A Very Simple Synthesis of 1-(Ethyl 6-*O*-Acetyl-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranos-4-yl)-1,2,3-triazole Derivatives

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Abstract: The copper-catalyzed reaction of ethyl 4-azido-6-*O*-acetoxy-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranoside with various functionalized alkynes gave the corresponding 1-(ethyl 6-*O*-acetyl-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranos-4-yl)-1,2,3-triazole derivatives in quite good yields, which could be transformed into (ethyl 2,3,6-tri-*O*-acetyl-4-deoxy-α-D-mannopyranosyl)-1*H*-1,2,3-triazole by a simple bis-hydroxylation.

Key words: 1,2,3-triazole based-carbohydrate, hexenopyranoside, cycloaddition, Cu catalyst

Glycoconjugates play important roles in many biological processes,[1–3] including particularly cellular recognition in the case of inflammation,[4–6] tumor metastasis,[7] immune response,[8,9] and bacterial and viral infections.[1] In the course of a project involving the synthesis and biological evaluation of a series of new aminosugars,[10–13] we were attracted by *N*-triazole derivatives of unsaturated carbohydrates where this heterocyclic nucleus is located at C-4 of the pyranosyl structure. Substituted triazoles have been shown to display important biological activity.[14–17] Surprisingly, in view of the ready availability of these potential glycomimetics, the literature reports only a handful examples of *N*-substituted triazole carbohydrates, most of them bearing the triazole structure at the anomeric position.[18–26] Herein, we describe some preliminary results dealing with the synthesis of some 1-(ethyl 6-*O*-acetyl-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranos-4-yl)-1,2,3-triazole derivatives.

We have recently described an easy access to ethyl 4-azido-6-*O*-acetoxy-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranoside (**2**) from unsaturated carbohydrate **1** by reaction of the latter with NaN_3 in the presence of $Pd(PPh_3)_4$ and 1,4-bis(diphenylphosphino)butane (dppb).[27] We expected that this unsaturated azido carbohydrate could be the precursor of the corresponding unsaturated 1,2,3-triazole derivative, which could be synthesized via a copper-catalyzed 1,3-dipolar cycloaddition reaction with the appropriate alkyne.[28,29] It is noteworthy that this copper-catalyzed reaction generally proceeds quantitatively under very mild conditions with very high regioselectivity and high tolerance of functionalities.

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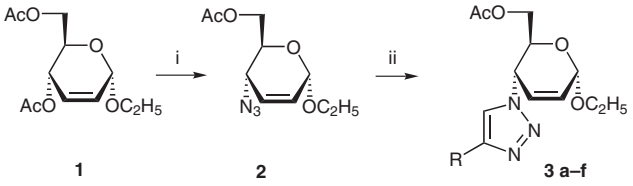
Ethyl 6-*O*-acetyl-4-azido-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranoside (**2**) reacted with ethynylbenzene in a 1:1 mixture of water and *tert*-butyl alcohol in the presence of copper(II) acetate and sodium ascorbate at room temperature to give ethyl 6-*O*-acetyl-2,3,4-trideoxy-4-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-α-D-*erythro*-hex-2-enopyranoside (**3a**) as the sole product in 82% yield after column chromatographical purification (Scheme 1). The regioselectivity of the 1,3-dipolar cycloaddition reaction was explained according to the previous results using this methodology and to the mechanism proposed by Sharpless.[28]

The scope of this copper-catalyzed introduction of the triazole moiety at C-4 of the unsaturated carbohydrate is remarkably efficient and can be used to link a variety of functionalities to this position of monosaccharides. Condensation of azido carbohydrate **2** with propargylic alcohol, methyl propiolate, and but-3-yn-2-one, gave the corresponding triazoles **3b**, **3c**, and **3d**, in 70%, 75%, and 83% yields, respectively, after purification by column chromatography. Reaction of *tert*-butyl prop-2-ynylcarbamate with azido carbohydrate **2** gave the unsaturated triazolylglycoside **3e** in 82% yield, showing the compatibility of the Boc group with the reaction conditions. Moreover, reaction of a racemic mixture of *N*-Boc-propargylglycine methyl ester gave triazole **3f** in 88% yield as a 1:1 mixture of the two epimers.

