SYNTHESIS OF A (1→3)-LINKED α-L-FUCOSE TETRASACCHARIDE

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Dedicated to Professor Miloslav Černý on the occasion of his 75th birthday in recognition of his outstanding contributions to carbohydrate chemistry.

Orthoester-protected benzyl and methyl 1-thiofucopyranosides could be opened to give fucopyranosides unblocked at position 3. Convergent glycosylations of such donors and acceptors led to the corresponding disaccharides, and their block condensation could be elaborated to give the (1→3)-linked α-L-fucose tetrasaccharide. Compounds of this structure are of interest with regard to the role of fucose in metastasis development in lung tissue.
Keywords: Fucose; Orthoesters; Thioglycosides; Oligosaccharides; Carbohydrates; α,(1→3)-Fucose tetrasaccharide; Glycosidations.

Placed at strategic sites of many biological active oligosaccharides, fucose has proved to play a particular important role in inflammatory diseases and cancer development[1]. In the latter case, fucose metabolism is typically activated and the sugar is found to be enriched in cell-surface oligosaccharides[2–4]. In lung tissue, fucose-specific lectins are considered to be responsible for interacting with disseminated fucose-presenting cancer cells and are therefore connected with the colonisation process of lung tissue with metastasis[5]. It was observed that blocking of these lectins was more efficient with the fucose-containing polymer fucoidin than with fucose itself[6], and this stimulated our interest in the development of a variety of derivatised, oligomeric and multivalent fucose derivatives[7–10]. Recently, fucoidin was discussed to be dominantly built of α,(1→3)-linkages[11].

Oligomers of fucose were previously obtained by Flowers et al. who synthesised all possible fucobiosides[12–15]. In the case of the α-fucosyl-(1→3)-α-fucose, they performed the Koenigs–Knorr reaction and used regioselective benzylation as the protection group strategy. (1→2)-Oligomers were obtained by Matta et al.[16,17] and ourselves[7] by using various isopropylidenated thio donors, and van Boom et al. investigated the synthesis of (1→4)-α-fucose oligomers employing thioglycoside donors[18]. Synthesic

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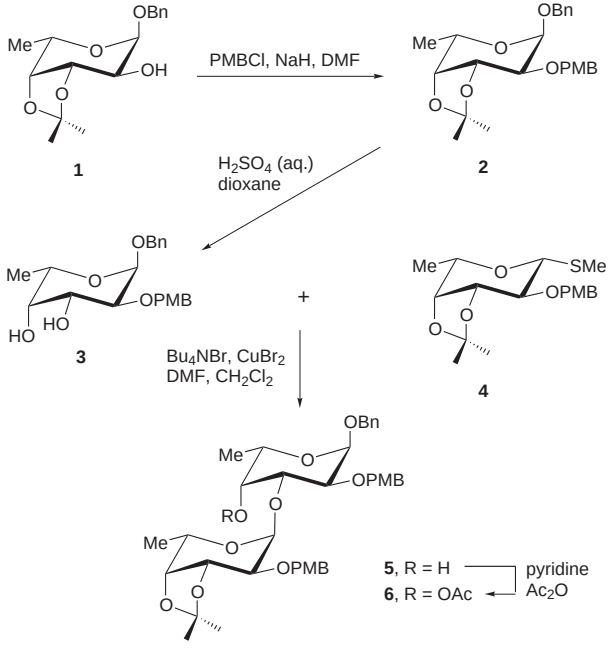
and NMR studies of sulfated and non-sulfated α-fucose (1→3)-trisaccharides as fragments of fucoidin were reported recently[19].

This paper reports on the convergent synthesis of fucose oligomers with an α-glycoside linkage pattern. To enable further elongation up to the tetrasaccharide, we investigated the protecting group strategy via ortho-esters[20] as well as regioselective glycosylations.

RESULTS AND DISCUSSION

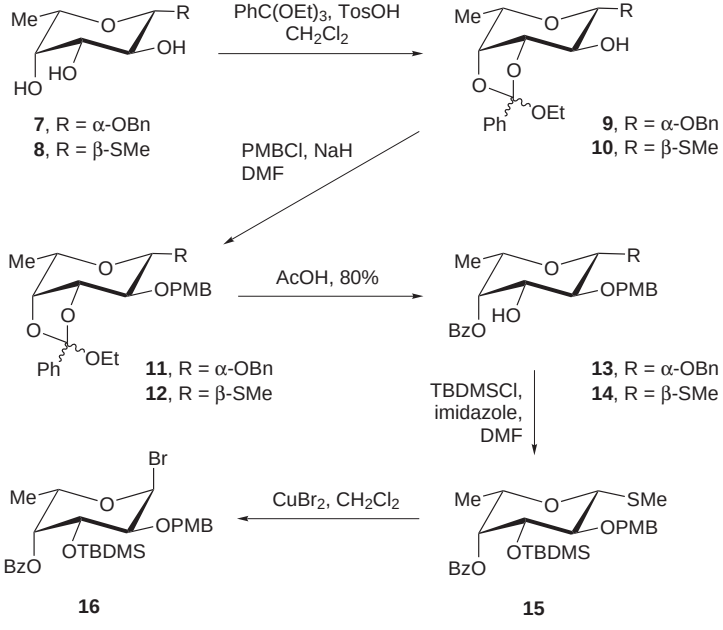
Except for heterogeneous promoters[21], the axial 4-OH group in *galacto*-configurated sugars is much less reactive and this may be advantageously used. By simple temporary introduction of an isopropylidene group into benzyl α-fucopyranoside[22] and protection of the 2-position with a 4-methoxybenzyl group (PMB), a suitable acceptor for regioselective glycosylations was obtained. Treatment of this derivative **3** with one equivalent of thiodonor[7] **4** under mild glycosylating conditions ($CuBr_2$/*t*-Bu_4NBr) led to disaccharide **5** which was acetylated to give **6** to facilitate analysis (Scheme 1).



SCHEME 1
Regioselective glycosylation at the equatorial 3-position of fucopyranose

Surprisingly, the resulting disaccharide contained some α,(1→4)-linked product (5%) and a considerable amount of β,(1→3)-glycoside (ca. 25%). Thus, to avoid purification problems in the growing saccharide chain, it was decided to protect the 4-position with a benzoate group via an orthoester. In a one-pot synthesis, treatment of the unprotected fucopyranosides **7** and **8** with triethyl orthobenzoate gave the corresponding diastereomeric 3,4-orthoesters **9** and **10**, and their subsequent 4-methoxybenzylation at position 2 led to the fully protected glycosides **11** and **12** (Scheme 2).

