Pergamon

Tetrahedron, Vol. 52, No. 10, pp. 3575-3592, 1996

0040-4020/96 $15.00 + 0.00

S0040-4020(96)00034-8

Iodonium Ion-Assisted Synthesis of Tetrameric Fragments Corresponding to the Cell Wall Phenolic Glycolipids of *Mycobacterium kansasii* serovars II and IV

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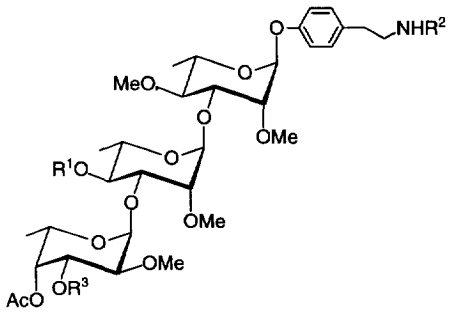
Abstract: The spacer-containing tetramers **3** and **4**, derivatives of the phenolic glycolipids of *Mycobacterium kansasii* serovars II and IV were prepared by iodonium ion-mediated mannosylation of trimeric acceptor 4-[2-(benzyloxycarbonylamino)ethyl]phenyl 2,4-di-*O*-methyl-3-*O*-[4-*O*-benzyl-2-*O*-methyl-3-*O*-(4-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl]-α-L-rhamnopyranoside (**2**) with ethyl 1-thio-D-mannopyranoside donors **7**, **13**, and **24**. In addition, the glycosylating properties of donors **7**, **13**, **24**, **29-31**, each containing a different protective group at position 2, were examined by executing condensations with model acceptor **18**(L) and its enantiomer **18**(D).

INTRODUCTION

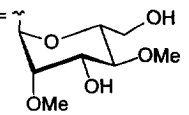
As part of a programme[1] to develop serodiagnostics and synthetic vaccines based on carbohydrates, we recently revealed[2] the assembly of the invariable *Mycobacterium kansasii* inner core trimeric fragment **1**, the terminal L-rhamnose unit of which is α-(*O*)-linked to a tyramine moiety suitable for conjugation with a protein.

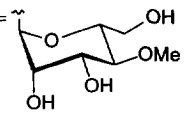
We here report that glycosylation of the HO-3 in the L-fucopyranosyl unit of the partially protected trisaccharide acceptor **2** with appropriately protected ethyl 1-thio-D-mannopyranoside donors (*i.e.* **7**, **13**, and **24**) gives access to the haptenic tetrameric fragments **3** and **4**, which correspond to the linear oligosaccharides of *M. kansasii* phenolic glycolipid serovars II[3] and IV[4], respectively.



1 $R^1=R^2=R^3=H$

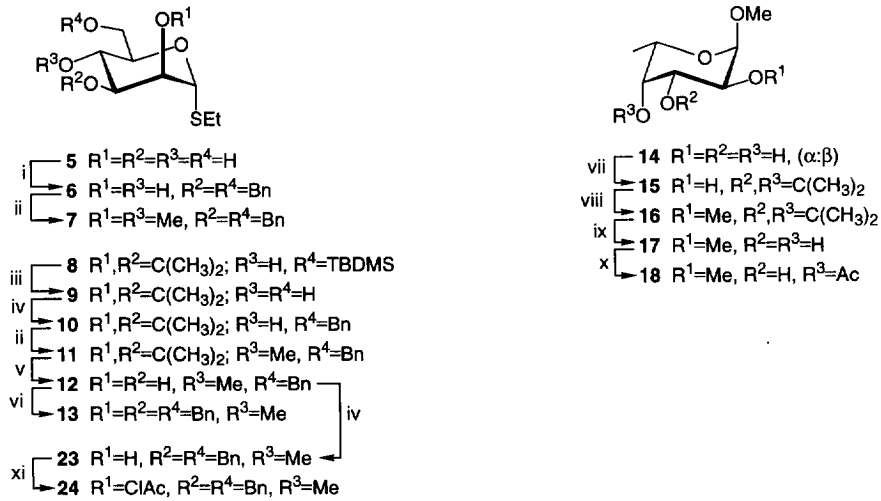
2 R^1=Bn, R^2=benzyloxycarbonyl(Z), $R^3=H$

3 $R^1=R^2=H$, $R^3=$ 

4 $R^1=R^2=H$, $R^3=$ 

RESULTS AND DISCUSSION

The readily accessibility[2] of the partially protected trimeric fragment **2** prompted us to investigate whether **2** could be used as a starting compound for the construction of the target tetramers **3** and **4**. A crucial step in the synthesis of tetrameric fragments **3** and **4** entails in both cases the stereoselective formation of a *trans* α-(1→3)-interglycosidic bond between the HO-3 of the L-fucosyl unit in the trimeric acceptor **2** and an appropriately protected D-mannopyranosyl donor. However, the presence of an acetyl group at the O-4 position of the L-fucose residue in acceptor **2** restricts the use of mannopyranosyl donors bearing O-2 participating groups (*i.e.* acetyl or benzoyl). The limited choice in protecting groups imposed on the mannopyranosyl donors, and our broad experience in applying ethyl 1-thio-glycosides as building blocks,[1,2,5-8] were decisive factors in selecting ethyl 1-thio-α-D-mannopyranosides for the elongation of **2**. Thus, condensation of acceptor **2** with ethyl 3,6-di-*O*-benzyl-2,4-di-*O*-methyl-1-thio-α-D-mannopyranoside (**7**) in the presence of the thiophilic promoter *N*-iodosuccinimide (NIS) and catalytic triflic acid (TfOH)[5] would give the fully protected tetramer **21**, a precursor of fragment **3**. Similarly, glycosylation of **2** with ethyl 2,3,6-tri-*O*-benzyl-4-*O*-methyl-1-thio-α-D-mannopyranoside (**13**) would result in the formation of tetramer **22**, a precursor of fragment **4**.



Reagents and conditions: (i) Bu_2SnO, MeOH, 2.5 h; BnBr, CsF, DMF, 18 h, 59%. (ii) MeI, NaH, DMF, 1 h, **7** 85%, **11** 95%. (iii) TBAF, dioxane, 1.5 h, 79%. (iv) Bu_2SnO, MeOH, 1.5 h; BnBr, CsF, DMF, 18 h, **10** 75%, **23** 80%. (v) 90% HOAc, 50°C, 17 h, 89%. (vi) BnBr, NaH, DMF, 1.5 h, 88%. (vii) HCl-MeOH (1 N), reflux, 1.5 h; $CH_3C(OCH_3)_2$, acetone, TsOH, 1.5 h, **15**-α 42% and **15**-β 27%. (viii) MeI, NaH, DMF, 1 h, 94%. (ix) 90% HOAc, 50°C, 17 h, 100%. (x) $CH_3C(OCH_3)_3$, CSA, CH_3CN, 45 min; 80% HOAc, 15 min, 81%. (xi) $(ClAc)_2O$, $NaHCO_3$, DMF, 24 h, 87%.

Scheme 1

The preparation of the required donors **7** and **13** starting from ethyl 1-thio-α-D-mannopyranoside[8] (**5**) is depicted in Scheme 1. Thus, regioselective benzylation of the distannylidene complex[9] of **5** with benzyl bromide, followed by methylation of the resulting 3,6-di-*O*-benzyl derivative **6**, gave donor **7** in 50% overall yield. On the other hand, desilylation of known[8b] ethyl 2,3-*O*-isopropylidene-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-α-D-mannopyranoside (**8**) and regioselective benzylation[10] of diol **9** gave the mono-benzylated derivative **10**. Methylation of **10** and subsequent deacetonation of **11** afforded, after benzylation of diol **12**, the partially benzylated donor **13** in 46% overall yield.

Prior to the intended elongation of trimeric fragment **2** with the mannopyranosyl donors **7** and **13**, we first focused our attention on the stereochemistry of the glycosylation of these donors with the model compound methyl 2-*O*-methyl-4-*O*-acetyl-α-L-fucopyranoside [**18**(L)], prepared in four steps (see steps vii-x

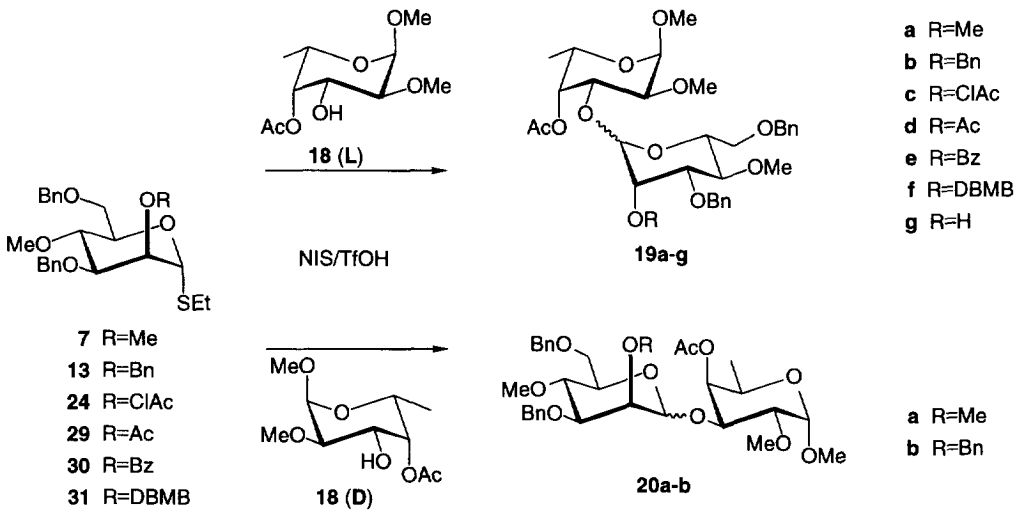
Table 1 *Relevant data on the NIS/TfOH(cat.)-assisted glycosylation* of fucopyranoside acceptor 18(L) and 18(D) with D-mannopyranoside donors 7, 13, 24, and 29-31.*

entry	donor	acceptor	dimer	yield (%)	α:β(:28)
1	**7** R=Me	**18**(L)	**19a**	74	2:1
2	**13** R=Bn	**18**(L)	**19b**	72	4:1
3	**7** R=Me	**18**(D)	**20a**	68	4:1
4	**13** R=Bn	**18**(D)	**20b**	65	6:1
5	**24** R=ClAc	**18**(L)	**19c, 28**	78	6:1(:6)
6	**24** R=ClAc**	**18**(L)	**19c**	79	6:1
7	**29** R=Ac	**18**(L)	**19d**	63	1:0
8	**30** R=Bz	**18**(L)	**19e**	92	1:0
9	**31** R=DBMB	**18**(L)	**19f**	94	1:0

* Acceptor (1 equiv.), Donor (1.2 equiv.), NIS (1.2 equiv.), TfOH (0.1 equiv.), 1,2-dichloroethane-Et_2O, 0°C, 15 min.

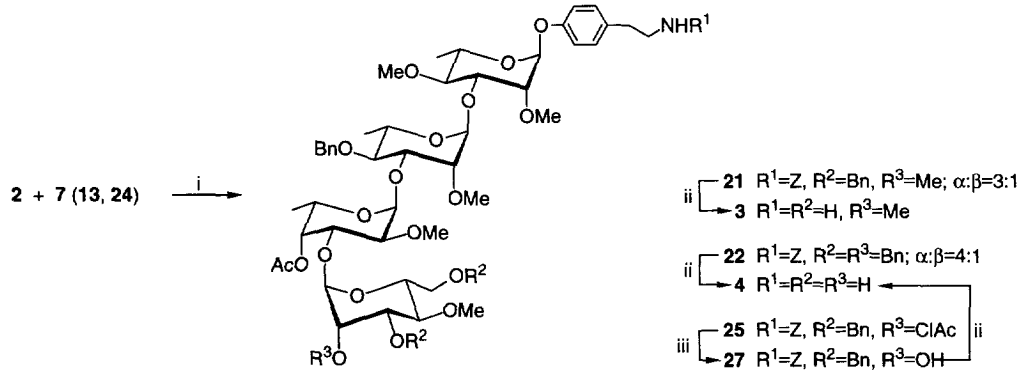
** 0.3 equiv. TfOH was used.

in Scheme 1) from methyl α(β)-L-fucopyranoside[11] (**14**). The yield and stereochemical outcome of those pilot mannosylations are summarised in Table 1. It can be seen (Table 1, entries 1-2) that NIS/TfOH(cat.)-assisted glycosylations of acceptor **18**(L) with 2-*O*-Me- and 2-*O*-Bn-mannopyranosides **7** and **13** resulted in the formation of a high percentage β-linked dimers **19a** and **19b** (Scheme 2). The unfavourable outcome of the latter glycosylations might be ascribed to the occurrence of double stereodifferentiation[12] (DSD). In order to validate this assumption, the enantiomeric acceptor **18**(D), prepared in three steps (*i.e.* steps viii-x in Scheme 1) from **15**(D)[13], was also condensed with the same donors **7** and **13**. Iodonium ion-mediated glycosylation of **18**(D) with mannopyranosyl donors **7** and **13** gave the respective dimers **20a** and **20b** as a mixture of anomers (Table 1, entries 3-4). A comparison between the stereochemical outcome of the latter glycosylations demonstrates that different α:β ratios are observed in the coupling of the individual enantiomers of **18** with both donors **7** (R=Me) and **13** (R=Bn), indicating that the occurrence of DSD, albeit to a minor degree, is not excluded.



Scheme 2

In the light of the aforementioned pilot glycosylations, it was anticipated that the stereochemistry of the condensation of the L-trimeric acceptor **2** with the D-mannopyranosyl donors **7** and **13** would not deviate substantially from those of the same donors with the L-acceptor **18** (see Table 1, entries 1-2). Indeed, NIS/TfOH(cat.)-promoted D-mannosylation of **2** with **7** (see Scheme 3) gave tetramer **21** as a mixture of anomers (α:β=3:1). Separation of the individual anomers by silica gel chromatography afforded the requisite α-mannosylated tetramer **21** in 63% yield. Similar to the synthesis of **21**, purification of the crude mannosylation mixture (α:β=4:1) resulting from the elongation of **2** with **13** gave the α-mannosylated tetramer **22** in 60% yield. Removal of the benzyl (Bn) and benzyloxycarbonyl (Z) groups from both tetramers **21** and **22** led, after purification by Sephadex LH20 gel-filtration, to the isolation of the respective target tetramers **3** and **4**, the structures of which were firmly established by NMR-spectroscopy.



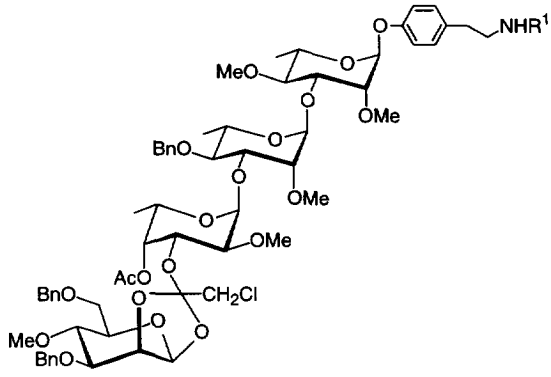
Reagents and conditions: (i) NIS/TfOH(cat.), 1,2-dichloroethane-Et_2O, 0°C, 15 min, **21** 83%, **22** 74%, **25+26** 76%. (ii) H_2, Pd(C), isopropanol-H_2O-HOAc, 66 h, **3** 86%, **4** 86%, 85%. (iii) HDTC, HOAc, lutidine, 0°C, 30 min, 86%.

Scheme 3

At this stage, we were interested to find out whether the rather low α-stereoselectivity in the mannosylation of L-acceptor **2** with the D-donors **7** and **13** could be increased by the known[14] α-directing nature of the participating medium diethyl ether. Pilot experiments indicated that α-mannosylation of **18**(L) by **7** at 20°C in diethyl ether proceeded with a high degree of stereoselectivity to give dimer **19a** as a mixture of anomers in the ratio α:β=7:1. As expected, the latter beneficial stereochemical effect was also observed in the glycosylation of trimeric acceptor **2** with both donors **7** and **13**. Thus, the individual tetrameric fragments **21** and **22** were obtained as an anomeric mixture (α:β ratio 10:1 and 12:1, respectively) and in excellent yield (≈90%).

It was expected that the formation of the unwanted β-anomer could be suppressed by replacing the non-participating 2-*O*-benzyl by a participating chloroacetyl group, the removal of which is compatible with the presence of a 4-*O*-acetyl group in the fucosyl moiety.

The requisite donor ethyl 3,6-di-*O*-benzyl-2-*O*-chloroacetyl-4-*O*-methyl-1-thio-α-D-mannopyranoside (**24** in Scheme 1) was obtained in 69% overall yield via regioselective benzylation of the equatorial hydroxyl group in **12** and subsequent chloroacetylation of **23**. However, glycosylation of **2** with the 2-*O*-chloroacetyl-D-mannopyranosyl donor **24** in the presence of NIS and variable amounts of TfOH (0.1 or 0.3 equiv.) gave tetrameric fragment **25** (Scheme 3) and its 1,2-orthoester derivative **26** (see Figure 3), as evidenced by NMR spectroscopy[15]. Unfortunately, every attempt to convert **26** into **25** via acid-catalysed (TfOH) rearrangement[16] was accompanied by the formation of the trimeric fragment fragment **2**. Selective removal of the chloroacetyl group in **25** with hydrazine dithiocarbonate[17] (HDTC) and subsequent hydrogenolysis of resulting **27** gave, after purification by Sephadex LH20 gel-filtration, homogeneous **4**, which was in every aspect identical with the same tetrasaccharide obtained by hydrogenolysis of **22**.