Condensation of unsaturated azido carbohydrate **2** (2 equiv) with 1,4-diethynylbenzene (1 equiv) afforded also cleanly 4,4′-[(1,4-phenylene)-bis(ethyl 6-*O*-acetyl-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranosyl)]-di-1*H*-1,2,3-triazole (**4**) in 89% yield after column chromatography (Scheme 2). Compound **4** was then subjected to the bis-hydroxylation reaction in the presence of a catalytic amount of OsO_4 and *N*-methylmorpholine-*N*-oxide (NMO). As expected, 4,4′-[(1,4-phenylene)-bis(ethyl 2,3,6-*O*-acetyl-4-deoxy-α-D-mannopyranosyl)]-1*H*-1,2,3-triazole (**5**) was obtained in 86% yield after acetylation of the crude mixture as the unique product. This compound resulted from the bis-hydroxylation on the less hindered side of the double bond, as expected from preceding results in this field.[30,31] The assigned configurations are mainly based on the coupling constants $J_{4,5}$ = 10.6 Hz and $J_{3,4}$ = 10.9 Hz, which are characteristic for axial–axial coupling of H-4/H-5 and H-3/H-4.

Copper-catalyzed [3+2] cycloaddition of ethyl 4-azido-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranoside (**2**) with various functionalized alkynes afforded the corresponding 1-(ethyl 2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranos-4-yl)-1,2,3-triazole derivatives **3a–f** in quite good yields. Bis-hydroxylation of these intermediates gave the corresponding (4-deoxy-α-D-mannopyranosyl)]-1*H*-1,2,3-triazole.



a: R = C_6H_5 (82% yield)
b: R = C_6H_4Br (67% yield)
c: R = CO_2Me (75% yield)
d: R = $COCH_3$ (83% yield)
e: R = CH_2NHBoc (82% yield)
f: R = (*R*,*S*)-$CH_2CH(CO_2Et)NHBoc$ (88% yield)

Scheme 1 *Reagents and conditions:* i) NaN_3, cat. $Pd(PPh_3)_4$ + dppb, THF, 25 °C; ii) R–C≡C–H, H_2O–*tert*-BuOH (1:1), $Cu(OAc)_2$ (20 mol%), and sodium ascorbate (40 mol%)

All commercially available reagents were used as received. All reactions were monitored by TLC analysis (TLC plates GF_{254}, Merck). Air- and moisture-sensitive reactions were performed with inert-atmosphere techniques. Melting points were determined on a Büchi apparatus and are uncorrected. Column chromatography was performed on silica gel 60 (230–240 mesh, Merck). Optical rotations were recorded using a Perkin-Elmer 241 polarimeter. NMR spectra were recorded with a Bruker AMX 300 spectrometer and were referenced as follows: ^1H (300 MHz), internal standard $SiMe_4$ at δ = 0.00 ppm, ^{13}C (75 MHz), internal standard $CDCl_3$ at δ = 77.23 ppm. Ethyl 4-azido-6-*O*-acetoxy-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranoside (**2**)[27] and racemic *N*-Boc-propargylglycine methyl ester[32] were prepared according to the literature. Hexanes used have bp 40–65 °C.

Preparation of 1,4-Disubstituted 1,2,3-Triazoles (3); General Procedure

4-Azido sugar **2** (241 mg, 1.05 mmol) and alkyne derivative (3 mmol) were suspended in *tert*-BuOH–H_2O (1:1, 4 mL). To this solution was added a mixture of $Cu(OAc)_2$ (36 mg, 0.20 mmol) and sodium ascorbate (79.5 mg, 0.401 mmol) in *tert*-BuOH–H_2O (1:1, 1 mL). The contents were stirred overnight under N_2 at r.t. When TLC analysis indicated complete consumption of the product, H_2O (3 mL) was added and the product was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave a residue that was purified by column chromatography (hexanes–EtOAc, ratios as specified below) to give compounds **3**.

