Prearranged Glycosides

Part 13

Intramolecular Mannosylations of Glucosamine, Galactose, Mannose, and Rhamnose Derivatives *via* Prearranged Glycosides

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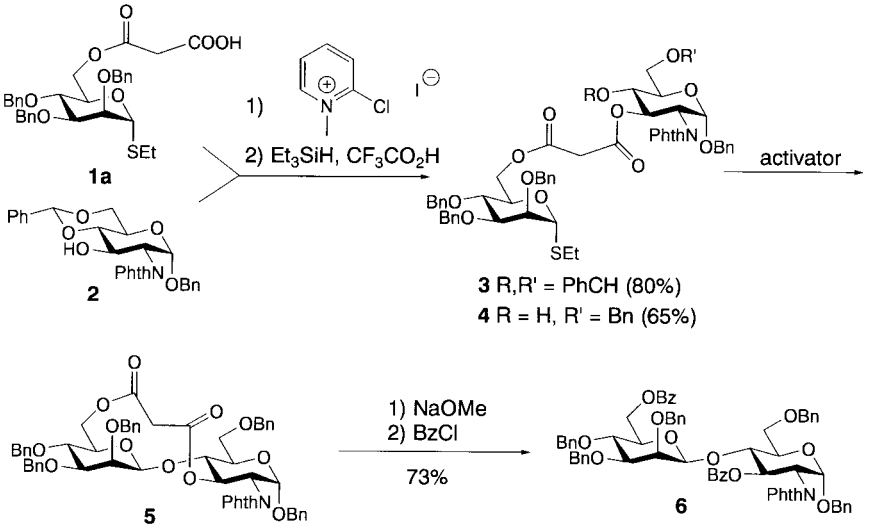
A series of prearranged glycosides **4**, **9**, **14**, **16**, **22**, **28**, **33**, **41**, and **46**, having a benzyl-protected 1-thiomannosyl donor linked through its position 6 *via* malonate and succinate tethers to various positions of glucosamine, galactose, mannose, and rhamnose acceptors, were prepared and cyclized to the corresponding disaccharides. The configuration at the anomeric center of the products strongly depended on the position of the tether in the acceptor part and could be predicted from the calculated thermodynamic stability of the products. No strong dependence of the diastereoselectivity of the intramolecular glycosylations on the activation conditions and the solvent was observed.

Introduction. – In the preceding paper [1], a series of prearranged glycosides have been prepared and used for intramolecular glycosylation leading to D-Man*p*-(1 → 4)-D-Glc*p* disaccharides. These prearranged glycosides were constructed from suitably protected mannosyl donors tethered *via* positions 2, 3, 4, and 6 by stable succinate and malonate linkers, respectively, to various positions of glucose acceptors. Together with previously studied examples in this series [2–6], it has been demonstrated that the outcome of the configuration at the anomeric center on intramolecular (1 → 4)-selective mannosylation strongly depends on the size of the ring formed and the positions that were involved for linking donor and acceptor. Similar results have recently been obtained for comparable intramolecular glycosylations by others [7–13]. Furthermore, it has been shown that simple force-field calculations on the thermodynamic stability of the tethered disaccharides allowed in most cases to predict which anomer would be formed as major product [1][4]. In continuation of this study toward intramolecular mannosylation *via* prearranged glycosides, we extended this principle to the synthesis of the important disaccharide structures D-Man*p*-(1 → 4)-D-GlcNAc*p*, D-Man*p*-(1 → 4)-D-Gal*p*, D-Man*p*-(1 → 4)-D-Man*p*, and D-Man*p*-(1 → 4)-L-Rha*p*, with the major goal to find conditions which allow for highly β-D-selective mannosylations in the aforementioned cases [2]. It should be noted, though, that the selective chemical construction of β-D-mannosidic linkages is still a difficult task and that 'useful' general procedures for that purpose are limited [14–20].

Results. – The prearranged glycosides used here for the construction of the disaccharides D-Man*p*-(1 → 4)-D-GlcNAc*p*, D-Man*p*-(1 → 4)-D-Gal*p*, D-Man*p*-(1 → 4)-D-Man*p*, and D-Man*p*-(1 → 4)-L-Rha*p* were prepared essentially as outlined in the preceding paper [1]. Starting from ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(carboxyacetyl)-1-thio-

α-D-mannopyranoside (**1a**) [4], condensation with benzyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-α-D-glucopyranoside (**2**) [21] using *Mukaiyama*'s method [22][23] afforded the malonate-tethered disaccharide **3** in 80% yield (*Scheme 1*). It should be noted that condensation of **1a** and **2** with dicyclohexylcarbodiimide (DCC) as previously performed for other saccharides [1] gave compound **3** in significantly lower yield (30%). Next, regioselective ring opening of the benzylidene moiety of **3** following *Garegg*'s procedure ($NaCNBH_3$, HCl) [24] gave prearranged glycoside **4** having a malonate tether at position 6 of the mannosyl donor and at position 3 of the glucosamine acceptor in poor 35% yield. Therefore, *DeNinno*'s procedure (Et_3SiH, CF_3COOH) [25] was applied for the benzylidene opening of **3**, which afforded **4** in 65% yield. Finally, cyclization of the latter under various conditions (see below, *Table*) resulted in exclusive formation of the tethered β-D-(1 → 4)-linked disaccharide **5**. That indeed a β-D-linked disaccharide was formed was established by removal of the acyl groups in **5**, followed by benzoylation of the intermediate to give disaccharide **6** (73%), which showed a characteristic [26] C,H-coupling constant of 154.8 Hz for the anomeric center of the mannosyl residue.

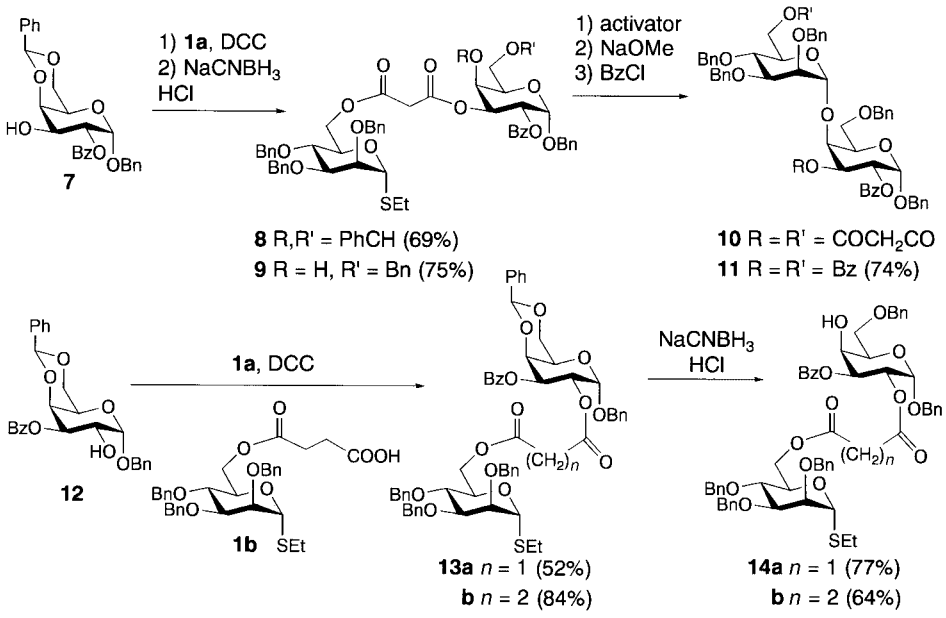
Scheme 1



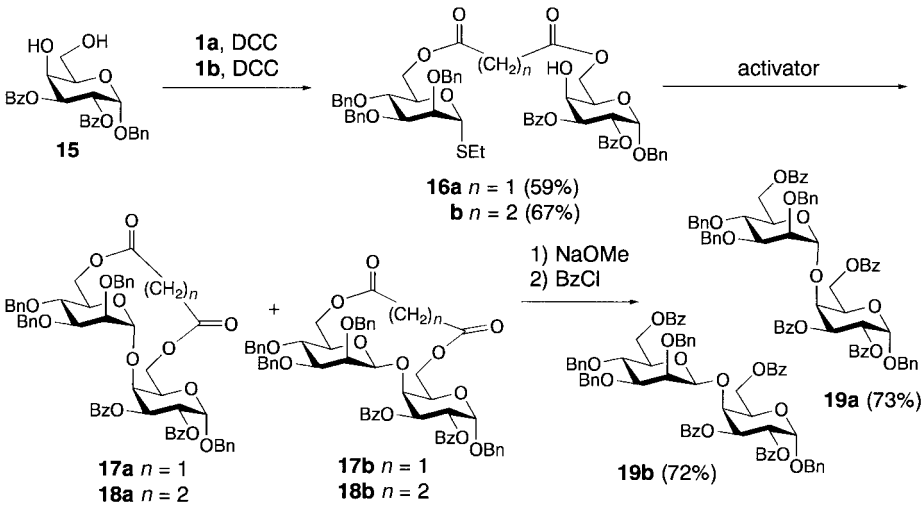
For the preparation of the disaccharide D-Man*p*-(1 → 4)-D-Gal*p*, a series of prearranged glycosides, which had succinate and malonate tethers at various positions of the galactose acceptor, were prepared as follows. First, benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside (**7**) [27] was condensed with compound **1a** (DCC, cat. *N*,*N*-dimethylpyridin-4-amine (DMAP)), and the resulting intermediate **8** (69%) was opened ($NaCNBH_3$, HCl) to give the prearranged glycoside **9** in 75% yield (*Scheme 2*). However, cyclization of the latter under various conditions (see below, *Table*) gave solely the α-D-(1 → 4)-linked disaccharide **10**. This was clearly evident from the C,H-coupling constant for the anomeric center of the mannosyl residue of **10** (^1J = 172.8 Hz) as well as from the corresponding coupling constant of the deacylated and

benzoylated disaccharide **11** ($^1J = 173.1$ Hz). Therefore, two tethered glycosides having position 2 of the galactose acceptor linked by succinate and malonate to position 6 of the mannosyl donor were prepared similarly. Condensation of benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside (**12**) [27] with **1a** [1] and **1b** [4] afforded intermediates **13a** and **13b**, respectively, which were converted as described above into prearranged glycosides **14a** and **14b**. However, all attempts to cyclize these prearranged glycosides under various conditions (see below, *Table*) resulted in complete decomposition of the starting material as could be judged from the TLC of the crude reaction mixtures; no product corresponding to a tethered disaccharide could be detected. Since the cyclization of **14a** and **14b** was obviously disfavored (see *Discussion*), two other prearranged glycosides having position 6 of the galactose acceptor tethered to the mannosyl donor were tested. Once again, condensation of benzyl 2,3-di-*O*-benzoyl-α-D-galactopyranoside (**15**) [28] with **1a** and **1b** in the presence of DCC gave regioselectively the tethered glycosides **16a** (59%) and **16b** (67%) (*Scheme 3*), respectively, which were used directly for the cyclizations (see below, *Table*). In the case of the malonate-tethered glycoside **16a**, cyclization afforded solely the corresponding β-D-linked disaccharide **17b** (49–55%). In contrast, cyclization of the succinate-tethered glycoside **16b** gave an anomer mixture of **18**, the composition of which depended on the reaction conditions (see below, *Table*). In both cases, the structure of the resulting disaccharides was assigned by measuring the coupling constant for the anomeric center of the protected mannosyl residue ($^1J = 158.7$ (**17b**), 170.7 (**18a**), and 154.0 Hz (**18b**)) and for that of the deacylated and benzoylated counterparts ($^1J = 174.2$ (**19a**) and 158.2 Hz (**19b**)). Therefore, the conversion **16a** → **17b** gave the desired β-D-(1 → 4)-linked disaccharide in medium yield.

Scheme 2

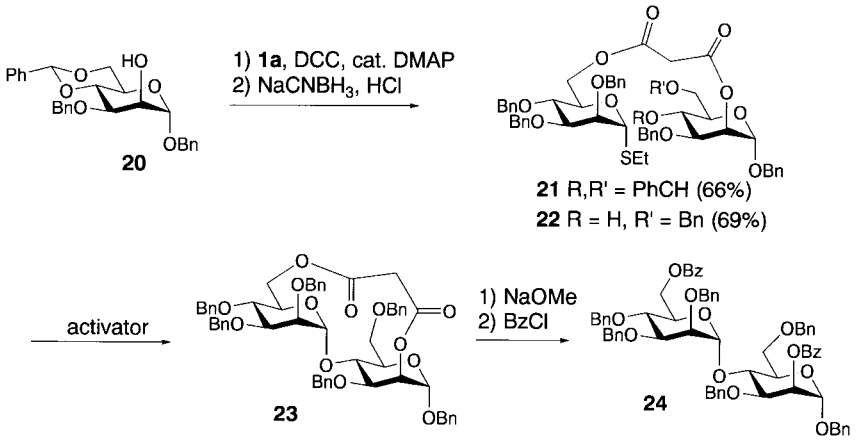


Scheme 3

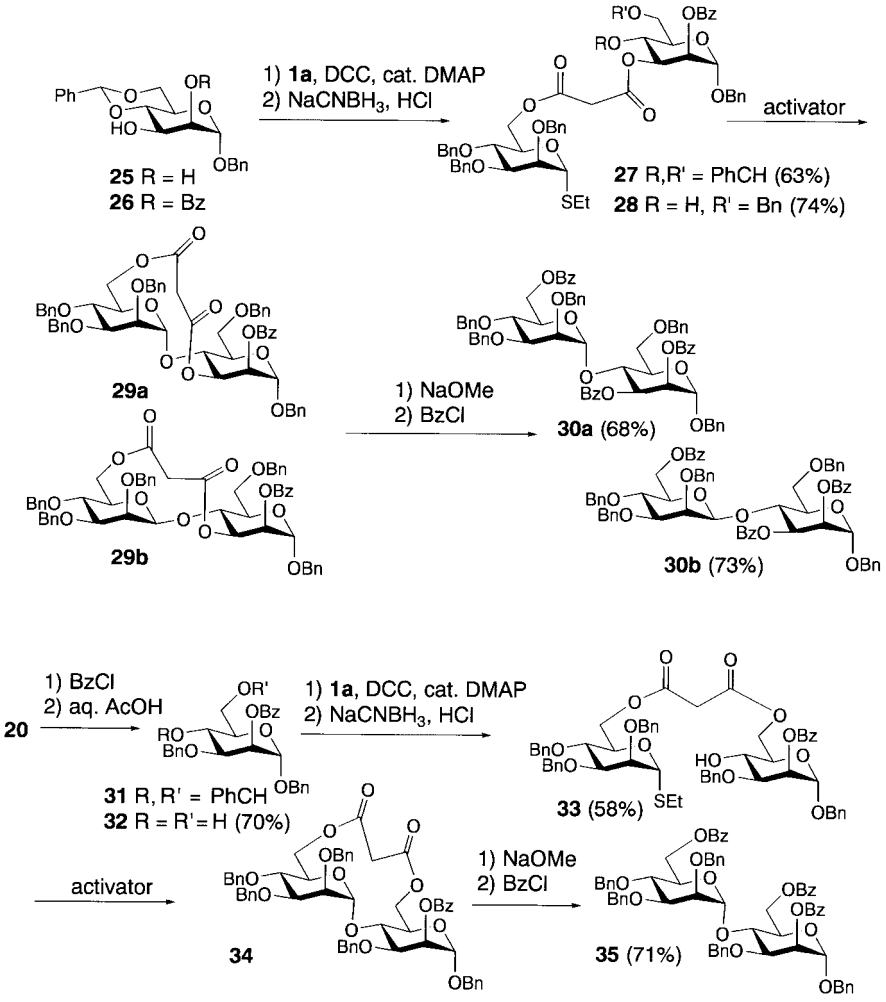


For the synthesis of the disaccharide D-Man*p*-(1 → 4)-D-Man*p*, a malonate tether at position 6 of the mannosyl donor (*i.e.*, compound **1a**) was combined with all possible positions of the mannosyl acceptor. Thus, mannoside **1a** was condensed with **20** [29] (*Scheme 4*), with **26** (prepared in 58% yield by regioselective benzoylation of benzyl 4,6-*O*-benzylidene-*α*-D-mannopyranoside (**25**) [29] under phase-transfer conditions), and with **32** (prepared from **20** by sequential benzoylation and hydrolysis of the benzylidene group) (*Scheme 5*). Thus, the tethered glycosides **21**, **27**, and **33**, respectively, were obtained. As outlined above, compounds **21** and **27** were regioselectively opened at their benzylidene rings to give **22** (69%) and **28** (74%), respectively, followed by intramolecular glycosylation under various conditions to give

Scheme 4



Scheme 5

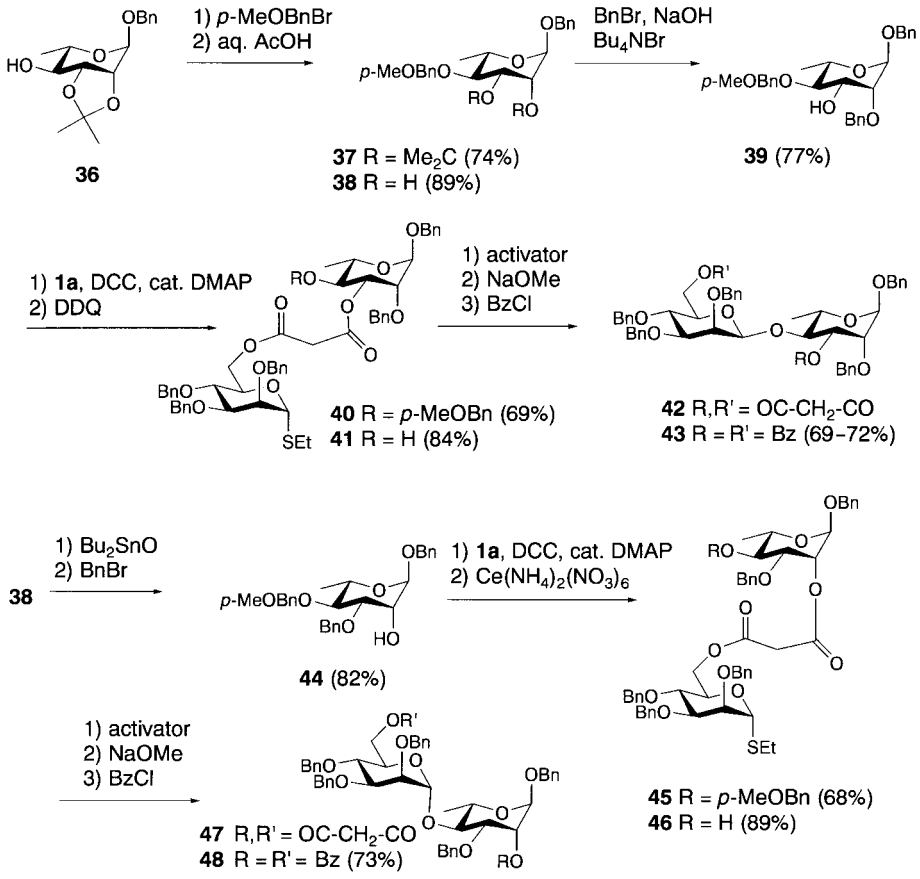


disaccharides **23** and **29** (see below, *Table*). The prearranged glycoside **33** was directly cyclized to disaccharide **34**. Both, **22** and **33** underwent exclusive formation of the α-D-linked disaccharides, which were both sequentially deacylated and benzoylated to afford compounds **24** ($^1J = 171.0$ Hz) and **35** ($^1J = 173.5$ Hz). In contrast, prearranged glycoside **28** gave an anomer mixture of **29a** ($^1J = 166.3$ Hz) and **29b** ($^1J = 150.9$ Hz), which were separated and transformed into the disaccharides **30a** ($^1J = 170.6$ Hz) and **30b** ($^1J = 151.6$ Hz) in order to establish their structures unambiguously.

