Prearranged Glycosides

Part 12

Intramolecular Mannosylations of Glucose Derivatives *via* Prearranged Glycosides

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A series of prearranged glycosides **5**, **17**, **23**, **28**, **37**, and **41**, having a benzyl-protected 1-thiomannosyl donor linked through its positions 2, 3, 4, and 6 *via* succinate and malonate tethers, respectively, to positions 2, 3, and 6 of a benzyl glucopyranoside acceptor, were prepared by condensation of the respective mannosyl succinates and malonates with suitably protected benzyl glucopyranosides. The prearranged glycosides were intramolecularly coupled under various conditions to give the corresponding tethered $(1 \rightarrow 4)$-linked disaccharides. The yields and anomer ratios of the products of these couplings were interpreted in terms of the thermodynamic stability of the resulting disaccharides. In the case of prearranged glycoside **17**, having positions 3 of both the donor and the acceptor linked by a succinate tether, a strong dependence of the diastereoselectivity of the intramolecular glycosylation on the activation procedure was observed. All other cases did not show a significant dependence of the outcome of the anomeric configuration in intramolecular glycosylation on the activation procedure or the solvent.

Introduction. – Intramolecular glycosylation provides an alternative route for the construction of *O*-glycosidic bonds in all those cases where classical glycosylation procedures (*i.e.*, intermolecular condensation of a glycosyl donor and a glycosyl acceptor) are less effective. Two different strategies can be envisaged for the intramolecularization of chemical glycosylation reactions. First, the glycosyl donor and glycosyl acceptor are connected by a suitable temporary linker, which is cleaved during the formation of the glycosidic bond. Acetal [1–11] and silylene-acetal linkers [12–16] have been among the first to have been used systematically for this purpose. Furthermore, carbonates [17–19], orthoesters [20], and cobaltcarbonyl complexes of alkynes [21] have also been applied as temporary linkers for this approach. However, thorough investigations of intramolecular glycosylations of this type revealed that also intermolecular processes may be involved during the formation of the *O*-glycosidic bond [19][20]. The second strategy for establishing intramolecular glycosylation resembles *Ogawa*'s cycloglycosylation [22–24] and makes use of stable persisting tethers between donor and acceptor that are not cleaved during glycosidic-bond formation [25–42]. The most significant advantage of the latter strategy of intramolecular glycosylation *via* prearranged glycosides is the fact that rings are formed during the glycosylation step. Therefore, the outcome of the configuration at the anomeric center on glycosylation strongly depends on the size of the ring formed and, thus, can simply be controlled by selection of an appropriate tether. Furthermore, also the diastereoselectivity of ring formation can be controlled by the positions to which the tether is linked in the glycosyl donor and the glycosyl acceptor, respectively. For

example, it has been demonstrated that a double diastereoselection governs the outcome of the anomer configuration in intramolecular glycosylations in these cases [34].

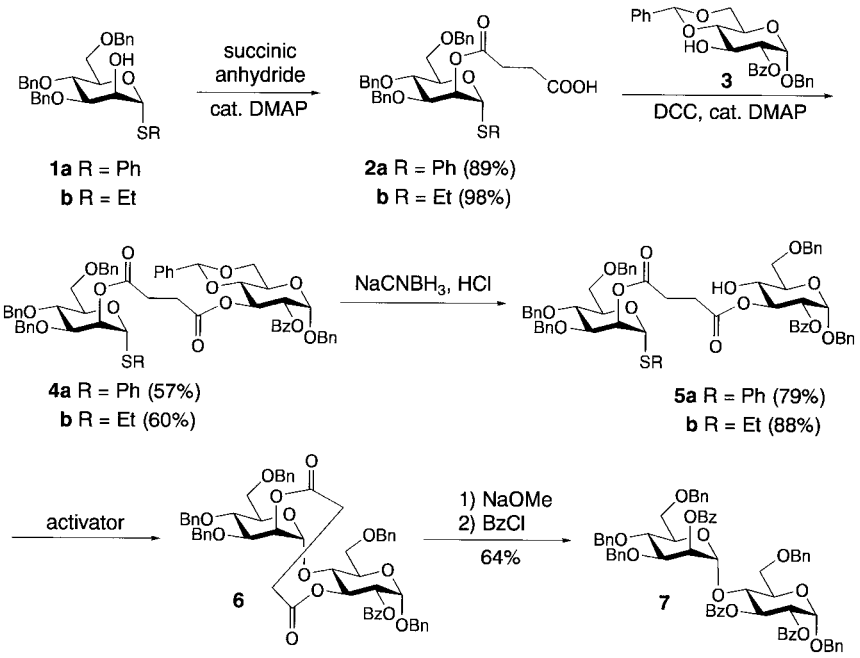
Attractive applications of the strategy of intramolecular glycosylation *via* prearranged glycosides are β-selective L-rhamnosylations [25][26][30] and D-mannosylations [27], which are still difficult to perform with classical approaches. Recently, we disclosed such highly diastereoselective intramolecular β-mannosylations for the construction of the disaccharide residues β-D-Man*p*-(1 → 4)-D-Glc*p*, β-D-Man*p*-(1 → 4)-D-GlcNAc*p*, β-D-Man*p*-(1 → 4)-D-Gal*p*, and β-D-Man*p*-(1 → 4)-D-Man*p* [35], all of which are important structures found in many naturally occurring oligosaccharides. Furthermore, intramolecular β-mannosylations and β-rhamnosylations were also shown to be well suited for the construction of tetrasaccharide fragments related to bacterial exopolysaccharides [30][40]. Of the various factors which may influence the diastereoselectivity of intramolecular β-mannosylations in the case of syntheses of D-Man*p*-(1 → 4)-D-Glc*p* fragments, we have systematically studied the influence of ring size when a dicarboxylic tether was linked to position 6 of the mannosyl donor and to position 3 of the glucosyl acceptor. Highest β-selectivities have been found in these cases for succinate and malonate tethers [41]. However, to gain more insight into additional factors which may influence the outcome of anomer configuration in intramolecular glycosylations, it is important to study further examples.

In continuation of these systematic studies, we now extended the intramolecular mannosylation with succinate and malonate tethers to mannosylations where the tether is linked to different positions of the donor and of the acceptor, respectively.

Results. – For the synthesis of D-Man*p*-(1 → 4)-D-Glc*p* fragments from mannosyl donors tethered with succinate and malonate, respectively, at various positions, we followed the previously published route for prearranged 1-thioglycosides [25][41]. Treatment of phenyl (**1a**) [43][44] and ethyl 3,4,6-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (**1b**) [45] with succinic anhydride and a catalytic amount of *N*,*N*-dimethylpyridin-4-amine (DMAP) afforded glycosides **2a** (89%) and **2b** (99%), respectively (*Scheme 1*). Next, the latter were condensed with glucoside **3** [26] in the presence of dicyclohexylcarbodiimide (DCC), and the benzylidene group of the intermediate succinyl-linked glycosides **4** (57–60%) was regioselectively opened using *Garegg*'s procedure ($NaCNBH_3$, HCl in THF) [46] to give the prearranged glycosides **5a** (79%) and **5b** (87%) [34]. Both glycosides **5** were then cyclized under various conditions (see below, *Table*) to the succinyl-tethered α-D-(1 → 4)-linked disaccharide **6**, the structure of which was unambiguously assigned by NMR spectroscopy [27]. No β-D-linked product was obtained. The α-D-linkage in **6** was also established by deacylation (cat. NaOMe, MeOH) and benzoylation (BzCl, pyridine) to give disaccharide **7** in 64% yield. In its NMR spectrum, **7** showed a C,H-coupling constant for the anomeric center of the mannosyl residue ($^1J = 175.5$ Hz) that is characteristic for α-D-mannosides [47].

To prepare prearranged glycosides having the tether attached at position 3 of the mannosyl donor, 1-thiomannosides **8** [48–50] were blocked at positions 6 with (*tert*-butyl)chlorodiphenylsilane, and the intermediates **9a** (78%) and **9b** (80%) were treated with 2,2-dimethoxypropane (DMP, acetone, cat. TsOH) to give 1-thiomannosides **10a**

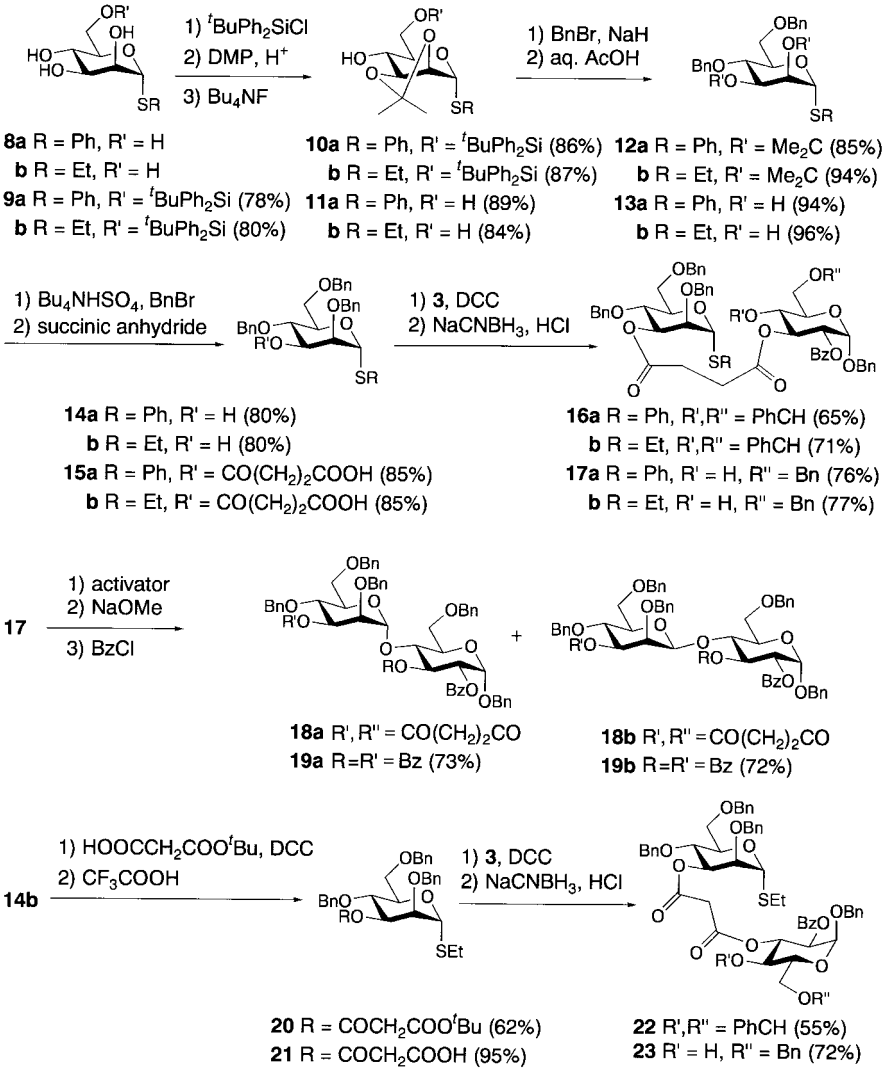
Scheme 1



(86%) and **10b** (87%), respectively (*Scheme 2*). Next, fluoride-catalyzed desilylation (cat. Bu_4NF, THF) afforded compounds **11** (84–89%), which were benzylated (BnBr, NaH, DMF) at positions 4 and 6 to give intermediates **12** (85–94%). Final removal of the isopropylidene group (70% $AcOH/H_2O$) and phase-transfer benzylation (BnBr, $NaOH/H_2O$, CH_2Cl_2, cat. $(Bu_4N)HSO_4$) of the axial OH group of the intermediates **13** afforded in 80% yield mannosides **14a** and **14b**, which were succinylated at position 3 with succinic anhydride to give 1-thiomannosides **15** in 85% yield. The latter were condensed with glucoside **3** as described above for compounds **4**, and the benzylidene groups of the resulting intermediates **16** were regioselectively opened to give prearranged glycosides **17**. Once again, cyclization of these succinyl-tethered glycosides under various conditions (see below, *Table*) gave mixtures of the corresponding α- and β-D-$(1\rightarrow4)$-linked disaccharides **18**. Also the tethered disaccharides **18a** and **18b** could be separated by chromatography, but the anomer configuration of the mannosyl residue could not be assigned since the relevant C,H-coupling constants for **18a** ($^1J=$ 168.4 Hz) and for **18b** ($^1J=167.1$ Hz) were not significantly different. Furthermore, rather unusual vicinal coupling constants ($^3J(1,2)=5.3$ Hz) were found for both disaccharides, which may be attributed to a conformation different from the usual $^4C_1$ conformation of glycopyranosides. Therefore, a deacylation-benzoylation sequence similar to that described above for the conversion **6** → **7** was performed with compounds **18a** and **18b**, yielding the disaccharides **19a** (73%) and **19b** (72%), which now allowed the assignment of the anomer configuration of the mannosyl residue by their NMR data ($^1J=164.8$ Hz for **19a** and 153.8 Hz for **19b**). In a similar sequence

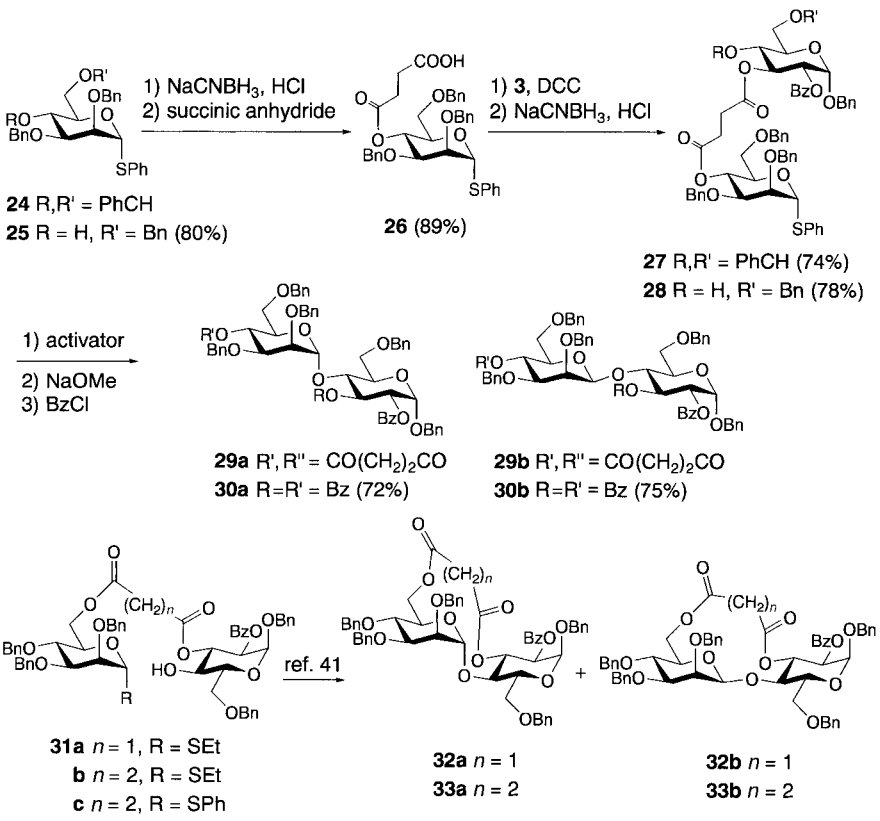
[41], **14b** was also treated with *tert*-butyl hydrogen malonate (DCC, 1-hydroxy-1*H*-benzotriazole) to give first ethyl 1-thiomannoside **20** (62%), the *tert*-butyl group of which was then removed with CF_3COOH to afford malonate **21** (95%). Condensation of the latter with glucoside **3** provided **22** (55%), which afforded the corresponding malonyl-tethered glycoside **23** upon regioselective opening of the benzylidene ring of the glucosyl residue. However, all attempts to cyclize compound **23** under conditions similar to those for cyclization of **17** failed. Solely products of decomposition of the starting material could be detected on TLC of the crude reaction mixture.

Scheme 2



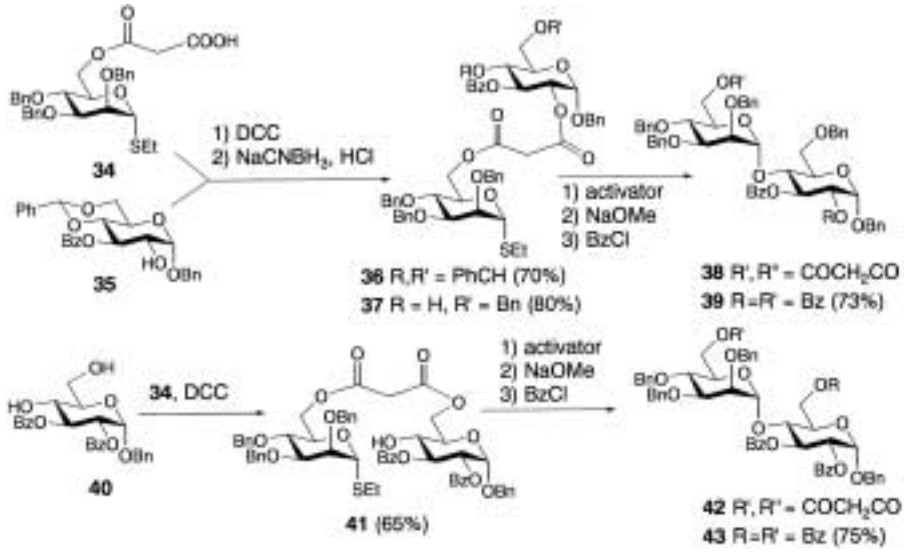
Prearranged glycosides tethered *via* position 4 of the respective mannosyl residues were prepared as follows. First, a suitably protected mannoside was needed to allow the introduction of the succinyl tether. Thus, phenyl 1-thiomannoside **25** was first prepared by opening of the benzylidene ring [46] of phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (**24**) [51] (*Scheme 3*). Next, succinylation at position 4 afforded monosaccharide **26** (89%), which was again condensed with glucoside **3**. The thus-obtained succinyl-tethered glycoside **27** (74%) was converted as described above to compound **28** (78%) and cyclized (see below, *Table*) to the tethered disaccharides **29**. As previously observed for the tethered disaccharides **18**, no assignment of the anomer configuration of saccharides **29a** and **29b** could be made by NMR spectroscopy (C(1) of the mannosyl residue at 100.4 (**29a**) and 100.8 ppm (**28a**); corresponding $^1J = 175.0$ (**29a**) and 173.7 Hz (**29b**)). Therefore, disaccharides **29** were each deacylated and benzoylated to give saccharides **30**, which now showed characteristic C,H-coupling constants ($^1J = 174.1$ Hz (**30a**) and 156.9 Hz (**30b**)). For comparison reasons, the *Table* (see below) also shows the already known results of the cyclization of compound **31**, which established the formation of anomer mixtures of tethered disaccharides **32** and **33**, respectively, depending on the reaction conditions [41].