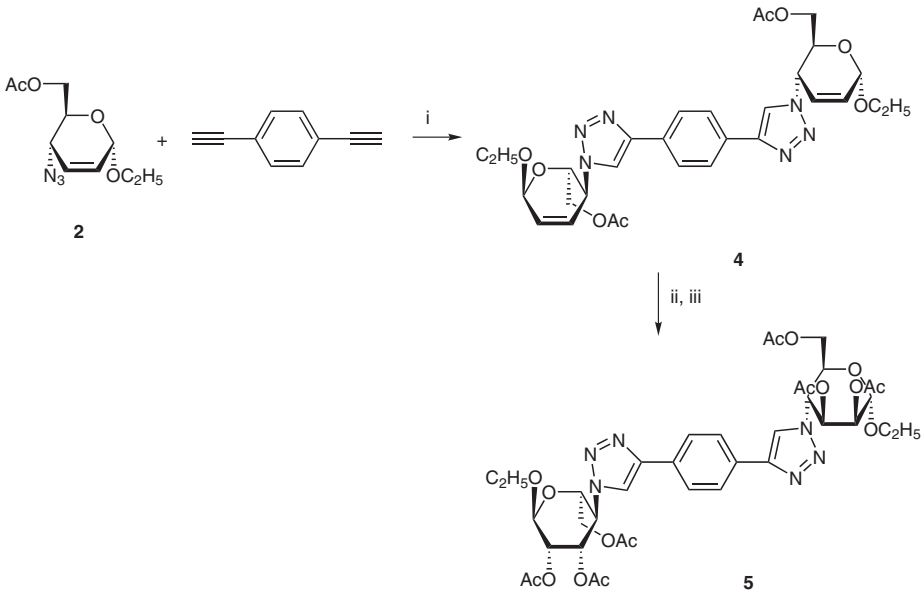
Ethyl 6-*O*-Acetyl-2,3,4-trideoxy-4-(4-phenyl-1*H*-1,2,3-triazol-1-yl]-α-D-*erythro*-hex-2-enopyranoside (3a)

Colorless oil; yield: 295 mg (82%); R_f = 0.3 (hexanes–EtOAc, 7:3); $[\alpha]_D^{20}$ +169 (*c* 2.0, CH_2Cl_2).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.1 Hz, 3 H, CH_3,), 2.08 (s, 3 H, CH_3CO), 3.67 (dq, *J* = 9.7, 7.1 Hz, 1 H, OCH_2CH_3), 3.90 (dq, *J* = 9.7, 7.1 Hz, 1 H, OCH_2CH_3), 4.12 (dd, *J* = 12.2, 5.1 Hz, 1 H, H-6), 4.23 (dd, *J* = 12.2, 2.8 Hz, 1 H, H-6), 4.35 (ddd, *J* = 9.9, 5.1, 2.8 Hz, 1 H, H-5), 5.20 (br s, 1 H, H-1), 5.47 (dd, *J* = 9.9, 1.7 Hz, 1 H, H-4), 6.05 (br d, *J* = 10.0 Hz, 1 H, H-3), 6.40 (ddd, *J* = 10.0, 2.8, 2.8 Hz, 1 H, H-2), 7.36 (dd, *J* = 7.5, 7.5 Hz, 1 H, H_{arom}), 7.43 (dd, *J* = 7.5 Hz, 2 H, H_{arom}), 7.83–7.87 (m, 3 H, H_{arom}, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.7, 21.1, 55.8, 63.3, 65.0, 68.7, 94.4, 118.4, 126.1, 129.3, 127.8, 128.8, 130.0, 130.6, 148.8, 170.8.

Anal. Calcd for $C_{18}H_{21}O_4N_3$: C, 62.96; H, 6.16. Found: C, 62.66; H, 5.98.



Scheme 2 *Reagents and conditions:* i) H_2O–*tert*-BuOH (1:1), $Cu(OAc)_2$ (20 mol%), and sodium ascorbate (40 mol%); ii) cat. OsO_4, NMO, acetone–water, r.t.; iii) Ac_2O, pyridine

Ethyl 6-*O*-Acetyl-[4-(4-bromophenyl)-1*H*-1,2,3-triazol -1-yl]-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranoside (3b)
Colorless oil; yield: 297 mg (67%); R_f = 0.4 (hexanes–EtOAc, 6:4); $[\alpha]_D^{20}$ +154.6 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.06 (s, 3 H, CH_3CO), 3.64 (dq, *J* = 9.7, 7.1 Hz, 1 H, OCH_2CH_3), 3.87 (dq, *J* = 9.7, 7.1 Hz, 1 H, OCH_2CH_3), 4.09 (dd, *J* = 12.2, 5.1 Hz, 1 H, H-6), 4.22 (dd, *J* = 12.2, 2.9 Hz, 1 H, H-6), 4.32 (ddd, *J* = 10.0, 5.1, 2.9 Hz, 1 H, H-5), 5.18 (br s, 1 H, H-1), 5.44 (br dd, *J* = 10.0, 1.7 Hz, 1 H, H-4), 6.01 (br d, *J* = 10.2 Hz, 1 H, H-3), 6.13 (ddd, *J* = 10.2, 2.8, 2.8, Hz, 1 H, H-2), 7.55 (d, *J* = 8.5 Hz, 2 H, H_{arom}), 7.70 (d, *J* = 8.5 Hz, 2 H, H_{arom}), 7.84 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.7, 21.1, 55.8, 63.2, 65.1, 68.7, 94.4, 118.5, 122.7, 127.6, 130.1, 127.6, 132.4, 129.6, 129.6, 147.8, 170.8.

