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Note

A facile preparation of trehalose analogues: 1,1-thiodisaccharides

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ABSTRACT

The synthesis of 1,1-thiodisaccharide trehalose analogues in good to excellent yields by a Lewis acid ($BF_3{\cdot}Et_2O$)-catalysed coupling of sugar per-*O*-acetate with thiosugar is described. The reactivity of different sugar per-*O*-acetates and thiosugars is explored.

Trehalose is a non-reducing disaccharide in which two molecules of glucose are linked via a 1,1-glycosidic bond.[1] Of the anomers possible, it is only the α,α-configuration that is found in animals, plants and microorganisms,[2] where it serves as a source of energy and carbon.[1] In addition, trehalose-derivatised lipids are important components of bacterial cell walls, and are therefore crucial to cell growth.[3] Thiotrehalose, in which the glycosidic oxygen is replaced by a sulfur atom, possesses greater chemical and enzymatic stability than its *O*-linked isostere. Thiodisaccharides that are structurally related to trehalose (including thiotrehalose) have attracted interest as enzyme inhibitors. For example, growth of *Escherichia coli* is inhibited by trehalose analogue 1-thio-β-D-galactopyranosyl-β-D-galactopyranoside.[4] Thiotrehalose analogues have also found other applications, including use in enzyme purification,[5–7] and in the study of enzyme kinetics.[8–10] The physical properties of these molecules have also been extensively studied, for example rotatory dispersion[11] and molecular dynamics.[12,13]

There are several reported methods for the synthesis of 1,1-thiodisaccharides. Initial reports described the condensation of per-*O*-acetylated chlorosugars with potassium alkylxanthate (to give the α,α-isomer),[14,15] or the reaction between a thiosugar and acetobromosugar.[16] Since then other methods have been developed in order to improve reaction yields, including the tri(diethylamino)-phosphine-promoted mono-desulfurisation of glycosyl disulfides.[17,18] This method affords *cis*-related 1-thioglycosides, but requires the prior synthesis of a glycosyl disulfide, which is not always straightforward. Using another procedure, a mixture of α,α-1-, α,β-1- and β,β-1-thiotrehaloses was obtained by the hydrogen fluoride-mediated reaction of D-glucose with hydrogen sulfide.[19] The use of toxic reagents and the need for specialised apparatus are drawbacks to this method. More recently, the reaction of sugar-thiouronium bromides with acetohalosugars either at room temperature[20] or under microwave conditions[21] afforded 1,1-thiodisaccharides in good yields. Methods involving a two-phase system have also been employed, for instance using sodium sulfide[22] and sodium hydrogensulfate[23,24] or thioacetamide.[25] In summary, the methods described here generally involve long reaction times and frequently require the use of toxic and malodorous reagents. There is therefore a clear need for alternative strategies.

The Lewis acid $BF_3{\cdot}Et_2O$ has found wide application in the synthesis of thioglycosides, not least in promoting the reaction between per-*O*-acetylated sugars and alkyl- and aryl-thiols or alkyl- and aryl-thiotrimethylsilanes.[26–28] Our interest in the chemical biology of thiodisaccharides[29,30] meant we required a facile route to thiotrehalose analogues. We investigated the use of $BF_3{\cdot}Et_2O$ in the synthesis of such molecules. Initially we explored the $BF_3{\cdot}Et_2O$-catalysed reaction of glucose per-*O*-acetate **1a** with per-*O*-acetylated 1-thioglucose **2a** (Table 1). This reaction, first introduced by Ferrier and Furneaux,[31] can also be used for the synthesis of alkyl- and aryl-thioglycosides.[26] The desired 1,1-thiodisaccharide **3a** was obtained in good yield with minimal by-products (Table 2, entry 1). Significantly, this method avoided the need to synthesise the acetobromosugar glycosyl donor, thereby reducing the number of steps in the synthesis. The study was extended to different sugar per-*O*-acetates **1a–i** and to different 1-thiosugars **2a–g** (Table 3).

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Table 1
Per-*O*-acetate sugars and thiosugars that were studied

Series	Per-*O*-Acetate sugar (**1**)	1-Thio sugar (**2**)
D-Glucose	OAc-Glc-β-OAc **1a** OAc-Glc-α-OAc **1b**	OAc-Glc-β-SH **2a**
D-Galactose	OAc-Gal-β-OAc **1c**	OAc-Gal-β-SH **2c**
D-Mannose	OAc-Man-α-OAc **1d** OAc-Man-β-OAc **1e**	OAc-Man-α-SH **2d**
L-Fucose	OAc-Fuc-β-OAc **1f** OAc-Fuc-α-OAc **1g**	OAc-Fuc-β-SH **2f** OAc-Fuc-α-SH **2g**
L-Rhamnose	OAc-Rha-β-OAc **1h** OAc-Rha-α-OAc **1i**	

This methodology was further investigated by varying the reaction time for OAc-Glc-β-OAc **1a** and OAc-Glc-β-SH **2a** (Table 2). OAc-Gal-β-OAc **1c** was more reactive than OAc-Glc-β-OAc **1a**, with a reaction time of 2 h sufficient to complete the consumption of **1c** (Table 2, entry 3), as expected.[32] It was found in the case of β,β-thio-diglucose **3a**, however, that 2.0 equiv of **2a** and longer reaction times (18 h) were optimal (Table 2, entries 1 and 2). Based on the reactivity of **1a**, a series of reactions were carried out overnight (Table 3). Reaction yield was dependent on the anomeric configuration of the glycosyl donor as observed previously.[31] No reaction was observed when using alpha-glucose derivative OAc-Glc-α-OAc **1b** as donor. The study was extended to investigate the reactivity of both fully acetylated anomers of mannose (entries 5 and 6), fucose (entries 10 and 11) and rhamnose (entries 12 and 13) with per-*O*-acetylated 1-β-thioglucose **2a**.

The results obtained are partly in contrast to those of a previous study,[33] in which unsuccessful attempts were made to synthesise alkyl thiomannosides from D-mannose per-*O*-acetate using $BF_3{\cdot}Et_2O$. Use of the alternative Lewis acid, $FeCl_3$, solved this problem in that instance.[33] Others have since employed $BF_3{\cdot}Et_2O$ to successfully synthesise aryl thiomannosides.[34,35] In this study, mannosyl thiodisaccharides were obtained, albeit in slightly lower yields than the corresponding glucosyl derivatives (Table 3, entries 5–7).

