Reiterative Intramolecular Glycosylation Supported by a Rigid Spacer

Soumendu Paul,[a] Matthias Müller,[a] and Richard R. Schmidt*[a]

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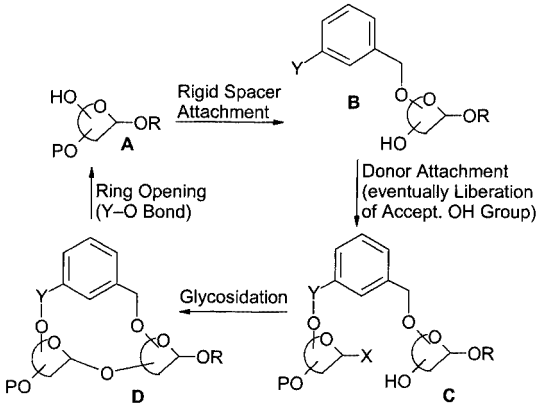
This paper describes a synthesis of trisaccharide **1** by reiterative intramolecular glycosidation with 5-(bromomethyl)-2-methylbenzoic acid (**5a**) as starting material for the generation of a rigid spacer. Intramolecular glycosidation of donor–acceptor-tethered compound **24** yielded disaccharide **25**. Transesterification of **25** afforded **26**, which generated a new linking centre for the next spacer. Repetition of the previous cycle on **26** yielded trisaccharide **1**, which again presents an extension point for the synthesis of higher saccharides.

Introduction

Thanks to the prominent role of carbohydrates in biology,[1] glycoside bond formation is an area of intense activity in contemporary research in organic chemistry. The importance of carbohydrates in biology stems from Nature's ability to effect glycosylation with absolute stereoselectivity, a feature which in many cases is still only a desire in chemists' repertoire of methodology. In recent years, intramolecular glycosylation[2] has emerged as a powerful tool for stereoselective construction of glycosidic linkages. The various approaches to intramolecular glycosylation[2,3] include the spacer-mediated linkages of donor and acceptor through nonreacting centres,[2,3−5] and among these we have devised the *rigid spacer-mediated concept*,[2,6−10] which offers the advantages of good yields and a high degree of anomeric stereocontrol. To allow for reiterative glycosylation by this approach, we envisioned the use of unsymmetrical rigid spacers.[9] Scheme 1 depicts a general outline for reiterative glycosylation by this approach. As shown for **A**, an acceptor with two selectively accessible hydroxy groups is required. Selective attachment of the rigid spacer by one handle to one of the hydroxy groups of **A** affords **B**. Then, tethering of the donor, which also has two selectively accessible hydroxy groups, to the other handle of the rigid spacer yields **C**. Glycosidation (→ **D**) and ring-opening of the spacer−disaccharide macrocycle to liberate 1 equiv. of **A** concludes this conceptual approach.

As our first attempt, we describe the synthesis of trisaccharide **1** (Scheme 2), which we selected as a target for our synthetic endeavours. As indicated in Scheme 2, **1** can be assembled from known building blocks **2**,[9,11,12] **3**,[13] and **4**.[14] *tert*-Butyl 5-(bromomethyl)-2-methylbenzoate (**5a**) (**5**: Y = CO_2tBu, R = Me) was used to provide the desired rigid spacer. The 2-methyl group of **5a** was introduced to reduce the conformational space in favour of the reacting centres (Scheme 2, b). A [3-(bromomethyl)phenyl]silyl rigid spacer **5b** (**5**: Y = SiiPr$_2$Cl, R = H) was also investigated.

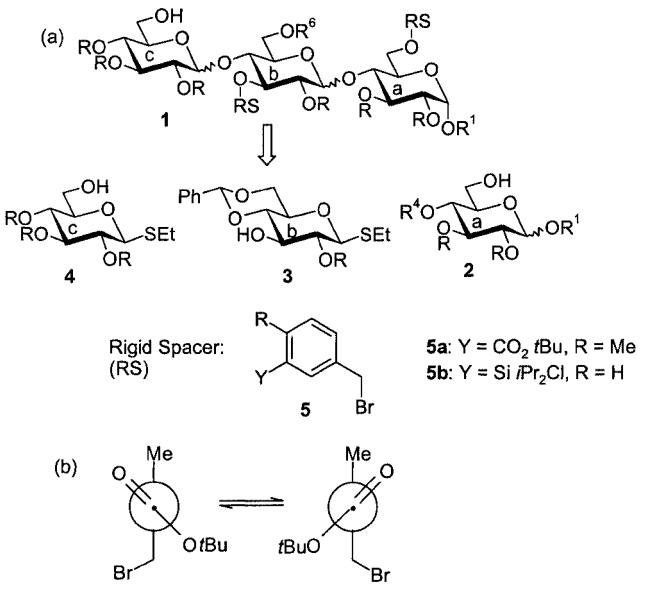


Scheme 1. Reiterative intramolecular oligosaccharide synthesis, R increasing with each cycle

Results and Discussion

Compound **2a**[9] reacted smoothly with spacer **5a** under standard base-catalysed conditions, to yield **6** in 65% yield with NaH as base and DMF as solvent (Scheme 3). To achieve the desired (1→4)-glycosidic linkage, and also to facilitate spacer linkage to acceptor **3**, so as to yield a 14-membered macrocycle,[2,7] it was necessary to replace the methoxyphenylmethyl (MPM) group. Hence, **6** was treated with DDQ/dichloromethane to yield the deprotected compound, which was treated without purification with levulinic acid in the presence of DCC/DMAP to furnish the 4-

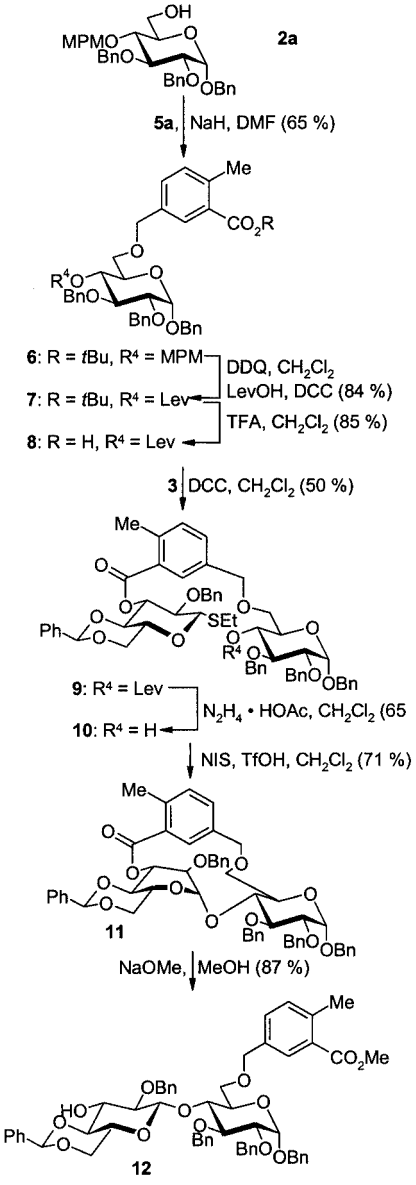
[a] Fachbereich Chemie, University of Konstanz,
Postfach M 725, 78457 Konstanz, Germany
Fax: (internat.) + 49-(0)7531/88-3135
E-mail: Richard.Schmidt@uni-konstanz.de



Scheme 2. (a) Retrosynthesis of target molecule **1**; (b) preferred conformers of **5a**; R = Bn; R^1 = Bn, Me; R^4 = MPM, H; R^6 = PhCHOMe; RS = rigid spacer

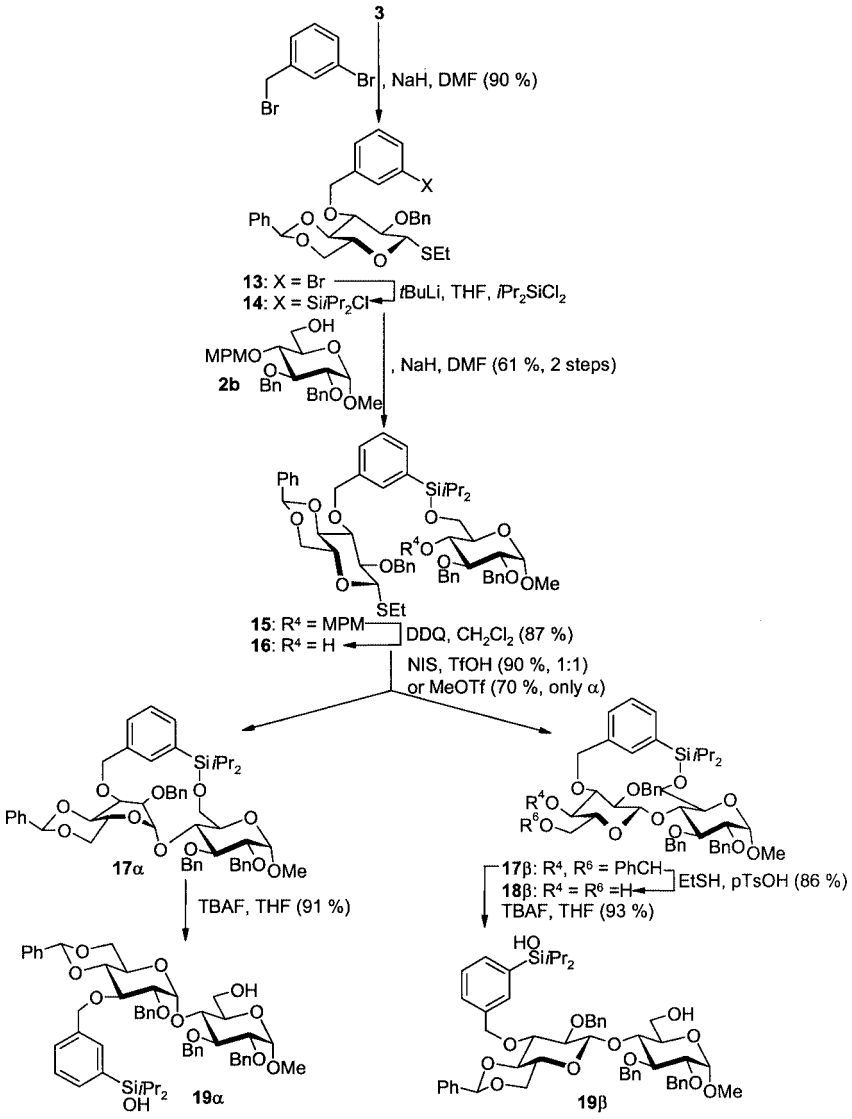
O-levulinoyl derivative **7** in 84% yield. Removal of the *tert*-butyl group of **7** with TFA in dichloromethane yielded acid **8**, which, when treated with **3** under standard esterification conditions (DCC/DMAP), furnished ester **9** in 50% yield. To set the stage for the generation of a 14-membered macrocycle for glycosylation, the levulinoyl group of **9** was removed with hydrazinium acetate in dichloromethane to yield donor−acceptor-tethered compound **10**. Glycosylation of **10** under *N*-iodosuccinimide/triflic acid (NIS/TfOH) mediated conditions afforded the disaccharide **11** in 71% yield. The reaction proceeded stereoselectively to yield the β anomer. This result was unexpected, because 3-L(β)-donor/5,4-L-*threo*-acceptor tethering with a rigid *m*-xylylene spacer had produced the Glcα(1−4)Glc linkage.[2,4−7] To generate an anchoring point for further glycosylation, **11** was untethered by transesterification with sodium methoxide in methanol, to provide **12** in quantitative yield. The 3′-hydroxy group of **12** was able to serve as the centre for the next spacer linkage.

