Pergamon

Tetrahedron Vol. 51, No. 19, pp. 5657-5670, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00225-1

Synthesis and Glycosylating Properties of Ketopyranosyl Donors

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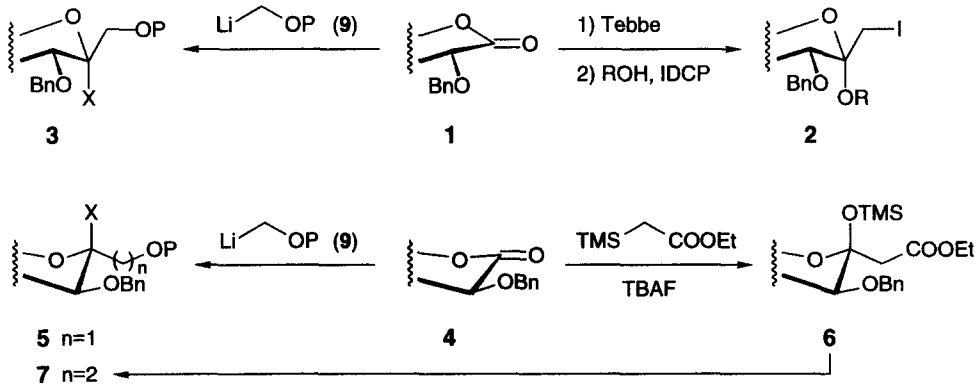
Abstract: *The preparation of heptulopyranosyl donors* ***13-15, 28, 29*** *and 3-octulopyranosyl donors* ***34, 35****, having a non-participating group at C-3 or C-4, respectively, is described. Glycosylations of various acceptors with these donors gave exclusively α-linked ketosides. On the other hand, condensation of 3-O-benzoyl heptulopyranosyl donor* ***19*** *with an acceptor furnished an anomeric mixture of ketodisaccharides.*

Introduction

The stereoselective synthesis of oligosaccharides containing ketopyranosyl units still presents, despite many efforts, a major problem in sugar chemistry. For example, zinc chloride promoted coupling[1] of *exo*-cyclic epoxides with various glycosyl acceptors led to anomeric mixtures of ketoglycosides. On the other hand, α-linked 1-deoxy-1-iodo-ketoglycosides **2** (see Scheme 1) could be prepared[2] successfully *via* iodonium di-*sym*-collidine perchlorate (IDCP) mediated condensation of an *exo*-cyclic glycal, readily



P=protective group; X=leaving group.

Scheme 1

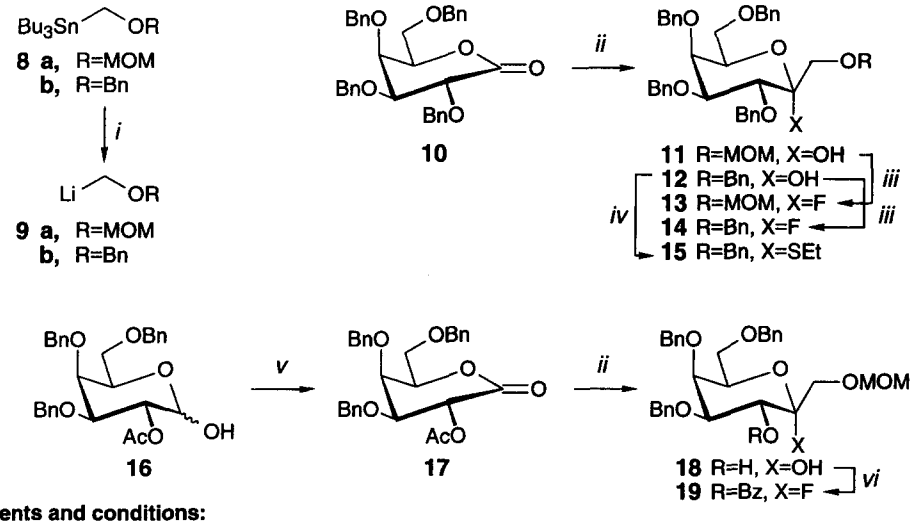
accessible by Tebbe methylenation[3] of the corresponding δ-lactone **1**, with an appropriate acceptor (ROH). Unfortunately, the neopentylic nature of the iodine atom in the resulting ketoglycoside **2** encumbers[4,5], or may even prohibit[6,7] its transformation into the required hydroxyl group.

Preliminary studies from this laboratory revealed[8] that the latter disadvantage could be circumvented by condensing glycosyl acceptors with ketopyranosyl donors **3** (X=SEt, F, see Scheme 1), the common precursor (**3**, X=OH) of which was readily prepared by the addition of an α-alkoxymethylating agent (*i.e.* **9**) to lactone **1**.

We here report in detail on the use of the respective D-*galacto*- and L-*fuco*-heptulopyranosides **3** and **5** (X=OH, F or SEt) in the synthesis of α-ketopyranosides. Moreover, it will be shown that the L-*fuco*-3-octulopyranosides **7** (X=SEt), accessible by fluoride ion promoted reaction of δ-lactone **4** with ethyl trimethylsilylacetate[9] and elaboration of the resulting addition product **6**, are effective glycosyl donors.

Results and discussion

The requisite D-*galacto*-heptulopyranosyl donors **13-15** were prepared by the sequence of reactions portrayed in Scheme 2. Thus, addition of [(methoxymethoxy)methyl]lithium **9a**, generated[10] *in situ* by



Reagents and conditions:

(i) BuLi, THF, -78°C; *(ii)* **9a,b**, THF, -78°C (**11**: 89%, **12**: 65%, **18**: 74%); *(iii)* DAST, CH_2Cl_2, -20°C (**13**: 88%, **14**: 85%); *(iv)* EtSH, $BF_3{\cdot}OEt_2$, CCl_3CN (64%); *(v)* Swern oxidation (78%); *(vi)* DAST, THF, -20°C; (b) BzCl, pyridine (75%, 2 steps).

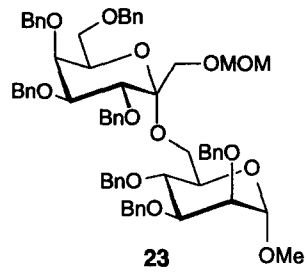
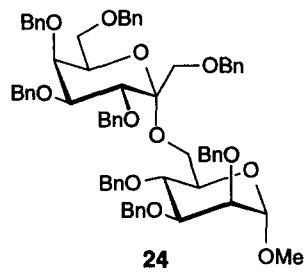
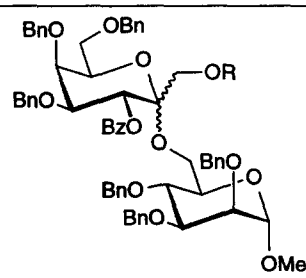
Scheme 2

tin/lithium exchange of the corresponding stannane derivative **8a**[11], to the known[12] perbenzylated D-galactono-1,5-lactone **10** afforded the anomerically pure α-D-*galacto*-heptulopyranose **11**. Transformation[13] of the anomeric hydroxyl group in **11** under the agency of diethylaminosulfur trifluoride (DAST) yielded the homogeneous α-fluoride **13**, as gauged by the large coupling constant (*i.e.* 23.2 Hz)[14] between H-3 and the fluorine atom. In a similar fashion, the partially benzylated heptulopyranose **12** was obtained by treatment of **10** with the benzyloxymethylating agent **9b**. DAST mediated fluorination or glycosidation[15] of

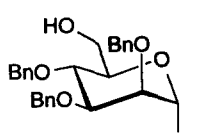
12 with ethanethiol in the presence of boron trifluoride etherate ($BF_3{\cdot}OEt_2$) led to the α-ketopyranosyl donors **14** and **15**, respectively.

The results of the glycosylations of the acceptor methyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside[16] (**20**) with the individual donors **13-15** are recorded in Table 1. It can be seen (entry 1) that condensation of

Table 1. Relevant Data on the Glycosylations of Acceptor 20 with D-*Galacto*-donors 13-15 and 19.

Entry	Donor	Acceptor	Promoter	Product	Yield[a] (α/β)
1	**13**	**20**	Cp_2ZrCl_2, AgOTf	 **23**	54% (1/0)
2	**14**	**20**	$BF_3{\cdot}OEt_2$	 **24**	58% (1/0)
3	**15**	**20**	IDCP	**24**	75% (1/0)
4	**19**	**20**	Cp_2ZrCl_2, AgOTf	 **25** R=MOM **26** R=H	32% (1/1) 17% (1/0)

[a]Based on donor.



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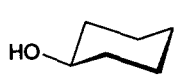

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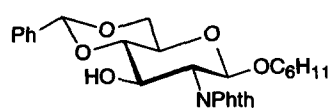
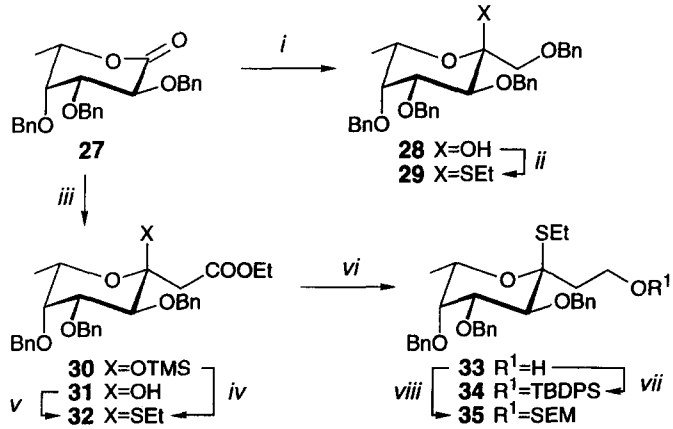


22

fluoride **13** in the presence of the promoter bis(cyclopentadienyl)zirconium dichloride/silver triflate[17] with acceptor **20** led to the exclusive formation of dimer **23**, the α-configuration of which was corroborated by ^{1}H NMR 2D NOESY experiments. A similar result was obtained (entry 2) in the BF_3·OEt_2 mediated[18] glycosylation of acceptor **20** with the fully benzylated donor **14**. It is also worth noting (entry 3) that glycosylation of **20** with the ethyl α-thioglycosyl donor **15** in the presence of the thiophilic promoter IDCP[19] resulted in a higher yield of disaccharide **24** (*cf.* entry 2). The stereoselective outcome of the above mentioned glycosylations urged us to examine whether the stereochemistry could be reversed by the use of the α-fluoride donor **19** (see Scheme 2) having a participating benzoyl group at O-3. To this end, 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-galactopyranose (**16**), accessible *via* regioselective acid hydrolysis of the orthoester function in 3,4,6-tri-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-α-D-galactopyranose[20], was oxidized (Swern) to give the δ-lactone **17**. Treatment of **17** with **9a** yielded the deacetylated ketose derivative **18** which, after fluorination and then benzoylation, resulted in the isolation of the α-fluoride **19**. Glycosylation of **20** with **19** in the presence of bis(cyclopentadienyl)zirconium dichloride/silver triflate (Table 1, entry 4) gave, after work-up and purification, disaccharide **25** (α/β mixture) as well as the anomerically pure dimer **26**, lacking the MOM protective group. The presence of the α-linkage in the latter dimer was firmly established on the basis of ^{1}H NMR 2D NOESY experiments performed with the corresponding fully protected derivative obtained by reaction of **26** with chloromethyl methyl ether.