Single anomer per-*O*-acetyl glycosyl donors generally yielded an anomeric mixture of thiodisaccharides (at the donor anomeric carbon). This result is consistent with that previously reported when alkyl thiols were used as glycosyl acceptors.[33] In the case of OAc-β-Glc-OAc and OAc-β-Gal-OAc we observed that the proportion of α anomer obtained was very low. These minor products were not isolated in this study. The ratio of anomers was determined by analysis of the proton NMR spectrum of the crude reaction mixture. With mannose per-*O*-acetate as donor, the α-anomer was favoured (α:β ratio of ca. 3:1) as observed previously by Ferrier and Furneaux.[36] For the fully acetylated 6-deoxy sugars, an α:β ratio of ca. 1:1 was obtained with L-fucose per-*O*-acetate while L-rhamnose per-*O*-acetate gave an α:β ratio of ca. 2:1. Compound characterisation was achieved using ^1H, 2D COSY and HMQC NMR experiments. The Pearl effect suggests that for monosaccharides, the $^1J_{(C\text{-}1,H\text{-}1)}$ coupling constant is higher (ca. 10 Hz) in the α anomer.[37,38] Based on this principle, the anomeric configurations of the mannosides and rhamnosides were confirmed.

In conclusion, the preparation of a series of 1,1-thiodisaccharides using the Lewis acid $BF_3{\cdot}Et_2O$ is reported. The method described herein has the advantage of producing thiotrehalose and analogues (including non-symmetrical thiodisaccharides) in a convenient, facile manner. Significantly, it was not necessary to activate the glycosyl donor by conversion to an acetohalosugar before coupling with the thiol. The methodology outlined is applicable to the synthesis of a wide range of thiodisaccharides, which have potential as enzyme inhibitors and molecular probes to aid understanding in complex biological systems.

1. Experimental

1.1. General methods

Optical rotations were measured using a PerkinElmer 341 polarimeter. NMR spectra were generated on a JEOL ECA-600 spectrometer (^1H at 600 MHz and ^{13}C at 150.9 MHz) or a Bruker DPX-400 spectrometer (^1H at 400 MHz and ^{13}C at 100.6 MHz). Chemical shifts are reported in ppm downfield relative to tetramethylsilane (solvent $CDCl_3$). Spectral assignment was accomplished using 2D COSY and HMQC measurements as well as coupling constant analysis where possible. Non-decoupled ^{13}C NMR experiments were employed to determine the $^1J_{(C\text{-}1,H\text{-}1)}$

Table 2
Importance of reaction time

per-*O*-acetate sugar + thiosugar $\xrightarrow{BF_3.Et_2O}$ **thiodisaccharide**

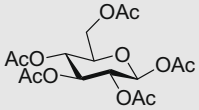
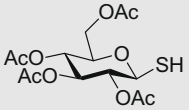
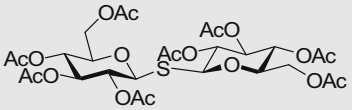
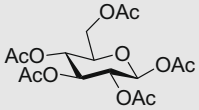
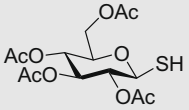
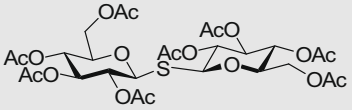
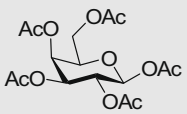
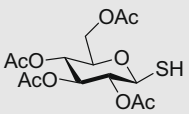
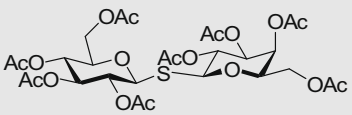
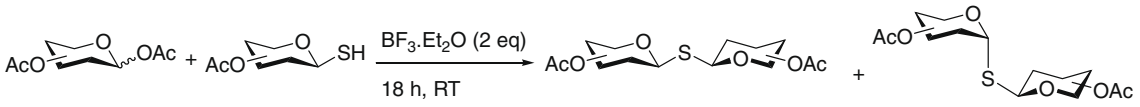
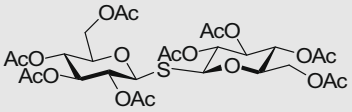
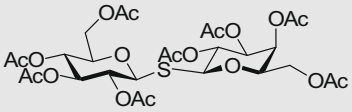
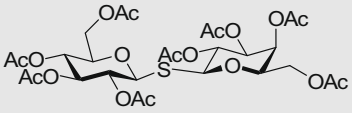
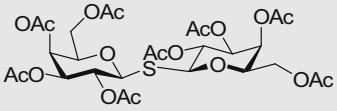
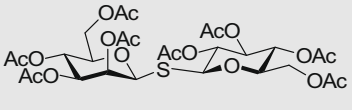
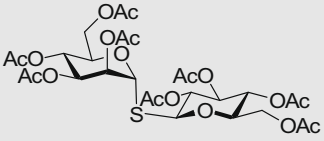
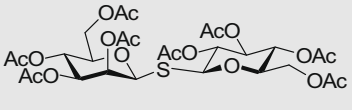
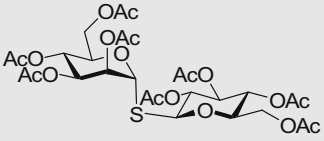
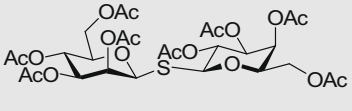
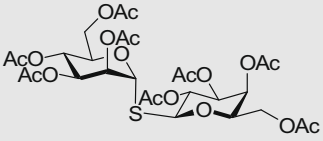
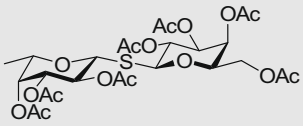
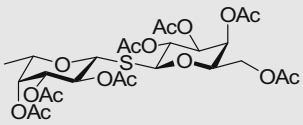
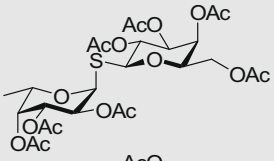
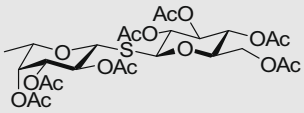
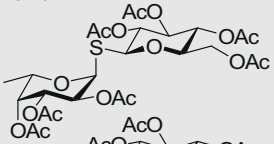
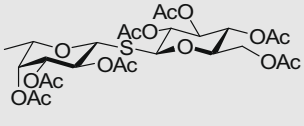
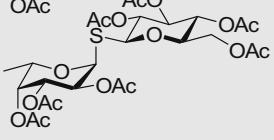
Entry	Per-*O*-acetate sugar	**2**	Product	Yield (%)
1				86
	1a	(2.0 eq **2a**, 18h)	**3a**	
2				37
	1a	(2.0 eq **2a**, 2h)	**3a**	
3				70
	1c	(2.0 eq **2a**, 2h)	**3b**	

