Note

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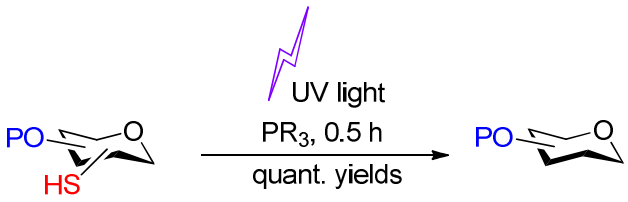
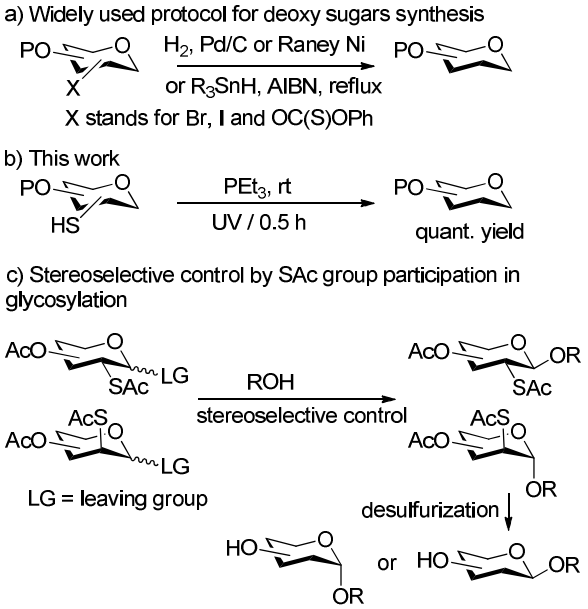
ABSTRACT



This study was performed to develop a highly efficient method whereby desulfurization could be completed in 0.5 hours under ultraviolet light, at room temperature, and in the presence of trialkylphosphine. Using this method, deoxy glycosides could be produced from sulfur-containing glycosides in almost quantitative yields. The much higher reactivity of desulfurization with triethylphosphine versus triethylphosphite was also discussed.

Deoxy glycosides are frequently the main constituents of glycosidic chains in many biologically active natural products, including antibiotics and cardiac glycosides, in which they are thought to play significant roles in bioactivity.[1-4] Consequently, the synthesis of deoxy sugars and further synthesis of related natural products, particularly 2-deoxy glycosides and their derivatives, has been identified as an important and challenging area of carbohydrate chemistry.[5-15] Several deoxy sugar production methods have been reported, including the reduction of glycals,[16] glyco-epoxides,[17] and glycosides with halides[18-22] and thiocarbonyl group,[23-28] all of which have their respective advantages and shortcomings (Scheme 1a). Hydrogenolytic desulfurization, catalyzed by either Raney nickel or Pd/Al_2O_3, was first used to synthesize unprotected peptide segments via native chemical ligation.[29-31] Later, a desulfurization method involving tris-(2-carboxyethyl) phosphine (TCEP) and a radical initiator was developed to overcome the shortcomings of the Raney nickel or palladium method.[32,33]

We recently noticed a report in which Raney nickel-catalyzed desulfurization was used to produce 2-deoxy β-disaccharides,[34,35] wherein C-2 thioacetate group participation controlled β-stereoselectivity. However, desulfurization was otherwise rarely reported regarding deoxy glycoside synthesis, possibly because of a lack of efficient means to obtain sulfur-containing glycosides. In this study, we developed a UV light-triggered desulfurization method (Scheme 1b) whereby sulfur-containing glycosides could be completely desulfurized within 0.5 h at room temperature and in the presence of trialkylphosphines (PEt_3). We then used this method to synthesize almost quantitative yields of various deoxy glycosides.

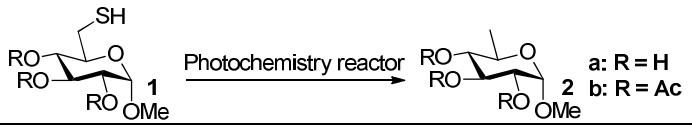


Scheme 1. Methods for deoxy glycoside synthesis

We have been making an efforts to develop methods for sulfur-containing glycoside synthesis over the years,[36-39] which inspired us to explore the efficient method of deoxy glycoside synthesis via desulfurization of sulfur-containing glycosides. More importantly, because C-2 thioacetate group participation can effectively control the stereochemistry of disaccharide formation,[34] it should be simple to construct 2-deoxy disaccharides with excellent α/β-selectivity via a glycosylation donor with a C-2 thioacetate group, followed by efficient desulfurization (Scheme 1c). In the 1950s, Hoffmann et al. identified a desulfurization reaction promoted by trialkylphosphite derivatives under thermal or photochemical conditions,[40] and Walling and Rabinowitz proposed a radical reaction mechanism shortly thereafter.[41-43] Based on those findings, we hypothesized that deoxy glycosides could be obtained by

treating sulfur-containing glycosides with $P(OEt)_3$ under UV light. We initially tested methyl 6-thio-α-D-glucoside **1a** in our proposed desulfurization reaction to explore optimized conditions (Table 1). The reactions were performed in a commercial photochemistry reactor with a 500-watt mercury lamp and cooling circuit (all glassware are pyrex). However, although complete desulfurization with $P(OEt)_3$ was reported under irradiation from a 100-watt S-4 bulb within 6.25 h,[40] or from a 300-watt visible light bulb within 36 h,[44] our experiments with $P(OEt)_3$ were unsuccessful (Entries 1 -3 in Table 1). Surprisingly, compound **1a** was successfully desulfurized under UV light in the presence of PEt_3 instead (Entries 4 - 8). Using the solvent DMF, which yielded the best results, we obtained a quantitative desulfurization yield of compound **1a** in the presence of 1.6 equiv. of PEt_3 (Entry 8). Although methanol could also be used as the solvent, 3.0 equiv. of PEt_3 were required to obtain a quantitative yield of compound **2a** (Entry 9). Other trialkylphosphines, including tributylphosphine and TCEP, also led to good yields (Entries 10 and 11). However, triphenylphosphine and tris(diethyla-mino)phosphine yielded no or little desulfurization (Entries 12 and 13). These reactions did not occur under visible light (Entry 14), and the desulfurization yield decreased by 35% (30-min reaction) when the power of the mercury lamp decreased by 200-watt (Entry 15). We also tested methyl 2,3,4-tri-OAc-6-thio-α-D-glucoside **1b** under a 200-watt UV light (Entry 16) and achieved a result identical to that obtained with **1a**, indicating that groups in other positions had no effect on desulfurization. A complex mixture was obtained when the reaction was performed with a radical initiator (AIBN) likely due to more side-reactions aroused by higher reaction temperature (50-70 ^{o}C) (Entry 17). Regarding solvents, our previous experiments indicated that in this reaction DMF was superior to methanol, likely due to a higher oxygen level in methanol. For confirmation, we performed desulfurization reactions both in normal and degassed methanol (Entries 18 and 19). As expected, the desulfurization yield with degassed methanol increased quantitatively from the 55% yield with normal methanol. Ultimately, we selected 1.6 equiv. of PEt_3 per thiol group, a 30-min reaction time, and DMF as the optimized conditions.

