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# Synthesis and Reactivity of a New Glycosyl Donor: *O*-(1-Phenyltetrazol-5-yl) Glucoside

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**Abstract**—A new glycosyl donor possessing an anomeric *O*-(1-phenyltetrazol-5-yl) group is prepared from 2,3,4,6-tetra-*O*-benzyl-D-glucose (**2**) and commercially available 5-chloro-1-phenyl-1*H*-tetrazole (**1**). The synthesis of glycosides derived from the donor and a few primary and secondary alcohols is reported.

## Introduction

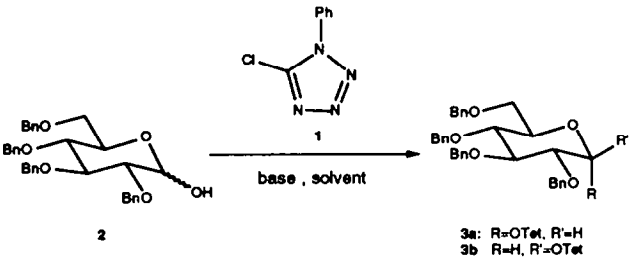
High yielding, selective and rapid *O*-glycosidation methods using stoichiometric amounts of donors and acceptors are a long-standing and important goal of carbohydrate chemistry.[1-6] Shortcomings of the classical Koenigs–Knorr method[7] (e.g. harsh conditions required to generate glycosyl halides which often are thermally unstable and the requirement for heavy metal salts as promoters) have spurred the search for new glycosyl donors. Many donors other than halides have been investigated. These include *N*-methyl imidates,[8,9] alkyl- and aryl thioglycosides,[10-17] *O*- and *S*-carbonates,[18-21] phosphates and phosphites,[22-33] *O*-pentenyl glycosides,[34,35] glycals,[36-44] sulfonamides[45,46] and *O*-selenides,[47-49] among others.

Among the most successful glycosyl donors are Schmidt's trichloroacetimidates[50] which are readily generated in one step from the corresponding hemiacetals. Glycosidation by these donors is promoted by a variety of Lewis acids. Stereoselectivity can be controlled by choice of solvent, temperature and promoter and chemical yields are generally high. Drawbacks of the method include lower chemical yields with poorly reactive glycosyl acceptors due to a competing rearrangement of the trichloroacetimidates to *N*-trichloroacetyl glycosylamines. Like other donors, the trichloroacetimidates cannot be used to make β-D-mannopyranosides selectively.

An improved glycosyl donor must include all the advantages of the trichloroacetimidates and avoid their drawbacks. Trichloroacetimidates are representatives of a class of donors characterized by an iminoether function carrying electron-withdrawing substituents, and one may expect to find similarly advantageous properties with other members of this class of compounds. One such donor is derived from 2-chloro-3,5-dinitropyridine and leads to good yields and selectivity in the synthesis of β-glycosides.[51] We speculated that a promising donor could be derived from the commercially available 5-chloro-1-phenyl-1*H*-tetrazole (**1**). This halogen compound should react with hemiacetals to yield 5-alkoxytetrazoles which may display a similar reactivity as trichloroacetimidates. The analogous thio-derivatives have been obtained by Ogura and co-workers[52] from *S*,*S*'-bis(1-phenyl-1*H*-tetrazol-5-yl) dithiocarbonate. Yields were unsatisfactory, however, and glycosidations required the use of AgOTf or $PdCl_2(CH_3CN)_2$/2AgOTf as promoters, led to poor stereoselectivity, and proceeded in variable chemical yields.[53] We report preliminary results on the synthesis of a glycosyl donor having an anomeric *O*-(1-phenyltetrazol-5-yl) (OTet) group and on its reactivity with MeOH, and a few primary and secondary alcohols.

## Results and Discussion

We focused our initial investigations on the reaction of 2,3,4,6-tetra-*O*-benzyl-D-glucose (**2**)[54] with 5-chloro-1-phenyl-1*H*-tetrazole (**1**, Scheme I).

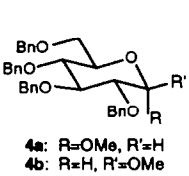



**Scheme I.**

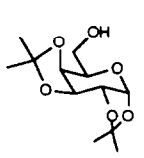
As shown in Table 1, various bases promote the formation of the α and/or β anomers of *O*-1-(1'-phenyl-1*H*-tetrazolyl) 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose **3a** and **3b**. The axial anomer **3a** was formed using either KOH in DMSO or *n*-BuLi in THF (entries 1 and 2). The former conditions lead presumably to equilibration of the hemiacetals and to the thermodynamically preferred α-D-anomer. It has been suggested that the axial lithium alkoxide derived from 2,3,4,6-tetra-*O*-benzyl-D-glucose (**2**) is stabilized by coordination between the lithium cation and the C(2) benzyloxy group.[31] Conditions for the preparation of pure **3b** have not yet been found; however, approximately 1:4 mixtures of **3a** and **3b** were obtained in high yield (entries 3 and 4). Although these anomers are stable on silica gel

provided that 1 % $Et_3N$ is added to the eluant, and do not interconvert, they could not be separated by column chromatography, and the mixtures were used for glycosidations. The ratio of anomers was determined by integration of the H-C(1) signal in the $^1H$ NMR spectrum of the mixture. The α-D anomer **3a** is characterized by an H-C(1) doublet ($J$=3.1 Hz) at 6.51 ppm and the β-D-anomer **3b** by a doublet ($J$ = 7.4 Hz) at 5.96 ppm.

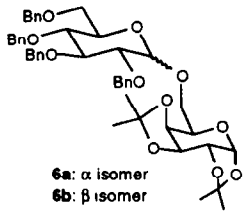
To evaluate the reactivity of **3**, we examined its solvolysis in MeOH. Boiling a 3.5:1 mixture of **3a**:**3b** in dry MeOH for 4 h converted it cleanly and quantitatively to the methyl 2,3,4,6-tetra-*O*-benzyl-α- and β-glycosides (**4a** and **4b**). The ratio of **4a**:**4b** was 1:3.5 from the integration of the methoxyl signals at 3.39 and 3.59 ppm respectively. This result suggested that inversion of configuration with reactive alcohols occurs in the absence of a promoter. Glycosidation of the pure α-D-anomer **3a**, however, led almost quantitatively to a 1:9 mixture of **4a**:**4b**, showing that methanolysis in the absence of a promoter does not proceed exclusively by an $S_N2$ mechanism.




**4a**: R=OMe, R'=H
**4b**: R=H, R'=OMe




**5**




**6a**: α isomer
**6b**: β isomer

Simply heating equimolar amounts of more complex primary alcohols and **3a** in a solvent such as THF, benzene, $CH_3CN$ or $CH_2Cl_2$ gave no reaction: the glycosyl donors and alcohols were recovered quantitatively. This result illustrates the thermal stability of the glycosyl donor. A few typical glycosidations of primary and secondary alcohols were studied in the presence of promoters. The results obtained by treating 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (**5**) with **3a** or mixtures of **3a** and **3b** depend on the solvent, temperature and Lewis acid, and are summarized in Table 2.

