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Acetolysis of 6-Deoxysugar Disaccharide Building Blocks: *exo* versus *endo* Activation

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Two different protocols for the mild and selective acetolysis of 6-deoxysugar methyl disaccharides under thermodynamic or kinetic control have been developed. The structures of the disaccharides obtained depend on the protocol used and, in the kinetically controlled cases, on the 6-deoxysugar configuration and protecting group pattern too. The behavior of 6-deoxyhexose oligosaccharides of different series (*rhamno*, *quinovo*, and *fuco*) under these two reaction conditions has been studied and rationalized based on the competition between *exo* versus *endo* oxygen activation in the acetolysis mechanism.

Introduction

Acetolysis of carbohydrates is a widely used reaction that involves the cleavage of the glycosidic bond and the simultaneous acetylation of the hydroxy groups thus formed and/or present before the solvolysis. Acetolysis finds extensive application as a selective degradation method in the structural elucidation of polysaccharides.[1] Similarly, the conversion of alkyl and aryl glycosides of mono- and oligosaccharides into 1-*O*-acetylated species is a key reaction in oligosaccharide synthesis because the products can be easily converted into both glycosyl donors and glycosyl acceptors.

Owing to the importance of such reactions, several studies of the mechanism of monosaccharide acetolysis have appeared in literature.[2] The mechanism can be summarized as shown in Scheme 1. Briefly, the acetylium ion, formed from Ac_2O under acid conditions, can activate the endocyclic as well as the exocyclic oxygen towards glycoside cleavage. Activation of the *exo* site provides 1-*O*-Ac-pyranoside products **B** after acetic acid attack on the oxocarbenium ion, whereas *endo* activation affords open-chain products **C**, which can react further under acid conditions. Indeed, they can be activated by a second acetylium ion to afford 1,1-diacetate **D** and/or 1-*O*-Ac-furanoside derivatives **E**. It has been shown that *endo* activation proceeds more rapidly, even if the relative rates of the two activation mechanisms are rather dependent on the sugar configuration.[2h] Nevertheless, acetolysis is usually governed not by kinetic, but by thermodynamic conditions, thus giving products **B** in much higher yields than **C**, **D**, and/or **E**. Indeed, the acetolysis of common hexose glycosides has been reported to produce high yields of the latter products by kinetic control in very few cases.[2d,2e,3,4] To the best of our knowledge, only one example of prevalent *endo* activation has been reported for the acetolysis of 6-deoxyhexose glycosides: a 6-deoxy-L-Tal-(1→2)-L-Rha-O*t*Bu building block afforded mainly an **E**-like disaccharide.[5]

Deoxyhexoses, and above all 6-deoxyhexoses, are frequently found in several natural sources: they have been found as constituents of O-antigen lipopolysaccharides[6] and also as components of glycoproteins, glycolipids, and other glycoconjugates such as cardioglycosides, natural antibiotics, and anticancer agents.[7] Because the biological role of the deoxyhexose components is very often crucial within these natural molecules, the synthesis of deoxyhexose-containing targets has been widely investigated. To the best of our knowledge, no comprehensive studies on the acetolysis of 6-deoxyhexose glycosides exist in the literature. Very recently we reported a mild, selective acetolysis of 6-deoxysugar oligosaccharide building blocks governed by the armed–disarmed effect: by using suitable protecting group patterns on the oligosaccharides we were able to convert the methyl glycosides into 1-*O*-Ac-pyranoside derivatives (**B**-like products) without cleaving the interglycosidic bonds.[8] In this work we have investigated the possibility of obtaining kinetically controlled **C**-, **D**-, and **E**-like disaccharide products. In fact, acetolysis of 6-deoxyhexoses under kinetic control should be more easily achieved with respect to common non-deoxyhexoses because the lack of the electron-withdrawing oxygen atom at the 6-position enhances the nucleophilicity of the endocyclic oxygen, thus favoring further the kinetically controlled *endo* activation pathway. A method in which one 6-deoxypyranose ring is selectively converted into a furanose cycle (kinetically controlled product **E**) at the disaccharide level could be very attractive for

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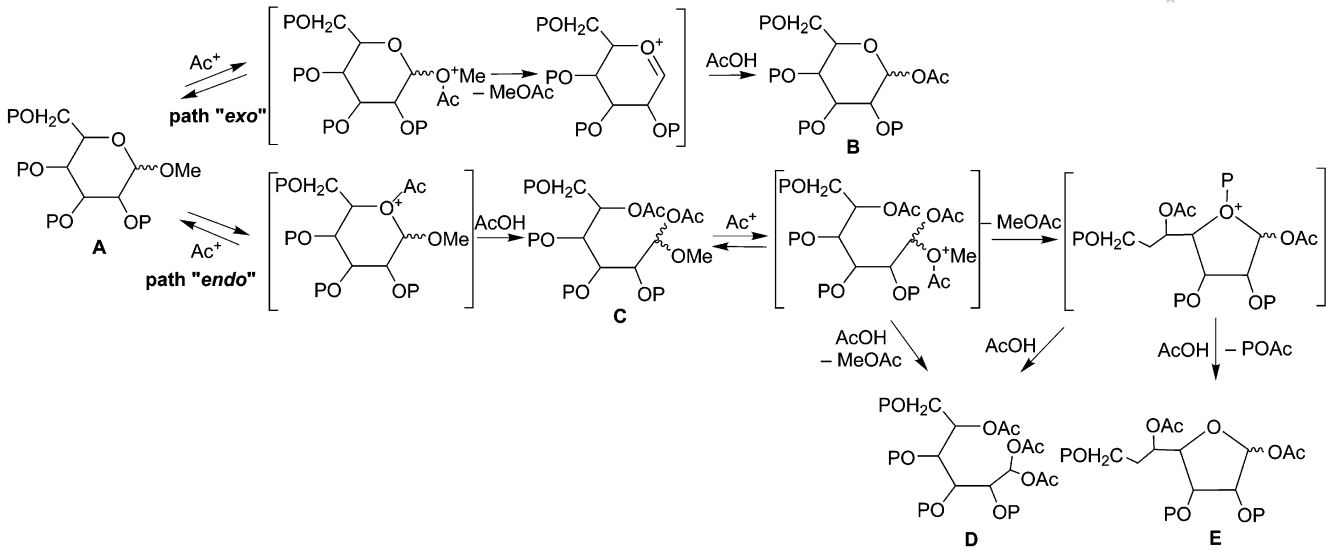


Scheme 1. *endo* versus *exo* activation mechanism for the acetolysis reaction.

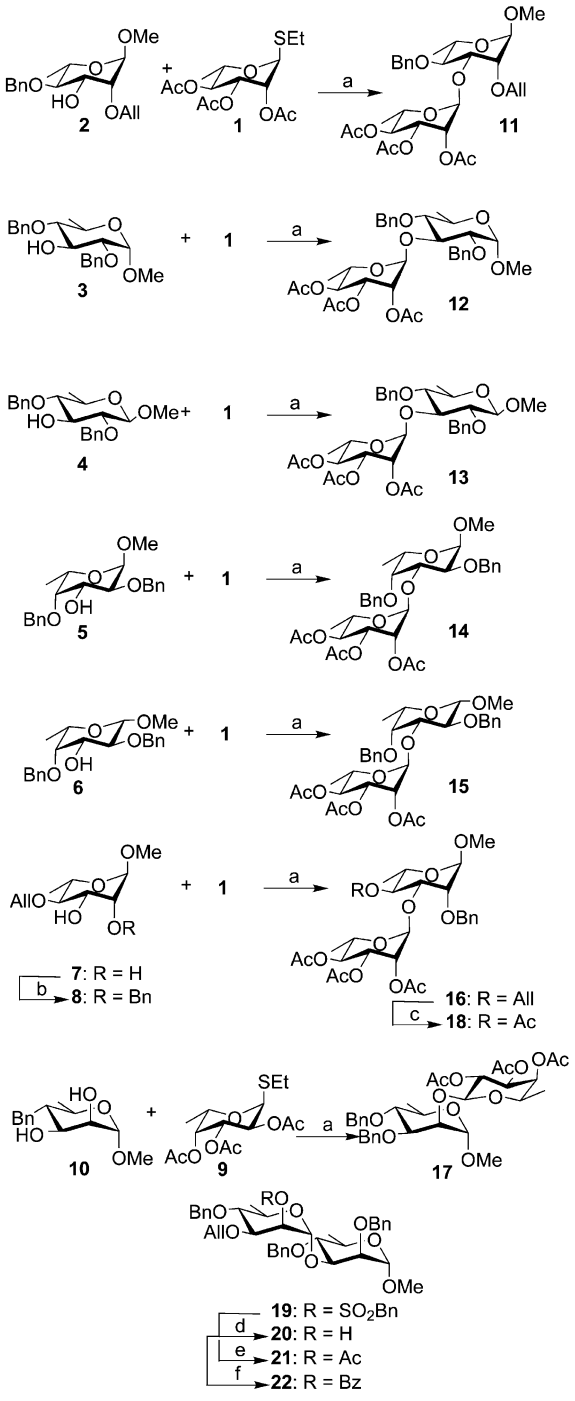
the synthesis of glycofuranose-containing oligosaccharides. These molecules have been the targets of much synthetic effort over the last 10 years[9] as they are present in some pathogenic microorganisms, such as the *Mycobacteria*,[10] *Trypanosoma*, and *Leishmania*[11] species. Therefore, the synthesis of 6-deoxyglycofuranose-containing structures could afford useful analogues and aid the understanding of the biosynthesis and the role of glycofuranose in microorganisms as well as the design of novel drugs for the treatment of diseases caused by such pathogenic species.

Results and Discussion

The first step of the work was the synthesis of a set of 6-deoxysugar disaccharide methyl glycosides. This was accomplished by the standard glycosylation reaction of L-rhamnose thioglycoside **1**[12] with the known glycosyl acceptors **2**,[13] **3**,[14] **4**,[14] **5**,[15] **6**,[15] and the novel acceptor **8** (obtained by phase-transfer benzylation of diol **7**)[16] as well as the reaction of L-fucose thioglycoside **9**[12] with glycosyl acceptor **10**[17] (Scheme 2). Glycosylations under the NIS/TfOH protocol proceeded in moderate to excellent yields to give the disaccharide methyl glycosides **11**–**17**. De-*O*-allylation of **16** with $PdCl_2$ and subsequent acetylation of the resulting alcohol afforded disaccharide **18**. Disaccharides **21** and **22** were obtained by de-*O*-benzenesulfonylation of **19**[18] with sodium amide and subsequent acetylation or benzoylation of the resulting alcohol **20**. Note that all the disaccharides were synthesized with a disarming ester protecting group at the 2-position of the non-pseudo-reducing unit in order to avoid the acetolytic cleavage of the glycosidic linkage.[8]

The next step of the work was the screening of the acetolysis conditions that would allow a kinetically controlled *endo* activation mechanism and at the same time be mild enough to allow the armed–disarmed effect in order to obtain selectively 1-*O*-Ac-furanoside disaccharide products. First, model compound **17** was treated with 10:10:1 (v/v/v) Ac_2O/AcOH/TFA.[19] By conducting the reaction at 70 °C,[8] 1-*O*-Ac-pyranoside derivative **23** was obtained in 95% yield, as expected through a thermodynamically controlled *exo* activation mechanism (Table 1, entry 1). By lowering the reaction temperature to 5 °C, no reaction was observed and the starting compound was recovered quantitatively even after 8 d (entry 2). Replacement of TFA with a stronger acid such as H_2SO_4 (100:1 Ac_2O/H_2SO_4 at 0 °C) led very rapidly, even at low temperatures, to an uncontrollable reaction, which produced a very complex mixture with derivative **24** as the main product (25% yield; entry 3). Finally, a slight modification[20] of the known procedure using freshly fused $ZnCl_2$ in 2:1 (v/v) Ac_2O/AcOH[21] (10 instead of 20 equiv. of $ZnCl_2$, 5 °C instead of room temp.; entry 4) afforded the desired 1-*O*-Ac-furanoside derivative **25** in good yield (76%) together with a small quantity of 1-*O*-Ac-pyranoside **23** (16%). The identity of **25** was confirmed by MALDI-TOF MS and NMR spectroscopy. The $^1J_{H,H}$ values ($J_{1,2}$ = 0.8 Hz, $J_{2,3}$ = 5.4 Hz, $J_{3,4}$ = 3.2 Hz, $J_{4,5}$ = 9.8 Hz) of the 1-*O*-acetylated residue were typical of a *manno*-configured furanose cycle[22] and the resonance at δ = 5.01 ppm for 5_A-H confirmed the acetylation of its geminal hydroxy group.

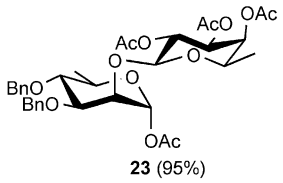
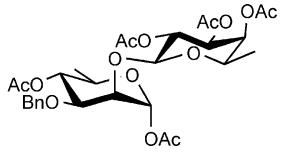
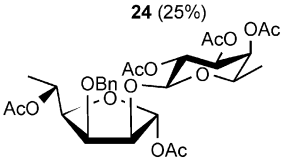
The synthesized disaccharides **11**–**16**, **18**, **21**, and **22** were subjected to acetolysis by the $ZnCl_2$ protocol described above as well as with the 10:10:1 (v/v/v) Ac_2O/AcOH/TFA procedure at 70 °C. The results are summarized in Table 2. As expected,[8] the latter protocol allowed in all cases the



Scheme 2. Synthesis of a set of 6-deoxysugar disaccharide methyl glycosides. Reagents and conditions: (a) NIS, TfOH, AW-300 MS (4 Å), CH_2Cl_2, –20 °C, **11**: 49%; **12**: 83%; **13**: 82%; **14**: 87%; **15**: 88%; **16**: 40%; **17**: 94%; (b) BnBr, KOH, TBAI, toluene, room temp., 72%; (c) i. $PdCl_2$, 1:1 (v/v) CH_2Cl_2/MeOH, room temp.; ii. Ac_2O, py, room temp., 75% (after two steps); (d) $NaNH_2$, DMF, 70 °C, 64%; (e) Ac_2O, py, room temp., 99%; (f) BzCl, py, room temp., 83%.

selective acetolysis of the glycosidic bond involving the monose unit protected with an arming benzyl group at the 2-*O* position through an *exo* activation mechanism: This

Table 1. Screening of acetolysis conditions on model compound **17**.