Table 1 Comparison of results by variation of reaction conditions[a]



Entry	Reagent (equiv.)	Solvent	Time (min.)	Yield %
1	$P(OEt)_3$ (1.2)	MeOH	30 - 120	-[g]
2	$P(OEt)_3$ (1.2)	Acetone	60	-[g]
3	$P(OEt)_3$ (1.2)	DMF	60	-[g]
4	PEt_3 (1.2)	MeOH	30	37
5	PEt_3 (1.2)	Acetone	30	36
6	PEt_3 (1.2)	DMF	30	81
7	PEt_3 (1.4)	DMF	30	92
8	PEt_3 (1.6)	DMF	30	Quant.
9	PEt_3 (3.0)	MeOH	30	Quant.
10	PBu_3 (1.6)	DMF	30	Quant.
11	TCEP (1.6)	DMF	30	90
12	PPh3 (1.6)	DMF	30	0
13	$P(NEt_2)_3$ (1.6)	DMF	30	25
14[b]	$P(Et)_3$ (1.6)	DMF	30	-[g]
15[c]	$P(Et)_3$ (1.6)	DMF	30	35
16[c,d]	$P(Et)_3$ (1.6)	DMF	30	35
17[e]	$P(Et)_3$ (1.6)	DMF	30	-[h]
18	$P(Et)_3$ (1.8)	MeOH	20	55
19[f]	P(Et)3 (1.8)	MeOH	20	Quant.

Reaction conditions: [a] Substrate **1a** (50 mg, 0.24 mmol), solvent (1 mL), 500-watt mercury lamp, r.t. [b] Visible light. [c] 200-watt mercury lamp. [d] Substrate **1b** (80 mg, 0.24 mmol). [e] AIBN (0.3 equiv), 50 – 70 ^{o}C. [f] Degassed by vacuum and then filled with N_2. [g] No reaction. [h] Complex mixture.

We next performed experiments under optimized conditions (Figure 1) to desulfurize methyl 6-thio glycopyranosides **3**, **5**, **7** and **9**; methyl 2-thio glycopyranosides **11** and **13**; methyl 4-thio glycopyranosides **15**, **17**, **19** and **20**; 3-thio glycopyranoside **21**; 2,4-dithio glycopyranosides **23** and **25**; and 1-thio glycopyranosides **27** and **29**. We achieved excellent isolation yields (> 90%) for desulfurized compounds **3**, **5**, **7**, **9**, **11**, **13**, **15**, **17**, **19**, **20** and **21** (TLC indicating full conversion) and relative low yields (55 – 58%) for the dithio glycosides **23** and **25** because of complicated side products. We still achieved a high isolated yield (98%) from large-scale testing of 6-thio-α-D-glucoside **1** (1 g), thus demonstrating the method's robustness. Unexpectedly, although the desulfurization of 1-thio glycopyranosides **27** lead to the high-yield synthesis (89%) of deoxy glycoside **28**, the desulfurization of 1-thio 2,3,4,6-tetra-OAc-glycosides **29** led to complex mixtures likely due to the migration of acetyl

group.[45,46] The disulfide dimer **30** (dimer **13**-**13**) was also tested under these conditions, leading to a high-yield (95%) isolation of deoxy glycoside **14** and indicating that our method could be used to desulfurize disulfide dimers. These results differed from those of an earlier report by Walling in which $P(OEt)_3$ led to sulfide production.[41-43] Our experiments have shown that $P(OEt)_3$ could not lead to UV excited desulfurization. In light of Walling's report, the reaction between thiyl radicals and $P(Et)_3$ is about 6 time faster than the reaction with $P(OEt)_3$.[43] As we used excess amounts of PEt_3 (1.6 equiv. per thiol group) in our case, it is probably that there are high concentration of thiyl radical in Walling's case whereas low concentration of thiyl radical in our case since the thiyl radical will be consumed by $P(Et)_3$ immediately once it forms. As a result, there are no sulfides found in our experiments. Furthermore, we performed deuteration experiments and demonstrated that the captured hydrogen atom by deoxy glycoside **14** came from trace water in the solvents (Figure S1 in SI). It is because that PEt_3 cleaves the disulfide according to the classical two electron process,[47] and hydrolysis of the intermediates by the water generates two equivalents of thiol. These are then desulfurized in the same manner as the other thiols in Figure 1.

