Synthesis of Anomeric Sulfimides and Their Use as a New Family of Glycosyl Donors

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Dedicated to Professor Joachim Thiem on the occasion of his 60th birthday

Keywords: Anomeric sulfimides / Glycosyl donors / Glycosylations

We introduce a convenient synthesis of anomeric sulfimides, the ability of which to act as glycosyl donors has been tested with various thiophilic reagents and acceptors.

Introduction

Since the recognition of the biologically important role of oligosaccharides, there has been an ongoing demand for new and more efficient methods for their synthesis. Thus, the development of stereoselective glycosylation reactions is a longstanding topic in carbohydrate chemistry.[1] Thioglycosides have attracted considerable attention in oligosaccharide synthesis over recent years, due to their stability under various different chemical conditions and their versatility of application.[2] The *S*-linked anomeric moiety may therefore act as a temporary protective group, and can also be activated by various thiophilic reagents when required. These interesting characteristics have given rise to the development of miscellaneous anomeric thio derivatives including xanthates[3] and sulfoxides.[4,5]

With the goal of developing a new family of thio-functionalised glycosyl donors, we have investigated the synthesis of carbohydrate-derived sulfimides.[6] These anomeric sulfimides are analogues of the corresponding sulfoxides, with the oxygen atom replaced by a substituted nitrogen atom. Our first syntheses were carried out on various protected ethyl 1-thio-glucopyranosides. In this paper, the work has been extended to different peracetylated thioglycosides of D-galactose, D-mannose, D-xylose, 2-amino-2-deoxy-D-glucose, L-rhamnose and L-fucose. Furthermore, the glycosyl-donating aptitude of the anomeric sulfimides has been tested with various acceptors and thiophilic activators.

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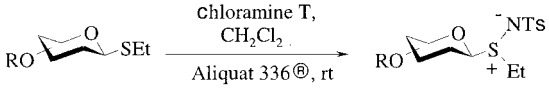
Results and Discussion

Sulfimide Synthesis

N-Tosylsulfimides are usually prepared by means of the reaction between chloramine T (the sodium salt of *N*-chloro-*p*-toluenesulfonamide) and sulfides in aqueous media, together with a cosolvent.[7] However, use of the aqueous system often results in significant formation of sulfoxides as by-products. Johnson and co-workers demonstrated that sulfoxide formation could be minimized under phase-transfer conditions.[8] By use of a similar methodology, it has been possible to obtain anomeric *N*-tosylsulfimides easily by means of the reaction between alkyl thioglycosides and chloramine T under phase-transfer catalysis conditions (Scheme 1).



Scheme 1

Our syntheses were initially focused on a series of diversely protected ethyl 1-thio-β-D-glucopyranosides. These turned out to be more reactive than their phenyl 1-thio counterparts in the reaction with chloramine T. The latter substrates gave only the corresponding sulfoxides, which may be due to steric hindrance. The anomeric sulfimides **1**−**5** (Scheme 2) prepared from ethyl 1-thio-β-D-glucopyranosides have been obtained in good yields (80−90%) and with high stereoselectivity, achieving a *de* of > 90% in most cases (Table 1).

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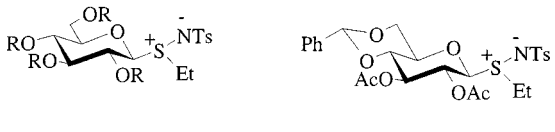
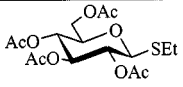
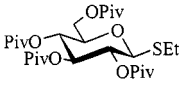
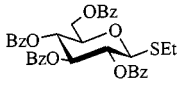
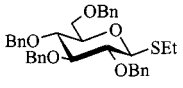
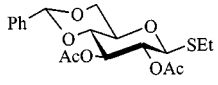


1 : R = Ac
2 : R = Piv
3 : R = Bz
4 : R = Bn

5

Scheme 2

Table 1. Sulfimides derived from variously protected ethyl 1-thio-β-D-glucopyranosides

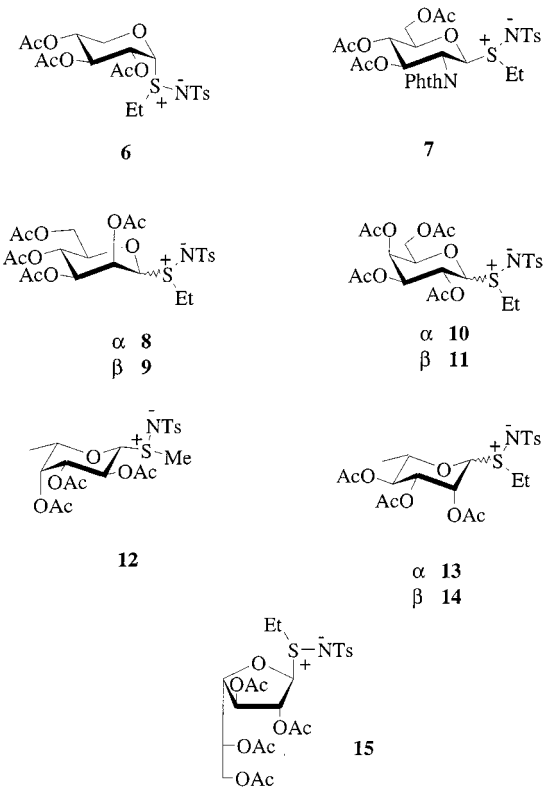
thioglycosides	time (h)	yield (%)	compd.	*de*[a]
	3	86	**1**	> 90%
	12	83	**2**	> 90%
	2	91	**3**	> 90%
	4	87	**4**	40%
	2	92	**5**	> 90%

[a] *de* values were estimated by ^{1}H NMR spectra.

These encouragingly good yields and stereoselectivities induced us to explore the scope of this reaction with further carbohydrate compounds. Peracetylated alkyl 1-thio-glycopyranosides derived from D-galactose, D-mannose, D-xylose, L-fucose, L-rhamnose, and D-glucosamine were chosen, due to the abundance of these sugars in naturally occurring oligosaccharides. Generally, the sulfimides **6**−**15** (Scheme 3) were obtained in good yields and with good stereoselectivities (Table 2). Only in some cases was the yield moderate, due to concomitant sulfoxide formation.

The formation of sulfimide is believed to proceed through an ionic mechanism, one feature of this being that the sulfonium intermediate may be intercepted by water to produce sulfoxides.[9] A possible source of water may originate from incomplete removal of crystal water from chloramine T.[10] The more reactive sugars, such as the deoxy derivatives (L-Fuc, L-Rha), displayed higher tendencies to yield undesired sulfoxide by-products.

Treatment of ethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-1-thio-β-D-glucopyranoside[11] with chloramine T under the standard reaction conditions furnished only the corresponding oxazoline.[12] The formation of oxazolines from *N*-acetylglucosamine is a well-known reaction that occurs upon activation of the anomeric centre.[13]



6 **7**

α **8**
β **9**

α **10**
β **11**

12

α **13**
β **14**

15

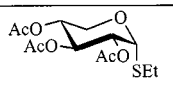
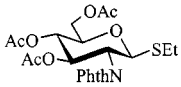
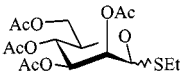
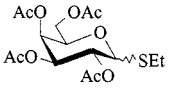
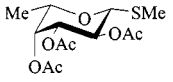
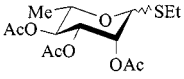
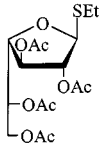
Scheme 3

Satisfactory spectroscopic data were obtained for all compounds, and their ^{1}H NMR spectra permitted estimation of the product composition (i.e., the *de* values with respect to the newly formed stereogenic centre at the sulfur atom). The crystallisation of some anomeric sulfimides was attempted, with the aim of establishing the absolute configuration at the sulfur atom by X-ray crystallography. This, however, was severely hampered by their intrinsic instability and was ultimately unsuccessful.

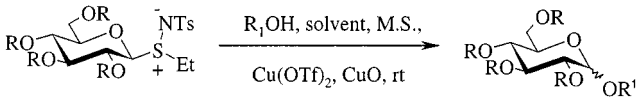
Glycosylation Reactions

In order to test their glycosyl-donating aptitudes and to find suitable reaction conditions for glycosylation, the anomeric sulfimides were submitted to various thiophilic activators, with different solvents and glycosyl acceptors. Preliminary experiments focused on the activation of the per-*O*-benzylated D-gluco sulfimide **4** as donor, with MeOH as a simple and reactive model acceptor and with use of Kahne-type activation.[4] Triflic anhydride and trimethylsilyl triflate, however, proved totally inefficient, while other hard Lewis acids such as $BF_3{\cdot}Et_2O$ gave only poor glycosylation yields, never exceeding 40%. In contrast, softer Lewis acids[14,15] such as cupric salts [$Cu(OTf)_2$, for example] proved to be much more efficient promoters for the glycosylation reaction (Scheme 4).

Table 2. Sulfimides derived from diversely peracetylated thioglycosides

thioglycosides		time (h)	yield (%)	product	*de*[a]
		12	94	**6**	> 90%
		2	65	**7**	> 90%
	α	12	70	**8**	67%
	β	14	70	**9**	60%
	α	10	87	**10**	60%
	β	8	65	**11**	> 90%
		3	50	**12**	> 90%
	α	6	70	**13**	50%
	β	8	70	**14**	> 90%
		2	70	**15**	> 90%

[a] *de* values were estimated by ^{1}H NMR spectra.

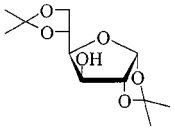
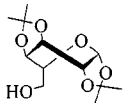


Scheme 4

Satisfactory glycosylation results were obtained only with excesses of glycosyl donor and promoter.[6] For example, 3 equiv., based on 1 equiv. of glycosyl acceptor, of the benzylated glucosyl donor **4** were used, together with 3.3 equiv. of $Cu(OTf)_2$. Under these reaction conditions, short reaction times (typically 5 min) were sufficient. In the case of peracetylated donors such as the D-gluco derivative **1**, the use of 2 equiv. of donor and 2.2 equiv. of $Cu(OTf)_2$ (based on 1 equiv. of acceptor) was appropriate, these conditions requiring reactions times of ca. 5 h.

