A Short Route to Malto-trisaccharide Synthons: Synthesis of the Branched Nonasaccharide, 6‴-α-Maltotriosyl-maltohexaose

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Abstract: A short route to phenyl 1-thio-β-maltotrioside derived building blocks and their use for the synthesis of the branched nonasaccharide, 6‴-α-maltotriosyl-maltohexaose, is described. Instead of using glucose and maltose as starting materials, maltotriose was used and synthetically manipulated in a well designed strategy to obtain phenyl *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-1-thio-β-D-glucopyranoside, phenyl *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside and phenyl *O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside. The described methodology has shortened multi-step synthesis of the desired branched nonasaccharide from 40 to 23 steps. It has also provided maltotriose derived building blocks that independently or in combination with corresponding glucose or maltose derived building blocks permit synthesis of any desired part of the amylopectin or amylose molecule.

Key words: 1,3-benzodithiolan-2-ylium protecting group, carbohydrates, glycosides, 6‴-α-maltotriosyl-maltohexaose, phase transfer catalysis

One of the difficulties in oligosaccharide synthesis is in obtaining stereoselective coupling of building blocks. A second difficulty originates from the polyfunctionality of carbohydrate oligomers, which necessitates the use of elaborate protective group chemistry if complex carbohydrates are to be synthesised. Therefore, facilitation of the chemical synthesis of a desired oligosaccharide may be obtained by developing a new coupling procedure or by establishing a well designed building block strategy to shorten a multi-step route. Recently, we reported[1] chemical synthesis of the branched nonasaccharide 6‴-α-maltotriosyl-maltohexaose (**22**) in 40 steps from a combined set of glucose-[1] and maltose-derived[2] building blocks (Figure 1). The synthesised branched nonasaccharide **22** was used for investigation of the action of starch synthase II[3] involved in the biosynthesis of starch. To determine the three-dimensional structure of **22** by X-ray crystallography and for further investigation of the action of enzymes involved in starch biosynthesis using compound **22** as a substrate, more material was needed demanding a shorter synthetic route. Here, we report a convenient route to chemical synthesis of three essential trisaccharide synthons **9**, **15**, and **21** starting from maltotriose. These synthons can be used in the synthesis of linear and branched complex oligosaccharides. The availability of these new synthons reduces the multi-step synthesis of **22**[1] from 40 to 23 steps (Figure 1).

The synthetic strategy to obtain the desired glycosyl acceptor **9** from maltotriose (**1**) is shown in Scheme 1. 1,6-Anhydro derivatives of D-glucopyranose and of di- and trisaccharides including maltose, cellobiose, and maltotriose are readily available from the parent saccharides[4–6] and are used as versatile synthons in carbohydrate chemistry.[7–12] Per-*O*-acetylated 1-β-linked pentachlorophenyl glycosides are the best suited precursors for the synthesis of the corresponding per-*O*-acetylated 1,6-anhydro sugars.[12,13] Further, phase transfer catalysis (PTC) has been extensively used in the field of carbohydrate chemistry[2,14–16] in particular to achieve nucleophilic substitutions at the anomeric center of glycosyl halides using a wide variety of nucleophiles[17] including aryloxides.[18,19] Therefore, maltotriose (**1**) was acetylated in a standard procedure using anhydrous sodium acetate and acetic anhydride to obtain maltotriose hendecaacetate (**2**) as an α,β-anomeric mixture (α:β ratio, 1:4) in quantitative yield.[20] The hendecaacetate **2** was converted into the corresponding per-*O*-acetylated- maltotriosyl bromide[12] using a hydrogen bromide–acetic acid solution in acetic acid −dichloromethane and subsequently treated with pentachlorophenol under PTC conditions using tetrabutylammonium hydrogen sulfate (TBAHS) as the catalyst to provide pentachlorophenyl glycoside derivative **3** in 76% yield. Compound **3** was previously prepared in a different manner.[12] Conversion of **3** to the 1,6-anhydro derivative **4** was accomplished in 85% yield as previously described[12] using aqueous potassium hydroxide and subsequent acetylation with acetic anhydride and anhydrous sodium acetate. The 1,6-anhydro ring of compound **4** was cleaved selectively using Hanessian's reagent[21] as reported by Sakairi[22] but using our described modification

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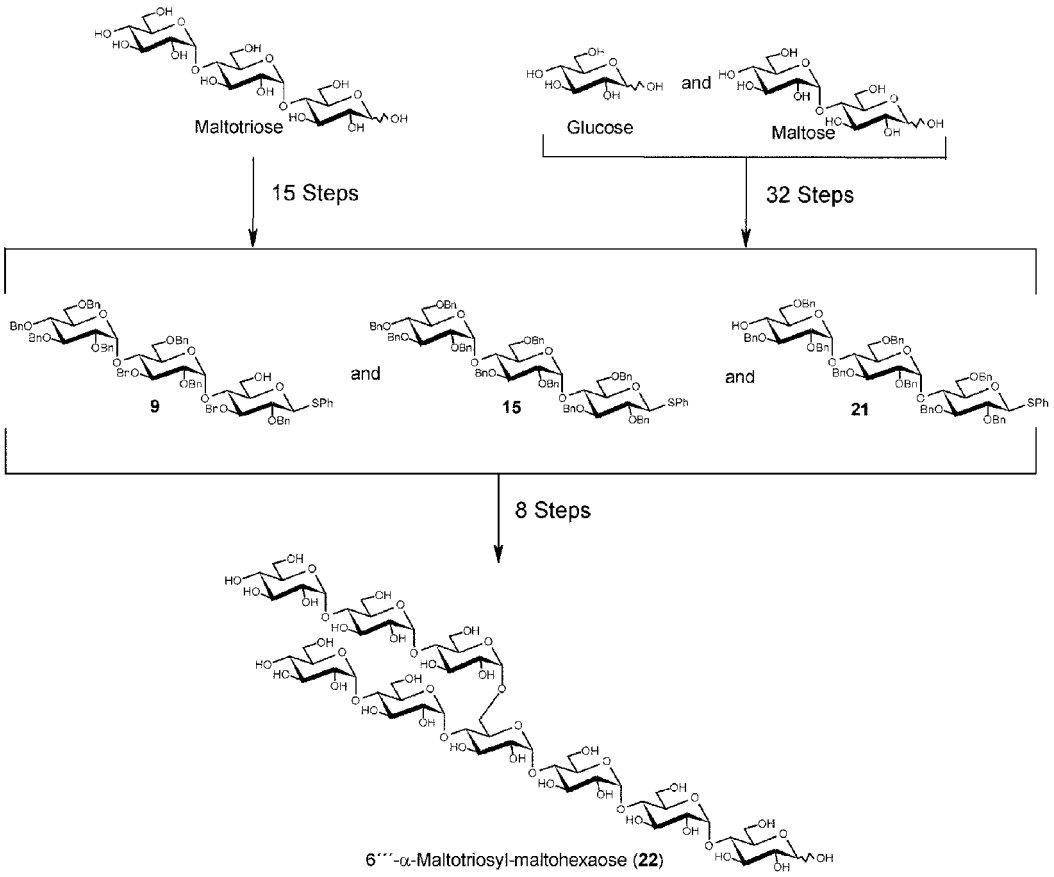
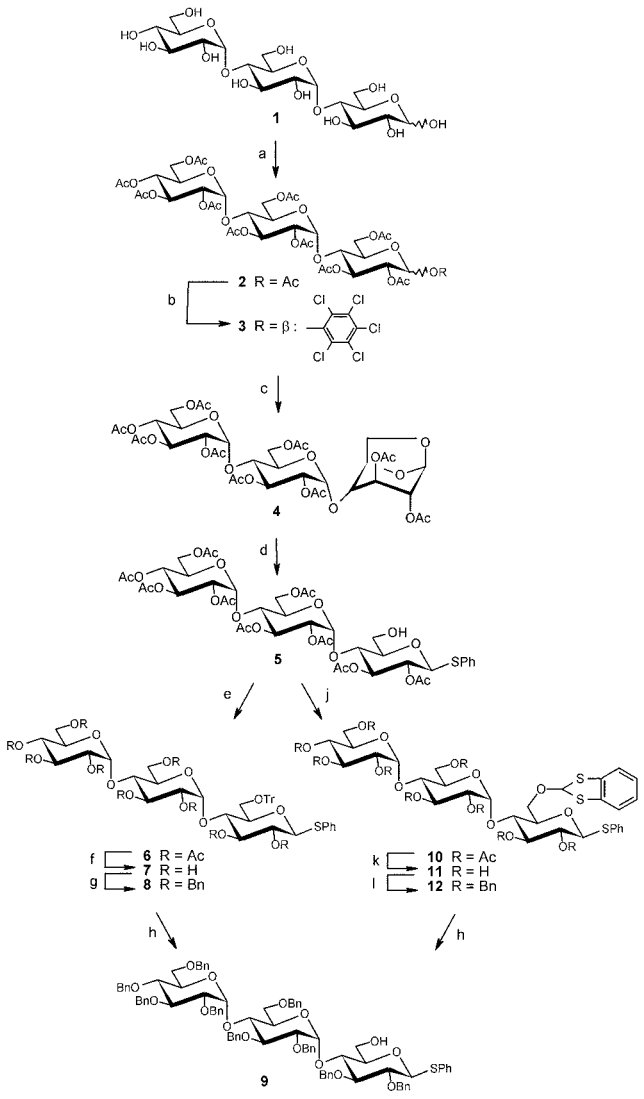


