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Benzoylated ethyl 1-thioglycosides: direct preparation from per-O-benzoylated sugars

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ABSTRACT

D-Glucose, lactose, maltose, and melibiose were benzoylated with Bz_2O–Et_3N reagent to give fully benzoylated β products. Under the same conditions, D-mannose produced a mixture where the β-benzoate predominated. Treatment of the foregoing compounds with EtSH at slightly elevated temperature (50–60 °C) in the presence of $BF_3{\cdot}Et_2O$ as a promoter gave the corresponding ethyl 1-thio glycosides in high yields. The α-products predominated in all cases in the anomeric mixtures formed. Individual products of all reactions were isolated by chromatography, they were obtained in analytically pure state, and were fully characterized by ^1H and ^{13}C NMR data and physical constants.

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1. Introduction

Because of their long shelf-life, 1-thioglycosides are very popular glycosyl donors.[1,2] While synthesis of per-O-acetylated 1-thioglycosides is fairly simple,[3–6] their benzoylated counterparts are normally prepared indirectly from acetylated thioglycosides, by sequential deacetylation and benzoylation.[7–12] Alternatively, fully benzoylated thioglycosides were prepared from the corresponding glycosyl thiocyanates[13] or iodides.[14] Cao et al.[15] prepared ethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside (**13**) from the corresponding penta-O-benzoate by treatment with EtSH in presence of $SnCl_4$.

Following reports on the use of 1-O-β-acetates of common sugars as glycosyl donors in trifluoromethanesulfonate (TMSOTf)-catalyzed glycosylation,[16,17] we have extended the method to the use of the corresponding 1-*O*-β-benzoyl derivatives.[18] More than a decade later, Gallo-Rodriguez et al. reported similar approach in their oligosaccharide synthesis.[19] Here, we describe a similar approach, but to glycosylation of EtSH, which allows direct preparation of 1-thioglycosides from fully-O-benzoylated saccharides using $BF_3{\cdot}Et_2O$ as a promoter (Scheme 1). To our knowledge, such conversion has not been described in accessible literature.

2. Results and discussion

Transfer of the acetyl group during glycosylation reactions from 2-O-acetylated glycosyl donors to the free hydroxyl group of glycosyl acceptors is a well established undesirable side reaction, which often occurs during Lewis acid mediated glycosylations.[16,17,20] For example, formation of as much as ~30% of methyl 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside was observed when methyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranoside was glycosylated with 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose in the presence of TMSOTf.[18] The significance of 2-O-benzoylated glycosyl donors in glycoside or oligosaccharide synthesis lies in the fact that the aforementioned transesterification does not take place when such donors are used.[18,21] Also, benzoylated glycosyl donors are often stable at base-deficient conditions, which are required for isomerization of the intermediate orthoesters into glycosides.[21] In view of the above, developing a more straightforward protocol for making benzoylated 1-thio-glycosides than through the corresponding acetates is desirable.

Knowing that 1,2-*trans*-O-acetates are normally more reactive than their 1,2-*cis* counterparts,[1,2] we searched for a simple preparation of this class of benzoyl derivatives, and have found it in the work by Luo[22] et al. who showed one example of using benzoic anhydride–triethylamine (Bz_2O–Et_3N) reagent in stereoselective 1-O-benzoylation. When treated in this way, D-glucose (**1**), lactose (**14**), maltose (**18**), and melibiose (**22**) produced virtually only β-anomers. The product formed from mannose (**5**) was an anomeric mixture of per-O-benzoates where the β-compound predominated (Table 1). There was no advantage to using the Bz_2O–Et_3N reagent for benzoylation of D-galactose (**10**). Several products were formed, one major of which co-chromatographed with the authentic sample[22,23] of 1,2,3,4,6-penta-*O*-benzoyl-α-D-galactopyranose (**11**).[23,24] It has been reported that high proportion of furanoses is formed during benzoylation of D-galactose at both elevated[19] and sub-ambient[25] temperatures. The products were difficult to

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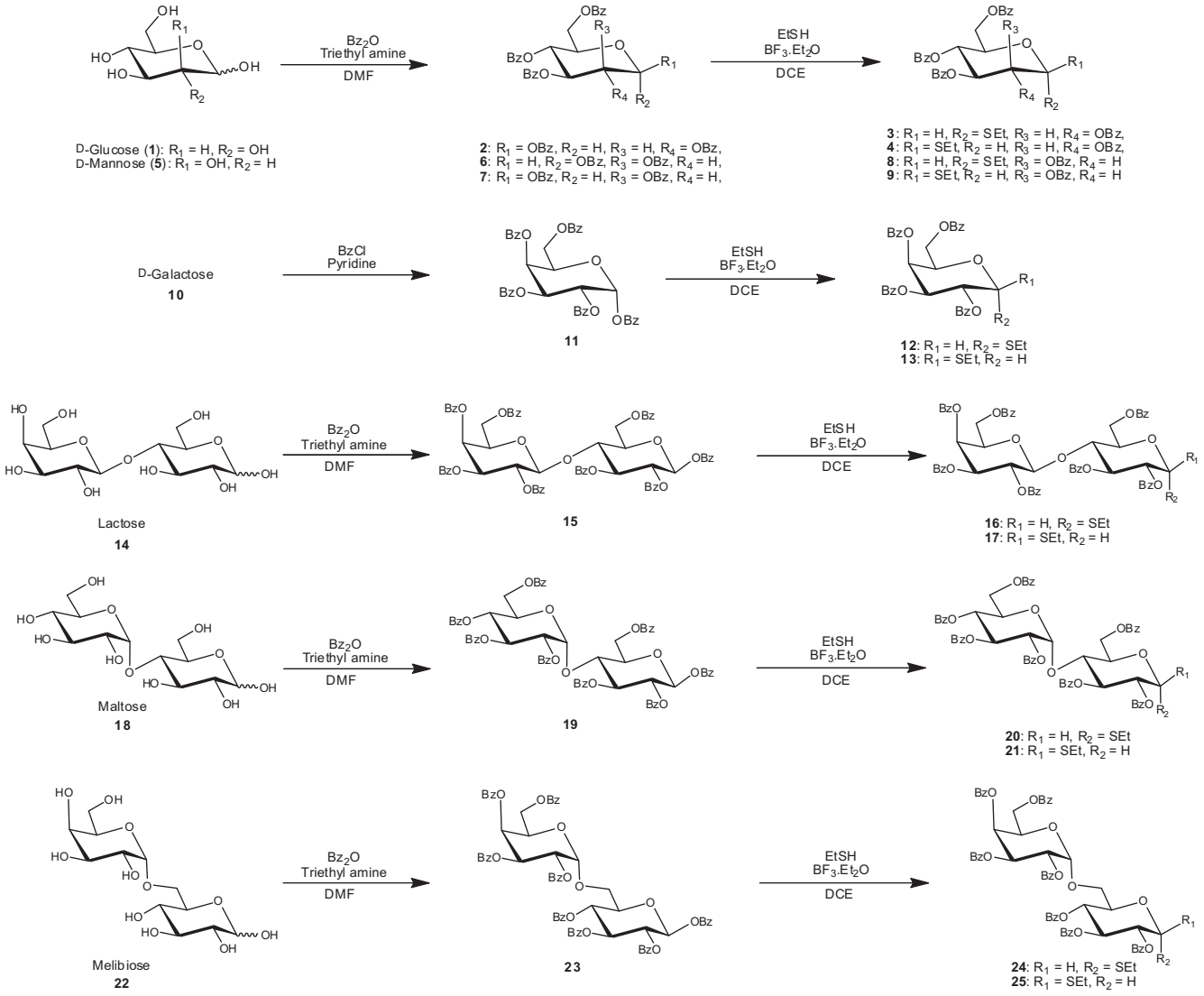

