

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

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β-D-Ribofuranosyl-(1→3)-α-L-rhamnopyranosyl-(1→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 system[5] (TCTM system) consisting of trimethylsilyl bromide (Me_3SiBr), cobalt(II) bromide, tetrabutylammonium bromide (TBAB), and molecular sieves 4A (MS4A) to oligosaccharide synthesis.

The TCTM system[5] is an in situ activating reagent system[6] 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).

$$\mathrm{DOH} + \mathrm{AOH} \rightarrow \mathrm{DOA} + \mathrm{H_2O} \quad (1)$$

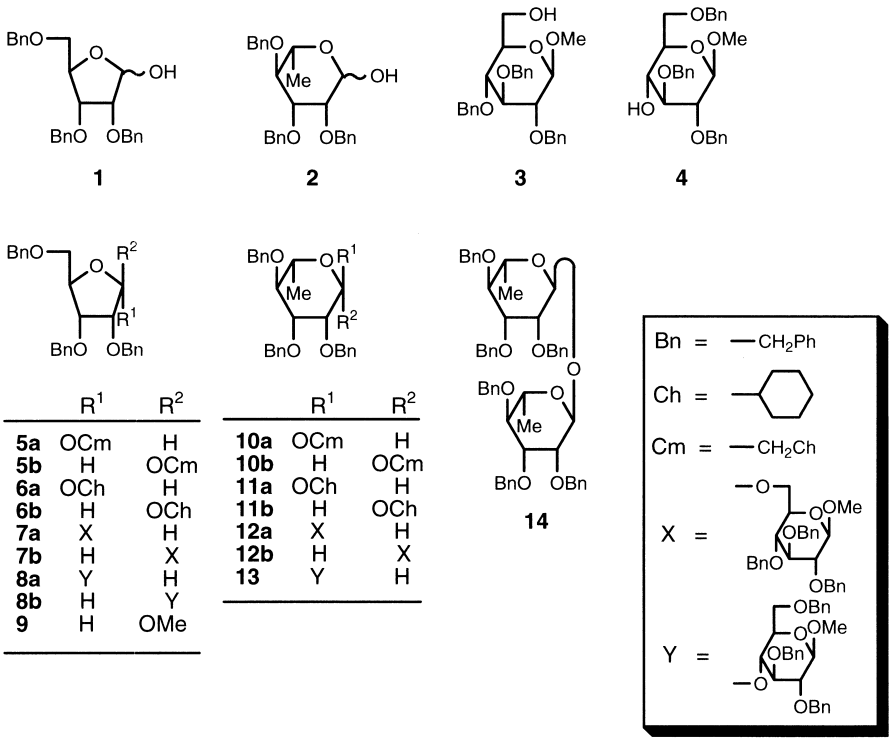
This reaction can be conducted at room temperature. This is a convenient reaction, because an acceptor can be added into the reaction system *before* adding of the activating reagent(s) for the donor (*one-pot-one-stage* method).[6b] We have now applied the TCTM system to 2,3,5-tri-*O*-benzyl-D-ribofuranose (**1**)[7] and 2,3,4-tri-*O*-benzyl-L-rhamnopyranose (**2**)[8,9] (Fig. 1) in their condensation with model acceptors, such as cyclohexylmethanol (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-glucopyanoside (**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-methane[5] 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→3)-α-L-rhamnopyranosyl-(1→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 monobenzylation 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 dibenzylation 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 tritylation[14] 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 tritylation[15] 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-



	R^1	R^2
5a	OCm	H
5b	H	OCm
6a	OCh	H
6b	H	OCh
7a	X	H
7b	H	X
8a	Y	H
8b	H	Y
9	H	OMe

	R^1	R^2
10a	OCm	H
10b	H	OCm
11a	OCh	H
11b	H	OCh
12a	X	H
12b	H	X
13	Y	H

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), $CoBr_2$ (1.3 eq), Bu_4NBr (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 alkylation[17] 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 regioselecitve 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-

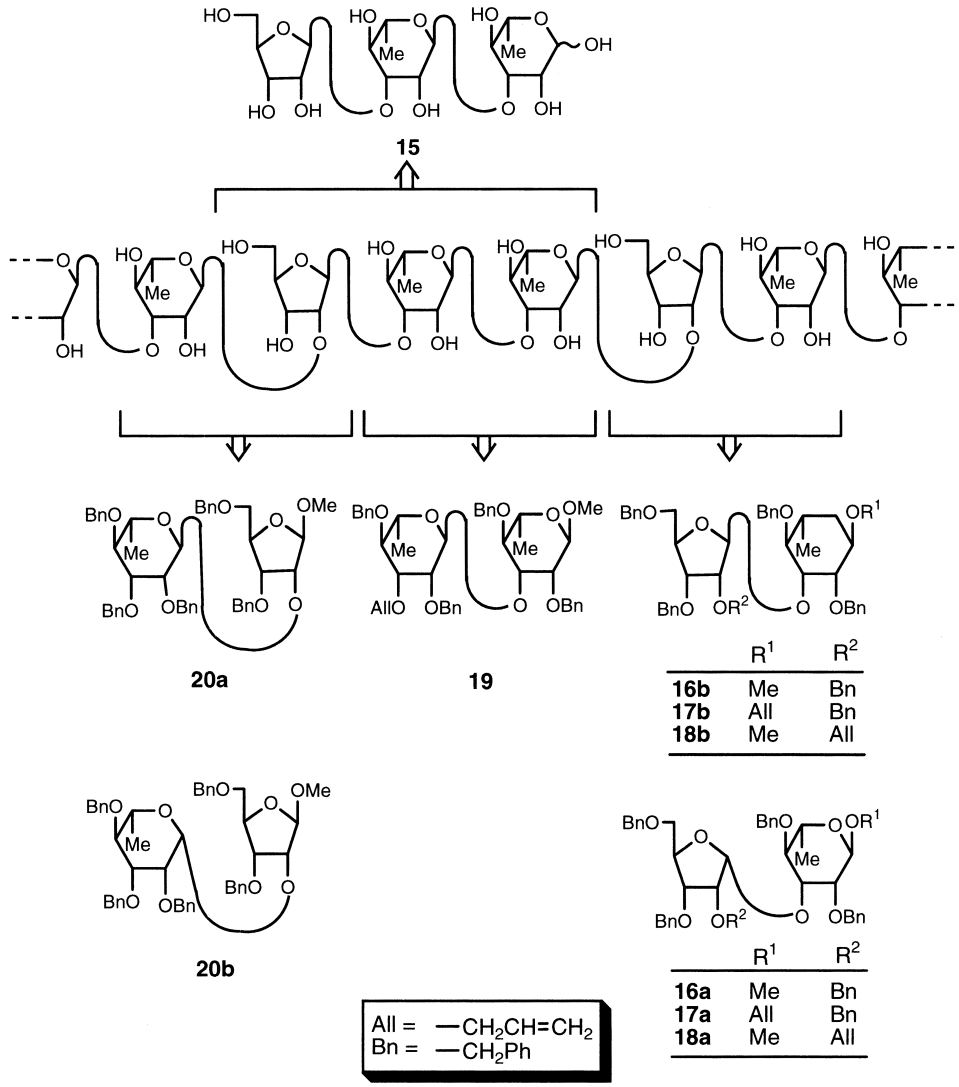


Fig. 2. The *C. freundii* O28, 1c O-specific polysaccharide and the related oligosaccharide fragments.

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

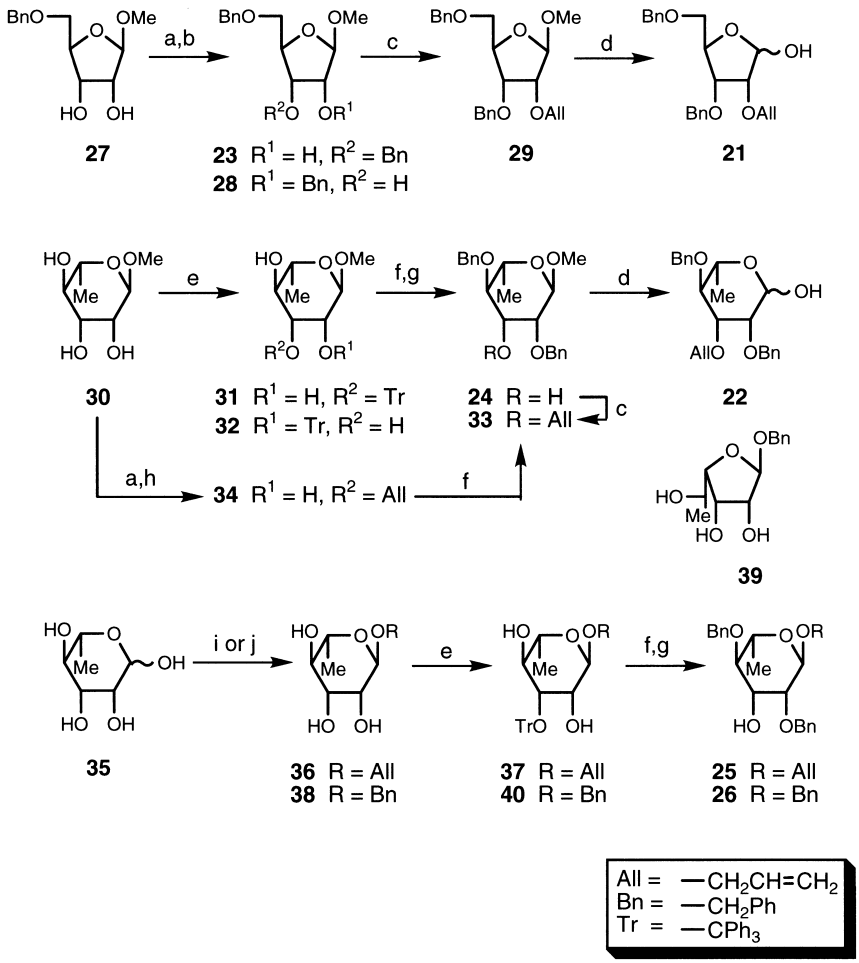


Fig. 3. The synthetic routes to the monosaccharide building units: a. BnBr, Bu_4NBr, Bu_2SnO, MS4A/C_6H_6, Δ; b. AllBr, NaH/Δ; c. aq AcOH (80%), H_2SO_4/Δ; d. TrCl, C_5H_5N/Δ; e. BnBr, NaH/DMF, 0 °C → room temperature (rt); f. MeOH, $CF_3CO_2H/CHCl_3$, rt; g. Bu_2SnO/MeOH, Δ; h. AllBr/DMF; i. AllOH, $MeSO_3H$/Δ; j. BnOH, $MeSO_3H$/Δ; k. (i) AcBr/AcOH, 0 °C, (ii) BnOH, $Hg(CN)_2$/$MeNO_2$, rt, (iii) dil NaOMe, rt.

glycosides stereoselectively (Run 8).

