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Graphical Abstract

**Photoinitiated hydrothiolation of pyranoid exo-glycals: the D-galacto and D-xylo cases**

János József, László Juhasz, Tünde Zita Illyés, Magdolna Csavás, Anikó Borbás, László Somsák

- Photoinitiated thiol-ene reaction of O-acetylated exo-glycals.
- Synthesis of β-β-d-glycopyranosylmethyl-sulfide type glycomimetics.
- Exclusive regio- and stereoselectivity with exo-galactal.
- Exclusive regio- and very high stereoselectivity with exo-xylal.
- Disaccharide mimicks of Gly-CH$_2$S-Gly scaffolds.

Highlights

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Photoinitiated hydrothiolation of pyranoid exo-glycals: the \( \delta \)-galacto and \( \delta \)-xylo cases

János József \(^a\), László Juhász \(^a\), Tünde Zita Illyés \(^a\), Magdolna Csávás \(^b\), Anikó Borbás \(^b\), László Somsák \(^a, *\)

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**A R T I C L E  I N F O**

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**A B S T R A C T**

Radical-mediated addition reactions of thiols to O-peracetylated exo-galactal and exo-xyral with 2,2-dimethoxy-2-phenylacetophenone as the photoinitiator resulted in high yielding formation of the corresponding \( \beta \)-\( \delta \)-glycopyranosylmethyl-sulfide derivatives (2,6-anhydro-1-deoxy-1-\( \delta \)-substituted-1-thioalditols) with exclusive regio- and very high stereoselectivity, including disaccharide mimics with Gly-\( \chi \)-\( \delta \)-Gly scaffolds.

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Keywords:
Thiol-ene click reaction
Exo-galactal
Exo-xyral
Disaccharide mimics

Glycomimetic compounds are widely used for deciphering the biological roles of carbohydrate derivatives.\(^1\) Glycomimetics resemble natural carbohydrates in their structure and/or biological function and often serve as lead compounds for drug design.\(^1\) One of the most important features of such compounds is their hydrolytic stability of the bond(s), which replace the natural O-glycosidic linkage(s). A wide range of such replacements were suggested, among others S-glycosides and C-glycosyl derivatives with a sulfur atom or a methylene group, respectively, in the position of the glycosidic oxygen.\(^1\) In addition, in a number of examples two (or even more) atoms are inserted between the glycon and aglycon\(^3\) in the form of e.g., S–S, \(^4\) S–Se, \(^5\)–\(^8\) SO\(_2\)–N–C(=O)–N linking moieties.\(^14\)–\(^17\)

Carbohydrate derivatives displaying Gly-\( \chi \)-\( \delta \)-S-R scaffolds are much less represented among glycomimetics although some synthetic methods, mostly limited to the application of O-perbenzylated exo-glycals, can be found in the literature. Thus, exo-glucal was transformed in several steps into a Glc-\( \chi \)-\( \delta \)-I derivative,\(^18\)–\(^20\) which was reacted under basic conditions with allylic and aromatic thiols including sulfur derivatives to give the above structures. Ring openings by nucleophiles of an exo-glucal-derived spiro-epoxide\(^21\) as well as a spiro-episulfonium ion\(^22\) resulted in ulose derivatives featuring the above structure. Radical-mediated addition of AcSH to exo-glycals furnished \( S-(\beta \)-\( \delta \)-glycosylmethyl) thioacetates.\(^23\)

The thiol-ene addition chemistry,\(^24\)\(^25\) either in ionic or radical-mediated versions, has found several applications in carbohydrate chemistry for S-glycoconjugation, wherein the sugar derivative generally plays the role of the thiol or is functionalized by O- or C-appended unsaturated moieties.\(^26\) Much less work has been devoted to additions of thiols to sugar ‘ene-’s in which the double bond is part of or directly attached to the sugar ring; thus, additions to sugar derived enones\(^27\) and some reactions of endoeneg-\(^8\)–\(^30\) and recently also exo-glycals\(^30\)–\(^33\) as well as derivatives with an exo-methylene group in the 4- and a 5-position of a furanose and a pyranose,\(^34\) respectively, and a 3-exomethylene-glucofuranose\(^31\)–\(^32\) have been reported.

