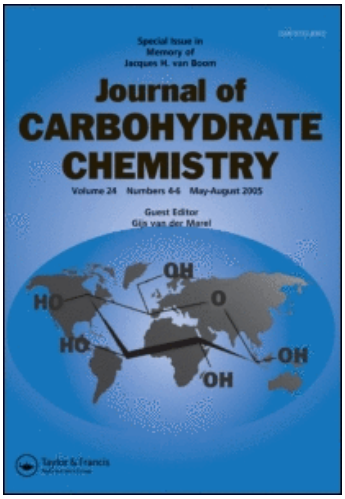

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Synthesis of α,ω-Diazidoalditol Derivatives via Both *bis*- or *tris*-Cyclic Sulfites and Peracetylated α,ω-Dibromoalditols as Bielectrophilic Intermediates

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ABSTRACT

The α,ω-diazidoalditol derivatives with *erythro*, *threo*, *xylo*, *ribo*, D-*arabino*, D-*manno*, and D-*gluco* configuration were efficiently synthesized, respectively, from *bis*- or *tris*-cyclic sulfite or peracetylated α,ω-dibromoalditol intermediates. The cyclic sulfite intermediates has the advantage to lead directly to the free α,ω-diazido-α,ω-dideoxyalditols.

Key Words: Diazidoalditol; Anhydroalditol; Dibromoalditol; Cyclic sulfite; Bielectrophilic intermediate; Azidation.

INTRODUCTION

The α,ω-diazidoalditol derivatives are potential precursors of corresponding diamino derivatives used as copolymers in polyamide syntheses,[1] chelating reagents,[2] and inhibitors of HIV-1 retrovirus proteases.[3]

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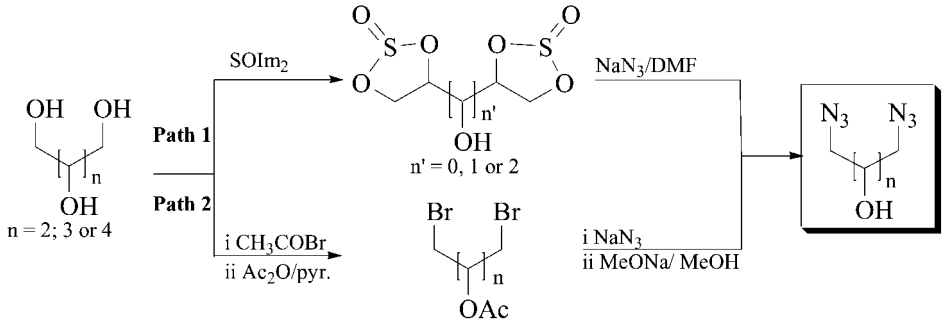
Azidation reactions are usually carried out by nucleophilic azide substitution for some leaving groups such as sulfonates,[3,4] cyclic sulfites,[5] and cyclic sulfates,[6] by opening of epoxides,[7] more directly using PPh_3/*N*-chlorosuccinimide and azide salts.[8] The most commonly used syntheses of α,ω-diazidoalditols involve *bis*-epoxides,[7] *bis*-sulfonates,[9] or *bis*- halogenated[10] intermediates obtained from partially protected alditols.

In this article, we report two efficient syntheses of α,ω-diazidoalditols (Sch. 1). The first one used the *bis*-cyclic sulfite alditol derivatives (Path 1), and the second one used the peracetylated α,ω-dibromoalditol derivatives as key intermediates (Path 2).[11]

The alditol cyclic sulfite synthesis was realized with the *N*,*N*′-di-imidazolylthione (Im_2SO) and alditols in THF as solvent. The *bis*-cyclic sulfite of erythritol **2**, D,L-threitol **8**, xylitol **12**, ribitol **20**, and D-arabinitol **28** derivatives (Sch. 2) were obtained, respectively, from the corresponding tetritols (**1** and **7**) and pentitols (**11**, **19**, and **27**) in excellent yields (>95%). With the hexitols [D-mannitol (**33**) and D-glucitol (**39**)], the *tris*-cyclic sulfite derivatives **34** and **40** were isolated in almost quantitative yield (Sch. 3). In each case, a mixture of *bis*- or *tris*-cyclic sulfite derivatives was obtained. The chiral nature of the sulfite, which is responsible for the complex mixture of isomers, could be overcome by oxidizing the products to sulfates. This was especially carried out with tetritol derivatives **2** and **8** which led, respectively, to only one *bis*-cylic sulfate derivative by oxidation.[12] With pentitols and hexitols sulfite, any interesting results were accomplished until now.

Treatment of the *bis*-cyclic sulfite derivative of erythritol **2**, by NaN_3 (6 equiv.) in DMF under optimal conditions (Table 1, entry 1), led to the 1,4-diazido-1,4-dideoxyerythritol (**3**) in excellent yield (80%). A regioselective monoazidation leading to 1-azido-D,L-erythritol **5** (59%) was observed when the reaction was carried out at room temperature during 36 hr (entry 2). With D,L-*threo bis*-cyclic sulfite **8**, the diazido derivative **9** was obtained in excellent yield (89%) (entry 3). No trace of monoazido derivative was observed even when the reaction occurred at room temperature.

With the pentitols, the azidation reaction has appeared slower because 3 hr were needed for a complete disappearance of the substrate. The diazidopentitol derivatives **13** (*xylo*), **21** (*ribo*), and **29** (D-*arabino*) (Sch. 2) were obtained in reasonable to good yields (72%, 56%, and 55%, respectively) (Table 1, entries 4–6). As by-products, the azidoanhydro derivatives **17** (D,L-*xylo*), **25** (D,L-*ribo*), and **31** (D-*arabino*) were observed (entries 4–6). In the case of the compound **32** (acetylated derivative of **31**), the coupling constant $J_{23} = 0.4$ Hz is in favor of a trans configuration resulting from a regioselective



Scheme 1.

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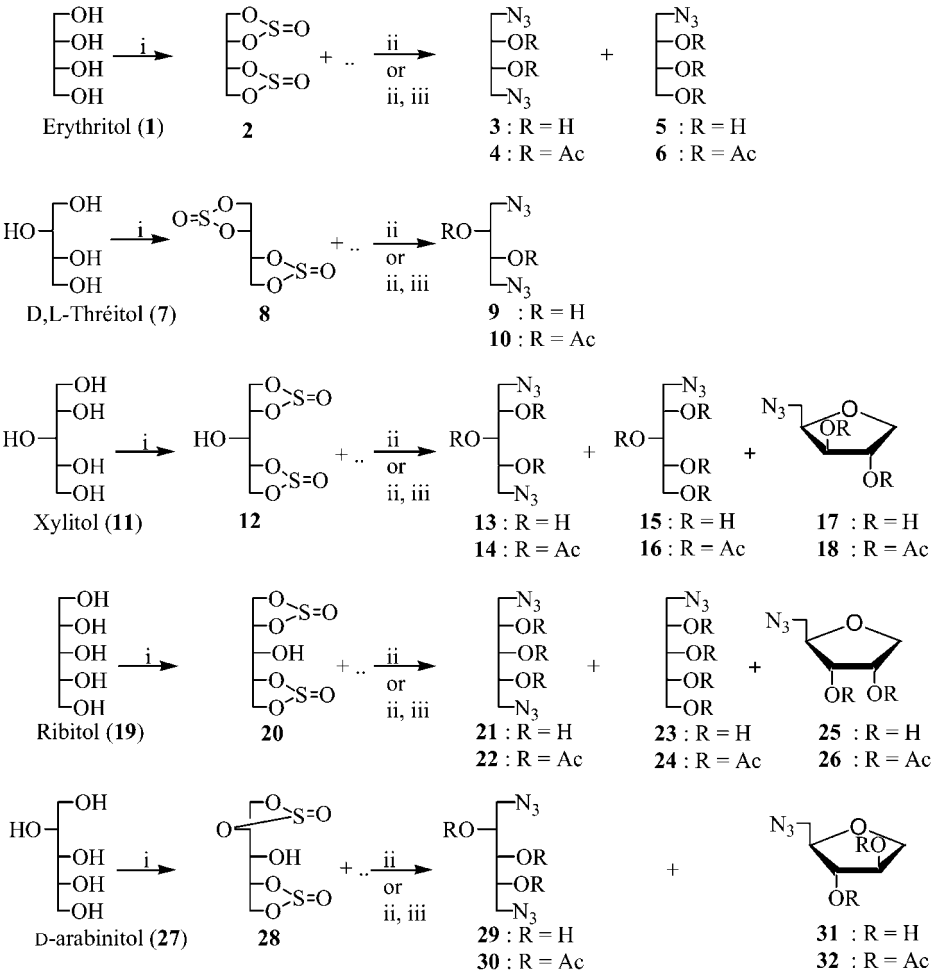

Scheme 2. (i) Im_2SO, THF; (ii) NaN_3, DMF; (iii) Ac_2O, pyridine.

