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Expedient Synthesis of α -S-(1 \rightarrow 6)-Linked Pentaglucoyl Thiol

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Abstract: An α -S-(1 \rightarrow 6)-linked pentaglucoyl thiol has been synthesized in a convenient and stereoselective way. Key steps of the synthesis involved thioglycosylation of 6-iodinated sugars with α -glycoyl thiols under phase transfer conditions. The α -configuration of glycosidic linkages was thus introduced prior to the coupling steps, and relied on the intrinsic configurational stability of α -glycoyl thiols. This work also demonstrated the great utility of MMTr as effective anomeric S-protecting group.

Introduction

The rapid development of glycobiology has created a great demand for structurally defined carbohydrates and their mimetics as biological probes. Among them, S-glycosides have attracted considerable attention due to their resistance to chemical and enzymatic hydrolysis. Also, S-glycosides often exhibit similar solution conformation and similar or even more potent biological activities compared to the corresponding O-glycosides.¹ For example, an S-linked glycopeptide mimic of tyrocidine displayed a greater inhibitory activity against *B. subtilis* than the natural antibiotic.² Carbohydrate epitopes of conjugate vaccines have also been modified to contain S-linked residues and the resulting S-linked immunogens generated an antigen-specific immune response that even exceeded the response to the native oligosaccharides.³ Owing to these

properties, *S*-glycosides including thiooligosaccharides and *S*-glycoconjugates, have frequently been the synthetic targets in carbohydrate chemistry in the past few decades.⁴

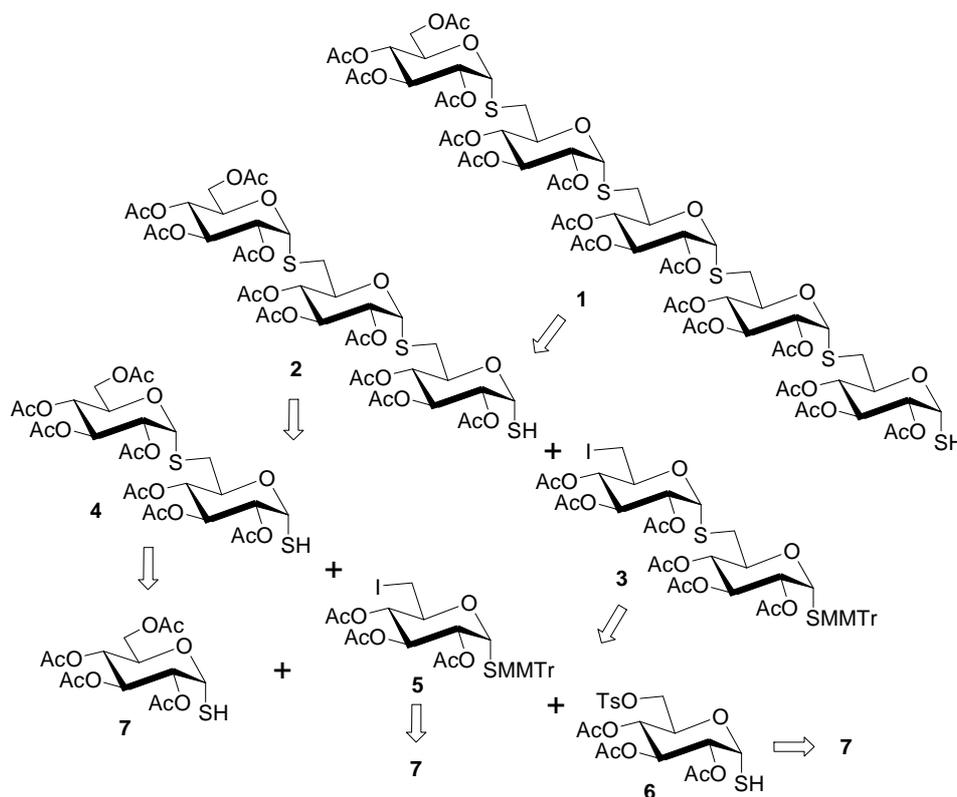
Literature survey revealed many *S*-glycosides have been synthesized by normal glycosidation procedures, i.e. using a glycosyl donor with a leaving group at its anomeric centre as the electrophile and an acceptor containing a free sulfhydryl group as the nucleophile.⁵ However, this conventional approach could often lead to the desired thioglycosides in unsatisfactory overall yields as the introduction of the sulfhydryl group onto the acceptor is often not straightforward giving rise to the nucleophile in low yield.⁶ Furthermore, application of the normal glycosidation approach to the synthesis of *S*-1,2-*cis* glycosides could be limited because 1,2-*cis* stereocontrol is generally difficult.⁷ Therefore, nonconventional approaches involving glycosyl thiols (sometimes called 1-thiosugars) as the nucleophile has recently emerged as the method of choice for synthesizing various *S*-glycosides.⁸ Unlike the normal sugar hemiacetals, which could mutarotate easily under most conditions, glycosyl thiols are quite stable in terms of configuration, and their mutarotation does not occur readily. In contrast, it is highly restricted and even blocked under basic conditions,⁹ as such, the anomeric configuration of glycosyl thiols can be maintained during the glycosylation process.

As part of our ongoing program on glycosyl thiol chemistry,¹⁰ we wish to report here the synthesis of an α -*S*-(1 \rightarrow 6)-linked pentaglycosyl thiol which could be used for ligation with electrophilic aglycones for the construction of complex *S*-glycoconjugates. A number of *S*-linked oligoglucosides have been synthesized by different methods including S_N2 displacement of a leaving group by a 1-thiosugar derivatives,¹¹ polymer-supported glycosyl thiolate-mediated S_N2 reaction,¹² ring-opening of a sugar epoxide or thiirane with a glycosyl thiol,¹³ or photoinduced coupling of a glycosyl thiol with a sugar alkene.^{8b} For example, Defaye and coworkers synthesized a series of thiooligoglucosides as enzymatically stable phytoalexin-elicitor analogues, in which all the thioglycosidic bonds were introduced through S_N2 reaction between glycosyl thiols and nonanomeric leaving groups,^{11a} and all the analogues were found to be active in eliciting phytoalexin accumulation in soybean cotyledon tissue and in binding to a glucan-binding protein of soybean. Ferrier reactions between glycals and thiosugars were also used to synthesize precursors to *S*-linked diglucosides.¹⁴ Oligoglucosides containing *S*-maltosyl-6-

thiomaltosyl structure have been synthesized as potential inhibitors for starch-debranching enzymes in which the key step involved also S_N2 displacement of 6-halogenated sugars by 1-thiosugar derivatives.¹⁵ Despite the enormous progress in the synthesis of *S*-glycosides,⁴ and the above different procedures for the synthesis of *S*-oligoglucosides, normal α -glycosyl thiols, such as α -glucosyl thiol, have been rarely used for the synthesis of oligosaccharides incorporating α -*S*-glycosidic linkage. Direct use of α -glycosyl thiols is rare due presumably to the difficulty in the preparation of configurationally pure α -glycosyl thiols. In a few examples, most notably by Driguez and coworkers,^{11b,15} α -glycosyl thioacetates were used as precursors to α -thiols to introduce α -*S*-glycosidic bonds. However, in these procedures, de-*O*-acetylation could also occur during thioglycosylation and dry conditions were often required for the coupling steps.¹⁵ Other precursors, such as glycosyl isothiureas¹⁶ and thiosilanes,¹⁷ have not been used for the synthesis of α -thiooligosaccharides. In addition, the low availability of these α -configurational precursors has also restricted their application in the synthesis of α -thiooligosaccharides.