Encouraged by the results achieved with the 3-(methoxycarbonyl)benzyl spacer **5**, we decided to explore the efficacy of using a 3-silylbenzyl spacer in intramolecular glycosidation (Scheme 4). The 3-*O*-unprotected glucoside **3**,[13] when treated with *m*-bromobenzyl bromide in the presence of NaH in DMF, furnished 3-bromobenzyl derivative **13** in 90% yield. Compound **13**, on treatment with diisopropylsilyl dichloride in the presence of *tert*-butyllithium in THF at −100 °C, furnished silyl chloride derivative **14**. Next, **14** was treated with acceptor **2b**[11] under standard basic conditions (NaH, DMF) to yield the spacer-linked compound **15**. In the light of our previous success, glycosylation through the intermediacy of a 14-membered macrocycle was an obvious choice, so **15** was treated with DDQ to remove the methoxyphenylmethyl (MPM) group to provide **16** in 87% yield. Glycosidation of **16** under NIS/TfOH-mediated conditions gave a 1:1 mixture of **17α** and **17β** in an overall yield of 90%, whereas glycosidation under methyl triflate mediated conditions yielded the α anomer **17α** in 70% yield. The silyl tethers of compounds **17α** and **17β** were cleaved by tetrabutylammonium fluoride (TBAF) in tetrahydrofuran to furnish **19α** and **19β** in 91% and 93% yields, respectively. The benzylidene ring of **17β** was cleaved with ethanethiol and *p*-toluenesulfonic acid (PTSA) to afford **18β** in 86% yield.



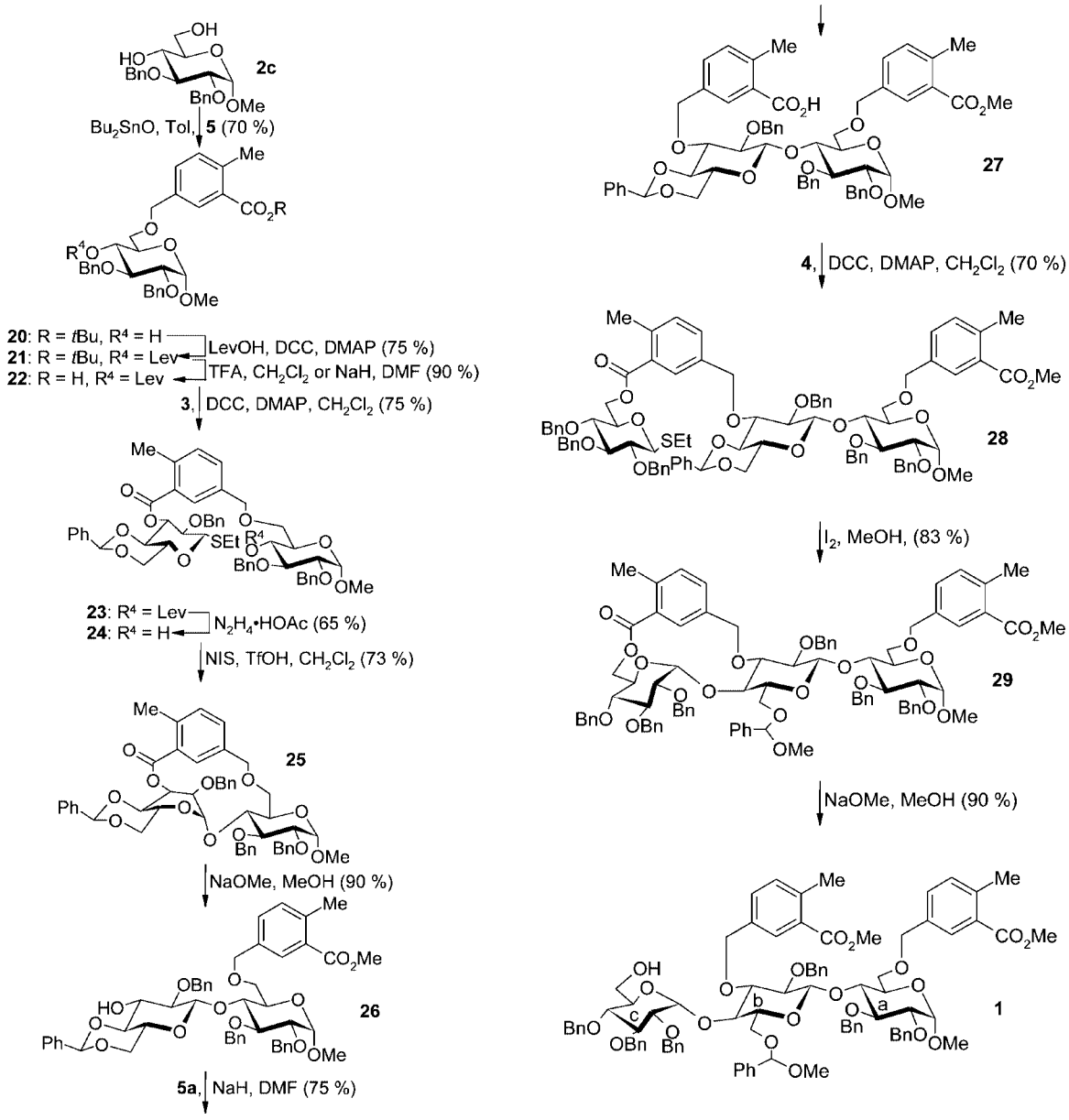
Scheme 3. Synthesis of disaccharide **12** with a 3-(methoxycarbonyl)-benzyl spacer

With the success of the methods described above behind us, we chose to reflect on the suitability of either of the two methods for the synthesis of target molecule **1**. Close evaluation revealed the 3-(bromomethyl)benzoyl spacer **5a**



Scheme 4. Synthesis of disaccharides **19** with a 3-silylbenzyl spacer

to be better suited with regard both to its ease of synthesis and to the stereoselectivity of the glycosylation reaction. The target molecule **1** was synthesised by the sequence of reactions outlined in Scheme 5. Acceptor **2c**[12] was transformed into compound **20** (70%) via the dibutylstannylene acetal (Bu_2SnO/toluene) and subsequent treatment with spacer **5a**. The 4-hydroxy group of **20**, which was destined to act as an acceptor in the glycosylation reaction, was protected as the levulinoyl ester **21** under standard conditions (DCC/DMAP). The *tert*-butyl ester group of **21** was cleaved with trifluoroacetic acid in dichloromethane to yield the acid **22**. Esterification of **22** with **3** (DCC/DMAP) afforded **23** (75%), the levulinoyl group of which was removed by the action of hydrazinium acetate to yield donor−acceptor-tethered **24** (65%). Glycosylation of **24** under NIS/TfOH conditions furnished the disaccharide **25** in 73% yield; it was also gratifying to observe that the reaction had proceeded selectively to yield the β anomer. To enable further glycosylation, **25** was transesterified with sodium methoxide in methanol to yield 3′-*O*-unprotected disaccharide **26** (90%). The spacer **5a** was now linked to the 3′-hydroxy group of **26** under standard basic conditions (NaH, DMF). Much to our surprise, however, this reaction proceeded with a concomitant hydrolysis of the *tert*-butyl ester group to furnish benzoic acid derivative **27** in 75% yield. This, which to the best of our knowledge has not previously been reported, constitutes a novel method for base-assisted cleavage of the *tert*-butyl ester group.[15] Esterification of **27** with donor **4**[14] under standard conditions yielded donor−acceptor-tethered intermediate **28** (70%). Since, in our earlier glycosylations (Schemes 3 and 4), the nucleophile (i.e., the hydroxy group of the glycosyl acceptor) had been unprotected and not part of a rigid ring system, we conjectured that it would be of interest to investigate glycosylation with an acceptor in which the reactive centre was part of an acid-sensitive ring. We therefore decided to use



Scheme 5. Synthesis of target molecule **1**

28 directly for glycosylation, without cleavage of the benzylidene acetal ring. Iodine in methanol, previously reported for the cleavage of acetals,[3,16] seemed to be a good reagent for glycosylation of **28**; we surmised that iodine, being a soft atom, would coordinate to the softer sulfur atom at the anomeric centre, in preference to the oxygen of the acetal ring. Thus, a carbocation would be generated at the anomeric carbon atom, which might invite an attack from the secondary oxygen atom of the benzylidene ring (4′-*O* of **28**) in preference to the primary oxygen atom (i.e. 6′-*O* of **28**), furnishing a fourteen-membered ring, due to its proximity to the anomeric centre, and bring about glycosylation. This hypothesis worked in practice; **28**, when treated with a 5% (w/v) solution of iodine in methanol, reacted smoothly at room temperature to yield **29** (α anomer only) in 83% yield. It needs to be mentioned, however, that longer reaction times resulted in the cleavage both of the newly formed glycosidic linkage as well as of the α-methoxybenzyl group. Transesterification of **29** with sodium methoxide in methanol yielded the target molecule **1** in 90% yield. Compound **1**, by virtue of its 6′′-hydroxy group, presents an extension point for further synthesis.

Conclusion

In conclusion, we have successfully demonstrated the utility of the rigid spacer-based intramolecular glycosidation method in the stereoselective construction of glycosidic linkages for the synthesis of higher saccharides by reiterat-

ive glycosylation. Without anchimeric assistance α- and β-linkages were stereoselectively generated.

Experimental Section

General: All air- and/or water-sensitive reactions were carried out under argon in dry solvents under anhydrous conditions. Reactions were monitored by TLC on Merck silica gel coated plastic sheets (60 F_{254}) with UV light as visualising 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 with 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 a 3-nitrobenzyl alcohol matrix. MALDI mass spectra were recorded with a Kratos compact spectrometer with a 2,5-dihydroxybenzoic acid matrix.