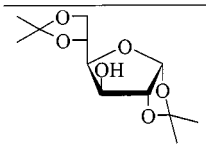
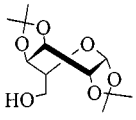
With these conditions established, the scope of the reaction was explored by treatment of **4** with two acceptors of different reactivity (Table 3). For donors without a participating group at C(2) the solvent may have a directing effect on the stereochemistry at the anomeric centre, so the reactions with disaccharides **16** and **17** were studied in different solvents. As expected, an α-orienting effect was observed in

Table 3. Reaction with the per-*O*-benzylated donor **4**

R^{1}OH	disaccharide	Et_2O		CH_2Cl_2		CH_3CN	
		yield	α/β[a]	yield	α/β[a]	yield	α/β[a]
	**16**	86	65/35	76	8/2 *4*[b]	76	55/45 *12*[b]
	**17**	91	8/2	quant.	6/4	quant.	2/8

[a] α/β ratios were determined by ^{1}H NMR. [b] The yields in italics correspond to rearranged products resulting from the 5,6→3,5 migration of an isopropylidene group.

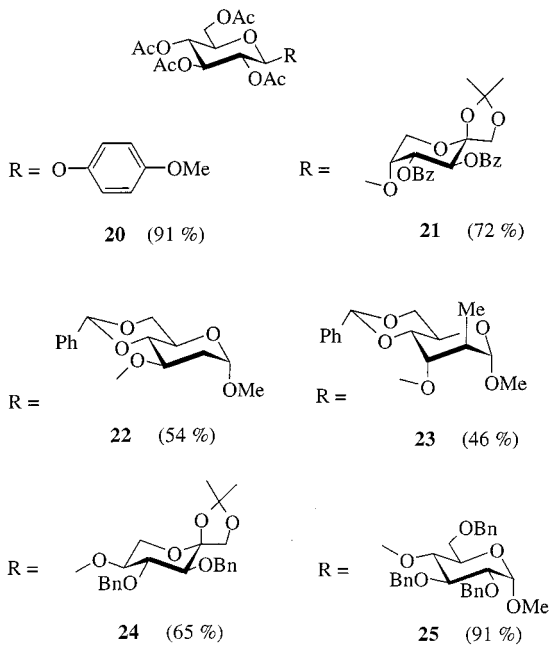
Table 4. Reactions with the per-*O*-acetylated donor **1**

R^{1}OH	disaccharide	solvent	yield	α/β[a]
	**18**	CH_2Cl_2	33+*26*[b]	0/1
	**19**	CH_2Cl_2	72	0/1

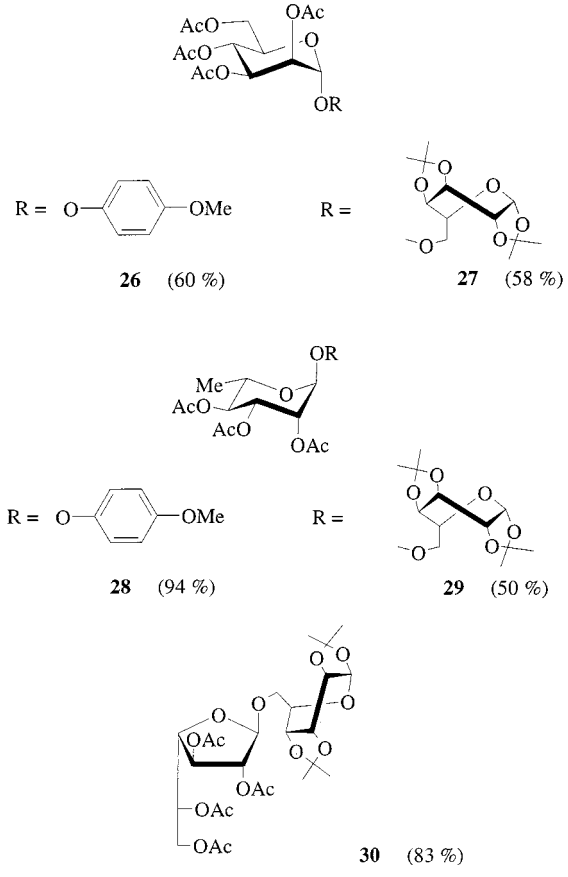
[a] α/β ratios were determined by ^{1}H NMR. [b] The yields in italics correspond to rearranged products resulting from the 5,6→3,5 migration of an isopropylidene group.

Et_2O and in CH_2Cl_2, while CH_3CN exhibited a β-orienting effect.[16] A higher amount of β-linked glycoside was usually obtained from donors with a participating group − such as an acetoxy moiety − at C(2), which often favoured the exclusive formation of a 1,2-*trans*-*O*-glycosidic orientation. Treatment of **1** with the same acceptors[6] as used above selectively provided the β-D-linked glycosides **18** and **19** (Table 4). In addition to **1**, further pyranoid or furanoid peracetylated donors with different stereochemistries, such as **8**, **13** and **15**, have been investigated.

Neighbouring participation by the 2-*O*-acetyl group also induced the exclusive formation of the 1,2-*trans*-*O*-glycosidic linkage in these cases. In most cases the yields were good, although moderate yields were obtained (for disaccharides **21**−**24**, Scheme 5, for example) with acceptors of low reactivity or when the hydroxyl group of the glycosyl acceptor was sterically hindered. In such cases though, the glycosyl acceptor and/or the acetylated acceptor could be recovered.



Scheme 5



Scheme 6

Conclusion

In summary, we describe the preparation of anomeric sulfimides as a new family of carbohydrate-derived sulfur compounds. Those sulfimides were easily prepared from the corresponding thioglycosides by use of chloramine T, an inexpensive and easily handled reagent.

Without the necessity of intermediate purification, anomeric sulfimides were successfully employed as glycosyl donors. Compared to other glycosylation methods, the yields and the stereoselectivity were similar, but the reaction conditions were mild, reaction times were short − especially for activated donors − and the promoter was easy to manipulate.

Experimental Section

General: Solvents were dried and distilled by standard methods. All reagents were of commercial quality (Acros, Aldrich or Lancaster) and were used without purification. Reactions were carried out under dry argon and monitored by TLC analysis on silica gel plates (Kieselgel 60 F_{254}, Merck). Compounds were viewed under UV light and by heat treatment with 10% sulfuric acid in ethanol. Column chromatography was performed on 60 M silica gel (0.036−0.063 mm, Merck). ^{1}H NMR (250 MHz) and ^{13}C NMR (62.59 MHz) spectra ($CDCl_3$, TMS as internal standard) were recorded with a Bruker AVANCE DPX 250; for compound **6**, ^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra ($CDCl_3$, TMS as internal standard) were recorded with a Bruker AMX 500. NMR simulations for **6** and **10** were produced with a Bruker program (PANIC) fixing the chemical shift and with free coupling constants. Chemical shifts (δ) are reported in ppm units by reference to TMS; coupling constants (*J*) are reported in Hertz and refer to apparent peak multiplicity. Assignments are based on H,H and C,H COSY experiments. Mass spectra were obtained with an API 300 Perkin−Elmer SCIEX spectrometer, using the ionspray method. HR-ESI-TOF-MS was carried out by Technologie Servier (Orléans, France). Optical rotations were measured in chloroform at room temperature with a Perkin−Elmer 41 polarimeter.

General Procedure for the Synthesis of Sulfimides (Procedure A): A dichloromethane solution of the thioglycoside was treated with chloramine T (1.5 equiv.) and 1 drop of Aliquat 336®. The suspension was stirred at room temperature and after completion of the reaction, the mixture was diluted with dichloromethane. The organic phase was washed with 5% aqueous NaOH, dried with $MgSO_4$ and filtered, and the solvents were evaporated under reduced pressure. The crude product could be purified by column chromatography on silica gel to afford the pure sulfimide.

General Procedure for Glycosylation (Procedure B): The glycosyl acceptor (1 equiv.) and CuO (1 equiv.) were added to a solution of the dried crude perbenzylated sulfimide **4** (3 equiv.) in an anhydrous solvent (Et_2O, CH_2Cl_2 or CH_3CN). The mixture was stirred with powdered molecular sieves (3 or 4 Å, depending on the solvent) for about 15 min in order to remove traces of water, and then treated with $Cu(OTf)_2$ (3.3 equiv.). The reaction mixture was stirred until complete consumption of the starting material, 2 drops of triethylamine were then added, and the mixture was stirred for another 5 min and filtered through Celite®. The filtrate was concentrated under reduced pressure and the crude product was chromatographed on silica gel to afford the pure glycoside.

General Procedure for Glycosylation (Procedure C): The glycosyl acceptor (1 equiv.) and CuO (1 equiv.) were added to a solution of the dried crude peracetylated sulfimide (2.5 equiv.) in anhydrous dichloromethane. The mixture was stirred with 4 Å powered molecular sieves for about 15 min in order to remove traces of water, and then treated with $Cu(OTf)_2$ (2 equiv.). The reaction mixture was stirred until complete consumption of the starting material, and 2 drops of triethylamine were then added. The mixture was then stirred for another 5 min and filtered through Celite®, and the filtrate was concentrated under reduced pressure. The crude product was chromatographed on silica gel to afford the pure glycoside.

Ethyl 2,3,4,6-Tetra-*O*-acetyl-*S*-(*N*-tosylimino)-1-thio-β-D-glucopyranoside (1): Preparation from crystalline ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside[17] (250 mg, 0.637 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 2:8) gave amorphous **1** (307 mg, yield 86%) in the form of one epimer. $[\alpha]_D = -166$ (c = 1.0; $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.13 (t, J_{vic} = 7.8 Hz, 3 H, SCH_2CH_3), 1.99, 2.01, 2.06, 2.11 (4 s, 12 H, 4 $COCH_3$), 2.38 (s, 3 H, CH_3Ar), 2.93 (dq, 1 H, $J_{gem} = -13.5$, SCH_2CH_3), 3.16 (dq, 1 H, SCH_2CH_3), 3.83 (ddd,1 H, $J_{5,6a}$ = 4.6, H-5), 4.14 (dd, 1 H, $J_{5,6b}$ = 2.2, H-6b), 4.30 (dd, 1 H, $J_{6a,6b} = -12.7$, H-6a), 4.59 (d 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 4.98 (t, 1 H, $J_{2,3}$ = 10.0 Hz, H-2), 5.02 (t, 1 H, $J_{3,4} = J_{4,5}$ = 10.0 Hz, H-4), 5.24 (t, 1 H, H-3),7.22 (d, J_{vic} = 8.1 Hz, 2 H, CH_3Ar), 7.76 (d, J_{vic} = 8.1 Hz, 2 H, CH_3Ar). ^{13}C NMR ($CDCl_3$): δ = 7.8 (SCH_2CH_3), 20.8, 20.9, 21.1 (4 $COCH_3$), 21.9 (CH_3Ar), 36.4 (SCH_2CH_3), 61.5 (C-6), 67.1 (C-4),68.0 (C-2), 74.1 (C-3), 76.6 (C-5), 90.5 (C-1), 126.3, 129.6 (2 × 2 CH, CH_3Ar), 139.2, 142.0 (2 C-arom. quat.), 169.3, 169.6, 170.0, 170.4 (4 $COCH_3$). HRMS ($C_{23}H_{31}NO_{11}S_2$): calcd. 561.1337; found 561.1344.

