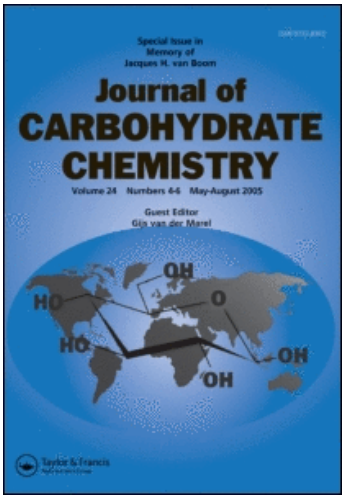

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SYNTHESIS OF 1,6-ANHYDRO-2-O-TRIFLUOROMETHANESULPHONYL-β-D-MANNOPYRANOSE DERIVATIVES AND THEIR CONVERSION INTO THE CORRESPONDING 1,6-ANHYDRO-2-AZIDO-2-DEOXY-β-D-GLUCOPYRANOSES: A CONVENIENT AND EFFICIENT APPROACH†

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ABSTRACT

Acid catalysed treatment of 1,6-anhydro-β-D-mannopyranose 1 with either benzaldehyde-, 4-methoxybenzaldehyde- or acrolein dimethyl acetal afforded the corresponding dioxolane acetals 2-4. The C-4 hydroxyl function was subsequently protected by a variety of protective groups to give fully protected mannose derivatives 5-7. Reductive opening of the endo isomers of the benzylidene, 4-methoxybenzylidene and prop-2-enylidene acetals in compounds 5-7 gave the corresponding axial ethers 8, 10 and 11. Oxidative opening of a mixture of isomers of the 4-methoxybenzylidene acetal in 6 resulted in the regioselective formation of axial 4-methoxybenzoyl esters 9. Triflation at the C-2 position of compounds 8-11, followed by treatment with lithium azide at room temperature yielded the corresponding 1,6-anhydro-2-azido-2-deoxy-β-D-glucopyranose derivatives 16-19 in high yields.

† Part of this work was presented at the XIIth International Carbohydrate Symposium, Utrecht, July 1984.

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INTRODUCTION

The presence of an azido function[1] at C-2 of sugars has been shown to be of great value in the preparation of complex aminosugars[2]. The reason for this is twofold: (i) the non-participating nature of the azido group enables, depending *inter alia* on the glycosidation conditions[2] together with the nature[3] and substitution pattern[4,5] of the protecting groups in the glycon, the formation of α- or β-glycoside linkages, and (ii) the azido function can be smoothly converted under reductive conditions into the free amino function[1,6].

Well-known procedures for the synthesis of 2-azido-2-deoxy-D-glucopyranoses are azidonitration[7,8] or chloroazidation[9] of commercially available 3,4,6-tri-O-acetyl-D-arabino-hex-1-enitol. In order to make selective extension possible, the fully-protected 2-azido derivatives have to be deacetylated and appropriately reprotected[10].

A more general approach was developed by Paulsen[11,12], which consisted of conversion of 1,6:2,3-dianhydro-β-D-mannopyranose (Cerný-epoxide)[13] into 1,6-anhydro-2-azido-2-deoxy-β-D-glucopyranose derivatives. This approach seems to be superior in many aspects over the previous one. Thus, the presence of a 1,6-anhydride linkage protects simultaneously the anomeric and primary hydroxyl groups. Acetolysis of the anhydride linkage affords building units which can in principle be extended at the anomeric centre and the C-6 position. Further, the 1,6-anhydride bond, which enforces the molecule to adopt the $^{1}C_{4}$(D)-conformation, enhances the nucleophilicity of the hydroxyl group at C-4[14].

Unfortunately, the synthesis of the Cerny-epoxide is time-consuming and its reaction with azide ions is sluggish and has to be performed at a rather high temperature.

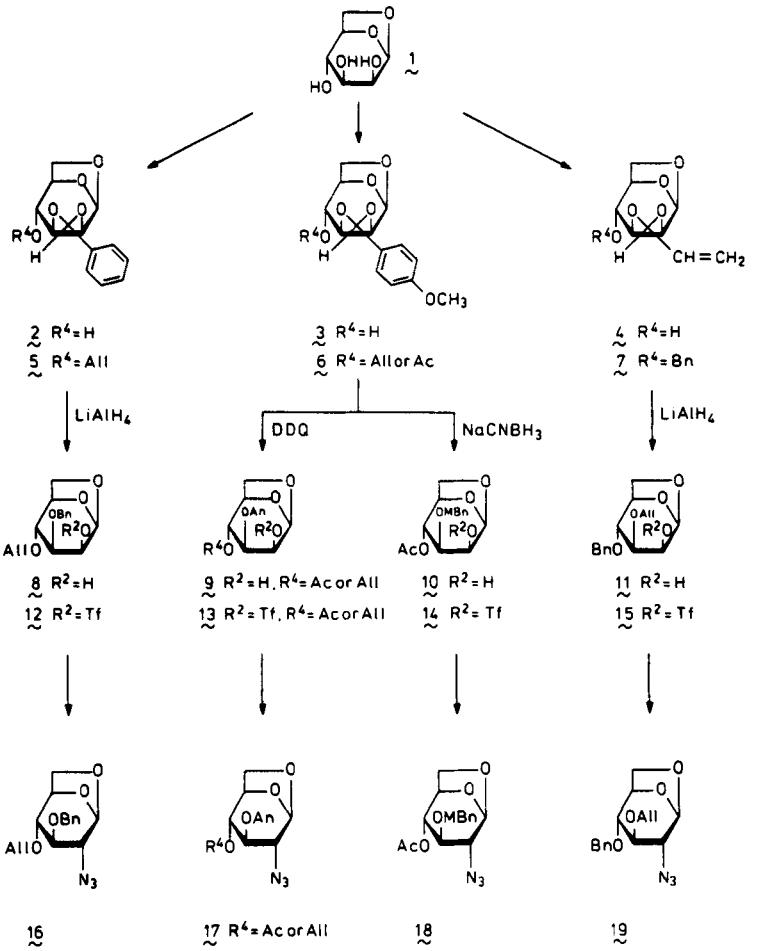
We now report that the easily accessible C-2-O-triflated 1,6-anhydro-β-D-mannopyranose derivatives 12-15 can be smoothly and efficiently converted with lithium azide into the corresponding 1,6-anhydro-2-azido-2-deoxy-β-D-glucopyranoses 16-19.