In order to probe the validity of the stereoselective formation of α-ketodisaccharides starting from D-*galacto*-heptulopyranosyl donors, we also prepared (see Scheme 3) the L-*fuco*-heptulo- and L-*fuco*-3-octulopyranosyl donors **28, 29** and **34, 35**, respectively. The former two donors are readily accessible, as depicted in Scheme 3, by benzyloxymethylation of 2,3,4-tri-*O*-benzyl-L-fucono-1,5-lactone[21] (**27**) with reagent **9b** and subsequent transformation of **28** into the corresponding α-oriented ethyl thioglycoside **29**.



Reagents and conditions:

(i) **9b**, THF, -78°C (92%); *(ii)* EtSH, BF_3·OEt_2, CCl_3CN (85%) *(iii)* $TMSCH_2COOEt$, TBAF, THF, 50°C (**30**: 71%, **31**: 13%); *(iv)* EtSH, TMSOTf, CH_2Cl_2 (94%); *(v)* DIPEA, Tf_2O, EtSH, CH_2Cl_2 (83%); *(vi)* $LiAlH_4$, THF, reflux (100%); *(vii)* TBDPSCl, pyridine (91%); *(viii)* SEMCl, DIPEA, dioxane (87%).

Scheme 3

On the other hand, extension of lactone **27** with ethyl trimethylsilylacetate under the influence of tetra-*n*-butylammonium fluoride (TBAF), according to the procedure of Csuk *et al.*[9], gave the expected α-trimethylsilyl derivative **30** as major product together with the desilylated product **31**. Reaction of **30** with ethanethiol and trimethylsilyl triflate proceeded with retention of configuration to give the ethyl α-thioglycoside **32**. In addition, conversion of the minor product **31** into **32** could be effected by triflation of **31** with triflic anhydride in the presence of diisopropylethylamine (DIPEA) and subsequent addition of ethanethiol. Reduction of the ester moiety in **32** with lithium aluminium hydride led to the isolation of ethyl 4,5,6-tri-*O*-benzyl-2-deoxy-3-thio-α-L-*fuco*-3-octulopyranoside (**33**). Reaction of the primary hydroxyl group in **33** with either *tert*-butyldiphenylsilyl chloride (TBDPSCl) or 2-(trimethylsilyl)ethoxymethyl chloride (SEMCl) gave the respective fully protected glycosyl donors **34** and **35**.

The stereochemistry and yield of the glycosylations of acceptors **20-22** with the four L-*fuco* donors **28-29** and **34-35** are summarized in Table 2. Perusal of the data in Table 2 reveals that all glycosylations proceeded with a high degree of α-stereoselectivity. Further, $BF_3{\cdot}OEt_2$ assisted condensation (entry 1) of the primary hydroxyl group in acceptor **20** with donor **28** gave an acceptable yield of dimer **36**. It is also evident that the secondary alcoholic function of cyclohexanol (**21**) could be effectively glycosylated (entries 2 and 4) in the presence of the thiophilic promoter IDCP or iodonium di-*sym*-collidine triflate[22] (IDCT) with the ethyl α-thioglycosides **29** and **34**. On the other hand, iodonium ion mediated condensation (entry 3) of the secondary hydroxyl group in cyclohexyl 4,6-*O*-benzylidene-2-deoxy-2-phtalimido-β-D-glucopyranoside[23] (**22**) with donor **29** proceeded less effectively. Moreover, the concomitant formation of the elimination product **41** (entry 5) resulted in a further decrease of yield of disaccharide **40**.

In conclusion, the methodology presented in this paper promises to be an effective synthetic route towards the preparation of highly functionalized α-ketosaccharides. Thus, we believe that this versatile approach facilitates the future design and synthesis of multisubstrate analogues[7] for glycosyltransferases.

Experimental

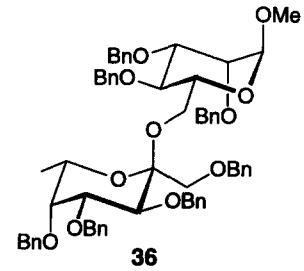
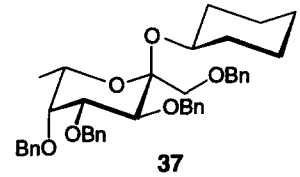
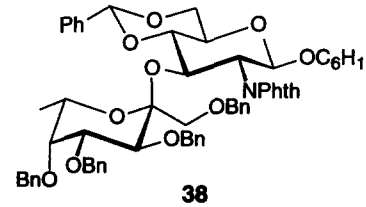
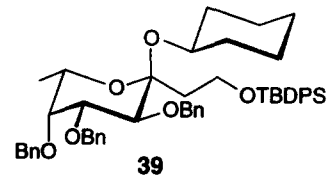
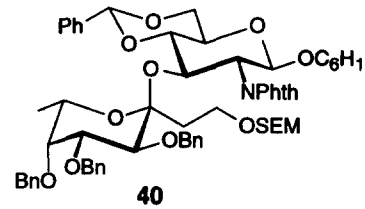
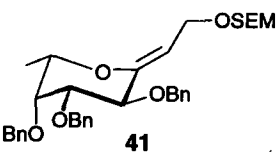
General procedures.

1,2-Dichloroethane, dichloromethane, diethyl ether and toluene were distilled from P_2O_5. Dioxane, pyridine and tetrahydrofuran (THF) were dried by refluxing with CaH_2 (5 g/L) and then distilled. All anhydrous solvents were stored on 0.4 nm molecular sieves. Trichloroacetonitrile was distilled before use. Schleicher and Schüll DC Fertigfolien F 1500 LS 254 were used for TLC analysis. Compounds were visualized by UV light (254 nm) and by charring with 20% sulfuric acid in methanol. Column chromatography was performed on silica gel 60, 230-400 mesh (Merck). The petroleum ether used for elution during chromatography was light boiling (40-60°C). Gel filtration was performed on Sephadex LH-20 from Pharmacia. ^1H NMR (200 MHz) and ^{13}C NMR spectra (50.1 MHz) were recorded using a Jeol JNM-FX 200 spectrometer, unless stated otherwise. ^1H NMR (300 MHz) spectra were recorded using a Bruker WM-300 spectrometer and ^1H NMR (400 MHz) spectra were recorded using a Bruker MSL-400 spectrometer. ^1H and ^{13}C chemical shifts (δ) are given in ppm relative to tetramethylsilane as internal standard.

3,4,5,7-Tetra-*O*-benzyl-1-*O*-methoxymethyl-α-D-*galacto*-heptulopyranose (11).

To a solution of $Bu_3SnCH_2OCH_2OCH_3$ (**8a**, 2.19 g, 6.0 mmol), dried by evaporation with toluene (3 × 5 ml), in THF (15 mL) was added *n*-BuLi (1.6 M in hexane, 3.7 mL, 5.9 mmol) under nitrogen with stirring while the temperature was maintained below -75°C. After 5 min, a solution of 2,3,4,6-tetra-*O*-benzyl-D-galactono-1,5-lactone (**10**, 1.07 g, 2.0 mmol), previously dried by evaporation with toluene (3 × 5 ml), in THF (5 mL) was added *via* syringe. After 15 min TLC analysis indicated complete

Table 2. Relevant Data on the Glycosylations of Acceptors 20-22 with L-*Fuco*-donors 28, 29, 34 and 35.

Entry	Donor	Acceptor	Promoter	Product	Yield[a] (α/β)
1	**28**	**20**	$BF_3{\cdot}OEt_2$	 **36**	65% (1/0)
2	**29**	**21**	IDCP (IDCT)	 **37**	85% (1/0)
3	**29**	**22**	IDCP (IDCT)	 **38**	66% (1/0)
4	**34**	**21**	IDCT (IDCP)	 **39**	95% (1/0)
5	**35**	**22**	IDCT (IDCP)	 **40**	55% (1/0)
				 **41**	13%

[a]Based on donor.

disappearance of the lactone. The reaction mixture was quenched with a 10% NH_4Cl solution and extracted with diethyl ether. The organic layer was washed with water, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by column chromatography (diethyl ether/petroleum ether, 0/1 to 1/2, v/v) to afford **11** as a colourless oil (1.09 g, 89%). R_f 0.45 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR (300 MHz) ($CDCl_3$) δ 3.31 (s, 3 H, OCH_3), 3.52 (dd, 1 H, H-7, $J_{6,7}$ = 5.7 Hz, $J_{7,7'}$ = -9.1 Hz), 3.55 (AB, 2 H, H-1), 3.58 (dd, 1 H, H-7', $J_{6,7'}$ = 7.6 Hz), 3.66 (d, 1 H, OH, $J_{OH,3}$ = -0.8 Hz), 3.91 (bd, 1 H, H-3, $J_{3,4}$ = 10.5 Hz), 4.01 (dd, 1 H, H-4, $J_{4,5}$ = 2.7 Hz), 4.02 (dd, 1 H, H-5, $J_{5,6}$ = 1.8 Hz), 4.13 (ddd, 1 H, H-6, $J_{5,6}$ = 1.8 Hz), 4.43-4.79 (5 × AB, 10 H, 4 × CH_2 benzyl, O-CH_2-O), 7.20-7.48 (m, 20 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 55.3 (OCH_3), 68.5, 70.3 (C-1, C-7), 69.9, 74.3, 75.9, 80,4 (C-3, C-4, C-5, C-6), 72.3, 73.2, 74,3 75.2 (4 × CH_2 benzyl), 96.9, 97.4 (C-2, O-CH_2-O), 127.3-128.2 ($CH_{arom.}$), 137.9-138.7 ($C_{arom.}$).

1,3,4,5,7-Penta-*O*-benzyl-α-D-*galacto*-heptulopyranose (12).

