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Note

Regioselective debenzylation of *C*-glycosyl compounds by boron trichloride

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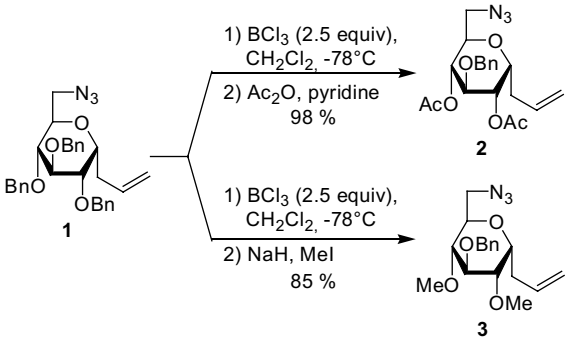
Abstract—Boron trichloride has been found to promote selective deprotection of 1,2- or 1,3-cis oriented secondary benzyl ethers of per-benzylated *C*-glycosyl derivatives. The reactivity towards BCl_3 follows the order: C-4 ⩾ C-2 > C-6 > C-3 for *C*-glucopyranosyl derivatives and C-3 ⩾ C-4 > C-6 > C-2 for *C*-galactopyranosyl derivatives. Preparatively useful selective debenzylation at secondary positions was possible after careful control of reaction conditions.

Keywords: Boron trichloride; *C*-Glycosyl compounds; Regioselective debenzylation

C-Glycosyl compounds, especially *C*-alcenyl derivatives, are useful precursors not only for the synthesis of metabolically and chemically stable glycoconjugates,[1] but also for the construction of natural products such as ciguatoxin,[2] brevetoxin B,[3] hemibrevetoxin B,[4,5] gambierol,[5,6] maitotoxin,[7] prelaureatin,[8] okadaic acid,[9] verrucarol[10] or ezomycins.[11] In these multistep syntheses, the protection–deprotection strategy is a basic approach. Among the wide range of protecting groups, the benzyl ether is frequently used owing to its ease of formation, inherent stability and variety of methods available for its deprotection. Selective removal of a benzyl ether functionality in an easily available per-*O*-benzylated precursor would be of considerable interest to minimize the number of transformations required. Several debenzylation methods (acetolysis, catalytic hydrogenolysis and Lewis acids such as $SnCl_4$, $TiCl_4$ or $CrCl_2$/LiI) have been studied for the preparation of partially benzylated monosaccharides.[12] The selective debenzylation has equally been achieved with TIBAL/DIBAL-H,[13] TMSI,[12a] NIS or a combination of diacetoxyiodobenzene/iodine.[14]

During the course of our research towards the synthesis of selectively protected *C*-glycosyl building blocks, we have recently discovered a new regioselective debenzylation reaction by boron trichloride (Scheme 1). BCl_3 has been used in the cleavage of methylene or benzylidene acetals and methyl or benzyl ethers/esters,[15] or in the



Scheme 1.

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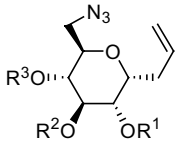
regeneration of free amino acids from *N*-benzyloxycarbonyl-5-oxazolidinones and from *N*-benzyloxycarbonylamino derivatives.[16] However, the regioselectivity of the BCl_3 promoted deprotection reaction has never been reported.[17] We describe herein the utility of this reagent for the regioselective debenzylation of per-benzylated *C*-glycosyl compounds.

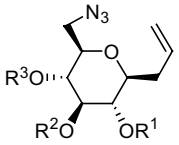
Treatment of α-*C*-allyl-D-glucosyl derivative **1**[18] with BCl_3 at −78 °C followed by acetylation gave **2** as the sole product in nearly quantitative yield (Scheme 1). This debenzylation is optimal with 2.5 equiv of BCl_3 (Table 1, entry 1–3). The 3-*O*-benzyl group is not cleaved even with an excess of reagent (entry 3). This remarkable selectivity may be explained by prior complexation of the oxygenophilic boron atom with the *cis*-oriented C-2 and C-4 benzyloxy groups, which allowed the subsequent deprotection. It is to be noted that the use of $BCl_3{\cdot}SMe_2$[19] instead of BCl_3 led to a mixture of several debenzylated products. The regioselective deprotection of **1** can be applied to large-scale preparations (up to 20 mmol). Other protecting groups can easily be introduced in 2- and 4-positions: compound **3** was isolated in 85% overall yield (Scheme 1).

In order to study the scope and regioselectivity of this reaction, a panel of per-benzylated *C*-glycosyl compounds has been studied and the results are compiled in Tables 1 and 2. Reaction of β-*C*-allyl-D-glucosyl derivative **4**[18] with BCl_3 (2.5 equiv) followed by acetylation led to a mixture of 2,4-di-*O*-acetyl (**5a**, 67%) and 2,3,4-tri-*O*-acetyl (**5b**, 31%) derivatives, separable by chromatography on silica gel (entry 4). In the case of the β-*C*-vinyl D-glucosyl derivative **6**,[20] the 4-*O*-benzyl ether was split more readily than the 2-*O*-benzyl group (entries 5 and 6). On prolonged treatment, 4-*O*-acetyl (**7a**, 25%), 2,4-di-*O*-acetyl (**7b**, 38%) and peracetylated derivatives (**7c**, 15%) have been isolated (entry 7). Complete deprotection can be achieved with an excess of BCl_3 in 64% yield (entry 8). It is not excluded that the cis-oriented allyl or vinyl group assisted the 3-*O*-benzyl ether cleavage in **4** and **6** as compared to **1**. The per-benzylated α-*C*-glucosyl compound **8**[21] seemed to be more reactive than the azido derivatives **1** and **6**: 1.25 equiv of BCl_3 was sufficient to convert all the starting material into the 2,4-di-*O*-acetyl (**9a**, 70%) and 2,4,6-tri-*O*-acetyl derivative (**9b**, 11%) (entry 9). On prolonged treatment, compound **9b** became predominant (entry 11 vs 10) and an excess of reagent brought progressively the reaction to complete deprotection (entries 12 and 13), accompanied by partial decomposition of the product (entry 13). These results show that the ease of cleavage of