Figure 1 The three phenyl 1-thio-β-D- maltotrioside derived building blocks **9**, **15**, and **21** were synthesised from maltotriose as starting material instead of a combination of glucose and maltose derivatives as previously described[1] shortening the multi-step synthesis of 6´´´-α-maltotriosyl-maltohexaose (**22**) from 40 to 23 steps.

procedure[23] with phenylthio-trimethylsilane and zinc iodide to accomplish conversion of **4** to the phenyl thioglycoside **5** in 90% yield. In the ^{1}H NMR spectrum of **5**, the doublet at δ 4.80 with J = 10.1 Hz reflects the β-anomeric proton. In the corresponding ^{13}C NMR spectrum, the diagnostic signal at δ 85.4 ppm reflects the β-anomeric carbon. Formation of the α-anomer of **5** was not observed. The free hydroxyl group at the 6-position of **5** was then protected with a trityl group introduced by the use of triphenylchloromethane in pyridine[24] to afford **6** in 88% yield. Deacetylation of the tritylated derivative **6** by treatment with sodium methoxide in methanol resulted in **7** (91% yield). Benzylation of **7** with benzyl bromide and sodium hydride in THF in the presence of tetrabutylammonium iodide (TBAI) afforded **8** in 48% yield. An alternative protection of the free OH group at the 6-position of **5** was accomplished using 1,3-benzodithiol-2-ylium (BDT) as protecting group. BDT is a well known protecting group in nucleoside chemistry[25] but has not previously been employed in carbohydrate chemistry. Compound **10** was obtained in quantitative yield by treating **5** with 1,3-benzodithiol-2-ylium tetrafluoroborate in pyridine. A stronger base like dimethylaminopyridine cannot be used in the reaction since it activates 1,3-benzodithiol-2-ylium tetrafluoroborate to form the dimer, dibenzotetrathiafulvalene instead.[25] Quantitative conversion of the 1,3-benzodithiolan-2-yl derivative **10** into **11** was achieved by deacetylation using methanolic ammonia. Standard benzylation of **11** using benzyl bromide and sodium hydride in DMF provided **12** in 51% yield. Compound **8** and **12** were independently treated with aqueous acetic acid resulting in the desired building block **9** in 71% and quantitative yield, respectively. The overall yield for the four steps involved in the manipulation of **5**, **10**, **11**, and **12** into compound **9** was calculated to be 51%. The parallel approach based on the use of the trityl group as protecting group gave an overall yield of 27%. The deacetylation and the benzylation methods reported for the two kind of protecting groups are different, but experiments using both methods for each type of protecting group were made and the method providing the highest yield is reported here. Hence, the 1,3-benzodithiol-2-ylium group can be used as an alternative temporary protecting group.

The synthesis of the two desired building blocks **15** and **21** is outlined in Scheme 2. Thiophenolysis of maltotriose hendecaacetate (**2**) with phenylthio-trimethylsilane using $BF_3{\cdot}Et_2O$ as the promoter afforded the phenyl thioglycoside **13** in 70% yield. Minor amounts of the α-anomer of **13** (< 2%) were removed by chromatography. Although **13** is a known compound[26] only its optical rotation has been reported. Neither its NMR data nor any other exper-



Scheme 1 Reagents and conditions: a) Ac_2O, CH_3COONa, 170 °C, 1 h; b) i. 33% HBr–HOAc, CH_2Cl_2–HOAc, 10−15 °C, 5 h ii. pentachlorophenol, TBAHS, EtOAc, 1 M aq Na_2CO_3, r.t., 18 h; c) i. 4 M aq KOH, 120 °C, 20 h ii. 3 M H_2SO_4 iii. Ac_2O, CH_3COONa, 170 °C, 2.5 h;[12] d) $PhSSi(CH_3)_3$, ZnI_2, r.t., 17 h; e) TrCl, pyridine, 140 °C, 1 h; f) NaOMe–MeOH, THF, r.t., 3 h; g) BnBr, TBAI, THF, NaH, r.t., 40 h h) CH_3COOH, H_2O, 100 °C, 10 min; j) 1,3-benzodithiolan-2-ylium tetrafluoroborate, pyridine, r.t., 1.5 h; k) 2 M NH_3–MeOH, r.t., overnight; l) BnBr, DMF, NaH, r.t., 24 h.

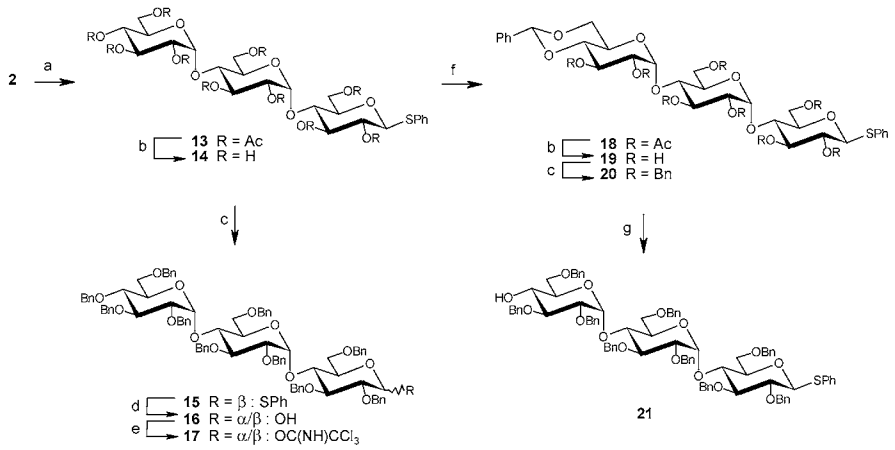
imental details have been reported. Deacetylation of **13** using sodium methoxide in methanol gave **14** in quantitative yield. Reaction of **14** with benzyl bromide and sodium hydride afforded the desired building block **15**[1] in 79% yield. The other desired building block **21** was successfully obtained from **14** (Scheme 2). Cyclic acetals constitute one of the most useful derivatives for regioselective *O*-protection in carbohydrate chemistry[23,27–30] and is used in the present strategy. The best results were obtained using α,α-dibromotoluene in pyridine.[2,27,28,30] Benzylidenation of **14** under base catalysed conditions using α,α-dibromotoluene in pyridine and subsequent in situ acetylation using acetic anhydride in pyridine to facilitate the work up to obtain the 4″,6″-*O*-benzylidene derivative gave **18** in 64% yield. In the ^{1}H NMR spectrum of **18**, a singlet at δ 5.47 reflects the benzylic proton. In the related ^{13}C NMR spectrum, a signal at 101.6 ppm reflects the benzylic carbon. Quantitative conversion of **18** into **19** was achieved using sodium methoxide in methanol. Benzylation of **19** using benzyl bromide and sodium hydride resulted in **20** (71% yield) after chromatographic purification. Regioselective reductive cleavage of the benzylidene function of **20** was achieved using sodium cyanoborohydride, ethereal solution of hydrogen chloride, and ether in THF[31] resulting in the desired building block **21** in 43% yield with a free hydroxyl group at the C-4″-position and a benzyl ether group at the C-6″-position.

The thioglycoside **5** is a glycosyl acceptor and was first used in a coupling reaction with the glycosyl donor **17**[1] using trimethylsilyl triflate (TMS triflate) as catalyst in anhydrous ether to provide the branched hexasaccharide **23** in 92% yield (Scheme 3). The acetyl groups of **23** were easily removed using methanolic ammonia resulting in quantitative yield of **24**. However, numerous trials to obtain the fully benzylated **25** were unsuccessful. Steric hindrance could be a likely explanation for incomplete benzylation of the hexasaccharide. Therefore, we decided to convert **5** into the analogue compound **9**, which is protected with benzyl groups instead of acetyl groups, thereby avoiding the troublesome benzylation of the hexasaccharide.

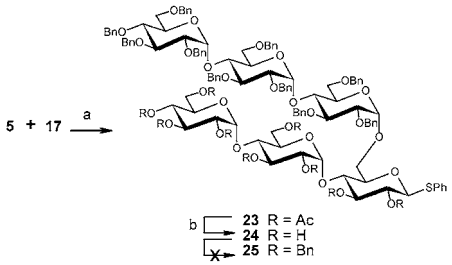
Synthesis of the nonasaccharide, 6‴-α-maltotriosyl-maltohexaose was smoothly carried out in 6 steps by coupling of the three trisaccharide building blocks **9**, **17**, and **21** as previously described.[1]

In conclusion, we have developed a more efficient and convenient route to obtain the three phenylthio maltotrioside building blocks **9**, **15**, and **21** using maltotriose as the starting material. The phenylthio group was chosen for two main reasons. First, thioglycosides are relatively stable to conditions used for manipulating other protecting groups and second, the phenylthio group can easily be removed.[32] The 1,3-benzodithiolan-2-yl group was shown to be a useful temporary protecting group in carbohydrate chemistry and it can be an alternative to the trityl group. The three building blocks **9**, **15**, and **21** were used for synthesis of the branched nonasaccharide, 6‴-α-maltotriosyl-maltohexaose, but may equally well be used as versatile building blocks in the chemical synthesis of other complex carbohydrates.

