Use of the [β-(Trimethylsilyl)ethoxy]methyl (SEM) Protecting Group in Carbohydrate Chemistry. Fully Functionalized Rhamnose Acceptors and Donors for Use in Oligosaccharide Synthesis

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The use of the [β-(trimethylsilyl)ethoxy]methyl (SEM) acetal as a protecting group in carbohydrate chemistry is described. The compatibility of this group with a variety of protection/deprotection conditions normally encountered in oligosaccharide synthesis is demonstrated, by way of example, with the preparation of fully functionalized rhamnose acceptors and donors and their subsequent use in glycosylation reactions. Thus, reaction of allyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside with SEM chloride resulted in a fully protected and functional key monosaccharide, namely allyl 2-*O*-benzoyl-3-*O*-[[β-(trimethylsilyl)ethoxy]methyl]-4-*O*-benzyl-α-L-rhamnopyranoside. Isomerization of the 1-*O*-allyl group to the prop-1-enyl group, followed by hydrolysis, yielded the hemiacetals. These were then treated with a Vilsmeier–Haack reagent to give a glycosyl chloride, a monosaccharide donor molecule. Alternatively, transesterification of the 2-*O*-benzoate in the key monosaccharide, followed by benzylation of the resultant alcohol, and acidic cleavage of the SEM acetal yielded the glycosyl acceptor, allyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside. Glycosylation of this acceptor with the monosaccharide donor above under Konigs–Knorr conditions afforded a disaccharide which was, in turn, converted into a disaccharide acceptor by methanolysis of the 2′-*O*-benzoate group. Similar glycosylation of allyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside with the monosaccharide chloride gave a second disaccharide that was converted into its chloride (a donor molecule) as described before. The disaccharides offer attractive rhamnopyranosyl synthons which can be used for the elaboration of higher order oligosaccharides.

Introduction

The biological roles of complex carbohydrates in processes as diverse as immune responses, hormone regulation, signalling of disease states, cell–cell recognition, and cell development are the subject of intensive investigation.[1] Indeed, advances in the understanding of biological processes mediated by carbohydrate recognition markers have led to a significant increase in activity at the carbohydrate frontier in recent years.[2] An integral component of this activity has involved the development of efficient chemical[3] and chemoenzymatic[4] methods of oligosaccharide synthesis together with methodology for the selective protection/deprotection and functional group manipulation in both mono- and oligosaccharides.[3] The quest for versatile protecting groups which can be selectively manipulated at will under specific conditions and which can be used to attenuate the reactivity of glycosyl acceptors and donors in glycosylation reactions[3] continues to be a worthy objective. We describe herein the use of such a protecting group, namely the [β-(trimethylsilyl)ethoxy]methyl (SEM) acetal.[5] In particular, we describe, by way of example, the use of SEM acetals as protecting groups to yield fully functionalized rhamnose glycosides. We describe also the selective manipulation of different functionality in these substrates to demonstrate the compatibility of the SEM acetals to various protection/deprotection conditions. Finally, we report the use of these fully functionalized rhamnose acceptors and donors in glycoside synthesis under conditions that are frequently encountered in oligosaccharide synthesis. The work is of interest since oligosaccharides containing rhamnose are widespread in the cell walls and lipopolysaccharide O-chains of bacteria and serve as recognition markers for the immune system.[7]

Results and Discussion

We chose as our starting monosaccharide allyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (**1**),[8] a compound that has served as a key unit in our laboratory for the synthesis of penta- up to heptasaccharides corresponding to the biological repeating unit of *Shigella flexneri* variant Y O-antigens[8-10] and for the synthesis of portions of the bacterial cell-wall polysaccharide of the β-hemolytic *Streptococci* Group A.[7c,11] Thus, protection of the remaining 3-OH in **1** as a SEM acetal was accomplished in 80% yield by use of [β-(trimethylsilyl)ethoxy]methyl (SEM) chloride and Hunig's base, as described by Lipshutz and Pegram.[6] It was essential at this point to verify that the SEM group could be removed selectively. This was of some concern since the original report[6] describing some SEM-protected monosaccharides had not indicated that the SEM group could be removed by use of fluoride ion, as was the case in some simpler molecules. Indeed, treatment of **2** with tetrabutylammonium fluoride (1 M) failed to remove the SEM group. Realization that this protecting group was in fact an acetal, led us to consider the use of acid catalysis for its removal, and reaction of **2** with methanolic hydrogen chloride (1.5%) afforded the alcohol **1** in 80% yield. Having established conditions for the selective removal of the SEM group, we proceeded

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(2) For example: Knight, P. *Biotechnology* **1989**, *7*, 35.

(3) Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 155. Paulsen, H. In *Organic Synthesis An Interdisciplinary Challenge*; Streith, J., Prinzbach, H., Schill, G., Eds.; Blackwell: Oxford, 1985; p 317.

(4) For example: Bednarski, M. D.; Chenault, H. K.; Simon, E. S.; Whitesides, G. M. *J. Am. Chem. Chem.* **1987**, *109*, 1283. David, S.; Auge, C. *Pure Appl. Chem.* **1987**, *59*, 1501. Palcic, M. M.; Srivastava, O. P.; Hindsgaul, O. *Carbohydr. Res.* **1987**, *159*, 315. Hindsgaul, O.; Tahir, S. H.; Srivastava, O. P.; Pierce, M. *Carbohydr. Res.* **1988**, *173*, 263. Sabesan, S.; Paulsen, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 2068.

(5) Although this group has been described previously,[6] its scope in the field of carbohydrate chemistry has not been evaluated.

(6) Lipshutz, B. H.; Pegram, J. J. *Tetrahedron Lett.* **1980**, *21*, 3343.

(7) (a) For example: Bundle, D. R.; Gidney, M. A. J.; Josephson, S.; Wessel, H.-P. *ACS Symp. Ser.* **1983**, *231*, 49. (b) Carlin, N. I. A.; Gidney, M. A. J.; Lindberg, A. A.; Bundle, D. R. *J. Immunol.* **1986**, *137*, 2361. (c) Reimer, K. B.; Pinto, B. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2103.

(8) Pinto, B. M.; Morissette, D. G.; Bundle, D. R. *J. Chem. Soc., Perkin Trans. 1* **1987**, 9.

(9) Pinto, B. M.; Reimer, K. B.; Morissette, D. G.; Bundle, D. R. *J. Org. Chem.* **1989**, *54*, 2650.

(10) Pinto, B. M.; Reimer, K. B.; Morissette, D. G.; Bundle, D. R. *J. Chem. Soc., Perkin Trans. 1*, in press.

(11) Andrews, J. S.; Pinto, B. M. *J. Chem. Soc., Perkin Trans. 1*, submitted.

