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N-*p*-Methoxybenzylidene derivatives of 2-amino-2-deoxy-D-glucose as glycosyl donors: a reinvestigation*

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ABSTRACT

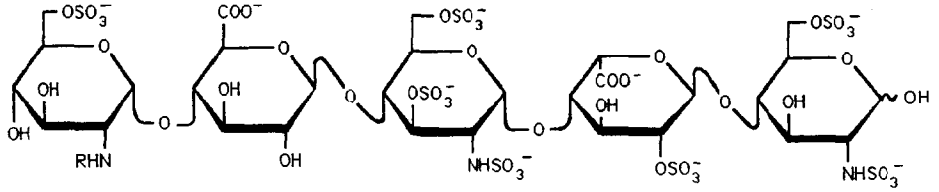
6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*p*-methoxybenzylideneamino-D-glucopyranosyl chloride, 3,4,6-tri-*O*-acetyl-2-deoxy-2-*p*-methoxybenzylideneamino-α-D-glucopyranosyl bromide, 3,4,6-tri-*O*-acetyl-2-deoxy-2-*p*-methoxybenzylideneamino-α- and -β-D-glucopyranosyl trichloroacetimidate, and 3,4,6-tri-*O*-acetyl-2-deoxy-2-*p*-nitrobenzylideneamino-α-D-glucopyranosyl bromide have been synthesised, and their behaviour as glycosylation agents with various soluble promoters has been investigated. The results obtained question the accepted non-participating character of the *N*-*p*-methoxybenzylideneamino group.

INTRODUCTION

The pentasaccharide sequence **1** (R = Ac or SO_3^-) in heparin is required for binding to the plasma protein Antithrombin III[1,2].

We have synthesised[3] **1** (R = SO_3^-), using 6-*O*-acetyl-2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl bromide[4] as a block for the D unit. In order to obtain **1** with R = Ac, it was necessary to use another glycosyl donor for the D unit and the sequence **2** →**3**→**4** was investigated.

α-Glycosylation (**2**→**3**) was expected to occur since *p*-methoxybenzylideneamino is considered to be a non-participating group in glycosylation reactions[5–8]. The results obtained indicate that this view should be questioned.



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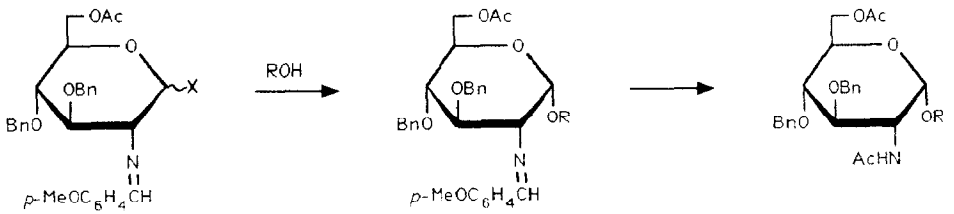


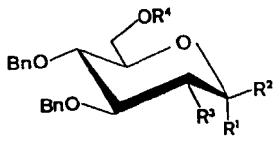
2 3 4

RESULTS AND DISCUSSION

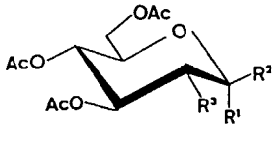
6-*O*-Acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*p*-methoxybenzylideneamino-*α*,*β*-D-glucopyranosyl chloride (**9**) was prepared from benzyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-*β*-D-glucopyranoside[9] (**5**) by acetolysis (→**6**), followed by acid hydrolysis[10] (→**7**). Treatment of **7** with *p*-anisaldehyde in the presence of aqueous sodium hydroxide gave the Schiff base **8**, which was converted (HCl–acetyl chloride) into **9** that was used immediately for glycosylation reactions, without further purification.

Condensation of **9** with methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranoside[11] (**19**) in dichloromethane at −30°, in the presence of silver triflate and 2,4,6-trimethylpyridine, gave, surprisingly, 68% of the amorphous *β*-disaccharide derivative **24**. The $J_{1',2'}$ value of 8.0 Hz indicated H-1′ to be axial. Furthermore, the chemical shift of the resonance of C-1′ was in the range (101–106 p.p.m.) for similar *β*-glucosides [see Experimental: **13** and **25**–**27**; *cf.* 97–98 p.p.m. for the *α* derivatives (see **29**)]. The *α* isomer of **24** was not detected. Likewise, when **9** was condensed with methyl 2,3,6-tri-*O*-benzyl-*α*-D-glucopyranoside[12] (**20**) in dichloromethane at room temperature in the presence of silver triflate and 2,4,6-trimethylpyridine, the crystalline *β*-disaccharide derivative **32** (18%) was the only product isolated and 76% of **20** was recovered. The *β* configuration of the new glycosidic linkage in **32** was indicated by the $J_{1',2'}$ value of 7.8 Hz. These results are in sharp contrast with those of Umezawa's group[6,7], who reported high yields of *α*-D-glucosides by using 3,4,6-tri-*O*-acetyl-2-deoxy-2-*p*-methoxybenzylideneamino-*α*-D-glucopyranosyl bromide[13] (**10**) as glycosyl donor and mercury(II) cyanide as promoter. These results were ascribed to the presence of the non-participating *p*-methoxybenzylideneamino group. However, on reinvestigation, condensation of **10** with the primary alcohol **19** in dichloromethane at −30° in the presence of silver triflate and 2,4,6-trimethylpyridine gave 71% of the crystalline *β*-disaccharide derivative **25** and ~8% of the *α* isomer **28**. Condensation of **10** with the secondary alcohol **20** at room temperature gave 23% of the *β*-disaccharide derivative **33** and 24% of the *α* isomer **34**, and 36% of **20** was recovered.

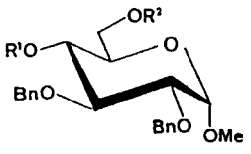
When mercury(II) cyanide was used as a promoter, condensation of **10** with methanol (8 equiv.) in dichloromethane at room temperature gave 74% of methyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-*p*-methoxybenzylideneamino-*β*-D-glucopyranoside[13] (**11**) together with ~7% of the cyano derivative **12**, the *α* configuration of which was



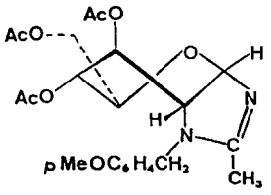
5 R^1 = H, R^2 = OBn, R^3 = NHAc, R^4 = Bn
6 R^1 = H, R^2 = OBn, R^3 = NHAc, R^4 = Ac
7 R^1 = OH, R^2 = R^4 = H, R^3 = $NH_3{}^+Cl^-$
8 R^1 = R^4 = H, R^2 = OH, R^3 = pMeOC$_6$H$_4$CH=N
9 R^1, R^2 = H, Cl, R^3 = pMeOC$_6$H$_4$CH=N, R^4 = Ac



10 R^1 = Br, R^2 = H, R^3 = pMeOC$_6$H$_4$CH=N
11 R^1 = H, R^2 = OMe, R^3 = pMeOC$_6$H$_4$CH=N
12 R^1 = OMe, R^2 = H, R^3 = pMeOC$_6$H$_4$CH(CN)NH
13 R^1 = H, R^2 = OMe, R^3 = pMeOC$_6$H$_4$CH(CN)NH
14 R^1, R^2 = H, OH, R^3 = pMeOC$_6$H$_4$CH=N
15 R^1 = OCNHCCl$_3$, R^2 = H, R^3 = pMeOC$_6$H$_4$CH=N
16 R^1 = H, R^2 = OCNHCCl$_3$, R^3 = pMeOC$_6$H$_4$CH=N
17 R^1 = H, R^2 = OAc, R^3 = pNO$_2$C$_6$H$_4$CH=N
18 R^1 = Br, R^2 = H, R^3 = pNO$_2$C$_6$H$_4$CH=N



19 R^1 = Bn, R^2 = H
20 R^1 = H, R^2 = Bn
21 R^1 = Bn, R^2 = pMeOC$_6$H$_4$CH(CN)



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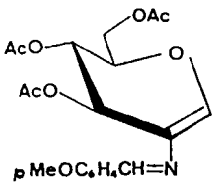
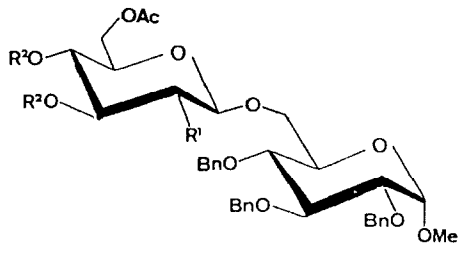
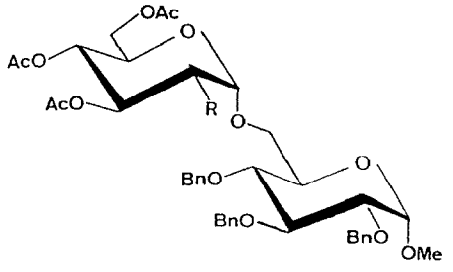


23

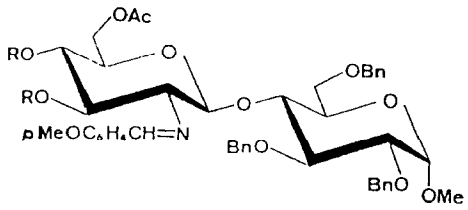
indicated by the $J_{1,2}$ value of 3.5 Hz; no β isomer was detected. Condensation of **10** (1.2 equiv.) with **19** under similar conditions gave 11% of the β-linked disaccharide derivative **25** and 40% of the cyano derivative **29** as a mixture of two diastereomers, which was resolved to give the pure components that were analysed by ^{1}H- and ^{13}C-n.m.r. spectroscopy (see Experimental). The minor product **21** (4%) was isolated also as a ~6:4 mixture of diastereomers. When the condensation reaction was performed in tetrahydrofuran, hardly any disaccharide was obtained, but 14% of the *p*-anisaldehyde acetal **35** was isolated. Thus, in glycosylations catalysed by mercury(II) cyanide, hydrocyanation of the aldimine accompanies α-glycosylation but β-glycosides are not hydrocyanated.

