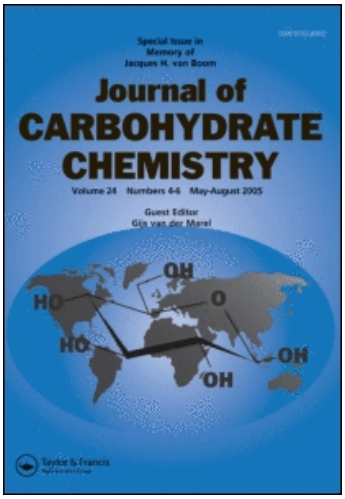

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2-*O*-Benzylation in *D*-Gluconamide Derivative Under Basic Conditions with Complete Retention of Stereo-Integrity: Convenient Access to 2-*O*-benzyl-3,4:5,6-di-*O*-isopropylidene-D-glucitol and other Differently Protected D-glucitol Derivatives

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A new and convenient synthesis of 2-*O*-benzyl-3, 4: 5, 6-di-*O*-isopropylidene-D-glucitol has been accomplished and has been generalized with the syntheses of differently protected D-glucitols at C-2 position. In the course of our new route to the differently protected D-glucitols at C-2 position, a new D-*gluco* configured building block, 1-morpholino-(3, 4: 5, 6-di-*O*-isopropylidene)-D-gluconamide has been achieved.

Keywords D-gluconolactone, morpholine, D-gluconamide, D-glucitol

2-*O*-benzyl and D-*gluco*-configured acyclic aldehyde **1** has served as a key building block during the synthesis of a new conformationally constrained 2,7-anhydrosialic acid derivative,[1] through the imine **2**. Due to the diverse and significant biological roles played by sialic acids,[2] conformationally rigid

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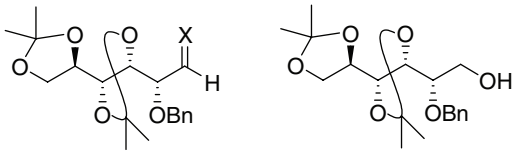


1 X = O
2 X = NBn

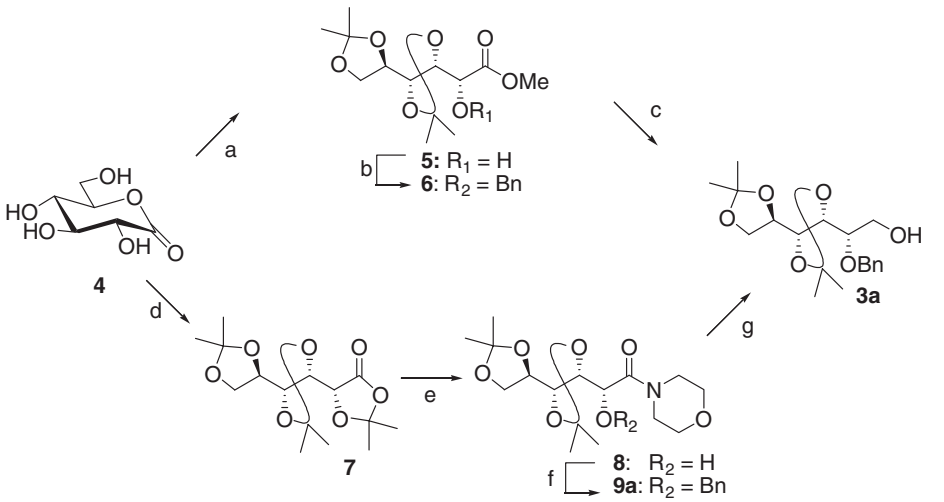
3a

Figure 1: 2-*O*-benzyl glucitol derivative **3a**—A precursor of valuable intermediates **1** and **2**.

structures[3,4] have been very attractive and important synthetic targets. These have served as valuable tools for the investigation of biological questions. Although aldehyde **1** is conveniently obtained by oxidation of **3a** using Dess-Martin reagent, it is the ready availability of **3a** that is more crucial and important.

Our three-step protocol[5] constituting conversion of *D*-glucono-lactone **4** to α-hydroxy-methyl ester **5** by a known method[6] and subsequent 2-*O*-benzylation under nonbasic conditions, followed by reduction with lithium aluminum hydride, continues to remain the only reported procedure in the literature. It has been used by Yao[1] to arrive at alcohol **3a** (Sch. 1). Our subsequent experience has shown that the *O*-benzylation using Ag_2O/BnBr is not free of difficulties. On a smaller scale (1 mmol), the reaction was satisfactory; however, the conversion always remained incomplete, despite long hours of reaction time, when conducted on a scale greater than 1 mmol. Even with excess equivalents of Ag_2O/BnBr and a change of solvents, isolated yields of **6** did not improve to more than 45% after careful and tedious silica gel column chromatography. Confronted by this difficulty and the immediate need of glucitol derivative **3a** as a chiral building block for other synthetic targets in our group, we searched for a convenient alternative. Presented herein are the results that not only provided an efficient synthesis of **3a** on multigram scale, but also paved the way for a general high-yielding route to differently protected glucitol derivatives **3b–i**. The alternative procedure starts with 1,2:3,4:5,6-tri-*O*-isopropylidene-D-gluconate **7**, conveniently available on a multigram scale in a single step from D-gluconolactone by a procedure attributed to Jarosz.[7] Lactone **7** on heating with morpholine in toluene at 90°C furnished a hitherto unknown α-hydroxy morpholine amide **8** in an isolated yield of 95% as a solid (Sch. 1).

The α-hydroxy amide **8** was subjected to *O*-benzylation using sodium hydride as base and in anhydrous DMF at room temperature. A clean reaction ensued in 30 min, giving the α-*O*-benzyl amide **9a** in an isolated yield of 90%. Since 2-*O*-benzylation has been done under basic conditions using sodium hydride, all associated apprehensions of any tampering of the stereochemistry at C-2 center were completely alleviated by comparing the product obtained through the benzylation of α-hydroxy amide **8** to that of the product obtained



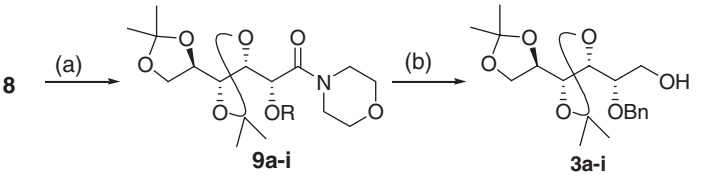
Reagents and conditions:
(a) Reference [6]; (b) Ag_2O (2eq.), BnBr (1.1eq.), CH_2Cl_2, rt, 48h, 45%;
(c) $NaBH_4$ (1.5 eq.), MeOH, rt, 12h, 90%; (d) Reference [7];
(e) Morpholine (4eq.), toluene, 90°C, 18h, 95%;
(f) NaH (1.1eq.), BnBr (1.1eq.), DMF, 0°C-rt, 30min, 90% or Ag_2O, BnBr, CH_2Cl_2, rt, 48h, 50%;
(g) $NaBH_4$ (10eq.), EtOH, 60°C, 12h, 86%.

