Synthesis of a Fucose Hexasaccharide

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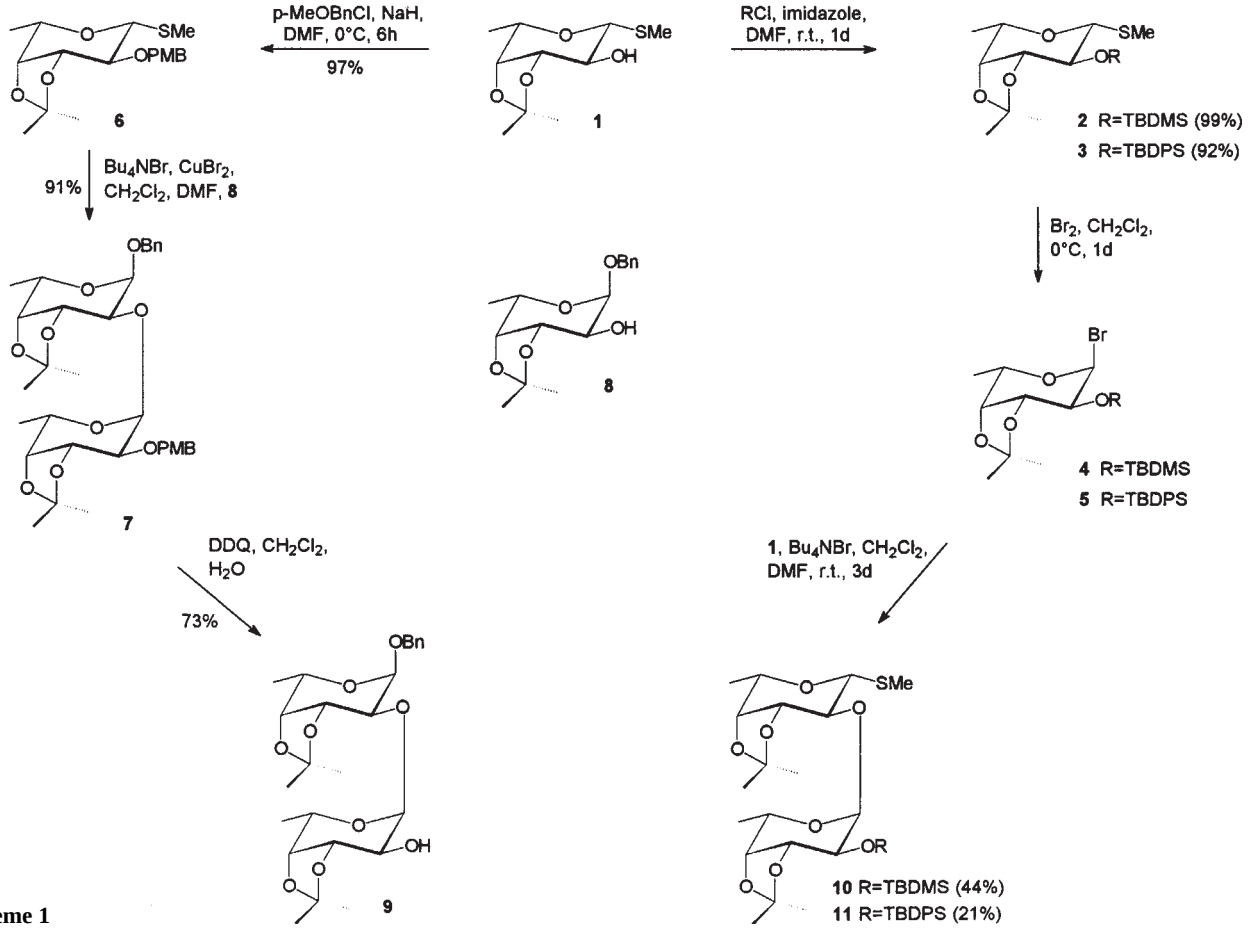
The facile synthesis of a homogeneously α,1 → 2 interglycosidically linked fucose hexasaccharide **17** via the disaccharide methylthio donor **10** is reported. Compound **10** in turn was synthesised from a monosaccharide thiomethyl precursor in three consecutive steps. Glycosylation employing thioglycosides activated by copper bromide/tetrabutylammonium bromide proved to be selective for the formation of α-glycosidic linkages.

Recently, results from in vitro and in vivo tests[1] have shown that adhesion of disseminated tumour cells to organ-specific lectins[2] could be prevented by specific sugars. In the case of mice lung cells, the use of the sulfated fucose polymer fucoidin was found to be advantageous compared to fucose itself. Since the cluster effect is discussed as an enhancing factor of lectin inhibition,[3] we are investigating several aspects, such as oligomerisation, clustering and glycopeptide syntheses of fucose conjugates.

Linear fucose oligomers were previously obtained by Flowers et al. using the Koenigs–Knorr reaction[4] and by Matta et al. performing a $CuBr_2/Bu_4NBr$ catalysed thioglycoside glycosylation with consecutive chain elongation by methyl 3,4-*O*-isopropylidene-2-*O*-(*p*-methoxybenzyl)-1-thio-*β-L-fucopyranoside (***6**).[5] However, we observed decreasing yields for glycosylation of higher oligomers and poor stereospecificity with stronger activation methods.

Therefore, a convergent synthesis from disaccharide building blocks seemed to be more suitable. Toth et al. synthesised a fucobiose thiomethyl donor as an example for the so called "armed-disarmed" strategy,[6] but have not yet applied it in any synthesis. Since this concept required an unfavourable protection group pattern, we synthesised a disaccharide methylthio donor from methyl 3,4-*O*-isopropylidene-1-thio-*β-L-fucopyranoside (***1**) by simple introduction of a TBDMS protecting group at the 2 position and treatment of the completely protected compound **2** with bromine to obtain the corresponding bromide **4**. The glycosylation of thioglycoside **1**[5c] was carried out in the presence of tetrabutylammonium bromide. The TBDMS protecting group was not completely stable under these glycosylation conditions and cross-coupling products were obtained. Nevertheless, the disaccharide donor **10** could be isolated in 44% after treating deprotected **10** with TBDMSCl.



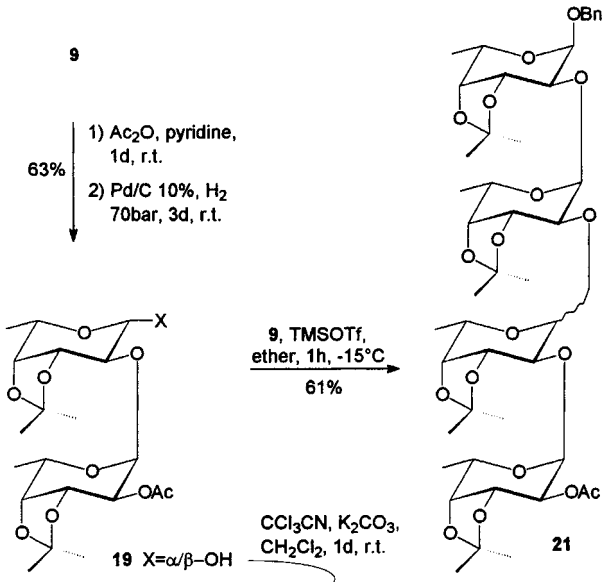
Scheme 1

The preparation of the disaccharide acceptor was carried out with benzyl 3,4-*O*-isopropylidene-α-L-fucopyranoside (**8**) and the *p*-methoxybenzyl protected donor **6**, using $CuBr_2/Bu_4NBr$ as activator. After oxidative deprotection of the 2′-position with DDQ traces of the β-glycosylation product could be removed easily by column chromatography.

The tetrasaccharide **12** was obtained from the disaccharide donor **10** and the disaccharide acceptor **9** in the presence of $CuBr_2/Bu_4NBr$ in a moderate yield (54%). The removal of 5% β-glycosylation byproduct was carried out after deprotection of the 2′-position. Another glycosylation step without formation of any β-glycoside led to the hexasaccharide **15** in 33% yield. Compound **15** was quantitatively deprotected to give the hexafucoside **17**.

By substitution of the TBDMS protecting group with a TBDPS group the moderate yields could not be improved. Activation of the thioglycosides with NIS led to better overall yields, but unfavourably changed the α/β-ratio to about 3:2.