1,4-*O*-heterocyclization. This suggests an initial regioselective nucleophilic attack on the C-5 carbon atom of **28** by an azide ion to give **28a** (Path 1) or **28b** (Path 2) as intermediates (Sch. 4). The subsequent *O*-heterocyclization involving the C-1 as electrophilic site and the O-4 as intramolecular nucleophilic atom led to **31** identified as their peracetylated derivative **32**.

The 1,5-diazido derivative **30** (D-*arabino*) (acetylated derivative of **29**) has a *syn*-methine ($J_{23} = 2.5$ Hz) and *anti*-methine ($J_{34} = 8.5$ Hz) coupling sequence in agreement with the planar and zigzag structure.[13,14]

With D-mannitol (**33**) and D-glucitol (**39**) (Sch. 3), the azidation was performed with the corresponding *tris*-cyclic sulfite derivatives **34** and **40**, respectively. With the D-*manno* derivative **34**, the azidation at 130°C gave mainly 1,6-diazido-1,6-dideoxy-D-mannitol (**35**) in 47% yield and as by-product the 1,6-diazido-3,4-*O*-sulfinyl **37** isolated in 39% yield (Table 2, entry 1). The subsequent acetylation of **37** gave quantitatively **38**.

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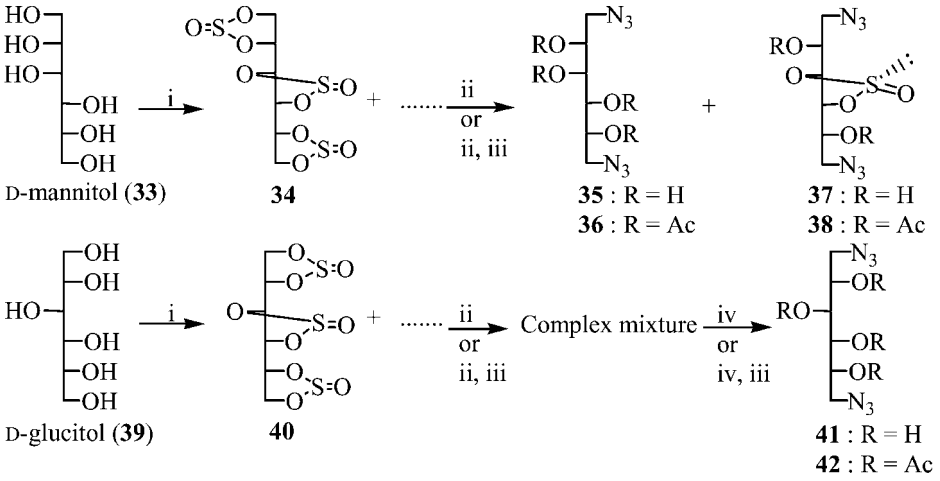

Scheme 3. (i) Im_2SO, THF; (ii) NaN_3, DMF; (iii) Ac_2O, pyridine; (iv) MeONa, MeOH.

At lower temperature (90°C) and with a prolonged time (2 hr) (entry 2), the yield of the 3,4-*O*-sulfinyl derivative **37** reached 58% while the yield of **35** was decreased to 15%. These results suggest the initial formation of **37** which undergoes subsequently a partial hydrolysis to lead to **35** in 49% yield. The yield of **35** was increased to 67% by treatment of the crude product after azidation by MeONa/MeOH during 24 hr at room temperature (Table 2, entry 3).

The *tris*-cyclic sulfite formation was avoided by a 3,4-di-*O*-benzyl protection leading to **43**[15] (Sch. 5). Surprisingly, the azidation of the 3,4-di-*O*-benzyl-1,2 : 5,6-di-*O*-sulfinyl-D-mannitol (**44**) led to the unexpected 2,5-anhydro-6-azido-6-deoxy-D-glucitol (**47**) in excellent yield (89%) through a 2,5-*O*-heterocylization. This compound was identified in its acetylated form **48** which in ^1H NMR showed a coupling constant $J_{3,4} = 1$ Hz in agreement with a *trans*-configuration of H-3 and H-4.

This 2,5-*O*-heterocyclization could be explained by the mechanism shown in the Sch. 6. Thus, the 5-*exo-tet O*-heterocyclization occurred regioselectively on the C-2 (≡C-5) with an inversion of the configuration from the possible intermediates **44a** (Path 1) or **44b** (Path 2). This type of intramolecular cyclization has already been reported in the literature with

Table 1. Azidation reaction of compounds **2**, **8**, **12**, **20**, and **28**.

Entry	Substrate	NaN_3 (equiv.)	*t* (°C)	Time (hr)	Isolated yield (%)		
					Diazido	Monoazido	Anhydro
1	**2** (*erythro*)	6	130	1	**3** (80)	—	—
2	**2** (*erythro*)	6	Rt	36	**3** (15)	**5** (59)	—
3	**8** (D,L-*threo*)	6	130	1	**9** (89)	—	—
4	**12** (*xylo*)	6	130	3	**13** (72)	**15** (10)	**17** (10)
5	**20** (*ribo*)	6	130	3	**21** (56)	**23** (9)	**25** (9)
6	**28** (D-*arabino*)	6	130	3	**29** (55)	—	**31** (10)

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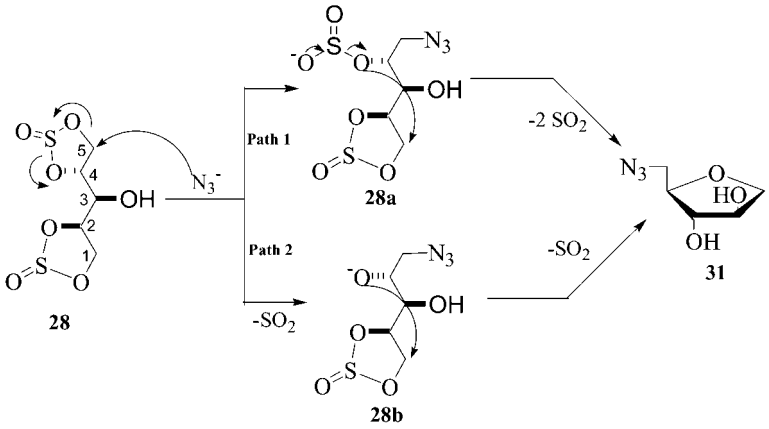


Scheme 4.

1,2 : 5,6-*bis*-epoxyhexane[16] and 1,2 : 5,6-*bis*-aziridine-D-mannitol.[17] In all cases the 6-*endo-tet* process are disfavored. This is in agreement with Baldwin's rules.[18]

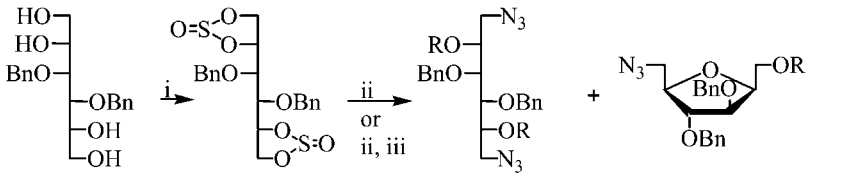
Unlike the *tris*-cyclic sulfite derivative **34** with a *manno* configuration, the azidation of the *tris*-cyclic sulfite of D-glucitol **40** led to a complex mixture of 1,6-diazido-*O*-sulfinyl regio- and stereoisomers (entry 4). When the azidation reaction was followed by methanolysis (MeONa/MeOH), 1,6-diazido-1,6-dideoxy-D-glucitol (**41**) was isolated in 52% yield.

To complement our work on the α,ω-regioselective azidation of alditols, another method for diazidoalditol synthesis was considered. This involved the peracetylated α,ω-dibromoalditol derivatives **49**, **50**, **51**, **52**, **53**, **54**, and **55** as bielectrophilic intermediates (Table 3). The latter were readily afforded by direct bromination of unprotected alditols using AcBr in 1,4-dioxane.[11] The bromination of the alditols **1**, **7**, **19**, **27**, **33**, and **39**, by this reagent, led in a one-pot reaction to complex mixtures of partially acetylated regioisomeric α,ω-dibromo-α,ω-dideoxyalditol derivatives. A subsequent acetylation, followed by a treatment of the resulting crude product by NaN_3 in DMF at 80°C overnight, led to the peracetylated α,ω-diazido-α,ω-dideoxyalditol derivatives **4** (*erythro*, 75%), **10** (D,L-*threo*,

Table 2. Azidation reaction of compounds **34** and **40**.

