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Synthesis and NMR analysis of ^{13}C-labeled oligosaccharides corresponding to the major glycolipid from *Mycobacterium leprae*

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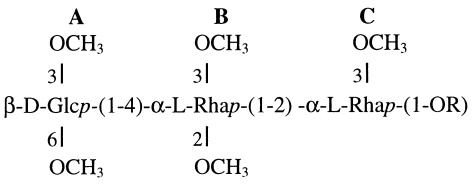
Abstract

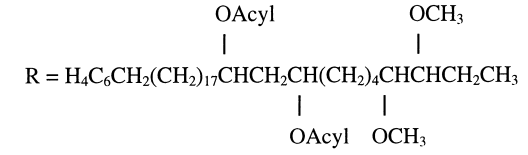
An improved synthesis of propyl 4-*O*-(3,6-di-*O*-methyl-β-D-glucopyranosyl)-2,3-di-*O*-methyl-α-L-rhamnopyranoside, a disaccharide corresponding to the phenolic glycolipid of *Mycobacterium leprae* using a trichloroacetimidate as a glycosyl donor is described. The synthetic strategy is also applied to the preparation of three corresponding disaccharide analogues containing ^{13}C-labeled methyl groups. The preparation of the trisaccharide, propyl 2-*O*-[4-*O*-(3,6-di-*O*-methyl-β-D-glucopyranosyl)-2,3-di-*O*-methyl-α-L-rhamnopyranosyl]-3-*O*-methyl-α-L-rhamnopyranoside is also reported. The di- and tri-saccharides were characterized by ^{1}H and ^{13}C NMR spectroscopy.

Keywords: Mycobacterium leprae; Synthesis; Oligosaccharide haptens; ^{13}C-labeled

1. Introduction

Mycobacterium leprae produces a unique phenolic glycolipid [1,2]:





Antibodies against oligosaccharides of this glycolipid have been detected in the sera of leprosy patients [2–5], suggesting that the oligosaccharides might be of value as diagnostic reagents or as components of vaccines. Synthetic [6–18] and conformational [18] studies of the di- and tri-saccharides have been reported, and immunochemical studies [7,8] have shown that the disaccharide **1**

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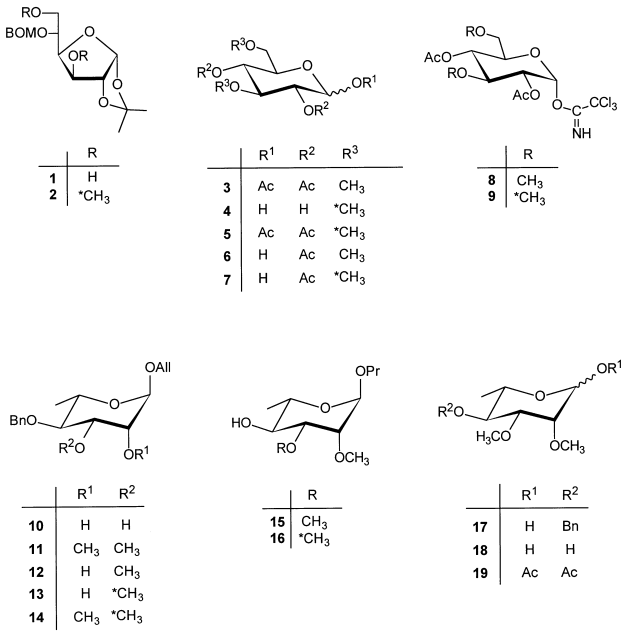
bound to antibodies and was also effective in the serodiagnosis of leprosy. The design of superior immunodiagnostic reagents requires a detailed understanding of the interaction between hapten and antibody. The use of ^{13}C-labeled compounds should thus prove useful [19–25].

We report herein the improved synthesis and NMR characterization of propyl 4-*O*-(3,6-di-*O*-methyl-β-D-glucopyranosyl)-2,3-di-*O*-methyl-α-L-rhamnopyranoside and three corresponding ^{13}C-labeled disaccharide analogues. These compounds will serve as initial substrates with which to test the NMR methods of analysis. The preparation and NMR of the trisaccharide hapten, propyl 2-*O*-[4-*O*-(3,6-di-*O*-methyl-β-D-glucopyranosyl)-2,3-di-*O*-methyl-α-L-rhamnopyranosyl]-3-*O*-methyl-α-L-rhamnopyranoside, is also reported.

2. Results and discussion

The unlabeled glycosyl donor **8** was prepared from the known diacetate **3** [6,15]. The corresponding labeled derivative **9** was synthesized from the benzoxymethylether **1** [26]. Methylation of **1** with an excess of methyl-^{13}C iodide gave the dimethyl ether **2** in 93% yield. The ^{1}H NMR spectrum of **2** showed two methyl signals which appeared as doublets ($^1J_{13C,H} = 141$ and 142 Hz), and signals corresponding to H-3, H-6 and H-6′ showed additional coupling (4.5, 2.5, and 4 Hz, respectively) to the labelled $^{13}CH_3$. Hydrolysis of compound **2** gave the triol **4** that was, in turn, acetylated to yield the triacetate **5**. Treatment of **3** and **5** with hydrazine acetate [27] gave the corresponding hemiacetals **6** and **7**, which were converted to the trichloroacetimidates **8** and **9**, respectively, by reaction with trichloroacetonitrile and K_2CO_3 [28].

The preparation of disaccharides **24**–**27** and trisaccharide **32** was accomplished using allyl 4-*O*-benzyl-α-L-rhamnopyranoside **10** [29] as a common precursor. Methylation of the diol **10** with methyl iodide in DMF containing sodium hydride gave the dimethylated compound **11** quantitatively. Regioselective monomethylation of the equatorial hydroxyl group of the diol **10** with methyl iodide was achieved via the corresponding stannylene acetal [30] and gave the methyl ether **12** (71%). The regioselectivity of the methylation reaction was confirmed by the downfield shift of C-3 (71.5 to 80.0 ppm) in the ^{13}C NMR spectrum; the shift of C-2 (67.3 ppm) was similar to that (67.9 ppm) in the spectrum of **10**. The labeled compound **13** was similarly obtained by monomethylation of **10** with ^{13}C-labeled methyl iodide. Compound **13** (54%) was, in turn, methylated at O-2 with unlabeled methyl iodide to give the dimethyl ether **14** quantitatively. The compound was labeled at O-3 (not)-2) because of its proximity to the glucosyl unit at O-4 in the disaccharide, with the expectation that this would facilitate analysis of conformations about the glycosidic linkage. Hydrogenolysis of the benzyl ether in compounds **11** and **14** led, as expected, to reduction of the allyl group to a propyl group, and gave the glycosyl acceptors **15** and **16**, respectively. Substitution at O-3 by a ^{13}C-labeled methyl group and at O-2 by an unlabeled methyl group in compound **16** was confirmed by an inverse ^{13}C–^{1}H correlation NMR experiment, optimized for long-range correlations. The spectrum showed an intense cross peak between the ^{13}C-labeled methyl signal (56.9 ppm) and the H-3 signal (3.43 ppm), corresponding to $^3J^{13}_{CH_3,H-3}$, and a less intense cross peak between the unlabeled methyl signal (58.9 ppm) and the H-2 signal, corresponding to $^3J_{CH_3,H-2}$. An additional crosspeak was observed between the ^{13}C labeled methyl signal and the H-4 signal (3.54 ppm), corresponding to $^4J^{13}_{CH_3,H-4}$. The allyl glycoside **11** was also treated with palladium (II) chloride [31] and the resulting hemiacetal **17** was hydrogenolyzed to give the diol **18**. Acetylation of **18** gave the diacetate **19** which was used as a glycosyl donor in the synthesis of the trisaccharide **30** (see below).



	R
1	H
2	*CH$_3$

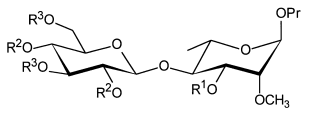
	R^1	R^2	R^3
3	Ac	Ac	CH$_3$
4	H	H	*CH$_3$
5	Ac	Ac	*CH$_3$
6	H	Ac	CH$_3$
7	H	Ac	*CH$_3$

	R
8	CH$_3$
9	*CH$_3$

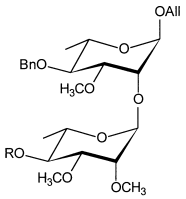
	R^1	R^2
10	H	H
11	CH$_3$	CH$_3$
12	H	CH$_3$
13	H	*CH$_3$
14	CH$_3$	*CH$_3$

	R
15	CH$_3$
16	*CH$_3$

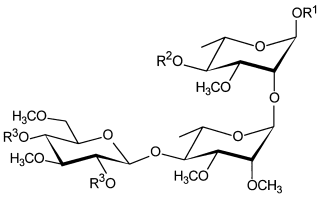
	R^1	R^2
17	H	Bn
18	H	H
19	Ac	Ac



	R^1	R^2	R^3
20	CH_3	Ac	CH_3
21	*CH_3	Ac	CH_3
22	CH_3	Ac	*CH_3
23	*CH_3	Ac	*CH_3
24	CH_3	H	CH_3
25	*CH_3	H	CH_3
26	CH_3	H	*CH_3
27	*CH_3	H	*CH_3



	R
28	Ac
29	H



	R^1	R^2	R^3
30	All	Bn	Ac
31	All	Bn	H
32	Pr	H	H

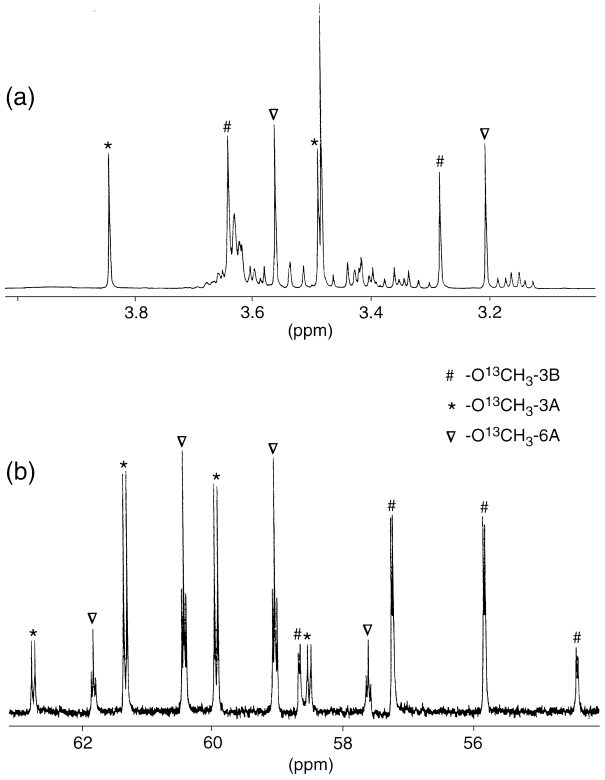


Fig. 1. Partial (a) ^1H and (b) ^{13}C NMR spectra of the ^{13}C-labeled disaccharide **27**.