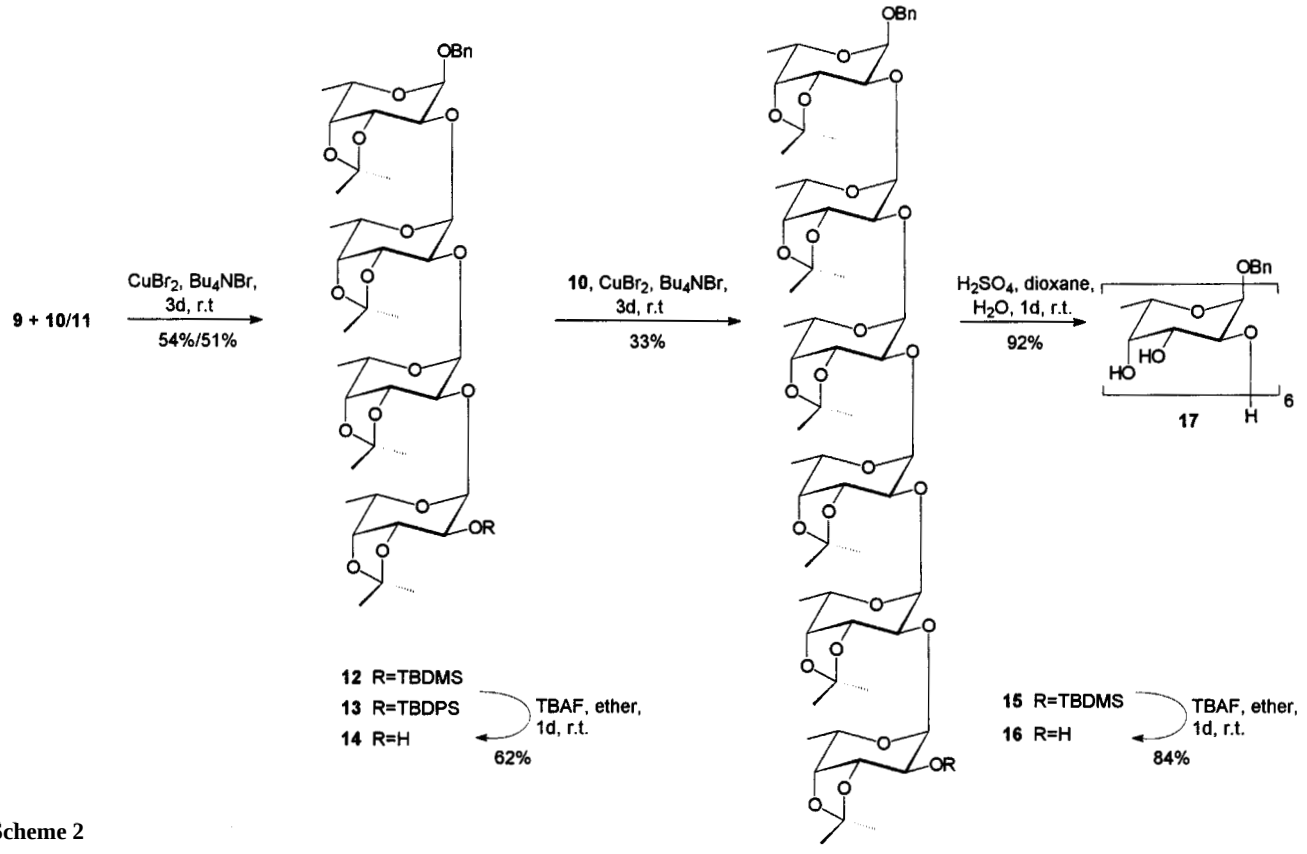
Similar results were obtained using the trichloroacetimidate glycosylation method. After acetylation of **9** at the 2′-position the benzyl group could be removed with a large excess of catalyst and the comparatively stable disaccharide β-imidate **20** formed stereospecifically. However, in contrast to reports about uniform α-formation employing monosaccharide imidates,[6] glycosylation with **9** as acceptor in the presence of TMSOTf resulted in a 1:1-mixture of the α- and β-linked tetrasaccharides (**21**).



Scheme 3

In conclusion, contrary to other methods glycosylation employing thioglycosides activated by $CuBr_2/Bu_4NBr$ proved to be selective for the formation of α-glycosidic linkages.

NMR spectra were recorded with a Bruker AMX-400 spectrometer, reference TMS. Some assignments were made with support of ^1H_1H- and $^1H^{13}C$-COSY experiments. Optical rotations were measured with a Perkin–Elmer polarimeter 243. TLC was performed on silica gel



Scheme 2

coated foil (silica gel 60 F_{254} Merck, Darmstadt). Preparative column chromatography was performed with silica gel 60 (63–200 μm, Merck, Darmstadt). ^{i}Pr denotes $(CH_3)_2C$.

Thioglycoside Activation with Copper Bromide/Tetrabutylammonium Bromide; General Procedure:

Donor and acceptor were evaporated three times with toluene and stirred together with freshly activated molecular sieves (4Å) in DMF/CH_2Cl_2 1:1 for 1h under Ar. Bu_4NBr was added, and after 1 h the reaction was started with $CuBr_2$ and carried out for at least 1 d at r.t. Subsequently, the solution was filtered over Celite, diluted with EtOAc, washed with sat. $NaHCO_3$ (same vol. 3 ×) and sat. brine (same vol., 1 ×), dried, evaporated and purified by flash column chromatography.

Methyl 2-*O*-*tert*-Butyldimethylsilyl-3,4-*O*-isopropylidene-1-thio-β-L-fucopyranoside (2):

To a stirred solution of **1**[5c] (1.0g, 4.27 mmol) in anhyd DMF (6 mL) imidazole (680 mg, 10 mmol) and TBDMSCl (1g, 6.9 mmol) was added. After 12 h DMF was evaporated in vacuo, the residue diluted with CH_2Cl_2 (30 mL), washed with sat. Na_2CO_3 (2 × 50 mL) and brine (50 mL), dried and concentrated in vacuo to give 1.48g (4.23 mmol, 99%) of white crystalline product; $[\alpha]_D^{20}$ + 1.7 (*c* = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 0.14 (2 × s, 6H, $SiMe_2$), 0.90 (s, 9H, ^{t}Bu), 1.35 (s, 3H, ^{i}Pr), 1.39 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6), 1 .51 (s, 3H, ^{i}Pr), 2.18 (s, 3H, SMe), 3.58 (dd, 1H, $J_{1,2}$ = 9.1 Hz, $J_{2,3}$ = 6.1 Hz, H-2), 3.82 (dq, 1H, $J_{4,5}$ = 2.0 Hz, $J_{5,6}$ = 6.5 Hz, H-5), 3.96 (dd ≈ t, 1H, $J_{2,3}$ = $J_{3,4}$ = 6.1 Hz, H-3), 4.03 (dd, 1H, $J_{3,4}$ = 5.6 Hz, $J_{4,5}$ = 2.0 Hz, H-4), 4.17 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-l).

$C_{16}H_{32}O_4SiS$	calcd	C	55.13	H	9.25
(348.57)	found		55.00		9.15

Methyl 2-*O*-*tert*-Butyldiphenylsilyl-3,4-*O*-isopropylidene-1-thio-β-L-fucopyranoside (3):

A solution of **1** (1.0g, 4.27 mmol), imidazole (680 mg, 10 mmol) and TBDPSCl (1.8 mL, 7.03 mmol) in anhyd DMF (6 mL) was stirred for 12 h. Then, DMF was evaporated in vacuo, the residue diluted with CH_2Cl_2 (30 mL), washed with sat. Na_2CO_3 (2 × 50 mL) and brine (50 mL), dried and concentrated in vacuo. Column chromatography (petroleum ether/EtOAc 10:1) gave 1.95g (3.91 mmol, 92%) of a colourless syrup; $[\alpha]_D^{20}$ + 0.4 (*c* = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.07 (s, 9H, ^{t}Bu), 1.16 (s, 3H, ^{i}Pr), 1.21 (s, 3H, ^{i}Pr), 1.32 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.84 (s, 3H, SMe), 3.72 (dd, 1H, $J_{1,2}$ = 8.1 Hz, $J_{2,3}$ = 5.8 Hz, H-2), 3.87 (dq, 1H, $J_{4,5}$ = 2.0 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.01 (dd, 1H, $J_{3,4}$ = 6.1 Hz, $J_{4,5}$ = 2.0 Hz, H-4), 4.19 (dd ≈ t, 1H, $J_{2,3}$ = $J_{3,4}$ = 6.1 Hz, H-3), 4.17 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-l), 7.37 (m, 6H, Ph), 7.71 (m, 4H, Ph).

$C_{26}H_{36}O_4SiS$	calcd	C	66.06	H	7.68
(472.71)	found		66.94		7.71

Methyl 3,4-*O*-Isopropylidene-2-*O*-(*p*-methoxybenzyl)-1-thio-β-L-fucopyranoside (6):

A solution of **1** (1.44 g, 6.14 mmol) in anhyd DMF (30 mL) under Ar was cooled to 0 °C and NaH (0.3 g, 10 mmol, 80% in paraffin) was added. After hydrogen formation decreased, *p*-methoxybenzyl chloride (1.16 g, 7.41 mmol) was added dropwise, the solution was stirred for another 6 h and warmed up to r.t. The excess of NaH was destroyed by MeOH (2 mL), the mixture evaporated in vacuo to dryness, diluted with CH_2Cl_2, washed with sat. Na_2CO_3 (50 mL), H_2O (50 mL) and brine (50 mL), dried and concentrated under reduced pressure. Column chromatography (petroleum ether/EtOAc 5:1) gave 2.12 g (5.98 mmol, 97%) of a bright yellow syrup;$[\alpha]_D^{20}$–3.4 (*c* = 1.0, $CHCl_3$)
^{1}H NMR ($CDCl_3$): δ = 1.37 (s, 3H, ^{i}Pr), 1.39 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.48 (s, 3H, ^{i}Pr), 2.18 (s, 3H, SMe), 3.42 (dd, 1H, $J_{1,2}$ = 9.7 Hz, $J_{2,3}$ = 6.6 Hz, H-2), 3.79 (s≈m, 3H, OMe), 3.80 (dq≈m, 1H, $J_{4,5}$ = 2.0 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.05 (dd, 1H, $J_{3,4}$ = 5.6 Hz, $J_{4,5}$ = 2.0 Hz, H-4), 4.18 (dd≈t, 1H, $J_{2,3}$ = $J_{3,4}$ = 6.1 Hz, H-3), 4.26 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 4.68 (d, 1H, J_{Bn} = 11.2 Hz, Bn), 4.79 (d, 1H, J_{Bn} = 11.2 Hz, Bn), 6.87 (m, 2H, Bn), 7.35 (m, 2H, Bn).

$C_{18}H_{26}O_5S$	calcd	C	60.99	H	7.39
(354.46)	found		60.99		7.58

Benzyl 3,4-*O*-Isopropylidene-2-*O*-p-methoxybenzyl-α-L-fucopyranosyl-(1→ 2)-3,4-*O*-isopropylidene-α-L-fucopyranoside (7):

Compounds **6** (1.0 g, 2.82 mmol) and **8** (0.7 g, 2.38 mmol) were converted together with Bu_4NBr (2.4 g, 7.44 mmol), $CuBr_2$ (1.68 g, 7.52 mmol), molecular sieves (3 g) and 30 mL solvent according to the general glycosylation procedure. Column chromatography (toluene/EtOAc 5:1) furnished **7** (1.31 g, 2.17 mmol, 91%) as a colourless syrup containing 15% β-anomer.

