Synthesis of Trisaccharides and Tetrasaccharides by Means of Intramolecular Glycosylation Supported by Rigid Spacers

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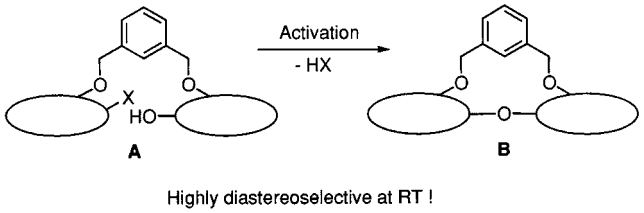
Treatment of α,α′-dibromo-*m*-xylylene with 6-*O*-unprotected thiomaltoside **4** as glycosyl donor (→ **5**), followed by 4-*O*-unprotected galactoside derivative **6** as acceptor, afforded β-linked macrocyclic trisaccharide **9β** in high yield after removal of the 3-*O*-MPM protective group and subsequent intramolecular glycoside bond formation. Similarly, by the same sequence of steps, the corresponding tetrasaccharide **14β** was obtained from **5** and 4b-*O*-unprotected lactoside **11**. For reiterative glycoside bond formation, treatment of α,α′-dibromo-*m*-xylylene with 3-*O*-unprotected thioglycoside **15** as donor (→ **16**), followed by 4,6-*O*-unprotected glucoside, and subsequent glycosylation afforded macrocyclic maltotrioside **22**, which was transformed into known maltotrioside **23**. A slight modification of the protecting-group pattern in maltotrioside synthesis resulted in generally higher yields in the ligation of the building blocks to the *m*-xylylene spacer, particularly in the second glycosylation step, thus providing macrocyclic maltotrioside **40α**, which was transformed into known maltotriosides **41α** and **41β**.

Introduction

Although the advantages, in terms of stereoselectivity and regioselectivity, of intramolecular reactions are well known, only rather recent investigations have been reported to apply this principle to glycosylation reactions. Three conceptually different methods have been investigated:[1] (1) "leaving group based intramolecular reactions", that is, linkage of the acceptor to the leaving group of the donor by a spacer;[2−7] (2) "accepting atom based intramolecular glycosylation", linkage of the accepting atom to functional groups of the donor through a spacer;[8−12] and (3) "spacer-mediated linkage" through nonreacting centers of donor and acceptor.[13−18] These methodologies have in part produced excellent results; however, intramolecular reaction courses have not been confirmed for all cases in which the leaving group or the accepting atom participates in spacer connection [methods (1) and (2)].[4−6] Method (3) results in formation of macrocyclic glycosides, and so intramolecular reaction versus intermolecular reaction is not generally an issue.

In order to ensure close proximity between glycosyl donor and acceptor and to limit the conformational space of the reacting centers in method (3), we designed the "rigid spacer" concept (Scheme 1).[13,14] With the aid of the rigid *m*-xylylene spacer, excellent results were obtained in terms of yield and anomeric selectivity, particularly when 14-membered macrocycles were generated; hydrogenolytic *O*-debenzylation and/or *O*-debenzylidenation ensured concomitant removal of the *m*-xylylene spacer. The success of this concept in trisaccharide and tetrasaccharide synthesis is demonstrated in this paper.



Scheme 1

Results and Discussion

Linking of a Disaccharide Donor to a Monosaccharide or Disaccharide Acceptor

A maltose thioglycoside was selected as a disaccharide donor (Scheme 2). To this end, maltose derivative **1** was prepared, following known procedures.[2] Regioselective 6a-*O*-silylation with thexyldimethylsilyl (TDS) chloride in the presence of imidazole as base afforded 6a-*O*-TDS-protected derivative **2**, which on treatment with benzyl bromide and sodium hydride in DMF afforded tetra-*O*-benzyl maltothioglycoside **3**. Removal of the TDS group with tetrabutylammonium fluoride (TBAF) in THF furnished compound **4**. The introduction of the spacer arm was achieved by treatment of **4** with excess α,α′-dibromo-*m*-xylylene in the presence of sodium hydride in DMF (see above), affording compound **5**, which was transformed with 4-*O*-unprotected galactoside **6**,[14] under the conditions described above, into **7**, with disaccharide and monosaccharide residues linked by a spacer. The 3-*O*-methoxyphenylmethyl (MPM) group could be selectively removed by treatment with dichlorodicyanoquinone (DDQ) in dichloromethane as solvent, thus providing **8**, possessing an *m*-xylylene-linked maltosyl donor and a galactose-derived acceptor. Glycosylation of 6(β)/

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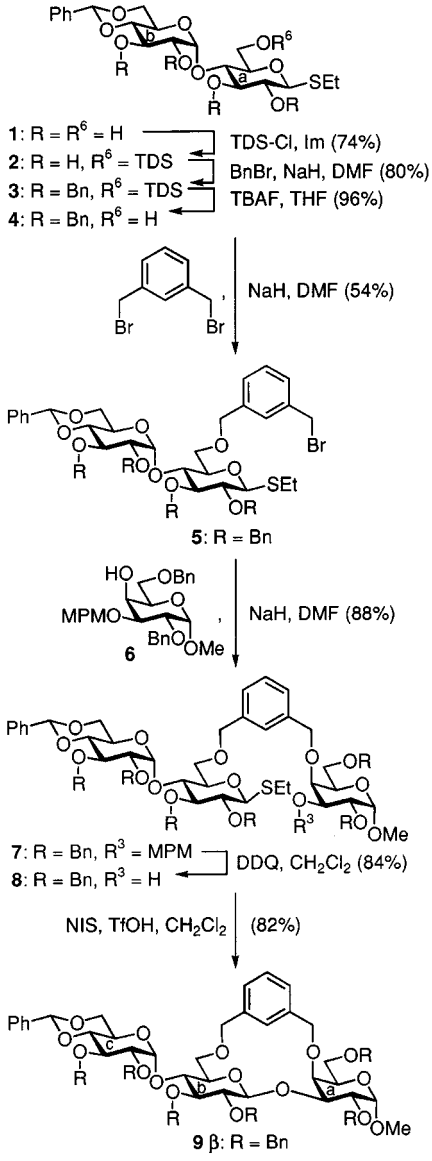
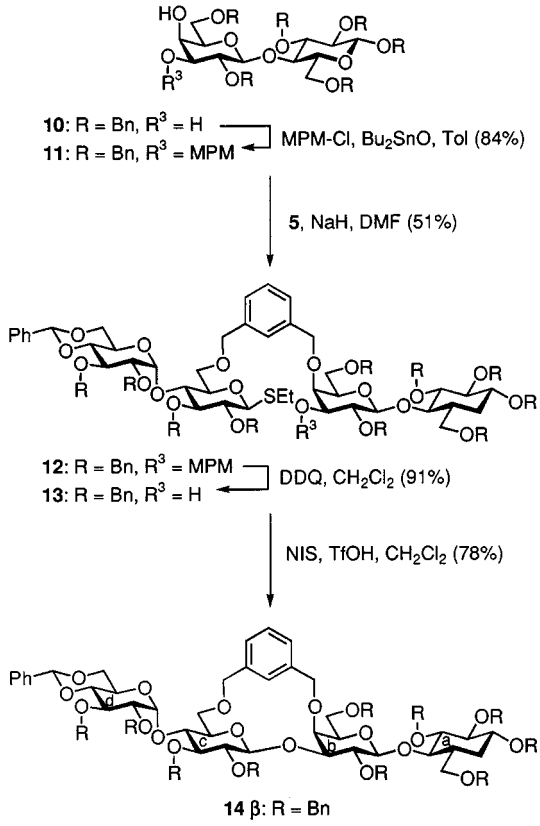


Scheme 2



Scheme 3

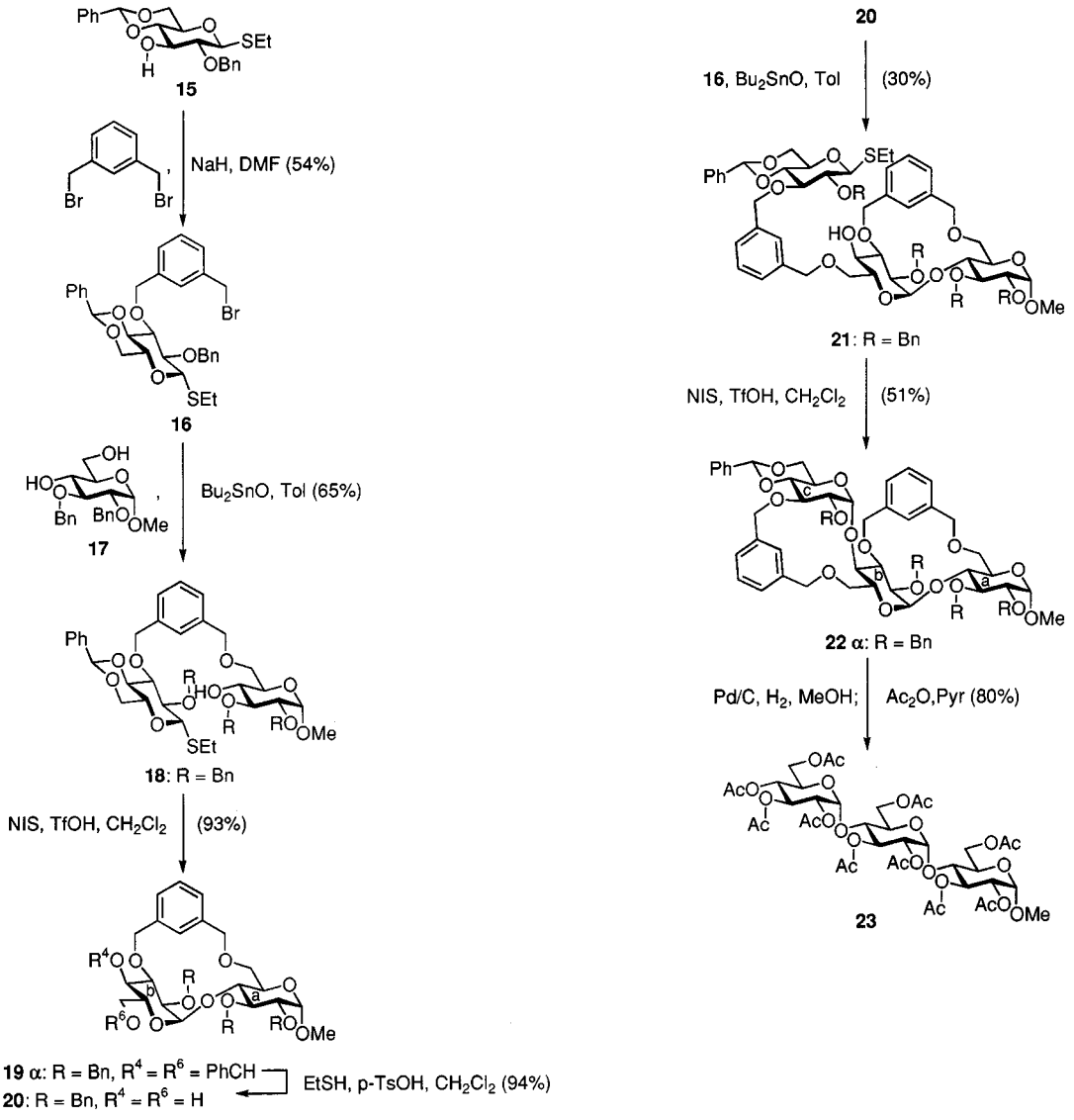
4(4,3-L-*erythro*)-linked **8**[20] under standard conditions [*N*-iodosuccinimide (NIS) (2 equiv.) and trifluoromethanesulfonic acid (TfOH) (0.2 equiv.) as promotor system] gave rise exclusively to a β(1−3) linkage between the maltosyl and the galactose moiety, even at room temperature without anchimeric assistance. In this way, trisaccharide **9β** was isolated in 82% yield and structurally assigned by NMR-spectroscopic data (^{1}H NMR: 1b-H, $J_{1,2}$ = 7.9 Hz; 1c-H, $J_{1,2}$ = 4.1 Hz).

For production of a glycosidic linkage between two disaccharide residues, a 3b-*O*-unprotected lactose was selected as acceptor, since β-glycosides with 3b-hydroxy groups are frequently found in nature. To this end, known 3b,4b-*O*-unproteced lactose derivative **10**[21] (Scheme 3) was treated with MPM-Cl as alkylating agent to afford 3b-*O*-MPM-protected derivative **11**. Treatment of **11** with **5** under standard conditions resulted in linkage of the two disaccharides by the *m*-xylylene spacer (→ **12**).

