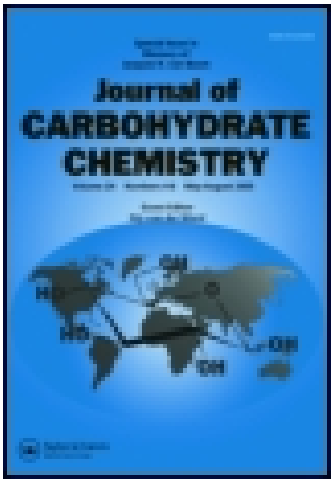

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Glycoside Synthesis with Anomeric 1-N-Glycobiosyl-1,2,3-triazoles[1]

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GLYCOSIDE SYNTHESIS WITH ANOMERIC 1-*N*-GLYCOBIOSYL-1,2,3-TRIAZOLES[1]

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ABSTRACT

1,3-Dipolar cycloaddition of the acetylated 1,2-*trans*- and 1,2-*cis*-cellobiosyl, -lactosyl, -maltosyl, and -melibiosyl azides with various acetylenedicarboxylic acid esters gave the corresponding 1-*N*-glycobiosyl-1,2,3-triazoles (**1a,b,c-8a,b,c**) which have been used as glycosyl donors for the synthesis of oligosaccharides (**15-17**) and an anthracycline type antibiotic (**18**).

INTRODUCTION

Glycoconjugates and complementary carbohydrate-binding proteins have a wide variety of physiological and pathological functions. The biological role of the complex carbohydrates was discovered to be important in intercellular recognition (receptors for pathogens, toxins, viruses, bacteria), adhesion and in the cell regulation (cell growth, glycosylation, etc.).[3] Studies on their biological activities have increased the need for synthetic carbohydrate derivatives as well as development of stereoselective, economic synthetic methods towards oligosaccharides.[4] Numerous methods using a variety of

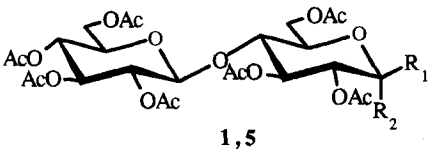
glycosyl donors have been used to form the corresponding glycosides: glycosyl halides (e.g. the Koenigs-Knorr,[5] Helferich[6] and the glycosyl fluoride[7] methods), orthoesters,[8] imidates,[9] thioglycosides,[10] pent-4-*enyl* glycosides[11] and tetrazoles.[12]

Azido groups often serve both as anomeric protecting groups and amino-group precursors in the synthesis of *N*-glycopeptides.[13,14] Furthermore, glycosyl azides are potential glycosyl donors when they are converted to glycosyl fluorides,[14] or *N*-glycosyl-triazoles.[13,14]

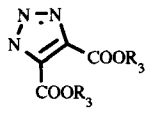
We intended to use *N*-glycosyl-1,2,3-triazoles as glycosyl donors in oligosaccharide synthesis. There are two reported synthetic routes to these heterocycles. By one route they are obtained by glycosylation of 1,2,3-triazoles.[15] Unfortunately, regioisomers often form in the above reaction. In an alternative approach, glycosyl azides are reacted directly with acetylenes or with alkylidene- or arylidene-phosphoranes.[13,16-21] In such a cycloaddition approach mainly 1,2-*trans*-glycosyl azides were used and only a single example is known when a 1,2-*cis*-glycosyl azide was utilized.[20] Herein we report on an extention of his reaction to disaccharides and 1,2-*cis*-glycosyl azides.

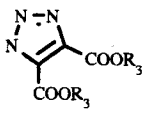
RESULTS AND DISCUSSION

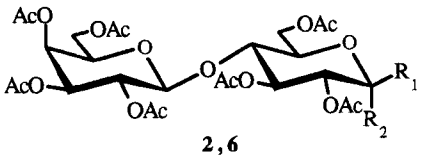
1,3-Dipolar cycloaddition reactions of 1,2-*trans*- and 1,2-*cis*-disaccharide (cellobiose, lactose, maltose, melibiose)[22] azides were carried out in refluxing toluene with various acetylene dicarboxylic acid esters (methyl, ethyl, *tert*-butyl) to afford 1-(hepta-*O*-acetyl-β- (**1a,b,c-4a,b,c**) and -α- (**5a,b,c-8a,b,c**) -glycobiosyl-1,2,3-triazole-4,5-dicarboxylic acid esters (**Scheme 1**) in excellent yield. Noticeable differences were observed between the reaction times of 1,2-*trans*- and 1,2-*cis*-glycobiosyl azides. Cycloadditions of the 1,2-*trans* azides occurred twice as fast as those of the corresponding 1,2-*cis* azides.



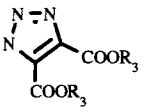
1,5

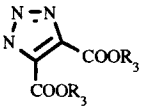
1	R_1	R_2		R_3
		H	**a**	CH_3
			b	CH_2CH_3
			c	$C(CH_3)_3$

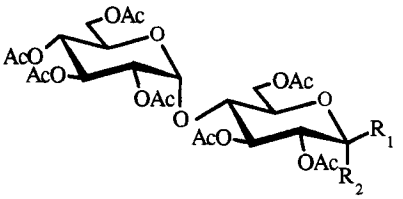
5	R_1	R_2		R_3
	H		**a**	CH_3
			b	CH_2CH_3
			c	$C(CH_3)_3$



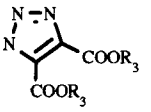
2,6

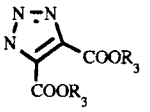
2	R_1	R_2	R_3
		H	**a** CH_3
			b CH_2CH_3
			c $C(CH_3)_3$

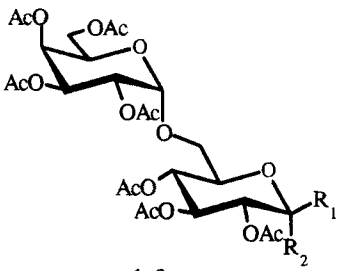
6	R_1	R_2	R_3
	H		**a** CH_3
			b CH_2CH_3
			c $C(CH_3)_3$



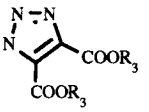
3,7

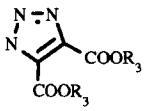
3	R_1	R_2	R_3
		H	**a** CH_3
			b CH_2CH_3
			c $C(CH_3)_3$

7	R_1	R_2	R_3
	H		**a** CH_3
			b CH_2CH_3
			c $C(CH_3)_3$



4,8

4	R_1	R_2	R_3
		H	**a** CH_3
			b CH_2CH_3
			c $C(CH_3)_3$

8	R_1	R_2	R_3
	H		**a** CH_3
			b CH_2CH_3
			c $C(CH_3)_3$

Scheme 1

This phenomenon can be explained by the steric interaction between the C-2 protecting group and the bulky anomeric triazole group.

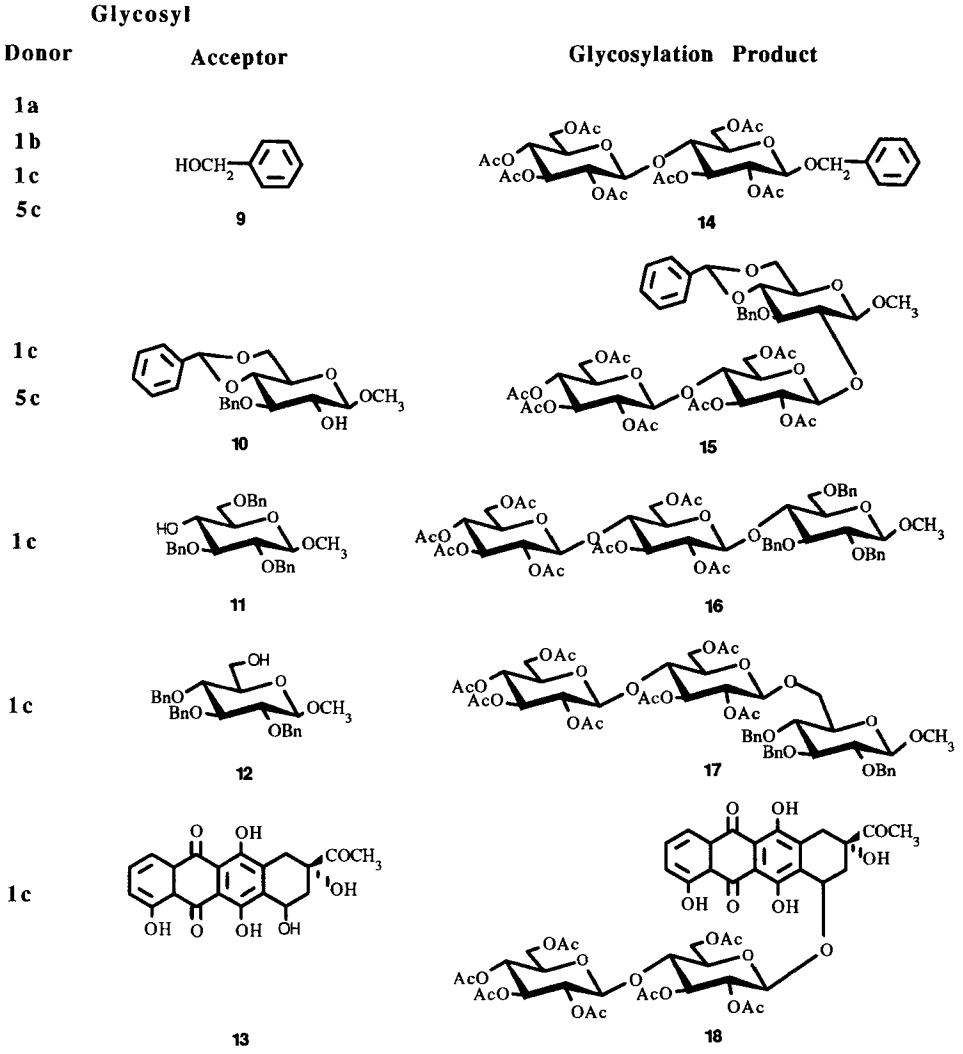
The *N*-glycobiosyl triazoles were purified by column chromatography and characterized by ^{1}H and ^{13}C NMR. The chemical shifts of the anomeric protons bearing equatorial substituents (**1a,b,c-4a,b,c**) are 0.4-0.6 ppm upfield compared to the axial isomers (**5a,b,c-8a,b,c**); similar results were observed with the anomeric glycobiosyl azides. The chemical shifts of the anomeric carbon of the equatorial isomers appear 4 ppm downfield with respect to the corresponding axial isomers.[23] However, the chemical shifts of the interglycosidic anomeric protons, and carbons did not change significantly.