RESULTS AND DISCUSSION

1,6-Anhydro-2-azido-2-deoxy-β-D-glucopyranoses 16-19 were prepared starting from the readily available 1,6-anhydro-β-D-mannopyranose 1[15]. Initially, serious problems were encountered in preparing compound 1 by the original procedure of Fraser-Reid[15]. In a slightly modified approach, 1,6-anhydro-β-D-mannopyranose could be prepared on a relatively large (35 g) scale and in a reasonable yield. Nonetheless, crude 1 thus obtained could not be separated from accompanying sodium toluene-p-sulphonate. Fortunately, however, impure 1 could be applied successfully as starting compound in subsequent acetalation reactions (i.e. conversion of 1 into 2-4).

Apart from this, an essential requisite in our particular approach is the possible isolation, as the regiospecificity of the reductive opening of a dioxolane acetal depends on the chirality of the bridgehead carbon atom[16-19], of one pure isomer (i.e. *endo* isomers) of the dioxolane acetals 2-4.

When compound 1 in N,N-dimethylformamide (DMF) was treated with benzaldehyde-, 4-methoxybenzaldehyde- or acrolein dimethyl acetal, in the presence of toluene-p-sulphonic acid, at room temperature overnight the *endo* isomers of 2, 3 and 4 were formed predominantly (*exo*/*endo* ratio: 1/3 à 4). The absolute configuration at the acetal carbon atom of these compounds was unambiguously ascertained by ^{1}H NMR spectroscopy taking into consideration that the dioxolane acetal proton of an *exo* isomer is known to resonate at lower field when compared with the corresponding *endo* isomer[19,20]. Compounds 2 and 3 crystallised readily from dichloromethane-hexane as the pure *endo* isomers. The 1,6-anhydro-2,3-O-prop-2-enylidene-β-D-mannopyranose 4 resisted crystallisation and was therefore subsequently benzylated with benzyl bromide and sodium hydride in DMF to afford 7 which crystallised as the *endo* isomer. Allylation of 2 and 3 gave compounds 5 and 6 (R^4=All), respectively. Hydrogenolytic ring cleavage of the *endo* benzylidene acetal in 5 with lithium aluminum hydride and aluminum trichloride[16] afforded



Ac = acetyl; All = allyl; An = 4-methoxybenzoyl; Bn = benzyl; MBn = 4-methoxybenzyl; Tf = trifluoromethanesulphonyl

4-O-allyl-1,6-anhydro-3-O-benzyl-β-D-mannopyranose 8 (R^2=H). The identity of compound 8 was ascertained by ^{1}H NMR spectroscopy of the trichloroacetyl carbamoyl derivative of 8 (R^2=TAC) obtained by treating 8 (R^2=H) with the shift reagent trichloroacetyl isocyanate[21,22]. In addition, the analytical data of 8 (R^2=H) are in agreement with those reported by Bock et al.[23]. Hydrogenolysis of the *endo* prop-2-enylidene acetal in compound 7, using a mixture of aluminum trichloride and lithium aluminum hydride, gave compound

11. Acetylation of 3 and consequently reductive ring opening of the *endo* 4-methoxybenzylidene acetal with sodium cyanoborohydride-hydrogen chloride in oxolane[18,24] afforded compound 10.

Next, the oxidative acetal opening in compound 6 (R^4=All or Ac) with the reagent 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)[25-29] in a mixture of dichloromethane-water was examined. Contrary to the reductive openings of dioxolane acetals, the oxidative cleavage of the 4-methoxybenzylidene acetal in 6 (R^4=All, *exo/endo* ratio: 1/1) was shown to be independent of the chirality at the acetal carbon atom and only 4-O-allyl-1,6-anhydro-3-O-(4-methoxybenzoyl)-β-D-mannopyranose 9 (R^4=All)[28] was isolated in high yield. In addition, substitution of the allyl ether in 6 (R^4=All) by the acetyl ester did not have profound influence on the stereochemical outcome of the acetal ring opening mediated by DDQ. Thus, also in this case, the C-3-O-(4-methoxybenzoyl)-ester 9 (R^4=Ac) was exclusively isolated.

As was observed before[27-29], the oxidative opening of a 4-methoxybenzylidene dioxolane acetal in a 1,6-anhydro-β-D-glycopyranose leads to the formation of axially orientated 4-methoxybenzoyl esters, leaving the more nucleophilic equatorial hydroxyl group unprotected. Whether or not this phenomenon is a general or accidental case is at present under investigation.

Having established the preparation of compounds 8, 9 (R^4=Ac or All), 10 and 11 with C-2-OH free, the introduction of the azido group was now investigated. We found that treatment of compound 9 (R^4=All) with triflic anhydride[30] and pyridine in 1,2-dichloroethane followed, after usual work-up, by the addition of lithium azide in DMF afforded 4-O-allyl-1,6-anhydro-2-azido-2-deoxy-3-O-(4-methoxybenzoyl)-β-D-glucopyranose 17 (R^4=All) in high yield. Monitoring of the substitution reaction by TLC-analysis revealed the reaction to be complete within 5 min at 20°C. Zemplén deacylation of 17 (R^4=All) afforded 4-O-allyl-1,6-anhydro-2-azido-2-deoxy-β-D-glucopyranose which was in every aspect - TLC-analysis, ^{1}H NMR and ^{13}C NMR spectroscopy - identical with the main product obtained by treatment of 4-O-allyl-1,6:2,3-dianhydro-β-D-mannopyranose

with lithium azide[28]. This result also indicated that no acyl migration or elimination reactions[30a] had occurred during the conversion of 13 into 17. The observed mild Walden inversion of the triflate ester in 13 (R^4=All) by azide ions was also applicable to compounds 12, 13 (R^4=Ac), 14 and 15. Thus, the corresponding 1,6-anhydro-2-azido-2-deoxy-β-D-glucopyranoses 16, 17 (R^4=Ac), 18 and 19 could be isolated in high yields.