**Exo-glycals offer themselves for the construction of Gly-\( \chi \)-\( \delta \)-S-R type compounds in thio-ene couplings provided that a sufficient degree of reactivity as well as of regio- and stereoselectivities can be achieved and the reaction conditions are compatible with the protective groups. Base induced anionic additions of thiocyanates can be expected ineffective with the electron-rich double bond,\(^33\) and acid-catalyzed reactions of thiols yield S-glycosides due to the stability of the glycosylon ion.\(^35\) Radical-mediated additions must be highly favourable due to the electrophilic nature of thiyl radicals\(^36\) and a good regioselectivity may also be foreseen based on the better stabilization of the tertiary glycosyl versus the primary glycosylmethyl radical. Although radical-mediated hydrothiolations...
could be performed with O-benzylated substrates, such protecting groups may be labile under those conditions (cf. a discussion in Ref. 31). On the other hand, O-acyl protection is usually advantageous and stable in radical-mediated reactions, as it was demonstrated recently also by hydrothiolations of O-perbenzoylated exo-1-glucal. In this case both the regio- and stereo-selectivities proved excellent as the formation of β-D-glucopyranosylmethyl-sulfides was observed only. As a continuation of these studies, herein we disclose our findings with the photoinitiated thiol-ene reactions of O-peracetylated exo-galactal and exo-xylal.

The O-peracetylated exo-glycals 1 and 4 were synthesized from the corresponding glycosyl cyanides according to our proven procedure. The thiol additions were carried out in toluene at room temperature by irradiation at $\lambda_{max}$ 365 nm for 15 min in the presence of 2,2-dimethoxy-2-phenylacetophenone (DPAP, 0.1 equiv) as the photoinitiator. The progress of the reaction was controlled by TLC after the first reaction period and irradiation and addition of DPAP were repeated if necessary. The thioles were applied in 10-fold excess for 2a–c and in slightly more than equimolar amounts for 2d–f. The results are summarized in Table 1 for exo-galactal 1 and in Table 2 for exo-xylal 4.

Each transformation needed two irradiation cycles after which time total consumption of the exo-glycals 1 or 4 was observed. The β-D-galactosylnitromethylene-sulfides 3 were isolated by column chromatography in good to high yields (59–87 %, Table 1). In several reactions of 4 the formation of two products 5 and 6 could be seen. In each of these cases compounds 5 were the major products (52–75 %) and 6 could be isolated in very small amounts (<10 %, Table 2).

The structure of the products was established by NMR methods. For the D-galactose derivatives 3 the $^1$C$_4$ conformation of the pyranoid ring and the equatorial position of the CH$_2$–S–R substituent (corresponding to a β-D-C-glycosidic configuration of the C-2 centre) was deduced from the proton spectra. The D-xylene derived 5 existed also in a $^1$C$_4$ conformation with a β-α-configured C-2 as revealed by the large three-bond coupling constants of ~10 Hz throughout the spectra of these compounds. On the other hand, the proton spectra of 6 exhibited several broad singlet-like signals, which were not well resolved. This was indicative of a pyranoid ring in the $^1$C$_4$ conformation (or more probably in a conformational equilibrium involving the $^1$C$_4$ chair and boat as well as skew-boat conformations). However, the configuration of the C-2 carbon could not be established on the basis of the proton spectra since both axial and equatorial orientation of substituents of that centre must result in small vicinal couplings in the given conformation. Therefore, the $^{1}$JC$_2$H$_2$ coupling constants were determined for the pair 5c and 6c by $^1$H decoupled and undecoupled HSQC measurements. $^{1}$JC$_4$H coupling constants were obtained by measuring the distance of peaks maxima in F2 ($^1$H) dimension from undecoupled HSQC spectra. The practically equal values of these couplings (Table 3, 148.2 Hz for 5c and 147.4 Hz for 6c) indicated the axial position of H-2 in both compounds, thereby revealing the α-D configuration for the C-2 atom in 6c. Variations in the $^{1}$JC$_4$H values of the other carbons may also indicate the conformational equilibrium for these derivatives.

For the other xylose derivatives the amounts of the isolated substances did not allow to carry out similar pairwise measurements, therefore, the analogous structure is made probable by the similarities of the $^{1}$H NMR spectra.

**Table 1**

<table>
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<tr>
<th>R</th>
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<td>b</td>
<td>Ph</td>
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<tr>
<td>c</td>
<td>Bn</td>
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</tr>
<tr>
<td>d</td>
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</tr>
<tr>
<td>e</td>
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<td>87</td>
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<tr>
<td>f</td>
<td>1:1</td>
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*Total conversion of 1 was detected after two irradiations of 15 min.*

*Isolated yields after purification by column chromatography.*
The optical rotations also corroborate these assumptions at least for compounds with non-sugar appendages as derivatives 6a–e are more dextrorotatory than 5a–c, respectively. The S-glycosyl moieties of the disaccharide like 3d–f, 5d–f, and 6d–f gave the expected signals in the NMR spectra.

