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# Photoinitiated thiol-ene reactions of glycals: Effect of C2-substitution on reactivity and regio- and stereoselectivity

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ABSTRACT

The photoinitiated thiol-ene reaction is a metal-free click chemistry method for the synthesis of thioglycosides and sulfur-linked glycomimetics. Here we present a comparative study on the thiol-ene reactions of C2-substituted and unsubstituted glycals with some selected thiols, such as thioacetic acid, *tert*-butyl mercaptan, and per-*O*-acetylated 1-thio-β-D-galactose and 1-thio-β-D-lactose derivatives at −80 °C in the presence of 2,2-dimethoxy-2-phenylacetophenone photoinitiator. 2-Acetoxyglycals gave the 1,2-*cis*-α-thioglycosides with complete regio- and stereoselectivity, in high yields with all thiols tested, except for *tert*-butyl mercaptan. Unsubstituted glucal and galactal gave the 1-deoxy-2-thiolated products regioselectively, and in most cases as a mixture of C2 epimers. Hydrothiolation of galactal always yielded the *galacto*-isomer in greater proportion than the *talo*-isomer. In hydrothiolation of glucal, either *manno*- or *gluco*-selectivity prevailed, depending on the thiol size and reaction temperature. Remarkably, unsubstituted glycals showed higher reactivity towards thiols than C2-substituted glycals.

## 1. Introduction

Thioglycosides and thio-linked glycomimetics are resistant to enzymatic and acidic hydrolysis, thus exhibiting high stability under physiological conditions, making them attractive structures for the development of biological probes and carbohydrate-based drug candidates [1–5].

In recent decades, free-radical thiol-ene coupling (TEC) has emerged as an efficient, atom-economic click method in many areas of synthetic chemistry, for the formation of thioether bonds [6]. Due to its mild conditions, high protecting group tolerance, and insensitivity to air and water, this method has gained widespread application in carbohydrate chemistry to prepare thiosugars, thioglycosides, thioglycoconjugates, and thio-linked glycoclusters [7–10].

The thiol–ene coupling reaction requires a thiyl radical, which adds regioselectively to an electron-rich double bond in a chain process (Scheme 1A) [11,12]. Among the many methods used to generate thiyl radicals, one of the most effective is irradiation with low-energy UVA light in the presence of DPAP (2,2-dimethoxy-2-phenylacetophenone) as a cleavable photoinitiator (Scheme 1B) [13,14]. The TEC reaction on cyclic olefins, including furanosyl and pyranosyl endo- and exoglycals, generally proceeds in a stereoselective manner, and often with opposite stereochemical outcomes compared to the common nucleophilic substitution-based thioglycosylation/thioconjugation methods [9]. However, the level of diastereoselectivity is highly dependent on the position of the double bond and the degree of ring substitution [9,15,16].

Our group systematically investigated the thiol-ene coupling of C2-substituted hexopyranosyl glycals and showed that the reaction proceeds with complete stereoselectivity, exclusively yielding the challenging 1,2-*cis*-α-linked thiodisaccharides and thioglycoconjugates [16–21]. Our study revealed that the sugar configuration of C2-substituted glycals does not affect the stereoselectivity of the thiol-ene coupling, but does affect the reactivity, e.g. *galacto*-configured

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glycals show lower reactivity at room temperature than glucose-derived glycals [16,20]. It was found that cooling promotes the thiol-ene coupling reaction by increasing the lifetime of the intermediate carbon-centered radical, thereby shifting the equilibrium of the reversible propagation step of the radical chain process towards product formation, and we have amply demonstrated that performing the photoinitiated thiol-ene coupling of enoses at −80 °C is a very efficient method for the stereoselective synthesis of thioglycosides and thioglycoconjugates [9,16–22]. However, we also showed that the efficiency of TEC is also significantly affected by the type of the thiols [14–16, 20–22], and further investigation of the reactions of thiols with low reactivity is warranted.

In contrast to C2-substituted glycals, thiol-ene coupling reactions of unsubstituted glycals have remained understudied, and limited to additions with thioacetic acid [23], and some 1-thiosugars [16,24]. These studies showed that the addition regioselectively gives the 1-deoxy-2--*S*-substituted products, but the efficiency and stereoselectivity of the reactions depend strongly on the configuration of the glycal (Scheme 1C). Igarashi and co-workers reported that although addition of thioacetic acid to D-glucal triacetate in the presence of the free radical initiator cumene hydroperoxide gave exclusively the C2–*S*-acetyl 1, 5-anhydro sugars, only moderate diastereoselectivity was observed in favor of the mannitol product [23]. Dondoni's group investigated the photoinduced coupling of tri-*O*-acetyl-D-glycals with various sugar thiols at room temperature, as a strategy for the preparation of 1-deoxy-2--*S*-disaccharides [24]. They found that a large excess of thiol (6 equiv.) was required for efficient reactions, and in the case of glucal, very modest *manno* selectivity was observed, while the hydrothiolation of galactal occurred with moderate *galacto* selectivity. Our group investigated the hydrothiolation of unsubstituted D- and L-glycals with 1-thioglucose at −80 °C. We found that at this low temperature, the thiol-ene coupling was significantly more efficient than at room temperature, with complete conversion occurring even with a small excess of thiol of 1.2 equiv, and in most cases the stereoselectivity also increased significantly in favor of the axially C2–*S*-linked products [16].

In this study, we selected some thiols with very different reactivity in thiol-ene reactions and reacted them with two C2-substituted glycals and two glycals at −80 °C to investigate the efficiency and stereochemical outcome of the reactions as a function of the double bond substitution, the configuration of the glycals and the type of thiols (Fig. 1).

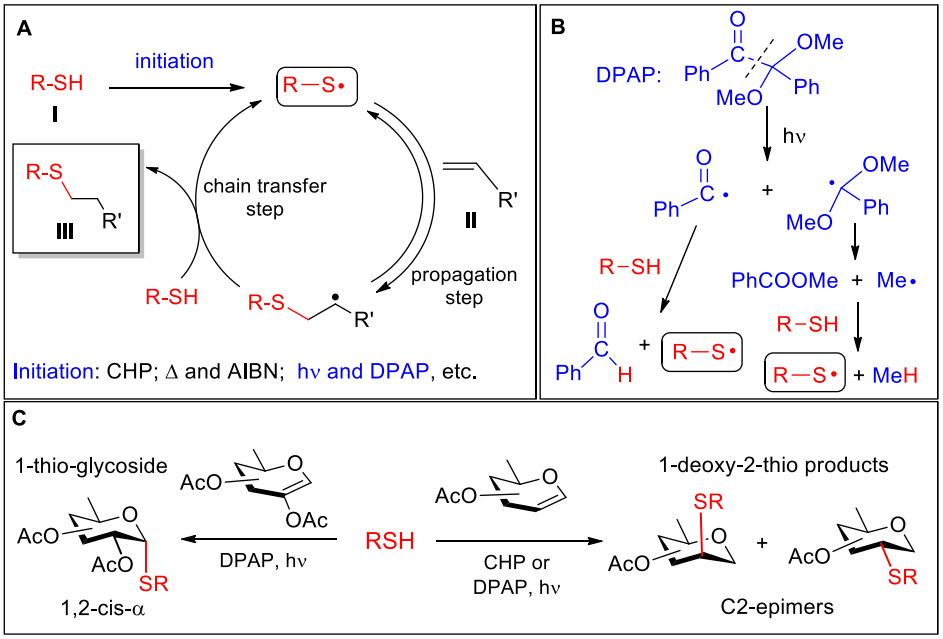
## 2. Results and discussion

Peracetylated glycals derived from D-glucose and D-galactose, including C2-substituted glycals **1** and **2** and unsubstituted glycals **3** and **4**, were involved in this study (Fig. 1). Thioacetic acid (**5**) and *tert*-butyl mercaptan (**6**), which previously showed low reactivity in the hydrothiolation reactions of 2-acetoxyglycals [13,16], were used in large excess (10 equivalents) to achieve satisfactory conversions. In contrast, ester-protected 1-thiosugars show high reactivity in radical-mediated thiol-ene couplings [15–22], therefore, 1-thiogalactose **7** and 1-thiolactose **8** were used in slightly above equimolar amounts (1.2 equiv.) in all cases. The reactions were carried out in toluene at −80 °C under UVA irradiation, in the presence of 0.1 equiv DPAP per irradiation cycle, the different conditions indicated in Tables 1 and 2.

We have recently developed an efficient procedure for the hydrothiolation of 2-acetoxyglycals with thioacetic acid, affording the α-SAc hexopyranoses in near quantitative yields [21]. Key elements of the method include the use of acetic acid as a solvent, long UV irradiation of ~2 h, and initiation with a synergistic combination of DPAP-MAP (4-methoxyacetophenone), first used by the Scanlan group [25,26].

Inspired by a recent work describing the thiol-ene reactions of 4,5-enoses [27], we now carried out the reaction of **1** and **2** in neat HSAc without solvent, which proved to be slightly more efficient than the reactions performed in acetic acid, affording the α-SAc glucose (**9**) and galactose (**10**) derivatives in 89% and 95% yields, respectively (Table 1, entries 1 and 2). The outstanding efficiency of the solvent-free reaction is likely attributable to the high concentration of the reaction mixture, as the specific kinetics of the thiol-ene reaction (very fast reversibility of the addition of the thiyl radical) [9,16,21] makes high concentrations of the reagents a key condition for efficient addition. Importantly, the unusually long UV irradiation of 180 min was also required for the efficient generation of the thiyl radical from thioacetic acid.

In our previous study of the thiol-ene reaction of 2-acetoxyglucal **1** with alkyl and aryl thiols at room temperature, we found that *tert*-butyl




**Scheme 1.** Mechanism and application of the free-radical hydrothiolation on glycals. **A**: Radical-mediated addition of thiol to terminal alkene. **B**: Generation of thiyl radicals upon UV irradiation in the presence of DPAP. **C**: Regio- and stereoselectivity of the thiol-ene coupling reaction of glycals and C2-substituted glycals. (CHP: cumene hydroperoxide, AIBN: 2,2′-azobis(isobutyronitrile), DPAP: 2,2-dimethoxy-2-phenylacetophenone.

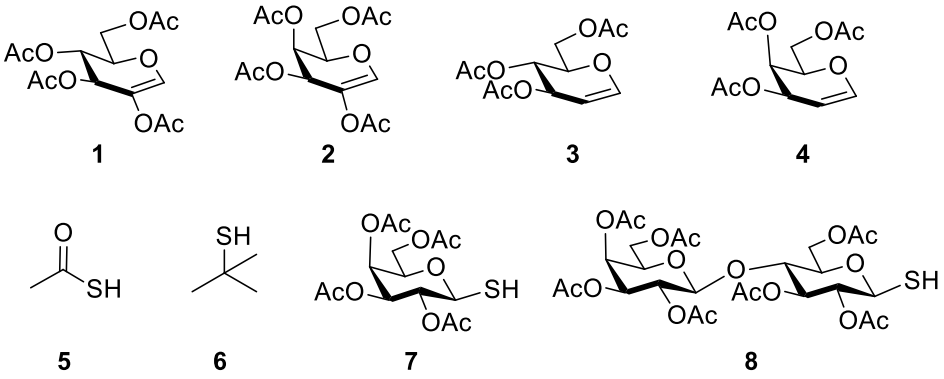



**Fig. 1.** Glycals and thiols involved in the study.

mercaptan showed much lower reactivity than *n*-alkyl thiols, and even with a large excess of thiol (15 equiv.), only modest conversion was achieved, yielding α-thioglycoside **11** with 25% yield (Table 1) [14]. In the present work, the reaction was carried out with 10 equiv. of *tert*-butyl mercaptan (**6**) at −80 °C, resulting in a ~20% increase in the yield of **11** (Table 1, entry 3). An even higher yield of 48% was achieved in the thiol-ene reaction of galactal **2** and thiol **6** at −80 °C (Table 1, entry 4). We studied whether MAP, forming a synergistic photoinitiator-photosensitizer pair with DPAP, could enhance the efficiency of hydrothiolation with *tert*-butyl mercaptan, similarly to the reactions with thioacetic acid, but unfortunately no beneficial effect of MAP was observed (Table 1, entry 5).

