Synthesis of selectively functionalized carbosilane dendrimers with carbohydrate core

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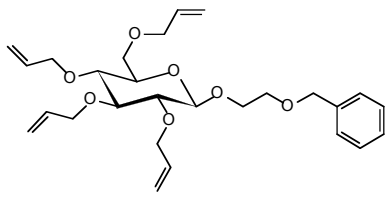
Supporting Information

General methods. Dry THF and dry diethyl ether were obtained by distillation from sodium/potassium ketyl under an atmosphere of nitrogen. Dry DMF was purchased from Fluka AG. Reactions which demanded use of Schlenk-techniques (all manipulations under an atmosphere of nitrogen) are denoted specially. TLC was performed on silica gel plates (GF_{254}, Merck). Detection was effected by UV irradiation and subsequent charring with 10% sulphuric acid in ethanol followed by heat treatment. Flash chromatography was performed on silica gel 60 (230-400 mesh, particle size 0.040-0.063 mm, Merck). Optical rotations were measured on a Perkin-Elmer 241 polarimeter (sodium-D-line: 589 nm, length of cell 1 dm) in chloroform. Melting points were measured with an Apotec apparatus and are uncorrected. NMR spectra were recorded on Bruker AMX 400 (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C) and DRX 500 (500.13 MHz for ^{1}H, 125.76 MHz for ^{13}C). The spectra were calibrated on the solvent peak ($CDCl_3$, 7.24 ppm for ^{1}H and 77.0 ppm for ^{13}C). Assignment of the peaks was achieved with the aid of 2D NMR techniques (^{1}H-^{1}H-COSY and HMQC). In the reported data the abbreviation 'su' denotes a sugar moiety. MALDI-TOF mass spectra were recorded on a Bruker Biflex III with 19 kV acceleration voltage and DHB (2,4-dihydroxy benzoic acid) as matrix (c = 10 μg/μl in 40% acetonitrile/water). Ionisation was effected with a nitrogen laser at 337 nm. Elemental analyses were performed in the microanalytic laboratory at the Department of Chemistry of the University of Hamburg.

Preparative procedures

(2-Benzyloxyethyl) 2,3,4,6-tetra-*O*-allyl-β-D-*gluco*-hexopyranoside (3)



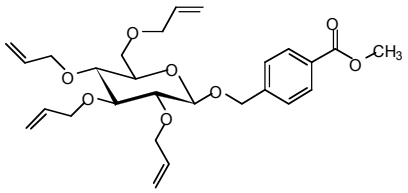
Glucoside **1** (2.29 g, 7.29 mmol) was dissolved in dry DMF (90 ml) under an argon atmosphere. At 0°C sodium hydride (1.46 g, 55-65% suspension in paraffin oil corresponding to 875 mg, 36.45 mmol pure sodium hydride, 5.0 eq) was added. After hydrogen evolvement had deceased the mixture was allowed to warm to rt and 3-bromo-1-propene (allyl bromide, 3.1 ml, 4.41 g, 36.45 mmol, 5.0 eq) was added and the mixture was stirred at rt until the starting material **1** had been completely consumed (checked by TLC, petrol ether/ethyl acetate 2:1). Water (60 ml) and dichloromethane (130 ml) were added, the phases were separated and the aqueous one was three times extracted with 40 ml dichloromethane. The combined organic phases were subsequently washed three times with 30 ml of water and then dried over magnesium sulphate. Filtration and evaporation of the solvents yielded the crude product **3** which was purified by flash chromatography (silica gel, petrol ether/diethyl ether 3:1).