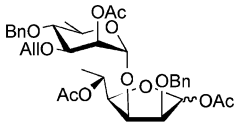
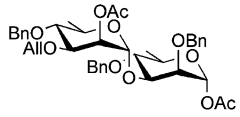
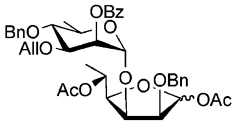
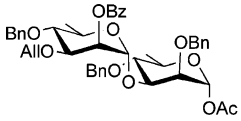
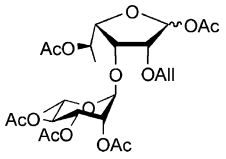
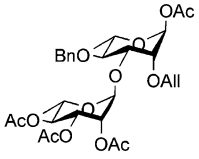
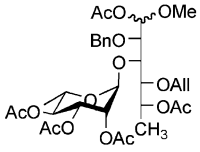
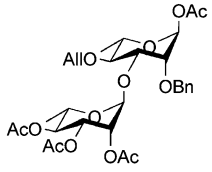
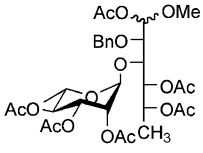
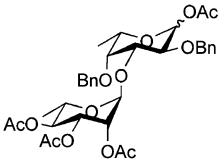
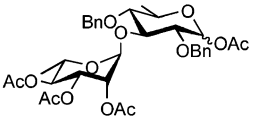
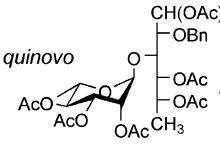
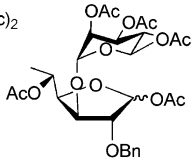
Entry	Protocol [a]	Product (% Yield)[b]
1	*A*	 **23** (95%)
2	*B*	no reaction
3	*C*	 **24** (25%)
4	*D*	 **25** (76%)

[a] Reaction conditions: ***A***: 10:10:1 (v/v/v) Ac_2O/AcOH/TFA, 70 °C; ***B***: 10:10:1 (v/v/v) Ac_2O/AcOH/TFA, 5 °C; ***C***: 100:1 (v/v) Ac_2O/H_2SO_4, 0 °C; ***D***: $ZnCl_2$ (10 equiv.), 2:1 (v/v) Ac_2O/AcOH, 5 °C. [b] Isolated yield.

afforded 1-*O*-Ac-pyranoside disaccharide derivatives in good to excellent yields regardless of the 6-deoxyhexose configuration (entries 1B–9B). In the same manner, acetolysis conducted by the $ZnCl_2$ protocol selectively involved the armed monose unit, but the products obtained depended strictly on the configuration of the 6-deoxyhexose sugar. In fact, with *rhamno*-configured units, acetolysis with $ZnCl_2$ always afforded the products under kinetic control: compounds **11**, **21**, and **22** were transformed into 1-*O*-Ac-furanoside disaccharide derivatives (**E**-like products) in good yields (entries 1A–3A), whereas compounds **16** and **18** gave predominantly the open-chain 1-*O*-acetyl-1-*O*-methyl acetals (**C**-like products) **32** and **34**, respectively (entries 4A and 5A). 1-*O*-Ac-pyranoside derivatives were isolated in reactions 1A–5A as minor products (15–25% yields). In the case of substrate **18**, the formation of the **C**-like derivative **34** could be supposedly due to the lower electron-donating effect of the acetyl-protecting group at the 4_A-*O* position of **16** as compared with the benzyl group at the same position in compounds **11**, **21**, and **22**. This avoids the conversion of **C**- into **E**-like products, whereas this transformation is rather easier in the presence of a benzyl group at the 4_A-*O* position. The preference for compound **16** to afford the **C**-like derivative **32** cannot be easily rationalized and therefore will be the object of future more detailed investigations.

In contrast to the rhamnose-rhamnose species, the acetolysis by $ZnCl_2$ of rhamnose-fucose methyl disaccharides **14** and **15** seems to proceed through an *exo* activation mechanism giving the thermodynamically controlled 1-*O*-Ac-pyranoside derivative **35** (entries 6A and 7A). The formation of traces of 1-*O*-Ac-furanosides could be detected

Table 2. Acetolysis of 6-deoxysugar disaccharide methyl glycosides.

Entry	Methyl disaccharide	Residue A configuration	Products (% yield)[a]	
			Protocol ***A***: $ZnCl_2$ (10 equiv.), Ac_2O, 5°C	Protocol ***B***: 1:1:0.1 v/v/v Ac_2O/AcOH/TFA
1	**21**	*rhamno*	 **26** (74%; α/β = 2.5:1)[b]	 **27** (71%)
2	**22**	*rhamno*	 **28** (75%; α/β = 2:1)[c]	 **29** (62%)
3	**11**	*rhamno*	 **30** (64%; α/β = 2:1)[b]	 **31** (55%)
4	**16**	*rhamno*	 **32** (77%; *dr* = 6:1)[b]	 **33** (73%)
5	**18**	*rhamno*	 **34** (63%; *dr* = 1.3:1)[b]	not determined
6	**14**	*fuco*	 **35** (82%; α/β = 3:1)[b] **35** (73%; α/β = 3:1)[b]	**35** (87%; α/β = 3:1)[b]
7	**15**	*fuco*		**35** (93%; α/β = 3:1)[b]
8	**12**	*quinovo*	 **36** (96%; α/β=6:1)[b]	**36** (83%; α/β = 6:1)[b]
9	**13**	*quinovo*	 **37** (43%)	 **38** (41%; α/β = 4:1)[b] **36** (56%; α/β = 4.5:1)[b]

[a] Isolated yield. [b] Anomeric ratio measured by ^1H NMR spectroscopy. [c] Anomeric ratio measured by isolation of the two anomers.

by MALDI-TOF MS analysis of the crude reaction mixtures, but such compounds were not isolable by chromatography due to their very low yield. The behavior of rhamnose-quinovose species **12** and **13** was strictly dependent on the configuration of the methyl aglycon: α-configured disaccharide **12** was acetolyzed by an *exo* activation mechanism, which furnished 1-*O*-Ac-pyranoside derivative **36** in almost quantitative yield (entry 8A), whereas β-derivative **13** gave open-chain derivative **37** and **E**-like derivative **38** in a 1:1 molar ratio (entry 9A). Interestingly, the low tendency of the *fuco*-configured moiety to undergo *endo* activation by the $ZnCl_2$ protocol fits well with the kinetic data reported for the acetolysis of sugars in the *galacto*, *gluco*, and *manno* series. First-order rate constants for *exo* activation of *galacto*-configured sugars are higher than for *gluco*-configured substrates.[2g] In addition, the first-order rate constant measured for *endo* activation of a *manno*-configured substrate is higher than for the *gluco* series.[2h] This can be summarized with a relative order for the tendency to give an acetolysis reaction through an *endo* anomeric kinetically controlled mechanism, that is: *manno* > *gluco* > *galacto*, whereas the *exo* anomeric activation follows a different order (*galacto* > *manno* > *gluco*), which has recently been demonstrated to be mainly dictated by the less electron-withdrawing power of axial over equatorial oxygens.[23] Therefore, when subjected to the $ZnCl_2$ protocol, *rhamno*-configured substrates **11**, **16**–**18**, **21**, and **22** gave predominantly kinetically controlled products, *fuco*-configured derivatives **14** and **15** preferred an *exo* activation mechanism even under $ZnCl_2$ conditions, whereas the results of the reactions of the two substrates of the *quinovo* series, **12** and **13**, were highly dependent on the anomeric configuration. The major tendency for the β-quinovose to give kinetically controlled products with respect to the α moiety can be ascribed, in general, to the greater nucleophilicity of the endocyclic oxygen in the β anomer. In fact, in contrast with the α anomer, the endocyclic oxygen is not involved in nσ* donation to the C1–O bond in the β anomer, whereas the exocyclic oxygen is involved in the *exo* anomeric effect in both anomers.[2e] Anyway, a precise and detailed understanding of the effect of the 6-deoxysugar configuration on the acetolysis reaction with $ZnCl_2$ will surely also require a future analysis of how Zn^{II}–sugar coordination influences the nucleophilicity of the *exo* and *endo* anomeric oxygen atoms.

Conclusions

A mild and selective acetolysis of 6-deoxysugar methyl disaccharides based on the armed–disarmed concept can be accomplished by two different protocols. The first one [10:10:1 (v/v/v) Ac_2O/AcOH/TFA at 70 °C] affords 1-*O*-acetylated disaccharides in the pyranose form as the products of a thermodynamically controlled mechanism with activation at the *exo* anomeric oxygen, whatever the configuration of the sugar,[8] whereas the second one [10 equiv. of $ZnCl_2$ in 2:1 (v/v) AcO/AcOH at 5 °C] affords kinetically controlled products (1-*O*-acetyl disaccharides with the pseudo-reducing unit in the furanose form and/or open-chain acyl acetals) with suitably protected *rhamno* and β-*quinovo* species. Further studies on the competition between the *exo* and *endo* activation mechanisms in the acetolysis of oligosaccharides as well as the application of these findings to the synthesis of biologically relevant oligosaccharides containing 6-deoxyhexose moieties are currently underway.

Experimental Section

General Methods: ^1H and ^{13}C NMR spectra were recorded with Varian XL-200 (^1H: 200 MHz; ^{13}C: 50 MHz), Varian Gemini-300 (^1H: 300 MHz; ^{13}C: 75 MHz), Bruker DRX-400 (^1H: 400 MHz; ^{13}C: 100 MHz), or Varian INOVA 500 (^1H: 500 MHz; ^{13}C: 125 MHz) instruments in $CDCl_3$ ($CHCl_3$ as internal standard: ^1H: C*H*Cl_3 at δ = 7.26 ppm; ^{13}C: *C*DCl_3 at δ = 77.0 ppm). Assignment of the proton chemical shifts was based on 1D HOHAHA experiments. Positive MALDI-TOF MS spectra were recorded with an Applied Biosystem Voyager DE-PRO MALDI-TOF mass spectrometer in the positive mode: compounds were dissolved in CH_3CN at a concentration of 1 mg/mL and one microliter of these solutions was mixed with one microliter of a 20 mg/mL solution of 2,5-dihydroxybenzoic acid in 7:3 CH_3CN/water. Optical rotations were measured with a JASCO *P*-1010 polarimeter. Analytical thin-layer chromatography (TLC) was performed on aluminium plates precoated with Merck Silica Gel 60 F_{254} as the adsorbent. The plates were developed with a 10% H_2SO_4 ethanolic solution and by heating to 130 °C. Column chromatography was performed on Merck Kieselgel 60 (63–200 mesh).

Methyl 4-*O*-Allyl-2-*O*-benzyl-α-L-rhamnopyranoside (8): Diol **7** (301 mg, 1.38 mmol) was dissolved in toluene (15 mL) and treated with TBAI (476 mg, 1.28 mmol), BnBr (328 μL, 2.75 mmol), and then KOH (690 mg, 10.8 mmol). The mixture was stirred at room temp. for 30 min and then treated with 1:1 AcOEt/water (25 mL) and stirred overnight. After that the organic layer was collected, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was subjected to column chromatography (7 to 10% ethyl acetate in petroleum ether) to afford **8** (310 mg, 72%) as a yellowish oil. $[a]_D$ = –9 (c = 0.8, CH_2Cl_2). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.34 (m, 5 H, Ar-H), 5.93 (m, 1 H, OCH_2CH=CH_2), 5.26 (dq, J_{vic} = 17.4, J_{gem} = $J_{long\text{-}range}$ = 1.4 Hz, 1 H, *trans* OCH_2CH=C*H*H), 5.13 (d, J_{vic} = 10.2, J_{gem} = $J_{long\text{-}range}$ = 1.4 Hz, 1 H, *cis* OCH_2CH=C*H*H), 4.73 (dt, J_{gem} = 11.6 Hz, 1 H, OC*H*HPh), 4.68 (d, $J_{1,2}$ = 1.4 Hz, 1 H, 1-H), 4.58 (d, J_{gem} = 11.6 Hz, 1 H, OC*H*HPh), 4.33 (ddt, J_{gem} = 12.4, J_{vic} = 5.6, $J_{long\text{-}range}$ = 1.4 Hz, 1 H, OC*H*HCH=CH_2), 4.13 (ddt, J_{gem} = 12.4, J_{vic} = 5.6, $J_{long\text{-}range}$ = 1.4 Hz, 1 H, OC*H*HCH=CH_2), 3.83 (br. m, 1 H, 3-H), 3.69 (dd, $J_{2,3}$ = 3.6, $J_{2,1}$ = 1.6 Hz, 1 H, 2-H), 3.59 (dq, $J_{5,4}$ = 9.2, $J_{5,6}$ = 6.2 Hz, 1 H, 5-H), 3.31 (s, 3 H, OCH_3), 3.18 (t, $J_{4,3}$ = $J_{4,5}$ = 9.2 Hz, 1 H, 4-H), 1.31 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 137.7 (C_{ipso}-Bn), 135.0 (OCH_2CH=CH_2), 128.5–127.8 (C-Ar), 116.8 (OCH_2CH=CH_2), 98.0 (C-1) 81.9, 78.5, 73.8, 73.0, 71.4, 67.0 (C-2, C-3, C-4, C-5, OCH_2Ph, OCH_2CH=CH_2), 54.6 (OCH_3), 18.0 (C-6) ppm. MS (MALDI-TOF): calcd. for $C_{17}H_{24}O_5$ $[M]^+$ 308.16; found 330.99 $[M + Na]^+$. $C_{17}H_{24}O_5$ (308.37): calcd. C 66.21, H 7.84; found C 66.00, H 7.70.

