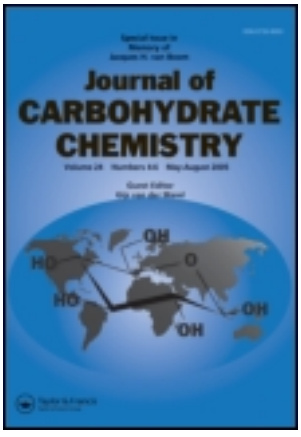

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lcar20

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

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Version of record first published: 27 Jun 2008.

To cite this article: Pintu Kumar Mandal , Gour Hari Maiti & Anup Kumar Misra (2008): Catalyst-free Efficient Synthesis of 3-Thio-2-deoxysugar Derivatives in Water , Journal of Carbohydrate Chemistry, 27:4, 238-257

To link to this article: http://dx.doi.org/10.1080/07328300802120893

Journal of Carbohydrate Chemistry, 27:238–257, 2008

ISSN: 0732-8303 print 1532-2327 online
DOI: 10.1080/07328300802120893

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]

Received October 6, 2007; accepted April 10, 2008.
C.D.R.I. communication no. 7250.
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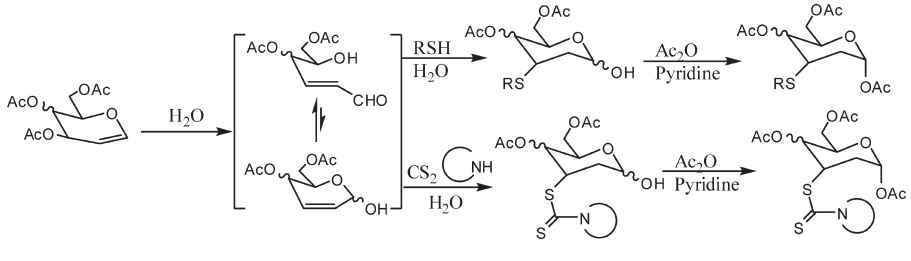
Recently, two elegant reaction protocols for the addition of thiols[6] and dithiocarbamates[7] to the activated olefins in water without using catalyst were disclosed. Prompted by these reports, it has been envisaged that water-mediated addition of a thiol or thiocarbamate anion generated in situ to 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.

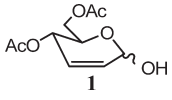
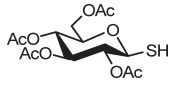
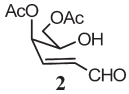
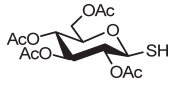
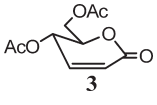
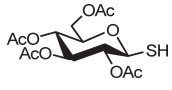
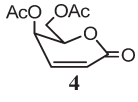
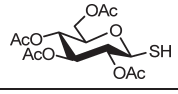
After achieving satisfactory yield of thia-Michael adducts of 2,3-unsaturated glyconolactols and lactones, we turned our attention to the preparation of 3-dithiocarbamoyl-2-deoxy sugar derivatives. For this purpose, we have applied the reaction protocol reported by Saidi et al.[7] In a model experiment, 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 GF_{254} coated TLC plates. The spots on TLC were visualized by UV lamp and warming ceric sulphate (2%$Ce(SO_4)_2$ in 2 N H_2SO_4) 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		$HSCH_2COOEt$	15	88	1:4
7			30	80	1:6
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		$HSCH_2COOEt$	15	85	4.6:1
19			30	82	5:1
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	1:0

[a]Determined from the integration values of the corresponding signals in ^1H NMR spectra.

^{1}H and ^{13}C NMR, 2D COSY, and HSQC spectra were recorded on a Brucker 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

^{1}H 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 *C*OCH_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 CO*C*H_3); ***R*-isomer**: ^{1}H 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 *C*OCH_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 CO*C*H_3); ESI-MS: $m/z = 405.4$ $[M + Na]^+$; Anal. Calcd. for $C_{18}H_{22}O_7S$ (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

^{1}H 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 *C*O*C*H_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 CO*C*H_3), 20.7 (*C*H_3); ***R*-isomer**: ^{1}H 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 *C*OCH$_3$), 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 CO*C*H$_3$, *C*H$_3$); ESI-MS: $m/z = 419.5$ $[M + Na]^+$; Anal. Calcd. for $C_{19}H_{24}O_7S$ (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