Yield: 2.90 g (6.11 mmol 84%), viscous oil, $[\alpha]_D^{20}$ = - 3.5° (c = 1.05, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.34 (5H, m, 5 aryl-H), 5.82-5.99 (4H, m, 4 CH_2=C**H**-CH_2), 5.06-5.29 (8H, m, 4 C**H$_2$**=CH-CH_2), 4.50-4.58 (2H, m, CH_2-Ph), 3.96-4.40 (10H, m, H-1, 4 CH_2=CH-C**H$_2$**, suO-C**H$_A$**H$_B$), 3.55-3.77 (5H, m, H-6, H-6‘, suO-CH_2-C**H$_2$**, suO-CH_A**H$_B$**), 3.28-3.39 (3H, m, H-3, H-4, H-5), 3.20 (1H, dd, H-2) ppm; $^3J_{1,2}$ = 7.6, $^3J_{2,3}$ = 8.7 Hz; ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 138.3 (C, aryl-C), 135.3, 135.2, 134.9, 134.7 (CH, 4 CH_2=CH-CH_2), 128.3, 127.6, 127.5 (CH, 5 aryl-C), 116.9, 116.6 (CH_2, 4 CH_2=CH-CH_2), 103.6 (CH, C-1), 84.1, 77.5, 74.8 (CH, C-3, -4, -5), 81.6 (CH, C-2), 74.4, 73.8, 73.5, 73.1, 72.4 (CH_2, 4 CH_2=CH-CH_2, O-CH_2-Ph), 69.3, 69.0 (CH_2, C-6, suO-CH_2-CH_2-O) ppm.

Per-allylation reaction of methyl ester 2

Glucoside **2** (1.045 g, 3.18 mmol) was dissolved in dry DMF (40 ml) under an argon atmosphere. After cooling to 0°C, sodium hydride (610 mg of a 55-65% suspension in paraffin oil corresponding to approximately 366 mg, 15.26 mmol, 4.8 eq pure sodium hydride) was added. After the evolvement of hydrogen had stopped, the solution was allowed to warm to rt. 3-Bromo-1-propene (1.3 ml, 15.90 mmol, 5.0 eq) was added and the mixture stirred at rt until the starting material **2** was consumed completely (TLC, petrol ether/ethyl acetate 2:1). Then water (25 ml) and dichloromethane (55 ml) were added and the phases were separated. The aqueous phase was extracted three times with dichloromethane (20 ml) and the combined organic phases were three times washed with water (30 ml) and then dried over magnesium sulphate. Filtration followed by evaporation of the solvents yielded the crude mixture of compounds **4** and **5** which could be separated by flash chromatography (silica gel, petrol ether/ethyl acetate 4:1).

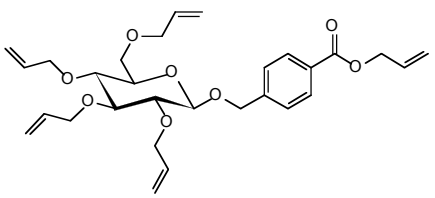
[(4-Methoxycarbonylphenyl)-methyl] 2,3,4,6-tetra-*O*-allyl-β-D-*gluco*-hexopyranoside (4):



second fraction, 830 mg (1.70 mmol, 53%), colourless solid; $[\alpha]_D^{20}$ = - 14.0° (c = 0.70, $CHCl_3$); mp = 64.0-64.8°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (2H, ddd ≈ d, 2 aryl-H), 7.41 (2H, ddd ≈ d, 2 aryl-H), 5.82-5.99 (4H, m, 4 CH_2=C**H**-CH_2), 5.10-5.29 (8H, m, 4 C**H$_2$**=CH-CH_2), 4.95 (1H, d, suO-C**H$_A$**H$_B$), 4.66 (1H, d, suO-CH_A**H$_B$**), 3.96-4.38 (9H, m, H-1, 4 CH_2=CH-C**H$_2$**), 3.89 (3H, s, O-CH_3), 3.69 (1H, dd, H-6‘), 3.60 (1H, dd, H-6), 3.30-3.39 (3H, m, H-3, H-4, H-5), 3.26 (1H, dd, H-2) ppm; $^3J_{1,2}$ = 7.6, $^3J_{2,3}$ = 9.2, $^3J_{5,6}$ = 4.1, $^3J_{5,6‘}$ = 1.5, $^2J_{6,6‘}$ = 10.7, $^2J_{A,B}$ = 13.2 Hz; ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 167.0 (C, **C**OO), 142.9 (C, aryl-C), 135.2, 135.0, 134.8, 134.7, (CH, 4 CH_2=**C**H-CH_2), 129.7, 127.2 (CH, 4 aryl-C), 129.4 (C, aryl-C), 117.1, 117.0, 116.9, 116.7 (CH_2, 4 **C**H_2=CH-CH_2), 102.7 (CH, C-1), 84.2, 77.5, 74.9 (CH, C-3, -4, -5), 81.6 (CH, C-2), 74.4, 73.8, 73.7, 72.5 (CH_2, 4 CH_2=CH-**C**H_2), 70.4 (CH_2, suO-CH_2), 68.9 (CH_2, C-6), 52.1 (CH_3, OCH_3) ppm; MALDI-TOF MS: *m/z* 511.3 ($(M + Na)^+$, calcd 511.2), 527.3 ($(M + K)^+$, calcd 527.2).

