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Catalyst-free Efficient Synthesis of 3-Thio-2-deoxysugar Derivatives in Water

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3-Thio- and 3-dithiocarbamoyl-2-deoxy carbohydrate derivatives have been synthesized using water as solvent without using a catalyst. In most of the cases yields obtained were excellent.

Keywords Carbohydrate, Deoxy sugars, Thia-Michael reaction, Dithiocarbamoyl, Water, Catalyst free

INTRODUCTION

Thiosugars as potential therapeutics have attracted considerable attention of medicinal chemists because of their ability to act as enzyme inhibitors.^[1] Application of thiosugars could be beneficial in designing therapeutics against infectious disease and cancers.^[2] Glycosyl dithiocarbamates could also serve as potential enzyme inhibitors. In order to design carbohydrate-derived molecules of medicinal interest, we were interested in synthesizing a series of 3-thio- or 3-dithiocarbamoyl-2-deoxy glycosides. Although a number of reports are available in the literature for the synthesis of thiosugars using thio-Michael reaction of carbohydrate-derived thiols and activated alkenes,^[3] synthesis of dithiocarbamate derivatives are limited and none of them used carbohydrate substrates.^[4,5]

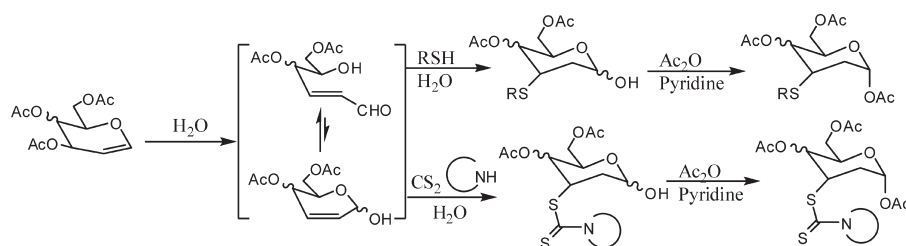
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Recently, two elegant reaction protocols for the addition of thiols^[6] and dithiocarbamates^[7] to the activated olefins in water without using catalyst were disclosed. Prompted by these reports, it has been envisaged that water-mediated addition of a thiol or thiocarbamate anion generated in situ to the glycal-derived 2,3-dideoxy-glyconolactol or lactone could result in 3-thio- or 3-thiocarbamoyl-2-deoxy glyconolactol or lactones. Organic reactions in water instead of using organic solvents have become attractive for environmental reasons. Here we report an expedient synthesis of 3-mercapto or 3-dithiocarbamoyl-2-deoxy-carbohydrate derivatives by the conjugate addition of thiols or dithiocarbamate anion to glycal-derived α,β -unsaturated carbonyl compounds in water at rt without the use of any catalyst. The reaction has been extended to a one-pot preparation of 3-mercapto or 3-dithiocarbamoyl-2-deoxy-carbohydrate derivatives starting from glycal derivatives (Sch. 1).

RESULTS AND DISCUSSION

In a set of initial experiments, 3,4,6-tri-*O*-acetyl-D-glucal (1 mmol) was taken in water (5 mL) and stirred at 80°C for 25 min to generate 4,6-di-*O*-acetyl-2,3-dideoxy-erythro-hex-2-eno-pyranose following a literature method.^[8] After complete consumption of the starting material, the reaction mixture was cooled to rt, thiophenol (1.1 mmol) was added, and the reaction mixture was allowed to stir vigorously at rt. The reaction was completed in 5 min. The crude product, isolated after workup, was acetylated using pyridine and acetic anhydride to furnish 1,4,6-tri-*O*-acetyl-2-deoxy-3-mercaptophenyl-D-glucopyranose in 90% yield. Variation of the amount of water did not show any significant role in product formation. In order to establish the generality of the reaction, 3,4,6-tri-*O*-acetyl-D-glucal was treated with water as mentioned earlier and the product obtained was allowed to react with a series of thiols in water at rt. Excellent yields were obtained in each case within 5 to 15 min. Use of carbohydrate-derived thiols instead of simple thiols also resulted in an excellent yield of thio-linked disaccharides in a slightly longer reaction time (~30 min). In order to prepare D-galactal-derived thio-adduct, 3,4,6-tri-*O*-acetyl-D-galactal



Scheme 1: Addition of thiols or dithiocarbamate anions to glycal-derived α,β -unsaturated carbonyl compounds in water.

was first treated with water in the presence of a catalytic amount of mercuric sulfate and sulfuric acid^[9] for 5 min, the resulting solution was filtered, and the filtrate was treated with a series of thiols as mentioned in the case of D-glucal-derived 2,3-unsaturated lactol. In every case excellent yields of 3-mercapto-2-deoxy-D-galactose derivatives were obtained. This methodology was then extended for the addition of thiols to α,β -unsaturated glyconolactones, which are also prepared by the treatment of 3,4,6-tri-*O*-acetyl-glycals with a combination of indium chloride and IBX in water.^[10] A solution of 4,6-di-*O*-acetyl-2,3-dideoxy-erythro-hex-2-eno-glyconolactone (1.0 mmol) and thiophenol (1.2 mmol) in water (2 mL) was allowed to stir at rt. Excellent yield of 4,6-di-*O*-acetyl-3-thiophenyl-2-deoxy-D-glyconolactone was achieved in 30 min. A series of aryl and alkyl thiols and sugar-derived thiols were also allowed to react with D-glucal- and D-galactal-derived 2,3-unsaturated glyconolactones to furnish the products in very good yield (Table 1). Stirring plays a significant role in the rate of reaction. In a control experiment, keeping a solution of D-glucal-derived 2,3-unsaturated glyconolactol and thiophenol in water without stirring at rt for 24 h furnished only a ~40% yield of the product.

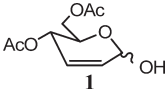
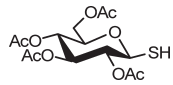
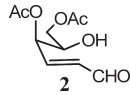
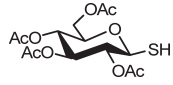
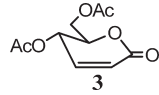
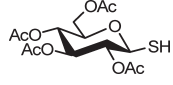
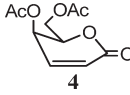
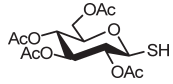
After achieving satisfactory yield of thia-Michael adducts of 2,3-unsaturated glyconolactols and lactones, we turned our attention to the preparation of 3-dithiocarbamoyl-2-deoxy sugar derivatives. For this purpose, we have applied the reaction protocol reported by Saidi et al.^[7] In a model experiment, a suspension of piperidine (1 mmol) and carbon disulfide (1.2 mmol) in water (5 mL) was allowed to stir at rt for 5 min. To the stirred reaction mixture was added 4,6-di-*O*-acetyl-2,3-dideoxy-erythro-hex-2-enopyranose and the resulting reaction mixture was stirred at rt. Gratifyingly, the reaction was completed in 1 h and the product was isolated by extracting the reaction mixture with ethyl acetate. In order to generalize the reaction conditions, a series of amines were allowed to react with D-glucal- and D-galactal-derived 2,3-unsaturated aldehydes (or glyconolactols) in the presence of carbon disulfide in water at rt. Excellent yields were achieved in every case (Table 1). All reactions can be scaled up for the preparation of compounds in larger quantities. For spectral analysis all products were conventionally acetylated using pyridine-acetic anhydride and characterized by NMR and mass spectroscopy.

EXPERIMENTAL

General Methods

All the reactions were monitored by thin layer chromatography over silica gel GF₂₅₄ coated TLC plates. The spots on TLC were visualized by UV lamp and warming ceric sulphate (2%Ce(SO₄)₂ in 2 N H₂SO₄) sprayed plates on a hot plate. Silica gel 230–400 mesh was used for flash column chromatography.

Table 1: Addition of thiols and dithiocarbamate to α,β -unsaturated lactols and lactones.

Entry	Substrate	Thiol/dithiocarbamate	Time (min)	Yield (%)	R/S ^a
1		PhSH	5	90	1:3.5
2		2-(Me)-PhSH	5	85	1:4
3		3-(Me)-PhSH	5	95	1:3.5
4		4-(Me)PhSH	5	90	1:4
5		KSAc	10	92	1:2
6		HSCH ₂ COOEt	15	88	1:4
7				30	80
8		2-Mercaptopyridine	15	82	1:4.5
9		Piperidine/CS ₂	60	78	1:6.6
10		Morpholine/CS ₂	60	75	1:9.6
11		Diethylamine/CS ₂	60	80	1:6
12		1,2,3,4-Tetrahydroisoquinoline/CS ₂	90	72	1:9.5
13		PhSH	5	92	4:1
14		2-(Me)-PhSH	5	88	4.5:1
15		3-(Me)-PhSH	5	95	3.6:1
16		4-(Me)PhSH	5	95	4:1
17		KSAc	15	90	2.5:1
18		HSCH ₂ COOEt	15	85	4.6:1
19				30	82
20		2-Mercaptopyridine	15	80	5:1
21		Piperidine/CS ₂	60	80	9.5:1
22		Morpholine/CS ₂	60	75	9.5:1
23		Diethylamine/CS ₂	60	82	9.5:1
24		1,2,3,4-Tetrahydroisoquinoline/CS ₂	90	75	9.5:1
25		PhSH	30	78	1:4
26		2-(Me)-PhSH	30	82	1:3.5
27		3-(Me)-PhSH	30	85	1:4
28		4-(Me)PhSH	30	90	1:4
29		KSAc	30	75	1:2.5
30			30	72	0:1
31		PhSH	25	88	9:1
32		2-(Me)-PhSH	30	80	9.5:1
33		3-(Me)-PhSH	30	90	9.5:1
34		4-(Me)PhSH	30	92	9.5:1
35				30	82

^aDetermined from the integration values of the corresponding signals in ¹H NMR spectra.

^1H and ^{13}C NMR, 2D COSY, and HSQC spectra were recorded on a Bruker Avance DPX 200 and 300 MHz using CDCl_3 as solvent and TMS as internal reference unless stated otherwise. Chemical shift values were expressed in (ppm). ESI-MS spectra were recorded on a MICROMASS QUTTRO II triple quadrupole mass spectrometer. Elementary analysis was carried out on a Carlo ERBA-1108 analyzer. Optical rotations were measured at 25°C on a Rudolf Autopol III polarimeter. Commercially available grades of organic solvents of adequate purity are used in many reactions.