7α: $[\alpha]_D^{20}$ –144.9 (*c* = 1.0, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ = 1.28 (d, 3H, $J_{5',6'}$ = 6.6 Hz, H-6'), 1.31 (d, 3H, $J_{5,6}$ = 7.1 Hz, H-6), 1.34 (s, 3H, ^{i}Pr), 1.35 (s, 3H, ^{i}Pr), 1.38 (s, 3H, ^{i}Pr), 1.51 (s, 3H, ^{i}Pr), 3.48 (dd, 1H, $J_{1',2'}$ = 3.5 Hz, $J_{2',3'}$ = 8.2 Hz, H-2'), 3.76 (s, 3H, OMe), 3,80 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 8,1 Hz, H-2), 4.04 (dd≈m, 1H, $J_{3,4}$ = 5.6 Hz. $J_{4,5}$ = 2.5 Hz, H-4), 4.07 (dd≈m, 1H, $J_{4',5'}$ = 2.5 Hz, H-4'), 4.12 (dq, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.32 (dd, 1H, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 5.6 Hz, H-3), 4.40 (dd, 1H, $J_{2',3'}$ = 8.2 Hz, $J_{3',4'}$ = 5.4 Hz, H-3'), 4.49 (dq, 1H, $J_{4',5'}$ = 2.5 Hz, $J_{5',6'}$ = 6.6 Hz, H-5'), 4.55 (d, 1H, J_{Bn} = 12.2 Hz, Bn), 4.61 (dd≈s, 2H, Bn), 4.68 (d, 1H, J_{Bn} = 12.2 Hz, Bn), 4.82 (d, 1H, $J_{1',2'}$ = 3.5 Hz, H-1'), 4.98 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 6.76 (m, 2H, BnOMe), 7.17 (m, 2H, BnOMe), 7.3 (m, 5H, Bn).
^{13}C NMR ($CDCl_3$): δ = 16.16 (C-6), 16.29 (C-6), 26.47 (^{i}Pr), 26.49 (^{i}Pr), 28.34 (^{i}Pr), 28.40 (^{i}Pr), 55.26 (OMe), 63.22 (C-5'), 63.43 (C-5), 70.05 (Bn), 71.35 (Bn), 73.76 (C-2), 74.65 (C-3), 75.31 (C-2'), 75.81 (C-3'), 76.22 (C-4, C-4'), 95,01 (C-1'), 95.25 (C-l), 108,67 (^{i}Pr), l08.73 (^{i}Pr), 113.67 (BnOMe), 127.00-130.00 (Bn,BnOMe), 137.21 (BnOMe), 159.15 (BnOMe).

7β:
^{1}H NMR ($CDCl_3$): δ = 3.37 (dd, 1H, H-2'), 3.95 (dd, 1H, H-4), 3.99 (dd, 1H, H-2), 4.19 (dq, 1H, H-5), 4.76 (d, 1H, H-1').

$C_{33}H_{44}O_{10}$	calcd	C	65.98	H	7.38
(600.71)	found		65.86		7.49

Benzyl 3,4-*O*-Isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranoside (9):

A stirred solution of **7** (870 mg, 1.45 mmol) in CH_2Cl_2/H_2O (25 mL, 18:1) was treated with 2,3-dicyano-5,6-dichloro-*p*-benzoquinone (DDQ, 490 mg, 2.1 mmol). After 40 min the solids were filtered off and the solution was washed with aq Na_2CO_3 (2 × 40 mL) and brine (40 mL). The solution was dried, the solvents evaporated and flash chromatography (petroleum ether/EtOAc 1.75:1) led to product **9** (509 mg, 1.06 mmol, 73%), and the respective, β-linked disaccharide (89 mg, 0.19 mmol, 13%).

9α: $[\alpha]_D^{20}$ –190.0 (*c* = 1.0. $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ = 1.30 (d, 3H, $J_{5',6'}$ = 6.6 Hz, H-6'), 1.45 (s, 3H, ^{i}Pr), 1.46 (d, 3H, H-6), 1.46 (s, 3H, ^{i}Pr), 1.51 (s, 3H, ^{i}Pr), 1.53 (s, 3H, ^{i}Pr), 2.20 (d, 1H, $J_{OH,2'}$ = 9.5 Hz, OH-2). 3.64 (ddd, 1H, $J_{1',2'}$ = 3.9 Hz, $J_{2',3'}$ = 7.1 Hz, $J_{OH,2'}$ = 9.5 Hz, H-2'), 3.80 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2.3}$ = 8.1 Hz, H-2), 4.05 (dd ≈ m, 1H, $J_{4,5}$ = 2.5 Hz, H-4), 4.06 (dd ≈ m, 1H, $J_{4',5'}$ = 2.5 Hz, H-4'), 4.12 (dd, 1H, H-3'), 4.13 (dq≈m, 1H, H-5), 4.24 (dd, 1H, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 5.4 Hz, H-3), 4.44 (dq, 1H, $J_{4',5'}$ = 2.0 Hz, $J_{5',6'}$ = 6.6 Hz, H-5'), 4.50 (d, 1H, J_{Bn} = 11.7 Hz, Bn), 4.70 (d, 1H, J_{Bn} = 11.7 Hz, Bn), 4.80 (d, 1H, $J_{1',2'}$ = 3.9 Hz, H-1'), 4.97 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 7.34 (m, 5H, Bn).
^{13}C NMR ($CDCl_3$): δ = 16. 16 (C-6'), 16.31 (C-6), 26.26 (^{i}Pr), 26.44 (^{i}Pr), 28.18 (^{i}Pr), 28.25 (^{i}Pr), 63.35 (C-5'), 63.55 (C-5), 69.87 (Bn), 70.13 (C-2'), 73.59 (C-2), 74.48 (C-3), 75.87 (C-4'), 76.16 (C-4), 76.88 (C-3'), 94.79 (C-l), 96. 18 (C-1'), 108.99 (^{i}Pr), 109.05 (^{i}Pr), 128.20 (Bn), 128.32 (Bn), 128.63 (Bn), 136.82 (Bn).

$C_{25}H_{36}O_9$	calcd	C	62.48	H	7.55
(480.56)	found		61.99		7.59

9β:
^{1}H NMR ($CDCl_3$): δ = 1.31 (d, 3H, $J_{5,6}$ = 6.5 Hz, H-6), 1.34 (s, 3H, ^{i}Pr), 1.35 (d ≈ m, 3H, H-6'), 1.37 (s, 3H, ^{i}Pr), 1.51 (s, 3H, ^{i}Pr), 1.55 (s, 3H, ^{i}Pr), 3.57 (dd≈t, 1H, $J_{1',2'}$ = $J_{2',3'}$ = 7.8 Hz, H-2'), 3.81 (dq, 1H, $J_{4',5'}$ = 2. 1 Hz, $J_{5',6'}$ = 6.5 Hz, H-5'), 3.87 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 8.6 Hz, H-2), 3.98 (dd, 1H, $J_{3',4'}$ = 5.6 Hz, $J_{4',5'}$ = 2.1 Hz, H-4'), 4.03 (dd, 1H, $J_{4',5'}$ = 5.1 Hz, $J_{4,5}$ = 2.5 Hz, H-4), 4.07 (dd, 1H, $J_{2',3'}$ = 7.1 Hz, $J_{3',4'}$ = 5.5 Hz, H-3'), 4.12 (dq, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.5 Hz, H-

5), 4,35 (dd, 1H, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 5.1 Hz, H-3), 4,47 (d, 1H, $J_{1',2'}$ = 8.1 Hz, H-1′), 4.59 (d, 1H, J_{Bn} = 12.2 Hz, Bn), 4.69 (d, 1H, J_{Bn} = 12.2 Hz, Bn), 5.03 (d, 1H, $J_{1,2}$ = 3,5 Hz, H-1), 7.32 (m, 5H, Bn).

^{13}C NMR ($CDCl_3$): δ = 16.25 (C-6), 16.59 (C-6′), 26.36 (^{i}Pr), 26.46 (^{i}Pr), 28.26 (^{i}Pr), 28.30 (^{i}Pr), 63.27 (C-5), 69.24 (C-5′), 69.96 (Bn), 73.57 (C-2′), 75.44 (C-3), 76.30 (C-4?), 76.34 (C-4?), 76.69 (C-2), 78.74 (C-3′), 97.99 (C-1), 102.57 (C-1′), 108.88 (^{i}Pr), 109.77 (^{i}Pr), 127.73 (Bn), 127.82 (Bn), 128.37 (Bn), 137.44 (Bn).

Methyl 2-*O*-*tert*-Butyldimethylsilyl-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1 → 2)-3,4-*O*-isopropylidene-1-thio-β-L-fucopyranoside (10):

1 (1240 mg, 5.29 mmol) was stirred with activated molecular sieves (4 g) in DMF/CH_2Cl_2 (2:1, 22 mL) for 1 h. To a solution of **2** (1470 mg, 4.22 mmol) in CH_2Cl_2 (20 mL) activated molecular sieves (0.5 g) was added, and after 1 h stirring the mixture was cooled to 0 °C and treated with abs bromine in CH_2Cl_2 (1:24, 5.53 mL, 4.3 mmol). After 20 min the solvent was evaporated at 0°C under reduced pressure and codistilled with CH_2Cl_2 until the orange colour disappeared. The crude residue was suspended in CH_2Cl_2 (7 mL) and together with Bu_4NBr (3.87 g, 12 mmol) added to the solution containing **1.** After stirring for 24 h workup was performed following the genera1 glycosylation procedure. Column chromatography (petroleum ether/EtOAc 7:1) furnished 731 mg (1.37 mmol, 32%) product as well as 211 mg (0.50 mmol, 12%) of product deprotected at position 2. This could be protected with TBDMSCl (see 3). Further starting material (2, 37%, anomeric mixture and **1**, 9%, anomeric mixture), β-linked disaccharide (108 mg, 5%) and the corresponding trisaccharide (32l mg, 11%) were isolated.