To build-up the trisaccharides, deallylation using palladium(II) chloride[18] 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 debenzylation of **42** afforded the methyl glycoside **44**. The structure of the synthesized **44** was assigned by the determination of its ^1H and ^{13}C NMR spectra in D_2O. The signal at δ 111.2 indicates the β-ribofuranosyl structure.[19a] The $J_{C1,H1}$ 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). Debenzylation of **45** gave the desired free trisaccharide **15**. The condensation of **25** and **43** furnished **46** (Ran 12). Deallylation of **46** yielded the trisaccharide donor **47**. Catalytic debenzylation of **47** afforded the above-described **15**. The ^1H and ^{13}C NMR spectra determined in D_2O of the synthesized trisaccharide **15** were consistent with its structure. The β-furanosyl structure was assigned by the signal at δ 110.5.[19a] The $J_{C1,H1}$ value, 170.1 Hz, of $C1^{II}$ indicates an α-rhamnopyranosyl linkage.[19b] NOE experiments as well as GHMQC experiments gave results consistent with the structure of **15**.

Two methyl glycosides of the disaccharide, which are structurally related to **15**, were synthesized. Debenzylation of **20a** gave the methyl glycoside **48**. A similar debenzylation of **16b** afforded the other disaccharide **49**. Deallylation of **18b** and subsequent debenzylation also afforded **49**. The structures of the methyl glycosides, **47** and **49**, were confirmed by determining their ^1H and ^{13}C NMR spectra in D_2O.

In summary, the TCTM system was useful for β-D-ribofuranosylation and α-L-rhamnopyranosylation. The utility of the TCTM system was shown in the first synthesis of the trisaccharide **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-

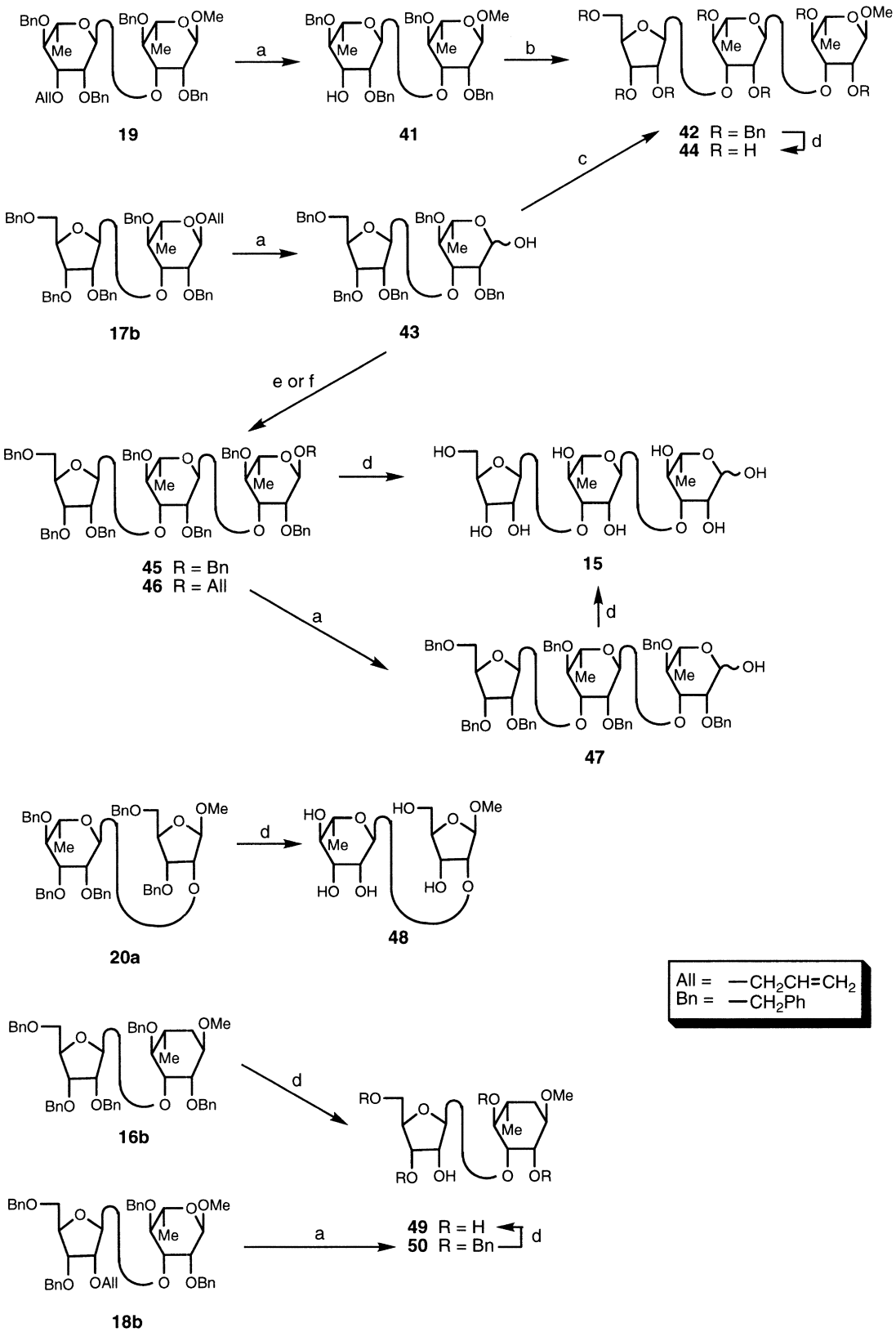


Fig. 4. Synthesis of β-D-Rib*f*-(1→3)-α-L-Rha*p*-(1→3)-L-Rha*p* and the related glycosides (TCTM = Me_3SiBr + $CoBr_2$ + Bu_4NBr + MS4A): a. $PdCl_2$, NaOAc/aq AcOH (95%), rt; b. **1**, TCTM/$(CH_2Cl)_2$, rt; c. **24**, TCTM/(CH_2Cl_2), rt; d. H_2, Pd–C (10%)/MeOH, rt; e. **26**, TCTM/$(CH_2Cl)_2$, rt; f. **25**, TCTM/$(CH_2Cl_2)_2$, rt.

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

Experimental[20]

The solvent systems for column chromatography on silica gel (Kanto Chemical, No. 37047; gradient elusion) and thin-layer chromatography (TLC) (Merck, DC-Plastikfolien Kieselgel 60 F_{254}, Art. 5735) were chloroform–MeOH (CM), 1,2–dichoroethane–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 H_2 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 ^{1}H and ^{13}C 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 (Me_3SiBr), $CoBr_2$, and tetrabutylammnomium bromide (Bu_4NBr) were products from Wako Pure Chemicals Industries. Molecular sieves, 4A, powder (MS4A) was bought from Hydrus 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 Ac_2O (0.2 mL) and pyridine (0.2 mL) containing one drop of Et_3N, 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 thier NMR spectra without their elemental analyses.

Glycosylation. To a vessel containing a donor (1.0–1.3 eq), an acceptor, $CoBr_2$ (1.3 eq), Bu_4NBr (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 $NaHCO_3$ 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 a anomeric mixture of glycosides. This was further separated with the solvent system specified below. The results are summarized in Tables 1 and 2.

Cylohexylmethyl 2,3,5-Tri-*O*-benzyl-α- and β-D-ribofuranosides (5a and 5b). 5a (the slower-moving (TK 20:1)): $[\alpha]_D$ +57° (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{33}H_{40}O_5Na$: 539.27733.

5b: $[\alpha]_D^{23}$ +17° (*c* 1.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{33}H_{40}O_5$: C, 76.71; H, 7.80%.

Cylohexyl 2,3,5-Tri-*O*-benzyl-α- and β-D-ribofuranosides (6a and 6b). 6a (the slower-moving (TK 20:1)): $[\alpha]_D$ +62° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{32}H_{38}O_5Na$: 525.26168.

6b: $[\alpha]_D^{23}$ −1.3° (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{32}H_{38}O_5$: C, 76.46; H, 7.62%.

Methyl *O*-(2,3,5-Tri-*O*-benzyl-α- and β-D-ribofuranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranosides (7a and 7b). 7a (the slower-moving (TK 20:1)): $[\alpha]_D^{20}$ +34° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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, $J_{2,3}$ = $J_{3,4}$ = 9Hz, $H3^I$), 3.73 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, $H4^I$), 3.80 (dd, $J_{5,6a}$ = 2 Hz, $J_{6a,6b}$ = 11.5Hz, $H6a^I$), 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, $H1^{II}$); ^{13}C NMR ($CDCl_3$, 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: $[\alpha]_D^{21}$ +8° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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, $H1^{II}$); ^{13}C NMR ($CDCl_3$, 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 $C_{54}H_{58}O_{10}$: C, 74.80; H, 6.74%.