					Isolated yield (%)		
Entry	Sulfite substrate	NaN_3 (equiv.)	*t* (°C)	Time	Diazido	Diazido-3,4-*O*-sulfinyl	Anhydro
1	**34** (D-*manno*)	4	130	15 min	**35** (47)	**37** (39)	—
2	**34** (D-*manno*)	4	90	2 hr	**35** (15)	**37** (58)	—
3	**34** (D-*manno*)	4	130	15 min	**35** (67)[a]	—	—
4	**40** (D-*gluco*)	4	130	15 min	Complex mixture		—
5	**40** (D-*gluco*)	4	130	15 min	**41** (52)[a]	—	—

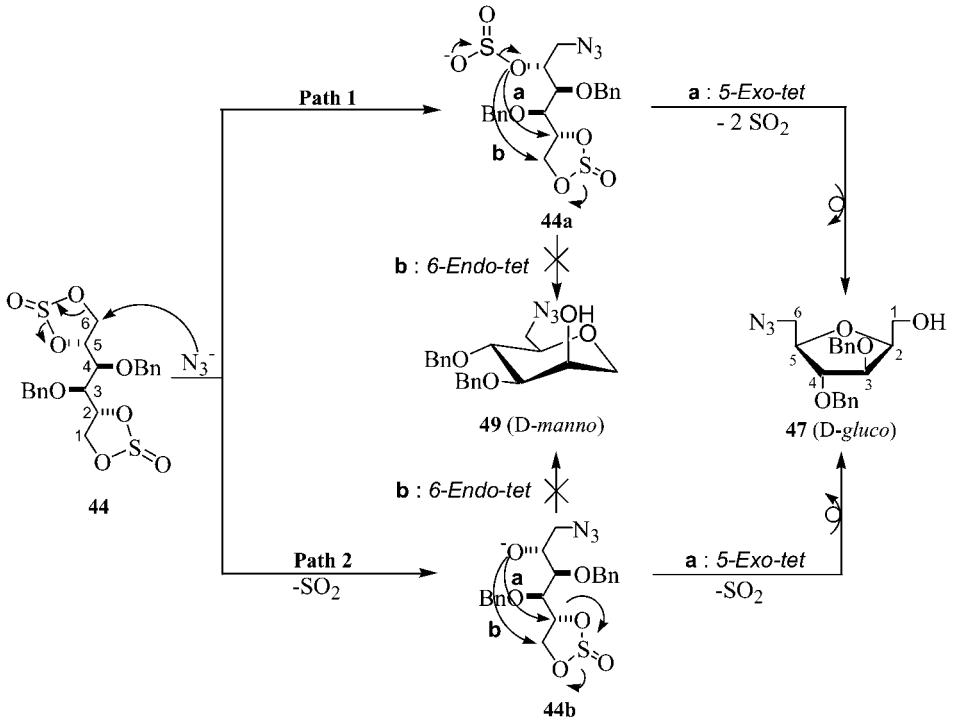
[a]Isolated after treatment with MeONa, MeOH, rt, 24 hr.



Scheme 5. (i) Im_2SO, THF; (ii) NaN_3, DMF; (iii) Ac_2O, pyridine; (iv) MeONa, MeOH.

76%), **14** (*xylo*, 64%), **22** (*ribo*, 50%), **30** (D-*arabino*, 70%), **36** (D-*manno*, 51%), and **42** (D-*gluco*, 42%) previously obtained from cyclic sulfite intermediates (Schs. 2 and 3).

In conclusion, we have reported two short and efficient syntheses of α,ω-diazidoalditols from both *bis*- and *tris*-cyclic sulfite derivatives and α,ω-dibromoalditols as intermediates. The synthesis via *bis*-cyclic sulfite intermediates was the preferred route because of the high yields of free diazido derivatives obtained in two steps from free alditols. The obtention in excellent yield of the unexpected and interesting 2,5-anhydro-6-azido-6-deoxy derivative **47** (89%) with D-*gluco* configuration from the tandem azidation-2,5-*O*-heterocyclization of 3,4-di-*O*-benzyl-*bis*-*O*-sulfinyl-D-mannitol **44** should also be noted.



Scheme 6.

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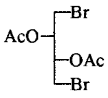
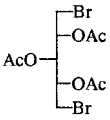
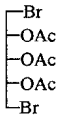
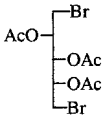
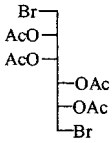
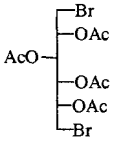
Table 3. Structure of peracetylated α,ω-dibromoalditol derivatives.

						
49	**50**	**51**	**52**	**53**	**54**	**55**
(*Erythro*)	(*Threo*)	(*Xylo*)	(*Ribo*)	(D-*arabino*)	(D-*manno*)	(D-*gluco*)

EXPERIMENTAL

General Methods

Melting points were determined with a Büchi 535 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 WB spectrometer; chemical shifts are reported in δ (ppm) relative to Me_4Si. All ^{13}C NMR signals were assigned through C,H-correlated spectra with hsqcgrad.routine experiment. TLC was performed on Silica Gel 60 F_{254} 230 mesh (E. Merck) with hexane–EtOAc or CH_2Cl_2–acetone as eluent, and detection by the vanillin–H_2SO_4 reagent. The silica gel used in column chromatography was 35–70 μ (Amicon). Elemental analyses were performed by the "Service de Microanalyse du CNRS" (Laboratoire de Chimie Bioorganique, Université de Reims Champagne Ardenne).

General Procedure I for the Preparation of *bis*-Cyclic Sulfite Derivatives of Alditols 2, 8, 12, 20, 28, 34, 40, and 44 (GPI)

Freshly distilled thionyl chloride (3 equiv. for tetritols **1** and **7**; 4 equiv. for pentitols and hexitols **11**, **19**, **27**, **33**, **39**, and **44**) was added dropwise to a solution of imidazole (12–16 equiv.) in THF (40 mL) under argon atmosphere at 0°C. The filtrate containing the diimidazolethionyl was directly added dropwise to a solution of alditol (1 g) in THF (10 mL) at −10°C. The mixture was stirred during 30 min. The residue obtained after the removal of the solvent in vacuum was dissolved in CH_2Cl_2 (20 mL) and washed twice by cold water, dried over Na_2SO_4, and evaporated under reduced pressure at 25°C to obtain the mixture of stereoisomeric *O*-sulfinyl derivatives.

Di-*O*-sulfinylerythritol (2). Reaction of **1** according to GPI gave **2** (1.74 g, 99%); colorless; m.p. 50–53°C; R_f 0.45 and 0.55 in 3:2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 81.2, 79.6, 79.2, 77.7 (C-2,3), 71.1, 70.3, 69.0, 68.6 (C-1,4); ^{1}H NMR ($CDCl_3$): δ 5.14–5.08 (m), 4.85–4.58 (m).

Di-*O*-sulfinyl-D,L-threitol (8). Reaction of **7** according to GPI gave **8** (1.72 g, 98%); syrup; R_f 0.25, 0.31, and 0.49 in 7:3 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 81.1, 80.1, 78.0, 76.9 (C-2,3), 68.6, 68.5, 67.7, 67.2, (C-1,4); ^{1}H NMR ($CDCl_3$): δ 5.18–4.90 (m), 4.80–4.39 (m).

Di-*O*-sulfinylxylitol Derivatives (12). Reaction of **11** according to GPI gave **12** (1.54 g, 96%), white powder; R_f 0.31–0.54 in 9:1 CH_2Cl_2-acetone; ^{13}C NMR (CD_3OD): δ 84.7–76.6 (C-2,3,4), 70.5–68.8 (CH_2OSO–), 63.0–61.2 (C-1,5).

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Di-*O*-sulfinylribitol (20). Reaction of **19** according to GPI gave **20** (1.57 g, 98%); white powder; R_f 0.44–0.90 in 9 : 1 CH_2Cl_2–acetone; ^{13}C NMR (CD_3OD): δ 84.0–75.0 (C-2,3,4), 70.7–66.4 (C-1,5), 61.9–58.0 (CH_2OH).