Glycosylation reactions with the trichloroacetimidate derivatives **8** and **9** were performed under catalysis with triethylsilyl triflate (TESOTf). Hence, glycosylation of **15** and **16** with the trichloroacetimidate **8** gave disaccharides **20** (99%) and **21** (93%), respectively. Similarly, glycosylation of **15** and **16** with the labeled trichloroacetimidate **9** gave disaccharides **22** (71%) and **23** (79%), respectively. Zemplén deacetylation of disaccharides **20–23** gave the deprotected disaccharides **24–27**, respectively. The ^{13}C NMR spectra of these disaccharides indicated that the $^3J^{13}_{CH_3-O-C-H}$ coupling pathways required for further NMR experiments with antibody-hapten complexes e.g., isotope-filtered experiments were clearly present (e.g. Fig. 1).

The trisaccharide **30** was synthesized as follows. The disaccharide **28** was prepared by glycosylation of the acceptor **12** with the diacetate **19** in the presence of BF_3–Et_2O as a catalyst [17]. The configuration of the glycosidic linkage was confirmed by the $^1J_{C-1,H-1}$ coupling constant of 171 Hz [32]. Zemplén deacetylation of disaccharide **28** gave the glycosyl acceptor **29** which was, in turn, glycosylated with the trichloroacetimidate **8** to give the trisaccharide **30**. Deprotection of the trisaccharide **30** by deacetylation followed by hydrogenolysis afforded the trisaccharide **32**.

3. Experimental

General methods.—Melting points (mps) were measured on a Fisher–Johns melting point apparatus and are uncorrected. Optical rotations were measured on a Rudolph Research Autopol II automatic polarimeter. ^1H NMR (400.13 MHz), ^{13}C NMR (100.6 MHz) spectra were recorded on a Bruker AMX-400 NMR in $CDCl_3$ (internal standard, for ^1H: residual $CHCl_3$ δ 7.24; for ^{13}C: $CDCl_3$ δ 77.0), unless otherwise stated. Chemical shifts and coupling constants were obtained from a first-order analysis of the spectra. ^1H-^1H COSY and inverse ^{13}C-^1H correlated spectra were acquired with data sets of 2K(F2)×512(F1), the FIDs were zero-filled to a 1K(F2)×1K(F1) data set, and processed using a sine-squared apodization function with a shift of 2 in F1 and F2. The spectra were displayed in the absolute value mode. For the inverse detection experiments, a 4-pulse sequence was used for the $^1H\{^{13}C\}$–^{13}C correlation [33]; the same sequence, incorporating a BIRD pulse in the preparation period, was used for the ^1H–^{13}C correlation [34]. The digital resolution in the inverse ^{13}C–^1H spectra was 1 Hz/pt. The inverse ^{13}C–^1H spectra for detecting long-range correlation were

acquired with data sets of 1K(F2)×250(F1). The mixing time was 90 ms and the digital resolution was 2 Hz/pt. Microanalyses were measured with an Elemental Analyzer-MDD 1106. The percentage of carbon was detected as the total number of moles of labeled and unlabeled CO_2 produced by the molecule. Whereas the molecular weight of a compound is sensitive to the presence of ^{13}C, the weight of carbon that it contains measured by elemental analysis is insensitive to the isotopic labeling. This was taken into account in the calculated analyses for the labeled compounds in which the molecular weights were calculated using 13.01 as the atomic weight of the labeled carbon while 12.01 was used for the calculation of the total weight of labeled and unlabeled carbon in the molecule.

Thin-layer chromatography (TLC) was performed on precoated aluminum plates with Kieselgel silica gel 60 F_{254} (E. Merck) and detected with UV light and/or charred with 5% sulfuric acid in EtOH solution. All compounds were purified by flash column chromatography with Kieselgel silica gel 60 (230–400 mesh) according to a published procedure [35]. Solvents were dried and distilled according to standard procedures [36]. Reactions performed under N_2 were carried out in deoxygenated solvents and transfers under N_2 were effected by means of standard Schlenk-tube techniques. Organic solutions were dried over Na_2SO_4 and concentrated below 40 °C under reduced pressure. Methyl–^{13}C iodide (99%–^{13}C) was purchased from Sigma Company.

5-O-*Benzoxymethyl-1,2*-O-*isopropylidene-3,6-di*-O-*^{13}C-methyl*-α-D-*glucofuranose* (**2**).—A solution of 5-*O*-benzoxymethyl-1,2-*O*-isopropylidene-α-D-glucofuranose **1** [26] (2.4 g, 6.9 mmol) in DMF (10 mL) was transferred under N_2 to a cooled suspension of NaH (1.4 g, 60% by weight in oil, 34 mmol) in DMF (3 mL). After stirring for 30 min at 0 °C, methyl–^{13}C iodide (2 g, 14 mmol) was added dropwise and the reaction was allowed to proceed for 6 h at room temperature. MeOH (4 mL) was added to destroy excess NaH, the mixture was poured into ice-water (50 mL), and the product was extracted with CH_2Cl_2 (2×50 mL). The extracts were washed with water (30 mL), dried, and concentrated. Chromatography of the residue (EtOAc–hexanes, 1:3) gave the *title compound* **2** as a syrup (2.4 g, 93%). ^1H NMR: δ 7.36 (m, 5 H, Ar), 5.86 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.88 (dd, 2 H, OCH_2O), 4.73 (d, 1 H, *J* 12 Hz, OC*H*HPh), 4.61 (d, 1 H, OCH*H*Ph), 4.58 (d, 1 H, H-2), 4.30 (dd, 1 H, $J_{4,3}$ 3 Hz, $J_{4,5}$ 9.5 Hz, H-4), 4.05 (m, 1 H, $J_{5,6}$ 2 Hz, $J_{5,6'}$ 3 Hz, H-5), 3.78 (dd, 1 H, $^3J_{H,^{13}C}$ 4.5 Hz, H-3), 3.76 (dt, 1 H, $J_{6,6'}$ 11 Hz, $^3J_{H,^{13}C}$ 2.5 Hz, H-6), 3.60 (dt, 1H, $^3J_{H,^{13}C}$, 4 Hz, H-6′), 3.39 (d, 3 H, $^1J_{H,^{13}C}$ 141 Hz, $O^{13}CH_3$), 3.37 (d, 3 H, $^1J_{H,^{13}C}$ 142 Hz, $O^{13}CH_3$), 1.50, 1.32 [2s, 2×3 H, $(CH_3)_2C$]. ^{13}C NMR: δ 138.0, 128.4, 127.8, 127.6 (Ar), 111.8 [$(CH_3)_2C$]; 105.1 (C-1), 94.7 (OCH_2O), 83.5 (C-3), 81.0 (C-2), 78.7 (C-4), 73.8 (C-5), 73.0 (C-6), 69.6 (OCH_2Ph), 59.3 (qt, $^1J_{13_{C,H}}$ 141 Hz, $^3J_{13_{C,H-6}} \sim 3$ Hz, $O^{13}CH_3$-6), 57.2 (qd, $^1J_{13_{C,H}}$ 142 Hz, $^3J_{13_{C,H-3}}$ 5 Hz, $O^{13}CH_3$-3), 26.8, 26.4 [2×(CH_3)$_2$C]. Anal. Calcd for $C_{17}{}^{13}C_2H_{28}O_7$: C, 61.59; H, 7.63. Found: C, 61.84; H, 7.68.

2,4-Di-O-*acetyl-3,6-di*-O-*methyl*-α-D-*glucopyranosyl trichloroacetimidate* (**8**).—Hydrazine acetate (250 mg, 2.8 mmol) was added to a solution of 1,2,4-tri-*O*-acetyl-3,6-di-*O*-methyl-α,β-D-glucopyranose [6,15] **3** (0.76 g, 2.2 mmol) in DMF (12 mL) and the reaction mixture was stirred for 24 h under N_2 at room temperature. The product was extracted with dichloromethane and washed with water. The organic phase was dried and concentrated to give the crude hemiacetal **6** as a syrup (910 mg) that was dried overnight under high vacuum and dissolved in anhydrous CH_2Cl_2 (50 mL). Anhydrous K_2CO_3 (3.1 g, 23 mmol), and trichloroacetonitrile (3.2 mL, 32 mmol) were added to the mixture that was stirred for 48 h at room temperature. Excess K_2CO_3 was removed by filtration through Celite 545 and the filtrate was concentrated. Chromatography (EtOAc–hexanes, 1:3) of the residue gave the trichloroacetimidate **8** as a colorless syrup (970 mg, 46%); its purity was confirmed by NMR spectroscopy and it was used directly in the glycosylation reactions. ^1H NMR: δ 8.60 (s, C=NH), 6.48 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.08 (dd, 1 H, $J_{4,3}+J_{4,5}=20$ Hz, H-4), 4.98 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 4.01 (m, 1 H, H-5), 3.80 (t, 1 H, H-3), 3.46 (dd, 1 H, $J_{6,5}$ 3 Hz, $J_{6,6'}$ 11 Hz, H-6), 3.43 (dd, 1 H, $J_{6',5}$ 5 Hz, H-6′), 3.46, 3.40 (2 s, 2×3 H, 2×OCH_3), 2.11, 2.02 (2 s, 2×3 H, 2×CH_3CO). ^{13}C NMR: δ 169.7, 169.3 (2×C=O), 160.8 (C=NH), 93.5 (C-1), 91.0 (CCl_3), 78.2 (C-3), 71.7 (C-2), 71.6 (C-5), 71.2 (C-6), 69.8 (C-4), 59.9, 59.3 (2×OCH_3), 20.7, 20.5 (2×CH_3CO).