Hydrothiolation of 2-acetoxyglycals, **1** and **2**, with 1-thiosugars **7** and **8** at −80 °C afforded the corresponding trehalose-type 1,2-*cis*-α-thioglycosides **13**–**16** in high yields and complete stereoselectivity (Table 1, entries 6-9), in line with our previous results [16–21,28]. The slightly lower yields of additions with β-1-thiolactose **8** can be attributed to incomplete conversion of the reactants.

We then moved on to the study the thiol-ene reactions of unsubstituted glycals **3** and **4** (Table 2). The reaction of D-glucal **3** and HSAc **5** in the presence of MAP, at −80 °C, after 2 × 60 min irradiation, yielded the 2-SAc products **17** and **18** with complete conversion, in a 63:37 D-*gluco*:D-*manno* ratio, with 96% combined yield (Table 2, entry 1). While the regioselectivity of the reaction was in agreement with literature results, the stereochemical outcome was very surprising, since according to literature data, hydrothiolation of D-glucal always resulted in the D-*manno* diastereomer as the main product - although usually with very modest selectivity -, regardless of the thiol type and reaction temperature [16,23,24]. To reveal the effect of temperature on the stereoselectivity, the reaction was carried out at 0 °C. The efficiency was unchanged, but the stereoselectivity reversed in favor of the D-*manno* product (**17**:**18** = 36:64, Table 2, entry 2). This stereochemical result was very similar to that of the CHP-mediated, room temperature reaction reported by the Igarashi group (**17**:**18** = 30:70) [23] and showed that in the case of HSAc addition, the proportion of the equatoriallly S-linked D-*gluco* product gradually increases with decreasing reaction temperature.

When D-galactal **4** was reacted with HSAc at both −80 °C and 0 °C, efficient reaction and preferred formation of the *galacto* product **19** were observed in both cases, but the stereoselectivity was significantly higher at the lower temperature (Table 2, entries 3 and 4).

*Tert*-butyl mercaptan **6** reacted with glycals **3** and **4** with surprisingly high affinity and exceptionally high stereoselectivity (Table 2, entries 5 and 6). Although complete conversions were not achieved, the overall yields of the thiolated products were high (74% from galactal and 66% from glucal), and high or complete stereoselectivity was observed in favor of the stereoisomers equatorially thiolated at the C2 position (**21** and **23**). Thus, at low temperatures, the same selectivity trend was observed upon addition of *tert*-butyl mercaptan and HSAc, but the selectivity was higher for the bulkier thiol **6**.

The thiol-ene coupling reaction of glycals, **3** and **4**, with a small excess of 1-thiosugars, **7** and **8**, at −80 °C afforded the corresponding C2 epimeric pairs of 1-deoxy-2-*S*-di- and trisaccharides (**25**–**32**) in good combined yields and moderate stereoselectivity (Table 2, entries 7-10). The structures and diastereomeric ratios of the products were determined by NMR spectroscopy, and the structures of **25** and **26** were also supported by X-ray diffraction measurements (Fig. 2) [29].

In the reactions with 1-thiogalactose **7** at −80 °C, glucal gave a higher proportion of mannitol (**26**) than glucitol (**25**), while the formation of galactitol **27** from galactal was preferred over talitol **28** (entries 7 and 8), these stereoselectivities are consistent with the results of the hydrothiolation of the Dondoni group at room temperature [24]. Furthermore, the same stereoselectivity was observed during the additions with 1-thiolactose **8** (entries 9 and 10). These results clearly show that neither temperature nor the size of the thiols have a significant effect on the stereoselectivity in the thiol-ene coupling reactions of glycals and 1-thiosugars, but rather the C4 configuration of the glycals determines the stereochemical outcome of the reactions.

### *2.1. Regio- and stereoselectivity of the thiol-ene coupling reactions of glycals*

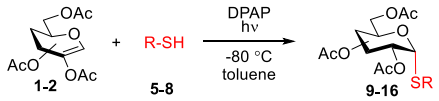
The regioselectivity of thiol-ene couplings is governed by the stability of the intermediate carbon-centered radicals. In the case of C2-substituted glycals (**1** and **2**), the more substituted C2- radical is significantly more stable than the anomeric radical, while in the case of unsubstituted glycals (**3** and **4**), the anomeric glycosyl radical is much more stable than the C2 radical due to its stabilization by the ring oxygen, which explains the complete and opposite regioselectivity of the addition reactions of the two different glycal types. (Scheme 2).

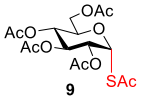
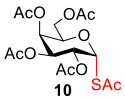
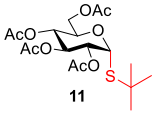
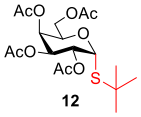
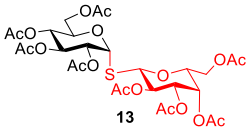
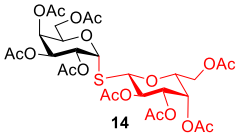
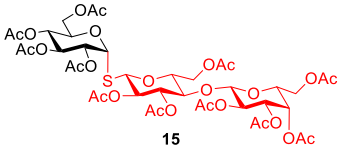
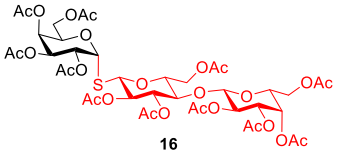
The stereoselectivity of the reactions is determined by the kinetically preferred trans diaxial addition of the thiyl and hydrogen radicals [30], as well as the stability of the carbon-centered radical intermediates of different conformations formed in the first, rapidly reversible thiyl addition step of the radical chain process [31].

In the case of 2-acetoxyglycals, the reactions proceed exclusively via the highly stable $^4C_1$ chair conformational forms of glucosyl and galactosyl C2-centered radical intermediates, which are formed by the upper-face attack of the thiyl radical on the $^4H_5$ conformational forms of the starting glycals, leading to the formation of 1,2-*cis*-α-thioglycosides (Scheme 2, top panel). All other attacks by the thiyl-radical on any conformational form of the starting glycals result in unstable carbon-centered radical intermediates of high-energy skew boat and $^1C_4$ conformations, which immediately decompose to the starting reactants, thus leading to no product formation [9,16,21].

In the case of unsubstituted glycals, two types of carbon-centered radical intermediates of similar stability can be formed by the addition of the thiyl radical both to glucal and galactal, which are stabilized

**Table 1**
Thiol-ene reactions of 2-acetoxy glycals.




| Entry | Glycal | Thiol | Reaction time | Product | Yield[a] |
|---|---|---|---|---|---|
| 1 | **1** | **5** | 180 min |  **9** | 82% in AcOH[b,c], [21]<br>89% in neat HSAc[c] |
| 2 | **2** | **5** | 180 min |  **10** | 95% in AcOH[b,c], [21]<br>95% in neat HSAc[c] |
| 3 | **1** | **6** | 2 x 120 min |  **11** | r.t., 25%[b], [14]<br>43% |
| 4<br>5 | **2**<br>**2** | **6**<br>**6** | 2 x 120 min |  **12** | 48%<br>43%[c] (MAP) |
| 6 | **1** | **7** | 3 x 20 min |  **13** | 89% |
| 7 | **2** | **7** | 3 x 20 min |  **14** | 89%[b], [28]<br>91% |
| 8 | **1** | **8** | 3 x 20 min |  **15** | 74% |
| 9 | **2** | **8** | 3 x 20 min |  **16** | 71% |

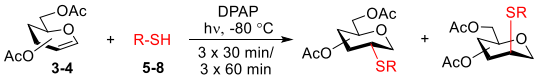
The reactions were performed in 0.5-3 mmol scale, using 10 equiv. of **5** and **6** and 1.2 equiv. of **7** and **8**.
[a] Isolated yield.
[b] Literature result.
[c] The reaction was performed in the presence of 0.3 equiv. of MAP.

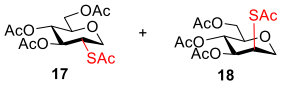
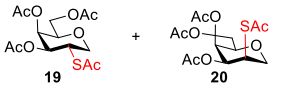
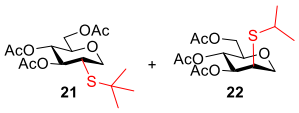
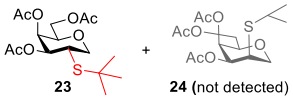
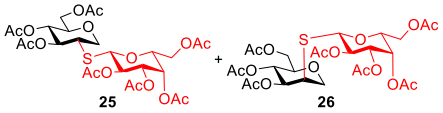
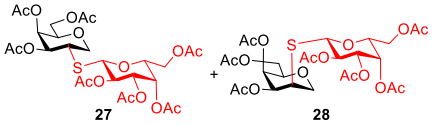
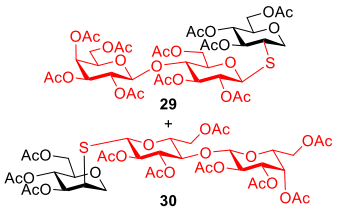
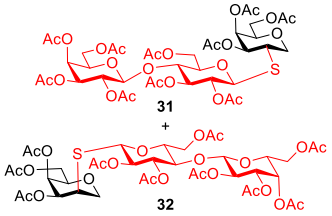
by the axial or quasi-axial C2 substituent through electronic effects (quasi-homo-anomeric effect) [32,33]. These stable intermediates are, on the one hand, the mannosyl and talosyl anomeric radicals existing in $^4C_1$ chair conformation, which are formed by the upper-face attack of the thiyl radical to the $^4H_5$ conformational form of glycals, and on the other hand, the skew-boat $^1S_5$ conformational form of glucosyl radical and the $^4H_5$ conformational form of galactosyl radical, which are formed by the upper-face attack of the thiyl radical to glycals in their $^4H_5$ conformational forms. Accordingly, *gluco* and *manno* products can be formed from glucal, and *galacto* and *talo* products can be formed from galactal (Scheme 2, bottom panel) [16].

In the hydrothiolation reactions of galactal **4**, the *galacto* diastereomer was always formed predominantly, regardless of the type of thiol and the reaction temperature. This can be explained by the fact that the talopyranosyl radical intermediate is less stable than the *galacto* intermediate due to the 1,3-diaxial repulsion between the C2 and C4 substituents in the *talo*-radical, and therefore decomposes faster, shifting the product ratio towards the *galacto* product.

