_2$ (G0 and G2)], 1.59 [d, 36H, J = 8.1 Hz, $18SiCH_2$ (G2)], 4.88 (m, 36H, $18CH_2$═), 5.79 (m, 18H, 18CH═); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) −3.29 (Me), 16.59 [CH_2 (G1)], 17.48 [CH_2 (G0)], 17.54 [CH_2 (G1)], 18.26 [CH_2 (G1)], 18.56 [CH_2 (G0)], 19.69 [$SiCH_2$ (G2)], 20.54 [CH_2 (G0)], 113.51 (CH_2═), 134.42 (CH═).

Bis{tris[tris(3-hydroxypropyl)silylpropyl]silylpropyl}dimethylsilane (36). This compound was prepared from **35** (510 mg, 0.458 mmol) in a similar manner as that described for **15** to give pure **36** (506 mg, 83.2%) as white amorphous solid: R_f 0.15 [65:25:4 (v/v) $CHCl_3$−MeOH−H_2O]; IR (neat) 3322 (ν_{O-H}), 2919 (ν_{C-H}), 1420 (ν_{Si-C}) cm^{-1}; ^1H NMR δ (400 MHz, DMSO-d_6) −0.82 (s, 6H, 2Me), −0.18 (m, 64H, $32SiCH_2$), 0.59 [m, 16H, $8SiCH_2CH_2$ (G0 and G1)], 0.75 [m, 36H, $18SiCH_2CH_2$ (G2)], 2.70 [t, 36H, J = 6.7 Hz, $18CH_2O$]; ^{13}C NMR δ (100.6 MHz, DMSO-d_6) −12.14 (Me), −0.30 [$SiCH_2$ (G2)], 9.04 [$SiCH_2$ (G1)], 9.18 [$SiCH_2$ (G0)], 9.37 [CH_2 (G1)], 10.42 [CH_2 (G0 and G1)], 11.94 [$SiCH_2CH_2$ (G0)], 18.62 [$SiCH_2CH_2$ (G2)], 56.59 (CH_2O).

Anal. Calcd for $C_{80}H_{180}O_{18}Si_9 \cdot 1H_2O$: C, 56.49; H, 10.78. Found: C, 56.32; H, 10.90.

Bis{tris[tris(3-methylsulfonyloxypropyl)silylpropyl]silylpropyl}-dimethylsilane (37). This compound was prepared from a polyol **36** (100 mg, 59.4 μmol) in the same manner as that described for **16** to give **37** (158 mg, 85.9%) as syrup, which was directly used for the next step without further purification: R_f 0.51 [10:1 (v/v) $CHCl_3$−MeOH]; IR (neat) 2914 (ν_{C-H}), 1414 (ν_{Si-C}), 1333 ($\nu_{O=S=O}$), 1173 ($\nu_{O=S=O}$) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) −0.11 (s, 6H, 2Me), 0.54 (m, 68H, $34SiCH_2$), 1.20 [m, 16H, $8SiCH_2CH_2$ (G0 and G1)], 1.66 [m, 36H, $18SiCH_2CH_2$ (G2)], 2.94 (s, 54H, $18CH_3$), 4.09 (t, 36H, J = 6.6 Hz, $18CH_2O$); ^{13}C NMR δ (100.6 MHz, $CDCl_3$) −4.4 (Me), 7.26 [$SiCH_2$ (G2)], 16.62 [$SiCH_2$ (G1)], 17.09 [CH_2 (G0)], 17.22 [CH_2 (G1)],18.08 [CH_2 (G1)], 18.19 [CH_2 (G0)], 20.13 [CH_2 (G0)], 23.46 [$SiCH_2CH_2$ (G2)], 36.95 (CH_3), 72.29 (CH_2O).

Bis{tris[tris(3-bromopropyl)silylpropyl]silylpropyl}dimethylsilane (38). This compound was prepared from a mesylate **37** (152 mg, 49.2 μmol) in the same manner as that described for **17** to give pure **38** (50 mg, 36.0%) as colorless syrup: R_f 0.30 [6:1 (v/v) *n*-hexane−ethyl acetate]; IR (neat) 2913 (ν_{C-H}), 1430 (ν_{Si-C}), 1239 (ν_{C-Br}) cm^{-1}; ^1H NMR δ (400 MHz, $CDCl_3$) −0.02 (s, 6H, 2Me), 0.62 (m, 68H, $34SiCH_2$), 1.31 [m, 16H, $8SiCH_2CH_2$ (G0 and G1)], 1.84 [m, 36H, $18SiCH_2CH_2$ (G2)], 3.40 [t, 36H, J = 6.8 Hz, $18CH_2O$]; ^{13}C NMR δ (100.6 MHz, $CDCl_3$) −3.09 (Me), 11.46 [$SiCH_2$ (G2)], 17.13 [$SiCH_2$ (G1)], 17.45 [CH_2 (G0)], 17.56 [CH_2 (G1)],18.42 [CH_2 (G1)], 18.58 [CH_2 (G0)], 20.56 [CH_2 (G0)], 27.70 [$SiCH_2CH_2$ (G2)], 37.09 (CH_2Br).

