Investigations on Leaving Group Based Intra- versus Intermolecular Glycoside Bond Formation

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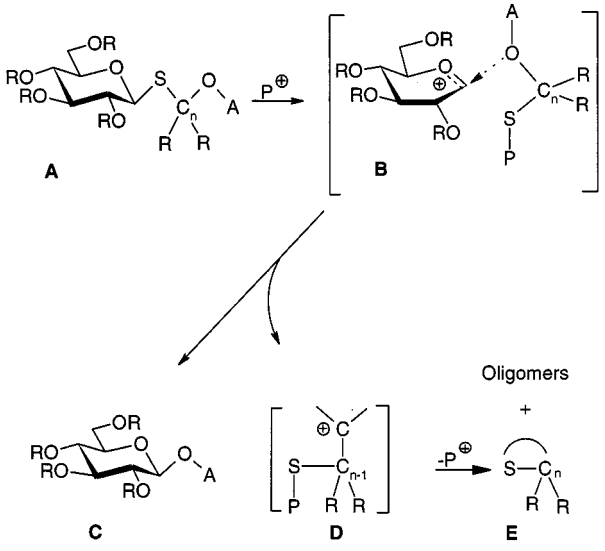
Dedicated to Professor Richard Neidlein on the occasion of his 70th birthday

Keywords: Carbohydrates / Glycosides / Glycosylations / Oligosaccharides

Ligation of the glycosyl donor to the glycosyl acceptor through the leaving group was performed with the aim of enforcing glycoside bond formation by an intramolecular (1.x)-shift. To this end, syntheses of alkoxymethyl (**2a** and **b**), 2-alkoxyethyl (**10a** and **b**, **13a**, **16a**), 3-alkoxypropenyl (**27a** and **b**), and 7-alkoxy-4-oxaheptadienyl thioglucopyranoside derivatives (**35a**,**b** and **d**) were carried out. Their activation with thiophilic promoter systems gave the expected glucopyranosides **5a**,**b** and **d** in up to high chemical yields, yet modest anomeric control. Competition experiments showed that an intermolecular reaction course is favored in these reactions, although model considerations imply that convenient intramolecular (1,3)-, (1,4)-, (1,5)-, and (1,9)-shifts, respectively, of the glycosyl donor to the acceptor are possible.

Introduction

Glycosyl transfer within the active site of a glycosyltransferase can be regarded as an intramolecular process in which the anomeric center of the glycosyl donor and the accepting moiety are held in close proximity, thus enforcing the regio- and diastereoselectivity of the reaction.[1,2] For corresponding in-vitro intramolecular glycosylations, linkers/spacers are required to connect the donor and the acceptor moieties appropriately. Linkers have been attached to functional groups on the donor;[3−15] mainly to the hydroxy group vicinal to the anomeric center,[3−10] thus preferentially furnishing either α- or β-products, depending on the configuration of the 2-hydroxy group. Particularly versatile and high yielding was the "rigid spacer" concept, recently introduced by us, which provides α- or β-products as desired.[15] We have also investigated linkage of the donor and the acceptor via the leaving group (leaving group based concept), which is rather attractive for preparative reasons.[11,13] However, success in this endeavor has thus far been erratic, because competition was occurring between intra- and intermolecular processes.[13] Building on this concept, we have now carried out a study using as glycosyl donors different thioglycosides bearing the glycosyl acceptor by means of a C_n bridge (n = 1,2,3, and 7) at the sulfur atom.[16,17] As shown in Scheme 1, after generation of a glycosyl cation intermediate **B** from **A**, with the help of a thiophilic promoter **P**, intramolecular attack could take place at the accepting oxygen atom, yielding glycoside **C** by an (n + 2)-shift with release of a (stabilized) carbenium ion **D**, and this in turn could provide **E** and **P**. The results of our study are communicated in this paper.



Scheme 1. General reaction scheme

Results and Discussion

For the construction of starting materials with a C_1 bridge, 2,3,4,6-tetra-*O*-benzyl-1-thioglucose (**1**)[18] (Scheme 2) was treated with chloromethyl ethyl ether in the presence of sodium hydride as base to afford ethoxymethyl thioglucoside **2a** directly. The corresponding *O*,*S*-acetal **2b**, with a sugar residue as acceptor, was obtained from methyl 6-*O*-acetyl-2,3,4-tri-*O*-benzylglucoside (**3**), which was converted with the Tebbe reagent[19] into enol ether **4**. Treatment of **4** and **1**[18] with $ZnCl_2$·OEt_2 complex as catalyst gave **2b** in 56% yield (1:1 mixture of diastereoisomers). Reaction of **2a** with various promoter systems (Table 1) furnished ethyl glucopyranosides **5aα,β**[20] in up to 69% yield; the α/β ratios exhibited only low anomer selectivity, al-

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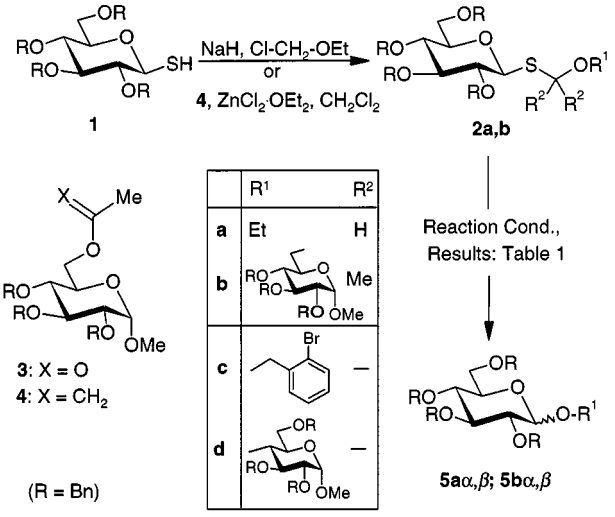
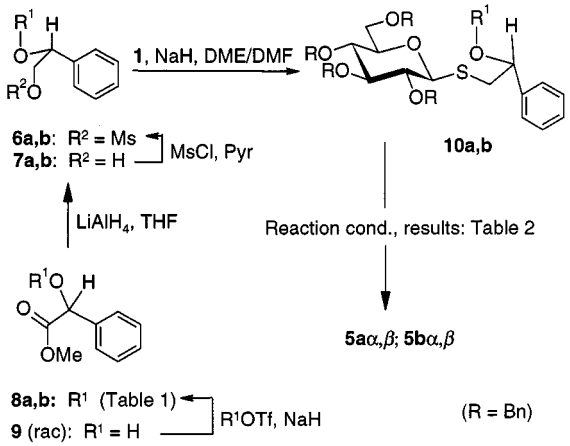


Scheme 2. Synthesis of starting materials **2a** and **b** and their transformations



Scheme 3. Synthesis of starting materials **10a** and **b** and their transformations

Table 1. Glycosylation results with **2a** and **b** in dichloromethane

	Temp.	Promoter	Product	Yield (%)	α,β
2a	room temp.	TMSOTf (0.7 equiv.)	**5a**	69	2:1
	−10 °C	TMSOTf (1.0 equiv.)	**5a**	39	2:3
	room temp.	$ZnCl_2$·OEt_2(2.0 equiv.)	**5a**	46	1:3
2b	room temp.	DMTST (1.1 equiv.)	**5b**	27	1:1

Table 2. Glycosylation results with **10a** and **10b** and DMTST (1.1 equiv.) as promoter

	Solvent	Temp.	Product	Yield (%)	α,β
10a	CH_2Cl_2	room temp.	**5a**	80	1:2
	CH_2Cl_2	0 °C	–	0	–
	MeCN	room temp.	**5a**	49	1:3
10b	CH_2Cl_2	room temp.	**5b**	51/43[a]	1.5:1/1.4:1[a]
	$ClCH_2CH_2Cl$	50	**5b**	60	2:1
	MeCN	room temp.	**5b**	44/44[a]	1:3/1:2[a]

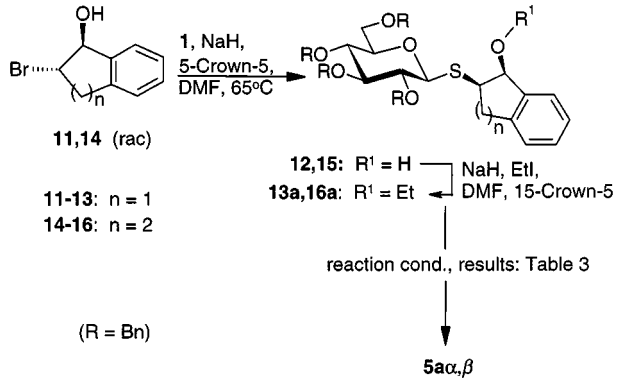
[a] Results from the two diastereoisomers.

though retention of configuration had been expected to be preferred. Similar results were obtained with **2b**, affording known disaccharides **5bα,β**.[21,25]

Therefore, we turned our attention to C_2-bridged systems in which the anomeric oxygen atom could be situated quite close conformationally to the anomeric center, via five connected atoms (Scheme 3). To this end, racemic methyl mandelate (**9**)[22] was *O*-alkylated with ethyl trifluoromethanesulfonate (R^1−OTf, R^1 = Et) and also with the 6-*O*-trifluoromethanesulfonate of methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside,[23] affording compounds **8a** and **b**. Reduction with lithium aluminum hydride in THF furnished diol derivatives **7a** and **b**, which upon treatment with methanesulfonyl (mesyl) chloride in pyridine gave mesylates **6a** and **b** in quantitative yields. Treatment of these with 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucose[18] (**1**), in DME/DMF mixtures as solvent and in the presence of NaH as base, afforded β-thioglycosides **10a** and **b** as mixtures of two diastereoisomers; **10b** was separated by chromatography (→ **10b*h*** and **10b*l***). Treatment of **10a** with dimethyl(methylthio)sulfonium triflate (DMTST) as promoter, in dichloromethane as solvent and under standard conditions,[24] afforded ethyl glycosides **5aα/β** in up to 80% yield with the expected preference for the β-anomer (Table 2). In acetonitrile as solvent, lower yields but slightly higher β-selectivities[11b,25] were observed. With **10b**, the two diastereoisomers **10b*h*** and **10b*l*** were investigated separately. In acetonitrile as solvent, yields and anomer selectivity in products **5b** was very similar, while in dichloromethane and 1,2-dichloroethane as solvent, even a preference for the formation of the α-anomers was observed.

Because of the conformational flexibility in the C_2-bridged systems **10a** and **b**, a related but more rigid cyclic system was investigated. To this end, *trans*-2-bromo-1-hydroxyindane (**11**)[22] and its homologue **14**[26] (Scheme 4) were transformed using 1-thioglucoside **1**[18] into *cis*-substituted derivatives **12*h,l*** and **15**, respectively. Treatment of these with ethyl iodide in the presence of NaH as base and 15-crown-5 in DMF as solvent furnished the desired model compounds **13a** and **16a**. From **13a** under standard glycosylation conditions,[24] yields of **5aα,β** were up to 80% (Table 3); however, only in acetonitrile at room temp. or in dichloromethane at −20 °C as solvents was the expected preference for the β-anomer observed. Transformation of **16a** into **5a** exhibited similar behavior, but somewhat lower product yields were obtained than those observed for the transformation of **13a**.

The low anomer selectivities with systems **2**, **10**, **13**, and **16** were reason to doubt the intramolecular reaction course in the glycosylations. Therefore, system **13** was investigated more carefully. Proper design of competition experiments can readily distinguish between intramolecular and intermolecular reaction courses.[13,17] To this end, two different glycosyl donor and acceptor moieties, each of approximately similar reactivity, have to be ligated through the leaving group. Tetra-*O*-benzylglucose **17**[27] and tetra-*O*-(3-methylbenzyl)glucose **18**[13,17] should fulfil this donor requirement (Scheme 5). Similar acceptor properties were ex-



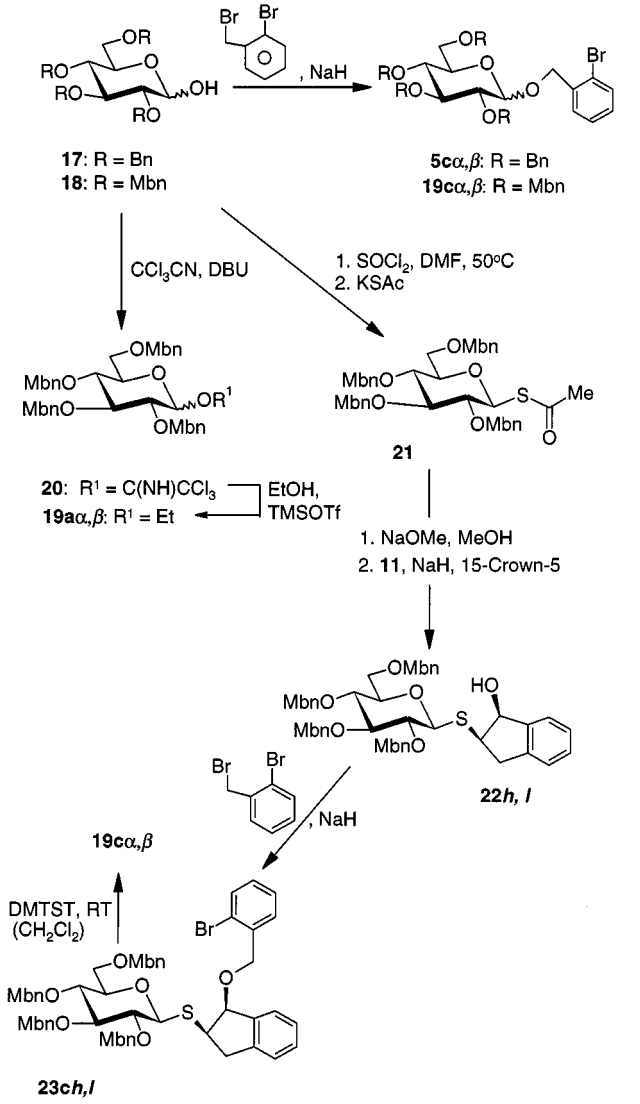
Scheme 4. Synthesis of **13a** and **16a** and their transformation into **5aα,β**