Scheme 3



The two prearranged glycosides tethered with a malonate spacer *via* position 6 of the mannosyl donor to position 2 and 6, respectively, of the glucosyl acceptor were prepared from ethyl 1-thiomannoside **34** [41]. Thus, condensation of the latter with benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**35**) [52], followed by regioselective opening of the benzylidene group of intermediate **36**, afforded the prearranged glycoside **37** (*Scheme 4*). Cyclization of compound **37** gave exclusively the tethered α-D-linked disaccharide **38** (see below, *Table*), which was deacylated and benzoylated to afford **39** in 73% yield. Both disaccharides showed C,H-coupling constants typical for an α-D-linkage ($^1J = 168.8$ (**38**) and 171.8 Hz (**39**)). Similarly, **34** was condensed regioselectively with benzyl 2,3-di-*O*-benzoyl-α-D-glucopyranoside (**40**) [53] to give the prearranged glycoside **41** (65%), cyclization of which (see below, *Table*) and subsequent deacylation and benzoylation afforded α-D-linked disaccharides **42** and **43**, respectively ($^1J = 172.5$ (**42**) and 172.0 Hz (**43**)).

Scheme 4



Discussion. – The *Table* summarizes the results for the cyclizations of tethered disaccharides **5**, **17**, **23**, **28**, **31**, **37**, and **41**. All cyclizations described here were performed in CH_2Cl_2 or MeCN with *N*-iodosuccinimide (NIS) for phenyl and ethyl 1-thioglycosides and with methyl trifluoromethanesulfonate (MeOTf) for ethyl 1-thioglycosides, as previously described [41]. The results of the cyclizations of prearranged glycosides **5** (*Table*, *Entries 1–3*) having the succinate tether at position 2 of the mannosyl donor and at position 3 of the glucosyl acceptor are in contrast to previously performed glycosylations with glucosyl or galactosyl instead of mannosyl donors [31][39][42]. In the case of **5**, solely α-D-(1 $\rightarrow$ 4)-linked disaccharides were found. It was originally expected for compounds **5** to give at least significant amounts of the corresponding β-D-linked disaccharides. That this was not the case may be explained by the results of force-field calculations [54] performed for the α-D-linked product **6** and its β-D-linked

counterpart and their comparison with those of galactosyl-derived analogues. For example, for disaccharides obtained from 1-thiogalactosides tethered *via* position 2 by succinate to position 3 of a glucose acceptor, the corresponding α-D-(1→4)-linked saccharides are *ca.* 7–12 kcal/mol more stable than the respective β-D-(1→4)-linked ones [39]. Contrarily, compound **6** is calculated to be *ca.* 36 kcal/mol more stable than the corresponding β-D-linked disaccharide. Thus, solely **6** was formed in the cyclizations of prearranged saccharides **5**.

Table. *Cyclization of Tethered Glycosides* **5**, **17**, **23**, **28**, **31**, *and* **41** *under Various Conditions to Tethered (1→4)-Linked Disaccharides*

Entry	Starting material (leaving group)	Tether (Man→Glc)	Tether linkage	Ring size	Conditions	Products (yield)	α-D/β-D
1	**5a** (PhS)	succinate	(2→3)	11	NIS, CH_2Cl_2, –30°	**6** (71%)	100:0
2					NIS, MeCN, –30°	**6** (73%)	100:0
3	**5b** (EtS)	succinate	(2→3)	11	NIS, MeCN, –30°	**6** (54%)[a])	100:0
4	**17a** (PhS)	succinate	(3→3)	12	NIS, CH_2Cl_2, –30°	**18a** (17%), **18b** (50%)	26:74
5					NIS, MeCN, –30°	**18a** (12%), **18b** (53%)	18:82
6	**17b** (EtS)	succinate	(3→3)	12	NIS, CH_2Cl_2, –30°	**18** (64%)	10:90[b])
7					NIS, MeCN, –30°	**18a** (0%), **18b** (66%)	0:100
8					MeOTf, CH_2Cl_2, r.t.	**18** (64%)	17:83[b])
9					MeOTf, MeCN, r.t.	**18a** (64%), **18b** (0%)	100:0
10	**23** (EtS)	malonate	(3→3)	11	NIS, CH_2Cl_2, –30°	–[c])	
11					MeOTf, CH_2Cl_2, r.t.	–[c])	
12	**28** (PhS)	succinate	(4→3)	12	NIS, CH_2Cl_2, –30°	**29a** (73%), **29b** (5%)	94:6
13					NIS, MeCN, –30°	**29a** (69%), **29b** (7%)	91:9
14	**31a** (EtS)	malonate	(6→3)	12	NIS, CH_2Cl_2, –30°	**32a** (17%), **32b** (53%)	24:76[d])
15					MeOTf, CH_2Cl_2, r.t.	**32a** (9%), **32b** (68%)	12:88[d])
16	**31b** (EtS)	succinate	(6→3)	13	NIS, CH_2Cl_2, –30°	**33a** (43%), **33b** (27%)	62:38[d])
17					MeOTf, CH_2Cl_2, r.t.	**33a** (31%), **33b** (37%)	45:55[d])
18	**31c** (PhS)	succinate	(6→3)	13	NIS, CH_2Cl_2, –30°	**33a** (53%), **33b** (21%)	71:29[d])
19	**37** (EtS)	malonate	(6→2)	13	NIS, CH_2Cl_2, –30°	**38** (69%)	100:0
20					NIS, MeCN, –30°	**38** (69%)	100:0
21					MeOTf, CH_2Cl_2, r.t.	**38** (68%)	100:0
22					MeOTf, MeCN, r.t.	**38** (71%)	100:0
23	**41** (EtS)	malonate	(6→6)	13	NIS, CH_2Cl_2, –30°	**42** (72%)	100:0
24					NIS, MeCN, –30°	**42** (68%)	100:0
25					MeOTf, CH_2Cl_2, r.t.	**42** (62%)	100:0
26					MeOTf, MeCN, r.t.	**42** (66%)	100:0

[a]) According to [34]. [b]) Determined from the ratio **19a**/**19b**. [c]) Decomposition of the starting material. [d]) According to [41].

For the prearranged glycosides **17** having succinate tethers between positions 3 of both donor and acceptor (*Table*, *Entries 4–9*), the outcome of the anomer configuration on cyclization strongly depends on the activation procedure and the solvent. Calculations performed for both anomers **18** showed that the α-D-linked disaccharide **18a** should be thermodynamically less stable by *ca.* 10 kcal/mol than the β-D-linked disaccharide **18b**. This is in good agreement for cyclizations of compound **17a** where **18b** was the major product (*Entries 4* and *5*). Similarly, reaction of **17b** with NIS resulted in predominant or exclusive formation of the β-D-linked disaccharide **18b** (*Entries 6–8*). However, when **17b** was cyclized with MeOTf (*Entry 9*), a complete inversion of this trend was observed, the α-D-(1 $\rightarrow$ 4)-linked disaccharide **18a** being formed as the sole product. Obviously, a change in the glycosylation mechanism takes place on changing the activator from NIS to MeOTf. Thus, the complete control of the generated anomer configuration in either direction on intramolecular glycosylation of **17b** by a simple change of the activation procedure is a useful and straightforward application of this methodology for the future preparation of oligosaccharides containing Man-(1 $\rightarrow$ 4)-Glc residues.

The complete failure of the cyclizations of the malonate-tethered prearranged glycoside **23** corresponding to **17** (*Table*, *Entries 10* and *11*) is due to the formation of thermodynamically unfavored 11-membered rings for both anomers. Calculations for the potential products showed that both anomers should be less stable by *ca.* 90 kcal/mol than the corresponding succinate-tethered disaccharides **18** having 12-membered rings. Thus, solely decomposition products were observed. Indeed, when the ring was enlarged to a 12- or 13-membered ring as for prearranged glycosides **28** (*Entries 12* and *13*) or **31** (*Entries 14–18*) [41] having positions 4 and 6, respectively, of the mannosyl donor connected by a succinate or malonate tether to position 3 of the glucosyl acceptor, cyclization proceeded well and gave the corresponding disaccharides **29**, **32**, and **33** in good overall yield. Once again, the calculated thermodynamic stability reflects the outcome of the anomer configuration in these intramolecular glycosylations [41].

When the attachment of the tether is changed from position 3 of the glucose acceptor (*cf.* compounds **31**) to position 2 as in **37** (*Entries 19–22*) or to position 6 as in **41** (*Entries 23–26*), only α-D-(1 $\rightarrow$ 4)-linked disaccharides **38** and **42** were obtained in good yield. Calculations of these cases showed again a significantly higher thermodynamic stability of the respective α-D-anomers. Therefore, simple force-field calculations of the thermodynamic stability of the tethered disaccharides can help to plan the length of the tether and the positions to which the tether has to be connected in the mannosyl donor and in the acceptor in order to find suitable conditions for preparing selectively either of the anomers. Solely in the case where a change in the activation procedure may result in a different glycosylation mechanism (*cf. Table*, *Entries 7* and *9*), calculated thermodynamic stabilities of the products do not properly reflect the reality.

Experimental Part

General. For workup, solns. in org. solvents were dried (Na_2SO_4) and evaporated at $< 40°/2$ kPa. TLC: Precoated plastic sheets, *Polygram SIL UV$_{254}$* (40 $\times$ 80 mm; *Macherey-Nagel*), toluene/AcOEt mixtures; detection by UV light, where applicable, and by charring with 5% H_2SO_4 in EtOH. Column chromatography

(CC): silica gel *60* (*Macherey-Nagel*), toluene/AcOEt mixtures. $[\alpha]_D$: at 25°; *Perkin-Elmer-241* automatic polarimeter. NMR Spectra: $CDCl_3$ solns. at 25°; *Bruker-AC-300F* and *-DRX-500* spectrometers; at 300 and 500 MHz for ^1H, and at 75 and 126 MHz for ^{13}C; ^1H assignments by first-order analysis and by H,H-COSY; ^{13}C assignments by mutual comparison of the spectra, by DEPT, and by C,H-COSY; δ in ppm rel. to Me_4Si as internal standard, J in Hz; for prearranged glycosides and disaccharides, unprimed locants refer to the glucose and primed ones to the mannose moiety.

Phenyl 3,4,6-Tri-O-*benzyl-2*-O-*(3-carboxypropanoyl)-1-thio-α*-D-*mannopyranoside* (**2a**). A soln. of *phenyl 3,4,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranoside* (**1a**) [43][44] (4.62 g, 8.51 mmol), succinic anhydride (6.81 g, 68.08 mmol), and a cat. amount of DMAP in pyridine (40 ml) was stirred for 24 h at 60°, then cooled to r.t., diluted with CH_2Cl_2, and washed with aq. HCl and $NaHCO_3$ soln. Evaporation afforded crude **2a** (4.84 g, 89%), which was used without further purification in the next step.

Ethyl 3,4,6-Tri-O-*benzyl-2*-O-*(3-carboxypropanoyl)-1-thio-α*-D-*mannopyranoside* (**2b**). As described for **2a**, with *ethyl 3,4,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranoside* (**1b**) [45] (0.93 g, 1.9 mmol), succinic anhydride (1.13 g, 11.3 mmol), DMAP, and pyridine (50 ml) (24 h at r.t.): **2b** (1.10 g, 98%). $[\alpha]_D = +75.2$ ($c = 1.1$, $CHCl_3$). ^1H-NMR ($CDCl_3$): 5.43 (dd, $J(1,2) = 1.3$, $J(2,3) = 2.5$, H–C(2)); 5.30 (d, $J(1,2) = 1.3$, H–C(1)); 4.13 (ddd, $J(4,5) = 8.4$, $J(5,6a) = 2.0$, $J(5,6b) = 4.4$, H–C(5)); 3.91–3.88 (m, H–C(3), H–C(4)); 3.82 (dd, $J(6a,6b) = -10.8$, H_a–C(6)); 3.68 (dd, H_b–C(6)); 2.69–2.55 (m, CH_2CH_2COOH, SCH_2); 1.27 (t, Me). ^{13}C-NMR ($CDCl_3$): 176.6, 171.4 (CO); 82.3 (C(1)); 78.5 (C(3)); 75.2 (Ph*C*H_2); 74.5 (C(4)); 73.4 (Ph*C*H_2); 71.73 (Ph*C*H_2); 71.68 (C(5)); 71.0 (C(2)); 68.8 (C(6)); 29.5, 29.1 (CO*C*H_2*C*H_2); 25.6 (CH_2S); 14.9 (Me). Anal. calc. for $C_{33}H_{38}O_8S$ (594.72): C 66.56, H 6.44, S 5.39; found: C 66.56, H 6.58, S 5.09.

Benzyl 2-O-*Benzoyl-4,6*-O-*benzylidene-3*-O-*[1,4-dioxo-4-(phenyl 3,4,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-2*-O-*yl)butyl]-α*-D-*glucopyranoside* (**4a**). A soln. of **2a** (4.69 g, 7.30 mmol), **3** [26] (3.75 g, 8.11 mmol), DCC (1.67 g, 8.11 mmol), and a cat. amount of DMAP in CH_2Cl_2 (50 ml) was stirred for 24 h at r.t. The resulting suspension was filtered through a layer of *Celite*, and the filtrate was washed with aq. HCl and $NaHCO_3$ soln., dried, and evaporated. CC (toluene/AcOEt 20:1) of the residue afforded **4a** (4.55 g, 57%). $[\alpha]_D = +103.7$ ($c = 0.8$, $CHCl_3$). ^1H-NMR ($CDCl_3$): 5.90 (t, $J(3,4) = 9.9$, H–C(3)); 5.52–5.48 (m, H–C(1′), H–C(2′)); 5.51 (s, PhC*H*); 5.30 (s, H–C(1)); 5.10 (dd, $J(2,3) = 9.9$, H–C(2)); 4.86 (t, $J = -10.8$, 1 H, PhCH_2); 4.78 (d, $J = -12.4$, 1 H, PhCH_2); 4.63 (d, $J = -12.0$, 1 H, PhCH_2); 4.58 (d, $J = -11.1$, 1 H, PhCH_2); 4.57 (d, $J = -12.4$, 1 H, PhCH_2); 4.48 (d, $J = -10.7$, 1 H, PhCH_2); 4.47 (s, 1 H, PhCH_2); 4.45 (d, $J = -12.2$, 1 H, PhCH_2); 4.35–4.32 (m, $J(5',6a') = 4.8$, H–C(5′)); 4.28 (dd, $J(6a,6b) = -10.1$, H_a–C(6)); 4.09 (dt, $J(5,6a) = 4.8$, $J(5,6b) = 9.9$, H–C(5)); 3.92–3.88 (m, H–C(3′), H–C(4′)); 3.83 (dd, $J(6a',6b') = -10.8$, H_a–C(6′)); 3.74 (t, H_b–C(6)); 3.70 (dd, H_b–C(6′)); 2.69–2.52 (m, $COCH_2CH_2CO$). ^{13}C-NMR ($CDCl_3$): 171.2, 171.0 (*C*O*C*H_2*C*H_2*C*O); 165.8 (Ph*C*O); 101.6 (Ph*C*H); 95.9 (C(1)); 85.9 (C(1′)); 79.1 (C(4)); 78.4 (C(3′)); 75.2 (Ph*C*H_2); 74.5 (C(4′)); 73.3 (Ph*C*H_2); 72.4 (C(5′)); 72.2 (C(2)); 71.7 (Ph*C*H_2); 70.5 (C(2′)); 70.0 (Ph*C*H_2); 69.2 (C(3)); 68.8 (C(6)); 64.0 (C(6′)); 62.8 (C(5)); 29.0 (2 C, CO*C*H_2*C*H_2CO). Anal. calc. for $C_{64}H_{62}O_{14}S$ (1087.25): C 70.70, H 5.75, S 2.95; found: C 70.50, H 5.76, S 2.97.

Benzyl 2-O-*Benzoyl-4,6*-O-*benzylidene-3*-O-*[4-(ethyl 3,4,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-2*-O-*yl)-1,4-dioxobutyl]-α*-D-*glucopyranoside* (**4b**). As described for **4a**, with **2b** (1.1 g, 1.9 mmol), **3** [26] (0.86 g, 1.9 mmol), DCC (2.06 g, 2.0 mmol), 1-hydroxy-1*H*-benzotriazole (126 mg, 0.93 mmol), DMAP, and CH_2Cl_2 (50 ml): **4b** (1.16 g, 60%). $[\alpha]_D = +88.4$ ($c = 1.0$, $CHCl_3$). ^1H-NMR ($CDCl_3$): 5.93 (t, $J(3,4) = 9.8$, H–C(3)); 5.31–5.25 (m, H–C(1′), H–C(2′)); 5.50 (s, PhC*H*); 5.29 (d, $J(1,2) = 3.8$, H–C(1)); 5.11 (dd, $J(2,3) = 10.0$, H–C(2)); 4.80 (d, $J = -10.5$, 1 H, PhCH_2); 4.76 (d, $J = -11.4$, 1 H, PhCH_2); 4.63 (d, $J = -12.2$, 1 H, PhCH_2); 4.55 (d, $J = -12.2$, 1 H, PhCH_2); 4.51 (d, $J = -11.0$, 1 H, PhCH_2); 4.45 (d, $J = -12.1$, 1 H, PhCH_2); 4.50 (s, 1 H, PhCH_2); 4.42 (d, $J = -11.4$, 1 H, PhCH_2); 4.37 (d, $J = -11.2$, 1 H, PhCH_2); 4.13–4.03 (m, H–C(5), H–C(5′)); 4.30 (dd, $J(5,6a) = 4.8$, $J(6a,6b) = -10.2$, H_a–C(6)); 4.13–4.03 (m, H–C(3′), H–C(4), H–C(4′), H_b–C(6), H_a–C(6′)); 3.67 (dd, H_b–C(6′)); 2.69–2.50 (m, 6 H, CH_2); 1.25 (t, Me). ^{13}C-NMR ($CDCl_3$): 171.3, 171.1 (*C*O*C*H_2*C*H_2*C*O); 165.8 (Ph*C*O); 101.6 (Ph*C*H); 96.0 (C(1)); 82.3 (C(1′)); 79.2 (C(4)); 78.5 (C(3′)); 75.1 (Ph*C*H_2); 74.5 (C(4′)); 73.3 (Ph*C*H_2); 72.3 (C(2)); 71.8 (C(5′)); 71.6 (Ph*C*H_2); 70.7 (C(2′)); 70.1 (Ph*C*H_2); 70.0 (C(6)); 69.2 (C(3)); 68.9 (C(6′)); 62.9 (C(5)); 29.4, 25.4, 20.0 (CH_2); 14.9 (Me). Anal. calc. for $C_{60}H_{62}O_{14}S$ (1039.20): C 69.35, H 6.01; found: C 69.14, H 6.04.