Typical Glycosylation Procedure: A mixture of the acceptor (173 μmol) and thioglycoside donor (222 μmol) was co-evaporated three times with toluene (2 mL). The residue was dried, mixed with NIS (282 μmol), and freshly activated with AW-300 molecular sieves (4 Å) under Ar, cooled to –20 °C, and suspended in CH_2Cl_2

(3.0 mL). A 0.57 M solution of TfOH in CH_2Cl_2 (100 μL, 57 μmol) was added. After 1 h stirring at –20 °C, the mixture was diluted with CH_2Cl_2 and washed with 1:1 (v/v) 1 M $NaHCO_3$/10% $Na_2S_2O_3$. The organic layer was collected, dried with anhydrous Na_2SO_4, filtered, concentrated, and purified by chromatography (ethyl acetate in toluene).

Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-allyl-4-*O*-benzyl-α-L-rhamnopyranoside (11): $[\alpha]_D$ = –50.6 (*c* = 1.8, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.30 (m, 5 H, Ar-H), 5.96 (m, 1 H, OCH_2CH=CH_2), 5.39–5.26 (m, 3 H, 2_B-H, 3_B-H, *trans* OCH_2CH=C*H*H), 5.23 (d, J_{vic} = 10.4 Hz, 1 H, *cis* OCH_2CH=C*H*H), 5.04 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1 H, 4_B-H), 5.03 (s, 1 H, 1_B-H), 4.80 (d, J_{gem} = 11.0 Hz, 1 H, OC*H*HPh), 4.65 (s, 1 H, 1_A-H), 4.62 (d, J_{gem} = 11.0 Hz, 1 H, OC*H*HPh), 4.22 (dd, J_{gem} = 13.0, J_{vic} = 5.6 Hz, 1 H, OC*H*HCH=CH_2), 4.07 (dd, J_{gem} = 13.0, J_{vic} = 5.6 Hz, OC*H*HCH=CH_2), 4.04–3.97 (m, 2 H, 3_A-H, 5_B-H), 3.65–3.56 (m, 3 H, 2_A-H, 4_A-H, 5_A-H), 3.32 (s, 3 H, OCH_3), 2.06, 2.05, 1.97 (3 s, 9 H, 3 $COCH_3$), 1.30 (d, $J_{6,5}$ = 5.7 Hz, 3 H, 6_A-H), 1.21 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 169.9–169.8 (3 CO), 138.1 (C_{ipso}-Bn), 134.9 (OCH_2CH=CH_2), 128.3–127.5 (C-Ar), 117.4 (OCH_2CH=CH_2), 99.1, 98.4 (C-1_A, C-1_B), 80.6, 78.3, 77.7, 75.3, 72.0, 71.1, 69.8, 69.1, 67.9, 66.8 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, OCH_2Ph, OCH_2CH=CH_2), 54.6 (OCH_3), 20.8–20.7 (3 CH_3CO), 17.9, 17.4 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{29}H_{40}O_{12}$ $[M]^+$ 580.25; found 603.00 $[M + Na]^+$. $C_{29}H_{40}O_{12}$ (580.62): calcd. C 59.99, H 6.94; found C 60.09, H 6.99.

Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-D-quinovopyranoside (12): $[\alpha]_D$ = –17.3 (*c* = 1.8, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.34–7.26 (m, 10 H, Ar-H), 5.38–5.27 (m, 3 H, 1_B-H, 2_B-H, 3_B-H), 4.97 (t, $J_{4,3}$ = $J_{4,5}$ = 10.0 Hz, 1 H, 4_B-H), 4.84 (d, J_{gem} = 11.2 Hz, 1 H, OC*H*HPh), 4.68 (d, J_{gem} = 12.0 Hz, 1 H, OC*H*HPh), 4.61 (d, J_{gem} = 11.2 Hz, 1 H, OC*H*HPh), 4.55 (d, J_{gem} = 12.0 Hz, 1 H, OC*H*HPh), 4.45 (d, $J_{1,2}$ = 3.4 Hz, 1 H, 1_A-H), 4.11 (t, $J_{3,4}$ = $J_{3,2}$ = 9.4 Hz, 1 H, 3_A-H), 4.02 (dq, $J_{5,4}$ = 10.0, $J_{5,6}$ = 6.2 Hz, 1 H, 5_B-H), 3.76 (dq, $J_{5,4}$ = 9.4, $J_{5,6}$ = 6.4 Hz, 1 H, 5_A-H), 3.51 (dd, $J_{2,3}$ = 9.4, $J_{2,1}$ = 3.4 Hz, 1 H, 2_A-H), 3.30 (s, 3 H, OCH_3), 3.09 (t, $J_{4,3}$ = $J_{4,5}$ = 9.4 Hz, 1 H, 4_A-H), 2.07, 1.99, 1.91 (3 s, 9 H, 3 CH_3CO), 1.27 (d, $J_{6,5}$ = 6.4 Hz, 3 H, 6_A-H), 0.88 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.1, 169.9, 169.8 (3 CO), 137.9, 137.6 (2 C_{ipso}-Bn), 128.4–127.2 (C-Ar), 97.6, 97.1 (C-1_A, C-1_B), 82.4, 81.0, 75.6, 74.9, 72.7, 70.9, 69.7, 69.2, 66.5, 66.1 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 2 OCH_2Ph), 54.9 (OCH_3), 20.7–20.6 (3 CH_3CO), 17.8, 16.9 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{33}H_{42}O_{12}$ $[M]^+$ 630.27; found 653.11 $[M + Na]^+$. $C_{33}H_{42}O_{12}$ (630.68): calcd. C 62.85, H 6.71; found C 62.59, H 6.59.

Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-D-quinovopyranoside (13): $[\alpha]_D$ = –50.3 (*c* = 3.0, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.33–7.26 (m, 10 H, Ar-H), 5.38 (d, $J_{1,2}$ = 1.0 Hz, 1 H, 1_B-H), 5.32–5.23 (m, 2 H, 2_B-H, 3_B-H), 4.98–4.81 (m, 3 H, 4_B-H, 2 OC*H*HPh), 4.70 (d, J_{gem} = 11.4 Hz, 1 H, OC*H*HPh), 4.56 (d, J_{gem} = 11.8 Hz, 1 H, OC*H*HPh), 4.27 (d, $J_{1,2}$ = 7.8 Hz, 1 H, 1_A-H), 4.03 (dq, $J_{5,4}$ = 10.0, $J_{5,6}$ = 6.2 Hz, 1 H, 5_B-H), 3.83 (t, $J_{3,4}$ = $J_{3,2}$ = 9.2 Hz, 1 H, 4_A-H), 3.54 (s, 3 H, OCH_3), 3.48–3.38 (m, 2 H, 2_A-H, 5_A-H), 3.15 (t, $J_{3,2}$ = $J_{3,4}$ = 9.2 Hz, 1 H, 3_A-H), 2.03, 1.97, 1.90 (3 s, 9 H, 3 CH_3CO), 1.37 (d, $J_{6,5}$ = 6.0 Hz, 3 H, 6_A-H), 0.87 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.1, 169.8, 169.7 (3 CO), 138.0, 137.7 (2 C_{ipso}-Bn), 128.2–127.3 (C-Ar), 104.2, 97.2 (C-1_A, C-1_B), 82.9, 82.0, 76.3, 75.2, 74.3, 71.1, 70.8, 69.4, 69.1, 66.1 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 2 OCH_2Ph), 56.9 (OCH_3), 20.7–20.6 (3 CH_3CO), 17.8, 16.9 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{33}H_{42}O_{12}$ $[M]^+$ 630.27; found 652.89 $[M + Na]^+$. $C_{33}H_{42}O_{12}$ (630.68): calcd. C 62.85, H 6.71; found C 62.70, H 6.67.

Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-D-fucopyranoside (14): $[\alpha]_D$ = –71.0 (*c* = 2.1, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.28 (m, 10 H, Ar-H), 5.46 (dd, $J_{3,4}$ = 9.9, $J_{3,4}$ = 3.3 Hz, 1 H, 3_B-H), 5.18 (dd, $J_{2,3}$ = 3.3, $J_{2,1}$ = 1.8 Hz, 1 H, 2_B-H), 5.08 (t, $J_{4,3}$ = $J_{4,5}$ = 9.9 Hz, 1 H, 4_B-H), 5.01 (s, 1 H, 1_B-H), 4.90 (d, J_{gem} = 11.7 Hz, 1 H, OC*H*HPh), 4.79 (d, J_{gem} = 12.0 Hz, 1 H, OC*H*HPh), 4.67 (m, 2 H, 1_A-H, OC*H*HPh), 4.59 (d, J_{gem} = 12.0 Hz, 1 H, OC*H*HPh), 4.20 (dq, $J_{5,4}$ = 9.9, $J_{5,6}$ = 6.0 Hz, 1 H, 5_B-H), 4.15 (dd, $J_{3,2}$ = 10.2, $J_{3,4}$ = 2.7 Hz, 1 H, 3_A-H), 3.98 (dd, $J_{2,3}$ = 10.2, $J_{2,1}$ = 3.6 Hz, 1 H, 2_A-H), 3.84 (q, $J_{5,6}$ = 6.0 Hz, 1 H, 5_A-H), 3.68 (d, $J_{3,4}$ = 2.7 Hz, 1 H, 4_A-H), 3.35 (s, 3 H, OCH_3), 2.16, 2.02, 2.00 (3 s, 9 H, 3 CH_3CO), 1.16 (d, $J_{6,5}$ = 6.0 Hz, 3 H, 6_A-H), 1.12 (d, $J_{6,5}$ = 6.0 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.4, 170.0, 169.9 (3 CO), 138.3, 138.2 (2 C_{ipso}-Bn), 129.0–127.7 (C-Ar), 98.4, 93.9 (C-1_A, C-1_B), 75.5, 74.6, 74.5, 74.4, 73.3, 71.1, 70.3, 68.9, 66.6, 65.8 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 2 OCH_2Ph), 55.3 (OCH_3), 20.9, 20.7, 20.6 (3 CH_3CO), 17.5, 16.7 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{33}H_{42}O_{12}$ $[M]^+$ 630.27; found 653.01 $[M + Na]^+$. $C_{33}H_{42}O_{12}$ (630.68): calcd. C 62.85, H 6.71; found C 62.82, H 6.72.

Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-β-D-fucopyranoside (15): $[\alpha]_D$ = –61.0 (*c* = 2.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.27 (m, 10 H, Ar-H), 5.40 (dd, $J_{3,4}$ = 9.9, $J_{3,4}$ = 3.3 Hz, 1 H, 3_B-H), 5.18 (dd, $J_{2,3}$ = 3.3, $J_{2,1}$ = 1.8 Hz, 1 H, 2_B-H), 5.03 (t, $J_{4,3}$ = $J_{4,5}$ = 9.9 Hz, 1 H, 4_B-H), 4.96 (s, 1 H, 1_B-H), 4.93 (d, J_{gem} = 10.5 Hz, 1 H, OC*H*HPh), 4.91 (d, J_{gem} = 11.4 Hz, 1 H, OC*H*HPh), 4.71 (d, J_{gem} = 10.5 Hz, 1 H, OC*H*HPh), 4.60 (d, J_{gem} = 11.4 Hz, 1 H, OC*H*HPh), 4.26 (d, $J_{1,2}$ = 7.2 Hz, 1 H, 1_A-H), 4.16 (dq, $J_{5,4}$ = 9.9, $J_{5,6}$ = 6.0 Hz, 1 H, 5_B-H), 3.74 (m, 2 H, 2_A-H, 3_A-H), 3.56 (s, 1 H, 4_A-H), 3.55 (s, 3 H, OCH_3), 3.48 (q, $J_{5,6}$ = 6.3 Hz, 1 H, 5_A-H), 2.15, 2.01, 2.00 (3 s, 9 H, 3 CH_3CO), 1.23 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_A-H), 0.96 (d, $J_{6,5}$ = 6.0 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.2, 169.9, 169.7 (3 CO), 138.6, 138.2 (2 C_{ipso}-Bn), 129.0–127.4 (C-Ar), 105.0, 94.0 (C-1_A, C-1_B), 77.7, 77.3, 75.3, 75.1, 75.0, 71.6, 70.4, 70.2, 69.0, 66.4 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 2 OCH_2Ph), 56.9 (OCH_3), 20.9–20.8 (3 CH_3CO), 17.2, 17.0 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{33}H_{42}O_{12}$ $[M]^+$ 630.27; found 653.15 $[M + Na]^+$. $C_{33}H_{42}O_{12}$ (630.68): calcd. C 62.85, H 6.71; found C 62.75, H 6.62.

Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-allyl-2-*O*-benzyl-α-L-rhamnopyranoside (16): $[\alpha]_D$ = –40.1 (*c* = 2.0, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.28 (m, 5 H, Ar-H), 5.87 (m, 1 H, OCH_2CH=CH_2), 5.34 (m, 2 H, 1_B-H, 3_B-H), 5.24 (d, J_{vic} = 16.8 Hz, 1 H, OCH_2CH=C*H*H), 5.10 (d, J_{vic} = 9.9 Hz, 1 H, OCH_2CH=C*H*H), 5.01 (m, 2 H, 2_B-H, 4_B-H), 4.75 (d, J_{gem} = 12.3 Hz, 1 H, OC*H*HPh), 4.66 (br. s, 1 H, 1_A-H), 4.64 (d, J_{gem} = 12.3 Hz, 1 H, OC*H*HPh), 4.25 (dd, J_{gem} = 12.2, J_{vic} = 5.7 Hz, 1 H, OC*H*HCH=CH_2), 4.10 (dd, J_{gem} = 12.4, J_{vic} = 5.7 Hz, 1 H, OC*H*HCH=CH_2), 3.94 (dd, $J_{3,4}$ = 9.3, $J_{3,2}$ = 3.3 Hz, 1 H, 3_A-H), 3.80 (dq, $J_{5,4}$ = 9.6, $J_{5,6}$ = 6.3 Hz, 1 H, 5_B-H), 3.65 (dd, $J_{2,3}$ = 3.0, $J_{2,1}$ = 1.8 Hz, 1 H, 2_A-H), 3.58 (dq, $J_{5,4}$ = 9.6, $J_{5,6}$ = 6.3 Hz, 1 H, 5_A-H), 3.46 (t, $J_{4,3}$ = $J_{4,5}$ = 9.6 Hz, 1 H, 4_A-H), 3.30 (s, 3 H, OCH_3), 2.10, 2.02, 1.97 (3 s, 9 H, 3 CH_3CO), 1.29 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_A-H), 1.09 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 169.7 (3 CO), 138.0 (C_{ipso}-Bn), 134.6 (OCH_2CH=CH_2), 128.3–127.5 (C-Ar), 116.7 (OCH_2CH=CH_2), 99.2, 98.3 (C-1_A, C-1_B), 80.4, 78.3, 77.7, 74.1, 72.4, 71.1, 69.8, 69.0,

68.0, 66.8 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, O*C*H_2Ph, O*C*H_2CH=CH_2), 54.6 (OCH_3), 20.7–20.6 (3 *C*H_3CO), 17.8, 17.4 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{29}H_{40}O_{12}$ $[M]^+$ 580.25; found 603.18 $[M + Na]^+$. $C_{29}H_{40}O_{12}$ (580.62): calcd. C 59.99, H 6.94; found C 59.75, H 6.82.

Methyl 2,3,4-Tri-*O*-acetyl-β-L-fucopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-D-rhamnopyranoside (17): $[\alpha]_D$ = +32.0 (*c* = 1.8, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.27 (m, 10 H, Ar-H), 5.33 (dd, $J_{2,3}$ = 10.2, $J_{2,1}$ = 8.4 Hz, 1 H, 2_B-H), 5.23 (d, $J_{4,3}$ = 3.3 Hz, 1 H, 4_B-H), 5.01 (dd, $J_{3,2}$ = 10.2, $J_{3,4}$ = 3.3 Hz, 1 H, 3_B-H), 4.90–4.74 (m, 4 H, 1_B-H, 3 OC*H*HPh), 4.54 (d, J_{gem} = 10.8 Hz, 1 H, OC*H*HPh), 4.50 (br. s, 1 H, 1_A-H), 4.05 (dd, $J_{3,4}$ = 8.4, $J_{3,2}$ = 2.1 Hz, 1 H, 3_A-H), 3.86 (br. s, 1 H, 2_A-H), 3.79 (q, $J_{5,6}$ = 6.3 Hz, 1 H, 5_B-H), 3.60 (m, 2 H, 4_A-H, 5_A-H), 3.26 (s, 3 H, OCH_3), 2.18, 1.97, 1.81 (3 s, 9 H, 3 CH_3CO), 1.27 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_A-H), 1.19 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.4, 170.0, 169.3 (3 CO), 138.8, 138.2 (2 C_{ipso}-Bn), 128.4–127.3 (C-Ar), 101.6, 99.7 (C-1_A, C-1_B), 80.2, 80.1, 77.5, 74.8, 73.4, 71.6, 70.4, 69.6, 69.0, 67.7 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 2 O*C*H_2Ph), 54.4 (OCH_3), 20.6–20.5 (3 *C*H_3CO), 17.9, 16.1 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{33}H_{42}O_{12}$ $[M]^+$ 630.27; found 653.09 $[M + Na]^+$. $C_{33}H_{42}O_{12}$ (630.68): calcd. C 62.85, H 6.71; found C 62.77, H 6.65.

Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-acetyl-2-*O*-benzyl-α-L-rhamnopyranoside (18): Compound **16** (30.4 mg, 52.2 μmol) was dissolved in 1:1 (v/v) CH_2Cl_2/MeOH (0.6 mL) and then treated with $PdCl_2$ (3.7 mg, 20.9 μmol). The mixture was vigorously stirred at room temp. for 2 h and then filtered through a Celite pad, diluted with CH_2Cl_2, and washed with water. The organic phase was collected, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was dissolved in 1:1 (v/v) Ac_2O/py (1.0 mL) and stirred at room temp. overnight. The solution was then concentrated. The residue was diluted with CH_2Cl_2 and the resulting solution washed with 1 M HCl. The organic phase was collected, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by chromatography (10 to 50% ethyl acetate in petroleum ether) to give **18** (22.9 mg, 75%) as a yellowish oil. $[\alpha]_D$ = –34.7 (*c* = 1.1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.37 (m, 5 H, Ar-H), 5.30 (dd, $J_{3,4}$ = 10.0, $J_{3,2}$ = 3.2 Hz, 1 H, 3_B-H), 5.21 (t, $J_{4,3}$ = $J_{4,5}$ = 9.8 Hz, 1 H, 4_A-H), 5.12 (dd, $J_{2,3}$ = 3.2, $J_{2,1}$ = 2.0 Hz, 1 H, 2_B-H), 5.02 (t, $J_{4,3}$ = $J_{4,5}$ = 10.0 Hz, 1 H, 4_B-H), 4.89 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1_B-H), 4.74–4.68 (m, 3 H, 1_A-H, O*C*H_2Ph), 4.00 (dd, $J_{3,4}$ = 9.8, $J_{3,2}$ = 3.2 Hz, 1 H, 3_A-H), 3.82 (dq, $J_{5,4}$ = 9.8, $J_{5,6}$ = 6.2 Hz, 1 H, 5_A-H), 3.70 (m, 2 H, 2_A-H, 5_B-H), 3.33 (s, 3 H, OCH_3), 2.13, 2.12, 2.03, 1.99 (4 s, 12 H, 4 CH_3CO), 1.20 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_B-H), 1.07 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_A-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.2, 170.1, 170.0, 169.6 (4 CO), 138.0 (C_{ipso}-Bn), 128.5–127.6 (C-Ar), 98.6, 98.5 (C-1_A, C-1_B), 76.9, 72.7, 72.6, 71.2, 71.1, 70.2, 68.6, 66.9, 66.8 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, O*C*H_2Ph), 54.9 (OCH_3), 20.9–20.7 (4 *C*H_3CO), 17.6, 17.4 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{28}H_{38}O_{13}$ $[M]^+$ 582.23; found 605.09 $[M + Na]^+$. $C_{28}H_{38}O_{13}$ (582.59): calcd. C 57.72, H 6.57; found C 57.57, H 6.62.

Methyl 3-*O*-Allyl-4-*O*-benzyl-α-D-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-D-rhamnopyranoside (20): Compound **19** (250 mg, 317 μmol) was dissolved in dry DMF (5.0 mL) under Ar and then $NaNH_2$ (542 mg, 13.9 mmol) was added. The mixture was stirred at 70 °C for 48 h and then diluted with MeOH. AcOH was added dropwise until the pH was neutral. The solution was concentrated and the residue was dissolved in CH_2Cl_2 and washed with 1 M $NaHCO_3$ and brine. The organic layer was collected, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by chromatography (8 to 16% ethyl acetate in toluene) to afford **20** (129 mg, 64%) as a yellowish oil. $[\alpha]_D$ = +26.5 (*c* = 2.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.19 (m, 15 H, Ar-H), 5.91 (m, 1 H, OCH_2C*H*=CH_2), 5.26 (dd, J_{vic} = 17.2, J_{gem} = 1.6 Hz, 1 H, *trans* OCH_2CH=C*H*H), 5.16–5.13 (m, 2 H, *cis* OCH_2CH=C*H*H, 1_B-H), 4.87 (d, J_{gem} = 11.0 Hz, 1 H, OC*H*HPh), 4.78 (d, J_{gem} = 11.0 Hz, 1 H, OC*H*HPh), 4.70 (s, 2 H, OCH_2Ph), 4.64 (s, 1 H, 1_A-H), 4.63 (d, J_{gem} = 11.0 Hz, 1 H, OC*H*HPh), 4.62 (d, J_{gem} = 11.6 Hz, 1 H, OC*H*HPh), 4.07 (dd, J_{gem} = 11.8, J_{vic} = 6.6 Hz, 1 H, OC*H*HCH=CH_2), 4.05 (dd, J_{gem} = 11.8, J_{vic} = 6.6 Hz, 1 H, OC*H*HCH=CH_2), 4.00 (d, $J_{2,1}$ = 1.3 Hz, 1 H, 2_B-H), 3.80 (m, 1 H, 5_B-H), 3.75–3.61 (m, 3 H, 3_A-H, 3_B-H, 2_A-H), 3.66 (m, 1 H, 5_A-H), 3.58 (t, $J_{4,5}$ = $J_{4,3}$ = 9.3 Hz, 1 H, 4_B-H), 3.42 (t, $J_{4,5}$ = $J_{4,3}$ = 9.3 Hz, 1 H, 4_A-H), 3.31 (s, 3 H, OCH_3), 1.32 (d, $J_{6,5}$ = 5.8 Hz, 3 H, 6_A-H), 1.25 (d, $J_{6,5}$ = 6.0 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 138.7, 138.2, 138.1 (3 C_{ipso}-Bn), 134.6 (OCH_2*C*H=CH_2), 128.4–127.8 (C-Ar), 117.2 (OCH_2CH=*C*H_2), 100.8, 98.6 (C-1_A, C-1_B), 81.1, 79.9, 79.5, 77.3, 76.7, 75.3, 75.1, 72.7, 70.9, 69.0, 67.9, 67.8 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 3 O*C*H_2Ph, O*C*H_2CH=CH_2), 54.9 (OCH_3), 18.2 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{37}H_{46}O_9$ $[M]^+$ 634.31; found 657.33 $[M + Na]^+$. $C_{37}H_{46}O_9$ (634.76): calcd. C 70.01, H 7.30; found C 70.18, H 7.45.

Methyl 2-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-α-D-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-D-rhamnopyranoside (21): Alcohol **20** (67.0 mg, 106 μmol) was dissolved in 1:1 Ac_2O/pyridine (1.5 mL). The solution was stirred overnight at room temp. and then co-evaporated four times with toluene. The residue was dissolved in CH_2Cl_2 and washed with water. The organic layer was collected, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by chromatography (6% ethyl acetate in toluene) to give **21** (71.0 mg, 99%) as a colorless oil. $[\alpha]_D$ = +28.2 (*c* = 0.9, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.26 (m, 15 H, Ar-H), 5.87 (m, 1 H, OCH_2C*H*=CH_2), 5.44 (br. s, 1 H, 2_B-H), 5.25 (d, J_{vic} = 17.4 Hz, 1 H, *trans* OCH_2CH=CHH), 5.13–5.10 (m, 2 H, *cis* OCH_2CH=CHH, 1_A-H), 4.94 (d, J_{gem} = 11.0 Hz, 1 H, OC*H*HPh), 4.83 (d, J_{gem} = 11.0 Hz, 1 H, OC*H*HPh), 4.72 (s, 2 H, OCH_2Ph), 4.66–4.61 (m, 3 H, 2 OC*H*HPh, 1_B-H), 4.16–4.06 (m, 2 H, OC*H*HCH=CH_2, 3_A-H), 3.98 (dd, J_{gem} = 12.0, J_{vic} = 5.4 Hz, 1 H, OC*H*HCH=CH_2), 3.88 (dd, $J_{3,2}$ = 3.3, $J_{3,4}$ = 9.3 Hz, 1 H, 3_B-H), 3.85 (m, 1 H, 5_B-H), 3.71 (br. s, 1 H, 2_A-H), 3.65 (t, $J_{4,5}$ = $J_{4,3}$ = 9.0 Hz, 1 H, 4_B-H), 3.41 (m, 1 H, 5_A-H), 3.36 (t, $J_{4,5}$ = $J_{4,3}$ = 9.6 Hz, 1 H, 4_A-H), 3.31 (s, 3 H, OCH_3), 2.09 (s, 3 H, $COCH_3$), 1.32 (d, $J_{6,5}$ = 5.4 Hz, 3 H, 6_A-H), 1.29 (d, $J_{6,5}$ = 5.7 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 169.9 (CO), 138.8, 138.1, 138.0 (3 C_{ipso}-Bn), 134.6 (OCH_2*C*H=CH_2), 128.4–127.5 (C-Ar), 117.1 (OCH_2CH=*C*H_2), 99.2, 98.5 (C-1_A, C-1_B), 81.0, 80.9, 79.9, 77.7, 77.4, 77.0, 75.2, 72.8, 70.6, 69.1, 68.2, 67.9 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 3 O*C*H_2Ph, O*C*H_2CH=CH_2), 54.6 (OCH_3), 20.9 (*C*H_3CO), 18.0, 17.9 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{39}H_{48}O_{10}$ $[M]^+$ 676.32; found 699.29 $[M + Na]^+$. $C_{39}H_{48}O_{10}$ (676.79): calcd. C 69.21, H 7.15; found C 69.15, H 7.09.

