Synthesis of Disaccharides, Containing Sulfur in the Ring of the Reducing Monosaccharide Unit, Through a Nonglycosylating Chemical Strategy

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Abstract: The synthesis of disaccharides containing sulfur in the reducing ring through a nonglycosylating chemical strategy is described. Lactose, maltose and cellobiose were transformed in several steps into the appropriately protected 4-*O*-glycosyl-2,3-*O*-isopropyliden-*aldehydo*-D-glucose dimethyl acetals (**6**, **11**, **18** and **27**) and 4-*O*-glycosyl-2,3-*O*-isopropyliden-*aldehydo*-L-idose dimethyl acetals (**42a** and **42b**). Compounds **6**, **11**, **18** and **27** were converted into the corresponding 4-*O*-glycosyl-5,6-dideoxy-5,6-epithio-2,3-*O*-isopropylidene-*aldehydo*-L-idose dimethyl acetals **33e–h** via the 5,6-cyclic sulfates **31a–d**, by reaction with potassium thioacetate or potassium thiocyanate and treatment with NaOMe/MeOH. Nucleophilic ring opening of the episulfide ring of **33e–h**, with sodium acetate followed by acidic hydrolysis, Zemplén de-*O*-acetylation and acetylation gave the thio disaccharides 4-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-galactopyranosyl-, -*α*-D-glucopyranosyl- and -*β*-D-glucopyranosyl)-1,2,3,6-tetra-*O*-acetyl-5-thio-*α*,*β*-L-idopyranoses (**38–40**).

Keywords: carbohydrates · cyclic sulfates · disaccharides · small ring systems · thiodisaccharides

1,2,3-Tri-*O*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-galactopyranosyl]-6-deoxy-5-thio-*α*,*β*-L-idopyranose (**37**) was obtained by treatment of 4-*O*-(2′,6′-di-*O*-acetyl-3′,4′-*O*-isopropylidene-*β*-D-galactopyranosyl)-2,3-*O*-isopropylidene-6-*S*-cyano-5-*O*-sulfonate-6-thio-*aldehydo*-D-glucose dimethyl acetal potassium salt (**32a**) with lithium aluminium hydride followed by acidic hydrolysis and acetylation. The analogous thio maltose and cellobiose (**47c** and **47d**) were synthesised following a similar strategy (5,6-cyclic sulfate →episulfide →thiosugar) from compounds **42a** and **42b**.

Introduction

The synthesis of sugar hetereoanalogues as potential inhibitors have received great attention in recent years. Most of the research in this respect is addressed toward the stability of the natural compounds under hydrolytic conditions and the enhancement of their affinity towards enzymes. Much of the activity has been focused in the synthesis of sugar heteroanalogues that fall in two main categories (see Figure 1): di/oligosaccharide heteroanalogues in which the interglycosidic oxygen atom has been replaced (type I) and those in which the ring oxygen atom has been substituted (type II). The synthesis of analogues of type I with a carbon,[1–15] sulfur,[16–36] selenium[36–38] or nitrogen atom[39–41] in the interglycosidic linkage has been described. Monosaccharide azasugars[42–47] have become increasingly important targets due to their potential value as enzyme inhibitors and therapeutic agents.

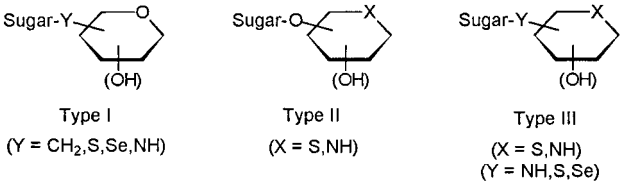

Figure 1. Sugar heteroanalogues.

Of the several different azasugars developed, some of them have been incorporated in analogues of type II.[48, 49] Furthermore, the synthesis of type II disaccharides containing sulfur in the ring of the reducing[48, 50] and nonreducing[36–38, 41, 50–55] sugar residues has been reported. Different thia sugars have also been incorporated in analogues of the blood group antigen trisaccharides Lewis X[56, 57] and H-type 2.[56] In addition, some novel disaccharide heteroanalogues with both the interglycosidic and the ring oxygen atoms substituted by heteroatoms (type III) have been recently reported. Pinto et al. have introduced sulfur as the X atom and sulfur,[36–38] selenium[36–38] or nitrogen[41] as the Y atom (see Figure 1) and Hashimoto et al.[39] described the synthesis of an azapyranosyl disaccharide with a thioglycosidic linkage.

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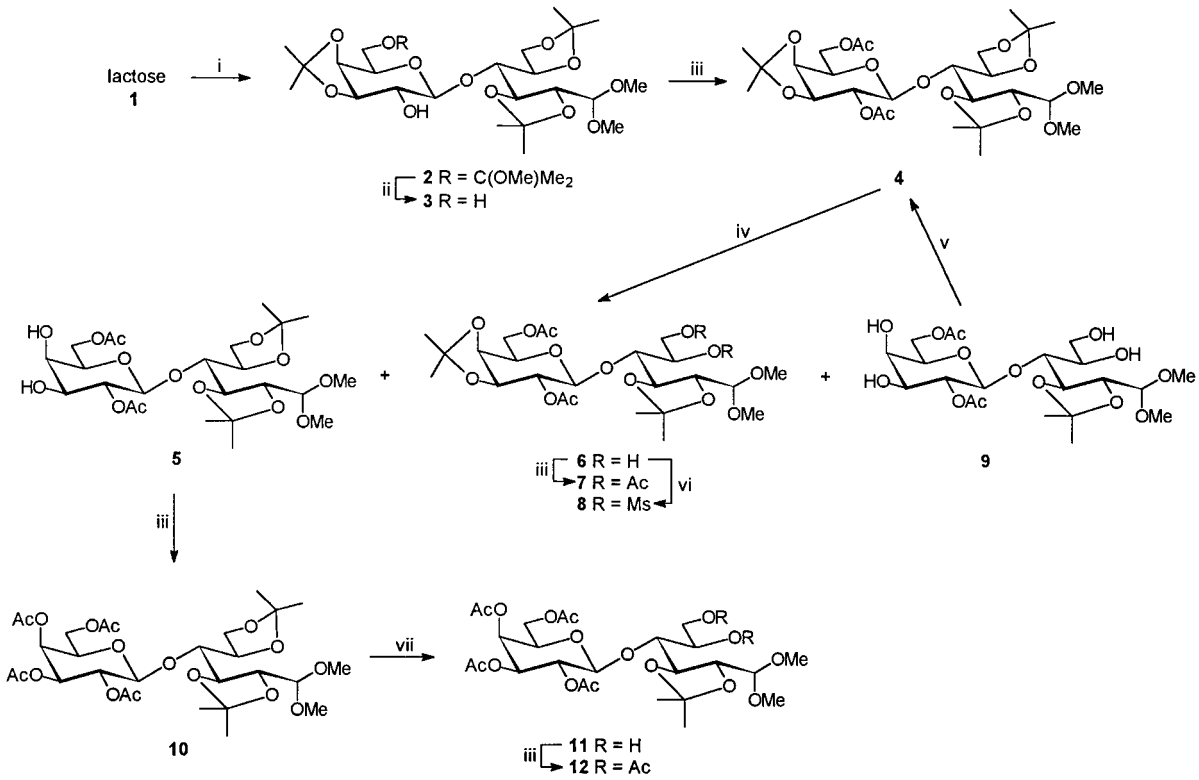
To the best of our knowledge, all the syntheses of thioanalogues of type II have been performed by chemical glycosylations using thio sugars and the appropriate glycosyl acceptors or by enzymatic methods. Only the synthesis of methyl 5′-thio-α-isomaltoside[55] has been performed from gentobiose through a novel ring-opening–recyclisation approach of the nonreducing sugar residue. This alternative strategy, which employs an easily available natural oligosaccharide in which an appropriate interglycosidic bond is already present, avoids the use of chemical or enzymatic glycosylation reactions between two monosaccharides and the consequent related steps in the synthesis, such as the multiple manipulation of protective groups. In this paper we extend this idea by means of the synthesis of thio sugars from vicinal diols via cyclic sulfates as described previously by our group,[58] using natural disaccharides (lactose, maltose and cellobiose) as starting materials.

Results and Discussion

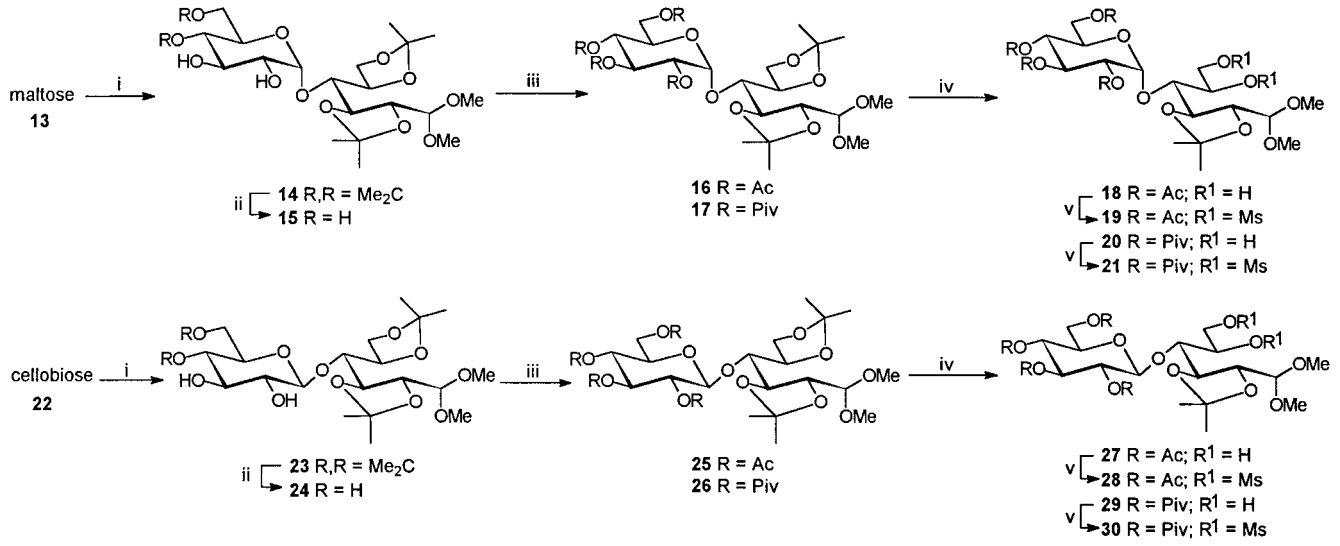
As mentioned above, we have developed[58] a new easy and expeditious strategy for the synthesis of thiiranes using cyclic sulfates of vicinal diols that allows access to these compounds in two steps. The versatility of this methodology was demonstrated by its application in carbohydrate chemistry. Thus, the preparation of several 4-thiopentofuranoses and 5-thiohexopyranoses, including L-thiofucose, was performed in good yields by the synthesis of 4,5-dideoxy-4,5-epithio pentoses and 5,6-dideoxy-5,6-epithio hexoses followed by nucleophilic ring opening of the episulfide with acetate or hydride and acidic hydrolysis. Considering the importance of sugar heteroanologues as potential inhibitors, we thought that this methodology could also be appropriate for the preparation of disaccharides containing sulfur in the ring of the reducing monosacharide unit. Although some enzymatic syntheses of this type of disaccharide heteroanalogues have been previously described,[48, 50] no general chemical synthesis is hitherto available. In order to get the highest efficiency in the synthesis it would be desirable to use appropriate disaccharide derivatives in which the interglycosidic bond is already present. In addition, the 5,6-hydroxyl groups of the reducing unit of such disaccharides should be free for the formation of a cyclic sulfate and the rest of the hydroxyl groups protected with temporary or semipermanent protecting groups that can be easily introduced and removed. In this context, the reported kinetic acetonation of lactose (**1**),[59, 60] maltose (**13**)[61] and cellobiose (**22**)[62] that leads to the corresponding dimethyl acetals (**3**, **14** and **23**, respectively) provides the appropriate starting materials (Schemes 1 and 2). The acetonation reactions were performed by the method described by Ueno et al.[61] with slight modifications in the reaction time and in the work-up (see Experimental Section). Hough et al.[59] were the first to report the isopropylidenation of lactose with an excess of 2,2-dimethoxypropane in the presence of *p*-toluensulfonic acid isolating the tri-*O*-isopropylidene dimethylacetal **3** as the major product. Later reinvestigation of this reaction by Yoshino et al.[60] showed that 2,3:5,6:3′,4′-tri-*O*-isopropylidene-6′-*O*-(2-methoxyisopropyl)lactose dimethyl acetal (**2**) was formed as a minor product. When we carried out the acetonation of lactose (**1**) following the method of Ueno et al.,[61] compound **3** was isolated in good yield (70%) together with a small amount of **2** (4%). The latter acetal can be readily transformed into **3** by boiling in methanol for 1 hour as previously described by Yoshino et al. (Scheme 1).[60] Acetylation of the 2′,6′-hydroxyl groups of **3** was followed by selective hydrolysis in 70% AcOH at RT, taking advantage of the different acid lability of the four acetal functions. Compounds **5** (14.0%), **6** (14.0%) and **9** (15.0%) were obtained together with a 20% of the starting material **4**. The low regioselectivity observed in the hydrolysis is compensated, since **5** and **6** are useful precursors for the pursued target compounds and **9** could be reacetonated giving again **4** in high yield (96%). Compound **6** fulfils all the requirements indicated above because it has the 5,6-hydroxyl groups ready for the formation of the corresponding cyclic sulfate derivative, whereas the rest of the hydroxyl groups are protected. Furthermore, compound **5** gave access to diol **11** by acetylation of the 3′- and 4′-hydroxyl groups and selective hydrolysis of the 5,6-*O*-isopropylidene group (48% overall yield from **5**). Diols **6** and **11** were characterised together with their corresponding 5,6-di-*O*-acetates derivatives **7** and **12**, respectively, (Scheme 1).

Isopropylidenation of maltose (**13**) and cellobiose (**22**) using the procedure of Ueno et al.[61] led to the tri-*O*-isopropylidene derivatives **14** and **23**, respectively (Scheme 2). Whereas **14** was the sole product isolated in the reaction with maltose, formation of the di-*O*-isopropylidene

Abstract in Spanish: *En el presente artículo se describe la síntesis de disacáridos que contienen azufre en la unidad reductora a través de una estrategia química no glicosidante. Los disacáridos naturales lactosa, maltosa y celobiosa fueron transformados, en varias etapas, en los 4-O-glicosil-2,3-O-isopropiliden-aldehido* D-*glucosa (**6**, **11**, **18** y **27**) y 4-O-glicosil-2,3-O-aldehido* L-*idosa (**42a** y **b**) dimetil acetales adecuadamente protegidos. Los compuestos **6**, **11**, **18** y **27** se transformaron en los correspondientes 4-O-glicosil-5,6-dideoxi-5,6-epitio-2,3-O-isopropiliden-aldehido-*L-*idosa dimetil acetales **33e–h** a través de los 5,6-sulfatos cíclicos **31a–d**, por reacción con tioacetato potásico o tiocianato potásico y tratamiento con NaOMe/MeOH. La apertura nucleofílica del anillo episulfuro de **33e–h** con acetato sódico seguido de hidrólisis ácida, des-O-acetilación de Zemplén y acetilación condujo a los tiodisacáridos 4-O-(2′, 3′,4′,6′-tetra-O-acetil-β-*D*-galactopiranosil-, -α-*D*-glucopiranosil- y -β-*D*-glucopiranosil)-1,2,3,6-tetra-O-acetil-5-tio-α,β-*L*-idopiranosas (**38–40**). Así mismo, el tiodisacárido 1,2,3-tri-O-acetil-4-O-[2′,3′,4′,6′-tetra-O-acetil-β-*D*-galactopiranosil]-6-deoxy-5-tio-α,β-*L*-idopiranosa (**37**) se obtuvo por tratamiento de la sal potásica de 4-O-(2′,6′-di-O-acetil-3′,4′-O-isopropiliden-β-*D*-galactopiranosil)-2,3-O-isopropiliden-6-S-ciano-5-O-sulfonato-6-tio-aldehido-*D*-glucosa dimetil acetal (**32a**) con hidruro de aluminio y litio seguido de hidrólisis ácida y acetilación. Los tioazúcares análogos de maltosa y celobiosa (**47c** y **d**) se sintetizaron siguiendo una estrategia similar (5,6-sulfato cíclico →episulfuro →tioazúcar) a partir de los compuestos **42a** y **b**.*



Scheme 1. Synthesis of partially protected derivatives of lactose. Reaction conditions: i) 2,2-dimethoxypropane, 1,4-dioxane, *p*-TsOH; ii) MeOH, reflux; iii) Ac_2O/Py; iv) 70% AcOH, RT; v) acetone, 2,2-dimethoxypropane, H^+; vi) MsCl/Py; vii) 80% AcOH, 50 °C.



Scheme 2. Synthesis of partially protected derivatives of maltose and cellobiose. Reaction conditions: i) 2,2-dimethoxypropane, 1,4-dioxane, *p*-TsOH; ii) MeOH, reflux; iii) Ac_2O, Py for **16** and **25** or Me_3COCl, Py for **17** and **26**; iv) 80% AcOH, 50 °C; v) MsCl/Py.

derivative **24** also occurs in the reaction with cellobiose. Selective hydrolysis of the 4′,6′-acetal in **14** and **23** with boiling methanol containing traces of acetic acid allowed the easy transformation into **15** and **24**, respectively. These compounds were subsequently converted into the tetra-*O*-acetyl derivatives **16** and **25** and then treated with 80% acetic acid at 50 °C yielding the diols **18** and **27;** these are then ready to be used for the formation of the corresponding cyclic sulfate. In all these transformations the reactions exhibited good to high yields (Scheme 2).

The disaccharide diols **6**, **11**, **18** and **27** were then transformed into the episulfides **33e–h** via the cyclic sulfates **31a–d**. Formation of these sulfates was performed by reaction with $SOCl_2/Et_3N$ followed by oxidation of the resulting cyclic sulfite by means of the procedure reported by Gao and Sharpless.[63] These two reactions were perfomed in a one-pot procedure to give the cyclic sulfates in high yields (82–96%). Two routes were now followed for the synthesis of episulfides **33e–h** from the cyclic sulfate derivatives. First, nucleophilic opening of the sulfate ring with potassium thiocyanate in

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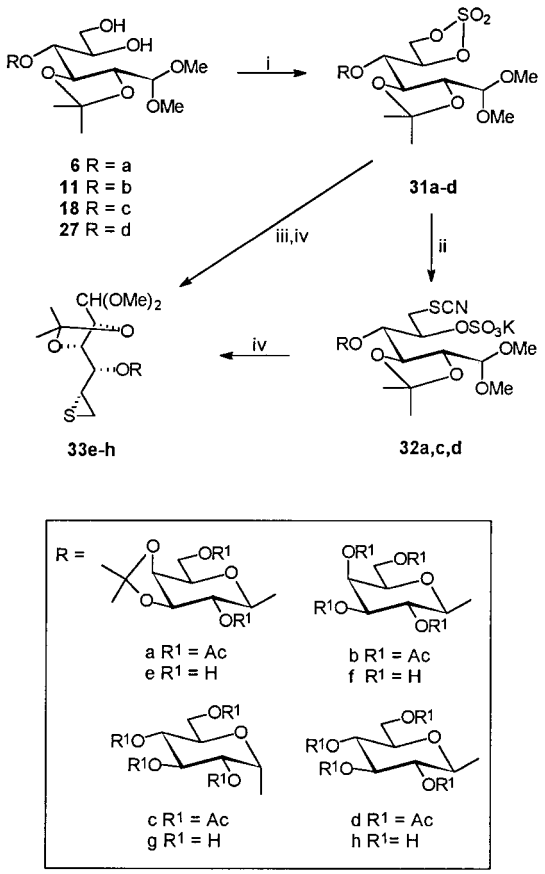
compounds **31a**, **c** and **d** gave the potassium salts **32a**, **c** and **d** in 79–99% yield. Subsequent treatment of these salts with sodium methoxide in methanol afforded the episulfides **33e**, **g** and **h** in high yields (85–90%). The second route studied used potassium thioacetate as nucleophile for the opening of the cyclic sulfate and introduction of a sulfur atom at the C-6 atom of the disaccharide derivatives. The corresponding 6-*S*-acetyl potassium salts were not isolated, but were directly treated with NaOMe/MeOH yielding the episulfides **33e–h** in a more straightforward fashion and with improved yields (88–100% from **31a–d**; Scheme 3). As a result of these reactions an



Scheme 3. Synthesis of episulfides **33e–h**. Reaction conditions: i) a) $SOCl_2$, Et_3N, CH_2Cl_2; b) $RuCl_3$, $NaIO_4$, MeCN, CCl_4, H_2O; ii) KSCN, acetone; iii) KSAC, acetone; iv) NaOMe, MeOH.

inversion of the configuration at the C-5 carbon atom occurred and therefore L-thio sugars will be obtained by the nucleophilic opening of the episulfide ring.