Finally, the disaccharide D-Man*p*-(1→4)-L-Rha*p* was prepared from suitable prearranged glycosides in a similar manner as follows. First, benzyl 2,3-*O*-isopropylidene-α-L-rhamnospyranoside [30] (**36**) was temporarily blocked at position 4 with a 4-methoxybenzyl (*p*-MeOBn) group, and intermediate **37** (74%) was deprotected to

afford diol **38** in 89% yield (*Scheme 6*). Regioselective benzylation of the latter under phase-transfer conditions gave **39** (77%), which was condensed with 1-thiomannoside **1a** to afford saccharide **40** (69%). Next, oxidative cleavage of the 4-methoxybenzyl group with 4,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) gave the desired prearranged glycoside **41** (84%), which was cyclized under various conditions (see below, *Table*) to afford disaccharide **42**. The TLC of each of the crude cyclization mixtures showed a single spot; however, the NMR spectra of **42** revealed a mixture of two isomers that could not be attributed. Therefore, **42** was deacylated and benzoylated as described above. Surprisingly, a single product **43** was obtained from all cyclization experiments, which turned out to be the β-D-linked disaccharide ($^1J(1',H-C(1')) = 157.0$ Hz for mannosyl unit). A similar observation during intramolecular glycosylations of prearranged glycosides has been made previously for rhamnosyl donors [31] and has been explained in terms of the presence of conformers for the tethered disaccharides. Similar conformations must be present in the case of **42** because conversion to **43** led to a single product.

Scheme 6



A corresponding malonate-tethered glycoside having the tether at position 2 of the rhamnosyl acceptor was prepared similarly. First, **38** was regioselectively benzylated at position 3 *via* stannylene intermediates to give **44** in 82% yield. Next, in a sequence similar to the preparation of **41**, compound **44** was condensed with **1a** followed by oxidative cleavage of the 4-methoxybenzyl group of the intermediate **45** with ceric ammonium nitrate to afford **46** in 89% yield. Intramolecular glycosylation of the latter (see below, *Table*) gave solely the α-D-linked disaccharide **47** ($^1J(1',H-C(1')) = 171.8$ Hz), the structure of which was once again established by its conversion to **48** ($^1J(1',H-C(1')) = 171.4$ Hz). No conformers were found in the case of **47**.

Discussion. – The *Table* summarizes the results of the intramolecular glycosylations of prearranged glycosides **4**, **9**, **14**, **16**, **22**, **28**, **33**, **41**, and **46** with either *N*-iodosuccinimide (NIS) or methyl trifluoromethanesulfonate (MeOTf) in CH_2Cl_2 and MeCN, respectively, as descibed in the preceding paper [1]. In general, the cyclizations showed no significant dependence of the anomer ratio of the disaccharides on the activation procedure or on the solvent. This was also observed in most previously performed cyclizations of prearranged glycosides [1][4–6]. For intramolecular mannosylations of glucosamine acceptors (*Table*, *Entries 1–4*, compound **4**), solely β-D-(1 → 4)-linked disaccharide **5** was obtained. This is in contrast to the corresponding intramolecular mannosylations of glucose acceptors, which always resulted in the formation of anomer mixtures [1][4]. Calculations of the thermodynamic stability of **5** and of its α-D-linked counterpart by means of MacroModel and the AMBER force field as described in [1][4] revealed no significant difference of the stability of these anomers. Nevertheless, disaccharide **5** represents an important structure found in many naturally occurring oligosaccharides. Thus, intramolecular glycosylation *via* prearranged glycosides provides an attractive access to these structures [2].

From our studies toward understanding the influence of the relative configuration of the donor and acceptor on the outcome of the anomeric configuration in intramolecular glycosylations [6], we expected that changing from a glucose acceptor as in **4** to a galactose acceptor as in **9** (the equatorial conformation at C(4) of the acceptor is now inverted to an axial one) would result in a complete inversion of the anomeric selectivity; this was indeed observed, solely the corresponding α-D-(1 → 4)-linked disaccharide **10** being obtained (*Table*, *Entries 5–8*). In this latter case, the calculation of the thermodynamic stability of the two diastereoisomers established that **10** is more stable by 26.6 kcal/mol than the β-D-linked counterpart and, thus, reflects well the experimental findings. Extending the ring size for 1,4-selective mannosylations of galactose derivatives from a 12-membered ring as in **10** to 13- and 14-membered rings as in the cyclization products expected from **14** by linking position 2 of the galactose acceptor resulted in complete decomposition of the starting material (*Table*, *Entries 9* and *10*). Although the calculated thermodynamic stability of the expected tethered disaccharides derived from prearranged glycosides **14** are similar as for **10**, intermolecular glycosylations affording mixtures of oligosaccharides predominated here. Therefore, it was argued that tethering of the galactosyl acceptor through its position 6 should result in a higher flexibility of the 13- and 14-membered rings formed and, thus, enable intramolecular glycosylation. Indeed, intramolecular mannosylations with malonate-tethered glycosides **16a** (*Entries 11–14*) and with succinate-tethered glycosides **16b** (*Entries 15–18*) proceeded smoothly. In all cases, the β-D-(1 → 4)-linked

Table. *Cyclizations of Tethered Glycosides* **4**, **9**, **14**, **16**, **22**, **28**, **33**, **41**, *and* **46** *under Various Conditions to Tethered (1 → 4)-Linked Disaccharides*

Entry	Starting material (acceptor)	Tether (Man → acceptor)	Tether linkage	Ring size	Conditions	Products (yield)	α-D/β-D
1	**4** (GlcNPhth)	malonate	(6 → 3)	12	NIS, CH_2Cl_2, −30°	**5** (47%)	0 : 100
2					NIS, MeCN, −30°	**5** (51%)	0 : 100
3	**4** (GlcNPhth)	malonate	(6 → 3)	12	MeOTf, CH_2Cl_2, r.t.	**5** (49%)	0 : 100
4					MeOTf, MeCN, r.t.	**5** (52%)	0 : 100
5	**9** (Gal)	malonate	(6 → 3)	12	NIS, CH_2Cl_2, −30°	**10** (60%)	100 : 0
6					NIS, MeCN, −30°	**10** (60%)	100 : 0
7	**9** (Gal)	malonate	(6 → 3)	12	MeOTf, CH_2Cl_2, r.t.	**10** (64%)	100 : 0
8					MeOTf, MeCN, r.t.	**10** (60%)	100 : 0
9	**14a** (Gal)	malonate	(6 → 2)	13	[a])	–[b])	
10	**14b** (Gal)	succinate	(6 → 2)	14	[a])	–[b])	
11	**16a** (Gal)	malonate	(6 → 6)	13	NIS, CH_2Cl_2, −30°	**17a** (traces), **17b** (49%)	> 1 : 99
12					NIS, MeCN, −30°	**17a** (0%), **17b** (50%)	0 : 100
13	**16a** (Gal)	malonate	(6 → 6)	13	MeOTf, CH_2Cl_2, r.t.	**17a** (0%), **17b** (55%)	0 : 100
14					MeOTf, MeCN, r.t.	**17a** (0%), **17b** (55%)	0 : 100
15	**16b** (Gal)	succinate	(6 → 6)	14	NIS, CH_2Cl_2, −30°	**18a** (7%), **18b** (51%)	12 : 88
16					NIS, MeCN, −30°	**18a** (5%), **18b** (51%)	9 : 91
17	**16b** (Gal)	succinate	(6 → 6)	14	MeOTf, CH_2Cl_2, r.t.	**18a** (5%), **18b** (50%)	9 : 91
18					MeOTf, MeCN, r.t.	**18a** (0%), **18b** (54%)	0 : 100
19	**22** (Man)	malonate	(6 → 2)	13	NIS, CH_2Cl_2, −30°	**23** (69%)	100 : 0
20					NIS, MeCN, −30°	**23** (68%)	100 : 0
21	**22** (Man)	malonate	(6 → 2)	13	MeOTf, CH_2Cl_2, r.t.	**23** (67%)	100 : 0
22					MeOTf, MeCN, r.t.	**23** (65%)	100 : 0
23	**28** (Man)	malonate	(6 → 3)	12	NIS, CH_2Cl_2, −30°	**29a** (50%), **29b** (20%)	71 : 29
24					NIS, MeCN, −30°	**29a** (47%), **29b** (23%)	67 : 33
25	**28** (Man)	malonate	(6 → 3)	12	MeOTf, CH_2Cl_2, r.t.	**29a** (40%), **29b** (27%)	60 : 40
26					MeOTf, MeCN, r.t.	**29a** (36%), **29b** (36%)	50 : 50
27	**33** (Man)	malonate	(6 → 6)	13	NIS, CH_2Cl_2, −30°	**34** (71%)	100 : 0
28					NIS, MeCN, −30°	**34** (68%)	100 : 0
29	**33** (Man)	malonate	(6 → 6)	13	MeOTf, CH_2Cl_2, r.t.	**34** (64%)	100 : 0
30					MeOTf, MeCN, r.t.	**34** (60%)	100 : 0
31	**41** (Rha)	malonate	(6 → 3)	12	NIS, CH_2Cl_2, −30°	**42** (67%)	0 : 100
32					NIS, MeCN, −30°	**42** (68%)	0 : 100
33	**41** (Rha)	malonate	(6 → 3)	12	MeOTf, CH_2Cl_2, r.t.	**42** (66%)	0 : 100
34					MeOTf, MeCN, r.t.	**42** (71%)	0 : 100
35	**46** (Rha)	malonate	(6 → 2)	13	NIS, CH_2Cl_2, −30°	**47** (74%)	100 : 0
36					NIS, MeCN, −30°	**47** (75%)	100 : 0
37	**46** (Rha)	malonate	(6 → 2)	13	MeOTf, CH_2Cl_2, r.t.	**47** (69%)	100 : 0
38					MeOTf, MeCN, r.t.	**47** (70%)	100 : 0

[a]) According to conditions of *Entries 1–4*. [b]) Decomposition of the starting material.

disaccharides **17b** and **18b**, respectively, were found as the major anomers. Once again, this is in good agreement with the calculated thermodynamic stability of products **17** and **18**, the β-D-anomers being more stable by *ca*. 10 kcal/mol than the α-D-anomers **17a** and **18a**, respectively.

Problems were encountered for the preparation of β-D-Man-(1 → 4)-D-Man disaccharides. Originally, it was expected that prearranged glycosides **22**, **28**, and **33**, similar to compound **4** but having a mannose acceptor instead of a glucosamine residue, should give significant amounts of β-D-anomers. However, in all cases tested here

(*Table*, *Entries 19–30*), cyclization gave either solely the α-D-linked disaccharides **23** (*Entries 19–22*) and **34** (*Entries 27–30*) or, in the best case, an anomer mixture **29** (*Entries 23–26*). Calculation of the thermodynamic stability of all products showed that, in fact, the tethered α-D-(1 → 4)-linked disaccharides are more stable by 3.8–7.4 kcal/mol than the corresponding β-D-(1 → 4)-linked ones. Thus, not only the relative configuration at the positions directly involved in the formation of the ring play an important role, but other substituents in the donor and acceptor influence as well the outcome of the anomer configuration in the intramolecular glycosylation.

Finally, (1 → 4)-selective mannosylations of L-rhamnose acceptors were investigated as well (*Table*, *Entries 31–38*). When a malonate tether was chosen for position 3 of the acceptor, prearranged glycoside **41** afforded the β-D-linked disaccharide **42** exclusively (*Entries 31–34*). Contrarily, changing the tether from position 3 to position 2, as in prearranged glycoside **46**, which allows the formation of a 13- instead of a 12-membered ring, gave solely α-D-linked disaccharide **47** (*Entries 35–38*). Both results are mirrored by calculation of the thermodynamic stability of the products which showed the anomer obtained to be more stable by 3.5–5.2 kcal/mol.

In summary, the intramolecular glycosylations as shown here and in the previous paper [1] allow for the selective preparation of both anomers of the disaccharides D-Man-(1 → 4)-D-Glc, D-Man-(1 → 4)-D-GlcN, D-Man-(1 → 4)-D-Gal, and D-Man-(1 → 4)-L-Rha all of which are important naturally occurring structures.

Experimental Part

General. See [1]. NMR: for prearranged glycosides and disaccharides, unprimed locants refer to the glucose, glucosamine, mannose (acceptor), and rhamnose moiety, and primed ones to the mannose (donor) moiety.

*Benzyl 4,6-Di-*O*-benzylidene-2-deoxy-3-*O*-[3-(ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-*D*-mannopyranosid-6-*O*-yl)-1,3-dioxopropyl]-2-phthalimido-α-*D*-glucopyranoside* (**3**). *a*) A soln. of **1a** [4] (1.26 g, 2.17 mmol), **2** [21] (0.9 g, 1.85 mmol), and Bu_3N (1.06 ml, 4.44 mmol) in CH_2Cl_2 (15 ml) was added at r.t. under Ar to a suspension of 2-chloro-1-methylpyridinium iodide [22][23] (0.57 g, 2.22 mmol) in CH_2Cl_2 (5 ml). The mixture was stirred for 2.5 h and evaporated. CC (toluene/AcOEt 15 : 1) of the residue afforded **3** (1.55 g, 80%). $[\alpha]_D = +101.4$ ($c =$ 1.1, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 6.80 (*dd*, *J*(3,4) = 9.4, H–C(3)); 5.50 (*s*, PhC*H*); 5.27 (*d*, *J*(1′,2′) = 1.4, H–C(1′)); 4.97 (*d*, *J*(1,2) = 3.8, H–C(1)); 4.83 (*d*, *J* = −10.8, 1 H, PhCH_2); 4.72 (*d*, *J* = −12.6, 1 H, PhCH_2); 4.68 (*d*, *J* = −12.4, 1 H, PhCH_2); 4.62 (*d*, *J* = −12.3, 1 H, PhCH_2); 4.55 (*dd*, *J*(2,3) = 11.2, H–C(2)); 4.53 (*s*, 2 H, PhCH_2); 4.45 (2*d*, *J* = −10.6, −12.7, 2 H, PhCH_2); 4.24 (*dd*, *J*(5,6a) = 5.0, *J*(6a,6b) = −9.9, H_a–C(6)); 4.16 (*dt*, *J*(5,6b) = 9.9, H–C(5)); 4.09–3.99 (*m*, H–C(5′), 2 H–C(6′)); 3.78 (*dd*, *J*(2′,3′) = 3.2, H–C(2′)); 3.76–3.66 (*m*, H–C(3′), H–C(4′)); 3.74 (*t*, H_b–C(6)); 3.69 (*t*, *J*(4,5) = 9.4, H–C(4)); 3.27 (*d*, *J* = −15.7, 1 H, $COCH_2$); 3.19 (*d*, *J* = −15.8, 1 H, $COCH_2$); 2.57–2.43 (*m*, Me*CH*$_2$S); 1.19 (*t*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 165.9, 164.1 (2 C each, NCO, *C*OCH_2); 101.4 (Ph*C*H); 97.1 (C(1)); 81.8 (C(1′)); 80.8 (C(4)); 80.1 (C(3′)); 76.1 (C(2′)); 75.0 (Ph*C*H_2); 74.6 (C(4′)); 72.0, 71.9 (Ph*C*H_2); 69.9 (C(5′)); 69.8 (Ph*C*H_2); 68.7 (C(6)); 67.3 (C(3)); 64.2 (C(6′)); 62.9 (C(5)); 54.0 (C(2)); 41.1 (CO*C*H_2); 25.4 (Me*C*H_2S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{60}H_{59}NO_{14}S$ (1050.19): C 68.62, H 5.66, N 1.33, S 3.05; found: C 68.69, H 5.70, N 1.39, S 2.99.

b) A soln. of **1a** (1.45 g, 2.97 mmol), **2** (1.57 g, 2.70 mmol), DCC (0.61 g, 2.97 mmol), and a cat. amount of DMAP in CH_2Cl_2 (12 ml) was stirred for 24 h at r.t. The resulting suspension was filtered through a layer of *Celite* and the filtrate washed with aq. HCl and $NaHCO_3$ soln., dried, and evaporated. CC (toluene/acetone 13 : 1) of the residue afforded **3** (0.85 g, 30%).

*Benzyl 6-*O*-Benzyl-2-deoxy-3-*O*-[3-(ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-*D*-mannopyranosid-6-*O*-yl)-1,3-dioxopropyl]-2-phthalimido-α-*D*-glucopyranoside* (**4**). *a*) A sat. soln. of dry HCl in Et_2O was added dropwise at r.t. to a suspension of **3** (0.44 g, 0.42 mmol), $NaCNBH_3$ (0.33 g, 5.25 mmol), and 3-Å molecular sieves in THF (10 ml) until the evolution of gas ceased. The mixture was diluted with CH_2Cl_2 and filtered through a layer of *Celite*. The filtrate was washed with aq. $NaHCO_3$ soln., dried, and evaporated. CC (toluene/AcOEt 5 : 1) of the residue

afforded **4** (153 mg, 35%). $[\alpha]_D = +115.1$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 6.62 (*dd*, *J*(3,4) = 9.0, H–C(3)); 5.29 (*d*, *J*(1′,2′) = 1.2, H–C(1′)); 4.99 (*d*, *J*(1,2) = 3.6, H–C(1)); 4.88 (*d*, *J* = –10.9, 1 H, PhCH_2); 4.73 (*d*, *J* = –12.6, 1 H, PhCH_2); 4.68 (*d*, *J* = –12.4, 1 H, PhCH_2); 4.64 (*d*, *J* = –10.7, 1 H, PhCH_2); 4.60–4.53 (*m*, 5 H, PhCH_2); 4.45 (*dd*, *J*(2,3) = 11.5, 1 H, H–C(2)); 4.44 (*d*, *J* = –12.7, 1 H, PhCH_2); 4.28–4.21 (*m*, 2 H–C(6′)); 4.18–4.03 (*m*, H–C(5), H–C(5′)); 3.85 (*t*, *J*(4′,5′) = 9.2, H–C(4′)); 3.81–3.78 (*m*, H–C(2′), H–C(3′)); 3.76–3.71 (*m*, H–C(4), 2 H–C(6)); 3.45 (br. *s*, OH); 3.28 (*s*, $COCH_2$); 2.59–2.45 (*m*, MeCH_2S); 1.20 (*t*, *J* = 7.4, *Me* CH_2S). ^{13}C-NMR ($CDCl_3$): 167.6, 166.8, 166.1 (CO); 96.2 (C(1)); 82.0 (C(1′)); 80.1 (C(3′)); 76.0 (C(2′)); 75.0 (PhCH_2); 74.2 (C(4′)); 73.5 (PhCH_2); 72.0 (2 C, PhCH_2); 71.8 (C(3)); 71.4 (C(5′)); 71.1 (C(4)); 69.8 (C(5)); 69.4 (PhCH_2); 68.9 (C(6)); 64.5 (C(6′)); 53.8 (C(2)); 41.3 ($COCH_2$); 25.5 (MeCH_2S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{60}H_{61}NO_{14}S$ (1052.21): C 68.49, H 5.84, N 1.33, S 3.05; found: C 68.56, H 5.88, N 1.21, S 3.20.

b) A soln. of **3** (0.5 g, 0.48 mmol), Et_3SiH (0.38 ml, 2.40 mmol), and CF_3COOH (0.24 ml, 2.40 mmol) in CH_2Cl_2 (10 ml) was stirred for 5 min at 0° and 2.5 h at r.t. and evaporated. CC (toluene/AcOEt 5:1) of the residue afforded **4** (0.33 g, 65%).

