2-HALOETHYL 1-THIOGLYCOSIDES AS NEW TOOLS IN GLYCOSIDE SYNTHESES. PART 1: PREPARATION, CHARACTERISTICS, GENERAL REACTIONS

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Dedicated to Professor Miloslav Černý on the occasion of his 75th birthday.

2-Haloethyl 1-thioglycosides are excellent leaving groups when the 2-haloethyl function is activated with silver salts or Lewis acids. These thioglycosides can be synthesized on the original Černý route or for better compatibility with the needs of a more complex glycoside synthesis, in stepwise procedures via 2-(2-tetrahydropyran-2-yloxy)ethyl glycosides or trityl 1-thioglycosides. The initial step in glycosidation reaction presumably proceeds via a thiiranium ion, which is responsible for their increased reactivity compared with normal thioethers as leaving groups in glycoside syntheses. Basic features of this new system with respect to reactivity and selectivity in disaccharide syntheses are described.

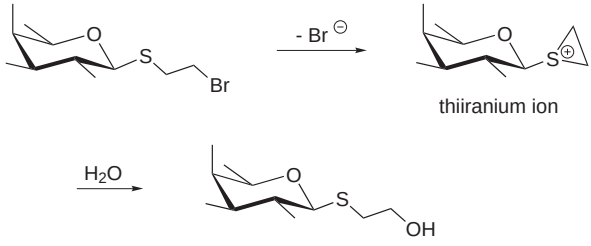
Keywords: Glycosides; Thioglycosides; Carbohydrates; Disaccharides; Glycosidation; Protecting groups; Leaving groups.

In 2-haloethyl 1-thioglycosides, a class of compounds first synthesized and described by Černý et al.[1] in 1959, the C–halogen bond in the aglycon is easily hydrolyzed, as it was demonstrated by the same group[2] in 1975. The often observed ease of such type of reactions, widely used in general chemistry, is a consequence of a β-positioned hetero atom relative to a leaving group, which supports the bond cleavage (anchimeric assistance)[3]. The reaction is regarded to proceed via a thiiranium ion, which is opened in a second step by the nucleophile.

As shown in Scheme 1, the attack of the nucleophile on the thiiranium ion generated from 2-haloethyl 1-thioglycosides may proceed at the two equivalent positions of the ring, resulting in compounds mentioned above.

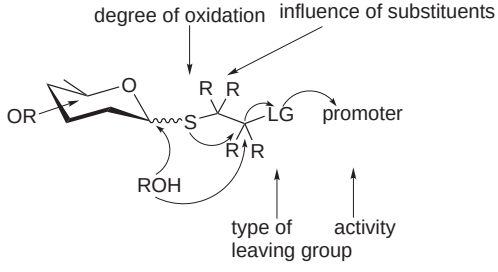
If the carbon of the C–S bond of the thiiranium ion is attacked by a nucleophile, for example an alcohol, a glycoside should be formed under

expelling a neutral ethylene sulfide. Herein we describe, that this way can be favoured by the reaction conditions to such an extent, that glycosides are the only products. With that, 2-haloethyl 1-thioglycosides represent a new type of leaving groups in glycoside syntheses, in which the anomeric sulfur is activated from a "remote" position (remote activation)[4].



SCHEME 1
Substition reaction of 2-haloethyl 1-thioglycosides via thiiranium ions according to Černý

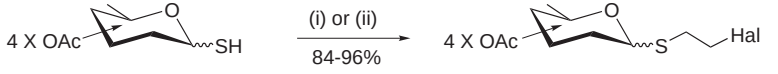
Scheme 2 indicates a large variety of possible manipulations at the leaving group. Besides the oxidation state of the sulfur, the ethylene moiety allows different substitution pattern to influence the reaction. The leaving group can be arranged in the way that it fits best to a promotor. In this paper we describe various appraoches to 2-haloethyl 1-thioglycosides, reflecting their availability for more complex glycoside syntheses and their reaction with inreactive hydroxy groups of carbohydrate derivatives to yield disaccharides[5]. In the following paper we will report a more complex synthesis of a spacered tetrasaccharide based on the methods described here.



SCHEME 2
Possible manipulations at the leaving groups

New Preparations of 2-Haloethyl 1-Thioglycosides by the Černý Route

The original procedure seems to be independent of the configuration of the starting material. There are no significant differences starting from the unprotected 1-thiols with the configurations shown in Scheme 3 (*gluco*-, *galacto*- or *manno*-configuration) to obtain either the 2-bromo- (**4**β [1], **5**β [2], **6**α) or 2-chloroethyl products (**7**β, **8**β)[6] in high yield. As it will be shown later, these compounds can be used directly in glycoside synthesis, but they do not allow any further manipulation at the glycosyl residue, due to the mentioned reactivity of their aglyconic part.



1-3 **4-6** Hal = Br; **7-8** Hal= Cl

1, 4, 7 β–D-*gluco*
2, 5, 8 β–D-*galacto*
3, 6 α-D-*manno*

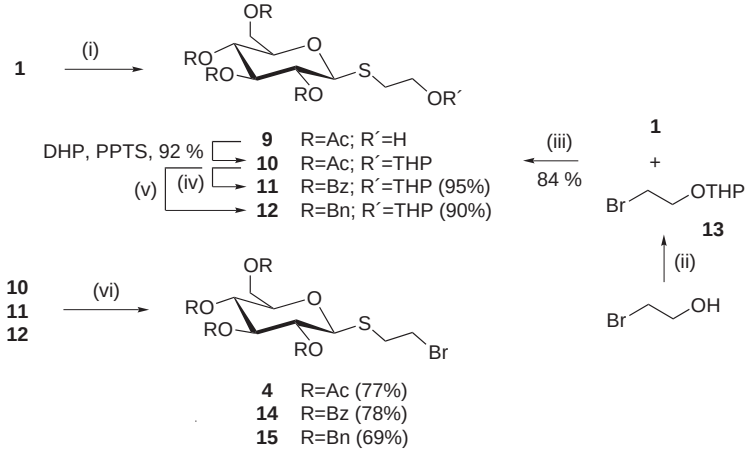
(i) 1,2-dibromomethane, K_2CO_3, H_2O, acetone; (ii) 1-bromo-2-chloroethane, K_2CO_3, H_2O, acetone

SCHEME 3
Preparation of 2-haloethyl 1-thioglycosides from 1-thiols (analogue Černý)

New Routes to 2-Haloethyl 1-Thioglycosides

For more advanced applications of 2-haloethyl 1-thioglycosides in glycoside syntheses, it is necessary that their reactivity at the glycosyl residue be diminished during synthetic manipulations. There are several options for this purpose: An interesting one is indicated in Scheme 4. Instead of using the dihalo compounds for the alkylation of the 1-unprotected thiols, 2-bromoethanol can be used to yield the corresponding 2-hydroxyethyl 1-thioglycosides of type **9** [6]. The hydroxy group in the aglycon part of the molecule can be protected as a normal reactive hydroxy group, for example as a tetrahydropyranyl (THP) ether **10**. The same product is directly available from the THP ether of 2-bromoethanol (**13**)[7] and the 1-unprotected thiol function in **1**. Such compounds can be deacetylated for example, reesterified to a tetrabenzoate **11** or rebenzylated to a tetrabenzyl ether **12**, allowing therefore small variations in the aglycon part of the molecule. The use of the THP ether as a protection group for the hydroxy group in the aglycon part has the advantage that this function can be transformed directly into a bromo function (**4**β, **14**, **15**) by applying the mild Appel sys-

tem[8] PPh_3/CBr_4. This allows to reactivate the leaving group at an appropriate time in synthesis.

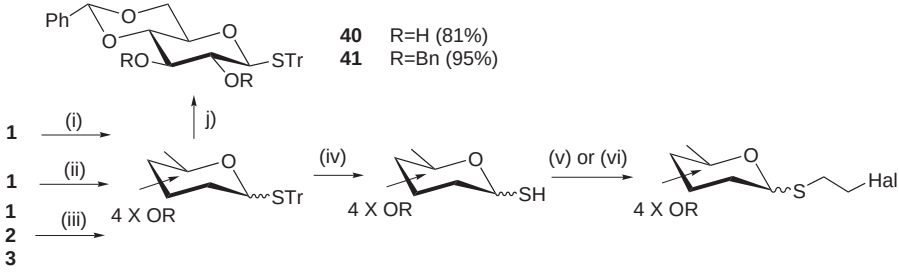


(i) 2-bromoethanol, K2CO3, H2O, acetone; (ii) DHP, PPTS, CH2Cl2, quant.;
(iii) K2CO3, H2O, acetone; (iv) 1. NaOMe, MeOH, 2. BzCl, pyridine;
(v) 1. NaOMe, MeOH, 2. BnBr, NaH, DMF; (vi) PPh2/CBr4, CH2Cl2

SCHEME 4
Preparation of 2-bromoethyl 1-thioglycosides from THP ethers

In this study, most of the newly described 2-haloethyl 1-thioglycosides are synthesized starting from the 1-unprotected thiol and using the trityl group as an intermediate protection for the anomeric centre. The acetylated *S*-trityl-protected compounds (**16**[9], **20**[10], **23**[11]) are available from the unprotected thiols using two different procedures. Under basic conditions with trityl chloride in pyridine or in dichloromethane and triethylamine (Scheme 5, (i), (ii)) or to advantage, under nearly neutral conditions with trityl alcohol and a catalytic amount of CF_3CO_2H (Scheme 5, (iii))[12]. As summarized in Scheme 5, the average yields are excellent for the isolated products **16**, **20** and **23** and independent of the configuration of the starting materials. The *S*-trityl-protected anomeric centre allows for example deacetylation at the glycosyl residue, incorporation of a benzylidene acetal with benzaldehyde and sulfuric acid (**40**) in a typical strong acidic procedure, or benzylation with NaH/benzyl bromide as the typical strong basic procedure (**41**). The yields for both reactions are excellent, indicating that the *S*-trityl protected anomeric centre allows a large variety of synthetic manipulations on the glycosyl part of the molecule.

The cleavage to the 1-unprotected thiols (**1**–**3** and **26** [13]–**32**) is easily carried out with the system CF_3CO_2H/Et_3SiH in dichloromethane described by Pearson et al.[14] The subsequent generation of the 2-haloethyl 1-thioglycosides proceeds in high yields using the Černý route (**14**, **15**, **33**, **34** and **35**–**39**), as summarized in Scheme 5.



β–D-*gluco* **16** R=Ac (82%)
(vii): **17** R=Bz (96%)
(viii): **18** R=Piv (70%)
(ix): **19** R=Bn (90%)

β–D-*galacto* **20** R=Ac (91%)
(vii): **21** R=Bz (95%)
(ix): **22** R=Bn (86%)

α–D-*manno* **23** R=Ac (84%)
(vii): **24** R=Bz (93%)
(ix): **25** R=Bn (76%)

1
26 R=Bz (α+β; 89%)
27 R=Piv (β; 92%)
28 R=Bn (β; 86%)

2
29 R=Bz (β; 88%)
30 R=Bn (β; 88%)

3
31 R=Bz (α; 87%)
32 R=Bn (α; 83%)

14(β) R=Bz, Hal=Br (78%)
33(β) R=Bz, Hal=Cl (95%)
34(β) R=Piv, Hal=Br (92%)
15(β) R=Bn, Hal=Br (69%)
35(β) R=Bn, Hal=Cl (90%)

36(β) R=Bz, Hal=Br (92%)
37(β) R=Bn, Hal=Br (85%)

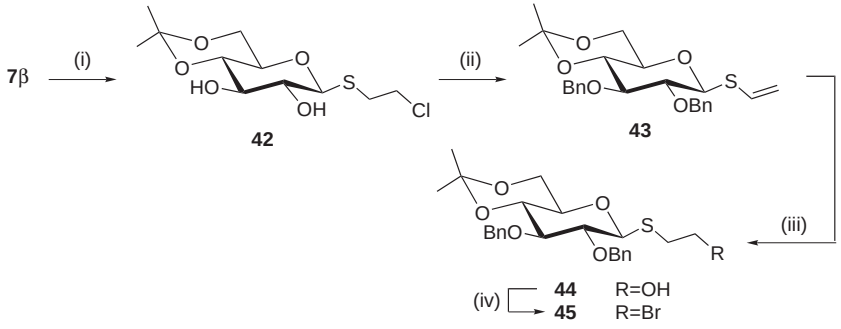
38(α) R=Bz, Hal=Br (89%)
39(α) R=Bn, Hal=Br (80%)

(i) TrCl, pyridine; (ii) TrCl, Et_3N, CH_2Cl_2; (iii) TrOH, CF_3COOH, CH_2Cl_2; (iv) CF_3COOH, Et_3SiH, CH_2Cl_2; (v) 1,2-dibromoethane, K_2CO_3, H_2O, acetone; (vi) 1-bromo-2-chloroethane, K_2CO_3, H_2O, acetone; (vii) 1. NaOMe, MeOH, 2. BzCl, pyridine; (viii) 1. NaOMe, MeOH, 2. PivCl, pyridine; (ix) 1. NaOMe, MeOH, 2. BnBr, NaH, DMF; (x) 1. NaOMe, MeOH, 2. PhCHO, H_2SO_4, DMF

SCHEME 5
Preparation of 2-bromoethyl 1-thioglycosides from trityl 1-thioglycosides

A singular result (Scheme 6) demonstrates the differences between a *S*-trityl-protected and a 2-chloroethyl-protected anomeric centre **7**β. Both allow deacetylation of the glycosyl residue. While the former allows the benzylidenation at the glycosyl part under strong acidic conditions (Scheme 4, (xi)), the latter can only be isopropylidenated in a fast reaction to compound **42**. This compound suffers from elimination in a clean reaction during benzylation with NaH/BnBr in DMF in the aglyconic part to yield the *S*-vinyl ether **43**. Interestingly, this compound showed a very low reactivity in the synthesis with thioglycosides under the reaction condi-

tions, normally supporting the glycoside synthesis. The vinyl group in **43** can be refunctionalized by hydroboration to the 2-hydroxyethyl moiety (**44**) and by bromination with the Classon[15] system Br_2/$ClPPh_2$/imidazole.



