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Note

Practical preparation of 2-azido-2-deoxy-β-D-mannopyranosyl carbonates and their application in the synthesis of oligosaccharides

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Abstract—1-*O*-Allyloxycarbonyl (or ethyloxycarbonyl)-2-azido-2-deoxy-3-*O*-benzyl (or allyl, or benzoyl)-4,6-*O*-isopropylidene-β-D-mannopyranose derivatives were prepared from the corresponding 2-hydroxy-β-D-glucopyranosyl carbonates in high yields via triflation of the 2-hydroxyl group and subsequent S_N2 displacement with azide ion. An *N*-acetyl-mannosamine-containing trisaccharide, a fragment of the putative O10 antigen from *Acinetobacter baumannii*, was efficiently synthesized using these derivatives.
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Keywords: 2-Azido-2-deoxy-β-D-mannopyranose; Triflation; Azide displacement

N-Acetyl-mannosamine (ManNAc) is the biosynthetic precursor of sialic acids, *N*-acetyl-neuraminic acid,[1] and is as a high-affinity ligand for the natural killer cell activating protein NKR-P1.[2] The ManNAc unit has been found in many bacterial polysaccharides,[3] and some oligosaccharides containing ManNAc have been found to possess immunostimulatory activity.[4] Because of the biological significance and utility of this monosaccharide, the synthesis of ManNAc and corresponding analogues has been an interesting topic in carbohydrate chemistry. As a synthetic intermediate, the corresponding azido derivative has been used extensively. Usually, the azido derivative is prepared by either azidonitration of glucal derivatives[5] or S_N2 inversion of the configuration at the C-2 atom of D-glucose derivatives.[6a–h]

There have been several publications regarding the preparation of 1,3,4,6-tetra-*O*-acetyl-2-azido-2-deoxy-α-D-mannopyranose from 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose via a two-step process.[6c,g,h] However, the instability of the target compound during work-up process is a major limitation of these approaches. Although the reasons for the instability of the product and the breakdown mechanism remain unclear, we speculate that the decomposition may be partially due to the interaction of azido group with the *cis*-3-*O*-acetyl group, as the corresponding 2-azido-2-deoxy-glucose[6c] and 3-O-unprotected 2-azido-2-deoxy-mannose derivatives[6g] are relatively stable. A previous study demonstrated the regio- and stereoselective esterification of 3-*O*-allyl (or benzyl, or benzoyl)-4,6-*O*-isopropylidene-D-glucopyranose with allyl (or ethyl) chloroformate, to afford the corresponding 2-hydroxy-β-D-glucopyranosyl carbonates in good yields.[7] With these compounds in hand, we envisioned that the corresponding 2-azido-2-deoxy-mannose derivatives could be conveniently prepared from these intermediates. We report here the results we recently obtained on this approach, which provides a new and practical method for the synthesis of 2-azido-2-deoxy-mannose derivatives. As an example of the methodology, it was used to synthesize efficiently a ManNAc-containing trisaccharide, a fragment of the putative O10 antigen from *Acinetobacter baumannii*.[8]

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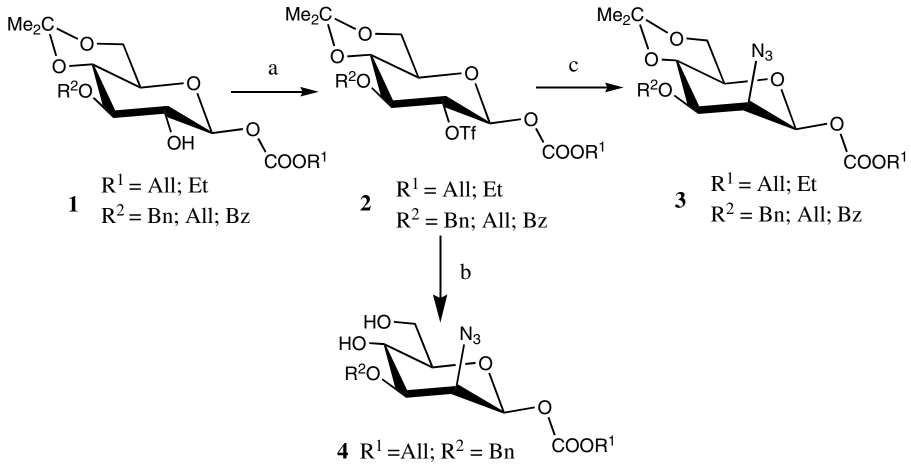
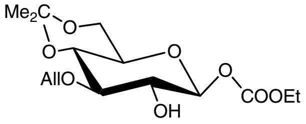
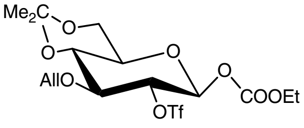
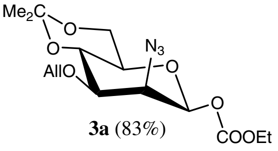
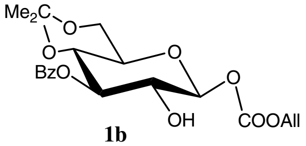
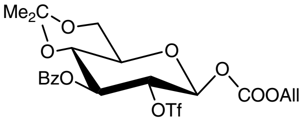
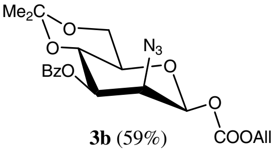
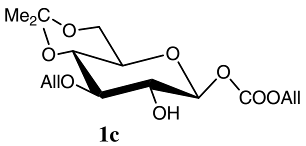
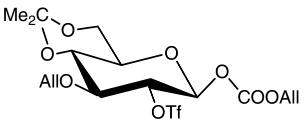
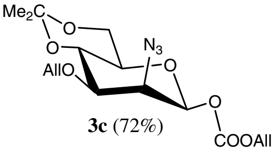
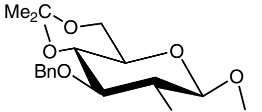
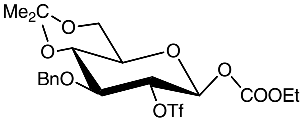
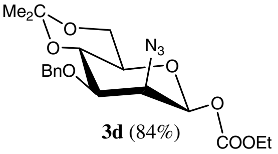
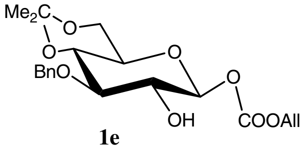
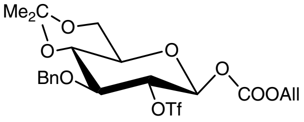
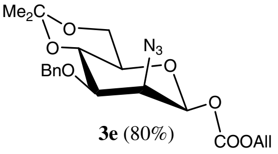


Scheme 1. Synthesis of 2-azido-2-deoxy-β-D-mannopyranoside derivatives. Reagents and conditions: (a) Tf_2O, pyridine; (b) NaN_3, DMF, 70 °C; (c) NaN_3, DMF, Et_3N, 70 °C.