By subsequent stereoselective opening of the orthoesters without isolation or purification of any intermediate, the 3-OH free fucopyranosides **13** and **14** were obtained. In this way, from both the benzyl and methyl 1-thiofucopyranosides, all necessary building blocks for the construction of oligomers could be prepared. In the case of the thiomethyl donor, a TBDMS-group was introduced into the 3-position of **14** to give fully protected thiofucopyranoside **15**. Attempts to use compound **12** directly as a

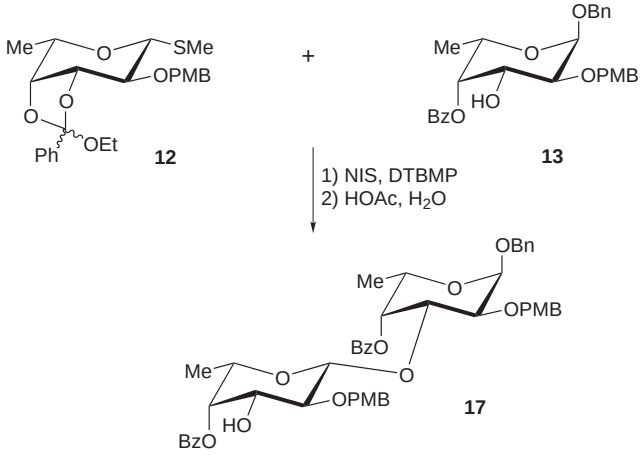


SCHEME 2
Regioselective protection of fucopyranosides via the orthoester route

glycosylation reagent proved to be difficult since the orthoester tended to opening under glycosylation conditions. Nevertheless, glycosylation of **13** could be performed under basic conditions which, however, led to the undesired corresponding β-glycoside **17** (Scheme 3).

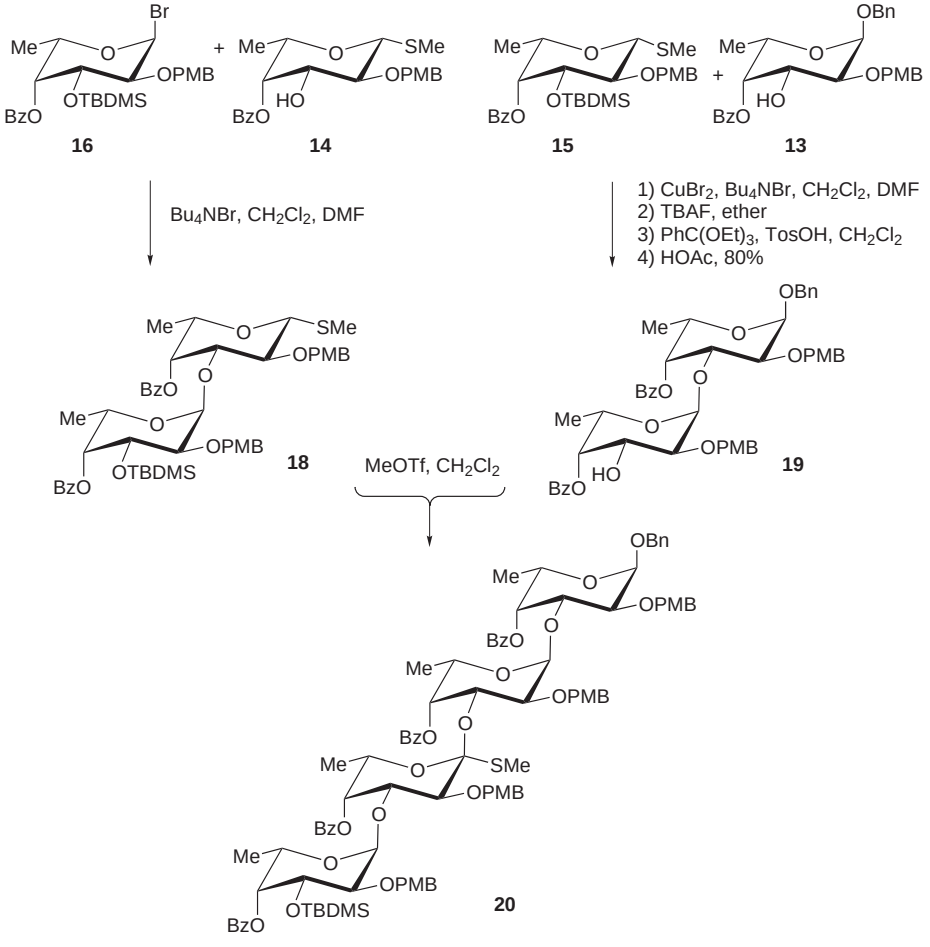
Glycosylation of acceptor **13** with donor **15** under activation of copper(II) bromide and tetrabutylammonium bromide gave stereospecifically the α-linked disaccharide **19**. However, deprotection of the 3-position in the terminal sugar ring turned out to be difficult since the benzoate tended to migrate to the equatorial position. A deprotection under acid conditions without affecting the PMB group could not be realised. Also, employing fluoride-containing acetic acid buffer did not result in any reaction. Finally, this could be overcome by removing both the TBDMS group together with the benzoate completely, followed by its re-introduction via an orthoester to give compound **19**.

For further elongation of the disaccharide acceptor **19**, a disaccharide donor was constructed. Using copper(II) bromide, donor **15** was converted into the corresponding bromide **16**, and this subsequently coupled to the thio acceptor **14** with tetrabutylammonium bromide as catalyst to give the disaccharide donor **18** in good yields. Treatment of **14** under glycosylation conditions led to a disaccharide in reasonable yields as well. However, since it proved to be impossible to introduce a TBDMS group at the 3′-position even when using TBDMSOTf, this was not further investigated.



SCHEME 3
Glycosylation using an fucopyranosyl donor under basic conditions

The decreased reactivity of the 3′-position was also evident in acceptor **19** since its glycosylation with disaccharide donor **18** under common activation of copper(II) bromide/tetrabutylammonium bromide did not give any coupling product at all. Methyl triflate as promotor, however, led to the stereoselective formation of tetrasaccharide **20** in good yield (Scheme 4).



SCHEME 4
Convergent block synthesis of a fucosetetrasaccharide derivative

CONCLUSIONS

Employment of orthoesters and their regioselective opening provided a simple and efficient approach to obtain fucopyranose derivatives with unblocked positions 3. Although the resulting axial benzoate tended to migrate to the thermodynamically more stable equatorial position, this did not occur under glycosylation conditions or with silyl-protected derivatives. However, it remained difficult to remove silyl groups without affecting the benzoate.

The reactivity of the 3-OH group appeared to be considerably reduced in disaccharides. Comparatively bulky protective groups at the 2- and 4-positions did neither affect the deprotection of a TBDMS group nor glycosylation in the monosaccharide. However, in order to perform these reactions for the corresponding disaccharide, a much more effective activation via a strong methylating agent had to be employed for the formation of the tetrasaccharide.

EXPERIMENTAL

Optical rotations (in 10^{-1} deg cm^2 g^{-1}) were determined with a Perkin–Elmer 241 polarimeter. NMR spectra were recorded on a Bruker AMX-400 or Bruker DRX-500 instrument with tetramethylsilane (TMS) as reference. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. All reactions were monitored by TLC on silica gel ($60F_{254,}$ Merck) with detection by UV or 10% ethanolic sulfuric acid. Flash chromatography was carried out with silica gel 60 (230–400 mesh, 40–63 μm, Merck). Microanalyses were made in the Microanalytical Laboratory, Department of Chemistry, University of Hamburg.