Scheme 1. Benzoylation of D-glucose, D-mannose, D-galactose, lactose, maltose, and melibiose, and thioglycosidation of their per-*O*-benzoyl derivatives.

Table 1
Benzoylation of saccharides with benzoic anhydride: product composition and yields

Starting material	Product(s) formed	Combined yield %	α/β ratio[a]
D-Glucose (**1**)	**2**	91	β Only
D-Mannose (**5**)	**6**, **7**	83	1/1.5
Lactose (**14**)	**15**	82	β Only
Maltose (**18**)	**19**	74	β Only
Melibiose (**22**)	**23**	75	β Only

[a] Determined after separation by chromatography.

Table 2
Glycosidation of per-O-benzoates with EtSH: combined yields and product composition

Starting material	Products formed	Combined yield %	α/β ratio
2	**3**, **4**	91	2[a]
6	**8**, **9**	93	8.7[a]
7	**8**, **9**	89	7.9[a]
11	**12**, **13**	80	2.7[b]
15	**16**, **17**	76	1.6[b]
19	**20**, **21**	90	2.8[b]
23	**24**, **25**	87	3.8[b]

[a] Ratio determined after separation by chromatography.
[b] Ratio in the crude product determined by NMR.

separate; hence accurate yield of individual compounds formed could not be determined. As we later discovered during this work, when thioglycosidation was conducted at elevated temperature 1,2-*cis*-O-benzoates served our purpose equally well, which agreed with Xu et al.'s[26] similar observation concerning the corresponding penta-*O*-acetyl derivatives. Thus, α-D-galactopyranose **11**[22,23] was used in the conversion into the corresponding 1-thio-glycosides **12** and **13**.

Reactions of *O*-benzoyl derivatives with EtSH in the presence of $BF_3{\cdot}Et_2O$ as a promoter were examined next. The reactions at room temperature were impractically slow. At moderately elevated temperature, mixtures of anomers were formed in all cases here examined (Table 2), with ethyl 1-thio-α-glycosides predominating. Anomerization of initially formed kinetic products in the presence of Lewis acid cannot be excluded. Ethyl 1-thio-β-glycosides of D-galactose and melibiose, (**13**) and (**25**), respectively, were found to co-chromatograph with the starting benzoates. This precluded monitoring of the progress of the reaction by thin-layer chromatography. In these situations small-scale experiments were conducted in NMR tubes using dichloroethane-d_4 as solvent, and the reaction times required for complete conversion (see Section 3)

of benzoates **11** and **23** were determined by ^{1}H NMR spectroscopy, by monitoring the disappearance of the low-field signals for H-1 of the starting materials. All products were fully characterized and produced NMR spectra consistent with the expected structures.

3. Experimental

3.1. General methods

Optical rotations were measured at ambient temperature for solution in $CHCl_3$ with a digital Jasco automatic polarimeter, Model P-2000. Melting points were measured on a Kofler hot stage. All reactions were monitored by thin-layer chromatography (TLC) on Silica Gel 60 coated glass slides. Column chromatography was performed by elution from prepacked columns of silica gel (Varian, Inc.) with the Isolera Flash Chromatograph (Biotage). Nuclear Magnetic Resonance (NMR) spectra were measured at 400 MHz (^{1}H) and 100 MHz (^{13}C) or at 600 MHz (^{1}H) and 150 MHz (^{13}C) with Bruker Avance spectrometers. Assignments of NMR signals were made by homonuclear and heteronuclear 2-dimensional correlation spectroscopy, run with the software supplied with the spectrometers. When reporting assignments of NMR signals of disaccharides, sugar residues are serially numbered, beginning with the one bearing the aglycon, and are identified by a Roman numeral superscript in listings of signal assignments. Liquid Chromatography–Electron Spray-Ionization Mass Spectrometry (ESI-MS) was performed with a Waters LCT Premier spectrometer. Reactions were carried out in closed flasks. Rubber septa used to close reaction flasks containing organic solvents were protected with a thin Teflon™ sheet (Laboratory Supplies Co., Inc., Hicksville, NY), to avoid leaching. Solutions in organic solvents were dried with anhydrous Na_2SO_4, and concentrated at 40 °C/2 kPa.

3.2. General procedures for benzoylation

The free sugar (2–5 mmol) was dissolved in DMF (10 mL/mmol), Et_3N (4 equiv/OH) was added followed by addition of Bz_2O (2 equiv/OH), and the mixture was stirred at conditions specified below. When the conversion was complete (TLC), excess of MeOH was added and the mixture was stirred overnight at room temperature. After concentration, a solution of the residue in CH_2Cl_2 was washed with saturated solution of sodium bicarbonate. The organic phase was dried, concentrated, and the crude mixture was chromatographed, to give pure substances and, occasionally, mixed fractions. For combined yields, see Table 1.

3.3. General procedure for thioglycosidation

$BF_3{\cdot}Et_2O$ was added to a solution of EtSH and sugar per-O-benzoate in 1,2-dichloroethane, and the mixture was stirred until all starting material was consumed (TLC). For amounts of solvent, reagents, and reaction conditions, see individual preparations (below). Et_3N (excess of over the molar amount of $BF_3{\cdot}Et_2O$) was added, the mixture was concentrated, and a solution of the residue in CH_2Cl_2 was washed with saturated solution of sodium bicarbonate. After concentration of the organic phase, chromatography of the material in the residue gave pure substances or mixtures of anomers. For combined yields, see Table 2.