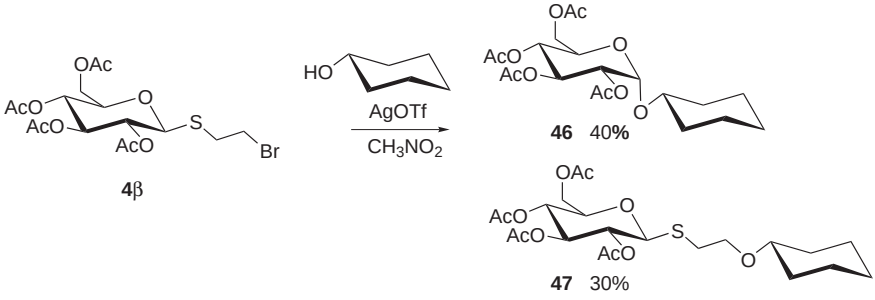
(i) 1. NaOMe, MeOH, 2. 2,2-dimethoxypropane, TsOH, 72%; (ii) NaH, BnBr, DMF, 82%; (iii) $BH_3{\cdot}SMe_2/H_2O_2$, 72%; (iv) Br_2, $ClPPh_2$, imidazole, 85%

SCHEME 6
2-Haloethyl compounds with varying protecting groups

Applications of 2-Bromoethyl Thioglycosides in Glycoside Syntheses

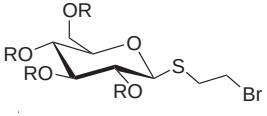
Compared to the corresponding chloro compounds the 2-bromoethyl 1-thioglycosides show, as it can be expected, always a higher reactivity. Here, only this type of compounds is regarded. In a basic experiment, compound **4**β reacts in nitromethane with 1.5 equivalents of the very reactive cyclohexanol under the promotion of silver triflate in a smooth reaction to two different compounds. One is the substitution product at the ethylene moiety (**47**) (30%), the other is cyclohexyl glycoside **46** [16] (40%) (Scheme 7). The most striking aspect of this reaction is the α-configuration of the formed cyclohexyl glycoside. This fits very good with the idea, as already discussed, that the reaction proceeds via a thiiranium ion, which, if attacked by the nucleophile at the ethylene moiety, leads to the substitution product **47**, or, if attacked by the nucleophile at the anomeric centre and expelling the neutral and very soft thiirane, results in glycoside **46**. The latter process has to be so fast and dominant that the expected neighboring group participation of the ester function at C-2 does not take place. This effect could no longer be observed if the ester functions were changed in the glycosyl acceptor (for example benzoates or pivalates) or if the reactivity of

the glycosyl donor was much lower compared to cyclohexanol. Nevertheless this basic finding indicates the new type of assistance in the glycosidation process.

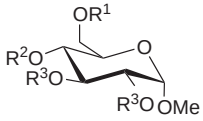


SCHEME 7
Glycosidation reaction of **4**β with cyclohexanol

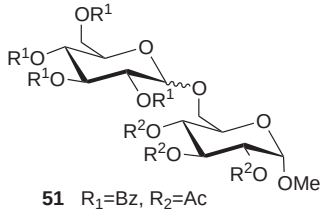
The basic behaviour of β-bromoethyl 1-*S*-glyosides in glycoside syntheses with less reactive glycosyl donors are summarized in Table I. Compound **14** represents ester-functionalized, compound **15** ether-functionalized glycosyl donors. The 6-unprotected compounds carry either acetate groups[17] (**48**) or benzyl groups[18] (**49**), represent the more reactive glycosyl donors, the 4-unprotected compound[19] (**50**) has in general a very low reactivity. The glycosidations were carried out under standard conditions (1.0 equivalent of glycosyl donor, 1.2 equivalents of hydroxy compound, 1.5 equivalents of the silver salt or a Lewis acid, room temperature) without any special precautions with respect to yield and selectivity, to make the results of the reactions comparable. As it can be seen in Table I, independently of the type of glycosyl donor and glycosyl acceptors, the yields are generally high or even excellent. In polar solvents nitromethane, dioxane and acetonitrile, silver triflate is an excellent promoter, surprisingly in the less polar solvent dichloromethane $SnCl_4$ is the best. The donor **14** with β-configuration always results in the β-linked disaccharides (entries 1–4), indicating a neighboring group participation during the bond formation. The donor **15** with β-configuration, a compound without the possibility of neighboring group assistance, shows in the solvents nitromethane, dioxane and dichloromethane an interestingly high tendency to form the α-linked disaccharides (entries 5, 6 and 8). In acetonitrile the opposite tendency can be observed, indicating the occurrence of an intermediate nitrilium ion[20]. Additional examples will be discussed in the next paper.



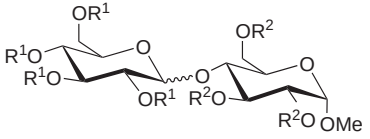
14 R=Bz
15 R=Bn



48 R_1=H, R_2, R_3= Ac
49 R_1=H, R_2, R_3= Bn
50 R_1, R_3=Bn, R_2=H



51 R_1=Bz, R_2=Ac
52 R_1=Bz, R_2=Bn
53 R_1, R_2=Bn



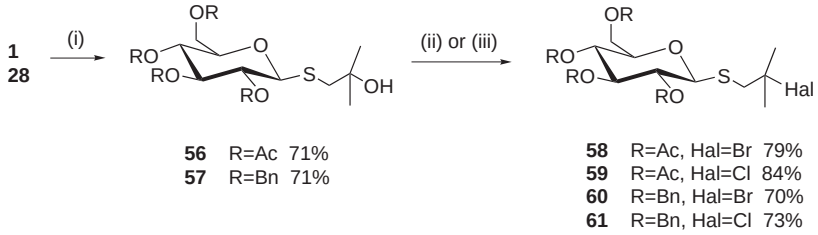
54 R_1=Bz, R_2=Bn
55 R_1,R_2=Bn

TABLE I
Selected glycosidation reactions with standard hydroxy compounds

Entry	Glycosyl donor	Glycosyl acceptor	Product	Promoter	Solvent	Yield, %	Selectivity (α:β)
1	**14**	**48**	**51**[21]	AgOTf	CH_3NO_2	78	0:1
2	**14**	**49**	**52**[22]	AgOTf	CH_3NO_2	80	0:1
3	**14**	**50**	**54**[23]	AgOTf	CH_3NO_2	71	0:1
4	**14**	**48**	**51**	$SnCl_4$	CH_2Cl_2	83	0:1
5	**15**	**49**	**53**[24]	AgOTf	dioxane	81	6:1
6	**15**	**49**	**53**	$SnCl_4$	CH_2Cl_2	84	4:1
7	**15**	**49**	**53**	AgOTf	CH_3CN	92	1:6
8	**15**	**50**	**55**[23]	AgOTf	dioxane	74	8:1

2,2-Dialkyl-2-haloethyl 1-Thioglycosides

The results described above refer to the basic system without any substituents at the ethylene moiety in the aglycon part. To clarify the influence of substituents in this part of the molecule the 2,2-dimethyl-2-bromoethyl 1-thioglycosides **56** and **57** were synthesized. The syntheses (Scheme 8) follow the general methods already described (**58**–**61**).



56 R=Ac 71%
57 R=Bn 71%

58 R=Ac, Hal=Br 79%
59 R=Ac, Hal=Cl 84%
60 R=Bn, Hal=Br 70%
61 R=Bn, Hal=Cl 73%

(i) 2-chloro-2-methylpropan-1-ol, K_2CO_3, acetone, H_2O; (ii) PBr_3, $CHCl_3$; (iii) PCl_3, $CHCl_3$

SCHEME 8
Preparation of 2,2-dialkyl-2-haloethyl 1-thioglycosides

In particular the glycosyl donor **60** and the glycosyl acceptor **49** show a very clear result with respect to the application of such compounds in glycoside syntheses. In general, compounds of type **60** exhibit a higher reactivity, compared with the basic system. Therefore the glycosylations were carried out at lower temperatures (Table II). In diethyl ether, toluene, nitromethane, tetrahydrofurane, *N*,*N*-dimethylformamide and dichloromethane, solvents covering a broad spectrum of polarities, only the product of substitution in the aglycon part, **62**, could be isolated in varying amounts (entries 1, 2, 5–9). This is in good accordance with the idea that, caused by the substituents, a "harder" electrophilic centre will favour the attack of a "hard" nucleophile (the OH function) in this part of the molecule. In case of acetonitrile, as it was already described for the basic system, the nitrilium ion is involved. When this is formed, the resulting reaction product is a glycoside, obtained with an excellent yield and selectivity (entries 3 and 4).

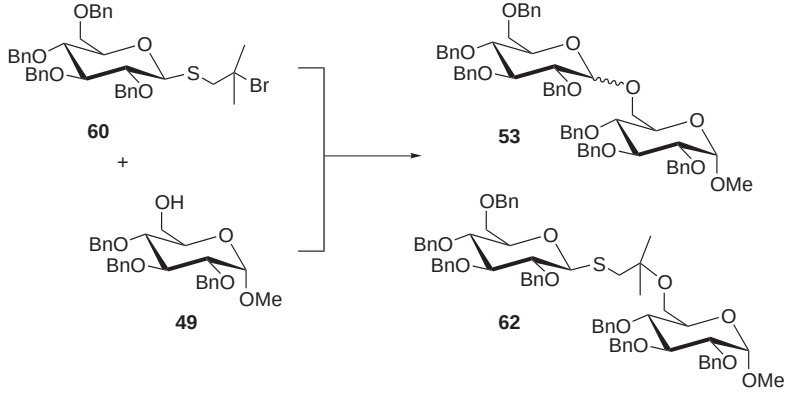


TABLE II
Orientation glycosidation reactions[a] with tertiary reaction centre

Entry	Solvent	Temperature, °C	Yield, %	Product	Selectivity (α:β)
1	Et_2O	0→20	72	**62**	–
2	Et_2O	–20	62	**62**	–
3	CH_3CN	0→20	89	**53**	1:7
4	CH_3CN	–20	91	**53**	1:22
5	Toluene	–20	70	**62**	–
6	CH_3NO_2	–20	60	**62**	–
7	THF	–20	34	**62**	–
8	DMF	–20	17	**62**	–
9	CH_2Cl_2	–20	75	**62**	–

[a] General procedure: 100 mg (0.14 mmol) of **60** was glycosylated with the hydroxy compound **49** according to General procedure 5 (see Experimental)

CONCLUSIONS

The availability of 2-halogenoethyl 1-thioglyosides, originally described by Černý et al., can be extended, covering especially the necessities for glycoside syntheses. This new type of leaving group in glycoside syntheses shows excellent reactivity and good tendencies to selectivity.

EXPERIMENTAL

All reactions were monitored by TLC on silica gel (Merck, GF_{254}) using mixtures of cylohexane and ethyl acetate (CH/EA). All solvents were distilled. Detection was carried out by UV spectra, reaction with 0.2% ethanolic naphthalene-1,3-diol solution/1 M H_2SO_4 (1:1) and heating. Separations were carried out using preparative column chromatography on silica gel (70–230 mesh) at normal pressure or on silica gel 60 (230–400 mesh) at 0.2–0.4 MPa using the solvent mixtures mentioned above. Melting points were measured on an electrothermal melting point apparatus and were not corrected. Optical rotations were measured on a Perkin–Elmer polarimeter 241 using 1 dm cells, $[\alpha]_D^{20}$ values are given in 10^{-1} deg cm^2 g^{-1}. ^{1}H NMR spectra were recorded on a Bruker WM 300 (^{1}H: 300.13 MHz, ^{13}C: 75.48 MHz) spectrometer using TMS as internal standard. All spectra were analyzed as first-order spectra. Coupling constants (*J*) are given in Hz. Acetylation of remaining free OH groups led to compounds having ^{1}H NMR spectra which could be easily analyzed because of the downfield shift of the corresponding hydrogen atoms. Therefore, compounds with free hydroxy groups are characterized as acetates (see General procedure 1). All evaporations were carried out at 40 °C in vacuo.