Anal. Calcd for $C_{18}H_{20}O_4N_3Br$: C, 51.20; H, 4.77. Found: C, 51.26; H, 4.95.

Ethyl 6-*O*-Acetyl-2,3,4-trideoxy-4-(4-methoxycarbonyl-1*H*-1,2,3-triazol-1-yl)-α-D-*erythro*-hex-2-enopyranoside (3c)
Colorless oil; yield: 256 mg (75%); R_f = 0.2 (hexanes–EtOAc, 6:4); $[\alpha]_D^{20}$ +101.5 (*c* 1.3, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.06 (s, 3 H, CH_3CO), 3.63 (dq, *J* = 9.7, 7.1 Hz, 1 H, OCH_2CH_3), 3.85 (dq, *J* = 9.7, 7.1 Hz, 1 H, OCH_2CH_3), 3.96 (s, 3 H, OCH_3), 4.04 (dd, *J* = 12.2, 5.0 Hz, 1 H, H-6), 4.20 (dd, *J* = 12.2, 3.0 Hz, 1 H, H-6), 4.30 (ddd, *J* = 9.8, 5.0, 3.0 Hz, 1 H, H-5), 5.17 (br s, 1 H, H-1), 5.45 (dd, *J* = 9.8, 1.5 Hz, 1 H, H-4), 5.95 (br d, *J* = 10.2 Hz, 1 H, H-3), 6.1 (ddd, *J* = 10.2, 2.8, 2.8 Hz, 1 H, H-2), 8.18 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.6, 21.0, 52.7, 56.1, 63.0, 65.1, 68.7, 94.3, 126.7, 126.8, 130.6, 140.9, 161.2, 170.7.

Anal. Calcd for $C_{14}H_{19}O_6N_3$: C, 51.69; H, 5.89. Found: C, 52.26; H, 6.28.

Ethyl 6-*O*-Acetyl-4-(4-acetyl-1*H*-1,2,3-triazol-1-yl)-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranoside (3d)
White solid; yield: 269 mg (83%); mp 65–66 °C; R_f = 0.4 (hexanes–EtOAc, 1:1); $[\alpha]_D^{20}$ +118.0 (*c* 1.7, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.2 Hz, 3 H, CH_3), 2.07 (s, 3 H, CH_3CO), 2.69 (s, 3 H, CH_3CO), 3.60 (dq, *J* = 9.7, 7.2 Hz, 1 H, OCH_2CH_3), 3.80 (dq, *J* = 9.7, 7.2 Hz, 1 H, OCH_2CH_3), 4.04 (dd, *J* = 12.3, 5.0 Hz, 1 H, H-6), 4.19 (dd, *J* = 12.3, 2.8 Hz, 1 H, H-6), 4.29 (ddd, *J* = 9.9, 5.0, 2.8 Hz, 1 H, H-5), 5.17 (br s, 1 H, H-1), 5.43 (ddd, *J* = 9.9, 3.6, 1.9 Hz, 1 H, H-4), 5.94 (br d, *J* = 10.0 Hz, 1 H, H-3), 6.13 (ddd, *J* = 10.0, 2.6, 2.6 Hz, 1 H, H-2), 8.15 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.6, 21.0, 27.6, 55.9, 63.0, 65.1, 68.8, 94.4, 124.5, 126.7, 130.6, 148.9, 170.7, 193.0.

Anal. Calcd for $C_{14}H_{19}O_5N_3$: C, 54.36; H, 6.19. Found: C, 54.57; H, 6.09.