Di-*O*-sulfinyl-D-arabinitol (28). Reaction of **27** according to GPI gave **28** (1.56 g, 97%); white powder; R_f 0.45–0.89 in 9 : 1 CH_2Cl_2–acetone; ^{13}C NMR (CD_3OD): δ 86.5–76.3 (C-2,3,4), 71.2–67.0 (CH_2OSO), 62.8–60.0 (C-1,5).

Tri-*O*-sulfinyl-D-mannitol (34). Reaction of **33** according to GPI gave **34** (1.74 g, 99%); syrup; R_f 0.75 in 96 : 04 CH_2Cl_2–acetone; ^{13}C NMR ($CDCl_3$): δ 82.8–77.9 (C-2,3,4,5), 71.0–67.6 (C-1,6).

Tri-*O*-sulfinyl-D-glucitol (40). Reaction of **39** according to GPI gave **40** (1.74 g, 99%); syrup; R_f 0.51–0.76 in 96 : 04 CH_2Cl_2–acetone; ^{13}C NMR ($CDCl_3$): δ 85.2–78.2 (C-2,3,4,5), 71.5–67.4 (C-1,6).

3,4-Di-*O*-benzyl-1,2 : 5,6-di-*O*-sulfinyl-D-mannitol (44). Reaction of **43** according to GPI gave **44**. A part of the mixture of the stereoisomers crystallized in hexane as solvent. Thus, two different mixtures of stereoisomers were obtained. One resulting from the crystalization (**a**) and the second resulting from the recovered filtrate after concentration (**b**). (**a**): Yield 70 mg (60%); colorless crystal; R_f 0.69 and 0.74 in CH_2Cl_2; ^{13}C NMR ($CDCl_3$): δ 137.3–128.2 (Ph), 82.4-77.6 (C-2,3,4,5), 75.5, 75.3, 75.2 ($\underline{C}H_2Ph$), 68.5, 68.2 (C-1,6). (**b**): 0.45 g; yield 39%; R_f 0.54 and 0.63 in CH_2Cl_2; ^{13}C NMR ($CDCl_3$): δ 137.3–128.7 (Ph), 82.7–77.6 (C-2,3,4,5), 75.5–74.2 ($\underline{C}H_2Ph$), 69.2–67.8 (C-1,6).

General Procedure II for the Azidation of Alditol Cyclic-Sulfite Derivatives (GPII)

Sodium azide (NaN_3, 6 equiv., 39.5 mmol) was added to a solution of *bis*-cyclic sulfite derivatives (1 g) in DMF (50 mL) during the desired time. The crude product obtained after concentration was then dissolved in EtOH, filtered, and the filtrate was evaporated and chromatographed on silica gel.

1,4-Diazido-1,4-dideoxyerythritol (3). According to GPII, the reaction was carried out at 130°C during 1 hr. The crude product was chromatographed on silica gel (1 : 4 hexane–EtOAc). Compound **3** (1.13 g, 80%); colorless crystals; m.p. 85–86°C; R_f 0.50 in 7 : 3 hexane–EtOAc; ^{13}C NMR (CD_3OD): δ 73.7 (C-2,3), 56.1 (C-1,4); ^1H NMR (CD_3OD): δ 3.64 (dd, 2H, $J_{1,2}$, $J_{3,4}$ 5.9 Hz, $J_{1',2}$, $J_{3,4'}$ 1.6 Hz, H-2,3), 3.49 (dd, 2H, $J_{1,1'}$, $J_{4,4'}$ 12.8 Hz, H-1′,4′), 3.36 (dd, 2H, $J_{1,1'}$, $J_{4,4'}$ 12.8 Hz, H-1,4).

Anal. Calcd for $C_4H_8N_6O_2$: C, 27.91; H, 4.68; N, 48.82; O, 18.59. Found: C, 28.01; H, 4.76; N, 48.75.

1-Azido-1-deoxy-D,L-erythritol (5). According to GPII, the reaction was carried out at room temperature during 36 hr. The crude product was chromatographed on silica gel (2 : 8 hexane–EtOAc). Compound **5** (0.71 g, 59%); syrup; R_f 0.20 in EtOAc; ^{13}C NMR (C_5D_5N): δ 74.8 (C-3), 74.0 (C-2), 65.2 (C-4), 56.2 (C-1); ^1H NMR (C_5D_5N): δ 4.45 (m, 1H, $J_{2,3}$ 4.9 Hz, H-2), 4.36 (m, 1H, $J_{3,4}$ 5.7 Hz, $J_{3,4'}$ 6.1 Hz, H-3), 4.15 (dd, 1H, $J_{4,4'}$ 12.4 Hz, H-4′), 4.10 (dd, 1H, H-4), 4.01 (dd, 1H, $J_{1',2}$ 1.7 Hz, $J_{1,1'}$ 12.5 Hz, H-1′), 3.93 (dd, 1H, $J_{1,2}$ 5.8 Hz, H-1).

Anal. Calcd for $C_4H_9N_3O_3$: C, 32.65; H, 6.17; N, 28.56; O, 32.62. Found: C, 32.49; H, 6.21; N, 28.61.

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1,4-Diazido-1,4-dideoxy-D,L-threitol (9). According to GPII, the reaction was carried out at 130°C during 1 hr. The crude product was chromatographed on silica gel (2 : 8 hexane–AcOEt). Compound **9** (1.27 g, 89%); syrup; R_f 0.42 in 7 : 3 hexane–EtOAc; ^{13}C NMR (CD_3OD): δ 70.7 (C-2,3), 53.5(C-1,4); ^{1}H NMR (CD_3OD): δ 3.69 (dd, 2H, $J_{1,2}$, $J_{3,4}$ 4.8 Hz, H-2,3), 3.45 (dd, 2H, $J_{1',2}$, $J_{3,4'}$ 3.6 Hz, H-1′,4′), 3.38 (dd, 2H, $J_{1,1'}$, $J_{4,4'}$ 12.4 Hz, H-1,4).

Anal. Calcd for $C_4H_8N_6O_2$: C, 27.91; H, 4.68; N, 48.82; O, 18.59. Found: C, 27.82; H, 4.72; N, 48.94.

1,5-Diazido-1,5-dideoxyxylitol (13). According to GPII, the reaction was carried out at 130°C during 3 hr. The crude product was chromatographed on silica gel (85 : 15 CH_2Cl_2–acetone). Compound **13** (0.96 g, 72%); syrup; R_f 0.38 in 7 : 3 CH_2Cl_2–acetone; ^{13}C NMR (CD_3OD): δ 73.8 (C-3), 73.2 (C-2,4), 54.5 (C-1,5); ^{1}H NMR (CD_3OD): δ 3.83 (ddd, 2H, $J_{1,2}$, $J_{4,5}$ 6.1 Hz, H-2,4), 3.51 (t, 1H, $J_{2,3}$, $J_{3,4}$ 4.0 Hz, H-3), 3.41 (dd, 2H, $J_{1',2}$, $J_{4,5'}$ 2.4 Hz, H-1′,5′), 3.38 (dd, 2H, $J_{1,1'}$, $J_{5,5'}$ 11.2 Hz, H-1,5).

Anal. Calcd for $C_5H_{10}N_6O_3$: C, 29.70; H, 4.99; N, 41.57; O, 23.74. Found: C, 29.81; H, 4.92; N, 41.63.

1-Azido-1-deoxy-D,L-xylitol (15). Yield 0.12 g (10%); syrup; R_f 0.33 in 7 : 3 CH_2Cl_2–acetone; ^{13}C NMR (CD_3OD): δ 71.2, 70.8, 65.8 (C-2,3,4), 63.3 (C-5), 55.0 (C-1).

Anal. Calcd for $C_5H_{11}N_3O_4$: C, 33.90; H, 6.26; N, 23.72; O, 36.12. Found: C, 33.79; H, 6.43; N, 23.80.

1,4-Anhydro-5-azido-5-deoxy-D,L-xylitol (17). Yield 0.10 g (10%); syrup; R_f 0.33 in 7 : 3 CH_2Cl_2–acetone; ^{13}C NMR (CD_3OD): δ 80.7, 78.5, 77.9 (C-4,3,2), 74.4 (C-1), 51.4 (C-5).

Anal. Calcd for $C_5H_9N_3O_3$: C, 37.74; H, 5.70; N, 26.40; O, 30.16. Found: C, 37.63; H, 5.75; N, 26.32.