Melting points were determined using a Mettler FP81 MBC cell connected to a Mettler FP80 Central Processor unit. Optical rotations were measured at either 27 °C ± 1 °C with an Optical Activity Ltd AA-1000 Polarimeter or at 23 °C ± 1 °C with an Optical Activity Ltd AA-10 Polarimeter. All reactions were monitored by TLC on aluminium sheets coated with silica gel $60F_{254}$ (0.2 mm thickness, E. Merck, Darmstadt, Germany) and reactants and products were visualised by charring with 10% H_2SO_4 in MeOH. Column chromatography was carried out using silica gel (particle size 0.040−0.063 mm, 230−400 mesh ASTM, E. Merck) and stepwise elution with the solvent mixtures known from TLC chromatography



Scheme 2 Reagents and conditions: a) $PhSSi(CH_3)_3$, $BF_3{\cdot}Et_2O$, CH_2Cl_2, r.t., 16 h; b) NaOMe–MeOH, r.t.; c) BnBr, DMF, NaH, r.t.; d) NBS, acetone−water, r.t., 5 min;[1] e) CCl_3CN, K_2CO_3, CH_2Cl_2, r.t., 23 h;[1] f) i. α,α-dibromotoluene, pyridine, 140 °C, 2 h. ii. Ac_2O, r.t., 19 h; g) $NaBH_3CN$, THF, 4 Å MS, HCl–Et_2O, 0 °C, 20 min.



Scheme 3 Reagents and conditions: a) TMS triflate, Et_2O, 4 Å MS, r.t., 1 h; b) 2 M NH_3–MeOH, THF, r.t., overnight.

to permit separation of the individual components. Solvent extracts were dried with anhyd $MgSO_4$ unless otherwise specified. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer. In D_2O, dioxane was used as internal reference [δ_H(dioxane) = 3.75; δ_C(dioxane) = 67.4]. In $CDCl_3$, acetone-d_6 and MeOH-d_4, the δ_H values are relative to internal Me_4Si. In DMSO-d_6 a δ_H value of 2.49 ppm was used as internal reference. The δ_C-values are referenced to the solvent [$\delta_C(CDCl_3)$ = 77.0; δ_C(DMSO-d_6) = 39.4; δ_C(MeOH-d_4) = 49.0; δ_C(acetone-d_6) = 206 ppm]. Since no ^{13}C NMR data and no full ^1H NMR assignment have been reported for the known compounds **2**, **3**, and **4** they are reported here. FAB spectra were recorded on a Jeol AX505W mass spectrometer. Microanalysis was performed at DBLab-Danish Bioprotein A/S, Stenhuggervej 22, P.O. Box 829, DK-5230 Odense M, Denmark.

Maltotriose Hendecaacetate (2)

Maltotriose (25 g, 49.56 mmol) was added in three portions to a stirred mixture of anhyd NaOAc (25 g) and Ac_2O (250 mL) at reflux. Stirring was continued for 1 h at reflux after which the reaction mixture was cooled. and the solvent evaporated. The residue was coevaporated with toluene (3 × 200 mL) and dissolved in EtOAc (400 mL). The organic phase was washed with H_2O (3 × 400 mL), sat. aq $NaHCO_3$ (300 mL), brine (300 mL), and then dried. The solvent was evaporated and the residue was coevaporated with toluene (3 × 200 mL) to afford **2** as a white solid as an α,β anomeric mixture (1:4) in quantitative yield (47.72 g). The β anomer was crystallised from EtOH to afford white crystals; mp 136.1 °C, Lit.[33] 134−136 °C $[\alpha]_D^{27}$ +87.4 (*c* = 0.53, $CHCl_3$), Lit.[33] $[\alpha]_D^{25}$ +89.5 (*c* = 2.9, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 2.00, 2.00, 2.01, 2.02, 2.03, 2.04, 2.06, 2.10, 2.11, 2.16, 2.17 (11 s, 33 H, 11 COC*H*$_3$), 3.88 (m, 1 H, H-5), 3.92−3.97 (m, 3 H, H-4′, H-5′, H-5′′), 4.01 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.1 Hz, H-4), 4.06 (dd, 1 H, $J_{5'',6''a}$ = 2.2 Hz, $J_{6'',6''a,6''b}$ = 12.5 Hz, H-6′′a), 4.17 (dd, 1 H, $J_{5',6'b}$ = 2.9 Hz, $J_{6'a,6'b}$ = 12.5 Hz, H-6′b), 4.25 (dd, 1 H, $J_{5'',6''b}$ = 3.4 Hz, H-6′′b), 4.31 (dd, 1 H, $J_{5,6b}$ = 4.2 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6b), 4.45 (dd, 1 H, $J_{5,6a}$ = 2.6 Hz, H-6a), 4.47 (dd, 1 H, $J_{5',6'a}$ = 2.0 Hz, H-6′a), 4.74 (dd, 1 H, $J_{2',3'}$ = 10.5 Hz, H-2′), 4.85 (dd, 1 H, $J_{2'',3''}$ = 9.9 Hz, H-2′′), 4.97 (dd, 1 H, $J_{2,3}$ = 9.1 Hz, H-2), 5.07 (t, 1 H, $J_{3'',4''} = J_{4'',5''}$ = 9.9 Hz, H-4′′), 5.27 (d, 1 H, $J_{1',2'}$ = 4.0 Hz, H-1′), 5.30 (t, 1 H, H-3), 5.35 (t, 1 H, H-3′′), 5.39 (dd, 1 H, $J_{3',4'}$ = 10.5 Hz, H-3′), 5.46 (d, 1 H, $J_{1'',2''}$ = 4.1 Hz, H-1′′), 5.75 (d, 1 H, $J_{1,2}$ = 8.6 Hz, H-1).

^{13}C NMR ($CDCl_3$): δ = 20.5 (6 × COC*H*$_3$), 20.7 (4 × CO*C*H$_3$), 20.8 (CO*C*H$_3$), 61.3 (C-6′′), 62.2 (C-6′), 62.6 (C-6), 67.8, 68.4, 69.0, 69.3, 70.0, 70.3, 70.9, 71.6, 72.4, 72.9, 73.4, 75.0 (C-2, C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′, C-2′′, C-3′′, C-4′′, C-5′′), 91.2 (C-1), 95.6 (C-1′′), 95.8 (C-1′), 168.7 (C=O), 169.3 (C=O), 169.5 (2 × C=O), 169.7 (C=O), 169.8 (C=O), 170.2 (C=O), 170.4 (2 × C=O), 170.5 (2 × C=O).

Anal. Calcd for $C_{40}H_{54}O_{27}$ (966.85): C, 49.69; H, 5.63. Found: C, 49.52; H, 5.70.

Pentachlorophenyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (3)

To a stirred soln of **2** (10.00 g, 10.30 mmol) in CH_2Cl_2−HOAc (75 mL, 2:1) was added dropwise HBr (6.5 mL, 33 wt% soln in HOAc) at −15 °C (acetone-ice bath). Stirring was continued at 10−15 °C for 5 h, the solvent was evaporated first and the residue coevaporated with toluene (3 × 100 mL). To a stirred soln of the residue in EtOAc (200 mL) was added tetrabutylammonium hydrogen sulfate (4.00 g, 11.78 mmol), pentachlorophenol (14.00 g, 52.56 mmol) dissolved in the minimum amount of EtOAc and 1 M aq Na_2CO_3 (200 mL). The mixture was vigorously stirred at r.t. for 18 h. The organic phase was separated and washed with H_2O (3 × 200 mL), 1 M aq NaOH (200 mL), H_2O (3 × 200 mL), brine (3 × 200 mL), then dried and evaporated. The residue was chromatographed on silica gel (210 g) with Et_2O−pentane (3:2) to remove all impurities. Elution with Et_2O afforded compound **3**, which was crystallised from EtOH as white crystals (9.18 g, 76%): mp 116.2 °C, Lit.[12] mp 109−112 °C.

$[\alpha]_D^{23}$ +116.4 (c = 0.08, $CHCl_3$), Lit.[12] $[\alpha]_D^{23}$ +114 (c = 0.63, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 2.00, 2.00, 2.03, 2.03, 3.03, 2.04, 2.08, 2.10, 2.11, 2.16 (10 s, 30 H, 10 COCH_3), 3.67 (m, 1 H, H-5), 3.89−3.96 (m, 3 H, H-4´, H-5´, H-5´´), 4.05 (dd, 1 H, $J_{5´´,6´´a}$ = 2.0 Hz, $J_{6´´a,6´´b}$ = 12.3 Hz, H-6´´a), 4.09 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, H-4), 4.18 (dd, 1 H, $J_{5´,6´b}$ = 2.3 Hz, $J_{6´a,6´b}$ = 12.3 Hz, H-6´b), 4.24 (dd, 1 H, $J_{5´´,6´´b}$ = 3.7 Hz, H-6´´b), 4.29 (dd, 1 H, $J_{5,6b}$ = 4.3 Hz, $J_{6a,6b,}$ = 12.3 Hz, H-6b), 4.41 (dd, 1 H, $J_{5,6a}$ = 3.3 Hz, H-6a), 4.46 (bd, 1 H, H-6´a), 4.74 (dd, 1 H, $J_{2´,3´}$ = 10.7 Hz, H-2´), 4.85 (dd, 1 H, $J_{2´´,3´´}$ = 10.7 Hz, H-2´´), 5.07 (t, 1 H, $J_{3´´4´´}$ = $J_{4´´,5´´}$ = 10.3 Hz, H-4´´), 5.23 (dd, 1 H, $J_{2,3}$ = 8.5 Hz, H-2), 5.27 (d, 1 H, $J_{1,2}$ = 7.9 Hz, H-1), 5.31 (d, 1 H, $J_{1´,2´}$ = 4.3 Hz, H-1´), 5.34 (dd, 1 H, H-3), 5.35 (dd, 1 H, H-3´´), 5.37 (t, 1 H, $J_{3´,4´}$ = 10.7 Hz, H-3´), 5.41 (d, 1 H, $J_{1´´,2´´}$ = 4.3 Hz, H-1´´).