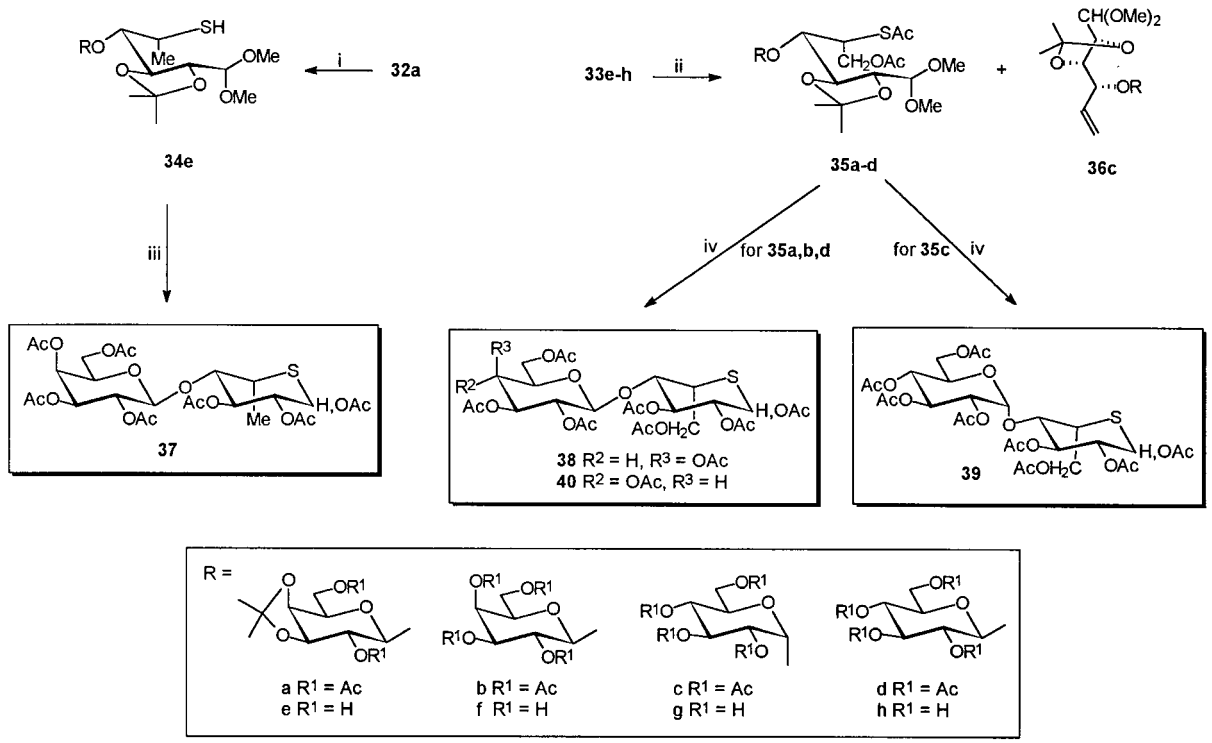
A different strategy for the synthesis of monosaccharide 5,6-episulfides has been used by Hashimoto et al.[64] for the synthesis of 5-thio-L-fucose by formation of 5,6-di-*O*-*p*-toluensulfonylesters derived from sugars and selective displacement of the 6-*O*-tosyl group with potassium thioacetate followed by treatment with NaOMe/MeOH. For this reason, the synthesis of di-*O*-methanesulfonylesters **8**, **19** and **28** was performed. Our experience showed that no selectivity was observed in the reactions of these dimesylate disaccharide derivatives with potassium thioacetate and mixtures of mono- and di-substituted compounds were obtained.

Incorporation of the sulfur atom into the carbohydrate ring in order to get the desired thio sugars was first carried out by thiirane opening with sodium acetate in acetic anhydride and acetic acid. This reaction allowed the conversion of episulfides **33e–h** into the 5-thioacetyl derivatives **35a–d** in good yields (57–87%). A yield decrease in the case of the preparation of the episulfide **33c** was due to concomitant formation of olefin **36c** as a by-product (33% yield). This process is not unusual, since thiirane thermal desulfurisation has previously been reported.[65–71] Acidic hydrolysis of the acetal groups in **35a–d** followed by Zemplen de-*O*-acetylation and acetylation afforded the disaccharide thio sugars **38–40** as an α,β mixture of anomers in 55–63% yield. On the other hand, treatment of the thiocyanate salt **32a** with an excess of lithium aluminium hydride led directly to the thiol derivative **34e**, which was then subsequently hydrolysed with aqueous acetic acid and acetylated. By this route, the 6-deoxy disaccharide thio sugar **37** was obtained in 38.0% overall yield from **32a** (Scheme 4).

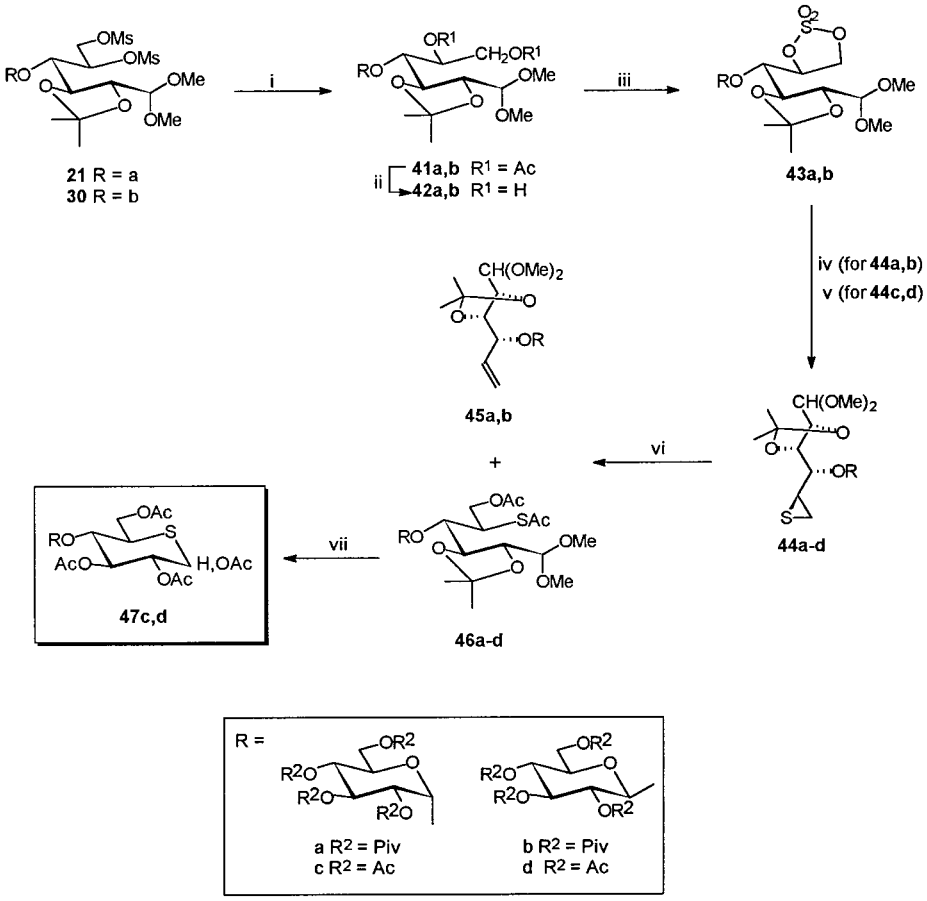
Considering the inversion of the configuration that occurs at the C-5 carbon in the formation of the episulfides **33e–h**, the synthesis of the thioanalogous of the naturally occurring disaccharides using a similar strategy requires an additional previous inversion in the configuration of C-5. In order to achieve this goal, it is necessary to use orthogonal protection that allows discrimination of the 5,6-hydroxyl groups. For these reasons, compounds **15** and **24** were transformed into the tetra-pivalate derivatives **17** and **26**, respectively. Selective hydrolysis of the 5,6-*O*-isopropylidene group followed by treatment with methanesulfonyl chloride led to the 5,6-di-*O*-methanesulfonyl derivatives **21** and **30** (see Scheme 2). Subsequent reaction with sodium acetate in acetic anydride allowed the desired inversion at C-5 and the isolation of compounds **41a** and **b** (Scheme 5). The selective deprotection of the acetyl esters in the presence of the pivaloyl esters was performed with guanidine or sodium methoxide at 0°C yielding compounds **42a** and **b**. Application of a strategy identical to that used for the diols **6**, **11**, **18** and **27** led to episulfides **44a** and **b** via the cyclic sulfates **43a** and **b**. However, the nucleophilic opening of these episulfides with sodium acetate occurred with low yields and formation of the olefin **45a** as the major product was observed in the case of episulfide **44a**. The presence of the bulky pivaloyl groups in these compounds can be pointed out as the likely cause for these results. An improvement in this transformation was possible by using the tetra-*O*-acetyl derivatives **44c** and **d**, which were obtained from **43a** and **b** by treatment with sodium methoxide in methanol followed by conventional acetylation. Opening of the thiirane ring in compounds **44c** and **d** happened in 16 and 52% yield, respectively, and the resulting acyclic 5-thio sugars **46c** and **d** were thus obtained and then converted into the thiodisaccharides thiomaltose and thiocellobiose **47c** and **d**.

Conclusion

We report the first synthesis of 1→4-linked disaccharides containing sulfur in the reducing ring unit by means of a nonglycosylating strategy and starting from the natural



Scheme 4. Synthesis of thiodisaccharides **37**–**40**. Reaction conditions: i) $LiAlH_4$, THF; ii) Ac_2O, AcOH, NaOAc; iii) a) $AcOH/H_2O$; b) Ac_2O/Py; iv) a) $AcOH/H_2O$; b) NaOMe, MeOH; c) Ac_2O/Py.



Scheme 5. Synthesis of thiomaltose **47c** and thiocellobiose **47d**. Reaction conditions: i) $NaOAc/Ac_2O/AcOH$; ii) NaOMe/MeOH, 0 °C or guanidine, Cl_2CH_2, EtOH; iv) a) KSAc, acetone; b) NaOMe, MeOH; v) a) KSAc, acetone; b) NaOMe, MeOH; c) Ac_2O, Py; vi) NaOAc, Ac_2O, AcOH; vii) a) AcOH, H_2O; b) NaOMe, MeOH; c) Ac_2O, Py.

disaccharides lactose, maltose and cellobiose. The methodology used takes advantage of an easy protection–deprotection manipulation of those natural disaccharides based on kinetic acetonation and selective hydrolysis; this allows the synthesis of partially protected disaccharide derivatives that have the 5,6-hydroxyl groups free. This in turn enables the introduction of the sulfur in the ring of the reducing unit through the sequence diol→cyclic sulfate →thiirane →thio sugar.

Experimental Section

General details: Thin-layer chromatography (TLC) was performed on precoated plates of silica gel $60F_{254}$ (Merck) with detection by UV light and the spots were visualised with a spray containing 5% sulfuric acid in ethanol followed by heating. Organic solutions were dried over Na_2SO_4. Column chromatography was performed on silica gel 60 (270–230 mesh, Merck). Optical rotations were measured with a Perkin–Elmer 141 polarimeter at RT. Infrared data were obtained with a Perkin–Elmer IR 983 spectrometer; only

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bands of spectral structural significance are listed. ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz (Bruker AM 300) and when specified at 400 MHz or 500 MHz (AM 400 or AM 500 instruments, respectively). The ^{1}H and ^{13}C resonances for compounds **3**, **14**, **17**, **26**, **37**, **38**, **39**, **40** and **42a** were assigned by ^{1}H-^{1}H COSY and ^{13}C-^{1}H NOESY correlation experiments. Mass spectra data (*m/z*) were obtained by the chemical ionisation mode using methane as the ionizing gas with a Fisons VG Platform II instrument and molecular weights were obtained with a Fisons VG Autospec-Q instrument. Microanalyses were performed by the University of Granada Microanalytical Service.

Reaction of lactose (1), maltose (13) and cellobiose (22) with 2,2-dimethoxypropane: general procedure: The reactions were carried out by the method of Ueno et al.[61, 62] with slight modifications. 2,2-Dimethoxypropane (40 mL, 0.33 mol) and *p*-toluenesulfonic acid (1.0 g) was added to a suspension of anhydrous disaccharide **1**, **13** or **22** (10.0 g, 29.24 mmol) in anhydrous 1,4-dioxane (100 mL) and the mixture was stirred at 70–80 °C (6 h for lactose and cellobiose and 1.5 h for maltose). After cooling, triethylamine was added dropwise until the solution became basic (pH paper) and the solvent was evaporated. The residue was purified by column chromatography.

2,3:5,6-Di-*O*-isopropylidene-4-*O*-(3′,4′-*O*-isopropylidene-β-D-galactopyranosyl)-*aldehydo*-D-glucose dimethyl acetal (3), and its 6′-*O*-(1-methyloxy-1-methylethyl) derivative (2): Column chromatography (ether) first gave **2** (0.71 g, 4.2 %), which was isolated as a syrup. $[\alpha]_D^{22} = +19.0$ ($c = 4.0$, chloroform); IR (neat) $\tilde{\nu} = 3450$, 1456, 1370, 1246, 1216, 1155, 1127, 1083 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 4.47$ (dd, $J = 7.7$, 6.1 Hz, 1H; H-2), 4.35 (d, $J = 8.2$ Hz, 1H; H-1′), 4.34 (d, $J = 6.1$ Hz, 1H; H-1), 4.24 (ddd, $J = 6.7$, 6.6, 2.6 Hz, 1H; H-5), 4.11 (dd, $J = 5.4$, 2.0 Hz, 1H; H-4′), 4.10 (dd, $J = 8.6$, 6.7 Hz, 1H; H-6), 4.04 (dd, $J = 2.4$, 1.7 Hz, 1H; H-4), 4.04 (dd, $J = 7.2$, 5.5 Hz, 1H; H-3′), 3.97 (dd, $J = 8.8$, 6.7 Hz, 1H; H-6), 3.87 (dd, $J = 7.6$, 1.5 Hz, 1H; H-3), 3.79 (ddd, $J = 6.3$, 6.3, 2.1 Hz, 1H; H-5′), 3.70–3.50 (m, 4H; H-2′,6′,6′,OH), 3.39, 3.38, 3.15 (3s, 9H; 3MeO), 1.46, 1.44, 1.33, 1.30, 1.29, 1.27 (6s, 24H; 4CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 110.0$, 109.9, 108.2, 100.5, 105.0, 104.1, 79.0, 77.9, 77.8, 76.6, 74.8, 74.4, 73.5, 72.8, 64.8, 60.0, 56.0, 53.0, 48.5, 28.2, 27.2, 26.4, 26.2, 25.7, 24.6, 24.3, 24.2.

Compound **3** (10.4 g, 70.2 %) was eluted second. M.p. 125–126 °C (from ether/hexane; lit. 133–134 °C,[59] 129–131 °C,[72] 129–130 °C[60]), $[\alpha]_D^{22} = +38.0$ ($c = 1.5$, chloroform) {lit. $[\alpha]_D^{22} = +39.1$ ($c = 1$, chloroform),[59] +37.3 ($c = 1.3$, chloroform)[72]}; IR (KBr): $\tilde{\nu} = 3450$, 1456, 1380, 1210, 1116, 906, 871, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$, D_2O): $\delta = 4.61$ (dd, $J = 7.8$, 6.8 Hz, 1H; H-2), 4.43 (d, $J = 8.3$ Hz, 1H; H-1′), 4.37 (d, $J = 6.7$ Hz, 1H; H-1), 4.34 (ddd, $J = 7.3$, 5.1, 2.5 Hz, 1H; H-5), 4.22 (dd, $J = 8.8$, 5.1 Hz, 1H; H-6), 4.09 (dd, $J = 6.0$, 5.3 Hz, 1H; H-3′), 4.07–3.97 (m, 3H; H-4, 4′, 6), 3.95–3.85 (m, 2H; H-3,6′), 3.82 (brd, $J = 9.0$ Hz, 1H; H-5′), 3.67 (dt, $J = 12.0$, 2.0 Hz, 1H; H-6′), 3.54 (dd, $J = 8.3$, 6.0 Hz, 1H; H-2′), 3.50, 3.49 (2s, 6H; 2MeO), 1.51, 1.39, 1.33, 1.32 (4s, 18H; 3CMe_2); ^{13}C NMR ($CDCl_3$): $\delta =$ 110.5, 110.0, 108.4 (3CMe_2), 107.2 (C-1), 103.5 (C-1′), 79.4 (C-3′), 78.1 (C-3), 77.5 (C-5), 75.8 (C-4′), 75.4 (C-2), 74.7 (C-5′), 74.1 (C-2′), 73.5 (C-4), 64.5 (C-6), 62.4 (C-6′), 57.5, 54.3 (2MeO), 28.1, 27.0, 26.2, 26.2, 25.6, 23.9 (3CMe_2). Compound **3** was also obtained in quantitative yield by treatment of **2** in boiling methanol for 1 h.

2,3:5,6-Di-*O*-isopropylidene-4-*O*-(4′,6′-*O*-isopropylidene-α-D-glucopyranosyl)-*aldehydo*-D-glucose dimethyl acetal (14): Column chromatography with ethyl acetate and then methanol/chloroform 1:10 gave **14** (8.2 g, 55.2 %) as a syrup. $[\alpha]_D^{22} = +58.0$ ($c = 1$, chloroform); IR (neat): $\tilde{\nu} = 3470$, 1457, 1373, 1266, 1211, 1065, 1026, 850 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 5.06$ (d, $J = 3.9$ Hz, 1H; H-1′), 4.40 (d, $J = 5.9$ Hz, 1H; H-1), 4.24–4.20 (m, 2H; H-2,5), 4.15 (dd, $J = 6.6$, 4.0 Hz, 1H; H-3), 4.03 (dd, $J = 8.0$, 6.4 Hz, 1H; H-6), 3.96 (dd, $J = 8.0$, 6.5 Hz, 1H; H-6), 3.87–3.84 (m, 2H; H-4, 6′), 3.80–3.70 (m, 3H; H-3′,5′,6′), 3.55 (dt, $J = 9.5$, 3.9 Hz, 1H; H-2′), 3.52 (t, $J = 9.3$ Hz, 1H; H-4′), 3.45, 3.42 (2s, 6H; 2OMe), 3.13 (d, $J = 9.8$ Hz, 1H; HO-2′), 2.62 (s, 1H; OH-3′), 1.51, 1.46, 1.43, 1.35 (4s, 18H; 3CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 110.1$, 108.8, 99.6 (3CMe_2), 104.9 (C-1), 100.8 (C-1′), 79.7 (C-4), 78.3 (C-3), 75.6, 75.3 (C-2,5), 73.4, 73.3 (C-2′,4′), 72.1 (C-5′), 65.8 (C-6), 63.8 (C-3′), 62.1 (C-6′), 56.6, 53.7 (2MeO), 29.0, 27.2, 27.0, 26.3, 24.9, 19.0 (3CMe_2).

2,3:5,6-Di-*O*-isopropylidene-4-*O*-(4′,6′-*O*-isopropylidene-β-D-glucopyranosyl)-*aldehydo*-D-glucose dimethyl acetal (23) and 4-*O*-β-D-glucopyranosyl-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (24): Column chromatography (ethyl acetate) first gave **23** (5.5 g, 37 %) as a syrup. $[\alpha]_D^{22} = -10.0$, $[\alpha]_{436}^{22} = -18.0$ ($c = 1$, chloroform); IR (neat): $\tilde{\nu} =$ 3426, 1456, 1369, 1209, 1073, 854 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 4.58$ (d, $J = 7.6$ Hz, 1H; H-1′), 4.43 (dd, $J = 7.3$, 6.4 Hz, 1H; H-2), 4.37 (d, $J = 6.3$ Hz, 1H; H-1), 4.31 (ddd, $J = 7.1$, 6.3, 1.8 Hz, 1H; H-5), 4.19 (dd, $J = 8.8$, 6.3 Hz, 1H; H-6), 4.07 (m, 1H; H-4), 4.02 (dd, $J = 8.8$, 7.1 Hz, 1H; H-6), 3.90 (dd, $J = 7.4$, 1.7 Hz, 1H; H-3), 3.83 (dd, $J = 10.8$, 5.9 Hz, 1H; H-6′), 3.80–3.58 (m, 4H; H-3′,4′,6′,OH), 3.48 (t, $J = 8.0$ Hz, 1H; H-2′), 3.41, 3.39 (2s, 6H; 2MeO), 3.27 (m, 1H; H-5′), 2.71 (brs, 1H; OH), 1.52, 1.44, 1.38, 1.35 (4s, 18H; 3CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 110.3$, 108.4, 99.9, 105.0, 104.8, 78.1, 77.9, 75.5, 74.7, 73.8, 73.0, 67.6, 64.6, 62.1, 55.9, 52.8, 29.1, 27.3, 26.5, 25.6, 24.2, 19.2; HR-MS (FAB+) $C_{23}H_{40}O_{12}Na$ calcd for [M^++Na] 531.2417; found 531.2421.

Further elution with ethyl acetate/methanol 20:1 provided the second title product **24** (2.2 g, 15.5 %) isolated as a hygroscopic foam solid. M.p. 126–129 °C; $[\alpha]_D^{22} = -9.0$ ($c = 1$, methanol); IR (neat): $\tilde{\nu} = 3450$, 1456, 1371, 1253, 1217, 1160, 1079, 992, 856 cm^{-1}; ^{1}H NMR ([D$_6$]DMSO): $\delta = 5.04$ (d, $J =$ 4.7 Hz, 1H; OH), 4.95 (d, $J = 4.8$ Hz, 1H; OH), 4.91 (d, $J = 5.1$ Hz, 1H; OH), 4.40 (dd, $J = 7.2$, 6.4 Hz, 1H; H-2), 4.37 (d, $J = 6.5$ Hz, 1H; H-1), 4.31 (d, $J = 7.8$ Hz, 1H; H-1′), 4.13 (m, 1H; H-5), 4.07 (dd, $J = 8.5$, 5.5 Hz, 1H; H-6), 4.02 (dd, $J = 7.3$, 1.0 Hz, 1H; H-3), 3.93 (dd, $J = 8.6$, 5.8 Hz, 1H; H-6), 3.89 (dd, $J = 7.9$, 4.3 Hz, 1H; HO–C-6′), 3.39 (m, 1H; H-6′; dd, $J = 11.7$, 6.5 Hz after isotopic exchange), 3.32, 3.30 (2s, 6H; 2MeO), 3.60, 3.17–2.92 (2m, 6H; H-4, 2′,3′,4′,5′,6′), 1.31, 1.28, 1.24 (3s, 18H; 3CMe_2); ^{13}C NMR ([D$_6$]DMSO): $\delta = 108.8$, 108.0, 105.3, 103.3, 77.1, 76.7, 76.1, 75.9, 74.5, 73.8, 70.3, 65.5, 61.6, 55.7, 53.3, 27.1, 26.6, 25.5; $C_{20}H_{36}O_{12} \cdot 1/2\,H_2O$ (477.51): calcd C 50.31, H 7.76; found C 50.70, H 7.84.