General Experimental Condition

3-Mercapto-2-dideoxy-D-glycose

A solution of tri-*O*-acetyl-D-glucal (1 mmol) in distilled water (5 mL) was placed on a preheated oil bath at 80°C for 25 min. [In case of tri-*O*-acetyl-D-galactal: to a solution of tri-*O*-acetyl-D-galactal (1 mmol) in water (5 mL) was added catalytic amount of HgSO_4 (5 mg) and 0.1 N H_2SO_4 (2–3 drops) and the reaction mixture was stirred at rt for 5 min.] After consumption of the starting glycal derivative (TLC), the reaction mixture was cooled to rt, appropriate thiol (1.2 mmol) was added to it, and the reaction mixture was stirred vigorously for the appropriate time (Table 1). The reaction mixture was extracted with EtOAc (20 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was acetylated using acetic anhydride and pyridine to furnish acetylated product, which was purified by column chromatography using hexane-EtOAc to afford pure acetylated product. Following the similar reaction condition a series of 3-mercapto-2-deoxy sugar derivatives and (1-3)-linked thiodisaccharides were synthesized.

3-Mercapto-2-deoxy-D-glyconolactone

To a solution of tri-*O*-acetyl-D-glucal (1 mmol) in distilled water (5 mL) were added InCl_3 (0.1 mmol) and IBX (2.5 mmol) and the reaction mixture was allowed to stir at 80°C for 6 h. After consumption of the starting material (TLC) the reaction mixture was cooled to rt and extracted with EtOAc (25 mL). The organic layer was washed with aq. NaHCO_3 , dried (Na_2SO_4), and concentrated. To a solution of the crude lactone (1 mmol) in water (5 mL) was added an appropriate thiol (1.2 mmol) and the reaction mixture was stirred vigorously at rt for the appropriate time (Table 1). The reaction mixture was extracted with EtOAc (20 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by column chromatography using hexane-EtOAc to furnish pure product. Following the similar reaction condition a series of 3-mercapto-2-deoxy glyconolactone derivatives were synthesized.

3-Dithiocarbamoyl-2-deoxy-D-glycose

To a solution of a secondary amine (1 mmol) in water (5 mL) was added carbon disulfide (1.2 mmol) at rt and the reaction mixture was allowed to stir at rt for 5 min. Glycal-derived 2,3-unsaturated glyconolactol was added to the reaction mixture and the reaction mixture was allowed to stir at rt for the appropriate time (Table 1). After completion (TLC), the reaction mixture was extracted with EtOAc (25 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was acetylated using acetic anhydride and pyridine and purified by column chromatography using hexane-EtOAc (3:1) to furnish pure acetylated product, which was characterized by NMR and mass spectral analysis. Following the similar reaction condition a series of 3-dithiocarbamoyl-2-deoxy glyconolactol derivatives were synthesized in excellent yield.

1,4,6-Tri-O-acetyl-3-mercaptophenyl-2-deoxy- α -D-glucopyranose (Table 1, entry 1): S-isomer

^1H NMR (CDCl_3 , 200 MHz): δ 7.49–7.28 (m, 5H, Ar-H), 6.20–6.06 (m, 1H, H-1), 5.05–4.87 (m, 1H, H-4), 4.35–4.10 (m, 2H, H-3, H-6_a), 4.08–3.90 (m, 2H, H-5, H-6_b), 2.12, 2.09, 2.07 (3 s, 9H, 3 COCH_3), 2.16–1.87 (m, 2H, H-2_{ae}); ^{13}C NMR (CDCl_3 , 50 MHz): δ 170.7, 170.1, 169.9 (3 COCH_3), 134.2–128.0 (Ar-C), 91.2 (C-1), 71.6 (C-5), 68.6 (C-4), 62.7 (C-6), 44.0 (C-3), 33.4 (C-2), 21.4, 21.3, 21.0 (3 COCH_3); **R-isomer**: ^1H NMR (CDCl_3 , 200 MHz): δ 7.50–7.26 (m, 5H, Ar-H), 6.15–6.02 (m, 1H, H-1), 5.0–4.84 (m, 1H, H-4), 4.40–4.18 (m, 2H, H-3, H-6_a), 4.10–3.95 (m, 1H, H-6_b), 3.78–3.66 (m, 2H, H-5), 2.09, 2.07, 1.95 (3 s, 9H, 3 COCH_3); ^{13}C NMR (CDCl_3 , 50 MHz): δ 170.1, 169.6, 169.0 (3 COCH_3), 134.3–128.0 (Ar-C), 92.8 (C-1), 75.7 (C-5), 69.0 (C-4), 62.7 (C-6), 47.0 (C-3), 35.7 (C-2), 21.2, 21.0, 20.9 (3 COCH_3); ESI-MS: $m/z = 405.4$ [$\text{M} + \text{Na}$] $^+$; Anal. Calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_7\text{S}$ (382.43): C, 56.53; H, 5.80; found: C, 56.35; H, 6.05.

1,4,6-Tri-O-acetyl-3-mercapto (2-methylphenyl)-2-deoxy- α -D-glucopyranose (Table 1, entry 2): S-isomer

^1H NMR (CDCl_3 , 200 MHz): δ 7.45–7.13 (m, 4H, Ar-H), 6.20–6.13 (m, 1H, H-1), 5.0–4.90 (m, 1H, H-4), 4.45–4.20 (m, 1H, H-3), 3.88–4.10 (m, 2H, H-6_{ab}), 3.68–3.50 (m, 1H, H-5), 2.40 (s, 3H, CH_3), 2.18–1.90 (m, 2H, H-2_{ea}), 2.11, 2.09, 2.06 (3 s, 9H, 3 COCH_3); ^{13}C NMR (CDCl_3 , 50 MHz): δ 170.8, 170.7, 169.9 (3 COCH_3), 140.8–126.8 (Ar-C), 91.1 (C-1), 71.6 (C-5), 69.9 (C-4), 62.7 (C-6), 43.6 (C-3), 35.6 (C-2), 21.4, 21.3, 21.0 (3 s, 9H, 3 COCH_3), 20.7 (CH_3); **R-isomer**: ^1H NMR: δ 7.45–7.13 (m, 4H, Ar-H), 6.18–6.12 (m, 1H, H-1), 5.02 (t, $J = 9.4$ Hz, 1H, H-4), 4.40–4.18 (m, 1H, H-3), 4.15–4.0 (m, 2H, H-6_{ab}), 3.40–3.28 (m, 1H, H-5), 2.42 (s, 3H, CH_3), 2.20–1.90 (m, 2H, H-2_{ea}), 2.09, 2.06, 2.03 (3 s, 9H, 3 COCH_3); ^{13}C NMR (CDCl_3 , 50 MHz): δ 170.1, 169.9,

169.0 (3 COCH₃), 140.8–126.8 (Ar-C), 92.7 (C-1), 75.7 (C-5), 69.9 (C-4), 63.3 (C-6), 43.9 (C-3), 36.5 (C-2), 21.7, 21.4, 21.0, 20.8 (3 COCH₃, CH₃); ESI-MS: $m/z = 419.5$ [M + Na]⁺; Anal. Calcd. for C₁₉H₂₄O₇S (396.45): C, 57.56; H, 6.10; found: C, 57.35; H, 6.35.

1,4,6-Tri-O-acetyl-3-mercapto (3-methylphenyl)-2-deoxy- α -D-glucopyranose
(Table 1, entry 3): *S*-isomer

¹H NMR (CDCl₃, 200 MHz): δ 7.26–7.08 (m, 4H, Ar-H), 6.15–6.10 (m, 1H, H-1), 4.98–4.92 (m, 1H, H-4), 4.30–4.18 (m, 2H, H-3, H-6_a), 4.0–3.98 (m, 2H, H-5, H-6_b), 2.35 (s, 3H, CH₃), 2.12–1.87 (m, 2H, H-2_{ea}), 2.08, 2.06 (2 s, 9H, 3 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.1 (2 C), 170.0 (3 COCH₃), 138.7–127.6 (Ar-C), 90.5 (C-1), 71.2 (C-4), 68.0 (C-5), 62.7 (C-6), 43.2 (C-3), 35.0 (C-2), 21.1, 21.0, 20.8 (3 COCH₃), 20.7 (CH₃); **R-isomer:** ¹H NMR (CDCl₃, 200 MHz): δ 5.80–5.70 (m, 1H, H-1), 5.0–4.90 (m, 1H, H-4), 4.30–4.20 (m, 2H, H-3, H-6_a), 3.98–3.92 (m, 2H, H-5, H-6_b), 2.33 (s, 3H, CH₃), 2.12, 1.95, 1.93 (3 s, 9H, 3 COCH₃), 2.10–1.85 (m, 2H, H-2_{ea}); ¹³C NMR (CDCl₃, 50 MHz): δ 169.3, 168.3 (2 C; 3 COCH₃), 138.5–128.3 (Ar-C), 92.2 (C-1), 75.2 (C-4), 68.5 (C-5), 62.1 (C-6), 43.9 (C-3), 33.6 (C-2), 20.9, 20.8, 20.5 (2 C) (3 COCH₃, CH₃); ESI-MS: $m/z = 419.5$ [M + Na]⁺; Anal. Calcd. for C₁₉H₂₄O₇S (396.45): C, 57.56; H, 6.10; found: C, 57.32; H, 6.35.

1,4,6-Tri-O-acetyl-3-mercapto (4-methylphenyl)-2-deoxy- α -D-glucopyranose
(Table 1, entry 4): *S*-isomer

¹H NMR (CDCl₃, 200 MHz): δ 7.37–7.08 (m, 4H, Ar-H), 6.15–6.08 (m, 1H, H-1), 5.0–4.85 (m, 1H, H-4), 4.30–4.07 (m, 2H, H-3, H-6_a), 4.0–3.85 (m, 2H, H-5, H-6_b), 2.35 (s, 3H, CH₃), 2.10–1.80 (m, 2H, H-2_{ea}), 2.08, 2.06 (2 s, 9H, 3 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.3, 170.2, 169.6 (3 COCH₃), 138.3–129.7 (Ar-C), 90.9 (C-1), 71.3 (C-5), 69.1 (C-4), 62.3 (C-6), 43.6 (C-3), 35.1 (C-2), 20.9 (CH₃), 20.6, 20.5, 20.4 (3 COCH₃); **R-isomer:** ¹H NMR (CDCl₃, 200 MHz): δ 7.37–7.08 (m, 4H, Ar-H), 5.77–5.65 (m, 1H, H-1), 5.02–4.88 (m, 1H, H-4), 4.30–4.10 (m, 2H, H-3, H-6_a), 4.02–3.85 (m, 2H, H-6_b), 2.31 (s, 3H, CH₃), 2.11, 2.06, 2.00 (3 s, 9H, 3 COCH₃), 2.10–1.82 (m, 2H, H-2_{ea}); ¹³C NMR (CDCl₃, 50 MHz): δ 169.6, 169.3, 168.5 (3 COCH₃), 138.3–127.4 (Ar-C), 92.4 (C-1), 75.4 (C-4), 68.2 (C-5), 62.3 (C-6), 44.7 (C-3), 33.7 (C-2), 21.1, 21.0, 20.9 (2 C) (3 COCH₃, CH₃); ESI-MS: $m/z = 419.5$ [M + Na]⁺; Anal. Calcd. for C₁₉H₂₄O₇S (396.45): C, 57.56; H, 6.10; found: C, 57.35; H, 6.38.

