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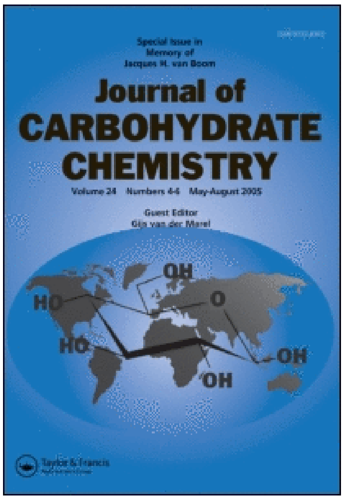

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PREPARATION OF PRIMARY AND SECONDARY AZIDOSUGARS FROM DIOLS USING THE DIOXAPHOSPHORANE METHODOLOGY

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ABSTRACT

Treatment of methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (**1**), methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside (**4**), 3-*O*-benzyl-1,2-*O*-(1-methylethylidene)-α-D-glucofuranose (**6**), 3-*O*-acetyl-1,2-*O*-(1-methylethylidene)-α-D-glucofuranose (**9**), 1,2-*O*-(1-methylethylidene)-α-D-xylofuranose (**11**) and methyl 2,3-di-*O*-acetyl-α-D-galactopyranoside (**15**) with diisopropylazodicarboxylate-triphenylphosphine in tetrahydrofuran led to the corresponding dioxaphosphoranes, which were opened by trimethylsilyl azide affording the silylated primary azidodeoxysugars. When the same reaction was performed on methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside (**20**), an inversion of the regioselectivity of the dioxaphosphorane opening was observed, leading mainly to the 4-azido-4-deoxy-α-D-glucopyranoside derivative **27**.

INTRODUCTION

Synthetic approaches to 6-azido-6-deoxy- and 4-azido-4-deoxysugars have been widely described, since these compounds are precursors of aminodeoxysugars which constitute part of antibiotics such as hybrimycin, ribostamycin, kanamycin[1,2] or glycocyanomoylspermidines[3] for example. More recently, 4-amino-4-deoxysugar derivatives have been used for the syntheses of 4-guanidinosugars[4] and β-lactams.[5] We have also prepared a series of amphiphilic 6-aminocarbonyl derivatives from 6-azido-6-deoxy-D-glucose.[6]

The present paper deals with the syntheses of primary 5- or 6-azidodeoxysugars as well as a secondary 4-azido-4-deoxysugar, by reacting triphenylphosphine-diisopropyl-azodicarboxylate (DIAD) and trimethylsilyl azide with appropriate diols.

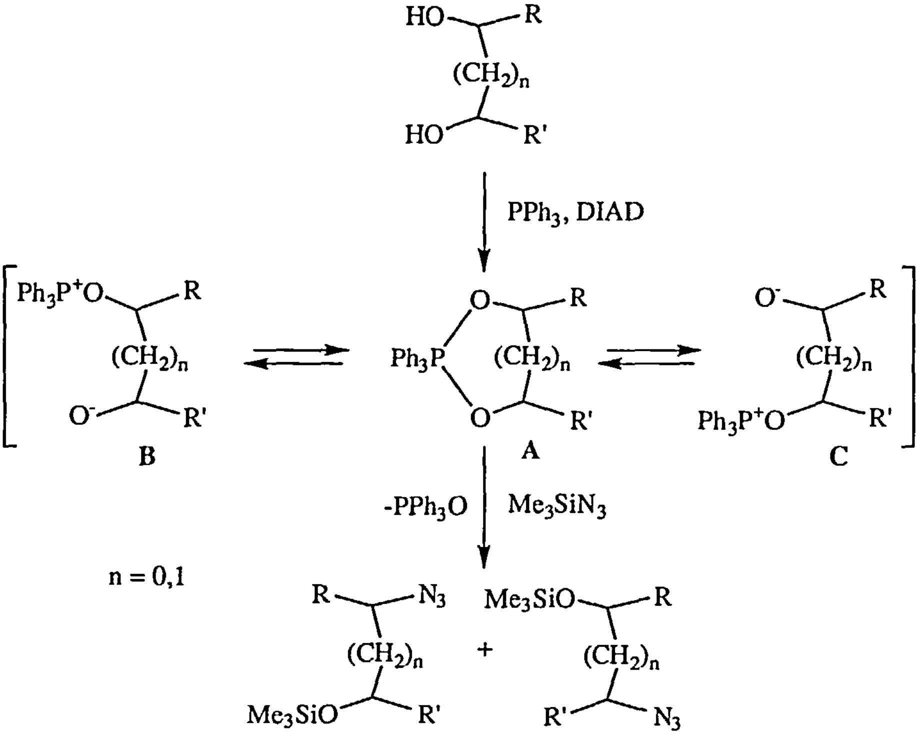
RESULTS AND DISCUSSION

Syntheses of primary azidodeoxysugars are well-documented in the literature. The 6-azido-6-deoxy derivatives are mostly obtained by nucleophilic displacement of leaving groups at C-6 (halogens[7-10] or sulfonates[11-13]) or by methods which involve an oxy-phosphonium type of activation, such as Mitsunobu reaction with diphenylphosphoryl azide[12] or zinc azide/bis-pyridine complex[14] as the nucleophile. Highly regioselective ring-opening of cyclic sulfites[15] or sulfates[12,16] with sodium azide have also been reported, affording 6-primary, as well as secondary azidodeoxysugar derivatives. On the other hand, 4-azido-4-deoxy-D-glucose derivatives are mainly obtained by displacement with sodium azide of 4-*O*-mesyl[17,18] or 4-*O*-triflyl-D-galactose[19] precursors.