General Procedure 1: Esterification (*O*-Acetylation, *O*-Pivaloylation, *O*-Benzoylation)

The carbohydrate compound (1 mmol per equivalent OH) was dissolved in anhydrous pyridine (3 ml). Ac_2O (0.1 ml, 1.1 mmol) or PivCl (6 equiv. per mmol OH) or benzoyl chloride (6 equiv. per mmol OH) and a catalytic amount of DMAP was added. After the reaction was complete, the mixture was concentrated under reduced pressure, codistilled with toluene (when using benzoyl chloride was used, washing of the organic layer with 10% HCl, a saturated sodium hydrogencarbonate solution and water were preferred) and purified by column chromatography.

General Procedure 2: De-*O*-acetylation

The carbohydrate compound was dissolved in methanol. Sodium methanolate was added until pH 10–11 was reached. After the reaction was complete (TLC monitoring), the mixture was neutralized with acid ion exchange resin (Dowex 50 WX8, H^+-form). The resin was filtered off, washed with methanol and the solvent was removed in vacuo.

General Procedure 3: *O*-Benzylation

The carbohydrate compound was dissolved in anhydrous *N*,*N*-dimethylformamide, cooled in an ice bath and sodium hydride (60 or 80% dispersion in mineral oil, 2 equiv. per OH group) was added. After 30 min, benzyl bromide (1.5 equiv. per OH group) was slowly dropped to the suspension and stirred at room temperature. After the reaction was complete excess of sodium hydride was destroyed with methanol, and the solution was reduced in high vacuo. The residue was extracted with ethyl acetate/water, the organic layer dried with anhydrous $MgSO_4$, filtered and reduced. Column chromatography followed.

General Procedure 4: *S*-Alkylation of Thioglycosides

The thioglycoside (1 mmol) was dissolved in acetone (1–2 ml) and the alkylation reagent (2 equiv., with 1,2-dibromoethane and 1-bromo-2-chloroethane 4 equiv.) was added. A solution of 1.2 mmol K_2CO_3 in 1–2 ml of water was added. With acetyl derivatives, the reaction was quenched after 1 h, otherwise deacetylation took place. Therefore, 10–20 ml of water was added and the solution was extracted (3×) with 40 ml of ethyl acetate. The organic layer was dried with anhydrous $MgSO_4$, filtered and concentrated. Column chromatography followed.

General Procedure 5: Glycosidation with Silver Salts

Under argon atmosphere the glycosyl compound (1.0 equiv.) and the hydroxy compound (1.2 equiv.) were dissolved in an anhydrous. solvent (5 ml per 100 mg) and stirred with powdered molecular sieve 4A for 4 h. After that the silver salt (1.5 equiv.) was added and the reaction mixture was stirred in the dark. After stirring overnight, the reaction mixture was filtered over Celite, washed with saturated aqueous sodium hydrogencarbonate, dried, concentrated and purified by column chromatography.

General Procedure 6: Glycosidation with Lewis Acids

Under argon atmosphere the glycosyl compound (1.0 equiv.) and the hydroxy compound (1.2 equiv.) were dissolved in the anhydrous solvent (5 ml per 100 mg) and stirred with

powdered molecular sieve 4A for 4 h. After that the Lewis acid (1.5 equiv.) was added. After stirring overnight, triethylamine (1.0 equiv.) was added and the mixture was stirred for another hour. The molecular sieves were filtered off and the resulting solution was concentrated and purified by column chromatography.

General Procedure 7: Halogenation with Phosphorus(III) Halides

The alcohol was dissolved in anhydrous. chloroform (4 ml per mmol) and stirred for 1 h with powdered molecular sieve 4A. After cooling to 0 °C phosphorus halide (0.4 equiv.) was dropped slowly to the solution. After 60-min cooling it was stirred at room temperature for 5 h. The reaction was quenched with methanol and solid sodium hydrogencarbonate was added. After filtration, the solution was concentrated, the residue was extracted with dichloromethane, washed with water and dried. The crude product was purified by column chromatography.

General Procedure 8: Detritylation of Trityl 1-Thioglycosides

The trityl 1-thioglycoside was dissolved in anhydrous dichloromethane (5 ml per mmol) and the same amount of trifluoroacetic acid was added. Triethylsilane (1.2 equiv.) was directly given to the solution, which led to decolorization. After 10 min the reaction was usually complete. The mixture was concentrated under reduced pressure. The residue was diluted with dichloromethane and washed with water, saturated sodium hydrogencarbonate solution and water, dried with anhydrous $MgSO_4$, filtered and the solvent was removed. The crude product was purified by column chromatography.

2-Bromoethyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**4**β)

a) Compound **1** (6.20 g, 17 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 5/1). Yield 6.97 g (87%), white crystals, m.p. 104 °C, $[\alpha]_D^{20}$ –32.1 (*c* 1.0 in MeOH); reported[1] m.p. 106–108 °C, $[\alpha]_D^{20}$ –29.7 (*c* 1.07 in $CHCl_3$). For $C_{16}H_{23}BrO_9S$ (471.4) calculated: 40.77% C, 4.92% H; found: 40.71% C, 4.85% H.

b) Tetrabromoethane (283 mg, 0.85 mmol) was added under argon atmosphere to a solution of compound **10** (300 mg, 0.61 mmol) in anhydrous dichloromethane. After 10 min the reaction mixture was cooled to 0 °C and 450 mg (2.8 mmol) triphenylphosphine was added. After stirring at room temperature overnight, the mixture was passed through a small silica gel layer. The filtrate was concentrated followed by a column chromatography (CH/EA = 5/1). Yield 221 mg (77%).

2-Bromoethyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (**5**β)

Compound **2** (4.50 g, 12.36 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 5/1). Yield 5.59 g (96%), white crystals, $[\alpha]_D^{20}$ –5.0 (*c* 0.9 in $CDCl_3$); reported[2] $[\alpha]_D^{20}$ –5.7 (*c* 1.0 in $CHCl_3$).

2-Bromoethyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (**6**α)

Compound **3** (2.00 g, 3.27 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 6/1). Yield 2.09 g (89%), white crystals, m.p. 79–81 °C, $[\alpha]_D^{20}$ –17.0 (*c* 1.0 in $CHCl_3$).

2-Chloroethyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**7**β)

Compound **1** (9.84 g, 27 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 5/1). Yield 10.37 g (90%), white crystals, m.p. 98 °C, $[\alpha]_D^{20}$ –25.4 (*c* 1.0 in MeOH); reported[6] m.p. 97–98 °C, $[\alpha]_D^{20}$ –38 (*c* 0.7 in $CHCl_3$). For $C_{16}H_{23}ClO_9S$ (426.9) calculated: 45.02% C, 5.43% H; found: 45.27% C, 5.42% H.

2-Chloroethyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (**8**β)

Compound **2** (0.75 g, 2.06 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 5/1). Yield 880 mg (92%), white crystals, m.p. 75–77 °C, $[\alpha]_D^{20}$ –8.6 (*c* 1.0 in $CDCl_3$); reported[6] m.p. 76–78 °C, $[\alpha]_D^{20}$ –10 (*c* 1.2 in $CHCl_3$).

2-Hydroxyethyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**9**)

Compound **1** (1.00 g, 2.74 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 2/1). Yield 884 mg (79%), colorless crystals, m.p. 70 °C, $[\alpha]_D^{20}$ –28.0 (*c* 1.0 in MeOH); reported[6] m.p. 70–73 °C, $[\alpha]_D^{20}$ –14 (*c* 0.5 in $CHCl_3$). For $C_{16}H_{24}O_{10}S$ (408.5) calculated: 47.04% C, 5.93% H; found: 47.12% C, 5.98% H.

Acetate ^{1}H NMR (300 MHz, $CDCl_3$): 5.22 dd, 1 H, *J*(2,3) = 9.4, *J*(3,4) = 9.4 (H-3); 5.07 dd, *J*(2,3) = 9.4, *J*(1,2) = 10.0 (H-2); 5.02 dd, *J*(3,4) = 9.4, *J*(4,5) = 9.8 (H-4); 4.54 d, *J*(1,2) = 10.0 (H-1); 4.25 m, 2 H (CH_2OCOCH_3); 4.22 dd, *J*(5,6) = 5.0, *J*(6,6′) = 12.2 (H-6); 4.14 dd, 1 H, *J*(5,6′) = 2.6, *J*(6,6′) = 12.2 (H-6′); 3.72 ddd, 1 H, *J*(4,5) = 9.8, *J*(5,6) = 5.0, *J*(5,6′) = 2.6 (H-5); 2.89 m, 2 H (SCH_2); 2.08, 2.06, 2.05, 2.02, 2.00 5 × s, 5 × 3 H (5 × OAc). ^{13}C NMR (75 MHz, $CDCl_3$): 170.63, 170.60, 170.20, 169.54, 169.36 (OAc), 83.61 (C-1), 75.98, 73.71, 69.74, 68.20 (C-2, C-3, C-4, C-5), 63.57, 62.02 (CH_2OAc or C-6), 28.69 (SCH_2), 20.82, 20.76, 20.72, 20.65, 20.55 ($OCOCH_3$).

2-(Tetrahydropyran-2-yloxy)ethyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**10**)

From the alcohol **9** [5]: Compound **9** (900 mg, 2.20 mmol) was dissolved in anhydrous dichloromethane (15 ml), 3,4-dihydro-2*H*-pyrane (0.3 ml, 3.30 mmol) and pyridinium tosylate (PPTS) (55 mg, 0.22 mmol) were added and the solution was stirred overnight. For work-up 20 ml diethyl ether was added, the organic layer was washed with half-concentrated sodium chloride solution and dried with anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography (CH/EA = 4/1). Yield 996 mg (92%), colorless syrup, diastereomeric mixture (1:1), $[\alpha]_D^{20}$ –28.0 (*c* 1.0 in MeOH). Selected ^{1}H NMR data: 4.65–4.58 m (H-1, THP acetal-H); 3.96–3.80 (THP-CH_2); 3.73–3.65 m (H-5), 3.64–3.59 m (CH_2OTHP); 3.55–3.45 m (THP-CH_2); 3.03–2.90 m (SCH_2′); 2.85–2.73 m (SCH_2); 2.07, 2.04, 2.01 1.99 4 × s (4 × OAc); 1.90–1.35 m (THP-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, double signals): 98.99, 98.71 (THP acetal-C), 83.78, 83.68 (C-1), 75.88, 73.90, 70.06 (C-2, C-3, C-4),

TABLE III
^{1}H NMR of 2-haloethyl 2,3,4,6-tetra-*O*-acetyl-1-thioglycosides

Compound	H-1	$J_{1,2}$	H-2	$J_{2,3}$	H-3	$J_{3,4}$	H-4	$J_{4,5}$	H-5	$J_{5,6}$	$J_{5,6'}$	H-6	$J_{6,6'}$	H-6′	SCH_2, CH_2Hal	OR
4β	4.52	10.0	5.20	9.2	5.00	9.6	5.03	10.0	3.70	3.4	4.6	4.15	10.0	4.15	3.02, 3.52	1.98, 2.00, 2.03, 2.08 (OAc)
5β	4.49	10.2	5.17	10.2	4.99	3.4	5.37	1.0	3.90	–	–	4.01–4.12	–	4.01–4.12	3.05, 3.43–3.58	1.92, 2.01, 2.01, 2.11 (OAc)
6α	5.28	1.6	5.26	3.0	5.15	9.8	5.22	9.4	4.36	2.2	6.4	4.10	12.2	4.26	2.96–3.16, 3.48	1.97, 2.04, 2.09, 2.10 (OAc)
7β	4.52	10.0	5.20	9.2	5.00	9.6	5.03	10.0	3.74–3.60	–	–	4.13–4.18	–	4.13–4.18	2.97, 3.74–3.60	1.98, 2.00, 2.03, 2.07 (OAc)
8β	4.49	10.0	5.17	9.8	5.04	3.4	5.43	1.0	3.92	–	–	4.05–4.17	–	4.05–4.17	2.96–3.17 3.56–3.68	1.94, 1.99, 2.01, 2.12 (OAc)

TABLE IV
^{13}C NMR of 2-haloethyl 2,3,4,6-tetra-*O*-acetyl-1-thioglycosides

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-arom.	CH_2	OR
5β	84.32	66.96	67.20	71.61	74.62	61.60	–	30.54, 32.66	20.43–20.63 (4×), 169.40, 169.81, 169.98, 170.24 (OAc)
6α	83.06	66.20	69.11	69.25	70.66	62.45	–	29.82, 33.79	20.53, 20.61, 20.67, 20.79, 169.80, 169.56, 169.72, 170.36, (OAc)
8β	85.42	67.96	68.22	72.61	74.95	62.30	–	31.12, 33.47	20.43, 20.47, 20.54, 20.60, 169.42, 169.99, 170.11, 170.29 (OAc)

68.35 (C-5), 67.37, 67.24, 62.32, 62.12 (THP-C-6, C-6), 30.52, 29.93, 29.76, 26.89, 25.37 (THP-C-3, THP-C-4, SCH_2, CH_2OTHP), 20.96, 20.64, 20.54 ($OCOCH_3$), 19.45, 19.31 (THP-C-4).