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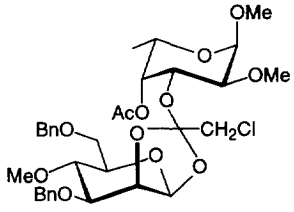

28

In this respect it is of interest to note that mannosylation (Table 1, entry 5) of **18**(L) with donor **24**, having a participating 2-*O*-chloroacetyl group, led to an anomeric mixture of dimer **19c** (Scheme 2) and its 1,2-ortho-ester derivative **28**. The identity of compound **28** was ascertained by ^{1}H- and ^{13}C-NMR spectroscopy[15] and its quantitative acid-catalysed (TfOH) rearrangement[16] into the α-linked dimer of **19c** (*cf.* conversion **26**→**25**). Apart from this, it was established that the formation of the rather acid-stable orthoester **28** could be prevented by executing the NIS-mediated mannosylation in the presence of relative excess triflic acid (see entry 6 in Table 1).[18] The formation of the undesired β-dimer of **19c** in the latter two mannosylations may be due to the less effective participating aptitude of the 2-O-chloroacetyl group. Indeed, exclusive α-mannosylation of **18**(L) occurred (Table 1, entries 7-8) using the corresponding 2-*O*-acetyl (**29**) or benzoyl (**30**) derivatives, obtained by acetylation or benzoylation of **23**, as the glycosylating agents.

The stereoselective introduction of the 1,2-*trans* linkage between 2-*O*-benzoyl-D-mannopyranoside **30** and the L-fucopyranoside acceptor **18** urged us to explore whether the D-mannopyranoside **31**, in which HO-2 is protected with the versatile 2-dibromomethylbenzoyl (DBMB) group[19], is a viable building unit in the synthesis of the partially protected dimer **19g** (see Scheme 2). The requisite mannopyranoside donor **31** was readily accessible by acylation of **23** with 2-dibromomethylbenzoyl chloride. Iodonium ion-mediated glycosylation of the L-fucosyl acceptor **18** with **31** proceeded in a stereoselective manner to give the α-linked disaccharide **19f** in an excellent yield (see entry 9 in Table 1). Treatment of **31** with silver perchlorate in acetone-water in the presence of 2,6-lutidine, and subsequent addition of morpholine to the resulting 2-*O*-(2-formyl)benzoyl derivative, gave partially protected dimer **19g** in 84% over the two steps. The successful synthesis of **19g** clearly demonstrates that the two-step removal of the DBMB is compatible with the presence of the 4-*O*-acetyl in the fucosyl moiety. It may therefore not be excluded that the DBMB group presents an attractive alternative for the recently proposed[20] 2-(2-chloroacetoxyethyl)benzoyl group, which is cleavable besides other acyl groups via a rather sluggish two-step process.

EXPERIMENTAL

General methods and materials: Methanol was dried by refluxing with magnesium methoxide and then distilled. Toluene and 1,2-dichloroethane were distilled from P_2O_5. *N,N*-Dimethylformamide (DMF) was stirred with calcium hydride for 20 h, then distilled under reduced pressure. Pyridine and dioxane were dried by refluxing 18 h with calcium hydride and then distilled. Acetonitrile (p.a. Rathburne) was dried by storage over molecular sieves 4 Å (Aldrich). Diethyl ether was distilled from $LiAlH_4$. Methanol was stored over molecular sieves 3 Å. Toluene and diethyl ether were stored over sodium wire. DMF, dioxane, pyridine and 1,2-dichloroethane were stored over molecular sieves 4 Å.

Reactions were performed under anhydrous conditions at room temperature unless stated otherwise. Evaporation of solvents was performed under reduced pressure at 40°C. TLC-analyses were conducted on DC Fertigfolien (Schleicher & Schüll

F 1500, LS 254). Compounds were visualised with UV light (254 nm) and by charring with concentrated sulfuric acid/ethanol (1/4, v/v). Column chromatography was performed on columns of silica gel 60, 230-400 mesh (Merck). The petroleum ether used for eluting the columns was low boiling (40-60°C). Sephadex LH20 (Pharmacia) was used for gel-filtration.

Optical rotations were determined with a Propol polarimeter for solutions in $CHCl_3$ (p.a. Baker) at 20°C. ^{1}H-NMR (200 MHz) and ^{13}C-NMR (50.1 MHz) spectra were recorded using a Jeol JNM-FX-200 spectrometer. Spectra were also recorded using a Bruker WM-300 spectrometer equipped with an Aspect 2000 computer, and a Bruker MSL-400 connected with an Aspect 3000 computer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane as an internal standard. Mass spectra of compounds dissolved in methanol-water (4/1, v/v) were recorded with a Finnigan MAT TSQ-70 equipped with a custom-made Electrospray Interface (ESI).

Ethyl 3,6-di-*O*-benzyl-1-thio-α-D-mannopyranoside (6) - To a solution of ethyl 1-thio-α-D-mannopyranoside (**5**, 1.13 g, 5.0 mmol) in methanol (41 ml) was added dibutyltin oxide (2.65 g, 10.6 mmol). The mixture was heated under reflux for 2.5 h. The solvent was removed and the residue was dried by evaporation with toluene. The distannylidene derivative was dissolved in DMF (34 ml), cesium fluoride (2.14 g, 14.1 mmol) and benzyl bromide (1.70 ml, 14.4 mmol) were added and the reaction mixture was stirred for 18 h at room temperature. The solvent was evaporated and the residue was redissolved in diethyl ether (20 ml). The organic layer was washed twice with aq. KF (1 M, 15 ml) and once with H_2O (10 ml), dried ($MgSO_4$), filtered, and concentrated. The oily residue was purified by column chromatography (ethyl acetate in petroleum ether 0→30%) to furnish compound **6** (1.20 g, 3.0 mmol).

^{13}C{^{1}H}-NMR ($CDCl_3$): δ 14.9 (CH_3 SEt), 24.9 (CH_2 SEt), 70.0 (C-6), 71.7, 73.4 (2× CH_2 Bn), 67.4, 69.4, 71.8, 79.9 (C-2, C-3, C-4, C-5), 84.0 (C-1), 126.9, 127.2, 127.6, 127.9, 128.1, 128.3, 128.5 (CH Bn), 137.9, 138.3 (qC Bn).

Anal. calcd. for $C_{22}H_{28}O_5S$ (404.53): C 65.32, H 6.98; found C 65.44, H 7.06%.

Ethyl 3,6-di-*O*-benzyl-2,4-di-*O*-methyl-1-thio-α-D-mannopyranoside (7) - Methyl iodide (0.49 ml, 7.8 mmol) was added at 0°C to a suspension of compound **6** (1.20 g, 3.0 mmol) and sodium hydride (60%, 360 mg, 9.0 mmol) in DMF (6 ml). After stirring for 45 min at room temperature, the reaction was quenched with methanol (1 ml) and the solvents were evaporated. A solution of the residue in diethyl ether (20 ml) was washed with H_2O (15 ml) and aq. $NaHCO_3$ (10%, 15 ml), dried ($MgSO_4$), filtered, and concentrated. Purification of the oily residue by column chromatography (0→10% ethyl acetate in petroleum ether) gave mannopyranoside donor **7** (1.09 g, 2.5 mmol).

^{1}H-NMR ($CDCl_3$): δ 1.27 (t, 3H, CH_3 SEt, $J_{H,H}$ 7.4 Hz), 2.61 (AB, 2H, CH_2 SEt), 3.44, 3.49 (2× s, 6H, 2× CH_3 Me), 3.52 (dd, 1H, H-2, $J_{2,1}$ 1.5 Hz, $J_{2,3}$ 3.1 Hz), 3.61-3.80 (m, 3H, H-6, H-3), 4.01 (ddd, 1H, H-5, $J_{5,4}$ 9.2 Hz, $J_{5,6}$ 4.6 Hz, $J_{5,6}$ 2.0 Hz), 4.48-4.72 (m, 4H, 2× CH_2 Bn), 5.40 (d, 1H, H-1, $J_{1,2}$ 1.5 Hz), 7.31-7.40 (m, 10H, CH Bn); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 14.9 (CH_3 SEt), 25.1 (CH_2 SEt), 58.2, 60.6 (2× CH_3 Me), 69.2 (C-6), 72.1, 73.1 (2× CH_2 Bn), 71.9, 76.5, 79.4, 80.1 (C-2, C-3, C-4, C-5), 81.0 (C-1), 127.3, 127.5, 127.7, 128.1, 128.2 (CH Bn), 138.3, 138.4 (qC Bn).

Anal. calcd. for $C_{24}H_{32}O_5S$ (432.58): C 66.64, H 7.46; found C 66.53, H 7.39%.

Ethyl 2,3-*O*-isopropylidene-1-thio-α-D-mannopyranoside (9) - Compound **8** (3.87 g, 11.2 mmol) was dried by repeated evaporation with dioxane and dissolved in the same solvent (37 ml). A solution of tetrabutylammonium fluoride (TBAF) in dioxane (1 M, 20 ml) was added and the mixture was stirred for 1.5 h. After concentration of the reaction mixture, the crude product was purified by column chromatography. The column was eluted with 40→60% ethyl acetate in petroleum ether. Concentration of the appropriate fractions yielded compound **9** (2.33 g, 8.8 mmol).

^{13}C{^{1}H}-NMR ($CDCl_3$): δ 14.4 (CH_3 SEt), 24.1 (CH_2 SEt), 26.2, 28.0 (2× CH_3 Isopr), 61.7 (C-6), 69.4, 69.7, 76.4, 78.3 (C-2, C-3, C-4, C-5), 79.5 (C-1), 109.5 (qC Isopr).

Ethyl 6-*O*-benzyl-2,3-*O*-isopropylidene-1-thio-α-D-mannopyranoside (10) - To a solution of compound **9** (845 mg, 3.2 mmol) in methanol (20 ml) was added dibutyltin oxide (876 mg, 3.5 mmol). The mixture was heated under reflux for 1 h, and concentrated. The residue was dried by repeated evaporation with toluene and redissolved in DMF (20 ml). Benzyl bromide (0.57 ml, 4.8 mmol) and cesium fluoride (634 mg, 4.2 mmol) were added. After stirring for 18 h, DMF was removed and the residue was taken up in diethyl ether (25 ml). The solution was washed twice with aq. KF (1 M, 15 ml), once with water (15 ml), dried ($MgSO_4$), filtered, and the solvent was evaporated. The crude product was purified by silica gel column chromatography. Elution

of the column with 0→60% ethyl acetate in petroleum ether gave **10** (749 mg, 2.4 mmol) and starting compound **9** (85 mg, 0.3 mmol).

9: $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 14.3 (CH_3 SEt), 23.9 (CH_2 SEt), 26.2, 28.0 (2× CH_3 Isopr), 69.6 (C-6), 73.3 (CH_2 Bn), 69.4, 70.1, 76.3, 78.3 (C-2, C-3, C-4, C-5), 79.2 (C-1), 109.4 (qC Isopr), 126.8, 127.4, 128.2 (CH Bn), 138.1 (qC Bn).

Ethyl 6-*O*-benzyl-4-*O*-methyl-1-thio-α-D-mannopyranoside (12) - Compound **10** (749 mg, 2.4 mmol) was dissolved in DMF (4 ml) and sodium hydride (60%, 145 mg, 3.6 mmol) and methyl iodide (0.19 ml, 3.1 mmol) were added at 0°C. After stirring for 1 h at room temperature, the reaction was quenched with methanol (2 ml), and the solvents were removed. The residue was taken up in diethyl ether (15 ml). The solution was washed with water (10 ml) and aq. $NaHCO_3$ (10%, 10 ml), dried ($MgSO_4$), filtered, and concentrated. The thus obtained fully protected mannopyranoside **11** was dissolved in acetic acid-water (9/1, v/v, 18 ml) and the mixture was heated at 50°C for 17 h. The solution was concentrated and the residue was evaporated with toluene. The residue was purified by a silica gel column chromatography. Elution with ethyl acetate in petroleum ether (0→60%) yielded compound **12** (701 mg, 2.1 mmol).

$^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 14.7 (CH_3 SEt), 24.6 (CH_2 SEt), 60.2 (CH_3 Me), 69.1 (C-6), 73.1 (CH_2 Bn), 71.0, 72.0, 72.3, 77.4 (C-2, C-3, C-4, C-5), 84.1 (C-1), 127.3, 127.5, 128.1 (CH Bn), 138.0 (qC Bn).

Anal. calcd. for $C_{16}H_{24}O_5S$ (328.43): C 58.51, H 7.37; found C 58.59, H 7.32%.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-methyl-1-thio-α-D-mannopyranoside (13) - To a cooled (0°C) solution of compound **12** (313 mg, 1.0 mmol) in DMF (2 ml) were added sodium hydride (60%, 120 mg, 3.0 mmol) and benzyl bromide (0.31 ml, 2.6 mmol). After stirring for 1.5 h, the reaction was quenched with methanol (1 ml) and the solvents were evaporated. The residue was redissolved in diethyl ether (15 ml), and the solution was washed with water (10 ml) and aq. $NaHCO_3$ (10%, 10 ml), dried ($MgSO_4$), and filtered. The filtrate was concentrated and the residual oil was purified by column chromatography. The column was eluted with ethyl acetate in petroleum ether (0→5%) to give pure **13** (471 mg, 0.9 mmol).

$[\alpha]_D$ +103.0° (c 1); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 15.0 (CH_3 SEt), 25.2 (CH_2 SEt), 60.8 (CH_3 Me), 69.3 (C-6), 71.9, 72.0, 73.3 (3× CH_2 Bn), 72.2, 76.5, 76.7, 80.3 (C-2, C-3, C-4, C-5), 81.8 (C-1), 127.3, 127.5, 127.8, 128.3 (CH Bn), 138.2, 138.4, 138.5 (qC Bn).

Anal. calcd. for $C_{30}H_{36}O_5S$ (508.68): C 70.82, H 7.13; found C 70.90, H 7.06%.

Methyl 3,4-*O*-isopropylidene-α-L-fucopyranoside [15(L)] - L-Fucopyranose (5.10 g, 31.1 mmol) was treated with HCl in methanol (0.5 M, 100 ml), according to Schuler *et al.*[14] to give, after neutralisation of the reaction mixture and evaporation of the solvent, methyl pyranoside **14**(L).

Compound **14**(L) was dissolved in a mixture of acetone (30 ml) and dimethoxypropane (16 ml). *p*-Toluenesulfonic acid (571 mg, 3 mmol) was added and the reaction mixture was stirred for 2 h. The solution was neutralised with Et_3N and the solvents were evaporated. The residue was taken up in ethyl acetate (150 ml) and the solution was washed with water (100 ml) and aq. $NaHCO_3$ (10%, 100 ml), dried ($MgSO_4$), and filtered. Ethyl acetate was evaporated and the oily residue was purified by column chromatography. The column was eluted with 0→40% ethyl acetate in petroleum ether to give the α-fucopyranoside **15**(L)-α (2.82 g, 12.9 mmol) and the β-linked anomer **15**(L)-β (1.71 g, 7.8 mmol).

15(L)-α: ^1H-NMR ($CDCl_3$): δ 1.33 (d, 3H, H-6, $J_{6,5}$ 6.7 Hz), 1.36, 1.52 (2× s, 6H, 2× CH_3 Isopr), 2.28 (d, 1H, OH, $J_{HO,2}$ 6.7 Hz), 3.44 (s, 3H, CH_3 1-*O*-Me), 3.79 (dt, 1H, H-2, $J_{2,1}$ 3.9 Hz, $J_{2,3}\approx J_{2,HO}$ 6.7 Hz), 4.01-4.13 (m, 2H, H-3, H-4), 4.18 (q, 1H, H-5, $J_{5,6}$ 6.2 Hz), 4.72 (d, 1H, H-1, $J_{1,2}$ 3.9 Hz); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 16.2 (C-6), 25.9, 27.8 (2× CH_3 Isopr), 55.3 (CH_3 1-*O*-Me), 63.5, 69.4, 75.6, 76.2 (C-2, C-3, C-4, C-5), 98.7 (C-1), 109.0 (qC Isopr).

15(L)-β: ^1H-NMR ($CDCl_3$): δ 1.36 (s, 3H, CH_3 Isopr), 1.43 (d, 3H, H-6, $J_{6,5}$ 6.7 Hz), 1.53 (s, 3H, CH_3 Isopr), 2.47 (d, 1H, OH, $J_{HO,2}$ 2.3 Hz), 3.48 (dd, 1H, H-3, $J_{3,2}$ 8.4 Hz, $J_{3,4}$ 5.5 Hz), 3.54 (s, 3H, CH_3 1-*O*-Me), 3.87 (dq, 1H, H-5, $J_{5,4}$ 2.1 Hz, $J_{5,6}$ 6.6 Hz), 4.01-4.10 (m, 3H, H-1, H-2, H-4); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 16.4 (C-6), 26.2, 28.1 (2× CH_3 Isopr), 56.7 (CH_3 1-*O*-Me), 68.9, 73.4, 76.2, 78.8 (C-2, C-3, C-4, C-5), 103.1 (C-1), 109.6 (qC Isopr).

Methyl 3,4-*O*-isopropylidene-2-*O*-methyl-α-L-fucopyranoside [16(L)] - Compound **15** was (1.84 g, 8.4 mmol) treated with sodium hydride (60%, 504 mg, 12.6 mmol) and methyl iodide (0.68 ml, 10.9 mmol) in DMF (16 ml), as described for the preparation of compound **12**, to give crude **16**(L) (1.83 g, 7.8 mmol).