Methyl 3-*O*-Allyl-2-*O*-benzoyl-4-*O*-benzyl-α-D-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-D-rhamnopyranoside (22): Alcohol **21** (86.3 mg, 136 μmol) was dissolved in pyridine (1.0 mL), treated with BzCl (40 μL, 345 μmol), and stirred overnight at room temp. The mixture was diluted with CH_2Cl_2 and washed with 1 M HCl and water. The organic layer was collected, dried with anhydrous Na_2SO_4, filtered, concentrated, and purified by chromatography (6 to 9% ethyl acetate in toluene) to give **22** (83.0 mg, 83%) as a colorless oil. $[\alpha]_D$ = –0.8 (*c* = 0.9, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.06–7.24 (m, 20 H, Ar-H), 5.88 (m, 1 H,

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$OCH_2CH{=}CH_2$), 5.71 (dd, $J_{2,1}$ = 1.6, $J_{2,3}$ = 3.0 Hz, 1 H, 2_B-H), 5.24 (dd, J_{vic} = 15.6, J_{gem} = 1.8 Hz, 1 H, *trans* $OCH_2CH{=}CHH$), 5.26 (br. s, 1 H, 1_B-H), 5.09 (dd, J_{vic} = 10.2, J_{gem} = 1.8 Hz, 1 H, *cis* $OCH_2CH{=}CHH$), 4.98 (d, J_{gem} = 11.0 Hz, 1 H, $OCHHPh$), 4.92 (d, J_{gem} = 11.0 Hz, 1 H, $OCHHPh$), 4.77 (s, 2 H, $OCHHPh$), 4.67–4.62 (m, 3 H, 2 $OCHHPh$, 1_A-H), 4.22 (dd, J_{gem} = 11.5, J_{vic} = 5.2 Hz, 1 H, $OCHHCH{=}CH_2$), 4.16–3.88 (m, 4 H, $OCHHCH{=}CH_2$, 3_A-H, 5_A-H, 5_B-H), 3.77 (dd, $J_{2,1}$ = 2.0, $J_{2,3}$ = 3.0 Hz, 1 H, 2_A-H), 3.71–3.67 (m, 2 H, 3_B-H, 4_A-H), 3.54 (t, $J_{4,5}$ = $J_{4,3}$ = 9.2 Hz, 1 H, 4_B-H), 3.33 (s, 3 H, OCH_3), 1.36–1.30 (m, 6 H, 6_A-H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 165.4 (CO), 138.7, 138.1, 138.0 (3 C_{ipso}-Bn), 134.7 ($OCH_2CH{=}CH_2$), 133.0 (C_{ipso}-Bz), 129.8–127.5 (C-Ar), 117.0 ($OCH_2CH{=}CH_2$), 99.2, 98.6 (C-1_A, C-1_B), 80.9, 80.0, 77.7, 77.5, 75.3, 75.1, 72.8, 70.5, 69.6, 69.5, 68.3, 67.9 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 3 OCH_2Ph, $OCH_2CH{=}CH_2$), 54.6 (OCH_3), 18.2, 17.9 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{44}H_{50}O_{10}$ $[M]^+$ 738.34; found 761.39 $[M + Na]^+$. $C_{44}H_{50}O_{10}$ (738.86): calcd. C 71.52, H 6.82; found C 71.45, H 6.77.

Typical Acetolysis Procedure ($ZnCl_2$ Protocol): Methyl glycoside (66 μmol) was dissolved in a 2:1 (v/v) Ac_2O/AcOH mixture (1.0 mL), cooled to 5 °C, and then treated with freshly fused $ZnCl_2$ (660 μmol). The solution was stirred at 5 °C until TLC (ethyl acetate in toluene) showed the disappearance of the starting material. The solution was then diluted with CH_2Cl_2 and washed with 1 M $NaHCO_3$ and then collected, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by chromatography (ethyl acetate in toluene).

Typical Acetolysis Procedure (TFA Protocol): Methyl glycoside (66 μmol) was dissolved in a 1:1:0.1 (v/v/v) Ac_2O/AcOH/TFA mixture (2.1 mL). The solution was stirred at 70 °C until TLC (ethyl acetate in toluene) showed disappearance of the starting material. The reaction was quenched by cooling to room temp. The mixture was diluted with CH_2Cl_2 and washed with 1 M $NaHCO_3$. The organic layer was collected, dried with anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by chromatography (ethyl acetate in toluene).

Acetyl 2,3,4-Tri-*O*-acetyl-β-L-fucopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-D-rhamnopyranoside (23): $[\alpha]_D$ = +27.5 (c = 1.9, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.44–7.16 (m, 10 H, Ar-H), 5.98 (d, $J_{1,2}$ = 2.0 Hz, 1 H, 1_A-H), 5.35 (dd, $J_{2,3}$ = 10.2, $J_{2,1}$ = 8.0 Hz, 1 H, 2_B-H), 5.25 (d, $J_{4,3}$ = 3.4 Hz, 1 H, 4_B-H), 5.03 (dd, $J_{3,2}$ = 10.2, $J_{3,4}$ = 3.4 Hz, 1 H, 3_B-H), 4.92–4.74 (m, 4 H, 1_B-H, 3 $OCHHPh$), 4.57 (d, J_{gem} = 10.6 Hz, 1 H, $OCHHPh$), 4.11 (dd, $J_{3,4}$ = 9.0, $J_{3,2}$ = 3.0 Hz, 1 H, 3_A-H), 3.87–3.73 (m, 3 H, 2_A-H, 5_A-H, 5_B-H), 3.65 (t, $J_{4,3}$ = $J_{4,5}$ = 9.4 Hz, 1 H, 4_A-H), 2.20, 2.05, 2.00, 1.89 (4 s, 12 H, 4 CH_3CO), 1.30 (d, $J_{6,5}$ = 5.7 Hz, 3 H, 6_A-H), 1.18 (d, $J_{6,5}$ = 6.6 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.2, 170.1, 168.8, 168.7 (4 CO), 138.3, 138.1 (2 C_{ipso}-Bn), 129.0–127.6 (C-Ar), 101.4 (C-1_B), 92.4 (C-1_A), 79.7, 78.8, 75.1, 73.5, 71.4, 70.4, 70.3, 69.5, 69.1 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, OCH_2Ph), 21.1, 20.9, 20.6, 20.5 (4 CH_3CO), 17.8, 16.0 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{34}H_{42}O_{13}$ $[M]^+$ 658.26; found 680.89 $[M + Na]^+$. $C_{34}H_{42}O_{13}$ (658.69): calcd. C 62.00, H 6.43; found C 61.86, H 6.32.

Acetyl 2,3,4-Tri-*O*-acetyl-β-L-fucopyranosyl-(1→2)-4-*O*-acetyl-3-*O*-benzyl-α-D-rhamnopyranoside (24): $[\alpha]_D$ = +30 (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.27 (m, 5 H, Ar-H), 6.01 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1_A-H), 5.27–5.21 (m, 3 H, 2_B-H, 4_A-H, 4_B-H), 4.99 (dd, $J_{3,2}$ = 10.5, $J_{3,4}$ = 3.5 Hz, 1 H, 3_B-H), 4.87 (d, J_{gem} = 12.1 Hz, 1 H, $OCHHPh$), 4.75 (d, J_{gem} = 12.1 Hz, 1 H, $OCHHPh$), 4.63 (d, $J_{1,2}$ = 8.0 Hz, 1 H, 1_B-H), 4.04 (dd, $J_{3,4}$ = 10.0, $J_{3,2}$ = 3.1 Hz, 1 H, 3_A-H), 3.82–3.75 (m, 3 H, 2_A-H, 5_A-H, 5_B-H), 2.19, 2.11, 2.08, 2.06, 1.99 (5 s, 15 H, 4 CH_3CO), 1.18 (d, $J_{6,5}$ = 6.0 Hz, 6 H, 6_A-H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.6, 170.3, 169.3, 169.2, 168.6 (5 CO), 138.1 (C_{ipso}-Bn), 129.0–127.6 (C-Ar), 101.6 (C-1_B), 92.6 (C-1_B), 76.2, 76.1, 73.6, 72.8, 71.2, 70.3, 69.3, 69.2, 68.9 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, OCH_2Ph), 21.1, 21.0, 20.7, 20.6, 20.5 (5 CH_3CO), 17.5, 16.1 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{29}H_{38}O_{14}$ $[M]^+$ 610.23; found 632.99 $[M + Na]^+$. $C_{29}H_{38}O_{14}$ (610.60): calcd. C 57.04, H 6.27; found C 56.96, H 6.20.

Acetyl 2,3,4-Tri-*O*-acetyl-β-L-fucopyranosyl-(1→2)-5-*O*-acetyl-3-*O*-benzyl-α-D-rhamnofuranoside (25): $[\alpha]_D$ = +24.6 (c = 1.1, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.36 (m, 5 H, Ar-H), 6.20 (d, $J_{1,2}$ = 0.8 Hz, 1 H, 1_A-H), 5.31 (dd, $J_{2,3}$ = 10.6, $J_{2,1}$ = 7.8 Hz, 1 H, 2_B-H), 5.25 (d, $J_{4,3}$ = 3.4 Hz, 1 H, 4_B-H), 5.04–4.97 (m, 2 H, 3_B-H, 5_A-H), 4.84 (d, J_{gem} = 11.8 Hz, 1 H, $OCHHPh$), 4.64–4.54 (m, 3 H, 1_B-H, 3_A-H, $OCHHPh$), 4.38 (dd, $J_{4,5}$ = 9.8, $J_{4,3}$ = 3.2 Hz, 1 H, 4_A-H), 3.92 (dd, $J_{2,3}$ = 5.4, $J_{2,1}$ = 0.8 Hz, 1 H, 2_A-H), 3.84 (q, $J_{5,6}$ = 6.2 Hz, 1 H, 5_B-H), 2.14, 2.10, 2.06, 2.04, 1.99 (5 s, 15 H, 5 CH_3CO), 1.27 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_A-H), 1.21 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.4, 170.2, 170.1, 170.0, 169.3 (5 CO), 138.1 (C_{ipso}-Bn), 129.0–125.2 (C-Ar), 101.3, 99.4 (C-1_A, C-1_B), 81.2, 81.0, 76.7, 73.0, 71.3, 70.1, 70.0, 69.5, 68.7 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, OCH_2Ph), 21.4, 21.2, 20.6, 20.5, 20.4 (5 CH_3CO), 16.1, 14.7 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{29}H_{38}O_{14}$ $[M]^+$ 610.23; found 632.90 $[M + Na]^+$. $C_{29}H_{38}O_{14}$ (610.60): calcd. C 57.04, H 6.27; found C 56.88, H 6.11.

Acetyl 3-*O*-Allyl-2-*O*-acetyl-4-*O*-benzyl-α-D-rhamnopyranosyl-(1→3)-5-*O*-acetyl-2-*O*-benzyl-D-rhamnofuranoside (26): ^{1}H NMR (400 MHz, $CDCl_3$) (α anomer): δ = 7.34 (m, 10 H, Ar-H), 6.20 (d, $J_{1,2}$ = 2.7 Hz, 1 H, 1_A-H), 5.92 (m, 1 H, $OCH_2CH{=}CH_2$), 5.30 (dd, J_{vic} = 18.0, J_{gem} = 1.8 Hz, 1 H, *trans* $OCH_2CH{=}CHH$), 5.19–5.05 (m, 3 H, 2_B-H, 5_A-H, *cis* $OCH_2CH{=}CHH$), 4.90 (d, J_{gem} = 11.1 Hz, 1 H, $OCHHPh$), 4.78 (d, $J_{1,2}$ = 1.5 Hz, 1 H, 1_B-H), 4.66–4.56 (m, 3 H, 3 $OCHHPh$), 4.39 (t, $J_{3,4}$ = $J_{3,2}$ = 4.8 Hz, 1 H, 3_A-H), 4.22–4.01 (m, 4 H, 4_A-H, 5_B-H, $OCH_2CH{=}CH_2$), 3.94 (dd, $J_{2,3}$ = 4.8, $J_{2,3}$ = 2.7 Hz, 1 H, 2_A-H), 3.84 (dd, $J_{3,4}$ = 9.2, $J_{3,2}$ = 3.0 Hz, 1 H, 3_B-H), 3.38 (t, $J_{4,3}$ = $J_{4,5}$ = 4.8 Hz, 1 H, 4_B-H), 2.14, 2.06, 2.05 (3 s, 9 H, 3 CH_3CO), 1.29 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_A-H), 1.18 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) (α anomer): δ = 170.0, 169.8, 169.6 (3 CO), 138.7, 137.1 (2 C_{ipso}-Bn), 134.5 ($OCH_2CH{=}CH_2$), 128.5–127.4 (C-Ar), 117.3 ($OCH_2CH{=}CH_2$), 99.6, 98.4 (C-1_A, C-1_B), 81.4, 80.8, 79.8, 77.3, 76.7, 75.0, 72.6, 70.8, 69.4, 68.6, 68.5 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 2 OCH_2Ph, $OCH_2CH{=}CH_2$), 21.3, 21.1, 21.0 (3 CH_3CO), 18.0, 16.4 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{35}H_{44}O_{12}$ $[M]^+$ 656.28; found 679.21 $[M + Na]^+$. $C_{35}H_{44}O_{12}$ (656.72): calcd. C 64.01, H 6.75; found C 64.23, H 6.66.