***tert*-Butyl 5-(Bromomethyl)-2-methylbenzoate (5a):** Hydrogen bromide in acetic acid (33%, 13 mL) was added to a mixture of 2-methylbenzoic acid (4.08 g, 30.0 mmol), paraformaldehyde (2.50 g, 83.0 mmol) and *O*-phosphoric acid (85%, 7.0 mmol), and the mixture was stirred for a period of 3 h at 115 °C. The system was allowed to cool and poured into ice-cold water (500 mL), and the precipitated solid material was filtered off and purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) to yield pure 5-(bromomethyl)-2-methylbenzoic acid (4.26 g, 62%) as colourless crystals. TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.34; m.p. 120−122 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.66 (s, 3 H, CH_3), 4.51 (s, 2 H, ArCH_2Br), 7.27 (d, J = 7.8 Hz, 1 H, 3-H), 7.49 (dd, J = 7.8, J = 2.0 Hz, 1 H, 4-H), 8.10 (d, J = 2.0 Hz, 1 H, 6-H) ppm. EI MS: m/z = 230 [M^+], 149 [M − Br]$^+$. $C_9H_9BrO_2$ (229.1): calcd. C 47.19, H 3.96; found C 47.53, H 4.24. This compound (4.58 g, 20.0 mmol) was dissolved in dichloromethane (200 mL) and cyclohexane (200 mL), and *tert*-butyl trichloroacetimidate[17] (8.74 g, 40.0 mmol) in cyclohexane (20 mL) was added, followed by the dropwise addition of boron trifluoride−diethyl ether (0.63 mL, 5.0 mmol). The mixture was stirred for a period of 1 h at room temp and washed with sodium bicarbonate solution (100 mL), the organic phase was dried with sodium sulfate, and the solvent was evaporated in vacuo. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 97:3) to yield pure **5a** as a colourless oil. TLC (petroleum ether/ethyl acetate, 9:1): R_f = 0.47. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.60 [br. s, 9 H, C$(CH_3)_3$], 2.56 (s, 3 H, CH_3), 4.49 (s, 2 H, ArCH_2Br), 7.18 (d, J = 7.9 Hz, 1 H, 3-H), 7.39 (dd, J = 7.9, J = 2.0 Hz, 1 H, 4-H), 7.82 (d, J = 2.0 Hz, 1 H, 6-H) ppm. EI MS: m/z = 286 [M^+], 205 [M − Br]$^+$. $C_{13}H_{17}BrO_2$ (285.2): calcd. C 54.75, H 6.01; found C 54.87, H 5.97.

***tert*-Butyl 5-[Benzyl 2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-α-D-glucopyranosid-6-yloxymethyl]-2-methylbenzoate (6):** NaH (96 mg, 4.00 mmol) and **2a**[9] (1.14 g, 2.0 mmol) were added to a solution of **5** (856 mg; 3.00 mmol) in DMF (20 mL). The mixture was stirred at room temp. for 20 h, by which time the reaction had proceeded to completion. The reaction mixture was diluted with MeOH (10 mL) and ethyl acetate (100 mL) and washed with brine (100 mL). The aqueous phase was reextracted with ethyl acetate (3×50 mL); the combined organic extract was washed with water and brine, dried with sodium sulfate and concentrated in vacuo to yield the crude compound as an oil, which was purified by flash chromatography (petroleum ether/ethyl acetate, 5:1) to provide **6** as a colourless oil (1.00 g; 65%). R_f = 0.58. $[\alpha]_D$ = +39 (c = 1.00, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.58 (s, 9 H), 2.56 (s, 3 H, ArCH_3), 3.54−3.82 (m, 8 H, 2-H, 4-H, 5-H, 6−H_2, OCH_3), 4.05 (dd, $J_{3,4}$ = $J_{3,2}$ = 9.2 Hz, 1 H, 3-H), 4.38−4.87 (m, 11 H, 1-H, 10 ArCHH), 5.03 (d, J = 10.9 Hz, 1 H), 6.79 (d, J = 8.6 Hz, 2 H, Ar), 7.02 (d, J = 8.6 Hz, 2 H, Ar), 7.17−7.44 (d, J = 1.8 Hz, 1 H, Ar) ppm. FAB MS: m/z = 797 [M^+ + Na^+]. $C_{48}H_{54}O_9$ (774.9): calcd. C 74.40, H 7.02; found C 73.83, H 6.99.

***tert*-Butyl 5-(Benzyl 2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-glucopyranosid-6-yloxy-methyl)-2-methylbenzoate (7):** Water (5 mL) and DDQ (152 mg, 0.67 mmol) were added to a solution of **6** (470 mg, 0.61 mmol) in dichloromethane, and the reaction mixture was stirred at room temp. for a period of 5 h. It was then washed with sodium bicarbonate solution (10 mL) and water (10 mL), and the organic phase was dried with sodium sulfate and evaporated in vacuo. The residue was taken up in dichloromethane (50 mL), and DCC (629 mg, 3.05 mmol), levulinic acid (709 mg, 6.10 mmol) and DMAP (0.02 g) were added. The reaction mixture was stirred for a period of 20 h and then filtered, and the organic phase was concentrated in vacuo to yield the crude compound, which was purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) to yield pure **7** as a colourless oil (386 mg, 84%). R_f = 0.44. $[\alpha]_D$ = +19 (c = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.58 [s, 9 H, C$(CH_3)_3$], 2.11 (s, 3 H, COCH_3), 2.28−2.63 (m, 7 H, CCH_2CH_2C, ArCH_3), 3.45−3.60 (m, 3 H, 2-H, 6-H_2), 3.90 (m, 1 H, 5-H), 3.99 (dd, $J_{3,2}$ = $J_{2,3}$ = 9.5 Hz, 1 H, 3-H), 4.47−4.68 (m, 7 H, 7 ArCHH), 4.83 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.90 (d, J = 11.6 Hz, 1 H, ArCHH), 5.07 (dd, $J_{4,3}$ = $J_{4,5}$ = 10.1 Hz, 1 H, 4-H), 7.16−7.43 (m, 17 H, Ar), 7.74 (d, J = 1.8 Hz, 1 H, Ar) ppm. FAB MS: m/z = 775 [M^+ + Na^+]. $C_{45}H_{52}O_{10}$ (752.9): calcd. C 71.79, H 6.96; found C 71.35, H 7.02.

5-(Benzyl 2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-glucopyranosid-6-yloxymethyl)-2-methylbenzoic Acid (8): Trifluoroacetic acid (5 mL) was added to a solution of **7** (0.33 g, 0.44 mmol) in dichloromethane (30 mL) and the reaction mixture was stirred for 5 h at room temp. Toluene (30 mL) was added, and the solvent was evaporated in vacuo to yield crude **8**, which was purified by flash chromatography (toluene/ethyl acetate, 1:1) to furnish pure **8** as a crystalline compound, which was recrystallised from petroleum ether/ethyl acetate. TLC (toluene/ethyl acetate, 1:1): R_f = 0.27; m.p. 84 °C. $[\alpha]_D$ = +36 (c = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, COCH_3), 2.28−2.68 (m, 7 H, CCH_2CH_2C, ArCH_3), 3.48−3.60 (m, 3 H, 2-H, 6-H_2), 3.88 (m, 1 H, 5-H), 3.99 (dd, $J_{3,4}$ = $J_{3,2}$ = 9.4 Hz, 1 H, 3-H), 4.50−4.71 (m, 7 H, 7 ArCHH), 4.83 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.90 (d, J = 11.6 Hz, 1 H, ArCHH), 5.08 (dd, $J_{4,3}$ = $J_{4,5}$ = 10.1 Hz, 1 H, 4-H), 7.22−7.49 (m, 17 H, Ar), 7.97 (d, J = 1.8 Hz, 1 H, Ar) ppm. $C_{41}H_{44}O_{10}$ (696.8): calcd. C 70.67, H 6.36; found C 70.63, H 6.46.

Spacer-Linked Monosaccharide−Monosaccharide 9: DCC (0.223 g, 1.08 mmol) and a catalytic amount of DMAP (0.02 g) were added to a solution of **8** (0.502 g, 0.72 mmol) and **3** (0.346 mg, 0.86 mmol) in dichloromethane (30 mL). The reaction mixture was stirred for 20 h at room temp., by which time the reaction had reached completion. The reaction mixture was filtered, and the solvent was removed in vacuo. The crude compound thus obtained was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) to yield pure **9** as a colourless foam (370 mg, 50%). TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.32. $[\alpha]_D$ = +15 (c = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.34 (t, J = 7.4 Hz, 3 H, SCH_2CH_3), 2.05 (s, 3 H, COCH_3), 2.22−2.67 (m, 7 H, CCH_2CH_2C, ArCH_3), 2.76−2.83 (m, 2 H, SCH_2CH_3), 3.45 (dd, $J_{6,6}$ = 10.8, $J_{6,5}$ = 4.6 Hz, 1 H, 6a-H), 3.52 (m, 2 H, 2a-H, 6a-H),

3.58 (m, 1 H, 5a-H), 3.64 (dd, $J_{2,1} = J_{2,3} = 9.2$ Hz, 1 H, 2b-H), 3.73−3.79 (m, 2 H, 4b-H, 6b-H), 3.85 (m, 1 H, 5a-H), 3.97 (dd, $J_{3,2} = J_{3,4} = 9.4$ Hz, 1 H, 3a-H), 4.38 (m, 5 H, 1b-H, 4 ArC*H*H), 4.43−4.53 (m, 4 H, 4 ArC*H*H), 4.60−4.69 (m, 5 H, 1b-H, 4 ArC*H*H), 4.81 (d, $J_{1,2} = 3.6$ Hz, 1 H, 1a-H), 4.86 (d, $J = 11.7$ Hz, 1 H, ArC*H*H), 5.09 (dd, $J_{4,3} = J_{4,5} = 9.7$ Hz, 1 H, 4a-H), 5.48 (s, 1 H, PhC*H*), 5.62 (dd, $J_{3,4} = J_{3,2} = 9.2$ Hz, 1 H, 3b-H), 7.14−7.39 (m, 27 H, Ar), 7.76 (s, 1 H, Ar) ppm. MALDI MS: *m*/*z* = 1103 [MNa$^+$], 1119 [MK$^+$]. $C_{63}H_{68}O_{14}S$ (1081.3): calcd. C 69.98, H 6.34; found C 69.53, H 6.31.

