Pergamon

Tetrahedron 56 (2000) 563–579

TETRAHEDRON

Synthesis of 4-*O*-D-Mannopyranosyl-α-D-glucopyranosides by Intramolecular Glycosylation of 6-*O*-Tethered Mannosyl Donors

Gregor Lemanski and Thomas Ziegler*

Institute of Organic Chemistry, University of Cologne, Greinstraße 4, D-50939 Cologne, Germany

Received 29 October 1999; accepted 3 December 1999

Abstract—A series of mannosyl donors linked via position 6 by a carbonate, oxalate, malonate, succinate, and phthalate tether, respectively, to position 3 of a glucoside and glucosamine acceptor afforded during intramolecular glycosylation, anomeric mixture of the corresponding disaccharides. The dependence of the diastereoselectivity on the glycosylation procedure, the solvent, and the blocking groups in comparison to an intermolecular mannosylation is studied.

Introduction

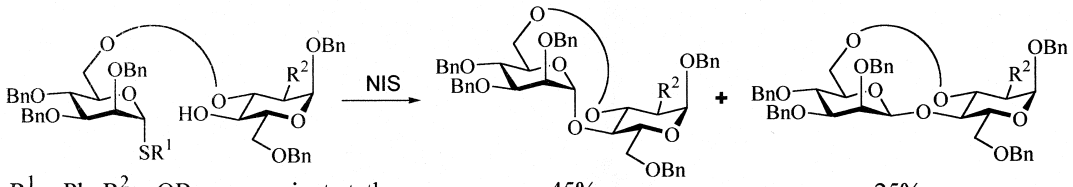
The disaccharide fragment β-D-Man*p*-(1→4)-D-Glc*p*/GlcNAc*p* is a very common structural disaccharide motif found in a huge number of naturally occurring oligosaccharides. For example, the Complex Carbohydrate Structure Database (CCSD) at the University of Georgia (http://128.192.9.29/carbbank/) contains more than 7,000 entries for this disaccharide fragment. In particular, this structure is found in the core region of *N*-glycanes of glycoproteins, in glycosphingolipids, and in various lipopolysaccharides. Without any doubt, it can be regarded as one of the most significant disaccharide structures found in nature. Due to the importance of β-D-Man*p*-(1→4)-D-Glc*p*/GlcNAc*p* fragments significant efforts toward the chemical synthesis of that structure have been undertaken in recent years and novel approaches for the construction of the difficult β-mannosidic linkage have been developed.[1–7]

Recently, we disclosed a new procedure for the synthesis of β-D-mannose containing saccharides using the intramolecular glycosylation approach via prearranged glycosides.[8] Thus, a suitably protected mannosyl donor was first linked by a succinyl or malonyl tether at its position 6 to a glucosyl acceptor followed by intramolecular glycosylation/cyclisation to afford the corresponding disaccharides (Scheme 1).[8,9]

For the disaccharide D-Man*p*-(1→4)-D-Glc*p* an α/β-ratio of 64:36 was obtained[9] whereas the disaccharide β-D-Man*p*-(1→4)-D-GlcNAc*p* was exclusively formed.[8] In order to understand the factors which influence the anomeric outcome of these intramolecular mannosylations we now made systematic variations of the length and flexibility of the tether as well as variations of the leaving group of the donor. Furthermore, solvent effects and different activation procedures have been studied in relation to the diastereoselectivity of intramolecular mannosylations as well.

Results and Discussion

As a basis for the comparison of the diastereoselectivity of intramolecular glycosylations and of the factors which may

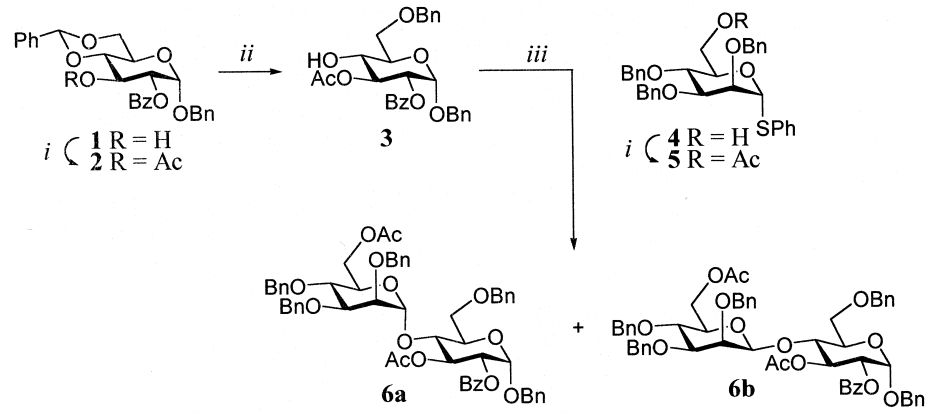


Scheme 1. Intramolecular glycosylation with 6-*O*-tethered mannosyl donors.

Keywords: intermolecular glycosylation; diastereoselectivity.

* Corresponding author. Fax: +49-221-470-5057; e-mail: thomas.ziegler@uni-koeln.de

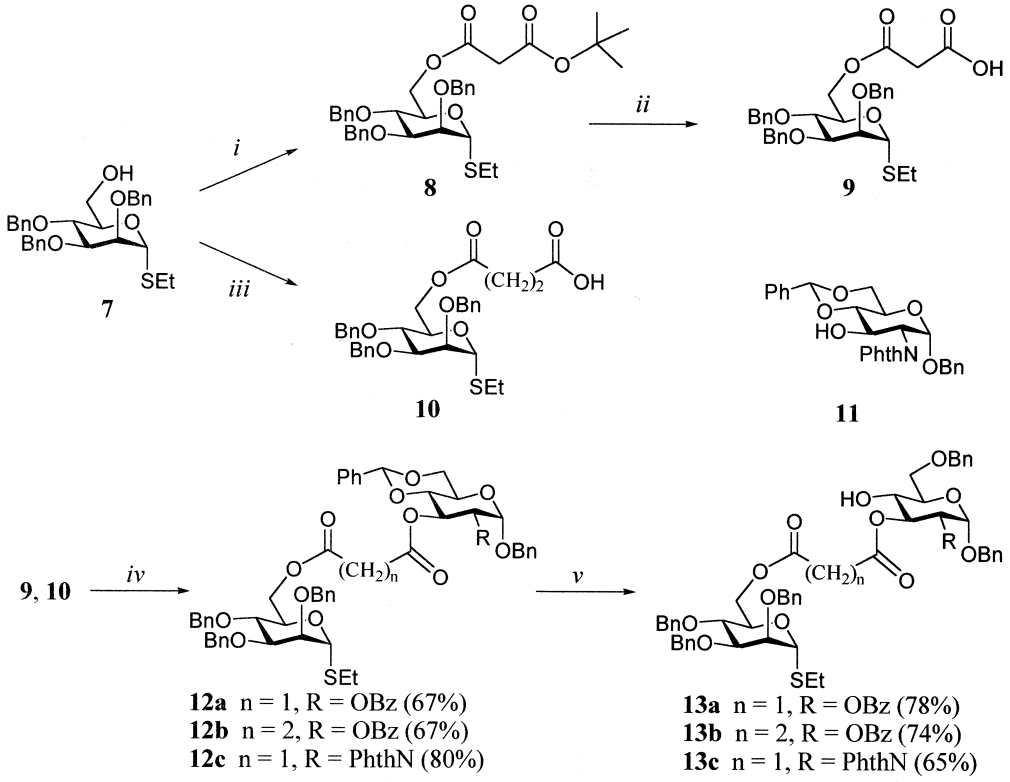
0040–4020/00/$ - see front matter
PII: S0040-4020(99)01053-4



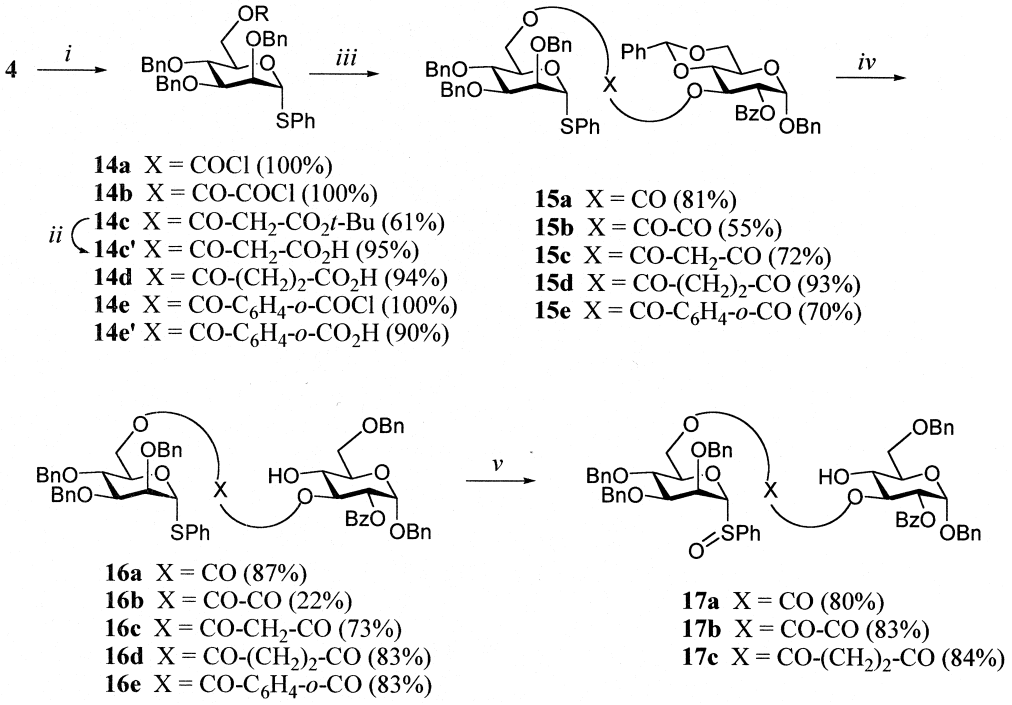
Scheme 2. (i) Ac_2O, pyridine, 87% **2**, 86% **5**; (ii) $NaCNBH_3$, HCl in Et_2O, 82%; (iii) NIS, cat. TMSOTf, −30°C, MeCN, 21% **6a**, 3% **6b**.

influence this selectivity we first prepared the disaccharides **6** by a classical approach as follows (Scheme 2). Benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside[10] (**1**) was conventionally acetylated to give **2**, the benzylidene acetal of which was regioselectively opened[11] to afford acceptor **3**. Next, phenyl 1-thio-mannoside donor **5** was prepared via intermediate **4** from phenyl 1-thio-α-D-mannopyranoside[12] by sequential tritylation (Trt-Cl, pyridine), benzylation (BnBr, NaH, DMF), detritylation (aqueous HCl, acetone), and acetylation (Ac_2O, pyridine). Coupling of **3** and **5** under activation with *N*-iodosuccinimide (NIS) and a catalytic amount of trimethylsilyl trifluoromethanesulfonate (TMSOTf) then afforded disaccharides **6** in 24% overall yield. Compound **6** was formed as a 88:12 mixture of the anomers **6a** and **6b**, respectively.

Next, for the systematic variation of the tethers and of the activation procedures for intramolecular mannosylations a series of differently linked prearranged glycosides **13**, **16**, and **17** were prepared (Schemes 3 and 4). Starting from known ethyl 2,3,4-tri-*O*-benzyl-1-thio-α-D-mannopyranoside[13] (**7**), esterification with *t*-butyl malonate[14] and dicyclohexyl carbodiimide (DCC) afforded compound **8**, the *t*-butyl group of which was hydrolyzed with CF_3CO_2H to give mannoside **9**. Similarly, **7** was treated with succinic anhydride as previously described[8,9,10b,11a] to afford the succinate **10**. Acids **9** and **10** were condensed with benzylidene protected glucosides **1** and **11**,[15] respectively, and the intermediates **12a**–**c** were finally converted into the prearranged glycosides **13a**–**c** (Scheme 3). In the case of compounds **12a**,**b** and **13a**,**b**, respectively, the condensation



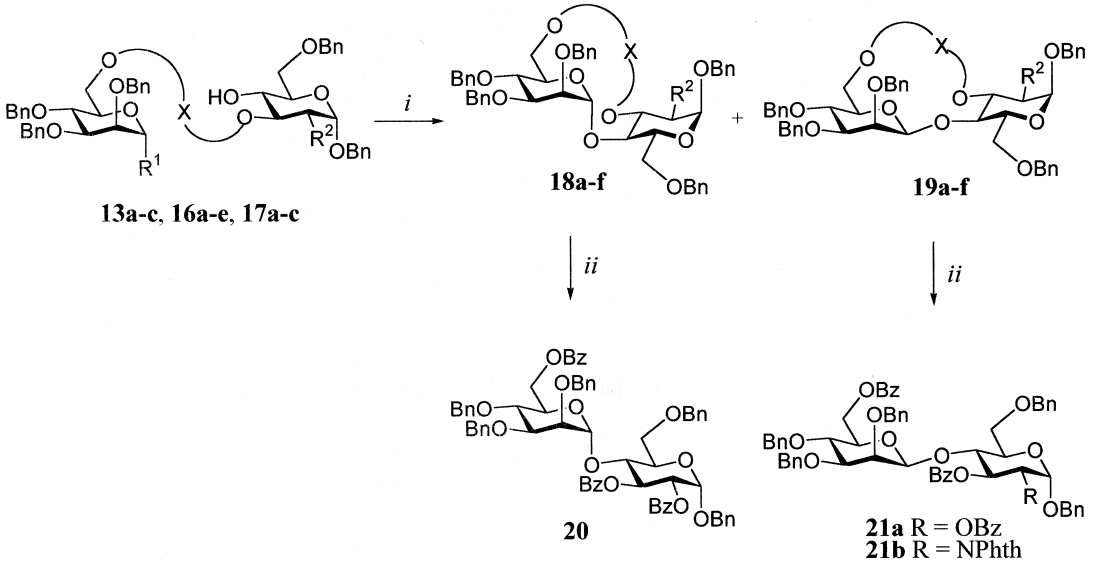
Scheme 3. (i) $HO_2C–CH_2–CO_2t$-Bu, DCC (64%); (ii) CF_3CO_2H (100%); (iii) succinic anhydride, pyridine, cat. DMAP (85%); (iv) (a,b) **1**, DCC, cat. DMAP; (c) **11**, 2-chloro-1-methyl pyridiniumiodide, $(n\text{-Bu})_{33}N$; (v) (a,b) $NaCNBH_3$, HCl in Et_2O; (c) Et_3SiH, CF_3CO_2H.



Scheme 4. (i) (a) $COCl_2$, pyridine; (b) $(CO)_2Cl_2$, pyridine; (c) $HO_2C–CH_2–CO_2t$-Bu, DCC; (d) succinic anhydride, pyridine, cat. DMAP; (e) phthaloyl dichloride, pyridine or phthalic anhydride, pyridine, cat. DMAP; (ii) CF_3CO_2H; (iii) (a) **1**, pyridine; (b) **1**, DCC, cat. DMAP; (iv) $NaCNBH_3$, HCl in Et_2O; (v) *m*-chloroperbenzoic acid.

and reductive ring opening of the benzylidene group could be performed conventionally as described above. However, the condensation of **9** and **11** with DCC as well as reduction of the benzylidene group of **12c** with $NaCNBH_3$ proceeded sluggishly and gave **13c** in poor yield. A similar observation has been previously made.[15] Therefore, Mukaiyama's method (2-chloro-1-methyl pyridiniumiodide, tri-*n*-butylamine)[16] was applied for the condensation step and DeNinno's method (Et_3SiH, CF_3CO_2H)[17] for the regioselective benzylidene ring opening which both gave satisfactory yields.

In similar sequences, phenyl 2,3,4-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (**4**) was used for the introduction of different tethers as outlined in Scheme 4. Treatment of **4** with phosgene and oxallylchloride in pyridine, respectively, afforded compounds **14a** and **14b**, which were both used without further purification. Esterification of the latter with glucoside **1** then gave first intermediates **15a** and **15b**, which were once again converted into the prearranged glycosides **16a** and **16b** by reduction with $NaCNBH_3$. Furthermore, the corresponding sulfoxides **17a** and **17b** were prepared as well according to Kahne's procedure[18]



Scheme 5. (i) For activation, R^1, R^2, and X see Table 1; (ii) (1) cat. NaOMe in MeOH; (2) BzCl, pyridine.

Table 1. Intramolecular glycosylation of compounds **13**, **16**, and **17**

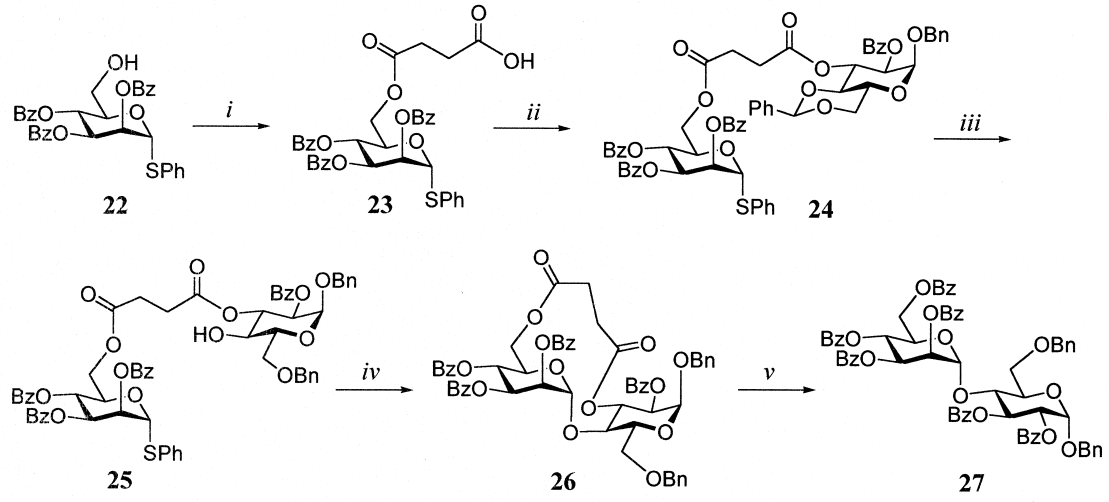
Entry	Starting material	R1	R2	X	Ring size	Activation[a]	Solvent	Yield (%) **18**	Yield (%) **19**	Ratio α:β
1	**13a**	SEt	OBz	Malonate	12	A	MeCN	13 **18a**	58 **19a**	18:82
2						A	CH_2Cl_2	17 **18a**	53 **19a**	24:76
3						B	MeCN	6 **18a**	73 **19a**	8:92
4						B	CH_2Cl_2	9 **18a**	68 **19a**	12:88
5	**13b**	SEt	OBz	Succinate	13	A	MeCN	38 **18b**	33 **19b**	53:47
6						A	CH_2Cl_2	43 **18b**	27 **19b**	61:39
7						B	MeCN	27 **18b**	43 **19b**	39:61
8						B	CH_2Cl_2	31 **18b**	37 **19b**	46:54
9						C	MeCN	36 **18b**	37 **19b**	49:51
10						C	CH_2Cl_2	40 **18b**	32 **19b**	56:44
11	**13c**	SEt	NPhth	Malonate	12	A	MeCN	0 **18c**	51 **19c**	0:100
12						A	CH_2Cl_2	0 **18c**	47 **19c**	0:100
13						B	MeCN	0 **18c**	52 **19c**	0:100
14						B	CH_2Cl_2	0 **18c**	49 **19c**	0:100
15	**16a**	SPh	OBz	Carbonate	10	A, D, E	MeCN CH_2Cl_2	–	–	–[b]
16						C, B	MeCN CH_2Cl_2	–	–	–[c]
17	**17a**	SOPh	OBz	Carbonate	10	F	MeCN	76 **18d**	0 **19d**	100:0
18						F	CH_2Cl_2	79 **18d**	0 **19d**	100:0
19	**16b**	SPh	OBz	Oxalate	11	A, B, D, E	MeCN CH_2Cl_2	–	–	–[b]
20						C	MeCN CH_2Cl_2	–	–	–[c]
21	**17b**	SOPh	OBz	Oxalate	11	F	MeCN	72 **18e**	0 **19e**	100:0
22						F	CH_2Cl_2	75 **18e**	0 **19e**	100:0
23	**16c**	SPh	OBz	Malonate	12	A	MeCN	22 **18a**	54 **19a**	29:71
24						A	CH_2Cl_2	25 **18a**	50 **19a**	33:67
25	**16d**	SPh	OBz	Succinate	13	A	MeCN	45 **18b**	25 **19b**	64:36
26						A	CH_2Cl_2	53 **18b**	21 **19b**	72:28
27	**17c**	SOPh	OBz	Succinate	13	F	MeCN	48 **18b**	23 **19b**	67:33
28						F	CH_2Cl_2	54 **18b**	23 **19b**	70:30
29	**16e**	SPh	OBz	Phthalate	13	A	MeCN	69 **18f**	9 **19f**	89:11
30						A	CH_2Cl_2	63 **18f**	10 **19f**	86:14

[a] A: NIS, cat TMSOTf, −30°C; B: MeOTf, 20°C; C: IDCP, 20°C; D: DMTST, 20°C; E: Br_2, AgOTf, 25°C; F: Tf_2O, 2,6-di-*t*-butyl-pyridine, −50 to 20°C.
[b] Decomposition.
[c] No reaction.