Benzyl 2-O-*Benzoyl-6*-O-*benzyl*-3-O-*[1,4-dioxo-4-(phenyl 3,4,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-2*-O-*yl)butyl]-α*-D-*glucopyranoside* (**5a**). A sat. soln. of dry HCl in Et_2O was added dropwise at r.t. to a suspension of **4a** (0.80 g, 0.78 mmol), $NaCNBH_3$ (0.61 g, 9.75 mmol) and 3-Å molecular sieves in THF (15 ml) until the gas evolution ceased. The mixture was diluted with CH_2Cl_2 and filtered through a layer of *Celite*, and the filtrate was washed with aq. $NaHCO_3$ soln., dried, and evaporated. CC (toluene/acetone 13:1) of the residue afforded **5b** (0.63 g, 79%). $[\alpha]_D = +27.6$ ($c = 0.7$, $CHCl_3$). ^1H-NMR ($CDCl_3$): 5.68 (dd, $J(3,4) = 9.2$, H–C(3));

5.61 (br. *d*, H–C(2′)); 5.51 (*d*, *J*(1,2) = 1.5, H–C(1′)); 5.28 (*d*, *J*(1,2) = 3.7, H–C(1)); 5.00 (*dd*, *J*(2,3) = 10.3, H–C(2)); 4.87 (*d*, *J* = –10.8, 1 H, PhC*H*$_2$); 4.78 (*d*, *J* = –12.4, 1 H, PhC*H*$_2$); 4.68 (*d*, *J* = –11.2, 1 H, PhC*H*$_2$); 4.65–4.63 (*m*, 2 H, PhC*H*$_2$); 4.63 (*d*, *J* = –10.5, 1 H, PhC*H*$_2$); 4.56 (*d*, *J* = –12.2, 1 H, PhC*H*$_2$); 4.52 (*d*, *J* = –11.0, 1 H, PhC*H*$_2$); 4.50 (*d*, *J* = –10.8, 1 H, PhC*H*$_2$); 4.43 (*d*, *J* = –11.9, 1 H, PhC*H*$_2$); 4.32 (*ddd*, *J*(5′,6a′) = 4.3, *J*(5′,6b′) = 1.8, H–C(5′)); 4.01–3.91 (*m*, H–C(3′), H–C(4′), H–C(5)); 3.84 (*dd*, *J*(6a′,6b′) = –10.8, H$_a$–C(6′)); 3.80–3.72 (*m*, H–C(4), H$_a$–C(6), H$_b$–C(6)); 3.70 (*dd*, H$_b$–C(6′)); 3.33 (br. *s*, OH); 2.81–2.44 (*m*, COCH$_2$CH$_2$CO). ^{13}C-NMR (CDCl$_3$): 172.2, 171.3 (*C*OCH$_2$CH$_2$*C*O); 165.7 (Ph*C*O); 95.2 (C(1)); 85.6 (C(1′)); 78.3 (C(3′)); 75.2 (Ph*C*H$_2$); 74.3 (C(4′)); 73.6 (Ph*C*H$_2$); 73.5 (C(3)); 73.3 (Ph*C*H$_2$); 72.3 (C(5′)); 71.8 (Ph*C*H$_2$); 71.4 (C(2)); 70.5 (C(2′)); 70.4 (C(5)); 69.5 (C(4), Ph*C*H$_2$); 69.2 (C(6)); 68.6 (C(6′)); 29.3, 29.1 (CO*C*H$_2$*C*H$_2$CO). Anal. calc. for $C_{64}H_{64}O_{14}S$ (1089.27): C 70.57, H 5.92; found: C 70.44, H 5.98.

Benzyl 2-O-*Benzoyl-6*-O-*benzyl-3*-O-*[4-(ethyl 3,4,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-2*-O-*yl)-1,4-dioxobutyl]-α*-D-*glucopyranoside* (**5b**). As described for **5a**, with **4b** (0.52 g, 0.5 mmol) and NaCNBH$_3$ (0.29 g, 4.64 mmol): **5b** (0.46 g, 88%). $[\alpha]_D = +86.2$ ($c = 1.3$, CHCl$_3$). ^{1}H-NMR (CDCl$_3$): 5.98 (*dd*, *J*(2,3) = 10.1, *J*(3,4) = 9.2, H–C(3)); 5.43 (*dd*, *J*(1,2) = 1.5, *J*(2,3) = 2.4, H–C(2′)); 5.25–5.21 (*m*, H–C(1), H–C(1′)); 5.00–4.38 (*m*, 11 H, H–C(2), PhC*H*$_2$), 3.88 (*ddd*, *J*(5′,6a′) = 1.8, *J*(5′,6b′) = 3.3, H–C(5′)); 3.89–3.76 (*m*, H–C(3′), H–C(4′), H–C(5)); 3.66 (*dd*, *J*(6a′,6b′) = –10.7, H$_a$–C(6′)); 4.99 (*dd*, *J*(5,6a) = 3.7, *J*(6a,6b) = –10.3, H$_a$–C(6)); 3.85–3.79 (*m*, H$_b$–C(6)); 3.74 (*dd*, *J*(6a′,6b′) = –10.7, H$_b$–C(6′)); 3.45 (*s*, OH); 2.78–2.36 (*m*, COCH$_2$CH$_2$CO); 1.28 (*t*, Me). ^{13}C-NMR (CDCl$_3$; significant signals): 95.2 (C(1)); 82.4 (C(1′)); 78.3 (C(3′)); 74.4 (C(4′)); 71.7 (C(5′)); 70.7 (C(2′)); 69.4 (C(2)); 69.3 (C(6)); 68.6 (C(6′)); 29.4, 29.3 (CO*C*H$_2$*C*H$_2$CO); 25.7 (CH$_2$S); 14.9 (Me). Anal. calc. for $C_{60}H_{64}O_{14}S$ (1041.22): C 69.21, H 6.20, S 3.08; found: C 69.00, H 6.33, S 3.25.

Benzyl O-*(3,4,6-Tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1 → 4)-2*-O-*benzoyl-6*-O-*benzyl-α*-D-*glucopyranoside 2′,3-Succinate* (**6**). *a*) A suspension of **5a** (0.64 g, 0.59 mmol) and 3-Å molecular sieves (*ca.* 0.2 g) in CH$_2$Cl$_2$ (20 ml) was stirred under Ar for 20 min at r.t. and cooled to –30°. NIS (0.66 g, 2.94 mmol) and Me$_3$SiOTf (27 µl, 0.15 mmol) were added, and the mixture was stirred for 5 min. The reaction was quenched by addition of pyridine, the mixture warmed to r.t., diluted with CH$_2$Cl$_2$ and filtered, and the filtrate washed with aq. NaHCO$_3$ and Na$_2$S$_2$O$_3$ soln., dried, and evaporated. CC (toluene/acetone 18:1) of the residue afforded **6** (0.41 g, 71%). $[\alpha]_D = +128.4$ ($c = 1.0$, CHCl$_3$). ^{1}H-NMR (CDCl$_3$): 5.80 (*dd*, *J*(3,4) = 9.2, H–C(3)); 5.24 (*d*, *J*(1,2) = 3.7, H–C(1)); 5.11 (br. *s*, H–C(1′)); 5.04 (*dd*, *J*(2,3) = 10.5, H–C(2)); 4.82 (*dd*, *J*(2′,3′) = 2.9, H–C(2′)); 4.73 (*d*, *J* = –12.4, 1 H, PhC*H*$_2$); 4.63 (*d*, *J* = –11.7, 1 H, PhC*H*$_2$); 4.53 (*d*, *J* = –12.2, 1 H, PhC*H*$_2$); 4.54–4.51 (*m*, 1 H, PhC*H*$_2$); 4.46 (*d*, *J* = –10.4, 1 H, PhC*H*$_2$); 4.42 (*s*, 2 H, PhC*H*$_2$); 4.40 (*d*, *J* = –12.3, 1 H, PhC*H*$_2$); 4.37 (*d*, *J* = –12.1, 1 H, PhC*H*$_2$); 4.26 (*d*, *J* = –11.8, 1 H, PhC*H*$_2$); 4.12 (br. *d*, H–C(3′)); 4.05–3.96 (*m*, H–C(5)), H–C(5′)); 3.89 (*t*, *J*(4,5) = 9.4, H–C(4)); 3.79–3.69 (*m*, 2 H–C(6′)); 3.77 (br. *d*, H–C(4′)); 3.56 (br. *d*, H–C(6)); 3.49 (br. *t*, H$_b$–C(6)); 2.86–2.37 (*m*, COCH$_2$CH$_2$CO). ^{13}C-NMR (CDCl$_3$): 172.7, 170.0 (*C*OCH$_2$CH$_2$*C*O); 165.7 (Ph*C*O); 102.4 (*J*(1′, H–C(1′)) = 170.6, C(1′)); 94.9 (C(1)); 80.0 (C(3′)); 75.6 (C(4)); 74.9 (C(4′)); 73.9 (C(2)); 73.0 (Ph*C*H$_2$); 72.9 (Ph*C*H$_2$); 72.7 (C(5′)); 72.4 (Ph*C*H$_2$); 71.8 (C(5)); 71.3 (Ph*C*H$_2$, C(3)); 70.2 (C(2′)); 69.7 (Ph*C*H$_2$); 69.4 (C(6)); 68.3 (C(6′)); 31.2, 30.0 (CO*C*H$_2$*C*H$_2$CO). Anal. calc. for $C_{58}H_{58}O_{14}$ (979.10): C 71.15, H 5.97; found: C 71.29, H 6.02.

b) Exactly as described in *Exper. a*, with **5a** (0.95 g, 0.87 mmol), NIS (0.99 g, 2.94 mmol), Me$_3$SiOTf (40 µl, 0.22 mmol), and MeCN (30 ml): **6** (0.63 g, 73%).

c) Exactly as described in *Exper. a*, with **5b** (0.63 g, 0.62 mmol), NIS (0.67 g, 3.0 mmol), Me$_3$SiOTf (27 µl, 0.15 mmol), and MeCN (100 ml): **6** (0.33 g, 45%).

Benzyl O-*(2*-O-*Benzoyl-3,4,6-tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1 → 4)-2,3-di*-O-*benzoyl-6*-O-*benzyl-α*-D-*glucopyranoside* (**7**). A soln. of **6** (122 mg, 0.115 mmol) and a cat. amount of NaOMe in MeOH (5 ml) were stirred for 24 h at r.t. Then, the mixture was neutralized with ion-exchange resin (H$^+$ form) and evaporated, the residue dissolved in pyridine (3 ml), BzCl (70 µl, 0.6 mmol) added, and the mixture stirred at r.t. for 24 h, then poured into H$_2$O, and extracted with CH$_2$Cl$_2$. The extracts were washed with aq. HCl and NaHCO$_3$ soln., dried and evaporated. CC (hexane/AcOEt 5:1) of the residue afforded **7** (82 mg, 64%). $[\alpha]_D = +60.3$ ($c = 1.4$, CHCl$_3$). ^{1}H-NMR (CDCl$_3$): 6.10 (*t*, *J*(3,4) = 10.0, H–C(3)); 5.60 (*t*, *J*(2′,3′) = 2.5, H–C(2′)); 5.50 (*d*, *J*(1′,2′) = 1.9, H–C(1′)); 5.13 (*d*, *J*(1,2) = 3.7, H–C(1)); 5.07 (*dd*, *J*(2,3) = 9.9, H–C(2)); 4.88 (*d*, *J* = –10.9, PhC*H*$_2$); 4.74 (*d*, *J* = –11.7, 1 H, PhC*H*$_2$); 4.64 (*d*, *J* = –12.1, 1 H, PhC*H*$_2$); 4.61 (*d*, *J* = –12.2, 1 H, PhC*H*$_2$); 4.57 (*d*, *J* = –11.5, 1 H, PhC*H*$_2$); 4.56 (*d*, *J* = –11.2, 1 H, PhC*H*$_2$); 4.55 (*d*, *J* = –10.9, 1 H, PhC*H*$_2$); 4.50–4.47 (*m*, 3 H, PhC*H*$_2$); 4.21 (*t*, *J*(4,5) = 10.1, H–C(4)); 4.07 (*dd*, *J*(3′,4′) = 9.5, H–C(3′)); 4.00–3.93 (*m*, H–C(4′), H–C(5′), H–C(5)); 3.73 (br. *d*, 2 H–C(6′)); 3.66 (br. *t*, 2 H–C(6)). ^{13}C-NMR (CDCl$_3$): 166.3, 166.1, 165.7 (Ph*C*O); 97.8 (*J*(1′, H–C(1′) = 175.5, C(1′)); 95.3 (C(1)); 77.9 (C(3′)); 75.1 (Ph*C*H$_2$); 74.6 (C(3)); 74.2 (C(4′)); 73.9 (C(4)); 73.4

(2 C, Ph*C*H$_2$); 72.4 (C(5′)); 71.6 (Ph*C*H$_2$); 71.3 (C(2)); 69.6 (Ph*C*H$_2$); 69.5 (C(2′)); 69.3 (C(5)); 69.1, 69.0 (C(6), C(6′)). Anal. calc. for $C_{68}H_{64}O_{14}$ (1105.25): C 73.90, H 5.84; found: C 74.15, H 5.90.

*Phenyl 6-*O*-[(*tert*-Butyl)diphenylsilyl]-1-thio-α-*D*-mannopyranoside* (**9a**). A soln. of **8a** [48] (7.49 g, 27.5 mmol), 1*H*-imidazole (4.86 g, 68.75 mmol), and (*tert*-butyl)chlorodiphenylsilane (8.6 ml, 33.0 mmol) in DMF (200 ml) was stirred for 24 h at r.t., poured into H_2O, and extracted with CH_2Cl_2. The extracts were washed with aq. $NaHCO_3$ soln., dried, and evaporated. Traces of DMF were removed by repetitive co-evaporation of toluene. Chromatography (toluene/AcOEt 1:1.5 containing 1% pyridine) afforded **9a** (11.0 g, 78%). $[\alpha]_D = +141.7$ ($c = 1.31$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.46 (*d*, *J*(1,2) = 1.2, H–C(1)); 4.17 (*dd*, *J*(2,3) = 3.2, H–C(2)); 4.15–4.10 (*m*, *J*(5,6a) = 4.5, *J*(5,6b) = 4.8, H–C(5)); 3.93–3.86 (*m*, H–C(4)); 3.91 (*dd*, *J*(6a,6b) = –10.8, H_a–C(6)); 3.83 (*dd*, *J*(3,4) = 9.3, H–C(3)); 3.78 (*dd*, H_b–C(6)); 2.97 (br. *s*, 3 H, OH); 1.04 (*s*, ^{t}Bu). ^{13}C-NMR ($CDCl_3$): 87.8 (C(1)); 72.1 (C(3)); 71.9 (C(2)); 71.7, 70.6 (C(4), C(5)); 65.0 (C(6)); 26.8 (Me$_3$*C*); 19.2 (*Me*$_3$C). Anal. calc. for $C_{28}H_{34}O_5SSi$ (510.73): C 65.85, H 6.71; found: C 66.16, H 6.80.

*Ethyl 6-*O*-[(*tert*-Butyl)diphenylsilyl]-1-thio-α-*D*-mannopyranoside* (**9b**). As described for **9a**, with **8b** [59][50] (6.48 g, 28.9 mmol), 1*H*-imidazole (4.92 g, 72.23 mmol), (*tert*-butyl)chlorodiphenylsilane (8.9 ml, 34.7 mmol), and DMF (130 ml): **9b** (10.71 g, 80%). $[\alpha]_D = +89.7$ ($c = 1.65$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.27 (*d*, *J*(1,2) < 1, H–C(1)); 4.08–4.02 (*m*, *J*(5,6a) = 5.0, H–C(5)); 3.98 (*dd*, *J*(2,3) = 2.9, H–C(2)); 3.93 (*dd*, *J*(6a,6b) = –10.6, H_a–C(6)); 3.86 (*dd*, *J*(5,6b) = 5.2, H_b–C(6)); 3.82–3.77 (*m*, H–C(3), H–C(4)); 3.12 (br. *s*, 3 H, OH); 2.65–2.43 (*m*, MeC*H*$_2$S); 1.22 (*t*, *J* = 7.4, MeCH$_2$S); 1.05 (*s*, ^{t}Bu). ^{13}C-NMR ($CDCl_3$): 83.6 (C(1)); 72.2 (C(3)); 71.8 (C(2)); 71.1, 70.5 (C(4), C(5)); 65.0 (C(6)); 26.8 (*Me*$_3$C); 24.7 (Me*C*H$_2$S); 19.1 (Me$_3$); 14.7 (*Me*CH$_2$S). Anal. calc. for $C_{24}H_{43}O_5SSi$ (462.68): C 62.30, H 7.41, S 6.93; found: C 62.61, H 7.49, S 7.03.

*Phenyl 6-*O*-[(*tert*-Butyl)diphenylsilyl]-2,3-di-*O*-isopropylidene-1-thio-α-*D*-mannopyranoside* (**10a**). A soln. of **9a** (3.66 g, 7.17 mmol) and TsOH (0.87 g, 4.56 mmol) in 2,2-dimethoxypropane (64 ml) was stirred for 24 h at r.t., neutralized by the addition of Et_3N, diluted with CH_2Cl_2, washed with H_2O, dried, and evaporated. CC (hexane/AcOEt 5:1) of the residue afforded **10a** (3.40 g, 86%). $[\alpha]_D = +108.1$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.75 (*d*, *J*(1,2) < 1.0, H–C(1)); 4.35 (*dd*, *J*(2,3) = 5.7, H–C(2)); 4.19 (*dd*, *J*(3,4) = 7.3, H–C(3)); 4.11–4.04 (*m*, *J*(5,6a) = 4.1, *J*(5,6b) = 4.7, H–C(5)); 3.95 (*dd*, *J*(4,5) = 10.1, H–C(4)); 3.89 (*dd*, *J*(6a,6b) = –10.9, H_a–C(6)); 3.83 (*dd*, H_b–C(6)); 1.54 (*s*, 3 H, Me$_2$C); 1.38 (*s*, 3 H, Me$_3$C); 1.04 (*s*, ^{t}Bu). ^{13}C-NMR ($CDCl_3$): 109.8 (Me$_2$C); 84.0 (C(1)); 78.2 (C(3)); 76.1 (C(2)); 71.4 (C(5)); 70.2 (C(4)); 64.5 (C(6)); 28.1 (*Me*$_2$C); 26.8 (*Me*$_3$C); 26.4 (*Me*$_2$C), 19.2 (Me$_3$*C*). Anal. calc. for $C_{31}H_{38}O_5SSi$ (550.79): C 67.60, H 6.95; found: C 67.73, H 6.89.

*Ethyl 6-*O*-[(*tert*-Butyl)diphenylsilyl]-2,3-di-*O*-isopropylidene-1-thio-α-*D*-mannopyranoside* (**10b**). As described for **10a**, with **9b** (4.05 g, 8.75 mmol), TsOH (1.07 g, 5.60 mmol), acetone (60 ml), and 2,2-dimethoxypropane (60 ml): **10b** (3.83 g, 87%). $[\alpha]_D = +67.2$ ($c = 1.63$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.56 (*s*, H–C(1)); 4.15 (*dd*, *J*(2,3) = 5.7, H–C(2)); 4.13–4.09 (*m*, *J*(3,4) = 7.0, H–C(3)); 4.02–3.95 (*m*, H–C(5)); 3.90 (*m*, 2 H–C(6)); 3.83 (*ddd*, *J*(4,5) = 9.9, *J*(4,OH) = 3.0, H–C(4)); 2.68 (*d*, OH); 2.65–2.43 (*m*, MeC*H*$_2$S); 1.52 (*s*, 3 H, Me$_2$C); 1.35 (*s*, 3 H, Me$_2$C); 1.24 (*t*, *J* = 7.4, *Me*CH$_2$S); 1.06 (*s*, ^{t}Bu). ^{13}C-NMR ($CDCl_3$): 109.6 (Me$_2$*C*); 79.1 (C(1)); 78.3 (C(3)); 76.3 (C(2)); 71.4 (C(4)); 69.6 (C(5)); 64.5 (C(6)); 28.1 (*Me*$_2$C); 26.7 (*Me*$_3$C); 26.3 (*Me*$_2$C); 24.0 (Me*C*H$_2$S); 19.2 (Me$_3$*C*); 14.4 (*Me*CH$_2$S). Anal. calc. for $C_{27}H_{38}O_5SSi$ (502.74): C 64.51, H 7.62, S 6.38; found: C 64.52, H 7.63, S 6.25.