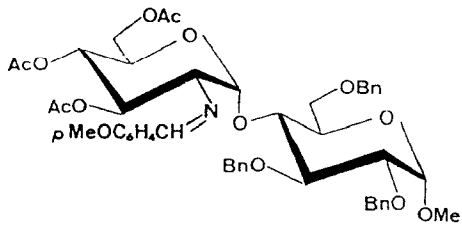




24 R^1 = *p*MeOC$_6$H$_4$CH=N, R^2 = Bn
25 R^1 = *p*MeOC$_6$H$_4$CH=N, R^2 = Ac
26 R^1 = *p*MeOC$_6$H$_4$CH(CN)NH, R^2 = Ac
27 R^1 = *p*NO$_2$C$_6$H$_4$CH=N, R^2 = Ac

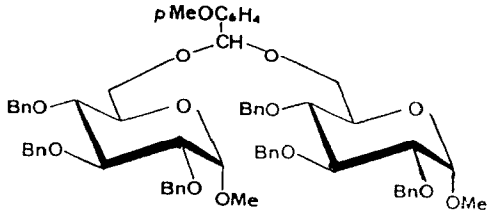
28 R = *p*MeOC$_6$H$_4$CH=N
29 R = *p*MeOC$_6$H$_4$CH(CN)NH
30 R = AcNH
31 R = *p*NO$_2$C$_6$H$_4$CH=N





32 R = Bn
33 R = Ac

34



35

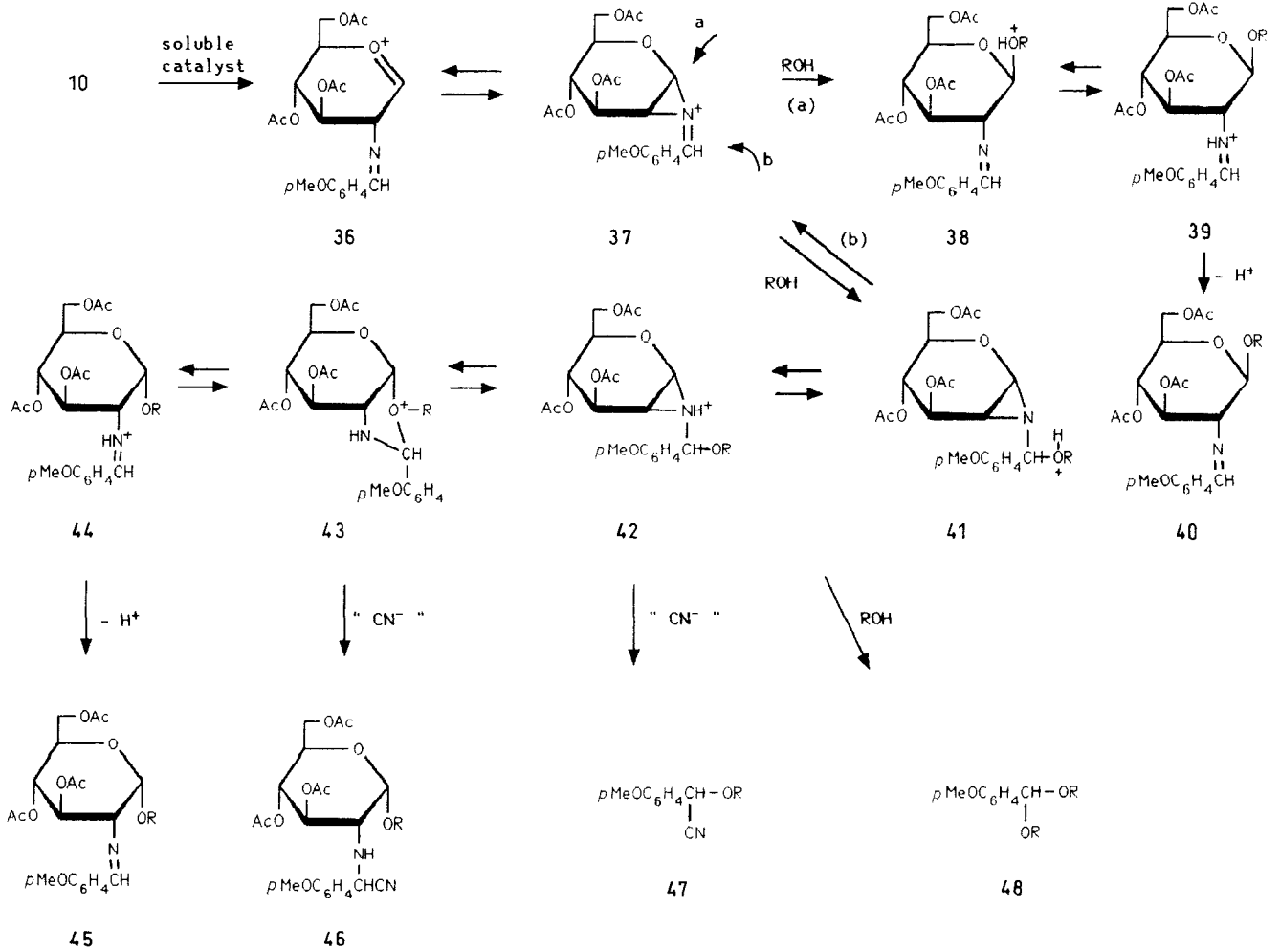
Umezawa *et al.*[6] reported that condensation of **10** with the secondary hydroxyl group of a derivative of streptamine, using mercury(II) cyanide as a promoter in dry benzene–1,4-dioxane at room temperature, gave 85% of an α-disaccharide derivative. We observed no reaction on using this solvent system. In subsequent[7,14] investigations using benzene as the solvent, the *N*-*p*-methoxybenzylidene group of the crude condensation product was converted into the *N*-acetyl group by acid hydrolysis (acetic acid in methanol) followed by *N*-acetylation. When this treatment was applied to the disaccharide derivative **29**, 60% of the crystalline acetamido derivative **30** was indeed obtained. In investigating further this selective hydrocyanation reaction, it was shown that addition of cyanhydric acid (generated *in situ* from potassium cyanide and acetic acid) to an ethanolic solution of **11**, **25**, and **28** occurred to give, respectively, **13**, **26**, and **29**, as mixtures of diastereomers. Compounds **26** and **29** were stable under basic conditions (aqueous saturated sodium hydrogencarbonate at room temperature, triethylamine in toluene at 80°, 1,8-diazabicyclo[5.4.0]undec-7-ene in dichloromethane at room temperature) or in methanol containing (±)-10-camphorsulphonic acid (room temperature, 4 h). Thus, the cyano α-glycosides are formed by a mechanism which is not possible for the β-glycosides.

The formation of 1,2-aziridine-type intermediates from 2-amino-2-deoxy-D-pyranoses has been suggested[15–19], and it is now proposed that a *p*-methoxybenzylideneamino substituent might be capable of neighbouring group participation. The initial formation of the oxycarbenium **36** from **10** is triggered by a soluble catalyst, such as silver triflate or mercury(II) cyanide. Participation of the nitrogen atom of the *p*-methoxybenzylideneamino group then gives **37**. Type (a) attack on **37** by an alcohol, favoured in the presence of silver triflate, provides a β-D-glycoside (→**38**→**39**→**40**). Type (b) attack yields **41** then **42** by rapid intramolecular proton transfer. Rearrangement of the kinetic species **42** to the more stable species **43** would explain the formation of α-D-glucopyranoside (**43**→**44**→**45**). Explanation of the formation of the by-products **47** (*e.g.*, **21**) and **48** (*e.g.*, **35**) from **42** is straightforward.

It is postulated that cyanation of the intermediate **43** occurs and not that of the species **44** (or **39**), thereby explaining the selectivity.

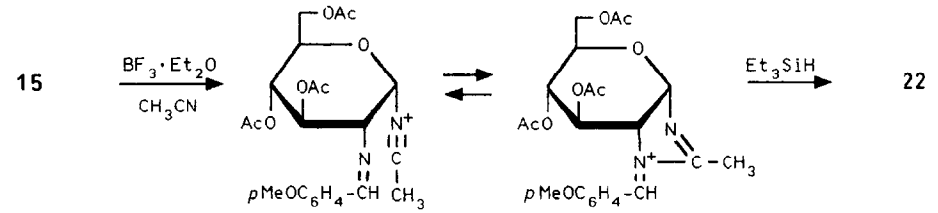
The neighbouring group participation of a benzylideneamino group should be enhanced by the presence of an electron-donating (*e.g.*, *p*-methoxy) substituent, and the presence of an electron-withdrawing (*e.g.*, *p*-nitro) group should decrease the formation of β-glycosides. Indeed, when crystalline 3,4,6-tri-*O*-acetyl-2-deoxy-2-*p*-nitrobenzylideneamino-α-D-glucopyranosyl bromide (**18**), prepared from the known[20] acetate **17**, was condensed with **19** in dichloromethane at −30° in the presence of silver triflate and 2,4,6-trimethylpyridine, 54% of the crystalline β-disaccharide derivative **27** and 12% of the α isomer **31** were obtained.

In order to evaluate the various conditions of glycosylation for preparative purposes, the α- (**15**) and β-trichloroacetimidates (**16**) were prepared. The bromide **10** was transformed into hemiacetal **14**, then into crystalline **15** (42%) and **16** (26%). Glycosylation of the primary alcohol **19** in dichloromethane with **15** or **16** in the


10
soluble catalyst
36
37
38
39
40
41
42
43
44
45
46
47
48
ROH
(a)
(b)
- H+
" CN- "
ROH

presence of trimethylsilyl triflate did not occur and the use of boron trifluoride etherate as promoter gave only traces of disaccharide derivatives.