As shown in Scheme 1, the preparation of the target 2-azido-2-deoxy-β-D-mannopyranose derivative, **3**, was achieved via S_N2 inversion by azide ion of triflate, **2**, which was prepared from the corresponding 2-hydroxy-glucopyranosyl carbonate **1**. The results of the reaction using different glucopyranosyl carbonate derivatives (**1a**–**e**) as the starting materials are listed in Table 1.

It was found that triflation of **1a**–**e** with triflic anhydride (2.2 equiv) in dichloromethane in the presence of pyridine (2.4 equiv) at −15 °C proceeded smoothly. Complete esterification occurred and intermediates

Table 1. Results of triflation and azide displacement reactions

Entry	Reactant **1a**–**e**	Triflate **2a**–**e** (yield)[a]	Product **3a**–**e** (yield)[a]	$J_{1,2}$ (Hz)
1	 **1a**	 **2a** (96%)	 **3a** (83%)	**2a** (8.2) **3a** (1.6)
2	 **1b**	 **2b** (94%)	 **3b** (59%)	**2b** (8.1) **3b** (1.5)
3	 **1c**	 **2c** (95%)	 **3c** (72%)	**2c** (8.2) **3c** (1.6)
4	 **1d**	 **2d** (93%)	 **3d** (84%)	**2d** (8.2) **3d** (1.6)
5	 **1e**	 **2e** (95%)	 **3e** (80%)	**2e** (8.2) **3e** (1.5)

[a] Isolated yield.

2a–e were obtained in high yields after a simple work-up procedure and silica gel column chromatography (8:1 petroleum ether–EtOAc, containing 0.5% of Et_3N). The use of low reaction temperatures was necessary to ensure the high yields. The ^1H NMR spectra of all triflates provided clear information to support the assigned structures.

These triflates were quite unstable and turned dark brown after 3–4 days of storage in a refrigerator, even at −15 °C. Therefore, to minimize decomposition, the triflates were used in the next step soon after purification. When the displacement reaction of **2a** with sodium azide was carried out in DMF at an elevated temperature (70 °C), the desired product, **3a**, was formed within 4 h in very low yield (17%) due to the removal of the 4,6-*O*-isopropylidene group under these conditions, thus giving **4** as the main product (61%). To solve this problem, several drops of Et_3N were added to the reaction mixture, and using this modification, **3a** was obtained in a high yield (83%). Under these optimized conditions, the triflates **2b–e** were converted to the corresponding azido derivatives in good yields (72–84%) except for **2b** (59%), presumably because of the instability of 3-*O*-benzoyl group under the basic reaction conditions. The inversion of configuration at C-2 was readily identified by comparison of ^1H NMR spectral data as indicated in Table 1 As expected, compounds with the β-*gluco* configuration showed large coupling constants for H-1 ($J_{1,2}$ 8.1–8.2 Hz), while those with the β-*manno* configuration showed small coupling constants ($J_{1,2}$ 1.5–1.6 Hz).

These 2-azido-2-deoxy-β-D-mannopyranose derivatives are useful building blocks for the preparation of ManNAc-containing oligosaccharides and glycoconjugates, as they can be readily converted either to 2-azido-2-deoxy-α-D-mannopyranosyl donors or to 2-azido-2-deoxy-β-D-mannopyranosyl carbonate acceptors. As an example, a trisaccharide containing 2-acetamido-2-deoxy-α-D-mannose was synthesized efficiently (Scheme 2). This trisaccharide is the core structure of the repeating unit of the putative O10 antigen from *A. baumannii*.[8]

Thus, dealloxycarbonylation of **3b** with the palladium catalyst, $Pd[P(C_6H_5)_3]_4$, (0.05 equiv), in the presence of triphenylphosphine (0.3 equiv) and triethylamine (2 equiv) in THF,[9] followed by C-1 activation with trichloroacetonitrile,[10] furnished the 2-azido-2-deoxy-α-D-mannopyranosyl donor **5** in 73% yield over the two steps. When rhamnose diol **6**[11] was treated with allyl chloroformate in dichloromethane at −15 °C in the presence of 4 equiv of pyridine, the C-3 hydroxyl group was selectively blocked, giving acceptor **7** in 92% yield.[12]