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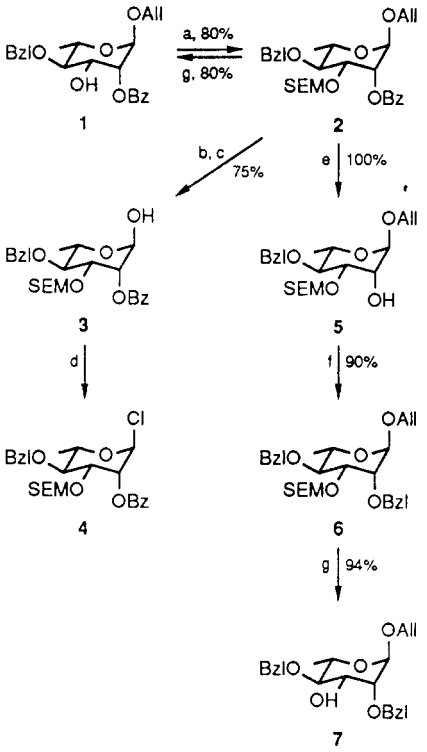
to test its compatibility with a variety of conditions normally encountered in oligosaccharide chemistry.

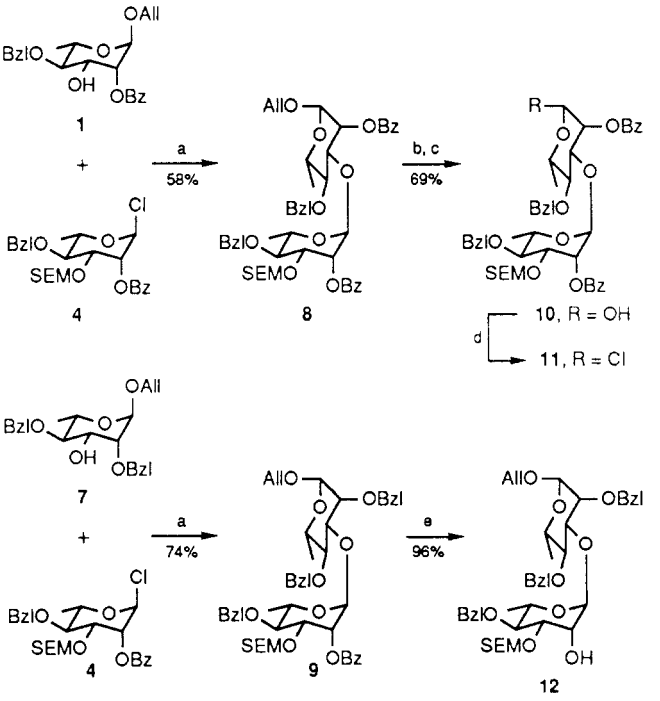
A key role of allyl glycosides in oligosaccharide synthesis is their ready manipulation to provide glycosyl donors.[7c,8-11] The reactions proceed via isomerization to the prop-1-enyl glycosides with Wilkinson's catalyst,[12] followed by hydrolysis of the vinyl ethers,[13] and treatment of the resultant hemiacetals with Vilsmeier–Haack reagents to give the glycosyl halides.[14] Application of this sequence of reactions to **2** was quite successful and afforded first the hemiacetal **3** and then the glycosyl chloride **4**. The conversion of the hemiacetal to the glycosyl chloride by use of dimethyl(chloromethylene)ammonium chloride was carried out in the presence of pyridine to ensure the stability of the SEM acetal.



(a) $[(CH_3)_2CH]_2NC_2H_5$, $(CH_3)_3SiCH_2CH_2OCH_2Cl$, CH_2Cl_2, 22 h; (b) $Rh(PPh_3)_3Cl$, EtOH–H_2O (9:1), reflux 14 h; (c) HgO/$HgCl_2$, $(CH_3)_2CO$ –H_2O (10:1), 18 h; (d) $[(CH_3)_2N{=}CClH]Cl$, py, CH_2Cl_2, 0.5 h; (e) NaOMe (0.1 M), 5 h; (f) NaH, THF, $C_6H_5CH_2Br$, 16 h, –35° to 25 °C; (g) HCl in MeOH (1.5%), 16 h

In order to test the stability of SEM acetals to methanolysis and benzylation, we next removed the 2-*O*-benzoate in **2** by base-catalyzed methanolysis (0.1 M NaOMe in MeOH) to give the 2-OH compound **5** in quantitative yield. Benzylation of **5** with sodium hydride and benzyl bromide in THF gave the dibenzylated monosaccharide **6** in 90% yield. Cleavage of the SEM acetal as described above then afforded the monosaccharide acceptor **7** (94% yield) for use in future glycosylation reactions.

We next turned our attention to evaluating the resistance of the SEM acetals to Konigs–Knorr glycosylation conditions by investigating the reactions of the monosaccharide acceptors **1** and **7** with the fully functionalized glycosyl donor **4**. Thus, reaction of **1**[8] with **4** using silver trifluoromethanesulfonate as promoter in the presence of 1,1,3,3-tetramethylurea[15] afforded the disaccharide **8** in 58% yield. Glycosylation of **7** with **4** under analogous conditions afforded the disaccharide **9** in 74% yield. The allyl glycosides **8** and **9** were then manipulated further to give a disaccharide acceptor and donor. Thus, **8** was converted, via the hemiacetal **10**, to the disaccharide chloride **11** (69%), and **9** was converted to the disaccharide acceptor **12** (96%), as described above for the case of **2**. These disaccharides will serve as useful substrates for the block synthesis of higher order oligosaccharides.



(a) CF_3SO_3Ag, TMU, CH_2Cl_2, 18 h, –78 to 25 °C; (b) $Rh(PPh_3)_3Cl$, EtOH –H_2O (9:1), reflux 12 h; (c) HgO/$HgCl_2$, $(CH_3)_2CO$ –H_2O (10:1), 24 h; (d) $[(CH_3)_2N{=}CClH]Cl$, py, CH_2Cl_2, 1.5 h; (e) NaOMe (0.1 M), 12 h

The assigned structures were in accord with their ^1H and ^{13}C NMR spectral data. Compounds were characterized by use of routine ^1H, ^{13}C, and $^{13}C\{^1H\}$ spectra. In the case of compounds **8** and **9**, ^1H homonuclear chemical shift correlated (COSY) experiments[16] and ^{13}C–^1H chemical shift correlated experiments[17] were performed in order to facilitate assignments. A COSY spectrum was also performed on **12**. The vicinal coupling constants of the ring protons in the monosaccharide units within the oligosaccharides were found to be consistent with a $^1C_4$ (L) conformation for the rhamnopyranosyl units.