Scheme 1. Synthesis of 2-*O*-benzyl-3, 4: 5, 6-di-*O*-isopropylidene-D-glucitol **3a**.

using a combination of silver oxide and benzyl bromide. The products obtained by either of the methods matched extremely well in optical rotation and their IR spectra were completely superimposable in the fingerprint region. The amide **9a** further underwent clean reduction with sodium borohydride in ethanol at 60°C, furnishing the 2-*O*-benzyl glucitol derivative **3a** in an isolated yield of 86%. The optical rotation and spectral data of the obtained material perfectly matched with that obtained through the conversion **6** → **3a** using lithium aluminium hydride as reported earlier[5] or using sodium borohydride. This further unambiguously proved the complete retention of the stereochemistry at the C-2 position in the amide while affecting the *O*-benzylation reaction under basic conditions. The convenience in using $NaBH_4$ for the reduction of the amide **9a** to glucitol **3a**, as opposed to the use of $LiAlH_4$ for the conversion **6** → **3a**, offered a significant advantage to this alternative preparative procedure for **3a**. The conversion of α-hydroxy amide **8** to 2-*O*-benzyl-protected glucitol derivative **3a** has been generalized, and this has enabled incorporation of other protecting groups at the C-2 hydroxy (Table 1).

The convenient availability of 2-*O*-benzyl morpholine amide **9a**, a crystalline solid with an indefinite shelf life, on multigram scale makes it a valuable building block with D-gluco configuration. Its ready conversion to differently protected D-glucitol is illustrated herein. The x-ray crystal structure data

Table 1: Differently protected glucitol at C-2 position **3a–i**



Reagents and Conditions : (a) : NaH, DMF, RX, (X = Cl / Br / I), 0°C - rt, 30 min.
(b) : $NaBH_4$, EtOH, 60°C, 12h.

		(%) Isolated Yield		Optical Rotation	
Entry	**RX**	**Amide 9a–i**	**Glucitol 3a–i**	**Amide 9a–i**	**Glucitol 3a–i**
a	$C_6H_5CH_2Br$	90	86	+10.79	+26.38
b	4-(MeO)-$C_6H_4CH_2Cl$	95	90	+15.79	+20.58
c	3,4-$(MeO)_2$-$C_6H_3CH_2Cl$	90	80	+16.49	+13.70
d	$HC{\equiv}CCH_2Cl$	94	75	+35.12	+12.39
e	$CH_2{=}CHCH_2Br$	97	90	+10.19	+4.99
f	$CH_3O(CH_2)_2OCH_2Cl$	90	82	+25.18	−8.39
g	CH_3I	86	91	+6.19	+14.49
h	CH_3CH_2I	77	89	+15.189	+22.183
i	$CH_3CH_2CH_2CH_2Br$	78	83	+11.99	+15.58

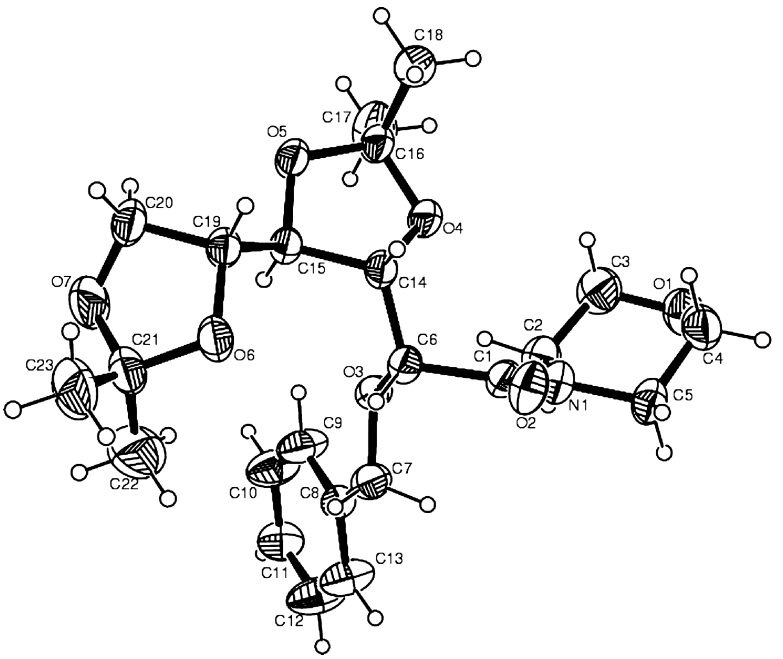


Figure 2. ORTEP plot[8] of compound **9a** with thermal ellipsoids drawn at 50% probability level (Johnson, 1976).

Table 2: Summary of crystal data and data collection parameters for 1-morpholino-(2-*O*-benzyl-3, 4: 5, 6-di-*O*-isopropylidene)-D-gluconamide (**9a**)

Chemical formula	$C_{23}H_{33}NO_7$
Formula weight	435.5
Crystal system	Monoclinic
Space groups	P 21
Unit cell dimensions	
a(Å)	9.7811 (6)
b(Å)	11.3116 (13)
c(Å)	11.0365 (16)
α, β, γ (°)	90.000(10), 99.229(7), 90.000(7)
V(Å)^3	1205.3 (2)
Z	4
D_{calcd} (mg m^{-3})	1.200
Absorption coefficient μ (mm^{-1})	0.729
F(000)	468
Index ranges	$0 \leq h \leq 11, 0 \leq k \leq 13, -13 \leq l \leq 13$
Crystal size (mm)	$0.3 \times 0.2 \times 0.2$
Measured data	2398
Unique data	2277
Parameters	299
Restraints	1
R (all data)	0.0454
wR_2	0.1110
Goodness of fit	1.035
Mean and maximum shift/esd	0.000, 0.000
Maximum and minimum difference electron density (e Å^{-3})	0.272 and –0.118

for the crystalline solid (**9a**) confirmed the complete structure and retention of stereointegrity at the C-2 position (Figure 2, Table 2). The D-*gluco*-configured α-hydroxy morpholine amide **8** and the 2-*O*-benzyl morpholine amide **9a** are potential building blocks, which, via suitable protection/deprotection strategies, can be usefully manipulated for different synthetic endeavors based on one's imagination and creativity.