Attempts were made to trap the postulated intermediate **37** by reduction to give a stable aziridine[21] derivative. When the α-imidate **15** was treated in acetonitrile at −15° with boron trifluoride etherate and triethylsilane, 28% of the imidazoline derivative **22** was isolated as a stable 1:1 complex with boron trifluoride. The probable mechanism is **15**→**49**→**50**→**22**. Several authors[22-27] have proved the existence of anomeric acetonitrilium ions by trapping the kinetic α-nitrilium ion intermediate. The ^{1}H-n.m.r. spectrum (400 MHz, $CDCl_3$) of **22** accorded with the structure, and the *J* values compared well with those obtained by Foces-Foces *et al.*[28] for 3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-D-glucopyrano[2,1-*d*]-2-oxazolines, for which a $^0S_2$ conformation was found. The crystalline glycal derivative **23** was also isolated (26%) and similar results were obtained with the β-imidate **16**.



49 **50**

The preparation of 2-methyl-(1,2-dideoxy-α-D-glucopyrano)[2,1-*d*]-1-imidazolines by a different route has been reported[29].

The use of dichloromethane instead of acetonitrile as the solvent in the above reduction of **15** led to complex mixtures in which the glycal derivative **23** preponderated (^{1}H-n.m.r. analysis). When the reaction was performed in acetonitrile or dichloromethane in the presence of trimethylsilyl triflate instead of boron trifluoride etherate, similar complex mixtures were obtained.

Thus, the chloride **9** and the bromide **10**, in the presence of silver triflate, are very efficient donors for selective β-glycosylation of primary alcohols, and the trichloroacetimidates **15** and **16** offer an easy approach to imidazoline derivatives.

EXPERIMENTAL

General methods. — Melting points were determined with a Büchi Model 510 capillary apparatus and are uncorrected. Optical rotations were measured at 20 ±2° with a Perkin–Elmer Model 241 polarimeter. Elemental analyses were performed at the University Pierre et Marie Curie (Paris VI). C.i. (ammonia)-mass spectra were obtained with a Nermag R10-10 spectrometer. ^{1}H-N.m.r. spectra were recorded with a Cameca 250 and a Bruker AM-400 spectrometer for solutions in the stated solvent (internal Me_4Si). ^{13}C-N.m.r. spectra (100.57 MHz) were recorded for solutions in $CDCl_3$, adopt-

ing δ 77.0 for the central line of $CDCl_3$. Assignments were aided by the J-MOD technique[30,31]. Reactions were monitored by t.l.c. on Silica Gel 60 F_{254} (Merck) and detection by charring with sulfuric acid. Flash column chromatography[32] was performed on Silica Gel 60 (230–400 mesh, Merck). Mercury(II) cyanide was dried[6] for 2 h at 110°, 10 Pa.

*Benzyl 2-acetamido-6-*O*-acetyl-3,4-di-*O*-benzyl-2-deoxy-β-*D*-glucopyranoside* (**6**). — To a solution of **5**[9] (9.64 g, 16.6 mmol) in acetic anhydride (150 mL) at 0° was added a solution of sulfuric acid (2.1 mL) in acetic acid (65 mL). After 1 h at 0°, the mixture was diluted with dichloromethane (300 mL), washed with cold water and saturated aqueous sodium hydrogencarbonate, dried ($MgSO_4$), and concentrated. The crude product was triturated with ethanol to give **6** as an amorphous solid (4.52 g, 51%), $[\alpha]_D$ −10° (*c* 1, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 7.44–7.28 (m, 15 H, 3 Ph), 5.54 (d, 1 H, $J_{2,NH}$ 8.0 Hz, NH), 4.90 and 4.62 (2 d, 2 H, *J* 10.8 Hz, PhCH_2), 4.88 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1), 4.85 and 4.70 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.84 and 4.58 (2 d, 2 H, *J* 11.8 Hz, PhCH_2), 4.42 (dd, 1 H, $J_{5,6a}$ 2.2, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.29 (dd, 1 H, $J_{5,6b}$ 4.5 Hz, H-6b), 4.10 (dd, 1 H, $J_{3,4}$ 7.8, $J_{4,5}$ 9.6 Hz, H-4), 3.70–3.51 (m, 3 H, H-2,3,5), 2.08 and 1.83 (2 s, 6 H, 2 Ac).

Anal. Calc. for $C_{31}H_{35}NO_7$: C, 69.77; H, 6.61; N, 2.62. Found: C, 69.95; H, 6.63; N, 2.77.

*2-Amino-3,4-di-*O*-benzyl-2-deoxy-α-*D*-glucopyranose hydrochloride* (**7**). — A solution of **6** (4.40 g, 8.2 mmol) in tetrahydrofuran (100 mL) and 3M hydrochloric acid (200 mL) was boiled under reflux for 14 h, then cooled to room temperature, and partially concentrated to give **7** as a white powder (2.48 g, 76%), $[\alpha]_D$ +37° (*c* 1, methanol). ^{1}H-N.m.r. data [250 MHz, $(CD_3)_2SO$ + D_2O]: δ 7.44–7.30 (m, 10 H, 2 Ph), 5.33 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.81 and 4.69 (2 s, 4 H, 2 PhCH_2), 3.91 (dd, 1 H, $J_{2,3}$ 10.5, $J_{3,4}$ 9.5 Hz, H-3), 3.78 (m, 1 H, H-5), 3.69–3.62 (m, 2 H, 2 H-6), 3.59 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 3.17 (dd, 1 H, H-2).

Anal. Calc. for $C_{20}H_{26}ClNO_5$: C, 60.68; H, 6.62; N, 3.54. Found: C, 60.78; H, 6.65; N, 3.51.

*3,4-Di-*O*-benzyl-2-deoxy-2-*p*-methoxybenzylideneamino-β-*D*-glucopyranose* (**8**). — A solution of **7** (2.37 g, 6 mmol) in methanol (20 mL) was treated at room temperature with M sodium hydroxide (6.5 mL) and freshly distilled *p*-anisaldehyde (0.73 mL, 6 mmol). After 2 h, the mixture was neutralized with acetic acid and concentrated to give crude **8**, a solution of which in dichloromethane was washed with water, dried ($MgSO_4$), and concentrated. Trituration of the residue with ether gave **8** as a white powder (2.18 g, 76%), $[\alpha]_D$ +162° (*c* 1.2, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 8.29 (s, 1 H, PhC*H*), 7.75–7.70 (m, 2 H, *m*-H of PhOMe), 7.37–7.05 (m, 10 H, 2 Ph), 6.93–6.88 (m, 2 H, *o*-H of PhOMe), 5.13 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.89 and 4.67 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.67 and 4.51 (2 d, 2 H, *J* 10.5 Hz, PhCH_2), 3.95–3.85 (m, 2 H, H-3,4), 3.83 (s, 3 H, MeO), 3.75–3.67 (m, 1 H, H-5), 3.64–3.54 (m, 2 H, 2 H-6), 3.21 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2).

Anal. Calc. for $C_{28}H_{31}NO_6$: C, 70.42; H, 6.54; N, 2.93. Found: C, 70.16; H, 6.62; N, 2.96.

6-O-Acetyl-3,4-di-O-benzyl-2-deoxy-2-p-methoxybenzylideneamino-α,β-D-glucopyranosyl chloride (**9**). — To a solution of **8** (480 mg, 1 mmol) in acetyl chloride (10 mL) at 0° was added ice-cold acetyl chloride (10 mL) saturated with hydrogen chloride. The mixture was kept overnight at room temperature and then concentrated, and toluene was evaporated from the residue, a solution of which in dichloromethane (100 mL) was washed with cold saturated aqueous sodium hydrogencarbonate (20 mL), dried ($MgSO_4$), and concentrated. The resulting crude **9** (510 mg) was used immediately for glycosylation reactions without further purification. ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ, amongst others, 8.34 (s, 0.8 H, PhC*H*α), 8.29 (s, 0.2 H, PhC*H*β), 5.98 (d, 0.8 H, $J_{1,2}$ 3.5 Hz, H-1α), 5.52 (d, 0.2 H, $J_{1,2}$ 8.7 Hz, H-1β), 3.64 (dd, 0.8 H, $J_{2,3}$ 9.5 Hz, H-2α), 3.43 (dd, 0.2 H, $J_{2,3}$ 9.0 Hz, H-2β), 2.06 (s, 0.6 H, Acβ), 2.05 (s, 2.4 H, Acα). Mass spectrum: m/z 538 $(M + 1)^+$.

Methyl 3,4,6-tri-O-acetyl-2-deoxy-2-p-methoxybenzylideneamino-β-D-glucopyranoside (**11**). — A mixture of **10**[13] (146 mg, 0.3 mmol), mercury(II) cyanide (150 mg, 0.6 mmol), activated 4 Å powdered molecular sieve (200 mg), and anhydrous dichloromethane (1 mL) was stirred for 15 min at room temperature. Anhydrous methanol (100 μL, 2.4 mmol) was added and stirring was continued for 3 h at room temperature. The mixture was diluted with dichloromethane, filtered through a bed of Celite, and concentrated. The residue was eluted from a column of silica gel with 3:1 toluene–ethyl acetate (containing 0.3% of triethylamine) to give, first, syrupy methyl 3,4,6-tri-*O*-acetyl-2-(1-cyano-1-*p*-methoxyphenylmethylamino)-2-deoxy-α-D-glucopyranoside (**12**, contaminated by **11**) as a single diastereomer (10 mg, 7%). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 7.44–7.40 (m, 2 H, *m*-H of PhOMe), 7.00–6.96 (m, 2 H, *o*-H of PhOMe), 5.24 (dd, 1 H, $J_{3,4}$ 9.3, $J_{4,5}$ 10.3 Hz, H-4), 5.07 (dd, 1 H, $J_{2,3}$ 10.2 Hz, H-3), 4.93 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.80 (d, 1 H, *J* 8.6 Hz, PhC*H*), 4.33 (dd, 1 H, $J_{5,6a}$ 4.5, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.10 (dd, 1 H, $J_{5,6b}$ 2.3 Hz, H-6b), 3.96 (ddd, 1 H, H-5), 3.86 and 3.44 (2 s, 6 H, 2 MeO), 3.11 (ddd, 1 H, $J_{2,NH}$ 9.6 Hz, H-2), 2.13 (dd, 1 H, NH), 2.13, 2.11, and 2.05 (3 s, 9 H, 3 Ac). Mass spectrum: m/z 465 $(M + 1)^+$.