*Phenyl 2,3-Di-*O*-isopropylidene-1-thio-α-*D*-mannopyranoside* (**11a**). A soln. of **10a** (3.28 g, 5.96 mmol) and Bu_4NF (5 ml of a 1M soln. in THF) in THF (15 ml) was stirred for 0.5 h at r.t. and evaporated. CC (toluene/acetone 3:1) of the residue afforded **11a** (1.66 g, 89%). M.p. 152–154° (hexane/acetone). $[\alpha]_D = +181.8$ ($c = 1.28$, acetone). ^{1}H-NMR ((D$_6$)acetone): 5.73 (*s*, H–C(1)); 4.50 (*d*, *J* = 5.3, OH); 4.33 (*dd*, *J*(2,3) = 5.7, H–C(2)); 4.11 (*dd*, *J*(3,4) = 7.4, H–C(3)); 3.98–3.92 (*m*, H–C(5)); 3.77–3.64 (*m*, H–C(4), 2 H–C(6)); 3.43 (*t*, *J* = 6.2, OH); 1.42 (*s*, 3 H, Me$_2$C); 1.31 (*s*, 3 H, Me$_2$C). ^{13}C-NMR ((D$_6$)acetone): 109.7 (Me$_2$*C*); 85.0 (C(1)); 79.7 (C(3)); 77.0 (C(2)); 73.0 (C(5)); 70.3 (C(4)); 62.3 (C(6)); 28.3, 26.6, (*Me*$_2$C). Anal. calc. for $C_{15}H_{20}O_5S$ (312.38): C 57.68, H 6.45, S 10.26; found: C 57.69, H 6.89, S 10.43.

*Ethyl 2,3-Di-*O*-isopropylidene-1-thio-α-*D*-mannopyranoside* (**11b**). As described for **11a**, with **10b** (12.33 g, 24.5 mmol), Bu_4NF (14 ml of a 1M soln. in THF), and THF (60 ml): **11b** (5.43 g, 84%). M.p. 127–129° (hexane/acetone). $[\alpha]_D = +173.5$ ($c = 1.36$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.59 (*s*, H–C(1)); 4.18 (*dd*, *J*(2,3) = 5.5, H–C(2)); 4.12 (*dd*, *J*(3,4) = 7.3, H–C(3)); 3.97–3.91 (*m*, H–C(5)); 3.87–3.82 (*m*, 2 H–C(6)); 3.81–3.76 (*m*, H–C(4)); 3.42 (*d*, *J*(4,OH) = 4.2, OH); 2.73–2.48 (*m*, MeC*H*$_2$S, OH); 1.50 (*s*, 3 H, Me$_2$C); 1.31 (*s*, 3 H, Me$_2$C); 1.26 (*t*, *J* = 7.4, *Me*CH$_2$S). ^{13}C-NMR ($CDCl_3$): 109.6 (Me$_2$*C*); 79.6 (C(1)); 78.3 (C(3)); 76.5 (C(2)); 69.8, 69.7 (C(5)); 62.0 (C(6)); 28.1 (*Me*$_2$C); 26.3 (*Me*$_2$C); 24.3 (Me*C*H$_2$S); 14.4 (*Me*CH$_2$S). Anal. calc. for $C_{11}H_{20}O_5S$ (264.34): C 49.98, H 7.63, S 12.13; found: C 49.89, H 7.61, S 12.10.

Phenyl 4,6-Di-O-*benzyl-2,3-di*-O-*isopropylidene-1-thio-α*-D-*mannopyranoside* (**12a**). BnBr (2.3 ml, 18.67 mmol) was added at 0° to a suspension of **11a** (1.66 g, 5.31 mmol) and NaH (0.42 g, 17.37 mmol) in DMF (30 ml), and the mixture was stirred for 1 h at r.t. The excess of NaH was hydrolyzed by careful addition of MeOH to the suspension, and the resulting soln. was poured into H_2O and extracted with CH_2Cl_2. The extracts were washed with H_2O, dried, and evaporated. CC (hexane/AcOEt 8:1) of the residue afforded **12a** (2.23 g, 85%). M.p. 84° (EtOH). $[\alpha]_D = +183.0$ ($c = 1.01$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.80 (*s*, H−C(1)); 4.88 (*d*, $J = -11.4$, 1 H, PhCH_2); 4.56 (*dd*, $J = -11.3$, 1 H, PhCH_2); 4.54 (br. *s*, 1 H, PhCH_2); 4.42 (*d*, $J = -12.1$, 1 H, PhCH_2); 4.38–4.33 (*m*, 2 H−C(2), H−C(3)); 4.26 (*ddd*, J(5,6a) = 2.7, J(5,6b) = 4.2, H−C(5)); 3.74–3.66 (*m*, J(4,5) = 10.1, H−C(4), 2 H−C(6)); 1.52 (*s*, 3 H, Me_2C); 1.38 (*s*, 3 H, Me_2C). ^{13}C-NMR ($CDCl_3$): 109.6 (Me_2C); 84.1 (C(1)); 78.5, 76.4 (C(2), C(3)); 76.0 (C(4)); 73.3, 73.0 (Ph*C*H$_2$); 70.0 (C(5)); 69.1 (C(6)); 27.9 (Me_2C); 26.4 (Me_2C). Anal. calc. for $C_{29}H_{32}O_5S$ (492.63): C 70.71, H 6.55; found: C 70.72, H 6.34.

Ethyl 4,6-Di-O-*benzyl-2,3-di*-O-*isopropylidene-1-thio-α*-D-*mannopyranoside* (**12b**). As described for **12b**, with **11b** (3.19 g, 12.1 mmol), BnBr (5.1 ml, 42.41 mmol), NaH (0.95 g, 39.45 mmol), and DMF (60 ml): **12b** (5.09 g, 94%). M.p. 55–57° (EtOH). $[\alpha]_D = +128.9$ ($c = 1.35$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.58 (*s*, J(1,2) = 1.0, H−C(1)); 4.86 (*d*, $J = -11.5$, 1 H, PhCH_2); 4.61 (*d*, $J = -12.1$, 1 H, PhCH_2); 4.54 (*d*, $J = -11.6$, 1 H, PhCH_2); 4.50 (*d*, $J = -12.1$, 1 H, PhCH_2); 4.31–4.27 (*m*, H−C(3)); 4.17 (*dd*, J(2,3) = 5.7, H−C(2)); 4.12 (*ddd*, J(5,6a) = 2.6, H−C(5)); 3.74 (*dd*, J(6a,6b) = −10.7, H_a−C(6)); 3.70–3.68 (*m*, J(5,6b) = 4.6, H_b−C(6)); 3.63 (*dd*, J(4,5) = 10.3, H−C(4)); 2.75–2.47 (*m*, 2 H, MeCH_2S); 1.51 (*s*, 3 H, Me_2C); 1.36 (*s*, 3 H, Me_2C). ^{13}C-NMR ($CDCl_3$): 109.4 (Me_2C); 79.5 (C(1)); 78.6 (C(3)); 76.7 (C(2)); 76.2 (C(4)); 73.3 (Ph*C*H$_2$); 72.9 (Ph*C*H$_2$); 69.2 (C(6)); 68.9 (C(5)); 28.0 (Me_2C); 26.4 (Me_2C); 24.1 (Me*C*H$_2$S); 14.4 (*Me*CH$_2$S). Anal. calc. for $C_{25}H_{32}O_5S$ (444.59): C 67.54, H 7.26, S 7.21; found: C 67.44, H 7.24, S 7.13.

Phenyl 4,6-Di-O-*benzyl-1-thio-α*-D-*mannopyranoside* (**13a**). A soln. of **12a** (2.23 g, 4.53 mmol) in 70% AcOH/H_2O (70 ml) was stirred for 2.5 h at 70°, evaporated, and co-evaporated several times with toluene. Crystallization of the residue from hexane/acetone afforded **13a** (1.93 g, 94%). M.p. 118–120°. $[\alpha]_D = +198.0$ ($c = 1.33$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.53 (*d*, J(1,2) = 1.4, H−C(1)); 4.75 (*d*, $J = -11.3$, 1 H, PhCH_2); 4.60 (*d*, $J = -11.9$, 1 H, PhCH_2); 4.58 (*d*, $J = -11.3$, 1 H, PhCH_2); 4.44 (*d*, $J = -11.9$, 1 H, PhCH_2); 4.26 (*ddd*, J(5,6a) = 2.0, J(5,6b) = 3.9, H−C(5)); 4.09 (*dd*, J(2,3) = 3.3, H−C(2)); 3.91 (*dd*, J(3,4) = 9.1, H−C(3)); 3.84–3.79 (*m*, J(6a,6b) = −10.8, H_a−C(6)); 3.80 (*t*, J(4,5) = 9.5, H−C(4)); 3.67 (*dd*, H_b−C(6)). ^{13}C-NMR ($CDCl_3$): 87.7 (C(1)); 75.9 (C(4)); 74.7 (Ph*C*H$_2$); 73.4 (Ph*C*H$_2$); 72.4 (C(2)); 72.3 (C(3)); 71.8 (C(5)); 68.8 (C(6)). Anal. calc. for $C_{26}H_{28}O_5S$ (452.57): C 69.00, H 6.24; found: C 68.94, H 6.20.

Ethyl 4,6-Di-O-*benzyl-1-thio-α*-D-*mannopyranoside* (**13b**). As described for **13a**, with **12b** (7.09 g, 15.96 mmol) and 70% AcOH/H_2O (100 ml): **13b** (6.81 g, 96%). M.p. 76–78° (hexane/acetone). $[\alpha]_D = +160.4$ ($c = 0.72$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.31 (*d*, J(1,2) = 1.1, H−C(1)); 5.24 (*d*, $J = -11.3$, 1 H, PhCH_2); 4.64 (*d*, $J = -12.1$, 1 H, PhCH_2); 4.55 (*d*, $J = -11.3$, 1 H, PhCH_2); 4.49 (*d*, $J = -12.0$, 1 H, PhCH_2); 4.12 (*ddd*, J(4,5) = 9.5, J (5,6a) = 3.8, J(5,6b) = 2.0, H−C(5)); 3.94 (*dd*, J(2,3) = 3.3, H−C(2)); 3.86 (*dd*, J(3,4) = 9.1, H−C(3)); 3.83–3.78 (*m*, H_a−C(6)); 3.76 (*t*, J(4,5) = 9.5, H−C(4)); 3.67 (*dd*, J(6a,6b) = −10.8, H_b−C(6)); 2.69–2.51 (*m*, MeCH_2S); 2.80 (br. *s*, 2 OH); 1.25 (*t*, $J = 7.5$, *Me*CH$_2$S). ^{13}C-NMR ($CDCl_3$): 84.0 (C(1)); 75.9 (C(4)); 74.5 (PhCH$_2$); 73.5 (Ph*C*H$_2$); 72.4, 72.3 (C(2), C(3)); 71.0 (C(5)); 68.8 (C(6)); 24.9 (MeCH$_2$S); 14.8 (*Me*CH$_2$S). Anal. calc. for $C_{22}H_{28}O_5S$ (404.52): C 65.32, H 6.98, S 7.93; found: C 65.21, H 6.96, S 7.97.

Phenyl 2,4,6-Tri-O-*benzyl-1-thio-α*-D-*mannopyranoside* (**14a**). A mixture of **13a** (1.93 g, 4.24 mmol), Bu_4NHSO_4 (0.29 g, 0.85 mmol), BnBr (0.88 ml, 7.42 mmol), and 5% aq. NaOH soln. (6.15 ml) in CH_2Cl_2 (23 ml) was refluxed for 24 h. The mixture was cooled to r.t., diluted with CH_2Cl_2, washed with H_2O, dried, and evaporated. CC (hexane/AcOEt 4:1) of the residue afforded **14a** (1.84 g, 80%). $[\alpha]_D = +108.2$ ($c = 2.23$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.70 (*s*, H−C(1)); 4.90 (*d*, $J = -11.1$, 1 H, PhCH_2); 4.79 (*d*, $J = -11.6$, 1 H, PhCH_2); 4.68 (*d*, $J = -12.0$, 1 H, PhCH_2); 4.58 (*d*, $J = -11.1$, 1 H, PhCH_2); 4.52 (*s*, 1 H, PhCH_2); 4.51 (*d*, $J = -11.9$, 1 H, PhCH_2); 4.33–4.29 (*m*, J(5,6a) = 4.8, J(5,6b) = 2.0, H−C(5)); 4.03–3.99 (*m*, H−C(2), H−C(3)); 3.87 (*dd*, J(6a,6b) = −10.9, H_a−C(6)); 3.82 (*t*, J(4,5) = 9.7, H−C(4)); 3.77 (*dd*, H_b−C(6)); 2.20 (br. *s*, OH). ^{13}C-NMR ($CDCl_3$): 85.0 (C(1)); 79.7 (C(2)); 76.8 (C(4)); 74.9 (Ph*C*H$_2$); 73.3 (Ph*C*H$_2$); 72.3 (C(3)); 72.1 (PhCH$_2$); 72.0 (C(5)); 69.1 (C(6)). Anal. calc. for $C_{33}H_{34}O_5S$ (542.69): C 73.04, H 6.32, S 5.91; found: C 72.95, H 6.34, S 5.84.

Ethyl 2,4,6-Tri-O-*benzyl-1-thio-α*-D-*mannopyranoside* (**14b**). As described for **14a**, with **13b** (3.51 g, 8.68 mmol), Bu_4NHSO_4 (0.59 g, 1.74 mmol), BnBr (1.8 ml, 15.2 mmol), 5% aq. NaOH soln. (11.2 ml), and CH_2Cl_2 (42 ml): **14b** (3.43 g, 80%). $[\alpha]_D = +76.9$ ($c = 2.15$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.48 (*s*, H−C(1)); 4.85 (*d*, $J = -11.1$, 1 H, PhCH_2); 4.77 (*d*, $J = -11.7$, 1 H, PhCH_2); 4.67 (*d*, $J = -12.1$, 1 H, PhCH_2); 4.52 (2*d*, $J = -11.7$, 2 H, PhCH_2); 4.51 (*d*, $J = -12.1$, 1 H, PhCH_2); 4.12 (*ddd*, J(5,6a) = 4.6, J(5,6b) = 2.0, H−C(5)); 3.95 (*dd*, J(3,4) = 9.3, H−C(3)); 3.83 (*dd*, J(2,3) = 3.8, H−C(2)); 3.81–3.78 (*m*, H_a−C(6)); 3.75 (*t*, J(4,5) = 9.6,

H–C(4)); 3.71 (*dd*, *J*(6a,6b) = –10.8, H_b–C(6)); 2.71–2.51 (*m*, Me*C*H_2S); 2.38 (*d*, *J*(3,OH) = 9.5, OH); 1.26 (*s*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 80.9 (C(1)); 79.8 (C(2)); 76.8 (C(4)); 74.8 (Ph*C*H_2), 73.3 (Ph*C*H_2); 72.3 (C(3)); 72.1 (Ph*C*H_2); 71.2 (C(5)); 69.0 (C(6)); 25.0 (Me*C*H_2S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{29}H_{34}O_5S$ (494.65): C 70.42, H 6.93, S 6.48; found: C 70.20, H 7.00, S 6.49.

Phenyl 2,4,6-Tri-O-*benzyl-3*-O-*(3-carboxypropanoyl)-1-thio-α*-D-*mannopyranoside* (**15a**). As described for **2a**, with **14a** (2.39 g, 4.40 mmol), succinic anhydride (3.50 g, 35.2 mmol), DMAP, and pyridine (20 ml): crude **15a** (2.39 g, 85%), which was used without further purification in the next step.

Ethyl 2,4,6-Tri-O-*benzyl-3*-O-*(3-carboxypropanoyl)-1-thio-α*-D-*mannopyranoside* (**15b**). As described for **2a**, with **14b** (4.03 g, 8.15 mmol), succinic anhydride (6.53 g, 65.20 mmol), DMAP, and pyridine (60 ml), followed by chromatography (toluene/acetone 7:1 → 3:1): **15b** (4.12 g, 85%). $[\alpha]_D = +47.7$ ($c = 2.95$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.37 (*d*, *J*(1,2) = 1.6, H–C(1)); 5.18 (*dd*, *J*(3,4) = 9.2, H–C(3)); 4.68 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.65 (*d*, *J* = –10.5, 1 H, PhCH_2); 4.64–4.51 (*m*, 2 H, PhCH_2); 4.52 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.49 (*d*, *J* = –11.8, 1 H, PhCH_2); 4.21–4.16 (*m*, *J*(5,6a) = 4.2, *J*(5,6b) = 1.8, H–C(5)); 4.09 (*t*, *J*(4,5) = 9.5, H–C(4)); 3.96 (*dd*, *J*(2,3) = 3.3, H–C(2)); 3.82 (*dd*, *J*(6a,6b) = –11.0, H_a–C(6)); 3.68 (*dd*, H_b–C(6)); 2.67–2.43 (*m*, CO*C*H_2*C*H_2COOH, Me*C*H_2S); 1.25 (*t*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 177.3 (COOH); 171.4 (*C*OCH_2CH_2); 81.7 (C(1)); 77.3 (C(2)); 74.6 (Ph*C*H_2); 74.5 (C(3)); (2 C, C(4), Ph*C*H_2); 72.4 (Ph*C*H_2); 71.7 (C(5)); 68.8 (C(6)); 28.8, 28.5 (CO*C*H_2*C*H_2COOH); 25.1 (Me*C*H_2S); 14.8 (*Me*CH_2S). Anal. calc. for $C_{33}H_{38}O_7S$ (578.72): C 68.49, H 6.62, S 5.54; found: C 68.61, H 6.57, S 5.60.