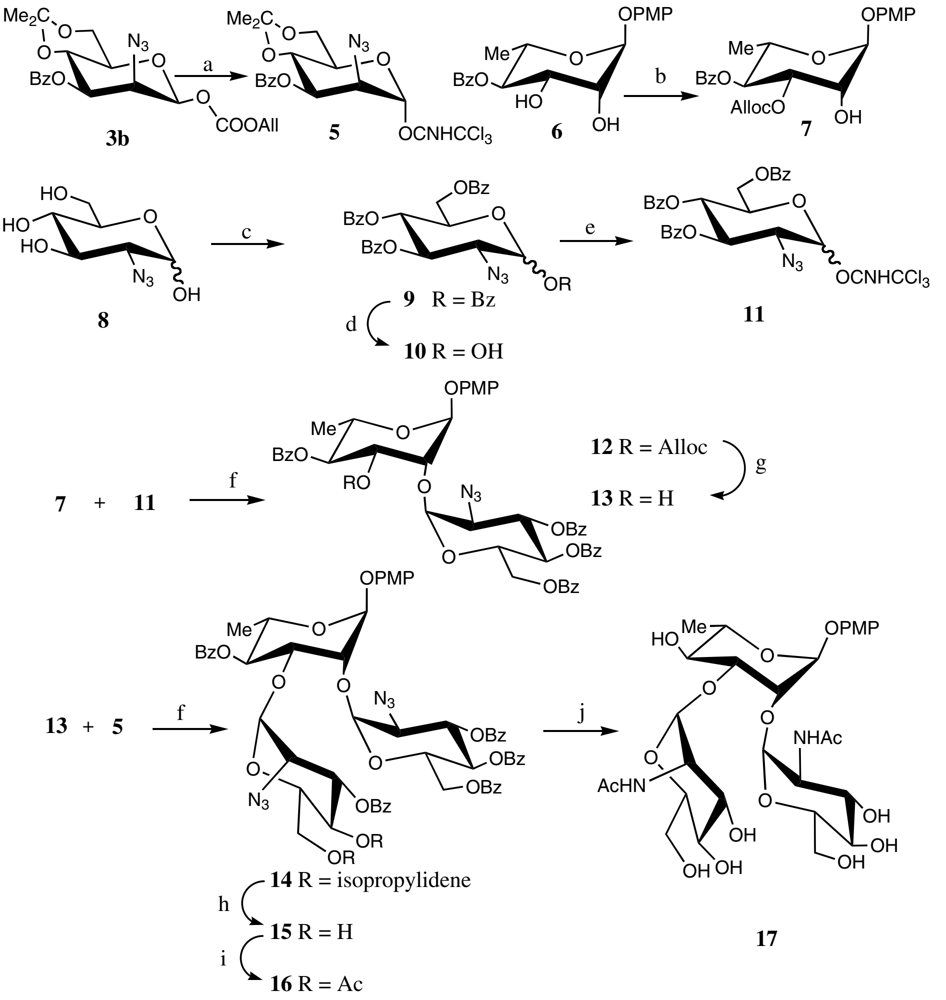
Assembly of trisaccharide **14** was achieved in three steps. First, glycosylation of **11**, which was prepared from 2-azido-2-deoxy-glucopyranose **8**[13] through benzoylation, C-1 debenzoylation, and conversion to the trichloroacetimidate, with acceptor **7** was accomplished within 40 min at room temperature using TMSOTf as the catalyst, giving the α-linked disaccharide **12** after silica gel column chromatography. Second, deallyloxycarbonylation of **12** under the same conditions as those used for the deallyloxycarbonylation of **3b** afforded the disaccharide acceptor **13** in 73% yield. Finally, TMSOTf-catalyzed coupling of the 2-azido-2-deoxy-α-D-mannopyranosyl donor **5** with **13** proceeded smoothly at 0 °C. However, some byproducts with identical chromatographic mobilities to trisaccharide **13** were produced and purification of the product was difficult. Therefore, a solution of 0.3% acetyl chloride in methanol was added to the reaction mixture immediately after completion of the coupling reaction, which, after stirring for 6 h at room temperature, led to the successful removal of the isopropylidene acetal furnishing the trisaccharide diol **15** (71% for 2 steps) as an amorphous solid. Subsequent acetylation with acetic anhydride in pyridine readily gave acetylated trisaccharide **16** (88%). The azido groups were transformed into the corresponding acetamido groups by reduction of **16** with activated zinc in a mixture of acetic anhydride, acetic acid, and THF,[14] and then the *O*-acyl groups were cleaved with a catalytic amount of sodium methoxide in methanol, furnishing the desired trisaccharide (56% for 2 steps). Construction of the (1→6)-linked dimer and trimer of this trisaccharide is in progress.

In conclusion, an efficient and practical method was developed for the synthesis of 2-azido-2-deoxy-β-D-mannopyranoside derivatives. Large-scale preparation of these building blocks is possible thus providing a valuable supplement to the present efforts for the synthesis of 2-azido-2-deoxymannose derivatives.

1. Experimental

1.1. General methods

Optical rotations were determined with a Perkin–Elmer model 241-MC automatic polarimeter for solution in a 1-dm, jacketed cell. NMR spectra were recorded in $CDCl_3$ solution on a Bruker DPX300 spectrometer, using tetramethylsilane as the internal standard. Elemental analysis was performed on a Yanaco CHN Corder MF-3 automatic elemental analyzer. Thin-layer chromatography (TLC) was performed on Silica Gel HF with detection by charring with 30% (v/v) H_2SO_4 in MeOH or by UV detection. Column chromatography was conducted by elution of a column (8 × 100 mm, 16 × 240 mm, 18 × 300 mm, or 35 × 400 mm) of silica gel (200–300 mesh) with mixtures of EtOAc–petroleum ether (bp 60–90 °C) as the eluent. Solutions were concentrated at a temperature <60 °C under diminished pressure.



Scheme 2. Synthesis of antigenic trisaccharide **17**. Reagents and conditions: (a) Pd[P(C_6H_5)$_3$]$_4$, P(C_6H_5)$_3$, Et_3N, THF, rt then Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 73% for 2 steps; (b) AllocCl, pyridine, CH_2Cl_2, −15 °C, 89%; (c) BzCl, pyridine; (d) MeOH, THF, NH_3; (e) Cl_3CCN, DBU, CH_2Cl_2, 0 °C, 62% from **8**; (f) TMSOTf, CH_2Cl_2, rt, 67% for **12**; (g) Pd[P(C_6H_5)$_3$]$_4$, P(C_6H_5)$_3$, Et_3N, THF, rt, 69%; (h) 0.3% CH_3COCl–MeOH, 71% for two steps; (i) Ac_2O–pyridine, 88%; (j) Zn, THF–Ac_2O–HOAc (3:2:1); then NaOMe, MeOH, 56%.

1.2. General procedure for the preparation of the triflates 2a–e

A 100-mL two-neck round-bottom flask equipped with two addition funnels was charged with pyridine (0.90 mL, 11 mmol) and dry CH_2Cl_2 (40 mL). A solution of triflic anhydride (1.65 mL, 10.0 mmol) in dry CH_2Cl_2 (10 mL) was placed in a funnel and a solution of **1a–e** (5.0 mmol) in dry CH_2Cl_2 (20 mL) was placed in the other funnel. The flask was cooled to −15 °C in an ice-salt-acetone bath and the triflic anhydride solution was added dropwise. A thick white precipitate began to form during the addition. After addition was complete, the suspension was allowed to stir for an additional 10 min. The sugar solution was added dropwise and stirring continued for an additional 0.5 h. The reaction mixture was poured into 50 mL of ice-water; the aqueous layer was extracted with two 30 mL portions of CH_2Cl_2. The combined organic layer and extracts were dried over Na_2SO_4 and the solution was concentrated under diminished pressure to give a residue, which was subjected to silica gel column chromatography (8:1–10:1 petroleum ether–EtOAc, containing 0.5% Et_3N) to give the desired triflates in almost quantitative yield.

