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First Synthesis of the β-D-Rhamnosylated Trisaccharide Repeating Unit of the *O*-Antigen from *Xanthomonas campestris* pv. *campestris* 8004

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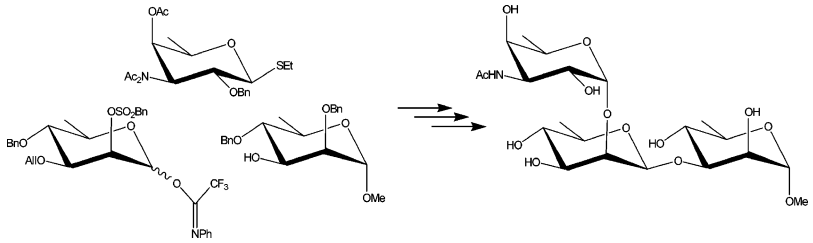

The trisaccharide repeating unit of the *O*-antigen of the lipopolysaccharide from *Xanthomonas campestris* pv. *campestris* 8004, a pathogen of cruciferous crops, presents some structural features that renders it a challenging synthetic target: the presence of a β-D-rhamnosidic linkage, the steric crowd on a 1,2-cis-diglycosylated D-rhamnose, and finally the noncommercial availability of its monosaccharide constituents. The synthesis of this trisaccharide as methyl glycoside has been accomplished by exploiting a strategy whose key steps were the sequential β-D-rhamnosylation with a 2-*O*-benzylsulfonyl-*N*-phenyltrifluoroacetimidate donor, debenzylsulfonylation, and coupling with a D-Fuc*p*3NAc thioglycoside donor.

Introduction

Almost 80% of the Gram-negative outer membrane cell surface is covered by lipopolysaccharides (LPSs), which are amphiphilic macromolecules consisting in three different domains: a lipid part (Lipid-A), an oligosaccharide region (Core), and a polysaccharide portion (*O*-specific chain, or simply *O*-chain).[1] LPSs are highly involved in bacterial pathogenesis both in animals and in plants: the mechanisms of interaction between bacteria and eukaryotic hosts cells have been addressed by several studies on Gram-negative bacteria that are pathogenic for animals and humans,[2] whereas very little is known about LPS−plant interactions to date. One of the most widely studied effects of LPSs on plant cells is the ability, induced by avirulent bacteria, to prevent the hypersensitive response (HR), a programmed cell death response triggered by live bacteria. The mechanism of this effect, usually named as localized induced resistance (LIR),[3] is far from being completely elucidated. A recent work showed that the lipid A moiety may be at least partially responsible for LPS perception by plant cells;[4] nevertheless, oligosaccharides, in particular synthetic oligorhamnans mimicking the general structure of the *O*-chains from phytopathogenic bacteria, have also been proved to prevent the hypersensitive response (HR).[5] The aim to investigate deeper the molecular basis of HR and LIR effects on plants prompted the synthesis of model oligosaccharides related to the *O*-chains from phytopathogenic bacteria. These are typically constituted by a repeating unit with a rhamnanic backbone, which usually bears a single monosaccharide as branch.[6] One of the most interesting *O*-chain structure is that from *Xanthomonas campestris* pv. *campestris* (*Xcc*) strain 8004, a

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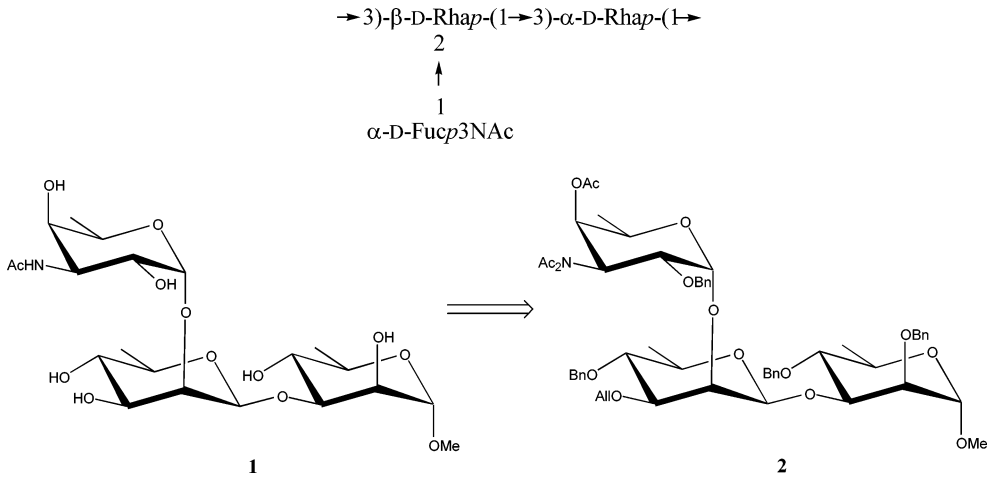

FIGURE 1. Structure of the repeating unit of the O-antigen from *Xcc* and of the related compounds that have been synthesized.

pathogen of cruciferous crops that is the causative agent of black rot, a disease of worldwide importance.[7] Additionally, a very recent study has demonstrated the effectiveness of both Lipid-A and oligosaccharides extracted from this bacterium to be active in LIR triggering and, moreover, with two independent mechanisms.[8]

The trisaccharide repeating unit of the O-chain from *Xcc* 8004 consists of a D-rhamnose disaccharide backbone with a 3-acetamido-3,6-dideoxy-D-galactopyranose (D-Fuc*p*3NAc) unit as branch (Figure 1).[9] The presence of a β-rhamnosidic linkage, the "steric crowd" on the 1,2-cis-diglycosylated D-rhamnose unit, and finally the noncommercial availability of both D-rhamnose and D-Fuc*p*3NAc surely render the synthesis of oligosaccharides related to this *O*-chain challenging. In this article is reported the synthesis of compound **1**, the methyl glycoside of the trisaccharide repeating unit of the O-antigen from *Xcc*, from the fully protected trisaccharide **2**. The latter was equipped with a suitable protecting-group pattern, which might allow its further elongation to higher oligosaccharides.