X-RAY DIFFRACTION ANALYSIS OF 2-*O*-BENZYL MORPHOLINE AMIDE 9a

X-ray diffraction data for 2-*O*-benzyl morpholine amide **9a** were collected on an ENRAF NONIUS CAD4-F single crystal diffractometer equipped with graphite mono-chromated Cu-Kα radiations. Unit cell parameters and orientation matrix were obtained using 36 reflections collected by a random search routine from different zones and indexed by a method of short vectors followed by least squares refinement. The intensity data were collected by a ω-2θ scan technique at 293°K. Structure was solved by a direct method technique

using the SIR92 (WINGX) program.[9] The nonhydrogen atoms were anisotropically refined. Hydrogen atoms were fixed at geometrically meaningful positions and were given riding model refinement. Full matrix least squares refinement using F^2 was continued until maximum shift/esd converged to zero. The SHELXL97 (WINGX)[10] program was used for refinement. The x-ray diffraction data of compound **9a** is deposited in the Cambridge Crystallographic Data Centre (12, Union Road, Cambridge, CB2 1EZ, UK) and the data deposition number is CCDC 719428.

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EXPERIMENTAL SECTION

All solvents were distilled before use. Anhydrous DMF was prepared by using standard procedures that involved drying over calcium hydride followed by vacuum distillation. Melting points were determined in capillaries and are uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with deuteriochloroform ($CDCl_3$) as the solvent and tetramethylsilane as reference. Mass spectra were recorded on a MICRO-Q TOF mass spectrometer by using the ESI technique at 10 eV. Optical rotations were measured with an Autopol IV polarimeter at rt. All the reactions were monitored by TLC on precoated silica gel plates. The TLC was performed and spots were developed by dipping the silica gel plate in a solution that was prepared by adding ammonium ceric sulfate (1 g) and ammonium molybdate (21 g) to concentrated sulfuric acid (31 mL) and making the volume up to 500 mL with distilled water. The TLC plate was later heated to 100°C to develop.

Preparation of 1-morpholino-(3, 4: 5, 6-di-O-isopropylidene)-D-gluconamide (8)

To a solution of the triacetonide **7** (5 g, 5.8 mmol) in toluene (16 mL), morpholine (5.5 mL, 63.3 mmol) was added and the reaction mixture was stirred at 90°C for 18 h. On completion of the reaction, as monitored by thin layer chromatography, the reaction mixture was allowed to cool and toluene was evaporated under reduced pressure. Morpholine was removed by addition of

toluene (2 × 10 mL) and distillation of the azeotropic mixture under reduced pressure. The crude product was subjected to silica gel column chromatography (ethyl acetate:hexane, 2:8) to obtain a white solid (5.2 g, 95% yield); m.p. 46–48°C;R_f 0.16 (ethyl acetate/hexane, 4:6); $[\alpha]_D^{25} = -15.8$ (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1} 3430, 1650, 1371, 1247, 1213, 1112, 1063, 847, 511. ^1H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.26, 1.31, 1.34, 1.37 (4 × s, 12H, 4 × CH_3); 3.37–3.72 (m, 8H, morpholinyl); 3.76 (d, $J = 9.2$ Hz, 1H, -OH); 3.87–3.94 (m, 2H, CH_2CH); 3.95–4.14 (m, 3H, 3 × CH); 4.51 (d, $J = 9.2$ Hz, 1H, CHCO); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 26.6, 27.2, (4 × CH_3); 42.9, 45.4 (2 × N-CH_2); 66.3 (*C*H_2CH); 66.4, 66.7 (2 × O-CH_2); 68.0 (CH_2*C*H); 77.1, 77.6 (2 × CH); 80.5 (*C*HCO); 109.6, 110.6, (2 ×*C*Me_2); 170.3 (CO); HRMS (TOF MS ES+) m/z $[M+H]^+$ calcd. for $C_{16}H_{27}NO_7$ 345.1866, found 345.1870.

Representative Procedure for 2-O-Alkylation on the α-Hydroxy Morpholine Amide 8

*1-morpholino-(2-O-benzyl-3, 4: 5, 6-di-O-isopropylidene)- D-gluconamide (**9a**)*

A solution of the α-hydroxy amide **8** (4 g, 11.6 mmol) in dry DMF (6 mL) was added to oil-free sodium hydride (0.306 g, 12.7 mmol) in DMF (1 mL) at 0°C under inert atmosphere. This was followed by addition of benzyl bromide (1.5 mL, 12.7 mmol) and then the reaction mixture was allowed to stir at rt for 30 min. On completion of the reaction, as monitored by thin layer chromatography, the product was extracted using ethyl acetate (20 mL) and the DMF was removed by washings with brine solution (2 × 50 mL). The organic layer was separated and evaporated under reduced pressure to obtain a syrupy liquid. The crude product was subjected to silica gel column chromatography (ethyl acetate:hexane, 2:8) to obtain a syrupy liquid (5 g, 90% yield). The syrupy liquid was crystallized by addition of 1 mL of ethyl acetate and allowing the mixture undisturbed overnight to obtain colorless crystals. m.p. 67–69°C; R_f 0.20 (ethyl acetate/hexane, 4:6); $[\alpha]_D^{25} = +10.79$ (*c* 1.0, $CHCl_3$); IR (neat) $\nu_{max}cm^{-1}$1637, 1456, 1371, 1252, 1114, 1070, 847, 738, 699, 584. ^1H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.25, 1.29 (2 × s, 12H, 4 × CH_3); 3.20–3.33 (m, 1H, morpholinyl); 3.40–3.70 (m, 6H, morpholinyl); 3.78–3.88 (m, 2H, C$H_a$$H_b$CH, morpholinyl); 3.97–4.11 (m, 3H, 2 × CH, $CH_a$$H_b$CH); 4.12–4.20 (m, 1H, H-2); 4.31 (d, $J = 2.8$ Hz, 1H, CHCO); 4.42 (d, $J = 11.5$ Hz, 1H, PhC$H_a$$H_b$); 4.59 (d, $J = 11.5$ Hz, 1H, PhC$H_a$$H_b$); 7.21–7.32 (m, 5H, Ar-H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 25.2, 26.61, 26.67, 27.2 (4 × CH_3); 43.2, 45.9 (2 × N-CH_2); 66.9, 67.1 (2 × O-CH_2, morpholinyl); 67.6 (*C*H_2CH); 72.9 (*C*H_2Ph); 76.94, 76.96 (C-4, C-5); 80.7 (C-3); 81.3 (*C*HCO); 109.7, 109.9 (2 ×*C*Me_2); 127.8, 128.1, 128.5, 136.9 (Aromatic); 168.5 (CO); HRMS (TOF MS ES+) m/z $[M+H]^+$ calcd. for $C_{23}H_{33}NO_7$ 436.2335, found 436.2340.