Several alcohols were glycosylated using 1-(hepta-*O*-acetyl-β- and -α-D-cellobiosyl-1,2,3-triazol-4,5-dicarboxylic acid methyl (**1a**), ethyl (**1b**), and *tert*-butyl (**1c,5c**) esters as glycosyl donors, in the presence of trimethylsilyl trifluoromethanesulfonate, as activating agent[14] to give the 1,2-*trans* glycosides (**14-18**) (**Scheme 2**) in good yields. The anomeric configuration of the glycosyl donor (**1c,5c**) did not exert any effect on the formation of the glycosidic bond (see synthesis of **9** from **1a**, **1b**, **1c** or **5c** in the Experimental part). The novel trisaccharides (**15-17**) and a new disaccharide glycoside of carminomycinone (**18**) (for the synthesis of anthracycline glycosides see Ref. 24) were characterized by ^{1}H and ^{13}C NMR sprectoscopy.

In summary, the outlined short procedure represents a reliable, effective and stereoselective method for synthesizing oligosaccharides under controlled conditions without using any exotic catalysts or reagents.

EXPERIMENTAL

General methods. Optical rotations were measured (λ=589 nm) at room temperature using a Perkin-Elmer 241 polarimeter in 10-cm 1mL cell. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, in deuteriochloroform as solvent using a Gemini 300 spectrometer. Chemical shifts (δ) are given in ppm relative to Me_4Si signal for ^{1}H, ^{13}C and APT. The mass spectra were obtained on a TSQ 70 (triple quadrupole) instrument. TLC was performed on DC Alurolle (Kieselgel) thin layer chromatography plates (Merck) with UV light detection and/or charring with 50% sulfuric-acid in ethanol. Column chromatography was performed on Silica gel 60 (particle size 0.2-0.063 mm, Merck). Solvent evaporations were conducted under reduced pressure in a 40 °C bath. Dichloromethane was dried by distillation from phosphorus pentoxide and stored over 4Å molecular sieves.



Scheme 2

Synthesis of 1-*N*-1,2-*trans*- and 1,2-*cis*-glycobiosyl-1,2,3-triazoles. 0.661 g (1.00 mmol) glycobiosyl azide was refluxed in toluene (10 mL) with the appropriate acetylene dicarboxylate (1.50 mmol) for 1-4 days. After complete conversion of the starting material, monitored by TLC, the reaction mixture was allowed to cool to room temperature and the solvent was evaporated. The residue was subjected to column chromatography to give the title compounds.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4,5-dimethoxycarbonyl-1,2,3-triazole (1a). Reaction time: one day; 97%; mp 199-201 °C (ethanol); $[\alpha]_D$ -36.4° (*c* 0.56, chloroform); *Rf*. 0.41 (toluene-ethyl acetate 1:1); ^{1}H NMR ($CDCl_3$) δ 1.85-2.15 (5s, 21H, CO*CH*$_3$), 3.78 (ddd, 1H, H-5'), 3.85 (ddd, 1H, H-5), 3.94 (dd~t, 1H, H-4), 3,98, 4.04 (2s, 6H, O*CH*$_3$), 4.06 (dd, 1H, H-6'b), 4.13 (dd, 1H, H-6a), 4.40 (dd, 1H, H-6'a), 4.52 (dd, 1H, H-6b), 4.56 (d, 1H, H-1' $J_{1',2'}$=7.5 Hz), 4.96 (dd, 1H, H-2'), 5.09 (dd, 1H, H-4'), 5.17 (dd, 1H, H-3'), 5.38 (dd, 1H, H-3), 5.90 (dd, 1H, H-2), 6.11 (d, 1H, H-1 $J_{1,2}$=9.8 Hz); ^{13}C NMR ($CDCl_3$) δ 20.12, 20.37, 20.50, 20.57 (7C, CO*CH*$_3$), 52.70, 53.50 (2C, O*CH*$_3$), 61.31 (C-6), 61.40 (C-6'), 67.62 (C-4'), 69.60 (C-2), 71.43 (C-2'), 71.92 (C-5'), 72.49 (C-3'), 72.72 (C-3), 75.46 (C-4), 75.83 (C-5), 84.98 (C-1), 100.60 (C-1'), 130.56, 140.05 ($C_{4,5}$ triazole), 158.27, 159.85 (*C*=*O* triazole), 168.53, 168.89, 169.17, 169.66, 169.94, 170.02, 170.33 (*CO*CH$_3$).

Anal. Calcd for $C_{32}H_{41}O_{21}N_3$: C, 47.82, H, 5.13, N, 5.22. Found: C, 47.95, H, 5.34, N, 5.30.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4,5-diethoxycarbonyl-1,2,3-triazole (1b). Reaction time: one day; 98%; mp 88-90 °C (ethanol); $[\alpha]_D$ -35.4° (*c* 0.61, chloroform); *Rf*. 0.37 (toluene-ethyl acetate 1:1); ^{1}H NMR ($CDCl_3$) δ 1.36-1.48 (q, 6H, OCH$_2$*CH*$_3$), 1.85-2.10 (5s, 21H, CO*CH*$_3$), 3.70 (ddd, 1H, H-5'), 3.84 (ddd, 1H, H-5), 3.92 (dd~t, 1H, H-4), 4.04 (dd, 1H, H-6'b), 4.12 (dd, 1H, H-6a), 4.36 (dd, H-6'a), 4.44, 4.48 (2q, 2H, O*CH*$_2$CH$_3$), 4.53 (dd, 1H, H-6b), 4.56 (d, 1H, H-1' $J_{1',2'}$=7.5 Hz), 4.95 (dd~t, 1H, H-2'), 5.10 (dd~t, 1H, H-4'), 5.18 (dd~t, 1H, H-3'), 5.38 ((dd, 1H, H-3), 5.92 (dd~t, 1H, H-2), 6.11 (d, 1H, H-1 $J_{1,2}$=9.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.74, 14.02 (OCH$_2$*CH*$_3$), 20.17, 20.38, 20.53 (7C, CO*CH*$_3$), 61.49 (C-6), 61.50 (C-6'), 61.95, 63.05 (O*CH*$_2$CH$_3$), 67.71 (C-4'), 69.61 (C-2), 71.51 (C-2'), 72.00 (C-5'), 72.70 (C-3'), 72.78 (C-3), 75.50 (C-4), 75.85 (C-5), 84.84 (C-1), 100.63 (C-1'), 130.51, 140.02 ($C_{4,5}$ triazole), 157.85, 159.61 (*C*=*O* triazole), 168.51, 168.90, 169.17, 169.69, 169.95, 170.02, 170.34 (*CO*CH$_3$).