Table 3. Formation of glycosides **5aα,β** from **13a** and **16a**

	Solvent	Temp.	Promoter	Yield (%)	α,β
13a	CH_2Cl_2	room temp.	DMTST (1.1 equiv.)	80	1:1
	CH_2Cl_2	−20 °C	DMTST (2.0 equiv.)	24	1:3
	CH_2Cl_2	room temp.	MeOTf (1.2 equiv.)	78	1:1
	Toluene	room temp.	MeOTf (2.0 equiv.)	70	1:1
	MeCN	room temp.	DMTST (1.5 equiv.)	47	1:3
16a	CH_2Cl_2	room temp.	MeOTf (1.2 equiv.)	60	1:1

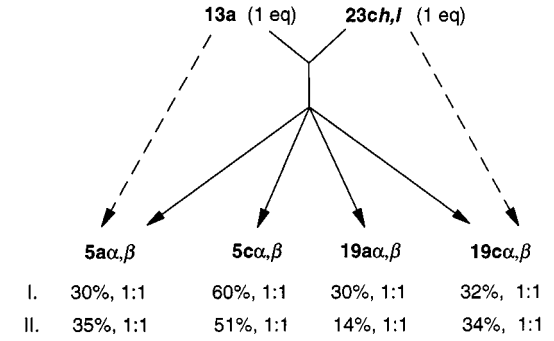
pected for primary alcohols ethanol and 2-bromobenzyl alcohol, which can readily be distinguished analytically. Transformation of **18** into trichloroacetimidate **20**,[13,17] followed by reaction with ethanol under standard conditions, gave ethyl glucosides **19aα,β**. The required Mbn-protected starting material was also obtained from **18**; reaction with thionyl chloride, and then with potassium thioacetate, gave 1-acetylthio derivative **21**. Removal of the *S*-acetyl group with sodium methoxide/methanol (similar to Zemplén conditions)[29] and immediate reaction with indane derivative **11** gave hydroxyindanyl thioglycosides **22*h,l***, which were separated by chromatography. Anomeric *O*-alkylation of **22*h,l*** with 2-bromobenzyl bromide furnished the desired starting material **23*h,l*** required for the competition experiments. Activation of **23c*h,l*** under standard conditions (DMTST, room temp., CH_2Cl_2) was also a means to obtain glycosides **19cα,β** (yield 64%, α:β = 1:1).

Competition experiments with **13a** (1 equivalent) and **23c*h,l*** (1 equivalent) in the presence of DMTST (total 5 equivalents) provided not only **5a** and **19c**, but also crossover products **5c** and **19a** (Scheme 6), thus clearly exhibiting that the glycosylations were mainly or exclusively following an intermolecular reaction course. In order to increase further the ring size for the potential intramolecular glycosyl transfer process, systems of structure **27** (Scheme 7), requiring a 1,5-shift, were investigated. This system, with the two heterocyclic rings in perpendicular arrangement, should also adopt a favorable conformation for the intramolecular glycosyl transfer;[17] facile cleavage of the C−O bond between the acceptor and the xanthene system should also be available, thus releasing the resonance-stabilized xanthylium moiety. For the synthesis of the starting material, 2-chloro-

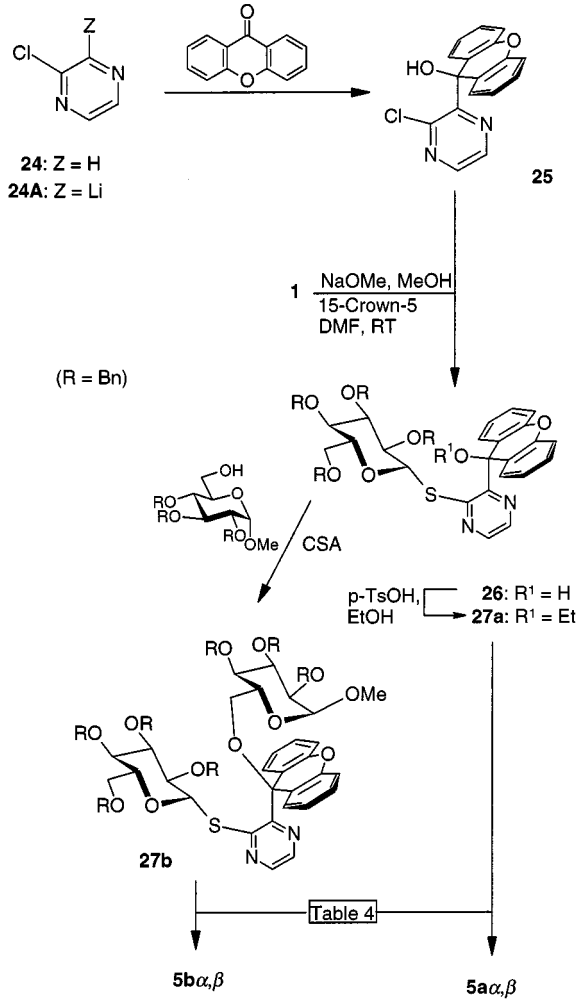


Scheme 5. Synthesis of **19a** and **c** and **23c** required for the competition experiments

pyrazine (**24**)[22] was *ortho*-lithiated (→ **24A** as intermediate);[30] reaction with xanthenone furnished addition product **25** in 82% yield. Transformation of **1**[18] into the sodium salt, and dissolution in dry DMF led, with **25** as electrophile, to thioglycoside **26** (carbinol base). Acceptor attachment to the 10-position of the xanthenol moiety could readily be achieved by acid catalysis. Thus, with excess ethanol in the presence of *p*TsOH as catalyst, 10-*O*-ethyl derivative **27a** was obtained; similarly, treatment with methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[31] and camphorsulfonic acid (CSA) as catalyst in the presence of molecular sieves furnished the corresponding 10-*O*-(glucopyranosid-6-yl) derivative **27b**. Transformation of **27a** and **27b** into glycosides **5a** and **5b**, respectively, could readily be accomplished with silver triflate as promoter (Table 4). Quite high product yields were obtained for both systems, but the α/β selectivities again were low. Addition of molecular sieves led to an increase of the retentive process, but these reactions were far from yielding a single product, as would



Scheme 6. Competition experiments with **13a** and 23***ch,l***; reagents and conditions: DMTST (5 equiv.), CH_2CI_2, room temp.; I: with **22c*h***; II: with **22c*l***



Scheme 7. Synthesis of **27a** and **b** and their transformations

be expected for an ideal intramolecular glycosyl transfer to the acceptor.

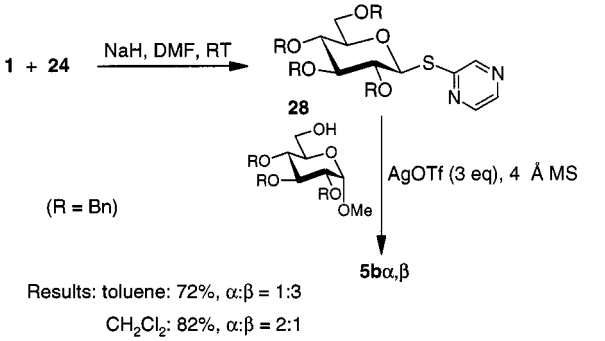
The pyrazinylthio group was investigated independently as a leaving group in glycosylation reactions (Scheme 8), since it should exhibit interesting properties.[31]

To this end, 1-thioglucose derivative **1** was transformed with **24** into the desired glycosyl donor **28**. In the context of this work, reaction with methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[32] as acceptor under the conditions described in Table 4 was investigated. The results were very similar, thus supporting the intermolecular reaction course of the transformations of **27a** and **b**.

Table 4. Glycosylation results with **27a** and **27b** at room temperature; conc. ca. 5×10^{-2} M

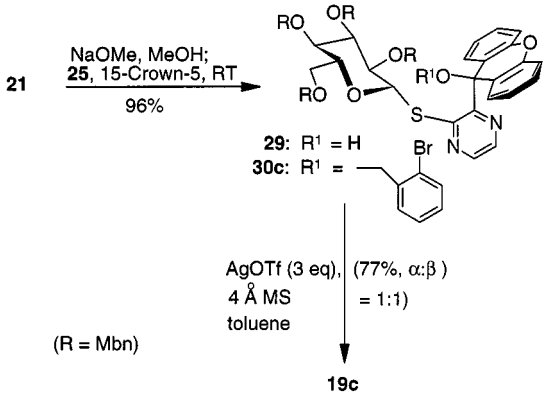
	Solvent	Promoter[a]	Product	Yield [%]	α,β
27a	Toluene	AgOTf (1+2 equiv.)	**5a**	64	1:3
	Toluene	AgOTf (3 equiv.)	**5a**	74	1:3
	CH_2Cl_2	AgOTf (3 equiv.)	**5a**	82	3:2
	CH_2Cl_2	MeOTf[b][c] (1.2 equiv.)	**5a**	10	1:1
27b	Toluene	AgOTf (3 equiv.)	**5b**	66	1:7
	Toluene	AgOTf (3 equiv.)	**5b**	69	1:3
	CH_2Cl_2	AgOTf (3 equiv.)	**5b**	75	3:2

[a] With molecular sieves (4 Å). – [b]With 2,6-di-*tert*-butylpyridine (1.2 equiv.). – [c] Without molecular sieves.



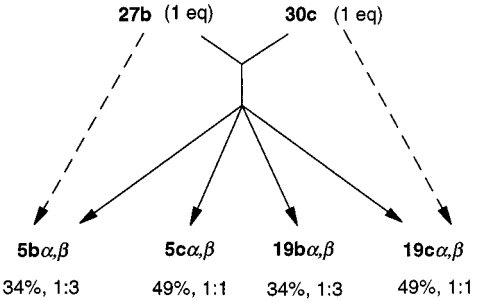
Scheme 8. Thioglycoside **28** as glycosyl donor

This expectation was confirmed by competition experiments (Scheme 9). To this end, Mbn-protected 1-acetylthioglucose **21** was transformed into the sodium thiolate and then treated with 2-chloropyrazine derivative **25** to afford thioglycoside **29**; reaction with 2-bromobenzyl alcohol in the presence of molecular sieves and CSA as catalyst furnished the desired starting material **30c** for the competition experiments. In order to prove the efficiency of **30c** as glycosyl donor/acceptor unit, activation with silver triflate was performed, leading to **19c** in good yield. For reasons of comparison, disaccharide **19b**[13] was also required.



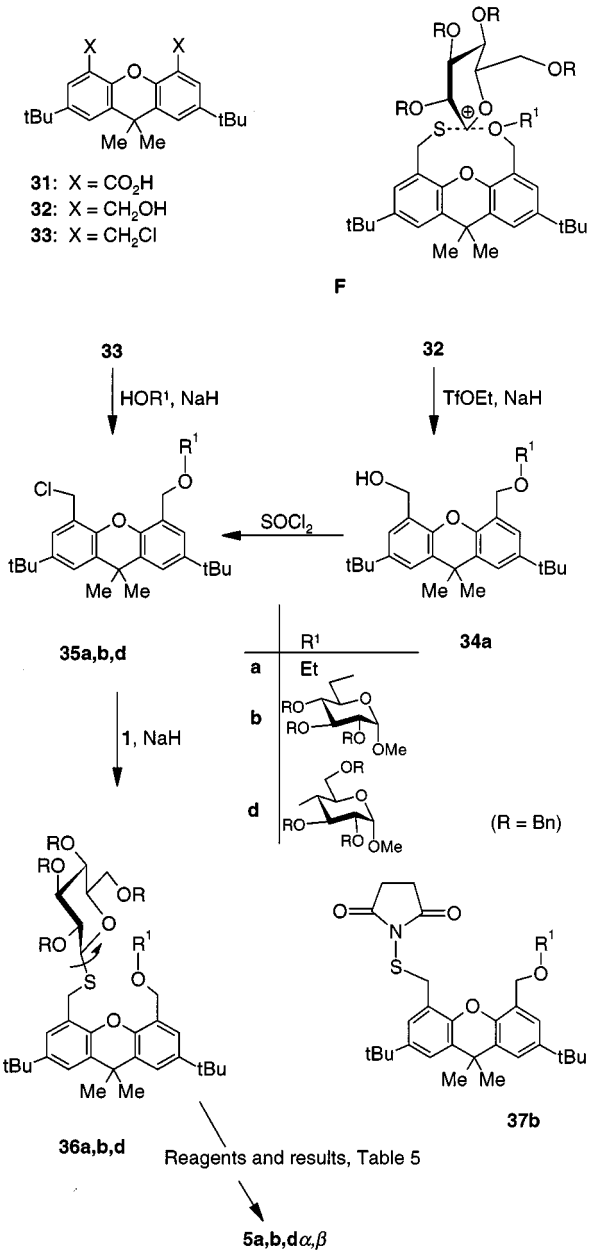
Scheme 9. Synthesis of **19c** and **30c** required for the competition experiments

With these compounds in hand, competition experiments could be carried out (Scheme 10). Treatment of **27b** and **30c** (one equivalent each) under standard glycosylation conditions furnished not only glycosides **5bα,β** and **19cα,β** but also the crossover products **5cα,β** and **19bα,β** in similar yields and anomer ratios. Once more, therefore, at least the prevalence of the intermolecular reaction course had been proven.



Scheme 10. Competition experiments with **27b** and **30c**; reagents and conditions: AgOTf(6 equiv.), molecular sieves (4 Å), toluene, room temp.