Results and Discussion

The 1,2-cis-diglycosylated moiety present on the β-D-rhamnose unit clearly suggested a synthetic approach in which the β-D-rhamnosidic linkage is first built up to give a rhamnose disaccharide with an orthogonal protecting-group pattern that allows the selective deprotection on the *O*-2_B position and the subsequent α-coupling with a suitable D-Fuc*p*3NAc donor. The *manno* configuration of D-rhamnose makes its β-stereoselective coupling part of a synthetic challenge on which several research groups focused their attention during the last two decades.[10] Nevertheless, many protocols for β-mannosylation require the use of 4,6-benzylidene-protected donor and therefore are not applicable to the rhamnose series. Recently, Crich developed three different β-rhamnosylation methods,[11] one of which is specific for D-rhamnose and employs a (2-(2-iodophenyl)ethylthiocarbonyl)benzylidene-protected D-mannose donor, which is coupled with high β-stereoselectivity; the benzylidene cycle is then reductively cleaved to give regioselectively the 6-deoxy functionality of β-D-rhamnose.[11b] Even if this protocol has been already successfully used for the synthesis of a tetrasaccharide containing two units of D-rhamnose,[12] we preferred to explore the possibility to apply a "nonbenzylidene requiring" method of β-D-mannosylation to the D-rhamnose series. Among such protocols,[13] the attention was focused on the use of a 2-*O*-sulfonate group whose electron-withdrawing effect was already demonstrated to be β-directing in glycosylation with L-rhamno-chlorides[14] and more recently extended to thioglycosides.[11c] Among the several different sulfonate groups already reported for this purpose, the benzylsulfonyl has been recently exploited by the Schmidt group on a β-glycosylation of a thioglycoside and a trichloroacetimidate mannosyl donor.[13f] Since a benzylsulfonyl group can be very easily installed on a hydroxyl function and selectively cleaved in the presence of ether-based protecting groups,[15] its use as both β-directing and

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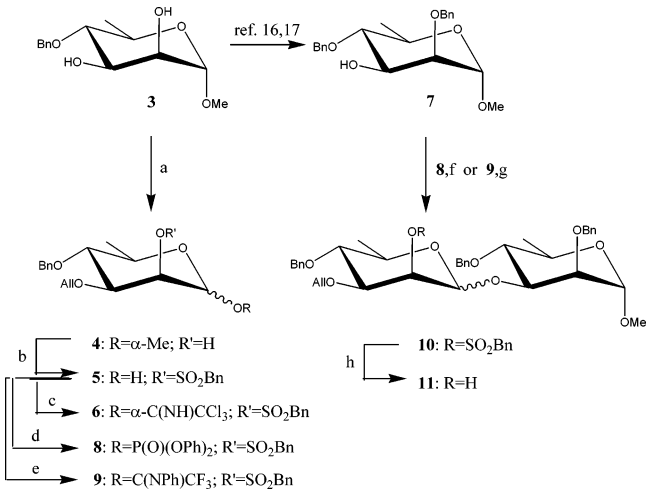
SCHEME 1. Synthesis of 11[a]



[a] (a) i. BuSnO, 10:1 benzene/methanol, 60 °C, 90 min; ii. TBAB, AllBr, toluene, 65 °C, 60 min, 82% over two steps; (b) i. $BnSO_2Cl$, py, rt, 45 min; ii. 73:26:1 Ac_2O/AcOH/H_2SO_4, rt, 3 h; iii. hydrazine acetate, DMF, rt, 2 h, 57% over three steps (α/β = 3:1); (c) Cl_3CCN, DBU, CH_2Cl_2, rt, 2 h, 35%; (d) $(PhO)_2POCl$, DMAP, CH_2Cl_2, −30 to −10 °C, overnight; (e) $CF_3C(NPh)Cl$, NaH, CH_2Cl_2, 0 °C, 4 h, 69% (α/β = 1:1); (f) see Table 1, entry 3; (g) see Table 1, entries 4 and 5; (h) $NaNH_2$, DMF, rt, 4 days, 62%.

temporary protecting group could be advantageous in the synthesis of the target compound **1**.

Thus, to prepare a suitable 2-*O*-benzylsulfonylated D-rhamnosyl donor, the known methyl 4-*O*-benzyl-α-D-rhamnopyranoside **3**[16] was regioselectively allylated at position *O*-3 with the stannylidene method, giving **4** in 82% yield (Scheme 1), and this alcohol was then subjected to benzylsulfonylation with $BnSO_2Cl$ in pyridine; without any intermediate chromatography, subsequent acetolysis and cleavage of the anomeric acetate gave the hemi-acetal **5** in 57% yield after three steps.

Conversion of the hemi-acetal into trichloroacetimidate surprisingly proceeded with low yield (35%). This result was explained with the high instability of compound **6**, which was degraded during the chromatographic purification on a neutral alumina support. Despite this low stability, we attempted the coupling of **6** with the D-rhamnose acceptor **7**, which was synthesized in one step from **3** according to the known phase-transfer procedure,[16,17] but the total consumption of the donor was observed giving no disaccharide product (Table 1). To have a glycosyl donor that was effective in glycosylate **7** and that did not degrade too quickly, alternative glycosylation procedures were investigated. Gin dehydrative coupling[18] between hemi-acetal **5** and acceptor **7** was first tested, but it did not proceed at all: no product was detected by TLC analysis, even when the reaction was conducted for 2 days. Actually, ESI-MS analysis revealed the presence of a small peak related to disaccharide formation, which was quantified in less than 10% yield by NMR analysis. Since glycosyl phosphates are known to be β-directing glycosyl donor,[13k] hemi-acetal **5** was converted into the diphenyl phosphate donor **8** by treatment with diphenyl chlorophosphate in CH_2Cl_2 at −10 °C in the presence of DMAP.[19] Analogously to **6**, **8** was demonstrated to be highly unstable by TLC analysis and chromatography on neutral alumina support, which did not allow the recovery of any glycosyl phosphate. Thus, crude **8** (α/β = 2.5:1) was directly subjected to glycosylation reaction without any chromatographic purification: upon coupling **8** and **7** with stoichiometric TMSOTf in CH_2Cl_2 at −78 °C, the desired disaccharide **10** was obtained in 58% yield. The stereoselectivity of the coupling was quite low: the β-disaccharide **10**β was recovered in 31% yield, whereas **10**α was recovered in 27% yield. The configuration of the new glycosidic bond in **10**α and **10**β was ascertained by comparing the chemical shifts values of H-3_B and H-5_B, which are upfield shifted in **10**β (H-3: 3.34 ppm; H-5: 3.24 ppm) with respect to **10**α (H-3, H-5: 3.84 ppm). To enhance the yield of the coupling, an *N*-phenyltrifluoroacetimidate was chosen as alternative leaving group on the anomeric position,[20] since it leads to glycosyl donors that are more stable and sometimes also more effective in glycosylation reactions than trichloroacetimidate ones.[21] Hemi-acetal **5** was therefore treated with $CF_3C(NPh)CCl$ and NaH[22] to give **9**, after chromatography on neutral alumina, in a rather better yield (69%; α/β = 1:1) than **6**. Coupling of **9** with **7** in CH_2Cl_2 at −25 °C using catalytic TMSOTf gave **10** in excellent yield and acceptable ratio of anomeric glycosides (99%; α/β = 2:3; 59% of isolated **10**β). A slight modification in the solvent mixture (addition of hexane to enhance the S_N2 character of the glycosyl acceptor attack on the supposed intermediate glycosyl triflate/oxacarbenium ion)[13f] afforded **10** in slightly lower yield (see Table 1, entry 5). Cleavage of the benzylsulfonyl protecting group on **10**β with sodium amide in DMF afforded the disaccharide acceptor **11** (62%).

The installation of the D-Fuc*p*3NAc unit was first attempted with the known *N*-phenyltrifluoroacetimidate **12**, the sole D-Fuc*p*3NAc donor reported to date.[23] The glycosylation with TMSOTf in an α-stereodirecting ternary solvent mixture (4:1:1 dioxane/DME/toluene)[24] afforded the trisaccharide **13** in only 17% yield (see Table 2, entry 1).