From the thiol **1**: Compound **1** (2.40 g, 6.59 mmol) was alkylated according to General procedure 4 with 2-[(2-bromoethyl)oxy)]tetrahydropyran (**13**; 2.76 g, 13.2 mmol). The crude product was purified by column chromatography (CH/EA = 4/1). Yield 2.27 g (84%), colorless syrup.

2-[2-(Bromoethyl)oxy]tetrahydropyran (**13**)

2-Bromoethanol (3.0 ml, 42.3 mmol) was dissolved in anhydrous dichloromethane (30 ml), 3,4-dihydro-2*H*-pyran (5.79 ml, 63.5 mmol) and pyridinium tosylate (PPTS) (1.06 g, 4.23 mmol) were added, and the solution was stirred overnight. For work-up diethyl ether (30 ml) was added, the organic layer was washed with half concentrated sodium chloride solution and dried with anhydrous $MgSO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography (CH/EA = 3/1). Yield 8.84 g (quantitatively), colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$): 4.58–4.64 m, 1 H (OCHO); 3.95 ddd, 1 H, J = 6.4, J' = 6.6, J'' = 11.4 (CH_2'Br); 3.78–3.88 m, 1 H (THP-CH_2); 3.70 ddd, 1 H, J = 6.4, J' = 6.6, J'' = 11.4 (CH_2Br); 3.40–3.51 m, 3 H (THP-CH_2, CH_2OTHP, CH_2'OTHP); 1.41–1.87 m, 6 H (THP-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): 98.22 (THP-C-2), 67.45 (CH_2OTHP), 62.13 (THP-C-6), 30.69 (CH_2Br), 30.35 (THP-C-3), 24.78 (THP-C-5), 19.16 (THP-C-4).

2-(Tetrahydropyran-2-yloxy)ethyl 2,3,4,6-Tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (**11**)

The peracetylated THP ether **10** (500 mg, 1.01 mmol) was deacetylated according to General procedure 2. After that, the crude product was benzoylated according to General procedure 1. The crude product was purified by column chromatography (CH/EA = 4/1). Yield 714 mg (95%), colorless syrup, diastereomeric mixture (1:1). For $C_{41}H_{40}O_{11}S$ (740.9) calculated: 66.46% C, 5.45% H; found: 66.55% C, 5.59% H.

Selected ^{1}H NMR data: 8.10–7.24 m (arom. H); 4.65–4.57 m (H-1, THP acetal-H); 3.95–3.80 (THP-CH_2); 3.73–3.65 m (H-5); 3.66–3.59 m (CH_2OTHP); 3.53–3.45 m (THP-CH_2); 2.93–3.08 m (SCH_2'); 2.88–2.79 m (SCH_2); 1.91–1.39 m (THP-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, double signals): 165.94, 165.21, 164.34, 163.92 (OCOPh), 133.14, 133.09, 132.89, 132.61 (C_i), 129.97–125.69 (arom. C), 98.90, 98.67 (THP acetal-C), 78.75 (C-1), 70.82, 69.89, 68.67, 68.52 (C-2, C-3, C-4, C-5), 67.17, 66.24, 62.30, 61.98 (THP-C-6, C-6), 30.52, 30.11, 29.93, 29.46, 26.85, 25.37 (THP-C-3, THP-C-5, SCH_2, CH_2OTHP), 19.35, 19.12 (THP-C-4).

2-(Tetrahydropyran-2-yloxy)ethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**12**)

The peracetylated THP ether **10** (500 mg, 1.01 mmol) was deacetylated according to General procedure 2. After that, the crude product was benzylated according to General procedure 3. The crude product was purified by column chromatography (CH/EA = 15/1). Yield 633 mg (90%), colorless syrup, diastereomeric mixture (1:1). Selected ^{1}H NMR data: 7.75–7.18 m (arom. H); 5.17–4.80 m ($PhCH_2$); 4.70–4.55 m (H-1, THP acetal-H); 4.05–3.63 m (H-2, H-3, H-4, H-6, THP-CH_2); 3.61–3.33 m (H-5, CH_2OTHP); 3.08–2.97 m (SCH_2'); 2.93–2.78 m (SCH_2); 1.91–1.30 m (THP-CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, double signals): 138.35, 138.00, 137.87, 137.62 (C_i), 129.41–127.68 (arom. C), 98.90, 98.76 (THP acetal-C), 87.41 (C-1), 85.69, 81.14, 79.06, 78.23 (C-2, C-3, C-4, C-5), 75.76, 75.61, 75.32, 73.40 ($PhCH_2$), 68.97

(C-6), 63.90, 62.54 (THP-C-6, C-6), 31.71, 30.54, 25.37 (THP-C-3, THP-C-5, SCH_2), 19.42, 19.33 (THP-C-4).

2-Bromoethyl 2,3,4,6-Tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (**14**)

Under argon atmosphere tetrabromoethane (410 mg, 1.23 mmol) was added to a solution of compound **11** (650 mg, 0.88 mmol) in anhydrous dichloromethane. After 10 min the reaction mixture was cooled to 0 °C and triphenylphosphine (645 mg, 2.39 mmol) was added. After stirring at room temperature overnight, the mixture was passed through a small silica gel layer. The filtrate was reduced, a column chromatography followed (CH/EA = 8/1). Yield 487 mg (78%), colorless crystals, m.p. 112–115 °C, $[\alpha]_D^{20}$ +23.8 (*c* 1.0 in $CHCl_3$). For $C_{36}H_{31}BrO_9$ (719.6) calculated: 60.08% C, 4.35% H; found: 60.22% C, 4.30% H.

2-Bromoethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**15**)

Tetrabromoethane (510 mg, 1.5 mmol) was added under argon atmosphere to a solution of compound **12** (750 mg, 1.10 mmol) in anhydrous dichloromethane. After 10 min the reaction mixture was cooled to 0 °C and triphenylphosphine (830 mg, 2.8 mmol) was added. After stirring at room temperature overnight, the mixture was passed through a small silica gel layer. The filtrate was reduced, a column chromatography followed (CH/EA = 12/1). Yield 503 mg (69%), colorless crystals, m.p. 121–123 °C, $[\alpha]_D^{20}$ +47.6 (*c* 1.0 in $CHCl_3$). For $C_{36}H_{39}BrO_5S$ (663.7) calculated: 65.14% C, 5.93% H; found: 65.20% C, 5.84% H.

Triphenylmethyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**16**)

a) Preparation with pyridine. Compound **1** (30.0 g, 82.4 mmol) was dissolved in anhydrous pyridine (500 ml), trityl chloride (40.0 g, 140.1 mmol, 1.7 equiv.) and catalytic amount of 4-(dimethylamino)pyridine were added. The solution was heated for several hours under reflux (black solution). After cooling down to room temperature, water (400 ml) was added and the resulting solution was concentrated and codistilled with toluene. The residue was diluted with dichloromethane and washed with water, dried with anhydrous $MgSO_4$, filtered and purified by column chromatography (CH/EA = 3/1). Yield 32.5 g (69%), colorless crystals, m.p. 176–178 °C (EtOH), $[\alpha]_D^{20}$ –6.1 (*c* 1.0 in $CHCl_3$); reported[9] m.p. 182–183 °C, $[\alpha]_D^{20}$ –2.0 (*c* 1.0 in $CHCl_3$). For $C_{33}H_{34}O_9S$ (606.7) calculated: 65.32% C, 5.66% H; found: 65.42% C, 5.69% H.

b) Preparation with triethylamine. Compound **1** (25.0 g, 68.6 mmol) was dissolved in anhydrous dichloromethane (200 ml) and trityl chloride (23.0 g, 82.3 mmol, 1.2 equiv.) was added. Under stirring, triethylamine (14.3 ml, 102.9 mmol, 1.5 equiv.) was dropped slowly to the reaction mixture. After the reaction was complete (TLC monitoring) the mixture was neutralized with 2 M hydrochloric acid, washed several times with water, dried with anhydrous $MgSO_4$, filtered and concentrated. The product was crystallized from ethanol. Yield 31.7 g (76%).

c) Preparation with trifluoroacetic acid. Compound **1** (25.0 g, 68.6 mmol) was dissolved in anhydrous dichloromethane (150 ml) and trityl chloride (21.5 g, 82.3 mmol, 1.2 equiv.) was added. Trifluoroacetic acid (50 ml) was given in one portion to the reaction mixture, which became brown. After 20 min the reaction was usually complete. The mixture was concentrated under reduced pressure. The residue was diluted with dichloromethane and washed with water, saturated sodium hydrogencarbonate solution and again with water,

dried with anhydrous $MgSO_4$, filtered and the solvent was removed. The product was crystallized from ethanol. Yield 34.1 g (82%).

Triphenylmethyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-galactopyranoside (**20**)

Preparation with trifluoroacetic acid. Compound **2** (35.0 g, 96.15 mmol) was dissolved in anhydrous dichloromethane (150 ml) and trityl chloride (30.0 g, 115.4 mmol, 1.2 equiv.) was added. Trifluoroacetic acid (150 ml) was given in one portion to the reaction mixture, which directly got brown. After 20 min the reaction was usually complete. The mixture was concentrated under reduced pressure. The residue was diluted with dichloromethane and washed with water, saturated sodium hydrogencarbonate solution and again with water, dried with anhydrous $MgSO_4$, filtered and the solvent was removed. The crude product was purified by column chromatography (CH/EA = 3/1). Yield 53.02 g (91%), m.p. 81–82 °C, $[\alpha]_D^{20}$ –10.1 (*c* 1.0 in $CHCl_3$). For $C_{33}H_{34}O_9S$ (606.7) calculated: 65.32% C, 5.66% H; found: 65.39% C, 5.67% H.

Triphenylmethyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-mannopyranoside (**23**)

Preparation with trifluoroacetic acid. Compound **3** (8.5 g, 23.35 mmol) was dissolved in anhydrous dichloromethane (150 ml) and trityl chloride (7.29 g, 28.0 mmol, 1.2 equiv.) was added. Trifluoroacetic acid (30 ml) was given in one portion to the reaction mixture, which became brown. After 20 min the reaction was usually complete. The mixture was concentrated under reduced pressure. The residue was diluted with dichloromethane and washed with water, saturated sodium hydrogencarbonate solution and again with water, dried with anhydrous $MgSO_4$, filtered and the solvent was removed. The crude product was purified by column chromatography (CH/EA = 3/1). Yield 11.75 g (84%), $[\alpha]_D^{20}$ +19.9 (*c* 1.0 in $CHCl_3$). For $C_{33}H_{34}O_9S$ (606.7) calculated: 65.32% C, 5.66% H; found: 65.37% C, 5.71% H.

Triphenylmethyl 2,3,4,6-Tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (**17**)

Compound **16** (46.7 g, 77.1 mmol) was deacetylated according to General procedure 2. After that, the crude product was benzoylated according to General procedure 1. The crude product was purified by column chromatography (CH/EA = 6/1). Yield 63.2 g (96%), colorless solid, m.p. 67 °C, $[\alpha]_D^{20}$ +19.8 (*c* 1.0 in $CHCl_3$). For $C_{53}H_{42}O_9S$ (855.0) calculated: 74.45% C, 4.96% H; found: 74.55% C, 4.92% H.

Triphenylmethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**18**)

Compound **16** (23.9 g, 39.4 mmol) was deacetylated according to General procedure 2. After that, the crude product was benzylated according to General procedure 3. The crude product was purified by column chromatography (CH/EA = 20/1). Yield 28.3 g (90%), yellow syrup, $[\alpha]_D^{20}$ +21.0 (*c* 1.0 in $CHCl_3$). For $C_{53}H_{50}O_5S$ (799.1) calculated: 79.66% C, 6.32% H; found: 79.55% C, 6.42% H.

Triphenylmethyl 2,3,4,6-Tetra-*O*-pivaloyl-1-thio-β-D-glucopyranoside (**19**)

Compound **16** (500 mg, 0.83 mmol) was deacetylated according to General procedure 2. After that, the crude product was pivaloylated according to General procedure 1. The crude product was purified by column chromatography (CH/EA = 4/1). Yield 447 mg (70%), color-

less syrup, $[\alpha]_D^{20}$ –67.8 (*c* 1.0 in $CHCl_3$). For $C_{45}H_{58}O_9S$ (775.1) calculated: 69.73% C, 7.56% H; found: 69.91% C, 7.47% H.