Benzyl 2-O-*Benzoyl-4,6*-O-*benzylidene-3*-O-*[1,4-dioxo-4-(phenyl 2,4,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranoside-3*-O-*yl)butyl]-α*-D-*glucopyranoside* (**16a**). As described for **4a**, with crude **15a** (2.39 g, 3.7 mmol), **3** [26] (1.72 g, 3.7 mmol), DCC (0.77 g, 3.7 mmol), DMAP, and CH_2Cl_2 (20 ml): **16a** (2.43 g, 65%). $[\alpha]_D = +100.0$ (c = 0.81, $CHCl_2$). ^{1}H-NMR ($CDCl_3$): 5.88 (*t*, *J*(3,4) = 9.9, H–C(3)); 5.55 (*d*, *J*(1′,2′) = 1.8, H–C(1′)); 5.30 (*d*, *J*(1,2) = 3.5, H–C(1)); 5.52 (*s*, PhC*H*); 5.11 (*dd*, *J*(3′,4′) = 9.3, H–C(3′)); 5.09 (*dd*, *J*(2,3) = 9.9, H–C(2)); 4.76 (*d*, *J* = –12.4, 1 H, PhCH_2); 4.66 (*d*, *J* = –11.9, 1 H, PhCH_2); 4.63 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.58 (*s*, 1 H, PhCH_2); 4.56 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.48 (*d*, *J* = –11.3, 1 H, PhCH_2); 4.46 (*d*, *J* = –11.9, 1 H, PhCH_2); 4.44 (*d*, *J* = –12.2, 1 H, PhCH_2); 4.30 (*ddd*, *J*(5′,6a′) = 4.6, *J*(5′,6b′) = 1.9, H–C(5′)); 4.25 (*dd*, *J*(5,6a) = 5.0, *J*(5,6b) = 10.3, *J*(6a,6b) = –10.3, H_a–C(6)); 4.16–4.10 (*m*, H–C(5)); 4.09 (*t*, *J*(4′,5′) = 9.8, H–C(4′)); 4.04 (*dd*, *J*(2′,3′) = 3.3, H–C(2′)); 3.82 (*dd*, *J*(6a′,6b′) = –11.0, H_a–C(6′)); 3.78 (*t*, H_b–C(6)); 3.73 (*t*, *J*(4,5) = 9.7, H–C(4)); 3.79 (*dd*, H_b–C(6′)); 2.51–2.35 (*m*, $COCH_2CH_2CO$). ^{13}C-NMR ($CDCl_3$): 171.1, 171.0 (*C*OCH_2CH_2*C*O); 165.8 (Ph*C*O); 95.9 (C(1)); 85.5 (C(1′)); 79.1 (C(4)); 77.0 (C(2′)); 74.6 (Ph*C*H_2); 74.2 (C(3′)); 73.6 (C(4′)); 73.3 (2 C, Ph*C*H_2); 72.3 (C(5′), Ph*C*H_2); 72.2 (C(2)); 70.0 (C(6′)); 69.3 (C(3)); 68.9 (C(6)); 62.8 (C(5)); 28.8 (CO*C*H_2*C*H_2CO). Anal. calc. for $C_{64}H_{62}O_{14}S$ (1087.25): C 70.70, H 5.75, S 2.95; found: C 70.57, H 5.78, S 3.02.

Benzyl 2-O-*Benzoyl-4,6*-O-*benzylidene-3*-O-*[4-(ethyl 2,4,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranoside-3*-O-*yl)-1,4-dioxobutyl]-α*-D-*glucopyranoside* (**16b**). As described for **16a**, with **15b** (4.12 g, 6.93 mmol), **3** [26] (3.21 g, 6.93 mmol), DMAP, DCC (1.72 g, 8.92 mmol), and CH_2Cl_2 (30 ml): **16b** (5.13 g, 71%). $[\alpha]_D = +83.5$ (c = 1.24, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.87 (*t*, *J*(3,4) = 9.9, H–C(3)); 5.51 (*s*, PhC*H*); 5.34 (*d*, *J*(1′,2′) = 1.8, H–C(1′)); 5.29 (*d*, *J*(1,2) = 3.8, H–C(1)); 5.08 (2 *dd*, *J*(3′,4′) = 9.4, *J*(2,3) = 10.0, H–C(2), H–C(3′)); 4.76 (*d*, *J* = –12.4, 1 H, PhCH_2); 4.69 (*d*, *J* = –12.2, 1 H, PhCH_2); 4.67 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.55 (*d*, *J* = –12.4, 1 H, PhCH_2); 4.52 (*d*, *J* = –11.6, 1 H, PhCH_2); 4.49 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.47 (*d*, *J* = –12.2, 1 H, PhCH_2); 4.44 (*d*, *J* = –11.4, 1 H, PhCH_2); 4.27 (*dd*, *J*(6a,6b) = –10.2, H_a–C(6)); 4.16 (*ddd*, *J*(5′,6a′) = 1.8, *J*(5′,6b′) = 4.1, H–C(5′)); 4.13–4.08 (*m*, *J*(5,6a) = 4.9, *J*(5,6b) = 10.2, H–C(5)); 4.04 (*t*, *J*(4′,5′) = 9.6, H–C(4′)); 3.88 (*dd*, *J*(2′,3′) = 3.3, H–C(2′)); 3.81–3.77 (*m*, *J*(6a′,6b′) = –11.0, H_a–C(6′)); 3.78 (*t*, H_b–C(6)); 3.72 (*t*, *J*(4,5) = 9.7, H–C(4)); 3.67 (*dd*, H_b–C(6′)); 2.67–2.32 (*m*, $COCH_2CH_2CO$, Me*C*H_2S); 1.25 (*t*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 170.0 (*C*OCH_2CH_2*C*O); 165.8 (Ph*C*O); 101.6 (Ph*C*H); 95.9 (C(1)); 81.7 (C(1′)); 79.1 (C(4)); 77.1 (C(2′)); 74.5 (Ph*C*H_2); 74.4 (C(3′)); 73.6 (C(4′)); 73.4 (2 C, Ph*C*H_2); 72.3 (Ph*C*H_2); 72.2 (C(2)); 71.6 (C(5′)); 69.9 (C(6′)); 69.2 (C(3)); 68.9 (C(6)); 62.8 (C(5)); 29.0, 28.8 (CO*C*H_2*C*H_2CO); 25.1 (Me*C*H_2S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{60}H_{62}O_{14}S$ (1039.21): C 69.35, H 6.01; found: C 69.24, H 5.99.

Benzyl 2-O-*Benzoyl-6*-O-*benzyl-3*-O-*[1,4-dioxo-4-(phenyl 2,4,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranoside-3*-O-*yl)butyl]-α*-D-*glucopyranoside* (**17a**). As described for **5a**, with **16a** (2.25 g, 2.1 mmol) and $NaCNBH_3$ (1.71 g, 27.1 mmol): **17a** (1.63 g, 76%). $[\alpha]_D = +87.7$ ($c = 1.58$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.66 (*dd*, *J*(3,4) = 9.1, H–C(3)); 5.57 (*d*, *J*(1′,2′) = 1.9, H–C(1′)); 5.28 (*d*, *J*(1,2) = 3.7, H–C(1)); 5.17 (*dd*, *J*(3′,4′) = 9.3, H–C(3′)); 5.06 (*dd*, *J*(2,3) = 10.2, H–C(2)); 4.76 (*d*, *J* = –12.4, 1 H, PhCH_2); 4.67 (*d*, *J* = –11.9, 1 H, PhCH_2); 4.66 (*d*, *J* = –12.2, 1 H, PhCH_2); 4.65 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.62 (*s*, 3 H, PhCH_2); 4.55 (*d*, *J* = –12.4, 1 H, PhCH_2); 4.50 (*d*, *J* = –11.3, 1 H, PhCH_2); 4.47 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.31 (*ddd*, *J*(5′,6a′) = 4.3, *J*(5′,6b′) = 1.9, H–C(5′)); 4.11 (*t*, *J*(4′,5′) = 9.6, H–C(4′)); 4.08 (*dd*, *J*(2′,3′) = 3.2, H–C(2′)); 3.98–3.93 (*m*, H–C(5)); 3.91–3.82 (*m*, 2 H–C(6)); 3.87 (*dd*, *J*(6a′,6b′) = –10.9, H_a–C(6′)); 3.84 (*t*, *J*(4,5) = 9.3, H–C(4)); 3.71

(*dd*, H_b–C(6′)); 3.00 (br. *s*, OH); 2.53–2.46 (*m*, $COCH_2CH_2CO$). ^{13}C-NMR ($CDCl_3$): 172.3, 171.7 ($COCH_2CH_2CO$); 165.7 (Ph*C*O); 95.2 (C(1)); 85.4 (C(1′)); 77.3 (C(2′)); 74.6 (Ph*C*H_2); 73.8 (C(3′)); 73.7 (C(4′)); 73.6 (2 C, C(3), Ph*C*H_2); 73.3, 72.2 (Ph*C*H_2); 71.8 (C(5′)); 71.4 (C(2)); 70.4 (C(5)); 70.2 (C(4)); 69.4 (C(6)); 69.3 (Ph*C*H_2); 69.0 (C(6′)); 29.1, 29.0 ($COCH_2CH_2CO$). Anal. calc. for $C_{64}H_{64}O_{14}S$ (1089.27): C 70.57, H 5.92, S 2.94; found: C 70.45, H 5.98, S 3.00.

Benzyl 2-O-*Benzoyl-6*-O-*benzyl-3*-O-*[4-(ethyl 2,4,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranoside-3*-O-*yl)-1,4-dioxobutyl]-α*-D-*glucopyranoside* (**17b**). As described for **5a**, with **16b** (3.15 g, 3.03 mmol) and $NaCNBH_3$ (2.38 g, 37.9 mmol): **17b** (2.44 g, 77%). $[\alpha]_D = +67.3$ ($c = 1.04$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.63 (*t*, *J*(3,4) = 9.7, H–C(3)); 5.36 (*d*, *J*(1′,2′) = 1.5, H–C(1′)); 5.26 (*d*, *J*(1,2) = 3.7, H–C(1)); 5.13 (*dd*, *J*(3′,4′) = 9.2, H–C(3′)); 5.04 (*dd*, *J*(2,3) = 10.2, H–C(2)); 4.74 (*d*, *J* = –12.4, 1 H, PhCH_2); 4.68 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.66 (*d*, *J* = –12.2, 1 H, PhCH_2); 4.62–4.55 (*m*, 4 H, PhCH_2); 4.49 (2*d*, *J* = –12.2, 2 H, PhCH_2); 4.48 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.16 (*ddd*, *J*(5′,6a′) = 2.5, *J*(5′,6b′) = 1.7, H–C(5′)); 4.06 (*t*, *J*(4′,5′) = 9.5, H–C(4′)); 3.95–3.91 (*m*, *J*(2′,3′) = 3.3, H–C(2′)); H–C(5)); 3.85–3.80 (*m*, H–C(4), H_a–C(6′)); 3.79–3.70 (*m*, 2 H–C(6)); 3.67 (*dd*, *J*(6a′,6b′) = –11.0, H_b–C(6′)); 2.95 (br. *d*, *J*(4,OH) = 4.2, OH); 2.66–2.52 (*m*, Me*C*H_2S); 2.45 (*s*, $COCH_2CH_2CO$); 1.25 (*t*, *J* = 7.3, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 172.3, 171.7 ($COCH_2CH_2CO$); 165.8 (Ph*C*O); 95.3 (C(1)); 81.7 (C(1′)); 77.2 (C(2′)); 74.6 (Ph*C*H_2); 73.7 (C(3′), Ph*C*H_2); 73.6 (C(4′)); 73.5 (C(3)); 73.4 (Ph*C*H_2); 72.3 (Ph*C*H_2); 71.7 (C(5′)); 71.4 (C(2)); 70.4 (C(5)); 70.2 (C(4)); 69.6 (Ph*C*H_2); 69.4 (C(6)); 68.9 (C(6′)); 29.2, 29.0 ($COCH_2CH_2CO$); 25.2 (Me*C*H_2S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{60}H_{64}O_{14}S$ (1041.23): C 69.21, H 6.20, S 3.08; found: C 69.26, H 6.28, S 2.99.

Benzyl O-*(2,4,6-Tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1 → 4)-2*-O-*benzoyl-6*-O-*benzyl-α*-D-*glucopyranoside 3,3′-Succinate* (**18a**) *and Benzyl* O-*(2,4,6-Tri*-O-*benzyl-β*-D-*mannopyranosyl)-(1 → 4)-2*-O-*benzoyl-6*-O-*benzyl-α*-D-*glucopyranoside 3,3′-Succinate* (**18b**). *a*) As described for **6** (*Exper. a*) with **17a** (0.58 g, 0.53 mmol), NIS (0.62 g, 2.78 mmol), Me_3SiOTf (26 µl, 0.14 mmol), and CH_2Cl_2 (15 ml), followed by CC (toluene/acetone 20:1): **18a** (86 mg, 17%), then **18b** (257 mg, 50%).

Data of **18a**: $[\alpha]_D = +105.7$ ($c = 1.61$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.96 (*t*, *J*(3,4) = 10.2, H–C(3)); 5.80 (br. *d*, H–C(3′)); 5.31 (*d*, *J*(1,2) = 3.8, H–C(1)); 5.15 (*d*, *J*(1′,2′) = 6.8, H–C(1′)); 5.13 (*dd*, *J*(2,3) = 10.4, H–C(2)); 4.78 (*d*, *J* = –12.5, Ph*C*H_2); 4.74 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.69 (*d*, *J* = –11.8, 1 H, PhCH_2); 4.60–4.51 (*m*, 5 H, PhCH_2); 4.46 (*d*, *J* = –12.2, 1 H, PhCH_2); 4.44 (*d*, *J* = –11.7, 1 H, PhCH_2); 4.08–4.02 (*m*, H–C(4′)); 3.80 (*t*, *J*(4,5) = 9.9, H–C(4)); 3.73 (*dd*, *J*(5,6a) = 3.0, *J*(6a,6b) = –10.5, H_a–C(6)); 3.72 (*dd*, *J*(2′,3′) = 2.8, H–C(2′)); 3.72–3.66 (*m*, *J*(6a′,6b′) = –11.2, H_a–C(6′)); 3.66–3.61 (*m*, *J*(5,6b) = 4.8, H–C(5)); 3.51 (*dd*, H_b–C(6′)); 3.50 (*dd*, H_b–C(6)); 2.50–2.31 (*m*, 2 H, $COCH_2CH_2CO$); 2.14–2.07 (*m*, 2 H, $COCH_2CH_2CO$). ^{13}C-NMR ($CDCl_3$): 171.8, 171.2 ($COCH_2CH_2CO$); 165.5 (Ph*C*O); 95.2 (C(1)); 92.1 (*J*(1′, H–C(1′) = 168.4, C(1′)); 76.6 (C(4)); 75.3 (C(4′)); 73.6 (Ph*C* H_2); 73.0 (Ph*C*H_2, C(2′)); 71.7 (Ph*C*H_2); 71.5 (C(2)); 69.8 (Ph*C*H_2, C(5)); 68.7 (Ph*C*H_2); 68.2 (C(6′)); 67.9 (C(6)); 67.8, 73.4, 67.2 (C(3), C(3′), C(5′)); 30.2, 28.5 ($COCH_2CH_2CO$). Anal. calc. for $C_{58}H_{58}O_{14}$ (979.10): C 71.15, H 5.97; found: C 70.96, H 6.03.

Data of **18b**: $[\alpha]_D = +62.1$ ($c = 0.96$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.96 (*t*, *J*(3,4) = 10.3, H–C(3)); 5.32 (*d*, *J*(1,2) = 3.8, H–C(1)); 5.20 (br. *t*, H–C(3′)); 5.15 (*dd*, *J*(2,3) = 10.6, H–C(2)); 4.99 (*d*, *J*(1′,2′) = 5.3, H–C(1′)); 4.74 (*d*, *J* = –12.4, 1 H, PhCH_2); 4.70 (*d*, *J* = –11.9, 1 H, PhCH_2); 4.67 (*d*, *J* = –11.9, 1 H, PhCH_2); 4.56–4.50 (*m*, 4 H, PhCH_2); 4.54 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.44 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.43 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.02–3.97 (*m*, H–C(4)); 3.77 (*dd*, *J*(2′,3′) = 2.5, H–C(2′)); 3.70–3.60 (*m*, 3 H, *J*(5,6a) = 3.1, *J*(5,6b) = 4.4, H–C(4′), H–C(5′), H–C(5)); 3.52 (*dd*, *J*(6a,6b) = –10.7, H_a–C(6)); 3.43 (*dd*, H_b–C(6)); 3.33–3.28 (*m*, 1 H_a–C(6′)); 3.17–3.06 (*m*, H_b–C(6′)); 2.43–2.29 (*m*, 2 H, $COCH_2CH_2CO$); 2.16–2.03 (*m*, 2 H, $COCH_2CH_2CO$). ^{13}C-NMR ($CDCl_3$): 172.2, 171.0 ($COCH_2CH_2CO$); 165.6 (Ph*C*O); 95.4 (C(1)); 93.9 (*J*(1′, H–C(1′) = 167.1, C(1′)); 75.2 (C(4)); 73.4, 73.2 (Ph*C*H_2); 72.7, 71.5 (C(2′), C(4′)); 71.3 (2 C, C(2), Ph*C*H_2); 70.6 (C(3)); 69.9, 69.8 (C(5), C(5′)); 69.7 (C(3′)); 69.6 (Ph*C*H_2); 69.4 (C(6′), Ph*C*H_2); 68.7 (C(6)). Anal. calc. for $C_{58}H_{58}O_{14}$ (979.10): C 71.15, H 5.97; found: C 70.91, H 6.00.

b) As described for **6** (*Exper. b*), with **17a** (0.62 g, 0.57 mmol), NIS (0.68 g, 3.0 mmol), Me_3SiOTf (29 µl, 0.16 mmol), and MeCN (20 ml), followed by CC (toluene/acetone 20:1): **18a** (67 mg, 12%) and **18b** (297 mg, 53%).

c) As described for **6** (*Exper. a*), with **17b** (0.47 g, 0.45 mmol), NIS (0.51 g, 2.25 mmol), Me_3SiOTf (20 µl, 0.11 mmol), and CH_2Cl_2 (20 ml), followed by CC (toluene/AcOEt 15:1): **18a**/**18b** 1:9 (0.28 g, 64%).

d) As described for **6** (*Exper. b*), with **17b** (0.94 g, 0.90 mmol), NIS (1.02 g, 4.5 mmol), Me_3SiOTf (41 µl, 0.23 mmol) and MeCN (30 ml), followed by CC (toluene/AcOEt 15:1): **18b** (0.59 g, 66%).

e) A suspension of **17b** (0.44 g, 0.42 mmol), 4-Å molecular sieves (1.1 g), and MeOTf (0.23 ml, 2.12 mmol) in CH_2Cl_2 (20 ml) was stirred for 6 h at r.t. The mixture was neutralized by the addition of Et_3N, diluted with

CH_2Cl_2, and filtered. The filtrate was washed with H_2O, dried, and evaporated. CC (toluene/acetone 20:1) of the residue afforded **18a**/**18b** 17:83 (0.26 g, 64%).

f) As described in *Exper. e*, with **17b** (0.55 g, 0.53 mmol), 4-Å molecular sieves (1.32 g), MeOTf (0.40 ml, 3.7 mmol), and MeCN (20 ml), followed by CC (toluene/acetone 20:1): **18a** (0.33 g, 64%).