1,4,6-Tri-O-acetyl-3-mercaptoacetyl-2-deoxy- α -D-glucopyranose (Table 1, entry 5): *S*-isomer

¹H NMR (CDCl₃, 200 MHz): δ 6.18–6.10 (m, 1H, H-1), 6.05.92 (m, 1H, H-4), 5.0–4.85 (m, 1H, H-3), 4.30–4.0 (m, 3H, H-5, H-6_{ab}), 2.33 (s, 3H, SCOCH₃), 2.18–2.0 (m, 2H, H-2_{ea}), 2.11, 2.07, 2.03 (3 s, 9H, 3 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 192.9 (SCOCH₃), 169.8, 169.0, 168.8 (3 COCH₃), 90.6

(C-1), 72.8 (C-5), 66.5 (C-4), 61.7 (C-6), 39.5 (C-3), 32.4 (C-2), 20.8 (2 C), 20.7 (2 C) (3 COCH₃, SCOCH₃); **R-isomer**: ¹H NMR (CDCl₃, 200 MHz): δ 6.15–6.08 (m, 1H, H-1), 5.88–5.78 (m, 1H, H-4), 5.05–4.92 (m, 1H, H-3), 4.32–4.05 (m, 3H, H-5, H-6_{ab}), 2.36 (s, 3H, SCOCH₃), 2.20, 2.15, 2.09 (3 s, 9H, 3 COCH₃), 2.18–2.0 (m, 2H, H-2_{ea}); ¹³C NMR (CDCl₃, 50 MHz): δ 193.7 (SCOCH₃), 169.0, 168.0, 168.0 (3 COCH₃), 91.6 (C-1), 74.9 (C-5), 67.5 (C-4), 62.5 (C-6), 38.2 (C-3), 33.0 (C-2), 21.0, 20.9, 20.8 (2 C); ESI-MS: *m/z* = 371.4 [M + Na]⁺; Anal. Calcd. for C₁₄H₂₀O₈S (348.37): C, 48.27; H, 5.79; found: C, 48.05; H, 6.0.

1,4,6-Tri-O-acetyl-3-(ethylglycoloyl)mercapto-2,3-dideoxy-α-D-glucopyranose
(Table 1, entry 6): *S-isomer*

¹H NMR (CDCl₃, 200 MHz): δ 6.10–6.08 (m, 1H, H-1), 4.80 (t, *J* = 9.6 Hz, 1H, H-4), 4.28–4.21 (m, 4H, H-6_{ab}, OCH₂CH₃), 4.04–3.98 (m, 1H, H-3), 3.65–3.58 (m, 1H, H-5), 3.34–3.23 (m, 2H, SCH₂COOEt), 2.22–2.15 (m, 1H, H-2_e), 2.11, 2.09, 2.08 (3 s, 9H, 3 COCH₃), 2.01–1.85 (m, 1H, H-2_a), 1.30 (t, *J* = 7.5 Hz, 1H, CH₂CH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.2 (COOEt), 169.3, 169.2, 168.5 (3 COCH₃), 92.2 (C-1), 72.9 (C-5), 67.2 (C-4), 63.0 (COOCH₂CH₃), 61.3 (C-6), 44.2 (C-3), 36.2 (SCH₂COOEt), 32.5 (C-2), 21.0, 20.8, 20.7 (3 COCH₃), 14.1 (CH₂CH₃); **R-isomer**: ¹H NMR (CDCl₃, 200 MHz): δ 6.17–6.10 (m, 1H, H-1), 4.91 (t, *J* = 9.4 Hz, 1H, H-4), 4.28–4.14 (m, 4H, H-6_{ab}, OCH₂CH₃), 3.99–3.94 (m, 1H, H-3), 3.73–3.66 (m, 1H, H-5), 3.26–3.15 (m, 2H, SCH₂COOEt), 2.31–2.20 (m, 1H, H-2_e), 2.12, 2.09, 2.08 (3 s, 9H, 3 COCH₃), 2.0–1.80 (m, 1H, H-2_a), 1.30 (t, *J* = 7.4 Hz, 3H, COOCH₂CH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.2, 169.7, 169.5, 169.3 (COOEt, 3 COCH₃), 90.7 (C-1), 71.4 (C-5), 68.4 (C-4), 62.2 (COOCH₂CH₃), 61.3 (C-6), 41.4 (C-3), 35.5 (SCH₂COOEt), 31.7 (C-2), 20.9, 20.7, 20.6 (3 COCH₃), 14.1 (CH₂CH₃); ESI-MS: *m/z* = 415.4 [M + Na]⁺; Anal. Calcd. for C₁₆H₂₄O₉S (392.42): C, 48.97; H, 6.16; found: C, 48.75; H, 6.35.

1,4,6-Tri-O-acetyl-3-mercapto (2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2-deoxy-α-D-glucopyranose (Table 1, entry 7): *S-isomer*

¹H NMR (CDCl₃, 300 MHz): δ 5.23 (t, *J* = 9.9 Hz, 1H, H-3'), 5.14 (t, *J* = 9.9 Hz, 1H, H-2'), 4.98 (t, *J* = 9.6 Hz, 1H, H-4'), 4.93–4.87 (m, 1H, H-4), 4.70–4.65 (m, 1H, H-1), 4.54 (d, *J* = 9.9 Hz, 1H, H-1'), 4.50–4.36 (m, 1H, H-3), 4.31–3.98 (m, 4H, H-6_{ab}, H-6'_{ab}), 3.74–3.70 (m, 2H, H-5, H-5'), 2.39–2.12 (m, 2H, H-2_{ea}), 2.13, 2.12, 2.11, 2.10, 2.08, 2.07, 2.02 (7 s, 21H, 7 COCH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 170.1, 169.9, 169.5, 169.2, 168.9, 168.7, 168.4 (7 COCH₃), 90.3 (C-1), 82.6 (C-1'), 75.4, 73.4, 69.6, 67.9 (2 C), 66.5, 62.7 (C-6), 61.8 (C-6'), 40.8 (C-3), 36.6 (C-2), 20.7 (2 C), 20.6 (2 C), 20.5 (2 C), 20.3; **R-isomer**: ¹H NMR (CDCl₃, 300 MHz): δ 5.20 (t, *J* = 9.9 Hz, 1H, H-3'), 5.15 (t, *J* = 9.9 Hz, 1H, H-2'), 5.0 (t, *J* = 9.6 Hz, 1H, H-4'), 4.90–4.82 (m, 1H, H-4), 4.72–4.68 (m, 1H, H-1), 4.60 (d, *J* = 9.9 Hz, 1H, H-1'),

4.48–4.38 (m, 1H, H-3), 4.30–4.0 (m, 4H, H-6_{ab}, H-6'_{ab}), 3.90–3.82 (m, 2H, H-5, H-5'), 2.40–2.15 (m, 2H, H-2_{ea}), 2.14, 2.12, 2.11, 2.09, 2.07, 2.06, 2.0 (7 s, 21H, 7 COCH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 170.4, 170.0, 169.5, 169.3, 168.9, 168.7, 168.4 (7 COCH₃), 90.7 (C-1), 83.7 (C-1'), 75.7, 73.5, 69.6, 67.7, 67.4, 66.7, 61.6 (C-6), 61.1 (C-6'), 37.3 (C-3), 33.5 (C-2), 20.9 (2 C), 20.7 (2 C), 20.6 (2 C), 20.5; ESI-MS: *m/z* = 659.6 [M + Na]⁺; Anal. Calcd. for C₂₆H₃₆O₁₆S (636.62): C, 49.05; H, 5.70; found: C, 48.80; H, 6.0.

1,4,6-Tri-O-acetyl-3-mercapto (2-pyridyl)-2-deoxy-α-D-glucopyranose (Table 1, entry 8): S-isomer

¹H NMR (CDCl₃, 200 MHz): δ 8.43–8.37 (m, 1H, Ar-H), 7.51–7.43 (m, 1H, Ar-H), 7.17–6.96 (m, 2H, Ar-H), 6.20–6.17 (m, 1H, H-1), 5.17–5.10 (m, 2H, H-3, H-4), 4.39–4.19 (m, 2H, H-6_{ab}), 4.10–4.0 (m, 1H, H-5), 2.35–2.0 (m, 2H, H-2_{ea}), 2.18, 2.14, 2.10 (3 s, 9H, 3 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.2, 170.1, 169.3 (3 COCH₃), 157.1–119.6 (Ar-C), 90.9 (C-1), 73.0 (C-5), 67.7 (C-4), 62.2 (C-6), 37.5 (C-3), 32.6 (C-2), 20.9, 20.8 (2 C) (3 COCH₃); **R-isomer:** ¹H NMR (CDCl₃, 200 MHz): δ 8.43–8.37 (m, 1H, Ar-H), 7.51–7.43 (m, 1H, Ar-H), 7.17–6.96 (m, 2H, Ar-H), 6.10–6.0 (m, 1H, H-1), 5.17–5.08 (m, 1H, H-4), 5.0–4.90 (m, 1H, H-3), 4.40–4.20 (m, 2H, H-6_{ab}), 4.08–4.0 (m, 1H, H-5), 2.30–1.95 (m, 2H, H-2_{ea}), 2.10, 1.90, 1.87 (3 s, 9H, 3 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 169.3, 169.1, 168.3 (3 COCH₃), 157.1–119.6 (Ar-C), 90.7 (C-1), 75.3 (C-4), 67.7 (C-5), 62.1 (C-6), 38.1 (C-3), 33.5 (C-2), 21.1, 20.9, 20.5 (3 COCH₃); ESI-MS: *m/z* = 406.4 [M + Na]⁺; Anal. Calcd. for C₁₇H₂₁NO₇S (383.82): C, 53.25; H, 5.52; found: C, 53.02; H, 5.75.

