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Syntheses of *O*-Protected 2-amino-2-deoxy-gentiobioside hydrohalides

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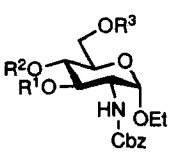
The syntheses of ethyl 3,4-di-*O*-acyl(benzyl)-2-benzyloxycarbonylamino-2-deoxy-6-*O*-trityl-α-D-glucopyranosides (**2-4**) and methyl 3,4-di-*O*-acyl(benzyl)-2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-6-*O*-trityl-α-D-glucopyranosides (**12-14**) are reported. The partially protected D-glucosamine derivatives ethyl 3,4-di-*O*-benzyl- (**5**) and 3-benzyl-2-benzyloxycarbonylamino-2-deoxy-α-D-glucopyranoside (**6**), ethyl 3,4-di-*O*-benzoyl-2-benzyloxycarbonylamino-2-deoxy-α-D-glucopyranoside (**9**), methyl 3,4-di-*O*-acyl(benzyl)-2-deoxy-2-dimethoxycarbonylvinylamino-α-D-glucopyranosides (**15-17**) have been prepared or isolated as by-products. The preparation of ethyl 3,4-di-*O*-acetyl- (**18**), 3,4-di-*O*-benzoyl- (**19**), and 3,4-di-*O*-benzyl-2-benzyloxycarbonylamino-2-deoxy-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranosides (**20**), and methyl 3,4-di-*O*-acetyl- (**21**), 3,4-di-*O*-benzoyl- (**22**), and 3,4-di-*O*-benzyl-2-deoxy-2-dimethoxycarbonylamino-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranosides (**23**) through glycosylation reactions using **2**, **3**, **4**, **12**, **13**, and **14** respectively as glycosyl acceptors and acetobromoglucose as glycosyl donor is described. The *N*-protecting group of **18**, **19**, and **21** was removed to give the alkyl hexa-*O*-acyl-2-amino-2-deoxy gentiobioside hydrohalides **24-26** respectively.

The syntheses of oligosaccharides, and glycosides of 2-amino-2-deoxy sugars are currently topics of interest in carbohydrate chemistry and biochemistry[1-4] .The aminosugars are valuable intermediates in the syntheses of glycoconjugates and *neo*-glycoconjugates[5] and frequently are components of complex synthetic and natural oligosaccharides[6], which play a key role in cell-cell and cell-virus recognition[1]. On the other hand gentiobiose [β-D-Glc*p*-(1→6)-D-Glc*p*] is an expensive sugar which is widespread in naturally occuring glycosides and found as a partial sequence in many oligo- and polysaccharides such as glycoglycerolipids and nephritogenic glycopeptides[7]. Several methods have been described for the preparations of (1→6)-linked disaccharides derivatives[8] and synthetic intermediates of (1→6)-linked oligosaccharides[9]. There are many data [1,10a-10d] on the use of D-glucosamine derivatives as glycosyl donors in glycosylation reactions, however little attention has been directed to their use as glycosyl acceptors, and mostly this use is limited to the syntheses of chitobiose derivatives[10e-10f]. We now report the preparation of the *N*-protected alkyl 2-amino-2-deoxygentiobiosides **18-23** which were obtained through glycosylation reactions using 6-*O*-trityl-D-glucosamine derivatives as glycosyl acceptors. The alkoxycarbonylvinyl and

benzyloxycarbonyl groups, both of them easy to remove[11], were used as *N*-protecting groups. The partially *O*-protected sugar derivatives **1**, **5**, **6**, **9**, **15-17**, useful precursors for specific functionalisation[12], have been directly obtained or isolated as by-products of the glycosylation reactions. As far as we are aware, there are no precedents for the synthesis of *N*-unprotected 2-amino-2-deoxygentiobioside derivatives; in this paper we report the preparation of the *O*-protected alkyl 2-amino-2-deoxygentiobiosides hydrohalides **24-26** from the corresponding *N*-protected derivatives **18**, **19**, **21**. During the deprotection the glycosidic bonds were not affected.