10α: $[\alpha]_D^{20}$ –94.0 (*c* = 1.0, $CHCl_3$),

^{1}H NMR ($CDCl_3$): δ = 0.11 (s, 3H, SiMe), 0.12 (s, 3H, SiMe), 0.92 (s, 9H, ^{t}Bu), 1.31 (d, 3H, $J_{5',6'}$ = 6.6 Hz, H-6′), 1.36 (s, 3H, ^{i}Pr), 1.37 (s, 3H, ^{i}Pr), 1.39 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.51 (s, 3H, ^{i}Pr), 1.53 (s, 3H, ^{i}Pr), 2.18 (s, 3H, SMe), 3.71 (dd≈m, 1H, $J_{1,2}$ = 9.2 Hz, $J_{2,3}$ = 6.6 Hz, H-2), 3.73 (dd ≈ m, 1H, $J_{1',2'}$ = 3.5 Hz, $J_{2',3'}$ = 7.1 Hz, H-2′), 3.81 (dq, 1H, $J_{4,5}$ = 2.0 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.05 (dd, 1H, $J_{3,4}$ = 5.6 Hz, $J_{4,5}$ = 2.0 Hz, H-4), 4.08 (dd, 1H, $J_{3',4'}$ = 5.6 Hz, $J_{4',5'}$ = 2.5 Hz, H-4′), 4.11 (dd ≈ t, 1H, $J_{2',3'}$ = $J_{3',4'}$ = 6.1 Hz, H-3′), 4.16 (dd ≈ t, 1H, $J_{2,3}$ = $J_{3,4}$ = 5.8 Hz, H-3), 4.23 (d, 1H, $J_{1,2}$ = 9.2 Hz, H-1), 4.55 (dq, 1H, $J_{4',5'}$ = 2.5 Hz, $J_{5',6'}$ = 6.6 Hz, H-5′), 5.21 (d, 1H, $J_{1',2'}$ = 3.5 Hz, H-1′).

^{13}C NMR ($CDCl_3$): δ = –4.56 (SiMe). –4.42 (SiMe), 12.49 (SMe), 16.19 (C-6′), 16.79 (C-6), 18.25 (^{t}Bu. q), 25.80 (^{t}Bu, s), 26.42 (2 × ^{i}Pr), 28.07 (^{i}Pr), 28.44 (^{i}Pr), 62.99 (C-5′), 71.59 (C-2′), 71.91 (C-5), 74.14 (C-2), 76.19 (C-4′), 76.31 (C-4), 76,66 (C-3′), 78.58 (C-3), 84.04 (C-1), 98.13 (C-1′), 108.50 (^{i}Pr), 109.45 (^{i}Pr).

$C_{25}H_{46}O_8SSi$	calcd	C	56.15	H	8.67	S	5.99
(534.79)	found		56.98		8.93		5.49

10β:

^{1}H NMR ($CDCl_3$): δ = 0.08 (s, 3H, SiMe), 0.12 (s, 3H, SiMe), 0.90 (s, 9H, ^{t}Bu), 1.37 (m, 9H, H-6, H-6′, 2 × ^{i}Pr), 1.51 (s, 6H, 2 × ^{i}Pr), 2.18 (s, 3H, SMe), 3.49 (dd, 1H, $J_{1,2}$ = 8.1, $J_{2,3}$ = 6.1 Hz, H-2), 3.80 (dq ≈ m, 1H, $J_{4,5}$ = 2.0 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 3.82 (dq≈m, 1H, $J_{4',5'}$ = 2.0 Hz, $J_{5',6'}$ = 6.6 Hz, H-5′), 3.98 (m, 3H, H-2′, H-3, H-4), 4.02 (dd, 1H, $J_{3,4}$ = 5.6 Hz, $J_{4,5}$ = 2.0 Hz, H-4′), 4.11 (dd≈t, 1H, $J_{2',3'}$ = $J_{3',4'}$ = 6.7 Hz, H-3′), 4.27 (d, 1H, $J_{1,2}$ = 8.6 Hz, H-1), 4.64 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1′).

^{13}C NMR ($CDCl_3$): δ = –4.59 (SiMe), –4.20 (SiMe), 11.84 (SMe), l6.49 (C-6?), 16.72 (C-6?), 18.24 (^{t}Bu, q), 25.87 (^{t}Bu, s), 26.46 (^{i}Pr), 26.49 (^{i}Pr), 28.15 (^{i}Pr), 28.17 (^{i}Pr), 69.00 (C-5), 72.50 (C-5′), 73.63 (C-2′), 74.11 (C-2), 76.42 (C-4′), 76.85 (C-4), 79.18 (C-3′), 80.91 (C-3), 83.27 (C-l′), 99.75 (C-1), 109.35 (^{i}Pr), 109.48 (^{i}Pr).

Methyl 2-*O*-*tert*-Butyldiphenylsilyl-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1 → 2)-3,4-*O*-isopropylidene-1-thio-β-L-fucopyranoside (11):

Using **3** (1.9 g, 4.02 mmol), **1** (1.0 g, 4.27 mmol), bromine in CH_2Cl_2 (1:24, 5.53 mL, 4.3 mmol), and Bu_4NBr (3870 mg, 12 mmol) this compound was prepared in the same way as **10**. Column chromatography yielded 568 mg (0.86 mmol, 21%) of product, byproducts were not isolated; $[\alpha]_D^{20}$ –62.5 (*c* = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.08 (s, 9H, ^{t}Bu), 1.14 (s, 3H, ^{i}Pr), 1.25 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.27 (s, 3H, ^{i}Pr), 1.35 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.36 (s, 3H, ^{i}Pr), 1.39 (s, 3H, ^{i}Pr), 1.94 (s, 3H, SMe), 3.71 (dd, 1H, $J_{1.2}$ = 8.6, $J_{2,3}$ = 6.1 Hz, H-2), 3.79 (dq, 1H, $J_{4,5}$ = 2.0 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 3.85 (dd, 1H, $J_{1',2'}$ = 3.5 Hz, $J_{2',3'}$ = 7.1 Hz, H-2′), 4.02 (dd, 1H, $J_{3,4}$ = 6.1 Hz, $J_{4,5}$ = 2.0 Hz, H-4), 4.06 (dd, 1H, $J_{3',4'}$ = 5.6 Hz, $J_{4',5'}$ = 2.5 Hz, H-4′), 4.09 (d, 1H, $J_{1,2}$ = 8.6 Hz, H-1), 4.16 (dd≈t, 1H, $J_{2,3}$ = $J_{3,4}$ = 6,1 Hz, H-3), 4.30 (dd, 1H, $J_{2',3'}$ = 7.1 Hz, $J_{3',4'}$ = 5.6 Hz, H-3′), 4.49 (dq, 1H, $J_{4',5'}$ = 2.5 Hz, $J_{5',6'}$ = 6.6 Hz, H-5′), 5.09 (d, 1H, $J_{1',2'}$ = 3.5 Hz, H-l′), 7.38 (m, 6H, Ph), 7.72 (m, 4H, Ph).

^{13}C NMR ($CDCl_3$): δ = 12.33 (SMe), 16.20 (C-6), 16.71 (C-6), 19.61 (^{t}Bu, q), 26.22 (^{i}Pr), 26.38 (^{i}Pr). 27,00 (^{t}Bu, s), 27.72 (^{t}Pr), 27.82 (^{i}Pr), 63.12 (C-5′), 71.71 (C-5), 71.76 (C-2′), 73.13 (C-2), 76.03 (C-4′), 76.11 (C-4), 76.43 (C-3′), 78.24 (C-3), 83.52 (C-1), 96.88 (C-1′), 108.55 (^{i}Pr), 109.43 (^{i}Pr), 127–l37 (Ph).

$C_{35}H_{50}O_8SSi$	calcd	C	63.80	H	7.65		
(658.92)	found		63.84		7.40		

Benzyl 2-*O*-*tert*-Butyldimethylsilyl-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1 → 2)-3,4-*O*-isopropylidene-α-L-fucopyranoside (12):

Compounds **9** (320 mg, 0.67 mmol) and **10** (360 mg, 0.67 mmol) were treated according to the general glycosylation procedure with Bu_4NBr (640 mg, 2 mmol), $CuBr_2$ (440 mg, 2 mmol), DMF/CH_2Cl_2 (15 mL) and molecular sieves (1 g). After a reaction time of 8 d and standard workup column chromatography (toluene/EtOAc 7.5:1) furnished 350 mg (0.36 mmol, 54%) of product containing 15% β-linked tetrasaccharide. Further starting material (**9**, 41%) and the corresponding disaccharide bromide (23%) and its hydrolysate (12%) were isolated.

12α: $[\alpha]_D^{20}$ –145.8 (*c* = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 0.10 (s, 3H, SiMe), 0.11 (s, 3H, SiMe), 0.88 (s, 9H, ^{t}Bu), 1.2–1.7 (m, 36H, 4 × H-6, 8 × ^{i}Pr), 3.65 (dd ≈ m, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 6.6 Hz, H-2), 3.67 (dd≈m, 1H, $J_{1,2}$ = 3.5 Hz, H-2), 3.7–3.8 (m, 3H, 2 × H-2, H-4), 4.0–4.1 (m, 4H, 3 × H-4, H-5), 4.14 (dd, 1H, $J_{2,3}$ = 5,6 Hz, $J_{3,4}$ = 8.1 Hz, H-3), 4.20 (dd ≈ t, 1H, $J_{2,3}$ = $J_{3,4}$ = 5.6 Hz, H-3), 4.26 (dd, 1H, $J_{2,3}$ = 8.2 Hz, $J_{3,4}$ = 5.1 Hz, H-3), 4.31 (dd, 1H, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 5.6 Hz, H-3), 4.35 (dq, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6,6 Hz, H-5), 4.42 (dq ≈ m, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.46 (dq ≈ m, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.58 (d, 1H, J_{Bn} = 11.8 Hz, Bn), 4.72 (d, 1H, J_{Bn} =11.9 Hz, Bn), 4.88 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.94 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), 4.99 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-l), 5.01 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 7.3-7.4 (m, 5H, Bn).