1,4,6-Tri-O-acetyl-3-(N-piperidinodithiocarbamoyl)-2-deoxy-α-D-glucopyranose (Table 1, entry 9): S-isomer

¹H NMR (CDCl₃, 200 MHz): δ 6.18–6.15 (m, 1H, H-1), 5.32–5.23 (m, 1H, H-4), 4.82–4.68 (m, 1H, H-3), 4.55–4.0 (m, 5H, H-5, H-6_{ab}, NCH₂), 3.93–3.82 (m, 2H, NCH₂), 2.70–2.57 (m, 1H, H-2_e), 2.02–1.87 (m, 1H, H-2_a), 2.11, 2.09, 2.06 (3 s, 9H, 3 COCH₃), 1.80–1.62 (m, 6H, 3-CH₂-); ¹³C NMR (CDCl₃, 50 MHz): δ 192.5 (CS), 170.5, 170.3, 168.9 (3 COCH₃), 91.1 (C-1), 71.8 (C-4), 66.8 (C-5), 62.2 (C-6), 52.9 (CH₂), 51.5 (CH₂), 48.1 (C-3), 35.9 (C-2), 25.4 (CH₂), 24.2 (2 C, CH₂), 21.1, 21.0, 20.9 (3 COCH₃); **R-isomer:** ¹H NMR (CDCl₃, 200 MHz): δ 6.47–6.36 (m, 1H, H-1), 5.20–5.10 (m, 1H, H-4), 5.02–4.94 (m, 1H, H-3), 4.50–4.0 (m, 5H, H-5, H-6_{ab}, NCH₂), 2.96–2.80 (m, 1H, H-2_e), 2.42–2.20 (m, 1H, H-2_a), 2.12, 2.09, 2.06 (3 s, 9H, 3 COCH₃), 1.78–1.60 (m, 6H, 3 CH₂-); ¹³C NMR (CDCl₃, 50 MHz): δ 192.4 (CS), 169.8, 169.6, 168.6 (3 COCH₃), 91.5 (C-1), 71.0 (C-4), 68.1 (C-5), 62.6 (C-6), 53.0 (CH₂), 51.5 (CH₂), 49.1 (C-3), 39.5 (C-2), 25.4 (CH₂), 24.2 (2 C, CH₂), 21.0, 20.9, 20.8 (3 COCH₃); ESI-MS: *m/z* = 456.5 [M + Na]⁺; Anal. Calcd. for C₁₈H₂₇NO₇S₂ (433.54): C, 49.87; H, 6.28; found: C, 49.64; H, 6.55.

1,4,6-Tri-O-acetyl-3-(N-morpholinodithiocarbamoyl)-2-deoxy- α -D-glucopyranose (Table 1, entry 10): S-isomer

^1H NMR (CDCl_3 , 200 MHz): δ 6.18–6.13 (m, 1H, H-1), 5.14–5.04 (m, 1H, H-4), 4.74–4.64 (m, 1H, H-3), 4.52–4.02 (m, 7H, H-5, H-6_{ab}, N(CH₂)₂), 3.84–3.66 (m, 4H, 2 OCH₂), 2.65–2.53 (m, 1H, H-2_e), 2.12, 2.10, 2.08 (3 s, 9H, 3 COCH₃), 1.97–1.82 (m, 1H, H-2_a); ^{13}C NMR (CDCl_3 , 50 MHz): δ 194.5 (CS), 170.3, 169.6, 168.7 (3 COCH₃), 91.0 (C-1), 71.8 (C-4), 66.5 (C-5), 66.0 (2 C, 2 OCH₂), 62.1 (C-6), 50.4 (2 C, 2 NCH₂), 48.2 (C-3), 35.9 (C-2), 21.0, 20.9, 20.7 (3 COCH₃); ESI-MS: $m/z = 458.5$ [M + Na]⁺; Anal. Calcd. for C₁₇H₂₅NO₈S₂ (435.51): C, 46.88; H, 5.79; found: C, 46.66; H, 6.0.

1,4,6-Tri-O-acetyl-3-(N,N-diethylaminodithiocarbamoyl)-2-deoxy- α -D-glucopyranose (Table 1, entry 11): S-isomer

^1H NMR (CDCl_3 , 200 MHz): δ 6.17–6.11 (m, 1H, H-1), 5.29–5.25 (m, 1H, H-4), 4.80–4.65 (m, 1H, H-3), 4.52–4.26 (m, 1H, H-6_a), 4.08–3.95 (m, 4H, 2 NCH₂CH₃), 3.77–3.70 (m, 2H, H-5, H-6_b), 2.62–2.55 (m, 1H, H-2_e), 2.37–2.29 (m, 1H, H-2_a), 2.14, 2.10, 2.05 (3 s, 9H, 3 COCH₃), 1.38–1.26 (m, 6H, 2 NCH₂CH₃); ^{13}C NMR (CDCl_3 , 50 MHz): δ 192.4 (CS), 170.4, 170.3, 169.6 (3 COCH₃), 91.5 (C-1), 74.0 (C-4), 66.8 (C-5), 62.5 (C-6), 46.5 (2 C, 2 CH₂CH₃), 44.4 (C-3), 31.4 (C-2), 21.2, 20.8, 20.6 (3 COCH₃), 12.8, 12.5 (2 CH₂CH₃); **R-isomer:** ^1H NMR (CDCl_3 , 200 MHz): δ 6.14–6.10 (m, 1H, H-1), 5.20–5.10 (m, 1H, H-4), 5.0–4.92 (m, 1H, H-3), 4.56–4.36 (m, 1H, H-6_a), 4.28–4.15 (m, 4H, 2 NCH₂CH₃), 3.95–3.88 (m, 2H, H-5, H-6_b), 2.95–2.77 (m, 1H, H-2_e), 2.30–2.0 (m, 1H, H-2_a), 2.14, 2.10, 2.08 (3 s, 9H, 3 COCH₃), 1.35–1.24 (m, 6H, 2 CH₂CH₃); ^{13}C NMR (CDCl_3 , 50 MHz): δ 192.6 (CS), 169.0, 168.9, 168.4 (3 COCH₃), 90.7 (C-1), 75.4 (C-4), 69.6 (C-5), 62.2 (C-6), 49.5 (2 C, 2 CH₂CH₃), 46.7 (C-3), 31.4 (C-2), 21.2, 21.1, 20.8 (3 COCH₃), 12.9, 12.6 (2 CH₂CH₃); ESI-MS: $m/z = 444.5$ [M + Na]⁺; Anal. Calcd. for C₁₇H₂₇NO₇S₂ (421.53): C, 48.44; H, 6.46; found: C, 48.20; H, 6.62.

1,4,6-Tri-O-acetyl-3-(1,2,3,4-tetrahydroisoquinolinodithiocarbamoyl)-2-dideoxy- α -D-glucopyranose (Table 1, entry 12): S-isomer

^1H NMR (CDCl_3 , 200 MHz): δ 7.29–7.21 (m, 4H, Ar-H), 6.18–6.12 (m, 1H, H-1), 5.36–5.24 (m, 1H, H-4), 5.15–4.95 (m, 1H, H-3), 4.60–4.30 (m, 3H, H-5, H-6_{ab}), 4.26–4.18 (m, 2H, NCH₂CH₂-), 4.14–4.0 (m, 2H, NCH₂CH₂-), 3.04–3.0 (m, 2H, NCH₂), 2.69–2.56 (m, 1H, H-2_e), 2.44–2.27 (m, 1H, H-2_a), 2.10, 2.08, 2.05 (3 s, 9H, 3 COCH₃); ^{13}C NMR (CDCl_3 , 50 MHz): δ 193.3 (CS), 170.4, 170.3, 169.5 (3 COCH₃), 134.1–126.1 (Ar-C), 91.1 (C-1), 74.0 (C-4), 71.7 (C-5), 62.1 (C-6), 53.7 (NCH₂CH₂-), 50.1 (NCH₂CH₂-), 48.0 (C-3), 35.8 (C-2), 28.9 (NCH₂), 21.2, 21.0, 20.7 (3 COCH₃); ESI-MS: $m/z = 504.6$ [M + Na]⁺; Anal. Calcd. for C₂₂H₂₇NO₇S₂ (481.58): C, 54.87; H, 5.65; found: C, 54.64; H, 6.87.

1,4,6-Tri-O-acetyl-3-mercaptophenyl-2-deoxy- α -D-galactopyranose (Table 1, entry 13): R-isomer

^1H NMR (CDCl_3 , 200 MHz): δ 7.48–7.30 (m, 5H, Ar-H), 6.46–6.44 (m, 1H, H-1), 5.58–5.52 (m, 1H, H-4), 5.30–5.20 (m, 1H, H-3), 4.40–4.10 (m, 2H, H-6_{ab}), 4.0–3.86 (m, 1H, H-5), 2.18–2.0 (m, 2H, H-2_{ea}), 2.09, 2.03 (2 s); ^{13}C NMR (CDCl_3 , 50 MHz): δ 170.7, 170.4, 170.3 (3 COCH_3), 145.7–128.6 (Ar-C), 91.6 (C-1), 73.1 (C-5), 64.3 (C-4), 62.2 (C-6), 44.6 (C-3), 30.9 (C-2), 21.4, 21.1, 21.0 (3 COCH_3); **S-isomer**: ^1H NMR (CDCl_3 , 200 MHz): δ 7.48–7.30 (m, 5H, Ar-H), 6.20–6.12 (m, 1H, H-1), 5.30–5.22 (m, 1H, H-4), 4.73–4.68 (m, 1H, H-3), 4.38–4.10 (m, 2H, H-6_{ab}), 3.50–3.42 (m, 1H, H-3), 2.18–2.0 (m, 2H, H-2_{ea}), 2.10, 2.05, 2.03 (3 s, 3 COCH_3); ^{13}C NMR (CDCl_3 , 50 MHz): δ 170.7, 170.5, 170.3 (3 COCH_3), 145.8–128.5 (Ar-C), 91.2 (C-1), 71.2 (C-5), 64.0 (C-4), 62.8 (C-6), 44.5 (C-3), 30.1 (C-2), 21.4, 21.1, 21.0 (3 COCH_3); ESI-MS: $m/z = 405.4$ [$\text{M} + \text{Na}$] $^+$; Anal. Calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_7\text{S}$ (382.43): C, 56.53; H, 5.80; found: C, 56.38; H, 6.02.