The data presented in this paper indicate that the easily accessible 1,6-anhydro-β-D-mannopyranose 1 is a key intermediate for the preparation of the differently protected D-mannose (2-4 and 8-11) as well as D-glucosamine (16-19) building blocks. Further, in the 1,6-anhydro-2-azido-2-deoxy-β-D-glucopyranose derivatives 16-19, selective removal of protective groups is feasible. For instance deallylation, using standard procedures[31], of compounds 16 and 19 will afford 2-azido-2-deoxy-D-glucopyranoses having C-4-OH and C-3-OH, respectively, free for modification or glycosylation. Furthermore, Zemplén deacylation of 17 (R^4=All) affords 4-O-allyl-1,6-anhydro-2-azido-2-deoxy-β-D-glucopyranose[28], whereas deallylation will give 17 (R^4=H). In addition, deesterification of 18 will afford a 2-azido-2-deoxy-D-glucopyranose moiety having a free C-4-OH, while selective removal of the 4-methoxybenzyl ether in the presence of the acetyl ester and the azido group can be performed using DDQ[6]. Finally, acetolysis of the 1,6-anhydride bond in compounds 16-19 will yield derivatives which can be used, after activation of the anomeric centre, for further glycosidation.

In conclusion, we believe that the easily accessible compounds 2-4, 8-11 and 16-19 promise to become valuable and versatile building units for the preparation of complex oligosaccharides.

EXPERIMENTAL

General methods and materials. Oxolane, pyridine and dichloromethane were dried by refluxing with CaH_2 for 16 h and then distil-

led. Pyridine was redistilled from p-toluenesulphonyl chloride (60 g/l) and stored over molecular sieves 4Å. Oxolane was redistilled from $LiAlH_4$ (5 g/l) and stored over molecular sieves 5Å. N,N-Dimethylformamide was stirred with CaH_2 for 16 h and then distilled under reduced pressure and stored over molecular sieves 4Å. Methanol was dried by refluxing with magnesium methoxide, distilled and stored over molecular sieves 3Å. Trichloroacetyl isocyanate was purchased from Merck. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was purchased from Janssen. DDQ was dissolved in hot dichloromethane, filtered to remove $DDQH_2$ and crystallized at 0°C. TLC analysis was carried out on silica gel (Schleicher & Schull, F 1500 LS 254) using the following solvents: A: dichloromethane/methanol, 99/1, v/v; B: dichloromethane/methanol, 49/1, v/v); C: dichloromethane/methanol, 19/1, v/v; D: dichloromethane/acetone, 97/3, v/v. Compounds were visualized by UV light or by spraying with the appropriate reagents. Thus, compounds containing allyl were visualized by spraying the TLC plates with $KMnO_4$ (1%) in aqueous Na_2CO_3 (2%); sugars were visualized by treatment with conc. H_2SO_4/methanol (2/8, v/v) followed by charring at 140°C for a few minutes. Column chromatography was carried out on Merck Kieselgel 60 (230-400 mesh, ASTM). Evaporations were carried out below 40°C under reduced pressure (15 mm or 0.5 mm Hg). Optical rotations were measured at 25°C using a Perking Elmer 141 Polarimeter. ^1H NMR spectra were measured at 300 MHz using a Bruker WM-300 spectrometer, equipped with an ASPECT-2000 computer, operating in the Fourier transform mode. ^{13}C NMR spectra were measured at 50.1 MHz using a Jeol JNM-FX 200 spectrometer on line with a JEC 980 B computer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane (TMS) as internal standard.

1,6-Anhydro-2,3-O-*endo*-benzylidene-β-D-mannopyranose (2). D-Mannose (70 g, 389 mmol), which had been dried for 24 h at 60°C over phosphorus pentoxide, was dissolved in anhydrous pyridine (200 ml) and evaporated to dryness. Pyridine (300 ml) was added and a solution of toluene-p-sulphonyl chloride (77 g, 404 mmol) in

pyridine (150 ml) was added dropwise with stirring at 0°C under an atmosphere of oxygen-free nitrogen. TLC analysis (dichloromethane/methanol, 65/35, v/v), after 2 h, showed almost complete conversion of D-mannose (Rf 0.24) into 6-O-toluene-p-sulphonyl-D-mannopyranose (Rf 0.80). The reaction mixture was quenched with water (50 ml). Then M sodium hydroxide was added dropwise with stirring until the pH was 10, which was kept at pH 10 for the next 3 h by carefully adding additional amounts of M sodium hydroxide. TLC analysis (dichloromethane/methanol, 4/1, v/v) showed conversion of 6-O-tosyl-D-mannopyranose (Rf 0.45) into compound 1 (Rf 0.29). The pH was subsequently adjusted to 7 using 3 M hydrogen chloride, the mixture was concentrated in vacuo and coevaporated twice with pyridine (150 ml) and toluene (200 ml). The residual oil was dissolved in a mixture of dichloromethane and methanol (4/1, v/v), filtrated and applied to a column of silicagel (1.4 kg, eluent dichloromethane/methanol, 4/1, v/v). Elution of the column and evaporation of the appropriate fractions afforded a mixture (51.3 g), consisting of compound 1 (35.3 g, 56%) and sodium toluene-p-sulphonate (16 g, as estimated from ^{1}H NMR spectroscopy). ^{1}H NMR ($CDCl_3/CD_3OD$): δ 2.35 (s, 1H, CH_3 tosyl); 3.66 (dd, 1H, H6*exo*); 3.82 (s, 1H, H4); 3.79, 3.97 (2xbd, 2H, H2, H3); 4.21 (dd, 1H, H6*endo*); 4.45 (bd, 1H, H5); 5.34 (s, 1H, H1); 7.18, 7.70 (2xd, 2x2/3H, H2(6) and H3(5) tosyl).

Crude compound 1 obtained above was directly used for the synthesis of compounds 2-4. To crude compound 1 (12.5 g, 53 mmol) in dry DMF (75 ml) benzaldehyde dimethyl acetal (9.9 g, 65 mmol) was added and the solution was acidified to pH 4 using toluene-p-sulphonic acid. After stirring for 18 h at 20°C, TLC analysis (solvent C) indicated complete conversion of starting material 1 (Rf 0.04) into product 2 (Rf 0.65) and the reaction was quenched with aqueous sodium bicarbonate (20 ml, 10%, w/v). The crude product was concentrated in vacuo, the residue dissolved in dichloromethane (100 ml), washed with water (25 ml), dried ($MgSO_4$) and evaporated to dryness. Compound 2 was obtained in pure form by column

chromatography (eluent solvent B; yield 11.1 g (84%), *exo/endo* ratio 1:3), followed by crystallisation from dichloromethane-hexane. Yield 6.89 g (52%). Rf 0.21 (solvent D); M.p. 184°C, lit[32] M.-p. 188-189°C. ^{1}H NMR ($CDCl_3$): δ 3.84 (dd, 1H, H6*exo*); 4.06 (dd, 1H, H6*endo*, J5,6*endo* 1.47 Hz, J6*endo*,6*exo* -7.47 Hz); 4.09 (bd, 1H, H4); 4.22 (m, 2H, H2, H3); 4.59 (m, 1H, H5); 5.30 (s, 1H, H1); 5.76 (s, 1H, H7); 7.2-7.7 (m, 5H, phenyl).