Anal. Calcd for $C_{34}H_{45}O_{21}N_3$: C, 49.10, H, 5.44, N, 5.05. Found: C, 48.93, H, 5.41, N, 4.95.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4,5-di-*tert*-butyloxycarbonyl-1,2,3-triazole (1c). Reaction time: one day; 87%; mp 160-161 °C (ethanol); $[\alpha]_D$ -27.7° (*c* 0.83, chloroform); *Rf*. 0.13 (diethyl ether-hexane 4:1); ^{1}H NMR ($CDCl_3$) δ 1.60, 1.62 [2s, 18H, OC(*CH*$_3$)$_3$], 1.85-2.10 (5s, 21H, CO*CH*$_3$), 3.70 (ddd, 1H, H-5'), 3.85 (ddd, 1H, H-5), 3.98 (dd~t, 1H, H-4), 4.08 (dd, 1H, H-6'b), 4.10 (dd, 1H, H-6a), 4.38 (dd, H-

6'a), 4.50 (dd, 1H, H-6b), 4.57 (d, 1H, H-1' $J_{1',2'}$=7.5 Hz), 4.96 (dd~t, 1H, H-2'), 5.08 (dd~t, 1H, H-4'), 5.17 (dd~t, 1H, H-3'), 5.37 ((dd~t, 1H, H-3), 5.99 (dd~t, 1H, H-2), 6.13 (d, 1H, H-1 $J_{1,2}$=9.8 Hz); ^{13}C NMR ($CDCl_3$) δ 20.24, 20.38, 20.52, 20.57 (7C, CO*CH*$_3$), 27.81, 27.97 [6C OC*(CH*$_3$*)*$_3$*]*, 61.49 (C-6), 61.50 (C-6'), 67.73 (C-4'), 69.45 (C-2), 71.53 (C-2'), 71.99 (C-5'), 72.80 (C-3'), 73.03 (C-3), 75.60 (C-4), 75.72 (C-5), 83.17 [O*C*(CH$_3$)$_3$], 84.16 (C-1), 85.25 [O*C*(CH$_3$)$_3$], 100.65 (C-1'), 130.91, 141.84 (*C*$_{4,5}$ triazole), 156.73, 158.93 (*C*=*O* triazole), 168.45, 168.93, 169.17, 169.77, 170.01, 170.34 (7C, *CO*CH$_3$).

Anal. Calcd for $C_{38}H_{53}O_{21}N_3$: C, 51.41, H, 6.01, N, 4.73. Found: C, 51.24, H, 6.00, N, 4.74.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4,5-dimethoxycarbonyl-1,2,3-triazole (2a). Reaction time: one day; 96%; mp 104-106 °C (diethyl ether-hexane); $[\alpha]_D$ -16.9° (*c* 0.56, chloroform); *Rf.* 0.41 (toluene-ethyl acetate 1:1); ^{1}H NMR ($CDCl_3$) δ 1.85-2.15 (7s, 21H, CO*CH*$_3$), 3.75 (ddd, 1H, H-5'), 3.82-3.88 (m, 2H, H-5, H-4), 3,92, 3.98 (2s, 6H, O*CH*$_3$), 4.05-4.12 (m, 2H, 2H-6), 4.42-4.46 (m, 2H, 2H-6), 4.52 (d, 1H, H-1' $J_{1',2'}$=7.5 Hz), 4.92 (dd, 1H, H-3'), 5.12 (dd, 1H, H-2'), 5.35 (m, 2H, H-4', H-3), 5.85 (dd, 1H, H-2), 6.09 (d, 1H, H-1 $J_{1,2}$=9.8 Hz); ^{13}C NMR ($CDCl_3$) δ 20.40, 20.59, 20.73, 20.83 (7C, CO*CH*$_3$), 52.92, 53.72 (2C, O*CH*$_3$), 61.13, 61.77 (C-6,6'), 66.92, 69.38, 70.09, 71.12, 73.16, 75.51, 76.22 (8C, C-2,3,4,5,2',3',4',5'), 85.31 (C-1), 101.17 (C-1'), 130.87, 140.40 (*C*$_{4,5}$ triazole), 158.59, 160.19 (*C*=*O* triazole), 168.85, 169.18, 169.90, 170.11, 170.23, 170.48 (7C, *CO*CH$_3$).

Anal. Calcd for $C_{32}H_{41}O_{21}N_3$: C, 47.82, H, 5.13, N, 5.22. Found: C, 47.90, H, 5.17, N, 4.92.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4,5-diethoxycarbonyl-1,2,3-triazole (2b). Reaction time: one day; 95%; mp 97-98 °C (diethyl ether-hexane); $[\alpha]_D$ -33.4° (*c* 0.50, chloroform); *Rf.* 0.33 (toluene-ethyl acetate 1:1); ^{1}H NMR ($CDCl_3$) δ 1.38-1.48 (q, 6H, OCH$_2$*CH*$_3$), 1.88-2.18 (5s, 21H, CO*CH*$_3$), 3.84-3.98 (m, 3H, H-5',H-5, H-4), 4.05-4.18 (m, 3H, 3H-6), 4.39, 4.44 (m, 4H, O*CH*$_2$CH$_3$), 4.46 (dd, 1H, H-6), 4.54 (d, 1H, H-1' $J_{1',2'}$=7.5 Hz), 4.95 (dd, 1H, H-3'), 5.12 (dd, 1H, H-2'), 5.36-5,42 (m, 2H, H-4', H-3), 5.95 (dd, 1H, H-2), 6.11 (d, 1H, H-1 $J_{1,2}$=9.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.50, 13.76 (2C, OCH$_2$*CH*$_3$), 19.92, 20.09, 20.22, 20.32, (7C, CO*CH*$_3$), 60.71, 61.42 (C-6,6'), 61.68, 62.83 (O*CH*$_2$CH$_3$), 66.50, 68.82, 69.48, 70.47, 70.59, 72.67, 75.06, 76.58 (C-2,3,4,5,2',3',4',5'), 84.58 (C-1), 100.58 (C-1'), 130.41, 140.10 (*C*$_{4,5}$ triazole), 157.59, 159.34 (*C*=*O* triazole), 168.34, 168.74, 169.45, 169.59, 169.77, 169.98 (7C, *CO*CH$_3$).

Anal. Calcd for $C_{34}H_{45}O_{21}N_3$: C, 49.10, H, 5.44, N, 5.05. Found: C, 49.15, H, 5.38, N, 5.00.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4,5-di-*tert*-butyloxycarbonyl-1,2,3-triazole (2c). Reaction time: one day; 93%; mp 101-103 °C (diethyl ether-hexane); $[\alpha]_D$ -22.8° (*c* 0.86, chloroform); *Rf*. 0.47 (toluene-ethyl acetate 6:5), 0.09 (diethyl ether-hexane 4:1); ^{1}H NMR ($CDCl_3$) δ 1.62, 1.64 [2s, 18H, $OC(CH_3)_3$], 1.90-2.20 (5s, 21H, $COCH_3$), 3.82-3.88 (m, 2H, H-5',5), 3.92 (dd, 1H, H-4), 4.05-4.14 (m, 2H, 2H-6), 4.45 (dd, 1H, H-6), 4.52 (d, 1H, H-1' $J_{1',2'}$=7.5 Hz), 4.98 (dd, 1H, H-3'), 5.12 (dd, 1H, H-2'), 5.34-5,48 (m, 2H, H-4',3), 5.98 (dd, 1H, H-2), 6.14 (d, 1H, H-1 $J_{1,2}$=9.8 Hz); ^{13}C NMR ($CDCl_3$) δ 20.25, 20.33, 20.47, 20.59 (7C, $COCH_3$), 27.82, 27.98 [6C, $OC(CH_3)_3$], 60.84, 61.65 (C-6,6'), 66.62, 69.08, 69.57, 70.78, 70.85, 73.33, 75.39, 75.72 (C-2,3,4,5,2',3',4',5'), 83.17 [$OC(CH_3)_3$], 84.15 (C-1), 85.24 [$OC(CH_3)_3$], 100.91 (C-1'), 130.93, 141.87 ($C_{4,5}$ triazole), 156.74, 158.93 (C=O triazole), 168.52, 168.96, 169.75, 169.85, 169.95 170.05, 170.21 (7C, $COCH_3$).

Anal. Calcd for $C_{38}H_{53}O_{21}N_3$: C, 51.41, H, 6.01, N, 4.73. Found: C, 50.98, H, 6.00, N, 4.77.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4,5-dimethoxycarbonyl-1,2,3-triazole (3a). Reaction time: one day; 96%; mp 144-146 °C (ethanol); $[\alpha]_D$ +38.1° (*c* 0.62, chloroform); *Rf*. 0.45 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.85-2.15 (7s, 21H, $COCH_3$), 3.88-3.98 (m, 2H, H-5,5'), 4.00, 4.06 (2s, 6H, OCH_3), 4.07 (dd, 1H, H-6), 4.10-4.25 (m, 2H), 4.25 (dd, 1H, H-6), 4.51 (dd, 1H, H-6), 4.90 (dd, 1H, H-6), 5.08 (dd~t, 1H), 5.48 (d, 1H, H-1' $J_{1',2'}$=3.8 Hz), 5.38-5.55 (m, 2H), 5.88 (dd~t, 1H, H-2), 6.22 (d, 1H, H-1 $J_{1,2}$=9.8 Hz); ^{13}C NMR ($CDCl_3$) δ 20.16, 20.46, 20.57, 20.59, 20.76 (7C, $COCH_3$), 52.75, 53.56 (OCH_3), 61.40, 62.17 (C-6',6), 67.88, 68.61, 69.13, 69.92, 69.99, 72.17, 75.30, 75.44 (C-2,3,4,5,2',3',4',5'), 84.61 (C-1), 95.78 (C-1'), 130.58, 140.18 ($C_{4,5}$ triazole), 158.18, 159.88 (C=O triazole), 168.76, 169.28, 169.79, 170.12, 170.16, 170.38 (7C, $COCH_3$).