**Table 1**. Synthesis of glycosyl donors **3a** and **3b** from 2,3,4,6-tetra-*O*-benzyl-D-glucose (**2**) and 5-chloro-1-phenyl-1 *H*-tetrazole (**1**)

| Entry | Base | Solvent | Temp (°C) | Time (h) | 3a:3b (α:β) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | KOH | DMSO | rt | 3.0 | pure 3α | 88 |
| 2 | *n*BuLi | THF | rt | 46 | pure 3α | 70 |
| 3 | NaH | $CH_2Cl_2$ | rt | 1.5 | ~1:4 | 87 |
| 4 | $Cs_2CO_3$ | $CH_2Cl_2$ | rt | 26 | ~1:4 | 73 |
| 5 | $K_2CO_3$ and $Et_4NBr$ | $CH_2Cl_2$ | rt | 96 | ~2.5:1 | 83 |

According to entries 1 and 3, **3a** and **3b** were obtained in gram quantities. Once purified, **3a** or mixtures of **3a** and **3b** could be stored under a $N_2$ atmosphere in a refrigerator for several weeks without detectable decomposition or rearrangement.

**Table 2**. Glycosidation of **3a** or **3b** with **5** to the disaccharides **6a** and **6b**

| Entry | 3a:3b | Promoter (Eq.) | Solvent | Temp (°C) | Time (h)[a] | Yield (%)[b] | 6a:6b[c] |
|---|---|---|---|---|---|---|---|
| 1 | >99:1 | $BF_3$•$OEt_2$ (0.5) | $CH_3CN$ | -20 | 1.0 | 75 | <1:95 |
| 2 | 7:1 | $BF_3$•$OEt_2$ (0.5) | THF | -20 | 1.0 | 49 | 1:4 |
| 3 | >99:1 | $BF_3$•$OEt_2$ (0.5) | $CH_2Cl_2$ | -20 | 1.0 | 69 | 1:3 |
| 4 | >99:1 | TMSOTf (0.5) | $CH_2Cl_2$ | -78 | 1.0 | 70 | 1:3 |
| 5 | >99:1 | TMSOTf (0.2) | $CH_3CN$ | -20 | 1.0 | 80 | <1:95 |
| 6 | >99:1 | TMSOTf (0.2) | $CH_2Cl_2$ | rt | 2.5 | 98 | 1.5:1 |
| 7 | >99:1 | TMSOTf (0.2) | $Et_2O$ | -78 | 3.0 | 82 | 1:1 |
| 8 | >99:1 | AgOTf (1.6) | $CH_2Cl_2$ | 0 | 2.0 | 82 | 1:1 |
| 9 | >99:1 | p-TsOH (0.5) | $CH_2Cl_2$ | rt | 17 | 54 | 2:1 |
| 10 | >99:1 | p-TsOH (0.5) | $CH_2Cl_2$-hexane (1:1) | 0 | 6.0 | 75 | 1.5:1 |
| 11 | >99:1 | p-TsOH (0.5) | $CH_2Cl_2$ | reflux | 1.5 | 58 | 1.4:1 |
| 12 | <1:99 | TMSOTf (0.2) | $CH_2Cl_2$ | -78 | 0.5 | 86 | 1:1.7 |
| 13 | 1:3.5 | p-TsOH (0.5) | $CH_2Cl_2$ | rt | 13.5 | 73 | 2:1 |
| 14 | 1:3.5 | TMSOTf (0.2) | $Et_2O$ | rt | 0.8 | 67 | 7:1 |
| 15 | >99:1 | TMSOTf (0.2) | $Et_2O$ | rt | 0.5 | 97 | 6:1 |
| 16 | 1:4 | TMSOTf (0.2) | $CH_3CN$ | -20 | 1.0 | 83 | <1:95 |

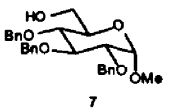
[a]With the exception of entries 9, 10 and 13, most reactions were complete after minutes; [b]yields were not optimized. Generally, lower yields were not due to the formation of side-products, but to the formation of 2,3,4,6-tetra-O-benzyl-D-glucose (**1**), indicative of traces of water in the reaction mixture; [c]the disaccharides were not separated. Ratios of isomers were determined from integration of the respective H-C(1) signals of the galactose residue in the $^1H$ NMR spectrum of the mixture.

Several conclusions are evident. The glycosyl donors **3a** or **3b** react with the glycosyl acceptor **5** in equimolar amounts and in the presence of a variety of promoters to form 6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (**6a**) and 6-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (**6b**) in good to excellent yields. TMSOTf led consistently to high yields, and the stereoselectivity could be controlled primarily by choice of the solvent. Entries 14 and 15 illustrate that the configuration of the donor is not relevant. TMSOTf as promoter and $Et_2O$ as solvent leads mostly to the α-D-linked disaccharide (**6a**).

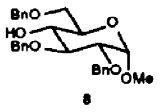
This suggests a dominating $S_N1$ mechanism. The solvent effect is consistent with similar observations reported mainly by Schmidt and coworkers.[55–57] As expected, diastereoselectivity increased with temperature (*c.f.* entries 7 and 15).

In contrast to this, formation of the β-linked disaccharide **6b** was favored at lower temperatures, with either $BF_3{\cdot}OEt_2$ or TMSOTf as promoter, and, most importantly, $CH_3CN$ as solvent (entries 1 and 5). The nitrile solvent effect is well-precedented.[55–65] Comparison of entries 5 and 16 illustrates that the β-linked disaccharide **6b** is formed predominantly when TMSOTf in $CH_3CN$ is used, independent of the anomeric configuration of the donor.

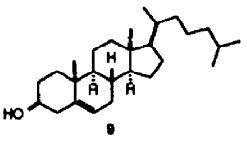
In the glycosidation by **3a** of methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**7**), methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**8**), and cholesterol (**9**) (Table 3) we attempted to prepare both the α- and β-D-glycosides from the axial (α) glycosyl donor **3a** by choosing the solvent, temperature and promoter, as worked out for the glycosidation of **5**.




**7**




**8**



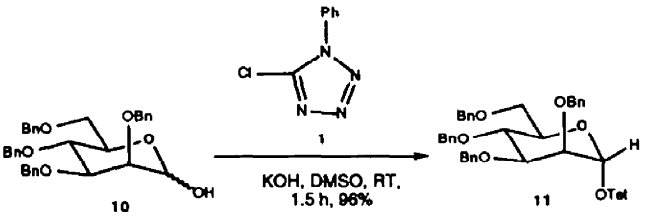

**9**

Good yield and β selectivity in the reaction of **3a** with the primary alcohol **7** were realized with TMSOTf as promoter and $CH_3CN$ as the solvent (entry 1). Reasonable selectivity, but a lower yield resulted under conditions favouring the α glycoside (entry 2). As the lower yield was due to the formation of numerous side-products, none of which were identified, this reaction was repeated at 0 °C. This decreased the selectivity without affecting the yield (entry 3). Performing the reaction with 2 equivalents of glycosyl acceptor **7** in $Et_2O$ at rt and with TMSOTf as promoter, however, increased the yield to 73 % (entry 4).