1,5-Diazido-1,5-dideoxy-ribitol (21). According to GPII, the reaction was carried at 130°C during 3 hr. The crude product was chromatographed on silica gel (85 : 15 CH_2Cl_2–acetone). Compound **21** (0.74 g, 56%); syrup; R_f 0.44 in 7 : 3 CH_2Cl_2–acetone; ^{13}C NMR (CD_3OD): δ 73.9 (C-3), 73.3 (C-2,4), 54.9 (C-1,5); ^{1}H NMR (CD_3OD): δ 4.72 (s, 3H, OH), 3.75 (ddd, 2H, $J_{1,2}$, $J_{4,5}$ 6.8 Hz, H-2,4), 3.48 (t, 1H, $J_{2,3}$, $J_{3,4}$ 6.5 Hz, H-3), 3.41 (dd, 2H, $J_{1',2}$, $J_{4,5'}$ 3.2 Hz, H-1′,5′), 3.38 (dd, 2H, $J_{1,1'}$, $J_{5,5'}$ 12.7 Hz, H-1,5).

Anal. Calcd for $C_5H_{10}N_6O_3$: C, 29.70; H, 4.99; N, 41.57; O, 23.74. Found: C, 29.73; H, 5.07; N, 41.47.

1-Azido-1-deoxy-D,L-ribitol (23). Yield 0.10 g (9%); syrup; R_f 0.40 in 7 : 3 CH_2Cl_2–acetone; ^{13}C NMR (CD_3OD): δ 73.1, 72.9, 65.8 (C-2,3,4), 64.7 (C-5), 56.1 (C-1).

Anal. Calcd for $C_5H_{11}N_3O_4$: C, 33.90; H, 6.26; N, 23.72; O, 36.12. Found: C, 33.74; H, 6.39; N, 23.65.

1,4-Anhydro-5-azido-5-deoxy-D,L-ribitol (25). Yield 0.09 g (9%); syrup; R_f 0.40 in 7 : 3 CH_2Cl_2–acetone; ^{13}C NMR (CD_3OD): δ 83.0, 75.3, 75.1 (C-4,3,2), 75.0 (C-1), 54.4 (C-5).

Anal. Calcd for $C_5H_9N_3O_3$: C, 37.74; H, 5.70; N, 26.40; O, 30.16. Found: C, 37.70; H, 5.65; N, 26.53.

1,5-Diazido-1,5-dideoxy-D-arabinitol (29). According to GPII, the reaction was carried at 130°C during 3 hr. The crude product was chromatographed on silica gel (85 : 15 CH_2Cl_2–acetone). Compound **29** (0.73 g, 55%); colorless crystals; m.p.

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85–86°C, $[\alpha]_D^{22}$ −29.5° (*c* 1.10 in MeOH); R_f 0.50 in 7 : 3 CH_2Cl_2–acetone; ^{13}C NMR (CD_3OD): δ 72.8 (C-3), 71.7 (C-4), 70.4 (C-2), 55.6 (C-5), 55.2 (C-1); ^1H NMR (CD_3OD): δ 4.78 (s, 3H, OH), 3.99 (m, 1H, $J_{1,2}$ 5.1 Hz, $J_{2,3}$ 2.7 Hz, H-2), 3.80 (m, 1H, $J_{3,4}$ 8.2 Hz, $J_{4,5'}$ 2.9 Hz, H-4), 3.54 (dd, 1H, $J_{5,5'}$ 13.0 Hz, H-5′), 3.42 (m, 3H, H-1′,3,5), 3.30 (dd, 1H, $J_{1,1'}$ 12.5 Hz, H-1).

Anal. Calcd for $C_5H_{10}N_6O_3$: C, 29.70; H, 4.99; N, 41.57; O, 23.74. Found: C, 29.75; H, 4.96; N, 41.70.

1,4-Anhydro-5-azido-5-deoxy-D-arabinitol (31). Yield 0.10 g (10%); syrup; R_f 0.45 in 7 : 3 CH_2Cl_2–acetone; ^{13}C NMR (CD_3OD): δ 85.7, 81.0, 80.4 (C-4,3,2), 74.5 (C-1), 53.6 (C-5).

Anal. Calcd for $C_5H_9N_3O_3$: C, 37.74; H, 5.70; N, 26.40; O, 30.16. Found: C, 37.68; H, 5.79; N, 26.49.

1,6-Diazido-1,6-dideoxy-D-mannitol (35). According to GPII, the reaction was carried out at 130°C during 15 min. The crude product was chromatographed on silica gel (CH_2Cl_2). Compound **35** (0.60 g, 47%); colorless crystals; m.p. 92–93°C; $[\alpha]_D^{28}$ +18.4° (*c* 1.00 in MeOH), R_f 0.36 in 6 : 4 CH_2Cl_2–acetone; ^{13}C NMR (D_2O): δ 72.1 (C-2,5), 71.9 (C-3,4), 56.4 (C-1,6); ^1H NMR (D_2O): δ 4.78 (s, 4H, OH), 3.91 (m, 2H, $J_{1,2}$, $J_{5,6}$ 6.0 Hz, H-2,5), 3.83 (d, 2H, $J_{2,3}$, $J_{4,5}$ 9.0 Hz, H-3,4), 3.68 (dd, 2H, $J_{1',2}$, $J_{5,6'}$ 2.3 Hz, H-1′,6′), 3.52 (dd, 2H, $J_{1,1'}$, $J_{6,6'}$ 13.0 Hz, H-1,6).

Anal. Calcd for $C_6H_{12}N_6O_4$: C, 31.04; H, 5.21; N, 36.19; O, 27.56. Found: C, 31.15; H, 5.33; N, 36.12.

1,6-Diazido-1,6-dideoxy-3,4-*O*-sulfinyl-D-mannitol (37). According to GPII, the reaction was carried out at 90°C during 2 hr. The crude product was chromatographed on silica gel (CH_2Cl_2). Compound **37** (0.89 g, 58%); syrup; $[\alpha]_D^{23}$ +103.5° (*c* 1.80 in CH_2Cl_2), R_f 0.65 in 9 : 1 CH_2Cl_2–acetone; ^{13}C NMR ($CDCl_3$): δ 84.5 (C-4), 82.0 (C-3), 71.2 (C-5), 70.3 (C-2), 53.0 (C-1,6); ^1H NMR ($CDCl_3$): δ 4.92 (dd, 1H, $J_{2,3}$ 7.5 Hz, $J_{3,4}$ 5.0 Hz, H-3), 4.64 (dd, 1H, $J_{4,5}$ 7.0 Hz, H-4), 4.09 (m, 1H, $J_{5,6}$ 5.3, $J_{5,6'}$ 3.8 Hz, H-5), 3.79 (m, 1H, $J_{1,2}$ 3.5 Hz, $J_{1',2}$ 5.8 Hz, H-2), 3.62–3.42 (m, 4H, H-1,6).

Anal. Calcd for $C_6H_{10}N_6O_5S$: C, 25.90; H, 3.62; N, 30.20; O, 28.75; S, 11.52. Found: C, 25.78; H, 3.73; N, 30.33.

1,6-Diazido-1,6-dideoxy-D-glucitol (41). According to GPII, the reaction was carried out at 130°C during 20 min. After evaporation of the solvent, the crude product was hydrolyzed by a catalytic amount of MeONa in 40 mL of MeOH at rt during one night under argon. The crude product was then neutralized by an acid resin Amberlyst 15 wet and filtered. The filtrate was evaporated under reduced pressure and chromatographed on silica gel (3 : 2 CH_2Cl_2–acetone). Compound **41** (0.66 g, 52%); colorless crystals; m.p. 62.5–63.5°C, $[\alpha]_D^{19}$ +13.4° (*c* 0.70 in MeOH), R_f 0.40 in 6 : 4 CH_2Cl_2–acetone; ^{13}C NMR (D_2O): δ 74.1 (C-2), 73.5 (C-4), 72.1 (C-3), 71.3 (C-5), 55.9 (C-6), 55.4 (C-1); ^1H NMR (D_2O): δ 4.79 (s, 4H, OH), 3.96 (m, 1H, H-2), 3.90 (m, 1H, H-5), 3.85 (dd, 1H, $J_{2,3}$ 6.0 Hz, H-3), 3.65 (dd, 1H, $J_{3,4}$ 1.7 Hz, H-4), 3.61 (dd, 1H, $J_{5,6'}$ 1.9 Hz, H-6′), 3.52 (dd, 1H, $J_{1,1'}$ 13.8, $J_{1',2}$ 3.3 Hz, H-1′), 3.50 (dd, 1H, $J_{5,6}$ 7.2 Hz, $J_{6,6'}$ 13.0 Hz, H-6), 3.47 (dd, 1H, $J_{1,2}$ 6.3 Hz, H-1).