^{13}C NMR ($CDCl_3$): δ = 20.5 (3 × COCH_3), 20.6 (2 × COCH_3), 20.8 (3 × COCH_3), 20.9 (2 × COCH_3), 61.4 (C-6´´), 62.2 (C-6), 62.3 (C-6´), 67.9, 68.5, 69.0, 69.3, 70.0, 70.4, 71.7, 72.2, 72.3, 72.5, 73.5, 74.9 (C-2, C-3, C-4, C-5, C-2´, C-3´, C-4´, C-5´, C-2´´, C-3´´, C-4´´, C-5´´), 95.6, 95.7, 100.3 (C-1, C-1´, C-1´´), 128.6 (2 × Ar-C), 130.6 (Ar-C), 132.0 (2 × Ar-C), 147.8 (Ar-C), 169.4 (COCH$_3$), 169.6 (COCH$_3$), 169.7 (COCH$_3$), 169.8 (COCH$_3$), 170.1 (2 × COCH$_3$), 170.3 (COCH$_3$), 170.5 (3 × COCH$_3$).

Anal. Calcd for $C_{44}H_{51}Cl_5O_{26}$ (1173.14): C, 45.05; H, 4.38. Found: C, 44.86; H, 4.51.

O-(2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-acetyl-α-D-glucopyranosyl)-(1→ 4)-2,3-di-O-acetyl-1,6-anhydro-β-D-glucopyranose (4)

A stirred suspension of **3** (9.18 g, 7.83 mmol) in 4 M aq KOH (50 mL) was refluxed at 120 °C for 20 h. The mixture was cooled to 0 °C, neutralised with 3 M H_2SO_4 and filtered. The filtrate was evaporated first and then coevaporated with toluene (3 × 50 mL). The residue obtained was refluxed at 170 °C for 2.5 h with anhyd NaOAc (9 g) and Ac_2O (90 mL). The mixture was cooled to r.t., evaporated first, then the residue coevaporated with toluene (3 × 50 mL). The residue was dissolved in EtOAc (200 mL) and sat. aq $NaHCO_3$ (150 mL). The organic phase was separated and washed with 1 M aq NaOH (15 mL), H_2O (15 mL) and brine (15 mL), then dried and evaporated. The residue was chromatographed on silica gel (210 g) with $CHCl_3$−EtOAc (1:1) as eluent to afford **4**, which crystallised from EtOH as white crystals (5.74 g, 85%): mp 155.0 °C, Lit.[12] mp 159−161 °C, Lit.[34] mp 156.5−157 °C.

$[\alpha]_D^{27}$ +83.2 (c = 0.38, $CHCl_3$), Lit.[12] $[\alpha]_D^{23}$ +89 (c = 0.46, $CHCl_3$), Lit.[34] $[\alpha]_D^{15}$ +82.4 (c = 1.5, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 2.00, 2.01, 2.03, 2.04, 2.04, 2.10, 2.10, 2.13, 2.21 (9 s, 27 H, COCH_3), 3.48 (br s, 1 H, H-4), 3.81 (dd,1 H, $J_{5,6a}$ = 5.3 Hz, $J_{6a,6b}$ = 7.6 Hz, H-6a), 3.96−4.03 (m, 3 H, H-6b, H-4´, H-5´´), 4.06 (dd, 1 H, $J_{5´´,6´´a}$ = 2.3 Hz, $J_{6´´a,6´´b}$ = 12.3 Hz, H-6´´a), 4.22 (dd, 1 H, $J_{5´,6´b}$ = 3.8 Hz, $J_{6´a,6´b}$ = 12.6 Hz, H-6´b), 4.25 (dd, 1 H, $J_{5´´,6´´b}$ = 3.5 Hz, H-6´´b), 4.40 (dt, 1 H, $J_{5´,6´a}$ = 2.6 Hz, $J_{4´,5´}$ = 9.9 Hz, H-5´), 4.51 (dd, 1 H, H-6´a), 4.60 (br s, 1 H, H-2), 4.72 (dd, 1 H, $J_{2´,3´}$ = 10.2 Hz, H-2´), 4.78 (bd, $J_{5,6b}$ = 5.3 Hz, H-5), 4.84 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 1.5 Hz, H-3), 4.89 (dd, 1 H, $J_{2´´,3´´}$ = 10.5 Hz, H-2´´), 5.08 (t, 1 H, $J_{3´´,4´´}$ = 9.7 Hz, $J_{4´´,5´´}$ = 9.9 Hz, H-4´´), 5.19 (d, 1 H, $J_{1´,2´}$ = 3.8 Hz, H-1´), 5.37 (dd, 1 H, H-3´´), 5.42 (d, 1 H, $J_{1´´,2´´}$ = 3.8 Hz, H-1´´), 5.50 (br s, 1 H, H-1), 5.57 (dd, 1 H, $J_{3´,4´}$ = 9.1 Hz, H-3´).

^{13}C NMR ($CDCl_3$): δ 20.5 (4 × COCH_3), 20.6, 20.8 (3 × COCH_3), 20.9 (2 × COCH_3), 61.3 (C-6´´), 62.7 (C-6´), 64.9 (C-6), 68.0 (C-4´´), 68.3 (C-5´´), 68.4 (C-5´), 68.5 (C-2), 69.2 (C-3´´), 69.9 (C-2´´), 70.3 (C-3), 71.1 (C-2´), 72.2 (C-3´), 72.6 (C-4´), 74.2 (C-5), 76.7 (C-4), 95.7 (C-1´´), 96.8 (C-1´), 99.0 (C-1), 169.3 (2 × C=O), 169.6 (C=O), 169.7 (C=O), 170.0 (C=O), 170.4 (3 × C=O), 170.5 (C=O).

Phenyl O-(2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-acetyl-α-D-glucopyranosyl)-(1→4)-2,3-di-O-acetyl-1-thio-β-D-glucopyranoside (5)

To a stirred soln of **4** (18.34 g, 21.21 mmol) in anhyd CH_2Cl_2 (400 mL) was added phenylthio-trimethylsilane (24 mL, 127.26 mmol), zinc iodide (40.62 g, 127.26 mmol) and stirring was continued at r.t. for 17 h. The reaction mixture was filtered through a pad of sea sand over a silica gel layer. To the filtrate was added solid $NaHCO_3$ (15 g), the solvent was evaporated and the residue obtained was dissolved in EtOAc (400 mL) and sat. aq $NaHCO_3$ (300 mL). The organic phase was separated and washed with 1 M aq NaOH (300 mL), water (3 × 300 mL), and brine (300 mL), then dried and evaporated. The residue was chromatographed on silica gel (320 g) with Et_2O−pentane (4:1) as eluent to remove all impurities. Elution with Et_2O afforded compound **5**, which crystallised from EtOH as white crystals (18.69 g, 90%): mp 141.1 °C.

$[\alpha]_D^{23}$ +72.0 (c = 0.36, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.98, 2.00, 2.00, 2.03, 2.04, 2.05, 2.06, 2.10, 2.15 (9 s, 27 H, 9 COCH_3), 3.58 (m, 1 H, H-5), 3.85 (dd, 1 H, $J_{5,6b}$ = 3.5 Hz, $J_{6a,6b}$ = 12.7 Hz, H-6b), 3.86−3.98 (m, 3 H, H-4´, H-5´, H-5´´), 4.01 (dd, 1 H, $J_{5,6a}$ = 2.4 Hz, H-6a), 4.05 (dd, 1 H, $J_{5´´,6´´a}$ = 2.5 Hz, $J_{6´´a,6´´b}$ = 12.7 Hz, H-6´´a), 4.08 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, H-4), 4.20−4.28 (m, 2 H, H-6´b, H-6´´b), 4.47 (dd, 1 H, $J_{5´,6´a}$ = 2.0 Hz, $J_{6´a,6´b}$ = 12.3 Hz, H-6´a), 4.71 (dd, 1 H, $J_{2´,3´}$ = 10.4 Hz, H-2´), 4.79 (t, 1 H, $J_{2,3}$ = 10.1 Hz, H-2), 4.80 (d, 1 H, $J_{1,2}$ = 10.1 Hz, H-1), 4.85 (dd, 1 H, $J_{2´´,3´´}$ = 10.4 Hz, H-2´´), 5.06 (t, 1 H, $J_{3´´,4´´}$ = $J_{4´´,5´´}$ = 10.2 Hz, H-4´´), 5.31 (d, 1 H, $J_{1´,2´}$ = 4.1 Hz, H-1´), 5.33 (dd, 1 H, H-3), 5.37 (t, 1 H, $J_{3´,4´}$ = 10.4 Hz, H-3´), 5.38 (t, 1 H, H-3´´), 5.40 (d, 1 H, $J_{1´´,2´´}$ = 4.1 Hz, H-1´´), 7.33−7.48 (m, 5 H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 20.9 (COCH_3), 21.0 (COCH_3), 21.1 (4 × COCH_3), 21.2 (COCH_3), 21.3 (COCH_3), 22.7 (COCH_3), 61.8, 61.8, 63.1 (C-6, C-6´, C-6´´), 68.0, 68.4, 68.7, 69.4, 69.9, 70.6, 70.9, 71.0, 71.8, 72.5, 76.4, 78.5 (C-2, C-3, C-4, C-5, C-2´, C-3´, C-4´, C-5´, C-2´´, C-3´´, C-4´´, C-5´´), 85.4 (C-1´), 95.2, 95.6 (C-1, C-1´´), 128.8 (Ar-C), 129.5 (2 × Ar-C), 132.1 (Ar-C), 133.2 (2 × Ar-C), 169.9 (2 × C=O), 170.1 (C=O), 170.3 (C=O), 170.6 (C=O), 170.9 (2 × C=O), 171.0 (2 × C=O).