The other 2-*O*-alkylated D-*gluco*-configured morpholine amides, **9b–i**, were prepared adapting the above procedure and using corresponding alkyl halide.

1-morpholino-(2-O-para-methoxy-benzyl-3,4:5,6-di-O-isopropylidene)-D-gluconamide ***(9b)***

R_f 0.11 (ethyl acetate/hexane, 4:6); $[\alpha]_D^{25} = +15.79$ (*c* 1.0, $CHCl_3$); IR (neat) $\nu_{max}cm^{-1}$1627, 1514, 1248, 1067, 906, 724, 647, 513. ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.24, 1.27 (2 × s, 12H, 2 × $C(CH_3)_2$); 3.20–3.30 (m, 1H, morpholinyl); 3.43–3.67 (m, 5H, morpholinyl); 3.71 (s, 3H, -OCH_3), 3.78–3.87 (m, 2H, morpholinyl); 3.94–4.10 (m, 4H, H-4, H-5, H-6, H-6′); 4.12–4.17 (m, 1H, H-3); 4.26–4.28 (m, 1H, CHCO); 4.35 (d, J_{gem} = 11.2 Hz, 1H, $ArCH_aH_b$); 4.51 (d, J_{gem} = 11.2 Hz, 1H, $ArCH_aH_b$); 6.79 (d, J = 8.4 Hz, 2H, aromatic); 7.15 (d, J = 8.4 Hz, 2H, aromatic); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 25.2, 26.5, 26.6, 27.1 (2 × $C(CH_3)_2$); 43.1, 45.9 (2 × N-CH_2); 55.2 (OCH_3); 66.9, 67.5 (2 × O-CH_2, morpholinyl); 68.0 (CH_2CH); 72.5 (-OCH_2Ar); 76.9, 80.5, 80.7, 80.9 (4 × CH); 109.6, 109.8 (2 × CMe_2); 113.8, 128.8, 129.6, 159.5 (aromatic); 168.5 (CO); HRMS (TOF MS ES+) m/z $[M+H]^+$ calcd. for $C_{24}H_{35}NO_8$ 466.2441, found 466.2445.

1-morpholino-{2-O-(3′,4′-dimethoxy-benzyl)-3,4:5,6-di-O-isopropylidene}-D-gluconamide ***(9c)***

R_f 0.11 (ethyl acetate/hexane, 4:6); $[\alpha]_D^{25} = +16.49$ (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1}1632, 1515, 1455, 1240, 1066, 1026, 845, 512. ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.24, 1.27 (2 × s, 12H, 2 × $C(CH_3)_2$); 3.20–3.40 (m, 1H, morpholinyl); 3.40–3.70 (m, 6H, morpholinyl); 3.86, 3.87 (2s, 3H, -OCH_3), 3.95–4.01 (m, 2H); 4.02–4.09 (m, 2H); 4.13–4.17 (m, 1H, H-3); 4.28–4.29 (d, J = 2.4 Hz, 1H, CHCO); 4.37 (d, J = 11.2 Hz, 1H, $ArCH_aH_b$); 4.53 (d, J = 11.2 Hz, 1H, $ArCH_aH_b$); 6.82–6.86 (m, 3H, aromatic); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 25.2, 26.6, 26.7, 27.2 (2 × $C(CH_3)_2$); 43.1, 45.9 (2 × N-CH_2); 55.90, 55.95 (2 × OCH_3); 66.9, 67.5 (CH_2-O-CH_2); 68.0 (CH_2CH); 72.9 (-OCH_2Ar); 76.9, 80.5, 80.7, 80.9 (4 × CH); 109.6, 109.8 (2 × CMe_2); 120.6, 121.0, 148.9, 159.5 (aromatic); 168.5 (CO); HRMS (TOF MS ES+) m/z $[M+H]^+$ calcd. for $C_{25}H_{37}NO_9$ 480.1225, found 480.1219.

*1-morpholino-(2-O-prop-2′-enyl-3,4:5,6-di-*O*-isopropylidene)-D-gluconamide* ***(9d)***

R_f 0.20 (ethyl acetate/hexane, 4:6); $[\alpha]_D^{25} = +10.19$ (*c* 1.0, $CHCl_3$); IR (neat) $\nu_{max}cm^{-1}$2986, 1635, 1457, 1437, 1371, 1252, 1214, 1114, 1067, 846, 750. ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.26, 1.34, 1.38, 1.39 (4 × s, 12H, 2 × $C(CH_3)_2$); 3.60–3.92 (m, 8H, morpholino); 3.93–3.99 (m, 2H,); 4.03–4.10 (m, 1H); 4.11–4.17 (m, 3H); 4.19–4.23 (dd, J_1 = 6.8 Hz, J_2 = 2.4 Hz,1H, $OCHCH_2$); 4.31 (d,

J = 2.8 Hz, 1H, CHCO); 5.20 (d, J = 10.8 Hz, 1H, olefin CH_cH$_t$); 5.26–5.32 (d, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1H, olefin CH$_c$$H_t$); 5.86–5.95 (m, 1H, olefin CH); ^{13}C NMR (CDCl$_3$/TMS, 100 MHz): δ 25.1, 26.59, 26.61, 27.2 (2 × C(CH$_3$)$_2$); 43.3, 45.9 (2 × N-CH$_2$); 67.0, 67.2 (2 × O-CH$_2$, morpholinyl); 67.7 (OCHCH$_2$); 71.5 (-OCH$_2$CHCH$_2$); 76.8, 77.0, 80.8, 81.2 (4 × CH); 109.7, 109.8 (2 ×CMe$_2$); 117.7 (olefin CH$_2$) ; 133.4 (olefin CH); 168.7 (CO); HRMS (TOF MS ES+) m/z [M+H]$^+$ calcd. for C$_{19}$H$_{31}$NO$_7$ 386.2179, found 386.2170.