^{1}H-NMR ($CDCl_3$): δ 1.36 (d, 3H, H-6, $J_{6,5}$ 6.7 Hz), 1.36, 1.55 (2× s, 6H, 2× CH_3 Isopr), 3.36 (dd, 1H, H-3, $J_{3,2}$ 7.8 Hz), 3.41, 3.53 (2× s, 6H, 2× CH_3 Me), 4.02-4.14 (m, 2H, H-4, H-5), 4.23 (br dd, 1H, H-2, $J_{2,1}$ 5.4 Hz, $J_{2,3}$ 7.7 Hz), 4.79 (d, 1H, H-1, $J_{2,1}$ 3.6 Hz); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 15.8 (C-6), 25.8, 27.9 (2× CH_3 Isopr), 54.8 (CH_3 1-*O*-Me), 58.1 (CH_3 Me), 62.4 (C-5), 75.4, 75.6, 78.8 (C-2, C-3, C-4), 97.4 (C-1), 108.4 (qC Isopr).

Methyl 2-*O*-methyl-α-L-fucopyranoside [17(L)] - Crude **16**(L) (1.83 g, 7.8 mmol) was dissolved in acetic acid-water (9/1, v/v, 5 ml) and stirred for 17 h at 50°C. Concentration of the solution followed by evaporation of the residue with toluene gave **17**(L) (1.47 g, 7.8 mmol) which was used without further purification.

^{1}H-NMR ($CDCl_3$); δ 1.30 (d, 3H, H-6, $J_{6,5}$ 6.7 Hz), 3.16 (s, 2H, 2× OH), 3.41, 3.49 (2× s, 6H, 2× CH_3 Me), 3.52 (dd, 1H, H-3, $J_{3,2}$ 9.8 Hz, $J_{3,4}$ 3.6 Hz), 3.80 (d, 1H, H-4, $J_{4,3}$ 3.3 Hz), 3.84-3.97 (m, 2H, H-2, H-5, $J_{2,3}$ 9.8 Hz, $J_{2,1}$ 3.1 Hz, $J_{5,6}$ 6.3 Hz), 4.90 (d, 1H, H-1, $J_{1,2}$ 3.6 Hz); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 15.9 (C-6), 54.7 (CH_3 1-*O*-Me), 57.5 (CH_3 Me), 65.3 (C-5), 69.3, 71.7, 77.6 (C-2, C-3, C-4), 97.0 (C-1).

Methyl 4-*O*-acetyl-2-*O*-methyl-α-L-fucopyranoside [18(L)] - To a solution of compound **17**(L) (1.47 g, 7.8 mmol) in acetonitrile (23 ml) were added trimethyl orthoacetate (2.0 ml, 15.6 mmol) and camphorsulfonic acid (182 mg, 0.78 mmol). After stirring for 45 min, a mixture of acetic acid-water (4/1, v/v, 45 ml) was added and stirring was continued for 15 min. The solution was diluted with dichloromethane (50 ml) and the layers were separated. The organic layer was washed with H_2O (30 ml) and aq. $NaHCO_3$ (10%, 30 ml), dried ($MgSO_4$), and filtered. The organic solvents were removed and the oily residue was purified by column chromatography (ethyl acetate in petroleum ether, 20→60%) to yield **18**(L) (1.48 g, 6.4 mmol).

$[\alpha]_D$ -168.6° (c 1); ^{1}H-NMR ($CDCl_3$): δ 1.16 (d, 3H, H-6, $J_{6,5}$ 6.7 Hz), 2.19 (s, 3H, CH_3 Ac), 2.42 (d, 1H, OH, $J_{HO,3}$ 2.8 Hz), 3.43 (dd, 1H, H-2/H-3, $J_{H,H}$ 3.6 Hz, $J_{H,H}$ 9.8 Hz), 3.43, 3.53 (2× s, 6H, 2× CH_3 Me), 4.04 (q, 1H, H-5, $J_{6,5}$ 6.7 Hz), 4.08-4.11 (m, 1H, H-2/H-3), 4.92 (d, 1H, H-1/H-4 $J_{H,H}$ 3.3 Hz), 5.24 (d, 1H, H-1/H-4, $J_{H,H}$ 3.6 Hz); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 15.6 (C-6), 20.3 (CH_3 Ac), 54.9 (CH_3 1-*O*-Me), 57.8 (CH_3 Me), 64.1 (C-5), 67.3, 73.0, 77.7 (C-2, C-3, C-4), 97.0 (C-1), 170.7 (C=O Ac).

Anal. calcd. for $C_{10}H_{18}O_6$ (234.25): C 51.27, H 7.75; found C 51.38, H 7.83%.

Methyl 3,4-*O*-isopropylidene-2-*O*-methyl-α-D-fucopyranoside [16(D)] - Known[10] methyl 3,4-*O*-isopropylidene-α-D-fucopyranoside [**15**(D), 0.90 g, 4.1 mmol] was treated with sodium hydride and methyl iodide, as described for the preparation of **12**, to yield compound **16**(D) (0.90 g, 3.9 mmol).

^{1}H-NMR ($CDCl_3$): δ 1.36 (d, 3H, H-6, $J_{6,5}$ 6.4 Hz), 1.36, 1.55 (2× s, 6H, 2× CH_3 Isopr), 3.36 (dd, 1H, H-2, $J_{2,1}$ 3.5 Hz, $J_{2,3}$ 7.8 Hz), 3.41, 3.49 (2× s, 6H, 2× CH_3 Me), 4.01-4.05 (m, 1H, H-4), 4.11 (dq, 1H, H-5, $J_{5,4}$ 2.4 Hz, $J_{5,6}$ 6.6 Hz), 4.23 (dd, 1H, H-3, $J_{3,2}$ 7.8 Hz, $J_{3,4}$ 5.2 Hz), 4.79 (d, 1H, H-1, $J_{1,2}$ 3.4 Hz); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 15.9 (C-6), 25.9, 27.9 (2× CH_3 Isopr), 54.9 (CH_3 1-*O*-Me), 58.2 (CH_3 Me), 62.5, 75.5, 75.7, 78.9 (C-2, C-3, C-4, C-5), 97.4 (C-1), 108.2 (qC Isopr).

Methyl 2-*O*-methyl-α-D-fucopyranoside [17(D)] - Crude **16**(D) (0.90 g, 3.9 mmol) was dissolved in acetic acid-water (9/1, v/v, 20 ml) and stirred for 18 h at 50°C. The solvents were evaporated under reduced pressure and the residual acetic acid was removed by repeated evaporation with toluene to afford compound **17**(D) (0.75 g, 3.9 mmol).

^{1}H-NMR ($CDCl_3$): δ 1.31 (d, 3H, H-6, $J_{6,5}$ 6.9 Hz), 2.46 (br s, 1H, OH), 2.69 (br s, 1H, OH), 3.40-3.49 (m, 2H, H-2, H-3), 3.43, 3.49 (2× s, 6H, 2× CH_3 Me), 3.59 (dd, 1H, H-4, $J_{4,3}$ 3.4 Hz, $J_{4,5}$ 1.7 Hz), 3.94 (br q, 1H, H-5, $J_{5,6}$ 6.6 Hz), 4.01-4.05 (m, 1H, H-4), 4.23 (dd, 1H, H-3, $J_{3,2}$ 7.8 Hz, $J_{3,4}$ 5.2 Hz), 4.91 (d, 1H, H-1, $J_{1,2}$ 3.4 Hz); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 15.9 (C-6), 25.9, 27.9 (2× CH_3 Isopr), 54.9 (CH_3 1-*O*-Me), 58.2 (CH_3 Me), 62.5, 75.5, 75.7, 78.9 (C-2, C-3, C-4, C-5), 97.4 (C-1), 108.2 (qC Isopr).

Methyl 4-*O*-acetyl-2-*O*-methyl-α-D-fucopyranoside [18(D)] - Crude **17**(D) (0.75 g, 3.9 mmol) was converted in compound **18**(D) (0.73 g, 3.1 mmol) as described for the enantiomer **18**(L).

$[\alpha]_D$ +137.2°; ^{1}H-NMR ($CDCl_3$): δ 1.16 (d, 3H, H-6, $J_{6,5}$ 6.6 Hz), 2.19 (s, 3H, CH_3 Ac), 2.28 (d, 1H, OH, $J_{HO,2}$ 2.8 Hz), 3.43 (s, 3H, CH_3 Me), 3.49 (dd, 1H, H-2/H-3, $J_{H,H}$ 3.4 Hz, $J_{H,H}$ 3.4 Hz), 3.51 (s, 3H, CH_3 Me), 4.03 (q, 1H, H-5, $J_{5,6}$ 6.6 Hz), 4.07-4.14 (m, 1H, H-2/H-3), 4.92 (d, 1H, H-1/H-4, $J_{H,H}$ 3.6 Hz), 5.23 (d, 1H, H-1/H-4, $J_{H,H}$ 3.6 Hz); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ

15.5 (C-6), 20.1 (CH_3 Ac), 54.6 (CH_3 1-*O*-Me), 57.6 (CH_3 Me), 64.0, 67.2, 73.0, 77.6 (C-2, C-3, C-4, C-5), 96.9 (C-1), 170.4 (C=O Ac).

Anal. calcd. for $C_{10}H_{18}O_6$ (234.25): C 51.27, H 7.75; found C 51.35, H 7.69%.

General glycosylation of the fucosyl acceptors 18(L) or 18(D)

A solution of glycosyl donor (0.3 mmol) and fucosyl acceptor **18** (58 mg, 0.25 mmol) in 1,2-dichloroethane-diethyl ether (1/1, v/v, 2 ml) was stirred in the presence of activated molecular sieves (4 Å) for 30 min. The mixture was cooled (0°C), and a suspension of NIS (68 mg, 0.3 mmol) and TfOH (2.8 µl, 32 µmol) in the same solvent mixture (2 ml) was added. After stirring for 15 min, the reaction was quenched with pyridine, filtered, and diluted with ethyl acetate (15 ml). The solution was washed with aq. $Na_2S_2O_3$ (20%, 10 ml) and aq. $NaHCO_3$ (10%, 10 ml), dried ($MgSO_4$), filtered, and concentrated. The reaction mixture was purified by silica gel column chromatography. The column was eluted with ethyl acetate in petroleum ether (0→40%) to give the individual pure dimers (unless stated otherwise).

Methyl 4-*O*-acetyl-3-*O*-(3,6-di-*O*-benzyl-2,4-di-*O*-methyl-α-D-mannopyranosyl)-2-*O*-methyl-α-L-fucopyranoside (19a-α) and **Methyl 4-*O*-acetyl-3-*O*-(3,6-di-*O*-benzyl-2,4-di-*O*-methyl-β-D-mannopyranosyl)-2-*O*-methyl-α-L-fucopyranoside (19a-β)** - Glycosylation of acceptor **18**(L) with donor **7** gave, after column chromatography, the α–linked dimer **19a-α** (86 mg, 0.11 mmol) and by the β-linked isomer **19a-β** (45 mg, 0.07 mmol).

The glycosylation of acceptor **18**(L) with donor **7** was also performed in diethyl ether at room temperature. After stirring donor and acceptor in the presence of molecular sieves (4 Å) for 30 min, NIS was added followed by a solution of TfOH in diethyl ether. The reaction was further processed as described above. Purification by column chromatography gave an anomeric mixture of **19a** (136 mg, 0.23 mmol) in the ratio α:β=7:1, based on the ^{1}H-NMR spectrum.

19a-α: $[\alpha]_D$ -21.7° (c 1); ^{1}H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.03 (d, 3H, H-6, $J_{6,5}$ 6.5 Hz), 2.04 (s, 3H, CH_3 Ac), 3.40, 3.44 (2× s, 6H, 2× CH_3 Me), 3.42 (dd, 1H, H-2', $J_{2,1}$ 1.6 Hz, $J_{2,3}$ 3.4 Hz), 3.43, 3.49 (2× s, 6H, 2× CH_3 Me), 3.49 (dd, 1H, H-2, $J_{2,1}$ 3.6 Hz, $J_{2,3}$ 10.2 Hz), 3.60 (dd, 1H, H-3', $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.2 Hz), 3.58 (t, 1H, H-4', $J_{4,3}$≈$J_{4,5}$ 9.2 Hz), 3.56-3.85 (m, 3H, H-5', H-6'), 3.88 (dq, 1H, H-5, $J_{5,4}$ 1.2 Hz, $J_{5,6}$ 6.5 Hz), 4.09 (dd, 1H, H-3, $J_{3,2}$ 10.2 Hz, $J_{3,4}$ 3.5 Hz), 4.61, 4.72 (2× AB, 4H, 2× CH_2 Bn), 4.85 (d, 1H, H-1, $J_{1,2}$ 3.6 Hz), 5.14 (d, 1H, H-1', $J_{1,2}$ 1.8 Hz), 5.17 (dd, 1H, H-4, $J_{4,3}$ 3.5 Hz, $J_{4,5}$ 1.2 Hz), 7.15-7.43 (m, 10H, CH Bn); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 15.7 (C-6), 20.4 (CH_3 Ac), 55.1, 58.4, 60.2 (3× CH_3 Me), 64.5 (C-5), 69.0 (C-6'), 71.9, 72.8 (2× CH_2 Bn), 71.9, 73.0, 76.3, 78.2, 78.5 (CH sugar rings), 97.3, 98.5 (C-1, C-1', $^1J_{C,H}$ 171.4, 170.0 Hz, respectively), 127.0, 127.3, 127.4, 127.9, 128.0, 128.7 (CH Bn), 138.5 (qC Bn), 170.4 (C=O Ac).

Anal. calcd. for $C_{32}H_{44}O_{11}$ (604.70): C 63.56, H 7.33; found C 63.62, H 7.41%.

19a-β: $[\alpha]_D$ -79.4° (c 1); ^{1}H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.15 (d, 3H, H-6, $J_{6,5}$ 6.6 Hz), 2.16 (s, 3H, CH_3 Ac), 3.28 (ddd, 1H, H-5', $J_{5,4}$ 9.5 Hz, $J_{5,6}$ 2.3 Hz, $J_{5,6}$ 4.8 Hz), 3.39 (s, 3H, CH_3 Me), 3.40 (dd, 1H, H-3', $J_{3,2}$ 3.1 Hz, $J_{3,4}$ 9.0 Hz), 3.47 (dd, 1H, H-4', $J_{4,3}$≈$J_{4,5}$ 9.3 Hz), 3.51 (dd, 1H, H-2, $J_{2,1}$ 3.7 Hz, $J_{2,3}$ 10.2 Hz), 3.51, 3.53 (2× s, 6H, 2× CH_3 Me), 3.53 (d, 1H, H-2', $J_{2,3}$ 3.6 Hz), 3.56 (s, 3H, CH_3 Me), 3.74 (dd, 1H, H-6', $J_{6,5}$ 4.8 Hz, $J_{6,6}$ 11.3 Hz), 3.79 (dd, 1H, H-6', $J_{6,5}$ 2.4 Hz, $J_{6,6}$ 11.2 Hz), 3.99 (dq, 1H, H-5, $J_{5,4}$ 1.3 Hz, $J_{5,6}$ 6.6 Hz), 4.24 (dd, 1H, H-3, $J_{3,2}$ 10.0 Hz, $J_{3,4}$ 3.5 Hz), 4.70 (s, 1H, H-1'), 4.84 (d, 1H, H-1, $J_{1,2}$ 3.7 Hz), 5.22 (dd, 1H, H-4, $J_{4,3}$ 3.5 Hz, $J_{4,5}$ 1.3 Hz), 7.22-7.42 (m, 10H, CH Bn); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 15.9 (C-6), 20.7 (CH_3 Ac), 55.2, 59.9, 60.6, 61.3 (4× CH_3 Me), 63.8 (C-5), 69.2 (C-6'), 71.8, 73.5 (2× CH_2 Bn), 70.5, 74.4, 76.2, 76.4, 77.8, 81.9 (CH sugar rings), 98.5 (C-1, $^1J_{C,H}$ 172.9 Hz), 98.7 (C-1', $^1J_{C,H}$ 153.9 Hz), 127.2, 127.4, 127.6, 127.7, 128.1, 128.2, 128.8 (CH Bn), 138.6 (qC Bn), 170.7 (C=O Ac).

Methyl 4-*O*-acetyl-3-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-methyl-α-D-mannopyranosyl)-2-*O*-methyl-α-L-fucopyranoside (19b-α) and Methyl 4-*O*-acetyl-3-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-methyl-β-D-mannopyranosyl)-2-*O*-methyl-α-L-fucopyranoside (19b-β) - Condensation of **18**(L) with **13** gave, after elution of the silica gel column, the α-linked dimer **19b-α** (102 mg, 0.15 mmol) and the β-linked anomer **19b-β** (24 mg, 0.03 mmol).