Anal. Calcd for $C_{27}H_{36}O_8$ (488.6): C, 66.38; H, 7.43. Found: C 65.707; H, 7.40.

[(4-Allyloxycarbonylphenyl)-methyl] 2,3,4,6-tetra-*O*-allyl-β-D-*gluco*-hexopyranoside (5):

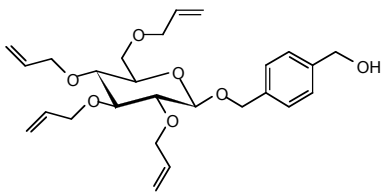


first fraction, 50 mg (0.97 mmol, 31%), colourless waxlike solid; $[\alpha]_D^{20}$ = - 27.0° (c = 0.60, $CHCl_3$); mp = 31.4-31.7°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (2H, ddd ≈ d, 2 aryl-H), 7.41 (2H, ddd ≈ d, 2 aryl-H), 5.83-6.07 (5H, m, 4 CH_2=C**H**-CH_2-Osu, CH_2=C**H$_a$**-CH_2-OOC), 5.39 (1H, ddt ≈ dq,

4.96 (1H, d, suO-C**H**$_A$H$_B$), 4.80 (2H, ddd ≈ dt, CH_2=CH-C**H**$_d$**H**$_e$-OOC), 4.66 (1H, d, suO-CH_A**H**$_B$), 3.96-4.39 (9H, m, H-1, 4 CH_2=CH-C**H$_2$**-Osu), 3.69 (1H, dd, H-6‘), 3.60 (1H, dd, H-6), 3.31-3.39 (3H, m, H-3, H-4, H-5), 3.26 (1H, dd, H-2) ppm; $^3J_{1,2}$ = 7.6, $^3J_{2,3}$ = 9.2, $^3J_{5,6}$ = 4.1, $^3J_{5,6‘}$ = 1.5, $^2J_{6,6‘}$ = 10.7, $^2J_{A,B}$ = 13.2, $^3J_{a,b}$ = 17.3, $^4J_{a,d}$ = $^4J_{a,e}$ = 1.5 Hz; ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 166.1 (C, **C**OO), 143.0 (C, aryl-C), 135.2, 135.0, 134.8, 134.7, (CH, 4 CH_2=**C**H-CH_2-Osu), 132.4 (CH, CH_2=**C**H-CH_2-OOC), 129.7, 127.2 (CH, 4 aryl-C), 129.4 (C, aryl-C), 118.2 (CH_2, **C**H$_2$=CH-CH_2-OOC), 117.0, 116.9, 116.7 (CH_2, 4 **C**H_2=CH-CH_2-Osu), 102.7 (CH, C-1), 84.2, 77.5, 74.9 (CH, C-3, -4, -5), 81.6 (CH, C-2), 74.4, 73.8, 73.7, 72.5 (CH_2, 4 CH_2=CH-**C**H_2-Osu), 70.3 (CH_2, suO-CH_2), 68.9 (CH_2, C-6), 65.5 (CH_2, CH_2=CH-**C**H_2-OOC) ppm; MALDI-TOF MS: *m/z* 537.3 ((M + Na)$^+$, calcd 537.2), 553.3 ((M + K)$^+$, calcd 553.2).

Anal. Calcd for $C_{29}H_{38}O_8$ (514.6): C, 67.69; H, 7.44. Found: C, 67.17; H, 7.45.