*1-morpholino-(2-O-prop-2′-ynyl-3,4:5,6-di-O-isopropylidene)-D-gluconamide (**9e**)*

R_f 0.20 (ethyl acetate/hexane, 4:6); $[\alpha]_D^{25}$ = +35.12 (c 1.0, CHCl$_3$); IR (neat) ν_{max}cm^{-1}2986, 1632, 1440, 1372, 1250, 1214, 1113, 1065, 1029, 845, 752, 666, 513. ^{1}H NMR (CDCl$_3$/TMS, 400 MHz): δ 1.27, 1.29, 1.32, 1.34 (4 × s, 12H, 2 × C(CH$_3$)$_2$); 2.42 (m, 1H, alkyne); 3.30–3.70 (m, 8H, morpholino); 3.84–3.90 (dd, J = 8.0, 4.8 Hz, 1H, OCH_aH$_b$CH); 3.91–4.18 (multiplets, 5H); 4.20–4.28 (dd, J_1 = 16.0, 2.4 Hz, 1H, OCH_aH$_b$CH); 4.41 (d, J = 2.8 Hz, 1H, CHCO); ^{13}C NMR (CDCl$_3$/TMS, 100 MHz): δ 25.1, 26.6, 27.1 (2 × C(CH$_3$)$_2$); 43.2, 46.1 (2 × N-CH$_2$); 57.9 (propargyl CH$_2$), 66.9 (2 × O-CH$_2$, morpholinyl); 67.6 {(CH$_3$)$_2$COCH$_2$}; 75.6 (CH, alkyne); 76.9, 77.0, 79.7, 80.4 (4 × CH); 109.8, 110.2 (2 ×CMe$_2$); 167.9(CO); HRMS (TOF MS ES+) m/z [M+H]$^+$ calcd. for C$_{19}$H$_{29}$NO$_7$ 384.2022, found 384.2032.

*1-morpholino-{2-O-(2′-methoxyethoxy)methyl-3,4:5,6-di-O-isopropylidene}-D-gluconamide (**9f**)*

R_f 0.03 (ethyl acetate/hexane, 4: 6); $[\alpha]_D^{25}$ = +25.18 (c 1.0, CHCl$_3$); IR (neat) ν_{max}cm^{-1}2895, 1636, 1456, 1371, 1248, 1214, 1113, 1065, 1019, 846. ^{1}H NMR (CDCl$_3$/TMS, 400 MHz): δ 1.27, 1.30, 1.33, 1.34 (4 × s, 12H, 2 × C(CH$_3$)$_2$); 3.29 (s, 3H, OCH$_3$); 3.32–3.40 (m, 1H, morpholinyl); 3.45 (t, J = 4.4 Hz, 2H, OCH_2CH$_2$OMe); 3.54–3.71 (m, 6H+2H, morpholinyl, CH_2OCH$_3$); 3.72–3.81 (m, 1H, morpholinyl); 3.82–3.87 (dd, J_{gem} = 7.6 Hz, $J_{6a,5}$ = 5.6 Hz, 1H, H$_a$-6); 3.92–3.97 (m, 1H, CH); 3.98–4.10 (m, 2H, 2 × CH); 4.12–4.16 (dd, J_{gem} = 7.2 Hz, $J_{6b,5}$ = 3.2 Hz, 1H, H$_b$-6); 4.50 (d, $J_{2,3}$ = 2.8 Hz, 1H, CHCO); 4.72 (s, 2H, OCH$_2$O); ^{13}C NMR (CDCl$_3$/TMS, 100 MHz): δ 25.1, 26.4, 26.7, 27.2 (2 × C(CH$_3$)$_2$); 42.9, 46.1 (2 × N-CH$_2$); 58.9 (OCH$_3$); 66.9, 67.3 (2 × O-CH$_2$, morpholinyl); 67.4 (CH$_2$OCH$_3$); 67.9 (C-6); 71.5 (-OCH$_2$CH$_2$OMe); 76.8, 76.9, 77.3, 80.3 (4 × CH); 95.6 (OCH$_2$O); 109.6, 110.1 (2 ×CMe$_2$); 168.2 (CO); HRMS (TOF MS ES+) m/z [M+H]$^+$ calcd. for C$_{20}$H$_{35}$NO$_9$ 434.2390, found 434.2392.

*1-morpholino-(2-O-methyl-3, 4: 5, 6-di-O-isopropylidene)-D-gluconamide (**9g**)*

R_f 0.28 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{25}$ = +6.195 (c 1.0, CHCl$_3$); IR (neat) ν_{max}cm^{-1}1653, 1456, 1380, 1252, 1114, 1070, 847, 845, 512. ^{1}H NMR (CDCl$_3$/TMS, 400 MHz): δ 1.34, 1.36, 1.37, 1.40 (4 × s, 12H, 2 × C(CH$_3$)$_2$); 3.42 (s, 3H, OCH$_3$); 3.60–3.92 (m, 8H, morpholinyl); 3.94–3.98 (dd, 1H, J_{gem} = 8.0,

$J_{6,5}$ = 4.0 Hz, OCH_aH$_b$CH); 4.01–4.21 (m, 5H, H-2, H-3, H-4, H-5, H$_b$-6); ^{13}C NMR ($CDCl_3$/TMS, 400 MHz): δ 25.2, 26.6, 26.67, 27.0, (2 × C(CH_3)$_2$); 43.2, 45.6 (2 × N-CH_2); 66.0, 67.2 (2 × O-CH_2, morpholinyl); 67.6 (OCH_2CH); 80.6, 77.0, 76.6 (3 × CH); 83.5 (*C*HCO); 109.6, 109.7 (2 ×*C*Me$_2$); 168.3 (CO); HRMS (TOF MS ES+) m/z [M+H]$^+$ calcd. for $C_{17}H_{30}NO_7$, 360.2022, found 360.2019.

*1-morpholino-(2-O-ethyl-3, 4: 5, 6-di-O-isopropylidene)-D-gluconamide (**9h**)*

R_f 0.20 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{25}$ = +15.189 (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1}1637, 1458, 1371, 1253, 1215, 1151, 1068, 846; ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.09–1.12 (t, 3H, J = 6.8 Hz, OCH_2CH_3); 1.21, 1.23, 1.24, 1.27, (4 × s, 12H, 2 × C(CH_3)$_2$); 3.21–3.39 (m, 2H, OCH_2CH$_3$); 3.47–3.80 (m, 8H, morpholinyl); 3.81–3.84 (dd, 1H, J_{gem} = 8.0 Hz, $J_{6a,5}$ = 4.4 Hz, OCH_aH$_b$CH); 3.88–3.98 (m, 2H, 2 × CH); 3.99–4.02 (dd, J_{gem} = 8.0 Hz, $J_{6b,5}$ = 5.2 Hz, 1H, OCH$_a$$H_b$); 4.04–4.07 (dd, 1H,$J_{3,4}$ = 7.2, $J_{3,2}$ = 2.4 Hz, *CH*CHCO); 4.11–4.12 (d, J = 2.4 Hz, 1H, CHCO); ^{13}C NMR ($CDCl_3$/TMS, 400 MHz): δ 14.9 (CH_2*C*H$_3$); 25.2, 26.6, 26.67, 27.0 (2 × C(CH_3)$_2$); 43.1, 45.7 (2 × N-CH_2); 66.1 (O*C*H$_2$CH$_3$); 66.8, 67.1 (2 × O-CH_2, morpholinyl); 67.5 (*C*H$_2$CH); 76.7, 76.9, 80.8, (3 × CH); 81.7, (*C*HCO); 109.6, 109.7 (2 ×*C*Me$_2$); 168.8 (CO); HRMS (TOF MS ES+) m/z [M+Na]$^+$ calcd. for $C_{18}H_{31}NO_7Na$, 396.1998, found 396.1991.