Benzyl 3,4-*O*-Isopropylidene-2-*O*-(4-methoxybenzyl)-α-L-fucopyranoside (**2**)

Compound **1** (1.18 g, 4.01 mmol) was dissolved in DMF (30 ml) and treated with sodium hydride (240 mg, 8 mmol, 80% in paraffin oil) at 0 °C. After stirring for 30 min, 4-methoxybenzyl chloride (0.7 ml, 5.16 mmol) was slowly added and the mixture was stirred overnight in the melting ice bath. The solvent was then evaporated in vacuo, the residue dissolved in ethyl acetate and washed with water and a sodium hydrogencarbonate solution. After drying with anhydrous magnesium sulfate and evaporation of the filtered solution, column chromatography (petroleum ether–ethyl acetate 5:1) yielded 1.56 g (3.76 mmol, 94%) of a white amorphous solid: $[\alpha]_D^{20}$ –131.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 7.35 (m, 5 H, Bn); 7.21 (m, 2 H, PMB); 6.81 (m, 2 H, PMB); 4.80 (d, 1 H, $J_{1,2}$ = 3.6, H-1); 4.70 (d, 1 H, *J* = 12.7, Bn); 4.65 (d, 1 H, *J* = 12.2, Bn); 4.57 (d, 1 H, *J* = 12.2, Bn); 4.53 (d, 1 H, *J* = 12.7, Bn); 4.35 (dd, 1 H, $J_{2,3}$ = 7.8, $J_{3,4}$ = 5.6, H-3); 4.11 (dq, 1 H, $J_{4,5}$ = 2.5, $J_{5,6}$ = 6.6, H-5); 4.03 (dd, 1 H, $J_{3,4}$ = 5.6, $J_{4,5}$ = 2.5, H-4); 3.79 (s, 3 H, OMe); 3.50 (dd, 1 H, $J_{1,2}$ = 3.6, $J_{2,3}$ = 7.8, H-2); 1.41 (s, 3 H, iPr); 1.34 (s, 3 H, iPr); 1.30 (d, 3 H, $J_{5,6}$ = 6.6, H-6). For $C_{24}H_{30}O_6$ (414.5) calculated: 69.55% C, 7.30% H; found: 69.31% C, 7.41% H.

Benzyl 2-*O*-(4-Methoxybenzyl)-α-L-fucopyranoside (**3**)

Compound **2** (500 mg, 1.19 mmol) was treated with a mixture of dioxane and 1% aqueous sulfuric acid (25 ml, 1:1) and stirred overnight. Subsequently, barium carbonate was added and after 2-h stirring, the solids were filtered off. After evaporation of the solvent, 443 mg (1.18 mmol, 99%) of a white solid remained as product: $[\alpha]_D^{20}$ –138.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 7.35 (m, 5 H, Bn); 7.20 (m, 2 H, PMB); 6.83 (m, 2 H, PMB); 4.88 (d, 1 H, $J_{1,2}$ = 3.6, H-1); 4.68 (d, 1 H, *J* = 12.2, Bn); 4.51 (d, 1 H, *J* = 12.2, Bn); 4.50 (d, 1 H, *J* = 11.7, Bn); 4.43 (d, 1 H, *J* = 11.7, Bn); 4.04 (ddd ≈ dt, 1 H, $J_{2,3}$ = 8.7, $J_{3,4}$ = $J_{3,OH}$ = 3.0, H-3); 3.98 (dq, 1 H, $J_{4,5}$ < 1.0, $J_{5,6}$ = 6.6, H-5); 3.79 (ddd ≈ m, 1 H, H-4); 3.79 (s, 3 H, OMe); 3.68 (dd, 1 H, $J_{1,2}$ = 3.6, $J_{2,3}$ = 8.7, H-2); 2.58 (d, 1 H, $J_{3,OH}$ = 3.0, OH-3); 2.40 (d, 1 H, $J_{4,OH}$ = 2.0, OH-4); 1.27 (d, 3 H, $J_{5,6}$ = 6.6, H-6). For $C_{21}H_{26}O_6$ (374.4) calculated: 67.36% C, 7.00% H; found: 67.07% C, 7.12% H.

Benzyl 3,4-*O*-Isopropylidene-2-*O*-(4-methoxybenzyl)-α-L-fucopyranosyl-(1→3)-2-*O*-(4-methoxybenzyl)-α-L-fucopyranoside (**5**)

Acceptor **3** (350 mg, 0.93 mmol) and donor **4** (280 mg, 0.80 mmol)[7] were coevaporated twice with toluene, set under argon and stirred in dichloromethane–DMF (10 ml, 1:1) together with molecular sieve (4A, 500 mg) for 1 h. Subsequently, tetrabutylammonium bromide (1200 mg, 3.72 mmol) and, 1 h later, copper(II) bromide (840 mg, 3.76 mmol) were added, and the mixture was stirred overnight. The mixture was then filtered through Celite, diluted with ethyl acetate and washed with a sodium hydrogencarbonate solution and brine, dried with anhydrous magnesium sulfate, filtered and evaporated. Column chromatography (toluene–ethyl acetate 5:1) furnished 249 mg (0.37 mmol, 46%) of the disaccharide as colourless syrup, which contained approximately 25% of β-linked product and 5% of (1→4)-linked product: $[\alpha]_D^{20}$ –107.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 7.30 (m, 5 H, Bn); 7.25 (m, 2 H, PMB); 7.18 (m, 2 H, PMB); 6.85 (m, 2 H, PMB); 6.81 (m, 2 H, PMB); 4.82 (d, 1 H, $J_{1,2}$ = 3.5, H-1); 4.80 (d, 1 H, *J* = 12.1, Bn-a); 4.72 (d, 1 H, $J_{1',2'}$ = 3.6, H-1′); 4.67 (d, 1 H, *J* = 12.2, Bn-b); 4.59 (d, 1 H, *J* = 12.1, Bn-a); 4.57 (d, 1 H, *J* = 12.2, Bn-b); 4.46 (d, 1 H, *J* = 11.7, Bn-c); 4.42 (d, 1 H, *J* = 11.7, Bn-c); 4.37 (dq, 1 H, $J_{4',5'}$ = 2.5, $J_{5',6'}$ = 6.6, H-5′); 4.36 (dd, 1 H, $J_{2',3'}$ = 7.6, $J_{3',4'}$ = 5.6, H-3′); 4.00 (dd, 1 H, $J_{2,3}$ = 9.6, $J_{3,4}$ = 3.0, H-3); 3.88 (m, 2 H, H-4′, H-5); 3.79 (s, 6 H, 2 × OMe); 3.75 (dd ≈ m, 1 H, $J_{1,2}$ = 3.6, H-2); 3.70 (ddd ≈ m, 1 H, H-4); 3.48 (dd, 1 H, $J_{1',2'}$ = 3.6, $J_{2',3'}$ = 7.6, H-2′); 1.44 (s, 3 H, iPr); 1.34 (s, 3 H, iPr); 1.25 (d, 3 H, $J_{5,6}$ = 6.6, H-6); 1.19 (d, 3 H, $J_{5',6'}$ = 6.6, H-6′). ^{13}C NMR (100 MHz, $CDCl_3$): 159.45 (PMB); 159.25 (PMB); 137.54 (Bn); 127.00–130.00 (Bn, PMB); 113.89 (PMB); 113.70 (PMB); 108.66 (iPr); 95.92 (C-1*); 94.02 (C-1*); 76.51, 76.21, 75.88, 74.92, 74.23, 68.17, 65.08, 63.36 (2 × C-2, 2 × C-3, 2 × C-4, 2 × C-5); 72.81 (PMB); 72.67 (PMB); 69.21 (Bn); 55.28 (2 × OMe); 28.34 (iPr); 26.43 (iPr); 16.29 (C-6*); 16.16 (C-6*). For $C_{38}H_{48}O_{11}$ (680.8) calculated: 67.04% C, 7.11% H; found: 67.03% C, 7.28% H.