1,4,6-Tri-O-acetyl-3-mercapto (2-methylphenyl)-2-deoxy- α -D-galactopyranose (Table 1, entry 14): R-isomer

^1H NMR (CDCl_3 , 200 MHz): δ 7.40–7.15 (m, 4H, Ar-H), 6.15 (dd, $J = 8.0$, 2.2 Hz, 1H, H-4), 5.70–5.60 (m, 1H, H-1), 4.60–4.58 (m, 1H, H-3), 4.0–3.85 (m, 2H, H-6_{ab}), 3.30–3.22 (m, 1H, H-5), 2.41 (s, 3H, CH_3), 2.20, 2.12, 2.09 (3 s, 9H, 3 COCH_3), 2.11–1.88 (m, 2H, H-2_{ea}); ^{13}C NMR (CDCl_3 , 50 MHz): δ 168.3, 168.2 (2 C) (3 COCH_3), 140.2–126.4 (Ar-C), 92.4 (C-1), 74.3 (C-4), 65.0 (C-5), 63.3 (C-6), 46.2 (C-3), 31.9 (C-2), 21.0–20.6 (3 C, 3 COCH_3), 20.4 (CH_3); **S-isomer**: ^1H NMR (CDCl_3 , 200 MHz): δ 7.40–7.15 (m, 4H, Ar-H), 6.23 (d, $J = 2.2$ Hz, 1H, H-4), 5.25–5.22 (m, 1H, H-1), 4.76–4.74 (m, 1H, H-3), 4.15–4.06 (m, 2H, H-6_{ab}), 3.52–3.61 (m, 1H, H-5), 2.43 (s, 3H, CH_3), 2.09, 2.05 (2 s, 9H, 3 COCH_3), 2.12–1.90 (m, 2H, H-2_{ea}); ^{13}C NMR (CDCl_3 , 50 MHz): δ 169.8, 169.4 (2 C) (3 COCH_3), 140.2–126.4 (Ar-C), 90.9 (C-1), 70.6 (C-4), 65.5 (C-5), 63.3 (C-6), 43.2 (C-3), 30.2 (C-2), 21.1, 20.6 (2 C) (3 COCH_3), 20.3 (CH_3); ESI-MS: $m/z = 419.5$ [$\text{M} + \text{Na}$] $^+$; Anal. Calcd. for $\text{C}_{19}\text{H}_{24}\text{O}_7\text{S}$ (396.45): C, 57.56; H, 6.10; found: C, 57.38; H, 6.33.

1,4,6-Tri-O-acetyl-3-mercapto (3-methylphenyl)-2-deoxy- α -D-galactopyranose (Table 1, entry 15): R-isomer

^1H NMR (CDCl_3 , 200 MHz): δ 7.29–7.09 (m, 4H, Ar-H), 6.32–6.26 (m, 1H, H-1), 5.30–5.25 (m, 1H, H-4), 5.82–5.77 (m, 1H, H-3), 4.18–4.06 (m, 2H, H-6_{ab}), 3.80–3.72 (m, 1H, H-5), 2.35 (s, 3H, CH_3), 2.17, 2.10, 2.09 (3 s, 9H, 3 COCH_3), 2.20–1.85 (m, 2H, H-2_{ea}); ^{13}C NMR (CDCl_3 , 50 MHz): δ 170.0, 169.6, 168.6 (3 COCH_3), 138.9–127.0 (Ar-C), 90.7 (C-1), 70.6 (C-5), 67.3 (C-4), 62.6 (C-6), 43.8 (C-3), 30.3 (C-2), 21.1, 20.8, 20.6, 20.4 (3 COCH_3 , CH_3); **S-isomer**: ^1H NMR (CDCl_3 , 200 MHz): δ 7.30–7.10 (m, 4H, Ar-H), 6.20–6.12

(m, 1H, H-1), 5.24–5.20 (m, 1H, H-4), 4.55–4.48 (m, 1H, H-3), 4.18–4.06 (m, 2H, H-6_{ab}), 3.60–3.50 (m, 1H, H-5), 2.33 (s, 3H, CH₃), 2.05, 2.03 (2 s, 9H, 3 COCH₃), 2.20–1.87 (m, 2H, H-2_{ea}); ¹³C NMR (CDCl₃, 50 MHz): δ 168.6, 168.5, 168.4 (3 COCH₃), 138.9–127.0 (Ar-C), 92.7 (C-1), 74.4 (C-5), 65.2 (C-4), 62.4 (C-6), 47.6 (C-3), 31.9 (C-2), 21.1, 20.8, 20.6, 20.4 (3 COCH₃, CH₃); ESI-MS: *m/z* = 419.5 [M + Na]⁺; Anal. Calcd. for C₁₉H₂₄O₇S (396.45): C, 57.56; H, 6.10; found: C, 57.35; H, 6.38.

1,4,6-Tri-O-acetyl-3-mercapto (4-methylphenyl)-2-deoxy-α-D-galactopyranose
(Table 1, entry 16): *R-isomer*

¹H NMR (CDCl₃, 200 MHz): δ 7.38–7.11 (m, 4H, Ar-H), 6.10 (dd, *J* = 8.0, 2.4 Hz, 1H, H-4), 5.75–5.65 (m, 1H, H-1), 4.52–4.50 (m, 1H, H-3), 3.98–3.80 (m, 2H, H-6_{ab}), 3.17–3.10 (m, 1H, H-5), 2.34 (s, 3H, CH₃), 2.19–2.16 (m, 1H, H-2_e), 2.11, 2.06, 2.03 (3 s, 9H, 3 COCH₃), 2.05–1.90 (m, 1H, H-2_a); ¹³C NMR (CDCl₃, 50 MHz): δ 168.5 (2 C), 168.4 (3 COCH₃), 138.4–127.8 (Ar-C), 92.8 (C-1), 74.5 (C-5), 65.3 (C-4), 62.4 (C-6), 48.3 (C-3), 31.9 (C-2), 21.0, 20.9 (2 C) (3 COCH₃), 20.7 (CH₃); **S-isomer**: ¹H NMR (CDCl₃, 200 MHz): δ 7.38–7.11 (m, 4H, Ar-H), 6.21 (d, *J* = 2.4 Hz, 1H, H-4), 5.20–5.21 (m, 1H, H-1), 4.75–4.74 (m, 1H, H-3), 4.13–4.09 (m, 2H, H-6_{ab}), 3.56–3.38 (m, 1H, H-5), 2.35 (s, 3H, CH₃), 2.14, 2.08, 2.02 (3 s, 9H, 3 COCH₃), 2.19–2.16 (m, 1H, H-2_e), 2.05–1.90 (m, 1H, H-2_a); ¹³C NMR (CDCl₃, 50 MHz): δ 170.0, 169.7, 169.6 (3 COCH₃), 138.4, 128.8 (Ar-C), 91.1 (C-1), 69.8 (C-5), 65.5 (C-4), 62.4 (C-6), 44.4 (C-3), 30.4 (C-2), 21.3, 21.2, 21.1 (3 COCH₃), 20.8 (CH₃); ESI-MS: *m/z* = 419.5 [M + Na]⁺; Anal. Calcd. for C₁₉H₂₄O₇S (396.45): C, 57.56; H, 6.10; found: C, 57.37; H, 6.38.

1,4,6-Tri-O-acetyl-3-mercaptoacetyl-2-deoxy-α-D-galactopyranose (Table 1, entry 17): *R-isomer*

¹H NMR (CDCl₃, 200 MHz): δ 6.20 (d, *J* = 2.4 Hz, 1H, H-4), 5.22–5.20 (m, 1H, H-1), 4.93–4.90 (m, 1H, H-3), 4.34–4.28 (m, 1H, H-5), 4.28–3.97 (m, 2H, H-6_{ab}), 2.30 (s, 3H, SCOCH₃), 2.11, 2.02 (2 s, 9H, 3 COCH₃), 2.0–1.80 (m, 2H, H-2_{ea}); ¹³C NMR (CDCl₃, 50 MHz): δ 193.9 (SCOCH₃), 170.5, 170.1, 170.0 (3 COCH₃), 93.0 (C-1), 74.7 (C-4), 70.3 (C-5), 62.6 (C-6), 39.9 (C-3), 30.1 (C-2), 21.5–20.9 (4 C, SCOCH₃, 3 COCH₃); **S-isomer**: ¹H NMR (CDCl₃, 200 MHz): δ 5.81–5.77 (m, 1H, H-4), 5.17–5.14 (m, 1H, H-1), 4.64–4.62 (m, 1H, H-3), 4.24–4.21 (m, 1H, H-5), 4.22–3.92 (m, 2H, H-6_{ab}), 2.31 (s, 3H, SCOCH₃), 2.13, 2.10, 2.06 (3 s, 9H, 3 COCH₃), 2.05–1.82 (m, 2H, H-2_{ea}); ¹³C NMR (CDCl₃, 50 MHz): δ 193.6 (SCOCH₃), 170.0, 169.2, 168.8 (3 COCH₃), 98.2 (C-1), 84.3 (C-4), 70.3 (C-5), 62.4 (C-6), 39.9 (C-3), 31.3 (C-2), 21.5–20.8 (4 C, SCOCH₃, 3 COCH₃); ESI-MS: *m/z* = 371.4 [M + Na]⁺; Anal. Calcd. for C₁₄H₂₀O₈S (348.37): C, 48.27; H, 5.79; found: C, 48.02; H, 6.0.