In the hydrothiolation reactions of glucal **3**, the stereoselectivity was significantly influenced by the reaction temperature and also by the thiol type. This suggests that the stability of the *manno*- and *gluco*-configured anomeric radical intermediates strongly depends on the type and size of the thiol, and consequently the stereochemical outcome of the reactions is difficult to predict. Nevertheless, the results so far show

**Table 2**
Thiol-ene reactions of glycals.




| Entry | Glycal | Thiol | Products | Product ratio[a] | Yield[b] |
|---|---|---|---|---|---|
| 1 | **3** | **5** |  **17** + **18** | −80 °C, **17:18** 63:37[c] | 96% |
| 2 | | | | 0 °C, **17:18** 36:64[c] | 93% |
| | | | | r.t., **17:18** 30:70[d], [23] | 87% |
| 3 | **4** | **5** |  **19** + **20** | −80 °C, **19:20** 68:32[c] | 97% |
| 4 | | | | 0 °C, **19:20** 53:47[c] | 86% |
| 5 | **3** | **6** |  **21** + **22** | **21:22** 88:12 | 66% |
| 6 | **4** | **6** |  **23** + **24** (not detected) | **23** > 99:1 | 74% |
| 7 | **3** | **7** |  **25** + **26** | −80 °C, **25:26** 42:58 | 85% |
| | | | | rt, **25:26** 46:54[e], [24] | 100% |
| 8 | **4** | **7** |  **27** + **28** | −80 °C, **27:28** 64:36 | 86% |
| | | | | rt, **27:28** 62:38[e], [24] | 100% |
| 9 | **3** | **8** |  **29** + **30** | −80 °C, **29:30** 37:63 | 84% |
| | | | | 0 °C, **29:30** 37:63 | 81% |
| 10 | **4** | **8** |  **31** + **32** | 31:32 69:31[f] | 81% |

The reactions were performed in 0.5-1 mmol scale, using 10 equiv. of **5** and **6** and 1.2 equiv. of **7** and **8**; reactions were generally carried out at −80 °C, other temperatures are indicated. For thiol **5**, 2 × 60 min of UV irradiation were used, for thiol **6**, 3 × 60 min, and for 1-thiosugars **7** and **8**, 3 x 30 min.

[a] Ratio determined by $^1$H NMR.

[b] Isolated yield.

[c] The reaction was performed in the presence of 0.3 equiv. of MAP.

[d] Literature result; the reaction was initiated by cumene hydroperoxide at r.t. [23].

[e] Literature result, the reaction was performed using 6 equiv. of thiol [24]; Disulfide was formed from thiol **8** as a byproduct, which eluted with **32** during the first column chromatographic purification.

that the formation of mannitol products is more favored in additions with thiosugars.

## 3. Conclusion

A small comparative study on the low-temperature photoinduced radical mediated hydrothiolation of C2-substituted hexoglycals and unsubstituted hexoglycals were performed, which was the first to show that unsubstituted glycals show greater reactivity towards thiols than C2-substituted glycals in the thiol-ene reactions performed at −80 °C. This difference in reactivity was most evident for the least reactive thiol, *tert*-butyl mercaptan.

Hydrothiolation of 2-acetoxyglycals proceeded with good/excellent yields with all thiols tested, except for *tert*-butyl mercaptan, which

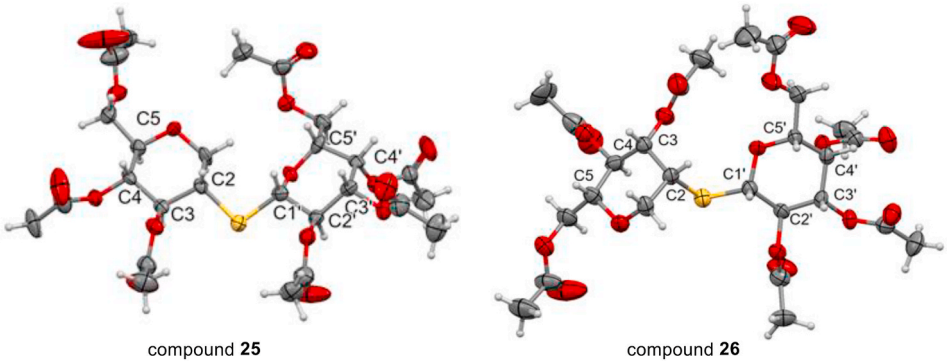
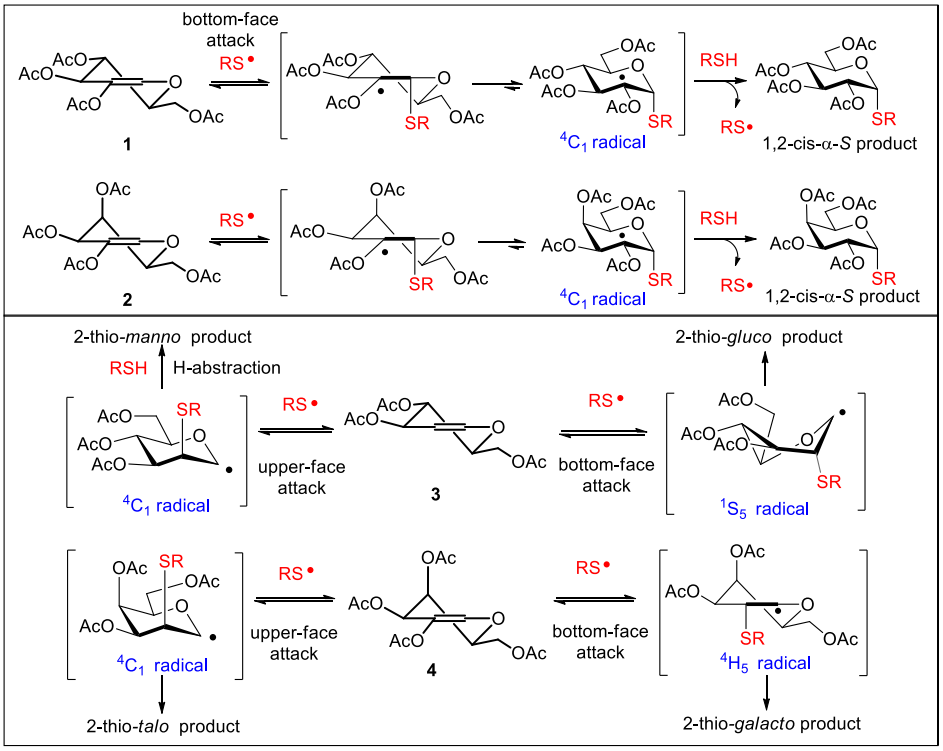



**Fig. 2.** ORTEP view of thiodisaccharide mimetics **25** and **26** ORTEP at 30% probability level [29].




**Scheme 2.** Stable glycopyranosyl radical intermediates formed upon upper-face attack by the thiyl radicals to the $^4H_5$ conformational form of C2-substituted glycals **1** and **2** (top panel) and upon upper- and bottom-face attacks by the thiyl radicals to the $^4H_5$ conformational form of glycals **3** and **4** (bottom panel). The conformational changes follow the pseudorotational itinerary of the pyranosyl ring interconversion map [34].

showed only moderate conversion. In agreement with our previous results, the reactions gave the 1,2-*cis*-α-thioglycosides with complete stereoselectivity, and cooling always promoted the reaction.

Hydrothiolation of unsubstituted glycals gave the 2-thiolated products regioselectively, and in most cases as a mixture of C2 epimers. In the case of galactal, the *galacto*-configured product was always formed in a higher proportion than the *talo*-isomer, and the *galacto*-selectivity increased with increasing thiol size and decreasing reaction temperature, and even reached 100% with the addition of *tert*-butyl mercaptan.

In the case of glucal, the stereoselectivity was highly variable, with either *manno*- or *gluco*-selectivity prevailing depending on the thiol type/size and the reaction temperature. This contrasts with previous results [16,24], which always reported *manno*-selectivity, and points out that it is worth further studying the thiol-ene coupling reactions of glycals.

## 4. Experimental

### 4.1. General information

2,3,4,6-Tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**1**) [6,35]-tetra-*O*-acetyl-1,5-anhydro-D-*lyxo*-hex-1-enitol (**2**) [6,35]-tetra-*O*-acetyl-1-thio-β-D-galactopyranose (**7**) [6,36]-tetra-*O*-acetyl-β-D-galactopyranosyl-(1 → 4)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranose (**8**) 4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-acetyl-1-thio-β-D-glucopyranose [37] were prepared according to the literature procedures. 3,4,6-Tri-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (3,4,6-tri-*O*-acetyl-D-glucal, **3**), thioacetic acid (**5**), 2,2-dimethoxy-2-phenylacetophenone (DPAP) and 4-methoxyacetophenone (MAP) were purchased from Sigma Aldrich Chemical Co, Germany; 3,4,6-tri-*O*-acetyl-1,5-anhydro-D-*lyxo*-hex-1-enitol (3,4,6-tri-*O*-acetyl-D-galactal, **4**) was purchased from Fluorochem, UK; and *tert*-butyl-mercaptane (**6**) was purchased from Fluka, Germany. Optical rotations were measured at

room temperature with a PerkinElmer 241 automatic polarimeter. Melting points were measured in open capillary tubes on a Büchi Melting Point B-540 apparatus. TLC was performed on Kieselgel 60 $F_{254}$ (Merck) with detection by UV-light (254 nm) and immersing into sulfuric acidic ammonium-molibdenate solution or 5% ethanolic sulfuric acid followed by heating. Flash column chromatography was performed on Silica gel 60 (Merck 0.040-0.063 mm). Organic solutions were dried over $Na_2SO_4$ or $MgSO_4$, and concentrated in vacuum. $^1H$ and J-modulated $^{13}C$ NMR spectra and and two-dimensional COSY and HSQC spectra spectra were recorded with Bruker Avance II 500 (500/125 MHz for $^1H/^{13}C$) and Bruker Avance Neo 700 MHz (700/175 MHz for $^1H/^{13}C$) spectrometers at 25 °C. Chemical shifts are referenced to $Me_4Si$ (0.00 ppm for $^1H$) and to the residual solvent signals ($CDCl_3$: 77.16 for $^{13}C$). In NMR assignment of thiodi- and trisaccharides, the C/H atoms of the thiol component are indicated by apostrophes. MALDI-TOF MS analyses of the compounds were carried out in the positive reflectron mode using a BIFLEX III mass spectrometer (Bruker, Germany) equipped with delayed-ion extraction. 2,5-Dihydroxybenzoic acid (DHB) was used as matrix and $F_3CCOONa$ as cationising agent in DMF. ESI-TOF HRMS spectra were recorded by a microTOF-Q type QqTOFMS mass spectrometer (Bruker) in the positive ion mode using MeOH as the solvent. The photoinitiated reactions were carried out in a borosilicate vessel by irradiation with a Hg-lamp giving maximum emission at 365 nm, without any caution to exclude air or moisture. Reactions at −80 °C were performed in a Dewar flask in an acetone-liquid nitrogen bath. Before irradiation, the entire set-up was covered with an aluminum foil tent to protect the laboratory personnel from UV light.

Single crystals of **25** and **26** could be grown by evaporation their solution. Diffraction intensity data was collected at ambient temperture for **25** and at low temperature (150 K) for **26** on a Bruker-D8 Venture diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) equipped with INCOATEC IμS 3.0 (Incoatec GmbH, Geesthacht, Germany) dual (Cu and Mo) sealed tube micro sources and a Photon II Charge-Integrating Pixel Array detector (Bruker AXS GmbH, Karlsruhe, Germany) using Cu Kα (λ = 1.541 Å) radiation. High-multiplicity data collection and integration were performed using APEX3 (version 2017.3-0, Bruker AXS Inc., 2017, Madison, WI, USA) software. Data reduction and multiscan absorption correction were performed using SAINT (version 8.38A, Bruker AXS Inc., 2017, Madison, WI, USA). The structures could be solved using direct methods and refined on $F^2$ using SHELXL program [38]. incorporated into the APEX4 suite. Refinement was performed anisotropicaly for all non-hydrogen atoms. Hydrogens were placed into geometric positions.