Liberation of the 3b-hydroxy group with DDQ produced **13**, featuring donor and acceptor linked by the rigid *m*-xylylene spacer in the same stereochemical arrangement as **8**. Treatment of **13** under standard conditions at room temperature again resulted only in β(1−3) linkage between the maltosyl and the lactoside residues, affording tetrasaccharide **14β**. The structural assignment could again be determined on the basis of the NMR-spectroscopic data (^{1}H NMR: 1b-H, $J_{1,2}$ = 7.4 Hz; 1c-H, $J_{1,2}$ = 7.9 Hz; 1d-H, $J_{1,2}$ = 3.8 Hz). Thus, transformation of **8** into **9β** and of **13** into **14β** furnished results corresponding to those observed for the glycosidic linkage between identically connected glucosyl and galactoside residues.[14]

Reiterative Procedure for the Synthesis of Maltotriosides

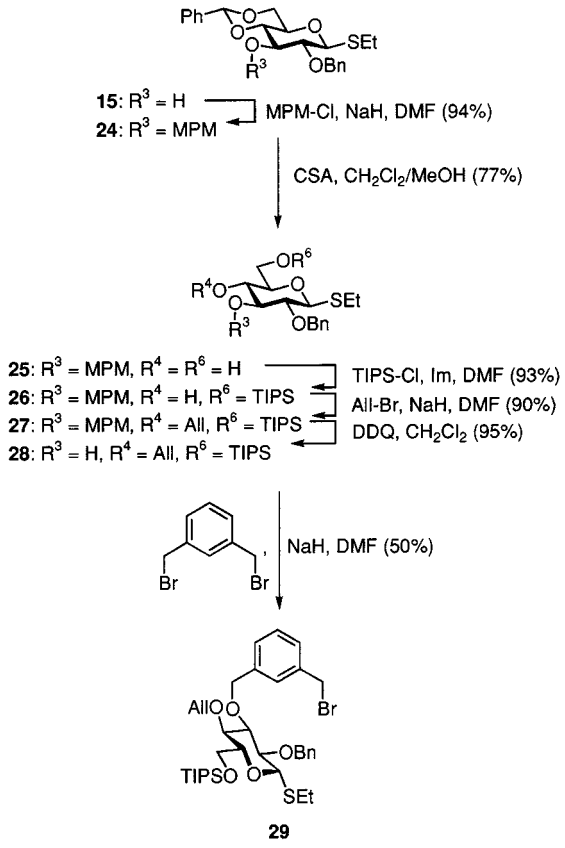
This great success in the generation of various types of glycosidic linkages was reason to investigate a reiterative procedure. The important α(1−4) linkage between glucosyl residues was selected as a suitable system for this endeavor, and was shown to be accessible in high yield in the 3(β)/6(5,4-L-*threo*) donor/acceptor arrangement through the rigid *m*-xylylene spacer.[14] To this end, known thioglycoside **15**[22] (Scheme 4) was treated with α,α′-dibromo-*m*-xylylene to afford **16**, which, when treated with 4,6-*O*-unprotected glucoside **17**,[23] gave the desired intermediate **18**. Glycoside bond formation under standard conditions confirmed the reported[14] exclusive formation of the α(1−4) linkage, thus



Scheme 4

providing macrocyclic disaccharide **19α**. Removal of the *O*-benzylidene group with *p*-toluenesulfonic acid (*p*TsOH) in the presence of ethanethiol as nucleophile afforded 4b,6b-*O*-unprotected derivative **20**. Treatment of **20** with dibutyltin oxide and then with bromoxylyl derivative **16** in the presence of tetrabutylammonium bromide (TBAB) furnished the desired *m*-xylylene spacer linked compound **21**, possessing a glucosyl donor and maltoside as acceptor. Glycosylation of **21** under standard conditions afforded macrocyclic (octacyclic in total) trisaccharide **22α**, although only in 51% yield. Assignment of the α-linkage was based on the NMR-spectroscopic data (^{1}H NMR: 1b-H, $J_{1,2}$ = 2.8 Hz; 1c-H, $J_{1,2}$ = 3.0 Hz). Hydrogenolytic cleavage of *O*-benzyl, *O*-benzylidene, and *O*-xylylene protective groups with Pd/C as catalyst, followed by *O*-acetylation with acetic anhydride in pyridine, afforded known maltotrioside **23**, which had analytical data in accordance with those reported.[24]

The relatively low yields in the dibutyltin oxide mediated linkage step between residues **16** and **20**, and also in the second glycosylation step, were reason to investigate a donor system with orthogonal temporary protective groups in the 1-, 3-, 4-, and 6-positions for the maltotrioside synthesis. This should make highly regioselective reactions accessible, thanks to separate spacer attachment in the 3- and 6-positions and, for chain extension, glycosylation at the anomeric center and at the 4-position. To this end, thioglycoside **15**[22] (Scheme 5) was treated with MPM-Cl and sodium hydride in DMF to afford 3-*O*-MPM-protected thioglucoside **24** in high yield. Removal of the *O*-benzylidene moiety with camphorsulfonic acid (CSA) as catalyst in dichloromethane/methanol afforded 4,6-*O*-unprotected derivative **25**, which on treatment with triisopropylsilyl (TIPS) chloride in the presence of imidazole afforded 6-*O*-TIPS-protected thioglycoside **26**. Treatment of **26** with allyl bromide under standard conditions resulted in 4-*O*-allylation, affording compound **27**, possessing the desired orthogonal groups in all positions. In order to allow for the desired 3(β)/6(5,4-L-*threo*) arrangement through the *m*-xylylene



Scheme 5

spacer, 3-*O*-deprotection of **27** with DDQ was first required; this furnished compound **28** in excellent yield. Treatment of **28** with excess α,α′-dibromo-*m*-xylylene under standard conditions provided spacer-linked donor **29** in good yield.

For the acceptor synthesis, known 4,6-*O*-unprotected glucoside **30**[25] was chosen as starting material (Scheme 6); on treatment with *tert*-butyldiphenylsilyl (TBDPS) chloride in the presence of imidazole as base, this furnished 6-*O*-TBDPS-protected derivative **31**. Treatment of **31** with MPM-Cl under standard conditions gave 4-*O*-MPM-protected intermediate **32**. Desilylation with TBAF in THF (→ **33**) followed by treatment with **29**, again in the presence of sodium hydride as base and DMF as solvent, afforded spacer-linked intermediate **34**, which on treatment with DDQ liberated the 4a-hydroxy group (→ **35**), thus permitting glycosidation. In this case, with the standard promoter system at room temperature, minor amounts of the β isomer were also generated; however, a high overall yield of **36α** and **36β** (84%, α/β = 7:1) was obtained. The anomers could readily be separated. Comparison with the structurally closely related transformation of **18** into **19α** (which had provided the α anomer exclusively) demonstrated that changes in the steric bulk of the protective groups can influence anomeric stereocontrol, which may reflect differences in the preferred conformational space of donor and/or acceptor moieties. Treatment of **36α** with TBAF resulted in 6b-*O*-desilylation (→ **37α**), thus permitting treatment with spacer-linked glycosyl donor **16** under standard conditions, giving 6b-*O*-alkylation product **38**. Removal of the 4b-*O*-allyl group with Wilkinson's catalyst in the presence of ethanol furnished the desired intermediate **39**, required for the next glycosylation step. This time, under standard glycosylation conditions, the α linkage was generated exclusively, furnishing protected trisaccharide **40α** in high yield. The structural assignment was determined on the basis of the NMR-spectroscopic data (^{1}H NMR: 1a-H, $J_{1,2}$ = 3.6 Hz; 1b-H, $J_{1,2}$ = 2.8 Hz; 1c-H, $J_{1,2}$ = 3.0 Hz). Hydrogenolysis with Pd/C as catalyst, removing the *O*-benzyl, *O*-benzylidene, and *O*-xylylene moieties, followed by *O*-acetylation with acetic anhydride in pyridine, afforded known *O*-acetyl-protected maltotriosides **41α** and **41β**, the analytical data for which were in accordance with those reported,[26] thus confirming the structural assignments.

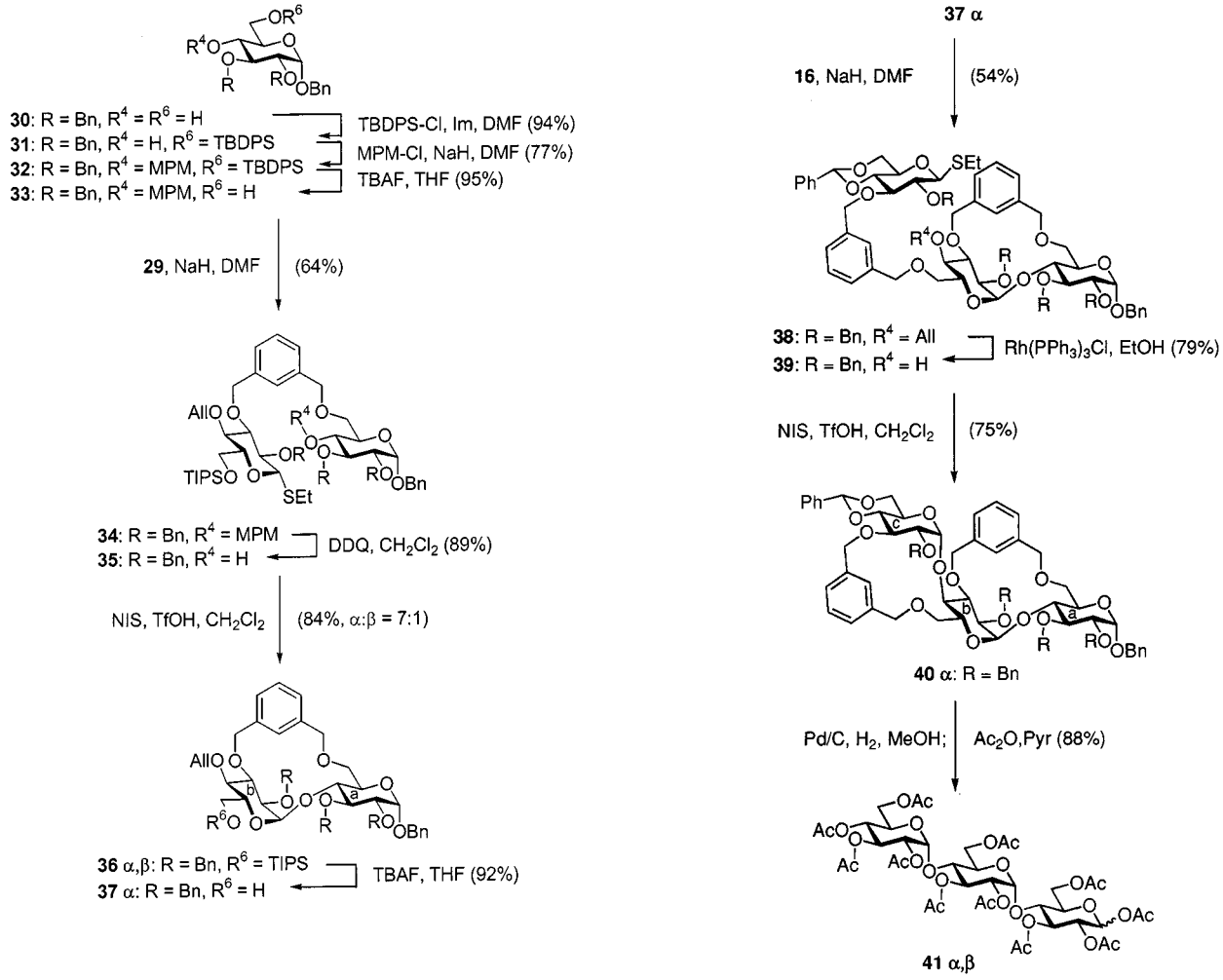
Conclusion

It was possible to extend intramolecular glycosylation based on the rigid *m*-xylylene spacer to trisaccharide and tetrasaccharide synthesis. Highly stereoselective and high-yielding glycosidations, producing macrocycles, were found even at room temperature. The *m*-xylylene spacer could readily be removed by hydrogenolysis.

Experimental Section

General: All air-sensitive and/or water-sensitive reactions were carried out under argon with dry solvents under anhydrous conditions. − Reactions were monitored by TLC carried out on Merck silica gel-coated plastic sheets (60 F_{254}) using UV light as visualizing agent and 5% $(NH_4)_2MoO_4$, 0.1% $Ce(SO_4)_2$ in 10% H_2SO_4 and heat as developing agents. − Baker silica gel (particle size 0.040−0.063 mm) was used for flash chromatography. − NMR spectra were recorded with Bruker DRX 600 (600 MHz) and AC 250 (250 MHz) instruments and calibrated using tetramethylsilane as internal standard. − Optical rotations were recorded with a Perkin−Elmer 241 MC polarimeter in a 1-dm cell at 22 °C. − FAB mass spectra were recorded with a Finnigan MAT 312/AMD 5000 spectrometer with 3-nitrobenzyl alcohol matrix. − MALDI mass spectra were recorded with a Kratos compact spectrometer with 2,5-dihydrobenzoic acid matrix.