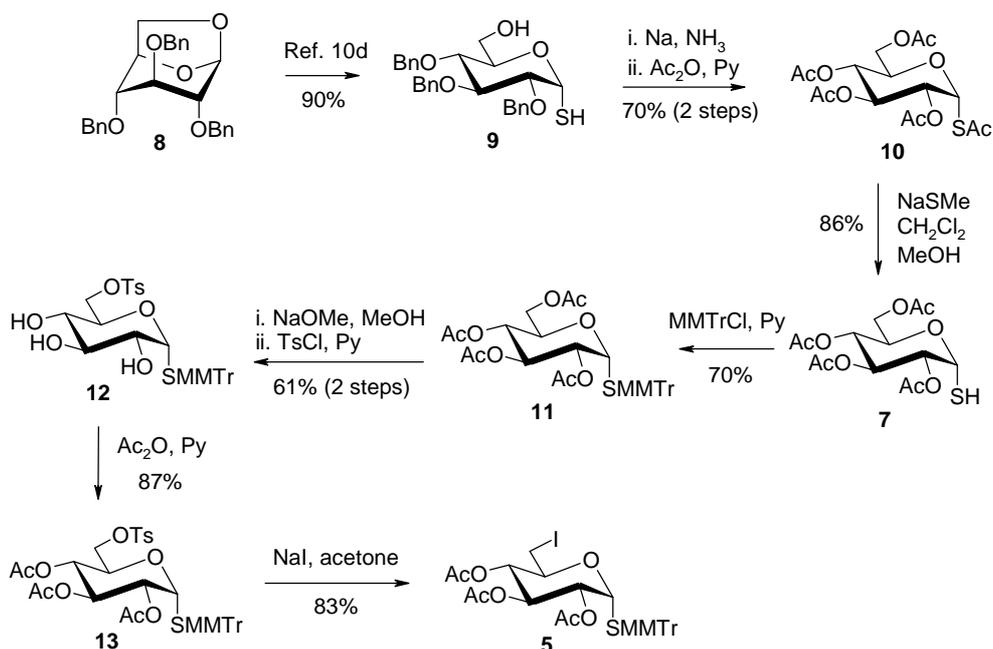
Results and discussion

Recently we developed a highly stereoselective procedure for the synthesis of α -glycosyl thiols by direct ring-opening of 1,6-anhydrosugars with commercially available bis(trimethylsilyl)sulfide.^{10d} This ring-opening procedure is a significant advance in glycosyl thiol chemistry because there have not been any reports on direct stereoselective preparation of α -glycosyl thiols prior to our work. Based on this work, we envisioned that the target structure **1** (Scheme 1) could be assembled stepwise from α -glucosyl thiol **7**, which could be readily prepared by our own procedure. The retrosynthetic analysis revealed a convergent [3+2] strategy to be attractive, i.e. coupling of trisaccharide **2** and disaccharide **3** would lead to the target molecule **1**. Trisaccharide **2** could be accessed from disaccharide **4** and iodide **5**, and in turn, **4** could be synthesized from thiol **7** and iodide **5**. Iodide **5** could also be obtained from thiol **7**. Meanwhile, disaccharide **3** could be derived from iodide **5** and thiol **6** which could also be prepared from thiol **7**. Iodo was chosen as the leaving group for all S_N2 coupling steps in view of its high performance in the synthesis of *S*-glycosides,¹⁵ while MMTTr was used to mask anomeric sulfhydryl groups as it was used previously as an anomeric *S*-protecting group for the synthesis of glycosyl thiols.^{10a}



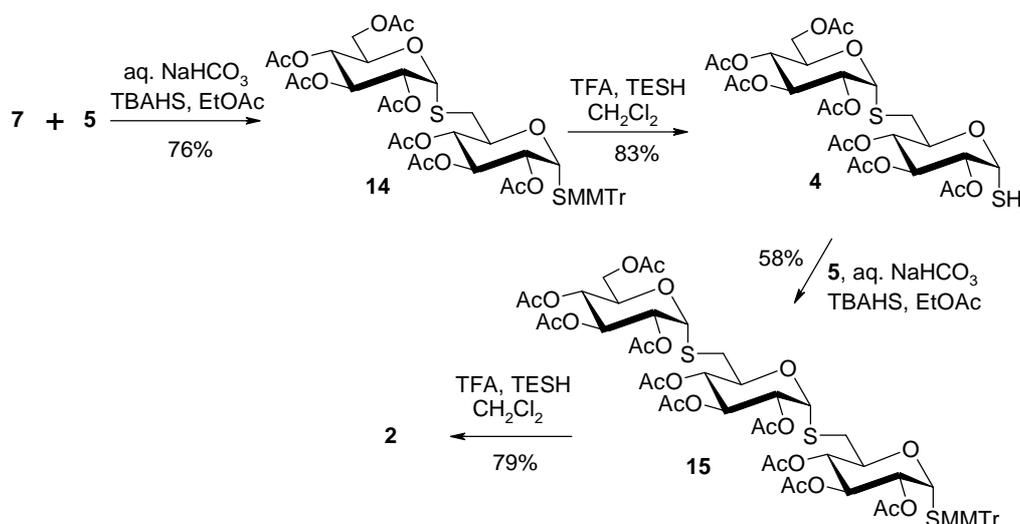
Scheme 1. Retrosynthetic analysis of *S*-pentaglycosyl thiol **1**.

To carry out the above synthetic scheme, α -glucosyl thiol **9**^{10d} was first prepared from benzylated levoglucosan **8** following the previous procedure (Scheme 2). As reported earlier,^{10d} **9** was produced exclusively as α -anomer, which made the purification very simple and straightforward. Birch reduction was then performed on **9** followed by acetylation, leading to the fully acetylated thiosugar **10** in 70% yield. The anomeric acetyl group of **10** was subsequently removed with 20% aqueous NaSMe in CH₂Cl₂-MeOH to give α -thiol **7** in 86% yield. Thus, the nucleophilic building block for thioglycosylation was made available. To obtain the other electrophilic coupling partner **5**, **7** was first treated with MMTrCl in pyridine to produce thioglycoside **11** in 70% yield, which was then subjected to deacetylation with NaOMe in MeOH and selective 6-*O*-tosylation with TsCl in pyridine to furnish intermediate **12** in 61% yield. Next, **12** was acetylated to give thioglycoside **13** in 87% yield, which subsequently reacted with NaI in acetone to produce the sugar iodide **5** in 83% yield.