Anal. Calcd for $C_6H_{12}N_6O_4$: C, 31.04; H, 5.21; N, 36.19; O, 27.56. Found: C, 31.12; H, 5.18; N, 36.26.

1,6-Diazido-3,4-di-*O*-benzyl-1,6-dideoxy-D-mannitol (45). According to GPII, the reaction was carried out at 90°C during 16 hr. The crude product was chromatographed on silica gel (9 : 1 hexane–EtOAc). Compound **45** (0.11 g, 10%); syrup; R_f 0.60 in 7 : 3

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hexane–EtOAc; ^{13}C NMR (CD_3OD): δ 140.5 (Ph-ipso), 130.5, 130.1, 129.7 (Ph), 81.4 (C-3,4), 76.7 ($\underline{C}H_2Ph$), 72.4 (C-2,5), 56.6 (C-1,6); ^{1}H NMR (CD_3OD): δ 7.30 (m, 10H, Ph), 4.68 (m, 4H, $C\underline{H}_2Ph$), 3.98 (m, 2H, $J_{2,3}$ 7.5 Hz, $J_{3,4}$ 5.0 Hz, H-2,5), 3.88 (d, 2H, $J_{2,3}$, $J_{4,5}$ 8.5 Hz, H-3,4), 3.55 (dd, 2H, $J_{1,1'}$, $J_{6,6'}$ 12.6 Hz, $J_{1',2}$, $J_{5,6'}$ 2.8 Hz, H-1′,6′), 3.37 (dd, 2H, $J_{1,2}$, $J_{5,6}$ 5.4 Hz, H-1,6).

Anal. Calcd for $C_{20}H_{24}N_6O_4$: C, 58.25; H, 5.83; N, 20.39. Found: C, 58.32; H, 5.85; N, 19.98.

2,5-Anhydro-1-azido-3,4-di-*O*-benzyl-1-deoxy-D-glucitol (47). According to GPII, the reaction was carried out at 90°C during 16 hr. The crude product was chromatographed on silica gel (9 : 1 hexane–EtOAc). Compound **47** (0.91 g, 89%); syrup; R_f 0.43 in 7 : 3 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 137.5 (Ph-ipso), 128.6, 128.0, 127.7 (Ph), 83.9, 83.1, 82.4, 81.6 (C-4,5,3,2), 72.0, 71.9 ($\underline{C}H_2Ph$), 61.3 (C-6), 52.6 (C-1); ^{1}H NMR ($CDCl_3$): δ 7.34 (m, 10H, Ph), 4.52 (q, 4H, CH_2Ph), 4.71–3.86 (4m, 6H, H-5,4,3,2,6,6′), 3.30 (dd, 2H, H-1,1′), 3.05 (m, 1H, OH).

Anal. Calcd for $C_{20}H_{23}N_3O_4$: C, 65.03; H, 6.28; N, 11.37; O, 17.32. Found: C, 64.93; H, 6.33; N, 11.29.

General Procedure III for Acetylation (GPIII)

After azidation, the crude product was directly dissolved in pyridine (20 mL) and an excess of acetic anhydride was added dropwise. After one night at room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 (15 mL) and washed twice by 2 × 15 mL of HCl (0.1 M), 2 × 15 mL of saturated HCO_3Na and 2 × 15 mL of water. The organic layer was evaporated and chromatographed on silica gel.

2,3-Di-*O*-acetyl-1,4-diazido-1,4-dideoxyerythritol (4). Reaction of crude product obtained from **2** according to GPII followed by GPIII gave **4** after chromatography on silica gel (8 : 2 hexane-AcOEt). Compound **4** (1.85 g, 88%); colorless crystals; m.p. 62–63°C; R_f 0.50 in 8 : 2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 169.4 (CO), 70.7 (C-2,3), 50.3 (C-1,4), 20.5 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.10 (m, 2H, H-2,3), 3.50 (dd, 2H, $J_{1',2}$, $J_{3,4'}$ 5.4 Hz, H-1′,4′), 3.40 (dd, 2H, $J_{1,2}$, $J_{3,4}$ 2.9 Hz, $J_{1,1'}$, $J_{4,4'}$ 13.4 Hz, H-1,4), 2.08 (s, 6H, CH_3).

Anal. Calcd for $C_8H_{12}N_6O_4$: C, 37.50; H, 4.72; N, 32.80; O, 24.98. Found: C, 37.70; H, 4.80; N, 32.53.

2,3,4-Tri-*O*-acetyl-1-azido-1-deoxy-D,L-erythritol (6). Yield 0.71 g (65%); syrup; R_f 0.20 in 8 : 2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 169.9, 169.4, 169.3 (CO), 69.9 (C-3), 69.3 (C-2), 61.3 (C-4), 50.1 (C-1), 20.2 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.25 (m, 1H, $J_{2,3}$ 5.2 Hz, H-3), 5.00 (m, 1H, H-2), 4.25 (dd, 1H, $J_{3,4'}$ 3.3 Hz, $J_{4,4'}$ 12.2 Hz, H-4′), 4.10 (dd, 1H, $J_{3,4}$ 5.5 Hz, H-4), 3.32 (dd, 1H, $J_{1',2}$ 4.3, $J_{1,1'}$ 13.5 Hz, H-1′), 3.25 (dd, 1H, $J_{1,2}$ 8.8 Hz, H-1), 1.89, 1.87, 1.82 (3s, 9H, CH_3).

Anal. Calcd for $C_{10}H_{15}N_3O_6$: C, 43.96; H, 5.53; N, 15.38; O, 35.13. Found: C, 43.63; H, 6.01; N, 15.53.

2,3-Di-*O*-acetyl-1,4-diazido-1,4-dideoxy-D,L-threitol (10). Reaction of crude product obtained from **8** according to GPII followed by GPIII gave **10** after chromatography on silica gel (8 : 2 hexane–AcOEt). Compound **10** (1.99 g, 95%); syrup; R_f 0.42 in 8 : 2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 169.7 (CO), 70.4 (C-2,3), 50.3 (C-1,4),

20.4 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.06 (m, 2H, H-2,3), 3.33 (dd, 2H, $J_{1',2}$, $J_{3,4'}$ 4.5 Hz, H-1′,4′), 3.26 (dd, 2H, $J_{1,2}$, $J_{3,4}$ 7.2 Hz, $J_{1,1'}$, $J_{4,4'}$ 13.3 Hz, H-1,4), 2.00, 1.97 (2s, 6H, CH_3).

Anal. Calcd for $C_8H_{12}N_6O_4$: C, 37.50; H, 4.72; N, 32.80; O, 24.98. Found: C, 37.93; H, 4.62; N, 32.14.

2,3,4-Tri-*O*-acetyl-1,5-diazido-1,5-dideoxyxylitol (14). Reaction of crude product obtained from **12** according to GPII followed by GPIII gave **14** after chromatography on silica gel (9 : 1 hexane–AcOEt). **14** (1.62 g, 75%); colorless crystals; m.p. 54–55°C; R_f 0.40 in 8 : 2 hexane–AcOEt; ^{13}C NMR ($CDCl_3$): δ 169.8, 169.7 (CO), 69.9 (C-2,4), 69.7 (C-3), 50.7 (C-1,5), 20.5, 20.4 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.30 (t, 1H, $J_{2,3}$, $J_{3,4}$ 5.2 Hz, H-3), 5.05 (m, 2H, $J_{1,2}$, $J_{4,5}$ 5.8 Hz, H-2,4), 3.40 (dd, 2H, $J_{1',2}$, $J_{4,5'}$ 4.1 Hz, H-1′,5′), 3.32 (dd, 2H, $J_{1,1'}$, $J_{5,5'}$ 13.2 Hz, H-1,5), 2.10, 2.00 (2s, 3H, 6H, CH_3).

Anal. Calcd for $C_{11}H_{16}N_6O_6$: C, 40.25; H, 4.91; N, 25.60; O, 29.24. Found: C, 40.53; H, 4.61; N, 25.71.

2,3,4,5-Tetra-*O*-acetyl-1-azido-1-deoxy-D,L-xylitol (16). Yield 0.23 g (10%); syrup; R_f 0.60 in 6 : 4 hexane–AcOEt; ^{13}C NMR ($CDCl_3$): δ 170.0, 169.8 (CO), 69.8 (C-2), 69.2 (C-3), 68.5 (C-4), 61.6 (C-5), 50.1 (C-1), 20.3, 20.1, 19.9 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.30 (dd, 1H, $J_{2,3}$ 5.0, $J_{3,4}$ 5.3 Hz, H-3), 5.10 (ddd, 1H, H-4), 5.01 (ddd, 1H, H-2), 4.22 (dd, 1H, $J_{4,5'}$ 4.0 Hz, $J_{5,5'}$ 12.2 Hz, H-5′), 3.89 (dd, 1H, $J_{4,5}$ 6.3 Hz, H-5), 3.38 (dd, 1H, $J_{1',2}$ 4.3, $J_{1,1'}$ 13.5 Hz, H-1′), 3.33 (dd, 1H, $J_{1,2}$ 6.0 Hz, H-1), 2.00, 1.97, 1.95, 1.93 (4s, 12H, CH_3).

