

Synthesis of β -D-Ribofuranosyl-(1 $\rightarrow$ 3)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-L-rhamnopyranose by in situ Activating Glycosylation Using 1-OH Sugar Derivative and Me_3SiBr – CoBr_2 – Bu_4NBr –Molecular Sieves 4A System

Motoko Hirooka,* Yoko Mori, Akiko Sasaki, Shinkiti Koto,* Yoshika Shinoda, and Aya Morinaga

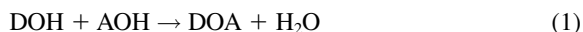
School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108-8641

(Received February 14, 2001)

β -D-Ribofuranosyl-(1 $\rightarrow$ 3)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-L-rhamnopyranose, the trisaccharide repeating unit of the *C. freundii* O28,1c O-specific polysaccharide, was synthesized using in situ activating glycosylation of the 1-OH sugar derivatives and a reagent mixture of trimethylsilyl bromide, cobalt(II) bromide, tetrabutylammonium bromide, and molecular sieves 4A. Regioselective tritylation was useful for synthesizing the 3-OH derivatives of methyl, allyl, and benzyl α -L-rhamnosides.

The development of new methods for glycosylation has always been important in synthetic carbohydrate chemistry.¹ Several modern glycosylation reactions giving high yield with high stereoselectivity have been established.² In addition, recent efforts to simplify the glycosylation procedure have developed various kinds of in situ activating glycosylations using a 1-OH sugar derivative and a reagent mixture.³ However, such methods have not been well applied for oligosaccharide synthesis.⁴ We wish to report on new results of the application of a reagent system⁵ (TCTM system) consisting of trimethylsilyl bromide (Me_3SiBr), cobalt(II) bromide, tetrabutylammonium bromide (TBAB), and molecular sieves 4A (MS4A) to oligosaccharide synthesis.

The TCTM system⁵ is an in situ activating reagent system⁶ for a 1-OH sugar derivative, such as 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (DOH), as a donor in the presence of an acceptor (AOH) to give an anomeric mixture of the corresponding glycosides DOA (Eq. 1).



This reaction can be conducted at room temperature. This is a convenient reaction, because an acceptor can be added into the reaction system *before* adding of the activating reagent(s) for the donor (*one-pot-one-stage* method).^{6b} We have now applied the TCTM system to 2,3,5-tri-*O*-benzyl-D-ribofuranose (**1**)⁷ and 2,3,4-tri-*O*-benzyl-L-rhamnopyranose (**2**)^{8,9} (Fig. 1) in their condensation with model acceptors, such as cyclohexyl-methanol (CmOH), cyclohexanol (ChOH), methyl 2,3,4-tri-*O*-benzyl- β -D-glucopyranoside (**3**),¹⁰ and methyl 2,3,6-tri-*O*-benzyl- β -D-glucopyranoside (**4**).¹¹ The results summarized in Table 1 show that the ribosyl donor **1** gives the corresponding glycosides with β -selectivity (Runs 1–8). In the case of Run 5 using acceptor **3** in dichloromethane as a solvent, a small amount of methyl riboside **9** was formed. There have been reported in situ activating β -D-ribofuranosylations using the lactol **1**.^{3x} The present case is a new example of β -D-ribofuranosylations.

On the other hand, the L-rhamnosyl donor **2** produces its α - or β -glycoside as a main condensate, depending on the acceptor used (Runs 9–16). The reaction with **4** (Runs 15 and 16) showed almost complete α -selectivities. 1,2-Dichloroethane instead of dichloro-methane⁵ as the solvent raised yields of glycosides (Runs 6, 8, 14, and 16). A self-condensation product **14** was formed^{4a} in the case of a less-reactive acceptor **4** in dichloromethane (Run 15).

The results mentioned above prompted us to synthesize β -D-ribofuranosyl-(1 $\rightarrow$ 3)- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-L-rhamnopyranose (**15**)¹² (Fig. 2) and the related oligosaccharides to show the utility of the TCTM system. The trisaccharide **15** is a trisaccharide repeating unit of the *C. freundii* O28,1c O-specific polysaccharide. To our knowledge, **15** has not been synthesized.

First, we tried to synthesize various protected disaccharides (**16b**, **17b**, **18b**, **19**, and **20a**) to check the feasibility of this plan (Fig. 3). All of these disaccharides are structurally related to the above-described polysaccharide. For this purpose, donors **21** and **22** as well as acceptors **23**, **24**, **25**, and **26** were conveniently prepared as described below.

The ribofuranose derivatives, **21** and **23**, were prepared from known monobenyl ether **27**.¹³ It was found that a tin-mediated monobenzoylation of **27** afforded the desired 2-OH derivative **23** in 54% yield. The reaction was not regioselective to give by-product **28** in 45% yield. However, tin-mediation was essential to avoid the dibenzoylation of **27**. Allylation of **23** afforded **29**, which was hydrolyzed into **21**; the yield from **27** was 42%.

Some years ago, we synthesized the donor **22**⁹ via the regioselective tritylation¹⁴ of 2-methoxyethyl α -L-rhamnopyranoside, and showed the utility of the trityl group at the secondary OH group. For an extension of the utility of such tritylation,¹⁴ an analogous tritylation¹⁵ of **30**¹⁶ was performed. The desired 3-*O*-trityl ether **31** was obtained mainly in 76% yield; the by-product was 2-*O*-substituted **32**. Compound **31** was benzylated and then hydrolyzed to afford the 3-OH derivative **24**. Ally-

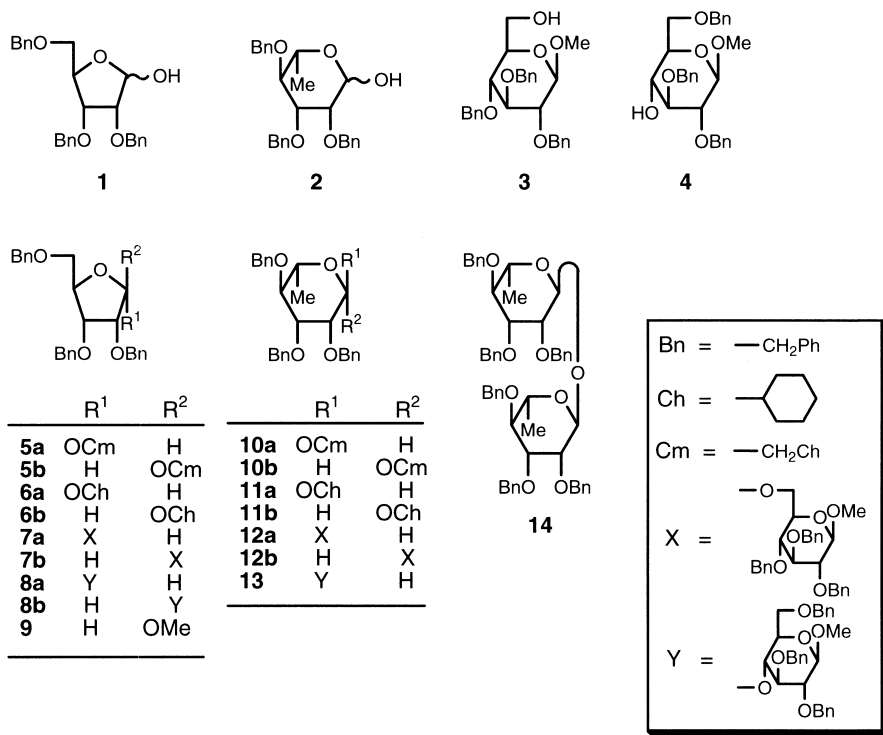


Fig. 1. Syntheses of D-ribofuranosides and L-rhamnopyranosides.

Table 1. Results of Glycosylation Using the TCTM System^{a),b)}

Run	Donor	Acceptor	Glycosides	Solvent	Yield/% (α/β)
1	1	CmOH	5a + 5b	M	91 (10/90)
2	1	CmOH	5a + 5b	E	80 (16/84)
3	1	ChOH	6a + 6b	M	70 (15/85)
4	1	ChOH	6a + 6b	E	68 (25/75)
5	1	3	7a + 7b	M	61 (21/79) ^{c)}
6	1	3	7a + 7b	E	77 (31/69)
7	1	4	8a + 8b	M	54 (49/51)
8	1	4	8a + 8b	E	75 (45/55)
9	2	CmOH	10a + 10b	M	96 (20/80)
10	2	CmOH	10a + 10b	E	88 (36/64)
11	2	ChOH	11a + 11b	M	96 (71/29)
12	2	ChOH	11a + 11b	E	94 (75/25)
13	2	3	12a + 12b	M	59 (39/61)
14	2	3	12a + 12b	E	81 (42/58)
15	2	4	13	M	65 ^{d)}
16	2	4	13	E	79

a) For acceptor (0.060 mmol), donor (1.3 eq), TMSBr (1.3 eq), CoBr₂ (1.3 eq), Bu₄NBr (1.3 eq), MS4A (2.0 mg/mg of donor), and solvent (0.30 mL) were used. The reactions were conducted under anhydrous conditions at 25 °C. b) ChOH = cyclohexanol, CmOH = cyclohexylmethanol, E = 1,2-dichloroethane, M = dichloromethane. c) **9** was isolated (8% yield). d) **14** was isolated (> 20% yield).

lation of **24** furnished **33**, which was hydrolyzed into the 1-OH derivative **22** in 30% yield from **30**. It was found that a tin-mediated alkylation¹⁷ of **30** selectively formed the 3-O-allyl derivative **34**, the precursor of **33**. The yield of **22** from **30** by this short route was 22% yield. A regioselective tritylation was also applied to the other rhamnosides, **36** and **38**, to yield the 3-O-trityl compound **37** (82%) and **40** (74%), respectively. Similar to the case of **24**, **37** and **40** were readily transformed

into the 3-OH derivatives, **25** and **26**, respectively. In preparing rhamnosides **30**, **36**, and **38**, methanesulfonic acid as catalyst was a good substitute for pungent hydrogen chloride.

For the disaccharide synthesis, β -D-ribofuranosylation reactions were first carried out. Condensation between **1** and **24** in the presence of the TCTM system stereoselectively gave the desired **16b** in ca. 40% yield (Table 2, Runs 1 and 2). A similar glycosylation of **25** with **1** afforded **17b** as the main con-

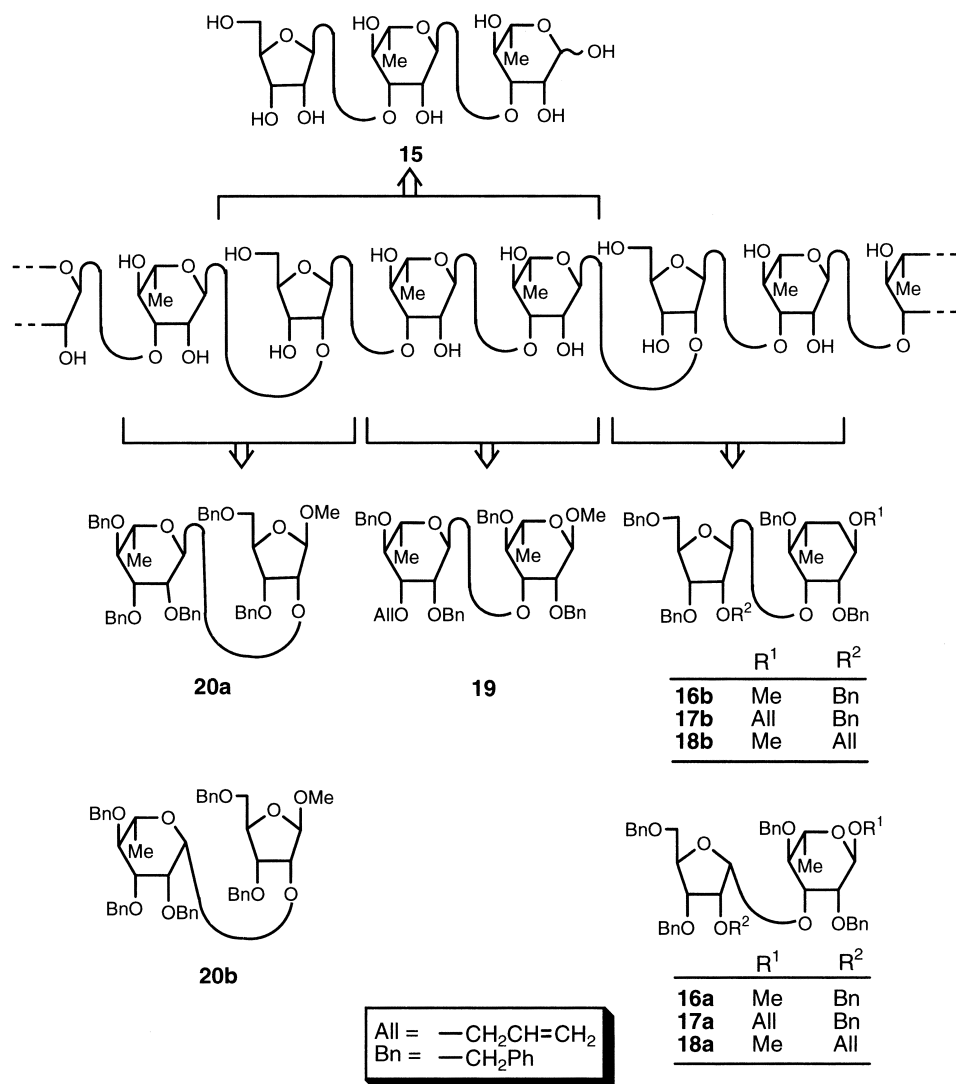
Fig. 2. The *C. freundii* O28, 1c O-specific polysaccharide and the related oligosaccharide fragments.

Table 2. Results of Oligosaccharide Synthesis Using the TCTM System

Run	DOH	mg	AOH	mg	Solvent ^{a)}	DOA	%(α/β)
1	1	39.4	24	33.6	M	16a + 16b	53 (21/79)
2	1	38.7	24	33.0	E	16a + 16b	56 (23/77)
3	1	43.5	25	39.8	M	17a + 17b	46 (30/70)
4	1	41.2	25	37.7	E	17a + 17b	59 (32/68)
5	21	90.4	24	89.8	M	18a + 18b	77 (48/52)
6	21	33.1	24	31.7	E	18a + 18b	57 (46/54)
7	22	223.1	24	208.0	E	19	50
8	2	66.5	23	52.7	M	20a + 20b	59 (73/27)
9	1	25.1	41	40.8	E	42	45
10	43	34.0	24	16.4	E	42	40
11	43	36.5	26	21.2	E	45	42
12	43	41.8	25	21.5	E	46	52

a) E = 1,2-dichloroethane, M = dichloromethane.

densate (Run 3). The use of 1,2-dichloroethane slightly increased the yields of the glycosides (Run 4). Glycosylation of **24** with **21** having an allyl group instead of a benzyl group at the C-2 position yielded **18b** with poor stereoselectivity (Runs

5 and 6). An α -L-Rhamnopyranosylation reaction of **24** was also performed using **22** and the TCTM system to afford the desired **19** in 50% yield with complete selectivity (Run 7). However, a similar reaction using **2** and **23** did not produce the

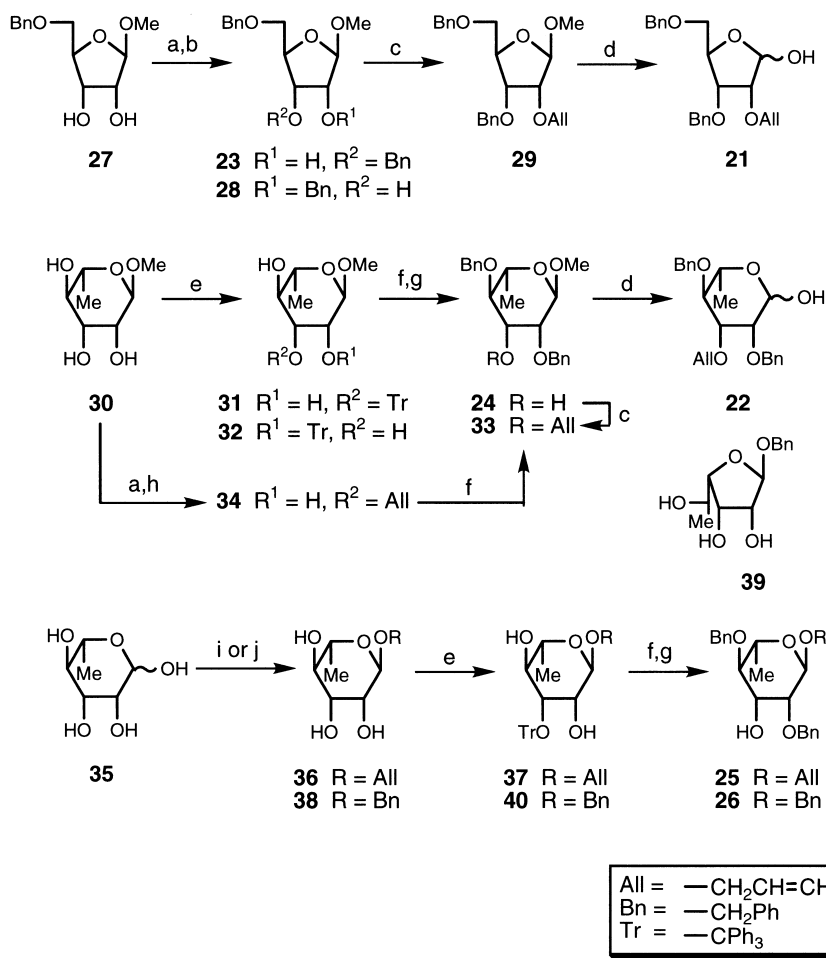


Fig. 3. The synthetic routes to the monosaccharide building units: a. BnBr, Bu₄NBr, Bu₂SnO, MS4A/C₆H₆, Δ ; b. AllBr, NaH/ Δ ; c. aq AcOH (80%), H₂SO₄/ Δ ; d. TrCl, C₅H₅N/ Δ ; e. BnBr, NaH/DMF, 0 $^\circ\text{C}$ $\rightarrow$ room temperature (rt); f. MeOH, CF₃CO₂H/CHCl₃, rt; g. Bu₂SnO/MeOH, Δ ; h. AllBr/DMF; i. AllOH, MeSO₃H/ Δ ; j. BnOH, MeSO₃H/ Δ ; k. (i) AcBr/AcOH, 0 $^\circ\text{C}$, (ii) BnOH, Hg(CN)₂/MeNO₂, rt, (iii) dil NaOMe, rt.

glycosides stereoselectively (Run 8).

To build-up the trisaccharides, deallylation using palladium(II) chloride¹⁸ effectively converted **19** into the disaccharide acceptor **41** in 81% yields (Fig. 4). Condensation of **41** with **1** proceeded with complete β -selectivity to give **42** in 45% yield (Run 9). This was also obtained by way of a stereoselective condensation of the resulting disaccharide donor **43**, the deallylated product of **17b**, with **24** (Run 10). Catalytic debenzyla-tion of **42** afforded the methyl glycoside **44**. The structure of the synthesized **44** was assigned by the determination of its ¹H and ¹³C NMR spectra in D₂O. The signal at δ 111.2 indicates the β -ribofuranosyl structure.^{19a} The $J_{\text{C1,H1}}$ values, 169.6 Hz and 170.9 Hz, show the α -pyranosyl frameworks.^{19b} The NOE's were observed between H1^{II} and H3^I as well as between H1^{III} and H3^{II}. This indicates linkage 1^{II} to the 3^I linkage and linkage 1^{III} to the 3^{II} linkage. These linkages were also assigned by GHMQC experiments; three-bond cross peaks were seen between H1^{II} and C3^I as well as between H1^{III} and C3^{II}. The condensation of **26** with the disaccharide donor **43** in the presence of the TCTM system proceeded well to give the desired trisaccharide derivative **45** in 42% yield (Run 11). Debenzyla-tion of **45** gave the desired free trisaccharide **15**. The

condensation of **25** and **43** furnished **46** (Run 12). Deallylation of **46** yielded the trisaccharide donor **47**. Catalytic debenzyla-tion of **47** afforded the above-described **15**. The ¹H and ¹³C NMR spectra determined in D₂O of the synthesized trisaccha-ride **15** were consistent with its structure. The β -furanosyl structure was assigned by the signal at δ 110.5.^{19a} The $J_{\text{C1,H1}}$ value, 170.1 Hz, of C1^{II} indicates an α -rhamnopyranosyl link-age.^{19b} NOE experiments as well as GHMQC experiments gave results consistent with the structure of **15**.