1.3. 3-*O*-Allyl-1-*O*-ethyloxycarbonyl-4,6-*O*-isopropylidene-2-*O*-trifluoromethanesulfonyl-β-D-glucopyranose (2a)

2.15 g (96%), syrup. $[\alpha]_D^{25}$ +27.2 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 5.95–5.87 (m, 1H, CH_2=C*H*–CH_2O), 5.63 (d, 1H, *J* = 8.2 Hz, H-1), 5.31–5.20 (m, 2H, C*H*$_2$=CH–CH_2O), 4.66 (dd, *J* = 8.2, 8.8 Hz, 1H, H-2), 4.40–4.15 (m, 4H, CH_2=CH–C*H*$_2$O, CH_3C*H*$_2$O), 3.98 (dd, 1H, *J* = 5.4, 10.9 Hz, H-6a), 3.80–3.66 (m, 3H, H-3, H-4, H-6b), 3.46–3.73 (m, 1H, H-5), 1.50, 1.43 (2s, 6H, $\mathit{Me}_2\mathrm{C}$), 1.30 (t, 3H, 7.14, $\mathrm{C\mathit{H}_3CH_2}$). Anal. Calcd for $C_{16}H_{23}F_3O_{10}S$: C, 41.38; H, 4.99. Found: C, 41.19; H, 5.02.

1.4. 1-*O*-Allyloxycarbonyl-3-*O*-benzoyl-4,6-*O*-isopropylidene-2-*O*-trifluoromethanesulfonyl-β-D-glucopyranose (2b)

2.54 g (94%), white solid. $[\alpha]_D^{25}$ +7.8 (*c* 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.08–7.44 (m, 5H, Bz-*H*), 5.97–5.88 (m, 1H, $\mathrm{CH_2{=}C\mathit{H}{-}CH_2OCO}$), 5.78 (d, 1H, $J = 8.1$ Hz, H-1), 5.66 (dd, 1H, $J = 9.5$ Hz, H-3), 5.42–5.29 (m, 2H, $\mathrm{C\mathit{H}_2{=}CH{-}CH_2OCO}$), 4.97 (dd, 1H, $J = 8.1$, 9.5 Hz, H-2), 4.73–4.69 (m, 2H, $\mathrm{C\mathit{H}_2{=}CH{-}C\mathit{H}_2OCO}$), 4.07–3.65 (m, 3H, H-4, H-6a, H-6b), 3.63 (m, 1H, H-5), 1.45, 1.36 (2s, 6H, $\mathit{Me}_2\mathrm{C}$). Anal. Calcd for $C_{21}H_{23}F_3O_{11}S$: C, 46.67; H, 4.29. Found: C, 46.55; H, 4.46.

1.5. 3-*O*-Allyl-1-*O*-allyloxycarbonyl-4,6-*O*-isopropylidene-2-*O*-trifluoromethanesulfonyl-β-D-glucopyranose (2c)

2.26 g (95%), colorless oil. $[\alpha]_D^{25}$ +19.6 (*c* 1.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.96–5.86 (m, 2H, $\mathrm{CH_2{=}C\mathit{H}{-}CH_2O}$, $\mathrm{CH_2{=}C\mathit{H}{-}CH_2OCO}$), 5.66 (d, 1H, $J = 8.2$ Hz, H-1), 5.41–5.20 (m, 4H, $\mathrm{CH_2{=}CH{-}CH_2O}$, $\mathrm{CH_2{=}CH{-}CH_2OCO}$), 4.71–4.67 (m, 3H, $\mathrm{CH_2{=}CH{-}C\mathit{H}_2OCO}$, H-2), 4.40–4.10 (m, 2H, $\mathrm{CH_2{=}CH{-}CH_2O}$), 3.97 (dd, 1H, $J = 5.4$, 10.9 Hz, H-6a), 3.80–3.61 (m, 3H, H-3, H-4, H-6b), 3.42 (m, 1H, H-5), 1.50, 1.43 (2s, 6H, $\mathit{Me}_2\mathrm{C}$). Anal. Calcd for $C_{17}H_{23}F_3O_{10}S$: C, 42.86; H, 4.87. Found: C, 42.90; H, 5.00.

1.6. 3-*O*-Benzyl-1-*O*-ethoxycarbonyl-4,6-*O*-isopropylidene-2-*O*-trifluoromethanesulfonyl-β-D-glucopyranose (2d)

2.40 g (93%), white solid. $[\alpha]_D^{25}$ +9.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36–7.25 (m, 5H, Ar-*H*), 5.66 (d, 1H, $J = 8.2$ Hz, H-1), 4.86–4.69 (m, 3H, $\mathrm{PhC\mathit{H}_2}$, H-2), 4.32–4.21 (m, 2H, $\mathrm{CH_3C\mathit{H}_2OCO}$), 3.99 (dd, 1H, $J = 5.4$, 10.9 Hz, H-6a), 3.82–3.73 (m, 3H, H-3, H-4, H-6b), 3.43 (m, 1H, H-5), 1.48, 1.43 (2s, 6H, $\mathit{Me}_2\mathrm{C}$), 1.32 (t, 3H, $J = 7.1$ Hz, $\mathrm{C\mathit{H}_3CH_2OCO}$). Anal. Calcd for $C_{20}H_{25}F_3O_{10}S$: C, 46.69; H, 4.90. Found: C, 46.33; H, 4.66.

1.7. 1-*O*-Allyloxycarbonyl-3-*O*-benzyl-4,6-*O*-isopropylidene-2-*O*-trifluoromethanesulfonyl-β-D-glucopyranose (2e)

2.50 g (95%), white solid. $[\alpha]_D^{25}$ +3.9 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.39–7.32 (m, 5H, Ar-*H*), 5.92–5.86 (m, 1H, $\mathrm{CH_2{=}C\mathit{H}{-}CH_2OCO}$), 5.65 (d, 1H, $J = 8.2$ Hz, H-1), 5.40–5.28 (m, 2H, $\mathrm{C\mathit{H}_2{=}CH{-}CH_2OCO}$), 4.86–4.66 (m, 5H, H-2, $\mathrm{PhC\mathit{H}_2}$, $\mathrm{CH_2{=}CH{-}C\mathit{H}_2OCO}$), 3.95 (dd, 1H, $J = 5.4$, 10.9 Hz, H-6a), 4.07–3.65 (m, 3H, H-3, H-4, H-6b), 3.44 (m, 1H, H-5), 1.47, 1.44 (2s, 6H, $\mathit{Me}_2\mathrm{C}$). Anal. Calcd for $C_{21}H_{25}F_3O_{10}S$: C, 47.91; H, 4.79. Found: C, 48.16; H, 5.04.