Ethyl 2,3,4,6-Tetra-*O*-pivaloyl-*S*-(*N*-tosylimino)-1-thio-β-D-glucopyranoside (2): A solution of ethyl 1-thio-β-D-glucopyranoside[18] (2 g, 8.9 mmol) in pyridine (10 mL) was treated with pivaloyl chloride (8 equiv.); an exothermic reaction occurred, with formation of a precipitate. After 6 h, DMAP (0.1 equiv.) was added to activate the reaction and stirring was maintained overnight. Standard workup involved treatment with methanol (6 equiv.) at 0 °C, dilution in dichloromethane, washing with water and drying with $MgSO_4$; the crude solid obtained after evaporation of the solvents and coevaporation with toluene was crystallised from 2-propanol/water to afford ethyl 2,3,4,6-tetra-*O*-pivaloyl-1-thio-β-D-glucopyranoside (2.1 g, yield 42%). Colourless crystals, $[\alpha]_D = -14$ (c = 1.6; $CHCl_3$), m.p. 128−130 °C. ^1H NMR ($CDCl_3$): δ = 1.11, 1.14, 1.16, 1.21 (4 s, 36 H, Piv), 1.26 (t, J_{vic} = 7.4 Hz, 3 H, SCH_2CH_3), 2.28−2.56 (m, 2 H, SCH_2CH_3), 3.73 (ddd, 1 H, H-5), 4.05 (d, 1 H, $J_{5,6b}$ = 5.3, H-6b), 4.21 (d, 1 H, $J_{5,6a}$ = 1.5, $J_{6a,6b} = -12.3$, H-6a), 4.51 (d 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 5.06, 5.11 (2t, 2 H, H-2, H-4), 5.33 (t, $J_{3,4}$ = 9.3 Hz, 1 H, $J_{2,3}$ = 9.3, H-3). ^{13}C NMR ($CDCl_3$): δ = 15.3 (SCH_2CH_3), 24.2 (SCH_2CH_3), 27.4, 27.5, 27.6 (CH_3 Piv), 39.0, 39.1, 39.2 (C quat. Piv), 62.5 (C-6), 68.2 (C-5), 69.9, 73.6 (C-2, C-4), 76.8 (C-3), 83.8 (C-1), 176.8, 176.9, 177.5, 178.4 (4 CO Piv). HRMS ($C_{28}H_{48}O_9S$): calcd. 560.3016; found 560.3021. Treatment of the above thioglucosidic precursor (170 mg, 0.303 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 7:3) gave amorphous **2** (184 mg, yield 83%) in the form of one epimer. $[\alpha]_D = -135$ (c = 1.23, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.06−1.17 (m, 39 H, Piv, SCH_2CH_3), 2.34 (s, 3 H, CH_3Ar), 2.91 (dq, 1 H, $J_{gem} = -13.4$, SCH_2CH_3), 3.19 (dq, 1 H, SCH_2CH_3), 3.84 (dt, 1 H, $J_{5,6a} = J_{5,6b}$ = 2.8, H-5), 4.18 (d, 2 H, H-6a, H-6b), 4.57 (d 1 H, $J_{1,2}$ = 10.2 Hz, H-1), 4.84 (t, 1 H, $J_{2,3}$ = 10.2 Hz, H-2), 5.11 (t, 1 H, $J_{3,4} = J_{4,5}$ = 10.2 Hz, H-4), 5.35 (t, 1 H, H-3), 7.17 (d, 2 H, J = 8.3, CH_3Ar), 7.67 (d, 2 H, J = 8.3, CH_3Ar). ^{13}C NMR ($CDCl_3$): δ = 8.1 (SCH_2CH_3), 21.8 (CH_3Ar), 27.3, 27.4, 27.5 (CH_3 Piv), 34.7 (SCH_2CH_3), 37.8, 37.9, 38.0 (C quat. Piv), 60.9 (C-6), 66.8 (C-4), 68.1 (C-2), 72.3 (C-3), 77.8 (C-5), 91.3 (C-1), 126.8, 129.6 (2 × 2 CH, CH_3Ar), 139.9, 141.1 (2 C-arom. quat.), 175.2, 175.7, 176.6, 176.8 (4 CO Piv). HRMS ($C_{35}H_{55}NO_{11}S_2$): calcd. 729.3214; found 729.3211.

Ethyl 2,3,4,6-Tetra-*O*-benzoyl-*S*-(*N*-tosylimino)-1-thio-β-D-glucopyranoside (3): Preparation from crystalline ethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside[19] (130 mg, 0.202 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 6:4) gave amorphous **3** (149 mg, yield 91%) in the form ofone epimer. $[\alpha]_D = -123$ (c = 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.21 (t, J_{vic} = 7.5 Hz, 3 H, SCH_2CH_3), 2.31 (s, 3 H, CH_3Ar), 3.12 (dq, 1 H, $J_{gem} = -12.8$, SCH_2CH_3), 3.28 (dq, 1 H, SCH_2CH_3), 4.30 (m, 1 H, H-5), 4.48 (dd, 1 H, $J_{5,6b}$ = 4.2, H-6b), 4.76 (dd, 1 H, $J_{5,6a}$ = 2.9, $J_{6a,6b} = -12.8$, H-6a), 4.97 (d 1 H, $J_{1,2}$ = 9.8 Hz, H-1), 5.40 (t, $J_{2,3}$ = 9.8 Hz, 1 H, H-2), 5.68 ("t", 1 H, $J_{3,4}$ = 9.8, $J_{4,5}$ = 9.8 Hz, H-4), 5.95 (t, 1 H, H-3), 6.99 (d, J_{vic} = 8.1 Hz, 2 H, CH_3Ar), 7.24−7.59 (m, 14 H, Bz, CH_3Ar), 7.80−7.87 (m, 4 H, Bz), 7.96−8.04 (m, 4 H, Bz). ^{13}C NMR ($CDCl_3$): δ = 8.1 (SCH_2CH_3), 21.8 (CH_3Ar), 36.3 (SCH_2CH_3), 62.5 (C-6), 68.5 (C-4), 68.8 (C-2), 73.1 (C-3), 77.8 (C-5), 91.1 (C-1), 126.3−142.3 (24 CH, 6 C-arom. quat., 4Bz, CH_3Ar), 165.4, 165.7, 166.1, 166.3 (4 CO Bz). HRMS ($C_{43}H_{39}NO_{11}S_2$): calcd. 809.1963; found 809.1972.

Ethyl 2,3,4,6-Tetra-*O*-benzyl-*S*-(*N*-tosylimino)-1-thio-β-D-glucopyranoside (4): Preparation from crystalline ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside[18] (342 mg, 0.585 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 6:4) gave amorphous **4** (384 mg, yield 87%) as a 4:1 mixture of diastereomers. $[\alpha]_D = -31$ (c = 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$) for the major epimer: δ = 1.07 (t, J_{vic} = 7.4 Hz, 3 H, SCH_2CH_3), 2.36 (s, 3 H, CH_3Ar), 2.36 (dq, 1 H, $J_{gem} = -12.8$, SCH_2CH_3), 2.71 (dq, 1 H, SCH_2CH_3), 3.63−4.02 (m, 6 H, H-2, H-3, H-4, H-5, H-6a, H-6b), 4.47−4.97 (m, 9 H, 1-H, 4 CH_2Ph), 7.17 (d, J_{vic} = 7.9 Hz, 2 H, CH_3Ar), 7.23−7.39 (m, 20 H, 4 CH_2Ph), 7.83 (d, J_{vic} = 8.3 Hz, 2 H, CH_3Ar); for the minor epimer: δ = 1.12 (t, J_{vic} = 7.4 Hz, 3 H, SCH_2CH_3), 2.38 (s, 3 H, CH_3Ar), 2.86 (dq, 1 H, $J_{gem} = -14.8$, SCH_2CH_3), 3.20 (dq, 1 H, SCH_2CH_3), 3.58−4.20 (m, 6 H, H-2, H-3, H-4, H-5, H-6a, H-6b), 4.34−4.96 (m, 9 H, 1-H, 4 CH_2Ph), 7.19 (d, 2 H, J = 7.9, CH_3Ar), 7.27−7.35 (m, 20 H, 4 CH_2Ph), 7.85 (d, J_{vic} = 8.1 Hz, 2 H, CH_3Ar). ^{13}C NMR ($CDCl_3$) for the major epimer: δ = 7.9 (SCH_2CH_3), 21.9 (CH_3Ar), 38.6 (SCH_2CH_3), 68.7 (C-6), 75.9, 76.0, 76.7, 76.8 (4 CH_2Ph), 77.3, 78.8, 80.5, 86.4 (C-2, C-3, C-4, C-5), 92.8 (C-1), 127.0−130.0 (24 CH, 4 CH_2Ph, CH_3Ar), 141.9, 142.0 (2 C-arom. quat., CH_3Ar), 137.4, 138.1, 138.2, 138.3 (4 C-arom. quat., 4 CH_2Ph); for the minor epimer: δ = 7.8 (SCH_2CH_3), 21.8 (CH_3Ar), 39.9 (SCH_2CH_3), 69.1 (C-6), 73.8, 75.5, 75.6, 76.9 (4 CH_2Ph), 77.4, 77.9, 80.5, 80.8 (C-2, C-3, C-4, C-5), 88.9 (C-1), 126.4−129.5 (24 CH, 4 CH_2Ph, CH_3Ar), 137.8−142.1 (6 C-arom. quat, 4 CH_2Ph, CH_3Ar). HRMS ($C_{43}H_{47}NO_7S_2$): calcd. 753.2792; found 753.2801.