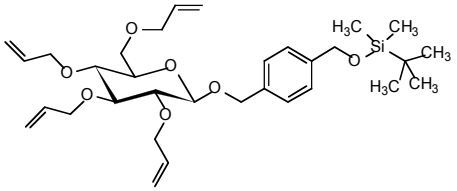
[(4-Hydroxymethylphenyl)-methyl] 2,3,4,6-tetra-*O*-allyl-β-D-*gluco*-hexopyranoside (6)



The methyl ester **4** (100 mg, 0.21 mmol) was dissolved in dry diethyl ether (2 ml) and added dropwise to a suspension of lithiumaluminumhydride (4 mg, 0.11 mmol, 0.55 eq) in dry diethyl ether (5 ml) under an atmosphere of argon. Subsequently the mixture was stirred at rt and after 45 min starting ester **4** had been completely consumed (checked by TLC, petrol ether/ethyl acetate 2:1). After cooling to 0°C, ice water was added to the mixture until hydrogen evolvement had ceased, then it was carefully treated with 10% sulphuric acid until the precipitated hydroxides just had dissolved. The aqueous phase was separated, three times extracted with 5 ml of diethyl ether and the combined organic phases were washed with brine. Drying over magnesium sulphate, filtration and evaporation of solvent yielded the pure title compound **6**.

Yield: 94 mg (0.20 mmol, 100%), colourless solid, $[\alpha]_D^{20}$ = - 27.0° (c = 1.05, $CHCl_3$), mp = 65.1-66.4°C, ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.36 (4H, m, 4 aryl-H), 5.83-5.99 (4H, m, 4 CH_2=C**H**-CH_2), 5.10-5.31 (8H, m, 4 C**H$_2$**=CH-CH_2), 4.89 (1H, d, suO-C**H**$_A$H$_B$), 4.67 (2H, s, C**H$_2$**-OH), 4.60 (1H, d, suO-CH_A**H**$_B$), 3.98-4.40 (9H, m, H-1, 4 CH_2=CH-C**H$_2$**), 3.70 (1H, dd, H-6‘), 3.61 (1H, dd, H-6), 3.30-3.38 (3H, m, H-3, H-4, H-5), 3.25 (1H, dd, H-2), 1.69 (1H, s, OH) ppm; $^3J_{1,2}$ = 7.6, $^3J_{5,6}$ = 4.1, $^3J_{5,6‘}$ = 1.0, $^2J_{6,6‘}$ = 10.7, $^2J_{A,B}$ = 13.2 Hz; ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 140.3, 137.1 (C, 2 aryl-C), 135.3, 135.1, 134.8, 134.7, (CH, 4 CH_2=C**H**-CH_2), 128.0, 127.0 (CH, 4 aryl-C), 117.0, 116.9, 116.8, 116.6 (CH_2, 4 CH_2=CH-CH_2), 102.4 (CH, C-1), 84.2, 81.6, 77.5, 74.8 (CH, C-2, C-3, C-4, C-5), 74.4, 73.8, 73.6, 72.5 (CH_2, 4 CH_2=CH-CH_2), 70.7 (CH_2, suO-CH_2), 69.0 (CH_2, C-6), 65.1 (CH_2, CH_2-OH) ppm.

{[4-(*tert*-Butyldimethylsiloxymethyl)-phenyl]-methyl} 2,3,4,6-tetra-*O*-allyl-β-D-*gluco*-hexopyranoside (7)



tert-Butyldimethylsilyltrifluoromethanesulfonate (0.08 ml, 96 mg, 0.37 mmol 1.0 eq) was dissolved together with pyridine (0.04 ml, 35 mg, 0.44 mmol, 1.2 eq) in 3 ml of dry acetonitrile under an atmosphere of argon. This solution was stirred at room temperature while alcohol **6** (168 mg, 0.37 mmol, 1.0 eq) dissolved in dry acetonitrile (2 ml) was slowly added. Stirring was continued until the starting material **6** had been completely consumed (controlled by TLC, petrol ether/ethyl acetate 2:1). For

sodium hydrogencarbonate. After separation of the phases, the aqueous one was extracted five times with 5 ml n-hexane and the combined organic phases were washed with water until the smell of pyridine had been dispelled, dried over magnesium sulphate and filtered. Evaporation of solvents yielded the crude title compound **7** which was purified by flash chromatography (silica gel, petrol ether/diethyl ether 5:1).