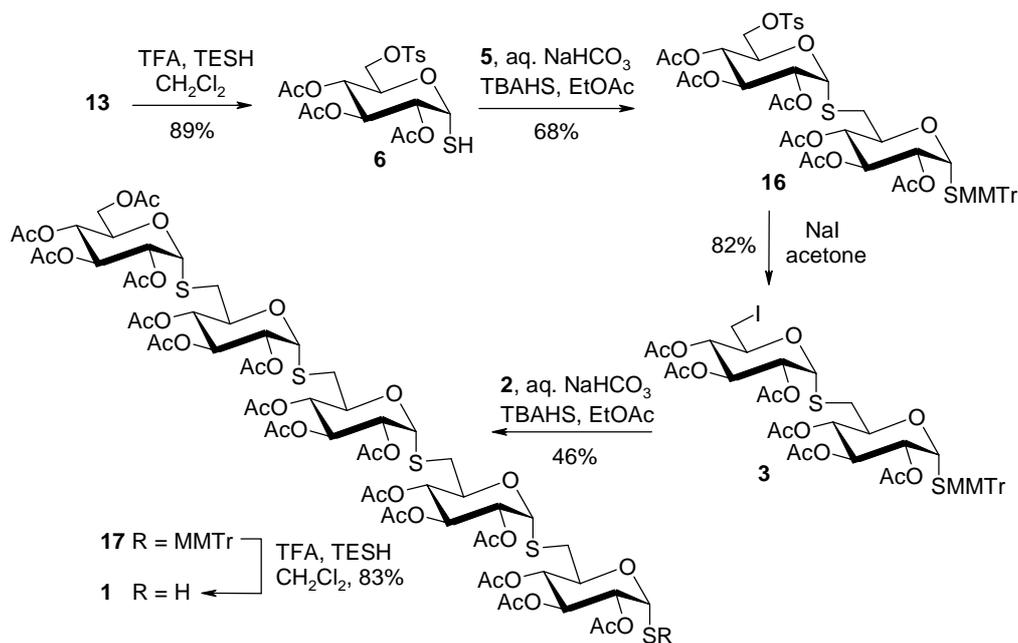
Scheme 2. Synthesis of monosaccharide building blocks **7** and **5**.

With the requisite building blocks **7** and **5** in hand, their coupling was performed in the presence of tetra-*n*-butylammonium hydrogensulfate (TBAHS) in ethyl acetate and a saturated aqueous solution of NaHCO_3 ,¹⁸ i.e. phase-transfer conditions (PTC), as shown in Scheme 3. As expected, *S*-linked disaccharide **14** was smoothly obtained in high yield (76%). In this coupling, the thiolate anion was generated in situ by the action of NaHCO_3 , and the α -*S*-disaccharide was then readily formed by nucleophilic displacement of the iodo atom in **5**. It is worth mentioning that the α -stereochemical integrity at the anomeric centre of **7** was maintained during the reaction. In comparison, no reaction took place when thioacetate **10** instead of thiol **7** was exposed to the above PTC conditions in the presence of **5**. Disaccharide **14** was then treated with trifluoroacetic acid (TFA) in CH_2Cl_2 in the presence of triethylsilane (TESH)^{10a} in order to expose the anomeric sulfhydryl group for the next coupling. The reaction occurred smoothly giving rise to disaccharidyl thiol **4** in 83% yield. Coupling between thiol **4** and iodide **5** was subsequently conducted under the above described PTC conditions, again, the desired trisaccharide **15** was produced in very good yield (58%). Next, **15** was converted into the key building block, trisaccharidyl thiol **2**, in 79% yield by treatment with the above TFA/TESH conditions.



Scheme 3. Synthesis of trisaccharidyl thiol **2**.

Meanwhile, thioglycoside **13** was also subjected to the same acidic conditions (TFA/TESH), as shown in Scheme 4, to provide the anomeric thiol **6** in 89% yield. We subsequently investigated the use of tosyl group-containing thiol **6** as a nucleophile. When **6** was treated with iodide **5** under the PTC conditions, fortunately, the desired disaccharide **16** was efficiently obtained in 68% yield and self-condensation of **6** was not detected in the reaction. Seeing that intermediate **6** contains both nucleophilic and electrophilic groups, its successful use in the above synthesis suggests that the current strategy could also be used for the synthesis of more complex oligosaccharides. To access the target pentasaccharide, the tosyl group of **16** was then displaced with iodo group by treatment with NaI in acetone to give rise to the key disaccharide building block **3** in 82% yield. Thioglycosylation of **3** with trisaccharidyl thiol **2** was then conducted in a mixture of EtOAc/aqueous NaHCO₃ and in the presence of TBAHS, to our delight, the desired pentasaccharide **17** was isolated in 46% yield. Here it should be mentioned that all the above thioglycosylation reactions proceeded well as indicated by TLC, although a small amount of glycosyl thiols remained unreacted in all cases. In the case of the relatively low yield of **17**, the formation of a small amount of disulfide byproduct was also observed. Finally, removal of the anomeric MMTr protecting group from **17** furnished the target α -S-(1 \rightarrow 6)-linked pentaglycoside **1** in 83% yield.



Scheme 4. Synthesis of target molecule **1**.

Conclusions

In conclusion, as an extension of our previous project, in this report, an α -S-(1 \rightarrow 6)-linked pentaglycosyl thiol was efficiently synthesized via a [3+2] thioglycosylation strategy. All the glycosylation reactions were conducted under PTC conditions, thus extremely simple in execution and in workup, and all the α -thioglycosidic bonds were introduced in highly stereoselective mode by virtue of configurational stability of anomeric thiols. In addition, the synthesized thiosugars including **4** and **2** could be ligated with electrophilic aglycones for the construction of complex S-glycoconjugates, which would deliver excellent mimics of naturally occurring glycoconjugates containing α -O-(1 \rightarrow 6)-linked oligoglucosides.¹⁹ Apparently, the synthetic strategy presented here could also be extended to the synthesis of other α -S-(1 \rightarrow 6)-linked or more complex oligosaccharides. Studies on the application of the synthetic methodology to specific, biorelevant glycoconjugate targets are in progress.

Experimental Section

General information

Unless otherwise stated, all moisture-sensitive reactions were performed in oven-dried glassware under nitrogen using dry solvents. Solvents were evaporated under reduced pressure while maintaining the water bath temperature below 40 °C. All reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 F₂₅₄ and the compounds visualized by UV or by treatment with 8% H₂SO₄ in methanol followed by heating. Flash chromatography was performed with the appropriate solvent system using 160-200 mesh silica. Optical rotations were measured at 20 °C. ¹H NMR spectra were obtained on a 600 MHz and reported in parts per million (δ) relative to the response of the solvent or to tetramethylsilane (0.00 ppm). Coupling constants (J) are reported in Hertz (Hz). ¹³C NMR spectra were recorded at 150 MHz and reported in δ relative to the response of the solvent. The HRMS data were recorded on an LC-time of flight mass spectrometer. Yields refer to chromatographically pure compounds and are calculated based on reagents consumed.