Ethyl 2,3-Di-*O*-acetyl-4,6-*O*-benzylidene-*S*-(*N*-tosylimino)-1-thio-β-D-glucopyranoside (5): Preparation from crystalline ethyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[20] (97 mg, 0.244 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 3:7) gave amorphous **5** (127 mg, yield: 92%) in the form of one epimer. $[\alpha]_D = -177$ (c = 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.13 (t, J_{vic} = 7.4 Hz, 3 H, SCH_2CH_3), 2.02, 2.07 (2 s, 6 H, 2 $COCH_3$), 2.37 (s, 3 H,

CH$_3$Ar), 2.93 (dq, 1 H, J_{gem} = −14.2, S*CH*$_2$CH$_3$), 3.10 (dq, 1 H, S*CH*$_2$CH$_3$), 3.55−3.71 (m, 3 H, H-4, H-5, H-6b), 4.38 (dd, 1 H, $J_{5,6a}$ = 2.7, $J_{6a,6b}$ = −9.4, H-6a), 4.59 (d 1 H, $J_{1,2}$ = 10.1 Hz, H-1), 5.00 (t, 1 H, $J_{2,3}$ = 10.1 Hz, H-2), 5. 33 (t, 1 H, $J_{3,4}$ = 10.1 Hz, H-3), 5.43 (s, 1 H, H-7), 7.22 (d, J_{vic} = 8.1 Hz, 2 H, CH$_3$*Ar*), 7.32−7.41 (m, 5 H, Ph), 7.74 (d, J_{vic} = 8.1 Hz, 2 H, CH$_3$*Ar*). ^{13}C NMR (CDCl$_3$): δ = 8.0 (SCH$_2$*CH*$_3$), 21.9, 21.8, 21.4 (2 CO*CH*$_3$, *CH*$_3$Ar), 36.7 (S*CH*$_2$CH$_3$), 65.2 (C-6), 68.2 (C-2), 71.7, 77.9 (C-4, C-5), 72.6 (C-3), 92.4 (C-1), 102.1 (C-7), 126.5−129.9 (9 CH, Ph, CH$_3$*Ar*), 130.1, 141.4, 142.5 (3 C-arom. quat.), 169.9, 170.1 (2 *CO*CH$_3$). HRMS ($C_{26}H_{31}NO_9S_2$): calcd. 565.1439; found 565.1441.

Ethyl 2,3,4-Tri-*O*-acetyl-*S*-(*N*-tosylimino)-1-thio-α-D-xylopyranoside (6): Preparation from syrupy ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-D-xylopyranoside[21] (136 mg, 0.425 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 2:8) gave amorphous **6** (196 mg, yield 94%) in the form of one epimer. [α]$_D$ = −70 (*c* = 1.0, CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ = 1.16 (t, J_{vic} = 7.4 Hz, 3 H, SCH$_2$*CH*$_3$), 2.02, 2.05 2.10 (3 s, 9 H, 3 CO*CH*$_3$), 2.34 (s, 3 H, *CH*$_3$Ar), 2.91 (dq, 1 H, J_{gem} = −14.3, S*CH*$_2$CH$_3$), 3.08 (dq, 1 H, S*CH*$_2$CH$_3$), 3.93 (dd, 1 H, $J_{4,5a}$ = 1.8, H-5a), 4.16 (ddd, 1 H, $J_{3,5b}$ = 1.7, $J_{4,5b}$ = 2.1, $J_{5a,5b}$ = −13.3, H-5b), 4.74 (m, 1 H, H-4), 4.84 (d, $J_{1,2}$ = 1.8 Hz, 1 H, H-1), 5.03 (ddd, 1 H, $J_{2,3}$ = 2.8, $J_{2,4}$ = 1.2 Hz, H-2), 5.35 (ddd, 1 H, $J_{3,4}$ = 3.1 Hz, H-3), 7.19 (d, J_{vic} = 8.1 Hz, 2 H, CH$_3$*Ar*), 7.69 (d, J_{vic} = 8.3 Hz, 2 H, CH$_3$*Ar*). ^{13}C NMR (CDCl$_3$): δ = 6.5 (SCH$_2$*CH*$_3$), 20.4, 20.7, 20.8 (3 CO*CH*$_3$), 21.4 (*CH*$_3$Ar), 40.1 (S*CH*$_2$CH$_3$), 64.4 (C-2), 65.0 (C-3), 65.8 (C-4), 68.1 (C-5), 88.8 (C-1), 126.3, 129.3 (2 × 2 CH, CH$_3$*Ar*), 140.7, 142.0 (2 C-arom. quat., CH$_3$*Ar*), 168.1, 168.8, 169.4 (3 *CO*CH$_3$). HRMS ($C_{20}H_{27}NO_9S_2$): calcd. 489.1126; found 489.1120.

Ethyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-*S*-(*N*-tosylimino)-1-thio-β-D-glucopyranoside (7): Preparation from ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[22] (160 mg, 0.334 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 2:8) gave amorphous **7** (141 mg, yield 65%) in the form of one epimer. [α]$_D$ = −46 (*c* = 1.0, CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ = 1.11 (t, J_{vic} = 7.3 Hz, 3 H, SCH$_2$*CH*$_3$), 1.82, 2.00, 2.07 (3 s, 9 H, 3 CO*CH*$_3$), 2.32 (s, 3 H, *CH*$_3$Ar), 2.92 (dq, 1 H, J_{gem} = −13.5, S*CH*$_2$CH$_3$), 3.07 (dq, 1 H, S*CH*$_2$CH$_3$), 3.94 (ddd, 1 H, $J_{5,6a}$ = 4.6, H-5), 4.18 (dd, 1 H, $J_{5,6b}$ = 1.9, H-6b), 4.30 (dd, 1 H, $J_{6a,6b}$ = −12.7, H-6a), 4.51 (dd, 1 H, $J_{2,3}$ = 10.1 Hz, H-2), 5.09 (dd, 1 H, $J_{3,4}$ = 9.5, $J_{4,5}$ = 10.3 Hz, H-4), 5.45 (d 1 H, $J_{1,2}$ = 10.8 Hz, H-1), 5.83 (dd, 1 H, H-3), 7.06 (d, J_{vic} = 8.5 Hz, 2 H, CH$_3$*Ar*), 7.48 (d, J_{vic} = 8.3 Hz, 2 H, CH$_3$*Ar*), 7.71−7.85 (m, 4 H, Phth). ^{13}C NMR (CDCl$_3$): δ = 7.2 (SCH$_2$*CH*$_3$), 20.4−21.5 (3 CO*CH*$_3$), 21.6 (*CH*$_3$Ar), 37.8 (S*CH*$_2$CH$_3$), 61.4 (C-6), 67.8 (C-4), 70.7 (C-3), 74.7 (C-2), 77.7 (C-5), 87.3 (C-1), 123.8−134.7 (8 CH, CH$_3$*Ar*), 141.2−142.2 (4 C-arom. quat., Phth, CH$_3$*Ar*), 167.7−170.9 (2 *CO*-Phth, 3 *CO*CH$_3$).). HRMS ($C_{29}H_{32}N_2O_{11}S_2$): calcd. 648.1447; found 648.1432.

Ethyl 2,3,4,6-Tetra-*O*-acetyl-*S*-(*N*-tosylimino)-1-thio-α-D-mannopyranoside (8): Preparation from ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside[21] (184 mg, 0.469 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 2:8) gave amorphous **8** (184 mg, yield 70%) as a 5:1 mixture of diastereomers. [α]$_D$ = +63 (*c* = 1.0, CHCl$_3$). ^{1}H NMR (CDCl$_3$) for the major epimer: δ = 1.35 (t, J_{vic} = 7.3 Hz, 3 H, SCH$_2$*CH*$_3$), 1.99, 2.05, 2.08, 2.13 (4 s, 12 H, 4 CO*CH*$_3$), 2.39 (s, 3 H, *CH*$_3$Ar), 2.92−3.12 (m, 2 H, S*CH*$_2$CH$_3$), 3.88 (ddd, 1 H, $J_{5,6a}$ = 5.8, H-5), 4.09 (dd, 1 H, $J_{5,6b}$ = 2.7, H-6b), 4.23 (dd, 1 H, $J_{6a,6b}$ = −12.5, H-6a), 4.98 (d, $J_{1,2}$ = 2.2 Hz, 1 H, H-1), 5.20 (t, $J_{4,5}$ = 9.3 Hz, 1 H, H-4), 5.37 (dd, 1 H, $J_{3,4}$ = 9.3 Hz, H-3), 5.59 (dd, 1 H, $J_{2,3}$ = 3.4 Hz, H-2), 7.25 (d, J_{vic} = 8.3 Hz, 2 H, CH$_3$*Ar*), 7.82 (d, J_{vic} = 8.3 Hz, 2 H, CH$_3$*Ar*); for the minor epimer: δ = 1.22 (t, J_{vic} = 7.4 Hz, 3 H, SCH$_2$*CH*$_3$), 2.02, 2.06, 2.07, 2.09 (4 s, 12 H, 4 CO*CH*$_3$), 2.30 (s, 3 H, *CH*$_3$Ar), 2.92−3.12 (m, 2 H, S*CH*$_2$CH$_3$), 4.09 (dd, 1 H, $J_{5,6b}$ = 2.7, H-6b), 4.28 (dd, 1 H, $J_{5,6a}$ = 5.2, $J_{6a,6b}$ = −12.6, H-6a), 4.42−4.45 (m, 1 H, H-5), 4.91 (d, $J_{1,2}$ = 3.2 Hz, 1 H, H-1), 5.23 (t, 1 H, $J_{4,5}$ = 10.5 Hz, H-4), 5.38 (dd, 1 H, $J_{3,4}$ = 10.5 Hz, H-3), 5.59 (dd, 1 H, $J_{2,3}$ = 3.4 Hz, H-2), 7.24 (d, J_{vic} = 8.2 Hz, 2 H, CH$_3$*Ar*), 7.81 (d, J_{vic} = 8.3 Hz, 2 H, CH$_3$*Ar*). ^{13}C NMR (CDCl$_3$) for the major epimer: δ = 6.3 (SCH$_2$*CH*$_3$), 20.1−21.2 (4 CO*CH*$_3$), 20.3 (*CH*$_3$Ar), 40.9 (S*CH*$_2$CH$_3$), 62.4 (C-6), 65.7 (C-5), 66.1 (C-4), 67.5 (C-3), 71.3 (C-2), 91.0 (C-1), 126.0−129.3 (4 CH, CH$_3$*Ar*), 141.7, 141.8 (2 C-arom. quat., CH$_3$*Ar*), 168.4−170.3 (4 *CO*CH$_3$); for the minor epimer: δ = 7.5 (SCH$_2$*CH*$_3$), 20.1−21.2 (4 CO*CH*$_3$), 22.1 (*CH*$_3$Ar), 39.5 (S*CH*$_2$CH$_3$), 61.7 (C-6), 65.9 (C-5), 66.3 (C-4), 68.7 (C-3), 69.4 (C-2), 89.2 (C-1), 127.4−129.3 (4 CH, CH$_3$*Ar*), 140.7, 141.8 (2 C-arom. quat, CH$_3$*Ar*), 168.4−170.3 (4 *CO*CH$_3$). HRMS ($C_{23}H_{31}NO_{11}S_2$): calcd. 561.1337; found 561.1333.