Benzyl 3,4-*O*-Isopropylidene-2-*O*-(4-methoxybenzyl)-α-L-fucopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-(4-methoxybenzyl)-α-L-fucopyranoside (**6**)

Compound **5** (230 mg, 0.34 mmol) was acetylated with a mixture of pyridine–acetic acid anhydride (15 ml, 1:1) overnight. The liquids were removed in vacuo to furnish 223 mg (0.31 mmol, 91%) of a syrupy product mixture: $[\alpha]_D^{20}$ –121.1 (*c* 1.0, $CHCl_3$). Isomer **6**α: ^{1}H NMR (400 MHz, $CDCl_3$): 7.3 (m, 5 H, Bn); 7.23 (m, 2 H, PMB); 7.18 (m, 2 H, PMB); 6.86

(m, 2 H, PMB); 6.82 (m, 2 H, PMB); 5.36 (dd ≈ d, 1 H, $J_{3,4}$ = 3.6, $J_{4,5}$ < 1.0, H-4); 5.01 (d, 1 H, $J_{1',2'}$ = 3.6, H-1′); 4.87 (d, 1 H, $J_{1,2}$ = 3.6, H-1); 4.70 (d, 1 H, *J* = 2.7, Bn-a); 4.63 (d, 1 H, *J* = 12.2, Bn-b); 4.60 (d, 1 H, *J* = 12.7, Bn-a); 4.57 (d, 1 H, *J* = 12.2, Bn-b); 4.54 (d, 1 H, *J* = 11.2, Bn-c); 4.48 (d, 1 H, *J* = 11.2, Bn-c); 4.39 (dq, 1 H, $J_{4',5'}$ = 2.5, $J_{5',6'}$ = 6.6, H-5′); 4.26 (dd, 1 H, $J_{2',3'}$ = 8.1, $J_{3',4'}$ = 5.6, H-3′); 4.24 (dd, 1 H, $J_{2,3}$ = 8.1, $J_{3,4}$ = 3.6, H-3); 4.01 (dq, 1 H, $J_{4,5}$ < 1.0, $J_{5,6}$ = 6.6, H-5); 3.79 (s, 6 H, 2 × OMe); 3.79 (m, 1 H, H-2); 3.71 (dd, 1 H, $J_{3',4'}$ = 5.6, $J_{4',5'}$ = 2.5, H-4′); 3.43 (dd, 1 H, $J_{1',2'}$ = 3.6, $J_{2',3'}$ = 8.1, H-2′); 1.97 (s, 3 H, OAc); 1.30 (s, 3 H, iPr); 1.28 (s, 3 H, iPr); 1.19 (d, 3 H, $J_{5,6}$ = 6.6, H-6*); 1.04 (d, 3 H, $J_{5,6}$ = 6.6, H-6*). ^{13}C NMR (100 MHz, $CDCl_3$): 170.92 (OAc); 159.17 (2 × PMB); 137.57 (Bn); 130.63, 129.81, 129.71, 129.08, 129.04, 128.46, 128.41, 128.35, 128.23, 128.03, 127.76, 125.31 (Bn, PMB); 113.67 (PMB); 113.60 (PMB); 108.59 (iPr); 96.60 (C-1*); 92.48 (C-1*); 75.44, 74.64, 69.99, 68.95, 65.08, 63.36 (2 × C-2, 2 × C-3, 2 × C-4); 64.78, 62.93 (2 × C-5); 72.52 (PMB); 71.81 (PMB); 69.62 (Bn); 55.29 (OMe); 55.27 (OMe); 28.09 (iPr); 26.38 (iPr); 20.68 (OAc); 16.44 (C-6*); 16.17 (C-6*). Isomer **6**β: ^{1}H NMR (400 MHz, $CDCl_3$): 5.31 (dd ≈ d, 1 H, $J_{3,4}$ = 3.6, $J_{4,5}$ < 1.0, H-4); 4.81 (d, 1 H, $J_{1,2}$ = 3.6, H-1*); 4.31 (dd, 1 H, $J_{2,3}$ = 10.1, $J_{3,4}$ = 3.6, H-3); 3.91 (dd, 1 H, $J_{3',4'}$ = 5.6, $J_{4',5'}$ = 2.5, H-4′); 3.87 (dd, 1 H, $J_{1,2}$ = 3.6, $J_{2,3}$ = 10.1, H-2); 3.30 (dd ≈ t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 7.6, H-2). α(1→4)-product: ^{1}H NMR (400 MHz, $CDCl_3$): 5.19 (dd, 1 H, $J_{2,3}$ = 10.7, $J_{3,4}$ = 3.1, H-3).

Methyl (*R*,*S*)-3,4-*O*-(α-Ethoxybenzylidene)-2-*O*-(4-methoxybenzyl)-1-thio-β-L-fucopyranoside (**12**)