Acetyl 2-*O*-Acetyl-3-*O*-allyl-4-*O*-benzyl-α-D-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-D-rhamnopyranoside (27): $[\alpha]_D$ = +69.6 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.26 (m, 15 H, Ar-H), 6.13 (d, $J_{1,2}$ = 2.0 Hz, 1 H, 1_A-H), 5.86 (m, 1 H, $OCH_2CH{=}CH_2$), 5.43 (dd, $J_{2,1}$ = 1.8, $J_{2,3}$ = 3.4 Hz, 1 H, 2_B-H), 5.25 (dd, J_{vic} = 17.0, J_{gem} = 1.6 Hz, 1 H, *trans* $OCH_2CH{=}CHH$), 5.12 (dd, J_{vic} = 10.0, J_{gem} = 1.6 Hz, 1 H, *cis* $OCH_2CH{=}CHH$), 5.08 (d, $J_{1,2}$ = 1.6 Hz, 1 H, 1_B-H), 4.93 (d, J_{gem} = 11.0 Hz, 1 H, $OCHHPh$), 4.84 (d, J_{gem} = 11.0 Hz, 1 H, $OCHHPh$), 4.76 (d, J_{gem} = 11.8 Hz, 1 H, $OCHHPh$), 4.67 (d, J_{gem} = 11.8 Hz, 1 H, $OCHHPh$), 4.63 (d, J_{gem} = 10.8 Hz, 1 H, $OCHHPh$), 4.61 (d, J_{gem} = 11.0 Hz, 1 H, $OCHHPh$), 4.09 (dd, J_{gem} = 12.8, J_{vic} = 5.5 Hz, 1 H, $OCHHCH{=}CH_2$), 4.07 (dd, $J_{3,2}$ = 3.2, $J_{3,4}$ = 9.4 Hz, 1 H, 3_A-

H), 4.03 (dd, J_{gem} = 12.8, J_{vic} = 5.5 Hz, 1 H, OC*H*HCH=CH_2), 3.85 (dd, $J_{3,2}$ = 3.4, $J_{3,4}$ = 9.3 Hz, 1 H, 3_B-H), 3.78 (m, 2 H, 5_A-H, 5_B-H), 3.72 (dd, $J_{2,1}$ = 1.6, $J_{2,3}$ = 2.2 Hz, 1 H, 2_A-H), 3.70 (t, $J_{4,5}$ = $J_{4,3}$ = 9.4 Hz, 1 H, 4_B-H), 3.39 (t, $J_{4,5}$ = $J_{4,3}$ = 9.4 Hz, 1 H, 4_A-H), 2.11 (s, 3 H, CH_3CO), 2.07 (s, 3 H, CH_3CO), 1.32 (d, $J_{6,5}$ = 6.1 Hz, 3 H, 6_A-H), 1.24 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.0, 169.1 (2 CO), 138.6, 137.8, 137.5 (3 C_{ipso}-Bn), 134.6 ($OCH_2CH=CH_2$), 129.0–127.6 (C-Ar), 117.1 ($OCH_2CH=CH_2$), 99.4 (C-1_B), 91.2 (C-1_A), 80.1, 79.8, 77.4, 77.3, 76.7, 75.4, 75.1, 72.6, 70.7, 70.6, 69.2, 69.1 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 3 OCH_2Ph, $OCH_2CH=CH_2$), 21.0, 20.9 (2 CH_3CO), 18.0, 17.9 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{40}H_{48}O_{11}$ $[M]^+$ 704.32; found 727.39 $[M + Na]^+$. $C_{40}H_{48}O_{11}$ (704.80): calcd. C 68.16, H 6.86; found C 68.23, H 6.97.

Acetyl 3-*O*-Allyl-2-*O*-benzoyl-4-*O*-benzyl-α-D-rhamnopyranosyl-(1→3)-5-*O*-acetyl-2-*O*-benzyl-α-D-rhamnofuranoside (28α): $[\alpha]_D$ = +5.9 (*c* = 0.8, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.07–7.26 (m, 15 H, Ar-H), 6.22 (d, $J_{1,2}$ = 3.0 Hz, 1 H, 1_A-H), 5.87 (m, 1 H, $OCH_2CH=CH_2$), 5.38 (dd, $J_{2,3}$ = 3.4, $J_{2,1}$ = 2.0 Hz, 1 H, 2_B-H), 5.28 (dd, J_{vic} = 18.0, J_{gem} = 1.5 Hz, 1 H, *trans* $OCH_2CH=CHH$), 5.18 (q, $J_{5,6}$ = $J_{5,4}$ = 6.0 Hz, 1 H, 5_A-H), 5.12 (dd, J_{vic} = 10.0, J_{gem} = 1.5 Hz, 1 H, *cis* $OCH_2CH=CHH$), 4.94 (d, J_{gem} = 11.0 Hz, 1 H, OC*H*HPh), 4.91 (d, $J_{1,2}$ = 2.0 Hz, 1 H, 1_B-H), 4.64 (m, 3 H, 3 OC*H*HPh), 4.43 (t, $J_{3,4}$ = $J_{3,2}$ = 5.4 Hz, 1 H, 3_A-H), 4.20 (m, 2 H, 4_A-H, OC*H*HCH=CH_2), 4.09 (m, 2 H, 5_B-H, OC*H*HCH=CH_2), 3.96 (m, 2 H, 2_A-H, 3_B-H), 3.49 (t, $J_{4,5}$ = $J_{4,3}$ = 9.0 Hz, 1 H, 4_B-H), 2.08 (s, 3 H, CH_3CO), 2.06 (s, 3 H, CH_3CO), 1.31 (d, $J_{6,5}$ = 6.0 Hz, 3 H, 6_A-H), 1.21 (d, $J_{6,5}$ = 6.0 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 169.9, 169.8, 165.5 (3 CO), 138.6, 137.1 (2 C_{ipso}-Bn), 134.6 ($OCH_2CH=CH_2$), 133.1 (C_{ipso}-Bz), 129.9–127.6 (C-Ar), 117.3 ($OCH_2CH=CH_2$), 99.5, 98.3 (C-1_A, C-1_B), 81.4, 80.8, 79.7, 77.4, 76.6, 75.0, 72.5, 70.6, 69.7, 68.6, 68.5 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 2 OCH_2Ph, $OCH_2CH=CH_2$), 21.4, 21.2 (2 CH_3CO), 18.2, 16.4 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{40}H_{46}O_{12}$ $[M]^+$ 718.30; found 741.03 $[M + Na]^+$. $C_{40}H_{46}O_{12}$ (718.79): calcd. C 66.84, H 6.45; found C 66.68, H 6.32.

Acetyl 3-*O*-Allyl-2-*O*-benzoyl-4-*O*-benzyl-α-D-rhamnopyranosyl-(1→3)-5-*O*-acetyl-2-*O*-benzyl-α-D-rhamnofuranoside (28β): $[\alpha]_D$ = –6 (*c* = 0.3, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ = 8.07–7.28 (m, 15 H, Ar-H), 6.25 (d, $J_{1,2}$ = 4.5 Hz, 1 H, 1_A-H), 5.88 (m, 1 H, $OCH_2CH=CH_2$), 5.36 (dd, J_{vic} = 18.0, J_{gem} = 1.6 Hz, 1 H, *trans* $OCH_2CH=CHH$), 5.30 (dd, $J_{2,3}$ = 3.4, $J_{2,1}$ = 2.0 Hz, 1 H, 2_B-H), 5.13 (m, 2 H, 5_A-H, *cis* $OCH_2CH=CHH$), 4.95 (d, J_{gem} = 11.0 Hz, 1 H, OC*H*HPh), 4.85 (d, $J_{1,2}$ = 1.8 Hz, 1 H, 1_B-H), 4.69 (d, J_{gem} = 13.0 Hz, 1 H, OC*H*HPh), 4.63 (d, J_{gem} = 11.0 Hz, 1 H, OC*H*HPh), 4.61 (d, J_{gem} = 13.0 Hz, 1 H, OC*H*HPh), 4.32 (dq, $J_{5,4}$ = 10.0, $J_{5,6}$ = 6.0 Hz, 1 H, 5_B-H), 4.23 (m, 2 H, 3_A-H, OC*H*HCH=CH_2), 4.10 (dd, J_{gem} = 13.0, J_{vic} = 6.0 Hz, 1 H, OC*H*HCH=CH_2), 4.00 (dd, $J_{3,4}$ = 10.0, $J_{3,2}$ = 3.4 Hz, 1 H, 3_B-H), 3.94 (dd, $J_{4,5}$ = 8.5, $J_{4,3}$ = 4.0 Hz, 1 H, 4_A-H), 3.85 (t, $J_{2,3}$ = $J_{2,1}$ = 4.5 Hz, 1 H, 2_A-H), 3.50 (t, $J_{4,5}$ = $J_{4,3}$ = 10.0 Hz, 1 H, 4_B-H), 2.11 (s, 3 H, CH_3CO), 2.09 (s, 3 H, CH_3CO), 1.36 (d, $J_{6,5}$ = 6.0 Hz, 3 H, 6_A-H), 1.15 (d, $J_{6,5}$ = 6.0 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 170.5, 170.3, 165.6 (3 CO), 138.9, 137.1 (2 C_{ipso}-Bn), 135.2, 134.8 ($OCH_2CH=CH_2$, C_{ipso}-Bz), 129.9–127.4 (C-Ar), 117.3 ($OCH_2CH=CH_2$), 99.8, 93.2 (C-1_A, C-1_B), 82.7, 80.1, 77.7, 77.2, 76.6, 75.0, 72.6, 70.1, 69.8, 68.6, 68.3 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 2 OCH_2Ph, $OCH_2CH=CH_2$), 21.4, 21.3 (2 CH_3CO), 18.1, 16.9 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{40}H_{46}O_{12}$ $[M]^+$ 718.30; found 740.56 $[M + Na]^+$. $C_{40}H_{46}O_{12}$ (718.79): calcd. C 66.84, H 6.45; found C 66.55, H 6.25.

Acetyl 3-*O*-Allyl-2-*O*-benzoyl-4-*O*-benzyl-α-D-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-α-D-rhamnopyranoside (29): $[\alpha]_D$ = –2.5 (*c* = 1.2, CH_2Cl_2). ^1H NMR (200 MHz, $CDCl_3$): δ = 8.07–7.16 (m, 20 H, Ar-H), 6.14 (d, $J_{1,2}$ = 2.0 Hz, 1 H, 1_A-H), 5.84 (m, 1 H, $OCH_2CH=CH_2$), 5.68 (dd, $J_{2,1}$ = 1.6, $J_{2,3}$ = 3.4 Hz, 1 H, 2_B-H), 5.25–5.21 (m, 2 H, 1_B-H, *trans* $OCH_2CH=CHH$), 5.08 (dd, J_{vic} = 10.2, J_{gem} = 1.8 Hz, 1 H, *cis* $OCH_2CH=CHH$), 4.95 (d, J_{gem} = 11.0 Hz, 1 H, OC*H*HPh), 4.90 (d, J_{gem} = 11.0 Hz, 1 H, OC*H*HPh), 4.79 (d, J_{gem} = 12.0 Hz, 1 H, OC*H*HPh), 4.72–4.62 (m, 3 H, 3 OC*H*HPh), 4.19 (dd, J_{gem} = 12.0, J_{vic} = 5.0 Hz, 1 H, OC*H*HCH=CH_2), 4.12–4.05 (m, 2 H, 3_A-H, OC*H*HCH=CH_2), 3.98 (dd, $J_{3,2}$ = 3.2, $J_{3,4}$ = 9.2 Hz, 1 H, 3_B-H), 3.91–3.65 (m, 4 H, 2_A-H, 4_A-H, 5_A-H, 5_B-H), 3.51 (t, $J_{4,5}$ = $J_{4,3}$ = 9.6 Hz, 1 H, 4_B-H), 2.06 (s, 3 H, CH_3CO), 1.32 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_B-H), 1.29 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_A-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 169.2, 165.5 (2 CO), 138.6, 137.8, 137.5 (3 C_{ipso}-Bn), 134.6 ($OCH_2CH=CH_2$), 133.1 (C_{ipso}-Bz), 129.8–125.3 (C-Ar), 117.1 ($OCH_2CH=CH_2$), 99.5 (C-1_B), 91.2 (C-1_A), 80.1, 79.9, 77.6, 77.4, 76.7, 75.5, 75.2, 72.6, 72.5, 70.6, 69.6, 68.4 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, 3 OCH_2Ph, $OCH_2CH=CH_2$), 21.0 (CH_3CO), 18.2, 18.1 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{45}H_{50}O_{11}$ $[M]^+$ 766.34; found 789.42 $[M + Na]^+$. $C_{45}H_{50}O_{11}$ (766.87): calcd. C 70.48, H 6.57; found C 70.28, H 6.34.

Acetyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-5-*O*-acetyl-2-*O*-allyl-α-L-rhamnofuranoside (30): ^1H NMR (400 MHz, $CDCl_3$): δ = 6.27 (d, $J_{1,2}$ = 4.5 Hz, 1 H_β, $1_{A\text{-}\beta}$-H), 6.19 (d, $J_{1,2}$ = 2.9 Hz, 1 H_α, $1_{A\text{-}\alpha}$-H), 5.87 (m, 1 H_β + 1 H_α, $OCH_2CH=CH_2$), 5.39 (dd, $J_{3,4}$ = 9.9, $J_{3,2}$ = 3.6 Hz, 1 H_α, $3_{B\text{-}\beta}$-H), 5.32 (dd, J_{vic} = 17.2, J_{gem} = 1.5 Hz, 1 H_α + 1 H_β, *trans* $OCH_2CH=CHH$), 5.26–5.18 (m, 3H_α + 2H_β, *cis* $OCH_2CH=CHH$, $2_{B\text{-}\alpha}$-H, $2_{B\text{-}\beta}$-H, $3_{B\text{-}\alpha}$-H), 5.18–5.01 (m, 2H_α + 2H_β, $4_{B\text{-}\alpha}$-H, $4_{B\text{-}\beta}$-H, $5_{A\text{-}\alpha}$-H, $5_{A\text{-}\beta}$-H), 4.78 (d, $J_{1,2}$ = 1.5 Hz, 1 H_α, $1_{B\text{-}\alpha}$-H), 4.74 (d, $J_{1,2}$ = 1.7 Hz, 1 H_β, $1_{B\text{-}\beta}$-H), 4.46 (dq, $J_{5,4}$ = 9.9, $J_{5,6}$ = 6.2 Hz, 1 H_β, $5_{B\text{-}\beta}$-H), 4.35 (t, $J_{3,2}$ = $J_{3,4}$ = 4.9 Hz, 1 H_α, $3_{A\text{-}\alpha}$-H), 4.26–4.19 (m, 2 H_α + 1 H_β, $3_{A\text{-}\beta}$-H, $4_{A\text{-}\alpha}$-H, $5_{B\text{-}\alpha}$-H), 4.13–4.03 (m, 2 H_α + 2 H_β, $OCH_2CH=CH_2$), 3.99 (dd, $J_{2,3}$ = 5.9, $J_{2,1}$ = 4.5 Hz, 1 H_β, $2_{A\text{-}\beta}$-H), 3.94 (dd, $J_{2,3}$ = 4.6, $J_{2,1}$ = 2.9 Hz, 1 H_α, $2_{A\text{-}\alpha}$-H), 3.91 (t, $J_{4,3}$ = $J_{4,5}$ = 5.9 Hz, 1 H_β, $4_{A\text{-}\beta}$-H), 2.18 (s, 3 H_β, CH_3CO), 2.13 (2 s, 3 H_α + 3 H_β, CH_3CO), 2.08 (s, 3 H_α, CH_3CO), 2.04 (2 s, 6 H_α, CH_3CO), 2.03 (s, 3 H_β, CH_3CO), 2.01 (s, 3 H_β, CH_3CO), 1.99 (s, 3 H_β, CH_3CO), 1.98 (s, 3 H_α, CH_3CO), 1.35 (d, $J_{6,5}$ = 6.2 Hz, 3 H_β, $6_{A\text{-}\beta}$-H), 1.31 (d, $J_{6,5}$ = 6.3 Hz, 3 H_α, $6_{A\text{-}\alpha}$-H), 1.17 (d, $J_{6,5}$ = 6.2 Hz, 3 H_α, $6_{B\text{-}\alpha}$-H), 1.16 (d, $J_{6,5}$ = 6.2 Hz, 3 H_β, $6_{B\text{-}\beta}$-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.1–169.6 (5 CO_α + 5 CO_β), 133.8 (α $OCH_2CH=CH_2$), 133.6 (β $OCH_2CH=CH_2$), 118.4 (α $OCH_2CH=CH_2$), 117.7 (β $OCH_2CH=CH_2$), 99.5, 98.4 (C-$1_{A\text{-}\alpha}$, C-$1_{B\text{-}\alpha}$), 98.8, 93.0 (C-$1_{A\text{-}\beta}$, C-$1_{B\text{-}\beta}$), 81.7, 81.0, 78.6, 71.7, 71.0, 69.9, 68.8, 68.7, 67.0 (α C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, $OCH_2CH=CH_2$), 82.8, 78.2, 72.4, 72.1, 71.5, 70.6, 68.8, 68.7, 66.7 (β C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, $OCH_2CH=CH_2$), 21.3–20.7 (5 CH_3CO_α + 5 CH_3CO_β), 17.6, 16.3 (C-$6_{A\text{-}\alpha}$, C-$6_{B\text{-}\alpha}$), 17.5, 16.7 (C-$6_{A\text{-}\beta}$, C-$6_{B\text{-}\beta}$) ppm. MS (MALDI-TOF): calcd. for $C_{25}H_{36}O_{14}$ $[M]^+$ 560.21; found 582.90 $[M + Na]^+$. $C_{25}H_{36}O_{14}$ (560.55): calcd. C 53.57, H 6.47; found C 53.70, H 6.40.

Acetyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2-*O*-allyl-4-*O*-benzyl-α-L-rhamnopyranoside (31): $[\alpha]_D$ = –39.2 (*c* = 1.4, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32 (m, 5 H, Ar-H), 6.09 (d, $J_{1,2}$ = 2.1 Hz, 1 H, 1_A-H), 5.98 (m, 1 H, $OCH_2CH=CH_2$), 5.40–5.34 (m, 3 H, 2_B-H, 3_B-H, *trans* $OCH_2CH=CHH$), 5.26 (dd, J_{vic} = 10.5, J_{gem} = 1.2 Hz, 1 H, *cis* $OCH_2CH=CHH$), 5.08 (t, $J_{4,3}$ = $J_{4,5}$ = 9.9 Hz, 1 H, 4_B-H), 5.05 (br. s, 1 H, 1_B-H), 4.84 (d, J_{gem} = 11.1 Hz, 1 H, OC*H*HPh), 4.64 (d, J_{gem} = 11.1 Hz, 1 H, OC*H*HPh), 4.27 (dd, J_{gem} = 12.9, J_{vic} = 5.4 Hz, 1 H,

OC*H*HCH=CH_2), 4.12–3.98 (m, 3 H, 3_A-H, 5_B-H, OC*H*HCH=CH_2), 3.77 (dq, $J_{5,4}$ = 9.6, $J_{5,6}$ = 6.3 Hz, 1 H, 5_A-H), 3.67 (dd, $J_{2,3}$ = 3.0, $J_{2,1}$ = 2.1 Hz, 1 H, 2_A-H), 3.63 (t, $J_{4,3}$ = $J_{4,5}$ = 9.6 Hz, 1 H, 4_A-H), 2.09, 2.07, 2.06, 1.99 (4 s, 12 H, 4 CH_3CO), 1.31 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_A-H), 1.20 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 170.0, 169.9, 169.8, 169.1 (4 CO), 137.8 (C_{ipso}-Bn), 134.3 ($OCH_2CH=CH_2$), 128.4–127.8 (C-Ar), 117.9 ($OCH_2CH=CH_2$), 99.4 ($C\text{-}1_B$), 91.2 ($C\text{-}1_A$), 79.7, 78.5, 76.7, 75.6, 71.8, 70.9, 70.6, 69.8, 69.0, 66.9 ($C\text{-}2_A$, $C\text{-}2_B$, $C\text{-}3_A$, $C\text{-}3_B$, $C\text{-}4_A$, $C\text{-}4_B$, $C\text{-}5_A$, $C\text{-}5_B$, OCH_2Ph, $OCH_2CH=CH_2$), 21.0–20.8 (4 CH_3CO), 18.0, 17.5 ($C\text{-}6_A$, $C\text{-}6_B$) ppm. MS (MALDI-TOF): calcd. for $C_{30}H_{40}O_{13}$ $[M]^+$ 608.25; found 630.74 [M + Na]$^+$. $C_{30}H_{40}O_{13}$ (608.63): calcd. C 59.20, H 6.62; found C 59.11, H 6.70.

2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-1,5-di-*O*-acetyl-4-*O*-allyl-2-*O*-benzyl-1-*O*-methyl-D-rhamnose Acetal (32): ^1H NMR (500 MHz, $CDCl_3$) (major diastereoisomer): δ = 7.32 (m, 5 H, Ar-H), 5.99 (d, $J_{1,2}$ = 7.0 Hz, 1 H, 1_A-H), 5.85 (m, 1 H, $OCH_2CH=CH_2$), 5.35 (dd, $J_{2,3}$ = 3.0, $J_{2,1}$ = 1.5 Hz, 1 H, 2_B-H), 5.24 (dd, $J_{3,4}$ = 10.2, $J_{3,2}$ = 3.0 Hz, 1 H, 3_B-H), 5.19 (d, J_{vic} = 17.5 Hz, 1 H, *trans* $OCH_2CH=CHH$), 5.08 (m, 2 H, 1_B-H, 4_B-H), 5.04 (d, J_{vic} = 10.5 Hz, 1 H, *trans* $OCH_2CH=CHH$), 4.81 (dq, $J_{5,6}$ = 6.6, $J_{5,4}$ = 1.8 Hz, 1 H, 5_A-H), 4.62 (s, 2 H, OCH_2Ph), 4.15 (m, 3 H, $OCH_2CH=CH_2$, 5_B-H), 3.80 (m, 2 H, 3_A-H, 4_A-H), 3.52 (m, 4 H, 2_A-H, OCH_3), 2.12 (s, 6 H, 2 CH_3CO), 2.07 (s, 3 H, CH_3CO), 2.02 (s, 3 H, CH_3CO), 1.97 (s, 3 H, CH_3CO), 1.04 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_B-H), 1.02 (d, $J_{6,5}$ = 6.6 Hz, 3 H, 5_A-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) (major diastereoisomer): δ = 170.5, 170.2, 169.9, 169.8, 169.7 (5 CO), 137.5 (C_{ipso}-Bn), 134.8 ($OCH_2CH=CH_2$), 128.5–127.9 (C-Ar), 116.5 ($OCH_2CH=CH_2$), 98.7, 98.0 ($C\text{-}1_A$, $C\text{-}1_B$), 80.6, 78.8, 77.7, 73.7, 73.5, 71.0, 70.8, 69.8, 69.6, 67.1 ($C\text{-}2_A$, $C\text{-}2_B$, $C\text{-}3_A$, $C\text{-}3_B$, $C\text{-}4_A$, $C\text{-}4_B$, $C\text{-}5_A$, $C\text{-}5_B$, OCH_2Ph, $OCH_2CH=CH_2$), 57.7 (OCH_3), 21.3, 21.2, 20.9, 20.8, 20.7 (5 CH_3CO), 17.4, 13.7 ($C\text{-}6_A$, $C\text{-}6_B$) ppm. MS (MALDI-TOF): calcd. for $C_{33}H_{46}O_{15}$ $[M]^+$ 682.28; found 704.73 [M + Na]$^+$. $C_{33}H_{46}O_{15}$ (682.71): calcd. C 58.06, H 6.79; found C 57.88, H 6.65.

Acetyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-4-*O*-allyl-2-*O*-benzyl-α-L-rhamnopyranoside (33): $[\alpha]_D$ = –32 (c = 0.9, CH_2Cl_2). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.39 (m, 5 H, Ar-H), 6.15 (d, $J_{1,2}$ = 2.0 Hz, 1 H, 1_A-H), 5.89 (m, 1 H, $OCH_2CH=CH_2$), 5.34–5.03 (m, 6 H, 1_B-H, 2_B-H, 3_B-H, 4_B-H, $OCH_2CH=CH_2$), 4.82 (d, J_{gem} = 12.0 Hz, 1 H, OC*H*HPh), 4.62 (d, J_{gem} = 12.0 Hz, 1 H, OC*H*HPh), 4.30 (dd, J_{gem} = 12.8, J_{vic} = 5.6 Hz, 1 H, OC*H*HCH=CH_2), 4.16 (dd, J_{gem} = 12.8, J_{vic} = 5.6 Hz, 1 H, OC*H*HCH=CH_2), 3.95 (dd, $J_{3,4}$ = 9.4, $J_{3,2}$ = 3.2 Hz, 1 H, 3_A-H), 3.79–3.67 (m, 3 H, 2_A-H, 5_A-H, 5_B-H), 3.54 (t, $J_{4,3}$ = $J_{4,5}$ = 9.4 Hz, 1 H, 4_A-H), 2.13, 2.08, 2.04, 2.00 (4 s, 12 H, 4 CH_3CO), 1.31 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_A-H), 1.07 (d, $J_{6,5}$ = 6.2 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 169.8–169.7 (4 CO), 137.5 (C_{ipso}-Bn), 134.4 ($OCH_2CH=CH_2$), 128.5–127.7 (C-Ar), 117.2 ($OCH_2CH=CH_2$), 99.5 ($C\text{-}1_B$), 91.2 ($C\text{-}1_A$), 79.7, 78.4, 77.2, 74.4, 72.3, 71.0, 70.9, 69.9, 69.0, 66.9 ($C\text{-}2_A$, $C\text{-}2_B$, $C\text{-}3_A$, $C\text{-}3_B$, $C\text{-}4_A$, $C\text{-}4_B$, $C\text{-}5_A$, $C\text{-}5_B$, OCH_2Ph, $OCH_2CH=CH_2$), 20.8–20.7 (4 CH_3CO), 18.0, 17.5 ($C\text{-}6_A$, $C\text{-}6_B$) ppm. MS (MALDI-TOF): calcd. for $C_{30}H_{40}O_{13}$ $[M]^+$ 608.25; found 631.11 [M + Na]$^+$. $C_{30}H_{40}O_{13}$ (608.63): calcd. C 59.20, H 6.62; found C 59.02, H 6.54.