Ethyl 6-*O*-Acetyl-2,3,4-trideoxy-4-[4-*N*-(*tert*-butoxycarbonyl)methyl-1*H*-1,2,3-triazol-1-yl]-α-D-*erythro*-hex-2-enopyranoside (3e)
Colorless oil; yield: 341 mg (82%); R_f = 0.4 (hexanes–EtOAc, 3:7); $[\alpha]_D^{20}$ +86.8 (*c* 2.2, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.45 (s, 9 H, Me_3Si), 2.07 (s, 3 H, CH_3CO), 3.62 (dq, *J* = 9.8, 7.1 Hz, 1 H, OCH_2CH_3), 3.85 (dq, *J* = 9.8, 7.1 Hz, 1 H, OCH_2CH_3), 4.01 (dd, *J* = 12.2, 5.1 Hz, 1 H, H-6), 4.16 (dd, *J* = 12.2, 2.6 Hz, 1 H, H-6), 4.28 (ddd, *J* = 9.9, 5.1, 2.6 Hz, 1 H, H-5), 4.40 (d, *J* = 5.8 Hz, 2 H, CH_2N), 5.15 (br s, 2 H, H-1, NH), 5.37 (dd, *J* = 9.9, 1.7 Hz, 1 H, H-4), 5.94 (br d, *J* = 10.1 Hz, 1 H, H-3), 6.07 (ddd, *J* = 10.1, 2.6, 2.6 Hz, 1 H, H-2), 7.57 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.6, 21.1, 28.8, 36.5, 55.6, 63.1, 65.0, 68.6, 80.2, 94.4, 120.8, 127.6, 129.9, 146.5, 156.2, 170.8.

Anal. Calcd for $C_{18}H_{28}O_6N_4$: C, 54.53; H, 7.12. Found: C, 54.36; H, 7.16.

Ethyl 6-*O*-Acetyl-2,3,4-trideoxy-4-[4-(*R*,*S*)-*tert*-butyloxycarbonyl)-2-amino-2-ethoxycarbonylethyl)-1*H*-1,2,3-triazol-1-yl]-α-D-*erythro*-hex-2-enopyranoside (3f)
Colorless oil; yield: 446 mg (88%); R_f = 0.6 (hexanes–EtOAc, 4:6).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.26 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.43 (s, 9 H, Me_3C), 2.07 (s, 3 H, CH_3CO), 3.23 (d, *J* = 5.3 Hz, 2 H, CH_2CH), 3.62 (dq, *J* = 9.7, 7.1 Hz, 1 H, OCH_2CH_3), 3.84 (dq, *J* = 9.7, 7.1 Hz, 1 H, OCH_2CH_3), 3.98 and 4.00 [dd, *J* = 12.2, 5.1 Hz, 1 H, H-6 (*R*) and H-6 (*S*) 1:1], 4.13–4.27 (m, 4 H, OCH_2CH_3, H-5, H-6), 4.58 (br s, 1 H, CH), 5.14 (br s, 1 H, H-1), 5.35 (br d, *J* = 9.8 Hz, 1 H, H-4), 5.48 [d, *J* = 7.7 Hz, 0.5 H, NH (*R*) or (*S*)], 5.53 [d, *J* = 8.1 Hz, 0.5 H, NH (*S*) or (*R*)], 5.92 (br d, *J* = 10.0 Hz, 0.5 H, H-3), 5.94 (br d, *J* = 10.0 Hz, 0.5 H, H-3), 6.06 (ddd, *J* = 10.0, 2.6, 2.6 Hz, 1 H, H-2), 7.43 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5, 15.6, 21.1, 28.7, 29.0, 55.5, 61.9, 63.1, 65.0, 68.7, 80.2, 94.4, 120.9, 127.6, 129.9, 144.1, 155.8, 170.8, 171.7 and 171.8 (*R* and *S*).

Anal. Calcd for $C_{22}H_{34}O_8N_4$: C, 54.76; H, 7.10. Found: C, 54.90; H, 7.26.

4,4′-[(1,4-Phenylene)-bis(ethyl 6-*O*-acetyl-2,3,4-trideoxy-α-D-*erythro*-hex-2-enopyranosyl)]-di-1*H*-1,2,3-triazole (4)
4-Azido carbohydrate **2** (53 mg, 0.22 mmol) and 1,4-diethynylbenzene (13 mg, 0.10 mmol) were suspended in *tert*-BuOH–H_2O (1:1, 2 mL). To this solution was added a mixture of $Cu(OAc)_2$ (8 mg, 0.045 mmol) and sodium ascorbate (18 mg, 0.091 mmol) in *tert*-BuOH–H_2O (1:1) (1 mL). H_2O (3 mL) was added and the product was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried over Na_2SO_4. Evaporation of the organic solvent under reduced pressure gave a mixture that was purified by column chromatography (hexanes–EtOAc, 2:8) to give compound **4**.