Table 3
Synthesis of thiodisaccharides

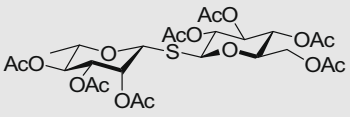
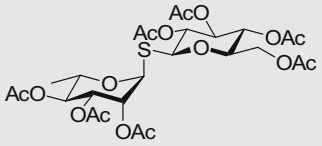
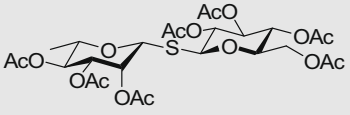
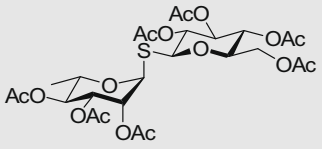
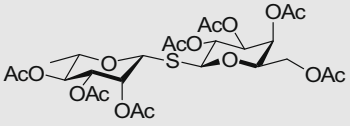
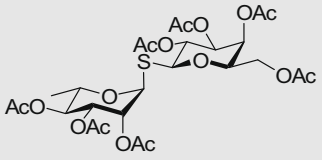
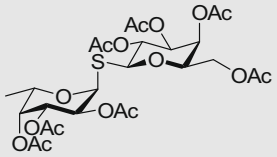
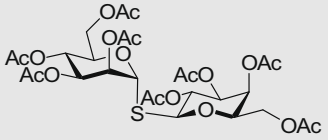


1 (1 eq) **2** (2 eq) **3** **4**

	1	2	3		4		Ratio 3:4[a]
1	**1a**	**2a**		**3a** (86%)	No isolated	–	9:1
2	**1c**	**2a**		**3b** (70%)[b]	Not isolated	–	9:1
3	**1a**	**2c**		**3b** (80%)	Not isolated	–	9:1
4	**1c**	**2c**		**3c** (85%)[b]	Not isolated	–	9:1
5	**1d**	**2a**		**3d** (14%)		**4d** (39%)	1:2.8
6	**1e**	**2a**		**3d** (11%)		**4d** (32%)	1:2.9
7	**1e**	**2c**		**3e** (15%)		**4e** (42%)	1:2.8
8	**1c**	**2f**		**3f** (68%)[b]	Not isolated	–	9:1
9	**1g**	**2c**		**3f** (45%)		**4f** (40%)	1.1:1
10	**1g**	**2a**		**3g** (24%)		**4g** (21%)	1.1:1
11	**1f**	**2a**		**3g** (48%)		**4g**(26%)	1.8:1

(*continued on next page*)

Table 3 (*continued*)

	1	2	3		4		Ratio 3:4[a]
12	**1h**	**2a**		**3h** (26%)		**4h** (44%)	1:1.7
13	**1i**	**2a**		**3h** (27%)		**4h** (50%)	1:1.9
14	**1i**	**2c**		**3i** (14%)		**4i** (20%)	1:1.4
15	**1c**	**2g**	Not isolated	–		**4f** (35%)[b]	1:9
16	**1c**	**2d**	Not isolated	–		**4e** (70%)[b]	1:9

[a] Determined by ^{1}H analysis of the crude reaction mixture.
[b] Reaction time 2 h.

coupling constants where indicated; in accordance with the findings of Bock and Pedersen[38] the assignment of configuration has been made on the basis that $^1J_{\alpha(C\text{-}1,H\text{-}1)} > {}^1J_{\beta(C\text{-}1,H\text{-}1)}$. Low resolution mass spectra (LRMS) were generated using a Micromass Quattro Ultima mass spectrometer. Analytical thin-layer chromatography (TLC) was performed on plates precoated with silica gel 60 F_{254} (Merck). Visualisation of the plates was carried out using UV light (254 nm), and/or a solution of 10% H_2SO_4 in EtOH followed by heating. Flash column chromatography was carried out on silica gel (Merck). All solvents were of reagent grade. **1a**, **1c** and **2a** were obtained commercially from Sigma–Aldrich. Compound **1c** was prepared from D-glucose (Ac_2O, I_2).[39] Other reducing sugars were per-*O*-acetylated (Ac_2O, pyridine) and the mixture of anomers was purified by preparative high-performance liquid chromatography (HPLC) to give the respective sugar peracetates **1d**, **1e**, **1f**, **1g**, **1h** and **1i**. Thiosugars **2c**, **2d**, **2f** and **2g** were prepared from the corresponding per-*O*-acetylated sugars in two steps: (1) bromination at the anomeric carbon using HBr–AcOH, and (2) reaction of the acetobromosugar with thiourea, followed by basic hydrolysis.[40] HPLC analysis and purification were performed on an Agilent Technologies 1200 HPLC system with diode array detection, using C_{18} reversed phase columns (Agilent Eclipse XDB—analytical: 4.6 × 100 mm; preparative: 21.2 × 150 mm), solvent A (90% H_2O, 10% MeCN + 0.05% TFA) and solvent B (90% MeCN, 10% H_2O + 0.05% TFA). Compounds were eluted using: 20% B (0–2 min), 20–60% B (2–7 min, linear gradient), 60–70% B (7–8 min, linear gradient), 70–100% B (8–13 min, linear gradient), 100% B (13 -18 min), 100–20% B (18–20 min, linear gradient).

1.2. General procedure for the synthesis of thiodisaccharides

$BF_3{\cdot}Et_2O$ (1.0 mmol) and 1-thiosugar **2** (1.0 mmol) were added to a stirred solution of sugar per-*O*-acetate **1** (0.50 mmol) in anhydrous CH_2Cl_2 (5 mL) under an argon atmosphere. The reaction mixture was stirred for 2 h (galactose per-*O*-acetate) and 18 h (glucose, mannose, rhamnose and fucose per-*O*-acetates). Thereafter, CH_2Cl_2 (50 mL) was added and the mixture was extracted with satd aq $NaHCO_3$ (50 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (1:1 petroleum ether–EtOAc) gave the desired thiodisaccharide. Mixtures of anomers otherwise inseparable by this method were separated by preparative HPLC after flash chromatography.

1.2.1. 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (3a)

Amorphous solid, lyophilised from water: R_f 0.42 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ − 34.0 ± 1.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.98, 2.01, 2.02, 2.09 (s, 12H, 4OAc), 3.66 (m, 1H, H-5), 4.13 (dd, 1H, $J_{5,6a}$ 2.0 Hz, $J_{6a,6b}$ 12.3 Hz, H-6a,), 4.24 (dd, 1H, $J_{5,6b}$ 4.8 Hz, $J_{6a,6b}$ 12.3 Hz, H-6b), 4.80 (d, 1H, $J_{1,2}$ 10.3 Hz, H-1), 5.03 (dd, 1H, $J_{1,2}$ 10.3 Hz, $J_{2,3}$ 9.6 Hz, H-2), 5.07 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 9.6 Hz, H-4), 5.20 (dd, 1H, $J_{3,4}$ 9.6 Hz, $J_{4,5}$ 8.9 Hz, H-3); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 20.67, 20.72, 20.85 (8 × OCH_3), 62.12 (2 × C-6), 68.24 (2 × C-4), 70.20 (2 × C-2), 73.89 (2 × C-3), 76.22 (2 × C-5), 80.69 (2 × C-1), 169.40, 169.46, 170.24, 170.67 (8 × CO); HRMS (ESI) calcd for $C_{28}H_{42}O_{18}NS$ $[M+NH_4]^+$ 712.2117. Found 712.2127; lit.[14] $[\alpha]_D^{20}$ − 35.

