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Silver(I) oxide-mediated regioselective 2-monoacylation in 3-*O*-benzyl-α-L-rhamnopyranosides and application in synthesis of a protected tetrasaccharide fragment of potent cytotoxic saponins gleditsiosides C and D

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Abstract—The axial 2-hydroxyl group of methyl and allyl 3-*O*-benzyl-α-L-rhamnopyranosides was selectively acylated in 56–78% yields by reaction with 1.1 equiv of acyl chloride in the presence of 1.5 equiv of silver(I) oxide. Use of the method permitted a convenient synthesis of a protected tetrasaccharide fragment of triterpene saponins gleditsiosides C and D.

Keywords: Silver(I) oxide; Acylation; Regioselectivity; L-Rhamnose; Gleditsioside

1. Introduction

It is now well understood that protein- and lipid-bound saccharides play essential roles in many vital biological processes.[1] The rapid development of glycobiology promotes a great need for efficient synthesis of pure and structurally well-defined oligosaccharides and glycoconjugates. One of the major obstacles to construction of these compounds through chemical synthesis is the tedious protecting group manipulation during the synthetic sequence. Therefore, development of various selective reaction strategies of multiple hydroxyl groups in carbohydrate units is highly desirable in the field of glycoscience.[2]

Rhamnose is a very common component of many bioactive natural oligosaccharides.[3] Access to differentially protected rhamnose building blocks is of particular interest due to their use in assembly of architecturally complex rhamnopyranosides. Typically, the regioselectivity is difficult to control due to the similar reactivity of the secondary 2-, 3-, and 4-hydroxyl groups in rhamnose. Although a series of highly elegant and powerful techniques, such as the stannylene acetal method,[4] the regioselective opening of (2-naphthyl)methylene acetals,[5] and the one-pot orthoesterification, orthoester rearrangement[6] have been developed, practical procedures providing unique regioselectivity are always useful. Noting recent reports of a variety of silver(I) oxide-mediated selective reactions, including both the monosubstitution of symmetrical diols in non-carbohydrate substrates,[7] and the highly selective protection of 2,3-diols in 4,6-*O*-benzylidene-blocked gluco- and galactopyranosides,[8] we were therefore drawn to explore the application of this reagent system in selective protection of hydroxyl groups in rhamnose. Described here is the development of the highly regioselective 2-monoacylation in 3-O-benzylated α-L-rhamnopyranosides in the presence of a stoichiometric amount of silver(I) oxide. In addition, we demonstrate the validity of this approach in a convenient synthesis of a protected tetrasaccharide fragment of saponins gleditsiosides C and D

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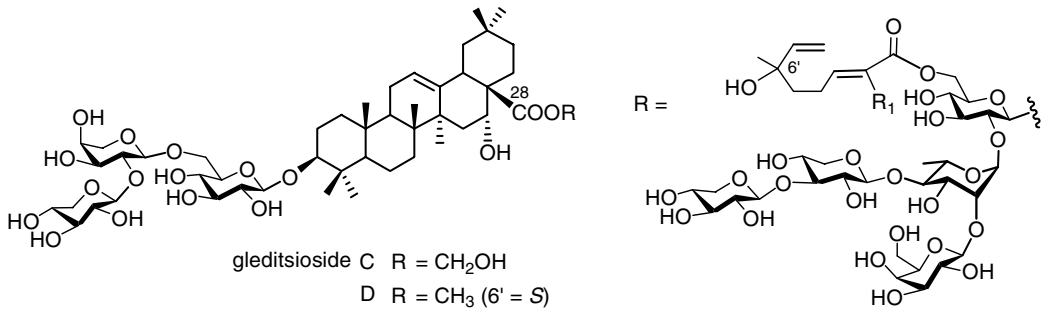
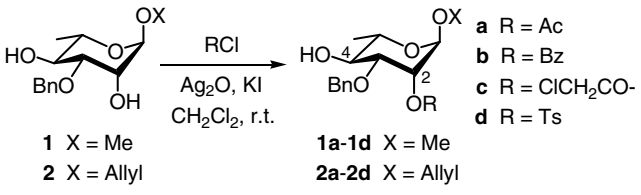


Chart 1. Structures of gleditsiosides C and D.

(Chart 1). Part of this work has already been published in a preceding communication.[9]

2. Results and discussion

Methyl and allyl 3-*O*-benzyl-α-L-rhamnopyranosides (**1**[10] and **2**,[11] Scheme 1) with free 2,4-dihydroxyl groups were prepared according to literature procedures. The solution of **1** (3.19 mmol) in anhydrous dichloromethane (32 mL) was treated with freshly prepared silver(I) oxide (4.79 mmol) and acetyl chloride (3.51 mmol) in the presence of catalytic amounts of potassium iodide (0.96 mmol) at room temperature to provide 56% yield of 2-acetylated ester **1a** (Table 1, entry 1). Indeed, no traces of 4-substituted or 2,4-disubstituted byproducts were isolated and the unreacted starting material **1** was recovered in ca. 10% yield after chromatographic separation at this stage. In the ^{1}H NMR spectrum of **1a**, the H-2 signal appeared downfield at δ 5.35 ppm (dd, J 1.6, 3.2 Hz) that was characteristic of a proton in a CH_3CO–O–C–H moiety, indicating that position 2 was acetylated. The structure of **1a** was further confirmed unambiguously on the basis of its 2D-COSY NMR spectral data. In an attempt to optimize the reaction efficiency, the influence of different reaction parameters on the yield of **1a** was investigated. We found that none or only a poor yield (20%) of the desired product was obtained when the reaction was conducted with *N*,*N*-dimethylformamide (DMF) or tetrahydrofuran (THF) as solvent (Table 1, entries 2 and 3, respectively). A



Scheme 1. Silver(I) oxide-mediated regioselective 2-monoacylation in 3-*O*-benzyl-α-L-rhamnopyranosides. Yields of products are summarized in Table 1.