Since **12** has been already reported to glycosylate selectively armed acceptors,[21b] its coupling with **11**, whose sterical crowd around the hydroxyl function renders it a quite disarmed acceptor, proceeds not surprisingly with low yield. A different D-Fuc*p*3NAc donor was therefore required. Since thiofucosides have been already reported to act as efficient donors in glycosylations in which glycosyl trihaloacetimidates failed,[25] the synthesis of a D-Fuc*p*3NAc thioglycoside was attempted (Scheme 2).

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TABLE 1. Glycosylation Reactions of Acceptor 7 To Give Disaccharide 10

entry	donor	acceptor	solvent	activator	temperature	yield[a] (α/β)[b]
1	**5**	**7**	CH_2Cl_2/toluene 3:1	Tf_2O/Ph_2SO/DTBMP	−78 °C to room temperature	traces
2	**6**	**7**	CH_2Cl_2	TMSOTf	−50 °C to room temperature	no product
3	**8**	**7**	CH_2Cl_2	TMSOTf	−78 °C to −15 °C	58% (1:1.1)
4	**9**	**7**	CH_2Cl_2	TMSOTf	−60 °C to −25 °C	99% (2:3)
5	**9**	**7**	CH_2Cl_2/hexane 1:1	TMSOTf	−50 °C	95% (1.1:1)

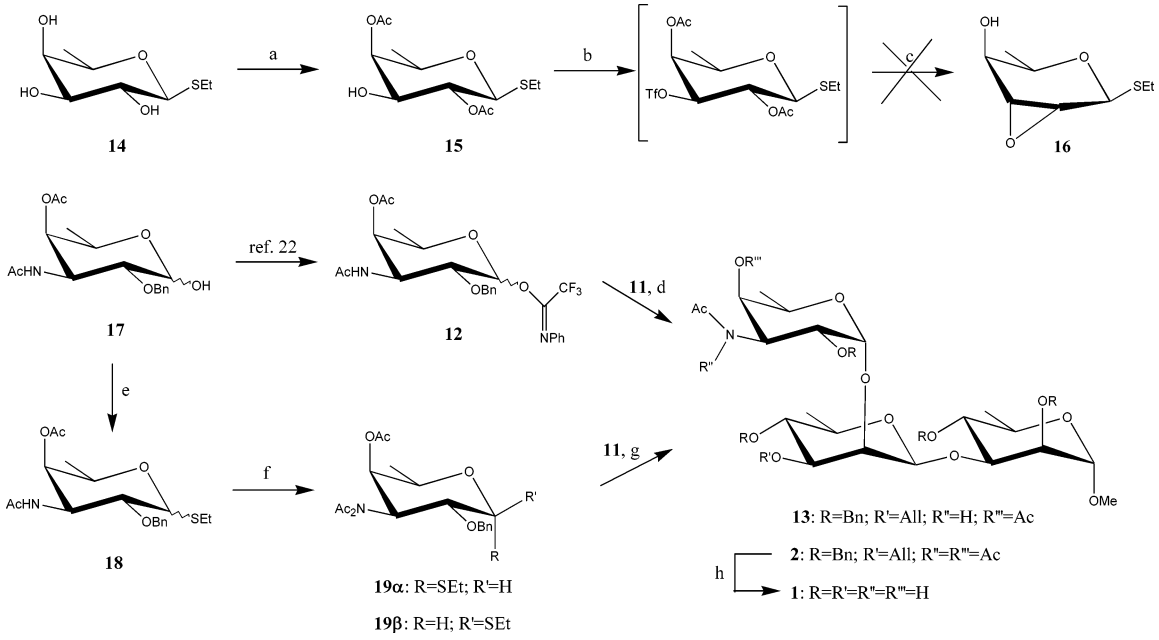
[a] Isolated yield. [b] Measured after isolation of the two anomers.

TABLE 2. Glycosylation Reactions of Disaccharide Acceptor 11

entry	donor	acceptor	solvent	activator	temperature	yield	product
1	**12**	**11**	dioxane/DME/toluene 4:1:1	TMSOTf	0 °C to room temperature	17%	**13**
2	**18**	**11**	CH_2Cl_2/Et_2O 1:1	NIS/TfOH	−20 °C	traces	**13**
3	**19α**	**11**	CH_2Cl_2/Et_2O 1:1	NIS/TfOH	−20 °C	15%	**2**
4	**19β**	**11**	CH_2Cl_2/Et_2O 1:1	NIS/TfOH	−20 °C	40% (55%)[a]	**2**

[a] Yield calculated on reacted acceptor.

SCHEME 2. Synthesis of 1[a]



[a] (a) i. CSA, 2:7 DMF/MeC(OMe)$_3$, 100 mbar, rt, 20 min; ii. Ac_2O, py, rt, overnight; iii. 80% AcOH, rt, 10 min, 82% over three steps; (b) Tf_2O, 1:1 py/CH_2Cl_2, 0 °C, 45 min; (c) Na, 1:1 MeOH/CH_2Cl_2, rt; (d) see Table 2, entry 1; (e) i. Ac_2O, py, rt, overnight; ii. EtSH, $BF_3{\cdot}OEt_2$, rt, overnight, 79% over two steps (α/β = 1:1); (f) AcCl, DIPEA, CH_2Cl_2, rt, overnight, 91%; (g) see Table 2, entries 3 and 4; (h) i. $PdCl_2$, 1:1 CH_2Cl_2/MeOH, rt, overnight; ii. 0.4 M NaOMe, 1:1 CH_2Cl_2/MeOH, rt, 3 h; iii. H_2, Pd/C, MeOH, rt, 4 days then HCOOH, ultrasound bath, rt, 3 h, 84% over three steps.

Thus, compound **14**[26] was subjected to a *one-pot* sequence of three reactions (orthoesterification, acetylation, and orthoester regioselective opening; 82% over three steps) to afford the alcohol **15**. Unfortunately, the treatment of the triflate derivative of **15** with sodium in methanol gave a complex mixture in which we detected only traces of the desired 2,3-epoxide **16**, which was required for the subsequent insertion of the 3-amino functionality via the intramolecular cyclization of an epoxytrichloroacetimidate.[23] For this reason, it was decided to install a thioalkyl group directly on a D-Fuc*p*3NAc building block, whose position 3 is namely already aminated. Thus, hemi-acetal **17**[23] was acetylated and then treated with EtSH/$BF_3{\cdot}OEt_2$ in CH_2Cl_2 to give the thioglycoside **18** (79%; α/β = 1:1 as an inseparable mixture). The NIS/TfOH mediated coupling of this donor and acceptor **11** in 1:1 CH_2Cl_2/Et_2O afforded only traces of the desired α-trisaccharide **13**. To enhance the yield, a more efficient D-Fuc*p*3NAc donor was required. Since it has been reported that the failure of a glycosylation can be sometimes ascribed to the inhibitory effect of a NHAc group on the glycosyl donor[27] or acceptor,[28] compound **18** was treated with AcCl/DIPEA in CH_2Cl_2 to give