Anal. Calcd for $C_{80}H_{162}Br_{18}Si_9$: C, 34.13; H, 5.80. Found: C, 34.74; H, 5.83.

Preparation of Carbosilane Compound Carrying Globotriaosyl Moieties (3−8). To a stirred solution of **39**[15] in liq NH_3 was added Na at −35 to −33 °C, and the mixture was stirred for ca. 30 min, giving thiolate anion **40**. The stirred mixture was treated with appropriate amount of NH_4Cl for 5 min, and then, a solution of various dendrimers in 1,2-dimethoxyethane 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, −50, or −75 with 5% aq AcOH as an eluent to give water-soluble carbosilane dendrimers having Gb3 trisaccharide moieties as white powder after lyophilization. The results are summarized in Table 1.

The gel filtration also gave a mixture of mercaptan **41** and disulfide **42**, which was acetylated by the usual way to afford thioacetate **43** and disulfide **44**, respectively.[15]

Ball(0)4 (3). R_f 0.16 [7:12:3 (v/v/v) $CHCl_3$−MeOH−H_2O]; IR (KBr) 3413 (ν_{O-H}), 2920 (ν_{C-H}), 1417 (ν_{Si-C}), 1074 (ν_{C-O-C}) cm^{-1}; ^1H NMR δ (400 MHz, D_2O) 0.70 (br s, 8H, $4SiCH_2$), 1.70 (m, 24H, $12CH_2$), 2.57 (br s, 16H, $8SCH_2CH_2$), 4.31 (t, 4H, J = 6.4 Hz), 4.41 (d, 4H, $J_{1,2}$ = 7.6 Hz, H-1), 4.48 (d, 4H, $J_{1',2'}$ = 7.5 Hz, H-1′), 4.91 (d, 4H, $J_{1'',2''}$ = 3.5 Hz, H-1″); ^{13}C NMR δ (100.6 MHz, D_2O) 11.84 ($SiCH_2$), 24.25 (CH_2), 25.99 (CH_2), 28.70 (CH_2), 31.61 (CH_2), 35.70 (CH_2), 60.38, 60.54, 60.68, 68.72, 69.09, 69.29, 70.01, 71.06, 72.38, 73.11, 74.69, 74.94, 75.59, 77.54, 78.76, 100.47 (C-1″), 102.41 (C-1), 103.42 (C-1′); FAB MS Calcd for [M + H^+]: 2562.96. Found: *m*/*z* 2562.85.

Ball(1)12 (4). IR (KBr) 3382 (ν_{O-H}), 2918 (ν_{C-H}), 1419 (ν_{Si-C}), 1075 (ν_{C-O-C}), 698 (ν_{Si-C}) cm^{-1}; ^1H NMR δ (400 MHz, D_2O) 0.69 (br s, 40H, $20SiCH_2$), 2.58 (br s, 48H, $24SCH_2CH_2$), 4.41 (d, 12H, $J_{1,2}$ = 7.2 Hz, H-1), 4.48 (d, 12H, $J_{1',2'}$ = 7.1 Hz, H-1′), 4.91 (br s, 12H, H-1″); ^{13}C NMR δ (100.6 MHz, D_2O) 10.00 [$SiCH_2$ (G1)], 21.45 [CH_2 (G1)], 24.39 [CH_2 (G1)], 26.03 [CH_2 (G1)], 28.76 [CH_2 (G1)], 31.78 [CH_2 (G1)], 35.86 [SCH_2 (G1)], 60.43, 60.56, 60.72, 68.74, 69.11, 69.31, 71.01, 71.07, 72.42, 73.12, 74.71, 74.95, 75.60, 77.56, 78.77, 100.48 (C-1″), 102.44 (C-1), 103.41 (C-1′); MALDI MS Calcd for [M + H^+]: 7935.0. Found: *m*/*z* 7935.5.

Ball(2)36 (5). IR (KBr) 3402 (ν_{O-H}), 2914 (ν_{C-H}), 1417 (ν_{Si-C}), 1076 (ν_{C-O-C}), 702 (ν_{Si-C}) cm^{-1}; ^1H NMR δ (400 MHz, D_2O) 0.72 (br s, 136H, $68SiCH_2$), 2.61 (br s, 144H, $72SCH_2CH_2$), 4.44 (d, 36H, $J_{1,2}$ = 5.6 Hz, H-1), 4.52 (d, 36H, $J_{1',2'}$ = 6.2 Hz, H-1′), 4.92 (br d, 36H, $J_{1'',2''}$ = ∼2.5 Hz, H-1″); ^{13}C NMR δ (100.6 MHz, D_2O) 12.12 [$SiCH_2$ (G2)],13.53 [CH_2 (G0)], 15.26 [CH_2 (G0)], 18.02 [CH_2 (G0)], 19.05 [CH_2 (G1)], 19.29 [CH_2 (G1)], 23.39 [CH_2 (G1)], 24.44 [CH_2 (G2)], 26.08 [CH_2 (G2)], 28.81 [CH_2 (G2)], 31.84 [CH_2 (G2)], 35.95 [SCH_2 (G2)], 60.43, 60.56, 60.72, 68.74, 69.11, 69.31, 71.01, 71.07, 72.42, 73.12, 74.71, 74.95, 75.60, 77.56, 78.77, 100.48 (C-1″), 102.44 (C-1), 103.41 (C-1′); MALDI TOF MS Calcd for [M + Na^+]: 23986.1. Found: *m*/*z* 23988.2.