Eluted second was **11** (97 mg, 74%), m.p. 122–124° (from ethyl acetate–hexane), $[\alpha]_D$ +88° (*c* 1, chloroform); lit.[13] m.p. 126–128°, $[\alpha]_D$ +88.9° (methanol). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 8.20 (s, 1 H, PhC*H*), 7.67–7.63 (m, 2 H, *m*-H of PhOMe), 6.92–6.88 (m, 2 H, *o*-H of PhOMe), 5.40 (dd, 1 H, $J_{2,3}$ 9.7, $J_{3,4}$ 9.6 Hz, H-3), 5.11 (dd, 1 H, $J_{4,5}$ 9.7 Hz, H-4), 4.64 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.35 (dd, 1 H, $J_{5,6a}$ 4.7, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.15 (dd, 1 H, $J_{5,6b}$ 2.2 Hz, H-6b), 3.82 (ddd, 1 H, H-5), 3.81 and 3.48 (2 s, 6 H, 2 MeO), 3.28 (dd, 1 H, H-2), 2.10, 2.03, and 1.86 (3 s, 9 H, 3 Ac).

Methyl 3,4,6-tri-O-acetyl-2-(1-cyano-1-p-methoxyphenylmethylamino)-2-deoxy-β-D-glucopyranoside (**13**). — To a stirred solution of **11** (130 mg, 0.3 mmol) in ethanol (4 mL) at 0° were added potassium cyanide (21 mg, 0.33 mmol) and acetic acid (20 μL, 0.33 mmol). The mixture was allowed to reach room temperature overnight, then concentrated. The residue was eluted from a column of silica gel with 4:1 toluene–ethyl acetate (containing 0.3% of triethylamine) to give, first, **13** (diastereomer *A*), isolated as a syrup (63 mg, 45%), $[\alpha]_D$ +44° (*c* 0.8, chloroform). N.m.r. data: ^{1}H (250 MHz, $CDCl_3$), δ 7.36–7.32 (m, 2 H, *m*-H of PhOMe), 6.91–6.87 (m, 2 H, *o*-H of PhOMe), 5.14 (dd, 1 H,

$J_{3,4}$ 9.2, $J_{4,5}$ 10.0 Hz, H-4), 4.96 (d, 1 H, J 10.5 Hz, PhC*H*), 4.94 (dd, 1 H, $J_{2,3}$ 10.2 Hz, H-3), 4.30 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 4.30 (dd, 1 H, $J_{5,6a}$ 4.3, $J_{6a,6b}$ 12.2 Hz, H-6a), 4.12 (dd, 1 H, $J_{5,6b}$ 2.3 Hz, H-6b), 3.80 (s, 3 H, MeO), 3.63 (ddd, 1 H, H-5), 3.59 (s, 3 H, MeO), 3.05 (ddd, 1 H, $J_{2,NH}$ 2.0 Hz, H-2), 2.15, 2.11, and 2.03 (3 s, 9 H, 3 Ac), 1.94 (dd, 1 H, NH); ^{13}C, δ 172.04, 170.71, and 169.35 (3 C=O), 160.05 (*p*-C of PhCH), 128.32 (*m*-C of PhOMe), 127.08 (*p*-C of PhOMe), 119.79 (CN), 114.32 (*o*-C of PhOMe), 105.71 (C-1), 73.40, 71.58, 68.50, 60.89 (C-2,3,4,5), 61.94 (C-6), 57.36 and 55.33 (2 CH_3O), 53.43 (*C*HCN), 20.88, 20.72, and 20.57 (3 *C*H_3CO). Mass spectrum: m/z 465 $(M + 1)^+$.

Anal. Calc. for $C_{22}H_{28}N_2O_9$: C, 56.89; H, 6.08; N, 6.03. Found: C, 56.78; H, 6.19; N, 5.93.

Eluted second was an ~1:1:1 mixture (60 mg) of diastereomer *A*, **11**, and diastereomer *B*. ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ, amongst others, 7.31–7.27 (m, 2 H, *m*-H of PhOMe), 6.91–6.87 (m, 2 H, *o*-H of PhOMe), 4.87 (d, 1 H, J 8.7 Hz, PhC*H*), 2.87 (m, 1 H, H-2).

3,4,6-Tri-O-*acetyl-2-deoxy-2*-p-*methoxybenzylideneamino*-D-*glucopyranose* (**14**). — A mixture of **10**[13] (980 mg, 2 mmol), silver carbonate (550 mg, 2 mmol), and 20:1 acetone–water (10 mL) was stirred for 15 min at room temperature, then eluted from a column of silica gel with 1:1 ethyl acetate–hexane (contaning 0.3% of triethylamine) to give **14** (790 mg, 92%) as an ~6:4 α,β-mixture. ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ, amongst others, 8.27 (s, 0.4 H, PhC*H*α), 8.24 (s, 0.6 H, PhC*H*β), 7.74–7.68 (m, 2 H, *m*-H of PhOMe), 6.99–6.92 (m, 2 H, *o*-H of PhOMe), 5.27 (d, 0.4 H, $J_{1,2}$ 3.5 Hz, H-1α), 5.16 (d, 0.6 H, $J_{1,2}$ 7.8 Hz, H-1β), 3.88 (s, 1.2 H, MeOα), 3.86 (s, 1.8 H, MeOβ), 3.56 (dd, 0.4 H, $J_{2,3}$ 9.8 Hz, H-2α), 3.31 (dd, 0.6 H, $J_{2,3}$ 10.0 Hz, H-2β), 2.13 and 1.89 (2 s, 2.4 H, 2 Acα), 2.12 and 1.88 (2 s, 3.6 H, 2 Acβ), 2.05 (s, 3 H, Ac).

Anal. Calc. for $C_{20}H_{25}NO_9$: C, 56.73; H, 5.95; N, 3.31. Found: C, 56.87; H, 5.95; N, 3.28.

3,4,6-Tri-O-*acetyl-2-deoxy-2*-p-*methoxybenzylideneamino-α*-(**15**) *and -β*-D-*glucopyranosyl trichloroacetimidate* (**16**). — To a stirred solution of **14** (254 mg, 0.6 mmol) in anhydrous dichloromethane (2 mL) at 0° were added trichloroacetonitrile (600 μL, 6 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (180 μL, 1.2 mmol). The mixture was stirred for 2 h at 0°, then eluted from a column of silica gel with 3:2 hexane–ethyl acetate (containing 0.3% of triethylamine) to give, first, **15** (140 mg, 42%), m.p. 122–124° (from ethyl acetate–hexane), $[\alpha]_D$ +94° (*c* 1.1, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 8.65 (s, 1 H, NH), 8.31 (s, 1 H, PhC*H*), 7.71–7.67 (m, 2 H, *m*-H of PhOMe), 6.97–6.93 (m, 2 H, *o*-H of PhOMe), 6.45 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.75 (dd, 1 H, $J_{2,3}$ 10.2, $J_{3,4}$ 9.6 Hz, H-3), 5.27 (dd, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 4.42–4.34 (m, 2 H, H-5,6a), 4.24–4.16 (m, 1 H, H-6b), 3.86 (s, 3 H, MeO), 3.84 (dd, 1 H, H-2), 2.12, 2.08, and 1.91 (3 s, 9 H, 3 Ac).

Anal. Calc. for $C_{22}H_{25}Cl_3N_2O_9$: C, 46.54; H, 4.44; N, 4.93. Found: C, 46.88; H, 4.51; N, 4.94.

Eluted second was **16** (88 mg, 26%), m.p. 156–157° (from ethyl acetate–hexane), $[\alpha]_D$ +59° (*c* 1, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 8.68 (s, 1 H, NH), 8.28 (s, 1 H, PhC*H*), 7.70–7.66 (m, 2 H, *m*-H of PhOMe), 6.96–6.92 (m, 2 H, *o*-H of PhOMe),

6.08 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 5.58 (dd, 1 H, $J_{2,3}$ 9.6 $J_{3,4}$ 9.4 Hz, H-3), 5.26 (dd, 1 H, $J_{4,5}$ 10.2 Hz, H-4), 4.44 (dd, 1 H, $J_{5,6a}$ 4.3, $J_{6a,6b}$ 12.5 Hz, H-6a), 4.22 (dd, 1 H, $J_{5,6b}$ 2.3 Hz, H-6b), 4.05 (ddd, 1 H, H-5), 3.86 (s, 3 H, MeO), 3.66 (dd, 1 H, H-2), 2.12, 2.06, and 1.93 (3 s, 9 H, 3 Ac).

Anal. Found: C, 46.76; H, 4.42; N, 4.87.

*3,4,6-Tri-*O*-acetyl-2-deoxy-2-*p*-nitrobenzylideneamino-α-*D*-glucopyranosyl bromide* (**18**). — To a stirred solution of **17**[20] (960 mg, 2 mmol) in anhydrous dichloromethane (10 mL) and ethyl acetate (1 mL) at 0° was added titanium tetrabromide (3.7 g, 10 mmol). The mixture was allowed to reach room temperature in the dark. After 3 days, the solution was diluted with anhydrous dichloromethane (15 mL), toluene (15 mL), and acetonitrile (3 mL), stirred with anhydrous sodium acetate (10 g) for 2 h, filtered through a bed of Celite, and concentrated. The residue was eluted from a short column (3 × 10 cm) of silica gel with 30:1 dichloromethane–acetone to give **18** (310 mg, 31%), m.p. 125–127° (from ethyl acetate–hexane), $[\alpha]_D$ +188° (*c* 1, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 8.47 (s, 1 H, PhC*H*), 8.37–8.33 (m, 2 H, *o*-H of $PhNO_2$), 8.03–7.99 (m, 2 H, *m*-H of $PhNO_2$), 6.38 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 5.78 (dd, 1 H, $J_{2,3}$ 10.2, $J_{3,4}$ 9.2 Hz, H-3), 5.27 (dd, 1 H, $J_{4,5}$ 10.6 Hz, H-4), 4.53 (ddd, 1 H, $J_{5,6a}$ 4.2, $J_{5,6b}$ 2.0 Hz, H-5), 4.45 (dd, 1 H, $J_{6a,6b}$ 12.6 Hz, H-6a), 4.21 (dd, 1 H, H-6b), 3.72 (dd, 1 H, H-2), 2.14, 2.10, and 1.91 (3 s, 9 H, 3 Ac).