2,4-Di-O-*acetyl-3,6-di*-O-*^{13}C-methyl*-α-D-*glucopyranosyl trichloroacetimidate* (**9**).—A solution of **2** (2.3 g, 6.3 mmol) in a mixture of dioxane (13 mL) and 0.5 N aq HCl (16 mL) was refluxed for 1 h. Toluene was added and the solvents were evaporated. Chromatography (EtOAc–hexanes–MeOH, 4:4:1.5) gave an anomeric mixture of 3,6-di-*O*-^{13}C-

methyl-α,β-D-glucopyranose (**4**) as a white solid (2.1 g, 100%). ^{1}H NMR[D_2O, internal standard: sodium trimethylsilyl-(2,2,3,3-tetradeutero)propionate, δ 0.0]: δ 5.14 (d, $J_{1,2}$ 4 Hz, H-1α), 4.58 (d, $J_{1,2}$ 8 Hz, H-1β), 3.56 (d, $^1J_{H,^{13}C}$ 143 Hz, O^{13}CH$_3$-α), 3.33 (d, $^1J_{H,^{13}C}$ 143 Hz, O^{13}CH$_3$-α). A solution of the triol **4** (2.1 g, 6.3 mmol) in Ac_2O–pyridine (1:2, 30 mL) was stirred for 24 h at room temperature. The mixture was poured into ice-water (200 mL) and the product was extracted with CH_2Cl_2(2×50 mL). The extracts were washed successively with 1 *N* aq HCl, satd aq $NaHCO_3$, satd NaCl, combined, dried, and concentrated. Chromatography of the residue (EtOAc–hexanes, 1:2) gave an anomeric mixture of 1,2,4-tri-*O*-acetyl-3,6-di-*O*^{13}C-methyl-α,β-D-glucopyranose (**5**) as a white solid (1.5 g, 74%). The triacetate **5** (550 mg, 1.6 mmol) was converted to the hemiacetal **7** as described for the preparation of the hemiacetal **6**. The crude hemiacetal **7** (570 mg) was then converted to the trichloroacetimidate **9** as described for the preparation of the trichloroacetimidate **8**. The trichloroacetimidate **9** was purified by chromatography (EtOAc–hexanes, 1:3) and was obtained as a colorless syrup (410 mg, 64%); its purity was confirmed by NMR spectroscopy and it was used directly in the glycosylation reactions, $[\alpha]^{22}_D$ +96.5° (*c* 0.48, CH_2Cl_2). ^{1}H NMR: δ 8.6 (s, C=NH), 6.48 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.08 (dd, 1 H, $J_{4,3}+J_{4,5}$ = 20 Hz, H-4), 4.98 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 4.01 (m, 1 H, H-5), 3.80 (td, 1 H, $^3J_{3,^{13}C}$ 6 Hz, H-3), 3.43 (m, 2 H, H-6, H-6′), 3.46 (d, 3 H, $^1J_{H,^{13}C}$ 142 Hz, O^{13}CH$_3$), 3.31 (d, 3 H, $^1J_{H,^{13}C}$ 142 Hz, O^{13}CH$_3$), 2.11, 2.02 (2 s, 2×3 H, 2×CH$_3$CO). ^{13}C NMR: δ 169.7, 169.4 (2×C=O), 160.7 (C=NH), 93.4 ($J_{C,H}$ 179.9 Hz, C-1), 90.9 (CCl_3), 78.2 (C-3), 71.6 (C-2), 71.5 (C-5), 71.2 (C-6), 69.7 (C-4), 59.9 (qd, $^1J_{13_{C,H}}$ 142 Hz, $^3J_{13_{C,H-3}}$ 6 Hz, O^{13}CH$_3$-3), 59.3 (qt, $^1J_{13_{C,H}}$ 142 Hz, $^3J_{13_{C,H-6}}$ 3 Hz, O^{13}CH$_3$-6), 20.8, 20.5 (2×CH$_3$CO).

*Allyl 4-*O*-benzyl-2,3-di-*O*-methyl-α-L-rhamnopyranoside* (**11**).—A solution of allyl 4-*O*-benzyl-α-L-rhamnopyranoside **10** (3.2 g, 11 mmol) [29] in DMF (20 mL) was transferred under N_2 to a suspension of NaH (2.0 g, 60% by weight in oil, 82 mmol) in DMF (10 mL) stirred at 0 °C. After stirring for 15 min at 0 °C, methyl iodide (2 mL, 32 mmol) was added slowly to the mixture that was then stirred for 2 h at room temperature. MeOH (5 mL) was added to destroy the excess NaH and the mixture was poured into ice-water (60 mL). The product was extracted with CH_2Cl_2 (60 mL, 2×30 mL) and the extracts were combined, dried, and concentrated. Chromatography (EtOAc–hexanes, 1:3) of the residue gave **11** as a syrup (3.5 g, 100%), $[\alpha]^{22}_D$ −67° (*c* 1.5, CH_2Cl_2). ^{1}H NMR: δ 7.35 (m, 5 H, Ar), 5.89 (m, 1 H, OCH$_2$C*H*=CH$_2$), 5.23 (m, 2 H, OCH$_2$CH=C*H*$_2$), 4.91 (d, 1 H, *J* 11 Hz, OC*H*HPh), 4.89 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 4.60 (d, 1 H, OCH*H*Ph), 4.05 (m, 2 H, OC*H*$_2$CH=CH$_2$), 3.68 (m, 1 H, H-5), 3.62–3.60 (m, 2 H, H-2, H-3), 3.51 (s, 6 H, 2×OCH$_3$), 3.43 (t, 1 H, $J_{4,3}+J_{4,5}$ = 19 Hz, H-4), 1.32 (d, 3 H, H-6). ^{13}C NMR: δ 133.8 (OCH$_2$*C*H=CH$_2$), 128.3, 127.9, 127.5 (Ar), 117.3 (OCH$_2$CH=CH$_2$), 96.0 ($J_{C,H}$ 167 Hz, C-1), 81.5 (C-4), 80.4 (C-3), 77.4 (C-2), 75.2 (O*C*H$_2$Ph), 67.8 (C-5 and O*C*H$_2$CH=CH$_2$), 59.0 (OCH$_3$), 57.7 (OCH$_3$), 17.8 (C-6). Anal. Calcd for $C_{18}H_{26}O_5$: C, 67.05; H, 8.14. Found: C, 66.98; H, 8.24.

*Allyl 4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranoside* (**12**).—A mixture of allyl 4-*O*-benzyl-α-L-rhamnopyranoside **10** (1.8 g, 6.1 mmol) and dibutyltin oxide (1.8 g, 7.2 mmol) in benzene (80 mL) was refluxed for 3 h with azeotropic removal of the water. The mixture was cooled to room temperature, toluene was added and the solvents were evaporated. The dried residue was dissolved in DMF (8 mL), methyl iodide (0.42 mL, 6.7 mmol) was added dropwise and the mixture was stirred overnight at 35–40 °C. The solution was concentrated and chromatography of the residue (EtOAc–hexanes, 1:1) gave the monomethyl ether **12** as a colorless syrup (1.3 g, 71%), $[\alpha]^{22}_D$ −89° (*c* 0.9, CH_2Cl_2). ^{1}H NMR: δ 7.36 (m, 5 H, Ar), 5.88 (m, 1 H, OCH$_2$C*H*=CH$_2$), 5.24 (m, 2 H, OCH$_2$CH=C*H*$_2$), 4.85 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 4.84, 4.62 (2×d, 1 H, *J* 11 Hz, 2×OCH*H*Ph), 4.07 (dd, 1 H, $J_{2,3}$ 3.5 Hz, H-2), 4.06 (m, 2 H, OC*H*$_2$CH=CH$_2$), 3.72 (m, 1 H, H-5), 3.59 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 3.50 (s, 3 H, OCH$_3$), 3.37 (t, 1 H, $J_{4,3}+J_{4,5}$ = 19 Hz, H-4), 2.43 (bs, 1 H, O*H*), 1.30 (d, 3 H, H-6). ^{13}C NMR: δ 133.9 (OCH$_2$*C*H=CH$_2$), 138.6, 128.4, 127.9, 127.7 (Ar), 117.4 (OCH$_2$CH=*C*H$_2$), 98.3 (C-1), 81.8, 80.0 (C-3, C-4), 75.2 (O*C*H$_2$Ph), 68.0 (C-5), 67.9, 67.3 (C-2, O*C*H$_2$CH=CH$_2$), 57.4 (OCH$_3$), 17.9 (C-6). Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.20; H, 7.86. Found: C, 66.42; H, 8.05.

*Propyl 2,3-di-*O*-methyl-α-L-rhamnopyranoside* (**15**).—The benzyl ether **11** (1.1 g, 3.5 mmol) was dissolved in EtOH–80% aq AcOH (1:2, 45 mL) and hydrogenolyzed overnight at 52 psi over Pd/C (10%, 0.10 g). The black solid was removed by filtration and the filtrate was concentrated to

dryness by coconcentration with toluene. Chromatography (EtOAc–hexanes, 1:1) of the residue gave the alcohol **15** as a colorless syrup (0.81 g, 100%), $[\alpha]^{22}_{D}$ −32.4° (*c* 0.7, CH_2Cl_2). ^{1}H NMR: δ 4.81 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 3.61 (dt, 1 H, $OCH_aH_bCH_2CH_3$), 3.58–3.57 (m, 2 H, H-2 and H-5), 3.51 (t, 1 H, $J_{4,3}+J_{4,5}=19$ Hz, H-4), 3.45, 3.43 (2 s, 2×3 H, 2×OCH_3), 3.39 (dd, 1 H, $J_{3,4}$ 9.5 Hz, $J_{3,2}$ 3 Hz, H-3), 3.34 (dt, 1 H, $OCH_aH_bCH_2CH_3$), 1.57 (m, 2 H, $OCH_2CH_2CH_3$), 1.27 (d, 3 H, $J_{6,5}$ 6 Hz, H-6), 0.9 (t, 3 H, $OCH_2CH_2CH_3$). ^{13}C NMR: δ 97.2 ($^1J_{C,H}$ 167 Hz, C-1), 81.3 (C-3), 76.1 (C-2), 71.8 (C-4), 69.2 ($OCH_2CH_2CH_3$), 68.1 (C-5), 58.9, 56.9 (2×OCH_3), 22.8 ($OCH_2CH_2CH_3$), 17.7 (C-6), 10.6 ($OCH_2CH_2CH_3$). Anal. Calcd for $C_{11}H_{22}O_5$: C, 56.38; H, 9.48. Found: C, 56.43; H, 9.52.