Ethyl *O*-(4,6-*O*-Benzylidene-α-D-glucopyranosyl)-(1→4)-6-*O*-thexyldimethylsilyl-1-thio-β-D-glucopyranoside (2): TDSCl (8.80 mL, 45.0 mmol) was added at 0 °C to a solution of compound **1** (18.0 g, 38.0 mmol) and imdazole (4.63 g, 68.0 mmol) in dimethylformamide (70 mL). The resulting mixture was warmed to room temp. and stirred for 4 h. The reaction mixture was then diluted with H_2O (200 mL) and extracted with dichloromethane (3 × 100 mL), and the organic layer was dried with $MgSO_4$. After evaporation of the solvent, the residue was purified by flash chromatography (toluene/acetone, 1:1) to afford compound **2** (17.3 g, 74%) as a colorless solid. − TLC (ethyl acetate/methanol, 9:1): R_f = 0.57. − $[\alpha]_D^{22}$ = +33 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.09, 0.11 [2 s, 6 H, $Si(CH_3)_2$], 0.86, 0.88, 0.89 (3 s, 12 H, 4 CH_3), 1.29 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 1.60 [m, 1 H, $CH(CH_3)_2$], 2.65−2.75 (m, 2 H, SCH_2CH_3), 3.33−3.96 (m, 11 H, 2a-H, 3a-H,



Scheme 6

4a-H, 5a-H, 2 6a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H), 4.21 (dd, $^2J_{6,6}$ = 10.2, $^3J_{6,5}$ = 4.8 Hz, 1 H, 6b-H), 4.27 (d, $^3J_{1,2}$ = 9.6 Hz, 1 H, 1a-H), 5.05 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1b-H), 5.51 (s, 1 H, PhCH), 7.35−7.51 (m, 5 H, Ph). − $C_{29}H_{48}O_{10}SSi$ (616.8): calcd. C 56.47, H 7.84; found C 56.01, H 7.84.

Ethyl *O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-thexyldimethylsilyl-1-thio-β-D-glucopyranoside (3): Sodium hydride (1.50 g, 62.4 mmol) was added at room temp. to a solution of compound **2** (8.02 g, 13.0 mmol) and benzyl bromide (6.80 mL, 57.2 mmol) in dimethylformamide (100 mL), and the resulting mixture was stirred for 4 h. Methanol (10 mL) was added, followed by ethyl acetate (100 mL) and brine (100 mL). The organic layer was separated and the aqueous phase was extracted with ethyl acetate (2 × 100 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 9:1) to afford compound **3** (10.2 g, 80%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 9:1): R_f = 0.45. − $[\alpha]_D^{22}$ = +2 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.13, 0.15 [2 s, 6 H, $Si(CH_3)_2$], 0.85, 0.86, 0.89 (3 s, 12 H, 4 CH_3), 1.32 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 1.64 [m, 1 H, $CH(CH_3)_2$], 2.71−2.80 (m, 2 H, SCH_2CH_3), 3.38−4.04 (m, 11 H, 2a-H, 3a-H, 4a-H, 5a-H, 2 6a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H), 4.29 (dd, $^2J_{6,6}$ = 10.0, $^3J_{6,5}$ = 4.6 Hz, 1 H, 6b-H), 4.48−4.90 (m, 9 H, 1b-H, 8 PhC*H*H), 5.53 (s, 1 H, PhCH), 5.60 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1a-H), 7.18−7.50 (m, 25 H, Ph). − Maldi MS: m/z = 1000 [MNa^+]. − $C_{57}H_{72}O_{10}$ SSi (977.3): calcd. C 70.05, H 7.43; found C 70.13, H 6.69.

Ethyl *O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-1-thio-β-D-glucopyranoside (4): nBu$_4$NF solution (1 M in tetrahydrofuran, 10.2 mL, 10.2 mmol) was added to a solution of **3** (8.31 g, 8.50 mmol) in tetrahydrofuran (100 mL), and the mixture was stirred for 4 h at room temp. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) to afford compound **4** (6.79 g, 96%) as a colorless foam. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.23. − $[\alpha]_D^{22}$ = 0 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.33 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.70−2.80 (m, 2 H, SCH_2CH_3), 3.44−4.03 (m, 11 H, 2a-H, 3a-H, 4a-H, 5a-H, 2 6a-H, 2b-H, 3b-H, 4b-H, 5b-H, 6b-H), 4.32 (dd, $^2J_{6,6}$ = 10.0, $^3J_{6,5}$ = 4.7 Hz, 1 H, 6b-H), 4.49−4.94 (m, 9 H, 1b-H, 8 PhC*H*H), 5.54 (s, 1 H, PhCH), 5.66 (d, $^3J_{1,2}$ = 4.0 Hz, 1 H, 1a-H), 7.11−7.51 (m, 25 H, Ph). − $C_{49}H_{54}O_{10}$ S (835.0): calcd. C 70.48, H 6.52; found C 70.43, H 6.62.

Ethyl *O*-(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-(3-bromomethylbenzyl)-1-thio-β-D-glucopyranoside (5): Compound **4** (2.51 g, 3.01 mmol) was added to a suspension of α,α′-dibromo-*m*-xylylene (3.17 g, 12.0 mmol) and sodium hydride (96 mg, 4.0 mmol) in dimethylformamide (50 mL)

and the mixture was stirred for 20 h at room temp. Ethyl acetate (100 mL) and brine (100 mL) were added and the organic layer was separated. The aqueous phase was extracted with ethyl acetate (2 × 100 mL) and the combined organic layers were dried with $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography (petroleum ether/ethyl acetate, 9:1→7:1) afforded compound **5** (1.65 g 54%) as a colorless foam. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.47. − $[\alpha]_D^{22}$ = +3 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.35 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.72−2.81 (m, 2 H, SCH_2CH_3), 3.48−4.18 (m, 12 H, 2a-H, 3a-H, 4a-H, 5a-H, 2 6a-H, 2b-H, 3b-H, 4b-H, 5b-H, 2 6b-H), 4.42−4.93 (m, 13 H, 10 PhC*H*H, $PhCH_2$Br, 1b-H), 5.54 (s, 1 H, PhCH), 5.69 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1a-H), 7.13−7.52 (m, 29 H, Ph). − Maldi MS: *m*/*z* = 1039, 1041 [M + Na^+]. − $C_{57}H_{61}BrO_{10}S$ (1018.1): calcd. C 67.24, H 6.04; found C 67.13, H 6.09.

Spacer-Linked Disaccharide−Monosaccharide 7: Sodium hydride (18 mg, 0.75 mmol) was added to a solution of compound **5** (641 mg, 0.630 mmol) and compound **6** (312 mg, 0.631 mmol) in dimethylformamide (50 mL), and the mixture was stirred for 3 h at room temperature. Methanol (5 mL), ethyl acetate (100 mL), and brine (100 mL) were added and the organic layer was separated. The aqueous phase was extracted with ethyl acetate (2 × 100 mL) and the combined organic layers were dried with $MgSO_4$. After evaporation of the solvent, the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) to afford compound **7** (790 mg, 88%) as a colorless foam. − TLC (toluene/ethyl acetate, 4:1): R_f = 0.53. − $[\alpha]_D^{22}$ = +6 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.34 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.67−2.81 (m, 2 H, SCH_2CH_3), 3.39 (s, 1 H, OCH_3), 3.53−3.65 (m, 7 H, 2 6a-H, 2b-H, 5b-H, 2c-H, 4c-H, 6c-H), 3.81−3.83 (m, 5 H, 3b-H, 6b-H, OCH_3), 3.90−3.93 (m, 5 H, 3a-H, 4a-H, 5a-H, 6b-H, 5c-H), 4.03−4.05 (m, 2 H, 2a-H, 3c-H), 4.15−4.17 (m, 2 H, 4b-H, 6c-H), 4.41 (d, ^2J = 11.8 Hz, 1 H, PhC*H*H), 4.48−4.98 (m, 19 H, 1a-H, 1b-H, 2 7′-H, 2 8′-H, 13 PhC*H*H), 5.55 (s, 1 H, PhCH), 5.71 (d, $^3J_{1,2}$ = 3.9 Hz, 1 H, 1c-H), 6.90 (d, ^3J = 8.6 Hz, 2 H, Ph), 7.21−7.39 (m, 39 H, Ph), 7.52 (m, 2 H, Ph). − ^{13}C NMR (151 MHz, $CDCl_3$): δ = 15.3 (SCH_2CH_3), 24.7 (SCH_2CH_3), 55.3 (2 OCH_3), 63.3 (5c-C), 69.0 (6c-C), 69.2 (6b-C), 69.3 (6a-C, 5a-C), 72.4 (4b-C), 72.7, 73.4, 73.5, 73.6, 73.9, 74.8, 75.2, 75.3 (7 $PhCH_2$, 7′-C, 8′-C), 75.4 (4a-C), 76.4 (2a-C), 78.6 (5b-C), 78.7 (2c-H), 78.8 (3a-C, 3c-C), 81.9 (2b-C), 82.4 (4c-C), 84.9 (1b-C), 86.7 (3b-C), 97.6 (1c-C), 98.8 (1a-C), 101.1 (PhCH). − Maldi MS: *m*/*z* = 1453 [M + Na^+]. − $C_{86}H_{94}O_{17}S$ (1431.7): calcd. C 72.15, H 6.62; found C 72.23, H 6.79.

Spacer-Linked Disaccharide−Monosaccharide 8: DDQ (98 mg, 0.43 mmol) was added to a solution of compound **7** (558 mg, 0.390 mmol) in dichloromethane (40 mL) and H_2O (4 mL) and the mixture was stirred for 6 h at room temp. The reaction mixture was diluted with dichloromethane (50 mL) and washed with aqueous $NaHCO_3$ solution (20 mL) and H_2O (20 mL). The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to afford compound **8** (430 mg, 84%) as a colorless foam. − TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.29. − $[\alpha]_D^{22}$ = +15 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.32 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.26 (d, ^3J = 4.9 Hz, 1 H, OH), 2.67−2.83 (m, 2 H, SCH_2CH_3), 3.32 (s, 1 H, OCH_3), 3.46−4.18 (m, 18 H, 2a-H, 3a-H, 4a-H, 5a-H, 2 6a-H, 2b-H, 3b-H, 4b-H, 5b-H, 2 6b-H, 2c-H, 3c-H, 4c-H, 5c-H, 2 6c-H), 4.38−4.96 (m, 18 H, 1a-H, 1b-H, 2 7′-H, 2 8′-H, 12 PhC*H*H), 5.52 (s, 1 H, PhCH), 5.69 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1c-H), 7.12−7.51 (m, 39 H, Ph). − Maldi MS: *m*/*z* = 1332 [MNa^+], 1351 [MK^+]. − $C_{78}H_{86}O_{16}S$ (1311.6): calcd. C 71.43, H 6.61; found C 71.45, H 6.71.