Benzyl O-*(2,3,4-Tri*-O-*benzyl-β*-D-*mannopyranosyl)-(1 → 4)-6*-O-*benzyl-2-deoxy-2-phthalimido-α*-D-*glucopyranoside 3,6′-Malonate* (**5**). *a*) A suspension of **4** (0.31 g, 0.30 mmol) and 3-Å molecular sieves (*ca.* 0.2 g) in CH_2Cl_2 (12 ml) was stirred under Ar for 20 min at r.t. and cooled to –30°. NIS (0.34 g, 1.5 mmol) and Me_3SiOTf (14 µl, 75 µmol) 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_2Cl_2, and filtered. The filtrate was washed with aq. $NaHCO_3$ and $Na_2S_2O_3$ soln., dried, and evaporated. CC (toluene/AcOEt 7:1) of the residue afforded **5** (0.14 g, 47%). $[\alpha]_D = +86.8$ ($c = 1.2$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 6.51 (*dd*, *J*(3,4) = 8.2, H–C(3)); 4.95 (*d*, *J*(1,2) = 4.0, H–C(1)); 4.93 (*d*, *J* = –11.1, 1 H, PhCH_2); 4.90 (*d*, *J* = –12.7, 1 H, PhCH_2); 4.72 (*d*, *J* = –12.7, 1 H, PhCH_2); 4.71 (*d*, *J* = –12.8, 1 H, PhCH_2); 4.67–4.60 (*m*, *J*(2,3) = 11.1, *J*(6a′,6b′) = –11.4, H–C(2)), H_a–C(6′)); 4.59 (*d*, *J* = –12.7, 1 H, PhCH_2); 4.57 (*d*, *J* = –11.2, 1 H, PhCH_2); 4.47–4.44 (*m*, 2 H, PhCH_2); 4.40 (*d*, *J* = –11.9, 1 H, PhCH_2); 4.32 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.26 (*s*, H–C(1′)); 4.09 (*dd*, *J*(5′,6b′) = 6.0, H_b–C(6′)); 4.03–3.97 (*m*, H–C(4), H–C(5)); 3.82 (*t*, *J*(4′,5′) = 9.4, H–C(4′)); 3.57 (br. *d*, *J*(2′,3′) = 2.9, H–C(2′)); 3.47 (br. *s*, 2 H–C(6)); 3.44–3.41 (*m*, H–C(5′)); 3.26 (*dd*, *J*(3′,4′) = 9.3, H–C(3′)); 3.20 (*d*, *J* = –12.1, 1 H, $COCH_2$); 3.12 (*d*, *J* = –12.1, 1 H, $COCH_2$). ^{13}C-NMR ($CDCl_3$): 167.3, 166.3 ($COCH_2$); 163.4 (2 C, NCO); 102.3 (*J*(1′,H–C(1′)) = 157.7, C(1′)); 96.3 (C(1)); 82.0 (C(3′)); 78.1 (C(4)); 75.9 (C(4′)); 75.0 (PhCH_2); 73.7 (2 C, PhCH_2, C(2′)); 73.5 (PhCH_2); 71.4 (PhCH_2); 70.6 (C(5′)); 70.4 (C(3)); 70.0 (C(5)); 69.5 (PhCH_2); 68.1 (C(6)); 63.4 (C(6′)); 53.8 (C(2)); 42.9 ($COCH_2$). Anal. calc. for $C_{58}H_{55}NO_{14}$ (990.08): C 70.36, H 5.60, N 1.42; found: C 70.07, H 5.64, N 1.28.

b) Exactly as described in *Exper. a*, with **4** (0.3 g, 0.29 mmol), NIS (0.32 g, 1.43 mmol), Me_3SiOTf (13 µl, 71 µmol), and MeCN (10 ml); **5** (144 mg, 51%).

c) A suspension of **4** (0.35 g, 0.33 mmol), 4-Å molecular sieves (0.86 g), and MeOTf (0.13 ml, 1.67 mmol) in CH_2Cl_2 (12 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. Chromatography (toluene/AcOEt 7:1) of the residue afforded **5** (0.16 g, 49%).

d) Exactly as described in *Exper. c*, with **4** (0.4 g, 0.38 mmol), MeOTf (0.21 ml, 1.92 mmol), and MeCN (12 ml): **5** (199 mg, 52%).

Benzyl O-*(6*-O-*Benzoyl-2,3,4-tri*-O-*benzyl-β*-D-*mannopyranosyl)-(1 → 4)-3*-O-*benzoyl-6*-O-*benzyl-2-deoxy-2-phthalimido-α*-D-*glucopyranoside* (**6**). A soln. of **5** (125 mg, 0.126 mmol) and a cat. amount of NaOMe in MeOH (6 ml) was stirred for 24 h at r.t. and neutralized with ion-exchange resin (H^+ form). After evaporation, the residue was dissolved in pyridine (6 ml), and BzCl (74 µl, 0.64 mmol) was added. The mixture was stirred at r.t. for 24 h, poured into H_2O, and extracted with CH_2Cl_2. The extracts were washed with aq. HCl and $NaHCO_3$ soln., dried, and evaporated. CC (hexane/AcOEt 3:1) of the residue afforded **6** (104 mg, 73%). $[\alpha]_D = +8.4$ ($c = 1.14$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 6.84 (*dd*, *J*(3,4) = 9.3, H–C(3)); 5.02 (*d*, *J*(1,2) = 3.5, H–C(1)); 4.90 (*d*, *J* = –11.3, 1 H, PhCH_2); 4.88 (*d*, *J* = –12.5, 1 H, PhCH_2); 4.82 (*dd*, *J*(2,3) = 11.1, H–C(2)); 4.74 (*d*, *J* = –12.4, 1 H, PhCH_2); 4.66 (*d*, *J* = –12.5, 1 H, PhCH_2); 4.55 (*d*, *J* = –12.6, 1 H, PhCH_2); 4.53 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.48 (*s*, H–C(1′)); 4.46–4.41 (*m*, 2 H, PhCH_2); 4.38 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.30–4.23 (*m*, H–C(4), H–C(5)); 4.22 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.18–4.11 (*m*, *J*(6a′,6b′) = –12.0, H_a–C(6′)); 4.13 (*dd*, *J*(5′,6b′) = 4.8, H_b–C(6′)); 3.80 (*t*, *J*(4′,5′) = 9.3, H–C(4′)); 3.73 (br. *d*, 2 H–C(6)); 3.68 (br. *d*, *J*(2′,3′) = 3.0, H–C(2′)); 3.24 (*dd*, *J*(3′,4′) = 9.2, H–C(3′)); 3.20–3.13 (*m*, H–C(5′)). ^{13}C-NMR ($CDCl_3$): 166.1, 165.8 (PhCO); 163.4 (2 C, NCO); 100.2 (*J*(1′,H–C(1′)) = 154.8, C(1′)); 96.6 (C(1)); 81.8 (C(3′)); 75.2 (PhCH_2); 74.8 (C(4)); 73.9 (C(5′)); 73.7 (C(4′)); 73.6 (2 C, C(2′), PhCH_2); 72.9 (C(3)); 72.1 (PhCH_2); 70.4 (C(5)); 69.6 (PhCH_2); 68.4 (C(6)); 62.8 (C(6′)); 54.0 (C(2)). Anal. calc. for $C_{69}H_{63}NO_{14}$ (1130.26): C 73.33, H 5.62, N 1.24; found: C 73.16, H 5.58, N 1.10.

Benzyl 2-O-*Benzoyl-4,6-O-benzylidene-3*-O-*[3-(ethyl 2,3,4-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-6*-O-*yl)-1,3-dioxopropyl]-α*-D-*galactopyranoside* (**8**). As described for **3** (*Exper. b*), with **1a** [1] (1.03 g, 1.77 mmol), **7** [27] (0.90 g, 1.95 mmol), DCC (0.40 g, 1.95 mmol), DMAP, and CH_2Cl_2 (40 ml): **8** (1.38 g, 69%). $[\alpha]_D = +137.4$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.66 (*dd*, $J(3,4) = 3.4$, H–C(3)); 5.55 (*dd*, $J(2,3) = 10.8$, H–C(2)); 5.52 (*s*, PhC*H*); 5.42 (*s*, $J(1,2) = 3.5$, H–C(1)); 5.28 (*s*, H–C(1′)); 4.88 (*d*, $J = -10.8$, 1 H, PhCH_2); 4.72 (*d*, $J = -12.4$, 1 H, PhCH_2); 4.65 (*s*, 2 H, PhCH_2); 4.57 (*d*, $J = -12.6$, 1 H, PhCH_2); 4.55 (*s*, 2 H, PhCH_2); 4.54 (*d*, $J = -10.8$, 1 H, PhCH_2); 4.49 (br. *d*, H–C(4)); 4.31 (*dd*, J(6a′,6b′) = –11.8, H_a–C(6′)); 4.24 (*dd*, H_b–C(6′)); 4.22 (*dd*, J(6a,6b) = –12.5, H_a–C(6)); 4.12–4.08 (*m*, $J(5',6a') = 5.2$, $J(5',6b') = 2.3$, H–C(5′)); 3.99 (*dd*, H_b–C(6)); 3.87 (*t*, $J(4',5') = 9.1$, H–C(4′)); 3.82–3.77 (*m*, $J(3',4') = 9.1$, H–C(2′), H–C(3′)); 3.73 (br. *s*, $J(5,6a) = 1.4$, $J(5,6b) = 1.5$, H–C(5)); 3.34 (br. *d*, 2 H, $COCH_2$); 2.55–2.41 (*m*, MeCH_2S); 1.16 (*t*, $J = 7.5$, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 166.1, 165.8, 165.6 (CO); 100.8 (PhCH); 96.2 (C(1)); 81.9 (C(1′)); 80.3 (C(3′)); 76.1 (C(2′)); 75.0 (PhCH_2); 74.4 (C(4′)); 73.9 (C(4)); 72.1 (2 C, PhCH_2); 70.1 (PhCH_2); 70.0 (C(5′)); 69.5 (C(3)); 69.0 (C(6)); 68.5 (C(2)); 64.4 (C(6′)); 62.5 (C(5)); 40.9 ($COCH_2$); 25.3 (MeCH_2S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{59}H_{60}O_{14}S$ (1025.18): C 69.12, H 5.90, S 3.13; found: C 69.32, H 5.95, S 3.02.

Benzyl 2-O-*Benzoyl-6*-O-*benzyl-3*-O-*[3-(ethyl 2,3,4-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-6*-O-*yl)-1,3-dioxopropyl]-α*-D-*galactopyranoside* (**9**). As described for **3** (*Exper. a*), with **8** (1.10 g, 1.07 mmol) and $NaCNBH_3$ (0.84 g, 13.38 mmol): **9** (0.82 g, 0.75 mmol). $[\alpha]_D = +102.9$ ($c = 1.01$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.46 (*dd*, $J(3,4) = 2.9$, H–C(3)); 5.36 (*d*, $J(1',2') = 1.7$, H–C(1′)); 5.30 (*dd*, $J(2,3) = 10.7$, H–C(2)); 5.28 (*d*, $J(1,2) = 3.0$, H–C(1)); 4.91 (*d*, $J = -10.9$, 1 H, PhCH_2); 4.87 (*d*, $J = -12.1$, 1 H, PhCH_2); 4.76 (*d*, $J = -12.2$, 1 H, PhCH_2); 4.72 (*d*, $J = -10.3$, 1 H, PhCH_2); 4.67 (*d*, $J = -12.5$, 1 H, PhCH_2); 4.59–4.51 (*m*, 4 H, PhCH_2); 4.49 (*d*, $J = -11.8$, 1 H, PhCH_2); 4.39 (br. *d*, H–C(4)); 4.32–4.20 (*m*, 2 H–C(6′)); 4.18–4.10 (*m*, H–C(5′), H–C(5)); 3.98 (*t*, $J(4',5') = 9.3$, H–C(4′)); 3.85–3.77 (*m*, H–C(2′), H–C(3′)); 3.68 (br. *s*, 2 H–C(6)); 3.30 (*s*, $COCH_2$); 2.62–2.47 (*m*, MeCH_2S); 1.22 (*t*, $J = 7.4$, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 166.7, 165.7, 165.4 (CO); 95.6 (C(1)); 82.3 (C(1′)); 80.5 (C(3′)); 76.3 (C(2′)); 74.2 (C(4′)); 73.9 (C(3)); 71.8 (C(5′)); 69.9 (C(5)); 69.6 (C(6)); 68.8 (C(4)); 67.7 (C(2)); 64.5 (C(6′)); 41.3 (MeCH_2S); 15.0 (*Me*CH_2S). Anal. calc. for $C_{59}H_{62}O_{14}S$ (1027.20): C 68.99, H 6.08; found: C 69.09, H 6.09.

Benzyl O-*(2,3,4-Tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1→4)-2*-O-*benzoyl-6*-O-*benzyl-α*-D-*galactopyranoside 3,6′-Malonate* (**10**). a) Exactly as described for **5** (*Exper. a*), with **9** (383 mg, 0.37 mmol), NIS (0.43 g, 1.87 mmol), Me_3SiOTf (17 µl, 93 µmol), and CH_2Cl_2 (10 ml): **10** (217 mg, 60%). $[\alpha]_D = +131.9$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.80 (*dd*, $J(3,4) = 3.1$, H–C(3)); 5.38 (*d*, $J(1,2) = 3.7$, H–C(1)); 5.21 (*dd*, $J(2',3') = 11.0$, H–C(2′)); 5.00 (*d*, $J(1',2') = 3.0$, H–C(1′)); 4.84 (br. *d*, J(6a′,6b′) = –10.7, H_a–C(6′)); 4.72 (*d*, $J = -11.7$, 1 H, PhCH_2); 4.69–4.64 (*m*, 5 H, PhCH_2); 4.52 (*d*, $J = -12.4$, 1 H, PhCH_2); 4.50 (*d*, $J = -11.7$, 1 H, PhCH_2); 4.43 (*d*, $J = -11.6$, 1 H, PhCH_2); 4.37 (*d*, $J = -11.6$, 1 H, PhCH_2); 4.24 (br. *d*, $J(4,5) = 3.0$, H–C(4)); 4.16–4.05 (*m*, $J(5',6b') = 10.1$, $J(5,6b) = 6.1$, H–C(5′), H–C(5)); 3.89 (*dd*, $J(3',4') = 6.6$, H–C(3′)); 3.86–3.85 (*t*, $J(2',3') = 3.0$, H–C(2′)); 3.78 (*dd*, H_b–C(6′)); 3.60–3.53 (*m*, J(6a,6b) = –9.4, H–C(4′), H_a–C(6)); 3.46 (*d*, $J = -15.8$, 1 H, $COCH_2$); 3.40 (*dd*, H_b–C(6)); 3.24 (*dd*, $J = -15.8$, 1 H, $COCH_2$). ^{13}C-NMR ($CDCl_3$): 165.6, 165.5 (2 C, 1 C, CO); 100.7 (J(1′,H–C(1′)) = 172.8, C(1′)); 95.5 (C(1)); 78.8 (C(3′)); 76.9 (C(2′)); 76.1 (C(4)); 75.8 (C(4′)); 73.5, 72.9, 72.8 (2 C, 1 C, 1 C, PhCH_2); 70.5 (C(5′)); 70.0 (PhCH_2); 69.9 (C(2)); 69.4 (C(3)); 68.9 (C(5)); 67.5 (C(6)); 64.9 (C(6′)); 42.1 ($COCH_2$). Anal. calc. for $C_{57}H_{56}O_{14}$ (965.07): C 70.94, H 5.85; found: C 70.73, H 5.85.

b) Exactly as described for **5** (*Exper. a*), with **9** (0.4 g, 0.39 mmol), NIS (0.44 g, 1.95 mmol), Me_3SiOTf (18 µl, 0.10 mmol), and MeCN (12 ml): **10** (225 mg, 60%).

c) Exactly as described for **5** (*Exper. c*), with **9** (0.43 g, 0.42 mmol), MeOTf (0.23 ml, 2.09 mmol), and CH_2Cl_2 (12 ml): **10** (260 mg, 64%).

d) Exactly as described for **5** (*Exper. d*), with **9** (0.62 g, 0.60 mmol), MeOTf (0.46 ml, 4.23 mmol), and MeCN (15 ml): **10** (364 mg, 60%).

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-*galactopyranoside* (**11**). Exactly as described for **6**, with **10** (160 mg, 0.17 mmol), NaOMe in MeOH, BzCl (0.12 ml, 1.0 mmol), and pyridine (5 ml): **11** (135 mg, 74%). $[\alpha]_D = +58.0$ ($c = 1.2$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.79 (*dd*, $J(3,4) = 3.2$, H–C(3)); 5.54 (*dd*, $J(2,3) = 11.0$, H–C(2)); 5.37 (*d*, $J(1,2) = 3.7$, H–C(1)); 5.01 (*d*, $J(1',2') = 1.8$, H–C(1′)); 4.84 (*d*, $J = -10.8$, 1 H, PhCH_2); 4.80 (*d*, $J = -11.7$, 1 H, PhCH_2); 4.73 (2*d*, $J = -11.8$, –12.4, 2 H, PhCH_2); 4.69 (*d*, $J = -12.3$, 1 H, PhCH_2); 4.59 (br. *d*, H–C(4)); 4.57 (*d*, $J = -12.3$, 1 H, PhCH_2); 4.56 (*d*, $J = -12.2$, 1 H, PhCH_2); 4.49 (*dd*, J(6a′,6b′) = –11.6, H_a–C(6′)); 4.46–4.42 (*m*, H_b–C(6′)); 4.45 (*s*, 2 H, PhCH_2); 4.44 (d, $J = -10.7$, 1 H, PhCH_2); 4.24 (br. *t*, $J(5,6a) = 6.9$, H–C(5)); 4.09 (br. *s*, $J(5',6a') = 2.1$, H–C(3′), H–C(4′), H–C(5′)); 3.88 (br. *s*, H–C(2′)); 3.45 (br. *dd*, J(6a,6b) = –11.6, 2 H–C(6)). ^{13}C-NMR ($CDCl_3$): 166.0, 165.9 (1 C, 2 C, CO); 99.1 (J(1′,H–C(1′)) = 173.1, C(1′)); 95.7 (C(1)); 79.9 (C(3′)); 75.3 (C(2′)); 75.1 (PhCH_2); 74.6 (C(4)); 74.0 (C(4′)); 73.6 (PhCH_2); 72.7 (2 C, PhCH_2); 70.7 (C(5′)); 70.0 (PhCH_2); 69.8

(C(3)); 69.2 (C(2)); 68.7 (C(5)); 67.9 (C(6)); 62.9 (C(6′)). Anal. calc. for $C_{68}H_{64}O_{14}$ (1105.25): C 73.90, H 5.84; found: C 74.00, 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-*galactopyranoside* (**13a**). As described for **3** (*Exper. b*), with **1a** [1] (1.15 g, 1.98 mmol), **12** [27] (0.92 g, 1.98 mmol), DCC (0.41 g, 1.98 mmol), DMAP, and CH_2Cl_2 (35 ml), followed by CC (toluene/acetone 40:1): **13a** (1.06 g, 52%). $[\alpha]_D = +143.8$ ($c = 1.2$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.61 (br. *t*, *J*(3,4) = 3.0, H−C(2), H−C(3)); 5.49 (*s*, PhC*H*); 5.36 (*d*, *J*(1,2) = 2.8, H−C(1)); 5.29 (*s*, H−C(1′)); 4.88 (*d*, *J* = −10.9, 1 H, PhCH_2); 4.74 (*d*, *J* = −12.1, 1 H, PhCH_2); 4.70–4.64 (*m*, 3 H, PhCH_2); 4.62–4.51 (*m*, 4 H, H−C(4), PhCH_2); 4.30–4.26 (*m*, 2 H−C(5′)); 4.21 (*dd*, *J*(6a,6b) = −12.6, H_a−C(6)); 4.11 (*ddd*, *J*(5′,6a′) = 3.2, *J*(5′,6b′) = 5.0, H−C(5′)); 4.01 (*dd*, H_b−C(6)); 3.81 (br. *s*, *J*(4′,5′) = 8.4, *J*(5,6a) = 1.5, *J*(5,6b) = 1.6, H−C(2′), H−C(3′), H−C(4′), H−C(5)); 3.30 (*s*, $COCH_2$); 2.57–2.43 (*m*, Me*C*H_2S); 1.17 (*t*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 166.1, 165.7 (1 C, 2 C, CO); 100.6 (Ph*C*H); 96.3 (C(1)); 81.7 (C(1′)); 80.2 (C(3′)); 76.0 (C(2′)); 75.0 (Ph*C*H_2); 74.5 (C(4′)); 74.0 (C(4)); 72.0, 71.9, 70.4 (1 C, 2 C, 1 C, Ph*C*H_2); 70.0 (C(5′)); 69.2 (C(2), C(3)); 69.0 (C(6)); 64.5 (C(6′)); 62.5 (C(5)); 40.8 (CO*C*H_2); 25.3 (Me*C*H_2S); 14.8 (*Me*CH_2S). Anal. calc. for $C_{59}H_{60}O_{14}S$ (10.25.18): C 69.12, H 5.90, S 3.13; found: C 69.09, H 5.90, S 3.23.