Lactone **10** (2.15 g, 4.0 mmol) was treated with reagent **8b** (3.29 g, 8.0 mmol) as described for the preparation of derivative **11**. Work-up and purification gave **12** as an oil in 65% yield (1.72 g). R_f 0.42 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR (300 MHz) ($CDCl_3$) δ 3.43 (d, 1 H, H-1, $J_{1,1'}$ = -10.4 Hz), 3.48 (d, 1 H, OH, $J_{OH,3}$ = -0.5 Hz), 3.53 (d, 1 H, H-1'), 3.56 (dd, 1 H, H-7, $J_{6,7}$ = 5.8 Hz, $J_{7,7'}$ = -9.1 Hz), 3.62 (dd, 1 H, H-7', $J_{6,7'}$ = 7.6 Hz), 3.97 (bd, 1 H, H-3, $J_{3,4}$ = 9.0 Hz), 3.99-4.05 (m, 2 H, H-4, H-5), 4.16 (ddd, 1 H, H-6, $J_{5,6}$ = 1.4 Hz), 4.46-5.10 (4 × AB, 8 H, 4 × CH_2 benzyl), 4.57 (s, 2 H, CH_2 benzyl), 7.20-7.48 (m, 25 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 68.5, 71.8 (C-1 and C-7), 69.9, 74.2, 75.5, 80.3 (C-3, C-4, C-5, C-6), 72.1, 73.0, 73.4, 74.2, 75.0 (5 × CH_2 benzyl), 97.8 (C-2), 127.2-128.0 ($CH_{arom.}$), 137.6-138.6 ($C_{arom.}$).

3,4,5,7-Tetra-*O*-benzyl-1-*O*-methoxymethyl-α-D-*galacto*-heptulopyranosyl Fluoride (13).

DAST (0.25 mL, 1.9 mmol) was added to a solution of compound **11** (1.00 g, 1.6 mmol), dried by evaporation with toluene (3 × 5 ml), in THF (10 ml) under nitrogen with stirring at -20°C. TLC analysis showed complete conversion of the starting material to the fluoride after 45 min. The reaction mixture was quenched with methanol (5 mL) and concentrated *in vacuo*. The residue was dissolved in dichloromethane and washed with saturated aqueous $NaHCO_3$ and water. Drying over $MgSO_4$ and evaporation of the solvent yielded **13** (880 mg, 88%). R_f 0.83 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR (300 MHz 2D COSY) ($CDCl_3$) δ 3.31 (s, 3 H, OCH_3), 3.58 (dd, 1 H, H-7, $J_{6,7}$ = 5.6 Hz, $J_{7,7'}$ = -9.1 Hz), 3.64 (dd, 1 H, H-7', $J_{6,7'}$ = 7.7 Hz), 3.65 (dd, 1 H, H-1, $J_{1,1'}$ = -11.0 Hz, $J_{1,F}$ = 2.9 Hz), 3.81 (dd, 1 H, H-1', $J_{1',F}$ = 9.3 Hz), 3.99 (dd, 1 H, H-4, $J_{3,4}$ = 10.1 Hz, $J_{4,5}$ = 2.7 Hz), 4.08 (dd, 1 H, H-5, $J_{5,6}$ = 1.3 Hz), 4.12 (ddd, 1 H, H-6), 4.19 (dd, 1 H, H-3, $J_{3,F}$ = 23.2 Hz), 4.46-4.77 (5 × AB, 10 H, 4 × CH_2 benzyl, O-CH_2-O), 7.20-7.47 (m, 20 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 55.2 (OCH_3), 66.6 (d, C-1, $J_{1,F}$ = 36.6 Hz), 67.8 (C-7), 72.1, 73.6, 79.7 (C-4, C-5, C-6), 74.7 (d, C-3, $J_{3,F}$ = 24.9 Hz), 72.3, 73.2, 74.3, 75.2 (4 × CH_2 benzyl), 96.4 (O-CH_2-O), 112.9 (d, C-2, $J_{2,F}$ = 225.7 Hz), 127.0-128.2 ($CH_{arom.}$); 137.6-138.5 (C_{arom}).

Anal. calcd. for $C_{37}H_{41}O_7F$ (616.73): C 72.06, H 6.70; found C 72.11, H 6.79%.

1,3,4,5,7-Penta-*O*-benzyl-1-α-D-*galacto*-heptulopyranosyl Fluoride (14).

Compound **12** (700 mg, 1.0 mmol) was treated with DAST (0.17 mL, 1.3 mmol) as described for the preparation of fluoride **13**, to give **14** in 85% yield (600 mg). R_f 0.80 (diethyl ether/petroleum ether, 1/1, v/v); ^1H NMR (300 MHz 2D COSY) ($CDCl_3$) δ 3.38 (dd, 1 H, H-1, $J_{1,F}$ = 2.0 Hz, $J_{1,1'}$ = -11.0 Hz), 3.61 (dd, 1 H, H-7, $J_{6,7}$ = 5.6 Hz, $J_{7,7'}$ = -9.1 Hz), 3.68 (t, 1 H, H-7', J = 8.4 Hz), 3.87 (dd, 1 H, H-1', $J_{1',F}$ = 7.3 Hz), 3.98 (dd, 1 H, H-4, $J_{3,4}$ = 10.1 Hz, $J_{4,5}$ = 2.7 Hz), 4.09 (bd, 1 H, H-5), 4.14 (bt, 1 H, H-6), 4.31 (dd, 1 H, H-3, $J_{3,F}$ = 23.4 Hz), 4.43-5.01 (5 × AB, 10 H, 5 × CH_2 benzyl), 7.22-7.46 (m, 25 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 68.1 (C-7), 69.4 (d, C-1, $J_{1',F}$ = 38.1 Hz), 72.4, 73.9, 79.9 (C-4, C-5, C-6), 74.8 (d, C-3, $J_{3,F}$ = 23.4 Hz), 72.5, 73.3, 73.4, 74.4, 75.4 (5 × CH_2 benzyl), 113.5 (d, C-2, $J_{2,F}$ =225.7 Hz), 127.3-128.3 ($CH_{arom.}$), 137.7-138.6 ($C_{arom.}$).

Anal. calcd. for $C_{42}H_{43}O_6F$ (662.80): C 76.11, H 6.54, F 2.87; found C 76.21, H 6.70, F 2.91%.

Ethyl 1,3,4,5,7-Penta-*O*-benzyl-2-thio-α-D-*galacto*-heptulopyranoside (15).

Compound **12** (500 mg, 0.76 mmol) was dried by evaporation with toluene (3 × 5 mL), dissolved in trichloroacetonitrile (5 mL) and stirred for 5 min with crushed molecular sieves (0.4 nm). EtSH (100 µL, 1.35 mmol) and BF_3·OEt_2 (93 µL, 0.76 mmol) were added. After stirring for 2.5 h, TLC analysis showed complete disappearance of the starting compound. The reaction mixture was quenched with TEA, filtered and concentrated *in vacuo*. The residue was redissolved in dichloromethane and washed with saturated aqueous $NaHCO_3$ and water. Drying ($MgSO_4$), evaporation of the solvent and subsequent purification of

the crude product by column chromatography (diethyl ether/petroleum ether, 0/1 to 1/3, v/v) yielded **15** as an oil (340 mg, 64%). R_f 0.54 (diethyl ether/petroleum ether, 1/1, v/v); ^1H NMR (300 MHz 2D COSY) ($CDCl_3$) δ 1.20 (t, 3 H, $SCH_2\underline{CH_3}$), 2.50 (ABX, 2 H, $S\underline{CH_2}CH_3$), 3.62 (dd, 1 H, H-7, $J_{6,7}$ = 6.2 Hz, $J_{7,7'}$ = -9.4 Hz), 3.62 (dd, 1 H, H-7', $J_{6,7'}$ = 6.6 Hz), 3.71 (d, 1 H, H-1, $J_{1,1'}$ = -11.6 Hz), 4.02 (dd, 1 H, H-5, $J_{4,5}$ = 2.8 Hz, $J_{5,6}$ = 1.1 Hz), 4.04 (d, 1 H, H-1'), 4.10 (dd, 1 H, H-4, $J_{3,4}$ = 9.9 Hz), 4.14 (ddd, 1 H, H-6), 4.37-5.05 (4 × AB, 1 s, 10 H, 5 × CH_2 benzyl), 4.60 (d, 1 H, H-3), 7.12-7.38 (m, 25 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 14.9 ($SCH_2\underline{C}H_3$), 20.1 ($S\underline{C}H_2CH_3$), 69.2, 72.8 (C-1 and C-7), 72.1, 74.5, 75.9, 81.2 (C-3, C-4, C-5, C-6), 73.2, 73.3, 73.6, 74.3, 75.2 (5 × CH_2 benzyl), 92.2 (C-2), 127.0-128.2 ($CH_{arom.}$), 137.0-139.0 ($C_{arom.}$).
Anal. calcd. for $C_{44}H_{48}O_6S$ (704.93): C 74.97, H 6.87; found C 75.09, H 6.96%.

2-*O*-Acetyl-3,4,5,7-tetra-*O*-benzyl-α-D-galactono-1,5-lactone (17).
A solution of DMSO (0.53 mL, 7.4 mmol) in dichloromethane (1 mL) was added to a cooled (-60°C) solution of oxalylchloride (0.30 mL, 3.4 mmol) in dichloromethane (15 mL) under a nitrogen atmosphere. After stirring for 15 min at -60°C compound **16** (1.60 g, 3.1 mmol), dissolved in dichloromethane (2 mL), was added dropwise and stirring was continued for 30 min at this temperature. TEA (2 mL) was added and the reaction mixture was allowed to warm to room temperature. After quenching with water the mixture was extracted with dichloromethane. The organic layer was washed with water, dried ($MgSO_4$) and concentrated *in vacuo*. Subsequent purification of the crude product by column chromatography (diethyl ether/petroleum ether, 0/1 to 1/3, v/v) furnished lactone **17**. Yield 1.30 g (81%); R_f 0.55 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR ($CDCl_3$) δ 2.08 (s, 3 H, CH_3 acetyl), 3.69 (dd, 1 H, H-6, $J_{5,6}$ = 5.9 Hz, $J_{6,6'}$ = -9.0 Hz), 3.73 (t, 1 H, H-6', J = 9.3 Hz), 4.02 (dd, 1 H, H-3, $J_{2,3}$ = 10.0 Hz, $J_{3,4}$ = 2.2 Hz), 4.23 (bt, 1 H, H-4, J = 1.8 Hz), 4.43 (ddd, 1 H, H-5), 5.46 (d, 1 H, H-2), 4.46-4.98 (3 × AB, 6 H, 3 × CH_2 benzyl), 7.25-7.37 (m, 15 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 20.3 (CH_3 acetyl), 67.2 (C-6), 71.1, 71.6, 77.3, 77.4 (C-2, C-3, C-4, C-5), 71.7, 73.3, 74.6 (3 × CH_2 benzyl), 127.0-128.2 ($CH_{arom.}$), 137.1-137.3 (C_{arom}), 166.4 (C-1)169.9 (C=O acetyl).