1,6-Anhydro-2,3-O-*endo*-(4-methoxybenzylidene)-β-D-mannopyranose (3). Crude compound 1 (12.5 g, 53 mmol) was dissolved in dry DMF and treated with 4-methoxybenzaldehyde dimethyl acetal[27] (11.1 g, 61 mmol) and toluene-p-sulphonic acid as described for the synthesis of compound 2. After usual work-up, crystallisation of the residual oil from dichloromethane/hexane afforded pure *endo* isomer 3 (yield 5.6 g, 40%). Column chromatography (eluent solvent B) of the mother liquid gave an extra crop of both isomers of 3 (7.3 g, 49%, *exo/endo* ratio 1:1) from which the *endo* isomer crystallised completely. Rf 0.51 (solvent C); $[\alpha]_D^{20}$ -81.5° (c 1.0, chloroform); M.p. 141-142°C. ^{1}H NMR ($CDCl_3$): δ 3.81 (s, 3H, CH_3-OØ); 3.85 (dd, 1H, H6*exo*); 4.04 (bs, 1H, H4); 4.07 (dd, 1H, H6-*endo*, J5,6*endo* 1.21 Hz, J6*endo*,6*exo* -7.42 Hz); 4.19 (m, 2H, H2+H3); 4.58 (bd, 1H, H5); 5.49 (t, 1H, H1); 5.72 (s, 1H, H7); 6.92 (d, 2H, H3+H5, methoxyphenyl); 7.60 (d, 2H, H2+H6, methoxyphenyl). ^{13}C NMR ($CDCl_3/CD_3OD$): δ 55.5 (CH_3O); 65.0 (C6); 69.8, 72.1, 76.6, 79.1 (C2-C5); 99.7 (C1); 104.9 (C7); 114.2 (C3+C5, methoxyphenyl); 129.2 (C1, methoxyphenyl); 129.8 (C2+C6, methoxyphenyl); 161.0 (C4, methoxyphenyl). $J1_{C-1_H}$ 175 Hz.

4-O-Allyl-1,6-anhydro-2,3-O-*endo*-benzylidene-β-D-mannopyranose (5). A mixture of compound 2 (1.63 g, 6.55 mmol), sodium hydride (0.4 g, 13 mmol), allyl bromide (1.45 ml, 16.8 mmol) and N,N-dimethylformamide (35 ml) was stirred for 1 h. TLC analysis (solvent D) showed complete conversion of starting material (Rf 0.21) into product 5 (Rf 0.66). Methanol and water were added successively and the mixture was evaporated. Dichloromethane (50 ml) was added to the residue and the organic layer was washed

with water (25 ml), dried ($MgSO_4$) and concentrated in vacuo. The residual oil was applied to a column of silica gel (30 g) suspended in dichloromethane. Yield 1.68 g (88%). Rf 0.56 (solvent A). $[\alpha]_D^{20}$ -61 (c 1.0, chloroform) (lit.[23] $[\alpha]_D^{22}$ -15 (c 0.2, chloroform). ^1H NMR ($CDCl_3$): δ 3.75 (bs, 1H, H2); 3.84 (dd, 1H, H6*exo*); 3.98 (dd, 1H, H6*endo*, J5,6*endo* 1.16 Hz, J6*endo*,6*exo* -7.39 Hz); 4.18 (m, 2H, H3, H4); 4.66 (bdd, 1H, H5); 5.20-5.37 (m, 2H, CH_2=CH-CH_2); 5.51 (bs, 1H, H1); 5.76 (s, 1H, H7); 5.90-5.99 (m, 1H, CH_2=CH-CH_2); 7.36-7.68 (m, 5H, phenyl).

4-O-Acetyl-1,6-anhydro-2,3-*endo*-(4-methoxybenzylidene)-β-D-mannopyranose (6, R^4=Ac). Compound 3 (2 g, 7.14 mmol) was treated with acetic anhydride (10 ml) in dry pyridine (15 ml) at 20°C. After 2 h, the reaction mixture was concentrated under reduced pressure and subsequently dissolved in dichloromethane (30 ml), washed with aqueous sodium bicarbonate (15 ml, 10%, w/v) and water (15 ml). The dried ($MgSO_4$) organic layer was concentrated in vacuo and twice coevaporated with toluene (20 ml), absolute alcohol (20 ml) and dichloromethane (20 ml) to give 6 (R^4=Ac) as a white solid, which crystallised from ethanol. Yield 2.30 g (91%). Rf 0.74 (solvent C); $[\alpha]_D^{20}$ -98.7° (c 1.0, chloroform); M.p. 153°C. ^1H NMR ($CDCl_3$): δ 2.17 (s, 3H, CH_3 acetyl); 3.81 (s, 3H, CH_3OØ); 3.86 (dd, 1H, H6*exo*, J5,6*exo* 6.36 Hz); 4.09 (dd, 1H, H6*endo*, J5,6*endo* 1.39 Hz, J6*endo*,6*exo* -7.61 Hz); 4.16 (bs, 1H, H3); 4.19 (d, 1H, H2, J1,2 2.90 Hz); 4.63 (m, 1H, H5); 5.11 (bs, 1H, H4); 5.53 (d, 1H, H1); 5.73 (s, 1H, H7); 6.92 (d, 2H, H3+H5, methoxyphenyl); 7.58 (d, 2H, H2+H6, methoxyphenyl). ^{13}C NMR ($CDCl_3$): δ 20.9 (CH_3, acetyl); 55.2 (CH_3OØ); 64.6 (C6); 71.0, 71.3, 73.3, 75.7 (C2-C5); 99.1 (C1); 104.4 (C7); 113.8 (C3+C5, methoxyphenyl); 129.1 (C2+C6, methoxyphenyl); 160.8 (C4, methoxyphenyl); 169.8 (C=O).

