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# Regioselective and stereoselective benzoylation of 2-*N*-protected 4,6-*O*-ketal derivatives of D-glucosamines with 1-(benzoyloxy)benzotriazole

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**Abstract**

A highly regioelective and stereoselective benzoylation of the 2-*N*-protected 4,6-*O*-ketal derivatives of D-glucosamines with 1-(benzoyloxy)benzotriazole that affords the corresponding β anomeric benzoates in excellent yields is described herein. 

*Keywords:* Benzoylation; 1-(Benzoyloxy)benzotriazole; Glucosamines

## 1. Introduction

*N*-Acetyl-D-glucosamine (GlcNAc) is a key component of numerous biologically important oligosaccharides. For example, Lewis group antigens[1] and hyaluronic acid[2] possess linkages of GlcNAc with various sugar units at C-1 and C-3, respectively. A convenient route to generate a free 3-hydroxyl for further glycosylation from the inexpensive, commercially available D-glucosamine requires a three-step transformation that includes the protection of the primary amine, cyclic ketal protection at O-4 and O-6, and regioselective protection at the anomeric hydroxyl group. Distinguishing between the hydroxyl groups at C-1 and C-3 is, however, a challenge for chemists.[3] We have explored herein a highly regioselective and stereoselective benzoylation of 2-*N*-protected 4,6-*O*-ketal derivatives of D-glucosamines with 1-(benzoyloxy)benzotriazole (BzOBT)[4] at the anomeric (C-1) position.

## 2. Results and discussion

Typical benzoylation of **1**, which is generated from D-glucosamine in two steps via transformation of an amino group into an azido group,[5] followed by *O*-benzylidene protection[6] and benzoylation with benzoyl chloride in pyridine at 0 °C, led to a mixture of 1-*O*-Bz, 3-*O*-Bz and 1,3-di-*O*-Bz products. When the diols **1**–**5** were treated with BzOBT in dichloromethane at room temperature using triethylamine as a base, the β anomeric benzoates **7**–**11** were afforded in good yields (Table 1), respectively. Due to the poor solubility of **6**, the reaction concentration was dilute and the adduct **12** was isolated in 42% yield (entry 6). The β configurations of **7**–**12** were determined by the *trans*-diaxial coupling constants of anomeric protons ($J_{1,2}$ 7.5–8.8

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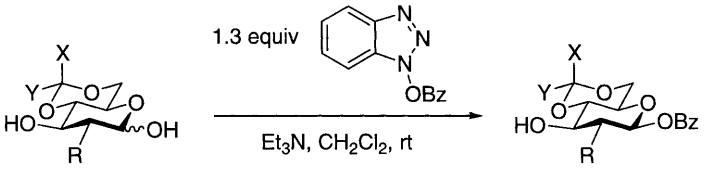
Table 1
Regioselective and stereoselective benzoylation of 2-*N*-protected 4,6-*O*-ketal derivatives of D-glucosamines with 1-(benzoyloxy)benzotriazole




| Entry | Starting material | Time (h) | Product | Yield (%) | $J_{1,2}$ (Hz) |
|---|---|---|---|---|---|
| 1 | **1**: R = $N_3$, X = H, Y = Ph | 36 | **7** | 89 | 8.4 |
| 2 | **2**: R = $N_3$, X = H, Y = *p*-OMe–Ph | 48 | **8** | 96 | 8.4 |
| 3 | **3**: R = $N_3$, X = Y = Me | 48 | **9** | 88 | 7.5 |
| 4 | **4**: R = NHAc, X = H, Y = Ph | 24 | **10** | 84 | 8.7 |
| 5 | **5**: R = NHAc, X = Y = Me | 24 | **11** | 93 | 8.7 |
| 6 | **6**: R = NHTroc, X = H, Y = Ph | 24 | **12** | 42 | 8.4 |