Benzyl 3-O-*Benzoyl-4,6*-O-*benzylidene-2*-O-*[4-(ethyl 2,3,4-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-6*-O-*yl)-1,4-dioxobutyl]-α*-D-*galactopyranoside* (**13b**). As described for **3** (*Exper. b*), with **1b** [4] (1.11 g, 1.87 mmol), **12** [27] (0.95 g, 2.05 mmol), DCC (0.43 g, 2.05 mmol), DMAP, and CH_2Cl_2 (35 ml), followed by CC (toluene/acetone 30:1): **13b** (1.71 g, 84%). $[\alpha]_D = +131.9$ ($c = 1.4$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.60 (br. *t*, H−C(2), H−C(3)); 5.50 (*s*, PhC*H*); 5.32 (*d*, *J*(1′,2′) < 1, H−C(1′)); 5.30 (*d*, *J*(1,2) = 2.4, H−C(1)); 4.90 (*d*, *J* = −10.9, 1 H, PhCH_2); 4.74 (*d*, *J* = −12.1, 1 H, PhCH_2); 4.71–4.56 (*m*, 5 H, H−C(4), PhCH_2); 4.62 (*d*, *J* = −12.3, 1 H, PhCH_2); 4.53 (*d*, *J* = −10.9, 1 H, PhCH_2); 4.26–4.20 (*m*, *J*(6a,6b) = −12.5, 2 H−C(6′), H_a−C(6)); 4.15–4.10 (*m*, H−C(5′)); 4.02 (*dd*, H_b−C(6)); 3.88 (*t*, *J*(4′,5′) = 9.3, H−C(4′)); 3.83–3.80 (*m*, *J*(2′,3′) = 3.1, *J*(5,6b) = 1.5, H−C(2′), H−C(5)); 3.81 (*dd*, *J*(3′,4′) = 9.9, H−C(3′)); 2.61–2.47 (*m*, $COCH_2CH_2CO$, Me*C*H_2S); 1.20 (*t*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 171.7, 171.5 (CO*C*H_2*C*H_2*C*O); 166.1 (Ph*C*O); 100.6 (Ph*C*H); 96.4 (C(1)); 81.9 (C(1′)); 80.3 (C(3′)); 76.1 (C(2′)); 75.1 (Ph*C*H_2); 74.6 (C(4′)); 74.0 (C(4)); 72.0 (2 C, Ph*C*H_2); 70.2 (2 C, C(5′), Ph*C*H_2); 69.4, 68.1 (C(2), C(3)); 69.0 (C(6)); 63.7 (C(6′)); 62.5 (C(5)); 28.8, 28.7 (CO*C*H_2*C*H_2*C*O); 25.4 (Me*C*H_2S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{60}H_{62}O_{14}S$ (1039.20): C 69.35, H 6.01, S 3.09; found: C 69.64, H 6.07, S 3.20.

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-*galactopyranoside* (**14a**). As described for **3** (*Exper. a*), with **13a** (0.92 g, 0.90 mmol) and $NaCNBH_3$ (0.71 g, 11.25 mmol): **14a** (0.71 g, 77%). $[\alpha]_D = +129.9$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.58 (*dd*, *J*(2,3) = 10.7, H−C(2)); 5.48 (*dd*, *J*(3,4) = 2.9, H−C(3)); 5.29 (*d*, *J*(1′,2′) = 1.5, H−C(1′)); 5.27 (*s*, H−C(1)); 4.88 (*d*, *J* = −10.8, 1 H, PhCH_2); 4.72 (*d*, *J* = −12.0, 1 H, PhCH_2); 4.69 (*d*, *J* = −12.3, 1 H, PhCH_2); 4.63 (*d*, *J* = −10.2, 1 H, PhCH_2); 4.59 (*d*, *J* = −12.3, 1 H, PhCH_2); 4.55 (*s*, 4 H, PhCH_2); 4.53 (*d*, *J* = −11.7, 1 H, PhCH_2); 4.43 (br. *s*, H−C(4)); 4.27 (br. *d*, 2 H−C(6′)); 4.13–4.07 (*m*, H−C(5′), H−C(5)); 3.85 (*t*, *J*(4′,5′) = 9.1, H−C(4′)); 3.81–3.77 (*m*, *J*(3′,4′) = 9.1, H−C(2′), H−C(3′)); 3.71 (br. *d*, 2 H−C(6)); 3.29 (*s*, $COCH_2$); 2.95 (*d*, *J*(4,OH) = 2.7, OH); 2.58–2.43 (*m*, Me*C*H_2S); 1.19 (*t*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 165.3 (3 C, CO); 95.9 (C(1)); 81.9 (C(1′)); 80.3 (C(3′)); 76.1 (C(2′)); 75.1 (Ph*C*H_2); 74.5 (C(4′)); 73.8 (Ph*C*H_2); 72.0 (2 C, Ph*C*H_2); 71.1 (C(3)); 70.1 (2 C, C(5′), Ph*C*H_2); 70.0 (C(6)); 69.1, 69.0 (C(2), C(4)); 68.3 (C(5)); 64.4 (C(6′)). Anal. calc. for $C_{59}H_{62}O_{14}S$ (1027.20): C 68.99, H 6.08; found: C 69.06, H 6.08.

Benzyl 3-O-*Benzoyl-6*-O-*benzyl-2*-O-*[4-(ethyl 2,3,4-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-6*-O-*yl)-1,4-dioxobutyl]-α*-D-*galactopyranoside* (**14b**). As described for **3** (*Exper. a*), with **13b** (1.43 g, 1.38 mmol) and $NaCNBH_3$ (1.08 g, 17.25 mmol), followed by CC (toluene/AcOEt 6:1): **14b** (0.92 g, 64%). $[\alpha]_D = +76.1$ ($c = 1.2$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.55 (*dd*, *J*(2,3) = 10.7, H−C(2)); 5.49 (*dd*, *J*(3,4) = 2.8, H−C(3)); 5.32 (*s*, H−C(1′)); 5.22 (*d*, *J*(1,2) = 3.5, H−C(1)); 4.89 (*d*, *J* = −10.9, 1 H, PhCH_2); 4.73 (*d*, *J* = −12.1, 1 H, PhCH_2); 4.70 (*d*, *J* = −12.3, 1 H, PhCH_2); 4.63 (*d*, *J* = −11.8, 1 H, PhCH_2); 4.60-4.56 (*m*, 4 H, PhCH_2); 4.54 (*d*, *J* = −11.2, 1 H, PhCH_2); 4.53 (*d*, *J* = −11.0, 1 H, PhCH_2); 4.41 (br. *s*, H−C(4)); 4.25 (br. *d*, 2 H−C(6′)); 4.15–4.09 (*m*, H−C(5′), H−C(5)); 3.88 (*t*, *J*(4′,5′) = 9.3, H−C(4′)); 3.84–3.79 (*m*, *J*(3′,4′) = 9.9, H−C(2′), H−C(3′)); 3.72 (br. *d*, 2 H−C(6)); 2.93 (*d*, *J*(4,OH) = 2.7, OH); 2.61–2.46 (*m*, $COCH_2CH_2CO$, Me*C*H_2S); 1.21 (*t*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 171.7, 171.6 (CO*C*H_2*C*H_2*C*O); 165.8 (Ph*C*O); 95.9 (C(1)); 81.9 (C(1′)); 80.2 (C(3′)); 76.1 (C(2′)); 75.1 (Ph*C*H_2); 74.6 (C(4′)); 73.8 (Ph*C*H_2); 72.0 (2 C, Ph*C*H_2); 71.2 (C(3)); 70.2 (C(5′)); 70.0 (C(6)); 69.9 (Ph*C*H_2); 69.1, 68.3 (1 C, 2 C, C(2), C(4), C(5)); 63.6 (C(6′)); 28.9, 28.7 (CO*C*H_2*C*H_2*C*O); 25.4 (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 69.20, H 6.14, S 2.97.

*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*-galactopyranoside* (**16a**). As described for **3** (*Exper. b*), with **1a** [1] (0.95 g, 1.64 mmol), **15** [28] (0.86 g, 1.80 mmol), DCC (0.37 g, 1.80 mmol), DMAP, and CH_2Cl_2 (20 ml), followed by CC (toluene/AcOEt 8:1): **16a** (1.11 g, 59%). $[\alpha]_D = +46.7$ ($c = 1.5$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.73 (*dd*, $J(3,4) = 3.0$, H–C(3)); 5.67 (*dd*, $J(2,3) = 10.7$, 2 H–C(2)); 5.32 (*d*, $J(1',2') = 1.1$, H–C(1′)); 5.29 (*d*, $J(1,2) = 3.5$, H–C(1)); 4.93 (*d*, $J = -10.8$, 1 H, PhCH_2); 4.76 (*d*, $J = -12.4$, 1 H, PhCH_2); 4.68 (*d*, $J = -12.3$, 1 H, PhCH_2); 4.63 (*d*, $J = -12.4$, 1 H, PhCH_2); 4.57 (br. *s*, $J = -10.8$, 4 H, PhCH_2); 4.46–4.34 (*m*, $J(6a',6b') = -11.9$, H_a–C(6′), 2 H–C(6)); 4.43 (*dd*, H_b–C(6′)); 4.31–4.24 (*m*, H–C(4), H–C(5)); 4.16 (*ddd*, $J(5',6a') = 2.2$, $J(5',6b') = 4.6$, H–C(5′)); 3.94 (*t*, $J(4',5') = 9.4$, H–C(4′)); 3.82 (2*d*, $J(2',3') = 3.0$, $J(3',4') = 10.2$, H–C(2′), H–C(3′)); 3.42 (*s*, $COCH_2$); 2.62 (*d*, $J(4,OH) = 2.1$, OH); 2.60–2.46 (*m*, MeCH_2S); 1.21 (*t*, $J = 7.4$, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 166.1, 166.0, 165.8 (*C*OCH_2); 95.7 (C(1)); 82.0 (C(1′)); 80.2 (C(3′)); 76.2 (C(2′)); 75.1 (Ph*C*H_2); 74.3 (C(4′)); 72.0 (2 C, Ph*C*H_2); 70.8 (C(3)); 70.1 (C(5′)); 69.9 (Ph*C*H_2); 68.7 (C(2)); 67.8, 67.7 (C(4), C(5)); 64.4 (C(6′)); 63.7 (C(6)); 41.2 (CO*C*H_2); 25.4 (Me*C*H_2S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{59}H_{64}O_{15}S$ (1041.18): C 68.06, H 5.81, S 3.08; found: C 68.20, H 5.84, S 3.10.

*Benzyl 2,3-Di-*O*-benzoyl-6-*O*-[4-(ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-*D*-mannopyranosid-6-*O*-yl)-1,4-dioxobutyl]-α-*D*-galactopyranoside* (**16b**). As described for **3** (*Exper. b*), with **1b** [4] (1.72 g, 2.89 mmol), **15** [28] (1,53 g, 3.19 mmol), DCC (0.66 g, 3.19 mmol), DMAP, and CH_2Cl_2 (40 ml), followed by CC (toluene/AcOEt 7:1): **16b** (2.25 g, 67%). $[\alpha]_D = +108.1$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.75 (*dd*, $J(3,4) = 3.0$, H–C(3)); 5.66 (*dd*, $J(2,3) = 10.7$, H–C(2)); 5.32 (*s*, *d*, each 1 H, $J(1,2) = 3.6$, H–C(1′), H–C(1)); 4.92 (*d*, $J = -10.8$, 1 H, PhCH_2); 4.78 (*d*, $J = -12.3$, 1 H, PhCH_2); 4.68 (*d*, $J = -12.3$, 1 H, PhCH_2); 4.62 (*d*, $J = -12.3$, 1 H, PhCH_2); 4.58 (*s*, 3 H, PhCH_2); 4.56 (*d*, $J = -11.2$, 1 H, PhCH_2); 4.43–43.9 (*m*, H_a–C(6)); 4.35–4.33 (*m*, 2 H–C(6′)); 4.31–4.25 (*m*, H–C(4), H–C(5), H_b–C(6)); 4.17–4.11 (*m*, $J(5',6a') = 2.5$, H–C(5′)); 3.91 (*t*, $J(4',5') = 9.3$, H–C(4′)); 3.84–3.81 (*m*, H–C(2′), H–C(3′)); 2.66–2.49 (*m*, $COCH_2CH_2CO$, MeCH_2S, OH); 1.23 (*t*, $J = 7.4$, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 172.0, 171.9 (*C*OCH_2CH_2*C*O); 165.8, 165.7 (Ph*C* O); 95.7 (C(1)); 81.9 (C(1′)); 80.1 (C(3′)); 76.3 (C(2′)); 75.1 (Ph*C*H_2); 74.5 (C(4′)); 72.1, 71.9 (Ph*C*H_2); 70.8 (C(3)); 70.2 (C(5′)); 69.7 (Ph*C*H_2); 68.7 (C(2)); 67.8 (C(4), C(5)); 63.7 (C(6′)); 62.8 (C(6)); 29.0, 28.9 ($COCH_2$*C*H_2CO); 25.4 (Me*C*H_2S); 15.0 (*Me*CH_2S). Anal. calc. for $C_{60}H_{62}O_{15}$ (1055.21): C 68.30, H 5.92, S 3.04; found: C 68.52, H 6.00, S 3.06.

Benzyl O*-(2,3,4-Tri-*O*-benzyl-α-*D*-mannopyranosyl)-(1→4)-2,3-di-*O*-benzoyl-α-*D*-galactopyranoside 6,6′-Malonate* (**17a**) *and Benzyl* O*-(2,3,4-Tri-*O*-benzyl-β-*D*-mannopyranosyl)-(1→4)-2,3-di-*O*-benzoyl-α-*D*-galactopyranoside 6,6′-Malonate* (**17b**). *a*) Exactly as described for **5** (*Exper. a*), with **16a** (0.40 g, 0.38 mmol), NIS (0.43 g, 1.87 mmol), Me_3SiOTf (17 µl, 93 µmol), and CH_2Cl_2 (10 ml), followed by CC (toluene/acetone 20:1): **17a** (< 1.0 mg; not further characterized), then **17b** (183 mg, 49%). **17b**: $[\alpha]_D = +68.3$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.81 (*dd*, $J(3,4) = 3.2$, H–C(3)); 5.68 (*dd*, $J(2,3) = 10.7$, H–C(2)); 5.34 (*d*, $J(1,2) = 3.6$, H–C(1)); 5.06 (*d*, $J = -12.5$, 1 H, PhCH_2); 4.93 (*d*, $J = -12.5$, 1 H, PhCH_2); 4.81 (*d*, $J = -11.3$, 1 H, PhCH_2); 4.77 (*d*, $J = -13.5$, 1 H, PhCH_2); 4.61 (*d*, $J = -12.5$, 1 H, PhCH_2); 4.61–4.57 (*m*, $J(6a',6b') = -14.2$, H_a–C(6′)); 4.48 (*d*, $J = -11.2$, 1 H, PhCH_2); 4.42–4.39 (*m*, H–C(4), H_a–C(6)); 4.30–4.19 (*m*, H–C(1′), H–C(5), H_b–C(6)); 4.15 (*d*, $J = -11.6$, 1 H, PhCH_2); 4.02 (br. *d*, $J(2',3') = 3.0$, H–C(2′)); 3.91 (*d*, $J = -11.5$, 1 H, PhCH_2); 3.86 (*dd*, H_b–C(6′)); 3.62 (*t*, $J(4',5') = 9.3$, H–C(4′)); 3.36 (br. *d*, $COCH_2$); 3.03 (*dd*, $J(3',4') = 9.0$, H–C(3′)). ^{13}C-NMR ($CDCl_3$): 165.8, 165.6, 165.3 (1 C, 1 C, 2 C, CO); 104.1 ($J(1',H–C(1')) = 158.7$, C(1′)); 95.9 (C(1)); 82.6 (C(3′)); 76.2 (C(4′)); 75.9 (C(4)); 75.0, 74.0 (PhCH_2); 72.9 (C(2′)); 71.0 (Ph*C*H_2); 70.7 (C(5′)); 70.5 (C(3)); 70.2 (Ph*C*H_2); 68.9 (C(2)); 66.5 (C(5)); 64.6 (C(6′)); 61.3 (C(6)); 42.4 ($COCH_2$). Anal. calc. for $C_{57}H_{54}O_{15}$ (979.05): C 69.93, H 5.56; found: C 69.88, H 5.55.

b) Exactly as described for **5** (*Exper. a*), with **16a** (0.44 g, 0.42 mmol), NIS (0.48 g, 2.12 mmol), Me_3SiOTf (19 µl, 0.11 mmol), and MeCN (12 ml): **17b** (205 mg, 50%).

c) Exactly as described for **5** (*Exper. c*), with **16a** (0.42 g, 0.40 mmol), MeOTf (0.22 ml, 2.0 mmol), and CH_2Cl_2 (12 ml): **17b** (214 mg, 55%).

d) Exactly as described for **5** (*Exper. d*), with **16a** (0.80 g, 0.77 mmol), MeOTf (0.95 ml, 3.85 mmol), and MeCN (15 ml): **17b** (410 mg, 55%).

Benzyl O*-(2,3,4-Tri-*O*-benzyl-α-*D*-mannopyranosyl)-(1→4)-2,3-di-*O*-benzoyl-α-*D*-galactopyranoside 6,6′-Succinate* (**18a**) *and Benzyl* O*-(2,3,4-Tri-*O*-benzyl-β-*D*-mannopyranosyl)-(1→4)-2,3-di-*O*-benzoyl-α-*D*-galactopyranoside 6,6′-Succinate* (**18b**). *a*) Exactly as described for **5** (*Exper. a*), with **16b** (0.46 g, 0.44 mmol), NIS (0.50 g, 2.20 mmol), Me_3SiOTf (20 µl, 110 µmol), and CH_2Cl_2 (15 ml), followed by CC (toluene/acetone 13:1): **18a** (29.3 mg, 7%), then **18b** (220 mg, 51%).

Data of **18a**: $[\alpha]_D = +98.5$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.70 (*dd*, $J(3,4) = 2.8$, H–C(3)); 5.62 (*dd*, $J(2,3) = 10.6$, H–C(2)); 5.38 (*d*, $J(1,2) = 3.7$, H–C(1)); 5.18 (*d*, $J(1',2') = 2.5$, H–C(1′)); 4.76–4.72 (*m*, 3 H, PhCH_2); 4.64 (*d*, $J = -11.5$, 1 H, PhCH_2); 4.63–4.57 (*m*, $J(6a',6b') = -11.4$, H–C(4), H_a–C(6′)); 4.60 (*s*, 1 H,

PhCH_2); 4.54 (d, $J=-11.7$, 1 H, PhCH_2); 4.45 (d, $J=-11.7$, 1 H, PhCH_2); 4.33 (d, $J=-11.6$, 1 H, PhCH_2); 4.30–4.23 (m, H–C(5), H_a–C(6)); 4.13–4.08 (m, H_b–C(6)); 3.94 (dd, J(5′,6b′) = 2.9, H_b–C(6′)); 3.85–3.80 (m, H–C(2′), H–C(3′); 3.64–3.60 (m, H–C(5′)); 3.56 (t, J(4′,5′) = 7.8, H–C(4′)); 2.82–2.61 (m, $COCH_2CH_2$-CO). ^{13}C-NMR ($CDCl_3$): 171.5, 170.4 ($COCH_2CH_2CO$); 166.1, 166.0 (PhCO), 96.0 (C(1)); 95.2 (J(1′,H–C(1′)) = 170.7, C(1′)); 79.2 (C(3′)); 76.0 (C(2′)); 74.8 (C(4′)); 73.9 (PhCH_2); 73.5 (PhCH_2); 72.9 (PhCH_2); 72.0 (C(5′)); 70.3 (C(3)); 70.1 (PhCH_2); 69.3 (C(2)); 67.6 (C(4)); 67.2 (C(5)); 63.3 (C(6′)); 61.7 (C(6)); 29.8, 29.5 ($COCH_2CH_2CO$). Anal. calc. for $C_{50}H_{56}O_{15}$ (993.08): C 70.15, H 5.68; found: C 70.30, H 5.75.

Data of **18b**: $[\alpha]_D = +83.5$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.78 (dd, J(3,4) = 2.6, H–C(3)); 5.73 (dd, J(2,3) = 10.6, H–C(2)); 5.33 (d, J(1,2) = 3.6, H–C(1)); 5.08 (d, $J=-12.5$, 1 H, PhCH_2); 4.93 (d, $J=-12.5$, 1 H, PhCH_2); 4.81 (d, $J=-10.7$, 1 H, PhCH_2); 4.79 (d, $J=-12.3$, 1 H, PhCH_2); 4.62 (d, $J=-12.4$, 1 H, PhCH_2); 4.51 (t, J(6a′,6b′) = –10.2, H_a–C(6′)); 4.45 (d, $J=-10.8$, 1 H, PhCH_2); 4.42 (br. s, H–C(4)); 4.33–4.24 (m, H–C(5), H_a–C(6)); 4.24 (s, H–C(1′)); 4.17 (d, $J=-11.5$, 1 H, PhCH_2); 4.11–3.99 (m, J(2′,3′) = 3.0, H–C(2′), H_b–C(6′), H_b–C(6)); 3.91 (d, $J=-11.4$, 1 H, PhCH_2); 3.57 (t, J(4′,5′) = 9.4, H–C(4′)); 3.33 (dt, J(5′,6a′) = 10.0, J(5′,6b′) = 2.3, H–C(5′)); 3.03 (dd, J(3′,4′) = 9.2, H–C(3′)); 2.88–2.41 (m, $COCH_2CH_2$-CO). ^{13}C-NMR ($CDCl_3$): 171.7, 170.8 ($COCH_2CH_2CO$); 165.8, 165.6 (PhCO); 103.8 (J(1′,H–C(1′)) = 154.0, C(1′)); 95.9 (C(1)); 82.5 (C(3′)); 76.4 (C(4)); 75.2 (PhCH_2); 75.0 (C(4′)); 74.1 (PhCH_2); 73.2 (2 C, C(2′), C(5′)); 71.0 (C(3)); 70.0 (PhCH_2); 68.8 (C(2)); 66.9 (C(5)); 64.7 (C(6)); 61.3 (C(6′)); 30.0, 29.4 ($COCH_2CH_2CO$). Anal. calc. for $C_{58}H_{56}O_{15}$ (993.08): C 70.15, H 5.68; found: C 69.92, H 5.71.

b) Exactly as described for **5** (*Exper. a*), with **16b** (0.47 g, 0.45 mmol), NIS (0.47 g, 1.45 mmol), Me_3SiOTf (20 µl, 0.11 mmol), and MeCN (15 ml), followed by CC (toluene/acetone 13:1): **18a** (22.8 mg, 5%) and **18b** (228 mg, 51%).

c) Exactly as described for **5** (*Exper. c*), with **16b** (0.50 g, 0.49 mmol), MeOTf (0.26 ml, 2.39 mmol), and CH_2Cl_2 (20 ml), followed by (toluene/acetone 13:1): **18a** (24 mg, 5%) and **18b** (244 mg, 50%).

d) Exactly as described for **5** (*Exper. d*), with **16b** (0.52 g, 0.49 mmol), MeOTf (0.27 ml, 2.45 mmol), and MeCN (15 ml): **18b** (260 mg, 54%).