1.8. General procedure for the preparation of azides 3a–e

A mixture of **2a–e** (2.50 mmol) and NaN_3 (0.81 g, 12.5 mmol) in dry DMF (15 mL, containing four drops of Et_3N) was stirred under N_2 atmosphere at 70 °C for 4 h, at which time TLC (8:1–10:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with satd aq $NaHCO_3$, and the organic layer was dried over Na_2SO_4. The solution was concentrated under diminished pressure, and the residue was purified by column chromatography on a silica gel column (8:1–10:1 petroleum ether–EtOAc) to give **3a–e**.

1.9. 3-*O*-Allyl-2-azido-2-deoxy-1-*O*-ethyloxycarbonyl-4,6-*O*-isopropylidene-β-D-mannopyranose (3a)

740 mg (83%), white solid. $[\alpha]_D^{25}$ +68.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.92–5.86 (m, 1H, $\mathrm{CH_2{=}C\mathit{H}{-}CH_2O}$), 5.59 (d, 1H, $J = 1.6$ Hz, H-1), 5.37–5.20 (m, 2H, $\mathrm{C\mathit{H}_2{=}CH{-}CH_2O}$), 4.31–3.80 (m, 8H), 3.67–3.63 (m, 1H, H-6b), 3.33–3.23 (m, 1H, H-5), 1.55, 1.41 (2s, 6H, $\mathit{Me}_2\mathrm{C}$), 1.28 (t, 3H, $J = 7.2$ Hz, $\mathrm{\mathit{CH}_3CH_2}$). Anal. Calcd for $C_{15}H_{23}N_3O_7$: C, 50.41; H, 6.49; N, 11.76. Found: C, 50.58; H, 6.35; N, 11.26.

1.10. 1-*O*-Allyloxycarbonyl-2-azido-3-*O*-benzoyl-2-deoxy-4,6-*O*-isopropylidene-β-D-mannopyranose (3b)

640 mg (59%), white solid. $[\alpha]_D^{25}$ +9.3 (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.11–7.45 (m, 5H, Bz-*H*), 5.98–5.89 (m, 1H, $\mathrm{CH_2{=}C\mathit{H}{-}CH_2OCO}$), 5.79 (d, 1H, $J = 1.5$ Hz, H-1), 5.42–5.25 (m, 3H, $\mathrm{C\mathit{H}_2{=}CH{-}CH_2OCO}$, H-3), 4.70–4.68 (m, 2H, $\mathrm{CH_2{=}CH{-}C\mathit{H}_2OCO}$), 4.38 (dd, 1H, $J = 1.5$, 3.7 Hz, H-2), 4.16 (dd, 1H, *J* 9.7, 9.7 Hz, H-4), 4.01–3.84 (m, 2H, H-6), 3.49 (m, 1H, H-5), 1.53, 1.37 (2s, 6H, $\mathit{Me}_2\mathrm{C}$). Anal. Calcd for $C_{20}H_{23}N_3O_8$: C, 55.42; H, 5.35; N, 9.70. Found: C, 55.76; H, 5.40; N, 9.47.

1.11. 3-*O*-Allyl-1-*O*-allyloxycarbonyl-2-azido-2-deoxy-4,6-*O*-isopropylidene-β-D-mannopyranose (3c)

670 mg (73%), colorless oil. $[\alpha]_D^{25}$ −5.7 (*c* 1.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.97–5.87 (m, 2H, $\mathrm{CH_2{=}C\mathit{H}{-}CH_2O}$, $\mathrm{CH_2{=}C\mathit{H}{-}CH_2OCO}$), 5.59 (d, 1H, $J = 1.6$ Hz, H-1), 5.42–5.20 (m, 4H, $\mathrm{C\mathit{H}_2{=}CH{-}CH_2O}$, $\mathrm{C\mathit{H}_2{=}CH{-}CH_2OCO}$), 4.69–4.67 (m, 2H, $\mathrm{CH_2{=}CH{-}C\mathit{H}_2OCO}$), 4.30–4.12 (m, 2H, $\mathrm{CH_2{=}CH{-}C\mathit{H}_2O}$), 4.10 (dd, 1H, $J = 1.5$, 3.6 Hz, H-2), 4.010–3.33 (m, 4H, H-3, H-4, H-6), 3.30 (m, 1H, H-5), 1.52, 1.41 (2s, 6H, $\mathit{Me}_2\mathrm{C}$). Anal. Calcd for $C_{16}H_{23}N_3O_7$: C, 52.03; H, 6.28; N, 11.38. Found: C, 52.29; H, 6.36; N, 11.51.

1.12. 2-Azido-3-*O*-benzyl-2-deoxy-1-*O*-ethoxycarbonyl-4,6-*O*-isopropylidene-β-D-mannopyranose (3d)

860 mg (84%), white solid. $[\alpha]_D^{25}$ −17.0 (*c* 2.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): *δ* 7.39–7.28 (m, 5H, Ar-*H*), 5.52 (d, 1H, *J* = 1.6 Hz, H-1), 4.88 (d, 1H, *J* = 12.3, PhC*H*$_2$), 4.71 (d, 1H, *J* = 12.3, PhC*H*$_2$), 4.23 (m, 2H, CH_3C*H*$_2$OCO), 4.06 (d, 1H, *J* = 9.5, H-4), 3.98 (dd, 1H, *J* = 1.6, 3.4 Hz, H-2), 3.94–3.77 (m, 2H, H-6), 3.66 (dd, 1H, *J* = 3.4, 9.5 Hz, H-3), 3.26 (m, 1H, H-5), 1.51, 1.41 (2s, 6H, *Me*$_2$C), 1.30 (t, 3H, *J* = 7.2 Hz, C*H*$_3$$CH_2$OCO). Anal. Calcd for $C_{19}H_{25}N_3O_7$: C, 56.01; H, 6.18; N, 10.31. Found: C, 56.05; H, 6.46; N, 10.19.