The transformations described in the foregoing sections clearly illustrate the viability of the SEM acetal as a protecting group in carbohydrate systems. The compatibility of this group with the conditions required for other selective functional group transformations, together with its stability under glycosylation conditions and its possible selective removal make it an important addition to the repertoire of the synthetic oligosaccharide chemist.[18]

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(18) We note also that the SEM protecting group can be used to advantage in attenuating the reactivity of the substrates in glycosylation reactions. For example, in connection with a separate project, we have employed[11] a β-D-Glc*p*NPhth-(1–3)-α-L-Rha*p* glycosyl donor containing SEM at the 3, 4, and 6 positions of glucosamine in the synthesis of a β-D-Glc*p*NPhth-(1–3)-α-L-Rha*p*-(1–3)-α-L-Rha*p* trisaccharide. In contrast, the corresponding reaction employing benzyl ethers as protecting groups showed poor stereoselectivity and yielded mainly elimination products.[19]

Furthermore, the SEM protecting group has distinct advantages over other simple acetal protecting groups such as the (2-methoxyethoxy)methyl (MEM)[20] and methoxymethyl (MOM) groups[21] for carbohydrates since it is removed under much milder acidic conditions.[22] It is likely that the removal of the SEM acetal with only 1.5% methanolic HCl occurs because of the acid-promoted attack of methanol at silicon, which results in the extrusion of ethylene and formaldehyde, as originally proposed by Lipshutz and Pegram[6] for the fluoride-assisted removal of SEM acetals. We note also that SEM and MEM acetals offer an ideal complementarity as alcohol protecting groups since the removal of the latter group requires fairly robust acidic conditions.[22] Finally, we note that the fully functionalized compounds synthesized in the present study could be used for the elaboration of higher order oligosaccharides corresponding to the cell wall polysaccharides of the β-hemolytic *Streptococci* Group A.[23]

Experimental Section

General. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM400 spectrometer and in deuteriochloroform unless otherwise stated. Chemical shifts and coupling constants were obtained from a first-order analysis of the spectra. NMR resonances for the SEM and allyl protecting groups are only cited for compound **2**, since they remain essentially unchanged for the series of compounds. The ^1H homonuclear chemical shift correlated (COSY) spectra made use of a final 2K × 1K data set with 512 experiments and the ^{13}C–^1H chemical shift correlated experiments made use of a final 2K × 1K data set and 256 experiments. Optical rotations were measured on a Perkin-Elmer P_{22} spectropolarimeter.

Analytical thin-layer chromatography (TLC) was performed on precoated aluminum plates with Merck silica gel 60F-254 as the adsorbent. The developed plates were air-dried, exposed to UV light and/or sprayed with 10% sulfuric acid in ethanol, and heated at 150 °C. All compounds were purified by medium-pressure column chromatography on Kieselgel 60 (230–400 mesh) according to a published procedure.[24]

Solvents were distilled before use and were dried, as necessary, by literature procedures. Solvents were evaporated under reduced pressure and below 40 °C. Reactions performed under nitrogen were also carried out in deoxygenated solvents. Transfers under nitrogen were effected by means of standard Schlenk-tube techniques.

Allyl 2-*O*-Benzoyl-3-*O*-[[β-(trimethylsilyl)ethoxy]methyl]-4-*O*-benzyl-α-L-rhamnopyranoside (2). Allyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (**1**)[8] (2.27 g, 5.70 mmol) was dissolved in anhydrous dichloromethane (2.5 mL). To this solution were successively added *N,N*-diisopropylethylamine (6.0 mL, 34.2 mmol) and [β-(trimethylsilyl)ethoxy]methyl chloride (2.0 mL, 11.4 mmol), and the mixture was stirred under a nitrogen atmosphere for 22 h. The solution was diluted with dichloromethane and washed successively with 0.5 N aqueous hydrogen chloride (2×) and water (2×). The organic layer was dried (Na_2SO_4), the solvent was evaporated, and the resulting yellow syrup was chromatographed with hexane–ethyl acetate (10:1) as eluant: R_f 0.35. The title compound (**2**) was obtained as a clear light yellow syrup (2.41 g, 80%): $[\alpha]^{25}_D$ −5.3° (*c* 0.94 in CH_2Cl_2); δ_C (100.6 MHz) −1.6 ($OCH_2OCH_2CH_2Si(CH_3)_3$), 17.9 and 18.0 (C-6 and $OCH_2OCH_2CH_2Si(CH_3)_3$), 65.6 ($OCH_2OCH_2CH_2Si(CH_3)_3$), 67.9 (C-5), 68.1 ($OCH_2CH{=}CH_2$), 71.6 (C-2), 75.2 and 75.9 (C-3 and $OCH_2C_6H_5$), 80.1 (C-4), 94.5 ($OCH_2OCH_2CH_2Si(CH_3)_3$), 96.6 (C-1), 117.4 ($OCH_2CH{=}CH_2$), 133.6 ($OCH_2CH{=}CH_2$), 165.7 (C=O); δ_H (400.13 MHz) −0.11 (9 H, s, $OCH_2OCH_2CH_2Si(CH_3)_3$), 0.88 (2 H, m, $OCH_2OCH_2CH_2Si(CH_3)_3$), 1.33 (3 H, d, $J_{5,6}$ = 6.3 Hz, 6-H), 3.55 (1 H, t, $J_{3,4} + J_{4,5}$ = 19.0 Hz, 4-H), 3.53 and 3.62 (2 × 1 H, m's, $OCH_2OCH_2CH_2Si(CH_3)_3$), 3.85 (1 H, dq, $J_{4,5}$ = 9.5, $J_{5,6}$ = 6.2 Hz, 5-H), 3.99 and 4.17 (2 × 1 H, m's, $OCH_2CH{=}CH_2$), 4.22 (1 H, dd, $J_{2,3}$ = 3.5, $J_{3,4}$ = 9.5 Hz, 3-H), 4.67 and 4.88 (2 × 1 H, d's, J_{gem} = 11.0 Hz, $OCH_2C_6H_5$), 4.77 and 4.84 (2 × 1 H, d's, J_{gem} = 7.0 Hz, $OCH_2OCH_2CH_2Si(CH_3)_3$), 4.87 (1 H, d, $J_{1,2}$ = 1.5 Hz, 1-H), 5.19 (1 H, m, *Z*-$OCH_2CH{=}CH_2$), 5.29 (1 H, m, *E*-$OCH_2CH{=}CH_2$), 5.48 (1 H, dd, $J_{1,2}$ = 1.5, $J_{2,3}$ = 3.5 Hz, 2-H), 5.93 (1 H, m, $OCH_2CH{=}CH_2$). Anal. Calcd for $C_{29}H_{40}O_7Si$: C, 65.88; H, 7.63. Found: C, 65.50; H, 7.66.