Anal. Calcd for $C_{32}H_{41}O_{21}N_3$: C, 47.82, H, 5.13, N, 5.22. Found: C, 47.61, H, 5.18, N, 5.18.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4,5-diethoxycarbonyl-1,2,3-triazole (3b). Reaction time: one day; 97%; mp 176-177 °C (ethanol); $[\alpha]_D$ +28.4° (*c* 0.79, chloroform); *Rf*. 0.40 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.64 (q, 6H, OCH_2CH_3), 1.85-2.15 (7s, 21H, $COCH_3$), 3.88-3.98 (m, 2H, H-5,5'), 4.04 (dd, 1H, H-6), 4.12-4.24 (m,

2H), 4.28 (dd, 1H, H-6), 4.48 (m, 4H, O$CH_2$$CH_3$), 4.50 (dd, 1H, H-6), 4.88 (dd, 1H, H-6), 5.08 (dd~t, 1H), 5.48 (d, 1H, H-1' $J_{1',2'}$=3.8 Hz), 5.34-5.50 (m, 2H), 5.86 (dd~t, 1H, H-2), 6.18 (d, 1H, H-1 $J_{1,2}$=9.8 Hz); ^{13}C NMR ($CDCl_3$) δ 13.80, 14.03 (OCH$_2$*CH$_3$*), 20.19, 20.45, 20.54, 20.76 (7C, CO*CH$_3$*), 61.41, 61.98 (C-6',6), 62.22, 63.11 (O*CH$_2$*CH$_3$), 67.91, 68.62, 69.17, 69.94 (2C), 72.24, 75.27, 75.57 (C-2,3,4,5, 2',3',4',5'), 84.43 (C-1), 95.81 (C-1'), 130.54, 140.54 (*C$_{4,5}$* triazole), 157.74, 159.60 (*C*=*O* triazole), 168.74, 169.27, 169.78, 170.12, 170.19, 170.37 (7C, *CO*CH$_3$).

Anal. Calcd for $C_{34}H_{45}O_{21}N_3$: C, 49.10, H, 5.44, N, 5.05. Found: C, 49.05, H, 5.48, N, 5.08.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4,5-di-*tert*-butyloxycarbonyl-1,2,3-triazole (3c). Reaction time: one day; 93%; mp 148 °C (diethyl ether-hexane); $[\alpha]_D$ +18.4° (*c* 0.61, chloroform); *Rf.* 0.61 (toluene-ethyl acetate 6:5), 0.27 (diethyl ether-hexane 4:1); ^{1}H NMR ($CDCl_3$) δ 1.58, 1.60 [2s, 18H, OC*(CH$_3$)$_3$*], 1.80-2.15 (7s, 21H, CO*CH$_3$*), 3.90-4.00 (m, 2H, H-5,5'), 4.06 (dd, 1H, H-6), 4.10-4.26 (m, 2H), 4.28 (dd, 1H, H-6), 4.48 (dd, 1H, H-6), 4.86 (dd, 1H, H-6), 5.08 (dd~t, 1H), 5.48 (d, 1H, H-1' $J_{1',2'}$=3.8 Hz), 5.32-5.50 (m, 2H), 5.94 (dd~t, 1H, H-2), 6.22 (d, 1H, H-1 $J_{1,2}$=9.8 Hz); ^{13}C NMR ($CDCl_3$) δ 20.24, 20.43, 20.50, 20.54 (7C, CO*CH$_3$*), 27.84, 27.97 [6C, OC*(CH$_3$)$_3$*], 61.40, 62.33 (C-6',6), 67.93, 68.60, 69.20, 69.77, 69.92, 72.32, 75.16, 75.90 (C-2,3, 4,5,2',3',4',5'), 83.18 [O*C*(CH$_3$)$_3$], 83.79 (C-1), 85.33 [O*C*(CH$_3$)$_3$], 95.82 (C-1'), 130.99, 141.82 (*C$_{4,5}$* triazole), 156.71, 158.89 (*C*=*O* triazole), 168.71, 169.23, 169.75, 170.13, 170.24, 170.32 (7C, *CO*CH$_3$).

Anal. Calcd for $C_{38}H_{53}O_{21}N_3$: C, 51.41, H, 6.01, N, 4.73. Found: C, 51.30, H, 5.98, N, 4.74.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-(1→6)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4,5-dimethoxycarbonyl-1,2,3-triazole (4a). Reaction time: one day; 94%; mp 88-90 °C (diethyl ether-hexane); $[\alpha]_D$ +84.0° (*c* 0.32, chloroform); *Rf.* 0.26 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.85-2.15 (7s, 21H, CO*CH$_3$*), 3.60 (dd, 1H, H-6), 3.76 (dd, 1H, H-6), 3.94-4.18 (m, 10H, 3.44, 4.04 2s, 6H, O*CH$_3$*, 2H-5, 2H-6), 5.04-5.12 (m, 2H, ~5.08 d, 1H, H-1' $J_{1',2'}$≈4.0 Hz), 5.22-5.48 (m, 4H), 5.96 (dd~t, 1H, H-2), 6.18 (d, 1H, H-1 $J_{1,2}$=9.5 Hz); ^{13}C NMR ($CDCl_3$) δ 20.07, 20.42, 20.51, (7C, CO*CH$_3$*), 52.66, 53.70 (O*CH$_3$*), 61.44, 65.98 (C-6',6), 66.38, 67.27, 67.76, 67.82, 67.87, 69.56, 73.06, 75.92 (C-2,3,4,5,2',3',4',5'), 84.82 (C-1), 96.27 (C-1'), 130.47, 140.23 (*C$_{4,5}$* triazole), 158.22, 159.87 (*C*=*O* triazole), 168.28, 168.98, 169.58, 169.96, 170.01, 170.12, 170.34 (7C, *CO*CH$_3$).

Anal. Calcd for $C_{32}H_{41}O_{21}N_3$: C, 47.82, H, 5.13, N, 5.22. Found: C, 47.89, H, 5.20, N, 5.08.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-(1→6)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4,5-diethoxycarbonyl-1,2,3-triazole (4b). Reaction time: one day; 83%; amorphous; $[\alpha]_D$ +52.0° (*c* 0.61, chloroform); *Rf.* 0.32 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.44 (q, 6H, OCH_2CH_3), 1.88-2.12 (6s, 21H, $COCH_3$), 3.62 (dd, 1H, H-6), 3.76 (dd, 1H, H-6), 3.94-4.02 (m, 3H, H-5, 2H-6), 4.12 (dd, 1H, H-6), 4.48 (m, 4H, OCH_2CH_3), 5.08-5.12 (m, 2H, ~5.08 d, 1H, H-1' $J_{1',2'}$≈4.0 Hz), 5.24-5.48 (m, 4H), 5.96 (dd~t, 1H, H-2), 6.18 (d, 1H, H-1 $J_{1,2}$=9.5 Hz); ^{13}C NMR ($CDCl_3$) δ 13.64, 13.86 (OCH_2CH_3), 19.99, 20.31, (7C, $COCH_3$), 61.34, 65.84 (C-6',6), 61.83, 63.17 (OCH_2CH_3), 66.27, 67.19, 67.68, 67.78, 69.44, 73.02, 75.74, 76.36 (C-2,3,4,5,2',3',4',5'), 84.60 (C-1), 96.16 (C-1'), 130.34, 140.43 ($C_{4,5}$ triazole), 157.66, 159.47 (C=O triazole), 168.16, 168.89, 169.44, 169.90, 170.00, 170.23, (7C, $COCH_3$).

Anal. Calcd for $C_{34}H_{45}O_{21}N_3$: C, 49.10, H, 5.44, N, 5.05. Found: C, 49.05, H, 5.47, N, 5.10.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-(1→6)-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl]-4,5-di-*tert*-butyloxycarbonyl-1,2,3-triazole (4c). Reaction time: one day; 98%; mp 84-86 °C (diethyl ether-hexane); $[\alpha]_D$ +61.7° (*c* 0.42, chloroform); *Rf.* 0.45 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.58, 1.60 [2s, 18H, $OC(CH_3)_3$], 1.90-2.12 (6s, 21H, $COCH_3$), 3.60 (dd, 1H, H-6), 3.74 (dd,1H, H-6), 3.90-4.04 (m, 3H, H-5, 2H-6),4.12 (dd, 1H, H-6), 5.04-5.08 (m, 2H, ~5.08 d, 1H, H-1' $J_{1',2'}$≈4.0 Hz), 5.30-5.46 (m, 4H), 5.98 (dd~t, 1H, H-2), 6.18 (d, 1H, H-1 $J_{1,2}$=9.5 Hz); ^{13}C NMR ($CDCl_3$) δ 20.19, 20.43, 20.49 (7C, $COCH_3$), 27.84, 28.00 [6C, $OC(CH_3)_3$], 61.41, 66.19 (C-6',6), 66.39, 67.38, 67.87 (3C), 69.62, 73.35, 75.82 (C-2,3,4,5,2',3',4',5'), 83.15 [$OC(CH_3)_3$], 84.32 (C-1), 85.45 [$OC(CH_3)_3$], 96.57 (C-1'), 131.02, 141.73 ($C_{4,5}$ triazole), 156.90, 158.87 (C=O triazole), 168.24, 168.93, 169.53, 169.97, 170.13, 170.42, (7C, $COCH_3$).