(*m*-chloroperbenzoic acid). The malonyl tether was introduced via **14c** and **15c** as described above. Similarly, succinates **14d**, **15d**, **16d**, and **17c** were obtained accordingly and as described previously.[8] For the synthesis of the phthaloyl tethered glycosides, two approaches have been tested. First, **4** was condensed with phthalicdichloride to give crude **14e**. However, all attempts to esterify the latter with glucoside **1** failed. Therefore, **4** was treated with phthalic anhydride to give the acid **14e′** the condensation of which with **1** and DCC proceeded without any problems and afforded **15e** in 70% yield. Finally, ring opening of the benzylidene acetal of the latter with $NaCNBH_3$ gave prearranged glycoside **16e**.

All prearranged glycosides **13**, **16**, and **17** were used for intramolecular mannosylations (Scheme 5) using NIS and a catalytic amount of TMSOTf at −30°C (procedure A),[19] methyl trifluoromethanesulfonate (MeOTf) at 20°C (procedure B),[20] iodoniumdicollidine perchlorate (IDCP) at 20°C (procedure C),[21] dimethyl methylthiosulfoniumtriflate (DMTST) at 20°C (procedure D),[20a,22] Br_2 and silver trifluoromethanesulfonate (AgOTf) at 20°C (procedure E),[23] and trifluoromethanesulfonic anhydride (Tf_2O) at −50 to 20°C (procedure F).[24] The results are summarized in Table 1. The anomeric configurations of the obtained disaccharides were determined by measuring the $^1J_{C\text{-}1,1\text{-}H}$-coupling constants at the anomeric centers of the mannose residues of all individual compounds. Typically, coupling constants of 153–160 Hz are indicative for β-linked mannose residues and constants of 162–173 Hz are indicative for α-linked mannosides.[25] For α-linked disaccharides **18**, the coupling constants were found to be in the range 164.3–168.5 Hz, and for β-linked disaccharides **19** in the range 153.1–153.4 Hz. Furthermore, deacylation of tethered compounds **18** and **19** followed by rebenzoylation of the intermediates afforded disaccharides **20** and **21** (Scheme 5) which also showed significant coupling constants of 171.8, 156.8, and 154.8 Hz, respectively.

In general, the following global properties of intramolecular glycosylations could be deduced from the experiments. (1) All intramolecular glycosylations (except those performed on carbonate and oxalate tethered 1-thio-glycosides **16a** and **16b** with procedures A–E, cf. Table 1, entries 15 and 19) proceeded with significantly higher yield than the intermolecular mannosylation between **3** and **5** (Scheme 2). Particularly, under identical conditions (activation with NIS), intramolecular mannosylations (Table 1, entries 1, 5, 23, 25, and 29) gave a 70–80% yield of the corresponding disccharides **18** and **19** whereas the intermolecular mannosylation afforded disaccharides **6** in poor 24% yield. Similar observations have been previously made for intramolecular (1→4)-selective rhamnosylations of galactosides.[26] (2) Except for intramolecular mannosylations with



Scheme 6. (i) Succinic anhydride, pyridine, cat. DMAP, 82%; (ii) **1**, DCC, cat. DMAP, 73%; (iii) $NaCNBH_3$, HCl in Et_2O, 93%; (iv) (a) NIS, cat. TMSOTf, MeCN, 63%; (b) NIS, cat. TMSOTf, CH_2Cl_2, 70%; (v) (1) cat. NaOMe in MeOH; (2) BzCl, pyridine, 81%.

phthalate tethered prearranged glycoside **16e** (entry 29) which resulted in an anomeric mixture of α:β=89:11, all other glycosylations proceeded with significantly higher β-content (up to α:β=8:92 in entry 3) than the intermolecular mannosylation of **3** and **5** which gave an α:β mixture of 88:12 (Scheme 2). (3) There was no strong solvent dependence of the diastereoselectivity as was previously observed for other intramolecular glycosylations.[27] (4) No dramatic change in diastereoselectivity could be observed for different activation procedures (cf. entries 1–4 vs. 23 and 24, 5–10 vs. 25–28). In contrast, a complete inversion of the anomeric selectivity has been found for intramolecular condensations with succinate tethers at position 3 of the mannosyl donor.[8] (5) Highest yields of β-(1→4)-linked products were obtained when a 12-membered ring was formed with malonate tethered compounds **13a** (entries 3 and 4) and **13c** (entries 11–14).

Obviously, a strong influence of the tether on the diastereoselectivity of intramolecular mannosylations is operative. When a 10-membered ring is formed (carbonate tethers, entries 15–18) solely activation of the sulfoxide **17a** gave α-linked product **18d**. No β-linked product **19d** was found in this case. Similarly, for an 11-membered ring (oxalate tether, entries 19–22) **17b** resulted in exclusive formation of the corresponding α-linked disaccharide **18e**. No reaction or decomposition of the starting materials **16a**, and **16b**, respectively, was observed for other activation procedures. The formation of 12-membered rings (i.e. a malonate tether, entries 1–4, 11–14, 23, and 24) resulted in high contents of the β-linked products **19a** and **19c**, respectively, whereas the formation of 13-membered rings (i.e. succinate and phthalate tethers, entries 5–10, 25–30) gave again higher contents of α-linked disaccharides **18b** and **18f**, respectively.

The influence of the tether on the anomeric selectivity of intramolecular mannosylations can be put down at least in part to the differences in the thermodynamic stability of the disaccharides **18** and **19**. A similar observation has been made previously for intramolecular galactosylations.[28] Molecular modeling studies for compounds **18** and **19** using a Monte-Carlo conformation search with the AMBER force field implemented in MacroModel[29] showed the α-linked products **18b**, **18d**, **18e**, and **18f** to be 26.6–55.5 kJ/mol more stable than the corresponding β-linked disaccharides. Solely, for malonate tethered disaccharides the β-linked products **19b** and **19c** were ca. 4 kJ/mol more stable than the α-linked counterpart. However, additional factors like the activation procedure used for the ring closure and the blocking groups at the mannosyl donor play also a significant role for the anomeric outcome. The latter influence was previously encountered for other intramolecular glycosylations[9,11a,26–28] and was also demonstrated here for prearranged glycoside **25** which had neighboring active benzoyl groups instead of benzyl groups as in compounds **13b**, **16d**, and **17c**.

Compound **25** was prepared as outlined above by succinoylation of **22**[12] to give first succinate **23**, condensation of which with **1** then afforded **24**, and reductive ring opening of the latter finally gave **25** (Scheme 6). When glycoside **25** was treated with NIS under identical conditions as in Table 1, solely the α-linked disaccharide **26** was obtained in 70% yield whereas the corresponding benzyl protected glycoside **16d** afforded a 72:28 α/β-mixture in 74% yield (Table 1, entry 26). Once again, the α-linkage in **26** was unambiguously assigned by the found CH-coupling constant of 168.2 Hz and by converting **26** into **27** which also had $J_{C\text{-}1,1\text{-}H}$=167.5 Hz.

Experimental

General

The NMR data were obtained from spectra measured in $CDCl_3$ solutions (with Me_4Si as internal standard) at 25°C with Bruker AC 300F and DRX 500 spectrometers at 300 and 500 MHz for ^1H NMR spectra, and 75 and 126 MHz for ^{13}C NMR spectra, respectively. ^1H NMR signal assignments were made by first-order analysis of the spectra and by HH-COSY spectra. Of the two magnetically non-equivalent geminal protons at C-6, the one resonating at lower field was

allocated 6a-H and the one resonating at higher field 6b-H. ^{13}C NMR assignments were made by mutual comparison of the spectra, by DEPT spectra, and by CH-COSY spectra. Optical rotations were measured at 25°C with a Perkin–Elmer automatic polarimeter, Model 241. TLC was performed on precoated plastic sheets, Polygram SIL UV_{254}, 40×80 mm (Macherey–Nagel) using appropriately adjusted mixtures of toluene/ethyl acetate. Detection was effected by UV light, where applicable, and by charring with 5% H_2SO_4 in ethanol. CC was performed by eluting from columns of Silica Gel 60 (Merck) with appropriately adjusted mixtures of toluene/ethyl acetate. Solutions in organic solvents were dried with anhydrous Na_2SO_4 and concentrated at 2 kPa, <40°C.

Benzyl 3-*O*-acetyl-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (2). A solution of benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside[10] (**1**, 1.16 g, 2.51 mmol) and acetic anhydride (1.42 ml, 15.06 mmol) in pyridine (15 ml) was stirred at 20°C for 24 h, poured into water and extracted with dichloromethane. The organic extracts were washed with aqueous HCl solution, dried and concentrated. Chromatography (*n*-hexane/ethyl acetate 5:1) of the residue afforded **2** (1.10 g, 87%), $[\alpha]_D=+134.8$ ($c=0.9$, $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta=5.85$ (t, 1H, $J_{3,4}=9.9$ Hz, 3-H), 5.53 (s, 1H, PhCH), 5.27 (d, 1H, $J_{1,2}=4.1$ Hz, 1-H), 5.07 (dd, 1H, $J_{2,3}=10.0$ Hz, 2-H), 4.75 (d, 1H, $J=-12.4$ Hz, $PhCH_2$), 4.54 (d, 1H, $J=-12.4$ Hz, $PhCH_2$), 4.26 (dd, 1H, $J_{5,6a}=4.9$ Hz, $J_{6a,6b}=-10.1$ Hz, 6a-H), 4.08 (dt, 1H, $J_{5,6b}=10.2$ Hz, 5-H), 3.79 (t, 1H, 6b-H), 1.99 (s, 3H, $COCH_3$). ^{13}C NMR ($CDCl_3$): $\delta=169.9$, 165.7 (CO), 101.6 (PhCH), 95.9 (C-1), 79.2 (C-4), 72.3 (C-2), 69.9 ($PhCH_2$), 68.9 (C-3), 68.3 (C-6), 62.8 (C-5), 20.8 ($COCH_3$). Anal. calcd for $C_{29}H_{28}O_8$: C, 69.04; H, 5.59; Found: C, 69.00; H, 5.66.

Benzyl 3-*O*-acetyl-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (3). A solution of HCl in Et_2O was added portionwise at 20°C to a stirred suspension of **2** (0.93 g, 1.84 mmol), 3 Å molecular sieves (ca. 0.5 g) and $NaCNBH_3$ (1.45 g, 23 mmol) in THF (15 ml) until the evolution of gas ceased. The mixture was diluted with dichloromethane and filtered through a layer of Celite. The filtrate was washed with aqueous $NaHCO_3$ solution and water, dried and concentrated. Chromatography (CCl_4/acetone 6:1) of the residue afforded **3** (0.77 g, 82%), $[\alpha]_D=+118.1$ ($c=1.1$, $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta=5.59$ (dd, 1H, $J_{3,4}=9.1$ Hz, 3-H), 5.23 (d, 1H, $J_{1,2}=3.7$ Hz, 1-H), 5.04 (dd, 1H, $J_{2,3}=10.2$ Hz, 2-H), 4.73 (d, 1H, $J=-12.4$ Hz, $PhCH_2$), 4.63 (d, 1H, $J=-12.0$ Hz, $PhCH_2$), 4.57 (d, 1H, $J=-12.1$ Hz, $PhCH_2$), 4.52 (d, 1H, $J=-12.4$ Hz, $PhCH_2$), 3.97–3.91 (m, 1H, $J_{5,6a}=4.2$ Hz, $J_{5,6b}=4.0$ Hz, 5-H), 3.88–3.84 (m, 1H, $J_{4,5}=9.5$ Hz, 4-H), 3.78 (dd, 1H, $J_{6a,6b}=-10.4$ Hz, 6a-H), 3.70 (dd, 1H, 6b-H), 2.88 (d, 1H, $J_{4,OH}=3.8$ Hz, OH), 2.02 (s, 2H, $COCH_3$). ^{13}C NMR ($CDCl_3$): $\delta=171.5$ ($COCH_3$), 165.7 (PhCO), 95.2 (C-1), 73.4 ($PhCH_2$), 73.0 (C-3), 71.4 (C-2), 70.5 (C-5), 70.3 (C-4), 69.7 ($PhCH_2$), 69.5 (C-6), 20.9 ($COCH_3$). Anal. calcd for $C_{29}H_{30}O_8$: C, 68.76; H, 5.97; Found: C, 68.96; H 6.10.

Phenyl 2,3,4-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (4). (a) A solution of phenyl 1-thio-α-D-mannopyranoside[12] (4.81 g, 17.7 mmol) and tritylchloride (4.56 g, 16.4 mmol) in pyridine (20 ml) was stirred at 20°C for 24 h. The mixture was poured into water and extracted with dichloromethane. The extracts were washed with water, dried and concentrated to give crude phenyl 6-*O*-trityl-1-thio-α-D-mannopyranoside (7.65 g). BnBr (5.27 ml, 44.6 mmol) was added at 0°C to a solution of the crude tritylated intermediate and NaH (2.06 g, 85.8 mmol) in DMF (30 ml) and the mixture was stirred at 20°C for 3 h. Excess NaH was destroyed by careful addition of MeOH and the mixture was poured into water and extracted with dichloromethane. The extracts were washed with aqueous $NaHCO_3$ solution, dried and concentrated. Chromatography (CCl_4/acetone 5:1) of the residue afforded phenyl 2,3,4-tri-*O*-benzyl-6-*O*-trityl-1-thio-α-D-mannopyranoside (9.0 g, 70%), $[\alpha]_D=+80.1$ ($c=1.1$, $CHCl_3$). ^1H NMR (significant signal, $CDCl_3$): $\delta=5.70$ (d, 1H, $J_{1,2}=1.4$ Hz, 1-H). ^{13}C NMR ($CDCl_3$): $\delta=85.3$ (C-1), 80.2 (C-3), 77.1 (C-4), 75.2 (C-2), 72.8 (C-5), 62.8 (C-8). Anal. calcd for $C_{52}H_{48}O_5S$: C, 79.56; H, 6.16; S, 4.09; Found: C, 79.39; H, 6.21; S, 3.85.

(b) A solution of phenyl 2,3,4-tri-*O*-benzyl-6-*O*-trityl-1-thio-α-D-mannopyranoside (5.95 g, 7.6 mmol) and 1 M aqueous HCl solution (15 ml) in acetone (150 ml) was stirred at 60°C for 24 h. The mixture was cooled to 20°C, washed with aqueous $NaHCO_3$ solution, dried and concentrated. Chromatography (CCl_4/acetone 15:1) of the residue afforded **4** (2.51 g, 61%), $[\alpha]_D=+86.1$ ($c=1.0$, $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta=5.51$ (d, 1H, $J_{1,2}=1.6$ Hz, 1-H), 4.69 (d, 1H, $PhCH_2$), 4.67 (s, 2H, $PhCH_2$), 4.65 (d, 1H, $PhCH_2$), 4.61 (d, 1H, $PhCH_2$), 4.60 (d, 1H, $PhCH_2$), 4.15–4.09 (m, 1H, 5-H), 4.05 (t, 1H, $J_{3,4}=J_{4,5}=9.5$ Hz, 4-H), 3.99 (dd, 1H, $J_{2,3}=3.1$ Hz, 2-H), 3.88 (dd, 1H, 3-H), 3.81–3.75 (m, 2H, 6a-H, 6b-H). ^{13}C NMR ($CDCl_3$): $\delta=86.0$ (C-1), 80.3 (C-3), 76.4 (C-4), 75.3 ($PhCH_2$), 74.7 (C-2), 73.2 (C-5), 72.3, 72.2 ($PhCH_2$), 62.2 (C-6). Anal. calcd for $C_{33}H_{34}O_5S$: C, 73.04; H, 6.31; S, 5.91; Found: C, 72.82; H, 6.28; S, 5.74.

Phenyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-1-thio-α-D-mannopyranoside (5). Treatment of **4** (3.07 g, 5.7 mmol) with acetic anhydride (3.2 ml, 34 mmol) in pyridine (30 ml) as described for compound **2** afforded **5** (2.84 g, 86%), $[\alpha]_D=+75.8$ ($c=2.0$, $CHCl_3$). ^1H NMR ($CDCl_3$): $\delta=5.57$ (d, 1H, $J_{1,2}=1.6$ Hz, 1-H), 4.95 (d, 1H, $J=-10.8$ Hz, $PhCH_2$), 4.72 (d, 1H, $J=-12.3$ Hz, $PhCH_2$), 4.63 (d, 1H, $J=-10.8$ Hz, $PhCH_2$), 4.61–4.57 (m, 3H, $PhCH_2$), 4.35–4.29 (m, 3H, $J_{5,6a}=4.6$ Hz, 5-H, 6a-H, 6b-H), 4.00 (dd, 1H, $J_{2,3}=2.9$ Hz, 2-H), 3.97–3.93 (m, 1H, 4-H), 3.88 (dd, 1H, $J_{3,4}=9.2$ Hz, 3-H), 2.01 (s, 3H, $COCH_3$). ^{13}C NMR ($CDCl_3$): $\delta=170.8$ ($COCH_3$), 85.5 (C-1), 80.1 (C-3), 76.0 (C-2), 75.3 ($PhCH_2$), 74.6 (C-4), 72.1, 71.9 ($PhCH_2$), 70.9 (C-5), 63.5 (C-6), 20.8 ($COCH_3$). Anal. calcd for $C_{35}H_{36}O_6S$: C, 71.89; H, 6.20; S, 5.48; Found: C, 72.00; H, 6.25; S, 5.40.