2-*O*-Benzoyl-3-*O*-[[β-(trimethylsilyl)ethoxy]methyl]-4-*O*-benzyl-α-L-rhamnopyranose (3). Tris(triphenylphosphine)rhodium(I)chloride (50 mg, 0.054 mmol) and 1,4-diazabicyclo[2.2.2]octane (60 mg, 0.53 mmol) were added to a solution of the allyl glycoside (**2**) (0.488 g, 0.923 mmol) in ethanol–water (9:1) (45 mL). The mixture was heated at reflux for 14 h under nitrogen. The solvent was evaporated to yield a dark brown residue, which was dissolved in ethyl acetate and filtered through a short column of silica gel. Removal of the solvent gave a light brown syrup. The syrup was dissolved in 90% aqueous acetone (65 mL), the solution was stirred, and yellow mercury(II) oxide (0.21 g, 0.96 mmol) was added followed by the dropwise addition, over 3 min, of mercury(II) chloride (0.20 g, 0.74 mmol) in 90% aqueous acetone (2.5 mL), followed by the dropwise addition of 90% aqueous acetone (15 mL). The reaction was stirred for 18 h, the solvent was evaporated, and the resulting residue was dissolved in ethyl acetate and filtered through Celite. The filtrate was washed successively with saturated aqueous potassium iodide (2×), sodium thiosulfate (2×), and water (2×). The organic layer was dried over anhydrous sodium sulfate, the solvent was evaporated, and the resulting yellow syrup was chromatographed on a silica gel column with hexane–ethyl acetate (3:1) as eluant. The title compound (**3**) was obtained as a clear syrup (0.34 g, 75%): δ_C (100.6 MHz) 17.9 and 18.1 (C-6 and $OCH_2OCH_2CH_2Si(CH_3)_3$), 67.8 (C-5), 72.1 (C-2), 75.0 and 75.4 (C-3 and $OCH_2C_6H_5$), 80.1 (C-4), 92.1 (C-1), 165.8 (C=O); δ_H (400.13 MHz) 1.34 (3 H, d, $J_{5,6}$ = 6.5 Hz, 6-H), 2.83 (1 H, d, $J_{1,OH}$ = 3.8 Hz, OH), 3.58 (1 H, t, $J_{3,4} + J_{4,5}$ = 19.0 Hz, 4-H), 4.08 (1 H, dq, $J_{4,5}$ = 9.5, $J_{5,6}$ = 6.5 Hz, 5-H), 4.30 (1 H, dd, $J_{2,3}$ = 3.5, $J_{3,4}$ = 9.5 Hz, 3-H), 4.70 and 4.93 (2 × 1 H, d's, J_{gem} = 11.0 Hz, $OCH_2C_6H_5$), 5.26 (1 H, m, 1-H), 5.51 (1 H, dd, $J_{1,2}$ = 2.0, $J_{2,3}$ = 3.3 Hz, 2-H).

2-*O*-Benzoyl-3-*O*-[[β-(trimethylsilyl)ethoxy]methyl]-4-*O*-benzyl-α-L-rhamnopyranosyl Chloride (4). Oxalyl chloride (2.9 mL, 33.2 mmol) was added to a stirred solution of *N,N*-dimethylformamide (2.55 mL, 32.9 mmol) in anhydrous dichloromethane (13 mL), and the mixture was stirred under nitrogen for 5 min. The solvent was evaporated under reduced pressure, and the white salt was dried under vacuum for 45 min. The dimethyl(chloromethylene)ammonium chloride was then dissolved in anhydrous dichloromethane (25 mL), and a solution of the hemiacetal (**3**) (3.23 g, 6.61 mmol) in anhydrous dichloromethane (8 mL) and pyridine (2.7 mL, 33.4 mmol) was transferred to this flask under nitrogen by means of a cannula. The flask was rinsed with additional portions of the solvent (3 × 2 mL), and the solvent was transferred as before. The reaction was stirred for 0.5 h and then quenched with cold aqueous sodium hydrogen carbonate. The organic layer was diluted with dichloromethane and washed successively with aqueous sodium hydrogen carbonate, aqueous hydrogen chloride (0.15 M), aqueous sodium hydrogen carbonate, and aqueous sodium chloride. Drying over anhydrous potassium carbonate and evaporation of the solvent yielded a dark yellow syrup (3.35 g), which was dried under vacuum and used in the subsequent glycosylation reaction: δ_C (100.6 MHz) 17.7 and 17.9 (C-6 and $OCH_2OCH_2CH_2Si(CH_3)_3$), 70.9 (C-5), 73.8, 74.7, and 75.3 (C-2, C-3, and $OCH_2C_6H_5$), 79.3 (C-4), 90.0 (C-1), 165.4 (C=O); δ_H (400.13 MHz) 1.39 (3 H, d, $J_{5,6}$ = 6.2 Hz, 6-H), 3.51–3.68 (3 H, m, 4-H and $OCH_2OCH_2CH_2Si(CH_3)_3$), 4.13 (1 H, dq, $J_{4,5}$ = 9.5, $J_{5,6}$ = 6.2 Hz, 5-H), 4.49 (1 H, dd, $J_{2,3}$ = 3.3, $J_{3,4}$ = 9.5 Hz, 3-H), 4.73 and 4.94 (2 × 1 H, d's, J_{gem} = 11.2 Hz, $OCH_2C_6H_5$), 5.62 (1 H, dd, $J_{1,2}$ = 1.8, $J_{2,3}$ = 3.3 Hz, 2-H), 6.11 (1 H, d, $J_{1,2}$ = 1.5 Hz, 1-H).