Methyl *O*-(2,3,5-Tri-*O*-benzyl-α- and β-D-ribofuranosyl-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (8a and 8b). 8a (the slower-moving (TK 20:1)): $[\alpha]_D$ +31° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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^{II}), 3.77 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{I}), 3.82 (t, $J_{2,3}$ = $J_{3,4}$ = 9 Hz, H3^{I}), 4.08 (dt, $J_{3,4}$ = 2 Hz, $J_{4,5a}$ = $J_{4,5b}$ = 4 Hz, H4^{II}), 4.35 (d, $J_{1,2}$ = 8 Hz, H1^{I}), 5.56 (d, $J_{1,2}$ = 4.5 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 57.1 (Me), 70.1 (C6^{I}), 70.3 (C5^{II}), 74.2 (C5^{I}), 74.3 (C4^{I}), 75.0 (C3^{II}), 77.3 (C2^{II}), 82.3 (C4^{II}), 82.4 (C2^{I}), 84.4 (C3^{I}), 101.8 (C1^{II}, $J_{C1,H1}$ = 175.2 Hz), 104.6 (C1^{I}, $J_{C1,H1}$ = 158.1 Hz); MS (FAB) *m/z* 889.3928 $(M+Na)^+$. Calcd for $C_{54}H_{58}O_{10}Na$: 889.39273.

8b: $[\alpha]_D^{21}$ +9° (*c* 9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.39 (dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 9 Hz, H2^{I}), 3.40 (ddd, $J_{4,5}$ = 9 Hz, $J_{5,6a}$ = 4 Hz, $J_{5,6b}$ = 2 Hz, H5^{I}), 3.48 (d, $J_{4,5}$ = 5 Hz, H5^{II}), 3.56 (s, Me), 3.59 (t, $J_{2,3}$ = $J_{3,4}$ = 9 Hz, H3^{I}), 3.64 (dd, $J_{5,6a}$ = 4 Hz, $J_{6a,6b}$ = 11 Hz, H6a^{I}), 3.70 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{I}), 3.73 (dd, $J_{5,6b}$ = 2 Hz, $J_{6a,6b}$ = 11 Hz, H6b^{I}), 3.82 (dd, $J_{1,2}$ = 3 Hz, $J_{2,3}$ = 5 Hz, H2^{II}), 3.93 (t, $J_{2,3}$ = $J_{3,4}$ = 5 Hz, H3^{II}), 4.23 (dt, $J_{3,4}$ = $J_{4,5}$ = 5 Hz, H4^{II}), 4.27 (d, $J_{1,2}$ = 7.5 Hz, H1^{I}), 5.38 (d, $J_{1,2}$ = 3 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 56.9 (Me), 69.1 (C6^{I}), 70.9 (C5^{II}), 74.9 (C5^{I}), 76.7 (C4^{I}), 77.4 (C3^{II}), 80.4 (C2^{II}), 80.5 (C4^{II}), 82.3 (C2^{I}), 83.1 (C3^{I}), 104.6 (C1^{I}, $J_{C1,H1}$ = 154.2 Hz, 106.5 (C1^{II}, $J_{C1,H1}$ = 169.0 Hz).

Found: C, 74.13; H, 6.79%. Calcd for $C_{54}H_{58}O_{10}$: 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**: $[\alpha]_D^{25}$ +23° (*c* 0.5, 1,4-dioxane) (Ref. 7, $[\alpha]_D^{20}$ +22.4° (*c* 3.6, 1,4-dioxane)); ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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)): $[\alpha]_D^{19}$ −2.5° (*c* 1.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6), 68.0 (C5), 75.3 (C2), 80.3 (C3), 80.7 (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 $C_{34}H_{42}O_5$: C, 76.95; H, 7.98%.

10b: mp 80–83 °C; $[\alpha]_D$ +35° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{34}H_{42}O_5Na$: 553.29297.

Cylohexyl 2,3,4-Tri-*O*-benzyl-α- and β-L-rhamnopyranosides (11a and 11b). **11a** (the faster-moving (TK 20:1)): $[\alpha]_D^{24}$ −20° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.32 (d, $J_{5,6}$ = 6 Hz, H6), 3.61 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H_4), 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); ^{13}C NMR ($CDCl_3$, 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; $[\alpha]_D$ +15° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 $C_{33}H_{40}O_5$: 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)): $[\alpha]_D^{23}$ −17° (*c* 0.3, $CHCl_3$) (Ref. 21a $[\alpha]_D^{16}$ −12.9° (*c* 2.05, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.36 (d, $J_{5,6}$ = 6 Hz, H6^{II}), 3.43 (t, $J_{1,2}$ = $J_{2,3}$ =8 Hz, H2^{I}), 3.435 (dd, $J_{3,4}$ = 8 Hz, $J_{4,5}$ = 9 Hz, H4^{I}), 3.440 (m, H5^{I}), 3.54 (s, Me), 3.56 (dd, $J_{5,6a}$ = 6.5 Hz, $J_{6a,6b}$ = 11.5 Hz, H6a^{I}), 3.665 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{II}), 3.668 (t, $J_{2,3}$ = $J_{3,4}$ = 8 Hz, H3^{I}), 3.76 (t, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^{II}), 3.81 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^{II}), 3.92 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^{II}), 3.93 (dd, $J_{5,6b}$ = 5 Hz, $J_{6a,6b}$ = 11.5 Hz, H6b^{I}), 4.31 (d, $J_{1,2}$ = 8 Hz, H1^{I}), 4.80 (d, $J_{1,2}$ = 2 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6^{II}), 56.8 (Me), 66.5 (C6^{I}), 68.1 (C5^{II}), 74.3 (C5^{I}), 75.2 (C2^{II}), 78.0 (C4^{I}), 79.9 (C3^{II}), 80.6 (C4^{II}), 82.3 (C2^{I}), 84.6 (C3^{I}), 98.5 (C1^{II}, $J_{C1,H1}$ = 167.0 Hz), 104.5 (C1^{I}, $J_{C1,H1}$ = 158.5 Hz).

12b: $[\alpha]_D^{23}$ +24° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.37 (d, $J_{5,6}$ = 6 Hz, H6^{II}), 3.33 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^{II}), 3.37 (ddd, $J_{4,5}$ = 9 Hz, $J_{5,6a}$ = 2 Hz, $J_{5,6b}$ = 3 Hz, H5^{I}), 3.40 (t, $J_{1,2}$ = $J_{2,3}$ = 8 Hz, H2^{I}), 3.47 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^{II}), 3.56 (s, Me), 3.61 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{II}), 3.64 (dd, $J_{2,3}$ = 8 Hz, $J_{3,4}$ = 9 Hz, H3^{I}), 3.71 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{I}), 3.78 (dd, $J_{5,6a}$ = 2 Hz, $J_{6a,6b}$ = 11.5 Hz, H6a^{I}), 4.00 (d, $J_{1,2}$ = 0 Hz, $J_{2,3}$ = 3 Hz, H2^{II}), 4.26 (dd, $J_{5,6b}$ = 3 Hz, $J_{6a,6b}$ = 11.5 Hz, H6b^{I}), 4.30 (d, $J_{1,2}$ = 8 Hz, H1^{I}), 4.50 (s, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6^{II}), 57.2 (Me), 67.1 (C6^{I}), 72.0 (C5^{II}), 74.0 (C2^{II}), 74.6 (C5^{I}), 77.7 (C4^{I}), 80.3 (C4^{II}), 82.2 (C3^{II}), 82.4 (C2^{I}), 84.5 (C3^{I}), 101.6 (C1^{II}, $J_{C1,H1}$ = 152.9 Hz), 104.9 (C1^{I}, $J_{C1,H1}$ = 153.7 Hz).

Found: **12a**, C, 75.04; H, 6.99%. **12b**, C, 74.69; H, 6.96%. Calcd for $C_{55}H_{60}O_{10}$: 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). $[\alpha]_D^{20}$ −17° (*c* 2.4, $CHCl_3$) (Ref. 4a and 21b, $[\alpha]_D^{20}$ −23° (*c* 2, $CHCl_3$), $[\alpha]_D^{20}$ −15° (*c* 1, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.08 (d, $J_{5,6}$ = 6 Hz, H6^{II}), 3.35 (ddd, $J_{4,5}$ = 9 Hz, $J_{5,6a}$ = 4 Hz, $J_{5,6b}$ = 2 Hz, H5^{I}), 3.502 (dd, $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 8 Hz, H2^{I}), 3.503 (dd, $J_{5,6a}$ = 4 Hz, $J_{6a,6b}$ = 10.5 Hz, H6a^{I}), 3.53 (dd, $J_{2,3}$ = 8 Hz, $J_{3,4}$ = 9 Hz, H3^{I}), 3.58 (s, Me), 3.59 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{II}), 3.62 (dd, $J_{5,6b}$ = 2 Hz, $J_{6a,6b}$ = 10.5 Hz, H6b^{I}), 3.73 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^{II}), 3.79 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{I}), 3.83 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^{II}), 3.93 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^{II}), 4.31 (d, $J_{1,2}$ = 7.5 Hz, H1^{I}), 5.09 (d, $J_{1,2}$ = 2 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.8 (C6^{II}), 56.9 (Me), 68.7 (C5^{II}), 69.0 (C6^{I}), 75.10 (C2^{II}), 75.14 (C5^{I}), 75.4 (C4^{I}), 79.7 (C3^{II}), 80.7 (C4^{II}), 82.6 (C2^{I}), 82.7 (C3^{I}), 98.4 ($J_{C1,H1}$ = 167.6 Hz), 104.7 (C1^{I}, $J_{C1,H1}$ = 158.2 Hz).

Found: C, 75.10; H, 7.03%. Calcd for $C_{55}H_{60}O_{10}$: C, 74.98; H, 6.86%.