Triphenylmethyl 2,3,4,6-Tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside (**21**)

Compound **20** (35.0 g, 96.15 mmol) was deacetylated according to General procedure 2. After that, the crude product was benzoylated according to General procedure 1. The crude product was purified by column chromatography (CH/EA = 3/1). Yield 53.02 g (91%), colorless solid, m.p. 81–82 °C, $[\alpha]_D^{20}$ –10.1 (*c* 1.0 in $CHCl_3$). For $C_{53}H_{42}O_9S$ (855.0) calculated: 74.45% C, 4.96% H; found: 74.50% C, 4.91% H.

Triphenylmethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (**22**)

Compound **20** (15.0 g, 24.8 mmol) was deacetylated according to General procedure 2. After that, the crude product was benzylated according to General procedure 3. The crude product was purified by column chromatography (CH/EA = 20/1). Yield 28.3 g (90%), yellow syrup, $[\alpha]_D^{20}$ –8.7 (*c* 1.0 in $CHCl_3$).

Triphenylmethyl 2,3,4,6-Tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside (**24**)

Compound **23** (6.30 g, 10.39 mmol) was deacetylated according to General procedure 2. After that, the crude product was benzoylated according to General procedure 1. The crude product was purified by column chromatography (CH/EA = 6/1). Yield 8.26 g (93%), colorless solid, m.p. 78–80 °C, $[\alpha]_D^{20}$ –6.5 (*c* 1.0 in $CHCl_3$). For $C_{53}H_{42}O_9S$ (855.0) calculated: 74.45% C, 4.96% H; found: 74.55% C, 4.92% H.

Triphenylmethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-mannopyranoside (**25**)

Compound **23** (2.30 g, 3.79 mmol) was deacetylated according to General procedure 2. After that, the crude product was benzylated according to General procedure 3. The crude product was purified by column chromatography (CH/EA = 20/1). Yield 2.30 g (76%), yellow syrup, $[\alpha]_D^{20}$ +9.2 (*c* 1.0 in $CHCl_3$).

2,3,4,6-Tetra-*O*-benzoyl-1-thio-α-D-glucopyranose (**26**α) and
2,3,4,6-Tetra-*O*-benzoyl-1-thio-β-D-glucopyranose (**26**β)

Compound **17** (15.5 g, 18.15 mmol) was detritylated according to General procedure 8. The crude product was purified by column chromatography (CH/EA = 3/1). Two substances could be identified.

Compound **26**α: yield 3.34 g (30%), colorless solid, m.p. 87–88 °C, $[\alpha]_D^{20}$ +83.5 (*c* 1.0 in $CHCl_3$). For $C_{34}H_{28}O_9S$ (612.7) calculated: 66.65% C, 4.62% H; found: 66.61% C, 4.56% H.

Compound **26**β: yield 6.56 g (59%), colorless solid, m.p. 104–106 °C, $[\alpha]_D^{20}$ +20.6 (*c* 1.0 in $CHCl_3$); reported[13] $[\alpha]_D^{23}$ +62.1 (*c* 2.0 in $CHCl_3$). For $C_{34}H_{28}O_9S$ (612.7) calculated: 66.65% C, 4.62% H; found: 66.60% C, 4.66% H.

2,3,4,6-Tetra-*O*-pivaloyl-1-thio-β-D-glucopyranose (**27**)

Compound **18** (500 mg, 0.65 mmol) was detritylated according to General procedure 8. The crude product was purified by column chromatography (CH/EA = 5/1). Yield 316 mg (92%),

colorless syrup, $[\alpha]_D^{20}$ +13.2 (*c* 1.0 in $CHCl_3$); reported[26] m.p. 115–116 °C, $[\alpha]_D^{20}$ +18.8 (*c* 1.18 in $CHCl_3$). For $C_{26}H_{44}O_9S$ (532.8) calculated: 58.61% C, 8.34% H; found: 58.74% C, 8.46% H.

2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranose (**28**)

Compound **19** (12.5 g, 15.66 mmol) was detritylated according to General procedure 8. The crude product was purified by column chromatography (CH/EA = 10/1). Yield 7.49 g (86%), colorless syrup, $[\alpha]_D^{20}$ –18.2 (*c* 1.0 in $CHCl_3$); reported[27] m.p. 83.5–84 °C, $[\alpha]_D^{20}$ –18.1 (*c* 1.0 in $CHCl_3$). For $C_{34}H_{36}O_5S$ (556.8) calculated: 73.34% C, 6.53% H; found: 73.24% C, 6.61% H.

2,3,4,6-Tetra-*O*-benzoyl-1-thio-β-D-galactopyranose (**29**)

Compound **21** (11.00 g, 12.88 mmol) was detritylated according to General procedure 8. The crude product was purified by column chromatography (CH/EA = 8/1). Yield 6.94 g (88%), colorless crystals, m.p. 89–90 °C, $[\alpha]_D^{20}$ –24.3 (*c* 1.0 in $CHCl_3$). For $C_{34}H_{28}O_9S$ (612.7) calculated: 66.65% C, 4.62% H; found: 66.62% C, 4.66% H.

2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-galactopyranose (**30**)

Compound **22** (1.25 g, 1.56 mmol) was detritylated according to General procedure 8. The crude product was purified by column chromatography (CH/EA = 15/1). Yield 763 mg (88%), colorless syrup, $[\alpha]_D^{20}$ –13.7 (*c* 1.0 in $CHCl_3$).

2,3,4,6-Tetra-*O*-benzoyl-1-thio-α-D-mannopyranose (**31**)

Compound **24** (6.50 g, 7.61 mmol) was detritylated according to General procedure 8. The crude product was purified by column chromatography (CH/EA = 4/1). Yield 4.05 g (87%), colorless syrup, $[\alpha]_D^{20}$ –30.5 (*c* 1.0 in $CHCl_3$). For $C_{34}H_{28}O_9S$ (612.7) calculated: 66.65% C, 4.62% H; found: 66.58% C, 4.73% H.

2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-mannopyranose (**32**)

Compound **25** (2.50 g, 3.13 mmol) was detritylated according to General procedure 8. The crude product was purified by column chromatography (CH/EA = 15/1). Yield 1.45 g (83%), colorless syrup, $[\alpha]_D^{20}$ +54.7 (*c* 1.0 in $CHCl_3$).

2-Chloroethyl 2,3,4,6-Tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside (**33**)

Compound **26** (650 mg, 1.06 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 8/1). Yield 680 mg (95%), colorless crystals, m.p. 134 °C, $[\alpha]_D^{20}$ +67.4 (*c* 1.0 in $CHCl_3$). For $C_{36}H_{39}ClO_5S$ (619.3) calculated: 69.82% C, 6.36% H; found: 69.86% C, 6.30% H.

2-Bromoethyl 2,3,4,6-Tetra-*O*-pivaloyl-1-thio-β-D-glucopyranoside (**34**)

Compound **27** (450 mg, 0.85 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 6/1). Yield 497 mg (92%), colorless syrup, $[\alpha]_D^{20}$ –42.9 (*c* 1.0 in $CHCl_3$). For $C_{28}H_{47}BrO_9S$ (639.7) calculated: 52.57% C, 7.42% H; found: 52.48% C, 7.50% H.

2-Chloroethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**35**)

Compound **28** (800 mg, 1.44 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 15/1). Yield 801 mg (90%), colorless solid, m.p. 96–97 °C, $[\alpha]_D^{20}$ +39.2 (*c* 1.0 in $CHCl_3$). For $C_{36}H_{39}ClO_5S$ (619.3) calculated: 69.82% C, 6.36% H; found: 69.86% C, 6.30% H.

2-Bromoethyl 2,3,4,6-Tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside (**36**)

Compound **29** (6.00 g, 9.8 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 8/1). Yield 6.48 g (92%), colorless solid, m.p. 112–114 °C, $[\alpha]_D^{20}$ –39.9 (*c* 1.0 in $CHCl_3$). For $C_{36}H_{31}BrO_9S$ (719.6) calculated: 60.08% C, 4.35% H; found: 60.15% C, 4.33% H.

2-Bromoethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (**37**)

Compound **30** (130 mg, 0.23 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 15/1). Yield 132 mg (85%), colorless solid, m.p. 61–63 °C, $[\alpha]_D^{20}$ –14.5 (*c* 1.0 in $CHCl_3$). For $C_{36}H_{39}BrO_5S$ (663.7) calculated: 65.14% C, 5.93% H; found: 65.27% C, 6.10% H.

2-Bromoethyl 2,3,4,6-Tetra-*O*-benzoyl-1-thio-α-D-mannopyranoside (**38**)

Compound **31** (2.00 g, 3.27 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 6/1). Yield 2.09 g (89%), colorless solid, m.p. 79–81 °C, $[\alpha]_D^{20}$ –17.0 (*c* 1.0 in $CHCl_3$). For $C_{36}H_{31}BrO_9S$ (719.6) calculated: 60.08% C, 4.35% H; found: 59.94% C, 4.26% H.

2-Bromoethyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-α-D-mannopyranoside (**39**)

Compound **32** (650 mg, 1.17 mmol) was alkylated according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 15/1). Yield 620 mg (80%), colorless syrup, $[\alpha]_D^{20}$ +39.8 (*c* 1.0 in $CHCl_3$).

Triphenylmethyl 4,6-*O*-Benzylidene-1-thio-β-D-glucopyranoside (**40**)

Compound **16** (10.0 g, 16.5 mmol) was deacetylated according to General procedure 2. The residue was codistilled several times with toluene. Under argon atmosphere the dry compound was dissolved in anhydrous *N*,*N*-dimethylformamide (35 ml), and distilled benzaldehyde (10 ml, 98.4 mmol) and concentrated sulfuric acid (12 drops) were added and stirred for three days. The reaction mixture was neutralized with concentrated ammonia, the residue concentrated in high vacuo and purified by column chromatography (CH/EA = 3/1). Yield 7.03 g (81%), colorless solid, m.p. 123–125 °C, $[\alpha]_D^{20}$ +10.9 (*c* 1.0 in MeOH). For $C_{32}H_{30}O_5S$ (526.7) calculated: 72.97% C, 5.75% H; found: 72.90% C, 5.69% H.

Diacetate ^{1}H NMR (300 MHz, $CDCl_3$): 7.19–7.44 m, 20 H (arom. H); 5.36 s, 1 H (benzylidene-H); 5.10 m, 2 H (H-2, H-3); 4.13 d, 1 H, *J*(1,2) = 9.0 (H-1); 3.85 dd, 1 H, *J*(5,6′) = 4.8, *J*(6,6′) = 9.0 (H-6′); 3.52 m, 1 H (H-4); 3.47 dd, 1 H, *J*(5,6′) = 9.8, *J*(6,6′) = 9.0 (H-6′); 2.75 ddd, 1 H, *J*(4,5) = 9.0, *J*(5,6) = 9.0, *J*(5,6′) = 4.8 (H-5); 2.16, 2.01 2 s, 2 × 3 H (OAc). ^{13}C NMR (75 MHz, $CDCl_3$): 170.02, 169.36 (OAc), 144.29 (CPh_3), 136.76 (C_i), 120.03–129.80

(arom. H), 101.29 (benzylidene-C), 84.17 (C-1), 78.11, 73.16, 70.67, 70.13 (C-5, C-4, C-3, C-2), 68.17 (C-6), 20.79, 20.69 ($OCOCH_3$).

Triphenylmethyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (**41**)

Compound **40** (600 mg, 1.14 mmol) was benzylated according to General procedure 3. The crude product was purified by column chromatography (CH/EA = 15/1). Yield 765 mg (95%), colorless solid, m.p. 89 °C, $[\alpha]_D^{20}$ +34.9 (*c* 1.0 in $CHCl_3$). For $C_{46}H_{42}O_5S$ (706.9) calculated: 78.16% C, 5.99% H; found: 78.29% C, 6.12% H. ^{1}H NMR (300 MHz, $CDCl_3$): 7.14–7.48 m, 30 H (arom. H); 5.42 s, 1 H (benzylidene-H); 5.08 d, 1 H, *J* = 9.8 ($PhCH_2$); 4.95 d, 1 H, *J* = 9.8 ($PhCH_2$); 4.89 d, 1 H, *J* = 10.2 ($PhCH_2$); 4.76 d, 1 H, *J* = 10.2 ($PhCH_2$); 4.16 d, 1 H, *J*(1,2) = 9.4 (H-1); 3.75 dd, 1 H, *J*(5,6′) = 4.8, *J*(6,6′) = 9.8 (H-6′); 3.66 dd, 1 H, *J*(3,4) = 7.6, *J*(4,5) = 9.0 (H-4); 3.36–3.56 m, 3 H (H-6, H-3, H-2); 2.61 ddd, 1 H, *J*(4,5) = 9.0, *J*(5,6) = 9.0, *J*(5,6′) = 4.8 (H-5). ^{13}C NMR (75 MHz, $CDCl_3$): 144.54 (CPh_3), 138.36, 138.14, 137.28 (C_i), 129.89–125.86 (arom. H), 100.86 (benzylidene-C), 85.73 (C-1), 83.20, 81.32, 81.18 (C-2, C-3, C-4), 76.21, 75.14 ($PhCH_2$), 69.62 (C-5), 68.34 (C-6).