2,3,4,6-Tetra-*O*-acetyl-1-*S*-acetyl-1-thio- α -D-glucopyranose (10): To liquid NH₃ (25 mL) at -78 °C was added Na^o until the solution became blue. A solution of 2,3,4-tri-*O*-benzyl-1-thio- α -D-glucopyranose **9** (1.77 g, 3.8 mmol) in THF (8 mL) was then added to the above solution, and the resulting mixture was stirred for 2 h at -78 °C. The reaction was quenched by the addition of ammonium chloride until the blue color disappeared. The NH₃ was allowed to evaporate slowly, and the crude residue was degassed for 2.5 h. Ac₂O (5 mL) was added to a slurry of the crude residue in pyridine (20 mL), and the reaction was stirred at room temperature overnight and then concentrated in vacuo. The crude product was then poured into aqueous NaHCO₃ and extracted with CH₂Cl₂ (3x25 mL). The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc, 5:1) to give the title compound **10** (1.08 g, 70%) as a white amorphous solid: [α]_D +129.1 (*c* 2.2, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 6.19 (d, J = 5.4 Hz, 1H), 5.22 (dd, J = 10.3, 5.5 Hz, 1H), 5.16 (t, J = 9.7 Hz, 1H), 5.07 (t, J = 10.0 Hz, 1H), 4.26 (dd, J = 12.5, 4.1 Hz, 1H), 4.03 (dd, J = 12.5, 2.2 Hz, 1H), 3.94 (ddd, J = 6.2, 4.0, 2.3 Hz, 1H), 2.41 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H); ¹³C NMR (150MHz, CDCl₃) δ 191.3, 170.5, 169.9, 169.3, 169.29, 80.35, 71.5, 71.1, 69.0, 67.9, 61.6, 31.4, 20.6, 20.55, 20.5; ESI-HRMS calcd for C₁₆H₂₂NaO₁₀S [M + Na]⁺ 429.0831, found 429.0835.

2,3,4,6-Tetra-*O*-acetyl-1-thio- α -D-glucopyranose (7): Compound **10** (1.62 g, 4.0 mmol) was dissolved in CH₂Cl₂ (14 mL) and MeOH (7 mL), and the solution was cooled at 0 °C. Nitrogen was bubbled through the solution for 5 min, followed by the addition of 20% aqueous NaSMe (1.1 mL, 4.0 mmol). The mixture was stirred for 3 min under nitrogen, after which time TLC indicated that the reaction was complete. The solution was then transferred to a separatory funnel containing 10 mL of 1% aqueous HCl and 10 mL of H₂O, and extracted with CH₂Cl₂ (3×25 mL). The combined CH₂Cl₂ layers were washed with H₂O (5 mL) and brine (5 mL), dried over Na₂SO₄, filtered and concentrated to give a residue, which was purified by flash column chromatography (petroleum ether/EtoAc, 6:1) to give the product **7** (1.25 g, 86%) as a white amorphous solid: $[\alpha]_D +166.3$ (*c* 3.0, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 5.95 (t, *J* = 5.8 Hz, 1H), 5.40 (t, *J* = 9.8 Hz, 1H), 5.08 (t, *J* = 10.0 Hz, 1H), 5.04 (dd, *J* = 10.2, 5.7 Hz, 1H), 4.45 (ddd, *J* = 10.3, 4.1, 2.2 Hz, 1H), 4.31 (dd, *J* = 12.5, 4.3 Hz, 1H), 4.12 (dd, *J* = 12.5, 2.2 Hz, 1H), 2.11 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.93 (d, *J* = 5.8 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 170.6, 169.9, 169.6, 169.5, 77.1, 70.3, 69.9, 68.28, 68.26, 61.6, 20.67, 20.64, 20.60, 20.55; ESI-HRMS calcd for C₁₄H₂₀NaO₉S [M + Na]⁺ 387.0726, found 387.0724.

4'-Monomethoxytrityl 2,3,4,6-Tetra-*O*-acetyl-1-thio- α -D-glucopyranoside (11): To a solution of the thiol **7** (2.10 g, 5.76 mmol) in dry pyridine (20 mL) was added MMTrCl (2.50 g, 8.10 mmol). The resulting mixture was stirred overnight at room temperature. Pyridine was then removed in vacuo and the residue was purified by flash column chromatography (petroleum ether/EtOAc, 5:1) to give the desired compound **11** (2.57 g, 70%) as a white amorphous solid: $[\alpha]_D +100.0$ (*c* 0.5, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.38 (d, *J* = 8.0 Hz, 4H), 7.31-7.26 (m, 8H), 6.82 (d, *J* = 8.9 Hz, 2H), 5.32 (t, *J* = 9.4 Hz, 1H), 5.07-5.04 (m, 3H), 4.42 (dt, *J* = 10.1, 2.6 Hz, 1H), 4.26 (dd, *J* = 12.4, 3.1 Hz, 1H), 3.84 (dd, *J* = 12.4, 2.3 Hz, 1H), 3.82 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 170.7, 169.9, 169.5, 169.3, 158.5, 144.67, 144.6, 136.3, 131.0, 129.7, 127.9, 127.1, 113.2, 82.5, 70.9, 69.7, 69.2, 69.0, 68.4, 61.7, 55.3, 20.83, 20.78, 20.6; ESI-HRMS calcd for C₃₄H₃₆NaO₁₀S [M + Na]⁺ 659.1927, found 659.1909.

4'-Monomethoxytrityl 6-*O*-Tosyl-1-thio- α -D-glucopyranoside (12): A solution of NaOMe (1.0 M) in MeOH was added to a solution of compound **11** (1.0 g, 1.57 mmol) in MeOH (10 mL)

until a pH of approximately 10 was reached. The reaction mixture was stirred at room temperature for 2 h, after which Amberlite-120 acidic resin was added to neutralize the solution. The mixture was then filtered and concentrated in vacuo to give a residue, which was azeotroped three times with toluene and directly used in the next step without purification. The crude deacetylated product was dissolved in pyridine (15 mL) and cooled at 0 °C. TsCl (0.36 g, 1.90 mmol) was added to the solution, and the resulting mixture was stirred at room temperature for 4 h. The mixture was then concentrated in vacuo to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc, 1:1) to afford the title compound **12** (0.6 g, 61%) as a colorless syrup: $[\alpha]_D^{25} +232.0$ (*c* 0.5, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.35-7.14 (m, 14H), 6.82 (d, *J* = 8.9 Hz, 2H), 4.71 (d, *J* = 4.8 Hz, 1H), 4.38 (s, 1H), 4.19 (dd, *J* = 10.9, 5.1 Hz, 1H), 4.08 (dd, *J* = 13.2, 7.6 Hz, 2H), 3.98 (s, 1H), 3.78 (s, 3H), 3.43-3.35 (m, 2H), 3.28 (t, *J* = 8.8 Hz, 1H), 3.06 (s, 1H), 2.41 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 158.4, 144.9, 144.8, 144.7, 136.2, 132.6, 131.4, 130.04, 129.96, 129.86, 128.1, 127.9, 127.1, 127.0, 113.2, 85.7, 75.3, 71.5, 71.4, 69.6, 69.5, 69.3, 55.3, 21.7; ESI-HRMS calcd for C₃₃H₃₄NaO₈S₂ [M + Na]⁺ 645.1593, found 645.1575.