2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-1,4,5-tri-*O*-acetyl-2-*O*-benzyl-1-*O*-methyl-D-rhamnose Acetal (34): ^1H NMR (500 MHz, $CDCl_3$): δ = 7.41–7.33 (m, 5 H′ + 5 H′′, Ar-H), 6.00 (d, $J_{1,2}$ = 5.0 Hz, 1 H′′, $1_{A''}$-H), 5.98 (d, $J_{1,2}$ = 6.0 Hz, 1 H′, $1_{A'}$-H), 5.45 (m, 1 H′ + 1 H′′, $4_{A'}$-H, $4_{A''}$-H), 5.25 (m, 1 H′ + 1 H′, $3_{B'}$-H, $3_{B''}$-H), 5.15 (dd, $J_{2,3}$ = 3.0, $J_{2,1}$ = 1.8 Hz, 1 H′′, $2_{B''}$-H), 5.13 (dd, $J_{2,3}$ = 3.0, $J_{2,1}$ = 1.8 Hz, 1 H′, $2_{B'}$-H), 5.06 (t, $J_{4,3}$ = $J_{4,5}$ = 10.0 Hz, 1 H′ + 1 H′′, $4_{B'}$-H, $4_{B''}$-H), 4.96 (m, 1 H′ + 1 H′′, $5_{A'}$-H, $5_{A''}$-H), 4.91 (d, $J_{1,2}$ = 1.8 Hz, 1 H′, $1_{B'}$-H), 4.86 (d, $J_{1,2}$ = 1.8 Hz, 1 H′′, $1_{B''}$-H), 4.78 (d, J_{gem} = 12.0 Hz, 1 H′, OC*H*HPh′), 4.69–4.61 (m, 2 H′ + 1 H′′, OC*H*HPh′, OC*H*HPh′′), 4.08 (dq, $J_{5,4}$ = 10.0, $J_{5,6}$ = 6.2 Hz, 1 H′ + 1 H′′, $5_{B'}$-H, $5_{B''}$-H), 3.93 (dd, $J_{3,4}$ = 8.0, $J_{3,2}$ = 1.8 Hz, 1 H′, $3_{A'}$-H), 3.89 (dd, $J_{3,4}$ = 8.0, $J_{3,2}$ = 3.0 Hz, 1 H′′, $3_{A''}$-H), 3.66 (dd, $J_{2,1}$ = 5.0, $J_{2,3}$ = 3.0 Hz, 1 H′′, $2_{A''}$-H), 3.57 (dd, $J_{2,1}$ = 6.0, $J_{2,3}$ = 1.8 Hz, 1 H′, $2_{A'}$-H), 3.53 (s, 3 H′, OCH_3'), 3.52 (s, 3 H′′, OCH_3''), 2.17 (s, 3 H′′, CH_3CO''), 2.14 (s, 3 H′, CH_3CO'), 2.13 (s, 3 H′′, CH_3CO''), 2.11 (s, 3 H′, CH_3CO'), 2.07 (s, 3 H′, CH_3CO'), 2.06 (s, 3 H′ + 3 H′′, CH_3CO', CH_3CO''), 2.05 (s, 3 H′′, 3 CH_3CO''), 1.97 (s, 6 H′ + 6 H′′, 2 CH_3CO', 2 CH_3CO''), 1.11 (d, $J_{6,5}$ = 6.2 Hz, 3 H′′, $6_{B''}$-H), 1.05 (d, $J_{6,5}$ = 6.2 Hz, 3 H′, $6_{B'}$-H), 1.03 (d, $J_{6,5}$ = 6.6 Hz, 3 H′′, $6_{A''}$-H), 1.00 (d, $J_{6,5}$ = 6.6 Hz, 3 H′, $6_{A'}$-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 170.4–169.7 (5 CO′, 5 CO′′), 137.6 (C_{ipso}-Bn′, C_{ipso}-Bn′′), 128.5–127.8 (C-Ar), 98.8, 97.1 ($C\text{-}1_{A''}$, $C\text{-}1_{B''}$), 98.5, 97.7 ($C\text{-}1_{A'}$, $C\text{-}1_{B'}$), 79.1, 76.8, 73.6, 73.1, 71.0, 70.1, 68.9, 68.8, 67.2 ($C\text{-}2_{A'}$, $C\text{-}2_{B'}$, $C\text{-}3_{A'}$, $C\text{-}3_{B'}$, $C\text{-}4_{A'}$, $C\text{-}4_{B'}$, $C\text{-}5_{A'}$, $C\text{-}5_{B'}$, OCH_2Ph'), 79.1, 77.2, 73.9, 72.9, 71.1, 70.0, 68.9, 68.8, 67.2 ($C\text{-}2_{A''}$, $C\text{-}2_{B''}$, $C\text{-}3_{A''}$, $C\text{-}3_{B''}$, $C\text{-}4_{A''}$, $C\text{-}4_{B''}$, $C\text{-}5_{A''}$, $C\text{-}5_{B''}$, OCH_2Ph''), 57.9 (OCH_3'), 53.4 (OCH_3''), 21.2–20.7 (5 CH_3CO', 5 CH_3CO''), 19.2, 14.5 ($C\text{-}6_{A''}$, $C\text{-}6_{B''}$), 17.3, 14.4 ($C\text{-}6_{A'}$, $C\text{-}6_{B'}$) ppm. MS (MALDI-TOF): calcd. for $C_{32}H_{44}O_{16}$ $[M]^+$ 684.26; found 706.80 [M + Na]$^+$. $C_{32}H_{44}O_{16}$ (684.68): calcd. C 56.13, H 6.48; found C 56.00, H 6.32.

Acetyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-L-fucopyranoside (35): ^1H NMR (300 MHz, $CDCl_3$) (α-anomer): δ = 7.42–7.32 (m, 10 H, Ar-H), 6.44 (d, $J_{1,2}$ = 2.7 Hz, 1 H, 1_A-H), 5.41 (dd, $J_{5,4}$ = 9.9, $J_{5,6}$ = 3.6 Hz, 1 H, 3_B-H), 5.20 (dd, $J_{2,3}$ = 3.6, $J_{2,1}$ = 1.8 Hz, 1 H, 2_B-H), 5.06 (t, $J_{4,3}$ = $J_{4,5}$ = 9.9 Hz, 1 H, 4_B-H), 5.00 (s, 1 H, 1_B-H), 4.93 (d, J_{gem} = 11.1 Hz, 1 H, OC*H*HPh), 4.71 (d, J_{gem} = 11.4 Hz, 1 H, OC*H*HPh), 4.62 (d, J_{gem} = 11.4 Hz, 1 H, OC*H*HPh), 4.60 (d, J_{gem} = 11.1 Hz, 1 H, OC*H*HPh), 4.18 (dq, $J_{5,4}$ = 9.9, $J_{5,6}$ = 6.3 Hz, 1 H, 5_B-H), 4.12 (d, $J_{4,3}$ = 2.4 Hz, 1 H, 4_A-H), 3.99 (q, $J_{5,6}$ = 6.6 Hz, 1 H, 5_A-H), 3.69–3.61 (m, 2 H, 2_A-H, 3_A-H), 2.16, 2.11, 2.03, 2.00 (4 s, 12 H, 4 CH_3CO), 1.18 (d, $J_{6,5}$ = 6.6 Hz, 3 H, 6_A-H), 0.98 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) (α anomer): δ = 170.3, 169.9, 169.7, 169.3 (4 CO), 137.9, 137.7 (2 C_{ipso}-Bn), 128.9–127.7 (C-Ar), 94.1 ($C\text{-}1_B$), 90.6 ($C\text{-}1_A$), 76.1, 75.6, 74.3, 73.4, 73.0, 70.9, 70.3, 69.0, 68.9, 66.5 ($C\text{-}2_A$, $C\text{-}2_B$, $C\text{-}3_A$, $C\text{-}3_B$, $C\text{-}4_A$, $C\text{-}4_B$, $C\text{-}5_A$, $C\text{-}5_B$, 2 OCH_2Ph), 21.0–20.7 (4 CH_3CO), 17.0, 16.8 ($C\text{-}6_A$, $C\text{-}6_B$) ppm. MS (MALDI-TOF): calcd. for $C_{34}H_{42}O_{13}$ $[M]^+$ 658.26; found 680.88 [M + Na]$^+$. $C_{34}H_{42}O_{13}$ (658.69): calcd. C 62.00, H 6.43; found C 62.18, H 6.61.

Acetyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-benzyl-D-quinovopyranoside (36): ^1H NMR (400 MHz, $CDCl_3$) (α-anomer): δ = 7.34–7.24 (m, 10 H, Ar-H), 6.25 (d, $J_{1,2}$ = 3.6 Hz, 1 H, 1_A-H), 5.39–5.28 (m, 3 H, 1_B-H, 2_B-H, 3_B-H), 4.99 (t, $J_{4,3}$ = $J_{4,5}$ = 9.9 Hz, 1 H, 4_B-H), 4.86 (d, J_{gem} = 11.1 Hz, 1 H, OC*H*HPh), 4.72 (d, J_{gem} = 11.1 Hz, 1 H, OC*H*HPh), 4.63 (d, J_{gem} = 11.1 Hz, 1 H, OC*H*HPh), 4.50 (d, J_{gem} = 11.1 Hz, 1 H, OC*H*HPh), 4.10 (t, $J_{3,4}$ = $J_{3,2}$ = 9.6 Hz, 1 H, 3_A-H), 4.05 (dq, $J_{5,4}$ = 9.9, $J_{5,6}$ = 6.3 Hz, 1 H, 5_B-H), 3.91 (dq, $J_{5,4}$ = 9.6, $J_{5,6}$ = 6.3 Hz, 1 H, 5_A-H), 3.66 (dd, $J_{2,3}$ = 9.6, $J_{2,1}$ = 3.3 Hz, 1 H, 2_A-H), 3.17 (t, $J_{4,3}$ = $J_{4,5}$ = 9.6 Hz, 1 H, 4_A-H), 2.13, 2.07, 2.01, 1.94 (4 s, 12 H, 4 CH_3CO), 1.32 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_A-H), 0.91 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) (α-anomer): δ = 170.0, 169.8, 169.7, 169.4 (4 CO), 137.6, 136.9 (2 C_{ipso}-Bn), 128.9–127.3 (C-Ar), 97.6 ($C\text{-}1_B$), 89.0 ($C\text{-}1_A$), 81.9, 79.8, 75.4, 75.0, 72.8, 71.0, 69.6, 69.5, 69.2, 66.4 ($C\text{-}2_A$, $C\text{-}2_B$, $C\text{-}3_A$, $C\text{-}3_B$, $C\text{-}4_A$, $C\text{-}4_B$, $C\text{-}5_A$, $C\text{-}5_B$, 2 OCH_2Ph), 21.0–20.8 (4 CH_3CO), 18.0, 17.1 ($C\text{-}6_A$, $C\text{-}6_B$) ppm.

MS (MALDI-TOF): calcd. for $C_{34}H_{42}O_{13}$ $[M]^+$ 658.26; found 681.15 $[M + Na]^+$. $C_{34}H_{42}O_{13}$ (658.69): calcd. C 62.00, H 6.43; found C 62.20, H 6.56.

2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-1,1,4,5-tetra-*O*-acetyl-2-*O*-benzyl-D-quinovose Acetal (37): $[a]_D$ = –15 (*c* = 0.1, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (m, 5 H, Ar-H), 6.95 (d, $J_{1,2}$ = 3.2 Hz, 1 H, 1_A-H), 5.33 (s, $J_{4,3}$ = 2.3 Hz, 1 H, 4_A-H), 5.28 (dd, $J_{3,4}$ = 10.0, $J_{3,2}$ = 4.8 Hz, 1 H, 3_B-H), 5.19 (dd, $J_{2,3}$ = 4.8, $J_{2,1}$ = 3.2 Hz, 1 H, 2_B-H), 5.11 (q, $J_{5,6}$ = 6.3 Hz, 1 H, 5_A-H), 5.06 (t, $J_{4,3}$ = $J_{4,5}$ = 10.0 Hz, 1 H, 4_B-H), 5.03 (br. s, 1 H, 1_B-H), 4.75 (d, J_{gem} = 11.6 Hz, 1 H, OC*H*HPh), 4.70 (d, J_{gem} = 11.5 Hz, 1 H, OC*H*HPh), 4.06 (dd, $J_{3,2}$ = 6.8, $J_{3,4}$ = 2.3 Hz, 1 H, 3_A-H), 4.00 (dq, $J_{5,4}$ = 10.0, $J_{5,6}$ = 6.4 Hz, 1 H, 5_B-H), 3.80 (dd, $J_{2,3}$ = 6.8, $J_{2,1}$ = 3.2 Hz, 1 H, 2_A-H), 2.10, 2.07, 2.06, 2.05, 2.04, 2.03, 1.97 (7 s, 21 H, 7 CH_3CO), 1.24 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_A-H), 1.21 (d, $J_{6,5}$ = 6.4 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.1, 170.0, 169.9, 169.7, 168.6, 168.5, 168.4 (7 CO), 134.7 (C_{ipso}-Bn), 128.4–127.9 (C-Ar), 100.8, 98.9 (C-1_A, C-1_B), 87.7, 74.5, 74.1, 72.9, 70.9, 69.6, 69.0, 68.8, 67.5 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, O*C*H_2Ph), 21.1–20.7 (7 *C*H_3CO), 17.3, 15.8 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{33}H_{44}O_{17}$ $[M]^+$ 712.29; found 734.61 $[M + Na]^+$. $C_{33}H_{44}O_{17}$ (712.69): calcd. C 55.61, H 6.22; found C 55.42, H 6.10.

Acetyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→3)-5-*O*-acetyl-2-*O*-benzyl-D-quinovofuranoside (38): ^1H NMR (300 MHz, $CDCl_3$) (β-anomer): δ = 7.31 (m, 5 H, Ar-H), 6.21 (s, 1 H, 1_A-H), 5.25–5.00 (m, 4 H, 2_B-H, 3_B-H, 4_B-H, 5_A-H), 4.76 (s, 1 H, 1_B-H), 4.69 (d, J_{gem} = 11.7 Hz, 1 H, OC*H*HPh), 4.60 (d, J_{gem} = 11.7 Hz, 1 H, OC*H*HPh), 4.36 (dd, $J_{4,5}$ = 7.2, $J_{4,3}$ = 4.5 Hz, 1 H, 4_A-H), 4.29 (d, $J_{3,4}$ = 4.5 Hz, 1 H, 3_A-H), 4.08 (s, 1 H, 2_A-H), 3.79 (dq, $J_{5,4}$ = 9.3, $J_{5,6}$ = 6.3 Hz, 1 H, 5_B-H), 2.15, 2.09, 2.06, 2.04, 1.98 (5 s, 15 H, 5 CH_3CO), 1.38 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_A-H), 1.24 (d, $J_{6,5}$ = 6.3 Hz, 3 H, 6_B-H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) (β-anomer): δ = 170.1–169.6 (5 CO), 136.8 (C_{ipso}-Bn), 128.5–127.7 (C-Ar), 99.2 (C-1_B), 95.8 (C-1_A), 84.2, 83.6, 76.9, 72.4, 70.6, 69.8, 68.9, 68.5, 67.5 (C-2_A, C-2_B, C-3_A, C-3_B, C-4_A, C-4_B, C-5_A, C-5_B, O*C*H_2Ph), 21.3–20.7 (5 *C*H_3CO), 17.6, 17.2 (C-6_A, C-6_B) ppm. MS (MALDI-TOF): calcd. for $C_{29}H_{38}O_{14}$ $[M]^+$ 610.23; found 632.97 $[M + Na]^+$. $C_{29}H_{38}O_{14}$ (610.60): calcd. C 57.04, H 6.27; found C 57.00, H 6.24.

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