Methyl 4,6′-*O*-(1,3-Xylylene)-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1′′→4′)-(2,3-di-*O*-benzyl-β-D-glucopyranosyl)-(1′→3)-2,6-di-*O*-benzyl-α-D-galactopyranoside (9β): TfOH (3 μL) was added to a solution of compound **8** (197 mg, 0.150 mmol) and NIS (67 mg, 0.30 mmol) in dichloromethane (15 mL) and the mixture was stirred for 30 min at room temp. The reaction mixture was washed with aqueous $NaHCO_3$ solution (2 mL) and aqueous $Na_2S_2O_3$ solution (2 mL) and dried with $MgSO_4$. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) to afford compound **9β** (155 mg, 82%) as a colorless foam. − TLC (toluene/ethyl acetate, 4:1): R_f = 0.61. − $[\alpha]_D^{22}$ = +1 (*c* = 0.5, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.02 (dd, $^2J_{6,6}$ = 10.6, $^3J_{6,5}$ = 3.8 Hz, 1 H, 6a-H), 3.23 (s, 1 H, OCH_3), 3.38 (d, $^2J_{6,6}$ = 11.2 Hz, 1 H, 6b-H), 3.48 (dd, $^2J_{6,6}$ = 10.6, $^3J_{6,5}$ = 7.3 Hz, 1 H, 6a-H), 3.52−3.55 (m, 3 H, 2b-H, 5b-H, 2c-H), 3.63 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.7 Hz, 1 H, 4c-H), 3.71−3.74 (m, 3 H, 4a-H, 5a-H, 6c-H), 3.81 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 9.1 Hz, 1 H, 3b-H), 3.85 (dd, $^3J_{3,4}$ = 2.9, $^3J_{3,2}$ = 10.3 Hz, 1 H, 3a-H), 4.00 (dd, $^3J_{2,1}$ = 3.8, $^3J_{2,3}$ = 10.3 Hz, 1 H, 2a-H), 4.03−4.06 (m, 2 H, 3c-H, 5c-H), 4.18 (dd, $^2J_{6,6}$ = 11.2, $^3J_{6,5}$ = 2.3 Hz, 1 H, 6b-H), 4.32−4.39 (m, 4 H, 6c-H, 8′-H, 2 PhC*H*H), 4.46−4.48 (m, 2 H, 1a-H, PhC*H*H), 4.51 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.4 Hz, 1 H, 4b-H), 4.59 (d, ^2J = 11.8 Hz, 1 H, PhC*H*H), 4.62 (d, $^3J_{1,2}$ = 7.9 Hz, 1 H, 1b-H), 4.65 (d, ^2J = 11.4 Hz, 1 H, PhC*H*H), 4.67 (d, ^2J = 12.2 Hz, 1 H, PhC*H*H), 4.71 (d, ^2J = 11.9 Hz, 1 H, PhC*H*H), 4.78 (d, ^2J = 11.1 Hz, 1 H, PhC*H*H), 4.79 (d, ^2J = 11.9 Hz, 1 H, PhC*H*H), 4.86 (d, ^2J = 11.0 Hz, 1 H, 7′-H), 4.93 (d, ^2J = 11.1 Hz, 1 H, PhC*H*H), 4.96 (d, ^2J = 15.3 Hz, 1 H, 8′-H), 4.97 (d, ^2J = 11.9 Hz, 1 H, PhC*H*H), 4.98 (d, ^2J = 12.0 Hz, 1 H, 7′-H), 5.07 (d, ^2J = 11.9 Hz, 1 H, PhC*H*H), 5.56 (s, 1 H, PhCH), 5.81 (d, $^3J_{1,2}$ = 4.1 Hz, 1 H, 1c-H), 6.93 (m, 1 H, Ph), 7.05−7.54 (m, 37 H, Ph), 8.10 (s, 1 H, Ph). − ^{13}C NMR (151 MHz, $CDCl_3$): δ = 54.9 (OCH_3), 63.3 (5c-C), 68.4 (6b-C), 69.3 (6c-C), 69.9 (5a-C), 70.1 (4b-C), 70.4 (8′-C), 70.8 (6a-C), 71.5 (4a-C), 72.5 (7′-H), 73.3−73.7 (5 $PhCH_2$, 5b-C), 75.3 ($PhCH_2$), 76.1 (2a-C), 78.6 (2c-C), 79.0 (3c-C), 81.2 (2b-C), 82.2 (4c-C), 82.4 (3a-C), 84.4 (3b-C), 97.1 (1c-C), 98.4 (1a-C), 101.1 (PhCH), 106.0 (1b-C). − Maldi MS: *m*/*z* = 1272 [M + Na^+], 1289 [M + K^+]. − $C_{76}H_{80}O_{16}$ (1249.5): calcd. C 73.06, H 6.45; found C 72.97, H 6.50.

Benzyl *O*-[2,6-Di-*O*-benzyl-3-*O*-(4-methoxybenzyl)-β-D-galactopyranosyl]-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (11): $n$$Bu_2SnO$ (747 mg, 3.00 mmol) was added to a solution of compound **10** (2.21 g, 2.50 mmol) in toluene (40 mL) and the resulting mixture was refluxed with removal of H_2O, using a Dean−Stark apparatus, for 4 h. Toluene (20 mL) was distilled off, and the reaction mixture was cooled to room temp. $n$$Bu_4NBr$ (806 mg, 2.50 mmol) and PMBCl (502 μL, 3.70 mmol) were added, and the mixture was heated to 90 °C and stirred for 3 h. The solvents were removed under reduced pressure and the residue was purified by flash chromatography (toluene/ethyl acetate, 1:0→9:1) to afford compound **11** (2.10 g, 84%) as a colorless oil. − TLC (toluene/ethyl acetate, 3:1): R_f = 0.57. − $[\alpha]_D^{22}$ = +15 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.33−4.00 (m, 15 H, 2a-H, 3a-H, 4a-H, 5a-H, 2 6a-H, 2b-H, 3b-H, 4b-H, 5b-H, 2 6b-H, OCH_3), 4.38−4.99 (m, 16 H, 1a-H, 1b-H, 14 PhC*H*H), 6.85 (m, 2 H, ^3J = 8.6 Hz, Ph), 7.21−7.40 (m, 32 H, Ph). − $C_{62}H_{66}O_{11}$ (1003.2): calcd. C 74.23, H 6.63; found C 74.00, H 6.67.

Spacer-Linked Disaccharide−Disaccharide 12: Sodium hydride (22 mg, 0.91 mmol) was added to a solution of compound **5** (774 mg, 0.760 mmol) and compound **11** (762 mg, 0.760 mmol) in

dimethylformamide (50 mL), and the mixture was stirred for 5 h at room temp. Methanol (5 mL), ethyl acetate (100 mL), and brine (100 mL) were added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (2 × 100 mL) and the combined organic layers were dried with $MgSO_4$. After evaporation of the solvent, the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 5:1) to afford compound **12** (750 mg, 51%) as a colorless foam. − TLC (toluene/ethyl acetate, 4:1): R_f = 0.56. − $[\alpha]_D^{22}$ = +2 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.28 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.66−2.75 (m, 2 H, SCH_2CH_3), 3.34−3.36 (m, 4 H, 5a-H, 3b-H, 5b-H, 6b-H), 3.46−3.60 (m, 8 H, 2a-H, 3a-H, 6b-H, 2c-H, 5c-H, 2d-H, 4d-H, 6d-H), 3.72−3.86 (m, 11 H, 2 6a-H, 2b-H, 4b-H, 3c-H, 2 6c-H, 5d-H, OCH_3), 3.93 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.3 Hz, 1 H, 4a-H), 3.99 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 9.3 Hz, 1 H, 3d-H), 4.11 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.2 Hz, 1 H, 4c-H), 4.15 (dd, $^2J_{6,6}$ = 10.2, $^3J_{6,5}$ = 4.9 Hz, 1 H, 6d-H), 4.22, 4.30 (2 d, 2 H, ^2J = 11.8 Hz, 2 PhC*H*H), 4.41 (m, 27 H, 1a-H, 1b-H, 1c-H, 2 7′-H, 2 8′-H, 20 PhC*H*H), 5.50 (s, 1 H, PhCH), 5.66 (d, $^3J_{1,2}$ = 3.9 Hz, 1 H, 1d-H), 6.81 (d, ^3J = 8.6 Hz, 2 H, Ph), 7.09−7.32 (m, 59 H, Ph), 7.48 (m, 2 H, Ph). − ^{13}C NMR (151 MHz, $CDCl_3$): δ = 15.2 (SCH_2CH_3), 24.7 (SCH_2CH_3), 55.2 (OCH_3), 63.2 (5d-C), 68.2 (6b-C), 68.4 (6a-C), 68.9 (6d-C), 69.1 (6c-C), 70.9 (7′-C), 72.2 ($PhCH_2$), 72.4 (4c-C), 73.1 (5b-C, $PhCH_2$), 73.4 ($PhCH_2$), 73.7 (4b-C, $PhCH_2$), 73.9, 74.0, 74.7, 75.0, 75.2, 75.3 (8′-C, 7 $PhCH_2$), 75.4 (5a-C), 76.8 (4a-C), 78.5 (5c-C), 78.7 (2d-C, 3d-C), 79.9 (2b-C), 81.9 (2a-C, 2c-C), 82.3 (3b-C), 83.0 (3a-C), 84.7 (1c-C), 86.7 (3c-C), 97.6 (1d-C), 101.1 (PhCH), 103.5 (1a-C), 102.8 (1b-C). − Maldi MS: *m*/*z* = 1962 [M + Na^+]. − $C_{119}H_{126}O_{22}S$ (1940.4): calcd. C 73.66, H 6.54; found C 73.95, H 6.38.

Spacer-Linked Disaccharide−Disaccharide 13: DDQ (747 mg, 3.00 mmol) was added to a solution of compound **12** (388 mg, 0.200 mmol) in dichloromethane (40 mL) and H_2O (4 mL), and the mixture was stirred for 6 h at room temp. The reaction mixture was diluted with dichloromethane (50 mL) and washed with aqueous $NaHCO_3$ solution (20 mL) and H_2O (20 mL). The organic layer was dried with $MgSO_4$ and the solvent was evaporated under reduced pressure. Purification of the residue by flash chromatography (petroleum ether/ethyl acetate, 4:1→3:1) afforded compound **13** (330 mg, 91%) as a colorless foam. − TLC (toluene/ethyl acetate, 4:1): R_f = 0.45. − $[\alpha]_D^{22}$ = −2 (*c* = 0.5, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.30 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.21 (d, ^3J = 5.8 Hz, 1 H, OH), 2.69−2.77 (m, 2 H, SCH_2CH_3), 3.38−4.17 (m, 24 H, 2a-H, 3a-H, 4a-H, 5a-H, 2 6a-H, 2b-H, 3b-H, 4b-H, 5b-H, 2 6b-H, 2c-H, 3c-H, 4c-H, 5c-H, 2 6c-H, 2d-H, 3d-H, 4d-H, 5d-H, 2 6d-H), 4.24−5.03 (m, 27 H, 1a-H, 1b-H, 1c-H, 2 7′-H, 2 8′-H, 20 PhC*H*H), 5.51 (s, 1 H, PhCH), 5.68 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1d-H), 7.12−7.49 (m, 59 H, Ph). − Maldi MS: *m*/*z* = 1844 [M + Na^+]. − $C_{111}H_{118}O_{21}S$ (1820.2): calcd. C 73.25, H 6.53; found C 72.91, H 6.58.

Benzyl 4′,6′′-*O*-(1,3-Xylylene)-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1′′′→4′′)-(2,3-di-*O*-benzyl-β-D-glucopyranosyl)-(1′′→3′)-(2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1′→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (14β): TfOH (2 μL) was added to a solution of compound **13** (182 mg, 0.100 mmol) and NIS (45 mg, 0.20 mmol) in dichloromethane (10 mL), and the reaction mixture was stirred for 30 min at room temp. The mixture was washed with aqueous $NaHCO_3$ solution (2 mL) and aqueous $Na_2S_2O_3$ solution (2 mL), and the organic layer was dried with $MgSO_4$. Evaporation of the solvent under reduced pressure and flash chromatography (petroleum ether/ethyl acetate, 4:1) of the residue afforded compound **14β** (137 mg, 78%) as a colorless foam. − TLC (petroleum ether/ethyl acetate, 2:1): R_f = 0.58. − $[\alpha]_D^{22}$ = +10 (*c* = 0.5, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.20−3.23 (m, 2 H, 5b-H, 6b-H), 3.26 (ddd, 1 H, $^3J_{5,4}$ = 10.0, $^3J_{5,6}$ = 4.4 Hz, 1.8 Hz, 5a-H), 3.36 (dd, $^3J_{3,2}$ = 9.7, $^3J_{3,4}$ = 2.9 Hz, 1 H, 3b-H), 3.35−3.43 (m, 4 H, 2a-H, 6b-H, 2c-H, 6c-H), 3.49−3.51 (m, 2 H, 5c-H, 2d-H), 3.57−3.65 (m, 4 H, 3a-H, 2 6a-H, 4d-H), 3.71−3.74 (m, 3 H, 2b-H, 4b-H, 6d-H), 3.77 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 9.1 Hz, 1 H, 3c-H), 3.98−4.03 (m, 3 H, 4a-H, 3d-H, 5d-H), 4.15 (d, ^2J = 11.8 Hz, 1 H, PhC*H*H), 4.19 (dd, $^2J_{6,6}$ = 11.7, $^3J_{6,5}$ = 2.6 Hz, 1 H, 6c-H), 4.29 (d, ^2J = 15.6 Hz, 1 H, 8′-H), 4.30−4.35 (m, 3 H, 6d-H, 2 PhC*H*H), 4.41 (d, $^3J_{2,1}$ = 7.4 Hz, 1 H, 1b-H), 4.44−4.45 (m, 3 H, 1a-H, 4c-H, PhC*H*H), 4.52 (d, $^3J_{1,2}$ = 7.9 Hz, 1 H, 1c-H), 4.57 (d, ^2J = 11.8 Hz, 1 H, PhC*H*H), 4.65 (d, ^2J = 12.0 Hz, 1 H, PhC*H*H), 4.66−4.79 (m, 9 H, 7′-Hz, 8 PhC*H*H), 4.88−4.98 (m, 7 H, 7′-H, 8′-H, 5 PhC*H*H), 5.12 (d, ^2J = 10.6 Hz, 1 H, PhC*H*H), 5.57 (s, 1 H, PhCH), 5.76 (d, $^3J_{1,2}$ = 3.8 Hz, 1 H, 1d-H), 7.00−7.40 (m, 55 H, Ph), 7.53 (m, 3 H, Ph), 7.96 (s, 1 H, Ph). − ^{13}C NMR (151 MHz, $CDCl_3$): δ = 63.3 (5d-C), 68.3 (6a-C), 69.1 (6c-C), 69.3 (6d-C), 69.8 (6b-C), 70.1 (4b-C), 70.8 ($PhCH_2$), 70.9 (4c-C), 71.3 (8′-C), 72.3 (7′-C), 73.0, 73.2, 73.8 (4 $PhCH_2$), 74.0 (5c-C), 74,3 (5b-C, $PhCH_2$), 74.7, 75.0 ($PhCH_2$), 75.1 (5a-C), 75.2, 75.3 (2 $PhCH_2$), 76.0 (4a-C), 78.7 (2d-C), 78.9 (3d-C), 79.5 (2b-C), 81.0 (2c-C), 81.8 (2a-C), 82.2 (4d-C), 82.9 (3a-C), 84.4 (3c-C), 85.0 (3b-C), 97.3 (1d-C), 101.2 (PhCH), 102.4 (1a-C), 102.7 (1b-C), 105.4 (1c-C). − Maldi MS: *m*/*z* = 1780 [M + Na^+]. − $C_{109}H_{112}O_{21}$ (1758.1): calcd. C 74.47, H 6.42; found C 74.30, H 6.53.