The β-(1→4)-linked disaccharide derivative (< 4% in Run 15 and < 6% in Run 16: ^{13}C NMR ($CDCl_3$, 75 MHz) δ 98.8 (C1^{II}), 104.6 (C1^{I}); 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**; $[\alpha]_D^{22}$ −27° (*c*

0.3, $CHCl_3$)[#] (Ref. 4a, $[\alpha]_D^{20}$ −74° (*c* 0.9, $CHCl_3$)); ^{1}H 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, $J_{C1,H1}$ = 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: $[\alpha]_D^{25}$ −23° (*c* 0.5, $CHCl_3$) (Ref. 22, $[\alpha]_D$ +17.4° (*c* 0.4, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.71 (d, $J_{2,OH}$ = 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, $J_{2,OH}$ = 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 $C_{20}H_{24}O_5$: C, 69.75; H, 7.02%.

28: $[\alpha]_D^{22}$ +13° (*c* 2, $CHCl_3$) (Ref. 23, $[\alpha]_D^{20}$ +4° (*c* 1, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.59 (d, $J_{3,OH}$ = 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, $J_{3,OH}$ = 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 $C_{20}H_{24}O_5Na$: 367.15214.

The NMR data of the acetate of **23**: ^{1}H 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**: ^{1}H 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 °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 °C for 2 h. Evaporation and chromatography with the TK system (20:1) afforded **29** (1.073 g, 88%), $[\alpha]_D^{22}$ +11° (*c* 1.2, $CHCl_3$); ^{1}H 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 $C_{23}H_{28}O_5$: 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 °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%); $[\alpha]_D^{22}$ +43° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) (65%α) δ 3.34 (d, $J_{1,OH}$ = 6.5 Hz, 1-OHβ), 3.47 (dd, $J_{4,5a}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5aα), 3.48 (dd, $J_{4,5a}$ = 3 Hz, $J_{5a,5b}$ = 10.5 Hz, H5aβ), 3.52 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5bα), 3.66 (dd, $J_{4,5b}$ = 2.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5bβ), 3.81 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4 Hz, H2β), 3.94 (dd, $J_{1,2}$ = 4 Hz, $J_{2,3}$ = 5 Hz, H2α), 4.01 (dd, $J_{2,3}$ = 5 Hz, $J_{3,4}$ = 2.5 Hz, H3α), 4.14 (d, $J_{1,OH}$ = 10 Hz, 1-OHα), 4.23 (dd, $J_{2,3}$ = 4 Hz, $J_{3,4}$ = 7 Hz, H3β), 4.28 (ddd, $J_{3,4}$ = 7 Hz, $J_{4,5a}$ = 3 Hz, $J_{4,5b}$ = 2.5 Hz, H4β), 4.36 (dt, $J_{3,4}$ = 2.5 Hz, $J_{4,5a}$ = $J_{4,5b}$ = 4 Hz, H4α), 5.28 (dd, $J_{1,2}$ = 1 Hz, $J_{1,OH}$ = 6.5 Hz, H1β), 5.31 (dd, $J_{1,2}$ = 4 Hz, $J_{1,OH}$ = 10.0 Hz, H1α); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 69.4 (C5β), 70.0 (C5α), 77.2 (C3β), 77.7 (C3α), 77.8 (C2α), 80.8 (C2β), 80.9 (C4α), 81.0 (C4β), 96.2 (C1α), 100.4 (C1β), 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 (benzy-β).

Found: C, 70.17; H, 7.07%. Calcd for $C_{22}H_{26}O_5 \cdot 0.5H_2O$: C, 69.64; H, 7.17%.

Methyl 2- and 3-*O*-Trityl-α-L-rhamnopynosides (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; ^{1}H 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, $J_{C1,H1}$ = 170.0 Hz). A mixture of **30** (3.50 g, 19.7 mmol), trityl chloride (10.7 g, 38.4 mmol), and pyridine (10mL) was stirred at 60 °C for 16 h. After the addition of Et_3N (10 mL),[14] the mixture was evaporated to dryness and chromatographed with the TKsystem (3:1) to give **31** (6.277 g, 76%); $[\alpha]_D^{20}$ −42° (*c* 1.7, $CHCl_3$) (Ref. 15, $[\alpha]_D^{20}$ −50.6° (*c* 2.7, $CHCl_3$)); ^{1}H 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, $J_{5,6}$ = 6Hz, 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 $C_{26}H_{28}O_5Na$: 443.18344.

Further elution gave **32** (0.224 mg, 7.5%); $[\alpha]_D^{20}$ +52° (*c* 0.5, $CHCl_3$) (Ref. 15, $[\alpha]_D^{20}$ +45° (*c* 1.1, $CHCl_3$)); ^{1}H 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: ^{1}H 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: ^{1}H 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, $CHCl_3$)); ^{1}H 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: ^{1}H 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).

Mthyl 3-*O*-Allyl-2,4-di-*O*-benzyl-α-L-rhamnopyanoside (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, $CHCl_3$)); ^{1}H 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-rhamnopynoside (**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)); ^{1}H 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: ^{1}H 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, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) (60%α) δ 1.31 (d, $J_{5,6}$ = 6 Hz, H6α), 1.34 (d, $J_{5,6}$ = 6 Hz, H6β), 2.65 (d, $J_{1,OH}$ = 3 Hz, OH-1α), 3.35 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5β), 3.47 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3α), 3.53 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4β), 3.59 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4α), 3.61 (dd, $J_{2,3}$ = 2 Hz, $J_{3,4}$ = 9 Hz, H3β), 3.80 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2α), 3.85 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 2 Hz, H2β), 3.92 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5α), 4.61 (d, $J_{1,2}$ = 1 Hz, H1β), 5.16 (dd, $J_{1,2}$ = 1.5 Hz, $J_{1,OH}$ = 3 Hz, H1α); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9 (C6β), 18.0 (C6α), 68.2 (C5α), 71.5 (C5β), 75.0 (C3β), 76.3 (C2β), 79.3 (C2α), 79.8 (C4β), 80.4 (C4α), 82.9 (C3α), 93.1 (C1α), 93.3 (C1β); 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-rhamnopyanoside (37). A mixture of **35** (monohydrate, 2.0 g, 11 mmol), allyl alcohol (10 mL, 15 mmol), and $MeSO_3H$ (33 µL, 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, $CHCl_3$)); ^{1}H NMR (D_2O, 300 MHz) δ

The previous value[9] 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, $J_{C1,H1}$ = 169.5 Hz); 71.7, 121.9, 136.8 (allyl).

Found: C, 51.75; H, 8.08%. Calcd for $C_9H_{16}O_5 \cdot 0.25H_2O$: 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%); $[\alpha]_D^{21}$ −46° (*c* 5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27 (d, $J_{5,6}$ = 6 Hz, H6), 1.65 (d, $J_{4,OH}$ = 3 Hz, OH-4), 2.29 (d, $J_{2,OH}$ = 3 Hz, OH-2), 3.00 (dt, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = $J_{2,OH}$ = 3 Hz, H2), 3.48 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5), 3.73 (dt, $J_{4,OH}$ = 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 $C_{28}H_{30}O_5$: C, 75.31; H, 6.77%.

The NMR data of the acetate of **37** was as follows: ^{1}H 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 CF_3CO_2H (5.0mL, 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%), $[\alpha]_D^{22}$ −2° (*c* 0.5, CH_2Cl_2) (Ref. 26, $[\alpha]_D^{25}$ +0.5° (*c* 1.10, CH_2Cl_2)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.34 (d, $J_{5,6}$ = 6 Hz, H6), 2.31 (d, $J_{3,OH}$ = 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, $J_{3,4}$ = $J_{3,OH}$= 9Hz, 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 $C_{23}H_{28}O_5$: C, 71.85; H, 7.34%.

The NMR data of the acetate of **25** was as follows: ^{1}H 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-rhamnopyanoside (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-rhamnofuranoside (**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: $[\alpha]_D^{20}$ −59° (*c* 1.1, H_2O) (Ref. 27, $[\alpha]_D^{20}$ −63° (*c* 1, H_2O), $[\alpha]_D$ −87° (*c* 0.5, MeOH)); ^{1}H 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, $J_{C1,H1}$ = 169.5 Hz), 73.1 (benzyl).

Found: C, 60.50; H, 7.25%. Calcd for $C_{13}H_{18}O_5 \cdot 0.25H_2O$: C, 60.33; H, 7.21%.

39: $[\alpha]_D^{20}$ −83° (*c* 1.6, MeOH); ^{1}H 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, $J_{C1,H1}$ = 172.1 Hz), 69.6 (benzyl).

Found: C, 61.23; H, 7.31%. Calcd for $C_{13}H_{18}O_5$: 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%), $[\alpha]_D^{21}$ −27° (*c* 1.0, $CHCl_3$); ^{1}H 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, $J_{C1,H1}$ = 167.7 Hz), 82.1 (trityl).

Found: C, 76.81; H, 6.75%. Calcd for $C_{32}H_{32}O_5$: C, 77.40; H, 6.50%.

The NMR data of the acetate of **40** was as follows: ^{1}H 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 purebenzyl ether (1.17 g). This was treated with CF_3CO_2H (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%), $[\alpha]_D^{24}$ −31° (*c* 2.1, $CHCl_3$) (Ref. 28, $[\alpha]_D$ −38.5° ($CHCl_3$)); ^{1}H 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, $J_{C1,H1}$ = 166.0 Hz).

Found: C, 74.50; H, 7.04%. Calcd for $C_{27}H_{30}O_5$: C, 74.63; H,

6.96%.