Benzyl *O*-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-3-*O*-acetyl-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (6a) and benzyl *O*-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-3-*O*-acetyl-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (6b). A mixture of **3** (0.67 g, 1.32 mmol), **5** (0.92 g, 1.58 mmol), NIS (1.50 g, 6.6 mmol) and 4 Å molecular sieves (ca. 0.5 g) in MeCN (20 ml) was cooled under Ar to −30°C. TMSOTf

(61 μl, 0.33 mmol) was added with a syringe, the mixture was stirred for 10 min, neutralized by addition of pyridine, diluted with dichloromethane and filtered. The filtrate was washed with aqueous $NaHCO_3$ and $Na_2S_2O_3$ solution, dried and concentrated. Chromatography (toluene/acetone 25:1) of the residue afforded first **6a** (278 mg, 21%), $[\alpha]_D$=+84.8 (c=1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.61 (t, 1H, $J_{3,4}$=8.9 Hz, 3-H), 5.22 (d, 1H, $J_{1,2}$=3.6 Hz, 1-H), 5.08 (s, 1H, 1′-H), 4.95 (dd, 1H, $J_{2,3}$=10.3 Hz, 2-H), 4.86 (d, 1H, J=−10.9 Hz, $PhCH_2$), 4.72 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.66–4.59 (m, 6H, $PhCH_2$), 4.64 (d, 1H, J=−11.7 Hz, $PhCH_2$), 4.56 (d, 1H, J=−12.7 Hz, $PhCH_2$), 4.22 (bs, 2H, 6a′-H, 6b′-H), 3.98–3.79 (m, 6H, 3′-H, 4′-H, 4-H, 5′-H, 5-H, 6a-H), 3.71–3.67 (m, 2H, 2′-H, 6b-H), 1.98 (s, 3H, $COCH_3$), 1.73 (s, 3H, $COCH_3$). ^{13}C NMR ($CDCl_3$): δ=170.7, 169.9 ($COCH_3$), 165.6 (PhCO), 100.0 (C-1′, $J_{C\text{-}1',1'\text{-}H}$=170.3 Hz), 94.9 (C-1), 79.6 (C-3′), 76.1, 74.2 (C-4,4′), 74.9 (2 C, C-2′, $PhCH_2$), 73.4 ($PhCH_2$), 72.4 ($PhCH_2$), 72.3 (C-3), 72.1 ($PhCH_2$), 71.8 (C-2), 71.3 (C-5), 70.1 (C-5′), 69.8 ($PhCH_2$), 68.5 (C-6), 63.6 (C-6′), 20.8 (2 C, $COCH_3$). Anal. calcd for $C_{58}H_{60}O_{14}$: C, 71.01; H, 6.16; Found: C, 70.89; H, 6.09.

Eluted next was **6b** (44.4 mg, 3%), $[\alpha]_D$=+45.0 (c=1.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.76 (t, 1H, $J_{3,4}$=9.8 Hz, 3-H), 5.28 (d, 1H, $J_{1,2}$=3.8 Hz, 1-H), 5.02 (dd, 1H, $J_{2,3}$=10.3 Hz, 2-H), 4.91 (d, 1H, J=−10.9 Hz, $PhCH_2$), 4.84 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.73 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.65 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.64 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.57 (d, 1H, J=−12.9 Hz, $PhCH_2$), 4.55 (d, 1H, J=−12.5 Hz, $PhCH_2$), 4.51 (bs, 1H, $PhCH_2$), 4.42 (d, 1H, J=−11.9 Hz, $PhCH_2$), 4.40 (d, 1H, J=−12.1 Hz, $PhCH_2$), 4.33 (s, 1H, 1′-H), 4.28 (bd, 2H, 6a′-H, 6b′-H), 4.01 (t, 1H, $J_{4,5}$=9.7 Hz, 4-H), 3.92–3.89 (m, 1H, 5-H), 3.78 (t, 1H, $J_{4',5'}$=9.4 Hz, 4′-H), 3.65 (bd, $J_{2',3'}$=2.9 Hz, 2′-H), 3.58 (bd, 2H, 6a-H, 6b-H), 3.33–3.30 (m, 1H, 5′-H), 3.29 (dd, 1H, $J_{3',4'}$=9.3 Hz, 3′-H), 2.00 (s, 3H, $COCH_3$), 1.95 (s, 3H, $COCH_3$). ^{13}C NMR ($CDCl_3$): δ=170.8, 170.4 ($COCH_3$), 165.7 (PhCO), 100.9 (C-1′, $J_{C\text{-}1',1'\text{-}H}$=152.2 Hz), 95.3 (C-1), 82.2 (C-3′), 75.0 ($PhCH_2$), 74.9 (C-4), 74.3 (C-4′), 73.8 (C-2′), 73.6 (1 C, 2 C, C-5′, $PhCH_2$), 71.8 (C-2), 71.3 ($PhCH_2$), 70.1 (C-5), 69.8 ($PhCH_2$), 69.7 (C-3), 68.1 (C-6), 63.6 (C-6′), 20.8, 20.7 ($COCH_3$). Anal. calcd for $C_{58}H_{60}O_{14}$: C, 71.01; H, 6.16; Found: C, 71.20; H, 6.10.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(*t*-butyloxycarbonylethanoyl)-1-thio-α-D-mannopyranoside (8). DCC (0.96 g, 4.65 mmol) was added at 0°C to a solution of **7**[13] (2.09 g, 4.23 mmol), *t*-butyl malonate[14] (0.75 g, 4.65 mmol) and 1-hydroxy-1*H*-benzotriazole (0.69 g, 5.08 mmol) in dichloromethane (30 ml). The mixture was stirred at 20°C for 24 h, diluted with dichloromethane and filtered through a layer of Celite. The filtrate was subsequently washed with aqueous HCl and $NaHCO_3$ solution, dried and concentrated. Chromatography (*n*-hexane/ethyl acetate 6:1) of the residue afforded **8** (1.73 g, 64%), $[\alpha]_D$=+58.0 (c=1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.33 (d, 1H, $J_{1,2}$=1.0 Hz, 1-H), 4.92 (d, 1H, J=−10.7 Hz, $PhCH_2$), 4.71 (d, 1H, J=−12.5 Hz, $PhCH_2$), 4.65 (d, 1H, J=−12.5 Hz, $PhCH_2$), 4.60–4.56 (m, 3H, $PhCH_2$), 4.44 (dd, 1H, $J_{5,6a}$=5.1 Hz, $J_{6a,6b}$=−11.8 Hz, 6a-H), 4.36 (dd, 1H, $J_{5,6b}$=2.2 Hz, 6b-H), 4.18 (ddd, 1H, 5-H), 3.93 (t, 1H, $J_{4,5}$=9.4 Hz, 4-H), 3.83 (2 dd, 2H, $J_{2,3}$=3.2 Hz, $J_{3,4}$=10.1 Hz, 2-H, 3-H), 3.29 (s, 2H, $COCH_2$), 2.66–2.47 (m, 2H, SCH_2CH_3), 1.44 (s, 9H, $C(CH_3)_3$), 1.23 (t, 3H, J=7.4 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ=166.9 (CO), 165.4 (CO), 82.0 ($C(CH_3)_3$), 81.9 (C-1), 80.2 (C-3), 76.2 (C-2), 75.2 ($PhCH_2$), 74.6 (C-4), 72.0 (2 C, $PhCH_2$), 70.1 (C-5), 64.3 (C-6), 42.6 ($COCH_2$), 27.9 ($C(CH_3)_3$), 25.4 (SCH_2CH_3), 14.9 (SCH_2CH_3). Anal. calcd for $C_{36}H_{44}O_8S$: C, 67.90; H, 6.96; S, 5.04; Found: C, 67.94; H, 7.08; S, 5.11.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(hydroxycarbonylethanoyl)-1-thio-α-D-mannopyranoside (9). Trifluoroacetic acid (5.3 ml, 51.8 mmol) was added at room temperature to a solution of **8** (1.65 g, 2.59 mmol) in dichloromethane (80 ml), the mixture was stirred for 3 h and concentrated. Coevaporation of toluene (three times) afforded crude **9** (2.58 g, 100%) which was used without further purification in the next step.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(3-hydroxycarbonylpropanoyl)-1-thio-α-D-mannopyranoside (10). A solution of **7**[13] (2.33 g, 4.71 mmol), succinic anhydride (3.8 g, 37.7 mmol) and a catalytic amount of DMAP (ca. 0.1 g) in pyridine (50 ml) was stirred at 20°C for 24 h and concentrated. The residue was dissolved in dichloromethane, washed with aqueous HCl and $NaHCO_3$ solution and water, dried and concentrated to give crude **10** (2.36 g, 85%) which was used without further purification in the next step.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranos-3-yloxy)-carbonylethanoyl]-1-thio-α-D-mannopyranoside (12a). Treatment of crude **9** (1.29 g, 2.2 mmol) and **1**[10] (1.13 g, 2.44 mmol) with DCC (0.5 g, 2.44 mmol) and a catalytic amount of DMAP in dichloromethane (40 ml) at 20°C for 24 h as described for the preparation of **8** and chromatography (toluene/acetone 10:1) afforded **12a** (1.67 g, 67%), $[\alpha]_D$=+101.4 (c=1.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.87 (t, 1H, $J_{3,4}$=9.9 Hz, 3-H), 5.49 (s, 1H, PhCH), 5.30 (d, 1H, $J_{1,2}$=3.8 Hz, 1-H), 5.28 (d, 1H, $J_{1',2'}$<1.0 Hz, 1′-H), 5.05 (dd, 1H, $J_{2,3}$=9.9 Hz, 2-H), 4.86 (d, 1H, J=−10.8 Hz, $PhCH_2$), 4.74 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.68 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.61 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.55–4.53 (m, 3H, $PhCH_2$), 4.50 (d, 1H, J=−10.8 Hz, $PhCH_2$), 4.25 (dd, 1H, $J_{5,6a}$=5.0 Hz, $J_{6a,6b}$=−10.4 Hz, 6a-H), 4.22–4.19 (m, 2H, 6a′-H, 6b′-H), 4.16–4.02 (m, 2H, 5-H, 5′-H), 3.83–3.68 (m, 3H, 2′-H, 4-H, 6b-H), 3.71 (t, 1H, $J_{4',5'}$=9.7 Hz, 4′-H), 3.32 (s, 2H, $COCH_2$), 2.56–2.41 (m, 2H, SCH_2CH_3), 1.17 (t, 3H, J=7.4 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ=165.8 (CO), 165.6 (CO), 165.3 (CO), 101.5 (PhCH), 95.8 (C-1), 81.8 (C-1′), 80.2 (C-3′), 78.9 (C-4), 76.0 (C-2′), 75.0 ($PhCH_2$), 74.6 (C-4′), 72.2 (C-2), 72.0 (2 C, $PhCH_2$), 70.0 (2 C, C-3, C-5′), 69.9 ($PhCH_2$), 68.8 (C-6), 62.8 (C-5), 64.3 (C-6′), 41.1 ($COCH_2$), 25.3 (SCH_2CH_3), 14.9 (SCH_2CH_3). Anal. calcd for $C_{59}H_{60}O_{14}S$: C, 69.12; H, 5.90; S, 3.13; Found: C, 68.82; H, 5.92; S, 3.14.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-[3-(2-*O*-benzoyl-1-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranos-3-yloxy)-carbonylpropanoyl]-1-thio-α-D-mannopyranoside (12b). Treatment of crude **10** (1.58 g, 2.7 mmol) and **1**[10] (1.23 g, 2.7 mmol) with DCC (0.61 g, 3.0 mmol) and a catalytic

amount of DMAP in dichloromethane (15 ml) at 20°C for 30 h as described for the preparation of **8** and chromatography (toluene/ethyl acetate 8:1) afforded **12b** (1.85 g, 67%), $[\alpha]_D$=+103.1 (*c*=1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.88 (t, 1H, $J_{3,4}$=9.8 Hz, 3-H), 5.52 (s, 1H, PhCH), 5.33 (s, 1H, 1′-H), 5.29 (d, 1H, $J_{1,2}$=3.8 Hz, 1-H), 5.08 (dd, 1H, $J_{2,3}$=10.0 Hz, 2-H), 4.90 (d, 1H, *J*=−10.9 Hz, $PhCH_2$), 4.76 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.69–4.57 (m, 4H, $PhCH_2$), 4.55 (d, 1H, *J*=−12.3 Hz, $PhCH_2$), 4.53 (d, 1H, *J*=−10.9 Hz, $PhCH_2$), 4.27 (dd, 1H, $J_{6a,6b}$=−10.1 Hz, 6a-H), 4.19–4.17 (m, 2H, 6a′-H, 6b′-H), 4.13–4.04 (m, 2H, $J_{5,6a}$=4.9 Hz, 5-H, 5′-H), 3.93–3.78 (m, 4H, 2′-H, 3′-H, 4′-H, 6b-H), 3.74 (t, 1H, $J_{4,5}$=9.7 Hz, 4-H), 2.60–2.53 (m, 6H, C*H*$_2$CH$_2$, SC*H*$_2$CH$_3$), 1.21 (t, 3H, *J*=7.4 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ=171.6 (*C*OCH_2CH_2), 171.1 (*C*OCH_2CH_2), 165.7 (PhCO), 101.5 (PhCH), 95.9 (C-1), 81.9 (C-1′), 80.3 (C-3′), 79.1 (C-4), 76.1 (C-2′), 75.1 ($PhCH_2$), 74.5 (C-4′), 72.2 (C-2), 72.0 (2 C, $PhCH_2$), 69.9 ($PhCH_2$), 69.2 (C-3), 68.8 (C-6), 63.5 (C-6′), 62.8 (C-5), 29.0, 28.9 (CO*C*H$_2$CH$_2$), 25.3 (S*C*H$_2$CH$_3$), 14.9 (SCH_2CH_3). Anal. calcd for $C_{60}H_{62}O_{14}S$: C, 69.35; H, 6.01; S, 3.09; Found: C, 69.29; H, 6.02; S, 3.07.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-[(1-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-α-D-glucopyranos-3-yloxy)-carbonylethanoyl]-1-thio-α-D-mannopyranoside (12c). A solution of crude **9** (1.26 g, 2.17 mmol), **11**[15] (0.9 g, 1.85 mmol) and *n*-Bu_3N (1.1 ml, 4.44 mmol) in dichloromethane (15 ml) was added at 20°C under Ar to a suspension of 2-chloro-1-methyl-pyridiniumiodide (0.57 g, 2.22 mmol) in dichloromethane (5 ml). The mixture was stirred for 2.5 h and concentrated. Chromatography (toluene/ethyl acetate 15:1) of the residue afforded **12c** (1.55 g, 80%), $[\alpha]_D$=+101.4 (*c*=1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=6.80 (dd, 1H, $J_{3,4}$=9.4 Hz, 3-H), 5.50 (s, 1H, PhCH), 5.27 (d, 1H, $J_{1',2'}$=1.4 Hz, 1-H), 4.97 (d, 1H, $J_{1,2}$=3.8 Hz, 1-H), 4.83 (d, 1H, *J*=−10.8 Hz, $PhCH_2$), 4.72 (d, 1H, *J*=−12.6 Hz, $PhCH_2$), 4.68 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.62 (d, 1H, *J*=−12.3 Hz, $PhCH_2$), 4.55 (dd, 1H, $J_{2,3}$=11.2 Hz, 2-H), 4.53 (s, 2H, $PhCH_2$), 4.45 (2 d, 2H, *J*=−10.6 Hz, *J*=−12.7 Hz, $PhCH_2$), 4.24 (dd, 1H, $J_{5,6a}$=5.0 Hz, $J_{6a,6b}$=−9.9 Hz, 6a-H), 4.16 (dt, 1H, $J_{5,6b}$=9.9 Hz, 5-H), 4.09–3.99 (m, 3H, 5′-H, 6a′-H, 6b′-H), 3.78 (dd, 1H, $J_{2',3'}$=3.2 Hz, 2′-H), 3.76–3.66 (m, 2H, 3′-H, 4′-H), 3.74 (t, 1H, 6b-H), 3.69 (t, 1H, $J_{4,5}$=9.4 Hz, 4-H), 3.27 (d, 1H, *J*=−15.7 Hz, $COCH_2$), 3.19 (d, 1H, *J*=−15.8 Hz, $COCH_2$), 2.57–2.43 (m, 2H, SC*H*$_2$CH$_3$), 1.19 (t, 3H, *J*=7.4 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ=165.9, 164.1 (2 C, 2 C, NCO, *C*O$COCH_2$), 101.4 (PhCH), 97.1 (C-1), 81.8 (C-1′), 80.8 (C-4), 80.1 (C-3′), 76.1 (C-2′), 75.0 ($PhCH_2$), 74.6 (C-4′), 72.0, 71.9 ($PhCH_2$), 69.9 (C-5′), 69.8 ($PhCH_2$), 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 (SCH_2CH_3), 14.9 (SCH_2CH_3). Anal. calcd for $C_{60}H_{59}NO_{14}S$: 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.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxy)-carbonylethanoyl]-1-thio-α-D-mannopyranoside (13a). Treatment of **12a** (0.8 g, 0.78 mmol) in THF (15 ml) with $NaCNBH_3$ (0.61 g, 9.75 mmol) and HCl in Et_2O as described for the preparation of **3** and chromatography (toluene/acetone 15:1) afforded **13a** (0.63 g, 78%), $[\alpha]_D$=+81.9 (*c*=1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.67 (dd, 1H, $J_{3,4}$=9.1 Hz, 3-H), 5.30 (s, 1H, 1′-H), 5.25 (d, 1H, $J_{1,2}$=3.7 Hz, 1-H), 4.97 (dd, 1H, $J_{2,3}$=10.3 Hz, 2-H), 4.90 (d, 1H, *J*=−11.0 Hz, $PhCH_2$), 4.74 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.68 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.61–4.58 (m, 2H, $PhCH_2$), 4.55 (s, 3H, $PhCH_2$), 4.54 (d, 1H, *J*=−11.0 Hz, $PhCH_2$), 4.52 (d, 1H, *J*=−12.6 Hz, $PhCH_2$), 4.37–4.30 (m, 2H, 6a′-H, 6b′-H), 4.13 (ddd, 1H, $J_{5',6a'}$=2.6 Hz, 5′-H), 4.00–3.94 (m, 1H, 5-H), 3.92 (t, 1H, $J_{4',5'}$=9.6 Hz, 4′-H), 3.82–3.67 (m, 3H, 2′-H, 3′-H, 4-H), 3.54 (d, 1H, $J_{4,OH}$=4.9 Hz, OH), 3.38 (d, 1H, *J*=−16.1 Hz, $COCH_2$), 3.30 (d, 1H, *J*=−16.1 Hz, $COCH_2$), 2.54–2.47 (m, 2H, SC*H*$_2$CH$_3$), 1.19 (t, 3H, *J*=7.4 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ=167.1 (PhCO), 165.8 (CO), 165.7 (CO), 95.1 (C-1), 82.0 (C-1′), 80.1 (C-3′), 76.0, 74.5 (C-2′,4), 75.1 ($PhCH_2$), 74.1 (C-3), 73.6 ($PhCH_2$), 71.9 (2 C, $PhCH_2$), 71.4 (C-2), 70.7 (C-5′), 69.8 (C-5), 69.5 ($PhCH_2$), 69.2 (C-4), 69.0 (C-6), 64.6 (C-6′), 41.4 (CO*C*H$_2$), 25.5 (S*C*H$_2$CH$_3$), 14.9 (SCH_2CH_3). Anal. calcd for $C_{59}H_{62}O_{14}S$: C, 68.99; H, 6.08; Found: C, 69.09; H, 6.02.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-[3-(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxy)-carbonylpropanoyl]-1-thio-α-D-mannopyranoside (13b). Treatment of **12b** (2.11 g, 2.03 mmol) in THF (25 ml) with $NaCNBH_3$ (1.59 g, 25.34 mmol) and HCl in Et_2O as described for the preparation of **3** and chromatography (toluene/ethyl acetate 3:1) afforded **13b** (1.57 g, 74%), $[\alpha]_D$=+89.2 (*c*=1.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.66 (dd, 1H, $J_{3,4}$=9.2 Hz, 3-H), 5.34 (d, 1H, $J_{1',2'}$=1.0 Hz, 1′-H), 5.24 (d, 1H, $J_{1,2}$=3.7 Hz, 1-H), 5.00 (dd, 1H, $J_{2,3}$=10.2 Hz, 2-H), 4.91 (d, 1H, *J*=−10.9 Hz, $PhCH_2$), 4.72 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.69 (d, 1H, *J*=−12.3 Hz, $PhCH_2$), 4.62 (d, 1H, *J*=−11.8 Hz, $PhCH_2$), 4.57 (d, 1H, *J*=−10.4 Hz, $PhCH_2$), 4.56 (s, 3H, $PhCH_2$), 4.53 (d, 1H, *J*=−10.7 Hz, $PhCH_2$), 4.52 (d, 1H, *J*=−12.3 Hz, $PhCH_2$), 4.28–4.22 (m, 2H, 6a′-H, 6b′-H), 4.12 (ddd, 1H, $J_{5',6a'}$=2.7 Hz, $J_{5',6b'}$=2.7 Hz, 5′-H), 3.99–3.93 (m, 1H, 5-H), 3.90 (t, 1H, $J_{4',5'}$=9.4 Hz, 4′H), 3.83–3.77 (m, 3H, 2′-H, 3′-H, 4-H), 3.73 (dd, 1H, 6b-H), 3.30 (bs, 1H, OH), 2.70–2.43 (m, 6H, C*H*$_2$CH$_2$, SC*H*$_2$CH$_3$), 1.22 (t, 3H, *J*=7.4 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ=172.2 (2 C, *C*O$COCH_2CH_2$), 165.7 (PhCO), 95.1 (C-1), 81.8 (C-1′), 80.2 (C-3′), 76.2, 74.4 (C-2′,4), 75.1 ($PhCH_2$), 73.6 ($PhCH_2$), 73.4 (C-3), 72.0 ($PhCH_2$), 71.9 ($PhCH_2$), 71.5 (C-2), 70.5 (C-5′), 70.1 (C-5), 69.7 (C-4), 69.5 ($PhCH_2$), 69.2 (C-6), 63.7 (C-6′), 29.2 (2 C, CO*C*H$_2$CH$_2$), 25.4 (S*C*H$_2$CH$_3$), 15.0 (SCH_2CH_3). Anal. calcd for $C_{60}H_{64}O_{14}S$: C, 69.21; H, 6.20; S, 3.08; Found: C, 69.38; H, 6.22; S, 3.29.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-[(1,6-di-*O*-benzyl-2-deoxy-2-phthalimido-α-D-glucopyranos-3-yloxy)-carbonylethanoyl]-1-thio-α-D-mannopyranoside (13c). Et_3SiH (0.38 ml, 2.4 mmol) and CF_3CO_2H (0.24 ml, 2.4 mmol) was added at 0°C to a solution of **12c** (0.5 g, 0.48 mmol) in dichloromethane (10 ml), the mixture was stirred at 20°C for 2.5 h and concentrated. Chromatography (toluene/ethyl acetate 5:1) of the residue afforded **13c** (0.33 g, 65%), $[\alpha]_D$=+115.1 (*c*=1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=6.62 (dd, 1H, $J_{3,4}$=9.0 Hz, 3-H), 5.29 (d, 1H, $J_{1',2'}$=1.2 Hz, 1′-H), 4.99 (d, 1H, $J_{1,2}$=3.6 Hz, 1-H), 4.88 (d, 1H, *J*=−10.9 Hz, $PhCH_2$), 4.73 (d, 1H, *J*=−12.6 Hz, $PhCH_2$), 4.68 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.64 (d, 1H, *J*=−10.7 Hz, $PhCH_2$),