Anal. Calcd for $C_{42}H_{54}O_{24}S$ (974.93): C, 51.74; H, 5.58; S, 3.29. Found: C, 51.33; H, 5.63; S, 3.46.

Phenyl O-(2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-acetyl-α-D-glucopyranosyl)-(1→4)-2,3-di-O-acetyl-6-O-(triphenylmethyl)-1-thio-β-D-glucopyranoside (6)

To a stirred soln of **5** (12.00 g, 12.3 mmol) in anhyd pyridine (100 mL) was added triphenylchloromethane (34.3 g, 61.5 mmol). The mixture was refluxed at 140 °C for 1 h with exclusion of moisture by fitting a $CaCl_2$ tube on top of the condenser. The solvent was evaporated and the residue was coevaporated with toluene (3 × 100 mL). The residue was chromatographed on silica gel (320 g) with pentane and Et_2O–pentane (4:1) afforded **6**, which crystallised from EtOH as white crystals (13.12 g, 88%): mp 155.1 °C.

$[\alpha]_D^{23}$ +80.0 (c = 0.24, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.95, 1.96, 1.98, 2.00, 2.02, 2.06, 2.09, 2.09, 2.11 (9 s, 27 H, 9 COCH_3), 3.32−3.40 (m, 2 H, H-5, H-5´), 3.48−3.53 (m, 2 H, H-6a, H-6b), 3.65−3.82 (m, 4 H, H-4, H-4´, H-5´´, H-6´b), 3.89 (dd, 1 H, $J_{5´,6´a}$ = 2.0 Hz, $J_{6´a,6´b}$ = 12.1 Hz, H-6´a), 4.02 (dd, 1 H, $J_{5´´,6´´a}$ = 2.3 Hz, $J_{6´´a,6´´b}$ = 12.5 Hz, H-6´´a), 4.25 (dd, 1 H, $J_{5´´,6´´b}$ = 3.4 Hz, H-6´´b), 4.63 (dd, 1 H, $J_{2´,3´}$ = 10.5 Hz, H-2´), 4.73 (d, 1 H, $J_{1,2}$ = 10.1 Hz, H-1), 4.84−4.92 (m, 2 H, H-2, H-2´´), 4.99 (d, 1 H, $J_{1´,2´}$ = 4.0 Hz, H-1´), 5.10 (t, 1 H, $J_{3´´,4´´}$ = 9.8 Hz, $J_{4´´,5´´}$ = 10.4 Hz, H-4´´), 5.17 (dd, 1 H, $J_{2,3}$ = $J_{3,4}$ = 8.7 Hz, H-3), 5.19 (dd, 1 H, $J_{3´,4´}$ = 9.0 Hz, H-3´), 5.38 (d, 1 H, $J_{1´´,2´´}$ = 4.0 Hz, H-1´´), 5.43 (dd, 1 H, $J_{2´´,3´´}$ = 9.8 Hz, H-3´´), 7.18−7.60 (m, 20 H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 20.5 (3 × CO*C*H$_3$), 20.6 (2 × CO*C*H$_3$), 20.7 (2 × CO*C*H$_3$), 20.9 (2 × CO*C*H$_3$), 61.3 (C-6´´), 62.2 (C-6´), 64.0 (C-6), 68.0 (C-4´), 68.4, 68.4 (C-5´, C-5´´), 69.5 (C-3´´), 69.7, 70.3 (C-2, C-2´´), 70.9 (C-2´), 71.6 (C-4´), 72.1 (C-3´), 74.0 (C-4), 76.5 (C-3), 77.8 (C-5), 85.9 (C-1), 87.2 (*C*(Ph)$_3$), 95.4 (C-1´), 95.5 (C-1´´), 127.2−146.9 (Ar-C), 169.3 (C=O), 169.6 (C=O), 169.7 (C=O), 169.9 (C=O), 170.0 (C=O), 170.2 (C=O), 170.4 (C=O), 170.5 (C=O), 170.6 (C=O).

Anal. Calcd for $C_{61}H_{68}O_{24}S$ (1217.25): C, 60.19; H, 5.63; S, 2.63. Found: C, 60.02; H, 5.74; S, 2.72.

Phenyl *O*-(α-D-Glucopyranosyl)-(1→4)-*O*-(α-D-glucopyranosyl)-(1→4)-6-*O*-(triphenylmethyl)-1-thio-β-D-glucopyranoside (7)

NaOMe (5 mL, 30% in MeOH) was added to a stirred soln of **6** (10.5 g, 8.63 mmol) in MeOH−THF (21 mL, 2:1) at 0 °C and stirring was continued at r.t. for 3 h. After neutralisation with Dowex 50W-X8 (H^+ form, 200−400 mesh), the resin was filtered off and washed with MeOH (3 × 50 mL). The residue was obtained upon evaporation of the combined filtrates and then coevaporated with toluene (3 × 100 mL). Chromatography on silica gel (60 g) with $CHCl_3$−MeOH (90:10) as eluent afforded **7** as a white solid (6.56 g, 91%). An analytical sample was obtained by crystallisation from EtOH.

$[\alpha]_D^{23}$ +65.3 (*c* = 0.23, MeOH).

^{1}H NMR (MeOH-d_4): δ = 3.01−3.87 (m, 18 H, skeleton protons), 4.76 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 5.08 (d, 1 H, $J_{1',2'}$ = 3.8 Hz, H-1´), 5.11 (d, 1 H, $J_{1'',2''}$ = 3.9 Hz, H-1´´), 7.17−7.65 (20 H, Ar-H).

^{13}C NMR (MeOH-d_4): δ = 61.1, 62.8 (C-6´, C-6´´), 65.6 (C-6), 71.4, 72.8, 73.6, 73.6, 74.3, 74.6, 74.6, 75.1, 79.2, 79.8, 80.9, 81.0 (C-2, C-3, C-4, C-5, C-2´, C-3´, C-4´, C-5´, C-2´´, C-3´´, C-4´´, C-5´´), 88.2 (C-1), 89.4 (*C*(Ph)$_3$), 102.1, 103.3, (C-1´, C-1´´), 128.0−145.5 (Ar-C).

Anal. Calcd for $C_{43}H_{50}O_{15}S.H_2O$ (856.93): C, 60.27; H, 6.12; S, 3.74. Found: C, 59.85; H, 6.10; S, 3.85.

Phenyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-(triphenylmethyl)-1-thio-β-D-glucopyranoside (8)

To a stirred soln of **7** (500 mg, 0.60 mmol) in anhyd THF (30 mL) at 0 °C was added NaH (860 mg, 60% in mineral oil) under Ar and stirring was continued at r.t. for 20 min. After addition of tetrabutylammonium iodide (4.10 g, 10.88 mmol), the reaction mixture was cooled to 0 °C, BnBr (2.55 mL, 21.47 mmol) was added dropwise and stirring was continued at r.t. for 40 h. After cooling to 0 °C and addition of MeOH to decompose excess NaH, the soln was stirred for an additional 10 min and then concentrated in vacuo. The mixture was diluted with EtOAc (25 mL) and H_2O (15 mL). The organic phase was washed with H_2O (4 × 15 mL) and brine, then dried and evaporated. The residue was chromatographed on silica gel (50 g) with pentane and Et_2O−pentane (1:9) as eluent and afforded **8** as a colourless syrup (470 mg, 48%).

$[\alpha]_D^{23}$ +43.7 (*c* = 0.41, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 5.34 (d, 1 H, $J_{1',2'}$ = 4.1 Hz, H-1´), 5.70 (d, 1 H, $J_{1'',2''}$ = 3.8 Hz, H-1´´), 7.00−7.72 (m, 65 H, Ar-H). H-1$_\beta$ was overlapped by the signals from the methylene protons of the benzyl groups.