^{13}C NMR ($CDCl_3$): δ = -4,46 (SiMe), -4.33 (SiMe), 16.18, 16.27 (4 × C-6), 18,31 (^{t}Bu, q), 26.00 (^{t}Bu, s), 26.21 (^{i}Pr), 26.40 (^{i}Pr), 26.49 (^{i}Pr), 26.55 (^{i}Pr), 28.20 (^{i}Pr), 28.38 (^{i}Pr), 28.41 (2 × ^{i}Pr), 63.15 (C-5), 63.45 (C-5), 63.54 (C-5), 63.63 (C-5), 69.59 (Bn), 71.91 (C-2), 74.44, 74.91 (C-2, 2 × C-3), 76.20, 76.29, 76.37, 76.70, 76.84, 77,02, 77.34 (2 × C-2, 2 × C-3, 4 × C-4), 95.38 (C-1), 95.79 (C-1), 96.80 (C-1), 98.21 (C-1), 108.45 (2 × ^{i}Pr), 108.48 (^{i}Pr), 108.66 (^{i}Pr), 127–137 (Bn).

12β:

^{1}H NMR ($CDCl_3$): δ = 3.80 (H-2), 3.91 (H-2), 3.95 (H-4), 4.98 (H-l), 5.40 (H-1).

$C_{49}H_{78}O_{17}Si$	calcd	C	60.85	H	8.13
(967.23)	found		61.26		8.17

Benzyl 2-*O*-*tert*-Butyldiphenylsilyl-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1 → 2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1 → 2)-3,4-*O*-isopropylidene-α-L-fucopyranoside (13):

13 was prepared in the same way as compound **12**, using **9** (300 mg, 0.62 mmol), **11** (200 mg, 0.30 mmol), Bu_4NBr (640 mg, 2 mmol), $CuBr_2$ (440 mg, 2 mmol), DMF/CH_2Cl_2 (10 mL) and molecular sieves (0.5 g). After stirring for 14 d and standard workup column chromatography (toluene/EtOAc 7.5:1) yielded 168 mg (0.15 mmol, 5l%) of product as a syrup, containing 15% β-linked tetrasaccharide.

13α: $[\alpha]_D^{20}$ –141,8 (c = 1.0, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ = 1.04 (s, 9H, ^{t}Bu), 1.2–1.35 (m, 30H, 4 × H-6, 6 × ^{i}Pr), 1.47 (s, 3H, ^{i}Pr), 1.52 (s, 3H, ^{i}Pr), 3.65 (dd ≈ m, 1H. $J_{1,2}$ = 3.0, $J_{2,3}$ = 8.1 Hz, H-2), 3.67 (dd ≈ m, 1H, $J_{1,2}$ = 3.0 Hz. H-2), 3.73 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 8.1 Hz, H-2), 3.85 (dd, 1H. $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 7.1 Hz, H-2), 3.98 (dd, 1H, $J_{3,4}$ = 5.6 Hz, $J_{4,5}$ = 2.5 Hz, H-4), 4.01-4.15 (m, 5H, H-3, 3 × H-4, H-5), 4,25–4.47 (m, 6H, 3 × H-3, 3 × H-5), 4.56 (d, 1H, J_{Bn} = 12.2 Hz, Bn), 4.75 (d, 1H, J_{Bn} = 12.2, Bn), 4.84 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.86 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-l), 4.96 (d, 1H, $J_{1,2}$ = 3.0 Hz, H-1), 5.00 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-l), 7.3–7.4 (m, 15H, Bn, Ph), 7.71 (m, 5H, Ph).

^{13}C NMR ($CDCl_3$): δ = 16.21, 16.27, 16.33 (4 × C-6), 19.50 (^{t}Bu, q), 26.14 (^{i}Pr), 26.30 (^{i}Pr), 26.50 (^{i}Pr), 27.00 (^{i}Pr), 27.14 (^{t}Bu, s), 27.47 (^{i}Pr), 28.19 (^{i}Pr), 28.29 (^{i}Pr), 28.43 (^{i}Pr), 63.42 (C-5), 63.49 (C-5), 63.62 (C-5), 63.72 (C-5), 69.49 (Bn), 72.44 (C-2), 74.78 (C-3). 74.86 (C-3), 74.93 (C-3, C-2), 75.89 (C-2), 75.96 (C-2), 76.13 (C-4), 76.27 (3 × C-4), 76.40 (C-3), 95.74 (C-1), 95.90 (C-1), 96.81 (C-1), 98.12 (C-1), 108.38 (^{i}Pr), 108.44 (^{i}Pr), 108.57 (^{i}Pr), 108.71 (^{i}Pr), 127–137 (Bn).

13β:
^{1}H NMR ($CDCl_3$): δ = 3.51 (H-2), 3.56 (H-2), 3.88 (H-2), 4.89 (H-1).

$C_{59}H_{82}O_{17}Si$	calcd	C	64.93	H	7.57
(1091.38)	found		64.59		7.57

Benzyl 3,4-*O*-Isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1 → 2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranoside (14):
12 (322 mg, 0.33 mmol) was treated with 1 M TBAF in THF (10 mL) for 4 h. Subsequently, the solvent was evaporated, the syrup dissolved in EtOAc (20 mL), washed with aq Na_2CO_3 (2 × 20 mL) and brine (20 mL) dried and again evaporated under reduced pressure. Column chromatography (petroleum ether/EtOAc 2:1) and following preparative TLC (petroleum ether/EtOAc 1:1) gave both, 177 mg (0.20 mmol, 62%) of product and 48 mg (0.06 mmol, 17%) of β-linked tetrasaccharide.

14α: $[\alpha]_D^{20}$ –228.2 (c = 1.0, $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ = 1.23 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1 .30 (d ≈ m, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1,31 (d ≈ m, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.33 (s, 9H, 3 × ^{i}Pr), 1.35 (s, 3H, ^{i}Pr), 1.36 (d ≈ m, 3H, H-6), 1.44 (s, 3H, ^{i}Pr), 1.51 (s, 3H, ^{i}Pr), 1.52 (s, 3H, ^{i}Pr), 1.53 (s, 3H, ^{i}Pr), 3.11 (d, 1H, $J_{2,OH}$ = 5.6 Hz, OH-2), 3.66 (ddd ≈ m, 1H, H-2‴), 3.77 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 8.1 Hz, H-2), 3.85 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 8.3 Hz, H-2), 3.93 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 6.1 Hz, H-2), 4.00 (dd, 1H, $J_{3,4}$ = 5.6 Hz, $J_{4,5}$ = 2.5 Hz, H-4), 4.02–4.09 (m, 4H, 3 × H-4, H-5), 4.18 (m ≈ dd, 3H, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 5.8 Hz, 2 × H-3, H-5), 4.28–4.33 (m, 2H, 2 × H-3), 4.41–4.48 (ddd, 2H, 2 × H-5), 4.55 (d, 1H, J_{Bn} =12.2 Hz, Bn), 4.67 (d, 1H, J_{Bn} =12.2 Hz, Bn), 4.91 (m ≈ d, 2H, $J_{1,2}$ = 3.5 Hz, 2 × H-l), 4.99 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1), 5.38 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-l), 7.3–7.4 (m, 5H, Bn).

^{13}C NMR ($CDCl_3$): δ = 16.21 (2 × C-6), 16.26 (C-6), 16.42 (C-6), 25.91 (^{i}Pr), 26.35 (^{i}Pr), 26.41 (2 × ^{i}Pr), 27.52 (^{i}Pr), 28.25 (^{i}Pr), 28.27 (^{i}Pr), 28.39 (^{i}Pr), 62.80 (C-5), 63.32 (2 × C-5), 64.49 (C-5), 69.58 (Bn), 70.11 (C-2), 76.63 (C-2), 72.18 (C-2), 73.27 (C-2), 74.32 (C-3), 74.37 (C-3), 74.42 (C-3), 75.93 (C-4), 76.01 (2 × C-4), 76.20 (C-3, C-4), 93.14 (C-1), 93.19 (C-l), 94.63 (C-1), 95.78 (C-1), 108.64 (^{i}Pr), l08.78 (^{i}Pr), 109.04 (^{i}Pr), 109.28 (^{i}Pr), 128.01 (Bn), 128.15 (Bn), 128.57 (Bn), 137.04 (Bn).

FAB (matrix: *m*-nitrobenzyl alcohol m = 852.41) = 837.5 (m–l5), 853.6 (m+1) 875.6 (m+Na).

$C_{43}H_{64}O_{17}$	calcd	C	60.55	H	7.56
(852.97)	found		59.95		7.29

14β: $[\alpha]_D^{20}$ –323.2 (c = 2.0 $CHCl_3$).
^{1}H NMR ($CDCl_3$): δ = 0.96 (s, 3H, ^{i}Pr), 1.23 (s, 3H, ^{i}Pr), 1.27 (m ≈ d, 6H, $J_{5,6}$ = 7.1 Hz, 2 × H-6), 1.31 (d ≈ m, 3H, $J_{5,6}$ = 8.1 Hz, H-6), 1.32 (s ≈ m, 3H, ^{i}Pr), 1.35 (s, 3H, ^{i}Pr), 1.37 (s, 3H, ^{i}Pr), 1.39 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.53 (s, 3H, ^{i}Pr), 1.55 (s, 3H, ^{i}Pr), 1.56 (s, 3H, ^{i}Pr), 3.58 (dd ≈ t, 1H, $J_{1'',2''}$ = $J_{2'',3''}$ = 8,1 Hz, H-2″), 3.63 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 8.6 Hz, H-2), 3.72–3.82 (m, 3H, 2 × H-2, H-5″), 3.90 (dd, 1H, $J_{3'',4''}$ = 5,1 Hz, $J_{4'',5''}$ = 1.5 Hz, H-4″), 3.98 (dd, 1H, $J_{3,4}$ = 5.1 Hz, $J_{4,5}$ = 2.5 Hz, H-4), 4.01–4.11 (m, 3H, H-3, H-4, H-5), 4.12 (dd, 1H, $J_{3,4}$ = 5.6 Hz, $J_{4,5}$ = 2.5 Hz, H-4), 4.17 (dd, 1H, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 5,6 Hz, H-3), 4.22 (dd, 1H, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 5.1 Hz, H-3), 4.41 (dd, 1H, $J_{2.3}$ = 8.4 Hz, $J_{3,4}$ = 5.6 Hz, H-3), 4.46 (m, 2H, $J_{1'',2''}$ = 8.1 Hz, H-1, H-5), 4.62 (m, 2H, J_{Bn} =11.2 Hz, H-5, Bn), 4.77 (d, 1H, J_{Bn} =11.2 Hz, Bn), 5.08 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), 5.18 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), 5.47 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 7.3–7.4 (m, 5H, Bn).