The C(4) hydroxyl group of glucose is known to be poorly reactive in glycosidation reactions.[9] The glycosyl acceptor **8** reacted with **3a** in the presence of TMSOTf as promoter and in $CH_3CN$ at –20 °C for 1.5 h to yield 70 % of the pure β-linked disaccharide **10** (entry 5). This unoptimized yield and excellent stereoselectivity suggests that the *O*-1-phenyltetrazol-5-yl group (OTet) will be a useful leaving group even with poorly reactive glycosyl acceptors. Attempts to form the α glycoside from **3a** using the poorly reactive acceptor **8** were, however, unsuccessful.

The conditions which favoured β-D-glycosides (TMSOTf and $CH_3CN$) were not suitable for the glycosidation of cholesterol (**9**) due to its limited solubility in that solvent. Instead, $BF_3{\cdot}OEt_2$ was used as promoter and $CH_2Cl_2$ as solvent: reaction of equimolar amounts of **3a** with **9** at –20 °C for 1 h gave a 1:3.3 mixture of α and β glycosides in 54 % yield (entry 6). When two equivalents of cholesterol (**9**) were used in the presence of TMSOTf, the yield increased to 70 %, but selectivity was slightly lower (entry 7). Attempts to form the α glycoside were unsuccessful: using TMSOTf in $Et_2O$ at rt gave only trace amounts of product. A less reactive promoter, camphor-10-sulfonic acid (CSA), improved yields marginally (entry 8).

Preliminary experiments using 2,3,4,6-tetra-*O*-benzyl-D-mannose (**10**)[66] have also been carried out. Reaction of **10** with 5-chloro-1-phenyl-1*H*-tetrazole (**1**) and KOH in DMSO at rt for 2 h gave *O*-1-(1'-phenyl-1*H*-tetrazolyl) 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranose (**11**) in 96 % yield (Scheme II).




**Scheme II.**

**Table 3**. Glycosidation of **3a** with **7**, **8**, or **9**

| Entry | Glycosyl Acceptor | Promoter (Eq.) | Solvent | Temp (°C) | Time (h) | Yield (%)[a] | Product α:β[b] |
|---|---|---|---|---|---|---|---|
| 1 | **7** | TMSOTf (0.2) | $CH_3CN$ | -20 | 0.25 | 79 | 1:13 |
| 2 | **7** | TMSOTf (0.2) | $Et_2O$ | rt | 1.0 | 66 | 7:1 |
| 3 | **7** | TMSOTf (0.2) | $Et_2O$ | 0 | 0.5 | 61 | 4.2:1 |
| 4 | **7**[c] | TMSOTf (0.2) | $Et_2O$ | rt | 0.5 | 73 | 6:1 |
| 5 | **8** | TMSOTf (0.2) | $CH_3CN$ | -20 | 1.5 | 70 | pure β |
| 6 | **9** | $BF_3{\cdot}OEt_2$ (0.5) | $CH_2Cl_2$ | -20 | 1.0 | 54 | 1:3.3 |
| 7 | **9**[c] | TMSOTf (0.2) | $CH_2Cl_2$ | -20; rt | 0.5; 0.5 | 70 | 1:2.2 |
| 8 | **9**[c] | CSA (0.5) | $Et_2O$ | rt | 24.0 | 35 | 2.2:1 |

[a]Yields are unoptimized; [b]anomer ratios were determined from the integration of suitable signals in the $^1H$ NMR spectra of the mixtures; [c]2 equivalents of glycosyl acceptor were used.

As in the *gluco* series, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (**5**) was used as a glycosyl acceptor in glycosidation reactions using **11** as glycosyl donor. Results using various solvents, temperatures and promoters are summarized in Table 4.

As shown by entry 1, the nitrile effect which was successfully used in the *gluco* series to form predominantly β-linked disaccharides was not strong enough to overcome the well-known kinetic preference for α-linked disaccharide formation.[67–75] In fact, the best β selectivity obtained in these initial investigations was only 50 % using a palladium promoter (entry 5). Using either TMSOTf or AgOTf in $CH_2Cl_2$ gave preferentially the α-linked disaccharide in excellent yields (entries 2–4). Analogous to observations made in the *gluco* series, higher temperatures under otherwise identical conditions favoured α anomer formation (compare entries 2 and 3).

These results show that *O*-1-phenyltetrazol-5-yl (OTet) is a promising new *O*-glycosyl leaving group. Further work is being done on the formation of glycosyl donors having protective groups other than benzyl and on the optimization of conditions to form both α and β glycosides using a variety of glycosyl acceptors.

## Experimental

### *General*

All reactions were done under a $N_2$ atmosphere with exclusion of moisture. Solvents were distilled under an inert atmosphere before use: $CH_2Cl_2$, toluene, benzene, $CH_3CH_2CN$ and $CH_3CN$ from $CaH_2$; $Et_2O$ and THF from Na/benzophenone; and MeOH from $Mg/I_2$. $K_2CO_3$ was flame-dried and cooled under $N_2$ before use. Other commercial reagents were used as received. TLC: Merck precoated silica gel 60 $F_{254}$ plates, with the solvent systems indicated: detection by spraying the plates with 5 % $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and 0.1 % $Ce(SO_4)_2$ in 10 % $H_2SO_{4(aq.)}$ solution followed by heating at *ca* 200 °C. Flash chromatography: silica gel Merck 60 (0.040–0.063 mm). Mps were performed using a Büchi apparatus and are uncorrected. Optical rotations were performed using a Jasco DIP-370 digital polarimeter with a 1-dm cell at 25 °C and at 589 nm. IR spectra were recorded as *ca* 3 % solutions in $CHCl_3$ using a Perkin Elmer 1600 series FT-IR. NMR spectra were recorded using Varian Gemini instruments: at 300 or 500 MHz and 50 or 125 MHz for $^1H$ and $^{13}C$ respectively.