*1-morpholino-(2-O-1butyl-3, 4: 5, 6-di-O-isopropylidene)-D-gluconamide (**9i**)*

R_f 0.2 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{25}$ = +11.99 (*c* 1.0, $CHCl_3$); IR (neat) ν_{max}cm^{-1}2923, 1637, 1458, 1371, 1253, 1215, 1068, 846 H NMR ($CDCl_3$/TMS, 400 MHz): δ 0.85 (t, 3H, J = 7.2, CH_3CH$_2$); 1.12–1.21 (m, 2H, butyl); 1.27, 1.28, 1.30, 1.32 (4s, 12H, 2 × C(CH_3)$_2$); 1.46–1.57 (m, 2H, butyl); 3.25–3.39 (m, 2H, OCH_2CH$_2$); 3.49–3.90 (m, 8H, morpholinyl); 3.81–4.04 (m, 3H, H-4, H-5, H$_a$-6); 4.05–4.09 (m, 1H, H$_b$-6); 4.09–4.13 (dd, $J_{3,4}$ = 6.4, $J_{3,2}$ = 2.0 Hz, 1H,*CH*CHCO), 4.14–4.18 (d, J = 2.0 Hz, 1H, CHCO);^{13}C NMR ($CDCl_3$/TMS, 400 MHz): δ 13.8 (*C*H$_3$CH$_2$); 19.23 (*C*H$_2$CH$_3$); 25.1, 26.5, 26.6, 27.2 (2 × C(CH_3)$_2$); 31.7(CH_2, butyl) 43.2, 45.8 (2 × NCH_2); 67.1, 67.3 (2 × O-CH_2, morpholinyl); 67.6 (O*C*H$_2$, butyl); 70.8 (O*C*H$_2$CH); 76.8, 77.0, 81.0 (3 × CH); 82.2 (*C*HCO); 109.7, 109.8 (2 ×*C*Me$_2$); 169.0 (CO) HRMS (TOF MS ES+) m/z [M+Na]$^+$ calcd. for $C_{20}H_{35}NO_7Na$ 424.2311, found 424.2311.

Representative Procedure for the Reduction of 2-O-alkylated Morpholine Amides 9a–i to the Corresponding D-glucitols 3a–i

*2-O-benzyl-3, 4: 5, 6-di-O-isopropylidene-D-glucitol (**3a**)*

To a solution of the α-*O*-benzyl amide **9a** (5 g, 11.5 mmol) in 10 mL of ethanol, sodium borohydride (7.4 g, 185 mmol) was added and the reaction mixture was stirred at 60°C for 12 h. On completion of the reaction, as monitored

by thin layer chromatography, the reaction mixture was allowed to cool and ethanol was evaporated under reduced pressure. The residue obtained was dissolved in 25 mL of water and the solution was neutralized using acetic acid . The product was extracted using diethylether (2 × 30 mL) and the combined ether extracts were evaporated under reduced pressure to obtain the crude product. This was subjected to silica gel column chromatography (ethyl acetate:hexane, 2.5:7.5) to give a colorless syrup (3.5 g, 86%). R_f 0.33 (ethyl acetate/hexane, 4:6); $[\alpha]_D^{25} = +26.38$ (*c* 1.0, $CHCl_3$); IR (neat) $\nu_{max}cm^{-1}$3481, 1217, 1071, 772, 698, 669. ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.35, 1.39, 1.42 (3 × s, 12H, 4 × CH_3); 3.60–4.20 (multiplets, 8H), 4.68 (d, $J = 11.7$ Hz, 1H, PhCH_aH$_b$); 4.78 (d, $J = 11.7$ Hz, 1H, PhCH$_a$$H_b$); 7.25–7.39 (m, 5H, Ar-H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 25.2, 26.4, 26.7, 27.2 (4 × CH_3); 62.2 (CH_2OH); 67.9 (C-O-*C*H$_2$); 72.5 (C-O-CH$_2$*C*H); 77.4, 77.9 (2 × CH); 78.1 (PhCH$_2$); 81.9 (*C*HCH$_2$OH); 109.77, 109.79 (2 ×*C*Me$_2$); 127.7, 127.8, 127.9,128.5, 138.3 (aromatic); HRMS (TOF MS ES+) m/z $[M+Na]^+$ calcd. for $C_{19}H_{28}O_6$ 375.1784, found 375.1789.

2-*O*-alkylated morpholine amides **9b–i** were reduced using the above procedure to the glucitols **3b–i**.

*2-O-para-methoxy-benzyl-3, 4: 5, 6-di-O-isopropylidene-D-glucitol (**3b**)*

R_f 0.53 (ethyl acetate/hexanes, 4:6); $[\alpha]_D^{25} = +20.58$ (*c* 1.0, $CHCl_3$); IR (neat) $\nu_{max}cm^{-1}$3478, 1513, 1371, 1246, 1213, 1068, 1035, 845, 752, 667, 512. ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.27, 1.30, 1.31, 1.32 (4 × s, 12H, 2 × C(CH_3)$_2$); 3.51–3.55 (m, 1H, H$_a$-6); 3.65–3.70 (dd, $J_{gem} = 12.0$ Hz, $J_{1,2} = 4.4$ Hz, 1H, CH_aH$_b$OH); 3.72 (s, 3H, OCH_3); 3.74–3.80 (dd, $J_{gem} = 12.0$ Hz, $J_{1,2} = 4.4$ Hz, 1H, CH$_a$$H_b$OH); 3.81–3.86 (dd, $J_{gem} = 8.4$ Hz, $J_{6b,5} = 5.6$ Hz, 1H, H$_b$-6); 3.90–4.01 (m, 2H, 2 × CH); 4.02–4.09 (m, 2H, 2 × CH); 4.53 (d, $J_{gem} = 11.2$ Hz, 1H, ArCH_aH$_b$); 4.60 (d, $J_{gem} = 11.5$ Hz, 1H, ArCH$_a$$H_b$); 6.78–6.81 (m, 2H, aromatic); 7.21–7.23 (m, 2H, aromatic); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 25.4, 26.7, 26.9, 27.4 (2 × C(*C*H$_3$)$_2$); 55.5 (OCH_3); 62.5 (CH_2OH); 68.1 (C-6); 72.5 (O*C*H$_2$Ar); 77.3, 77.5, 77.7, 81.9 (4 × CH); 109.6, 109.8 (2 ×*C*Me$_2$); 113.8, 129.4, 129.6, 159.5 (aromatic); HRMS (TOF MS ES+) m/z $[M+H]^+$ calcd. for $C_{20}H_{29}O_7$ 383.2441, found 383.2445.