E. Zbiral et al. have described the structural modifications of partly silylated carbohydrates, having two or three contiguous hydroxyl groups, with triphenylphosphine-DIAD and a nucleophile.[20,21] When the reaction was performed on methyl 2,6-bis-*O-tert*-butyldimethylsilyl-β-D-glucopyranoside, methyl 3-deoxy-3-halogeno-D-allopyranosides were obtained using triphenylphosphine hydrobromide or methyl iodide as nucleophiles whereas, in the corresponding α-series, methyl 4-deoxy-4-halogeno-D-galactopyranosides were formed. Methyl 3-azido-3-deoxy-D-allopyranoside was also obtained from methyl 6-*O-tert*-butyldimethylsilyl-β-D-glucopyranoside, using triphenylphosphine-DIAD and hydrazoic acid. These reactions proceed via a dioxaphosphorane intermediate (A) in equilibrium with two zwitterionic open forms (B and C). The regio- and stereoselectivity of the nucleophilic attack on the latter are governed by stereoelectronic factors (Scheme 1).

To our knowledge, this reaction was neither extended to the 4,6-diols in the hexopyranose series nor to the 5,6- or 3,5-diols in the hexo- or pentofuranoside series.

Treatment of methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[22] (1) with a slight excess of DIAD and triphenylphosphine in tetrahydrofuran, followed by addition of trimethylsilyl azide (2.5 eq) at 0 °C, afforded methyl 6-azido-2,3-di-*O*-benzyl-6-deoxy-4-*O*-trimethyl-silyl-α-D-glucopyranoside (2) in 88% yield. The reaction was assumed to proceed by the intermediate of a cyclic phosphorane[23] which was opened by attack of the azide at the less hindered C-6 with simultaneous silylation at O-4. Such a result was not unexpected, even though the same reaction performed on 1,2-propanediol affords the 2-azido-1-trimethylsilyloxypropane with a very high regioselectivity (>99%).[24] The attack of the nucleophile at the secondary position, in this latter example, is due to inductive effects which largely overcome steric hindrance. Desilylation of product **2** with potassium carbonate in methanol gave rise to methyl 6-azido-2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside[25] (**3**) in high yield. Similar results were obtained from methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside[26] (**4**) which was transformed into the 6-azido-4-*O*-silylated product **5** by the intermediate of a dioxaphophorane (^{31}P NMR δ -57.5 ppm in THF). 3-*O*-Benzyl-1,2-*O*-(1-methylethylidene)-α-D-glucofuranose[27] (**6**) or its 3-*O*-acetyl analogue[28] **9**, treated in the same conditions, afforded 6-azido-6-deoxy-5-*O*-trimethylsilyl products **7** and **10** with the same regioselectivity in 78% and 81% yields respectively. As observed with compound **1**, the reaction was regiospecific and only one compound was oberved by ^{1}H NMR of the crude reaction mixture. The regiospecificity of the reaction was again directed towards the less hindered primary position. Further desilylation of **7** afforded the azido-alcohol **8** already described in the literature.[29]



Scheme 1

Treatment of 1,2-*O*-(1-methylethylidene)-α-D-xylofuranose[30] (**11**) with triphenylphosphine-DIAD and trimethylsilyl azide led to 5-azido-5-deoxy-1,2-*O*-(1-methylethylidene)-3-*O*-trimethylsilyl-α-D-xylofuranose (**12**) accompanied with 10% of 1,2-*O*-(1-methylethylidene)-3,5-di-*O*-trimethylsilyl-α-D-xylofuranose (**13**). The latter could be the result of the silylation of the diol **11**, before the formation of the dioxaphosphorane adduct. The structure of **13** was ascertained by direct silylation of the diol **11** with trimethylsilyl triflate and triethylamine in dichloromethane. Desilylation of the mixture **12**/**13** afforded 5-azido-5-deoxy-1,2-*O*-(1-methylethylidene)-α-D-xylofuranose[31] (**14**) in 73% overall yield.

The azidosilylation of methyl 2,3-di-*O*-acetyl-α-D-galactopyranoside[32] (**15**) afforded a mixture of three compounds, *i. e.*, the expected 6-azido-6-deoxy-4-*O*-silylated derivative **16** (67%), the 6-azido-6-deoxy-3-*O*-silylated derivative **17** (7%) and the 4,6-di-*O*-silylated product **18** (9%). The formation of compound **17** results of the migration of the 3-*O*-acetyl group whereas that of **18** probably results of the silylation of diol **15** (scheme 2). Azidosilylation of methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside[18] (**20**), using a lower excess of trimethylsilyl azide (1.5 eq) proceeded quite differently and afforded a mixture from which the components (**20**-**23**) were separated only after desilylation (K_2CO_3 in methanol). The major compound (66% overall yield from **20**) was identified as methyl 4-azido-2,3-di-*O*-benzyl-4-deoxy-α-D-glucopyranoside (**23**)[18] and resulted of a nucleophilic attack with inversion at the secondary position C-4. The minor derivatives were shown to be methyl 4,6-diazido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-glucopyranoside (**21**) (3%), methyl 6-azido-2,3-di-*O*-benzyl-6-deoxy-α-D-galactopyranoside (**22**) (3%) and methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside (**20**) (3%). Compound **22** is the hydrolysed form of the azidosilyl adduct due to the attack of the nucleophile at C-6, whereas compound **20** is the hydrolyzed form of the 4,6-di-*O*-silyl intermediate **24**. The formation of the diazido derivative **21** could result from the slight excess of PPh_3-DIAD still present in the reaction mixture after a first nucleophilic attack. Silylation of compounds **20**, **22** and **23** to **24**, **26** and **27**, respectively, confirmed the formation of the three products during the reaction by comparison of their ^{13}C NMR spectra with that of the crude azidosilylation mixture.

The most striking feature concerns the regioselectivity of the nucleophilic attack in pyranose rings. The latter is directed towards the primary position in compounds **1**, **4** and **15**, whereas it is directed towards the secondary position in compound **20**. The explanation could lay in the geometry of the dioxaphosphorane rings (*e.g.*, **19**) or in the equilibrium between cyclic dioxaphosphorane and open phosphonium intermediates (*e.g.*, **19a** or **19b**). Nevertheless, ^{31}P NMR of reaction mixtures did not reveal any difference in the azidosilylation of **20** and the other pyranose 4,6-diols. In our opinion, that discrepancy is more probably due to the steric hindrance governing the approach of the nucleophile. The disfavoured axial attack of leaving groups at the C-4 position of D-*gluco* derivatives is well examplified and could explain the substitution at C-6 in compounds **1** and **4**. The equatorial substitution at C-4 of the dioxaphosphorane **25** (or phosphonium **25a**) is also in agreement with the usual equatorial attack at C-4 of D-*galacto* derivatives. The reverse regioselectivity observed in the 3-*O*-acetyl derivative **15** could, in our opinion, be explained by the participation of the acetyl group that shifts the phosphorane (**19**)/phosphonium (**19a** and **19b**) equilibrium to **19c**. Then, the substitution at C-6 results from a nucleophilic attack on the latter (scheme 2).