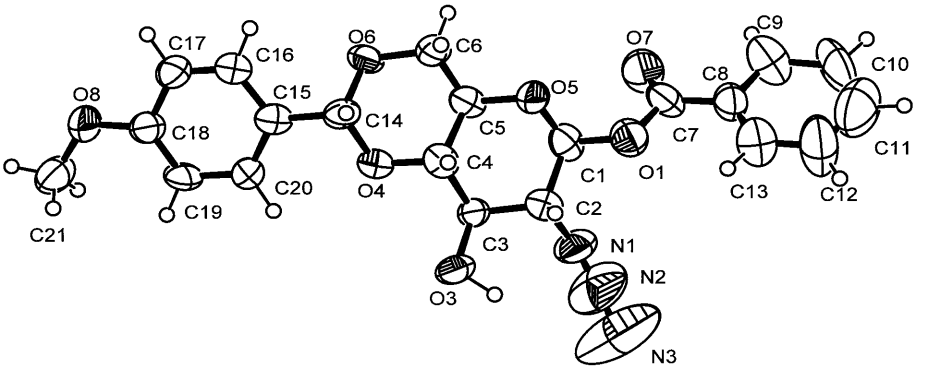



Fig. 1. The stereo ORTEP drawing of **8**.

Hz). The absolute structure of **8** was firmly determined by single-crystal X-ray analysis. An ORTEP drawing of the structure is shown in Fig. 1. The crystal data, data collection parameters, and refinement results for **8** are listed in Table 2, and atomic coordinates and their isotropic thermal parameters are provided in Table 3.

Since the proton of the 1-hydroxy group is more acidic than the 3-hydroxy group, the high regioselectivity is perhaps induced by the formation of a higher concentration of the anomeric species in the presence of triethylamine, which predominantly reacts with the mild benzoylating reagent BzOBT. Due to the kinetic stereoelectronic effect or 1,3-diaxial repulsion,[7] the $O^-$ is oriented in the equatorial position and only the β anomer is formed.

In conclusion, we have successfully developed a highly regioselective and stereoselective benzoylation of *N*-protected 4,6-*O*-ketal derivatives of D-glucosamines with BzOBT to afford the corresponding β anomeric benzoates in good yields.

## 3. Experimental

*General methods.*—Solvents were purified and dried by distillation. Flash chromatography was carried out as recommended with Silica Gel 60 (230–400 mesh, E. Merk). TLC was performed on precoated glass plates of Silica Gel 60 $F_{254}$ (0.25 mm, E. Merck); detection was carried out by spraying with a solution of $Ce(NH_4)_2(NO_3)_6$, $(NH_4)_6Mo_7O_{24}$, as well as $H_2SO_4$ in water and subsequent heating on a hot plate. Melting points were determined with a Büchi B-540 apparatus and are

uncorrected. Optical rotations were measured with a JASCO DIP-370 polarimeter at ~25 °C. $^1$H and $^{13}$C NMR spectra were recorded with Bruker AC 300 and AMX 400 instruments. Chemical shifts are in ppm from $Me_4Si$, generated from the $CHCl_3$ lock signal at $\delta$ 7.26. Mass spectra were obtained with a VG 70-250S mass spectrometer in the EI and FAB modes. IR spectra were taken with a Perkin–Elmer Paragon 1000 FT-IR spectrometer. Elemental analyses were determined with a Perkin–Elmer 2400 CHN instrument.

*General procedure for regioselective benzoylation.*—To a solution of the diol (3.0 mmol) in $CH_2Cl_2$ (10 mL) was sequentially added BzOBT (3.9 mmol) and $Et_3N$ (9.0 mmol) at rt under nitrogen. After stirring for 24–48 h (Table 1), the mixture was concentrated at reduced pressure, and the residue was purified by flash column chromatography on silica gel to afford the desired adduct (the yields were listed in Table 1).