^{13}C NMR ($CDCl_3$): δ = 63.9 (C-6), 68.0 (C-6´), 68.6 (C-6´´), 70.7, 70.9, 72.2, 74.7, 77.7, 78.4, 79.3, 79.6, 81.0, 81.7, 82.0 (C-2, C-4, C-5, C-2´, C-3´, C-4´, C-5´, C-2´´, C-3´´, C-4´´, C-5´´), 73.1 (2 × *C*H$_2$Ph), 73.4 (2 × *C*H$_2$Ph), 73.8 (*C*H$_2$Ph), 74.1 (*C*H$_2$Ph), 74.8 (*C*H$_2$Ph), 75.1 (*C*H$_2$Ph), 75.4 (*C*H$_2$Ph), 86.1 (C-3), 86.8 (C(Ph)$_3$), 87.6 (C-1), 96.2 (C-1´), 97.2 (C-1´´), 126.3−143.9 (Ar-C).

Phenyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-1-thio-β-D-glucopyranoside (9)

A stirred soln of either **8** (296 mg, 0.18 mmol) or **12** (229 mg, 0.15 mmol) in HOAc (3 mL, 99.8%) was heated to 100 °C and H_2O (2 mL) was added until the reaction mixture became turbid. HOAc was then added to obtain clear soln and stirring continued for 10 min. The mixture was evaporated and the residue coevaporated with toluene (3 × 10 mL). The residue was chromatographed on silica gel (30 g) with Et_2O−pentane (10:90 and 30:70) as eluent to give **9**[1] as colourless syrup in 71% yield from **8** and in quantitative yield from **12**.

Phenyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-acetyl-6-*O*-(1,3-benzodithiolan-2-yl)-1-thio-β-D-glucopyranoside (10)

To a stirred soln of **5** (3.0 g, 3.08 mmol) in anhyd CH_2Cl_2 (20 mL) was added 1,3-benzodithiol-2-ylium tetrafluoroborate (2.26 g, 9.23 mmol) and pyridine (0.75 mL, 9.29 mmol) under N_2 and stirring was continued at r.t. for 1.5 h. Et_3N (3 mL) was added and the mixture was filtered through a pad of sea sand and a layer of silica gel. The solvent was evaporated and the residue was dissolved in EtOAc (25 mL). The organic phase was separated and successively washed with sat. aq $NaHCO_3$ (20 mL), H_2O (3 × 20 mL) until neutral pH, then with brine (20 mL), dried and evaporated. The residue was chromatographed on silica gel (90 g) with CH_2Cl_2−EtOAc (9:1 and 7:3) as eluent to give **10** as a white solid in quantitative yield (3.47 g). An analytical sample was obtained by crystallisation from EtOH.

$[\alpha]_D^{23}$ +139.1 (*c* = 0.34, acetone).

^{1}H NMR (acetone-d_6): δ = 1.97, 1.98, 1.98, 2.00, 2.00, 2.01, 2.03, 2.05, 2.08 (9 s, 27 H, 9 × CO*CH*$_3$), 3.86−3.96 (m, 4 H, H-4, H-5, H-6a, H-6b), 4.01−4.12 (m, 4 H, H-4´, H-5´, H-5´´, H-6´´a), 4.18 (dd, 1 H, $J_{5',6'b}$ = 3.6 Hz, $J_{6'a,6'b}$ = 12.2 Hz, H-6´b), 4.25 (dd, 1 H, $J_{5'',6''b}$ = 4.1 Hz, $J_{6''a,6''b}$ = 12.7 Hz, H-6´´b), 4.41 (dd, 1 H, $J_{5',6'a}$ = 1.5 Hz, H-6´a), 4.70 (dd, 1 H, $J_{2',3'}$ = 10.4 Hz, H-2´), 4.80 (dd, 1 H, $J_{2,3}$ = 9.9 Hz, H-2), 4.88 (dd, 1 H, $J_{2'',3''}$ = 10.6 Hz, H-2´´), 5.02 (d, 1 H, $J_{1,2}$ = 9.9 Hz, H-1), 5.09 (t, 1 H, $J_{3'',4''}$ = $J_{4'',5''}$ = 9.9 Hz, H-4´´), 5.25 (d, 1 H, $J_{1',2'}$ = 3.9 Hz, H-1´), 5.33 (t, 1 H, $J_{3,4}$ = 9.1 Hz, H-3), 5.39 (d, 1 H, $J_{1'',2''}$ = 4.1 Hz, H-1´´), 5.39 (t, 1 H, $J_{3',4'}$ = 10.4 Hz, H-3´), 5.43 (dd, 1 H, H-3´´), 7.08 (s, 1 H, SC*H*S), 7.18−7.40 (m, 9 H, Ar-H).

^{13}C NMR (acetone-d_6): δ = 20.5 (CO*C*H$_3$), 20.6 (3 × CO*C*H$_3$), 20.7 (2 × CO*C*H$_3$), 20.8 (CO*C*H$_3$), 21.0 (2 × CO*C*H$_3$), 62.3 (C-6´´), 63.6 (C-6´), 64.8 (C-6), 69.1, 69.4, 69.9, 70.1, 70.8, 71.4, 71.4, 72.3, 73.6 , 74.1, 76.6, 77.9 (C-2, C-3, C-4, C-5, C-2´, C-3´, C-4´, C-5´, C-2´´, C-3´´, C-4´´, C-5´´), 85.1 (C-1), 91.3 (SC*H*S), 96.2 (C-1´), 96.7 (C-1´´), 122.8−136.9 (Ar-C), 169.8 (2 × C=O), 170.2 (2 × C=O), 170.4 (C=O), 170.6 (C=O), 170.7 (C=O), 170.9 (C=O), 171.0 (C=O).

Anal. Calcd for $C_{49}H_{58}O_{24}S_3.H_2O$ (1145.17): C, 51.39; H, 5.28; S, 8.40. Found: C, 51.10; H, 5.26; S, 8.07.

Phenyl *O*-(α-D-Glucopyranosyl)-(1→4)-*O*-(α-D-glucopyranosyl)-(1→4)-6-*O*-(1,3-benzodithiolan-2-yl)-1-thio-β-D-glucopyranoside (11)

Compound **10** (1.0 g, 0.89 mmol) was treated with methanolic NH_3 (40 mL, 2.0 M). The mixture was stirred at r.t. overnight, evaporated and the residue coevaporated with toluene (3 × 25 mL). The residue was suspended in $CHCl_3$ and the solid product was filtered off and washed with $CHCl_3$ (3 × 20 mL) to give **11** in quantitative yield (664 mg). An analytical sample of **11** was obtained by crystallisation MeOH as white crystals: mp 188 °C dec.

$[\alpha]_D^{23}$ –144.7 ° (*c* = 0.15, DMSO).

^{1}H NMR (DMSO-d_6): δ = 4.61 (d, 1 H, $J_{1,2}$ = 9.6 Hz, H-1), 5.01 (d, 1 H, $J_{1',2'}$ = 3.7 Hz, H-1′), 5.01 (d, 1 H, $J_{1'',2''}$ = 3.7 Hz, H-1′′), 6.85 (s, 1 H, SC*H*S), 7.10−7.50 (m, 9 H, Ar-H).

^{13}C NMR (DMSO-d_6): δ = 60.7, 61.0 (C-6′, C-6′′), 66.4 (C-6), 70.0, 72.0, 72.0, 72.1, 72.6, 73.3, 73.5, 73.7, 76.7, 77.6, 79.8, 79.8 (C-2, C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′, C-2′′, C-3′′, C-4′′, C-5′′), 86.8 (C-1), 90.6 (S*C*HS), 101.0, 101.1 (C-1′, C-1′′), 122.7−135.6 (Ar-C).

MS (FAB): *m/z* = 771 [M$^+$ + Na].

Phenyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-benzyl-6-*O*-(1,3-benzodithiolan-2-yl)-1-thio-β-D-glucopyranoside (12)

To a stirred soln of **11** (450 mg, 0.60 mmol) in anhyd DMF (10 mL) at 0 °C was added NaH (1.21g, 60% in mineral oil) under N_2 and stirring was continued at r.t. for 1 h. The reaction mixture was cooled to 0 °C and BnBr (3.6 mL diluted with 1 mL anhyd DMF) was added dropwise. Stirring was continued at r.t. for 24 h. After cooling to 0 °C and addition of MeOH to decompose excess NaH, the soln was concentrated in vacuo and diluted with EtOAc (50 mL) and H_2O (25 mL). The organic phase was separated, washed with H_2O (4 × 25 mL), brine (25 mL), dried and evaporated. The residue was chromatographed on silica gel (90 g) with Et_2O−pentane (2:8, 3:7 and 4:6) as eluent to afford **12** as a colourless syrup (409 mg, 51%): $[\alpha]_D^{23}$ +29.0 (*c* = 0.05, acetone).

^{1}H NMR (acetone-d_6): δ = 5.53 (d, 1 H, *J* = 3.5 Hz, H-1,internal), 5.69 (d, 1 H, *J* = 3.7 Hz, H-1,internal), 7.18−7.60 (m, 54 H, Ar-H). H-1$_\beta$ was overlapped by the signals from the methylene protons of the benzyl groups.

^{13}C NMR (acetone-d_6): δ = 66.1 (C-6), 69.8, 70.4 (C-6′, C-6′′), 72.0, 72.1, 73.3, 74.4, 78.3, 78.9, 80.4, 80.9, 81.6, 82.1, 82.7 (C-2, C-4, C-5, C-2′, C-3′, C-4′, C-5′, C-2′′, C-3′′, C-4′′, C-5′′), 73.4 (2 × *C*H$_2$Ph), 73.8 (2 × *C*H$_2$Ph), 74.3 (*C*H$_2$Ph), 74.8 (*C*H$_2$Ph), 75.3 (*C*H$_2$Ph), 75.5 (*C*H$_2$Ph), 75.9 (*C*H$_2$Ph), 86.8 (C-3), 87.3 (C-1), 91.6 (S*C*HS), 96.9, 96.9 (C-1′, C-1′′), 123.0−140.1 (Ar-C).

Phenyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (13)

To a stirred soln of **2** (19.17 g, 19.82 mmol) and $PhSSi(CH_3)_3$ (6.0 mL, 31.18 mmol) in anhyd CH_2Cl_2 (50 mL) was added $BF_3{\cdot}Et_2O$ (15 mL, 119.4 mmol) and stirring was continued at r.t. for 16 h under Ar. Solid $NaHCO_3$ (20 g) was added, the mixture was diluted with EtOAc (300 mL), H_2O (200 mL) and this mixture was stirred for an additional 10 min. The organic phase was separated washed with H_2O (4 × 100 mL), NaOH (4 × 100 mL, 1 N), brine (100 mL), dried and evaporated. The residue was chromatographed on silica gel (320 g) with Et_2O−pentane (1:1 and 4:1) as eluent to afford **13**, which was crystallised from EtOH as white crystals (14.02 g, 70%): mp 102.1 °C.

$[\alpha]_D^{27}$ +78.8 (*c* = 0.45, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.97, 2.00, 2.00, 2.01, 2.03, 2.05, 2.06, 2.10, 2.15, 2.15 (10 s, 30 H, 10 × COC*H*$_3$), 3.76 (m, 1 H, H-5), 3.85−3.99 (m, 4 H, H-4, H-4′, H-5′, H-5′′), 4.05 (dd, 1 H, $J_{5'',6''a}$ = 2.4 Hz, $J_{6''a,6''b}$ = 12.6 Hz, H-6′′a), 4.18 (dd, 1 H, $J_{5',6'b}$ = 3.4 Hz, $J_{6'a,6'b}$ = 12.3 Hz, H-6′b), 4.25 (dd, 1 H, $J_{5'',6''b}$ = 3.8 Hz, H-6′′b), 4.30 (dd, 1 H, $J_{5,6b}$ = 4.7 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6b), 4.46 (dd, 1 H, $J_{5',6'a}$ = 2.1 Hz, H-6′a), 4.54 (dd, 1 H, $J_{5,6a}$ = 2.7 Hz,) H-6a), 4.73 (dd, 1 H, $J_{2',3'}$ = 10.1 Hz, H-2′), 4.73 (d, 1 H, $J_{1,2}$ = 10.2 Hz, H-1), 4.76 (dd, 1 H, $J_{2,3}$ = 8.7 Hz, H-2), 4.85 (dd, 1 H, $J_{2'',3''}$ = 10.4 Hz, H-2′′), 5.06 (dd, 1 H, $J_{3'',4''}$ = 9.9 Hz, $J_{4'',5''}$ = 10.1 Hz, H-4′′), 5.25 (d, 1 H, $J_{1',2'}$ = 4.1 Hz, H-1′), 5.29 (t, 1 H, $J_{3,4}$ = 8.7 Hz, H-3), 5.35 (t, 1 H, H-3′′), 5.38 (t, 1 H, $J_{3',4'}$ = 10.1 Hz, H-3′), 5.40 (d, 1 H, $J_{1'',2''}$ = 4.1 Hz, H-1′′), 7.28−7.50 (m, 5 H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 20.5 (4 × CO*C*H$_3$), 20.6, (2 × CO*C*H$_3$), 20.7 (CO*C*H$_3$), 20.8 (3 × CO*C*H$_3$), 61.3, 62.3, 62.9 (C-6, C-6′, C-6′′), 67.9, 68.5, 68.9, 69.3, 70.0, 70.4, 70.6, 71.7, 72.4, 73.5, 76.0, 76.3 (C-2, C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′, C-2′′, C-3′′, C-4′′, C-5′′), 84.9, 95.6, 95.7 (C-1C-1′C-1′′), 128.4 (Ar-C), 128.8 (2 × Ar-C), 131.1 (Ar-C), 133.4 (Ar-C), 169.4 (C=O), 169.5 (C=O), 169.6 (C=O), 169.8 (C=O), 170.0 (C=O), 170.3 (2 × C=O), 170.4 (C=O), 170.5 (2 × C=O).

Anal. Calcd for $C_{44}H_{56}O_{25}S$ (1016.97): C, 51.97; H, 5.55; S, 3.15. Found: C, 52.14; H, 5.62; S, 3.33.

Phenyl *O*-(α-D-Glucopyranosyl)-(1→4)-*O*-(α-D-glucopyranosyl)-(1→4)-1-thio-β-D-glucopyranoside (14)

Compound **13** (10.13 g, 9.96 mmol) was deacetylated and worked up as described for **7**. Compound **14** was obtained after crystallisation from MeOH as white crystals in quantitative yield (5.94 g): mp 146.6 °C.

$[\alpha]_D^{27}$ +133.3 (*c* = 0.29, H_2O).

^{1}H NMR (DMSO-d_6): δ = 3.08−3.75 (m, 18 H, skeleton protons), 4.67 (d, 1 H, $J_{1,2}$ = 9.7 Hz, H-1), 5.01 (d, 1 H, *J* = 3.5 Hz, H-1,internal), 5.05 (d, 1 H, *J* = 3.5 Hz, H-1,internal), 7.23−7.48 (m, 5 H, Ar-H).

^{13}C NMR (DMSO-d_6): δ = 60.4, 60.7, 61.0 (C-6, C-6′, C-6′′), 70.0, 71.9, 72.0 72.0, 72.5, 73.3, 73.3, 73.6, 77.8, 79.2, 79.4, 79.6 (C-2, C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′, C-2′′, C-3′′, C-4′′, C-5′′), 86.9 (C-1), 100.6, 100.9 (C-1′, C-1′′), 126.9 (Ar-C), 129.2 (2 × Ar-C), 130.1 (2 × Ar-C), 134.6 (Ar-C).

Anal. Calcd for $C_{24}H_{36}O_{15}S.2H_2O$ (632.63): C, 45.56; H, 6.37; S, 5.07. Found: C, 45.83; H, 6.32; S, 5.19.

Phenyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (15)

Compound **14** (3.30 g, 5.53 mmol) was benzylated and worked up as described for **12**. The residue was chromatographed on silica gel (210 g) with Et_2O−pentane (3:7) as eluent to afford **15** as colourless syrup (6.51g, 79%). Optical rotation and the ^{1}H NMR and ^{13}C NMR spectral data were identical to literature data.[1]

Phenyl *O*-(2,3-Di-acetyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranoside (18)

To a stirred soln of **14** (7.14 g, 12.10 mmol) in anhyd pyridine (50 mL) was added α,α-dibromotoluene (4 mL, 24.20 mmol) under Ar. The reaction mixture was refluxed at 140 °C for 2 h with exclusion of moisture by fitting a $CaCl_2$ tube on top of the condenser. The mixture was cooled to 0 °C, Ac_2O (60 mL, 0.64 mol) was added and stirred at r.t. for 19 h. The solvent was evaporated and the residue coevaporated with toluene (3 × 100 mL), the residue was dissolved in EtOAc (200 mL) and sat. aq $NaHCO_3$ (150 mL) was added. The organic phase was separated and washed with H_2O until neutral pH, then with brine (150 mL), dried and evaporated. The residue was chromatographed on silica gel (200 g) with Et_2O−pentane (4:6) as eluent to give **18**, which was crystallised from EtOH as white solid (7.97 g, 64%).

$[\alpha]_D^{23}$ +28.6 ° (*c* = 0.14, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.97, 2.01, 2.01, 2.04, 2.06, 2.06, 2.12, 2.15 (8 s, 24 H, 8 × COC*H*$_3$), 3.62 (t, 1 H, $J_{3'',4''}$ = $J_{4'',5''}$ = 9.9 Hz, H-4′′), 3.70−3.77 (m, 2 H, H-5, H-6′′), 3.83 (m, 1 H, H-5′′), 3.90−3.97 (m, 3 H, H-4, H-4′, H-5′), 4.17−4.32 (m, 3 H, H-6b, H-6′b, H-6′′), 4.52 (dd, 1 H, $J_{5',6'a}$ = 1.6 Hz, $J_{6'a,6'b}$ = 12.5 Hz, H-6′a), 4.58 (dd, 1 H, $J_{5,6a}$ = 2.7 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.72 (d, 1 H, $J_{1,2}$ = 9.9 Hz, H-1), 4.67−4.79 (m, 2 H, H-2, H-2′), 4.87 (dd, 1 H, $J_{2'',3''}$ = 10.3 Hz, H-2′′), 5.24 (d, 1 H, $J_{1',2'}$ = 4.3 Hz, H-1′), 5.29 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 8.6 Hz, H-3), 5.35 (d, 1 H, $J_{1'',2''}$ = 4.1 Hz, H-1′′), 5.39

(t, 1 H, $J_{2',3'} = J_{3',4'}$ = 9.9 Hz, H-3´), 5.45 (t, 1 H, H-3´´), 5.47 (s, 1 H, OC*H*O), 7.26−7.51 (m, 10 H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 20.5 (CO*C*H$_3$), 20.6 (CO*C*H$_3$), 20.7 (2 × CO*C*H$_3$), 20.8 (4 × CO*C*H$_3$), 62.1 (C-6´), 62.7 (C-6), 63.7 (C-5´´), 68.4 (C-6´´), 68.4, 69.0, 70.4, 70.7, 70.8, 71.8, 72.4, 73.3, 76.1, 76.4, 78.7 (C-2, C-3, C-4, C-5, C-2´, C-3´, C-4´, C-5´, C-2´´, C-3´´, C-4´´), 84.8 (C-1), 95.7 (C-1´), 96.4 (C-1´´), 101.6 (O*C*HO), 126.2−136.6 (Ar-C), 169.5 (C=O), 169.6 (2 × C=O), 170.0 (C=O), 170.1 (C=O), 170.2 (C=O), 170.6 (C=O), 170.8 (C=O).