Two methyl glycosides of the disaccharide, which are struc-turally related to **15**, were synthesized. Debenzyla-tion of **20a** gave the methyl glycoside **48**. A similar debenzyla-tion of **16b** afforded the other disaccharide **49**. Deallylation of **18b** and subsequent debenzyla-tion also afforded **49**. The structures of the methyl glycosides, **47** and **49**, were confirmed by determin-ing their ¹H and ¹³C NMR spectra in D₂O.

In summary, the TCTM system was useful for β -D-ribofura-nosylation and α -L-rhamnopyranosylation. The utility of the TCTM system was shown in the first synthesis of the trisac-charide **15** as well as its methyl glycoside **44**. Through this work, the convenience of regioselective 3-*O*-tritylation^{9,14} of α -L-rhamnopyranosides **30**, **36**, and **38**, as well as of tin-medi-

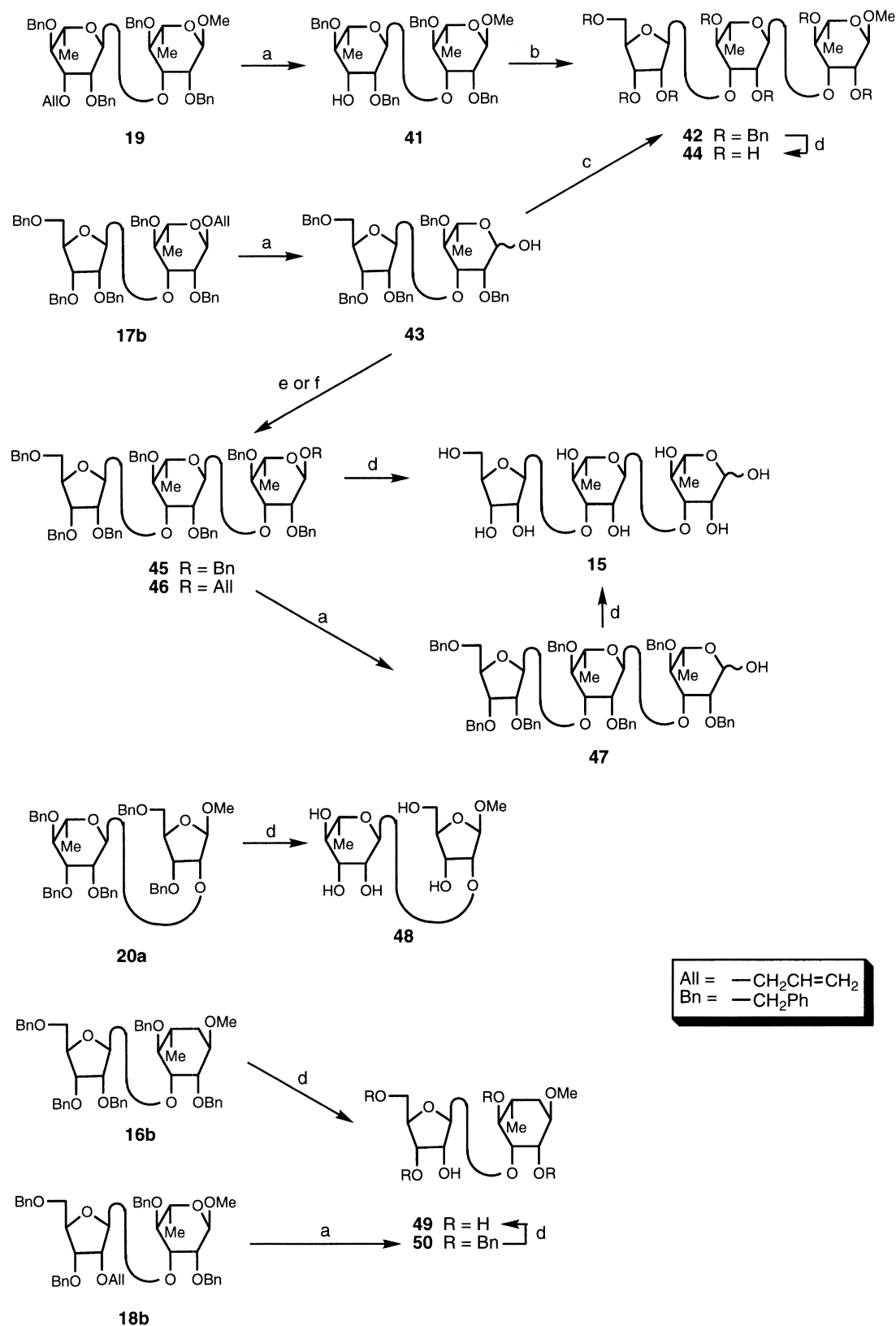


Fig. 4. Synthesis of β -D-Ribf-(1 $\rightarrow$ 3)- α -L-Rhap-(1 $\rightarrow$ 3)-L-Rhap and the related glycosides (TCTM = $\text{Me}_3\text{SiBr} + \text{CoBr}_2 + \text{Bu}_4\text{NBr} + \text{MS4A}$): a. PdCl_2 , $\text{NaOAc}/\text{aq AcOH}$ (95%), rt; b. **1**, TCTM/ $(\text{CH}_2\text{Cl}_2)_2$, rt; c. **24**, TCTM/ $(\text{CH}_2\text{Cl}_2)_2$, rt; d. H_2 , Pd-C (10%)/MeOH, rt; e. **26**, TCTM/ $(\text{CH}_2\text{Cl}_2)_2$, rt; f. **25**, TCTM/ $(\text{CH}_2\text{Cl}_2)_2$, rt.

ated alkylations of **27** and **30** were shown.

Experimental²⁰

The solvent systems for column chromatography on silica gel (Kanto Chemical, No. 37047; gradient elution) and thin-layer chromatography (TLC) (Merck, DC-Plastikfolien Kieselgel 60 F₂₅₄, Art. 5735) were chloroform–MeOH (CM), 1,2-dichloroethane–AcOEt (DE), AcOEt–MeOH (EM), hexane–AcOEt (HE), and PhMe–2-butanone (TK). Hydrogenolytic debenzylation was carried out using a Parr-3911 hydrogenation apparatus under 340 kPa of H₂ at room temperature. Evaporation was carried out under reduced pressure. The optical rotations were measured on a JASCO DIP-180 Digital Polarimeter at room temperature (20–25 °C), unless otherwise specified. The ¹H and ¹³C NMR spectra were recorded with a Varian VXR300 spectrometer or a Varian XL-400 spectrometer, along with measurements of the H,H-COSY, C,H-COSY, and DEPT spectra. For assigning of the anomeric configuration of the rhamnosides, their $J_{C1,H1}$ values^{19b} were determined by gated decoupling with the NOE experiment. The assignments of the spectra of **15** and **44** were made by auxiliary measurements of HOHAHA, NOE difference, and HMQC spectra.

L-Rhamnose (**35**, monohydrate) and NaH (ca. 60% dispersion in oil) were products of Wako Pure Chemicals Industries. Compounds **1**,⁷ **2**,⁹ **3**,¹⁰ **4**,¹¹ and **27**¹³ were prepared by known methods. Trimethylsilyl bromide (Me₃SiBr), CoBr₂, and tetrabutylammonium bromide (Bu₄NBr) were products from Wako Pure Chemicals Industries. Molecular sieves, 4A, powder (MS4A) was bought from Hydrys Chemical, Inc.

The preparation of the acetates of **23**, **24**, **25**, **26**, **28**, **31**, **32**, **34**, **37**, and **40** was carried out as follows: a sample (ca. 20 mg) was treated with Ac₂O (0.2 mL) and pyridine (0.2 mL) containing one drop of Et₃N, at room temp overnight, quenched with EtOH (0.2 mL) at 20 °C, evaporated to dryness, and chromatographed using the HE system (3:1) to give a chromatographically pure acetate. All of the thus-obtained acetates were usable for determining their NMR spectra without their elemental analyses.

Glycosylation. To a vessel containing a donor (1.0–1.3 eq), an acceptor, CoBr₂ (1.3 eq), Bu₄NBr (1.3 eq), MS4A (2.0 mg/mg of donor), and solvent (5–10 mL/mmol of acceptor), TMSBr (1.3 eq) was added under stirring at room temp (ca. 25 °C). The mixture was stirred for 16–24 h under anhydrous conditions. To the mixture, PhMe and NaHCO₃ were added; the mixture was then stirred for 15 min and transferred onto a silica-gel column, which was subsequently eluted with the TK system (gradient) to give an anomeric mixture of glycosides. This was further separated with the solvent system specified below. The results are summarized in Tables 1 and 2.

Cyclohexylmethyl 2,3,5-Tri-O-benzyl- α - and β -D-ribofuranosides (5a and 5b). **5a** (the slower-moving (TK 20:1)): [α]_D²³ +57° (c 0.3, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 3.39 (dd, $J_{4,5a}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a), 3.47 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b), 3.78 (dd, $J_{1,2}$ = 4 Hz, $J_{2,3}$ = 6.5 Hz, H2), 3.84 (dd, $J_{2,3}$ = 6.5 Hz, $J_{3,4}$ = 4 Hz, H3), 4.22 (dt, $J_{3,4}$ = $J_{4,5a}$ = $J_{4,5b}$ = 4 Hz, H4), 4.98 (d, $J_{1,2}$ = 4 Hz, H1); ¹³C NMR (CDCl₃, 75 MHz) δ 70.2 (C5), 75.8 (C3), 77.7 (C2), 81.3 (C4), 101.6 (C1, $J_{C1,H1}$ = 170.4 Hz); 25.8, 25.9, 26.7, 30.2 (2C), 37.8, 74.0 (cyclohexylmethyl); MS (FAB) m/z 539.2773 (M+Na)⁺. Calcd for C₃₃H₄₀O₅Na: 539.27733.

5b: [α]_D²³ +17° (c 1.9, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 3.52 (dd, $J_{4,5a}$ = 6 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a), 3.61 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b), 3.87 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4.5 Hz,

H2), 4.02 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 7 Hz, H3), 4.35 (ddd, $J_{3,4}$ = 7 Hz, $J_{4,5a}$ = 6.0 Hz, $J_{4,5b}$ = 4 Hz, H4), 5.00 (d, $J_{1,2}$ = 1 Hz, H1); ¹³C NMR (CDCl₃, 75 MHz) δ 71.7 (C5), 79.0 (C3), 80.0 (C2), 80.4 (C4), 105.6 (C1, $J_{C1,H1}$ = 171.0 Hz); 25.8 (2C), 26.6, 30.0 (2C), 37.8, 73.6 (cyclohexylmethyl).

Found: C, 76.65; H, 8.02%. Calcd for C₃₃H₄₀O₅: C, 76.71; H, 7.80%.

Cyclohexyl 2,3,5-Tri-O-benzyl- α - and β -D-ribofuranosides (6a and 6b). **6a** (the slower-moving (TK 20:1)): [α]_D²⁰ +62° (c 0.4, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 3.38 (dd, $J_{4,5a}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a), 3.47 (dd, $J_{4,5b}$ = 3.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b), 3.77 (dd, $J_{1,2}$ = 4 Hz, $J_{2,3}$ = 6.5 Hz, H2), 3.85 (dd, $J_{2,3}$ = 6.5 Hz, $J_{3,4}$ = 4 Hz, H3), 4.24 (dt, $J_{3,4}$ = $J_{4,5a}$ = 4 Hz, $J_{4,5b}$ = 3.5 Hz, H4), 5.18 (d, $J_{1,2}$ = 4 Hz, H1); ¹³C NMR (CDCl₃, 75 MHz) δ 70.1 (C5), 75.8 (C3), 77.5 (C2), 80.9 (C4), 99.7 (C1, $J_{C1,H1}$ = 167.9 Hz); 24.4, 24.5, 25.7, 32.0, 33.8, 76.2 (cyclohexyl); MS (FAB) m/z 525.2617 (M+Na)⁺. Calcd for C₃₂H₃₈O₅Na: 525.26168.

6b: [α]_D²³ –1.3° (c 1.4, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 3.53 (dd, $J_{4,5a}$ = 6 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a), 3.61 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b), 3.85 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 5 Hz, H2), 4.02 (dd, $J_{2,3}$ = 5 Hz, $J_{3,4}$ = 6.5 Hz, H3), 4.33 (ddd, $J_{3,4}$ = 6.5 Hz, $J_{4,5a}$ = 6.0 Hz, $J_{4,5b}$ = 4 Hz, H4), 5.18 (d, $J_{1,2}$ = 1.5 Hz, H1); ¹³C NMR (CDCl₃, 75 MHz) δ 71.8 (C5), 78.9 (C3), 80.2 (C4), 80.4 (C2), 103.3 (C1, $J_{C1,H1}$ = 171.0 Hz); 24.0, 24.2, 25.7, 31.5, 33.6, 75.2 (cyclohexyl).

Found: C, 76.21; H, 7.61%. Calcd for C₃₂H₃₈O₅: C, 76.46; H, 7.62%.

Methyl O-(2,3,5-Tri-O-benzyl- α - and β -D-ribofuranosyl-(1 $\rightarrow$ 6)-2,3,4-tri-O-benzyl- β -D-glucopyranosides (7a and 7b). **7a** (the slower-moving (TK 20:1)): [α]_D²⁰ +34° (c 0.5, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 3.34 (dd, $J_{1,2}$ = 8 Hz, $J_{2,3}$ = 9 Hz, H2^I), 3.38 (ddd, $J_{4,5}$ = 9 Hz, $J_{5,6a}$ = 2 Hz, $J_{5,6b}$ = 4 Hz, H5^I), 3.45 (dd, $J_{4,5a}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a^{II}), 3.48 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b^{II}), 3.53 (s, Me), 3.60 (t, $J_{2,3}$ = $J_{3,4}$ = 9 Hz, H3^I), 3.73 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^I), 3.80 (dd, $J_{5,6a}$ = 2 Hz, $J_{6a,6b}$ = 11.5 Hz, H6a^I), 3.88 (dd, $J_{1,2}$ = 3 Hz, $J_{2,3}$ = 3.5 Hz, H2^{II}), 3.89 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 7 Hz, H3^{II}), 4.11 (dd, $J_{5,6b}$ = 4 Hz, $J_{6a,6b}$ = 11.5 Hz, H6b^I), 4.24 (dt, $J_{3,4}$ = 7 Hz, $J_{4,5a}$ = $J_{4,5b}$ = 4 Hz, H4^{II}), 4.30 (d, $J_{1,2}$ = 8 Hz, H1^I), 5.17 (d, $J_{1,2}$ = 3 Hz, H1^{II}); ¹³C NMR (CDCl₃, 75 MHz) δ 56.9 (Me), 66.8 (C6^I), 70.0 (C5^{II}), 74.7 (C5^I), 76.2 (C3^{II}), 77.8 (C4^I), 78.0 (C2^{II}), 81.5 (C4^{II}), 82.4 (C2^I), 84.6 (C3^I), 102.2 (C1^{II}, $J_{C1,H1}$ = 169.5 Hz), 104.6 (C1^I, $J_{C1,H1}$ = 159.1 Hz).

7b: [α]_D²¹ +8° (c 0.8, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 3.39 (m, H5^I), 3.42 (t, $J_{1,2}$ = $J_{2,3}$ = 8 Hz, H2^I), 3.45 (dd, $J_{3,4}$ = 8 Hz, $J_{4,5}$ = 9 Hz, H4^I), 3.51 (s, Me), 3.56 (dd, $J_{4,5a}$ = 6.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a^{II}), 3.60 (t, $J_{2,3}$ = $J_{3,4}$ = 8 Hz, H3^I), 3.63 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b^{II}), 3.90 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4.5 Hz, H2^{II}), 4.05 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 6.5 Hz, H3^{II}), 4.26 (d, $J_{1,2}$ = 8 Hz, H1^I), 4.36 (dt, $J_{3,4}$ = $J_{4,5a}$ = 6.5 Hz, $J_{4,5b}$ = 4 Hz, H4^{II}), 5.10 (d, $J_{1,2}$ = 1 Hz, H1^{II}); ¹³C NMR (CDCl₃, 75 MHz) δ 56.9 (Me), 66.8 (C6^I), 71.7 (C5^{II}), 74.4 (C5^I), 78.1 (C4^I), 78.9 (C3^{II}), 79.9 (C2^{II}), 80.7 (C4^{II}), 82.3 (C2^I), 84.6 (C3^I), 104.5 (C1^I, $J_{C1,H1}$ = 155.9 Hz), 105.8 (C1^{II}, $J_{C1,H1}$ = 171.6 Hz). Found: **7a**: C, 74.22; H, 6.89%. **7b**: C, 74.47; H, 6.84%. Calcd for C₅₄H₅₈O₁₀: C, 74.80; H, 6.74%.

Methyl O-(2,3,5-Tri-O-benzyl- α - and β -D-ribofuranosyl-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranosides (8a and 8b). **8a** (the slower-moving (TK 20:1)): [α]_D²¹ +31° (c 0.7, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 3.42 (dd, $J_{1,2}$ = 8 Hz, $J_{2,3}$ = 9 Hz, H2^I), 3.61 (s, Me), 3.66 (dd, $J_{1,2}$ = 4.5 Hz, $J_{2,3}$ = 6.5 Hz, H2^{II}),

3.74 (dd, $J_{2,3} = 6.5$ Hz, $J_{3,4} = 2$ Hz, H3^H), 3.77 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4^L), 3.82 (t, $J_{2,3} = J_{3,4} = 9$ Hz, H3^L), 4.08 (dt, $J_{3,4} = 2$ Hz, $J_{4,5a} = J_{4,5b} = 4$ Hz, H4^H), 4.35 (d, $J_{1,2} = 8$ Hz, H1^L), 5.56 (d, $J_{1,2} = 4.5$ Hz, H1^H); ¹³C NMR (CDCl₃, 75 MHz) δ 57.1 (Me), 70.1 (C6^L), 70.3 (C5^H), 74.2 (C5^L), 74.3 (C4^L), 75.0 (C3^H), 77.3 (C2^H), 82.3 (C4^H), 82.4 (C2^L), 84.4 (C3^L), 101.8 (C1^H, $J_{C1,H1} = 175.2$ Hz), 104.6 (C1^L, $J_{C1,H1} = 158.1$ Hz); MS (FAB) m/z 889.3928 (M+Na)⁺. Calcd for C₅₄H₅₈O₁₀Na: 889.39273.

8b: [α]_D²¹ +9° (c 9, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 3.39 (dd, $J_{1,2} = 7.5$ Hz, $J_{2,3} = 9$ Hz, H2^L), 3.40 (ddd, $J_{4,5} = 9$ Hz, $J_{5,6a} = 4$ Hz, $J_{5,6b} = 2$ Hz, H5^L), 3.48 (d, $J_{4,5} = 5$ Hz, H5^H), 3.56 (s, Me), 3.59 (t, $J_{2,3} = J_{3,4} = 9$ Hz, H3^L), 3.64 (dd, $J_{5,6a} = 4$ Hz, $J_{6a,6b} = 11$ Hz, H6a^L), 3.70 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4^L), 3.73 (dd, $J_{5,6b} = 2$ Hz, $J_{6a,6b} = 11$ Hz, H6b^L), 3.82 (dd, $J_{1,2} = 3$ Hz, $J_{2,3} = 5$ Hz, H2^H), 3.93 (t, $J_{2,3} = J_{3,4} = 5$ Hz, H3^H), 4.23 (dt, $J_{3,4} = J_{4,5} = 5$ Hz, H4^H), 4.27 (d, $J_{1,2} = 7.5$ Hz, H1^L), 5.38 (d, $J_{1,2} = 3$ Hz, H1^H); ¹³C NMR (CDCl₃, 75 MHz) δ 56.9 (Me), 69.1 (C6^L), 70.9 (C5^H), 74.9 (C5^L), 76.7 (C4^L), 77.4 (C3^H), 80.4 (C2^H), 80.5 (C4^H), 82.3 (C2^L), 83.1 (C3^L), 104.6 (C1^L, $J_{C1,H1} = 154.2$ Hz), 106.5 (C1^H, $J_{C1,H1} = 169.0$ Hz).