1.13. 1-*O*-Allyloxycarbonyl-2-azido-3-*O*-benzyl-2-deoxy-4,6-*O*-isopropylidene-β-D-mannopyranose (3e)

840 mg (80%), white solid. $[\alpha]_D^{25}$ +10.2 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): *δ* 7.38–7.28 (m, 5H, Ar-*H*), 5.98–5.87 (m, 1H, CH_2=C*H*–CH_2OCO), 5.53 (d, 1H, *J* = 1.5 Hz, H-1), 5.41–5.21 (m, 2H, C*H*$_2$=CH–CH_2O-CO), 4.89 (d, 1H, *J* = 12.2 Hz, PhC*H*$_2$), 4.73 (d, 1H, *J* = 12.2 Hz, PhC*H*$_2$), 4.70–4.65 (m, 2H, CH_2=CH–C*H*$_2$OCO), 4.06 (dd, 1H, *J* = 9.5, 9.5 Hz, H-4), 3.98 (dd, 1H, *J* = 9.5 Hz, H-4), 3.95 (dd, 1H, *J* = 1.5, 3.6 Hz, H-2), 3.94–3.79 (m, 2H, H-6), 3.67 (dd, 1H, *J* = 3.6, 9.5 Hz, H-3), 3.26 (m, 1H, H-5), 1.55, 1.51 (2s, 6H, *Me*$_2$C). Anal. Calcd for $C_{20}H_{25}N_3O_7$: C, 57.27; H, 6.01; N, 10.02. Found: C, 57.50; H, 5.88; N, 9.89.

1.14. 2-Azido-3-*O*-benzoyl-2-deoxy-4,6-*O*-isopropylidene-α-D-mannopyranosyl trichloroacetimidate (5)

A solution of the allyloxycarbonate **3b** (600 mg, 1.4 mmol) and Et_3N (0.39 mL, 2.77 mmol) in THF (10 mL) was mixed with PPh_3 (110 mg 0.42 mmol) and $Pd[P(C_6H_5)_3]_4$ (80 mg, 0.07 mmol), and the mixture was stirred at 25 °C until TLC (6:1 petroleum ether–EtOAc) indicated the completion of the reaction. The reaction mixture was concentrated under diminished pressure and the residue was purified by flash chromatography on a silica gel column (7:1 petroleum ether–EtOAc) to give the deallyloxycarbonation product as a white solid. This solid was dried under high vacuum for 4 h and then was dissolved in CH_2Cl_2 (10 mL). Under N_2 atmosphere, CCl_3CN (0.5 mL, 5 mmol) and DBU (70 μL, 0.5 mmol) were added, the mixture was stirred for 2 h, at which time TLC (6:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated under diminished pressure to give a residue that was purified on a silica gel column with 8:1 petroleum ether–EtOAc as the eluent to give the desired compound (500 mg, 73%) as a foamy solid: $[\alpha]_D^{25}$ +100.0 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): *δ* 8.7 (s, 1H, $CNHCCl_3$), 8.11–7.45 (m, 5H, Bz-*H*), 6.26 (d, 1H, *J* = 1.6 Hz, H-1), 5.63 (dd, 1H, *J* = 3.9, 10.1 Hz, H-3), 4.46 (dd, 1H, *J* = 1.6, 3.9 Hz, H-2), 4.33 (dd, 1H, *J* = 10.1, 10.1 Hz, H-4), 4.04–3.82 (m, 3H, H-5, H-6), 1.56, 1.39 (2s, 6H, *Me*$_2$C). Anal. Calcd for $C_{18}H_{19}Cl_3N_4O_6$: C, 43.79; H, 3.88; N, 11.35. Found: C, 43.53; H, 3.67; N, 11.62.

1.15. 4-Methoxylphenyl 3-*O*-allyloxycarbonyl-4-*O*-benzoyl-α-L-rhamnopyranoside (7)

Compound **6** (3.74 g, 10 mmol) was dissolved in dry CH_2Cl_2 (40 mL) containing pyridine (8.1 mL, 100 mmol), then under N_2 atmosphere, allyl chloroformate (1.2 mL, 11 mmol) in anhyd CH_2Cl_2 (10 mL) was added dropwise to the solution over 30 min at 0 °C. The reaction mixture was slowly raised to room temperature and stirred for 2 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was diluted with CH_2Cl_2 (100 mL), washed with water, 1 M HCl, and dried (Na_2SO_4). The solution was concentrated, and purification of the residue by column chromatography on silica gel (3:1 petroleum ether–EtOAc) gave compound **7** (4.21 g, 92%) as a syrup; $[\alpha]_D^{25}$ −50.3 (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): *δ* 8.05–7.41 (m, 5H, Bz-*H*), 7.07–6.83 (m, 4H, Ar-*H*), 5.76–5.67 (m, 1H, CH_2=C*H*–CH_2OCO), 5.54–5.47 (m, 3H, H-1, H-3, H-4), 5.21–5.04 (m, 2H, C*H*$_2$=CH–CH_2OCO), 4.51–4.48 (m, 2H, CH_2=CH–C*H*$_2$OCO), 4.38 (dd, 1H, *J* = 0.5, 2.7 Hz, H-2), 4.13 (m, 1H, H-5), 3.77 (s, 3H, C*H*$_3$O), 1.25 (d, 3H, *J* = 6.3 Hz, H-6). Anal. Calcd for $C_{24}H_{26}O_9$: C, 62.88; H, 5.72. Found: C, 63.03; H, 5.66.

1.16. 2-Azido-3,4,6-tri-*O*-benzoyl-2-deoxy-α,β-D-glucopyranosyl trichloroacetimidate (11)

To a solution of 2-azido-2-deoxy-α,β-D-glucopyranose **8** (6.20 g, 30 mmol) in pyridine (100 mL) was added benzoyl chloride (21 mL, 180 mmol) at −5 °C. The reaction mixture was slowly warmed to room temperature and stirred for 12 h, at which time TLC (4:1 petroleum ether–EtOAc) indicated that the reaction was complete. Water (300 mL) was added to the reaction mixture, and stirring was continued for 30 min. The aq solution was extracted with CH_2Cl_2 (3 × 100 mL), the combined extracts were washed with 1 M HCl and satd aq $NaHCO_3$, dried (Na_2SO_4), and concentrated to give **9** (18.1 g, 97%) as a white solid. Compound **9** (15.54 g, 25.0 mmol) was dissolved in a 2 M solution of ammonia–MeOH (200 mL) and stirred for 4 h, at which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The solution was concentrated, and purification of the residue by flash chromatography on a silica gel column (3:1 petroleum ether–EtOAc) gave compound **10** (10.5 g, 81%) as a syrup. A mixture of