*2-O-(3′,4′-dimethoxy-benzyl)-3, 4: 5, 6-di-O-isopropylidene-D-glucitol (**3c**)*

R_f 0.46 (ethyl acetate/hexane, 4:6); $[\alpha]_D^{25} = +13.70$ (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1}3512, 2934, 1515, 1371, 1260, 1238, 1213, 1068, 1027, 845, 751, 666, 512. ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.27, 1.31, 1.32, 1.34 (4 × s, 12H, 2 × C(CH_3)$_2$); 3.52–3.56 (m, 1H, H$_a$-6), 3.67–3.73 (dd, $J_{gem} = 12.0$ Hz, $J_{1,2} = 4.4$ Hz, 1H, CH_aH$_b$OH); 3.76–3.78 (m, 1H, CH$_a$$H_b$OH); 3.79, 3.81 (2 × s, 6H, 2 × OCH_3), 3.82–3.87 (dd, $J_{gem} = 8.4$ Hz, $J_{6b,5} = 5.6$ Hz, 1H, H$_b$-6); 3.91–4.02 (m, 2H, 2 × CH); 4.05–4.11 (m, 2H, 2 × CH); 4.54 (d, $J_{gem} = 11.6$ Hz, 1H, ArCH_aH$_b$);

4.62 (d, J_{gem} = 11.6 Hz, 1H, $ArCH_aH_b$); 6.75 (d, J = 8.0 Hz,1H, Ar-H); 6.80–6.83 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz,1H, Ar-H); 6.88 (d, J = 1.6 Hz,1H, Ar-H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 25.1, 26.4, 26.7, 27.2 (2 × $C(CH_3)_2$); 55.8, 55.9 (2 × OCH_3); 62.3 (CH_2OH); 67.8 (CH_2CH); 72.5 (OCH_2Ar); 77.2, 77.5, 77.9, 81.9 (4 × CH); 109.76, 109.78 (2 × CMe_2); 111.0, 111.3, 120.3, 130.9, 148.7, 149.1 (Aromatic); HRMS (TOF MS ES+) m/z $[M+H]^+$ calcd. for $C_{21}H_{31}O_8$ 397.3351, found 397.3346.

*2-O-prop-2′-enyl-3,4:5,6-di-O-isopropylidene-D-glucitol (**3d**)*

R_f 0.34 (ethyl acetate/hexane, 4:6); $[\alpha]_D^{25}$ = +4.99 (*c* 1.0, $CHCl_3$); IR (neat) $\nu_{max}cm^{-1}$3448, 2986, 1371, 1248, 1212, 1152, 1067, 845, 512. ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.28, 1.31, 1.35 (3 × s, 12H, 2 × $C(CH_3)_2$); 3.46–3.52 (m, 1H); 3.68–3.80 (ddd, J_1 = 12.0 Hz, J_2 = 4.8 Hz, J_3 = 0.8 Hz, 2H, -OCH_2CHCH_2); 3.85–4.20 (multiplets, 7H); 5.10 (d, J = 11.2 Hz, 1H, olefin CH_cH_t); 5.19–5.27 (m, J_1 = 16.6 Hz, 1H, olefin CH_cH_t); 5.81–5.94 (m, 1H, olefin CH); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 25.2, 26.4, 26.6, 27.1 (2 × $C(CH_3)_2$); 62.2 (CH_2OH); 67.9 (C-6); 71.7 (-OCH_2CHCH_2); 77.3, 77.8, 81.8 (4 × CH); 109.7, 109.8 (2 × CMe_2); 117.0 (olefin CH_2) ; 134.8 (olefin CH); HRMS (TOF MS ES+) m/z $[M+Na]^+$ calcd. for $C_{15}H_{26}O_6$ 325.1627, found 325.1622.

*2-O-prop-2′-ynyl-3,4:5,6-di-O-isopropylidene-D-glucitol (**3e**)*

R_f 0.40 (ethyl acetate/hexane, 4:6); $[\alpha]_D^{25}$ = +12.39 (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1}3432, 2986, 1440, 1372, 1250, 1214, 1113, 1065, 1029, 845, 752, 666, 513. ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.36, 1.38, 1.42, 1.44 (4 × s, 12H, 2 × $C(CH_3)_2$); 2.45 (m, 1H, alkyne); 3.72–3.77 (dd, J_1 = 8.4 Hz, J_2 = 4.4 Hz,1H, $CHCH_2OH$); 3.78–3.84 (dd, J = 12.0, 4.4 Hz, 1H, CH_aH_bOH); 3.86–3.92 (dd, J = 12.0, 4.4 Hz, 1H, CH_aH_bOH); 3.93–3.98 (dd, J = 8.4, 5.6 Hz, 1H); 4.00 (d, J = 7.2 Hz, 1H); 4.03–4.10 (m, 1H); 4.11–4.15 (dd, J = 7.2, 4.4 Hz, 1H); 4.16–4.20 (dd, J_1 = 8.4, 6.0 Hz, 1H); 4.32–4.47 (m, 1H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 25.2, 26.4, 26.7, 27.2 (2 × $C(CH_3)_2$); 57.8 (propargyl CH_2), 62.2 (CH_2OH); 67.9 {$(CH_3)_2COCH_2$}; 74.8 (CH, alkyne); 77.3, 77.6, 77.8, 81.8 (4 × CH); 109.90, 109.92 (2 × CMe_2); HRMS (TOF MS ES+) m/z $[M+H]^+$ calcd. for $C_{15}H_{24}O_6$ 301.1122, found 301.1120.