RESULTS AND DISCUSSION

The reaction of ethyl 2-benzyloxycarbonylamino-2-deoxy-α-D-glucopyranoside[13] with trityl chloride yielded the 6-*O*-trityl derivative **1**. Acetylation, or benzoylation, or treatment of **1** with benzyl bromide gave the 3,4-disubstituted derivatives **2-4**, respectively. The results of the benzylations of **1** at rt with different amounts of benzyl bromide and different crystallisation times (EtOH) are shown in Table I. When the crystallisation was left for 24 h (entries 2 and 3) detrytilation took place and the partially protected D-glucosamine derivatives **5** and **6** were isolated. The regioselectivity of the benzylations is also dependent on the BnBr/**1** ratio (entries 1-3). The formation of **6** during the contact with ethanol implies that **8** was obtained during the benzylation although this compound was not isolated. The acetyl derivative **7** was prepared in order to complete the structural study of **6**. The removal of the 6-*O*-trityl group of **3** with AcOH/HBr led to the formation of **9** and ethyl 6-*O*-acetyl-2-benzyloxycarbonylamino-3,4-di-*O*-benzoyl-α-D-glucopyranoside (**10**).



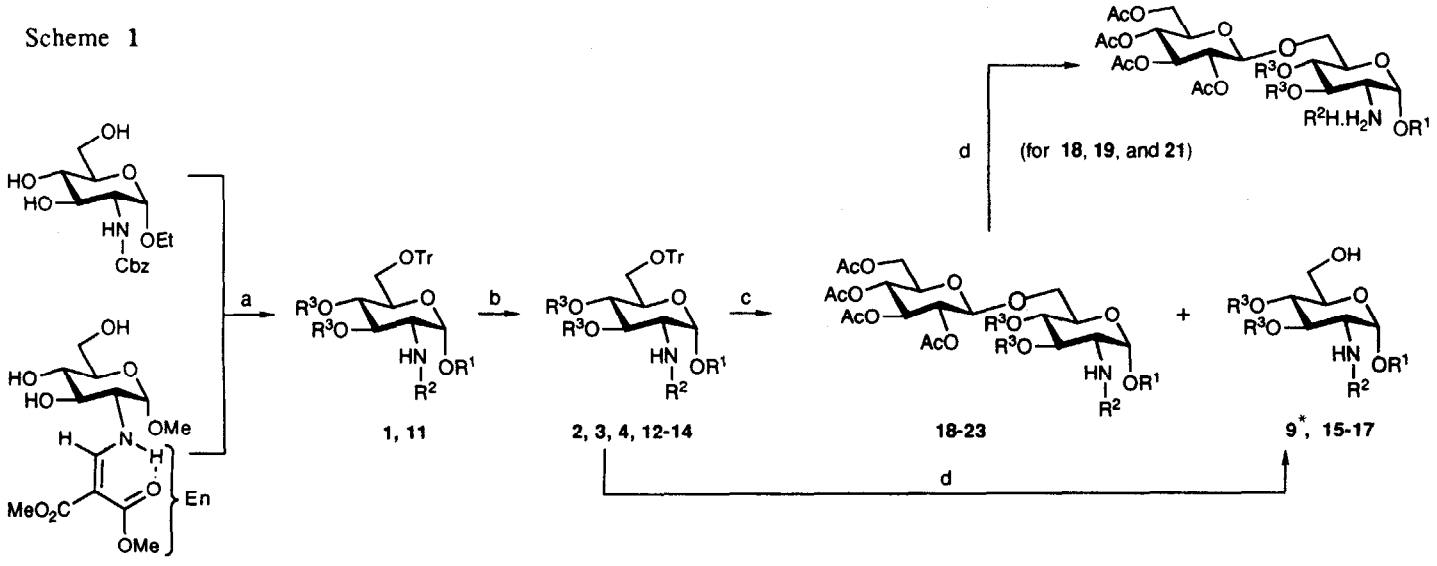
	1	**4**	**5**	**6**	**7**	**8**
R1	H	Bn	Bn	Bn	Bn	Bn
R2	H	Bn	Bn	H	Ac	H
R3	Tr	Tr	H	H	Ac	Tr

Table 1. Benzylations of **1** at rt.