1.2.2. 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (3b)

Amorphous solid, lyophilised from water: R_f 0.42 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ − 10.0 ± 1.0 (*c* 0.37, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 1.95, 1.97, 2.00, 2.02, 2.02, 2.04, 2.07, 2.13 (8s, 24H, 8OAc), 3.66 (m, 1H, H-5_{Glc}), 3.88 (dd, 1H, $J_{5,6a}$ 6.4 Hz, $J_{5,6b}$ 6.7 Hz, H-5_{Gal}), 4.08–4.14 (m, 3H, H-$6a_{Glc}$, H-$6a_{Gal}$, and H-$6b_{Gal}$), 4.23 (dd, 1H, $J_{5,6b}$ 4.9 Hz, $J_{6a,6b}$ 12.3 Hz, H-$6b_{Glc}$), 4.78 (d, 1H, $J_{1,2}$ 9.6 Hz, H-1_{Gal}), 4.80 (d, 1H, $J_{1,2}$ 9.6 Hz, H-1_{Glc}), 5.00 (dd, 1H, $J_{1,3}$ 9.6 Hz, $J_{2,3}$ 9.6 Hz, H-2_{Glc}), 5.02 (dd, 1H, $J_{3,4}$ 3.1 Hz, $J_{2,3}$ 9.6 Hz, H-3_{Gal}), 5.06 (dd, 1H, $J_{3,4}$ 9.6 Hz, $J_{4,5}$ 9.6 Hz, H-4_{Glc}), 5.17–5.20 (m, 2H, H-2_{Gal}, H-3_{Glc}), 5.41 (d, 1H, $J_{3,4}$ 3.1 Hz, H-4_{Gal}); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 20.66, 20.74, 20.77, 20.78, 20.80, 20.83 (8 × OCH_3), 61.45 (C-6_{Gal}), 62.14 (C-6_{Glc}), 67.16 (C-4_{Gal}), 67.34 (C-3_{Glc}), 68.25 (C-4_{Glc}), 70.16 (C-2_{Glc}), 71.85 (C-3_{Gal}), 73.88 (C-2_{Gal}), 74.75 (C-5_{Gal}), 76.17 (C-5_{Glc}), 80.73 (C-1_{Glc}), 81.28 (C-1_{Gal}), 169.38, 169.46, 169.56, 170.08, 170.24, 170.25, 170.42, 170.61 (8 × CO); HRMS (ESI) calcd for $C_{28}H_{42}O_{18}NS$ $[M+NH_4]^+$ 712.2117. Found 712.2117.

1.2.3. 2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (3c)

Amorphous solid, lyophilised from water: R_f 0.46 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ + 6.0 ± 2.0 (*c* 0.45, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 1.07, 2.05, 2.05, 2.16 (4s, 12H, 4OAc), 3.90 (m, 1H, H-5), 4.10 (dd, 1H, $J_{5,6a}$ 6.6 Hz, $J_{6a,6b}$ 11.3 Hz, H-6a), 4.16 (dd, 1H, $J_{5,6b}$ 6.7 Hz, $J_{6a,6b}$ 11.3 Hz, H-6b), 4.79 (d, 1H, $J_{1,2}$ 10.1 Hz, H-1), 5.04 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 9.9 Hz, H-3), 5.21 (dd, 1H, $J_{2,3}$ 9.9 Hz, $J_{1,2}$ 10.1 Hz, H-2), 5.43 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 20.66, 20.77, 20.79, 20.87 (8 × OCH_3), 61.47 (2 × C-6), 67.22 (2 × C-4), 67.36 (2 × C-2), 71.92 (2 × C-3), 74.77 (2 × C-5), 81.45 (2 × C-1), 169.57, 170.11, 170.27, 170.45 (8 × CO); HRMS (ESI) calcd for $C_{28}H_{42}O_{18}NS$ $[M+NH_4]^+$ 712.2117. Found 712.2125.

1.2.4. 2,3,4,6-Tetra-*O*-acetyl-β-D-mannopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (3d)

Amorphous solid, lyophilised from water: R_f 0.44 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ − 47.0 ± 1.0 (*c* 0.27, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 1.96, 1.99, 2.02, 2.03, 2.04, 2.10, 2.10, 2.16 (8s, 24H, 8OAc), 3.66–3.70 (m, 2H, H-5_{Glc}, and H-5_{Man}), 4.09–4.17 (m, 2H, H-$6a_{Man}$, and H-$6a_{Glc}$), 4.24 (dd, 1H, $J_{5,6b}$ 4.6 Hz, $J_{6a,6b}$ 12.5 Hz, H-$6b_{Glc}$), 4.29 (dd, 1H, $J_{5,6b}$ 5.6 Hz, $J_{6a,6b}$ 12.5 Hz, H-$6b_{Man}$), 4.81 (d, 1H, $J_{1,2}$ 10.0 Hz, H-1_{Glc}), 5.00 (dd, 1H, $J_{1,2}$ 10.1 Hz, $J_{2,3}$ 9.3 Hz, H-2_{Glc}), 5.05 (d, 1H, $J_{1,2}$ 1.2 Hz, H-1_{Man}), 5.06–5.11 (m, 2H, H-3_{Man}, and H-4_{Glc}), 5.20–5.26 (m, 2H, H-3_{Glc}, and H-4_{Man}), 5.48 (dd, 1H, $J_{1,2}$ 1.2 Hz, $J_{2,3}$ 3.3 Hz, H-2_{Man}); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 20.62, 20.66, 20.71, 20.75, 20.76, 20.85, 20.90 (8 × OCH_3), 61.94 (C-6_{Glc}), 62.83 (C-6_{Man}), 65.73, 68.17, 70.06, 70.27, 71.75, 73.76 (C-2_{Glc}, C-3_{Glc}, C-4_{Glc}, C-2_{Man}, C-3_{Man} and C-4_{Man}), 76.14, 76.71 (C-5_{Glc} and C-5_{Man}), 79.27 (C-1_{Man}), 80.94 (C-1_{Glc}), 169.37, 169.43, 169.96, 170.07, 170.27, 170.71, 170.75 (8 × CO); HRMS (ESI) calcd for $C_{28}H_{42}O_{18}NS$ $[M+NH_4]^+$ 712.2117. Found 712.2121.