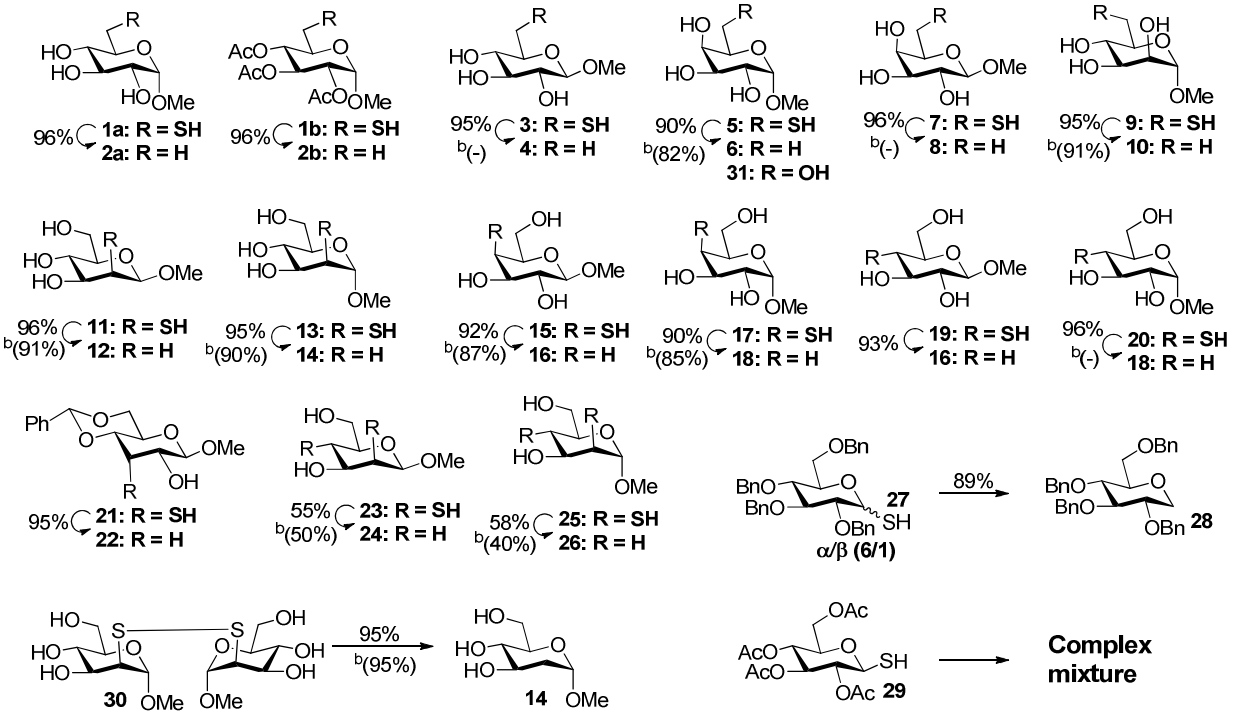
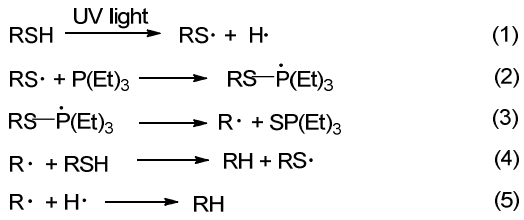


Figure 1. UV-light promoted synthesis of deoxy glycosides.[a] React condition: [a] Substrate (50 mg), $P(Et)_3$ (1.6 equiv.), DMF (1 mL), 500-watt mercury lamp, r.t., 0.5 h. [b] Substrate (50 mg), $P(Et)_3$ (3.0 equiv.), mathanol (1 mL), 500-watt mercury lamp, r.t., 0.5 h.

Though additional PEt_3 is needed for desulfurization when methanol is used as the solvent, this solvent is usually superior to DMF because it is easily removed from the reaction mixture. Therefore, we tested desulfurization using 3.0 equiv. of PEt_3 per thiol group, a 30-min reaction time, and methanol. Under these conditions, we observed somewhat lower yields of deoxy products following the desulfurization of compounds **5**, **9**, **11**, **13**, **15**, **17**, **23**, **25** and **30** (due to trace side-products). For example, a small amount of the side product methyl α-galactoside **31** was observed in the desulfurization of compound **5**. No reactions were observed in the desulfurization of compound **3**, **7**, and **20**. These unexpected results might be attributable to the oxygen present in methanol.

Similar to Walling and Rabinowitz proposed radical reaction mechanism,[41-43] the desulfurization with PEt_3 via phosphoranyl radical intermediate was shown in eqs 1-5.



To further understand differences in desulfurization reactivities with PEt_3 and with $P(OEt)_3$, density functional calculations were performed using ethylsulfanyl radical to mimic the sulfur-containing glycoside radical generated upon UV excitation (see SI for details). Here, a complex (phosphoranyl radical) forms between the two reactants, with partial electron transfer from the phosphorus moiety to the sulfur center. Reaction approaches involving two different phosphoranyl radical configurations suggested by Giles and Robert[48] were compared in the calculation, supporting a lower barrier of transition state in desulfurization with PEt_3. In addition, the lower desulfurization reactivity with $P(OEt)_3$ may be attributed to β-oxygen effect,[49-51] because there is a strong possibility that the phosphoranyl radical obtained by thiyl radical addition to $P(OEt)_3$ could undergo competing decay by fragmentation of a C-O bond to give an ethyl radical and a P=O bond. This is exactly the type of competition (C-O vs C-S fragmentation) that occurs in xanthate reduction.[52,53] This pathway is not available in the PEt_3 series.

In conclusion, we have developed a highly efficient method for desulfurizing thio-containing glycosides under UV light and in the presence of 1.6 equiv. of PEt_3 in DMF. Using this method, we could generally obtain quantitative yields of desulfurization products after 30-min reactions in a commercial photochemistry reactor and could synthesize deoxy glycosides with high efficiency. This method may provide a new approach to synthesize 2-deoxy glycosides (Scheme 1c) via the stereoselective control of C-2 thioacetate groups.

Experimental section

General: All commercially available starting materials and solvents were of reagent grade and used without further purification. Chemical reactions were monitored with thin-layer chromatography using precoated silica gel 60 (0.25 mm thickness) plates. Flash column chromatography was performed on silica gel 60 (SDS 0.040-0.063 mm). ^{1}H NMR spectra were recorded at 298K in $CDCl_3$ and D_2O, using the residual signals from $CHCl_3$ (^{1}H: = 7.26 ppm) and D_2O (^{1}H: = 4.80 ppm) as internal standard. ^{1}H peak assignments were made by first order analysis of the spectra, supported by standard ^{1}H-^{1}H correlation spectroscopy (COSY).

General deacylation of thiolacetate carbohydrate derivatives:[37] Sodium hydroxide (1.1 equiv for each of thioacetyl groups) was added in the solution of acylated thio-containing methyl D-glycoside derivatives in methanol. The reaction mixture was stirred at room temperature for 4-8 h under nitrogen protection and monitored with TLC. Then the mixture was neutralized with Amberlite IR-120 (H^+) ion exchange resin and filtered. DTT (3.0-5.0 equiv) was added to the filtration. The mixture was stirred at room temperature for 12 h. The solvent was removed under vacuum. Purification of the residue by flash column chromatography (CH_2Cl_2/MeOH 30:1-100:1) afforded the deprotected products.

General procedure of desulfurization reaction under UV light: Substrates (50 mg) were allowed to react with triethylphosphine (1.6 – 2.0 equiv. to per thiol group) in DMF/methanol (0.5 mL) under UV light (a photochemistry reactor with a 500-watt mercury lamp and a cooling circuit) at room temperature for 30 minutes. The reaction mixture was concentrated in vacuo. The residue was directly purified by

flash column chromatography (EtOAc-CH_3OH = 30:1 to 100:1) to afford the pure products.

Large scale: Thio-glucoside **1a** (1 g) were allowed to react with triethylphosphine (1.1 mL) in DMF (6 mL) under UV light (a photochemistry reactor with a 500-watt mercury lamp and a cooling circuit) at room temperature for 30 minutes. The reaction mixture was concentrated in vacuo. The residue was directly purified by flash column chromatography (EtOAc : CH_3OH = 30:1 to 100:1) to afford the pure product **2a** (0.83 g, 98% yield).