In none of the systems **2**, **10**, **13**, and **27** − with C_1, C_2, and C_3 bridges, respectively − was the expected retention of configuration at the anomeric center observed in glycoside bond formation; obviously, intramolecular 1,3-, 1,4-, or 1,5-glycosyl cation shifts were disfavored. Therefore, systems capable of producing medium-sized rings in the glycosyl transfer were planned. In this way, S_N2-type shifts between donor and acceptor, as shown with transition state **F** in Scheme 11, might be accessible, leading to inversion of configuration at the anomeric center. To this end, 1,8-dicarboxyxanthene **31**[22] (Scheme 11) was reduced to diol **32**, which upon treatment with thionyl chloride gave 1,8-bis(chloromethyl) derivative **33**. Compound **33** could be treated with methyl 2,3,4-[32] and 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside,[33] to produce mainly monoethers **35b** and **d**. Reaction of **32** with ethyl triflate in the presence of NaH as base afforded **34a**, which, on treatment with thionyl chloride, gave chloromethyl derivative **35a**, thus offering an alternative route for the synthesis of compounds of type **35**. Reaction of **35a,b** and **d** with **1**[18] and NaH as base furnished target molecules **36a,b** and **d**. Activation of these, again under standard glycosylation conditions, gave glycosides **5aα,β,bα,β** and **dα,β** (Table 5). However, neither the epected preference for the inversion products (i.e., the α-anomers) nor even high product yields were observed. Instead, upon activation of, for instance, **36b** with *N*-iodosuccinimide (NIS) in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (DTP), a large amount (86%) of sulfenamide **37b** was obtained, thus precluding the envisaged intramolecular reaction course. Possibly, the glycosyl donor moiety and the glycosyl acceptor moiety populate conformationally different sides of the flat tricyclic xanthene system (this is also supported by model calculations), hence once again disfavoring generation of transition state **F**, required for the intramolecular glycosyl transfer to the acceptor.



Scheme 11. Synthesis of **36a,b** and **d** and their transformations

Table 5. Glycosylation results with **36a,b** and **d** in dichloromethane

	Temp.	Promoter	Product	Yield ([%)	α,β
36a	room temp.	DMTST (1.4 equiv.)	**5a**	64	1:1
	0 °C	DMTST (1.2 equiv.)	**5a**	74	2:3
36b	room temp.	DMTST (2 equiv.)	**5b**	36	5:2
36d	room temp.	DMTST (1.5 equiv.)	**5d**	15	3:2

In conclusion, the leaving group based glycosylations studied in this paper follow an intermolecular rather than an intramolecular reaction course, although intramolecular (1,3)-, (1,4)-, and (1,5)-shifts (Schemes 2−4 and Scheme 7)

of the donor to the acceptor seem to be readily available. Activation of the glycosyl donor moiety in these systems obviously leads to solvent-and/or counterion-stabilized intermediates, which experience a lifetime long enough to search intermolecularly for sites of reactivity. This finally leads to product formation in up to high yields; yet the desired stereocontrol of an intramolecular reaction course is not attained. Of particular interest is the xanthene-derived system (Scheme 11) in which, according to model considerations, an intramolecular inversion 1,9-shift of the donor to the acceptor could take place, yet the results do not support this reaction course. Presumably, the 10-membered cyclic transition state as shown in **F** (Scheme 11) is conformationally disfavored. Obviously, structural modification of the xanthene skeleton could consider these conformational aspects, thus enforcing intramolecular leaving group based glycosylations. The xanthene system is also valuable for "rigid spacer based" intramolecular glycosylations,[15] which turned out to be very successful.

Experimental Section

General Methods: Optical rotations were determined with a Perkin−Elmer 241 MC polarimeter at 20° C. − ^{1}H NMR spectra were recorded (internal Me_4Si) with a Bruker WM 250 Cryospec and a Bruker DRX 600 instrument. TLC was performed on silica gel 60 F_{254} (Merck). − Chromatography was performed with silica gel (Baker, particle size 40 μm). Chromatography under elevated pressure (MPLC) was performed with LiChroprep Si 60 (Merck; 15−25 μm). The boiling range of the petroleum ether was 35−60 °C; anhydrous solvents were used. Molecular sieves (beads) were activated (250 °C; HV) before use; silver triflate was dried over KOH.

Ethoxymethyl 2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-thio-β-D-glucopyranoside (2a): To compound **1**[18] (0.12 g, 0.22 mmol) in CH_2Cl_2 was added NEt_3 (45 μL, 0.32 mmol) and chloromethyl ethyl ether (30 μL, 0.32 mmol). The solution was diluted with ethyl acetate and washed with water. The organic layer was concentrated in vacuo. The pure product **2a** (0.14 g, 100%) was isolated as a colorless oil. − TLC (petroleum ether/diethyl ether, 2:1): R_f = 0.36. − $[\alpha]_D$ = −24.7 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.17 (t, ^3J = 7.1 Hz, 3 H, CH_3), 3.49−3.57, 3.67−3.75 (2 m, 8 H, 2-H, 3-H, 4-H, 5-H, 2 6-H, CH_2Me), 4.53 (d, ^2J = 12.2 Hz, 1 H, SCH), 4.57 (d, ^2J = 11.7 Hz, 1 H, PhCH), 4.60 (d, $^3J_{1,2}$ = 10 Hz, 1 H, 1-H), 4.61 (d, ^2J = 12.2 Hz, 1 H, SCH), 4.75 (d, ^2J = 11.7 Hz, 1 H, PhCH), 4.77 (d, ^2J = 10.4 Hz, 1 H, PhCH), 4.81 (d, ^2J = 11.0 Hz, 1 H, PhCH), 4.85 (d, ^2J = 11.0 Hz, 1 H, PhCH), 4.91 (d, ^2J = 11.0 Hz, 1 H, PhCH), 4.92 (d, ^2J = 10.3 Hz, 1 H, PhCH), 5.04 (d, ^2J = 11.5 Hz, 1 H, PhCH), 7.15−7.37 (m, 20 H, 4 Ph). − $C_{37}H_{42}O_6S$ (614.8): calcd. C 72.28, H 6.89; found C 72.11, H 6.88.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosylthio)prop-2-yl]-α-D-glucopyranoside (2b): To compounds **4** (1.0 g, 1.98 mmol) and **1** (1.06 g, 1.90 mmol) in dioxane was added zinc chloride−diethyl ether (2.5 M in Et_2O, 0.2 mL, 0.5 mmol), while stirring. After 24 h, the mixture was neutralized with sat. $NaHCO_3$ solution. The mixture was diluted with ethyl acetate. The organic layer was separated; concentration in vacuo and then chromatography (petroleum ether/diethyl ether, 2:1) yielded **2b** (1.17 g, 56%) as a slightly yellow oil. − TLC (petroleum ether/diethyl ether, 2:1): R_f = 0.28. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.48 (s, 3 H, CH_3), 1.68 (s, 3 H, CH_3), 3.19 (s, 3 H, OCH_3), 3.32−3.72, 3.88−3.95 (2 m, 12 H, 2-H, 3-H, 4-H, 5-H, 2 6-H, 2′-H, 3′-H, 4′-H, 5′-H, 2 6′-H), 4.48−4.98 (m, 16 H, 1-H, 1′-H, 7 $PhCH_2$), 7.16−7.35 (m, 35 H, 7 Ph).

Methyl 6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3): To methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[32] (1.0 g, 2.15 mmol) in pyridine (10 mL) was added acetic anhydride (5 mL). At the end of the reaction, water and ethyl acetate were added. The layers were separated and concentrated in vacuo. Chromatography (toluene/ethyl acetate, 10:1) yielded **3** (1.0 g, 92%) as a colorless oil. TLC (toluene/ethyl acetate, 6:1): R_f = 0.40. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.02 (s, 3 H, OAc), 3.37 (s, 3 H, OCH_3), 3.48 (dd, $^3J_{4,5}$ = 10.0 Hz, $^3J_{4,3}$ = 9.0 Hz, 1 H, 4-H), 3.53 (dd, $^3J_{2,1}$ = 3.6 Hz, $^3J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 3.81 (ddd, $^3J_{5,6}$ = 3.8 Hz, $^3J_{5,4}$ = 10.1 Hz, 1 H, 5-H), 4.01 (dd, ^3J = 9.3 Hz, 1 H, 3-H), 4.20−4.31 (m, 2 H, 2 6-H), 4.53−5.03 (m, 7 H, 1-H, 3 $PhCH_2$), 7.24−7.38 (m, 15 H, 3 Ph). The NMR spectroscopic data correspond to those reported in ref.[34]

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(propen-2-yl)-α-D-glucopyranoside (4): To compound **3** (1.20 g, 2.37 mmol) was added a solution of dimethyldicyclopentadienyltitanium[19] (1.0 g, 4.8 mmol in 10 mL toluene) and the mixture was warmed up to 70 °C. After 15 h, dimethyldicyclopentadienyltitanium (0.5 g, 2.4 mmol in 5 mL toluene) was once again added. After 5 h, the solution was concentrated in vacuo. Chromatography (petroleum ether/diethyl ether, 3:1) yielded **4** (1.10 g, 92%) as a slightly yellow oil. − TLC (petroleum ether/diethyl ether, 2:1): R_f = 0.42. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.82 (s, 3 H, CH_3), 3.37 (s, 3 H, OCH_3), 3.55 (dd, $^3J_{2,1}$ = 3.6 Hz, $^3J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 2.64 (dd, $^3J_{4,3}$ = 9.1 Hz, $^3J_{4,5}$ = 9.1 Hz, 1 H, 4-H), 3.79−3.87 (m, 5 H, C=CH_2, 5-H, 2 6-H), 3.66 (dd, $^3J_{3,2}$ = 9.1 Hz, $^3J_{4,5}$ = 9.1 Hz, 1 H, 3-H), 4.51 (d, ^2J = 10.7 Hz, 1 H, PhCH), 4.61 (d, $^3J_{1,2}$ = 3.6 Hz, 1 H, 1-H), 4.66 (d, ^2J = 12.1 Hz, 1 H, PhCH), 4.78−4.86 (m, 3 H, 3 PhCH), 4.98 (d, ^2J = 10.8 Hz, 1 H, PhCH), 7.22−7.38 (m, 15 H, 3 Ph).

Ethyl 2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranoside (5aα,β). − General procedure for Table 1: To compound **2a** (0.16 g, 0.28 mmol) in CH_2Cl_2 (2 mL) was added DMTST (77 mg, 0.31 mmol). At the end of the reaction, sat. $NaHCO_3$ solution was added. The layers were separated and concentrated in vacuo. Chromatography (toluene/ethyl acetate, 20:1) yielded **5aα,β** (86 mg, 69%, α:β = 1:2) as a colorless oil. − General procedure for Table 2: To compound **10a** (123 mg, 0.17 mmol) in CH_2Cl_2 (1 mL) was added DMTST (49 mg, 0.19 mmol in 1 mL CH_2Cl_2). After the end of the reaction, sat. $NaHCO_3$ solution was added. The layers were separated and concentrated in vacuo. Chromatography (toluene/ethyl acetate, 20:1) yielded **5aα,β** (77 mg, 80%, α:β = 1:1) as a colorless oil. − General procedure for Table 3: To compound **13a** (0.16 g, 0.28 mmol) in CH_2Cl_2 (2 mL) was added DMTST (77 mg, 0.31 mmol). After the end of the reaction, sat. $NaHCO_3$ solution was added. The layers were separated and concentrated in vacuo. Chromatography (toluene/ethyl acetate, 20:1) yielded **5aα,β** (86 mg, 69%, α/β = 1:2) as a colorless oil. The physical data of **5aα,β** are in accordance with literature data.[20]

Methyl 6-*O*-(2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (5bα,β): The title compound was prepared following the general procedure (Table 1 and 2) given above for **5aα,β.** The physical data are in accordance with literature data.[21] − General procedure for Table 4: Molecular sieves (4 Å, ca. 0.7 g) and **27b** (90 mg, 0.07 mmol) were stirred in CH_2Cl_2 (1.5 mL) for 15 min at room temp. After addition of silver triflate

(54 mg, 0.21 mmol), the reaction mixture was stirred for 24 h under exclusion of light. CH_2Cl_2 and sat. $Na_2S_2O_3$ solution were added to the dark orange reaction mixture, which was then stirred for 2 h. After the usual workup, chromatography (toluene/ethyl acetate, 12:1) yielded **5bα,β** (52 mg, 75%, α:β = 1.5:1).

From Compound 28: Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[31] (58 mg, 0.13 mmol), **28** (80 mg, 0.13 mmol), and molecular sieves (4 Å, ca. 0.5 g) were stirred in toluene (2.0 mL) for 30 min at room temp. After addition of silver triflate (90 mg, 0.35 mmol), the reaction mixture was stirred for 3 h under exclusion of light. Purification as described above yielded **5bα,β** (90 mg, 72%, α:β = 1:3).

2-Bromobenzyl 2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranoside (5cα,β). − From Compounds 23c*l* and 13a: To compound **23c*l*** (110 mg, 0.12 mmol) and compound **13a** (86 mg, 0.12 mmol) in CH_2Cl_2 (2.0 mL) was added DMTST (0.25 M in CH_2Cl_2, 2.0 mL, 0.50 mmol) at room temp. After 45 min, sat. $NaHCO_3$ solution was added, followed by the usual workup. The resulting syrup was co-evaporated twice with toluene. Chromatography with toluene/ethyl acetate, 60:1 first gave a fraction containing **19cα,β** (31 mg, 34%, α:β = 1:1) and **5cα,β** (43 mg, 51%, α:β = 1:1); changing to toluene/ethyl acetate, 30:1 gave a fraction containing **19aα,β** (10 mg, 14%, α:β = 1:1) and **5aα,β** (24 mg, 35%, α:β = 1:1).

From Compounds 23c*h* and 13a: To compound **23c*h*** (110 mg, 0.12 mmol) and compound **13a** (86 mg, 0.12 mmol) in CH_2Cl_2 (2.0 mL) was added DMTST (0.25 M in CH_2Cl_2, 2.0 mL, 0.50 mmol). After 45 min, the reaction mixture was purified as described above. Products were **19cα/β** (29 mg, 32%, α:β = 1:1), **5cα,β** (51 mg, 60%, α:β = 1:1), **19aα,β** (16 mg, 30%, α:β = 1:1), and **5aα,β** (20 mg, 30%, α:β = 1:1).