1.2.5. 2,3,4,6-Tetra-*O*-acetyl-β-D-mannopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (3e)

Amorphous solid, lyophilised from water: R_f 0.41 (1:2 petroleum ether–EtOAc) ; $[\alpha]_D^{20}$ − 65.0 ± 5.0 (*c* 0.03, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 1.96, 1.97, 2.03, 2.05, 2.05, 2.09, 2.15, 2.16 (8s, 24H, 8OAc), 3.66–3.68 (m, 1H, H-5_{Man}), 3.91 (dd, 1H, $J_{5,6a}$ 6.6 Hz, $J_{5,6a}$ 6.6 Hz, H-5_{Gal}), 4.10–4.17 (m, 3H, H-$6a_{Gal}$, H-$6b_{Gal}$, and H-$6a_{Man}$), 4.29 (dd, 1H, $J_{5,6b}$ 5.8 Hz, $J_{6a,6b}$ 12.3 Hz, H-$6b_{Man}$), 4.78 (d, 1H, $J_{1,2}$ 10.1 Hz, H-1_{Gal}), 5.04 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 9.9 Hz, H-3_{Gal}), 5.06 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1_{Man}), 5.08 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.9 Hz, H-3_{Man}), 5.20 (dd, 1H, $J_{1,2}$ 10.1 Hz, $J_{2,3}$ 9.9 Hz, H-2_{Gal}), 5.24 (dd, 1H, $J_{3,4}$ 9.9 Hz, $J_{4,5}$ 9.9 Hz, H-4_{Man}), 5.43 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4_{Gal}), 5.49 (dd, 1H, $J_{1,2}$ 1.0 Hz, $J_{2,3}$ 3.4 Hz, H-2_{Man}); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 20.63, 20.64, 20.71, 20.76, 20.79, 20.86, 20.90 (8 × OCH_3), 61.47 (C-6_{Gal}), 62.47 (C-6_{Man}), 65.77 (C-4_{Man}), 67.12 (C-4_{Gal}), 67.36 (C-2_{Gal}), 70.35 (C-2_{Man}), 71.78, 71.81 (C-3_{Gal} and C-3_{Man}), 74.75 (C-5_{Gal}), 76.96 (C-5_{Man}), 79.36 (C-1_{Man}), 81.43 (C-1_{Gal}), 169.68, 169.74, 169.93, 170.06, 170.11, 170.27, 170.45, 170.68 (8 × CO); $^1J_{\beta\text{-Man(C-1,H-1)}}$ 156.0 Hz; HRMS (ESI) calcd for $C_{28}H_{42}O_{18}NS$ $[M+NH_4]^+$ 712.2117. Found 712.2108.

1.2.6. 2,3,4-Tri-*O*-acetyl-β-L-fucopyranosyl 2,3,4,6-*O*-acetyl-1-thio-β-D-galactopyranoside (3f)

Amorphous solid, lyophilised from water: R_f 0.57 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ + 6.0 ± 1.0 (*c* 0.31, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 1.21 (d, 3H, ^3J 6.3 Hz, CH_3), 1.96, 1.97, 2.02, 2.04, 2.15, 2.18 (6s, 21H, 7OAc), 3.83–3.86 (m, 1H, H-5_{Fuc}), 3.95 (ddd, 1H, $J_{4,5}$ 1.0 Hz, $J_{5,6a}$ 6.8 Hz, $J_{5,6b}$ 6.5 Hz, H-5_{Gal}), 4.07 (dd, 1H, $J_{5,6a}$ 6.8 Hz, $J_{6a,6b}$ 11.3 Hz, H-$6a_{Gal}$), 4.19 (dd, 1H, $J_{5,6b}$ 6.5 Hz, $J_{6a,6b}$ 11.3 Hz, H-$6b_{Gal}$), 4.58 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1_{Fuc}), 4.74 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1_{Gal}), 5.01 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 9.9 Hz, H-3_{Fuc}), 5.04 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 9.9 Hz, H-3_{Gal}), 5.22–5.27 (m, 3H, H-2_{Gal}, H-2_{Fuc}, H-4_{Fuc}), 5.41 (dd, 1H, $J_{4,5}$ 1.0 Hz, $J_{3,4}$ 3.4 Hz, H-4_{Gal}); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 16.41 (C-6_{Fuc}), 20.68, 20.74, 20.76, 20.80, 20.89 (7 × OCH_3), 61.48 (C-6_{Gal}), 67.31 (C-4_{Gal}), 67.56, 68.03, 70.49 (C-2_{Gal}, C-2_{Fuc} and C-4_{Fuc}), 72.07 (C-3_{Gal}), 72.60 (C-3_{Fuc}), 73.84 (C-5_{Fuc}), 74.78 (C-5_{Gal}), 81.51 (C-1_{Fuc}), 81.82 (C-1_{Gal}), 169.22, 169.37, 170.29, 170.33, 170.56, 170.70 (7 × CO); $^1J_{\beta\text{-Fuc(C-1,H-1)}}$ 155.3 Hz; HRMS (ESI) calcd for $C_{26}H_{40}O_{16}NS$ $[M+NH_4]^+$ 654.2062. Found 654.2067.

1.2.7. 2,3,4-Tri-*O*-acetyl-β-L-fucopyranosyl 2,3,4,6-*O*-acetyl-1-thio-β-D-glucopyranoside (3g)

Clear oil, becomes amorphous solid on standing: R_f 0.12 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ − 7.9 ± 0.2 (*c* 1.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.20 (d, 3H, ^3J 6.4 Hz, CH_3), 1.96, 1.99, 2.02, 2.03, 2.08, 2.18 (6s, 21H, 7OAc), 3.73 (m, 1H, H-5_{Glc}), 3.85 (q, 1H, $J_{5,6}$ 6.4 Hz, H-5_{Fuc}), 4.13 (d, 1H, $J_{6a,6b}$ 12.4 Hz, H-$6a_{Glc}$), 4.25 (dd, 1H, $J_{5,6b}$ 5.2 Hz, $J_{6a,6b}$ 12.4 Hz, H-$6b_{Glc}$), 4.58 (d, 1H, *J* 10.0 Hz, H-1_{Glc}), 4.74 (d, 1H, *J* 10.0 Hz, H-1_{Fuc}), 4.99–5.05 (m, 2H, H-2_{Fuc}, H-3_{Fuc}), 5.09 (1H, t, $J_{3,4=4,5}$ 9.6 Hz, H-4_{Glc}), 5.20 (t, 3H, $J_{2,3=3,4}$ 9.6 Hz, H-3_{Glc}), 5.25–5.27 (m, 2H, H-2_{Glc}, H-4_{Fuc}); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 15.88 (C-6_{Fuc}), 20.19, 20.32, 20.34 (7C, OCH_3), 62.05 (C-6_{Glc}), 67.74, 67.98, 70.07, 70.35 (C-2_{Glc}, C-2_{Fuc}, C-4_{Glc}, C-4_{Fuc}), 72.40 (C-3_{Fuc}), 73.68 (C-5_{Fuc}), 74.00 (C-3_{Glc}), 76.15 (C-5_{Glc}), 81.05 (2C, C-1_{Glc}, C-1_{Fuc}), 169.66, 169.74, 169.88, 170.65, 170.85, 171.08, 171.23 (7C, CO); HRMS (ESI) calcd for $C_{26}H_{36}O_{16}S$ $[M+NH_4]^+$ 654.2062. Found 654.2059.