10 (10.3 g, 20 mmol), trichloroacetonitrile (8.0 mL, 80 mmol), and 1,8-diazabicyclo[5.4.0]undecene (DBU) (0.50 mL, 4.04 mmol) in dry CH_2Cl_2 (50 mL) was stirred under N_2 atmosphere for 5 h and then concentrated in vacuo. The residue was purified by flash chromatography (4:1 petroleum ether–EtOAc) to give **11** (10.5 g, 79%) as a foamy solid; $[\alpha]_D^{25}$ +31.3 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.7 (2s, 1H, α,β-CN*H*CCl_3), 8.00–7.31 (m, 15H, Bz-*H*), 6.63 (d, 0.17H, *J* = 3.6 Hz, α-H-1), 6.11 (dd, 0.17H, *J* = 9.7, 9.7 Hz, α-H-3), 5.96 (d, 0.83 H, *J* = 8.3, β-H-1), 5.69–5.59 (m, 1.83 H, β-H-3, α, β-H-4), 4.62–4.45 (m, 2H), 4.23–4.06 (m, 2 H). Anal. Calcd for $C_{29}H_{23}Cl_3N_4O_8$: C, 52.62; H, 3.50; N, 8.46. Found: C, 52.58; H, 3.71; N, 8.60.

1.17. 4-Methoxylphenyl 2-azido-3,4,6-tri-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl-(1→2)-3-*O*-allyloxycarbonyl-4-*O*-benzoyl-α-L-rhamnopyranoside (12)

Compounds **7** (275 mg, 0.60 mmol) and **11** (437 mg, 0.66 mmol) were dried together under high vacuum for 4 h, then dissolved in anhyd CH_2Cl_2 (10 mL). TMSOTf (7.0 μL, 0.04 mmol) was added at 25 °C under a N_2 atmosphere. The reaction mixture was stirred for 2 h, neutralized with Et_3N, concentrated to dryness under diminished pressure, and the residue was purified by flash chromatography (4:1 petroleum ether–EtOAc) to give **12** (380 mg, 66%) as a syrup; $[\alpha]_D^{25}$ −30.7 (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.08–7.36 (m, 20H, Bz-*H*), 7.01–6.84 (m, 4H, Ar-*H*), 6.04 (dd, 1H, *J* = 9.4, 10.7 Hz), 5.77–5.59 (m, 4H), 5.55 (d, 1H, *J* = 1.3 Hz, H-1), 5.21 (d, 1H, *J* = 3.8 Hz, H-1′), 5.15–4.92 (m, 2H, C*H*$_2$=CH–CH_2OCO), 4.80–4.76 (m, 1H, CH_2=CH–C*H*HOCO), 4.63 (dd, 1H, *J* = 2.7, 12.7 Hz), 4.48–4.41 (m, 3H), 4.31 (dd, 1H, *J* = 3.7, 12.6 Hz), 4.15 (m, 1H, H-5), 3.78 (s, 3H, C*H*$_3$O), 3.49 (dd, 1H, *J* = 3.8, 10.6 Hz), 1.34 (d, 3H, *J* = 6.2 Hz, H-6). Anal. Calcd for $C_{51}H_{47}N_3O_{16}$: C, 63.94; H, 4.95; N, 4.39. Found: C, 63.83; H, 5.10; N, 4.54.

1.18. 4-Methoxylphenyl 2-azido-3,4,6-tri-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl-(1→2)-4-*O*-benzoyl-α-L-rhamnopyranoside (13)

A solution of compound **12** (770 mg, 0.8 mmol) and Et_3N (0.22 mL, 1.6 mmol) in THF (15 mL) was mixed with PPh_3 (63 mg, 0.24 mmol) and $Pd[P(C_6H_5)_3]_4$ (46 mg, 0.04 mmol) and the mixture was stirred at 25 °C until TLC (2:1 petroleum ether–EtOAc) indicated the completion of the reaction. The reaction mixture was concentrated under diminished pressure, and the residue was purified by flash chromatography on a silica gel column (3:1 petroleum ether–EtOAc) to give compound **13** (510 mg, 73%) as a white solid; $[\alpha]_D^{25}$ −11.0 (*c* 1.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.07–7.36 (m, 20H, Bz-*H*), 7.06–6.84 (m, 4H, Ar-*H*), 6.08 (dd, 1H, *J* = 9.4, 10.6 Hz), 5.69 (dd, 1H, *J* = 10.2, 10.2 Hz), 5.59 (d, 1H, *J* = 1.0 Hz, H-1), 5.32 (d, 1H, *J* = 3.8 Hz, H-1′), 5.28 (dd, 1H, *J* = 9.7 Hz), 4.88 (m, 1H), 4.68–4.30 (m, 4H), 4.16 (m, 1H, H-5), 3.78 (s, 3H, C*H*$_3$O), 3.55 (dd, 1H, *J* = 3.7, 10.7 Hz), 1.34 (d, 3H, *J* = 6.2 Hz, H-6); ^{13}C NMR δ 167.1, 166.1, 165.5, 165.4, 155.2, 150.3, 133.4, 133.4, 133.3, 133.0, 129.9, 129.8, 129.8, 129.7, 129.5, 129.5, 129.0, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 97.9, 96.2, 78.1, 75.6, 70.3, 69.6, 69.3, 68.8, 67.2, 62.6, 61.4, 55.6, 29.3, 17.5. Anal. Calcd for $C_{47}H_{43}N_3O_{14}$: C, 64.60; H, 4.96; N, 4.81. Found: C, 64.44; H, 5.08; N, 5.11.