Benzyl O-*(6-*O-*Benzoyl-2,3,4-tri-*O-*benzyl-α-*D-*mannopyranosyl)-(1 → 4)-2,3,6-tri-*O-*benzoyl-α-*D-*galacto-pyranoside* (**19a**). Exactly as described for **6**, with **18a** (85 mg, 0.09 mmol), NaOMe in MeOH, BzCl (0.06 ml, 0.51 mmol), and pyridine (5 ml): **19a** (70.1 mg, 73%). $[\alpha]_D = +56.8$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.75 (dd, J(3,4) = 3.0, H–C(3)); 5.64 (dd, J(2,3) = 10.4, H–C(2)); 5.42 (d, J(1′,2′) = 2.6, H–C(1′)); 5.39 (d, J(1,2) = 3.6, H–C(1)); 4.85 (d, $J=-12.5$, 1 H, PhCH_2); 4.79 (d, $J=-11.8$, 1 H, PhCH_2); 4.78 (d, $J=-12.1$, 1 H, PhCH_2); 4.77–4.70 (m, H–C(4)); 4.71–4.67 (m, H_a–C(6)); 4.62–4.59 (m, J(6a′,6b′) = –11.7, H_a–C(6′), H_b–C(6)); 4.61 (d, $J=-11.7$, 1 H, PhCH_2); 4.56 (d, $J=-11.8$, 1 H, PhCH_2); 4.47–4.43 (m, H–C(5)); 4.44 (d, $J=-11.7$, 1 H, PhCH_2); 4.42 (d, $J=-11.5$, 1 H, PhCH_2); 4.38 (dd, J(5′,6b′) = 2.0, 1 H, H_b–C(6′)); 4.30 (d, $J=-12.0$, 1 H, PhCH_2); 4.05–4.00 (m, H–C(3′)); 3.96 (t, J(4′,5′) = 9.3, H–C(4′)); 3.88–3.83 (m, H–C(2′)); 3.65–3.61 (m, H–C(5′)). ^{13}C-NMR ($CDCl_3$): 166.3, 165.8, 165.7, 165.5 (PhCO); 95.4 (C(1)); 93.8 (J(1′,H–C(1′)) = 174.2, C(1′)); 78.8 (C(3′)); 76.3 (C(2′)); 74.0, 73.6 (PhCH_2); 73.4 (C(4′)); 73.0 (PhCH_2); 71.4 (C(5′)); 71.0 (PhCH_2); 70.1 (C(3)); 69.4 (C(2)); 68.5 (C(5)); 66.0 (C(4)); 65.2 (C(6′)); 61.2 (C(6)). Anal. calc. for $C_{68}H_{62}O_{15}$ (1119.24): C 72.97, H 5.58; found: C 72.86, H 5.50.

Benzyl O-*(6-*O-*Benzoyl-2,3,4-tri-*O-*benzyl-β-*D-*mannopyranosyl)-(1 → 4)-2,3,6-tri-*O-*benzoyl-α-*D-*galacto-pyranoside* (**19b**). *a*) Exactly as described for **6**, with **17b** (0.30 g, 0.31 mmol), NaOMe in MeOH, BzCl (0.21 ml, 1.83 mmol), and pyridine (4 ml): **19b** (251 mg, 72%). $[\alpha]_D = +48.9$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.85 (dd, J(3,4) = 3.0, H–C(3)); 5.75 (dd, J(2,3) = 10.6, H–C(2)); 5.34 (d, J(1,2) = 3.5, H–C(1)); 5.17 (d, $J=-12.2$, 1 H, PhCH_2); 4.97 (d, $J=-12.2$, 1 H, PhCH_2); 4.86 (d, $J=-10.6$, 1 H, PhCH_2); 4.74–4.68 (m, H_a–C(6)); 4.72 (d, $J=-12.2$, 1 H, PhCH_2); 4.60–4.50 (m, 2 H, H–C(4), H_b–C(6)); 4.52 (d, $J=-10.7$, 1 H, PhCH_2); 4.50 (d, $J=-12.0$, 1 H, PhCH_2); 4.50–4.45 (m, H–C(5), 2 H–C(6′)); 4.42 (d, $J=-11.7$, 1 H, PhCH_2); 4.22 (d, $J=-11.7$, 1 H, PhCH_2); 4.08 (br. d, J(2′,3′) = 2.8, H–C(2′)); 3.96 (t, J(4′,5′) = 9.6, H–C(4′)); 3.34 (dt, J(5′,6a′) = 3.5, J(5′,6b′) = 9.6, H–C(5′)); 3.23 (dd, J(3′,4′) = 9.4, H–C(3′)). ^{13}C-NMR ($CDCl_3$): 166.2, 165.9, 165.4 (1 C, 2 C, 1 C, CO); 102.4 (J(1′,H–C(1′)) = 158.2, C(1′)); 95.3 (C(1)); 82.1 (C(3′)); 75.3 (PhCH_2); 74.8 (C(4)); 74.2 (PhCH_2); 73.9, 73.8 (C(4′), C(5′)); 73.5 (C(2′)); 71.0 (PhCH_2); 70.8 (C(3)); 69.3 (PhCH_2); 68.9 (C(2)); 68.2 (C(5)); 64.2 (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 72.89, H 5.51.

b) Exactly as described for **6**, with **18b** (0.10 g, 0.10 mmol), NaOMe in MeOH, BzCl (0.07 ml, 0.6 mmol), and pyridine (8 ml): **19b** (84.2 mg, 74%).

*Benzyl 3-*O-*Benzyl-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-*mannopyranoside* (**21**). As described for **3** (*Exper. b*), with **1a** [1] (1.92 g, 3.31 mmol), **20** [29] (1.48 g, 3.30 mmol), DCC (0.68 g, 3.30 mmol), DMAP, and CH_2Cl_2 (50 ml), followed by CC (toluene/acetone 40:1): **21** (2.19 g, 66%). $[\alpha]_D = +50.2$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.62 (s, PhCH); 5.47

(*dd*, *J*(2,3) = 2.9, H–C(2)); 5.33 (*d*, *J*(1′,2′) = 1.1, H–C(1′)); 4.95 (*d*, *J*(1,2) = 1.6, H–C(1)); 4.93 (*d*, *J* = – 10.0, 1 H, PhCH_2); 4.70 (*d*, *J* = – 12.2, 1 H, PhCH_2); 4.68 (*s*, 1 H, PhCH_2); 4.66 (*d*, *J* = – 11.7, 1 H, PhCH_2); 4.63 (*d*, *J* = – 12.2, 1 H, PhCH_2); 4.60 (*d*, *J* = – 10.9, 1 H, PhCH_2); 4.56 (*s*, 3 H, PhCH_2); 4.48 (*d*, *J* = – 11.8, 1 H, PhCH_2); 4.44 – 4.41 (*m*, 2 H–C(6′)); 4.23 – 4.17 (*m*, *J*(5,6a) = 10.2, H–C(5′), H_a–C(6)); 4.50 – 4.03 (*m*, H–C(3), H–C(4)); 3.93 (*t*, *J*(4′,5′) = 9.4, H–C(4′)); 3.86 – 3.82 (*m*, H–C(2′), H–C(3′, H–C(5′)); 4.80 (*t*, *J*(6a,6b) = – 10.2, H_b–C(6)); 3.52 (*d*, *J* = – 16.2, 1 H, COCH_2); 3.45 (*d*, *J* = – 16.2, 1 H, COCH_2); 2.63 – 2.49 (*m*, MeCH_2S); 1.23 (*t*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 166.0, 165.5 (*C*OCH_2); 101.4 (Ph*C*H); 97.9 (C(1)); 81.9 (C(1′)); 80.3 (C(3′)); 78.2 (C(4)); 76.1 (C(2′)); 75.2 (PhCH_2); 74.5 (C(4′)); 73.7 (C(3)); 72.1 (PhCH_2); 72.0 (2 C, PhCH_2); 70.8 (C(2)); 70.1 (C(5′)); 69.7 (PhCH_2); 68.6 (C(6)); 64.5 (C(6′)); 64.0 (C(5)); 41.0 (CO*C*H_2); 25.4 (Me*C*H_2S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{59}H_{62}O_{13}$ (1011.20): C 70.08, H 6.18, S 3.17; found: C 70.24, H 6.24, S 3.24.

Benzyl 3,6-Di-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-*mannopyranoside* (**22**). As described for **3** (*Exper. a*), with **21** (1.59 g, 1.57 mmol) and $NaCNBH_3$ (1.24 g, 19.63 mmol): **14a** (1.10 g, 69%). $[\alpha]_D$ = +37.3 (*c* = 0.98, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.41 (*dd*, *J*(2,3) = 2.8, H–C(2)); 5.31 (*d*, *J*(1′,2′) = 1.0, H–C(1′)); 4.96 (*d*, *J*(1,2) = 1.8, H–C(1)); 4.90 (*d*, *J* = – 10.8, 1 H, PhCH_2); 4.71 (*d*, *J* = – 11.2, 1 H, PhCH_2); 4.70 (*d*, *J* = – 11.7, 1 H, PhCH_2); 4.66 (*d*, *J* = – 11.7, 1 H, PhCH_2); 4.64 (*d*, *J* = – 12.4, 1 H, PhCH_2); 4.59 – 4.53 (*m*, 5 H, PhCH_2); 4.48 (*d*, *J* = – 11.7, 1 H, PhCH_2); 4.41 (*d*, *J* = – 11.3, 1 H, PhCH_2); 4.39 (br. *d*, 2 H–C(6′)); 4.20 – 4.14 (*m*, H–C(5′)); 3.91 (*t*, *J*(4,5) = 9.4, H–C(4)); 3.85 – 3.78 (*m*, 5 H, H–C(2′), H–C(3′), H–C(3), H–C(4′), H–C(5)); 3.73 – 3.71 (*m*, 2 H–C(6)); 3.43 (*s*, COCH_2); 2.61 – 2.46 (*m*, MeCH_2S); 2.35 (*s*, OH); 1.21 (*t*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 166.0, 165.7 (*C*OCH_2); 97.0 (C(1)); 82.0 (C(1′)); 80.3 (C(3′)); 77.4 (C(3)); 76.1 (C(2′)); 75.1 (PhCH_2); 74.6 (C(4′)); 73.5 (PhCH_2); 72.0 (2 C, PhCH_2); 71.6 (PhCH_2); 71.4 (C(5′)); 70.1 (C(5)); 69.8 (PhCH_2); 69.3 (C(6)); 69.1 (C(2)); 64.5 (C(6′)); 41.0 (CO*C*H_2); 25.4 (Me*C*H_2S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{59}H_{64}O_{13}S$ (1013.22): C 69.94, H 6.37, S 3.16; found: C 70.03, H 6.35, S 3.22.

Benzyl O-*(2,3,4-Tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1 → 4)-3,6-di*-O-*benzyl-α*-D-*mannopyranoside 2,6′-Malonate* (**23**). *a*) Exactly as described for **5** (*Exper. a*), with **22** (0.33 g, 0.33 mmol), NIS (0.37 g, 1.65 mmol), Me_3SiOTf (15 µl, 83 µmol), and CH_2Cl_2 (10 ml), followed by CC (toluene/AcOEt 15 : 1): **23** (217 mg, 69%). $[\alpha]_D$ = +23.8 (*c* = 0.63, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.45 (*t*, *J*(2,3 = 1.9, H–C(2)); 5.40 (*d*, *J*(1′,2′) = 1.9, H–C(1′)); 4.97 (*d*, *J*(1,2) = 1.8, H–C(1)); 4.83 (*d*, *J* = – 11.6, 1 H, PhCH_2); 4.80 (*d*, *J* = – 11.9, 1 H, PhCH_2); 4.75 (*dd*, *J*(5′,6a′) = 8.6, H_a–C(6′)); 4.73 (*d*, *J* = – 11.9, 1 H, PhCH_2); 4.57 – 4.43 (*m*, 7 H, PhCH_2); 4.55 – 4.43 (*m*, *J*(4,5) = 10.0, H–C(4)); 4.40 (*d*, *J* = – 12.4, 1 H, PhCH_2); 4.30 (*d*, *J* = – 11.9, 1 H, PhCH_2); 4.08 (br. *t*, H–C(5′)); 4.00 – 3.93 (*m*, *J*(6a′,6b′) = H–C(3), H_b–C(6′)); 3.78 (*dt*, *J*(5,6a) = 5.5, H–C(5)); 3.66 (*t*, *J*(4′,5′) = 8.3, H–C(4′)); 3.65 – 3.56 (*m*, H–C(2′), H–C(3′), 2 H–C(6)); 3.55 (*d*, *J* = – 11.3, 1 H, COCH_2); 3.25 (*d*, *J* = – 11.3, 1 H, COCH_2). ^{13}C-NMR ($CDCl_3$): 164.5, 164.1 (*C*OCH_2*C*O); 96.5 (C(1)); 95.1 (*J*(1′,H–C(1′)) = 170.7, C(1′)); 79.4 (C(3′)); 79.1 (C(3)); 75.0 (C(2′)); 74.8 (C(4′)); 74.4 (PhCH_2); 73.4 (PhCH_2); 72.7 (C(5)); 72.4 (PhCH_2); 71.7 (PhCH_2); 71.3 (C(5′)); 70.5 (C(2)); 70.4 (PhCH_2); 69.0 (PhCH_2); 68.8 (C(6)); 65.1 (C(4)); 64.5 (C(6′)); 43.4 (CO*C*H_2). Anal. calc. for $C_{57}H_{58}O_{13}$ (951.09): C 71.98, H 6.15; found: C 71.86, H 6.11.

b) Exactly as described for **5** (*Exper. a*), with **22** (0.34 g, 0.34 mmol), NIS (0.38 g, 1.70 mmol), Me_3SiOTf (15 µl, 83 µmol), and MeCN (10 ml), followed by CC (toluene/AcOEt 15 : 1): **23** (221 mg, 68%).

c) Exactly as described for **5** (*Exper. c*), with **22** (0.36 g, 0.36 mmol), MeOTf (0.20 ml, 1.80 mmol), and CH_2Cl_2 (12 ml), followed by CC (toluene/AcOEt 15 : 1): **23** (228 mg, 67%).

d) Exactly as described for **5** (*Exper. d*), with **22** (0.41 g, 0.41 mmol), MeOTf (0.23 ml, 2.05 mmol), and MeCN (15 ml): **23** (267 mg, 65%).

Benzyl O-*(6*-O-*Benzoyl-2,3,4-tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1 → 4)-2*-O-*benzoyl-3,6-di*-O-*benzyl-α*-D-*mannopyranoside* (**24**). Exactly as described for **6**, with **23** (0.11 g, 0.12 mmol), NaOMe in MeOH, BzCl (34 µl, 0.29 mmol), and pyridine (6 ml): **24** (93.3 mg, 73%). $[\alpha]_D$ = +14.6 (*c* = 1.01, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.66 (*dd*, *J*(2,3) = 2.9, H–C(2)); 5.26 (*d*, *J*(1′,2′) = 1.9, H–C(1′)); 5.08 (*d*, *J*(1,2) = 1.8, H–C(1)); 4.88 (*d*, *J* = – 10.7, 1 H, PhCH_2); 4.80 (2*d*, 1 H each, *J* = – 10.4, – 11.7, PhCH_2); 4.67 (*d*, *J* = – 11.7, 1 H, PhCH_2); 4.63 (*d*, *J* = – 12.5, 1 H, PhCH_2); 4.61 (*d*, *J* = – 12.7, 1 H, PhCH_2); 4.59 (*s*, 4 H, PhCH_2); 4.58 (*d*, *J* = – 10.3, 1 H, PhCH_2); 4.56 – 4.52 (*m*, *J*(4,5) = 9.5, H–C(4)); 4.45 (*dd*, *J*(5′,6a′) = 3.5, *J*(6a′,6b′) = – 11.9, H_a–C(6a′)); 4.35 – 4.31 (*m*, *J*(5′,6b′) = 2.0, H_b–C(6′)); 4.32 (*d*, *J* = – 10.9, 1 H, PhCH_2); 4.19 – 4.05 (*m*, H–C(4′), H–C(5), H–C(5′)); 4.02 (*dd*, *J*(3,4) = 9.1, H–C(3)); 3.90 (*dd*, *J*(3′,4′) = 9.5, H–C(3′)); 3.87 – 3.81 (*m*, 2 H–C(6)); 3.70 – 3.67 (*m*, H–C(2′)). ^{13}C-NMR ($CDCl_3$): 166.3 (Ph*C*O); 100.1 (*J*(1′,H–C(1′)) = 171.0); 96.9 (C(1)); 79.8 (C(3′)); 78.5 (C(3)); 75.8 (C(2′)); 75.2 (PhCH_2); 74.6, 73.9 (C(4), C(4′)); 73.4, 72.0 (1 C, 2 C, PhCH_2); 71.3, 71.2 (C(5), C(5′)); 71.1 (PhCH_2); 69.6 (2 C, PhCH_2, C(6)); 68.1 (C(2)); 63.6 (C(6′)). Anal. calc. for $C_{68}H_{66}O_{14}$ (1107.27): C 73.76, H 6.01; found: C 73.84, H 5.98.

*Benzyl 2-*O*-Benzoyl-4,6-*O*-benzylidene-α-*D*-mannopyranoside* (**26**). At −5°, 5% aq. NaOH soln. (37.31 ml) was added to a soln. of BzCl (2.56 ml, 22.07 mmol), benzyl 4,6-*O*-benzylidene-α-D-mannopyranoside (**25**) [29] (5.33 g, 14.87 mmol), and $Bu_4N(HSO_4)$ (1.03 g, 3.02 mmol) in CH_2Cl_2 (250 ml) and vigorously stirred for 1.5 h. The org. layer was separated, washed with H_2O, dried, and evaporated. CC (toluene/AcOEt 15:1) of the residue afforded **26** (3.97 g, 58%). $[\alpha]_D = +10.5$ ($c = 2.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.59 (*s*, PhCH); 5.45 (*dd*, *J*(2,3) = 3.6, H−C(2)); 5.00 (*d*, *J*(1,2) = 1.4, H−C(1)); 4.70 (*d*, *J* = −11.8, 1 H, PhCH_2); 4.51 (*d*, *J* = −11.8, 1 H, PhCH_2); 4.30 (*dd*, *J*(3,4) = 9.6, H−C(3)); 4.24 (*dd*, *J*(5,6a) = 4.2, *J*(6a,6b) = 9.8, H_a−C(6)); 4.02 (*t*, *J*(4,5) = 9.5, H−C(4)); 3.92 (*dt*, H−C(5)); 3.82 (*t*, *J*(5,6b) = 9.7, H_b−C(6)); 2.82 (br. *s*, OH). ^{13}C-NMR ($CDCl_3$): 166.0 (Ph*C*O); 102.2 (Ph*C*H); 98.0 (C(1)); 79.4 (C(4)); 72.6 (C(2)); 69.8 (Ph*C*H_2); 68.8 (C(6)); 67.5 (C(3)); 63.6 (C(5)). Anal. calc. for $C_{27}H_{26}O_7$ (462.50): C 70.12, H 5.67; found: C 70.07, H 5.67.