19b-α: $[\alpha]_D$ -28.0° (c 1); ^{1}H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.01 (d, 3H, H-6, $J_{6,5}$ 6.6 Hz), 2.03 (s, 3H, CH_3 Ac), 3.32, 3.39 (2× s, 6H, 2× CH_3 Me), 3.45 (dd, 1H, H-2, $J_{2,1}$ 3.5 Hz, $J_{2,3}$ 10.2 Hz), 3.51 (s, 3H, CH_3 Me), 3.59 (dd, 1H, H-3', $J_{3,2}$ 3.1 Hz, $J_{3,4}$ 9.3 Hz), 3.68 (t, 1H, H-4', $J_{4,3}$≈$J_{4,5}$ 9.2 Hz), 3.71 (dd, 1H, H-2', $J_{2,1}$ 2.0 Hz, $J_{2,3}$ 2.8 Hz), 3.76 (AB, 2H, H-6', $J_{6,5}$ 2.3 Hz, $J_{6,5}$ 4.7 Hz), 3.85 (dq, 1H, H-5, $J_{5,4}$ 1.4 Hz, $J_{5,6}$ 6.4 Hz), 4.87 (ddd, 1H, H-5', $J_{5,4}$ 9.6 Hz, $J_{5,6}$ 2.1 Hz, $J_{5,6}$ 4.2 Hz), 4.10 (dd, 1H, H-3, $J_{3,2}$ 10.2 Hz, $J_{3,4}$ 3.5 Hz), 4.54-4.77 (m, 6H, 3× CH_2 Bn), 4.83 (d, 1H, H-1, $J_{1,2}$ 3.6 Hz), 5.15 (dd, 1H, H-4, $J_{4,3}$ 3.6

Hz, $J_{4,5}$ 1.2 Hz), 5.16 (d, 1H, H-1', $J_{1,2}$ 1.8 Hz), 7.26-7.42 (m, 15H, CH Bn); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 15.7 (C-6), 20.5 (CH_3 Ac), 55.1, 58.6, 60.3 (3× CH_3 Me), 64.5 (C-5), 69.3 (C-6'), 71.7, 71.9, 72.9 (3× CH_2 Bn), 72.1, 72.8, 73.0, 74.1, 76.5, 78.2, 79.0 (CH sugar rings), 97.4, 99.2 (C-1, C-1', $^1J_{C,H}$ 171.1, 172.9 Hz, respectively), 127.0, 127.3, 127.7, 128.0, 128.1 (CH Bn), 138.1, 138.6, 138.7 (qC Bn), 170.0 (C=O Ac).

Anal. calcd. for $C_{38}H_{48}O_{11}$ (680.80): C 67.04, H 7.11; found C 67.13, H 7.05%.

19b-β: ^1H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.15 (d, 3H, H-6, $J_{6,5}$ 6.6 Hz), 2.05 (s, 3H, CH_3 Ac), 3.31-3.36 (m, 1H, H-5'), 3.40 (s, 3H, CH_3 Me), 3.45 (dd, 1H, H-3', $J_{3,2}$ 2.9 Hz, $J_{2,3}$ 9.4 Hz), 3.53, 3.54 (2× s, 6H, 2× CH_3 Me), 3.67 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.5 Hz), 3.72 (d, 1H, H-2', $J_{2,3}$ 2.8 Hz), 3.80 (d, 1H, H-6', $J_{6,5}$ 4.1 Hz), 3.81 (d, 1H, H-6', $J_{6,5}$ 2.9 Hz), 4.00 (dq, 1H, H-5, $J_{5,4}$ 1.2 Hz, $J_{5,6}$ 6.6 Hz), 4.31 (dd, 1H, H-3, $J_{3,2}$ 10.0 Hz, $J_{3,4}$ 3.5 Hz), 4.53 (s, 1H, H-1'), 4.59 (s, 2H, CH_2 Bn), 4.69, 4.78 (2× AB, 4H, 2× CH_2 Bn), 4.85 (d, 1H, H-1, $J_{1,2}$ 3.7 Hz), 5.24 (dd, 1H, H-4, $J_{4,3}$ 3.6 Hz, $J_{4,5}$ 1.2 Hz), 7.21-7.40 (m, 15H, CH Bn); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 15.9 (C-6), 20.5 (CH_3 Ac), 55.2, 59.9, 60.7 (3× CH_3 Me), 63.8 (C-5), 69.4 (C-6'), 71.7, 73.6, 73.9 (3× CH_2 Bn), 70.4, 74.1, 75.1, 76.4, 76.5, 82.4 (CH sugar rings), 98.3 (C-1', $^1J_{C,H}$ 153.9 Hz), 98.8 (C-1, $^1J_{C,H}$ 171.4 Hz), 127.3, 127.4, 127.6 127.7, 128.0, 128.1, 128.3, 128.4 (CH Bn), 138.7, 139.0, 139.3 (qC Bn), 171.1 (C=O Ac).

Methyl 4-*O*-acetyl-3-*O*-(3,6-di-*O*-benzyl-2,4-di-*O*-methyl-D-mannopyranosyl)-2-*O*-methyl-α-D-fucopyranoside (20a-α) and Methyl 4-*O*-acetyl-3-*O*-(3,6-di-*O*-benzyl-2,4-di-*O*-methyl-α,β-D-mannopyranosyl)-2-*O*-methyl-α-D-fucopyranoside (20a-α,β) - Condensation of **18**(D) with **7** gave, after column chromatography, first the α-linked dimer **20a-α** (65.1 mg, 0.11 mmol). Further elution of the column gave a mixture of two anomers (α:β=2:3, 38 mg, 0.06 mmol).

20a-α: $[\alpha]_D$ +138.4° (c 1); ^1H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.14 (d, 3H, H-6, $J_{6,5}$ 6.5 Hz), 2.10 (s, 3H, CH_3 Ac), 3.22 (dd, 1H, H-2', $J_{2,1}$ 1.8 Hz, $J_{2,3}$ 2.7 Hz), 3.37 (s, 3H, CH_3 Me), 3.39 (dd, 1H, H-2, $J_{2,3}$ 10.2 Hz), 3.40, 3.47, 3.48 (3× s, 9H, 3× CH_3 Me), 3.63-3.77 (m, 4H, H-3', H-4', H-6'), 3.82 (ddd, 1H, H-5', $J_{5,4}$ 7.8 Hz, $J_{5,6}$ 1.7 Hz, $J_{5,6}$ 3.5 Hz), 3.97 (dq, 1H, H-5, $J_{5,4}$ 1.1 Hz, $J_{5,6}$ 6.5 Hz), 4.16 (dd, 1H, H-3, $J_{3,2}$ 10.2 Hz, $J_{3,4}$ 3.4 Hz), 4.59, 4.70 (2× AB, 4H, 2× CH_2 Bn), 4.83 (d, 1H, H-1, $J_{1,2}$ 3.7 Hz), 5.10 (d, 1H, H-1', $J_{1,2}$ 1.7 Hz), 5.21 (dd, 1H, H-4, $J_{4,3}$ 3.4 Hz, $J_{4,5}$ 1.0 Hz), 7.24-7.41 (m, 10H, CH Bn); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 16.0 (C-6), 20.7 (CH_3 Ac), 55.2 (CH_3 1-*O*-Me), 58.7, 59.5, 60.4 (3× CH_3 Me), 68.9 (C-6'), 72.0, 73.0 (2× CH_2 Bn), 63.9, 68.9, 69.6, 70.6, 71.3, 76.0, 76.6, 77.8, 78.8 (CH sugar rings), 92.9 (C-1', $^1J_{C,H}$ 170.0 Hz), 97.9 (C-1, $^1J_{C,H}$ 168.5 Hz), 127.2, 127.4, 127.7, 128.0, 128.1 (CH Bn), 138.6 (qC Bn), 170.5 (C=O Ac).

20b-β: $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 97.6 (C-1, $^1J_{C,H}$ 167.1 Hz), 102.6 (C-1', $^1J_{C,H}$ 152.4 Hz).

Anal. calcd. for $C_{32}H_{44}O_{11}$ (604.70): C 63.56, H 7.33; found C 63.45, H 7.45%.

Methyl 4-*O*-acetyl-3-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-methyl-α-D-mannopyranosyl)-6-deoxy-2-*O*-methyl-α-D-galactopyranoside (20b-α) and **Methyl 4-*O*-acetyl-3-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-methyl-α,β-D-mannopyranosyl)-6-deoxy-2-*O*-methyl-α-D-galactopyranoside (20b-α,β)** - The two anomers were isolated in a total ratio of α:β=6:1 after the glycosylation of **18**(D) with **13**. Elution of the column gave the pure α-linked dimer **20b-α** (87 mg, 0.13 mmol). Further elution yielded a mixture of the anomers in a ratio α:β=1:2 (23 mg, 0.03 mmol).

20b-α: $[\alpha]_D$ +84.8° (c 1); ^1H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.14 (d, 3H, H-6, $J_{6,5}$ 6.5 Hz), 2.09 (s, 3H, CH_3 Ac), 3.36-3.41 (m, 1H, H-2), 3.36, 3.39 (2× s, 6H, 3× CH_3 Me), 3.50-3.53 (m, 1H, H-2'), 3.50 (s, 3H, CH_3 Me), 3.67 (dd, 1H, H-3', $J_{3,2}$ 2.8 Hz, $J_{3,4}$ 8.8 Hz), 3.73-3.78 (m, 4H, H-4', H-5', H-6'), 3.97 (q, 1H, H-5, $J_{5,6}$ 6.6 Hz), 4.18 (dd, 1H, H-3, $J_{3,2}$ 10.1 Hz, $J_{3,4}$ 3.1 Hz), 4.51, 4.62, 4.70 (3× AB, 6H, 3× CH_2 Bn), 4.82 (d, 1H, H-1, $J_{1,2}$ 3.6 Hz), 5.16 (br s, 1H, H-1'), 5.21-5.24 (m, 1H, H-4), 7.21-7.48 (m, 15H, CH Bn); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 16.0 (C-6), 20.6 (CH_3 Ac), 55.2 (CH_3 1-*O*-Me), 59.5, 60.5 (2× CH_3 Me), 69.0 (C-6'), 71.6 (2×), 73.0 (3× CH_2 Bn), 63.9, 69.5, 70.3, 71.4, 74.4, 76.0, 76.6, 78.8 (CH sugar rings), 93.1 (C-1', $^1J_{C,H}$ 170.0 Hz), 97.9 (C-1, $^1J_{C,H}$ 170.0 Hz), 127.1, 127.4, 127.7, 128.0 (CH Bn), 138.5 (qC Bn), 170.3 (C=O Ac).

20b-β: $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 97.6, 103.0 (C-1, C-1').

Anal. calcd. for $C_{38}H_{48}O_{11}$ (680.80): C 67.04, H 7.11; found C 67.10, H 7.01%.

4-[2-(Benzyloxycarbonylamino)ethyl]phenyl 2,4-di-*O*-methyl-3-*O*-{4-*O*-benzyl-2-*O*-methyl-3-*O*-[4-*O*-acetyl-2-*O*-methyl-3-*O*-(3,6-di-*O*-benzyl-2,4-di-*O*-methyl-α-D-mannopyranosyl)-α-L-fucopyranosyl]-α-L-rhamnopyranosyl}-α-L-rhamnopyranoside (21-α) and **4-[2-(Benzyloxycarbonylamino)ethyl]phenyl 2,4-di-*O*-methyl-3-*O*-{4-*O*-benzyl-2-*O*-methyl-3-*O*-[4-*O*-acetyl-2-*O*-methyl-3-*O*-(3,6-di-*O*-benzyl-2,4-di-*O*-methyl-β-D-mannopyranosyl)-α-L-fucopyranosyl]-α-L-rhamnopyranosyl}-α-L-rhamnopyranoside (21-β)** - Mannopyranosyl donor **7** (52 mg, 0.12 mmol) and trimer acceptor **2** (90 mg, 0.10

mmol) were dissolved in a mixture of 1,2-dichloroethane-diethyl ether (1/1, v/v, 1 ml). After stirring for 25 min in the presence of activated molecular sieves (4 Å), the reaction mixture was cooled (0°C), and a suspension of NIS (27 mg, 0.12 mmol) and TfOH (1.3 µl, 15 µmol) in the same solvent mixture (1.5 ml) was added. Stirring was continued for 15 min. The reaction was quenched with pyridine (0.1 ml), filtered, and diluted with ethyl acetate (15 ml). The organic solution was washed with aq. $Na_2S_2O_3$ (20%, 10 ml) and aq. $NaHCO_3$ (10%, 10 ml), dried ($MgSO_4$), and filtered. The solvents were removed and the residue was purified by silica gel column chromatography (0→3% acetone in dichloromethane) to give the α-linked tetramer **21-α** (80 mg, 63 µmol) and the β-linked anomer **21-β** (26 mg, 21 µmol).

The glycosylation of **2** with **7** was also performed in diethyl ether at room temperature using the same procedure as described above, while NIS was added as a solid followed by a solution of TfOH in diethyl ether. Column chromatography gave tetramer **21** (112 mg, 88 µmol), in an anomeric ratio of α:β=10:1, as was evidenced by ^{1}H-NMR spectroscopy.

21-α: $[\alpha]_D$ -49.4° (c 1); ^{1}H-NMR ($CDCl_3$, 400 MHz, HH-COSY): δ 1.06 (d, 3H, H-6", $J_{6,5}$ 6.5 Hz), 1.26 (d, 3H, H-6, $J_{6,5}$ 6.1 Hz), 1.33 (d, 3H, H-6', $J_{6,5}$ 6.2 Hz), 2.04 (s, 3H, CH_3 Ac), 2.76 (t, 2H, CH_2 spacer, $J_{H,H}$ 6.8 Hz), 3.20 (s, 3H, CH_3 Me), 3.21 (t, 1H, H-4, $J_{4,3}\approx J_{4,5}$ 9.6 Hz), 3.41 (s, 6H, 2× CH_3 Me), 3.45 (t, 2H, CH_2 spacer, $J_{H,H}$ 6.5 Hz), 3.46 (dd, 1H, H-2", $J_{2,1}$ 4.3 Hz, $J_{2,3}$ 10.9 Hz), 3.48, 3.50 (2× s, 6H, 2× CH_3 Me), 3.51 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.9 Hz), 3.53 (s, 3H, CH_3 Me), 3.66 (dq, 1H, H-5, $J_{5,4}$ 9.4 Hz, $J_{5,6}$ 6.4 Hz), 3.69 (dd, 1H, H-2', $J_{2,1}$ 1.9 Hz, $J_{2,3}$ 3.2 Hz), 3.72 (dd, 1H, H-2, $H_{2,1}$ 2.0 Hz, $J_{2,3}$ 3.4 Hz), 3.77 (dd, 1H, H-6"', $J_{5,6}$ 4.7 Hz, $J_{6,6}$ 10.8 Hz), 3.41-3.85 (m, 5H, H-2, H-3, H-4, H-5, H-6 all Man*p*), 3.93 (dq, 1H, H-5', $J_{5,4}$ 9.4 Hz, $J_{5,6}$ 6.3 Hz), 4.00 (dd, 1H, H-3', $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.6 Hz), 4.08 (dd, 1H, H-3, $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.6 Hz), 4.24 (dd, 1H, H-3", $J_{2,3}$ 10.3 Hz, $J_{3,4}$ 3.5 Hz), 4.28 (dq, 1H, H-5", $J_{5,4}$ 1.2 Hz, $J_{5,6}$ 6.6 Hz), 4.62, 4.72 (2× AB, 4H, 2× CH_2 Bn), 4.67-4.76 (m, 1H, H-1'"), 4.85 (AB, 2H, CH_2 Bn), 5.10 (s, 2H, CH_2 Z), 5.16 (d, 1H, H-1', $J_{1,2}$ 1.7 Hz), 5.18 (d, 1H, H-1", $J_{1,2}$ 2.8 Hz), 5.23 (dd, 1H, H-4", $J_{4,3}$ 3.4 Hz, $J_{4,5}$ 1.2 Hz), 5.46 (d, 1H, H-1, $J_{1,2}$ 1.9 Hz), 6.97-7.11 (m, 4H, CH spacer), 7.23-7.42 (m, 20H, arom); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 16.2, 17.8, 18.1 (C-6, C-6', C-6"), 20.6 (CH_3 Ac), 35.2, 42.2 (2× CH_2 spacer), 57.6, 58.3, 58.6, 58.8, 60.4, 61.0 (6× CH_3 Me), 66.5 (CH_2 Z), 69.2 (C-6'"), 72.1, 73.1, 75.0 (3× CH_2 Bn), 65.3, 68.6, 68.7, 71.9, 73.2, 73.3, 76.4, 78.3, 78.5, 78.7, 79.2, 79.6, 80.1, 80.5, 81.5, 81.9 (CH sugar rings), 94.8 (C-1, $^1J_{C,H}$ 170.0 Hz), 98.2, 98.7, 99.4 (C-1', C-1", C-1'", $^1J_{C,H}$ 167.1, 170.0, 167.1 Hz, respectively), 116.4 (CH spacer), 127.2, 127.3, 127.4, 127.6, 128.0, 128.2, 128.4, 129.7 (CH arom), 132.4, 138.6, 139.0, 155.0, 156.2 (qC arom, C=O Z), 170.2 (C=O Ac).

Anal. calcd. for $C_{69}H_{89}NO_{21}$ (1268.47): C 65.33, H 7.07, N 1.10; found C 65.24, H 7.16, N 1.03%.