Yield: 136 mg (0.24 mmol, 65%), colourless oil, $[\alpha]_D^{20}$ = - 12.8° (c = 0.50, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.31 (4H, m, 4 aryl-H), 5.84-5.99 (4H, m, 4 CH_2=C**H**-CH_2), 5.09-5.31 (8H, m, 4 C$\mathbf{H_2}$=CH-CH_2), 4.88 (1H, d, suO-C$\mathbf{H_A}H_B$), 4.71 (2H, s, CH_2-OTBDMS), 4.59 (1H, d, suO-$CH_A\mathbf{H_B}$), 4.08-4.40 (9H, m, H-1, 4 CH_2=CH-C$\mathbf{H_2}$), 3.70 (1H, dd ≈ d, H-6‘), 3.67 (1H, dd, H-6), 3.29-3.38 (3H, m, H-3, H-4, H-5), 3.25 (1H, dd ≈ t, H-2), 0.92 (9H, s, $C(CH_3)_3$ TBDMS), 0.07 (6H, s, CH_3 TBDMS) ppm; $^3J_{1,2}$ = 8.1, $^3J_{5,6}$ = 4.1, $^2J_{6,6'}$ = 11.2, $^2J_{A,B}$ = 12.2 Hz; ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 140.9, 136.1 (C, 2 aryl-C), 135.3, 135.1, 134.9, 134.8, (CH, 4 CH_2=$\underline{C}$H-CH_2), 127.7, 126.0 (CH, 4 aryl-C), 117.0, 116.9, 116.8, 116.6 (CH_2, 4 $\underline{C}H_2$=CH-CH_2), 102.4 (CH, C-1), 84.2, 77.6, 74.8 (CH, C-3,-4,-5), 81.7 (CH, C-2), 74.4, 73.8, 73.6, 72.5 (CH_2, 4 CH_2=CH-$\underline{C}H_2$), 70.8 (CH_2, suO-$\underline{C}H_2$), 69.0 (CH_2, C-6), 64.8 (CH_2, $\underline{C}H_2$-OTBDMS), 25.9 (CH_3, C($\underline{C}H_3$)$_3$ TBDMS), 18.4 (C, $\underline{C}(CH_3)_3$ TBDMS), -5.3 (CH_3, CH_3 TBDMS) ppm.

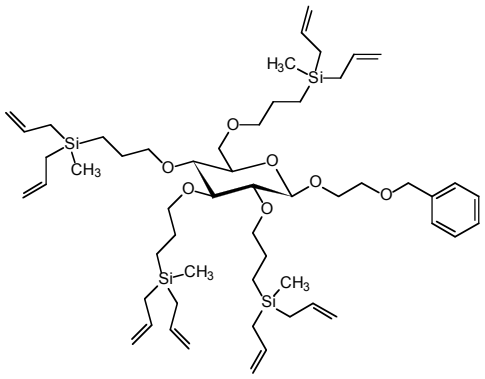
Preparation of carbosilan dendrimers from tetraallylated glucosides:

a) Hydrosilylation of tetraallylated compounds with dichloromethylsilane and Speier's catalyst
b) Grignard-Addition of allyl magnesiumbromide to Si-Cl bonds

a) This reaction demanded the use of Schlenk-technique. All manipulations were performed under an atmosphere of nitrogen.
The tetraallyl compound (**3** or **7**) was dissolved in dry THF (concentration dependent on amount of starting material 0.11-0.37 mol/l). After addition of dichloromethylsilane (6 eq, 1.5 eq per C=C-double bond) and 1-4 drops of Speier's catalyst the mixture was stirred at rt for 1 h and afterwards under reflux for another 10 h. After cooling to rt the solvent and the excess of dichloromethylsilane were removed under vacuum as far as possible. The resulting oily crude product (chlorosilane **8** or **9**) which still contained residual solvent and silane reagent was used in the next synthetic step without any further purification. A complete characterisation of the hydrosilylated products by NMR was made impossible by the catalyst and its paramagnetic byproducts which remain in the crude product. However, ^{1}H NMR clearly showed the complete consumption of all double bonds during the reaction.