In conclusion, the photoinitiated addition of thiols to O-per-acetylated exo-galactal and exo-xylal gave the expected D-glycosylmethyl-sulfide type compounds in good yields with exclusive regioselectivity. The D-galactose derivatives were formed with complete β-stereoselectivity, while in the cases of the D-xylose derivatives besides the major β-C-glycosyl derivatives the α-counterparts were also isolated in small amounts. This study demonstrated that the thiol-ene reaction of exo-glycals with a wide range of thiols can be extended to sugars other than glucose. These reactions of very high regio- and stereoselectivities may be valuable tools for the construction of new types of glycomimetic compounds.

1. Experimental

1.1. General methods

Melting points were measured in open capillary tubes or on a Kofler hot-stage and are uncorrected. Optical rotations were determined with a Perkin-Elmer 241 polarimeter at room temperature. NMR spectra were recorded with Bruker 360 (360/90 MHz for $^1$H/$^13$C), Bruker 400 (400/100 MHz for $^1$H/$^13$C) or Bruker Avance II 500 spectrometer equipped with TXI z-gradient probeheads (500/125.77 MHz for $^1$H/$^13$C) spectrometer. Chemical shifts are referenced to TMS as the internal reference ($^1$H), or to the

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<td>c</td>
<td>1:10</td>
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<td>d</td>
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<td>53</td>
<td>4</td>
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* Total conversion of 4 was detected after two irradiations of 15 min.

* Isolated yields after purification by column chromatography.

* The formation of 6 was not detected.

Table 3
Selected $^1$C NMR data of compounds 5c and 6c

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<td>J_C,H</td>
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<td>154.0</td>
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<td>149.5</td>
<td>164.0</td>
<td>147.4</td>
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residual solvent signals (12C). JCH coupling constants were determined by measuring the distance of peak maximums in F2 (1H) dimension from undecoupled HSQC spectra. The assignments of the 1H NMR signals of compounds 3d, 3f, 5c and 5f were performed by their COSY spectra. Mass spectra were recorded with a Thermo LTQ XL mass spectrometer (Thermo Electron Corp., San Jose, CA, USA) operated in a full scan positive ion ESI mode. TLC was performed on DC-Alugols Kieselgel 60 F254 (Merck). TLC plates were visualized under UV light, and by gentle heating. For column chromatography Kieselgel 60 (Merck, particle size (0.063–0.200 mm) was applied. Thiols 2a–c were purchased from Sigma–Aldrich or prepared according to literature procedures (2d, 2e, 2f).

1.2. General procedure for the photoinitiated reaction of exo-glycals with thiols

To a solution of the starting glycal (1 or 4, 50–100 mg) in dry toluene (4 mL/100 mg), a thiol 2 (10 equiv of 2a–c, 11 equiv of 2d–f) and 2,2-dimethoxy-2-phenylacetophenone (DPA, 0.1 equiv) were added. The solution was irradiated by a mercury vapor lamp (λmax = 365 nm) at rt for 15 min. After addition of another 0.1 equiv of DPA photolysis irradiation was continued and, when the starting material disappeared (TLC, eluent 5:1 hexane–acetone), the solvent was removed under diminished pressure, then the residue was purified using column chromatography (eluent A 5:1 hexane–acetone; eluent B 6:1 hexane–acetone; eluent C 2:1 hexane: acetone).

1.2.1. 3,4,5,7-Tetra-O-acetyl-2,6-anhydro-1-deoxy-1-S-propyl-1-thio-o-glycero-α-manno-heptitol (3a)