Selective hydrolysis of 4′,6′-acetal of 14 and 23. Synthesis of 15 and 24: A solution of **14** or **23** (6.2 g, 12.2 mmol) and acetic acid (2 drops) in methanol (100 mL) was boiled for 24 h. The solvent was removed under vacuum and the residue was purified by column chromatography.

4-*O*-α-D-Glucopyranosyl-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (15): Column chromatography (methanol/ethyl acetate 1:15) of the crude product gave first the starting material **14** (1.15 g, 16.1 %). Compound **15** (4.02 g, 70.4 %) was eluted second as a syrup. $[\alpha]_D^{22} = +76.0$ ($c = 1$, methanol); IR (neat): $\tilde{\nu} = 3402$, 1374, 1253, 1216, 1053, 1047 cm^{-1}; ^{1}H NMR ([D$_6$]DMSO): $\delta = 4.93$ (d, $J = 5.1$ Hz, 1H; OH),4.88 (d, $J = 5.3$ Hz, 1H; OH), 4.84 (d, $J = 4.6$ Hz, 1H; OH), 4.78 (d, $J = 3.5$ Hz, 1H; H-1′), 4.73 (dd, $J = 7.4$, 7.1 Hz, 1H; H-2), 3.89 (t, $J = 5.2$ Hz, 1H; HO–C-6′), 4.33 (d, $J = 6.4$ Hz, 1H; H-1), 4.05, 3.62–3.00 (several m, 11H; H-3,4,5,6,6,2′,3′,4′,5′,6′,6′), 3.33, 3.29 (2s, 6H; 2MeO), 1.36, 1.30, 1.29, 1.24 (4s, 12H; 2CMe_2); ^{13}C NMR ([D$_6$]DMSO): $\delta = 108.5$, 107.7, 105.1, 101.3, 79.6, 78.0, 75.3, 73.2, 72.7, 72.1, 70.0, 66.8, 60.9, 55.6, 52.80, 27.4, 26.8, 26.5, 25.1; HR-MS (FAB+) $C_{20}H_{36}O_{12}Na$ calcd for [M^++Na] 491.2104; found 491.2087; $C_{20}H_{36}O_{12} \cdot H_2O$ (486.51): calcd C 49.37, H 7.87; found C 49.20, H 8.14.

4-*O*-β-D-Glucopyranosyl-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (24): Column chromatography (ethyl acetate) of the crude product gave **24** (3.78 g, 66.3 %) which showed physical properties identical to those described above.

Acetylation of 3, 15 and 24: Conventional acetylation of **3**, **15** and **24** (5.0 g) with acetic anhydride-pyridine (25:25 mL) at RT overnight gave after conventional work-up a crude product that was purified by column chromatography.

4-*O*-(2′,6′-Di-*O*-acetyl-3′,4′-*O*-isopropylidene-β-D-galactopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (4): Column chromatography (ether) gave **4** (5.1 g, 88 %). M.p. 105–106 °C (lit. m.p. 113–115 °C[59]); $[\alpha]_D^{22} = +25.0$ ($c = 1$, chloroform)(lit. $[\alpha]_D^{22} = +25.2$[59]). The ^{1}H and ^{13}C NMR data are identical to the reported by Yoshino et al.[60]

4-*O*-(2′,3′4′,6′-Tetra-*O*-acetyl-α-D-glucopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (16): Column chromatography (ether/hexane 5:1) gave **16** (5.43 g, 80 %). M.p. 115–117 °C; $[\alpha]_D^{22} = +93.0$ ($c = 2$, chloroform) {lit. $[\alpha]_D^{22} = +116.7$ ($c = 0.06$, chloroform)[61]}; IR (KBr): $\tilde{\nu} = 1744$, 1369, 1224, 1161, 1142, 1085, 1058, 1029 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.49$ (dd, $J = 10.5$, 9.4 Hz, 1H; H-3′), 5.32 (d, $J = 3.6$ Hz, 1H; H-1′), 5.09 (dd, $J = 10.2$, 9.4 Hz, 1H; H-4′), 4.95 (dd, $J = 10.5$, 3.6 Hz, 1H; H-2′), 4.36 (ddd, $J = 10.3$, 3.8, 2.2 Hz, 1H; H-5), 4.32 (d, $J = 5.9$ Hz, 1H; H-1), 4.30–4.20, 4.12–3.90 (several m, 7H; H-3,4,6,6,5′,6′,6′), 4.15 (dd, $J = 7.4$, 5.9 Hz, 1H; H-2), 3.45, 3.44 (2s, 6H; 2MeO), 2.10, 2.08, 2.02, 2.00 (4s, 12H; 4Ac), 1.45, 1.42, 1.41, 1.35 (4s, 12H; 2CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.7$, 170.2, 170.0, 169.6, 110.2, 108.5, 105.9, 97.1, 78.8, 78.8, 76.0, 75.7, 70.7, 70.0, 68.4,

67.6, 65.7, 61.9, 57.0, 54.7, 27.2, 26.9, 26.4, 25.1, 20.7, 20.6; $C_{28}H_{44}O_{16}$ (636.65): calcd C 52.83, H 6.97; found C 53.14, H 7.11.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (25): Column chromatography (ether/hexane 5:1) gave **25** (5.67 g, 83.5 %) as an amorphous solid. M.p. 60–61 °C; $[\alpha]_D^{22} = -11.0$ ($c = 1$, chloroform) {lit. $[\alpha]_D^{22} = -12.0$ ($c = 0.51$, chloroform)[62]}; ^{1}H NMR ($CDCl_3$): $\delta = 5.20$ (t, $J = 9.3$ Hz, 1H; H-3′), 5.13 (t, $J = 8.9$ Hz, 1H; H-4′), 5.07 (dd, $J = 9.4$, 7.3 Hz, 1H; H-2′), 4.98 (d, $J =$ 7.9 Hz, 1H; H-1), 4.43–4.33, 3.95–3.91 (2m, 5H; H-2,3,6,6,1′), 4.31 (ddd, $J = 6.8$, 6.7, 2.3 Hz, 1H; H-5), 4.22 (dd, $J = 12.3$, 4.3 Hz, 1H; H-6′), 4.12 (t, $J = 1.7$ Hz, 1H; H-4), 4.07 (dd, $J = 12.2$, 2.3 Hz, 1H; H-6′), 3.69 (ddd, $J =$ 9.8, 4.2, 2.4 Hz, 1H; H-5′), 3.38, 3.36 (2s, 6H; 2MeO), 2.08, 2.06, 2.01, 1.99 (4s, 12H; 4Ac), 1.50, 1.36, 1.31 (3s, 12H; 2CMe_2); ^{13}C NMR ($CDCl_3$): $\delta =$ 170.7, 170.3, 169.5, 169.4, 110.9, 108.1, 105.1, 100.5, 78.3, 78.1, 74.9, 74.0, 73.1, 71.6, 71.3, 68.7, 64.4, 62.0, 55.7, 52.6, 27.3, 26.3, 26.1, 24.4, 20.7; MS (FAB+): m/z: 659 [M^++Na], 637 [M^++H]; $C_{28}H_{44}O_{16}$ (636.65): calcd C 52.83, H 6.97; found C 52.49, H 7.18.

Pivalation of 15 and 24. Synthesis of 17 and 26: Pivaloyl chloride (3.5 mL) and a catalytic amount of DMAP was added to a solution of **15** or **24** (4.7 mmol) in dry pyridine (10 mL). The reaction was kept at RT for 72 h and then at 60 °C for 24 h. The reaction mixture was poured into ice water (100 mL) and extracted with chloroform (100 mL). The organic phase was successively washed with hydrochloric acid (2 × 75 mL), saturated aqueous solution of sodium hydrogen carbonate (100 mL) and water (50 mL). The organic phase was evaporated and the residue was purified by column chromatography (ether/hexane 1:1)

4-*O*-(2′,3′,4′,6′-Tetra-*O*-pivaloyl-*α*-D-glucopyranosyl)-2,3:5,6-di-*O*-isopropylidene-aldehyde-D-glucose dimethyl acetal (17): Column chromatography gave **17** (3.06 g, 81 %), as a syrup. $[\alpha]_D^{22} = +84.0$ ($c = 1$, chloroform); IR (neat): $\tilde{\nu} = 1741$, 1700, 1141, 1039 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.62$ (d, $J =$ 3.7 Hz, 1H; H-1′), 5.61 (t, $J = 9.8$ Hz, 1H; H-3′), 5.12 (dd, $J = 10.4$, 9.5 Hz, 1H; H-4′), 4.88 (dd, $J = 10.3$, 3.7 Hz, 1H; H-2′), 4.70 (ddd, $J = 10.4$, 4.7, 1.3 Hz, 1H; H-5′), 4.30 (d, $J = 5.6$ Hz, 1H; H-1), 4.23–4.18 (m, 2H; H-3,6), 4.11 (dd, $J = 7.6$, 2.7 Hz, 1H; H-4 or H-5), 4.04–3.96 (m, 4H; H-2,6,6′,6′), 3.91 (dd, $J = 7.6$, 6.3 Hz, 1H; H-5 or H-4), 3.47, 3.45 (2s, 6H; 2MeO), 1.48, 1.43, 1.37, 1.34 (4s, 12H; 2CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 178.1$, 177.5, 177.0 (4CO), 110.4, 108.6 (2CMe_2), 105.6 (C-1), 94.7 (C-1′), 79.1 (C-4 or C-5), 77.6 (C-2), 75.0 (C-3), 74.8 (C-5 or C-4), 70.9 (C-2′), 69.4 (C-3′), 68.1 (C-4′), 67.3 (C-5′), 64.1 (C-6′), 61.9 (C-6), 57.0, 54.6 (2MeO), 38.9, 38.8, 38.6 (Me_3C), 27.3, 27.2, 27.1, 27.0 26.9, 26.5, 26.4, 25.5 (4Me_3C, 2Me_2C); $C_{40}H_{68}O_{16}Na$: HR-MS (FAB+) calcd [M^++Na] 827.4405; found 827.4384.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-pivaloyl-*β*-D-glucopyranosyl)-2,3:5,6-di-*O*-isopropylidene-aldehyde-D-glucose dimethyl acetal (26): Column chromatography gave **26** (2.61 g, 69 %) as a solid. M.p. 131–132 °C; $[\alpha]_D^{22} = -16.0$ ($c = 1$, chloroform); IR (KBr): $\tilde{\nu} = 1745$, 1138 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.25$ (dd, $J = 9.2$, 7.0 Hz, 1H; H-3′), 5.16 (dd, $J = 9.7$, 9.2 Hz, 1H; H-4′), 5.12–5.05 (m, 2H; H-1′, 2′), 4.36–4.31 (m, 2H; H-1,2), 4.26 (dd, $J = 6.8$, 3.3 Hz, 1H; H-5), 4.18 (br s, 1H; H-4), 4.16 (dd, $J = 12.4$, 1.5 Hz, 1H; H-6′), 4.03 (m, 1H; H-3), 4.02 (dd, $J = 12.4$, 4.6 Hz, 1H; H-6′), 3.95 (m, 2H; H-6,6), 3.68 (ddd, $J = 9.9$, 4.5, 1.5 Hz, 1H; H-5′), 3.36, 3.36 (2s, 6H; 2OMe), 1.46, 1.34, 1.29, 1.21 (4s, 12H; 2CMe_2), 1.20, 1.15, 1.12, 1.09 (4s, 36H; 4Me_3C); ^{13}C NMR ($CDCl_3$): $\delta = 178.2$, 177.3, 177.2, 176.6 (CO), 110.8, 108.2 (2CMe_2), 105.1 (C-1), 99.5 (C-1′), 78.1 (C-5), 77.9 (C-3), 75.2 (C-2), 72.9 (C-3′), 72.3 (C-5′), 72.2 (C-4), 71.7 (C-2′), 68.1 (C-4′), 64.9 (C-6), 61.8 (C-6′), 55.5, 53.6 (2OMe), 38.7 (Me_3C), 27.7, 27.3, 27.3, 27.2, 27.1, 26.8, 26.5, 24.9 (4Me_3C, 2Me_2C); HR-MS (FAB+) $C_{40}H_{68}O_{16}Na$: calcd for [M^++Na] 827.4405; found 827.4402; $C_{40}H_{68}O_{16}$ (804.97): calcd C 59.68, H 8.52; found C 59.41, H 8.65.

Treatment of 4 with aqueous acetic acid. Synthesis of 5, 6 and 9: Compound **4** (7.6 g, 12.82 mmol) was hydrolysed with aqueous 70 % acetic acid for 70 h at RT. Water (25 mL) was added, the mixture was neutralised with sodium hydrogen carbonate. The solution was extracted with ethyl acetate (6 × 65 mL). The organic phase was dried and concentrated. The residue was chromatographed (ether) to give the starting material **4** (1.4 g, 20.0 %).

4-*O*-(2′,6′-Di-*O*-acetyl-*β*-D-galactopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (5): Compound **5** (1 g, 14.1 %) as a solid was obtained after further elution with ethyl acetate. M.p. 123–124 °C; $[\alpha]_D^{22} = +9.0$, $[\alpha]_{436}^{22} = +20.0$ ($c = 1$, methanol); IR (KBr): $\tilde{\nu} = 3440$, 1742, 1373, 1250, 1226, 1156, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.03$ (dd, $J = 9.8$, 8.1 Hz, 1H; H-2′), 4.85 (d, $J = 8.0$ Hz, 1H; H-1′), 4.47 (dd, $J = 6.6$, 6.2 Hz, 1H; H-2), 4.36 (d, $J = 6.2$ Hz, 1H; H-1), 4.40–4.25 (m, 2H; H-5,6′), 4.19 (dd, $J = 11.5$, 6.5 Hz, 1H; H-6′), 4.10 (m, 1H; H-4), 4.01 (dd, $J = 6.7$, 1.4 Hz, 1H; H-3), 3.97 (m, 2H; H-6,6), 3.90 (d, $J = 2.8$ Hz, 1H; H-4′), 3.68 (dd, $J = 6.4$, 6.1 Hz, 1H; H-5′), 3.62 (dd, $J = 9.8$, 3.0 Hz, 1H; H-3′), 3.41, 3.40 (2s, 6H; 2MeO), 2.16, 2.08 (2s, 6H; 2Ac), 1.50, 1.37, 1.33 (3s, 12H; 2CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 171.3$, 171.0, 111.0, 108.0, 105.0, 100.5, 78.2, 78.1, 75.4, 74.0, 72.9, 72.5, 72.2, 69.0, 64.6, 62.9, 55.4, 53.3, 27.6, 26.4, 26.1, 24.6, 20.9, 20.8; $C_{24}H_{40}O_{14} \cdot 1/2\,H_2O$ (561.58): calcd C 51.34, H 7.31; found C 51.49, H 7.30.

4-*O*-(2′,6′-Di-*O*-acetyl-3′,4′-*O*-isopropylidene-*β*-D-galactopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (6): Upon further elution compound **6** was obatined as a syrup (1.0 g, 14.1 %). $[\alpha]_D^{22} = +11.0$, $[\alpha]_{436}^{22} = +24.0$ ($c = 1$, methanol); IR (neat): $\tilde{\nu} = 3475$, 1747, 1454, 1373, 1226, 1157, 1132, 1082 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 4.97$ (dd, $J = 8.0$, 6.8 Hz, 1H; H-2′), 4.66 (d, $J = 8.0$ Hz, 1H; H-1′), 4.45 (dd, $J = 7.4$, 5.8 Hz, 1H; H-2), 4.36 (d, $J = 5.7$ Hz, 1H; H-1), 4.35 (dd, $J = 10.7$, 5.1 Hz, 1H; H-6′), 4.26 (dd, $J =$ 11.6, 7.1 Hz, 1H; H-6′), 4.17–4.11 (m, 3H; H-3′,4′, OH), 4.09 (dd, $J = 7.4$, 1.5 Hz, 1H; H-3), 3.95 (ddd, $J = 7.0$, 5.1, 1.8 Hz, 1H; H-5′), 3.88 (dd, $J = 5.2$, 1.4 Hz, 1H; H-4), 3.81 (m, 1H; H-5), 3.75–3.70 (m, 3H; H-6,6,OH), 3.43, 3.42 (2s, 6H; 2MeO), 2.10, 2.07 (2s, 6H; 2Ac), 1.52, 1.39, 1.31 (3s, 12H; 2CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.9$, 169.7, 110.9, 110.8, 105.2, 100.2, 77.3, 77.0, 76.7, 75.7, 73.5, 72.9, 72.8, 71.0, 63.3, 63.2, 55.9, 53.8, 27.6, 27.4, 26.4, 26.3, 21.0, 20.8; MS (CI+) m/z: 537 [$M^+ - CH_3$], 521 [M^++1 − CH_3OH], 287 [$C_{13}H_{19}O_7$]; HR-MS (FAB+) $C_{24}H_{41}O_{14}$: calcd for [M^++H] 553.2496; found 553.2494.

4-*O*-(2′,6′-Di-*O*-acetyl-*β*-D-galactopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (9): Further elution with chloroform-methanol 5:1 gave **9** (1 g, 15.2 %) as a solid. M.p. 157–160 °C; $[\alpha]_D^{22} =$ +10.0, $[\alpha]_{436}^{22} = +20.0$ ($c = 1$, methanol); IR (KBr): $\tilde{\nu} = 3412$, 1743, 1375, 1241, 1139, 1064 cm^{-1}; ^{1}H NMR ([D$_6$]DMSO, D$_2$O): $\delta = 4.83$ (dd, $J = 9.9$, 8.1 Hz, 1H; H-2′), 4.54 (d, $J = 8.1$ Hz, 1H; H-1′), 4.38 (t, $J = 6.4$ Hz, 1H; H-2), 4.29 (d, $J = 6.2$ Hz, 1H; H-1), 4.20–3.20 (several m, 10H; H-3,4,5,6,6,3′,4′,5′,6′,6′), 3.30, 3.26 (2s, 6H; 2MeO), 2.01, 2.00 (2s, 6H; 2Ac),1.27, 1.25 (2s, 6H; CMe_2); ^{13}C NMR ([D$_6$]DMSO): $\delta = 170.3$, 169.0, 109.1, 104.8, 99.8, 77.0, 76.1, 74.9, 72.1, 72.0, 71.6, 70.7, 68.4, 63.5, 61.7, 54.9, 52.6, 27.8, 26.6, 20.9, 20.5; $C_{21}H_{36}O_{14}$ (512.51): calcd C 49.21, H 7.08. found: C 49.36, H 7.04.

Acetonation of 9: 2,2-Dimethoxypropane (10 mL) and *p*-toluenesulfonic acid (50 mg) was added to a solution of **9** (0.74 g) in anhydrous acetone (20 mL). The mixture was stirred for 1 h at RT. Triethylamine was then added until the solution became basic and the solvent was evaporated. The residue was chromatographed (ether) to give **4** (0.82 g, 96 %).

Acetylation of 5 and 6. Synthesis of 10 and 7: Conventional acetylation of **5** and **6** (1.0 g) with acetic anhydride/pyridine (7:7 mL) at RT overnight followed by conventional work-up gave a crude product that was purified by column chromatography.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2,3:5,6-di-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (10): Column chromatography (ether/hexane 5:1) of the crude product gave **10** (1.14 g, 99 %), as a syrup. $[\alpha]_D^{22} = -8.0$, $[\alpha]_{436}^{22} = -13.0$ ($c = 1$, chloroform); IR (neat): $\tilde{\nu} = 1749$, 1458, 1376, 1218, 1154, 1076, 721, 664 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.38$ (d, $J = 3.4$ Hz, 1H; H-4′), 5.21 (dd, $J = 10.5$, 8.0 Hz, 1H; H-2′), 4.99 (dd, $J =$ 10.4, 3.5 Hz, 1H; H-3′), 4.97 (d, $J = 7.9$ Hz, 1H; H-1′), 4.45 (dd, $J = 7.1$, 6.1 Hz, 1H; H-2), 4.36 (d, $J = 6.1$ Hz, 1H; H-1), 4.33 (m, 1H; H-5), 4.15–3.93 (m, 7H; H-3,4,6,6,5′,6′,6′), 3.41 (s, 6H; 2MeO), 2.16, 2.10, 2.04, 1.98 (4s, 12H; 4Ac), 1.49, 1.40, 1.38, 1.31 (4s, 12H; 2CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.4$, 170.2, 169.6, 110.9, 108.0, 105.2, 100.8, 78.2, 78.1, 75.2, 73.7, 71.1, 70.5, 68.9, 67.1, 64.4, 61.2, 55.7, 53.2, 27.5, 26.3, 26.1, 24.3, 20.8, 20.7, 20.6; MS m/z (CI+): 621 [$M^+ - CH_3$], 605 [M^++1 − CH_3OH], 331 ($C_{14}H_{19}O_9$); HR-MS (FAB+) $C_{28}H_{45}O_{16}$: calcd for [M^++H] 637.2707; found 637.2699.

4-*O*-(2′,6′-Di-*O*-acetyl-3′,4′-*O*-isopropylidene-*β*-D-galactopyranosyl)-5,6-di-*O*-acetyl-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (7): Column chromatography (ether/hexane 5:1) of the crude product gave **7** (1.10 g, 95.5 %), as a syrup. $[\alpha]_D^{22} = +18.0$, $[\alpha]_{436}^{22} = +38.0$ ($c = 2.0$, chloroform); IR (neat): $\tilde{\nu} = 1749$, 1437, 1373, 1224, 1156, 1132, 1080 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.30$ (ddd, $J = 8.5$, 2.8, 2.2 Hz, 1H; H-5), 4.99 (dd, $J = 7.9$, 7.1 Hz, 1H; H-2′), 4.65 (d, $J = 8.0$ Hz, 1H; H-1′), 4.60 (dd, $J = 12.5$, 2.2 Hz, 1H; H-6), 4.40–4.00 (m, 9H; H-1,2,3, 4,6,3′,4′,6′,6′), 3.94 (ddd, $J = 7.1$, 5.2, 1.9 Hz, 1H; H-5′), 3.44, 3.43 (2s, 6H; 2MeO), 2.17, 2.11, 2.06 (3s, 12H; 4Ac), 1.57, 1.39, 1.37, 1.35 (4s, 12H; 2CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.9$,

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170.8, 170.0, 169.5, 111.0, 110.9, 105.3, 99.5, 77.9, 77.2, 75.6, 75.5, 74.2, 73.5, 72.9, 71.1, 63.3, 62.7, 55.8, 53.7, 27.6, 27.5, 26.4, 26.3, 21.2, 20.9, 20.8; MS (CI+): m/z: 621 [$M^+ - CH_3$], 605 [$M^+ + 1 - CH_3OH$], 287 [$C_{13}H_{19}O_7$]; HR-MS (FAB+) $C_{28}H_{45}O_{16}$: calcd for [M^++H] 637.2708; found 637.2717.