Propyl 2-O-*methyl-3*-O-*^{13}C-methyl*-α-L-*rhamnopyranoside* (**16**).—Allyl 4-*O*-benzyl-α-L-rhamnopyranoside **10** (1.6 g, 5.6 mmol) was selectively methylated at O-3 with methyl-^{13}C iodide as described for the preparation of the unlabeled methyl ether **12**. The dimethyl ether **13** was purified by chromatography (EtOAc–hexanes, 1:1) and isolated as a syrup (0.94 g, 54%). A solution of **13** (0.94 g, 3.0 mmol) in DMF (4.5 mL) was transferred under N_2 to a cooled (0 °C) suspension of NaH (0.31 g, 60% by weight in oil, 7.9 mmol) in DMF (2 mL). After stirring for 30 min at 0 °C, methyl iodide (0.41 g, 6.1 mmol) was added dropwise and the reaction mixture was stirred under N_2 for 2 h at room temperature. MeOH (2 mL) was added to destroy the excess NaH and the reaction mixture was poured into ice-water (10 mL). The product was extracted with EtOAc (20 mL, 3×10 mL), the extracts were washed with water, combined, dried, and concentrated to give crude **14** as a syrup (1.1 g). The syrup was dissolved in EtOH–80% aq AcOH (1:2, 45 mL) and hydrogenolyzed overnight at 52 psi over Pd/C (10% on charcoal, 0.13 g). More catalyst (56 mg) was added and the reaction was allowed to proceed for 24 h. The catalyst was removed by filtration through Celite 545 and the filtrate was extracted with CH_2Cl_2 (3×20 mL). The extracts were washed with satd aq $NaHCO_3$ (2×20 mL), combined, dried, and concentrated. Chromatography (EtOAc–hexanes, 1:1) of the residue yielded pure **16** as a colorless syrup (570 mg, 80% based on **14**), $[\alpha]^{22}_{D}$ −33.6° (*c* 0.7, CH_2Cl_2). ^{1}H NMR: δ 4.85 (d, 1 H, $J_{1,2}$ 2 Hz, H-1), 3.61 (m, 3 H, H-2, H-5, $OCH_aH_bCH_2CH_3$), 3.54 (t, 1 H, $J_{4,3}+J_{4,5}=19$ Hz, H-4), 3.48 (s, 3 H, OCH_3-2), 3.46 (d, 3 H, $J_{H,^{13}C}$ 141 Hz, $O^{13}CH_3$-3), 3.41 (dt, 1 H, $J_{3,4}$ 9.5 Hz, $J_{3,2}$ 3.5 Hz, $^3J_{H,^{13}C}$, 3.5 Hz, H-3), 3.36 (dt, 1 H, $OCH_aH_bCH_2CH_3$), 2.4–2.3 (bs, 1 H, O*H*), 1.60 (m, 2 H, $OCH_2CH_2CH_3$), 1.30 (d, 3 H, $J_{6,5}$ 6 Hz, H-6), 0.92 (t, 3 H, $OCH_2CH_2CH_3$). ^{13}C NMR: δ 97.2 ($^1J_{C,H}$ 167 Hz, C-1), 81.2 (C-3), 76.1 (C-2), 71.8 (C-4), 69.2 ($OCH_2CH_2CH_3$), 68.1 (C-5), 58.9 ($^1J_{C,H}$ 142 Hz, $^3J_{C,H\text{-}2}$ 5 Hz, OCH_3-2), 56.9 (qd, $^1J_{13_{C,H}}$ 142 Hz, $^3J_{13_{C,H\text{-}3}}$ 4 Hz, $O^{13}CH_3$-3), 22.8 ($OCH_2CH_2CH_3$), 17.7 (C-6), 10.6 ($OCH_2CH_2CH_3$). Anal. Calcd for $C_{10}{}^{13}C_1H_{22}O_5$: C, 56.13; H, 9.44. Found: C, 56.30; H, 9.47.

Propyl 4-O-*(2,4-di*-O-*acetyl-3,6-di*-O-*methyl*-β-D-*glucopyranosyl)-2,3-di*-O-*methyl*-α-L-*rhamnopyranoside* (**20**).—A mixture of the acceptor **15** (192 mg, 0.82 mmol), the trichloroacetimidate **8** (415 mg, 0.95 mmol) and activated molecular sieves (4Å) in anhydrous CH_2Cl_2 (20 mL) was stirred for 1 h under N_2. The mixture was cooled to −78 °C and triethylsilyl triflate(TESOTf) (30 μL, 0.13 mmol) was added. After stirring for 15 min at −78 °C, the reaction was allowed to proceed 15 min at room temperature and quenched by addition of triethylamine (~25 μL). The molecular sieves were removed by filtration and the filtrate was concentrated. Chromatography (EtOAc–hexanes, 1:1) of the residue gave the disaccharide **20** as a colorless oil (420 mg, 100%), $[\alpha]^{22}_{D}$ −51° (*c* 0.7, CH_2Cl_2). ^{1}H NMR: δ 4.98 (t, 1 H, $J_{4,3}+J_{4,5}=$ 18 Hz, H-4A), 4.90 (dd, 1 H, $J_{2,1}$ 8 Hz, $J_{2,3}$ 10 Hz, H-2A), 4.82 (d, 1 H, $J_{1,2}$ 2 Hz, H-1B), 4.74 (d, 1 H, H-1A), 3.61–3.51 (m, 4 H, H-6′A, H-6A, H-5B, $OCH_aH_bCH_2CH_3$), 3.56 (dd, 1 H, $J_{2,3}$ 3 Hz, H-2B), 3.48–3.30 (m, 5 H, H-3B, H-4B, H-3A, H-5A, $OCH_aH_bCH_2CH_3$), 3.48, 3.42, 3.38, 3.30(4s, 4×3 H, 4×OCH_3), 3.34(dd, 1H, $OCH_aH_bCH_2CH_3$), 2.30, 2.50 (2s, 2×3 H, CH_3CO), 1.32(m, 2H, $OCH_2CH_2CH_3$), 1.13(d, 3H, H-6B), 0.96 (t, 3 H, $CH_2CH_2CH_3$). ^{13}C NMR: δ 169.3, 168.9 (2×C=O), 100.9 ($^1J_{C,H}$ 167 Hz, C-1A), 96.6 ($^1J_{C,H}$ 167 Hz, C-1B), 81.5, 81.3 (C-3B, C-4B), 77.6, 76.7 (C-2B, C-6A), 73.0, 72.4, 72.0 (C-2A, C-3A, C-5A), 70.2 (C-4A), 69.3 ($OCH_2CH_2CH_3$), 67.0 (C-5B), 59.6, 58.9, 58.3, 57.0 (4×OCH_3), 22.6 ($OCH_2CH_2CH_3$), 20.9, 20.8 (2×CH_3CO), 17.7 (C-6B), 10.5 ($OCH_2CH_2CH_3$). Anal. Calcd for $C_{23}H_{40}O_{12}$: C, 54.33; H, 7.87. Found: C, 54.42; H, 8.03.

Propyl 4-O-*(2,4-di*-O-*acetyl-3,6-di*-O-*methyl*-β-D-*glucopyranosyl)-2*-O-*methyl-3*-O-*^{13}C-methyl*-α-L-*rhamnopyranoside* (**21**).—Glycosylation of the acceptor **16** (162 mg, 0.69 mmol) with the trichloroacetimidate **8** (297 mg, 0.68 mmol) was performed

as described for the preparation of disaccharide **20**. The disaccharide **21** was purified by chromatography (EtOAc–hexanes, 1:1) and was isolated as a syrup (321 mg, 93%). ^{1}H NMR: δ 4.98 (t, 1 H, $J_{4,3}+J_{4,5}=18$ Hz, H-4A), 4.90 (dd, 1 H, $J_{2,1}$ 8 Hz, $J_{2,3}$ 10 Hz, H-2A), 4.82 (d, 1 H, $J_{1,2}$ 2 Hz, H-1B), 4.74 (d, 1 H, H-1A), 3.59 (m, 1 H, H-5B), 3.61 (dd, 1 H, OCH_aH$_b$CH$_2$CH$_3$), 3.56 (dd, $J_{2,3}$ 3 Hz, H-2B), 3.56–3.51 (m, 2 H, H-6′A and H-6A), 3.48–3.42 (m, 3 H, H-3B, H-4B, H-5A), 3.43 (d, 3 H, $^1J_{13_{C,H}}$ 141 Hz, O^{13}CH$_3$-3B), 3.48, 3.38, 3.32 (3s, 3×3 H, 3×OCH$_3$), 3.44 (t, 1 H, $J_{3,2}+J_{3,4}=20$ Hz, H-3A), 3.34 (dd, 1 H, OCH$_a$$H_bCH_2CH_3$), 2.30, 2.50 (2s, 2×3 H, 2×CH$_3$CO), 1.32 (OCH$_2$CH_2CH$_3$), 1.13 (d, 3 H, H-6B), 0.96 (OCH$_2$CH$_2$CH_3). ^{13}C NMR: δ 101.0(C-1A), 96.7(C-1B), 81.5, 81.4 (C-3B, C-4B), 77.7, 76.8 (C-2B, C-6A), 73.0, 72.5, 72.1 (C-2A, C-3A, C-5A), 70.3 (C-4A), 69.4 (OC_{H_2}CH$_2$CH$_3$), 67.0 (C-5B), 59.6 (OCH$_3$-6A), 58.9 (OCH$_3$-2B), 58.2 (OCH$_3$-3A), 57.1 ($^1J_{13_{C,H}}$ 141 Hz, $^3J_{13_{C,H-3}}$ 4 Hz, O^{13}CH$_3$-3B), 22.7 (OCH$_2$CH$_2$CH$_3$), 21.0, 20.8 (2×CH$_3$CO), 17.8(C-6B), 10.6 (OCH$_2$CH$_2$CH$_3$).