21-β: ^{1}H-NMR ($CDCl_3$, 400 MHz, HH-COSY): δ 1.16 (d, 3H, H-6", $J_{6,5}$ 6.5 Hz), 1.26 (d, 3H, H-6, $J_{6,5}$ 6.2 Hz), 1.29 (d, 3H, H-6', $J_{6,5}$ 6.2 Hz), 2.16 (s, 3H, CH_3 Ac), 2.76 (t, 2H, CH_2 spacer, $J_{H,H}$ 6.4 Hz), 3.22 (t, 1H, H-4, $J_{4,3}\approx J_{4,5}$ 9.6 Hz), 3.33 (t, 1H, H-4'", $J_{4,3}\approx J_{4,5}$ 10.3 Hz), 3.43 (t, 2H, CH_2 spacer, $J_{H,H}$ 6.7 Hz), 3.30-3.60 (m, 5H, H-2, H-3, H-5, H-6 all Man*p*), 3.41 (s, 3H, CH_3 Me), 3.45 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.7 Hz), 3.47, 3.48, 3.49 (3× s, 9H, 3× CH_3 Me), 3.49 (dd, 1H, H-2") 3.53, 3.54 (2× s, 6H, 2× CH_3 Me), 3.66 (dq, 1H, H-5, $J_{5,4}$ 9.5 Hz, $J_{5,6}$ 6.3 Hz), 3.68-3.71 (m, 2H, H-2, H-2'), 3.91 (dq, 1H, H-5', $J_{5,4}$ 9.4 Hz, $J_{5,6}$ 6.2 Hz), 4.03 (dd, 1H, H-3', $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.6 Hz), 4.07 (dd, 1H, H-3, $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.7 Hz), 4.34 (dq, 1H, H-5", $J_{5,4}$ 1.2 Hz, $J_{5,6}$ 6.2 Hz), 4.38 (dd, 1H, H-3", $J_{2,3}$ 10.0 Hz, $J_{3,4}$ 3.5 Hz), 4.70 (s, 2H, CH_2 Z), 5.18 (s, 1H, H-1'"), 5.19 (d, 1H, H-1', $J_{1,2}$ 1.6 Hz), 5.19 (d, 1H, H-1", $J_{1,2}$ 3.8 Hz), 5.29 (dd, 1H, H-4", $J_{4,3}$ 3.6 Hz, $J_{4,5}$ 0.8 Hz), 5.45 (d, 1H, H-1, $J_{1,2}$ 1.9 Hz), 6.97-7.12 (m, 4H, CH spacer), 7.22-7.44 (m, 20H, CH arom); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 16.3, 17.8, 18.1 (C-6, C-6', C-6"), 20.8 (CH_3 Ac), 35.2, 42.2 (2× CH_2 spacer), 57.7, 58.8, 59.8, 60.7, 61.0, 61.2 (6× CH_3 Me), 66.6 (CH_2 Z), 69.5 (C-6'"), 71.9, 73.6, 75.1 (3× CH_2 Bn), 64.5, 68.6, 68.8, 70.6, 74.3, 76.3, 76.4, 77.9, 79.4, 80.1, 80.7, 81.1, 82.0 (CH sugar rings), 95.0 (C-1, $^1J_{C,H}$ 168.5 Hz), 98.2 (C-1'", $^1J_{C,H}$ 155.3 Hz), 98.2, 100.6 (C-1', C-1", $^1J_{C,H}$ 166.9, 168.5 Hz, respectively), 116.5 (CH spacer), 127.3, 127.6, 127.7, 127.9, 128.0, 128.2, 128.3, 128.4, 129.7 (CH arom), 132.4, 138.3, 138.6, 139.0, 155.1, 156.2 (qC arom, C=O Z), 170.8 (C=O Ac).

4-(Aminoethyl)phenyl 2,4-di-*O*-methyl-3-*O*-{2-*O*-methyl-3-*O*-[4-*O*-acetyl-2-*O*-methyl-3-*O*-(2,4-di-*O*-methyl-α-D-mannopyranosyl)-α-L-fucopyranosyl]-α-L-rhamnopyranosyl}-α-L-rhamnopyranoside (3) - To a solution of tetramer **21** (80 mg, 63 µmol) in a mixture of isopropanol-water-acetic acid (10/5/2, v/v/v, 7 ml) was added palladium on carbon (5%). The reaction mixture was stirred for 66 h under a blanket of hydrogen. The reaction mixture was filtered and the filtrate were evaporated to give, after purification of the residual oil by gel-filtration (methanol), the required tetramer **3** (47 mg, 54 µmol).

^{1}H-NMR (D_2O, 400 MHz, HH-COSY): δ 1.13 (d, 3H, H-6", $J_{6,5}$ 6.6 Hz), 1.23 (d, 3H, H-6, $J_{6,5}$ 6.3 Hz), 1.33 (d, 3H, H-6', $J_{6,5}$ 6.3 Hz), 2.19 (s, 3H, CH_3 Ac), 2.86 (t, 2H, CH_2 spacer, $J_{H,H}$ 7.3 Hz), 3.09 (t, 2H, CH_2 spacer, $J_{H,H}$ 7.1 Hz), 3.27 (t, 1H, H-4, $J_{4,3}\approx J_{4,5}$ 9.7 Hz), 3.31 (t, 1H, H-4'", $J_{4,3}\approx J_{4,5}$ 9.7 Hz), 3.45, 3.49, 3.50, 3.52, 3.54 (5× s, 15H, 5× CH_3 Me), 3.56 (dd, 1H, H-2'", $J_{2,1}$ 1.6 Hz, $J_{2,3}$ 3.6 Hz), 3.57 (s, 3H, CH_3 Me), 3.59 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.7 Hz), 3.65 (m, 1H, H-5'"), 3.71 (dd, 1H,

H-2", $J_{2,1}$ 3.7 Hz, $J_{2,3}$ 10.6 Hz), 3.71 (m, 1H, H-6'''), 3.74 (dd, 1H, H-2', $J_{2,1}$ 1.6 Hz, $J_{2,3}$ 3.7 Hz), 3.74 (dd, 1H, H-3''', $J_{3,2}$ 3.6 Hz, $J_{3,4}$ 10.0 Hz), 3.78 (dq, 1H, H-5, $J_{5,4}$ 9.8 Hz, $J_{5,6}$ 6.5 Hz), 3.83 (dd, 1H, H-6''', $J_{6,5}$ 2.1 Hz, $J_{6,6}$ 12.0 Hz), 3.86 (dq, 1H, H-5', $J_{5,4}$ 9.5 Hz, $J_{5,6}$ 6.2 Hz), 3.91 (dd, 1H, H-2, $J_{2,1}$ 1.9 Hz, $J_{2,3}$ 3.4 Hz), 3.98 (dd, 1H, H-3', $J_{3,2}$ 3.3 Hz, $J_{3,4}$ 9.8 Hz), 4.16 (dd, 1H, H-3, $J_{3,2}$ 3.4 Hz, $J_{3,4}$ 9.7 Hz), 4.23 (dd, 1H, H-3", $J_{3,2}$ 3.4 Hz, $J_{3,4}$ 10.4 Hz), 4.29 (dq, 1H, H-5", $J_{5,4}$ 1.1 Hz, $J_{5,6}$ 6.6 Hz), 5.18 (d, 1H, H-1''', $J_{1,2}$ 1.6 Hz), 5.25 (d, 1H, H-1', $J_{1,2}$ 1.6 Hz), 5.31 (dd, 1H, H-4", $J_{4,3}$ 3.5 Hz, $J_{4,5}$ 0.9 Hz), 5.44 (d, 1H, H-1", $J_{1,2}$ 3.8 Hz), 5.70 (d, 1H, H-1, $J_{1,2}$ 1.8 Hz), 7.09-7.27 (m, 4H, CH spacer); $^{13}C\{^1H\}$-NMR (D_2O, 100 MHz, CH-COSY): δ 15.9, 17.4, 17.6 (C-6, C-6', C-6"), 20.8 (CH_3 Ac), 34.6, 41.9 (2× CH_2 spacer), 58.4, 58.8, 59.1, 59.4, 61.4 (5× CH_3 Me), 60.6 (C-6'''), 66.5 (C-5"), 69.3 (C-5), 70.3 (C-5'), 70.4 (C-5'''), 72.1, 72.9, 73.5, 74.1 (4× CH), 77.7 (C-4'''), 78.7 (CH), 78.8 (C-3'), 79.3 (C-3), 80.1 (C-2), 81.0 (2× CH), 82.5 (C-4), 95.1 (C-1), 98.9, 99.0 (C-1', C-1'''), 99.2 (C-1"), 118.0, 131.0 (CH spacer), 133.3, 154.9 (qC spacer), 174.2 (C=O Ac); MS: $[M+H]^+$ for $C_{32}H_{52}NO_{14}$: m/z 864.5.

4-[2-(Benzyloxycarbonylamino)ethyl]phenyl 2,4-di-*O*-methyl-3-*O*-[4-*O*-benzyl-2-*O*-methyl-3-*O*-[4-*O*-acetyl-2-*O*-methyl-3-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-methyl-α-D-mannopyranosyl)-α-L-fucopyranosyl]-α-L-rhamnopyranosyl]-α-L-rhamnopyranoside (22-α) and **4-[2-(benzyloxycarbonylamino)ethyl]phenyl 2,4-di-*O*-methyl-3-*O*-[4-*O*-benzyl-2-*O*-methyl-3-*O*-[4-*O*-acetyl-2-*O*-methyl-3-*O*-(2,3,6-tri-*O*-benzyl-4-*O*-methyl-β-D-mannopyranosyl)-α-L-fucopyranosyl]-α-L-rhamnopyranosyl}-α-L-rhamnopyranoside (22-β)** - A suspension of NIS (27 mg, 0.12 mmol) and TfOH (1.3 µl, 15 µmol) in 1,2-dichloroethane-diethyl ether (1/1, v/v, 1 ml) was added at 0°C to a stirred mixture of trimer acceptor **2** (90 mg, 0.10 mmol), mannopyranosyl donor **13** (61 mg, 0.12 mmol), and activated molecular sieves (4 Å) in the same solvent mixture (1 ml). After stirring at 0°C for 15 min, the reaction was quenched with pyridine (0.1 ml), and filtered. The filtrate was diluted with ethyl acetate (10 ml), washed with aq. $Na_2S_2O_3$ (20%, 7 ml) and aq. $NaHCO_3$ (10%, 5 ml), dried ($MgSO_4$), filtered, and concentrated. The oily residue was purified by column chromatography (0→60% ethyl acetate in petroleum ether). Concentration of the appropriate fractions gave the α-linked tetramer **22-α** (77 mg, 57 µmol). Further elution of the column gave the β-linked anomer of **22-β** (18 mg, 13 µmol).

Donor **13** and acceptor **2** were also coupled in diethyl ether (4 ml) at room temperature under the agency of NIS and TfOH. NIS was added to a mixture of donor **13**, acceptor **2** and activated molecular sieves (4 Å), followed by a solution of TfOH in diethyl ether. An anomeric mixture of tetramer **22** (123 mg, 91 µmol) was isolated after column chromatography, in a ratio of α:β =12:1 as was established by ^1H-NMR spectroscopy.

22-α: $[\alpha]_D$ -66.2° (c 1); ^1H-NMR ($CDCl_3$, 400 MHz, HH-COSY): δ 1.05 (d, 3H, H-6", $J_{6,5}$ 6.6 Hz), 1.26 (d, 3H, H-6, $J_{6,5}$ 6.1 Hz), 1.33 (d, 3H, H-6', $J_{6,5}$ 6.2 Hz), 2.03 (s, 3H, CH_3 Ac), 2.76 (t, 2H, CH_2 spacer, $J_{H,H}$ 6.9 Hz), 3.11 (s, 3H, CH_3 Me), 3.21 (t, 1H, H-4, $J_{4,3}\approx J_{4,5}$ 9.6 Hz), 3.40 (s, 3H, CH_3 Me), 3.41 (dd, 1H, H-2''', $J_{2,1}$ 1.9 Hz, $J_{2,3}$ 3.9 Hz), 3.42 (m, 2H, CH_2 spacer), 3.43 (dd, 1H, H-2", $J_{2,1}$ 10.3 Hz, $J_{2,3}$ 3.5 Hz), 3.51 (s, 6H, 2× CH_3 Me), 3.52 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.6 Hz), 3.53 (s, 3H, CH_3 Me), 3.60 (dd, 1H, H-3''', $J_{3,2}$ 3.1 Hz, $J_{3,4}$ 9.4 Hz), 3.67 (dq, 1H, H-5, $J_{5,4}$ 9.4 Hz, $J_{5,6}$ 6.2 Hz), 3.68 (dd, 1H, H-2', $J_{2,1}$ 1.6 Hz, $J_{2,3}$ 3.3 Hz), 3.70 (t, 1H, H-4''', $J_{4,3}\approx J_{4,5}$ 9.6 Hz), 3.72 (dd, 1H, H-2, $J_{2,1}$ 1.8 Hz, $J_{2,3}$ 3.5 Hz), 3.76 (dd, 1H, H-6''', $J_{6,5}$ 2.0 Hz, $J_{6,6}$ 10.9 Hz), 3.82 (dd, 1H, H-6''', $J_{6,5}$ 4.8 Hz, $J_{6,6}$ 10.9 Hz), 3.89 (ddd, 1H, H-5''', $J_{5,4}$ 9.8 Hz, $J_{5,6}$ 2.0 Hz, $J_{5,6}$ 4.7 Hz), 3.94 (dq, 1H, H-5', $J_{5,4}$ 9.4 Hz, $J_{5,6}$ 6.2 Hz), 4.00 (dd, 1H, H-3', $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.5 Hz), 4.08 (dd, 1H, H-3, $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.6 Hz), 4.25 (dd, 1H, H-3", $J_{3,2}$ 10.3 Hz, $J_{3,4}$ 3.5 Hz), 4.27 (dq, 1H, H-5", $J_{5,4}$ 1.1 Hz, $J_{5,6}$ 6.2 Hz), 4.54-4.75 (m, 7H, 3× CH_2 Bn, CH from CH_2 Bn), 5.09 (s, 2H, CH_2 Z), 5.17 (m, 1H, CH from CH_2 Bn), 5.17 (d, 1H, H-1", $J_{1,2}$ 3.6 Hz), 5.18 (d, 1H, H-1', $J_{1,2}$ 1.9 Hz), 5.18 (d, 1H, H-1''', $J_{1,2}$ 1.9 Hz), 5.23 (dd, 1H, H-4", $J_{4,3}$ 3.5 Hz, $J_{4,5}$ 1.1 Hz), 5.47 (d, 1H, H-1, $J_{1,2}$ 1.9 Hz), 6.95-7.09 (m, 4H, CH spacer), 7.21-7.43 (m, 25H, CH arom); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 16.2, 17.8, 18.1 (C-6, C-6', C-6"), 20.6 (CH_3 Ac), 35.2, 42.2 (2× CH_2 spacer), 57.5, 58.2, 58.8, 60.4, 61.0 (5× CH_3 Me), 66.5 (CH_2 Z), 69.5 (C-6'''), 71.8, 71.9, 73.1, 75.0 (4× CH_2 Bn), 65.3, 68.6, 68.7, 72.1, 72.9, 73.2, 74.4, 76.6, 78.5, 79.1, 79.2, 79.6, 80.1, 80.5, 81.6, 82.0 (CH sugar rings), 94.9 (C-1, $^1J_{C,H}$ 170.0 Hz), 98.3, 99.4 (C-1', C-1", C-1''', $^1J_{C,H}$ 171.5, 167.1 (2×) Hz, respectively), 116.4 (CH spacer), 127.2, 127.3, 127.4, 127.7, 128.1, 128.4, 129.7 (CH arom), 132.4, 138.2, 138.7, 139.2, 155.1, 156.2 (qC arom, C=O Z), 170.1 (C=O Ac).

Anal. calcd. for $C_{75}H_{93}NO_{21}$ (1344.57): C 67.00, H 6.97, N 1.04; found C 66.88, H 6.90, N 1.15%.

22-β: ^1H-NMR ($CDCl_3$, 400 MHz, HH-COSY): δ 1.16 (d, 3H, H-6", $J_{6,5}$ 6.5 Hz), 1.26 (d, 3H, H-6, $J_{6,5}$ 6.1 Hz), 1.29 (d, 3H, H-6', $J_{6,5}$ 6.2 Hz), 2.04 (s, 3H, CH_3 Ac), 2.76 (t, 2H, CH_2 spacer, $J_{H,H}$ 6.8 Hz), 3.22 (t, 1H, H-4, $J_{4,3}\approx J_{4,5}$ 9.6 Hz), 3.35 (ddd, 1H, H-5''', $J_{5,4}$ 9.7 Hz, $J_{5,6}$ 2.3 Hz, $J_{5,6}$ 4.7 Hz), 3.39 (s, 3H, CH_3 Me), 3.44 (m, 2H, CH_2 spacer), 3.47 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.7 Hz), 3.47 (dd, H-3''', $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 10.2 Hz), 3.48, 3.49, 3.50 (3× s, 9H, 3× CH_3 Me), 3.52 (dd, 1H, H-2", $J_{2,1}$ 3.7 Hz, $J_{2,3}$ 10.3 Hz), 3.54 (s, 3H, CH_3 Me), 3.60 (t, 1H, H-4''', $J_{4,3}\approx J_{4,5}$ 9.5 Hz), 3.66 (dq, 1H, H-5, $J_{5,4}$ 9.6 Hz, $J_{5,6}$ 6.2 Hz), 3.69-3.70 (m, 1H,

H-2), 3.71-3.72 (m, 1H, H-2'), 3.73 (d, 1H, H-2''', $J_{2,1}$ 3.6 Hz), 3.91 (dq, 1H, H-5', $J_{5,4}$ 9.4 Hz, $J_{5,6}$ 6.2 Hz), 4.03 (dd, 1H, H-3', $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.5 Hz), 4.08 (dd, 1H, H-3, $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.6 Hz), 4.37 (dq, 1H, H-5'', $J_{5,4}$ 1.5 Hz, $J_{5,6}$ 6.4 Hz), 4.44 (dd, 1H, H-3'', $J_{3,2}$ 10.1 Hz, $J_{3,4}$ 3.5 Hz), 5.09 (s, 2H, CH_2 Z), 5.19-5.21 (m, 3H, H-1', H-1'', H-1'''), 5.32 (dd, 1H, H-4'', $J_{4,3}$ 3.4 Hz, $J_{4,5}$ 2.1 Hz), 5.45 (d, 1H, H-1, $J_{1,2}$ 1.9 Hz), 6.97-7.10 (m, 4H, CH spacer), 7.22-7.42 (m, 25H, CH arom); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 16.4, 17.8, 18.1 (C-6, C-6', C-6''), 20.8 (CH_3 Ac), 35.2, 42.3 (2× CH_2 spacer), 57.7, 58.9, 59.8, 60.8, 61.1 (5× CH_3 Me), 66.6 (CH_2 Z), 69.6 (C-6'''), 71.8, 73.6, 75.0, 75.2 (4× CH_2 Bn), 64.6, 68.6, 68.8, 70.4, 75.0, 76.6, 76.7, 79.4, 79.6, 80.1, 80.7, 81.3, 82.0, 85.5 (CH sugar rings), 95.0 (C-1, $^1J_{C,H}$ 168.5 Hz), 98.0 (C-1''', $^1J_{C,H}$ 161.2 Hz), 98.3, 100.6 (C-1', C-1'', $^1J_{C,H}$ 167.0, 168.5 Hz, respectively), 116.5 (CH spacer), 127.2, 127.3, 127.4, 127.5, 127.6, 127.9, 128.0, 128.1, 128.2, 128.3, 128.5, 129.8 (CH arom), 132.4, 138.5, 138.6, 139.1, 155.2, 156.2 (qC arom, C=O Z), 170.9 (C=O Ac).