4'-Monomethoxytrityl 2,3,4-Tri-*O*-acetyl-6-*O*-tosyl-1-thio- α -D-glucopyranoside (13): Ac₂O (3.0 mL) was added to a solution of **12** (0.50 g, 0.8 mmol) in pyridine (10 mL) and the reaction was stirred at room temperature overnight. The mixture was then concentrated in vacuo to give a residue which was purified by flash column chromatography (petroleum ether/EtOAc, 5:1) to give the product **13** (0.52 g, 87%) as a white foam: $[\alpha]_D^{25} +155.8$ (*c* 0.8, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.36-7.23 (m, 14H), 6.84 (d, *J* = 8.9 Hz, 2H), 5.24 (t, *J* = 9.6 Hz, 1H), 4.88 (m, 3H), 4.45-4.39 (m, 1H), 3.98 (dd, *J* = 11.0, 4.5 Hz, 1H), 3.92 (dd, *J* = 11.0, 2.58 Hz, 1H), 3.83 (s, 3H), 2.47 (s, 3H), 2.10 (s, 3H), 1.983 (s, 3H), 1.981 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 169.9, 169.4, 169.1, 158.5, 145.0, 144.6, 144.5, 136.15, 132.5, 131.0, 129.80, 129.78, 129.7, 128.2, 127.94, 127.92, 127.14, 127.12, 113.2, 82.3, 70.6, 69.4, 69.2, 68.8, 68.7, 67.6, 55.3, 21.7, 20.8, 20.6, 20.5; ESI-HRMS calcd for C₃₉H₄₀KO₁₁S₂ [M + K]⁺ 787.1649, found 787.1611.

4'-Monomethoxytrityl 6-Deoxy-6-iodo-2,3,4-tri-*O*-acetyl-1-thio- α -D-glucopyranoside (5): To a solution of **13** (0.48 g, 0.64 mmol) in acetone (10 mL) was added NaI (1.44 g, 9.6 mmol). The

mixture was stirred at 60 °C for 23 h. The solvent was then removed under diminished pressure and the crude product was then poured into H₂O (30 mL) and extracted with CH₂Cl₂ (3x25 mL). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc, 6:1) to give the title compound **5** (0.37 g, 83%) as a white foam: $[\alpha]_D +135.3$ (*c* 1.2, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.42 (d, *J* = 7.9 Hz, 4H), 7.33-7.24 (m, 8H), 6.83 (d, *J* = 8.9 Hz, 2H), 5.34 (dd, *J* = 10.6, 9.0 Hz, 1H), 5.11 (d, *J* = 5.7 Hz, 1H), 5.04 (dd, *J* = 10.6, 5.7 Hz, 1H), 4.92 (t, *J* = 9.3 Hz, 1H), 3.91 (dt, *J* = 9.6, 3.4 Hz, 1H), 3.82 (s, 3H), 3.10 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.03 (dd, *J* = 11.2, 3.7 Hz, 1H), 2.15 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 170.0, 169.33, 169.27, 158.5, 144.7, 144.6, 136.3, 131.0, 129.7, 129.67, 128.0, 127.0, 113.2, 82.0, 72.9, 70.7, 69.7, 68.8, 68.7, 61.7, 55.3, 20.83, 20.78, 20.6; ESI-HRMS calcd for C₃₂H₃₃INaO₈S [M + Na]⁺ 727.0839, found 727.0833.

4'-Monomethoxytrityl 2,3,4,6-Tetra-O-acetyl-1-thio- α -D-glucopyranosyl-S-(1 \rightarrow 6)-2,3,4-tri-O-acetyl-1-thio- α -D-glucopyranoside (14): A pH 8.5 solution of NaHCO₃ (5 mL) followed by TBAHS (475 mg, 1.4 mmol) were added to a solution of iodide **5** (268 mg, 0.38 mmol) and glucosyl thiol **7** (126 mg, 0.35 mmol) in EtOAc (5 mL) under N₂. The mixture was vigorously stirred at room temperature for 24 h, and was then diluted with EtOAc and washed successively with saturated aqueous NaHCO₃ and brine. The organic layer was dried over MgSO₄ and concentrated in vacuo to give a residue which was purified by flash column chromatography (petroleum ether/EtOAc, 2:1) to give disaccharide **14** (247 mg, 76%) as a white amorphous solid: $[\alpha]_D +157.5$ (*c* 0.9, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.39 (d, *J* = 7.8 Hz, 4H), 7.32-7.23 (m, 8H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.59 (d, *J* = 5.8 Hz, 1H), 5.38 (t, *J* = 9.8 Hz, 1H), 5.28 (t, *J* = 9.6 Hz, 1H), 5.08 (t, *J* = 9.8 Hz, 1H), 5.03-4.95 (m, 4H), 4.44-4.39 (m, 2H), 4.32 (dd, *J* = 12.4, 4.5 Hz, 1H), 4.10 (dd, *J* = 12.3, 1.8 Hz, 1H), 3.81 (s, 3H), 2.66 (dd, *J* = 14.5, 3.1 Hz, 1H), 2.51 (dd, *J* = 14.5, 4.7 Hz, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.99 (s, 3H), 1.94 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 170.65, 169.86, 169.84, 169.7, 169.66, 169.2, 158.4, 144.7, 144.6, 136.3, 131.1, 129.81, 129.76, 128.0, 127.1, 113.2, 82.19, 82.16, 70.9, 70.78, 70.75, 70.5, 70.4, 69.6, 69.2, 68.5, 67.7, 61.9, 55.3, 30.0, 20.9, 20.73, 20.66, 20.62, 20.59, 20.53; ESI-HRMS calcd for C₄₆H₅₂NaO₁₇S₂ [M + Na]⁺ 963.2544, found 963.2523.