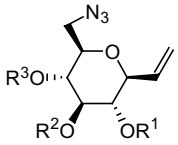
Table 1. BCl_3-promoted debenzylation of *C*-glucopyranosyl compounds



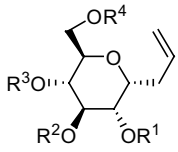
1: $R^1{=}R^2{=}R^3{=}Bn$
2: $R^2{=}Bn$, $R^1{=}R^3{=}Ac$



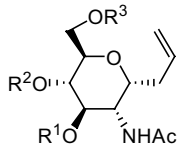
4: $R^1{=}R^2{=}R^3{=}Bn$
5a: $R^2{=}Bn$, $R^1{=}R^3{=}Ac$
5b: $R^1{=}R^2{=}R^3{=}Ac$



6: $R^1{=}R^2{=}R^3{=}Bn$
7a: $R^1{=}R^2{=}Bn$, $R^3{=}Ac$
7b: $R^2{=}Bn$, $R^1{=}R^3{=}Ac$
7c: $R^1{=}R^2{=}R^3{=}Ac$



8: $R^1{=}R^2{=}R^3{=}R^4{=}Bn$
9a: $R^2{=}R^4{=}Bn$, $R^1{=}R^3{=}Ac$
9b: $R^2{=}Bn$, $R^1{=}R^3{=}R^4{=}Ac$
9c: $R^1{=}R^2{=}R^3{=}R^4{=}Ac$

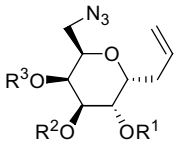


10: $R^1{=}R^2{=}R^3{=}Bn$
11a: $R^2{=}R^3{=}Bn$, $R^1{=}Ac$
11b: $R^2{=}Bn$, $R^1{=}R^3{=}Ac$
11c: $R^1{=}R^2{=}R^3{=}Ac$

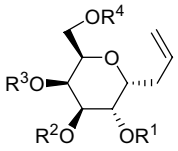
Entry	Reactant	BCl_3 (equiv)	Time (h)	Product (% yield)[a]				
				SM[b]	Glu(OAc)	$Glu(OAc)_2$	$Glu(OAc)_3$	$Glu(OAc)_4$
1	**1**	1.25	2	**1**[c]	—	—	—	—
2	**1**	2.5	2	—	—	**2** (98%)[d]	—	—
3	**1**	7.5	2	—	—	**2** (85%)[d]	—	—
4	**4**	2.5	2	—	—	**5a** (67%)[d]	**5b** (31%)[d]	—
5	**6**	1.25	2	**6** (28%)	**7a** (30%)	—	—	—
6	**6**	2.5	1	**6** (12%)	**7a** (36%)	—	—	—
7	**6**	2.5	2	—	**7a** (25%)	**7b** (38%)	**7c** (15%)	–
8	**6**	7.5	1	—	—	—	**7c** (64%)	—
9	**8**	1.25	1	—	—	**9a** (70%)	**9b** (11%)	—
10	**8**	2.5	1	—	—	**9a** (60%)	**9b** (20%)	—
11	**8**	2.5	2	—	—	**9a** (35%)	**9b** (40%)	—
12	**8**	7.5	0.5	—	—	**9a** (10%)	**9b** (38%)	**9c** (25%)
13	**8**	7.5	2	—	—	—	—	**9c** (44%)
14	**10**	2.5	1	**10** (33%)	**11a** (32%)	—	—	—
15	**10**	3.5	1	—	**11a** (19%)	**11b** (12%)	**11c** (40%)	—
16	**10**	3.5	2	—	—	**11b** (35%)	**11c** (55%)	—

[a] Isolated yield after acetylation and purification by preparative thin-layer chromatography.
[b] Starting material.
[c] Majority of the starting material was recovered.
[d] Isolated yield after flash chromatography on 3 mmol scale.

Table 2. BCl_3-promoted debenzylation of α-*C*-allyl-galactopyranosyl compounds



12: $R^1=R^2=R^3=Bn$
13a: $R^1=Bn$, $R^2=R^3=Ac$
13b: $R^1=R^2=R^3=Ac$



14: $R^1=R^2=R^3=R^4=Bn$
15a: $R^1=R^3=R^4=Bn$, $R^2=Ac$
15b: $R^1=R^4=Bn$, $R^2=R^3=Ac$
15c: $R^1=Bn$, $R^2=R^3=R^4=Ac$
15d: $R^1=R^2=R^3=R^4=Ac$

Entry	Reactant	BCl_3 (equiv)	Time (h)	Product (% yield)[a]				
				SM[b]	Gal(OAc)	$Gal(OAc)_2$	$Gal(OAc)_3$	$Gal(OAc)_4$
1	**12**	1.25	2	**12** (15%)	—	**13a** (51%)	—	—
2	**12**	2.5	2	—	—	**13a** (67%)	**13b** (20%)	—
3	**12**	7.5	1	—	—	**13a** (25%)	**13b** (15%)	—
4	**14**	1.25	2	**14** (17%)	**15a** (5%)	**15b** (42%)	**15c** (28%)	—
5	**14**	2.5	2	—	—	**15b** (20%)	**15c** (25%)	**15d** (35%)
6	**14**	5	2	—	—	—	**15c** (40%)	**15d** (53%)
7	**14**	7.5	2	—	—	—	**15c** (20%)	**15d** (60%)

[a] Isolated yield after acetylation and purification by preparative thin-layer chromatography.
[b] Starting material.

per-benzylated *C*-glucosyl compounds follows the order C-4 ⩾ C-2 > C-6 > C-3.