Ethyl 2,3,4,6-Tetra-*O*-acetyl-*S*-(*N*-tosylimino)-1-thio-β-D-mannopyranoside (9): Ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-mannopyranoside was obtained as a syrupy by-product in the synthesis of its α-counterpart.[21] [α]$_D$ = +37 (*c* = 1.1, CHCl$_3$). ^{1}H NMR (CDCl$_3$): δ = 1.23 (t, J_{vic} = 7.4 Hz, 3 H, SCH$_2$*CH*$_3$), 1.90, 1.97, 2.00, 2.11 (4 s, 12 H, 4 CO*CH*$_3$), 2.67 (bd, 2 H, S*CH*$_2$CH$_3$), 3.65 (ddd, 1 H, H-5), 4.06 (dd, 1 H, $J_{5,6b}$ = 2.5, H-6b), 4.20 (dd, 1 H, $J_{5,6a}$ = 5.9, $J_{6a,6b}$ = 12.2, H-6a), 4.74 (d 1 H, $J_{1,2}$ = 1.0 Hz, H-1), 5.01 (dd, 1 H, $J_{3,4}$ = 10.1 Hz, H-3), 5.18 (dd, 1 H, $J_{4,5}$ = 10.1 Hz, H-4), 5.43 (dd, 1 H, $J_{2,3}$ = 3.4 Hz, H-2). ^{13}C NMR (CDCl$_3$): δ = 15.3 (SCH$_2$*CH*$_3$), 20.5−20.8 (4 CO*CH*$_3$), 26.2 (S*CH*$_2$CH$_3$), 62.8 (C-6), 63.1 (C-4), 70.5 (C-2), 71.9 (C-3), 76.4 (C-5), 82.9 (C-1), 169.6−170.6 (4 *CO*CH$_3$). Preparation from ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-mannopyranoside (80 mg, 0.203 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 2:8) gave amorphous **9** (80 mg, yield 70%) as a 4:1 mixture of diastereomers. [α]$_D$ = −18 (*c* = 1.0, CHCl$_3$). ^{1}H NMR (CDCl$_3$) for the major epimer: δ = 1.22 (t, J_{vic} = 7.4 Hz, 3 H, SCH$_2$*CH*$_3$), 1.96, 2.04, 2.06, 2.08 (4 s, 12 H, 4 CO*CH*$_3$), 2.37 (s, 3 H, *CH*$_3$Ar), 3.05−3.15 (m, 2 H, S*CH*$_2$CH$_3$), 3.87 (ddd, 1 H, H-5), 4.15 (dd, 1 H, $J_{5,6b}$ = 2.6, H-6b), 4.22 (dd, 1 H, $J_{5,6a}$ = 5.3, $J_{6a,6b}$ = −12.5, H-6a), 4.94 (d 1 H, $J_{1,2}$ = 1.1 Hz, H-1), 5.12 (dd, 1 H, $J_{3,4}$ = 10.1 Hz, H-3), 5.23 (dd, 1 H, $J_{4,5}$ = 10.3 Hz, H-4), 5.74 (dd, 1 H, $J_{2,3}$ = 3.2 Hz, H-2), 7.21 (d, J_{vic} = 7.9 Hz, 2 H, CH$_3$*Ar*), 7.71 (d, J_{vic} = 8.2 Hz, 2 H, CH$_3$*Ar*); for the minor epimer: δ = 1.22 (t, J_{vic} = 7.4 Hz, 3 H, SCH$_2$*CH*$_3$), 2.03, 2.04, 2.08 (3 s, 12 H, 4 CO*CH*$_3$), 2.38 (s, 3 H, *CH*$_3$Ar), 3.03−3.15 (m, 2 H, S*CH*$_2$CH$_3$), 4.06−4.39 (m, 3 H, H-5, H-6a, H-6b), 4.92 (d, $J_{1,2}$ = 1.0 Hz, 1 H, H-1), 5.16−5.28 (m, 2 H, H-3, H-4), 5.67 (dd, 1 H, $J_{2,3}$ = 3.8 Hz, H-2), 7.24 (d, J_{vic} = 7.7 Hz, 2 H, CH$_3$*Ar*), 7.76 (d, J_{vic} = 8.2 Hz, 2 H, CH$_3$*Ar*). ^{13}C NMR (CDCl$_3$) for the major epimer: δ = 7.1 (SCH$_2$*CH*$_3$), 20.9−21.8 (4 CO*CH*$_3$), 22.0 (*CH*$_3$Ar), 41.0 (S*CH*$_2$CH$_3$), 62.9 (C-6), 65.7 (C-4), 66.5 (C-3), 71.4 (C-2), 77.9 (C-5), 90.1 (C-1), 126.3−129.7 (4 CH, CH$_3$*Ar*), 141.0, 143.0 (2 C-arom. quat., CH$_3$*Ar*), 169.8−171.3 (4 *CO*CH$_3$); for the minor epimer: δ = 7.2 (SCH$_2$*CH*$_3$), 20.9−21.8 (4 CO*CH*$_3$), 22.2 (*CH*$_3$Ar), 42.1 (S*CH*$_2$CH$_3$), 61.3 (C-6), 65.3 (C-4), 66.3 (C-3), 71.4 (C-2), 78.1 (C-5), 89.5 (C-1), 126.3−129.7 (4 CH, CH$_3$*Ar*), 141.0, 143.0 (2 C-arom. quat., CH$_3$*Ar*), 169.8−171.3 (4 *CO*CH$_3$). HRMS ($C_{23}H_{31}NO_{11}S_2$): calcd. 561.1337; found 561.1339.

Ethyl 2,3,4,6-Tetra-*O*-acetyl-*S*-(*N*-tosylimino)-1-thio-α-D-galactopyranoside (10): Preparation from syrupy ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-galactopyranoside[21] (73 mg, 0.186 mmol) according to

Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 2:8) gave amorphous **10** (91 mg, yield 87%) as a 4:1 mixture of diastereomers. $[\alpha]_D^{20} = +97$ ($c = 1.0$, $CHCl_3$). ^1H NMR ($CDCl_3$) for the major epimer: δ = 1.12 (t, J_{vic} = 7.3 Hz, 3 H, SCH_2CH_3), 2.04, 2.06, 2.13, 2.18 (4 s, 12 H, 4 $COCH_3$), 2.38 (s, 3 H, CH_3Ar), 2.81−2.90 (m, 2 H, SCH_2CH_3), 4.02 (dd, 1 H, $J_{5,6b}$ = 3.9, H-6b), 4.14−4.18 (m, 1 H, H-5), 4.29 (dd, 1 H, $J_{5,6a}$ = 7.8, $J_{6a,6b}$ = −11.5, H-6a), 5.32−5.35 (m, 1 H, H-1), 5.51−5.54 (m, 2 H, H-2, H-3), 5.55−5.59 (m, 1 H, H-4), 7.24 (d, J_{vic} = 8.5 Hz, 2 H, CH_3Ar), 7.76 (d, J_{vic} = 8.1 Hz, 2 H, CH_3Ar), for the minor epimer: δ = 1.26 (t, J_{vic} = 7.2 Hz, 3 H, SCH_2CH_3), 2.04, 2.07, 2.13, 2.18 (4 s, 12 H, 4 $COCH_3$), 2.37 (s, 3 H, CH_3Ar), 3.03 (dq, 1 H, J_{gem} = 13.5 Hz, SCH_2CH_3), 3.20 (dq, 1 H, SCH_2CH_3), 4.04−4.19 (m, 3 H, H-5, H-6a, H-6b), 5.33 (d, $J_{1,2}$ = 3.4 Hz, 1 H, H-1), 5.56−5.59 (m, 2 H, H-2, H-4), 5.79 (dd, 1 H, $J_{2,3}$ = 10.7, $J_{3,4}$ = 3.2 Hz, H-3), 7.24 (d, J_{vic} = 8.5 Hz, 2 H, CH_3Ar), 7.82 (d, J_{vic} = 8.3 Hz, 2 H, CH_3Ar). ^{13}C NMR ($CDCl_3$) for the major epimer: δ = 6.4 (SCH_2CH_3), 20.9−21.8 (4 $COCH_3$), 22.5 (CH_3Ar), 40.1 (SCH_2CH_3), 61.3 (C-6), 66.6, 66.7, 67.6, 74.1 (C-2, C-3, C-4, C-5), 87.6 (C-1), 126.6−129.7 (4 CH, CH_3Ar), 141.8−142.3 (2 C-arom. quat., CH_3Ar), 169.6−170.7 (4 $COCH_3$); for the minor epimer: δ = 8.5 (SCH_2CH_3), 20.9−21.8 (4 $COCH_3$), 22.2 (CH_3Ar), 39.9 (SCH_2CH_3), 61.0 (C-6), 61.3−74.1 (C-2, C-3, C-4, C-5), 86.6 (C-1), 126.6−129.7 (4 CH, CH_3Ar), 141.8−142.3 (2 C-arom. quat., CH_3Ar), 169.6−170.7 (4 $COCH_3$). HRMS ($C_{23}H_{31}NO_{11}S_2$): calcd. 561.1337; found 561.1328.