Anal. Calcd for $C_{38}H_{53}O_{21}N_3$: C, 51.41, H, 6.01, N, 4.73. Found: C, 51.40, H, 5.89, N, 4.70.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-4,5-dimethoxycarbonyl-1,2,3-triazole (5a). Reaction time: four days; 94%; mp 94-96 °C (ethanol); $[\alpha]_D$ +66.0° (*c* 0.53, chloroform); *Rf.* 0.21 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.90-2.15 (6s, 21H, $COCH_3$), 3.73 (ddd, 1H, H-5'), 3.85 (dd~t, 1H, H-4), 3.98, 4.00 (s, 6H, OCH_3), 4.07 (dd, 1H, H-6'a), 4.14 (dd, 1H, H-6a), 4.34 (dd, 1H, H-6'b), 4.38 (ddd, 1H, H-5), 4.42 (dd, 1H,

H-6b), 4.65 (d, 1H, H-1' $J_{1',2'}$=7.5 Hz), 4.95 (dd~t, 1H, H-2'), 5.08 (dd, 1H, H-4'), 5.14 (dd, 1H, H-3'), 5.38 (dd, 1H, H-3), 6.16 (dd, 1H, H-2), 6.68 (d, 1H, H-1 $J_{1,2}$=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.13, 20.39, 20.63, (7C, CO*CH*$_3$), 52.74, 53.75 (2C, O*CH*$_3$), 61.28 (C-6), 61.45 (C-6'), 67.75 (C-4'), 68.87 (C-2,3), 71.46 (C-2'), 71.90 (C-5'), 72.63 (C-5), 72.92 (C-3'), 75.60 (C-4), 80.97 (C-1), 99.91 (C-1'), 131.65, 139.29 (*C*$_{4,5}$ triazole), 158.30, 160.01 (*C*=*O* triazole), 168.74, 169.01, 169.13, 169.69, 169.98, 170.07, 170.32 (*CO*CH_3).

Anal. Calcd for $C_{32}H_{41}O_{21}N_3$: C, 47.82, H, 5.13, N, 5.22. Found: C, 47.90, H, 5.16, N, 5.30.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-4,5-diethoxycarbonyl-1,2,3-triazole (5b). Reaction time: four days; 96%; mp 76-78 °C (diethyl ether-hexane); $[\alpha]_D$ +55.6° (*c* 0.45, chloroform); *Rf*. 0.30 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.44 (q, 6H, OCH$_2$*CH*$_3$), 1.92-2.15 (6s, 21H, CO*CH*$_3$), 3.72 (ddd, 1H, H-5'), 3.98 (dd~t, 1H, H-4), 4.02-4.18 (m, 2H, H-6'a,6a), 4.36 (dd, 1H, H-6'b), 4.38-4.52 (m, 6H, H-5,6b, 2x O*CH*$_2$CH$_3$), 4.64 (d, 1H, H-1' $J_{1',2'}$=7.5 Hz), 4.95 (dd~t, 1H, H-2'), 5.10 (dd, 1H, H-4'), 5.16 (dd, 1H, H-3'), 5.42 (dd, 1H, H-3), 6.18 (dd, 1H, H-2), 6.68 (d, 1H, H-1 $J_{1,2}$=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 13.66, 13.96 (OCH$_2$*CH*$_3$), 20.13, 20.37, 20.60, (7C, CO*CH*$_3$), 61.31 (C-6), 61.49 (C-6'), 61.82, 63.28 (O*CH*$_2$CH$_3$), 67.80 (C-4'), 68.93 (C-2,3), 71.49 (C-2'), 71.90 (C-5'), 72.53 (C-5), 72.93 (C-3'), 75.57 (C-4), 80.87 (C-1), 99.85 (C-1'), 131.70, 140.08 (*C*$_{4,5}$ triazole), 157.89, 159.66 (*C*=*O* triazole), 168.71, 168.99, 169.12, 169.67, 170.05, 170.31 (7C, *CO*CH_3).

Anal. Calcd for $C_{34}H_{45}O_{21}N_3$: C, 49.10, H, 5.44, N, 5.05. Found: C, 49.18, H, 5.50, N, 5.00.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-4,5-di-*tert*-butyloxycarbonyl-1,2,3-triazole (5c). Reaction time: four days; 90%; mp 88-90 °C (diethyl ether-hexane); $[\alpha]_D$ +56.8° (*c* 1.02, chloroform); *Rf*. 0.34 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.58, 1.64 [s, 18H, OC*(CH*$_3$*)*$_3$], 1.92-2.16 (6s, 21H, CO*CH*$_3$), 3.75 (ddd, 1H, H-5'), 3.85 (dd~t, 1H, H-4), 4.04 (dd, 1H, H-6'a), 4.12 (dd, 1H, H-6a), 4.32 (dd, 1H, H-6'b), 4.38 (ddd, 1H, H-5), 4.42 (dd, 1H, H-6b), 4.66 (d, 1H, H-1' $J_{1',2'}$=7.5 Hz), 4.95 (dd~t, 1H, H-2'), 5.08 (dd, 1H, H-4'), 5.12 (dd, 1H, H-3'), 5.40 (dd, 1H, H-3), 6.22 (dd~t, 1H, H-2), 6.66 (d, 1H, H-1 $J_{1,2}$=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.21, 20.38, 20.64 (7C, CO*CH*$_3$),27.69, 27.95 [6C, OC*(CH*$_3$*)*$_3$*]*, 61.33 (C-6), 61.48 (C-6'), 67.76 (C-4'), 69.04 (C-2,3), 71.45 (C-2'), 71.85 (C-5'), 72.20 (C-5), 72.94 (C-3'), 75.59 (C-4), 80.47 (C-1), 83.17, 85.75 [O*C*(CH$_3$)$_3$], 99.79 (C-1'), 132.43, 140.63 (*C*$_{4,5}$ triazole), 156.85,

158.83 (*C=O* triazole), 168.67, 168.96, 169.13, 169.76, 169.96, 170.07, 170.32 (*CO*CH_3).

Anal. Calcd for $C_{38}H_{53}O_{21}N_3$: C, 51.41, H, 6.01, N, 4.73. Found: C, 51.50, H, 5.96, N, 4.68.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-4,5-dimethoxycarbonyl-1,2,3-triazole (6a). Reaction time: four days; 93%; mp 93-95 °C (ethanol); $[\alpha]_D$ +58.3° (*c* 0.54, chloroform); *Rf.* 0.20 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.90-2.20 (6s, 21H, CO*CH_3*), 3.72-3.82 (m, 2H), 3,98, 4.08 (2s, 6H, O*CH_3*), 4.04-4.18 (m, 3H), 4.36-4.48 (m, 2H, H-5,6), 4.62 (d, 1H, H-1' $J_{1',2'}$=7.5 Hz), 4.98 (dd, 1H, H-6), 5.14 (dd~t, 1H), 5.34-5.42 (m, 2H), 6.16 (dd~t, 1H, H-2), 6.68 (d, 1H, H-1 $J_{1,2}$=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.12, 20.43, 20.61, (7C, CO*CH_3*), 52.70, 53.71 (2C, O*CH_3*), 60.84, 61.44 (C-6'6,), 66.66, 68.94 (2C), 69.25, 70.76, 70.98, 72.68, 75.49, (8C, C-2,3,4,5,2',3',4',5'), 81.03 (C-1), 100.39 (C-1'), 131.65, 139.14 (*$C_{4,5}$* triazole), 158.33, 160.08 (*C=O* triazole), 168.72, 168.94, 169.69, 170.02, (7C, *CO*CH_3).