Spacer-Linked Monosaccharide−Monosaccharide 10: Hydrazinium acetate (0.028 g, 0.30 mmol) was added to a solution of **9** (0.342 g, 0.30 mmol) in dichloromethane (10 mL) and MeOH (1 mL), followed by pyridine (1 mL). The mixture was stirred for 2 h at room temp and then filtered, and the solvent was removed in vacuo. The crude compound thus obtained was flash chromatographed to yield pure **10** (0.192 g, 65%). TLC (petroleum ether/ethyl acetate, 2:1): $R_f = 0.38$. $[\alpha]_D = +5$ ($c = 0.5$, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.34 (t, $J = 7.4$ Hz, 3 H, SCH_2CH_3), 2.50 (s, 3 H, $ArCH_3$), 2.76−2.83 (m, 2 H, SCH_2CH_3), 3.50 (dd, $J_{6,6} = 9.6$, $J_{6,5} = 3.6$ Hz, 1 H, 6a-H), 3.55−3.88 (m, 9 H, 2a-H, 3a-H, 4a-H, 5a-H, 6a-H, 2b-H, 4b-H, 5b-H, 6b-H), 4.38 (dd, $J_{6,5} = 4.8$, $J_{6,6} = 10.3$ Hz, 1 H, 6b-H), 4.50−4.75 (m, 9 H, 1b-H, 8 ArC*H*H), 4.83 (d, $J_{1,2} = 3.6$ Hz, 1 H, 1a-H), 4.87 (d, $J = 10.7$ Hz, 1 H, ArC*H*H), 5.02 (d, $J = 11.4$ Hz, 1 H, ArC*H*H), 5.49 (s, 1 H, PhC*H*), 5.63 (dd, 1H, $J_{3,4} = J_{3,2} = 9.0$ Hz, 3b-H), 7.14−7.42 (m, 27 H, Ar), 7.72 (d, $J = 1.8$ Hz, 1 H, Ar) ppm. MALDI MS: *m*/*z* = 1005 [MNa$^+$], 1021 [MK$^+$]. $C_{58}H_{62}O_{12}S$ (983.2): calcd. C 70.86, H 6.36; found C 70.52, H 6.35.

Benzyl 6,3′-*O*-(2-Methyl-5-methylene-benzoyl)-(2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1−4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (11): *N*-Iodosuccinimide (0.090 g, 0.40 mmol) and a catalytic amount of trifluoromethanesulfonic acid (4 μm) were added to a solution of **10** (0.195 g, 0.20 mmol) in dichloromethane, and the reaction mixture was stirred for a period of 30 min. The reaction mixture was then washed with sodium bicarbonate solution (10 mL) and sodium thiosulfate solution (10 mL). The aqueous phase was reextracted with dichloromethane (50 mL), the combined organic extracts were washed with water and brine and dried with sodium sulfate, and the solvent was removed in vacuo to yield the crude product, which was purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) to yield pure **11** (131 mg, 71%). TLC (petroleum ether/ethyl acetate, 2:1): $R_f = 0.42$. $[\alpha]_D = +5$ ($c = 1.0$, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.63 (s, 3 H, $ArCH_3$), 3.42 (d, $J_{1,2} = 2.2$ Hz, 1 H, 2b-H), 3.55−3.58 (m, 2 H, 2a-H, 4a-H), 3.63 (dd, $J_{5,6} = 6.0$, $J_{6,6} = 10.2$ Hz, 1 H, 6a-H), 3.80 (dd, 1 H, $J_{5,6} = 10.8$, $J_{6,6} = 10.8$ Hz, 6b-H), 3.86 (d, $J_{6,6} = 10.2$ Hz, 1 H, 6a-H), 4.12 (dd, $J_{5,6} = 5.4$, $J_{5,4} = 9.6$ Hz, 1 H, 5a-H), 4.22 (dd, $J_{5,6} = 10.8$ Hz, $J_{5,4} = 10.2$ Hz, 1 H, 5b-H), 4.34 (dd, $J_{3,4} = J_{3,2} = 7.8$ Hz, 1 H, 3a-H), 4.42 (dd, $J_{6,5} = 5.4$, $J_{6,6} = 10.8$ Hz, 1 H, 6b-H), 4.51−4.55 (m, 8 H, 4b-H, 7′-H, 6 ArC*H*H), 4.80 (d, $J = 15.6$ Hz, 1 H, 7′-H), 4.86−4.89 (m, 3 H, 1a-H, 2 ArC*H*H), 5.33 (d, $J_{3,4} = 7.2$ Hz, 1 H, 3b-H), 5.54 (s, 1 H, PhC*H*), 5.56 (br. s, 1 H, 1b-H), 7.15−7.26 (m, 23 H, Ar), 7.50 (m, 4 H, Ar), 8.15 (s, 1 H, Ar) ppm. $C_{56}H_{56}O_{12}$ (924.9): calcd. C 73.03, H 6.13; found C 73.01, H 6.54.

Benzyl *O*-(2-*O*-Benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1−4)-2,3-di-*O*-benzyl-6-*O*-(3-methoxycarbonyl-4-methylbenzyl)-α-D-glucopyranoside (12): Sodium methoxide solution (1 mmol/mL in MeOH, 0.5 mL, 5 mmol) was added to a solution of **11** (0.090 g, 0.10 mmol) in dichloromethane (5 mL), and the reaction mixture was stirred for a period of 2 h at room temp., by which time the reaction had proceeded to completion. The reaction mixture was neutralised with ion-exchange resin (Amberlite IR-120, H$^+$), the mixture was filtered, and the solvent was evaporated in vacuo. The crude compound was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) to yield pure **12** (0.083 g, 87%) as a colourless oil. TLC (toluene/ethyl acetate, 3:1): $R_f = 0.54$. $[\alpha]_D = +4$ ($c = 1.0$, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.56 (s, $ArCH_3$), 3.07 (m, 1 H, 5b-H), 3.20 (dd, $J_{2,1} = J_{2,3} = 7.8$ Hz, 1 H, 2b-H), 3.37−3.45 (m, 3 H, 6a-H, 4b-H, 6b-H) 3.50−3.54 (m, 2 H, 2a-H, 3b-H), 3.68 (m, 1 H, 5a-H), 3.82−3.84 (m, 4 H, 6a-H, OCH_3), 3.90 (m, 2 H, 3a-H, 4a-H), 4.13 (dd, $J_{5,6} = 4.8$, $J_{6,6} = 10.2$ Hz, 1 H, 6b-H), 4.30 (2 H, 1b-H, ArC*H*H), 4.54 (d, $J = 12.0$ Hz, 1 H, ArC*H*H), 4.57−4.60 (m, 2 H, 2 ArC*H*H), 4.68−4.83 (m, 6 H, 1a-H, 5 ArC*H*H), 4.92 (d, $J = 10.2$ Hz, 1 H, ArC*H*H), 5.42 (s, 1 H, PhC*H*), 7.20−7.50 (m, 27 H, Ar), 7.82 (s, 1 H, Ar) ppm. MALDI MS: *m*/*z* = 975 [MNa$^+$], 991 [MK$^+$].

Ethyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-(3-bromobenzyl)-1-thio-β-D-glucopyranoside (13): *m*-Bromobenzyl bromide (7.50 g, 30.0 mmol) was added in portions to a suspension of **3**[13] (10.1 g, 25.0 mmol) and sodium hydride (0.72 g, 30.0 mmol) in dry DMF (150 mL). The reaction mixture was stirred for a period of 3 h at room temp and then quenched by MeOH, and the solvent was evaporated in vacuo. The residue was taken up in ethyl acetate (250 mL) and washed with water (2×50 mL) and brine (50 mL), and the aqueous phase was reextracted with ethyl acetate (50 mL). The combined organic extracts were dried with sodium sulfate, and the solvent was evaporated in vacuo. The crude compound was purified by flash chromatography (petroleum ether/ethyl acetate, 10:1) to yield pure **13** as a colourless oil (15.4 g, 90%). TLC (toluene/ethyl acetate, 9:1): $R_f = 0.57$. $[\alpha]_D = -31$ ($c = 1.0$, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.32 (t, $J = 7.4$ Hz, 3 H, SCH_2CH_3), 2.74−2.82 (m, 2 H, SCH_2CH_3), 3.42−3.50 (m, 2 H, 2-H, 5-H), 3.66−3.82 (m, 3 H, 3-H, 4-H, 5-H), 4.36 (dd, $J_{6,6} = 10.4$, $J_{6,5} = 5.0$ Hz, 1 H, 6 H), 4.56 (d, $J_{1,2} = 9.8$ Hz, 1 H, 1-H), 4.71−4.96 (m, 4 H, 4 ArC*H*H), 5.57 (s, 1 H, PhCH), 7.10−7.50 (m, 14 H, Ar), 7.50 (m, 4 H, Ar) ppm. MALDI MS: *m*/*z* = 596 [MNa$^+$]. $C_{29}H_{31}BrO_5S$ (571.5): calcd. C 60.94, H 5.47; found C 61.00, H 5.41.

Ethyl 2-*O*-Benzyl-4,5-*O*-benzylidene-3-*O*-[3-(chlorodiisopropylsilyl)-benzyl]-1-thio-β-D-glucopyranoside (14): A solution of **13** (1.71 g, 3.0 mmol) in dry THF (15 mL) was cooled to −100 °C. *tert*-Butyllithium (1.6 mol/L in hexane, 3.75 mL, 6.0 mmol) was added dropwise over a period of 1 h at −100 °C, after which dichlorodiisopropylsilane (1.62 mL, 9.0 mL) was added. The temperature was now gradually raised to −50 °C and the mixture was stirred at that temperature for a period of 1 h, after which it was gradually warmed to room temp. and the solvent was evaporated in vacuo. The excess dichlorodiisopropylsilane (b.p. 66 °C at 27 mbar) was removed by the application of high vacuum to provide pure **14** as an oil, which was immediately used in the next step.

Ethyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-{3-[methyl 2,3-di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-α-D-glucopyranosid-6-yloxy]diisopropylsilylbenzyl}-1-thio-β-D-glucopyranoside (15): Sodium hydride (0.10 g, 4.20 mmol) was added to a solution of **2b**[11] (1.79 g, 3.60 mmol) in DMF (10 mL), followed by the dropwise addition of a solution of **14** (192 g, 3.0 mmol). The reaction mixture was stirred for a period of 20 h and then quenched with MeOH, and the solvent was evaporated in vacuo. The residue was taken up in ethyl acetate (50 mL) and washed with water (20 mL) and brine (20 mL), and the organic extract was dried with sodium sulfate and concentrated in vacuo. The crude compound was purified by flash chromatography (petroleum ether/ethyl acetate, 9:1) to yield pure **15** as

a colourless oil (2.01 g, 61%). TLC (toluene/ethyl acetate, 6:1): R_f = 0.75. $[\alpha]_D$ = −22 (c = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.93, 0.99 [2m, 12 H, 2 CH(CH_3)$_2$], 1.16 [m, 2 H, 2 CH(CH_3)$_2$], 1.32 (t, J = 7.4 Hz, 3 H, SCH$_2$CH_3), 2.72−2.77 (m, 2 H, CH_2CH$_3$), 3.33 (s, 3 H, OCH_3), 3.43−3.47 (m, 2 H, 2b-H, 5b-H), 3.50−3.52 (m, 2 H, 2a-H, 4a-H), 3.65 (m, 1 H, 5a-H), 3.70 (dd, $J_{4,3}$ = $J_{4,5}$ = 9.3 Hz, 1 H, 4b-H), 3.76−3.86 (m, 6 H, 6a-H, 3b-H, 6b-H, OCH_3), 3.90 (dd, $J_{6,6}$ = 10.8, $J_{6,6}$ < 1.0 Hz, 1 H, 6a-H), 3.98 (dd, $J_{3,4}$ = $J_{3,2}$ = 9.3 Hz, 1 H, 3a-H), 4.35 (dd, $J_{6,6}$ = 10.4, $J_{6,5}$ = 5.0 Hz, 1 H, 6b-H), 4.55 (m, 2 H, 2 ArCHH), 4.61 (d, $J_{1,2}$ = 3.3 Hz, 1 H, 1a-H), 4.65 (d, J = 12.5 Hz, 1 H, ArCHH), 4.62−4.66 (m, 2 H, 2 ArCHH), 4.73 (d, J = 12.0 Hz, 1 H, ArCHH), 4.76−4.86 (m, 2 H, 2 ArCHH), 4.94−497 (m, 2 H, 2 ArCHH), 5.56 (s, 1 H, PhCH), 6.78 (d, J = 8.5 Hz, 2 H, Ar), 7.12 (d, J = 8.5 Hz, 2 H, Ar), 7.25−7.46 (m, 20 H, Ar) ppm. MALDI MS: m/z = 1121 [MNa$^+$], 1161 [MK$^+$]. $C_{64}H_{76}O_{11}SSi$ (1098.4): calcd. C 69.98, H 6.97; found C 70.08, H 7.33.