Dumbbell(1)4 (6). R_f 0.17 [3:5:1 (v/v/v) $CHCl_3$−MeOH−H_2O]; IR (KBr) 3401 (ν_{O-H}), 2911 (ν_{C-H}), 1419 (ν_{Si-C}), 1073 (ν_{C-O-C}), 705

(ν_{Si-C}) cm^{-1}; ^1H NMR δ (400 MHz, D_2O) 1.00 (br s, 12H, 4Me), 0.67 (br s, 16H, 8$SiCH_2$), 2.58 (br s, 16H, 8SCH_2CH_2), 4.45 (br s, 4H, H-1), 4.52 (d, 4H, $J_{1',2'} = \sim 1$ Hz, H-1′), 4.95 (br s, 4H, H-1″); ^{13}C NMR δ (100.6 MHz, D_2O) −4.43 (Me), −2.31 (Me), 13.50 [$SiCH_2$ (G1)], 18.80 [CH_2 (G0)], 18.80 [CH_2 (G0)], 20.32 [CH_2 (G0)], 24.45 [CH_2 (G1)], 26.92 [CH_2 (G1)], 28.84 [CH_2 (G1)], 31.81 [CH_2 (G1)], 35.87 [SCH_2 (G1)], 60.44, 60.60, 60.74, 68.76, 69.12, 69.34, 71.05, 71.05, 72.42, 73.14, 74.74, 74.96, 75.63, 77.55, 78.71, 100.49 (C-1″), 102.57 (C-1), 103.43 (C-1′); FAB MS Calcd for [M + H^+]: 2764.1. Found: *m*/*z* 2764.1.

Dumbbell(1)6 (7). R_f 0.10 [7:12:4 (v/v/v) $CHCl_3$−MeOH−H_2O]; IR (KBr) 3404 (ν_{O-H}), 2919 (ν_{C-H}), 1416 (ν_{Si-C}), 1076 (ν_{C-O-C}), 703 (ν_{Si-C}) cm^{-1}; ^1H NMR δ (400 MHz, D_2O) −0.04 (br s, 6H, 2Me), 0.7 (m, 20H, 10$SiCH_2$), 2.57 (br s, 24H, 12SCH_2CH_2), 4.41 (d, 6H, $J_{1,2} =$ 6.7 Hz, H-1), 4.48 (d, 6H, $J_{1',2'} = 6.9$ Hz, H-1′), 4.91 (d, 6H, $J_{1'',2''} =$ 3.1 Hz, H-1″); ^{13}C NMR δ (100.6 MHz, D_2O) −2.15 (Me), 12.01 [$SiCH_2$ (G1)],17.54 [CH_2 (G0)], 18.77 [CH_2 (G0)], 20.38 [CH_2 (G0)], 24.36 [CH_2 (G1)], 26.07 [CH_2 (G1)], 28.78 [CH_2 (G1)], 31.77 [CH_2 (G1)], 35.86 [SCH_2 (G1)], 60.45, 60.57, 60.71, 68.72, 69.10, 69.31, 71.04, 71.04, 72.39, 73.14, 74.71, 74.93, 75.60, 77.54, 78.72, 100.47 (C-1″), 102.48 (C-1), 103.41 (C-1′); FAB MS Calcd for [M + H^+]: 4000.5. Found: *m*/*z* 4001.0.

Dumbbell(2)18 (8). IR (KBr) 3361 (ν_{O-H}), 2915 (ν_{C-H}), 1420 (ν_{Si-C}), 1074 (ν_{C-O-C}), 706 (ν_{Si-C}) cm^{-1}; ^1H NMR δ (400 MHz, D_2O) 0.00 (br s, 6H, 2Me), 0.69 (br s, 68H, 34$SiCH_2$), 2.57 (br s, 72H, 36SCH_2-CH_2), 4.42 (d, 18H, $J_{1,2} = \sim 7$ Hz, H-1), 4.47 (d, 18H, $J_{1',2'} = \sim 8$ Hz, H-1′), 4.90 (br d, 18H, $J_{1'',2''} = \sim 4$ Hz, H-1″); ^{13}C NMR δ (100.6 MHz, D_2O) 12.03 [$SiCH_2$ (G2)], 24.34 [CH_2 (G2)], 26.10 [CH_2 (G2)], 28.77 [CH_2 (G2)], 31.85 [CH_2 (G2)], 35.87 [SCH_2 (G2)], 60.34, 60.57, 60.72, 68.73, 69.10, 69.34, 71.07, 71.07, 72.42, 73.13, 74.71, 74.96, 75.61, 77.53, 78.72, 100.48 (C-1″), 102.51 (C-1), 103.42 (C-1′); MALDI TOF MS Calcd for [M + H^+]: 12048.6. Found: *m*/*z* 12049.9.

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