4-O-Allyl-1,6-anhydro-2,3-O-*endo*-(4-methoxybenzylidene)-β-D-mannopyranose (6, R^4=All). A mixture of *endo*/*exo* isomers of compound 3 (2 g, 7.1 mmol) was treated with allyl bromide in the same way as described for the synthesis of compound 5. After the usual work-up, followed by column chromatography (40 g, eluent dichloro-

methane) compound 6 (R^4=All) was obtained as a mixture of both isomers (*exo/endo*, 1/1, yield 1.95 g (86%)) from which the *endo* isomer crystallised upon standing at 0°C in ethanol. Rf 0.54 (solvent A); $[\alpha]_D^{20}$ -76° (c 1.0, chloroform); M.p. 121°C. ^{1}H NMR ($CDCl_3$): δ 3.72 (s, 1H, H4); 3.80 (s, 3H, $CH_3O\emptyset$); 3.82 (dd, 1H, H6*exo*); 3.98 (dd, 1H, H6*endo*); 4.18 (m, 4H, H2, H3, CH_2=CH-$\underline{CH}_2$); 4.63 (bd, 1H, H5); 5.21-5.36 (m, 2H, $\underline{CH}_2$=CH-CH_2); 5.50 (bs, 1H, H1); 5.71 (s, 1H, H7); 5.80-6.0 (m, 1H, CH_2=$\underline{CH}$-CH_2); 6.91 (d, 2H, H3+H5, methoxyphenyl); 7.59 (d, 2H, H2+H6, methoxyphenyl). ^{13}C NMR ($CDCl_3$): δ 55.3 (CH_3O); 63.6 (C6); 70.7 (CH_2=CH-$\underline{CH}_2$); 71.6, 73.7, 75.8, 76.2 (C2-C5); 99.0 (C1); 104.3 (C7); 113.8 (C3+C5, methoxyphenyl); 118.1 ($\underline{CH}_2$=CH-CH_2); 128.4 (C1, methoxyphenyl); 129.1 (C2+C6, methoxyphenyl); 133.9 (CH_2=$\underline{CH}$-CH_2); 160.8 (C4, methoxyphenyl).

1,6-Anhydro-4-O-benzyl-2,3-O-prop-2-enylidene-β-D-mannopyranose (7). Crude compound 1 (12.5 g, 53 mmol) was treated with 3,3-dimethoxy-1-propene (7.85 ml, 66.25 mmol) in the same way as described for the synthesis of compound 2. After the usual work-up, crude compound 4 was dissolved in a mixture of dry N,N-dimethylformamide (35 ml) and sodium hydride (6.4 g, 265 mmol), after which benzyl bromide (10.1 ml, 84.8 mmol) was added dropwise with stirring at 0°C. Within 2 h, TLC analysis (diethyl ether/petroleum ether, b.p. 40-60°C, 1/1, v/v) showed almost complete conversion of 4 (Rf 0.07) into product 7 (Rf 0.41). Excess sodium hydride was destroyed with methanol and the reaction mixture evaporated. Ether (75 ml) was added to the residue and the organic layer was washed with water (30 ml), dried ($MgSO_4$) and evaporated. The crude product 7 could be purified by crystallisation (absolute alcohol, yield 3.0 g (37%) *endo* isomer) after which the mother layer was applied to a column of silica gel (100 g) suspended in diethyl ether/petroleum ether, b.p. 40-60°C (1/1, v/v). Yield 7.99 g (52%). Rf 0.55 (solvent A); $[\alpha]_D^{20}$ -44.4° (c 1.0, chloroform); M.p. 76°C. ^{1}H NMR ($CDCl_3$): δ 3.73 (dd, 1H, H6*exo*); 3.73 (bs, 1H, H4); 3.91 (dd, 1H, H6*endo*, J5,6*endo* 1.43 Hz, J6*endo*,6*exo* -7.34 Hz); 4.14, 4.62 (2xdd, 2H, H2, H3, J2,3 6.2 Hz); 4.68 (AB, 2H, $\underline{CH}_2\emptyset$);

5.26 (d, 1H, H7, JH7, $\underline{CH}=CH_2$ 7.05 Hz); 5.38 (bs, 1H, H1); 5.37-5.51 (m, 2H, $CH=\underline{CH_2}$); 5.92-6.04 (m, 1H, $\underline{CH}=CH_2$); 7.36 (m, 5H, phenyl). ^{13}C NMR ($CDCl_3$): δ 64.5 (C6); 71.4 ($\underline{CH_2}Ø$); 71.9, 73.4, 75.4, 75.7 (C2-C5); 98.9 (C1); 104.9 (C7); 121.3 ($CH=\underline{CH_2}$); 127.7, 128.0, 134.7 (C2-C6, phenyl); 134.7 ($\underline{CH}=CH_2$); 137.3 (C1, phenyl).

4-O-Allyl-1,6-anhydro-3-O-benzyl-β-D-mannopyranose (8). To a solution of compound 5 (1.25 g, 4.31 mmol) in dry dichloromethane (100 ml) lithium aluminum hydride (2.8 g, 73.7 mmol) was added and the mixture was cooled to 0°C with stirring. Then a solution of aluminum trichloride (6.4 g, 48 mmol) in dry diethyl ether (40 ml) was added dropwise over a period of 15 min. The mixture was stirred for 1 h at 0°C and excess of reagent was destroyed by adding ethyl acetate (20 ml) and water (5 ml). The organic layer was separated and the solid residue was extracted twice with diethyl ether (100 ml). The combined extracts were washed with water, dried ($MgSO_4$) and evaporated. The residue was applied to a column of silica gel (20 g) suspended in solvent A. Evaporation of the appropriate fractions afforded 8 as an oil. Yield 0.78 g (62%). Rf 0.34 (solvent A); $[\alpha]_D^{20}$ -70° (c 0.6, chloroform), lit.[23] $[\alpha]_D^{23}$ -66° (c 0.6, chloroform). ^1H NMR ($CDCl_3$): δ 3.00 (d, 1H, OH, JH2,-OH 11.45 Hz); 3.48 (t, 1H, H4, J3,4 ≃ J4,5 ≃ 1.77 Hz); 3.69-4.05 (m, 5H, H2, H3, H6*exo*, $CH_2=CH-\underline{CH_2}$); 4.12 (dd, 1H, H6*endo*, J5,6*endo* 1.12 Hz, J6*endo*,6*exo* -7.11 Hz); 4.53 (m, 1H, H5); 4.63 (s, 2H, $\underline{CH_2}Ø$); 5.19-5.28 (m, 2H, $\underline{CH_2}=CH-CH_2$); 5.35 (t, 1H, H1, J1,2 ≃ J1,5 ≃ 1.42 Hz); 5.82-5.94 (m, 1H, $CH_2=\underline{CH}-CH_2$); 7.35 (m, 5H, phenyl). ^{13}C NMR ($CDCl_3$): δ 64.7 (C6); 70.5 ($CH_2=CH-\underline{CH_2}$); 73.9 ($\underline{CH_2}Ø$); 66.4, 73.7, 75.8, 76.1 (C2-C5); 101.8 (C1); 117.9 ($\underline{CH_2}=CH-CH_2$); 127.9, 128.2, 128.7 (C2-C6, phenyl); 134.3 ($CH_2=\underline{CH}-CH_2$); 137.2 (C1, phenyl).