Methyl 6,3′-*O*-(1,3-Xylylene)-(2-*O*-benzyl-α-D-glucopyranosyl)-(1′→4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (20): Ethanethiol (388 μL, 5.00 mmol) and *p*TsOH (50 mg) were added to a solution of compound **19α** (816 mg, 1.00 mmol) in dichloromethane (30 mL), and the resulting mixture was stirred for 2 h. The reaction mixture was neutralized by addition of Et_3N and the solvents were then removed under reduced pressure. Flash chromatography of the residue (toluene/ethyl acetate, 2:1→3:2) afforded compound **20** (686 mg, 94%) as a colorless oil. − TLC (toluene/acetone, 1:1): R_f = 0.50. − $[\alpha]_D^{22}$ = −4 (*c* = 0.8, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.00 (m, 1 H, 6a-H), 3.33−3.57 (m, 9 H, 2a-H, 4a-H, 2b-H, 4b-H, 5b-H, 6b-H, OCH_3), 3.78 (dd, 1 H, $^2J_{6,6}$ = 11.0 Hz, $^3J_{6,5}$ < 1.0 Hz, 6a-H), 4.00−4.12 (m, 3 H, 3a-H, 5a-H, 6b-H), 4.48−5.07 (m, 12 H, 1a-H, 3b-H, 2 7′-H, 2 8′-H, 6 PhC*H*H), 5.42 (d, $^3J_{1,2}$ = 2.7 Hz, 1 H, 1b-H), 7.14−7.49 (m, 19 H, Ph). − MALDI MS: *m*/*z* = 751 [M + Na^+]. − $C_{42}H_{48}O_{11}$ (728.0): calcd. C 69.21, H 6.64; found C 69.13, H 7.02.

Spacer-Linked Monosaccharide−Disaccharide 21: Compound **20** (369 mg, 0.507 mmol) and nBu_2SnO (149 mg, 0.599 mmol) were dissolved in toluene (20 mL) and the resulting mixture was refluxed with removal of H_2O, using a Dean−Stark apparatus, for 20 h, after which toluene (10 mL) was distilled off. After the mixture had cooled to room temp., nBu_4NBr (226 mg, 0.701 mmol) and compound **16** (410 mg, 0.700 mmol) were added. The reaction mixture was heated to 90 °C and stirred for 2 h and the solvents were then removed under reduced pressure and the residue purified by flash chromatography (toluene/ethyl acetate, 1:0→9:1) to afford **21** (185 mg, 30%) as a colorless oil. − TLC (toluene/ethyl acetate, 4:1): R_f = 0.28. − $[\alpha]_D^{22}$ = −2 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.33 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.71−2.78 (m, 2 H, SCH_2CH_3), 3.10−3.54 (m, 12 H, 2a-H, 6a-H, 2b-H, 4b-H, 5b-H, 2 6b-H, 2c-H, 5c-H, OCH_3), 3.68−3.76 (m, 5 H, 4a-H, 6a-H, 3c-H, 4c-H, 6c-H), 4.01−4.14 (m, 3 H, 3a-H, 5a-H, 3b-H), 4.31−4.99 (m, 19 H, 1a-H, 1c-H, 6c-H, 16 PhC*H*H), 5.41 (d, $^3J_{1,2}$ = 2.7 Hz, 1 H, 1b-H), 5.54 (s, 1 H, PhCH), 7.14−7.51 (m, 33 H, Ph). − FAB MS: *m*/*z* = 1255 [M + Na^+]. − $C_{72}H_{80}O_{16}S$ (1233.5): calcd. C 70.11, H 6.54; found C 70.27, H 6.61.

Methyl 6′,3′′-*O*-(1,3-Xylylene)-(2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1′′→4′)-6,3′-*O*-(1,3-xylylene)-(2-*O*-benzyl-α-D-glucopyranosyl)-(1′→4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (22α): TfOH (2 μL) was added to a solution of **21** (124 mg, 0.10 mmol) and NIS (45 mg, 0.20 mmol) in dichloromethane (10 mL), and the resulting mixture was stirred for 1 min. The reaction mixture was washed with aqueous $NaHCO_3$ solution (2 mL) and aqueous $Na_2S_2O_3$ solution (2 mL), dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash chromatography (toluene/ethyl acetate, 19:1→14:1) to afford **22α** (60 mg, 51%) as a colorless oil. − TLC (toluene/ethyl acetate 2:1): R_f = 0.64. − $[\alpha]_D^{22}$ = −6 (*c* = 0.8, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.22−3.28 (m, 4 H, 6a-H, 4b-H, 6b-H, 5c-H), 3.35 (dd, 1 H, $^3J_{2,1}$ = 2.9, $J_{2,3}$ = 9.8 Hz, 2c-H), 3.40 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.5 Hz, 1 H, 4c-H), 3.45 (br. s, 4 H, OCH_3, 2b-H), 3.65 (m, 2 H, 2a-H, 6c-H), 3.71 (m, 2 H, 4a-H, 5b-H), 3.78−3.81 (m, 2 H, 6a-H, 6b-H), 4.02−4.14 (m, 4 H, 3a-H, 5a-H, 3c-H, PhC*H*H), 4.20−4.26 (m, 4 H, 3b-H, 6c-H, 2 PhC*H*H), 4.41 (d, ^2J = 13.6 Hz, 1 H, PhC*H*H), 4.56−4.67 (m, 8 H, 7 PhC*H*H, 1a-H), 4.72−4.78 (m, 4 H, 4 PhC*H*H), 5.00 (d, ^2J = 11.0 Hz, 1 H, PhC*H*H), 5.14 (d, ^2J = 11.2 Hz, 1 H, PhC*H*H), 5.31 (d, $^3J_{1,2}$ = 3.0 Hz, 1 H, 1c-H), 5.33 (d, $^3J_{1,2}$ = 2.8 Hz, 1 H, 1b-H), 5.41 (s, 1 H, PhCH), 6.92 (m, 1 H, Ph), 7.12−7.40 (m, 31 H, Ph), 7.64 (s, 1 H, Ph). − FAB MS: *m*/*z* = 1193 [M + Na^+]. − $C_{70}H_{74}O_{16}$ (1171.6): calcd. C 71.78, H 6.37; found C 71.46, H 6.50.

Methyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside (23): A mixture of compound **22α** (23 mg, 0.020 mmol) and palladium on carbon (10%, 10 mg) in methanol/ethyl acetate (1:1, 4 mL) and formic acid (0.2 mL) was stirred under hydrogen for 20 h. After filtration and concentration under reduced pressure, the residue was dissolved in acetic anhydride/pyridine (1:1, 4 mL) and stirred for 20 h. The solution was concentrated under reduced pressure, coevaporated with toluene, and purified by flash chromatography (toluene/ethyl acetate, 1:1) to afford known compound **23** (15 mg, 80%) as a colorless oil.[24]

Ethyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-(4-methoxybenzyl)-1-thio-β-D-glucopyranoside (24): *p*-Methoxybenzyl chloride (5.56 mL, 41.0 mmol) was added at 0 °C to a suspension of compound **15** (15.0 g, 37.3 mmol) and sodium hydride (1.08 g, 44.8 mmol) in dimethylformamide (200 mL). After warming to room temp., the mixture was stirred for 2 h and then quenched by addition of methanol (10 mL). The solvents were removed under reduced pressure. The residue was dissolved in ethyl acetate (200 mL) and washed with H_2O (20 mL) and brine (20 mL). The aqueous layer was reextracted with ethyl acetate (20 mL) and the combined organic layers were dried with $MgSO_4$ and the solvents then removed under reduced pressure. Purification of the residue by flash chromatography (petroleum ether/ethyl acetate, 9:1→6:1) afforded compound **24** (18.4 g, 94%) as a colorless solid. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.71. − $[\alpha]_D^{22}$ = −32 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.32 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.72−2.77 (m, 2 H, SCH_2CH_3), 3.40−3.49 (m, 2 H, 2-H, 5-H), 3.65−3.83 (m, 6 H, OCH_3, 3-H, 4-H, 6-H), 4.32−4.38 (m, 1 H, 6-H), 4.55 (d, $^3J_{1,2}$ = 9.8 Hz, 1 H, 1-H), 4.71−4.89 (m, 4 H, 4 PhC*H*H), 5.58 (s, 1 H, PhCH), 6.81 (d, ^3J = 8.7 Hz, 2 H, Ph), 7.24−7.51 (m, 12 H, Ph). − Maldi MS: *m*/*z* = 546 [M + Na^+]. − $C_{30}H_{34}O_6S$ (522.7): calcd. C 68.94, H 6.56; found C 68.84, H 6.67.

Ethyl 2-*O*-Benzyl-3-*O*-(4-methoxybenzyl)-1-thio-β-D-glucopyranoside (25): Compound **24** (17.8 g, 34.0 mmol) was dissolved in a mixture of dichloromethane (150 mL) and methanol (150 mL) and 10-camphorsulfonic acid (200 mg) was added. After stirring for 20 h at room temp. the solution was neutralized by addition of Et_3N. The solvents were removed under reduced pressure and the residue was purified by flash chromatography (toluene/ethyl acetate, 1:1) to afford compound **25** (11.5 g, 77%) as a colorless solid; m.p. 78−80 °C. − TLC (toluene/ethyl acetate, 1:1): R_f = 0.24. − $[\alpha]_D^{22}$ = −24 (*c* = 0.5, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.15 (t, ^3J = 6.6 Hz, 1 H, OH), 2.18 (s, 1 H, OH), 2.63−2.73 (m, 2 H, SCH_2CH_3), 3.20−3.47 (m, 4 H, 2-H, 3-H, 4-H, 5-H), 3.61−3.81 (m, 5 H, 2 6-H, OCH_3), 4.42 (d, $^3J_{1,2}$ = 9.4 Hz, 1 H, 1-H), 4.57 (d, ^2J = 11.2 Hz, 1 H, PhC*H*H), 4.66 (d, ^2J = 10.3 Hz, 1 H, PhC*H*H), 4.81 (d, ^2J = 11.2 Hz, 1 H, PhC*H*H), 4.87 (d, ^2J = 10.3 Hz, 1 H, PhC*H*H), 6.79 (d, ^3J = 8.6 Hz, 2 H, Ph), 7.15−7.36 (m, 7 H, Ph). − Maldi MS: *m*/*z* = 457 [M + Na^+]. − $C_{23}H_{30}O_6S$ (434.6): calcd. C 63.57, H 6.96; found C 63.59, H 6.67.