4.60–4.53 (m, 5H, $PhCH_2$), 4.45 (dd, 1H, $J_{2,3}$=11.5 Hz, 2-H), 4.44 (d, 1H, J=−12.7 Hz, $PhCH_2$), 4.28–4.21 (m, 2H, 6a′-H, 6b′-H), 4.18–4.03 (m, 2H, 5-H, 5′-H), 3.85 (t, 1H, $J_{4',5'}$=9.2 Hz, 4′-H), 3.81–3.78 (m, 2H, 2′-H, 3′-H), 3.76–3.71 (m, 3H, 4-H, 6a-H, 6b-H), 3.45 (bs, 1H, OH), 3.28 (s, 2H, $COCH_2$), 2.59–2.45 (m, 2H, SCH_2CH_3), 1.20 (t, 3H, J 7.4 Hz, SCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ=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 (SCH_2CH_3), 14.9 (SCH_2CH_3). Anal. calcd for $C_{60}H_{61}NO_{14}S$: 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.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-chlorocarbonyl-1-thio-α-D-mannopyranoside (14a). Pyridine (0.19 ml, 2.3 ml) and a solution of **4** (1.25 g, 2.3 mmol) in toluene (15 ml) was added at −15°C to a 2.12 M solution of phosgene in toluene (1.3 ml, 2.76 mmol) and the mixture was stirred at 20°C for 17 h. Filtration of the mixture and concentration of the filtrate afforded crude **14a** (1.31 g, 94%) which was used without further purification for the next step.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-chlorooxalyl-1-thio-α-D-mannopyranoside (14b). Pyridine (0.22 ml, 2.7 ml) and a solution of **4** (1.47 g, 2.7 mmol) in toluene (30 ml) was added at 0°C to a solution of oxalylchloride (0.28 ml, 3.25 mmol) in toluene (30 ml) and the mixture was stirred at 20°C for 17 h. Filtration of the mixture and concentration of the filtrate afforded crude **14b** (1.72 g, 100%) which was used without further purification for the next step.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(*t*-butyloxycarbonylethanoyl)-1-thio-α-D-mannopyranoside (14c). Treatment of **4** (2.15 g, 4.0 mmol) and *t*-butyl malonate[14] (0.63 g, 4.0 mmol) with DCC (0.87 g, 4.23 mmol) in dichloromethane (40 ml) at 20°C for 16 h and workup as described for the preparation of **8** and chromatography (*n*-hexane/ethyl acetate 10:1) afforded **14c** (1.64 g, 61%), $[\alpha]_D$=+71.6 (c=1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.55 (d, 1H, $J_{1,2}$=1.5 Hz, 1-H), 4.94 (d, 1H, J=−10.7 Hz, $PhCH_2$), 4.71 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.61 (d, 1H, J=−12.2 Hz, $PhCH_2$), 4.62 (d, 1H, J=−10.7 Hz, $PhCH_2$), 4.60 (s, 2H, $PhCH_2$), 4.44 (dd, 1H, $J_{5,6a}$=5.3 Hz, $J_{6a,6b}$=−11.8 Hz, 6a-H), 4.37 (dd, 1H, $J_{5,6b}$=2.1 Hz, 6b-H), 4.33–4.28 (m, 1H, 5-H), 3.99 (dd, 1H, $J_{2,3}$=2.9 Hz, 2-H), 3.97 (t, 1H, $J_{4,5}$=9.3 Hz, 4-H), 3.87 (dd, 1H, $J_{3,4}$=9.2 Hz, 3-H), 3.26 (s, 2H, $COCH_2$), 1.43 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ=166.8 ($COCH_2$), 165.5 ($COCH_2$), 82.1 ($C(CH_3)_3$), 85.6 (C-1), 80.1 (C-3), 76.1 (C-2), 75.3 ($PhCH_2$), 74.6 (C-4), 72.1 ($PhCH_2$), 72.0 ($PhCH_2$), 70.8 (C-5), 64.3 (C-6), 42.6 ($COCH_2$), 27.9 ($C(CH_3)_3$). Anal. calcd for $C_{40}H_{44}O_8S$: C, 70.15; H, 6.47; S, 4.68; Found: C, 70.11; H, 6.56; S, 4.62.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(hydroxycarbonylethanoyl)-1-thio-α-D-mannopyranoside (14c′). Trifluoroacetic acid (3.2 ml, 41.8 mmol) was added at room temperature to a solution of **14c** (1.43 g, 2.1 mmol) in dichloromethane (60 ml), the mixture was stirred for 2 h and concentrated. Coevaporation of toluene (three times) afforded crude **14c′** (1.25 g, 95%) which was used without further purification in the next step.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(3-hydroxycarbonylpropanoyl)-1-thio-α-D-mannopyranoside (14d). Treatment of **4** (1.02 g, 1.9 mmol), succinic anhydride (1.51 g, 15.04 mmol) and a catalytic amount of DMAP (ca. 0.1 g) in pyridine (20 ml) at 20°C for 19 h as described for the preparation of **10** and chromatography (CCl_4/acetone 3:1) afforded **14d** (1.13 g, 94%), $[\alpha]_D$=+61.5 (c=1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.56 (d, 1H, $J_{1,2}$=1.5 Hz, 1-H), 4.94 (d, 1H, $PhCH_2$), 4.72 (d, 1H, $PhCH_2$), 4.64 (d, 1H, $PhCH_2$), 4.61 (s, 2H, $PhCH_2$), 4.59 (d, 1H, $PhCH_2$), 4.40 (dd, 1H, $J_{5,6a}$=5.0 Hz, $J_{6a,6b}$=−11.9 Hz, 6a-H), 4.38–4.35 (m, 1H, 6b-H), 4.28 (ddd, 1H, $J_{4,5}$=9.2 Hz, $J_{5,6b}$=2.2 Hz, 5-H), 4.00 (dd, 1H, $J_{2,3}$=2.8 Hz, 2-H), 3.98 (t, 1H, $J_{3,4}$=9.3 Hz, 4-H), 3.87 (dd, 1H, 3-H), 2.57 (s, 4H, CH_2–CH_2). ^{13}C NMR ($CDCl_3$): δ=176.9 ($COOH$), 171.8 (OCO–CH_2), 85.6 (C-1), 80.1 (C-3), 76.2 (C-4), 75.3 ($PhCH_2$), 74.5 (C-2), 72.1 ($PhCH_2$), 70.9 (C-5), 63.6 (C-6), 28.9, 28.8 (CH_2–CH_2). Anal. calcd for $C_{37}H_{38}O_8S$: C, 69.14; H, 5.96; S, 4.99; Found: C, 68.95; H, 5.96; S, 4.76.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-chlorocarbonylbenzoyl)-1-thio-α-D-mannopyranoside (14e). Pyridine (0.24 ml, 2.9 ml) and a solution of **4** (1.59 g, 2.93 mmol) in toluene (5 ml) was added at 0°C to a solution of phthaloylchloride (0.51 ml, 3.5 mmol) in toluene (15 ml) and the mixture was stirred at 20°C for 15 h. Filtration of the mixture and concentration of the filtrate afforded crude **14e** (1.92 g, 93%) which was used without further purification for the next step.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-hydroxycarbonylbenzoyl)-1-thio-α-D-mannopyranoside (14e). Treatment of **4** (1.53 g, 2.8 mmol), phthalic anhydride (0.5 g, 3.38 mmol) and a catalytic amount of DMAP (ca. 0.1 g) in pyridine (20 ml) at 20°C for 15 h as described for the preparation of **10** afforded **14e** (1.75 g, 90%) which was used without further purification for the next step.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranos-3-yloxy)-carbonyloxy]-1-thio-α-D-mannopyranoside (15a). A solution of crude **14a** (1.31 g, 2.17 mmol) in dichloromethane (15 ml) was added at −10°C to a solution of **1**[10] (1.0 g, 2.17 mmol) in pyridine (20 ml), the mixture was stirred at 20°C for 20 h, poured into water and extracted with dichloromethane. The extracts were washed with aqueous HCl and $NaHCO_3$ solution, dried and concentrated. Chromatography (toluene/ethyl acetate 15:1) of the residue afforded **15a** (1.81 g, 81%), $[\alpha]_D$=+93.3 (c=1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.69 (t, 1H, $J_{3,4}$=9.8 Hz, 3-H), 5.49 (s, 1H, PhCH), 5.41 (d, 1H, $J_{1',2'}$=1.4 Hz, 1′-H), 5.34 (d, 1H, $J_{1,2}$=3.8 Hz, 1-H), 5.01 (dd, 1H, $J_{2,3}$=9.9 Hz, 2-H), 4.74 (d, 1H, J=−10.4 Hz, $PhCH_2$), 4.73 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.63 (d, 1H, J=−12.5 Hz, $PhCH_2$), 4.52 (d, 1H, J=−12.2 Hz, $PhCH_2$), 4.50 (d, 1H, J=−11.5 Hz, $PhCH_2$), 4.43–4.33 (m, 2H, 6a′-H, 6b′-H), 4.32–4.15 (m, 3H, $PhCH_2$), 4.26 (dd, 1H, $J_{5,6a}$=4.8 Hz, $J_{5,6b}$=9.9 Hz, $J_{6a,6b}$=−10.1 Hz, 6a-H), 4.21–4.15 (m, 1H, 5′-H), 4.07 (dt, 1H, 5-H), 3.94 (t, 1H, $J_{4',5'}$=9.6 Hz, 4′-H), 3.91 (bd, 1H, $J_{2',3'}$=2.5 Hz, 2′-H), 3.80 (dd, 1H, $J_{3',4'}$=9.7 Hz,