4-(Aminoethyl)phenyl 2,4-di-*O*-methyl-3-*O*-{2-*O*-methyl-3-*O*-[4-*O*-acetyl-2-*O*-methyl-3-*O*-(4-*O*-methyl-α-D-mannopyranosyl)-α-L-fucopyranosyl]-α-L-rhamnopyranosyl}-α-L-rhamnopyranoside (4) - Compound **22** (77 mg, 57 μmol) was dissolved in a mixture of isopropanol-water-acetic acid (5/2/1, v/v/v, 6 ml) and hydrogenated in the presence of palladium on carbon for 66 h. The reaction mixture was filtered and the solvents were concentrated. Purification of the residue using gel-filtration (methanol) gave tetramer **4** (41 mg, 48 μmol).

^{1}H-NMR (D_2O, 400 MHz, HH-COSY): δ 1.14 (d, 3H, H-6'', $J_{6,5}$ 6.5 Hz), 1.26 (d, 3H, H-6, $J_{6,5}$ 6.2 Hz), 1.30 (d, 3H, H-6', $J_{6,5}$ 6.3 Hz), 2.21 (s, 3H, CH_3 Ac), 2.96 (t, 2H, CH_2 spacer, $J_{H,H}$ 7.3 Hz), 3.25 (t, 2H, CH_2 spacer, $J_{H,H}$ 7.2 Hz), 3.29 (t, 1H, H-4, $J_{4,3}\approx J_{4,5}$ 9.4 Hz), 3.41 (t, 1H, H-4''', $J_{4,3}\approx J_{4,5}$ 9.7 Hz), 3.51 (s, 6H, 2× CH_3 Me), 3.51, 3.56, 3.59 (3× s, 9H, 3× CH_3 Me), 3.60 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.7 Hz), 3.71 (dd, 1H, H-2'', $J_{2,1}$ 3.6 Hz, $J_{2,3}$ 10.6 Hz), 3.72 (dd, 1H, H-2', $J_{2,1}$ 1.7 Hz, $J_{2,3}$ 3.5 Hz), 3.78 (dq, 1H, H-5, $J_{5,4}$ 9.5 Hz, $J_{5,6}$ 6.3 Hz), 3.70-3.80 (m, 3H, H-3, H-5, H-6 all Man*p*), 3.85 (dd, 1H, H-6''', $J_{6,5}$ 2.9 Hz, $J_{6,6}$ 12.0 Hz), 3.87 (dq, 1H, H-5', $J_{5,4}$ 9.5 Hz, $J_{5,6}$ 6.3 Hz), 3.92 (dd, 1H, H-2, $J_{2,1}$ 2.0 Hz, $J_{2,3}$ 3.0 Hz), 3.95 (dd, 1H, H-2''', $J_{2,1}$ 1.5 Hz, $J_{2,3}$ 3.3 Hz), 3.98 (dd, 1H, H-3', $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.9 Hz), 4.18 (dd, 1H, H-3, $J_{3,2}$ 3.4 Hz, $J_{3,4}$ 9.7 Hz), 4.22 (dd, 1H, H-3'', $J_{3,2}$ 10.4 Hz, $J_{3,4}$ 3.5 Hz), 4.29 (q, 1H, H-5'', $J_{5,6}$ 6.6 Hz), 5.06 (d, 1H, H-1''', $J_{1,2}$ 1.2 Hz), 5.26 (d, 1H, H-1', $J_{1,2}$ 0.8 Hz), 5.31 (d, 1H, H-4'', $J_{4,3}$ 3.5 Hz), 5.43 (d, 1H, H-1'', $J_{1,2}$ 3.9 Hz), 5.72 (d, 1H, H-1, $J_{1,2}$ 1.5 Hz), 7.08-7.27 (m, 4H, CH spacer); $^{13}C\{^1H\}$-NMR (D_2O): δ 15.8, 17.4, 17.5 (C-6, C-6', C-6''), 20.8 (CH_3 Ac), 32.7, 41.3 (2× CH_2 spacer), 58.4, 58.8, 59.1, 60.4, 61.6 (5× CH_3 Me), 61.4 (C-6'''), 66.5, 69.3, 70.3, 70.6, 71.0, 72.2, 72.9, 73.2, 74.1, 77.3, 78.6, 78.8, 79.3, 80.1, 81.0, 82.4 (CH sugar rings), 95.0 (C-1), 99.0, 99.2, 102.2 (C-1', C-1'', C-1'''), 118.3, 131.0 (CH spacer), 132.0, 155.1 (qC spacer), 174.2 (C=O Ac). MS: $[M+H]^+$ for $C_{39}H_{63}NO_{19}$: m/z 650.2.

Ethyl 3,6-di-*O*-benzyl-4-*O*-methyl-1-thio-D-mannopyranoside (23) - Dibutyltin oxide (2.05 g, 8.2 mmol) was added to a solution of compound **12** (2.44 g, 7.5 mmol) in methanol (45 ml) and the suspension was heated under reflux for 2 h. The clear solution was concentrated and the residue was dried by evaporation with toluene. The stannylidene derivative was dissolved in DMF (80 ml), cesium fluoride (1.50 g, 9.9 mmol) and benzyl bromide (1.3 ml, 10.9 mmol) were added. After stirring for 18 h, DMF was evaporated, and the oily residue was taken up in diethyl ether (50 ml). This solution was washed twice with aq. KF (1 M, 20 ml), once with water (15 ml), dried ($MgSO_4$), and filtered. The filtrate was concentrated and the crude product was purified by column chromatography (0→30% ethyl acetate in petroleum ether). Concentration of the appropriate fractions gave compound **23** (2.51 g, 6.0 mmol).

^{1}H-NMR ($CDCl_3$): δ 1.27 (t, 3H, CH_3 SEt, $J_{H,H}$ 7.5 Hz), 2.60 (ABX, 2H, CH_2 SEt), 3.48 (s, 3H, CH_3 OMe), 3.67 (dd, 1H, H-6, $J_{6,5}$ 2.7 Hz, $J_{6,6}$ 11.2 Hz), 3.54-3.81 (m, 1H, H-3), 3.77 (dd, 1H, H-6, $J_{6,5}$ 4.2 Hz, $J_{6,6}$ 10.8 Hz), 3.89 (t, 1H, H-4, $J_{4,3}\approx J_{4,5}$ 9.4 Hz), 4.02-4.10 (m, 1H, H-5), 4.05 (dd, 1H, H-2, $J_{2,1}$ 1.7 Hz, $J_{2,3}$ 3.2 Hz), 4.60 (AB, 2H, CH_2 Bn), 4.67 (s, 2H, CH_2 Bn), 5.36 (s, 1H, H-1), 7.28-7.38 (m, 10H, CH Bn); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 14.4 (CH_3 SEt), 24.4 (CH_2 SEt), 60.2 (CH_3 Me), 68.6 (C-6), 71.2, 72.8 (2× CH_2 Bn), 69.3, 71.0, 75.8, 79.8 (C-2, C-3, C-4, C-5), 83.3 (C-1), 127.0, 127.3, 127.8, 127.9 (CH Bn), 137.5, 137.8 (qC Bn).

Anal. calcd. for $C_{23}H_{30}O_5S$ (418.53): C 66.01, H 7.22; found C 65.87, H 7.14%.

Ethyl 3,6-di-*O*-benzyl-2-*O*-chloroacetyl-4-*O*-methyl-1-thio-α-D-mannopyranoside (24) - To a solution of compound **23** (827 mg, 2.0 mmol) in DMF (20 ml) were added chloroacetic anhydride (673 mg, 4.0 mmol) and aq. $NaHCO_3$ (360 mg, 4.0 mmol). After stirring for 24 h, the reaction mixture was poured into ice water (20 ml) and extracted with dichloromethane (3× 15 ml). The organic layers were collected, washed with water (15 ml) and aq. $NaHCO_3$ (10%, 15 ml), dried over ($MgSO_4$), filtered, and

concentrated to dryness. The residue was purified by silica gel column chromatography. The column was eluted with 0→20% ethyl acetate in petroleum ether to afford pure **24** (813 mg, 1.7 mmol).

$[\alpha]_D$ 75.4° (c 1); ^{1}H-NMR ($CDCl_3$): δ 1.27 (t, 1H, CH_3 SEt, $J_{H,H}$ 7.3 Hz), 2.62 (ABX, 2H, CH_2 SEt), 3.47 (s, 3H, CH_3 Me), 3.60 (t, 1H, H-4, $J_{4,3}\approx J_{4,5}$ 9.5 Hz), 3.63-3.70 (m, 1H, H-3), 3.78 (d 1H, H-6, $J_{6,5}$ 3.1 Hz), 3.83 (d, 1H, H-6, $J_{6,5}$ 3.8 Hz), 4.02-4.08 (m, 1H, H-5), 4.59, 4.60 (2× AB, 4H, 2× CH_2 Bn), 5.31 (s, 1H, H-1), 5.45 (dd, 1H, H-2, $J_{2,1}$ 1.4 Hz, $J_{2,3}$ 3.0 Hz), 7.29-7.33 (m, 10H, CH Bn); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 14.3 (CH_3 SEt), 24.8 (CH_2 SEt), 40.3 (CH_2 ClAc), 60.2 (CH_3 Me), 68.3 (C-6), 71.3, 72.7 (2× CH_2 Bn), 71.4, 71.9, 75.5, 77.8 (C-2, C-3, C-4, C-5), 81.3 (C-1), 127.0, 127.2, 127.5, 127.7, 127.8 (CH Bn), 137.1, 137.7 (qC Bn), 166.1 (C=O ClAc).

Anal. calcd. for $C_{25}H_{31}O_6SCl$ (495.04): C 60.66, H 6.31; found C 60.74, H 6.40%.

4-[2-(Benzyloxycarbonylamino)ethyl]phenyl 2,4-di-*O*-methyl-3-*O*-{4-*O*-benzyl-2-*O*-methyl-3-*O*-[4-*O*-acetyl-2-*O*-methyl-3-*O*-(3,6-di-*O*-benzyl-2-*O*-chloroacetyl-4-*O*-methyl-α-D-mannopyranosyl)-α-L-fucopyranosyl]-α-L-rhamnopyranosyl}-α-L-rhamnopyranoside (25) and **1,2-(3,6-di-*O*-Benzyl-4-*O*-methyl-α-D-mannopyranose) 3-*O*-{4-[2-(benzyloxycarbonylamino)ethyl]phenyl 2,4-di-*O*-methyl-3-*O*-[4-*O*-benzyl-2-*O*-methyl-3-*O*-(4-*O*-acetyl-2-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl]-α-L-rhamnopyranoside} orthochloroacetate (26)** - To a mixture of trimer acceptor **2** (222 mg, 0.25 mmol), mannopyranoside donor **24** (148 mg, 0.30 mmol) and activated molecular sieves (4 Å) in 1,2-dichloroethane-diethyl ether (1/1, v/v, 2 ml) was added at 0°C a suspension of NIS (68 mg, 0.30 mmol) and TfOH (3.3 µl, 37 µmol) in the same solvent mixture (2 ml). After stirring for 15 min, the reaction was quenched with pyridine, diluted with dichloromethane (10 ml) and filtered. The solution was washed with aq. $Na_2S_2O_3$ (20%, 7 ml) and aq. $NaHCO_3$ (10%, 5 ml), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography [ethyl acetate in petroleum ether (0→50%)]. Elution of the column gave the α-linked tetramer **25-α** (123 mg, 93 µmol) and the 1,2-orthoester linked tetramer **26** (67 mg, 50 µmol).

25-α: $[\alpha]_D$ -63.6° (c 1); ^{1}H-NMR ($CDCl_3$, 400 MHz, HH-COSY): δ 1.08 (d, 3H, H-6", $J_{6,5}$ 6.5 Hz), 1.26 (d, 3H, H-6, $J_{6,5}$ 6.1 Hz), 1.35 (d, 3H, H-6', $J_{6,5}$ 6.2 Hz), 2.05 (s, 3H, CH_3 Ac), 2.75 (t, 2H, CH_2 spacer, $J_{H,H}$ 6.8 Hz), 3.22 (t, 1H, H-4, $J_{4,3}\approx J_{4,5}$ 9.6 Hz), 3.31, 3.43 (2× s, 6H, 2× CH_3 Me), 3.40-3.45 (m, 2H, CH_2 spacer), 3.47, 3.49, 3.53 (3× s, 9H, 3× CH_3 Me), 3.48-3.54 (m, 2H, H-2", H-4'), 3.57 (t, 1H, H-4"', $J_{4,3}\approx J_{4,5}$ 9.7 Hz), 3.65-3.72 (m, 5H, H-2, H-5, H-2', H-3"', H-6"'), 3.81 (AB, 1H, H-6"', $J_{6,6}$ 11.0 Hz, $J_{6,5}$ 4.0 Hz), 3.89-3.93 (m, 1H, H-5"'), 3.95 (dq, 1H, H-5', $J_{5,4}$ 10.0 Hz, $J_{5,6}$ 6.5 Hz), 4.00 (dd, 1H, H-3', $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.5 Hz), 4.09 (dd, 1H, H-3, $J_{3,2}$ 3.1 Hz, $J_{3,4}$ 9.6 Hz), 4.11 (AB, 2H, CH_2 ClAc), 4.25 (dd, 1H, H-3", $J_{3,2}$ 10.2 Hz, $J_{3,4}$ 3.5 Hz), 4.32 (q, 1H, H-5", $J_{5,6}$ 6.8 Hz), 4.62, 4.63, 4.81 (3× AB, 6H, 3× CH_2 Bn), 5.09 (s, 2H, CH_2 Z), 5.14 (d, 1H, H-1"', $J_{1,2}$ 1.3 Hz), 5.19 (d, 1H, H-1", $J_{1,2}$ 4.0 Hz), 5.20 (d, 1H, H-1', $J_{1,2}$ 2.0 Hz), 5.22 (d, 1H, H-4", $J_{4,3}$ 4.0 Hz), 5.39 (dd, 1H, H-2"', $J_{2,1}$ 2.0 Hz, $J_{2,3}$ 3.0 Hz), 5.47 (d, 1H, H-1, $J_{1,2}$ 1.6 Hz), 6.97-7.10 (m, 4H, CH spacer), 7.26-7.41 (m, 20H, CH arom); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 16.1, 17.7, 18.0 (C-6, C-6', C-6"), 20.5 (CH_3 Ac), 35.0, 42.2 (2× CH_2 spacer), 40.9 (CH_2 ClAc), 57.5, 58.4, 58.7, 60.5, 61.0 (5× CH_3 Me), 66.5 (CH_2 Z) 69.1 (C-6"'), 71.7, 73.1, 75.1 (3× CH_2 Bn), 65.2, 68.4, 68.6, 70.6, 71.6, 72.8, 73.1, 75.6, 76.9, 78.4, 79.1, 79.4, 80.0, 80.4, 81.5, 81.8 (CH sugar rings), 94.7 (C-1, $^1J_{C,H}$ 168.5 Hz), 98.0, 98.8, 99.3 (C-1', C-1", C-1"', $^1J_{C,H}$ 174.4, 165.6, 167.0 Hz, respectively), 116.3 (CH spacer), 127.3, 127.5, 127.6, 127.7, 128.0, 128.8, 128.3, 129.6 (CH arom), 132.3, 137.7, 138.2, 138.6, 154.9 (qC arom, C=O Z), 166.7 (C=O ClAc), 170.3 (C=O Ac).

Anal. calcd. for $C_{70}H_{88}NO_{22}Cl$ (1330.93): C 63.17, H 6.66, N 1.05; found C 63.10, H 6.78, N 1.13%.