4,5,7-Tri-*O*-benzyl-1-*O*-methoxymethyl-α-D-*galacto*-heptulopyranose (18).
Compound **17** (1.40 g, 2.9 mmol) was treated with reagent **8a** (3.2 g, 8.7 mmol) as described for the preparation of derivative **11**. Work-up and purification afforded **18** as an oil in 74% yield (1.11 g). R_f 0.10 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR ($CDCl_3$) δ 3.37 (s, 3 H, OCH_3), 3.39-3.78 (m, 4 H, H-4, H-6, H-7), 3.77 (AB, 2 H, H-1), 3.97 (d, 1 H, H-3, $J_{3,4}$ = 9.8 Hz), 4.02 (dd, 1 H, H-5, $J_{4,5}$ = 2.6 Hz, $J_{5,6}$ = 1.0 Hz), 4.13 (ddd, 1 H, H-6, $J_{6,7}$ = 5.9 Hz, $J_{6,7'}$ = 7.2 Hz), 4.46-4.91 (s, 3 × AB, 8 H, 3 × CH_2 benzyl, O-CH_2-O), 7.24-7.38 (m, 15 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 55.2 (OCH_3), 68.6, 70.6 (C-1, C-7), 69.1, 69.9, 73.6, 79.8 (C-3, C-4, C-5, C-6), 72.1, 73.1, 74.2 (3 × CH_2 benzyl), 96.8 (C-2, O-CH_2-O), 127.3-128.2 ($CH_{arom.}$), 137.7-138.4 ($C_{arom.}$).

3-*O*-Benzoyl-4,5,7-tri-*O*-benzyl-1-*O*-methoxymethyl-α-D-*galacto*-heptulopyranosyl Fluoride (19).
Compound **18** (740 mg, 1.4 mmol) was treated with DAST (0.21 mL, 1.6 mmol) as described for the preparation of fluoride **13** to give the anomeric fluoride [610 mg, R_f 0.48 (diethyl ether/petroleum ether, 2/1, v/v)], which was subsequently dried by evaporation with pyridine (3 × 3 mL) and dissolved in pyridine (5 mL). Benzoyl chloride (0.16 mL, 1.4 mmol) was added and after stirring for 2 h TLC analysis indicated completion of the reaction. Water was added and the mixture was concentrated *in vacuo*. A solution of the residue in dichloromethane was washed with saturated aqueous $NaHCO_3$ and water, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was purified by column chromatography (diethyl ether/petroleum ether, 0/1 to 1/2, v/v) to give pure **19**. Yield: 670 mg (75% over two steps) R_f 0.81 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR (400 MHz 2D COSY) ($CDCl_3$) δ 3.24 (s, 3 H, OCH_3), 3.48-3.72 (m, 4 H, H-7, H-1), 4.03 (dd, 1 H, H-4, $J_{3,4}$ = 10.3 Hz, $J_{4,5}$ = 2.6 Hz), 4.13 (bd, 1 H, H-5), 4.19 (bt, 1 H, H-6, $J_{6,7}$ = $J_{6,7'}$ = 6.9 Hz), 4.46-5.01 (4 × AB, 8 H, 3 × CH_2 benzyl, O-CH_2-O), 5.96 (dd, 1 H, H-3, $J_{3,F}$ = 23.1 Hz), 7.11-8.08 (m, 19 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 55.2 (OCH_3), 67.1 (d, C-1, $J_{1,F}$ = 32.3 Hz), 67.9 (C-7), 69.0 (d, C-3, $J_{3,F}$ =24.9 Hz), 71.9, 73.3, 74.4 (3 × CH_2 benzyl), 72.4, 72.8, 77.2 (C-4, C-5, C-6), 96.5 (O-CH_2-O), 112.6 (d, C-2, $J_{2,F}$ =227.1 Hz), 127.3-133.1 ($CH_{arom.}$), 137.4-138.2 ($C_{arom.}$), 165.3 (C=O, benzoyl).
Anal. calcd. for $C_{37}H_{39}O_8F$ (630.72): C 70.46, H 6.23; found C 70.51, H 6.21%.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,5,7-tetra-*O*-benzyl-1-*O*-methoxymethyl-α-D-*galacto*-heptulo-pyranosyl)-α-D-mannopyranoside (23).

Cp_2ZrCl_2 (190 mg, 0.65 mmol) and activated AgOTf (165 mg, 0.64 mmol) were dissolved in dichloromethane (5 mL) and stirred for 5 min with crushed molecular sieves (0.4 nm) under a nitrogen atmosphere and under the exclusion of light. A solution of compound **20** (300 mg, 0.65 mmol), dried by evaporation with toluene (3 × 2 mL), in dichloromethane (1 mL) was added and stirring was continued. After 5 min donor **13** (200 mg, 0.32 mmol), dried by evaporation with toluene (3 × 2 mL), dissolved in dichloromethane (1 mL) was added at -25°C and stirring was continued for 1 h at this temperature, when TLC analysis showed complete disappearance of the fluoride. The reaction mixture was quenched with TEA, filtered and washed with a 10% NH_4Cl solution and with water. After drying ($MgSO_4$) and concentration, the crude product was purified by gel filtration (dichloromethane/methanol, 2/1, v/v) to give **23** as an oil. Yield 186 mg (54 %), R_f 0.83 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR (300 MHz 2D COSY) ($CDCl_3$) δ 3.11 (s, 3 H, Man: OCH_3), 3.26 (s, 3 H, Gal: OCH_3), 3.55 (dd, 1 H, Gal: H-7, $J_{6,7}$ = 5.6 Hz, $J_{7,7'}$ = -9.4 Hz), 3.59 (d, 1 H, Gal: H-1, $J_{1,1'}$ = -10.7 Hz), 3.62-3.80 (m, 6 H, Gal: H-7', Man: H-2, H-4, H-5, H-6, H-6'), 3.75 (d, 1H, Gal: H-1'), 3.84 (dd, 1 H, Man: H-3, $J_{2,3}$ = 3.2 Hz, $J_{3,4}$ = 8.7 Hz), 3.99 (dd, 1 H, Gal: H-5, $J_{4,5}$ = 2.8 Hz, $J_{5,6}$ = 1.3 Hz), 4.03 (dd, 1 H, Gal: H-4, $J_{3,4}$ = 10.0 Hz), 4.17 (ddd, 1 H, Gal: H-6, $J_{6,7'}$ = 5.6 Hz), 4.29 (d, 1 H, Gal: H-3), 4.57 (s, 2 H, CH_2 benzyl), 4.61 (d, 1 H, Man: H-1), 4.44-4.83 (7 × AB, 14 H, 6 × CH_2 benzyl, O-CH_2-O), 7.14-7.35 (m, 35 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 54.3 (Man: OCH_3), 55.4 (Gal: OCH_3), 61.6 (Man: C-6), 67.3, 68.6 (Gal: C-1, C-7), 69.0, 69.9, 71.5, 74.6, 75.5, 76.1, 79.9, 80.3 (Gal: C-3, C-4, C-5, C-6, Man: C-2, C-3, C-4, C-5), 69.0, 72.1, 72.2, 72.5, 73.0, 74.2, 74.7 (7 × CH_2 benzyl), 96.7 (O-CH_2-O), 98.5 (Man: C-1), 101.1 (Gal: C-2), 127.1-128.2 ($CH_{arom.}$), 138.2-139.0 ($C_{arom.}$). ^1H NMR (300MHz 2D NOESY): A NOE effect was observed between H-1 and H-3 of the galactose moiety.

Anal. calcd. for $C_{65}H_{72}O_{13}$ (1061.28): C 73.57, H 6.84; found C 73.72, H 6.91%.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(1,3,4,5,7-penta-*O*-benzyl-α-D-*galacto*-heptulopyranosyl)-α-D-mannopyranoside (24).

Method A: Donor **14** (125 mg, 0.19 mmol) and methyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (**20**, 105 mg, 0.23 mmol) were dried by evaporation with toluene (3 × 2 mL), dissolved in dichloromethane (5 mL) and stirred for 5 min with crushed molecular sieves (0.4 nm) under a nitrogen atmosphere at -20°C. $BF_3{\cdot}OEt_2$ (10 µL, 0.081 mmol) was added and stirring was continued for 45 min, when TLC analysis (diethyl ether/petroleum ether, 2/1, v/v) showed complete disappearance of the fluoride. The reaction mixture was quenched with TEA, filtered, diluted with dichloromethane and washed with a 10% NH_4Cl solution and water. Drying ($MgSO_4$), evaporation of the solvent and subsequent purification of the residue by column chromatography (diethyl ether/petroleum ether, 0/1 to 1/2, v/v) yielded **24** as an oil (122 mg, 58%).

Method B: Compound **15** (55 mg, 0.078 mmol) and acceptor **20** (36 mg, 0.078 mmol) were dried by evaporation with 1,2-dichloroethane (3 × 2 mL), dissolved in dichloroethane/diethyl ether (1/4, v/v, 5 mL) and stirred for 30 min with crushed molecular sieves (0.4 nm) under a nitrogen atmosphere. IDCP (73 mg, 0.156 mmol) was added and stirring was continued for 1 h, when TLC analysis (diethyl ether/petroleum ether, 1/1, v/v) showed complete disappearance of the donor. The reaction mixture was filtered, diluted with diethyl ether and washed with a 1 M $Na_2S_2O_3$ solution, saturated aqueous $NaHCO_3$, dried over $MgSO_4$ and concentrated *in vacuo*. Purification as described for *method A* yielded **24** as an oil (65 mg, 75%), R_f 0.44 (diethyl ether/petroleum ether, 1/1, v/v); ^1H NMR (300 MHz 2D COSY) ($CDCl_3$) δ 3.09 (s, 3 H, OCH_3), 3.53 (d, 1 H, Gal: H-1, $J_{1,1'}$ = -10.8 Hz), 3.59 (dd, 1 H, Gal: H-7, $J_{6,7}$ = 5.7 Hz, $J_{7,7'}$ = -9.3 Hz), 3.60-3.73 (m, 6 H, Gal: H-7', Man: H-2, H-4, H-5, H-6, H-6'), 3.77 (d, 1 H, Gal: H-1'), 3.83 (dd, 1 H, Man: H-3, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 8.7 Hz), 4.01 (bs, 1 H, Gal: H-5), 4.02 (bd, 1 H, Gal: H-4, $J_{3,4}$ = 11.7 Hz), 4.18 (bt, 1 H, Gal: H-6, $J_{6,7}$, $J_{6,7'}$ = 6.6 Hz), 4.34 (d, 1 H, Gal: H-3), 4.61 (d, 1 H, Man: H-1, $J_{1,2}$ = 1.8 Hz), 4.32-5.03 (2 × s and 5 × AB, 14 H, 7 × CH_2 benzyl), 7.13-7.37 (m, 35 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 54.3 (OCH_3), 61.6 (Man: C-6), 68.7, 70.2 (Gal: C-1, C-7), 70.0, 71.6, 74.6, 75.0, 75.5, 76.2, 79.8, 80.2 (Gal; C-3, C-4, C-5, C-6, Man: C-2, C-3, C-4, C-5), 72.0, 72.2, 72.5, 73.0, 73.4, 74.3, 2 × 74.8 (8 × CH_2 benzyl), 98.4 (Man: C-1), 101.5 (Gal: C-2), 127.0-128.2 ($CH_{arom.}$ benzyl), 138.2-139.1 ($C_{arom.}$ benzyl).