Entry	[BnBr]/1	Time crystallisation (h)	Isolated product and yield (%)		
1	6	0.5	**4** (85%)	---	---
2	6	24	---	**5** (53%)	---
3	3	24	---	**5** (31%)	**6** (15%)

The structures of **1-7**, **9** and **10** were based on UV, IR, ^{1}H NMR, ^{13}C NMR analytical and/or HRMS data (see experimental). These compounds showed IR bands at ≈3300 and ≈1670 cm^{-1} for

Scheme 1



	1	2	3	4	9	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
R^1	Et	Et	Et	Et	Et	Me	Me	Me	Me	Me	Me	Me	Et	Et	Et	Me	Me	Me	Et	Et	Me
R^2	Cbz	Cbz	Cbz	Cbz	Cbz	En	En	En	En	En	En	En	Cbz	Cbz	Cbz	En	En	En	Br	Br	Cl
R^3	H	Ac	Bz	Bn	Bz	H	Ac	Bz	Bn	Ac	Bz	Bn	Ac	Bz	Bn	Ac	Bz	Bn	Ac	Bz	Ac

* Together with **9** the 6-*O*-Ac derivative **10** was obtained.

(a) ClTr, 80°C; (b) Ac_2O/Py (**2**, **12**); ClBz/Py (**3**, **13**); BrBn, NaOH 50% (**4**, **14**); (c) $AgClO_4$, $MeNO_2$, drierite and acetobromoglucose, 0°C, 5 min. under nitrogen; (d) 33% HBr in AcOH, 0°C, 3 min.; (e) 33% HBr in AcOH, 0°C, 2.5 h. for **18** and **19**; Cl_2 in CH_2Cl_2 for **21**.

NH group, and **1**, **5**, **6**, and **9** had a strong absorption for OH (3428-3324 cm^{-1}). The values of $J_{1,2}$ (≈3.7 Hz) and the high and positive optical rotations are indicative of α(D) configuration. The assignments of the carbon resonances were based on APT[14] spectra and are in agreement with data reported for related compounds[15]. The EIMS of **1-4** contained a strong peak at *m/z* 243 (Ph_3C^+) and significant signals at 165, 152, and 77 which come from 243. The primary fragments of **2** and **4** were $M^{+\cdot}$-BnOH and $M^{+\cdot}$-Tr$^{\cdot}$ and also $M^{+\cdot}$-Ph$^{\cdot}$ for **2** and $M^{+\cdot}$-BnOH-Ph$^{\cdot}$ for **3**. The HREIMS of **7** showed as primary fragmentations losses of Ac$^{\cdot}$, Bn$^{\cdot}$, EtO$^{\cdot}$, tropilium cation and H_2NCO_2Bn. Other MS data are given in experimental section.

The enamino sugar **11** was prepared by reaction of methyl 2-deoxy-2[2',2'-dimethoxycarbonylvinyl)amino]-α-D-glucopyranoside[11c] with trityl chloride. Acetylation, or benzoylation, or benzylation of **11** yielded the *O*-protected derivatives **12-14** respectively. The structures **11-14** were assigned on the basis of analytical, UV, IR, ^1H and ^{13}C NMR and MS data. APT[14] spectra and a heteronuclear 2D correlated spectrum (**11**) were used to assist in carbon signal assignments. Compounds **11-14** had two ^{13}C resonances at ≈169.0 (C=O chelated) and ≈165.8 ppm (C=O free). The former is indicative of the hydrogen bond shown in the structure. This chelated structure is also supported by the chemical shift of N*H* (≈9.2 ppm), the $J_{NH,=CH}$ value (≈14 Hz) corresponding to antiperiplanar protons, and the IR C=O band (≈1667 cm^{-1}) of a CO_2Me group[16]. The HREIMS spectra of **12-14** showed loss of MeO$^{\cdot}$ and the characteristic fragments of Tr and the corresponding *O*-substituent groups. Additionally **12** and **13** had molecular ions. The base peak or a prominent fragment for **11-14** was *m/z* 243 (Tr^+). The FABMS spectra of **11** and **14** had pseudomolecular peaks $[M+H]^+$ and/or $[M+Na]^+$.