However, the 3-*O*-benzyl group is split first when the 2-*O*-benzyl ether is replaced by an acetamido group (compound **10**,[22] entry 14). Because of the presence of the acetamido group, 3.5 equiv of BCl_3 were necessary to consume all the starting material (entries 15 and 16). The relative ease of removal of benzyl groups follows the order C-3 > C-6 > C-4 for the amino *C*-glucosyl compound **10**. The regioselective *O*-debenzylation by anchimeric assistance has already been observed.[23]

Table 2 reports on the debenzylation of per-benzylated α-*C*-allyl-D-galactopyranosyl compounds. Entries 1 and 2 show that the cis-oriented C-3 and C-4 benzyloxy groups of compound **12** are more reactive than the C-2 substituent. The 3,4-di-*O*-acetyl compound **13a** can be isolated in 67% yield (entry 2). However, as in the case of compound **8** (Table 1, entry 13), use of 7.5 equiv of BCl_3 led to lower yields of products (entry 3). Concerning the tetra-*O*-benzylated α-*C*-galactosyl compound **14**,[21] a moderate regioselectivity was observed (entries 4 and 5). Treatment of **14** with more than 5 equivalents of reagent furnished the tri- and tetra-*O*-debenzylated derivatives **15c** and **15d** (entries 6 and 7). In the light of these results, the reactivity of α-*C*-galactosyl compounds towards BCl_3 follows the order: C-3 ⩾ C-4 > C-6 > C-2. Furthermore, the trans-oriented C-2 benzyl group in **12** and **14** was only partially deprotected with an excess of reagent (entries 3, 6 and 7).

In conclusion, we have reported a new regioselective debenzylation of *C*-glycosyl compounds. BCl_3 has been found to be efficient to promote selective deprotection of 1,2- or 1,3-cis oriented secondary benzyl ethers. This process, with an operationally simple protocol, complements the already existing methodologies and unravels possibilities for selectivities that have not been achieved with other methods. Preparatively useful selective debenzylation of per-benzylated *C*-glycosyl compounds at secondary positions was possible after careful control of reagent amount and reaction time. Finally, all the partially debenzylated products reported are new *C*-glycosyl derivatives, which should be useful synthetic intermediates.

1. Experimental

1.1. General methods

^1H and ^{13}C NMR spectra were recorded on a Bruker AGH-250 spectrometer in $CDCl_3$ solns. Optical rotations were measured using a Perkin–Elmer 141 polarimeter and a 10-cm cell. Column chromatography was performed on E. Merck Silica Gel 60 (230–400 mesh). Analytical thin-layer chromatography was performed on E. Merck aluminum precoated plates of Silica Gel 60F-254 with detection by UV and by spraying with 6 N H_2SO_4 and heating about 2 min at 300 °C. Dichloromethane and pyridine were distilled over CaH_2. Microanalyses were performed at the Service de Microanalyse de l'Université Pierre et Marie Curie.

1.2. General procedure for the debenzylation of per-benzylated *C*-glycosyl compounds

To a soln of the per-benzylated *C*-glycosyl derivative (0.1 mmol) in dry CH_2Cl_2 (2 mL) under an argon atmosphere, was added slowly boron trichloride (1 M soln in CH_2Cl_2) via a syringe at −78 °C, and the mixture was further stirred at this temperature. After the indicated time (Tables 1 and 2), the reaction was quenched with 1:1 MeOH–CH_2Cl_2 (2 mL) and concentrated under diminished pressure. The resulting residue was dissolved

in 2:1 pyridine–Ac_2O (1.5 mL) and stirred for 15 h at rt. After concentration under diminished pressure, the residue was dissolved in EtOAc, washed with water, dried over $MgSO_4$, concentrated and purified by preparative TLC (Et_2O–cyclohexane or EtOAc–cyclohexane).

1.2.1. 3-(2′,4′-Di-*O*-acetyl-6′-azido-3′-*O*-benzyl-6′-deoxy-α-D-glucopyranosyl)-1-propene (2). $[\alpha]_D$ +47.5 (*c* 0.91, CH_2Cl_2), R_f 0.62 (2:3 EtOAc–cyclohexane); ^1H NMR ($CDCl_3$, 250 MHz): 7.32–7.23 (m, 5H, Ph), 5.82–5.66 (m, 1H, CH═), 5.14–5.06 (m, 2H, CH_2═), 4.91 (dd, *J* 6.3, 4.0 Hz, 1H, H-2′), 4.82 (t, *J* 6.0 Hz, 1H, H-4′), 4.66 (d, *J* 12.0 Hz, 1H, CH–Ph), 4.57 (d, *J* 11.8 Hz, 1H, CH–Ph), 4.16-4.06 (m, 1H, H-1′), 3.87 (ddd, *J* 8.1, 5.8, 3.9 Hz, 1H, H-5′), 3.75 (t, *J* 6.3 Hz, 1H, H-3′), 3.51 (dd, *J* 13.1, 8.1 Hz, 1H, H-6′a), 3.17 (dd, *J* 13.1, 3.9 Hz, 1H, H-6′b), 2.52–2.35 (m, 1H, H-3a), 2.33–2.15 (m, 1H, H-3b), 2.02 (s, 3H, Ac), 1.97 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 170.3, 170.1 (CO), 137.9 (C_{ipso}), 133.5 (CH═), 128.9, 128.4, 128.1 (Ph), 118.3 (CH_2═), 75.5 (C-3′), 74.1 (CH_2–Ph), 72.8 (C-5′), 70.7 (C-2′), 69.9, 69.8 (C-1′,4′), 50.7 (C-6′), 33.1 (C-3), 21.3 (Me). Anal. Calcd for $C_{20}H_{25}N_3O_6$: C, 59.54; H, 6.25; N, 10.42. Found: C, 59.88; H, 6.30; N, 10.29.