Ethyl 2,3,4,6-Tetra-*O*-acetyl-*S*-(*N*-tosylimino)-1-thio-β-D-galactopyranoside (11): Preparation from syrupy ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside[17] (140 mg, 0.357 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 2:8) gave amorphous **11** (130 mg, yield 65%) in the form of one epimer. $[\alpha]_D = -122$ ($c = 1.0$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.13 (t, J_{vic} = 7.4 Hz, 3 H, SCH_2CH_3), 1.95, 2.02, 2.10, 2.12 (4 s, 12 H, 4 $COCH_3$), 2.36 (s, 3 H, CH_3Ar), 2.92 (dq, 1 H, $J_{gem} = -13.5$, SCH_2CH_3), 3.15 (dq, 1 H, SCH_2CH_3), 4.05−4.18 (m, 3 H, H-5, H-6a, H-6b), 4.56 (d 1 H, $J_{1,2}$ = 9.9 Hz, H-1), 5.08 (dd, 1 H, $J_{3,4}$ = 3.1 Hz, H-3), 5.13 (t, $J_{2,3}$ = 9.9 Hz, 1 H, H-2), 5.43 (d, 1 H, $J_{4,5} < 0.5$, H-4), 7.21 (d, J_{vic} = 8.2 Hz, 2 H, CH_3Ar), 7.71 (d, J_{vic} = 8.2 Hz, 2 H, CH_3Ar). ^{13}C NMR ($CDCl_3$): δ = 9.5 (SCH_2CH_3), 20.8, 20.9, 21.0 (4 $COCH_3$), 23.5 (CH_3Ar), 37.7 (SCH_2CH_3), 61.7 (C-6), 67.3 (C-3), 68.8 (C-4), 72.9 (C-2), 78.1 (C-5), 93.1 (C-1), 126.3, 129.9 (2 × 2 CH, CH_3Ar), 144.1, 142.9 (2 C-arom. quat., CH_3Ar), 171.3, 171.8, 172.4, 172.5 (4 $COCH_3$). HRMS ($C_{23}H_{31}NO_{11}S_2$): calcd. 561.1337; found 561.1335.

Methyl 2,3,4-Tri-*O*-acetyl-*S*-(*N*-tosylimino)-1-thio-β-L-fucopyranoside (12): Preparation from crystalline methyl 2,3,4-tri-*O*-acetyl-1-thio-β-L-fucopyranoside[23] (62 mg, 0.193 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 2:8) gave amorphous **12** (47 mg, yield: 50%) in the form of one epimer. $[\alpha]_D = +104$ ($c = 1.0$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.26 (d, J_{vic} = 6.4 Hz, 3 H, CH_3), 1.97, 2.11, 2.15 (3 s, 9 H, 3 $COCH_3$), 2.39 (s, 3 H, CH_3Ar), 2.68 (s, 3 H, SCH_3), 3.97 (dq, 1 H, H-5), 4.54 (d, $J_{1,2}$ = 9.8 Hz, 1 H, H-1), 4.99 (t, 1 H, $J_{2,3}$ = 9.8, H-2), 5.09 (dd 1 H, $J_{3,4}$ = 3.2 Hz, H-3), 5.29 (dd, 1 H, $J_{4,5}$ = 0.9 Hz, H-4), 7.26 (d, J_{vic} = 8.3 Hz, 2 H, CH_3Ar), 7.75 (d, J_{vic} = 8.0 Hz, 2 H, CH_3Ar). ^{13}C NMR ($CDCl_3$): δ = 16.2 (CH_3), 20.6, 20.7, 20.9 (3 $COCH_3$), 21.8 (CH_3Ar), 25.6 (SCH_3), 65.3 (C-4), 69.8 (C-3), 71.2 (C-2), 75.1 (C-5), 90.4 (C-1), 126.6, 129.7 (2 × 2 CH, CH_3Ar), 141.4, 142.4 (2 C-arom. quat., CH_3Ar), 169.9, 170.4, 170.9 (3 $COCH_3$). HRMS ($C_{20}H_{27}NO_9S_2$): calcd. 489.1126; found 489.1114.

Ethyl 2,3,4-Tri-*O*-acetyl-*S*-(*N*-tosylimino)-1-thio-α-L-rhamnopyranoside (13): Preparation from syrupy ethyl 2,3,4-tri-*O*-acetyl-1-thio-α-L-rhamnopyranoside[24] (230 mg, 0.688 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 2:8) gave amorphous **13** (242 mg, yield: 70%) as a 3:1 mixture of diastereomers. $[\alpha]_D = -76$ ($c = 1.0$, $CHCl_3$). ^1H NMR ($CDCl_3$) for the major epimer: δ = 1.22 (d, J_{vic} = 6.1 Hz, 3 H, CH_3), 1.38 (t, J_{vic} = 7.4 Hz, 3 H, SCH_2CH_3), 1.95, 2.04, 2.12 (3 s, 9 H, 3 $COCH_3$), 2.34 (s, 3 H, CH_3Ar), 2.85−3.07 (m, 2 H, SCH_2CH_3), 3.72 (dq, 1 H, H-5), 4.91 (d, $J_{1,2}$ = 1.7 Hz, 1 H, H-1), 5.00 (t, 1 H, $J_{4,5}$ = 9.5, H-4), 5.25 (d 1 H, $J_{3,4}$ = 9.5 Hz, H-3), 5.52 (dd, 1 H, $J_{2,3}$ = 3.6 Hz, H-2), 7.23 (d, J_{vic} = 8.2 Hz, 2 H, CH_3Ar), 7.80 (d, J_{vic} = 8.2 Hz, 2 H, CH_3Ar); for the minor epimer: δ = 1.22 (d, J_{vic} = 6.5 Hz, 3 H, CH_3); 1.38 (t, J_{vic} = 6.5 Hz, 3 H, SCH_2CH_3), 1.97, 2.05, 2.13 (3 s, 9 H, 3 $COCH_3$), 2.36 (s, 3 H, CH_3Ar), 2.85−3.07 (m, 2 H, SCH_2CH_3), 3.92 (dq, 1 H, H-5), 4.36 (d, $J_{1,2}$ = 2.1 Hz, 1 H, H-1), 5.02 (t, 1 H, $J_{4,5}$ = 9.5, H-4), 5.21 (d 1 H, $J_{3,4}$ = 9.5 Hz, H-3), 5.65 (dd, 1 H, $J_{2,3}$ = 3.5 Hz, H-2), 7.21 (d, J_{vic} = 7.8 Hz, 2 H, CH_3Ar), 7.78 (d, J_{vic} = 8.8 Hz, 2 H, CH_3Ar). ^{13}C NMR ($CDCl_3$) for the major epimer: δ = 7.1 (SCH_2CH_3), 17.9 (CH_3), 20.7−21.8 (3 $COCH_3$), 21.9 (CH_3Ar), 40.9 (SCH_2CH_3), 66.6 (C-2), 68.2 (C-3), 70.6 (C-4), 73.5 (C-5), 91.5 (C-1), 126.2−129.9 (4 CH, CH_3Ar), 135.8, 139.9 (2 C-arom. quat., CH_3Ar), 169.0−169.7 (3 $COCH_3$); for the minor epimer: δ = 7.0 (SCH_2CH_3), 17.8 (CH_3), 20.0−21.9 (3 $COCH_3$), 21.8 (CH_3Ar), 34.3 (SCH_2CH_3), 66.6 (C-2), 69.3 (C-3), 71.6 (C-4), 75.4 (C-5), 90.7 (C-1), 126.2−129.9 (4 CH, CH_3Ar), 141.4, 143.5 (2 C-arom. quat., CH_3Ar), 168.3−169.7 (3 $COCH_3$). HRMS ($C_{21}H_{29}NO_9S_2$): calcd. 503.1283; found 503.1269.

Ethyl 2,3,4-Tri-*O*-acetyl-*S*-(*N*-tosylimino)-1-thio-β-L-rhamnopyranoside (14): Preparation from syrupy ethyl 2,3,4-tri-*O*-acetyl-1-thio-β-L-rhamnopyranoside[24] (112 mg, 0.335 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 2:8) gave amorphous **14** (118 mg, yield 70%) in the form of one epimer. $[\alpha]_D = +97$ ($c = 1.0$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.23 (d, J_{vic} = 6.1 Hz, 3 H, CH_3), 1.27 (t, J_{vic} = 7.3 Hz, 3 H, SCH_2CH_3), 1.98, 2.06, 2.09 (3 s, 9 H, 3 $COCH_3$), 2.38 (s, 3 H, CH_3Ar), 2.99−3.15 (m, 2 H, SCH_2CH_3), 3.68 (dq, 1 H, H-5), 4.81 (d, $J_{1,2}$ = 1.2 Hz, 1 H, H-1), 5.04−5.06 (m, 2 H, H-3, H-4), 5.73 (dd, 1 H, $J_{2,3}$ = 2.7 Hz, H-2), 7.22 (d, J_{vic} = 8.5 Hz, 2 H, CH_3Ar), 7.73 (d, J_{vic} = 8.3 Hz, 2 H, CH_3Ar). ^{13}C NMR ($CDCl_3$): δ = 7.3 (SCH_2CH_3), 17.9 (CH_3), 20.9−21.1 (3 $COCH_3$), 21.8 (CH_3Ar), 40.8 (SCH_2CH_3), 65.9 (C-2), 69.9, 71.3 (C-3, C-4), 76.8 (C-5), 89.6 (C-1), 126.3, 129.7 (2 × 2 CH, CH_3Ar), 141.1, 142.4 (2 C-arom. quat., CH_3Ar), 169.3−170.2 (3 $COCH_3$). HRMS ($C_{21}H_{29}NO_9S_2$): calcd. 503.1283; found 503.1277.