White solid; yield: 56 mg (89%); mp 120–123 °C; R_f = 0.6 (hexanes–EtOAc, 2:8); $[\alpha]_D^{20}$ +245 (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (t, *J* = 7.0 Hz, 6 H, CH_3), 2.07 (s, 6 H, CH_3CO), 3.65 (dq, *J* = 9.7, 7.0 Hz, 2 H, OCH_2CH_3), 3.88 (dq, *J* = 9.7, 7.0 Hz, 2 H, OCH_2CH_3), 4.11 (dd, *J* = 12.2, 5.1 Hz, 2 H, H-6), 4.23 (dd, *J* = 12.2, 2.8 Hz, 2 H, H-6), 4.35 (ddd, *J* = 9.9, 5.1, 2.8 Hz, 2 H, H-5), 5.19 (br s, 2 H, H-1), 5.47 (dd, *J* = 9.9, 1.7 Hz, 2 H, H-4), 6.03 (br d, *J* = 10.0 Hz, 2 H, H-3), 6.14 (ddd, *J* = 10.0, 2.8, 2.8 Hz, 2 H, H-2), 7.88 (s, 2 H, H_{triaz}), 7.91 (s, 4 H, H_{arom}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.7, 21.1, 55.8, 63.2, 65.1, 68.8, 94.4, 118.5, 126.6, 127.7, 130.1, 130.6, 148.4, 170.8.

Anal. Calcd for $C_{30}H_{36}O_8N_6$: C, 59.20; H, 5.96. Found: C, 59.11; H, 5.72.

HRMS-FAB: *m*/*z* $[M + H]^+$ calcd for $C_{30}H_{37}O_8N_6$: 609.2673; found: 609.2671.

4,4′-[(1,4-Phenylene)-bis(ethyl 2,3,6-tri-*O*-acetyl-4-deoxy-α-D-mannopyranosyl)]-di-1*H*-1,2,3-triazole (5)
To a solution of 2,3-unsaturated triazole carbohydrate **4** (30 mg, 0.049 mmol) in acetone–H_2O (4:1, 2 mL) was added OsO_4 (0.25 mg, 1.0 μmol, 2 mol%) and NMO (465 mg, 3.97 mmol) at 0 °C. After stirring at r.t. for 20 h, $NaHSO_3$ (25 mg, 0.24 mmol) was added, and the mixture was stirred at r.t. for 30 min. H_2O (2.5 mL) was added, the mixture was extracted with EtOAc (2 × 5 mL), and the or-

ganic layers were dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave a residue that was directly acetylated using Ac_2O (102 mg, 1.00 mmol) in pyridine (2 mL) for 1 d. After removing the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (EtOAc) to afford compound **5**.

White solid; yield: 36 mg (86%); mp 116–118 °C; $R_f = 0.5$ (EtOAc); $[\alpha]_D^{20}$ +57.6 (*c* 1.5, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.0 Hz, 6 H, CH_3), 1.86 (s, 6 H, CH_3CO), 2.04 (s, 6 H, CH_3CO), 2.22 (s, 6 H, CH_3CO), 3.63 (dq, *J* = 9.8, 7.0 Hz, 2 H, OCH_2CH_3), 3.84 (dq, *J* = 9.8, 7.0 Hz, 2 H, OCH_2CH_3), 3.98 (dd, *J* = 12.4, 4.7 Hz, 2 H, H-6), 4.15 (dd, *J* = 12.4, 3.2 Hz, 2 H, H-6), 4.35 (ddd, *J* = 10.6, 4.7, 3.2 Hz, 2 H, H-5), 4.96 (br s, 2 H, H-1), 5.00 (dd, *J* = 10.9, 10.6 Hz, 2 H, H-4), 5.37 (dd, *J* = 3.2, 1.9 Hz, 2 H, H-2), 5.88 (br d, *J* = 10.9 Hz, 2 H, H-3), 7.88 (s, 2 H, H_{triaz}), 7.91 (s, 4 H, H_{arom}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.7, 20.8, 21.0, 21.3, 57.9, 63.0, 64.8, 68.7, 69.0, 69.2, 97.9, 118.5, 126.6, 130.4, 147.8, 169.6, 170.6, 170.7.

Anal. Calcd for $C_{38}H_{48}O_{16}N_6$: C, 54.02; H, 5.73. Found: C, 53.66; H, 5.84.

HRMS-FAB: *m/z* [M + H] $^+$ calcd for $C_{38}H_{48}O_{16}N_6$: 845.3205; found: 845.3209.

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