From Compounds 27b and 30c: Molecular sieves (4 Å, 0.6 g), compound **30c** (112 mg, 0.11 mmol), and compound **27b** (135 mg, 0.11 mmol) were stirred in toluene (6 mL) for 10 min at room temp. After addition of silver triflate (163 mg, 0.63 mmol), the reaction mixture was stirred under exclusion of light. After 2 h, TLC indicated that 50% of the starting materials had been consumed. Also, however, two new, characteristically UV-active intermediates could be detected. Their R_f values fitted with those which would be expected for the transetherification products of **30c** and **27b**. After 24 h, CH_2Cl_2 (6 mL) and sat. $Na_2S_2O_3$ solution (8 mL) were added to the red-brown reaction mixture. After stirring for 4 h, the usual workup followed. Chromatography and analysis, as described earlier, yielded **19cα,β** (40 mg, 49%, α/β = 1:1), **5cα,β** (37 mg, 49%, α/β = 1:1), **19bα,β** (38 mg, 34%), and **5bα,β** (35 mg, 34%). A ratio of α/β = 1:3.5 was determined for the last two.

Methyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (5dα/β). − General procedure for Table 5: To compound **36d** (90 mg, 0.07 mmol) in CH_2Cl_2 (2.0 mL) at room temp. was added DMTST (20 mg, 0.08 mmol). After 15 h, sat. $NaHCO_3$ solution was added, followed by the usual workup. Chromatography (toluene/ethyl acetate, 15:1) yielded first a fraction of **5dα,β** (10 mg, 15%, α:β = 1.5:1).

2-Ethoxy-2-phenylethyl Methanesulfonate (6a): To compound **7** (0.8 g, 4.8 mmol) in pyridine (8 mL) was added mesyl chloride (0.45 mL, 5.8 mmol). After 30 min, the solution was diluted with ethyl acetate. After filtration through silica gel, the solution was concentrated in vacuo. Chromatography (toluene/ethyl acetate, 20:1) yielded **7a** (1.18 g, 100%) as a colorless oil. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3), 3.00 (s, 3 H, SO_2CH_3), 3.37−3.55 (m, 2 H, CH_2CH_3), 4.22 (dd, ^3J = 3.8, ^2J = 11.2 Hz, 1 H, C*H*OMes), 4.33 (dd, ^3J = 8.1, ^2J = 11.2 Hz, 1 H, C*H*OMes), 4.60 (dd, ^3J = 3.7 Hz, 1 H, PhCH), 7.15−7.42 (m, 5 H, Ph).

2-(Methyl 2,3,4-Tri-*O*-benzyl-α-D-glucopyranosid-6-yl)-2-phenylethyl Methanesulfonate (6b*h,l*): Compound **6b*h*** was prepared using **7b*h***, following the procedure given for **6a**; colorless solid, 67% yield. − TLC (toluene/ethyl acetate, 10:1): R_f = 0.38. − $[\alpha]_D$ = −6.0 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.89 (s, 3 H, SO_2CH_3), 3.36 (s, 3 H, OCH_3), 3.45−3.53 (m, 3 H, 2-H, 4-H, 6-H), 3.63 (dd, $^3J_{6,5}$ = 1.6 Hz, $^2J_{6,6'}$ = 11.1 Hz, 1 H, 6-H), 3.72 (ddd, $^3J_{5,6}$ = 1.6 Hz, $^3J_{5,6'}$ = 4.9, $^3J_{5,4}$ = 10.2 Hz, 1 H, 5-H), 3.98 (dd, $J_{3,2}$ = 9.2 Hz, $J_{3,4}$ = 9.2 Hz, 1 H, 3-H), 4.21 (dd, ^3J = 4.8 Hz, ^2J = 11.0 Hz, 1 H, C*H*OMes), 4.31 (dd, ^3J = 7.8 Hz, ^2J = 11.0 Hz, 1 H, C*H*OMes), 4.54−4.61 (m, 3 H, 1-H, 2 PhCH), 4.66 (d, ^2J = 12.2 Hz, 1 H, PhCH), 4.79 (d, ^2J = 12.2 Hz, 1 H, PhCH), 4.80 (d, ^2J = 10.9 Hz, 1 H, PhCH), 4.87 (d, ^2J = 11.1 Hz, 1 H, PhCH), 4.97 (d, ^2J = 10.9 Hz, 1 H, PhCH), 7.16−7.40 (m, 20 H, 4 Ph). − $C_{37}H_{42}O_9S$ (662.8): calcd. C 67.05, H 6.39; found C 67.26, H 6.37.

Compound 6b*l*: prepared using **7b*l***, following the procedure given for **6a**; colorless solid, 93% yield. − TLC (toluene/ethyl acetate, 3:2): R_f = 0.60. − ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.90 (s, 3 H, SO_2CH_3), 3.36 (s, 3 H, OCH_3), 3.47−3.99 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 2 6-H), 4.21 (dd, ^3J = 3.7 Hz, ^2J = 11.2 Hz, 1 H, C*H*OMes), 4.37 (dd, ^3J = 8.1 Hz, ^2J = 11.2 Hz, 1 H, C*H*OMes), 4.42 (d, ^2J = 10.8 Hz, 1 H, PhCH), 4.57 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.66 (dd, ^3J = 3.7 Hz, ^3J = 8.1 Hz, 1 H, PhC*H*CH_2), 4.68 (d, ^2J = 12.1 Hz, 1 H, PhCH), 4.79 (d, ^2J = 9.9 Hz, 1 H, PhCH), 4.80 (d, ^2J = 12.2 Hz, 1 H, PhCH), 4.81 (d, ^2J = 11.1 Hz, 1 H, PhCH), 4.98 (d, ^2J = 9.8 Hz, 1 H, PhCH), 7.04−7.37 (m, 20 H, 4 Ph). − $C_{37}H_{42}O_9S$ (662.8): calcd. C 67.05, H 6.39; found C 67.06, H 6.53.

2-Ethoxy-2-phenylethanol (7a): To a suspension of lithium aluminum hydride (0.18 g, 4.7 mmol) in dry Et_2O (10 mL) was added **8a** (1.3 g, 6.7 mmol) in Et_2O (7 mL). The mixture was refluxed. At the end of the reaction, ethyl acetate and water were added. The solid residue was dissolved in dilute sulfuric acid. The organic layer was separated and concentrated in vacuo. Chromatography (toluene/ethyl acetate, 20:1) yielded **7a** (0.90 g, 81%) as a colorless oil. − TLC (toluene/ethyl acetate, 10:1). − R_f = 0.23. − ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.22 (t, ^3J = 7.0 Hz, 3 H, CH_3), 2.50 (br. s, 1 H, OH), 3.40 (dq, ^3J = 7.0 Hz, ^2J = 9.3 Hz, 1 H, OC*H*CH_3), 3.50 (dq, ^3J = 7.0 Hz, ^2J = 9.3 Hz, 1 H, OC*H*CH_3), 3.63−3.71 (m, 2 H, C*H*$_2$OH), 4.20 (dd, 1 H, PhCH, ^3J = 4.3 Hz, ^3J = 8.1 Hz). This compound had been prepared previously.[35] NMR-spectroscopic data had not been provided.

Methyl 2,3,4-Tri-*O*-benzyl-6-(2-hydroxy-1-phenylethyl)-α-D-glucopyranoside (7b*h,l*): The title compound was prepared from **8b**, following the procedure described above for **7a**, in 56% yield.

Compound 7b*h*: Colorless oil, TLC (toluene/ethyl acetate, 3:2): R_f = 0.38. − $[\alpha]_D$ = −19.5 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.44 (br. s, 1 H, OH), 3.37 (s, 3 H, OCH_3), 3.40−4.00 (m, 8 H, 2-H, 3-H, 4-H, 5-H, 2 6 H, C*H*$_2$OH), 4.38 (dd, ^3J = 3.9 Hz, ^3J = 8.3 Hz, 1 H, PhC*H*CH_2), 4.56 (d, ^3J = 11.0 Hz, 1 H, PhCH), 4.61 (d, $^3J_{1,2}$ = 3.5 Hz, 1 H, 1-H), 4.66 (d, ^2J = 12.2 Hz, 1 H, PhCH), 4.68 (d, ^2J = 12.2 Hz, 1 H, PhCH), 4.81 (d, ^2J = 10.8 Hz, 1 H, PhCH), 4.88 (d, ^2J = 11.0 Hz, 1 H, PhCH), 4.98 (d, ^2J = 10.8 Hz, 1 H, PhCH), 7.16−7.37 (m, 20 H, 4 Ph). − $C_{36}H_{40}O_7$ (584.7): calcd. C 73.95, H 6.90; found C 73.51, H 6.87.

Compound 7b*l*: Colorless oil. − TLC (toluene/ethyl acetate, 3:2): R_f = 0.23. − $[\alpha]_D$ = 46.0 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz,

$CDCl_3$): δ = 2.59 (br. s, 1 H, OH), 3.39 (s, 3 H, OCH_3), 3.55 (dd, $J_{2,1}$ = 3.5 Hz, $J_{2,3}$ = 9.6 Hz, 1 H, 2-H), 3.61−3.99 (m. 7 H, 3-H, 4-H, 5-H, 2 6-H, CH_2OH), 4.42−4.49 (m, 1 H, PhCHCH$_2$), 4.65 (d, $^3J_{1,2}$ = 3.3 Hz, 1 H, 1-H), 4.68 (d, ^2J = 11.8 Hz, 1 H, PhCH), 4.78−4.86 (m, 3 H, 3 PhCH), 4.99 (d, ^2J = 10.8 Hz, 1 H, PhCH), 7.06−7.38 (m, 20 H, 4 Ph). − $C_{36}H_{40}O_7$ (584.7): calcd. C 73.95, H 6.90; found C 73.55, H 7.03.

Methyl 2-Ethoxy-2-phenylacetate (8a): To compound **9** (1.5 g, 9.0 mmol) in CH_2Cl_2 (50 mL) was added NaH (0.22 g, 9.0 mmol). At the end of H_2 evolution, ethyl triflate (1.42 mL, 9.9 mmol) was added. When the reaction was complete, sat. NH_4Cl solution was added. After extraction with ethyl acetate, the organic layer was concentrated in vacuo. Chromatography (toluene/ethyl acetate, 10:1) yielded **8a** (1.35 g, 77%) as a colorless oil. − TLC (toluene/ethyl acetate, 10:1): R_f = 0.61. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.28 (t, ^3J = 7.0 Hz, 3 H, CH_3), 3.59 (dq, ^3J = 7.0 Hz, ^2J = 9.1 Hz, 1 H, OCHMe), 3.61 (dq, ^3J = 7.0, ^2J = 9.1 Hz, 1 H, OCHMe), 3.71 (s, 3 H, OCH_3), 4.89 (s, 1 H, PhCH), 7.32−7.48 (m, 5 H, Ph). This compound had been prepared previously.[35] NMR-spectroscopic data had not been provided.

Methyl 2-(Methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosid-6-yl)-2-phenylacetate (8b): This compound was prepared using methyl 2,3,4-tri-*O*-benzyl-6-*O*-trifluoromethanesulfonyl-α-D-glucopyranoside[23] and following the procedure given for **8a**; colorless oil, 76% yield. − TLC (toluene/ethyl acetate, 10:1): R_f = 0.32. − $[\alpha]_D$ = 20.0 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.35 (s, 3 H, OCH_3), 3.48−3.92 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 2 6-H), 3.63, 3.64 (2 s, 3 H, CO_2CH_3), 3.99 (dd, ^3J = 9.2 Hz, 1 H), 4.49−5.00 (m, 8 H, 1-H, 7 PhCH), 7.15−7.44 (m, 20 H, 4 Ph). − $C_{37}H_{40}O_8$ (612.7): calcd. C 72.53, H 6.58; found C 72.60, H 6.65.

2-Ethoxy-2-phenyl-1-(2,3,4,6-tetra-*O*-benzyl-1-deoxy-β-D-glucopyranosylthio)ethane (10a*h,l*): To compound **1** (1.0 g, 1.8 mmol) in DME and DMF (30 mL, ratio 2:1) was added NaH (43 mg, 1.8 mmol). To the solution was added 15-crown-5 (0.36 mL, 1.8 mmol), and it was then warmed up to 60 °C. To the solution was added **6a** (0.5 g, 2.0 mmol). After 3 h, the solution was neutralized with sat. NH_4Cl solution. After extraction with ethyl acetate, the organic layer was concentrated in vacuo. Chromatography (toluene/ethyl acetate, 20:1) yielded **10a** (1.08 g, 85%).

Compound 10a*h*: Colorless oil. − TLC (toluene/ethyl acetate, 10:1): R_f = 0.34. − $[\alpha]_D$ = 6.0 (c = 1.0, $CHCl_3$). −^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.17 (t, ^3J = 7.0 Hz, 3 H, CH_3), 2.83 (dd, ^2J = 13.6 Hz, ^3J = 4.8 Hz, 1 H, SCH), 3.18 (dd, ^2J = 13.6 Hz, ^3J = 8.3 Hz, 1 H, SCH), 3.37 (q, ^3J = 7.0 Hz, 2 H, OCH_2Me), 3.41−3.47 (m, 2 H, 2-H, 5-H), 3.57−3.78 (m, 4 H, 3-H, 4-H, 2 6-H), 4.49−4.95 (m, 10 H, 1-H, 9 PhCH), 7.15−7.39 (m, 25 H, 5 Ph). − $C_{44}H_{48}O_6S$ (704.9): C 74.97, H 6.86; found C 74.58, H 6.87.

Compound 10a*l*: Colorless oil. − TLC (toluene/ethyl acetate): R_f = 0.29. − $[\alpha]_D$ = −17 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.16 (t, ^3J = 7.0 Hz, 3 H, CH_3), 2.98 (dd, ^2J = 11.5 Hz, ^3J = 6.1 Hz, 1 H, SCH), 3.05 (dd, ^2J = 11.5 Hz, ^3J = 6.1 Hz, 1 H, SCH), 3.33−3.44, 3.59−3.72 (2 m, 8 H, CH_2Me, 2-H, 3-H, 4-H, 5-H, 2 6-H), 4.30 (d, $^3J_{1,2}$ = 9.7 Hz, 1 H, 1-H), 4.47−4.63 (m, 4 H, 4 Ph), 4.69 (d, ^2J = 10.2 Hz, 1 H, PhCH), 4.80 (d, ^2J = 10.8 Hz, 1 H, PhCH), 4.82 (d, ^2J = 11.0 Hz, 1 H, PhCH), 4.88 (d, ^2J = 10.3 Hz, 1 H, PhCH), 4.90 (d, ^2J = 11.0 Hz, 1 H, PhCH), 7.14−7.37 (m, 25 H, 5 Ph). − $C_{44}H_{48}O_6S$ (704.9): calcd. C 74.97, H 6.86; found C 74.71, H 6.94.