### *O-1-(1'-Phenyl-1H-tetrazolyl) 2,3,4,6-tetra-O-benzyl-α-D-glucopyranose (3a) Method A*

A mixture of 2,3,4,6-tetra-*O*-benzyl-D-glucose (**2**, 0.618 g, 1.14 mmol), KOH (0.128 g, 2.28 mmol) and 5-chloro-1-phenyl-1*H*-tetrazole (**1**, 0.216 g, 1.19 mmol) was dissolved in DMSO (40 mL) which had been dried by storage over 4 Å molecular sieves and stirred at rt for 3 h. Water was added and the mixture was extracted with EtOAc (3 ×). The combined extracts were washed successively with $H_2O$ (2 ×) and brine. After drying over $MgSO_4$ and removal of the solvent, a yellow oil was isolated. Purification by column chromatography using 40:10:1 hexane:EtOAc:$Et_3N$ as eluant gave pure **3a** as a thick colourless oil (0.684 g, 88 %). There was no evidence of anomer **3b** as determined by $^1H$ NMR. Data for **3a**: $R_f$ (hexane:EtOAc 1:1) 0.62. $[\alpha]_D$ = +70.5 (*c* = 0.91, $CHCl_3$). IR: 3007 m, 2917 m, 2871 m, 1597m, 1555 s, 1506 s, 1454 s, 1361 m, 1295 m, 1158 s, 1107 s, 1071 s, 1047 s, 1028 s, 993 m. $^1H$ NMR (300 MHz, $CDCl_3$): 7.72–7.65 (m, 2 arom H), 7.55–7.45 (m, 3 arom H), 7.35–7.20 (m, 18 arom H), 7.15–7.10 (m, 2 arom H), 6.51 (d, 1H, *J* = 3.1 Hz, H-C(1)), 4.93 (d, 1H, *J* = 11.0 Hz, PhC$H_2$), 4.84 (d, 1H, *J* = 10.5 Hz, PhC$H_2$); 4.82 (d, 1H, *J* = 11.0 Hz, PhC$H_2$), 4.75 (br s, 1H, PhC$H_2$), 4.60 (d, 1H, *J* = 12.1 Hz, PhC$H_2$), 4.54 (d, 1H, *J* = 10.5 Hz, PhC$H_2$); 4.49 (d, 1H, *J* = 12.1, PhC$H_2$); 3.95–3.89 (m, 1H, H-C(3)), 3.87–3.80 (m, 3H, H-C(2), H-C(4), H-C(5)), 3.75 (dd, 1H, *J* = 10.8, 2.0 Hz, $H_B$-C(6)), 3.65 (d, 1H, *J* = 10.8 Hz, $H_A$-C(6)). $^{13}C$ NMR (50 MHz, $CDCl_3$): 159.52 (tetrazolyl C); 138.32, 137.78, 137.71, 137.21, 133.22 (5 arom C); 129.73–127.65 (arom *C*H); 122.14 (arom *C*H); 101.32 (C-1); 81.16 (C-4); 79.21 (C-2); 76.57 (C-5); 75.68 (C-3); 75.49, 73.79, 73.78, 73.67 (4 $CH_2$Ph); 67.80 (C-6). FAB-MS: 685 (2, $M^+$); 181 (37); 91 (100). Anal. calcd for $C_{41}H_{40}N_4O_6$ (684.79): C, 71.91; H, 5.89; N, 8.18. Found: C, 71.78; H, 5.90; N, 8.09.

### *O-1-(1'-Phenyl-1H-tetrazolyl) 2,3,4,6-tetra-O-benzyl-α-D-glucopyranose (3a) Method B*

To a solution of 2,3,4,6-tetra-*O*-benzyl-D-glucose (**2**, 0.179 g, 0.331 mmol) in THF (5.0 mL) at 0 °C was added dropwise *n*-BuLi (1.6 M, 0.21 mL, 0.33 mmol). After stirring for 10 min, a solution of 5-chloro-1-phenyl-1*H*-tetrazole (**1**, 0.069 g, 0.38 mmol) in THF (5.0 mL) was

**Table 4**. Glycosidation of **11** with **5**

| Entry | Promoter (Eq.) | Solvent | Temp (°C) | Time (h) | Yield (%)[a] | Product α:β[b] |
|---|---|---|---|---|---|---|
| 1 | TMSOTf (0.2) | $CH_3CN$ | -20 | 1.0 | 88 | 3:1 |
| 2 | TMSOTf (0.2) | $CH_2Cl_2$ | -78 | 1.5 | 92 | 1.2:1 |
| 3 | TMSOTf (0.2) | $CH_2Cl_2$ | rt | 0.6 | 92 | 2.9:1 |
| 4 | AgOTf (1.3) | $CH_2Cl_2$ | 0-rt | 12 | 97 | 2.4:1 |
| 5 | $PdCl_2{\cdot}CH_3CN$ (0.09) | $CH_2Cl_2$ | -20; 0 | 3.0; 2.0 | 63 | 1:1 |

[a]Yields are unoptimized; [b]anomer ratios were determined from the integration of suitable signals in the $^1H$ NMR spectra of the mixtures.

added. The mixture was allowed to come to rt and was stirred for 46 h. Brine was added and the mixture was extracted with EtOAc (3 ×). After drying the combined extracts over $MgSO_4$ and removal of the solvent, a yellow oil was obtained. Purification by column chromatography using 4:1 hexane:EtOAc containing 1 % $Et_3N$ gave pure **3a** (0.158 g, 70 %). Spectral characteristics were identical to those obtained for **3a** prepared via Method A, and there was no evidence of the β anomer **3b** as determined by $^1H$ NMR.

*O-1-(1'-Phenyl-1H-tetrazolyl) 2,3,4,6-tetra-O-benzyl-α-D-glucopyranose (3a) and O-1-(1'-phenyl-1H-tetrazolyl) 2,3,4,6-tetra-O-benzyl-β-D-glucopyranose (3b) (mixture of anomers) Method C*

A slurry of NaH (95 %, 8.1 mg, 0.34 mmol) in $CH_2Cl_2$ (1.0 mL) was stirred at rt. A solution of 2,3,4,6-tetra-*O*-benzyl-D-glucose (**2**, 0.152 g, 0.281 mmol) in $CH_2Cl_2$ (4.0 mL) was added, followed by a solution of 5-chloro-1-phenyl-1*H*-tetrazole (**1**, 0.061 g, 0.34 mmol) in $CH_2Cl_2$ (2.0 mL). The reaction mixture was stirred at rt for 1.5 h, then quenched by the addition of brine. The mixture was extracted with $CH_2Cl_2$ (3 ×) and the combined extracts were dried over $MgSO_4$. Removal of the solvent gave a yellow oil which was purified by column chromatography using 4:1 hexane:EtOAc containing 1 % $Et_3N$ as eluant. A mixture of **3a** and **3b** (1:4) was isolated as a thick colourless oil (0.167 g, 87 %). Spectral characteristics were consistent with those listed above in the preparation of pure **3a**. The β anomer **3b** showed a characteristic C(1) proton signal (d, $J$ = 7.4 Hz) at 5.96 ppm in the $^1H$ NMR of the mixture and the ratio of **3a:3b** was determined from integration of the respective C(1) proton signals.

*O-1-(1'-Phenyl-1H-tetrazolyl) 2,3,4,6-tetra-O-benzyl-α-D-glucopyranose (3a) and O-1-(1'-phenyl-1H-tetrazolyl) 2,3,4,6-tetra-O-benzyl-β-D-glucopyranose (3b) (mixture of anomers) Method D*

To a solution of $Cs_2CO_3$ (0.205 g, 0.629 mmol) in $CH_2Cl_2$ (1.0 mL) was added successively a solution of 2,3,4,6-tetra-*O*-benzyl-D-glucose (**2**, 0.203 g, 0.375 mmol) in $CH_2Cl_2$ (4.0 mL) and a solution of 5-chloro-1-phenyl-1*H*-tetrazole (**1**, 0.108 g, 0.601 mmol) in $CH_2Cl_2$ (4.0 mL). The mixture was stirred at rt for 26 h, then water was added. After extraction with $CH_2Cl_2$ (3 ×) the combined extracts were dried over $MgSO_4$. Removal of the solvent gave a yellow oil which was purified by column chromatography using 4:1 hexane:EtOAc containing 1 % $Et_3N$ as eluant. A 1:4 mixture of **3a** and **3b** (0.188 g, 73 %) was obtained as a colourless oil. Spectral characteristics were consistent with those described above.