Found: C, 74.13; H, 6.79%. Calcd for C₅₄H₅₈O₁₀: C, 74.80; H, 6.74%.

Methyl 2,3,5-Tri-*O*-benzyl- β -D-ribofuranoside (9). In the case of Run 5, **9** (8%) was eluted before the appearance of **7b**: [α]_D²⁵ +23° (c 0.5, 1,4-dioxane) (Ref. 7, [α]_D²⁰ +22.4° (c 3.6, 1,4-dioxane)); ¹H NMR (CDCl₃, 300 MHz) δ 3.32 (s, Me), 3.51 (dd, $J_{4,5a} = 6$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a), 3.61 (dd, $J_{4,5b} = 4$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b), 3.83 (dd, $J_{1,2} = 1$ Hz, $J_{2,3} = 4.5$ Hz, H2), 4.02 (dd, $J_{2,3} = 4.5$ Hz, $J_{3,4} = 7$ Hz, H3), 4.34 (ddd, $J_{3,4} = 7$ Hz, $J_{4,5a} = 6$ Hz, $J_{4,5b} = 4$ Hz, H4), 4.92 (d, $J_{1,2} = 1$ Hz, H1); ¹³C NMR (CDCl₃, 75 MHz) δ 55.1 (Me), 71.4 (C5), 78.5 (C3), 79.8 (C2), 80.5 (C4), 106.4 (C1); MS (FAB) m/z 457 (M+Na)⁺.

Cyclohexylmethyl 2,3,4-Tri-*O*-benzyl- α - and β -L-rhamnopyranosides (10a and 10b). **10a** (the faster-moving (TK 20:1)): [α]_D¹⁹ -2.5° (c 1.8, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 1.32 (d, $J_{5,6} = 6$ Hz, H6), 3.61 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4), 3.65 (dq, $J_{4,5} = 9$ Hz, $J_{5,6} = 6$ Hz, H5), 3.75 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2), 3.85 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.0$ Hz, H3), 4.70 (d, $J_{1,2} = 2$ Hz, H1); ¹³C NMR (CDCl₃, 75 MHz) δ 18.0 (C6), 68.0 (C5), 75.3 (C2), 80.3 (C3), 80.1 (C4), 98.1 (C1, $J_{C1,H1} = 165.8$ Hz); 25.8, 25.9, 26.6, 29.9, 30.1, 37.9, 73.1 (cyclohexylmethyl).

Found: C, 77.05; H, 8.23%. Calcd for C₃₄H₄₂O₅: C, 76.95; H, 7.98%.

10b: mp 80–83 °C; [α]_D +35° (c 1.0, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 1.39 (d, $J_{5,6} = 6$ Hz, H6), 3.31 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5), 3.45 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3), 3.63 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4), 3.91 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 3$ Hz, H2), 4.31 (s, H1); ¹³C NMR (CDCl₃, 75 MHz) δ 18.0 (C6), 72.0 (C5), 74.0 (C2), 80.3 (C4), 82.4 (C3), 102.0 (C1, $J_{C1,H1} = 151.7$ Hz); 25.9 (2C), 26.6, 29.9, 30.2, 38.2, 75.7 (cyclohexylmethyl); MS (FAB) m/z 553.2930 (M+Na)⁺. Calcd for C₃₄H₄₂O₅Na: 553.29297.

Cyclohexyl 2,3,4-Tri-*O*-benzyl- α - and β -L-rhamnopyranosides (11a and 11b). **11a** (the faster-moving (TK 20:1)): [α]_D²⁴ -20° (c 0.9, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 1.32 (d, $J_{5,6} = 6$ Hz, H6), 3.61 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4), 3.72 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2), 3.77 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5), 3.89 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3), 4.87 (d, $J_{1,2} = 2$ Hz, H1); ¹³C NMR (CDCl₃, 75 MHz) δ 18.0 (C6), 68.1 (C5), 75.8 (C2), 80.3 (C3), 80.8 (C4), 95.8 (C1, $J_{C1,H1} = 164.9$ Hz); 23.7, 24.0, 25.7, 31.3, 33.3, 74.6 (cyclohexyl).

11b: mp 80–82 °C; [α]_D +15° (c 0.4, CHCl₃); ¹H NMR

(CDCl₃, 300 MHz) δ 1.37 (d, $J_{5,6} = 6$ Hz, H6), 3.30 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5), 3.45 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3), 3.62 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4), 3.85 (dd, $J_{1,2} = 0.5$ Hz, $J_{2,3} = 3$ Hz, H2), 4.47 (d, $J_{1,2} = 0.5$ Hz, H1); ¹³C NMR (CDCl₃, 75 MHz) δ 18.1 (C6), 71.9 (C5), 74.6 (C2), 80.3 (C4), 82.5 (C3), 99.2 (C1, $J_{C1,H1} = 152.7$ Hz); 23.7, 23.8, 25.8, 31.5, 33.4, 76.2 (cyclohexyl).

Found: **11a**, C, 76.28; H, 7.81%. **11b**, C, 76.86; H, 7.99%. Calcd for C₃₃H₄₀O₅: C, 76.71; H, 7.80%.

Methyl *O*-(2,3,4-Tri-*O*-benzyl- α - and β -L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl- β -D-glucopyranosides (12a and 12b). **12a** (the faster-moving (TK 20:1)): [α]_D²³ -17° (c 0.3, CHCl₃) (Ref. 21a [α]_D¹⁶ -12.9° (c 2.05, CHCl₃)); ¹H NMR (CDCl₃, 300 MHz) δ 1.36 (d, $J_{5,6} = 6$ Hz, H6^H), 3.43 (t, $J_{1,2} = J_{2,3} = 8$ Hz, H2^L), 3.435 (dd, $J_{3,4} = 8$ Hz, $J_{4,5} = 9$ Hz, H4^L), 3.440 (m, H5^L), 3.54 (s, Me), 3.56 (dd, $J_{5,6a} = 6.5$ Hz, $J_{6a,6b} = 11.5$ Hz, H6a^L), 3.665 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4^H), 3.668 (t, $J_{2,3} = J_{3,4} = 8$ Hz, H3^L), 3.76 (t, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2^H), 3.81 (dq, $J_{4,5} = 9$ Hz, $J_{5,6} = 6$ Hz, H5^H), 3.92 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9$ Hz, H3^H), 3.93 (dd, $J_{5,6b} = 5$ Hz, $J_{6a,6b} = 11.5$ Hz, H6b^L), 4.31 (d, $J_{1,2} = 8$ Hz, H1^L), 4.80 (d, $J_{1,2} = 2$ Hz, H1^H); ¹³C NMR (CDCl₃, 75 MHz) δ 18.0 (C6^H), 56.8 (Me), 66.5 (C6^L), 68.1 (C5^H), 74.3 (C5^L), 75.2 (C2^H), 78.0 (C4^L), 79.9 (C3^H), 80.6 (C4^H), 82.3 (C2^L), 84.6 (C3^L), 98.5 (C1^H, $J_{C1,H1} = 167.0$ Hz), 104.5 (C1^L, $J_{C1,H1} = 158.5$ Hz).

12b: [α]_D²³ +24° (c 0.4, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 1.37 (d, $J_{5,6} = 6$ Hz, H6^H), 3.33 (dq, $J_{4,5} = 9$ Hz, $J_{5,6} = 6$ Hz, H5^H), 3.37 (ddd, $J_{4,5} = 9$ Hz, $J_{5,6a} = 2$ Hz, $J_{5,6b} = 3$ Hz, H5^L), 3.40 (t, $J_{1,2} = J_{2,3} = 8$ Hz, H2^L), 3.47 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9$ Hz, H3^H), 3.56 (s, Me), 3.61 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4^H), 3.64 (dd, $J_{2,3} = 8$ Hz, $J_{3,4} = 9$ Hz, H3^L), 3.71 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4^L), 3.78 (dd, $J_{5,6a} = 2$ Hz, $J_{6a,6b} = 11.5$ Hz, H6a^L), 4.00 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 3$ Hz, H2^H), 4.26 (dd, $J_{5,6b} = 3$ Hz, $J_{6a,6b} = 11.5$ Hz, H6b^L), 4.30 (d, $J_{1,2} = 8$ Hz, H1^L), 4.50 (s, H1^H); ¹³C NMR (CDCl₃, 75 MHz) δ 18.0 (C6^H), 57.2 (Me), 67.1 (C6^L), 72.0 (C5^H), 74.0 (C2^H), 74.6 (C5^L), 77.7 (C4^L), 80.3 (C4^H), 82.2 (C3^H), 82.4 (C2^L), 84.5 (C3^L), 101.6 (C1^H, $J_{C1,H1} = 152.9$ Hz), 104.9 (C1^L, $J_{C1,H1} = 153.7$ Hz).

Found: **12a**, C, 75.04; H, 6.99%. **12b**, C, 74.69; H, 6.96%. Calcd for C₅₅H₆₀O₁₀: C, 74.98; H, 6.86%.

Methyl *O*-(2,3,4-Tri-*O*-benzyl- α -L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl- β -D-glucopyranosides (13). [α]_D²⁰ -17° (c 2.4, CHCl₃) (Ref. 4a and 21b, [α]_D²⁰ -23° (c 2, CHCl₃), [α]_D²⁰ -15° (c 1, CHCl₃)); ¹H NMR (CDCl₃, 300 MHz) δ 1.08 (d, $J_{5,6} = 6$ Hz, H6^H), 3.35 (ddd, $J_{4,5} = 9$ Hz, $J_{5,6a} = 4$ Hz, $J_{5,6b} = 2$ Hz, H5^L), 3.502 (dd, $J_{1,2} = 7.5$ Hz, $J_{2,3} = 8$ Hz, H2^L), 3.503 (dd, $J_{5,6a} = 4$ Hz, $J_{6a,6b} = 10.5$ Hz, H6a^L), 3.53 (dd, $J_{2,3} = 8$ Hz, $J_{3,4} = 9$ Hz, H3^L), 3.58 (s, Me), 3.59 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^H), 3.62 (dd, $J_{5,6b} = 2$ Hz, $J_{6a,6b} = 10.5$ Hz, H6b^L), 3.73 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2^H), 3.79 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4^L), 3.83 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3^H), 3.93 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5^H), 4.31 (d, $J_{1,2} = 7.5$ Hz, H1^L), 5.09 (d, $J_{1,2} = 2$ Hz, H1^H); ¹³C NMR (CDCl₃, 75 MHz) δ 17.8 (C6^H), 56.9 (Me), 68.7 (C5^H), 69.0 (C6^L), 75.10 (C2^H), 75.14 (C5^L), 75.4 (C4^L), 79.7 (C3^H), 80.7 (C4^H), 82.6 (C2^L), 82.7 (C3^L), 98.4 ($J_{C1,H1} = 167.6$ Hz), 104.7 (C1^L, $J_{C1,H1} = 158.2$ Hz).

Found: C, 75.10; H, 7.03%. Calcd for C₅₅H₆₀O₁₀: C, 74.98; H, 6.86%.

The β -(1→4)-linked disaccharide derivative (< 4% in Run 15 and < 6% in Run 16: ¹³C NMR (CDCl₃, 75 MHz) δ 98.8 (C1^H), 104.6 (C1^L); MS (FAB) m/z 903 (M+Na)⁺) could not be isolated in pure state.

***O*-(2,3,4-Tri-*O*-benzyl- α -L-rhamnopyranosyl-(1→1)-2,3,4-Tri-*O*-benzyl- α -L-rhamnopyranoside (14)**. In the case of Run 15, **14** (20%) was eluted after the appearance of **13**: [α]_D²² -27° (c

0.3, CHCl_3)[#] (Ref. 4a, $[\alpha]_{\text{D}}^{20} -74^\circ$ (c 0.9, CHCl_3)); ^1H NMR (CDCl_3 , 300 MHz) δ 1.25 (d, $J_{5,6} = 6$ Hz, H6), 3.41 (dq, $J_{4,5} = 9$ Hz, $J_{5,6} = 6$ Hz, H5), 3.57 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2), 3.59 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4), 3.67 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.0$ Hz, H3), 4.96 (d, $J_{1,2} = 2$ Hz, H1); ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.0 (C6), 68.7 (C5), 74.4 (C2), 79.5 (C3), 80.4 (C4), 93.5 (C1, $J_{\text{C1,H1}} = 168.9$ Hz); MS (FAB) m/z 873 (M+Na)⁺.

Methyl 2,5- and 3,5-Di-O-benzyl- β -D-ribofuranosides (28 and 23). A mixture of **27**¹³ (3.14 g, 12.3 mmol), Bu_2SnO (4.13 g, 16.6 mmol), Bu_4NBr (4.13 g, 12.8 mmol), BnBr (6.9 mL, 58 mmol), PhH (69 mL), and MS4A (13.8 g) was refluxed for 2 h under stirring. After evaporation to dryness, the residue was chromatographed with the TK system (10:1) to give **28** (1.9 g, 45%), and **23** (2.3 g, 54%).

23: $[\alpha]_{\text{D}}^{25} -23^\circ$ (c 0.5, CHCl_3) (Ref. 22, $[\alpha]_{\text{D}} +17.4^\circ$ (c 0.4, CHCl_3)); ^1H NMR (CDCl_3 , 300 MHz) δ 2.71 (d, $J_{2,\text{OH}} = 3$ Hz, OH), 3.32 (s, Me), 3.55 (2H, d, $J_{4,5} = 5.5$ Hz, H5), 4.03 (dd, $J_{1,2} = 0$ Hz, $J_{2,3} = 5$ Hz, $J_{2,\text{OH}} = 3$ Hz, H2); 4.08 (dd, $J_{2,3} = 5$ Hz, $J_{3,4} = 6$ Hz, H3), 4.24 (dt, $J_{3,4} = 6$ Hz, $J_{4,5} = 5.5$ Hz, H4), 4.87 (s, H1); ^{13}C NMR (CDCl_3 , 75 MHz) δ 55.0 (Me), 71.6 (C5), 73.4 (C2), 79.6 (C3), 80.6 (C4), 108.6 (C1).

Found: C, 69.97; H, 7.16%. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_5$: C, 69.75; H, 7.02%.

28: $[\alpha]_{\text{D}}^{22} +13^\circ$ (c 2, CHCl_3) (Ref. 23, $[\alpha]_{\text{D}}^{20} +4^\circ$ (c 1, CHCl_3)); ^1H NMR (CDCl_3 , 300 MHz) δ 2.59 (d, $J_{3,\text{OH}} = 8.5$ Hz, OH), 3.34 (s, Me), 3.55 (dd, $J_{4,5a} = 6$ Hz, $J_{5a,5b} = 11$ Hz, H5a), 3.67 (dd, $J_{4,5b} = 4$ Hz, $J_{5a,5b} = 11$ Hz, H5b), 3.87 (dd, $J_{1,2} = 1$ Hz, $J_{2,3} = 5$ Hz, H2), 4.10 (dt, $J_{3,4} = J_{4,5a} = 6$ Hz, $J_{4,5b} = 4$ Hz, H4), 4.17 (ddd, $J_{2,3} = 5$ Hz, $J_{3,4} = 6$ Hz, $J_{3,\text{OH}} = 8.5$ Hz, H3); 4.92 (d, $J_{1,2} = 1$ Hz, H1); ^{13}C NMR (CDCl_3 , 75 MHz) δ 55.2 (Me), 71.6 (C5), 71.8 (C3), 82.0 (C2), 83.2 (C4), 105.8 (C1); MS (FAB) m/z 367.1521 (M+Na)⁺. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_5\text{Na}$: 367.15214.

The NMR data of the acetate of **23**: ^1H NMR (CDCl_3 , 300 MHz) δ 2.12 (s, Ac), 3.33 (s, Me), 3.50 (dd, $J_{4,5a} = 5.5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a), 3.61 (dd, $J_{4,5b} = 3.5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b); 4.13 (dd, $J_{2,3} = 4.5$ Hz, $J_{3,4} = 7.5$ Hz, H3), 4.22 (ddd, $J_{3,4} = 7.5$ Hz, $J_{4,5a} = 3.5$ Hz, $J_{4,5b} = 5.5$ Hz, H4), 4.88 (s, H1), 5.20 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 4.5$ Hz, H2), ^{13}C NMR (CDCl_3 , 75 MHz) δ 55.0 (Me), 71.1 (C5), 74.1 (C2), 77.9 (C3), 80.4 (C4), 106.3 (C1), 20.9, 170.0 (Ac).

The NMR data of the acetate of **28**: ^1H NMR (CDCl_3 , 300 MHz) δ 2.07 (s, Ac), 3.35 (s, Me), 3.57 (dd, $J_{4,5a} = 5.5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a), 3.61 (dd, $J_{4,5b} = 5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b), 4.09 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 5$ Hz, H2), 4.34 (dt, $J_{3,4} = J_{4,5b} = 5$ Hz, $J_{4,5a} = 5.5$ Hz, H4), 4.92 (d, $J_{1,2} = 2$ Hz, H1), 5.15 (t, $J_{2,3} = J_{3,4} = 5$ Hz, H3); ^{13}C NMR (CDCl_3 , 75 MHz) δ 55.4 (Me), 71.2 (C5), 73.4 (C3), 80.3 (C4), 80.9 (C2), 107.0 (C1), 20.8, 170.0 (Ac).

A sample (6.9 mg) of **23** was benzylated with PhCH_2Br (24 μL) and NaH (ca. 60%, 8.0 mg) in DMF (0.20 mL) at 20 $^\circ\text{C}$ for 2 h, followed by quenching with MeOH, evaporation, and chromatography, to give **9** quantitatively.

Methyl 2-O-Allyl-3,5-Di-O-benzyl- β -D-ribofuranosides (29). A mixture of **23** (1.097 g, 3.2 mmol), NaH (60% in oil, 0.20 g, 6.5 mmol), and allyl bromide (10 mL) was stirred at 80 $^\circ\text{C}$ for 2 h. Evaporation and chromatography with the TK system (20:1) afforded **29** (1.073 g, 88%), $[\alpha]_{\text{D}}^{22} +11^\circ$ (c 1.2, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 3.35 (s, Me), 3.53 (dd, $J_{4,5a} = 6$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a), 3.63 (dd, $J_{4,5b} = 4$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b), 3.81 (dd, $J_{1,2} = 1$ Hz, $J_{2,3} = 5$ Hz, H2), 4.05 (dd, $J_{2,3} = 5$ Hz, $J_{3,4} = 7$ Hz, H3), 4.33 (ddd, $J_{3,4} = 7$ Hz, $J_{4,5a} = 6$ Hz, $J_{4,5b} = 4$ Hz, H4),

4.93 (d, $J_{1,2} = 1$ Hz, H1), 5.95 (m, allyl); ^{13}C NMR (CDCl_3 , 75 MHz) δ 55.0 (Me), 71.2 (C5), 78.3 (C3), 79.8 (C2), 80.4 (C4), 106.4 (C1); 71.4, 117.5, 134.3 (allyl).

Found: C, 71.22; H, 7.33%. Calcd for $\text{C}_{23}\text{H}_{28}\text{O}_5$: C, 71.85; H, 7.34%.