Anal. Calcd for $C_{32}H_{41}O_{21}N_3$: C, 47.82, H, 5.13, N, 5.22. Found: C, 47.69, H, 5.09, N, 5.16.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-4,5-diethoxycarbonyl-1,2,3-triazole (6b). Reaction time: four days; 96%; mp 149-150 °C (ethanol); $[\alpha]_D$ +56.3° (*c* 0.64, chloroform); *Rf.* 0.26 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.44 (q, 6H, OCH_2*CH_3*), 1.92-2.18 (6s, 21H, CO*CH_3*), 3.90-4.20 (m, 5H, H-5,6), 4.38-4.48 (m, 6H, H-6, O*CH_2*CH_3), 4.64 (d, 1H, H-1' $J_{1',2'}$=7.5 Hz), 4.94 (dd, 1H, H-6), 5.12 (dd, 1H), 5.38-5.46 (m, 2H), 6.16 (dd~t, 1H, H-2), 6.70 (d, 1H, H-1 $J_{1,2}$=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 13.71, 14.02 (OCH_2*CH_3*), 20.18, 20.36, 20.47, 20.65 (7C, CO*CH_3*), 60.90, 61.52 (C-6',6), 61.99, 63.40 (O*CH_2*CH_3), 66.73, 69.05 (2C), 69.37, 70.82, 71.05, 72.63, 75.52, (8C, C-2,3,4,5,2',3',4',5'), 80.97 (C-1), 100.37 (C-1'), 131.75, 139.65 (*$C_{4,5}$* triazole), 157.97, 159.71 (*C=O* triazole), 168.71, 168.95, 169.71, 169.90, 170.04, (7C, *CO*CH_3).

Anal. Calcd for $C_{34}H_{45}O_{21}N_3$: C, 49.10, H, 5.44, N, 5.05. Found: C, 49.05, H, 5.42, N, 5.10.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-4,5-di-*tert*-butyloxycarbonyl-1,2,3-triazole (6c). Reaction time: four days; 90%; syrup; $[\alpha]_D$ +23.3° (*c* 0.40, chloroform); *Rf.* 0.52 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.62, 1.66 [s, 18H, OC*$(CH_3)_3$*], 1.85-2.12 (6s, 21H, CO*CH_3*), 3.94-4.04 (m, 3H), 4.06-4.18 (m, 2H), 4.48 (ddd, 1H, H-5),

4.62 (d, 1H, H-1' $J_{1',2'}$=7.5 Hz), 4.90 (dd, 1H, H-6), 5.08 (dd~t, 1H), 5.32-5.50 (m, 3H), 5.92 (dd~t, 1H, H-2), 6.68 (d, 1H, H-1 $J_{1,2}$=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.31, 20.49, 20.87, (7C, CO*CH*$_3$), 27.92, 28.05 [6C, OC(*CH*$_3$)$_3$], 60.78, 61.46 (C-6',6), 66.76, 68.88 (2C), 69.34, 70.78, 71.04, 72.58, 75.46, (8C, C-2,3,4,5,2',3',4',5'), 80.97 (C-1), 83.08, 84.98 [O*C*(CH$_3$)$_3$], 100.37 (C-1'), 131.68, 139.46 (*C*$_{4,5}$ triazole), 157.86, 159.48 (*C*=*O* triazole), 168.69, 168.93, 169.71, 169.86, 170.02, (7C, *CO*CH$_3$).

Anal. Calcd for $C_{38}H_{53}O_{21}N_3$: C, 51.41, H, 6.01, N, 4.73. Found: C, 51.50, H, 6.08, N, 4.65.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-4,5-dimethoxycarbonyl-1,2,3-triazole (7a). Reaction time: two days; 95%; syrup; $[\alpha]_D$ +132.7° (*c* 0.45, chloroform); *Rf*. 0.28 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.90-2.14 (7s, 21H, CO*CH*$_3$), 3.92 (ddd, 1H, H-5), 3.98, 4.00 (2s, 6H, O*CH*$_3$), 4.08-4.24 (m, 4H), 4.38-4.52 (m, 2H), 4.90 (dd, 1H, H-6), 5.01 (t, 1H), 5.34 (2dd, 2H), 5.48 (d, 1H, H-1' $J_{1',2'}$=4.0 Hz), 6.08 (dd~t, 1H, H-2), 6.68 (d, 1H, H-1 $J_{1,2}$=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.04, 20.38, 20.55, 20.65 (7C, CO*CH*$_3$), 52.68, 53.68 (O*CH*$_3$), 61.37, 62.11 (C-6',6), 67.95, 68.48, 68.71, 69.25, 69.87, 71.70, 72.54, 72.72 (C-2,3,4,5,2',3',4',5'), 81.11 (C-1), 95.75 (C-1'), 131.40, 139.31 (*C*$_{4,5}$ triazole), 158.36, 160.00 (*C*=*O* triazole), 169.20, 169.27, 169.57, 170.11, 170.29, 170.45 (7C, *CO*CH$_3$).

Anal. Calcd for $C_{32}H_{41}O_{21}N_3$: C, 47.82, H, 5.13, N, 5.22. Found: C, 47.70, H, 5.17, N, 5.29.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-4,5-diethoxycarbonyl-1,2,3-triazole (7b). Reaction time: two days; 97%; syrup; $[\alpha]_D$ +127.9° (*c* 0.46, chloroform); *Rf*. 0.38 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.42 (q, 6H, OCH$_2$*CH*$_3$), 1.88-2.12 (7s, 21H, CO*CH*$_3$), 3.98 (ddd, 1H, H-5), 4.10 (dd, 1H, H-6), 4.22 (ddd, dd, 2H, H-5,6), 4.45 (2dd, 2H, O*CH*$_2$CH$_3$, m, 3H, incl. H-6), 4.90 (dd, 1H, H-6), 5.08 (t, 1H), 5.38 (2dd, 2H), 5.48 (d, 1H, H-1' $J_{1',2'}$=4.0 Hz), 6.12 (dd, 1H, H-2), 6.68 (d, 1H, H-1 $J_{1,2}$=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 13.65, 13.97 (OCH$_2$*CH*$_3$), 20.08, 20.38, 20.57, 20.65 (7C, CO*CH*$_3$), 61.36, 62.11 (C-6',6), 61.93, 63.04 (O*CH*$_2$CH$_3$), 67.95, 68.46, 68.77, 69.25, 69.86, 71.81, 72.40, 72.69 (C-2,3,4,5,2',3',4',5'), 80.95 (C-1), 95.76 (C-1'), 131.48, 139.58 (*C*$_{4,5}$ triazole), 157.94, 159.64 (*C*=*O* triazole), 169.20, 169.28, 169.60, 170.11, 170.30, 170.48 (7C, *CO*CH$_3$).

Anal. Calcd for $C_{34}H_{45}O_{21}N_3$: C, 49.10, H, 5.44, N, 5.05. Found: C, 50.00, H, 5.48, N, 5.12.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-4,5-di-*tert*-butyloxycarbonyl-1,2,3-triazole (7c). Reaction time: two days; 97%; syrup; $[\alpha]_D$ +138.3° (*c* 0.42, chloroform); *Rf*. 0.50 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.56, 1.64 [s, 18H, OC*(CH$_3$)$_3$*], 1.90-2.18 (7s, 21H, CO*CH$_3$*), 3.94 (ddd, 1H, H-5), 4.08 (dd, 1H, H-6), 4.12-4.42 (m, dd, 5H, incl. H-5,6), 4.88 (dd, 1H, H-6), 5.08 (t, 1H), 5.38 (2dd, 2H), 5.48 (d, 1H, H-1' $J_{1',2'}$=4.0 Hz), 6.18 (dd, 1H, H-2), 6.64 (d, 1H, H-1 $J_{1,2}$=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.21, 20.46, 20.53, 20.65, 20.74 (7C, CO*CH$_3$*), 27.77, 28.03 [6C, OC*(CH$_3$)$_3$*], 61.42, 62.25 (C-6',6), 68.04, 68.50, 69.05, 69.33, 69.92, 72.10, 72.16, 72.74 (C-2,3,4,5,2', 3',4',5'), 80.59 (C-1), 83.21, 85.80 [O*C*(CH$_3$)$_3$], 95.69 (C-1'), 132.30, 140.79 (*C$_{4,5}$* triazole), 156.97, 158.92 (*C*=*O* triazole), 169.25, 169.37, 169.57, 169.78, 170.17, 170.39, 170.63 (7C, *CO*CH$_3$).

Anal. Calcd for $C_{38}H_{53}O_{21}N_3$: C, 51.41, H, 6.01, N, 4.73. Found: C, 51.49, H, 6.11, N, 4.80.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-(1→6)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-4,5-dimethoxycarbonyl-1,2,3-triazole (8a). Reaction time: two days; 94%; syrup; $[\alpha]_D$ +145.5° (*c* 0.44, chloroform); *Rf*. 0.31 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.90-2.15 (7s, 21H, CO*CH$_3$*), 3.52 (dd, 1H, H-6), 3.70 (dd, 1H, H-6), 3.98, 4.02 (s, O*CH$_3$*), 4.02 (1H), 4.10-4.20 (m, 2H, H-5,6), 4.44 (dd, 1H, H-5), 5.00 (dd, 1H), 5.12 (d, 1H, H-1' $J_{1',2'}$=3.2 Hz), 5.22-5.48 (m, 4H), 6.18 (dd~t, 1H, H-2), 6.74 (d, 1H, H-1 $J_{1,2}$=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.05, 20.42 (7C, CO*CH$_3$*), 52.67, 53.76 (O*CH$_3$*), 61.54, 65.48 (C-6',6), 66.28, 67.32, 67.92, 68.00, 68.19, 68.79, 70.08, 72.70 (C-2,3,4,5,2',3',4',5'), 80.86 (C-1), 96.13 (C-1'), 131.84, 139.36 (*C$_{4,5}$* triazole), 158.23, 160.01 (*C*=*O* triazole), 169.32, 169.55, 169.99, 170.15, 170.37 (7C, *CO*CH$_3$).