1.2.2. 3-(6′-Azido-3′-*O*-benzyl-6′-deoxy-2′,4′-di-*O*-methyl-α-D-glucopyranosyl)-1-propene (3). Compound **1**[18] (3.2 g, 6.41 mmol) in dry CH_2Cl_2 (200 mL) was debenzylated with BCl_3 (2.5 equiv, 16 mL) during 1 h 30 at −78 °C as described above. The reaction mixture was then quenched with 1:1 MeOH–CH_2Cl_2 (130 mL) and concentrated under diminished pressure. The residue was dissolved in EtOAc and washed with 5% aq $NaHCO_3$, water and brine, dried over $MgSO_4$ and concentrated. A soln of the resulting residue (2.04 g) in dry DMF (10 mL) was added to a mixture of NaH (450 mg, 18.8 mmol) in DMF (15 mL) at 0 °C. After 30 min, MeI (1.1 mL, 18.8 mmol) was added. The mixture was allowed to warm at rt and was then stirred overnight. After concentration, the residue was diluted in EtOAc and water and extracted. The organic layer was washed with brine, dried ($MgSO_4$) and concentrated to give **3** as an oil (1.88 g, 85%). $[\alpha]_D$ +71.6 (*c* 1, CH_2Cl_2), R_f 0.47 (1:4 EtOAc–cyclohexane); ^1H NMR ($CDCl_3$, 250 MHz): δ 7.39–7.26 (m, 5H, Ph), 5.92–5.73 (m, 1H, CH═), 5.19–5.10 (m, 2H, CH_2═), 4.88 (d, *J* 11.0 Hz, 1H, CH–Ph), 4.75 (d, *J* 11.0 Hz, 1H, CH–Ph), 4.21–4.13 (m, 1H, H-1′), 3.65–3.55 (m, 2H, H-3′,5′), 3.53 (s, 3H, OMe), 3.47 (s, 3H, OMe), 3.48–3.41 (m, 2H, H-2′,6′b), 3.34 (dd, *J* 13.1, 5.3 Hz, 1H, H-6′a), 3.15 (dd, *J* 9.5, 8.5 Hz, 1H, H-4′), 2.40–2.38 (m, 2H, H-3). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 138.8 (C_{ipso}), 134.4 (CH═), 128.5, 128.0, 127.8 (Ph), 117.2 (CH_2═), 81.9, 81.8 (C-2′,3′), 80.7 (C-4′), 75.2 (CH_2–Ph), 73.1 (C-1′), 71.2 (C-5′), 60.9, 58.8 (OMe), 51.8 (C-6′), 30.3 (C-3). Anal. Calcd for $C_{18}H_{25}N_3O_4$: C, 62.23; H, 7.25; N, 12.10. Found: C, 62.01; H, 7.33; N, 12.19.

1.2.3. 3-(2′,4′-Di-*O*-acetyl-6′-azido-3′-*O*-benzyl-6′-deoxy-β-D-glucopyranosyl)-1-propene (5a). $[\alpha]_D$ −8.6 (*c* 1, CH_2Cl_2), R_f 0.69 (2:3 EtOAc–cyclohexane); ^1H NMR ($CDCl_3$, 250 MHz) 7.29–7.17 (m, 5H, Ph), 5.89–5.72 (m, 1H, CH═), 5.07–5.01 (m, 2H, CH_2═), 4.92 (t, *J* 9.8 Hz, 1H, H-2′ or 4′), 4.91 (t, *J* 9.5 Hz, 1H, H-4′ or 2′), 4.56 (s, 2H, CH_2–Ph), 3.63 (t, *J* 9.3 Hz, 1H, H-3′), 3.52–3.43 (m, 1H, H-5′), 3.40–3.34 (m, 1H, H-1′), 3.26 (dd, *J* 13.3, 7.5 Hz, 1H, H-6′a), 3.07 (dd, *J* 13.3, 2.5 Hz, 1H, H-6′b), 2.25–2.22 (m, 2H, H-3), 1.95 (s, 3H, Ac), 1.92 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 169.7, 169.6 (CO), 138.0 (C_{ipso}), 133.2 (CH═), 128.6, 127.9, 127.8 (Ph), 117.9 (CH_2═), 81.7 (C-3′), 77.7 (C-1′,5′), 74.2 (CH_2–Ph), 73.1, 71.4 (C-2′,4′), 51.7 (C-6′), 36.1 (C-3), 21.0, 20.9 (Me). Anal. Calcd for $C_{20}H_{25}N_3O_6$: C, 59.54; H, 6.25; N, 10.42. Found: C, 59.09; H, 6.21; N, 10.51.

1.2.4. 3-(2′,3′,4′-Tri-*O*-acetyl-6′-azido-6′-deoxy-β-D-glucopyranosyl)-1-propene (5b). $[\alpha]_D$ +7.1 (*c* 1, CH_2Cl_2), R_f 0.54 (2:3 EtOAc–cyclohexane); ^1H NMR ($CDCl_3$, 250 MHz): 5.89–5.78 (m, 1H, CH═), 5.17 (t, *J* 9.8 Hz, 1H), 5.11–5.04 (m, 2H, CH_2═), 4.97 (t, *J* 9.8 Hz, 1H), 4.91 (t, *J* 9.5 Hz, 1H), 3.63 (ddd, *J* 9.5, 7.0, 3.3 Hz, 1H, H-5′), 3.54 (ddd, *J* 9.8, 7.0, 4.0 Hz, 1H, H-1′), 3.29 (dd, *J* 12.8, 7.0 Hz, 1H, H-6′a), 3.21 (dd, *J* 13.3, 3.0 Hz, 1H, H-6′b), 2.34–2.25 (m, 2H, H-3), 2.04 (s, 3H, Ac), 2.03 (s, 3H, Ac), 2.00 (s, 3H, Ac). ^{13}C NMR: ($CDCl_3$, 62.9 MHz) δ 170.6, 169.7 (CO), 132.7 (CH═), 118.3 (CH_2═), 77.3, 74.3, 71.7, 69.9 (CH), 51.4 (C-6′), 36.0 (C-3), 20.8 (Me). Anal. Calcd for $C_{15}H_{21}N_3O_7$: C, 50.70; H, 5.96; N, 11.83. Found: C, 50.51; H, 6.01; N, 11.77.