Allyl 3-*O*-[[β-(Trimethylsilyl)ethoxy]methyl]-4-*O*-benzyl-α-L-rhamnopyranoside (5). Allyl 2-*O*-benzoyl-3-*O*-

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[[β-(trimethylsilyl)ethoxy]methyl]-4-*O*-benzyl-α-L-rhamnopyranoside (**2**) (1.62 g, 3.06 mmol) was dissolved in a 0.1 M sodium methoxide-methanol solution (6 mL) and stirred for 5 h at room temperature under nitrogen. The solution was quenched in a 0.5 N aqueous hydrogen chloride solution (40 mL), the compound was extracted with dichloromethane (3×), and the organic layer was washed with saturated aqueous sodium thiosulfate and water. The organic layer was then dried (Na_2SO_4), and the solvent was evaporated to give a syrup, which was chromatographed using hexane–ethyl acetate (3.5:1) as eluant: R_f 0.37. The title compound (**5**) was obtained as a light yellow syrup (1.29 g, quantitative): $[\alpha]^{25}_D$ −20.0° (*c* 1.00 in CH_2Cl_2); δ_C (100.6 MHz) 17.8 and 18.1 (C-6 and $OCH_2OCH_2CH_2Si(CH_3)_3$), 67.4 (C-5), 67.8 ($OCH_2CH{=}CH_2$), 70.1 (C-2), 75.1 ($OCH_2C_6H_5$), 78.4 (C-3), 79.9 (C-4), 98.3 (C-1); δ_H (400.13 MHz) 1.30 (3 H, d, $J_{5,6}$ = 6.5 Hz, 6-H), 2.53 (1 H, d, $J_{2,OH}$ = 2.8 Hz, OH), 3.44 (1 H, t, $J_{3,4} + J_{4,5}$ = 19.0 Hz, 4-H), 3.76 (1 H, dq, $J_{4,5}$ = 9.5, $J_{5,6}$ = 6.3 Hz, 5-H), 3.95 (1 H, dd, $J_{2,3}$ = 3.5, $J_{3,4}$ = 9.5 Hz, 3-H), 4.04 (1 H, m, 2-H), 4.71 and 4.82 (2 × 1 H, d's, J_{gem} = 11.0 Hz, $OCH_2C_6H_5$), 4.83 (1 H, 1-H). Anal. Calcd for $C_{22}H_{36}O_6Si$: C, 62.23; H, 8.55. Found: C, 62.19; H, 8.28.

Allyl 2,4-Di-*O*-benzyl-3-*O*-[[β-(trimethylsilyl)ethoxy]methyl]-α-L-rhamnopyranoside (6). Allyl 3-*O*-[[β-(trimethylsilyl)ethoxy]methyl]-4-*O*-benzyl-α-L-rhamnopyranoside (**5**) (170 mg, 0.400 mmol) was dissolved in dry, freshly distilled THF (0.5 mL), and the solution was added dropwise to a cooled (−35 °C) suspension of sodium hydride (40 mg) in THF (1 mL). The flask was rinsed with additional portions of THF (2 × 0.5 mL). The mixture was taken out of the cooling medium, and benzyl bromide (0.07 mL, 0.60 mmol) was then added dropwise to the reaction mixture. After stirring for 16 h at room temperature, TLC [hexane–ethyl acetate (2:1)] indicated completion of reaction. The reaction was quenched with anhydrous methanol and stirred for 10 min till the solution became clear. The mixture was poured into cold water and extracted with ethyl acetate (3×). The extract was washed successively with aqueous hydrogen chloride (1 N), aqueous sodium hydrogen carbonate, and water. The organic layer was dried over sodium sulfate, concentrated, and chromatographed using hexane–ethyl acetate as eluant (R_f 0.59 in hexane–ethyl acetate (4:1)). The title compound (**6**) was obtained as a syrup (186 mg, 90%): $[\alpha]^{25}_D$ −6.9° (*c* 1.30 in CH_2Cl_2); δ_C (100.6 MHz) 17.9 and 18.1 (C-6 and $OCH_2OCH_2CH_2Si(CH_3)_3$), 67.7 and 68.0 (C-5 and $OCH_2CH{=}CH_2$), 72.9 and 75.1 (2 $OCH_2C_6H_5$), 76.9 and 77.3 (C-2 and C-3), 80.6 (C-4), 97.0 (C-1); δ_H (400.13 MHz) 1.31 (3 H, d, $J_{5,6}$ = 6.5 Hz, 6-H), 3.58 (1 H, t, $J_{3,4} + J_{4,5}$ = 18.5 Hz, 4-H), 3.73 (1 H, m, 5-H), 3.79 (1 H, dd, $J_{1,2}$ = 1.5, $J_{2,3}$ = 3.3 Hz, 2-H), 4.03 (1 H, dd, $J_{2,3}$ = 3.0, $J_{3,4}$ = 9.5 Hz, 3-H), 4.62 and 4.88 (2 × 1 H, d's, J_{gem} = 11.0 Hz, $OCH_2C_6H_5$), 4.71 and 4.79 (2 × 1 H, d's, J_{gem} = 12.5 Hz, $OCH_2C_6H_5$), 4.78 (1 H, d, $J_{1,2}$ = 1.8 Hz, 1-H). Anal. Calcd for $C_{29}H_{42}O_6Si$: C, 67.67; H, 8.22. Found: C, 67.57; H, 8.25.

Allyl 2,4-Di-*O*-benzyl-α-L-rhamnopyranoside (7). Methanolic hydrogen chloride (3.5 mL) [prepared by treating anhydrous methanol (25 mL) with acetyl chloride (1 mL)] was added to a stirred solution of allyl 2,4-di-*O*-benzyl-3-*O*-[[β-(trimethylsilyl)-ethoxy]methyl]-α-L-rhamnopyranoside (**6**) (71.9 mg, 0.139 mmol) in anhydrous methanol (3.5 mL), and the mixture was kept at room temperature for 16 h, after which TLC [hexane–ethyl acetate (4:1)] indicated completion of reaction. The mixture was made basic by addition of triethylamine. The solvent was evaporated, and the resulting product was dissolved in ethyl acetate. The organic layer was washed with water (2×) and dried over sodium sulfate. Evaporation of the solvent gave a syrup that was chromatographed with hexane–ethyl acetate (4:1) as eluant: R_f 0.27. The title compound (**7**) was obtained as a colorless syrup (50.4 mg, 94%): $[\alpha]^{25}_D$ +0.5° (*c* 1.10 in CH_2Cl_2); δ_C (100.6 MHz) 17.8 (C-6), 67.2 and 67.5 (C-5 and $OCH_2CH{=}CH_2$), 71.5 (C-3), 72.8 and 74.6 (2 $OCH_2C_6H_5$), 78.6 (C-2), 82.1 (C-4), 96.1 (C-1); δ_H (400.13 MHz), 1.35 (3 H, d, $J_{5,6}$ = 6.5 Hz, 6-H), 2.32 (1 H, d, $J_{3,OH}$ = 9.3 Hz, OH), 3.35 (1 H, t, $J_{3,4} + J_{4,5}$ = 18.8 Hz, 4-H), 3.72 (1 H, dq, $J_{4,5}$ = 9.5, $J_{5,6}$ = 6.5 Hz, 5-H), 3.77 (1 H, dd, $J_{1,2}$ = 1.5, $J_{2,3}$ = 3.8 Hz, 2-H), 3.99 (1 H, ddd, $J_{2,3}$ = 3.5, $J_{3,4}$ = 9.3, $J_{3,OH}$ = 9.3 Hz, 3-H), 4.60 and 4.76 (2 × 1 H, d's, J_{gem} = 12.0 Hz, $OCH_2C_6H_5$), 4.67 and 4.92 (2 × 1 H, d's, J_{gem} = 11.0 Hz, $OCH_2C_6H_5$), 4.87 (1 H, d, $J_{1,2}$ = 1.2 Hz, 1-H). Anal. Calcd for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34. Found: C, 71.87; H, 7.43.