2-Chloroethyl 4,6-*O*-Isopropylidene-1-thio-β-D-glucopyranoside (**42**)

Compound **7** (5.07 g, 11.9 mmol) was deacetylated according to General procedure 2. The residue was dissolved in anhydrous acetone (400 ml), and 2,2-dimethoxypropane (6 ml, 48.8 mmol) and catalytic amount of 4-toluenesulfonic acid were added. After stirring overnight, the reaction mixture was neutralized with concentrated ammonia and the solution was concentrated in vacuo. The resulting residue was extracted with hot dichloromethane. After reducing the solvent, the crude product was purified by column chromatography (CH/EA = 1/1). Yield 2.56 g (72%), colorless syrup, $[\alpha]_D^{20}$ –42.6 (*c* 1.0 in MeOH). For $C_{16}H_{23}ClO_7S$ (394.9) calculated: 48.67% C, 5.87% H; found: 48.52% C, 5.90% H.

Diacetate ^{1}H NMR (300 MHz, $CDCl_3$): 5.12 dd, 1 H, *J*(1,2) = 10.2, *J*(2,3) = 9.2 (H-2); 4.93 dd, 1 H, *J*(2,3) = 9.6, *J*(3,4) = 9.2 (H-3); 4.52 d, 1 H, *J*(1,2) = 10.2 (H-1); 3.93 dd, *J*(5,6) = 5.4, *J*(6,6′) = 10.9 (H-6); 3.77–3.57 m, 4 H (CH_2Cl, H-6′, H-4); 3.37 ddd, *J*(4,5) = 10.0, *J*(5,6) = 5.4, *J*(5,6′) = 10.2 (H-5); 2.96 m, 2 H (SCH_2); 2.03, 2.01 2 s, 2 × 3 H (2 × OAc); 1.44, 1.35 2 s, 2 × 3 H (2 × isoprop.-CH_3).

Vinyl 2,3-Di-*O*-benzyl-4,6-*O*-isopropylidene-1-thio-β-D-glucopyranoside (**43**)

Compound **42** (2.56 g, 8.57 mmol) was benzylated according to General procedure 3. The crude product was purified by column chromatography (CH/EA = 10/1). Yield 2.11 g (82%), colorless crystals, m.p. 61 °C, $[\alpha]_D^{20}$ +3.5 (*c* 1.0 in MeOH). For $C_{25}H_{30}O_5S$ (442.6) calculated: 67.85% C, 6.83% H; found: 67.54% C, 7.11% H. ^{1}H NMR (300 MHz, $CDCl_3$): 7.36–7.25 m, 10 H (arom. H); 6.47 dd, 1 H, *J* = 10.0 (=CH_2); 5.39 d, 1 H, *J* = 16.9 (=CH_2); 5.34 d, 1 H, *J* = 10.0 (=CH_2); 4.87, 4.74 2 d, 2 × 1 H ($PhCH_2$); 4.78 s, 2 H ($PhCH_2$); 4.63 d, 1 H, *J*(1,2) = 9.7 (H-1); 3.94 dd, 1 H, *J*(5,6) = 5.4, *J*(6,6′) = 10.9 (H-6); 3.75 dd, 1 H, *J*(5,6′) = 9.6, *J*(6,6′) = 10.9 (H-6′); 3.72 dd, 1 H, *J*(3,4) = 9.1, *J*(4,5) = 9.5 (H-4); 3.64 dd, 1 H, *J*(2,3) = 8.2, *J*(3,4) = 9.1 (H-3); 3.49 dd, 1 H, *J*(1,2) = 9.7, *J*(2,3) = 8.2 (H-2); 3.30 ddd, 1 H, *J*(4,5) = 9.5, *J*(5,6) = 5.4, *J*(5,6′) = 9.6 (H-5); 1.49, 1.41 2 s, 2 × 3 H (2 × isoprop.-CH_3).

TABLE V
^{1}H NMR data of trityl 1-thioglycosides

Compound	H-1	$J_{1,2}$	H-2	$J_{2,3}$	H-3	$J_{3,4}$	H-4	$J_{4,5}$	H-5	$J_{5,6}$	$J_{5,6'}$	H-6	$J_{6,6'}$	H-6′	OR
16	3.77	10.4	5.10	9.0	4.92	9.4	4.97	9.8	2.88	2.2	4.8	3.75	12.2	4.00	1.93, 1.95, 1.96, 2.06 (OAc), 7.17–7.43 (arom. H)
17	4.08	10.0	5.89	9.0	5.30	9.4	5.81	10.0	3.28	3.28	2.8	4.14	11.6	4.23	7.08–8.08 (arom. H)
18	3.67	10.2	5.16	8.6	5.01	9.2	5.08	9.6	2.87	2.87	3.0	3.80	–	3.80	1.08, 1.09, 1.11, 1.19 (OPiv), 7.15–7.43 (arom. H)
19	3.83	9.4	3.39–3.66	–	3.39–3.66	–	3.39–3.66	–	2.58	2.58	2.8	3.22	11.0	3.48	4.39–5.06 (8× $PhCH_2$), 7.08–7.48 (arom. H)
20	3.76	10.2	5.28	10.2	4.74	3.5	5.23	1.0	3.18	6.4	7.0	3.81	11.0	3.89	1.89, 1.93, 2.06, 2.13 (OAc), 7.19–7.45 (arom. H)
21	4.10	10.2	5.86	10.0	5.33	3.6	5.82	1.0	3.56	7.2	6.4	4.14	11.4	4.27	7.10–8.08 (arom. H)
22	4.00	9.8	3.91	8.6	3.37	2.8	3.85	0.8	3.08–3.17	5.0	2.0	2.85	8.4	3.45	4.21–5.04 (8× $PhCH_2$), 7.03–7.78 (arom. H)
23	4.82	1.4	5.20–5.31	–	5.20–5.31	–	5.20–5.31	–	3.87–3.95	–	–	4.22–4.31	–	4.22–4.31	1.96, 2.01 (2×), 2.09 (OAc), 7.19–8.10 (arom. H)
24	5.14	1.2	5.81	2.8	5.83	8.8	6.11	9.4	4.68	2.4	9.4	4.40–4.46	–	4.40–4.46	7.19–8.10 (arom. H)
25	4.83	1.6	4.36	2.8	4.42	8.2	4.50	9.0	3.91–4.03	1.8	4.4	4.19	10.6	4.29	4.51–4.90 (8× $PhCH_2$), 7.12–7.39 (arom. H)

TABLE VI
^{13}C NMR data of trityl 1-thioglycosides

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-(CPh_3)	C-arom.	OR
16	83.59	68.16	69.68	74.29	75.27	61.76	144.29	126.96–129.92	20.44, 20.52, 20.57, 20.71, 169.16, 170.16, 170.31, 170.47 (OAc)
18	83.96	75.82	72.38	69.57	68.28	61.51	144.36	126.84, 127.53, 129.83	26.86, 27.00, 27.08, 27.16, 38.53, 38.79, 176.14, 176.37, 177.18, 178.03 (OPiv)
19	85.31	76.12	79.44	81.07	83.14	68.22	144.80	126.74–130.14	72.59, 73.88, 74.56, 76.12, 137.83, 137.95, 138.36, 138.65 ($PhCH_2$, C_i-Bn)
20	84.14	66.86	66.98	72.14	73.87	60.88	144.26	126.91, 127.67, 129.85	20.48, 20.50, 20.62, 20.81, 169.34, 169.99, 170.11, 170.21 (OAc)
22	86.03	76.16	77.85	78.69	84.90	67.89	145.28	126.87–130.52	67.89, 73.00, 73.58, 73.81, 74.88, 138.30, 138.74, 138.96, 139.12 ($PhCH_2$, C_i-Bn)
24	82.99	66.89	70.68	70.98	73.02	62.93	144.12	127.06–129.87	132.94, 133.19, 133.33, 164.77, 165.28, 165.41, 166.07 (PhOCO, C_i-Bz)

TABLE VII
^{1}H NMR data of the *gluco*-, *galacto*- and *manno*-configurated 1-SH-compounds

Compound	H-1	$J_{1,2}$	H-2	$J_{2,3}$	H-3	$J_{3,4}$	H-4	$J_{4,5}$	H-5	$J_{5,6}$	$J_{5,6'}$	H-6	$J_{6,6'}$	H-6′	SH	$J_{1,SH}$	OR
26α	6.20	5.8	4.52	10.4	5.73	10.0	6.09	10.0	4.87	4.8	3.0	4.50	12.4	4.65	2.09	10.4	7.27–7.94 (arom. H)
26β	4.91	9.8	5.72	10.0	5.90	9.2	5.51	10.0	4.18	5.2	3.2	4.49	12.4	4.64	2.48	10.0	7.24–8.06 (arom. H)
27β	4.53	9.8	5.00	9.0	5.30	9.4	5.17	10.0	3.73	4.8	2.0	4.10	12.4	4.19	2.23	10.0	1.12, 1.15, 1.18, 1.23 (OPiv)
28β	4.50	9.4	3.33–3.41 or 3.59–3.69	–	3.33–3.41 or 3.59–3.69	–	3.33–3.41 or 3.59–3.69	8.2	3.47	4.2	2.2	3.67	11.6	3.73	2.30	8.0	4.53–4.94 ($PhCH_2$), 7.22–7.37 (arom. H)
29β	4.76	10.0	5.79	9.8	5.98	3.8	5.51	1.0	4.10	6.2	7.8	4.43	12.2	4.61	2.35	10.0	7.18–8.05 (arom. H)
30β	4.44	9.2	3.75	9.4	3.52	2.8	3.95	0	3.55–3.62	–	–	3.55–3.62	–	3.55–3.62	2.28	8.2	4.40–4.94 ($PhCH_2$) 7.20–7.39 (arom. H)
31α	5.86	1.6	5.80	3.0	5.91	9.4	6.18	9.4	4.80	3.6	2.4	4.50	11.6	4.73	2.45	6.2	7.16–8.13 (arom. H)
32α	5.66	1.6	3.81	2.8	3.87	8.2	4.01	9.0	4.11	1.8	4.6	3.68	10.2	3.79	2.01	6.6	4.51–4.86 ($PhCH_2$), 7.15–7.39 (arom. H)

TABLE VIII
^{13}C NMR data of the *gluco*-, *galacto*- and *manno*-configurated 1-SH-compounds

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-arom.	OR
26α	76.15	68.48	68.77	69.89	70.80	62.24	125.99–129.50	132.64, 132.79, 133.00, 133.14, 164.72, 164.81, 165.22, 165.64 ($PhCH_2$, C_i-Bz)
26β	79.13	76.72	74.23	73.83	69.44	63.14	128.26–129.77	133.07, 133.14, 133.21, 133.40, 165.08, 165.39, 165.69, 166.08 ($PhCH_2$, C_i-Bz)
27β	79.15	67.83	73.76	76.79	77.64	61.97	–	27.09, 27.20, 27.27, 176.44, 176.91, 177.21, 178.16 (OPiv)
28β	86.58	77.77	79.47	79.77	84.86	68.75	127.70–128.38	73.51, 74.99, 75.48, 75.62, 137.79, 137.96, 138.09, 138.40 ($PhCH_2$, C_i-Bn)
29β	79.83	76.92	74.02	72.88	69.47	62.24	128.50–129.56	133.03, 133.24, 133.44, 133.56, 165.08, 165.43, 165.69, 166.12 ($PhCH_2$, C_i-Bz)
30β	83.88	75.86	77.72	80.34	81.72	68.55	127.52–128.38	72.66, 73.54, 73.70, 74.61, 137.76, 138.10, 138.23, 138.58 ($PhCH_2$, C_i-Bn)
31α	66.82	69.94	69.96	72.18	77.43	62.50	128.32–129.80	133.03, 133.19, 133.30, 133.49, 165.24, 165.35, 165.48, 166.06 ($PhCH_2$, C_i-Bz)
32α	79.55	77.99	77.32	75.43	73.17	69.50	127.98–130.22	72.56, 72.63, 73.82, 75.63, 138.44, 138.58, 138.75, 138.85 (PhOCO, C_i-Bn)