Ethyl 2-*O*-Benzyl-3-*O*-(4-methoxybenzyl)-6-*O*-triisopropylsilyl-1-thio-β-D-glucopyranoside (26): TIPSCl (7.00 mL, 32.7 mmol) was added at 0 °C to a solution of **25** (11.5 g, 26.5 mmol) and imidazole (3.25 g, 47.5 mmol) in dimethylformamide (100 mL). The mixture was warmed to room temp. and stirred for 4 h. After addition of H_2O (200 mL), the aqueous layer was extracted with dichloromethane (3 × 100 mL) and the organic layer was dried with $MgSO_4$. Evaporation of the solvent under reduced pressure and purification of the residue by flash chromatography (petroleum ether/ethyl acetate, 7:1) afforded compound **26** (14.5, 93%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.63. − $[\alpha]_D^{22}$ = −20 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.03−1.16 [m, 21 H, 3 C*H*(CH_3)$_2$], 1.29 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.69−2.76 (m, 2 H, SCH_2CH_3), 3.33−3.40 (m, 2 H, 2-H, 5-H), 3.53 (dd, $^3J_{3,4}$ = $^3J_{4,5}$ = 8.8 Hz, 1 H, 3-H), 3.67 (dd, $^3J_{4,5}$ = $^3J_{4,3}$ = 8.8 Hz, 1 H, 4-H), 3.79 (s, 1 H, OCH_3), 3.86−3.96 (m, 2 H, 2 6 H), 4.47 (d, $^3J_{1,2}$ = 9.6 Hz, 1 H, 1-H), 4.75−4.91 (m, 4 H, 4 PhC*H*H), 6.85 (d, ^3J = 8.6 Hz, 2 H, Ph), 7.25−7.42 (m, 7 H, Ph). − Maldi MS: *m*/*z* = 614 [M + Na^+]. − $C_{32}H_{50}O_6SSi$ (590.9): calcd. C 65.05, H 8.55; found C 65.09, H 8.50.

Ethyl 4-*O*-Allyl-2-*O*-benzyl-3-*O*-(4-methoxybenzyl)-6-*O*-triisopropylsilyl-1-thio-β-D-glucopyranoside (27): Allyl bromide (2.00 mL, 23.6 mmol) was added to a suspension of compound **26** (12.5 g, 21.2 mmol) and sodium hydride (609 mg, 25.4 mmol) in dimethylformamide (50 mL). The mixture was stirred for 3 h at room temp., methanol (5 mL) was added, and the solvents were removed under reduced pressure. The residue was dissolved in ethyl acetate (100 mL) and washed with H_2O (20 mL) and brine (20 mL). The organic layer was dried with $MgSO_4$ and evaporated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 19:1) to afford compound **27** (12.0 g, 90%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.77. − $[\alpha]_D^{22}$ = +16 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.06−1.11 [br. s, 21 H, 3 C*H*(CH_3)$_2$], 1.28 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.62−2.81 (m, 2 H, SCH_2CH_3), 3.23−3.28 (m, 1 H, 5-H), 3.35 (dd, $^3J_{2,1}$ = 9.7, $^3J_{2,3}$ = 8.7 Hz, 1 H, 2-H), 3.50 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 3.60 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 9.7 Hz, 1 H, 3-H), 3.79 (s, 3 H, OCH_3), 3.87 (dd, $^2J_{6,6}$ = 11.2, $^3J_{6,5}$ = 4.0 Hz, 1 H, 6-H), 3.97 (dd, $^2J_{6,6}$ = 11.2, $^3J_{6,5}$ = 1.8 Hz, 1 H, 6-H), 4.15−4.25, 4.29−4.38 (2 m, 2 H, $OCH_2CH{=}CH_2$), 4.42 (d, $^3J_{1,2}$ = 9.7 Hz, 1 H, 1-H), 4.72−4.88 (m, 3 H, 3 PhC*H*H), 4.89 (d, ^2J = 10.3 Hz, 1 H, PhC*H*H), 5.14−5.18, 5.22−5.29 (2 m, 2 H, CH=CH_2), 5.83−6.00 (m, 1 H, C*H*=CH_2), 6.85 (d, ^3J = 8.7 Hz, 2 H, Ph), 7.23−7.42 (m, 7 H, Ph). − Maldi MS: *m*/*z* = 653 [M + Na^+]. − $C_{35}H_{54}O_6SSi$ (631.0): calcd. C 66.63, H 8.63; found C 66.61, H 8.55.

Ethyl 4-*O*-Allyl-2-*O*-benzyl-6-*O*-triisopropylsilyl-1-thio-β-D-glucopyranoside (28): DDQ (5.20 g, 22.9 mmol) was added to a solution of compound **27** (12.0 g, 19.0 mmol) in dichloromethane (100 mL) and H_2O (10 mL) and the mixture was stirred for 5 h. The reaction mixture was washed with aqueous $NaHCO_3$ solution (50 mL) and H_2O (20 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. Purification of the residue by flash chromatography (petroleum ether/ethyl acetate, 9:1) afforded compound **28** (9.23 g, 95%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.65. − $[\alpha]_D^{22}$ = −5 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.01−1.05 [br. s, 21 H, 3 C*H*(CH_3)$_2$], 1.22 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.45 (br. s, 1 H, OH), 2.62−2.71 (m, 2 H, SCH_2CH_3), 3.15−3.23 (m, 2 H, 2-H, 5-H), 3.35 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.5 Hz, 1 H, 4-H), 3.62 (dd, $^3J_{3,4}$ = $^3J_{3,2}$ = 9.5 Hz, 1 H, 3-H), 3.82 (dd, $^2J_{6,6}$ = 11.2, $^3J_{6,5}$ = 4.1 Hz, 1 H, 6-H), 3.89 (dd, $^2J_{6,6}$ = 11.2, $^3J_{6,5}$ = 1.7 Hz, 1 H, 6-H), 4.05−4.17, 4.18−4.28 (2 m, 2 H, $OCH_2CH{=}CH_2$), 4.35 (d, $^3J_{1,2}$ = 9.6 Hz, 1 H, 1-H), 4.60 (m, 1 H, ^2J = 10.9 Hz, PhC*H*H), 4.89 (d, ^2J = 10.9 Hz, 1 H, PhC*H*H), 5.06−5.11, 5.13−5.23 (2 m, 2 H, $CH{=}CH_2$), 5.75−5.91 (m, 1 H, $CH{=}CH_2$), 7.19−7.36 (m, 5 H, Ph). − Maldi MS: m/z = 533 [M + Na^+]. − $C_{27}H_{46}O_5SSi$ (510.8): calcd. C 63.49, H 9.08; found C 63.51, H 8.99.

Ethyl 4-*O*-Allyl-2-*O*-benzyl-3-*O*-(3-bromomethylbenzyl)-6-*O*-triisopropylsilyl-1-thio-β-D-glucopyranoside (29): Compound **28** (5.11 g, 10.0 mmol), dissolved in dimethylformamide (20 mL), was added to a suspension of α,α′-dibromo-*m*-xylylene (10.6 g, 40.0 mmol) and sodium hydride (312 mg, 13.0 mmol) in dimethylformamide (50 mL). The resulting mixture was stirred for 20 h at room temp. and then H_2O (200 mL) was added. After extraction of the mixture with ethyl acetate (5 × 50 mL), the organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. Flash chromatography (petroleum ether/ethyl acetate, 29:1) of the residue afforded compound **29** (3.50 g, 50%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 9:1): R_f = 0.39. − $[\alpha]_D^{22}$= +11 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.05−1.10 [br. s, 21 H, 3 C*H*(CH_3)$_2$], 1.29 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.69−2.78 (m, 2 H, SCH_2CH_3), 3.28 (m, 1 H, 5-H), 3.37 (dd, $^3J_{2,1}$ = $^3J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 3.48−3.61 (m, 2 H, 3-H, 4-H), 3.85−4.03 (m, 2 H, 2 6-H), 4.15−4.38 (m, 2 H, $OCH_2CH{=}CH_2$), 4.42−4.46 (m, 3 H, 1-H, 2 PhC*H*H), 4.70 (d, ^2J = 10.4 Hz, 1 H, PhC*H*H), 4.83 (s, 2 H, $PhCH_2Br$), 4.92 (d, ^2J = 10.4 Hz, 1 H, PhC*H*H), 5.13−5.17, 5.21−5.29 (2 m, 2 H, $CH{=}CH_2$), 5.86−5.94 (m, 1 H, $CH{=}CH_2$), 7.25−7.40 (m, 5 H, Ph). − Maldi MS: m/z = 715, 717 [M + Na^+]. − $C_{35}H_{53}BrO_5SSi$ (693.9): calcd. C 60.59, H 7.70; found C 60.56, H 7.44.

Benzyl 2,3-Di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-α-D-glucopyranoside (31): Compound **30** (21.2 g, 47.0 mmol) and imidazole (5.79 g, 85.0 mmol) were dissolved in dimethylformamide (200 mL) and the resulting mixture was cooled to 0 °C. After addition of TBDPSCl (14.6 mL, 56.0 mmol), the solution was warmed to room temp. and stirred for 4 h. H_2O (400 mL) was added, and the aqueous layer was extracted with dichloromethane (3 × 200 mL). The combined organic extracts were dried with $MgSO_4$ and the solvents were removed under reduced pressure. Flash chromatography (toluene/ethyl acetate, 19:1) of the residue afforded compound **31** (30.5 g, 94%) as a colorless oil. − TLC (toluene/ethyl acetate, 9:1): R_f = 0.58. − $[\alpha]_D^{22}$ = +53 (c = 1.5, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.05 [br. s, 9 H, $C(CH_3)_3$], 2.40 (d, ^3J = 1.1 Hz, 1 H, OH), 3.48−3.91 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 2 6-H), 4.50−4.85 (m, 6 H, 1-H, 5 PhC*H*H), 4.99 (d, ^2J = 11.3 Hz, 1 H, PhC*H*H), 7.15−7.42 (m, 21 H, Ph), 7.67−7.72 (m, 4 H, Ph). − Maldi MS: m/z = 711 [M + Na^+]. − $C_{43}H_{48}O_6Si$ (689.9): calcd. C 74.86, H 7.01; found C 74.88, H 7.09.

Benzyl 2,3-Di-*O*-benzyl-6-*O*-(*tert*-butyldiphenylsilyl)-4-*O*-(4-methoxybenzyl)-α-D-glucopyranoside (32): *p*-Methoxybenzyl chloride (6.50 mL, 47.9 mmol) was added to a suspension of **31** (30.0 g, 43.5 mmol) and sodium hydride (1.25 g, 52.2 mmol) in dimethylformamide (100 mL) at room temp. and the resulting mixture was stirred for 20 h. The reaction mixture was quenched by addition of methanol (10 mL), followed by the evaporation of the solvents under reduced pressure. The residue was dissolved in ethyl acetate (200 mL) and washed with H_2O (2 × 100 mL). The aqueous layer was reextracted with ethyl acetate (50 mL) and the combined organic layer was dried with $MgSO_4$. Purification of the residue by flash chromatography (petroleum ether/ethyl acetate, 9:1) afforded compound **32** (27.0 g, 77%) as a colorless oil. − TLC (toluene/ethyl acetate, 9:1): R_f = 0.63. − $[\alpha]_D^{22}$ = +12 (c = 0.5, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.05 [br. s, 9 H, $C(CH_3)_3$], 3.52−3.82 (m, 8 H, 2-H, 4-H, 5-H, 2 6-H, OCH_3), 4.05 (dd, $^3J_{3,4}$ = $^3J_{3,2}$ = 9.2 Hz, 1 H, 3-H), 4.52−4.87 (m, 8 H, 1-H, 7 PhC*H*H), 4.99 (d, 1 H, ^{2} = 10.8 Hz, PhC*H*H), 6.76 (d, ^3J = 8.6 Hz, 2 H, Ph), 7.06 (d, ^3J = 8.6 Hz, 2 H, Ph), 7.29−7.43 (m, 23 H, Ph), 7.68−7.73 (m, 2 H, Ph). − Maldi MS: m/z = 832 [M + Na^+]. − $C_{51}H_{56}O_7Si$ (810.1): calcd. C 75.62, H 6.97; found C 75.50, H 7.08.

Benzyl 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-α-D-glucopyranoside (33): nBu$_4$NF solution (1M in tetrahydrofuran, 35.0 mL, 35.0 mmol) was added to a solution of **32** (26.0 g, 32.1 mmol) in tetrahydrofuran (200 mL), and the mixture was stirred for 20 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1→2:1) to afford compound **33** (17.4 g, 95%) as a colorless solid. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.14. − $[\alpha]_D^{22}$ = +57 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.48−3.52 (m, 2 H, 2-H, 6-H), 3.67−3.79 (m, 7 H, 4-H, 5-H, 6-H, OH, OCH_3), 4.05 (dd, $^3J_{3,4}$ = $^3J_{3,2}$ = 9.2 Hz, 1 H, 3-H), 4.52−4.87 (m, 8 H, 1-H, 7 PhC*H*H), 5.01 (d, ^2J = 10.9 Hz, 1 H, PhC*H*H), 6.85 (d, ^3J = 8.6 Hz, 2 H, Ph), 7.20−7.37 (m, 17 H, Ph). − Maldi MS: m/z = 594 [M + Na^+]. − $C_{35}H_{38}O_7$ (570.7): calcd. C 73.66, H 6.71; found C 73.66, H 6.60.