Table 1. Silver(I) oxide-mediated selective 2-monoacylation in 3-*O*-benzyl-α-L-rhamnopyranosides[a]

Entry	Carb.	Acyl chloride	Time (h)	Yield[b] (%)	Product
1	**1**	AcCl	10	56	**1a**
2[c]	**1**	AcCl	18	—	No reaction
3[d]	**1**	AcCl	10	20	**1a**
4[e]	**1**	AcCl	18	57	**1a**
5	**1**	BzCl	15	68	**1b**
6	**1**	$ClCH_2COCl$	12	61	**1c**
7	**1**	TsCl	10	72	**1d**
8	**2**	AcCl	8	60	**2a**
9	**2**	BzCl	15	78	**2b**
10	**2**	$ClCH_2COCl$	12	68	**2c**
11	**2**	TsCl	8	66	**2d**

[a] All reactions were performed at room temperature using Ag_2O (1.5 equiv), acyl chloride (1.1 equiv), and KI (0.3 equiv) in CH_2Cl_2, unless otherwise indicated.
[b] Isolated yield based on the corresponding substrate **1** or **2**.
[c] In DMF.
[d] In THF.
[e] At 45 °C.

higher temperature (45 °C), even with prolonged reaction time (18 h), also caused no significant improvement of the yield (entry 4).

With this knowledge in hand, the stage was set for extension of the protocol scope by reaction of **1** with various acylating reagents under the effective conditions (1.1 equiv acyl chloride, 1.5 equiv Ag_2O, 0.3 equiv KI, dichloromethane, room temperature). To our delight, the frequently used hydroxyl-protecting groups, including benzoyl, chloroacetyl, and *p*-toluenesulfonyl groups, were also introduced selectively at C-2 of **1**, thereby giving rise to the corresponding acylated products **1b**, **1c**, and **1d**, respectively, in 68%, 61%, and 72% yields (entries 5–7). In a similar fashion, substrate **2**, bearing an allyl functionality on the anomeric carbon, was subjected to the same approach to afford solely 2-monoacylated esters **2a**–**2d** in equally satisfying yields (entries 8–11). It is important to note that, in all cases, the esterifications occurred invariably at the axial 2-*O*-positions without concomitant formation of other products that reflected the robustness of the methodology.

The synthetic utility of the Ag_2O-mediated reaction for the formation of partially protected rhamnosides was demonstrated in an expedient synthesis of a protected tetrasaccharide fragment **11**, which might be an essential intermediate for preparation of C-28 side chain of triterpene saponins gleditsiosides C and D[12] (Chart 1). Isolated from the anomalous fruits of a Chinese medicinal herb called *Gleditsia sinensis* Lam., gleditsiosides C and D exhibit remarkable cytotoxicity against a variety of tumor cell lines in vitro, especially acute promyelocytic leukemia (HL-60) cell with the IC_{50} values of 2.2 ± 0.2 μM for C and 3.5 ± 0.1 μM for D, respectively.[13] The exceedingly potent bioactivity in combination with the intricate oligosaccharide architecture within gleditsiosides C and D have engaged our efforts in their synthesis.

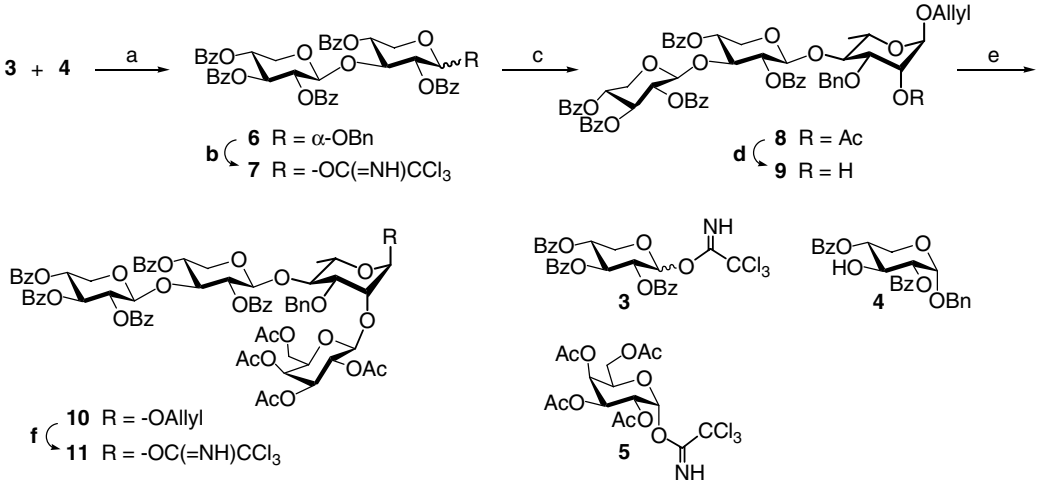
The synthesis of the tetrasaccharide **11** is depicted in Scheme 2. Since a notable feature of **11** is the presence of structurally different sugar residues attaching, respectively, to positions 2 and 4 of a rhamnopyranose core within its scaffold, we envisioned that the alcohol **2a** could be a potential glycosyl acceptor in its construction. Three known monosaccharide synthons **3**,[14] **4**,[15] and **5**[16] are used to assemble **11**. To this end, glycosidic coupling of the xylopyranosyl imidate **3** with **4** yielded (1→3)-linked disaccharide **6** in 75% yield. Through successive debenzylation and trichloroacetimidation with trichloroacetonitrile, **6** was converted to the corresponding imidate **7**[14] as an inseparable α/β mixture in a ratio of ca. 1:1. Ready glycosylation of **7** with the rhamnoside acceptor **2a** activated by trimethylsilyl trifluoromethanesulfonate at −40 °C in dichloromethane furnished the 4-O-glycosylated rhamnoside **8** with complete β-selectivity in 77% yield. Treatment of the trisaccharide **8** with ca. 3% AcCl–MeOH[17] smoothly effected 2-deacetylation and afforded 89% of alcohol **9**, which was then coupled with the galactopyranose donor **5** using an inverse glycosylation procedure[18] to give the expected tetrasaccharide **10** in 69% isolated yield. Eventually, selective removal of the anomeric allyl group within **10**, and subsequent trichloroacetimidate formation of the resulting hemiacetal delivered the target imidate **11** (61% over two steps).