Methyl 6-*O*-[2-(2,3,4,6-Tetra-*O*-benzyl-1-deoxy-β-D-glucopyranosylthio)-1-phenylethyl]-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (10b*h,l*): Compound **10b*h*** was prepared using **6b*h***, following the procedure given for **10a*h,l***; colorless oil, 36% yield. − TLC (toluene/ethyl acetate, 10:1): R_f = 0.43. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.99 (dd, ^3J = 6.0 Hz, ^2J = 13.4 Hz, 1 H, SCH), 3.09 (dd, ^3J = 7.3 Hz, ^2J = 13.4 Hz, 1 H, SCH), 3.25 (dd, $^3J_{5,6}$ = 2.6 Hz, $^3J_{5,4}$ = 9.2 Hz, 1 H, 5a-H or 5b-H), 3.32 (s, 3 H, OCH_3), 3.36−3.65 (m, 10 H, 2a-H, 2b-H, 3a-H, 3b-H, 4a-H, 4b-H, 2 6a-H, 2 6b-H), 3.96 (ddd, $^3J_{5,6}$ = 2.7 Hz, $^3J_{5,4}$ = 9.0 Hz, 1 H, 5b-H or 5a-H), 4.16 (d, $^3J_{1b,2b}$ = 9.6 Hz, 1 H, 1b-H), 4.45−4.98 (m, 16 H, 1a-H, 15 PhCH), 7.12−7.23 (m, 40 H, 8 Ph). − $C_{70}H_{74}O_{11}S$ (1123.4): calcd. C 74.84, H 6.64; found C 74.35, H 6.62.

Compound 10b*l*: Prepared using **6b*l***, following the procedure given for **10a**; colorless oil, 46% yield. − TLC (toluene/ethyl acetate, 10:1): R_f = 0.43. − $[\alpha]_D$ = 12.0 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.88 (dd, ^3J = 5.4 Hz, ^2J = 13.3 Hz, 1 H, SCH), 3.27 (dd, ^3J = 7.7 Hz, ^2J = 13.3 Hz, 1 H, SCH), 3.35 (s, 3 H, OCH_3), 3.40−3.76 (m, 3 H), 3.96 (dd, ^3J = 9.3 Hz, 1 H, 2a-H, 2b-H, 3a-H, 3b-H, 4a-H, 4b-H, 5a-H, 5b-H, 2 6a-H, 2 6b-H), 4.33 (d, ^3J = 10.8 Hz, 1 H), 4.49−4.97 (m, 16 H, 1a-H, 1b-H, 14 PhCH), 6.99−7.37 (m, 40 H, 8 Ph). − $C_{70}H_{74}O_{11}S$ (1123.4): calcd. C 74.84, H 6.64; found C 75.05, H 6.79.

D,L-*erythro*-1-Hydroxy-2-(2,3,4,6-tetra-*O*-benzyl-1-deoxy-β-D-glucopyranosylthio)indane (12*h,l*): To compound **1**[18] (0.18 g, 0.32 mmol) and 15-crown-5 (64 μL, 0.32 mmol) in DMF (2 mL) was added NaH (7 mg, 31 mmol). After 10 min, 2-bromo-1-hydroxyindane (**11**)[22] (0.14 g, 0.65 mmol) was added; 10 min later, sat. $NaHCO_3$ solution was added. After extraction with ethyl acetate, the organic layer was concentrated in vacuo. Chromatography (petroleum ether/ethyl acetate, 4:1) yielded **12*h,l*** (0.97 g, 78%) as a colorless oil. − TLC (toluene/ethyl acetate, 9:1): R_f = 0.38. − $C_{43}H_{44}O_6S$ (688.9): calcd. C 74.97, H 6.44; found C 74.82, H 6.46. − The diastereomers were separated by MPLC (toluene/ethyl acetate, 20:1) and acetylated, to afford **12*h*-*Ac*** and **12*l*-*Ac***, respectively.

Compound 12*h*: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.03 (dd, ^2J = 15.6 Hz, ^3J = 8.7 Hz, 1 H, SCHCH), 3.22 (dd, ^2J = 15.8 Hz, ^3J = 7.7 Hz, 1 H, SCH−CH), 3.39−3.92 (m, 7 H, SCH, 2-H, 3-H, 4-H, 5-H, 2 6-H), 4.49−5.05 (m, 10 H, 1-H, 9 PhCH), 7.12−7.40 (m, 24 H, C_6H_4, Ph).

Compound 12*h*-*Ac*: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, Ac), 3.19−3.34 (m, 2 H, 2 3′-H), 3.40−3.77 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 2 6-H), 3.86−3.95 (m, 1 H, SCH), 4.52−4.64 (m, 4 H, 1-H, 3 PhCH), 4.74−4.95 (m, 5 H, 5 PhCH), 6.20 (d, ^3J = 5.6 Hz, 1 H, 1′-H), 7.16−7.49 (m, 24 H, C_6H_4, 4 Ph).

Compound 12*l*: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.99 (ddd, $J_{5,4}$ = 9.4 Hz, $J_{5,6}$ = 3.0 Hz, 1 H, 5-H), 3.13 (dd, ^2J = 16.5 Hz, ^3J = 5.3 Hz, 1 H, 3′-H), 3.34 (dd, ^2J = 16.6 Hz, ^3J = 7.7 Hz, 1 H, 3′-H), 2.26 (dd, ^3J = 9.6 Hz, 1 H), 3.55 (dd, ^2J = 9.0 Hz, 1 H), 3.61−3.68 (m, 5 H, 2-H, 3-H, 4-H, 2 6-H), 3.91 (ddd, ^3J = 7.8, 5.6 Hz, 1 H, SCH), 4.31 (d, $^3J_{1,2}$ = 9.8 Hz, 1 H, 1-H), 4.49−4.90 (m, 8 H, 8 PhCH), 5.18 (dd, ^3J = 6.7 Hz, 1 H, PhCHOH), 7.11−7.36 (m, 24 H, C_6H_4, 4 Ph).

Compound 12*l*-*Ac*: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.97 (s, 3 H, Ac), 3.20 (dd, ^2J = 9.3 Hz, 1 H, SCHCH), 3.31 (dd, ^2J = 16.0 Hz, ^3J = 7.6 Hz, 1 H, SCHCH), 3.45 (dd, $^3J_{2,1}$ = 9.0 Hz, $^3J_{2,3}$ = 9.0 Hz, 1 H, 2-H), 3.48−3.53 (m, 1 H, 5-H), 3.60 (dd, $J_{4,5}$ = $J_{4,3}$ = 8.7 Hz, 1 H, 4-H), 3.63−3.75 (m, 3 H, 3-H, 2 6-H), 3.91 (ddd, ^3J = 9.0 Hz, 7.7 Hz, 5.5 Hz, 1 H, SCH), 4.50−4.94 (m, 9 H, 1-H, 4 PhCH$_2$), 6.21 (d, ^3J = 5.5 Hz, 1 H, AcOCH), 7.17−7.44 (m, 24 H, C_6H_4, 4 Ph).

D,L-*erythro*-1-Ethoxy-2-(2,3,4,6-tetra-*O*-benzyl-1-deoxy-β-D-glucopyranosylthio)indane (13a): To compound **12h,*l*** (148 mg, 0.21 mmol) and 15-crown-5 (43 μL, 0.21 mmol) in DMF (5 mL) were added NaH (5 mg, 0.21 mmol) and ethyl iodide (0.5 mL, 6.2 mmol). At the end of the reaction, the solution was diluted with Et_2O and washed with water. The organic layer was concentrated in vacuo. Chromatography (toluene/ethyl acetate, 14:1) yielded **13a** (130 mg, 86%) as colorless solid. − TLC (toluene/ethyl acetate, 9:1): R_f = 0.57. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20, 1.21 (2 t, ^3J = 7.0 Hz, 3 H, CH_3), 3.24−3.76 (m, 10 H, CH_2Me, CH_2CS, 2-H, 3-H, 4-H, 5-H, 2 6-H), 3.83 (mc, 0.5 H, SCH), 3.96 (mc, 0.5 H, SCH), 4.50−4.99 (m, 10 H, 1-H, 9 PhCH), 7.12−7.41 (m, 24 H, C_6H_4, 4 Ph). − $C_{45}H_{48}O_6S$ (716.9): calcd. C 75.39, H 6.75; found C 74.88, H 6.69.

D,L-*erythro*-1-Hydroxy-2-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosylthio)-1′,2′,3′,4-tetrahydronaphthalene (15): To compound **1**[18] (1.0 g, 1.8 mmol) and 15-crown-5 (0.36 mmol) in DMF (10 mL) was added NaH (43 mg, 1.8 mmol). After 10 min, **14**[26] (0.82 g, 3.6 mmol) was added. After 7 h, the solution was diluted with Et_2O and washed with water. The organic layer was concentrated in vacuo. Chromatography (toluene/ethyl acetate, 20:1) yielded **15** (0.70 g, 55%) as a colorless oil. − TLC (toluene/ethyl acetate, 20:1): R_f = 0.36. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.00−2.35 (m, 2 H, 2 3′-H), 2.73−3.05 (m, 2 H, 2 4′-H), 3.36−3.75 (m, 8 H, 2-H, 3-H, 4-H, 5-H, 2 6-H, 2′-H, OH), 4.47−4.96 (m, 10 H, 1-H, 1′-H, 8 PhCH), 708−7.40 (m, 24 H, C_6H_4, 4 Ph). − $C_{44}H_{46}O_6S$ (702.9): calcd. C 75.18, H 6.60; found C 74.87, H 6.66.

D,L-*erythro*-1-Ethoxy-2-(-2,3,4,6-tetra-*O*-benzyl-1-deoxy-β-D-glucopyranosylthio)-1′,2′,3′,4-tetrahydronaphthalene (16a): To compound **15** (0.70 g, 1.0 mmol) and 15-crown-5 (0.20 mL, 1.0 mmol) in dioxane (10 mL) and DMF (2 mL) was added NaH (24 mg, 1.0 mmol). After 10 min, ethyl iodide (0.16 mL, 2.0 mmol) was added. After 4 h, the solution was diluted with ethyl acetate and washed with water. The organic layer was concentrated in vacuo. Chromatography (toluene/ethyl acetate, 20:1) yielded **16a** (0.54 g, 74%) as a colorless oil. − TLC (toluene/ethyl acetate, 9:1): R_f = 0.51. − ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.20, 1.21 (2 s, 3 H, CH_3), 2.04−2.44 (m, 2 H, 2 3′-H), 2.70−2.83 (m, 1 H, 4′-H), 2.98−3.09 (m, 1 H, 4′-H), 3.42−3.77 (m, 9 H, 2-H, 3-H, 4-H, 5-H, 2 6 H, 2′-H, CH_2Me), 4.47−4.97 (m, 10 H, 1-H, 1′-H, 8 PhCH), 7.12−7.39 (m, 24 H, C_6H_4, 4 Ph). − $C_{46}H_{50}O_6S$ (731.0): calcd. C 75.59, H 6.89; found C 75.40, H 7.03.

Ethyl 2,3,4,6-Tetra-*O*-(3-methylbenzyl)-α/β-D-glucopyranoside (19aα/β): To compound **20α/β**[13] (600 mg, 0.809 mmol, α/β = 4:1) and EtOH (94 μL, 1.62 mmol) in CH_2Cl_2 (1.0 mL) at −78 °C was added trimethylsilyl triflate (0.2 M in CH_2Cl_2, 120 μL, 0.02 mmol). The reaction mixture was allowed to reach 0 °C over 1.5 h. After addition of NEt_3 and coevaporation with toluene, chromatography (at first, petroleum ether/ethyl acetate, 8:1) yielded **19aβ** (434 mg, 86%) as a colorless syrup. A change to petroleum ether/ethyl acetate, 6:1 gave **19aα** (29 mg, 6%) as a colorless syrup.

Compound 19aα: TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.46. − $[\alpha]_D$ = 15.5 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, 3 H, $CHCH_3$), 2.29−2.32 (m, 12 H, 4 PhCH_3), 3.47−3.79 (m, 7 H, OCH_2Me, 2-, 4-, 5-, 6-, 6′-H), 3.98 (dd, 1 H, 3-H), 4.39−4.44 (m, 2 H, 2 MePhCH), 4.57−4.64 (m, 2 H, 2 MePhCH), 4.74−4.82 (m, 4 H, 3 MePhCH, 1-H), 4.97 (d, ^3J = 10.7 Hz, 1 H, MePhCH), 6.93 (m, 2 H, 2 MePh-H), 7.05−7.26 (m, 14 H, 14 MePhH).

Compound 19aβ: TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.50. − $[\alpha]_D$ = 8.0 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.30 (t, 3 H, $OCCH_3$), 2.30 (m, 12 H, 4 PhCH_3), 3.41−3.78 (m, 7 H, CHMe, 2-, 3-, 4-, 5-, 6-, 6′-H), 4.05 (m, 1 H, CHMe), 4.40 (d, ^3J = 7.8 Hz, 1 H, 1-H), 4.46−4.95 (m, 8 H, 4 MePhCH_2), 6.95 (m, 2 H, 2 MePhH), 7.09−7.24 (m, 14 H, 14 MePhH). − $C_{40}H_{48}O_6$ (624.8): calcd. C 76.89, H 7.74; found C 77.13, H 7.75.

2-Bromobenzyl 2,3,4,6-Tetra-*O*-benzyl-α/β-D-glucopyranoside (19cα/β): These compounds were prepared following the general procedures for Table 3 and 4.