The $^3J_{H,H}$ values for **1-6**, **8-10** and **11-13** were consistent with the $^4C_1$(D) conformation for solutions in chloroform.

Treatment of the 6-*O*-trityl derivatives **2-4** with acetobromoglucose in the presence of silver perchlorate[9b,17] gave the corresponding 2-deoxy-2-benzyloxycarbonylaminogentiobiosides **18-20** in a 37-65% yield. When the same reaction was performed on the enamino sugars **12-14** the disaccharide derivatives **21-23** (25-33%) were obtained together with **15-17** as by-products. Similar yield was obtained when the reaction was carried out on **12** using silver triflate instead of silver perchlorate as promotor. The structures of **18-23** were based on UV, IR, ^1H NMR, ^{13}C NMR, ^{15}N NMR, HRMS and/or analytical data. Thus, **18-23** had similar UV absorptions to the corresponding starting materials (**2-4**, **12-14**), had no IR or NMR signals for OH or trityl groups, and the signals for the benzyloxycarbonyl (**18-20**) or enamino (**21-23**) groups were similar to those for **2-4** or **12-14** respectively. Assignments of the ^1H and ^{13}C resonances were based on homonuclear (COSY and TOCSY-HOHAHA[18]) and heteronuclear 2D correlated experiments performed on **18-21**. The assignment of ^{13}C resonances was also supported by APT[14] and DEPT spectra and is in agreement with data reported for gentiobiosylenamines[9b]. A 2D inverse correlation ^1H-^{15}N experiment performed on **20** showed that the chemical shift for the resonance of N*H* group is 303 ppm upfield from $MeNO_2$. The $J_{1',2'}$ values (7.6-7.9 Hz) were in the range for antiperiplanar protons and indicated that the glucosyloxy moieties of **18-23** were β. This configuration was also confirmed by the

chemical shift of the C-1' resonance (≈100.6 ppm)[9b,19]. The $^4C_1$(D) conformation for each sugar ring of **18-23** was evident from the $^3J_{H,H}$ values.

The EI mass spectra of **18-20** showed no $M^{+\cdot}$, and had peaks for losses of AcOH, AcO', BnOH and a signal at *m/z* 331, corresponding to the tetra-*O*-acetylglucosyl moiety, similar to that described for gentiobiosylenamines[9b]. In the FABMS of **18-20** $[M+Na]^+$ ions were observed. The HREIMS of **21-23** contained a peak for $M^{+\cdot}$, the peak *m/z* 331 and the characteristic signals of the corresponding *O*-substituent group (see experimental). In the case of the **21** the assignments have been verified by a study of metastable transitions through B^2/E linked scans.

Compounds **15-17** which have HO-6 unsubstituted showed an IR absorption at 3400-3500 cm^{-1} and a ^1H NMR resonance at 2.30-2.82 ppm for hydroxyl group. The IR, ^1H, and ^{13}C NMR spectroscopic data for the enamino group and the conformational assignments were similar to those above described for **11-14**. The HREIMS showed $M^{+\cdot}$, signals for $M^{+\cdot}$-H_2O (**15**), $M^{+\cdot}$-MeO' (**16, 17**), $M^{+\cdot}$-MeOH (**16, 17**), and the characteristic peaks of the corresponding *O*-substituent.

The reaction of **18** and **19** with HBr/AcOH[11a] and the treatment of **21** with chlorine in dichloromethane[11b,c] gave the *O*-protected 2-amino-2-deoxygentiobioside hydrohalides **24-26**. However when the *N*-deprotection with HBr/AcOH was tried on **20** a complex mixture of products was formed. The partially protected gentiobioside **27** could be identified by HRMS[20] in this mixture but not isolated from it. Compounds **24-26** showed the broad and strong IR absorption (3000-2800 cm^{-1}) and the proton resonance at $\delta \approx 8.5$ ppm for the ammonium group. The $^3J_{H,H}$ values confirmed the $^4C_1$(D) conformation for each sugar ring. The FABMS of **24-26** contained the molecular ions and significant peaks corresponding to losses of the halogen atom, EtOH (**24, 25**) or MeOH (**26**), and AcOH (**24, 26**) or BzOH (**25**) from $M^{+\cdot}$. The rupture of the glycosidic bond with formation of the ion *m/z* 331[9b] was also a primary fragmentation. The exact mass of the ammonium ion of **24-26** was measured by HREIMS.