In conclusion, a silver(I) oxide-mediated regioselective 2-monoacylation in 3-*O*-benzyl-α-L-rhamnopyranosides has been developed. This novel method allows for the convenient generation of a variety of differentially functionalized L-rhamnose building blocks. Use of the monomer **2a** as a glycosylating partner permitted an efficient assembly of the branched tetrasaccharide portion **11** of saponins gleditsiosides C and D. Further demonstration of the synthetic applicability of the method, as well as construction of the gleditsioside-type saponins is ongoing.

3. Experimental

3.1. Materials and methods

Solvents used in the reactions were distilled from appropriate drying agents prior to use. Silver(I) oxide was prepared from silver nitrate.[19] All reactions were performed under a nitrogen atmosphere and monitored by thin-layer chromatography (TLC) using Silica Gel GF254 plates with detection by charring with 10% (v/v) H_2SO_4 in EtOH or by UV detection. Silica gel (100–200 mesh) was used for column chromatography. Opti-



Scheme 2. Synthesis of tetrasaccharide fragment **11**. Reagents and conditions: (a) TMSOTf (cat.), 4 Å molecular sieves, CH_2Cl_2, −40 °C, 75%; (b) (i) 10% Pd/C, EtOH, 50 °C; (ii) CCl_3CN, DBU, CH_2Cl_2, 71% over two steps; (c) **2a** (1.05 equiv), TMSOTf (cat.), 4 Å molecular sieves, CH_2Cl_2, −40 °C, 77%; (d) AcCl (4.0 equiv), CH_3OH–CH_2Cl_2 (10:1), 0 °C to rt, 89%; (e) **5** (2.5 equiv), TMSOTf (cat.), 4 Å molecular sieves, CH_2Cl_2, −40 °C, 69%; (f) (i) $PdCl_2$, NaOAc, AcOH–H_2O (9:1), 35 °C; (ii) CCl_3CN, DBU, CH_2Cl_2, 61% over two steps.

cal rotations were measured with a PE-314 automatic polarimeter at 20 ± 1 °C for solutions in a 1.0 dm cell. HRESIMS spectra were acquired on BioTOF Q. ^{1}H, ^{13}C NMR spectra and 2D-COSY NMR experiments were obtained on Bruker AC-E 200 or Varian INOVA-400/54 spectrometers in $CDCl_3$ with tetramethylsilane (TMS) as internal reference. Chemical shifts (δ) are expressed in ppm downfield from the internal TMS absorption.

3.2. Typical procedure for silver(I) oxide-mediated regioselective monoacylation

To a stirred soln of methyl or allyl 3-*O*-benzyl-α-L-rhamnopyranoside (**1** or **2**, 2.7 mmol) in anhydrous CH_2Cl_2 (27 mL) was added freshly prepared Ag_2O (4.05 mmol). The reaction mixture was stirred for 30 min at room temperature, then acyl chloride (2.97 mmol) and KI (0.81 mmol) were added. The mixture was shielded from light and allowed to stir at room temperature for the desired time (indicated in Table 1) until the reaction was complete as judged by TLC analysis. The reaction mixture was filtered and concentrated under diminished pressure. The crude product was subjected to column chromatography on silica gel eluted with petroleum ether–EtOAc to afford the corresponding products.

3.2.1. Methyl 2-*O*-acetyl-3-*O*-benzyl-α-L-rhamnopyranoside (1a). From **1** (68.3 mg), colorless syrup (45.0 mg, 56%): $[\alpha]_D^{21}$ −13.7 (*c* 1.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.38 (m, 5H, Ph*H* of Bn), 5.35 (dd, 1H, *J* 1.6, 3.2 Hz, H-2), 4.70 (d, 1H, *J* 10.8 Hz, PhCH_2), 4.64 (d, 1H, *J* 1.6 Hz, H-1), 4.40 (d, 1H, *J* 10.8 Hz, PhCH_2), 3.70 (dd, 1H, *J* 3.2, 9.6 Hz, H-3), 3.66 (dd, 1H, *J* 6.0, 9.2 Hz, H-5), 3.54 (t, 1H, *J* 9.2 Hz, H-4), 3.36 (s, 3H, OCH_3), 2.02 (s, 3H, CH_3CO), 1.33 (d, 3H, *J* 6.4 Hz, H-6); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.1 (CH_3CO), 137.5, 128.3, 127.9, 127.8, 98.8 (C-1), 77.5, 71.4, 71.2 (Ph*C*H_2), 67.9, 67.8, 54.7 (O*C*H_3), 20.7 (*C*H_3CO), 17.5 (C-6). HRESIMS: calcd for $C_{16}H_{22}O_6$ $[M+Na]^+$, 333.1314, found *m*/*z* 333.1309. Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.76; H, 7.18.