CONCLUSION

In conclusion, the use of triphenylphosphine-DIAD-trimethylsilylazide allows the preparation of primary azidodeoxysugars from primary-secondary diols, in good yields and with a high regioselectivity, in the D-*xylo* and D-*gluco* series. In the D-*galacto* series, the regioselectivity depends on the protecting groups at the neighbouring position. This one-pot methodology complements the other methods described in the literature and avoids the use of protection/deprotection steps for the regioselective azidations of unprotected diols.

EXPERIMENTAL

General methods. Tetrahydrofuran was dried by refluxing under argon with sodium-benzophenone prior to distillation. Methanol was refluxed with sodium methylate before distillation. Dichloromethane was washed with H_2SO_4 and water prior to distillation. Melting points were determined on a Büchi apparatus and were uncorrected. TLC analyses were performed on aluminium sheets coated with silica gel 60 F 254 Merck. Compounds were visualized by spraying the TLC plates with dilute 15 % aqueous sulfuric acid, followed by charring at 150 °C for a few minutes. Column chromatographies were performed on silica gel Geduran Si 60 Merck. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter in a 1 dm cell at 21 °C. ^1H and ^{13}C NMR spectra were recorded with Bruker AC-200 or AM-300 spectrometers operating at 200 or 300 MHz and 50 or 75.5 MHz respectively with tetramethylsilane as internal standard. Mass spectra were recorded on Finnigan MAT 95 XL spectrometer. Elemental analyses were carried out by the "Laboratoire Central d'Analyses du CNRS" (Vernaison, France).

General procedure for the azidosilylation reaction. To a suspension of the sugar (1.0 mmol) in dry THF (5 mL) were added successively diisopropylazodicarboxylate (203 µL, 1.05 mmol) and triphenylphosphine (0.275 g, 1.05 mmol). The mixture was stirred at rt for one hour, then cooled to 0 °C before addition of trimethylsilyl azide (328 µL, 2.5 mmol, unless otherwise stated). The solution was allowed to reach rt and stirring was maintained overnight. The reaction mixture was then poured into sat aq $NaHCO_3$ (20 mL) and the aqueous layer was extracted twice with CH_2Cl_2 (2x20 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude product which was purified by column chromatography.

General procedure for the desilylation reaction. To a solution of the silylated sugar (0.5-0.8 mmol) in dry MeOH (20 mL) was added anhydrous K_2CO_3 (0.5 g, 1.51 mmol). The mixture was stirred overnight, concentrated and the products were then extracted twice with CH_2Cl_2 (2x30 mL). The combined organic layers were washed with water (10 mL), dried (Na_2SO_4) and concentrated under reduced pressure to afford the crude product which was purified by column chromatography.

General procedure for the silylation reaction. To a solution of the sugar (0.20 mmol) in CH_2Cl_2 (5 mL), was added successively at -20 °C triethylamine (3 eq/OH) and trimethylsilyltrifluoromethane sulfonate (1.5 eq/OH). The solution was stirred for 16 h, then allowed to reach to rt and concentrated. The residue was applied at the top on a short column of silica-gel; elution with EtOAc/petroleum ether (1:4 v/v) afforded the pure product as an oil.

Methyl 6-Azido-2,3-di-*O*-benzyl-6-deoxy-4-*O*-trimethylsilyl-α-D-glucopyranoside (2). Obtained by the azidosilylation procedure described above from methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[22] (1). Purification by column chromatography (EtOAc/petroleum ether 1:5 v/v) afforded pure product **2** (0.410 g, 88% yield). Compound **2** : liquid; R_f 0.78 (EtOAc/petroleum ether 1:5 v/v); $[\alpha]_D$ +56.4° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.10 (s, 9 H, 3 CH_3Si), 3.34 (dd, 1 H, $J_{5,6b}$ = 5.3 Hz, $J_{6a,6b}$ = 12.8 Hz, H-6b), 3.40 (s, 3H, OCH_3), 3.41 (dd, 1 H, $J_{5,6a}$ = 2.5 Hz, H-6a), 3.50 (dd, 1 H, $J_{1,2}$ = 3.6 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 3.54 (dd, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 3.74 (m, 2 H, H-3,5), 4.49 (d, 1 H, H-1), 4.60 and 4.72 (2d, 2 H, J = 12.0 Hz, CH_2Ph), 4.74 and 5.01 (2d, 2 H, J = 11.3 Hz, CH_2Ph), 7.29-7.35 (m, 10 H, 2 C_6H_5); ^{13}C NMR ($CDCl_3$) δ 0.51 (3 C, 3 CH_3Si), 51.33 (C-6), 55.20 (OCH_3), 71.03, 71.71 (C-4,5), 73.25, 75.26 (2 C, 2 CH_2Ph), 81.20, 81.39 (C-2,3), 97.91 (C-1), 127.15-128.36, 137.96, 138.91 (12 C, 2 C_6H_5).

Anal. Calcd for $C_{24}H_{33}N_3O_9Si$ (471.61): C, 61.11; H, 7.05; N, 8.91. Found: C, 60.90; H, 7.22; N, 8.67.