*2-Azido-1-*O*-benzoyl-2-deoxy-4,6-*O*-benzylidene-β-*D*-glucopyranose* (**7**).—$R_f$ 0.26 (1:4 EtOAc–hexanes); mp 190–191 °C; $[\alpha]_D^{27}$ −118° (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) 3522, 2871, 2114, 1738, 1452, 1262, 1082, 991, 760 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.09 (d, 2 H, *J* 7.4 Hz, Bz*H*), 7.61 (t, 1 H, *J* 7.4 Hz, Bz*H*), 7.49–7.45 (m, 4 H, Bz*H*, Ph*H*), 7.40–7.36 (m, 3 H, Ph*H*), 5.82 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 5.54 (s, 1 H, PhC*H*), 4.37 (dd, 1 H, $J_{6eq,6ax}$ 10.2 Hz, H-6eq), 3.86 (dt, 1 H, $J_{3,OH}$ 2.6, $J_{3,4}$ 9.2 Hz, H-3), 3.77 (dd, 1 H, $J_{2,3}$ 9.2 Hz, H-2), 3.74 (t, 1 H, H-6ax), 3.64 (dd, 1 H, $J_{4,5}$ 10.2 Hz, H-4), 3.62 (dt, 1 H, $J_{5,6ax}$ 10.2, $J_{5,6eq}$ 4.0 Hz, H-5), 2.75 (d, 1 H, O*H*-3); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.43 (C), 136.62 (C), 134.02 (CH), 130.10 (CH), 129.48 (CH), 128.62 (CH), 128.42 (CH), 126.27 (CH), 102.11 (CH), 93.70 (CH), 80.40 (CH), 72.37 (CH), 68.26 ($CH_2$), 66.96 (CH), 65.55 (CH); FABHRMS ($MH^+$): Anal. Calcd for $C_{20}H_{20}N_3O_6$ 398.1352. Found 398.1337. Anal. Calcd for $C_{20}H_{19}N_3O_6$: C, 60.45; H, 4.82; N, 10.57. Found: C, 60.44; H, 4.65; N, 10.62.

*2-Azido-1-*O*-benzoyl-2-deoxy-4,6-*O*-(p-methoxybenzylidene)-β-*D*-glucopyranose* (**8**).—$R_f$ 0.36 (1:2 EtOAc–hexanes); mp 194–195 °C; $[\alpha]_D^{29}$ −115.0° (*c* 0.5, $CHCl_3$); IR ($CHCl_3$) 3528, 2930, 2118, 1740, 1613, 1514, 1085, 816, 712 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.08 (d, 2 H, *J* 8.0 Hz, Bz*H*), 7.39 (t, 1 H, *J* 8.0 Hz, Bz*H*), 7.47 (t, 2 H, *J* 8.0 Hz, Bz*H*), 7.40 (d, 2 H, *J* 6.8, Ar*H*), 6.89 (d, 2 H, *J* 6.8 Hz, Ar*H*), 5.81 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 5.51 (s, 1 H, PhC*H*), 4.36 (dd, 1 H, $J_{6eq,6ax}$ 9.8 Hz, H-6eq), 3.85 (td, 1 H, $J_{3,4}$ 9.8, $J_{3,OH}$ 2.8 Hz, H-3), 3.79 (s, 3 H, OMe), 3.73 (dt, 1 H, $J_{5,6eq}$ 3.7, $J_{5,6ax}$ 9.8 Hz, H-5), 3.71 (dd, $J_{2,3}$ 9.6 Hz, H-2), 3.63 (t, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 3.60 (t, 1 H, H-6ax), 2.76 (d, 1 H, O*H*); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.43 (C), 160.37 (C), 133.98 (CH), 130.07 (CH), 129.10 (C), 128.59 (CH), 128.46 (C), 127.63 (CH), 113.77 (CH), 102.00 (CH), 93.67 (CH), 80.35 (CH), 72.28 (CH), 68.19 ($CH_2$), 66.93 (CH), 65.50 (CH), 55.28 ($CH_3$); FABHRMS ($MH^+$): Anal. Calcd for $C_{21}H_{22}N_3O_7$ 428.1459. Found 428.1424. Anal. Calcd for $C_{21}H_{21}N_3O_7$: C, 59.01; H, 4.95; N, 9.83. Found: C, 59.10; H, 4.93; N, 9.83.