The NMR data of the acetate of **26** was as follows: ^{1}H 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→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 mol), $CoBr_2$ (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 °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; $[\alpha]_D$ +5° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30 (d, $J_{5,6}$ = 6 Hz, H6^I), 3.29 (s, Me), 3.40 (dd, $J_{4,5a}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a^{II}), 3.47 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b^{II}), 3.62 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^I), 3.68 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^I), 3.86 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^I), 3.88 (dd, $J_{1,2}$ = 4 Hz, $J_{2,3}$ = 6.5 Hz, H2^{II}), 3.93 (dd, $J_{2,3}$ = 6.5 Hz, $J_{3,4}$ = 3.5 Hz, H3^{II}), 4.20 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^I), 4.32 (dt, $J_{3,4}$ = 3.5 Hz, $J_{4,5a}$ = $J_{4,5b}$ = 4 Hz, H4^{II}), 4.63 (d, $J_{1,2}$ = 2 Hz, H1^I), 5.27 (d, $J_{1,2}$ = 4 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6^I), 54.6 (Me), 68.0 (C5^I), 70.1 (C5^{II}), 75.0 (C2^I), 75.5 (C3^{II}), 76.7 (C3^I), 78.4 (C2^{II}), 79.4 (C4^I), 82.0 (C4^{II}), 99.2 (C1^{II}, $J_{C1,H1}$ = 162.7 Hz), 99.4 (C1^I, $J_{C1,H1}$ = 168.8 Hz).

16b; $[\alpha]_D^{19}$ +2° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30 (d, $J_{5,6}$= 6 Hz, H6^I), 3.33 (s, Me), 3.45 (dd, $J_{4,5a}$ = 5.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a^{II}), 3.55 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^I), 3.61 (dd, $J_{4,5b}$ = 3.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b^{II}), 3.69 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^I), 3.79 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2^I), 3.92 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4.5 Hz, H2^{II}), 4.01 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 7 Hz, H3^{II}), 4.07 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^I), 4.33 (ddd, $J_{3,4}$ = 7 Hz, $J_{4,5a}$ = 5.5 Hz, $J_{4,5b}$ = 3.5 Hz, H4^{II}), 4.55 (d, $J_{1,2}$ = 1.5 Hz, H1^I), 5.41 (d, $J_{1,2}$ = 1 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6^I), 68.0 (C5^I), 71.0 (C5^{II}), 77.8 (C3^{II}), 78.3 (C3^I), 78.6 (C2^I), 80.2 (2C, C2^{II} and C4^{II}), 80.7 (C4^I), 99.3 (C1^I, $J_{C1,H1}$ = 166.0 Hz), 106.7 (C1^{II}, $J_{C1,H1}$ = 172.5 Hz).

A similar reaction (Run 2) using $(CH_2Cl)_2$ 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 $C_{47}H_{52}O_9$: C, 74.19; H, 6.89%.

Allyl *O*-(2,3,5-Tri-*O*-benzyl-α- and β-D-ribofuranosyl)-(1→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 mol) 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;$[\alpha]_D^{21}$ +5° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.29 (d, $J_{5,6}$ = 6 Hz, H6^I), 3.41 (dd, $J_{4,5a}$ = 3.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a^{II}), 3.47 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b^{II}), 3.63 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^I), 3.73 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^I), 3.877 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^I), 3.878 (dd, $J_{1,2}$ = 4 Hz, $J_{2,3}$ = 6.5 Hz, H2^{II}), 3.94 (dd, $J_{2,3}$ = 6.5 Hz, $J_{3,4}$ = 3.5 Hz, H3^{II}), 4.23 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^I), 4.33 (dt, $J_{3,4}$ = $J_{4,5a}$ = 3.5 Hz, $J_{4,5b}$ = 4 Hz, H4^{II}), 4.77 (d, $J_{1,2}$ = 2 Hz, H1^I), 5.28 (d, $J_{1,2}$ = 4 Hz, H1^{II}), 5.82 (m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9 (C6^I), 68.1 (C5^I), 70.0 (C5^{II}), 74.9 (C2^I), 75.4 (C3^{II}), 76.7 (C3^I), 78.3 (C2^{II}), 79.5 (C4^I), 82.0 (C4^{II}), 97.5 (C1^I, $J_{C1,H1}$ = 170.0 Hz), 99.3 (C1^{II}, $J_{C1,H1}$ = 172.4 Hz), 67.7, 117.0, 134.0 (allyl).

17b; $[\alpha]_D^{20}$ −9° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30 (d, $J_{5,6}$ = 6 Hz, H6^I), 3.45 (dd, $J_{4,5a}$ = 5 Hz, $J_{5a,5b}$ = 10 Hz, H5a^{II}), 3.55 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^I), 3.61 (dd, $J_{4,5b}$ = 3.5 Hz, $J_{5a,5b}$ = 10 Hz, H5b^{II}), 3.73 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^I), 3.82 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2^I), 3.93 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4 Hz, H2^{II}), 4.00 (dd, $J_{2,3}$ = 4 Hz, $J_{3,4}$ = 7 Hz, H3^{II}), 4.10 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^I), 4.34 (ddd, $J_{3,4}$ = 7 Hz, $J_{4,5a}$ = 5 Hz, $J_{4,5b}$ = 3.5 Hz, H4^{II}), 4.70 (d, $J_{1,2}$ = 1.5 Hz, H1^I), 5.41 (d, $J_{1,2}$ = 1 Hz, H1^{II}), 5.87 (m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9 (C6^I), 68.1 (C5^I), 71.1 (C5^{II}), 77.7 (C3^{II}), 78.4 (C3^I), 78.6 (C2^I), 80.08 (C2^{II}), 80.11 (C4^{II}), 80.7 (C4^I), 97.3 (C1^I), 106.7 (C1^{II}, $J_{C1,H1}$ = 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 $C_{49}H_{54}O_9$: C, 74.78; H, 6.92%.

A similar ribofuranosylation using $(CH_2Cl)_2$ 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→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%); $[\alpha]_D^{23}$ −3° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (d, $J_{5,6}$ = 6 Hz, H6^I), 3.31 (s, Me), 3.42 (dd, $J_{4,5a}$ = 5.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a^{II}), 3.52 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^I), 3.58 (dd, $J_{4,5b}$ = 3.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b^{II}), 3.66 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^I), 3.77 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2^I), 3.83 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4.5 Hz, H2^{II}), 3.98 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 7.5 Hz, H3^{II}), 4.03 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^I), 4.26 (ddd, $J_{3,4}$ = 7.5 Hz, $J_{4,5a}$ = 5.5 Hz, $J_{4,5b}$ = 3.5 Hz, H4^{II}),4.52 (d, $J_{1,2}$ = 1.5 Hz, H1^I), 5.31 (d, $J_{1,2}$ = 1 Hz, H1^{II}), 5.74 (m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9 (C6^I), 67.9 (C5^I), 70.9 (C5^{II}), 77.6 (C3^{II}), 78.3 (C3^I), 78.5 (C2^I), 80.0 (2C, C2^{II} and C4^{II}), 80.6 (C4^I), 99.2 (C1^I), 106.8 (C1^{II}); 54.6 (Me), 71.1, 117.2, 134.3 (allyl); MS (FAB) *m/z* 733.3353 $(M+Na)^+$. Calcd for $C_{43}H_{50}O_9Na$: 733.33522.

Further elution afforded **18a** (64.3 mg, 37%): $[\alpha]_D^{24}$ +9° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.31 (d, $J_{5,6}$ = 6 Hz, H6^I), 3.30 (s, Me), 3.41 (dd, $J_{4,.5a}$ = 3.5 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}), 3.62 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^I), 3.69 (dq $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^I), 3.84 (dd, $J_{1,2}$ = 4 Hz, $J_{2,3}$ = 6.5 Hz, H2^{II}), 3.85 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^I), 3.93 (dd, $J_{2,3}$ = 6.5 Hz, $J_{3,4}$ = 3.5 Hz, H3^{II}), 4.19 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^I), 4.31 (m, H4^{II}), 4.66 (d, $J_{1,2}$ = 2 Hz, H1^I), 5.24 (d, $J_{1,2}$ = 4 Hz, H1^{II}), 5.89 (m, allyl); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6^I), 68.0 (C5^I), 70.1 (C5^{II}), 74.6 (C2^I), 75.4 (C3^{II}), 76.7 (C3^I), 78.6 (C2^{II}), 79.4 (C4^I), 82.0 (C4^{II}), 99.2 (C1^{II}), 99.4 (C1^I); 54.5 (Me); 71.7, 117.7, 134.7 (allyl); MS (FAB) *m/z* 733.3353 $(M+Na)^+$. Calcd for $C_{43}H_{50}O_9Na$: 733.33522.

In the case of Run 6 using $(CH_2Cl)_2$, **18a** (26%) and **18b** (31%) were obtained.

Methyl *O*-(3-*O*-Allyl-2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→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 $(CH_2Cl)_2$ (3.5 mL), followed by chromatography with the TK system (10:1) to afford **19** (269.1 mg, 50%); $[\alpha]_D^{20}$ −22° (*c* 1.3, $CHCl_3$) (Ref. 29, $[\alpha]_D$ −39° (*c* 0.3, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.278 (d, $J_{5,6}$ = 6 Hz, H6^{II}), 1.283 (d, $J_{5,6}$ = 6 Hz, H6^{I}), 3.30 (s, Me), 3.56 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{II}), 3.59 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^{II}), 3.67 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 9 Hz, H5^{II}), 3.72 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^{II}), 3.77 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2^{I}), 3.80 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^{I}), 3.82 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{I}), 4.07 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^{I}), 4.63 (d, $J_{1,2}$ = 2 Hz, H1^{II}), 5.16 (d, $J_{1,2}$ = 1.5 Hz, H1^{I}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6^{II}), 18.1 (C6^{I}), 68.0 (C5^{II}), 68.7 (C5^{I}), 75.7 (C2^{I}), 77.8 (C3^{I}), 78.0 (C2^{II}), 79.7 (C4^{I}), 80.5 (C3^{II}), 80.9 (C4^{II}), 98.7 (C1^{II}, $J_{C1,H1}$ = 168.3 Hz), 99.9 (C1^{I}, $J_{C1,H1}$ = 169.1 Hz), 54.7 (Me), 71.0, 116.4, 135.1 (allyl).