^{1}H NMR (CDCl$_3$, 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, C*H*$_3$), 2.12–1.87 (m, 2H, H-2$_{ea}$), 2.08, 2.06 (2 s, 9H, 3 COC*H*$_3$); ^{13}C NMR (CDCl$_3$, 50 MHz): δ 170.1 (2 C), 170.0 (3 *C*OCH$_3$), 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 CO*C*H$_3$), 20.7 (*C*H$_3$); ***R*-isomer**: ^{1}H NMR (CDCl$_3$, 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, C*H*$_3$), 2.12, 1.95, 1.93 (3 s, 9H, 3 COC*H*$_3$), 2.10–1.85 (m, 2H, H-2$_{ea}$); ^{13}C NMR (CDCl$_3$, 50 MHz): δ 169.3, 168.3 (2 C; 3 *C*OCH$_3$), 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 CO*C*H$_3$, *C*H$_3$); ESI-MS: $m/z = 419.5$ $[M + Na]^+$; Anal. Calcd. for $C_{19}H_{24}O_7S$ (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

^{1}H NMR (CDCl$_3$, 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, C*H*$_3$), 2.10–1.80 (m, 2H, H-2$_{ea}$), 2.08, 2.06 (2 s, 9H, 3 COC*H*$_3$); ^{13}C NMR (CDCl$_3$, 50 MHz): δ 170.3, 170.2, 169.6 (3 *C*OCH$_3$), 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 (*C*H$_3$), 20.6, 20.5, 20.4 (3 CO*C*H$_3$); ***R*-isomer**: ^{1}H NMR (CDCl$_3$, 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, C*H*$_3$), 2.11, 2.06, 2.00 (3 s, 9H, 3 COC*H*$_3$), 2.10–1.82 (m, 2H, H-2$_{ea}$); ^{13}C NMR (CDCl$_3$, 50 MHz): δ 169.6, 169.3, 168.5 (3 *C*OCH$_3$), 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 CO*C*H$_3$, C*H*$_3$); ESI-MS: $m/z = 419.5$ $[M + Na]^+$; Anal. Calcd. for $C_{19}H_{24}O_7S$ (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

^{1}H NMR (CDCl$_3$, 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, SCOC$\underline{H}_3$), 2.18–2.0 (m, 2H, H-2$_{ea}$), 2.11, 2.07, 2.03 (3 s, 9H, 3 COC*H*$_3$); ^{13}C NMR (CDCl$_3$, 50 MHz): δ 192.9 (S*C*OC*H*$_3$), 169.8, 169.0, 168.8 (3 *C*OCH$_3$), 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 COCH$_3$, SCOCH$_3$); ***R*-isomer**: ^{1}H NMR ($CDCl_3$, 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, SCOC*H*$_3$), 2.20, 2.15, 2.09 (3 s, 9H, 3 COC*H*$_3$), 2.18–2.0 (m, 2H, H-2$_{ea}$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 193.7 (SCOCH$_3$), 169.0, 168.0, 168.0 (3 *C*OCH$_3$), 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 $C_{14}H_{20}O_8S$ (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