3.3.1. 1,2,3,4,6-Penta-*O*-benzoyl-β-D-glucopyranose (2)

Reaction conditions: 16 h, rt; flash chromatography, 4:1 hexane–acetone; yield, starting from **1** (0.9 g, 5.0 mmol), 3.2 g (91%); R_f = 0.3 (4:1 hexane–acetone); Mp 182–185 °C (MeOH); $[\alpha]_D$ +24.4 (*c* 1.0, $CHCl_3$); lit.[27] Mp 189–192 °C (AcOH); $[\alpha]_D$ +24.2 (*c* 2.6, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.30 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1), 6.05 (t, 1H, J = 9.5 Hz, H-3), 5.90–5.81 (m, 2H, H-2, H-4), 4.66 (dd, 1H, $J_{6a,6b}$ = 12.3, $J_{5,6a}$ = 3.0 Hz, H-6a), 4.52 (dd, 1H, $J_{5,6b}$ = 4.8 Hz, H-6b), 4.41 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, H-5); ^{13}C NMR (150 MHz, $CDCl_3$) δ 92.65 (C-1), 73.12 (C-5), 72.76 (C-3), 70.78 (C-2), 68.99 (C-4), 62.62 (C-6); ESI-HRMS calc. for $C_{41}H_{36}NO_{11}$ $[M+NH_4]^+$: 718.2288; Found: 718.2292. Anal. Calcd For $C_{41}H_{32}O_{11}$: C, 70.28; H, 4.60. Found: C, 70.46; H, 4.65.

3.3.2. Ethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α- (3) and β-D-glucopyranoside (4)

Reaction conditions: EtSH (0.45 mL, 6.0 mmol), $BF_3{\cdot}Et_2O$ (0.554 mL, 4.4 mmol), 1 h, 50 °C; flash chromatography, 30:1→20:1 toluene–EtOAc; yield, starting from **2** (2.80 g, 4.0 mmol), 1.53 g (60%) of **3** and 0.80 g (31%) of **4**.

Compound **3**: R_f = 0.7 (15:1 toluene–EtOAc); Mp 137–138 °C (CH_2Cl_2–MeOH); $[\alpha]_D$ +104.2 (*c* 1.0, $CHCl_3$); lit.[7] Mp 135 °C (toluene–pet. ether); $[\alpha]_D$ +104 (*c* 2.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.08 (t, 1H, J = 9.9 Hz, H-3), 5.95 (d, 1H, $J_{1,2}$ = 5.8 Hz, H-1), 5.68 (t, 1H, J = 9.8 Hz, H-4), 5.51 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H-2), 4.88 (ddd, 1H, $J_{4,5}$ = 10.1, $J_{5,6b}$ = 5.4, $J_{5,6a}$ = 2.8 Hz, H-5), 4.60 (dd, 1H, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.52 (dd, 1H, $J_{5,6b}$ = 5.5 Hz, H-6b), 2.70–2.55 (m, 2H, CH_2), 1.25 (t, 3H, J = 7.4 Hz, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 81.98 (C-1), 71.63 (C-2), 70.87 (C-3), 69.49 (C-4), 68.08 (C-5), 63.02 (C-6), 24.24 (*C*H_2), 14.61 (*C*H_3); ESI-HRMS calcd for $C_{36}H_{36}NO_9S$ $[M+NH_4]^+$: 658.2111; found: 658.2123; Anal. Calcd for $C_{36}H_{32}O_9S$: C, 67.49; H, 5.03. Found: C, 67.71; H, 5.03.

Compound **4**: The solid obtained after freeze-drying of a solution in benzene could not be crystallized. R_f = 0.6 (15:1 toluene–EtOAc); $[\alpha]_D$ +29.1 (*c* 1.0, $CHCl_3$); lit.[7] Mp 108–109 °C (ether–petroleum ether); $[\alpha]_D$ +27 (*c* 1.8, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.93 (t, 1H, J = 9.5 Hz, H-3), 5.67 (t, 1H, J = 9.8 Hz, H-4), 5.57 (t, 1H, J = 9.7 Hz, H-2), 4.87 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1), 4.63 (dd, 1H, $J_{6a,6b}$ = 12.2, $J_{5,6a}$ = 3.1 Hz, H-6a), 4.50 (dd, 1H, $J_{5,6b}$ = 5.5 Hz, H-6b), 4.18 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, H-5), 2.84–2.69 (m, 2H, SCH_2CH$_3$), 1.26 (t, 3H, J = 7.4 Hz, SCH$_2$CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ 83.90 (C-1), 76.25 (C-5), 74.05 (C-3), 70.54 (C-2), 69.57 (C-4), 63.30 (C-6), 24.38 (SCH$_2$CH$_3$), 14.90 (SCH$_2$CH$_3$); ESI-HRMS calcd for $C_{36}H_{36}NO_9S$ $[M+NH_4]^+$: 658.2111; found: 658.2114. Anal. Calcd for $C_{36}H_{32}O_9S$: C, 67.49; H, 5.03. Found: C, 67.56; H, 5.01.

3.3.3. 1,2,3,4,6-Penta-*O*-benzoyl-α- (6) and β-D-mannopyranose (7)

Compound **5**: Reaction conditions: 40 h, rt; flash chromatography, 50:1→30:1 toluene–EtOAc; yield, starting from **5** (0.180 g, 1.0 mmol), 0.234 g (33%) of **6** and 0.342 g (50%) of **7**.

Compound **6**: R_f = 0.5 (19:1 toluene–EtOAc); Mp 150.5–152 °C (MeOH); $[\alpha]_D$ −20.2 (*c* 1.0, $CHCl_3$); lit.[27] Mp 152–153 °C; $[\alpha]_D$ −18.6 (*c* 1.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (d, 1H, $J_{1,2}$ = 2.0 Hz, H-1), 6.28 (t, 1H, J = 10.2 Hz, H-4), 6.07 (dd, 1H, $J_{3,4}$ = 10.2, $J_{2,3}$ = 3.3 Hz, H-3), 5.91 (dd, 1H, H-2), 4.70 (dd, 1H, $J_{6a,6b}$ = 12.2, $J_{5,6a}$ = 2.5 Hz, H-6a), 4.57 (dt, 1H, $J_{4,5}$ = 10.0 Hz, H-5), 4.50 (dd, 1H, $J_{5,6b}$ = 3.7 Hz, H-6b); ^{13}C NMR (100 MHz, $CDCl_3$) δ 91.37 (C-1, $J_{C\text{-}1,H\text{-}1}$ = 178.8 Hz), 71.18 (C-5), 69.99 (C-3), 69.43 (C-2), 66.18 (C-4), 62.34 (C-6); ESI-HRMS calcd for $C_{41}H_{36}NO_{11}$ $[M+NH_4]^+$: 718.2288; found: 718.2274. Anal. Calcd for $C_{41}H_{32}O_{11}$: C, 70.28; H, 4.60. Found: C, 70.56; H, 4.80.