Ethyl 2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-{3-[methyl 2,3-di-*O*-benzyl-α-D-glucopyranosid-6-yloxy]-diisopropylsilylbenzyl}-1-thio-β-D-glucopyranoside (16): Compound **15** (1.10 g, 1.0 mmol) was taken up in CH_2Cl_2 (30 mL) and water (5 mL), and DDQ (272 mg, 1.20 mmol) was added. The reaction mixture was stirred for a period of 20 h at room temp, after which it was diluted to 50 mL, washed with sodium bicarbonate solution (2×10 mL) and water (10 mL), and dried with sodium sulfate. The solvent was removed in vacuo. The crude compound was purified by flash chromatography (toluene/ethyl acetate, 19:1) to yield pure **16** as a colourless oil (851 mg, 87%). TLC (toluene/ethyl acetate, 9:1): R_f = 0.38. $[\alpha]_D$ = −9 (c = 0.8, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.92, 0.99 [2 m, 12 H, 2 CH(CH_3)$_2$], 1.18 [m, 2 H, 2 CH(CH$_3$)$_2$], 1.29 (t, J = 7.4 Hz, 3 H, SCH$_2$CH_3), 2.71−2.75 (m, 2 H, SCH_2CH$_3$), 3.34 (s, 3 H, OCH_3), 3.42−3.47 (m, 3 H, 2a-H, 2b-H, 5b-H), 3.53 (ddd, $J_{4,3}$ = $J_{4,5}$ = 9.1, $J_{4,OH}$ = 2.0 Hz, 1 H, 4a-H), 3.62 (m, 1 H, 5a-H), 3.70 (dd, $J_{4,3}$ = $J_{4,5}$ = 9.4 Hz, 1 H, 4b-H), 3.75 (dd, $J_{6,6}$ = 10.9, $J_{6,5}$ = 5.3 Hz, 1 H, 6a-H), 3.90 (dd, $J_{6,6}$ = 10.9, $J_{6,5}$ = 3.8 Hz, 1 H, 6a-H), 4.32 (dd, $J_{6,6}$ = 10.6, $J_{6,5}$ = 5.0 Hz, 1 H, 6b-H), 4.55 (d, $J_{1,2}$ = 9.7 Hz, 1 H, 1b-H), 4.59 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1a-H), 4.63 (d, J = 12.0 Hz, 1 H, ArCHH), 4.72−4.80 (m, 4 H, 4 ArCHH), 4.84 (d, J = 10.3 Hz, 1 H, ArCHH), 4.93−4.97 (m, 2 H, 2 ArCHH), 5.55 (s, 1 H, PhCH), 7.24−7.35 (m, 24 H, Ar) ppm. MALDI MS: m/z = 1101 [MNa$^+$], 1118 [MK$^+$]. $C_{56}H_{68}O_{11}SSi$ (978.0): calcd. C 68.75, H 7.01; found C 68.68, H 7.19.

Methyl 6,3′-*O*-[-3-(Diisopropylsilyl)benzyl]-(2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1−4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (17α) and Methyl 6,3′-*O*-[-3-(Diisopropylsilyl)benzyl]-(2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1−4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (17β). a) With NIS: Compound **16** (0.196 g, 0.20 mmol) was taken up in dry dichloromethane (20 mL), and to this solution were added NIS (0.090 g, 0.40 mmol) and a catalytic amount of trifluoromethanesulfonic acid (4 μL). The reaction mixture was stirred at room temp. for a period of 30 min and was then washed with sodium bicarbonate solution (10 mL) and sodium thiosulfate (10 mL). The aqueous phase was reextracted with dichloromethane (20 mL), the organic extracts were combined and dried with sodium sulfate, and the solvent was removed in vacuo. The crude compound was purified by flash chromatography (petroleum ether/ethyl acetate, 13:1 to 9:1) to yield the two anomers **17α** (0.083 g, 45%), and **17β** (0.083 g, 45%). **b) With MeOTf:** Methyl triflate (88 μL, 0.80 mmol) was added to a solution of **16** (0.196 g, 0.20 mmol) in dry dichloromethane (20 mL). After 2 h of stirring at room temp., the reaction mixture was neutralised with triethylamine, diluted with dichloromethane (20 mL) and washed with water (10 mL) and brine (10 mL). The aqueous phase was reextracted with CH_2Cl_2 (30 mL), the combined organic extracts were dried with sodium sulfate, and the solvent was evaporated in vacuo. The residue was purified by flash chromatography (toluene/ethyl acetate, 29:1) to yield pure **17β** as a colourless foam (0.129 g, 70%). **17α:** TLC (toluene/ethyl acetate, 9:1): R_f = 0.38. $[\alpha]_D$ = −14 (c = 0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 1.01 [m, 3 H, CH(CH_3)$_2$), 1.05 [m, 3 H, CH(CH_3)$_2$], 1.11 [m, 3 H, CH(CH_3)$_2$], 1.14 [m, 3 H, CH(CH_3)$_2$], 1.21 [m, 2 H, 2 CH(CH$_3$)$_2$], 3.32 (ddd, $J_{5,6}$ = 4.7 Hz, $J_{6,6}$ = 10 Hz, $J_{4,5}$ = 9.7 Hz, 1 H, 5b-H), 3.45 (m, 4 H, 4a-H, OCH_3), 3.51 (dd, $J_{2,3}$ = 9.4, $J_{2,1}$ = 3.5 Hz, 1 H, 2a-H), 3.56 (dd, $J_{6,6}$ = $J_{6,5}$ = 10.3 Hz, 1 H, 6b-H), 3.62 (dd, $J_{6,6}$ = 10.3, $J_{6,5}$ = 8.2 Hz, 1 H, 6a-H), 3.88 (dd, $J_{5,6}$ = 8.2, $J_{5,4}$ = 10.6 Hz, 1 H, 5a-H), 4.03 (dd, $J_{3,2}$ = $J_{3,4}$ = 9.1 Hz, 1 H, 3a-H), 4.07 (dd, $J_{6,6}$ = 10.6, $J_{6,5}$ = 4.7 Hz, 1 H, 6b-H), 4.19 (dd, 1 H, $J_{6,6}$ = 10.3, $J_{6,5}$ < 1.0 Hz, 6a-H), 4.34 (dd, $J_{3,4}$ = $J_{3,2}$ = 9.7 Hz, 1 H, 3b-H), 4.54−4.58 (m, 3 H, 1a-H, 2 ArCHH), 4.66−4.74 (m, 3 H, 3 ArCHH), 4.85−4.91 (m, 2 H, 2 ArCHH), 5.01 (d, J = 11.0 Hz, 1 H, ArCHH), 5.35 (s, 1 H, PhCH), 5.38 (d, $J_{1,2}$ = 2.9 Hz, 1 H, 1b-H), 7.20−7.32 (m, 22 H, Ar), 7.50 (m, 1 H, Ar), 7.72 (m, 1 H, Ar) ppm. FAB MS: m/z = 939 [MNa$^+$]. $C_{54}H_{64}O_{11}$ (918.2): calcd. C 70.64, H 7.03; found C 70.17, H 6.90. **17β:** TLC (toluene/ethyl acetate, 9:1): R_f = 0.50. ^1H NMR (600 MHz, $CDCl_3$): δ = 0.95 [m, 3 H, CH(CH_3)$_2$], 1.01 [m, 6 H, CH(CH_3)$_2$], 1.09 [m, 3 H, CH(CH_3)$_2$], 1.15 [m, 2 H, 2 CH(CH_3)$_2$], 3.34 (dd, $J_{4,3}$ = 8.2 Hz, 10 Hz, $J_{4,5}$ = 9.7 Hz, 1 H, 4a-H), 3.35 (s, OCH_3), 3.51 (dd, $J_{2,3}$ = 9.1, $J_{2,1}$ = 3.5 Hz, 1 H, 2a-H), 3.54 (dd, $J_{2,1}$ = 2.1, $J_{2,1}$ < 1.0 Hz, 1 H, 2b-H), 3.60 (dd, $J_{6,6}$ = $J_{6,5}$ = 10.3 Hz, 1 H, 6b-H), 3.73−3.80 (m, 2 H, 5a-H, 6a-H), 3.84 (dd, $J_{3,4}$ = 7.3, $J_{3,2}$ < 1.0 Hz, 1 H, 3b-H), 3.88 (dd, $J_{6,6}$ = 10.3, $J_{6,5}$ < 1.0 Hz, 1 H, 6a-H), 3.97 (dd, $J_{5,6}$ = 5.0 Hz, $J_{5,4}$ = 10.3 Hz, 5b-H), 4.07 (dd, $J_{3,4}$ = $J_{3,2}$ = 8.8 Hz, 1 H, 3a-H), 4.18−4.20 (m, 2 H, 6b-H, ArCHH), 4.31 (d, J = 11.6 Hz, 1 H, ArCHH), 4.40 (dd, $J_{4,5}$ = 10.6, $J_{4,3}$ = 7.3 Hz, 1 H, 4b-H),4.45 (d, J = 13.8 Hz, 1 H, 8′-H), 4.49 (d, J = 12.0 Hz, 1 H, ArCHH), 4.64 (d, $J_{1,2}$ = 3.5 Hz, 1 H, 1a-H), 4.72 (d, J = 12.0 Hz, 1 H, ArCHH), 4.88 (d, J = 10.3 Hz, 1 H, ArCHH), 5.01 (d, J = 10.3 Hz, 1 H, ArCHH), 5.11 (d, J = 12.0 Hz, 1 H, 8′-H), 5.22 (br. s, 1 H, $J_{1,2}$ < 1.0 Hz, 1b-H), 5.48 (s, 1 H, PhCH), 7.12−7.37 (m, 23 H, Ar), 7.46 (s, 1 H, Ar).