Found: C, 72.36; H, 7.17%. Calcd for $C_{44}H_{52}O_9$: C, 72.91; H, 7.23%.

Methyl *O*-(2,3,4-Tri-*O*-benzyl-α- and β-L-rhamnopyranosyl)-(1→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 µL, 0.17 mmol), $CoBr_2$ (36.9 mg, 0.17 mmol), Bu_4NBr (54.3 mg, 0.17 mmol), and MS4A (153 mg) in CH_2Cl_2 (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: $[\alpha]_D^{24}$ −4° (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.36 (d, $J_{5,6}$ = 6 Hz, H6^{II}), 3.32 (s, Me), 3.53 (dd, $J_{4,.5a}$ = 5.5 Hz, $J_{5a,5b}$ = 10 Hz, H5a^{I}), 3.63 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 10 Hz, H5b^{I}), 3.64 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{II}), 3.78 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^{II}), 3.85 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^{II}), 3.91 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^{II}), 4.07 (dd, $J_{2,3}$ = 4 Hz, $J_{3,4}$ = 7 Hz, H3^{I}), 4.11 (d, $J_{1,2}$ = 0 Hz, $J_{2,3}$ = 4 Hz, H2^{I}), 4.25 (ddd, $J_{3,4}$ = 7 Hz, $J_{4,5a}$ = 5.5 Hz, $J_{4,5b}$ = 4 Hz, H4^{I}), 4.85 (s, H1^{I}), 5.04 (d, $J_{1,2}$ = 2 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6^{II}), 54.9 (Me), 68.6 (C5^{II}), 71.4 (C5^{I}), 75.1 (C2^{II}), 77.1 (C2^{I}), 79.3 (C3^{I}), 79.9 (C3^{II}), 80.1 (C4^{I}), 80.4 (C4^{II}), 98.3 (C1^{II}, $J_{C1,H1}$ = 168.3 Hz), 107.6 (C1^{I}, $J_{C1,H1}$ = 168.3 Hz).

20b: $[\alpha]_D^{22}$ +45° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.40 (d, $J_{5,6}$ = 6 Hz, H6^{II}), 3.37 (dq, $J_{4,5a}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^{II}), 3.38 (s, Me), 3.49 (dd, $J_{4,.5b}$ = 5 Hz, $J_{5a,5b}$ = 11.5 Hz, H5a^{I}), 3.50 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^{II}), 3.58 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{II}), 3.69 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 11.5 Hz, H5b^{I}), 3.97 (d, $J_{1,2}$ = 0 Hz, $J_{2,3}$ = 3 Hz, H2^{II}), 4.07 (ddd, $J_{3,4}$ = 7.5 Hz, $J_{4,5a}$ = 5 Hz, $J_{4,5b}$ = 4 Hz, H4^{I}), 4.38 (d, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4.5 Hz, H2^{I}), 4.45 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 7.5 Hz, H3^{I}), 4.60 (s, H1^{II}), 4.96 (d, $J_{1,2}$ = 1 Hz, H1^{I}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6^{II}), 55.1 (Me), 71.1 (C5^{I}), 72.1 (C5^{II}), 73.9 (C2^{II}), 77.6 (2C, C3^{I} and C4^{I}), 80.1 (C4^{II}), 81.2 (C2^{I}), 81.9 (C3^{II}), 99.9 (C1^{II}, $J_{C1,H1}$ = 153.9 Hz), 106.4 (C1^{I}, $J_{C1,H1}$ = 168.0 Hz).

Found: **20a**, C, 73.66; H, 7.00%. **20b**, C, 73.61; H, 6.85%. Calcd for $C_{47}H_{52}O_9$: C, 74.19; H, 6.89%.

Methyl *O*-(2,4-Di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (41). A mixture of **19** (109.4 mg, 0.151 mmol), $PdCl_2$ (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%); $[\alpha]_D^{20}$ −18° (*c* 0.3, $CHCl_3$) (Ref. 29, $[\alpha]_D$ −17.2° (*c* 1.0, $CHCl_3$)); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.28 (d, $J_{5,6}$ = 6 Hz, H6^{II}), 1.32 (d, $J_{5,6}$ = 6 Hz, H6^{I}), 2.27 (d, $J_{3,OH}$ = 9.5 Hz, OH-3^{II}), 3.31 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{II}), 3.33 (s, Me), 3.61 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{I}), 3.707 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4 Hz, H2^{II}), 3.708 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 3 Hz, H2^{I}), 3.709 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^{I}), 3.79 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^{II}), 3.99 (dt, $J_{2,3}$ = 4 Hz, $J_{3,4}$ = $J_{3,OH}$ = 9.5 Hz, H3^{II}), 4.10 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^{I}), 4.66 (d, $J_{1,2}$ = 1 Hz, H1^{II}), 5.19 (d, $J_{1,2}$ = 1 Hz, H1^{I}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0 (C6^{I}), 18.1 (C6^{II}), 67.8 (C5^{II}), 68.2 (C5^{I}), 71.6 (C3^{II}), 77.9 (2C, C2^{I} and C3^{I}), 79.2 (C2^{II}), 81.0 (C4^{I}), 82.3 (C4^{II}), 98.80 (C1^{II}, $J_{C1,H1}$ = 168.3 Hz), 98.84 (C1^{I}, $J_{C1,H1}$ = 169.0 Hz), 54.7 (Me).

Found: C, 71.36; H, 7.11%. Calcd for $C_{41}H_{48}O_9$: C, 71.91; H, 7.06%.

***O*-(2,3,5-Tri-*O*-benzyl-β-D-ribofuranosyl)-(1→3)-2,4-di-*O*-benzyl-L-rhamnopyranose (43).** Compound **17b** (36.1 mg, 0.046 mmol) was treated with $PdCl_2$ (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%); $[\alpha]_D^{22}$ +13° (*c* 1.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) (50%α) δ 1.27 (d, $J_{5,6}$ = 6 Hz, H6α^{I}), 1.29 (d, $J_{5,6}$ = 6 Hz, H6β^{I}), 3.35 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5β^{I}), 3.45 (dd, $J_{4,5a}$ = 4.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5aβ^{II}), 3.47 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4β^{I}), 3.50 (dd, $J_{4,5a}$ = 4.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5aα^{II}), 3.56 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4α^{I}), 3.61 (dd, $J_{4,5b}$ = 3.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5bβ^{II}), 3.67 (dd, $J_{4,5b}$ = 3 Hz, $J_{5a,5b}$ = 10.5 Hz, H5bα^{II}), 3.79 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3β^{I}), 3.818 (dd, $J_{2,3}$ = 1.5 Hz, $J_{3,4}$ = 3 Hz, H2α^{I}), 3.822 (d, $J_{1,2}$ = 0 Hz, $J_{2,3}$ = 3 Hz, H2β^{I}), 3.87 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4.5 Hz, H2α^{II}), 3.92 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 4.5 Hz, H2β^{II}), 3.94 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5α^{I}), 4.00 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 7.5 Hz, H3β^{II}), 4.05 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 7.5 Hz, H3α^{II}), 4.14 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3a^{I}), 4.32 (ddd, $J_{3,4}$ = 7.5 Hz, $J_{4,5a}$ = 4.5 Hz, $J_{4,5b}$ = 3 Hz, H4α^{II}), 4.33 (ddd, $J_{3,4}$ = 7.5 Hz, $J_{4,5a}$ = 4.5 Hz, $J_{4,5b}$ = 3.5 Hz, H4β^{II}), 4.66 (s, H1β^{I}), 5.05 (d, $J_{1,2}$ = 1.5 Hz, H1α^{I}), 5.42 (d, $J_{1,2}$ = 1 Hz, H1α^{II} and H1β^{II}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.8 (C6β^{I}), 18.0 (C6α^{I}), 68.2 (C5α^{I}), 69.9 and 70.8 (C5α^{II} and C5β^{II}), 71.4 (C5β^{I}), 76.7 and 77.5 (C3α^{II} and C3β^{II}), 77.6 (C3α^{I}), 78.6 (C2β^{II}), 79.8 (C2β^{I}), 79.87 (C2α^{I}), 79.90 (C2α^{II}), 79.99 (C4β^{II}), 80.00 (C4α^{II}), 80.2 (C3β^{I}), 80.3 (C4β^{I}), 80.6 (C4α^{I}), 93.0 (C1α^{I}), 93.1 (C1β^{I}), 106.4 and 106.6 (C1α^{II} and C1β^{II}).

Found: C, 73.71; H, 6.95%. Calcd for $C_{46}H_{50}O_9$: C, 73.97; H, 6.75%.