Methyl 6-Azido-2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (3). Obtained as described above from methyl 6-azido-2,3-di-*O*-benzyl-6-deoxy-4-*O*-trimethylsilyl-α-D-glucopyranoside (2) (0.377 g, 0.80 mmol). Purification by column chromatography (EtOAc/petroleum ether 1:2 v/v) afforded pure product 3 (0.303 g, 95% yield). Compound 3[25] : liquid; R_f 0.85 (EtOAc/petroleum ether 1:2 v/v); $[\alpha]_D$ +13.8° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.23 (d, 1 H, $J_{4,OH}$ = 2.3 Hz, O*H*), 3.35-3.45 (m, 5 H, H-6a,6b, OCH_3), 3.47 (dd, 1 H, $J_{3,4}$ = 9.0 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.54 (dd, 1 H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 3.72 (m, 1 H, H-5), 4.66 (d, 1 H, H-1), 4.68 and 4.79 (2d, 2 H, J = 12.0 Hz, CH_2Ph), 4.69 and 5.05 (2d, 2 H, J = 11.5 Hz, CH_2Ph), 7.29-7.35 (m, 10 H, 2 C_6H_5); ^{13}C NMR ($CDCl_3$) δ 51.59 (C-6), 55.46 (OCH_3), 70.41, 70.76 (C-4,5), 73.17, 75.43 (2 C, 2 CH_2Ph), 79.90, 81.19 (C-2,3), 98.14 (C-1), 128.03-128.72, 138.00, 138.73 (12 C, 2 C_6H_5).

Methyl 2,3-Di-*O*-acetyl-6-azido-6-deoxy-4-*O*-trimethylsilyl-α-D-glucopyranoside (5). Obtained as described above from methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside[26] (4) (0.278 g, 1.00.mmol). Purification by column chromatography (EtOAc/petroleum ether 1:3 v/v) afforded pure product 5 (0.311 g, 83% yield). Compound 5 : liquid; R_f 0.76 (EtOAc/petroleum ether 1:3 v/v); $[\alpha]_D$ +116.5° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.10 (s, 9 H, 3 CH_3Si), 2.07 (s, 6 H, 2 CH_3COO), 3.37 (dd, 1 H, $J_{5,6b}$ = 4.8 Hz, $J_{6a,6b}$ = 13.1 Hz, H-6b), 3.42 (s, 3H, OCH_3), 3.52 (dd, 1 H, $J_{5,6a}$ = 2.3 Hz, H-6a), 3.73 (dd, 1 H, $J_{3,4}$ = 8.5 Hz, $J_{4,5}$ = 9.5 Hz, H-4), 3.83 (ddd, 1 H, H-5), 4.81 (dd, 1 H, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.1 Hz, H-2), 4.90 (d, 1 H, H-1), 5.37 (dd, 1 H, H-3); ^{13}C NMR ($CDCl_3$) δ 0.27 (3 C, 3 CH_3Si), 20.64, 21.01 (2 C, 2 CH_3COO), 50.88 (C-6), 55.22 (CH_3O), 70.14, 70.94, 71.20, 72.40 (4 C, C-2,3,4,5), 96.85 (C-1), 169.59, 170.20 (2 C, 2 CH_3CO).

Anal. Calcd for $C_{14}H_{25}N_3O_7Si$ (375.45): C, 44.78; H, 6.71; N, 11.19. Found: C, 44.85; H, 6.94; N, 10.83.

6-Azido-3-*O*-benzyl-6-deoxy-1,2-*O*-(1-methylethylidene)-5-*O*-trimethylsilyl-α-D-glucofuranose (7). Obtained as described above from 3-*O*-benzyl-1,2-*O*-(1-methylethylidene)-α-D-glucofuranose[27] (6) (0.310 g, 1.0 mmol). Purification by column chromatography (EtOAc/petroleum ether 1:4 v/v) afforded pure product 7 (0.318 g, 78% yield). Compound 7 : liquid; R_f 0.70 (EtOAc/petroleum ether 1:4 v/v); $[\alpha]_D$ -43.1° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.13 (s, 9 H, 3 CH_3Si), 1.32, 1.52 (2s, 6 H, 2 CH_3C), 3.39 (ddd, 1 H, $J_{4,6b} = J_{5,6b}$ = 2.1 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6b), 3.59 (bd, 1 H, $J_{5,6a}$ < 1.0 Hz, H-6a), 4.05 (bs, 1 H, H-3), 4.19 (bs, 2 H, H-4,5), 4.60 (d, 1 H, $J_{1,2}$

= 3.7 Hz, H-2), 4.57 and 4.69 (2d, 2 H, J = 11.6 Hz, CH_2Ph), 5.87 (d, 1 H, H-1), 7.30-7.40 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 0.49 (3 C, 3 CH$_3$Si), 26.40, 26.88 (2 C, 2 CH$_3$C), 55.23 (C-6), 68.62 (C-5), 71.70 (CH$_2$Ph), 80.70, 81.35, 81.76 (C-2,3,4), 105.12 (C-1), 111.97 (C(CH_3)$_2$), 127.38-128.53, 137.55 (C_6H$_5$).

Anal. Calcd for $C_{19}H_{29}N_3O_5Si$ (407.53): C, 56.00; H, 7.17; N, 10.31. Found: C, 56.32; H, 6.91; N, 10.28.

6-Azido-3-*O*-benzyl-6-deoxy-1,2-*O*-(1-methylethylidene)-α-D-glucofuranose (8). Obtained as described above from 6-azido-3-*O*-benzyl-6-deoxy-1,2-*O*-(1-methylethylidene)-5-*O*-trimethylsilyl-α-D-glucofuranose (7) (0.265 g, 0.65 mmol). Purification by column chromatography (EtOAc/petroleum ether 1:2 v/v) afforded pure product **8**[29] (0.207 g, 95% yield). Compound **8** : liquid; R_f 0.35 (EtOAc/ petroleum ether 1:4 v/v); $[\alpha]_D$ -61.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.34, 1.50 (2s, 6 H, 2 CH_3C), 2.32 (d, 1 H, $J_{5,OH}$ = 3.3 Hz, H-5), 3.42 (m, 1 H, H-6b), 3.56 (dd, 1 H, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a), 4.11 (bs, 3 H, H-3,4,5), 4.64 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-2), 4.54 and 4.75 (2d, 2 H, J = 11.8 Hz, CH_2Ph), 5.93 (d, 1 H, H-1), 7.32-7.42 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 26.34, 26.87 (2 C, 2 CH$_3$C), 54.65 (C-6), 68.40 (C-5), 72.13 (CH$_2$Ph), 80.11, 81.67, 82.15 (C-2,3,4), 105.26 (C-1), 112.02 (C(CH_3)$_2$), 127.93-128.80, 137.21 (C_6H$_5$).