*Benzyl 2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-[3-(ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-*D*-mannopyranosid-6-*O*-yl)-1,3-dioxopropyl]-α-*D*-mannopyranoside* (**27**). As described for **3** (*Exper. b*), with **1a** [1] (1.37 g, 2.36 mmol), **26** (1.09 g, 2.36 mmol), DCC (0.49 g, 2.36 mmol), DMAP, and CH_2Cl_2 (40 ml), followed by CC (toluene/acetone 50:1): **27** (1.53 g, 63%). $[\alpha]_D = +27.1$ ($c = 1.4$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.63–5.60 (*m*, H−C(2), H−C(3)); 5.59 (*s*, PhC*H*); 5.29 (*s*, H−C(1′)); 5.02 (*d*, *J*(1,2) = 1.0, H−C(1)); 4.85 (*d*, *J* = −10.8, 1 H, PhCH_2); 4.75 (*d*, *J* = −11.9, 1 H, PhCH_2); 4.68 (*d*, *J* = −12.4, 1 H, PhCH_2); 4.61 (*d*, *J* = −12.4, 1 H, PhCH_2); 4.59 (*d*, *J* = −11.9, 1 H, PhCH_2); 4.54 (*s*, 2 H, PhCH_2); 4.52 (*d*, *J* = −12.2, 1 H, PhCH_2); 4.26 (*dd*, 1 H, *J*(6a,6b) = −10.0, H_a−C(6)); 4.23–4.18 (*m*, 2 H−C(6′)); 4.16–4.14 (*m*, H−C(4)); 4.10–4.02 (*m*, H−C(5′)); 4.04 (*dt*, *J*(5,6a) = 4.6, *J*(5,6b) = 9.7, H−C(5)); 3.87 (*t*, *J*(4′,5′) = 10.0, H−C(4′)); 3.81–3.77 (*m*, *J*(3′,4′) = 10.0, H−C(2′), H−C(3′), H_b−C(6)); 3.34 (*d*, *J* = −16.1, 1 H, COCH_2); 3.27 (*d*, *J* = −16.1, 1 H, COCH_2); 2.58–2.43 (*m*, 2 H, MeCH_2S); 1.19 (*t*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 165.6, 165.3, 165.2 (CO); 101.8 (Ph*C*H); 96.9 (C(1)); 80.9 (C(1′)); 79.4 (C(3′)); 75.5, 75.2 (C(4), C(2′)); 74.2 (Ph*C*H_2); 73.8 (C(4′)); 71.1 (2 C, Ph*C*H_2); 69.7 (C(5′)); 69.2 (C(2)); 69.0 (Ph*C*H_2); 68.8 (C(3)); 67.9 (C(6)); 63.6 (C(6′)); 63.2 (C(5)); 40.0 (CO*C*H_2); 24.5 (Me*C*H_2S); 14.1 (*Me*CH_2S). Anal. calc. for $C_{59}H_{60}O_{14}S$ (1025.18): C 69.12, H 5.90, S 3.13; found: C 69.38, H 5.96, S 3.20.

*Benzyl-2-*O*-Benzoyl-6-*O*-benzyl-3-*O*-[3-(ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-*D*-mannopyranosid-6-*O*-yl)-1,3-dioxopropyl]-α-*D*-mannopyranoside* (**28**). As described for **3** (*Exper. a*), with **27** (1.08 g, 1.05 mmol) and $NaCNBH_3$ (0.83 g, 13.13 mmol): **28** (0.80 g, 74%). $[\alpha]_D = +58.7$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.52 (br. *d*, *J*(2,3) = 3.3, H−C(2)); 5.45 (*dd*, *J*(3,4) = 9.7, H−C(3)); 5.28 (*s*, H−C(1′)); 5.02 (*d*, *J*(1,2) = 1.4, H−C(1)); 4.87 (*d*, *J* = −11.0, 1 H, PhCH_2); 4.76 (*d*, *J* = −12.0, 1 H, PhCH_2); 4.68 (*d*, *J* = −11.9, 1 H, PhCH_2); 4.63 (*d*, *J* = −12.1, 1 H, PhCH_2); 4.60 (*s*, 1 H, PhCH_2); 4.58 (*d*, *J* = −12.0, 1 H, PhCH_2); 4.55 (*d*, *J* = −10.6, 1 H, PhCH_2); 4.54 (*s*, 2 H, PhCH_2); 4.53 (*d*, *J* = −10.7, 1 H, PhCH_2); 4.30 (*dd*, *J*(5′,6a′) = 2.5, *J*(6a′,6b′) = −11.9, H_a−C(6′)); 4.27–4.23 (*m*, H_b−C(6′)); 4.18 (*t*, *J*(4,5) = 9.8, H−C(4)); 4.14–4.08 (*m*, H−C(5′)); 3.98–3.93 (*m*, *J*(5,6a) = 2.7, *J*(5,6b) = 4.2, H−C(5)); 3.90–3.83 (*m*, *J*(2′,3′) = 3.0, H−C(2′)); 3.79–3.76 (*m*, 3 H, H−C(3′), 2 H−C(6)); 3.33 (*s*, COCH_2); 2.58–2.42 (*m*, MeCH_2S); 2.35 (*s*, OH); 1.15 (*t*, *J* = 7.4, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 166.6 (CO); 165.5 (2 C, CO); 96.8 (C(1)); 81.9 (C(1′)); 80.2 (C(3′)); 75.9 (C(2′)); 75.0 (Ph*C*H_2); 74.1 (C(4′)); 73.7 (C(3)); 73.6 (Ph*C*H_2); 71.9 (1 C, 2 C, C(5), Ph*C*H_2); 70.2 (C(5′)); 69.8 (C(2)); 69.4 (2 C, C(6), Ph*C*H_2); 65.8 (C(4)); 64.4 (C(6′)); 41.4 (CO*C*H_2); 25.2 (Me*C*H_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 69.04, H 6.07.

Benzyl O*-(2,3,4-Tri-*O*-benzyl-α-*D*-mannopyranosyl)-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-*D*-mannopyranoside 3,6′-Malonate* (**29a**) *and Benzyl* O*-(2,3,4-Tri-*O*-benzyl-β-*D*-mannopyranosyl)-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-*D*-mannopyranoside 3,6′-Malonate* (**29b**). *a*) Exactly as described for **5** (*Exper. a*), with **28** (0.41 g, 0.40 mmol), with NIS (0.45 g, 2.0 mmol), Me_3SiOTf (18 µl, 100 µmol), and CH_2Cl_2 (12 ml), followed by CC (toluene/acetone 20:1): **29a** (192 mg, 50%), then **29b** (77 mg, 20%).

Data of **29a**: $[\alpha]_D = +32.2$ ($c = 0.8$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.87 (br. *t*, *J*(2,3) = 2.6, H−C(2)); 5.38 (*dd*, *J*(3,4) = 11.1, H−C(3)); 4.96 (*s*, H−C(1)); 4.93 (*dd*, *J*(6a′,6b′) = −10.8, H_a−C(6′)); 4.88 (*s*, *d*, 1 H each, *J* = −11.5, H−C(1′), PhCH_2); 4.78 (*d*, *J* = −12.1, 1 H, PhCH_2); 4.62 (*d*, *J* = −11.6, 1 H, PhCH_2); 4.61 (*d*, *J* = −11.8, 1 H, PhCH_2); 4.58 (*d*, *J* = −11.8, 1 H, PhCH_2); 4.57–4.51 (*m*, 3 H, PhCH_2); 4.47 (*d*, *J* = −11.9, 1 H, PhCH_2); 4.46 (*d*, *J* = −11.7, 1 H, PhCH_2); 4.41–4.37 (*m*, *J*(4,5) = 10.9, H−C(4)); 4.01 (*dt*, *J*(5′,6a′) = 2.5, *J*(5′,6b′) = 10.8, H−C(5′)); 3.75 (*dd*, *J*(3′,4′) = 9.1, H−C(3′)); 3.62 (*t*, H_b−C(6′)); 3.60 (*t*, *J*(4′,5′) = 9.6, H−C(4′)); 3.54–3.51 (*m*, *J*(5,6a) = 1.8, H−C(5)); 3.46 (*dd*, *J*(6a,6b) = −10.9, H_a−C(6)); 3.36 (br. *d*, *J*(2′,3′) = 3.2, H−C(2′), H_b−C(6)); 3.35 (*d*, *J* = −14.1, 1 H, COCH_2); 3.16 (*d*, *J* = −14.1, 1 H, COCH_2). ^{13}C-NMR ($CDCl_3$): 165.7, 165.4, 165.1 (CO); 96.3 (C(1)); 92.8 (*J*(1′,H−C(1′)) = 166.3, C(1′)); 79.2 (C(3′)); 75.5 (C(2′), C(4′)); 74.5 (Ph*C*H_2); 73.8 (Ph*C*H_2); 73.1 (Ph*C*H_2); 72.7 (Ph*C*H_2); 70.6 (C(4)); 69.8 (2 C, C(2), C(3)); 69.5 (Ph*C*H_2); 69.2 (C(5′), C(5)); 96.1 (C(6)); 64.6 (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 70.73, H 5.86.

Data of **29b** (77 mg, 20%). $[\alpha]_D = +18.8$ ($c = 0.8$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.64 (*dd*, *J*(2,3) = 3.3, H–C(2)); 5.40 (*dd*, *J*(3,4) = 9.3, H–C(3)); 5.00 (*s*, *J*(1,2) = 2.0, H–C(1)); 4.85 (*d*, *J* = –11.3, 1 H, PhCH_2); 4.76 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.73–4.68 (*m*, 3 H, PhCH_2); 4.63 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.57–4.51 (*m*, 3 H, PhCH_2); 4.55 (br. *s*, H_a–C(6′)); 4.30 (*d*, *J* = –12.2, 1 H, PhCH_2); 4.15–4.10 (*m*, H–C(1′), H–C(4)); 3.88–3.81 (*m*, H_b–C(6′)); 3.77–3.73 (*m*, H–C(5)); 3.69–3.66 (*m*, H–C(4′), H–C(5′)); 3.44 (br. *d*, H–C(2′), H_a–C(6)); 3.36–3.32 (*m*, 3 H, H–C(3′), H_b–C(6), $COCH_2$); 3.16 (*d*, *J* = –13.8, 1 H, $COCH_2$). ^{13}C-NMR ($CDCl_3$): 165.9, 165.5, 164.7 (CO); 103.4 (*J*(1′, H–C(1′)) = 150.9, C(1′)); 96.7 (C(1)); 82.8 (C(3′)); 76.8, 76.7 (C(4), C(4′)); 74.8 (Ph*C*H_2); 74.7 (C(2′)); 73.9 (Ph*C*H_2); 73.5 (Ph*C*H_2); 72.9 (C(3)); 72.4 (Ph*C*H_2); 70.8 (C(5)); 70.2 (C(5′)); 69.6 (Ph*C*H_2); 69.4 (C(2)); 68.3 (C(6)); 64.6 (C(6′)); 42.8 (CO*C*H_2). Anal. calc. for $C_{57}H_{56}O_{14}$ (965.07): C 70.94, H 5.85; found: C 70.61, H 5.86.

b) Exactly as described for **5** (*Exper. a*), with **28** (0.36 g, 0.35 mmol), NIS (0.40 g, 1.75 mmol), Me_3SiOTf (14 µl, 80 µmol), and MeCN (10 ml), followed by CC (toluene/acetone 20:1): **29a** (158 mg, 47%) and **29b** (79 mg, 23%).

c) Exactly as described for **5** (*Exper. c*), with **28** (0.39 g, 0.38 mmol), MeOTf (0.29 ml, 2.66 mmol), and CH_2Cl_2 (10 ml), followed by CC (toluene/acetone 20:1): **29a** (147 mg, 40%) and **29b** (99 mg, 27%).

d) Exactly as described for **5** (*Exper. d*), with **28** (0.65 g, 0.64 mmol), MeOTf (0.48 ml, 4.41 mmol), and MeCN (15 ml): **29a** (218 mg, 36%) and **29b** (219 mg, 36%).

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-*mannopyranoside* (**30a**). Exactly as described for **6**, with **29a** (0.10 g, 0.11 mmol), NaOMe in MeOH, BzCl (75 µl, 0.65 mmol), and pyridine (6 ml): **30a** (81.5 mg, 68%). $[\alpha]_D = +25.8$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.79 (*dd*, *J*(3,4) = 9.6, H–C(3)); 5.63 (*dd*, *J*(2,3) = 3.3, H–C(2)); 5.21 (*d*, *J*(1′,2′) = 2.0, H–C(1′)); 5.09 (*d*, *J*(1,2) = 1.8, H–C(1)); 4.85 (*d*, *J* = –10.8, 1 H, PhCH_2); 4.83 (*d*, *J* = –11.9, 1 H, PhCH_2); 4.65 (*d*, *J* = –11.6, 1 H, PhCH_2); 4.63 (*s*, 2 H, PhCH_2); 4.52 (br. *d*, *J* = –11.8, 2 H, PhCH_2); 4.47 (*d*, *J* = –11.8, 1 H, PhCH_2); 4.46 (*dd*, *J*(6a′,6b′) = –11.9, H_a–C(6′)); 4.45 (*t*, *J*(4,5) = 9.7, H–C(4)); 4.36 (*dd*, H_b–C(6′)); 4.16 (*d*, *J* = –11.8, 1 H, PhCH_2); 4.08–4.02 (*m*, 3 H, H–C(4′), H–C(5), PhCH_2); 3.94–3.89 (*m*, *J*(5′,6a′) = 3.2, *J*(5′,6b′) = 2.0, *J*(5,6b) = 1.7, *J*(6a,6b) = –10.8, H–C(5′), H_a–C(6)); 3.86 (*dd*, *J*(3′,4′) = 9.2, H–C(3′)); 3.80 (*dd*, H_b–C(6)); 3.56 (br. *t*, *J*(2′,3′) = 2.8, H–C(2′)). ^{13}C-NMR ($CDCl_3$): 166.3, 165.4, 165.2 (Ph*C*O); 100.2 (*J*(1′,H–C(1′)) = 170.6, C(1′)); 96.7 (C(1)); 79.7 (C(3′)); 75.6 (C(2′)); 75.2 (Ph*C*H_2); 73.7 (C(4′)); 73.5 (2 C, C(4), Ph*C*H_2); 72.8 (C(3)); 72.4 (Ph*C*H_2); 71.8 (Ph*C*H_2); 70.6 (C(2)); 69.7 (Ph*C*H_2); 69.2 (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 74.10, H 5.82.

Benzyl O-*(6*-O-*Benzoyl-2,3,4-tri*-O-*benzyl-β*-D-*mannopyranosyl)-(1→4)-2,3-di*-O-*benzoyl-6*-O-*benzyl-α*-D-*mannopyranoside* (**30b**). Exactly as described for **6**, with **29b** (0.07 g, 0.07 mmol), NaOMe in MeOH, BzCl (48 µl, 0.04 mmol), and pyridine (4 ml): **30b** (55.1 mg, 73%). $[\alpha]_D = +2.9$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.88 (*dd*, *J*(3,4) = 9.9, H–C(3)); 5.61 (*dd*, *J*(2,3) = 3.4, H–C(2)); 5.07 (*d*, *J*(1,2) = 1.8, H–C(1)); 4.84 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.78 (*d*, *J* = –10.8, 1 H, PhCH_2); 4.76 (*d*, *J* = –11.8, 1 H, PhCH_2); 4.74 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.67 (*d*, *J* = –12.0, 1 H, PhCH_2); 4.62 (*d*, *J* = –12.1, 1 H, PhCH_2); 4.56 (*t*, *J*(4,5) = 10.0, H–C(4)); 4.51 (*s*, 2 H, PhCH_2); 4.47 (*d*, *J* = –11.7, 1 H, PhCH_2); 4.40 (*d*, *J* = –11.4, 1 H, PhCH_2); 4.28 (*dd*, *J*(6a′,6b′) = –11.9, H_a–C(6′)); 4.02 (*dd*, H_b–C(6′)); 4.01–3.98 (*m*, *J*(5,6b) = 2.0, H–C(5)); 3.89 (*t*, *J*(4′,5′) = 9.6, H–C(4′)); 3.78–3.72 (*m*, *J*(2′,3′) = 2.8, *J*(6a,6b) = –11.2, H–C(2′), H_a–C(6)); 3.69 (*dd*, H_b–C(6)); 3.38 (*dd*, *J*(3′,4′) = 9.3, H–C(3′)); 3.28 (*ddd*, *J*(5′,6a′) = 3.8, *J*(5′,6b′) = 2.1, H–C(5′)). ^{13}C-NMR ($CDCl_3$): 166.1, 165.4, 165.2 (Ph*C*O); 101.1 (*J*(1′,H–C(1′)) = 151.6, C(1′)); 96.8 (C(1)); 82.2 (C(3′)); 75.1 (Ph*C*H_2); 74.5 (C(2′)); 73.7 (3 C, C(4′), C(5′), Ph*C*H_2); 73.5 (2 C, Ph*C*H_2); 73.3 (C(4)); 71.4 (C(5)); 71.0 (C(2)); 69.6 (2 C, C(3), Ph*C*H_2); 68.8 (C(6)); 63.4 (C(6′)). Anal. calc. for $C_{68}H_{64}O_{14}$ (1105.25): C 73.90, H 5.84; found: C 73.85, H 5.92.

Benzyl 2-O-*Benzoyl-3*-O-*benzyl-4,6*-O-*benzylidene-α*-D-*mannopyranoside* (**31**). BzCl (1.0 ml, 8.45 mmol) was added at r.t. to a soln. of **20** (3.16 g, 7.04 mmol) in pyridine (40 ml). The mixture was stirred for 24 h, then poured into H_2O and extracted with CH_2Cl_2. The extracts were washed with aq. HCl and $NaHCO_3$ soln., dried, and evaporated to give crude **31** (3.0 g), which was used without further purification for the next step.

Benzyl 2-O-*Benzoyl-3*-O-*benzyl-α*-D-*mannopyranoside* (**32**). A soln. of crude **31** (3.0 g) in 70% AcOH/H_2O (50 ml) was stirred at 60° for 3 h, evaporated, and co-evaporated with toluene. Chromatography (toluene/AcOEt 4:1) of the residue afforded **32** (2.27 g, 70%). $[\alpha]_D = +86.7$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.62 (*dd*, *J*(2,3) = 3.1, H–C(2)); 5.03 (*d*, *J*(1,2) = 1.8, H–C(1)); 4.77 (*d*, *J* = –11.1, 1 H, PhCH_2); 4.73 (*d*, *J* = –11.0, 1 H, PhCH_2); 4.54 (*d*, *J* = –11.8, 1 H, PhCH_2); 4.45 (*d*, *J* = –11.2, 1 H, PhCH_2); 4.07 (*ddd*, *J*(4,5) = 9.5, *J*(4,OH) = 2.3, H–C(4)); 3.94 (*dd*, *J*(3,4) = 9.4, H–C(3)); 3.89–3.85 (*m*, 2 H–C(6)); 3.78 (*dt*, *J*(5,6a) = 4.0, *J*(5,6b) = 9.4, H–C(5)); 2.50 (*d*, OH); 2.09 (*dd*, *J*(6a,OH) = 6.0, *J*(6b,OH) = 7.0, OH). ^{13}C-NMR ($CDCl_3$): 165.7 (Ph*C*O); 97.5 (C(1)); 77.8 (C(3)); 72.2 (C(5)); 71.5 (Ph*C*H_2); 69.6 (Ph*C*H_2); 68.4 (C(2)); 67.1 (C(4)); 62.6 (C(6)). Anal. calc. for $C_{27}H_{28}O_7$ (464.52): C 69.81, H 6.08; found: C 69.99, H 6.10.