Methyl 6-thio-α-D-glucopyranoside 1a[54]: Methyl 4-*O*-acetyl-6-*S*-acetyl-α-D-glucopyranoside (colorless syrup) was synthesized via methyl 6-tosyl-α-D-glucopyranoside starting from methyl α-D-glucopyranoside in light of reference.[38] Sodium hydroxide (1.1 equiv, 75 mg) was added in the solution of methyl 4-*O*-acetyl-6-*S*-acetyl-α-D-glucopyranoside (500 mg, 1.7 mmol) in methanol, performed as described in the general deacylation of thiolacetate carbohydrate derivatives. Purification of the residue by flash column chromatography (CH_2Cl_2/MeOH= 30:1) afforded **1a** (318 mg, 89%) as colorless oil. ^{1}H NMR (D_2O, 400 MHz): δ = 4.70 (H-1, in water peak), 3.63-3.50 (m, 2H, H-5, H-3), 3.48 (dd, 1H, J = 9.7 Hz, H-2), 3.30 (t, J = 9.2 Hz, 1H, H-4), 3.34 (s, 3H, OMe), 2.90 (dd, J = 14.2 Hz, 1.2 Hz, 1H, H-6a), 2.63 (dd, J = 14.2 Hz, 7.4 Hz, 1H, H-6b) ppm; ^{13}C NMR(CD_3OD, 100 MHz): δ = 99.9, 73.6, 72.7, 72.3, 72.2, 54.2, 25.6 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5SNa$ 233.0460; found 233.0461.

Methyl 6-deoxy-α-D-glucopyranoside 2a[28]: To a solution of methyl 6-thio-α-D-glucopyranoside **1a** (100 mg, 0.48 mmol) and $P(Et)_3$ (130 uL, 0.77 mmol) in DMF (1mL), performed as described in the general procedure of desulfurization reaction under UV light, affording **2a** as colorless oil (elution with methanol / ethyl acetate = 1:30 (v/v); 83.7 mg, 98% yield). ^{1}H NMR (D_2O, 400 MHz) δ = 4.66 (H-1, in water peak), 3.76-3.50 (m, 3H, H-2, H-4, H-5), 3.40 (s, 3H, OMe), 3.14 (t, J = 8.8 Hz, 1H, H-3), 1.27 (d, J = 6.2 Hz, 3H, H-6) ppm; ^{13}C NMR (CD_3OD, 100 MHz) δ = 99.9, 76.0, 73.5, 72.4, 67.2, 54.1, 16.6 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5Na$ 201.0739; found 201.0731.

Methyl 2,3,4-Tri-*O*-acetyl-6-deoxy-α-D-glucopyranoside 2b[55]: To a solution of methyl 2,3,4-Tri-*O*-acetyl-6-thio-α-D-glucopyranoside **1b**[56] (120 mg, 0.36 mmol) and $P(Et)_3$ (100 uL, 0.77 mmol) in DMF

(1 mL), performed as described in the general procedure of desulfurization reaction under UV light, affording **2b** as white solid (elution with ethyl acetate/petroleum ether = 1:5 (v/v); 105 mg, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 5.43 (dd, *J* = 10.4 Hz, 1H, H-3), 4.93-4.84 (m, 2H, H-1, H-2), 4.80 (t, *J* = 9.6 Hz, 1H, H-4), 3.88 (dq, *J* = 9.6 Hz, 1H, H-5), 3.40 (s, 3H, OMe), 1.20 (d, *J* = 6.4 Hz, 3H, H-6) ppm; ^{13}C NMR (CD_3OD, 100 MHz) δ = 170.2, 170.1, 169.8, 96.6, 73.8, 71.2, 70.1, 64.9, 55.2, 22.4, 20.7, 20.6, 17.2 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{20}O_8Na$ 327.1056; found 327.1053.

Methyl 6-thio-β-D-glucopyranoside 3: Sodium hydroxide (1.1 equiv, 75 mg) was added in the solution of methyl 4-*O*-acetyl-6-*S*-acetyl-β-D-glucopyranoside[38] (500 mg, 1.7 mmol) in methanol, performed as described in the general deacylation of thiolacetate carbohydrate derivatives. Purification of the residue by flash column chromatography (CH_2Cl_2/MeOH = 30:1) afforded **3** (314 mg, 89%) as colorless oil. $[\alpha]_D^{25}$ = −23.1 (c = 2.0 in CH_3OH); ^{1}H NMR (D_2O, 400 MHz) *δ* = 4.25 (d, *J* = 8.0 Hz, 1H, H-1), 3.45 (s, 3H, OMe), 3.37-3.23 (m, 3H, H-3, H-4, H-5), 3.11 (dd, 1H, *J* = 8.0 Hz , 9.2 Hz, H-2), 2.86 (dd, *J* = 2.4 Hz, 14.4 Hz, 1H, H-6a), 2.58 (dd, *J* = 7.2 Hz, 14.4 Hz, 1H, H-6b) ppm; ^{13}C NMR (CD_3OD, 100 MHz) *δ* = 103.9, 76.5, 76.4, 73.8, 72.4, 55.9, 25.6 ppm. IR (film) v = 3360, 2920, 1662, 1447, 1395, 1074, 931, 614 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5SNa$ 233.0460; found 233.0455.

Methyl-6-deoxy-β-D-glucopyranoside 4[57]: To a solution of methyl 6-thio-β-D-glucopyranoside **3** (56 mg, 0.27 mmol) and $P(Et)_3$ (74 uL, 0.44 mmol) in DMF (0.6 mL), performed as described in the general procedure of desulfurization reaction under UV light, affording **4** as colorless oil (elution with methanol / ethyl acetate = 1:30 (v/v); 46 mg, 95% yield). ^{1}H NMR (D_2O, 400 MHz) δ = 4.24 (d, *J* = 7.8 Hz, 1H, H-1), 3.44 (s, 3H, OMe), 3.41-3.30 (m, 2H, H-3, H-5), 3.14 (t, *J* = 8.4 Hz, 1H, H-2), 3.14 (t, *J* = 9.2 Hz, 1H, H-4), 1.27 (d, *J* = 6.4 Hz, 3H, H-6) ppm; ^{13}C NMR (CD_3OD, 100 MHz) δ = 103.9, 76.4, 75.6, 73.9, 71.9, 55.8, 16.6 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5Na$ 201.0739; found 201.0734.