*O-1-(1'-Phenyl-1H-tetrazolyl) 2,3,4,6-tetra-O-benzyl-α-D-glucopyranose (3a) and O-1-(1'-phenyl-1H-tetrazolyl) 2,3,4,6-tetra-O-benzyl-β-D-glucopyranose (3b) (mixture of anomers) Method E*

A solution of 2,3,4,6-tetra-*O*-benzyl-D-glucose (**2**, 0.071 g, 0.13 mmol), 5-chloro-1-phenyl-1*H*-tetrazole (**1**, 0.032 g, 0.18 mmol), $K_2CO_3$ (0.033 g, 0.24 mmol), and $Et_4NBr$ (0.048 g, 0.23 mmol) in $CH_2Cl_2$ (5.0 mL) was stirred at rt for 4 days. Brine was added and the mixture was extracted with $CH_2Cl_2$ (3 ×). After drying the combined extracts over $MgSO_4$ and removal of the solvent, a yellow oil was obtained. Purification by column chromatography using 4:1 hexane:EtOAc containing 1 % $Et_3N$ as eluant gave a mixture of **3a** and **3b** (2.5:1) as a colourless oil (0.074 g, 83 %). Spectral characteristics were consistent with those described above.

*General methanolysis procedure to form methyl 2,3,4,6-tetra-O-benzyl-α- and β-D-glucopyranosides (4a and 4b)*

A 3.5:1 mixture of *O*-1-(1'-phenyl-1*H*-tetrazolyl) 2,3,4,6-tetra-*O*-benzyl-α- and β-D-glucopyranoses **3a** and **3b** or pure **3a** was refluxed in the presence of 4 Å powdered molecular sieves in dry MeOH for 4 h. After cooling to rt, water was added and the mixture was extracted with $CH_2Cl_2$ (3 ×). The combined extracts were dried over $MgSO_4$, and the solvent was removed to yield a yellow oil. Flash column chromatography using 4:1 hexane:EtOAc as eluant gave mixtures of **4a** and **4b**. The ratio of anomers was determined by integration of the methoxyl proton peaks at 3.39 and 3.59 ppm respectively in the $^1H$ NMR spectrum of the mixture. Further column chromatography of part of the mixture using 9:1 hexane:EtOAc was done to obtain pure samples of each isomer. Data for **4a**: $R_f$ (hexane:EtOAc, 2:1) 0.42. $[\alpha]_D$ = +23.7 ($c$ = 1.1, $CHCl_3$) (lit: $[\alpha]_{578}^{24}$ = +20.9 ($c$ = 1.17, $CHCl_3$);[76] $[\alpha]_D^{20}$ = +32.2 ($c$ = 5, $CHCl_3$);[54] $[\alpha]_D^{25}$ = +18.7 ($c$ = 1.5, $CHCl_3$)).[77] IR: 3008 m, 2915 m, 1497 m, 1454 m, 1362 m, 1160 m, 1134 m, 1070 s, 1047 s, 1028 s, 1004m. $^1H$ NMR (300 MHz, $CDCl_3$): 7.38–7.13 (m, 20 arom H), 4.99 (d, 1H, $J$ = 10.9 Hz, PhC$H_2$), 4.84 (d, 1H, $J$ = 10.7 Hz, PhC$H_2$), 4.83 (d, 1H, $J$ = 10.9 Hz, PhC$H_2$), 4.80 (d, 1H, $J$ = 11.0 Hz, PhC$H_2$), 4.67 (d, 1H, $J$ = 13.1 Hz, PhC$H_2$), 4.64 (d, 1H, $J$ = 4.0, H-C(1)), 4.62 (d, 1H, $J$ = 12.6 Hz, PhC$H_2$), 4.49 (br d, 2H, $J$ = 12.0 Hz, 2 PhC$H_2$), 3.99 (dd, 1H, $J$ = 9.9, 9.0 Hz, H-C(4)), 3.78–3.60 (m, 3H, H-C(5), 2 H-C(6), H-C(3)), 3.57 (dd, 1H, $J$ = 9.6, 3.6 Hz, H-C(2)), 3.39 (s, 3H, $CH_3$). $^{13}C$ NMR (50 MHz, $CDCl_3$): 138.83, 138.21, 138.19, 137.95 (arom C); 129.44–127.61 (arom *C*H); 98.24 (C-1); 82.17 (C-4); 79.86 (C-2); 77.69 (C-5); 75.79, 75.06, 73.51, 73.43 (4 *C*$H_2$Ph); 70.08 (C-3); 68.50 (C-6); 55.20 (*C*$H_3$). Data for **4b**: $R_f$ (hexane:EtOAc, 2:1) 0.48. $[\alpha]_D$ = +13.1 ($c$ = 1.1, dioxane)(lit: $[\alpha]_{578}^{20}$ = +13.1 ($c$ = 1, $CHCl_3$);[76] $[\alpha]_D$ = +11 ($c$ = 5.3, dioxane);[78] $[\alpha]_D$ = +14 ($c$ = 1.0, dioxane)).[79] Mp: 68.5–69 °C (lit: 68 °C;[76] 65–66 °C;[78] 74–75 °C[79]). IR: 3008 m,, 2912 m, 2868 m, 1454 s, 1360 m, 1067 s, 1028 s, 1006 m. $^1H$ NMR (300 MHz, $CDCl_3$): 7.38–7.13 (m, 20 arom H), 4.94 (d, 1H, $J$ = 10.9 Hz, PhC$H_2$), 4.93 (d, 1H, $J$ = 11.0 Hz, PhC$H_2$), 4.83 (d, 1H, $J$ = 10.8 Hz, PhC$H_2$), 4.80 (d, 1H, $J$ = 10.9 Hz, PhC$H_2$), 4.72 (d, 1H, $J$ = 11.0 Hz, PhC$H_2$); 4.64 (d, 1H, $J$ = 12.2 Hz, PhC$H_2$), 4.56 (d, 1H, $J$ = 12.1 Hz, PhC$H_2$), 4.54 (d, 1H, $J$ = 10.9 Hz, PhC$H_2$), 4.32 (d, 1H, $J$ = 7.7 Hz, H-C(1)), 3.77 (dd, 1H, $J$ = 10.7, 2.0 Hz, $H_A$-C(6)), 3.70 (dd, 1H, $J$ = 10.7, 4.6 Hz, $H_B$-C(6)), 3.65–3.56 (m, 1H, H-C(4)), 3.59 (s, 3H, $CH_3$), 3.50–3.41 (m, 2H, H-C(5), H-C(2)). $^{13}C$ NMR (50

MHz, $CDCl_3$): 138.66, 138.60, 138.23, 138.17 (arom C); 128.41–127.65 (arom *C*H); 104.77 (C-1); 84.71 (C-4); 82.39 (C-2); 77.94 (C-5); 75.73, 75.07 (2 × *C*$H_2$Ph); 74.92 (C-3); 74.80, 73.56 (2 × *C*$H_2$Ph); 69.00 (C-6); 57.16 (*C*$H_3$). Anal. calcd for $C_{35}H_{38}O_6$ (554.7): C, 75.79; H, 6.90. Found: C, 75.53; H, 6.83.