A solution of compound **8** (1.0 g, 5.15 mmol)[17] in dichloromethane (20 ml) was treated with a speck of 4-toluenesulfonic acid before triethyl orthobenzoate (3.4 ml, 15 mmol) was slowly added. After stirring the mixture overnight, a small amount of sodium hydroxide was added and the solvent was removed. The residue was evaporated twice with toluene and dissolved in anhydrous DMF (20 ml). Sodium hydride (0.45 g, 15 mmol) was added, and after stirring the mixture for 20 min, 4-methoxybenzyl chloride (2.23 ml, 16.44 mmol) was dropped slowly into the solution. After stirring for another night, methanol (1 ml) was added and, 20 min later, the solvent was removed in vacuo. The residue was again dissolved in dichloromethane, washed with water and brine, dried over anhydrous magnesium sulfate and filtered. The solvent was removed and the crude product was purified by column chromatography (petroleum ether–ethyl acetate 4:1) to give 640 mg (1.43 mmol, 28%) of pure syrupy product (diastereomeric mixture) and another 1.9 g of crude product: $[\alpha]_D^{20}$ –5.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 7.64–7.28 (m, 5 H, Ph); 7.10 (m, 2 H, PMB); 6.75 (m, 2 H, PMB); 4.59 (d, 1 H, *J* = 11.2, Bn); 4.51 (dd ≈ t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 6.2, H-3); 4.45 (dd, 1 H, $J_{3,4}$ = 6.2, $J_{4,5}$ = 2.0, H-4); 4.42 (d, 1 H, *J* = 11.2, Bn); 4.21 (d, 1 H, $J_{1,2}$ = 10.2, H-1); 3.88 (dq, 1 H, $J_{4,5}$ = 2.0, $J_{5,6}$ = 6.6, H-5); 3.76 (s, 3 H, OMe); 3.50 (dt, 1 H, J_d = 7.1, J_t = 9.7, O-CH_2); 3.38 (dt, 1 H, J_d = 7.1, J_t = 9.5, O-CH_2); 3.24 (d, 1 H, $J_{1,2}$ = 10.2, $J_{2,3}$ = 6.6, H-2); 2.02 (s, 3 H, SMe); 1.51 (d, 3 H, $J_{5,6}$ = 6.6, H-6); 1.19 (dd ≈ t, 3 H, *J* = 7.1, OEt).

Benzyl 4-*O*-Benzoyl-2-*O*-(4-methoxybenzyl)-α-L-fucopyranoside (**13**)

Compound **7** (1.5 g, 5.99 mmol)[22] was processed in the same way as compound **8** in the previous procedure using triethyl orthobenzoate (3.95 ml, 17.4 mmol), a speck of 4-toluenesulfonic acid, dichloromethane (25 ml), anhydrous DMF (20 ml), sodium hydride (80% in paraffin oil, 522 mg, 17.4 mmol), and 4-methoxybenzyl chloride (1.62 ml, 12 mmol). After having performed the benzylation overnight, acetic acid (5 ml) and a few drops of water

were added, and the mixture was stirred for another night. For workup, the solvent was exchanged for dichloromethane and washed with a sodium hydrogencarbonate solution and brine, dried with anhydrous magnesium sulfate and evaporated. Column chromatography (petroleum ether–ethyl acetate 2:1) yielded 1.50 g (3.13 mmol, 52%) of the product: $[\alpha]_D^{20}$ –119.6 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 8.02 (m, 2 H, Bz); 7.59 (m, 1 H, Bz); 7.45 (m, 2 H, Bz); 7.39 (m, 5 H, Bn); 7.20 (m, 2 H, PMB); 6.82 (m, 2 H, PMB); 5.48 (dd ≈ d, 1 H, $J_{3,4}$ = 3.6, $J_{4,5}$ < 1.0, H-4); 4.99 (d, 1 H, $J_{1,2}$ = 3.1, H-1); 4.73 (d, 1 H, *J* = 12.2, Bn); 4.57 (d, 1 H, *J* = 12.2, Bn); 4.52 (2 × d, 2 H, Bn); 4.32 (dd, 1 H, $J_{2,3}$ = 10.7, $J_{3,4}$ = 3.6, H-3); 4.17 (dq, 1 H, $J_{4,5}$ < 1.0, $J_{5,6}$ = 6.6, H-5); 3.82 (dd, 1 H, $J_{1,2}$ = 3.1, $J_{2,3}$ = 10.7, H-2); 3.79 (s, 3 H, OMe); 1.14 (d, 3 H, $J_{5,6}$ = 6.6, H-6). For $C_{28}H_{30}O_7$ (478.5) calculated: 70.28% C, 6.32% H; found: 70.20% C, 6.56% H.

Methyl 4-*O*-Benzoyl-2-*O*-(4-methoxybenzyl)-1-thio-β-L-fucopyranoside (**14**)

Compound **12** (100 mg, 0.22 mmol) was dissolved in dichloromethane (20 ml) and treated with acetic acid (1 ml). The solution was stirred overnight, washed twice with aqueous $NaHCO_3$ and water, dried over anhydrous magnesium sulfate, filtered and evaporated. Column chromatography (petroleum ether–ethyl acetate 2:1) yielded 91 mg (0.217 mmol, 98%) of the product: $[\alpha]_D^{20}$ –60.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (m, 2 H, Bz); 7.61 (m, 1 H, Bz); 7.47 (m, 2 H, Bz); 7.34 (m, 2 H, PMB); 6.86 (m, 2 H, PMB); 5.45 (dd ≈ d, 1 H, $J_{3,4}$ = 3.2, $J_{4,5}$ < 1.0, H-4); 4.92 (d, 1 H, *J* = 10.6, PMB); 4.64 (d, 1 H, *J* = 10.6, PMB); 4.40 (d, 1 H, $J_{1,2}$ = 9.8, H-1); 3.90 (dd, 1 H, $J_{2,3}$ = 9.1, $J_{3,4}$ = 3.2, H-3); 3.85 (dq, 1 H, $J_{4,5}$ < 1.0, $J_{5,6}$ = 6.6, H-5); 3.76 (s, 3 H, OMe); 3.61 (dd ≈ t, 1 H, $J_{1,2}$ = 9.8, $J_{2,3}$ = 9.1, H-2); 2.31 (s, 3 H, SMe); 1.25 (d, 3 H, $J_{5,6}$ = 6.6, H-6). For $C_{22}H_{26}O_6S$ (418.5) calculated: 63.14% C, 6.26% H; found: 62.51% C; 6.50% H.

Methyl 4-*O*-Benzoyl-3-*O*-(*tert*-butyldimethylsilyl)-2-*O*-(4-methoxybenzyl)-1-thio-β-L-fucopyranoside (**15**)

Compound **14** (2.83 g, 6.75 mmol) was dissolved in DMF (10 ml), treated with imidazole (1.01 g, 15.8 mmol) and *tert*-butyldimethylsilyl chloride (1.58 g, 10.9 mmol), and stirred at room temperature overnight. For workup, the solvent was removed under reduced pressure and the residue dissolved in dichloromethane. The solution was washed twice with $NaHCO_3$ solution and water, dried over anhydrous magnesium sulfate, filtered and evaporated. The crude residue was purified by column chromatography (petroleum ether–ethyl acetate 5:1) to give 2.25 g (4.22 mmol, 63%) of pure product: $[\alpha]_D^{20}$ +10.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (m, 2 H, Bz); 7.59 (m, 1 H, Bz); 7.46 (m, 2 H, Bz); 7.35 (m, 2 H, PMB); 6.86 (m, 2 H, PMB); 5.34 (dd ≈ d, 1 H, $J_{3,4}$ = 3.6, $J_{4,5}$ < 1.0, H-4); 4.78 (d, 1 H, *J* = 10.2, PMB); 4.69 (d, 1 H, *J* = 10.2, PMB); 4.39 (d, 1 H, $J_{1,2}$ = 9.7, H-1); 3.88 (dd, 1 H, $J_{2,3}$ = 9.2, $J_{3,4}$ = 3.6, H-3); 3.80 (s, 3 H, OMe); 3.80 (dq ≈ m, 1 H, H-5); 3.61 (dd ≈ t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 9.5, H-2); 2.25 (s, 3 H, SMe); 1.25 (d, 3 H, $J_{5,6}$ = 6.6, H-6); 0.80 (s, 9 H, *t*-Bu); 0.13 (s, 3 H, SiMe); 0.08 (s, 3 H, SiMe). For $C_{28}H_{40}O_6SiS$ (532.8) calculated: 63.12% C, 7.57% H; found: 63.15% C, 7.67% H.