By the general procedure, starting from 1 (100 mg, 0.29 mmol) to give 3a (eluent A) as a colorless oil (72% mg; 59%), Rf = 0.42 (eluent C), [α]D +5.0 (c = 0.52, CHCl3). 1H NMR (400 MHz, CDCl3) δ: 5.41 (dd, 1H, J = 11.0, 3.5 Hz, H-5), 5.12 (pt, 1H, J = 9.8 Hz, H-3), 5.02 (dd, 1H, J = 3.5, 9.8 Hz, H-4), 4.13 (dd, 1H, J = 6.5, 11.3 Hz, H-7α), 4.07 (dd, 1H, J = 6.5, 11.3 Hz, H-7β), 3.90 (dd, 1H, J = 1.1, 6.5, 6.5 Hz, H-6), 3.60 (dd, 1H, J = 3.7, 7.2, 9.8 Hz, H-2), 2.69 (dd, 1H, J = 7.2, 14.2 Hz, H-1a), 2.48 (dd, 1H, J = 1.3, 14.2 Hz, H-1b), 2.53–2.62 (m, 2H, CH2–CH2), 2.05, 2.04, 1.97 (4 × s, 4 × HOC, OA), 1.66–1.53 (m, 2H, CH2), 0.97 (t, 3H, J = 7.3 Hz, CH3). 13C NMR (101 MHz, CDCl3) δ: 170.41 (CO), 79.95, 74.34, 72.15, 69.16, 67.76 (C-2–C-6), 61.74 (C-7), 35.54, 33.58 (C-1, CH2), 22.97, 20.98, 20.84, 20.76, 13.56 (CH3), C18H28O12S (M+ 420.47 g/mol); MS: [M+H]+ = 421.58; [M+K]+ = 459.50.

1.2.2. 3,4,5,7-Tetra-O-acetyl-2,6-anhydro-1-deoxy-1-S-phenyl-1-thio-o-glycero-α-manno-heptitol (3b)

By the general procedure, starting from 1 (100 mg, 0.29 mmol) to give 3b (eluent A) as a yellow oil (82% mg; 62%), Rf = 0.37 (eluent C), [α]D −15.0 (c = 0.53, CHCl3). 1H NMR (400 MHz, CDCl3) δ: 7.39–7.33 (m, 2H, aromatic), 7.32–7.25 (m, 2H, aromatic), 7.23–7.17 (m, 1H, aromatic), 5.40 (dd, 1H, J = 1.3, 13.5 Hz, H-5), 5.22 (pseudo t, 1H, J = 10.0 Hz, H-3), 5.02 (dd, 1H, J = 3.5, 10.0 Hz, H-4), 4.10 (dd, 1H, J = 6.8, 11.3 Hz, H-7α), 4.04 (dd, 1H, J = 6.8, 11.3 Hz, H-7β), 3.91 (dd, 1H, J = 1.3, 11.2 Hz, H-6), 3.62 (dd, 1H, J = 4.4, 6.7 Hz, H-2), 3.08 (dd, 1H, J = 4.4, 13.6 Hz, H-1a), 3.12 (dd, 1H, J = 6.7, 13.6 Hz, H-1b), 2.16, 2.05, 2.04, 1.98 (4 × s, 4 × HOC, OA). 13C NMR (101 MHz, CDCl3) δ: 170.55, 170.37, 170.28, 170.01 (4 × CO), 130.01, 129.05, 126.63 (aromatic), 77.98, 74.37, 72.08, 69.25, 67.09 (C-2–C-6), 61.35 (C-7), 36.33 (C-1), 20.97, 20.84, 20.74 (CH3), C18H28O12S (M+ 424.49 g/mol); MS: [M+H]+ = 445.58; [M+K]+ = 483.50.

1.2.3. 3,4,5,7-Tetra-O-acetyl-2,6-anhydro-1-deoxy-1-S-benzyl-1-thio-o-glycero-α-manno-heptitol (3c)

By the general procedure, starting from 1 (100 mg, 0.29 mmol) to give 3c (eluent A) as a colorless oil (102% mg; 75%), Rf = 0.37 (eluent C), [α]D −10.0 (c = 0.56, CHCl3). 1H NMR (400 MHz, CDCl3) δ: 7.40–7.46 (m, 5H, aromatic), 5.41 (dd, 1H, J = 12, 3.4 Hz, H-5), 5.16 (pseudo t, 1H, J = 10.1 Hz, H-3), 5.00 (dd, 1H, J = 3.4, 10.1 Hz, H-4), 4.16
to give 3a (eluent B) as a colorless oil (80 mg; 63%). Rf = 0.47 (eluent C), [x]D −50.2 (c = 0.59, CHCl3). 1H NMR (400 MHz, CDCl3): δ = 5.40 (dd, 1H, J = 3.6, 14.4 Hz, H-1), 2.56 (dd, 1H, J = 7.2, 14.4 Hz, H-1a), 2.52 (dd, 1H, J = 3.6, 14.4 Hz, H-1b), 2.16, 2.05, 1.98, 1.97 (4 × 3H, OAc). 13C NMR (101 MHz, CDCl3): δ = 170.56, 170.37, 170.29, 169.82 (CO), 138.18, 129.18, 128.58, 127.19 (aromatic), 79.64, 74.35, 72.10, 68.98, 67.73 (C-2→C-6), 61.81 (C-7), 31.74, 32.27 (C-1, SCH2), 20.87, 20.83, 20.73 (CH3). C23H26O4S2, M+: 620.66 g/mol; MS: [M+H+] = +638.25.