^{1}H NMR ($CDCl_3$, 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$_{ab}$, OC*H*$_2$C*H*$_3$), 4.04–3.98 (m, 1H, H-3), 3.65–3.58 (m, 1H, H-5), 3.34–3.23 (m, 2H, SC*H*$_2$COOEt), 2.22–2.15 (m, 1H, H-2$_e$), 2.11, 2.09, 2.08 (3 s, 9H, 3 COC*H*$_3$), 2.01–1.85 (m, 1H, H-2$_a$), 1.30 (t, $J = 7.5$ Hz, 1H, CH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.2 (*C*OOEt), 169.3, 169.2, 168.5 (3 *C*OCH$_3$), 92.2 (C-1), 72.9 (C-5), 67.2 (C-4), 63.0 (COO*C*H$_2$CH$_3$), 61.3 (C-6), 44.2 (C-3), 36.2 (S*C*H$_2$COOEt), 32.5 (C-2), 21.0, 20.8, 20.7 (3 CO*C*H$_3$), 14.1 (CH$_2$*C*H$_3$); ***R*-isomer**: ^{1}H NMR ($CDCl_3$, 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$_{ab}$, OC*H*$_2$C*H*$_3$), 3.99–3.94 (m, 1H, H-3), 3.73–3.66 (m, 1H, H-5), 3.26–3.15 (m, 2H, SC*H*$_2$COOEt), 2.31–2.20 (m, 1H, H-2$_e$), 2.12, 2.09, 2.08 (3 s, 9H, 3 COC*H*$_3$), 2.0–1.80 (m, 1H, H-2$_a$), 1.30 (t, $J = 7.4$ Hz, 3H, COOCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.2, 169.7, 169.5, 169.3 (*C*OOEt, 3 *C*OCH$_3$), 90.7 (C-1), 71.4 (C-5), 68.4 (C-4), 62.2 (COO*C*H$_2$CH$_3$), 61.3 (C-6), 41.4 (C-3), 35.5 (S*C*H$_2$COOEt), 31.7 (C-2), 20.9, 20.7, 20.6 (3 CO*C*H$_3$), 14.1 (CH$_2$*C*H$_3$); ESI-MS: $m/z = 415.4$ $[M + Na]^+$; Anal. Calcd. for $C_{16}H_{24}O_9S$ (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

^{1}H NMR ($CDCl_3$, 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 COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.1, 169.9, 169.5, 169.2, 168.9, 168.7, 168.4 (7 *C*OCH$_3$), 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**: ^{1}H NMR ($CDCl_3$, 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 COCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.4, 170.0, 169.5, 169.3, 168.9, 168.7, 168.4 (7 *C*OCH_3), 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 $C_{26}H_{36}O_{16}S$ (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

^{1}H NMR ($CDCl_3$, 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 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.2, 170.1, 169.3 (3 *C*OCH_3), 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 CO*C*H_3); ***R*-isomer**: ^{1}H NMR ($CDCl_3$, 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 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 169.3, 169.1, 168.3 (3 *C*OCH_3), 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 CO*C*H_3); ESI-MS: $m/z = 406.4$ $[M + Na]^+$; Anal. Calcd. for $C_{17}H_{21}NO_7S$ (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

^{1}H NMR ($CDCl_3$, 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}, NCH_2), 3.93–3.82 (m, 2H, NCH_2), 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 COCH_3), 1.80–1.62 (m, 6H, 3-CH_2-); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 192.5 (*C*S), 170.5, 170.3, 168.9 (3 *C*OCH_3), 91.1 (C-1), 71.8 (C-4), 66.8 (C-5), 62.2 (C-6), 52.9 (*C*H_2), 51.5 (*C*H_2), 48.1 (C-3), 35.9 (C-2), 25.4 (*C*H_2), 24.2 (2 C, *C*H_2), 21.1, 21.0, 20.9 (3 COCH_3); ***R*-isomer**: ^{1}H NMR ($CDCl_3$, 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}, NCH_2), 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 COCH_3), 1.78–1.60 (m, 6H, 3 CH_2-); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 192.4 (*C*S), 169.8, 169.6, 168.6 (3 *C*OCH_3), 91.5 (C-1), 71.0 (C-4), 68.1 (C-5), 62.6 (C-6), 53.0 (*C*H_2), 51.5 (*C*H_2), 49.1 (C-3), 39.5 (C-2), 25.4 (*C*H_2), 24.2 (2 C, *C*H_2), 21.0, 20.9, 20.8 (3 CO*C*H_3); ESI-MS: $m/z = 456.5$ $[M + Na]^+$; Anal. Calcd. for $C_{18}H_{27}NO_7S_2$ (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

^{1}H 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(CH_2-)$_2$), 3.84–3.66 (m, 4H, 2 OCH_2), 2.65–2.53 (m, 1H, H-2_e), 2.12, 2.10, 2.08 (3 s, 9H, 3 COCH_3), 1.97–1.82 (m, 1H, H-2_a); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 194.5 (*C*S), 170.3, 169.6, 168.7 (3 *C*OCH_3), 91.0 (C-1), 71.8 (C-4), 66.5 (C-5), 66.0 (2 C, 2 O*C*H$_2$), 62.1 (C-6), 50.4 (2 C, 2 N*C*H$_2$), 48.2 (C-3), 35.9 (C-2), 21.0, 20.9, 20.7 (3 CO*C*H$_3$); ESI-MS: $m/z = 458.5$ $[M + Na]^+$; Anal. Calcd. for $C_{17}H_{25}NO_8S_2$ (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