Methyl 6-thio-α-D-galactopyranoside 5: Sodium hydroxide (1.1 equiv, 58 mg) was added in the solution of methyl 2,3,4-tri-*O*-acetyl-6-*S*-acetyl-α-D-galactopyranoside[58] (500 mg, 1.32 mmol) in methanol, performed as described in the general deacylation of thiolacetate carbohydrate derivatives.

Purification of the residue by flash column chromatography (CH_2Cl_2/MeOH = 30:1) afforded **5** (236 mg, 85%) as colorless oil. $[\alpha]_D^{25}$ = +79.3 (c = 2.0 in CH_3OH); ^{1}H NMR (D_2O, 400 MHz) δ = 4.75 (H-1, in water peak), 3.98 (s, 1H, H-3), 3.80-3.74 (m, 3H, H-5, H-2, H-4), 3.37 (s, 3H, OMe), 2.68 (m, 2H, H-6a, H-6b) ppm; ^{13}C NMR (D_2O, 100 MHz) δ = 99.5, 72.2, 69.6, 69.5, 68.1, 55.2, 23.9 ppm. IR (film) v = 3412, 2925, 2854, 1662, 1418, 1362, 1044, 939, 662 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5SNa$ 233.0460; found 233.0460.

Methyl 6-deoxy-α-D-galactopyranoside 6[57]: To a solution of methyl 6-thio-α-D-galactopyranoside **5** (55 mg, 0.26 mmol) and $P(Et)_3$ (74 uL, 0.43 mmol) in DMF (0.6 mL), performed as described in the general procedure of desulfurization reaction under UV light, affording **6** as colorless oil (elution with methanol / ethyl acetate = 1:30 (v/v); 42 mg, 90% yield). ^{1}H NMR (D_2O, 400 MHz) δ = 4.65 (d, *J* = 3.2 Hz, 1H, H-1), 3.92 (dd, *J* = 6.4 Hz, 13.2 Hz, 1H, H-5), 3.73-3.64 (m, 3H, H-2, H-3, H-4), 3.28 (s, 3H, OMe), 1.11 (d, *J* = 6.4 Hz, 3H, H-6) ppm; ^{13}C NMR (D_2O, 100 MHz) δ = 99.5, 71.8, 69.6, 67.9, 66.5, 55.1, 15.3 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5Na$ 201.0739; found 201.0733.

Methyl 6-thio-β-D-galactopyranoside 7: Sodium hydroxide (1.1 equiv, 58 mg) was added in the solution of methyl 2,3,4-tri-*O*-acetyl-6-*S*-acetyl-β-D-galactopyranoside (500 mg, 1.32 mmol) in methanol, performed as described in the general deacylation of thiolacetate carbohydrate derivatives. Purification of the residue by flash column chromatography (CH_2Cl_2/MeOH = 30:1) afforded **7** (236 mg, 85%) as white solid. Although this compound has been reported in literatures,[39] its full spectroscopic data are not available. $[\alpha]_D^{25}$ = -10.5 (c = 1.5 in CH_3OH); mp = 114−115°C; ^{1}H NMR (D_2O, 400 MHz) δ = 4.20 (d, *J* = 8 Hz, 1H, H-1), 3.91 (d, *J* = 3.2 Hz, 1H, H-4), 3.52 (m, 2H, H-3, H-5), 3.46 (s, 3H, OMe), 3.37 (dd, 1H, H-2), 2.72 (dd, *J* = 7.6 Hz, 13.6 Hz, 1H, H-6a), 2.59 (dd, *J* = 6.0 Hz , 13.6 Hz, 1H, H-6b) ppm; ^{13}C NMR (D_2O, 100 MHz) δ = 103.8, 76.4, 72.8, 70.6, 68.9, 57.2, 23.7 ppm. IR (film) v = 3359, 2917, 2868, 1647, 1419, 1397, 1057, 900, 656 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5SNa$ 233.0460; found 233.0462.

Methyl 6-deoxy-β-D-galactopyranoside 8[57]: To a solution of methyl 6-thio-β-D-galactopyranoside **7** (55 mg, 0.26 mmol) and $P(Et)_3$ (74 uL, 0.43 mmol) in DMF (0.6 mL), performed as described in the

general procedure of desulfurization reaction under UV light, affording **8** as colorless oil (elution with methanol / ethyl acetate = 1:30 (v/v); 44 mg, 96% yield). ^{1}H NMR (D_2O, 400 MHz) δ = 4.18 (d, *J* = 7.6 Hz, 1H, H-1), 3.68 (q, *J* = 6.4 Hz, 1H, H-5), 3.63 (dd, *J* = 3.2 Hz, 1H, H-4), 3.53(dd, *J* = 3.2 Hz, 9.2 Hz, 1H, H-3), 3.43 (s, 3H, OMe), 3.34 (dd, *J* = 7.6 Hz, 9.2 Hz, 1H, H-2), 1.15 (d, *J* = 6.4 Hz, 3H, H-6) ppm; ^{13}C NMR (CD_3OD, 100 MHz) δ = 104.5, 73.8, 71.6, 70.9, 70.5, 55.7, 15.3 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5Na$ 201.0739; found 201.0733.

Methyl 6-deoxy-α-D-mannopyranoside 10[57]: To a solution of methyl 6-thio-α-D-mannopyranoside **9**[36] (96 mg, 0.46 mmol) and $P(Et)_3$ (130 uL, 0.74 mmol) in DMF (1 mL), performed as described in the general procedure of desulfurization reaction under UV light, affording **10** as colorless oil (elution with methanol / ethyl acetate = 1:30 (v/v); 77.8 mg, 95% yield). Analytical data found for **10** are in accordance with those reported previously. ^{1}H NMR (D_2O, 400 MHz) δ = 4.66 (d, *J* = 1.7 Hz, 1H, H-1), 3.78 (dd, *J* = 3.5, 1.7 Hz, 1H, H-2), 3.61 (dd, *J* = 9.4, 3.5 Hz, 1H, H-3), 3.57-3.48 (m, 1H, H-5), 3.38 (pt, *J* = 9.5 Hz, 1H, H-4), 3.35 (s, 3H, OMe), 1.27 (d, *J* = 6.2 Hz, 3H, H-6) ppm; ^{13}C NMR (D_2O, 100 MHz) δ = 101.4, 72.6, 71.0, 70.8, 68.2, 53.7, 16.8 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5Na$ 201.0739; found 201.0734.