^{13}C NMR ($CDCl_3$): δ = 16.00 (C-6), 16.14 (C-6), 16.23 (C-6), 17.09 (C-6), 26.19 (^{i}Pr), 26.39 (^{i}Pr), 26.46 (^{i}Pr), 26.55 (^{i}Pr), 27.31 (^{i}Pr), 28.33 (^{i}Pr), 28.47 (^{i}Pr), 28.54 (^{i}Pr), 62.46 (C-5), 62.61 (C-5), 63.29 (C-5), 68.76 (C-5″), 70.57 (C-2), 71.75 (Bn), 74.49 (C-3), 74.51 (C-3), 75.40 (C-2, C-2″), 75.96 (C-4), 76.10 (C-3), 76.24 (C-4), 76.32 (C-4), 76.43 (C-4), 77.78 (C-3″), 81.25 (C-2), 96.93 (C-1), 96.94 (C-1), 98.22 (C-1), 105.71 (C-1″), 108.54 (^{i}Pr), 108.74 (^{i}Pr), 109.16 (^{i}Pr), 109.45 (^{i}Pr), 127,60 (Bn), 128.13 (Bn), 128.57 (Bn), 137.09 (Bn).

Benzyl 2-*O*-*tert*-Butyldimethylsilyl-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranoside (15):
Applying the general glycosylation procedure **14** (200 mg, 0.24 mmol), **10** (220 mg, 0.41 mmol), Bu_4NBr 450 mg (1.4 mmol), $CuBr_2$ (310 mg, 1.4 mmol), DMF/CH_2Cl_2 (10 mL) and molecular sieves (1 g) were converted in a reaction time of 10 d. Standard workup and column chromatography (toluene/EtOAc 10:1) furnished 104 mg (0.08 mmol, 33%) of product containing less than 5% β-linked hexasaccharide. Furthermore starting material (**14**, 30%) and disaccharide bromide (31%) were isolated; $[\alpha]_D^{20}$ –193.0 (c = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 0.08 (s, 3H, SiMe), 0.10 (s, 3H, SiMe), 0.87 (s, 9H, ^{t}Bu), 1.21 (s, 3H, ^{i}Pr), 1.23–l.35 (m, 27H, 5 × H-6, 4 × ^{i}Pr), 1.36 (d, 3H, $J_{5,6}$ =6.6 Hz. H-6), 1.47 (s, 6H, 2 × ^{i}Pr), 1.52 (s, 3H, ^{i}Pr), 1.53 (s, 6H, 2 × ^{i}Pr), 1.54 (s, 3H, ^{i}Pr), 1.65 (s, 3H, ^{i}Pr), 3.57 (dd, 1H, $J_{1,2}$ = 3.1 Hz, $J_{2,3}$ = 8.1 Hz, H-2), 3.59–3.64 (m, 3H, 3 × H-2), 3.69 (dd ≈ m, 1H, $J_{1,2}$ = 3.5 Hz, H-2), 3.71 (dd ≈ m, 1H, $J_{1,2}$ = 3.5 Hz, H-2), 3.82 (dd, 1H, $J_{3,4}$ = 5.6 Hz, $J_{4,5}$ = 3.0 Hz, H-4), 3.93–4.01 (m, 3H, 2 × H-3, H-4), 4.03 (dd, 1H, $J_{3,4}$ = 5.1 Hz, $J_{4,5}$ = 2.6 Hz, H-4), 4.07 (dd, 1H, $J_{3,4}$ = 5.1 Hz, $J_{4,5}$ = 3.0 Hz, H-4), 4.14 (m, 2H, H-3, H-5), 4.19 (dd, 1H, $J_{3,4}$ = 5.4 Hz, $J_{4,5}$ = 3.5 Hz, H-4), 4.22 (dd, 1H, $J_{3,4}$ = 5.6 Hz, $J_{4.5}$ = 2.5 Hz, H-4), 4.27–4.35 (m, 3H, 3 × H-3), 4.39–4.51 (m, 4H, 4 × H-5), 4.59 (dq, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.71 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.73 (d, 1H, J_{Bn} = 12.2 Hz, Bn), 4.79 (d, 1H, J_{Bn} =l2.2 Hz, Bn), 4.85 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), 4.89 (d ≈ m, 1H, $J_{1,2}$ = 3.5 Hz, H-l), 4.90 (d ≈ m, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 4.96 (d, 1H, $J_{1,2}$ = 3.l Hz, H-1), 5.10 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1), 7.3–7.4 (m, 5H, Bn).

^{13}C NMR ($CDCl_3$): δ = –4.41 (SiMe), –4.26 (SiMe), 15.93 (C-6), l6.06 (C-6), 16.14 (C-6), 16.18 (C-6), 16.24 (C-6), 16.35 (C-6), 18.34 (^{t}Bu, q), 26.05 (^{t}Bu, s), 26.32 (^{i}Pr), 26.67 (2 × ^{i}Pr), 26.69 (^{i}Pr), 26.72 (^{i}Pr), 27.05 (^{i}Pr), 28.50 (2 × ^{i}Pr), 28.52 (^{i}Pr), 28.60 (^{i}Pr), 28.71 (^{i}Pr), 29.70 (^{i}Pr), 63.15, 63.19, 63.39, 63.95 (6 × C-5), 70.76 (Bn), 72.71 (C-2), 74.32 (C-3), 74.55 (C-3), 74.59 (C-3), 74.68 (C-3), 74.73 (C-3), 76–80 (5 × C-2, C-3, 6 × C-4), 97.55 (3 × C-l), 97.92 (C-l), 100.15 (C-1), 101.27 (C-l), 108.14 (^{i}Pr), 108.35 (^{i}Pr), 108.38 (^{i}Pr), l08.51 (^{i}Pr), 108.62 (^{i}Pr), 108.65 (^{i}Pr), 127.35 (Bn), 127.52 (Bn), 128.32 (Bn), 138.31 (Bn).

$C_{67}H_{106}O_{25}Si$	calcd	C	60.07	H	7.98
(1339.65)	found		59.76		8.09

Benzyl 3,4-*O*-Isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranoside (16):
1 M TBAF in THF (4 mL) was added to **15** (100 mg, 0.07 mmol) and stirred for 3 h. For workup the solvent was evaporated, EtOAc (20 mL) was added, the solution agitated with sat. Na_2CO_3 (3 × 20 mL)

and sat. brine (20 mL), dried, evaporated and column chromatography (petroleum ether/EtOAc 1:1.5) yielded 78 mg (0.06 mmol, 84%) of product containing traces of TBAF; $[\alpha]_D^{20}$ –168.2 (c = 0.8, $CHCl_3$). ^{1}H NMR 500M Hz ($CDCl_3$): δ = 1.26 (s, 3H, ^{i}Pr), 1.28 (s, 3H, ^{i}Pr), 1.29–l.40 (m, 30H, 6 × H-6, 4 × ^{i}Pr), 1.51 (s, 6H, 2 × ^{i}Pr), 1.53 (s, 3H, ^{i}Pr), 1.54 (s, 3H, ^{i}Pr), 1.55 (s, 6H, 2 × ^{i}Pr), 2.97 (d, 1H, $J_{2,OH}$ = 7.0 Hz, OH-2), 3.70 (ddd, 1H, $J_{1,2}$ = 3.8 Hz, $J_{2,3} \approx J_{2,OH}$ = 7.3 Hz, H-2′′′′), 3.77 (dd ≈ m, 1H, $J_{1,2}$ = 3.8 Hz, H-2), 3.79 (dd ≈ m, 1H, $J_{1,2}$ = 3.8 Hz, H-2), 3.86 (dd ≈ m, 1H, $J_{1,2}$ = 3.8 Hz, H-2), 3.87 (dd ≈ m, 1H, $J_{1,2}$ = 3.2 Hz, H-2), 3.98–4.06 (m, 4H, H-2, 2 × H-4, H-5), 4.08–4.15 (m, 4H, 4 × H-4), 4.23 (dd, 1H, $J_{2,3}$ = 7.6 Hz, $J_{3,4}$ = 5.7 Hz, H-3′′′′), 4.28 (dd, 1H, $J_{2,3}$ = 7.6 Hz, $J_{3,4}$ = 5.7 Hz, H-3), 4.31–4.41 (m, 7H, 4 × H-3, 3 × H-5), 4.43 (dq, 1H, $J_{4,5}$ = 2.2 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.47 (dq, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.8 Hz, H-5), 4.67 (d ≈ s, 1H, J_{Bn} = 12.0 Hz, Bn), 4.70 (d ≈ s, 1H, J_{Bn} = 12.0 Hz, Bn), 4.97 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-l), 5.02 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 5.08 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1′′′′), 5.27 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1), 5.36 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-l), 5.41 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 7.3–7.5 (m, 5H, Bn).