3.2.2. Methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-rhamnopyranoside (1b). From **1** (88.9 mg), colorless syrup (88.4 mg, 68%): $[\alpha]_D^{21}$ +48.2 (*c* 1.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–8.08 (m, 5H, Ph*H* of Bz), 7.23–7.27 (m, 5H, Ph*H* of Bn), 5.57 (dd, 1H, *J* 2.0, 2.8 Hz, H-2), 4.78 (s, 1H, H-1), 4.75 (d, 1H, *J* 11.2 Hz, PhCH_2), 4.44 (d, 1H, *J* 11.2 Hz, PhCH_2), 3.81 (dd, 1H, *J* 3.2, 9.2 Hz, H-3), 3.75 (dd, 1H, *J* 6.0, 9.6 Hz, H-5), 3.68 (t, 1H, *J* 9.2 Hz, H-4), 3.39 (s, 3H, OCH_3), 1.37 (d, 3H, *J* 6.0 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8 (Ph*C*O), 137.7, 133.3, 129.9, 129.8, 128.5, 128.4, 128.1, 127.9, 99.0 (C-1), 77.8, 72.0, 71.3 (Ph*C*H_2), 68.5, 68.0, 55.0 (O*C*H_3), 17.9 (C-6); HRESIMS: calcd for $C_{21}H_{24}O_6$ $[M+Na]^+$, 395.1471, found 395.1465. Anal. Calcd for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50. Found: C, 67.76; H, 6.57.

3.2.3. Methyl 3-*O*-benzyl-2-*O*-chloroacetyl-α-L-rhamnopyranoside (1c). From **1** (76.8 mg), white foamy solid (60.1 mg, 61%): $[\alpha]_D^{21}$ −5.1 (*c* 1.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.38 (m, 5H, Ph*H* of Bn), 5.41 (dd, 1H, *J* 1.6, 3.2 Hz, H-2), 4.70 (d, 1H, *J* 11.2 Hz, PhCH_2), 4.67 (d, 1H, *J* 1.6 Hz, H-1), 4.42 (d, 1H, *J* 11.2 Hz, PhCH_2), 4.13 (s, 2H, ClCH_2CO), 3.73 (dd, 1H, *J* 3.2, 9.6 Hz, H-3), 3.69 (dd, 1H, *J* 6.4, 9.6 Hz, H-5), 3.52 (t, 1H, *J* 9.6 Hz, H-4), 3.37 (s, 3H, OCH_3), 1.33 (d, 3H, *J* 6.4 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8 (ClCH_2*C*O), 137.3, 128.6, 128.2, 128.1, 98.5 (C-1), 77.6, 71.7 (Ph*C*H_2), 71.5, 69.9, 68.0, 55.0 (O*C*H_3), 40.6 (Cl*C*H_2CO), 17.6 (C-6); HRESIMS: calcd for $C_{16}H_{21}O_6Cl$ $[M+Na]^+$, 367.0924, found *m*/*z* 367.0915. Anal. Calcd for $C_{16}H_{21}O_6Cl$: C, 55.74; H, 6.14. Found: C, 55.86; H, 6.37.

3.2.4. Methyl 3-*O*-benzyl-2-*O*-(*p*-tolylsulfonyl)-α-L-rhamnopyranoside (1d). From **1** (69.5 mg), white foamy solid (78.9 mg, 72%): $[\alpha]_D^{21}$ −40.3 (*c* 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.83 (m, 5H, Ph*H* of Ts), 7.20–7.25 (m, 5H, Ph*H* of Bn), 4.87 (dd, 1H, *J* 1.2, 3.2 Hz, H-2), 4.76 (d, 1H, *J* 1.6 Hz, H-1), 4.42 (d, 1H, *J* 11.2 Hz, PhCH_2), 4.21 (d, 1H, *J* 11.2 Hz, PhCH_2), 3.65 (dd, 1H, *J* 3.2, 9.6 Hz, H-3), 3.61 (dd, 1H, *J* 6.0, 9.6 Hz, H-5), 3.52 (t, 1H, *J* 9.2 Hz, H-4), 3.33 (s, 3H, OCH_3), 2.38 (s, 3H, CH_3 of Ts), 1.29 (d, 3H, *J* 6.4 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 137.4, 133.7, 129.8, 128.5, 128.0, 127.9, 127.8, 98.8 (C-1), 76.9, 74.6, 71.2 (Ph*C*H_2), 68.0, 55.0 (O*C*H_3), 21.6 (*C*H_3 of Ts), 17.7 (C-6); HRESIMS: calcd for $C_{21}H_{26}SO_7$ $[M+Na]^+$, 445.1297, found *m*/*z* 445.1291. Anal. Calcd for $C_{21}H_{26}SO_7$: C, 59.70; H, 6.20. Found: C, 59.86; H, 6.24.

3.2.5. Allyl 2-*O*-acetyl-3-*O*-benzyl-α-L-rhamnopyranoside (2a). From **2** (72.3 mg), colorless syrup (49.6 mg, 60%): $[\alpha]_D^{21}$ −11.6 (*c* 1.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.40 (m, 5H, Ph*H* of Bn), 5.88 (ddt, 1H, *J* 5.6, 10.8, 16.8 Hz, CH_2–C*H*=CH_2), 5.38 (dd, 1H, *J* 1.6, 3.2 Hz, H-2), 5.29 (dd, 1H, *J* 1.6, 16.4 Hz, H-*Z*), 5.21 (dd, 1H, *J* 1.2, 10.4 Hz, H-*E*), 4.80 (d, 1H, *J* 1.6 Hz, H-1), 4.72 (d, 1H, *J* 11.2 Hz, PhCH_2), 4.42 (d, 1H, *J* 11.2 Hz, PhCH_2), 4.14–4.19 (m, 1H, CH_2–CH=CH_2), 3.95–4.00 (m, 1H, CH_2–CH=CH_2), 3.75 (dd, 1H, *J* 3.2, 9.6 Hz, H-3), 3.71 (dd, 1H, *J* 6.4, 9.6 Hz, H-5), 3.56 (t, 1H, *J* 9.2 Hz, H-4), 2.12 (s, 3H, CH_3CO), 1.32 (d, 3H, *J* 6.4 Hz, H-6); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.3 (CH_3CO), 137.6, 133.4 (CH_2–*C*H=CH_2), 128.5, 128.1, 128.0, 117.6 (CH_2–

CH=*C*H_2), 97.0 (C-1), 77.6, 71.6, 71.4 (Ph*C*H_2), 68.1, 68.0 (*C*H_2–CH=CH_2), 20.9 (*C*H_3CO), 17.7 (C-6); HRESIMS: calcd for $C_{18}H_{24}O_6$ $[M+Na]^+$, 359.1471, found *m*/*z* 359.1465. Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 64.50; H, 7.21.