Methyl 2-deoxy-β-D-mannopyranoside 12[59]: To a solution of methyl 2-thio-β-D-mannopyranoside **11**[36] (50 mg, 0.24 mmol) and $P(Et)_3$ (68 uL, 0.39 mmol) in DMF (0.5 mL), performed as described in the general procedure of desulfurization reaction under UV light, affording **12** as colorless oil (elution with methanol / ethyl acetate = 1:30 (v/v); 41 mg, 96% yield). ^{1}H NMR (D_2O, 400 MHz) δ = 4.54 (dd, *J* = 2.0 Hz, 10.0 Hz, 1H, H-1), 3.84 (dd, *J* = 2.0 Hz, 12.0 Hz, 1H, H-4), 3.67-3.59 (m, 2H, H-3, H-5), 3.43 (s, 3H, OMe), 3.28 (m, 1H, H-6a), 3.16 (m, 1H, H-6b), 2.16 (ddd, *J* = 1.6 Hz, 4.8 Hz, 12.4 Hz, 1H, H-2a), 1.67 (ddd, *J* = 9.8 Hz, 12.0 Hz,12.0 Hz, 1H, H-2b) ppm; ^{13}C NMR (D_2O, 100 MHz) δ = 100.8, 76.6, 71.7, 71.1, 61.6, 55.4, 38.9 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5Na$ 201.0739; found 201.0734.

Methyl 2-deoxy-α-D-mannopyranoside 14[60]: Procedure A: to a solution of methyl 2-thio-α-D-mannopyranoside **13**[36] (73 mg, 0.35 mmol) and $P(Et)_3$ (98 uL, 0.56 mmol) in DMF (0.7 mL), performed

as described in the general procedure of desulfurization reaction under UV light, affording **14** as white solid (elution with methanol / ethyl acetate = 1:30 (v/v); 59 mg, 95% yield). Procedure B: to a solution of (methyl 2-thio-α-mannopyranosyl)-(methyl 2-thio-α-mannopyranosyl) disulfide **31** (50 mg, 0.12 mmol) and $P(Et)_3$ (110 uL, 0.56 mmol) in DMF (0.6 mL), performed as described in the general procedure of desulfurization reaction under UV light, affording **14** as white solid (elution with methanol / ethyl acetate = 1:30 (v/v); 40 mg, 95% yield). ^{1}H NMR (D_2O, 400 MHz) δ = 4.78 (d, *J* = 3.2 Hz, 1H, H-1), 3.78-3.69 (m, 2H, H-3, H-6a), 3.64 (m, 1H, H-6b), 3.47 (m, 1H, H-5), 3.26-3.18 (m, 1H, H-4), 3.23 (s, 3H, OMe), 2.10 (dd, *J* = 5.2 Hz, 13.6 Hz, 1H, H-2a), 1.67 (ddd, *J* =4.0 Hz, 12.4 Hz,13.6 Hz, 1H, H-2b) ppm.

Methyl 4-deoxy-β-D-xylo-hexopyranoside 16[61]: To a solution of methyl 4-thio-β-D-galactopyranoside **15**[39] or methyl 4-thio-β-D-glucopyranoside **19** (55 mg, 0.26 mmol) and $P(Et)_3$ (74 uL, 0.43 mmol) in DMF (0.6 mL), performed as described in the general procedure of desulfurization reaction under UV light, affording 1**6** as colorless oil (elution with methanol / ethyl acetate = 1:30 (v/v); 44 mg, 96% yield). ^{1}H NMR (D_2O, 400 MHz) δ = 4.18 (d, *J* = 7.6 Hz, 1H, H-1), 3.66-3.47 (m, 4H, H-3, H-6a, H-6b, H-5), 3.44 (s, 3H, OMe), 3.04 (t, *J* = 8.8 Hz, 1H, H-2), 1.86 (dd, *J* = 5.2 Hz, 12.8 Hz, 1H, H-4a), 1.28 (q, *J* = 12.8 Hz, 1H, H-4b) ppm; ^{13}C NMR (D_2O, 100 MHz) δ = 103.6, 74.9, 72.6, 70.4, 63.6, 57.1, 34.2 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5Na$ 201.0739; found 201.0735.

Methyl 4-deoxy-α-D-xylo-hexopyranoside 18[62]: To a solution of methyl 4-thio-α-D-galactopyranoside **17**[65] or methyl 4-thio-α-D-glucopyranoside **20**[63] (55 mg, 0.26 mmol) and $P(Et)_3$ (74 uL, 0.43 mmol) in DMF (0.6 mL), performed as described in the general procedure of desulfurization reaction under UV light, affording 1**8** as colorless oil (elution with methanol / ethyl acetate = 1:30 (v/v); 42 mg, 90% yield). ^{1}H NMR (D_2O, 400 MHz) δ = 4.72 (d, *J* = 4.0 Hz, 1H, H-1), 3.80 (m, 2H, H-2, H-3, H-5), 3.55 (dd, *J* = 3.2 Hz, 12.0 Hz, 1H, H-6a), 3.46 (dd, *J* = 6.4 Hz, 12.0 Hz, 1H, H-6b), 3.38 (dd, *J* = 3.6 Hz, 9.6 Hz, 1H, H-2), 3.28 (s, 3H, OMe), 1.86 (ddd, *J* = 2.0 Hz, 5.2 Hz, 12.0 Hz , 1H, H-4a), 1.31 (q, *J* = 12.0 Hz, 1H, H-4b) ppm; ^{13}C NMR (D_2O, 100 MHz) δ = 100.5, 74.1, 68.5, 67.5, 64.3, 54.3, 35.0 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5Na$ 201.0739; found 201.0734.

Methyl 4-thio-β-D-glucopyranoside 19: The deacylation of methyl 2,3,6-tri-*O*-benzoyl-4-*S*-acetyl-β-D-glucopyranoside[8] afforded **19** (CH_2Cl_2/MeOH = 30:1, 480 mg, 81%) as colorless oil. $[\alpha]_D^{25}$ = -81.2 (c = 0.2 in CH_3OH); ^{1}H NMR (D_2O, 400 MHz) δ = 4.28 (d, *J* = 7.6 Hz, 1H, H-1), 3.93 (dd, *J* = 2 Hz,12.4 Hz, 1H, H-6), 3.77 (dd, *J* = 5.2 Hz , 12.4 Hz, 1H, H-6), 3.46 (s, 3H, OMe), 3.44 (m, 1H, H-5), 3.31 (t, *J* = 9.6 Hz, 1H, H-3), 3.14 (t, *J* = 8 Hz, 1H, H-2), 2.59 (t, *J* = 10.8 Hz, 1H, H-4) ppm; ^{13}C NMR(CD_3OD, 100 MHz) δ = 103.9, 78.0, 77.6, 74.7, 61.8, 55.8, 41.9 ppm. IR (film) v = 3360, 2921, 2851, 1633, 1410, 1207, 1063, 891, 614 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5SNa$ 233.0460; found 233.0459.