*Propyl 4-*O*-(2,4-di-*O*-acetyl-3,6-di-*O*-^{13}C-methyl-*β*-*D*-glucopyranosyl)-2,3-di-*O*-methyl-*α*-*L*-rhamnopyranoside* (**22**).—Glycosylation of the acceptor **15** (55 mg, 0.24 mmol) with the trichloroacetimidate **9** (94 mg, 0.22 mmol) was performed as described for the preparation of disaccharide **20**. Disaccharide **22** was purified by chromatography (EtOAc–hexanes, 1:1) and was isolated as a syrup (78 mg, 71%), $[\alpha]_D^{22}$ −50.3° (*c* 2.3, CH_2Cl_2). ^{1}H NMR: δ 4.98 (t, 1 H, $J_{4,3}+J_{4,5}=18$ Hz, H-4A), 4.90 (dd, 1 H, $J_{2,1}$ 8 Hz, $J_{2,3}$ 10 Hz, H-2A), 4.82 (d, 1 H, $J_{1,2}$ 2 Hz, H-1B), 4.76 (d, 1 H, H-1A), 3.48 (s, 3 H, OCH$_3$), 3.38 (d, 3 H, $^1J_{13_{C,H}}$ 141 Hz, O^{13}CH$_3$), 3.32 (d, 3 H, $^1J_{13_{C,H}}$ 142 Hz, O^{13}CH$_3$), 3.49 (s, 3 H, OCH$_3$-2B), 3.34 (dt, 1 H, OCH$_a$$H_bCH_2CH_3$), 2.10, 2.08 (2s, 2×3 H, 2×CH$_3$CO), 1.59 (m, 2 H, OCH$_2$CH_2CH$_3$), 1.24 (d, 3 H, H-6B), 0.92 (t, 3 H, OCH$_2$CH$_2$CH_3). ^{13}C NMR: δ 169.6, 169.3 (2×C=O), 101.0 (C-1A), 96.6 (C-1B), 81.5, 81.4 (C-3B, C-4B), 77.7, 76.8 (C-2B, C-6A), 73.0, 72.4, 72.1 (C-2A, C-3A, C-5A), 70.7 (C-4A), 69.4, 67.0 (C-5B), 59.6 (qt, $^1J_{13_{C,H}}$ 141 Hz, $^3J_{13_{C,H-6A}}$ 4 Hz, O^{13}CH$_3$-6A), 58.9 (OCH$_3$-2$_B$), 58.2 (qd, $^1J_{13_{C,H}}$ 142 Hz, $^3J_{13_{C,H-3A}}$ 6 Hz, O^{13}CH$_3$-3A), 58.0 (OCH$_3$-3B), 22.7 (OCH$_2$CH$_2$CH$_3$), 21.0, 20.9 (CH$_3$CO), 17.8 (C-6B), 10.6 (OCH$_2$CH$_2$CH$_3$). Anal. Calcd for $C_{21}{}^{13}C_2H_{40}O_{12}$: C, 54.10; H, 7.91. Found: C, 54.21; H, 8.09.

*Propyl 4-*O*-(2,4-di-*O*-acetyl-3,6-di-O-^{13}C-methyl-*β*-*D*-glucopyranosyl)-2-*O*-methyl-3-*O*-^{13}C-methyl-*α*-*L*-rhamnopyranoside* (**23**).—Glycosylation of the acceptor **16** (58 mg, 0.25 mmol) with the trichloroacetimidate **9** (110 mg, 0.25 mmol) was performed as described for the preparation of disaccharide **20**. Chromatography (EtOAc–hexanes, 1:1) gave the disaccharide **23** as a syrup (0.12 g, 100%). $[\alpha]^{22}{}_D$ −51.5° (*c* 2.3, CH_2Cl_2). ^{1}H NMR: δ 4.98(t, 1 H, $J_{4,3}+J_{4,5}=18$ Hz, H-4A), 4.90 (dd, 1 H, $J_{2,1}$ 8 Hz, $J_{2,3}$ 10 Hz, H-2A), 4.82 (d, 1 H, $J_{1,2}$ 2 Hz, H-1B), 4.76 (d, 1 H, H-1A), 3.61 (dt, 1 H, OCH_aH$_b$CH$_2$CH$_3$), 3.44 (d, 3 H, $^1J_{13_{C-H}}$ 141 Hz, O^{13}CH$_3$), 3.38 (d, 3 H, $^1J_{13_{C,H}}$ 141 Hz, O^{13}CH$_3$), 3.32(d, 3 H, $^1J_{13_{C,H}}$ 142 Hz, O^{13}CH$_3$), 3.49 (s, 3 H, OCH$_3$-2B), 3.34 (dt, 1 H, OCH$_a$$H_bCH_2CH_3$), 2.10, 2.08 (2s, 2×3 H, 2×CH$_3$CO), 1.59 (m, 2 H, OCH$_2$CH_2CH$_3$), 1.24 (d, H-6B), 0.92 (t, 3 H, OCH$_2$CH$_2$CH_3). ^{13}C NMR: δ 169.6, 169.3(C=O), 101.0 (C-1A), 96.6 (C-1B), 81.5, 81.4 (C-3B, C-4B), 77.7, 76.8 (C-2B, C-6A), 73.0, 72.4, 72.1 (C-2A, C-3A, C-5A), 70.3 (C-4A), 69.4 (OCH$_2$CH$_2$CH$_3$), 67.0 (C-5B), 59.6 (qt, $^1J_{13_{C,H}}$ 141 Hz, $^3J_{13_{C,6A}}$ 4 Hz, O^{13}CH$_3$-6A), 58.9 (OCH$_3$-2B), 58.2 ($^1J_{13_{C,H}}$ 142 Hz, $^3J_{13_{C,3A}}$ 6 Hz, O^{13}CH$_3$-3A), 57.1 (qd, $^1J_{13_{C,H}}$ 141 Hz, $^3J_{13_{C,3B}}$ 5 Hz, O^{13}CH$_3$-3B), 22.7 (OCH$_2$CH$_2$CH$_3$), 23.0, 20.9 (2×CH$_3$CO), 17.8 (C-6B), 10.6 (OCH$_2$CH$_2$CH$_3$). Anal. Calcd for $C_{20}{}^{13}C_3H_{40}O_{12}$: C, 54.10; H, 7.90. Found C, 54.35; H, 7.85.

*Propyl 4-*O*-(3,6-di-*O*-methyl-*β*-*D*-glucopyranosyl)-2,3-di-*O*-methyl-*α*-*L*-rhamnopyranoside* (**24**).—A solution of the protected disaccharide **20** (410 mg, 0.81 mmol) in methanolic sodium methoxide (0.3 *N*, 4 mL) was stirred for 2 h at room temperature and neutralized with Dowex 50W-X8(H$^+$) resin. The resin was filtered off, rinsed with MeOH (5 mL) and the combined supernatant and washings were concentrated. Chromatography (EtOAc–hexanes–MeOH, 6:6:1) of the residue gave the disaccharide **24** that crystallized on standing (291 mg, 85%), mp 52–54 °C, $[\alpha]^{22}{}_D$ −53° (*c* 0.6, CH_2Cl_2) [lit [6]., $[\alpha]^{26}{}_D$ −46.1° (*c* 1.2, $CHCl_3$)]. ^{1}H NMR: δ 4.81 (d, 1H, $J_{1,2}$ 2 Hz, H-1B), 4.40 (d, 1H, $J_{1,2}$ 8 Hz, H-1A), 3.67 (s, 3H, OCH$_3$), 3.64 (H-5B), 3.63 (m, 2H, H-6A, H-6′A), 3.62 (m, 3H, H-2B, H-3B, H-4B), 3.59 (dt, 1H, OCH_aH$_b$CH$_2$CH$_3$), 3.52 (t, 1H, $J_{4,3}+J_{4,5}=18$ Hz, H-4A), 3.48 (s, 3H, OCH$_3$), 3.46 (s, 3H, OCH$_3$), 3.41 (m, 1H, H-5A), 3.38 (s, 3H, OCH$_3$), 3.15 (t, 1H, $J_{3,2}+J_{3,4}=20$ Hz, H-3A), 3.35 (dt, 1H, OCH$_a$$H_bCH_2CH_3$), 1.57 (OCH$_2CH_2CH_3$), 1.34 (d, 3H, H-6B), 0.90 (OCH$_2$CH$_2$CH_3). ^{13}C NMR: δ 105.6 ($^1J_{C,H}$ 159 Hz, C-1A), 96.8($^1J_{C,H}$ 168 Hz, C-1B), 85.6 (C-3A), 81.8 (C-3B), 80.7 (C-4B), 76.0 (C-2B), 75.0 (C-2A), 74.2

(C-5A), 72.8 (C-6A), 71.2 (C-4A), 69.3 ($OCH_2CH_2CH_3$), 67.5 (C-5B), 60.4, 59.5, 59.0, 56.4($4\times OCH_3$), 22.7 ($OCH_2CH_2CH_3$), 17.5 (C-6B), 10. 6 ($OCH_2CH_2CH_3$). Anal. Calcd for $C_{19}H_{36}O_{10}$: C, 53.75; H, 8.56. Found: C, 53.64; H, 8.62.