Selective hydrolysis of 5,6-acetal of 10, 16 and 25: general procedure: Compounds **10**, **16** and **25** (3.5 g, 5.5 mmol) were treated with aqueous 70% acetic acid (40 mL) at 45 °C (4 h for **10** and 2 h for **16** and **25**). The reaction mixtures were concentrated and coevaporated with toluene to give a crude product that was purified by column chromatography.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (11): Column chromatography (ethyl acetate/methanol 50:1) of the crude product gave, first, unreacted **10** (420 mg, 12%). Compound **11** (1.39 g, 48%) was eluted second. M.p. 85–90 °C; $[\alpha]_D^{22} = -13.0$, $[\alpha]_{436}^{22} = -25$ ($c = 1$, chloroform); IR (KBr): $\tilde{\nu} = 3450$, 1749, 1392, 1215, 1143, 1099, 1041 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.39$ (dd, $J = 3.0$, 1.0 Hz, 1H; H-4′), 5.21 (dd, $J = 10.5$, 7.9 Hz, 1H; H-2′), 5.03 (dd, $J = 10.5$, 3.4 Hz, 1H; H-3′), 4.83 (d, $J = 8.0$ Hz, 1H; H-1′), 4.45 (dd, $J = 7.4$, 5.9 Hz, 1H; H-2), 4.38 (d, $J = 5.9$ Hz, 1H; H-1), 4.15–3.75 (several m, 10H; H-3,4,5,6,6,5′,6′,6′,2OH), 3.44 (s, 6H; 2MeO), 2.16, 2.10, 2.05, 1.98 (4s, 12H; 4Ac), 1.44, 1.42 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.5$, 170.3, 170.2, 169.5, 110.8, 105.3, 100.7, 77.3, 77.0, 75.7, 73.0, 71.0, 70.8, 69.2, 67.1, 63.5, 61.2, 56.0, 54.0, 27.4, 26.4, 20.8, 20.7, 20.7, 20.6; MS (CI+): m/z: 581 [$M^+ - CH_3$], 565 [$M^+ + 1 - CH_3OH$], 331 [$C_{14}H_{19}O_9$]; $C_{25}H_{40}O_{16}$ (596.58): calcd C 50.33, H 6.76; found C 50.34, H 6.84.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-*α*-D-glucopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (18): Column chromatography (ethyl acetate) of the crude product gave, first, unreacted **16** (680 mg, 19.4%). Compound **18** (2.44 g, 74.4%) was eluted second as a syrup. $[\alpha]_D^{22} = +61.0$ ($c = 1$, chloroform); IR (neat): $\tilde{\nu} = 3510$, 1742, 1725, 1437, 1376, 1179, 1169, 1014 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.52$ (dd, $J = 10.4$, 9.4 Hz, 1H; H-3′), 5.20 (d, $J = 3.8$ Hz, 1H; H-1′), 5.05 (dd, $J = 10.3$, 9.5 Hz, 1H; H-4′), 4.95 (dd, $J = 10.4$, 3.8 Hz, 1H; H-2′), 4.42 (ddd, $J = 10.2$, 5.0, 2.5 Hz, 1H; H-5′), 4.33 (d, $J = 5.8$ Hz, 1H; H-1), 4.27 (dd, $J = 7.5$, 5.9 Hz, 1H; H-2), 4.20–4.09 (m, 3H; H-3,6′,6′), 3.98 (m, 1H; H-5), 3.77 (dd, $J = 3.4$, 3.1 Hz, 1H; H-4), 3.70 (m, 2H; H-6,6), 3.46 (s, 6H; 2MeO), 3.40 (d, $J = 8.2$ Hz, 1H; OH-5), 2.37 (br s, 1H; OH-6), 2.11, 2.09, 2.04, 2.01 (4s, 12H; 4Ac), 1.51, 1.43 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.8$, 170.2, 170.0, 169.7, 110.6, 106.1, 98.4, 80.6, 78.6, 76.5, 73.9, 70.8, 69.9, 68.6, 68.3, 63.8, 62.3, 57.2, 55.7, 27.2, 26.5, 20.8, 20.7; HR-MS (FAB+) $C_{25}H_{40}O_{16}Na$: calcd for [M^++Na] 619.2214; found 619.2199.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (27): Column chromatography (ethyl acetate/methanol 50:1) of the crude product gave, first, unreacted **25** (1.1 g, 31%). Compound **27** (1.84 g, 56%) was eluted second. M.p. 108–110 °C; $[\alpha]_D^{22} = -20.0$, $[\alpha]_{436}^{22} = -39.0$ ($c = 1$, chloroform); IR (KBr): $\tilde{\nu} = 3422$, 1756, 1364, 1230, 1176, 1067 cm^{-1}; ^{1}H NMR ([D$_6$]DMSO): $\delta = 5.23$ (dd, $J = 9.7$, 9.6 Hz, 1H; H-3′), 4.91 (d, $J = 8.0$ Hz, 1H; H-1′), 4.90 (t, $J = 9.8$ Hz, 1H; H-4′), 4.77 (d, $J = 4.4$ Hz, 1H; OH–C-5), 4.75 (dd, $J = 9.8$, 8.0 Hz, 1H; H-2′), 4.50 (t, $J = 5.0$ Hz, 1H; CH_2OH), 4.36–4.29, 3.96–3.40 (several m, 8H; H-2,3,4,5,6,6,5′,6′), 4.19 (d, $J = 6.4$ Hz, 1H; H-1), 4.11 (dd, $J = 12.0$, 4.5 Hz, 1H; H-6′), 3.32, 3.30 (2s, 6H; 2MeO), 1.99, 1.97, 1.93 (3s, 12H; 4Ac), 1.28, 1.25 (2s, 6H; CMe_2); ^{13}C NMR ([D$_6$]DMSO): $\delta = 170.1$, 169.5, 169.3, 168.8, 108.0, 104.8, 98.8, 76.7, 76.7, 74.7, 72.1, 71.5, 71.2, 70.3, 68.2, 62.0, 61.8, 55.3, 52.3, 27.6, 26.5, 20.3, 20.2; MS (CI+): m/z: 581 [$M^+ - CH_3$], 565 [$M^+ + 1 - CH_3OH$], 331 [$C_{14}H_{19}O_9$]; $C_{25}H_{40}O_{16}$ (596.58): calcd C 50.34, H 6.76; found C 50.38, H 6.93.

Synthesis of the 5,6-di-*O*-mesyl derivatives 8, 19 and 28: general procedure: Methanesulfonyl chloride (0.5 mL) was added to a solution of **6**, **18** or **27** (0.5 mmol) in dry pyridine (7 mL) and the reaction was kept at RT for 16 h. The reaction mixture was poured into ice water and extracted with chloroform (75 mL). The organic phase was successively washed with hydrochloric acid (2 × 50 mL), saturated aqueous solution of sodium hydrogen carbonate (50 mL) and water (50 mL). After evaporation of the organic phase, the residue was purified by column chromatography (ether).

4-*O*-(2′,6′-Di-*O*-acetyl-3′,4′-*O*-isopropylidene-*β*-D-galactopyranosyl)-2,3-*O*-isopropylidene-5,6-di-*O*-methanesulfonyl-*aldehydo*-D-glucose dimethyl acetal (8): Column chromatography gave **8** (172 mg, 48%) as a solid. M.p. 114–116 °C; $[\alpha]_D^{22} = +24.0$, $[\alpha]_{436}^{22} = +50.0$ ($c = 1$, chloroform); IR (KBr): $\tilde{\nu} = 1742$, 1353, 1227, 1177, 1094, 1042 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 4.98$ (dd, $J = 7.6$, 6.7 Hz, 1H; H-2′), 4.94 (ddd, $J = 7.6$, 3.2, 2.6 Hz, 1H; H-5), 4.78 (dd, $J = 12.1$, 2.1 Hz, 1H; H-6), 4.70 (d, $J = 7.7$ Hz, 1H; H-1′), 4.45 (dd, $J = 10.8$, 4.9 Hz, 1H; H-6′), 4.42 (dd, $J = 6.1$, 4.4 Hz, 1H; H-2), 4.40 (dd, $J = 11.9$, 3.7 Hz, 1H; H-6), 4. 38 (d, $J = 6.0$ Hz, 1H; H-1), 4.30 (dd, $J = 3.1$, 1.5 Hz, 1H; H-4), 4.25 (dd, $J = 11.6$, 7.3 Hz, 1H; H-6′), 4.22 (dd, $J = 6.6$, 5.4 Hz, 1H; H-3′), 4.17 (dd, $J = 5.6$, 2.1 Hz, 1H; H-4′), 4.01 (dd, $J = 7.5$, 1.4 Hz, 1H; H-3), 3.97 (ddd, $J = 7.1$, 4.7, 2.3 Hz, 1H; H-5′), 3.46, 3.44 (2s, 6H; 2MeO), 3.12, 3.08 (2s, 6H; 2Ms), 2.15, 2.10 (2s, 6H; 2Ac), 1.54, 1.40, 1.38, 1.33 (4s, 12H; 2CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.2$, 169.7, 111.2, 110.9, 105.3, 100.4, 82.0, 77.1, 76.6, 75.7, 73.4, 72.8, 71.3, 68.1, 63.2, 56.3, 53.9, 38.6, 37.6, 27.6, 27.4, 26.4, 26.2, 21.0, 20.8; MS (CI+): m/z: 693 [$M^+ - CH_3$], 287 [$C_{13}H_{19}O_7$]; HR-MS (FAB+) $C_{26}H_{43}O_{18}S_2$: calcd for [$M^+ - H$] 707.1891; found 707.1882; $C_{26}H_{44}O_{18}S_2$ (708.74): calcd C 44.07, H 6.21, S 9.04; found C 44.03, H 6.19, S 8.81.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-*α*-D-glucopyranosyl)-2,3-*O*-isopropylidene-5,6-di-*O*-methanesulfonyl-*aldehydo*-D-glucose dimethyl acetal (19): Column chromatography gave **19** (250 mg, 66%) as a solid foam. M.p. 62–66 °C; $[\alpha]_D^{22} = +82.0$ ($c = 2$, chloroform); IR (KBr): $\tilde{\nu} = 1749$, 1363, 1227, 1177, 1041 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.44$ (dd, $J = 10.4$, 9.6 Hz, 1H; H-3′), 5.41 (d, $J = 3.8$ Hz, 1H; H-1′), 5.08 (dd, $J = 10.1$, 9.8 Hz, 1H; H-4′), 5.07 (m, 1H; H-5), 4.92 (dd, $J = 10.5$, 3.8 Hz, 1H; H-2′), 4.68 (dd, $J = 11.6$, 2.2 Hz, 1H; H-6), 4.48 (dd, $J = 11.6$, 8.9 Hz, 1H; H-6), 4.46–4.37 (m, 2H; H-1,6′), 4.27–4.03 (m, 5H; H-2,3,4,5′,6′), 3.49, 3.44 (2s, 6H; 2MeO), 3.12, 3.09 (2s, 6H; 2Ms), 2.06, 2.05, 2.02, 2.01 (4s, 12H; 4Ac), 1.38, 1.38 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): δ: 170.7, 170.2, 170.0, 169.6 (4CO), 110.8 (CMe_2), 105.3, 97.3, 81.4, 79.7, 77.7, 77.0, 70.4, 69.7, 68.3, 68.1, 67.5, 61.2, 57.7, 54.9, 38.4, 37.8, 26.9, 26.8, 20.8, 20.7; $C_{27}H_{44}O_{20}S_2$ (752.75): calcd C 43.08, H 5.89, S 8.52; found C 42.90, H 5.92, S 8.54.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)-2,3-*O*-isopropylidene-5,6-di-*O*-methanesulfonyl-*aldehydo*-D-glucose dimethyl acetal (28): Column chromatography gave **28** (0.29 g, 77%), as a solid. M.p. 68–70 °C. $[\alpha]_D^{22} = -4.0$, $[\alpha]_{436}^{22} = -6.0$ ($c = 1$, chloroform); IR (KBr): $\tilde{\nu} = 1756$, 1364, 1230, 1176, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.24$ (dd, $J = 9.4$, 9.3 Hz, 1H; H-3′), 5.12 (dd, $J = 9.9$, 9.4 Hz, 1H; H-4′), 5.03 (dd, $J = 9.4$, 8.0 Hz, 1H; H-2′), 4.95 (ddd, $J = 8.4$, 2.6, 2.2 Hz, 1H; H-5), 4.90 (d, $J = 7.9$ Hz, 1H; H-1′), 4.77 (dd, $J = 12.1$, 2.1 Hz, 1H; H-6), 4.39 (dd, $J = 6.8$, 6.1 Hz, 1H; H-2), 4.38 (d, $J = 6.1$ Hz, 1H; H-1), 4.38 (dd, $J = 12.1$, 8.4 Hz, 1H; H-6), 4.33 (dd, $J = 2.7$, 1.6 Hz, 1H; H-4), 4.22 (dd, $J = 12.2$, 4.2 Hz, 1H; H-6′), 4.14 (dd, $J = 12.4$, 2.4 Hz, 1H; H-6′), 3. 98 (dd, $J = 6.8$, 1.4 Hz, 1H; H-3), 3.73 (ddd, $J = 9.9$, 4.3, 2.6 Hz, 1H; H-5′), 3.44, 3.40 (2s, 6H; 2MeO), 3.14, 3.07 (2s, 6H; 2Ms), 2.11, 2.07, 2.02, 2.00 (4s, 12H; 4Ac), 1.40, 1.37 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.7$, 170.2, 169.5, 111.1, 105.3, 100.4, 81.8, 77.0, 75.6, 73.0, 72.0, 71.7, 68.2, 67.8, 61.7, 56.6, 53.6, 38.7, 37.7, 27.4, 26.3, 20.6; MS (CI+): m/z: 721 [$M^+ - OCH_3$], 331 [$C_{14}H_{19}O_9$]; $C_{27}H_{44}O_{20}S_2$ (752.75): calcd C 43.09, H 5.85, S 8.51; found C 43.43, H 6.01, S 8.34.

Synthesis of 5,6-di-*O*-methanesulfonyl derivatives 21 and 30: general procedure: Compounds **17** and **26** (3.93 g, 4.90 mmol) were treated with aqueous 80% acetic acid (40 mL) at 45 °C for 12–14 h. The reaction mixture was concentrated and evaporated with toluene to give a crude product that was dissolved in dry pyridine (15 mL). Methanesulfonyl chloride (1.1 mL) was then added at 0 °C and the magnetically stirred solution was left at RT for 16 h. The reaction mixture was poured into ice water (100 mL) and extracted with chloroform (150 mL). The organic phase was successively washed with 5% hydrochloric acid (2 × 100 mL), sodium hydrogen carbonate saturated aqueous solution (100 mL) and water (50 mL). After evaporation of the organic phase, the residue was purified by column chromatography (ether).

4-O-(2′,3′,4′,6′-Tetra-*O*-pivalolyl-*α*-D-glucopyranosyl)-2,3-*O*-isopropylidene-5,6-di-*O*-methanesulfonyl-aldehyde-D-glucose dimethyl acetal (21): Column chromatography gave **21** (3.0 g, 66.6%) as a solid. M.p. 68–70 °C; $[\alpha]_D^{22}$ +64.0 ($c = 2.0$, chloroform); IR (KBr): $\tilde{\nu} = 1742$, 1177, 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.53$ (d, $J = 4.0$ Hz, 1H; H-1′), 5.52 (t, $J = 10.0$ Hz, 1H; H-3′), 5.17 (dd, $J = 10.2$, 9.6 Hz, 1H; H-4′), 5.13 (dt, $J = 5.6$, 5.5, 1.2 Hz, 1H; H-5), 4.90 (dd, $J = 10.3$, 4.0 Hz, 1H; H-2′), 4.53 (d, $J = 5.6$ Hz, 1H; H-6), 4.38 (d, $J = 4.6$ Hz, 1H; H-1), 4.32 (dt, $J = 10.3$, 1.2, 1.2 Hz, 1H; H-5′), 4.27–4.20 (m, 4H; H-4,6,6′,6′), 4.10 (dd, $J = 6.7$, 4.6 Hz, 1H; H-2), 4.04 (dd, $J = 8.0$, 6.7 Hz, 1H; H-3), 3.52, 3.46 (2s, 6H; 2MeO), 3.14, 3.10 (2s, 6H; 2MeSO$_2$), 1.41, 1.38 (2s, 6H; CMe_2), 1.23, 1.18, 1.15, 1.13 (4s, 36H; 4Me_3C); ^{13}C NMR ($CDCl_3$): $\delta = 178.0$, 177.4, 177.3, 177.2, 110.9, 105.1, 96.1, 79.8, 79.4, 77.8, 70.6, 69.5, 68.2, 67.6, 67.5, 60.9, 57.7, 54.7, 38.8, 38.3, 37.8, 27.3, 27.2, 27.2, 27.0, 27.0; HR-MS (FAB+) $C_{39}H_{68}O_{20}NaS_2$: calcd for [M^++Na] 943.3643;

found 943.3631; $C_{39}H_{68}O_{20}S_2$ (921.0): calcd C 50.85, H 7.44, S 6.96; found C 50.55, H 7.63, S 6.91.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-pivalolyl-*β*-D-glucopyranosyl)-2,3-*O*-isopropylidene-5,6-di-*O*-methanesulfonyl-aldehyde-D-glucose dimethyl acetal (30): Column chromatography gave **30** (2.95 g, 65%) as a solid foam. M.p. 70–73 °C; $[\alpha]_D^{22}$ −4.0 ($c = 1.0$, chloroform); IR (KBr): $\tilde{\nu} = 1744$, 1178, 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.35$ (dd, $J = 9.3$, 9.2 Hz, 1H; H-3′), 5.21 (dd, $J = 10.1$, 9.3 Hz, 1H; H-4′), 5.07 (dd, $J = 9.2$, 8.0 Hz, 1H; H-2′), 4.90 (d, $J = 8.0$ Hz, 1H; H-1′), 4.92 (ddd, $J = 8.1$, 3.3, 2.2 Hz, 1H; H-5), 4.87 (dd, $J = 12.2$, 2.2 Hz, 1H; H-6), 4.41–4.32 (m, 4H; H-1,2,4,6), 4.22 (dd, $J = 12.5$, 1.7 Hz, 1H; H-6′), 4.07 (dd, $J = 12.5$, 3.8 Hz, 1H; H-6′), 4.00 (dd, $J = 7.1$, 1.3 Hz, 1H; H-3), 3.76 (ddd, $J = 9.9$, 3.7, 1.7 Hz, 1H; H-5′), 3.43, 3.49 (2s, 6H; 2MeO), 3.13, 3.03 (2s, 6H; 2MeSO$_2$), 1.39, 1.36 (2s, 6H; C*Me*$_2$), 1.23, 1.19, 1.14, 1.12 (4s, 36H; 4Me$_3$C); ^{13}C NMR ($CDCl_3$): $\delta = 178.1$, 177.0, 176.3, 177.2, 111.1, 105.2, 99.8, 82.2, 76.6, 75.8, 74.9, 72.7, 72.4, 71.9, 68.0, 67.6, 61.4, 56.6, 54.0, 38.9, 38.6, 37.7, 27.5, 27.4, 27.3, 27.1, 26.4; HR-MS (FAB+) $C_{39}H_{68}O_{20}NaS_2$: calcd for $[M^+ + Na]$ 943.3643; found 943.3653; $C_{39}H_{68}O_{20}S_2$ (921.0): calcd C 50.85, H 7.44, S 6.96; found C 50.46, H 7.61, S 7.35.