3′-H), 3.76–3.71 (m, 2H, $J_{4,5}$=9.9 Hz, 4-H, 6b-H). ^{13}C NMR ($CDCl_3$): δ=165.5 (PhCO), 154.6 (OCO), 101.6 (PhCH), 95.7 (C-1), 85.5 (C-1′), 79.9 (C-3′), 79.0 (C-4), 75.7 (C-2′), 75.3 ($PhCH_2$), 74.2 (C-4′), 73.2 (C-3), 72.5 (C-2), 71.9 ($PhCH_2$), 71.6 ($PhCH_2$), 71.0 (C-5′), 70.0 ($PhCH_2$), 68.8 (C-6), 66.7 (C-6′), 62.7 (C-5). Anal. calcd for $C_{61}H_{58}O_{13}S$: C, 71.05; H, 5.67; S, 3.11; Found: C, 71.16; H, 5.69; S, 3.11.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranos-3-yloxy)-oxalyloxy]-1-thio-α-D-mannopyranoside (15b). Treatment of crude **14b** (1.72 g, 2.72 mmol) and **1**[10] (1.26 g, 2.72 mmol) in pyridine (10 ml) at 20°C for 16 h as described for the preparation of **15a** afforded **15b** (1.59 g, 55%), $[\alpha]_D$=+103.7 (*c*=1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.94 (t, 1H, $J_{3,4}$=9.8 Hz, 3-H), 5.54 (s, 1H, PhCH), 5.50 (d, 1H, $J_{1',2'}$=1.4 Hz, 1′-H), 5.35 (d, 1H, $J_{1,2}$=3.8 Hz, 1-H), 5.07 (dd, 1H, $J_{2,3}$=9.9 Hz, 2-H), 4.75 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.73 (d, 1H, *J*=−10.9 Hz, $PhCH_2$), 4.67–4.59 (m, 5H, $PhCH_2$), 4.54 (d, 1H, *J*=−12.3 Hz, $PhCH_2$), 4.40–4.21 (m, 4H, $J_{5,6a}$=4.8 Hz, $J_{6a,6b}$=−10.2 Hz, 5′-H, 6a-H, 6a′-H, 6b′-H), 4.12–4.05 (m, 1H, $J_{5,6b}$=9.7 Hz, 5-H), 4.01 (dd, 1H, $J_{2',3'}$=2.6 Hz, 2′-H), 3.93 (t, 1H, $J_{4',5'}$=9.2 Hz, 4′-H), 3.88–3.77 (m, 2H, $J_{3',4'}$=9.2 Hz, $J_{4,5}$=9.7 Hz, 3′-H, 4-H), 3.69 (t, 1H, 6b-H). ^{13}C NMR ($CDCl_3$): δ=165.5 (PhCO), 156.9, 156.3 (COCO), 101.7 (PhCH), 95.6 (C-1), 85.7 (C-1′), 80.2 (C-3′), 78.5 (C-4), 76.3 (C-2′), 75.2 ($PhCH_2$), 74.2 (C-4′), 72.2 (C-2), 72.1 ($PhCH_2$), 72.0 ($PhCH_2$), 71.8 (C-5′), 70.4 (C-3), 70.1 ($PhCH_2$), 68.7 (C-6), 65.8 (C-6′), 62.7 (C-5). Anal. calcd for $C_{62}H_{58}O_{14}S$: C, 70.31; H, 5.52; S, 3.03; Found: C, 70.22; H, 5.55; S, 3.02.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranos-3-yloxy)-carbonylethanoyl]-1-thio-α-D-mannopyranoside (15c). Treatment of crude **14c**′ (1.18 g, 1.9 mmol) and **1**[10] (0.86 g, 1.87 mmol) with DCC (0.43 g, 2.06 mmol) and a catalytic amount of DMAP in dichloromethane (40 ml) at 20°C for 14 h as described for the preparation of **8** and chromatography (*n*-hexane/ethyl acetate 5:1) afforded **15c** (1.44 g, 72%), $[\alpha]_D$=+104.1 (*c*=1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.88 (t, 1H, $J_{3,4}$=9.8 Hz, 3-H), 5.48 (d, 1H, $J_{1,2}$=1.6 Hz, 1′-H), 5.47 (s, 1H, PhCH), 5.29 (d, 1H, $J_{1,2}$=3.8 Hz, 1-H), 5.05 (dd, 1H, $J_{2,3}$=9.9 Hz, 2-H), 4.88 (d, 1H, *J*=−10.8 Hz, $PhCH_2$), 4.73 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.67 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.63–4.57 (m, 3H, $PhCH_2$), 4.53 (d, 1H, *J*=−12.6 Hz, $PhCH_2$), 4.52 (d, 1H, *J*=−10.8 Hz, $PhCH_2$), 4.27–4.15 (m, 4H, $J_{5,6b}$=9.8 Hz, 5′-H, 6a′-H, 6b′-H, 6a-H), 3.94 (bd, 1H, 2′-H), 3.82–3.72 (m, 3H, 3′-H, 4′-H, 6b-H), 3.69 (t, 1H, $J_{4,5}$=9.7 Hz, 4-H), 3.26 (s, 2H, $COCH_2$). ^{13}C NMR ($CDCl_3$): δ=165.7 (CO), 165.6 (CO), 165.3 (CO), 101.5 (PhCH), 95.8 (C-1), 85.4 (C-1′), 80.0 (C-3′), 78.9 (C-4), 75.9 (C-2′), 75.1 ($PhCH_2$), 74.6 (C-4′), 72.2 (C-2), 72.0 (2 C, $PhCH_2$), 70.7 (C-5′), 70.1 (C-3), 70.0 ($PhCH_2$), 68.8 (C-6), 64.3 (C-6′), 62.8 (C-5), 41.1 ($COCH_2$). Anal. calcd for $C_{64}H_{60}O_{14}S$: C, 70.51; H, 5.64; S, 2.99; Found: C, 70.37; H, 5.62; S, 3.09.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranos-3-yloxy)-3-car-bonylpropanoyl]-1-thio-α-D-mannopyranoside (15d). Treatment of **14d** (0.8 g, 1.24 mmol) and **1**[10] (0.58 g, 1.24 mmol) with DCC (0.31 g, 1.49 mmol) and a catalytic amount of DMAP in dichloromethane (20 ml) at 20°C for 22 h as described for the preparation of **8** and chromatography (CCl_4/acetone 10:1) afforded **15d** (1.25 g, 93%), $[\alpha]_D$=+101.7 (*c*=1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.87 (t, 1H, $J_{2,3}$=$J_{3,4}$=9.9 Hz, 3-H), 5.56 (d, 1H, $J_{1,2}$=1.5 Hz, 1-H), 5.50 (s, 1H, PhCH), 5.27 (d, 1H, $J_{1,2}$=3.7 Hz, 1-H), 5.06 (dd, 1H, 2-H), 4.94–4.53 (8d, 8H, Ph*CH*$_2$-), 4.38–4.35 (m, 2H, 6a-H, 6b-H), 4.31–4.20 (m, 2H, 5-H, 5-H), 4.18–4.16 (m, 1H, 4-H), 3.99 (dd, 1H, $J_{2,3}$=2.9 Hz, 2-H), 3.98–3.93 (m, 1H, 4-H), 3.87 (dd, 1H, $J_{3,4}$=9.1 Hz, 3-H), 3.80–3.68 (m, 2H, $J_{6a,6b}$=−10.4 Hz, 6a-H, 6b-H), 2.53–2.46 (m, 4H, *CH*$_2$–*CH*$_2$). ^{13}C NMR ($CDCl_3$): δ=171.8, 171.6 (*OCO*–CH_2), 165.8 (Ph*CO*), 101.6 (Ph*CH*), 95.9 (C-1), 85.5 (C-1), 80.1 (C-3), 79.1 (C-4), 76.1 (C-4), 75.9 (C-2), 75.3 (Ph*CH*$_2$), 74.5 (C-3), 72.3 (C-5), 72.1, 71.9, 69.9 (Ph*CH*$_2$), 69.2 (C-2), 68.8 (C-6), 63.6 (C-6), 62.8 (C-5), 28.9, 28.7 (*CH*$_2$–*CH*$_2$–). Anal. calcd for $C_{64}H_{62}O_{14}S$: C, 70.70; H, 5.75; S, 2.95; Found: C, 70.46; H, 5.86; S, 2.76.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranos-3-yloxy)-2-carbonylbenzoyl]-1-thio-α-D-mannopyranoside (15e). Treatment of crude **14e**′ (1.24 g, 1.8 mmol), **1**[10] (0.83 g, 1.8 mmol) and *p*-toluenesulfonic acid (30 mg, 0.18 mmol) with DCC (0.37 g, 1.8 mmol) and a catalytic amount of DMAP in pyridine (25 ml) at 20°C for 24 h as described for the preparation of **8** and chromatography (CCl_4/acetone 40:1) afforded **15e** (1.43 g, 70%), $[\alpha]_D$=+94.0 (*c*=1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=6.10 (t, 1H, $J_{3,4}$=9.8 Hz, 3-H), 5.57 (d, 1H, $J_{1',2'}$=1.5 Hz, 1′-H), 5.52 (s, 1H, PhCH), 5.31 (d, 1H, $J_{1,2}$=3.8 Hz, 1-H), 5.14 (dd, 1H, $J_{2,3}$=9.9 Hz, 2-H), 4.90 (d, 1H, *J*=−10.6 Hz, $PhCH_2$), 4.78 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.71 (d, 1H, *J*=−12.2 Hz, $PhCH_2$), 4.64 (s, 3H, $PhCH_2$), 4.63 (d, 1H, *J*=−12.1 Hz, $PhCH_2$), 4.55 (d, 1H, *J*=−12.1 Hz, $PhCH_2$), 4.35–4.22 (m, 4H, $J_{5,6a}$=4.7 Hz, $J_{5,6b}$=9.8 Hz, $J_{6a,6b}$=−10.3 Hz, 5′-H, 6a′-H, 6a-H, 6b′-H), 4.11 (dt, 1H, 5-H), 3.97 (t, 1H, $J_{4',5'}$=8.8 Hz, 4′-H), 3.88 (dd, 1H, $J_{3',4'}$=9.2 Hz, 3′-H), 3.76–3.73 (m, 1H, $J_{4,5}$=9.8 Hz, 4-H), 3.75 (t, 1H, 6b-H). ^{31}C NMR ($CDCl_3$): δ=167.0 (PhCO), 166.0, 165.8 (PhCOO), 101.3 (PhCH), 95.9 (C-1), 85.4 (C-1′), 80.2 (C-3′), 79.3 (C-4), 76.3 (C-2′), 75.3 ($PhCH_2$), 74.6 (C-4′), 72.2 (C-2), 72.1, 72.0 ($PhCH_2$), 70.9 (C-5′), 70.1 (C-3), 69.9 ($PhCH_2$), 68.8 (C-6), 63.9 (C-6′), 62.8 (C-5). Anal. calcd for $C_{68}H_{62}O_{14}S$: C, 71.94; H, 5.50; S, 2.82; Found: C, 71.82; H, 5.41; S, 2.90.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxy)-carbonyl]-1-thio-α-D-mannopyranoside (16a). Treatment of **15a** (1.06 g, 1.03 mmol) in THF (15 ml) with $NaCNBH_3$ (0.58 g, 9.27 mmol) and HCl in Et_2O as described for the preparation of **3** and chromatography (CCl_4/acetone 12:1) afforded **16a** (0.93 g, 87%), $[\alpha]_D$=+110.9 (*c*=1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.45 (t, 1H, $J_{3,4}$=9.7 Hz, 3-H), 5.41 (d, 1H, $J_{1',2'}$=1.4 Hz, 1′-H), 5.30 (d, 1H, $J_{1,2}$=3.7 Hz, 1-H), 4.97 (dd, 1H, $J_{2,3}$=10.2 Hz, 2-H), 4.92 (d, 1H, *J*=−10.6 Hz, $PhCH_2$), 4.70 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.64 (d, 1H, *J*=−12.1 Hz, $PhCH_2$), 4.62 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.57 (d, 1H, *J*=−10.6 Hz, $PhCH_2$), 4.56 (d, 1H, *J*=−12.6 Hz, $PhCH_2$), 4.51 (d, 1H, *J*=−12.3 Hz, $PhCH_2$),

4.50 (s, 3H, $PhCH_2$), 4.47 (dd, 1H, $J_{5',6a'}$=5.7 Hz, $J_{6a',6b'}$=−11.5 Hz, 6a′-H), 4.38 (dd, 1H, $J_{5',6b'}$=2.1 Hz, 6b′-H), 4.23 (ddd, 1H, 5′-H), 3.99–3.91 (m, 3H, $J_{2',3'}$=3.0 Hz, $J_{4',5'}$=9.8 Hz, $J_{5,6a}$=4.3 Hz, $J_{5,6b}$=3.7 Hz, 2′-H, 4′-H, 5-H), 3.86 (t, 1H, $J_{4,5}$=9.7 Hz, 4-H), 3.78 (dd, 1H, $J_{3',4'}$=9.3 Hz, 3′-H), 3.75 (dd, 1H, $J_{6a,6b}$=−10.5 Hz, 6a-H), 3.68 (dd, 1H, 6b-H), 2.72 (bs, 1H, OH). ^{13}C NMR ($CDCl_3$): δ=165.6 (PhCO), 155.4 (OCO), 95.1 (C-1), 85.5 (C-1′), 79.9 (C-3′), 76.9 (C-3), 75.7 (C-2′), 75.3 ($PhCH_2$), 74.5 (C-4′), 73.7 ($PhCH_2$), 71.9 ($PhCH_2$), 71.7 (C-2), 71.6 ($PhCH_2$), 70.9 (C-5′), 70.1, 70.0 (C-4,5), 69.7 ($PhCH_2$), 69.2 (C-6), 67.0 (C-6′). Anal. calcd for $C_{61}H_{60}O_{13}S$: C, 70.91; H, 5.85; S, 3.10; Found: C, 70.78; H, 5.96; S, 3.01.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxy)-oxalyloxy]-1-thio-α-D-mannopyranoside (16b). Treatment of **15b** (1.59 g, 1.5 mmol) in THF (20 ml) with $NaCNBH_3$ (0.85 g, 13.5 mmol) and HCl in Et_2O as described for the preparation of **3** and chromatography (CCl_4/acetone 10:1) afforded **16b** (0.35 g, 22%), $[\alpha]_D$=+118.2 (*c*=1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.70 (t, 1H, $J_{3,4}$=9.8 Hz, 3-H), 5.50 (d, 1H, $J_{1',2'}$=1.4 Hz, 1′-H), 5.31 (d, 1H, $J_{1,2}$=3.7 Hz. 1-H), 5.03 (dd, 1H, $J_{2,3}$=10.0 Hz, 2-H), 4.89 (d, 1H, *J*=−10.6 Hz, $PhCH_2$), 4.74 (d, 1H, *J*=−12.5 Hz, $PhCH_2$), 4.63 (d, 1H, *J*=−12.2 Hz, $PhCH_2$), 4.60 (d, 1H, *J*=−12.3 Hz, $PhCH_2$), 4.55 (d, 1H, *J*=−10.6 Hz, $PhCH_2$), 4.53 (d, 1H, *J*=−10.6 Hz, $PhCH_2$), 4.50 (d, 1H, *J*=−12.3 Hz, $PhCH_2$), 4.48 (bd, 3H, $PhCH_2$), 4.46–4.27 (m, 3H, 5′-H, 6a′-H, 6b′-H), 4.05 (dd, 1H, $J_{2',3'}$=2.9 Hz, 2′-H), 4.00-3.93 (m, 1H, $J_{5,6a}$=4.4 Hz, $J_{5,6b}$=3.9 Hz, 5-H), 3.96 (t, 1H, $J_{4,5}$=9.8 Hz, 4-H), 3.94 (t, 1H, $J_{4',5'}$=9.4 Hz, 4′-H), 3.81 (dd, 1H, $J_{3',4'}$=9.1 Hz, 3′-H), 3.80 (dd, 1H, $J_{6a,6b}$=−10.3 Hz, 6a-H), 3.63 (t, 1H, 6b-H), 2.75 (bs, 1H, OH). ^{13}C NMR ($CDCl_3$): δ=165.6 (PhCO), 157.4, 156.8 (COCO), 95.0 (C-1), 85.7 (C-1′), 80.2 (C-3′), 76.3 (C-2′), 75.2 ($PhCH_2$), 74.5 (C-4′), 74.1 (C-3), 73.4 ($PhCH_2$), 72.2, 72.1 ($PhCH_2$), 71.7 (C-5′), 71.4 (C-2), 70.0 (2 C, C-5, $PhCH_2$), 69.5 (C-4), 69.1 (C-6), 66.1 (C-6′). Anal. calcd for $C_{62}H_{60}O_{14}S$: C, 70.17; H, 5.70; S, 3.02; Found: C, 70.04; H, 5.81; S, 2.91.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxy)-carbonylethanoyl]-1-thio-α-D-mannopyranoside (16c). Treatment of **15c** (0.59 g, 0.55 mmol) in THF (15 ml) with $NaCNBH_3$ (0.43 g, 6.9 mmol) and HCl in Et_2O as described for the preparation of **3** and chromatography (*n*-hexane/ethyl acetate 3:1) afforded **16c** (0.39 g, 73%), $[\alpha]_D$=+101.9 (*c*=1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.65 (dd, 1H, $J_{3,4}$=9.2 Hz, 3-H), 5.52 (d, 1H, $J_{1',2'}$=1.5 Hz, 1′-H), 5.24 (d, 1H, $J_{1,2}$=3.7 Hz, 1-H), 4.97 (dd, 1H, $J_{2,3}$=10.2 Hz, 2-H), 4.90–4.83 (m, 4H, $PhCH_2$), 4.73 (d, 1H, *J*=−12.6 Hz, $PhCH_2$), 4.65–4.55 (m, 4H, $PhCH_2$), 4.51 (d, 1H, *J*=−12.5 Hz, $PhCH_2$), 4.33–4.24 (m, 3H, 5′-H, 6a′-H, 6b′-H), 3.97–3.95 (m, 2H, $J_{2',3'}$=2.8 Hz, 2′-H, 5-H), 3.94 (t, 1H, $J_{4',5'}$=9.2 Hz, 4′-H), 3.84 (dd, 1H, $J_{3',4'}$=9.2 Hz, 3′-H), 3.71–3.63 (m, 3H, 4-H, 6a-H, 6b-H), 3.57 (d, 1H, $J_{4,OH}$=3.2 Hz, OH), 3.29 (bd, 2H, $COCH_2$). ^{13}C NMR ($CDCl_3$): δ=167.0 (PhCO), 165.8 ($COCH_2$), 165.7 ($COCH_2$), 95.0 (C-1), 85.5 (C-1′), 80.0 (C-3′), 76.0 (C-2′), 75.3 ($PhCH_2$), 74.6, 74.3 (C-3,4), 73.6 ($PhCH_2$), 72.1 ($PhCH_2$), 72.0 ($PhCH_2$), 71.4 (C-2), 70.6, 70.7 (C-5,5), 69.6 ($PhCH_2$), 69.3 (C-4), 69.1 (C-6), 64.7 (C-6′), 41.5 ($COCH_2$). Anal. calcd for $C_{63}H_{62}O_{14}S$: C, 70.37; H, 5.81; S, 2.98; Found: C, 70.43; H, 5.93; S, 3.05.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxy)-3-carbonylpropanoyl]-1-thio-α-D-mannopyranoside (16d). Treatment of **15d** (1.25 g, 1.15 mmol) in THF (20 ml) with $NaCNBH_3$ (0.9 g, 14.4 mmol) and HCl in Et_2O as described for the preparation of **3** and chromatography (CCl_4/acetone 5:1) afforded **16d** (1.04 g, 83%), $[\alpha]_D$=+98.3 (*c*=1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.65 (t, 1H, $J_{2,3}$=$J_{3,4}$=9.7 Hz, 3-H), 5.55 (d, 1H, $J_{1,2}$=1.4 Hz, 1-H), 5.23 (d, 1H, $J_{1,2}$=3.7 Hz, 1-H), 4.99 (dd, 1H, 2-H), 4.93 (d, 1H, $PhCH_2$), 4.74 (d, 1H, $PhCH_2$), 4.70 (d, 1H, $PhCH_2$), 4.61–4.58 (m, 6H, $PhCH_2$, 5-H), 4.56 (d, 1H, $PhCH_2$), 4.52 (d, 1H, $PhCH_2$), 4.28–4.25 (m, 3H, $J_{5,6a}$=4.9 Hz, $J_{5,6b}$=2.6 Hz, 5-H, 6a-H, 6b-H), 3.97 (dd, 1H, 2-H), 3.92 (t, 1H, $J_{3,4}$=9.2 Hz, 4-H), 3.85 (dd, 1H, $J_{2,3}$=3.1 Hz, 3-H), 3.78–3.75 (m, 1H, $J_{4,5}$=9.6 Hz, 4-H), 3.73 (dd, 1H, $J_{5,6a}$=4.9 Hz, $J_{6a,6b}$=−10.6 Hz, 6a-H), 3.69 (dd, 1H, $J_{5,6b}$=3.2 Hz, 6b-H), 3.27 (d, 1H, $J_{4,OH}$=3.7 Hz, O*H*), 2.64–2.43 (m, 4H, CH_2–CH_2). ^{13}C-NMR ($CDCl_3$): δ=172.2 (2, OC*O*–CH_2), 165.7 (Ph*C*O–), 95.2 (C-1), 85.4 (C-1), 80.0 (C-3), 76.1 (C-4), 75.2 (Ph*C*H_2), 74.4 (C-2), 73.6 (Ph*C*H_2), 73.5 (C-3), 72.1, 71.9 (Ph*C*H_2), 71.5 (C-4), 70.8 (C-5), 70.5 (C-2), 69.7 (C-5), 69.5 (Ph*C*H_2), 69.2 (C-6), 63.7 (C-6), 29.2 (2C, *C*H_2–*C*H_2). Anal. calcd for $C_{64}H_{64}O_{14}S$: C, 70.57; H, 5.92; S, 2.94; Found: C, 70.72; H, 6.04; S, 2.79.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxy)-2-carbonylbenzoyl]-1-thio-α-D-mannopyranoside (16e). Treatment of **15e** (0.48 g, 0.42 mmol) in THF (15 ml) with $NaCNBH_3$ (0.33 g, 5.23 mmol) and HCl in Et_2O as described for the preparation of **3** and chromatography (CCl_4/acetone 15:1) afforded **16e** (0.4 g, 83%), $[\alpha]_D$=+139.4 (*c*=1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.96 (t, 1H, $J_{3,4}$=10.0 Hz, 3-H), 5.59 (d, 1H, $J_{1',2'}$=1.4 Hz, 1′-H), 5.29 (d, 1H, $J_{1,2}$=3.7 Hz, 1-H), 5.05 (dd, 1H, $J_{2,3}$=10.2 Hz, 2-H), 4.96 (d, 1H, *J*=−10.9 Hz, $PhCH_2$), 4.80 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.70 (d, 1H, *J*=−12.1 Hz, $PhCH_2$), 4.65–4.59 (m, 6H, $PhCH_2$), 4.56 (d, 1H, *J*=−12.7 Hz, $PhCH_2$), 4.45–4.36 (m, 3H, 5′-H, 6a′-H, 6b′-H), 4.06 (t, 1H, $J_{4',5'}$=9.5 Hz, 4′-H), 4.01–3.90 (m, 3H, $J_{3',4'}$=9.5 Hz, 3′-H, 4′-H, 5-H), 3.89 (t, 1H, $J_{4,5}$=9.7 Hz, 4-H), 3.80–3.67 (m, 3H, 6a-H, 6b-H, OH). ^{13}C NMR ($CDCl_3$): δ=168.5 (PhCO), 166.5, 165.7 (PhCOO), 95.2 (C-1), 85.3 (C-1′), 80.2 (C-3), 76.2, 74.8 (C-2′,4), 75.3 ($PhCH_2$), 74.3 (C-3′), 73.5 ($PhCH_2$), 72.1, 72.0 ($PhCH_2$), 71.5 (C-2), 70.8 (2 C, C-5′, C-5), 69.0 (C-4), 68.8 (C-6), 64.6 (C-6′). Anal. calcd for $C_{68}H_{64}O_{14}S$: C, 71.81; H, 5.67; S, 2.82; Found: C, 71.70; H, 5.80; S, 2.95.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxy)-carbonyl]-1-sulfoxy-α-D-mannopyranoside (17a). A solution of **16a** (207 mg, 0.2 mmol) and 55% *m*-chloroperbenzoic acid (87 mg, 0.28 mmol) in dichloromethane (10 ml) was stirred at 20°C for 24 h and concentrated. Chromatography (toluene/ethyl acetate 5:1) of the residue afforded **17a** (168 mg, 80%), $[\alpha]_D$=+38.2 (*c*=1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.45 (dd, 1H, $J_{3,4}$=8.7 Hz, 3-H), 5.28 (d, 1H, $J_{1,2}$=3.7 Hz, 1-H), 5.03 (dd, 1H, $J_{2,3}$=10.2 Hz, 2-H), 4.90