Compound **7**: R_f = 0.4 (19:1 toluene–EtOAc); Mp 160–161.5 °C (MeOH); $[\alpha]_D$ −84.2 (*c* 1.0, $CHCl_3$); lit.[28] Mp 161–161.5 °C (EtOH); $[\alpha]_D$ −80.7 ($CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.44 (d, 1H, $J_{1,2}$ = 1.2 Hz, H-1), 6.18 (t, 1H, J = 9.8 Hz, H-4), 6.11 (dd, 1H, $J_{2,3}$ = 3.2 Hz, H-2), 5.81 (dd, 1H, $J_{3,4}$ = 9.9 Hz, H-3), 4.76 (dd, 1H, $J_{6a,6b}$ = 12.3, $J_{5,6a}$ = 2.8 Hz, H-6a), 4.56 (dd, 1H, $J_{5,6b}$ = 4.3 Hz, H-6b), 4.38 (ddd, 1H, $J_{4,5}$ = 9.7 Hz, H-5); ^{13}C NMR (150 MHz, $CDCl_3$) δ 91.19 (C-1, $J_{C\text{-}1,H\text{-}1}$ = 163.3 Hz), 73.28 (C-5), 71.51 (C-3), 69.36 (C-2), 69.32 (C-4), 62.61 (C-6); ESI-HRMS calcd for $C_{41}H_{36}NO_{11}$

$[M+NH_4]^+$: 718.2288; found: 718.2292. Anal. Calcd for $C_{41}H_{32}O_{11}$: C, 70.28; H, 4.60. Found: C, 70.49; H, 4.69.

3.3.4. Ethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α- (8) and β-D-mannopyranoside (9)

Reaction conditions: EtSH (1.5 mL, 2.0 mmol), $BF_3{\cdot}Et_2O$ (0.23 mL, 1.8 mmol), 3 h (starting from **6**), 5 h (starting from **7**), 50 °C; flash chromatography, 50:1→25:1 toluene–EtOAc.

Compound **8**: yield, starting from **6** (0.700 g, 1 mmol), 0.536 g (84%), starting from **7** (0.700 g, 1 mmol), 0.504 g (79%); R_f = 0.7 (15:1 toluene–EtOAc); Mp 120–121.5 °C (EtOH); $[\alpha]_D$ −14.0 (*c* 1.0, $CHCl_3$); lit.[29]: Mp 124–125 °C (EtOH); $[\alpha]_D$ −15.8 (*c* 0.8, $CHCl_3$). ^1H NMR (600 MHz, $CDCl_3$) δ 6.17 (t, 1H, *J* = 10.0 Hz, H-4), 5.89 (dd, 1H, $J_{3,4}$ = 9.9, $J_{2,3}$ = 3.2 Hz, H-3), 5.87 (dd, 1H, $J_{1,2}$ = 1.3 Hz, H-2), 5.59 (br d, 1H, H-1), 4.85 (ddd, 1H, $J_{4,5}$ = 10.1, $J_{5,6b}$ = 4.5, $J_{5,6a}$ = 2.6 Hz, H-5), 4.69 (dd, 1H, $J_{6a,6b}$ = 12.2 Hz, H-6a), 4.54 (dd, 1H, H-6b), 2.95–2.58 (m, 2H, SCH_2CH$_3$), 1.35 (t, 3H, SCH$_2$CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 82.29 (C-1, $J_{C\text{-}1,H\text{-}1}$ = 168.3 Hz), 72.08 (C-2), 70.48 (C-3), 69.19 (C-5), 66.99 (C-4), 62.82 (C-6), 25.57 (SCH$_2$CH$_3$), 14.81 (SCH$_2$CH$_3$); ESI-HRMS calcd for $C_{36}H_{36}NO_9S$ $[M+NH_4]^+$: 658.2111; found: 658.2126. Anal. Calcd for $C_{36}H_{32}O_9S$: C, 67.49; H, 5.03. Found: C, 67.70; H, 5.09.

Compound **9**: Amorphous solid after freeze-drying of a solution in benzene; yield, starting from **6** (0.700 g, 1 mmol), 0.062 g (10%); yield, starting from **7** (0.700 g, 1 mmol), 0.061 g (10%); R_f = 0.5 (15:1 toluene–EtOAc); $[\alpha]_D$ −150.4 (*c* 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 6.02 (dd, 1H, $J_{2,3}$ = 3.3, $J_{1,2}$ = 0.9 Hz, H-2), 6.00 (t, 1H, *J* = 10.0 Hz, H-4), 5.67 (dd, 1H, $J_{3,4}$= 10.1 Hz, H-3), 5.11 (br d, 1H, H-1), 4.71 (dd, 1H, $J_{6a,6b}$ = 12.1, $J_{5,6a}$ = 2.9 Hz, H-6a), 4.54 (dd, 1H, $J_{5,6b}$ = 5.4 Hz, H-6b), 4.20–4.18 (m, 1H, H-5), 2.83–2.74 (m, 2H, SCH_2CH$_3$), 1.31 (t, 3H, *J* = 7.4 Hz, SCH$_2$CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 82.84 (C-1, $J_{C\text{-}1,H\text{-}1}$ = 152.2 Hz), 76.53 (C-5), 72.77 (C-3), 71.35 (C-2), 66.85 (C-4), 63.43 (C-6), 25.86 (SCH$_2$CH$_3$), 14.97 (SCH$_2$CH$_3$); ESI-HRMS calcd for $C_{36}H_{36}NO_9S$ $[M+NH_4]^+$: 658.2111; found: 658.2119; Anal. Calcd for $C_{36}H_{32}O_9S$: C, 67.49; H, 5.03. Found: C, 67.19; H, 4.99.

3.3.5. 1,2,3,4,6-Penta-*O*-benzoyl-α-D-galactopyranose (11)

This compound was prepared as described.[24] Mp 161.5–162.5 °C (EtOH); $[\alpha]_D$ +193.9 (*c* 1.0, $CHCl_3$); lit.[24] Mp 158–159 °C (MeOH); $[\alpha]_D$ +187.0 (*c* 4.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ: 6.96 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1), 6.20 (br d, 1H, H-4), 6.13 (dd, 1H, $J_{2,3}$ = 10.7, $J_{3,4}$ = 3.4 Hz, H-3), 6.03 (dd, 1H, H-2), 4.84 (t, 1H, *J* = 6.8 Hz, H-5), 4.64 (dd, 1H, $J_{6a,6b}$ = 11.4, $J_{5,6a}$ = 6.4 Hz, H-6a), 4.43 (dd, 1H, $J_{5,6b}$ = 6.9 Hz, H-6b); ^{13}C NMR (150 MHz, $CDCl_3$): δ 90.65 (C-1), 69.41 (C-5), 68.50 (C-3), 68.43 (C-4), 67.66 (C-2), 61.80 (C-6). ESI-HRMS calcd for $C_{41}H_{36}NO_{11}$ $[M+NH_4]^+$: 718.2288; found: 718.2258; Anal. Calcd for $C_{41}H_{32}O_{11}$: C, 70.28; H, 4.60. Found: 70.14; H, 4.70.