3-*O*-Acetyl-6-azido-6-deoxy-1,2-*O*-(1-methylethylidene)-5-*O*-trimethylsilyl-α-D-glucofuranose (10). Obtained as described above from 3-*O*-acetyl-1,2-*O*-(1-methylethylidene)-α-D-glucofuranose[28] (9) (0.262 g, 1.0 mmol). Purification by column chromatography (EtOAc/petroleum ether 1:4 v/v) afforded pure product **10** (0.318 g, 81% yield). Compound **10** : liquid; R_f 0.70 (EtOAc/petroleum ether 1:4 v/v); $[\alpha]_D$ -37.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9 H, 3 CH_3Si), 1.30, 1.52 (2s, 6 H, 2 CH_3C), 2.11 (s, 3 H, CH_3COO), 3.35 (ddd, 1 H, $J_{5,6a}$ = 2.6 Hz, $J_{5,6b}$ = 5.4 Hz, $J_{6a,6b}$ = 12.6 Hz, H-6b), 3.59 (dd, 1 H, H-6a), 4.05 (ddd, 1 H, $J_{4,5}$ = 8.8 Hz, H-5), 4.05 (ddd, 1 H, $J_{4,5}$ = 8.8 Hz, H-5), 4.24 (dd, 1 H, $J_{3,4}$ = 2.7 Hz, H-3), 4.48 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-2), 5.17 (d, 1 H, H-3), 5.84 (d, 1 H, H-1); ^{13}C NMR ($CDCl_3$) δ 0.12 (3 C, 3 CH$_3$Si), 20.90 (CH_3COO), 26.16, 26.57 (2 C, 2 CH$_3$C), 54.92 (C-6), 68.53 (C-5), 76.00 (C-3), 78.72 (C-4), 82.88 (C-2), 104.71 (C-1), 112.22 (C(CH_3)$_2$), 169.40 ($CH_3$$C$O).

Anal. Calcd for $C_{14}H_{25}N_3O_6Si$ (359.45): C, 46.78; H, 7.01; N, 11.69. Found: C, 46.69; H, 6.89; N, 11.49.

5-Azido-5-deoxy-1,2-*O*-(1-methylethylidene)-3-*O*-trimethylsilyl-α-D-xylofuranose (12) and 1,2-*O*-(1-methylethylidene)-3,5-di-*O*-trimethylsilyl-α-D-xylofuranose (13). Obtained as described above from 1,2-*O*-(1-methylethylidene)-α-D-xylofuranose[30] (**11**) (0.190 g, 1.0 mmol). The crude product was purified by column chromatography (EtOAc/petroleum ether 1:5 v/v) to afford products **12** and **13** as an inseparable mixture (0.274 g). Compound **12** : liquid; R_f 0.75 (EtOAc/petroleum ether 1:5 v/v); ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9 H, 3 CH_3Si), 1.30, 1.48 (2s, 6 H, 2 CH_3C), 3.35 (dd, 1 H, $J_{4,5b}$ = 2.6 Hz, $J_{5,6b}$ = 6.5 Hz, $J_{6a,6b}$ = 12.3 Hz, H-5b), 3.55 (dd, 1 H, $J_{4,5a}$ = 6.5 Hz, H-5a), 4.15 (d, 1 H, $J_{3,4}$ = 2.7 Hz, H-3), 4.23 (ddd, 1 H, H-4), 4.36 (dd, 1 H, $J_{1,2}$ = 3.6 Hz, H-2), 5.90 (d, 1 H, H-1); ^{13}C NMR ($CDCl_3$) δ -0.21 (3 C, 3 CH_3Si), 26.26, 26.80 (2 C, 2 CH_3C), 49.29 (C-5), 75.13 (C-3), 79.11 (C-4), 85.41 (C-2), 105.00 (C-1), 111.77 ($C(CH_3)_2$).

Compound **13** was also synthesized by direct silylation of the diol **11**: liquid; $[\alpha]_D$ -40.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.12, 0.15 (2s, 18 H, 6 CH_3Si), 1.32, 1.51 (2s, 6 H, 2 CH_3C), 3.73 (d, 2 H, $J_{5,6a}$ = $J_{5,6b}$ = 6.3 Hz, H-5a,5b), 4.20 (m, 2 H, H-3,4), 4.36 (dd, 1 H, $J_{1,2}$ = 3.6 Hz, H-2), 5.91 (d, 1 H, H-1); ^{13}C NMR ($CDCl_3$) δ -0.62, -0.21 (6 C, 2 CH_3Si), 26.35, 26.85 (2 C, 2 CH_3C), 59.49 (C-5), 75.29 (C-3), 81.09 (C-4), 85.56 (C-2), 105.00 (C-1), 111.51 ($C(CH_3)_2$).

Anal. Calcd for $C_{14}H_{30}O_5Si_2$ (334.55): C, 50.26; 9.04. Found: C, 50.73; H, 8.89.

5-Azido-5-deoxy-1,2-*O*-(1-methylethylidene)-α-D-xylofuranose (14). Obtained by the desilylation procedure from the mixture of **12** and **13** (0.274 g). The crude product was purified by column chromatography (EtOAc/petroleum ether 1:1 v/v) to afford the pure product **14** (0.158 g) in 73% yield [calculated from 1,2-*O*-(1-methylethylidene)-α-D-xylofuranose]. Compound **14** : mp 61-62 °C (lit.[31] mp 58.5-60 °C); R_f 0.72 (EtOAc/petroleum ether 1:1 v/v); $[\alpha]_D$ -34.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.32, 1.50 (2s, 6 H, 2 CH_3C), 2.39 (d, 1 H, $J_{3,OH}$ = 4.3 Hz, O*H*), 3.58 (dd, 1 H, $J_{4,5b}$ = 2.8 Hz, $J_{5,6b}$ = 6.3 Hz, $J_{6a,6b}$ = 12.3 Hz, H-5b), 3.65 (dd, 1 H, $J_{4,5a}$ = 6.3 Hz, H-5a), 4.26 (dd, 1 H, $J_{3,4}$ = 2.8 Hz, H-3), 4.29 (ddd, 1 H, H-4), 4.52 (dd, 1 H, $J_{1,2}$ = 3.7 Hz, H-2), 5.96 (d, 1 H, H-1); ^{13}C NMR ($CDCl_3$) δ 26.16, 26.71 (2 C, 2 CH_3C), 49.19 (C-5), 74.90 (C-3), 78.63 (C-4), 85.36 (C-2), 104.81 (C-1), 112.05 ($C(CH_3)_2$).