(d, 1H, J=−10.9 Hz, $PhCH_2$), 4.72 (d, 1H, J=−12.3 Hz, $PhCH_2$), 4.65 (d, 1H, J=−12.3 Hz, $PhCH_2$), 4.59 (d, 1H, J=−12.2 Hz, $PhCH_2$), 4.57 (bs, 4H, $PhCH_2$), 4.55 (d, 1H, J=−11.2 Hz, $PhCH_2$), 4.47 (d, 1H, J=−11.5 Hz, $PhCH_2$), 4.43 (s, 1H, 1′-H), 4.40 (dd, 1H, $J_{5',6a'}$=2.0 Hz, $J_{6a',6b'}$=−11.7 Hz, 6a′-H), 4.31 (bt, 1H, $J_{2',3'}$=3.2 Hz, 2′-H), 4.24 (dd, 1H, $J_{5',6b'}$=6.6 Hz, 6b′-H), 4.09 (dd, 1H, $J_{3',4'}$=9.0 Hz, 3′-H), 4.05–4.00 (m, 1H, 5′-H), 3.98–3.89 (m, 2H, $J_{5,6a}$=3.9 Hz, $J_{5,6b}$=3.6 Hz, 4-H, 5-H), 3.85 (t, 1H, $J_{4',5'}$=9.3 Hz, 4′-H), 3.78 (dd, 1H, $J_{6a,6b}$=−10.4 Hz, 6a-H), 3.70 (dd, 1H, 6b-H), 2.86 (d, 1H, $J_{4,OH}$=3.9 Hz, OH). ^{13}C NMR ($CDCl_3$): δ=165.5 (PhCO), 155.2 (OCO), 95.2, 95.1 (C-1,1′), 79.0 (C-3′), 77.1 (C-3), 75.8 (C-5′), 75.0 ($PhCH_2$), 73.7 ($PhCH_2$), 73.4 (C-4′), 72.3 ($PhCH_2$), 72.0 ($PhCH_2$), 71.6 (C-2), 71.2 (C-2′), 70.1 (2 C, C-4, C-5), 69.7 ($PhCH_2$), 69.2 (C-6), 67.2 (C-6′). Anal. calcd for $C_{61}H_{60}O_{14}S$: C, 69.83; H, 5.76; S, 3.06; Found: C, 69.49; H, 5.85; S, 3.09.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxy)-oxalyloxy]-1-sulfoxy-α-D-mannopyranoside (17b). Treatment of **16b** (218 mg, 0.21 mmol) and 55% *m*-chloroperbenzoic acid (89 mg, 0.28 mmol) in dichloromethane (10 ml) as described for the preparation of **17a** afforded **17b** (183 mg, 83%), $[\alpha]_D$=+90.8 (c=1.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.68 (t, 1H, $J_{3,4}$=9.9 Hz, 3-H), 5.29 (d, 1H, $J_{1,2}$=3.7 Hz, 1-H), 5.11 (dd, 1H, $J_{2,3}$=10.0 Hz, 2-H), 4.80 (d, 1H, J=−10.9 Hz, $PhCH_2$), 4.73 (d, 1H, J=−12.3 Hz, $PhCH_2$), 4.65 (d, 1H, J=−12.2 Hz, $PhCH_2$), 4.63 (d, 1H, J=−11.9 Hz, $PhCH_2$), 4.62–4.56 (m, 3H, $PhCH_2$), 4.55 (d, 1H, J=−12.0 Hz, $PhCH_2$), 4.53 (d, 1H, $J_{1',2'}$=1.5 Hz, 1′-H), 4.51 (d, 1H, J=−12.1 Hz, $PhCH_2$), 4.49 (d, 1H, J=−12.3 Hz, $PhCH_2$), 4.41 (dd, 1H, $J_{2',3'}$=3.3 Hz, 2′-H), 4.39–4.18 (m, 2H, 6a′-H, 6b′-H), 4.12 (dd, 1H, $J_{3',4'}$=9.3 Hz, 3′-H), 4.16–3.98 (m, 1H, 5′-H), 4.04 (t, 1H, $J_{4,5}$=9.7 Hz, 4-H), 4.02–3.95 (m, 1H, $J_{5,6a}$=4.3 Hz, $J_{5,6b}$=3.5 Hz, 5-H), 3.85 (t, 1H, $J_{4',5'}$=9.6 Hz, 4′-H), 3.83 (dd, 1H, $J_{6a,6b}$=−10.2 Hz, 6a-H), 3.61 (t, 1H, 6b-H), 2.80 (bs, 1H, OH). ^{13}C NMR ($CDCl_3$): δ=165.7 (PhCO), 157.2, 156.6 (COCO), 95.1 (C-1), 94.3 (C-1′), 79.2 (C-3′), 74.5 (2 C, C-5′, $PhCH_2$), 74.4 (C-3), 74.1 (C-4′), 73.4 ($PhCH_2$), 73.1 ($PhCH_2$), 71.2 ($PhCH_2$), 72.0 (C-2′), 71.1 (C-2), 70.1 (C-5), 70.0 ($PhCH_2$), 69.6 (C-4), 69.1 (C-6), 66.4 (C-6′). Anal. calcd for $C_{62}H_{60}O_{15}S$: C, 69.13; H, 5.61; S, 2.98; Found: C, 69.00; H, 5.74; S, 3.05.

Phenyl 2,3,4-tri-*O*-benzyl-6-*O*-[(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxy)-3-carbonylpropanoyl]-1-sulfoxy-α-D-mannopyranoside (17c). Treatment of **16d** (0.69 g, 0.63 mmol) and 55% *m*-chloroperbenzoic acid (0.25 g, 0.78 mmol) in dichloromethane (10 ml) as described for the preparation of **17a** afforded **17c** (0.59 g, 84%), $[\alpha]_D$=+69.2 (c=1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.63 (dd, 1H, $J_{3,4}$=9.3 Hz, 3-H), 5.22 (d, 1H, $J_{1,2}$=3.8 Hz, 1-H), 5.00 (dd, 1H, $J_{2,3}$=10.2 Hz, 2-H), 4.85 (d, 1H, J=−11.2 Hz, $PhCH_2$), 4.77 (d, 1H, $J_{1',2'}$=1.7 Hz, 1′-H), 4.71 (d, 1H, J=−10.6 Hz, $PhCH_2$), 4.69 (d, 1H, J=−12.8 Hz, $PhCH_2$), 4.65 (bs, 2H, $PhCH_2$), 4.62 (d, 1H, J=−12.3 Hz, $PhCH_2$), 4.61 (d, 1H, J=−11.5 Hz, $PhCH_2$), 4.57 (bd, 1H, $J_{2',3'}$=3.3 Hz, 2′-H), 4.55 (d, 1H, J=−12.3 Hz, $PhCH_2$), 4.52 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.49 (d, 1H, J=−11.0 Hz, $PhCH_2$), 4.26 (dd, 1H, $J_{3',4'}$=8.6 Hz, 3′-H), 4.10 (bd, 2H, 6a′-H, 6b′-H), 3.98-3.91 (m, 1H, 5′-H), 3.83 (t, 1H, $J_{4',5'}$=9.2 Hz, 4′-H), 3.80–3.70 (m, 3H, 5-H, 6a-H, 6b-H), 3.67–3.63 (m, 1H, 4-H), 3.17 (d, 1H, $J_{4,OH}$=3.7 Hz, OH), 2.60–2.38 (m, 4H, $COCH_2CH_2$). ^{13}C NMR ($CDCl_3$): δ=172.2, 172.0 ($COCH_2CH_2$), 165.7 (PhCO), 95.2 (C-1), 90.8 (C-1′), 79.2 (C-3′), 74.4 (2 C, C-5′, $PhCH_2$), 73.9 (C-4′), 73.7 ($PhCH_2$), 73.5 (C-3), 73.2 ($PhCH_2$), 72.8 ($PhCH_2$), 71.4 (2 C, C-2, C-2′), 70.4 (C-5), 69.9 (C-4), 69.6 ($PhCH_2$), 69.3 (C-6), 63.9 (C-6′), 29.1 (2 C, $COCH_2CH_2$). Anal. calcd for $C_{64}H_{64}O_{15}S$: C, 69.55; H, 5.84; S, 2.90; Found: C, 69.85; H, 5.77; S, 2.98.

General procedure A: According to Table 2, a solution of **13a**–**c** or **16a**–**e** and 4 Å molecular sieves in MeCN or dichloromethane were stirred under Ar for 0.5 h and cooled to −30°C. NIS and TMSOTf were added at −30°C, the mixture was stirred for 10 min, neutralized by addition of pyridine, diluted with dichloromethane and filtered. The filtrate was washed with aqueous $NaHCO_3$ and $Na_2S_2O_3$ solution, dried and concentrated. Chromatography (toluene/ethyl acetate) of the residue afforded compounds **18a**,**b**,**f** and **19a**–**c**,**f**.

General procedure B: According to Table 2, a solution of **13a**–**c** and **16a**,**b** and MeOTf in MeCN or dichloromethane was stirred at 20°C for 6 h, neutralized by addition of Et_3N, diluted with dichloromethane and filtered. The filtrate was washed with water, dried and concentrated. Chromatography (toluene/ethyl acetate) of the residue afforded compounds **18a**,**b** and **19a**–**c**.

General procedure C: According to Table 2, a solution of IDCP and **13b** and **16a**,**b** in MeCN or dichloromethane was stirred at 20°C until all starting material was consumed. The mixture was diluted with dichloromethane, filtered, and the filtrate was washed with aqueous $Na_2S_2O_3$ solution, dried and concentrated. Chromatography (toluene/ethyl acetate) of the residue afforded **18b** and **19b**.

General procedure D: According to Table 2, a solution of **16a**,**b** and DMTST in MeCN or dichloromethane was stirred at 20°C until all starting material was consumed. TLC showed complete decomposition of the starting material.

General procedure E: According to Table 2, AgOTf was added at 20°C to a solution of **16a**,**b** in MeCN or dichloromethane. Br_2 was added and the mixture was stirred until all starting material was consumed. TLC showed complete decomposition of the starting material.

General procedure F: According to Table 2, Tf_2O was added under Ar at −50°C to a solution of **17a**–**c** and 2,6-di-*t*-butylpyridine in MeCN or dichloromethane. The mixture was warmed to 20°C, stirred for 50 h, diluted with dichloromethane and filtered. The filtrate was washed with aqueous $NaHCO_3$ solution dried and concentrated. Chromatography (toluene/ethyl acetate) of the residue afforded **18b**,**d**,**e** and **19b**.

Benzyl *O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside-3,6-malonate (18a). $[\alpha]_D$=+140.1 (c=1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$):

Table 2. Intramolecular glycosylation of compounds **13**, **16** and **17** according to the general procedures A–F

Starting material (mg, mmol)	Solvent (ml)	Proc.	Activators (g or μl, mmol)	Products, yield (mg, %)
13a (460, 0.45)	MeCN (15)	A	NIS (0.50, 2.24), TMSOTf (20, 0.11)	**18a** (58, 13), **19a** (250, 58)
13a (410, 0.40)	CH_2Cl_2 (15)	A	NIS (0.45, 2.00), TMSOTf (18, 0.1)	**18a** (64, 17), **19a** (204, 53)
13a (460, 0.45)	MeCN (15)	B	MeOTf (340, 3.14)	**18a** (28, 6), **19a** (315, 73)
13a (520, 0.51)	CH_2Cl_2 (15)	B	MeOTf (280, 2.53)	**18a** (46, 9), **19a** (335, 68)
13b (470, 0.45)	MeCN (15)	A	NIS (0.51, 2.25), TMSOTf (20, 0.11)	**18b** (169, 38), **19b** (146, 33)
13b (400, 0.39)	CH_2Cl_2 (15)	A	NIS (0.44, 1.94), TMSOTf (18, 0.1)	**18b** (164, 43), **19b** (104, 27)
13b (640, 0.62)	MeCN (15)	B	MeOTf (340, 3.14)	**18b** (161, 27), **19b** (257, 43)
13b (390, 0.37)	CH_2Cl_2 (10)	B	MeOTf (200, 1.87)	**18b** (112, 31), **19b** (133, 37)
13b (380, 0.37)	MeCN (10)	C	IDCP (0.35, 0.74)	**18b** (129, 36), **19b** (132, 37)
13b (360, 0.34)	CH_2Cl_2 (10)	C	IDCP (0.32, 0.69)	**18b** (133, 40), **19b** (106, 32)
13c (300, 0.29)	MeCN (10)	A	NIS (0.32, 1.43), TMSOf (13, 0.07)	**19c** (144, 51)
13c (310, 0.30)	CH_2Cl_2 (12)	A	NIS (0.34, 1.50), TMSOf (14, 0.08)	**19c** (140, 47)
13c (400, 0.38)	MeCN (12)	B	MeOTf (214, 1.92)	**19c** (199, 52)
13c (350, 0.33)	CH_2Cl_2 (12)	B	MeOTf (128, 1.67)	**19c** (160, 49)
16a (214, 0.21)	MeCN (20)	A	NIS (0.23, 1.04), TMSOTf (5, 0.052)	–[a]
16a (250, 0.26)	CH_2Cl_2 (20)	A	NIS (0.29, 1.29), TMSOTf (12, 0.065)	–[a]
16a (166, 0.16)	MeCN (10)	B	MeOTf (90, 0.81)	–[b]
16a (213, 0.21)	CH_2Cl_2 (10)	B	MeOTf (110, 1.03)	–[b]
16a (157, 0.15)	MeCN (8)	C	IDCP (150, 0.31)	–[b]
16a (225, 0.22)	CH_2Cl_2 (12)	C	IDCP (210, 0.45)	–[b]
16a (240, 0.24)	MeCN (15)	D	DMTST (290, 1.12)	–[a]
16a (199, 0.19)	CH_2Cl_2 (10)	D	DMTST (230, 0.87)	–[a]
16a (250, 0.25)	MeCN (15)	E	AgOTf (124, 0.48), Br_2 (8.7, 0.17)	–[a]
16a (155, 0.15)	CH_2Cl_2 (10)	E	AgOTf (80, 0.30), Br_2 (5.5, 0.11)	–[a]
17a (350, 0.37)	MeCN (20)	F	Tf_2O (182, 2.2)	**18d** (257, 76)
17a (149, 0.14)	CH_2Cl_2 (10)	F	Tf_2O (66, 0.43)	**18d** (103, 79)
16b (350, 0.33)	MeCN (10)	A	NIS (0.37, 1.65), TMSOTf (15, 0.083)	–[a]
16b (300, 0.28)	CH_2Cl_2 (10)	A	NIS (0.32, 1.41), TMSOTf (13, 0.072)	–[a]
16b (294, 0.28)	MeCN (10)	B	MeOTf (152, 1.39)	–[a]
16b (261, 0.25)	CH_2Cl_2 (10)	B	MeOTf (135, 1.23)	–[a]
16b (303, 0.29)	MeCN (10)	C	IDCP (268, 0.57)	–[b]
16b (280, 0.26)	CH_2Cl_2 (12)	C	IDCP (248, 0.53)	–[b]
16b (330, 0.31)	MeCN (12)	D	DMTST (362, 1.4)	–[a]
16b (280, 0.26)	CH_2Cl_2 (12)	D	DMTST (307, 1.19)	–[a]
16b (294, 0.28)	MeCN (12)	E	AgOTf (142, 0.55), Br_2 (10, 0.20)	–[a]
16b (237, 0.22)	CH_2Cl_2 (12)	E	AgOTf (115, 0.45), Br_2 (8.0, 0.16)	–[a]
17a (320, 0.30)	MeCN (18)	F	Tf_2O (146, 0.89)	**18e** (204, 72)
17a (282, 0.26)	CH_2Cl_2 (10)	F	Tf_2O (129, 0.79)	**18e** (187, 75)
16c (211, 0.20)	MeCN (15)	A	NIS (0.22, 0.98), TMSOTf (15, 0.083)	**18a** (42, 22), **19a** (102, 54)
16c (364, 0.38)	CH_2Cl_2 (20)	A	NIS (0.42, 1.89), TMSOTf (17, 0.094)	**18a** (90, 25), **19a** (180, 50)
16d (520, 0.48)	MeCN (60)	A	NIS (0.54, 2.40), TMSOTf (20, 0.11)	**18b** (213, 45), **19b** (118, 25)
16c (370, 0.34)	CH_2Cl_2 (50)	A	NIS (0.38, 1.70), TMSOTf (14, 0.08)	**18b** (175, 53), **19a** (71, 21)
17c (330, 0.30)	MeCN (10)	F	Tf_2O (132, 0.60)	**18b** (142, 48), **19b** (67, 23)
17c (300, 0.27)	CH_2Cl_2 (10)	F	Tf_2O (119, 0.54)	**18b** (144, 54), **19b** (61, 23)
16e (290, 0.26)	MeCN (15)	A	NIS (0.29, 1.30), TMSOTf (12, 0.065)	**18f** (183, 69), **19f** (23, 9)
16e (340, 0.30)	CH_2Cl_2 (15)	A	NIS (0.34, 1.51), TMSOTf (14, 0.08)	**18f** (195, 63), **19f** (31, 10)

[a] Decomposition of the starting material.
[b] No reaction.