3.3.6. Ethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-α- (12) and β-D-galactopyranoside (13)

Reaction conditions: EtSH (0.375 mL, 5.0 mmol), $BF_3{\cdot}Et_2O$ (0.504 mL, 4.0 mmol), 16 h (optimum time determined by NMR spectroscopy), 60 °C; flash chromatography, 5:1 hexane–acetone; yield, starting from **11** (1.40 g, 2.0 mmol), 0.422 g of pure **12** (33%), 0.317 g of pure **13** (25%). Unresolved mixture of **12** and **13** (0.282 g, 22%) was also obtained.

Compound **12**: Amorphous solid after freeze-drying of a solution in benzene; R_f = 0.4 (3:1 hexane–acetone); $[\alpha]_D$ +166.6 (*c* 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 6.09–5.99 (m, 2H, H-1, H-4), 5.92–5.82 (m, 2H, H-2, H-3), 5.03 (dd, 1H, $J_{5,6a}$ = 7.0, $J_{5,6b}$ = 5.6 Hz, H-5), 4.62 (dd, 1H, $J_{6a,6b}$ = 11.5 Hz, H-6a), 4.44 (dd, 1H, H-6b), 2.74–2.49 (m, 2H, SCH_2CH$_3$), 1.25 (m, 3H, SCH$_2$CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 81.22 ($J_{C\text{-}1,H\text{-}1}$ = 168.5 Hz, C-1), 68.05, 67.96, 67.90 (C-2, C-3, C-4), 66.22 (C-5), 61.60 (C-6), 23.03 (SCH$_2$CH$_3$), 13.57 (SCH$_2$CH$_3$); ESI-HRMS calcd for $C_{36}H_{36}NO_9S$ $[M+NH_4]^+$: 658.2111; found: 658.2111; Anal. Calcd for $C_{36}H_{32}O_9S$: C, 67.49; H, 5.03. Found: C, 67.39; H, 5.00.

Compound **13**; Amorphous solid after freeze-drying of a solution in benzene; R_f = 0.3 (3:1 hexane–acetone); $[\alpha]_D$ +98.4 (*c* 1.0, $CHCl_3$); lit.[30] $[\alpha]_D$ +106 (*c* 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ: 6.04 (br d, 1H, H-4), 5.84 (t, 1H, *J* = 9.9 Hz, H-2), 5.65 (dd, 1H, $J_{2,3}$ = 9.9, $J_{3,4}$ = 3.5 Hz, H-3), 4.88 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1), 4.67 (dd, 1H, $J_{6a,6b}$ = 11.2, $J_{5,6a}$ = 6.5 Hz, H-6a), 4.41 (dd, 1H, $J_{5,6b}$ = 6.5 Hz, H-6b), 4.36 (t, 1H, *J* = 6.6 Hz, H-5), 2.95–2.72 (m, 2H, SCH_2CH$_3$), 1.32 (t, 3H, SCH$_2$SCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 84.31 ($J_{C\text{-}1,H\text{-}1}$ = 152.5 Hz, C-1), 75.03 (C-5), 72.70 (C-3), 68.36 (C-4), 68.19 (C-2), 62.60 (C-6), 24.53 (SCH$_2$CH$_3$), 14.98 (SCH$_2$CH$_3$); ESI-HRMS calcd for $C_{36}H_{36}NO_9S$ $[M+NH_4]^+$: 658.2111; found: 658.2111; Anal. Calcd for $C_{36}H_{32}O_9S$: C, 67.49; H, 5.03. Found: C, 67.73; H, 5.02.

3.3.7. 1,2,3,6-Tetra-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranose (Octa-*O*-benzoyl-β-lactose, 15)

Reaction conditions: 40 h, 50 °C; flash chromatography, 30:1→20:1 toluene–EtOAc; yield, starting from lactose monohydrate (1.44 g, 4.0 mmol), 3.85 g (82%); R_f = 0.5 (10:1 toluene–EtOAc); $[\alpha]_D$ +45.7 (*c* 1.0, $CHCl_3$); lit.[31] Mp 140–142 °C (acetone–MeOH); $[\alpha]_D$ +38.1 (*c* 0.9, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 6.15 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1′), 5.96 (t, 1H, *J* = 9.3 Hz, H-3), 5.80 (dd, 1H, $J_{2,3}$ = 9.6 Hz, H-2), 5.78–5.72 (m, 2H, H-2′,4′), 5.39 (dd, 1H, $J_{2',3'}$ = 10.4, $J_{3',4'}$ = 3.4 Hz, H-3′), 4.90 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1′), 4.60 (dd, 1H, $J_{6a,6b}$ = 12.4, $J_{5,6a}$ = 1.9 Hz, H-6a), 4.54 (dd, 1H, $J_{5,6b}$ = 3.9 Hz, H-6b), 4.41 (t, 1H, *J* = 9.4 Hz, H-4), 4.08 (ddd, 1H, $J_{4,5}$ = 9.9 Hz, H-5), 3.90 (t, 1H, *J* = 6.8 Hz, H-5′), 3.78 (dd, 1H, $J_{6a',6b'}$ = 11.3, $J_{5',6a'}$ = 6.4 Hz, H-6a′), 3.71 (dd, 1H, $J_{5',6b'}$ = 7.1 Hz, H-6b′); ^{13}C NMR (150 MHz, $CDCl_3$) δ 101.00 (C-1′), 92.53 (C-1), 75.48 (C-4), 73.75 (C-5), 72.76 (C-3), 71.69 (C-3′), 71.32 (C-5′), 70.61 (C-2), 69.73, 67.39 (C-2′,4′), 62.04 (C-6), 60.92 (C-6′); ESI-HRMS calcd for $C_{68}H_{58}NO_{19}$ $[M+NH_4]^+$: 1192.3603; found: 1192.3623; Anal. Calcd for $C_{68}H_{54}O_{19}$: C, 69.50; H, 4.63. Found: C, 69.53; H, 4.61.

3.3.8. Ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-1-thio-α- (16) and β-D-glucopyranoside (17) (Hepta-*O*-benzoyl-1-thio-α- and β-lactoside)

Reaction conditions: EtSH (0.15 mL, 2.0 mmol), $BF_3{\cdot}Et_2O$ (0.23 mL, 1.8 mmol), 2 h, 50 °C; chromatography, 50:1→25:1 toluene–EtOAc; yield, starting from **15** (1.175 g, 1.0 mmol), 1.024 g (76%) of mixture of **16** and **17**. Compound **16** crystallized from DCM–MeOH.