Spacer-Linked Monosaccharide−Monosaccharide 34: Compound **33** (3.14 g, 5.50 mmol) was added portionwise to a suspension of compound 29 (3.47 g, 5.00 mmol) and sodium hydride (144 mg, 6.00 mmol) in dimethylformamide (50 mL), and the resulting mixture was stirred for 5 h at room temp. H_2O (250 mL) and brine (50 mL) were added, and the mixture was extracted with ethyl acetate (3 × 100 mL). The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 9:1) to afford compound **34** (3.80 g, 64%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.66. − $[\alpha]_D^{22}$ = +26 (c = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.03−1.10 [br. s, 21 H, 3 C*H*(CH_3)$_2$], 1.28 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.67−2.77 (m, 2 H, SCH_2CH_3), 3.23 (m, 1 H, 5b-H), 3.34 (dd, $^3J_{2,1}$ = $^3J_{2,3}$ = 9.2 Hz, 1 H, 2b-H), 3.47 (dd, $^3J_{4,5}$ = $^3J_{4,3}$ = 9.4 Hz, 1 H, 4b-H), 3.52−3.62 (m, 4 H, 2a-H, 4a-H, 6a-H, 3b-H), 3.67 (dd, $^2J_{6,6}$ = 10.6, $^3J_{6,5}$ = 3.4 Hz, 1 H, 6a-H), 3.75−3.77 (m, 4 H, 5a-H, OCH_3), 3.88 (dd, $^2J_{6,6}$ = 10.5, $^3J_{6,5}$ = 3.4 Hz, 1 H, 6b-H), 3.96−4.00 (m, 2 H, 3a-H, 6b-H), 4.15, 4.27 (2 m, 2 H, $OCH_2CH{=}CH_2$), 4.39−4.43 (m, 3 H, 7′-H, 8′-H, 1b-H), 4.52−4.58 (m, 3 H, 8′-H, 2 PhC*H*H), 4.60−4.73 (m, 4 H, 7′-H, 3 PhC*H*H), 4.80−4.83 (m, 4 H, 1a-H, 3 PhC*H*H), 4.87 (d, ^2J = 10.9 Hz, 1 H, PhC*H*H), 4.98 (d, ^2J = 10.3 Hz, 1 H, PhC*H*H), 5.10, 5.18 (2 m, 2 H, $CH{=}CH_2$), 5.83−5.95 (m, 1 H, $CH{=}CH_2$), 6.76 (d, ^3J = 8.5 Hz, 2 H, Ph), 7.02 (d, ^3J = 8.5 Hz, 2 H, Ph), 7.24−7.35 (m, 24 H, Ph). − ^{13}C NMR (151 MHz, $CDCl_3$): δ = 12.0 {Si(*C*H(CH_3)$_2$)$_3$}, 15.0

(SCH_2CH_3), 18.0 {Si[CH(CH_3)$_2$]$_3$}, 24.1 (SCH_2CH_3), 55.2 (OCH_3), 62.5 (6b-C), 68.6 (6a-C), 69.1 ($PhCH_2$), 70.5 (5a-C), 73.0, 73.4 (2 $PhCH_2$), 73.7 ($OCH_2CH=CH_2$), 74.7, 75.3, 75.6, (4 $PhCH_2$), 77.4 (4b-C), 77.5 (4a-C), 79.9 (2a-C), 80.3 (5b-C), 81.7 (2b-C), 82.1 (3a-C), 84.2 (1b-C), 86.7 (3b-C), 95.7 (1a-C). − Maldi MS: *m*/*z* = 1207 [M + Na^+], 1223 [M + K^+]. − $C_{70}H_{90}O_{12}SSi$ (1183.6): calcd. C 71.03, H 7.66; found C 71.35, H 7.66.

Spacer-Linked Monosaccharide−Monosaccharide 35: DDQ (851 mg, 3.75 mmol) was added to a solution of compound **34** (3.70 g, 3.13 mmol) in dichloromethane (100 mL) and H_2O (10 mL), and the mixture was stirred for 5 h at room temp. The organic layer was washed with aqueous $NaHCO_3$ solution (2 × 50 mL) and H_2O (50 mL) and dried with $MgSO_4$. After evaporation of the solvent, the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 6:1→5:1) to afford compound **35** (2.95 g, 89%) as a colorless oil. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.63. − $[\alpha]_D^{22}$ = +20 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.97−1.04 [br. s, 21 H, 3 C*H*(CH_3)$_2$], 1.21 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.24 (br. s, 1 H, OH), 2.60−2.69 (m, 2 H, SCH_2CH_3), 3.19 (m, 1 H, 5b-H), 3.30 (dd, $^3J_{2,1}$ = $^3J_{2,3}$ = 8.7 Hz, 1 H, 2b-H), 3.40−3.58 (m, 6 H, 2a-H, 4a-H, 2 6a-H, 3b-H, 4b-H), 3.64−3.90 (m, 4 H, 3a-H, 5a-H, 2 6b-H), 4.10, 4.23 (2 m, 2 H, $OCH_2CH=CH_2$), 4.35 (d, ^2J = 10.9 Hz, 1 H, PhC*H*H), 4.42−4.83 (m, 12 H, 1a-H, 1b-H, 10 PhC*H*H), 4.94 (d, ^2J = 11.4 Hz, 1 H, PhC*H*H), 5.03−5.19, (m, 2 H, $CH=CH_2$), 5.75−5.87 (m, 1 H, C*H*=CH_2), 7.17−7.34 (m, 24 H, Ph). − Maldi MS: *m*/*z* = 1085 [M + Na^+], 1101 [M + K^+]. − $C_{62}H_{82}O_{11}SSi$ (1063.5): calcd. C 70.02, H 7.77; found C 69.94, H 8.05.

Benzyl 6,3′-*O*-(1,3-Xylylene)-(4-*O*-allyl-2-*O*-benzyl-6-*O*-triisopropyl-α-D-glucopyranosyl)-(1′→4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (36α) and Benzyl 6,3′-*O*-(1,3-Xylylene)-(4-*O*-allyl-2-*O*-benzyl-6-*O*-triisopropyl-β-D-glucopyranosyl)-(1′→4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (36β): TfOH (35 μL, 0.40 mmol) was added to a solution of compound **35** (2.01 g, 2.00 mmol) and NIS (900 mg, 4.00 mmol) in dichloromethane (200 mL). The resulting mixture was stirred for 30 min at room temp. and then washed with aqueous $NaHCO_3$ solution (20 mL) and aqueous $Na_2S_2O_3$ solution (20 mL). The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure. Flash chromatography (petroleum ether/ethyl acetate, 12:1→10:1) of the residue afforded compounds **36α** (1.42 g, 71%) and **36β** (0.25 g, 13%) as colorless oils.

Compound 36α: TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.82. − $[\alpha]_D^{22}$ = +41 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.87−0.91 [br. s, 21 H, 3 C*H*(CH_3)$_2$], 3.16 (dd, $^3J_{2,1}$ = 2.6, $^3J_{2,3}$ = 10.3 Hz, 1 H, 2b-H), 3.27 (dd, $^3J_{5,6}$ = 2.6, $^3J_{5,4}$ = 9.6 Hz, 1 H, 5b-H), 3.39 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 9.4 Hz, 1 H, 4b-H), 3.43−3.47 (m, 2 H, 6a-H, 6b-H), 3.52−3.59 (m, 3 H, 2a-H, 6a-H, 6b-H), 3.72 (dd, $^3J_{4,3}$ = $^3J_{4,5}$ = 10.0 Hz, 1 H, 4a-H), 3.97 (dd, $^3J_{5,4}$ = 10.6, $^3J_{5,6}$ = 6.5 Hz, 1 H, 5a-H), 4.02−4.06 (m, 2 H, 3a-H, OC*H*HCH=CH_2), 4.27−4.34 (m, 2 H, 3b-H, OC*H*HCH=CH_2), 4.37−4.43 (m, 3 H, 3 PhC*H*H), 4.48−4.56 (m, 3 H, 8′-H, 2 PhC*H*H), 4.64 (d, ^2J = 11.9 Hz, 1 H, PhC*H*H), 4.72 (d, ^2J = 13.0 Hz, 1 H, 8′-H), 4.76 (d, ^2J = 12.3 Hz, 1 H, PhC*H*H), 4.79−4.81 (m, 2 H, 1a-H, 7′-H), 4.91 (d, ^2J = 11.3 Hz, 1 H, 7′-H), 5.05 (d, ^2J = 11.9 Hz, 1 H, PhC*H*H), 5.10 (m, 1 H, CH=C*H*H), 5.17−5.19 (m, 2 H, 1b-H, CH=C*H*H), 5.84−5.87 (m, 1 H, C*H*=CH_2), 7.15−7.35 (m, 21 H, Ph), 7.44 (m, 2 H, Ph), 7.59 (s, 1 H, Ph). − ^{13}C NMR (151 MHz, $CDCl_3$): δ = 11.8 {Si[*C*H(CH$_3$)$_2$]$_3$}, 17.9 {Si[CH(*C*H$_3$)$_2$]$_3$}, 61.6 (6a-C), 66.3 (6b-C), 68.5 ($PhCH_2$), 68.7 (5a-C), 71.0 (8′-C), 71.4 (4a-C), 72.6, 73.1 (2 $PhCH_2$), 73.6 (3b-C, $OCH_2CH=CH_2$), 73.9 (7′-C), 74.3 (5b-C), 76.3 (4b-C), 78.5 (3a-C), 79.4 (2b-C), 80.7 (2a-C), 93.5 (1b-C), 94.6 (1a-C). − FAB MS: *m*/*z* = 1023 [MNa^+]. − $C_{60}H_{76}O_{11}Si$ (1001.3): calcd. C 71.91, H 7.65; found C 71.77, H 7.61.

Compound 36β: TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.74. − $[\alpha]_D$ = +37 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.85−0.93 [br. s, 21 H, 3 C*H*(CH_3)$_2$], 3.25 (d, $^2J_{6,6}$ = 10.6 Hz, 1 H, 6a-H), 3.28 (br. s, 1 H, 2b-H), 3.35 (dd, $^3J_{4,3}$ = 8.5, $^3J_{4,5}$ = 10.0 Hz, 1 H, 4a-H), 3.40 (dd, $^3J_{2,3}$ = 9.4, $^3J_{2,1}$ = 3.5 Hz, 1 H, 2a-H), 3.45 (dd, $^2J_{6,6}$ = 10.6, $^3J_{6,5}$ = 5.3 Hz, 1 H, 6a-H), 3.43−3.47 (m, 2 H, 6a-H, 6b-H), 3.72−3.82 (m, 5 H, 3b-H, 4b-H, 5b-H, 2 6b-H), 3.94 (dd, $^3J_{5,4}$ = 10.3, $^3J_{5,6}$ = 5.0 Hz, 1 H, 5a-H), 4.01 (m, 1 H, OC*H*HCH=CH_2), 4.13−4.18 (m, 3 H, 3a-H, OC*H*HCH=CH_2, PhC*H*H), 4.25−4.29 (m, 2 H, 8′-H, PhC*H*H), 4.37 (d, ^2J = 11.9 Hz, 1 H, PhC*H*H), 4.46−4.49 (m, 2 H, 2 PhC*H*H), 4.57 (br. s, 2 H, 2 7′-H), 4.67 (d, ^2J = 12.6 Hz, 1 H, PhC*H*H), 4.71 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1a-H), 4.84 (d, ^2J = 13.4 Hz, 1 H, 8′-H), 4.88 (d, ^2J = 10.1 Hz, 1 H, PhC*H*H), 4.99−5.04, 5.16−5.19 (2 m, 3 H, CH=CH_2, PhC*H*H), 5.36 (br. s, 1 H, 1b-H), 5.80−5.90 (m, 1 H, C*H*=CH_2), 6.93−7.01 (m, 4 H, Ph), 7.11−7.27 (m, 17 H, Ph), 7.34 (m, 2 H, Ph), 7.57 (s, 1 H, Ph). − ^{13}C NMR (151 MHz, $CDCl_3$): δ = 12.0 {Si[*C*H(CH$_3$)$_2$]$_3$}, 18.1 {Si[CH(*C*H$_3$)$_2$]$_3$}, 64.0 (6b-C), 68.3 (6a-C), 68.8 ($PhCH_2$), 69.9 (5a-C), 70.6 (7′-C), 71.1 ($PhCH_2$), 71.5 (8′-C, $OCH_2CH=CH_2$), 72.6 ($PhCH_2$), 74.5 (5b-C), 74.7 ($PhCH_2$), 76.2 (4b-C), 77.4 (4a-C), 77.6 (2b-C), 79.6 (3a-C), 80.8 (2a-C), 82.3 (3b-C), 94.9 (1a-C), 100.4 (1b-C), 116.3 (CH=*C*H_2). − $C_{60}H_{76}O_{11}Si$ (1001.3): calcd. C 71.91, H 7.65; found C 71.80, H 7.81.