Methyl 4-thio-α-D-glucopyranoside 20[63]: To a solution of methyl α-D-galactopyranoside (1.0 g, 5.15 mmol) in dry pyridine (7 mL), benzoyl chloride (1.97 mL, 3.3 equiv.) in DCM (15 mL) was added dropwise, and the mixture was stirred at -40 ^{o}C for 4h. Purification of the residue by flash column chromatography (hexane/ethyl acetate, 3:1) afforded methyl 2,3,4-tri-*O*-benzoyl-α-D-galactopyranoside as white solid (1.95 g, 75%). To a solution of methyl 2,3,4-tri-*O*-benzoyl-α-D-galactopyranoside (1.95 g, 3.85 mmol) in CH_2Cl_2 was added pyridine (760 mg) at –30 °C. Trifluoromethanesulfonic anhydride (2.73 g) in CH_2Cl_2 (2 mL) was added dropwise, and the mixture was stirred while allowing to warm from –30 °C to 10 °C over 2 h. The resulting mixture was subsequently diluted with CH_2Cl_2 and washed with 1M HCl, aqueous $NaHCO_3$, water, and brine. The organic phase was dried with Mg_2SO_4 and concentrated in vacuo at low temperature. The residue was solved in dry DMF (5.0 mL) which was used directly in the next step. KSAc (1.5 equiv.) was added to the solution. After stirring at room temperature for 24 h under nitrogen atmosphere, the mixture was diluted by ethyl acetate, and washed with brine. The organic phase was dried with $MgSO_4$ and concentrated in vacuum. Purification of the residue by flash column chromatography (ethyl acetate/petrol, 1:4-1:7) afforded methyl 2,3,6-tri-*O*-benzoyl-4-*S*-acetyl-α-D-glucopyranoside[63] (1.59 g, 73%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17-7.90 (m, 6H, Ph), 7.65-7.33 (m, 9H, Ph), 5.94 (dd, *J* = 11.1 Hz, 9.6 Hz, 1H, H-3), 5.30-5.20 (m, 2H, H-1, H-2), 4.65 (dd, *J* = 2.1 Hz, 12.1 Hz, 1H, H-6a), 4.56 (dd, *J* = 5.1 Hz, 12.1 Hz, 1H, H-6b), 3.95 (ddd, *J* = 2.1 Hz, 5.1 Hz, 11.1 Hz, 1H, H-5), 4.18 (t, *J* = 11.1 Hz, 1H, H-4), 3.43 (s, 3H, OMe), 2.21 (s, 3H, SAc)

ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ =192.5, 166.3, 165.8, 165.7, 133.3, 133.2, 133.1, 129.9, 129.8, 129.7, 129.2, 129.1, 128.4, 128.4, 128.3, 97.2, 77.2, 73.1, 69.3, 68.6, 63.8 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{28}O_9SNa$ 587.1352; found 587.1335. The deacylation of methyl 2,3,6-tri-*O*-benzoyl-4-*S*-acetyl-α-D-glucopyranoside afforded methyl 4-thio-α-D-glucopyranside **20** (CH_2Cl_2/MeOH = 30:1, 480 mg, 81%) as colorless oil. ^{1}H NMR (D_2O, 400 MHz) δ = 4.76 (d, J = 2.8 Hz, 1H, H-1), 3.83 (d, J = 3.6 Hz, 2H, H-6a,H-6b), 3.62 (ddd, J = 10.4, 3.6 Hz,1H, H-5), 3.46 (m, 2H, H-2, H-3), 3.31(s, 3H, OMe), 2.61 (t, J = 10.4 Hz, 1H, H-4) ppm; ^{13}C NMR(CD_3OD, 100 MHz) δ = 100.1, 74.2, 73.7, 73.1, 61.8, 54.2, 42.1 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_5SNa$ 233.0460; found 233.0457.

Methyl 3-thio-4,6-*O-benzylidene*-β-D-allopyranoside 21: The deacylation of methyl 3-*S*-acetyl-4,6-*O-benzylidene*-β-D-allopyranoside[38] afforded **21** (552 mg, 87%) as colorless oil. $[\alpha]_D^{25}$ = -128.5 (c = 0.15 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54-7.33 (m, 5H, Ph), 5.58 (s, 1H, CH), 4.73 (d, J = 7.6 Hz, 1H, H-1), 4.35 (dd, J = 10.4, 5.2 Hz, 1H, H-3), 4.17 (m, 1H, H-4), 4.11 (m, 1H, H-6a), 3.83 (dd, 1H, H-5), 3.80-3.70 (m, 2H, H-6, H-2), 3.57 (s, 3H, OMe), 2.61 (s, 1H, OH), 2.03 (s, 1H, SH) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 137.0, 129.3, 128.4, 126.3, 101.7, 101.5, 77.8, 70.4, 68.9, 63.9, 57.4, 43.2 ppm. IR (film) v = 3361, 2924, 2853, 1660, 1463, 1269, 1090, 851, 714 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H1_8O_5SNa$ 321.0733; found 321.0739.

Methyl 3-deoxy-4,6-*O-benzylidene*-β-D-allopyranoside 22: To a solution of methyl 3-thio-4,6-*O*-benzylidene-β-D-allopyranoside **21** (70 mg, 0.24 mmol) and $P(Et)_3$ (65 uL, 0.38 mmol) in DMF (0.6 mL), performed as described in the general procedure of desulfurization reaction under UV light, affording **22** as colorless oil (elution with methanol / ethyl acetate = 1:30 (v/v); 42 mg, 90% yield). $[\alpha]_D^{25}$ = -54.7 (c = 0.15 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54-7.33 (m, 5H, Ph), 5.53 (s, 1H, CH), 4.34 (dd, J = 4.8, 10.4 Hz, 1H, H-5), 4.25 (d, J = 7.6 Hz, 1H, H-1), 3.77 (t, J = 10.0 Hz, 1H, H-6a), 3.63-3.56 (m, 2H, H-2, H-4), 3.58 (s, 3H, OMe), 3.46 (m, 1H, H-6b), 2.45 (dt, J = 4.8, 12.0 Hz, 1H, H-3a), 1.75 (q, J = 11.6, 1H, H-3b) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 137.3, 129.1, 128.4, 126.2, 106.4, 101.8, 76.2, 70.6, 69.2, 69.1, 57.3, 35.0 ppm. IR (film) v = 3371, 2925, 2852, 1612, 1432, 1216,

1081, 908, 696 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{18}O_5Na$ 289.1052; found 289.1039.