2-O-Allyl-3,5-Di-O-benzyl- β -D-ribofuranose (21). A mixture of **29** (890 mg, 2.3 mmol), aq AcOH (89 mL), and aq H_2SO_4 (30%, 0.35 mL) was stirred at 80 $^\circ\text{C}$ for 1 h. After the mixture was diluted with H_2O (50 mL) and PhMe (100 mL), the organic layer was washed with aq NaHCO_3 (5%) and H_2O . Evaporation and chromatography with the TK system (10:1) afforded **21** (750 mg, 99%); $[\alpha]_{\text{D}}^{22} +43^\circ$ (c 0.9, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) (65% α) δ 3.34 (d, $J_{1,\text{OH}} = 6.5$ Hz, 1-OH β), 3.47 (dd, $J_{4,5a} = 4$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a α), 3.48 (dd, $J_{4,5a} = 3$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a β), 3.52 (dd, $J_{4,5b} = 4$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b α), 3.66 (dd, $J_{4,5b} = 2.5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b β), 3.81 (dd, $J_{1,2} = 1$ Hz, $J_{2,3} = 4$ Hz, H2 β), 3.94 (dd, $J_{1,2} = 4$ Hz, $J_{2,3} = 5$ Hz, H2 α), 4.01 (dd, $J_{2,3} = 5$ Hz, $J_{3,4} = 2.5$ Hz, H3 α), 4.14 (d, $J_{1,\text{OH}} = 10$ Hz, 1-OH α), 4.23 (dd, $J_{2,3} = 4$ Hz, $J_{3,4} = 7$ Hz, H3 β), 4.28 (ddd, $J_{3,4} = 7$ Hz, $J_{4,5a} = 3$ Hz, $J_{4,5b} = 2.5$ Hz, H4 β), 4.36 (dt, $J_{3,4} = 2.5$ Hz, $J_{4,5a} = J_{4,5b} = 4$ Hz, H4 α), 5.28 (dd, $J_{1,2} = 1$ Hz, $J_{1,\text{OH}} = 6.5$ Hz, H1 β), 5.31 (dd, $J_{1,2} = 4$ Hz, $J_{1,\text{OH}} = 10.0$ Hz, H1 α); ^{13}C NMR (CDCl_3 , 75 MHz) δ 69.4 (C5 β), 70.0 (C5 α), 77.2 (C3 β), 77.7 (C3 α), 77.8 (C2 α), 80.8 (C2 β), 80.9 (C4 α), 81.0 (C4 β), 96.2 (C1 α), 100.4 (C1 β), 71.5, 117.7, 134.1 (allyl- α), 71.5, 117.6, 134.4 (allyl- β), 72.8, 73.5 (benzyl- α), 72.5, 73.5 (benzyl- β).

Found: C, 70.17; H, 7.07%. Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_5 \cdot 0.5\text{H}_2\text{O}$: C, 69.64; H, 7.17%.

Methyl 2- and 3-O-Trityl- α -L-rhamnopyranosides (32 and 31). The glycoside **30**¹⁶ was prepared by a modified methanolysis. A mixture of **35** (monohydrate, 9.0 g, 49 mmol), MeOH (45 mL), and MeSO_3H (0.30 mL, 4.6 mmol) was refluxed for 5 h. To a cooled solution, NaHCO_3 (0.60 g) was added. Evaporation and chromatography with the CM system (10:1) afforded an anomeric mixture of the pyranosides. This was rechromatographed with the EM system to give **30** (6.32 g, 72%) as the main product; ^1H NMR (D_2O , 300 MHz) δ 1.29 (d, $J_{5,6} = 6$ Hz, H6), 3.39 (s, Me), 3.42 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4), 3.67 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5), 3.70 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, H3), 3.92 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3.5$ Hz, H2), 4.69 (d, $J_{1,2} = 2$ Hz, H1); ^{13}C NMR (D_2O , 75 MHz) δ 20.6 (C6), 58.1 (Me), 71.8 (C5), 73.4 (C2), 73.7 (C3), 75.5 (C4), 104.3 (C1, $J_{\text{C1,H1}} = 170.0$ Hz). A mixture of **30** (3.50 g, 19.7 mmol), trityl chloride (10.7 g, 38.4 mmol), and pyridine (10 mL) was stirred at 60 $^\circ\text{C}$ for 16 h. After the addition of Et_3N (10 mL),¹⁴ the mixture was evaporated to dryness and chromatographed with the TK system (3:1) to give **31** (6.277 g, 76%); $[\alpha]_{\text{D}}^{20} -42^\circ$ (c 1.7, CHCl_3) (Ref. 15, $[\alpha]_{\text{D}}^{20} -50.6^\circ$ (c 2.7, CHCl_3)); ^1H NMR (CDCl_3 , 300 MHz) δ 1.28 (d, $J_{5,6} = 6$ Hz, H6), 2.09 (OH), 2.17 (OH), 3.18 (s, Me), 3.45 (dq, $J_{4,5} = 9$ Hz, $J_{5,6} = 6$ Hz, H5), 3.61 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3$ Hz, H2), 3.71 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4), 3.84 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9$ Hz, H3), 4.43 (d, $J_{1,2} = 1.5$ Hz, H1); ^{13}C NMR (CDCl_3 , 75 MHz) δ 17.9 (C6), 54.7 (Me), 68.0 (C5), 69.6 (C2), 72.0 (C4), 74.5 (C3), 100.4 (C1); 87.5 (trityl); MS (FAB) m/z 443.1834 (M+Na)⁺. Calcd for $\text{C}_{26}\text{H}_{28}\text{O}_5\text{Na}$: 443.18344.

Further elution gave **32** (0.224 mg, 7.5%); $[\alpha]_{\text{D}}^{20} +52^\circ$ (c 0.5, CHCl_3) (Ref. 15, $[\alpha]_{\text{D}}^{20} +45^\circ$ (c 1.1, CHCl_3)); ^1H NMR (CDCl_3 , 300 MHz) δ 1.33 (d, $J_{5,6} = 6$ Hz, H6), 2.50–2.55 (2H, OH), 3.37 (s, Me), 3.44 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4), 3.64 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5), 3.74 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, H3), 3.92 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3.5$ Hz, H2), 4.67 (d, $J_{1,2} = 1.5$ Hz, H1); ^{13}C NMR (CDCl_3 , 75 MHz) δ 17.5 (C6), 54.9 (Me), 67.6 (C5),

The previous value^{4a} was corrected.

70.9 (C2), 71.9 (C3), 73.6 (C4), 100.7 (C1, $J_{C1,H1}$ = 167 Hz).

Found: C, 73.65; H, 6.85%. Calcd for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71%.

The NMR data of the acetate of **31** was as follows: 1H NMR ($CDCl_3$, 300 MHz) δ 1.14 (d, $J_{5,6}$ = 6 Hz, H6); 1.89, 2.22 (s, Ac), 3.15 (s, Me), 3.50 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5), 3.91 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, H3), 4.20 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3.5 Hz, H2), 4.47 (d, $J_{1,2}$ = 2 Hz, H1), 5.30 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.7 (C6), 66.7 (C5), 69.5 (C3), 71.9 (C2), 72.4 (C4), 97.8 (C1); 21.2, 21.3, 170.2 (2C) (Ac); 54.9 (Me), 87.4 (trityl).

The NMR data of the acetate of **32** was as follows: 1H NMR ($CDCl_3$, 300 MHz) δ 1.29 (d, $J_{5,6}$ = 6 Hz, H6); 1.93, 2.06 (s, Ac), 3.00 (s, Me), 3.55 (d, $J_{1,2}$ = 1.5 Hz, H1), 3.75 (dq, $J_{4,5}$ = 10 Hz, $J_{5,6}$ = 6 Hz, H5), 3.92 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.5 Hz, H2), 5.13 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 10 Hz, H3), 5.47 (t, $J_{3,4}$ = $J_{4,5}$ = 10 Hz, H4); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9 (C6), 66.3 (C5), 70.7 (C3), 71.8 (C2), 71.9 (C4), 99.3 (C1, $J_{C1,H1}$ = 170 Hz); 20.9, 21.0, 170.0 (2C) (Ac); 55.0 (Me), 87.9 (trityl).

Methyl 2,4-Di-O-benzyl- α -L-rhamnopyranosides (24). To a mixture of **31** (1.525 g, 3.6 mmol), $PhCH_2Br$ (3.0 mL, 25 mmol), and DMF (19 mL), NaH (60% in oil, 0.93 mg, 23 mmol) was added at 0 °C and the mixture was stirred for 15 min. The mixture was then stirred for 20 °C for 1 h. To the mixture, MeOH (4 mL) was added at 0 °C under stirring. After stirring at 20 °C for 1 h, the mixture was evaporated and chromatographed with the TK system (20:1) to give chromatographically pure benzyl ether (2.45 g). This was treated with CF_3CO_2H (2.0 mL, 27 mmol) in CH_2Cl_2 (29 mL) containing MeOH (5 mL) at room temp for 1 h. Evaporation at 25 °C and chromatography with the TK system (5:1) afforded **24** (1.074 g, 83%), $[\alpha]_D^{22}$ -13° (c 2.1, $CHCl_3$) (Ref. 24, $[\alpha]_D^{23}$ -15.42° (c 1.1, $CHCl_3$)); 1H NMR ($CDCl_3$, 300 MHz) δ 1.35 (d, $J_{5,6}$ = 6 Hz, H6), 2.48 (br, OH), 3.32 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4), 3.33 (s, Me), 3.67 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5), 3.73 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 4 Hz, H2), 3.94 (dd, $J_{2,3}$ = 4 Hz, $J_{3,4}$ = 9 Hz, H3), 4.72 (d, $J_{1,2}$ = 1.5 Hz, H1); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6), 54.7 (Me), 67.0 (C5), 71.6 (C3), 78.6 (C2), 82.2 (C4), 97.9 (C1).

Found: C, 70.39; H, 7.52%. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31%.

The NMR data of the acetate of **24** was as follows: 1H NMR ($CDCl_3$, 300 MHz) δ 1.35 (d, $J_{5,6}$ = 6 Hz, H6), 1.96 (s, Ac), 3.34 (s, Me), 3.63 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4), 3.77 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5), 3.86 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3.5 Hz, H2), 4.65 (d, $J_{1,2}$ = 2 Hz, H1), 5.19 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9 Hz, H3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6), 54.7 (Me), 67.6 (C5), 73.8 (C3), 76.2 (C2), 79.1 (C4), 98.8 (C1), 21.0, 170.0 (Ac).

Methyl 3-O-Allyl-2,4-di-O-benzyl- α -L-rhamnopyranoside (33). A mixture of **24** (1.95 g, 5.4 mmol), allyl bromide (20 mL), and NaH (ca. 60% dispersion in oil, 0.65 g, 16.3 mmol) was stirred at 80 °C for 2 h. Evaporation and chromatography using the TK system (20:1) **33** (1.798 g, 83%), $[\alpha]_D^{22}$ -39° (c 0.9, $CHCl_3$) (Ref. 24, $[\alpha]_D^{23}$ -40.64° (c 1.2, $CHCl_3$)); 1H NMR ($CDCl_3$, 300 MHz) δ 1.34 (d, $J_{5,6}$ = 6 Hz, H6), 3.30 (s, Me), 3.58 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4), 3.66 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5), 3.73 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3), 3.76 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2), 4.65 (d, $J_{1,2}$ = 1.5 Hz, H1), 5.95 (m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6), 54.5 (Me), 67.8 (C5), 74.7 (C2), 79.8 (C3), 80.4 (C4), 99.1 (C1); 71.0, 116.5, 135.0 (allyl).

Found: C, 72.37; H, 7.79%. Calcd for $C_{24}H_{30}O_5$: C, 72.34; H, 7.59%.

This was done alternatively as follows: A mixture of **30** (1.54 g,

8.6 mmol), Bu_2SnO (2.4 g, 9.6 mmol), and MeOH (100 mL) was stirred at 75 °C under reflux for 80 min. After evaporation to dryness, the residue was heated in DMF (65 mL) containing allyl bromide (3.8 mL, 45 mmol) at 65 °C under stirring for 16 h. After evaporation to dryness on a boiling water-bath, the residue was chromatographed with the CM system (10:1) to give methyl 3-O-allyl- α -L-rhamnopyranoside (**34**) (1.03 g, 55%); $[\alpha]_D^{22}$ -28° (c 0.4, H_2O) (Ref. 24, $[\alpha]_D^{23}$ -39.18° (c 1.1, H_2O)); 1H NMR ($CDCl_3$, 300 MHz) δ 1.30 (d, $J_{5,6}$ = 6 Hz, H6), 2.65 (s, OH), 3.521 (dd, $J_{2,3}$ = 2.5 Hz, $J_{3,4}$ = 9 Hz, H3), 3.523 (s, Me), 3.53 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4), 3.62 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5), 3.89 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 2.5 Hz, H2), 4.68 (d, $J_{1,2}$ = 1.5 Hz, H1); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.6 (C6), 54.8 (Me), 67.6 (C5), 67.7 (C2), 71.4 (C4), 79.3 (C3), 100.4 (C1); 70.4, 118.0, 134.3 (allyl); MS (FAB) m/z 241.1052 ($M+Na$)⁺. Calcd for $C_{10}H_{18}O_5Na$: 241.1052.

The NMR data of the acetate of **34** was as follows: 1H NMR ($CDCl_3$, 300 MHz) δ 1.20 (d, $J_{5,6}$ = 6 Hz, H6), 2.07, 2.12 (s, Ac), 3.35 (s, Me), 3.73 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 10 Hz, H3), 3.77 (dq, $J_{4,5}$ = 10 Hz, $J_{5,6}$ = 6 Hz, H5), 4.62 (d, $J_{1,2}$ = 1.5 Hz, H1), 4.98 (t, $J_{3,4}$ = $J_{4,5}$ = 10 Hz, H4), 5.25 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2), 5.79 (m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.4 (C6), 55.0 (Me), 66.3 (C5), 68.7 (C2), 72.5 (C4), 74.4 (C3), 98.7 (C1), 20.9, 21.0, 169.9, 170.3 (Ac).

To a mixture of **34** (2.00 g, 92 mmol), $PhCH_2Br$ (2.4 mL, 20 mmol), and DMF (10 mL), NaH (60% in oil, 0.80 g, 20 mmol) was added at 0 °C, and the mixture was stirred for 15 min. The mixture was then stirred for 20 °C for 1 h, followed by quenching with MeOH (0.4 mL) and chromatography with the TK system, as described above, to give **33** (2.50 g, 68%).

3-O-Allyl-2,4-Di-O-benzyl-L-rhamnopyranose (22). A mixture of **33** (2.40 g, 60 mmol), aq AcOH (25 mL), and aq H_2SO_4 (30%, 0.5 mL) was stirred at 85 °C for 1 h. After dilution with H_2O (50 mL) and PhMe (100 mL), the separated organic layer was washed with aq $NaHCO_3$ (5%). Evaporation and chromatography using the HE system (2:1) afforded **22** (1.39 g, 60%), $[\alpha]_D^{21}$ -15° (c 0.5, $CHCl_3$)[#] (Ref. 9, $[\alpha]_D$ -22° (c 1.0, $CHCl_3$)); 1H NMR ($CDCl_3$, 300 MHz) (60% α) δ 1.31 (d, $J_{5,6}$ = 6 Hz, H6 α), 1.34 (d, $J_{5,6}$ = 6 Hz, H6 β), 2.65 (d, $J_{1,OH}$ = 3 Hz, OH-1 α), 3.35 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5 β), 3.47 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3 α), 3.53 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4 β), 3.59 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4 α), 3.61 (dd, $J_{2,3}$ = 2 Hz, $J_{3,4}$ = 9 Hz, H3 β), 3.80 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2 α), 3.85 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 2 Hz, H2 β), 3.92 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5 α), 4.61 (d, $J_{1,2}$ = 1 Hz, H1 β), 5.16 (dd, $J_{1,2}$ = 1.5 Hz, $J_{1,OH}$ = 3 Hz, H1 α); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9 (C6 β), 18.0 (C6 α), 68.2 (C5 α), 71.5 (C5 β), 75.0 (C3 β), 76.3 (C2 β), 79.3 (C2 α), 79.8 (C4 β), 80.4 (C4 α), 82.9 (C3 α), 93.1 (C1 α), 93.3 (C1 β); 71.1, 116.6, 135.0 (allyl- α); 71.6, 117.0, 134.6 (allyl- β); 72.9, 75.3 (benzyl- α), 74.8, 75.4 (benzyl- β); MS (FAB) m/z 407.1834 ($M+Na$)⁺. Calcd for $C_{23}H_{28}O_5Na$: 407.18344.

Allyl 3-O-Trityl- α -L-rhamnopyranoside (37). A mixture of **35** (monohydrate, 2.0 g, 11 mmol), allyl alcohol (10 mL, 15 mmol), and $MeSO_3H$ (33 μ L, 0.51 mmol) was stirred at 95 °C for 3 h. After the addition of $NaHCO_3$ (0.13 g, 1.6 mmol), the mixture was evaporated to dryness and chromatographed with the CM system (10:1) to give an anomeric mixture of the pyranosides. This was chromatographed with the EM system to give allyl α -L-rhamnopyranoside (**36**) (1.83 g, 81%); $[\alpha]_D^{25}$ -69° (c 1.0, $CHCl_3$) (Ref. 25, $[\alpha]_D^{20}$ -49° (c 1.0, $CHCl_3$)); 1H NMR (D_2O , 300 MHz) δ

The previous value⁹ was corrected.

1.28 (d, $J_{5,6}$ = 6 Hz, H6), 3.43 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4), 3.69 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5), 3.74 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3), 3.93 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2), 4.83 (d, $J_{1,2}$ = 1.5 Hz, H1), 5.96 (m, allyl); ^{13}C NMR (D_2O , 75 MHz) δ 20.1 (C6), 72.1 (C5), 73.6 (C2), 73.8 (C3), 75.5 (C4), 102.5 (C1, $J_{\text{C1,H1}}$ = 169.5 Hz); 71.7, 121.9, 136.8 (allyl).

Found: C, 51.75; H, 8.08%. Calcd for $\text{C}_9\text{H}_{16}\text{O}_5 \cdot 0.25\text{H}_2\text{O}$: C, 51.79; H, 7.97%.

A mixture of **36** (1.573 g, 8.7 mmol), trityl chloride (4.274 g, 15 mmol), and pyridine (4.3 mL) was stirred at 60 °C for 16 h. After the addition of Et_3N (4.3 mL),¹⁴ the mixture was evaporated to dryness and chromatographed with the TK system (4:1) to give **37** (2.83 g, 82%); $[\alpha]_{\text{D}}^{21}$ -46° (c 5, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.27 (d, $J_{5,6}$ = 6 Hz, H6), 1.65 (d, $J_{4,\text{OH}}$ = 3 Hz, OH-4), 2.29 (d, $J_{2,\text{OH}}$ = 3 Hz, OH-2), 3.00 (dt, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = $J_{2,\text{OH}}$ = 3 Hz, H2), 3.48 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5), 3.73 (dt, $J_{4,\text{OH}}$ = 3 Hz, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4), 3.83 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3), 4.57 (d, $J_{1,2}$ = 2 Hz, H1), 5.74 (m, allyl); ^{13}C NMR (CDCl_3 , 75 MHz) δ 17.9 (C6), 68.3 (C5), 69.7 (C2), 72.0 (C4), 74.7 (C3), 98.6 (C1); 67.4, 116.1, 133 (allyl).

Found: C, 75.35; H, 7.09%. Calcd for $\text{C}_{28}\text{H}_{30}\text{O}_5$: C, 75.31; H, 6.77%.

The NMR data of the acetate of **37** was as follows: ^1H NMR (CDCl_3 , 300 MHz) δ 1.12 (d, $J_{5,6}$ = 6 Hz, H6); 1.87, 2.23 (s, Ac); 3.50 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5), 3.90 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3), 4.25 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2), 4.61 (d, $J_{1,2}$ = 2 Hz, H1), 5.30 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4), 5.71 (m, allyl); ^{13}C NMR (CDCl_3 , 75 MHz) δ 17.7 (C6), 67.0 (C5), 69.7 (C3), 72.1 (C2), 72.4 (C4), 96.2 (C1), 87.5 (trityl); 21.2, 21.3, 170.3 (2C, Ac); 67.8, 116.2, 133.5 (allyl).

Allyl 2,4-Di-O-benzyl- α -L-rhamnopyranosides (25). To a mixture of **37** (3.263 g, 7.3 mmol), PhCH_2Br (6.0 mL, 50 mmol), and DMF (32 mL), NaH (60% in oil, 1.88 g, 47 mmol) was added at 0 °C. The mixture was stirred for 15 min and then for 20 °C for 1 h, followed by quenching with MeOH (4 mL) and chromatography with the TK system (20:1), as described for **24**, to give chromatographically pure benzyl ether. This was treated with $\text{CF}_3\text{CO}_2\text{H}$ (5.0 mL, 67 mmol) in CHCl_3 (74 mL) containing MeOH (10 mL) at room temperature for 2 h. Evaporation at 25 °C and chromatography with TK system (10:1) afforded **25** (1.917 g, 68%), $[\alpha]_{\text{D}}^{25}$ -2° (c 0.5, CH_2Cl_2) (Ref. 26, $[\alpha]_{\text{D}}^{25}$ +0.5° (c 1.10, CH_2Cl_2)); ^1H NMR (CDCl_3 , 300 MHz) δ 1.34 (d, $J_{5,6}$ = 6 Hz, H6), 2.31 (d, $J_{3,\text{OH}}$ = 9 Hz, OH-3), 3.33 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4), 3.71 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5), 3.76 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3.5 Hz, H2), 3.98 (dt, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = $J_{3,\text{OH}}$ = 9 Hz, H3), 4.87 (d, $J_{1,2}$ = 1.5 Hz, H1), 5.86 (m, allyl); ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.0 (C6), 67.2 (C5), 71.7 (C3), 78.7 (C2), 82.3 (C4), 96.1 (C1); 67.7, 117.2, 133.7 (allyl).