^{1}H 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 NCH_2CH_3), 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 COCH_3), 1.38–1.26 (m, 6H, 2 NCH_2CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 192.4 (*C*S), 170.4, 170.3, 169.6 (3 *C*OCH_3), 91.5 (C-1), 74.0 (C-4), 66.8 (C-5), 62.5 (C-6), 46.5 (2 C, 2 *C*H$_2$CH$_3$), 44.4 (C-3), 31.4 (C-2), 21.2, 20.8, 20.6 (3 CO*C*H$_3$), 12.8, 12.5 (2 CH_2*C*H$_3$); ***R*-isomer**: ^{1}H 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 NCH_2CH_3), 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 COCH_3), 1.35–1.24 (m, 6H, 2 CH_2CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 192.6 (*C*S), 169.0, 168.9, 168.4 (3 CO*C*H$_3$), 90.7 (C-1), 75.4 (C-4), 69.6 (C-5), 62.2 (C-6), 49.5 (2 C, 2 *C*H$_2$CH$_3$), 46.7 (C-3), 31.4 (C-2), 21.2, 21.1, 20.8 (3 CO*C*H$_3$), 12.9, 12.6 (2 CH$_2$*C*H$_3$); ESI-MS: $m/z = 444.5$ $[M + Na]^+$; Anal. Calcd. for $C_{17}H_{27}NO_7S_2$ (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

^{1}H 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, NCH_2CH$_2$-), 4.14–4.0 (m, 2H, NCH$_2$CH_2-), 3.04–3.0 (m, 2H, NCH_2), 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 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 193.3 (*C*S), 170.4, 170.3, 169.5 (3 *C*OCH_3), 134.1–126.1 (Ar-C), 91.1 (C-1), 74.0 (C-4), 71.7 (C-5), 62.1 (C-6), 53.7 (N*C*H$_2$CH$_2$-), 50.1 (NCH$_2$*C*H$_2$-), 48.0 (C-3), 35.8 (C-2), 28.9 (N*C*H$_2$), 21.2, 21.0, 20.7 (3 CO*C*H$_3$); ESI-MS: $m/z = 504.6$ $[M + Na]^+$; Anal. Calcd. for $C_{22}H_{27}NO_7S_2$ (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

^{1}H 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 *C*OCH_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 CO*C*H_3); ***S*-isomer**: ^{1}H 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 *C*OCH_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 CO*C*H_3); ESI-MS: $m/z = 405.4$ $[M + Na]^+$; Anal. Calcd. for $C_{18}H_{22}O_7S$ (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

^{1}H 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, C*H*$_3$), 2.20, 2.12, 2.09 (3 s, 9H, 3 COC*H*$_3$), 2.11–1.88 (m, 2H, H-2_{ea}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 168.3, 168.2 (2 C) (3 *C*OCH_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 CO*C*H_3), 20.4 (*C*H_3); ***S*-isomer**: ^{1}H 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, C*H*$_3$), 2.09, 2.05 (2 s, 9H, 3 COC*H*$_3$), 2.12–1.90 (m, 2H, H-2_{ea}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 169.8, 169.4 (2 C) (3 *C*OCH_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 CO*C*H_3), 20.3 (*C*H_3); ESI-MS: $m/z = 419.5$ $[M + Na]^+$; Anal. Calcd. for $C_{19}H_{24}O_7S$ (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

^{1}H 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, C*H*$_3$), 2.17, 2.10, 2.09 (3 s, 9H, 3 COC*H*$_3$), 2.20–1.85 (m, 2H, H-2_{ea}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.0, 169.6, 168.6 (3 *C*OCH_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 CO*C*H_3, *C*H_3); ***S*-isomer**: ^{1}H 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, CH_3), 2.05, 2.03 (2 s, 9H, 3 COCH_3), 2.20–1.87 (m, 2H, H-2_{ea}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 168.6, 168.5, 168.4 (3 *C*OCH_3), 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 CO*C*H_3, *C*H_3); ESI-MS: $m/z = 419.5$ $[M + Na]^+$; Anal. Calcd. for $C_{19}H_{24}O_7S$ (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