Synthesis of 41a and b: general procedure: Anhydrous NaAcO (2.3 g) was added to a solution of compounds **21** or **30** (1.3 g, 1.4 mmol) in Ac_2O (20 mL). The reaction mixture was heated under reflux for 72 h. After this time water (200 mL) was added and the resulting solution was neutralised by the portion wise addition of sodium hydrogen carbonate. Extraction with CH_2Cl_2 (2 × 150 mL) was followed by washing with water (2 × 100 mL). After evaporation of the organic phase, the residue was purified by column chromatography.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-pivalolyl-*α*-D-glucopyranosyl)-2,3-*O*-isopropylidene-5,6-di-*O*-acetyl-aldehyde-L-idose dimethyl acetal (41a): Column chromatography (ether/hexane 1:1) first gave **41a** (712 mg, 60%) as a solid. M.p. 118 °C; $[\alpha]_D^{22} = +54.0$ ($c = 2.2$, chloroform); IR (KBr): $\tilde{\nu} = 1742$, 1220, 1134, 1039 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.52$ (dd, $J = 10.4$, 9.3 Hz, 1H; H-3′), 5.23 (m, 1H; H-5), 5.21 (d, $J = 3.5$ Hz, 1H; H-1′), 5.11 (dd, $J = 10.1$, 9.3 Hz, 1H; H-4′), 4.90 (dd, $J = 10.4$, 3.7 Hz, 1H; H-2′), 4.45 (dd, $J = 12.7$, 2.5 Hz, 1H; H-6), 4.27–4.04 (m, 7H; H-1,2,3,6,5′,6′,6′), 3.80 (dd, $J = 5.7$, 1.8 Hz, 1H; H-4), 3.38, 3.35 (2s, 6H; 2MeO), 2.00, 1.98 (2s, 6H; 2Ac), 1.44, 1.35 (2s, 6H; C*Me*$_2$), 1.16, 1.13, 1.06, 1.05 (4s, 36H; 4Me$_3$C); ^{13}C NMR ($CDCl_3$): $\delta = 177.9$, 177.8, 176.8, 176.2, 170.4, 170.1, 110.7, 105.9, 97.4, 76.9, 76.5, 76.2, 72.7, 71.1, 69.6, 68.7, 67.5, 63.2, 61.0, 57.2, 55.2, 38.9, 38.7, 27.2, 27.1, 27.1, 27.0, 26.9, 20.9, 20.7; HR-MS (FAB+) $C_{41}H_{68}O_{18}Na$: calcd for $[M^+ + Na]$ 871.4303; found 871.4315; $C_{41}H_{68}O_{18}$ (848.95): calcd C 58.00, H 8.07; found C 58.46, H 8.06. Unreacted **21** (445 mg, 34%) was eluted second.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-pivalolyl-*β*-D-glucopyranosyl)-2,3-*O*-isopropylidene-5,6-di-*O*-acetyl-aldehyde-L-idose dimethyl acetal (41b): Column chromatography (ether/hexane 2:1) gave **41b** (792 mg, 66%) as a syrup. $[\alpha]_D^{22} = -14.0$ ($c = 4.0$, chloroform); IR (neat): $\tilde{\nu} = 1742$, 1139 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.33$ (t, $J = 9.4$ Hz, 1H; H-3′), 5.20 (dd, $J = 10.0$, 9.3 Hz, 1H; H-4′), 5.17 (m, 1H; H-5), 5.09 (dd, $J = 9.5$, 8.0 Hz, 1H; H-2′), 4.89 (d, $J = 8.1$ Hz, 1H; H-1′), 4.40–4.28 (m, 5H; H-1,2,3,6,6) 4.22 (dd, $J = 12.4$, 1.5 Hz, 1H; H-6′), 4.07–3.98 (m, 2H; H-4,6′), 3.77 (ddd, $J = 10.0$, 4.4, 1.5 Hz, 1H; H-5′), 3.38, 3.36 (2s, 6H; 2MeO), 2.11, 2.04 (2s, 6H; 2Ac), 1.38, 1.34 (2s, 6H; C*Me*$_2$), 1.23, 1.15, 1.13, 1.11 (4s, 36H; 4Me$_3$C); ^{13}C NMR ($CDCl_3$): $\delta = 178.0$, 177.2, 176.3, 176.3, 170.4, 170.1, 111.1, 105.1, 99.2, 75.8, 75.3, 72.9, 72.8, 72.5, 72.5, 71.2, 67.8, 55.7, 53.0, 38.9, 38.7, 38.7, 38.7, 27.6, 27.3, 27.3, 27.2, 27.2, 27.1, 27.0, 26.9, 26.4, 21.1, 21.0; HR-MS (FAB+) $C_{41}H_{68}O_{18}Na$: calcd for $[M^+ + Na]$ 871.4303; found 871.4302.

Zemplén de-*O*-acetylation of 41a and b. Synthesis of 42a and b: general procedure: A 0.5 N solution of sodium methoxide in methanol (0.5 mL) was added to a solution of **41a** and **b** (1.84, 2.16 mmol) in anhydrous methanol (25 mL). The reaction mixture was left at RT for 30 min. Neutralisation with acetic acid was followed by concentration under vacuum giving a crude product that was purified by column chromatography (ether) giving **42a** and **b** in quantitative yields.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-pivalolyl-*α*-D-glucopyranosyl)-2,3-*O*-isopropylidene-aldehyde-L-idose dimethyl acetal (42a): Isolated as a syrup. $[\alpha]_D^{22} = +52.0$ ($c = 1.0$, chloroform); IR (neat): $\tilde{\nu} = 3450$, 1735, 1281, 1134, 1035 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.58$ (dd, $J = 10.4$, 9.2 Hz, 1H; H-3′), 5.31 (d, $J = 3.7$ Hz, 1H; H-1′), 5.11 (dd, $J = 10.2$, 9.2 Hz, 1H; H-4′), 4.98 (dd, $J = 10.4$, 3.7 Hz, 1H; H-2′), 4.33 (d, $J = 4.9$ Hz, 1H; H-1), 4.24–4.15 (m, 3H; H-2,3,5′), 4.14 (dd, $J = 12.5$, 1.8 Hz, 1H; H-6′), 4.02 (dd, $J = 12.5$, 5.4 Hz, 1H; H-6′), 3.93 (m, 1H; H-5); 3.82 (dd, $J = 11.5$, 4.7 Hz, 1H; H-6), 3.72–3.70 (m, 2H; H-4,6); 3.48, 3.43 (2s, 6H; 2MeO), 1.50, 1.42 (2s, 6H; C*Me*$_2$), 1.22, 1.19, 1.14, 1.11 (4s, 36H; 4Me$_3$C); ^{13}C NMR ($CDCl_3$): $\delta = 178.3$, 177.8, 176.6 (4CO), 110.4 (*C*Me$_2$), 106.1 (C-1), 97.5 (C-1′), 80.8 (C-4), 76.8, 76.6 (C-2,3), 71.6 (C-5), 70.9 (C-2′), 69.3 (C-3′), 68.9 (C-5′), 68.2 (C-4′), 62.3, 62.2 (C-6,6′), 57.7, 55.7 (2OMe), 39.0, 38.8 (*C*Me$_3$), 27.3, 27.3, 27.2, 27.1, 26.9 (*C*Me$_2$, *C*Me$_3$); HR-MS (FAB+) $C_{37}H_{64}O_{16}Na$: calcd for $[M^+ + Na]$ 787.4092; found 787.4093.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-pivalolyl-*β*-D-glucopyranosyl)-2,3-*O*-isopropylidene-aldehyde-L-idose dimethyl acetal (42b): Isolated as a solid. M.p. 62–65 °C; $[\alpha] = -15.0$ ($c = 1.0$, chloroform); IR (KBr): $\tilde{\nu} = 3418$, 1745, 1139 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.33$ (t, $J = 9.4$ Hz, 1H; H-3′), 5.21 (dd, $J = 9.8$, 9.4 Hz, 1H; H-4′), 5.09 (dd, $J = 9.4$, 8.0 Hz, 1H; H-2′), 4.81 (d, $J = 7.9$ Hz, 1H; H-1′), 4.46 (dd, $J = 7.4$, 5.7 Hz, 1H; H-2), 4.37 (d, $J = 5.7$ Hz, 1H; H-1), 4.21 (dd, $J = 12.4$, 1.7 Hz, 1H; H-6′), 4.11 (d, $J = 7.3$ Hz, 1H; H-3), 4.04 (dd, $J = 12.4$, 3.9 Hz, 1H; H-6′), 3.86–3.59 (m, 5H; H-4,5,6,6,5′), 3.42, 3.38 (2s, 6H; 2MeO), 2.80, 1.07 (2brs, 2H; 2OH), 1.41, 1.40 (2s, 6H; C*Me*$_2$), 1.23, 1.17, 1.14, 1.11 (4s, 36H; 4Me$_3$C); ^{13}C NMR ($CDCl_3$): $\delta = 178.1$, 177.6, 177.3, 176.4, 110.7, 105.1, 100.0, 76.4, 75.6, 75.5, 72.6, 72.4, 71.6, 71.3, 67.7, 61.5, 61.5, 56.3, 53.5, 39.0, 38.8, 27.5, 27.3, 27.3, 27.2, 27.1, 26.4; HR-MS (FAB+) $C_{37}H_{64}O_{16}Na$: calcd for $[M^+ + Na]$ 787.4092; found 787.4086; $C_{37}H_{64}O_{16}$ (764.88): calcd C 58.10, H 8.43; found C 58.00, H 8.79.

Synthesis of cyclic sulfates 31a–d and 43a and b: general procedure: $SOCl_2$ (1.5 mmol) in CH_2Cl_2 (5 mL) was added dropwise over a period of 10 min to an ice cooled and magnetically stirred solution of the diol **6**, **11**, **18**, **27**, **42a** or **42b** (1 mmol) and Et_3N (4 mmol) in dry CH_2Cl_2 (20 mL). Stirring was continued at 0 °C, until TLC (ether) showed complete disappearance of starting material (15–30 min). The mixture was diluted with CH_2Cl_2 (50 mL), and washed with water (2 × 50 mL) and brine (100 mL). The organic solution was dried (Na_2SO_4) and filtered. The filtrate was concentrated under vacuum giving a mixture of the corresponding cyclic sulfites, which was dissolved in MeCN/CCl_4 (10:10 mL). $NaIO_4$ (1.5 equiv) dissolved in water (10 mL) was then added followed by a catalytic amount of $RuCl_3 \cdot 3H_2O$. The resulting mixture was stirred for 45–60 min at RT until TLC (ether/hexane 5:1) showed complete disappearance of the starting material. The mixture was diluted with ether (100 mL) and washed with water (2 × 100 mL) and brine (100 mL). The organic solution was dried (Na_2SO_4) and filtered. After evaporation the crude product obtained was purified by short-column chromatography.

4-*O*-(2′,6′-Di-*O*-acetyl-3′,4′-*O*-isopropylidene-*β*-D-galactopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal 5,6-cyclic sulfate (31a): Column chromatography (ether/hexane 5:1) of the crude product gave **31a** (0.503 g, 82.2%) as a foam solid. M.p. 52–54 °C; $[\alpha]_D^{22} = +19.0$, $[\alpha]_{436}^{22} = +40.0$ ($c = 1$, chloroform); IR (KBr): $\tilde{\nu} = 1747$, 1385, 1214, 1155, 1132, 1085, 1047 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.10$ (ddd, $J = 8.4$, 6.7, 1.9 Hz, 1H; H-5), 5.00 (dd, $J = 7.6$, 7.0 Hz, 1H; H-2′), 4.79 (dd, $J = 8.9$, 8.4 Hz, 1H; H-6), 4.69 (dd, $J = 9.1$, 6.7 Hz, 1H; H-6), 4.67 (d, $J = 7.7$ Hz, 1H; H-1′), 4.49 (dd, $J = 7.3$, 5.6 Hz, 1H; H-2), 4.38 (d, $J = 5.6$ Hz, 1H; H-1), 4.35 (dd, $J = 11.6$, 5.3 Hz, 1H; H-6′), 4.28 (t, $J = 3.3$ Hz, 1H; H-4), 4.27 (dd, $J = 11.6$, 6.7 Hz, 1H; H-6′), 4.22 (dd, $J = 6.8$, 5.6 Hz, 1H; H-3′), 4.16 (dd, $J = 5.6$, 2.1 Hz, 1H; H-4′), 3.94 (dd, $J = 7.3$, 1.5 Hz, 1H; H-3), 3.93 (ddd, $J = 6.9$, 5.3, 2.1 Hz, 1H; H-5′), 3.44, 3.42 (2s, 6H; 2MeO), 2.12, 2.09 (2s, 6H; 2Ac), 1.53, 1.38, 1.35, 1.33 (4s, 12H; 2C*Me*$_2$); ^{13}C NMR ($CDCl_3$): $\delta = 111.6$, 110.9, 104.9, 100.7, 83.0, 77.0, 75.5, 73.2, 72.6, 72.6, 71.2, 69.7, 63.1, 56.5, 53.7, 27.6, 27.4, 26.3, 26.3, 20.2; $C_{24}H_{38}O_{16}S$ (614.62): calcd C 46.90, H 6.23; found C 46.70, H 6.45.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-*β*-D-galactopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal 5,6-cyclic sulfate (25b): Column chromatography (ether) of the crude product gave **31b** (0.554 g, 83.0%) as a foam solid. $[\alpha]_D^{22} = -1.5$, $[\alpha]_{436}^{22} = 4.0$ ($c = 1.0$, chloroform); IR (KBr): $\tilde{\nu} =$ 1750, 1373, 1215, 1073, 972 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.42$ (dd, $J = 3.4$, 1.0 Hz, 1H; H-4′), 5.20 (dd, $J = 10.5$, 7.8 Hz, 1H; H-2′), 5.13 (ddd, $J = 8.3$, 7.0, 1.3 Hz, 1H; H-5), 5.05 (dd, $J = 10.5$, 3.4 Hz, 1H; H-3′), 4.82 (d, $J =$ 7.8 Hz, 1H; H-1′), 4.78 (t, $J = 8.7$ Hz, 1H; H-6), 4.69 (dd, $J = 9.0$, 6.8 Hz, 1H; H-6), 4.50 (dd, $J = 7.3$, 5.7 Hz, 1H; H-2), 4.39 (d, $J = 5.7$ Hz, 1H; H-1), 4.37–4.31, 4.16–4.06, 3.97–3.90 (3m, 5H; H-3,4,5′,6′,6′), 3.46, 3.43 (2s, 6H; 2MeO), 2.16, 2.11, 2.05, 1.98 (4s, 12H; 4Ac), 1.43, 1.38 (2s, 6H; C*Me*$_2$); ^{13}C NMR ($CDCl_3$): $\delta = 170.3$, 170.1, 170.0, 169.9, 111.4, 105.1, 100.9, 82.6, 76.9, 75.5, 72.6, 70.8, 70.7, 68.8, 66.8, 69.5, 60.9, 56.6, 53.8, 27.2, 26.2, 20.6, 20.6, 20.5; $C_{25}H_{38}O_{18}S \cdot 1/2\ H_2O$ (667.64): calcd C 44.97, H 5.89, S 4.80; found C 44.90, H 6.08, S 4.80.

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4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-*α*-D-glucopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal 5,6-cyclic sulfate (31c): Column chromatography (ether/hexane 5:1) of the crude product gave **31c** (0.554 g, 84.3%) as a solid. M.p. 87 °C; $[\alpha]_D^{22} = +80.0$ ($c = 1.0$, chloroform); IR (KBr): $\tilde{\nu} = 1750, 1370, 1224, 1111, 638, 616\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta =$ 5.44 (dd, $J = 10.5, 9.5$ Hz, 1H; H-3′), 5.26 (d, $J = 3.9$ Hz, 1H; H-1′), 5.14 (t, $J = 10.4$ Hz, 1H; H-4′), 5.13 (ddd, $J = 8.5, 6.6, 1.7$ Hz, 1H; H-5), 5.06 (dd, $J = 10.5, 3.9$ Hz, 1H; H-2′), 4.91 (t, $J = 8.8$ Hz, 1H; H-6), 4.76 (dd, $J = 8.9, 6.6$ Hz, 1H; H-6), 4.35 (dd, $J = 12.8, 3.1$ Hz, 1H; H-6′), 4.35 (d, $J = 5.2$ Hz, 1H; H-1), 4.29–4.24 (m, 2H; H-4,5′), 4.10 (dd, $J = 7.8, 5.2$ Hz, 1H; H-2), 4.10 (dd, $J = 12.8, 2.5$ Hz, 1H; H-6′), 3.98 (dd, $J = 7.8, 3.6$ Hz, 1H; H-3), 3.48, 3.44 (2s, 6H; 2MeO), 2.10, 2.08, 2.04, 2.01 (4s, 12H; 4Ac), 1.43, 1.39 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.6$, 170.1, 169.8, 169.6, 110.8, 105.3, 98.0, 81.0, 77.5, 76.1, 75.9, 70.2, 69.9, 68.3, 67.7, 69.9, 61.5, 57.7, 55.5, 26.9, 26.5, 20.8, 20.7; $C_{25}H_{38}O_{18}S$ (658.63): calcd C 45.59, H 5.81, S 4.86; found C 45.76, H 6.22, S 4.55.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal 5,6-*O*-cyclic sulfate (31d): Column chromatography (ether/hexane 5:1) of the crude product gave **31d** (0.633 g, 96.3%) as a solid. M.p. 125–126 °C, $[\alpha]_D^{22} = -6.5$, $[\alpha]_{436}^{22} = -11.0$ ($c = 1.0$, chloroform); IR (KBr): $\tilde{\nu} = 1755, 1382, 1214, 1053, 973\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 5.26$ (dd, $J = 9.4, 9.3$ Hz, 1H; H-3′), 5.14 (dd, $J = 9.9, 9.1$ Hz, 1H; H-4′), 5.11 (m, 1H; H-5), 5.08 (dd, $J = 9.5, 7.8$ Hz, 1H; H-2′), 4.83 (d, $J = 7.8$ Hz, 1H; H-1′), 4.77 (dd, $J = 9.0, 8.2$ Hz, 1H; H-6), 4.68 (dd, $J = 9.0, 6.9$ Hz, 1H; H-6), 4.46 (dd, $J = 7.3, 5.7$ Hz, 1H; H-2), 4.36 (d, $J = 5.7$ Hz, 1H; H-1), 4.31 (dd, $J = 1.7, 1.5$ Hz, 1H; H-4), 4.25 (dd, $J = 12.2, 4.0$ Hz, 1H; H-6′), 4.12 (dd, $J = 12.2, 2.5$ Hz, 1H; H-6′), 3.93 (dd, $J = 7.3, 1.4$ Hz, 1H; H-3), 3.72 (ddd, $J = 9.9, 4.0, 2.5$ Hz, 1H; H-5′), 3.43, 3.39 (2s, 6H; 2MeO), 2.09, 2.08, 2.03, 2.00 (4s, 12H; 4Ac), 1.40, 1.37 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.5$, 170.0, 169.9, 169.6, 111.5, 105.2, 100.7, 82.6, 77.0, 75.5, 73.0, 72.8, 71.8, 71.4, 68.3, 69.5, 61.7, 56.7, 53.6, 27.3, 26.8, 20.6, 20.5; $C_{25}H_{38}O_{18}S$ (658.63): calcd C 45.59, H 5.81; found C 45.38, H 6.06.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-pivaloyl-*α*-D-glucopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-L-idose dimethyl acetal 5,6-*O*-cyclic sulfate (43a): Column chromatography (ether/hexane 2:1) of the crude product gave **43a** (745 mg, 90.4%) as a solid. M.p. 54–56 °C; $[\alpha]_D^{22} = +64.0$ ($c = 1.0$, chloroform); IR (KBr): $\tilde{\nu} = 1743, 1215, 1138\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 5.55$ (dd, $J = 10.4, 9.3$ Hz, 1H; H-3′), 5.24 (m, 1H; H-5), 5.24 (d, $J = 3.8$ Hz, 1H; H-1′), 5.16 (dd, $J = 9.8, 9.4$ Hz, 1H; H-4′), 5.00 (dd, $J = 10.4, 3.8$ Hz, 1H; H-2′), 4.78 (d, $J = 7.4$ Hz, 1H; H-1), 4.33 (br d, $J = 3.9$ Hz, 1H; H-3), 4.19–4.05 (m, 7H; H-2,4,6,6,5′,6′,6′), 3.50, 3.42 (2s, 6H; 2MeO), 1.46, 1.39 (2s, 6H; CMe_2), 1.23, 1.19, 1.15, 1.12 (4s, 36H; 4Me_3C); ^{13}C NMR ($CDCl_3$): $\delta = 178.0, 177.7, 177.1, 176.4, 110.9, 105.7, 97.6, 81.5, 76.4, 76.3, 75.0, 70.9, 69.7, 69.5, 69.1, 68.0, 61.7, 58.0, 56.0, 39.1, 39.0, 38.9, 27.4, 27.4, 27.3, 27.2, 26.9, 26.7$; HR-MS (FAB+) $C_{37}H_{62}O_{18}NaS$: calcd for $[M^+ + Na]$ 849.3555; found 849.3565.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-pivaloyl-*β*-D-glucopyranosyl)-2,3-*O*-isopropylidene-*aldehydo*-L-idose dimethyl acetal 5,6-*O*-cyclic sulfate (43b): Column chromatography (ether/hexane 2:1) of the crude product gave **43b** (740 mg, 90%) as a foam. M.p. 65–70 °C; $[\alpha]_D^{22} = -10.0$ ($c = 1.0$, chloroform); IR (KBr): $\tilde{\nu} = 1735, 1274, 1134\ cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 5.36$ (dd, $J = 9.5, 9.4$ Hz, 1H; H-3′), 5.22 (dd, $J = 9.9, 9.5$ Hz, 1H; H-4′), 5.10 (dd, $J = 9.4, 8.1$ Hz, 1H; H-2′), 5.08 (m, 1H; H-5), 4.90 (d, $J = 8.1$ Hz, 1H; H-1′), 4.79 (dd, $J = 9.0, 6.4$ Hz, 1H; H-6), 4.49 (dd, $J = 8.8, 8.4$ Hz, 1H; H-6), 4.43 (dd, $J = 6.8, 4.8$ Hz, 1H; H-2), 4.37 (d, $J = 4.8$ Hz, 1H; H-1), 4.23 (dd, $J = 12.4, 1.6$ Hz, 1H; H-6′), 4.12 (dd, $J = 8.7, 1.6$ Hz, 1H; H-4), 4.04 (dd, $J = 12.4, 4.0$ Hz, 1H; H-6′), 3.86 (dd, $J = 6.8, 1.6$ Hz, 1H; H-3), 3.75 (ddd, $J = 10.0, 4.0, 1.6$ Hz, 1H; H-5′), 3.44, 3.39 (2s, 6H; 2MeO), 1.37, 1.35 (2s, 6H; CMe_2), 1.23, 1.17, 1.15, 1.11 (4s, 36H; 4Me_3C); ^{13}C NMR ($CDCl_3$): $\delta = 178.0, 177.1, 176.6, 176.4, 111.9, 104.8, 99.9, 83.6, 75.8, 74.9, 74.8, 72.6, 72.3, 71.1, 69.5, 67.2, 61.5, 56.7, 54.6, 38.8, 27.3, 27.2, 27.1, 26.5$; HR-MS (FAB+) $C_{37}H_{62}O_{18}NaS$: calcd for $[M^+ + Na]$ 849.3555; found 849.3575.