Methyl 6,3′-*O*-[-3-(Diisopropylsilyl)benzyl]-(2-*O*-benzyl-β-D-glucopyranosyl)-(1−4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (18β): Ethanethiol (222 μL, 3.0 mmol) and *p*-toluenesulfonic acid (0.010 g) were added to a solution of **17β** (0.55 g, 0.6 mmol) in dichloromethane (30 mL). The reaction mixture was stirred at room temp. for a period of 5 h. The reaction mixture was neutralised with triethylamine and the solvent was evaporated in vacuo. The crude compound was purified by flash chromatography (toluene/ethyl acetate, 2:1) to yield the pure compound as an oil (0.43 g, 86%). TLC (toluene/ethyl acetate, 1:1): R_f = 0.34. $[\alpha]_D$ = +26 (c = 0.5, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 0.90 [m, 3 H, CH(CH_3)$_2$], 0.98 [m, 3 H, CH(CH_3)$_2$], 1.01 [m, 3 H, CH(CH_3)$_2$], 1.11 [m, 3 H, CH(CH_3)$_2$], 1.28 (m, 2 H, 2 CH(CH$_3$)$_2$], 2.59 (br. s, 1 H, 4b-OH), 2.69 (br. s, 1 H, 6b-OH), 3.32 (dd, $J_{4,3}$ = 8.5, $J_{4,5}$ = 9.9 Hz, 1 H, 4a-H), 3.40 (s, 3 H, OCH_3), 3.43 (br. s, $J_{2,3}$ = $J_{2,1}$ = 1.5 Hz, 1 H, 2b-H), 3.55 (m, 2 H, 2a-H, 2b-H), 3.64 (ddd, $J_{3,4}$ = 6.2, $J_{3,2}$ < 1.0, $J_{3,1}$ < 1.0 Hz, 1 H, 3b-H) 3.68−3.72 (m, 3 H, 6a-H, 5b-H, 6b-H), 3.79 (dd, $J_{5,6}$ = 6.6, $J_{5,4}$ = 10.1 Hz, 1 H, 5a-H), 3.85 (dd, $J_{6,6}$ = 10.3, $J_{6,5}$ < 1.0 Hz, 1 H, 6a-H), 4.09 (m, 2 H, 2 ArCHH), 4.20 (dd, $J_{3,4}$ = $J_{3,2}$ = 9.0 Hz, 1 H, 3a-H), 4.25 (bt, 1 H, 4b-H), 4.41 (d, J = 13.8 Hz, 1 H, ArCHH), 4.56 (d, J = 12.0 Hz, 1 H, ArCHH), 4.66 (m, 2 H, 1a-H, ArCHH), 4.74 (d, J = 10.6 Hz, 1 H, ArCHH), 4.86 (d, $J_{1,2}$ = 10.6 Hz, 1 H, ArCHH), 5.04 (br. s, $J_{1,2}$ < 1.0, $J_{1,3}$ < 1.0 Hz, 1 H, 1b-H), 5.12 (d, J = 13.8 Hz, 1

H, 8′-H), 7.00 (m, 2 H, Ar), 7.20−7.36 (m, 16 H, Ar) ppm. FAB MS: *m*/*z* = 859 [MNa$^+$]. $C_{47}H_{60}O_{10}Si$ (830.1): calcd. C 68.01, H 7.29; found C 67.79, H 7.22.

Methyl *O*-{2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-[3-(hydroxydiisopropylsilyl)benzyl]-α-D-glucopyranosyl}-(1−4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (19α): Tetrabutylammonium fluoride solution (1 mol/L in THF, 120 μL, 0.12 mmol) was added to a solution of **17α** (0.092 g, 0.10 mmol) in tetrahydrofuran (25 mL) and the mixture was stirred for a period of 2 h at room temp. The solvent was then removed in vacuo, and the crude product was purified by flash chromatography to yield **19α** (0.085 g, 91%) as a colourless oil. TLC (toluene/ethyl acetate, 4:1): R_f = 0.18. $[\alpha]_D$ = −10 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.90 [m, 6 H, CH(C*H*$_3$)$_2$], 0.99 [m, 6 H, CH(C*H*$_3$)$_2$], 1.12 [m, 2 H, 2 C*H*(CH$_3$)$_2$], 1.71 (s, 1 H, OH), 1.83 (t, *J* = 6.2 Hz, 1 H, OH), 3.37 (s, 3 H, OCH_3), 3.52−3.54 (m, 2 H, 2a-H, 2b-H), 3.62 (dd, $J_{4,3} = J_{4,5}$ = 9.4 Hz, 1 H, 4b-H), 3.69 (dd, $J_{6,5} = J_{6,6}$ = 10.3 Hz, 1 H, 6b-H), 3.80−3.85 (m, 3 H, 5a-H, 6a-H, 5b-H), 3.96 (dd, $J_{4,3} = J_{4,5}$ = 9.2 Hz, 1 H, 4a-H), 4.03 (dd, $J_{3,2} = J_{3,4}$ = 9.4 Hz, 1 H, 3b-H), 4.09 (dd, $J_{3,2} = J_{3,4}$ = 9.2 Hz, 1 H, 3a-H), 4.30 (dd, $J_{6,6}$ = 10.1, $J_{6,5}$ = 4.8 Hz, 1 H, 6b-H), 4.52−4.56 (m, 3 H, 1a-H, 2 ArC*H*H), 4.66 (d, *J* = 12.0 Hz, 1 H, ArC*H*H), 4.73−4.79 (m, 3 H, 3 ArC*H*H), 4.92 (d, *J* = 10.9 Hz, 1 H, ArC*H*H), 4.99 (d, *J* = 11.8 Hz, 1 H, ArC*H*H), 5.54 (s, 1 H, PhC*H*), 5.71 (d, $J_{1,2}$ = 3.9 Hz, 1 H, 1b-H), 7.16−7.48 (m, 24 H, Ar) ppm. FAB MS: *m*/*z* = 957 [MNa$^+$]. $C_{54}H_{66}O_{12}Si$ (935.2): calcd. C 69.35, H 7.11; found C 69.14, H 6.97.

Methyl *O*-{2-*O*-Benzyl-4,6-*O*-benzylidene-3-*O*-[3-(hydroxydiisopropylsilyl)benzyl]-β-D-glucopyranosyl}-(1−4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (19β): Tetrabutylammonium fluoride solution (1 mol/L in tetrahydrofuran, 120 μL, 0.12 mmol) was added to a solution of **17β** (0.092 g, 0.10 mmol) in tetrahydrofuran and the mixture was stirred for 2 h at room temp., after which the solvent was removed in vacuo and the residue was purified by flash chromatography (toluene/ethyl acetate, 4:1) to yield pure **19β** (0.087 g, 93%) as a colourless oil. TLC (toluene/ethyl acetate, 4:1), R_f = 0.18. $[\alpha]_D$ = −5 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.90 [m, 6 H, CH(C*H*$_3$)$_2$], 0.99 [m, 6 H, CH(C*H*$_3$)$_2$], 1.12 [m, 2 H, 2 C*H*(CH$_3$)$_2$], 1.58 (s, 1 H, OH), 1.75 (br. s, 1 H, OH), 3.32−3.36 (m, 4 H, 5b-H, OCH_3), 3.40−3.50 (m, 4 H, 2a-H, 5a-H, 2b-H, 6b-H), 3.61−3.66 (m, 2 H, 4b-H, 6a-H), 3.75−3.85 (m, 4 H, 3a-H, 4a-H, 3b-H, 6a-H), 4.15 (dd, $J_{6,6}$ = 10.5, $J_{6,5}$ = 5.0 Hz, 1 H, 6b-H), 4.52 (d, $J_{1,2}$ = 3.7 Hz, 1 H, 1a-H), 4.60−4.63 (m, 2 H, 1b-H, ArC*H*H), 4.75−4.81 (m, 4 H, 4 ArC*H*H), 4.86 (d, *J* = 11.2 Hz, 1 H, ArC*H*H), 4.91−4.92 (m, 2 H, 2 ArC*H*H), 5.49 (s, 1 H, PhC*H*), 7.24−7.46 (m, 24 H) ppm. FAB MS: *m*/*z* = 957 [MNa$^+$]. $C_{54}H_{66}O_{12}Si$ (935.2): calcd. C 69.35, H 7.11; found C 68.88, H 7.12.

***tert*-Butyl 5-[Methyl 2,3-di-*O*-benzyl-α-D-glucopyranosid-6-yloxymethyl]-2-methylbenzoate (20):** Compound **2c**[12] (6.5 g, 18 mmol) was taken up in toluene (60 mL), dibutyltin oxide (4.5 g, 18 mmol) was added, and the solution was heated under reflux for 5 h in a Dean−Stark apparatus. The solution was concentrated to a volume of 10 mL, to which **5** (4.25 g, 18 mmol), and TBAI (7.4 g, 20 mmol) were added, and was then heated under reflux for another 6 h. The solvent was now removed in vacuo, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to yield pure **20** as an oil (7.03 g, 70%). TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.41. $[\alpha]_D$ = −4.7 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.58 [s, 9 H, C(CH$_3$)$_3$], 2.61 (s, 3 H, $ArCH_3$), 3.38 (s, 3 H, OCH_3), 3.45−3.54 (m, 2 H, 6-H$_2$), 3.57 (m, 1 H, 2-H), 3.83 (m, 1 H, 5-H), 3.92 (m, 2 H, 3-H, 4-H), 4.47 (m, 1 H, ArC*H*H), 4.60 (d, *J* = 3.92 Hz, 1 H, 1-H), 4.64 (m, 1 H, ArC*H*H), 4.78 (m, 1 H, ArC*H*H), 4.86 (m, 1 H, ArC*H*H), 4.88 (m, 2 H, 2 ArC*H*H), 7.15−7.73 (m, 12 H, Ar), 7.72 (d, *J* = 1.80 Hz, 1 H, Ar) ppm. MALDI MS: *m*/*z* = 601 [MNa$^+$]. $C_{34}H_{42}O_8$ (578.6): calcd. C 70.58, H 7.26; found C 70.71, H 7.31.

***tert*-Butyl 5-[Methyl 2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-glucopyranosid-6-yl-oxymethyl]-2-methylbenzoate (21):** Levulinic acid (5.07 g, 43.65 mmol), DCC (9.06 g, 44 mmol), and DMAP (0.100 g) were added to a solution of **20** (4.70 g, 0.61 mmol) in dichloromethane, and the reaction mixture was stirred for a period of 24 h, by which time the reaction mixture had acquired a deep brown color. The reaction mixture was filtered and the solvent was evaporated. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, 3:2) to yield pure **21** as an oil (4.38 g, 75%); TLC (petroleum ether/ethyl acetate, 3:2). $[\alpha]_D$ = −6.2 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.58 [s, 9 H, C(CH$_3$)$_3$], 2.11 (s, 3 H, $COCH_3$), 2.28−2.52 (m, 4 H, CC*H*$_2$C*H*$_2$C), 2.61 (s, 3 H, $ArCH_3$), 3.38 (s, 3 H, OCH_3), 3.45−3.54 (m, 2 H, 6-H$_2$), 3.57 (m, 1 H, 2-H), 3.81 (m, 1 H, 5-H), 3.92 (m, 1 H, 3-H), 4.47 (m, 1 H, ArC*H*H), 4.60 (d, *J* = 3.9 Hz, 1 H, 1-H), 4.64 (m, 1 H, ArC*H*H), 4.76 (m, 1 H, ArC*H*H), 4.78 (m, 1 H, ArC*H*H), 4.86 (m, 1 H, ArC*H*H), 4.88 (m, 1 H, ArC*H*H), 5.03 (m, 1 H, 4-H), 7.15−7.73 (m, 12 H, Ar), 7.72 (d, *J* = 1.8 Hz, 1 H, Ar) ppm. FAB MS: *m*/*z* = 699 [MNa$^+$], 714 [MK$^+$]. $C_{39}H_{48}O_{10}$ (676.3): calcd. C 69.23, H 7.1; found C 69.47, H 7.56.