^{1}H NMR ($CDCl_3$, 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, CH_3), 2.19–2.16 (m, 1H, H-2_e), 2.11, 2.06, 2.03 (3 s, 9H, 3 COCH_3), 2.05–1.90 (m, 1H, H-2_a); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 168.5 (2 C), 168.4 (3 *C*OCH_3), 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 CO*C*H_3), 20.7 (*C*H_3); **S-isomer**: ^{1}H NMR ($CDCl_3$, 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, CH_3), 2.14, 2.08, 2.02 (3 s, 9H, 3 COCH_3), 2.19–2.16 (m, 1H, H-2_e), 2.05–1.90 (m, 1H, H-2_a); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.0, 169.7, 169.6 (3 *C*OCH_3), 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 CO*C*H_3), 20.8 (*C*H_3); ESI-MS: $m/z = 419.5$ $[M + Na]^+$; Anal. Calcd. for $C_{19}H_{24}O_7S$ (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

^{1}H NMR ($CDCl_3$, 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, SCOCH_3), 2.11, 2.02 (2 s, 9H, 3 COCH_3), 2.0–1.80 (m, 2H, H-2_{ea}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 193.9 (S*C*OCH_3), 170.5, 170.1, 170.0 (3 *C*OCH_3), 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, SCO*C*H_3, 3 CO*C*H_3); **S-isomer:** ^{1}H NMR ($CDCl_3$, 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, SCOCH_3), 2.13, 2.10, 2.06 (3 s, 9H, 3 COCH_3), 2.05–1.82 (m, 2H, H-2_{ea}); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 193.6 (S*C*OCH_3), 170.0, 169.2, 168.8 (3 *C*OCH_3), 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, SCO*C*H_3, 3 CO*C*H_3); ESI-MS: $m/z = 371.4$ $[M + Na]^+$; Anal. Calcd. for $C_{14}H_{20}O_8S$ (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

^{1}H 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 *C*OCH_3, *C*OOEt), 90.7 (C-1), 69.3 (C-5), 64.4 (C-4), 62.5 (C-6), 61.7 (O*C*H_2CH_3), 38.9 (C-3), 30.3 (C-2), 28.7 (S*C*H_2-), 20.9–20.4 (3 C, 3 CO*C*H_3), 13.9 (-CH_2*C*H_3); ***S*-isomer**: ^{1}H 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 (*C*OOEt, 3 *C*OCH_3), 92.5 (C-1), 73.9 (C-5), 63.7 (C-4), 62.7 (C-6), 61.6 (O*C*H_2CH_3), 39.9 (C-3), 31.4 (C-2), 28.6 (S*C*H_2-), 20.7–20.2 (3 C, 3 CO*C*H_3), 13.8 (-CH_2*C*H_3); ESI-MS: $m/z = 415.4$ $[M + Na]^+$; Anal. Calcd. for $C_{16}H_{24}O_9S$ (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

^{1}H 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 *C*OCH_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**: ^{1}H 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 *C*OCH_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: $m/z = 659.6$ $[M + Na]^+$; Anal. Calcd. for $C_{26}H_{36}O_{16}S$ (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

^{1}H 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 COCH_3); ^{13}C NMR ($CDCl_3$, 200 MHz): δ 169.8, 169.3, 168.5 (3 *C*OCH$_3$), 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 COCH_3); ***S*-isomer**: ^{1}H 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), 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 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 168.5, 168.2 (2 C, 3 *C*OCH$_3$), 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 CO*C*H$_3$); ESI-MS: $m/z = 406.4$ $[M + Na]^+$; Anal. Calcd. for $C_{17}H_{21}NO_7S$ (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

^{1}H NMR ($CDCl_3$, 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, NC$\underline{H}_2$), 4.14–3.92 (m, 2H, H-6_{ab}), 3.90–3.78 (m, 2H, NC$\underline{H}_2$), 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 COCH_3), 1.80–1.60 (m, 6H, 3 CH_2); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 192.0 (*C*S), 170.2, 169.5, 169.0 (3 *C*OCH$_3$), 91.5 (C-1), 70.2 (C-4), 67.2 (C-5), 62.5 (C-6), 53.0 (*C*H$_2$), 51.4 (*C*H$_2$), 45.8 (C-3), 29.5 (C-2), 25.3 (*C*H$_2$), 24.2 (2 C, 2 *C*H$_2$), 20.9, 20.7, 20.6 (3 CO*C*$\underline{H}_3$); ESI-MS: $m/z = 456.5$ $[M + Na]^+$; Anal. Calcd. for $C_{18}H_{27}NO_7S_2$ (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