3.2.6. Allyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-rhamnopyranoside (2b). From **2** (66.5 mg), colorless syrup (70.2 mg, 78%): $[\alpha]_D^{21}$ +36.7 (*c* 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–8.08 (m, 5 H, Ph*H* of Bz), 7.23–7.30 (m, 5H, Ph*H* of Bn), 5.92 (ddt, 1H, *J* 5.6, 10.8, 16.8 Hz, CH_2–C*H*=CH_2), 5.61 (dd, 1H, *J* 2.0, 3.2 Hz, H-2), 5.31 (ddd, 1H, *J* 1.6, 3.2, 17.2 Hz, H-*Z*), 5.22 (ddd, 1H, *J* 1.2, 2.8, 10.4 Hz, H-*E*), 4.94 (dd, 1H, *J* 1.6 Hz, H-1), 4.78 (d, 1H, *J* 11.2 Hz, PhCH_2), 4.45 (d, 1H, *J* 11.2 Hz, PhCH_2), 4.18–4.23 (m, 1H, CH_2–CH=CH_2), 3.99–4.04 (m, 1H, CH_2–CH=CH_2), 3.87 (dd, 1H, *J* 3.2, 9.2 Hz, H-3), 3.81 (dd, 1H, *J* 6.4, 9.6 Hz, H-5), 3.70 (dd, 1H, *J* 9.2, 9.6 Hz, H-4), 1.37 (d, 3H, *J* 6.4 Hz, H-6); ^{13}C NMR (50 MHz, $CDCl_3$): δ 165.7 (Ph*C*O), 137.5, 133.5 (CH_2–*C*H=CH_2), 133.2, 129.8, 129.7, 128.4, 128.3, 128.0, 127.8, 117.6 (CH_2–CH=*C*H_2), 97.0 (C-1), 77.8, 71.9, 71.3 (Ph*C*H_2), 68.6, 68.2, 68.0 (*C*H_2–CH=CH_2), 17.8 (C-6); HRESIMS: calcd for $C_{23}H_{26}O_6$ $[M+Na]^+$, 421.1627, found *m*/*z* 421.1622. Anal. Calcd for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58. Found: C, 69.45; H, 6.68.

3.2.7. Allyl 3-*O*-benzyl-2-*O*-chloroacetyl-α-L-rhamnopyranoside (2c). From **2** (82.7 mg), colorless syrup (70.8 mg, 68%): $[\alpha]_D^{21}$ −3.7 (*c* 1.27, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.38 (m, 5H, Ph*H* of Bn), 5.89 (m, 1H, *J* 5.6, 10.8, 16.8 Hz, CH_2–C*H*=CH_2), 5.42 (dd, 1H, *J* 1.6, 3.2 Hz, H-2), 5.29 (dd, 1H, *J* 1.2, 16.8 Hz, H-*Z*), 5.23 (dd, 1H, *J* 1.2, 10.4 Hz, H-*E*), 4.83 (d, 1H, *J* 1.2 Hz, H-1), 4.72 (d, 1H, *J* 10.8 Hz, PhCH_2), 4.42 (d, 1H, *J* 10.8 Hz, PhCH_2), 4.16–4.20 (m, 1H, CH_2–CH=CH_2), 3.97–4.02 (m, 1H, CH_2–CH=CH_2), 4.13 (s, 2H, ClCH_2CO), 3.78 (dd, 1H, *J* 3.2, 9.6 Hz, H-3), 3.72 (dd, 1H, *J* 6.0, 9.6 Hz, H-5), 3.52 (t, 1H, *J* 9.6 Hz, H-4), 1.32 (d, 3H, *J* 6.0 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8 (ClCH_2*C*O), 137.4, 133.3 (CH_2–*C*H=CH_2), 128.6, 128.2, 128.1, 127.9, 117.9 (CH_2–CH=*C*H_2), 96.5 (C-1), 77.6, 71.7 (Ph*C*H_2), 71.6, 70.0, 68.2, 68.1 (*C*H_2–CH=CH_2), 40.8 (Cl*C*H_2CO), 17.6 (C-6); HRESIMS: calcd for $C_{18}H_{23}O_6Cl$ $[M+Na]^+$, 393.1081, found *m*/*z* 393.1067. Anal. Calcd for $C_{18}H_{23}O_6Cl$: C, 58.30; H, 6.25. Found: C, 58.38; H, 6.18.