*2-Azido-1-*O*-benzoyl-2-deoxy-4,6-*O*-isopropylidine-β-*D*-glucopyranose* (**9**).—$R_f$ 0.32 (1:2 EtOAc–hexanes); mp 160–161°C; $[\alpha]_D^{30}$ −115° (*c* 0.7, $CHCl_3$); IR ($CHCl_3$) 3424, 2992,

Table 2
Crystal data, data collection parameters, and refinement results for **8** [a]

| | **8** |
|---|---|
| Formula | $C_{42}H_{42}N_6O_{14}$ |
| Formula weight | 854.82 |
| Crystal dimensions (mm$^3$) | $0.45\times0.38\times0.26$ |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| *a* (Å) | 8.2825(21) |
| *b* (Å) | 13.3590(13) |
| *c* (Å) | 38.155(7) |
| *V* (Å$^3$) | 4221.7(14) |
| *Z* | 4 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.345 |
| *F*(000) | 1792 |
| $\mu$ (Mo K$_\alpha$) (mm$^{-1}$) | 0.1 |
| $2\theta_{max}$ (°) | 50.0 |
| Measured reflections | 4240 |
| Unique reflections | 4240 |
| Observed reflections ($I>2.0\sigma(I)$) | 2492 |
| Variables | 561 |
| Min, max in final difference map (e Å$^{-3}$) | −0.24, 0.29 |
| *R*; *wR* | 0.064, 0.075 |

[a] $T=298$ K; diffractometer, Nonius CAD-4; radiation, Mo K$_\alpha$; $\lambda=0.7107$ Å.