Allyl 3-*O*-[2′-*O*-Benzoyl-3′-*O*-[[β-(trimethylsilyl)ethoxy]methyl]-4′-*O*-benzyl-α-L-rhamnopyranosyl]-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (8). Anhydrous dichloromethane (7 mL) and 1,1,3,3-tetramethylurea (1.2 mL, 10.0 mmol) were added to a well-dried mixture of allyl 2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranoside (**1**) (1.359 g, 3.411 mmol), silver trifluoromethanesulfonate (1.88 g, 7.32 mmol), and 4A molecular sieves, and this mixture was stirred under an atmosphere of nitrogen for 0.5 h in a flask fitted with a dropping funnel which was equipped with a cooling jacket. A solution of the glycosyl chloride (**4**) (2.64 g, 5.21 mmol) in anhydrous dichloromethane (4 mL), previously stirred with 4A molecular sieves for 0.5 h under nitrogen, was transferred under nitrogen pressure to the dropping funnel by means of a cannula. The flask was rinsed with additional portions (3 × 1.5 mL) of solvent which were transferred as before. Both the glycosyl chloride and the allyl glycoside solutions were cooled to −78 °C before the glycosyl chloride was added dropwise, during 20 min. The dropping funnel was also rinsed with additional portions of solvent (2 × 1 mL). The reaction mixture was allowed to warm up to room temperature while being stirred in the dark under a nitrogen atmosphere for 18 h. The solids were removed by filtration. The filtrate was diluted with dichloromethane and washed successively with aqueous sodium hydrogen carbonate and aqueous sodium chloride. The organic layer was dried (Na_2SO_4), and the solvent was evaporated to give a syrup which was chromatographed using hexane–ethyl acetate (3:1) as eluant: R_f 0.50. The title compound (**8**) was obtained as a clear syrup (1.710 g, 58%): $[\alpha]^{25}_D$ +1.5° (*c* 0.65 in CH_2Cl_2); δ_C (100.6 MHz) 17.9 (C-6′), 18.1 (C-6), 67.9 (C-5), 68.7 (C-5′), 71.7 (C-2′), 73.0 (C-2), 74.3 and 75.7 (2 × $OCH_2C_6H_5$), 75.5 (C-3′), 78.4 (C-3), 79.8 (C-4′), 80.3 (C-4), 96.3 (C-1), 99.6 (C-1′), 165.5 and 166.0 (2 C=O); δ_H (400.13 MHz), 1.17 (3 H, d, $J_{5',6'}$ = 6.3 Hz, 6′-H), 1.35 (3 H, d, $J_{5,6}$ = 6.3 Hz, 6-H), 3.49 (1 H, t, $J_{3',4'} + J_{4',5'}$ = 19.0 Hz, 4′-H), 3.64 (1 H, t, $J_{3,4} + J_{4,5}$ = 19.0 Hz, 4-H), 3.84 (1 H, m, 5-H), 3.85 (1 H, m, 5′-H), 4.13 (1 H, dd, $J_{2',3'}$ = 3.3, $J_{3',4'}$ = 9.5 Hz, 3′-H), 4.30 (1 H, dd, $J_{2,3}$ = 3.3, $J_{3,4}$ = 9.5 Hz, 3-H), 4.58 and 4.78 (2 × 1 H, d's, J_{gem} = 11.5 Hz, $OCH_2C_6H_5$), 4.69 and 5.02 (2 × 1 H, d's, J_{gem} = 10.8 Hz, $OCH_2C_6H_5$), 4.92 (1 H, d, $J_{1,2}$ = 1.5 Hz, 1-H), 5.18 (1 H, d, $J_{1',2'}$ = 1.5 Hz, 1′-H), 5.40 (1 H, dd, $J_{1,2}$ = 2.0, $J_{2,3}$ = 3.3 Hz, 2-H), 5.57 (1 H, dd, $J_{1',2'}$ = 1.7, $J_{2',3'}$ = 3.0 Hz, 2′-H). Anal. Calcd for $C_{49}H_{60}O_{12}Si$: C, 67.72; H, 6.96. Found: C, 67.56; H, 6.92.

Allyl 3-*O*-[2′-*O*-Benzoyl-3′-*O*-[[β-(trimethylsilyl)ethoxy]methyl]-4′-*O*-benzyl-α-L-rhamnopyranosyl]-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (9). A mixture of allyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside (**7**) (0.119 g, 0.311 mmol), silver trifluoromethanesulfonate (0.230 g, 0.895 mmol), 1,1,3,3-tetramethylurea (0.11 mL, 0.92 mmol), and 4A molecular sieves in anhydrous dichloromethane (1.0 mL) was stirred under an atmosphere of nitrogen for 0.5 h in a flask fitted with a dropping funnel which was equipped with a cooling jacket. A solution of the glycosyl chloride (**4**) (0.232 g, 0.440 mmol) in anhydrous dichloromethane (1.5 mL), previously stirred with 4A molecular sieves for 0.5 h under nitrogen, was transferred under nitrogen pressure to the dropping funnel by means of a cannula. The flask was rinsed with additional portions (3 × 0.5 mL) of solvent, which were transferred as before. Both the glycosyl chloride and the allyl glycoside solutions were cooled to −78 °C before the glycosyl chloride was added dropwise, during 25 min. The reaction mixture was allowed to warm up to room temperature while being stirred in the dark under a nitrogen atmosphere for 18 h. The solids were removed by filtration. The filtrate was diluted with dichloromethane and washed successively with aqueous sodium hydrogen carbonate and aqueous sodium chloride. The organic layer was dried (Na_2SO_4), and the solvent was evaporated to give a dark brown syrup, which was chromatographed using hexane–ethyl acetate (3:1) as eluant: R_f 0.43. The title compound (**9**) was obtained as a clear colorless syrup (0.196 g, 74%): $[\alpha]^{25}_D$ −8.4° (*c* 1.00 in CH_2Cl_2); δ_C (100.6 MHz) 17.9 (2 C) and 18.2 (C-6, C-6′, and $OCH_2OCH_2CH_2Si(CH_3)_3$), 68.3 (C-5), 68.4 (C-5′), 71.5 (C-2′), 72.7, 75.0, and 75.6 (3 $OCH_2C_6H_5$), 75.4 (C-3′), 78.1 (C-2), 78.2 (C-3), 80.2 (C-4′), 80.9 (C-4), 96.8 (C-1), 99.3 (C-1′), 165.4 (C=O); δ_H (400.13 MHz), 1.29 (3 H, d, $J_{5',6'}$ = 6.3 Hz, 6′-H), 1.30 (3 H, d, $J_{5,6}$ = 6.3 Hz, 6-H), 3.51–3.61 (3 H, m, 4′-H and $OCH_2OCH_2CH_2Si(CH_3)_3$), 3.54 (1 H, t, $J_{3',4'} + J_{4',5'}$ = 18.9 Hz, 4′-H), 3.64–3.72 (2 H, m, 4-H and 5-H), 3.76 (1 H, dd, $J_{1,2}$ = 2.1, $J_{2,3}$ = 3.5 Hz, 2-H), 3.94 (1 H, dq, $J_{4',5'}$ = 10.3, $J_{5',6'}$ = 6.2 Hz, 5′-H), 4.13 (1 H, dd, $J_{2,3}$ = 3.4, $J_{3,4}$ = 9.5 Hz, 3-H), 4.31 (1 H, dd, $J_{2',3'}$ = 3.4,