Methyl *O*-(2,3,5-Tri-*O*-benzyl-β-D-ribofuranosyl)-(1→3)-*O*-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→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 µL, 0.066 mmol), $CoBr_2$ (14.3 mg, 0.065 mmol), Bu_4NBr (21.1 mg, 0.065 mmol), and MS4A (40.0 mg) in $(CH_2Cl)_2$ (0.5 mL), followed by chromatography with the TK system (10:1), to afford **42** (29.4 mg, 45%); $[\alpha]_D^{23}$ −13° (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.24 (d, $J_{5,6}$ = 6 Hz, H6^{II}),1.25 (d, $J_{5,6}$ = 6 Hz, H6^{I}), 3.31 (s, Me), 3.37 (dd, $J_{4,.5a}$ = 5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a^{III}), 3.49 (dd, $J_{4,.5b}$ = 4.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b^{III}), 3.56 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{II}), 3.57 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{I}), 3.65 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^{I}), 3.71 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2^{I}), 3.81 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^{II}), 3.91 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$= 4.5 Hz, H2^{III}), 3.92 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2^{II}), 4.00 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 6.5 Hz, H3^{III}), 4.06 (dd, $J_{2,3}$ = 3, 9 Hz, H3^{I}), 4.17 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^{II}), 4.66 (d, $J_{1,2}$ = 1.5 Hz, H1^{I}), 5.11 (d, $J_{1,2}$ = 1.5 Hz, H1^{II}), 5.42 (d, $J_{1,2}$ = 1.5 Hz, H1^{III}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.9 (C6^{II}), 18.0 (C6^{I}), 54.6 (Me), 68.0 (C5^{I}), 68.6 (C5^{II}), 70.9 (C5^{III}), 77.3 (C3^{III}), 77.6 (C3^{I}), 77.8 (C2^{I}), 78.8 (C3^{II}), 79.2 (C2^{II}), 80.1 (C4^{III}), 80.4 (C2^{III}), 80.6 (C4^{II}), 80.8 (C4^{I}), 98.7 (C1^{I}, $J_{C1,H1}$ = 170 Hz), 99.8 (C1^{II}, $J_{C1,H1}$ = 170 Hz), 107.1 (C1^{III}, $J_{C1,H1}$ = 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 µL, 0.050 mmol), $CoBr_2$ (11.0 mg, 0.050 mmol), Bu_4NBr (16.2 mg, 0.050 mmol), and MS4A (50.0 mg) in $(CH_2Cl)_2$ (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→3)-*O*-α-L-rhamnopyranosyl-(1→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° (*c* 0.4, MeOH); ^{1}H NMR (D_2O, 400 MHz) δ 1.26 (d, $J_{5,6}$ = 6 Hz, H6^{II}), 1.28 (d, $J_{5,6}$ = 6 Hz, H6^{I}), 3.38 (s, Me), 3.48 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{II}), 3.52 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{I}), 3.67 (dd, $J_{4,5a}$ = 5 Hz, $J_{5a,5b}$ = 12 Hz, H5a^{III}), 3.69 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^{I}), 3.75 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^{I}), 3.81 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^{II}), 3.83 (dd, $J_{4,5b}$ = 3 Hz, $J_{5a,5b}$ = 12 Hz, H5b^{III}), 3.87 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^{II}), 3.99 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^{I}), 4.04 (ddd, $J_{3,4}$ = 7.5 Hz, $J_{4,5a}$ = 5 Hz, $J_{4,5b}$ = 3 Hz, H4^{III}), 4.14 (d, $J_{1,2}$ = 0 Hz, $J_{2,3}$ = 4.5 Hz, H2^{III}), 4.22 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^{II}), 4.30 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 7.5 Hz, H3^{III}), 4.64 (d, $J_{1,2}$ = 2 Hz, H1^{I}), 5.00 (d, $J_{1,2}$ = 2 Hz, H1^{II}), 5.19 (s, H1^{III}); ^{13}C NMR (D_2O, 100 MHz) δ 19.25 (C6^{I}), 19.31 (C6^{II}), 57.4 (Me), 64.4 (C5^{III}), 71.2 (C5^{I}), 71.7 (C5^{II}), 72.4 (C2^{I}), 72.5 (C2^{II}), 72.7 (C3^{III}), 73.6 (C4^{II}), 74.0 (C4^{I}), 77.3 (C2^{III}), 80.7 (C3^{I}), 81.5 (C3^{II}), 85.2 (C4^{III}), 103.4 (C1^{I}, $J_{C1,H1}$ = 169.6 Hz), 104.6 (C1^{II}, $J_{C1,H1}$ = 170.9 Hz), 111.2 (C1^{III}, $J_{C1,H1}$ = 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→3)-O-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→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 µL, 0.054 mmol), $CoBr_2$ (11.7 mg, 0.053 mmol), Bu_4NBr (17.3 mg, 0.054 mmol), and MS4A (50.0 mg) in $(CH_2Cl)_2$ (0.50 mL) to afford **45** (23.7 mg, 42%), $[\alpha]_D^{20}$ −26° (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.24 (d, $J_{5,6}$ = 6 Hz, H6^{II}), 1.26 (d, $J_{5,6}$ = 6 Hz, H6^{I}), 3.38 (dd, $J_{4,5a}$ = 5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a^{III}), 3.48 (dd, $J_{4,5b}$ = 4.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b^{III}), 3.56 (t, $J_{3,4}$ = $J_{4.5}$ = 9.5 Hz, H4^{II}), 3.60 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{I}), 3.74 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^{I}), 3.77 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^{I}), 3.82 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^{II}), 3.92 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 4.5 Hz, H2^{III}), 3.93 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2^{II}), 4.01 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 6.5 Hz, H3^{III}), 4.14 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^{I}), 4.17 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^{II}), 4.86 (d, $J_{1,2}$ = 2 Hz, H1^{I}), 5.12 (d, $J_{1,2}$ = 1.5 Hz, H1^{II}), 5.42 (d, $J_{1,2}$ = 1.5 Hz, H1^{III}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.9 (C6^{II}), 18.0 (C6^{I}), 68.4 (C5^{I}), 68.6 (C5^{II}), 70.8 (C5^{III}), 77.8 (C3^{I}), 77.88 (C3^{III}), 77.93 (C2^{I}), 78.8 (C3^{II}), 79.2 (C2^{II}), 80.1 (C4^{III}), 80.4 (C2^{III}), 80.6 (C4^{II}), 80.8 (C4^{I}), 96.9 (C1^{I}), 99.8 (C1^{II}), 107.1 (C1^{III}).

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→3)-*O*-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (46) (Run12)**.** 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 µL, 0.061 mmol), $CoBr_2$ (13.5 mg, 0.062 mmol), Bu_4NBr (19.8 mg, 0.061 mmol), and MS4A (85.0 mg) in $(CH_2Cl)_2$ (0.50 mL) to afford **46** (32.4 mg, 52%); $[\alpha]_D^{23}$ −15° (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.239 (d, $J_{5,6}$ = 6 Hz, H6^{II}), 1.244 (d, $J_{5,6}$ = 6 Hz, H6^{I}), 3.37 (dd, $J_{4,5a}$ = 5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5a^{III}), 3.48 (dd, $J_{4,5b}$ = 4.5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5b^{III}), 3.56 (t, $J_{3,4}$ = $J_{4.5}$ = 9.5 Hz, H4^{II}), 3.58 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^{I}), 3.70 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^{I}), 3.75 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2^{I}), 3.82 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^{II}), 3.91 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 4.5 Hz, H2^{III}), 3.93 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2^{II}), 4.01 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 6.5 Hz, H3^{III}), 4.12 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^{I}), 4.17 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^{II}), 4.31 (ddd, $J_{3,4}$ = 6.5 Hz, $J_{4,5a}$ = 5 Hz, $J_{4,5b}$ = 4.5 Hz, H4^{III}), 4.81 (d, $J_{1,2}$ = 1.5 Hz, H1^{I}), 5.12 (d, $J_{1,2}$ = 1.5 Hz, H1^{II}), 5.42 (d, $J_{1,2}$ = 1.5 Hz, H1^{III}), 5.85 (m, allyl); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.8 (C6^{II}), 18.0 (C6^{I}), 68.2 (C5^{I}), 68.6 (C5^{II}), 70.8 (C5^{III}), 77.7 (C3^{I}), 77.9 (C2^{I}), 78.0 (C3^{III}), 78.8 (C3^{II}), 79.2 (C2^{II}), 80.1 (C4^{III}), 80.4 (C2^{III}), 80.6 (C4^{II}), 80.8 (C4^{I}), 96.8 (C1^{I}, $J_{C1,H1}$ = 167.8 Hz), 99.8 (C1^{II}, $J_{C1,H1}$ = 169.2 Hz), 107.1 (C1^{III}, $J_{C1,H1}$ = 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→3)-*O*-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2,4-di-*O*-benzyl-L-rhamnopyranose (47).** Compound **46** (46.3 mg, 0.042 mmol) was treated with $PdCl_2$ (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° (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz) (56%α) δ 1.24 (d, $J_{5,6}$ = 6 Hz, H6α^{I}), 1.25 (d, $J_{5,6}$ = 6 Hz, H6α^{II}), 1.26 (d, $J_{5,6}$ = 6 Hz, H6β^{I}), 1.30 (d, $J_{5,6}$ = 6 Hz, H6β^{II}), 3.35 (dq, $J_{4,.5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5β^{I}), 3.38 (dd, $J_{4,5a}$ = 5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5aα^{III}), 3.39 (dd, $J_{4,5a}$ = 5 Hz, $J_{5a,5b}$ = 10.5 Hz, H5aβ^{III}), 3.50 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5bα^{III}), 3.54 (dd, $J_{4,5b}$ = 4 Hz, $J_{5a,5b}$ = 10.5 Hz, H5bβ^{III}), 3.55 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4β^{I}), 3.57 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4α^{I}), 3.59 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4α^{II}), 3.61 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4β^{II}), 3.76 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2α^{I}), 3.78 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2β^{I}), 3.82 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5α^{I}), 3.87 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5β^{II}), 3.88 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5α^{II}), 3.92 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 4.5 Hz, H2β^{III}), 3.93 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 4.5 Hz, H2α^{III}), 3.94 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2α^{II}), 3.97 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 3 Hz, H2β^{II}), 4.018 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$= 6.5 Hz, H3α^{III}), 4.020 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 6.5 Hz, H3β^{III}), 4.16 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3β^{I} and H3β^{II}), 4.17 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3α^{I} and H3α^{II}), 4.65 (s, H1β^{I}), 5.13 (d, $J_{1,2}$ = 1.5 Hz, H1α^{II}), 5.18 (d, $J_{1,2}$ = 1.5 Hz, H1α^{I}), 5.22 (d, $J_{1,2}$ = 1.5 Hz, H1β^{II}), 5.40 (d, $J_{1,2}$ = 1.5 Hz, H1β^{III}), 5.43 (d, $J_{1,2}$ = 1.5 Hz, H1α^{III}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.7 (C6β^{II}), 17.97 (C6α^{I} and C6α^{II}), 18.03 (C6β^{I}), 68.3 (C5α^{II}), 68.6 (C5α^{I}), 69.2 (C5β^{II}), 70.7 (C5β^{III}), 70.8 (C5α^{III}), 71.6 (C5β^{I}), 77.7 (C3β^{III}), 77.88 (C3α^{III}), 77.92 (C2α^{I}), 78.6 (C3β^{II}), 78.7 (C3α^{II}), 78.8 (C3α^{I} and C3β^{I}), 78.86 (C2β^{I}), 78.94 (C2β^{II}), 79.2 (C2α^{II}), 80.1 (C4α^{III}), 80.2 (C2β^{III} and C4β^{III}), 80.3 (C2α^{III}), 80.6 (C4α^{I} and C4β^{I}), 80.7 (C4β^{II}), 80.8 (C4α^{II}), 92.6 (C1α^{I}), 93.3 (C1β^{I}), 99.7 (C1α^{II}), 99.6 (C1β^{II}), 107.06 (C1β^{III}), 107.08 (C1α^{III}).