#### 4.1.1. 2,3,4,6-Tetra-O-acetyl-1-S-acetyl-1-thio-α-D-glucopyranose (9)

Thioacetic acid (**5**, 10.0 equiv., 30.28 mmol, 2.135 mL) was added to 2-acetoxy-D-glucal **1** (1 g, 3.027 mmol), forming a clear solution. Next, DPAP (0.1 equiv., 0.40 mmol, 78 mg) and MAP (0.3 equiv., 0.91 mmol, 137 mg) were added, the reaction mixture was cooled to −80 °C, and irradiated with UV light for 180 min. The temperature was monitored throughout the reaction time. Next, the solvent was evaporated in vacuo and the crude product was purified by flash column chromatography using $CH_2Cl_2$: acetone to give compound **9** (1.09 g, 89%) as white crystals. Characterisation data of the compound are consistent with those reported in the literature [21].

#### 4.1.2. 2,3,4,6-Tetra-O-acetyl-1-S-acetyl-1-thio-α-D-galactopyranose (10)

Thioacetic acid (**5**, 10.0 equiv., 30.28 mmol, 2.135 mL) was added to 2-acetoxy-D-galactal **2** (1 g, 3.027 mmol), forming a clear solution. Next, DPAP (0.1 equiv., 0.40 mmol, 78 mg) and MAP (0.3 equiv., 0.91 mmol, 137 mg) were added, the reaction mixture was cooled to −80 °C, and irradiated with UV light for 180 min. The temperature was monitored throughout the reaction time. Next, the solvent was evaporated in vacuo and the crude product was purified by flash column chromatography using $CH_2Cl_2$: acetone to give compound **10** (1.17 g, 95%) as white crystals. Characterisation data of the compound are consistent with those reported in the literature [21].

#### 4.1.3. tert-Butyl 2,3,4,6-tetra-O-acetyl-1-thio-α-D-glucopyranoside (11)

2-Acetoxy-3,4,6-tri-*O*-acetyl-D-glucal **1** (165 mg, 0.5 mmol), *tert*-butyl-mercaptan (**6**, 10.0 equiv, 0.562 mL, 5.0 mmol) and DPAP (0.1 equiv, 12 mg, 0.05 mmol) were dissolved in toluene (0.7 mL). The reaction mixture was cooled to −80 °C and was irradiated with UV light for 120 min. Afterwards, 0.1 equiv (12 mg) DPAP was added and the irradiation continued for 120 min at −80 °C. The crude product was concentrated under reduced pressure and was purified by flash column chromatography (hexane: acetone 85:15) to give compound **11** (90 mg, 43%) as colourless syrup. $R_f = 0.48$ (hexane: acetone 7:3), $[\alpha]_D$ +147.5 (*c* 0.28, $CHCl_3$) lit [14]. $[\alpha]_D$ +154.4. $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 5.88 (d, $J_{1,2} = 5.9$ Hz, 1H, H-1), 5.29 (t, $J_{3,4} = 9.9$ Hz, 1H, H-3), 5.05 (t, $J_{3,4} = 9.7$ Hz, 1H, H-4), 4.97 (dd, $J_{2,3} = 10.5$ Hz, $J_{1,2} = 5.9$ Hz, 1H), 4.50 (ddd, $J_{4,5} = 10.3$ Hz, $J_{5,6a} = 4.7$ Hz, $J_{5,6b} = 2.2$ Hz, 1H, H-5), 4.32 (dd, $J_{6a,6b} = 12.3$ Hz, $J_{5,6a} = 4.8$ Hz, 1H, H-6a), 4.07 (dd, $J_{6a,6b} = 12.4$ Hz, $J_{5,6b} = 2.3$ Hz, 1H), 2.09, 2.07, 2.05, 2.03 (4s, 4 × 3H, 4 x OAc, C*H*$_3$), 1.37 (1s, 9H, 3 x C*H*$_3$, *t*-Bu) ppm; $^{13}C$ NMR (126 MHz, $CDCl_3$) $\delta$ 170.8, 170.1, 170.0, 169.8 (4C, 4 x OAc, $C_q$), 80.3 (1C, C-1), 71.0, 70.7, 68.8, 67.8 (4C, skeleton carbons), 62.1 (1C, C-6), 44.6 (1C, $C_q$, *t*-Bu), 31.5 (3C, 3 x *C*H$_3$, *t*-Bu), 20.9, 20.8, 20.8, 20.8 (4C, 4 x OAc, *C*H$_3$) ppm; MALDI-TOF-HRMS *m/z* calcd for $C_{18}H_{28}NaO_9S^+$ $[M+Na]^+$ 443.1347, found 443.1347.

#### 4.1.4. tert-Butyl 2,3,4,6-tetra-O-acetyl-1-thio-α-D-galactopyranoside (12)

2-Acetoxy-3,4,6-tri-*O*-acetyl-D-galactal **2** (330 mg, 1.0 mmol), *tert*-butyl-mercaptan (**6**, 10.0 equiv, 1.125 mL, 10.0 mmol) and DPAP (0.1 equiv, 25 mg, 0.1 mmol) were dissolved in toluene (1.0 ml). The reaction mixture was cooled to −80 °C and was irradiated with UV light for 120 min. Afterwards, 0.1 equiv (25 mg) DPAP was added and the irradiation continued for 120 min at −80 °C. The crude product was concentrated under reduced pressure and was purified by flash column chromatography (hexane: acetone 85:15) to give compound **12** (201 mg, 48%) as colourless syrup. The reaction was repeated in the presence of 0.3 eq MAP as photosensitizer, yielding **12** in 43% yield. $R_f = 0.48$ (hexane: acetone 7:3), m.p. 119.6-121.8 °C; $[\alpha]_D$ +116.5 (*c* 0.31, $CHCl_3$), $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 5.94 (d, $J_{1,2} = 5.8$ Hz, 1H, H-1), 5.43 (dd, $J_{3,4} = 3.3$ Hz, $J_{4,5} = 1.3$ Hz, 1H, H-4), 5.22 (dd, $J_{2,3} = 11.1$ Hz, $J_{1,2} = 5.8$ Hz, 1H, H-2), 5.12 (dd, $J_{2,3} = 11.1$ Hz, $J_{3,4} = 3.4$ Hz, 1H, H-3), 4.65 (td, $J_{5,6} = 6.5$ Hz, $J_{4,5} = 1.4$ Hz, 1H, H-5), 4.10 (d, $J = 6.5$ Hz, 2H), 2.14, 2.07, 2.02, 1.99 (4s, 4 × 3H, 4 x OAc, C*H*$_3$), 1.35 (s, 9H, 3 x C*H*$_3$, *t*-Bu) ppm; $^{13}C$ NMR (126 MHz, $CDCl_3$) $\delta$ 170.3, 170.2, 170.1, 169.7 (4C, 4 x OAc, $C_q$), 80.8 (1C, C-1), 68.2, 68.1, 68.1, 66.6 (4C, skeleton carbons), 61.6 (1C, C-6), 44.1 (1C, $C_q$, *t*-Bu), 31.4 (3C, 3 x *C*H$_3$, *t*-Bu), 20.8, 20.6 (4C, 4 x OAc, *C*H$_3$) ppm; MALDI-TOF-HRMS *m/z* calcd for $C_{18}H_{28}NaO_9S^+$ $[M+Na]^+$ 443.1347, found 443.1340.

#### 4.1.5. 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl-(1 → 1)-2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (13)

2-Acetoxy-3,4,6-tri-*O*-acetyl-D-glucal **1** (165 mg, 0.5 mmol), 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D -galactopyranose **7** (1.2 equiv, 218 mg, 0.6 mmol) and DPAP (0.1 equiv, 12 mg, 0.05 mmol) were dissolved in toluene (1.0 mL). The reaction mixture was cooled to −80 °C and irradiated with UV light for 20 min. The addition of 0.1 equiv. of DPAP and the 20 min of irradiation was repeated two more times. The solvent was evaporated in vacuo and the crude product was purified by flash column chromatography (hexane: ethyl acetate 1:1) to give compound **13** (310 mg, 89%) as colourless foam. $R_f = 0.28$ (hexane: ethyl acetate 1:1), $[\alpha]_D$ +129.3 (*c* 0.16, $CHCl_3$), $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 5.96 (d, $J_{1,2} = 5.7$ Hz, 1H, H-1), 5.42 (d, $J_{3,4} = 2.8$ Hz, 1H, H-4′), 5.33 (t, $J_{3,4} = 9.9$ Hz, 1H, H-3), 5.26 (t, $J = 10.0$ Hz, 1H, H-2′), 5.14 (t, $J_{3,4} = 9.8$ Hz, 1H, H-4), 5.04 – 4.96 (m, 2H, H-3′, H-2), 4.56 (d, $J_{1,2} = 10.0$ Hz, 1H, H-1′), 4.43 (dt, $J_{4,5} = 10.2$ Hz, $J_{5,6a} = 2.6$ Hz, 1H, H-5), 4.38 (dd, $J_{6a,6b} = 12.5$ Hz, $J_{5,6a} = 2.9$ Hz, 1H, H-6a), 4.16 (dd, $J_{6a,6b} = 11.4$ Hz, $J_{5,6a} = 5.9$ Hz, 1H, H-6′), 4.10 (dd, $J_{6a,6b} = 12.3$ Hz, $J_{5,6b} = 2.4$ Hz, 1H, H-6b), 4.03 (dd, $J_{6a,6b} = 11.4$ Hz, $J_{5,6b} = 6.6$ Hz, 1H, H-6b′), 3.96 (t, $J = 5.7$ Hz, 1H, H-5′), 2.17,

2.10, 2.05, 2.04, 2.04, 2.02, 2.02, 1.98 (8s, 8 × 3H, 8 x OAc, C*H*$_3$) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 170.6, 170.4, 170.2, 170.0, 169.8, 169.7, 169.5, 169.2 (8C, 8 x OAc, $C_q$), 83.4 (1C, C-1′), 82.3 (1C, C-1), 74.9 (1C, C-5′), 71.8 (1C, C-3′), 70.7 (1C, C-2), 70.3 (1C, C-3), 68.5 (1C, C-5), 68.1 (1C, C-2′), 67.9 (1C, C-4), 67.3 (1C, C-4′), 61.8 (1C, C-6'), 61.2 (1C, C-6), 20.7, 20.6, 20.6, 20.6 (8C, 8 x OAc, *C*H$_3$) ppm; MALDI-TOF-HRMS *m/z* calcd for $C_{28}H_{38}NaO_{18}S^+$ $[M+Na]^+$ 717.1671, found 717.1665.

#### *4.1.6. 2,3,4,6-Tetra-O-acetyl-α-D-galactopyranosyl-(1 → 1)-2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (**14**)*

2-Acetoxy-3,4,6-tri-*O*-acetyl-D-galactal **2** (165 mg, 0.5 mmol) was reacted with thiol **7** (1.2 equiv, 218 mg, 0.6 mmol) as described for the synthesis of **13**, to give compound **14** (316 mg, 91%) as a white foam. $R_f$ = 0.3 (hexane: ethyl acetate 1:1), $[\alpha]_D$ +129.8, lit [28]. $[\alpha]_D$ +137.9 NMR data of the compound are consistent with those reported in the literature [28].