12.7. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-propyl-1-thio-gulo-hexitol (5a)

By the general procedure, starting from 4 (100 mg, 0.37 mmol) to give 5a (eluent B) as a colorless oil (80 mg; 63%). Rf = 0.47 (eluent C), [x]D −50.2 (c = 0.59, CHCl3). 1H NMR (360 MHz, CDCl3): δ = 5.18 (t, 1H, J = 9.4 Hz, H-4), 4.99 (ddd, 1H, J = 5.7, 9.4, 10.7 Hz, H-5), 4.95 (0.51, CHCl3). 13C NMR (90 MHz, CDCl3): δ = 172.7, 169.85, 169.72 (CO), 79.00, 73.74, 76.81, 72.61 (C-2→C-5), 66.79 (C-6), 35.41, 33.57 (C-1, SCH2), 22.86 (CH2CO). 1H NMR (400 MHz, CDCl3): 7.11, 7.31, 10.65, 11.31 (CO), 136.45, 138.43, 140.71, 141.13 (aromatic), 77.68, 73.70, 72.67, 66.75 (C-2→C-5), 66.68 (C-6), 36.11 (C-1), 20.68 (CH3), C23H26O4S2, M+: 384.41 g/mol; MS: [M+H+] = +349.58; [M+K+] = +387.58.

12.8. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-phenyl-1-thio-gulo-hexitol (5b)

By the general procedure, starting from 4 (100 mg, 0.37 mmol) to give 5b (eluent B) as a colorless oil (73 mg; 52%). Rf = 0.42 (eluent C), [x]D −49.0 (c = 0.53, CHCl3). 1H NMR (360 MHz, CDCl3): δ = 7.41→7.16 (m, 5H, aromatic), 5.01 (dd, 1H, J = 5.6, 9.4, 11.1 Hz, H-4, 0.51, CHCl3). 13C NMR (90 MHz, CDCl3): δ = 172.60, 169.69, 169.51 (CO), 79.32, 78.25, 78.73, 74.35, 74.72, 71.13, 68.74, 67.62, 67.32, 67.15 (C-2→C-6 and C-1′→C-5′), 61.34 (C-1), 61.31 (C-6), 30.58 (C-1), 20.85, 20.83, 20.73, 20.69, 20.66, 20.62 (CH3), C26H28O4S2, M+: 708.68 g/mol; MS: [M+Na]+ = +731.83.

12.9. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-benzyl-1-thio-gulo-hexitol (5c)

By the general procedure, starting from 4 (100 mg, 0.37 mmol) to give 5c (eluent B) as a colorless oil (99 mg; 68%). Rf = 0.38 (eluent C), [x]D +50.8 (c = 0.52, CHCl3). 1H NMR (360 MHz, CDCl3): δ = 7.35→7.19 (m, 5H, aromatic), 5.14 (t, 1H, J = 9.4 Hz, H-4), 4.97 (0.51, CHCl3). 13C NMR (90 MHz, CDCl3): δ = 173.50, 170.90, 169.88, 168.73, 169.51 (CO), 83.75, 82.75, 74.35, 74.74, 71.67, 69.78, 68.52, 67.60 (C-2→C-6 and C-1′→C-5′), 65.06 (C-7), 61.45 (C-5′), 311.3 (C-1), 20.91, 20.80, 20.70 (CH3), C27H30O4S2, M+: 736.62 g/mol; MS: [M+Na]+ = +659.92.

12.10. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-benzyl-1-thio-gulo-hexitol (5d)

By the general procedure, starting from 4 (50 mg, 0.185 mmol) to give 5d (eluent B) as a colorless oil (81 mg; 69%). Rf = 0.16 (eluent C), [x]D −47.0 (c = 0.58, CHCl3). 1H NMR (360 MHz, CDCl3): δ = 5.39 (dd, 1H, J = 1.1, 3.3 Hz, H-4), 5.19 (t, 1H, J = 10.0 Hz, H-8), 0.52 (1H, J = 9.5 Hz, H-5), 5.00 (dd, 1H, J = 5.7, 9.5, 10.5 Hz, H-6), 4.93 (0.52, CHCl3). 13C NMR (90 MHz, CDCl3): δ = 170.48, 169.75, 169.60 (CO), 138.03, 129.91, 128.51, 127.11 (aromatic), 81.62, 77.30, 71.59, 69.19 (C-2→C-5), 66.79 (C-6), 36.94 (C-1), 32.10 (SCH2), 20.76 (CH3), C27H30O4S2, M+: 396.45 g/mol; MS: [M+H+] = 397.58; [M+K+] = 435.58.