***S*-[2,3,4,6-Tetra-*O*-(3-methylbenzyl)-β-D-glucopyranosyl] Thioacetate (21):** To compound **18**[13] (500 mg, 0.84 mmol) in dist. $SOCl_2$ (1.6 mL, 22 mmol) was added DMF (8 μL, 0.10 mmol), and the mixture was warmed to 50 °C for 30 min. The reaction mixture was concentrated in vacuo and the resulting syrup was dried under high vacuum for 1 h. The residue was dissolved in DMF (1.5 mL) and potassium thioacetate (380 mg, 3.3 mmol) was added. After 2 d at room temp., the black reaction mixture was processed by the usual workup. After the first chromatography (petroleum ether/ethyl acetate, 6:1), a second elution [first toluene/ethyl acetate, 40:1, then (giving the compound) with toluene/ethyl acetate, 20:1] yielded **21** (464 mg, 84%) as a slightly red solid. − M.p. 52 °C (Et_2O/petroleum ether at −18 °C). − TLC (toluene/ethyl acetate, 10:1): R_f = 0.58. − $[\alpha]_D$ = 25.3 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.29−2.31 (m, 12 H, 4 PhCH_3), 2.37 (s, 3 H, $SCOCH_3$), 3.49−3.74 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H, 6′-H), 4.43 (d, ^2J = 12.0 Hz, 1 H, MePhCH), 4.50 (d, ^2J = 10.6 Hz, 1 H, MePhCH), 4.60 (d, ^2J = 12.0 Hz, 1 H, MePhCH), 4.69−4.84 (m, 5 H, 5 MePhCH), 5.16 (d, ^3J = 10.1 Hz, 1 H, 1-H), 6.94 (m, 2 H, 2 MePhH), 7.09−7.25 (m, 14 H, 14 MePhH). − $C_{40}H_{46}O_6S$ (654.9): calcd. C 73.36, H 7.08; found C 73.51, H 7.07.

D,L-*erythro*-1-Hydroxy-2-[2,3,4,6-tetra-*O*-(3-methylbenzyl)-β-D-glucopyranosylthio]indane (22*hl*): Compound **21** (3.00 g, 4.58 mmol) was suspended in MeOH (15 mL), and NaOMe (1 M in MeOH, 4.7 mL, 4.7 mmol) was added at room temp. After 40 min, MeOH was removed under vacuum and the resulting solid was dried under high vacuum for 45 min. The residue was dissolved under exclusion of O_2 in DMF (8 mL) at room temp. *trans*-2-Bromo-1-hydroxyindane (1.45 g, 6.80 mmol) and 15-crown-5 (0.91 mL, 4.6 mmol) were added and the solution was stirred for 2 h. Addition of sat. $NaHCO_3$ solution was followed by the usual workup. Chromatography (petroleum ether/ethyl acetate, 6:1, then petroleum ether/ethyl acetate, 3.5:1) yielded **22*hl*** (2.96 g, 87%, ***h*/*l*** = 1:1) as a colorless oil. The solvent system toluene/ethyl acetate, 12:1 allowed partial/total separation of **22*h*** and **22*l*** by chromatography/middle-pressure chromatography, although **22*l*** still contained 5% of a by-product only separable in the next step.

Compound 22*l*: TLC (toluene/ethyl acetate, 10:1): R_f = 0.38.

Compound 22*h*: M.p. 88 °C (Et_2O/petroleum ether). − TLC (toluene/ethyl acetate, 10:1): R_f = 0.44. − $[\alpha]_D$ = 16.8 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.31 (2 s, 6 H, 2 PhCH_3), 2.33 (2 s, 6 H, 2 PhCH_3), 3.03 (dd, ^2J = 15.8 Hz, ^3J = 8.9 Hz, 1 H, indane-3-H), 3.22 (dd, ^2J = 15.8 Hz, ^3J = 7.6 Hz, 1 H, indane-3′-H), 3.41−3.77 (m, 8 H, OH, indane-2-H, 2-H, 3-H, 4-H, 5-H, 6-H, 6′-H), 4.50−4.61 (m, 4 H, 3 MePhCH, 1-H), 4.73−4.92 (m, 5 H, 5 MePhCH), 5.04 (d, 1 H, indane-1-H), 7.00 (m, 2 H, 2 MePhH), 7.12−7.34 (m, 18 H, 14 MePhH, 4 indane-H). − $C_{47}H_{52}O_6S$ (745.0): calcd. C 75.77, H 7.04; found C 75.54, H 7.07.

D,L-*erythro*-1-(2-Bromobenzyloxy)-2-[2,3,4,6-tetra-*O*-(3-methylbenzyl)-β-D-glucopyranosylthio]indane (23c*h*): To compound **22*h*** (525 mg, 0.70 mmol) in DMF (2.0 mL) were added 2-bromob-

enzyl bromide (300 mg, 1.20 mmol) and NaH (30 mg, 1.25 mmol) at room temp. under exclusion of light. To quicken the reaction, 15-crown-5 (140 μL, 0.71 mmol) was added after 2 h. After a further 4 h, MeOH and then sat. $NaHCO_3$ solution were added, followed by the usual workup. Chromatography yielded **23c*h*** (540 mg, 84%) as a colorless solid. − M.p. 68 °C (Et_2O/petroleum ether). − TLC (toluene/ethyl acetate, 10:1): $R_f = 0.66$. − $[\alpha]_D = 2.0$ ($c = 1.0$, $CHCl_3$). − ^1H NMR (600 MHz, $CDCl_3$): δ = 2.26−2.31 (4 s, 12 H, 4 $PhCH_3$), 3.30 (dd, $^2J = 15.7$ Hz, $^3J = 7.3$ Hz, 1 H, indane-3-H), 3.35 (dd, $^2J = 15.7$ Hz, $^3J = 7.3$ Hz, 1 H, indane-3′-H), 3.47 (5-H), 3.50 (2-H), 3.60 (4-H), 3.66 (6-H), 3.69 (3-H), 3.74 (6′-H), 4.00 (indane-2-H), 4.47 (d, $^2J = 11.9$ Hz, 1 H, MePhCH), 4.53−4.55 (m, 2 H, 2 MePhCH), 4.62 (d, $^3J = 9.7$ Hz, 1 H, 1-H), 4.70−4.83 (m, 5 H, 3 MePhCH, $BrPhCH_2$), 4.90−4.92 (m, 2 H, 2 MePhCH), 4.96 (m, 1 H, indane-1-H), 7.00 (m, 2 H, 2 MePhH), 7.06−7.28 (m, 19 H, 14 MePhH, 4 indane-H, BrPhH), 7.37 (m, 1 H, BrPhH), 7.48 (m, 1 H, BrPhH), 7.65 (m, 1 H, BrPhH). − ^{13}C NMR (150.9 MHz, $CDCl_3$, selected data): δ = 39.3 (indane-3-C), 48.6 (indane-2-C), 69.4 (6-C), 70.1 (BrPhC), 78.0 (4-C), 79.1 (5-C), 82.0 (2-C), 83.4 (indane-1-C), 84.4 (1-C), 86.7 (3-C). − $C_{54}H_{57}BrO_6S$ (914.01): calcd. C 70.96, H 6.29; found C 70.61, H 6.28.

D,L-*erythro*-1-(2-Bromobenzyloxy)-2-[2,3,4,6-tetra-*O*-(3-methylbenzyl)-β-D-glucopyranosylthio]indane (23c*l*): To compound **22*l*** (425 mg, 0.57 mmol) in DMF (2.0 mL) at room temp. were added 2-bromobenzyl bromide (185 mg, 0.74 mmol) and NaH (20 mg, 0.8 mmol). After 2 h, purification as described for **23c*h*** yielded **23c*l*** (420 mg, 81%) as a colorless solid. − M.p. 105 °C (ethyl acetate/petroleum ether). − TLC (toluene/ethyl acetate, 10:1): $R_f = 0.66$. − $[\alpha]_D = -13.2$ ($c = 1.0$, $CHCl_3$). − ^1H NMR (600 MHz, $CDCl_3$): δ = 2.25−2.30 (4 s, 12 H, 4 $PhCH_3$), 3.32 (dd, $^2J = 15.8$ Hz, $^3J = 7.3$ Hz, 1 H, indane-3-H), 3.40 (dd, $^2J = 15.8$ Hz, $^3J = 7.3$ Hz, 1 H, indane-3′-H), 3.49 (2-H), 3.50 (5-H), 3.57 (4-H), 3.65 (6-H), 3.68 (3-H), 3.74 (6′-H), 3.87 (m, 1 H, indane-2-H), 4.50−4.56 (m, 3 H, 3 MePhCH), 4.61 (d, $^3J = 9.7$ Hz, 1 H, 1-H), 4.68−4.75 (m, 3 H, $BrPhCH_2$, MePhCH), 4.79−4.82 (m, 2 H, 2 MePhCH), 4.88−4.94 (m, 3 H, 2 MePhCH, indane-1-H), 7.01 (m, 2 H, 2 MePhH), 7.06−7.26 (m, 19 H, 14 MePhH, 4 indane-H, BrPhH), 7.38 (m, 1 H, BrPhH), 7.48 (m, 1 H, BrPhH), 7.65 (m, 1 H, BrPhH). − ^{13}C NMR (150.9 MHz, $CDCl_3$, selected data): δ = 40.3 (indane-3-C), 50.53 (indane-2-C), 69.4 (6-C), 69.8 (BrPhC), 78.0 (4-C), 79.0 (5-C), 82.2 (2-C), 85.9 (1-C), 86.6 (3-C). − $C_{54}H_{57}BrO_6S$ (914.0): calcd. C 70.96, H 6.29; found C 70.63, H 6.33.

9-(3-Chloro-2-pyrazinyl)-9-hydroxyxanthene (25): To THF (70 mL) was added *n*BuLi (1.6 M in hexane, 7.0 mL, 11.2 mmol) at −10 °C. This was cooled down to −70 °C. After addition of 2,2,6,6-tetramethylpiperidine (2.0 mL, 11.8 mmol), the reaction mixture was warmed up to 0 °C, and 30 min later cooled down to −70 °C. Chloropyrazine (**24**) (0.80 mL, 8.8 mmol) was added and the mixture was stirred for 2 h at −70 °C. 9-Xanthenone (1.96 g, 10 mmol) was added; the mixture was stirred for 2 h at −70 °C and quenched by addition of sat. $NaHCO_3$ solution. After warming, water was added and extraction performed with CH_2Cl_2. The organic phase was washed with water, 1 N hydrochloric acid, and sat. $NaHCO_3$ solution. Drying with $MgSO_4$ and concentration in vacuo yielded a solid, which was dissolved in CH_2Cl_2 (5 mL). Chromatography (petroleum ether/ethyl acetate, 2:1) yielded **25** (2.23 g, 82%) as a colorless solid. − M.p. 179 °C (CH_2Cl_2/Et_2O). − TLC (petroleum ether/ethyl acetate, 2:1): $R_f = 0.28$. − ^1H NMR (250 MHz, $CDCl_3$): δ = 6.93−7.05 (m, 4 H, 4 xanthene-H), 7.14 (s, 1 H, OH), 7.23 (m, 2 H, 2 xanthene-H), 7.34 (m, 2 H, 2 xanthene-H), 8.43 (d, $^2J = 2.5$ Hz, 1 H, pyrazine-H), 8.61 (d, $^2J = 2.5$ Hz, 1 H, pyrazine-H). − $C_{17}H_{11}ClN_2O_2$ (310.7): calcd. C 65.71, H 3.57, N 9.01; found C 65.69, H 3.52, N 8.98.

9-Hydroxy-9-[3-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosylthio)-2-pyrazinyl]xanthene (26): To compound **1** (212 mg, 0.38 mmol), suspended in MeOH (2 mL) was added NaOMe (1 M in MeOH, 380 μL, 0.38 mmol). After 10 min of stirring at room temp., the now clear solution was concentrated under high vacuum and dried for 45 min. The solid residue was dissolved under exclusion of O_2 in DMF (1.5 mL). Compound **25** (118 mg, 0.380 mmol) and 15-crown-5 (80 μL, 0.40 mmol) were added. After 24 h, the usual workup followed. Chromatography (petroleum ether/ethyl acetate, 2:1) yielded **26** (264 mg, 83%) as a colorless, solid foam. − TLC (petroleum ether/ethyl acetate, 2:1): $R_f = 0.27$. − $[\alpha]_D = -9.6$ ($c = 1.0$, $CHCl_3$). − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.31−3.61 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H, 6′-H), 4.16 (d, $^2J = 10.5$ Hz, 1 H, PhCH), 4.30−4.49 (m, 4 H, 4 PhCH), 4.72 (m, 3 H, 3 PhCH), 5.50 (d, $^3J = 10.2$ Hz, 1 H, 1-H), 6.77−7.34 (m, 28 H, 4 Ph, 8 xanthene-H), 7.39 (s, 1 H, OH), 8.36 (d, $^2J = 2.6$ Hz, 1 H, pyrazine-H), 8.40 (d, $^2J = 2.6$ Hz, 1 H, pyrazine-H). − $C_{51}H_{46}N_2O_7S$ (831.0): calcd. C 73.71, H 5.58, N 3.37; found C 73.62, H 5.57, N 3.53.

9-Ethoxy-9-[3-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosylthio)-2-pyrazinyl]xanthene (27a): To compound **26** (600 mg, 0.72 mmol) in EtOH (6 mL) and CH_2Cl_2 (2 mL) was added camphor-10-sulfonic acid (20 mg, 0.09 mmol) at room temp. After 3 h, enough NEt_3 to ensure basic conditions was added. After concentration in vacuo, chromatography (petroleum ether/ethyl acetate, 3:1, 1 vol-% NEt_3) yielded **27a** (560 mg, 91%) as a colorless, solid foam. − TLC (petroleum ether/ethyl acetate, 3:1): $R_f = 0.27$. − $[\alpha]_D = 41.4$ ($c = 1.0$, $CHCl_3$). − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 (t, $^3J = 7.0$ Hz, 3 H, CH_3), 3.12 (q, $^3J = 7.0$ Hz, 2 H, CH_2Me), 3.59−3.80 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H, 6′-H), 4.43 (d, $^2J = 12.1$ Hz, 1 H, PhCH), 4.55 (m, 2 H, 2 PhCH), 4.67−4.93 (m, 5 H, 5 PhCH), 5.65 (d, $^3J = 10.2$ Hz, 1 H, 1-H), 6.88−7.39 (m, 28 H, 4 Ph, 8 xanthene-H), 8.13 (s, 2 H, 2 pyrazine-H). − $C_{53}H_{50}N_2O_7S$ (859.1): calcd. C 74.10, H 5.87, N 3.26; found C 73.74, H 5.86, N 3.35.