Table 3
Atomic coordinates and isotropic thermal parameters for compound **8**

| Atom | *x* | *y* | *z* | $B_{iso}$ |
|---|---|---|---|---|
| O1 | 0.3935(8) | 0.0658(5) | 0.8522(2) | 5.7(3) |
| O3 | 0.3204(9) | 0.3791(4) | 0.9072(1) | 6.3(3) |
| O4 | 0.3796(7) | 0.3786(4) | 0.9733(1) | 4.2(3) |
| O5 | 0.3845(8) | 0.0705(4) | 0.9110(1) | 4.8(3) |
| O6 | 0.4054(8) | 0.1291(4) | 1.0045(1) | 5.1(4) |
| O7 | 0.6055(11) | −0.0373(6) | 0.8580(2) | 8.2(4) |
| O8 | 0.4520(9) | 0.4231(5) | 1.1304(1) | 6.0(3) |
| O31 | 0.0932(8) | 0.6396(4) | 0.8428(1) | 4.9(3) |
| O33 | 0.1263(7) | 0.4841(4) | 0.9550(1) | 4.5(3) |
| O34 | 0.1186(7) | 0.6881(4) | 0.9842(1) | 4.0(3) |
| O35 | 0.1630(7) | 0.7309(4) | 0.8905(1) | 4.1(3) |
| O36 | 0.1832(8) | 0.8561(4) | 0.9750(1) | 5.0(3) |
| O37 | −0.0772(9) | 0.7607(6) | 0.8246(2) | 7.1(4) |
| O38 | 0.0768(14) | 0.8500(10) | 1.1385(2) | 12.2(7) |
| N1 | 0.4680(13) | 0.2726(6) | 0.8495(2) | 6.9(5) |
| N2 | 0.3928(19) | 0.3156(11) | 0.8291(3) | 11.6(9) |
| N3 | 0.3132(24) | 0.2645(17) | 0.8091(4) | 20.3(15) |
| N31 | −0.0468(11) | 0.4849(5) | 0.8872(2) | 5.9(4) |
| N32 | −0.0317(16) | 0.4477(6) | 0.8592(2) | 9.6(6) |
| N33 | −0.0278(22) | 0.4034(9) | 0.8329(3) | 14.7(10) |
| C1 | 0.4462(11) | 0.1187(7) | 0.88151(25) | 4.9(5) |
| C2 | 0.3798(12) | 0.2249(6) | 0.87782(21) | 4.6(4) |
| C3 | 0.4029(11) | 0.2871(6) | 0.91131(20) | 3.9(4) |
| C4 | 0.3449(9) | 0.2267(6) | 0.94144(21) | 3.9(4) |
| C5 | 0.4258(10) | 0.1246(6) | 0.94232(22) | 4.2(4) |
| C6 | 0.3770(12) | 0.0682(6) | 0.97270(21) | 4.9(4) |
| C7 | 0.4976(16) | −0.0125(7) | 0.84110(29) | 5.9(6) |
| C8 | 0.4344(14) | −0.0566(7) | 0.80899(25) | 5.6(5) |
| C9 | 0.5129(17) | −0.1444(9) | 0.79792(33) | 8.9(8) |
| C10 | 0.4513(23) | −0.1839(10) | 0.76400(39) | 10.2(9) |
| C11 | 0.3306(24) | −0.1379(16) | 0.74637(41) | 11.7(12) |
| C12 | 0.2576(19) | −0.0567(12) | 0.75866(38) | 10.7(10) |
| C13 | 0.3049(16) | −0.0185(9) | 0.78907(32) | 7.6(7) |
| C14 | 0.3245(11) | 0.2228(6) | 1.00288(21) | 4.2(4) |
| C15 | 0.3567(10) | 0.2791(6) | 1.03555(21) | 4.0(4) |
| C16 | 0.3533(12) | 0.2301(6) | 1.06814(23) | 4.8(5) |
| C17 | 0.3871(13) | 0.2784(7) | 1.09764(21) | 5.2(5) |
| C18 | 0.4204(12) | 0.3834(7) | 1.09766(23) | 4.7(4) |
| C19 | 0.4164(12) | 0.4331(6) | 1.06735(23) | 5.1(5) |
| C20 | 0.3840(11) | 0.3809(6) | 1.03515(20) | 4.4(4) |
| C21 | 0.4893(14) | 0.5262(8) | 1.13360(24) | 6.4(6) |
| C31 | 0.0544(11) | 0.6595(6) | 0.87781(22) | 4.4(4) |
| C32 | 0.0774(10) | 0.5600(6) | 0.89819(20) | 4.1(4) |
| C33 | 0.0679(10) | 0.5718(6) | 0.93811(20) | 3.9(4) |
| C34 | 0.1582(10) | 0.6621(6) | 0.94948(19) | 3.5(4) |