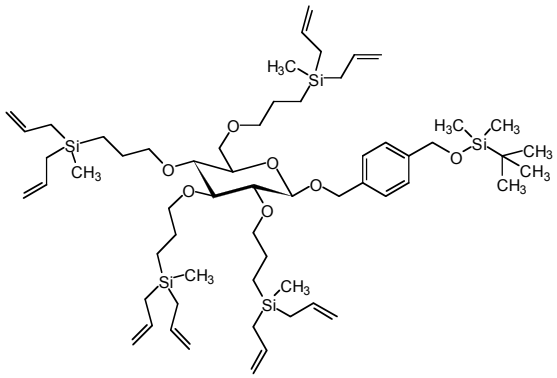
b) The reaction demanded the use of Schlenk-technique. Workup was performed under normal atmospheric conditions.
The crude chlorosilane (**8** or **9**) prepared by the previous procedure was dissolved in dry diethyl ether under an atmosphere of nitrogen (concentration of the starting compound dependent on amount 0.11-0.22 mol/l). To this solution allyl magnesiumbromide in diethyl ether (concentration of the solution 1 mol/l, 1.5 eq per Si-Cl bond, because of residual dichloromethylsilane in the crude product a bigger excess of Grignard-reagent should be used) was added dropwise. Precipitation of magnesium salts resulted instantly. After the addition was finished, the mixture was stirred under reflux for 12 h, then cooled to rt and poured on ice cold saturated ammonium chloride solution. The aqueous phase was extracted three times with diethyl ether and the combined organic phases were then twice washed with water and finally once with brine. Drying over magnesium sulphate, filtration and evaporation

(2-Benzyloxyethyl) 2,3,4,6-tetra-*O*-[3-(diallylmethylsilyl)-propyl]-β-D-*gluco*-hexopyranoside (10)



Amount of starting compound **3**: 1.06 g (2.23 mmol), eluant petrol ether/ethyl acetate 10:1
Yield: 1.13 g (1.15 mmol, 52%, two steps), colourless oil, $[\alpha]_D^{20}$ = - 0.3° (c = 1.60, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.34 (5H, m, 5 aryl-H), 5.67-5.81 (8H, m, 8 CH_2=C**H**-CH_2), 4.78-4.88 (16H, m, 8 C**H$_2$**=CH-CH_2), 4.50-4.58 (2H, m, CH_2-Ph), 4.26 (1H, d, H-1), 3.96-4.03 (1H, ddd ≈ m, suO-C**H$_A$**H$_B$), 3.14-3.84 (16H, m, H-3, H-4, H-5, H-6, H-6‘, 4 O-C**H$_2$**-CH_2-CH_2-Si, C**H$_2$**-O-CH_2-Ph, suO-CH_A**H$_B$**), 3.07 (1H, dd ≈ t, H-2), 1.46-1.61 (24H, m, 8 CH_2=CH-C**H$_2$**, 4 O-CH_2-C**H$_2$**-CH_2-Si), 0.42-0.56 (8H, m, 4 O-CH_2-CH_2-C**H$_2$**-Si), -0.02, -0.03, -0.05 (12H, each s, 4 Si-CH_3) ppm; $^3J_{1,2} \approx {}^3J_{2,3}$ = 8.1 Hz; ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 138.3 (C, aryl-C), 134.6, 134.5 (CH, 8 CH_2=<u>C</u>H-CH_2), 128.3, 127.6, 127.5 (CH, 4 aryl-C), 113.3, 113.2 (CH_2, 8 <u>C</u>H_2=CH-CH_2), 103.7 (CH, C-1), 84.8, 78.1, 75.0 (CH, C-3, -4, -5), 82.3 (CH, C-2), 76.4, 75.8, 75.6, 74.6 (CH_2, 4 O-<u>C</u>H_2-CH_2-CH_2-Si), 73.1 (CH_2, <u>C</u>H_2-Ph), 69.8, 69.3, 68.9 (CH_2, C-6, <u>C</u>H_2-O-CH_2-Ph, suO-CH_2), 24.6, 24.5, 24.4, 23.8 (CH_2, 4 O-CH_2-<u>C</u>H_2-CH_2-Si), 21.2 (CH_2, 8 CH_2=CH-<u>C</u>H_2), 9.1, (CH_2, 4 O-CH_2-CH_2-<u>C</u>H_2-Si), - 5.9 (CH_3, Si-CH_3) ppm; MALDI-TOF MS: *m/z* 1001.7 ($(M + Na)^+$, calcd 1001.6); 1017.7 ($(M + K)^+$, calcd 1017.6) for $C_{55}H_{94}O_7Si_4$ (M = 978.6); 875.6 ($(C_{48}H_{80}O_7Si_3Na)^+$, calcd 876.1).