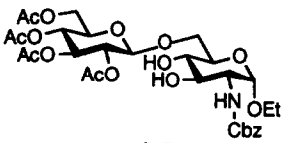


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Table 2. Combined yields for the syntheses of **24-26**

Transformation and yield (%)	Overall yield
1 → **2**(98) → **18**(37) → **24**(88)	31.9
1 → **3**(88) → **19**(65) → **25**(80)	45.8
11 → **12**(90) → **21**(33) → **26**(67)	19.9

The overall yields (Table 2) for the preparations of hexa-*O*-acyl-2-amino-2-deoxygentiobiosides from **1** or **11** are better when *N*-benzyloxycarbonyl compounds are used (**24**, **25**) than when N-dimethoxycarbonylvinyl compounds are used (**26**).

EXPERIMENTAL

General. Melting points are uncorrected. Optical rotations were measured at 22±1° for solutions in dichloromethane, UV spectra were obtained for solutions in dichloromethane. FTIR spectra were recorded for KBr discs. ^{1}H NMR spectra (200, 300, 400, and 500 MHz) were obtained for solutions in $CDCl_3$, *J* values are given in Hz. Assignments were confirmed by decoupling, H-D exchange, and homonuclear 2D COSY and TOCSY-HOHAHA[18] correlated experiments. ^{13}C NMR spectra were recorded at 50.3, 75.4, and 125.7 MHz. Proton decoupled attached proton test (APT[14]), DEPT and heteronuclear 2D correlated spectra were obtained in order to assist in carbon resonance assignments. ^{15}N NMR data (30.39 MHz) were measured through a ^{1}H/^{15}N inverse correlation 2D experiment not using ^{15}N decoupling during the adquisition. The chemical shift is expressed as δ value from nitromethane as external reference. EIMS spectra (70 eV) were measured with a Kratos MS-80RFA instrument, with an ionising current of 100 μA, an accelerating voltage of 4 KV, and a resolution of 1000 (10% valley definition). The elemental composition of the ions was determined with a resolution of 10000 (10% valley definition). The FABMS spectra were recorded with the same instrument. Ions were produced by a beam of xenon atoms (6-7 KeV) using a matrix consisting of glycerol or thioglycerol and NaI as salt, $(CsI)_{37}Cs$ was used as reference. TLC was performed on Silica Gel HF_{254} (Merck), with detection by UV light or charring with H_2SO_4. Silica Gel 60 (Merck, 230 mesh) was used for preparative chromatography.

Ethyl 2-benzyloxycarbonylamino-2-deoxy-6-*O*-trityl-α-D-glucopyranoside (**1**). To a stirred solution of ethyl 2-benzyloxycarbonyl-2-deoxy-α-D-glucopyranoside[13] (0.5 g, 1.46 mmol) in dry pyridine (5 mL) was added trityl chloride (0.53 g, 1.89 mmol). The mixture was heated for 18 h at 80 °C, then poured into ice-water (50 mL). Column chromatography (gradient 4:1→6:1 ether-hexane) of the crude amorphous solid gave **1** as a colourless foam (0.5 g, 59%); crystallised from ether was a white solid which had mp 86-88 °C; $[\alpha]^{22}_D$ +41.2° (*c* 0.9); UV 231 (ε 8200), 265 nm (ε 2300); IR ν_{max} 3420, 3317, 3050, 2926, 1714, 1640, 1500, 1449, 1380, 1260, 1050, 746, 700 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.50-7.10 (m, 20 H, 4 Ph), 5.20 (d, 1 H, $J_{2,NH}$ = 10.0, NH), 5.10 (s, 2 H, CH_2 of Cbz), 4.80 (d, 1 H, $J_{1,2}$ = 3.3, H-1), 3.67-3.35 (m, 8 H, H-2,3,4,5,6,6' and CH_2CH_3), 3.04, 2.80 (each bs, each 1 H, 2 OH), 1.19 (t, 3 H, $^3J_{H,H}$ = 7.0, CH_3); ^{13}C NMR (50.3 MHz) δ 156.5 (C=O), 143.6-127.0 (24 C, 4 Ph), 97.0 (C-1), 86.8 (Ph_3C), 73.6 (C-3), 72.3 (C-5), 69.9 (C-4), 67.2 (CH_2 of Cbz), 63.7 (C-6), 63.2 (CH_2CH_3), 54.7 (C-2), 14.8 (CH_3); EIMS *m/z* 475 (1, M$^{+\cdot}$-BnOH), 398 (1, 475-Ph$^\cdot$), 260 (5, TrOH$^+$), 243 (100, Tr$^+$), 183 (17, 260-Ph$^\cdot$), 165 (85, fluorenyl$^+$), 152 (15, biphenylene$^+$), 77 (24, Ph$^+$). Anal. Calcd for $C_{35}H_{37}O_7N$: C, 72.02; H, 6.39; N, 2.40. Found: C, 72.01; H, 6.54; N, 2.19.