Found: C, 71.46; H, 7.42%. Calcd for $\text{C}_{23}\text{H}_{28}\text{O}_5$: C, 71.85; H, 7.34%.

The NMR data of the acetate of **25** was as follows: ^1H NMR (CDCl_3 , 300 MHz) δ 1.34 (d, $J_{5,6}$ = 6 Hz, H6), 1.97 (s, Ac), 3.64 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4), 3.81 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5), 3.88 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2), 4.80 (d, $J_{1,2}$ = 2 Hz, H1), 5.23 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3), 5.86 (m, allyl); ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.0 (C6), 67.8 (C5), 73.8 (C3), 76.3 (C2), 79.2 (C4), 96.8 (C1); 67.9, 117.3, 133.7 (allyl); 21.1, 170.1 (Ac).

Benzyl 3-O-Trityl- α -L-rhamnopyranoside (40). A mixture of **35** (monohydrate, 2.00 g, 11 mmol), benzyl alcohol (4.0 mL, 39 mmol), and MeSO_3H (0.40 mL, 62 mmol) was stirred for 40 min at 75 °C. After the addition of CHCl_3 (5 mL) and Et_3N (1.6 mL), the mixture was chromatographed with the CM system (10:1) to

give benzyl α -L-rhamnopyranoside (**39**) (0.168 g, 6%), and then an anomeric mixture of the pyranosides. This was chromatographed with the EM system (4:1) affording benzyl α -L-rhamnopyranoside (**38**) (1.95 g, 70%) as the main product.

38: $[\alpha]_{\text{D}}^{20}$ -59° (c 1.1, H_2O) (Ref. 27, $[\alpha]_{\text{D}}^{20}$ -63° (c 1, H_2O), $[\alpha]_{\text{D}}$ -87° (c 0.5, MeOH)); ^1H NMR (D_2O , 300 MHz) δ 1.26 (d, $J_{5,6}$ = 6 Hz, H6), 3.44 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4), 3.71 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5), 3.74 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3), 3.93 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2), 4.89 (d, $J_{1,2}$ = 2 Hz, H1); ^{13}C NMR (D_2O , 75 MHz) δ 20.0 (C6), 72.2 (C5), 73.7 (C2), 73.8 (C3), 75.5 (C4), 102.9 (C1, $J_{\text{C1,H1}}$ = 169.5 Hz), 73.1 (benzyl).

Found: C, 60.50; H, 7.25%. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_5 \cdot 0.25\text{H}_2\text{O}$: C, 60.33; H, 7.21%.

39: $[\alpha]_{\text{D}}^{20}$ -83° (c 1.6, MeOH); ^1H NMR (D_2O , 300 MHz) δ 1.35 (d, $J_{5,6}$ = 6 Hz, H6), 3.86 (t, $J_{3,4}$ = $J_{4,5}$ = 5 Hz, H4), 4.11 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 5 Hz, H2), 4.15 (dq, $J_{4,5}$ = 5 Hz, $J_{5,6}$ = 6 Hz, H5), 4.48 (t, $J_{2,3}$ = $J_{3,4}$ = 5 Hz, H3), 5.06 (d, $J_{1,2}$ = 1.5 Hz, H1); ^{13}C NMR (D_2O , 75 MHz) δ 18.9 (C6), 68.0 (C5), 71.9 (C3), 76.5 (C2), 81.5 (C4), 106.7 (C1, $J_{\text{C1,H1}}$ = 172.1 Hz), 69.6 (benzyl).

Found: C, 61.23; H, 7.31%. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_5$: C, 61.40; H, 7.14%.

A mixture of **38** (665.0 mg, 2.62 mmol), trityl chloride (1.44 g, 5.2 mmol), and pyridine (1.44 mL) was stirred at 60 °C for 18 h. After the addition of Et_3N (1.4 mL),¹⁴ the mixture was evaporated to dryness and chromatographed with the TK system (10:1) to give **40** (0.98 g, 75%), $[\alpha]_{\text{D}}^{21}$ -27° (c 1.0, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.30 (d, $J_{5,6}$ = 6 Hz, H6), 2.88 (br, OH), 3.26 (br, OH), 3.46 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4), 3.69 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5), 3.79 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3), 3.94 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 3 Hz, H2), 4.84 (d, $J_{1,2}$ = 1 Hz, H1); ^{13}C NMR (CDCl_3 , 75 MHz) δ 17.5 (C6), 68.1 (C5), 69.2 (benzyl), 71.1 (C2), 71.9 (C3), 73.4 (C4), 98.9 (C1, $J_{\text{C1,H1}}$ = 167.7 Hz), 82.1 (trityl).

Found: C, 76.81; H, 6.75%. Calcd for $\text{C}_{32}\text{H}_{32}\text{O}_5$: C, 77.40; H, 6.50%.

The NMR data of the acetate of **40** was as follows: ^1H NMR (CDCl_3 , 300 MHz) δ 1.12 (d, $J_{5,6}$ = 6 Hz, H6); 1.85, 2.25 (s, Ac), 3.51 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5), 3.90 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3), 4.33 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2), 4.72 (d, $J_{1,2}$ = 2 Hz, H1), 5.33 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4), 4.28, 4.51 (d, J_{gem} = 12 Hz, benzyl); ^{13}C NMR (CDCl_3 , 75 MHz) δ 17.7 (C6), 67.1 (C5), 69.7 (C3), 72.1 (C2), 72.4 (C4), 96.5 (C1), 87.6 (trityl); 21.2, 21.3, 170.3 (2C) (Ac).

Benzyl 2,4-Di-O-benzyl- α -L-rhamnopyranosides (26). To a mixture of **40** (548 mg, 1.1 mmol), PhCH_2Br (1.0 mL, 8.4 mmol), and DMF (4.8 mL), NaH (60% in oil, 290 mg, 7.3 mmol) was added at 0 °C and the mixture was stirred for 15 min. The mixture was then stirred for 20 °C for 1 h, followed by quenching with MeOH (1 mL). Chromatography with the TK system (30:1), as described for **24**, gave chromatographically pure benzyl ether (1.17 g). This was treated with $\text{CF}_3\text{CO}_2\text{H}$ (1.0 mL, 13.5 mmol) in CH_2Cl_2 (15 mL) containing MeOH (2 mL) at room temp for 2 h. Evaporation at 25 °C and chromatography with the TK system (10:1) afforded **26** (411 mg, 86%), $[\alpha]_{\text{D}}^{24}$ -31° (c 2.1, CHCl_3) (Ref. 28, $[\alpha]_{\text{D}}$ -38.5° (CHCl_3)); ^1H NMR (CDCl_3 , 300 MHz) δ 1.35 (d, $J_{5,6}$ = 6 Hz, H6), 2.37 (s, OH-3), 3.37 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4), 3.76 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5), 3.78 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 4 Hz, H2), 4.02 (dd, $J_{2,3}$ = 4 Hz, $J_{3,4}$ = 9 Hz, H3), 4.92 (d, $J_{1,2}$ = 1.5 Hz, H1); ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.0 (C6), 67.5 (C5), 71.7 (C3), 78.7 (C2), 82.3 (C4), 96.3 (C1, $J_{\text{C1,H1}}$ = 166.0 Hz).

Found: C, 74.50; H, 7.04%. Calcd for $\text{C}_{27}\text{H}_{30}\text{O}_5$: C, 74.63; H,

6.96%.

The NMR data of the acetate of **26** was as follows: ^1H NMR (CDCl_3 , 300 MHz) δ 1.35 (d, $J_{5,6} = 6$ Hz, H6), 1.98 (s, Ac), 3.66 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4), 3.85 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5), 3.91 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3.5$ Hz, H2), 4.86 (d, $J_{1,2} = 2$ Hz, H1), 5.27 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, H3), ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.0 (C6), 68.0 (C5), 73.8 (C3), 76.3 (C2), 79.3 (C4), 97.0 (C1); 21.0, 170.1 (Ac).

Methyl O-(2,3,5-Tri-O-benzyl- α - and β -D-ribofuranosyl)-(1 $\rightarrow$ 3)-2,4-di-O-benzyl- α -L-rhamnopyranosides (16a and 16b) (Table 2, Run 1). To a mixture of **1** (39.4 mg, 0.094 mmol), **24** (33.6 mg, 0.094 mmol), CoBr_2 (22.5 mg, 0.103 mmol), Bu_4NBr (33.2 mg, 0.103 mmol), MS4A (94 mg), and CH_2Cl_2 (0.94 mL), TMSBr (13.6 μL , 0.103 mmol) was added under stirring at room temp (ca. 25 $^\circ\text{C}$). The mixture was then stirred well under anhydrous conditions for 24 h. After the addition of PhMe (2 mL) and NaHCO_3 (8.7 mg), the mixture was stirred for 15 min. The mixture was transferred onto a column of silica gel, which was eluted with the TK system (10:1) to give **16b** (30.1 mg, 42%) and **16a** (8.0 mg, 11%).

16a; $[\alpha]_{\text{D}}^{+5^\circ}$ (c 1.1, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.30 (d, $J_{5,6} = 6$ Hz, H6 $^{\text{H}}$), 3.29 (s, Me), 3.40 (dd, $J_{4,5a} = 4$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a $^{\text{H}}$), 3.47 (dd, $J_{4,5b} = 4$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b $^{\text{H}}$), 3.62 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4 $^{\text{H}}$), 3.68 (dq, $J_{4,5} = 9$ Hz, $J_{5,6} = 6$ Hz, H5 $^{\text{H}}$), 3.86 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2 $^{\text{H}}$), 3.88 (dd, $J_{1,2} = 4$ Hz, $J_{2,3} = 6.5$ Hz, H2 $^{\text{H}}$), 3.93 (dd, $J_{2,3} = 6.5$ Hz, $J_{3,4} = 3.5$ Hz, H3 $^{\text{H}}$), 4.20 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9$ Hz, H3 $^{\text{H}}$), 4.32 (dt, $J_{3,4} = 3.5$ Hz, $J_{4,5a} = J_{4,5b} = 4$ Hz, H4 $^{\text{H}}$), 4.63 (d, $J_{1,2} = 2$ Hz, H1 $^{\text{H}}$), 5.27 (d, $J_{1,2} = 4$ Hz, H1 $^{\text{H}}$); ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.0 (C6 $^{\text{H}}$), 54.6 (Me), 68.0 (C5 $^{\text{H}}$), 70.1 (C5 $^{\text{H}}$), 75.0 (C2 $^{\text{H}}$), 75.5 (C3 $^{\text{H}}$), 76.7 (C3 $^{\text{H}}$), 78.4 (C2 $^{\text{H}}$), 79.4 (C4 $^{\text{H}}$), 82.0 (C4 $^{\text{H}}$), 99.2 (C1 $^{\text{H}}$, $J_{\text{C1,H1}} = 162.7$ Hz), 99.4 (C1 $^{\text{H}}$, $J_{\text{C1,H1}} = 168.8$ Hz).

16b; $[\alpha]_{\text{D}}^{+2^\circ}$ (c 0.9, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.30 (d, $J_{5,6} = 6$ Hz, H6 $^{\text{H}}$), 3.33 (s, Me), 3.45 (dd, $J_{4,5a} = 5.5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a $^{\text{H}}$), 3.55 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4 $^{\text{H}}$), 3.61 (dd, $J_{4,5b} = 3.5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b $^{\text{H}}$), 3.69 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5 $^{\text{H}}$), 3.79 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3$ Hz, H2 $^{\text{H}}$), 3.92 (dd, $J_{1,2} = 1$ Hz, $J_{2,3} = 4.5$ Hz, H2 $^{\text{H}}$), 4.01 (dd, $J_{2,3} = 4.5$ Hz, $J_{3,4} = 7$ Hz, H3 $^{\text{H}}$), 4.07 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3 $^{\text{H}}$), 4.33 (ddd, $J_{3,4} = 7$ Hz, $J_{4,5a} = 5.5$ Hz, $J_{4,5b} = 3.5$ Hz, H4 $^{\text{H}}$), 4.55 (d, $J_{1,2} = 1.5$ Hz, H1 $^{\text{H}}$), 5.41 (d, $J_{1,2} = 1$ Hz, H1 $^{\text{H}}$); ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.0 (C6 $^{\text{H}}$), 68.0 (C5 $^{\text{H}}$), 71.0 (C5 $^{\text{H}}$), 77.8 (C3 $^{\text{H}}$), 78.3 (C3 $^{\text{H}}$), 78.6 (C2 $^{\text{H}}$), 80.2 (2C, C2 $^{\text{H}}$ and C4 $^{\text{H}}$), 80.7 (C4 $^{\text{H}}$), 99.3 (C1 $^{\text{H}}$, $J_{\text{C1,H1}} = 166.0$ Hz), 106.7 (C1 $^{\text{H}}$, $J_{\text{C1,H1}} = 172.5$ Hz).

A similar reaction (Run 2) using $(\text{CH}_2\text{Cl})_2$ as the solvent gave **16a** (13%) and **16b** (43%).

Found: **16a**, C, 73.94; H, 6.99%. **16b**, C, 73.92; H, 6.96%. Calcd for $\text{C}_{47}\text{H}_{52}\text{O}_9$: C, 74.19; H, 6.89%.

Allyl O-(2,3,5-Tri-O-benzyl- α - and β -D-ribofuranosyl)-(1 $\rightarrow$ 3)-2,4-di-O-benzyl- α -L-rhamnopyranosides (17a and 17b) (Run 3). Condensation of **1** (43.5 mg, 0.103 mmol) and **25** (39.8 mg, 0.103 mmol) in the presence of TMSBr (15.0 μL , 0.114 mmol), CoBr_2 (24.9 mg, 0.114 mmol), Bu_4NBr (36.7 mg, 0.114 mmol), and MS4A (103.4 mg) in CH_2Cl_2 (1.03 mL) gave **17b** (the faster-moving (TK 10:1), 25.8 mg, 32%) and **17a** (11.3 mg, 14%).

17a; $[\alpha]_{\text{D}}^{+5^\circ}$ (c 0.8, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.29 (d, $J_{5,6} = 6$ Hz, H6 $^{\text{H}}$), 3.41 (dd, $J_{4,5a} = 3.5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a $^{\text{H}}$), 3.47 (dd, $J_{4,5b} = 4$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b $^{\text{H}}$), 3.63 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4 $^{\text{H}}$), 3.73 (dq, $J_{4,5} = 9$ Hz, $J_{5,6} = 6$ Hz, H5 $^{\text{H}}$), 3.877 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2 $^{\text{H}}$), 3.878 (dd, $J_{1,2} = 4$ Hz, $J_{2,3} = 6.5$ Hz, H2 $^{\text{H}}$), 3.94 (dd, $J_{2,3} = 6.5$ Hz, $J_{3,4} = 3.5$ Hz, H3 $^{\text{H}}$), 4.23 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9$ Hz, H3 $^{\text{H}}$), 4.33 (dt, $J_{3,4} = J_{4,5a} = 3.5$

Hz, $J_{4,5b} = 4$ Hz, H4 $^{\text{H}}$), 4.77 (d, $J_{1,2} = 2$ Hz, H1 $^{\text{H}}$), 5.28 (d, $J_{1,2} = 4$ Hz, H1 $^{\text{H}}$), 5.82 (m, allyl); ^{13}C NMR (CDCl_3 , 75 MHz) δ 17.9 (C6 $^{\text{H}}$), 68.1 (C5 $^{\text{H}}$), 70.0 (C5 $^{\text{H}}$), 74.9 (C2 $^{\text{H}}$), 75.4 (C3 $^{\text{H}}$), 76.7 (C3 $^{\text{H}}$), 78.3 (C2 $^{\text{H}}$), 79.5 (C4 $^{\text{H}}$), 82.0 (C4 $^{\text{H}}$), 97.5 (C1 $^{\text{H}}$, $J_{\text{C1,H1}} = 170.0$ Hz), 99.3 (C1 $^{\text{H}}$, $J_{\text{C1,H1}} = 172.4$ Hz), 67.7, 117.0, 134.0 (allyl).

17b; $[\alpha]_{\text{D}}^{+9^\circ}$ (c 0.9, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.30 (d, $J_{5,6} = 6$ Hz, H6 $^{\text{H}}$), 3.45 (dd, $J_{4,5a} = 5$ Hz, $J_{5a,5b} = 10$ Hz, H5a $^{\text{H}}$), 3.55 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4 $^{\text{H}}$), 3.61 (dd, $J_{4,5b} = 3.5$ Hz, $J_{5a,5b} = 10$ Hz, H5b $^{\text{H}}$), 3.73 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5 $^{\text{H}}$), 3.82 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3$ Hz, H2 $^{\text{H}}$), 3.93 (dd, $J_{1,2} = 1$ Hz, $J_{2,3} = 4$ Hz, H2 $^{\text{H}}$), 4.00 (dd, $J_{2,3} = 4$ Hz, $J_{3,4} = 7$ Hz, H3 $^{\text{H}}$), 4.10 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3 $^{\text{H}}$), 4.34 (ddd, $J_{3,4} = 7$ Hz, $J_{4,5a} = 5$ Hz, $J_{4,5b} = 3.5$ Hz, H4 $^{\text{H}}$), 4.70 (d, $J_{1,2} = 1.5$ Hz, H1 $^{\text{H}}$), 5.41 (d, $J_{1,2} = 1$ Hz, H1 $^{\text{H}}$), 5.87 (m, allyl); ^{13}C NMR (CDCl_3 , 75 MHz) δ 17.9 (C6 $^{\text{H}}$), 68.1 (C5 $^{\text{H}}$), 71.1 (C5 $^{\text{H}}$), 77.7 (C3 $^{\text{H}}$), 78.4 (C3 $^{\text{H}}$), 78.6 (C2 $^{\text{H}}$), 80.08 (C2 $^{\text{H}}$), 80.11 (C4 $^{\text{H}}$), 80.7 (C4 $^{\text{H}}$), 97.3 (C1 $^{\text{H}}$), 106.7 (C1 $^{\text{H}}$, $J_{\text{C1,H1}} = 173.4$ Hz), 67.7, 117.1, 133.9 (allyl).

Found: **17a** C, 74.54; H, 6.97%. **17b** C, 74.86; H, 7.08%. Calcd for $\text{C}_{49}\text{H}_{54}\text{O}_9$: C, 74.78; H, 6.92%.

A similar ribofuranosylation using $(\text{CH}_2\text{Cl})_2$ as a solvent gave **17a** (19%) and **17b** (40%) (Run 4).