1,4,6-Tri-O-acetyl-3-(ethylglycoloyl)mercapto-2,3-dideoxy- α -D-galactopyranose
(Table 1, entry 18): *R*-isomer

^1H NMR (CDCl_3 , 200 MHz): δ 5.93–5.90 (m, 1H, H-1), 5.28–5.27 (m, 1H, H-4), 4.48–4.44 (m, 1H, H-5), 4.27–3.99 (m, 4H, H-6_{ab}, OCH_2CH_3), 3.66–3.57 (m, 1H, H-3), 3.48–3.28 (m, 2H, SCH_2COOEt), 2.17, 2.13, 2.12 (3 s, 9H, 3 COCH_3), 2.05–1.91 (m, 2H, H-2_{ea}), 1.29 (t, $J = 7.6$ Hz, 3H, OCH_2CH_3); ^{13}C NMR (CDCl_3 , 50 MHz): δ 169.9, 169.8, 169.6, 169.4 (3 COCH_3 , COOEt), 90.7 (C-1), 69.3 (C-5), 64.4 (C-4), 62.5 (C-6), 61.7 (OCH_2CH_3), 38.9 (C-3), 30.3 (C-2), 28.7 (SCH_2 -), 20.9–20.4 (3 C, 3 COCH_3), 13.9 ($-\text{CH}_2\text{CH}_3$); **S-isomer**: ^1H NMR (CDCl_3 , 200 MHz): δ 5.79–5.75 (m, 1H, H-1), 5.21 (brs, 1H, H-4), 4.40–4.32 (m, 1H, H-5), 4.20–3.95 (m, 4H, H-6_{ab}, OCH_2CH_3), 3.50–3.43 (m, 1H, H-3), 3.33–3.15 (m, 2H, SCH_2COOEt), 2.11, 2.08, 2.07 (3 s, 9H, 3 COCH_3), 2.03–1.87 (m, 2H, H-2_{ea}), 1.30 (t, $J = 7.5$ Hz, 3H, OCH_2CH_3); ^{13}C NMR (CDCl_3 , 50 MHz): δ 169.4, 168.5, 168.3, 168.2 (COOEt , 3 COCH_3), 92.5 (C-1), 73.9 (C-5), 63.7 (C-4), 62.7 (C-6), 61.6 (OCH_2CH_3), 39.9 (C-3), 31.4 (C-2), 28.6 (SCH_2 -), 20.7–20.2 (3 C, 3 COCH_3), 13.8 ($-\text{CH}_2\text{CH}_3$); ESI-MS: $m/z = 415.4$ [$\text{M} + \text{Na}$] $^+$; Anal. Calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_9\text{S}$ (392.42): C, 48.97; H, 6.16; found: C, 48.80; H, 6.38.

1,4,6-Tri-O-acetyl-3-mercapto (2,3,4,6-tetra-O-acetyl- β -D-glucopyranosyl)-2-deoxy- α -D-galactopyranose (Table 1, entry 19): *R*-isomer

^1H NMR (CDCl_3 , 300 MHz): δ 5.25 (brs, 1H, H-4), 5.15 (t, $J = 9.4$ Hz, 1H, H-3'), 5.08 (t, $J = 9.4$ Hz, 1H, H-2'), 5.12–4.98 (m, 2H, H-1, H-4'), 4.63 (d, $J = 9.9$ Hz, 1H, H-1'), 4.24–4.05 (m, 4H, H-6_{ab}, H-6'_{ab}), 3.96–3.87 (m, 1H, H-3), 3.74–3.69 (m, 1H, H-5), 3.50–3.40 (m, 1H, H-5'), 2.26–1.98 (m, 2H, H-2'_{ea}), 2.14, 2.13, 2.12, 2.10, 2.08, 2.06, 2.05 (7 s, 21H, 7 COCH_3); ^{13}C NMR (CDCl_3 , 75 MHz): δ 170.1, 169.7, 169.3, 169.1, 169.0, 168.6, 168.4 (7 COCH_3), 91.0 (C-1), 82.3 (C-1'), 75.9 (C-5), 73.4 (C-4), 69.9, 69.4, 68.1, 67.9, 62.3 (C-6), 61.7 (C-6'), 37.9 (C-3), 31.5 (C-2), 20.4 (3 C), 20.3 (4 C); **S-isomer**: ^1H NMR (CDCl_3 , 300 MHz): δ 5.21 (brs, 1H, H-4), 5.20–5.10 (m, 2H, H-2', H-3'), 5.10–4.95 (m, H-1, H-4'), 4.60 (d, $J = 9.9$ Hz, 1H, H-1'), 4.30–4.10 (m, 4H, H-6_{ab}, H-6'_{ab}), 3.93–3.85 (m, 1H, H-3), 3.70–3.65 (m, 1H, H-5), 3.28–3.22 (m, 1H, H-5'), 2.20–1.88 (m, 2H, H-2'_{ea}), 2.15, 2.13, 2.11, 2.09, 2.08, 2.06, 2.05 (7 s, 21H, 7 COCH_3); ^{13}C NMR (CDCl_3 , 75 MHz): δ 170.1 (2 C), 169.7, 169.2, 169.0 (2 C), 168.6 (7 COCH_3), 92.5 (C-1), 82.1 (C-1'), 76.1 (C-4), 74.6 (C-5), 70.4, 69.2, 67.5, 67.4, 62.0 (C-6), 61.6 (C-6'), 38.8 (C-3), 30.5 (C-2), 21.0 (2 C), 20.9 (2 C), 20.8 (3 C); ESI-MS: $m/z = 659.6$ [$\text{M} + \text{Na}$] $^+$; Anal. Calcd. for $\text{C}_{26}\text{H}_{36}\text{O}_{16}\text{S}$ (636.62): C, 49.05; H, 5.70; found: C, 48.82; H, 5.96.

1,4,6-Tri-O-acetyl-3-mercapto (2-pyridyl)-2-deoxy- α -D-galactopyranose
(Table 1, entry 20): *R*-isomer

^1H NMR (CDCl_3 , 200 MHz): δ 8.45–8.41 (m, 1H, Ar-H), 7.52–7.46 (m, 1H, Ar-H), 7.12–7.00 (m, 2H, Ar-H), 5.98–5.82 (m, 1H, H-1), 5.42 (brs, 1H, H-4),

4.70–4.60 (m, 1H, H-5), 4.42–4.35 (m, 1H, H-3), 4.20–3.95 (m, 2H, H-6_{ab}), 2.72–2.65 (m, 1H, H-2_e), 2.40–2.30 (m, 1H, H-2_a), 2.17, 2.15, 2.13 (3 s, 9H, 3 COCH₃); ¹³C NMR (CDCl₃, 200 MHz): δ 169.8, 169.3, 168.5 (3 COCH₃), 156.3–119.4 (Ar-C), 90.9 (C-1), 69.5 (C-5), 66.5 (C-4), 62.6 (C-6), 37.6 (C-3), 29.2 (C-2), 20.9–20.5 (3 C, 3 COCH₃); **S-isomer**: ¹H NMR (CDCl₃, 200 MHz): δ 8.45–8.41 (m, 1H, Ar-H), 7.52–7.46 (m, 1H, Ar-H), 7.12–7.00 (m, 2H, Ar-H), 6.09–6.0 (m, 1H, H-1), 5.34 (brs, 1H, H-4), 4.55–4.48 (m, 1H, H-5), 4.40–4.34 (m, 1H, H-3), 4.15–3.90 (m, 2H, H-6_{ab}), 2.88–2.77 (m, 1H, H-2_e), 2.40–2.32 (m, 1H, H-2_a), 2.17, 2.13, 2.11 (3 s, 9H, 3 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 168.5, 168.2 (2 C, 3 COCH₃), 156.3–119.3 (Ar-C), 90.9 (C-1), 70.4 (C-5), 67.2 (C-4), 62.2 (C-6), 39.7 (C-3), 30.2 (C-2), 20.6–20.4 (3 C, 3 COCH₃); ESI-MS: *m/z* = 406.4 [M + Na]⁺; Anal. Calcd. for C₁₇H₂₁NO₇S (383.82): C, 53.25; H, 5.52; found: C, 53.0; H, 5.74.

1,4,6-Tri-O-acetyl-3-(N-piperidinodithiocarbamoyl)-2-deoxy-α-D-galactopyranose (Table 1, entry 21): R-isomer

¹H NMR (CDCl₃, 200 MHz): δ 6.24–6.22 (m, 1H, H-1), 5.48 (brs, 1H, H-4), 4.81–4.74 (m, 1H, H-3), 4.40–4.29 (m, 1H, H-5), 4.24–4.17 (m, 2H, NCH₂), 4.14–3.92 (m, 2H, H-6_{ab}), 3.90–3.78 (m, 2H, NCH₂), 2.30–2.21 (m, 1H, H-2_e), 2.11–2.0 (m, 1H, H-2_a), 2.17, 2.12, 2.05 (3 s, 9H, 3 COCH₃), 1.80–1.60 (m, 6H, 3 CH₂); ¹³C NMR (CDCl₃, 50 MHz): δ 192.0 (CS), 170.2, 169.5, 169.0 (3 COCH₃), 91.5 (C-1), 70.2 (C-4), 67.2 (C-5), 62.5 (C-6), 53.0 (CH₂), 51.4 (CH₂), 45.8 (C-3), 29.5 (C-2), 25.3 (CH₂), 24.2 (2 C, 2 CH₂), 20.9, 20.7, 20.6 (3 COCH₃); ESI-MS: *m/z* = 456.5 [M + Na]⁺; Anal. Calcd. for C₁₈H₂₇NO₇S₂ (433.54): C, 49.87; H, 6.28; found: C, 49.66; H, 6.5.

1,4,6-Tri-O-acetyl-3-(N-morpholinodithiocarbamoyl)-2-deoxy-α-D-galactopyranose (Table 1, entry 22): R-isomer

¹H NMR (CDCl₃, 200 MHz): δ 6.27–6.25 (m, 1H, H-1), 5.50 (brs, 1H, H-4), 4.85–4.75 (m, 1H, H-3), 4.62–4.52 (m, 1H, H-5), 4.45–3.96 (m, 6H, H-6_{ab}, 2 NCH₂), 3.85–3.70 (m, 4H, 2 OCH₂), 2.86–2.80 (m, 1H, H-2_e), 2.41–2.23 (m, 1H, H-2_a), 2.20, 2.15, 2.05 (3 s, 9H, 3 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 193.8 (CS), 170.1, 169.6, 169.4 (3 COCH₃), 91.3 (C-1), 70.0 (C-4), 66.9 (C-5), 66.0 (2 C, OCH₂), 62.0 (C-6), 51.0 (2 C, NCH₂), 45.8 (C-3), 29.5 (C-2), 21.0, 20.9, 20.8 (3 COCH₃); ESI-MS: *m/z* = 458.5 [M + Na]⁺; Anal. Calcd. for C₁₇H₂₅NO₈S₂ (435.51): C, 46.88; H, 5.79; found: C, 46.64; H, 6.0.