1.19. 4-Methoxylphenyl 2-azido-3-*O*-benzoyl-2-deoxy-α-D-mannopyranosyl-(1→3)-[2-azido-3,4,6-tri-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl-(1→2)-]4-*O*-benzoyl-α-L-rhamnopyranoside (15)

To a cooled solution (0 °C) of **13** (350 mg, 0.4 mmol) and 2-azido-3-*O*-benzoyl-2-deoxy-4,6-*O*-isopropylidene-α-D-mannopyranosyl trichloroacetimidate (**5**) (237 mg, 4.8 mmol) in anhyd CH_2Cl_2 (30 mL) was added TMSOTf (7.2 μL, 0.04 mmol). The mixture was stirred at this temperature for 2 h, then MeOH (30 mL) and CH_3COCl (0.1 mL) were subsequently added to the reaction mixture. The mixture was stirred at room temperature for 6 h, and then concentrated. The residue was purified by silica gel column chromatography to give **15** (340 mg, 73%) as a foamy solid; $[\alpha]_D^{25}$ +19 (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 813–7.15 (m, 25H, Bz-*H*), 7.07–6.84 (m, 4H, Ar-*H*), 6.11 (dd, 1H, *J* = 9.8 Hz), 5.71 (dd, 1H, *J* = 9.9, 9.9 Hz), 5.70 (d, 1H, *J* = 1.9 Hz, H-1), 5.63 (dd, 1H, *J* = 9.5 Hz), 5.46 (dd, 1H, *J* = 3.6, 10.0 Hz), 5.43 (d, 1H, *J* = 2.5 Hz, H-1), 5.15 (d, 1H, *J* = 1.5 Hz, H-1), 5.01 (dd, 1H, *J* = 1.5, 10.8 Hz), 4.72 (m, 1H), 4.57–4.44 (m, 3H), 4.30 (d, 1H, *J* = 1.80, 3.50 Hz, H-2), 4.16–4.02 (m, 2H), 3.89 (m, 1H), 3.71 (m, 1H), 1.33 (d, 3H, *J* = 6.3 Hz, H-6); ^{13}C NMR (characteristic signals given) δ 166.4, 166.2, 165.9, 165.8, 165.5, 155.4, 150.1, 98.3, 97.4, 95.8, 17.6. Anal. Calcd for $C_{60}H_{56}N_6O_{19}$: C, 61.85; H, 4.84, N, 7.21. Found: C, 61.77; H, 4.69; N, 7.53.

1.20. 4-Methoxyphenyl 4,6-di-*O*-acetyl-2-azido-3-*O*-benzoyl-2-deoxy-α-D-mannopyranosyl-(1→3)-[2-azido-3,4,6-tri-*O*-benzoyl-2-deoxy-α-D-glucopyranosyl-(1→2)-]4-*O*-benzoyl-α-L-rhamnopyranoside (16)

To a solution of **15** (312 mg, 0.250 mmol) in pyridine (12 mL) was added Ac_2O (8 mL, 8 mmol). The reaction mixture was stirred at rt for 12 h, at which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The reaction mixture was concentrated, and then the residue was purified by silica gel column chromatography (2:1 petroleum ether–EtOAc) to give compound **16** (283 mg, 88%) as a foamy solid. $[\alpha]_D^{25}$ +16 (*c* 0.3, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 8.13–7.09 (m, 25 H, Bz-*H*), 7.09–6.85 (m, 4H, Ar-*H*), 6.05 (dd, 1H, $J = 9.9$, 9.9 Hz), 5.75 (dd, 1H, $J = 10.0$ Hz), 5.68 (d, 1H, $J = 2.0$ Hz, H-1), 5.60 (dd, 1H, $J = 9.8$ Hz), 5.51–5.39 (m, 2H), 5.25 (d, 1H, $J = 3.4$ Hz, H-1), 5.15 (d, 1H, $J = 1.20$ Hz, H-1), 4.90 (dd, 1H, $J = 2.0$, 10.0 Hz), 4.72 (m, 1H), 4.55–4.46 (m, 3H), 4.39 (d, 1H, $J = 1.20$, 3.40 Hz, H-2), 4.22–4.10 (m, 1H), 4.00–3.90 (m, 2H), 3.79 (s, 3H, OMe), 3.70 (m, 1H), 2.06 (s, 3H, OAc), 1.58 (s, 3H, OAc), 1.27 (d, 3H, $J = 6.4$ Hz, H-6); ^{13}C NMR (characteristic signals given) δ 170.6, 169.4, 165.7, 165.4, 165.3, 165.2, 165.1, 117.7, 114.8, 99.4, 96.9, 95.9, 20.7, 20.3, 17.5. Anal. Calcd for $C_{64}H_{60}N_6O_{21}$: C, 61.53; H, 4.84, N, 6.73. Found: C, 61.70; H, 4.61; N,6.49.

1.21. 4-Methoxyphenyl 2-acetamido-2-deoxy-α-D-mannopyranosyl-(1→3)-[2-acetamido-2-deoxy-α-D-glucopyranosyl-(1→2)-]α-L-rhamnopyranoside (17)

A solution of compound **16** (256 mg, 0.20 mmol) in THF–Ac_2O–acetic acid (8:3:1; 12 mL) was treated with activated zinc powder (activation with 2% $CuSO_4$ in water for 5–10 min). The mixture was stirred for 10 min at room temperature and then was filtered and washed with THF (5 × 1 mL) and acetic acid (5 × 0.5 mL) before being concentrated and co-distilled with toluene (5 × 2 mL) and then with MeOH–toluene (1:3; 5 × 2 mL) in vacuo. The residue was dried under high vacuum for 2 h and then dissolved in absolute MeOH (10 mL). Sodium methoxide (1.0 M, 5 drops) was added and the reaction mixture was stirred for 6 h at room temperature. The solution was neutralized by addition of acetic acid (5 drops), concentrated, and the residue was co-distilled with toluene in vacuo. Purification of the residue by silica gel chromatography on a short column (4:1–3:1 EtOAc–MeOH) gave **17** (76 mg, 56%) as a foamy solid. $[\alpha]_D^{25}$ +33 (*c* 1.0, H_2O); ^1H NMR ($CDCl_3$, 300 MHz) (characteristic signals given): δ 6.99–6.81 (m, 4H, Ar-*H*), 5.36 (d, 1H, $J = 2.3$ Hz, H-1), 5.18 (d, 1H, $J = 3.5$ Hz, H-1), 4.98 (s, 1H, H-1), 3.37 (s, 3H, OMe), 2.02 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.28 (d, 3H, $J = 6.2$ Hz, H-6); ^{13}C NMR (characteristic signals given) δ 174.2, 173.7, 156.7, 151.9, 119.0, 119.0, 115.7, 115.7, 98.4, 97.6, 96.5, 22.8, 22.7, 18.5; MALDI-TOF MS Calcd for $C_{29}H_{44}N_2O_{16}$: 676.27 [M]. Found: 699.43 [M+Na].

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Supplementary data

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