*Propyl 4-*O*-(3,6-di-*O*-methyl-*β*-*D*-glucopyranosyl)-2-*O*-methyl-3-*O*-^{13}C-methyl-*α*-*L*-rhamnopyranoside* (**25**).—Deacetylation of disaccharide **21** (193 mg, 0.38 mmol) was performed as described for the deprotection of disaccharide **20**. Chromatography (EtOAc–hexanes–MeOH, 4:4:1) gave the disaccharide **25** as a colorless syrup (161 mg, 100%), $[\alpha]^{22}_D$ −51.6° (*c* 1.2, CH_2Cl_2). ^{1}H NMR: *δ* 4.81 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1B), 4.40 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1A), 3.45 (d, $^1J_{13_{C,H}}$ 142 Hz, $O^{13}CH_3$-3B), 3.66 (s, 3H, OCH_3), 3.62 (m, 7H, overlapped, H-6A, H-6′A, H-2B, H-3B, H-4B, H-5B, $OCH_aH_bCH_2CH_3$), 3.53 (t, $J_{4,3}+J_{4,5}=20$ Hz, H-4A), 3.47 (s, 3H, OCH_3), 3.46–3.37(m, 2H, overlapped, H-2A, H-5A), 3.37 (s, 3H, OCH_3), 3.35 (dt, 1H, $OCH_aH_bCH_2CH_3$), 3.15 (t, 1H, $J_{2,3}+J_{3,4}=$ 18 Hz, H-3A), 1.57 (m, 2H, $OCH_2CH_2CH_3$), 1.34 (d, 3H, H-6B), 0.90 (t, 3H, $OCH_2CH_2CH_3$). ^{13}C NMR: *δ* 105.6 ($^1J_{C,H}$ 161 Hz, C-1A), 96.9($^1J_{C,H}$ 168 Hz, C-1B), 85.6 (C-3A), 81.9 (C-3B), 80.7 (C-4B), 76.1 (C-2B), 75.1 (C-2A), 74.2 (C-5A), 72.9 (C-6A), 71.2 (C-4A), 69.3 ($OCH_2CH_2CH_3$), 67.6 (C-5B), 60.4, 59.6, 59.0 ($3\times OCH_3$), 56.4 (qd, $^1J_{13_{C,H}}$ 142 Hz, $^3J_{13_{C,H\text{-}3B}}$ 3 Hz, $O^{13}CH_3$-3B), 22.8 ($OCH_2CH_2CH_3$), 17.5 (C-6B), 10.6 ($OCH_2CH_2CH_3$). Anal. Calcd for $C_{18}{}^{13}C_1H_{36}O_{10}$: C, 53.62; H, 8.54. Found: C, 53.49; H, 8.67.

*Propyl 4-*O*-(3,6-di-*O*-^{13}C-methyl-*β*-*D*-glucopyranosyl)-2,3-di-O-methyl-*α*-*L*-rhamnopyranoside* (**26**).—Deacetylation of disaccharide **22** (78 mg, 0.15 mmol) was performed as described for the deprotection of disaccharide **20**. Chromatography (EtOAc–hexanes–MeOH, 6:6:1) gave the disaccharide **26** as a colorless syrup (58 mg, 89%), $[\alpha]^{22}_D$ −45° (*c* 0.6, CH_2Cl_2). ^{1}H NMR: *δ* 4.82 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1B), 4.40 (d, 1H, $J_{1,2}$ 8 Hz, H-1A), 3.68–3.48 (m, 6H, overlapped, H-6A, H-6′A, H-2B, H-3B, H-4B, H-5B), 3.59 (dt, 1H, $OCH_aH_bCH_2CH_3$), 3.53 (H-4A), 3.41(m, 2H, overlapped, H-2A, H-5A), 3.67 (d, 3H, $^1J_{13_{C,H}}$ 142 Hz, $O^{13}CH_3$), 3.38 (d, 3H, $^1J_{13_{C,H}}$ 142 Hz, $O^{13}CH_3$), 3.48 (s, 3H, OCH_3), 3.46 (s, 3H, OCH_3), 3.35 (dt, 1H, $OCH_aH_bCH_2CH_3$), 3.16 (tt, 1H, $J_{3,2}+J_{3,4}=18$ Hz, $^3J_{13_{C,H}}$ 5 Hz, H-3A), 1.57 ($OCH_2CH_2CH_3$), 1.34 (d, 3H, $H\text{-}6_B$), 0.91 ($OCH_2CH_2CH_3$). ^{13}C NMR: *δ* 105.7 ($^1J_{C,H}$ 160 Hz, C-1A), 96.9 ($^1J_{C,H}$ 167 Hz, C-1B), 85.6 (C-3A), 81.9 (C-3B), 80.7 (C-4B), 76.0 (C-2B), 75.1 (C-2A), 74.1 (C-5A), 72.9 (C-6A), 71.3 (C-4A), 69.3 ($OCH_2CH_2CH_3$), 67.5 (C-5B), 60.4 (qd, $^1J_{13_{C,H}}$ 142 Hz, $^3J_{13_{C,H\text{-}3A}}$ 5 Hz, $O^{13}CH_3$-3A), 59.6 (qt, $^1J_{13_{C,H}}$ 142 Hz, $^3J_{13_{C,H\text{-}6A}}$ 4 Hz, $O^{13}CH_3$-6A), 59.0 (OCH_3-2B), 56.4(OCH_3-3B), 22.7 ($OCH_2CH_2CH_3$), 17.5 (C-6B), 10.6 ($OCH_2CH_2CH_3$).. Anal. Calcd for $C_{17}{}^{13}C_2H_{36}O_{10}$: C, 53.50; H, 8.52. Found: C, 53.70; H, 8.40.

*Propyl 4-*O*-(3,6-di-*O*-^{13}C-methyl-*β*-*D*-glucopyranosyl)-2-*O*-methyl-3-*O*-^{13}C-methyl-*α*-*L*-rhamnopyranoside* (**27**).—Deacetylation of disaccharide **23** (66 mg, 0.13 mmol) was performed as described for the deprotection of disaccharide **20**. Chromatography (EtOAc–hexanes–MeOH, 6:6:1) gave the disaccharide **27** as a colorless syrup (58 mg, 100%), $[\alpha]^{22}_D$ −44° (*c* 0.8, CH_2Cl_2). ^{1}H NMR: *δ* 4.82 (d, 1H, $J_{1,2}$ 1.5 Hz, H-1B), 4.40 (d, 1H, $J_{1,2}$ 8 Hz, H-1A), 3.68–3.48 (m, 6H, overlapped, H-6A, H-6′A, H-2B, H-3B, H-4B, H-5B), 3.59 (dt, 1H, $OCH_aH_bCH_2CH_3$), 3.53 (m, 1H, H-4A), 3.41 (m, 2H, H-2A, H-5A), 3.67 (d, 3H, $^1J_{13_{C,H}}$ 142 Hz, $O^{13}CH_3$), 3.46 (d, 3H, $^1J_{13_{C,H}}$ 142 Hz, $O^{13}CH_3$), 3.38 (d, 3H, $^1J_{13_{C,H}}$ 142 Hz, $O^{13}CH_3$), 3.48 (s, 3H, OCH_3), 3.35(dt, 1H, $OCH_aH_bCH_2CH_3$), 3.16 (dt, 1H, $J_{3,2}+J_{3,4}=9.0$ Hz, $^3J_{13_{C,H}}$ 5 Hz, H-3A), 1.57 ($OCH_2CH_2CH_3$), 1.34 (d, 3H, H-6B), 0.91 ($OCH_2CH_2CH_3$). ^{13}C NMR: *δ* 105.7 ($^1J_{C,H}$ 158 Hz, C-1A), 96.8 ($^1J_{C,H}$ 168 Hz, C-1B), 85.6 (C-3A), 81.9 (C-3B), 80.7 (C-4B), 76.0(C-2B), 75.1 (C-2A), 74.1 (C-5A), 72.9 (C-6A), 71.3 (C-4A), 69.3 ($OCH_2CH_2CH_3$), 67.5 (C-5B), 60.4 (qd, $^1J_{13_{C,H}}$ 142 Hz, $^3J_{13_{C,H\text{-}3A}}$ 5 Hz, $O^{13}CH_3$-3A), 59.6 (qt, $^1J_{13_{C,H}}$ 142 Hz, $^3J_{13_{C,H\text{-}6A}}$ 4 Hz, $O^{13}CH_3$-6A), 59.0 (OCH_3-2B), 56.4 (qd, $^1J_{13_{C,H}}$ 142 Hz, $^3J_{13_{C,H\text{-}3B}}$ 3 Hz, $O^{13}CH_3$-3B), 22.8 ($OCH_2CH_2CH_3$), 17.5(C-6B), 10.6 ($OCH_2CH_2CH_3$). Anal. Calcd for $C_{16}{}^{13}C_3H_{36}O_{10}$: C, 53.37; H, 8.50. Found: C, 53.55; H, 8.54.