Opening of cyclic sulfates 31,a,c,d with potassium thiocyanate: general procedure: KSCN (1.1 equiv) was added to a solution of the cyclic sulfate **31a**, **c** and **d** (1 equiv) in dry acetone (20 mL). The resulting solution was then stirred at RT until no cyclic sulfate remained (TLC; 4 d for **31a** and **d**, and 2 d for **31c**). The solution was then concentrated and the crude product was purified by column chromatography on silica gel.

4-*O*-(2′,6′-Di-*O*-acetyl-3′,4′-*O*-isopropylidene-*β*-D-galactopyranosyl)-2,3-*O*-isopropylidene-6-*S*-cyano-5-*O*-sulfonate-6-thio-*aldehydo*-D-glucose dimethyl acetal potassium salt (32a): Column chromatography (methanol/chloroform 1:5) of the crude product gave **32a** (635 mg, 89.3%) as a hygroscopic solid. M.p. 84–87 °C; $[\alpha]_D^{22} = +26.0$ ($c = 1$, methanol); IR (KBr): $\tilde{\nu} = 3482, 2159, 1748, 1374, 1227, 1155, 1132, 1078\ cm^{-1}$; ^1H NMR ([D$_6$]DMSO, 500 MHz): $\delta = 4.78$ (dd, $J = 8.2, 7.7$ Hz, 1H; H-2′), 4.70 (d, $J =$ 8.4 Hz, 1H; H-1′), 4.39–4.36, 4.22–4.18 (2m, 4H; H-2,4,5,4′), 4.31 (d, $J =$ 6.2 Hz, 1H; H-1), 4.23 (dd, $J = 7.4$, 5.4 Hz, 1H; H-3′), 4.16 (dd, $J = 11.4$, 4.2 Hz, 1H; H-6′), 4.10 (dd, $J = 11.5, 7.8$ Hz, 1H; H-6′), 4.01 (ddd, $J = 7.5$, 4.4, 2.0 Hz, 1H; H-5′), 3.93 (dd, $J = 6.8, 2.2$ Hz, 1H; H-3), 3.48 (dd, $J = 12.8$, 2.6 Hz, 1H; H-6), 3.34, 3.31 (2s, 6H; 2MeO), 3.13 (dd, $J = 13.0, 5.8$ Hz, 1H; H-6), 2.09, 2.03 (2s, 6H; 2Ac), 1.41, 1.29, 1.25, 1.25 (4s, 12H; 2CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.9$, 169.9, 114.2, 110.2, 109.9, 105.2, 100.1, 77.8, 77.3, 76.7, 76.3, 73.8, 73.1, 70.5, 63.1, 55.9, 54.2, 35.3, 27.9, 27.6, 26.6, 26.5, 21.1, 20.8; HR-MS (FAB+) $C_{25}H_{39}NO_{16}S_2K$: calcd for $[M^+ + H]$ 712.1347; found 712.1342; $C_{25}H_{38}O_{16}NS_2K \cdot 1/2\ H_2O$ (780.80): calcd C 41.65, H 5.45, N 1.95, S 8.89; found C 41.92, H 5.73, N 1.64, S 8.84.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-*α*-D-glucopyranosyl)-2,3-*O*-isopropylidene-6-*S*-cyano-5-*O*-sulfonate-6-thio-*aldehydo*-D-glucose dimethyl acetal potassium salt (32c): Column chromatography (methanol/chloroform 1:5) of the crude product gave **32c** (610 mg, 79%) as a solid. M.p. 105–108 °C; $[\alpha]_D^{22} =$ +88.0 ($c = 1$, methanol); IR (KBr): $\tilde{\nu} = 2158, 1750, 1370, 1226, 1140,$ $1041\ cm^{-1}$; ^1H NMR ([D$_6$]DMSO): $\delta = 5.37$ (t, $J = 10.0$ Hz, 1H; H-3′), 5.25 (d, $J = 3.7$ Hz, 1H; H-1′), 4.96 (t, $J = 10.0$ Hz, 1H; H-4′), 4.68 (dd, $J = 10.4$, 3.7 Hz, 1H; H-2′), 4.43–4.00 (several m, 6H; H-2,4,5,5′,6′,6′), 4.37 (d, $J =$ 6.7 Hz, 1H; H-1), 3.84 (t, $J = 6.5$ Hz, 1H; H-3), 3.44–3.32 (m, 2H; H-6,6), 3.38, 3.33 (2s, 6H; 2MeO), 1.99, 1.98, 1.97, 1.96 (4s, 12H; 4Ac), 1.30, 1.28 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.6$, 170.2, 170.0, 169.6, 114.0, 109.7, 105.1, 95.9, 81.1, 78.4, 76.8, 73.6, 70.5, 69.4, 67.9, 67.3, 56.6, 54.2, 35.1, 26.9, 26.8, 21.2, 20.8, 20.6; HR-MS (FAB+) $C_{26}H_{39}NO_{18}S_2K$ calcd for $[M^+ + H]$ 756.1128; found 756.1102; $C_{26}H_{38}O_{18}NS_2K \cdot H_2O$ (773.82): calcd C 40.35, H 5.21, N 1.81, S 8.28; found C 40.74, H 5.37, N 1.55, S 8.04.

4-*O*-(2′,3′,4′,6′-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)-6-deoxy-2,3-*O*-isopropylidene-6-*S*-cyano-5-*O*-sulfonate-6-thio *aldehydo*-D-glucose dimethyl acetal potassium salt (32d): Column chromatography (methanol/chloroform 1:3) of the crude product gave **32d** (750 mg, 99%) as a solid. M.p. 122–127 °C; $[\alpha]_D^{22} = -2.2$, $[\alpha]_{436}^{22} = -3.9$ ($c = 0.7$, methanol); IR (KBr): $\tilde{\nu} =$ $2113, 1753, 1373, 1226, 1062\ cm^{-1}$; ^1H NMR ([D$_6$]DMSO): $\delta = 5.23$ (dd, $J =$ 9.8, 9.6 Hz, 1H; H-3′), 4.98 (d, $J = 8.0$ Hz, 1H; H-1′), 4.90 (dd, $J = 9.8$, 9.6 Hz, 1H; H-4′), 4.78 (dd, $J = 9.8, 8.0$ Hz, 1H; H-2′), 4.38 (m, 1H; H-5), 4.37 (br s, 1H; H-4), 4.32 (d, $J = 6.2$ Hz, 1H; H-1), 4.22 (dd, $J = 6.7$, 6.5 Hz, 1H; H-2), 4.10 (dd, $J = 12.4, 4.9$ Hz, 1H; H-6′), 3.97 (dd, $J = 12.2, 2.4$ Hz, 1H; H-6′), 3.94 (dd, $J = 6.0, 2.0$ Hz, 1H; H-3), 3.87 (ddd, $J = 9.8, 4.7, 2.5$ Hz, 1H; H-5′), 3.47 (dd, $J = 12.5, 2.8$ Hz, 1H; H-6), 3.32, 3.28 (2s, 6H; 2MeO), 3.11 (dd, $J = 12.5, 9.3$ Hz, 1H; H-6), 2.05, 1.99, 1.97, 1.93 (4s, 12H; 4Ac), 1.29, 1.26 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.1, 169.5, 169.3, 113.8,$ $109.6, 104.6, 100.1, 78.1, 77.3, 76.5, 75.5, 72.1, 71.2, 70.5, 68.1, 61.8, 55.5, 53.0,$ $35.0, 27.3, 26.3, 20.5, 20.3, 20.2$; $C_{26}H_{38}O_{18}NS_2K$ (755.80): calcd C 41.31, H 5.07, N 1.85, S 8.48; found C 41.68, H 4.72, N 1.48, S 8.10.

Synthesis of 5,6-dideoxy-5,6-epithio derivatives 33e–h and 44a and b: general procedure:

a) From cyclic sulfates: KSAc (1.1 equiv) was added to a solution of the cyclic sulfate **31a–d** or **43a** and **b** (1 equiv) in dry acetone (20 mL) was added. The resulting solution was then stirred at RT until no cyclic sulfate remained (TLC; 1 d for **31b–d**, **43a** and **b** and 2.5 d for **31a**). The solution was then concentrated and the crude product was dissolved in dry methanol and then NaOMe (5 equiv) was added. The reaction mixture was left at RT until TLC (methanol/chloroform 1:5) showed complete disappearance of the starting material (1 h for **31b–d**, 2 h for **31a** and 4 h **43a** and **b**). The solution was neutralised with acetic acid and concentrated. The residue was purified by column chromatography on silica gel.

*b) From the 6-S-cyano-potassium salts **32a**, **c** and **d***: NaOMe (5 equiv) was added to a solution of the 6-*S*-cyano potassium salts **32a**, **c** and **d** (1 equiv) in dry methanol (25 mL). The reaction mixture was left at RT until TLC (methanol/chloroform 1:5) showed complete disappearance of the starting material (2–4 h). The solution was neutralised with acetic acid and concentrated. The residue was purified by column chromatography on silica gel using the solvent described above. Compounds **33e**, **g** and **h** were obtained in 85, 87 and 90% yield, respectively.

5,6-Dideoxy-5,6-epithio-4-*O*-[3′,4′-*O*-isopropylidene-*β*-D-galactopyranosyl]-2,3-*O*-isopropylidene-*aldehydo*-D-idose dimethyl acetal (33e): Column chromatography (ethyl acetate) of the crude product gave **33e**

(410 mg, 88%) as a solid. M.p. 117–118 °C; $[\alpha]_D^{22} = +4.0$, $[\alpha]_{436}^{22} = +6.0$ (c = 1.0, methanol); IR (KBr): $\tilde{\nu}$ = 3481, 1245, 1219, 1078 cm^{-1}; ^{1}H NMR ([D$_6$]DMSO): δ = 5.29 (d, J = 5.4 Hz, OH–C-2′), 4.45 (d, J = 7.9 Hz, 1H; H-1′), 4.41 (dd, J = 6.7, 4.6 Hz, 1H; CH$_2$O*H*), 4.36 (d, J = 5.9 Hz, 1H; H-1), 4.27 (dd, J = 7.2, 5.9 Hz, 1H; H-2), 4.10 (dd, J = 5.6, 1.9 Hz, 1H; H-4′), 3.99 (ddd, J = 7.2, 6.7, 1.7 Hz, 1H; H-6′; after isotopic exchange with D_2O was transformed in dd, J = 7.2, 1.7 Hz), 3.94 (dd, J = 6.8, 5.6 Hz, 1H; H-3), 3.62 (ddd, J = 5.9, 5.3, 1.6 Hz, 1H; H-5′), 3.60–3.15 (several m, 5H; H-4,5,2′,3′,6′), 3.29, 3.28 (2s, 6H; 2MeO), 2.55 (dd, J = 6.3, 1.5 Hz, 1H; H-6), 2.24 (dd, J = 5.3, 1.5 Hz, 1H; H-6), 1.35, 1.32, 1.30, 1.22 (4s, 12H; 2C*Me*$_2$); ^{13}C NMR ([D$_6$]DMSO): δ = 109.5, 108.5, 104.7, 101.7, 80.6, 79.5, 79.3, 75.2, 73.0, 72.9, 72.4, 60.2, 55.3, 53.6, 35.3, 28.1, 27.2, 26.6, 26.3, 20.7; HR-MS (FAB+) $C_{20}H_{35}O_{10}S$: calcd for [M^++H] 467.1951; found 467.1948; $C_{20}H_{35}O_{10}S$ (467.55): calcd C 51.48, H 7.35, S 6.87; found C 51.23, H 7.34, S 6.89.

5,6-Dideoxy-5,6-epithio-4-*O*-[*β*-D-galactopyranosyl]-2,3-*O*-isopropylidene-*aldehydo*-D-idose dimethyl acetal (33f): Column chromatography (methanol/chloroform 1:4) of the crude product gave **33f** (383 mg, 90%) as a solid. M.p. 78–80 °C; $[\alpha]_D^{22} = -15.0$ (c = 1.0, methanol); IR (KBr): $\tilde{\nu}$ = 3482, 1374, 1255, 1214, 1168, 1116 cm^{-1}; ^{1}H NMR (500 MHz; D_2O): δ = 4.71 (d, J = 7.8 Hz, 1H; H-1′), 4.62 (d, J = 6.7 Hz, 1H; H-1), 4.44 (dd, J = 7.0, 6.7 Hz, 1H; H-2), 4.33 (dd, J = 7.2, 1.9 Hz, 1H; H-3), 3.92 (d, J = 3.2 Hz, 1H; H-4′), 3.78 (dd, J = 11.6, 8.0 Hz, 1H; H-6′), 3.72 (dd, J = 11.6, 4.4 Hz, 1H; H-6′), 3.67 (dd, J = 9.8, 3.2 Hz, 1H; H-3′), 3.64 (m, 1H; H-5′), 3.58 (dd, J = 9.9, 7.6 Hz, 1H; H-2′), 3.51, 3.50 (2s, 6H; 2MeO), 3.50 (dd, J = 8.5, 1.9 Hz, 1H; H-4), 3.26 (ddd, J = 8.7, 6.1, 6.1 Hz, 1H; H-5), 2.62 (dd, J = 6.6, 1.9 Hz, 1H; H-6), 2.38 (dd, J = 5.7, 1.9 Hz, 1H; H-6), 1.52, 1.48 (2s, 6H; C*Me*$_2$); ^{13}C NMR ([D$_6$]DMSO): δ = 110.1, 105.3, 102.7, 80.8, 79.9, 75.4, 75.3, 73.8, 71.0, 68.2, 60.6, 56.0, 53.9, 35.8, 27.5, 27.1, 21.0; HR-MS (FAB+) $C_{17}H_{31}O_{10}S$: calcd for [M^++H] 427.1638; found 427.1641; $C_{17}H_{30}O_{10}S \cdot H_2O$ (444.49): calcd C 45.93, H 7.26, S 7.21; found C 45.92, H 7.10, S 6.76.

5,6-Dideoxy-5,6-epithio-4-*O*-[*α*-D-glucopyranosyl]-2,3-*O*-isopropylidene-*aldehydo*-D-idose dimethyl acetal (33g): Column chromatography (methanol/chloroform 1:5) of the crude product gave **33g** (424 mg, −100%) as a syrup. $[\alpha]_D^{22} = +70.0$ (c = 1, methanol); IR (neat): $\tilde{\nu}$ = 3422, 1253, 1216, 1145, 1054, 1022, 922 cm^{-1}; ^{1}H NMR ([D$_6$]DMSO, D_2O): δ = 4.76 (d, J = 3.7 Hz, 1H; H-1′), 4.45 (dd, J = 7.5, 6.3 Hz, 1H; H-2), 4.33 (d, J = 6.3 Hz, 1H; H-1), 3.94 (dd, J = 7.5, 1.6 Hz, 1H; H-3), 3.60–3.00 (several m, 8H; H-4,5,2′,3′,4′,5′,6′,6′), 3.29, 3.28 (2s, 6H; 2MeO), 2.51 (dd, J = 5.6, 2.6 Hz, 1H; H-6), 2.35 (dd, J = 5.6, 1.6 Hz, 1H; H-6), 1.37, 1.30 (2s, 6H; C*Me*$_2$); ^{13}C NMR ([D$_6$]DMSO): δ = 109.6, 105.0, 101.1, 83.6, 79.9, 74.9, 73.3, 73.1, 72.9, 69.9, 60.7, 56.0, 53.9, 36.0, 27.6, 27.0, 22.3; HR-MS (FAB+) $C_{17}H_{31}O_{10}S$: calcd for [M^++H] 427.1637; found 427.1631.

5,6-Dideoxy-5,6-epithio-4-*O*-[*β*-D-glucopyranosyl]-2,3-*O*-isopropylidene-*aldehydo*-D-idose dimethyl acetal (33h): Column chromatography (methanol/chloroform 1:4) of the crude product gave **33h** (384 mg, 90%) as a solid. M.p. 75–80 °C; $[\alpha]_D^{22} = -21.0°$ (c = 2, methanol); IR (KBr): $\tilde{\nu}$ = 3422, 1216, 1078 cm^{-1}; ^{1}H NMR (500 MHz, [D$_6$]DMSO, D_2O): δ = 4.43 (d, J = 6.0 Hz, 1H; H-1′), 4.36 (d, J = 6.1 Hz, 1H; H-1), 4.29 (dd, J = 7.2, 6.1 Hz, 1H; H-2), 4.00 (dd, J = 7.3, 1.5 Hz, 1H; H-3), 3.60 (br d, J = 11.4 Hz, 1H; H-6′), 3.37 (dd, J = 11.4, 6.0 Hz, 1H; H-6′), 3.29, 3.28 (2s, 6H; 2MeO), 3.18 (dd, J = 8.6, 1.5 Hz, 1H; H-4), 3.15–2.95 (m, 5H; H-5,2′,3′,4′,5′), 2.54 (dd, J = 6.4, 1.4 Hz, 1H; H-6), 2.24 (dd, J = 5.5, 1.4 Hz, 1H; H-6), 1.33, 1.31 (2s, 6H; C*Me*$_2$); ^{13}C NMR ([D$_6$]DMSO): δ = 109.8, 105.2, 102.1, 80.7, 79.6, 76.9, 76.8, 75.3, 73.7, 70.5, 61.8, 56.0, 53.9, 35.7, 27.4, 26.9, 21.0; MS(CI+): *m/z* 427 [M^++H], 411 [$M^+ - CH_3$], 395 [$M^+ - CH_3O$], 379 [$M^+ - CH_3 - CH_3OH$], 363 [$M^+ - CH_3O - S$]; HR-MS (FAB+) $C_{17}H_{31}O_{10}S$: calcd for [M^++H] 427.1638; found 427.1635; $C_{17}H_{30}O_{10}S$ (426.48): calcd C 47.87, H 7.09; found C 47.77, H 7.37.

5,6-Dideoxy-5,6-epithio-4-*O*-[2′,3′,4′,6′-tetra-*O*-pivaloyl-*α*-D-glucopyranosyl]-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (44a): Column chromatography (ether/hexane 1:2) of the crude product gave **44a** (514 mg, 67%) as a solid. M.p. 52–54 °C; $[\alpha]_D^{22} = +59.0$ (c = 1.0, chloroform); IR (KBr): $\tilde{\nu}$ = 1740, 1281, 1141, 1041 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 5.57 (dd, J = 10.4, 9.3 Hz, 1H; H-3′), 5.15 (d, J = 3.6 Hz, 1H; H-1′), 5.10 (dd, J = 10.2, 9.3 Hz, 1H; H-4′), 4.84 (dd, J = 10.4, 3.6 Hz, 1H; H-2′), 4.25 (m, 1H; H-5′), 4.24 (d, J = 5.8 Hz, 1H; H-1), 4.18 (dd, J = 7.6, 5.8 Hz, 1H; H-2), 4.12 (dd, J = 12.7, 2.1 Hz, 1H; H-6′), 4.08 (dd, J = 7.8, 2.3 Hz, 1H; H-3), 3.95 (dd, J = 12.5, 4.2 Hz, 1H; H-6′), 3.35, 3.34 (2s, 6H; 2MeO), 3.13 (ddd, J = 9.2, 5.8, 5.5 Hz, 1H; H-5), 2.92 (dd, J = 9.2, 2.2 Hz, 1H; H-4), 2.56 (dd, J = 6.0, 1.5 Hz, 1H; H-6), 2.34 (dd, J = 5.4, 1.5 Hz, 1H; H-6), 1.48, 1.39 (2s, 6H; C*Me*$_2$), 1.15, 1.11, 1.08, 1.06 (4s, 36H; 4Me$_3$C); ^{13}C NMR ($CDCl_3$): δ = 178.2, 179.9, 177.0, 176.5, 110.4, 106.1, 96.3, 84.3, 81.0, 76.1, 71.2, 69.5, 68.5, 68.0, 61.9, 57.3, 54.8, 38.9, 38.8, 34.0, 27.4, 27.3, 27.2, 27.1, 26.9, 26.2; HR-MS (FAB+) $C_{37}H_{62}O_{14}NaS$: calcd for [M^++Na] 785.3758; found 785.3759.

5,6-Dideoxy-5,6-epithio-4-*O*-[2′,3′,4′,6′-tetra-*O*-pivaloyl-*β*-D-glucopyranosyl]-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (44b): Column chromatography (ether/hexane 1:2) of the crude product gave **44b** (532 mg, 70%) as a solid. M.p. 107–110 °C; $[\alpha]_D^{22} = -16.5$ (c = 1.2, chloroform); IR (KBr): $\tilde{\nu}$ = 1744, 1158, 1132, 1105, 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 5.33 (dd, J = 9.6, 9.4 Hz, 1H; H-3′), 5.13 (dd, J = 10.0, 9.4 Hz, 1H; H-4′), 5.08 (dd, J = 9.6, 8.0 Hz, 1H; H-2′), 4.83 (d, J = 8.0 Hz, 1H; H-1′), 4.33 (d, J = 6.2 Hz, 1H; H-1), 4.27 (dd, J = 7.3, 6.2 Hz, 1H; H-2), 4.15 (dd, J = 12.2, 1.8 Hz, 1H; H-6′), 4.12 (dd, J = 7.2, 1.5 Hz, 1H; H-3), 4.01 (dd, J = 12.3, 5.3 Hz, 1H; H-6′), 3.68 (ddd, J = 10.1, 5.3, 1.8 Hz, 1H; H-5′), 3.36, 3.33 (2s, 6H; 2MeO), 3.32 (m, 1H; H-4), 3.05 (ddd, J = 8.4, 5.8, 5.4 Hz, 1H; H-5), 2.63 (dd, J = 5.9, 0.8 Hz, 1H; H-6), 2.29 (dd, J = 5.4, 0.8 Hz, 1H; H-6), 1.39, 1.35 (2s, 6H; C*Me*$_2$), 1.18, 1.15, 1.13, 1.09 (4s, 36H; 4Me$_3$C); ^{13}C NMR ($CDCl_3$): δ = 178.0, 177.2, 176.4, 176.2, 110.5, 104.9, 98.0, 80.2, 78.8, 75.0, 72.4, 71.3, 67.9, 61.9, 55.1, 53.6, 38.9, 38.8, 38.7, 32.9, 27.5, 27.3, 27.3, 27.2, 27.1, 27.0, 26.9, 25.0; $C_{37}H_{62}O_{14}S$ (762.95): calcd C 58.25, H 8.19; found C 58.14, H 8.33; HR-MS (FAB+) $C_{37}H_{62}O_{14}NaS$: calcd for [M^++Na] 785.3758; found 785.3752.