Compound **16**: R_f = 0.5 (19:1 toluene–EtOAc); Mp 221–222.5 °C (CH_2Cl_2–MeOH); $[\alpha]_D$ +91.3 (*c* 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 5.95 (t, 1H, *J* = 9.6 Hz, H-3), 5.82 (d, 1H, $J_{1,2}$ = 5.9 Hz, H-1), 5.75 (br d, partially overlapped, H-4′), 5.73 (dd, partially overlapped, $J_{2',3'}$ = 10.2, $J_{1',2'}$ = 8.0 Hz), 5.43 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H-2), 5.38 (dd, 1H, $J_{3',4'}$ = 3.4 Hz, H-3′), 4.92 (d, 1H, H-1′), 4.61– 4.52 (m, 3H, H-5, H-6a′, H-6b′), 4.21 (t, 1H, *J* = 9.5 Hz, H-4), 3.91 (t, 1H, *J* = 6.7 Hz, H-5′), 3.85 (d, 1H, $J_{6a',6b'}$ = 11.3, $J_{5',6a'}$ = 6.4 Hz, H-6a′), 3.76 (dd, 1H, $J_{5',6b'}$ = 7.1 Hz, H-6b′), 2.61–2.45 (m, 2H, SCH_2CH$_3$), 1.18 (t, *J* = 7.4 Hz, 3H, SCH$_2$CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 101.13 ($J_{C\text{-}1',H\text{-}1'}$ = 160.1 Hz, C-1′), 81.91 ($J_{C\text{-}1,H\text{-}1}$ = 168.2 Hz, C-1), 76.35 (C-4), 71.95 (C-3′), 71.49 (C-2), 71.30 (C-5′), 70.87 (C-3), 69.88 (C-2′), 68.78 (C-5), 67.45 (C-4′), 62.53 (C-6), 61.05 (C-6′), 24.23 (SCH$_2$CH$_3$), 14.55 (SCH$_2$CH$_3$); ESI-HRMS calcd for $C_{63}H_{58}NO_{17}S$ $[M+NH_4]^+$: 1132.3425; found: 1132.3457; Anal. Calcd for $C_{63}H_{54}O_{17}S$: C, 67.85; H, 4.88. Found: C, 67.94; H, 4.90.

The mother liquor contained predominantly ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-1-thio-β-D-glucopyranoside **17**, and a solvent suitable for separation by chromatography could not be found; R_f = 0.5 (19:1 toluene–EtOAc); amorphous solid; lit.[30] amorphous solid; ^1H NMR (600 MHz, $CDCl_3$) δ

5.82 (t, 1H, J = 9.3 Hz, H-3), 5.73 (m, partially overlapped, H-4′), 5.72 (dd, partially overlapped, $J_{2',3'}$ = 10.3, $J_{1'2'}$ = 7.9 Hz, H-2′), 5.50 (t, 1H, J = 9.7 Hz, H-2), 5.37 (dd, 1H, $J_{3',4'}$ = 3.4 Hz, H-3′), 4.87 (d, 1H, H-1′), 4.73 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1), 4.60 (dd, 1H, $J_{6a,6b}$ = 12.2, $J_{5,6a}$ = 1.8 Hz, H-6a), 4.49 (dd, 1H, $J_{5,6b}$ = 4.7 Hz, H-6b), 4.24 (t, 1H, J = 9.5 Hz, H-4), 3.90 (t, 1H, J = 6.8 Hz, H-5′), 3.86 (ddd, 1H, $J_{4,5}$ = 10.0 Hz, H-5), 3.72 (m, 2H, H-6a′, H-6b′), 2.75–2.61 (m, 2H, SCH_2CH$_3$), 1.20 (t, J = 7.5 Hz, 3H, SCH$_2$CH_3); ^{13}C NMR (150 MHz, CDCl$_3$) δ 100.92 ($J_{C\text{-}1',H\text{-}1'}$ = 161.4 Hz, C-1′), 83.74 ($J_{C\text{-}1,H\text{-}1}$ = 153.5 Hz, C-1), 77.00 (C-5), 75.92 (C-4), 73.97 (C-3), 71.75 (C-3′), 71.31 (C-5′), 70.48 (C-2), 69.82 (C-2′), 67.44 (C-4′), 62.65 (C-6), 60.98 (C-6′), 24.43 (SCH$_2$CH$_3$), 14.85 (SCH$_2$CH$_3$); ESI-HRMS calcd for $C_{63}H_{58}NO_{17}S$ [M+NH$_4$]$^+$: 1132.3425; found: 1132.3441; Anal. Calcd for $C_{63}H_{54}O_{17}S$: C, 67.85; H, 4.88. Found: C, 67.82; H, 4.80.

3.3.9. 1,2,3,6-tetra-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-β-D-glucopyranose (Octa-*O*-benzoyl-β-maltose, 19)

Reaction conditions: 40 h, 50 °C; flash chromatography, 50:1→25:1 toluene–EtOAc; yield, starting from 18 (1.71 g, 5.0 mmol), 4.32 g (74%); R_f = 0.5 (15:1 toluene–EtOAc); Mp 193–195 °C (MeOH); [α]$_D$ +62.0 (*c* 1.0, CHCl$_3$); lit.[32] Mp 190–192 °C (acetone–MeOH); [α]$_D$ +68.2 (*c* 1.0, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.27 (d, 1H, $J_{1,2}$ = 7.4 Hz, H-1), 6.11 (t, 1H, J = 10.0 Hz, H-3′), 5.85 (t, 1H, J = 8.6 Hz, H-3), 5.79 (d, 1H, $J_{1'2'}$ = 3.9 Hz, H-1′), 5.68 (t, 1H, J = 9.8 Hz, H-4′), 5.64 (dd, 1H, $J_{2,3}$ = 8.7 Hz, H-2), 5.26 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2′), 4.90 (dd, 1H, $J_{6a,6b}$ = 12.3, $J_{5,6a}$ = 2.5 Hz, H-6a), 4.78 (dd, 1H, $J_{5,6b}$ = 3.8 Hz, H-6b), 4.67 (t, 1H, J = 9.0 Hz, H-4), 4.44 (dt, 1H, $J_{4',5'}$ = 10.1 Hz, H-5′), 4.41 – 4.35 (m, 2H, H-6a′, H-5), 4.21 (dd, 1H, $J_{6a',6b'}$ = 12.3, $J_{5',6b'}$ = 3.5 Hz, H-6b′); ^{13}C NMR (150 MHz, CDCl$_3$) δ 96.37 (C-1′), 92.13 (C-1), 74.81 (C-3), 73.47 (C-5), 72.60 (C-4), 71.09 (C-2), 70.91 (C-2′), 69.80 (C-3′), 69.14 (C-5′), 68.94 (C-4′), 63.09 (C-6), 62.34 (C-6′); ESI-HRMS calcd for $C_{68}H_{58}NO_{19}$ [M+NH$_4$]$^+$: 1192.3603; found: 1192.3596; Anal. Calcd for $C_{68}H_{54}O_{19}$: C, 69.50; H, 4.63. Found: C, 69.39; H, 4.80.

3.3.10. Ethyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-1-thio-α- (20) and β-D-glucopyranoside (21) (Ethyl hepta-*O*-benzoyl-1-thio-α- and β-maltoside)

Reaction conditions: EtSH (0.34 mL, 4.5 mmol), BF$_3$·Et$_2$O (0.42 mL, 3.3 mmol), 3 h, 50 °C; chromatography, 50:1 toluene–EtOAc; yield, starting from **19** (3.525 g, 3.0 mmol), 3.02 g (90%) of mixture of **20** and **21**. Only small amounts of pure **20** and **21** could be isolated by flash chromatography.