2,3,4,6-Tetra-*O*-acetyl-1-thio- α -D-glucopyranosyl-*S*-(1 \rightarrow 6)-2,3,4-tri-*O*-acetyl-1-thio- α -D-glucopyranose (4): To a stirred solution of disaccharide **14** (170 mg, 0.18 mmol) in CH₂Cl₂ (30 ml) at 0 °C was added dropwise TFA (0.24 mL, 0.8%) followed by Et₃SiH (0.3 mL, 1%). The reaction was stirred at 0 °C overnight, after which time TLC indicated the disappearance of the starting material. The mixture was then concentrated in vacuo at room temperature, and azeotroped with toluene to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc, 3:1) to give the thiol **4** (100 mg, 83%) as a white solid: $[\alpha]_D +249.2$ (*c* 1.2, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 5.88 (t, *J* = 5.7 Hz, 1H), 5.76 (d, *J* = 5.8 Hz, 1H), 5.38-5.35 (m, 1H), 5.35-5.32 (m, 1H), 5.04 (q, *J* = 10.2 Hz, 2H), 5.01-4.97 (m, 2H), 4.43-4.36 (m, 2H), 4.28 (dd, *J* = 12.4, 4.3 Hz, 1H), 4.06 (dd, *J* = 12.4, 1.9 Hz, 1H), 2.83 (dd, *J* = 14.2, 2.9 Hz, 1H), 2.59 (dd, *J* = 14.2, 6.2 Hz, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.94 (d, *J* = 5.7 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 170.6, 169.9, 169.8, 169.7, 169.63, 169.61, 81.9, 76.9, 70.9, 70.7, 70.3, 69.8, 69.0, 68.4, 67.8, 61.8, 29.9, 20.74, 20.70, 20.66, 20.65, 20.64, 20.63, 20.59; ESI-HRMS calcd for C₂₆H₃₆NaO₁₆S₂ [M + Na]⁺ 691.1343, found 691.1323.

4'-Monomethoxytrityl 2,3,4,6-Tetra-*O*-acetyl-1-thio- α -D-glucopyranosyl-*S*-(1 \rightarrow 6)-2,3,4-tri-*O*-acetyl-1-thio- α -D-glucopyranosyl-*S*-(1 \rightarrow 6)-2,3,4-tri-*O*-acetyl-1-thio- α -D-glucopyranoside (15): A pH 8.5 solution of NaHCO₃ (5 mL) followed by TBAHS (272 mg, 0.8 mmol) were added to a solution of iodide **5** (169 mg, 0.24 mmol) and thiol **4** (137 mg, 0.20 mmol) in EtOAc (5 mL) under N₂. The mixture was vigorously stirred at room temperature for 24 h, and was then diluted with EtOAc and washed successively with saturated aqueous NaHCO₃ and brine. The organic layer was dried over MgSO₄ and concentrated in vacuo to give a residue which was purified by flash column chromatography (petroleum ether/EtOAc, 3:2) to give trisaccharide **15** (145 mg, 58%) as a white amorphous solid: $[\alpha]_D +247.5$ (*c* 0.4, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.40-7.38 (m, 4H), 7.31-7.28 (m, 8H), 6.81 (d, *J* = 8.9 Hz, 2H), 5.74 (d, *J* = 5.8 Hz, 1H), 5.45 (d, *J* = 5.7 Hz, 1H), 5.40 (t, *J* = 9.8 Hz, 1H), 5.33-5.29 (m, 1H), 5.29-5.25 (m, 1H), 5.08 (t, *J* = 9.8 Hz, 1H), 5.04-5.02 (m, 1H), 5.02-4.99 (m, 2H), 4.97-4.90 (m, 3H), 4.41-4.35 (m, 3H), 4.28 (dd, *J* = 12.5, 4.2 Hz, 1H), 4.09 (dd, *J* = 12.4, 1.9 Hz, 1H), 3.80 (s, 3H), 2.80 (dd, *J* = 13.9, 2.8 Hz, 1H), 2.68-2.62 (m, 2H), 2.47 (dd, *J* = 14.8, 4.2 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.04 (s, 9H), 2.02 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.91 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ

170.6, 169.89, 169.86, 169.84, 169.78, 169.77, 169.66, 169.65, 169.2, 158.4, 144.8, 144.4, 136.3, 130.9, 129.8, 129.7, 127.9, 127.1, 113.2, 82.3, 82.1, 81.4, 71.2, 70.8, 70.68, 70.64, 70.5, 70.4, 70.2, 69.65, 68.9, 68.4, 68.3, 67.8, 61.8, 55.3, 30.1, 29.7, 20.9, 20.72, 20.7, 20.67, 20.66, 20.64, 20.63, 20.61, 20.6, 20.5; ESI-HRMS calcd for C₅₈H₆₈NaO₂₄S₃ [M + Na]⁺ 1267.3160, found 1267.3155.

2,3,4,6-Tetra-*O*-acetyl-1-thio- α -D-glucopyranosyl-*S*-(1 \rightarrow 6)-2,3,4-tri-*O*-acetyl-1-thio- α -D-

glucopyranosyl-*S*-(1 \rightarrow 6)-2,3,4-tri-*O*-acetyl-1-thio- α -D-glucopyranose (2): To a stirred solution of trisaccharide **15** (165 mg, 0.13 mmol) in CH₂Cl₂ (30 mL) at 0 °C was added dropwise TFA (0.24 mL, 0.8%) followed by Et₃SiH (0.3 mL, 1%). The reaction was stirred at 0 °C overnight, after which time TLC indicated the disappearance of the starting material. The mixture was then concentrated in vacuo at room temperature, and azeotroped with toluene to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc, 2:1) to give the thiol **2** (100 mg, 79%) as a white amorphous solid: [α]_D +236.0 (*c* 3.0, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 5.87 (t, *J* = 5.5 Hz, 1H), 5.73 (d, *J* = 5.6 Hz, 1H), 5.68 (d, *J* = 5.6 Hz, 1H), 5.35 (d, *J* = 9.9 Hz, 1H), 5.32 (d, *J* = 9.7 Hz, 1H), 5.28 (d, *J* = 10.1 Hz, 1H), 5.06-5.00 (m, 2H), 4.97 (m, 3H), 4.90 (q, *J* = 5.8 Hz, 1H), 4.40-4.38 (m, 1H), 4.37-4.30 (m, 2H), 4.25 (dd, *J* = 12.3, 3.9 Hz, 1H), 4.02 (d, *J* = 12.4 Hz, 1H), 2.88 (d, *J* = 14.4 Hz, 1H), 2.76 (d, *J* = 13.8 Hz, 1H), 2.56 (m, 2H), 2.09 (s, 3H), 2.08 (s, 3H), 2.07 (s, 6H), 2.05 (s, 3H), 2.02 (s, 6H), 2.00 (s, 3H), 1.99 (m, 7H); ¹³C NMR (150 MHz, CDCl₃) δ 170.6, 169.94, 169.91, 169.83, 169.81, 169.78, 169.76, 169.72, 169.62, 169.60, 81.8, 81.5, 71.1, 70.70, 70.65, 70.6, 70.27, 70.25, 70.0, 69.8, 68.72, 68.71, 68.3, 67.8, 61.7, 30.1, 29.6, 20.74, 20.68, 20.63, 20.60; ESI-HRMS calcd for C₃₈H₅₂NaO₂₃S₃ [M + Na]⁺ 995.1959, found 995.1954.