| C35 | 0.1250(10) | 0.7528(6) | 0.92609(21) | 3.7(4) |
| C36 | 0.2302(13) | 0.8378(6) | 0.93975(24) | 5.5(5) |
| C37 | 0.0140(14) | 0.6968(7) | 0.81785(22) | 5.1(5) |
| C38 | 0.0566(14) | 0.6639(8) | 0.78192(25) | 5.8(5) |
| C39 | 0.0146(15) | 0.7100(8) | 0.75394(27) | 7.0(6) |
| C40 | 0.0312(19) | 0.6829(11) | 0.72026(33) | 8.8(8) |
| C41 | 0.1344(23) | 0.6090(13) | 0.71419(34) | 9.8(10) |
| C42 | 0.2076(19) | 0.5608(10) | 0.74376(33) | 10.1(9) |
| C43 | 0.1684(16) | 0.5873(8) | 0.77596(22) | 6.9(7) |
| C44 | 0.2107(10) | 0.7714(6) | 0.99686(24) | 4.3(4) |
| C45 | 0.1682(10) | 0.7946(7) | 1.03265(23) | 4.6(5) |
| C46 | 0.1241(12) | 0.8921(8) | 1.04305(28) | 6.2(5) |
| C47 | 0.0900(15) | 0.9146(9) | 1.07807(28) | 6.4(6) |
| C48 | 0.0988(16) | 0.8426(12) | 1.10209(36) | 8.6(8) |
| C49 | 0.1406(16) | 0.7451(12) | 1.09318(24) | 8.1(8) |
| C50 | 0.1735(12) | 0.7225(8) | 1.05875(28) | 6.0(5) |
| C51 | 0.0405(22) | 0.9291(21) | 1.15234(43) | 17.7(18) |
| Ho3 | 0.303 | 0.388 | 0.881 | 7.0 |
| Ho33 | 0.034 | 0.443 | 0.964 | 5.3 |
| H1 | 0.567 | 0.124 | 0.882 | 5.6 |
| H2 | 0.262 | 0.222 | 0.872 | 5.4 |
| H3 | 0.521 | 0.300 | 0.914 | 4.7 |
| H4 | 0.226 | 0.216 | 0.939 | 4.7 |
| H5 | 0.545 | 0.136 | 0.943 | 5.0 |
| H6a | 0.440 | 0.005 | 0.975 | 5.7 |
| H6b | 0.260 | 0.050 | 0.971 | 5.7 |
| H9 | 0.607 | −0.171 | 0.811 | 9.7 |
| H10 | 0.503 | −0.245 | 0.754 | 11.0 |
| H11 | 0.292 | −0.173 | 0.725 | 12.5 |
| H12 | 0.176 | −0.025 | 0.743 | 11.5 |
| H13 | 0.239 | 0.038 | 0.799 | 8.4 |
| H14 | 0.206 | 0.211 | 1.001 | 5.0 |
| H16 | 0.326 | 0.157 | 1.070 | 5.6 |
| H17 | 0.395 | 0.240 | 1.120 | 5.9 |
| H19 | 0.443 | 0.506 | 1.066 | 5.9 |
| H20 | 0.384 | 0.420 | 0.013 | 5.2 |
| H21a | 0.508 | 0.546 | 0.159 | 7.2 |
| H21b | 0.399 | 0.569 | 0.125 | 7.2 |
| H21c | 0.588 | 0.545 | 0.120 | 7.2 |
| H31 | −0.061 | 0.680 | 0.880 | 5.2 |
| H32 | 0.187 | 0.533 | 0.892 | 4.8 |
| H33 | −0.048 | 0.586 | 0.944 | 4.7 |
| H34 | 0.275 | 0.644 | 0.948 | 4.3 |
| H35 | 0.009 | 0.772 | 0.929 | 4.5 |
| H36a | 0.348 | 0.821 | 0.938 | 6.3 |
| H36b | 0.214 | 0.900 | 0.925 | 6.3 |
| H39 | −0.095 | 0.765 | 0.758 | 7.8 |
| H40 | −0.015 | 0.715 | 0.699 | 9.6 |
| H41 | 0.164 | 0.586 | 0.690 | 10.6 |
| H42 | 0.292 | 0.508 | 0.740 | 10.9 |
| H43 | 0.217 | 0.552 | 0.796 | 7.7 |
| H44 | 0.328 | 0.754 | 0.996 | 5.1 |
| H46 | 0.123 | 0.946 | 1.025 | 7.0 |
| H47 | 0.051 | 0.983 | 1.084 | 7.2 |
| H49 | 0.145 | 0.692 | 1.112 | 8.9 |
| H50 | 0.203 | 0.652 | 1.053 | 6.8 |
| H51a | 0.034 | 0.937 | 1.178 | 18.5 |
| H51b | −0.052 | 0.963 | 1.140 | 18.5 |
| H51c | 0.127 | 0.977 | 1.145 | 18.5 |