3.2.8. Allyl 3-*O*-benzyl-2-*O*-(*p*-tolylsulfonyl)-α-L-rhamnopyranoside (2d). From **2** (55.8 mg), white foamy solid (56.1 mg, 66%): $[\alpha]_D^{21}$ +38.7 (*c* 1.29, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.77 (m, 5H, Ph*H* of Ts), 7.13–7.29 (m, 5H, Ph*H* of Bn), 5.80 (ddt, 1H, *J* 5.6, 10.8, 16.8 Hz, CH_2–C*H*=CH_2), 5.20 (dd, 1H, *J* 1.6, 17.2 Hz, H-*Z*), 5.14 (dd, 1H, *J* 1.2, 10.4 Hz, H-*E*), 4.86 (d, 1H, *J* 2.0 Hz, H-1), 4.82 (dd, 1H, *J* 1.6, 3.2 Hz, H-2), 4.36 (d, 1H, *J* 11.6 Hz, PhCH_2), 4.24 (d, 1H, *J* 11.6 Hz, PhCH_2), 4.07–4.11 (m, 1H, CH_2–CH=CH_2), 3.87–3.92 (m, 1H, CH_2–CH=CH_2), 3.68 (dd, 1H, *J* 3.2, 9.6 Hz, H-3), 3.64 (dd, 1H, *J* 6.4, 9.6 Hz, H-5), 3.51 (t, 1H, *J* 9.6 Hz, H-4), 2.30 (s, 3H, CH_3 of Ts), 1.25 (d, 3 H, *J* 6.4 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 137.3, 133.3, 133.1 (CH_2–*C*H=CH_2), 129.4, 128.0, 127.6, 127.4, 127.4, 117.3 (CH_2–CH=*C*H_2), 96.4 (C-1), 76.5, 75.1, 71.0 (Ph*C*H_2), 68.1, 67.7 (*C*H_2–CH=CH_2), 21.2 (*C*H_3 of Ts), 17.2 (C-6); HRESIMS: calcd for $C_{23}H_{28}SO_7$ $[M+Na]^+$, 471.1453, found *m*/*z* 471.1448. Anal. Calcd for $C_{23}H_{28}SO_7$: C, 61.59; H, 6.29. Found: C, 61.46; H, 6.40.

3.3. Benzyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-α-D-xylopyranoside (6)

The donor **3** (1.99 g, 3.28 mmol) and the acceptor **4** (1.40 g, 3.12 mmol) were dried together under high vacuum for 2 h, then dissolved in CH_2Cl_2 (31 mL), followed by freshly activated 4 Å MS (5.2 g), after which it was cooled to −40 °C and a soln of TMSOTf (126 μL, 0.656 mmol) in CH_2Cl_2 (26 mL) was added dropwise. The reaction mixture was stirred for 3 h at the same temperature, then neutralized with satd aq $NaHCO_3$, concentrated, and purified by column chromatography (5:1, petroleum ether–EtOAc) to afford **6** as a colorless syrup (2.08 g, 75%): R_f 0.38 (3:1, petroleum ether–EtOAc); $[\alpha]_D^{21}$ −2.1 (*c* 1.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–8.13 (m, 5H, Ph*H*), 7.09–7.62 (m, 20H, Ph*H*), 5.64 (dd, 1H, *J* 6.0 Hz, H-3′), 5.31–5.38 (m, 1H, H-4), 5.26 (d, 1H, *J* 4.4 Hz, H-1′), 5.18 (d, 1H, *J* 3.6 Hz, H-1), 5.11 (dd, 1H, *J* 3.6 Hz, 9.6 Hz, H-2′), 5.03 (dd, 1H, *J* 5.2, 9.2 Hz, H-4′), 4.75 (d, 1H, *J* 12.0 Hz, PhCH_2), 4.69 (dd, 1H, *J* 9.6 Hz, H-3), 4.47 (d, 1H, *J* 12.0 Hz, PhCH_2), 4.28 (dd, 1H, *J* 3.6, 12.4 Hz, H-5e′), 4.06 (dd, 1H, *J* 6.0, 10.8 Hz, H-5e), 3.84 (t, 1H, *J* 10.8 Hz, H-5a), 3.58 (dd, 1H, *J* 5.2, 12.4 Hz, H-5a′); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 165.3, 165.2, 165.0, 164.5 (Ph*C*O), 133.4, 133.3, 133.2, 133.1, 132.8, 129.8, 129.8, 129.6, 129.5, 129.2, 128.9, 128.8, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 100.5, 95.2 (C-1), 75.3, 73.8, 70.3, 69.7 (Ph*C*H_2), 69.5, 68.7, 68.5, 60.3, 59.0; HRESIMS: calcd for $C_{52}H_{44}O_{14}$ $[M+Na]^+$, 915.2629, found *m*/*z* 915.2590. Anal. Calcd for $C_{52}H_{44}O_{14}$: C, 69.95; H, 4.97. Found: C, 70.08; H, 5.06.

3.4. 2,3,4-Tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-D-xylopyranosyl trichloroacetimidate (7)

To a soln of **6** (1.72 g, 1.93 mmol) in EtOH (48 mL) was added 10% Pd/C (516 mg). The mixture was stirred at 50 °C for 24 h, at the end of which time TLC indicated

the reaction was complete. The mixture was filtered and the filtrate was concentrated to dryness, the resulting residue was purified by column chromatography (5:2, petroleum ether–EtOAc) to afford the desired hemiacetal as a colorless syrup which was directly used in the next step. To a soln of the above hemiacetal (1.24 g, 1.54 mmol) and CCl_3CN (1.2 mL, 12.3 mmol) in CH_2Cl_2 (15 mL) was added catalytic DBU at 0 °C. The mixture was stirred for 1 h during which time it was gradually warmed to ambient temperature, and then concentrated in vacuo. The resulting residue was purified by column chromatography (3:1, petroleum ether–EtOAc) to afford a foamy solid, the titled compound **7** (1.31 g, 71% over two steps) as an inseparable α/β anomeric mixture. The ^{1}H NMR data of **7** were identical to that reported previously.[14]

3.5. Allyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-β-D-xylopyranosyl-(1→4)-2-*O*-acetyl-3-*O*-benzyl-α-L-rhamnopyranoside (8)