Anal. calcd. for $C_{70}H_{74}O_{12}$ (1107.36): C 75.93, H 6.74; found C 76.01, H 6.70%.

Methyl 6-*O*-(3-*O*-Benzoyl-4,5,7-tri-*O*-benzyl-1-*O*-methoxymethyl-α/β-D-*galacto*-heptulopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (25).

Donor **19** (100 mg, 0.16 mmol) was treated at -25°C with a mixture of Cp_2ZrCl_2 (90 mg, 0.32 mmol), activated AgOTf (82 mg, 0.32) and acceptor **20** (150 mg, 0.32 mmol) as described for the synthesis of disaccharide **23**. After 2.5 h TLC analysis showed

complete disappearance of the fluoride, and the mixture was worked up as described earlier. Three disaccharides were obtained after gel filtration (dichloromethane/methanol, 2/1, v/v), which were separated by silicagel column chromatography (diethyl ether/petroleum ether, 0/1 to 1/2, v/v). First **25α** was eluted (28 mg, R_f 0.59, diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR (400 MHz 2D COSY) ($CDCl_3$) δ 3.10 (s, 3 H, Man: OCH_3), 3.13 (s, 3 H, Gal: OCH_3), 3.55 (dd, 1 H, Gal: H-7, $J_{6,7}$ = 5.7 Hz, $J_{7,7'}$ = -9.2 Hz), 3.60 (s, 2 H, Gal: H-1), 3.61-3.88 (m, 7 H, Gal: H-7', Man: H-2, H-3, H-4, H-5, H-6), 4.03 (bs, 1 H, Gal: H-5), 4.04 (dd, 1 H, Gal: H-4, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 2.7 Hz), 4.15 (bt, 1 H, Gal: H-6, $J_{6,7}$ = 6.5 Hz), 4.37-5.02 (1 s, 6 × AB, 14 H, 6 × CH_2 benzyl, O-CH_2-O), 4.65 (d, 1 H, Man: H-1, $J_{1,2}$ = 1.9), 5.96 (d, 1 H, Gal: H-3), 7.07-8.07 (m, 35 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 54.1 (Man: OCH_3), 55.4 (Gal: OCH_3), 61.4 (Man: C-6), 67.3, 68.6 (Gal: C-1, C-7), 70.2, 71.2, 71.4, 73.6, 74.6, 75.5, 77.6, 80.4 (Gal: C-3, C-4, C-5, C-6, Man: C-2, C-3, C-4, C-5), 71.6, 72.0, 72.6, 72.2, 74.3, 75.1 (6 × CH_2 benzyl), 96.8 (O-CH_2-O), 98.6 (Man: C-1), 99.1 (Gal: C-2), 127.2-132.6 ($CH_{arom.}$), 130.6-138.8 ($C_{arom.}$), 165.7 (C=O).

Next **25β** was eluted: 26 mg; R_f 0.55; ^1H NMR (400 MHz 2D COSY) ($CDCl_3$) δ 3.18 (s, 3 H, Man: OCH_3), 3.22 (s, 3 H, Gal: OCH_3), 3.45 (dd, 1 H, Gal: H-7, $J_{6,7}$ = 5.2 Hz, $J_{7,7'}$ = -8.8 Hz), 3.52 (t, 1 H, Gal: H-7', $J_{6,7'}$, $J_{7,7'}$ = -8.5 Hz), 3.63-3.69 (m, 2 H, Man: H-2, H-5), 3.68 (d, 1 H, Gal: H-1, $J_{1,1'}$ = -10.6 Hz), 3.82 (dd, 1 H, Man: H-3, $J_{2,3}$ = 3.1 Hz, $J_{3,4}$ = 9.1 Hz), 3.88 (t, 1 H, Man: H-4, $J_{3,4}$, $J_{4,5}$ = 9.4 Hz), 4.04-4.08 (m, 2 H, Gal: H-5, Man: H-6), 4.08 (d, 1H, Gal: H-1'), 4.13 (dd, 1 H, Man: H-6', $J_{5,6'}$ = 4.6 Hz, $J_{6,6'}$ = -10.1 Hz), 4.18 (dd, 1 H, Gal: H-4, $J_{3,4}$ = 10.3 Hz, $J_{4,5}$ = 2.6 Hz), 4.30 (bdd, 1 H, Gal: H-6), 4.24; 4.43-5.02 (3 s, 4 × AB, 14 H, 6 × CH_2 benzyl O-CH_2-O), 4.64 (d, 1 H, Man: H-1, $J_{1,2}$ = 1.9), 6.16 (d, 1 H, Gal: H-3), 7.07-8.01 (m, 35 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 54.4 (Man: OCH_3), 55.4 (Gal: OCH_3), 60.5 (Man: C-6), 68.7, 71.2, 71.4, 72.0, 72.2, 73.3, 74.3 (Gal: C-1, C-7, 6 × CH_2 benzyl), 69.5, 71.1, 72.7, 72.9, 74.5, 74.6, 78.3, 80.3 (Gal: C-3, C-4, C-5, C-6, Man: C-2, C-3, C-4, C-5), 96.8 (O-CH_2-O), 98.4 (Man: C-1), 100.1 (Gal: C-2), 127.0-132.8 ($CH_{arom.}$), 130.4-139.1 ($C_{arom.}$), 165.1 (C=O).

Anal. calcd. for $C_{65}H_{70}O_{14}$ (1075.27): C 72.61, H 6.56; found C 72.53, H 6.61%.

Compound **26** was eluted last (28 mg, R_f 0.38); ^1H NMR ($CDCl_3$) δ (300 MHz 2D COSY) 3.15 (s, 3 H, OCH_3), 3.28 (bs, 1 H, Gal: H-1), 3.56-3.66 (m, 4 H, Gal: H-7', Man: H-2, H-5), 3.68 (bs, 1 H, Gal: H-1'), 3.75 (dd, 1 H, Man: H-6, $J_{5,6}$ = 4.4 Hz, $J_{6,6'}$ = -12.3 Hz), 3.83 (dd, 1 H, Man: H-3, $J_{2,3}$ = 3.0 Hz, $J_{3,4}$ = 9.5 Hz), 4.86-3.92 (m, 2 H, Gal: H-6, Man: H-6'), 3.99-4.03 (m, 2 H, Gal: H-4, H-5), 4.23 (t, 1 H, Man: H-4, J = 10.0 Hz), 4.24, 4.42-5.02 (6 AB, 12 H, 5 × CH_2 benzyl), 4.49 (d, 1 H, Man: H-1, $J_{1,2}$ = 1.8 Hz), 5.93 (d, 1 H, Gal: H-3, $J_{3,4}$ = 9.8 Hz), 7.01-8.14 (m, 35 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 54.6 (OCH_3), 59.9 (Man: C-6), 63.9 (Gal: C-1), 68.8 (Gal: C-7), 71.2, 72.0, 73.6, 74.8, 77.4, 79.8 (Gal: C-3, C-4, C-5, C-6, Man: C-2, C-3, C-4, C-5), 71.9, 72.0, 72.2, 73.4, 74.4, 74.8 (6 × CH_2 benzyl), 99.1 (Man: C-1), 99.4 (Gal: C-2), 127.4-132.5 ($CH_{arom.}$), 130.4-138.6 ($C_{arom.}$), 166.3 (C=O). Total yield: 49%.

^1H NMR (300 MHz 2D NOESY): A NOE effect was observed between H-3 and H-1 of the galactose moiety for **25α** while **25β** showed a NOE effect between H-4 and H-1.

1,3,4,5-Tetra-*O*-benzyl-α-L-*fuco*-heptulopyranose (28).

Compound **27** (2.15 g, 5.0 mmol) was treated with reagent **8b** (6.59 g, 16.0 mmol) as described for the preparation of derivative **11**. Work-up and purification furnished **28** as an oil in 92% yield (2.36 g). R_f 0.24 (diethyl ether/petroleum ether, 1/1, v/v); ^1H NMR ($CDCl_3$) δ 1.18 (d, 3 H, H-7, $J_{6,7}$ = 6.4 Hz), 3.44 (s, 1 H, OH), 3.47 (AB, 2 H, H-1), 3.69 (dd, 1 H, H-5, $J_{4,5}$ = 2.3 Hz, $J_{5,6}$ = 1.3 Hz), 3.95 (d, 1 H, H-3, $J_{3,4}$ = 9.8 Hz), 4.02 (dd, 1 H, H-4), 4.08 (dq, 1 H, H-6), 4.56-5.03 (2 s, 2 AB, 8 H, 4 × CH_2 benzyl), 7.17-7.41 (m, 20 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 16.8 (C-7), 67.2, 75.5, 77.1, 80.9 (C-3, C-4, C-5, C-6), 72.0, 73.4, 73.6, 74.4, 75.2 (C-1, 4 × CH_2 benzyl), 97.6 (C-2), 126.7-128.3 ($CH_{arom.}$), 137.7-138.5 ($C_{arom.}$).

Anal. calcd. for $C_{35}H_{38}O_6$ (554.69): C 75.79, H 6.91; found C 75.70, H 6.98%.

Ethyl 1,3,4,5-Tetra-*O*-benzyl-2-thio-α-L-*fuco*-heptulopyranoside (29).