*General glycosidation procedure*

A solution of glycosyl donor (**3a** or **3b**) and glycosyl acceptor was stirred in the presence of ground, dried 4 Å molecular sieves at the indicated temperature in the indicated solvent. The promoter was added dropwise and the mixture was stirred until TLC and $^1$H NMR showed complete disappearance of the glycosyl donor. A saturated solution of $NaHCO_{3(aq.)}$ was added, the mixture was extracted with either $CH_2Cl_2$ or EtOAc and the combined extracts were dried over $MgSO_4$. The solvent was removed and the crude product was purified by column chromatography. All glycosides are known compounds and characteristic data and comparison to the literature follow.

*6-O-(2,3,4,6-Tetra-O-benzyl-α-D-glucopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranoside*

This compound was always obtained as a mixture together with the corresponding β-linked disaccharide and the two isomers were inseparable by column chromatography. The characteristic signal in the $^1$H NMR spectrum (300 MHz, $CDCl_3$) was 5.53 (d, 1H, $J$ = 5.1 Hz, H-C(1))(lit.[31] 5.52 (d, 1H, $J$ = 5.3 Hz)). $R_f$ (hexane:EtOAc, 2:1) 0.42.

*6-O-(2,3,4,6-Tetra-O-benzyl-β-D-glucopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranoside*

$R_f$ (hexane:EtOAc, 2:1) 0.42. $[\alpha]_D$ = –32.5 ($c$ = 0.85, $CHCl_3$). IR: 3008 m, 2909 m, 1454 m, 1384 m, 1255 m, 1166 m, 1070 s, 1028 m, 1008 m. $^1$H NMR (300 MHz, $CDCl_3$): 7.44–7.41 (m, 2 arom H), 7.38–7.22 (m, 16 arom H), 7.14–7.10 (m, 2 arom H), 5.58 (d, 1H, $J$ = 5.1 Hz, H-C(1)), 5.07 (d, 1H, $J$ = 11.2 Hz, PhC*H*$_2$), 4.97 (d, 1H, $J$ = 10.9 Hz, PhC*H*$_2$), 4.82 (d, 1H, $J$ = 10.9 Hz, PhC*H*$_2$), 4.78 (d, 1H, $J$ = 11.0 Hz, PhC*H*$_2$), 4.73 (d, 1H, $J$ = 11.2 Hz, PhC*H*$_2$), 4.63 (d, 1H, $J$ = 12.4 Hz, PhC*H*$_2$), 4.60 (dd, 1H, $J$ = 7.9, 2.4 Hz, H-C(3)), 4.54 (d, 1H, $J$ = 12.2 Hz, PhC*H*$_2$), 4.51 (d, 1H, $J$ = 10.9, PhC*H*$_2$), 4.47 (d, 1H, $J$ = 7.8 Hz, H-C(1')), 4.33 (dd, 1H, $J$ = 5.0, 2.4 Hz, H-C(2)), 4.26 (dd, 1H, $J$ = 7.9, 1.9 Hz, H-C(4)), 4.18 (dd, 1H, $J$ = 10.5, 3.6 Hz, $H_A$-C(6)), 4.13–4.07 (m, 1H, H-C(5)), 3.76 (m, 1H, $H_B$-C(6)), 3.73–3.70 (m, 2H, 2 × H-C(6')); 3.66–3.60 (m, 2H, H-C(3'), H-C(4')), 3.51–3.42 (m, 2H, H-C(2'), H-C(5')), 1.51 (s, 3H, $CH_3$), 1.47 (s, 3H, $CH_3$), 1.33 (br s, 6H, 2 × $CH_3$). $^{13}$C NMR (50 MHz, $CDCl_3$): 138.72–138.17 (arom C), 128.66–127.49 (arom *C*H), 109.40, 108.60 (isoprop C); 104.41 (C-1'); 96.41 (C-1); 84.58 (C-4'); 81.65 (C-2'); 77.75 (C-5'); 75.68, 75.01 (2 × *C*$H_2$Ph); 74.77 (C-3'); 74.37, 73.53 (2 × *C*$H_2$Ph); 71.47 (C-4); 70.81 (C-2); 70.51 (C-5); 69.73 (C-6'); 68.79 (C-6); 67.38 (C-3); 26.06 (2 × $CH_3$); 25.06 ($CH_3$); 24.47 ($CH_3$). FAB-MS: 781 (M-1); 181 (27); 91 (100). Anal. calcd for $C_{46}H_{54}O_{11}$ (782.93): C, 70.57; H, 6.95. Found: C, 70.64; H, 6.95.

*Methyl 6-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside*

$R_f$ ($CHCl_3$:$Et_2O$, 20:1) 0.43. $[\alpha]_D$ = +59.8 ($c$ = 1.4, $CHCl_3$) (lit: $[\alpha]_D$ = +57 ($c$ = 1.2, $CHCl_3$)[55]). IR: 3008 m, 2928 m, 1497 m, 1454 m, 1361 m, 1161 m, 1136 m, 1090 s, 1072 s, 1028 s. $^1$H NMR (300 MHz, $CDCl_3$): 7.38–7.10 (m, 35 arom H), 4.99 (d, 1H, $J$ = 3.3 Hz H-C(1')), 4.98 (d, 1H, $J$ = 10.8 Hz, PhC*H*$_2$), 4.95 (d, 1H, $J$ = 10.9 Hz, PhC*H*$_2$), 4.93 (d, 1H, $J$ = 11.2 Hz, PhC*H*$_2$), 4.84 (d, 1H, $J$ = 11.0 Hz, PhC*H*$_2$), 4.82 (d, 1H, $J$ = 11.0 Hz, PhC*H*$_2$), 4.78 (d, 1H, $J$ = 10.9 Hz, PhC*H*$_2$), 4.72 (d, 1H, $J$ = 12.1 Hz, PhC*H*$_2$), 4.66 (br d, 3H, $J$ = 10.3 Hz, 3 × PhC*H*$_2$), 4.58 (br d, 2H, $J$ = 12.1 Hz, 2 × PhC*H*$_2$), 4.56 d, 1H, $J$ = 2.6 Hz, H-C(1)), 4.47 (d, 1H, $J$ = 10.0 Hz, PhC*H*$_2$), 4.43 (d, 1H, $J$ = 12.1 Hz, PhC*H*$_2$), 4.22–3.93 (m, 2H, H-C(3) and H-C(3')), 3.86–3.52 (m, 9H), 3.45 (dd, 1H, $J$ = 9.6, 3.6 Hz, H-C(2)), 3.35 (s, 3H, $OCH_3$) (lit: 3.35 (s, $OCH_3$)[31]).