Compound **20**: Amorphous solid after freeze-drying of a solution in benzene; R_f = 0.5 (19:1 toluene–EtOAc); [α]$_D$ +112.2 (*c* 1.0, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.11 (dd, 1H, $J_{2',3'}$ = 10.5, $J_{3',4'}$ = 9.6 Hz, H-3′), 5.96 (dd, 1H, $J_{2,3}$ = 10.0, $J_{3,4}$= 8.9 Hz, H-3), 5.82 (d, 1H, $J_{1,2}$ = 5.6 Hz, H-1), 5.77 (d, 1H, $J_{1',2'}$ = 3.9 Hz, H-1′), 5.68 (t, 1H, J = 9.8 Hz, H-4′), 5.29 (dd, partially overlapped, H-2′), 5.28 (dd, partially overlapped, H-2), 4.87 (dd, 1H, $J_{6a,6b}$ = 11.9, $J_{5,6a}$ = 2.1 Hz, H-6a), 4.83–4.80 (m, 1H, H-5), 4.78 (dd, 1H, $J_{5,6b}$ = 4.5 Hz, H-6b), 4.50 (dt, 1H, $J_{4',5'}$ = 10.1, $J_{5',6a',b'}$ = 3.4 Hz, H-5′), 4.45 (dd, 1H, $J_{6a',6b'}$ = 12.3, $J_{5',6a'}$ = 3.1 Hz, H-6a′), 4.42 (t, J = 9.3 Hz, H-4), 4.31 (dd, 1H, $J_{5',6b'}$ = 3.7 Hz, H-6b′), 2.65–2.55 (m, 2H, SCH_2CH$_3$), 1.25 (t, 3H, J = 7.4 Hz, SCH$_2$CH_3); ^{13}C NMR (150 MHz, CDCl$_3$) δ 96.72 ($J_{C\text{-}1',H\text{-}1'}$ = 176.2 Hz, C-1′), 81.78 ($J_{C\text{-}1,H\text{-}1}$ = 168.3 Hz, C-1), 73.90 (C-4), 72.74 (C-3), 72.03 (C-2), 70.83 (C-2′), 69.84 (C-3′), 69.17 (C-5′), 69.08 (C-4′), 68.62 (C-5), 63.54 (C-6), 62.44 (C-6′), 24.33 (SCH$_2$CH$_3$), 14.69 (SCH$_2$CH$_3$); ESI-HRMS calcd for $C_{63}H_{58}NO_{17}S$ [M+NH$_4$]$^+$: 1132.3425; found: 1132.3400; Anal. Calcd for $C_{63}H_{54}O_{17}S$: C, 67.85; H, 4.88. Found: C, 67.87; H, 4.80.

Compound **21**: R_f = 0.5 (19:1 toluene–EtOAc); Mp 146–148 °C (MeOH); [α]$_D$ +69.6 (*c* 1.0, CHCl$_3$); lit.[33], mode of preparation and characterization data were not disclosed; ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.08 (dd, 1H, $J_{2',3'}$ = 10.5, $J_{3',4'}$ = 9.6 Hz, H-3′), 5.80 (t, 1H, J = 9.2 Hz, H-3), 5.74 (d, 1H, $J_{1',2'}$ = 3.9 Hz, H-1′), 5.65 (t, 1H, J = 9.8 Hz, H-4′), 5.36 (t, 1H, J = 9.6 Hz, H-2), 5.24 (dd, 1H, H-2′), 4.93 (dd, 1H, $J_{6a,6b}$ = 12.1, $J_{5,6a}$ = 2.4 Hz, H-6a), 4.81 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 4.74 (dd, 1H, $J_{5,6b}$ = 4.4 Hz, H-6b), 4.49 (t, 1H, J = 9.3 Hz, H-4), 4.45 (dt, partially overlapped, $J_{4',5'}$ = 10.1, $J_{5',6a',b'}$ = 3.5 Hz, H-5′), 4.40 (dd, 1H, $J_{6a',6b'}$ = 12.2 Hz, $J_{5',6a'}$ = 3.1 Hz, H-6a′), 4.26 (dd, 1H, $J_{5',6b'}$ = 3.8 Hz, H-6b′), 4.10 (ddd, 1H, $J_{4,5}$ = 9.6 Hz, H-5), 2.86–2.58 (m, 2H, SCH_2CH$_3$), 1.22 (t, 3H, J = 7.5 Hz, SCH$_2$CH_3); ^{13}C NMR (150 MHz, CDCl$_3$) δ 96.3 ($J_{C\text{-}1',H\text{-}1'}$ = 175.7 Hz, C-1′), 83.5 ($J_{C\text{-}1,H\text{-}1}$ = 154.7 Hz, C-1), 76.76 (C-5), 76.11 (C-3), 73.03 (C-4), 70.98 (C-2), 70.87 (C-2′), 69.81 (C-3′), 69.12 (C-5′), 69.04 (C-4′), 63.62 (C-6), 62.48 (C-6′), 24.3 (SCH$_2$CH$_3$), 14.9 (SCH$_2$CH$_3$); ESI-HRMS calcd for $C_{63}H_{58}NO_{17}S$ [M+NH$_4$]$^+$: 1132.3425; found: 1132.3401; Anal. Calcd for $C_{63}H_{54}O_{17}S$: C, 67.85; H, 4.88. Found: C, 67.93; H, 4.76.

3.3.11. 1,2,3,4-tetra-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl)-β-D-glucopyranose (Octa-*O*-benzoyl-β-melibiose, 23)