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the *N*,*N*-diacetylated thioglycoside **19** in a ca. 1:1 α/*β* mixture, which was then easily separated by standard silica gel chromatography (**19**α: 44%; **19***β*: 47%). The α-anomer gave the α-trisaccharide **2** in 15% yield, whereas compound **19***β* afforded the same coupling product in higher yield (40%) together with a 27% recovery of unreacted acceptor **11** (55% yield based on reacted **11**) and 10% of compound **13**, whose formation is probably due to an acidic cleavage of the diamide function to NHAc group. The α-configuration of the newly formed glycosydic bond was ascertained by the $^3J_{H1-H2}$ value (3.4 Hz). In comparison with the NHAc group, the presence of an *N*,*N*′-diacetyl protecting group in **2** does not increase the number of the required deprotection steps, since conventional transesterification with NaOMe on an NAc_2 group retains one *N*-acetyl functionality, which occurs in the natural repeating unit of the O-antigen from *Xcc*. Thus, after a first de-*O*-allylation step with $PdCl_2$ in 1:1 MeOH/CH_2Cl_2, Zemplèn deacetylation and subsequent hydrogenolysis afforded the target compound **1** (84%). Interestingly, hydrogenolysis with Pd/C in MeOH under H_2 atmosphere allowed the cleavage of only two benzyl groups, even after a prolonged period of several days. The complete debenzylation was, however, accomplished by transfer hydrogenation under Perlin's conditions.[29]

Conclusion

In conclusion, the first synthesis of a methyl trisaccharide corresponding to the repeating unit of the *O*-antigen from *Xanthomonas campestris* pv. *campestris* 8004 has been reported. It is noteworthy that the proposed synthetic approach yields the orthogonally protected trisaccharide building block **2**, whose allyl protecting group could chemoselectively be cleaved to give a trisaccharide acceptor. This one would be ready for successive glycosylations to higher oligosaccharide fragments of the O-antigen from *Xcc*, suitable, as **1**, for phytopathological structure−activity studies.

Experimental Section

Methyl 3-*O*-Allyl-4-*O*-benzyl-α-D-rhamnopyranoside (4). Diol **3**[15] (1.337 g, 4.99 mmol) was dissolved in 10:1 benzene/methanol (34 mL), and Bu_2SnO (1.565 g, 6.29 mmol) was then added. After being stirred at 60° C for 90 min, the solvent was evaporated. Bu_4NBr (1.609 g, 4.99 mmol) was added to the residue under argon. The mixture was suspended in toluene (22 mL), AllBr (4.63 mL, 54.8 mmol) was then added, and stirring was conducted at 65 °C for 60 min, after that the solvent was evaporated. A column chromatography (6:1 petroleum ether/ethyl acetate) on the residue afforded **4** (1.258 g, 82%) as a yellowish oil. $[\alpha]_D$ +54.0 (*c* 0.9, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz) *δ* 7.33 (m, 5H), 5.93 (m, 1H), 5.32 (dd, 1H, J_{vic} = 17.0 Hz, J_{gem} = 1.6 Hz), 5.20 (dd, 1H, J_{vic} = 10.4 Hz, J_{gem} = 1.6 Hz), 4.87 (d, 1H, J_{gem} = 10.8 Hz), 4.69 (bs, 1H), 4.62 (d, 1H, J_{gem} = 10.8 Hz), 4.16 (m, 2H), 3.99 (bd, 1H, $J_{2,3}$ = 3.0 Hz), 3.68 (m, 2H), 3.40 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.6 Hz), 3.34 (s, 3H), 2.48 (s, 1H), 1.31 (d, 3H, $J_{6,5}$ = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) *δ* 138.4, 134.5, 128.3−127.7, 117.3, 100.0, 79.8, 79.6, 75.3, 70.9, 68.6, 67.0, 54.7, 17.9. ESI-MS for $C_{17}H_{24}O_5$ (*m*/*z*): M_r (calcd) 308.16, M_r (found) 331.39 $(M + Na)^+$. Anal. Calcd: C, 66.21; H, 7.84. Found: C, 66.50; H, 7.87.

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3-*O*-Allyl-2-*O*-benzensulfonyl-4-*O*-benzyl-D-rhamnopyranose (5). Compound **4** (0.577 g, 1.87 mmol) was dissolved in pyridine (12 mL), and then $BnSO_2Cl$ (0.899 g, 4.71 mmol) was added. The solution was stirred for 45 min at room temperature, and after that water (10 mL) was added. The mixture was diluted with CH_2Cl_2 and washed with water. The organic layer was collected, dried, and concentrated to give a brown oil that was dissolved in Ac_2O (10 mL) and cooled to 0 °C. A 25:20:0.5 v/v/v mixture of Ac_2O/AcOH/H_2SO_4 (15 mL) was added. The solution was allowed to gradually warm to room temperature, and after 3 h it was diluted with CH_2Cl_2 and washed with water, 1 M $NaHCO_3$, and water again. The organic layer was collected, dried, and concentrated to give a residue that was dissolved in DMF (5 mL). The solution was treated with hydrazine acetate (0.488 g, 5.10 mmol) and then stirred for 2 h at room temperature. Then it was diluted with CH_2Cl_2, washed with 5 N NaCl, dried, and concentrated. The residue was subjected to column chromatography (4:1 to 2:1 petroleum ether/ethyl acetate) to give **5** (0.478 g, 57%; α/*β* = 6:1) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 200 MHz) (α-anomer) *δ* 7.50−7.27 (m, 10H), 5.96 (m, 1H), 5.36 (dd, 1H, J_{vic} = 17.2 Hz, J_{gem} = 1.6 Hz), 5.23 (dd, 1H, J_{vic} = 10.5 Hz, J_{gem} = 1.6 Hz), 5.14 (d, 1H, $J_{1,2}$ = 1.6 Hz), 4.99 (dd, 1H, $J_{2,3}$ = 2.8 Hz, $J_{1,2}$ = 1.6 Hz), 4.92 (d, 1H, J_{gem} = 11.2 Hz), 4.64 (d, 1H, J_{gem} = 11.2 Hz), 4.54 (AB d, 1H, J_{gem} = 14.6 Hz), 4.45 (AB d, 1H, J_{gem} = 14.6 Hz), 4.23 (m, 2H), 3.91 (m, 2H), 3.37 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.6 Hz), 1.28 (d, 3H, $J_{6,5}$ = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) (α-anomer) *δ* 138.2, 134.2, 130.8−127.8, 117.7, 92.3, 79.8, 78.0, 75.6, 75.4, 71.5, 67.7, 57.4, 17.9. ESI-MS for $C_{23}H_{28}O_7S$ (*m*/*z*): M_r (calcd) 448.16, M_r (found) 471.41 $(M + Na)^+$. Anal. Calcd: C, 61.59; H, 6.29. Found: C, 61.70; H, 6.26.