4-*O*-Benzoyl-3-*O*-(*tert*-butyldimethylsilyl)-2-*O*-(4-methoxybenzyl)-α-L-fucopyranosyl Bromide (**16**)

Compound **15** (500 mg, 0.94 mmol) was set under argon, dissolved in dichloromethane (20 ml) and stirred for 2 h together with molecular sieve (4A, 300 mg). Subsequently, copper(II) bromide (628 mg, 2.81 mmol) was added. After stirring the solution overnight, the solids were filtered off, and the solution was washed with aqueous $NaHCO_3$ and water, dried over anhydrous magnesium sulfate and evaporated. This furnished 401 mg (0.71 mmol, 75%) of the product, which was used without further purification: $[\alpha]_D^{20}$ –257.5 (*c* 3.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 7.93 (m, 2 H, Bz); 7.51 (m, 1 H, Bz); 7.38 (m, 2 H, Bz); 7.21 (m, 2 H, PMB); 6.80 (m, 2 H, PMB); 5.96 (d, 1 H, $J_{1,2}$ = 4.0, H-1); 5.31 (dd, 1 H, $J_{3,4}$ = 3.5, $J_{4,5}$ = 1.0, H-4); 4.58 (d, 1 H, *J* = 11.7, PMB); 4.51 (d, 1 H, *J* = 11.7, PMB); 4.34 (dq ≈ q, 1 H, $J_{4,5}$ = 1.0, $J_{5,6}$ = 6.1, H-5); 4.17 (dd, 1 H, $J_{2,3}$ = 9.6, $J_{3,4}$ = 3.5, H-3); 3.82 (dd, 1 H, $J_{1,2}$ = 4.0, $J_{2,3}$ = 9.6, H-2); 3.73 (s, 3 H, OMe); 1.16 (d, 3 H, $J_{5,6}$ = 6.1, H-6); 0.69 (s, 9 H, *t*-Bu); 0.09 (s, 3 H, SiMe); 0.02 (s, 3 H, SiMe).

Benzyl 4-*O*-Benzoyl-2-*O*-(4-methoxybenzyl)-β-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-(4-methoxybenzyl)-α-L-fucopyranoside (**17**)

Compound **12** (158 mg, 0.36 mmol) and compound **13** (126 mg, 0.28 mmol) were mixed and evaporated twice with toluene. The mixture was dissolved in dichloromethane (10 ml) and molecular sieve (4A, 200 mg) and 2,6-di-*tert*-butyl-4-methylpyridine (206 mg, 1.0 mmol) were added under argon. After stirring for 1 h, the solution was cooled to –20 °C and *N*-iodosuccinimide (225 mg, 1.0 mmol) was added. The solution was stirred overnight, acetic acid (2 ml) and water (1 ml) were added, and the mixture was stirred for another night. For workup, some aqueous $NaHCO_3$ was added and the organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered and evaporated. The remaining crude product was purified by column chromatography (petroleum ether–ethyl acetate 2:1) to give 56 mg (0.066 mmol, 24%) of the product as colourless syrup: $[\alpha]_D^{20}$ –197.4 (*c* 1.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 8.13 (m, 2 H, Bz); 8.04 (m, 2 H, Bz); 7.54 (m, 2 H, Bz); 7.40 (m, 9 H, Bz, Bn); 7.18 (m, 2 H, PMB); 6.91 (m, 2 H, PMB); 6.79 (m, 2 H, PMB); 6.62 (m, 2 H, PMB); 5.66 (dd ≈ d, 1 H, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1.0, H-4*); 5.34 (dd ≈ d, 1 H, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1.0, H-4*); 4.94 (d, 1 H, $J_{1,2}$ = 3.6, H-1); 4.90 (d, 1 H, $J_{1',2'}$ = 7.6, H-1′); 4.74 (d, 1 H, *J* = 12.2, Bn-a); 4.69 (d, 1 H, *J* = 11.2, Bn-b); 4.63 (d, 1 H, *J* = 12.2, Bn-a); 4.62 (d, 1 H, *J* = 11.7, Bn-c); 4.51 (dd, 1 H, $J_{2,3}$ = 10.2, $J_{3,4}$ = 3.5, H-3*); 4.44 (d, 1 H, *J* = 11.7, Bn-c); 4.31 (d, 1 H, *J* = 11.2, Bn-b); 4.21 (dq ≈ q, 1 H, $J_{4,5}$ < 1.0, $J_{5,6}$ = 6.6, H-5*); 4.04 (dd, 1 H, $J_{2,3}$ = 10.2, $J_{3,4}$ = 3.5, H-3*); 3.77 (m, 2 H, H-2, H-5*); 3.77 (s, 3 H, OMe); 3.67 (s, 3 H, OMe); 3.37 (dd, 1 H, $J_{1',2'}$ = 7.6, $J_{2',3'}$ = 10.2, H-2′); 1.19 (d, 3 H, $J_{5,6}$ = 6.6, H-6*); 1.17 (d, 3 H, $J_{5,6}$ = 6.6, H-6*).

Methyl 4-*O*-Benzoyl-3-*O*-(*tert*-butyldimethylsilyl)-2-*O*-(4-methoxybenzyl)-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-(4-methoxybenzyl)-1-thio-β-L-fucopyranoside (**18**)