*Allyl 2-*O*-(4-*O*-acetyl-2,3-di-*O*-methyl-*α*-*L*-rhamnopyranosyl)-4-*O*-benzyl-3-*O*-methyl-*α*-*L*-rhamnopyranoside* (**28**).—A solution of the allyl glycoside **11** (2.1 g, 6.7 mmol) in 95% aq AcOH (120 mL) containing palladium (II) chloride (1.4 g, 8.0 mmol), and NaOAc (1.6 g, 20 mmol) was stirred for 48 h at room temperature. The reaction mixture was filtered, extracted with CH_2Cl_2 (3×50 mL), and the extracts were washed successively with water (2×40 mL), satd aq $NaHCO_3$ (4×40 mL), satd NaCl (2×40 mL), then combined, dried and concentrated. Chromatography (EtOAc–hexanes,

1:1) of the residue gave an anomeric mixture 4-*O*-benzyl-2,3-di-*O*-methyl-α,β-L-rhamnose (**17**) as a colorless syrup (1.7 g, 99%). Crystallization from EtAc–hexanes (1:8) gave white crystals that were estimated by NMR to be a 2:1 mixture of the α- and β-pyranoses. ^{1}H NMR: δ 7.32 (m, 5 H, Ar), 5.26 (bs, 1 Hα, H-1α), 4.90, 4.89, 4.61, 4.60 (4 d, 2 H α, 2 Hβ, OCH_2Ph), 4.65 (bs, 1 Hβ, H-1β), 3.43 (dd, 1 Hα, $J_{4,3}+J_{4,5}=18$ Hz, H-4α), 3.38 (dd, 1 Hβ, $J_{4,3}+J_{4,5}=18$ Hz, H-4β), 1.32 (d, 1 Hβ, $J_{5,6}$ 6 Hz, H-6β), 1.28 (d, 1 Hα, $J_{6,5}$ 6 Hz, H-6α). ^{13}C NMR: δ 138.8, 128.4, 128.3, 127.9, 127.8, 127.6 (Ar), 93.6 ($J_{C,H}$ 162 Hz, C-1β), 92.0 ($J_{C,H}$ 172 Hz, C-1α), 61.8 (OCH_3-β), 59.2 (OCH_3-α), 58.1 (OCH_3-β), 57.8 (OCH_3-α), 18.0 (C-6α), 17.9 (C-6β). The anomeric mixture **17** (1.6 g, 6.0 mmol) was hydrogenolyzed as described for the hydrogenolysis of **14**. Chromatography (EtAc–hexanes–MeOH, 4:4:1) gave the hemiacetal **18** as a syrup (1.1 g, 90%). Compound **18** (0.88 g, 4.6 mmol) was acetylated as described for the preparation of **4** to give 1,4-di-*O*-acetyl-2,3-di-*O*-methyl-α,β-L-rhamnopyronose (**19**) that, after chromatography (EtAc–hexanes, 1:1), gave an α:β (7:1) mixture as a syrup (0.97 g, 76%). ^{1}H NMR: δ 6.17 (d, 1 Hα, $J_{1,2}$ 2 Hz, H-1α), 5.60 (d, 1 Hβ, $J_{1,2}$ 1 Hz, H-1β), 5.08 (t, 1 Hα, $J_{4,3}$ 10 Hz, $J_{4,5}$ 10 Hz, H-4α), 4.99 (t, 1 Hβ, $J_{4,3}$ 10 Hz, $J_{4,5}$ 10 Hz, H-4β), 3.79 (m, 1 Hα, H-5α), 3.75 (dd, 1 Hβ, $J_{2,3}$ 3 Hz, H-2β), 3.61 (dd, 1 Hα, $J_{2,3}$ 3 Hz, H-2α), 3.59 (s, 3 Hβ, OCH_3), 3.54 (dd, 1 Hα, H-3α), 3.52 (s, 3 Hα, OCH_3), 3.47 (m, Hβ, H-5β), 3.43 (s, 3 Hα, OCH_3), 3.39 (s, 3 Hβ, OCH_3), 3.28 (dd, 1 Hβ, H-3β), 2.65, 2.42 (2s, 2×3 Hα, CH_3CO), 2.13, 2.05 (2s, 2×3 Hβ, CH_3CO), 1.91 (d, 3 Hα, $J_{6,5}$ 6 Hz, H-6α), 1.20 (d, 3 Hβ, $J_{6,5}$ 6 Hz, H-6β). ^{13}C NMR: δ 169.7, 168.9, 169.1 (C=O), 93.0 (C-1β), 91.3 (C-1α), 81.3 (C-3β), 78.5 (C-3α), 76.2 (C-2β), 76.0 (C-2α), 72.1 (C-4β), 7.20 (C-4α), 7.15 (C-5β), 69.2 (C-5α), 61.4, 59.2, 57.7, 57.8 ()CH^3), 29.6, 21.0, 20.9 (CH_3CO), 17.5 (C-6α), 17.4 (C-6β). A mixture of the acceptor **12** (327 mg, 1.1 mmol), the donor **19** (333 mg, 1.2 mmol) and activated molecular sieves (4Å) in anhydrous CH_2Cl_2 (50 mL) was stirred for 1 h under N_2 and BF_3-Et_2O (60 μL, 0.22 mmol) was added to the mixture. The reaction was allowed to proceed for 16 h at room temperature and was quenched by addition of NEt_3 (~25 μL). The molecular sieves were removed by filtration, rinsed with CH_2Cl_2 (10 mL), and the combined supernatant and washings were concentrated. Chromatography (EtOAc–hexanes, 1:1) of the residue gave disaccharide **28** (542 mg, 97%) that was isolated as white crystals from EtOH-hexanes, mp 109–110 °C, $[\alpha]^{22}_D$ −65.6° (*c* 0.7, CH_2Cl_2). ^{1}H NMR: δ 7.36 (m, 5 H, Ar), 5.87 (m, 1 H, $OCH_2CH=CH_2$), 5.23 (m, 2 H, $OCH_2CH=CH_2$), 5.10 (d, 1 H, $J_{1,2}$ 2 Hz, H-1B), 5.03 (t, 1 H, $J_{4,3}+J_{4,5}=20$ Hz, H-4B), 4.88 (d, 1 H, *J* 11 Hz OCHPh), 4.77 (d, 1 H, $J_{1,2}$ 2 Hz, H-1C), 4.63 (d, 1 H, OCHPh), 4.06 (dd, 1 H, $J_{2,3}$ 3 Hz, H-2C), 4.04 (m, 2 H, $OCH_2CH=CH_2$), 3.72 (dd, 1 H, $J_{2,3}$ 3 Hz, H-2B), 3.76 (m, 1 H, H-5B), 3.69 (m, 1 H, H-5C), 3.62 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3C), 3.56 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3B), 3.52, 3.48, 3.44 (3s, 3×3H, 3×OCH_3), 3.37 (t, 1 H, $J_{4,3}+J_{4,5}=20$ Hz, H-4C), 2.05 (s, 3 H, CH_3CO), 1.30 (d, 3 H, H-6C), 1.15 (d, 3 H, H-6B). ^{13}C NMR: δ 169.9 (C=O), 133.8 ($OCH_2CH=CH_2$), 138.6, 128.4, 128.0, 127.7 (Ar), 117.4 ($OCH_2CH=C_H2$), 99.2 ($^1J_{C,H}$ 171 Hz, C-1B), 98.1 ($^1J_{C,H}$ 170 Hz, C-1C), 81.9 (C-3C), 80.2 (C-4C), 78.7 (C-3B), 75.0 (OCH_2Ph), 77.1 (C-2B), 74.1 (C-2C), 73.1 (C-4B), 67.9, 67.8, 67.1 (C-5B, C-5C, $OCH_2CH=CH_2$), 59.1, 57.9, 57.8(2×OCH_3), 21.0 (CH_3CO), 17.9 (C-6C), 17.5 (C-6B). Anal. Calcd for $C_{27}H_{40}O_{10}$: C, 61.80; H, 7.70. Found: C, 62.01; H, 7.85.

*Allyl 2-*O*-(2,3-di-*O*-methyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyrano-side* (**29**).—Deacetylation of disaccharide **28** (397 mg, 0.76 mmol) was performed as described for the deprotection of disaccharide **20**. Chromatography (EtOAc–hexanes–MeOH, 4:8:1) gave the disaccharide **29** as a colorless syrup (242 mg, 66%), $[\alpha]^{22}_D$ −62.8° (*c* 0.8, CH_2Cl_2). ^{1}H NMR: δ 7.32 (m, 5 H, Ar), 5.87 (m, 1 H, $OCH_2CH=CH_2$), 5.22 (m, 2 H, $OCH_2CH=CH_2$), 5.13 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1B), 4.87 (d, 1 H, *J* 11 Hz, OCHPh), 4.78 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1C), 4.63 (d, 1 H, OCHPh), 4.07 (dd, 1 H, $J_{2,3}$ 3 Hz, H-2C), 4.04 (m, 2 H, $OCH_2CH=CH_2$), 3.73 (dd, 1 H, $J_{2,3}$ 3 Hz, H-2B), 3.68 (m, 2 H, H-5B, H-5C), 3.62 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-3C), 3.56 (t, 1 H, $J_{4,3}+J_{4,5}=19$ Hz, H-4B), 3.50, 3.49 (2s, 3 H and 6 H, 3×OCH_3), 3.45 (dd, $J_{3,4}$ 9.5 Hz, H-3B), 3.36 (t, 1 H, $J_{4,3}+J_{4,5}=19$ Hz, H-4C), 1.30 (d, 3 H, H-6C), 1.29 (d, 3 H, H-6B). ^{13}C NMR: δ 133.8 ($OCH_2CH=CH_2$), 138.7, 128.3, 128, 127.7 (Ar), 117.4 ($OCH_2CH=CH_2$), 98.9 ($^1J_{C,H}$ 163 Hz, C-1B), 98.1 ($^1J_{C,H}$ 165 Hz, C-1C), 82.0 (C-3C), 80.9 (C-3B), 80.2 (C-4C), 76.0 (C-2B), 75.0 (OCH_2Ph), 73.7 (C-2C), 71.7 (C-4B), 68.7, 67.9, 67.8 (C-5B, C-5C, $OCH_2CH=CH_2$), 58.8 (OCH_3-2B), 57.9 (OCH_3-3C), 57.0 (OCH_3-3B), 18.0, 17.7 (C-6B, C-6C). Anal. Calcd for $C_{25}H_{38}O_9$: C, 62.21; H, 7.95. Found: C, 62.00; H, 8.03.