3-*O*-Allyl-2-*O*-benzensulfonyl-4-*O*-benzyl-D-rhamnopyranosyl Trichloroacetimidate (6). Hemi-acetal **5** (0.459 g, 1.02 mmol) was dissolved under argon in CH_2Cl_2 (11 mL), and Cl_3CCN (0.565 mL, 5.60 mmol) and DBU (30 *μ*L, 0.20 mmol) were sequentially added. The solution was stirred at room temperature for 2 h, and then it was concentrated to give a residue, which, after neutral alumina (Brockman grade 1) column chromatography (10:1 petroleum ether/ethyl acetate), afforded **6** (0.214 g, 35%) as a colorless oil. $[\alpha]_D$ +6.1 (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz) *δ* 8.65 (s, 1H), 7.44−7.20 (m, 10H), 6.14 (bs, 1H), 5.92 (m, 1H), 5.31 (dd, 1H, J_{vic} = 17.2 Hz, J_{gem} = 1.6 Hz), 5.19 (dd, 1H, J_{vic} = 10.5 Hz, J_{gem} = 1.6 Hz), 5.05 (bd, 1H, $J_{2,3}$ = 2.8 Hz), 4.89 (d, 1H, J_{gem} = 11.1 Hz), 4.61 (d, 1H, J_{gem} = 11.1 Hz), 4.52 (d, 1H, J_{gem} = 14.7 Hz), 4.47 (m, 3H), 4.35−4.10 (m, 5H), 3.87 (m, 2H), 3.44 (m, 3H), 1.29 (d, 3H, $J_{6,5}$ = 6.2 Hz), 1.23 (d, 1H, $J_{6,5}$ = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) 159.7, 137.7, 133.9, 130.7−127.5, 118.4, 95.0, 78.8, 76.5, 75.6, 75.4, 71.5, 70.9, 57.6, 17.7. Anal. Calcd: C, 50.64; H, 4.76; N, 2.36. Found: C, 50.58; H, 4.73; N, 2.37.

3-*O*-Allyl-2-*O*-benzensulfonyl-4-*O*-benzyl-D-rhamnopyranosyl *N*-Phenyltrifluoroacetimidate (9). A mixture of **5** (0.544 g, 1.21 mmol) and freshly activated 4 Å molecular sieves was suspended under argon in CH_2Cl_2 (25 mL) and cooled to 0 °C. $CF_3C(NPh)Cl$ (195 *μ*L, 1.58 mmol) and NaH (60% oil suspension; 86 mg, 2.14 mmol) were sequentially added. The mixture was stirred at 0 °C for 4 h, and then it was filtered over a Celite pad and concentrated. Neutral alumina (Brockman grade 1) column chromatography (13:1 petroleum ether/ethyl acetate) on the residue afforded **9** (0.514 g, 69%; α:*β* = 1:1) as a yellowish oil. ^{1}H NMR ($CDCl_3$, 200 MHz) *δ* 7.45−6.79 (m, 15H), 6.08−5.90 (m, 3H), 5.79 (bm, 1H), 5.35 (2 dd, 2H, J_{vic} = 17.4 Hz, J_{gem} = 1.6 Hz), 5.21 (m, 3H), 5.11 (dd, 1H), 4.95 (d, 1H, J_{gem} = 10.8 Hz), 4.91 (d, 1H, J_{gem} = 10.8 Hz), 4.67 (d, 1H, J_{gem} = 10.8 Hz), 4.62 (d, 1H, J_{gem} = 10.8 Hz), 4.57 (d, 1H, J_{gem} = 14.4 Hz), 4.47 (m, 3H), 4.35−4.10 (m, 5H), 3.87 (m, 2H), 3.44 (m, 3H), 1.29 (d, 3H, $J_{6,5}$ = 6.2 Hz), 1.23 (d, 1H, $J_{6,5}$ = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) *δ* 135.9, 130.9, 130.7, 128.7−123.7, 119.3, 119.2, 94.0, 93.4, 78.8, 78.7, 77.5, 75.6, 75.5, 75.1, 72.9, 71.7, 71.1, 70.6, 57.6, 17.7. ESI-MS for $C_{31}H_{32}F_3NO_7S$ (*m*/*z*): M_r (calcd) 619.19, M_r (found) 619.65 (M

+ Na)$^+$. Anal. Calcd: C, 60.09; H, 5.21; N, 2.26. Found: C, 60.16; H, 5.22; N, 2.25.

Methyl (3-*O*-Allyl-2-*O*-benzensulfonyl-4-*O*-benzyl-*β*-D-rhamnopyranosyl)-(1 → 3)-2,4-di-*O*-benzyl-α-D-rhamnopyranoside (10). A mixture of acceptor **7** (0.182 g, 0.51 mmol) and donor **9** (0.362 g, 0.58 mmol) was coevaporated three times with toluene (5 mL). The residue was mixed with freshly activated AW-300 4 Å molecular sieves and suspended under argon in CH_2Cl_2 (20 mL). The mixture was cooled to −60 °C, and an 80 μM solution of TMSOTf in CH_2Cl_2 (75 μL, 6.0 μmol) was added. The temperature was allowed to gradually rise to −25 °C. After 4 h the mixture was neutralized by adding Et_3N, then filtered over Celite, and concentrated to give a residue that after column chromatography (9:1 to 6:1 petroleum ether/ethyl acetate) afforded, as first eluted compound, **10**α (0.165 g, 41%) as a yellowish oil. $[\alpha]_D$ −6.8 (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.40−7.24 (m, 20H), 5.91 (m, 1H), 5.27 (dd, 1H, J_{vic} = 17.4 Hz, J_{gem} = 1.6 Hz), 5.14 (dd, 1H, J_{vic} = 10.6 Hz, J_{gem} = 1.6 Hz), 5.07 (bd, 1H, $J_{2,3}$ = 2.7 Hz), 4.91 (d, 1H, J_{gem} = 11.1 Hz), 4.80 (d, 1H, J_{gem} = 10.8 Hz), 4.66 (d, 1H, $J_{1,2}$ = 1.5 Hz), 4.64 (bs, 1H), 4.62 (d, 1H, J_{gem} = 11.1 Hz), 4.57 (d, 1H, J_{gem} = 10.8 Hz), 4.42 (d, 1H, J_{gem} = 14.1 Hz), 4.35 (d, 1H, J_{gem} = 14.1 Hz), 4.17 (m, 1H), 4.02 (m, 2H, H-3$_A$), 3.84 (m, 2H), 3.70 (bd, 1H, $J_{2,3}$ = 2.7 Hz), 3.63 (dq, 1H, $J_{5,4}$ = 9.4 Hz, $J_{5,6}$ = 6.2 Hz), 3.57 (t, 1H, $J_{4,5}$ = $J_{4,3}$ = 9.4 Hz), 3.36 (t, 1H, $J_{4,5}$ = $J_{4,3}$ = 9.8 Hz), 3.30 (s, 3H), 1.26 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 138.4, 138.0, 134.3, 130.9, 128.7−127.8, 117.7, 99.1, 98.3, 80.5, 79.7, 78.4, 77.4, 77.3, 75.3, 75.2, 72.7, 71.3, 68.6, 67.9, 57.5, 54.7, 17.9. ESI-MS for $C_{44}H_{52}O_{11}S$ (*m/z*): M_r (calcd) 788.32, M_r (found) 810.91 (M + Na)$^+$. Anal. Calcd: C, 66.98; H, 6.64. Found: C, 66.88; H, 6.62.