δ=5.77 (t, 1H, $J_{3,4}$=10.0 Hz, 3-H), 5.11 (d, 1H, $J_{1,2}$=3.4 Hz, 1-H), 4.93 (dd, 1H, $J_{2,3}$=9.6 Hz, 2-H), 4.92 (s, 1H, 1′-H), 4.87 (d, 1H, J=−11.4 Hz, $PhCH_2$), 4.84–4.80 (m, 1H, 6a′-H), 4.82 (d, 1H, J=−11.2 Hz, $PhCH_2$), 4.81 (d, 1H, J=−10.9 Hz, $PhCH_2$), 4.75–4.66 (m, 4H, $PhCH_2$), 4.54 (d, 1H, J=−12.6 Hz, $PhCH_2$), 4.51 (s, 1H, $PhCH_2$), 4.43 (d, 1H, J=−12.2 Hz, $PhCH_2$), 4.11 (t, 1H, $J_{4,5}$=10.4 Hz, 4-H), 4.11–4.04 (m, 1H, 5′-H), 3.77–3.71 (m, 1H, 6b′-H), 3.73 (dd, 1H, $J_{3',4'}$=9.3 Hz, 3′-H), 3.64 (t, 1H, $J_{4',5'}$=9.3 Hz, 4′-H), 3.50–3.44 (m, 1H, $J_{5,6b}$=4.0 Hz, 5-H), 3.43–3.39 (m, 2H, $J_{2',3'}$=3.0 Hz, $J_{6a,6b}$=−10.9 Hz, 2′-H, 6a-H), 3.33–3.28 (m, 1H, 6b-H), 3.27 (d, 1H, J=−12.6 Hz, $COCH_2$), 3.18 (d, 1H, J=−12.6 Hz, $COCH_2$). ^{13}C NMR ($CDCl_3$): δ=165.6 ($COCH_2$), 165.4 ($COCH_2$), 164.5 (PhCO), 94.8 (C-1), 93.1 (C-1′, $J_{C\text{-}1',1'\text{-}H}$=166.0 Hz), 79.3 (C-3′), 75.5 (C-4′), 75.3 (C-2′), 74.5 ($PhCH_2$), 73.5 ($PhCH_2$), 73.2 (C-4), 73.0 (C-2), 72.8 ($PhCH_2$), 72.5 ($PhCH_2$), 69.5 ($PhCH_2$), 69.1, 68.9 (C-3,5,5), 68.8 (C-6), 64.8 (C-6′), 43.3 ($COCH_2$). Anal. calcd for $C_{57}H_{56}O_{14}$: C, 70.94; H, 5.85; Found: C, 70.60; H, 5.85.

Benzyl *O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside-3,6-succinate (18b). $[\alpha]_D$=+119.1 (c=1.0; $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=6.05 (t, 1H, $J_{2,3}$=$J_{3,4}$=10.0 Hz, 3-H), 5.14 (d, 1H, $J_{1,2}$=3.4 Hz, 1-H); 5.05 (d, 1H, $J_{1,2}$=1.6 Hz, 1-H), 4.92 (dd, 1H, 2-H), 4.86 (d, 1H, $PhCH_2$), 4.78 (d, 1H, $PhCH_2$), 4.60–4.52 (m, 6H, $PhCH_2$), 4.45 (d, 1H, $PhCH_2$), 4.42 (d, 1H, $PhCH_2$), 4.26–4.14 (m, 3H, $J_{6a,6b}$=−10.6 Hz, 5-H, 6a-H, 6b-H), 4.02 (dt, 1H, $J_{4,5}$=9.3 Hz, 5-H), 3.66–3.56 (m, 2H, 2-H, 4-H), 3.75 (dd, 1H, $J_{2,3}$=2.9 Hz, $J_{3,4}$=8.6 Hz, 3-H), 3.50–3.43 (m, 2H, 4-H, 6a-H), 3.36 (dd, 1H, 6b-H), 2.87–2.59 (m, 2H, CH_2–CH_2), 2.42–2.34 (m, 1H, CH_2–CH_2), 2.17–2.09 (m, 1H, CH_2–CH_2). ^{13}C NMR ($CDCl_3$): δ=171.5, 170.4 (O–*C*O–CH_2), 165.7 (Ph*C*O–), 95.0 (C-1), 92.8 (C-1, $J_{C\text{-}1,1\text{-}H}$=164.5 Hz), 80.0 (C-4), 79.2 (C-5), 75.2 (C-2), 74.8 (Ph*C*H_2), 73.6 (Ph*C*H_2), 73.2 (C-3), 72.8 (C-3), 72.5 (Ph*C*H_2), 72.3 (Ph*C*H_2), 71.0 (C-2), 70.8 (C-5), 69.7 (Ph*C*H_2), 68.6 (C-6), 67.4 (C-4), 64.2 (C-6), 29.9, 29.7 (*C*H_2-*C*H_2). Anal. calcd for $C_{58}H_{58}O_{14}$: C, 71.15; H, 5.97; Found: C, 70.94; H, 5.97.

Benzyl *O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside-3,6-carbonate (18d). $[\alpha]_D$=+121.7 (c=0.99, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.73 (t, 1H, $J_{3,4}$=9.9 Hz, 3-H), 5.17 (d, 1H, $J_{1,2}$=3.7 Hz, 1-H), 4.93 (dd, 1H, $J_{2,3}$=10.1 Hz, 2-H), 4.81 (s, 1H, 1′-H), 4.78 (d, 1H, J=−11.0 Hz, $PhCH_2$), 4.69 (d, 1H, J=−12.3 Hz, $PhCH_2$), 4.66 (d, 1H, J=−11.7 Hz, $PhCH_2$), 4.60 (d, 1H, J=−11.8 Hz, $PhCH_2$), 4.59 (d, 1H, J=−12.5 Hz, $PhCH_2$), 4.55 (d, 1H, J=−11.7 Hz, $PhCH_2$), 4.53 (d, 1H, J=−12.6 Hz, $PhCH_2$), 4.50 (s, 3H, $PhCH_2$), 4.34 (dd, 1H, $J_{5',6a'}$=1.7 Hz, $J_{6a',6b'}$=−11.5 Hz, 6a′-H), 4.30 (t, 1H, $J_{4,5}$=9.4 Hz, 4-H), 4.04–4.00 (m, 1H, $J_{5',6b'}$=4.9 Hz, 5′-H), 3.95 (dd, 1H, 6b′-H), 3.77–3.71 (m, 1H, 5-H), 3.67 (dd, 1H, $J_{3',4'}$=9.4 Hz, 3′-H), 3.65 (t, 1H, $J_{4',5'}$=8.9 Hz, 4′-H), 3.49 (bd, 1H, 6a-H), 3.45–3.35 (m, $J_{2',3'}$=2.5 Hz, 2′-H), 3.32 (bd, 1H, 6b-H). ^{13}C NMR ($CDCl_3$): δ=165.3 (PhCO), 154.1 (OCO), 94.9 (C-1), 93.7 (C-1′, $J_{C\text{-}1',1'\text{-}H}$=168.5 Hz), 79.0 (C-3′), 74.4 ($PhCH_2$), 74.2 (C-2′), 74.0 (C-4), 73.8 ($PhCH_2$), 73.4, 73.3 (C-2,4′), 73.0, 72.5 ($PhCH_2$), 71.9 (C-3), 71.0 (C-5′), 70.5 ($PhCH_2$), 68.2 (C-5), 68.8 (C-6), 67.0 (C-6′). Anal. calcd for $C_{55}H_{34}O_{13}$: C, 71.57; H, 5.90; Found: C, 71.64; H, 5.88.

Benzyl *O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside-3,6-oxalate (18e). $[\alpha]_D$=+128.6 (c=2.13, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.98 (t, 1H, $J_{3,4}$=9.8 Hz, 3-H), 5.18 (d, 1H, $J_{1,2}$=3.6 Hz, 1-H), 4.99 (dd, 1H, $J_{2,3}$=9.9 Hz, 2-H), 4.90 (d, 1H, $J_{1',2'}$=1.3 Hz, 1′-H), 4.88 (d, 1H, J=−10.7 Hz, $PhCH_2$), 4.76 (d, 1H, J=−11.8 Hz, $PhCH_2$), 4.66 (d, 1H, J=−11.8 Hz, $PhCH_2$), 4.59 (d, 1H, J=−12.5 Hz, $PhCH_2$), 4.56 (d, 1H, J=−10.7 Hz, $PhCH_2$), 4.53 (d, 1H, J=−11.0 Hz, $PhCH_2$), 4.52–4.46 (m, 4H, $PhCH_2$), 4.42 (t, 1H, $J_{4,5}$=9.9 Hz, 4-H), 4.33–4.14 (m, 1H, 6a′-H), 4.04–3.93 (m, 2H, 5′-H, 6b′-H), 3.78–3.72 (m, 1H, $J_{5,6a}$=4.2 Hz, 5-H), 3.74 (dd, 1H, $J_{3',4'}$=9.2 Hz, 3′-H), 3.67 (t, 1H, $J_{4',5'}$=9.3 Hz, 4′-H), 3.55–3.48 (m, 1H, $J_{2',3'}$=3.0 Hz, 2′-H), 3.54 (dd, 1H, $J_{6a,6b}$=−10.7 Hz, 6a-H), 3.30–3.24 (m, 1H, 6b-H). ^{13}C NMR ($CDCl_3$): δ=165.8 (PhCO), 157.6, 156.7 (COCO), 94.8 (C-1), 93.9 (C-1′, $J_{C\text{-}1',1'\text{-}H}$=165.6 Hz), 79.3 (C-3′), 75.4 ($PhCH_2$), 74.8 (C-2′), 73.4, 73.3 (C-4,4), 73.2 ($PhCH_2$), 73.1 (C-2), 72.0, 71.9 ($PhCH_2$), 71.8 (C-5′), 69.8 ($PhCH_2$), 69.1 (C-3), 68.7 (C-6), 68.2 (C-5), 66.2 (C-6′). Anal. calcd for $C_{56}H_{54}O_{14}$ (951.04): C, 70.72; H, 5.72; Found: C, 70.86; H, 5.69.

Benzyl *O*-(2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside-3,6-phthalate (18f). $[\alpha]_D$=+153.6 (c=1.36, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=6.35 (t, 1H, $J_{3,4}$=9.8 Hz, 3-H), 5.20 (d, 1H, $J_{1,2}$=3.4 Hz, 1-H), 5.15 (dd, 1H, $J_{2,3}$=9.3 Hz, 2-H), 5.14 (d, 1H, $J_{1',2'}$=1.7 Hz, 1′-H), 4.86 (d, 1H, J=−11.1 Hz, $PhCH_2$), 4.80 (d, 1H, J=−12.6 Hz, $PhCH_2$), 4.73 (d, 1H, J=−10.4 Hz, $PhCH_2$), 4.71 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.69 (d, 1H, J=−11.2 Hz, $PhCH_2$), 4.61 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.59 (d, 1H, J=−11.2 Hz, $PhCH_2$), 4.57 (d, 1H, J=−12.7 Hz, $PhCH_2$), 4.54 (d, 1H, J=−11.6 Hz, $PhCH_2$), 4.52 (s, 1H, $PhCH_2$), 4.44–4.41 (m, 1H, $J_{6a',6b'}$=−10.3 Hz, 6a′-H), 4.31 (t, 1H, $J_{5',6b'}$=10.3 Hz, 6b′-H), 4.08–3.98 (m, 2H, 4-H, 5′-H), 3.94–3.75 (m, 2H, 4′-H, 5-H), 3.69 (dd, 1H, $J_{3',4'}$=5.9 Hz, 3′-H), 3.62–3.42 (m, 3H, $J_{2',3'}$=2.9 Hz, 2′-H, 6a-H, 6b-H). ^{13}C NMR ($CDCl_3$): δ=167.5 (PhCO), 165.9, 165.7 (PhCOO), 94.8 (C-1), 93.9 (C-1′, $J_{C\text{-}1',1'\text{-}H}$=164.3 Hz), 75.7 (C-3′), 75.3, 74.6 (C-2′,4), 73.6 (C-4′), 73.4 ($PhCH_2$), 73.0 (C-2), 72.6, 72.5, 72.1 ($PhCH_2$), 71.3 (C-5′), 69.8 ($PhCH_2$), 69.6 (C-5), 68.3 (C-3), 68.2 (C-6), 64.9 (C-6′). Anal. calcd for $C_{62}H_{58}O_{14}$: C, 72.50; H, 5.69; Found: C, 72.32; H, 5.74.

Benzyl *O*-(2,3,4-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside-3,6-malonate (19a). $[\alpha]_D$=+80.3 (c=1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.74 (t, 1H, $J_{3,4}$=9.5 Hz, 3-H), 5.26 (d, 1H, $J_{1,2}$=3.8 Hz, 1-H), 5.00 (dd, 1H, $J_{2,3}$=10.1 Hz, 2-H), 4.91 (d, 1H, J=−11.3 Hz, $PhCH_2$), 4.81 (d, 1H, J=−12.6 Hz, $PhCH_2$), 4.73 (d, 1H, J=−12.5 Hz, $PhCH_2$), 4.70 (d, 1H, J=−12.6 Hz, $PhCH_2$), 4.64–4.60 (m, 1H, $J_{6a',6b'}$=−11.3 Hz, 6a′-H), 4.58 (d, 1H, J=−11.3 Hz, $PhCH_2$), 4.56 (d, 1H, J=−12.3 Hz, $PhCH_2$), 4.55 (d, 1H, J=−12.5 Hz, $PhCH_2$), 4.49 (s, 2H, $PhCH_2$), 4.29 (d, 1H, J=−12.1 Hz, $PhCH_2$), 4.22 (s, 1H, 1′-H), 4.01 (dd, 1H, 6b′-H), 3.97 (t, 1H, $J_{4,5}$=9.5 Hz, 4-H), 3.81–3.78 (m, 1H,

$J_{5,6a}$=1.8 Hz, 5-H), 3.78 (t, 1H, $J_{4',5'}$=9.3 Hz, 4′-H), 3.60 (ddd, 1H, $J_{5',6a'}$=4.8 Hz, $J_{5',6b'}$=7.8 Hz, 5′-H), 3.54 (bd, 1H, $J_{2',3'}$=3.0 Hz, 2′-H), 3.41 (dd, 1H, $J_{6a,6b}$=−10.9 Hz, 6a-H), 3.39–3.33 (m, 1H, 6b-H), 3.34 (dd, 1H, $J_{3',4'}$=9.0 Hz, 3′-H), 3.28 (d, 1H, J=−12.4 Hz, $COCH_2$), 3.18 (d, 1H, J=−12.4 Hz, $COCH_2$). ^{13}C NMR ($CDCl_3$): δ=165.9 ($COCH_2$), 165.5 ($COCH_2$), 164.3 (PhCO), 103.2 (C-1′, $J_{C\text{-}1',1'\text{-}H}$=153.2 Hz), 95.0 (C-1), 82.3 (C-3′), 78.4 (C-4), 76.6 (C-4′), 74.9 ($PhCH_2$), 73.6 (2 C, $PhCH_2$), 71.9 ($PhCH_2$), 69.7 ($PhCH_2$), 74.2 (C-2′), 72.6 (C-3), 72.2 (C-2), 70.2 (C-5′), 69.8 (C-5), 67.9 (C-6), 64.1 (C-6′), 42.9 ($COCH_2$). Anal. calcd for $C_{57}H_{56}O_{14}$: C, 70.94; H, 5.85; Found: C, 70.77; H, 5.88.

Benzyl *O*-(2,3,4-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside-3,6-succinate (19b). $[\alpha]_D$=+38.8 (c=1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=5.83 (dd, 1H, $J_{2,3}$=9.9 Hz, $J_{3,4}$=8.8 Hz, 3-H), 5.22 (d, 1H, $J_{1,2}$=3.6 Hz, 1-H), 5.00 (dd, 1H, 2-H), 4.90 (d, 1H, $PhCH_2$), 4.79 (d, 1H, $PhCH_2$), 4.69 (d, 1H, $PhCH_2$), 4.62–4.50 (m, 6H, 1-H, $PhCH_2$), 4.37–4.29 (m, 2H, $PhCH_2$), 4.26–4.16 (m, 2H, 6a-H, 6b-H), 4.02 (t, 1H, $J_{3,4}$=$J_{4,5}$=9.3 Hz, 4-H), 3.82 (d, 1H, $J_{2,3}$=3.1 Hz, 2-H), 3.72 (t, 1H, $J_{4,5}$=9.5 Hz, 4-H), 3.53–3.42 (m, 3H, 3-H, 5-H, 5-H), 3.36 (dd, 1H, $J_{5,6a}$=6.7 Hz, 6a-H), 3.32–3.26 (m, 1H, $J_{5,6b}$=2.8 Hz, 6b-H), 2.73–2.24 (m, 4H, CH_2–CH_2). ^{13}C NMR ($CDCl_3$): δ=171.0, 170.7 (O–*C*O–CH_2), 165.7 (Ph*C*O), 103.0 (C-1, $J_{C\text{-}1,1\text{-}H}$=153.1 Hz), 95.2 (C-1), 82.7 (C-4), 78.5 (C-5), 75.5 (C-2), 75.2 (Ph*C*H_2), 74.6 (C-3), 73.9 (Ph*C*H_2), 73.5 (Ph*C*H_2), 72.7 (C-3), 72.4 (C-2), 72.2 (C-5), 72.0 (Ph*C*H_2), 69.9 (C-4), 69.7 (Ph*C*H_2), 68.1 (C-6), 63.4 (C-6), 30.3, 29.8 (*C*H_2–*C*H_2). Anal. calcd for $C_{58}H_{58}O_{14}$: C, 71.15; H, 5.97; Found: C, 70.97; H, 6.01.

Benzyl *O*-(2,3,4-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-1,6-di-*O*-benzyl-2-deoxy-2-phthalimido-α-D-glucopyranoside-3,6-malonate (19c). $[\alpha]_D$=+86.8 (c=1.20, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=6.51 (dd, 1H, $J_{3,4}$=8.2 Hz, 3-H), 4.95 (d, 1H, $J_{1,2}$=4.0 Hz, 1-H), 4.93 (d, 1H, J=−11.1 Hz, $PhCH_2$), 4.90 (d, 1H, J=−12.7 Hz, $PhCH_2$), 4.72 (d, 1H, J=−12.7 Hz, $PhCH_2$), 4.71 (d, 1H, J=−12.8 Hz, $PhCH_2$), 4.67–4.60 (m, 2H, $J_{2,3}$=11.1 Hz, $J_{6a',6b'}$=−11.4 Hz, 2-H, 6a′-H), 4.59 (d, 1H, J=−12.7 Hz, $PhCH_2$), 4.57 (d, 1H, J=−11.2 Hz, $PhCH_2$), 4.47–4.44 (m, 2H, $PhCH_2$), 4.40 (d, 1H, J=−11.9 Hz, $PhCH_2$), 4.32 (d, 1H, J=−12.1 Hz, $PhCH_2$), 4.26 (s, 1H, 1′-H), 4.09 (dd, 1H, $J_{5',6b'}$=6.0 Hz, 6b′-H), 4.03–3.97 (m, 2H, 4-H, 5-H), 3.82 (t, 1H, $J_{4',5'}$=9.4 Hz, 4′-H), 3.57 (bd, 1H, $J_{2',3'}$=2.9 Hz, 2′-H), 3.47 (bs, 2H, 6a-H, 6b-H), 3.44–3.41 (m, 1H, 5′-H), 3.26 (dd, 1H, $J_{3',4'}$=9.3 Hz, 3′-H), 3.20 (d, 1H, J=−12.1 Hz, $COCH_2$), 3.12 (d, 1H, J=−12.1 Hz, $COCH_2$). ^{13}C NMR ($CDCl_3$): δ=167.3, 166.3 ($COCH_2$), 163.4 (2 C, NCO), 102.3 (C-1′, $J_{C\text{-}1',1'\text{-}H}$=157.7 Hz), 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. calcd for $C_{58}H_{55}NO_{14}$: C, 70.36; H, 5.60; N, 1.42; Found: C, 70.07; H, 5.64; N, 1.28.