*Methyl 6-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside*

$R_f$ ($CHCl_3$:$Et_2O$, 20:1) 0.33. $[\alpha]_D$ = +17.8 ($c$ = 0.82, $CHCl_3$) (lit: $[\alpha]_D^{22}$ = +18.9 ($c$ = 1.2, $CHCl_3$),[24] $[\alpha]_D^{21}$ = +20 ($c$ = 0.4, $CHCl_3$),[51] $[\alpha]_D^{20}$ = +17.1 ($c$ = 0.42, $CHCl_3$),[9] $[\alpha]_D^{20}$ = +18.4 ($c$ = 0.76, $CHCl_3$)[12]). Mp 130–131 °C (lit: 131–133 °C,[51] 133–133.5 °C,[9] 133–134 °C,[76] 130–131.5 °C[12]). IR: 3007 s, 2977 s, 2896 m, 1454 m, 1390 m, 1248 m, 1069 s, 1047 s, 877 m. $^1$H NMR (300 MHz, $CDCl_3$): 7.39–7.12 (m, 35 arom H), 5.15–4.47 (m, 15 H), 4.35 (d, 1H, $J$ = 7.6 Hz, H-C(1')), 4.19 (dd, 1H, $J$ = 10.7, 1.7 Hz); 4.00 (br t, 1H, $J$ = 9.2 Hz, H-C(3)), 3.88–3.40 (m, 10H), 3.33 (s, 3H, $OCH_3$) (lit: 3.33 (s, $OCH_3$)[31]).

*Methyl 4-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-2,3,6-tri-O-benzyl-α-D-glucopyranoside*

$R_f$ (hexane:EtOAc, 2:1) 0.42. $[\alpha]_D$ = +21.3 ($c$ = 0.62, $CHCl_3$) (lit: $[\alpha]_D^{22}$ = +16.9 ($c$ = 1.7, $CHCl_3$),[24] $[\alpha]_{578}^{20}$ = +25.3 ($c$ = 1, $CHCl_3$).[55] Mp 90–92 °C (lit: 85–88 °C[55]). IR: 3008 m, 2910 m, 2869 m, 1497 m, 1454 m, 1361 m, 1069 s, 1048 s, 1028 s. $^1$H NMR (500 MHz, $CDCl_3$): 7.45–39 (m, 2 arom H), 7.32–7.18 (m, 33 arom H), 5.08 (d, 1H, $J$ = 11.3 Hz), 4.86 (d, 1H, $J$ = 10.9 Hz); 4.80–4.70 (m, 6H), 4.62–4.54 (m, 4H), 4.45–4.35 (m, 4H), 3.96 (dd, 1H, $J$ = 9.9, 9.0 Hz), 3.87–3.81 (m, 2H), 3.71 (dd, 1H, $J$ = 11.0, 1.8 Hz), 3.61–3.57 (m, 2H), 3.54 (dd, 1H, $J$ = 11.0, 4.7 Hz); 3.50–3.43 (m, 3H), 3.36 (m, 1H), 3.36 (s, 3H, $OCH_3$), 3.29 (ddd, 1H, $J$ = 9.8, 4.6, 1.8 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$): 139.62, 138.63, 138.62, 138.59, 138.43, 138.36, 137.88 (7 × arom C); 128.46–126.77 (arom *C*H); 102.50 (C-1'); 98.44 (C-1); 84.90, 82.84, 80.44, 78.87, 78.08, 76.62 (6 × *C*H); 75.59, 75.38 (2 × *C*$H_2$); 75.20 (*C*H); 74.92, 74.79, 73.63, 73.37, 73.35 (5 × *C*$H_2$); 69.99 (*C*H); 69.03, 67.89 (2 × *C*$H_2$); 55.15 (*C*$H_3$) (lit: 102.49 (C-1'); 98.43 (C-1)[31]). Anal. calcd for $C_{62}H_{66}O_{11}$ (987.2): C, 75.43; H, 6.74. Found: C, 75.17; H, 6.79.

*Cholesteryl 2,3,4,6-tetra-O-benzyl-α-D-glucopyranoside*

$R_f$ ($CHCl_3$:petroleum ether, 1:1) 0.53. $[\alpha]_D$ = +48.7($c$ = 0.31, $CHCl_3$) (lit: $[\alpha]_D^{23}$ = +44 ($c$ = 1.2, $CHCl_3$),[80] $[\alpha]_D^{23}$

= +40 ($c$ = 1, $CHCl_3$).[10] Mp 138–139 °C (lit: 127–128 °C,[10] 142 °C,[80] 140–142 °C[55]). $^1$H NMR (300 MHz, $CDCl_3$): characteristic signal 5.29 (m, 1H, steroidal H-C(6)). Anal. calcd for $C_{61}H_{80}O_6$ (909.3): C, 80.58; H, 8.87. Found: C, 80.49; H, 8.90.

*Cholesteryl 2,3,4,6-tetra-O-benzyl-β-D-glucopyranoside*

$R_f$ ($CHCl_3$:petroleum ether, 1:1) 0.41. $[\alpha]_D$ = –0.97 ($c$ = 0.10, $CHCl_3$) (lit: $[\alpha]_D^{23}$ = –0.4 ($c$ = 1.2, $CHCl_3$),[80] $[\alpha]_D^{21}$ = +8.6 ($c$ = 0.9, $CHCl_3$),[51] (lit: $[\alpha]_D^{20}$ = +0.2 ($c$ = 1.6, $CHCl_3$)[55]). Mp 93–94 °C (lit: 108–109 °C,[55] 94.5–95.5 °C,[51] 96–97 °C[80]). $^1$H NMR (500 MHz, $CDCl_3$): characteristic signal 5.34 (m, 1H, steroidal H-C(6)). $^{13}$C NMR (125 MHz, $CDCl_3$): characteristic signal 102.26 (C-1) (lit: 102.3[80,26]).