2,3,4-Tri-*O*-acetyl-6-*O*-tosyl-1-thio- α -D-glucopyranose (6): To a stirred solution of the thioglycoside **13** (390 mg, 0.52 mmol) in CH₂Cl₂ (30 mL) at 0 °C was added dropwise TFA (0.24 mL, 0.8%) followed by Et₃SiH (0.3 mL, 1%). The reaction was stirred at 0 °C overnight, after which time TLC indicated the disappearance of the starting material. The mixture was then concentrated in vacuo at room temperature, and azeotroped with toluene to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc, 4:1) to give the thiol **6** (221 mg, 89%) as a colorless syrup: [α]_D +125.0 (*c* 1.2, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ

7.80 (d, $J = 8.2$ Hz, 2H), 7.37 (d, $J = 8.1$ Hz, 2H), 5.84 (t, $J = 5.6$ Hz, 1H), 5.34 (t, $J = 9.8$ Hz, 1H), 4.97 (t, $J = 9.8$ Hz, 1H), 4.92 (dd, $J = 10.2, 5.7$ Hz, 1H), 4.46 (dt, $J = 10.2, 3.6$ Hz, 1H), 4.14 (d, $J = 3.6$ Hz, 2H), 2.47 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.84 (d, $J = 5.6$ Hz, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 170.0, 169.6, 169.4, 145.1, 129.85, 128.1, 76.9, 70.1, 69.7, 68.4, 67.9, 67.3, 21.7, 20.63, 20.62, 20.5; ESI-HRMS calcd for $\text{C}_{19}\text{H}_{24}\text{NaO}_{10}\text{S}_2$ $[\text{M} + \text{Na}]^+$ 499.0709, found 499.0711.

4'-Monomethoxytrityl 2,3,4-Tri-*O*-acetyl-6-*O*-tosyl-1-thio- α -D-glucopyranosyl-*S*-(1 \rightarrow 6)-2,3,4-tri-*O*-acetyl-1-thio- α -D-glucopyranoside (16): A pH 8.5 solution of NaHCO_3 (5 mL) followed by TBAHS (435 mg, 1.28 mmol) were added to a solution of iodide **5** (271 mg, 0.38 mmol) and thiol **6** (152 mg, 0.32 mmol) in EtOAc (5 mL) under N_2 . The mixture was vigorously stirred at room temperature for 24 h, and was then diluted with EtOAc and washed successively with saturated aqueous NaHCO_3 and brine. The organic layer was dried over MgSO_4 and concentrated in vacuo to give a residue which was purified by flash column chromatography (petroleum ether/EtOAc, 2:1) to give the title compound **16** (229 mg, 68%) as a colorless syrup: $[\alpha]_{\text{D}} +120.7$ (c 1.4, CHCl_3); ^1H NMR (600 MHz, CDCl_3) δ 7.82 (d, $J = 8.2$ Hz, 2H), 7.42-7.39 (m, 4H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.32-7.23 (m, 8H), 6.82 (d, $J = 8.9$ Hz, 2H), 5.46 (d, $J = 5.8$ Hz, 1H), 5.28 (t, $J = 9.8$ Hz, 2H), 5.04-4.94 (m, 4H), 4.88 (dd, $J = 10.4, 5.8$ Hz, 1H), 4.44-4.40 (m, 1H), 4.37 (dt, $J = 9.7, 3.5$ Hz, 1H), 4.17-4.11 (m, 2H), 3.80 (s, 3H), 2.59 (dd, $J = 14.6, 3.1$ Hz, 1H), 2.47 (s, 3H), 2.46-2.41 (m, 1H), 2.13 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.97 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.88, 169.85, 169.73, 169.70, 169.4, 169.2, 158.4, 145.1, 144.7, 144.5, 136.3, 131.0, 129.9, 129.8, 129.7, 128.1, 127.9, 127.1, 113.2, 82.3, 82.1, 70.8, 70.5, 70.4, 70.24, 70.22, 69.7, 68.9, 68.5, 67.4, 67.3, 55.3, 29.9, 21.7, 20.9, 20.67, 20.63, 20.61, 20.51, 20.49; ESI-HRMS calcd for $\text{C}_{51}\text{H}_{56}\text{NaO}_{18}\text{S}_3$ $[\text{M} + \text{Na}]^+$ 1075.2527, found 1075.2474.

4'-Monomethoxytrityl 6-Deoxy-6-iodo-2,3,4-tri-*O*-acetyl-1-thio- α -D-glucopyranosyl-*S*-(1 \rightarrow 6)-2,3,4-tri-*O*-acetyl-1-thio- α -D-glucopyranoside (3): To a solution of **16** (154 mg, 0.15 mmol) in acetone (10 mL) was added NaI (225 mg, 1.5 mmol). The mixture was stirred at 60 $^\circ\text{C}$ for 23 h. The solvent was removed under diminished pressure, the crude product was then poured into H_2O (30 mL) and extracted with CH_2Cl_2 (3x25 mL). The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated to give a residue, which was purified by flash

column chromatography (petroleum ether/EtOAc, 3:1) to give the title compound **3** (124 mg, 82%) as a white amorphous solid: $[\alpha]_D +195.7$ (*c* 1.4, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.44-7.39 (m, 4H), 7.36-7.25 (m, 8H), 6.83 (d, *J* = 8.9 Hz, 2H), 5.53 (d, *J* = 5.8 Hz, 1H), 5.35 (t, *J* = 11.9 Hz, 1H), 5.31-5.26 (m, 1H), 5.03 (t, *J* = 9.4 Hz, 1H), 4.99-4.93 (m, 3H), 4.90 (t, *J* = 9.5 Hz, 1H), 4.41 (dt, *J* = 9.8, 3.8 Hz, 1H), 4.21 (m, 1H), 3.82 (s, 3H), 3.33 (dd, *J* = 11.0, 2.5 Hz, 1H), 3.20 (dd, *J* = 11.0, 7.8 Hz, 1H), 2.80 (dd, *J* = 14.9, 3.1 Hz, 1H), 2.55 (dd, *J* = 14.9, 4.4 Hz, 1H), 2.12 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 2.00 (s, 3H), 1.93 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 169.9, 169.8, 169.75, 169.71, 169.7, 169.2, 158.4, 144.75, 144.5, 136.4, 131.0, 129.8, 129.7, 128.0, 127.1, 113.3, 82.3, 82.1, 72.6, 70.82, 70.78, 70.68, 70.61, 69.9, 69.7, 69.0, 68.9, 55.3, 30.1, 20.89, 20.88, 20.71, 20.65, 20.6, 20.5; ESI-HRMS calcd for C₄₄H₄₉INaO₁₅S₂ [M + Na]⁺ 1031.1455, found 1031.1457.