Methyl 2,3-di-*O*-acetyl-6-azido-6-deoxy-4-*O*-trimethylsilyl-α-D-galactopyranoside (16), methyl 2,4-di-*O*-acetyl-6-azido-6-deoxy-3-*O*-trimethylsilyl-α-D-galactopyranoside (17) and methyl 2,3-di-*O*-acetyl-4,6-di-*O*-trimethylsilyl-α-D-galactopyranoside (18). Obtained by the azidosilylation procedure from methyl 2,3-di-*O*-acetyl-α-D-galactopyranoside[32] (**15**) (0.278 g, 1.0 mmol). Purification by column chromatography (EtOAc/petroleum ether 1:3 v/v) afforded a fraction of two compounds (R_f 0.74), plus pure product **16** (R_f 0.64).

16 : 0.252 g (67% yield) ; white solid, mp 92-93 °C; R_f 0.54 (EtOAc/petroleum ether 1:3 v/v); $[\alpha]_D$ +112.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9 H, 3 CH_3Si), 2.08 (s, 6 H, 2 CH_3COO), 3.16 (dd, 1 H, $J_{5,6a}$ = 5.3 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 3.43 (s, 3 H, CH_3O), 3.53 (dd, 1 H, $J_{5,6a}$ = 7.9 Hz, H-6a), 3.94 (ddd, 1 H, $J_{4,5}$ = 0.5 Hz, H-5), 4.09 (dd, 1 H, $J_{3,4}$ = 2.3 Hz, H-4), 4.98 (dd, 1 H, $J_{1,2}$ = 2.8 Hz, H-1), 5.20 (dd, 1 H, $J_{2,3}$ = 10.8 Hz, H-2), 5.31 (dd, 1 H, H-3); ^{13}C NMR ($CDCl_3$) δ 0.22 (3 C, 3 CH_3Si), 20.75, 20.90 (2 C, 2 CH_3COO), 51.10 (C-6), 55.36 (CH_3O), 68.21, 69.47, 69.83, 69.85 (4 C, C-2,3,4,5), 97.28 (C-1), 169.87, 170.21 (2 C, 2 CH_3CO).

Anal. Calcd for $C_{14}H_{25}N_3O_7Si$ (375.45): C, 44.78; H, 6.71; N, 11.19. Found: C, 44.54; H, 6.75; N, 11.14.

A new chromatographic separation of the first fraction (R_f 0.74) using ether/petroleum ether (3:4 v/v) as the eluent allowed the isolation of compounds **17** and **18**.

17 : 0.028 g (7%); liquid; R_f 0.69 (ether/petroleum ether 1:1 v/v); $[\alpha]_D$ +84.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.11, 0.13 (2s, 18 H, 6 CH_3Si), 2.07, 2.08 (2s, 6 H, 2 CH_3COO), 3.38 (s, 3 H, CH_3O), 3.61 (d, 2 H, $J_{5,6a}$ = $J_{5,6b}$ = 6.9 Hz, H-6a,6b), 3.79 (dt, 1 H, $J_{4,5}$ = 1.1 Hz, H-5), 4.20 (dd, 1 H, $J_{3,4}$ = 2.2 Hz, H-4), 4.95 (d, 1 H, $J_{1,2}$ = 2.8 Hz, H-1), 5.21 (dd, 1 H, $J_{2,3}$ = 10.8 Hz, H-2), 5.28 (dd, 1 H, H-3); ^{13}C NMR ($CDCl_3$) δ -0.10 (3 C, 3 CH_3Si), 20.76, 20.91 (2 C, 2 CH_3COO), 51.15 (C-6), 55.59 (CH_3O), 66.63, 68.21, 71.35, 71.53 (4 C, C-2,3,4,5), 97.42 (C-1), 170.50, 170.55 (2 C, 2 CH_3CO).

Anal. Calcd for $C_{14}H_{25}N_3O_7Si$ (375.45): C, 44.78; H, 6.71; N, 11.19. Found: C, 44.57; H, 6.51; N, 10.70.

18 : 0.040 g (9%); liquid; R_f 0.60 (ether/petroleum ether 1:1 v/v); $[\alpha]_D$ +113.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H, 3 CH_3Si), 2.11, 2.14 (2s, 6 H, 2 CH_3COO), 3.15 (dd, 1 H, $J_{5,6a}$ = 3.9 Hz, $J_{6a,6b}$ = 12.9 Hz, H-6b), 3.40 (s, 3 H, CH_3O), 3.45 (dd, 1 H, $J_{5,6a}$ = 8.6 Hz, H-6a), 4.04 (ddd, 1 H, $J_{4,5}$ = 1.1 Hz, H-5), 4.13 (dd, 1 H, $J_{2,3}$ = 9.9 Hz, $J_{3,4}$ = 3.7 Hz, H-3), 4.92 (dd, 1 H, $J_{1,2}$ = 3.6 Hz, H-2), 5.00 (dd, 1 H, H-1), 5.20 (dd, 1 H, H-4).

Anal. Calcd for $C_{17}H_{34}O_8Si_2$ (422.57): C, 48.32; H, 8.11. Found: C, 48.29; H, 8.03.