*O-1-(1'-Phenyl-1H-tetrazolyl) 2,3,4,6-tetra-O-benzyl-α-D-mannopyranose (11a)*

A mixture of 2,3,4,6-tetra-*O*-benzyl-D-mannose (**10**, 0.078 g, 0.14 mmol), KOH (0.020 g, 0.35 mmol) and 5-chloro-1-phenyl-1*H*-tetrazole (**1**, 0.026 g, 0.14 mmol) was dissolved in DMSO (5 mL) which had been dried by storage over 4 Å molecular sieves and stirred at rt for 2 h. Water was added and the mixture was extracted with EtOAc (3 ×). The combined extracts were washed successively with $H_2O$ (2 ×) and brine. After drying over $MgSO_4$ and removal of the solvent, a yellow oil was isolated. Purification by column chromatography using 40:10:1 hexane:EtOAc:$Et_3N$ as eluant gave pure **11a** as a thick colourless oil (0.094 g, 96 %). There was no evidence of the corresponding β anomer as determined by $^1$H NMR. Data for **11a**: $R_f$ (hexane:EtOAc, 2:1) 0.36. $[\alpha]_D$ = +58 ($c$ = 0.6, $CHCl_3$). IR: 3008 m, 2870 m, 1597 m, 1551 s, 1505 s, 1454 s, 1363 m, 1293 m, 1171 m, 1099 s, 1047 m, 1028 m, 985 m, 907 m. $^1$H NMR (300 MHz, $CDCl_3$): 7.55–7.15 (m, 25 arom H), 6.45 (d, 1H, $J$ = 2.2 Hz, H-C(1)), 4.88 (d, 1H, $J$ = 10.6 Hz, PhC$H_2$); 4.85 (d, 1H, $J$ = 12.2 Hz, PhC$H_2$), 4.81 (d, 1H, $J$ = 12.2 Hz, PhC$H_2$), 4.66 (d, 1H, $J$ = 12.1 Hz, PhC$H_2$); 4.60 (d, 1H, $J$ = 12.1 Hz, PhC$H_2$), 4.57 (d, 1H, $J$ = 10 Hz, PhC$H_2$) 4.56 (d, 1H, $J$ = 12.1, PhC$H_2$), 4.53 (d, 1H, $J$ = 9.9 Hz, PhC$H_2$), 4.17 (t, 1H, $J$ = 9.4 Hz, H-C(4)), 4.04 (dd, 1H, $J$ = 3.1, 2.2 Hz, H-C(2)), 3.83 (dd, 1H, $J$ = 9.2, 3.1 Hz, H-C(3)), 3.88–3.68 (m, 3H, H-C(5), 2 × H-C(6)). $^{13}$C NMR (50 MHz, $CDCl_3$): 158.49 (tetrazolyl C); 138.10, 137.93, 137.80, 137.51, 132.99 (5 arom C); 129.81–127.27 (arom *C*H); 121.81 (arom *C*H); 101.74 (C-1); 78.13, 75.42, 73.59, 72.94 (C-2, C-3, C-4, C-5); 73.94, 73.47, 72.31, 68.59 (4 *C*$H_2$Ph). FAB-MS: 685 (3, $M^+$); 253 (25); 181 (68); 91 (100). Anal. calcd for $C_{41}H_{40}N_4O_6$ (684.79): C, 71.91; H, 5.89; N, 8.18. Found: C, 71.64; H, 5.78; N, 8.14.

*6O-(2,3,4,6-Tetra-O-benzyl-α-D-mannopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranoside*

$R_f$ (hexane:EtOAc, 2:1) 0.34. $^1$H NMR (300 MHz, $CDCl_3$): 7.42–7.15 (m, 20 arom H); 5.54 (d, 1H, $J$ = 5.0 Hz H-C(1)), 5.04 (d, 1H, $J$ = 1.7 Hz, H-C(1')), 4.88 (d, 1H, $J$ = 10.9 Hz, PhC$H_2$), 4.77 (d, 1H, $J$ = 11.9 Hz, PhC$H_2$), 4.73 (d, 1H, $J$ = 11.9 Hz, PhC$H_2$), 4.70 (d, 1H, $J$ = 12.1 Hz, PhC$H_2$), 4.64–4.58 (m, 3H, H-C(3) and 2 × PhC$H_2$), 4.54 (d, 1H, $J$ = 12.0 Hz, PhC$H_2$), 4.52 (d, 1H, $J$ = 10.8 Hz, PhC$H_2$), 4.33 (dd, 1H, $J$ = 5.0, 2.4 Hz, H-C(2)), 4.17 (dd, 1H, $J$ = 8.0, 1.8 Hz, H-C(4)), 4.04 (t, 1H, $J$ = 9.2 Hz), 3.98 (dt, 1H, $J$ = 6.6, 1.6 Hz, H-C(5)), 3.92 (dd, 1H, $J$ = 9.3, 3.1 Hz), 3.85 (dd, 1H, $J$ = 3.1, 1.8 Hz, H-C(2')), 3.83–3.67 (m, 5H), 1.51 (s, 3H, $CH_3$), 1.44 (s, 3H, $CH_3$), 1.34 (br s, 6H, $CH_3$). Anal. calcd for $C_{46}H_{54}O_{11}$ (782.93): C, 70.57; H, 6.95. Found: C, 70.52; H, 6.86.

*6O-(2,3,4,6-Tetra-O-benzyl-β-D-mannopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranoside*

$R_f$ (hexane:EtOAc, 2:1) 0.28. $[\alpha]_D$ = –87.5 ($c$ = 0.55, $CHCl_3$). IR: 3007 m, 2910 m, 2869 m, 1454 m, 1384 m, 1256 m, 1166 m, 1103 s, 1070 s, 1028 m, 1009 m, 899 m. $^1$H NMR (300 MHz, $CDCl_3$): 7.55–7.45 (m, 2 arom H), 7.40–7.20 (m, 21 arom H), 7.19–7.12 (m, 2 arom H), 5.60 (d, 1H, $J$ = 5.0 Hz, H-C(1)), 5.02 (d, 1H, $J$ = 12.5 Hz, PhC$H_2$); 4.92 (d, 1H, $J$ = 12.3, PhC$H_2$), 4.91 (d, 1H, $J$ = 10.8 Hz, PhC$H_2$), 4.65 (d, 1H, $J$ = 12.1 Hz, PhC$H_2$), 4.62 (dd, 1H, $J$ = 7.6, 2.5 Hz, H-C(3)), 4.56 (d, 1H, $J$ = 12.1 Hz, PhC$H_2$), 4.51 (d, 1H, $J$ = 10.8 Hz, PhC$H_2$), 4.45 (br d, 2H, $J$ = 10.7 Hz, 2 × PhC$H_2$), 4.35 (d, 1H, $J$ = 11.8 Hz, PhC$H_2$), 4.34 (dd, 1H, $J$ = 5.0, 2.4 Hz, H-C(2)), 4.23 (dd, 1H, $J$ = 7.9, 1.9 Hz, H-C(4)), 4.22 (dd, 1H, $J$ = 10.8, 2.3 Hz, $H_A$-C(6)), 4.12 (br dt, 1H, $J$ = 8.2, 1.9 Hz, H-(5)), 4.01 (d, 1H, $J$ = 2.9 Hz, H-C(1')), 3.91 (t, 1H, $J$ = 9.5 Hz, H-C(3')); 3.84–3.72 (m, 3H), 3.63 (dd, 1H, $J$ = 10.7, 8.3 Hz, $H_B$-C(6)), 3.47 (dd, 1H, $J$ = 9.4, 3.0 Hz, H-C(2')), 3.43 (m, 1H), 1.49 (s, 3H, $CH_3$), 1.46 (s, 3H, $CH_3$), 1.35 (s, 3H, $CH_3$), 1.33 (s, 3H, $CH_3$). Anal. calcd for $C_{46}H_{54}O_{11}$ (782.93): C, 70.57; H, 6.95. Found: C, 70.57; H, 6.88.

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