Benzyl O-*(3*-O-*Benzoyl-2,4,6-tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1→4)-2,3-di*-O-*benzoyl-6*-O-*benzyl-α*-D-*glucopyranoside* (**19a**) *and Benzyl* O-*(3*-O-*Benzoyl-2,4,6-tri*-O-*benzyl-β*-D-*mannopyranosyl)-(1→4)-2,3-di*-O-*benzoyl-6-O-benzyl-α*-D-*glucopyranoside* (**19b**). *a*) As described for **7**, with **18a** (111 mg, 0.11 mmol), NaOMe in MeOH (4 ml), BzCl (79 µl, 0.68 mmol), and pyridine (4 ml): **19a** (92 mg, 73%). $[\alpha]_D = +43.6$ ($c = 1.82$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 6.10 (*dd*, $J(3,4) = 9.2$, H–C(3)); 5.60 (*dd*, $J(3',4') = 9.4$, H–C(3′)); 5.33 (*d*, $J(1,2) = 3.8$, H–C(1)); 5.19 (*dd*, $J(2,3) = 10.3$, H–C(2)); 5.14 (*d*, $J(1',2') = 1.8$, H–C(1′)); 4.74 (*d*, $J = -12.5$, 1 H, PhCH_2); 4.75 (*d*, $J = -12.5$, 1 H, PhCH_2); 4.65 (*d*, $J = -12.7$, 1 H, PhCH_2); 4.62 (*d*, $J = -12.3$, 1 H, PhCH_2); 4.60–4.55 (*m*, 2 H, PhCH_2); 4.45–4.40 (*m*, 2 H, PhCH_2); 4.40 (*t*, $J(4',5') = 9.5$, H–C(4′)); 4.19 (*d*, $J = -11.9$, 1 H, PhCH_2); 4.13 (*t*, $J(4,5) = 9.3$, H–C(4)); 4.12 (*d*, $J = -12.1$, 1 H, PhCH_2); 4.03–3.98 (*m*, $J(5,6a) = 4.1$, $J(5,6b) = 2.0$, H–C(5)); 3.95 (*dd*, $J(6a,6b) = -11.2$, H_a–C(6)); 3.86–3.80 (*m*, $J(5',6b') = 3.1$, H–C(5′), H_a–C(6′)); 3.84 (*dd*, $J(2',3') = 3.0$, H–C(2′)); 3.74 (*dd*, $J(6a',6b') = -11.6$, H_b–C(6′)); 3.73 (*dd*, H_b–C(6)). ^{13}C-NMR ($CDCl_3$): 165.6, 165.5, 165.4 (Ph*C*O); 98.8 ($J(1', H–C(1')) = 170.9$, C(1′)); 95.1 (C(1)); 77.7 (C(2′)); 76.3 (C(4)); 75.6 (C(4′)); 74.7 (Ph*C*H$_2$); 74.1 (Ph*C*H$_2$); 73.9, 73.7, 73.5 (1 C, 1 C, 2 C, C(5′), C(3), C(3′), Ph*C*H$_2$); 72.7 (Ph*C*H$_2$); 72.4 (C(2)); 70.2 (C(5)); 69.8 (Ph*C*H$_2$); 68.8 (C(6′)); 68.5 (C(6)). Anal. calc. for $C_{68}H_{64}O_{14}$ (1105.25): C 73.90, H 5.84; found: C 74.05, H 5.93.

b) As described for **7**, with **18b** (159 mg, 0.16 mmol), NaOMe, MeOH (4 ml), BzCl (113 µl, 0.98 mmol), and pyridine (4 ml): **19b** (130 mg, 72%). $[\alpha]_D = -32.3$ ($c = 1.10$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 6.10 (*t*, $J(3,4) = 9.8$, H–C(3)); 5.34 (*d*, $J(1,2) = 3.8$, H–C(1)); 5.21 (*dd*, $J(2,3) = 10.2$, H–C(2)); 5.00 (*dd*, H–C(3′)); 4.76 (*d*, $J = -12.6$, 1 H, PhCH_2); 4.75 (*d*, $J = -12.5$, 1 H, PhCH_2); 4.71 (*d*, $J = -12.7$, 1 H, PhCH_2); 4.60 (*d*, $J = -12.9$, 1 H, PhCH_2); 4.60–4.52 (*m*, 3 H, PhCH_2); 4.44 (*s*, H–C(1′)); 4.43 (*d*, $J = -12.1$, 1 H, PhCH_2); 4.42 (*d*, $J = -11.8$, 1 H, PhCH_2); 4.33 (*t*, $J(4,5) = 9.8$, H–C(4)); 4.15 (*d*, $J = 11.8$, 1 H, PhCH_2); 4.05–3.99 (*m*, $J(5,6a) = 2.8$, $J(5,6b) = 1.8$, H–C(5)); 4.00 (*t*, $J(4',5') = 9.7$, H–C(4′)); 3.89 (br. *d*, $J(2',3') = 3.1$, H–C(2′)); 3.74 (*dd*, $J(6a,6b) = -11.2$, H–C(6a)); 3.66 (*dd*, H_b–C(6)); 3.44 (*dd*, $J(6a',6b') = -11.4$, H_a–C(6′)); 3.34 (*dd*, H_b–C(6′)); 3.26–3.21 (*m*, $J(5',6a') = 4.5$, $J(5',6b') = 1.8$, H–C(5′)). ^{13}C-NMR ($CDCl_3$): 165.7, 165.6 (1 C, 2 C, Ph*C*O); 100.6 ($J(1', H–C(1')) = 158.5$, C(1′)); 95.3 (C(1)); 76.2, 76.0 (1 C, 2 C, C(2′), C(3′), C(5′)); 74.9 (C(4)); 74.6 (Ph*C*H$_2$); 74.3 (Ph*C*H$_2$); 73.7 (Ph*C*H$_2$); 73.1 (Ph*C*H$_2$); 73.0 (C(4′)); 72.2 (C(2)); 70.9, 70.2 (C(3), C(5)); 69.8 (Ph*C*H$_2$); 68.8 (C(6′)); 68.1 (C(6)). Anal. calc. for $C_{68}H_{64}O_{14}$ (1105.25): C 73.90, H 5.84; found: C 74.10, H 5.90.

c) As described for **7**, with **18a**/**18b** 1:9 (see above, *Exper. c*; 0.20 g, 0.2 mmol), NaOMe in MeOH (8 ml), BzCl (139 µl, 1.2 mmol), and pyridine (8 ml), followed by CC (hexane/AcOEt 5:1): **19a** (14 mg, 7%) and **19b** (141 mg, 64%).

d) As described for **7**, with **18a**/**18b** 17:83 (see above, *Exper. e*; 0.18 g, 0.18 mmol), NaOMe in MeOH (8 ml), BzCl (126 µl, 1.1 mmol), and pyridine (8 ml), followed by CC (hexane/AcOEt 5:1): **19a** (23 mg, 12%) and **19b** (105 mg, 58%).

Ethyl 2,4,6-Tri-O-*benzyl-3*-O-*[3-(*tert-*butoxy)-1,3-dioxopropyl]-1-thio-α*-D-*mannopyranoside* (**20**). A soln. of **14b** (1.78 g, 4.54 mmol), *tert*-butyl hydrogen malonate (0.61 g, 3.78 mmol), 1-hydroxy-1*H*-benzotriazole (0.61 g, 4.54 mmol), and DCC (0.78 g, 3.78 mmol) in CH_2Cl_2 (30 ml) was stirred for 1 h at 0° followed by 48 h at r.t. Workup as described for **4a** and CC (hexane/AcOEt 8:1) afforded **20** (1.50 g, 62%). $[\alpha]_D = +51.4$ ($c = 1.83$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.35 (*d*, $J(1,2) = 1.8$, H–C(1)); 5.27 (*s*, PhC*H*); 5.22 (*dd*, $J(3,4) = 9.1$, H–C(3)); 4.68 (*d*, $J = -12.0$, 1 H, PhCH_2); 4.67 (*d*, $J = -12.0$, 1 H, PhCH_2); 4.66 (*d*, $J = -11.1$, 1 H, PhCH_2); 4.58 (*d*, $J = -12.0$, 1 H, PhCH_2); 4.48 (*d*, $J = -12.0$, 1 H, PhCH_2); 4.46 (*d*, $J = -11.1$, 1 H, PhCH_2); 4.18 (*ddd*, $J(5,6a) = 4.2$, $J(5,6b) = 1.9$, H–C(5)); 4.09 (*t*, $J(4,5) = 9.5$, H–C(4)); 3.99 (*dd*, $J(2,3) = 3.3$, H–C(2)); 3.82 (*dd*, $J(6a,6b) = -11.0$, H_a–C(6)); 3.68 (*dd*, H_b–C(6)); 3.18 (br. *d*, $COCH_2$); 2.67–2.51 (*m*, MeCH_2S); 1.42 (*s*, *t*Bu); 1.24 (*t*, $J = 7.4$, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 166.2 (*C*OCH_2); 165.4 (*C*OCH_2); 82.1 (Me_3C); 81.7 (C(1)); 77.3 (C(2)); 75.1 (C(3)); 74.5 (Ph*C*H$_2$); 73.4 (C(4)); 73.3 (Ph*C*H$_2$); 72.4 (Ph*C*H$_2$); 71.7 (C(5)); 68.8 (Ph*C*H$_2$); 63.6 (C(6)); 42.7 (CO*C*H$_2$); 27.9 (Me_3C); 25.1 (Me*C*H$_2$S); 14.8 (*Me*CH_2S). Anal. calc. for $C_{36}H_{44}O_8S$ (636.80): C 67.90, H 6.96, S 5.04; found: C 67.58, H 6.92, S 5.06.

Ethyl 2,4,6-Tri-O-*benzyl-3*-O-*(carboxyacetyl)-1-thio-α*-D-*mannopyranoside* (**21**). A soln. of **20** (1.25 g, 1.96 mmol) and CF_3COOH (4.3 ml, 37.2 mmol) in CH_2Cl_2 (40 ml) was stirred for 3 h at r.t. Evaporation afforded crude **21** (1.08 g, 95%), which was used without further purification in the next step.

Benzyl 2-O-*Benzoyl-4,6*-O-*benzylidene-3*-O-*[3-(ethyl 2,4,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-3*-O-*yl)-1,3-dioxopropyl]-α*-D-*glucopyranoside* (**22**). As described for **4a**, with crude **21** (1.08 g, 1.9 mmol), **3** [26]

(0.91 g, 1.96 mmol), DCC (0.41 g, 1.96 mmol), DMAP, and CH_2Cl_2 (30 ml): **22** (1.1 g, 55%). $[\alpha]_D = -81.6$ ($c = 0.97$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.86 (t, $J(3,4) = 9.9$, H–C(3)); 5.44 (s, PhC*H*); 5.27 (d, $J(1,2) = 3.6$, H–C(1)); 5.26 (d, $J(1',2') = 1.7$, H–C(1')); 5.08 (dd, $J(3',4') = 9.7$, H–C(3')); 5.07 (dd, $J(2,3) = 10.0$, H–C(2)); 4.74 (d, $J = -12.4$, 1 H, PhCH_2); 4.64 (d, $J = -12.0$, 1 H, PhCH_2); 4.54 (d, $J = -12.5$, 1 H, PhCH_2); 4.53 (d, $J = -12.1$, 1 H, PhCH_2); 4.52 (d, $J = -11.3$, 1 H, PhCH_2); 4.46 (d, $J = -12.1$, 1 H, PhCH_2); 4.40 (d, $J = -12.1$, 1 H, PhCH_2); 4.32 (d, $J = -11.3$, 1 H, PhCH_2); 4.24 (dd, J(6a,6b) $= -10.2$, H_a–C(6)); 4.14–4.01 (m, $J(5,6a) = 4.9$, $J(5',6b') = 2.0$, H–C(5), H–C(5')); 3.94 (t, $J(4',5') = 9.6$, H–C(4')); 3.84 (dd, $J(2',3') = 3.3$, H–C(2')); 3.76–3.61 (m, J(6a',6b') $= -10.8$, H–C(4), H_a–C(6'), H_b–C(6)); 3.61 (dd, H_b–C(6')); 3.17 (s, $COCH_2$); 2.64–2.48 (m, MeCH_2S); 1.23 (t, $J = 7.4$, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 165.8 (CO); 165.3 (CO); 165.2 (CO); 101.5 (Ph*C*H); 95.9 (C(1)); 81.7 (C(1')); 78.9 (C(4)); 77.3 (C(2')); 75.2 (C(3')); 74.3 (PhCH_2); 73.4 (C(4')); 73.3 (PhCH_2); 72.5 (PhCH_2); 72.0 (C(2)); 71.5 (C(5')); 70.1 (C(3)); 70.0 (C(6')); 68.8 (C(6), PhCH_2); 62.7 (C(5)); 41.0 (COCH_2); 25.1 (MeCH_2S); 14.9 (MeCH_2S). Anal. calc. for $C_{59}H_{60}O_{14}S$ (1025.18): C 69.12, H 5.90, S 3.13; found: C 68.76, H 5.90, S 3.21.

Benzyl 2-O-*Benzoyl-6*-O-*benzyl-3*-O-*[3-(ethyl 2,4,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-3*-O-*yl)-1,3-dioxopropyl]-α*-D-*glucopyranoside* (**23**). As described for **5a**, with **22** (1.30 g, 1.25 mmol) and $NaCNBH_3$ (1.57 g, 25.0 mmol): **23** (0.93 g, 72%). $[\alpha]_D = +83.3$ ($c = 1.08$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.64 (t, $J(3,4) = 9.1$, H–C(3)); 5.37 (d, $J(1',2') = 1.9$, H–C(1')); 5.25 (d, $J(1,2) = 3.7$, H–C(1)); 5.15 (dd, $J(3',4') = 9.1$, H–C(3')); 5.04 (dd, $J(2,3) = 10.3$, H–C(2)); 4.75 (d, $J = -12.4$, 1 H, PhCH_2); 4.67 (d, $J = -12.0$, 1 H, PhCH_2); 4.66 (d, $J = -12.2$, 1 H, PhCH_2); 4.65 (d, $J = -12.2$, 1 H, PhCH_2); 4.63 (s, 1 H, PhCH_2); 4.59 (d, $J = -12.1$, 1 H, PhCH_2); 4.55 (d, $J = -12.4$, 1 H, PhCH_2); 4.52 (d, $J = -10.2$, 1 H, PhCH_2); 4.46 (d, $J = -12.2$, 1 H, PhCH_2); 4.44 (d, $J = -11.0$, 1 H, PhCH_2); 4.17 (ddd, $J(5',6a') = 4.0$, $J(5',6b') = 1.9$, H–C(5')); 4.06 (t, $J(4',5') = 9.5$, H–C(4')); 3.97–3.93 (m, H–C(5)); 3.92 (dd, $J(2',3') = 3.4$, H–C(2')); 3.80–3.77 (m, $J(4,5) = 9.4$, H–C(4)); 3.79 (dd, J(6a',6b') $= -11.0$, H_a–C(6')); 3.74–3.70 (m, 2 H–C(6)); 3.67 (dd, H–C(6')); 3.23 (d, $J = -16.3$, 1 H, $COCH_2$); 3.11 (d, $J = -16.3$, 1 H, $COCH_2$); 2.69–2.54 (m, MeCH_2S); 2.35 (br. d, OH); 1.26 (t, $J = 7.4$, MeCH_2S). ^{13}C-NMR ($CDCl_3$): 166.8 (CO); 165.8 (CO); 165.7 (CO); 95.3 (C(1)); 81.5 (C(1')); 77.1 (C(2')); 75.3, 74.8 (C(3), C(3')); 74.4 (PhCH_2); 73.6 (PhCH_2); 73.5 (2 C, C(4'), PhCH_2); 72.3 (PhCH_2); 71.6 (C(5')); 71.3 (C(2)); 70.5 (C(5)); 69.7 (PhCH_2); 69.0 (C(6)); 68.8 (C(6')); 41.9 (COCH_2); 25.2 (MeCH_2S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{59}H_{62}O_{14}S$ (1027.20): C 68.99, H 6.08; found: C 69.03, H 6.07.

Phenyl 2,3,6-Tri-O-*benzyl-1-thio-α*-D-*mannopyranoside* (**25**). As described for **5a**, with **24** [51] (4.63 g, 8.56 mmol) and $NaCNBH_3$ (6.70 g, 107.0 mmol), followed by CC (CCl_4/acetone 15:1): **25** (3.76 g, 80%). $[\alpha]_D = +32.9$ ($c = 1.74$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.61 (d, $J(1,2) = 1.3$, H–C(1)); 4.70 (d, $J = -12.2$, 1 H, PhCH_2); 4.61 (d, $J = -11.9$, 1 H, PhCH_2); 4.58 (d, $J = -11.7$, 1 H, PhCH_2); 4.53 (d, $J = -11.9$, 1 H, PhCH_2); 4.50 (d, $J = -11.6$, 1 H, PhCH_2); 4.48 (d, $J = -11.9$, 1 H, PhCH_2); 4.32–4.26 (m, H–C(5)); 4.13 (dt, $J(4,5) = 9.6$, J(4,OH) $= 2.1$, H–C(4)); 4.01 (dd, $J(2,3) = 3.0$, H–C(2)); 3.86–3.77 (m, 2 H–C(6)); 3.68 (dd, $J(3,4) = 9.4$, H–C(3)); 2.55 (d, OH). ^{13}C-NMR ($CDCl_3$): 85.5 (C(1)); 79.6 (C(3)); 75.5 (C(2)); 73.4 (PhCH_2); 72.4 (C(5)); 71.9, 71.7 (PhCH_2); 70.1 (C(6)); 67.8 (C(4)). Anal. calc. for $C_{33}H_{34}O_5S$ (542.69): C 73.04, H 6.32, S 5.91; found: C 72.91, H 6.27, S 6.10.

Phenyl 2,3,6-Tri-O-*benzyl-4*-O-*(3-carboxypropanoyl)-1-thio-α*-D-*mannopyranoside* (**26**). As described for **2a**, with **25** (1.78 g, 3.28 mmol), succinic anhydride (2.62 g, 26.24 mmol), DMAP, and pyridine (20 ml): **26** (1.72 g, 82%). $[\alpha]_D = +78.9$ ($c = 2.11$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.57 (d, $J(1,2) = 1.7$, H–C(1)); 5.41 (t, $J(4,5) = 9.8$, H–C(4)); 4.57 (d, $J = -12.3$, 1 H, PhCH_2); 4.56 (d, $J = -12.1$, 1 H, PhCH_2); 4.52 (d, $J = -11.9$, 1 H, PhCH_2); 4.50 (d, $J = -12.1$, 1 H, PhCH_2); 4.48 (d, $J = -12.0$, 1 H, PhCH_2); 4.46 (d, $J = -12.2$, 1 H, PhCH_2); 4.38–4.34 (m, $J(5,6a) = 5.8$, $J(5,6b) = 3.1$, H–C(5)); 4.04 (dd, $J(2,3) = 2.4$, H–C(2)); 3.84 (dd, $J(3,4) = 9.8$, H–C(3)); 3.61 (dd, J(6a,6b) $= -10.3$, H_a–C(6)); 3.54 (dd, H_b–C(6)); 2.58–2.39 (m, $COCH_2CH_2CO$). ^{13}C-NMR ($CDCl_3$): 177.2 (COOH); 171.4 (*C*OCH_2CH_2COOH); 86.3 (C(1)); 77.5, 76.4 (C(2), C(3)); 72.5, 72.1, 70.3 (PhCH_2); 70.0 (C(6)); 69.8, 69.7 (C(4), C(5)); 29.3, 29.2 (CO*C*H_2*C*H_2CO). Anal. calc. for $C_{37}H_{38}O_8S$ (642.77): C 69.14, H 5.96, S 4.99; found: C 69.30, H 5.90, S 5.15.