*2-O-(2′-methoxyethoxy)methyl-3,4:5,6-di-O-isopropylidene-D-glucitol (**3f**)*

R_f 0.15 (ethyl acetate/hexane, 6:4); $[\alpha]_D^{25}$ = +25.18 (*c* 1.0, $CHCl_3$); IR (neat) $\nu_{max}cm^{-1}$3467, 1456, 1380, 1249, 1212, 1126, 1065, 1035, 845. ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.34, 1.37, 1.40, 1.41 (4 × s, 12H, 2 × $C(CH_3)_2$); 3.39 (s, 3H, OCH_3); 3.56 (t, J = 4.4 Hz, 2H, $OCH_2CH_2OCH_3$); 3.67–3.75 (m, 2H, H-4, H_a-6); 3.76–3.80 (m, 2H, CH_2OH); 3.85–3.95 (m, 3H, CH_2OCH_3, H-5); 4.01–4.08 (m, 2H, H-2, H-3); 4.13–4.19 (m, 1H, H_b-6); 4.78–4.81 (d, 1H, J = 7.2 Hz, OCH_aH_bO); 4.90–4.94 (d, 1H, J = 7.2 Hz, OCH_aH_bO); ^{13}C NMR

($CDCl_3$/TMS, 100 MHz): δ 25.1, 26.4, 26.7, 27.1 (2 × C(CH_3)$_2$); 58.9 (OCH_3); 63.5 (CH_2OH); 67.5 (CH_2OCH_3); 67.9 (C-6); 71.6 (-OCH_2CH_2OMe); 77.3, 77.6, 80.9, 81.4 (4 × CH); 96.3 (OCH_2O); 109.7, 109.8 (2 ×CMe_2); HRMS (TOF MS ES+) m/z $[M+H]^+$ calcd. for $C_{16}H_{30}O_8$ 351.2019, found 351.2018.

*2-O-methyl-3, 4: 5, 6-di-O-isopropylidene-D-glucitol (**3g**)*

R_f 0.29 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{25} = +14.5$ (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1}3427, 1371, 1249, 1213, 1069, 846, 740, ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.28, 1.30, 1.34, 1.35 (4 × s, 12H, 2 × C(CH_3)$_2$); 2.60 (brs, OH); 3.30–3.34 (m, 1H); 3.43 (s, OCH_3); 3.67–3.83 (m, 2H, CH_2OH); 3.88–3.92 (m, 2H); 3.96–4.03 (m, 2H); 4.07–4.13 (m,1H); ^{13}C NMR ($CDCl_3$/TMS, 100 MHz): δ 25.1, 26.4, 26.6, 27.0 (2 × C(CH_3)$_2$); 58.5 (OCH_3); 61.5 (CH_2OH); 67.9 (C-6); 77.2, 77.3, 80.6, 81.7 (4 × CH); 109.6, 109.7 (2 ×CMe_2); HRMS (TOF MS ES+) m/z $[M+Na]^+$ calcd. for $C_{13}H_{24}O_6Na$ 299.1471, found 299.1473.

*2-O-ethyl-3, 4: 5, 6-di-O-isopropylidene-D-glucitol (**3h**)*

R_f 0.42 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{25} = +22.18$ (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1}3450, 1372, 1264, 1213, 1069, 846, 732, 512. ^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 1.14–1.18 (t, 3H, J = 6.8Hz, CH_3); 1.21, 1.23, 1.24,1.27 (4 × s, 12H, 2 × C(CH_3)$_2$); 3.42–3.44 (m, 1H, O$CH_a$$H_b$$CH_3$);3.48–3.58 (m, 1H, O$CH_a$$H_b$$CH_3$); 3.65–3.72 (m, 1H, $CH_a$$H_b$OH); 3.73–3.78 (dd, 1H, J = 12.0, 4.8 Hz, C$H_a$$H_b$OH); 3.86–3.90 (m, 1H, C$H_a$$H_b$CH); 3.91–4.12 (m, 5H, H-2, H-3, H-4, H-5, H_b-6); ^{13}C NMR ($CDCl_3$/TMS, 400 MHz): δ 15.37 (OCH_2CH_3); 25.1, 26.34, 26.5, 27.0 (2 × C(CH_3)$_2$); 62.2 (1 × CH_2OH); 66.23 (OCH_2CH_3); 67.81 (OCH_2CH); 76.7, 77.6, 78.06, 81.84 (4 × CH); 109.6, 109.7 (2 × C (CH_3)$_3$); HRMS (TOF MS ES+) m/z $[M+Na]^+$ calcd. for $C_{14}H_{26}NO_6Na$, 313.1627, found 313.1630.

*2-O-butyl-3, 4: 5, 6-di-O-isopropylidene-D-glucitol (**3i**)*

R_f 0.20 (ethyl acetate/hexane, 3:7); $[\alpha]_D^{25} = +15.58$ (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} cm^{-1}3499.9, 2992, 1370, 1210, 1067, 842, 735.^{1}H NMR ($CDCl_3$/TMS, 400 MHz): δ 0.88–0.93 (t, C$H_3$$CH_2$); 1.23 (m, 2H, CH_2CH_3); 1.32, 1.36,1.38, 1.39 (4s, 12H, 2 × C(CH_3)$_2$); 1.54–1.62 (m, 2H, OCH_2CH_2, butyl); 2.22–2.28 (brs, OH); 3.44–3.56 (m, 2H, OCH_2, butyl); 3.63–3.71 (m, 1H, H-2); 3.71–3.77 (dd, J_{gem} = 12.0 Hz, $J_{1,2}$ = 4.8 Hz, 1H, C$H_a$$H_b$OH); 3.81–3.87 (dd, J_{gem} = 12.0 Hz, $J_{1,2}$ = 4.8 Hz, 1H, $CH_a$$H_b$OH); 3.91–3.96 (dd, J_{gem} = 8.4 Hz, $J_{6a,5}$ = 5.2 Hz, 1H, H_a-6); 3.96–4.07 (m, 3H, H-3, H-4, H-5); 4.12–4.17 (dd, J_{gem} = 8.4 Hz, $J_{6a,5}$ = 5.6 Hz, 1H, H_b-6); ^{13}C NMR ($CDCl_3$/TMS, 400 MHz): δ 13.9 (CH_3CH_2); 19.4 (CH_2CH_3); 25.2, 26.4, 26.6, 27.1 (2 × C(CH_3)$_2$); 32.1 (OCH_2CH_2, butyl); 62.3 (CH_2OH); 67.9 (OCH_2butyl); 70.7 (C-6); 77.2, 77.3, 78.02, 82.1 (4 × CH); 109.72,109.77 (2 ×CMe_2); HRMS (TOF MS ES+) m/z $[M+Na]^+$ calcd. for $C_{16}H_{30}NO_6Na$, 341.1940, found 341.1941.

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