Methyl O-(2-O-Allyl-3,5-di-O-benzyl- α - and β -D-ribofuranosyl)-(1 $\rightarrow$ 3)-2,4-di-O-benzyl- α -L-rhamnopyranosides (18a and 18b) (Run 5). Acceptor **24** (89.8 mg, 0.25 mmol) was condensed with **21** (90.4 mg, 0.24 mol) in the presence of TMSBr (34.9 μL , 0.27 mmol), CoBr_2 (58.8 mg, 0.27 mmol), Bu_4NBr (86.8 mg, 0.27 mmol), and MS4A (246 mg) in CH_2Cl_2 (2.5 mL) to afford **18b** (the faster-moving by the TK system (10:1), 69.1 mg, 40%); $[\alpha]_{\text{D}}^{+3^\circ}$ (c 0.5, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.28 (d, $J_{5,6} = 6$ Hz, H6 $^{\text{H}}$), 3.31 (s, Me), 3.42 (dd, $J_{4,5a} = 5.5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a $^{\text{H}}$), 3.52 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4 $^{\text{H}}$), 3.58 (dd, $J_{4,5b} = 3.5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b $^{\text{H}}$), 3.66 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5 $^{\text{H}}$), 3.77 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3$ Hz, H2 $^{\text{H}}$), 3.83 (dd, $J_{1,2} = 1$ Hz, $J_{2,3} = 4.5$ Hz, H2 $^{\text{H}}$), 3.98 (dd, $J_{2,3} = 4.5$ Hz, $J_{3,4} = 7.5$ Hz, H3 $^{\text{H}}$), 4.03 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3 $^{\text{H}}$), 4.26 (ddd, $J_{3,4} = 7.5$ Hz, $J_{4,5a} = 5.5$ Hz, $J_{4,5b} = 3.5$ Hz, H4 $^{\text{H}}$), 4.52 (d, $J_{1,2} = 1.5$ Hz, H1 $^{\text{H}}$), 5.31 (d, $J_{1,2} = 1$ Hz, H1 $^{\text{H}}$), 5.74 (m, allyl); ^{13}C NMR (CDCl_3 , 75 MHz) δ 17.9 (C6 $^{\text{H}}$), 67.9 (C5 $^{\text{H}}$), 70.9 (C5 $^{\text{H}}$), 77.6 (C3 $^{\text{H}}$), 78.3 (C3 $^{\text{H}}$), 78.5 (C2 $^{\text{H}}$), 80.0 (2C, C2 $^{\text{H}}$ and C4 $^{\text{H}}$), 80.6 (C4 $^{\text{H}}$), 99.2 (C1 $^{\text{H}}$), 106.8 (C1 $^{\text{H}}$); 54.6 (Me), 71.1, 117.2, 134.3 (allyl); MS (FAB) m/z 733.3353 (M+Na) $^+$. Calcd for $\text{C}_{43}\text{H}_{50}\text{O}_9\text{Na}$: 733.33522.

Further elution afforded **18a** (64.3 mg, 37%); $[\alpha]_{\text{D}}^{+9^\circ}$ (c 0.8, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.31 (d, $J_{5,6} = 6$ Hz, H6 $^{\text{H}}$), 3.30 (s, Me), 3.41 (dd, $J_{4,5a} = 3.5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a $^{\text{H}}$), 3.48 (dd, $J_{4,5b} = 4$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b $^{\text{H}}$), 3.62 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4 $^{\text{H}}$), 3.69 (dq, $J_{4,5} = 9$ Hz, $J_{5,6} = 6$ Hz, H5 $^{\text{H}}$), 3.84 (dd, $J_{1,2} = 4$ Hz, $J_{2,3} = 6.5$ Hz, H2 $^{\text{H}}$), 3.85 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2 $^{\text{H}}$), 3.93 (dd, $J_{2,3} = 6.5$ Hz, $J_{3,4} = 3.5$ Hz, H3 $^{\text{H}}$), 4.19 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9$ Hz, H3 $^{\text{H}}$), 4.31 (m, H4 $^{\text{H}}$), 4.66 (d, $J_{1,2} = 2$ Hz, H1 $^{\text{H}}$), 5.24 (d, $J_{1,2} = 4$ Hz, H1 $^{\text{H}}$), 5.89 (m, allyl); ^{13}C NMR (CDCl_3 , 75 MHz) δ 18.0 (C6 $^{\text{H}}$), 68.0 (C5 $^{\text{H}}$), 70.1 (C5 $^{\text{H}}$), 74.6 (C2 $^{\text{H}}$), 75.4 (C3 $^{\text{H}}$), 76.7 (C3 $^{\text{H}}$), 78.6 (C2 $^{\text{H}}$), 79.4 (C4 $^{\text{H}}$), 82.0 (C4 $^{\text{H}}$), 99.2 (C1 $^{\text{H}}$), 99.4 (C1 $^{\text{H}}$); 54.5 (Me); 71.7, 117.7, 134.7 (allyl); MS (FAB) m/z 733.3353 (M+Na) $^+$. Calcd for $\text{C}_{43}\text{H}_{50}\text{O}_9\text{Na}$: 733.33522.

In the case of Run 6 using $(\text{CH}_2\text{Cl})_2$, **18a** (26%) and **18b** (31%) were obtained.

Methyl O-(3-O-Allyl-2,4-di-O-benzyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-2,4-di-O-benzyl- α -L-rhamnopyranosides (19) (Run 7). Acceptor **24** (208.0 mg, 0.58 mmol) was condensed with **22** (223.1 mg, 0.58 mol) in the presence of TMSBr (84.2 μL , 0.64 mmol), CoBr_2 (140.0 mg, 0.64 mmol), Bu_4NBr (206.0 mg, 0.64

mmol), and MS4A (342.5 mg) in (CH₂Cl)₂ (3.5 mL), followed by chromatography with the TK system (10:1) to afford **19** (269.1 mg, 50%); [α]_D²⁰ -22° (c 1.3, CHCl₃) (Ref. 29, [α]_D -39° (c 0.3, CHCl₃)); ¹H NMR (CDCl₃, 300 MHz) δ 1.278 (d, $J_{5,6}$ = 6 Hz, H6^{ll}), 1.283 (d, $J_{5,6}$ = 6 Hz, H6^l), 3.30 (s, Me), 3.56 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{ll}), 3.59 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^{ll}), 3.67 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 9 Hz, H5^{ll}), 3.72 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^{ll}), 3.77 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2^l), 3.80 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^l), 3.82 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^l), 4.07 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^l), 4.63 (d, $J_{1,2}$ = 2 Hz, H1^{ll}), 5.16 (d, $J_{1,2}$ = 1.5 Hz, H1^l); ¹³C NMR (CDCl₃, 75 MHz) δ 18.0 (C6^{ll}), 18.1 (C6^l), 68.0 (C5^{ll}), 68.7 (C5^l), 75.7 (C2^l), 77.8 (C3^l), 78.0 (C2^{ll}), 79.7 (C4^l), 80.5 (C3^{ll}), 80.9 (C4^{ll}), 98.7 (C1^{ll}, $J_{C1,H1}$ = 168.3 Hz), 99.9 (C1^l, $J_{C1,H1}$ = 169.1 Hz), 54.7 (Me), 71.0, 116.4, 135.1 (al-lyl).

Found: C, 72.36; H, 7.17%. Calcd for C₄₄H₅₂O₉: C, 72.91; H, 7.23%.

Methyl O-(2,3,4-Tri-O-benzyl- α - and β -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-3,5-di-O-benzyl- β -D-ribofuranoside (20a and 20b) (Run 8). Acceptor **23** (52.7 mg, 0.153 mmol) was condensed with **2** (66.5 mg, 0.153 mol) in the presence of TMSBr (21.9 μ L, 0.17 mmol), CoBr₂ (36.9 mg, 0.17 mmol), Bu₄NBr (54.3 mg, 0.17 mmol), and MS4A (153 mg) in CH₂Cl₂ (1.5 mL) to afford **20a** (the faster-moving by TK system (10:1), 49.5 mg, 43%) and **20b** (18.7 mg, 16%).

20a: [α]_D²⁴ -4° (c 1.4, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 1.36 (d, $J_{5,6}$ = 6 Hz, H6^{ll}), 3.32 (s, Me), 3.53 (dd, $J_{4,5a}$ = 5.5 Hz, $J_{5a,5b}$ = 10 Hz, H5a^l), 3.63 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 10 Hz, H5b^l), 3.64 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{ll}), 3.78 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^{ll}), 3.85 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^{ll}), 3.91 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^{ll}), 4.07 (dd, $J_{2,3}$ = 4 Hz, $J_{3,4}$ = 7 Hz, H3^l), 4.11 (d, $J_{1,2}$ = 0 Hz, $J_{2,3}$ = 4 Hz, H2^l), 4.25 (ddd, $J_{3,4}$ = 7 Hz, $J_{4,5a}$ = 5.5 Hz, $J_{4,5b}$ = 4 Hz, H4^l), 4.85 (s, H1^l), 5.04 (d, $J_{1,2}$ = 2 Hz, H1^{ll}); ¹³C NMR (CDCl₃, 75 MHz) δ 18.0 (C6^{ll}), 54.9 (Me), 68.6 (C5^{ll}), 71.4 (C5^l), 75.1 (C2^{ll}), 77.1 (C2^l), 79.3 (C3^l), 79.9 (C3^{ll}), 80.1 (C4^l), 80.4 (C4^{ll}), 98.3 (C1^{ll}, $J_{C1,H1}$ = 168.3 Hz), 107.6 (C1^l, $J_{C1,H1}$ = 168.3 Hz).

20b: [α]_D²² +45° (c 0.8, CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 1.40 (d, $J_{5,6}$ = 6 Hz, H6^{ll}), 3.37 (dq, $J_{4,5a}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^{ll}), 3.38 (s, Me), 3.49 (dd, $J_{4,5b}$ = 5 Hz, $J_{5a,5b}$ = 11.5 Hz, H5a^l), 3.50 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^{ll}), 3.58 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{ll}), 3.69 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 11.5 Hz, H5b^l), 3.97 (d, $J_{1,2}$ = 0 Hz, $J_{2,3}$ = 3 Hz, H2^{ll}), 4.07 (ddd, $J_{3,4}$ = 7.5 Hz, $J_{4,5a}$ = 5 Hz, $J_{4,5b}$ = 4 Hz, H4^l), 4.38 (d, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4.5 Hz, H2^l), 4.45 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 7.5 Hz, H3^l), 4.60 (s, H1^{ll}), 4.96 (d, $J_{1,2}$ = 1 Hz, H1^l); ¹³C NMR (CDCl₃, 75 MHz) δ 18.0 (C6^{ll}), 55.1 (Me), 71.1 (C5^l), 72.1 (C5^{ll}), 73.9 (C2^{ll}), 77.6 (2C, C3^l and C4^l), 80.1 (C4^{ll}), 81.2 (C2^l), 81.9 (C3^{ll}), 99.9 (C1^{ll}, $J_{C1,H1}$ = 153.9 Hz), 106.4 (C1^l, $J_{C1,H1}$ = 168.0 Hz).

Found: **20a**, C, 73.66; H, 7.00%. **20b**, C, 73.61; H, 6.85%. Calcd for C₄₇H₅₂O₉: C, 74.19; H, 6.89%.

Methyl O-(2,4-Di-O-benzyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-2,4-di-O-benzyl- α -L-rhamnopyranoside (41). A mixture of **19** (109.4 mg, 0.151 mmol), PdCl₂ (87.8 mg, 0.495 mol), NaOAc (49.2 mg, 0.600 mmol), and aq AcOH (95%, 6.6 mL) was stirred at 60 °C for 45 min. The mixture was evaporated to dryness at 25 °C and chromatographed with the TK (5:1) system to give **41** (83.6 mg, 81%); [α]_D²⁰ -18° (c 0.3, CHCl₃) (Ref. 29, [α]_D -17.2° (c 1.0, CHCl₃)); ¹H NMR (CDCl₃, 300 MHz) δ 1.28 (d, $J_{5,6}$ = 6 Hz, H6^{ll}), 1.32 (d, $J_{5,6}$ = 6 Hz, H6^l), 2.27 (d, $J_{3,OH}$ = 9.5 Hz, OH-3^{ll}), 3.31 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{ll}), 3.33 (s, Me), 3.61 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^l), 3.707 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4 Hz, H2^{ll}), 3.708

(dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 3 Hz, H2^l), 3.709 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^l), 3.79 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^{ll}), 3.99 (dt, $J_{2,3}$ = 4 Hz, $J_{3,4}$ = $J_{3,OH}$ = 9.5 Hz, H3^{ll}), 4.10 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^l), 4.66 (d, $J_{1,2}$ = 1 Hz, H1^{ll}), 5.19 (d, $J_{1,2}$ = 1 Hz, H1^l); ¹³C NMR (CDCl₃, 75 MHz) δ 18.0 (C6^l), 18.1 (C6^{ll}), 67.8 (C5^{ll}), 68.2 (C5^l), 71.6 (C3^{ll}), 77.9 (2C, C2^l and C3^l), 79.2 (C2^{ll}), 81.0 (C4^l), 82.3 (C4^{ll}), 98.80 (C1^{ll}, $J_{C1,H1}$ = 168.3 Hz), 98.84 (C1^l, $J_{C1,H1}$ = 169.0 Hz), 54.7 (Me).

Found: C, 71.36; H, 7.11%. Calcd for C₄₁H₄₈O₉: C, 71.91; H, 7.06%.

O-(2,3,5-Tri-O-benzyl- β -D-ribofuranosyl)-(1 $\rightarrow$ 3)-2,4-di-O-benzyl-L-rhamnopyranose (43). Compound **17b** (36.1 mg, 0.046 mmol) was treated with PdCl₂ (80.8 mg, 0.46 mmol) and NaOAc (15.0 mg, 0.18 mmol) in aq AcOH (95%, 2.05 mL) at room temp for 3 h, followed by purification, as described for **41**, to give **43** (24.9 mg, 73%); [α]_D²² +13° (c 1.6, CHCl₃); ¹H NMR (CDCl₃, 400 MHz) (50% α) δ 1.27 (d, $J_{5,6}$ = 6 Hz, H6 α^l), 1.29 (d, $J_{5,6}$ = 6 Hz, H6 β^l), 3.35 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5 β^l), 3.45 (dd, $J_{4,5a}$ = 4.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a β^l), 3.47 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4 β^l), 3.50 (dd, $J_{4,5a}$ = 4.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a α^l), 3.56 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4 α^l), 3.61 (dd, $J_{4,5b}$ = 3.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b β^l), 3.67 (dd, $J_{4,5b}$ = 3 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b α^l), 3.79 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3 β^l), 3.818 (dd, $J_{2,3}$ = 1.5 Hz, $J_{3,4}$ = 3 Hz, H2 α^l), 3.822 (d, $J_{1,2}$ = 0 Hz, $J_{2,3}$ = 3 Hz, H2 β^l), 3.87 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4.5 Hz, H2 α^l), 3.92 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4.5 Hz, H2 β^l), 3.94 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5 α^l), 4.00 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 7.5 Hz, H3 β^l), 4.05 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 7.5 Hz, H3 α^l), 4.14 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3a^l), 4.32 (ddd, $J_{3,4}$ = 7.5 Hz, $J_{4,5a}$ = 4.5 Hz, $J_{4,5b}$ = 3 Hz, H4 α^l), 4.33 (ddd, $J_{3,4}$ = 7.5 Hz, $J_{4,5a}$ = 4.5 Hz, $J_{4,5b}$ = 3.5 Hz, H4 β^l), 4.66 (s, H1 β^l), 5.05 (d, $J_{1,2}$ = 1.5 Hz, H1 α^l), 5.42 (d, $J_{1,2}$ = 1 Hz, H1 α^l and H1 β^l); ¹³C NMR (CDCl₃, 100 MHz) δ 17.8 (C6 β^l), 18.0 (C6 α^l), 68.2 (C5 α^l), 69.9 and 70.8 (C5 α^l and C5 β^l), 71.4 (C5 β^l), 76.7 and 77.5 (C3 α^l and C3 β^l), 77.6 (C3 α^l), 78.6 (C2 β^l), 79.8 (C2 β^l), 79.87 (C2 α^l), 79.90 (C2 α^l), 79.99 (C4 β^l), 80.00 (C4 α^l), 80.2 (C3 β^l), 80.3 (C4 β^l), 80.6 (C4 α^l), 93.0 (C1 α^l), 93.1 (C1 β^l), 106.4 and 106.6 (C1 α^l and C1 β^l).

Found: C, 73.71; H, 6.95%. Calcd for C₄₆H₅₀O₉: C, 73.97; H, 6.75%.

Methyl O-(2,3,5-Tri-O-benzyl- β -D-ribofuranosyl)-(1 $\rightarrow$ 3)-O-(2,4-di-O-benzyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-2,4-di-O-benzyl- α -L-rhamnopyranoside (42) (Run 9). Acceptor **41** (40.8 mg, 0.060 mmol) was condensed with **1** (25.1 mg, 0.060 mol) in the presence of TMSBr (8.7 μ L, 0.066 mmol), CoBr₂ (14.3 mg, 0.065 mmol), Bu₄NBr (21.1 mg, 0.065 mmol), and MS4A (40.0 mg) in (CH₂Cl)₂ (0.5 mL), followed by chromatography with the TK system (10:1), to afford **42** (29.4 mg, 45%); [α]_D²³ -13° (c 1.3, CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ 1.24 (d, $J_{5,6}$ = 6 Hz, H6^{ll}), 1.25 (d, $J_{5,6}$ = 6 Hz, H6^l), 3.31 (s, Me), 3.37 (dd, $J_{4,5a}$ = 5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a^{ll}), 3.49 (dd, $J_{4,5b}$ = 4.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b^{ll}), 3.56 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{ll}), 3.57 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^l), 3.65 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^{ll}), 3.71 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2^{ll}), 3.81 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^l), 3.91 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 4.5 Hz, H2^{ll}), 3.92 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2^l), 4.00 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 6.5 Hz, H3^{ll}), 4.06 (dd, $J_{2,3}$ = 3, 9 Hz, H3^l), 4.17 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^{ll}), 4.66 (d, $J_{1,2}$ = 1.5 Hz, H1^l), 5.11 (d, $J_{1,2}$ = 1.5 Hz, H1^{ll}), 5.42 (d, $J_{1,2}$ = 1.5 Hz, H1^{ll}); ¹³C NMR (CDCl₃, 100 MHz) δ 17.9 (C6^{ll}), 18.0 (C6^l), 54.6 (Me), 68.0 (C5^l), 68.6 (C5^{ll}), 70.9 (C5^{ll}), 77.3 (C3^{ll}), 77.6 (C3^l), 77.8 (C2^l), 78.8 (C3^{ll}), 79.2 (C2^{ll}), 80.1 (C4^{ll}), 80.4 (C2^{ll}), 80.6 (C4^{ll}), 80.8 (C4^l), 98.7 (C1^l, $J_{C1,H1}$ = 170 Hz), 99.8 (C1^{ll}, $J_{C1,H1}$ = 170 Hz), 107.1 (C1^{ll}, $J_{C1,H1}$ = 175

Hz).

Found: C, 73.64; H, 7.03%. Calcd for $C_{67}H_{74}O_{13}$: C, 74.01; H, 6.86%.

(Run 10): Acceptor **24** (16.4 mg, 0.046 mmol) was condensed with **43** (34.0 mg, 0.046 mol) in the presence of TMSBr (6.6 μ L, 0.050 mmol), CoBr₂ (11.0 mg, 0.050 mmol), Bu₄NBr (16.2 mg, 0.050 mmol), and MS4A (50.0 mg) in (CH₂Cl)₂ (0.50 mL), followed by iterative chromatography to separate unreacted **24** from **42** with DE (30:1) as well as the TK system (10:1) to afford **42** (20.0 mg, 40%).

Methyl O- β -D-Ribofuranosyl-(1 $\rightarrow$ 3)-O- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)- α -L-rhamnopyranoside (44). Hydrogenation of **42** (38.0 mg, 0.035 mmol) over Pd on C (56 mg) in MeOH (6 mL) at room temp overnight, removal of the catalyst by filtration, evaporation at 25 °C, and chromatography with the CM system (2:1) afforded **44** (8.9 mg, 56%); mp 125–127 °C, $[\alpha]_D^{22} -96^\circ$ (c 0.4, MeOH); ¹H NMR (D₂O, 400 MHz) δ 1.26 (d, $J_{5,6} = 6$ Hz, H6^l), 1.28 (d, $J_{5,6} = 6$ Hz, H6^l), 3.38 (s, Me), 3.48 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^l), 3.52 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^l), 3.67 (dd, $J_{4,5a} = 5$ Hz, $J_{5a,5b} = 12$ Hz, H5a^l), 3.69 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5^l), 3.75 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3^l), 3.81 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5^l), 3.83 (dd, $J_{4,5b} = 3$ Hz, $J_{5a,5b} = 12$ Hz, H5b^l), 3.87 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3^l), 3.99 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2^l), 4.04 (ddd, $J_{3,4} = 7.5$ Hz, $J_{4,5a} = 5$ Hz, $J_{4,5b} = 3$ Hz, H4^l), 4.14 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 4.5$ Hz, H2^l), 4.22 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2^l), 4.30 (dd, $J_{2,3} = 4.5$ Hz, $J_{3,4} = 7.5$ Hz, H3^l), 4.64 (d, $J_{1,2} = 2$ Hz, H1^l), 5.00 (d, $J_{1,2} = 2$ Hz, H1^l), 5.19 (s, H1^l); ¹³C NMR (D₂O, 100 MHz) δ 19.25 (C6^l), 19.31 (C6^l), 57.4 (Me), 64.4 (C5^l), 71.2 (C5^l), 71.7 (C5^l), 72.4 (C2^l), 72.5 (C2^l), 72.7 (C3^l), 73.6 (C4^l), 74.0 (C4^l), 77.3 (C2^l), 80.7 (C3^l), 81.5 (C3^l), 85.2 (C4^l), 103.4 (C1^l, $J_{C1,H1} = 169.6$ Hz), 104.6 (C1^l, $J_{C1,H1} = 170.9$ Hz), 111.2 (C1^l, $J_{C1,H1} = 175.5$ Hz).