Benzyl 2-O-*Benzoyl-4,6*-O-*benzylidene-3*-O-*[1,4-dioxo-4-(phenyl 2,3,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-4*-O-*yl)butyl]-α*-D-*glucopyranoside* (**27**). As described for **4a**, with **26** (1.72 g, 2.68 mmol), **3** [26] (1.36 g, 2.95 mmol), DCC (0.61 g, 2.95 mmol), DMAP, and CH_2Cl_2 (20 ml): **27** (2.15 g, 74%). $[\alpha]_D = +73.9$ ($c = 0.93$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.87 (t, $J(3,4) = 9.9$, H–C(3)); 5.54 (d, $J(1',2') = 1.8$, H–C(1')); 5.53 (s, PhC*H*); 5.36 (t, $J(4',5') = 9.7$, H–C(4')); 5.30 (d, $J(1,2) = 3.8$, H–C(1)); 5.08 (dd, $J(2,3) = 10.0$, H–C(2)); 4.74 (d, $J = -12.4$, 1 H, PhCH_2); 4.68 (d, $J = -12.3$, 1 H, PhCH_2); 4.59 (s, 1 H, PhCH_2); 4.57 (d, $J = -11.8$, 1 H, PhCH_2); 4.54 (d, $J = -12.3$, 1 H, PhCH_2); 4.49 (d, $J = -12.2$, 1 H, PhCH_2); 4.48 (d, $J = -11.8$, 1 H, PhCH_2); 4.39 (d, $J = -12.3$, 1 H, PhCH_2); 4.35–4.32 (m, $J(5',6a') = 6.0$, $J(5',6b') = 3.3$, H–C(5')); 4.27 (dd, $J(5,6a) = 4.8$, H_a–C(6)); 4.08 (dt, $J(5,6b) = 9.8$, H–C(5)); 3.98–3.94 (m, $J(2',3') = 2.4$, H–C(2')); 3.85 (t, J(6a,6b) $= -10.2$, H_b–C(6));

3.78–3.76 (*m*, H–C(4)); 3.73 (*dd*, *J*(3′,4′) = 9.7, H–C(3′)); 3.58 (*dd*, *J*(6a′,6b′) = –10.4, H_a–C(6′)); 3.53 (*dd*, H_b–C(6′)); 2.52–2.35 (*m*, 4 H, $COCH_2CH_2CO$). ^{13}C-NMR ($CDCl_3$): 171.1 ($COCH_2CH_2CO$); 170.8 ($COCH_2CH_2CO$); 165.8 (Ph*C*O); 101.6 (Ph*C*H); 96.4 (C(1)); 86.3 (C(1′)); 79.6 (C(4)); 77.4, 76.2 (C(2′), C(3′)); 73.7 (PhCH_2); 72.7 (C(3)); 72.6 (PhCH_2); 72.2 (PhCH_2); 71.6 (C(2)); 70.4 (PhCH_2); 69.9 (C(6′)); 69.7, 69.5 (C(4′), C(5′)); 69.3 (C(6)); 63.3 (C(5)); 29.5 (2 C, $COCH_2CH_2CO$). Anal. calc. for $C_{64}H_{62}O_{14}S$ (1087.25): C 70.70, H 5.75, S 2.98; found: C 70.53, H 5.80, S 3.08.

Benzyl 2-O-*Benzoyl-6*-O-*benzyl-3*-O-*[1,4-dioxo-4-(phenyl 2,3,6-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-4*-O-*yl)butyl]-α*-D-*glucopyranoside* (**28**). As described for **5a**, with **27** (1.54 g, 1.42 mmol) and $NaCNBH_3$ (1.12 g, 17.75 mmol): **28** (1.21 g, 78%). $[\alpha]_D = +58.9$ ($c = 0.93$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.63 (*dd*, *J*(3,4) = 9.1, H–C(3)); 5.54 (*d*, *J*(1′,2′) = 1.8, H–C(1′); 5.39 (*t*, *J*(4′,5′) = 9.7, H–C(4′)); 5.24 (*d*, *J*(1,2) = 3.7, H–C(1)); 5.04 (*dd*, *J*(2,3) = 10.2, H–C(2)); 4.73 (*d*, *J* = –12.4, 1 H, PhCH_2); 4.68 (*d*, *J* = –12.5, 1 H, PhCH_2); 4.62 (*d*, *J* = –10.2, 1 H, PhCH_2); 4.59 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.58 (*d*, *J* = –10.3, 1 H, PhCH_2); 4.50 (*d*, *J* = –11.7, 1 H, PhCH_2); 4.54–4.43 (*m*, 2 H, PhCH_2); 4.39–4.33 (*m*, H–C(5′)); 3.97–3.95 (*m*, *J*(2′,3′) = 3.0, H–C(2′)); 3.92–3.81 (*m*, H–C(4), H_a–C(6)); 3.76 (*dd*, *J*(3′,4′) = 9.6, H–C(3′)); 3.71–3.68 (*m*, H–C(5), H_b–C(6)); 3.62–3.59 (*m*, 2 H–C(6′)); 3.13 (*d*, *J*(4,OH) = 3.6, OH); 2.59–2.38 (*m*, $COCH_2CH_2CO$). ^{13}C-NMR ($CDCl_3$): 172.4 ($COCH_2CH_2CO$); 171.2 ($COCH_2CH_2CO$); 165.8 (Ph*C*O); 94.7 (C(1)); 85.3 (C(1′)); 76.4 (C(3′)); 75.2 (C(2′)); 73.0 (C(3)); 72.8 (PhCH_2); 71.7 (PhCH_2); 71.2 (PhCH_2); 71.0 (C(2)); 70.7 (C(5′)); 70.1 (C(4)); 69.4 (C(5)); 69.2 (C(6′)); 69.1 (PhCH_2); 68.8 (C(6)); 68.7 (C(4′)); 28.9 ($COCH_2CH_2CO$); 28.6 ($COCH_2CH_2CO$). Anal. calc. for $C_{64}H_{64}O_{14}S$ (1089.25): C 70.57, H 5.92, S 2.94; found: C 70.65, H 6.05, S 2.93.

Benzyl O-*(2,3,6-Tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1 → 4)-2*-O-*benzoyl-6*-O-*benzyl-α*-D-*glucopyranoside 3,4′-Succinate* (**29a**) *and Benzyl* O-*(2,3,6-Tri*-O-*benzyl-β*-D-*mannopyranosyl)-(1 → 4)-2*-O-*benzoyl-6*-O-*benzyl-α*-D-*glucopyranoside 3,4′-Succinate* (**29b**). *a*) As described for **6** (*Exper. a*), with **28** (0.49 g, 0.45 mmol), NIS (0.50 g, 2.24 mmol), Me_3SiOTf (20 µl, 0.11 mmol), and CH_2Cl_2 (20 ml), followed by CC (CCl_4/acetone 25 : 1): **29a** (0.32 g, 73%), then **29b** (21.8 mg, 5%).

Data of **29a**: $[\alpha]_D = +103.7$ ($c = 1.14$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.64 (*t*, *J*(3,4) = 10.0, H–C(3)); 5.31 (*m*, H–C(4′)); 5.22 (*d*, *J*(1,2) = 3.8, H–C(1)); 5.16 (*d*, *J*(1′,2′) = 1.7, H–C(1′)); 4.75 (*dd*, *J*(2,3) = 10.4, H–C(2)); 4.66 (*d*, *J* = –12.4, 1 H, PhCH_2); 4.65 (*d*, *J* = –11.8, 1 H, PhCH_2); 4.57–4.53 (*m*, 4 H, PhCH_2); 4.49 (*d*, *J* = –12.3, 1 H, PhCH_2); 4.48 (*d*, *J* = –12.3, 1 H, PhCH_2); 4.45 (*d*, *J* = –12.2, 1 H, PhCH_2); 4.04 (*d*, *J* = –12.3, 1 H, PhCH_2); 4.00–3.88 (*m*, H–C(3′), H–C(5′)); 3.98 (*t*, *J*(4,5) = 9.8, H–C(4)); 3.79–3.60 (*m*, H–C(2′), H–C(5), 2 H–C(6′), 2 H–C(6)); 2.97–2.86 (*m*, 1 H, $COCH_2CH_2CO$); 2.41–2.34 (*m*, 1 H, $COCH_2CH_2CO$); 2.16–2.03 (*m*, 2 H, $COCH_2CH_2CO$). ^{13}C-NMR ($CDCl_3$): 172.0, 169.9 ($COCH_2CH_2CO$); 166.0 (Ph*C*O); 100.8 (*J*(1′, H–C(1′) = 175.0, C(1′)); 95.5 (C(1)); 73.7, 72.3 (C(2), C(4)); 72.0 (C(2′)); 71.1 (C(5)); 71.0 (C(3′)); 70.6 (C(5′)); 69.7 (C(6′)); 69.5 (C(4′)); 68.8 (C(6)); 67.3 (C(3)); 30.7, 30.0 ($COCH_2CH_2CO$). Anal. calc. for $C_{58}H_{58}O_{14}$ (979.10): C 71.15, H 5.97; found: C 71.05, H 5.99.

Data of **29b**: $[\alpha]_D = +11.9$ ($c = 0.74$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.46 (*t*, *J*(3,4) = 10.0, H–C(3)); 5.45 (*t*, *J*(4′,5′) = 9.4, H–C(4′)); 5.34 (*d*, *J*(1,2) = 3.6, H–C(1)); 4.85 (*dd*, *J*(2,3) = 10.1, H–C(2)); 4.76 (*d*, *J* = –12.5, 1 H, PhCH_2); 4.74 (*d*, *J* = –11.8, 1 H, PhCH_2); 4.69 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.64 (*d*, *J* = –11.7, 1 H, PhCH_2); 4.61–4.52 (*m*, 4 H, PhCH_2); 4.46 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.45 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.44 (*s*, H–C(1′)); 4.00–3.89 (*m*, H–C(5)); 3.92–3.80 (*m*, H–C(2′), 2 H–C(6′)); 3.87 (*t*, *J*(4,5) = 9.9, H–C(4)); 3.80–3.76 (*m*, 2 H–C(6)); 3.70–3.66 (*m*, H–C(3′)); 3.58–3.50 (*m*, H–C(5′)). ^{13}C-NMR ($CDCl_3$): 171.8, 170.6 ($COCH_2CH_2CO$); 166.4 (Ph*C*O); 100.4 (*J*(1′, H–C(1′)) = 173.7, C(1′)); 95.7 (C(1)); 77.6 (C(4)); 74.8 (PhCH_2); 74.5 (C(3′)); 74.2 (PhCH_2); 73.4, 72.7 (PhCH_2); 72.4 (C(5)); 72.2 (C(5′)); 72.1 (C(3)); 71.4 (2 C, C(2′), C(2)); 69.9 (PhCH_2); 69.8 (C(4′)); 69.0 (C(6′)); 68.3 (C(6)). Anal. calc. for $C_{58}H_{58}O_{14}$ (979.10): C 71.15, H 5.97; found: C 70.98, H 6.12.

b) As described for **6** (*Exper. b*), with **28** (0.49 g, 0.45 mmol), NIS (0.51 g, 2.27 mmol), Me_3SiOTf (21 µl, 0.12 mmol), and MeCN (20 ml), followed by CC (CCl_4/acetone 25 : 1): **29a** (0.30 g, 69%) and **29b** (32.2 mg, 7%).

Benzyl O-*(4*-O-*Benzoyl-2,3,6-tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1 → 4)-2,3-di*-O-*benzoyl-6*-O-*benzyl-α*-D-*glucopyranoside* (**30a**). As described for **7**, with **29a** (180 mg, 0.18 mmol), NaOMe in MeOH (5 ml), BzCl (128 µl, 1.10 mmol), and pyridine (5 ml): **30a** (147 mg, 72%). $[\alpha]_D = +42.8$ ($c = 0.88$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.94 (*t*, *J*(3,4) = 9.4, H–C(3)); 5.61 (*t*, *J*(4′,5′) = 9.3, H–C(4′)); 5.40 (*d*, *J*(1,2) = 3.7, H–C(1)); 5.20 (*d*, *J*(1′,2′) = 1.8, H–C(1′)); 4.99 (*dd*, *J*(2,3) = 10.3, H–C(2)); 4.70 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.68 (*d*, *J* = –11.7, 1 H, PhCH_2); 4.60–4.53 (*m*, 4 H, PhCH_2); 4.50 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.48 (*d*, *J* = –12.3, 1 H, PhCH_2); 4.44 (*d*, *J* = –11.9, 1 H, PhCH_2); 4.17 (*dd*, *J*(3′,4′) = 9.2, H–C(3′)); 4.10–4.06 (*m*, *J*(5,6a) = 4.2, *J*(5,6b) = 2.1, *J* = –12.3, 2 H, H–C(5), PhCH_2); 4.05–4.00 (*m*, 2 H–C(6′)); 3.96 (*dd*, *J*(6a,6b) = –12.0, H_a–C(6)); 3.90 (*t*, *J*(4,5) = 9.6, H–C(4)); 3.88–3.80 (*m*, H–C(5′)); 3.77 (*dd*, H_b–C(6)); 3.73–3.68 (*m*, *J*(2′,3′) = 2.7, H–C(2′)). ^{13}C-NMR ($CDCl_3$): 166.4, 165.8, 165.6 (Ph*C*O); 99.9 (*J*(1′, H–C(1′)) = 174.1,

C(1′)); 95.3 (C(1)); 74.7 (C(4)); 74.4, 73.6 (Ph*C*H$_2$); 73.1 (C(3)); 72.4 (2 C, C(2′), Ph*C*H$_2$); 72.2 (C(2)); 72.0 (Ph*C*H$_2$); 71.5 (C(3′)); 71.0 (2 C, C(4′), C(5′)); 70.2 (C(5)); 69.9 (Ph*C*H$_2$); 69.1 (C(6′)); 68.8 (C(6)). Anal. calc. for $C_{68}H_{54}O_{14}$ (1105.25): C 73.90, H 5.84; found: C 74.15, H 5.94.

Benzyl O-*(4-*O-*Benzoyl-2,3,6-tri-*O-*benzyl-β-*D-*mannopyranosyl)-(1 → 4)-2,3-di-*O-*benzoyl-6-*O-*benzyl-α-*D-*glucopyranoside* (**30b**). As described for **7**, with **29b** (51 mg, 0.05 mmol), NaOMe in MeOH (3 ml), BzCl (36 µl, 0.31 mmol), and pyridine (3 ml): **30b** (43 mg, 75%). $[\alpha]_D = -33.1$ ($c = 0.65$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.96 (*t*, *J*(3,4) = 9.6, H−C(3)); 5.42 (*d*, *J*(1,2) = 3.6, H−C(1)); 5.38 (*t*, *J*(4′,5′) = 9.4, H−C(4′)); 5.04 (*dd*, *J*(2,3) = 10.0, H−C(2)); 4.78 (*d*, *J* = −12.1, 1 H, PhC*H*$_2$); 4.75 (*d*, *J* = −11.8, 1 H, PhC*H*$_2$); 4.73 (*d*, *J* = −12.5, 1 H, PhC*H*$_2$); 4.69 (*d*, *J* = −11.7, 1 H, PhC*H*$_2$); 4.65–4.55 (*m*, 4 H, PhC*H*$_2$); 4.51 (*s*, H−C(1′)); 4.49 (*d*, *J* = −12.1, 1 H, PhC*H*$_2$); 4.46 (*d*, *J* = −11.7, 1 H, PhC*H*$_2$); 4.13–4.08 (*m*, *J*(5,6a) = 4.1, *J*(5,6b) = 1.9, H−C(5)); 3.81–3.78 (*m*, 2 H−C(6′)); 3.78–3.73 (*m*, *J*(2′,3′) = 3.0, H−C(2′)); 3.75 (*dd*, *J*(6a,6b) = −12.2, H$_a$−C(6)); 3.74 (*t*, 1 *J*(4,5) = 9.5, H−C(4)); 3.72 (*dd*, H$_b$−C(6)); 3.68 (*dd*, *J*(3′,4′) = 9.3, H−C(3′)); 3.44–3.40 (*m*, H−C(5′)). ^{13}C-NMR ($CDCl_3$): 165.8, 165.5, 165.4 (Ph*C*O); 100.7 (*J*(1′,H−C(1′) = 156.9, C(1′)); 95.2 (C(1)); 75.0, 74.4 (Ph*C*H$_2$); 74.2 (C(3′)); 73.6 (Ph*C*H$_2$); 73.2 (C(5′)); 73.1 (C(4)); 72.8 (Ph*C*H$_2$); 72.3 (C(2)); 71.5 (C(3)); 71.1 (C(2′)); 70.1 (C(5)); 69.9 (Ph*C*H$_2$); 69.5 (C(4′)); 68.8 (C(6′)); 68.5 (C(6)). Anal. calc. for $C_{68}H_{54}O_{14}$ (1105.25): C 73.90, H 5.84; found: C 74.15, H 5.94.

*Benzyl 3-*O-*Benzoyl-4,6-*O-*benzylidene-2-*O-*[3-(ethyl 2,3,4-tri-*O-*benzyl-1-thio-α-*D-*mannopyranosid-6-*O-*yl)-1,3-dioxopropyl]-α-*D-*glucopyranoside* (**36**). As described for **4a**, with **34** [41] (1.44 g, 2.48 mmol), **35** [52] (1.45 g, 2.48 mmol), DCC (0.51 g, 2.48 mmol), DMAP, and CH_2Cl_2 (30 ml): **36** (1.74 g, 70%). $[\alpha]_D = +89.2$ (c = 1.31, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.91 (*t*, *J*(3,4) = 9.9, H−C(3)); 5.50 (*s*, 1 H, PhC*H*); 5.31 (*d*, *J*(1′,2′) = 1.0, H−C(1′)); 5.18 (*d*, *J*(1,2) = 3.8, H−C(1)); 4.94 (*dd*, *J*(2,3) = 10.0, H−C(2)); 4.88 (*d*, *J* = −10.9, 1 H, PhC*H*$_2$); 4.69 (*d*, *J* = −12.3, 1 H, PhC*H*$_2$); 4.62 (*d*, *J* = −12.4, 1 H, PhC*H*$_2$); 4.56–4.50 (*m*, 3 H, PhC*H*$_2$); 4.49 (*d*, *J* = −10.7, 1 H, PhC*H*$_2$); 4,46 (*d*, *J* = −10.8, 1 H, PhC*H*$_2$); 4.33–4.27 (*m*, 2 H−C(6′)); 4.26 (*dd*, *J*(5,6a) = 4.8, *J*(6a,6b) = −10.5, H$_a$−C(6)); 4.20–4.08 (*m*, H−C(5′)); 4.15–4.02 (*m*, H−C(5)); 3.83–3.68 (*m*, *J*(3′,4′) = 9.7, H−C(2′), H−C(3′), H−C(4), H$_b$−C(6)); 3.79 (*t*, *J*(4′,5′) = 9.6, H−C(4′)); 3.36 (*d*, *J* = −16.0, 1 H, COCH$_2$); 3.27 (*d*, *J* = −16.0, 1 H, COCH$_2$); 2.57–2.44 (*m*, MeC*H*$_2$S); 1.19 (*t*, *J* = 7.4, *Me*CH$_2$S). ^{13}C-NMR ($CDCl_3$): 165.4, 165.3, 165.1 (CO); 101.5 (Ph*C*H); 94.9 (C(1)); 82.0 (C(1′)); 80.2 (C(3′)); 79.3 (C(4)); 76.0 (C(2′)); 74.8 (Ph*C*H$_2$); 74.6 (C(4′)); 72.6 (C(2)); 71.9, 71.8 (Ph*C*H$_2$); 70.1 (C(5′)); 70.0 (Ph*C*H$_2$); 69.6 (C(3)); 68.8 (C(6)); 64.4 (C(6′)); 62.7 (C(5)); 41.2 (CO*C*H$_2$); 25.1 (Me*C*H$_2$S); 15.0 (*Me*CH$_2$S). Anal. calc. for $C_{59}H_{60}O_{14}S$ (1025.18): C 69.12, H 5.90; found: C 69.07, H 5.94.