Benzyl 2-O-*Benzoyl-3*-O-*benzyl-6*-O-*[3-(ethyl 2,3,4-tri*-O-*benzyl-1-thio-α*-D-*mannopyranosid-6*-O-*yl)-1,3-dioxopropyl]-α*-D-*mannopyranoside* (**33**). As described for **3** (*Exper. b*), with **1a** [1] (1.76 g, 3.03 mmol), **32** (1.07 g, 2.30 mmol), DCC (0.47 g, 2.30 mmol), DMAP, and CH_2Cl_2 (40 ml), followed by CC (toluene/AcOEt 10:1): **33** (1.38 g, 58%). $[\alpha]_D = +35.5$ ($c = 1.2$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.60 (*dd*, $J(2,3) = 3.4$, H–C(2)); 5.31 (*d*, $J(1',2') =$ H–C(1')); 5.00 (*d*, $J(1,2) = 1.7$, H–C(1)); 4.88 (*d*, $J = -10.7$, 1 H, PhCH_2); 4.76 (*d*, $J = -11.1$, 1 H, PhCH_2); 4.68 (*d*, $J = -12.5$, 1 H, PhCH_2); 4.63 (*d*, $J = -12.4$, 1 H, PhCH_2); 4.55–4.52 (*m*, 4 H, PhCH_2); 4.50–4.46 (*m*, 2 H, PhCH_2); 4.50–4.43 (*m*, 2 H–C(6)); 4.41–4.39 (*m*, J(6a',6b') = –11.8, H_b–C(6')); 4.40 (*dd*, H–C(6')); 4.19–4.14 (*m*, $J(5',6a') = 2.4$, $J(5',6b') = 5.0$, H–C(5')); 4.01 (*dt*, $J(4,5) = 9.3$, H–C(4)); 3.98–3.88 (*m*, H–C(5)); 3.93 (*dd*, $J(3,4) = 8.9$, H–C(3)); 3.87–3.82 (*m*, H–C(4')); 3.81–3.79 (*m*, $J(2',3') = 3.2$, H–C(2'), H–C(3')); 3.46 (*s*, $COCH_2$); 2.83 (*d*, $J(4,OH) = 2.8$, OH); 2.73–2.45 (*m*, MeCH_2S); 1.23 (*t*, $J = 7.5$, *Me*CH_2S). ^{13}C-NMR ($CDCl_3$): 166.2, 166.0, 165.6 (CO); 97.3 (C(1)); 81.9 (C(1')); 80.2 (C(3')); 77.6 (C(3)); 76.2 (C(2')); 75.2 (PhCH_2); 74.5 (C(4')); 72.1 (PhCH_2); 72.0 (PhCH_2); 71.6 (PhCH_2); 70.4 (C(5)); 70.1 (C(5')); 69.6 (PhCH_2); 68.4 (C(2)); 66.6 (C(4)); 64.5, 64.4 (C(6), C(6')); 41.3 ($COCH_2$); 25.3 (MeCH_2S); 14.9 (*Me*CH_2S). Anal. calc. for $C_{59}H_{62}O_{14}$ (1027.20): C 68.99, H 6.08, S 3.12; found: C 69.12, H 6.05, S 3.20.

Benzyl O-*(2,3,4-Tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1→4)-2*-O-*benzoyl-3*-O-*benzyl-α*-D-*mannopyranoside 6,6'-Malonate* (**34**). *a*) Exactly as described for **5** (*Exper. a*), with **33** (0.33 g, 0.32 mmol), NIS (0.36 g, 1.61 mmol), Me_3SiOTf (15 µl, 80 µmol), and CH_2Cl_2 (10 ml), followed by CC (toluene/AcOEt 20:1): **34** (219 mg, 71%). $[\alpha]_D = +38.0$ ($c = 0.8$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.62 (br. *s*, H–C(2)); 5.55 (*d*, $J(1',2') = 2.9$, H–C(1')); 5.04 (*s*, H–C(1)); 4.80 (*dd*, J(6a',6b') = –10.9, H_a–C(6')); 4.71 (*d*, $J = -11.7$, 1 H, PhCH_2); 4.66–4.61 (*m*, H_a–C(6)); 4.61 (*s*, 4 H, PhCH_2); 4.59 (*d*, $J = -12.6$, 1 H, PhCH_2); 4.50 (*t*, $J(4,5) = 9.6$, H–C(4)); 4.42 (*d*, $J = -10.9$, 1 H, PhCH_2); 4.40 (*d*, $J = -11.2$, 1 H, PhCH_2); 4.26 (*d*, $J = -12.1$, 1 H, PhCH_2); 4.20 (*d*, $J = -12.2$, 1 H, PhCH_2); 4.11–4.08 (*m*, $J(3,4) = 9.6$, H–C(3), H_b–C(6)); 3.95 (br. *d*, H_b–C(6')); 3.88 (br. *d*, H–C(5)); 3.76 (*dd*, $J(3',4') = 6.6$, H–C(3')); 3.70–3.64 (*m*, $J(2',3') = 2.4$, $J(5',6a') = 8.8$, H–C(2'), H–C(5')); 3.51 (*d*, $J = -15.7$, 1 H, $COCH_2$); 3.38 (*d*, $J = -15.7$, 1 H, $COCH_2$). ^{13}C-NMR ($CDCl_3$): 166.6, 165.6, 165.5 (CO); 99.5 (J(1',H–C(1')) = 172.2, C(1)); 97.4 (C(1)); 79.0 (C(3)); 78.6 (C(3')); 76.6 (C(2')); 75.1 (C(4')); 74.0 (PhCH_2); 73.4 (C(5')); 72.3 (PhCH_2); 72.1 (PhCH_2); 71.1 (PhCH_2); 70.7 (C(4)); 70.0 (PhCH_2); 69.0 (C(5)); 68.6 (C(2)); 64.5 (C(6')); 63.9 (C(6)); 42.6 ($COCH_2$). Anal. calc. for $C_{57}H_{56}O_{14}$ (965.07): C 70.94, H 5.85; found: C 70.97, H 5.87.

b) Exactly as described for **5** (*Exper. a*), with **33** (0.35 g, 0.34 mmol), with NIS (0.39 g, 1.70 mmol), Me_3SiOTf (16 µl, 85 µmol), and MeCN (10 ml), followed by CC (toluene/AcOEt 20:1): **34** (225 mg, 68%).

c) Exactly as described for **5** (*Exper. c*), with **33** (0.38 g, 0.37 mmol), MeOTf (0.28 ml, 2.59 mmol), and CH_2Cl_2 (10 ml), followed by CC (toluene/AcOEt 20:1): **34** (227 mg, 64%).

d) Exactly as described for **5** (*Exper. d*), with **33** (0.59 g, 0.57 mmol), MeOTf (0.44 ml, 3.99 mmol), and MeCN (15 ml): **34** (332 mg, 60%).

Benzyl O-*(6*-O-*Benzoyl-2,3,4-tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1→4)-2,6-di*-O-*benzoyl-3*-O-*benzyl-α*-D-*mannopyranoside* (**35**). Exactly as described for **6**, with **34** (0.15 g, 0.16 mmol), NaOMe in MeOH, BzCl (110 µl, 0.95 mmol), and pyridine (5 ml): **35** (125 mg, 71%). $[\alpha]_D = +32.1$ ($c = 0.9$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.68 (*t*, $J(2,3) = 2.4$, H–C(4)); 5.34 (*d*, $J(1',2') = 1.8$, H–C(1')); 5.06 (*d*, $J(1,2) = 1.6$, H–C(1)); 4.86 (*d*, $J = -10.7$, 1 H, PhCH_2); 4.83 (*d*, $J = -10.8$, 1 H, PhCH_2); 4.78–4.74 (*m*, H_a–C(6)); 4.76 (*d*, $J = -11.7$, 1 H, PhCH_2); 4.70–4.64 (*m*, 3 H, PhCH_2); 4.59–4.51 (*m*, 4 H, 2 H–C(6'), PhCH_2); 4.41–4.32 (*m*, H–C(5), H_b–C(6)); 4.25 (*t*, $J(4,5) = 9.6$, H–C(4)); 4.20 (*d*, $J = -11.8$, 1 H, PhCH_2); 4.14–4.11 (*m*, H–C(4')); 4.08–4.03 (*m*, $J(3,4) = 9.6$, H–C(3), H–C(5')); 4.03 (*d*, $J = -12.0$, 1 H, PhCH_2); 3.96 (*dd*, $J(3',4') = 9.4$, H–C(3')); 3.70 (*t*, $J(2',3') = 2.7$, H–C(2')). ^{13}C-NMR ($CDCl_3$): 166.2, 166.1, 165.6 (Ph*C*O); 100.3 (J(1',H–C(1')) = 173.5, C(1')); 97.8 (C(1)); 79.8 (C(3')); 78.5 (C(3)); 76.0 (C(2')); 75.2 (PhCH_2); 74.2 (C(4)); 73.8 (C(4')); 72.2 (PhCH_2); 72.1 (PhCH_2); 71.6 (C(5)); 71.2 (PhCH_2); 69.9 (C(5')); 69.8 (PhCH_2); 68.1 (C(2)); 63.5, 63.3 (C(6), C(6')). Anal. calc. for $C_{68}H_{64}O_{14}$ (1105.25): C 73.90, H 5.84; found: C 74.00, H 5.90.

Benzyl 2,3-O-*Isopropylidene-4*-O-*(4-methoxybenzyl)-α*-L-*rhamnopyranoside* (**37**). A suspension of benzyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (**36**) [30] (5.52 g, 18.75 mmol) and NaH (0.68 g, 28.13 mmol) in DMF (150 ml) was stirred for 30 min at 0°. Then, 4-methoxybenzyl chloride (3.18 ml, 23.44 mmol) was added dropwise at 0°, and the mixture was stirred at r.t. for 2.5 h. The excess of NaH was destroyed by careful addition of MeOH and the mixture poured into H_2O and extracted with CH_2Cl_2. The extracts were washed with H_2O, dried, and evaporated. CC (hexane/AcOEt 15:1) of the residue afforded **37** (5.77 g, 74%). $[\alpha]_D = -56.3$ ($c = 1.0$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.04 (*s*, H–C(1)); 4.83 (*d*, $J = -11.2$, 1 H, PhCH_2); 4.68 (*d*, $J = -11.7$, 1 H, PhCH_2); 4.55 (*d*, $J = -11.2$, 1 H, PhCH_2); 4.48 (*d*, $J = -11.7$, 1 H, PhCH_2); 4.28 (br. *t*, $J(3,4) = 7.0$, H–C(3)); 4.18 (*dd*, $J(2,3) = 5.8$, H–C(2)); 3.78 (*s*, MeO); 3.77–3.69 (*m*, $J(5,6) = 6.3$, H–C(5)); 1.51 (*s*, 3 H, Me_2C); 1.36 (*s*, 3 H, Me_2C); 1.26 (*d*, Me(6)). ^{13}C-NMR ($CDCl_3$): 109.1 (Me_2C); 96.1 (C(1)); 80.8 (C(4)); 78.7 (C(3)); 76.1

(C(2)); 72.6 (Ph*C*H$_2$); 69.0 (Ph*C*H$_2$); 64.7 (C(5)); 55.2 (MeO); 28.0 (*Me*$_2$C); 26.3 (*Me*$_2$C), 17.8 (C(6)). Anal. calc. for $C_{24}H_{30}O_6$ (414.50): C 69.55, H 7.30; found: C 69.60, H 7.25.

*Benzyl 4-*O*-(4-Methoxybenzyl)-α-*L*-rhamnopyranoside* (**38**). As described for **32**, with **37** (5.68 g, 13.70 mmol) and 70% AcOH/H$_2$O: **38** (4.54 g, 89%). $[\alpha]_D = -88.7$ ($c = 1.03$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 4.70 (*s*, H–C(1)); 4.66–4.61 (*m*, 3 H, PhC*H*$_2$); 4.47 (*d*, $J = -11.9$, 1 H, PhC*H*$_2$); 3.94–3.89 (*m*, $J(2,3) = 3.3$, H–C(2), H–C(3)); 3.78 (*s*, MeO); 3.34 (*t*, $J(4,5) = 9.1$, H–C(4)); 3.76–3.72 (*m*, $J(5,6) = 6.3$, H–C(5)); 2.60 (br. *s*, OH); 2.44 (br. *s*, OH); 1.34 (*d*, Me(6)). ^{13}C-NMR ($CDCl_3$): 98.6 (C(1)); 81.3 (C(4)); 74.8 (Ph*C*H$_2$); 71.5, 71.1 (C(2), C(3)); 69.1 (Ph*C*H$_2$); 67.5 (C(5)); 55.3 (MeO); 18.0(C(6)). Anal. calc. for $C_{21}H_{26}O_6$ (374.44): C 67.36, H 7.00; found: C 67.48, H 6.92.

*Benzyl 2-*O*-Benzyl-4-*O*-(4-methoxybenzyl)-α-*L*-rhamnopyranoside* (**39**). As described for **26**, with **38** (1.62 g, 4.33 mmol), BnBr (0.77 ml, 6.50 mmol), $Bu_4N(HSO_4)$ (0.44 g, 1.37 mmol), CH_2Cl_2 (15 ml), and 20% aq. NaOH soln. (10 ml) for 6 h: **39** (1.55 g, 77%). $[\alpha]_D = -31.7$ ($c = 2.4$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 4.89 (*d*, $J(1,2) = 1.3$, H–C(1)); 4.81 (*d*, $J = -10.7$, 1 H, PhC*H*$_2$); 4.70 (*d*, $J = -11.8$, 1 H, PhC*H*$_2$); 4.68 (*d*, $J = -11.9$, 1 H, PhC*H*$_2$); 4.60 (*s*, 1 H, PhC*H*$_2$); 4.55 (*d*, $J = -11.6$, 1 H, PhC*H*$_2$); 3.78 (*s*, MeO); 3.76 (*dd*, $J(2,3) = 3.8$, H–C(2)); 3.72–3.69 (*m*, $J(5,6) = 6.3$, H–C(5)); 3.33 (*t*, $J(4,5) = 9.3$, H–C(4)); 3.32 (*dt*, $J(3,4) = 9.1$, $J(3,OH) = 9.0$, H–C(3)); 2.28 (*d*, OH); 1.32 (*d*, Me(6)). ^{13}C-NMR ($CDCl_3$): 96.3 (C(1)); 82.0 (C(4)); 78.6 (C(2)); 74.8 (Ph*C*H$_2$); 73.0 (Ph*C*H$_2$); 71.7 (C(3)); 69.0 (Ph*C*H$_2$); 67.5 (C(5)); 55.3 (MeO); 18.1 (C(6)). Anal. calc. for $C_{28}H_{32}O_6$ (464.56): C 72.39, H 6.94; found: C 72.08, H 6.90.

*Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-{3-[benzyl 2-*O*-benzyl-4-*O*-(4-methoxybenzyl)-α-*L*-rhamnopyranosid-3-*O*-yl]-1,3-dioxopropyl}-1-thio-α-*D*-mannopyranoside* (**40**). As described for **3** (*Exper. b*), with **1a** [1] (1.29 g, 2.22 mmol), **39** (1.03 g, 2.22 mmol), DCC (0.52 g, 2.50 mmol), DMAP, and CH_2Cl_2 (40 ml), followed by CC (toluene/AcOEt 20:1): **40** (1.57 g, 69%). $[\alpha]_D = +21.3$ ($c = 0.9$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.31–5.26 (*m*, H–C(1′), H–C(3)); 4.91 (*d*, $J = -10.8$, 1 H, PhC*H*$_2$); 4.77 (*d*, $J(1,2) = 1.6$, H–C(1)); 4.69 (*d*, $J = -12.2$, 1 H, PhC*H*$_2$); 4.63 (*d*, $J = -10.7$, 1 H, PhC*H*$_2$); 4.61 (*d*, $J = -12.4$, 1 H, PhC*H*$_2$); 4.58 (*s*, 2 H, PhC*H*$_2$); 4.55 (*s*, 2 H, PhC*H*$_2$); 4.47 (*d*, $J = -12.0$, PhC*H*$_2$); 4.43 (*d*, $J = -12.3$, 1 H, PhC*H*$_2$); 4.38–4.33 (*m*, 2 H–C(6′)); 4.20–4.14 (*m*, H–C(5′)); 3.93–3.86 (*m*, $J(2,3) = 3.3$, H–C(2), H–C(4′)); 3.82–3.77 (*m*, H–C(2′), H–C(3′)); 3.80–3.75 (*m*, $J(5,6) = 6.2$, H–C(5)); 3.75 (*s*, MeO); 3.62 (*t*, $J(4,5) = 9.4$, H–C(4)); 3.32 (*d*, $J = -16.0$, 1 H, COC*H*$_2$); 3.26 (*d*, $J = -16.1$, 1 H, COC*H*$_2$); 2.61–2.22 (*m*, MeC*H*$_2$S); 1.28 (*d*, Me(6)); 1.19 (*t*, $J = 7.4$, *Me*CH$_2$S). ^{13}C-NMR ($CDCl_3$): 166.1, 165.5 (*C*OCH$_2$); 97.0 (C(1)); 81.9 (C(1′)); 80.3 (C(3′)); 78.5 (C(4)); 76.1 (C(2), C(2′)); 75.1 (C(3)); 74.6 (Ph*C*H$_2$, C(4′)); 73.3 (Ph*C*H$_2$); 72.0 (2 C, Ph*C*H$_2$); 70.1 (C(5′)); 68.9 (Ph*C*H$_2$); 67.9 (C(5)); 64.5 (C(6′)); 55.2 (MeO); 41.3 (CO*C*H$_2$); 25.4 (Me*C*H$_2$S); 17.9 (C(6)); 14.9 (*Me*CH$_2$S). Anal. calc. for $C_{60}H_{66}O_{13}S$ (1027.24): C 70.16, H 6.48, S 3.12; found: C 70.24, H 6.53, S 3.12.

*Ethyl 2,3,4-Tri-*O*-benzyl-6-*O*-[3-(Benzyl 2-*O*-benzyl-α-*L*-rhamnopyranosid-3-*O*-yl)-1,3-dioxopropyl]-1-thio-α-*D*-mannopyranoside* (**41**). A mixture of **40** (1.08 g, 1.05 mmol) and DDQ (0.29 g, 1.29 mmol) in CH_2Cl_2 (25 ml) and H_2O (6 ml) was stirred at r.t. for 3 h, diluted with CH_2Cl_2, and filtered. The org. layer of the filtrate was washed with aq. $NaHCO_3$ soln., dried, and evaporated. CC (toluene/acetone 15:1) of the residue afforded **41** (0.80 g, 84%). $[\alpha]_D = +24.5$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.32 (*s*, H–C(1′)); 5.16 (*dd*, $J(3,4) = 9.3$, H–C(3)); 4.92 (*d*, $J = -10.9$, 1 H, PhC*H*$_2$); 4.82 (*d*, $J(1,2) = 1.5$, H–C(1)); 4.71 (*d*, $J = -12.5$, 1 H, PhC*H*$_2$); 4.68 (*d*, $J = -12.5$, 1 H, PhC*H*$_2$); 4.63 (*d*, $J = -12.5$, 1 H, PhC*H*$_2$); 4.58 (*d*, $J = -10.6$, 1 H, PhC*H*$_2$); 4.56–4.53 (*m*, 3 H, PhC*H*$_2$); 4.49 (*d*, $J = -12.2$, 1 H, PhC*H*$_2$); 4.48 (*d*, $J = -12.0$, 1 H, PhC*H*$_2$); 4.29 (*dd*, $J(5′,6b′) = 2.1$, $J(6a′,6b′) = -12.2$, H_b–C(6′)); 4.19–4.15 (*m*, H–C(5′), H_a–C(6′)); 3.90 (*t*, $J(4′,5′) = 9.4$, H–C(4′)); 3.86–3.70 (*m*, $J(2,3) = 3.3$, $J(5,6) = 5.6$, $J(4,OH) = 3.8$, H–C(2), H–C(2′), H–C(3′), H–C(4), H–C(5)); 3.37 (*d*, $J = -16.0$, 1 H, COC*H*$_2$); 3.29 (*d*, $J = -16.0$, 1 H, COC*H*$_2$); 3.08 (*d*, OH); 2.65–2.48 (*m*, MeC*H*$_2$S); 1.32 (*d*, Me(6)); 1.22 (*t*, $J = 7.4$, *Me*CH$_2$S). ^{13}C-NMR ($CDCl_3$): 166.8, 165.9 (*C*OCH$_2$); 97.0 (C(1)); 81.8 (C(1′)); 80.1 (C(3′)); 75.9 (C(3)); 75.8, 75.7 (C(2), C(2′)); 75.1 (Ph*C*H$_2$); 74.3 (C(4′)); 73.1, 71.9, 71.8 (Ph*C*H$_2$); 70.7 (C(5)); 69.9 (C(5′)); 68.9 (Ph*C*H$_2$); 68.6 (C(4)); 64.6 (C(6′)); 41.5 (CO*C*H$_2$); 25.4 (Me*C*H$_2$S); 17.7 (C(6)); 14.9 (*Me*CH$_2$S). Anal. calc. for $C_{52}H_{58}O_{12}S$ (907.09): C 68.86, H 6.45; found: C 68.95, H 6.50.