Methyl 4,6-diazido-2,3-di-*O*-benzyl-4,6-dideoxy-α-D-glucopyranoside (21), methyl 6-azido-2,3-di-*O*-benzyl-6-dideoxy-α-D-galactopyranoside (22) and methyl 4-azido-2,3-di-*O*-benzyl-4-deoxy-α-D-glucopyranoside (23). Methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside[18] (20) (0.562 g, 1.50 mmol) was reacted as described above, using a smaller excess of trimethylsilyl azide (1.5 eq instead of 2.5 eq). After usual treatment, the crude mixture was applied at the top of a small silica gel column (EtOAc/petroleum ether 1:4 v/v) in order to separate the reaction products (R_f 0.62-0.75) from triphenylphosphine oxide and diisopropyloxycarbonylhydrazine. The fraction containing the mixture of sugars was concentrated and treated overnight with potassium carbonate (0.500 g) in MeOH (25 mL). MeOH was then evaporated and the residue was dissolved in CH_2Cl_2 (50 mL), and washed with water (10 mL). After drying (Na_2SO_4) and evaporation the organic extract afforded a mixture of four compounds which were purified by column chromatography (EtOAc/petroleum ether 1:4 v/v, then 1:1 v/v, then 2:1 v/v). Compounds **21**, **22**, **23** and **20** (0.015 g, 3%) were successively eluted.

21 (0.020 g 3% yield) : liquid; R_f 0.62 (EtOAc/petroleum ether 1:4 v/v); $[\alpha]_D$ +109.1° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 3.41 (s, 3 H, CH_3O), 3.39-3.46 (m, 3 H, H-4,6a,6b), 3.57 (dd, 1 H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H-2) 3.64 (ddd, 1 H, $J_{4,5}$ = 10.2 Hz, $J_{5,6a}$ = 2.5 Hz, $J_{5,6b}$ = 5.3 Hz, H-5), 3.90 (dd, 1 H, $J_{3,4}$ = 9.2 Hz, H-3), 4.64 (d, 1 H, H-1), 4.66 and 4.80 (2d, 2 H, J = 12.0 Hz, CH_2Ph), 4.83 and 4.99 (2d, 2 H, J = 10.5 Hz, CH_2Ph), 7.31-7.40 (m, 10 H, 2 C_6H_5); ^{13}C NMR ($CDCl_3$) δ 51.83 (C-6), 55.68 (OCH_3), 62.50 (C-4), 69.20 (C-5), 73.43, 75.83 (2 C, 2 CH_2Ph), 79.85, 79.94 (C-2,3), 98.21 (C-1), 128.15-128.64, 137.85, 137.95 (12 C, 2 C_6H_5). HRMS Calcd for $C_{21}H_{25}N_4O_4$ ($MH-N_2$): 397.18758. Found: 397.18764.

Anal. Calcd for $C_{21}H_{24}N_6O_4$ (424.44): C, 59.42; H, 5.70; N, 19.80. Found: C, 59.11; H, 5.89; N, 19.07.

22 (0.020 g, 3% yield) : mp 65-66 °C; R_f 0.81 (EtOAc/petroleum ether 1:1 v/v); $[\alpha]_D$ +20.0° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 3.27 (dd, 1 H, $J_{5,6b}$ = 4.5 Hz, $J_{6a,6b}$ = 12.7 Hz, H-6b), 3.41 (s, 3 H, CH_3O), 3.61 (dd, 1 H, $J_{5,6a}$ = 6.2 Hz, H-6a), 3.84 (dd, 1 H, $J_{1,2}$ = 3.3 Hz, $J_{2,3}$ = 9.3 Hz, H-2), 3.87 (dd, 1 H, $J_{3,4}$ = 3.0 Hz, H-3) 3.88 (ddd, 1 H, $J_{4,5}$ = 1.0 Hz, H-5), 3.92 (dd, 1 H, H-4), 4.70 (d, 1 H, H-1), 4.68 and 4.83 (2d, 2 H, J = 12.3 Hz, CH_2Ph), 4.71 and 4.84 (2d, 2 H, J = 11.4 Hz, CH_2Ph), 7.29-7.39 (m, 10 H, 2 C_6H_5); ^{13}C NMR ($CDCl_3$) δ 51.31 (C-6), 55.55 (OCH_3), 68.25, 68.87 (C-4,5), 73.14, 75.58 (2 C, 2 CH_2Ph), 75.61, 77.36 (C-2,3), 98.61 (C-1), 127.94-128.63, 138.02, 138.30 (12 C, 2 C_6H_5).

Anal. Calcd for $C_{21}H_{25}N_3O_5$ (399.43): C, 63.14; H, 6.31; N, 10.52. Found: C, 63.46; H, 6.44; N, 10.34.

23[18] (0.395 g, 66% yield) : liquid; R_f 0.56 (EtOAc/petroleum ether 1:1 v/v); $[\alpha]_D$ +97.8° (*c* 1.0, $CHCl_3$) (lit.[18] $[\alpha]_D$ +90°) ; ^1H NMR ($CDCl_3$) δ 1.78 (t, 1 H, $J_{6a,OH} = J_{6b,OH}$ = 5.9 Hz, 3.36 (s, 3 H, CH_3O), 3.48 (m, 1 H, H-5), 3.51 (dd, 1 H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 3.52 (dd, 1 H, $J_{3,4}$ = 9.5 Hz, H-3), 3.71 (ddd, 1 H, $J_{5,6b}$ = 5.1 Hz, $J_{6a,6b}$ = 11.0 Hz, H-6b), 3.80 (ddd, 1 H, $J_{5,6a}$ = 2.4 Hz, H-6a), 3.95 (dd, 1 H, $J_{4,5}$ = 9.5 Hz, H-4), 4.58 (d, 1 H, H-1), 4.65 and 4.80 (2d, 2 H, J = 10.6 Hz, CH_2Ph), 4.83 and 4.97 (2d, 2 H, J = 10.6 Hz, CH_2Ph), 7.29-7.41 (m, 10 H, 2 C_6H_5); ^{13}C NMR ($CDCl_3$) δ

55.49 (OCH_3), 61.57 (C-4), 61.96 (C-6), 70.70 (C-5), 73.39, 75.77 (2 C, 2 CH_2Ph), 79.96, 80.00 (C-2,3), 98.31 (C-1), 127.92-128.61, 137.94, 138.09 (12 C, 2 C_6H_5).