4-O-Allyl-1,6-anhydro-3-O-benzyl-2-O-(trichloroacetyl carbamoyl)-β-D-mannopyranose (8, R^2=TAC). To a solution of compound 8 (R^2=H, 10 mg) in $CDCl_3$ (0.4 ml), trichloroacetyl isocyanate[21] (20 µl) was added and the product thus obtained was analysed, without further work-up, by ^1H NMR spectroscopy: δ 3.49 (t, 1H, H4); 3.82

(dd, 1H, H6*exo*); 4.13 (m, 1H, H3); 4.61 (m, 1H, H5); 4.87 (dd, 1H, H2, J1,2 2 Hz, J2,3 6 Hz); 5.50 (t, 1H, H1).

4-O-Allyl-1,6-anhydro-3-O-(4-methoxybenzoyl)-β-D-mannopyranose (9, R^4=All). Compound 6 (R^4=All, *exo/endo* mixture; 1.20 g, 3.8 mmol) was dissolved in a mixture of dichloromethane and water (9 ml, 8/1, v/v) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 1.3 g, 5.7 mmol) suspended in dichloromethane (8 ml) was added at 25°C with exclusion of light under an atmosphere of oxygen-free nitrogen. After stirring overnight, TLC analysis (solvent A) indicated complete conversion of starting material 6 (R^4=All; Rf 0.55) into product 9 (R^4=All; Rf 0.27). Dichloromethane was added (30 ml) and the organic layer was separated, washed with water (30 ml), aqueous sodium bicarbonate (30 ml, 10%, w/v) and water (20 ml), dried ($MgSO_4$) and evaporated to dryness. The residue was purified by column chromatography (silica gel, 20 g, eluent dichloromethane). Yield 1.16 g (92%). Rf 0.27 (solvent A); $[\alpha]_D^{20}$ -60.5° (c 1.0, chloroform). ^{1}H NMR ($CDCl_3$): δ 2.55 (d, 1H, OH, JH2,OH 11.75 Hz); 3.56 (t, 1H, H4); 3.84 (dd, 1H, H6*exo*); 3.87 (s, 3H, $CH_3O\emptyset$); 3.94 (ddd, 1H, H2, J2,3 5.69 Hz, J1,2 1.80 Hz); 4.06 (d, 1H, H6*endo*,J6*endo*,6*exo* -7.51 Hz); 4.18-4.38 (c, 2H, CH_2=CH-$\underline{CH}_2$); 4.57 (bd, 1H, H5); 5.21-5.41 (m, 2H, $\underline{CH}_2$=CH-CH_2); 5.40 (dd, 1H, H3, J3,4 1.33 Hz); 5.46 (t, 1H, H1); 5.88-6.00 (m, 1H, CH_2=$\underline{CH}$-CH_2); 6.95 (d, 2H, H3+H5, methoxyphenyl); 8.01 (d, 2H, H2+H6, methoxyphenyl). ^{13}C NMR ($CDCl_3$): δ 55.5 (CH_3O); 65.1 (C6); 70.8 (CH_2=CH-$\underline{CH}_2$); 66.3, 69.3, 74.4, 76.4 (C2-C5); 101.5 (C1); 114.0 (C3+C5, methoxyphenyl); 118.1 ($\underline{CH}_2$=CH-CH_2); 131.7 (C2+C6, methoxyphenyl); 134.0 (CH_2=$\underline{CH}$-CH_2); 163.9, 165 (C4, C=O, methoxyphenyl).

4-O-Acetyl-1,6-anhydro-3-O-(4-methoxybenzoyl)-β-D-mannopyranose (9, R^4=Ac). Compound 6 (R^4=Ac, 6 g, 18.6 mmol) was treated as described for the preparation of compound 9 (R^4=All). After the usual work-up, the product was purified by column chromatography (100 g, eluent dichloromethane). Yield 5.61 g (89%). Rf 0.32 (solvent A). ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 3H, acetyl); 2.36 (d, 1H, OH, JH2,OH 11.42 Hz); 3.88 (s, 3H, $CH_3O\emptyset$); 3.89 (dd, 1H, H6*exo*); 3.95

(ddd, 1H, H2, J2,3 5.79 Hz); 4.21 (dd, 1H, H6*endo*, J5,6*endo* 1.00 Hz, J6*endo*,6*exo* -7.80 Hz); 4.64 (m, 1H, H5); 4.91 (t, 1H, H4, J3,4 ≃ J4,5 ≃ 1.82 Hz); 5.39 (dd, 1H, H3); 5.49 (t, 1H, H1, J1,2 ≃ J1,5 ≃ 1.70 Hz); 6.95 (d, 2H, H3+H5, methoxyphenyl); 8.00 (d, 2H, H2+H6, methoxyphenyl). ^{13}C NMR ($CDCl_3$): δ 20.9 (CH_3 acetyl); 55.5 (CH_3-OØ); 65.2 (C6); 66.2, 69.4, 71.6, 73.4 (C2-C5); 101.7 (C1); 114.0 (C3+C5, methoxyphenyl); 131.9 (C2+C6, methoxyphenyl); 164.0, 165.0 (C4, C=O, methoxyphenyl); 169.7 (C=O, acetyl).