*Benzyl 3-*O-*Benzoyl-6-*O-*benzyl-2-*O-*[3-(ethyl 2,3,4-tri-*O-*benzyl-1-thio-α-*D-*mannopyranosid-6-*O-*yl)-1,3-dioxopropyl]-α-*D-*glucopyranoside* (**37**9). As described for **5a**, with **36** (1.26 g, 1.23 mmol) and $NaCNBH_3$ (0.97 g, 15.38 mmol): **37** (1.01 g, 80%). $[\alpha]_D = +100.8$ (c = 1.02, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.71 (*dd*, *J*(3,4) = 9.3, H−C(3)); 5.32 (*d*, *J*(1′,2′) = 1.0, H−C(1′)); 5.10 (*d*, *J*(1,2) = 3.8, H−C(1)); 4.92 (*d*, *J* = −11.0, 1 H, PhC*H*$_2$); 4.86 (*dd*, *J*(2,3) = 10.1, H−C(2)); 4.75 (*d*, *J* = −12.3, 1 H, PhC*H*$_2$); 4.66 (*d*, *J* = −12.4, 1 H, PhC*H*$_2$); 4.63–4.56 (*m*, 3 H, PhC*H*$_2$); 4.55 (*d*, *J* = −11.0, 1 H, PhC*H*$_2$); 4.53 (*s*, 2 H, PhC*H*$_2$); 4.51 (*d*, *J* = −12.4, 1 H, PhC*H*$_2$); 4.46–4.40 (*m*, 2 H−C(6′)); 4.24–4.12 (*m*, H−C(5′)); 4.04–3.90 (*m*, H−C(5)); 3.99 (*t*, *J*(4′,5′) = 9.7, H−C(4′)); 3.82–3.67 (*m*, *J*(3′,4′) = 9.6, H−C(2′), H−C(3′), H−C(4), 2 H−C(6)); 3.56 (*d*, *J*(4,OH) = 5.0, OH); 3.36 (*d*, *J* = −16.0, 1 H, COCH$_2$); 3.31 (*d*, *J* = −16.0, 1 H, COCH$_2$); 2.55–2.45 (*m*, MeC*H*$_2$S); 1.19 (*t*, *J* = 7.4, *Me*CH$_2$S). ^{13}C-NMR ($CDCl_3$): 165.5, 165.3, 165.1 (CO); 94.2 (C(1)); 82.2 (C(1′)); 80.1 (C(3′)); 75.9 (C(2′)); 74.8 (Ph*C*H$_2$); 74.5 (C(4′)); 73.7 (C(3)); 73.6 (Ph*C*H$_2$); 72.0 (2 C, Ph*C*H$_2$); 71.8 (C(2)); 70.8 (C(5′)); 69.7 (2 C, Ph*C*H$_2$, C(5)); 69.6 (C(4)); 69.0 (C(6)); 64.7 (C(6′)); 41.2 (CO*C*H$_2$); 25.4 (Me*C*H$_2$S); 15.0 (*Me*CH$_2$S). Anal. calc. for $C_{59}H_{62}O_{14}S$ (1027.20): C 68.99, H 6.08, S 3.12; found: C 69.05, H 6.05, S 3.20.

Benzyl O-*(2,3,4-Tri-*O-*benzyl-α-*D-*mannopyranosyl)-(1 → 4)-3-*O-*benzoyl-6-*O-*benzyl-α-*D-*glucopyranoside 2,6′-Malonate* (**38**). *a*) As described for **6** (*Exper. a*), with **37** (0.56 g, 0.45 mmol), NIS (0.51 g, 2.25 mmol), Me_3SiOTf (20 µl, 0.11 mmol), and CH_2Cl_2 (15 ml), followed by CC (toluene/acetone 20:1): **38** (0.30 g, 69%). $[\alpha]_D = +115.4$ (c = 1.31, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.81 (*t*, *J*(3,4) = 9.8, H−C(3)); 4.96 (*d*, *J*(1,2) = 3.8, H−C(1)); 4.94 (*d*, *J*(1′,2′) = 1.0, H−C(1′)); 4.85 (*d*, *J* = −11.3, 1 H, PhC*H*$_2$); 4.84 (*dd*, *J*(2,3) = 10.0, H−C(2)); 4.83 (*d*, *J* = −11.2, 1 H, PhC*H*$_2$); 4.82 (*d*, *J* = −10.8, 1 H, PhC*H*$_2$); 4.81–4.78 (*m*, H$_a$−C(6′)); 4.78–4.67 (*m*, 4 H, PhC*H*$_2$); 4.56 (*d*, *J* = −12.5, 1 H, PhC*H*$_2$); 4.52 (*d*, *J* = −12.2, 1 H, PhC*H*$_2$); 4.50 (*d*, *J* = 12.1, 1 H, PhC*H*$_2$); 4.18–4.06 (*m*, H−C(5′)); 4.12 (*t*, *J*(4,5) = 9.8, H−C(4)); 3.82–3.73 (*m*, H$_b$−C(6′)); 3.76–3.62 (*m*, H−C(5)); 3.72 (*t*, *J*(4′,5′) = 9.4, H−C(4′)); 3.48–3.38 (*m*, H−C(2′), H−C(3′), H$_a$−C(6)); 3.37–3.24 (*m*, H$_b$−C(6)); 3.28 (*d*, *J* = −12.7, 1 H, COCH$_2$); 3.15 (*d*, *J* = −12.7, 1 H, COCH$_2$). ^{13}C-NMR ($CDCl_3$): 165.6, 165.4, 164.4 (CO); 93.9 (C(1)); 93.3 (*J*(1′,H−C(1′)) = 168.8, C(1′)); 79.3 (C(3′)); 75.5, 75.2, 73.6 (C(2′), C(4), C(4′)); 73.4 (C(2)); 69.0 (C(5′)); 68.8 (C(5)); 68.7 (C(3)); 68.6 (C(6)); 64.9 (C(6′)); 43.1 (CO*C*H$_2$). Anal. calc. for $C_{57}H_{56}O_{14}$ (965.07): C 70.94, H 5.85; found: C 71.13, H 5.90.

b) As described for **6** (*Exper. b*), with **37** (0.43 g, 0.42 mmol), NIS (0.47 g, 2.10 mmol), Me_3SiOTf (20 µl, 0.11 mmol), and MeCN (12 ml), followed by CC (toluene/acetone 20:1): **38** (0.28 g, 69%).

c) As described for **18** (*Exper. e*), with **37** (0.47 g, 0.46 mmol), 4-Å molecular sieves (1.3 g) and MeOTf (0.40 ml, 3.7 mmol), followed by CC (toluene/acetone 20:1): **38** (0.39 g, 68%).

d) As described for **18** (*Exper. f*), with **37** (0.50 g, 0.49 mmol), 4-Å molecular sieves (1.2 g), MeOTf (0.27 ml, 2.45 mmol), and MeCN (15 ml), followed by CC (toluene/acetone 20:1): **38** (0.34 g, 71%).

Benzyl O-*(6*-O-*Benzoyl-2,3,4-tri*-O-*benzyl*-α-D-*mannopyranosyl)-(1→4)-2,3-di*-O-*benzoyl-6*-O-*benzyl*-α-D-*glucopyranoside* (**39**). As described for **7**, with **38** (107 mg, 0.11 mmol), NaOMe in MeOH (8 ml), BzCl (77 µl, 0.66 mmol), and pyridine (8 ml): **39** (89 mg, 73%). $[\alpha]_D = +57.7$ ($c = 0.52$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 6.07 (*dd*, *J*(3,4) = 8.9, H–C(3)); 5.32 (*d*, *J*(1,2) = 3.7, H–C(1)); 5.16 (*dd*, *J*(2,3) = 10.3, H–C(2)); 5.14 (*d*, *J*(1′,2′) = 1.7, H–C(1′)); 4.87 (*d*, *J* = –10.8, 1 H, PhC*H*$_2$); 4.79 (*d*, *J* = –12.4, 1 H, PhC*H*$_2$); 4.61 (*d*, *J* = –11.6, 1 H, PhC*H*$_2$); 4.59 (*s*, 1 H, PhC*H*$_2$); 4.58 (*d*, *J* = –10.6, 1 H, PhC*H*$_2$); 4.57 (*d*, *J* = –12.1, 1 H, PhC*H*$_2$); 4.55–4.52 (*m*, 1 H, PhC*H*$_2$); 4.51 (*dd*, *J*(6a′,6b′) = –11.8, 1 H, H_a–C(6′)); 4.45–4.41 (*m*, 2 H, H_b–C(6′), PhC*H*$_2$); 4.13 (*t*, *J*(4′,5′) = 9.4, H–C(4′)); 4.06–4.00 (*m*, 2 H, *J*(5,6b) = 2.0, H–C(5), PhC*H*$_2$); 4.03 (*t*, *J*(4,5) = 9.5, H–C(4)); 3.96–3.91 (*m*, *J*(5′,6a′) = 3.1, H–C(3′), H–C(5′)); 3.89–3.83 (*m*, *J*(6a,6b) = –11.1, H_a–C(6)); 3.72 (*dd*, H_b–C(6)); 3.60 (*t*, *J*(2′,3′) = 2.4, H–C(2′)). ^{13}C-NMR ($CDCl_3$): 166.3, 165.6, 165.5 (Ph*C*O); 100.2 (*J*(1′,H–C(1′)) = 171.8, C(1′)); 95.1 (C(1)); 79.6 (C(3′)); 76.7 (C(4′)); 75.6 (C(2′)); 75.1 (Ph*C*H$_2$); 73.7 (C(4)); 73.5 (Ph*C*H$_2$); 72.9 (C(3)); 72.5 (Ph*C*H$_2$); 71.8 (C(2)); 71.6 (Ph*C*H$_2$); 71.4 (C(5′)); 70.2 (C(5)); 69.8 (Ph*C*H$_2$); 68.6 (C(6)); 63.5 (C(6′)). Anal. calc. for $C_{68}H_{64}O_{14}$ (1105.25): C 73.90, H 5.84; found: C 73.95, H 5.83.

Benzyl 2,3-Di-O-*benzoyl-6*-O-*[3-(ethyl 2,3,4-tri*-O-*benzyl-1-thio*-α-D-*mannopyranosid-6*-O-*yl)-1,3-dioxopropyl]*-α-D-*glucopyranoside* (**41**). As described for **4a**, with **34** [41] (2.24 g, 3.86 mmol), **40** [53] (2.03 g, 4.24 mmol), DCC (0.88 g, 4.27 mmol), DMAP, and CH_2Cl_2 (60 ml): **41** (2.88 g, 65%). $[\alpha]_D = +94.5$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.82 (*t*, *J*(3,4) = 9.3, H–C(3)); 5.31 (*d*, *J*(1′,2′) = 1.0, H–C(1′)); 5.24 (br. *d*, H–C(2)); 5.20 (*d*, *J*(1,2) = 3.7, H–C(1)); 4.91 (*d*, *J* = –10.8, 1 H, PhC*H*$_2$); 4.75 (*d*, *J* = –12.4, 1 H, PhC*H*$_2$); 4.68 (*d*, *J* = –12.5, 1 H, PhC*H*$_2$); 4.62 (*d*, *J* = –12.4, 1 H, PhC*H*$_2$); 4.58–4.50 (*m*, *J*(5,6a) = 3.9, *J*(6a,6b) = –12.1, 5 H, PhC*H*$_2$, H_a–C(6)); 4.47–4.39 (*m*, *J*(5′,6a′) = 5.0, *J*(6a′,6b′) = –11.8, 2 H–C(6′)); 4.34 (*dd*, *J*(5,6b) = 2.4, H_b–C(6)); 4.20–4.15 (*m*, H–C(5′)); 4.04 (*ddd*, H–C(5)); 3.90–3.79 (*m*, *J*(4,5) = 9.9, H–C(2′), H–C(3′), H–C(4′), H–C(4)); 3.47 (br. *d*, $COCH_2$); 3.36 (*d*, *J*(4,OH) = 5.1, OH); 2.62–2.48 (*m*, Me*C*H$_2$S); 1.22 (*t*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 167.0, 166.4, 166.2, 165.7 (CO); 95.3 (C(1)); 81.9 (C(1′)); 80.1 (C(3′)); 76.0 (C(2′)); 75.1 (Ph*C*H$_2$); 74.4 (C(4′)); 73.7 (C(3)); 72.0 (Ph*C*H$_2$); 71.9 (Ph*C*H$_2$); 71.2 (C(2)); 70.0 (C(4), C(5′)); 69.8 (Ph*C*H$_2$); 69.2 (C(4)); 64.5 (C(6)); 63.8 (C(6′)); 41.2 (CO*C*H$_2$); 25.4 (Me*C*H$_2$S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{59}H_{60}O_{15}S$ (1041.18): C 68.06, H 5.81, S 3.08; found: C 68.34, H 5.90, S 3.05.

Benzyl O-*(2,3,4-Tri*-O-*benzyl*-α-D-*mannopyranosyl)-(1→4)-2,3-di*-O-*benzoyl*-α-D-*glucopyranoside 6,6′-Malonate* (**42**). *a*) As described for **6** (*Exper. a*), with **41** (0.37 g, 0.36 mmol), NIS (0.41 g, 1.80 mmol), Me_3SiOTf (16 µl, 0.09 mmol), and CH_2Cl_2 (15 ml), followed by CC (toluene/acetone 30:1): **42** (354 mg, 72%). $[\alpha]_D = +91.1$ ($c = 1.03$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 6.13 (*t*, *J*(3,4) = 9.3, H–C(3)); 5.30 (*d*, *J*(1,2) = 3.8, H–C(1)); 5.28 (*s*, H–C(1′)); 5.12 (*dd*, *J*(2,3) = 10.3, H–C(2)); 4.83–4.77 (*m*, *J*(6a′,6b′) = –10.7, H_a–C(6′)); 4.78 (*d*, *J* = –11.5, 1 H, PhC*H*$_2$); 4.74 (*d*, *J* = –12.5, 1 H, PhC*H*$_2$); 4.69–4.62 (*m*, 2 H, PhC*H*$_2$, H_a–C(6)); 4.59 (*d*, *J* = –12.5, 1 H, PhC*H*$_2$); 4.47 (2*d*, *J* = –11.9, 1 H, PhC*H*$_2$); 4.43 (*s*, 1 H, PhC*H*$_2$); 4.38 (*t*, *J*(3,4) = 9.6, H–C(4)); 4.13–4.07 (*m*, H_b–C(6)); 3.97 (*d*, *J* = –11.7, 1 H, PhC*H*$_2$); 3.90 (br. *d*, H_b–C(6′)); 3.69–3.59 (*m*, *J*(3′,4′) = 6.8, H–C(2′), H–C(3′), H–C(5′)); 3.58 (*d*, *J* = –13.6, 1 H, $COCH_2$); 3.48 (*dd*, *J*(4′,5′) = 9.3, H–C(4′)); 3.39 (*d*, *J* = –15.6, 1 H, $COCH_2$). ^{13}C-NMR ($CDCl_3$): 166.5 (CO); 165.6 (2 C, CO); 165.2 (CO); 99.7 (*J*(1′,H–C(1′)) = 172.5, C(1′)); 95.4 (C(1)); 78.4 (C(3′)); 76.6 (C(2′)); 74.7 (C(4′)); 73.9 (Ph*C*H$_2$); 73.8 (C(5′)); 73.4 (C(3)); 73.0 (Ph*C*H$_2$); 72.9 (C(4)); 72.0 (Ph*C*H$_2$, C(2)); 70.3 (Ph*C*H$_2$); 67.8 (C(5)); 64.1 (C(6′)); 63.3 (C(6)); 42.5 (CO*C*H$_2$). Anal. calc. for $C_{57}H_{54}O_{15}$ (979.05): C 69.93, H 5.56; found: C 70.05, H 5.50.

b) As described for **6** (*Exper. b*), with **41** (0.42 g, 0.40 mmol), NIS (0.45 g, 2.02 mmol), Me_3SiOTf (19 µl, 0.10 mmol) and MeCN (15 ml), followed by CC (toluene/acetone 30:1): **42** (268 mg, 68%).

c) As described for **18** (*Exper. e*), with **41** (0.41 g, 0.39 mmol), 4-Å molecular sieves (1.02 g), and MeOTf (0.21 ml, 1.95 mmol), followed by CC (toluene/acetone 25:1): **42** (238 mg, 62%).

d) As described for **18** (*Exper. f*), with **41** (0.55 g, 0.53 mmol), 4-Å molecular sieves (1.38 g), MeOTf (0.29 ml, 2.65 mmol), and MeCN (25 ml), followed by CC (toluene/acetone 25:1): **42** (0.34 g, 66%).

Benzyl O-*(6*-O-*Benzoyl-2,3,4-tri*-O-*benzyl*-α-D-*mannopyranosyl)-(1→4)-2,3,6-tri*-O-*benzoyl*-α-D-*glucopyranoside* (**43**). As described for **7**, with **42** (176 mg, 0.18 mmol), NaOMe in MeOH (5 ml), BzCl (105 µl, 0.9 mmol), and pyridine (5 ml): **43** (151 mg, 75%). $[\alpha]_D = +29.7$ ($c = 0.88$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 6.10 (*t*, *J*(3,4) = 9.4, H–C(3)); 5.46 (*d*, *J*(1′,2′) = 1.5, H–C(1′)); 5.08 (*m*, *J*(1,2) = 3.6, H–C(1)); 5.07 (*dd*, *J*(2,3) = 10.0, H–C(2)); 4.88 (*d*, *J* = –10.9, 1 H, PhC*H*$_2$); 4.74–4.69 (*m*, 5H, 2 H–C(6′), PhC*H*$_2$); 4.65 (br. *d*, 2 H,

PhCH_2); 4.58 (d, $J = -10.9$, 1 H, PhCH_2); 4.52–4.45 (m, 1 H, PhCH_2); 4.49 (br. dd, J(5,6a) = 4.6, J(6a,6b) = −11.7, 2 H–C(6)); 4.13 (t, J(4,5) = 9.4, H–C(4)); 4.12–4.07 (m, H–C(4′), H–C(5′)); 4.09–4.03 (m, H–C(5)); 4.03–3.95 (m, H–C(3′)); 3.97–3.92 (m, H–C(2′)). ^{13}C-NMR ($CDCl_3$): 166.5, 166.3, 166.2, 166.1 (Ph*C*O); 99.3 (J(1′,H–C(1′)) = 172.0, C(1′)); 95.1 (C(1)); 79.0 (C(3′)); 75.4 (C(3)); 75.3 (C(2′)); 74.9 (Ph*C*H$_2$); 74.7 (C(4)); 74.2 (C(4′)); 72.3, 72.2 (Ph*C*H$_2$); 71.6 (C(2)); 71.5 (C(5′)); 69.7 (Ph*C*H$_2$); 68.5 (C(5)); 63.8 (C(6)); 63.2 (C(6′)). Anal. calc. for $C_{68}H_{62}O_{15}$ (1119.24): C 72.97, H 5.58; found: C 73.05, H 5.60.

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