Second eluted compound **10***β* (0.237 g, 59%) was recovered as a yellowish oil. $[\alpha]_D$ −22.1 (*c* 0.8, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.40−7.25 (m, 20H), 5.99 (m, 1H), 5.39 (dd, 1H, J_{vic} = 17.4 Hz, J_{gem} = 1.8 Hz), 5.23 (dd, 1H, J_{vic} = 10.5 Hz, J_{gem} = 1.8 Hz), 5.04 (d, 1H, $J_{2,3}$ = 2.1 Hz), 4.97 (d, 1H, J_{gem} = 10.8 Hz), 4.92 (d, 1H, J_{gem} = 10.8 Hz), 4.79 (d, 1H, J_{gem} = 12.0 Hz), 4.75 (bs, 1H), 4.65 (d, 1H, J_{gem} = 12.0 Hz), 4.61 (d, 1H, J_{gem} = 10.8 Hz), 4.52 (d, 3H), 4.44 (bs, 1H), 4.34 (dd, 1H, J_{gem} = 14.4 Hz, J_{vic} = 6.6 Hz), 4.11 (m, 2H, H-3$_A$), 3.75 (t, 1H, $J_{2,1}$ = $J_{2,3}$ = 5.8 Hz), 3.63 (dq, 1H, $J_{5,4}$ = 9.6 Hz, $J_{5,6}$ = 6.2 Hz), 3.55 (t, 1H, $J_{4,5}$ = $J_{4,3}$ = 9.6 Hz), 3.34 (m, 5H), 3.24 (dq, 1H, $J_{5,4}$ = 9.6 Hz, $J_{5,6}$ = 6.2 Hz), 1.28 (d, 6H, $J_{6,5}$ = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 138.8, 138.3, 134.3, 131.0, 130.9, 128.6−127.4, 117.7, 99.1, 96.8, 80.0, 79.9, 79.7, 78.1, 75.9, 75.7, 74.0, 72.8, 72.1, 71.2, 67.7, 57.9, 54.9, 18.2, 17.9. ESI-MS for $C_{44}H_{52}O_{11}S$ (*m/z*): M_r (calcd) 788.32, M_r (found) 810.91 (M + Na)$^+$. Anal. Calcd: C, 66.98; H, 6.64. Found: C, 67.11; H, 6.58.

Methyl (3-*O*-Allyl-4-*O*-benzyl-*β*-D-rhamnopyranosyl)-(1 → 3)-2,4-di-*O*-benzyl-α-D-rhamnopyranoside (11). A mixture of **10** (0.229 g, 0.29 mmol) and $NaNH_2$ (127 mg, 3.26 mmol) was suspended in DMF (5 mL) and stirred at room temperature. After 24 and 48 h additional aliquots of $NaNH_2$ (127 mg, 3.26 mmol) were added. After 4 days we added methanol (30 mL) and then, dropwise, AcOH (3 mL). The mixture was concentrated to give a residue that was dissolved in CH_2Cl_2, washed with 1 M $NaHCO_3$ and 5 M NaCl, dried, and concentrated. Column chromatography (6:1 petroleum ether/EtOAc) on the residue afforded **11** (0.114 g, 62%) as a yellowish oil. $[\alpha]_D$ −11.1 (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.39−7.26 (m, 15H), 5.98 (m, 1H), 5.34 (dd, 1H, J_{vic} = 17.2 Hz, J_{gem} = 1.6 Hz), 5.21 (dd, 1H, J_{vic} = 10.4 Hz, J_{gem} = 1.6 Hz), 4.95 (d, 1H, J_{gem} = 10.8 Hz), 4.90 (d, 1H, J_{gem} = 10.8 Hz), 4.77 (d, 1H, J_{gem} = 12.4 Hz), 4.72 (d, 1H, $J_{1,2}$ = 1.9 Hz), 4.61−4.56 (m, 3H), 4.28 (bs, 1H), 4.21 (m, 2H), 4.11 (m, 1H), 3.88 (d, 1H, $J_{2,3}$ = 3.0 Hz), 3.73−3.64 (m, 2H), 3.56 (t, 1H, $J_{4,3}$ = $J_{4,5}$ = 8.9 Hz), 3.45 (t, 1H, $J_{4,3}$ = $J_{4,5}$ = 9.3 Hz), 3.33 (s, 3H), 3.28 (dd, 1H, $J_{3,4}$ = 9.3 Hz, $J_{3,2}$ = 3.0 Hz), 3.19 (dq, $J_{5,4}$ = 9.3 Hz, $J_{5,6}$ = 6.2 Hz), 1.35 (d, 3H, $J_{6,5}$ = 6.2 Hz), 1.27 (d, 3H, $J_{6,5}$ = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 138.5, 138.0, 134.8, 134.7, 128.3−127.5, 117.2, 98.6, 97.1, 81.4, 79.7, 75.5, 75.0, 74.7, 72.5, 71.6, 70.5, 68.8, 67.5, 54.7, 18.1, 17.9. ESI-MS for $C_{37}H_{46}O_9$ (*m/z*): M_r (calcd) 634.31, M_r (found) 657.47 (M + Na)$^+$. Anal. Calcd: C, 70.01; H, 7.30. Found: C, 69.90; H, 7.30.

Ethyl 2,4-Di-*O*-acetyl-1-thio-*β*-D-fucopyranoside (15). Triol **14** (0.775 g, 3.72 mmol) was dissolved in 2:7 v/v DMF/$MeC(OMe)_3$ (9.0 mL), CSA (80 mg, 0.34 mmol) was then added, and the solution was evacuated at 100 mbar for 20 min. Then pyridine (7.0 mL) and Ac_2O (7.0 mL) were sequentially added. The solution was stirred overnight at room temperature, then coevaporated four times with toluene (10 mL each). The residue was dissolved in 80% AcOH, and the solution was stirred at room temperature for 10 min. Then it was coevaporated two times with toluene (5 mL each). The residue was subjected to column chromatography (5:2 petroleum ether/ethyl acetate) to give **15** (0.893 g, 82%) as a white solid. $[\alpha]_D$ −2.4 (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.17 (dd, 1H, $J_{4,3}$ = 3.2 Hz, $J_{4,5}$ = 0.8 Hz), 4.97 (t, 1H, $J_{2,3}$ = $J_{2,1}$ = 9.6 Hz), 4.37 (d, 1H, $J_{1,2}$ = 10.0 Hz), 3.79 (dd, 1H, $J_{3,2}$ = 9.6 Hz, $J_{3,4}$ = 3.2 Hz), 3.71 (dq, $J_{5,6}$ = 6.4 Hz, $J_{5,4}$ = 0.8 Hz), 2.67 (dq, 2H, J_{vic} = 7.2 Hz, J_{gem} = 3.2 Hz), 2.14, 2.07 (2s, 6H), 1.23 (t, 3H, J_{vic} = 7.2 Hz), 1.16 (d, 3H, $J_{6,5}$ = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 171.3, 171.0, 83.1, 73.4, 73.1, 72.4, 71.0, 24.1, 20.9, 20.8, 16.6, 14.7. ESI-MS for $C_{12}H_{20}O_6S$ (*m/z*): M_r (calcd) 292.10, M_r (found) 292.21 (M + Na)$^+$. Anal. Calcd: C, 49.30; H, 6.90. Found: C, 49.35; H, 6.85.