The mixture of **7** (1.27 g, 1.34 mmol) and the acceptor **2a** (474 mg, 1.41 mmol) were dried together under high vacuum for 2 h, then dissolved in CH_2Cl_2 (35 mL), followed by freshly activated 4 Å MS (1.74 g). The mixture was stirred at room temperature for 15 min and then cooled to −40 °C, and a soln of TMSOTf (51.3 μL, 0.268 mmol) in CH_2Cl_2 (5.4 mL) was added dropwise. After being stirred for 2 h at the same temperature, the reaction was quenched with satd aq $NaHCO_3$ and filtered. The filtrates were concentrated in vacuo to give a residue, which was purified by column chromatography (5:1, petroleum ether–EtOAc) to afford **8** (1.16 g, 77%) as a white foam: R_f 0.40 (7:2, petroleum ether–EtOAc); $[\alpha]_D^{21}$ −38.1 (*c* 1.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.98 (m, 10H, Ph*H*), 7.22–7.54 (m, 20H, Ph*H*), 5.88–5.98 (m, 1H, CH_2–C*H*=CH_2), 5.68 (t, 1H, *J* 6.8 Hz, H-3″), 5.33 (m, 2H, H-4′, H-2″), 5.29 (d, 1H, *J* 3.2 Hz, H-1′), 5.25–5.18 (m, 5H, H-*Z*, H-*E*, H-2, H-2′, H-1″), 5.10 (dd, 1H, *J* 4.4, 8.4 Hz, H-4″), 4.70 (s, 1H, H-1), 4.28–4.39 (m, 4H, H-3, H-3′, PhCH_2), 4.17–4.22 (m, 1H, CH_2–CH=CH_2), 3.94–3.99 (m, 1H, CH_2–CH=CH_2), 3.85 (dd, 1H, *J* 6.0, 10.8 Hz, H-5e″), 3.62–3.75 (m, 4H, H-4, H-5, H-5e′, H-5a′), 3.47 (dd, 1H, *J* 3.6, 9.2 Hz, H-5a″), 2.05 (s, 3H, CH_3CO), 1.30 (d, 3H, *J* 6.0 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2 (CH_3*C*O), 165.5, 165.4, 165.1, 165.0, 164.5 (Ph*C*O), 137.7, 133.5, 133.3, 133.2, 133.1, 133.0, 130.0, 129.9, 129.8, 129.8, 129.7, 129.5, 129.3, 129.1, 128.7, 128.6, 128.4, 128.3, 128.3, 128.2, 128.1, 127.5, 127.3, 118.0 (CH_2–CH=*C*H_2), 100.3, 99.0, 96.7 (C-1), 78.6, 75.7, 74.1, 71.2 (Ph*C*H_2), 70.4, 69.8, 69.6, 68.9, 68.6, 68.2 (*C*H_2–CH=CH_2), 67.0, 61.1, 59.6, 20.9 (*C*H_3CO), 18.2 (C-6); HRESIMS: calcd for $C_{63}H_{60}O_{19}$ $[M+Na]^+$, 1143.3626, found 1143.3660. Anal. Calcd for $C_{63}H_{60}O_{19}$: C, 67.49; H, 5.39. Found: C, 67.57; H, 5.29.

3.6. Allyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-β-D-xylopyranosyl-(1→4)-3-*O*-benzyl-α-L-rhamnopyranoside (9)

To a soln of sugar **8** (1.08 g, 0.96 mmol) in MeOH–CH_2Cl_2 (9:1, 10 mL) was added AcCl (0.28 mL) at 0 °C, then the reaction mixture was allowed to warm slowly to room temperature. When the starting material was no longer present (ca. 24 h), the mixture was concentrated to give a residue, which was purified by column chromatography (3:1, petroleum ether–EtOAc) to afford **9** (921 mg, 89%) as a white foam: R_f 0.26 (3:1, petroleum ether–EtOAc); $[\alpha]_D^{21}$ −122.8 (*c* 1.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–7.80 (m, 10H, Ph*H*), 7.12–7.57 (m, 20H, Ph*H*), 5.88–5.98 (m, 1H, CH_2–C*H*=CH_2), 5.66 (t, 1H, *J* 6.4 Hz, H-3″), 5.32 (dd, 1H, *J* 2.0, 7.6 Hz, H-4′), 5.29 (d, 1H, *J* 4.8 Hz, H-1″), 5.26 (d, 1H, *J* 4.4 Hz, H-1′), 5.16–5.23 (m, 5H, H-*Z*, H-*E*, H-2′, H-2″, H-4″), 4.81 (s, 1H, H-1), 4.32–4.40 (m, 3H, H-2, H-3, H-3′), 4.30 (d, 1H, *J* 11.2 Hz, PhCH_2), 4.17 (d, 1H, *J* 11.2 Hz, PhCH_2), 4.15–4.22 (m, 1H, CH_2–CH=CH_2), 3.95–4.00 (m, 1H, CH_2–CH=CH_2), 3.89 (dd, 1H, *J* 1.6, 3.2 Hz, H-5e″), 3.66–3.74 (m, 3H, H-4, H-5, H-5a′), 3.65 (dd, 1H, *J* 6.0, 11.6 Hz, H-5e′), 3.48 (dd, 1H, *J* 3.2, 8.8 Hz, H-5e″), 1.30 (d, 3H, *J* 6.0 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 165.4, 165.1, 164.8, 164.5 (Ph*C*O), 137.7, 133.8, 133.3, 133.2, 133.0, 132.9, 130.0, 129.9, 129.8, 129.8, 129.7, 129.6, 129.5, 129.3, 129.2, 129.1, 128.4, 128.4, 128.3, 128.2, 128.2, 127.8, 127.3, 117.6 (CH_2–CH=*C*H_2), 100.0, 99.6, 98.1 (C-1), 80.7, 75.9, 74.7, 71.4 (Ph*C*H_2), 71.0, 69.9, 69.7, 69.5, 68.8 68.1, 68.0 (*C*H_2–CH=CH_2), 66.7, 60.9, 60.2, 18.0 (C-6); HRESIMS: calcd for $C_{61}H_{58}O_{18}$ $[M+Na]^+$, 1101.3521, found *m*/*z* 1101.3488. Anal. Calcd for $C_{61}H_{58}O_{18}$: C, 67.89; H, 5.42. Found: C, 67.58; H, 5.26.