Benzyl 6,3′-*O*-(1,3-Xylylene)-(4-*O*-allyl-2-*O*-benzyl-α-D-glucopyranosyl)-(1′→4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (37α): *n*Bu_4NF solution (1 M in tetrahydrofuran, 1.10 mL, 1.10 mmol) was added at 0 °C to a solution of compound **36α** (1.00 g, 1.00 mmol) in tetrahydrofuran (50 mL), and the mixture was then warmed to room temp. and stirred for 3 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (toluene/ethyl acetate, 3:1) to afford compound **37α** (776 mg, 92%) as a colorless foam. − TLC (toluene/ethyl acetate, 2:1): R_f = 0.24. − $[\alpha]_D^{22}$ = +73 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.15−3.25 (m, 3 H, 2b-H, 4b-H, 5b-H), 3.39−3.67 (m, 6 H, 2a-H, 4a-H, 2 6a-H, 2 6b-H), 3.97−4.30 (m, 5 H, 3a-H, 5a-H, 3b-H, $OCH_2CH=CH_2$), 4.42−5.21 (m, 16 H, 1a-H, 1b-H, 2 7′-H, 2 8′-H, 8 PhC*H*H, CH=CH_2), 5.75−5.86 (m, 1 H, C*H*=CH_2), 7.16−7.53 (m, 24 H, Ph). − $C_{51}H_{55}O_{11}$ (844.0): calcd. C 72.58, H 6.57; found C 72.43, H 6.86.

Spacer-Linked Monosaccharide−Disaccharide 38: Compound **16** (972 mg, 1.66 mmol) was added to a suspension of compound **37α** (700 mg, 0.829 mmol), sodium hydride (40 mg, 1.67 mmol), and 15-crown-5 (0.40 mL, 1.64 mmol) in dimethylformamide. The resulting mixture was heated to 60 °C and stirred for 20 h. Methanol (10 mL) and brine (50 mL) were added and the mixture was extracted with ethyl acetate (3 × 50 mL). The organic layer was dried with $MgSO_4$ and the solvents were removed under reduced pressure. Purification of the residue by flash chromatography (petroleum ether/ethyl acetate, 5:1) afforded compound **38** (610 mg, 54%) as a colorless foam. − TLC (toluene/ethyl acetate, 3:1): R_f = 0.60. − $[\alpha]_D^{22}$ = +35 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.33 (t, ^3J = 7.4 Hz, 3 H, SCH_2CH_3), 2.74−2.79 (m, 2 H, SCH_2CH_3), 3.22 (d, $^2J_{6,6}$ = 10.0 Hz, 1 H, 6b-H), 3.28 (dd, $^3J_{2,1}$ = 2.7, $^3J_{2,3}$ = 10.3 Hz, 1 H, 2b-H), 3.34−3.39 (m, 3 H, 4b-H, 5b-H, 6b-H), 3.44−3.50 (m, 3 H, 6a-H, 2c-H, 5c-H), 3.55 (m, 2 H, 2a-H, 6a-H), 3.68−3.72 (m, 2 H, 4a-H, 3c-H), 3.78−3.82 (m, 2 H, 4c-H, 6c-H), 3.87 (m, 1 H, OC*H*HCH=CH_2), 4.03 (dd, $^3J_{5,6}$ = 6.5, $^3J_{5,4}$ = 10.5 Hz, 1 H, 5a-H), 4.09 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 9.2 Hz, 1 H, 3a-H), 4.20−4.26 (m, 3 H, 3b-H, 7′′-H, OC*H*HCH=CH_2), 4.36

(dd, $^3J_{5,6}$ = 5.0, $^2J_{6,6}$ = 10.5 Hz, 1 H, 6c-H), 4.40−4.47 (m, 4 H, 7′′-H, 3 PhC*H*H), 4.53−4.61 (m, 5 H, 1c-H, 7′-H, 3 PhC*H*H), 4.68 (d, ^2J = 13.0 Hz, 1 H, 7′-H), 4.75−4.83 (m, 5 H, 1a-H, 8′-H, 8′′-H, 2 PhC*H*H), 4.87−4.95 (m, 3 H, 8′-H, 8′′-H, PhC*H*H), 5.03−5.13 (m, 3 H, PhC*H*H, CH=CH_2), 5.25 (d, $^3J_{1,2}$ = 2.8 Hz, 1 H, 1b-H), 5.57 (s, 1 H, PhCH), 5.72−5.77 (m, 1 H, C*H*=CH$_2$), 7.19−7.46 (m, 37 H, Ph), 7.60 (s, 1 H, Ph). − FAB MS: *m*/*z* = 1372 [M + Na$^+$]. − $C_{81}H_{88}O_{16}S$ (1349.6): calcd. C 72.09, H 6.58; found C 72.12, H 6.78.

Spacer-Linked Monosaccharide−Disaccharide 39: [(Ph$_3$P)$_3$RhCl] (37 mg, 0.04 mmol) was added to a solution of compound **38** (550 mg, 0.407 mmol) and DBU (15 μL, 0.10 mmol) in ethanol (20 mL), and the resulting mixture was refluxed for 30 min. The solvents were removed under reduced pressure, the residue was dissolved in acetone/conc. HCl. (99:1, 20 mL), and the reaction mixture was refluxed for another 5 min. After neutralization of the reaction mixture with Et$_3$N, the solvents were removed under reduced pressure. The residue was dissolved in ethyl acetate (50 mL) and washed with brine (20 mL). The organic layer was dried with MgSO$_4$ and the solvent was removed under reduced pressure. Purification of the residue by flash chromatography (petroleum ether/ethyl acetate, 4:1) afforded compound **39** (423 mg, 79%) as a colorless foam. − TLC (toluene/ethyl acetate, 3:1): R_f = 0.40. − $[\alpha]_D^{22}$ = +23 (*c* = 1.0, CHCl$_3$). − ^{1}H NMR (600 MHz, CDCl$_3$): δ = 1.32 (t, ^3J = 7.4 Hz, 3 H, SCH$_2$C*H*$_3$), 2.74−2.79 (m, 2 H, SC*H*$_2$CH$_3$), 3.17 (ddd, 1 H, $^3J_{5,6}$ = 3.6 Hz, 3.6, $^3J_{5,4}$ = 9.4 Hz, 5b-H), 3.37−3.48 (m, 7 H, 6a-H, 2b-H, 4b-H, 2 6b-H, 2c-H, 5c-H), 3.54−3.59 (m, 2 H, 2a-H, 4a-H), 3.69−3.79 (m, 4 H, 6a-H, 3c-H, 4c-H, 6c-H), 4.08 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 9.9 Hz, 1 H, 3b-H), 4.11 (dd, $^3J_{3,2}$ = $^3J_{3,4}$ = 9.1 Hz, 1 H, 3a-H), 4.19 (dd, $^3J_{5,6}$ = 7.6, $^3J_{5,4}$ = 10.2 Hz, 1 H, 5a-H), 4.30 (d, ^2J = 12.4 Hz, 1 H, 7′′-H), 4.35 (dd, $^3J_{5,6}$ = 5.0, $^2J_{6,6}$ = 10.5 Hz, 1 H, 6c-H), 4.39 (d, ^2J = 12.4 Hz, 1 H, 7′′-H), 4.45 (d, ^2J = 11.6 Hz, 1 H, PhC*H*H), 4.52−4.67 (m, 8 H, 1c-H, 2 7′-H, 5 PhC*H*H), 4.75−4.90 (m, 7 H, 1a-H, 8′-H, 2 8′′-H, 3 PhC*H*H), 4.96 (d, ^2J = 11.2 Hz, 1 H, 8′-H), 5.03 (d, ^2J = 11.4 Hz, 1 H, PhC*H*H), 5.42 (d, $^3J_{1,2}$ = 2.7 Hz, 1 H, 1b-H), 5.55 (s, 1 H, PhCH), 7.18−7.55 (m, 38 H, Ph). − FAB MS: *m*/*z* = 1332 [M + Na$^+$]. − $C_{78}H_{84}O_{16}S$ (1309.6): calcd. C 71.54, H 6.46; found C 71.60, H 6.32.

Benzyl 6′,3′′-*O*-(1,3-Xylylene)-(2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1′′→4′)-6,3′-*O*-(1,3-xylylene)-(2-*O*-benzyl-α-D-glucopyranosyl)-(1′→4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (40α): TfOH (2 μL) was added to a solution of compound **39** (150 mg, 0.115 mmol) and NIS (52 mg, 0.23 mmol) in dichloromethane (11 mL), and the mixture was stirred for 1 min at room temp. The resulting mixture was washed with aqueous NaHCO$_3$ solution (2 mL) and aqueous Na$_2$S$_2$O$_3$ solution (2 mL), and the organic layer was dried with MgSO$_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 4:1→3:1) to afford compound **40α** (108 mg, 75%) as a colorless foam. − TLC (toluene/ethyl acetate, 3:1): R_f = 0.58. − $[\alpha]_D^{22}$ = +45 (*c* = 0.6, CHCl$_3$). − ^{1}H NMR (600 MHz, CDCl$_3$): δ = 3.22−3.26 (m, 3 H, 4b-H, 6b-H, 5c-H), 3.33−3.44 (m, 4 H, 6a-H, 2b-H, 2c-H, 4c-H), 3.65−3.82 (m, 6 H, 2a-H, 4a-H, 6a-H, 5b-H, 6b-H, 6c-H), 4.04−4.07 (m, 2 H, 3c-H, PhC*H*H), 4.17−4.27 (m, 6 H, 3a-H, 5a-H, 3b-H, 6c-H, 7′′-H, PhC*H*H), 4.45−4.67 (m, 9 H, 2 7′-H, 8′-H, 6 PhC*H*H), 4.90 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1a-H), 5.00 (d, ^2J = 11.1 Hz, 1 H, PhC*H*H), 5.15 (d, ^2J = 11.2 Hz, 1 H, 8′-H), 5.29 (d, $^3J_{1,2}$ = 2.8 Hz, 1 H, 1b-H), 5.31 (d, $^3J_{1,2}$ = 3.0 Hz, 1 H, 1c-H), 5.40 (s, 1 H, PhCH), 6.96 (m, 1 H, Ph), 7.11−7.47 (m, 36 H, Ph), 7.66 (s, 1 H, Ph). − ^{13}C NMR (151 MHz, CDCl$_3$): δ = 66.1 (5c-C), 67.1 (6a-C), 68.3 (6b-C), 68.6 (3c-C), 69.4 (6c-C), 69.2 (PhCH$_2$), 69.5 (5a-C), 70.2 (7′-C), 70.9 (4b-C), 71.5 (3b-C), 71.7 (7′′-C), 72.0 (PhCH$_2$), 72.1 (4a-C), 73.0 (8′-C, PhCH$_2$), 73.1 (PhCH$_2$), 73.6 (8′′-C), 74.3 (5b-C), 78.3 (3a-C), 79.7 (2c-C), 80.5 (2a-C), 81.1 (4c-C), 81.9 (2b-C), 93.0 (1b-C), 95.0 (1c-C), 95.4 (1a-C), 101.5 (PhCH). − FAB MS: *m*/*z* = 1269 [M + Na$^+$]. − $C_{76}H_{78}O_{16}$ (1247.4): calcd. C 73.18, H 6.30; found C 72.71, H 6.41.

Acetyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-(2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α/β-D-glucopyranoside (41α/β): A mixture of compound **40α** (25 mg, 0.020 mmol) and palladium on carbon (10%, 10 mg) in methanol/ethyl acetate (1:1, 4 mL) and formic acid (0.2 mL) was stirred under hydrogen for 20 h. After filtration and concentration under reduced pressure, the residue was dissolved in acetic anhydride/pyridine (1:1, 4 mL) and stirred for 20 h. The solution was concentrated under reduced pressure, coevaporated with toluene, and purified by flash chromatography (toluene/ethyl acetate, 1:1) to afford known compound **41α/β** (17 mg, 88%) as a colorless oil.[26]

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