2117, 1734, 1602, 1271, 1077, 840, 713 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.06 (d, 2 H, *J* 7.2 Hz, Bz*H*), 7.60 (t, 1 H, *J* 7.2 Hz, Bz*H*), 7.46 (t, 2 H, *J* 7.2 Hz, Bz*H*), 5.77 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 3.95 (dd, 1 H, H-6eq), 3.76 (t, 1

H, $J_{6a,6b}$ 10.4 Hz, H-6ax), 3.72 (dt, 1 H, $J_{3,4}$ 10.4, $J_{3,OH}$ 2.0 Hz, H-3), 3.66 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2), 3.62 (t, 1 H, $J_{4,5}$ 10.4 Hz, H-4), 3.44 (dt, 1 H, $J_{5,6eq}$ 5.6, $J_{5,6ax}$ 10.4 Hz, H-5), 2.79 (d, 1 H, O*H*-3), 1.51 (s, 3 H, Me), 1.43 (s, 3 H, Me); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.45 (C), 134.00 (CH), 130.11 (CH), 128.62 (CH), 128.52 (C), 100.12 (C), 93.78 (CH), 73.19 (CH), 72.79 (CH), 67.98 (CH), 65.76 (CH), 61.66 ($CH_2$), 28.90 ($CH_3$), 19.05 ($CH_3$); FABHRMS ($MH^+$): Anal. Calcd for $C_{16}H_{20}N_3O_6$ 350.1352. Found 350.1344. Anal. Calcd for $C_{16}H_{19}N_3O_6$: C, 55.01; H, 5.48. Found: C, 54.96; H, 5.44.

*2*-N-*Acetyl-1*-O-*benzoyl-2-deoxy-4,6*-O-*benzylidene-β*-D-*glucopyranose* (**10**).—$R_f$ 0.28 (3:2 EtOAc–hexanes); mp 188–189 °C; $[\alpha]_D^{32}$ −61° (*c* 0.5, 1:1 $CHCl_3$–MeOH); IR ($CHCl_3$) 3650, 3276, 3057, 2877, 1740, 1679, 1250, 1084, 753, 698 cm$^{-1}$; $^1$H NMR (400 MHz, 1:1 $CDCl_3$–$CD_3OD$) $\delta$ 8.07 (dd, 2 H, *J* 7.2, *J* 1.2 Hz, Bz*H*), 7.62 (tt, 1 H, *J* 7.2, *J* 1.2 Hz, Bz*H*), 7.54–7.46 (m, 4 H, Bz*H*, Ph*H*), 7.38–7.36 (m, 3 H, Ph*H*), 5.85 (d, 1 H, $J_{1,2}$ 8.8 Hz, H-1), 5.62 (s, 1 H, PhC*H*), 4.37 (dd, 1 H, H-6eq), 4.23 (t, 1 H, $J_{2,3}$ 8.8 Hz, H-2), 3.89 (t, 1 H, $J_{3,4}$ 8.8 Hz, H-3), 3.83 (dt, 1 H, $J_{5,6ax}$10.4, $J_{5,6eq}$ 4.4 Hz, H-5), 3.70 (dd, $J_{4,5}$ 10.4 Hz, H-4), 3.65 (dd, 1 H, $J_{6ax,6eq}$ 10.4 Hz, H-6ax), 1.94 (s, 3 H, Ac); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 172.37 (C), 165.17 (C), 137.03 (C), 133.60 (CH), 129.75 (CH), 128.79 (CH), 128.57 (C), 128.30 (CH), 127.81 (CH), 126.04 (CH), 101.65 (CH), 93.75 (CH), 81.04 (CH), 70.77 (CH), 68.10 ($CH_2$), 66.99 (CH), 55.05 (CH), 21.91 ($CH_3$); FABHRMS ($MH^+$): Anal. Calcd for $C_{22}H_{24}NO_7$ 414.1553. Found 414.1584.