4-O-Acetyl-1,6-anhydro-3-O-(4-methoxybenzyl)-β-D-mannopyranose (10). A solution of 6 (R^4=Ac, 0.40 g, 1.24 mmol) and sodium cyanoborohydride (1.45 g, 23.1 mmol) in dry oxolane (25 ml) containing 4Å molecular sieves was cooled to 0°C and a saturated solution of hydrogen chloride in diethyl ether was added until the evolution of gas ceased. The mixture was neutralized with aqueous sodium bicarbonate (5 ml, 10%, w/v), filtrated, concentrated in vacuo, dissolved in dichloromethane (50 ml) and washed with water. The dried ($MgSO_4$) organic layer was concentrated under reduced pressure. Silica gel column chromatography (10 g, eluent solvent D) afforded the desired product 10 as a colourless oil. Yield 0.29 g (73%). Rf 0.39 (solvent A); $[\alpha]_D^{20}$ -30° (c 1.0, chloroform.). ^1H NMR ($CDCl_3$): δ 2.17 (s, 3H, acetyl); 3.00 (d, 1H, OH, JH2,OH 11 Hz); 3.65 (m, 2H, H2, H3); 3.75 (dd, 1H, H6*exo*); 3.81 (s, 3H, CH_3OØ); 4.14 (dd, 1H, H6*endo*); 4.65 (AB, 2H, CH_2, methoxybenzyl); 4.98 (t, 1H, H4); 5.37 (bs, 1H, H1); 6.88 (d, 2H, H3+H5, methoxyphenyl); 7.27 (d, 2H, H2+H6, methoxyphenyl). ^{13}C NMR ($CDCl_3$): δ 20.0 (CH_3, acetyl); 54.2 (CH_3OØ); 63.9 (C6); 65.3, 69.6, 71.9, 72.5, 74.1 (C2-C5, CH_2, methoxybenzyl); 100.7 (C1); 113.0 (C3+C5, methoxyphenyl); 128.7 (C2+C6, methoxyphenyl); 158.5 (C4, methoxyphenyl); 169.2 (C=O, acetyl).

3-O-Allyl-1,6-anhydro-4-O-benzyl-β-D-mannopyranose (11). Compound 7 (0.3 g, 1.03 mmol) was reduced and the product was worked-up as described for the preparation of compound 8. Silica gel column chromatography (8 g, eluent solvent D) afforded the desired product 11 as a colourless oil. Yield 0.21 g (68%). Rf 0.32

(solvent A); $[\alpha]_D^{20}$ -40° (c 2.0, chloroform). ^{1}H NMR ($CDCl_3$): δ 2.98 (d, 1H, OH, JH2,OH 11.06 Hz); 3.52 (bs, 1H, H4); 3.70 (m, 2H, H3, H6*exo*); 3.73 (ddd, 1H, H2, J1,2 2.0 Hz, J2,3 5.87 Hz); 3.95 (m, 2H, CH_2=CH-CH_2); 4.04 (dd, 1H, H6*endo*, J5,6*endo* 0.71 Hz, J6-*endo*,6*exo* -7.24 Hz); 4.55 (bd, 1H, H5); 4.66 (s, 2H, $CH_2Ø$); 5.22 (m, 2H, CH_2=CH-CH_2); 5.35 (bs, 1H, H1); 5.77-5.90 (m, 1H, CH_2=CH-CH_2); 7.37 (m, 5H, phenyl). ^{13}C NMR ($CDCl_3$): δ 64.6 (C6); 71.2 (CH_2=CH-CH_2); 72.2 ($CH_2Ø$); 66.4, 73.5, 75.3, 75.6 (C2-C5); 101.7 (C1); 117.7 (CH_2=CH-CH_2); 127.7, 128.0, 128.5 (C2-C6, phenyl); 133.9 (CH_2=CH-CH_2); 137.5 (C1, phenyl).

4-O-Allyl-1,6-anhydro-2-azido-3-O-benzyl-2-deoxy-β-D-glucopyranose (16). Trifluoromethanesulphonic anhydride (0.54 ml, 3.22 mmol) in dry 1,2-dichloroethane (2 ml) was added under an atmosphere of oxygen-free nitrogen at -10°C to a stirred solution of pyridine (0.30 ml, 3.75 mmol) and dry 1,2-dichloroethane (10 ml). After 10 min, a solution of compound 8 (0.47 g, 1.61 mmol) in 1,2-dichloroethane (3 ml) was added to the mixture and stirring was continued for 1 h at 0°C. Then TLC analysis (solvent D) indicated complete conversion of starting compound 8 (Rf 0.19) into the C-2 triflyl ester 12 (Rf 0.68). Aqueous sodium bicarbonate (10 ml, 10%, w/v) and dichloromethane (50 ml) were added, the organic layer was separated and the aqueous layer extracted with dichloromethane. The combined extracts were washed with water, dried ($MgSO_4$), evaporated and coevaporated with toluene (10 ml). Crude compound 12 was dissolved in dry N,N-dimethylformamide (20 ml), lithium azide (0.91 g, 16 mmol) was added and the mixture stirred at 20°C for 4 min after which time TLC analysis (solvent D) showed complete conversion of the triflyl ester 12 (Rf 0.68) into the azido sugar 16 (Rf 0.65). The solution was evaporated to dryness, dissolved in dichloromethane (50 ml), washed with water (20 ml), dried ($MgSO_4$) and concentrated in vacuo. The residual oil was applied to a column of silica gel (10 g, eluent dichloromethane). Yield 0.43 g (85%). Rf 0.28 (dichloromethane); $[\alpha]_D^{20}$ +74° (c 1.0, chloroform); IR (neat) 2110 cm^{-1} (νN_3). ^{1}H NMR

($CDCl_3$): δ 3.27 (bs, 1H, H2); 3.37 (t, 1H, H4); 3.63 (m, 1H, H3); 3.76 (dd, 1H, H6*exo*, J5,6*exo* 5.79 Hz); 4.01-4.05 (m, 2H, CH_2=CH-$\underline{CH}_2$); 4.07 (dd, 1H, H6*endo*, J5,6*endo* 1.17 Hz, J6*endo*,6*exo* -7.18 Hz); 4.63 (AB, 2H, $\underline{CH}_2Ø$); 4.64 (m, 1H, H5); 5.18-5.31 (m, 2H, $\underline{CH}_2$=CH-CH_2); 5.48 (bs, 1H, H1); 5.82-5.96 (m, 1H, CH_2=$\underline{CH}$-CH_2). ^{13}C NMR ($CDCl_3$): δ 59.8 (C2); 65.3 (C6); 70.2 (CH_2=CH-$\underline{CH}_2$); 72.3 ($\underline{CH}_2$-Ø); 74.3, 76.3, 76.4 (C3-C5); 100.6 (C1); 117.6 ($\underline{CH}_2$=CH-CH_2); 127.7, 128.0, 128.5 (C2-C6, phenyl); 134.2 (CH_2=$\underline{CH}$-CH_2); 137.4 (C1, phenyl).