Found: C, 47.10; H, 7.32%. Calcd for $C_{18}H_{32}O_{13}$: C, 47.36; H, 7.07%.

Benzyl O-(2,3,5-Tri-O-benzyl- β -D-ribofuranosyl)-(1 $\rightarrow$ 3)-O-(2,4-di-O-benzyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-2,4-di-O-benzyl- α -L-rhamnopyranoside (45) (Run 11). Acceptor **26** (21.2 mg, 0.049 mmol) was condensed with **43** (36.5 mg, 0.049 mol) in the presence of TMSBr (7.1 μ L, 0.054 mmol), CoBr₂ (11.7 mg, 0.053 mmol), Bu₄NBr (17.3 mg, 0.054 mmol), and MS4A (50.0 mg) in (CH₂Cl)₂ (0.50 mL) to afford **45** (23.7 mg, 42%), $[\alpha]_D^{20} -26^\circ$ (c 0.3, CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ 1.24 (d, $J_{5,6} = 6$ Hz, H6^l), 1.26 (d, $J_{5,6} = 6$ Hz, H6^l), 3.38 (dd, $J_{4,5a} = 5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a^l), 3.48 (dd, $J_{4,5b} = 4.5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b^l), 3.56 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^l), 3.60 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^l), 3.74 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5^l), 3.77 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2^l), 3.82 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5^l), 3.92 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 4.5$ Hz, H2^l), 3.93 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3$ Hz, H2^l), 4.01 (dd, $J_{2,3} = 4.5$ Hz, $J_{3,4} = 6.5$ Hz, H3^l), 4.14 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3^l), 4.17 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3^l), 4.86 (d, $J_{1,2} = 2$ Hz, H1^l), 5.12 (d, $J_{1,2} = 1.5$ Hz, H1^l), 5.42 (d, $J_{1,2} = 1.5$ Hz, H1^l); ¹³C NMR (CDCl₃, 100 MHz) δ 17.9 (C6^l), 18.0 (C6^l), 68.4 (C5^l), 68.6 (C5^l), 70.8 (C5^l), 77.8 (C3^l), 77.88 (C3^l), 77.93 (C2^l), 78.8 (C3^l), 79.2 (C2^l), 80.1 (C4^l), 80.4 (C2^l), 80.6 (C4^l), 80.8 (C4^l), 96.9 (C1^l), 99.8 (C1^l), 107.1 (C1^l).

Found: C, 75.38; H, 6.86%. Calcd for $C_{73}H_{78}O_{13}$: C, 75.36; H, 6.76%.

Allyl O-(2,3,5-Tri-O-benzyl- β -D-ribofuranosyl)-(1 $\rightarrow$ 3)-O-(2,4-di-O-benzyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-2,4-di-O-benzyl- α -L-rhamnopyranoside (46) (Run 12). Acceptor **25** (21.5 mg, 0.056 mmol) was condensed with **43** (41.8 mg, 0.056 mol) in

the presence of TMSBr (8.1 μ L, 0.061 mmol), CoBr₂ (13.5 mg, 0.062 mmol), Bu₄NBr (19.8 mg, 0.061 mmol), and MS4A (85.0 mg) in (CH₂Cl)₂ (0.50 mL) to afford **46** (32.4 mg, 52%); $[\alpha]_D^{23} -15^\circ$ (c 1.4, CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ 1.239 (d, $J_{5,6} = 6$ Hz, H6^l), 1.244 (d, $J_{5,6} = 6$ Hz, H6^l), 3.37 (dd, $J_{4,5a} = 5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a^l), 3.48 (dd, $J_{4,5b} = 4.5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b^l), 3.56 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^l), 3.58 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4^l), 3.70 (dq, $J_{4,5} = 9$ Hz, $J_{5,6} = 6$ Hz, H5^l), 3.75 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3$ Hz, H2^l), 3.82 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5^l), 3.91 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 4.5$ Hz, H2^l), 3.93 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3$ Hz, H2^l), 4.01 (dd, $J_{2,3} = 4.5$ Hz, $J_{3,4} = 6.5$ Hz, H3^l), 4.12 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9$ Hz, H3^l), 4.17 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3^l), 4.31 (ddd, $J_{3,4} = 6.5$ Hz, $J_{4,5a} = 5$ Hz, $J_{4,5b} = 4.5$ Hz, H4^l), 4.81 (d, $J_{1,2} = 1.5$ Hz, H1^l), 5.12 (d, $J_{1,2} = 1.5$ Hz, H1^l), 5.42 (d, $J_{1,2} = 1.5$ Hz, H1^l), 5.85 (m, allyl); ¹³C NMR (CDCl₃, 100 MHz) δ 17.8 (C6^l), 18.0 (C6^l), 68.2 (C5^l), 68.6 (C5^l), 70.8 (C5^l), 77.7 (C3^l), 77.9 (C2^l), 78.0 (C3^l), 78.8 (C3^l), 79.2 (C2^l), 80.1 (C4^l), 80.4 (C2^l), 80.6 (C4^l), 80.8 (C4^l), 96.8 (C1^l, $J_{C1,H1} = 167.8$ Hz), 99.8 (C1^l, $J_{C1,H1} = 169.2$ Hz), 107.1 (C1^l, $J_{C1,H1} = 175.0$ Hz); 67.8, 116.9, 133.9 (allyl).

Found: C, 74.60; H, 7.04%. Calcd for $C_{69}H_{76}O_{13}$: C, 74.44; H, 6.88%.

O-(2,3,5-Tri-O-benzyl- β -D-ribofuranosyl)-(1 $\rightarrow$ 3)-O-(2,4-di-O-benzyl- α -L-rhamnopyranosyl)-(1 $\rightarrow$ 3)-2,4-di-O-benzyl-L-rhamnopyranose (47). Compound **46** (46.3 mg, 0.042 mmol) was treated with PdCl₂ (73.2 mg, 0.41 mmol) and NaOAc (13.6 mg, 0.17 mmol) in aq AcOH (95%, 1.9 mL) at room temp overnight, followed by purification, as described for **41**, to give **47** (27.3 mg, 61%); $[\alpha]_D^{22} -10^\circ$ (c 0.4, CHCl₃); ¹H NMR (CDCl₃, 400 MHz) (56% α) δ 1.24 (d, $J_{5,6} = 6$ Hz, H6 α^l), 1.25 (d, $J_{5,6} = 6$ Hz, H6 α^l), 1.26 (d, $J_{5,6} = 6$ Hz, H6 β^l), 1.30 (d, $J_{5,6} = 6$ Hz, H6 β^l), 3.35 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5 β^l), 3.38 (dd, $J_{4,5a} = 5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a α^l), 3.39 (dd, $J_{4,5a} = 5$ Hz, $J_{5a,5b} = 10.5$ Hz, H5a β^l), 3.50 (dd, $J_{4,5b} = 4$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b α^l), 3.54 (dd, $J_{4,5b} = 4$ Hz, $J_{5a,5b} = 10.5$ Hz, H5b β^l), 3.55 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4 β^l), 3.57 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4 α^l), 3.59 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4 α^l), 3.61 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4 β^l), 3.76 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3$ Hz, H2 α^l), 3.78 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3$ Hz, H2 β^l), 3.82 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5 α^l), 3.87 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5 β^l), 3.88 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5 α^l), 3.92 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 4.5$ Hz, H2 α^l), 3.93 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 4.5$ Hz, H2 α^l), 3.94 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3$ Hz, H2 α^l), 3.97 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 3$ Hz, H2 β^l), 4.018 (dd, $J_{2,3} = 4.5$ Hz, $J_{3,4} = 6.5$ Hz, H3 α^l), 4.020 (dd, $J_{2,3} = 4.5$ Hz, $J_{3,4} = 6.5$ Hz, H3 β^l), 4.16 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3 β^l and H3 β^l), 4.17 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3 α^l and H3 α^l), 4.65 (s, H1 β^l), 5.13 (d, $J_{1,2} = 1.5$ Hz, H1 α^l), 5.18 (d, $J_{1,2} = 1.5$ Hz, H1 α^l), 5.22 (d, $J_{1,2} = 1.5$ Hz, H1 β^l), 5.40 (d, $J_{1,2} = 1.5$ Hz, H1 β^l), 5.43 (d, $J_{1,2} = 1.5$ Hz, H1 α^l); ¹³C NMR (CDCl₃, 100 MHz) δ 17.7 (C6 β^l), 17.97 (C6 α^l and C6 α^l), 18.03 (C6 β^l), 68.3 (C5 α^l), 68.6 (C5 α^l), 69.2 (C5 β^l), 70.7 (C5 β^l), 70.8 (C5 α^l), 71.6 (C5 β^l), 77.7 (C3 β^l), 77.88 (C3 α^l), 77.92 (C2 α^l), 78.6 (C3 β^l), 78.7 (C3 α^l), 78.8 (C3 α^l and C3 β^l), 78.86 (C2 β^l), 78.94 (C2 β^l), 79.2 (C2 α^l), 80.1 (C4 α^l), 80.2 (C2 β^l and C4 β^l), 80.3 (C2 α^l), 80.6 (C4 α^l and C4 β^l), 80.7 (C4 β^l), 80.8 (C4 α^l), 92.6 (C1 α^l), 93.3 (C1 β^l), 99.7 (C1 α^l), 99.6 (C1 β^l), 107.06 (C1 β^l), 107.08 (C1 α^l).

Found: C, 73.75; H, 6.81%. Calcd for $C_{66}H_{72}O_{13}$: C, 73.86; H, 6.76%.

O- β -D-Ribofuranosyl-(1 $\rightarrow$ 3)-O- α -L-rhamnopyranosyl-(1 $\rightarrow$ 3)-L-rhamnopyranose (15). Hydrogenation of **47** (29.3 mg, 0.027 mmol) over Pd on C (20 mg) in MeOH (6 mL) containing H₂O (0.1 mL) at room temp overnight, removal of the catalyst

by filtration, evaporation at 25 °C, and chromatography with the EM system (3:1) afforded **15** (10.2 mg, 84%), mp 135–137 °C, $[\alpha]_D^{21} -59^\circ$ (c 0.6, MeOH); ^1H NMR (D_2O , 400 MHz) (67% α) δ 1.26 (d, $J_{5,6} = 6$ Hz, $\text{H6}\alpha^{\text{H}}$), 1.268 (d, $J_{5,6} = 6$ Hz, $\text{H6}\beta^{\text{H}}$), 1.274 (d, $J_{5,6} = 6$ Hz, H6^{H}), 3.44 (dq, $J_{4,5} = 9$ Hz, $J_{5,6} = 6$ Hz, $\text{H5}\beta^{\text{H}}$), 3.45 (t, $J_{3,4} = J_{4,5} = 9$ Hz, $\text{H4}\beta^{\text{H}}$), 3.49 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^{H}), 3.52 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, $\text{H4}\alpha^{\text{H}}$), 3.64 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9$ Hz, $\text{H3}\beta^{\text{H}}$), 3.68 (dd, $J_{4,5a} = 5$ Hz, $J_{5a,5b} = 12$ Hz, H5a^{H}), 3.837 (dd, $J_{4,5b} = 3$ Hz, $J_{5a,5b} = 12$ Hz, H5b^{H}), 3.838 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, $\text{H5}\alpha^{\text{H}}$), 3.87 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5^{H}), 3.876 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3^{H}), 3.882 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, $\text{H3}\alpha^{\text{H}}$), 3.98 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, $\text{H2}\alpha^{\text{H}}$), 3.99 (dd, $J_{1,2} = 1$ Hz, $J_{2,3} = 3$ Hz, $\text{H2}\beta^{\text{H}}$), 4.01 (ddd, $J_{3,4} = 7.5$ Hz, $J_{4,5a} = 5$ Hz, $J_{4,5b} = 3$ Hz, H4^{H}), 4.15 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 5$ Hz, H2^{H}), 4.23 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2^{H}), 4.31 (dd, $J_{2,3} = 5$ Hz, $J_{3,4} = 7.5$ Hz, H3^{H}), 4.86 (d, $J_{1,2} = 1$ Hz, $\text{H1}\beta^{\text{H}}$), 5.03 (d, $J_{1,2} = 2$ Hz, H1^{H}), 5.06 (d, $J_{1,2} = 2$ Hz, $\text{H1}\alpha^{\text{H}}$), 5.20 (s, H1^{H}); ^{13}C NMR (D_2O , 100 MHz) δ 18.65 (C6^{H}), 18.73 ($\text{C6}\beta^{\text{H}}$), 18.8 ($\text{C6}\alpha^{\text{H}}$), 63.8 (C5^{H}), 70.4 (C5^{H}), 71.0 ($\text{C5}\alpha^{\text{H}}$), 71.8 (C2^{H}), 72.0 (C3^{H}), 72.6 ($\text{C2}\alpha^{\text{H}}$), 72.9 ($\text{C4}\alpha^{\text{H}}$), 73.19 ($\text{C2}\beta^{\text{H}}$), 73.23 ($\text{C5}\beta^{\text{H}}$), 73.5 (C4^{H}), 73.8 ($\text{C4}\beta^{\text{H}}$), 76.7 (C2^{H}), 79.8 (C3^{H}), 80.8 ($\text{C3}\alpha^{\text{H}}$), 82.2 ($\text{C3}\beta^{\text{H}}$), 84.5 (C4^{H}), 95.4 ($\text{C1}\beta^{\text{H}}$, $J_{\text{C1,H1}} = 159.7$ Hz), 95.9 ($\text{C1}\alpha^{\text{H}}$, $J_{\text{C1,H1}} = 170.0$ Hz), 103.9 (C1^{H} , $J_{\text{C1,H1}} = 170.1$ Hz), 110.5 (C1^{H} , $J_{\text{C1,H1}} = 175.7$ Hz).

Found: C, 44.55; H, 7.00%. Calcd for $\text{C}_{17}\text{H}_{30}\text{O}_{13}\cdot\text{H}_2\text{O}$: C, 44.35; H, 7.00%.

A similar hydrogenation of **47** (11.5 mg, 0.010 mmol) over Pd on C (10%, 20 mg) in MeOH (6 mL), followed by chromatography with EM system, gave **15** (3.3 mg, 76%).

Methyl O- α -L-Rhamnopyranosyl-(1 $\rightarrow$ 2)- β -D-ribofuranoside (48). Hydrogenation of **20a** (35.2 mg, 40 mmol) over Pd on C (40 mg) in MeOH (6 mL) at room temp overnight and chromatography with the CM system (2:1) afforded **48** (33.0 mg, 23%); $[\alpha]_D -89^\circ$ (c 0.25, MeOH); ^1H NMR (D_2O , 400 MHz) δ 1.28 (d, $J_{5,6} = 6$ Hz, H6^{H}), 3.40 (s, Me), 3.44 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^{H}), 3.59 (dd, $J_{4,5a} = 6.5$ Hz, $J_{5a,5b} = 12$ Hz, H5a^{H}), 3.70 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5^{H}), 3.77 (dd, $J_{4,5b} = 3$ Hz, $J_{4a,4b} = 12$ Hz, H5b^{H}), 3.79 (dd, $J_{2,3} = 3.5$ Hz, $J_{3,4} = 9.5$ Hz, H3^{H}), 4.02 (dt, $J_{3,4} = J_{4,5a} = 6.5$ Hz, $J_{4,5b} = 3$ Hz, H4^{H}), 4.03 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3.5$ Hz, H2^{H}), 4.05 (d, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 5$ Hz, H2^{H}), 4.25 (dd, $J_{2,3} = 5$ Hz, $J_{3,4} = 6.5$ Hz, H3^{H}), 4.95 (d, $J_{1,2} = 2$ Hz, H1^{H}), 4.99 (d, $J_{1,2} = 1.5$ Hz, H1^{H}); ^{13}C NMR (D_2O , 100 MHz) δ 18.5 (C6^{H}), 57.4 (Me), 64.3 (C5^{H}), 71.2 (C5^{H}), 71.9 (C3^{H}), 72.0 (C2^{H}), 72.2 (C3^{H}), 73.9 (C4^{H}), 82.2 (C2^{H}), 85.2 (C3^{H}), 102.9 (C1^{H} , $J_{\text{C1,H1}} = 171.3$ Hz), 108.6 (C1^{H} , $J_{\text{C1,H1}} = 175.7$ Hz); MS (FAB) m/z 333.1162 ($\text{M}+\text{Na}^+$). Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_9\text{Na}$: 333.11614.

Methyl O-(3,5-Di-O-benzyl- β -D-ribofuranosyl)-(1 $\rightarrow$ 3)-2,4-di-O-benzyl- α -L-rhamnopyranoside (50). Compound **17b** (57.6 mg, 0.081 mmol) was treated with PdCl_2 (20.0 mg, 0.113 mmol) and NaOAc (37.0 mg, 0.45 mmol) in aq AcOH (95%, 3.0 mL) at 60 °C for 2 h, followed by purification, as described for **41**, to give **50** (32.1 mg, 50%); $[\alpha]_D^{27} -24^\circ$ (c 0.5, CHCl_3); ^1H NMR (CDCl_3 , 300 MHz) δ 1.30 (d, $J_{5,6} = 6$ Hz, H6^{H}), 1.57 (s, OH), 3.29 (s, Me), 3.45 (dd, $J_{4,5a} = 5$ Hz, $J_{5a,5b} = 10$ Hz, H5a^{H}), 3.52 (dd, $J_{4,5b} = 5$ Hz, $J_{5a,5b} = 10$ Hz, H5b^{H}), 3.54 (t, $J_{3,4} = J_{4,5} = 9$ Hz, H4^{H}), 3.65 (dq, $J_{4,5} = 9$ Hz, $J_{5,6} = 6$ Hz, H5^{H}), 3.74 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2^{H}), 3.993 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9$ Hz, H3^{H}), 3.994 (dd, $J_{2,3} = 5$ Hz, $J_{3,4} = 6$ Hz, H3^{H}), 4.10 (dd, $J_{1,2} = 1.5$ Hz, $J_{2,3} = 5$ Hz, H2^{H}), 4.19 (dt, $J_{3,4} = 6$ Hz, $J_{4,5a} = J_{4,5b} = 5$ Hz, H4^{H}), 4.54 (d, $J_{1,2} = 2$ Hz, H1^{H}), 5.27 (d, $J_{1,2} = 1.5$ Hz, H1^{H}); ^{13}C NMR (CDCl_3 , 75 MHz) δ 17.9 (C6^{H}), 67.9 (C5^{H}), 71.2 (C5^{H}), 73.8 (C2^{H}), 78.4 (C2^{H}), 78.7 (C3^{H}), 79.0 (C3^{H}), 80.2 (C4^{H}), 80.7 (C4^{H}), 99.2

(C1^{H}), 109.0 (C1^{H}); 54.6 (Me).

Found: C, 71.05; H, 6.95%. Calcd for $\text{C}_{40}\text{H}_{46}\text{O}_9$: C, 71.62; H, 6.91%.