Ethyl 2,3,4,6-Tetra-*O*-acetyl-*S*-(*N*-tosylimino)-1-thio-β-D-galactofuranoside (15): Preparation from syrupy ethyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactofuranoside[25] (115 mg, 0.293 mmol) according to Procedure A and purification by column chromatography (petroleum ether/ethyl acetate, 2:8) gave amorphous **15** (115 mg, yield 70%) in the form of one epimer. $[\alpha]_D = -47$ ($c = 1.8$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.26 (t, J_{vic} = 7.2 Hz, 3 H, SCH_2CH_3), 2.05, 2.11, 2.12 (3 s, 12 H, 4 $COCH_3$), 2.38 (s, 3 H, CH_3Ar), 2.88−3.10 (m, 2 H, SCH_2CH_3), 4.09 (dd, 1 H, $J_{5,6b}$ = 6.6, H-6b), 4.29 (dd, 1 H, $J_{5,6a}$ = 4.5, $J_{6a,6b}$ = −12.2, H-6a), 4.31 (dd, 1 H, $J_{4,5}$ = 4.5 Hz, H-4), 5.10 (d, $J_{1,2}$ = 1.5 Hz, 1 H, H-1), 5.14 (dd, 1 H, $J_{3,4}$ = 3.6 Hz, H-3), 5.24−5.31 (m, 1 H, H-5), 5.66 (d, 1 H, $J_{2,3} < 0.5$, H-2), 7.24 (d, J_{vic} = 7.9 Hz, 2 H, CH_3Ar), 7.79 (d, J_{vic} = 8.1 Hz, 2 H, CH_3Ar). ^{13}C NMR ($CDCl_3$): δ = 7.3 (SCH_2CH_3), 20.8−21.1 (4 $COCH_3$), 21.8 (CH_3Ar), 41.0 (SCH_2CH_3), 62.5 (C-6), 69.5 (C-3), 76.8 (C-5), 77.6 (C-2), 85.8 (C-4), 97.0 (C-1), 128.6, 129.6 (2 × 2

CH, CH_3*Ar*), 141.2, 142.4 (2 C-arom. quat., CH_3*Ar*), 168.8, 170.0, 170.2, 170.8 (4 *CO*CH_3). HRMS ($C_{23}H_{31}NO_{11}S_2$): calcd. 561.1337; found 561.1330.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-α-D-glucofuranose (16): Treatment of the glycosyl donor **4** with 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (50 mg, 0.192 mmol) as acceptor according to Procedure B (15 min) and purification by column chromatography (petroleum ether/ethyl acetate, 8:2) furnished **16** together with 1,2:3,5-di-*O*-isopropylidene-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α- and -β-D-glucopyranosyl)-α-D-glucofuranose as a side-product (Table 3). The physical data were in accordance with the literature.[26]

1,2:3,4-Di-*O*-isopropylidene-6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-α- and -β-D-galactopyranose (17): Treatment of **4** with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (55 mg, 0.211 mmol) as acceptor according to Procedure B (15 min; chromatography: petroleum ether/ethyl acetate, 7:3, 6:4 and 1:1) furnished **17**[27] (Table 3).

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucofuranose and 1,2:3,5-Di-*O*-isopropylidene-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucofuranose (18): Treatment of the glycosyl donor **1** with 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (77 mg, 0.296 mmol) as acceptor according to Procedure C (5 h; chromatography: petroleum ether/ethyl acetate, 7:3, 6:4 and 1:1) furnished **18**[28] (Table 4).

1,2:3,4-Di-*O*-isopropylidene-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-galactopyranose (19): Treatment of **1** with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (79 mg, 0.303 mmol) as acceptor according to Procedure C (4 h; chromatography: petroleum ether/ethyl acetate, 8:2) furnished **19**[27] (Table 4).

***p*-Methoxyphenyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (20):** Treatment of **1** with 4-methoxyphenol (13 mg, 0.105 mmol) as acceptor according to Procedure C (2.5 h; chromatography: petroleum ether/ethyl acetate, 7:3) furnished **20** (43 mg, yield 91%).[29]

5-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-3,4-di-*O*-benzoyl-1,2-*O*-isopropylidene-β-D-fructopyranose (21): Treatment of **1** with 1,2-*O*-isopropylidene-3,4-di-*O*-benzoyl-β-D-fructopyranose[30] (60 mg, 0.140 mmol) as acceptor according to Procedure C (5 h; chromatography: petroleum ether/ethyl acetate, 6:4) furnished **21** as a syrup (77 mg, yield 72%). $[\alpha]_D = -81$ (c = 3.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.41, 1.51 (2 s, 6 H, 2 CH_3 *iPrd*), 1.62, 2.03, 2.04 (3 s, 12 H, 4 COCH_3), 3.66−3.79 (dt, 1 H, H-5), 3.83 (dd, 1 H, $J_{5',6'b}$ = 2.9, H-6′b), 4.04−4.09 (m, 2 H, H-6a, H-6b), 3.98 (d, 1 H, $J_{1'a,1'b}$ = −8.5, H-1′b), 4.09 (d, 1 H, H-1′a), 4.13 (d, 1 H, $J_{5',6'a} < 0.5$, $J_{6'a,6'b} = -12.3$, H-6′a), 4.31 (dd, 1 H, H-2), 4.38−4.39 (m, 1 H, H-5′), 4.80 (dd, 1 H, $J_{4,5}$ = 9.4 Hz, H-4), 5.07 (t, 1 H, $J_{2,3} = J_{3,4}$ = 3.4 Hz, H-3), 5.48 (dd, 1 H, $J_{4',5'}$ = 3.4, H-4′), 5.57 (d, $J_{1,2}$ = 7.1 Hz, 1 H, H-1), 5.83 (d, 1 H, $J_{3',4'}$ = 10.4, H-3′), 7.29−7.38 (m, 2 H, Bz), 7.44−7.51 (m, 4 H, Bz), 7.89−8.00 (m, 4 H, Bz). $^{-13}$C NMR ($CDCl_3$): δ = 21.2−22.4 (4 COCH_3), 26.6, 26.9 (2 CH_3, *iPrd*), 63.3 (C-6), 63.9 (C-6′), 67.5 (C-3′), 67.7 (C-5), 68.3 (C-4), 69.9 (C-5′), 70.4 (C-3), 71.8 (C-4′), 72.2 (C-1′), 73.8 (C-2), 97.4 (C-1), 106.8 (C-2′), 114.4 (Cquat., *iPrd*), 124.0, 130.6 (2 C-arom. quat., Bz), 128.6−135.5 (10 CH Bz), 168.1, 168.2, 171.2, 171.7, 172.8 (4 *CO*CH_3, 2 *CO* Bz). HRMS ($C_{37}H_{42}O_{17}$): calcd. 758.2419; found 758.2415.

Methyl 3-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (22): Treatment of **1** with methyl 4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside[31] (33 mg, 0.124 mmol) as acceptor according to Procedure C (4 h; chromatography: petroleum ether/ethyl acetate, 6:4) furnished **22** (40 mg, yield 54%). $[\alpha]_D^{20} = +27$ (c = 2.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.78 (ddd, 1 H, $J_{2'b,3'}$ = 11.3, H-2′b), 2.13 (dd, 1 H, $J_{2'a,3'}$ = 5.3, $J_{2'a,2'b}$ = −13.4, H-2′a), 1.97, 1.99, 2.01 (3 s, 12 H, 4 COCH_3), 3.33 (s, 3 H, OMe), 3.44 (dt, 1 H, H-5), 3.65 (t, 1 H, $J_{3',4'} = J_{4',5'}$ = 9.4, H-4′), 3.72−3.82 (m, 2 H, H-6′b, H-3′), 3.87 (dd, 1 H, $J_{5,6b}$ = 2.3, H-6b), 4.08 (dd, 1 H, $J_{5,6a}$ = 3.8, $J_{6a,6b}$ = −12.1, H-6a), 4.16 (dt, 1 H, H-5′), 4.22 (m, 1 H, H-6′a), 4.67 (d, $J_{1,2}$ = 7.8 Hz, 1 H, H-1), 4.78 (d, 1 H, $J_{1',2'}$ = 3.4, H-1′), 4.96 (t, $J_{2,3}$ = 8.9 Hz, 1 H, H-2), 5.06 (t, 1 H, H-4), 5.13(t, $J_{3,4}$ = 8.9 Hz, 1 H, H-3), 5.58 (s, 1 H, H-7′), 7.33−7.49 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$): δ = 21.0−21.1 (4 COCH_3), 36.5 (C-2′), 55.2 (OMe), 61.9 (C-6), 63.2 (C-3′,), 68.4 (C-2), 69.4 (C-6′), 71.1 (C-5′), 72.2 (C-4), 73.3 (C-3), 75.2 (C-5), 82.3 (C-4′), 99.1 (C-1′), 101.1 (C-1), 101.9 (C-7′), 126.3−129.5 (5 CH, Ph), 139.8 (C-arom. quat., Ph), 171.6, 171.7, 172.7, 173.1 (4 *CO*CH_3). HRMS ($C_{28}H_{36}O_{14}$): calcd. 596.2103; found 596.2097.

Methyl 3-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-4,6-*O*-benzylidene-2-deoxy-2-*C*-methyl-α-D-altropyranoside (23): Treatment of **1** with methyl 4,6-*O*-benzylidene-2-deoxy-2-*C*-methyl-α-D-altropyranoside[32] (36 mg, 0.128 mmol) as acceptor according to Procedure C (6 h; chromatography: toluene/ethyl acetate, 7:3) furnished **23** (36 mg, yield 46%). $[\alpha]_D^{20} = +47$ (c = 1.7, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.15 (d, 3 H, J = 7.7, CH_3), 1.98, 1.99, 2.01, 2.06 (4 s, 12 H, 4 COCH_3), 2.38 (dd, 1 H, $J_{2',3'}$ = 2.6, 2′-H), 3.34 (s, 3 H, OMe), 3.60 (ddd, 1 H, $J_{5,6a}$ = 2.9, $J_{5,6b}$ = 4.1, 5-H), 3.72 (t, 1 H, $J_{5',6b'}$ = 10.0, 6′-Hb), 3.81 (dd, 1 H, $J_{3',4'}$ = 2.6, $J_{4',5'}$ = 9.4, 4′-H), 3.99 (t, 1 H, 3′-H), 4.10 (dd, 1 H, $J_{5',6a'}$ = 5.1, $J_{6a',6b'}$ = −10.0, 6′-Ha), 4.19 (ddd, 1 H, 5′-H), 4.10−4.36 (m, 2 H, 6-Ha, 6-Hb), 4.39 (s, 1 H, 1′-H), 4.90 (d, 1 H, $J_{1,2}$ = 7.4, 1-H), 5.07 (t, 1 H, $J_{3,4}$ = 9.4, 4-H), 5.12 (t, 1 H, 3-H), 5.21(t, 1 H, $J_{2,3}$ = 9.4, 2-H), 5.52 (s, 1 H, 7′-H), 7.33−7.57 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$): δ = 16.8 (CH_3), 21.0−21.1 (4 COCH_3), 40.2 (C-2′), 55.4 (OMe), 58.6 (C-5′), 62.4 (C-6′), 69.0 (C-5), 69.9 (C-6), 71.5 (C-4), 71.9 (C-2), 73.1 (C-3), 76.1 (C-3′), 77.3 (C-4′), 100.9 (C-1), 102.6 (C-1′, C-7′), 126.3−129.3 (5 CH, Ph), 137.5 (C-arom. quat., Ph), 169.3, 169.4, 170.4, 170.8 (4 *CO*CH_3). HRMS ($C_{29}H_{38}O_{14}$): calcd. 610.2259; found 610.2251.