5-[Methyl 2,3-di-*O*-benzyl-4-*O*-levulinoyl-α-D-glucopyranosid-6-yloxymethyl]-2-methylbenzoic Acid (22): Trifluoroacetic acid was added to a solution of **21** (3 g, 4.43 mmol) in dichloromethane, and the reaction mixture was stirred for a period of 4 h. Toluene (20 mL) was added, and the solvent was evaporated in vacuo to yield the crude compound, which was purified by flash chromatography (petroleum ether/ethyl acetate, 1:1) to yield pure **22** (2.75 g, 90%) as an oil. TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.15. $[\alpha]_D$ = −7.05 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.11 (s, 3 H, $COCH_3$), 2.28−2.52 (m, 4 H, CC*H*$_2$C*H*$_2$C), 2.61 (s, 3 H, $ArCH_3$), 3.38 (s, 3 H, OCH_3), 3.45−3.54 (m, 2 H, 6-H$_2$), 3.57 (m, 1 H, 2-H), 3.81 (m, 1 H, 5-H), 3.92 (m, 1 H, 3-H), 4.47 (m, 1 H, ArC*H*H), 4.60 (d, *J* = 3.88 Hz, 1 H), 4.64 (m, 1 H, ArC*H*H), 4.76 (m, 1 H, ArC*H*H), 4.78 (m, 1 H, ArC*H*H), 4.86 (m, 1 H, ArC*H*H), 4.88 (m, 2 H, 2 ArC*H*H), 5.03 (m, 1 H, 4-H), 7.15−7.73 (m, 12 H, Ar), 7.72 (d, *J* = 1.8 Hz, 1 H, Ar) ppm. MALDI MS: *m*/*z* = 643 [MNa$^+$], $C_{35}H_{40}O_{10}$ (620.4): calcd. C 67.74, H 6.45; found C 67.74, H 6.52.

Spacer-Linked Monosaccharide-Monosaccharide 23: DCC (3.09 g, 15 mmol) and a catalytic amount of DMAP (0.02 g) were added to a solution of **22** (2.00 g, 3.22 mmol) and **3**[13] (1.24 g, 3 mmol) in dichloromethane (50 mL). The reaction mixture was stirred for a period of 20 h at room temp and was then filtered, and the solvent was removed in vacuo. The crude compound was purified by flash chromatography (petroleum ether/ethyl acetate, 3:1) to yield pure **23** as colourless foam (2.42 g, 75%). TLC (petroleum ether/ethyl acetate, 3:2). $[\alpha]_D$ = −10.53 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 7.4 Hz, 3 H, SCH$_2$C*H*$_3$), 2.05 (s, 3 H, OCH_3), 2.22−2.56 (m, 4 H, CC*H*$_2$C*H*$_2$C), 2.61 (s, 3 H, $ArCH_3$), 2.7−2.83 (m, 2 H, SC*H*$_2$CH$_3$), 3.38 (s, 3 H, OCH_3), 3.45 (m, 1 H, 6a-H), 3.54 (m, 2 H, 6a-H, 2a-H), 3.61 (m, 1 H, 5-H), 3.64 (dd, $J_{2,1} = J_{2,3}$ = 9.2 Hz, 1 H, 2b-H) 3.73−3.79 (m, 2 H, 4b-H, 6b-H), 3.85 (m, 1 H, 5a-H), 3.92 (m, 1 H, 3a-H), 4.40−4.49 (m, 5 H, 4 ArC*H*H, 1b-H), 4.50−4.58 (m, 4 H, 4 ArC*H*H), 4.60 d, *J* = 3.9 Hz, 1 H, 1a-H), 5.48 (s, 1 H, PhC*H*), 7.12−7.37 (m, 23 H, Ar), 7.75 (s, 1 H, Ar) ppm. MALDI MS: *m*/*z* = 1025 [MNa$^+$]. $C_{57}H_{62}O_{14}S$ (1002.9): calcd. C 68.26, H 6.38; found C 68.50, H 6.74.

Spacer-Linked Monosaccharide-Monosaccharide 24: Hydrazinium acetate (0.074 g, 0.80 mmol) was added to a solution of **23** (0.80 g, 0.79 mmol) in dichloromethane and MeOH (2 mL), followed by pyr-

idine (1 mL). The mixture was stirred for 2 h at room temp and was then filtered, and the solvent was removed in vacuo to yield the crude compound, which was purified by flash chromatography to provide pure **24** as colourless foam (0.470 g, 65%). TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.43. $[\alpha]_D$ = −8.0 (c = 1.0, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.34 (t, J = 7.4 Hz, 3 H, SCH_2CH_3), 2.56 (s, 3 H, $ArCH_3$), 2.7−2.83 (m, 2 H, SCH_2CH_3), 3.38 (s, 3 H, OCH_3), 3.45 (m, 1 H, 6a-H), 3.54 (m, 3 H, 2a-H, 4a-H, 6a-H), 3.62 (m, 1 H, 5b-H), 3.64 (m, 1 H) 3.73−3.79 (m, 3 H, 4b-H, 6b-H_2), 3.81 (m, 1 H, 5a-H), 3.92 (m, 1 H, 3a-H), 4.40−4.49 (m, 5 H, 4 ArC*H*H, 1b-H), 4.50−4.58 (m, 4 H, 4 ArC*H*H), 4.60 (d, J = 3.9 Hz, 1 H, 1a-H), 5.48 (s, 1 H, PhC*H*), 5.63 (m, 1 H, 3b-H) 7.15−7.37 (m, 23 H, Ar), 7.75 (s, 1 H, Ar) ppm. MALDI MS: m/z = 929 [MNa^+]. $C_{52}H_{58}O_{12}S$ (906.6): calcd. C 68.87, H 6.40; found C 69.05, H 6.77.

Methyl 6,3′-*O*-(2-Methyl-5-methylenebenzoyl)-2-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl-(1−4)-2,3-di-*O*-benzyl-α-D-glucopyranoside (25): *N*-Iodosuccinimide (0.124 g, 0.55 mmol), followed by a catalytic amount of triflic acid (6 μL), were added to a solution of **24** (0.25 g, 0.275 mmol) in dichloromethane (20 mL). The reaction mixture was stirred at room temp. for a period of 10 min and was then washed with sodium bicarbonate solution (30 mL) and sodium thiosulfate solution (30 mL). The aqueous phase was reextracted with dichloromethane (50 mL), the organic extracts were combined, washed with water and brine and dried with sodium sulfate, and the solvent was removed in vacuo. The crude compound obtained was purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) to yield pure **25** (0.170 g, 73%) as a colourless foam. TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.48. $[\alpha]_D$ = −7.5 (c = 1.0, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$): δ = 2.56 (s, 3 H, $ArCH_3$), 3.35 (d, J = 2.2 Hz, 1 H, 2b-H), 3.43 (s, 3 H, OCH_3), 3.44−3.49 (m, 2 H, 2a-H, 4a-H), 3.50 (dd, $J_{6,6}$ = 10.3, $J_{6,5}$ = 6.0 Hz, 1 H, 6a-H), 3.77 (dd, $J_{6,6}$ = 10.8, $J_{6,5}$ = 6.2 Hz, 1 H, 6b-H), 3.86 (dd, 1 H, $J_{6,6}$ = 10.2 Hz, 6a-H), 3.98 (m, 1 H, 5a-H), 4.16 (m, 2 H, 3a-H, 5b-H), 4.35 (dd, 1 H, $J_{6,6}$ = 10.8, $J_{6,5}$ = 6.2 Hz, 1 H, 6b-H), 4.54 (d, $J_{1,2}$ = 4.0 Hz, 1 H, 1a-H), 4.61 (m, 1 H, 4b-H), 4.68 (m, 2 H, 2 ArC*H*H), 4.77 (m, 2 H, 2 ArC*H*H), 4.82 (m, 2 H, 2 ArC*H*H), 5.01 (m, 2 H, 2 ArC*H*H), 5.28 (d, $J_{3,4}$ = 6.8 Hz, 1 H, 3b-H), 5.56 (s, 1 H, PhC*H*), 5.66 (br. s, 1 H, 1b-H), 7.15−7.45 (m, 23 H, Ar), 8.09 (s, 1 H, Ar) ppm. MALDI MS: m/z = 867 [MNa^+]. $C_{50}H_{52}O_{12}$ (844.9): calcd. C 71.09, H 6.16; found C 71.30, H 6.27.

Methyl *O*-(2-*O*-Benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1−4)-2,3-di-*O*-benzyl-6-*O*-(3-methoxycarbonyl-4-methylbenzyl)-α-D-glucopyranoside (26): Sodium methoxide in MeOH (0.50 mmol) was added to a solution of **25** (400 mg, 0.473 mmol) in dichloromethane (20 mL) and the reaction mixture was stirred at room temp. for 2 h. The mixture was now neutralised with ion-exchange resin (IR-120H^+) and filtered, and the solvent was removed in vacuo. The crude compound was purified by flash chromatography (petroleum ether/ethyl acetate, 4:1) to yield pure **26** (0.375 g, 90%) as a colourless oil. TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.48. $[\alpha]_D$ = −8.7 (c = 1.0, $CHCl_3$). ^1H NMR (250 MHz): δ = 2.61 (s, 3 H, $ArCH_3$), 3.10 (m, 1 H, 5b-H), 3.22 (m, 1 H, 2b-H), 3.38 (s, 3 H, OCH_3), 3.42−3.56 (m, 5 H, 6a-H, 2a-H, 3b-H, 4b-H, 6b-H), 3.68 (m, 1 H, 5a-H), 3.80 (s, 3 H, $COOCH_3$), 3.82−3.84 (m, 2 H, 6a-H), 3.90 (m, 2 H, 3a-H, 4a-H), 4.13 (dd, $J_{6,6}$ = 10.2, $J_{5,6}$ = 4.6 Hz, 1 H, 6b-H), 4.24−4.30 (m, 2 H, 1b-H, ArC*H*H), 4.54 (d, J = 3.9 Hz, 1 H, 1a-H), 4.60 (m, 1 H, ArC*H*H), 4.70 (s, 1 H, ArC*H*H), 4.75 (m, 2 H, 2 ArC*H*H), 4.80 (m, 1 H, ArC*H*H), 4.82 (m, 1 H, ArC*H*H), 4.90 (s, 1 H, ArC*H*H), 5.48 (s, 1 H, PhC*H*), 7.3−7.6 (m, 23 H, Ar), 7.80 (s, 1 H, Ar) ppm. MALDI MS: m/z = 875 [M^+], 898 [MNa^+]. $C_{51}H_{56}O_{13}$ (876.7): calcd. C 69.86, H 6.39; found C 69.95, H 6.63.