{[4-(*tert*-Butyldimethylsiloxymethyl)-phenyl]-methyl} 2,3,4,6-tetra-*O*-[3-(diallylmethylsilyl)-propyl]-β-D-*gluco*-hexopyranoside (11)



Amount of starting compound **7** : 194 mg (0.34 mmol), eluant petrol ether/ethyl acetate 20:1
Yield: 131 mg (0.12 mmol, 36%, two steps), colourless oil, $[\alpha]_D^{20}$ = - 3.4° (c = 0.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.31 (4H, m, 4 aryl-H), 5.68-5.81 (8H, m, 8 CH_2=C**H**-CH_2), 4.77-4.90 (17H, m, 8 C**H$_2$**=CH-CH_2, suO-C**H$_A$**H$_B$), 4.71 (2H, s, CH_2-OTBDMS), 4.58 (1H, d, suO-CH_A**H$_B$**), 4.29 (1H, d, H-1), 3.15-3.82 (13H, m, H-3, H-4, H-5, H-6, H-6‘, 4 O-C**H$_2$**-CH_2-CH_2-Si), 3.11 (1H, dd ≈ t, H-2), 1.49-1.63 (24H, m, 8 CH_2=CH-C**H$_2$**, 4 O-CH_2-C**H$_2$**-CH_2-Si), 0.92 (9H, s, $C(CH_3)_3$ TBDMS), 0.45-0.59 (8H, m, 4 O-CH_2-CH_2-C**H$_2$**-Si), 0.08 (6H, s, 2 CH_3 TBDMS), -0.02, -0.03 (12H, each s, 4 Si-CH_3) ppm; $^3J_{1,2}$ = 7.6, $^2J_{A,B}$ = 12.2 Hz; ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 140.9, 136.2 (C, 2 aryl-C), 134.6, 134.5 (CH, 8 CH_2=<u>C</u>H-CH), 127.7, 126.0 (CH, 4 aryl-C), 113.3, 113.2 (CH_2, 8 <u>C</u>H_2=CH-CH), 102.2 (CH, C-1), 84.9, 78.2, 75.1 (CH, C-3, -4, -5), 82.3 (CH, C-2), 76.4, 75.8, 75.7 (CH_2, 4 O-<u>C</u>H_2-CH_2-CH_2-Si), 70.7 (CH_2, suO-CH_2), 69.8 (CH_2, C-6), 64.8 (CH_2, CH_2-OTBDMS), 25.9 (CH_3, C(<u>C</u>H_3)$_3$), 24.6, 24.5, 24.4, 23.9 (CH_2, 4 O-CH_2-<u>C</u>H_2-CH_2-Si), 21.2 (CH_2, 8 CH_2=CH-<u>C</u>H), 18.4 (C, <u>C</u>$(CH_3)_3$), 9.1, 9.0 (CH_2, 4 O-CH_2-CH_2-<u>C</u>H_2-Si), - 5.3 (CH_3, 2 CH_3 TBDMS), -5.9 (CH_3, 4 Si-CH_3) ppm; MALDI-TOF MS: *m/z* 1101.7 ($(M + Na)^+$, calcd 1101.7), 117.7 ($(M + K)^+$, cald 1117.6) for $C_{60}H_{106}O_7Si_5$ (M = 1078.7); 975.7 ($(C_{53}H_{92}O_7Si_4Na)^+$, calcd 975.6), 963.6 ($(C_{54}H_{91}O_7Si_4)^+$, calcd 963.6).