Allyl 2-O-[4-O-(2,4-di-O-acetyl-3,6-di-O-methyl-β-D-glucopyranosyl)-2,3-di-O-methyl-α-L-rhamnopyranosyl]-4-O-benzyl-3-O-methyl-α-L-rhamnopyranoside (**30**).—A mixture of the acceptor **29** (211 mg, 0.44 mmol), the trichloroacetimidate **8** (237 mg, 0.54 mmol) and activated molecular sieves (4Å) in anhydrous CH_2Cl_2 (20 mL) was stirred for 5 h under N_2. The mixture was cooled to −78 °C and TESOTf (20 μL, 0.08 mmol) was added. After stirring for 20 min at −78 °C, the reaction was allowed to proceed for 30 min at room temperature and was quenched by addition of triethylamine (~25 μL). The molecular sieves were removed by filtration, rinsed with CH_2Cl_2 (10 mL), and the combined supernatant and washings were concentrated. Chromatography (EtOAc–hexanes–MeOH, 4:8:1) of the residue gave the disaccharide **30** as a colorless oil (330 mg, 100%), $[\alpha]^{22}_D$ −63.7° (*c* 0.3, CH_2Cl_2). ^{1}H NMR: δ 7.35 (m, 5 H, Ar), 5.87 (m, 1 H, $OCH_2CH=CH_2$), 5.23 (m, 2 H, $OCH_2CH=CH_2$), 5.17 (d, $J_{1,2}$ 2 Hz, H-1B), 4.98 (t, 1 H, $J_{4,3}+J_{4,5}=19$ Hz, H-4A), 4.89(dd, 1 H, $J_{2,1}$ 8 Hz, $J_{2,3}$ 10 Hz, H-2A), 4.86 (d, 1 H, *J* 11 Hz, OC*H*HPh), 4.76 (d, 1 H, H-1A), 4.74 (d, 1 H, $J_{1,2}$ 2 Hz, H-1C), 4.64 (d, 1 H, OCH*H*Ph), 4.11 (m, 2 H, $OCH_2CH=CH_2$), 4.10 (dd, 1 H, $J_{2,3}$ 3 Hz, H-2C), 3.73–3.56 (m, 6 H, H-6A′, H-6A, H-2B, H-5B, H-3C, H-5C), 3.50–3.47 (m, 2 H, H-3B, H-4B), 3.50, 3.48, 3.47, 3.38, 3.32 (5s, 5×3 H, 5×OCH_3), 3.40–3.38 (m, 2 H, H-3A, H-5A), 3.37 (t, 1 H, *J* 8 Hz, *J* 7 Hz, H-4C), 2.70, 2.40 (2s, 2×3 H, 2×CH_3CO), 1.32, 1.25 (m, 2 H, H-6B, H-6C). ^{13}C NMR: δ 169.6, 169.1 (2×C=O), 133.8 ($OCH_2CH=CH_2$), 138.7, 128.3, 128.0, 127.7 (Ar), 117.5 ($OCH_2CH=CH_2$), 100.9 (C-1A), 98.2, 98.1 (C-1B, C-1C), 82.3 (C-3C), 81.5, 80.9 (C-3B, C-4B), 80.2 (C-4C), 77.5, 76.9 (C-2B, C-6A), 75.0 (OCH_2Ph), 73.1, 72.8, 72.3, 72.2 (C-2A, C-3A, C-5A, C-2C), 70.2 (C-4A), 67.9, 67.8, 67.7 (C-5B, C-5C, $OCH_2CH=CH_2$), 59.6, 58.87, 58.1, 57.9, 57.3 (5 x OCH3), 21.0, 20.9 (2×CH_3CO), 18.0, 17.8 (C-6B, C-6C). Anal. Calcd for $C_{37}H_{56}O_{16}$: C, 58.71; H, 7.47. Found: C, 58.49; H, 7.37.

Allyl 2-O-[4-O-(3,6-di-O-methyl-β-D-glucopyranosyl)-2,3-di-O-methyl-α-L-rhamnopyranosyl]-4-O-benzyl-3-O-methyl-α-L-rhamnopyranoside (**31**).—Deacetylation of trisaccharide **30** (371 mg, 0.44 mmol) was performed as described for the deprotection of disaccharide **20**. Chromatography (EtOAc–hexanes–MeOH, 4:4:1) gave the trisaccharide **31** as a colorless syrup (214 mg, 72%), $[\alpha]^{22}_D$ −62° (*c* 0.4, CH_2Cl_2). ^{1}H NMR: δ 7.43 (m, 5 H, Ar), 5.85 (m, 1 H, $OCH_2CH=CH_2$), 5.21 (m, 2 H, $OCH_2CH=CH_2$), 5.11 (d, $J_{1,2}$ 2 Hz, H-1B), 4.86 (d, 1H, *J* 11 Hz, OC*H*HPh), 4.72 (d, 1 H, $J_{1,2}$ 2 Hz, H-1C), 4.62 (d, 1 H, OCH*H*Ph), 4.40 (d, 1H, $J_{1,2}$ 8 Hz, H-1A), 4.00 (m, 2 H, $OCH_2CH=CH_2$), 4.04 (dd, 1 H, $J_{2,3}$ 3 Hz, H-2C), 3.74 (dd, 1 H, $J_{2,3}$ 3 Hz, H-2B), 3.67–3.50 (m, 6 H, H-6A′, H-6A, H-3B, H-4B, H-5B, H-5C), 3.67 (m, 1 H, H-3C), 3.55 (m, 1 H, H-4A), 3.44 (m, 1 H, H-2A), 3.42 (m, 1 H, H-5A), 3.67, 3.50, 3.49, 3.48, 3.39 (5s, 5×3H, 5×OCH_3), 3.32 (t, 1 H, $J_{4,3}+J_{4,5}=18$ Hz, H-4C), 3.19 (t, 1 H, $J_{3,4}+J_{3,2}=18$ Hz, H-3A), 1.32, 1.25 (H-6B, H-6C). ^{13}C NMR: δ 133.8 ($OCH_2CH=CH_2$), 138.6, 128.3, 127.9, 127.7 (Ar), 117.4 ($OCH_2CH=CH_2$), 105.5 ($^1J_{C,H}$ 161 Hz, C-1A), 98.5 ($^1J_{C,H}$ 171 Hz, C-1B), 98.0 ($^1J_{C,H}$ 170 Hz, C-1C), 85.5 (C-3A), 82.0, 81.5, 80.3, 80.2 (C-3B, C-4B, C-3C, C-4C), 75.9, 75.0 (C-2B, C-5A), 74.0 (OCH_2Ph), 73.8 (C-2A), 73.4 (C-2C), 72.9 (C-6A), 71.2 (C-4A), 68.1, 67.9, 67.8 (C-5B, C-5C, $OCH_2CH=CH_2$), 60.3, 59.6, 58.8, 57.9, 56.4 (5×OCH_3), 18.0, 17.5 (C-6B, C-6C). Anal. Calcd for $C_{33}H_{52}O_{14}$: C, 58.90; H, 7.81. Found: C, 58.60; H, 8.08.

Propyl 2-O-[4-O-(3,6-di-O-methyl-β-D-glucopyranosyl)-2,3-di-O-methyl-α-L-rhamnopyranosyl]-3-O-methyl-α-L-rhamnopyranoside (**32**).—The trisaccharide **31** (238 mg, 0.35 mmol) was dissolved in a mixture of 80% aq AcOH–EtOH (0.8:1, 18 mL) and hydrogenolyzed for 6 h at 52 psi in the presence of 10% Pd/C catalyst (78 mg). More catalyst (30 mg) was added and the reaction was allowed to proceed at 52 psi for 3 h. The catalyst was removed by filtration and the filtrate co-concentrated with toluene. The dry residue was dissolved in CH_2Cl_2 (30 mL) and the solution was washed successively with satd aq $NaHCO_3$ (20 mL), satd aq NaCl (20 mL), dried, and concentrated. Chromatography (EtOAc–hexanes–MeOH, 4:4:1) of the residue gave the trisaccharide **32** as a syrup (0.19 g, 90%). $[\alpha]^{22}_D$ −46° (*c* 1, CH_2Cl_2). ^{1}H NMR: Λ 5.06 (d, $J_{1,2}$ 2 Hz, H-1B), 4.70 (d, $J_{1,2}$ 2 Hz, H-1C), 4.40 (d, $J_{1,2}$ 8 Hz, H-1A), 4.05 (dd, $J_{2,1}$ 2 Hz, $J_{2,3}$ 2.5 Hz, H-2C), 3.70 (m, 2 H, H-2B, H-5B), 3.67 (s, 3 H, OCH_3-3A), 3.64 (m, 1 H, H-5C), 3.62 (m, 1H, H-4B), 3.61(m, 1 H, H-3B), 3.53 (t, 1 H, H-4A), 3.50 (t, 1H, H-4C), 3.48 (s, 3H, OCH_3-2B), 3.47 (s, 3H, OCH_3-3C), 3.46 (s, 3H, OCH_3-3B), 3.43 (m, 1 H, H-3C), 3.40 (m, 2 H, H-2A, H-5A), 3.38 (s, 3H, OCH_3-6A), 3.15 (t, *J* 9.5 Hz, H-3A), 3.59 (dd, 1 H, $OCH_aH_bCH_2CH_3$), 3.34 (dd, 1 H, $OCH_aH_bCH_2CH_3$), 3.58 (m, 2H, H-6A, H-6′A),

1.59 (m, 2 H, $OCH_2CH_2CH_3$), 1.32, 1.25(2d, 2×3H, H-6B, H-6C), 0.92 (t, 3H, $OCH_2CH_2CH_3$). ^{13}C NMR: δ 105.6 ($^1J_{C,H}$ 158 Hz, C-1A), 99.1 ($^1J_{C,H}$ 169 Hz, C-1C), 98.3 ($^1J_{C,H}$ 170 Hz, C-1B), 85.6 (C-3A), 81.9 (C-3C), 81.6 (C-3B), 80.3 (C-4B), 75.9 (C-2B), 75.1 (C-2A), 74.2 (C-5A), 72.9 (C-6A), 72.2 (C-2C), 72.0 (C-4C), 71.2 (C-4A), 69.2 ($OCH_2CH_2CH_3$), 68.2 (overlapped, C-5B, C-5C), 60.4 (OCH_3-3A), 59.6 (OCH_3-6A), 59.0 (OCH_3-2B), 57.5 (OCH_3-3C), 56.5 (OCH_3-3B), 22.7 ($OCH_2CH_2CH_3$), 17.7 (C-6C), 17.6 (C-6B), 10.6 ($OCH_2CH_2CH_3$). Anal. Calcd for $C_{26}H_{48}O_{14}$: C, 53.40; H, 8.29. Found: C, 53.20; H, 8.28.

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