Synthesis of 5,6-dideoxy-5,6-epithio derivatives 44c and d: general procedure: The 5,6-dideoxy-5,6-epithio derivatives **44c** and **d** were prepared according to the general procedure outlined for **44a** and **b** starting from the parent cyclic sulfates **43a** and **b** (1 mmol) and treatment with NaOMe (5 equiv). After 18 h evaporation of the solvent gave a crude product, which was conventionally acetylated with by treatment with acetic anhydride-pyridine (5:5 mL) at RT overnight. Conventional work-up gave a crude product that was purified by column chromatography (ether/hexane 2:1).

5,6-Dideoxy-5,6-epithio-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-*α*-D-glucopyranosyl]-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (44c): Column chromatography gave **44c** (505 mg, 85%) as a syrup. $[\alpha]_D^{22} = +32.0$ (c = 0.5, chloroform); IR (neat): $\tilde{\nu}$ = 1751, 1225, 1041 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 5.53 (t, J = 9.9 Hz, 1H; H-3′), 5.12 (d, J = 3.7 Hz, 1H; H-1′), 5.10 (t, J = 9.8 Hz, 1H; H-4′), 4.93 (dd, J = 10.4, 3.7 Hz, 1H; H-2′), 4.30 (d, J = 6.0 Hz, 1H; H-1), 4.32–4.00 (m, 5H; H-2,3,4,6,6′), 3.44, 3.42 (2s, 6H; 2MeO), 3.21 (dt, J = 9.0, 5.6, 5.6 Hz,1H; H-5′), 2.95 (dd, J = 9.0, 2.2 Hz, 1H; H-5), 2.58 (br d, J = 6.0 Hz, 1H; H-6), 2.41 (br d, J = 5.1 Hz, 1H; H-6), 2.01, 2.08, 2.04, 2.00 (4s, 12H; 4Ac), 1.52, 1.45 (2s, 6H; C*Me*$_2$); ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.2, 170.0, 169.6, 110.3, 106.2, 97.9, 85.6, 80.9, 75.9, 70.7, 69.8, 68.6, 68.1, 62.1, 57.1, 55.1, 33.6, 27.1, 26.7, 25.5, 20.8, 20.7, 20.6; HR-MS (FAB+) $C_{25}H_{38}O_{14}NaS$: calcd for [M^++Na] 617.1880; found 617.1865.

5,6-Dideoxy-5,6-epithio-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyl]-2,3-*O*-isopropylidene-*aldehydo*-D-glucose dimethyl acetal (44d): Column chromatography gave **44d** (450 mg, 77%) as a syrup. $[\alpha]_D^{22} = -17.0$ (c = 2.0, chloroform); IR (KBr): $\tilde{\nu}$ = 1756, 1222, 1043 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 5.22 (dd, J = 9.5, 9.4 Hz, 1H; H-3′), 5.08 (dd, J = 9.8, 9.4 Hz, 1H; H-4′), 5.06 (dd, J = 9.5, 7.9 Hz, 1H; H-2′), 4.81 (d, J = 7.9 Hz, 1H; H-1′), 4.36 (d, J = 6.2 Hz, 1H; H-1), 4.31 (dd, J = 6.9, 6.3 Hz, 1H; H-2), 4.21 (dd, J = 12.3, 5.0 Hz, 1H; H-6′), 4.12 (dd, J = 6.8, 1.6 Hz, 1H; H-4), 4.10 (dd, J = 12.3, 2.6 Hz, 1H; H-6′), 3.66 (ddd, J = 10.0, 5.0, 2.6 Hz, 1H; H-5′), 3.48 (dd, J = 7.0, 1.6 Hz, 1H; H-3), 3.40, 3.38 (2s, 6H; 2MeO), 3.11 (m, 1H; H-5), 2.57 (d, J = 6.0 Hz, 1H; H-6), 2.37 (d, J = 5.7 Hz, 1H; H-6), 2.07, 2.05, 2.03, 2.01 (4s, 12H; 4Ac), 1.43, 1.40 (2s, 6H; C*Me*$_2$); ^{13}C NMR ($CDCl_3$): δ = 170.6, 170.3, 169.5, 169.2, 110.5, 105.2, 99.1, 80.2, 78.9, 75.1, 72.9, 71.8, 71.5, 68.6, 62.1, 55.6, 53.5, 33.2, 27.4, 26.5, 23.8, 20.7, 20.6; HR-MS (FAB+) $C_{25}H_{38}O_{14}NaS$: calcd for [M^++Na] 617.1880; found 617.1879.

Synthesis of 6-deoxy-4-*O*-[2′,3′-*O*-isopropylidene-*β*-D-galactopyranosyl]-2,3-*O*-isopropylidene-5-thio-*aldehydo*-L-idose dimethyl acetal (34e): A mixture of **32a** (0.711 g, 1 mmol) and lithium aluminium hydride (0.267 g, 7 mmol) in dry THF (30 mL) was stirred at RT for 1.5 h. Ethyl acetate (25 mL) was added and the solution filtered through celite and evaporated. Water (50 mL) was added to the residue, which was then extracted with ethyl acetate (3 × 50 mL). The organic phase was dried and evaporated. Column chromatography (ethyl acetate) of the crude product gave **34e** (0.135 g, 45.5%) as a solid. M.p. 123–125 °C; $[\alpha]_D^{22} = +31.5$ (c = 2.0, chloroform); IR (KBr): $\tilde{\nu}$ = 3450, 2542, 1243, 1217, 1152, 1121, 1074, 1036 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 4.69 (d, J = 8.3 Hz, 1H; H-1′), 4.64 (dd,

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$J = 7.9$, 6.7 Hz, 1H; H-2), 4.36 (d, $J = 6.7$ Hz, 1H; H-1), 4.17–3.38 (several m, 11H; H-3,4,5,2′,3′,4′,5′,6′,6′ and 2OH), 3.52, 3–51 (2s, 6H; 2OMe), 2.04 (d, $J = 5.5$ Hz, 1H; SH), 1.50, 141, 1.40, 1.33 (4s, 12H; 2CMe_2), 1.35 (d, $J =$ 6.9 Hz, 3H; Me); ^{13}C NMR ($CDCl_3$): $\delta = 110.6$, 109.8, 107.7, 102.7, 81.4, 79.6, 76.9, 75.8, 75.0, 74.6, 73.7, 62.5, 57.8, 54.8, 38.2, 28.2, 27.1, 26.6, 26.3, 21.0; MS (CI+): m/z: 453 [$M^+ - CH_3$], 451 [$M^+ + 1 - H_2O$], 203 [$C_9H_{15}O_5$]; $C_{20}H_{36}O_{10}S$ (468.56): calcd C 51.26, H 7.74, S 6.84; found C 51.49, H 7.84, S 6.53.

Opening of episulfides 33e–h and 44a–d with sodium acetate: general procedure: A mixture of episulfide (**33e–h** or **44a–d**; 1 mmol) and anhydrous sodium acetate (6.0 g) in acetic anhydride (30 mL) and acetic acid (6.0 mL) was heated at 140 °C under an argon atmosphere until TLC (ether) showed complete disappearance of the starting material (2.5 d for **33e**, 2 d for **33f**, 4 d for **33g**, 3 d for **33h**, 6 d for **44a–c** and 12 d for **44d**). After cooling, the reaction mixture was poured into ice water and the aqueous solution was extracted with chloroform (100 mL). The chloroform solution was washed with a saturated solution of sodium hydrogen carbonate (3×100 mL) followed by water (100 mL), was dried and evaporated.

6-*O*-Acetyl-5-*S*-acetyl-4-*O*-[2′,6′-di-*O*-acetyl-3′,4′-*O*-isopropyliden-*β*-D-galactopyranosyl]-2,3-*O*-isopropylidene-5-thio-*aldehydo*-L-idose dimethyl acetal (35a): Column chromatography (ether) gave **35a** (0.516 g, 86%) as a syrup. $[\alpha]_D^{22} = +0.5$; $[\alpha]_{436}^{22} = +1.1$ ($c = 2.0$, chloroform); IR (neat): $\tilde{\nu} =$ 1743, 1696, 1374, 1229, 1044 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.02$ (dd, $J = 8.0$, 7.3 Hz, 1H; H-2′), 4.71 (d, $J = 8.0$ Hz, 1H; H-1′), 4.42–3.99 (several m, 9H; H-1,2,3,6,6,3′,4′,6′,6′), 3.84 (br d, $J = 4.5$ Hz, 1H; H-4), 3.45–3.40 (m, 1H; H-5), 3.41, 3.38 (2s, 6H; 2OMe), 2.36 (s, 3H; MeCOS), 2.10, 2.08, 2.06 (3s, 9H; 3MeCO), 1.56, 1.37, 1.36, 1.35 (4s, 12H; 2CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 194.5$, 170.7, 170.5, 169.3, 111.1, 110.8, 105.2, 98.4, 77.2, 76.4, 75.4, 75.2, 73.6, 72.5, 71.2, 63.1, 61.9, 55.3, 53.3, 44.6, 30.7, 27.6, 26.3, 26.2, 21.2, 20.9, 20.7; MS (CI+): m/z: 653 [M^++1], 637 [$M^+ - CH_3$], 621 [$M^+ - CH_3O$], 563 [$M^+ - CH_3O - CH_3CO$]; HR-MS (FAB+) $C_{28}H_{45}O_{15}S$: calcd for [M^++H] 653.2479; found 653.2469.

6-*O*-Acetyl-5-*S*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-galactopyranosyl]-2,3-*O*-isopropylidene-5-thio-*aldehydo*-L-idose dimethyl acetal (35b): Column chromatography (ether/hexane 5:1) gave **35b** (0.44 g, 63%) isolated as a syrup. $[\alpha]_D^{22} = -8.0$ ($c = 1.0$, chloroform); IR (neat): $\tilde{\nu} = 1747$, 1692, 1368, 1224, 1077 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.41$ (dd, $J = 3.3$, 0.8 Hz, 1H; H-4′), 5.22 (dd, $J = 10.3$, 7.8 Hz, 1H; H-2′), 5.09 (dd, $J = 10.4$, 3.4 Hz, 1H; H-3′), 4.86 (d, $J = 7.8$ Hz, 1H; H-1′), 4.41–3.80 (several m, 10H; H-1,2,3,4,5,6,6,5′,6′,6′), 3.41, 3.38 (2s, 6H; 2OMe), 2.37 (s, 3H; MeCOS), 2.16, 2.07, 2.04, 2.03, 1.98 (5s, 15H; 5MeCO), 1.39, 1.38 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 194.4$, 170.5, 170.5, 170.4, 170.2, 169.3, 111.1, 105.4, 99.4, 76.6, 75.8, 75.6, 71.1, 70.9, 68.8, 67.1, 61.9, 61.0, 55.6, 53.5, 44.9, 30.8, 27.6, 26.3, 20.9, 20.8, 20.6; HR-MS (FAB+) $C_{29}H_{44}O_{17}S$: calcd for [M^++Na] 719.2231; found 719.2215.

6-*O*-Acetyl-5-*S*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-*α*-D-glucopyranosyl]-2,3-*O*-isopropylidene-5-thio-*aldehydo*-L-idose dimethyl acetal (35c) and 4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-*α*-D-glucopyranosyl]-2,3-*O*-isopropylidene-*aldehydo*-D-xylo-hex-5-ene dimethyl acetal (36c): Column chromatography (ether/hexane 5:1) gave first **36c** (0.190 g, 33%) as a syrup. $[\alpha]_D^{22} =$ +67.0 ($c = 1.7$, chloroform); IR (neat): $\tilde{\nu} = 1749$, 1699, 1646, 1223, 1145, 1041 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 6.02$ (ddd, $J = 17.3$, 10.3, 8.5 Hz, 1H; H-5), 5.56 (t, $J = 10.0$ Hz, 1H; H-3′), 5.40–5.25 (m, 2H; H-6,6), 5.29 (d, $J =$ 3.7 Hz, 1H; H-1′), 5.10 (t, $J = 10.2$ Hz, 1H; H-4′), 4.89 (dd, $J = 10.2$, 3.7 Hz, 1H; H-2′), 4.36 (d, $J = 5.9$ Hz, 1H; H-1), 4.25 (dd, $J = 12.3$, 4.0 Hz, 1H; H-6′), 4.14 (ddd, $J = 10.4$, 4.1, 4.0 Hz, 1H; H-5′), 4.10–3.96 (m, 3H; H-2,3,6′), 3.48, 3.47 (2s, 6H; 2OMe), 2.11, 2.10, 2.05, 2.04 (4s, 12H; 4MeCO), 1.51, 1.45 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.7$, 170.2, 170.0, 169.6, 135.7, 118.3, 110.3, 105.3, 97.1, 81.8, 81.1, 76.1, 71.0, 70.1, 68.5, 67.5, 61.6, 56.4, 54.3, 27.4, 26.9, 20.7, 20.6; HR-MS (FAB+) $C_{25}H_{38}O_{14}$: calcd for [M^++Na] 585.2159; found 585.2158.

Compound **35c** (0.4 g, 57%) was eluted second and was isolated as a solid. M.p. 115–117 °C; $[\alpha]_D^{22} = +32.0$ ($c = 1.0$, chloroform); IR (KBr): $\tilde{\nu} = 1747$, 1683, 1239, 1159, 1138, 1091, 1036 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.48$ (dd, $J = 10.3$, 9.6 Hz, 1H; H-3′), 5.32 (d, $J = 3.8$ Hz, 1H; H-1′), 5.11 (t, $J =$ 9.8 Hz, 1H; H-4′), 4.96 (dd, $J = 10.5$, 3.8 Hz, 1H; H-2′), 4.43 (dd, $J = 11.4$, 6.0 Hz, 1H; H-6), 4.38 (dd, $J = 12.5$, 3.8 Hz, 1H; H-6′), 4.29 (d, $J = 5.9$ Hz, 1H; H-1), 4.26–4.11 (m, 5H; H-3,5,6,5′,6′), 4.00 (dd, $J = 7.0$, 6.0 Hz, 1H; H-2), 3.84 (t, $J = 3.4$ Hz, 1H; H-4), 3.42, 3.41 (2s, 6H; 2OMe), 2.36 (s, 3H; MeCOS), 2.09, 2.07, 2.05, 2.05, 2.01 (5s, 15H; 5MeCO), 1.44, 1.39 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 194.2$, 170.7, 170.5, 170.2, 169.6, 110.8, 105.7, 98.5, 80.3, 78.1, 70.6, 70.5, 69.9, 68.5, 68.2, 62.9, 61.7, 57.0, 54.7, 45.0, 30.6, 27.4, 26.8, 20.9, 20.7; MS (CI+): m/z: 681 [M^++1], 637 [$M^+ - CH_3$], 331 [$C_{14}H_{19}O_9$]; $C_{29}H_{44}O_{16}S$ (680.72): calcd C 51.16, H 6.51, S 4.71; found C 51.26, H 6.61, S 4.37.

6-*O*-Acetyl-5-*S*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-*β*-D-glucopyranosyl]-2,3-*O*-isopropylidene-5-thio-*aldehydo*-L-idose dimethyl acetal (35d): Column chromatography (ether/hexane 3:1) gave **35d** (0.61 g, 87%) isolated as a syrup. $[\alpha]_D^{22} = -14.0$ ($c = 1$, chloroform); IR (neat): $\tilde{\nu} = 1749$, 1696, 1227, 1041 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.30$ (dd, $J = 9.5$, 9.3 Hz, 1H; H-3′), 5.17 (dd, $J = 9.7$, 9.6 Hz, 1H; H-4′), 5.08 (dd, $J = 9.5$, 8.1 Hz, 1H; H-2′), 4.94 (d, $J = 8.1$ Hz, 1H; H-1′), 4.38–4.00 (m, 7H; H-1,2,3,6,6,6′,6′), 4.00 (m, 1H; H-5), 3.87 (br d, $J = 4.4$ Hz, 1H; H-4), 3.81 (ddd, $J = 10.0$, 4.1, 2.5 Hz, 1H; H-5′), 3.38 (s, 6H; 2OMe), 2.38 (s, 3H; MeCOS), 2.08, 2.08, 2.06, 2.05, 2.03 (5s, 15H; 5MeCO), 1.39, 1.38 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta =$ 194.4, 170.7, 170.5, 170.3, 169.5, 169.2, 111.0, 105.2, 98.8, 76.5, 75.7, 75.2, 73.1, 71.9, 71.2, 68.4, 61.8, 55.6, 52.7, 44.9, 30.8, 27.6, 26.3, 20.9, 20.7, 20.5; HR-MS (FAB+) $C_{29}H_{44}O_{17}NaS$: calcd for [M^++Na] 719.2197; found 719.2170.

4-*O*-[2′,3′,4′,6′-Tetra-*O*-pivaloyl-*α*-D-glucopyranosyl]-2,3-*O*-isopropylidene-*aldehydo*-D-xylo-hex-5-ene dimethyl acetal (45a) and 6-*O*-Acetyl-5-*S*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-pivaloyl-*α*-D-glucopyranosyl]-2,3-*O*-isopropylidene-5-thio-*aldehydo*-D-glucose dimethyl acetal (46a): Column chromatography (ether/hexane 1:1) gave first unreacted **44a** (208 mg, 27%). Compound **45a** (310 mg, 31%) was eluted second and isolated as a syrup $[\alpha]_D^{22} = +61.0$ ($c = 1.0$, chloroform); IR (neat): $\tilde{\nu} = 1735$, 1281, 1138, 1037 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 6.00$ (ddd, $J = 17.3$, 10.2, 8.7 Hz, 1H; H-5), 5.60 (dd, $J = 10.2$, 9.4 Hz, 1H; H-3′), 5.32 (br d, $J = 17.4$ Hz, 1H; H-6), 5.26 (dd, $J = 10.2$, 1.4 Hz, 1H; H-6), 5.25 (d, $J = 3.6$ Hz, 1H; H-1′), 5.15 (dd, $J = 10.2$, 9.4 Hz, 1H; H-4′), 4.88 (dd, $J = 10.2$, 3.7 Hz, 1H; H-2′), 4.32 (d, $J =$ 5.5 Hz, 1H; H-1), 4.17 (ddd, $J = 10.2$, 3.0, 2.7 Hz, 1H; H-5′), 4.10 (dd, $J =$ 7.0, 5.4 Hz, 1H; H-2), 4.07–4.04 (m, 3H; H-6′,6′,4), 3.99 (dd, $J = 7.0$, 4.3 Hz, 1H; H-3), 3.45, 3.43 (s, 6H; 2OMe), 1.48, 1.41 (2s, 6H; CMe_2), 1.23, 1.19, 1.15, 1.12 (4s, 36H; 4CMe_3); ^{13}C NMR ($CDCl_3$): $\delta = 178.2$, 177.8, 176.5, 135.8, 118.7, 110.4, 105.4, 96.2, 81.6, 81.0, 76.5, 71.2, 69.8, 67.9, 61.7, 56.6, 54.6, 38.9, 27.4, 27.3, 27.2, 27.1, 27.0; HR-MS (FAB+) $C_{37}H_{62}O_{14}Na$: calcd for [M^++Na] 753.4037; found 753.4029.

Compound **46a** (490 mg, 42%) was eluted third and isolated as a syrup. $[\alpha]_D^{22} = +51.0$ ($c = 1.0$, chloroform); IR (neat): $\tilde{\nu} = 1735$, 1689, 1281, 1140, 1037 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.49$ (dd, $J = 10.3$, 9.6 Hz, 1H; H-3′), 5.47 (d, $J = 4.0$ Hz, 1H; H-1′), 5.20 (dd, $J = 10.1$, 9.6 Hz, 1H; H-4′), 4.91 (dd, $J =$ 10.3, 4.0 Hz, 1H; H-2′), 4.37–4.11 (several m, 9H; H-1,2,3,4,6,6,5′,6′,6′), 3.95 (dd, $J = 7.3$, 2.0 Hz, 1H; H-5), 3.45, 3.44 (2s, 6H; 2OMe), 2.37 (s, 3H; MeCOS), 2.12 (s, 3H; Ac), 1.39, 1.25 (2s, 6H; CMe_2), 1.24, 1.18, 1.15, 1.12 (4s, 36H; 4CMe_3); ^{13}C NMR ($CDCl_3$): $\delta = 192.9$, 178.3, 178.1, 177.5, 177.1, 167.4, 105.3, 96.6, 78.9, 70.6, 69.8, 68.1, 67.7, 62.0, 61.4, 57.1, 54.2, 44.3, 31.5, 30.3, 29.8, 27.4, 27.3, 27.2, 20.9; HR-MS (FAB+) $C_{41}H_{68}O_{17}NaS$: calcd for [M^++Na] 887.4075; found 887.4066.