1.2.8. 2,3,4-Tri-*O*-acetyl-β-L-rhamnopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (3h)

Amorphous solid, lyophilised from water: R_f 0.67 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ − 13.0 ± 1.0 (*c* 0.23, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 1.26 (d, 3H, ^3J 6.1 Hz, CH_3), 1.96, 1.99, 2.02, 2.02, 2.04, 2.10, 2.15 (7s, 21H, 7OAc), 3.34–3.49 (m, 1H, H-5_{Rha}), 3.72–3.75 (m, 1H, H-5_{Glc}), 4.11 (dd, 1H, $J_{5,6a}$ 2.1 Hz, $J_{6a,6b}$ 12.4 Hz, H-$6a_{Glc}$), 4.25 (dd, 1H, $J_{5,6b}$ 4.9 Hz, $J_{6a,6b}$ 12.4 Hz, H-$6b_{Glc}$), 4.55 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1_{Glc}), 4.96 (d, 1H, $J_{1,2}$ 1.1 Hz, H-1_{Rha}), 4.99–5.05 (m, 3H, H-2_{Glc}, H-3_{Rha}, and H-4_{Rha}), 4.19–5.17 (m, 2H, H-3_{Glc}, and H-4_{Glc}), 5.47 (dd, 1H, $J_{1,2}$ 1.1 Hz, $J_{2,3}$ 3.0 Hz, H-2_{Rha}); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 17.56 (C-6_{Rha}), 20.66, 20.69, 20.82, 20.88 (7 × OCH_3), 62.21 (C-6_{Glc}), 67.93 (C-4_{Glc}), 70.08, 70.55, 71.28, 71.82 (C-2_{Glc}, C-2_{Rha}, C-3_{Rha} and C-4_{Rha}), 74.40 (C-3_{Glc}), 75.17 (C-5_{Rha}), 76.58 (C-5_{Glc}), 79.10 (C-1_{Rha}), 82.02 (C-1_{Rha}), 169.16, 169.57, 170.02, 170.34, 170.41, 170.91 (7 × CO); $^1J_{\beta\text{-Rha(C-1,H-1)}}$ 153.8 Hz; HRMS (ESI) calcd for $C_{26}H_{40}O_{16}NS$ $[M+NH_4]^+$ 654.2062. Found 654.2054.

1.2.9. 2,3,4-Tri-*O*-acetyl-β-L-rhamnopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (3i)

Clear oil, becomes amorphous solid on standing: R_f 0.16 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ + 4.5 ± 1.0 (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.29 (d, 3H, ^3J 6.0 Hz, CH_3), 1.98, 2.04, 2.05, 2.06, 2.16, 2.17 (6s, 21H, 7OAc), 3.56 (m, 1H, H-5_{Rha}), 3.97 (t, 1H, $J_{5,6}$ 6.8 Hz, H-5_{Gal}), 4.14 (d, 1H, *J* 6.8 Hz, H-6_{Gal}), 4.58 (d, 1H, $J_{1,2}$ 10.0 Hz, H-1_{Gal}), 4.96–5.06 (m, 3H, H-3_{Gal}, H-3_{Rha}, H-4_{Rha}), 4.99 (br s, 1H, H-1_{Rha}), 5.28 (t, 1H, *J* 10.0 Hz, H-2_{Gal}), 5.42 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4_{Gal}), 5.49 (d, 1H, *J* 0.8 Hz, H-2_{Rha}); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 17.21 (C-6_{Rha}), 20.23, 20.26, 20.31, 20.34, 20.42 (7C, OCH_3), 61.32 (C-6_{Gal}), 67.25 (C-4_{Gal}), 67.53 (C-2_{Gal}), 70.02, 71.06, 71.72, 72.17 (C-2_{Rha}, C-3_{Gal}, C-3_{Rha}, C-4_{Rha}), 74.92 (C-5_{Gal}), 75.19 (C-5_{Rha}), 79.85 (C-1_{Rha}), 82.76 (C-1_{Gal}), 169.60, 170.33, 170.62, 170.73, 170.82, 170.95 (7C, CO); $^1J_{\beta\text{-Rha(C-1,H-1)}}$ 157.4 Hz; HRMS (ESI) calcd for $C_{26}H_{36}O_{16}S$ $[M+NH_4]^+$ 654.2062. Found 654.2066.

1.2.10. 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (4d)

Amorphous solid, lyophilised from water: R_f 0.46; $[\alpha]_D^{20}$ + 28.0 ± 0.5 (*c* 0.49, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 1.98, 1.98, 2.01, 2.03, 2.06, 2.07, 2.10, 2.17 (8s, 24H, 8OAc), 3.71–3.79 (m, 1H, H-5_{Man}), 4.10 (dd, 1H, $J_{5,6a}$ 2.2 Hz, $J_{6a,6b}$ 12.5 Hz, H-$6a_{Glc}$), 4.14–4.19 (m, 2H, H-6_{Man}, and H-$6b_{Man}$), 4.25–4.28 (m, 1H, H-5_{Glc}), 4.38 (dd, 1H, $J_{5,6a}$ 3.4 Hz, $J_{6a,6b}$ 12.5 Hz, H-$6b_{Glc}$), 4.62 (d, 1H, H-1_{Glc}), 5.06 (2dd, 2H, 2*J* 9.6 Hz, H-3_{Glc}, and H-4_{Man}), 5.16 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 9.6 Hz, H-3_{Glc}), 5.18 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.6 Hz, H-3_{Man}), 5.31 (dd, 1H, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.4 Hz, H-2_{Man}), 5.38 (dd, 1H, $J_{3,4}$ 9.6 Hz, $J_{4,5}$ 9.6 Hz, H-4_{Glc}), 5.57 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1_{Man}); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 20.66, 20.68, 20.77, 20.79, 20.81, 20.99 (8 × OCH_3), 61.85 (C-6_{Man}), 61.97 (C-6_{Glc}), 65.63 (C-4_{Man}), 67.88 (C-4_{Glc}), 69.36, 70.05, 70.80, 70.94 (C-2_{Glc}, C-2_{Man}, C-3_{Man} and C-5_{Man}), 73.85 (C-3_{Glc}), 76.51 (C-5_{Glc}), 81.59 (C-1_{Man}), 82.80 (C-1_{Glc}), 169.36, 169.44, 169.68, 169.89, 170.05, 170.26, 170.71, 170.77 (8 × CO); HRMS (ESI) calcd for $C_{28}H_{42}O_{18}NS$ $[M+NH_4]^+$ 712.2117. Found 712.2114.