5-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-3,4-di-*O*-benzyl-1,2-*O*-isopropylidene-β-L-sorbopyranose (24): Treatment of **1** with 3,4-di-*O*-benzyl-1,2-*O*-isopropylidene-β-L-sorbopyranose[33] (61 mg, 0.152 mmol) as acceptor according to Procedure C (3 h; chromatography: petroleum ether/ethyl acetate, 7:3) furnished **24** (72 mg, yield: 65%). $[\alpha]_D = -22$ (c = 3.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 1.43, 1.48 (2 s, 6 H, 2 CH_3 *iPrd*), 1.81, 1.99, 2.02, 2.08 (4 s, 12 H, 4 COCH_3), 3.35 (d, $J_{3,4}$ = 8.9 Hz, 1 H, H-3), 3.65−3.84 (m, 5 H, H-4′, H-5, H-5′, H-6′a, H-6′b), 3.80 (d, 1 H, $J_{1'a,1'b}$ = −8.5, H-1′b), 3.89 (d, 1 H, H-1′a), 4.12 (dd, 1 H, $J_{5,6b}$ = 2.3, $J_{6a,6b}$ = −12.1, H-6b), 4.24 (dd, 1 H, $J_{5,6a}$ = 4.6, H-6a), 4.60 (d, 1 H, J = −11.5, CH_2Ph), 4.77 (s, 2 H, CH_2Ph), 4.85 (d, $J_{1,2}$ = 7.8 Hz, 1 H, H-1), 4.90 (d, 1 H, J = −11.5, CH_2Ph), 5.02 (dd, 1 H, H-2), 5.06 (t, $J_{4,5}$ = 9.4 Hz, 1 H, H-4), 5.20 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.4 Hz, H-3), 7.24−7.38 (m, 10 H, 2 CH_2*Ph*). ^{13}C NMR ($CDCl_3$): δ = 20.7, 20.8, 20.9, 21.1 (4 COCH_3), 26.5, 27.5 (2 CH_3, *iPrd*), 62.3, 62.4 (C-6, C-6′), 68.8 (C-4), 71.8, 72.1 (C-2, C-5), 73.4 (C-3), 75.7, 75.8 (2 CH_2Ph), 78.5 (C-3′), 79.9, 83.1 (C-4′, C-5′), 101.4 (C-1), 105.2 (C-2′), 112.6 (C-quat., *iPrd*), 126.3−130.1 (10 CH, 2 CH_2*Ph*), 138.3, 138.6 (2 C-arom. quat., CH_2*Ph*), 169.6, 169.8, 170.6, 170.9 (4 *CO*CH_3). HRMS ($C_{37}H_{46}O_{15}$): calcd. 730.2834; found 730.2828.

Methyl 4-*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (25): Treatment of **1** with methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside[34] (63 mg, 0.136 mmol) as acceptor according to Procedure C (4 h; chromatography: petroleum ether/ethyl acetate, 7:3) furnished **25** (98 mg, yield 91%).[35]

***p*-Methoxyphenyl 2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranoside (26):** Treatment of the glycosyl donor **8** with 4-methoxyphenol (30 mg, 0.241 mmol) as acceptor according to Procedure C (2.5 h; chromatography: petroleum ether/ethyl acetate, 7:3) furnished **26** (66 mg, yield 60%).[36]

1,2:3,4-Di-*O*-isopropylidene-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-galactopyranose (27): Treatment of **8** with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (48 mg, 0.184 mmol) as acceptor according to Procedure C (5 h; chromatography: petroleum ether/ethyl acetate, 7:3) furnished **27** (92 mg, yield 85%). $[\alpha]_D = +3$ ($c = 3.0$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.32, 1.40, 1.53 (3 s, 12 H, 4 CH_3, *iPrd*), 1.96, 2.02, 2.08, 2.13 (4 s, 12 H, 4 COCH_3), 3.69 (dd, 1 H, $J_{5,6b} = 3.9$, $J_{6a,6b} = -10.2$, H-6b), 3.77 (dd, 1 H, $J_{5,6a} = 4.6$, H-6a), 3.95 (dt, 1 H, $J_{5',6'a} = J_{5',6'b} = 6.3$, H-5′), 4.03−4.14 (m, 2 H, H-5, H-6′b), 4.22 (dd, 1 H, $J_{4',5'} = 1.9$, H-4′), 4.27−4.32 (m, 2 H, H-2′, H-6′a), 4.60 (dd, 1 H, $J_{2',3'} = 2.4$, $J_{3',4'} = 7.9$, H-3′), 4.84 (d, $J_{1,2} = 1.8$ Hz, 1 H, H-1), 5.22−5.34 (m, 3 H, H-2, H-3, H-4), 5.48 (d, 1 H, $J_{1',2'} = 4.9$, H-1′). ^{13}C NMR ($CDCl_3$): δ = 21.0, 21.1, 21.2, 21.3 (4 COCH_3), 24.7, 25.3, 26.3, 26.5 (4 CH_3, *iPrd*), 62.7(C-6′), 66.7 (C-5′), 67.4 (C-6), 68.9 (C-5), 66.4, 69.6, 69.8 (C-2, C-3, C-4), 70.9 (C-2′, C-3′), 71.2 (C-4′), 96.6 (C-1′), 98.2 (C-1), 109.1, 109.7 (2 C-quat., *iPrd*), 170.2, 170.3, 170.4, 171.1 (4 *CO*CH_3). HRMS ($C_{26}H_{38}O_{15}$): calcd. 590.2208; found 590.2211.

***p*-Methoxyphenyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranoside (28):** Treatment of the glycosyl donor **13** with 4-methoxyphenol as acceptor (17 mg, 0.137 mmol) according to Procedure C (2.5 h; chromatography: petroleum ether/ethyl acetate, 8:2) furnished **28** (51 mg, yield 94%). $[\alpha]_D = -61$ ($c = 2.5$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.2 (d, $J_{vic} = 6.4$ Hz, 3 H, CH_3), 2.02, 2.05, 2.17 (3 s, 9 H, 3 COCH_3), 3.76 (s, 3 H, OMe), 4.05 (dt, 1 H, H-5), 5.13 (t, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 5.33 (s, 1 H, $J_{1,2} < 0.5$, H-1), 5.41 (d, $J_{2,3} = 3.4$ Hz, 1 H, H-2), 5.49 (dd, 1 H, H-3), 6.82 (d, $J_{vic} = 9.1$ Hz, 2 H, *Ph*OMe), 6.99 (d, $J_{vic} = 8.9$ Hz, 2 H, *Ph*OMe). ^{13}C NMR ($CDCl_3$): δ = 19.2 (CH_3), 22.4, 22.5, 22.6 (3 COCH_3), 57.3 (OMe), 68.7 (C-5), 70.7 (C-3), 71.5 (C-2), 72.7 (C-4), 98.2 (C-1), 116.3, 119.3 (2 × 2 CH, *Ph*OMe), 151.6, 156.9 (2 C-arom. quat.), 171.6, 171.7, 171.8 (3 *CO*CH_3). HRMS ($C_{19}H_{24}O_9$): calcd. 396.1419; found 396.1424.

1,2:3,4-Di-*O*-isopropylidene-6-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-D-galactopyranose (29): Treatment of **13** with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (52 mg, 0.200 mmol) as acceptor according to Procedure C (5 h; chromatography: petroleum ether/ethyl acetate, 7:3) furnished **29** (53 mg, yield 50%).[37]

1,2:3,4-Di-*O*-isopropylidene-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactofuranosyl)-α-D-galactopyranose (30): Treatment of the glycosyl donor **15** with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (27 mg, 0.104 mmol) as acceptor according to Procedure C (3 h; chromatography: petroleum ether/ethyl acetate, 6:4) furnished **30** (51 mg, yield 83%). $[\alpha]_D = -70$ ($c = 1.0$, $CHCl_3$). ^1H NMR ($CDCl_3$): δ = 1.31, 1.32, 1.43, 1.52 (4 s, 12 H, 4 CH_3, *iPrd*), 2.04, 2.06, 2.08, 2.12 (4 s, 12 H, 4 COCH_3), 3.57 (dd, 1 H, $J_{5',6'b} = 6.6$, $J_{6'a,6'b} = -9.6$, H-6′b), 3.84 (dd, 1 H, $J_{5',6'a} = 6.6$, H-6′a), 3.96 (m, 1 H, H-5′), 4.17 (dd, 1 H, $J_{5,6b} = 7.7$, H-6b), 4.24 (dd, 1 H, $J_{4',5'} = 1.9$, $J_{3',4'} = 7.9$, H-4′), 4.29 (dd, 1 H, $J_{4,5} = 7.5$ Hz, H-4), 4.30 (dd, 1 H, H-2′), 4.37 (dd, 1 H, $J_{5,6a} = 3.6$, $J_{6a,6b} = -11.9$, H-6a), 4.59 (dd, 1 H, $J_{2',3'} = 2.3$, $J_{3',4'} = 7.9$, H-3′), 4.94 (dd, 1 H, $J_{3,4} = 5.7$, H-3), 5.06 (d, $J_{2,3} = 1.9$ Hz, 1 H, H-2), 5.08 (s, 1 H, $J_{1,2} < 0.5$, H-1), 5.41 (m, 1 H, H-5), 5.50 (d, 1 H, $J_{1',2'} = 5.1$, H-1′). ^{13}C NMR ($CDCl_3$): δ = 20.7, 20.8, 20.9 (4 COCH_3), 24.7, 24.9, 25.9, 26.1 (4 CH_3, *iPrd*), 63.1 (C-6), 64.9 (C-6′), 65.5 (C-5′), 69.3 (C-5), 70.8, 70.5 (C-3, C-4′), 76.6 (C-3), 77.4 (C-4), 80.1 (C-2′), 81.1 (C-2), 96.2 (C-1′), 104.8 (C-1), 108.6, 109.3 (2 C-quat., *iPrd*), 169.6, 169.9, 170.1, 170.7 (4 *CO*CH_3). HRMS ($C_{26}H_{38}O_{15}$): calcd. 590.2208; found 590.2202.

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