Anal. Calc. for $C_{19}H_{21}BrN_2O_9$: C, 45.52; H, 4.22; N, 5.59. Found: C, 45.81; H, 4.14; N, 5.52.

*2-Methyl-3-*p*-methoxyphenylmethyl-(3,4,6-tri-*O*-acetyl-1,2-dideoxy-α-*D*-gluco-pyrano)[2,1-*d*]-1-imidazoline, boron trifluoride complex* (**22**). — To a stirred solution of **15** (284 mg, 0.5 mmol) in anhydrous acetonitrile (3 mL) at −15° was added triethylsilane (480 μL, 3 mmol) and then boron trifluoride ethyl etherate (380 μL, 3 mmol). The mixture was stirred for an additional 30 min at −15°, then triethylamine (~0.5 mL) was added. The solution was concentrated, and eluted from a column of silica gel with hexane–ethyl acetate (2:1 then 1:2, containing 0.3% of triethylamine) to give, first, 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-2-*p*-methoxybenzylideneamino-*D*-*arabino*-hex-1-enitol (**23**; 52 mg, 26%), m.p. 132–133° (from ethyl acetate–hexane), $[\alpha]_D$ −164° (*c* 1.1, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 7.98 (s, 1 H, PhC*H*), 7.71–7.65 (m, 2 H, *m*-H of PhOMe), 7.07 (s, 1 H, H-1), 6.95–6.89 (m, 2 H, *o*-H of PhOMe), 5.88 (dd, 1 H, $J_{3,4}$ 3.4, $J_{3,5}$ ~0.7 Hz, H-3), 5.24 (m, 1 H, H-4), 4.53–4.43 (m, 2 H, H-5,6a), 4.28–4.19 (m, 1 H, H-6b), 3.85 (s, 3 H, MeO), 2.11, 2.10, and 2.07 (3 s, 9 H, 3 Ac).

Anal. Calc. for $C_{20}H_{23}NO_8$: C, 59.25; H, 5.72; N, 3.45. Found: C, 59.11; H, 5.67; N, 3.42.

Eluted second was **22** (72 mg, 28%), $[\alpha]_D$ −92° (*c* 1.4, chloroform). ^{1}H-N.m.r. data [400 MHz, $CDCl_3$; 32k data points were acquired, using a 1501-Hz spectral width giving 0.1-Hz digital resolution. The experimental and calculated (PANIC program) spectra from the best resulting values matched satisfactorily. The positive sign of $^4J_{2,4}$ was determined using COSY45[33] and spin-decoupling[34] experiments.]: δ 7.17–7.14 (m, 2 H, *m*-H of PhOMe), 6.95–6.92 (m, 2 H, *o*-H of PhOMe), 5.91 (ddd, 1 H, $J_{1,2}$ 9.3, $J_{1,3}$ 0.3, $J_{1,5}$ 0.7 Hz, H-1), 5.28 (ddd, 1 H, $J_{2,3}$ 2.7, $J_{3,4}$ 1.8 Hz, H-3), 4.96 (ddd, 1 H, $J_{4,5}$ 8.5, $J_{2,4}$ 1.4 Hz,

H-4), 4.72 and 4.37 (2 d, 2 H, *J* 16.0 Hz, PhCH_2), 4.27 (dd, 1 H, $J_{5,6a}$ 2.8, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.17 (dd, 1 H, $J_{5,6b}$ 6.6 Hz, H-6b), 3.85 (ddd, 1 H, H-2), 3.81 (s, 3 H, MeO), 3.59 (dddd, 1 H, H-5), 2.53 (s, 3 H, Me), 2.12, 2.10, and 2.05 (3 s, 9 H, 3 Ac). Mass spectrum: *m/z* 534 $(M + 18)^+$, 497 $(M - F)^+$, 449 $(M + 1 - BF_3)^+$.

Anal. Calc. for $C_{22}H_{28}N_2O_8 \cdot BF_3$: C, 51.18; H, 5.47; N, 5.43. Found: C, 51.20; H, 5.54; N, 5.42.

When the reaction was performed with the imidate **16**, similar results were obtained.

*Methyl 6-O-(6-O-acetyl-3,4-di-O-benzyl-2-deoxy-2-*p*-methoxybenzylideneamino-β-*D*-glucopyranosyl)-2,3,4-tri-O-benzyl-α-*D*-glucopyranoside* (**24**). — A mixture of **19**[11] (93 mg, 0.2 mmol), freshly prepared **9** (160 mg, 0.3 mmol), 2,4,6-trimethylpyridine (40 μL, 0.3 mmol), activated 4 Å powdered molecular sieve (200 mg), and anhydrous dichloromethane (1 mL) was stirred for 30 min at room temperature then cooled to −30°. Silver triflate (154 mg, 0.6 mmol) was added and stirring was continued for 3 h at −30° in the dark. The mixture was diluted with dichloromethane, filtered through a bed of Celite, and concentrated. The residue was eluted from a column of silica gel with 5:2 toluene–ether (containing 0.3% of triethylamine) to give **24** (131 mg, 68%), $[\alpha]_D$ +89° (*c* 0.8, chloroform). N.m.r. data: ^{1}H (400 MHz, C_6D_6), δ 8.27 (s, 1 H, PhC*H*), 7.67–7.64 (m, 2 H, *m*-H of PhOMe), 7.36–7.00 (m, 25 H, 5 Ph), 6.70–6.66 (m, 2 H, *o*-H of PhOMe), 4.94 and 4.75 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.90 and 4.57 (2 d, 2 H, *J* 11.3 Hz, PhCH_2), 4.88 and 4.80 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.82 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.75 and 4.71 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.59 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.52 (dd, 1 H, $J_{5',6'a}$ 1.8, $J_{6'a,6'b}$ 12.0 Hz, H-6'a), 4.44 and 4.35 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.42 (dd, 1 H, $J_{5',6'b}$ 4.5 Hz, H-6'b), 4.29 (m, 1 H, H-6a), 4.19 (dd, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 8.7 Hz, H-3), 4.00 (dd, 1 H, $J_{2',3'}$ 9.5, $J_{3',4'}$ 9.0 Hz, H-3'), 3.91–3.84 (m, 2 H, H-5,6b), 3.79 (dd, 1 H, $J_{4,5}$ 10.0 Hz, H-4), 3.75 (dd, 1 H, $J_{4',5'}$ 9.8 Hz, H-4'), 3.62 (dd, 1 H, H-2'), 3.50 (ddd, 1 H, H-5'), 3.44 (dd, 1 H, H-2), 3.20 and 3.08 (2 s, 6 H, 2 MeO), 1.67 (s, 3 H, Ac); ^{13}C, δ 170.81 (C=O), 163.58 (PhC*H*=), 161.73 (*p*-C of PhCH=), 138.82, 138.50, 138.12, 137.76, and 137.74 (quaternary C), 129.98 (*m*-C of PhOMe), 128.78 (*p*-C of PhOMe), 128.46–127.34 (aromatic C), 113.88 (*o*-C of PhOMe), 102.31 (C-1'), 98.07 (C-1), 83.69, 81.96, 79.46, 77.16, 77.10, 76.41, 73.09, and 69.49 (C-2,3,4,5,2',3',4',5'), 75.41, 75.20, 74.89, 74.70, and 73.29 (5 PhCH_2), 67.97 (C-6), 63.22 (C-6'), 55.23 and 55.04 (2 CH_3O), 20.87 (CH_3CO). Mass spectrum: *m/z* 966 $(M + 1)^+$.

Anal. Calc. for $C_{58}H_{63}NO_{12} \cdot 0.5H_2O$: C, 71.44; H, 6.62; N, 1.44. Found: C, 71.38; H, 6.58; N, 1.47.

*Methyl 2,3,4-tri-O-benzyl-6-O-(3,4,6-tri-O-acetyl-2-deoxy-2-*p*-methoxybenzylideneamino-β- and -α-*D*-glucopyranosyl)-α-*D*-glucopyranoside* (**25** *and* **28**). — A mixture of **19**[11] (232 mg, 0.5 mmol), **10**[13] (292 mg, 0.6 mmol), 2,4,6-trimethylpyridine (100 μL, 0.75 mmol), activated 4 Å powdered molecular sieve (500 mg), and anhydrous dichloromethane (3 mL) was stirred for 30 min at room temperature then cooled to −30°. Silver triflate (260 mg, 1 mmol) was added and stirring was continued for 1.5 h at −30° in the dark. The mixture was diluted with dichloromethane, filtered through a bed of Celite, and concentrated. The residue was eluted from a column of silica gel with 2:1 toluene–

ethyl acetate (containing 0.3% of triethylamine) to give, first, **28** (35 mg, 8%) contaminated by **25**. ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ, amongst others, 8.25 (s, 1 H, PhC*H*), 7.83–7.79 (m, 2 H, *m*-H of PhOMe), 7.47–7.12 (m, 15 H, 3 Ph), 6.82–6.78 (m, 2 H, *o*-H of PhOMe), 5.20 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1'), 4.38 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 3.62 and 3.31 (2 s, 6 H, 2 MeO), 2.11, 2.06, and 1.86 (3 s, 9 H, 3 Ac).