Methyl *O*-[2-*O*-Benzyl-3-*O*-(3-hydroxycarbonyl-4-methylbenzyl)-4,6-*O*-benzylidene-β-D-glucopyranosyl]-(1−4)-[2,3-di-*O*-benzyl-6-*O*-(3-methoxycarbonyl-4-methyl)benzyl]-α-D-glucopyranoside (27): NaH (32 mg, 1.368 mmol) was added to a solution of **26** (200 mg, 0.228 mmol) in DMF and the mixture was stirred for 15 min. Compound **5** (195 mg, 0.684 mmol) was added, and the reaction mixture was stirred for a period of 3 h. It was then quenched by the addition of MeOH (5 mL), and the solvent was evaporated in vacuo. The residue was taken in water and acidified, which yielded a white precipitate. The aqueous solution was extracted with ethyl acetate (3×50 mL). The organic extracts were combined and the solvent was evaporated in vacuo to yield the crude compound, which was purified by flash chromatography (petroleum ether/ethyl acetate, 1:4) to yield pure **27** (0.172 g, 75%). TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.27. $[\alpha]_D$ = −11 (c = 1.0, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.59 (s, 3 H, $ArCH_3$), 2.61 (s, 3 H, $ArCH_3$), 3.26 (m, 1 H, 5b-H), 3.28 (m, 1 H, 2b-H), 3.38 (s, 3 H, OCH_3), 3.42−3.56 (m, 5 H, 6a-H, 2a-H, 3b-H, 4b-H, 6b-H), 3.65 (s, 3 H), 3.68 (m, 1 H, 5a-H), 3.70−3.92 (m, 3 H, 6a-H, 3a-H, 4a-H), 4.13−4.30 (m, 2 H, 1b-H, 1ArC*H*H), 4.55 (d, $J_{1,2}$ = 3.9 Hz, 1 H, 1a-H), 4.6−4.95 (m, 9 H, 9 ArC*H*H), 5.48 (s, 1 H, PhC*H*), 7.15−7.50 (m, 25 H, Ar), 7.76 (s, 1 H, Ar) ppm. MALDI MS: m/z = 1047 [MNa^+]. $C_{60}H_{64}O_{15}$ (1024.8): calcd. C 70.37, H 5.76; found C 70.71, H 5.98.

Spacer-Linked Monosaccharide−Disaccharide 28: Compound **4**[14] (48 mg, 0.099 mmol) and DCC (101 mg, 0.495 mmol) were added to a solution of **27** (100 mg, 0.99 mmol) in dichloromethane, followed by a catalytic amount of DMAP (0.020 g). The reaction mixture was stirred for a period of 10 h and then filtered, and the solvent was removed in vacuo to yield the crude compound, which was purified by flash chromatography (petroleum ether/ethyl acetate, 2:1) to give pure **28** (0.103 g, 70%). TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.56. $[\alpha]_D$ = −12.56 (c = 1.0, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 1.34 (t, J = 7.4 Hz, 3 H, SCH_2CH_3), 2.60 (s, 3 H, $ArCH_3$), 2.61 (s, 3 H, $ArCH_3$), 2.7−2.83 (m, 2 H, SCH_2CH_3), 3.20−3.35 (m, 2 H, 2b-H, 5b-H), 3.38 (s, 3 H, OCH_3), 3.42−3.56 (m, 8 H, 6a-H, 2a-H, 3b-H, 4b-H, 6b-H, 2c-H, 4c-H, 5c-H), 3.65 (m, 4 H, 5a-H, CO-OCH_3), 3.70−3.92 (m, 3 H, 6a-H, 3a-H, 4a-H), 4.12−4.22 (m,1 H, 3c-H), 4.30−4.42 (m, 3 H, 6a-H, 1b-H, ArC*H*H), 4.43−4.49 (m, 2 H, 6a-H), 4.50−4.52 (m, 2 H, 2 ArC*H*H), 4.53−4.68 (m, 6 H, 1a-H, 1c-H, 4 ArC*H*H), 4.70−5.0 (m, 10 H, 10 ArC*H*H), 5.50 (s, 1 H, PhC*H*) 7.15−7.37 (m, 40 H, Ar), 7.78, (s, 1 H, Ar) ppm. MALDI MS: m/z = 1524 [MNa^+], 1539.8 [MK^+]. $C_{89}H_{96}O_{19}S$ (1500.8): calcd. C 71.20, H 6.40; found C 71.27, H 6.59.

Methyl 3′,6′′-*O*-[2-Methyl-5-(methylenebenzoyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl]-(1−4)-[2-*O*-benzyl-6-*O*-methoxybenzyl-β-D-glucopyranosyl]-(1−4)-2,3-di-*O*-benzyl-6-*O*-(3-methoxycarbonyl-4-methylbenzyl)-α-D-glucopyranoside (29): Compound **28** (20 mg, 0.013 mmol) was added to a solution of iodine in MeOH (5% w/v), and the reaction mixture was stirred at room temp. for a period of 0.5 h. Sodium thiosulfate solution was now added until the reaction was iodine-free, and the solvent was removed in vacuo. The residue was taken in dichloromethane (20 mL) and washed with water. The aqueous phase was reextracted with dichloromethane (2×30 mL). The organic extracts were combined, dried with sodium sulfate and concentrated to yield the crude compound, which was purified by PLC (preparative thin layer chromatography) to yield pure **29** as a colourless foam (16 mg, 83%). TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.42. $[\alpha]_D$ = −9.10 (c = 1.0, $CHCl_3$). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.60 (s, 3 H, $ArCH_3$), 2.61 (s, 3 H, $ArCH_3$), 3.1−3.2 (m, 2 H, 2b-H, 5b-H), 3.33 (s, 3 H, OCH_3), 3.37 (s, 3 H, OCH_3), 3.42−3.60 (m, 8 H, 6a-H, 2a-H, 2b-H, 4b-H, 6b-H, 2c-H, 4c-H, 5c-H), 3.65 (m, 4 H, 5a-H, $COOCH_3$), 3.80−3.98 (m, 4 H, 6a-H, 3a-H,

4a-H, 3b-H), 4.12−4.22 (m, 1 H, 3c-H), 4.30 (m, 1 H, ArC*H*H), 4.39 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1b-H), 4.43−4.49 (m, 2 H, 6c-H), 4.51 (s, 1 H, ArC*H*H), 4.57 (d, $J_{1,2}$ = 3.9 Hz, 1 H, 1a-H), 4.61 (s, 1 H, ArC*H*H), 4.62 (m, 2 H, ArC*H*H), 4.65 (m, 3 H, 3 ArC*H*H), 4.72 (m, 1 H, ArC*H*H), 4.76 (d, J = 11.2 Hz, 1 H, ArC*H*H), 4.78−4.83 (m, 2 H, 2 ArC*H*H), 4.85−4.91 (m, 2 H, 2 ArC*H*H), 4.93 (m, 1 H, ArC*H*H), 4.97 (br. s, 1 H, ArC*H*H), 5.10 (br. s, 1 H, ArC*H*H), 5.47 (s, 1 H, PhC*H*), 7.15−7.42 (m, 40 H, Ar), 7.78 (s, 1 H, Ar). $C_{88}H_{94}O_{20}$ (1470.9): calcd. C 71.83, H 6.39; found C 71.91, H 6.58.

Methyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1−4)-[2-*O*-benzyl-3-*O*-3-(methoxycarbonyl-4-methylbenzyl)-6-*O*-(methoxyphenyl-methyl)-β-D-glucopyranosyl]-(1−4)-2,3-di-*O*-benzyl-6-*O*-(3-methoxycarbonyl-4-methylbenzyl)-α-D-glucopyranoside (1): Sodium methoxide in MeOH (0.5 mmol) was added to a solution of **29** (10 mg, 0.007 mmol) in dichloromethane, and the solution was stirred for a period of 2 h at room temp. Next, the reaction mixture was neutralised by the addition of ion-exchange resin (Amberlite IR 120H$^+$) and filtered, and the solvent was evaporated in vacuo. The crude compound was purified by PLC (preparative thin layer chromatography) to yield pure **1** (9 mg, 90%). TLC (petroleum ether/ethyl acetate, 3:2): R_f = 0.42. $[\alpha]_D$ = −9.42 (c = 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.51 (s, 3 H, $ArCH_3$), 2.53 (s, 3 H, $ArCH_3$), 3.14−3.16 (m, 1 H, 5b-H), 3.33 (s, 3 H, OCH_3), 3.34 (m, 1 H, 2b-H), 3.37 (s, 3 H, OCH_3), 3.42−3.46 (m, 3 H, 6b-H, 6a-H, 4c-H), 3.50−3.52 (m, 3 H, 2a-H, 2c-H, 3b-H), 3.55−3.56 (m, 2 H, 5a-H, 4b-H), 3.58 (m, 1 H, 6c-H), 3.65 (s, 3 H, $COOCH_3$), 3.67 (s, 3 H, $COOCH_3$), 3.81 (m, 2 H, 6a-H, 3a-H), 3.88−3.91 (m, 2 H, 4a-H, 5c-H), 4.01 (t, J = 4.0 Hz, 1 H, 3c-H) 4.18−4.25 (m, 2 H, 6b-H, ArC*H*H), 4.39 (d, $J_{1,2}$ = 7.73 Hz, 1 H, 1b-H), 4.42 (m, 1 H, ArC*H*H), 4.44−4.48 (dd, 1 H, $J_{5,6}$ = 5.3, $J_{6,6}$ = 9.6 Hz, 6-H), 4.55 (m, 1 H, ArC*H*H), 4.57 (d, $J_{1,2}$ = 4.3 Hz, 1 H, 1c-H), 4.58 (d, $J_{1,2}$ = 3.9 Hz, 1 H, 1a-H), 4.61−4.63 (m, 1 H, ArC*H*H), 4.68−4.72 (m, 2 H, 2 ArC*H*H), 4.76−4.81 (m, 5 H, 5 ArC*H*H), 4.86−4.90 (m, 3 H, 3 ArC*H*H), 4.97 (d, J = 8.2 Hz, 1 H, ArC*H*H), 5.47 (s, 1 H, PhC*H*), 7.22−7.45 (m, 40 H, Ar), 7.79 (s, 1 H, Ar). $C_{89}H_{98}O_{21}$ (1502.9): calcd. C 71.10, H 6.52; found C 71.16, H 6.59.

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