TABLE IX
^{1}H NMR data of 2-haloethyl 1-thioglycosides

Compound	H-1	$J_{1,2}$	H-2	$J_{2,3}$	H-3	$J_{3,4}$	H-4	$J_{4,5}$	H-5	$J_{5,6}$	$J_{5,6'}$	H-6	$J_{6,6'}$	H-6′	SCH_2, CH_2Hal	OR
33	4.91	10.2	5.65	9.6	5.93	9.8	5.55	10.0	4.19	5.8	3.0	4.47	12.8	4.66	2.99–3.31, 3.51–3.60	7.26–8.07 (arom. H)
14	4.76	10.2	5.65	9.4	5.90	9.8	5.50	10.0	4.24	5.6	3.4	4.47	12.2	4.66	2.97–3.12, 3.16–3.34	7.19–8.10 (arom. H)
34	4.55	10.0	5.06	9.4	5.34	9.4	5.12	9.8	3.74	5.4	1.8	4.05	12.4	4.23	2.90–3.24, 3.47–3.56	1.12, 1.16, 1.17, 1.23 (OPiv)
15	4.46	9.8	3.42	8.4	3.53–3.73	–	3.53–3.73	–	3.46	5.0	2.0	3.53–3.73	–	3.53–3.73	3.11, 3.53–3.73	4.52–4.90 ($PhCH_2$), 7.15–7.36 (arom. H)
35	4.46	10.0	3.40	8.2	3.52–3.79	–	3.52–3.79	–	3.49	5.2	2.0	3.52–3.79	–	3.52–3.79	3.02, 3.52–3.79	4.55–4.94 ($PhCH_2$) 7.10–7.39 (arom. H)
36	4.75	10.0	5.80	10.0	5.39	3.4	3.77	1.0	3.77	7.8	5.6	4.21	12.0	4.29	3.09, 3.42–3.65	7.10–8.08 (arom. H)
37	4.45	9.8	3.81	8.8	3.45–3.66	–	3.93	–	3.45–3.66	–	–	3.45–3.66	–	3.45–3.66	3.08, 3.45–3.66	4.37–4.94 ($PhCH_2$), 7.16–7.38 (arom. H)
38	5.62	0.8	5.78–5.86	–	5.78–5.86	9.0	6.14	10.4	4.85	5.0	2.6	4.57	12.2	4.72	3.09–3.29, 3.52–3.69	7.23–8.14 (arom. H)
39	5.36	1.8	3.81	3.2	3.77	9.0	3.97	10.0	4.10	2.0	5.2	3.70	10.8	3.77	2.99, 3.49	4.46–4.86 ($PhCH_2$), 7.14–7.39 (arom. H)

TABLE X
^{13}C NMR data of 2-haloethyl 1-thioglycosides

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-arom.	CH_2	OR
33	84.66	77.80	74.24	70.84	69.70	63.43	128.64–130.19	31.05, 33.04	133.56, 133.62, 133.77, 133.85, 165.50, 166.07, 166.27, 166.39 (PhCH$_2$, C$_i$-Bz)
14	84.62	69.71	71.85	74.00	77.82	65.49	127.94–130.89	33.25, 43.71	133.46, 133.59, 133.77, 133.95, 165.60, 166.13, 166.27, 166.41 (PhCH$_2$, C$_i$-Bz)
34	83.53	76.70	73.02	69.42	67.63	61.88	–	30.63, 31.90	26.89, 27.05, 27.13, 38.67, 38.85, 176.28, 176.47, 177.01, 177.90 (OPiv)
15	86.48	85.63	81.49	79.03	77.78	68.97	127.68–128.39	31.31, 33.37	73.47, 75.32, 75.49, 75.70, 137.69, 137.95, 138.05, 138.37 (PhCH$_2$, C$_i$-Bn)
35	86.44	77.75	78.98	81.49	85.50	68.95	127.59–128.30	33.30, 43.64	73.39, 74.91, 75.39, 75.79, 137.71, 137.95, 138.12, 138.35 (PhCH$_2$, C$_i$-Bn)
36	84.31	65.91	67.22	72.23	74.00	62.40	128.14–129.83	30.44, 32.67	133.01, 133.19, 133.28, 133.43, 169.47, 169.89, 170.05, 170.29 (PhCH$_2$, C$_i$-Bz)
37	85.73	75.75	78.11	83.74	84.11	68.88	126.87–129.50	31.27, 33.00	72.75, 73.57, 74.48, 75.49, 137.79, 138.06, 138.17, 138.60 (PhCH$_2$, C$_i$-Bn)
38	83.15	66.98	69.78	70.25	71.83	62.91	128.28–129.79	29.91, 33.85	133.06, 133.23, 133.47, 133.53, 165.29, 165.34, 165.41, 166.04 (PhCH$_2$, C$_i$-Bz)
39	83.27	80.04	76.23	74.98	72.35	69.16	125.26–129.00	30.70, 33.94	72.20, 72.25, 73.35, 75.05, 137.89, 138.06, 138.18, 138.31 (PhCH$_2$, C$_i$-Bn)

2-Hydroxyethyl 2,3-Di-*O*-benzyl-4,6-*O*-isopropylidene-1-thio-β-D-glucopyranoside (**44**)

Compound **43** (940 mg, 2.21 mmol) was dissolved in anhydrous tetrahydrofurane (6 ml) and under argon atmosphere and ice cooling 2 M borane–dimethyl sulfide complex in THF (1.2 ml) was added during 30 min. After stirring at room temperature for 3 h, 3 M sodium hydroxide solution (0.3 ml) was added and the reaction mixture was cooled to 0 °C. Hydrogen peroxide solution (30%, 0.28 ml) was dropped to the mixture (temperature should not reach more than 5 °C), after that the solution was heated up to 40–50 °C. After 2-h stirring at this temperature, the mixture was poured into ice water (15 ml) and extracted several times with diethyl ether. The organic layer was dried with anhydrous $MgSO_4$ and the crude product was purified by column chromatography (CH/EA = 2/1). Yield 722 mg (72%), colorless syrup, $[\alpha]_D^{20}$ –7.3 (*c* 1.0 in MeOH). For $C_{27}H_{34}O_7S$ (502.6) calculated: 64.52% C, 6.82% H; found: 64.40% C, 6.88% H.

Acetate ^{1}H NMR (300 MHz, $CDCl_3$): 7.35–7.25 m, 10 H (arom. H); 4.84, 4.73 d, 2 × 1 H, *J* = 11.4 ($PhCH_2$); 4.79 s, 2 H ($PhCH_2$); 4.51 d, 1 H, *J*(1,2) = 9.8 (H-1); 4.23 td, 2 H, *J* = 1.8, *J*(1,2) = 6.8 (CH_2OAc); 3.91 dd, 1 H, *J*(5,6) = 5.4, *J*(6,6′) = 10.9 (H-6); 3.74 dd, 1 H, *J*(5,6′) = 9.6, *J*(6,6′) = 10.9 (H-6′); 3.71 dd, 1 H, *J*(3,4) = 9.1, *J*(4,5) = 9.5 (H-4); 3.61 dd, 1 H, *J*(2,3) = 8.2, *J*(3,4) = 9.8 (H-3); 3.37 dd, 1 H, *J*(2,1) = 9.8, *J*(2,3) = 8.2 (H-2); 3.26 ddd, 1 H, *J*(4,5) = 9.5, *J*(5,6) = 5.4, *J*(5,6′) = 9.6 (H-5); 2.90 m, 2 H (SCH_2); 2.02 s, 3 H (OAc); 1.48, 1.40 2 s, 2 × 3 H (2 × isoprop.-CH_3).

2-Bromoethyl 2,3-Di-*O*-benzyl-4,6-*O*-isopropylidene-1-thio-β-D-glucopyranoside (**45**)

Compound **44** (3.19 g, 6.94 mmol) was dissolved in anhydrous toluene (100 ml), and chlorodiphenylphosphane (1.98 g, 8.97 mmol) and bromine (1.05 g, 15.42 mmol) were added. The reaction mixture was cooled in an ice-bath, and bromine (ca. 1.1 g) was dropped slowly to the solution until the mixture stayed light brown. After the reaction was complete (10 min), it was washed with saturated sodium hydrogencarbonate solution, saturated sodium chloride solution and water. The organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (CH/EA = 3/1). Yield 3.10 g (85%), colorless syrup, $[\alpha]_D^{20}$ –3.8 (*c* 1.0 in $CHCl_3$). For $C_{25}H_{31}BrO_5S$ (523.5) calculated: 57.36% C, 5.97% H; found: 57.03% C, 5.81% H. ^{1}H NMR (300 MHz, $CDCl_3$): 7.35–7.25 m, 10 H (arom. H); 4.87, 4.73 d, 2 × 1 H, *J* = 11.2 ($PhCH_2$); 4.78 s, 2 H ($PhCH_2$); 4.49 d, 1 H, *J*(1,2) = 10.0 (H-1); 3.92 dd, 1 H, *J*(5,6) = 5.4, *J*(6,6′) = 10.9 (H-6); 3.74 dd, 1 H, *J*(5,6′) = 9.6, *J*(6,6′) = 10.9 (H-6′); 3.71 dd, 1 H, *J*(3,4) = 9.4, *J*(4,5) = 9.5 (H-4); 3.62 dd, 1 H, *J*(2,3) = 8.2, *J*(3,4) = 9.4 (H-3); 3.49 m, 2 H (CH_2Br); 3.37 dd, 1 H, *J*(2,1) = 10.0, *J*(2,3) = 8.2 (H-2); 3.26 ddd, 1 H, *J*(4,5) = 9.5, *J*(5,6) = 5.4, *J*(5,6′) = 9.6 (H-5); 3.20–2.95 m, 2 H (SCH_2); 1.48, 1.41 2 s, 2 × 3 H (2 × isoprop.-CH_3).

Cyclohexyl 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranoside[16] (**46**)

Compound **4** (100 mg, 0.23 mmol) and cyclohexanol (1.2 equiv.) were glycosylated according to General procedure 5. Temperature 0 °C, solvent nitromethane. Yield 39.6 mg (40%) of **46**, the substitution product **47** was not further characterized.

Compound **46**, colorless syrup. ^{1}H NMR (300 MHz, $CDCl_3$): 5.47 dd, 1 H, *J*(2,3) = 10.4, *J*(3,4) = 9.6 (H-3); 5.20 d, 1 H, *J*(1,2) = 3.8 (H-1); 5.01 dd, 1 H, *J*(3,4) = 9.6, *J*(4,5) = 9.8 (H-4); 4.78 dd, 1 H, *J*(1,2) = 3.8, *J*(2,3) = 10.4 (H-2); 4.22 dd, 1 H, *J*(5,6) = 4.8, *J*(6,6′) = 12.4 (H-6);

4.14–4.04 m, 2 H (H-5, H-6′); 3.59–3.54 m, 1 H (cyclohexyl-H); 2.06, 2.03, 2.01, 1.99 4 s, 4 × 3 H (4 × OAc); 1.86–1.22 m, 10 H (cyclohexyl-H). ^{13}C NMR (75 MHz, $CDCl_3$): 94.1 (C-1α).

Methyl 2,3,4,6-Tetra-*O*-benzoyl-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-acetyl-α-D-glucopyranoside[21] (**51**αβ)

a) Compound **14** (100 mg, 0.139 mmol) and the hydroxy compound **48** (1.2 equiv.) were glycosylated according to General procedure 5. Solvent nitromethane, column chromatography (CH/EA = 3/1). Yield 92 mg (78%), colorless crystals. For $C_{47}H_{46}O_{18}$ (898.9) calculated: 62.79% C, 5.17% H; found: 62.83% C, 5.20% H.

b) Compound **14** (100 mg, 0.139 mmol) and the hydroxy compound **48** (1.2 equiv.) were glycosylated according to General procedure 6. Solvent dichloromethane, column chromatography (CH/EA = 3/1). Yield 86 mg (83%), colorless crystals.

Methyl 2,3,4,6-Tetra-*O*-benzoyl-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[22] (**52**αβ)

Compound **14** (100 mg, 0.139 mmol) and the hydroxy compound **49** (1.2 equiv.) were glycosylated according to General procedure 5. Solvent nitromethane, column chromatography (CH/EA = 6/1). Yield 116 mg (80%), colorless crystals.

Methyl 2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[24] (**53**αβ)

a) Compound **15** (100 mg, 0.151 mmol) and the hydroxy compound **49** (1.2 equiv.) were glycosylated according to General procedure 5. Solvent dioxane, column chromatography (CH/EA = 6/1). Yield 115 mg (81%), colorless syrup.

b) Compound **15** (100 mg, 0.151 mmol) and the hydroxy compound **49** (1.2 equiv.) were glycosylated according to General procedure 5. Solvent acetonitrile, column chromatography (CH/EA = 6/1). Yield 130 mg (92%), colorless syrup.

c) Compound **15** (100 mg, 0.151 mmol) and the hydroxy compound **49** (1.2 equiv.) were glycosylated according to General procedure 6. Solvent dichloromethane, column chromatography (CH/EA = 6/1). Yield 119 mg (84%), colorless syrup.

Methyl 2,3,4,6-Tetra-*O*-benzoyl-α/β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside[23] (**54**αβ)

Compound **14** (100 mg, 0.139 mmol) and the hydroxy compound **50** (1.2 equiv.) were glycosylated according to General procedure 5. Solvent nitromethane, column chromatography (CH/EA = 6/1). Yield 40 mg (71%), colorless crystals.