1.2.5. (4′-*O*-Acetyl-6′-azido-2′,3′-di-*O*-benzyl-6′-deoxy-β-D-glucopyranosyl)-ethene (7a). $[\alpha]_D$ +3.4 (*c* 0.7, CH_2Cl_2), R_f 0.62 (1:2 EtOAc–cyclohexane); ^1H NMR ($CDCl_3$, 250 MHz): 7.36–7.26 (m, 10H, Ph), 6.05–5.91 (m, 1H, CH═), 5.52–5.30 (m, 2H, CH_2═), 4.98 (t, *J* 9.5 Hz, 1H, H-4′), 4.88 (d, *J* 11.5 Hz, 1H, CH–Ph), 4.76 (d, *J* 10.8 Hz, 1H, CH–Ph), 4.68 (d, *J* 11.5 Hz, 1H, CH–Ph), 4.66 (d, *J* 10.8 Hz, 1H, CH–Ph), 3.85 (dd, *J* 9.5, 5.5 Hz, 1H, H-1′), 3.69 (t, *J* 9.3 Hz, 1H, H-3′), 3.56 (ddd, *J* 9.5, 6.6, 3.3 Hz, 1H, H-5′), 3.38 (t, *J* 9.3 Hz, 1H, H-2′), 3.31 (dd, *J* 13.5, 6.5 Hz, 1H, H-6′a), 3.22 (dd, *J* 13.3, 3.0 Hz, 1H, H-6′b), 1.94 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 169.9 (CO), 138.3, 137.8 (C_{ipso}), 134.4 (CH═), 128.6, 128.2, 128.1, 127.9 (Ph), 118.1 (CH_2═), 83.9 (C-3′), 82.5 (C-2′), 79.7 (C-1′), 77.2 (C-5′), 75.4 (CH_2–Ph), 71.5 (C-4′), 51.7 (C-6′), 21.0 (Me). Anal. Calcd for $C_{24}H_{27}N_3O_5$: C, 65.89; H, 6.22; N, 9.60. Found: C, 65.74; H, 6.33; N, 9.69.

1.2.6. (2′,4′-Di-*O*-acetyl-6′-azido-3′-*O*-benzyl-6′-deoxy-β-D-glucopyranosyl)-ethene (7b). R_f 0.44 (1:2 EtOAc–cyclohexane); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.34–7.23 (m, 5H, Ph), 5.83–5.69 (m, 1H, CH=), 5.39–5.24 (m, 2H, CH_2=), 5.02 (t, *J* 9.5 Hz, 1H, H-2′), 4.97 (t, *J* 9.5 Hz, 1H, H-4′), 4.62 (s, 2H, CH_2–Ph), 3.81 (dd, *J* 9.7, 6.8 Hz, 1H, H-1′), 3.72 (t, *J* 9.3 Hz, 1H, H-3′), 3.59 (ddd, *J* 9.3, 7.0, 3.0 Hz, 1H, H-5′), 3.35 (dd, *J* 13.5, 6.8 Hz, 1H, H-6′a), 3.23 (dd, *J* 13.5, 3.0 Hz, 1H, H-6′b), 1.99 (s, 3H, Ac), 1.97 (s, 3H, Ac).

1.2.7. (2′,3′,4′-Tri-*O*-acetyl-6′-azido-6′-deoxy-β-D-glucopyranosyl)-ethene (7c). $[\alpha]_D$ +20.3 (*c* 0.4, CH_2Cl_2), R_f 0.35 (1:2 EtOAc–cyclohexane); ^{1}H NMR ($CDCl_3$, 250 MHz): 5.81–5.68 (m, 1H, CH=), 5.41–5.30 (m, 2H, CH_2=), 5.22 (t, *J* 9.5 Hz, 1H, H-3′), 5.02 (t, *J* 9.8 Hz, 1H, H-4′), 4.92 (t, *J* 9.5 Hz, 1H, H-2′), 3.90 (dd, *J* 10.0, 6.5 Hz, 1H, H-1′), 3.72–3.64 (m, 1H, H-5′), 3.32–3.31 (m, 2H, H-6′), 2.03 (s, 3H, Ac), 2.02 (s, 3H, Ac), 2.00 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 170.4, 169.6, 169.5 (CO), 133.0 (CH=), 119.7 (CH_2=), 78.9 (C-1′), 76.9 (C-5′), 73.9 (C-3′), 71.4 (C-2′), 69.7 (C-4′), 51.2 (C-6′), 20.7 (Me). Anal. Calcd for $C_{14}H_{19}N_3O_7$: C, 49.27; H, 5.61; N, 12.31. Found: C, 49.50; H, 5.67; N, 5.50.