9-(Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosid-6-yl)-9-[3-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosylthio)-2-pyrazinyl]xanthene (27b): To methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (205 mg, 0.44 mmol), compound **26** (350 mg, 0.42 mmol), and molecular sieves (4 Å, 5 g) in CH_2Cl_2 (10 mL) at room temp. was added camphor-10-sulfonic acid (4 × 25 mg, 4 × 0.108 mmol) in four portions at hourly intervals. After 19 h, NEt_3 was added to the then neutral reaction mixture. The solution was separated from the molecular sieves, which were washed with ethyl acetate. After filtration, the combined extracts were concentrated and co-evaporated with toluene. Chromatography (toluene/ethyl acetate, 20:1, 1 vol-% NEt_3) yielded **27b** (439 mg, 82%) as a colorless, solid foam. − TLC (toluene/ethyl acetate, 10:1): $R_f = 0.24$. − $[\alpha]_D = 34.5$ ($c = 1.0$, $CHCl_3$ + 1 vol-% pyridine). − ^1H NMR (250 MHz, $CDCl_3$ + 1 vol-% [D_5]pyridine): δ = 3.21 (dd, $^2J = 10.0$ Hz, $^3J = 5.7$ Hz, 1 H, 6b-H), 3.33−3.79 (m, 13 H, OMe, 2a-H, 2b-H, 3a-H, 4a-H, 4b-H, 5a-H, 5b-H, 6a-H, 6′a-H, 6′b-H), 3.94 (dd, 1 H, 3b-H), 4.22 (d, $^2J = 10.9$ Hz, 1 H, PhCH), 4.42 (d, $^2J = 12.0$ Hz, 1 H, PhCH), 4.53 (d, $^2J = 12.0$ Hz, 1 H, PhCH), 4.57−4.86 (m, 11 H, 10 PhCH, 1b-H), 4.93 (d, $^2J = 10.7$ Hz, 1 H, PhCH), 5.67 (d, $^3J = 10.3$ Hz, 1 H, 1a-H), 6.67 (m, 1 H, xanthene-H), 6.82 (m, 2 H, 2 xanthene-H), 6.96 (m, 1 H, xanthene-H), 7.08−7.40 (m, 39 H, 7 Ph, 4 xanthene-H), 8.09 (d, $^3J = 2.3$ Hz, 1 H, pyrazine-H), 8.13 (d, $^3J = 2.3$ Hz, 1 H, pyrazine-H). − $C_{79}H_{76}N_2O_{13}S$ (1277.5): calcd. C 74.27, H 6.00, N 2.19; found C 73.96, H 6.09, N 2.49.

2-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosylthio)pyrazine (28): To compound **1** (285 mg, 0.51 mmol) in DMF (1.5 mL) at 0 °C was

added NaH (14 mg, 0.58 mmol). Chloropyrazine (**24**) (73 μL, 0.82 mmol) was added after 10 min, the ice-bath was removed, and the reaction was stirred for 2 h at room temp. Addition of sat. $NaHCO_3$ solution was followed by the usual workup. Chromatography (toluene/ethyl acetate, 8:1) yielded **28** (282 mg, 87%) as a colorless solid. − TLC (toluene/ethyl acetate, 8:1): R_f = 0.23. − $[\alpha]_D$ = 15.0 (c = 1.0, $CHCl_3$). − ^1H NMR (250 MHz, $CDCl_3$): δ = 3.58−3.83 (m, 6 H, 2-H 3-H, 4-H, 5-H, 6-H, 6′-H), 4.46 (d, ^2J = 12.1 Hz, 1 H, PhCH), 4.55−4.60 (m, 2 H, 2 PhCH), 4.77−4.95 (m, 5 H, 5 PhCH), 5.46 (d, ^2J = 9.7 Hz, 1 H, 1-H), 7.14−7.33 (m, 20 H, 4 Ph), 8.26 (m, 1 H, pyrazine-H), 8.36 (m, 1 H, pyrazine-H), 8.55 (m, 1 H, pyrazine-H). − $C_{38}H_{38}N_2O_5S$ (634.8): calcd. C 71.90, H 6.03, N 4.41; found C 71.55, H 6.09, N 4.42.

9-Hydroxy-9-{3-[2,3,4,6-tetra-*O*-(3-methylbenzyl)-β-D-glucopyranosylthio]-2-pyrazinyl}xanthene (29): To compound **21** (633 mg, 0.97 mmol), suspended in MeOH (1.5 mL), was added NaOMe (1 M in MeOH, 1 mL, 1 mmol). After 20 min at room temp., the clear solution was concentrated under high vacuum and dried for 45 min. The residue was dissolved in DMF (2 mL) under exclusion of O_2. Compound **25** (300 mg, 0.97 mmol) and 15-crown-5 (192 μL, 0.97 mmol) were added and the mixture was stirred for 13 h. The usual workup followed. Chromatography (petroleum ether/ethyl acetate, 3:1) yielded **29** (826 mg, 96%) as a colorless syrup. − TLC (petroleum ether/ethyl acetate, 3:1): R_f = 0.28. − $[\alpha]_D$ = − 6.5 (c = 1.0, $CHCl_3$). − ^1H NMR (250 MHz, $CDCl_3$): δ = 2.24−2.28 (m, 12 H, 4 $PhCH_3$), 3.33 (dd, ^3J = 10.1 Hz, ^3J = 9.8 Hz, 1 H, 2-H), 3.44−3.57 (m, 5 H, 3-H, 4-H, 5-H, 6-H, 6′-H), 4.12 (d, ^2J = 10.4 Hz, 1 H, MePhCH), 4.27 (d, ^2J = 12.0 Hz, 1 H, MePhCH), 4.29 (d, ^2J = 10.4 Hz, 1 H, MePhCH), 4.40 (d, ^2J = 12.0 Hz, 1 H, MePhCH), 4.43 (d, ^2J = 10.6 Hz, 1 H, MePhCH), 4.63−4.73 (m, 3 H, 3 MePhCH), 5.50 (d, ^3J = 10.1 Hz, 1 H, 1-H), 6.71−7.33 (m, 24 H, 16 MePhH, 8 xanthene-H), 7.38 (s, 1 H, OH), 8.35 (d, ^3J = 2.5 Hz, 1 H, pyrazine-H), 8.39 (d, ^3J = 2.5 Hz, 1 H, pyrazine-H). − $C_{55}H_{54}N_2O_7S$ (887.1): calcd. C 74.47, H 6.14, N 3.16; found C 74.81, H 6.21, N 3.28.

9-(2-Bromobenzyloxy)-9-{3-[2,3,4,6-tetra-*O*-(3-methylbenzyl)-β-D-glucopyranosylthio]-2-pyrazinyl}xanthene (30c): To compound **29** (420 mg, 0.47 mmol), 2-bromobenzyl alcohol (89 mg, 0.47 mmol), and molecular sieves (4 Å, 3.0 g) in CH_2Cl_2 (5 mL) was added camphor-10-sulfonic acid (2 × 55 mg, 2 × 0.24 mmol), in two portions, separated by 2 h. After 2 h, the then neutral reaction mixture was processed as described for **27b**. Chromatography (petroleum ether/ethyl acetate, 5:1, 1 vol-% NEt_3) yielded 448 mg (90%) of **30c** (448 mg, 90%) as a colorless syrup. − TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.42. − $[\alpha]_D$ = 11.1 (c = 1.0, $CHCl_3$ + 1 vol-% pyridine). − ^1H NMR (250 MHz, $CDCl_3$ + 1 vol-% [D_5]pyridine): δ = 2.24 (s, 3 H, $PhCH_3$), 2.27−2.29 (m, 9 H, 3 $PhCH_3$), 3.47−3.76 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H, 6′-H), 4.23 (dd, 2 H, $BrPhCH_2$), 4.38 (d, ^2J = 12.0 Hz, 1 H, MePhCH), 4.44 (d, ^2J = 10.4 Hz, 1 H, MePhCH), 4.50 (d, ^2J = 10.4 Hz, 1 H, MePhCH), 4.52 (d, ^2J = 12.0 Hz, 1 H, MePhCH), 4.74−4.86 (m, 4 H, 2 $MePhCH_2$), 5.65 (d, ^3J = 10.3 Hz, 1 H, 1-H), 6.90−7.54 (m, 26 H, 16 MePhH, 8 xanthene-H), 7.62 (m, 2 H, 2 BrPhH), 8.09 (d, ^3J = 2.3 Hz, 1 H, pyrazine-H), 8.13 (d, ^3J = 2.3 Hz, 1 H, pyrazine-H).

2,7-Di-*tert*-butyl-4,5-bis(hydroxymethyl)-9,9-dimethylxanthene (32): To compound **31** (3.36 g, 8.19 mmol) in THF (50 mL), in a reaction flask with a 12-inch Vigreux column, was added borane−dimethyl sulfide (10 M in THF, 3.3 mL, 33 mmol) at room temp. The reaction mixture was heated to reflux and the dimethyl sulfide was distilled off. After 4 h, the reaction mixture was cooled and water (30 mL) was added carefully. The mixture was extracted with Et_2O (2 × 200 mL). The combined organic phase was washed twice with sat. $NaHCO_3$ solution, then with water and brine. After drying with $MgSO_4$, concentration in vacuo gave a solid, which was dissolved in refluxing ethyl acetate (15 mL). After cooling and addition of petroleum ether (40 mL), **32** (2.76 g, 88%) crystallized as colorless crystals. Chromatography (petroleum ether/ethyl acetate, 3:2) of the concentrated mother liquor yielded further **32** (0.28 g, 9%). − M.p. 196° (ethyl acetate). − TLC (petroleum ether/ethyl acetate, 1:1): R_f = 0.58. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.33 (s, 18 H, 2 tBu), 1.65 (s, 6 H, 2 Me), 2.38 (br. s, 1 H, 2 OH), 4.80 (s, 4 H, CH_2O), 7.18 (d, ^4J = 2.3 Hz, 2 H, 2 xanthene-H), 7.40 (d, ^4J = 2.3 Hz, 2 H, 2 xanthene-H). − EI-MS (70 eV); m/z (%): 382 (9) $[M]^+$, 367 (100) $[M - CH_3]^+$. − $C_{25}H_{34}O_3$ (382.5): calcd. C 78.49, H 8.96; found C 78.17, H 9.20.

2,7-Di-*tert*-butyl-4,5-bis(chloromethyl)-9,9-dimethylxanthene (33): To dist. $SOCl_2$ (2.1 mL, 29 mmol) in CH_2Cl_2 (17 mL) was added **32** (1.84 g, 4.82 mmol) in CH_2Cl_2 (17 mL) over a period of 30 min at room temp. After 2 h, the reaction mixture was concentrated in vacuo. The usual workup, without chromatography, yielded **33** (1.86 g, 92%) as a colorless solid. − M.p. 202 °C (Et_2O/petroleum ether). − TLC (petroleum ether/ethyl acetate, 10:1): R_f = 0.71. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.34 (s, 18 H, 2 tBu), 1.64 (s, 6 H, 2 Me), 4.87 (s, 4 H, 2 CH_2Cl), 7.28 (d, ^4J = 2.3 Hz, 2 H, 2 xanthene-H), 7.41 (d, ^4J = 2.3 Hz, 2 H, 2 xanthene-H). − $C_{25}H_{32}Cl_2O$ (419.4): calcd. C 71.59, H 7.69; found C 71.80, H 7.65.

2,7-Di-*tert*-butyl-4-ethoxymethyl-5-hydroxymethyl-9,9-dimethylxanthene (34a): To compound **32** (350 mg, 0.92 mmol) in CH_2Cl_2 (20 mL) at −20 °C were added NaH (60% in oil, 46 mg, 1.15 mmol), 15-crown-5 (200 μL, 1.00 mmol), and ethyl triflate (120 μL, 0.93 mmol). After warming to 14 °C over a period of 2 h, stirring was continued for another 1 h at 14 °C. The addition of sat. NH_4Cl solution was followed by extraction with CH_2Cl_2. The organic phase was washed with water and brine, dried with $MgSO_4$, and concentrated in vacuo. Chromatography (toluene/ethyl acetate, 15:1) yielded **34a** (340 mg, 91%) as a colorless solid. − M.p. 190 °C (Et_2O/petroleum ether). − TLC (toluene/ethyl acetate, 3:1): R_f = 0.58. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.21 (t, 3 H, $CHCH_3$), 1.33 (s, 9 H, tBu), 1.34 (s, 9 H, tBu), 1.64 (2 s, 6 H, xanthene-CH_3), 3.50 (q, 2 H, CH_2Me), 4.68 (s, 2 H, CH_2O), 4.77 (s, 2 H, CH_2O), 7.16 (m, 2 H, xanthene-H), 7.37 (d, 1 H, xanthene-H), 7.41 (d, 1 H, xanthene-H). − EI-MS (70 eV); m/z (%): 410 (9) $[M]^+$, 395 (100) $[M - CH_3]^+$). − $C_{27}H_{38}O_3$ (410.7): calcd. C 78.98, H 9.33; found C 78.96, H 9.23.

2,7-Di-*tert*-butyl-4-chloromethyl-5-ethoxymethyl-9,9-dimethylxanthene (35a): To compound **34a** (235 mg, 0.57 mmol) in CH_2Cl_2 (6 mL) at room temp. was added dist. $SOCl_2$ (125 μL, 1.7 mmol). After 2 h, the reaction mixture was concentrated in vacuo. Chromatography (petroleum ether/ethyl acetate, 40:1) yielded **35a** (218 mg, 89%) as a colorless syrup. − TLC (petroleum ether/ethyl acetate, 40:1): R_f = 0.64. − ^1H NMR (250 MHz, $CDCl_3$): δ = 1.31 (t, ^3J = 7.0 Hz, 3 H, $OCCH_3$), 1.33 (s, 9 H, tBu), 1.34 (s, 9 H, tBu), 1.64 (2 s, 6 H, 2 xanthene-CH_3), 3.69 (q, ^3J = 7.0 Hz, 2 H, CH_2Me), 4.77 (s, 2 H, xanthene-CH_2), 4.79 (s, 2 H, xanthene-CH_2), 7.25 (d, 1 H, xanthene-H), 7.34 (d, 2 H, xanthene-H), 7.40 (d, ^4J = 2.3 Hz, 1 H, xanthene-H). − EI-MS (70 eV); m/z (%): 428 (7) $[M]^+$, 413 (100) $[M - CH_3]^+$. − $C_{27}H_{37}ClO_2$ (429.0): calcd. C 75.59, H 8.69; found C 75.71, H 8.69.