Ethyl 3,4-di-*O*-acetyl- (**2**) and 3,4-di-*O*-benzoyl-2-benzyloxycarbonylamino-2-deoxy-6-*O*-trityl-α-D-glucopyranoside (**3**). Conventional[21] treatment of **1** (3.0 g, 5.14 mmol) with pyridine (10 mL) and acetic anhydride (2 mL, 21.4 mmol) or pyridine (12.8 mL) and benzoyl chloride (2.4 mL, 20.6 mmol) gave **2** (amorphous solid) or **3** (syrup), respectively. Compounds **2** and **3** were purified as indicated.

Compound **2** (3.35 g, 98%) crystallised from ethanol (30 min, 0 °C) had mp 115-116 °C; $[\alpha]^{22}_D$ +93.8° (*c* 1.0); UV 231 nm (ε 5000); IR ν_{max} 3334, 3060, 2968, 2920, 1746, 1714, 1680, 1507, 1445, 1360, 1238, 1047, 762, 698 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.46-7.24 (m, 20 H, 4 Ph), 5.17 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 10.2, H-3), 5.15, 5.04 (each d, each 1 H, $^2J_{H,H}$ = 12.5, CH_2 of Cbz), 5.08 (t, 1 H, $J_{4,5}$ = 10.2, H-4), 5.04 (d, 1 H, $J_{2,NH}$ = 10.2, NH), 4.92 (d, 1 H, $J_{1,2}$ = 3.6, H-1), 4.08 (td, 1 H, H-2), 3.90 (m, 1 H, H-5), 3.87-3.42 (m, 2 H, CH_2CH_3), 3.19 (dd, 1 H, $J_{5,6}$ = 2.8, $J_{6,6'}$ = 10.2, H-6), 3.09 (dd, 1 H, $J_{5,6'}$ = 5.1, H-6'),

1.87, 1.71 (each s, each 3 H, 2 Ac), 1.25 (t, 3 H, $^3J_{H,H}$ = 7.3, CH_2CH_3); ^{13}C NMR (50.3 MHz) δ 171.1, 169.3 (2 $COCH_3$), 155.6 (C=O of Cbz), 143.5-126.8 (24 C, 4 Ph), 96.9 (C-1), 86.4 (Ph_3C), 71.8 (C-3), 69.0, 68.8 (C-4,5), 66.8 (CH_2 of Cbz), 63.5 (C-6), 62.1 (CH_2CH_3), 53.6 (C-2), 20.5, 20.3 (2 $COCH_3$), 14.9 (CH_2CH_3); EIMS *m/z* 667 (1, $M^{+\cdot}$), 590 (1, $M^{+\cdot}$-Ph$^\cdot$), 559 (1, $M^{+\cdot}$-BnOH), 530 (1, 559-CO), 482 (7, 559-Ph$^\cdot$), 424 (1, $M^{+\cdot}$-Tr$^\cdot$), 260 (9, $TrOH^+$), 259 (11, TrO^+), 243 (100, Tr^+), 183 (5, 260-Ph$^\cdot$), 165 (52, fluorenyl$^+$), 152 (8, biphenylene$^+$), 108 (32, $BnOH^+$), 105 (22, Bz^+), 91 (20, tropylium$^+$), 77 (17, Ph^+), 43 (12, Ac^+). Anal. Calcd for $C_{39}H_{41}O_9N$: C, 70.14; H, 6.20; N, 2.09. Found: C, 69.86; H, 6.25; N, 2.13.