#### *4.1.7. 2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl-(1 → 4)-2,3,6-tri-O-acetyl-1-thio-β-D-glucopyranosyl-(1 → 1)-2,3,4,6-tetra-O-acetyl-1-thio-α-D-glucopyranoside (**15**)*

2-Acetoxy-3,4,6-tri-*O*-acetyl-D-glucal **1** (165 mg, 0.5 mmol), β-1-thiolactose-peracetate **8** (1.2 equiv, 390 mg, 0.6 mmol) and DPAP (0.1 equiv, 12 mg, 0.05 mmol) were dissolved in toluene (1.0 mL). The reaction mixture was cooled to −80 °C and irradiated with UV light for 20 min. The addition of 0.1 equiv. of DPAP and the 20 min of irradiation was repeated two more times. The solvent was evaporated in vacuo and the crude product was purified by flash column chromatography (hexane: ethyl acetate 1:1) to give compound **15** (365 mg, 74%) as colourless foam. $R_f$ = 0.49 (hexane: ethyl acetate 4:6); $[\alpha]_D$ +121.7 (*c* 0.29, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.92 (t, *J* = 5.3 Hz, 1H, H-1), 5.38 – 5.29 (m, 1H), 5.26 (td, *J* = 9.9 Hz, *J* = 5.5 Hz, 1H), 5.20 – 5.02 (m, 3H), 5.01 – 4.91 (m, 3H), 4.62 – 4.50 (m, 3H, H-1′, H-1″, H-6), 4.41 (ddd, *J* = 12.6 Hz, *J* = 5.1 Hz, *J* = 2.9 Hz, 1H, H-6), 4.32 (ddd, *J* = 10.2 Hz, *J* = 5.0 Hz, *J* = 2.6 Hz, 1H), 4.17 – 4.04 (m, 3H, 3 x H-6), 4.03 – 3.97 (m, 1H, H-6), 3.95 (t, *J* = 6.2 Hz, 1H, H-5), 3.80 (td, *J* = 9.5 Hz, *J* = 4.1 Hz, 1H, H-5), 3.71 – 3.64 (m, 1H, H-5), 2.21 – 1.87 (m, 11 × 3H 11 x OAc, C*H*$_3$) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 170.2, 170.0, 170.0, 169.8, 169.7, 169.5, 169.4, 169.3, 169.2, 169.0, 168.7 (11C, 11 x OAc, $C_q$), 100.7 (1C, C-1″), 81.8 (1C, C-1'), 81.4 (1C, C-1), 76.8, 75.4, 73.4, 71.1, 70.7, 70.4, 70.2, 70.0, 68.9, 68.4, 67.6, 66.5 (12C, skeleton carbons), 61.7, 61.0, 60.7 (3C, 3 x C-6), 20.7, 20.5, 20.4, 20.3, 13.9 (11C, 11 x OAc, *C*H$_3$) ppm; MALDI-TOF-HRMS *m/z* calcd for $C_{40}H_{54}NaO_{26}S^+$ $[M+Na]^+$ 1005.2517, found 1005.2544.

#### *4.1.8. 2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl-(1 → 4)-2,3,6-tri-O-acetyl-1-thio-β-D-glucopyranosyl-(1 → 1)-2,3,4,6-tetra-O-acetyl-1-thio-α-D-galactopyranoside (**16**)*

2-Acetoxy-3,4,6-tri-*O*-acetyl-D-galactal **2** (165 mg, 0.5 mmol) and β-1-thiolactose-peracetate **8** (1.2 equiv, 390 mg, 0.6 mmol) and DPAP (0.1 equiv, 12 mg, 0.05 mmol) were dissolved in toluene (1.0 mL). The reaction mixture was cooled to −80 °C and irradiated with UV light for 20 min. The addition of 0.1 equiv. of DPAP and the 20 min of irradiation was repeated two more times. The solvent was evaporated in vacuo and the crude product was purified by flash column chromatography (hexane: ethyl acetate 1:1) to give compound **16** (349 mg, 71%) as colourless foam. $R_f$ = 0.43 (hexane: ethyl acetate 4:6); $[\alpha]_D$ +87.3 (*c* 0.11, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.87 (d, *J* = 5.5 Hz, 1H, H-1), 5.38 (s, 1H), 5.27 (t, *J* = 3.5 Hz, 1H), 5.16 – 4.98 (m, 4H), 4.94 – 4.86 (m, 2H), 4.53 – 4.41 (m, 4H), 4.10 – 4.03 (m, 4H, 4 x H-6), 4.03 – 3.92 (m, 1H), 3.84 (t, *J* = 6.7 Hz, 1H, H-5), 3.75 (td, *J* = 9.5 Hz, *J* = 2.5 Hz, 1H, H-5), 3.62 – 3.54 (m, 1H, H-5), 2.11 – 1.86 (m, 11 × 3H, 11 x OAc, C*H*$_3$) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 170.2, 170.1, 170.1, 170.0, 169.9, 169.9, 169.8, 169.6, 169.6, 169.3, 168.9 (11C, 11 x OAc, $C_q$), 100.9 (1C, C-1″), 82.1 (1C, C-1'), 81.8 (1C, C-1), 76.9, 75.5, 73.6, 71.3, 70.9, 70.6, 69.0, 67.8, 67.7, 67.2, 67.0, 66.6 (12C, skeleton carbons), 61.7, 60.8, 60.2 (3C, 3 x C-6), 20.7, 20.5, 20.4 (11C, 11 x OAc, *C*H$_3$) ppm; MALDI-TOF-HRMS *m/z* calcd for $C_{40}H_{54}NaO_{26}S^+$ $[M+Na]^+$ 1005.2517, found 1005.2523.

#### *4.1.9. 3,4,6-Tri-O-acetyl-1,5-anhydro-2-thio-2-S-acetyl-D-glucitol (17) and 3,4,6-tri-O-acetyl-1,5-anhydro-2-thio-2-S-acetyl-D-mannitol (**18**)*

3,4,6-Tri-*O*-acetyl-D-glucal **3** (272 mg, 1.0 mmol), MAP (0.3 equiv, 45 mg, 0.3 mmol) and DPAP (0.2 equiv, 50 mg, 0.2 mmol) were dissolved in thioacetic acid (10.0 equiv, 0.710 mL, 10.0 mmol). The reaction mixture was cooled to −80 °C and was irradiated with UV light for 2 × 60 min. The crude product was concentrated under reduced pressure and was purified by flash column chromatography (hexane: acetone 85:15) to give compound **17** (176 mg) and a mixture of **17** and **18** (160 mg) as colourless syrup. The total combined yield was 96%, the **17**:**18** ratio was 63:37.

The reaction was repeated at 0 °C, the total combined yield was 93%, the **17**:**18** ratio was 36:64 (41 mg of compound **17**, 28 mg of compound **18**, 254 mg of a mixture of **17** and **18** were isolated).

Compound **17**: white foam; $R_f$ = 0.31 (hexane: acetone 7:3); $[\alpha]_D$ +10.9 (*c* 0.42, $CHCl_3$); lit [23]. $[\alpha]_D$ +7.8; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.11 (dd, $J_{2,3}$ = 11.2 Hz, $J_{3,4}$ = 9.1 Hz, 1H, H-3), 5.04 (dd, $J_{4,5}$ = 9.8 Hz, $J_{3,4}$ = 9.0 Hz, 1H, H-4), 4.24 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 4.9 Hz, 1H, H-6a), 4.12 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6b}$ = 2.2 Hz, 1H, H-1b), 4.05 (dd, $J_{1a,1b}$ = 11.6 Hz, $J_{1a,2}$ = 5.2 Hz, 1H, H-1a), 3.77 (td, $J_{2,3}$ = 11.4 Hz, $J_{1,2a}$ = 5.2 Hz, 1H, H-2), 3.62 (ddd, $J_{4,5}$ = 9.8 Hz, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 2.2 Hz, 1H, H-5), 3.42 (t, $J_{1a,1b}$ = 11.6 Hz, 1H, H-1b), 2.34 (s, 3H, SAc, C*H*$_3$), 2.10, 2.03, 2.02 (3s, 3 × 3H, 3 x OAc, C*H*$_3$) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 193.2 (1C, SAc, $C_q$), 170.7, 170.3, 169.5 (3C, 3 x OAc, $C_q$), 76.6 (1C, C-5), 71.9 (1C, C-3), 69.6 (1C, C-4), 69.1 (1C, C-1), 62.3 (1C, C-6), 43.1 (1C, C-2), 30.8 (1C, SAc, *C*H$_3$), 20.8, 20.6, 20.6 (3C, 3 x OAc, *C*H$_3$) ppm; MALDI-TOF-HRMS *m/z* calcd for $C_{14}H_{20}NaO_8S^+$ $[M+Na]^+$ 371.0772, found: 371.0777.

Compound **18**: colorless syrup; $R_f$ = 0.29 (hexane: acetone 7:3); $[\alpha]_D$ −4.87 (c 0.16, $CHCl_3$), lit [23]. $[\alpha]_D$ −10.0; $^1$H NMR (500 MHz, $CDCl_3$) δ 5.21 (dd, $J_{3,4}$ = 9.7 Hz, $J_{2,3}$ = 4.6 Hz, 1H, H-3), 5.07 (t, $J_{3,4}$ = 9.7 Hz, 1H, H-4), 4.24 (dt, $J_{2,3}$ = 4.5 Hz, $J_{1,2}$ = 2.1 Hz, 1H, H-2), 4.17 (dd, $J_{6a,6b}$ = 12.3 Hz, $J_{5,6a}$ = 5.2 Hz, 1H, H-6a), 4.12 (dd, $J_{6a,6b}$ = 12.4 Hz, $J_{5,6b}$ = 2.5 Hz, 1H, H-6b), 4.03 (dd, $J_{1a,1b}$ = 12.5 Hz, $J_{1a,2}$ = 2.1 Hz, 1H, H-1a), 3.91 (dd, $J_{1a,1b}$ = 12.5 Hz, $J_{1b,2}$ = 2.0 Hz, 1H, H-1b), 3.59 (ddd, $J_{4,5}$ = 9.6 Hz, $J_{5,6a}$ = 5.2 Hz, $J_{5,6b}$ = 2.5 Hz, 1H, H-5), 2.38 (s, 3H, s, 3H, SAc, $CH_3$), 2.11, 2.05, 1.98 (3s, 3 × 3H, 3 x OAc, $CH_3$) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) δ 194.2 (1C, SAc, $C_q$), 170.8, 170.2, 169.6 (3C, 3 x OAc, $C_q$), 77.3 (1C, C-5), 72.0 (1C, C-3), 69.9 (1C, C-1), 66.9 (1C, C-4), 62.6 (1C, C-6), 45.0 (1C, C-2), 30.7 (1C, SAc, $CH_3$), 20.8, 20.8, 20.8 (3C, 3 x OAc, $CH_3$) ppm; MALDI-TOF-HRMS m/z calcd for $C_{14}H_{20}NaO_8S^+$ $[M+Na]^+$ 371.0772, found: 371.0766.

#### *4.1.10. 3,4,6-Tri-O-acetyl-1,5-anhydro-2-thio-2-S-acetyl-D-galactitol (19) and 3,4,6-tri-O-acetyl-1,5-anhydro-2-thio-2-S-acetyl-D-talitol (**20**)*

3,4,6-Tri-*O*-acetyl-D-galactal **4** (272 mg, 1.0 mmol), MAP (0.3 equiv, 45 mg, 0.3 mmol) and DPAP (0.2 equiv, 50 mg, 0.2 mmol) were dissolved in thioacetic acid (10.0 equiv, 0.710 mL, 10.0 mmol). The reaction mixture was cooled to −80 °C and was irradiated with UV light for 2 × 60 min. The crude product was concentrated under reduced pressure and was purified by flash column chromatography (hexane: ethyl acetate 8:2) to give compound **19** (201 mg, 58%) and a mixture of **19** and **20** (135 mg, **19**:**20** = 1:3.8) as colourless syrup. The total combined yield was 97%, the **19**:**20** ratio was 68:32.

The reaction was repeated at 0 °C to give **19** (158 mg, 46%) as white crystal, and **20** (141 mg, 40%) as colourless syrup.