Compound **14** (381 mg, 0.91 mmol) was evaporated with toluene and stirred in a mixture of dichloromethane–DMF (10 ml, 1:1) together with molecular sieve (4A, 500 mg) for 1 h under argon. Subsequently, tetrabutylammonium bromide (665 mg, 2.07 mmol) and acceptor **16** (401 mg, 0.71 mmol) were added, and the mixture was stirred overnight. For workup, the solids were filtered off, the solution was washed with aqueous $NaHCO_3$ and water, dried over anhydrous magnesium sulfate, filtered and evaporated. The crude product was purified by

column chromatography (petroleum ether–ethyl acetate 10:1) to give 320 mg (0.35 mmol, 49%) of a colourless syrup: $[\alpha]_D^{20}$ –100.9 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 8.03 (m, 2 H, Bz); 7.97 (m, 2 H, Bz); 7.56 (m, 2 H, Bz); 7.44 (m, 4 H, Bz); 7.36 (m, 2 H, PMB); 7.06 (m, 2 H, PMB); 6.89 (m, 2 H, PMB); 6.68 (m, 2 H, PMB); 5.66 (dd ≈ d, 1 H, $J_{3,4}$ = 3.5, $J_{4,5}$.0, H-4*); 5.28 (d, 1 H, $J_{1',2'}$ = 3.6, H-1′); 5.22 (dd ≈ d, 1 H, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1.0, H-4*); 4.93 (d, 1 H, *J* = 10.2, Bn-a); 4.77 (d, 1 H, *J* = 10.2, Bn-a); 4.44 (d, 1 H, $J_{1',2'}$ = 9.7, H-1′); 4.43 (d, 1 H, *J* = 11.7, Bn-b); 4.30 (d, 1 H, *J* = 11.7, Bn-b); 4.26 (m, 2 H, 2 × H-3); 3.98 (dd, 1 H, $J_{1',2'}$ = 3.6, $J_{2',3'}$ = 9.7, H-2′); 3.82 (s, 3 H, OMe); 3.76 (s, 3 H, OMe); 3.85–3.72 (m, 3 H, H-2, 2 × H-5); 2.29 (s, 3 H, SMe); 1.22 (d, 3 H, $J_{5,6}$ = 6.6, H-6*); 0.99 (d, 3 H, $J_{5,6}$ = 6.6, H-6*); 0.69 (s, 9 H, *t*-Bu); 0.04 (s, 3 H, SiMe); –0.03 (s, 3 H, SiMe). ^{13}C NMR (100 MHz, $CDCl_3$): 166.39 (Bz); 166.29 (Bz); 159.51 (Bz); 158.80 (Bz); 133.05, 132.83, 130.38, 129.99, 129.95, 129.78, 129.29, 128.37, 128.28 (Bz, PMB); 113.95 (PMB); 113.37 (PMB); 93.87 (C-1′); 85.47 (C-1); 76.15, 75.94, 75.00, 74.56, 73.51, 69.60, 69.53, 65.40 (2 × C-2, 2 × C-3, 2 × C-4, 2 × C-5); 75.27 (PMB); 71.68 (PMB); 55.35 (OMe); 55.18 (OMe); 25.64 (*t*-Bu); 17.82 (*t*-Bu); 16.85 (C-6*); 16.20 (C-6*); 12.66 (SMe); –4.75 (SiMe); –4.97 (SiMe). For $C_{49}H_{62}O_{12}SSi$ (903.2) calculated: 65.16% C, 6.92% H; found: 64.88% C, 7.13% H.

Benzyl 4-*O*-Benzoyl-2-*O*-(4-methoxybenzyl)-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-(4-methoxybenzyl)-α-L-fucopyranoside (**19**)

Acceptor compound **13** (333 mg, 0.74 mmol), donor compound **15** (500 mg, 0.94 mmol), molecular sieve (4A, 1.0 g), tetrabutylammonium bromide (665 mg, 2.07 mmol), and copper(II) bromide (457 mg, 2.07 mmol) under argon in dichloromethane–DMF (10 ml, 1:1) were treated and worked up as described for the synthesis of disaccharide **5**. Column chromatography (petroleum ether–ethyl acetate 5:1) furnished 454 mg (0.47 mmol, 64%) of the disaccharide as a colourless syrup. This compound (410 mg, 0.43 mmol) and a 1 M solution of tetrabutylammonium fluoride in THF (5 ml) were stirred at room temperature overnight. The solvent was evaporated and the residue dissolved in dichloromethane, washed with water, dried with anhydrous magnesium sulfate, filtered and evaporated. The crude product was purified by column chromatography (petroleum ether–ethyl acetate 2:1) to yield 43 mg of the product **19** (0.051 mmol, 12%), 20 mg of the 3-*O*-benzylated product (0.024 mmol, 5%) and 262 mg of the product without benzoate at the non-reducing end (0.352 mmol, 82%).

The latter (230 mg, 0.321 mmol) was dissolved in dichloromethane (10 ml) and treated with triethyl orthobenzoate (0.22 ml, 0.983 mmol) and a speck of 4-toluenesulfonic acid and stirred at room temperature for 2 h. Acetic acid (5 ml) and water (1 ml) were added and the solvent was removed after 1-h stirring. Column chromatography (petroleum ether–ethyl acetate 2:1) yielded 156 mg (0.184 mmol, 57%) of the product resulting in an overall amount of 199 mg (0.235 mmol, 55%): $[\alpha]_D^{20}$ –122.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): 8.04 (m, 2 H, Bz); 7.94 (m, 2 H, Bz); 7.58 (m, 2 H, Bz); 7.40 (m, 9 H, Bz, Bn); 7.23 (m, 2 H, PMB); 7.05 (m, 2 H, PMB); 6.84 (m, 2 H, PMB); 6.69 (m, 2 H, PMB); 5.68 (dd ≈ d, 1 H, $J_{3,4}$ = 3.5, $J_{4,5}$ = 1.0, H-4*); 5.41 (d, 1 H, $J_{1',2'}$ = 3.6, H-1′); 5.29 (dd ≈ d, 1 H, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1.0, H-4*); 4.97 (d, 1 H, $J_{1,2}$ = 3.6, H-1); 4.74 (d, 1 H, *J* = 12.2, Bn-a); 4.64 (d, 1 H, *J* = 12.2, Bn-a); 4.61 (d, 1 H, *J* = 11.2, Bn-b); 4.55 (d, 1 H, *J* = 11.2, Bn-b); 4.50 (d, 1 H, *J* = 11.7, Bn-c); 4.46 (dd ≈ m, 1 H, $J_{3,4}$ = 3.5, H-3*); 4.42 (dq ≈ m, 1 H, $J_{4,5}$ < 1.0, $J_{5,6}$ = 6.6, H-5*); 4.32 (d, 1 H, *J* = 11.7, Bn-c); 4.20 (dd, 1 H, $J_{2,3}$ = 10.2, $J_{3,4}$ = 3.5, H-3*); 4.15 (dq ≈ q, 1 H, $J_{4,5}$ < 1.0, $J_{5,6}$ = 6.6, H-5*); 4.00 (dd, 1 H, $J_{1,2}$ = 3.6, $J_{2,3}$ = 10.2, H-2*); 3.81 (s, 3 H, OMe); 3.82 (dd ≈ m, 1 H,

H-2*); 3.71 (s, 3 H, OMe); 1.11 (d, 3 H, $J_{5,6}$ = 6.6, H-6*); 1.08 (d, 3 H, $J_{5,6}$ = 6.6, H-6*). ^{13}C NMR (100 MHz, $CDCl_3$): 171.25 (Bz); 166.47 (Bz); 159.39 (Bz); 159.23 (Bz); 137.60, 133.64, 133.19, 132.97, 130.27, 130.20, 130.01, 129.87, 129.76, 129.49, 129.47, 128.56, 128.40, 128.31, 128.00, 127.80 (Bn, Bz, PMB); 113.85, 113.77 (PMB); 97.72 (C-1*); 92.20 (C-1*); 74.97, 74.25, 73.80, 70.25, 70.06, 67.88 (2 × C-2, 2 × C-3, 2 × C-4); 72.65, 71.45, 69.69 (2 × PMB, Bn); 65.26 (2 × C-5); 55.32 (OMe); 55.16 (OMe); 16.25 (C-6*); 16.13 (C-6*). For $C_{49}H_{52}O_{13}$ (848.9) calculated: 69.33% C, 6.17% H; found: 69.04% C, 6.52% H.