^{13}C NMR ($CDCl_3$): δ = 16.09 (C-6), 16.23 (2 × C-6), 16.37 (3 × C-6), 26.13 (^{i}Pr), 26.38 (^{i}Pr), 26.42 (2 × ^{i}Pr), 26.54 (2 × ^{i}Pr), 27.84 (^{i}Pr), 28.29 (^{i}Pr), 28.36 (^{i}Pr), 28.39 (^{i}Pr), 28.42 (^{i}Pr), 28.47 (^{i}Pr), 62.64 (C-5), 62.77 (3 × C-5), 62.91 (C-5), 63.95 (C-5), 69.83 (Bn), 70.19 (C-2′′′′), 71.17 (C-2), 72.08 (C-2), 72.46 (C-2), 72.90 (2 × C-2), 74.05 (2 × C-3), 74.43 (3 × C-3), 75.97 (2 × C-4), 76.09 (3 × C-4), 76.20 (C-4), 76.53 (C-3), 92.11 (C-1), 92,42 (2 × C-1), 92.83 (C-1), 94.19 (C-l), 95.31 (C-1′′′′), 108.60 (^{i}Pr), 108.73 (^{i}Pr), 108.75 (^{i}Pr), 108.78 (2 × ^{i}Pr), 109.05 (^{i}Pr), 127.99 (Bn), 128.44 (Bn), 128.81 (Bn), 136.97 (Bn).

FAB (matrix: *m*-nitrobenzyl alcohol m =1224.59): 1209.6 (m–l5), 1247.8 (m+Na).

$C_{61}H_{92}O_{25}$	calcd	C	59.79	H	7.57
(1225.39)	found		60.15		7.89

Benzyl α-L-Fucopyranosyl-(1→2)-α-L-fucopyranosyl-(1→2)-α-L-fucopyranosyl-(1 → 2)-α-L-fucopyranosyl-(1 → 2)-α-L-fucopyranosyl-(1 → 2)-α-L-fucopyranoside (17):

16 (16 mg, 13 µmol) was treated with a mixture of dioxane and l% H_2SO_4 (1:1, 10ml) for 5 h. The mixture was neutralized with $BaCO_3$ and the solvent removed under reduced pressure to yield 12 mg (12 µmol, 92%) of crystalline white product; $[\alpha]_D^{20}$ –251.8 (c = 1.3, $CHCl_3$). ^{1}H NMR (D_2O): δ = 0.76 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.00–1.10 (m, 15H, 5 × H-6), 3.5–4.0 (m, 23H, 6 × H-2, 6 × H-3, 6 × H-4, 5 × H-5), 4.06 (dq ≈ q, 1H, $J_{4,5} \leq 1$ Hz, $J_{5,6}$ = 6.6 Hz), 4.62 (d ≈ m, 1H, Bn), 4.72 (d, 1H, J_{Bn} = 12.2 Hz, Bn), 4.97 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1), 4.98 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.16 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-1), 5.24 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), 5.31 (d ≈ s, 1H, H-1), 5.40 (d ≈ s, 1H, H-1), 7.2–7.4 (m, 5H, Bn).

^{13}C NMR (D_2O): δ = 15.29, 15.59, 15.67, 15.76, 15.82 (6 × C-6), 67.01, 67.14, 67.49, 67.57, 68.37, 68.58, 68.63, 68.68, 68.81, 69.79, 71.94, 72.12, 72.24 (6 × C-2, 6 × C-3, 6 × C-4, 6 × C-5), 94.91 (C-1), l28.68, 129.04, 129.65 (Bn).

$C_{42}H_{66}O_{25}$	calcd	C	51.95	H	6.85
(970.97)	found		52.33		6.99

Benzyl 2-*O*-Acetyl-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranoside (18):

9 (300 mg, 0.62 mmol) was treated with Ac_2O/pyridine (1:2, 30 mL) at 0 °C and stirred overnight at r.t. Evaporation with toluene (3 ×) and silica gel filtration (petroleum ether/EtOAc 2:1) furnished 320 mg (0.51 mmol, 99%) of a colourless syrup; $[\alpha]_D^{20}$ –203.0 (c = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.31 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.33 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.35 (s, 6H, 2 × ^{i}Pr), 1.53 (s, 6H, 2 × ^{i}Pr), 1.93 (s, 3H, OAc), 3.81 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 8.1 Hz, H-2), 4.05 (dd, 1H, $J_{3,4}$ = 5.6 Hz, $J_{4,5}$ = 2.6 Hz, H-4), 4.09 (dq, 1H, $J_{4,5}$ = 2.6 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.13 (dd, 1H, $J_{3,4}$ = 5.1 Hz, $J_{4,5}$ = 2.6 Hz, H-4), 4.29 (dd, 1H, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 5.1 Hz, H-3), 4.40 (dd, 1H, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 5.1 Hz, H-3), 4.48 (d, 1H, J_{Bn} = 12.2 Hz, Bn), 4.55 (dq, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.71 (d, 1H, J_{Bn} = 12.2 Hz, Bn), 4.80 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 8.1 Hz, H-2), 4.92 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 5.10 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1), 7.34 (m, 5H, Bn).

^{13}C NMR ($CDCl_3$): δ = 16.10 (C-6), 16.24 (C-6), 20.92 (OAc), 26.45 (2 × ^{i}Pr), 28.11 (^{i}Pr), 28.42 (^{i}Pr), 62.62 (C-5), 63.31 (C-5), 69.99 (Bn), 72.43, 73.25, 73.40, 74.50, 76.17 (2 × C-2, 2 × C-3, 2 × C-4), 93.32 (C-1), 95.27 (C-l), 108.81 (^{i}Pr), 109.20 (^{i}Pr), 127.43 (Bn), 127.83 (Bn), 128.43 (Bn), 137.33 (Bn), 170.82 (OAc).

$C_{27}H_{38}O_{10}$	calcd	C	62.06	H	7.33
(522.59)	found		61.76		7.34

2-*O*-Acetyl-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-L-fucopyranose (19):

To a stirred solution of **18** (312 mg, 0.60 mmol) in MeOH/EtOAc (2:1, 30 mL) HCO_2NH_4 (200 mg) and Pd/C (50 mg, 10%) were added. The suspension was hydrogenated under 70 bar for 2 d, the solids were replaced and hydrogenation was carried on for another 2 d. After filtration column chromatography (petroleum ether/EtOAc 1:1) yielded 166 mg (0.38 mmol, 64%) of the anomeric mixture (α/β 3:2) as a solid and unchanged starting material (31%); $[\alpha]_D^{20}$ –l78.3 (c = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.32 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6α), 1.33–1.37 (m, 18H, H-6α, H-6β, 2 × ^{i}Prα, 2 × ^{i}Prβ), 1.39 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6β), 1.52 (s, 3H, ^{i}Prα), 1.53 (s, 6H, ^{i}Prα, ^{i}Prβ), 1.55 (s, 3H, ^{i}Prβ), 2.11 (s, 3H, OAcβ), 2.13 (s, 3H, OAcα), 3.54 (dd ≈ t, 1H, $J_{1,2} \approx J_{2,3}$ = 7.6 Hz, H-2β), 3.81 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 6.6 Hz, H-2α), 3.89 (dq, 1H, $J_{4,5}$ = 2.0 Hz, $J_{5,6}$ = 6.6 Hz, H-5β), 4.00 (dd, 1H, $J_{3,4}$ = 5.2 Hz, $J_{4,5}$ = 2.0 Hz, H-4β), 4.05 (dd, 1H, $J_{3,4}$ = 6.1 Hz $J_{4,5}$ = 2.5 Hz, H-4α), 4.08 (dd, 1H, $J_{2,3}$ = 7,1 Hz, $J_{3,4}$ = 5.6 Hz, H-3β), 4.12 (dd, 2H, $J_{3,4}$ = 5.6 Hz, $J_{4,5}$ = 2.5 Hz, H-4α, H-4β), 4.25 (dq, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.6 Hz, H-5α), 4.28–4.36 (m, 3H, 2 × H-3α, H-3β), 4.40 (dq, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.6 Hz, H-5α), 4.54 (dq ≈ m, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.6 Hz, H-5β), 4.56 (d ≈ m, 1H, $J_{1,2}$ = 7.1 Hz, H-1β), 4.88 (dd ≈ m, 1H, $J_{1',2'}$ = 3.5 Hz, $J_{2',3'}$ = 8.2 Hz, H-2′β), 4.91 (dd ≈ m, 1H, $J_{1',2'}$ = 3.6 Hz, $J_{2',3'}$ = 8.0 Hz, H-2′α), 5.06 (d, 1H, $J_{1',2'}$ = 3.6 Hz, H-1′α), 5.18 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1α), 5.35 (d, 1H, $J_{1',2'}$ = 3.5 Hz, H-1′β).

^{13}C NMR ($CDCl_3$): δ = 16.17, 16.46, 16.58 (2 × C-6α, 2 × C-6β), 20.97 (OAcβ), 21.01 (OAcα), 26.01, 26.35, 26.45, 27.66, 27.94, 28.10 (4 × ^{i}Prα, 4 × ^{i}Prβ), 62.86 (C-5β), 63.42 (C-5α), 64.07 (C-5 α), 68.88 (C-5β), 71.79 (C-2′α), 72.02 (C-2′β), 73.13 (C-3α, C-3β), 73.89 (C-3α), 74.70 (C-2α), 75.66 (C-4α), 75.89 (C-4α), 76.23 (C-4β), 76.51 (C-4β), 77.61 (C-3β), 77.76 (C-2β), 89.74 (C-1α), 95.55 (C-1′α), 95.93 (C-1′β), 96.51 (C-1β).