1,4,6-Tri-O-acetyl-3-(N,N-diethylaminodithiocarbamoyl)-2-deoxy-α-D-galactopyranose (Table 1, entry 23): R-isomer

¹H NMR (CDCl₃, 200 MHz): δ 6.25–6.22 (m, 1H, H-1), 5.47 (brs, 1H, H-4), 4.80–4.72 (m, 1H, H-3), 4.41–4.36 (m, 1H, H-5), 4.15–4.06 (m, 1H, H-6_a), 4.04–3.95 (m, 4H, CH₂CH₃), 3.72–3.62 (m, 1H, H-6_b), 2.34–2.22 (m, 1H, H-2_e), 2.18, 2.12, 2.05 (3 s, 9H, 3 COCH₃), 2.16–2.01 (m, 1H, H-2_a), 1.28–1.24 (m, 6H,

2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 191.9 (CS), 170.0, 169.5, 168.9 (3 COCH₃), 91.7 (C-1), 70.2 (C-4), 67.2 (C-5), 62.7 (C-6), 46.7 (2 C, 2 CH₂CH₃), 45.8 (C-3), 28.8 (C-2), 21.1, 20.7, 20.6 (3 COCH₃), 12.4, 11.4 (2 CH₂CH₃); ESI-MS: *m/z* = 444.5 [M + Na]⁺; Anal. Calcd. for C₁₇H₂₇NO₇S₂ (421.53): C, 48.44; H, 6.46; found: C, 48.17; H, 6.68.

1,4,6-Tri-O-acetyl-3-(1,2,3,4-tetrahydroisoquinolinodithiocarbamoyl)-2-deoxy-α-D-galactopyranose (Table 1, entry 24): R-isomer

¹H NMR (CDCl₃, 200 MHz): δ 7.24–7.10 (m, 4H, Ar-H), 6.25–6.22 (m, 1H, H-1), 5.50 (brs, 1H, H-4), 4.88–4.81 (m, 1H, H-3), 4.42–4.38 (m, 1H, H-5), 4.21–4.07 (m, 2H, H-6_a, NCH₂CH₂), 4.03–3.92 (m, 2H, H-6_b, NCH₂CH₂), 3.0–2.92 (m, 2H, NCH₂), 2.40–2.22 (m, 1H, H-2_e), 2.16, 2.13, 2.05 (3 s, 9H, 3 COCH₃), 2.11–2.03 (m, 1H, H-2_a); ¹³C NMR (CDCl₃, 50 MHz): δ 193.0 (CS), 170.1, 169.5, 168.9 (3 COCH₃), 134.9–126.0 (Ar-C), 91.5 (C-1), 70.2 (C-4), 67.0 (C-5), 62.4 (C-6), 53.8 (NCH₂CH₂), 47.9 (NCH₂CH₂), 45.5 (C-3), 29.6 (C-2), 28.9 (NCH₂), 21.0, 20.8, 20.7 (3 COCH₃); ESI-MS: *m/z* = 504.6 [M + Na]⁺; Anal. Calcd. for C₂₂H₂₇NO₇S₂ (481.58): C, 54.87; H, 5.65; found: C, 54.65; H, 6.90.

4,6-Di-O-acetyl-3-mercaptophenyl-2-deoxy-D-glucono-1,5-lactone (Table 1, entry 25): S-isomer

¹H NMR (CDCl₃, 200 MHz): δ 7.50–7.31 (m, 5H, Ar-H), 5.21–5.10 (m, 1H, H-4), 4.50–4.35 (m, 1H, H-5), 4.30–4.20 (m, 2H, H-6_{ab}), 3.58–3.42 (m, 1H, H-3), 3.0–2.75 (m, 2H, H-2_{ea}), 2.05, 2.03 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.1, 169.3, 166.6 (2 COCH₃, C-1), 134.1–127.9 (Ar-C), 77.9 (C-5), 68.2 (C-4), 61.6 (C-6), 42.8 (C-3), 33.5 (C-2), 20.7, 20.5 (2 COCH₃); **R-isomer:** ¹H NMR (CDCl₃, 200 MHz): δ 7.50–7.31 (m, 5H, Ar-H), 5.29–5.20 (m, 1H, H-4), 4.90–4.79 (m, 1H, H-5), 4.28–4.21 (m, 2H, H-6_{ab}), 3.86–3.75 (m, 1H, H-3), 3.0–2.85 (m, 1H, H-2_e), 2.62–2.50 (m, 1H, H-2_a), 2.04, 2.03 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 169.8, 169.6, 167.2 (2 COCH₃, C-1), 134.2–127.9 (Ar-C), 77.2 (C-5), 67.2 (C-4), 62.8 (C-6), 42.9 (C-3), 34.5 (C-2), 20.6, 20.5 (2 COCH₃); ESI-MS: *m/z* = 361.4 [M + Na]⁺; Anal. Calcd. for C₁₆H₁₈O₆S (338.38): C, 56.79; H, 5.36; found: C, 56.55; H, 6.58.

4,6-Di-O-acetyl-3-mercapto (2-methylphenyl)-2-deoxy-D-glucono-1,5-lactone (Table 1, entry 26): S-isomer

¹H NMR (CDCl₃, 200 MHz): δ 7.40–7.10 (m, 4H, Ar-H), 5.15–5.06 (m, 1H, H-4), 4.78–4.68 (m, 1H, H-5), 4.28–4.05 (m, 2H, H-6_{ab}), 3.72–3.64 (m, 1H, H-3), 2.92–2.70 (m, 2H, H-2_{ea}), 2.36 (s, 3H, CH₃), 1.99, 1.97 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 169.8, 169.6, 166.8 (2 COCH₃, C-1), 141.0–126.8 (Ar-C), 77.0 (C-5), 67.4 (C-4), 62.8 (C-6), 42.2 (C-3), 33.7 (C-2), 20.9, 20.6, 20.5 (2 COCH₃, CH₃); **R-isomer:** ¹H NMR (CDCl₃, 200 MHz): δ 7.40–7.10 (m, 4H, Ar-H), 5.22–5.12 (m, 1H, H-4), 4.40–4.28 (m, 1H, H-5), 4.27–4.08 (m, 2H, H-6_{ab}), 4.52–4.40 (m, 1H, H-3), 2.99–2.85 (m, 1H, H-2_e),

2.60–2.40 (dd, $J = 17.4, 9.2$ Hz, 1H, H-2_a), 2.37 (s, 3H, CH₃), 2.02, 1.93 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.1, 169.2, 166.9 (2 COCH₃, C-1), 141.1–126.8 (Ar-C), 77.8 (C-5), 68.7 (C-4), 62.5 (C-6), 43.9 (C-3), 34.4 (C-2), 20.8, 20.6, 20.5 (2COCH₃, CH₃); ESI-MS: $m/z = 375.4$ [M + Na]⁺; Anal. Calcd. for C₁₇H₂₀O₆S (352.4): C, 57.94; H, 5.72; found: C, 57.70; H, 6.0.

4,6-Di-O-acetyl-3-mercapto (3-methylphenyl)-2-deoxy-D-glucono-1,5-lactone

(Table 1, entry 27): *S-isomer*

¹H NMR (CDCl₃, 200 MHz): δ 7.26–7.11 (m, 4H, Ar-H), 5.24–5.20 (m, 1H, H-4), 5.82–4.72 (m, 1H, H-5), 4.30–4.26 (m, 2H, H-6_{ab}), 4.88–4.76 (m, 1H, H-3), 3.02–2.76 (m, 2H, H-2_{ea}), 2.35 (s, 3H, CH₃), 2.04, 2.03 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.3, 169.8, 167.3 (2 COCH₃, C-1), 139.2–126.4 (Ar-C), 81.5 (C-5), 70.8 (C-4), 61.7 (C-6), 42.9 (C-3), 35.5 (C-2), 21.3, 20.8, 20.6 (2 COCH₃, CH₃); **R-isomer**: ¹H NMR (CDCl₃, 200 MHz): δ 7.28–7.11 (m, 4H, Ar-H), 5.18 (t, $J = 8.4$ Hz, 1H, H-4), 4.40–4.28 (m, 1H, H-5), 4.30–4.25 (m, 2H, H-6_{ab}), 3.58–3.42 (m, 1H, H-3), 3.06–2.82 (m, 1H, H-2_e), 2.60–2.20 (dd, $J = 17.6, 9.5$ Hz, 1H, H-2_a), 2.35 (s, 3H, CH₃), 2.04, 2.03 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.4, 170.0, 166.9 (2 COCH₃, C-1), 139.2–126.8 (Ar-C), 81.4 (C-5), 67.9 (C-4), 62.1 (C-6), 41.6 (C-3), 34.7 (C-2), 21.3, 20.9, 20.7 (2 COCH₃, CH₃); ESI-MS: $m/z = 375.4$ [M + Na]⁺; Anal. Calcd. for C₁₇H₂₀O₆S (352.4): C, 57.94; H, 5.72; found: C, 57.72; H, 5.95.

4,6-Di-O-acetyl-3-mercapto (4-methylphenyl)-2-deoxy-D-glucono-1,5-lactone

(Table 1, entry 28): *S-isomer*

¹H NMR (CDCl₃, 200 MHz): δ 7.38–7.10 (m, 4H, Ar-H), 5.11 (t, $J = 8.0$ Hz, 1H, H-4), 4.55–4.40 (m, 1H, H-5), 4.30–4.15 (m, 2H, H-6_{ab}), 3.50–3.32 (m, 1H, H-3), 3.0–2.77 (m, 1H, H-1_e), 2.60–2.40 (dd, $J = 17.5, 9.4$ Hz, 1H, H-2_a), 2.35 (s, 3H, CH₃), 2.08, 2.06 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 169.8, 169.6, 167.3 (2 COCH₃, C-1), 139.2–126.6 (Ar-C), 77.8 (C-5), 67.9 (C-4), 62.6 (C-6), 44.2 (C-3), 34.5 (C-2), 21.2, 20.7, 20.5 (2 COCH₃, CH₃); **R-isomer**: ¹H NMR (CDCl₃, 200 MHz): δ 7.38–7.12 (m, 4H, Ar-H), 5.22–5.18 (m, 1H, H-4), 4.82–4.72 (m, 1H, H-5), 4.28–4.10 (m, 2H, H-6_{ab}), 3.78–3.65 (m, 1H, H-3), 3.0–2.70 (m, 2H, H-2_{ea}), 2.35 (s, 3H, CH₃), 2.06, 2.03 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 169.9, 169.8, 166.7 (2 COCH₃, C-1), 139.2–126.6 (Ar-C), 77.3 (C-5), 67.2 (C-4), 62.9 (C-6), 43.1 (C-3), 33.4 (C-2), 20.8, 20.6, 20.5 (2 COCH₃, CH₃); ESI-MS: $m/z = 375.4$ [M + Na]⁺; Anal. Calcd. for C₁₇H₂₀O₆S (352.4): C, 57.94; H, 5.72; found: C, 57.70; H, 6.0.