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1.2.11. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-(2,3,4-tri-O-acetyl-β-oxypropionyl) -thio-1-ido-gulo-hexitol (5e)

By the general procedure, starting from 4 (50 mg, 0.185 mmol) to give 5e (eluent B) as a colorless oil (78 mg; 75%). Rf = 0.20 (eluent C), [α]D -96 (c = 0.52, CHCl3).1H NMR (360 MHz, CDCl3): δ: 5.14 (t, 1H, J = 9.4 Hz, H-4), 5.12 (t, 1H, J = 8.4 Hz, H-3), 4.99—4.82 (m, 4H, H-1, H-3, H-5, H-2, H-4), 4.58 (d, 1H, J = 8.4 Hz, H-1), 4.19 (dd, 1H, J = 5.0, 11.2 Hz, H-6eq), 4.09 (dd, 1H, J = 5.5, 11.2 Hz, H-6ax), 3.58 (dd, 1H, J = 2.9, 7.0 Hz, H-2), 3.34 (dd, 1H, J = 8.8, 11.7 Hz, H-5ax), 3.24 (t, 1H, J = 11.7 Hz, H-5eq), 2.90 (dd, 1H, J = 7.0, 14.0 Hz, H-1B), 2.63 (dd, 1H, J = 7.0, 14.0 Hz, H-1B), 2.05 (s, 3H, CH3), 1.56 (m, 5H, CH2), 1.34, 1.33 (4H, CH2). 13C NMR (91 MHz, CDCl3): δ: 170.43, 169.89, 169.85, 169.70, 169.53 (CO), 83.17, 78.04, 73.79, 71.93, 72.17, 69.64, 61.12, 68.82 (C-2—C5 and C-1—C4), 68.63 (C-6), 65.35 (C-5), 30.85, 20.79 (CH3). C23H32O14S, M+: 564.56 g/mol; MS: [M+Na]+ = 588.08.

1.2.12. 3,4,5-Tri-O-acetyl-2,6-anhydro-1-deoxy-1-S-(12,3,4,5-tetra-O-isopropylidene-β-o-galactopyranos-6-yl)-thio-1-ido-gulo-hexitol (5f)

By the general procedure, starting from 4 (100 mg, 0.38 mmol) to give 5f (eluent B) as a colorless oil (108 mg; 53%). Rf = 0.36 (eluent C), [α]D -71 (c = 0.58, CHCl3).1H NMR (360 MHz, CDCl3): δ: 5.47 (d, 1H, J = 5.5, 9.5 Hz, H-5), 5.13 (pseudo t, 1H, J = 9.5 Hz, H-4), 4.92 (dd, 1H, J = 5.5, 9.5 Hz, H-5), 4.86 (pseudo t, 1H, J = 9.5 Hz, H-3), 1H, 4.57 (dd, J = 2.4, 7.9 Hz, H-4), 4.27 (dd, 1H, J = 2.2, 5.1 Hz, H-2), 4.12 (dd, 1H, J = 2.2, 5.1 Hz, H-2), 3.85 (m, 1H, J = 5.5), 3.52 (dd, 1H, J = 2.7, 5.2 Hz, H-3), 3.24 (dd, 1H, J = 10.5, 11.5 Hz, H-3), 2.80—2.69 (m, 3H, CH3-1A and 2-6H), 2.57 (dd, 1H, J = 1.8, 14.3 Hz, H-1B), 2.00, 1.99, 198 (3H, 3×3, CH3O), 1.50, 1.40, 1.31, 128 (4×5, 4×3, CH3), 13C NMR (91 MHz, CDCl3): δ: 170.08, 169.86, 169.73 (CO), 109.29, 108.65 (C), 96.96, 78.97, 73.74, 71.74, 71.65, 70.95, 70.55, 69.23, 67.72 (C-2—C5 and C-1—C4), 66.75 (C-6), 33.96 (C1), 32.78 (C-6), 26.10, 26.05, 24.96, 24.51, 20.76 (CH3). C25H38O18S, M+: 548.60 g/mol; MS: [M+H]+ = 566.42.
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