Compound **19**: white crystals; $R_f$ = 0.22 (hexane: acetone 7:3); m.p. 111.3-113.7 °C $[\alpha]_D$ −3.64 (*c* 0.22, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.38 (dd, $J_{3,4}$ = 3.3 Hz, $J_{4,5}$ = 1.2 Hz, 1H, H-4), 4.98 (dd, $J_{2,3}$ = 11.9 Hz, $J_{3,4}$ = 3.2 Hz, 1H, H-3), 4.16 – 4.04 (m, 3H, H-1a, H-6a, H-6b), 3.99 (td, $J_{2,3}$ = 11.7 Hz, $J_{1,2}$ = 5.1 Hz, 1H, H-2), 3.83 (td, $J_{5,6}$ = 6.4, $J_{4,5}$ = 1.2 Hz, 1H, H-5), 3.43 (t, $J_{1a,1b}$ = 11.5 Hz, 1H, H-1b), 2.35 (s, 3H, SAc, C*H*$_3$), 2.18, 2.06, 2.00 (3s, 3 × 3H, 3 x OAc, C*H*$_3$) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 193.6 (1C, SAc, $C_q$), 170.5, 170.3, 170.0 (3C, 3 x OAc, $C_q$), 75.0

(1C, C-5), 69.8 (1C, C-3), 69.4 (1C, C-1), 67.3 (1C, C-4), 62.3 (1C, C-6), 39.8 (1C, C-2), 30.9 (1C, SAc, *C*H$_3$), 20.7, 20.7, 20.6 (3C, 3 x OAc, *C*H$_3$) ppm; MALDI-TOF-HRMS *m/z* calcd for $C_{14}H_{20}NaO_8S^+$ $[M+Na]^+$ 371.0772, found: 371.0780.

Compound **20**: colorless syrup; $R_f = 0.14$ (hexane: acetone 7:3); $[\alpha]_D$ −5.39 (c 0.23, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) δ 5.31 – 5.26 (m, 2H, H-3, H-4), 4.15 (dd, $J_{6a,6b} = 11.7$ Hz, $J_{5,6a} = 7.2$ Hz, 1H, H-6a), 4.11 (dd, $J_{6a,6b} = 11.8$ Hz, $J_{5,6b} = 5.8$ Hz, 1H, H-6b), 4.07 – 4.03 (m, 1H, H-2), 4.02 (dd, $J_{1a,1b} = 12.7$ Hz, $J_{1a,2} = 2.3$ Hz, 1H, H-1a), 3.91 (dd, $J_{1a,1b} = 12.6$ Hz, $J_{1b,2} = 2.3$ Hz, 1H, H-1b), 3.84 (ddd, $J_{5,6a} = 7.4$ Hz, $J_{5,6b} = 5.8$, $J_{4,5} = 1.7$ Hz, 1H, H-5), 2.37 (s, 3H, SAc, $CH_3$), 2.19, 2.05, 2.02 (3s, 3 × 3H, 3 x OAc, $CH_3$) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) δ 195.6 (1C, SAc, $C_q$), 170.6, 170.0, 169.7 (3C, 3 x OAc, $C_q$), 75.3 (1C, C-5), 70.7 (1C, C-1), 68.5 (1C, C-3), 66.5 (1C, C-4), 62.1 (1C, C-6), 41.6 (1C, C-2), 30.6 (1C, SAc, $CH_3$), 20.9, 20.8, 20.8 (3C, 3 x OAc, $CH_3$) ppm; MALDI-TOF-MS m/z calcd for $C_{14}H_{20}NaO_8S^+$ $[M+Na]^+$ 371.0772, found 371.0770.

#### *4.1.11. 3,4,6-Tri-O-acetyl-1,5-anhydro-2-thio-2-S-(tert-butyl)-D-glucitol (21) and 3,4,6-tri-O-acetyl-1,5-anhydro-2-thio-2-S-(tert-butyl)-D-mannitol (22)*

3,4,6-Tri-*O*-acetyl-D-glucal (**3**) (1.10 mmol, 300 mg), *tert*-butylmercaptan (10.0 equiv., 11.02 mmol, 1.25 mL), and DPAP (0.1 equiv., 0.11 mmol, 28 mg) were dissolved in toluene (1.0 mL). The reaction mixture was cooled to −80 °C and was irradiated with UV light for 60 min. After irradiation, another 0.1 equiv. DPAP was added, and the irradiation was continued for 60 min. The latter step was repeated one more time, after which the crude product was concentrated under reduced pressure and purified by flash column chromatography (hexane: ethyl acetate 8:2) to give compound **22** (31 mg, 8%) as a colorless syrup, and an inseparable mixture of **21** and glycal **1** in a 3:1 ratio (308 mg) as a colorless syrup. The total combined yield was 66%.

Compound **21** (from the mixture of **21** and **1**): $R_f = 0.53$ (hexane: ethyl acetate 6:4); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.00 (dd, $J = 10.0$, 9.1 Hz, 1H, H-4), 4.90 (dd, $J = 11.1$, 9.1 Hz, 1H, H-3), 4.27 (dd, $J = 12.3$, 4.8 Hz, 1H, H-6a), 4.10 – 4.05 (m, 2H, H-1$_{equatorial}$, H-6b), 3.59 (ddd, $J = 9.9$, 4.8, 2.2 Hz, 1H, H-5), 3.33 (t, $J = 12.1$ Hz, 1H, H-1$_{axial}$), 2.84 (ddd, $J = 11.9$, 11.0, 5.4 Hz, 1H, H-2), 2.10, 2.06, 2.02 (3s, 3 × 3H, 3 x OAc, C*H$_3$*), 1.32 (s, 9H, C(C*H$_3$*)$_3$) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.7, 170.2, 169.9 (3C, 3 x OAc, *C*q), 76.5 (1C, C-5), 73.9 (1C, C-3), 71.7 (1C, C-1), 69.8 (1C, C-4), 62.5 (1C, C-6), 43.8 (1C, *t*-Bu Cq), 42.7 (1C, C-2), 31.4 (3C, *t*-Bu ($CH_3$)$_3$), 20.9, 20.8, 20.7 (3C, 3 x OAc, *C*H$_3$) ppm; MALDI-TOF-HRMS: *m/z* calcd for $C_{16}H_{26}NaO_7S^+$ $[M+Na]^+$ 385.1297, found 385.1289.

Compound **22**: $R_f = 0.51$ (hexane: ethyl acetate 6:4); $[\alpha]_D$ −52.0 (*c* 0.10, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.10 – 5.01 (m, 2H, H-3, H-4), 4.21 (dd, $J = 12.2$, 5.5 Hz, 1H, C-6a), 4.11 (dd, $J = 12.2$, 2.6 Hz, 1H, H-6b), 4.01 (dd, $J = 11.8$, 3.2 Hz, 1H, H-1$_{equatorial}$), 3.86 (dd, $J = 11.8$, 2.1 Hz, 1H, H-1$_{axial}$), 3.58 (ddd, $J = 8.0$, 5.5, 2.4 Hz, 1H, H-5), 3.28 (dt, $J = 3.3$, 1.0 Hz, 1H, H-2), 2.09, 2.05 (3s, 3 × 3H, 3 x OAc, C*H$_3$*), 1.29 (s, 9H, C(C*H$_3$*)$_3$); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 171.0, 170.7, 169.5 (3C, 3 x OAc, *C*q), 76.5 (1C, C-5), 73.4 (1C, C-3), 71.4 (1C, C-1), 67.0 (1C, C-4), 62.6 (1C, C-6), 43.7 (1C, *t*-Bu Cq), 42.8 (1C, C-2), 31.1 (3C, *t*-Bu ($CH_3$)$_3$), 21.1, 20.9, 20.8 (3C, 3 x OAc, *C*H$_3$); HR-MALDI-TOF-MS: *m/z* calcd for $C_{16}H_{26}NaO_7S^+$ $[M+Na]^+$ 385.1291, found 385.1295.

#### *4.1.12. 3,4,6-Tri-O-acetyl-1,5-anhydro-2-thio-2-S-(tert-butyl)-D-galactitol (23)*

3,4,6-Tri-*O*-acetyl-D-galactal (**4**) (1.10 mmol, 300 mg), *tert*-butylmercaptan (10.0 equiv., 11.02 mmol, 1.25 mL), and DPAP (0.1 equiv., 0.11 mmol, 28 mg) were dissolved in toluene (1.0 mL). The reaction mixture was cooled to −80 °C and was irradiated with UV light for 60 min. After irradiation, another 0.1 equiv. DPAP was added, and the irradiation was continued for 60 min. The latter step was repeated one more time, after which the crude product was concentrated under reduced pressure and purified by flash column chromatography (hexane: ethyl acetate 8:2) to give compound **23** (297 mg, 74%) as a colorless syrup. $R_f = 0.51$ (hexane: ethyl acetate 6:4); $[\alpha]_D$ −30.7 (*c* 0.13, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.36 (dd, $J = 3.3$, 1.2 Hz, 1H, H-4), 4.75 (dd, $J = 11.6$, 3.2 Hz, 1H, H-3), 4.11 (dd, $J = 12.1$, 5.3 Hz, 1H, H-1$_{equatorial}$), 4.08 (d, $J = 6.1$ Hz, 2H, H-6ab), 3.79 (td, $J = 6.4$, 1.2 Hz, 1H, H-5), 3.34 (t, $J = 12.0$ Hz, 1H, H-1$_{axial}$), 3.03 (td, $J = 11.8$, 5.3 Hz, 1H, H-2), 2.17, 2.06, 2.02 (3s, 3 × 3H, 3 x OAc, C*H$_3$*), 1.33 (s, 9H, C(C*H$_3$*)$_3$) ppm; $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 170.6, 170.2, 169.9 (3C, 3 x OAc, *C*q), 75.00 (1C, C-5), 71.9 (1C, C-3), 71.8 (1C, C-1), 67.7 (1C, C-4), 62.4 (1C, C-6), 43.7 (1C, *t*-Bu *C*q), 38.6 (1C, C-2), 31.4 (3C, *t*-Bu ($CH_3$)$_3$), 20.8 (3C, 3 x OAc, *C*H$_3$) ppm; MALDI-TOF-HRMS: *m/z* calcd for $C_{16}H_{26}NaO_7S^+$ $[M+Na]^+$ 385.1297, found 385.1298.

#### *4.1.13. 3,4,6-Tri-O-acetyl-1,5-anhydro-2-thio-2-S-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-D-glucitol (25) and 3,4,6-tri-O-acetyl-1,5-anhydro-2-thio-2-S-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-D-mannitol (26)*

To a solution of 3,4,6-tri-*O*-acetyl-D-glucal **3** (300 mg, 1.00 equiv., 1.1 mmol) and 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranose **7** (482 mg, 1.2 equiv., 1.33 mmol) in toluene (1.00 mL), 0.1 equiv. of DPAP (30 mg, 0.11 mmol) per cycle was added. The reaction mixture was irradiated at −80 °C for 3 × 30 min. The crude product was purified by column chromatography (hexane: ethyl acetate 1:1) to give compounds **25** (202 mg, 36%) and **26** (337 mg, 49%), both as white crystals.