Methyl 2,3-di-*O*-benzyl-4,6-bis-*O*-trimethylsilyl-α-D-galactopyranoside (24). The general silylation procedure was applied to 20[18] (0.075 g, 0.20 mmol). Compound 23 (0.093 g, 90% yield) was recovered as a colorless liquid : R_f 0.72 (EtOAc/petroleum ether 1:4 v/v); $[\alpha]_D$ +30.8° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.10 and 0.13 (2s, 18 H, 6 CH_3Si), 3.40 (s, 3 H, CH_3O), 3.57 (dd, 1 H, $J_{5,6b}$ = 5.9 Hz, $J_{6a,6b}$ = 8.9 Hz, H-6b), 3.66 (bd, 1 H, H-6a), 3.73 (bd, 1 H, H-5), 3.81 (dd, 1 H, $J_{2,3}$ = 10.1 Hz, $J_{3,4}$ = 2.6 Hz, H-3), 3.93 (dd, 1 H, $J_{1,2}$ = 3.4 Hz, H-2), 4.18 (dd, 1 H, $J_{4,5}$ = 0.7 Hz, H-4), 4.71 (d, 1 H, H-1), 4.69 and 4.82 (2d, 2 H, J = 12.3 Hz, CH_2Ph), 4.74 and 4.86 (2d, 2 H, J = 11.4 Hz, CH_2Ph), 7.28-7.37 (m, 10 H, 2 C_6H_5); ^{13}C NMR ($CDCl_3$) δ -0.46 and 0.60 (2s, 6 C, 6 CH_3Si), 55.33 (OCH_3), 61.10 (C-6), 69.61, 71.14 (C-4,5), 73.37, 73.73 (2 C, 2 CH_2Ph), 75.98, 76.47 (C-2,3), 98.94 (C-1), 127.45-128.40, 138.60, 138.76 (12 C, 2 C_6H_5). HRMS Calcd for $C_{24}H_{42}O_6Si_2$: 518.25199. Found: 518.25.019.

Anal. Calcd for $C_{27}H_{42}O_6Si_2$ (518.78): C, 62.51; H, 8.16. Found: C, 61.84; H, 8.07.

Methyl 6-azido-2,3-di-*O*-benzyl-6-deoxy-4-*O*-trimethylsilyl-α-D-galactopyranoside (26). Obtained, as described above, from 22 (0.080 g, 0.20 mmol) as a colorless liquid (0.086 g, 91% yield) : R_f 0.66 (EtOAc/petroleum ether 1:4 v/v); $[\alpha]_D$ +30.8° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.14 (s, 9 H, 3 CH_3Si), 3.15 (dd, 1 H, $J_{5,6b}$ = 5.3 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6b), 3.48 (s, 3 H, CH_3O), 3.50 (ddd, 1 H, $J_{5,6a}$ = 7.9 Hz, H-6a), 3.81 (dd, 1 H, $J_{2,3}$ = 10.1 Hz, $J_{3,4}$ = 2.5 Hz, H-3), 3.82 (m, 1 H, H-5), 3.91 (dd, 1 H, $J_{1,2}$ = 3.3 Hz, H-2), 4.02 (m, 1 H, H-4), 4.71 (d, 1 H, H-1), 4.67 and 4.83 (2d, 2 H, J = 12.1 Hz, CH_2Ph), 4.73 and 4.87 (2d, 2 H, J = 11.3 Hz, CH_2Ph), 7.30-7.35 (m, 10 H, 2 C_6H_5); ^{13}C NMR ($CDCl_3$) δ - 0.60 (s, 3 C, 3 CH_3Si), 51.49 (C-6), 55.56 (OCH_3), 70.15 (C-4), 70.79 (C-5), 73.42, 74.02 (2 C, 2 CH_2Ph), 75.63, 77.58 (C-2,3), 98.94 (C-1), 127.61-128.47, 138.39, 138.44 (12 C, 2 C_6H_5).

Anal. Calcd for $C_{24}H_{33}N_3O_5Si$ (471.61): C, 61.12; H, 7.05; N, 8.91. Found: C, 61.16; H, 7.23; N, 8.67.

Methyl 4-azido-2,3-di-*O*-benzyl-4-deoxy-6-*O*-trimethylsilyl-α-D-glucopyranoside (27). Obtained, as described above, from 23 (0.080 g, 0.20 mmol) as a colorless liquid (0.088 g, 93 % yield) : R_f 0.66 (EtOAc/petroleum ether 1:4 v/v); $[\alpha]_D$ +77.1° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.14 (s, 9 H, 3 CH_3Si), 3.37 (s, 3 H, CH_3O), 3.44 (ddd, 1 H, $J_{4,5}$ = 10.2 Hz, $J_{5,6a}$ = 3.2 Hz, $J_{5,6b}$ = 1.8 Hz, H-5), 3.50 (dd, 1 H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.5 Hz, H-2), 3.61 (dd, 1 H, $J_{3,4}$ = 9.5 Hz, H-4), 3.75 (dd, 1

H, $J_{6a,6b}$ = 11.5 Hz, H-6b), 3.84 (ddd, 1 H, H-6a), 3.90 (dd, 1 H, H-3), 4.64 (d, 1 H, H-1), 4.65 and 4.80 (2d, 2 H, J = 12.1 Hz, CH_2Ph), 4.83 and 4.99 (2d, 2 H, J = 10.5 Hz, CH_2Ph), 7.31-7.44 (m, 10 H, 2 C_6H_5); ^{13}C NMR ($CDCl_3$) δ -0.47 (s, 3 C, 3 CH_3Si), 55.37 (OCH_3), 61.29 (C-4), 61.65 (C-6), 70.28 (C-5), 73.38, 75.86 (2 C, 2 CH_2Ph), 79.90, 80.22 (C-2,3), 98.33 (C-1), 127.93-128.53, 138.02, 138.14 (12 C, 2 C_6H_5).

Anal. Calcd for $C_{24}H_{33}N_3O_5Si$ (471.61): C, 61.12; H, 7.05; N, 8.91. Found: C, 61;13; H, 6.89; N, 8.77.

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