$J_{3',4'}$ = 9.5 Hz, 3'-H), 4.63 and 4.94 (2 × 1 H, d's, J_{gem} = 11.3 Hz, $OCH_2C_6H_5$), 4.68 and 4.92 (2 × 1 H, d's, J_{gem} = 11.0 Hz, $OCH_2C_6H_5$), 4.75 (2 H, s, $OCH_2C_6H_5$), 4.82 (1 H, d, $J_{1,2}$ = 2.0 Hz, 1-H), 5.22 (1 H, d, $J_{1',2'}$ = 1.8 Hz, 1'-H), 5.67 (1 H, dd, $J_{1',2'}$ = 1.9, $J_{2',3'}$ = 3.4 Hz, 2'-H). Anal. Calcd for $C_{49}H_{62}O_{11}Si$: C, 68.83; H, 7.31. Found: C, 69.08; H, 7.31.

3-*O*-[2'-*O*-Benzoyl-3'-*O*-[[β-(trimethylsilyl)ethoxy]methyl]-4'-*O*-benzyl-α-L-rhamnopyranosyl]-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranose (10). Tris(triphenylphosphine)rhodium(I) chloride (15.9 mg, 0.017 mmol) and 1,4-diazabicyclo[2.2.2]octane (16.3 mg, 0.145 mmol) were added to a solution of the allyl glycoside (**8**) (0.253 g, 0.291 mmol) in ethanol–water (9:1) (40 mL). The mixture was heated at reflux for 12 h under nitrogen. The solvent was evaporated to yield a dark brown residue, which was dissolved in ethyl acetate and filtered through a short column of silica gel. Removal of the solvent gave a light brown syrup. The syrup was dissolved in 90% aqueous acetone (15 mL), the solution was stirred, and yellow mercury(II) oxide (0.12 g, 0.55 mmol) was added followed by the dropwise addition, over 3 min, of mercury(II) chloride (0.11 g, 0.40 mmol) in 90% aqueous acetone (1 mL) and the dropwise addition of 90% aqueous acetone (12 mL). The reaction was stirred for 24 h, the solvent was evaporated, and the resulting residue was dissolved in ethyl acetate and filtered through Celite. The filtrate was washed successively with saturated aqueous potassium iodide (2×), sodium thiosulfate (2×), and water (2×). The organic layer was dried over anhydrous sodium sulfate, the solvent was evaporated, and the resulting yellow syrup was chromatographed on silica gel with hexane–ethyl acetate (3:1) as eluant. The title compound (**10**) was obtained as a white foam (0.167 g, 69%): δ_C (100.6 MHz) 17.7, 17.8, and 18.0 (C-6, C-6', and $OCH_2OCH_2CH_2Si(CH_3)_3$), 67.5 (C-5), 68.5 (C-5'), 71.6 (C-2'), 73.3 (C-2), 74.2 ($OCH_2C_6H_5$), 75.4 (C-3' and $OCH_2C_6H_5$), 77.6 (C-3), 79.7 (C-4'), 80.1 (C-4), 91.5 (C-1), 99.3 (C-1'), 165.5 and 166.0 (2 C=O); δ_H (400.13 MHz), 1.17 (3 H, d, $J_{5',6'}$ = 6.0 Hz, 6'-H), 1.34 (3 H, d, $J_{5,6}$ = 6.0 Hz, 6-H), 2.88 (1 H, s, OH), 3.50 (1 H, t, $J_{3',4'} + J_{4',5'}$ = 19.0 Hz, 4'-H), 3.65 (1 H, t, $J_{3,4} + J_{4,5}$ = 19.0 Hz, 4-H), 3.85 (1 H, dq, $J_{4',5'}$ = 9.5, $J_{5',6'}$ = 6.2 Hz, 5'-H), 4.04 (1 H, dq, $J_{4,5}$ = 9.5, $J_{5,6}$ = 6.2 Hz, 5-H), 4.13 (1 H, dd, $J_{2',3'}$ = 3.3, $J_{3',4'}$ = 9.5 Hz, 3'-H), 4.35 (1 H dd, $J_{2,3}$ = 3.3, $J_{3,4}$ = 9.5 Hz, 3-H), 4.58 and 4.78 (2 × 1 H, d's, J_{gem} = 11.5 Hz, $OCH_2C_6H_5$), 4.70 and 5.02 (2 × 1 H, d's, J_{gem} = 10.8 Hz, $OCH_2C_6H_5$), 5.18 (1 H, d, $J_{1',2'}$ = 1.5 Hz, 1'-H), 5.30 (1 H, 1-H), 5.40 (1 H, dd, $J_{1,2}$ = 2.0, $J_{2,3}$ = 3.5 Hz, 2-H), 5.57 (1 H, dd, $J_{1',2'}$ = 2.0, $J_{2',3'}$ = 3.3 Hz, 2'-H). Anal. Calcd for $C_{46}H_{56}O_{12}Si$: C, 66.64; H, 6.81. Found: C, 66.61; H, 6.66.