3.7. Allyl 2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→2)]-3-*O*-benzyl-α-L-rhamnopyranoside (10)

The alcohol **9** (421 mg, 0.39 mmol) was dried under high vacuum for 2 h, then dissolved in CH_2Cl_2 (7.8 mL), followed by freshly activated 4 Å MS (1.81 g). The mixture was stirred at room temperature for 15 min, after which it was cooled to −40 °C and a soln of TMSOTf (18.1 μL, 0.098 mmol) in CH_2Cl_2 (3.9 mL) was added dropwise. After being stirred for 5 min, the imidate **5** (483 mg, 0.98 mmol) dried separately under high vacuum for 2 h was added. The reaction mixture was stirred at −40 °C for 2 h, at the end of which time TLC indicated that the acceptor was completely disappeared. The reaction

was quenched with Et_3N, concentrated, and purified by column chromatography (2:1, hexane–EtOAc) to afford **10** (381 mg, 69%) as a colorless syrup: R_f 0.35 (2:1, hexane–EtOAc). Sugar **10** was found to decompose in NMR tube and was therefore used in the next step without further identification.

3.8. 2,3,4-Tri-*O*-benzoyl-β-D-xylopyranosyl-(1→3)-2,4-di-*O*-benzoyl-β-D-xylopyranosyl-(1→4)-[2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→2)]-3-*O*-benzyl-α-L-rhamnopyranosyl trichloroacetimidate (11)

A mixture of **10** (235 mg, 0.17 mmol), $PdCl_2$ (52.5 mg), and NaOAc (112.7 mg) in AcOH–H_2O (9:1, 1.2 mL) was stirred overnight at 35 °C. The insoluble material was filtered off; the filtrate was concentrated to give a residue which was extracted with EtOAc. The extract was washed with water (10 mL × 2), satd aq $NaHCO_3$ (15 mL × 2), and brine (15 mL), dried over anhyd Na_2SO_4, and concentrated. The resulting residue was purified by column chromatograph (3:2, petroleum ether–EtOAc) to afford the hemiacetal which was directly used for the next step without further purification. To a soln of the obtained hemiacetal (151 mg, 0.11 mmol) in CH_2Cl_2 (1.1 mL) was added CCl_3CN (88 μL, 0.88 mmol) and catalytic DBU at 0 °C. The mixture was stirred for 1 h during which time it was gradually warmed to ambient temperature, and then concentrated to give a residue which was purified by column chromatography (2:1, petroleum ether–EtOAc) to afford the tetrasaccharide imidate **11** (148 mg, 61% over two steps) as a white foam: R_f 0.45 (3:2, petroleum ether–EtOAc); $[\alpha]_D^{21}$ −43.6 (*c* 1.20, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.50 (s, 1H, N*H*), 7.75–8.03 (m, 10H, Ph*H*), 7.13–7.57 (m, 20H, Ph*H*), 6.16 (d, 1H, *J* 2.0 Hz, H-1), 5.56 (t, 1H, *J* 7.2 Hz, H-3″), 5.30 (dd, 1H, *J* 3.6, 8.0 Hz, H-2‴), 5.12–5.24 (m, 7H, H-1′, H-2′, H-4′, H-1″, H-2″, H-4″, H-3‴), 4.94 (dd, 1H, *J* 3.2, 10.4 Hz, H-4‴), 4.45 (d, 1H, *J* 12.0 Hz, PhC*H*$_2$), 4.30 (d, 1H, *J* 12.0 Hz, PhC*H*$_2$), 4.39–4.36 (m, 2H, H-3′, H-5‴), 4.38 (d, 1H, *J* 8.0 Hz, H-1‴), 4.26 (dd, 1H, *J* 3.6, 12.4 Hz, H-3), 4.08 (dd, 1H, *J* 6.4, 11.2 Hz, H-6a‴), 4.02 (dd, 1H, *J* 6.4, 11.2 Hz, H-6b‴), 3.65–3.81 (m, 6H, H-2, H-4, H-5, H-5e‴, H-5e′, H-5a′), 3.60 (dd, 1H, *J* 5.4, 12.4 Hz, H-5a″), 2.15, 2.00, 1.99, 1.91 (s, 12H, 4 × C*H*$_3$CO), 1.18 (d, 3H, *J* 6.0 Hz, H-6); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 170.2, 170.1, 169.2 (CH$_3$*C*O), 165.6, 165.4, 165.1, 164.8, 164.5 (Ph*C*O), 137.8, 133.8, 133.4, 133.3, 133.0, 132.9, 130.0, 129.9, 129.9, 129.8, 129.7, 129.6, 129.5, 129.3, 129.1, 128.4, 128.3, 128.2, 128.2, 128.0, 127.7, 127.3, 102.5, 99.9, 98.3, 96.8 (C-1), 79.6, 76.4, 75.4, 73.6, 72.9 (Ph*C*H$_2$), 71.0, 70.6, 70.4, 69.9, 69.7, 69.5, 68.8, 68.3, 68.1, 66.8, 61.0, 60.1, 20.6 (*C*H$_3$CO), 18.1 (C-6). Anal. Calcd for $C_{74}H_{72}Cl_3NO_{27}$: C, 61.60; H, 5.03. Found: C, 61.54; H, 5.18.

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Supplementary data

The ^1H and ^{13}C NMR spectra of compound **11** are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2007.03.001.

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