1.2.8. 3-(2′,4′-Di-*O*-acetyl-3′,6′-di-*O*-benzyl-α-D-glucopyranosyl)-1-propene (9a). $[\alpha]_D$ +45.0 (*c* 1, CH_2Cl_2), R_f 0.20 (2:3 Et_2O–cyclohexane); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.29–7.16 (m, 10H, Ph), 5.78–5.60 (m, 1H, CH=), 5.08–4.99 (m, 2H, CH_2=), 4.94 (t, *J* 5.5 Hz, 1H, H-4′), 4.86 (dd, *J* 6.0, 3.8 Hz, 1H, H-2′), 4.58 (s, 2H, CH_2–Ph), 4.44 (s, 2H, CH_2–Ph), 4.08–4.00 (m, 1H, H-1′), 3.91 (q, *J* 5.8 Hz, 1H, H-5′), 3.70 (t, *J* 6.0 Hz, 1H, H-3′), 3.61 (dd, *J* 10.5, 6.3 Hz, 1H, H-6′a), 3.54 (dd, *J* 10.5, 5.5 Hz, 1H, H-6′b), 2.45–2.33 (m, 1H, H-3a), 2.23–2.15 (m, 1H, H-3b), 1.99 (s, 3H, Ac), 1.90 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 170.1, 169.9 (CO), 137.9 (C_{ipso}), 133.7 (CH=), 128.6, 128.5, 127.9, 127.7 (Ph), 117.7 (CH_2=), 75.3 (C-3′), 73.5 (CH_2–Ph), 72.5 (C-5′), 70.6 (C-2′), 69.6 (C-1′), 69.1 (C-4′), 68.5 (C-6′), 33.2 (C-3), 21.1 (Me). Anal. Calcd for $C_{27}H_{32}O_7$: C, 69.21; H, 6.88. Found: C, 69.00; H, 6.95.

1.2.9. 3-(2′,4′,6′-Tri-*O*-acetyl-3′-*O*-benzyl-α-D-glucopyranosyl)-1-propene (9b). $[\alpha]_D$ +76.7 (*c* 0.3, CH_2Cl_2), R_f 0.11 (2:3 Et_2O–cyclohexane); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.29–7.19 (m, 5H, Ph), 5.76–5.58 (m, 1H, CH=), 5.07–5.00 (m, 2H, CH_2=), 4.90–4.83 (m, 2H, H-2′,4′), 4.63 (d, *J* 11.8 Hz, 1H, CH–Ph), 4.57 (d, *J* 11.8 Hz, 1H, CH–Ph), 4.35 (dd, *J* 12.0, 7.0 Hz, 1H, H-6′a), 4.15–4.08 (m, 1H, H-1′), 4.02 (dd, *J* 12.0, 3.8 Hz, 1H, H-6′b), 3.91–3.85 (m, 1H, H-5′), 3.71 (t, *J* 6.0 Hz, 1H, H-3′), 2.45–2.30 (m, 1H, H-3a), 2.22–2.12 (m, 1H, H-3b), 2.00 (s, 3H, Ac), 1.99 (s, 3H, Ac), 1.94 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 170.9, 170.1, 169.8 (CO), 137.4 (C_{ipso}), 133.5 (CH=), 128.6, 128.1, 127.8 (Ph), 117.7 (CH_2=), 75.2 (C-3′), 73.7 (CH_2–Ph), 71.3 (C-5′), 70.6, 69.5, 68.6 (C-1′,2′,4′), 61.8 (C-6′), 32.9 (C-3), 21.0 (Me). Anal. Calcd for $C_{22}H_{28}O_8$: C, 62.85; H, 6.71. Found: C, 62.62; H, 6.84.

1.2.10. 3-(3′-*O*-Acetyl-2′-*N*-acetylamino-4′,6′-di-*O*-benzyl-2′-deoxy-α-D-glucopyranosyl)-1-propene (11a). $[\alpha]_D$ +30.0 (*c* 0.6, CH_2Cl_2), R_f 0.43 (3:1 EtOAc–cyclohexane); ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.28–7.16 (m, 10H, Ph), 6.15 (d, *J* 8.8 Hz, 1H, NH), 5.79–5.63 (m, 1H, CH=), 5.07–4.97 (m, 3H, H-3′, CH_2=), 4.52 (s, 2H, CH_2–Ph), 4.51 (d, *J* 11.8 Hz, 1H, CH–Ph), 4.44 (d, *J* 12.0 Hz, 1H, CH–Ph), 4.10 (ddd, *J* 8.8, 6.8, 3.8 Hz, 1H, H-2′), 4.03–3.96 (m, 1H, H-1′), 3.90 (q, *J* 5.0 Hz, 1H, H-5′), 3.68 (dd, *J* 10.3, 5.3 Hz, 1H, H-6′a), 3.60 (t, *J* 5.8 Hz, 1H, H-4′), 3.56 (dd, *J* 10.3, 5.3 Hz, 1H, H-6′a), 2.35–2.10 (m, 2H, H-3), 1.89 (s, 3H, Ac), 1.80 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 170.8, 169.9 (CO), 138.0, 137.6 (C_{ipso}), 134.1 (CH=), 128.7, 128.6, 128.2, 127.9 (Ph), 117.4 (CH_2=), 73.9 (C-4′), 73.5 (C-5′, CH_2–Ph), 70.9 (C-3′), 70.5 (C-1′), 67.9 (C-6′), 50.1 (C-2′), 33.4 (C-3), 23.3 (Me), 21.1 (Me). Anal. Calcd for $C_{27}H_{33}NO_6$: C, 69.36; H, 7.11; N, 3.00. Found: C, 69.55; H, 7.02; N, 2.90.