4-O-Acetyl-1,6-anhydro-2-azido-2-deoxy-3-O-(4-methoxybenzoyl)-β-D-glucopyranose (17, R^4=Ac). Compound 9 (R^4=Ac, 6.1 g, 18.0 mmol) was treated as described for the preparation of compound 16. After the usual work-up, the product was purified by column chromatography (100 g, eluent dichloromethane). Yield 6.2 g (95%). Rf 0.22 (dichloromethane). IR (neat): 2115 cm^{-1} (νN_3). ^1H NMR ($CDCl_3$): δ 2.21 (s, 3H, CH_3, acetyl); 3.31 (bs, 1H, H2); 3.88 (s, 3H, $CH_3Ø$); 3.90 (dd, 1H, H6*exo*, J5,6*exo* 5.85 Hz); 4.26 (dd, 1H, H6*endo*, J5,6*endo* 0.59 Hz, J6*endo*,6*exo* -7.77 Hz); 4.73 (bd, 1H, H5); 4.82 (bs, 1H, H4); 5.17 (t, 1H, H3); 5.59 (bs, 1H, H1); 6.95 (d, 2H, H3+H5, methoxyphenyl); 7.97 (d, 2H, H2+H6, methoxyphenyl).

4-O-Allyl-1,6-anhydro-2-azido-2-deoxy-3-O-(4-methoxybenzoyl)-β-D-glucopyranose (17, R^4=All). Compound 17 (R^4=All) was prepared by treating 9 (R^4=All, 2.1 g, 6.23 mmol) in the same way as described for the synthesis of compound 16. Yield 1.98 g (88%). Rf 0.20 (dichloromethane); $[\alpha]_D^{20}$ +58° (c 1.0, chloroform). ^1H NMR ($CDCl_3$): δ 3.32 (bs, 1H, H2); 3.41 (bs, 1H, H4); 3.86 (dd, 1H, H6-*exo*, J5,6*exo* 5.93 Hz); 3.87 (s, 3H, $CH_3OØ$); 4.11 (d, 1H, H6*endo*, J6*endo*,6*exo* -7.60 Hz); 4.19-4.39 (m, 2H, CH_2=CH-$\underline{CH}_2$); 4.70 (bd, 1H, H5); 5.23 (m, 1H, H3); 5.21-5.40 (m, 2H, $\underline{CH}_2$=CH-CH_2); 5.58 (bs, 1H, H1); 5.89-6.02 (m, 1H, CH_2=$\underline{CH}$-CH_2); 6.95 (d, 2H, H3+H5, methoxyphenyl); 7.97 (d, 2H, H2+H6, methoxyphenyl). ^{13}C NMR ($CDCl_3$): δ 55.5 (CH_3O); 58.9 (C2); 65.2 (C6); 70.7 (CH_2=CH-$\underline{CH}_2$); 69.2, 74.0, 77.8 (C3-C5); 100.2 (C1); 113.9 (C3+C5, methoxyphenyl); 118.1 ($\underline{CH}_2$=CH-CH_2); 121.4 (C1, methoxyphenyl); 131.8 (C2+C6,

methoxyphenyl); 133.9 (CH_2=$\underline{C}$H-CH_2); 164.0, 164.8 (C=O, C4, methoxyphenyl).

4-O-Acetyl-1,6-anhydro-2-azido-2-deoxy-3-O-(4-methoxybenzyl)-β-D-glucopyranose (18). Compound 10 (0.13 g, 0.39 mmol) was treated as described for the preparation of compound 16. After the usual work-up, the product was purified by column chromatography (4 g, eluent dichloromethane). Yield 0.12 g (85%). Rf 0.15 (dichloromethane); $[\alpha]_D^{20}$ +58° (c 1.0, chloroform). ^{1}H NMR ($CDCl_3$): δ 2.16 (s, 3H, CH_3, acetyl); 3.21 (bs, 1H, H2); 3.57 (m, 1H, H3); 3.77 (dd, 1H, H6*exo*, J5,6*exo* 5.95 Hz); 3.81 (s, 3H, $CH_3O\emptyset$); 4.18 (dd, 1H, H6*endo*, J5,6*endo* 0.97 Hz, J6*endo*,6*exo* -7.43 Hz); 4.61 (m, 3H, CH_2 methoxybenzyl, H5); 4.77 (t, 1H, H4); 5.51 (t, 1H, H1); 6.88 (d, 2H, H3+H5, methoxyphenyl); 7.25 (d, 2H, H2+H6, methoxyphenyl). ^{13}C NMR ($CDCl_3$): δ 20.8 (CH_3, acetyl); 55.1 ($\underline{C}H_3O\emptyset$); 59.7 (C2); 65.1 (C6); 72.0 (CH_2, methoxybenzyl); 70.1, 73.9, 75.4 (C3-C5); 100.4 (C1); 113.8 (C3+C5, methoxyphenyl); 129.3 (C2+C6, methoxyphenyl); 159.3 (C4, methoxyphenyl); 170.1 (C=O).

3-O-Allyl-1,6-anhydro-2-azido-4-O-benzyl-2-deoxy-β-D-glucopyranose (19). Compound 19 was prepared by treating 11 (0.15 g, 0.52 mmol) in the same way as described for the synthesis of compound 16. Yield 145 mg (88%). Rf 0.24 (dichloromethane); $[\alpha]_D^{20}$ +22° (c 1.0, chloroform). ^{1}H NMR ($CDCl_3$): δ 3.22 (bs, 1H, H2); 3.36 (t, 1H, H4); 3.60 (m, 1H, H3); 3.70 (dd, 1H, H6*exo*, J5,6*exo* 5.97 Hz); 3.96 (dd, 1H, H6*endo*, J5,6*endo* 0.78 Hz, J6*endo*,6*exo* -7.32 Hz); 3.98-4.01 (m, 2H, CH_2=CH-$\underline{C}H_2$); 4.62 (bdd, 1H, H5); 4.68 (s, 2H, $\underline{C}H_2\emptyset$); 5.19-5.28 (m, 2H, $\underline{C}H_2$=CH-CH_2); 5.47 (bs, 1H, H1); 5.80-5.89 (m, 1H, CH_2=$\underline{C}$H-CH_2); 7.37 (m, 5H, phenyl). ^{13}C NMR ($CDCl_3$): δ 60.1 (C2); 65.3 (C6); 71.3, 71.4 ($CH_2\emptyset$, CH_2=CH-$\underline{C}H_2$); 74.3, 76.1, 76.4 (C3-C5); 100.5 (C1); 117.7 ($\underline{C}H_2$=CH-CH_2); 127.8, 127.9, 128.5 (C2-C6, phenyl); 133.9 (CH_2=$\underline{C}$H-CH_2); 135.7 (C1, phenyl).

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