Anal. Calcd for $C_{47}H_{56}O_{23}S.H_2O$ (1039.02): C, 54.33; H, 5.63; S, 3.09. Found: C, 54.05; H, 5.71; S, 3.23.

Phenyl *O*-(4,6-*O*-Benzylidene-α-D-glucopyranosyl)-(1→4)-*O*-(α-D-glucopyranosyl)-(1→4)-1-thio-β-D-glucopyranoside (19)

Compound **18** (6.10 g, 5.97 mmol) was deacetylated and worked up as described for **7** to give **19**, which crystallised from EtOH as white crystals in quantitative yield (4.09 g): mp 158.1 °C.

$[\alpha]_D^{23}$ +86.7 ° (*c* = 0.34, MeOH).

^{1}H NMR (MeOH-d_4): δ = 3.28−3.92 (m, 17 H, skeleton protons), 4.23 (dd, 1 H, $J_{5''6''b}$ = 4.7 Hz, $J_{6''a,6''b}$ = 9.9 Hz, H-6´´b), 4.62 (d, 1 H, $J_{1,2}$ = 9.9 Hz, H-1), 5.18 (d, 1 H, $J_{1',2'}$ = 3.7 Hz, H-1´) 5.18 (d, 1 H, $J_{1'',2''}$ = 3.7 Hz, H-1´´), 5.56 (s, 1 H, OC*H*O), 7.20−7.40 (m, 10 H, Ar-H).

^{13}C NMR (MeOH-d_4): δ = 62.3, 62.3 (C-6, C-6´), 69.8 (C-6´´), 65.0, 72.1, 73.3, 73.4, 73.7, 74.8, 74.9, 79.4, 80.6, 80.8, 81.8, 82.5 (C-2, C-3, C-4, C-5, C-2´, C-3´, C-4´, C-5´, C-2´´, C-3´´, C-4´´, C-5´´), 89.3 (C-1), 102.5 (O*C*HO), 103.0, 103.5 (C-1´, C-1´´), 128.4−139.1 (Ar-C).

Anal. Calcd for $C_{31}H_{40}O_{15}S.2H_2O$ (720.74): C, 51.66; H, 6.15; S, 4.45. Found: C, 51.37; H, 6.02; S, 4.60.

Phenyl *O*-(2,3-di-Benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (20)

A soln of **19** (500 mg, 0.73 mmol) in anhyd DMF (50 mL) was stirred with NaH (467 mg, 60% in mineral oil) for 4 h at r.t. The mixture was cooled to 0 °C, BnBr (1.5 mL) was added dropwise and stirring was continued at r.t. for 5 d. The reaction mixture was worked up as described for **12** and the residue was chromatographed on silica gel (45 g) with Et_2O−pentane (1:4 and 1:1) as eluent to afford **20** as colorless syrup (730 mg, 71%).

$[\alpha]_D^{23}$ +2.75 ° (*c* = 1.09, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 5.20 (d, 1 H, *J* = 3.5 Hz, H-1,internal), 5.30 (s, 1 H, OC*H*O), 5.66 (d, 1 H, *J* = 4.0 Hz, H-1,internal). 7.00−7.65 (m, 50 H, Ar-H). H-1$_\beta$ was overlapped by the signals from the methylene protons of the benzyl groups.

^{13}C NMR ($CDCl_3$): δ = 63.2 (C-5´´), 68.7, 68.9, 68.9 (C-6, C-6´, C-6´´), 70.6, 72.3, 73.5, 78.6, 78.8, 78.9, 79.5, 80.6, 81.6, 82.3, 86.5 (C-2, C-3, C-4, C-5, C-2´, C-3´, C-4´, C-5´, C-2´´, C-3´´, C-4´´), 73.1 (2 × *C*H$_2$Ph), 73.4 (*C*H$_2$Ph), 73.5 (*C*H$_2$Ph), 73.9 (*C*H$_2$Ph), 74.4 (*C*H$_2$Ph), 75.1 (*C*H$_2$Ph), 75.2 (*C*H$_2$Ph), 87.2 (C-1), 96.7, 97.4 (C-1´, C-1´´), 101.1 (O*C*HO), 126.0−138.8 (Ar-C).

Phenyl *O*-(2,3,6-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (21)

A soln of **20** (1.77 g, 1.26 mmol) and $NaBH_3CN$ (1.20 g, 11.34 mmol) in anhyd THF (45 mL) containing 4 Å molecular sieves was stirred at r.t. for 15 min. The mixture was cooled to 0 °C and a soln of HCl in Et_2O was gradually added until the soln became acidic (pH 1−2). After additional stirring for 20 min at 0 °C, the reaction mixture was diluted with EtOAc (100 mL) and filtered through a pad of sea sand over a silica gel layer. The filtrate was washed with H_2O (3 × 150 mL), sat. aq $NaHCO_3$ (3 × 150 mL), H_2O (3 × 150 mL), brine (150 mL), then dried and evaporated. The residue was chromatographed on silica gel (80 g) with Et_2O−pentane (2:3) as eluent to afford **21** as colorless syrup (760 mg, 43%). Optical rotation, ^{1}H NMR and ^{13}C NMR spectral data were identical to literature data.[1]

Phenyl *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-[(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)]-2,3-di-*O*-acetyl-1-thio-β-D-glucopyranoside (23)

A soln of **5** (1.00 g, 1.03 mmol) and **17**[1] (2.30 g, 1.48 mmol) in anhyd Et_2O (35 mL) was stirred with 4 Å molecular sieves (0.5 g, activated powder) under Ar at r.t. for 1 h. After cooling to −64 °C and dropwise addition of trimethylsilyl trifluoromethanesulfonate (48 µL, 0.26 mmol) in anhyd Et_2O (20 mL) , stirring was continued for 1 h during which time the temperature was raised to r.t. After addition of solid $NaHCO_3$ (1.5 g), the reaction mixture was stirred for additional 10 min, diluted with EtOAc (30 mL) and filtered through a pad of sea sand and a layer of silica gel. The filtrate was washed with sat. aq $NaHCO_3$ (25 mL), H_2O (3 × 25 mL) until neutral pH, brine (25 mL), dried and evaporated. The residue was chromatographed on silica gel (95 g) with Et_2O−pentane (1:1 and 4:1) as eluent to afford **23** as white foam (2.23 g, 92%). $[\alpha]_D^{23}$ +78.4 (*c* = 0.42, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 4.66 (d, 1 H, $J_{1,2}$ = 9.9 Hz, H-1), 5.11 (d, 1 H, *J* = 3.8 Hz, H-1internal), 5.25 (d, 1 H, *J* = 3.8 Hz, H-1internal), 5.46 (d, 1 H, *J* = 3.8 Hz, H-1internal), 5.67 (d, 2 H, *J* = 3.8 Hz, H-1internal).

^{13}C NMR ($CDCl_3$): δ = 85.2 (C-1), 95.2, 95.6, 96.2, 96.6, 96.7 (5 internal anomeric C).

Anal. Calcd for $C_{130}H_{144}O_{39}S.3H_2O$ (2416.65): C, 64.61; H, 6.26; S, 1.33. Found: C, 64.51; H, 6.24; S, 1.88.

Phenyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-[α-D-glucopyranosyl)-(1→4)-*O*-(α-D-glucopyranosyl)-(1→4)]-1-thio-β-D-glucopyranoside (24)

The procedure was the same as described for **11** using **23** (1.62 g, 0.69 mmol) dissolved in THF (3 mL) and methanolic NH_3 (50 mL, 2.0 M) to afford **24** as a white solid in quantitative yield (1.36 g).

$[\alpha]_D^{23}$ +19.7 (*c* = 0.30, DMSO).

^{1}H NMR (DMSO-d_6): δ = 4.68 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 4.94 (d, 1 H, *J* = 4.2 Hz, H-1internal), 4.97 (d, 1 H, *J* = 3.8 Hz, H-1internal), 5.02 (d, 1 H, *J* = 4.2 Hz, H-1internal), 5.50 (d, 2 H, *J* = 3.8 Hz, 2 H-1internal).

^{13}C NMR (DMSO-d_6): δ = 86.7 (C-1), 95.1 (2 C), 95.7, 96.2, 100.9, 101.2 (5 internal anomeric C).

Anal. Calcd for $C_{112}H_{126}O_{30}S.3H_2O$ (2038.32): C, 66.00; H, 6.53; S, 1.57. Found: C, 66.26; H, 6.51; S, 1.98.

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