Benzyl *O*-(2,3,4-tri-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside-3,6-phthalate (19f). $[\alpha]_D$=+80.9 (c=1.68, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=6.06 (dd, 1H, $J_{3,4}$=9.5 Hz, 3-H), 5.32 (d, 1H, $J_{1,2}$=3.5 Hz, 1-H), 5.12 (dd, 1H, $J_{2,3}$=10.2 Hz, 2-H), 4.98 (d, 1H, J=−10.8 Hz, $PhCH_2$), 4.85 (d, 1H, J=−12.5 Hz, $PhCH_2$), 4.75 (d, 1H, J=−11.5 Hz, $PhCH_2$), 4.70 (d, 1H, J=−11.7 Hz, $PhCH_2$), 4.68–4.58 (m, 3H, $PhCH_2$), 4.55 (s, 2H, $PhCH_2$), 4.48–4.44 (m, 1H, $J_{6a',6b'}$=11.4 Hz, 6a′-H), 4.34 (s, 1H, 1′-H), 4.43 (d, 1H, J=−12.5 Hz, $PhCH_2$), 4.33 (dd, 1H, $J_{5',6b'}$=9.0 Hz, 6b′-H), 4.18 (t, 1H, $J_{4,5}$=9.4 Hz, 4-H), 3.92 (t, 1H, $J_{4',5'}$=9.5 Hz, 4′-H), 3.91–3.82 (m, 1H, 5-H), 3.68–3.60 (m, 1H, 5′-H), 3.62–3.56 (m, 2H, $J_{2',3'}$=2.7 Hz, 2′-H, 3′-H), 3.52–3.44 (m, 2H, 6a-H, 6b-H). ^{13}C NMR ($CDCl_3$): δ=168.3 (PhCO), 165.2, 164.2 (PhCOO), 102.4 (C-1′, $J_{C\text{-}1',1'\text{-}H}$=153.4 Hz), 95.2 (C-1), 79.0 (C-3), 77.7 (C-4), 76.9 (C-3′), 75.9, 74.7 (C-2,4′), 75.1 ($PhCH_2$), 73.9, 73.5, 72.2 ($PhCH_2$), 71.3 (C-2), 70.2 (C-5), 69.5 ($PhCH_2$), 69.1 (C-5′), 67.8 (C-6), 64.1 (C-6′). Anal. calcd for $C_{62}H_{58}O_{14}$: C, 72.50; H, 5.69; Found: C, 72.34; H, 5.75.

Benzyl *O*-(6-*O*-benzoyl-2,3,4-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-2,3-di-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (20). (a) A solution of **18a** (90 mg, 0.09 mmol) and a catalytic amount of NaOMe in methanol (8 ml) was stirred at 20°C for 3 h, neutralized with Dowex ion exchange resin (H^+ form) and concentrated. The residue was dissolved in pyridine (8 ml) and benzoyl chloride (0.065 ml, 0.56 mmol) was added. The mixture was stirred at 20°C for 24 h, poured into water and extracted with dichloromethane. The extracts were washed with aqueous HCl and $NaHCO_3$ solution, dried and concentrated. Chromatography (*n*-hexane/ethyl acetate 4:1) of the residue afforded **20** (71.7 mg, 70%), $[\alpha]_D$=+57.7 (c=0.52, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=6.07 (dd, 1H, $J_{3,4}$=8.9 Hz, 3-H), 5.32 (d, 1H, $J_{1,2}$=3.7 Hz, 1-H), 5.16 (dd, 1H, $J_{2,3}$=10.3 Hz, 2-H), 5.14 (d, 1H, $J_{1',2'}$=1.7 Hz, 1′-H), 4.87 (d, 1H, J=−10.8 Hz, $PhCH_2$), 4.79 (d, 1H, J=−12.4 Hz, $PhCH_2$), 4.61 (d, 1H, J=−11.6 Hz, $PhCH_2$), 4.59 (s, 1H, $PhCH_2$), 4.58 (d, 1H, J=−10.6 Hz, $PhCH_2$), 4.57 (d, 1H, J=−12.1 Hz, $PhCH_2$), 4.55–4.52 (m, 1H, $PhCH_2$), 4.51 (dd, 1H, $J_{6a',6b'}$=−11.8 Hz, 6a′-H), 4.45–4.41 (m, 2H, 6b′-H, $PhCH_2$), 4.13 (t, 1H, $J_{4',5'}$=9.4 Hz, 4′-H), 4.06–4.00 (m, 2H, $J_{5,6b}$=2.0 Hz, 5-H, $PhCH_2$), 4.03 (t, 1H, $J_{4,5}$=9.5 Hz, 4-H), 3.96–3.91 (m, 2H, $J_{5',6a'}$=3.1 Hz, 3′-H, 5′-H), 3.89–3.83 (m, 1H, $J_{6a,6b}$=−11.1 Hz, 6a-H), 3.72 (dd, 1H, 6b-H), 3.60 (t, 1H, $J_{2',3'}$=2.4 Hz, 2′-H). ^{13}C NMR ($CDCl_3$): δ=166.3, 165.6, 165.5 (PhCO), 100.2 (C-1′, $J_{C\text{-}1',1'\text{-}H}$=171.8 Hz), 95.1 (C-1), 79.6 (C-3′), 76.7 (C-4′), 75.6 (C-2′), 75.1 ($PhCH_2$), 73.7 (C-4), 73.5 ($PhCH_2$), 72.9 (C-3), 72.5 ($PhCH_2$), 71.8 (C-2), 71.6 ($PhCH_2$), 71.4 (C-5′), 70.2 (C-5), 69.8 ($PhCH_2$), 68.6 (C-6), 63.5 (C-6′). Anal. calcd for $C_{68}H_{64}O_{14}$: C, 73.90; H, 5.84; Found: C, 73.95; H, 5.83. (b) Treatment of **18b** (198 mg, 0.2 mmol) as described under (A) afforded **20** (175 mg, 78%). (c) Treatment of **18d** (92 mg, 0.1 mmol) as described under (A) afforded **20** (81.7 mg, 74%). (d) Treatment of **18e** (86 mg, 0.09 mmol) as described under (A) afforded **20** (69.9 mg, 70%). (e) Treatment of **18f** (99 mg, 0.096 mmol) as described under (A) afforded **20** (74.7 mg, 70%).

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-glucopyranoside (21a). (A) Treatment of **19a** (324 mg,

0.34 mmol) as described for the preparation of **20** under (A) afforded **21a** (283 mg, 76%), $[\alpha]_D$=−45.6 (*c*=1.22, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=6.07 (t, 1H, $J_{3,4}$=9.8 Hz, 3-H), 5.33 (d, 1H, $J_{1,2}$=3.8 Hz, 1-H), 5.18 (dd, 1H, $J_{2,3}$=10.2 Hz, 2-H), 4.89 (d, 1H, *J*=−12.0 Hz, $PhCH_2$), 4.79 (d, 1H, *J*=−10.9 Hz, $PhCH_2$), 4.75 (d, 1H, *J*=−12.7 Hz, $PhCH_2$), 4.65 (d, 1H, *J*=−12.1 Hz, $PhCH_2$), 4.56 (d, 1H, *J*=−12.5 Hz, $PhCH_2$), 4.51 (d, 1H, *J*=−11.8 Hz, $PhCH_2$), 4.44 (bd, 2H, *J*=−11.8 Hz, 1′-H, $PhCH_2$), 4.42 (bd, 2H, *J*=−11.7 Hz, $PhCH_2$), 4.39 (d, 1H, *J*=−10.8 Hz, $PhCH_2$), 4.22 (t, 1H, $J_{4,5}$=9.8 Hz, 4-H), 4.13 (dd, 1H, $J_{6a',6b'}$=−11.7 Hz, 6a′-H), 4.08–4.02 (m, 2H, 5-H, 6b′-H), 3.76 (t, 1H, $J_{4',5'}$=9.4 Hz, 4′-H), 3.70–3.60 (m, 3H, $J_{2',3'}$=2.7 Hz, 2′-H, 6a′-H, 6b-H), 3.32 (bdd, 2H, $J_{3',4'}$=9.2 Hz, $J_{5',6a'}$=2.0 Hz, 2′-H, 5′-H). ^{13}C NMR ($CDCl_3$): δ=166.0, 165.7, 165.6 (PhCO), 100.8 (C-1′, $J_{C\text{-}1',1'\text{-}H}$=156.8 Hz), 95.3 (C-1), 82.1 (C-3′), 75.1 (C-4), 75.0 ($PhCH_2$), 74.1 (2 C, C-2′, C-4′), 73.7 ($PhCH_2$), 73.5 (2 C, C-5′, $PhCH_2$), 72.0 (C-2), 71.2 ($PhCH_2$), 70.2, 70.1 (C-3,5), 69.8 ($PhCH_2$), 68.2 (C-6), 63.5 (C-6′). Anal. calcd for $C_{68}H_{64}O_{14}$: C, 73.90; H, 5.84; Found: C, 73.92; H, 5.90. (B) Treatment of **19b** (105 mg, 0.11 mmol) as described under (A) afforded **21a** (88 mg, 75%). (C) Treatment of **19f** (89 mg, 0.087 mmol) as described under (A) afforded **21a** (69.5 mg, 73%).

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 (21b). (A) Treatment of **19c** (125 mg, 0.13 mmol) as described for the preparation of **20** under (A) afforded **21b** (104 mg, 73%), $[\alpha]_D$=+8.4 (*c*=1.14, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=6.84 (dd, 1H, $J_{3,4}$=9.3 Hz, 3-H), 5.02 (d, 1H, $J_{1,2}$=3.5 Hz, 1-H), 4.90 (d, 1H, *J*=−11.3 Hz, $PhCH_2$), 4.88 (d, 1H, *J*=−12.5 Hz, $PhCH_2$), 4.82 (dd, 1H, $J_{2,3}$=11.1 Hz, 2-H), 4.74 (d, 1H, *J*=−12.4 Hz, $PhCH_2$), 4.66 (d, 1H, *J*=−12.5 Hz, $PhCH_2$), 4.55 (d, 1H, *J*=−12.6 Hz, $PhCH_2$), 4.53 (d, 1H, *J*=−12.1 Hz, $PhCH_2$), 4.48 (s, 1H, 1′-H), 4.46–4.41 (m, 2H, $PhCH_2$), 4.38 (d, 1H, *J*=−12.0 Hz, $PhCH_2$), 4.30–4.23 (m, 2H, 4-H, 5-H), 4.22 (d, 1H, *J*=−12.1 Hz, $PhCH_2$), 4.18–4.11 (m, 1H, $J_{6a',6b'}$=−12.0 Hz, 6a′-H), 4.13 (dd 1H, $J_{5',6b'}$=4.8 Hz, 6b′-H), 3.80 (t, 1H, $J_{4',5'}$=9.3 Hz, 4′-H), 3.73 (bd, 2H, 6a-H, 6b-H), 3.68 (bd, 1H, $J_{2',3'}$=3.0 Hz, 2′-H), 3.24 (dd, 1H, $J_{3',4'}$=9.2 Hz, 3′-H), 3.20–3.13 (m, 1H, 5′-H). ^{13}C NMR ($CDCl_3$): δ=166.1, 165.8 (PhCO), 163.4 (2 C, NCO), 100.2 (C-1′, $J_{C\text{-}1',1'\text{-}H}$=154.8 Hz), 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. calcd for $C_{69}H_{63}NO_{14}$: C, 73.33; H, 5.62; N, 1.24; Found: C, 73.16; H, 5.58; N, 1.10.

Acknowledgements

We thank Dr H. Schmickler, and C. Schmitz, University of Cologne for performing the NMR spectra and elemental analyses. This work was financially supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

References

1. Barresi, F.; Hindsgaul, O. Synthesis of β-D-Mannose Containing Oligosaccharides. *Modern Methods in Carbohydrate Synthesis*; Khan, S. H., O'Neill, R. A., Eds.; Harwood Academic Publishers: Amsterdam, 1996; pp 251–276.
2. (a) Paulsen, H.; Lockhoff, O. *Chem. Ber.* **1981**, *114*, 3102–3114. (b) Paulsen, H.; Kutschker, W.; Lockhoff, O. *Chem. Ber.* **1981**, *114*, 3233–3241.(c) Crich, D.; Sun, S. *J. Org. Chem.* **1996**, *61*, 4506–4507. (d) Crich, D.; Sun, S. *J. Org. Chem.* **1997**, *62*, 1198–1199. (e) Crich, D.; Sun, S. *J. Am. Chem. Soc.* **1998**, *120*, 435–436. (f) Crich, D.; Dai, Z. *Tetrahedron* **1999**, *55*, 1569–1580.
3. Hodosi, G.; Kovac, P. *J. Am. Chem. Soc.* **1997**, *119*, 2335–2336.
4. (a) Kaji, E.; Lichtenthaler, F. W. *Trends Glycosci. Glycotechnol.* **1993**, *5*, 121–142. (b) Lichtenthaler, F. W.; Schneider-Adams, T. *J. Org. Chem.* **1994**, *59*, 6728–6734. (c) Lichtenthaler, F. W.; Schneider-Adams, T.; Immel, S. *J. Org. Chem.* **1994**, *59*, 6735–6738. (d) Lichtenthaler, F. W.; Metz, T. W. *Tetrahedron Lett.* **1997**, *38*, 5477–5480.
5. (a) Günther, W.; Kunz, H. *Carbohydr. Res.* **1992**, *228*, 217–241. (b) Seifert, J.; Unverzagt, C. *Tetrahedron Lett.* **1996**, *37*, 6527–6530. (c) Fürstner, A.; Konetzki, I. *Tetrahedron Lett.* **1998**, *39*, 5721–5724.
6. (a) Barresi, F.; Hindsgaul, O. *Synlett* **1992**, 759–761. (b) Stork, G.; Kim, G. *J. Am. Chem. Soc.* **1992**, *114*, 1087–1088. (c) Ito, Y.; Ogawa, T. *Angew. Chem.* **1994**, *106*, 1843–1845; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1765–1767. (d) Dan, A.; Ito, Y.; Ogawa, T. *J. Org. Chem.* **1995**, *60*, 4680–4681. (e) Lergenmller, M.; Nukada, T.; Kuramochi, K.; Dan, A.; Ogawa, T.; Ito, Y. *Eur. J. Org. Chem.* **1999**, 1367–1376.
7. (a) Ohtake, H.; Iimori, T.; Ikegami, S. *Tetrahedron Lett.* **1997**, *38*, 3413–3414. (b) Schmidt, R. R.; Moering, U.; Reichrath, M. *Chem. Ber.* **1982**, *115*, 39–49. (c) Hodosi, G.; Kovac, P. *J. Am. Chem. Soc.* **1997**, *119*, 2335–2336.
8. Ziegler, T.; Lemanski, G. *Angew. Chem.* **1998**, *110*, 3367–3369; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3129–3132.
9. Ziegler, T.; Lemanski, G.; Rakoczy, A. *Tetrahedron Lett.* **1995**, *36*, 8973–8976.
10. (a) Liptak, A.; Csik, E.; Nanasi, P. *Acta Chim. Acad. Sci. Hung.* **1977**, *94*, 267–273. (b) Ziegler, T.; Lemanski, G. *Eur. J. Org. Chem.* **1998**, 163–170.
11. (a) Schle, G.; Ziegler, T. *Liebigs Ann.* **1996**, 1599–1607. (b) Garegg, P.; Hultberg, H. *Carbohydr. Res.* **1981**, *93*, C10–C11.
12. Christensen, M. K.; Meldal, M.; Bock, K. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1453–1460.
13. Ottoson, H. *Carbohydr. Res.* **1990**, *197*, 101–107.
14. Backer, H. J.; Homan, J. D. H. *Recl. Trav. Chim. Pays-Bas* **1939**, *58*, 1048–1061.
15. Ziegler, T.; Ritter, A.; Hürttlen, J. *Tetrahedron Lett.* **1997**, *38*, 3715–3718.
16. (a) Saigo, K.; Usui, M.; Kikuchi, K.; Shimada, E.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1863–1866. (b) Mukaiyama, T. *Angew. Chem.* **1979**, *91*, 798–812; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 707–721.
17. DeNinno, M. P.; Etienne, J. B.; Duplantier, K. C. *Tetrahedron Lett.* **1995**, *36*, 669–672.
18. Kahne, D.; Walker, S.; Cheng, Y.; van Engen, D. *J. Am. Chem. Soc.* **1989**, *111*, 6881–6882.
19. (a) Demchenko, A.; Stauch, T.; Boons, G.-J. *Synlett* **1997**, 818–820. (b) Boons, G.-J.; Zhu, T. *Synlett* **1997**, 809–811.
20. (a) Fügedi, P.; Garegg, P. J.; Lönn, H.; Norberg, T. *Glycoconjugate J.* **1987**, *4*, 97–108. (b) Lönn, H. *Carbohydr. Res.* **1985**,

139, 115–121. (c) Lönn, H. *J. Carbohydr. Chem.* **1987**, *6*, 301–306.
21. (a) Zuurmond, H. M.; van der Laan, S. C.; van der Marel, G. A.; van Boom, J. H. *Carbohydr. Res.* **1991**, *215*, C1–C3. (b) Zegelaar-Jaarsveld, K.; van der Marel, G. A.; van Boom, J. H. *Tetrahedron* **1992**, *48*, 10 133–10 148. (c) Veeneman, G. H.; van Boom, J. H. *Tetrahedron Lett.* **1990**, *31*, 275–278.
22. (a) Andersson, F.; Fügedi, P.; Garegg, P. J.; Nashed, M. *Tetrahedron Lett.* **1986**, *27*, 3919–3922. (b) Andersson, F.; Birberg, W.; Fügedi, P.; Garegg, P. J.; Nashed, M.; Pilotti, A. *ACS Symp. Ser.* **1989**, *386*, 117–130. (c) Fügedi, P.; Garegg, P. J. *Carbohydr. Res.* **1986**, *149*, C9–C12.
23. Kihlberg, J. O.; Leigh, D. A.; Bundle, D. R. *J. Org. Chem.* **1990**, *55*, 2860–2863.
24. Dobarro-Rodriguez, A.; Trumtel, M.; Wessel, H. P. *J. Carbohydr. Chem.* **1992**, *11*, 255–263.
25. (a) Bock, K.; Pedersen, C. *J. Chem. Soc. Perkin Trans. 2* **1974**, 293–297. (b) Bock, K.; Pedersen, C. *Acta Chem. Scand.* **1975**, *B29*, 258–262. (c) Podlasek, C. A.; Wu, J.; Stripe, W. A.; Bondo, P. B.; Serianni, A. S. *J. Am. Chem. Soc.* **1995**, *117*, 8635–8644.
26. Ziegler, T.; Lau, R. *Tetrahedron Lett.* **1995**, *36*, 1417–1420.
27. Lau, R.; Schle, G.; Schwaneberg, U.; Ziegler, T. *Liebigs Ann.* **1995**, 1745–1754.
28. Ziegler, T.; Dettmann, R.; Ariffahdillah; Zettl, U. *J. Carbohydr. Chem.* **1999**, *18*, 1079–1095.
29. Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440–450.