26: $[\alpha]_D$ -64.0° (c 1); ^{1}H-NMR ($CDCl_3$, 400 MHz, HH-COSY): δ 1.12 (d, 3H, H-6", $J_{6,5}$ 6.5 Hz), 1.27 (d, 3H, H-6, $J_{6,5}$ 6.3 Hz), 1.33 (d, 3H, H-6', $J_{6,5}$ 6.3 Hz), 2.03 (s, 3H, CH_3 Ac), 2.75 (t, 2H, CH_2 spacer, $J_{H,H}$ 6.9 Hz), 3.23 (t, 1H, H-4, $J_{4,3}\approx J_{4,5}$ 9.6 Hz), 3.30 (s, 3H, CH_3 Me), 3.31 (t, 1H, H-4"', $J_{4,3}\approx J_{4,5}$ 9.3 Hz), 3.42 (q, 2H, CH_2 spacer, $J_{H,H}$ 6.5 Hz), 3.47 (s, 3H, CH_3 Me), 3.49 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.6 Hz), 3.50, 3.52 (2× s, 6H, 2× CH_3 Me), 3.52 (dd, 1H, H-2", $J_{2,1}$ 3.4 Hz, $J_{2,3}$ 10.1 Hz), 3.54 (s, 3H, CH_3 Me), 3.63-3.73 (m, 7H, H-2, H-5, H-2', H-3"', H-5"', H-6"'), 3.82 (AB, 2H, CH_2 ClAc), 3.95 (dq, 1H, H-5', $J_{5,4}$ 9.40 Hz, $J_{5,6}$ 6.3 Hz), 4.05 (dd, 1H, H-3', $J_{3,2}$ 3.1 Hz, $J_{3,4}$ 9.6 Hz), 4.09 (dd, 1H, H-3, $J_{3,2}$ 3.3 Hz, $J_{3,4}$ 9.7 Hz), 4.32 (dd, 1H, H-3", $J_{3,2}$ 10.4 Hz, $J_{3,4}$ 3.5 Hz), 4.33 (q, 1H, H-5", $J_{5,6}$ 6.0 Hz), 4.59 (t, 1H, H-2"', $J_{2,1}\approx J_{2,3}$ 3.3 Hz), 4.63, 4.76, 4.83 (3× AB, 6H, 3× CH_2 Bn), 5.09 (s, 2H, CH_2 Z), 5.22 (d, 1H, H-1", $J_{1,2}$ 3.7 Hz), 5.21 (s, 1H, H-1'), 5.28 (d, 1H, H-4", $J_{4,3}$ 3.7 Hz), 5.43 (d, 1H, H-1"', $J_{3,1}$ 3.1 Hz), 5.47 (d, 1H, H-1, $J_{1,2}$ 1.7 Hz), 6.97-7.10 (m, 4H, CH spacer), 7.25-7.43 (m, 20H, CH arom); ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz, CH-COSY): δ 16.2 (C-6"), 17.7 (C-6), 18.1 (C-6'), 20.8 (CH_3 Ac), 35.1, 42.2 (2× CH_2 spacer), 44.9 (CH_2 ClAc), 57.5, 58.8, 59.1, 60.5, 61.0 (5× CH_3 Me), 65.1 (C-5"), 66.5 (CH_2 Z), 68.5 (C-5), 68.7 (C-5'), 69.4 (C-6"'), 70.4 (C-3"), 71.5, 73.3 (2× CH_2 Bn), 73.5 (C-4"), 74.8 (CH_2 Bn), 75.3 (C-4"'), 75.8 (CH), 76.1 (C-2"'), 76.4 (CH), 77.3 (CH), 79.2 (CH), 79.6 (C-3), 80.1 (CH), 80.5 (CH), 81.3 (C-3'), 82.0 (C-4), 94.9 (C-1, $^1J_{C,H}$ 168.5 Hz), 97.9 (C-1"', $^1J_{C,H}$ 176.5 Hz), 98.2, 99.8 (C-1', C-1", $^1J_{C,H}$

171.4, 168.5 Hz, respectively), 116.4 (CH spacer), 121.3 (qC orthoester), 127.4, 127.7, 128.0, 128.2, 128.3, 128.4, 129.7 (CH arom), 132.4, 136.5, 137.9, 138.2, 155.1, 156.2 (qC arom, C=O Z), 170.8 (C=O Ac).

Anal. calcd. for $C_{70}H_{88}NO_{22}Cl$ (1330.93): C 63.17, H 6.66, N 1.05; found C 63.23, H 6.73, N 0.98%.

4-[2-(Benzyloxycarbonylamino)ethyl]phenyl 2,4-di-*O*-methyl-3-*O*-{4-*O*-benzyl-2-*O*-methyl-3-*O*-[4-*O*-acetyl-2-*O*-methyl-3-*O*-(3,6-di-*O*-benzyl-4-*O*-methyl-α-D-mannopyranosyl)-α-L-fucopyranosyl]-α-L-rhamnopyranosyl}-α-L-rhamnopyranoside (27) - To a solution of tetramer **25** (123 mg, 93 μmol) in a mixture of 2,6-lutidine and acetic acid (3/1, v/v, 1.63 ml) was added dropwise a freshly prepared solution of HDTC[14] (0.5 ml). After stirring for 30 min, TLC-analysis showed complete conversion of the starting material. The reaction mixture was diluted with dichloromethane (5 ml) and washed with water (3 ml) and aq. $NaHCO_3$ (10%, 3 ml). The organic layer was dried over ($MgSO_4$), filtered, and concentrated to dryness. The crude product was purified by column chromatography. Elution was performed with a gradient of ethyl acetate in petroleum ether (0→60%). Concentration of the appropriate fractions gave compound **27** (97 mg, 77 μmol).

$[\alpha]_D$ -67.6° (c 1); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 16.1, 17.7, 18.0 (3× C-6), 20.6 (CH_3 Ac), 35.2, 42.3 (2× CH_2 spacer), 57.5, 58.4, 58.8, 60.5, 61.1 (5× CH_3 Me), 66.6 (CH_2 Z), 69.1 (C-6'''), 71.9, 73.3, 75.0 (3× CH_2 Bn), 65.2, 68.6, 68.7, 68.8, 71.4, 73.0, 73.3, 75.9, 78.4, 79.2, 79.2, 79.7, 80.1, 80.6, 82.0 (CH sugar rings), 94.9 (C-1), 98.3, 99.6, 101.0 (C-1', C-1'', C-1'''), 116.5 (CH spacer), 127.2, 127.4, 127.7, 127.9, 128.1, 128.2, 128.4, 128.5, 129.0, 129.8 (CH arom), 132.4, 136.5, 138.2, 138.4, 139.0 (qC arom), 155.1, 156.3 (qC arom, C=O Z), 170.4 (C=O Ac).

Anal. calcd. for $C_{68}H_{87}NO_{21}$ (1254.45): C 65.11, H 6.99, N 1.11; found C 65.25, H 6.92, N 1.18%.

Ethyl 2-*O*-acetyl-3,6-di-*O*-benzyl-4-*O*-methyl-1-thio-D-mannopyranoside (29) - Mannopyranoside **23** (419 mg, 1.0 mmol) was dried by evaporation with pyridine and dissolved in the same solvent (4 ml). Acetic anhydride (0.14 ml, 1.5 mmol) and DMAP (12 mg, 0.1 mmol) were added. After stirring for 1 h, the reaction was quenched with addition of methanol (0.5 ml). The solution was concentrated and the residual acetic acid was removed by repeated evaporation of toluene. The residue was purified by silica gel column chromatography. The column was eluted with ethyl acetate in petroleum ether (0→10%) to yield after evaporation of the solvent, product **29** (401 mg, 0.9 mmol).

$[\alpha]_D$ +79.6° (c 1); ^1H-NMR ($CDCl_3$): δ 1.27 (t, 3H, CH_3 SEt, $J_{H,H}$ 7.4 Hz), 2.13 (s, 3H, CH_3 Ac), 2.61 (ABX, 2H, CH_2 SEt), 3.48 (s, 3H, CH_3 Me), 3.63 (t, 1H, H-4, $J_{4,3}\approx J_{4,5}$ 9.5 Hz), 3.68 (dd, 1H, H-6, $J_{6,6}$ 10.8 Hz, $J_{6,5}$ 2.0 Hz), 3.72-3.84 (m, 2H, H-3, H-6), 4.05 (ddd, 1H, H-5, $J_{5,4}$ 9.6 Hz, $J_{5,6}$ 1.8 Hz, $J_{5,6}$ 4.0 Hz), 4.59, 4.60 (2× AB, 4H, 2× CH_2 Bn), 5.29 (d, 1H, H-1, $J_{1,2}$ 1.3 Hz), 5.38 (dd, 1H, H-2, $J_{2,1}$ 1.7 Hz, $J_{2,3}$ 3.2 Hz), 7.27-7.36 (m, 10H, CH Bn); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 14.6 (CH_3 SEt), 20.8 (CH_3 Ac), 25.2 (CH_2 SEt), 60.6 (CH_3 Me), 68.7 (C-6), 71.5, 73.1 (2× CH_2 Bn), 70.3, 71.6, 75.8, 78.2 (C-2, C-3, C-4, C-5), 82.1 (C-1), 127.3, 127.4, 127.5, 127.7, 128.0, 128.2 (CH Bn), 137.6, 138.0 (qC Bn), 170.0 (C=O Ac).

Anal. calcd. for $C_{25}H_{32}O_6S$ (460.59): C 65.19, H 7.00; found C 65.12, H 7.07%.

Ethyl 2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-methyl-1-thio-α-D-mannopyranoside (30) - Compound **23** (423 mg, 1.0 mmol) was dissolved in pyridine (3 ml) and benzoyl chloride (0.17 ml, 1.5 mmol) was added. After stirring for 1 h, the reaction was quenched with water, and the solvents were removed. The residue was taken up in ethyl acetate (10 ml). The solution was washed with water (5 ml) and aq. $NaHCO_3$ (10%, 5 ml), dried ($MgSO_4$), and filtered. The organic layer was concentrated and the oily residue was purified by column chromatography. The column was eluted with ethyl acetate in petroleum ether (0→20%). Concentration of the appropriate fractions gave compound **30** (452 mg, 0.9 mmol).

$[\alpha]_D$ +29.0° (c 1); ^1H-NMR ($CDCl_3$): δ 1.29 (t, 1H, CH_3 SEt, $J_{H,H}$ 7.4 Hz), 2.64 (ABX, 2H, CH_2 SEt), 3.52 (s, 3H, CH_3 Me), 3.55-4.14 (m, 5H, H-3, H-4, H-5, H-6), 4.64 (CH_2 Bn), 5.40 (s, 1H, H-1), 5.64-5.66 (m, 1H, H-2), 7.25-7.37 (m, 13H, CH arom), 8.02-8.07 (m, 2H, CH Bz); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 14.5 (CH_3 SEt), 25.1 (CH_2 SEt), 60.4 (CH_3 Me), 68.7 (C-6), 71.1, 72.9 (2× CH_2 Bn), 70.5, 71.7, 75.7, 78.1 (C-2, C-3, C-4, C-5), 82.1 (C-1), 126.9, 127.0, 127.2, 127.5, 127.8, 127.9, 128.4, 129.4 (CH arom), 129.5 (qC Bz), 132.7 (CH Bz), 137.5, 138.1 (qC Bn), 165.0 (C=O Bz).

Anal. calcd. for $C_{30}H_{34}O_6S$ (522.67): C 78.23, H 7.44; found C 78.16, H 7.36%.

Ethyl 3,6-di-*O*-benzyl-2-*O*-(2-dibromomethyl)benzoyl-4-*O*-methyl-1-thio-α-D-mannopyranoside (31) - 2-Dibromomethylbenzoyl chloride (406 mg, 1.3 mmol) was added to a solution of compound **23** (419 mg, 1.0 mmol) pyridine. After stirring for 4 h at room temperature, the reaction mixture was quenched with water (1 ml) and diluted with ethyl acetate (10 ml). The solution

was washed with water (7 ml) and aq. $NaHCO_3$ (10%, 7 ml), dried ($MgSO_4$), and filtered. The solvents were removed and the residue was purified by column chromatography (0→20% ethyl acetate in petroleum ether) to give compound **31** (575 mg, 0.83 mmol).

$[\alpha]_D$ +27.2° (c 1); ^{1}H-NMR ($CDCl_3$): δ 1.29 (t, 3H, CH_3 SEt, $J_{H,H}$ 7.4 Hz), 2.64 (ABX, 2H, CH_2 SEt), 3.55 (s, 3H, CH_3 Me), 3.73 (dd, 1H, H-6, $^2J_{6,6}$ 10.9 Hz, $J_{6,5}$ 1.9 Hz), 3.87 (dd, 1H, H-6, $^2J_{6,6}$ 10.8 Hz, $J_{6,5}$ 3.8 Hz), 3.87 (t, 1H, H-4, $J_{4,3}\approx J_{4,5}$ 9.4 Hz), 3.93 (dd, 1H, H-3, $J_{3,2}$ 3.0 Hz, $J_{3,4}$ 9.2 Hz), 4.13 (ddd, 1H, H-5, $J_{5,4}$ 9.1 Hz, $J_{5,6}$ 1.8 Hz, $J_{5,6}$ 3.8 Hz), 4.60, 4.69 (2× AB, 4H, 2× CH_2 Bn), 5.43 (d, 1H, H-1, $J_{1,2}$ 1.5 Hz), 5.57 (dd, 1H, H-2, $J_{2,1}$ 1.8 Hz, $J_{2,3}$ 2.9 Hz), 7.19 (dt, 1H, CH DBMB, $J_{H,H}$ 7.7 Hz, $^4J_{H,H}$ 1.1 Hz), 7.23-7.37 (m, 10H, CH Bn), 7.57 (dt, 1H, CH DBMB, $J_{H,H}$ 7.7 Hz, $^4J_{H,H}$ 1.2 Hz), 7.84 (dd, 1H, CH DBMB, $J_{H,H}$ 8.0 Hz, $^4J_{H,H}$ 1.3 Hz), 7.98 (s, 1H, $CHBr_2$ DBMB), 8.12 (dt, 1H, CH DBMB, $J_{H,H}$ 8.0 Hz, $^4J_{H,H}$ 1.0 Hz); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 14.7 (CH_3 SEt), 25.3 (CH_2 SEt), 38.3 ($CHBr_2$ DBMB), 60.7 (CH_3 Me), 68.7 (C-6), 71.9, 73.1 (2× CH_2 Bn), 71.6, 72.0, 75.9, 78.1 (C-2, C-3, C-4, C-5), 81.8 (C-1), 124.5 (qC DBMB), 127.2, 127.2, 127.5, 127.7, 128.0, 128.1, 129.1, 129.9, 131.3, 132.9 (CH arom), 137.2, 137.9 (qC Bn), 142.6 (qC DBMB), 165 (C=O DBMB).

Anal. calcd. for $C_{31}H_{34}O_6SBr_2$ (694.50): C 53.61, H 4.93; found C 53.49, H 5.02%.

Methyl 4-*O*-acetyl-3-*O*-(3,6-di-*O*-benzyl-2-*O*-chloroacetyl-4-*O*-methyl-α-D-mannopyranosyl)-2-*O*-methyl-α-L-fucopyranoside (19c-α) and **Methyl 4-*O*-acetyl-3-*O*-(3,6-di-*O*-benzyl-2-*O*-chloroacetyl-4-*O*-methyl-β-D-mannopyranosyl)-2-*O*-methyl-α-L-fucopyranoside (19c-β)** and **1,2-(3,6-di-*O*-Benzyl-4-*O*-methyl-α-D-mannopyranose) 3-(methyl 4-*O*-acetyl-2-*O*-methyl-α-L-fucopyranoside) orthochloroacetate (28)** - According to the general glycosylation procedure, acceptor **18**(L) was coupled with donor **24** to furnish, after purification by column chromatography, the α-anomer **19c-α** (63 mg, 0.09 mmol) together with the β-linked dimer **19c-β** (10 mg, 0.02 mmol) and the orthoester-linked dimer **28** (57 mg, 0.09 mmol).

This glycosylation was also performed in the presence on 0.3 equiv. of TfOH. After purification of the crude reaction mixture, the individual dimers **19c-α** (112 mg, 0.17 mmol) and **19c-β** (17 mg, 0.03 mmol) were isolated.

19c-α $[\alpha]_D$ -36.0° (c 1); ^{1}H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.04 (d, 3H, H-6, $J_{6,5}$ 6.6 Hz), 2.05 (s, 3H, CH_3 Ac), 3.39 (s, 3H, CH_3 Me), 3.48 (s, 6H, 2× CH_3 Me), 3.53 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.7 Hz), 3.53 (dd, 1H, H-2, $J_{2,1}$ 3.5 Hz, $J_{2,3}$ 10.1 Hz), 3.71 (dd, 1H, H-3', $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.3 Hz), 3.71 (AB, 1H, H-6', $J_{6,6}$ 10.8 Hz, $J_{6,5}$ 1.8 Hz), 3.79 (AB, 1H, H-6', $J_{6,6}$ 11.0 Hz, $J_{6,5}$ 4.4 Hz), 3.88 (q, 1H, H-5, $J_{5,6}$ 6.4 Hz), 3.90 (ddd, 1H, H-5', $J_{5,4}$ 9.5 Hz, $J_{5,6}$ 2.0 Hz, $J_{5,6}$ 4.1 Hz), 4.10 (dd, 1H, H-3, $J_{3,2}$ 10.1 Hz, $J_{3,4}$ 3.5 Hz), 4.10 (AB, 2H, CH_2 ClAc), 4.61, 4.62 (2× AB, 4H, 2× CH_2 Bn), 4.85 (d, 1H, H-1, $J_{1,2}$ 3.5 Hz), 5.47 (d, 1H, H-1', $J_{1,2}$ 1.7 Hz), 5.15 (dd, 1H, H-4, $J_{4,3}$ 3.6 Hz, $J_{4,5}$ 1.1 Hz), 5.37 (dd, 1H, H-2', $J_{2,1}$ 1.8 Hz, $J_{2,3}$ 3.3 Hz), 7.23-7.38 (m, 10H, CH Bn); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 15.8 (C-6), 20.6 (CH_3 Ac), 40.9 (CH_2 ClAc), 55.3 (CH_3 1-*O*-Me), 58.8, 60.6 (2× CH_3 Me), 68.5 (C-6'), 71.8, 73.1 (CH_2 Bn), 64.5, 70.7, 71.9, 72.9, 75.8, 77.0, 78.3 (CH sugar rings), 97.5, 98.8 (C-1, C-1', $^1J_{C,H}$ 167.0, 174.9 Hz, respectively), 127.3, 127.4, 127.6, 127.8, 128.1, 128.3 (CH Bn), 137.8, 138.5 (qC Bn), 166.7 (C=O ClAc), 170.3 (C=O Ac).