1.2.11. 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (4e)

Amorphous solid, lyophilised from water: R_f 0.45 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ + 44.0 ± 2.0 (*c* 0.22, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 1.97, 1.98, 2.03, 2.08, 2.10, 2.14, 2.18 (7s, 24H, 8OAc), 3.95 (dd, 1H, $J_{5,6a}$ 6.5 Hz, $J_{5,6b}$ 6.5 Hz, H-5_{Gal}), 4.05 (dd, 1H, $J_{5,6a}$ 6.5 Hz, $J_{6a,6b}$ 11.2 Hz, H-$6a_{Gal}$), 4.10 (dd, 1H, $J_{5,6a}$ 2.2 Hz, $J_{6a,6b}$ 12.5 Hz, H-$6a_{Man}$), 4.14 (dd, 1H, $J_{5,6b}$ 6.5 Hz, $J_{6a,6b}$ 11.2 Hz, H-$6b_{Gal}$), 4.30–4.33 (m, 1H, H-5_{Man}), 4.35 (dd, 1H, $J_{5,6b}$ 3.6 Hz, $J_{6a,6b}$ 12.5 Hz, H-$6b_{Man}$), 4.61 (d, 1H, $J_{1,2}$ 10.1 Hz, H-1_{Gal}), 5.00 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 9.9 Hz, H-3_{Gal}), 5.22 (dd, 1H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 10.1 Hz, H-3_{Man}), 5.26 (dd, 1H, $J_{2,3}$ 9.9 Hz, $J_{1,2}$ 10.1 Hz, H-2_{Gal}), 5.32 (dd, 1H, $J_{1,2}$ 1.3 Hz, $J_{2,3}$ 3.4 Hz, H-2_{Man}), 5.38 (dd, 1H, $J_{4,5}$ 9.9 Hz, $J_{3,4}$ 10.1 Hz, H-4_{Man}), 5.41 (d, 1H, $J_{3,4}$ 3.4 Hz, H-4_{Gal}), 5.53 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1_{Man}); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 20.65, 20.68, 20.74, 20.76, 20.81, 20.88, 21.02 (8 × OCH_3), 61.53 (C-6_{Man}), 61.92 (C-6_{Gal}), 65.71 (C-4_{Man}), 67.24 (C-4_{Gal}), 67.84 (C-2Gal), 69.32, 69.87, 70.74 (C-2_{Man}, C-3_{Man} and C-5_{Man}), 71.73 (C-3_{Gal}), 74.90 (C-5_{Gal}), 81.90 (C-1_{Man}), 83.76 (C-1_{Gal}), 169.50, 169.67, 169.82, 170.07, 170.26, 170.47, 170.7 (8 × CO); $^1J_{\alpha\text{-Man(C-1,H-1)}}$ 171.9 Hz; HRMS (ESI) calcd for $C_{28}H_{42}O_{18}NS$ $[M+NH_4]^+$ 712.2117. Found 712.2119.

1.2.12. 2,3,4-Tri-*O*-acetyl-α-L-fucopyranosyl 2,3,4,6-*O*-acetyl-1-thio-β-D-galactopyranoside (4f)

Amorphous solid, lyophilised from water: R_f 0.67 (1:2 petroleum ether–EtOAc); $[\alpha]_D^{20}$ − 158.0 ± 1.0 (*c* 0.21, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 1.17 (d, 3H, ^3J 6.5 Hz, CH_3), 1.97, 1.97, 2.04, 2.05, 2.06, 2.14, 2.16 (7s, 21H, 7OAc), 3.89 (ddd, 1H, $J_{4,5}$ 1.0 Hz, $J_{5,6a}$ 6.5 Hz, $J_{5,6b}$ 6.7 Hz, H-5_{Gal}), 4.06 (dd, 1H, $J_{5,6a}$ 6.5 Hz, $J_{6a,6b}$ 11.3 Hz, H-$6a_{Gal}$), 4.13 (dd, 1H, $J_{5,6b}$ 6.7 Hz, $J_{6a,6b}$ 11.3 Hz, H-$6b_{Gal}$), 4.33–4.35 (m, 1H, H-5_{Fuc}), 4.63 (d, 1H, $J_{1,2}$ 10.2 Hz, H-1_{Gal}), 5.01 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 9.9 Hz, H-3_{Gal}), 5.11 (dd, 1H, $J_{3,4}$ 3.3 Hz, $J_{2,3}$ 10.9 Hz, H-3_{Fuc}), 5.26 (dd, 1H, $J_{1,2}$ 10.2 Hz, $J_{2,3}$ 9.9 Hz, H-2_{Gal}), 5.29 (d, 1H, $J_{3,4}$ 3.3 Hz, H-4_{Fuc}), 5.34 (dd, 1H, $J_{1,2}$ 5.7 Hz, $J_{2,3}$ 10.9 Hz, H-2_{Fuc}), 5.40 (dd, 1H, $J_{4,5}$ 1.0 Hz, $J_{3,4}$ 3.4 Hz, H-4_{Gal}), 5.86 (d, 1H, $J_{1,2}$ 5.7 Hz, H-1_{Fuc}); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 16.02 (C-6_{Fuc}), 20.66, 20.70, 20.75, 20.78, 20.84, 20.90 (7 × OCH_3), 61.35 (C-6_{Gal}), 65.66 (C-5_{Fuc}), 67.06, 67.27, 67.34 (C-2_{Gal}, C-2_{Fuc} and C-4_{Gal}), 68.66 (C-3_{Fuc}), 70.64 (C-4_{Fuc}), 72.04 (C-3_{Gal}), 74.67 (C-5_{Gal}), 80.34 (C-1_{Fuc}), 81.23 (C-1_{Gal}), 169.42, 170.03, 170.05, 170.17, 170.36, 170.60 (7 × CO); $^1J_{\alpha\text{-Fuc(C-1,H-1)}}$ 173.6 Hz; HRMS (ESI) calcd for $C_{26}H_{40}O_{16}NS$ $[M+NH_4]^+$ 654.2064. Found 654.2071.