Further elution gave **25** (310 mg, 71%), m.p. 138–140° (from ethyl acetate–hexane), $[\alpha]_D$ +48° (*c* 1, chloroform). N.m.r. data: ^{1}H (400 MHz, C_6D_6), δ 8.05 (s, 1 H, PhC*H*), 7.60–7.56 (m, 2 H, *m*-H of PhOMe), 7.28–6.99 (m, 15 H, 3 Ph), 6.59–6.55 (m, 2 H, *o*-H of PhOMe), 5.72 (dd, 1 H, $J_{2',3'}$ 9.6, $J_{3',4'}$ 9.7 Hz, H-3'), 5.43 (dd, 1 H, $J_{4',5'}$ 10.0 Hz, H-4'), 4.93 and 4.73 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.84 and 4.71 (2 d, 2 H, *J* 11.7 Hz, PhCH_2), 4.75 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.62 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.46 and 4.38 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.45 (dd, 1 H, $J_{5',6'a}$ 4.2, $J_{6'a,6'b}$ 12.3 Hz, H-6'a), 4.23 (dd, 1 H, $J_{5,6a}$ 1.5, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.19 (dd, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 9.0 Hz, H-3), 4.10 (dd, 1 H, $J_{5',6'b}$ 1.8 Hz, H-6'b), 3.89 (ddd, 1 H, $J_{4,5}$ 9.8, $J_{5,6b}$ 4.0 Hz, H-5), 3.81 (dd, 1 H, H-6b), 3.72 (dd, 1 H, H-4), 3.54 (dd, 1 H, H-2'), 3.46 (dd, 1 H, H-2), 3.37 (ddd, 1 H, H-5'), 3.16 and 3.10 (2 s, 6 H, 2 MeO), 1.75, 1.74, and 1.55 (3 s, 9 H, 3 Ac); ^{13}C, δ 170.69, 169.77, and 169.70 (3 C=O), 164.00 (PhCH=), 161.97 (*p*-C of PhCH=), 138.78, 138.45, and 138.10 (quaternary C), 130.11 (*m*-C of PhOMe), 128.33 (*p*-C of PhOMe), 128.25–127.37 (aromatic C), 113.88 (*o*-C of PhOMe), 102.27 (C-1'), 98.10 (C-1), 81.92, 79.53, 77.11, 73.81, 73.36, 71.78, 69.51, and 68.59 (C-2,3,4,5,2',3',4',5'), 75.40, 74.87, and 73.30 (3 PhCH_2), 68.21 (C-6), 62.27 (C-6'), 55.23 and 55.09 (2 CH_3O), 20.73, 20.66, and 20.50 (2 CH_3CO).

Anal. Calc. for $C_{48}H_{55}NO_{14}$: C, 66.27; H, 6.37; N, 1.61. Found: C, 66.13; H, 6.35; N, 1.63.

Methyl 2,3,4-tri-O-*benzyl-6*-O-*[3,4,6-tri*-O-*acetyl-2-(1-cyano-1*-p-*methoxyphenylmethylamino)-2-deoxy-β*-D-*glucopyranosyl]-α*-D-*glucopyranoside* (**26**). — To a stirred solution of **25** (174 mg, 0.2 mmol) in ethanol (5 mL) and dichloromethane (1 mL) at 0° were added potassium cyanide (65 mg, 1 mmol) and acetic acid (60 μL, 1 mmol). The mixture was allowed to reach room temperature overnight, then concentrated. The residue was eluted from a column of silica gel with 4:1 ethyl acetate–hexane (containing 0.3% of triethylamine) to give, first, **26** (diastereomer *A*), isolated as a syrup (102 mg, 57%), $[\alpha]_D$ +41° (*c*, 1.1, chloroform). N.m.r. data: ^{1}H (250 MHz, $CDCl_3$), δ, amongst others, 7.42–7.23 (m, 17 H, 3 Ph, *m*-H of PhOMe), 6.86–6.82 (m, 2 H, *o*-H of PhOMe), 5.10 (d, 1 H, *J* 10.8 Hz, PhC*H*), 4.52 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.26 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 3.75 and 3.30 (2 s, 6 H, 2 MeO); 3.47 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 3.11 (ddd, 1 H, $J_{2',3'}$ 10.2, $J_{2',NH}$ 2.5 Hz, H-2'), 2.16, 2.07, and 2.03 (3 s, 9 H, 3 Ac), 1.91 (dd, 1 H, NH); ^{13}C, δ 172.03, 170.56, and 169.23 (3 C=O), 160.00 (*p*-C of PhCH), 138.62, 138.05, and 137.91 (quaternary C), 128.38–127.55 (aromatic C), 126.97 (*p*-C of PhOMe), 119.72 (CN), 114.32 (*o*-C of PhOMe), 104.87 (C-1'), 97.83 (C-1), 81.73, 79.86, 78.07, 73.53, 71.51, 69.60, 68.45, and 60.70 (C-2,3,4,5,2',3',4',5'), 75.83, 74.65, and 73.22 (3 PhCH_2), 69.30 (C-6), 61.93 (C-6'), 55.23 (2 CH_3O), 53.35 (CHCN), 20.83, 20.60, and 20.50 (3 CH_3CO). Mass spectrum: *m/z* 897 $(M + 1)^+$, 871 $(M + 1 - CN)^+$.

Anal. Calc. for $C_{49}H_{56}N_2O_{14}$: C, 65.61; H, 6.29; N, 3.12. Found: C, 65.49; H, 6.39; N, 3.07.

Eluted second was an ~ 1:1 mixture (n.m.r. analysis) of the diastereomer *B* and **25** (50 mg).

*Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-*p*-nitrobenzylidene-amino-β-and -α-*D*-glucopyranosyl)-α-*D*-glucopyranoside* (**27** and **31**). — A mixture of **19** (ref. 11) (140 mg, 0.3 mmol), **18** (180 mg, 0.36 mmol), 2,4,6-trimethylpyridine (60 μL, 0.45 mmol), activated 4 Å powdered molecular sieve (300 mg), and anhydrous dichloromethane (2 mL) was stirred for 30 min at room temperature, then cooled to −30°. Silver triflate (150 mg, 0.6 mmol) was added and stirring was continued for 1 h at −30° in the dark. The mixture was diluted with dichloromethane, filtered through a bed of Celite, and concentrated. The residue was eluted from a column of silica gel with 30:1 dichloromethane–acetone (containing 0.3% of triethylamine) to give, first, **31** (32 mg, 12%), $[\alpha]_D$ +102° (*c* 1, chloroform). ^{1}H-N.m.r. data (400 MHz, C_6D_6): 7.76–7.73 (m, 2 H, *o*-H of $PhNO_2$), 7.68 (s, 1 H, PhC*H*), 7.51–7.48 and 7.30–7.02 (2 m, 15 H, 3 Ph), 7.48–7.45 (m, 2 H, *m*-H of $PhNO_2$), 6.11 (dd, 1 H, $J_{2',3'}$ 10.3, $J_{3',4'}$ 9.4 Hz, H-3'), 5.47 (dd, 1 H, $J_{4',5'}$ 10.0 Hz, H-4'), 5.22 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1'), 5.19 and 4.99 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.87 and 4.77 (2 d, 2 H, *J* 10.5 Hz, PhCH_2), 4.49–4.44 (m, 2 H, 2 H-6'), 4.47 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 4.29–4.24 (m, 1 H, H-5'), 4.26 and 4.19 (2 d, 2 H, *J* 12.3 Hz, PhCH_2), 4.17 (dd, 1 H, $J_{2,3}$ 9.4, $J_{3,4}$ 9.0 Hz, H-3), 4.09 (dd, 1 H, $J_{4,5}$ 9.8 Hz, H-4), 3.89 (dd, 1 H, $J_{5,6a}$ 3.7, $J_{6a,6b}$ 12.5 Hz, H-6a), 3.84–3.78 (m, 2 H, H-5,6b), 3.42 (dd, 1 H, H-2'), 3.10 (s, 3 H, MeO), 3.08 (dd, 1 H, H-2), 1.80, 1.75, and 1.59 (3 s, 9 H, 3 Ac).

Anal. Calc. for $C_{47}H_{52}N_2O_{15}$: C, 63.79; H, 5.92; N, 3.17. Found: C, 63.69; H, 5.85; N, 3.15.

Eluted second was **27** (143 mg, 54%), m.p. 121–122° (from ethyl acetate–hexane), $[\alpha]_D$ +49° (*c* 1, chloroform), N.m.r. data: ^{1}H (400 MHz, C_6D_6), δ 7.84 (s, 1 H, PhC*H*), 7.69–7.66 (m, 2 H, *o*-H of $PhNO_2$), 7.31–7.28 (m, 2 H, *m*-H of $PhNO_2$), 7.25–7.05 (m, 15 H, 3 Ph), 5.67 (dd, 1 H, $J_{2',3'}$ 9.8, $J_{3',4'}$ 9.5 Hz, H-3'), 5.44 (dd, 1 H, $J_{4',5'}$ 10.0 Hz, H-4'), 4.91 and 4.64 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.72 and 4.51 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.66 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1'), 4.59 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.48 and 4.40 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.44 (dd, 1 H, $J_{5',6'a}$ 4.0, $J_{6'a,6'b}$ 12.5 Hz, H-6'a), 4.17 (dd, 1 H, $J_{5,6a}$ 1.5, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.15 (dd, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 8.8 Hz, H-3), 4.08 (dd, 1 H, $J_{5',6'b}$ 2.0 Hz, H-6'b), 3.84 (ddd, 1 H, $J_{4,5}$ 10.0, $J_{5,6b}$ 4.0 Hz, H-5), 3.75 (dd, 1 H, H-6b), 3.56 (dd, 1 H, H-4), 3.46 (dd, 1 H, H-2'), 3.42 (dd, 1 H, H-2), 3.34 (ddd, 1 H, H-5'), 3.05 (s, 3 H, MeO), 1.76, 1.75, and 1.57 (3 s, 9 H, 3 Ac); ^{13}C, δ 170.55, 169.64, and 169.46 (3 C=O), 162.48 (PhCH=), 149.20 (*p*-C of PhCH=), 140.26 (*p*-C of $PhNO_2$), 138.36, 138.00, and 137.91 (quaternary C), 128.97 (*m*-C of $PhNO_2$), 128.33–127.43 (aromatic C), 123.71 (*o*-C of $PhNO_2$), 101.68 (C-1'), 98.01 (C-1), 81.75, 79.50, 77.18, 73.88, 72.86, 71.87, 69.30, and 68.33 (C-2,3,4,5,2',3',4',5'), 75.62, 74.70, and 73.14 (3 PhCH_2), 68.30 (C-6), 62.08 (C-6'), 55.09 (CH_3O), 20.65, 20.56 and 20.39 (3 CH_3CO).

Anal. Calc. for $C_{47}H_{52}N_2O_{15}$: C, 63.79; H, 5.92; N, 3.17. Found: C, 63.60; H, 6.06; N, 3.15.

*Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[3,4,6-tri-*O*-acetyl-2-(1-cyano-1-*p*-methoxyphenylmethylamino)-2-deoxy-α-*D*-glucopyranosyl]-α-*D*-glucopyranoside* (**29**). — (*a*) A mixture of **19**[11] (325 mg, 0.7 mmol), **10**[13] (490 mg, 1 mmol), activated 4 Å powdered

molecular sieve (500 mg), and anhydrous dichloromethane (3 mL) was stirred for 30 min at room temperature. Mercury(II) cyanide (500 mg, 2 mmol) was added and stirring was continued for 8 h at room temperature. The mixture was diluted with dichloromethane, filtered through a bed of Celite, and concentrated. The residue was eluted from a column of silica gel with toluene–ethyl acetate (from 5:1 to 3:1, containing 0.3% of triethylamine) to give, first, unstable methyl 2,3,4-tri-*O*-benzyl-6-*O*-(1-cyano-1-*p*-methoxyphenylmethyl)-*α*-D-glucopyranoside (**21**; 17 mg, 4%) as an ~6:4 mixture of diastereomers. N.m.r. data:^{1}H (250 MHz, $CDCl_3$), δ 7.36–7.16 (m, 17 H, 3 Ph, *m*-H of PhOMe), 6.89–6.85 (m, 2 H, *o*-H of PhOMe), 5.28 (s, 0.6 H, PhC*H*), 5.18 (s, 0.4 H, PhC*H*), 4.98 and 4.79 (2 d, 0.8 H, *J* 11.0 Hz, PhCH_2), 4.97 and 4.80 (2 d, 1.2 H, *J* 10.8 Hz, PhCH_2), 4.86 and 4.49 (2 d, 1.2 H, *J* 10.7 Hz, PhCH_2), 4.82 and 4.52 (2 d, 0.8 H, *J* 11.0 Hz, PhCH_2), 4.78 and 4.64 (2 d, 2 H, *J* 12.2 Hz, PhCH_2), 4.02–3.70 (m, 4 H), 3.80 (s, 1.2 H, PhO*Me*), 3.79 (s, 1.8 H, PhO*Me*), 3.58–3.47 (m, 2 H), 3.37 (s, 1.8 H, MeO), 3.35 (s, 1.2 H, MeO); ^{13}C, δ (amongst others) 125.40 and 125.36 (*p*-C of PhOMe), 117.33 and 117.28 (CN), 98.15 and 98.12 (C-1), 68.15 and 67.47 (PhCHCN). Mass spectrum: *m*/*z* 627 $(M + 18)^+$.

Eluted second was **29** (diastereomer *A*), isolated as a syrup (145 mg, 23%), $[\alpha]_D$ +95° (*c* 0.6, chloroform). N.m.r. data: ^{1}H (400 MHz, $CDCl_3$), δ 7.36–7.26 (m, 17 H, 3 Ph, *m*-H of PhOMe), 6.87–6.84 (m, 2 H, *o*-H of PhOMe), 5.14 (dd, 1 H, $J_{2',3'}$ 10.2, $J_{3',4'}$ 9.7 Hz, H-3′), 5.03 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-1′), 4.97 (dd, 1 H, $J_{4',5'}$ 10.3 Hz, H-4′), 4.96 and 4.77 (2 d, 2 H, *J* 10.8 Hz, PhCH_2), 4.91 and 4.61 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.73 (d, 1 H, *J* 8.5 Hz, PhC*H*), 4.61 and 4.53 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 4.54 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.19 (dd, 1 H, $J_{5',6'a}$ 4.3, $J_{6'a,6'b}$ 12.5 Hz, H-6′a), 3.98 (dd, 1 H, $J_{5',6'b}$ 2.0 Hz, H-6′b), 3.95 (dd, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 9.0 Hz, H-3), 3.86 (dd, 1 H, $J_{5,6a}$ 3.8, $J_{6a,6b}$ 11.3 Hz, H-6a), 3.86 (ddd, 1 H, H-5′), 3.73 (ddd, 1 H, $J_{4,5}$ 10.2, $J_{5,6b}$ 2.0 Hz, H-5), 3.72 (s, 3 H, MeO), 3.65 (dd, 1 H, H-6b), 3.47 (dd, 1 H, H-4), 3.39 (dd, 1 H, H-2), 3.36 (s, 3 H, MeO), 3.00 (ddd, 1 H, $J_{2',NH}$ 8.5 Hz, H-2′), 2.22 (dd, 1 H, NH), 2.07. 2.04, and 2.03 (3 s, 9 H, 3 Ac); ^{13}C, δ 170.50, 170.36, and 169.56 (3 C=O), 160.10 (*p*-C of PhCH), 138.49, 137.92, and 137.72 (quaternary C), 128.91–127.51 (aromatic C), 126.55 (*p*-C of PhOMe), 119.80 (CN), 114.27 (*o*-C of PhOMe), 98.10 (C-1), 97.84 (C-1′), 81.87, 80.36, 77.00, 72.48, 69.76, 68.45, 67.43, and 58.94 (C-2,3,4,5,2′,3′,4′,5′), 75.61, 74.79, and 73.22 (3 PhCH_2), 66.99 (C-6), 61.72 (C-6′), 55.44 (*C*HCN), 55.15 (2 CH_3O), 20.81, 20.59, and 20.56 (3 CH_3CO). Mass spectrum: *m*/*z* 871 $(M + 1 - CN)^+$.

Anal. Calc. for $C_{49}H_{56}N_2O_{14}$: C, 65.61; H, 6.29; N, 3.12. Found: C, 65.36; H, 6.28; N, 3.08.

Eluted third was **29** (diastereomer *B*), isolated as a syrup (106 mg, 17%), $[\alpha]_D$ +91° (*c* 1, chloroform). N.m.r. data: ^{1}H (400 MHz, $CDCl_3$), δ 7.36–7.26 (m, 17 H, 3 Ph, *m*-H of PhOMe), 6.89–6.86 (m, 2 H, *o*-H of PhOMe), 5.14 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-1′), 5.05 (dd, 1 H, $J_{2',3'}$ 10.3, $J_{3',4'}$ 9.7 Hz, H-3′), 4.99 and 4.81 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.94 and 4.61 (2 d, 2 H, *J* 11.3 Hz, PhCH_2), 4.89 (dd, 1 H, $J_{4',5'}$ 10.1 Hz, H-4′), 4.72 and 4.62 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.69 (d, 1 H, *J* 4.8 Hz, PhC*H*), 4.56 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.13 (dd, 1 H, $J_{5',6'}$ 4.3, $J_{6'a,6'b}$ 12.5 Hz, H-6′a), 3.99 (dd, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 9.0 Hz, H-3), 3.94 (dd, 1 H, $J_{5,6'b}$ 2.2 Hz, H-6′b), 3.83 (ddd, 1 H, H-5′), 3.83 (dd, 1 H, $J_{5,6a}$ 3.5, $J_{6a,6b}$ 11.3 Hz, H-6a),

3.78 (s, 3 H, MeO), 3.76 (ddd, 1 H, $J_{4,5}$ 10.6, $J_{5,6b}$ 1.8 Hz, H-5), 3.68 (dd, 1 H, H-6b), 3.47 (dd, 1 H, H-4), 3.41 (dd, 1 H, H-2), 3.38 (s, 3 H, MeO), 2.93 (ddd, 1 H, $J_{2',NH}$ 9.3 Hz, H-2'), 2.20 (dd, 1 H, NH), 2.02, 1.99, and 1.98 (3 s, 9 H, 3 Ac); ^{13}C, δ 170.60, 170.52, and 169.49 (3 C=O), 160.13 (*p*-C of PhCH), 138.46, 137.94, and 137.87 (quaternary C), 128.95–127.54 (aromatic C), 126.41 (*p*-C of PhOMe), 119.38 (CN), 114.29 (*o*-C of PhOMe), 97.76 and 97.23 (C-1,1'), 81.95, 79.97, 77.25, 71.64, 69.72, 68.44, 67.32, and 57.40 (C-2,3,4,5,2',3',4',5'), 75.71, 74.82, and 73.23 (3 PhCH_2), 66.59 (C-6), 61.70 (C-6'), 55.48 and 55.23 (2 CH_3O), 51.27 (*C*HCN), 20.90, 20.61, and 20.54 (3 CH_3CO). Mass spectrum: *m/z* 897 $(M + 1)^+$, 871 $(M + 1 - CN)^+$.

Anal. Calc. for $C_{49}H_{56}N_2O_{14}$: C, 65.61; H, 6.29; N, 3.12. Found: C, 65.59; H, 6.14; N, 3.07.

Further elution gave **25** (67 mg, 11%) identical with the compound obtained by use of silver triflate as promoter.

When the glycosylation was performed in 2:1 benzene-1,4-dioxane[6] instead of dichloromethane, compounds **10**[13] and **19**[11] were unchanged (t.l.c.) after 24 h at room temperature.

When the glycosylation was performed in tetrahydrofuran, **10**[13] disappeared but only traces of disaccharide derivatives were isolated. Also isolated was unstable, syrupy *p*-methoxybenzaldehyde bis(methyl 2,3,4-tri-*O*-benzyl-*α*-D-glucopyranosid-6-yl) acetal (**35**, 14%). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 7.36–7.10 (m, 32 H, 6 Ph, *m*-H of PhOMe), 6.84–6.80 (m, 2 H, *o*-H of PhOMe), 5,58 (s, 1 H, PhC*H*), 4.97 and 4.44 (2 d, 2 H, *J* 10.8 Hz, PhCH_2), 4.96 and 4.48 (2 d, 2 H, *J* 10.8 Hz, PhCH_2), 4.81 (s, 2 H, PhCH_2), 4.77 and 4.64 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.76 and 4.64 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.76 (s, 2 H, PhCH_2), 4.60 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.58 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1'), 4.01–3.36 (m, 12 H), 3.75 (s, 3 H, PhO*Me*), 3.34 (s, 6 H, 2 MeO). Mass spectrum: *m/z* 1064 $(M + 18)^+$.