Anal. Calcd for $C_{32}H_{41}O_{21}N_3$: C, 47.82, H, 5.13, N, 5.22. Found: C, 48.01, H, 5.20, N, 5.14.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-(1→6)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-4,5-diethoxycarbonyl-1,2,3-triazole (8b). Reaction time: two days; 96%; syrup; $[\alpha]_D$ +137.0° (*c* 0.48, chloroform); *Rf*. 0.38 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.38 (q, 6H, OCH$_2$*CH$_3$*) 1.88-2.15 (7s, 21H, CO*CH$_3$*), 3.52 (dd, 1H, H-6), 3.72 (dd, 1H, H-6), 4.02-4.22 (m, 3H), 4.38 (ddd, 1H, H-5), 4.45 (m, 4H, O*CH$_2$*CH$_3$), 5.05 (dd, 1H), 5.12 (d, 1H, H-1' $J_{1',2'}$=3.4 Hz), 5.24-5.46 (m, 4H), 6.18 (dd~t, 1H, H-2), 6.74 (d, 1H, H-1 $J_{1,2}$=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 13.52, 13.83 (OCH$_2$*CH$_3$*), 19.96, 20.30 (7C, CO*CH$_3$*), 61.37, 65.28 (C-6',6), 61.80, 63.31 (O*CH$_2$*CH$_3$), 66.12, 67.16, 67.74, 67.84, 68.00, 68.63, 69.93,

72.50 (C-2,3,4,5,2',3',4',5'), 80.60 (C-1), 96.00 (C-1'), 131.72, 139.43 ($C_{4,5}$ triazole), 157.67, 159.50 (C=O triazole), 169.17, 169.34, 169.41, 169.83, 169.98, 170.20 (7C, COCH$_3$).

Anal. Calcd for $C_{34}H_{45}O_{21}N_3$: C, 49.10, H, 5.44, N, 5.05. Found: C, 49.02, H, 5.46, N, 4.99.

1-[*O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)-(1→6)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl]-4,5-di-*tert*-butyloxycarbonyl-1,2,3-triazole (8c). Reaction time: two days; 92%; syrup; $[\alpha]_D$ +123.3° (*c* 0.86, chloroform); *Rf.* 0.46 (toluene-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.58, 1.62 [6s, 18H, OC$(CH_3)_3$], 1.90-2.12 (7s, 21H, COCH_3), 3.52 (dd, 1H, H-6), 3.72 (dd, 1H, H-6), 4.04-4.18 (m, 3H), 4.32 (ddd, 1H, H-5), 5.06 (dd, 1H), 5.16 (d, 1H, H-1' $J_{1',2'}$=3.2 Hz), 5.28-5.46 (m, 4H), 6.18 (dd~t, 1H, H-2), 6.68 (d, 1H, H-1 $J_{1,2}$=6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.17, 20.47 (7C, COCH_3), 27.75, 28.00 [6C, OC$(CH_3)_3$], 61.52, 65.50 (C-6',6), 66.35, 67.39, 67.93, 68.07, 68.20, 68.92, 70.25, 72.53 (C-2,3,4,5,2',3',4',5'), 80.50 (C-1), 83.18, 85.90 [OC(CH$_3$)$_3$], 96.37 (C-1'), 131.69, 140.58 ($C_{4,5}$ triazole), 156.85, 158.82 (C=O triazole), 169.32, 169.54, 169.64, 169.99, 170.14, 170.36 (7C, COCH$_3$).

Anal. Calcd for $C_{38}H_{53}O_{21}N_3$: C, 51.41, H, 6.01, N, 4.73. Found: C, 51.20, H, 5.94, N, 4.69

Glycosylation procedure:

Benzyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-*O*-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (14). 1a (0.080 g, 0.10 mmol), **1b** (0.083 g, 0.10 mmol), **1c** (0.088 g, 0.10 mmol), or **5c** (0.088 g, 0.10 mmol), benzyl alcohol (**9**) (0.041 mL, 0.40 mmol) and powdered 4Å molecular sieves (0.4 g) were suspended in dry dichloromethane (10 mL). Trimethylsilyl trifluoromethanesulfonate (TMSOTf) (0.036 mL, 0.2 mmol) was dropwise added and the reaction mixture was stirred at room temperature for one hour. The reaction was quenched with pyridine. The reaction mixture was diluted with dichloromethane (40 mL) and filtered through Celite. The filtrate was washed with water, saturated aqueous sodium bicarbonate, water, dried and the solvent was evaporated. Column chromatography (toluene-ethyl acetate 7:3→6:5 gave **14**[25] (0.050 g, 70%); (0.048 g, 68%); (0.046, 65%); (0.050 g, 70%), respectively: mp 191-192 °C (ethanol); $[\alpha]_D$ -47.1° (*c* 0.44, chloroform); [lit. mp[25a] 190 °C, $[\alpha]_D$[25b] -37.4° (*c* 1.3, chloroform)]; *Rf.* 0.50 (tolune-ethyl acetate 6:5); ^{1}H NMR ($CDCl_3$) δ 1.96, 1.98, 2.00, 2.02, 2.06, 2.16 (7s, COCH_3), 3.52 (ddd, 1H, H-5'), 3.62 (ddd, 1H, H-5), 3.72 (dd, 1H, H-6'b), 3.76 (t, 1H, H-4), 4.00 (dd, 1H, H-6b), 4.08 (dd, 1H, H-6a), 4.32 (dd, 1H, H-6a'), 4.42-4.50 (m, 4H, 4.46 d, 1H, H-1' $J_{1',2'}$≈7.7), 4.52 (d, 1H, OCH_2), 4.80 (d, 1H, OCH_2), 4.88 (t, 1H), 4.88-5.16 (m, 3H, 4.92 d, 1H, H-1 $J_{1,2}$=7.8), 7.15-7.35 (m, 5H,

OCH_2Ph); ^{13}C NMR ($CDCl_3$) δ 20.68, 20.99 (7C, $COCH_3$), 61.83, 62.12 (C-6,6'), 68.13, 71.85 (3C), 72.18, 72.76, 72.96, 73.17 (C-2,3,4,5,2',3',4',5'), 70.93 (OCH_2Ph), 99.35 (C-1), 100.90 (C-1'), 127.94, 128.19, 128.63, (5C, *Ph*), 136.87 (*q*, *Ph*), 169.16, 169.45, 169.70 (7C, $COCH_3$).

Methyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-*O*-(2, 3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→2)-*O*-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside (15). **1c** (0.088 g, 0.10 mmol); **5c** (0.088 g, 0.10 mmol), 4Å pulverized molecular sieves (0.2 g) and methyl *O*-(3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranoside[26] (**10**) (0.037 g, 0.1 mmol) were suspended in dry dichloromethane (10 mL). TMSOTf (0.036 mL, 0.20 mmol) was dropwise added to the solution, and the reaction mixture was stirred for one hour. The reaction was worked up as described for **14**, and the crude product was purified by column chromatography (toluene-ethyl acetate 7:3→6:5) to give **15** (0.077 g, 50%), and (0.034 g, 36%), respectively: $[\alpha]_D$ -51.0° (*c* 0.36, chloroform); ^1H NMR ($CDCl_3$) δ 1.86, 1.98, 2.01, 2.02, 2.03, 2.09, 2.12 ($COCH_3$), 3.40 (ddd, 1H, H-5), 3.54 (s, 3H, OCH_3), 3.57 (ddd, 1H, H-5), 3.62-3.85 (m, 6H), 4.04 (dd, 1H, H-6), 4.11 (dd, 1H), 4.34 (dd, 1H, H-6), 4.38 (dd, 1H, H-6), 4.41 (d, 1H, H-1, $J_{1,2}$=7.2), 4.48 (dd, 1H), 4.52 (dd, 1H, H-1', $J_{1',2'}$=7.9 Hz), 4.68, 4.83 (2d, 2H, OCH_2Ph), 4.91 (d, 1H, H-1'' $J_{1'',2''}$=7.8 Hz), 4.93, 4.97 (2t, 2H), 5.06 (t, 1H), 5.12, 5.15 (2t, 2H), 5.57 (s, 1H, *CH*Ph), 7.26-7.46 (m, 10H, OCH_2Ph, CH*Ph*); ^{13}C NMR ($CDCl_3$) δ 20.49, 20.57, 20.81 (7C, $COCH_3$), 57.01 (OCH_3), 61.52, 61.99, (C-6',6''), 65.70, 67.74, 71.01, 71.59, 72.09, 72.78, 72.84, 72.94, 76.43, 80.50, 80.69, 81.42 (C-2,3,4,5,2',3',4',5',2'',3'',4'',5''), 68.70 (C-6), 72.24 (OCH_2Ph), 100.40, 100.78 (C-1',1''), 101.20 (*CH*Ph), 103.43 (C-1), 125.93, 127.93, 128.26, 128.35, 128.44, 129.02 (10C, *Ph*), 137.09, 137.99 (2*q*, *Ph*), 168.98, 169.25, 169.73, 170.16, (7C, $COCH_3$).