Ethyl 3-Acetamido-4-*O*-acetyl-2-*O*-benzyl-1-thio-D-fucopyranoside (18). Hemi-acetal **17**[22] (100 mg, 297 μmol) was dissolved in pyridine (1.5 mL), and Ac_2O (2.0 mL) was added. The solution was stirred overnight at room temperature, then coevaporated twice with toluene (10 mL). The residue was dissolved in CH_2Cl_2, washed with 1 M HCl and 0.2 M $NaHCO_3$, dried, and concentrated to give a residue that was then dissolved in CH_2Cl_2 (2.0 mL) and treated with EtSH (25 μL, 0.34 mmol) and BF_3·OEt_2 (76 μL, 0.60 mmol). After being stirred overnight at room temperature the mixture was diluted with CH_2Cl_2 (40 mL), washed with 1 M KOH (50 mL) and water (50 mL), dried, and concentrated. The residue was subjected to column chromatography (1:1 petroleum ether/ethyl acetate) to afford **18** (90 mg, 79%; α/*β* = 1:1) as a white foam. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.36 (m, 10H), 5.57 (d, 1H, $J_{1,2}$ = 5.0 Hz), 5.33 (d, 1H, $J_{4,3}$ = 2.2 Hz), 5.20 (d, 1H, $J_{4,3}$ = 2.4 Hz), 5.02−4.87 (m, 2H), 4.86 (d, 1H, J_{gem} = 11.4 Hz), 4.78 (d, 1H, J_{gem} = 12.0 Hz), 4.57 (m, 2H), 4.46 (q, 1H, $J_{5,6}$ = 6.0 Hz), 4.38 (d, 1H, J_{gem} = 12.0 Hz), 4.33−4.16 (m, 2H), 3.87 (dd, 1H, $J_{2,3}$ = 11.2 Hz, $J_{2,1}$ = 5.0 Hz), 3.76 (q, 1H, $J_{5,6}$ = 6.6 Hz), 3.397 (t, 1H, $J_{2,3}$ = $J_{2,1}$ = 9.8 Hz), 2.79, 2.58 (2q, 4H, J_{vic} = 6.8 Hz), 2.09, 2.08 (2s, 6H), 1.82, 1.73 (2s, 6H), 1.33 (t, 6H, J_{vic} = 6.8 Hz), 1.13 (d, 3H, $J_{6,5}$ = 6.0 Hz), 1.07 (d, 3H, $J_{6,5}$ = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.1−169.9, 137.6, 137.4, 128.4−128.0, 85.8, 82.8, 75.4, 74.1, 73.6, 72.6, 72.2, 72.1, 71.2, 64.9, 53.3, 49.8, 25.2, 23.6, 23.0, 20.6, 16.7, 16.1, 14.9, 14.8. ESI-MS for $C_{19}H_{27}NO_5S$ (*m/z*): M_r (calcd) 381.16, M_r (found) 404.36 (M + Na)$^+$. Anal. Calcd: C, 59.82; H, 7.13; N, 3.67. Found: C, 59.89; H, 7.19; N, 3.68.

Ethyl 3,3-Diacetamido-4-*O*-acetyl-2-*O*-benzyl-1-thio-D-fucopyranoside (19). Compound **18** (71 mg, 186 μmol) was dissolved under argon in CH_2Cl_2 (2.0 mL). This solution was treated with DIPEA (148 μL, 0.86 mmol) and then, dropwise, with AcCl (183 μL, 2.58 mmol). The solution was stirred overnight at room temperature, then diluted with CH_2Cl_2, washed with 1 M $NaHCO_3$, dried, and concentrated. The residue was subjected to column chromatography (5:1 to 3:1 petroleum ether/ethyl acetate) to give, as first eluted compound, **19**α (35 mg, 44%) as a white foam. $[\alpha]_D$ +20.3 (*c* 2.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.30 (m, 5H), 5.55 (d, 1H, $J_{1,2}$ = 4.0 Hz), 5.11 (d, 1H), 4.68 (m, 2H), 4.58 (d, 1H, J_{gem} = 10.6 Hz), 4.47 (q, 1H, $J_{5,6}$ = 6.6 Hz), 4.26 (d, 1H, J_{gem} = 10.6 Hz), 2.51 (q, 2H, J_{vic} = 7.2 Hz), 2.21 (s, 6H), 2.12 (s, 3H), 1.27 (t, 3H, J_{vic} = 7.2 Hz), 1.15 (d, 3H, $J_{6,5}$ = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 173.9, 171.3, 137.1, 128.3−127.9, 83.6, 71.6, 71.3, 70.8, 65.7, 57.9, 27.0, 23.7, 21.0, 16.1, 14.9. ESI-MS for $C_{21}H_{29}NO_6S$ (*m/z*): M_r (calcd) 423.17, M_r (found) 446.41 (M +

$Na)^+$. Anal. Calcd: C, 59.55; H, 6.90; N, 3.31. Found: C, 59.56; H, 6.87; N, 3.29.

The second eluted compound, **19**β (37 mg, 47%), was recovered as a white foam. $[\alpha]_D$ −45.3 (*c* 0.9, CH_2Cl_2). ^1H NMR ($CDCl_3$, 200 MHz) δ 7.30 (m, 5H), 5.12 (bs, 1H), 4.99 (d, 1H, J_{gem} = 11.0 Hz), 4.50 (m, 3H), 4.33 (d, 1H, J_{gem} = 11.0 Hz), 3.82 (q, 1H, $J_{5,6}$ = 6.0 Hz), 2.79 (dq, 2H, J_{vic} = 7.6 Hz, J_{gem} = 2.0 Hz), 2.23 (s, 6H), 2.10 (s, 3H), 1.33 (t, 3H, J_{vic} = 7.6 Hz), 1.19 (d, 3H, $J_{6,5}$ = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 174.2, 171.5, 138.1, 128.3−127.4, 87.2, 74.4, 73.7, 73.5, 72.0, 62.5, 27.2, 25.0, 20.9, 16.6, 14.9. ESI-MS for $C_{21}H_{29}NO_6S$ (*m/z*): M_r (calcd) 423.17, M_r (found) 446.39 $(M + Na)^+$. Anal. Calcd: C, 59.55; H, 6.90; N, 3.31. Found: C, 59.59; H, 6.86; N, 3.28.