^{1}H NMR ($CDCl_3$, 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 NCH_2), 3.85–3.70 (m, 4H, 2 OCH_2), 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 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 193.8 (*C*S), 170.1, 169.6, 169.4 (3 *C*OCH$_3$), 91.3 (C-1), 70.0 (C-4), 66.9 (C-5), 66.0 (2 C, O*C*H$_2$), 62.0 (C-6), 51.0 (2 C, N*C*H$_2$), 45.8 (C-3), 29.5 (C-2), 21.0, 20.9, 20.8 (3 CO*C*H$_3$); ESI-MS: $m/z = 458.5$ $[M + Na]^+$; Anal. Calcd. for $C_{17}H_{25}NO_8S_2$ (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

^{1}H NMR ($CDCl_3$, 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, CH_2CH$_3$), 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 COCH_3), 2.16–2.01 (m, 1H, H-2_a), 1.28–1.24 (m, 6H,

2 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 191.9 (*C*S), 170.0, 169.5, 168.9 (3 *C*OCH$_3$), 91.7 (C-1), 70.2 (C-4), 67.2 (C-5), 62.7 (C-6), 46.7 (2 C, 2 *C*H$_2$CH$_3$), 45.8 (C-3), 28.8 (C-2), 21.1, 20.7, 20.6 (3 CO*C*H$_3$), 12.4, 11.4 (2 CH$_2$*C*H$_3$); ESI-MS: $m/z = 444.5$ $[M + Na]^+$; Anal. Calcd. for $C_{17}H_{27}NO_7S_2$ (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

^{1}H NMR ($CDCl_3$, 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$_a$, NC*H*$_2$CH$_2$), 4.03–3.92 (m, 2H, H-6$_b$, NCH$_2$C*H*$_2$), 3.0–2.92 (m, 2H, NC*H*$_2$), 2.40–2.22 (m, 1H, H-2$_e$), 2.16, 2.13, 2.05 (3 s, 9H, 3 COC*H*$_3$), 2.11–2.03 (m, 1H, H-2$_a$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 193.0 (*C*S), 170.1, 169.5, 168.9 (3 *C*OCH$_3$), 134.9–126.0 (Ar-C), 91.5 (C-1), 70.2 (C-4), 67.0 (C-5), 62.4 (C-6), 53.8 (N*C*H$_2$CH$_2$), 47.9 (NCH$_2$*C*H$_2$), 45.5 (C-3), 29.6 (C-2), 28.9 (N*C*H$_2$), 21.0, 20.8, 20.7 (3 CO*C*H$_3$); ESI-MS: $m/z = 504.6$ $[M + Na]^+$; Anal. Calcd. for $C_{22}H_{27}NO_7S_2$ (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

^{1}H NMR ($CDCl_3$, 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 COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.1, 169.3, 166.6 (2 *C*OCH$_3$, 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 CO*C*H$_3$); ***R*-isomer**: ^{1}H NMR ($CDCl_3$, 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 COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 169.8, 169.6, 167.2 (2 *C*OCH$_3$, 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 CO*C*H$_3$); ESI-MS: $m/z = 361.4$ $[M + Na]^+$; Anal. Calcd. for $C_{16}H_{18}O_6S$ (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

^{1}H NMR ($CDCl_3$, 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, C*H*$_3$), 1.99, 1.97 (2 s, 6H, 2 COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 169.8, 169.6, 166.8 (2 *C*OCH$_3$, 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 CO*C*H$_3$, *C*H$_3$); ***R*-isomer**: ^{1}H NMR ($CDCl_3$, 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, CH_3), 2.02, 1.93 (2 s, 6H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.1, 169.2, 166.9 (2 *C*OCH$_3$, 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 (2CO*C*H$_3$, *C*H$_3$); ESI-MS: $m/z = 375.4$ $[M + Na]^+$; Anal. Calcd. for $C_{17}H_{20}O_6S$ (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