1.2.13. 2,3,4-Tri-*O*-acetyl-α-L-fucopyranosyl 2,3,4,6-*O*-acetyl-1-thio-β-D-glucopyranoside (4g)

Clear oil, becomes amorphous solid on standing: R_f 0.20 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ − 158.2 ± 1.0 (*c* 2.12, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 1.17 (d, 3H, ^3J 6.6 Hz, CH_3), 1.97, 2.00, 2.01, 2.05, 2.06, 2.08, 2.17 (7s, 21H, 7OAc), 3.66 (m, 1H, H-1_{Glc}), 4.03 (dd, 1H, $J_{5,6a}$ 2.4 Hz, $J_{6a,6b}$ 12.6 Hz, H-$6a_{Glc}$), 4.28 (dd, 1H, $J_{5,6b}$ 5.4 Hz, $J_{6a,6b}$ 12.6 Hz, H-$6b_{Glc}$), 4.33 (q, 1H, $J_{5,6}$ 6.6 Hz, H-5_{Fuc}), 4.65 (d, 1H, $J_{1,2}$ 10.8 Hz, H-1_{Glc}), 5.03–5.11 (m, 3H, H-2_{Glc}, H-4_{Glc}, H-3_{Fuc}), 5.21 (t, 1H, $J_{2,3=3,4}$ 9.0 Hz, H-3_{Glc}), 5.29 (d, 1H, $J_{3,4}$ 1.8 Hz, H-4_{Fuc}), 5.33 (dd, 1H, $J_{1,2}$ 5.7 Hz, $J_{2,3}$ 10.8 Hz, H-2_{Fuc}), 5.87 (d, 1H, $J_{1,2}$ 5.7 Hz, H-1_{Fuc}); ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 15.53 (C-6_{Fuc}), 20.20, 20.24, 20.28, 20.31, 20.36, 20.40 (7C, OCH_3), 61.80 (C-6_{Glc}), 65.55 (C-5_{Fuc}), 66.80 (C-2_{Fuc}), 68.04, 68.44, 69.92 (C-2_{Glc}, C-3_{Fuc}, C-4_{Glc}), 70.42 (C-4_{Fuc}), 73.84 (C-3_{Glc}), 75.94 (C-5_{Glc}), 80.20 (C-1_{Fuc}), 80.54 (C-1_{Glc}), 169.71, 169.91, 170.46, 170.78, 170.99, 171.23 (7C, CO); HRMS (ESI) calcd for $C_{26}H_{36}O_{16}S$ $[M+NH_4]^+$ 654.2062. Found 654.2065.

1.2.14. 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (4h)

Amorphous solid, lyophilised from water: R_f 0.48 (1:2 petroleum ether–EtOAc) ; $[\alpha]_D^{20}$ − 101.0 ± 1.0 (*c* 0.63, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 1.24 (d, 3H, ^3J 6.1 Hz, CH_3), 1.96, 2.00, 2.00, 2.04, 2.06, 2.07, 2.14 (7s, 21H, 7OAc), 3.66–3.69 (m, 1H, H-5_{Glc}), 4.04–4.07 (m, 1H, H-5_{Rha}), 4.11 (dd, 1H, $J_{5,6a}$ 2.2 Hz, $J_{6a,6b}$ 12.3 Hz, H-$6a_{Glc}$), 4.25 (dd, 1H, $J_{5,6b}$ 4.5 Hz, $J_{6a,6b}$ 12.3 Hz, H-$6b_{Glc}$), 4.69 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1_{Glc}), 5.05 (dd, 1H, $J_{1,2}$ 9.9 Hz, $J_{2,3}$ 9.9 Hz, H-2_{Glc}), 5.07–5.15 (m, 3H, H-3_{Rha}, H-4_{Rha}, and H-4_{Glc}), 5.22 (dd, 1H, $J_{2,3}$ 9.9 Hz, $J_{3,4}$ 9.3 Hz, H-3_{Glc}), 5.35 (dd, 1H, $J_{1,2}$ 1.5 Hz, $J_{2,3}$ 3.3 Hz, H-2_{Rha}), 5.43 (dd, 1H, $J_{1,2}$ 1.5 Hz, H-1_{Rha}); ^{13}C NMR (150.9 MHz, $CDCl_3$) δ 17.42 (C-6_{Rha}), 20.64, 20.68, 20.69, 20.73, 20.79, 20.85, 20.95 (7 × OCH_3), 61.81 (C-6_{Glc}), 68.01 (C-4_{Glc}), 68.09 (C-5_{Rha}), 69.19 (C-3_{Rha}), 70.06 (C-2_{Glc}), 70.87 (C-2_{Rha}), 71.02 (C-4_{Rha}), 73.96 (C-3_{Glc}), 76.05 (C-5_{Glc}), 80.07 (C-1_{Rha}), 81.29 (C-1_{Glc}), 169.28, 169.45, 169.89, 169.92, 170.05, 170.41, 170.90 (7 × CO); $^1J_{\alpha\text{-Rha(C-1,H-1)}}$ 171.9 Hz; HRMS (ESI) calcd for $C_{26}H_{40}O_{16}NS$ $[M+NH_4]^+$ 654.2062. Found 654.2056.

1.2.15. 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (4i)

Clear oil, becomes amorphous solid on standing: R_f 0.16 (1:1 petroleum ether–EtOAc); $[\alpha]_D^{20}$ − 106.3° ± 1.3° (*c* 0.55, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.24 (d, 3H, ^3J 6.4 Hz, CH_3), 1.97, 1.98, 2.03, 2.05, 2.07, 2.15, 2.16 (7s, 21H, 7OAc), 3.92 (t, 1H, $J_{5,6}$ 6.8 Hz, H-5_{Gal}), 4.05–4.18 (m, 3H, H-6_{Gal}, H-5_{Rha}), 4.68 (d, 1H, $J_{1,2}$ 10.0 Hz, H-1_{Gal}), 5.05 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 10.0 Hz, H-3_{Gal}), 5.10 (t, 1H, $J_{3,4=4,5}$ 10.0 Hz, H-4_{Rha}), 5.16 (dd, 1H, $J_{2,3}$ 3.2 Hz, $J_{3,4}$ 10.4 Hz, H-3_{Rha}), 5.27 (t, 1H, *J* 10.0, H-2_{Gal}), 5.36 (dd, 1H, $J_{1,2}$ 1.2 Hz, $J_{2,3}$

3.2 Hz, H-2_{Rha}), 5.42 (d, 1H, $J_{3,4}$ 3.2 Hz, H-4_{Gal}), 5.45 (br s, 1H, H-1_{Rha}); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 16.95 (C-6_{Rha}), 20.19, 20.25, 20.31, 20.34, 20.40, 20.50 (7C, OCH_3), 61.05 (C-6_{Gal}), 66.96 (C-4_{Gal}), 67.21 (C-2_{Gal}), 67.97 (C-5_{Rha}), 69.02 (C-3_{Rha}), 70.91 (2C, C-2_{Rha}, C-4_{Rha}), 71.73 (C-3_{Gal}), 74.56 (C-5_{Gal}), 80.02 (C-1_{Rha}), 81.75 (C-1_{Gal}), 169.82, 170.28, 170.43, 170.59, 170.80, 170.89 (7C, CO); $^1J_{\alpha\text{-Rha(C-1,H-1)}}$ 171.9 Hz; HRMS (ESI) calcd for $C_{26}H_{36}O_{16}S$ $[M+NH_4]^+$ 654.2062. Found 654.2067.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2009.03.017.

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