Benzyl O*-(2,3,4-Tri-*O*-benzyl-β-*D*-mannopyranosyl)-(1→4)-2-*O*-benzyl-α-*L*-rhamnopyranoside 3,6′-Malonate* (**42**). *a*) Exactly as described for **5** (*Exper. a*), with **41** (0.31 g, 0.34 mmol), NIS (0.39 g, 1.70 mmol), Me_3SiOTf (15 µl, 80 µmol), and CH_2Cl_2 (12 ml), followed by CC (toluene/acetone 20:1): **42** (192 mg, 67%) as a mixture of 2 isomers.

b) Exactly as described for **5** (*Exper. a*), with **41** (0.69 g, 0.76 mmol), NIS (0.86 g, 3.80 mmol), Me_3SiOTf (35 µl, 190 µmol), and MeCN (25 ml), followed by CC (toluene/acetone 20:1): **42** (440 mg, 68%) as a mixture of 2 isomers.

c) Exactly as described for **5** (*Exper. c*), with **41** (0.33 g, 0.36 mmol), MeOTf (0.20 ml, 1.80 mmol), and CH_2Cl_2 (12 ml), followed by CC (toluene/acetone 20:1): **42** (201 mg, 66%) as a mixture of 2 isomers.

d) Exactly as described for **5** (*Exper. d*), with **41** (0.37 g, 0.41 mmol), MeOTf (0.22 ml, 2.04 mmol), and MeCN (15 ml): **42** (244 mg, 71%) as a mixture of 2 isomers.

Benzyl O-*(6*-O-*Benzoyl-2,3,4-tri*-O-*benzyl-β*-D-*mannopyranosyl)-(1 → 4)-3*-O-*benzoyl-2*-O-*benzyl-α*-L-*rhamnopyranoside* (**43**). Exactly as described for **6**, with the mixture **42** of isomers from *Exper. a* (see above; 123 mg, 0.15 mmol), NaOMe in MeOH, BzCl (51 µl, 0.44 mmol), and pyridine (5 ml): **43** (102 mg, 72%). Similarly, the mixtures **42** of isomers from *Exper. b–d* (see above) were converted separately to **43** (69, 72, and 70%, resp.). $[\alpha]_D = -12.6$ ($c = 2.3$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.47 (*dd*, *J*(3,4) = 9.6, H–C(3)); 4.99 (*d*, *J*(1,2) = 1.8, H–C(1)); 4.80 (*d*, *J* = –12.2, 1 H, PhC*H*$_2$); 4.77 (*d*, *J* = –12.7, 1 H, PhC*H*$_2$); 4.71 (*d*, *J* = –12.3, 1 H, PhC*H*$_2$); 4.64 (*d*, *J* = –10.5, 1 H, PhC*H*$_2$); 4.63 (*d*, *J* = –10.5, 1 H, PhC*H*$_2$); 4.62 (*d*, *J* = –12.6, 1 H, PhC*H*$_2$); 4.57 (*d*, *J* = –12.2, 1 H, PhC*H*$_2$); 4.55 (*d*, *J* = –10.4, 1 H, PhC*H*$_2$); 4.53 (*s*, H–C(1′)); 4.52 (*d*, *J* = –12.2, 1 H, PhC*H*$_2$); 4.47 (*d*, *J* = –11.8, 1 H, PhC*H*$_2$); 4.08–4.03 (*m*, *J*(6a′,6b′) = –11.6, H$_a$–C(6′)); 4.03 (*dd*, *J*(5′,6b′) = 2.5, H$_b$–C(6′)); 4.02–3.94 (*m*, H–C(4)); 3.93–3.82 (*m*, *J*(2,3) = 3.4, H–C(2), H–C(4′)); 3.82–3.74 (*m*, *J*(5,6) = 6.2, H–C(5)); 3.68 (br. *t*, *J*(2′,3′) = 2.9, H–C(2′)); 3.61–3.56 (*m*, H–C(5′)); 3.22 (*dd*, *J*(3′,4′) = 9.4, H–C(3′)); 1.11 (*d*, Me(6)). ^{13}C-NMR ($CDCl_3$): 166.4, 165.2 (Ph*C*O); 102.8 (*J*(1′,H–C(1′)) = 157.0, C(1′)); 97.0 (C(1)); 82.6 (C(3′)); 78.4 (C(2)); 76.1 (C(4)); 75.3 (Ph*C*H$_2$); 74.4 (C(2′)); 74.1 (Ph*C*H$_2$); 74.0 (C(4′)); 73.4 (C(5′)); 73.1 (Ph*C*H$_2$); 72.4 (C(3)); 70.9 (Ph*C*H$_2$); 70.7 (C(5)); 69.0 (Ph*C*H$_2$); 63.9 (C(6′)); 17.9 (C(6)). Anal. calc. for $C_{61}H_{60}O_{12}$ (985.15): C 74.37, H 6.14; found: C 74.50, H 6.10.

Benzyl 3-O-*Benzyl-4*-O-*(4-methoxybenzyl)-α*-L-*rhamnopyranoside* (**44**). A mixture of **38** (1.50 g, 4.01 mmol) and Bu_2SnO (1.17 g, 4.68 mmol) in benzene (150 ml) was refluxed at a *Dean-Stark* apparatus for 48 h, cooled to r.t., and evaporated. The residue was dissolved in benzene (70 ml), BnBr (0.59 ml, 4.93 mmol) and Bu_4NBr (1.34 g, 4.17 mmol) were added, the mixture was stirred for 22 h at 60°, cooled to r.t. and evaporated. CC (toluene/AcOEt 12 : 1) of the residue afforded **44** (1.53 g, 82%). $[\alpha]_D = -103.2$ ($c = 1.5$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 4.89 (*d*, *J*(1,2) = 1.2, H–C(1)); 4.80 (*d*, *J* = –10.5, 1 H, PhC*H*$_2$); 4.68 (*d*, *J* = –11.9, 1 H, PhC*H*$_2$); 4.57 (*d*, *J* = –10.5, 1 H, PhC*H*$_2$); 4.46 (*d*, *J* = –11.8, 1 H, PhC*H*$_2$); 4.07–4.05 (*m*, *J*(2,3) = 3.3, *J*(2,OH) = 2.2, H–C(2)); 3.87 (*dd*, *J*(3,4) = 9.1, H–C(3)); 3.80–3.75 (*m*, *J*(5,6) = 6.2, H–C(5)); 3.79 (*s*, MeO); 3.46 (*t*, *J*(4,5) = 9.4, H–C(4)); 2.51 (*d*, OH); 1.31 (*d*, Me(6)). ^{13}C-NMR ($CDCl_3$): 98.2 (C(1)); 80.1 (C(3)); 79.6 (C(4)); 75.0 (Ph*C*H$_2$); 72.0 (Ph*C*H$_2$); 69.0 (Ph*C*H$_2$); 68.6 (C(2)); 67.5 (C(5)); 55.2 (MeO); 17.9 (C(6)). Anal. calc. for $C_{28}H_{32}O_6$ (464.56): C 72.39, H 6.94; found: C 72.12, H 7.10.

Ethyl 2,3,4-Tri-O-*benzyl-6*-O-*{3-[benzyl 3*-O-*benzyl-4*-O-*(4-methoxybenzyl)-α*-L-*rhamnopyranosid-2*-O-*yl]-1,3-dioxopropyl}-1-thio-α*-D-*mannopyranoside* (**45**). As described for **3** (*Exper. b*), with **1a** [1] (1.87 g, 3.22 mmol), **44** (1.25 g, 2.69 mmol), DCC (0.58 g, 2.83 mmol), DMAP, and CH_2Cl_2 (40 ml), followed by CC (toluene/acetone 40 : 1): **45** (1.88 g, 68%). $[\alpha]_D = +31.4$ ($c = 1.78$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.43 (*dd*, *J*(2,3) = 3.3, H–C(2)); 5.33 (*d*, *J*(1′,2′) = 1.0, H–C(1′)); 4.92 (*d*, *J* = –10.8, 1 H, PhC*H*$_2$); 4.79 (*d*, *J* = –10.4, 1 H, PhC*H*$_2$); 4.71 (*d*, *J* = –12.4, 1 H, PhC*H*$_2$); 4.70 (*d*, *J* = –11.1, 1 H, PhC*H*$_2$); 4.65 (*d*, *J* = –12.5, 1 H, PhC*H*$_2$); 4.63 (*d*, *J* = –11.5, 1 H, PhC*H*$_2$); 4.56 (*s*, 1 H, PhC*H*$_2$); 4.50 (*d*, *J* = –10.4, 1 H, PhC*H*$_2$); 4.49 (*d*, *J* = –11.1, 1 H, PhC*H*$_2$); 4.45–4.43 (*m*, 1 H, PhC*H*$_2$); 4.85 (*d*, *J*(1,2) = 1.8, H–C(1)); 4.45–4.39 (*m*, *J*(5′,6a′) = 2.3, *J*(5′,6b′) = 5.0, 2 H–C(6′)); 4.18 (*ddd*, H–C(5′)); 3.95 (*dd*, *J*(3,4) = 9.3, H–C(3)); 3.92 (*t*, *J*(4′,5′) = 9.6, H–C(4′)); 3.85–3.81 (*m*, *J*(2′,3′) = 3.3, H–C(2′), H–C(3′)); 3.78 (*s*, MeO); 3.76–3.71 (*m*, *J*(5,6) = 6.2, H–C(5)); 3.47 (br. *d*, COCH_2); 3.39 (*t*, *J*(4,5) = 9.5, H–C(4)); 2.63–2.49 (*m*, MeCH_2S); 1.23 (*t*, *J* = 7.4, *Me*CH$_2$S); 1.28 (*d*, Me(6)). ^{13}C-NMR ($CDCl_3$): 166.1, 165.7 (*C*OCH$_2$); 96.9 (C(1)); 81.9 (C(1′)); 80.3 (C(3′)); 79.6 (C(4)); 77.9 (C(3)); 76.1 (C(2′)); 75.1 (Ph*C*H$_2$); 74.6 (C(4′)); 72.0 (2 C, Ph*C*H$_2$); 71.8 (Ph*C*H$_2$); 70.1 (C(2), C(5′)); 69.3 (Ph*C*H$_2$); 67.9 (C(5)); 64.5 (C(6′)); 55.2 (MeO); 41.1 (CO*C*H$_2$); 25.4 (Me*C*H$_2$S); 17.9 (C(6)); 14.9 (*Me*CH$_2$S). Anal. calc. for $C_{60}H_{66}O_{13}S$ (1027.24): C 70.16, H 6.48, S 3.12; found: C 70.37, H 6.52, S 3.10.

Ethyl 2,3,4-Tri-O-*benzyl-6*-O-*{3-(benzyl 3*-O-*benzyl-α*-L-*rhamnopyranosid-2*-O-*yl)-1,3-dioxopropyl}-1-thio-α*-D-*mannopyranoside* (**46**). A mixture of **45** (1.56 g, 1.52 mmol) and $Ce(NH_4)_2(NO_3)_6$ (4.17 g, 7.60 mmol) in MeCN/H_2O 4 : 1 (50 ml) was stirred for 30 min at r.t., diluted with CH_2Cl_2, washed with aq. NaCl soln., dried, and evaporated. CC (toluene/acetone 18 : 1) of the residue afforded **46** (1.22 g, 89%). $[\alpha]_D = +45.6$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.42 (*dd*, *J*(2,3) = 3.1, H–C(2)); 5.32 (*s*, H–C(1′)); 4.91 (*d*, *J* = –10.8, 1 H, PhC*H*$_2$); 4.88 (*d*, *J*(1,2) = 1.7, 1 H, H–C(1)); 4.71 (*d*, *J* = –11.2, 1 H, PhC*H*$_2$); 4.69 (*s*, 1 H, PhC*H*$_2$); 4.67 (*d*, *J* = –11.6, 1 H, PhC*H*$_2$); 4.65 (*d*, *J* = –12.4, 1 H, PhC*H*$_2$); 4.58 (*d*, *J* = –12.5, 1 H, PhC*H*$_2$); 4.56 (*s*, 2 H, PhC*H*$_2$); 4.46 (*d*, *J* = –11.7, 1 H, PhC*H*$_2$); 4.44 (*dd*, *J*(5′,6a′) = 5.3, *J*(6′,6b′) = –11.8, H$_a$–C(6′)); 4.38–4.33 (*m*, *J*(5′,6b′) = 2.2, H$_b$–C(6′)); 4.36 (*d*, *J* = –11.0, 1 H, PhC*H*$_2$); 4.20–4.15 (*m*, H–C(5′)); 3.90 (*t*, *J*(4′,5′) = 9.5, H–C(4′)); 3.85–3.80 (*m*, *J*(2′,3′) = 3.0, H–C(2′), H–C(3′)); 3.78–3.71 (*m*, *J*(5,6) = 6.2, H–C(5)); 3.76 (*dd*, *J*(3,4) = 9.4, H–C(3)); 3.53 (*t*, *J*(4,5) = 9.5, H–C(4)); 3.44 (*s*, COCH_2); 2.62–2.48 (*m*, MeCH_2S); 2.22 (*d*, *J*(4,OH) = 2.4, OH); 1.29 (*d*, Me(6)); 1.22 (*t*, *J* = 7.4, *Me*CH$_2$S). ^{13}C-NMR ($CDCl_3$): 166.0, 165.7 (*C*OCH$_2$); 97.1 (C(1)); 81.9 (C(1′)); 80.3 (C(3′)); 77.5 (C(3)); 76.6 (C(2′)); 76.1 (Ph*C*H$_2$); 75.2 (C(4′)); 74.6 (Ph*C*H$_2$); 72.0 (Ph*C*H$_2$); 71.5

(2 C, PhCH$_2$, C(4)); 70.1 (C(5′)); 69.3 (PhCH$_2$); 69.2 (C(2)); 68.3 (C(5)); 64.5 (C(6′)); 41.0 (MeCH$_2$S); 17.7 (C(6)); 14.9 (MeCH$_2$S). Anal. calc. for $C_{52}H_{58}O_{12}S$ (907.09): C 68.86, H 6.45; found: C 69.00, H 6.56.

Benzyl O-*(2,3,4-Tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1 → 4)-3*-O-*benzyl-α*-L-*rhamnopyranoside 2,6′-Malonate* (**47**). *a*) Exactly as described for **5** (*Exper. a*), with **46** (0.28 g, 0.31 mmol), NIS (0.35 g, 1.56 mmol), Me_3SiOTf (14 µl, 78 µmol), and CH_2Cl_2 (15 ml), followed by CC (toluene/acetone 25 : 1): **47** (195 mg, 745%). $[\alpha]_D = +19.3$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.47 (br. *t*, $J(2,3) = 2.6$, H–C(2)); 4.89 (*d*, $J(1',2') = 1.2$, H–C(1′)); 4.82 (*d*, $J(1,2) = 1.3$, H–C(1)); 4.75 (*d*, $J = -12.4$, 1 H, PhCH$_2$); 4.74 (*d*, $J = -11.4$, 1 H, PhCH$_2$); 4.69–4.64 (*m*, $J(6a',6b') = -10.8$, H_a–C(6′)); 4.67 (*d*, $J = -11.9$, 1 H, PhCH$_2$); 4.60–4.50 (*m*, $J(5',6b') = 9.9$, H–C(5′)); 4.59 (*d*, $J = -12.5$, 1 H, PhCH$_2$); 4.58 (*d*, $J = -11.4$, 1 H, PhCH$_2$); 4.52 (*s*, 2 H, PhCH$_2$); 4.49 (*d*, $J = -12.2$, 1 H, PhCH$_2$); 4.45 (*d*, $J = -11.7$, 1 H, PhCH$_2$); 4.28 (*t*, $J(4,5) = 10.0$, H–C(4)); 4.25 (*d*, $J = -11.5$, 1 H, PhCH$_2$); 3.89 (*dd*, H_b–C(6′)); 3.76 (*dd*, $J(3,4) = 10.3$, H–C(3)); 3.75–3.71 (*m*, $J(5,6) = 6.4$, H–C(5)); 3.68 (br. *s*, H–C(2′)); 3.58–3.54 (*m*, H–C(3′), H–C(4′)); 3.56 (*d*, $J = -11.8$, 1 H, COCH$_2$); 3.26 (*d*, $J = -11.8$, 1 H, COCH$_2$); 1.14 (*d*, Me(6)). ^{13}C-NMR ($CDCl_3$): 164.9, 164.8 (*C*OCH$_2$); 97.6 ($J(1',H–C(1')) = 171.8$, C(1′)); 96.6 (C(1)); 80.2 (C(3′)); 76.6 (C(3)); 75.5 (C(2′)); 75.2 (C(4′)); 74.2 (PhCH$_2$); 73.5 (PhCH$_2$); 72.7 (PhCH$_2$); 71.7 (PhCH$_2$); 71.4 (C(2)); 70.1, 70.0, 69.9 (C(4), C(5), C(5′)); 68.9 (PhCH$_2$); 64.9 (C(6′)); 43.2 (COCH$_2$); 18.1 (C(6)). Anal. calc. for $C_{50}H_{52}O_{12}$ (844.96): C 71.07, H 6.20; found: C 71.00, H 6.29.

b) Exactly as described for **5** (*Exper. a*), with **46** (0.28 g, 0.31 mmol), NIS (0.35 g, 1.54 mmol), Me_3SiOTf (14 µl, 77 µmol), and MeCN (15 ml), followed by CC (toluene/acetone 20 : 1): **47** (196 mg, 75%).

c) Exactly as described for **5** (*Exper. c*), with **46** (0.32 g, 0.35 mmol), with MeOTf (0.19 ml, 1.77 mmol), and CH_2Cl_2 (15 ml), followed by CC (toluene/acetone 20 : 1): **47** (206 mg, 69%).

d) Exactly as described for **5** (*Exper. d*), with **46** (0.35 g, 0.38 mmol), MeOTf (0.21 ml, 1.91 mmol), and MeCN (15 ml): **47** (225 mg, 70%).

Benzyl O-*(6*-O-*Benzoyl-2,3,4-tri*-O-*benzyl-α*-D-*mannopyranosyl)-(1 → 4)-2*-O-*benzoyl-3*-O-*benzyl-α*-L-*rhamnopyranoside* (**48**). Exactly as described for **6**, with **47** (170 mg, 0.20 mmol), NaOMe in MeOH, BzCl (152 µl, 1.31 mmol), and pyridine (5 ml): **48** (145 mg, 73%). $[\alpha]_D = +10.3$ ($c = 1.4$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 5.65 (*dd*, $J(2,3) = 2.8$, H–C(2)); 4.93 (*d*, $J(1,2) = 1.6$, H–C(1)); 4.79 (*d*, $J = -12.3$, 1 H, PhCH$_2$); 4.78 (*d*, $J(1',2') = 1.6$, H–C(1′)); 4.75 (*d*, $J = -11.6$, 1 H, PhCH$_2$); 4.64 (*d*, $J = -12.0$, 1 H, PhCH$_2$); 4.64–4.55 (*m*, $J(5',6b') = 2.2$, H–C(5′)); 4.61 (*d*, $J = -12.4$, 1 H, PhCH$_2$); 4.56 (*d*, $J = -11.5$, 1 H, PhCH$_2$); 4.52–4.46 (*m*, 4 H, PhCH$_2$); 4.36–4.31 (*m*, $J(6a',6b') = -10.9$, H_a–C(6′)); 4.33 (*t*, $J(4,5) = 9.6$, H–C(4)); 4.26 (*d*, $J = -11.6$, 1 H, PhCH$_2$); 4.25 (*dd*, H_b–C(6′)); 4.05–4.00 (*m*, $J(5,6) = 6.3$, H–C(5)); 4.02–3.98 (*m*, H–C(4′)); 3.84 (*dd*, $J(3,4) = 9.2$, H–C(3)); 3.73–3.69 (*m*, $J(2',3') = 3.0$, H–C(2′)); 3.60 (*dd*, $J(3',4') = 9.4$, H–C(3′)); 1.24 (*d*, Me(6)). ^{13}C-NMR ($CDCl_3$): 166.6, 166.3 (PhCO); 100.8 ($J(1',H–C(1')) = 171.4$, C(1′)); 97.0 (C(1)); 80.6 (C(3′)); 79.6 (C(4)); 76.3 (C(2′)); 76.0 (C(3)); 75.3 (PhCH$_2$); 74.3 (C(4′)); 73.4, 72.2, 71.0 (PhCH$_2$); 69.8 (C(5′)); 69.4 (PhCH$_2$); 69.0 (C(2)); 68.6 (C(5)); 64.1 (C(6′)); 18.9 (C(6)). Anal. calc. for $C_{61}H_{60}O_{12}$ (985.15): C 74.37, H 6.14; found: C 74.50, H 6.10.

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