^{1}H NMR ($CDCl_3$, 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, CH_3), 2.04, 2.03 (2 s, 6H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.3, 169.8, 167.3 (2 *C*OCH$_3$, 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 COCH_3, *C*H$_3$); ***R*-isomer:** ^{1}H NMR ($CDCl_3$, 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, CH_3), 2.04, 2.03 (2 s, 6H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.4, 170.0, 166.9 (2 *C*OCH$_3$, 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 COCH_3, *C*H$_3$); ESI-MS: $m/z = 375.4$ $[M + Na]^+$; Anal. Calcd. for $C_{17}H_{20}O_6S$ (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

^{1}H NMR ($CDCl_3$, 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, CH_3), 2.08, 2.06 (2 s, 6H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 169.8, 169.6, 167.3 (2 *C*OCH$_3$, 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 COCH_3, *C*H$_3$); ***R*-isomer**: ^{1}H NMR ($CDCl_3$, 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, CH_3), 2.06, 2.03 (2 s, 6H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 169.9, 169.8, 166.7 (2 *C*OCH$_3$, 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 COCH_3, *C*H$_3$); ESI-MS: $m/z = 375.4$ $[M + Na]^+$; Anal. Calcd. for $C_{17}H_{20}O_6S$ (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

^{1}H NMR ($CDCl_3$, 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, CH_3), 2.11, 2.08 (2 s, 6H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 171.2, 170.9, 170.6, 167.2 (3 *C*OCH$_3$, 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 CO*C*H$_3$); ***R*-isomer**: ^{1}H NMR ($CDCl_3$, 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, CH_3), 2.07, 2.05 (2 s, 6H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 171.4, 170.2, 170.0, 166.9 (3 *C*OCH$_3$, 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 CO*C*H$_3$); ESI-MS: $m/z = 327.3$ $[M + Na]^+$; Anal. Calcd. for $C_{12}H_{16}O_7S$ (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

^{1}H NMR ($CDCl_3$, 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 COCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.2, 170.1, 169.9, 169.5, 169.2, 169.0 (6 COCH_3), 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 $C_{24}H_{32}O_{15}S$ (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

^{1}H NMR ($CDCl_3$, 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 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.0, 169.2, 166.7 (2 *C*OCH$_3$, 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 CO*C*H$_3$); ESI-MS: $m/z = 361.4$ $[M + Na]^+$; Anal. Calcd. for $C_{16}H_{18}O_6S$ (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

^{1}H NMR ($CDCl_3$, 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, CH_3), 2.09, 2.05 (2 s, 6H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.0, 169.2, 166.7 (2 *C*OCH$_3$, 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 CO*C*H$_3$, *C*H$_3$); ESI-MS: $m/z = 375.4$

$[M + Na]^+$; Anal. Calcd. for $C_{17}H_{20}O_6S$ (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

^{1}H NMR ($CDCl_3$, 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, CH_3), 2.10, 2.05 (2 s, 6H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.0, 169.2, 166.8 (2 *C*OCH$_3$, 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 CO*C*H$_3$, *C*H$_3$); ESI-MS: $m/z = 375.4$ $[M + Na]^+$; Anal. Calcd. for $C_{17}H_{20}O_6S$ (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

^{1}H NMR ($CDCl_3$, 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, CH_3), 2.09, 2.05 (2 s, 6H, 2 COCH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ 170.5, 168.9, 166.7 (2 *C*OCH$_3$, 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 (2CO*C*H$_3$, *C*H$_3$); ESI-MS: $m/z = 375.4$ $[M + Na]^+$; Anal. Calcd. for $C_{17}H_{20}O_6S$ (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

^{1}H NMR ($CDCl_3$, 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 COCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.3, 170.1, 169.7, 169.4, 169.2, 169.0 (6 *C*OCH$_3$), 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 $C_{24}H_{32}O_{15}S$ (592.57): C, 48.65; H, 5.44; found: C, 48.48; H, 5.70.

ACKNOWLEDGMENTS

Instrumentation facilities from SAIF, CDRI, are gratefully acknowledged. P.K.M. thanks CSIR, New Delhi, for providing a Junior Research Fellowship. This work was partly funded by Ramanna fellowship, DST, New Delhi (AKM).

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