3-*O*-[2'-*O*-Benzoyl-3'-*O*-[[β-(trimethylsilyl)ethoxy]methyl]-4'-*O*-benzyl-α-L-rhamnopyranosyl]-2-*O*-benzoyl-4-*O*-benzyl-α-L-rhamnopyranosyl Chloride (11). Oxalyl chloride (0.07 mL, 0.80 mmol) was added to a stirred solution of *N*,*N*-dimethylformamide (0.06 mL, 0.77 mmol) in anhydrous dichloromethane (2 mL), and the mixture was stirred under nitrogen for 5 min. The solvent was evaporated under reduced pressure, and the white salt was dried under vacuum for 45 min. Dimethyl(chloromethylene)ammonium chloride was then dissolved in anhydrous dichloromethane (1.5 mL) and pyridine (0.06 mL, 0.74 mmol). A solution of the hemiacetal (**10**) (0.116 g, 0.140 mmol) in anhydrous dichloromethane (1.5 mL) was transferred under nitrogen pressure by means of a cannula. The flask was rinsed with additional portions of the solvent (3 × 1 mL), and the solvent was transferred as before. The reaction was stirred for 1.5 h and then quenched with cold aqueous sodium hydrogen carbonate. The organic layer was diluted with dichloromethane and washed successively with aqueous sodium hydrogen carbonate, aqueous hydrogen chloride (0.15 M), aqueous sodium hydrogen carbonate, and aqueous sodium chloride. Drying over anhydrous potassium carbonate and evaporation of the solvent yielded a dark yellow syrup (0.118 g): δ_C (100.6 MHz) 17.7, 17.8, and 17.9 (C-6, C-6', and $OCH_2OCH_2CH_2Si(CH_3)_3$), 69.0 and 70.9 (C-5 and C-5'), 71.6 (C-2'), 74.4 ($OCH_2C_6H_5$), 75.0, 75.5, and 75.8 (C-2, C-3', and $OCH_2C_6H_5$), 76.8 (C-3), 79.4 and 79.6 (C-4 and C-4'), 89.6 (C-1), 99.8 (C-1), 165.5 and 165.7 (2 C=O); δ_H (400.13 MHz) 1.22 (3 H, d, $J_{5',6'}$ = 6.2 Hz, 6'-H), 1.40 (3 H, d, $J_{5,6}$ = 6.2 Hz, 6-H), 3.54 (1 H, t, $J_{3',4'} + J_{4',5'}$ = 19.0 Hz, 4'-H), 3.75 (1 H, t, $J_{3,4} + J_{4,5}$ = 19.0 Hz, 4-H), 3.84 (1 H, dq, $J_{4',5'}$ = 9.5, $J_{5',6'}$ = 6.2 Hz, 5'-H), 4.13 (1 H, dq, $J_{4,5}$ = 9.5, $J_{5,6}$ = 6.2 Hz, 5-H), 4.15 (1 H, dd, $J_{2',3'}$ = 3.3, $J_{3',4'}$ = 9.5 Hz, 3'-H), 4.60 (1 H, dd, $J_{2,3}$ = 3.3, $J_{3,4}$ = 9.5 Hz, 3-H), 4.63 and 4.81 (2 × 1 H, d's, J_{gem} = 11.5 Hz, $OCH_2C_6H_5$), 4.75 and 5.08 (2 × 1 H, d's, J_{gem} = 10.8 Hz, $OCH_2C_6H_5$), 5.18 (1 H, d, $J_{1',2'}$ = 1.5 Hz, 1'-H), 5.55 (1 H, dd, $J_{1,2}$ = 1.8, $J_{2,3}$ = 3.2 Hz, 2-H), 5.63 (1 H, dd, $J_{1',2'}$ = 1.8, $J_{2',3'}$ = 3.0 Hz, 2'-H), 6.17 (1 H, d, $J_{1,2}$ = 1.5 Hz, 1-H).

Allyl 3-*O*-[3'-*O*-[[β-(Trimethylsilyl)ethoxy]methyl]-4'-*O*-benzyl-α-L-rhamnopyranosyl]-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (12). To the disaccharide (**9**) (0.142 g, 0.189 mmol) were added a 0.1 M sodium methoxide–methanol solution (3 mL) and a few drops of dichloromethane, to bring it in solution. This mixture was stirred under a nitrogen atmosphere at room temperature for 12 h. The solution was neutralized by stirring with Rexyn 101 (H^+) resin beads, which were removed by filtration. The beads were extensively washed with methanol, dichloromethane, and ethyl acetate. The filtrate was concentrated to yield a clear brown syrup. The syrup was chromatographed using hexane–ethyl acetate as eluant (4:1). The title compound (**12**) was obtained as a clear colorless syrup (0.12 g, 96%): $[\alpha]^{25}_D$ −49.3° (*c* 1.30 in CH_2Cl_2); δ_C (100.6 MHz) 17.9, 18.0, and 18.2 (C-6, C-6', and $OCH_2OCH_2CH_2Si(CH_3)_3$), 67.8 ($OCH_2CH{=}CH_2$), 68.0 and 68.3 (C-5 and, C-5'), 70.5 (C-2'), 72.7, 74.9, and 75.3 (3 $OCH_2C_6H_5$), 78.1 and 78.5 (C-2, C-3, and C-3'), 80.1 (C-4'), 81.1 (C-4), 96.9 (C-1), 101.2 (C-1'); δ_H (400.13 MHz), 1.24 and 1.32 (6 H, d's, $J_{5,6}$ = 6.2, $J_{5',6'}$ = 6.2 Hz, 6-H, and 6'-H), 2.38 (1 H, s, OH), 3.45 (1 H, t, $J_{3',4'} + J_{4',5'}$ = 18.5 Hz, 4'-H), 3.61 (1 H, t, $J_{3,4} + J_{4,5}$ = 18.5 Hz, 4-H), 3.65–3.73 (2 H, m, 5-H, and $OCH_2OCH_2CH_2Si(CH_3)_3$), 3.75 (1 H, dd, $J_{1,2}$ = 2.0, $J_{2,3}$ = 3.2 Hz, 2-H), 3.86 (1 H, dq, $J_{4',5'}$ = 9.5, $J_{5',6'}$ = 6.2 Hz, 5'-H), 4.01 (1 H, dd, $J_{2',3'}$ = 3.3, $J_{3',4'}$ = 9.0 Hz, 3'-H), 4.07–4.15 (3 H, m, 2'-H, 3-H, and $OCH_2CH{=}CH_2$), 4.62 (2 × 1 H, d's, J_{gem} = 11.0, J_{gem} = 11.5 Hz, 2 $OCH_2C_6H_5$), 4.73 (2 H, s, $OCH_2C_6H_5$), 4.78–4.84 (5 H, m, 1-H, $OCH_2OCH_2CH_2Si(CH_3)_3$, and 2 $OCH_2C_6H_5$), 5.13–5.17 (2 H, m, 1'-H, and *Z*-$OCH_2CH{=}CH_2$). Anal. Calcd for $C_{42}H_{58}O_{10}Si$: C, 67.17; H, 7.78. Found: C, 67.03; H, 7.90.

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