Methyl (3,3-Diacetamido-4-*O*-acetyl-2-*O*-benzyl-α-D-fucopyranosyl)-(1 → 2)-(3-*O*-allyl-4-*O*-benzyl-*β*-D-rhamnopyranosyl)-(1 → 3)-2,4-di-*O*-benzyl-α-D-rhamnopyranoside (2). A mixture of acceptor **11** (19.7 mg, 31.0 μmol) and donor **19**β (28 mg, 66 μmol) was coevaporated three times with toluene (1 mL). The residue was mixed with freshly activated AW-300 4 Å molecular sieves and suspended under argon in 1:1 v/v CH_2Cl_2/Et_2O (800 μL). NIS (16 mg, 71 μmol) was then added under argon, the mixture was cooled to −20 °C, and a 0.60 mM solution of TfOH in CH_2Cl_2 (20 μL, 12 μmol) was added. After 90 min of being stirred at −20 °C, the mixture was filtered over Celite, diluted with CH_2Cl_2, washed with 10% $Na_2S_2O_3$ and 1 M $NaHCO_3$, dried, and concentrated. The residue was then subjected first to column chromatography (6:1 petroleum ether/ethyl acetate) and then to HPLC (Phenomenex Proteo 90A C-18 column, 250 × 10 mm; eluent: $MeOH/CH_3CN/H_2O$ 2:2:1) to afford a first eluted fraction, containing **11** (5.4 mg, 27%), and a second fraction, which contained **2** (12.3 mg, 40%) as a white foam. $[\alpha]_D$ +5 (*c* 0.3, CH_2Cl_2). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.39−7.10 (m, 20H), 5.92 (m, 1H), 5.76 (d, 1H, $J_{1,2}$ = 3.4 Hz), 5.29 (d, 1H, J_{gem} = 18.0 Hz), 5.21 (d, 1H, J_{gem} = 10.4 Hz), 5.13 (bs, 1H), 5.04 (m, 2H), 4.85 (q, 1H, $J_{5,6}$ = 6.4 Hz), 4.75 (d, 1H, J_{gem} = 12.0 Hz), 4.71 (m, 2H), 4.64 (d, 1H, J_{gem} = 12.0 Hz), 4.52 (m, 2H), 4.39 (m, 2H), 4.28 (d, 1H, J_{gem} = 11.1 Hz), 4.24−4.07 (m, 4H), 3.67 (m, 2H), 3.49 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz), 3.44 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.3 Hz), 3.32 (s, 3H), 3.24 (m, 2H), 2.11 (s, 3H), 2.01 (s, 6H), 1.35 (d, 3H, $J_{6,5}$ = 6.0 Hz), 1.28 (d, 3H, $J_{6,5}$ = 6.2 Hz), 1.16 (d, 3H, $J_{6,5}$ = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) 174.3, 171.5, 138.8, 138.5, 138.3, 138.0, 134.5, 130.8−126.9, 117.6, 98.9, 98.4, 95.8, 83.2, 80.6, 80.5, 75.1, 75.0, 73.3, 72.5, 72.4, 72.2, 72.1, 72.0, 71.9, 71.5, 70.2, 68.2, 65.7, 56.7, 54.7, 23.8, 21.0, 18.5, 17.9, 16.2. ESI-MS for $C_{56}H_{69}NO_{15}$ (*m/z*): M_r (calcd) 995.47, M_r (found) 1018.50 $(M + Na)^+$. Anal. Calcd: C, 67.52; H, 6.98; N, 1.41; Found: C, 67.44; H, 7.02; N, 1.40.

Methyl 3-Acetamido-α-D-fucopyranosyl-(1 → 2)-*β*-D-rhamnopyranosyl-(1 → 3)-α-D-rhamnopyranoside (1). To a solution of **2** (8.6 mg, 8.6 μmol) in 1:1 CH_2Cl_2/MeOH (400 μL) $PdCl_2$ (0.6 mg, 3.4 μmol) was added, and the mixture was vigorously stirred at room temperature overnight. Then it was filtered over a Celite pad, diluted with CH_2Cl_2, washed with 5 N NaCl, dried, and concentrated. The residue was then dissolved in 1:1 CH_2Cl_2/MeOH (800 μL) and treated with a 0.4 M methanolic solution of NaOMe (30 μL). After 3 h of being stirred at room temperature, the solution was neutralized with Amberlist-15 (H^+), filtered, and concentrated. The residue was dissolved in MeOH (1.5 mL) and then added to a suspension of 10% Pd/C (catalyst amount) in MeOH (0.5 mL). After being stirred at room temperature for 4 days under a hydrogen atmosphere, HCOOH (100 μL) was added and the mixture was kept in an ultrasound bath for 3 h. Then it was filtered on Celite and concentrated to give **1** (3.7 mg, 84% yield). $[\alpha]_D$ +26 (*c* 0.2, H_2O). ^1H NMR (D_2O, 600 MHz) δ 5.18 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1_C), 4.81 (s, 1H, H-1_B), 4.74 (s, 1H, H-1_A), 4.54 (q, 1H, $J_{5,6}$ = 6.4 Hz, H-5_C), 4.27 (dd, 1H, $J_{3,2}$ = 9.5 Hz, $J_{3,4}$ = 3.2 Hz, H-3_C), 4.14 (bs, 1H, H-2_A), 4.12 (d, 1H, $J_{2,3}$ = 3.0 Hz, H-2_B), 3.92 (dd, 1H, $J_{3,4}$ = 9.8 Hz, $J_{3,2}$ = 3.0 Hz, H-3_A), 3.87 (dd, 1H, $J_{2,3}$ = 9.5 Hz, $J_{2,1}$ = 3.6 Hz, H-2_C), 3.72 (m, 3H, H-3_B, H-4_C, H-5_A), 3.53 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.5 Hz, H-4_A), 3.50 (t, 1H, $J_{4,3} = J_{4,5}$ = 9.3 Hz, H-4_B), 3.41 (m, 4H, H-5_B, OMe), 2.06 (s, 3H, NHAc), 1.33 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6_A), 1.31 (d, 3H, $J_{6,5}$ = 6.2 Hz, H-6_B), 1.18 (d, 3H, $J_{6,5}$ = 6.4 Hz, H-6_C); ^{13}C NMR ($CDCl_3$, 150 MHz) 174.4 ($NHCOCH_3$), 100.5 (C-1_A), 100.1 (C-1_C), 96.6 (C-1_B), 78.7 (C-2_B), 77.0 (C-3_A), 73.5 (C-3_B), 72.5 (C-4_B), 72.4 (C-5_B), 70.5 (C-4_A), 70.3 (C-4_C), 68.5 (C-5_A), 67.1 (C-2_A, C-5_C), 66.6 (C-2_C), 54.7 (OMe), 51.2 (C-3_C), 22.0 ($NHCOCH_3$), 16.7, 16.6 (C-6_A, C-6_B), 15.3 (C-6_C). ESI-MS for $C_{21}H_{37}NO_{13}$ (*m/z*): M_r (calcd) 511.23, M_r (found) 533.71 $(M + Na)^+$. Anal. Calcd: C, 49.31; H, 7.29; N, 2.74; Found: C, 48.79; H, 7.47; N, 2.67.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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