2,7-Di-*tert*-butyl-4-chloromethyl-9,9-dimethyl-5-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosid-6-yloxy)methylxanthene (35b): To methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (890 mg, 1.92 mmol) in THF (20 mL) at room temp. were added NaH (60% in oil, 96 mg, 2.4 mmol), 15-crown-5 (0.80 mL, 4.0 mmol), compound 33

(810 mg, 1.93 mmol), and anhydrous NaI (288 mg, 1.92 mmol). After 2 d under exclusion of light, sat. $NaHCO_3$ solution was added and the usual workup followed. Chromatography (toluene/ethyl acetate, 24:1) gave as first fraction **35b** (678 mg, 41%) as a colorless syrup. − TLC (toluene/ethyl acetate, 10:1): R_f = 0.60. − $[\alpha]_D$ = 19.0 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.29 (s, 9 H, *t*Bu), 1.32 (s, 9 H, *t*Bu), 1.54 (s, 3 H, xanthene-CH_3), 1.58 (s, 3 H, xanthene-CH_3), 3.38 (s, 3 H, OMe), 3.54−3.84 (m, 5 H, 2-H, 4-H, 5-H, 6-H, 6′-H), 3.96 (dd, 1 H, 3-H), 4.37 (d, ^3J = 10.6 Hz, 1 H, PhCH), 4.63−5.00 (m, 10 H, 5 PhCH, 2 xanthene-CH_2, 1-H), 6.98−7.38 (m, 19 H, 3 Ph, 4 xanthene-H). − $C_{53}H_{63}ClO_7$ (847.5): calcd. C 75.11, H 7.49; found C 74.86, H 7.46.

2,7-Di-*tert*-butyl-4-chloromethyl-9,9-dimethyl-5-(methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranosid-4-yloxy)methylxanthene (35d): To methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (1.11 g, 2.38 mmol) in THF (25 mL) at room temp. were added NaH (60% in oil, 170 mg, 4.3 mmol), 15-crown-5 (0.95 mL, 4.8 mmol), compound **33** (1.00 g, 2.38 mmol), and anhydrous NaI (360 mg, 2.40 mmol). The reaction was treated as described for **35b**. The first fraction was **35d** (1.29 g, 64%) as a colorless syrup. − TLC (toluene/ethyl acetate, 10:1): R_f = 0.59. − $[\alpha]_D$ = 57.0 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.30 (s, 9 H, *t*Bu), 1.33 (s, 9 H, *t*Bu), 1.60 (s, 3 H, xanthene-CH_3), 1.63 (s, 3 H, xanthene-CH_3), 3.40 (s, 3 H, OMe), 3.56−3.70 (m, 4 H, 2-H, 4-H, 6-H, 6′-H), 3.82 (m, 1 H, 5-H), 4.03 (dd, 1 H, 3-H), 4.40 (s, 2 H, xanthene-CH_2), 4.54 (d, ^3J = 11.3 Hz, 1 H, PhCH), 4.62−4.99 (m, 7 H, 1-H, xanthene-CH_2, 4 PhCH), 5.12 (d, ^3J = 12.7 Hz, 1 H, PhCH), 7.11−7.39 (m, 19 H, 4 xanthene-H, 3 Ph). − $C_{53}H_{63}ClO_2$ (847.5): calcd. C 75.11, H 7.49; found C 75.04, H 7.56.

2,7-Di-*tert*-butyl-5-ethoxymethyl-9,9-dimethyl-4-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosylthio)methylxanthene (36a): To compound **1** (187 mg, 0.33 mmol) and compound **35a** (142 mg, 0.33 mmol) in DMF (4 mL) at 0 °C were added NaH (17 mg, 0.7 mmol) and 15-crown-5 (66 μL, 0.33 mmol). After 2 h, MeOH and then sat. NH_4Cl solution were added and followed by the usual workup. Chromatography (toluene/ethyl acetate, 20:1) yielded **36a** (307 mg, 97%) as a colorless syrup. − TLC (petroleum ether/ethyl acetate, 4:1): R_f = 0.60. − $[\alpha]_D$ = − 83.7 (c = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.24 (t, 3 H, $CHCH_3$), 1.27 (s, 9 H, *t*Bu), 1.35 (s, 9 H, *t*Bu), 1.58 (s, 3 H, xanthene-CH_3), 1.65 (s, 3 H, xanthene-CH_3), 3.45 (5-H), 3.47 (2-H), 3.59 (3-H), 3.59 (4-H), 3.60 (m, 2 H, CH_2Me), 3.71 (6-H), 3.80 (6′-H), 4.11 (m, 2 H, CH_2S), 4.35 (d, ^3J = 9.5 Hz, 1 H, 1-H), 4.52−4.88 (m, 10 H, 4 $PhCH_2$, CH_2OEt), 6.94 (m, 2 H, 2 PhH), 7.06−7.40 (m, 24 H, 4 Ph, 4 xanthene-H (3: 7.12, 6: 7.21)). − ^{13}C NMR (150.9 MHz, $CDCl_3$, selected data): δ = 15.3 ($OCCH_3$), 29.1 (CH_2S), 66.2 (OCH_2Me), 67.9 (CH_2OEt), 69.2 (6-C), 78.1 (4-C), 79.0 (5-C), 81.8 (2-C), 82.7 (1-C), 86.6 (3-C). − INEPT: $^1J_{1\text{-H},1\text{-C}}$ = 157 Hz. − $C_{61}H_{72}O_7S$ (949.3): calcd. C 77.18, H 7.64; found C 77.36, H 7.63.

2,7-Di-*tert*-butyl-9,9-dimethyl-5-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosid-6-yloxy)methyl-4-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosylthio)methylxanthene (36b): To compound **1** (328 mg, 0.59 mmol) and compound **35b** (500 mg, 0.59 mmol) in DMF (5 mL) at 0 °C were added NaH (24 mg, 1.0 mmol) and 15-crown-5 (117 μL, 0.59 mmol). Ice-cooling was removed after 1 h and the reaction was stirred for 20 h at room temp. The reaction was worked up by addition of sat. $NaHCO_3$ solution and water, followed by extraction with Et_2O. The organic phase was washed with water and brine, dried with $MgSO_4$, and concentrated in vacuo. Chromatography (toluene/ethyl acetate, 5:1) yielded **36b** (640 mg, 79%) as a colorless syrup. − TLC (toluene/ethyl acetate, 10:1): R_f = 0.35. − $[\alpha]_D$ = − 65.6 (c = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.27 (s, 9 H, *t*Bu), 1.30 (s, 9 H, *t*Bu), 1.54 (s, 3 H, xanthene-CH_3), 1.63 (s, 3 H, xanthene-CH_3), 3.35 (s, 3 H, OMe), 3.43 (5a-H), 3.44 (2a-H), 3.55 (2b-H), 3.56 (3a-H), 3.59 (4a-H), 3.60 (4b-H), 3.69 (6b-H), 3.70 (5b-H), 3.71 (6a-H), 3.75 (6b′-H), 3.80 (6′a-H), 3.94 (3b-H), 4.09 (m, 2 H, CH_2S), 4.31 (d, ^3J = 9.8 Hz, 1 H, 1a-H), 4.43−4.48 (m, 2 H, 2 PhCH), 4.55 (d, ^2J = 10.7 Hz, 1 H, PhCH), 4.61 (d, 1 H, 1b-H), 4.61−4.66 (m, 4 H, 4 PhCH), 4.71 (d, ^2J = 10.6 Hz, 1 H, PhCH), 4.75−4.84 (m, 5 H, 5 PhCH), 4.86 (s, 2 H, xanthene-CH_2O), 4.94 (d, ^2J = 11.0 Hz, 1 H, PhCH), 6.89 (m, 2 H, 2 PhH), 7.05−7.41 (m, 37 H, 33 Ph-H, 4 xanthene-H (3: 7.10, 6: 7.34)). − ^{13}C NMR (150.9 MHz, $CDCl_3$, selected data): δ = 29.2 (CH_2S), 68.1 (xanthene-CH_2O), 68.7 (6b-C), 69.2 (6a-C), 70.2 (5b-C), 77.7 (4b-C), 78.0 (4a-C), 78.9 (5a-C), 79.9 (2b-C), 81.8 (2a-C), 82.1 (3b-C), 82.4 (1a-C), 86.6 (3a-C), 98.1 (1b-C). − INEPT: $^1J_{1\text{a-H},1\text{a-C}}$ = 157 Hz, $^1J_{1\text{b-H},1\text{b-C}}$ = 168 Hz. − $C_{87}H_{98}O_{12}S$ (1367.8): calcd. C 76.40, H 7.22; found C 76.39, H 7.27.

2,7-Di-*tert*-butyl-9,9-dimethyl-4-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosylthio)methyl-5-(methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranosid-4-yloxy)methylxanthene (36d): To compound **1** (668 mg, 1.20 mmol) and compound **35d** (1.03 g, 1.22 mmol) in DMF (9 mL) at 0 °C were added NaH (36 mg, 1.5 mmol) and 15-crown-5 (240 μL, 1.20 mmol). The reaction mixture was treated as described for **36b**. Chromatography (toluene/ethyl acetate, 18:1) yielded **36d** (1.53 g, 93%) as a colorless syrup. − TLC (toluene/ethyl acetate, 10:1): R_f = 0.57. − $[\alpha]_D$ = − 33.0 (c = 1.0, $CHCl_3$). − ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.28 (s, 9 H, *t*Bu), 1.31 (s, 9 H, *t*Bu), 1.54 (s, 3 H, xanthene-CH_3), 1.65 (s, 3 H, xanthene-CH_3), 3.36 (s, 3 H, OMe), 3.39 (5a-H), 3.41 (2a-H), 3.48 (6b-H), 3.55 (3a-H), 3.55 (2b-H), 3.58 (6′b-H), 3.60 (4b-H), 3.61 (4a-H), 3.69 (6a-H), 3.74 (6′a-H), 3.80 (5b-H), 3.96 (CH−S-1a-C), 4.01 (3b-H), 4.01 (CH−S-1a-C), 4.32 (1a-H), 4.32−4.38 (m, 2 H, 2 PhCH), 4.43 (d, ^2J = 9.8 Hz, 1 H, PhCH), 4.54−4.58 (m, 4 H, 2 $PhCH_2$), 4.58 (1b-H), 4.64 (d, ^2J = 12.0 Hz, 1 H, PhCH), 4.71−4.84 (m, 5 H, 5 PhCH), 4.93 (d, ^2J = 11.0 Hz, 1 H, PhCH), 5.03 (d, ^2J = 12.2 Hz, 1 H, CHO-4b-C), 5.08 (d, ^2J = 12.2 Hz, 1 H, CHO-4b-C), 6.86 (m, 2 H, 2 PhH), 7.00−7.26 (m, 37 H, 33 PhH, 4 xanthene-H (3: 7.11, 6: 7.30, 1: 7.31, 8: 7.35). − ^{13}C NMR (150.9 MHz, $CDCl_3$, selected data): δ = 29.6 (CH_2S), 55.1 (OMe), 69.2 (6a-C), 69.5 (6b-C), 69.9 (CO-4b-C), 70.2 (5b-C), 78.0 (4a-C), 78.5 (4b-C), 78.8 (5a-C), 80.2 (2b-C), 81.8 (2a-C), 82.2 (3b-C), 83.2 (1a-C), 86.7 (3a-C), 98.0 (1b-H). − $C_{87}H_{98}O_{12}$ (1367.8): calcd. C 76.40, H 7.22; found C 76.34, H 7.32.

2,7-Di-*tert*-butyl-9,9-dimethyl-5-(methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranosid-6-yloxy)methyl-4-(*N*-succinimidylthio)methylxanthene (37b): To compound **36b** (114 mg, 0.08 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (85 mg, 0.41 mmol) in CH_2Cl_2 (3.0 mL) was added *N*-iodosuccinimide (93 mg, 0.41 mmol). After 16 h under exclusion of light, the addition of sat. $Na_2S_2O_3$ solution was followed by the usual workup. Chromatography (toluene/ethyl acetate, 5:1) yielded **22b** (64 mg, 86%) as a colorless syrup. − TLC (toluene/ethyl acetate, 5:1): R_f = 0.23. − $[\alpha]_D$ = 22.2 (c = 1.0, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.29 (s, 9 H, *t*Bu), 1.30 (s, 9 H, *t*Bu), 1.52 (s, 3 H, xanthene-CH_3), 1.56 (s, 3 H, xanthene-CH_3), 2.53 (s, 4 H, CH_2CH_2), 3.38 (s, 3 H, OMe), 3.55 (dd, 1 H, 6-H), 3.59−3.98 (m, 5 H, 2-H, 3-H, 4-H, 5-H, 6′-H), 4.20 (d, ^2J = 12.2 Hz, 1 H, CH−S), 4.26 (d, ^2J = 12.2 Hz, 1 H, CHS), 4.40 (d, ^2J = 10.6 Hz, 1 H, PhCH), 4.63−5.06 (m, 8 H, 5 PhCH, xanthene-CH_2, 1-H), 6.98−7.03 (m, 3 H, 3 PhCH), 7.16−7.37 (m, 16 H, 12 PhH, 4 xanthene-H). − FAB MS (positive mode, matrix: 3-nitrobenzyl alcohol with NaI); *m/z*: 1115 (2́) [{MNaI}Na]$^+$, 964 (75), [MNa]$^+$, 478 (100). − $C_{57}H_{67}NO_9S$ (942.2): calcd. C 72.66, H 7.17, N 1.49; found C 72.51, H 7.20, N 2.00.

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