1.2.11. 3-(3′,6′-Di-*O*-acetyl-2′-*N*-acetylamino-4′-*O*-benzyl-2′-deoxy-α-D-glucopyranosyl)-1-propene (11b). $[\alpha]_D$ +39.3 (*c* 0.3, CH_2Cl_2), R_f 0.33 (3:1 EtOAc–cyclohexane); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.30–7.23 (m, 5H, Ph), 6.17 (d, *J* 9.0 Hz, 1H, NH), 5.79–5.63 (m, 1H, CH=), 5.08–4.99 (m, 3H, H-3′, CH_2=), 4.57 (s, 2H, CH_2–Ph), 4.31 (dd, *J* 11.8, 7.0 Hz, 1H, H-6′a), 4.17–4.10 (m, 2H, H-2′,6′b), 4.05–3.94 (m, 2H, H-1′,5′), 3.44 (t, *J* 4.8 Hz, 1H, H-4′), 2.34–2.10 (m, 2H, H-3), 2.01 (s, 3H, Ac), 1.97 (s, 3H, Ac), 1.81 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 170.7, 169.9 (CO), 137.2 (C_{ipso}), 133.9 (CH=), 128.8, 128.4, 128.1 (Ph), 117.6 (CH_2=), 73.4 (C-4′, CH_2–Ph), 72.6 (C-5′), 70.3 (C-3′), 67.0 (C-1′), 61.7 (C-6′), 49.7 (C-2′), 33.7 (C-3), 23.3 (Me), 21.2 (Me), 20.9 (Me). Anal. Calcd for $C_{22}H_{29}NO_7$: C, 62.99; H, 6.97; N, 3.34. Found: C, 63.15; H, 7.00; N, 3.26.

1.2.12. 3-(6′-Azido-2′,3′,4′-tri-*O*-benzyl-6′-deoxy-α-D-galactopyranosyl)-1-propene (12). This was prepared following the method described for **4**:[18] methanesulfonyl chloride (60 μL, 0.772 mmol) was added to a 0 °C soln of 3-(2′,3′,4′-tri-*O*-benzyl-α-D-galactopyranosyl)-1-propene[24] (260 mg, 0.537 mmol) and TEA (137 μL, 0.998 mmol) in CH_2Cl_2 (2 mL). The ice bath was removed, and stirring was continued for 18 h before MeOH (50 μL) was added. The soln was concentrated, dissolved in EtOAc (20 mL) and washed successively with water, $NaHCO_3$ 5% and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated to an oil, which was dissolved in DMF (2 mL) and added to

NaN_3 (175 mg, 2.685 mmol). The reaction mixture was heated at 90 °C for 20 h. After evaporation, the residue was diluted in EtOAc (20 mL), washed successively with water, brine, dried over $MgSO_4$, filtered, concentrated and purified by preparative thin-layer chromatography (1:2 Et_2O–cyclohexane) to afford **12** as an oil (41 mg, 15.3%). $[\alpha]_D$ +48.0 (*c* 1, CH_2Cl_2), R_f 0.52 (1:4 EtOAc–cyclohexane); ^1H NMR ($CDCl_3$, 250 MHz) δ 7.26–7.14 (m, 15H, Ph), 5.85–5.57 (m, 1H, CH=), 5.04–4.95 (m, 2H, CH_2=), 4.64–4.43 (m, 6H, $3\times CH_2$–Ph), 3.97–3.85 (m, 4H), 3.69–3.66 (m, 1H), 3.55–3.52 (m, 1H), 3.15 (dd, *J* = 13.0, 2.3 Hz, 1H, H-6′), 2.35–2.24 (m, 2H, H-3). ^{13}C NMR ($CDCl_3$, 62.9 MHz) δ 138.2, 138.1 (C_{ipso}), 134.7 (CH=), 128.5, 128.1, 127.9, 127.7 (Ph), 117.3 (CH_2=), 76.1, 74.9, 73.7, 73.5 (CH), 73.4, 73.1, 72.4 (CH_2–Ph), 69.3 (CH), 48.7 (C-6′), 33.3 (C-3). Anal. Calcd for $C_{30}H_{33}N_3O_4$: C, 72.12; H, 6.66; N, 8.41. Found: C, 72.41; H, 6.79; N, 8.21.

1.2.13. 3-(3′,4′-Di-*O*-acetyl-6′-azido-2′-*O*-benzyl-6′-deoxy-α-D-galactopyranosyl)-1-propene (13a). $[\alpha]_D$ +72.0 (*c* 1, CH_2Cl_2), R_f 0.33 (2:3 Et_2O–cyclohexane); ^1H NMR ($CDCl_3$, 250 MHz): δ 7.36–7.26 (m, 5H, Ph), 5.88–5.73 (m, 1H, CH=), 5.38 (dd, *J* 3.3, 2.5 Hz, 1H, H-4′), 5.20 (dd, *J* 9.3, 3.5 Hz, 1H, H-3′), 5.19–5.10 (m, 2H, CH_2=), 4.67 (d, *J* 11.8 Hz, 1H, CH–Ph), 4.59 (d, *J* 11.8 Hz, 1H, CH–Ph), 4.21–4.13 (m, 1H, H-1′), 3.99 (ddd, *J* 8.3, 4.0, 2.5 Hz, 1H, H-5′), 3.91 (dd, *J* 9.3, 5.5 Hz, 1H, H-2′), 3.48 (dd, *J* 10.5, 8.3 Hz, 1H, H-6′a), 3.08 (dd, *J* 10.5, 4.0 Hz, 1H, H-6′b), 2.51–2.47 (m, 2H, H-3), 2.13 (s, 3H, Ac), 2.03 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 170.2 (CO), 137.9 (C_{ipso}), 134.0 (CH=), 128.6, 128.1, 127.8 (Ph), 117.6 (CH_2=), 73.7 (C-2′), 73.4 (C-1′), 73.3 (CH_2–Ph), 69.6 (C-3′,5′), 68.9 (C-4′), 50.6 (C-6′), 30.2 (C-3), 21.0, 20.8 (Me). Anal. Calcd for $C_{20}H_{25}N_3O_6$: C, 59.54; H, 6.25; N, 10.42. Found: C, 59.70; H, 6.33; N, 10.30.