Anal. calcd. for $C_{33}H_{43}O_{12}Cl$ (667.16): C 59.41, H 6.50; found C 59.32, H 6.43%.

19c-β $[\alpha]_D$ -57.8° (c 0.5); ^{1}H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.15 (d, 3H, H-6, $J_{6,5}$ 6.6 Hz), 2.21 (s, 3H, CH_3 Ac), 3.33 (ddd, 1H, H-5', $J_{5,4}$ 9.4 Hz, $J_{5,6}$ 2.7 Hz, $J_{5,6}$ 3.6 Hz), 3.40 (s, 3H, CH_3 Me), 3.49 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.6 Hz), 3.49 (dd, 1H, H-2, $J_{2,1}$ 3.8 Hz, $J_{2,3}$ 9.9 Hz), 3.48, 3.51 (2× s, 6H, 2× CH_3 Me), 3.57 (dd, 1H, H-3', $J_{3,2}$ 3.2 Hz, $J_{3,4}$ 9.2 Hz), 3.78 (d, 1H, H-6', $J_{6,5}$ 2.5 Hz), 3.78 (d, 1H, H-6', $J_{6,5}$ 3.8 Hz), 3.97 (dq, 1H, H-5, $J_{5,4}$ 1.3 Hz, $J_{5,6}$ 6.5 Hz), 4.10 (AB, 2H, CH_2 ClAc), 4.28 (dd, 1H, H-3, $J_{3,2}$ 10.0 Hz, $J_{3,4}$ 3.5 Hz), 4.60 (d, 1H, H-1', $J_{1,2}$ 1.0 Hz), 4.63, 4.66 (2× AB, 4H, 2× CH_2 Bn), 4.82 (d, 1H, H-1, $J_{1,2}$ 3.7 Hz), 5.20 (dd, 1H, H-4, $J_{4,3}$ 3.5 Hz, $J_{4,5}$ 1.4 Hz), 5.44 (dd, 1H, H-2', $J_{2,1}$ 1.0 Hz, $J_{2,3}$ 3.1 Hz), 7.26-7.38 (m, 10H, CH Bn); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 16.0 (C-6), 20.8 (CH_3 Ac), 40.9 (CH_2 ClAc), 55.3 (CH_3 1-*O*-Me), 59.9, 60.9 (2× CH_3 Me), 68.8 (C-6'), 71.6, 73.5 (2× CH_2 Bn), 63.8, 70.0, 73.9, 75.7, 76.1, 76.3, 79.7 (CH sugar rings), 95.2 (C-1', $^1J_{C,H}$ 158.3 Hz), 98.6 (C-1, $^1J_{C,H}$ 175.8 Hz), 127.4, 127.6, 127.8, 128.0, 128.2, 128.4 (CH Bn).

28: $[\alpha]_D$ -67.8° (c 1); ^{1}H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.12 (d, 3H, H-6, $J_{6,5}$ 6.6 Hz), 2.18 (s, 3H, CH_3 Ac), 3.37-3.43 (m, 1H, H-5'), 3.41, 3.50, 3.53 (3× s, 9H, 3× CH_3 Me), 3.64 (dd, 1H, H-2, $J_{2,1}$ 3.6 Hz, $J_{2,3}$ 10.2 Hz), 3.63-3.77 (m, 4H, H-3', H-4', H-6'), 3.80 (AB, 2H, CH_2 ClAc), 3.97 (dq, 1H, H-5, $J_{5,4}$ 1.1 Hz, $J_{5,6}$ 6.5 Hz), 4.21 (dd, 1H, H-3, $J_{3,2}$ 10.2 Hz, $J_{3,4}$ 3.5 Hz), 4.58 (AB, 2H, CH_2 Bn), 4.61 (t, 1H, H-2', $J_{2,1}\approx J_{2,3}$ 3.2 Hz), 4.76 (AB, 2H, CH_2 Bn), 4.88 (d, 1H, H-1, $J_{1,2}$ 3.6 Hz), 5.25 (dd, 1H, H-4, $J_{4,3}$ 3.5 Hz, $J_{4,5}$ 1.2 Hz), 5.47 (d, 1H, H-1', $J_{1,2}$ 2.9 Hz), 7.22-7.45 (m, 10H, CH Bn); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 16.0 (C-6), 20.9 (CH_3 Ac), 45.3 (CH_2 ClAc), 55.2 (CH_3 1-*O*-Me), 59.4, 60.6 (2× CH_3 Me), 69.2 (C-6'), 71.5, 73.2 (2× CH_2 Bn),

64.5, 70.3, 73.4, 74.7, 75.2, 76.2, 76.3, 77.5 (CH sugar rings), 97.7 (C-1', $^1J_{C,H}$ 175.8 Hz), 98.0 (C-1, $^1J_{C,H}$ 170.0 Hz), 121.4 (qC orthoester), 127.3, 127.7, 127.7, 128.2, 128.3 (CH Bn), 137.9, 138.2 (qC Bn), 165.9 (C=O ClAc), 170.7 (C=O Ac).

Anal. calcd. for $C_{33}H_{43}O_{12}Cl$ (667.16): C 59.41, H 6.50; found C 59.48, H 6.61%.

Methyl 4-*O*-acetyl-3-*O*-(2-*O*-acetyl-3,6-di-*O*-benzyl-4-*O*-methyl-α-D-mannopyranosyl)-2-*O*-methyl-α-L-fucopyranoside (19d-α) - Glycosylation of donor **29** with model acceptor **18**(L) afforded, after silica gel column chromatography, exclusively the α-linked dimer **19d-α** (100 mg, 0.16 mmol).

$[\alpha]_D$ -46.6° (c 1); ^{1}H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.03 (d, 3H, H-6, $J_{6,5}$ 6.5 Hz), 2.04, 2.06 (2× s, 3H, CH_3 Ac), 3.38, 3.48, 3.49 (3× s, 9H, 3× CH_3 Me), 3.53 (dd, 1H, H-2, $J_{2,1}$ 3.6 Hz, $J_{2,3}$ 10.2 Hz), 3.56 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.6 Hz), 3.70 (dd, 1H, H-3', $J_{3,2}$ 3.4 Hz, $J_{3,4}$ 9.4 Hz), 3.72 (dd, 1H, H-6', $J_{6,6}$ 10.9 Hz, $J_{6,5}$ 1.9 Hz), 3.80 (dd, 1H, H-6', $J_{6,6}$ 11.0 Hz, $J_{6,5}$ 4.6 Hz), 3.87 (dq, 1H, H-5, $J_{5,4}$ 1.3 Hz, $J_{5,6}$ 6.5 Hz), 3.89 (ddd, 1H, H-5', $J_{5,4}$ 9.9 Hz, $J_{5,6}$ 1.9 Hz, $J_{5,6}$ 4.3 Hz), 4.10 (dd, 1H, H-3, $J_{3,2}$ 10.1 Hz, $J_{3,4}$ 3.6 Hz), 4.52-4.73 (m, 4H, 2× CH_2 Bn), 4.84 (d, 1H, H-1, $J_{1,2}$ 3.5 Hz), 5.08 (d, 1H, H-1', $J_{1,2}$ 1.8 Hz), 5.15 (dd, 1H, H-4, $J_{4,3}$ 3.6 Hz, $J_{4,5}$ 1.2 Hz), 5.34 (dd, 1H, H-2', $J_{2,1}$ 1.8 Hz, $J_{2,3}$ 3.4 Hz), 7.24-7.38 (m, 10H, CH Bn); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 15.8 (C-6), 20.6, 20.9 (2× CH_3 Ac), 55.3 (CH_3 1-*O*-Me), 58.9, 60.5 (2× CH_3 Me), 69.0 (C-6'), 71.5, 73.9 (2× CH_2 Bn), 64.5, 68.8, 71.9, 72.8, 72.9, 75.9, 77.1, 78.4 (CH sugar rings), 97.6, 99.1 (C-1, C-1', $^1J_{C,H}$ 171.4 Hz, both), 127.2, 127.4, 127.5, 127.7, 128.1, 128.2 (CH Bn), 138.10, 138.67 (qC Bn), 170.1, 170.2 (2× C=O Ac).

Anal. calcd. for $C_{33}H_{44}O_{12}$ (632.71): C 62.65, H 7.01; found C 62.74, H 6.91%.

Methyl 4-*O*-acetyl-3-*O*-(2-*O*-benzoyl-3,6-di-*O*-benzyl-4-*O*-methyl-α-D-mannopyranosyl)-2-*O*-methyl-α-L-fucopyranoside (19e-α) - Donor **30** was condensed with acceptor **18**(L) and the crude product was purified by column chromatography to give pure **19e-α** (157 mg, 0.23 mmol).

$[\alpha]_D$ -76.0° (c 1); ^{1}H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.06 (d, 3H, H-6, $J_{6,5}$ 6.5 Hz), 2.06 (s, 3H, CH_3 Ac), 3.38, 3.51, 3.53 (3× s, 9H, 3× CH_3 Me), 3.57 (dd, 1H, H-2, $J_{2,1}$ 3.6 Hz, $J_{2,3}$ 10.1 Hz), 3.78 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.3 Hz), 3.81-3.96 (m, 5H, H-5, H-3', H-5', H-6'), 4.14 (dd, 1H, H-3, $J_{3,2}$ 10.1 Hz, $J_{3,4}$ 3.5 Hz), 4.68, 4.69 (2× AB, 4H, 2× CH_2 Bn), 4.85 (d, 1H, H-1, $J_{1,2}$ 3.6 Hz), 5.20 (dd, 1H, H-4, $J_{4,3}$ 3.5 Hz, $J_{4,5}$ 1.3 Hz), 5.21 (d, 1H, H-1', $J_{1,2}$ 1.8 Hz), 5.58 (dd, 1H, H-2', $J_{2,1}$ 2.1 Hz, $J_{2,3}$ 2.7 Hz), 7.23-7.43 (m, 13H, CH arom), 8.01-8.06 (m, 2H, CH Bz); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 15.9 (C-6), 20.6 (CH_3 Ac), 55.3 (CH_3 1-*O*-Me), 59.0, 60.6 (2× CH_3 Me), 69.5 (C-6'), 71.3, 73.2 (2× CH_2 Bn), 64.6, 69.1, 72.1, 73.0, 73.1, 76.1, 77.1, 78.4 (CH sugar rings), 97.6, 99.2 (C-1, C-1', $^1J_{C,H}$ 166.9, 174.4 Hz, respectively), 127.2, 127.4, 127.6, 128.2, 129.8 (CH arom), 132.9 (CH Bz), 138.1, 138.8 (qC Bn), 165.5 (C=O Bz), 170.3 (C=O Ac).

Anal. calcd. for $C_{38}H_{46}O_{12}$ (694.78): C 65.69, H 6.67; found C 65.78, H 6.58%.

Methyl 4-*O*-acetyl-3-*O*-(3,6-di-*O*-benzyl-2-*O*-(2-dibromomethyl)benzoyl-4-*O*-methyl-α-D-mannopyranosyl)-2-*O*-methyl-α-L-fucopyranoside (19f-α) - Glycosylation of **18**(L) with **31** gave, after purification by silica gel column chromatography, exclusively **19f-α** (204 mg, 0.24 mmol).

$[\alpha]_D$ -42.2° (c 1); ^{1}H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.06 (d, 3H, H-6, $J_{6,5}$ 6.5 Hz), 2.09 (s, 3H, CH_3 Ac), 3.37-3.94 (m, 7H, H-2, H-5, H-3', H-4', H-5', H-6'), 3.40, 3.55, 3.56 (3× s, 9H, 3× CH_3 Me), 4.14 (dd, 1H, H-3, $J_{3,2}$ 10.2 Hz, $J_{3,4}$ 3.5 Hz), 4.62, 4.73 (2× AB, 4H, 2× CH_2 Bn), 4.87 (d, 1H, H-1, $J_{1,2}$ 3.6 Hz), 5.19 (br dd, 1H, H-4), 5.24 (d, 1H, H-1', $J_{1,2}$ 1.6 Hz), 5.49 (dd, 1H, H-2', $J_{2,1}$ 2.0 Hz, $J_{2,3}$ 2.6 Hz), 7.21 (dt, 1H, CH DBMB, $J_{H,H}$ 7.6 Hz, $^4J_{H,H}$ 0.9 Hz), 7.22-7.39 (m, 10H, CH Bn), 7.54 (dt, 1H, CH DBMB, $J_{H,H}$ 7.8 Hz, $^4J_{H,H}$ 1.2 Hz), 7.78 (dd, 1H, CH DBMB, $J_{H,H}$ 7.9 Hz, $^4J_{H,H}$ 1.2 Hz), 7.96 (s, 1H, $CHBr_2$ DBMB), 8.12 (dt, 1H, CH DBMB, $J_{H,H}$ 8.0 Hz, $^4J_{H,H}$ 0.8 Hz); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 15.7 (C-6), 20.4 (CH_3 Ac), 38.2 ($CHBr_2$ DBMB), 55.1 (CH_3 1-*O*-Me), 58.8, 60.5 (2× CH_3 Me), 68.8 (C-6'), 71.8, 72.9 (2× CH_2 Bn), 64.3, 70.3, 71.7, 72.7, 75.9, 76.8, 78.2 (CH sugar rings), 97.4, 98.5 (C-1, C-1', $^1J_{C,H}$ 168.5, 171.5 Hz, respectively), 124.7 (qC DBMB), 127.0, 127.1, 127.4, 127.5, 128.0, 128.1, 129.2, 129.8, 131.2, 132.8 (CH arom), 137.6, 138.3 (qC Bn), 142.4 (qC DBMB), 165.3 (C=O DBMB), 170.0 (C=O Ac).

Anal. calcd. for $C_{39}H_{46}O_{12}Br_2$ (866.61): C 54.05, H 5.35; found C 54.14, H 5.48%.

Methyl 4-*O*-acetyl-3-*O*-(3,6-di-*O*-benzyl-4-*O*-methyl-α-D-mannopyranosyl)-2-*O*-methyl-α-L-fucopyranoside (19g) - Silver perchlorate (141 mg, 0.68 mmol) and 2,6-lutidine (40 µl, 0.34 mmol) were added to a solution of disaccharide **19f** (98 mg, 0.11 mmol) in acetone-water (1.5 ml, 20/1, v/v). After stirring for 30 min, lithium bromide (87 mg, 1 mmol) was added to the

reaction mixture and silver bromide was filtered. The solids were washed with a mixture of acetone-water (2 ml, 20/1, v/v) and morpholine (0.4 ml, 4.6 mmol) was added to the filtrate. The reaction mixture was stirred for 45 min and neutralised with acetic acid. The solution was diluted with diethyl ether (10 ml) and washed with water (8 ml), dried ($MgSO_4$), filtered and concentrated. The residue was purified by column chromatography (30→60% ethyl acetate in petroleum ether) to yield compound **19g** (56 mg, 0.95 mmol).

$[\alpha]_D$ +27.2° (c 1); ^{1}H-NMR ($CDCl_3$, 300 MHz, HH-COSY): δ 1.03 (d, 3H, H-6, $J_{6,5}$ 6.6 Hz), 2.08 (s, 3H, CH_3 Ac), 3.40, 3.44, 3.48 (3× s, 9H, 3× CH_3 Me), 3.52 (dd, 1H, H-2, $J_{2,1}$ 3.2 Hz, $J_{2,3}$ 9.8 Hz), 3.54 (t, 1H, H-4', $J_{4,3}\approx J_{4,5}$ 9.3 Hz), 3.61 (dd, 1H, H-3', $J_{3,2}$ 3.0 Hz, $J_{3,4}$ 9.1 Hz), 3.69-3.75 (m, 2H, H-6'), 3.85-3.90 (m, 2H, H-5, H-5'), 3.98 (dd, 1H, H-2', $J_{2,1}$ 1.7 Hz, $J_{2,3}$ 3.0 Hz), 4.12 (dd, 1H, H-3, $J_{3,2}$ 10.2 Hz, $J_{3,4}$ 3.5 Hz), 4.61 (AB, 4H, 2× CH_2 Bn), 4.70 (s, 2H, CH_2 Bn), 4.85 (d, 1H, H-1, $J_{1,2}$ 3.6 Hz), 5.14 (d, 1H, H-1', $J_{1,2}$ 1.5 Hz), 5.16 (br dd, 1H, H-4), 7.25-7.40 (m, 10H, CH Bn); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 15.8 (C-6), 20.6 (CH_3 Ac), 55.3 (CH_3 1-*O*-Me), 58.7, 60.5 (2× CH_3 Me), 69.0 (C-6'), 71.9, 72.9 (2× CH_2 Bn), 64.6, 68.7, 71.5, 72.9, 76.0, 78.2, 79.1 (CH sugar rings), 97.5, 100.8 (C-1, C-1'), 127.3, 127.5, 127.7, 128.1, 128.4 (CH Bn), 138.0, 138.5 (qC Bn), 170.3 (C=O Ac).

Anal. calcd. for $C_{31}H_{42}O_{11}$ (590.67): C 63.04, H 7.17; found C 62.98, H 7.11%.

ACKNOWLEDGEMENT

This research was supported by the Netherlands Organisation for Scientific Research (NWO).

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(*Received in UK* 5 *December* 1995; *accepted* 8 *January* 1996)