Compound **28** (2.00 g, 3.61 mmol) was treated with EtSH (0.32 mL, 4.30 mmol) and $BF_3{\cdot}OEt_2$ (65 µL, 0.53 mmol) as described for the preparation of compound **15**. After 2 h, an additional amount of $BF_3{\cdot}OEt_2$ (65 µL) was added and stirring was continued for another 2 h when TLC analysis indicated completion of the reaction. Work-up and purification yielded **29** as an oil (1.94 g, 85%). R_f 0.70 (diethyl ether/petroleum ether, 1/1, v/v); ^1H NMR ($CDCl_3$) δ 1.21 (t, 3 H, $SCH_2\underline{CH_3}$), 1.25 (d, 3 H, H-7, $J_{6,7}$ = 6.4 Hz), 2.45 (ABX_3, 2 H, $SC\underline{H_2}CH_3$), 3.69 (d, 1 H, H-1, $J_{1,1'}$ = -11.6 Hz), 3.70 (bd, 1 H, H-5, $J_{4,5}$ = 2.8 Hz), 4.01 (bq, 1 H, H-6), 4.09 (dd, 1 H, H-4, $J_{3,4}$ = 9.9 Hz), 4.38-5.09 (s, 2 AB, 8 H, 3 × CH_2 benzyl), 4.56 (d, 1 H, H-3), 7.15-7.41 (m, 15 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 15.1 ($SCH_2\underline{CH_3}$), 17.0 (C-7), 20.2 ($S\underline{CH_2}CH_3$), 69.1, 75.8, 77.4, 81.9 (C-3, C-4, C-5, C-6),

72.7, 73.3, 73.6, 74.5, 75.1 (C-1, 4 × CH_2 benzyl), 92.2 (C-2), 127.0-128.2 ($CH_{arom.}$), 138.8-140.0 ($C_{arom.}$).
Anal. calcd. for $C_{37}H_{42}O_5S$ (598.81): C 74.22, H 7.07; found C 74.35, H 7.14%.

Ethyl 4,5,6-Tri-*O*-benzyl-2-deoxy-3-*O*-trimethylsilyl-α-L-*fuco*-3-octulopyranosonate (30) and Ethyl 4,5,6-Tri-*O*-benzyl-2-deoxy-α-L-*fuco*-3-octulopyranosonate (31).

Lactone **27** (3.0 g, 6.94 mmol), was dried by evaporation with toluene (3 × 5 mL) and dissolved in THF (30 mL). $TMSCH_2COOEt$ (2.54 mL, 13.88 mmol) and TBAF (2.1 mL, 1.0 M solution in THF) were added and the mixture was stirred for 3.5 h at 50°C. The mixture was diluted with diethyl ether, washed with ice water and brine, dried (Na_2SO_4) and concentrated *in vacuo*. Purification by column chromatography (diethyl ether/petroleum ether, 0/1 to 1/3, v/v) yielded **30** as an amorphous solid (2.92 g, 71%). R_f 0.93 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR ($CDCl_3$) δ 1.06 (d, 3 H, H-8, $J_{7,8}$ = 6.2 Hz), 1.14 (t, 3 H, $OCH_2C\underline{H}_3$), 2.64 (AB, 2 H, H-2), 3.33 (dd, 1 H, H-5, $J_{4,5}$ = 10.1 Hz, $J_{5,6}$ = 2.8 Hz), 3.44 (dd, 1 H, H-6, $J_{6,7}$ = 1.1 Hz), 3.66 (dq, 1 H, H-7), 3.74 (d, 1 H, H-4), 3.98 (ABX_3, 2 H, $OC\underline{H}_2CH_3$), 4.44-4.92 (3 AB, 6 H, 3 × CH_2 benzyl), 7.07-7.28 (m, 15 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 1.58 ($Si(CH_3)_3$), 14.1 ($OCH_2\underline{C}H_3$), 16.5 (C-8),38.0 (C-2), 60.0 ($O\underline{C}H_2CH_3$), 69.6, 77.4, 80.8, 83.0 (C-4, C-5, C-6, C-7), 72.8, 74.7 (3 × CH_2 benzyl), 101.4 (C-3), 127.0-128.1 ($CH_{arom.}$), 138.5-138.7 ($C_{arom.}$), 169.5 (C-1). Further elution gave **31** as an oil (0.47 g, 13%). R_f 0.70; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 13.8 ($OCH_2\underline{C}H_3$), 16.5 (C-8),40.5 (C-2), 60.7 ($O\underline{C}H_2CH_3$), 67.0, 77.3, 78.1, 80.6 (C-4, C-5, C-6, C-7), 72.5, 74.5 75.0 (3 × CH_2 benzyl), 97.3 (C-3), 126.7-128.4 ($CH_{arom.}$), 138.0-138.5 ($C_{arom.}$), 172.5 (C-1).

Ethyl (Ethyl 4,5,6-Tri-*O*-benzyl-2-deoxy-3-thio-α-L-*fuco*-3-octulopyranosid)onate (32).

Method A (from 30): Compound **30** (1.10 g, 1.86 mmol) was dried by evaporation with toluene (3 × 5 mL) and dissolved in dichloromethane (10 mL). Crushed molecular sieves (0.4 nm), EtSH (0.55 mL, 3.72 mmol) and TMSOTf (36 μL, 0.19 mmol) were added and the mixture was stirred for 10 min, when TLC analysis (diethyl ether/petroleum ether, 2/1, v/v) showed complete disappearance of the starting compound. The reaction mixture was quenched with TEA, filtered and washed with a 10% NH_4Cl solution and water. Drying ($MgSO_4$), evaporation of the solvent and subsequent purification of the crude product by column chromatography (diethyl ether/petroleum ether, 0/1 to 1/8, v/v) yielded **32** as an oil (0.99 g, 94%).

Method B (from 31): Compound **31** (410 mg, 0.79 mmol) was dried by evaporation with toluene (3 × 2 mL) and dissolved in 5 mL dichloromethane. Crushed molecular sieves (0.4 nm), DIPEA (0.15 mL, 0.86 mmol) and Tf_2O (0.14 mL, 0.83 mmol) were subsequently added. After stirring for 5 min, EtSH (0.24 mL, 1.61 mmol) was added and stirring was continued for 1 h, when TLC analysis showed completion of the reaction. The mixture was filtered and washed with saturated aqueous $NaHCO_3$ and with water. Drying ($MgSO_4$), evaporation of the solvent and subsequent purification as described for *method A* yielded **32** as an oil (370 mg, 83%). R_f 0.93 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR ($CDCl_3$) δ 1.08 (t, 3 H, $SCH_2C\underline{H}_3$), 1.19 (d, 3 H, H-8, $J_{7,8}$ = 6.4 Hz), 1.23 (t, 3 H, $OCH_2C\underline{H}_3$), 2.45 (ABX_3, 2 H, $SC\underline{H}_2CH_3$), 2.96 (AB, 2 H, H-2), 3.66 (bd, 1 H, H-6, $J_{5,6}$ = 1.9 Hz), 3.92-4.12 (m, 4 H, H-5, H-7, $OC\underline{H}_2CH_3$), 4.55-5.07 (s, 2 AB, 6 H, 3 × CH_2 benzyl), 4.64 (d, 1 H, H-4, $J_{4,5}$ = 9.6 Hz), 7.22-7.37 (m, 15 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 13.8, 14.1 ($SCH_2\underline{C}H_3$, $OCH_2\underline{C}H_3$), 16.4 (C-8),20.0 ($S\underline{C}H_2CH_3$), 43.8 (C-2), 60.3 ($O\underline{C}H_2CH_3$), 68.7, 77.2, 77.3, 81.6 (C-4, C-5, C-6, C-7), 72.3, 74.4, 75.0 (3 × CH_2 benzyl), 90.1 (C-3), 126.9-128.1 ($CH_{arom.}$), 138.4-138.8 ($C_{arom.}$), 168.6 (C-1).

Ethyl 4,5,6-Tri-*O*-benzyl-2-deoxy-3-thio-α-L-*fuco*-3-octulopyranoside (33).

Compound **32** (1.36 g, 2.41 mmol), dried by evaporation with toluene (3 × 5 ml) was dissolved in THF (5 mL) and added to a suspension of $LiALH_4$ (100 mg, 2.64 mmol) in THF (15 mL) at 0°C. The mixture was allowed to warm to room temperature and then refluxed until TLC analysis showed complete disappearance of the starting compound (15 min). After cooling to 0°C the excess $LiAlH_4$ was carefully destroyed with water, 20 mL of a 10% NH_4Cl solution and Celite were added and stirring was continued for 30 min. The mixture was filtered and extracted with diethyl ether. The organic layer was washed with brine, dried (Na_2SO_4) and concentrated *in vacuo* to give compound **33** in a quantitative yield. R_f 0.74 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR ($CDCl_3$) δ 1.17 (d, 3 H, H-8, $J_{7,8}$ = 6.4 Hz), 1.23 (t, 3 H, $SCH_2C\underline{H}_3$), 2.02-2.21 (m, 2 H, H-2), 2.31-2.59 (ABX_3, 2 H, $SC\underline{H}_2CH_3$), 2.74 (m, 1 H, OH), 3.40-3.59 (m, 2 H, H-1), 3.69 (bd, 1 H, H-6, $J_{5,6}$ = 2.6 Hz), 4.04 (bq, 1 H, H-7), 4.11 (dd, 1 H, H-5, $J_{4,5}$ = 9.9 Hz), 4.24 (d, 1 H, H-4), 4.62-5.05 (s, 2 AB, 6 H, 3 × CH_2 benzyl), 7.26-7.36 (m, 15 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 14.3 ($SCH_2\underline{C}H_3$), 16.6 (C-8), 20.0 ($S\underline{C}H_2CH_3$), 40.2 (C-2), 58.7 (C-1), 68.3, 76.5, 76.7, 81.9 (C-4, C-5, C-6, C-7), 72.2, 74.2, 74.8 (3 × CH_2 benzyl), 92.2 (C-3), 94.8 ($O\underline{C}H_2O$), 127.2-128.1 ($CH_{arom.}$), 138.0-138.5 ($C_{arom.}$).