4,6-Di-O-acetyl-3-mercaptoacetyl-2-deoxy-D-glucono-1,5-lactone (Table 1, entry 29): *S-isomer*

¹H NMR (CDCl₃, 200 MHz): δ 5.50–5.40 (m, 1H, H-4), 5.30–5.20 (m, 1H, H-5), 4.40–4.30 (m, 1H, H-3), 4.25–4.10 (m, 2H, H-6_{ab}), 2.80–2.40

(m, 2H, H-2_{ea}), 2.32 (s, 3H, CH₃), 2.11, 2.08 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 171.2, 170.9, 170.6, 167.2 (3 COCH₃, C-1), 71.2 (C-5), 70.0 (C-4), 62.2 (C-6), 40.9 (C-3), 35.4 (C-2), 21.3, 21.0, 20.9 (3 COCH₃); **R-isomer**: ¹H NMR (CDCl₃, 200 MHz): δ 5.32–5.28 (m, 1H, H-4), 5.25–5.20 (m, 1H, H-5), 4.30–4.28 (m, 1H, H-3), 4.26–4.10 (m, 2H, H-6_{ab}), 2.78–2.35 (m, 2H, H-2_a), 2.35 (s, 3H, CH₃), 2.07, 2.05 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 171.4, 170.2, 170.0, 166.9 (3 COCH₃, C-1), 70.8 (C-5), 69.8 (C-4), 62.2 (C-6), 40.2 (C-3), 35.2 (C-2), 21.3, 21.2, 21.0 (3 COCH₃); ESI-MS: *m/z* = 327.3 [M + Na]⁺; Anal. Calcd. for C₁₂H₁₆O₇S (304.32): C, 47.36; H, 5.30; found: C, 47.12; H, 5.52.

4,6-Di-O-acetyl-3-mercapto (2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2-deoxy-D-glucono-1,5-lactone (Table 1, entry 30): S-isomer

¹H NMR (CDCl₃, 300 MHz): δ 5.30–5.26 (m, 1H, H-4), 5.22 (t, *J* = 9.3 Hz, 1H, H-3'), 5.07–5.01 (2 t, *J* = 9.4, 9.4 Hz, 2H, H-2', H-4'), 4.68–2.62 (m, 1H, H-5), 4.52 (d, *J* = 9.8 Hz, 1H, H-1'), 4.46–4.41 (m, 1H, H-6'_a), 4.30–4.20 (m, 2H, H-6_{ab}), 4.10–4.04 (m, 1H, H-6'_b), 3.84–3.70 (m, 2H, H-3, H-5'), 2.96–2.87 (m, 1H, H-1_e), 2.78–2.62 (m, 1H, H-1_a), 2.18, 2.13, 2.09, 2.06, 2.02, 2.00 (6 s, 18H, 6 COCH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 170.2, 170.1, 169.9, 169.5, 169.2, 169.0 (6 COCH₃), 165.2 (C-1), 82.0 (C-1'), 77.8, 74.0, 73.5, 68.9, 68.8, 67.9, 62.5 (C-6), 61.7 (C-6'), 37.2 (C-3), 31.6 (C-2), 20.8 (2 C), 20.6 (2 C), 20.5 (2 C); ESI-MS: *m/z* = 615.5 [M + Na]⁺; Anal. Calcd. for C₂₄H₃₂O₁₅S (592.57): C, 48.65; H, 5.44; found: C, 48.46; H, 5.68.

4,6-Di-O-acetyl-3-mercaptophenyl-2-deoxy-D-galactono-1,5-lactone (Table 1, entry 31): R-isomer

¹H NMR (CDCl₃, 200 MHz): δ 7.50–7.34 (m, 5H, Ar-H), 5.12–5.06 (m, 2H, H-3, H-4), 4.22–4.19 (m, 2H, H-6), 3.77–3.70 (m, 1H, H-5), 3.06 (dd, *J* = 18.1, 6.7 Hz, 1H, H-2_e), 2.66 (dd, *J* = 18.1, 3.7 Hz, 1H, H-2_a), 2.09, 2.05 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.0, 169.2, 166.7 (2 COCH₃, C-1), 133.6–127.7 (Ar-C), 74.2 (C-5), 67.2 (C-4), 62.0 (C-6), 42.1 (C-3), 31.8 (C-2), 20.9, 20.6 (2 COCH₃); ESI-MS: *m/z* = 361.4 [M + Na]⁺; Anal. Calcd. for C₁₆H₁₈O₆S (338.38): C, 56.79; H, 5.36; found: C, 56.57; H, 6.53.

4,6-Di-O-acetyl-3-mercapto (2-methylphenyl)-2-deoxy-D-galactono-1,5-lactone (Table 1, entry 32): R-isomer

¹H NMR (CDCl₃, 200 MHz): δ 7.47–7.19 (m, 4H, Ar-H), 5.14–5.07 (m, 1H, H-3), 5.06–5.03 (m, 1H, H-4), 4.23–4.19 (m, 2H, H-6), 3.72–3.68 (m, 1H, H-5), 3.05 (dd, *J* = 18.0, 6.7 Hz, 1H, H-2_e), 2.60 (dd, *J* = 18.1, 3.7 Hz, 1H, H-2_a), 2.45 (s, 3H, CH₃), 2.09, 2.05 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.0, 169.2, 166.7 (2 COCH₃, C-1), 140.4–127.0 (Ar-C), 74.3 (C-5), 67.1 (C-4), 61.9 (C-6), 41.3 (C-3), 31.8 (C-2), 20.7, 20.6, 20.5 (2 COCH₃, CH₃); ESI-MS: *m/z* = 375.4

[M + Na]⁺; Anal. Calcd. for C₁₇H₂₀O₆S (352.4): C, 57.94; H, 5.72; found: C, 57.70; H, 5.96.

4,6-Di-O-acetyl-3-mercapto (3-methylphenyl)-2-deoxy-D-galactono-1,5-lactone
(Table 1, entry 33): *R-isomer*

¹H NMR (CDCl₃, 200 MHz): δ 7.28–7.13 (m, 4H, Ar-H), 5.12–5.05 (m, 2H, H-3, H-4), 4.22–4.18 (m, 2H, H-6), 3.74–3.70 (m, 1H, H-5), 3.0 (dd, *J* = 18.1, 6.7 Hz, 1H, H-2_e), 2.60 (dd, *J* = 18.1, 3.7 Hz, 1H, H-2_a), 2.36 (s, 3H, CH₃), 2.10, 2.05 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.0, 169.2, 166.8 (2 COCH₃, C-1), 139.4–127.9 (Ar-C), 74.2 (C-5), 67.2 (C-4), 62.0 (C-6), 42.0 (C-3), 31.8 (C-2), 21.3, 20.6, 20.5 (2 COCH₃, CH₃); ESI-MS: *m/z* = 375.4 [M + Na]⁺; Anal. Calcd. for C₁₇H₂₀O₆S (352.4): C, 57.94; H, 5.72; found: C, 57.75; H, 6.0.

4,6-Di-O-acetyl-3-mercapto (4-methylphenyl)-2-deoxy-D-galactono-1,5-lactone
(Table 1, entry 34): *R-isomer*

¹H NMR (CDCl₃, 200 MHz): δ 7.38–7.14 (m, 4H, Ar-H), 5.07–5.04 (m, 2H, H-3, H-4), 4.21–4.18 (m, 2H, H-6), 3.67–3.64 (m, 1H, H-5), 3.0 (dd, *J* = 18.1, 6.7 Hz, 1H, H-2_e), 2.60 (dd, *J* = 18.1, 3.7 Hz, 1H, H-2_a), 2.36 (s, 3H, CH₃), 2.09, 2.05 (2 s, 6H, 2 COCH₃); ¹³C NMR (CDCl₃, 50 MHz): δ 170.5, 168.9, 166.7 (2 COCH₃, C-1), 138.9–127.2 (Ar-C), 74.2 (C-5), 68.2 (C-4), 62.0 (C-6), 42.5 (C-3), 31.8 (C-2), 21.1, 21.1, 20.6 (2COCH₃, CH₃); ESI-MS: *m/z* = 375.4 [M + Na]⁺; Anal. Calcd. for C₁₇H₂₀O₆S (352.4): C, 57.94; H, 5.72; found: C, 57.72; H, 5.98.

4,6-Di-O-acetyl-3-mercapto (2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2-deoxy-D-galactono-1,5-lactone (Table 1, entry 35): *R-isomer*

¹H NMR (CDCl₃, 300 MHz): δ 5.29 (brs, 1H, H-4), 5.24–5.0 (m, 3H, H-2', H-3', H-4'), 4.65 (d, *J* = 9.7 Hz, 1H, H-1'), 4.28–4.06 (m, 4H, H-6_{ab}, H-6'_{ab}), 3.74–3.65 (m, 2H, H-5, H-5'), 3.0 (dd, *J* = 18.1, 6.6 Hz, 1H, H-2_e), 2.40 (dd, *J* = 18.1, 3.7 Hz, 1H, H-2_a), 2.16, 2.09, 2.07, 2.03, 2.02 (5 s, 18H, 6 COCH₃); ¹³C NMR (CDCl₃, 75 MHz): δ 170.3, 170.1, 169.7, 169.4, 169.2, 169.0 (6 COCH₃), 166.4 (C-1), 82.3 (C-1'), 78.2, 76.2, 73.4, 69.2, 68.0, 67.8, 62.7 (C-6), 61.9 (C-6'), 36.2 (C-3), 32.6 (C-2), 20.6 (2 C), 20.5 (2 C), 20.4 (2 C); ESI-MS: *m/z* = 615.5 [M + Na]⁺; Anal. Calcd. for C₂₄H₃₂O₁₅S (592.57): C, 48.65; H, 5.44; found: C, 48.48; H, 5.70.

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