Compound **3** was extracted with chloroform (4×30 mL). The combined extracts were washed with M H_2SO_4 (4×30 mL), saturated aqueous $NaHCO_3$ (4×30 mL) and water (4×30 mL), then dried ($MgSO_4$) and the solvent evaporated. The residue (3.6 g, 88%) crystallised from ethanol (30 min, 0 °C) had mp 128-129 °C; $[\alpha]^{22}_D$ +38.2° (*c* 1,0); UV 235 nm (ε 24700); IR ν_{max} 3334, 3060, 2905, 1742, 1720, 1640, 1600, 1580, 1507, 1452, 1445, 1380, 1289, 1113, 705 cm^{-1}; ^1H NMR (200 MHz) δ 8.20-7.00 (m, 30 H, 6 Ph), 5.61 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.2, H-3), 5.51 (t, 1 H, $J_{4,5}$ = 9.2, H-4), 5.19 (d, 1 H, $J_{2,NH}$ = 9.2, NH), 5.02 (d, 1 H, $J_{1,2}$ = 3.7, H-1), 4.94 (s, 2 H, CH_2 of Cbz), 4.32 (td, 1 H, H-2), 4.10 (m, 1 H, H-5), 3.89, 3.59 (each dq, each 1 H, $^2J_{H,H}$ = 10.0, CH_2CH_3), 3.24-3.21 (m, 2 H, H-6,6'), 1.30 (t, 3 H, $^3J_{H,H}$ = 7.0, CH_2CH_3); ^{13}C NMR (50.3 MHz) δ 166.4 (2 C, 2 COPh), 143.5-126.7 (36 C, 6 Ph), 155.6 (C=O of Cbz), 97.2 (C-1), 86.5 (Ph_3C), 72.2 (C-3), 69.6, 69.4 (C-4,5), 66.7 (CH_2 of Cbz), 63.6 (C-6), 62.4 (CH_2CH_3), 54.1 (C-2), 14.9 (CH_2CH_3); EIMS *m/z* 606 (2, $M^{+\cdot}$-BnOH-Ph$^\cdot$), 424 (8, $M^{+\cdot}$-BnOH-TrO$^\cdot$), 396 (2, $M^{+\cdot}$-TrH-H_2NCO_2Bn), 259 (5, TrO^+), 243 (62, Tr^+), 165 (29, fluorenyl$^+$), 152 (5, biphenylene$^+$), 122 (10, $BzOH^+$), 108 (65, $BnOH^+$), 105 (100, Bz^+), 91 (20, tropylium$^+$), 79 (91), 77 (60, Ph^+). Anal. Calcd for $C_{49}H_{45}O_9N$: C, 74.32; H, 5.72; N, 1.76. Found: C, 74.32; H, 6.01; N, 2.02.