*2*-N-*Acetyl-1*-O-*benzoyl-2-deoxy-4,6*-O-*isopropylidene-β*-D-*glucopyranose* (**11**).—$R_f$ 0.21 (EtOAc); mp 115–117 °C; $[\alpha]_D^{32}$ −37° (*c* 0.7, $CHCl_3$); IR ($CHCl_3$) 3630, 3288, 2994, 1735, 1655, 1264, 1076, 1026, 940, 859, 755 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.04 (d, 2 H, *J* 7.2 Hz, Bz*H*), 7.58 (t, 1 H, *J* 7.2 Hz, Bz*H*), 7.44 (d, 2 H, *J* 7.2 Hz, Bz*H*), 5.92 (bs, 1 H, NH), 5.89 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 4.23 (q, 1 H, $J_{2,3}$ 8.4 Hz, H-2), 3.95 (dd, 1 H, H-6eq), 3.83 (dd, 1 H, $J_{3,4}$ 9.6 Hz, H-3), 3.77 (t, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 3.69 (t, 1 H, $J_{6ax,6eq}$ 9.6 Hz, H-6ax), 3.45 (dt, 1 H, $J_{5,6ax}$ 9.6, $J_{5,6eq}$ 5.2 Hz, H-5), 1.95 (s, 3 H, Ac), 1.52 (s, 3 H, Me), 1.43 (s, 3 H, Me); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 171.66 (C), 165.47 (C), 133.97 (CH), 130.20 (CH), 128.62 (CH), 128.61 (C), 100.03 (C), 93.59 (CH), 73.98 (CH), 72.94 (CH), 68.10 (CH), 61.75 ($CH_2$), 56.03 (CH), 28.96 ($CH_3$), 23.33 ($CH_3$), 19.03 ($CH_3$).

*2-(2,2,2-Trichloroethoxycarbonylamino)-1-O-benzoyl-2-deoxy-4,6-O-benzylidine-β*-D-*glucopyranose* (**12**).—$R_f$ 0.32 (4:7 EtOAc–hexanes); mp 201–202 °C; $[\alpha]_D^{30}$ −57° (*c* 0.7, $CHCl_3$); IR ($CHCl_3$) 3636, 3315, 2867, 1739, 1704, 1684, 1534, 1265, 1081, 1026, 820, 750, 706 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.08 (dd, 2 H, *J* 7.4, 1.2, Bz*H*), 7.60 (tt, 1 H, *J* 7.4, 1.2 Hz, Bz*H*), 7.53–7.51 (m, 2 H, Bz*H*), 7.47–7.40 (m, 5H, Ph*H*), 5.93 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1), 5.59 (s, 1 H, PhC*H*), 5.18 (d, 1 H, NH), 4.85 (d, 1 H, *J* 12.0 Hz, $CCl_3CH_2O$), 4.54 (d, 1 H, $CCl_3CH_2O$), 4.41 (dd, 1 H, $J_{6eq,6ax}$ 10.4 Hz, H-6eq), 4.04 (q, 1 H, $J_{2,3}$ 8.4, $J_{2,NH}$ 8.4 Hz, H-2), 3.99 (dd, 1 H, $J_{3,4}$ 7.6 Hz, H-3), 3.80 (dt, 1 H, $J_{5,6ax}$ 10.4, $J_{5,6eq}$ 4.4 Hz, H-5), 3.71 (dd, 1 H, $J_{4,5}$ 10.4 Hz, H-4), 3.69 (dd, 1 H, H-6ax), 2.91 (s, 1 H, O*H*-3); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 165.01 (C), 154.74 (C), 136.82 (C), 133.97 (CH), 130.25 (CH), 129.59 (CH), 128.54 (CH), 128.40 (C), 126.40 (CH), 102.05 (CH), 95.25 (C), 93.45 (CH), 81.08 (CH), 74.49 ($CH_2$), 71.39 (CH), 68.34 ($CH_2$), 67.02 (CH), 57.02 (CH); FABHRMS ($MH^+$): Anal. Calcd for $C_{23}H_{23}Cl_3NO_8$ 546.0489. Found 546.0482.

## 4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 147253. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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