Compound **25**: $R_f = 0.19$ (hexane: ethyl acetate 1:1); M.p.: 188-190 °C; $[\alpha]_D$ +4.00 (*c* 0.1, $CHCl_3$); $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 5.43 – 5.41 (m, 1H, H-4′), 5.12 (t, $J = 10.6$ Hz, 1H, H-2′), 5.03 (t, $J = 11.0$ Hz, 1H, H-3), 5.00 (dd, $J = 10.0$, 3.4 Hz, 1H, H-3′), 4.97 (t, $J = 9.6$ Hz, 1H, H-4), 4.64 (d, $J = 10.2$ Hz, 1H, H-1′), 4.26 (dd, $J = 9.3$, 3.3 Hz, 1H, H-1a), 4.25 – 4.23 (m, 1H, H-6a), 4.16 (dd, $J = 11.4$, 6.9 Hz, 1H, H-6b), 4.12 – 4.09 (m, 1H, H-6′a), 4.09 – 4.06 (m, 1H, H-6′b), 3.92 (td, $J = 6.3$ Hz, 1H, H-5′), 3.60 (dt, $J = 10.0$, 4.8 Hz, 1H, H-5), 3.35 (t, $J = 11.9$ Hz, 1H, H-1b), 3.12 (td, $J = 11.5$, 5.1 Hz, 1H, H-2), 2.16, 2.08, 2.07, 2.07, 2.03, 2.02, 1.98 (7s, 7 × 3H, 7 x OAc, C*H$_3$*) ppm; $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 170.7, 170.4, 170.2, 170.1, 169.9, 169.8, 169.4 (7C, 7 x OAc, *C*q), 85.4 (1C, C-1′), 76.5 (1C, C-5), 74.9 (1C, C-5′), 74.6 (1C, C-3), 71.6 (1C, C-3′), 70.2 (1C, C-1), 69.4 (1C, C-4), 67.5 (1C, C-2′), 67.0 (1C, C-4′), 62.3 (1C, C-6), 61.4 (1C, C-6′), 45.5 (1C, C-2), 20.8, 20.7, 20.7, 20.7, 20.6, 20.6 (7C, 7 x OAc, *C*H$_3$) ppm; MALDI-TOF HRMS: *m/z* calcd for $C_{26}H_{36}NaO_{16}S^+$ $[M+Na]^+$ 659.1617, found 659.1622.

Compound **26**: $R_f = 0.12$ (hexane: ethyl acetate 1:1); M.p.: 138-140 °C; $[\alpha]_D$ −63.3 (*c* 0.18, $CHCl_3$), lit.[24] $[\alpha]_D$ −47.5 (c 0.5, $CHCl_3$); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.31 (dd, $J = 3.4$, 1.1 Hz, 1H, H-4′), 5.10 (t, $J = 10.0$ Hz, 1H, H-2′), 4.98 – 4.96 (m, 2H, H-4, H-3), 4.96 – 4.93 (m, 1H, H-3′), 4.62 (d, $J = 9.9$ Hz, 1H, H-1′), 4.13 (dd, $J = 12.3$, 5.7 Hz, 1H, H-6a), 4.06 (dd, $J = 12.4$, 3.0 Hz, 1H, H-1a), 4.01 (dd, $J = 12.2$, 2.5 Hz, 1H, H-6b), 4.00 – 3.95 (m, 2H, H-6′ab), 3.86 – 3.81 (m, 1H, H-5′), 3.75 (dd, $J = 12.4$, 2.3 Hz, 1H, H-1b), 3.55 – 3.53 (m, 1H, H-5), 3.54 – 3.50 (m, 1H, H-2), 2.05, 1.99, 1.98, 1.98, 1.95, 1.95, 1.87 (7s, 7 × 3H, 7 x OAc, C$H_3$) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 170.4, 170.2, 169.9, 169.9, 169.7, 169.2, 169.1 (7C, 7 x OAc, *C*q), 83.1 (1C, C-1′), 76.4 (1C, C-5), 74.4 (1C, C-5′), 72.2 (1C, C-3), 71.6 (1C, C-3′), 68.6 (1C, C-1), 67.2 (1C, C-4′), 67.1 (1C, C-2′), 66.1 (1C, C-4), 62.1 (1C, C-6), 61.3 (1C, C-6′), 44.2 (1C, C-2), 20.7, 20.5, 20.4, 20.3 (7C, 7 x OAc, *C*H$_3$) ppm; MALDI-TOF HRMS: *m/z* calcd for $C_{26}H_{36}NaO_{16}S^+$ $[M+Na]^+$ 659.1617, found 659.1622.

#### *4.1.14. 3,4,6-Tri-O-acetyl-1,5-anhydro-2-thio-2-S-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-D-galactitol (27) and 3,4,6-tri-O-acetyl-1,5-anhydro-2-thio-2-S-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-D-talitol (28)*

To a solution of 3,4,6-tri-*O*-acetyl-D-galactal **4** (300 mg, 1.00 equiv., 1.1 mmol) and 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranose **7** (482 mg, 1.2 equiv., 1.33 mmol) in toluene (1.00 mL), 0.1 equiv. DPAP (30 mg, 0.11 mmol) per cycle was added. The reaction mixture was irradiated at −80 °C for 3 × 30 min. The crude product was purified by column chromatography (hexane:ethyl acetate 1:1) to give compound **27** (385 mg, 55%) and **28** (219 mg, 31%), both as white foam.

Compound **27**: $R_f = 0.19$ (hexane: ethyl acetate 1:1); $[\alpha]_D$ +1.54 (*c* 0.13, $CHCl_3$); lit.[24] $[\alpha]_D = -1.5$ (c 1.0, CHCl3); $^1$H NMR (500 MHz,

$CDCl_3$) $\delta$ 5.31 (dd, $J = 3.4$, 1.2 Hz, 1H, H-4′), 5.24 (dd, $J = 3.3$, 1.2 Hz, 1H, H-4), 5.01 (t, $J = 10.0$ Hz, 1H, H-2′), 4.93 (dd, $J = 10.0$, 3.4 Hz, 1H. H-3′), 4.79 (dd, $J = 11.5$, 3.3 Hz, 1H, H-3), 4.60 (d, $J = 10.0$ Hz, 1H, H-1′), 4.17 (dd, $J = 11.9$, 5.0 Hz, 1H, H-1a), 4.07 (dd, $J = 11.3$, 6.9 Hz, 1H, H-6′a), 4.02 – 3.98 (m, 1H, H-6′b), 3.98 – 3.94 (m, 2H, H-6ab), 3.89 (td, $J = 6.6$, 1.2 Hz, 1H, H-5′), 3.72 (td, $J = 6.7$, 1.2 Hz, 1H, H-5), 3.31 (t, $J = 11.8$ Hz, 1H, H-1b), 3.16 (td, $J = 11.6$, 5.0 Hz, 1H, H-2), 2.06, 2.05, 1.95, 1.93 1.92, 1.92, 1.86 (7s, 7 × 3H, 7 x OAc, C*H*$_3$) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 170.2, 170.1, 169.9, 169.8, 169.7, 169.4, 169.1 (7C, 7 x OAc, *C*q), 84.9 (1C, C-1′), 74.7 (1C, C-5), 74.1 (1C, C-5′), 72.2 (1C, C-3), 71.3 (1C, C-3′), 70.2 (1C, C-1), 67.3 (1C, C-2′), 67.1 (1C, C-4), 66.8 (1C, C-4′), 61.9 (1C, C-6′), 61.1 (1C, C-6), 42.0 (1C, C-2), 20.5, 20.4, 20.4, 20.3, 20.3, 20.3 (7C, 7 x OAc, *C*H$_3$) ppm; MALDI-TOF HRMS: *m/z* calcd for $C_{26}H_{36}NaO_{16}S^+$ $[M+Na]^+$ 659.1617, found 659.1610.

Compound **28**: $R_f = 0.16$ (hexane: ethyl acetate 1:1); $[\alpha]_D$ −13.1 (*c* 0.16, $CHCl_3$); lit.[24] $[\alpha]_D$ −21.1 (*c* 0.8, CHCl*3*); $^1$H NMR (500 MHz, $CDCl_3$); $\delta$ 5.33 (dd, $J = 3.5$, 1.1 Hz, 1H, H-4′), 5.19 (t, $J = 4.7$ Hz, 1H, H-3), 5.15 – 5.10 (m, 2H, H-2′, H-4), 4.96 (dd, $J = 10.0$, 3.4 Hz, 1H, H-3′), 4.40 (d, $J = 10.0$ Hz, 1H, H-1′), 4.20 (dd, $J = 11.8$, 7.7 Hz, 1H, H-6a), 4.08 – 4.04 (m, 1H, H-6b), 4.04 – 4.02 (m, 1H, H-1a), 4.02 – 3.97 (m, 2H, H-6′ab), 3.88 – 3.85 (m, 1H, H-5′), 3.85 – 3.80 (m, 1H, H-5), 3.76 (dd, $J = 12.4$, 3.0 Hz, 1H, H-1b), 3.32 (t, $J = 4.0$ Hz, 1H, H-2), 2.08, 2.03, 2.00, 1.98, 1.97, 1.96, 1.89 (7s, 7 × 3H, 7 x OAc, C*H*$_3$) ppm; $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 170.4, 170.2, 170.0, 169.8, 169.6, 169.6, 169.2 (7C, 7 x OAc, *C*q), 83.4 (1C, C-1′), 74.6 (1C, C-5′), 74.2 (1C, C-5), 71.7 (1C, C-3′), 69.0 (1C, C-3), 67.2 (1C, C-4′), 66.9 (1C, C-4), 66.7 (1C, C-2′), 61.3 (1C, C-1), 61.2 (2C, C-6, C-6′), 41.7 (1C, C-2), 20.6, 20.6, 20.5, 20.5, 20.4 (7C, 7 x OAc, *C*H$_3$) ppm; MALDI-TOF HRMS: *m/z* calcd for $C_{26}H_{36}NaO_{16}S^+$ $[M+Na]^+$ 659.1617, found 659.1621.

#### *4.1.15. 3,4,6-Tri-O-acetyl-1,5-anhydro-2-thio-2-S-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1-4)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-D-glucitol (**29**) and 3,4,6-tri-O-acetyl-1,5-anhydro-2-thio-2-S-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1-4)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-D-mannitol (**30**)*

3,4,6-Tri-*O*-acetyl-D-glucal **3** (69 mg, 0.25 mmol), 2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-1-thio-β-D-lactose **8** (198 mg, 0.3 mmol, 1.2 equiv.) and DPAP (7 mg, 0.05 mmol, 0.1 equiv.) were dissolved in toluene (1 mL). The reaction mixture was cooled to −80 °C and was irradiated with UV light for 2 x 30 and 1 × 60 min. The crude product was concentrated under reduced pressure and purified by flash column chromatography (chloroform: acetone 94:6) to give compounds **29** (31 mg, 13%) and an inseparable mixture of **29** and **30** (167 mg, 71%) as white foam. The total combined yield was 84% with a **29**:**30** = 39:61 ratio.

The reaction was repeated at 0 °C, the total combined yield was 80%, the **29**:**30** ratio was 37:63 (58 mg of compound **29**, 128 mg of a mixture of **29** and **30** were isolated).