Methyl 2,4-di-deoxy-β-D-*threo*-Hexopyranoside 24: To a solution of methyl 2,4-di-thio-β-D-mannopyranoside **23**[36] (102 mg, 0.46 mmol) and $P(Et)_3$ (252 uL, 1.48 mmol) in DMF(1 mL), performed as described in the general procedure of desulfurization reaction under UV light, affording **24** as colorless oil (elution with methanol / ethyl acetate = 1:50 (v/v); 41 mg, 55% yield). $[\alpha]_D^{25}$ = +22.5 (c = 2.0 in CH_3OH); ^1H NMR (400 MHz, D_2O) δ = 4.40 (dd, *J* = 2.0, 9.2 Hz, 1H, H-1), 3.84 (m, 1H, H-3), 3.61-3.44 (m, 3H, H-5, H-6a, H-6b), 3.40 (s, 3H, OMe), 2.08 (ddd, *J* = 12.0 Hz, 1H, H-2a), 1.78 (d, *J* = 12.4 Hz, 1H, H-4a), 1.19-0.96 (m, 2H, H-2b, H-4b) ppm; ^{13}C NMR (100 MHz, CD_3OD) δ = 101.3, 72.9, 65.9, 64.5, 55.3, 40.4, 36.2 ppm. IR (film) v = 3388, 2923, 1645, 1460, 1383, 1175, 1029, 669 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_4Na$ 185.0790; found 185.0786.

Methyl 2,4-di-deoxy-α-D-*threo*-Hexopyranoside 26[64]: To a solution of methyl 2,4-di-thio-α-D-mannopyranoside **25**[36] (110 mg, 0.49 mmol) and $P(Et)_3$ (265 uL, 1.56 mmol) in DMF (1 mL), performed as described in the general procedure of desulfurization reaction under UV light, affording **26** as colorless oil (elution with methanol / ethyl acetate = 1:50 (v/v); 46 mg, 58% yield). $[\alpha]_D^{25}$ = +166.8 (c = 1.2 in CH_3OH); ^1H NMR (400 MHz, D_2O) δ = 4.89 (d, *J* = 3.6 Hz, 1H, H-1), 3.98 (m, 1H, H-3), 3.77 (m, 1H, H-5), 3.58 (dd, *J* = 3.2 Hz, 12.0 Hz, 1H, H-6a), 3.50 (dd, *J* = 6.4 Hz, 12.0 Hz, 1H, H-6b), 3.25 (s, 3H, OMe), 1.98 (m, 1H, H-2a), 1.84 (m, 1H, H-4a), 1.45 (ddd, *J* = 3.6 Hz, 11.6 Hz, 15.2 Hz , 1H, H-2b), 1.21 (q, *J* = 11.6 Hz, 1H, H-4b) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 99.0, 68.9, 64.2, 62.9, 54.3, 37.5, 35.2 ppm. IR (film) v = 3393, 2923, 1630, 1451, 1383, 1166, 1083, 669 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_7H_{14}O_4Na$ 185.0790; found 185.0789.

1,5-anhydro-2,3,4,6-tetra-*O*-benzyl-D-glucitol 28[66]: To a solution of 2,3,4,6-tetra-*O*-benzyl-1-thio-α/β-D-glucopyranose **27** (100 mg, 0.18 mmol) and $P(Bu)_3$ (90 uL, 0.35 mmol) in DMF(0.6 mL), performed as described in the general procedure of desulfurization reaction under UV light, affording **28** as colorless oil (elution with ethyl acetate/petroleum ether = 1:8 (v/v); 83 mg, 89% yield). ^1H NMR (400 MHz, $CDCl_3$) δ = 3.23-3.27 (m, 1H, H-2), 3.42 (ddd, J = 9.5 Hz, 4.2 Hz, 2.2 Hz, 1H, H-5), 3.60 (t, J =

9.5 Hz, 1H, H-4), 3.65-3.70 (m, 3H, H-1a, H-3, H-6), 3.72 (dd, J = 10.5 Hz, 2.2 Hz, 1H, H-6), 4.08 (dd, J = 11.3 Hz, 4.7 Hz, 1H, H-1b), 4.53, 4.87 (AB, J_{AB} = 10.7 Hz, 2H, CH_2Ph), 4.55, 4.63 (AB, J_{AB} = 12.1 Hz, 2H, CH_2Ph), 4.70, 4.76 (AB, J_{AB} = 11.5 Hz, 2H, CH_2Ph), 4.89, 5.01 (AB , J_{AB} = 11.0 Hz, 2H, CH_2Ph), 7.37 – 7.11(m, 20H, Ar-H) ppm.

(Methyl 2-thio-α-mannopyranosyl)-(Methyl 2-thio-α-mannopyranosyl) disulfide 31: A solution of methyl 2-thio-α-D-mannopyranoside (207 mg, 0.99 mmol) in CH_3OH (3 mL) was stirred at room temperature with the air oxidation until TLC indicated complete consumption of the starting material, purified by silica gel chromatography (CH_3OH:EtOAc 20:1) to give **31** (200 mg, 97%) as colorless oil. $[\alpha]_D^{25}$ = -87.1 (c = 1.4 in CH_3OH); ^{1}H NMR (400 MHz, D_2O) δ = 5.12 (s, 1H, H-1), 4.13 (dd, *J* = 9.5, 5.0 Hz, 1H, H-3), 3.86 (d, *J* = 12.4 Hz, 1H, H-6a), 3.74 (dd, *J* = 12.4, 5.7 Hz, 1H, H-6b), 3.69 – 3.59 (m, 1H, H-5), 3.52 (t, *J* = 9.5 Hz, 1H, H-4), 3.49 (d, *J* = 5.0 Hz, 1H, H-2), 3.42 (s, 3H, OMe) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 100.7, 72.8, 69.3, 67.3, 60.6, 59.6, 54.9 ppm. IR (film) v = 3364, 2923, 2852, 1659, 1413, 1253, 1120, 960, 610 cm^{-1}. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{26}O_{10}S_2Na$ 441.0865; found 441.0875.

Spectroscopic data of known products were in accordance with those reported in the literature.

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Supporting Information Available: Figure S1-8, ^{1}H NMR- and ^{13}C NMR-spectra of compounds **1 - 30**, Computational Methods and cartesian coordinates, and total energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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