Anal. Calcd for $C_{13}H_{19}N_3O_8$: C, 45.22; H, 5.55; N, 12.17; O, 37.07. Found: C, 45.33; H, 5.64; N, 12.51.

2,3-Di-*O*-acetyl-1,4-anhydro-5-azido-5-deoxy-D,L-xylitol (18). Yield 0.18 g (11%); syrup; R_f 0.35 in 8 : 2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 168.6 (CO), 77.4 (C-4), 76.3 (C-2), 75.2 (C-3), 70.7 (C-1), 48.7 (C-5), 19.7 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.00 (dd, 1H, $J_{2,3}$ 0.6 Hz, $J_{3,4}$ 3.6 Hz, H-3), 4.84 (m, 1H, H-2), 3.98 (dd, 1H, H-4), 3.85 (dd, 1H, $J_{1',2}$ 4.8 Hz, $J_{1,1'}$ 10.8 Hz, H-1′), 3.50 (dd, 1H, $J_{1,2}$ 2.0 Hz, H-1), 3.30 (m, 2H, $J_{5,5'}$ 11.9 Hz, H-5,5′), 1.89, 1.85 (2s, 12H, CH_3).

Anal. Calcd for $C_9H_{13}N_3O_5$: C, 44.44; H, 5.39; N, 17.28; O, 32.89. Found: C, 44.53; H, 5.73; N, 17.62.

2,3,4-Tri-*O*-acetyl-1,5-diazido-1,5-dideoxyribitol (22). Reaction of crude product obtained from **20** according to GPII followed by GPIII gave **22** after chromatography on silica gel (9 : 1 hexane–AcOEt). 1.25 g (58%); syrup; R_f 0.42 in 8 : 2 hexane–AcOEt; ^{13}C NMR ($CDCl_3$): δ 169.8, 169.3 (CO), 69.5 (C-2,4), 69.3 (C-3), 49.4 (C-1,5), 19.7, 19.6 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.23 (m, 2H, H-2,4), 5.13 (t, 1H, $J_{2,3}$, $J_{3,4}$ 5.2 Hz, H-3), 3.48 (dd, 2H, $J_{1',2}$, $J_{4,5'}$ 3.5 Hz, H-1′,5′), 3.37 (dd, 2H, $J_{1,2}$, $J_{4,5}$ 6.4 Hz, $J_{1,1'}$, $J_{5,5'}$ 13.5 Hz, H-1,5), 2.07, 2.05 (2s, 6H, 3H, CH_3).

Anal. Calcd for $C_{11}H_{16}N_6O_6$: C, 40.25; H, 4.91; N, 25.60; O, 29.24. Found: C, 40.63; H, 4.51; N, 25.65.

2,3,4,5-Tetra-*O*-acetyl-1-azido-1-deoxy-D,L-ribitol (24). Yield 0.23 g (10%); syrup; R_f 0.63 in 6 : 4 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 170.2, 169.7, 169.5 (CO), 70.1 (C-2), 69.5 (C-3), 69.2 (C-4), 61.3 (C-5), 49.7 (C-1), 20.7, 20.6, 20.5 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.25 (ddd, 1H, $J_{2,3}$ 5.2 Hz, $J_{3,4}$ 5.3 Hz, H-3), 5.15 (m, 1H, H-4), 5.05 (m, 1H, H-2), 4.20 (dd, 1H, $J_{4,5'}$ 3.0, $J_{5,5'}$ 12.5 Hz, H-5′), 3.99 (dd, 1H, $J_{4,5}$ 6.0 Hz, H-5), 3.41 (dd, 1H, $J_{1',2}$ 3.5 Hz, $J_{1,1'}$ 13.2 Hz, H-1′), 3.30 (dd, 1H, $J_{1,2}$ 6.9 Hz, H-1), 2.05, 2.00 (2s, 6H, 6H, CH_3).

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Anal. Calcd for $C_{13}H_{19}N_3O_8$: C, 45.22; H, 5.55; N, 12.17; O, 37.07. Found: C, 45.73; H, 5.51; N, 12.29.

2,3-Di-*O*-acetyl-1,4-anhydro-5-azido-5-deoxy-D,L-ribitol (26). Yield 0.21 g (13%); syrup; R_f 0.35 in 8 : 2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 169.6, 169.5 (CO), 77.9 (C-4), 72.5 (C-2), 71.3 (C-3), 70.1 (C-1), 49.5 (C-5), 19.9, 19.8 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.05 (m, 1H, $J_{2,3}$ 5.5 Hz, $J_{3,4}$ 6.3 Hz, H-2), 4.95 (d, 1H, H-3), 3.90 (dd, 1H, H-4), 3.85 (dd, 1H, $J_{1',2}$ 5.0 Hz, $J_{1,1'}$ 10.2 Hz, H-1′), 3.60 (dd, 1H, $J_{1,2}$ 3.4 Hz, H-1), 3.45 (dd, 1H, $J_{4,5'}$ 5.6 Hz, $J_{5,5'}$ 12.5 Hz, H-5′), 3.33 (dd, 1H, $J_{4,5}$ 3.7 Hz, H-5), 1.85, 1.83 (2s, 6H, CH_3).

Anal. Calcd for $C_9H_{13}N_3O_5$: C, 44.44; H, 5.39; N, 17.28; O, 32.89. Found: C, 44.48; H, 5.41; N, 17.35.

2,3,4-Tri-*O*-acetyl-1,5-diazido-1,5-dideoxy-D-arabinitol (30). Reaction of crude product obtained from **28** according to GPII followed by GPIII gave **30** after chromatography on silica gel (9 : 1 hexane–EtOAc). Yield 1.12 g (52%); colorless crystals; m.p. 29–30°C, $[\alpha]_D^{22}$ +38.0° (*c* 1.40 in CH_2Cl_2), R_f 0.41 in 8 : 2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 169.5, 169.4, 169.2 (CO), 69.5 (C-2), 68.9 (C-3), 68.7 (C-4), 50.7 (C-5), 50.3 (C-1), 20.0, 19.9, 19.8 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.31 (dd, 1H, $J_{2,3}$ 2.5 Hz, $J_{3,4}$ 8.5 Hz, H-3), 5.19 (m, 1H, H-4), 5.08 (m, 1H, H-2), 3.45 (dd, 1H, $J_{1',2}$ 3.3 Hz, $J_{1,1'}$ 13.6 Hz, H-1′), 3.33 (dd, 1H, $J_{4,5'}$ 5.2 Hz, $J_{5,5'}$ 13.0 Hz, H-5′), 3.29 (dd, 1H, $J_{4,5}$ 7.0 Hz, H-5), 3.24 (dd, 1H, J_{12} 5.3 Hz, H-1), 2.06, 2.01 (2s, 6H, 3H, CH_3).

Anal. Calcd for $C_{11}H_{16}N_6O_6$: C, 40.25; H, 4.91; N, 25.60; O, 29.24. Found: C, 40.88; H, 4.59; N, 25.65.

2,3-Di-*O*-acetyl-1,4-anhydro-5-azido-5-deoxy-D-arabinitol (32). Yield 0.24 g (15%); syrup; R_f 0.37 in 8 : 2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 168.6 (CO), 83.5 (C-4), 78.5 (C-3), 77.8 (C-3), 71.9 (C-1), 51.7 (C-5), 20.7 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.11 (m, 1H, H-2), 4.95 (dd, 1H, $J_{2,3}$ 0.4 Hz, $J_{3,4}$ 3.5 Hz, H-3), 3.99 (d, 2H, $J_{1,2}$, $J_{1',2}$ 2.7 Hz, H-1,1′), 3.87 (ddd, 1H, H-4), 3.52 (dd, 1H, $J_{4,5'}$ 5.9 Hz, $J_{5,5'}$ 13.1 Hz, H-5′), 3.37 (dd, 1H, $J_{4,5}$ 3.2′Hz, H-5), 2.02 (s, 6H, CH_3).

Anal. Calcd for $C_9H_{13}N_3O_5$: C, 44.44; H, 5.39; N, 17.28; O, 32.89. Found: C, 44.28; H, 5.62; N, 17.11.