(*b*) Treatment of **28** with potassium cyanide and acetic acid, as described for the preparation of **26**, gave, after similar work-up and purification, **29** (82%) as an ~3:2 mixture of diastereomers.

Methyl 6-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-glucopyranosyl)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**30**). — A solution of **29** (~1:1 mixture of the two diastereomers; 90 mg, 0.1 mmol) in methanol (5 mL) was treated overnight at room temperature with 50% aqueous acetic acid (3 mL). The solution was concentrated, toluene was evaporated from the residue, a solution of which in pyridine (2 mL) was then treated at room temperature with acetic anhydride (2 mL). After 3 h, the solution was concentrated, and toluene was evaporated from the residue which was eluted from a column of silica gel with 3:1 ethyl acetate–hexane to give **30** (48 mg, 60%), m.p. 141–143° (from ethyl acetate–hexane), $[\alpha]_D$ +83° (*c* 0.9, chloroform). ^{1}H-N.m.r. data (400 MHz, $CDCl_3$): δ 7.43–7.30 (m, 15 H, 3 Ph), 5.69 (d, 1 H, $J_{2',NH}$ 9.5 Hz, NH), 5.18 (dd, 1 H, $J_{2',3'}$ 10.2, $J_{3',4'}$ 9.5 Hz, H-3'), 5.12 (dd, 1 H, $J_{4',5'}$ 9.7 Hz, H-4'), 5.06 and 4.86 (2 d, 2 H, *J* 11.0 Hz, PhCH_2), 4.98 and 4.72 (2 d, 2 H, *J* 11.3 Hz, PhCH_2), 4.89 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1'), 4.84 and 4.72 (2 d, 2 H, *J* 12.2 Hz, PhCH_2), 4.60 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.33 (ddd, 1 H, H-2'), 4.15 (dd, 1 H, $J_{5',6'a}$ 4.4, $J_{6'a,6'b}$ 12.5 Hz, H-6'a), 4.06 (dd, 1 H, $J_{5',6'b}$ 2.2 Hz,

H-6'b), 4.05 (dd, 1 H, $J_{2,3}$ 9.6, $J_{3,4}$ 9.0 Hz, H-3), 3.95 (ddd, 1 H, H-5'), 3.87–3.79 (m, 2 H, H-5,6a), 3.69–3.65 (m, 1 H, H-6b), 3.53 (dd, 1 H, H-2), 3.44 (dd, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 3.43 (s, 3 H, MeO), 2.06, 2.05, 2.04, and 1.87 (4 s, 12 H, 4 Ac).

Anal. Calc. for $C_{42}H_{51}NO_{14}$: C, 63.54; H, 6.48; N, 1.76. Found: C, 63.63; H, 6.55; N, 1.91.

*Methyl 4-*O*-(6-*O*-acetyl-3,4-di-*O*-benzyl-2-deoxy-2-*p*-methoxybenzylideneamino-β-*D*-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-*D*-glucopyranoside* (**32**). — A mixture of **20**[12] (93 mg, 0.2 mmol), freshly prepared **9** (160 mg, 0.3 mmol), 2,4,6-trimethylpyridine (40 μL, 0.3 mmol), activated 4Å powdered molecular sieve (200 mg), and anhydrous dichloromethane (1 mL) was stirred for 30 min at room temperature. Silver triflate (154 mg, 0.6 mmol) was added and stirring was continued for 6 h at room temperature in the dark. The mixture was diluted with dichloromethane, filtered through a bed of Celite, and concentrated. The residue was eluted from a column of silica gel with 3:1 hexane–ethyl acetate (containing 0.3% of triethylamine) to give, first, **20** (70 mg, 76%) and then **32** (35 mg, 18%), m.p. 135–137° (from ethyl acetate–hexane), $[\alpha]_D$ +49° (*c* 0.5, chloroform). ^{1}H-N.m.r. data (400 MHz, C_6D_6): δ 8.21 (s, 1 H, PhC*H*), 7.61–7.59 (m, 2 H, *m*-H of PhOMe), 7.59–7.00 (m, 25 H, 5 Ph), 6.72–6.69 (m, 2 H, *o*-H of PhOMe), 5.45 and 4.93 (2 d, 2 H, *J* 11.5 Hz, PhCH_2), 5.25 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.87 and 4.56 (2 d, 2 H, *J* 11.2 Hz, PhCH_2), 4.72 and 4.63 (2 d, 2 H, *J* 10.5 Hz, PhCH_2), 4.70 and 4.58 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.59 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.54 and 4.38 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.45–4.41 (m, 2 H, 2 H-6'), 4.36 (dd, 1 H, $J_{3,4}$ 9.0, $J_{4,5}$ 9.8 Hz, H-4), 4.31 (dd, 1 H, $J_{5,6a}$ 3.3, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.22 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-3), 3.91 (dd, 1 H, $J_{2',3'}$ 9.5, $J_{3',4'}$ 9.0 Hz, H-3'), 3.84–3.78 (m, 2 H, H-5,6b), 3.73 (dd, 1 H, $J_{4',5'}$ 9.5 Hz, H-4'), 3.64 (ddd, 1 H, $J_{5',6'a} = J_{5',6'b}$ = 3.3 Hz, H-5'), 3.53 (dd, 1 H, H-2), 3.51 (dd, 1 H, H-2'), 3.19 and 2.96 (2 s, 6 H, 2 MeO), 1.61 (s, 3 H, Ac).

Anal. Calc. for $C_{58}H_{63}NO_{12}$·0.5 H_2O: C, 71.44; H, 6.62; N, 1.44. Found: C, 71.47; H, 6.67; N, 1.52.

*Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-*p*-methoxybenzylideneamino-β- and -α-*D*-glucopyranosyl)-α-*D*-glucopyranoside* (**33** *and* **34**). — A mixture of **20**[12] (93 mg, 0.2 mmol), **10**[13] (117 mg, 0.24 mmol), 2,4,6-trimethylpyridine (40 μL, 0.3 mmol), activated 4 Å powdered molecular sieve (200 mg), and anhydrous dichloromethane (1 mL) was stirred for 30 min at room temperature. Silver triflate (100 mg, 0.4 mmol) was added and stirring was continued for 4 h at room temperature in the dark. The mixture was diluted with dichloromethane, filtered through a bed of Celite, and concentrated. The residue was eluted from a column of silica gel with 4:1 toluene–ethyl acetate (containing 0.3% of triethylamine) to give, first, **20**[12] (33 mg, 36%), then **33** (40 mg, 23%), $[\alpha]_D$ −9° (*c* 0.7, chloroform). ^{1}H-N.m.r. data (250 MHz, $CDCl_3$): δ 8.15 (s, 1 H, PhC*H*), 7.71–7.67 (m, 2 H, *m*-H of PhOMe), 7.50–7.27 (m, 15 H, 3 Ph), 6.98–6.94 (m, 2 H, *o*-H of PhOMe), 5.22 (dd, 1 H, $J_{2',3'}$ 9.3, $J_{3',4'}$ 10.0 Hz, H-3'), 5.09 (dd, 1 H, $J_{4',5'}$ 9.5 Hz, H-4'), 5.09 and 4.78 (2 d, 2 H, *J* 11.3 Hz, PhCH_2). 4.84 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.76 and 4.61 (2 d, 2 H, *J* 12.3 Hz, PhCH_2), 4.66 and 4.49 (2 d, 2 H, *J* 12.2 Hz, PhCH_2), 4.55 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.26 (dd, 1 H, $J_{5',6'a}$ 4.3, $J_{6'a,6'b}$ 12.5 Hz, H-6'a), 3.94 (dd, 1 H, $J_{5',6'b}$ 2.0 Hz, H-6'b), 3.94–3.78 (m, 3 H), 3.86 (s, 3 H, MeO), 3.54–3.43 (m, 4 H), 3.29 (s, 3 H, MeO), 3.26 (dd, 1 H, H-2'), 2.03, 1.99, and 1.87 (3 s, 9 H, 3 Ac).

Anal. Calc. for $C_{48}H_{55}NO_{14}\cdot 0.5H_2O$: C, 65.59; H, 6.42; N, 1.59. Found: C, 65.69; H, 6.53; N, 1.77.

Further elution gave **34** (42 mg, 24%), $[\alpha]_D$ +19° (*c* 0.8, chloroform). ^{1}H-N.m.r. data (400 MHz, $CDCl_3$): δ 7.87 (s, 1 H, PhC*H*), 7.57–7.54 (m, 2 H, *m*-H of PhOMe), 7.36–7.13 and 6.83–6.79 (2 m, 15 H, 3 Ph), 6.90–6.83 (m, 2 H, *o*-H of PhOMe), 5.77 (d, 1 H, $J_{1',2'}$ 3.8 Hz, H-1'), 5.49 (dd, 1 H, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.4 Hz, H-3'), 5.02 (dd, 1 H, $J_{4',5'}$ 10.3 Hz, H-4'), 4.87 and 4.46 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.65 and 4.54 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.65 and 4.58 (2 d, 2 H, *J* 12.0 Hz, PhCH_2), 4.60 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.20 (dd, 1 H, $J_{5',6'a}$ 3.5, $J_{6'a,6'b}$ 12.3 Hz, H-6'a), 4.07 (dd, 1 H, $J_{2,3}$ 9.7, $J_{3,4}$ 8.7 Hz, H-3), 4.02 (ddd, 1 H, $J_{5',6'b}$ 2.0 Hz, H-5'), 4.00 (ddd, 1 H, $J_{5,6a}$ 4.8, $J_{5,6b}$ 1.8 Hz, H-5), 3.92 (dd, 1 H, H-4), 3.85 (s, 3 H, MeO), 3.81 (dd, 1 H, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.78 (dd, 1 H, H-6'b), 3.74 (dd, 1 H, H-6b), 3.52 (dd, 1 H, H-2), 3.43 (s, 3 H, MeO), 3.38 (dd, 1 H, H-2'), 2.04, 2.01, and 1.79 (3 s, 9 H, 3 Ac).

Anal Calc. for $C_{48}H_{55}NO_{14}\cdot 0.5H_2O$: C, 65.59; H, 6.42; N, 1.59. Found: C, 65.58; H, 6.34; N, 1.66.

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