Reaction conditions: 16 h, 50 °C; flash chromatography, 50:1→20:1 toluene–EtOAc; yield, starting from melibiose monohydrate (1.08 g, 3.0 mmol), 2.53 g (75%); R_f = 0.5 (15:1 toluene–EtOAc); Mp 165–168 °C (MeOH); [α]$_D$ +141.3 (*c* 1.0, CHCl$_3$); lit.[34] (anomeric configuration not specified; in the absence of NMR data, judging by physical constants, the compound reported previously is likely the α anomer): Mp 111–112 °C (EtOH), [α]$_D$ +174 (*c* 4.55, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.15 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 6.12 (dd, 1H, $J_{2',3'}$ = 10.7, $J_{3',4'}$ = 3.5 Hz, H-3′), 6.02–5.99 (m, partially overlapped, H-4′), 5.98 (t, partially overlapped, J 9.7 Hz, H-3), 5.71 (dd, 1H, $J_{1',2'}$ = 3.7 Hz, H-2′), 5.70 (t, 1 H, J = 9.8 Hz, H-4), 5.61 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 5.43 (d, 1H, H-1′), 4.65 (br t, 1H, H-5′), 4.36 (dd, 1H, $J_{6a',6b'}$ = 11.5, $J_{5',6a'}$ = 7.7 Hz, H-6′a′), 4.23 (ddd, 1H, $J_{4,5}$ = 10.1, $J_{5,6a}$ = 5.1, $J_{5,6b}$ = 1.8 Hz, H-5), 4.09 (dd, 1H, $J_{5',6b'}$ = 4.9 Hz, H-6b′), 4.02 (dd, 1H, $J_{6a,6b}$ = 11.4 Hz, H-6a), 3.83 (dd, 1H, H-6b); ^{13}C NMR (150 MHz, CDCl$_3$) δ 96.57 (C-1′), 92.92 (C-1), 74.20 (C-5), 72.87 (C-3), 70.85 (C-2), 69.35 (C-4′), 68.89 (C-2′), 68.59 (C-4), 68.55 (C-3′), 67.14 (C-5′), 65.68 (C-6), 62.86 (C-6′); ESI-HRMS calcd for $C_{68}H_{58}NO_{19}$ [M+NH$_4$]$^+$: 1192.3603; found: 1192.3628; Anal. Calcd for $C_{68}H_{54}O_{19}$: C, 69.50; H, 4.63. Found: C, 69.23; H, 4.89.

3.3.12. Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl)-1-thio-α- (24) and β-D-glucopyranoside (25) (Ethyl hepta-*O*-benzoyl-1-thio-α- and β-melibioside)

Reaction conditions: EtSH (0.19 mL, 2.5 mmol), BF$_3$·Et$_2$O (0.25 mL, 2.0 mmol), 16 h, 60 °C (optimum reaction time determined by NMR spectroscopy); chromatography, 50:1→30:1 toluene–EtOAc; yield, starting from **23** (1.175 g, 1.0 mmol), 0.320 g (29%) of **24**, 0.159 g (14%) of **25**. Unresolved mixture of **24** and **25** (0.495 g, 44%) was also obtained.

Compound **24**: Amorphous solid after freeze-drying of a solution in benzene; R_f = 0.6 (12:1 toluene–EtOAc); [α]$_D$ +165.0 (*c* 1.0, CHCl$_3$); ^{1}H NMR (600 MHz, CDCl$_3$) δ 6.05 (br d, 1H, $J_{3',4'}$ = 3.4 Hz, H-4′), 6.01 (dd, $J_{2',3'}$ = 10.5, Hz, H-3′), 5.98 (t, 1H, J = 9.9 Hz, H-3), 5.81 (d, 1H, $J_{1,2}$ = 5.9 Hz, H-1), 5.71 (dd, 1H, $J_{1',2'}$ = 3.7 Hz, H-2′), 5.48 (d, 1H, H-1′), 5.35 (t, 1H, J = 9.9 Hz, H-4), 5.05 (dd, 1H, $J_{2,3}$ = 10.1 Hz, H-2), 4.72 (br dd, 1H, H-5′), 4.69 (ddd, 1H, $J_{4,5}$ = 10.1, $J_{5,6a}$ = 6.5, $J_{5,6b}$ = 1.9 Hz, H-5), 4.51 (dd, 1H, $J_{6a',6b'}$ = 11.5, $J_{5',6a'}$ = 4.8 Hz, H-6a′), 4.43 (dd, 1H, $J_{5',6b'}$ = 7.7 Hz, H-6b′), 4.04 (dd, 1H, $J_{6a,6b}$ = 11.0 Hz, H-6a), 3.65 (dd, 1H, H-6b), 2.76–2.58 (m, 2H, SCH_2CH$_3$), 1.35 (t, 3H, J = 7.4 Hz, SCH$_2$CH_3); ^{13}C NMR (150 MHz, CDCl$_3$) δ 96.25 ($J_{C\text{-}1',H\text{-}1'}$ = 173.7 Hz, C-1′), 81.10 ($J_{C\text{-}1,H\text{-}1}$ = 170.0 Hz, C-1), 71.57 (C-2), 70.84 (C-3), 69.30 (C-4′), 69.17 (C-4), 69.08 (C-2′), 68.71 (C-5), 68.42 (C-3′), 67.18 (C-5′), 65.98 (C-6), 62.84 (C-6′), 23.93 (SCH$_2$CH$_3$), 14.45 (SCH$_2$CH$_3$); ESI-HRMS calcd for $C_{63}H_{58}NO_{17}S$ [M+NH$_4$]$^+$: 1132.3425; found: 1132.3422; Anal. Calcd for $C_{63}H_{54}O_{17}S$: C, 67.85; H, 4.88. Found: C, 67.82; H, 5.02.

Compound **25**: R_f = 0.5 (19:1 toluene–EtOAc); Mp 157–159 °C; $[\alpha]_D$ +128.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.06 (dd, 1H, $J_{2',3'}$ = 10.6, $J_{3',4'}$ = 3.4 Hz, H-3′), 6.03 (dd, 1H, $J_{4,5}$ = 1.2 Hz, H-4′), 5.85 (t, 1H, *J* = 9.6 Hz, H-3), 5.73 (dd, 1H, $J_{1',2'}$ = 3.7 Hz, H-2′), 5.59 (t, 1H, *J* = 9.6 Hz, H-4), 5.49 (d, 1H, H-1′), 5.33 (t, 1H, *J* = 9.7 Hz, H-2), 4.74 (d, 1H, $J_{1,2}$ = 10.0 Hz, H-1), 4.66 (br t, 1H, H-5′), 4.47 (dd, 1H, $J_{6a',6b'}$ = 11.4, $J_{5',6a'}$ = 7.2 Hz, H-6a′), 4.31 (dd, 1H, $J_{5',6b'}$ = 5.6 Hz, H-6b′), 4.06–3.98 (m, 2H, H-5, H-6a), 3.80–3.76 (m, 1H, H-6b), 2.64 (q, 2H, *J* = 7.4 Hz, SCH_2CH_3), 1.16 (t, 3H, *J* = 7.4 Hz, SCH_2CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 96.57 ($J_{C\text{-}1',H\text{-}1'}$ = 173.7 Hz, C-1′), 83.64 ($J_{C\text{-}1,H\text{-}1}$ = 153.0 Hz, C-1), 77.42 (C-5), 74.23 (C-3), 70.41 (C-2), 69.19 (C-4′), 69.02 (C-2′), 68.98 (C-4), 68.40 (C-3′), 67.15 (C-5′), 66.29 (C-6), 62.60 (C-6′), 23.84 (SCH_2CH_3), 14.69 (SCH_2CH_3); ESI-HRMS calcd for $C_{63}H_{58}NO_{17}S$ $[M+NH_4]^+$: 1132.3425; found: 1132.3397; Anal. Calcd for $C_{63}H_{54}O_{17}S$: C, 67.85; H, 4.88. Found: C, 67.96; H, 5.15.

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