6-*O*-Acetyl-5-*S*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-pivaloyl-*β*-D-glucopyranosyl]-2,3-*O*-isopropylidene-5-thio-*aldehydo*-D-glucose dimethyl acetal (46b): Column chromatography (ether/hexane 1:1) gave first unreacted **44b** (560 mg, 73%). Compound **46b** (190 mg, 22%) was eluted second and isolated as a syrup. $[\alpha]_D^{22} = -4.0$ ($c = 1.2$, chloroform); IR (neat): $\tilde{\nu} = 1745$, 1687, 1138 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.33$ (t, $J = 9.4$ Hz, 1H; H-3′), 5.16 (dd, $J = 10.0$, 9.4 Hz, 1H; H-4′), 5.09 (dd, $J = 9.5$, 7.9 Hz, 1H; H-2′), 4.79 (d, $J = 7.9$ Hz, 1H; H-1′), 4.58 (dd, $J = 11.0$, 4.5 Hz, 1H; H-6), 4.38–4.32 (m, 2H; H-1,6), 4.23–4.01 (several m, 6H, H-2,3,4,5,6,6′), 3.72 (ddd, $J = 10.0$, 4.6, 1.6 Hz, 1H; H-5′), 3.40, 3.39 (2s, 6H; 2OMe), 2.35 (s, 3H; MeCOS), 2.04 (s, 3H; Ac), 1.39, 1.35 (2s, 6H; CMe_2), 1.22, 1.17, 1.15, 1.111 (4s, 36H, 4CMe_3); ^{13}C NMR ($CDCl_3$): $\delta = 194.7$, 110.8, 105.2, 98.3, 78.2, 75.5, 73.5, 72.8, 72.6, 71.6, 67.9, 62.8, 61.7, 55.7, 53.6, 44.7, 30.7, 30.3, 27.5, 27.3, 27.2, 26.5, 20.8; HR-MS (FAB+) $C_{41}H_{68}O_{17}NaS$: calcd for [M^++Na] 887.4075; found 887.4071.

6-*O*-Acetyl-5-*S*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-*α*-D-glucopyranosyl]-2,3-*O*-isopropylidene-5-thio-*aldehydo*-D-glucose dimethyl acetal (46c): Column chromatography (ether/hexane 2:1) gave first **36c** (90 mg, 16%). Compound unreacted **44c** (300 mg, 50%) was eluted second. Compound **46c** (120 mg, 18%) was eluted third and isolated as a syrup. $[\alpha]_D^{22} = +60.0$ ($c = 1.0$, chloroform); IR (neat): $\tilde{\nu} = 1749$, 1697, 1665, 1619, 1158 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.43$ (dd, $J = 10.0$, 9.9 Hz, 1H; H-3′), 5.35 (d, $J =$ 3.8 Hz, 1H; H-1′), 5.12 (dd, $J = 9.9$, 9.6 Hz, 1H; H-4′), 4.89 (dd, $J = 10.5$, 3.8 Hz, 1H; H-2′), 4.42–3.85 (several m, 10H; H-1,2,3,4,5,6,6,5′,6′,6′), 3.45

(s, 6H; 2OMe), 2.37 (s, 3H; MeCOS), 2.12, 2.11, 2.07, 2.02, 2.01 (5s, 15H; 5 Ac), 1.40, 1.38 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 195.3$, 170.7, 170.5, 170.1, 169.9, 169.4, 110.5, 105.3, 97.4, 82.8, 78.9, 76.4, 70.2, 69.7, 68.2, 67.8, 62.1, 61.4, 56.9, 54.0, 44.4, 30.6, 27.1, 26.4, 20.7, 20.6, 20.2, 19.5; HR-MS (FAB+) $C_{29}H_{44}O_{17}NaS$: calcd for $[M^+ + Na]$ 719.2197; found 719.2195.

6-*O*-Acetyl-5-*S*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl]-2,3-*O*-isopropylidene-5-thio-*aldehydo*-D-glucose dimethyl acetal (46d): Column chromatography (ether) gave first unreacted **44d** (230 mg, 40%). Compound **46d** (365 mg, 52%) was elusted second and isolated as a syrup. $[\alpha]_D^{22} = -14.0$ ($c = 2.0$, chloroform); IR (neat): $\tilde{\nu} = 1752$, 1687, 1232, 1041 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.20$ (t, $J = 9.3$ Hz, 1H; H-3′), 5.11 (dd, $J = 9.6$, 9.3 Hz, 1H; H-4′), 5.03 (dd, $J = 9.4$, 7.9 Hz, 1H; H-2′), 4.76 (d, $J =$ 7.9 Hz, 1H; H-1′), 4.55–4.05 (several m, 8H; H-2,3,4,5,6,6,6′,6′), 4.34 (d, $J = 6.3$ Hz, 1H; H-1), 3.69 (ddd, $J = 9.6$, 4.1, 2.6 Hz, 1H; H-5′), 3.41, 3.39 (2s, 6H; 2OMe), 2.36 (s, 3H; MeCOS), 2.08, 2.07, 2.05, 2.02, 2.00 (5s, 15H; 5 Ac), 1.39, 1.37 (2s, 6H; CMe_2); ^{13}C NMR ($CDCl_3$): $\delta = 194.6$, 170.7, 170.5, 170.3, 169.4, 169.2, 110.8, 105.6, 99.6, 78.6, 76.7, 75.4, 73.0, 71.8, 71.4, 68.4, 62.6, 61.8, 56.1, 53.3, 45.5, 30.7, 30.4, 27.5, 26.4, 20.9, 20.7; HR-MS (FAB+) $C_{29}H_{44}O_{17}NaS$: calcd for $[M^+ + Na]$ 719.2197; found 719.2198.

Synthesis of 1,2,3-tri-*O*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosyl]-6-deoxy-5-thio-α,β-L-idopyranose (37): A solution of **34e** (90 mg, 0.19 mmol) in 80% aqueous acetic acid (20 mL) was heated at 70 °C for 4 h. After cooling the reaction mixture was evaporated and coevaporated with toluene (2 × 20 mL). The crude product was kept overnight with acetic anhydride (5 mL) and pyridine (3 mL) at RT. Standard work-up and purification by column chromatography (ether/hexane 4:1) gave first **37** (β anomer; 63 mg, 51.6%) as a solid. M.p. 180–181 °C; $[\alpha]_D^{22} = +68.0$ ($c = 1.0$, methanol); IR (KBr): $\tilde{\nu} = 1749$, 1222, 1081, 1045 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.08$ (d, $J = 3.6$ Hz, 1H; H-1), 5.47 (t, $J = 10.0$ Hz, 1H; H-3), 5.35 (d, $J = 3.3$ Hz, 1H; H-4′), 5.17 (dd, $J =$ 10.2, 3.6 Hz, 1H; H-2), 5.09 (dd, $J = 10.4$, 7.8 Hz, 1H; H-2′), 4.97 (dd, $J =$ 10.4, 3.4 Hz, 1H; H-3′), 4.51 (d, $J = 7.8$ Hz, 1H; H-1′), 4.13–4.06 (m, 3H; H-4,6′,6′), 3.89 (t, $J = 6.7$ Hz, 1H; H-5′), 3.05 (dq, $J = 7.2$, 5.4 Hz, 1H; H-5), 2.13, 2.11, 2.04, 2.03, 2.01, 1.97, 1.95 (7s, 21H; 7MeCO), 1.49 (d, $J = 7.4$ Hz, 3H; Me); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.5$, 170.2, 169.9, 169.8, 169.4, 168.9 (7CO), 99.9 (C-1′), 80.6 (C-4), 73.1 (C-2), 72.1 (C-1), 71.1 (C-3′), 70.9 (C-5′), 69.2 (C-2′), 67.0 (C-4′), 66.5 (C-3), 61.2 (C-6′), 37.3 (C-5), 21.2, 20.9, 20.8, 20.7 (7*Me*CO), 17.4 (C-6); MS (CI+): m/z: 577 $[M^+ + 1 - CH_3COOH]$, 517 $[M^+ + 1 - 2\,CH_3COOH]$, 331 $[C_{14}H_{19}O_9]$; $C_{26}H_{36}O_{16}S$ (636.62): calcd C 49.05, H 5.70, S 5.04; found C 49.46, H 5.77, S 4.70.

Compound **37** (α-anomer containing ~15% of the β-anomer; 42 mg, 32.8%) was eluted second and isolated as a syrup. ^{1}H NMR ($CDCl_3$): $\delta =$ 5.87 (d, $J = 5.8$ Hz, 1H; H-1), 5.37 (d, $J = 3.5$ Hz, 1H; H-4′), 5.36 (t, $J =$ 6.0 Hz, 1H; H-3), 5.19 (dd, $J = 10.3$, 8.0 Hz, 1H; H-2′), 5.09 (t, $J = 5.8$ Hz, 1H; H-2), 5.01 (dd, $J = 10.4$, 3.45 Hz, 1H; H-3′), 4.60 (d, $J = 7.9$ Hz, 1H; H-1′), 4.20–4.10 (m, 2H; H-6′,6′), 3.95 (br t, $J = 7.0$ Hz, 1H; H-5′), 3.85 (dd, $J = 6.0$, 3.1 Hz, 1H; H-4), 3.34 (dq, $J = 7.3$, 3.1 Hz, 1H; H-5), 2.13, 2.11, 2.08, 2.07, 2.06, 2.03, 1.98 (7s, 21H; 7MeCO), 1.31 (d, $J = 7.3$ Hz, 3H; Me); ^{13}C NMR ($CDCl_3$): $\delta = 170.6$, 170.2, 170.1, 169.5, 169.3, 169.0, 168.8 (7Me*CO*), 102.0, 79.1, 71.5, 71.0, 71.0, 69.2, 69.0, 68.6, 67.1, 61.2, 33.2, 20.8, 20.6, 15.6.

Synthesis of thio sugars 38–40: general procedure: A solution of the *S*-acetyl derivative (**35a–d**; 0.5 mmol) in 70% aqueous acetic acid (20 mL) was heated at 80 °C until TLC showed complete disappearance of the starting material (4 h). After cooling, the reaction mixture was concentrated and coevaporated with toluene (2 × 20 mL). The crude product was dissolved in anhydrous methanol (25 mL) and a 0.5 N solution of sodium methoxide in methanol (0.5 mL) was added. The reaction mixture was left at RT for 2 h. Neutralisation with acetic acid followed by concentration under vacuum gave a crude product that was acetylated with acetic anhydride-pyridine (10:8 mL) at RT overnight. Methanol (10 mL) was added and the solution was coevaporated with toluene to give a crude product, which was purified by column chromatography.

1,2,3,6-Tetra-*O*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-β-D-galactopyranosyl]-5-thio-α,β-L-idopyranose (38): Column chromatography (ether) first gave **38** (β anomer; 192 mg, 55.3%) as a solid. M.p. 173–175 °C; $[\alpha]_D^{22} =$ +34.0 ($c = 2$, chloroform); IR (KBr): $\tilde{\nu} = 1749$, 1220, 1049 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.03$ (d, $J = 3.4$ Hz, 1H; H-1), 5.42 (t, $J = 10.1$ Hz, 1H; H-3), 5.36 (d, $J = 3.3$ Hz, 1H; H-4′), 5.19 (dd, $J = 10.2$, 3.5 Hz, 1H; H-2), 5.09 (dd, $J = 10.4$, 7.7 Hz, 1H; H-2′), 4.99 (dd, $J = 10.4$, 3.4 Hz, 1H; H-3′), 4.66 (t, $J = 11.2$ Hz, 1H; H-6), 4.62 (d, $J = 7.8$ Hz, 1 H, H-1′), 4.27 (dd, $J = 11.4$, 4.3 Hz, 1H; H-6), 4.23 (dd, $J = 10.0$, 5.4 Hz, 1H; H-4), 4.15 (dd, $J = 11.2$, 6.6 Hz, 1H; H-6′), 4.09 (dd, $J = 11.2$, 6.8 Hz, 1H; H-6′), 3.91 (t, $J =$ 6.7 Hz, 1H; H-5′), 3.33 (m, 1H; H-5), 2.15, 2.13, 2.06, 2.05, 2.04, 2.03, 1.98, 1.96 (8s, 24H; 8MeCO), 1.49 (d, $J = 7.4$ Hz, 3H; Me); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.3$, 170.1, 169.8, 169.7, 169.3, 169.1 (8CO), 99.8 (C-1′), 79.2 (C-4), 72.8 (C-2), 71.7 (C-1), 71.0 (C-3′), 71.0 (C-5′), 69.1 (C-2′), 66.9 (C-4′), 66.8 (C-3), 62.6 (C-6), 61.6 (C-6′), 41.8 (C-5), 21.1, 20.8, 20.7, 20.6 (8*Me*CO); MS (CI+): m/z: 635 $[M^+ + 1 - CH_3COOH]$, 575 $[M^+ + 1 - 2\,CH_3COOH]$, 515 $[M^+ + 1 - 3\,CH_3COOH]$, 347 $[C_{14}H_{19}O_8S]$, 331 $[C_{14}H_{19}O_9]$; $C_{28}H_{38}O_{18}S$ (694.66): calcd C 48.41, H 5.47; found C 48.50, H 5.56.

A mixture of the α and β anomers of **38** in a 1:1 proportion (61 mg, 17.7%) was eluted second and isolated as a syrup. ^{1}H NMR ($CDCl_3$; selected signals for α-anomer) $\delta = 5.97$ (d, $J = 5.4$ Hz, 1H; H-1), 4.64 (d, $J = 8.0$ Hz, 1H; H-1′), 3.58 (m, 1H; H-5); ^{13}C NMR ($CDCl_3$; selected signals for α-anomer) $\delta = 102.0$ (C-1′), 37.1 (C-5).

1,2,3,6-Tetra-*O*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl]-5-thio-α,β-L-idopyranose (39): Column chromatography (ether/hexane 4:1) gave **39** (β anomer; 177 mg, 55%) as a syrup. $[\alpha]_D^{22} = +314.0$ ($c = 1.0$, chloroform); IR (KBr): $\tilde{\nu} = 1752$, 1700, 1228, 1158, 1126, 1043 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 6.05$ (d, $J = 3.4$ Hz, 1H; H-1), 5.58 (t, $J = 10.2$ Hz, 1H; H-3), 5.38 (dd, $J = 10.2$, 9.6 Hz, 1H; H-3′), 5.31 (d, $J = 4.0$ Hz, 1H; H-1′), 5.14 (dd, $J = 10.2$, 3.4 Hz, 1H; H-2), 5.02 (t, $J = 9.8$ Hz, 1H; H-4′), 4.85 (dd, $J = 10.3$, 4.0 Hz, 1H; H-2′), 4.62 (dd, $J = 11.6$, 8.1 Hz, 1H; H-6′), 4.59 (dd, $J = 11.7$, 5.7 Hz, 1H; H-6′), 4.34 (dd, $J = 10.1$, 5.5 Hz, 1H; H-4), 4.25 (dd, $J = 11.6$, 5.5 Hz, 1H; H-6), 4.17 (m, 1H; H-5′), 4.10 (dd, $J = 11.7$, 2.0 Hz, 1H; H-6), 3.40 (m, 1H; H-5), 2.18, 2.16, 2.08, 2.07, 2.03, 2.03, 2.00, 1.98 (8s, 24H; 8MeCO); ^{13}C NMR ($CDCl_3$): $\delta = 170.5$, 169.8, 169.6, 169.5, 169.2 (8CO), 96.7 (C-1′), 77.0 (C-4), 73.5 (C-2), 71.4 (C-1), 70.6 (C-2′), 69.7 (C-3′), 68.8 (C-3), 68.6 (C-4′), 68.5 (C-5′), 64.2 (C-6), 62.2 (C-6′), 42.7 (C-5), 20.8, 20.7, 20.6, 20.5 (8*Me*CO); HR-MS (FAB+) $C_{28}H_{38}O_{18}SNa$: calcd for $[M^+ + Na]$ 717.1677; found 717.1686; $C_{28}H_{38}O_{18}S$ (694.66): calcd C 48.41, H 5.51, S 4.62; found C 48.11, H 5.70, S 4.49.

1,2,3,6-Tetra-*O*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl]-5-thio-α,β-L-idopyranose (40): Column chromatography (ether) gave first **40** (β anomer; 53 mg, 15.5%) as a solid. M.p. 196–197 °C; $[\alpha]_D^{22} = +15.0$, $[\alpha]_{436}^{22} = +33.0$ ($c = 1.0$, chloroform); IR (KBr): $\tilde{\nu} = 1747$, 1233, 1042 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 6.05$ (d, $J = 3.4$ Hz, 1H; H-1), 5.44 (dd, $J = 10.2$, 10.0 Hz, 1H; H-3), 5.22 (dd, $J = 10.2$, 3.5 Hz, 1H; H-2), 5.20 (dd, $J = 9.5$, 9.3 Hz, 1H; H-3′), 5.10 (dd, $J = 9.8$, 9.5 Hz, 1H; H-4′), 4.90 (dd, $J = 9.3$, 7.9 Hz, 1H; H-2′), 4.70 (d, $J = 7.9$ Hz, 1H; H-1′), 4.68 (dd, $J = 11.2$, 10.0 Hz, 1H; H-6), 4.35 (dd, $J = 12.4$, 4.5 Hz, 1H; H-6′), 4.30 (dd, $J = 11.4$, 4.2 Hz, 1H; H-6), 4.25 (dd, $J = 10.0$, 5.5 Hz, 1H; H-4), 4.09 (dd, $J = 12.4$, 2.3 Hz, 1H; H-6′), 3.70 (ddd, $J = 9.8$, 4.5, 2.3 Hz, 1H; H-5′), 3.36 (ddd, $J = 10.2$, 5.5, 4.6 Hz, 1H; H-5), 2.17, 2.09, 2.08, 2.05, 2.04, 2.03, 2.00, 2.00 (8s, 24H; 8MeCO); ^{13}C NMR ($CDCl_3$): $\delta = 170.3$, 169.7, 169.6, 169.2 (8CO), 99.2 (C-1′), 79.3 (C-4), 72.9 (C-3′), 72.8 (C-2), 72.1 (C-5′), 71.7 (C-1), 71.6 (C-2′), 68.0 (C-4′), 66.7 (C-3), 62.7 (C-6), 61.7 (C-6′), 41.7 (C-5), 21.1, 20.8, 20.7, 20.6, 20.5 (8*Me*CO); MS (CI+): m/z: 635 $[M^+ + 1 - CH_3COOH]$, 575 $[M^+ + 1 - 2\,CH_3COOH]$, 515 $[M^+ + 1 - 3\,CH_3COOH]$, 347 $[C_{14}H_{19}O_8S]$, 331 $[C_{14}H_{19}O_9]$; $C_{28}H_{38}O_{18}S$ (694.66): calcd C 48.41, H 5.47, S 4.61; found C 48.23, H 5.50, S 4.25.

A mixture of the α and β anomers of **40** in a 1:5 proportion (0.142 g, 41%) was eluted second and isolated as a syrup. ^{1}H NMR ($CDCl_3$; selected signals for α-anomer): δ 6.01 (d, $J = 6.2$ Hz, 1H; H-1), 3.49 (m, 1H; H-5).

1,2,3,6-Tetra-*O*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl]-5-thio-α,β-D-glucopyranose (47c): Column chromatography (ether/hexane 2:1) gave **47c** (280 mg, 83%; 3:1 α:β mixture) as a syrup. IR (neat): $\tilde{\nu} =$ 1735, 1665, 1281 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 6.08$ (d, $J = 3.0$ Hz, 1H; H-1 α-anomer), 5.86 (d, $J = 5.1$ Hz; H-1 β-anomer), 5.51 (t, $J = 9.7$ Hz; H-3 α-anomer), 5.47 (d, $J = 3.9$ Hz; H-1′ α-anomer), 5.38 (dd, $J = 10.2$, 9.9 Hz; H-3′ α-anomer), 5.14 (dd, $J = 10.3$, 3.4 Hz; H-2 α-anomer), 5.08 (t, $J =$ 9.8 Hz; H-4′ α-anomer), 4.91 (dd, $J = 10.5$, 3.9 Hz; H-2′ α-anomer), 4.52 (dd, $J = 12.0$, 3.2 Hz; H-6 α-anomer), 4.39 (dd, $J = 12.0$, 4.5 Hz; H-6 α-anomer), 4.30–4.00 (m, 10H; H-1,2,3,4,5,6,6,5′,6′,6′), 3.59 (dt, $J = 10.2$, 3.8, 3.8 Hz; H-5 α-anomer), 3.4 (m; H-5 α-anomer), 2.20, 2.13, 2.11, 2.10, 2.03, 2.02, 2.02, 1.97 (8s; 8 Ac α-anomer), 2.55, 2.35, 2.26, 2.25, 2.15, 2.09, 2.08 (7s; 7Ac β-anomer); ^{13}C NMR ($CDCl_3$): $\delta = 170.6$, 170.3, 169.9, 169.8, 169.7, 169.5, 169.2, 96.1, 77.0, 73.5, 72.8, 70.4, 70.3, 69.5, 68.8, 68.1, 61.9, 61.7, 41.0, 21.0, 21.0, 20.8, 20.6, 20.5; HR-MS (FAB+) $C_{28}H_{38}O_{18}NaS$: calcd for $[M^+ + Na]$ 717.1676; found 717.1670.

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1,2,3,6-Tetra-*O*-acetyl-4-*O*-[2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl]-5-thio-α,β-D-glucopyranose (47d): Column chromatography (ether/hexane 5:1) gave **47d** (120 mg, 35%; α:β mixture) as a syrup. IR (neat): $\tilde{\nu}$ = 1735, 1665, 1281 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 6.34 (d, J = 3.8 Hz, 1H; H-1 α-anomer), 5.73 (d, J = 8.3 Hz; H-1′ α-anomer), 5.48 (t, J = 9.8 Hz; H-3 α-anomer), 5.26 (t, J = 9.3 Hz; H-3′ α-anomer), 5.18–5.08 (m, H-2,2′,4′ α-anomer, 4.33–4.11 (m, H-4,6,6,6′,6′), 4.10 (ddd, J = 9.5, 5.0, 2.2 Hz; H-5′ α-anomer), 3.85 (ddd, J = 9.8, 4.4, 2.2 Hz; H-5 α-anomer), 2.19, 2.12, 2.10, 2.09, 2.05, 2.04, 2.02 (7s; 8Ac α-anomer); ^{13}C NMR ($CDCl_3$): δ = 169.4, 91.8, 89.1, 72.9, 72.8, 70.3, 69.9, 69.2, 68.0, 67.8, 61.5, 61.5, 30.4, 21.1, 20.9, 20.7, 20.6, 20.5; HR-MS (FAB+) $C_{28}H_{38}O_{18}NaS$: calcd for [M^++Na] 717.1677; found 717.1671.

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