Compound **29**: $R_f = 0.33$ (hexane: ethyl acetate 1:2). $[\alpha]_D$ −7.2 (*c* 0.18, $CHCl_3$); $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 5.35 (dd, $J = 3.5$, 1.2 Hz, 1H, H-4″), 5.17 (t, $J = 9.2$ Hz, 1H, H-3′), 5.11 (dd, $J = 10.4$, 7.9 Hz, 1H, H-2″), 5.01 (dd, $J = 10.9$, 9.1 Hz, 1H, H-3), 5.00 – 4.93 (m, 2H, H-3″, H-4), 4.82 (dd, $J = 10.2$, 9.2 Hz, 1H, H-2′), 4.62 (d, $J = 10.2$ Hz, 1H, H-1′), 4.49 (dd, $J = 11.7$, 2.1 Hz, 1H, H-6′a, overlap with H-1″), 4.48 (d, $J = 7.7$, 1H, H-1″, overlap with H-6′a), 4.25 (dd, $J = 12.5$, 4.9 Hz, 1H, H-6a), 4.23 (dd, $J = 12.0$, 5.2 Hz, 1H, H-1β), 4.13 (dd, $J = 11.2$, 6.3 Hz, 1H, H-6″a), 4.11 – 4.06 (m, 3H, H-6b, H-6′b, H-6″b), 3.88 (ddd, $J = 7.5$, 6.3, 1.2 Hz, 1H, H-5″), 3.76 (dd, $J = 9.9$, 9.1 Hz, 1H, H-4′), 3.64 – 3.60 (m, 1H, H-5′), 3.60 – 3.58 (m, 1H, H-5), 3.33 (t, $J = 11.9$ Hz, 1H, H-1α), 3.08 (ddd, $J = 11.8$, 10.9, 5.2 Hz, 1H, H-2), 2.16, 2.14, 2.08, 2.07, 2.07, 2.06, 2.04, 2.02, 2.02, 1.97 (10s, 10 × 3H, 10 x OAc, C*H*$_3$) ppm; $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 170.7, 170.4, 170.4, 170.2, 170.1, 170.0, 169.8, 169.7, 169.5, 169.2 (10C, 10 x OAc, *C*q), 101.2 (1C, C-1″), 84.4 (1C, C-1′), 76.8 (1C, C-5), 76.5 (1C, C-5′), 76.1 (1C, C-4′), 74.6 (1C, C-3), 73.6 (1C, C-3′), 71.0 (1C, C-3″), 70.8 (1C, C-5″), 70.7 (1C, C-2′), 70.3 (1C, C-1), 69.5 (1C, C-4), 69.1 (1C, C-2″), 66.6 (1C, C-4″), 62.3 (1C, C-6), 62.1 (1C, C-6′), 60.9 (1C, C-6″), 45.6 (1C, C-2), 20.9, 20.8, 20.8, 20.7, 20.7, 20.7, 20.6 (10C, 10 x OAc, *C*H$_3$) ppm; MALDI-TOF HRMS: *m/z* calcd for $C_{38}H_{52}NaO_{24}S^+$ $[M+Na]^+$ 947.2461, found 947.2469.

Compound **30**: $R_f = 0.20$ (hexane: ethyl acetate 1:2). The NMR characterization was made from the NMR spectra of the mixture. $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 5.35 – 5.34 (m, 1H, H-4″), 5.19 (t, $J = 9.2$ Hz, 1H, H-3′), 5.09 (dd, $J = 10.4$, 8.0 Hz, 1H, H-2″), 5.08 – 5.03 (m, 2H, H-3, H-4), 4.95 (dd, $J = 10.5$, 3.6 Hz, 1H, H-3″), 4.92 (t, $J = 10.1$ Hz, 1H, H-2′), 4.68 (d, $J = 10.1$ Hz, 1H, H-1′), 4.46 (d, $J = 7.9$ Hz, 1H, H-1″), 4.42 (dd, $J = 12.1$, 2.0 Hz, 1H, H-6′a), 4.24 (dd, $J = 12.3$, 5.6 Hz, 1H, H-6a), 4.14 – 4.07 (m, 5H, H-6b, H-6′b, H-6″ab, H-1a), 3.87 (t, $J = 6.7$ Hz, 1H, H-5″), 3.81 (dd, $J = 12.4$, 2.4 Hz, 1H, H-1b), 3.77 (t, $J = 9.5$ Hz, 1H, H-4′), 3.63 – 3.57 (m, 3H, H-2, H-5, H-5′), 2.15, 2.12, 2.11, 2.07, 2.07, 2.05, 2.05, 2.04, 2.04, 1.96 (10s, 10 × 3H, 10 x OAc, C*H*$_3$) ppm; $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 170.9, 170.5, 170.5, 170.3, 170.2, 169.8, 169.7, 169.4, 169.2 (10C, 10 x OAc, $C_q$), 101.2 (1C, C-1″), 82.7 (1C, C-1′), 77.0 (1C, C-5′), 76.6 (1C, C-5), 76.1 (1C, C-4′), 73.8 (1C, C-3′), 72.5 (1C, C-3), 71.0 (1C, C-3″), 70.8 (1C, C-5″), 70.4 (1C, C-2′), 69.1 (1C, C-2″), 68.8 (1C, C-1), 66.7 (1C, C-4″), 66.2 (1C, C-4), 62.2 (2C, C-6, C-6′), 60.9 (1C, C-6″), 44.1 (1C, C-2), 20.9, 20.9, 20.9, 20.8, 20.8, 20.8, 20.7, 20.6 (10C, 10 x OAc, *C*H$_3$) ppm; MALDI-TOF HRMS: *m/z* calcd for $C_{38}H_{52}NaO_{24}S^+$ $[M+Na]^+$ 947.2461, found 947.2472.

#### *4.1.16. 3,4,6-Tri-O-acetyl-1,5-anhydro-2-thio-2-S-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1-4)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-D-galactitol (**31**) and 3,4,6-tri-O-acetyl-1,5-anhydro-2-thio-2-S-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-(1-4)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-D-talitol (**32**)*

3,4,6-Tri-*O*-acetyl-D-galactal **4** (136 mg, 0.5 mmol), 2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-1-thio-β-D-lactose **8** (391 mg, 0.6 mmol, 1.2 equiv.) and DPAP (13 mg, 0.05 mmol, 0.1 equiv.) were dissolved in toluene (1 mL). The reaction mixture was cooled to −80 °C and was irradiated with UV light for 2 x 30 and 1 × 60 min. The crude product was concentrated under reduced pressure and purified by flash column chromatography (chloroform: acetone 95:5) to give compounds **31** (128 mg, 28%) and an inseparable mixture of **31**, **32** and disulfide formed from thiol **8** (248 mg, 53%) as white amorphous. The total combined yield was 81%, **31**:**32** = 67:33.

Compound **31**: $R_f = 0.28$ (hexane: ethyl acetate 1:2). $[\alpha]_D$ −13.3 (*c* 0.12, $CHCl_3$). $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 5.36 – 5.32 (m, 2H, H-4, H-4″), 5.19 (t, $J = 9.1$ Hz, 1H, H-3′), 5.10 (dd, $J = 10.4$, 7.9 Hz, 1H, H-2″), 4.97 (dd, $J = 10.5$, 3.5 Hz, 1H, H-3″), 4.88 (dd, $J = 11.5$, 3.3 Hz, 1H, H-4), 4.83 (t, $J = 9.7$ Hz, 1H, H-2′), 4.66 (d, $J = 10.1$ Hz, 1H, H-1′), 4.52 – 4.47 (m, 2H, H-1″, H-6′a), 4.28 (dd, $J = 12.0$, 5.1 Hz, 1H, H-1β), 4.14 – 4.05 (m, 5H, H-6ab, H-6′b, H-6″ab), 3.90 (t, $J = 6.9$ Hz, 1H, H-5″), 3.81 (t, $J = 6.7$ Hz, 1H, H-5), 3.77 (t, $J = 9.5$ Hz, 1H, H-4′), 3.65 (ddd, $J = 10.0$, 5.8, 2.2 Hz, 1H, H-5′), 3.39 (t, $J = 11.9$ Hz, 1H, H-1α), 3.23 (td, $J = 11.6$, 5.0 Hz, 1H, H-2), 2.17, 2.15, 2.14, 2.06, 2.06, 2.04, 2.04, 2.03, 2.02, 1.96 (10s, 10 × 3H, 10 x OAc, C*H*$_3$) ppm; $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 170.4, 170.3, 170.3, 170.1, 170.0, 170.0, 169.7, 169.6, 169.4, 169.1 (10C, 10 x OAc, *C*q), 101.1 (1C, C-1″), 84.4 (1C, C-1′), 76.7 (1C, C-5′), 76.1 (1C, C-4′), 74.9 (1C, C-5), 73.5 (1C, C-3′), 72.2 (1C, C-3), 70.9 (1C, C-3″), 70.7 (1C, C-5″), 70.6 (1C, C-2′), 70.5 (1C, C-1), 69.1 (1C, C-2″), 67.3, 66.6 (2C, C-4, C-4″), 62.0, 62.0 (2C, C-6, C-6′), 60.8 (1C, C-6″), 42.4 (1C, C-2), 20.7, 20.7, 20.6, 20.6, 20.5, 20.4 (10C, 10 x OAc, *C*H$_3$) ppm; MALDI-TOF HRMS: *m/z* calcd for $C_{38}H_{52}NaO_{24}S^+$ $[M+Na]^+$ 947.2461, found 947.2472.

Compound **32**: Small amount of a mixture of **31**, **32** and disulfide was repurified by flash column chromatography (eluent: hexane: chloroform: acetone: methanol 3:1:1:0.1) to give compound **32** as analytical standard. Rf = 0.29 (hexane: chloroform: acetone: methanol 2:1:1:0.1, $[\alpha]_D$ −21.4 (*c* 1.24, $CHCl_3$). $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ 5.35 (dd, $J = 3.5$, 0.9 Hz, 1H, H-4″), 5.26 – 5.22 (m, 1H), 5.21 (t, $J = 2.9$ Hz, 1H), 5.18 (t, $J = 9.2$ Hz, 1H, H-3′), 5.10 (dd, $J = 10.4$, 7.9 Hz, 1H, H-2″), 4.95 (dd, $J = 10.4$, 3.3 Hz, 1H, H-3″, overlap with H-2′), 4.94 (t, $J = 9.7$ Hz, 1H, 1H, H-2′, overlap with H-3″), 4.46 (d, $J = 8.2$ Hz, 1H, H-1″, overlap with H-1′), 4.45 (d, $J = 9.8$ Hz, 1H, H-1′, overlap with H-1″), 4.43 (dd, $J = 12.1$,

2.0 Hz, 1H), 4.29 (dd, $J = 11.4$, 8.2 Hz, 1H), 4.14 – 4.05 (m, 5H), 3.89 (ddd, $J = 11.7$, 5.6, 3.6 Hz, 1H), 3.89 – 3.84 (m, 1H, H-5″), 3.79 (dd, $J =$ 12.0, 2.6 Hz, 1H), 3.77 (t, $J = 9.5$ Hz, 1H, H-4′), 3.59 (ddd, $J = 10.0$, 5.2, 2.0 Hz, 1H, H-5′), 3.31 (q, $J = 4.4$ Hz, 1H), 2.15, 2.13, 2.11, 2.07, 2.06, 2.06, 2.05, 2.04, 2.04, 1.97 (10s, 10 × 3H, 10 x OAc, C$H_3$) ppm; $^{13}$C NMR (176 MHz, $CDCl_3$) $\delta$ 170.8, 170.5, 170.5, 170.3, 170.2, 170.0, 169.9, 169.8, 169.7, 169.2 (10C, 10 x OAc, *C*q), 101.3 (1C, C-1″), 83.0 (1C, C-1′), 77.1 (1C, C-5′, overlap with $CDCl_3$ signal), 76.2 (1C, C-4′), 73.9 (1C, C-3′), 71.1 (1C, C-3″), 70.8 (1C, C-5″), 69.9 (1C, C-2’), 69.3, 69.2 (1C, C-2″), 67.1, 66.7 (1C, C-4”), 62.2, 61.6, 60.90, 41.8, 21.0, 20.9, 20.9, 20.8, 20.8, 20.8, 20.7 (10C, 10 x OAc, *C*$H_3$) ppm. MALDI-TOF HRMS: m\z calcd for $C_{38}H_{52}NaO_{24}S^+$ $[M+Na]^+$ 947.2461, found 947.2461.

## CRediT authorship contribution statement

**Ágnes Homolya:** Writing – original draft, Investigation. **Nawar Ahmad:** Writing – original draft, Investigation. **Rasha Ghanem Kattoub:** Investigation. **Fanni Hőgye:** Investigation. **Erika Mező:** Writing – original draft, Investigation. **Anikó Borbás:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carres.2026.109926.

## Data availability

Data will be made available on request.

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