4'-Monomethoxytrityl 2,3,4,6-Tetra-O-acetyl-1-thio- α -D-glucopyranosyl-S-(1 \rightarrow 6)-2,3,4-tri-O-acetyl-1-thio- α -D-glucopyranosyl-S-(1 \rightarrow 6)-2,3,4-tri-O-acetyl-1-thio- α -D-glucopyranosyl-S-(1 \rightarrow 6)-2,3,4-tri-O-acetyl-1-thio- α -D-glucopyranoside (17): A pH 8.5 solution of NaHCO₃ (5 mL) followed by TBAHS (177 mg, 0.52 mmol) were added to a solution of iodide **3** (158 mg, 0.16 mmol) and thiol **2** (124 mg, 0.13 mmol) in EtOAc (5 mL) under N₂. The mixture was vigorously stirred at room temperature for 24 h, and was then diluted with EtOAc and washed successively with saturated aqueous NaHCO₃ and brine. The organic layer was dried over MgSO₄ and concentrated in vacuo to give a residue which was purified by flash column chromatography (petroleum ether/EtOAc, 1:1) to give the title compound **17** (110 mg, 46%) as a white amorphous solid: $[\alpha]_D +182.3$ (*c* 0.4, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.4-7.38 (m, 4H), 7.33-7.24 (m, 8H), 6.82 (d, *J* = 8.9 Hz, 2H), 5.71 (t, *J* = 6.5 Hz, 2H), 5.66 (d, *J* = 5.7 Hz, 1H), 5.44 (d, *J* = 5.6 Hz, 1H), 5.38 (t, *J* = 7.4 Hz, 1H), 5.36 (t, *J* = 5.4 Hz, 1H), 5.34-5.32 (m, 1H), 5.32-5.30 (m, 1H), 5.30-5.26 (m, 1H), 5.09-5.06 (m, 1H), 5.06-5.02 (m, 4H), 5.02-4.99 (m, 2H), 4.99-4.97 (m, 2H), 4.96-4.94 (m, 1H), 4.94-4.89 (m, 1H), 4.43-4.39 (m, 1H), 4.38-4.35 (m, 4H), 4.28 (dd, *J* = 12.4, 4.3 Hz, 1H), 4.08-4.04 (m, 1H), 3.82 (s, 3H), 2.94 (dd, *J* = 14.0, 2.1 Hz, 1H), 2.85 (dd, *J* = 14.3, 2.1 Hz, 1H), 2.77 (dd, *J* = 14.1, 2.4 Hz, 1H), 2.67 (dd, *J* = 14.8, 2.7 Hz, 1H), 2.65-2.58 (m, 3H), 2.50 (dd, *J* = 14.8, 3.9 Hz, 1H), 2.13 (s, 6H), 2.12 (s, 3H), 2.10 (s, 6H), 2.09 (s, 3H), 2.08 (s, 3H), 2.06 (s, 6H), 2.05 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.94 (s, 3H); ¹³C NMR

(150 MHz, CDCl₃) δ 170.6, 169.93, 169.92, 169.88, 169.83, 169.82, 169.81, 169.79, 169.77, 169.7, 169.3, 158.4, 144.8, 144.4, 136.4, 130.9, 129.8, 129.7, 128.0, 127.1, 113.3, 82.5, 82.1, 81.8, 81.7, 81.2, 70.97, 70.96, 70.94, 70.92, 70.75, 70.65, 70.61, 70.60, 70.42, 70.40, 70.3, 70.2, 70.1, 69.7, 68.9, 68.82, 68.80, 68.4, 68.1, 67.8, 61.8, 55.3, 30.1, 30.0, 29.9, 29.7, 20.9, 20.75, 20.71, 20.69, 20.67, 20.66, 20.65, 20.6, 20.5; ESI-HRMS calcd for C₈₂H₁₀₀NaO₃₈S₅ [M + Na]⁺ 1875.4394, found 1875.4290.

2,3,4,6-Tetra-*O*-acetyl-1-thio- α -D-glucopyranosyl-*S*-(1 \rightarrow 6)-2,3,4-tri-*O*-acetyl-1-thio- α -D-glucopyranosyl-*S*-(1 \rightarrow 6)-2,3,4-tri-*O*-acetyl-1-thio- α -D-glucopyranosyl-*S*-(1 \rightarrow 6)-2,3,4-tri-*O*-acetyl-1-thio- α -D-glucopyranose (1):

To a stirred solution of pentasaccharide **17** (110 mg, 0.06 mmol) in CH₂Cl₂ (10 mL) at 0 °C was added dropwise TFA (80 μ L, 0.8%) followed by Et₃SiH (0.1 mL, 1%). The reaction was stirred at 0 °C overnight, after which time TLC indicated the disappearance of the starting material. The mixture was then concentrated in vacuo at room temperature, and azeotroped with toluene to give a residue, which was purified by flash column chromatography (petroleum ether/EtOAc, 1:1) to give the target molecule **1** (79 mg, 83%) a white foam: $[\alpha]_D^{+261.5}$ (*c* 2.6, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 5.89 (t, *J* = 5.6 Hz, 1H), 5.74 (d, *J* = 5.7 Hz, 1H), 5.68 (d, *J* = 5.7 Hz, 1H), 5.65 (d, *J* = 5.7 Hz, 1H), 5.63 (d, *J* = 5.6 Hz, 1H), 5.39-5.34 (m, 1H), 5.33-5.28 (m, 4H), 5.09-5.04 (m, 2H), 5.03-5.00 (m, *J* = 2H), 5.00-4.96 (m, 3H), 4.95-4.89 (m, 3H), 4.43-4.39 (m, 1H), 4.38-4.30 (m, 4H), 4.25 (dd, *J* = 12.4, 4.3 Hz, 1H), 4.06-4.02 (m, 1H), 2.93 (dd, *J* = 14.4, 2.7 Hz, 1H), 2.87 (dd, *J* = 14.2, 2.2 Hz, 1H), 2.84-2.80 (m, 1H), 2.78-2.73 (m, 1H), 2.60 (d, *J* = 6.7 Hz, 1H), 2.59-2.54 (m, 3H), 2.11 (s, 8H), 2.10 (s, 4H), 2.08 (s, 6H), 2.069 (s, 5H), 2.066 (s, 4H), 2.033 (s, 3H), 2.027 (s, 3H), 2.017 (s, 3H), 2.003 (m, 7H), 1.996 (s, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 170.6, 170.0, 169.98, 169.94, 169.90, 169.85, 169.83, 169.80, 169.76, 169.72, 169.70, 169.65, 169.64, 81.9, 81.8, 81.7, 71.0, 70.8, 70.71, 70.69, 70.66, 70.62, 70.58, 70.55, 70.3, 70.2, 70.14, 70.11, 70.05, 69.8, 68.9, 68.8, 68.70, 68.65, 68.3, 67.8, 61.8, 30.0, 29.9, 29.84, 29.79, 20.8, 20.70, 20.68, 20.65, 20.64, 20.60; ESI-HRMS calcd for C₆₂H₈₄NaO₃₇S₅ [M + Na]⁺ 1603.3193, found 1603.3190.

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