Benzyl 4-*O*-Benzoyl-3-*O*-(*tert*-butyldimethylsilyl)-2-*O*-(4-methoxybenzyl)-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-(4-methoxybenzyl)-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-(4-methoxybenzyl)-α-L-fucopyranosyl-(1→3)-4-*O*-benzoyl-2-*O*-(4-methoxybenzyl)-α-L-fucopyranoside (**20**)

Donor disaccharide **18** (45 mg, 49.8 (mol) and acceptor disaccharide **19** (57 mg, 67.1 μmol) were coevaporated twice with toluene, dissolved in dichloromethane (3 ml) and stirred for 1 h together with a freshly activated molecular sieve (4A, 300 mg). Then, methyl triflate (0.2 ml of a 10% solution in dichloromethane, 0.2 mmol) was added and the solution was stirred overnight under argon. For workup, first triethylamine (0.1 ml) and, after 1-h stirring, a small amount of solid sodium hydrogencarbonate were added. The mixture was evaporated together with silica gel and the residue purified by column chromatography (petroleum ether–ethyl acetate 3:1) yielded 56 mg (32.8 μmol, 66%) of a syrupy product: $[\alpha]_D^{20}$ –444.2 (*c* 2.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): 8.02 (m, 2 H, Bz); 7.97 (m, 2 H, Bz); 7.91 (m, 2 H, Bz); 7.86 (m, 2 H, Bz); 7.54 (m, 4 H, 4 × Bz); 7.38 (m, 13 H, 4 × Bz, Bn); 7.24 (m, 2 H, PMB); 7.08 (m, 2 H, PMB); 7.03 (m, 2 H, PMB); 6.98 (m, 2 H, PMB); 6.83 (m, 2 H, PMB); 6.72 (m, 2 H, PMB); 6.69 (m, 2 H, PMB); 6.64 (m, 2 H, PMB); 5.63 (dd ≈ d, 1 H, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1.0, H-4d); 5.49 (dd ≈ d, 1 H, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1.0, H-4a); 5.27 (d, 1 H, $J_{1,2}$ = 3.5, H-1a); 5.21 (dd ≈ d, 1 H, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1.0, H-4b); 5.11 (d, 1 H, $J_{1,2}$ = 3.5, H-1b); 5.03 (d, 1 H, $J_{1,2}$ = 3.5, H-1c); 5.00 (dd ≈ d, 1 H, $J_{3,4}$ = 3.5, $J_{4,5}$ < 1.0, H-4c); 4.92 (d, 1 H, $J_{1,2}$ = 3.6, H-1d); 4.74 (d, 1 H, *J* = 12.3, Bn-a); 4.64 (m ≈ d, 2 H, Bn-a, Bn-b); 4.60 (d, 1 H, *J* = 11.7, Bn-b); 4.52 (d, 1 H, *J* = 11.0, Bn-c); 4.48 (d, 1 H, *J* = 11.3, Bn-d); 4.42 (dd, 1 H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 3.6, H-3d); 4.36 (dq, 1 H, $J_{4,5}$ < 1.0, $J_{5,6}$ = 6.6, H-5a); 4.32 (m, 4 H, Bn-c, Bn-d, Bn-e, H-3a); 4.19 (dd, 1 H, $J_{2,3}$ = 10.2, $J_{3,4}$ = 3.6, H-3b); 4.10 (m, 4 H, Bn-e, H-5b, H-5c, H-5d); 4.04 (dd ≈ m, 1 H, $J_{2,3}$ = 10.5, $J_{3,4}$ = 3.5, H-3c); 4.01 (dd ≈ m, 1 H, $J_{1,2}$ = 3.6, H-2d); 3.98 (dd, 1 H, $J_{1,2}$ = 3.5, $J_{2,3}$ = 10.4, H-2a); 3.88 (dd, 1 H, $J_{1,2}$ = 3.5, $J_{2,3}$ = 10.1, H-2b); 3.80 (s, 3 H, OMe); 3.78 (s, 3 H, OMe); 3.76 (s, 3 H, OMe); 3.75 (s, 3 H, OMe); 3.63 (dd, 1 H, $J_{1,2}$ = 3.5, $J_{2,3}$ = 9.6, H-2c); 1.09 (d, 3 H, $J_{5,6}$ = 6.6, H-6*); 1.06 (d, 3 H, $J_{5,6}$ = 6.6, H-6*); 0.78 (d, 3 H, $J_{5,6}$ = 6.6, H-6*); 0.72 (d, 3 H, $J_{5,6}$ = 6.6, H-6*); 0.64 (s, 9 H, *t*-Bu); –0.12 (s, 3 H, $SiMe_2$); –0.20 (s, 3 H, $SiMe_2$). ^{13}C NMR (100 MHz, $CDCl_3$): 166.37 (OBz); 166.28 (OBz); 159.36 (OBz); 159.05 (OBz); 158.95 (OBz); 158.67 (OBz); 137.61, 133.12, 132.97, 132.73, 130.47, 130.41, 130.18, 130.10, 130.06, 130.03, 129.99, 129.95, 129.88, 129.86, 129.79, 129.76, 129.73, 129.41, 129.37, 128.41, 128.38, 128.28, 128.20, 128.17, 128.02, 127.78 (Bn, Bz, PMB); 113.83 (PMB); 113.58 (2 × PMB); 113.22 (PMB); 96.90 (C-1d); 93.34 (C-1a); 93.17 (C-1b); 93.00 (C-1c); 75.11 (C-4c); 73.95 (C-2c); 73.56 (C-2d); 73.21 (C-2a); 72.68 (Bn-b); 72.27 (Bn-c); 72.15 (C-2b); 71.58 (Bn-d); 71.18 (Bn-e); 70.88 (C-3d); 70.75 (C-3a); 70.43 (C-3b); 70.21 (C-4d); 70.15 (C-4a, C-4b); 69.66 (Bn-a); 69.48 (C-3c); 65.34 (C-5a, C-5*); 65.02 (C-5*); 64.82 (C-5*); 55.26 (OMe); 55.21 (2 × OMe); 55.12 (OMe); 25.60 (*t*-Bu); 17.74 (*t*-Bu); 16.28 (C-6*); 16.28 (C-6*);

16.25 (C-6*); 16.00 (C-6*); –4.92 (2 × SiMe). Maldi-Tof (M = 1702.01): 1605.57 (M – (Bz/PMB) + Na); 1621.57 (M – (Bz/PMB) + K); 1725.66 (M + Na); 1741.64 (M + K).

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