FAB-MS (mNBA) *m/z* [M+matrix] 1143.6.

Methyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-*O*-(2, 3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-*O*-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (16). To a solution of **1c** (0.198 g, 0.22 mmol), methyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside[27] (**11**) (0.091 g, 0.20 mmol) and powdered 4Å molecular sieves (0.5 g) in dry dichloromethane (10 mL), TMSOTf (0.058 mL, 0.30 mmol) was added dropwise. The reaction mixture was stirred for one hour and worked up as described previously. Column chromatography provided **16** (0.150 g, 70%): mp 206-208 °C (ethanol); $[\alpha]_D$ -10.6° (*c* 0.34, chloroform); ^1H NMR ($CDCl_3$) δ 1.93, 1.95, 1.98, 1.99, 2.00, 2.02, 2.08 ($COCH_3$), 3.12 (ddd, 1H, H-5), 3.33 (dd, 1H, H-5), 3.35 (dd, 1H), 3.38 (dd, 1H, H-6), 3.52 (dd, 1H), 3.55 (s, 3H, OCH_3), 3.65 (dd, 1H), 3.72 (m, 3H),

3.86 (t, 1H), 3.92 (dd, 1H), 4.01 (dd, 1H), 4.22 (dd, 1H), 4.26 (d, 1H, H-1 $J_{1,2}$=7.7 Hz), 4.36 (dd, 1H), 4.38 (d, 1H, H-1 $J_{1,2}$=7.7 Hz), 4.53 (d, 1H, OCH_2), 4.61 (d, 1H, H-1 $J_{1,2}$=7.7 Hz), 4.62 (d, 1H, OCH_2), 4.73, 4.74, 4.79, 4.80 (4d, 4H, OCH_2), 4.93, 4.97, 5.07, 5.08 (4t, 4H), 7.15-7.40 (m, 15H, *Ph*); ^{13}C NMR ($CDCl_3$) δ 20.53, 20.65, 20.70 (7C, COCH_3), 57.06 (s, 3H, OCH_3), 61.48, 61.78 (C-6',6"), 67.71, 71.43, 71.87, 72.17, 72.36, 72.90 (2C), 74.50, 76.17, 77.06, 81.62, 82.49 (C-2,3,4,5,2',3', 4',5',2",3",4",5"), 67.77 (C-6), 73.64, 74.61, 74.70 (OCH_2Ph), 99.83, 100.81 (C-1',1"), 104.59 (C-1), 126.92, 127.12, 127.50, 128.02, 128.08, 128.19, 128.60 (15C, OCH_2*Ph*), 137.83, 138.37, 139.28 (3*q*, OCH_2*Ph*), 169.00, 169.31, 169.48, 169.79, 170.20, 170.25, 170.50 (7C, *CO*CH_3).

FAB-MS (mNBA) *m/z* [M-H]$^-$ 1081.6, [M+matrix] 1235.6.

Methyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-*O*-(2, 3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1→6)-*O*-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (17). Glycosylation of methyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside[27,28] (**12**) (0.091 g, 0.20 mmol) with **1c** (0.198 g, 0.22 mmol) in dry dichloromethane (10 mL), in the presence 4Å molecular sieves (0.5 g) and TMSOTf (0.058 mL, 0.30 mmol) was carried out as described for compound **14** to give **17** (0.164 g, 76%): mp 70-72 °C (ethanol); $[\alpha]_D$ -77.8° (*c* 0.26, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.98, 2.01, 2.04, 2.08, 2.09 (7s, 21H, COCH_3), 3.36 (t, 1H), 3.40 (dd, 1H), 3.46 (ddd, 1H), 3.54 (ddd, 1H), 3.57 (s, 3H, OCH_3), 3.60-3.69 (m, 3H), 3.78 (t, 1H), 4.04 (dd, 1H), 4.08 (2dd, 2H), 4.27 (d, 1H, H-1 $J_{1,2}$=7.7 Hz), 4.38 (dd, 1H), 4.48-4.54 (m, 3H, incl. 4.49 d, 1H, H-1 $J_{1,2}$=7.9 Hz, 4.52 d, 1H, OCH_2), 4.60 (d, 1H, H-1 $J_{1,2}$=7.9 Hz), 4.69, 4.77, 4.84 (3d, 3H, OCH_2), 4.88-4.98 (m, 4H), 5.06 (t, 1H), 5.14 (m, 2H), 7.22-7.36 (m, 15H, *Ph*); ^{13}C NMR ($CDCl_3$) δ 20.54, 20.65, 20.71, 20.84 (7C, COCH_3), 57.18 (OCH_3), 61.52, 61.83, (C-6',6"), 68.28 (C-6), 67.75, 71.52, 71.57, 71.93, 72.63, 72.65, 72.91, 74.75, 76.36, 77.81, 82.19, 84.46 (C-2,3,4,5,2',3',4',5',2",3",4",5"), 74.75, 74.96, 75.68 (OCH_2Ph), 100.58, 100.81 (C-1',1"), 104.63 (C-1), 127.68, 127.88, 127.96, 128.09, 128.38, 128.52 (15C, OCH_2*Ph*), 137.81, 138.35, 138.40 (3*q* OCH_2*Ph*), 169.05, 169.31, 169.34, 169.84, 170.22, 170.31, 170.51 (7C, *CO*CH_3).

FAB-MS (mNBA) *m/z* [M-H]$^-$ 1081.5, [M+matrix] 1235.7.

(1*S*,3*S*)-3-acetyl-1,2,3,4,6,11-hexahydro-3,5,10,12-tetrahydroxy-6, 11-dioxo-1-naphthacenyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-*O*-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (18). TMSOTf (0.058 mL, 0.30 mmol) was added to the heterogeneous mixture of **1c** (0.198 g, 0.22 mmol), carminomycinone[29] (**13**) (0.077 g, 0.20 mmol) and powdered 4Å molecular sieves (0.5 g) in dry dichloromethane (10 mL). The reaction mixture was stirred at room temperature for

one hour. The reaction mixture was diluted with chloroform (50 mL), filtered through a pad of Celite, the filtrate was washed with water and concentrated. Column chromatography (toluene-methanol 99:1→95:5) gave **18** (0.188 g, 94%): $[\alpha]_D$ +8.8° (*c* 0.56, chloroform); ^{1}H NMR ($CDCl_3$) δ 1.84, 1.88, 1.94, 2.01, 2.03, 2.04, 2.08 2.42 (8s, 24H, CO*CH*$_3$), 2.94, 3.22 (2d, 2H, *CH*$_2$), 3.65 (2ddd, 2H), 3.72-3.82 (m, 2H, incl. *CH*$_2$), 4.04 (dd, 1H), 4.15 (m, 2H, *CH*$_2$), 4.36 (dd, 1H), 4.54 (d, 1H, H-1' $J_{1',2'}$=7.9), 4.68 (dd, 1H), 4.82-5.30 (m, 6H, 4.96 (d, 1H, H-1 $J_{1,2}$≈7.6), 7.30, 7.65, 7.86 (dd, t, 3H, *Ar*), 12.06, 12.90, 13.38 (3s, 3H, Ar*OH*); ^{13}C NMR ($CDCL_3$) δ 20.57, 20.68, 20.84 (7C, CO*CH*$_3$), 33.52, 34.66 (*C*$_{2,4}$ *anthracycline*), 61.45, 61.58 (C-6,6'), 67.77, 70.52, 71.54, 71.64, 71.93, 72.07, 72.91, 73.09, 76.40 (C-2,3,4,5,2',3',4',5' and *C*$_1$ *anthracycline*), 76.16 (*C*$_3$ *anthracycline*), 100.82, 101.75 (C-1,1', $J_{C1,H1}$=165 Hz β, $J_{C1',H1'}$=162 Hz β), 110.26, 111.50, 115.97, 132.32, 133.40, 137.93, 156.34, 156.87, 162.65 (*C*$_q$ *anthracycline*), 110.71, 124.86, 137.16 (*C*$_{7,8,9}$ *anthracycline*), 169.02, 169.33, 169.62, 169.72, 170.24, 170.29, 170.55 (*CO*CH$_3$), 186.16, 190.70 (*C*$_{6,11}$ *anthracycline*), 212.82 (*CO*CH$_3$ *anthracycline*).

FAB-MS (mNBA + NaOAc) *m/z* $[M-H]^-$ 1000.4, $[M+Na]^+$ 1024.6.

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