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→3)-*O*-α-L-rhamnopyranosyl-(1→3)-L-rhamnopyranose (15).** Hydrogenation of **47** (29.3 mg, 0.027 mmol) over Pd on C (20 mg) in MeOH (6 mL) containing H_2O (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° (*c* 0.6, MeOH); ^{1}H NMR (D_2O, 400 MHz) (67%α) δ 1.26 (d, $J_{5,6}$ = 6 Hz, H6α^I), 1.268 (d, $J_{5,6}$ = 6 Hz, H6β^I), 1.274 (d, $J_{5,6}$ = 6 Hz, H6^{II}), 3.44 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5β^I), 3.45 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4β^I),3.49 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{II}), 3.52 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4α^I), 3.64 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3β^{II}), 3.68 (dd, $J_{4,5a}$ = 5 Hz, $J_{5a,5b}$ = 12 Hz, H5a^{III}), 3.837 (dd, $J_{4,5b}$ = 3 Hz, $J_{5a,5b}$ = 12 Hz, H5b^{III}), 3.838 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5α^I), 3.87 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^{II}), 3.876 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^{II}), 3.882 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3α^I), 3.98 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2α^I), 3.99 (dd, $J_{1,2}$ = 1 Hz, $J_{2,3}$ = 3 Hz, H2β^I), 4.01 (ddd, $J_{3,4}$ = 7.5 Hz, $J_{4,5a}$ = 5 Hz, $J_{4,5b}$ = 3 Hz, H4^{III}), 4.15 (d, $J_{1,2}$ = 0 Hz, $J_{2,3}$ = 5 Hz, H2^{III}), 4.23 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^{II}), 4.31 (dd, $J_{2,3}$ = 5 Hz, $J_{3,4}$ = 7.5 Hz, H3^{III}), 4.86 (d, $J_{1,2}$ = 1 Hz, H1β^I), 5.03 (d, $J_{1,2}$ = 2 Hz, H1^{II}), 5.06 (d, $J_{1,2}$ = 2 Hz, H1α^I), 5.20 (s, H1^{III}); ^{13}C NMR (D_2O, 100 MHz) δ 18.65 (C6^{II}), 18.73 (C6β^I), 18.8 (C6α^I), 63.8 (C5^{III}), 70.4 (C5^{II}), 71.0 (C5α^I), 71.8 (C2^{II}), 72.0 (C3^{III}), 72.6 (C2α^I), 72.9 (C4α^I), 73.19 (C2β^I), 73.23 (C5β^I), 73.5 (C4^{II}), 73.8 (C4β^I), 76.7 (C2^{III}), 79.8 (C3^{II}), 80.8 (C3α^I), 82.2 (C3β^I), 84.5 (C4^{III}), 95.4 (C1β^I, $J_{C1,H1}$ = 159.7 Hz), 95.9 (C1α^I, $J_{C1,H1}$ = 170.0 Hz), 103.9 (C1^{II}, $J_{C1,H1}$ = 170.1 Hz), 110.5 (C1^{III}, $J_{C1,H1}$ = 175.7 Hz).

Found: C, 44.55; H, 7.00%. Calcd for $C_{17}H_{30}O_{13}\cdot H_2O$: 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→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° (*c* 0.25, MeOH); ^{1}H NMR (D_2O, 400 MHz) δ 1.28 (d, $J_{5,6}$ = 6 Hz, H6^{II}), 3.40 (s, Me), 3.44 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^{II}), 3.59 (dd, $J_{4,5a}$ = 6.5 Hz, $J_{5a,5b}$ = 12 Hz, H5a^I), 3.70 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^{II}), 3.77 (dd, $J_{4,5b}$ = 3 Hz, $J_{4a,4b}$ = 12 Hz, H5b^I), 3.79 (dd, $J_{2,3}$ = 3.5 Hz, $J_{3,4}$ = 9.5 Hz, H3^{II}), 4.02 (dt, $J_{3,4}$ = $J_{4,5a}$ = 6.5 Hz, $J_{4,5b}$ = 3 Hz, H4^I), 4.03 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3.5 Hz, H2^{II}), 4.05 (d, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 5 Hz, H2^I), 4.25 (dd, $J_{2,3}$ = 5 Hz, $J_{3,4}$ = 6.5 Hz, H3^I), 4.95 (d, $J_{1,2}$ = 2 Hz, H1^{II}), 4.99 (d, $J_{1,2}$ = 1.5 Hz, H1^I); ^{13}C NMR (D_2O, 100 MHz) δ 18.5 (C6^{II}), 57.4 (Me), 64.3 (C5^I), 71.2 (C5^{II}), 71.9 (C3^{II}), 72.0 (C2^{II}), 72.2 (C3^I), 73.9 (C4^{II}), 82.2 (C2^I), 85.2 (C3^I), 102.9 (C1^{II}, $J_{C1,H1}$ = 171.3 Hz), 108.6 (C1^I, $J_{C1,H1}$ = 175.7 Hz); MS (FAB) *m/z* 333.1162 $(M+Na)^+$. Calcd for $C_{12}H_{22}O_9Na$: 333.11614.

Methyl *O*-(3,5-Di-*O*-benzyl-β-D-ribofuranosyl)-(1→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° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.30 (d, $J_{5,6}$ = 6 Hz, H6^I), 1.57 (s, OH), 3.29 (s, Me), 3.45 (dd, $J_{4,5a}$ = 5 Hz, $J_{5a,5b}$ = 10 Hz, H5a^{II}), 3.52 (dd, $J_{4,5b}$ = 5 Hz, $J_{5a,5b}$ = 10 Hz, H5b^{II}), 3.54 (t, $J_{3,4}$ = $J_{4,5}$ = 9 Hz, H4^I), 3.65 (dq, $J_{4,5}$ = 9 Hz, $J_{5,6}$ = 6 Hz, H5^I), 3.74 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^I), 3.993 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9 Hz, H3^I), 3.994 (dd, $J_{2,3}$ = 5 Hz, $J_{3,4}$ = 6 Hz, H3^{II}), 4.10 (dd, $J_{1,2}$ = 1.5 Hz, $J_{2,3}$ = 5 Hz, H2^{II}), 4.19 (dt, $J_{3,4}$ = 6 Hz, $J_{4,5a}$ = $J_{4,5b}$ = 5 Hz, H4^{II}), 4.54 (d, $J_{1,2}$ = 2 Hz, H1^I), 5.27 (d, $J_{1,2}$ = 1.5 Hz, H1^{II}); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.9 (C6^I), 67.9 (C5^I), 71.2 (C5^{II}), 73.8 (C2^{II}), 78.4 (C2^I), 78.7 (C3^I), 79.0 (C3^{II}), 80.2 (C4^{II}), 80.7 (C4^I), 99.2 (C1^I), 109.0 (C1^{II}); 54.6 (Me).

Found: C, 71.05; H, 6.95%. Calcd for $C_{40}H_{46}O_9$: C, 71.62; H, 6.91%.

Methyl *O*-β-D-Ribofuranosyl-(1→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° (*c* 0.8, MeOH); ^{1}H NMR (D_2O, 400 MHz) δ 1.28 (d, $J_{5,6}$ = 6 Hz, H6^I), 3.38 (s, Me), 3.47 (t, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H4^I), 3.68 (dd, $J_{4,5a}$ = 5 Hz, $J_{5a,5b}$ = 12.5 Hz, H5a^I), 3.71 (dq, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6 Hz, H5^I), 3.73 (dd, $J_{2,3}$ = 3 Hz, $J_{3,4}$ = 9.5 Hz, H3^I), 3.83 (dd, $J_{4,5b}$ = 3 Hz, $J_{5a,5b}$ = 12.5 Hz, H5b^{II}), 4.01 (ddd, $J_{3,4}$ = 7.5 Hz, $J_{4,5a}$ = 5 Hz, $J_{4,5b}$ = 3 Hz, H4^{II}), 4.09 (dd, $J_{1,2}$ = 2 Hz, $J_{2,3}$ = 3 Hz, H2^I), 4.14 (d, $J_{1,2}$ = 0 Hz, $J_{2,3}$ = 4.5 Hz, H2^{II}), 4.31 (dd, $J_{2,3}$ = 4.5 Hz, $J_{3,4}$ = 7.5 Hz, H3^{II}), 4.67 (d, $J_{1,2}$ = 2 Hz, H1^I), 5.16 (s, H1^{II}); ^{13}C NMR (D_2O, 100 MHz) δ 19.3 (C6^I), 57.4 (Me), 64.3 (C5^{II}), 71.0 (C5^I), 72.3 (C2^I), 72.6 (C3^{II}), 73.6 (C4^I), 77.3 (C2^{II}), 81.6 (C3^I), 85.1 (C4^{II}), 103.2 (C1^I, $J_{C1,H1}$ = 170.4 Hz), 111.2 (C1^{II}, $J_{C1,H1}$ = 174.5 Hz).

Found: C, 46.15; H, 7.23%. Calcd for $C_{12}H_{22}O_9$: C, 46.45; H, 7.15%.

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

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