1.2.14. 3-(2′,3′,4′-Tri-*O*-acetyl-6′-azido-6′-deoxy-α-D-galactopyranosyl)-1-propene (13b). $[\alpha]_D$ +86.7 (*c* 0.3, CH_2Cl_2), R_f 0.19 (2:3 Et_2O–cyclohexane); ^1H NMR ($CDCl_3$, 250 MHz) δ 5.86–5.75 (m, 1H, CH=), 5.40–5.13 (m, 5H, H-2′,3′,4′, CH_2=), 4.36–4.29 (m, 1H, H-1′), 4.02–3.98 (m, 1H, H-5′), 3.51 (dd, *J* 12.8, 8.3 Hz, 1H, H-6′a), 3.10 (dd, *J* 12.8, 4.3 Hz, 1H, H-6′b), 2.56–2.28 (m, 2H, H-3), 2.14 (s, 3H, Ac), 2.07 (s, 3H, Ac), 2.03 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 170.1 (CO), 133.3 (CH=), 118.1 (CH_2=), 72.0 (C-1′), 69.9 (C-5′), 68.5, 68.2, 68.1 (C-2′,3′,4′), 50.5 (C-6′), 30.9 (C-3), 20.9 (Me). Anal. Calcd for $C_{15}H_{21}N_3O_7$: C, 50.70; H, 5.96; N, 11.83. Found: C, 50.90; H, 6.10; N, 11.74.

1.2.15. 3-(3′-*O*-Acetyl-2′,4′,6′-tri-*O*-benzyl-α-D-galactopyranosyl)-1-propene (15a). R_f 0.38 (2:3 Et_2O–cyclohexane); ^1H NMR ($CDCl_3$, 250 MHz) δ 7.33–7.26 (m, 15H, Ph), 5.78–5.64 (m, 1H, CH=), 5.09–5.02 (m, 3H, H-3′, CH_2=), 4.73–4.51 (m, 6H, $3\times CH_2$–Ph), 4.27–4.20 (m, 1H, H-5′), 4.06–3.98 (m, 2H, H-1′,6′a), 3.91 (dd, *J* 5.3, 3.0 Hz, 1H, H-4′), 3.78–3.71 (m, 2H, H-2′,6′b), 2.40–2.10 (m, 2H, H-3), 2.05 (s, 3H, Ac).

1.2.16. 3-(3′,4′-Di-*O*-acetyl-2′,6′-di-*O*-benzyl-α-D-galactopyranosyl)-1-propene (15b). $[\alpha]_D$ +60.0 (*c* 0.5, CH_2Cl_2), R_f 0.24 (2:3 Et_2O–cyclohexane); ^1H NMR ($CDCl_3$, 250 MHz): δ 7.38–7.25 (m, 10H, Ph), 5.89–5.73 (m, 1H, CH=), 5.48 (dd, *J* 3.3, 2.0 Hz, 1H, H-4′), 5.21 (dd, *J* 9.8, 3.3 Hz, 1H, H-3′), 5.20–5.08 (m, 2H, CH_2=), 4.66 (d, *J* 12.0 Hz, 1H, CH–Ph), 4.59 (d, *J* 12.0 Hz, 1H, CH–Ph), 4.56 (d, *J* 12.0 Hz, 1H, CH–Ph), 4.42 (d, *J* 12.0 Hz, 1H, CH–Ph), 4.20–4.12 (m, 1H, H-1′), 4.03 (td, *J* 6.3, 2.0 Hz, H-5′), 3.95 (dd, *J* 9.8, 5.8 Hz, 1H, H-2′), 3.52 (dd, *J* 9.5, 6.0 Hz, 1H, H-6′a), 3.42 (dd, *J* 9.8, 6.3 Hz, 1H, H-6′b), 2.55–2.49 (m, 2H, H-3), 2.04 (s, 3H, Ac), 2.00 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 170.2 (CO), 138.1, 137.9 (C_{ipso}), 134.5 (CH=), 128.5, 128.0, 127.8, 127.7 (Ph), 117.4 (CH_2=), 74.0 (C-1′,2′), 73.5, 73.3 (CH_2–Ph), 70.2 (C-3′), 68.9 (C-4′), 68.7 (C-5′), 67.9 (C-6′), 29.8 (C-3), 21.0, 20.8 (Me). Anal. Calcd for $C_{27}H_{32}O_7$: C, 69.21; H, 6.88. Found: C, 69.44; H, 6.97.

1.2.17. 3-(3′,4′,6′-Tri-*O*-acetyl-2′-*O*-benzyl-α-D-galactopyranosyl)-1-propene (15c). $[\alpha]_D$ +86.0 (*c* 0.3, CH_2Cl_2), R_f 0.18 (2:3 Et_2O–cyclohexane); ^1H NMR ($CDCl_3$, 250 MHz): δ 7.34–7.26 (m, 5H, Ph), 5.81–5.67 (m, 1H, CH=), 5.42 (dd, *J* 3.3, 2.3 Hz, 1H, H-4′), 5.21 (dd, *J* 9.0, 3.3 Hz, 1H, H-3′), 5.15–5.06 (m, 2H, CH_2=), 4.66 (d, *J* 11.8 Hz, 1H, CH–Ph), 4.57 (d, *J* 11.8 Hz, 1H, CH–Ph), 4.23–4.02 (m, 4H, H-1′,5′,6′), 3.89 (dd, *J* 9.0, 5.3 Hz, 1H, H-2′), 2.47–2.42 (m, 2H, H-3), 2.10 (s, 3H, Ac), 2.03 (s, 3H, Ac), 2.02 (s, 3H, Ac). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ 170.8, 170.3 (CO), 138.0 (C_{ipso}), 134.4 (CH=), 128.6, 128.1, 127.9 (Ph), 117.5 (CH_2=), 74.0 (C-2′), 73.4 (CH_2–Ph), 73.2 (C-5′ or C-1′), 67.9 (C-3′), 68.2 (C-4′, C-1′ or C-5′), 61.8 (C-6′), 30.5 (C-3), 20.9 (Me). Anal. Calcd for $C_{22}H_{28}O_8$: C, 62.85; H, 6.71. Found: C, 62.70; H, 6.59.

References

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