Ethyl 4,5,6-Tri-*O*-benzyl-1-*O*-*tert*-butyldiphenylsilyl-2-deoxy-3-thio-α-L-*fuco*-3-octulopyranoside (34).
Compound **33** (290 mg, 0.52 mmol) was dried by evaporation with toluene (3 × 5 mL), dissolved in pyridine (3 mL) and TBDPSCl was added (0.14 mL, 0.55 mmol). After stirring for 16 h water was added and the mixture was concentrated *in vacuo*. The residue was redissolved in dichloromethane, the solution was washed with saturated aqueous $NaHCO_3$ and with water. Drying ($MgSO_4$), evaporation of the solvent and subsequent purification of the crude product by column chromatography (diethyl ether/petroleum ether, 0/1 to 1/8, v/v) yielded **34** as an oil (380 mg, 91%). R_f 0.96 (diethyl ether/petroleum ether, 2/1, v/v); ^{1}H NMR ($CDCl_3$) δ 1.02 (s, 9 H, $C(CH_3)_3$), 1.14 (d, 3 H, H-8, $J_{7,8}$ = 6.4 Hz), 1.16 (t, 3 H, $SCH_2\underline{CH_3}$), 2.15-2.47 (m, 4 H, H-2, $SC\underline{H_2}CH_3$), 3.63 (dd, 1 H, H-6, $J_{5,6}$ = 2.3 Hz, $J_{6,7}$ = 1.1 Hz), 3.80-4.05 (m, 4 H, H-1, H-5, H-7), 4.13 (d, 1 H, H-4, $J_{3,4}$ = 9.6 Hz), 4.56-4.98 (s, 2 AB, 6 H, 3 × CH_2 benzyl), 7.20-7.40, 7.60-7.67 (m, 25 H, $H_{arom.}$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.6 ($SCH_2\underline{CH_3}$), 17.0 (C-8), 19.3 ($SiC(\underline{CH_3})_3$), 20.3 ($S\underline{CH_2}CH_3$), 27.0 ($SiC(\underline{CH_3})_3$), 42.4 (C-2), 60.4 (C-1), 68.5, 77.3, 79.3, 82.3 (C-4, C-5, C-6, C-7), 72.7, 74.5, 75.2 (3 × CH_2 benzyl), 90.9 (C-3), 127.3-129.5, 135.7 ($CH_{arom.}$), 134.0, 138.9 ($C_{arom.}$).
Anal. calcd. for $C_{47}H_{56}O_5SSi$ (761.12): C 74.17, H 7.42; found C 74.28, H 7.49%.

Ethyl 4,5,6-Tri-*O*-benzyl-2-deoxy-3-thio-1-*O*-[2-(trimethylsilyl)ethoxymethyl]-α-L-*fuco*-3-octulopyranoside (35).
Compound **33** (1.09 g, 2.09 mmol), dried by evaporation with toluene (3 × 5 ml), was dissolved in 15 mL dioxane. DIPEA (1.13 mL, 6.27 mmol) and SEMCl (0.92 mL, 5.23 mmol) were added and the mixture was stirred for 2.5 h. Excess SEMCl was destroyed with methanol (0.5 mL), water was added and the mixture was extracted with diethyl ether. The organic layer was washed with a 10% NH_4Cl solution and brine, dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the residue by column chromatography (diethyl ether/petroleum ether, 0/1 to 1/10, v/v) gave **35** as an oil in a 87% yield (1.19 g). R_f 0.98 (diethyl ether/petroleum ether, 2/1, v/v); ^{1}H NMR ($CDCl_3$) δ 0.82-0.91 (m, 2 H, $OCH_2C\underline{H_2}Si$), 1.18 (t, 3 H, $SCH_2\underline{CH_3}$), 1.24 (d, 3 H, H-8, $J_{7,8}$ = 6.4 Hz), 2.25-2.55 (m, 4 H, H-2, $SC\underline{H_2}CH_3$), 3.49-3.72 (m, 5 H, H-1, H-6, $OC\underline{H_2}CH_2Si$), 3.99 (bq, 1 H, H-7), 4.07 (dd, 1 H, H-5, $J_{4,5}$ = 9.2 Hz, $J_{5,6}$ = 2.1 Hz), 4.16 (d, 1 H, H-4), 4.52-5.02 (s, 3 AB, 8 H, 3 × CH_2 benzyl, $OC\underline{H_2}O$), 7.22-7.36 (m, 15 H, $H_{arom.}$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ -1.4 ($Si(CH_3)_3$), 14.1 ($SCH_2\underline{CH_3}$), 16.8 (C-8), 18.0 ($OCH_2\underline{CH_2}Si$), 20.2 ($S\underline{CH_2}CH_3$), 39.3 (C-2), 63.8, 64.9 (C-1, $O\underline{CH_2}CH_2Si$), 68.5, 77.2, 78.5, 82.1 (C-4, C-5, C-6, C-7), 72.6, 74.4, 75.1 (3 × CH_2 benzyl), 90.8 (C-3), 94.8 ($O\underline{CH_2}O$), 127.2-128.3 ($CH_{arom.}$), 138.5-139.0 ($C_{arom.}$).
Anal. calcd. for $C_{37}H_{52}O_6SSi$ (652.97): C 68.06, H 8.03; found C 68.13, H 8.14%.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(1,3,4,5-tetra-*O*-benzyl-α-L-*fuco*-heptulopyranosyl)-α-D-mannopyra-noside (36).
Donor **28** (100 mg, 0.18 mmol) and acceptor **20** (100 mg, 0.21 mmol) were dried by evaporation with toluene (3 × 2 mL), dissolved in trichloroacetonitril (5 mL) and stirred for 15 min with crushed molecular sieves (0.4 nm). $BF_3{\cdot}OEt_2$ (44 μL, 0.36 mmol) was added and stirring was continued. After 2 h TLC-analysis showed complete disappearance of the donor. The reaction mixture was quenched with TEA, filtered and concentrated *in vacuo*. The residue was redissolved in dichloromethane and washed with saturated aqueous $NaHCO_3$ and water. Drying ($MgSO_4$), evaporation of the solvent and subsequent purification of the crude product by column chromatography (diethyl ether/petroleum ether, 0/1 to 1/3, v/v) yielded **36** as an oil (115 mg, 65%). R_f 0.68 (diethyl ether/petroleum ether, 2/1, v/v); ^{1}H NMR (300 MHz 2D COSY) ($CDCl_3$) δ 1.18 (d, 3 H, Fuc: H-7, $J_{6,7}$ = 6.5 Hz), 3.22 (s, 3 H, OCH_3), 3.57 (dd, 1 H, Fuc: H-5, $J_{4,5}$ = 2.8 Hz, $J_{5,6}$ = 1.1 Hz), 3.56-3.61 (m, 1 H, Man: H-5)3.59 (d, 1 H, Fuc: H-1, $J_{1,1'}$ = -10.4 Hz), 3.70 (dd, 1 H, Man: H-6, $J_{5,6}$ = 4.5 Hz, $J_{6,6'}$ = -10.4 Hz), 3.76 (dd, 1 H, Man: H-2, $J_{1,2}$ = 1.7 Hz, $J_{2,3}$ = 3.1 Hz), 3.78 (d, 1 H, Fuc: H-1'), 3.80 (dd, 1 H, Man: H-6', $J_{5,6'}$ = 1.1 Hz), 3.84 (dd, 1 H, Man: H-3, $J_{3,4}$ = 9.5 Hz), 3.98 (dd, 1 H, Fuc: H-4, $J_{3,4}$ = 10.1 Hz), 4.04 (t, 1 H, Man: H-4), 4.14 (dq, 1 H, Fuc: H-6), 4.29 (d, 1 H, Fuc: H-3), 4.40-5.02 (2 s, 5 AB, 14 H, 4 × CH_2 benzyl), 4.66 (d, 1 H, Man: H-1), 7.02-7.48 (m, 35 H, $H_{arom.}$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 16.8 (Fuc: C-7), 54.3 (OCH_3), 60.0 (Man: C-6), 67.2, 71.4, 74.4, 75.6, 76.1, 77.2, 80.0, 80.4 (Fuc: C-3, C-4, C-5, C-6, Man: C-2, C-3, C-4, C-5), 70.3 (Fuc: C-1), 72.1, 72.2, 73.0, 73.4, 74.1, 74.6, 74.9 (7 × CH_2 benzyl), 98.9 (Man: C-1), 100.9 (Fuc: C-2), 126.7-128.2 ($CH_{arom.}$), 138.1-139.1 ($C_{arom.}$). ^{1}H NMR (300 MHz NOE-diff.): A NOE effect was observed between H-1 and H-3 of the fucose moiety.
Anal. calcd. for $C_{63}H_{68}O_{11}$ (1001.24): C 75.58, H 6.85; found C 75.66, H 6.61%.

Cyclohexyl 1,3,4,5-Tetra-*O*-benzyl-α-L-*fuco*-heptulopyranoside (37).
Donor **29** (200 mg, 0.32 mmol) and cyclohexanol **21** (67 μL, 0.64 mmol) were treated with IDCP (300 mg, 0.64 mmol) at -10°C as described for the synthesis of disaccharide **24** (*method B*). Reaction time: 15 min. After work-up and purification **37** was

isolated in 85% yield (180 mg). R_f 0.61 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR ($CDCl_3$) δ 1.22 (d, 3 H, H-7, $J_{6,7}$ = 6.4 Hz), 1.17-1.77 (m, 10 H, 5 × CH_2 Chex), 3.61 (d, 1 H, H-1, $J_{1,1'}$ = -10.5 Hz), 3.68-3.79 (m, 1H, OCH cHex), 3.71 (bd, 1 H, H-5, $J_{4,5}$ = 2.6 Hz), 3.84, (d, 1 H, H-1'), 3.97 (dq, 1 H, H-6), 4.00 (dd, 1 H, H-4, $J_{3,4}$ = 10.3 Hz), 4.40 (d, 1 H, H-3), 4.34-5.07 (s, 3 AB, 8 H, 4 × CH_2 benzyl), 7.17-7.77 (m, 20 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 16.9 (C-7), 24.5, 24.8, 25.4, 34.3, 34.9 (5 × CH_2 cHex), 67.7, 69.8, 76.1, 77.7, 80.7 (C-3, C-4, C-5, C-6, OCH cHex), 71.0 (C-1), 72.6, 73.4, 74.3, 75.0 (4 × CH_2 benzyl), 102.2 (C-2), 127.0-128.2 ($CH_{arom.}$), 138.5-139.1 ($C_{arom.}$).
Anal. calcd. for $C_{41}H_{48}O_6$ (636.83): C 77.33, H 7.60; found C 77.21, H 7.66%.