Methyl 2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α/β-D-glucopyranoside[25] (**55**αβ)

Compound **15** (100 mg, 0.151 mmol) and the hydroxy compound **50** (1.2 equiv.) were glycosylated according to General procedure 5. Solvent dioxane, column chromatography (CH/EA = 8/1). Yield 110 mg (74%), colorless syrup.

2-Hydroxy-2-methylpropyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**56**)

Compound **1** (5.19 g, 14.2 mmol) was alkylated with 1-chloro-2-methylpropan-2-ol according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 2/1). Yield 4.40 g (71%), colorless solid, m.p. 89 °C, $[\alpha]_D^{20}$ –67 (*c* 1.0 in $CHCl_3$). For $C_{18}H_{28}O_{10}S$ (436.5) calculated: 49.52% C, 6.49% H; found: 49.42% C, 6.44% H. ^{1}H NMR (300 MHz, $CDCl_3$): 5.08 dd, 1 H, *J*(2,3) = 9.2, *J*(3,4) = 9.40 (H-3); 4.84–4.96 m, 2 H (H-2, H-4); 4.43 d, 1 H, *J*(1,2) = 10.4 (H-1); 3.95–4.07 m, 2 H (H-6, H-6′); 3.63 ddd, 1 H, *J*(4,5) = 10.2, *J*(5,6) = 2.8, *J*(5,6′) = 5.4 (H-5); 2.75 d, 1 H, *J* = 14.4 (SCH_2'); 2.59 d, 1 H, *J* = 14.4 (SCH_2); 1.86, 1.88, 1.92, 1.95 4 s, 4 × 3 H (OAc); 1.14 s, 3 H (CH_3'); 1.13 s, 3 H (CH_3).

2-Hydroxy-2-methylpropyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**57**)

Compound **28** (500 mg, 0.89 mmol) was alkylated with 1-chloro-2-methylpropan-2-ol according to General procedure 4. The crude product was purified by column chromatography (CH/EA = 4/1). Yield 401 mg (71%), colorless syrup, $[\alpha]_D^{20}$ +30.6 (*c* 1.0 in $CHCl_3$). For $C_{38}H_{44}O_6S$ (628.9) calculated: 72.57% C, 7.07% H; found: 72.55% C, 7.10% H. ^{1}H NMR (300 MHz, $CDCl_3$): 7.12–7.38 m, 20 H (arom. H); 4.92 d, 1 H, *J* = 10.6 ($PhCH_2$); 4.90 d, 1 H, *J* = 11.2 ($PhCH_2$); 4.83 d, 1 H, *J* = 11.2 ($PhCH_2$); 4.79 d, 1 H, *J* = 11.0 ($PhCH_2$); 4.77 d, 1 H, *J* = 10.6 ($PhCH_2$); 4.59 d, 1 H, *J* = 12.4 ($PhCH_2$); 4.54 d, 1 H, *J* = 11.0 ($PhCH_2$); 4.50 d, 1 H, *J* = 12.4 ($PhCH_2$); 4.46 d, 1 H, *J*(1,2) = 10.0 (H-1); 3.57–3.72 m, 4 H (H-6, H-6′, H-2/H-3/H-4);

TABLE XI
Selected NMR data ($CDCl_3$) of disaccharides **51**–**55**

Product	^{1}H NMR, ppm	^{13}C NMR, ppm
51	OCH_3: 3.04	C1: 96.11
		C1′: 101.60
52	OCH_3: 3.32	C1: 96.20
		C1′: 102.18
53	OCH_3 (α): 3.35	C1: 97.9
	OCH_3 (β): 3.32	C1′ (α): 98.3
		C1: 98
		C1′ (β): 103.8
54	OCH_3: 3.30	C1: 96.36
		C1′: 103.49
55	OCH_3 (α): 3.37	C1: 97.8
	OCH_3 (β): 3.35	C1′ (α): 96.6
		C1: 98.3
		C1′ (β): 102.4

3.40–3.52 m, 2 H (H-5, H-2/H-3/H-4); 2.90 d, 1 H, *J* = 14.8 (SCH_2'); 2.76 d, 1 H, *J* = 14.8 (SCH_2); 1.28 s, 3 H (CH_3'); 1.25 s, 3 H (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 138.38, 138.13, 137.91, 137.81 (arom. C_i), 127.57–128.34 (arom. C), 87.13 (C-1), 77.62, 78.74, 81.43, 86.49 (C-2, C-3, C-4, C-5), 75.64, 75.49, 74.93, 73.48 ($PhCH_2$), 69.64 ($C(CH_3)_2OH$), 68.73 (C-6), 28.69, 28.34 (CH_3).

2-Bromo-2-methylpropyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**58**)

Compound **56** (650 mg, 1.49 mmol) was halogenated with phosphorus tribromide according to General procedure 7. The crude product was purified by column chromatography (CH/EA = 4/1). Yield 588 mg (79%), colorless solid, m.p. 78 °C, $[\alpha]_D^{20}$ +51 (*c* 1.0 in $CHCl_3$). For $C_{18}H_{27}BrO_9S$ (499.4) calculated: 43.29% C, 5.45% H; found: 43.37% C, 5.49% H. ^{1}H NMR (300 MHz, $CDCl_3$): 5.17 dd, 1 H, *J*(2,3) = 9.8, *J*(3,4) = 10.0 (H-3); 5.02 dd, 1 H, *J*(3,4) = 10.0, *J*(4,5) = 10.2 (H-4); 4.95 dd, 1 H, *J*(1,2) = 10.0, *J*(2,3) = 9.8 (H-2); 4.53 d, 1 H, *J*(1,2) = 10.0 (H-1); 4.19 dd, 1 H, *J*(5,6′) = 5.2, *J*(6,6′) = 12.2 (H-6′); 4.09 dd, 1 H, *J*(5,6) = 2.6, *J*(6,6′) = 12.2 (H-6); 3.67 ddd, 1 H, *J*(4,5) = 10.2, *J*(5,6) = 2.6, *J*(5,6′) = 5.2 (H-5); 3.22 d, 1 H, *J* = 13.6 (SCH_2'); 3.14 d, 1 H, *J* = 13.6 (SCH_2); 2.03, 2.01, 1.97, 1.95 4 s, 4 × 3 H (OAc); 1.77 s, 3 H (CH_3'); 1.76 s, 3 H (CH_3).

2-Chloro-2-methylpropyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**59**)

Compound **56** (500 mg, 1.15 mmol) was halogenated with phosphorus trichloride according to General procedure 7. The crude product was purified by column chromatography (CH/EA = 4/1). Yield 483 mg (84%), colorless solid, m.p. 69–71 °C, $[\alpha]_D^{20}$ +47 (*c* 1.0 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 5.16 dd, 1 H, *J*(2,3) = 9.4, *J*(3,4) = 9.4 (H-3); 5.02 dd, 1 H, *J*(3,4) = 9.4, *J*(4,5) = 10.0 (H-4); 4.94 dd, 1 H, *J*(1,2) = 10.2, *J*(2,3) = 9.4 (H-2); 4.54 d, 1 H, *J*(1,2) = 10.2 (H-1); 4.19 dd, 1 H, *J*(5,6′) = 5.2, *J*(6,6′) = 12.6 (H-6′); 4.09 dd, 1 H, *J*(5,6) = 2.6, *J*(6,6′) = 12.6 (H-6); 3.67 ddd, 1 H, *J*(4,5) = 10.0, *J*(5,6) = 2.6, *J*(5,6′) = 5.2 (H-5); 3.08 d, 1 H, *J* = 13.8 (SCH_2'); 2.99 d, 1 H, *J* = 13.8 (SCH_2); 2.03, 2.01, 1.97, 1.95 4 s, 4 × 3 H (OAc); 1.60 s, 3 H (CH_3'); 1.58 s, 3 H (CH_3).

2-Bromo-2-methylpropyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**60**)

Compound **57** (840 mg, 1.49 mmol) was halogenated with phosphorus tribromide according to General procedure 7. The crude product was purified by column chromatography (CH/EA = 12/1). Yield 647 mg (70%), colorless syrup. For $C_{38}H_{43}BrO_5S$ (691.8) calculated: 65.97% C, 6.28% H; found: 65.90% C, 6.33% H. ^{1}H NMR (300 MHz, $CDCl_3$): 7.10–7.35 m, 20 H (arom. H); 4.87 d, 1 H, *J* = 11.2 ($PhCH_2$); 4.85 d, 1 H, *J* = 10.4 ($PhCH_2$); 4.80 d, 1 H, *J* = 11.2 ($PhCH_2$); 4.77 d, 1 H, *J* = 11.0 ($PhCH_2$); 4.71 d, 1 H, *J* = 10.4 ($PhCH_2$); 4.55 d, 1 H, *J* = 12.2 ($PhCH_2$); 4.53 d, 1 H, *J* = 11.0 ($PhCH_2$); 4.49 d, 1 H, *J* = 12.2 ($PhCH_2$); 4.45 d, 1 H, *J*(1,2) = 10.0 (H-1); 3.54–3.73 m, 4 H (H-6, H-6′, H-2/H-3/H-4); 3.35–3.45 m, 2 H (H-5, H-2/H-3/H-4); 3.31 d, 1 H, *J* = 13.6 (SCH_2'); 3.23 d, 1 H, *J* = 13.6 (SCH_2); 1.81 s, 6 H (CH_3, CH_3'). ^{13}C NMR (75 MHz, $CDCl_3$): 138.43, 138.06, 137.99, 137.82 (arom. C_i), 127.58–128.32 (arom. C), 86.54 (C-1), 85.75, 81.99, 79.05, 77.78 (C-2, C-3, C-4, C-5), 75.65, 75.32, 74.94, 73.42 ($PhCH_2$), 68.45 (C-6), 47.11 (SCH_2), 33.02 (CH_3'), 32.94 (CH_3).

2-Chloro-2-methylpropyl 2,3,4,6-Tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**61**)

Compound **57** (350 mg, 0.56 mmol) was halogenated with phosphorus trichloride according to General procedure 7. The crude product was purified by column chromatography (CH/EA = 10/1). Yield 270 mg (73%), colorless syrup, $[\alpha]_D^{20}$ +25.6 (*c* 1.0 in $CHCl_3$). For $C_{38}H_{43}ClO_5S$ (647.3) calculated: 70.50% C, 6.71% H; found: 70.55% C, 6.64% H. ^{1}H NMR (300 MHz, $CDCl_3$): 7.08–7.44 m, 20 H (arom. H); 4.87 d, 1 H, *J* = 11.2 ($PhCH_2$); 4.86 d, 1 H, *J* = 10.6 ($PhCH_2$); 4.83 d, 1 H, *J* = 11.2 ($PhCH_2$); 4.77 d, 1 H, *J* = 11.0 ($PhCH_2$); 4.68 d, 1 H, *J* = 10.6 ($PhCH_2$); 4.59 d, 1 H, *J* = 12.0 ($PhCH_2$); 4.53 d, 1 H, *J* = 11.0 ($PhCH_2$); 4.49 d, 1 H, *J* = 12.0 ($PhCH_2$); 4.51 d, 1 H, *J*(1,2) = 10.0 (H-1); 3.52–3.73 m, 4 H (H-6, H-6′, H-2/H-3/H-4); 3.30–3.47 m, 2 H (H-5, H-2/H-3/H-4); 3.24 d, 1 H, *J* = 13.2 (SCH_2'); 3.03 d, 1 H, *J* = 13.2 (SCH_2); 1.61 s, 3 H (CH_3); 1.55 s, 3 H (CH_3').

Substitution Product (**62**)

^{1}H NMR (300 MHz, $CDCl_3$): 7.14–7.36 m, 35 H (arom. H); 4.96 d, 1 H, *J* = 11.2 ($PhCH_2$); 4.56–4.93 m, 11 H (11 × $PhCH_2$, H-1); 4.57 d, 1 H, *J* = 12.4 ($PhCH_2$); 4.56 d, 1 H, *J* = 11.2 ($PhCH_2$); 4.50 d, 1 H, *J* = 12.4 ($PhCH_2$); 4.46 d, 1 H, *J*(1,2) = 10.0 (H-1′); 3.96 dd, 1 H, *J*(1,2) = 9.4, *J*(1,2) = 9.4 (sugar-H); 3.31–3.74 m, 11 H (sugar-H); 3.33 s, 3 H (OCH_3); 2.85–2.89 m, 2 H (SCH_2); 1.26 s, 3 H (CH_3'); 1.24 s, 3 H (CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 138.90, 138.63, 138.53, 138.48, 138.42, 138.25, 138.06 (arom. C_i), 127.52–128.31 (arom. C), 97.88 (C-1′), 86.59 (C-1), 85.39, 82.33, 82.03, 80.17, 78.95, 77.92, 77.64 (sugar-C), 75.89, 75.64, 75.45, 75.36, 74.97, 74.77, 73.39, 73.23 (7 × $PhCH_2$, sugar-CH), 70.16, 69.08 (C-6, C-6′), 60.67 ($C(CH_3)_2O$), 54.96 (OCH_3), 41.32 (SCH_2), 24.80 (CH_3'), 24.57 (CH_3).

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