$C_{20}H_{32}O_{10}$	calcd	C	55.55	H	7.46
(432.47)	found		55.50		7.57

2-*O*-Acetyl-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-β-L-fucopyranosyl Trichloroacetimidate (20):

To a stirred solution of **19** (100 mg, 0.23 mmol) in CH_2Cl_2 (5 mL) under Ar were added K_2CO_3 (120 mg, 0.87 mmol) and trichloroacetonitrile (0.12 mL, 1.2 mmol). After 1 d the solids were filtered off, the solvent was evaporated and column chromatography (petroleum ether/EtOAc 1.5:1) yielded 80 mg (14 mmol, 60%) product; $[\alpha]_D^{20}$ –53.0 (c = 0.5, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.34 (s, 3H, ^{i}Pr), 1.35 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.38 (s, 3H, ^{i}Pr), 1.42 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.53 (s, 3H, ^{i}Pr), 1.59 (s, 3H, ^{i}Pr), 2.01 (s, 3H, OAc), 3.92 (dd ≈ t, 1H, $J_{1,2} \approx J_{2,3}$ = 7.8 Hz, H-2), 4.02 (dq, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.07 (dd, 1H, $J_{3,4}$ = 5.2 Hz, $J_{4,5}$ = 2.5 Hz, H-4), 4.12 (dd, 1H, $J_{3',4'}$ = 5.1 Hz, $J_{4',5'}$ = 2.5 Hz, H-4′), 4.20 (dd, 1H, $J_{2,3}$ = 7.1 Hz, $J_{3,4}$ = 5.1 Hz, H-3), 4.28 (dd, 1H, $J_{2',3'}$ = 8.4 Hz, $J_{3',4'}$ = 5.4 Hz, H-3′), 4.64 (dq, 1H, $J_{4',5'}$ = 2.5 Hz, $J_{5',6'}$ = 6.6 Hz, H-5′), 5.06 (dd, 1H, $J_{1',2'}$ = 3.5 Hz, $J_{2',3'}$ = 8.6 Hz, H-2′), 5.25 (d, 1H, $J_{1',2'}$ = 3.5 Hz, H-1′), 5.75 (d, 1H, $J_{1,2}$ = 8.6 Hz, H-1), 8.68 (s, 1H, NH).

^{13}C NMR ($CDCl_3$): δ = 16.11 (C-6), 16.42 (C-6), 21.06 (OAc), 26.33 (^{i}Pr), 26,54 (^{i}Pr), 27.90 (^{i}Pr), 28.14 (^{i}Pr), 62.95 (C-5), 69.95, 70.62 (C-2, C-5), 73.44, 74.44, 76.23, 76.33, 78.11 (C-2, 2 × C-3, 2 × C-4), 90.64 (CCl_3), 95.98 (C-1), 97.48 (C-1), 109.23 (^{i}Pr), 109.91 (^{i}Pr), l61.38 (CNH), 170.02 (OAc).

$C_{22}H_{32}O_{10}Cl_3N$	calcd	C	45.81	H	5.59	N	2.43
(576.86)	found		45.14		5.48		2.41

Benzyl 2-*O*-Acetyl-3,4-*O*-isopropylidene-α-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α,β-L-fucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-Lfucopyranosyl-(1→2)-3,4-*O*-isopropylidene-α-L-fucopyranoside (21):

Compounds **9** (75 mg, 156 μmol) and **20** (68 mg, 118 μmol) were dissolved in Et_2O and stirred with molecular sieves for 1 h. The solution was cooled to –15 °C and TMSOTf [0.5 mL, 0.2 mL in Et_2O (5 mL)] was added dropwise. After 1 h the mixture was treated with Na_2CO_3 (50 mg), filtered through Celite, washed with sat. Na_2CO_3, dried, and column chromatography (toluene/EtOAc 3:1) furnished two fractions, 28 mg (31 μmol, 27%) β-linked product and 36 mg (40 μmol, 34%) of an anomeric mixture (α/β 3:1).

21β:

^{1}H NMR ($CDCl_3$): δ = 1.17 (d, 3H, $J_{5''',6'''}$ = 6.6 Hz, H-6‴), 1.20 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.29 (d, 3H, $J_{5'',6''}$ = 6.6 Hz, H-6″), 1.31 (s, 3H, ^{i}Pr), 1.32 (s, 3H, ^{i}Pr), 1.33 (s, 3H, ^{i}Pr), 1.34 (s, 6H, 2 × ^{i}Pr), 1.40 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.49 (s, 3H, ^{i}Pr), 1.51 (s, 3H, ^{i}Pr), 1.56 (s, 3H, ^{i}Pr), 2.16 (s, 3H, OAc), 3.66 (dd ≈ t, 1H, $J_{1'',2''} \approx J_{2'',3''}$ = 7.6 Hz, H-2″), 3.70 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 8.6 Hz, H-2), 3.78 (ddd, 1H, $J_{4,5}$ = 2.1 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 3.89 (dd, 1H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 8.1 Hz, H-2), 3.94 (ddd ≈ m, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 3.97 (m, 2H, H-4, H-4″), 4.04 (dd, 1H, $J_{3,4}$ = 5.1 Hz, $J_{4,5}$ = 2.5 Hz, H-4), 4.10 (m, 2H, H-3″, H-4‴), 4.21 (dd, 1H, $J_{2,3}$ = 8.6 Hz, $J_{3,4}$ = 5.6 Hz, H-3), 4.27 (dd, 1H, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 5.6 Hz, H-3), 4.34 (dd, 1H, $J_{2''',3'''}$ = 8.6 Hz, $J_{3''',4'''}$ = 5.1 Hz, H-3‴), 4.54 (ddd, 1H, $J_{4,5}$ = 2.5 Hz, $J_{5,6}$ = 6.6 Hz, H-5), 4.58 (d ≈ m, 1H, J_{Bn} =11.7 Hz, Bn), 4.59 (ddd ≈ m, 1H, $J_{4''',5'''}$ = 2.5 Hz, H-5‴), 4.78 (d, 1H, J_{Bn} =11.7 Hz, Bn), 4.81 (d, 1H, $J_{1'',2''}$ = 8.5 Hz, H-1″), 4.90 (d, 1H, $J_{1,2}$ = 3.8 Hz, H-1), 4.94 (d, 1H, $J_{1,2}$ = 3.2 Hz, H-l), 5.06 (dd, 1H, $J_{1''',2'''}$ = 3.6 Hz, $J_{2''',3'''}$ = 8.6 Hz, H-2‴), 5.57 (d, 1H, $J_{1''',2'''}$ = 3.6 Hz, H-1‴), 7.3–7.4 (m, 5H, Bn).

^{13}C NMR ($CDCl_3$): δ = 16.05 (C-6), 16.13 (2 × C-6), 16.63 (C-6), 21.21 (OAc), 26.41 (^{i}Pr), 26.53 (^{i}Pr), 26.64 (2 × ^{i}Pr), 28.06 (^{i}Pr), 28.13 (^{i}Pr), 28.37 (^{i}Pr), 28.49 (^{i}Pr), 62.40 (C-5). 62.49 (C-5), 63.23 (C-5), 68.78 (C-5), 70.73 (Bn), 71.36, 73.51, 74.01, 74.42. 74.49, 74.63, 76.06, 76.28, 76.46, 78.20 (4 × C-2, 4 × C-3, 4 × C-4), 95.47 (C-1), 95.51 (C-1), 96.03 (C-1), 101.58 (C-1), 108.39 (2 × ^{i}Pr), 108.92 (^{i}Pr), 109.41 (^{i}Pr), 128.23 (Bn), 128.36 (Bn), 128.53 (Bn), 137.91 (Bn), 170.53 (OAc).

21α: $[\alpha]_D^{20}$ –159.8 (*c* = 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.22 (s, 3H, ^{i}Pr), 1.24 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6), 1.26–1.37 (m, 18H, 3 × H-6, 3 × ^{i}Pr), 1.46 (s, 3H, ^{i}Pr), 1.47 (s, 3H, ^{i}Pr), 1.51 (s, 3H, ^{i}Pr), 1.55 (s, 6H, 2 × ^{i}Pr), 2.15 (s, 3H, OAc), 3.59 (dd, 1H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 8.1 Hz, H-2), 3,68 (dd ≈ m, 1H, H-2), 3.76 (dd, 1H, $J_{1,2}$ = 3,5 Hz, $J_{2,3}$ = 8.6 Hz, H-2), 4.00–4.15 (m, 6H, H-3, 4 × H-4, H-5), 4.18–4.25 (m, 2H, H-3, H-5), 4.30 (dd, 1H, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 5.6 Hz, H-3), 4.34 (dd, 1H, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 5.3 Hz, H-3), 4.42–4.53 (m, 2H, 2 × H-5), 4.58 (d, 1H, J_{Bn} =12.2, Bn), 4.72 (d, 1H, J_{Bn} =12,2 Hz, Bn), 4.98 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.01 (m, 2H, H-1‴, H-2‴), 5.03 (d, 1H. $J_{1,2}$ = 3,5 Hz, H-1), 5.07 (dd, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 7.3–7.4 (m, 5H, Bn).

^{13}C NMR ($CDCl_3$): δ = 16.11, 16.13, 16.63 (4 × C-6), 21.14 (OAc), 26.26 (^{i}Pr), 26.33 (^{i}Pr), 26.42 (^{i}Pr), 26.52 (^{i}Pr), 27.99 (^{i}Pr), 28.25 (^{i}Pr), 28.35 (^{i}Pr). 28.42 (^{i}Pr), 62.82 (C-5), 62.88 (C-5), 63.36 (C-5), 63.50 (C-5), 69.75 (Bn), 69.74, 71.46, 73.31, 73.51, 74.42, 74.48, 75.14, 76.06, 76.13, 76.32, 76.86, 79.19 (4 × C-2, 4 × C-3, 4 × C-4), 93.85 (C-1), 94.23 (C-1), 94.49 (C-1), 95.19 (C-1), 108.60 (^{i}Pr), 108.64 (^{i}Pr), 108.69 (^{i}Pr), 109.10 (^{i}Pr), 127.61 (Bn), 128.33 (Bn), 128.49 (Bn), 128.97 (Bn), 170.91 (OAc).

$C_{45}H_{66}O_{18}$	calcd	C	60.39	H	7.43
(895.01)	found		59.95		7.22

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