2,3,4,5-Tetra-*O*-acetyl-1,6-diazido-1,6-dideoxy-D-mannitol (36). Reaction of crude product obtained from **34** according to GPII followed by GPIII gave **36** after chromatography on silica gel (8 : 2 hexane–EtOAc). 1.10 g (50%); syrup; $[\alpha] - D^{25}$ +33.0° (*c* 1.00 in CH_2Cl_2), R_f 0.39 in 7 : 3 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 168.8, 168.7 (CO), 67.5 (C-3,4), 67.1 (C-2,5), 49.7 (C-1,6), 19.7, 19.6 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.31 (d, 2H, $J_{2,3}$, $J_{4,5}$ 8.1 Hz, H-3,4), 4.94 (m, 2H, H-2,5), 3.38 (dd, 2H, $J_{1',2}$, $J_{5,6'}$ 3.2 Hz, $J_{1,1'}$, $J_{6,6'}$ 13.5 Hz, H-1′,6′), 3.18 (dd, 2H, $J_{1,2}$, $J_{5,6}$ 5.6 Hz, H-1,6), 2.00 (s, 12H, CH_3).

Anal. Calcd for $C_{14}H_{20}N_6O_8$: C, 42.00; H, 5.04; N, 20.99; O, 31.97. Found: C, 42.22; H, 5.14; N, 21.02.

2,5-Di-*O*-acetyl-1,6-diazido-1,6-dideoxy-3,4-O-sulfinyl-D-mannitol (38). Reaction of crude product obtained from **34** according GPII at 90°C followed by GPIII gave **38** after chromatography on silica gel (7 : 3 hexane–EtOAc). 1.23 g (62%); syrup; $[\alpha]_D^{24}$ +86.3°(*c* 4.7 in CH_2Cl_2), R_f 0.60 in 7 : 3 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 169.6 (CO), 81.3 (C-3), 81.2 (C-4), 71.9 (C-2), 70.8 (C-5), 50.2 (C-1), 49.5 (C-6), 20.6 (CH_3); ^{1}H NMR ($CDCl_3$): δ 5.20 (m, 1H, H-2), 5.00 (m, 1H, H-5), 4.86 (dd, 1H, $J_{3,4}$ 5.0 Hz, $J_{4,5}$ 4.6 Hz, H-4), 4.64 (dd, 1H, $J_{2,3}$ 7.0 Hz, H-3), 4.60 (dd, 1H, $J_{1',2}$ 3.4 Hz, $J_{1,1'}$

15.0 Hz, H-1′), 3.50 (d, 1H, $J_{1,2}$ 4.8 Hz, H-1) 3.46 (d, 2H, $J_{5,6}$, $J_{5,6'}$ 4.5 Hz, H-6,6′), 2.07, 2.06 (2s, 6H, CH_3).

Anal. Calcd for $C_{10}H_{14}N_6O_7S$: C, 33.15; H, 3.89; N, 23.20; O, 30.91; S, 8.85. Found: C, 33.52; H, 3.74; N, 22.95.

2,3,4,5-Tetra-*O*-acetyl-1,6-diazido-1,6-dideoxy-D-glucitol (42). Reaction of crude product obtained from **40** according to GPII followed by GPIII gave **42** after chromatography on silica gel (8 : 2 hexane–EtOAc). 1.16 g (53%); colorless crystals; m.p. 64–65°C, $[\alpha]_D^{25}$ +4.01° (*c* 1.0 in CH_2Cl_2), R_f 0.50 in 7 : 3 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 168.8, 168.7 (CO), 69.2 (C-2), 68.2 (C-5), 68.0 (C-4), 67.5 (C-3), 49.5 (C-1), 49.2 (C-6); ^{1}H NMR ($CDCl_3$): δ 5.38 (dd, 1H, $J_{2,3}$ 7.0 Hz, $J_{3,4}$ 3.6 Hz, H-3), 5.29 (dd, 1H, $J_{4,5}$ 7.1 Hz, H-4), 5.03 (m, 1H, H-2), 4.97 (m, 1H, H-5), 3.49 (dd, 1H, $J_{1,1'}$ 14.0 Hz, $J_{1',2}$ 2.6 Hz, H-1′), 3.43 (dd, 1H, $J_{5,6'}$ 3.7 Hz, $J_{6,6',2}$ 13.4 Hz, H-6′), 3.38 (dd, 1H, $J_{1,2}$ 5.2 Hz, H-1), 3.30 (dd, 1H, $J_{5,6}$ 5.6 Hz, H-6), 2.08, 2.04, 2.03, 2.01 (4s, 12H, CH_3).

Anal. Calcd for $C_{14}H_{20}N_6O_8$: C, 42.00; H, 5.04; N, 20.99; O, 31.97. Found: C, 42.33; H, 4.92; N, 20.77.

2,3-Di-*O*-acetyl-1,6-diazido-3,4-di-*O*-benzyl-1,6-dideoxy-D-mannitol (46). Reaction of crude product obtained from **44** according to GPII followed by GPIII gave **46** after chromatography on silica gel (9 : 1 hexane–EtOAc). 0.48 g (9%); syrup; R_f 0.48 in 9 : 1 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 169.8 (CO), 139.9 (Ph-ipso), 130.0, 129.7, 129.5 (Ph), 76.5 (C-3,4), 71.8 (CH_2Ph), 70.1 (C-2,5), 51.0 (C-1,6), 20.7 (CH_3); ^{1}H NMR ($CDCl_3$): δ 7.28 (m, 10H, Ph), 4.55 (m, 2H, H-2,5), 4.50 (m, 4H, CH_2Ph), 4.01 (d, 2H, $J_{2,3}$, $J_{4,5}$ 7.8 Hz, H-3,4), 3.35 (dd, 2H, $J_{1,1'}$, $J_{6,6'}$ 13.1 Hz, $J_{1',2}$, $J_{5,6'}$ 3.1 Hz, H-1′,6′), 3.18 (dd, 2H, $J_{1,2}$, $J_{5,6}$ 6.1′Hz, H-1,6), 2.01 (s, 6H, CH_3).

Anal. Calcd for $C_{24}H_{28}N_6O_6$: C, 58.06; H, 5.68; N, 16.93; O, 19.33. Found: C, 58.13; H, 5.65; N, 16.73.

1-*O*-Acetyl-2,5-anhydro-6-azido-3,4-di-*O*-benzyl-6-deoxy-D-glucitol (48). Yield 1.02 g (89%); syrup; $[\alpha]_D^{25}$ +49.3° (*c* 1.0 in CH_2Cl_2), R_f 0.58 in 8 : 2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 170.7 (CO), 137.3 (C-ipso), 128.5, 128.0, 127.8 (Ph), 83.3 (C-4), 83.0 (C-5), 82.4 (C-3), 79.2 (C-2), 71.8 (CH_2 benzyl), 63.1 (C-1), 52.4 (C-6), 20.8 (CH_3); ^{1}H NMR ($CDCl_3$): δ 7.33 (m, 10H, Ph), 4.38–4.58 (m, 5H, $C\underline{H}_2$Ph, H-1′), 4.22–4.29 (m, 2H, H-2,1), 4.07 (dt, 1H, $J_{1,2}$, $J_{1',2}$, 5.8 Hz, $J_{2,3}$, 2.9 Hz, H-5), 3.99 (dd, 1H, $J_{3,4}$ 1.0 Hz, $J_{4,5}$, 3.1 Hz, H-3), 3.91 (dd, 1H, H-4), 3.36 (d, 2H, H-6,6′), 2.03 (s, 3H, CH_3).

Anal. Calcd for $C_{22}H_{25}N_3O_5$: C, 64.22; H, 6.12; N, 10.21; O, 19.44. Found: C, 64.33; H, 6.15; N, 10.44.

General Procedure for Azidation of α,ω-Dibromoalditols Derivatives

To a solution in DMF (8 mL) of crude product of α,ω-dibromoalditols obtained after acetylation from 0.2 g of unprotected alditols,[11] was added sodium azide (3 equiv.), and the mixture was stirred during 16 hr at 80°C. The crude product obtained was chromatographed on silica gel with 6 : 1 hexane–EtOAc as an eluant. The peracetylated α,ω-diazidoalditol derivatives **4** (*erythro*, 75%), **10** (D,L-*threo*, 76%), **14** (*xylo*, 64%), **22** (*ribo*, 50%), **30** (D-*arabino*, 70%), **36** (D-*manno*, 51%) et.**42** (D-*gluco*, 42%) were obtained.

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