Cyclohexyl 3-*O*-(1,3,4,5-Tetra-*O*-benzyl-α-L-*fuco*-heptulopyranosyl)-4,6-*O*-benzylidene-2-deoxy-2-phtalimido-β-D-glucopyranoside (38).
Donor **29** (100 mg, 0.16 mmol) and acceptor **22** (100 mg, 0.21 mmol) were treated with IDCP (150 mg, 0.33 mmol) at -10°C as described for the synthesis of disaccharide **24** (*method B*). Reaction time: 10 min. After work-up and purification pure **38** was obtained in 65% yield (110 mg). R_f 0.79 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR (300 MHz 2D COSY) ($CDCl_3$) δ 0.98 (d, 3 H, Fuc: H-7, $J_{6,7}$ = 6.5 Hz), 1.02-1.82 (m, 10 H, 5 × CH_2 cHex), 3.64 (m, 1 H, Fuc: H-5), 3.53-3.69 (m, 3 H, GlcNPhth: H-4, H-6, OCH cHex), 3.72 (d, 1 H, Fuc: H-1, $J_{1,1'}$ = -10.4 Hz), 3.79 (d, 1 H, Fuc: H-1'), 3.79-3.86 (m, 1 H, GlcNPhth: H-5), 3.90 (dd, 1 H, Fuc: H-4, $J_{3,4}$ = 10.4 Hz, $J_{4,5}$ = 2.7 Hz), 3.98 (AB, 2 H, CH_2 benzyl), 4.09 (d, 1 H, Fuc: H-3), 4.12 (dq, 1 H, Fuc: H-6, $J_{5,6}$ = 1.1 Hz), 4.27 (dd, 1 H, GlcNPhth: H-2, $J_{1,2}$ = 8.6 Hz, $J_{2,3}$ = 10.1 Hz), 4.40 (dd, 1 H, GlcNPhth: H-6, $J_{5,6'}$ = 4.2 Hz, $J_{6,6'}$ = -10.2 Hz), 4.50 (AB, 2 H, CH_2 benzyl), 4.58 (s, 2 H, CH_2 benzyl), 4.69 (dd, 1 H, GlcNPhth: H-3, $J_{3,4}$ = 8.3 Hz), 5.39 (d, 1 H, GlcNPhth: H-1), 5.53 (s, 1 H, CHPh), 6.70-7.62 (m, 29 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 16.7 (Fuc: C-7), 23.3, 23.6, 25.3, 31.4, 33.1 (5 × CH_2 cHex), 56.0 (GlcNPhth: C-2), 66.3, 67.5, 69.9, 76.2, 77.2, 78.7, 80.1, 82.1 (Fuc: C-3, C-4, C-5, C-6, GlcNPhth: C-3, C-4, C-5, OCH cHex), 68.7, 69.4 (Fuc: C-1, GlcNPhth: C-6), 73.1, 73.4, 74.0, 74.2 (4 × CH_2 benzyl), 97.1 (GlcNPhth: C-1), 100.9 (CHPh), 101.9 (Fuc: C-2), 122.8-133.5 ($CH_{arom.}$), 137.2-139.3 ($C_{arom.}$).
Anal. calcd. for $C_{64}H_{65}O_{11}N$ (1024.23): C 75.05, H 6.40, N 1.37; found C 75.11, H 6.35, N 1.50%.

Cyclohexyl 4,5,6-Tri-*O*-benzyl-1-*O*-*tert*-butyldiphenylsilyl-2-deoxy-α-L-*fuco*-3-octulopyranoside (39).
Donor **34** (380 mg, 0.50 mmol) was condensed with cyclohexanol (**21**, 1.00 mL, 0.96 mmol) under the agency of IDCT (260 mg, 0.50 mmol), as described for the synthesis of compound **24** (*method B*) at -10°C. Reaction time: 5 min. Work-up and purification gave **39** as an oil (380 mg, 95%). R_f 0.96 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR ($CDCl_3$) δ 1.00 (s, 9 H, $SiC(CH_3)_3$), 1.09 (d, 3 H, H-8, $J_{7,8}$ = 6.7 Hz), 1.62-1.73 (m, 10 H, 5 × CH_2 cHex), 2.04-2.28 (m, 2 H, H-2), 3.62-3.64 (m, 2 H, H-6, OCH cHex), 3.80-3.92 (m, 4 H, H-1, H-4, H-7), 3.99 (dd, 1 H, H-5, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 2.6 Hz), 4.47-4.97 (s, 2 AB, 6 H, 3 × CH_2 benzyl), 7.15-7.64 (m, 25 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 16.7 (C-8), 19.0 ($SiC(\underline{C}H_3)_3$), 24.5, 24.8, 25.5, 34.0, 34.5 (5 × CH_2 cHex), 37.4 (C-2), 60.3 (C-1), 67.0, 69.3, 77.5, 78.0, 80.8 (C-4, C-5, C-6, C-7, OCH cHex), 72.2, 74.1, 74.5 (3 × CH_2 benzyl), 101.3 (C-3), 126.9-135.4 ($CH_{arom.}$), 133.8-139.0 ($C_{arom.}$).
Anal. calcd. for $C_{51}H_{62}O_6Si$ (799.14): C 76.66, H 7.82; found C 76.57, H 7.86%.

Cyclohexyl 3-*O*-(4,5,6-Tri-*O*-benzyl-2-deoxy-1-*O*-[2-(trimethylsilyl)ethoxymethyl]-α-L-*fuco*-3-octulopyranosyl}-4,6-*O*-benzylidene-2-deoxy-2-phtalimido-β-D-glucopyranoside (40).
Donor **35** (710 mg, 1.09 mmol) and acceptor **22** (525 mg, 1.09 mmol) were treated with IDCT (570 mg, 1.10 mmol) at -30°C as described for the synthesis of disaccharide **24** (*method B*). Reaction time: 15 min. After work-up and purification by column chromatography (diethyl ether/petroleum ether, 0/1 to 1/1, v/v) a mixture of **40** and **41** was obtained. The compounds were separated by gel filtration (dichloromethane/methanol, 2/1, v/v) to give pure **40** in 55% yield (640 mg) as an amorphous white solid. R_f 0.85 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR (400 MHz 2D COSY) ($CDCl_3$) δ 0.78 (s, 3 H, $OCH_2\underline{CH_2}Si$), 0.90 (d, 3 H, Fuc: H-8, $J_{7,8}$ = 6.6 Hz), 1.02-1.68 (m, 10 H, 5 × CH_2 cHex), 1.81 (ddd, 1 H, Fuc: H-2, $J_{1,2}$ = 6.2 Hz, $J_{1',2}$ = 9.6 Hz, $J_{2,2'}$ = -12.6 Hz), 2.32 (ddd, 1 H, Fuc: H-2', $J_{1,2'}$ = 9.3 Hz, $J_{1',2'}$ = 4.9 Hz), 2.71 (dt, 1 H, Fuc: H-1, $J_{1,1'}$, $J_{1,2'}$ = 9.4 Hz), 3.26-2.05 (m, 4 H, Fuc: H-1', H-4, $O\underline{CH_2}CH_2Si$), 3.50 (t, 1 H, GlcNPhth: H-4, $J_{3,4}$, $J_{4,5}$ = 8.9 Hz), 3.55, 4.24 (AB, 2 H, CH_2 benzyl), 3.58-3.64 (m, 2 H, GlcNPhth: H-5, OCH cHex), 3.60 (d, 1 H, Fuc: H-4, $J_{4,5}$ = 9.9 Hz), 3.83 (t, 1 H, GlcNPhth: H-6, $J_{5,6}$ = 2.8 Hz, $J_{6,6'}$ = -9.7 Hz), 4.07 (dq, 1 H, Fuc: H-7, $J_{6,7}$ = 1.0 Hz), 4.29 (dd, 1 H, GlcNPhth: H-2, $J_{1,2}$ = 8.6 Hz, $J_{2,3}$ = 10.3 Hz), 4.39 (dd, 1 H, GlcNPhth: H-6', $J_{5,6'}$ = 4.8 Hz), 4.18-1.88 (AB, 2 H, CH_2 benzyl), 4.79 (dd, GlcNPhth: 1 H, H-3), 5.42 (d, GlcNPhth: 1 H, H-1), 5.49 (s, 1 H, CHPh), 6.87-7.58 (m, 19 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ -1.6 ($Si(CH_3)_3$), 16.4 (Fuc:

C-8), 17.6 ($OCH_2\underline{C}H_2Si$), 23.2, 23.5, 25.1, 31.2, 31.6 (5 × CH_2 cHex), 33.3 (Fuc: C-2), 55.7 (GlcNPhth: C-2), 63.5, 64.4 (Fuc: C-1, $O\underline{C}H_2CH_2Si$), 66.1, 66.9, 69.1, 75.7, 76.9, 80.9, 82.2 (Fuc: C-4, C-5, C-6, C-7, Man: C-3, C-4, C-5, OCH cHex), 72.7, 73.2, 74.0 (3 × CH_2 benzyl), 94.3 ($O\underline{C}H_2O$), 97.0 (GlcNPhth: C-1), 100.5 (CHPh), 101.4 (Fuc: C-3), 122.6-133.3 ($CH_{arom.}$), 137.2-139.1 ($C_{arom.}$), 168.3 (C=O).

Anal. calcd. for $C_{64}H_{76}O_{13}NSi$ (1095.40): C 70.18, H 7.00, N 1.28; found C 70.10, H 7.14, N 1.26%.

Further elution yielded **41** (85 mg, 13%). R_f 0.92 (diethyl ether/petroleum ether, 2/1, v/v); ^1H NMR ($CDCl_3$) δ 0.88-0.97 (m, 2 H, $OCH_2\underline{C}H_2Si$), 1.26 (d, 3 H, H-8, $J_{7,8}$ = 6.4 Hz), 3.56-3.72 (m, 5 H, H-5, H-6, H-7, $O\underline{C}H_2CH_2Si$), 4.12 (ddd, 1 H, H-1, $J_{1,1'}$ = -11.8 Hz, $J_{1,2}$ = 6.4 Hz, $J_{1,4}$ = 1.7 Hz), 4.28 (dd, 1 H, H-1', $J_{1',2}$ = 7.7 Hz), 4.38 (bd, 1 H, H-4, $J_{3,4}$ = 9.2 Hz), 4.62-5.00 (2 s, 2 AB, 8 H, 3 × CH_2 benzyl, $O\underline{C}H_2O$), 5.31 (ddd, 1 H, H-2, $J_{2,4}$ = 1.7 Hz), 7.24-7.36 (m, 15 H, $H_{arom.}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ -1.5 ($Si(CH_3)_3$), 14.1 ($SCH_2\underline{C}H_3$), 16.8 (C-8), 18.0 ($OCH_2\underline{C}H_2Si$), 60.9, 64.8 (C-1, $O\underline{C}H_2CH_2Si$), 72.9, 73.7, 74.4 (3 × CH_2 benzyl), 75.7, 76.5, 76.9, 82.5 (C-4, C-5, C-6, C-7), 93.9 ($O\underline{C}H_2O$), 106.1 (C-2), 127.2-128.2 ($CH_{arom.}$), 138.4 ($C_{arom.}$), 153.1 (C-3).

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(*Received in UK* 27 *February* 1995; *accepted* 17 *March* 1995)