Methyl O- β -D-Ribofuranosyl-(1 $\rightarrow$ 3)- α -L-rhamnopyranoside (49). Hydrogenation of **16b** (23.3 mg, 0.031 mmol) over Pd on C (28 mg) in MeOH (6 mL) at room temp overnight and chromatography with the CM system (2:1) afforded **47** (2.8 mg, 40%); $[\alpha]_D^{23} -77^\circ$ (c 0.8, MeOH); ^1H NMR (D_2O , 400 MHz) δ 1.28 (d, $J_{5,6} = 6$ Hz, H6^{H}), 3.38 (s, Me), 3.47 (t, $J_{3,4} = J_{4,5} = 9.5$ Hz, H4^{H}), 3.68 (dd, $J_{4,5a} = 5$ Hz, $J_{5a,5b} = 12.5$ Hz, H5a^{H}), 3.71 (dq, $J_{4,5} = 9.5$ Hz, $J_{5,6} = 6$ Hz, H5^{H}), 3.73 (dd, $J_{2,3} = 3$ Hz, $J_{3,4} = 9.5$ Hz, H3^{H}), 3.83 (dd, $J_{4,5b} = 3$ Hz, $J_{5a,5b} = 12.5$ Hz, H5b^{H}), 4.01 (ddd, $J_{3,4} = 7.5$ Hz, $J_{4,5a} = 5$ Hz, $J_{4,5b} = 3$ Hz, H4^{H}), 4.09 (dd, $J_{1,2} = 2$ Hz, $J_{2,3} = 3$ Hz, H2^{H}), 4.14 (d, $J_{1,2} = 0$ Hz, $J_{2,3} = 4.5$ Hz, H2^{H}), 4.31 (dd, $J_{2,3} = 4.5$ Hz, $J_{3,4} = 7.5$ Hz, H3^{H}), 4.67 (d, $J_{1,2} = 2$ Hz, H1^{H}), 5.16 (s, H1^{H}); ^{13}C NMR (D_2O , 100 MHz) δ 19.3 (C6^{H}), 57.4 (Me), 64.3 (C5^{H}), 71.0 (C5^{H}), 72.3 (C2^{H}), 72.6 (C3^{H}), 73.6 (C4^{H}), 77.3 (C2^{H}), 81.6 (C3^{H}), 85.1 (C4^{H}), 103.2 (C1^{H} , $J_{\text{C1,H1}} = 170.4$ Hz), 111.2 (C1^{H} , $J_{\text{C1,H1}} = 174.5$ Hz).

Found: C, 46.15; H, 7.23%. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_9$: C, 46.45; H, 7.15%.

A similar debenzoylation of **50** (21.7 mg, 0.032 mmol) over Pd–C (10%, 46 mg) in MeOH (6 mL) furnished **49** (6.7 mg, 67%).

References

- N. L. Douglas, S. V. Ley, U. Lücking, and S. L. Warriner, *J. Chem. Soc., Perkin Trans. 1*, **1998**, 51; P. P. Deshpande, H. M. Kim, A. Zatorski, T.-K. Park, G. Ragupathi, P. O. Livingston, D. Live, and S. J. Danishefsky, *J. Am. Chem. Soc.*, **120**, 1600 (1998); H. Ohtake, T. Iimori, and S. Ikegami, *Synlett*, **1998**, 1420; G. Hodosi and P. Kováč, *Carbohydr. Res.*, **308**, 63 (1998); D. Crich and Z. Dai, *Tetrahedron Lett.*, **39**, 1681 (1998); S. Cassel, I. Plessis, H. P. Wessel, and P. Rollin, *Tetrahedron Lett.*, **39**, 8097 (1998); K. Fukase, Y. Nakai, T. Kanoh, and S. Kusumoto, *Chem. Lett.*, **1998**, 84; W. Wang and F. Kong, *Tetrahedron Lett.*, **39**, 1937 (1998); G. G. Cross and D. M. Whitfield, *Synlett*, **1998**, 487; M. Izumi and Y. Ichikawa, *Tetrahedron Lett.*, **39**, 2079 (1998); T. Zhu and G.-J. Boons, *Tetrahedron Lett.*, **39**, 2187 (1998); U. Schmid and H. Waldmann, *Chem. Eur. J.*, **1998**, 494; T. Ziegler and G. Lemanski, *Eur. J. Org. Chem.*, **1998**, 163; L. Green, B. Hinzen, S. J. Ince, P. Langer, S. V. Ley, and S. L. Warriner, *Synlett*, **1998**, 440; S. K. Chatterjee and P. Nuhn, *Chem. Commun.*, **1998**, 1729; H. B. Mereyala and S. R. Gurralla, *Chem. Lett.*, **1998**, 863; V. D. Bussolo, Y.-J. Kim, and D. Y. Gin, *J. Am. Chem. Soc.*, **120**, 13515 (1998); S. Yamago, K. Kokubo, H. Murakami, Y. Mino, O. Hara, and J. Yoshida, *Tetrahedron Lett.*, **39**, 7905 (1998); T. Ziegler, R. D. Ariffadhillah, and U. Zettl, *J. Carbohydr. Chem.*, **18**, 1079 (1999); T. Mukaiyama, Y. Wakiyama, K. Miyazaki, and K. Takeuchi, *Chem. Lett.*, **1999**, 933; H. Tanaka, H. Sakamoto, A. Sano, S. Nakamura, M. Nakajima, and S. Hashimoto, *Chem. Commun.*, **1999**, 1259; K. Tushima, K. Kasumi, and S. Matsumura, *Synlett*, **1999**, 813; K. Oshima and Y. Aoyama, *J. Am. Chem. Soc.*, **121**, 2315 (1999); I. Azumaya, T. Niwa, M. Kotani, T. Iimori, and S. Ikegami, *Tetrahedron Lett.*, **40**, 4683 (1999); M. Lergenmüller, T. Nukada, K. Kuramochi, A. Dan, T. Ogawa, and Y. Ito, *Eur. J. Org. Chem.*, **1999**, 1367; H. Yamada, T. Kato, and T. Takahashi, *Tetrahedron Lett.*, **40**, 4581 (1999); W. Wang and F. Kong, *Angew. Chem., Int. Ed. Engl.*, **38**, 1247 (1999); R. Caputo, H. Kunz, D. Mastroianni, G. Palumbo, S. Pedatella, and F. Sollà, *Eur. J. Org. Chem.*, **1999**, 3147; R. Geurtsen, F. Côté, M. G. Hahn, and G.-J. Boons, *J. Org. Chem.*, **64**, 7828 (1999); E. Kaji and N.

- Harita, *Tetrahedron Lett.*, **41**, 53 (2000); E. Kaji and Y. Hosokawa, *Heterocycles*, **52**, 579 (2000); J. C. Castro-Palmino and R. R. Schmidt, *Tetrahedron Lett.*, **41**, 629 (2000); V. D. Bussolo, J. Liu, L. G. Huffman, Jr., and D. Y. Gin, *Angew. Chem., Int. Ed. Engl.*, **39**, 204 (2000); K. Takeuchi, T. Tamura, and T. Mukaiyama, *Chem. Lett.*, **2000**, 122; K. Takeuchi, T. Tamura, and T. Mukaiyama, *Chem. Lett.*, **2000**, 124; K. Takeuchi, T. Tamura, H. Jona, and T. Mukaiyama, *Chem. Lett.*, **2000**, 692; T. Mukaiyama, H. Jona, and K. Takeuchi, *Chem. Lett.*, **2000**, 696; B. S. Babu, K. K. Balasubramanian, *Tetrahedron Lett.*, **41**, 1271 (2000); T. Takahashi, M. Adachi, A. Matsuda, and T. Doi, *Tetrahedron Lett.*, **41**, 2599 (2000); H. Jona, K. Takeuchi, T. Saitoh, and T. Mukaiyama, *Chem. Lett.*, **2000**, 1178; D. Magaud, R. Dolmazon, D. Anker, A. Doutheau, Y. L. Dory, and P. Deslongchamps, *Org. Lett.*, **2000**, 2275; R. Weingart and R. R. Schmidt, *Tetrahedron Lett.*, **41**, 8753 (2000); M. Adinolfi, G. Barone, L. Guariniello, and A. Iadonisi, *Tetrahedron Lett.*, **41**, 9005 (2000); M. Yun, Y. Shin, K. H. Chun, and J. E. N. Shin, *Bull. Korean Chem. Soc.*, **21**, 502 (2000); G. Scheffler, M. E. Behrendt, and R. R. Schmidt, *Eur. J. Org. Chem.*, **2000**, 3527; C. M. P. Seward, I. Cumpstey, M. Aloui, S. C. Ennis, A. J. Redgrave, and A. J. Fairbanks, *Chem. Commun.*, **2000**, 1409; G. Lemanski and T. Ziegler, *Helv. Chim. Acta*, **83**, 2655, 2676 (2000); M. Lahmann and S. Oscarson, *Org. Lett.*, **2**, 3881 (2000); D. Crich and M. Smith, *Org. Lett.*, **2**, 4067 (2000).
- 2 H. Paulsen, "Modern Methods in Carbohydrate Synthesis," ed by S. H. Khan and R. A. O'Neill, Harwood Academic Publishers (1996), p. 1; R. R. Schmidt and K.-H. Jung, "Preparative Carbohydrate Chemistry," ed by S. Hanessian, Marcel Dekker, Inc., New York (1997), p. 283; S. Hanessian, "Preparative Carbohydrate Chemistry," ed by S. Hanessian, Marcel Dekker, Inc., New York (1997), p. 381; S. L. Flitsch and G. M. Watt, "Glycopeptides and Related Compounds," ed by D. G. Large and C. D. Warren, Marcel Dekker, Inc., New York (1997), p. 207; O. Kanie and T. Ogawa, "Medicinal Chemistry: Today and Tomorrow," ed by M. Yamazaki, Blackwell Science Ltd., Oxford (1997), p. 221; G. H. Veeneman, "Carbohydrate Chemistry," by G.-J. Boons, Blackie Academic and Professional, London (1998), p. 98; C. S. Roberts and J. R. Merritt, "Bioorganic Chemistry: Carbohydrates," ed by S. M. Hecht, Oxford University Press, Oxford (1999), p. 89; S. Oscarson, *Carbohydrates*, **1999**, 150; B. G. Davis, *J. Chem. Soc., Perkin Trans. 1*, **2000**, 2137; G. Capozzi, S. Menichetti, and C. Nativi, *Methods Princ. Med. Chem.*, **7** (New Trends in Synthetic Medicinal Chemistry), 221 (2000); K. Toshima, *Carbohydr. Res.*, **327**, 15 (2000).
- 3 a) M. Kuhn and A. von Wartburg, *Helv. Chim. Acta*, **51**, 1631 (1968). b) E. Grochowski and J. Jurczak, *Carbohydr. Res.*, **50**, C15 (1976). c) W. A. Szarek, H. C. Jarrell, and J. K. N. Jones, *Carbohydr. Res.*, **57**, C13 (1977). d) J. Leroux and A. S. Perlin, *Carbohydr. Res.*, **67**, 163 (1978). e) G. Gryniewicz, *Pol. J. Chem.*, **53**, 1571 (1979). f) A. A. Pavia, J.-M. Rocheville, and A. N. Ung, *Carbohydr. Res.*, **79**, 79 (1980). g) J. A. Lacombe, A. A. Pavia, and J. M. Rocheville, *Can. J. Chem.*, **59**, 473 (1981). h) H. Tsutsumi and Y. Ishido, *Carbohydr. Res.*, **88**, 61 (1981). i) J. M. Lacombe and A. A. Pavia, *J. Org. Chem.*, **48**, 2557 (1983). j) W. Szeja, *Synthesis*, **1988**, 223. k) T. Mukaiyama and S. Suda, *Chem. Lett.*, **1990**, 1143. l) K. C. Nicolaou and R. D. Groneberg, *J. Am. Chem. Soc.*, **112**, 4085 (1990). m) N. Chida, M. Ohtsuka, K. Nakazawa, and S. Ogawa, *J. Org. Chem.*, **56**, 2976 (1991). n) S. Suda and T. Mukaiyama, *Chem. Lett.*, **1991**, 431. o) A. B. Smith, III, R. A. Rivero, K. J. Hale, and H. A. Vaccaro, *J. Am. Chem. Soc.*, **113**, 2092 (1991). p) T. Mukaiyama, K. Matsubara, and S. Suda, *Chem. Lett.*, **1991**, 981. q) N. Shimomura and T. Mukaiyama, *Chem. Lett.*, **1993**, 1941. r) J. Inanaga, Y. Yokoyama, and T. Hanamoto, *J. Chem. Soc., Chem. Commun.*, **1993**, 1090. s) T. Mukaiyama, K. Matsubara, and M. Hora, *Synthesis*, **1994**, 1368. t) N. Shimomura and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **67**, 2532 (1994). u) H. Susaki, *Chem. Pharm. Bull.*, **42**, 1917 (1994). v) P.-M. Aberg and B. Ernest, *Acta Chem. Scand.*, **48**, 356 (1994). w) W. R. Roush and X.-F. Lin, *J. Am. Chem. Soc.*, **117**, 2236 (1995). x) H. Uchiro and T. Mukaiyama, *Chem. Lett.*, **1996**, 79. y) H. Uchiro and T. Mukaiyama, *Chem. Lett.*, **1996**, 271. z) Y.-L. Li and Y.-L. Wu, *Tetrahedron Lett.*, **37**, 7413 (1996). aa) H. Uchiro, K. Miyazaki, and T. Mukaiyama, *Chem. Lett.*, **1997**, 403. bb) K. Takeuchi, S. Higuchi, and T. Mukaiyama, *Chem. Lett.*, **1997**, 969. cc) T. Kiyoi and H. Kondo, *Bioorg. Med. Chem. Lett.*, **8**, 2845 (1998). dd) C. Gallo-Rodriguez, O. Varela, and R. M. de Lederkremer, *Carbohydr. Res.*, **305**, 163 (1998). ee) M. Wakao, Y. Nakai, K. Fukase, and S. Kusumoto, *Chem. Lett.*, **1999**, 27. ff) K. Toshima, H. Nagai, and S. Matsumura, *Synlett*, **1999**, 1420. gg) D. Gueyrard, P. Rollin, T. T. T. Nga, M. Ourévitich, J.-P. Bégué, and D. Bonnet-Delpon, *Carbohydr. Res.*, **318**, 171 (1999). hh) T. Jyojima, N. Miyamoto, Y. Ogawa, S. Matsumura, and K. Toshima, *Tetrahedron Lett.*, **40**, 5023 (1999). ii) B. A. Garcia and D. Y. Gin, *J. Am. Chem. Soc.*, **122**, 4269 (2000).
- 4 a) S. Koto, N. Morishima, M. Uchino, M. Fukuda, M. Yamazaki, and S. Zen, *Bull. Chem. Soc. Jpn.*, **61**, 3943 (1988). b) S. Koto, H. Haigoh, S. Shichi, M. Hirooka, T. Nakamura, C. Maru, M. Fujita, A. Goto, T. Sato, M. Okada, S. Zen, K. Yago, and F. Tomonaga, *Bull. Chem. Soc. Jpn.*, **68**, 2331 (1995).
- 5 S. Koto, N. Morishima, C. Kusuhara, S. Sekido, T. Yoshida, and S. Zen, *Bull. Chem. Soc. Jpn.*, **55**, 2995 (1982).
- 6 a) One-pot-two-stage method (AOH is added into the system after activation of DOH): S. Koto, Y. Hamada, and S. Zen, *Chem. Lett.*, **1975**, 587; S. Koto, N. Morishima, M. Araki, T. Tsuchiya, and S. Zen, *Bull. Chem. Soc. Jpn.*, **54**, 1895 (1981). b) One-pot-one-stage method (AOH is added into the system before activation of DOH): S. Koto, N. Morishima, Y. Hamada, T. Sato, Y. Miyata and S. Zen, "The 8th International Symposium on Carbohydrate Chemistry," Kyoto, 1976, Abstr., No. 1D-4; S. Koto, N. Morishima, and S. Zen, *Bull. Chem. Soc. Jpn.*, **52**, 784 (1979); S. Koto, T. Sato, N. Morishima, and S. Zen, *Bull. Chem. Soc. Jpn.*, **53**, 1761 (1980); S. Koto, N. Morishima, and S. Zen, *Bull. Chem. Soc. Jpn.*, **55**, 1543 (1982); S. Koto, N. Morishima, M. Owa, and S. Zen, *Carbohydr. Res.*, **130**, 73 (1984); S. Koto, K. Yago, S. Zen, F. Tomonaga, and S. Shimada, *Bull. Chem. Soc. Jpn.*, **59**, 411 (1986); M. Hirooka and S. Koto, *Bull. Chem. Soc. Jpn.*, **71**, 2893 (1998).
- 7 R. Barker and H. G. Fletcher, Jr., *J. Org. Chem.*, **26**, 4605 (1961).
- 8 J. M. J. Fréchet and H. H. Baer, *Carbohydr. Res.*, **42**, 369 (1975).
- 9 S. Koto, N. Morishima, K. Takenaka, K. Kanemitsu, N. Shimoura, M. Kase, S. Kojiro, T. Nakamura, T. Kawase, and S. Zen, *Bull. Chem. Soc. Jpn.*, **62**, 3549 (1989).
- 10 S. S. Bhattacharjee and P. A. J. Gorin, *Can. J. Chem.*, **47**, 1195 (1969).
- 11 S. Koto, N. Morishima, R. Kawahara, K. Ishikawa, and S. Zen, *Bull. Chem. Soc. Jpn.*, **55**, 1092 (1982).
- 12 N. A. Kocharova, Y. A. Knirel, E. V. Kholodkova, and E. S. Stanislavsky, *Carbohydr. Res.*, **279**, 327 (1995).
- 13 T. Desai, J. Gigg, and R. Gigg, *Carbohydr. Res.*, **280**, 209 (1996).
- 14 S. Koto, N. Morishima, T. Yoshida, M. Uchino, and S. Zen, *Bull. Chem. Soc. Jpn.*, **56**, 1171 (1983).

- 15 T. Otake, T. Sonobe, and T. Suami, *Bull. Chem. Soc. Jpn.*, **52**, 3109 (1979).
- 16 P. A. Levene and I. E. Muskat, *J. Biol. Chem.*, **105**, 431 (1934); G. M. Bebault and G. G. S. Dutton, *Can. J. Chem.*, **50**, 3373 (1972).
- 17 G. Yang and F. Kong, *Carbohydr. Res.*, **211**, 179 (1991); W. Liao, Y. Liu, and D. Lu, *Carbohydr. Res.*, **260**, 151 (1994).
- 18 H. Paulsen, J. P. Lorentzen, and W. Kutschker, *Carbohydr. Res.*, **136**, 153 (1985).
- 19 a) K. Bock and C. Pedersen, *Adv. Carbohydr. Chem. Biochem.*, **41**, 27 (1983). b) K. Bock and C. Pedersen, *J. Chem. Soc., Perkin Trans. 2*, **1974**, 293.
- 20 S. Koto, A. Kusunoki, and M. Hirooka, *Bull. Chem. Soc. Jpn.*, **73**, 967 (2000); S. Koto, M. Hirooka, T. Yoshida, K. Takenaka, C. Asai, T. Nagamitsu, H. Sakuma, M. Sakurai, S. Masuzawa, M. Komiya, T. Sato, S. Zen, K. Yago, and F. Tomonaga, *Bull. Chem. Soc. Jpn.*, **73**, 2521 (2000).
- 21 a) M. Nishizawa, Y. Kan, W. Shimomoto, and H. Yamada, *Tetrahedron Lett.*, **31**, 2431 (1990). b) S. Kamiya, S. Esaki, and R. Ito, *Agric. Biol. Chem.*, **50**, 1321 (1986).
- 22 J. Ning and F. Kong, *Carbohydr. Res.*, **300**, 355 (1997).
- 23 T. M. Slaghek, A. H. van Oijen, A. A. M. Maas, J. P. Kamerling, and J. F. G. Vliegthart, *Carbohydr. Res.*, **207**, 237 (1990).
- 24 W. B. Severn and J. C. Richards, *J. Am. Chem. Soc.*, **115**, 114 (1993).
- 25 D. Chatterjee, S.-N. Cho, and P. J. Brennan, *Carbohydr. Res.*, **156**, 39 (1986); L. Valente, A. Olesker, R. Rabanal, L. E. S. Barata, G. Lukacs, and T. T. Thang, *Tetrahedron Lett.*, **1979**, 1153.
- 26 B. M. Pinto, M. M. W. Buiting, and K. B. Reimer, *J. Org. Chem.*, **55**, 2177 (1990).
- 27 J. S. Brimacombe, M. C. Cook, and L. C. N. Tucker, *J. Chem. Soc.*, **1965**, 2292; B. Danieli, F. Peri, G. Roda, G. Carrea, and S. Riva, *Tetrahedron*, **55**, 2045 (1999).
- 28 V. Pozsgay, *Carbohydr. Res.*, **69**, 284 (1979).
- 29 M. K. Gurjar and A. S. Mainkar, *Tetrahedron*, **48**, 6729 (1992).
-