Ethyl 3,4-di-*O*-benzyl-2-benzyloxycarbonylamino-2-deoxy-6-*O*-trityl-α-D-glucopyranoside (**4**). To a solution of crude **1** (3.0 g, 5.14 mmol) in dichloromethane (15 mL) were added aqueous 50% NaOH (15 mL) and a catalytic amount of tetrabutylammonium hydrogensulphate. After 5 min freshly distilled benzyl bromide (3.7 mL, 30.8 mmol) was added dropwise with vigorous stirring. The mixture was stirred at rt for 7 days, and then the aqueous layer was extracted with dichloromethane (2×10 mL), the combined organic layers were washed with water (3×15 mL), then dried ($MgSO_4$), and the solvent was evaporated under diminished pressure. The residue (3.34 g, 85%) crystallised from ethanol (30 min, 0 °C) had mp 137-138 °C; $[\alpha]^{22}_D$ +53.8° (*c* 1.0); UV 230 nm (ε 8500); IR ν_{max} 3274, 3082, 3061, 2974, 2926, 1724, 1695, 1597, 1554, 1446, 1360, 1226, 1057, 740, 702 cm^{-1}; ^1H NMR (500 MHz) δ 7.51-6.85 (m, 30 H, 6 Ph), 5.17, 5.11 (each d, each 1 H, $^2J_{H,H}$ = 12.0, CH_2 of Cbz), 4.94 (d, 1 H, $J_{2,NH}$ = 9.9, NH), 4.91 (d, 1 H, $J_{1,2}$ = 3.9, H-1), 4.82, 4.67 (each d, each 2 H, $^2J_{H,H}$ = 11.2, CH_2Ph), 4.66, 4.31 (each d, each 2 H, $^2J_{H,H}$ = 10.2, CH_2Ph), 4.10 (td, 1 H, $J_{2,3}$ = 9.9, H-2), 3.85-3.74 (m, 3 H, H-4,5 and $CHHCH_3$), 3.68 (t, 1 H, $J_{3,4}$ = 9.9, H-3), 3.53-3.47 (m, 1 H, $CHHCH_3$), 3.52 (dd, 1 H, $J_{5,6}$ = 1.0, $J_{6,6'}$ = 10.0, H-6), 3.24 (dd, 1 H, $J_{5,6'}$ = 3.5, H-6'), 1.19 (t, 3 H, $^3J_{H,H}$ = 7.0, CH_2CH_3); ^{13}C NMR (50.3 MHz) δ 155.9 (C=O), 143.8-126.4 (36 C, 6 Ph), 97.5 (C-1), 86.1 (Ph_3C), 81.3 (C-3), 78.4 (C-4), 75.4, 74.8 (2 CH_2Ph), 70.7 (C-5), 66.8 (CH_2 of Cbz), 63.0 (C-6), 62.3 (CH_2CH_3), 54.8 (C-2), 14.9 (CH_2CH_3), EIMS *m/z* 655 (1, $M^{+\cdot}$-BnOH), 520 (1, $M^{+\cdot}$-Tr$^\cdot$), 412 (30, $M^{+\cdot}$-BnOH-Tr$^\cdot$), 243 (88, Tr^+), 165 (60, fluorenyl$^+$), 152 (10, biphenylene$^+$), 108 (30, $BnOH^+$), 105 (32, Bz^+), 91 (100, tropylium$^+$), 77 (35, Ph^+). Anal. Calcd for $C_{49}H_{49}O_7N$: C, 77.04; H, 6.46; N, 1.83. Found: C, 77.15; H, 6.34; N, 2.10.

Ethyl 3,4-di-*O*-benzyl-2-benzyloxycarbonylamino-2-deoxy-α-D-glucopyranoside (**5**). Compound **1** (1.0 g, 1.71 mmol) was processed as indicated for the preparation of **4** until the dryng with $MgSO_4$. The residue was dissolved in warm ethanol and cooled. The crystals formed were left in the same ethanol for 24 h at rt, and the solution obtained was evaporated to dryness. Column chromatography (EtOAc-hexane, 2:3) of the residue gave **5** as amorphous solid (0.48 g, 53%); $[\alpha]^{22}_D$ +78.5° (*c* 1,0); UV 226 (ε 400), 258 nm (ε 500); IR ν_{max} 3324, 3222, 3063, 3031, 2936, 2888, 1688, 1682, 1590, 1543, 1448, 1365, 1269, 1031, 743, 696 cm^{-1}; ^1H NMR (500 MHz) δ 7.38-7.23 (m, 15 H, 3 Ph), 5.17, 5.02 (each d, each 1 H, $^2J_{H,H}$ = 12.1, CH_2 of Cbz), 4.91 (d, 1 H, $J_{2,NH}$ =

10.2, NH), 4.87, 4.67 (each d, each 1 H, $^2J_{H,H}$ = 10.9, CH_2Ph), 4.84, 4.71 (each d, each 1 H, $^2J_{H,H}$ = 11.2, CH_2Ph), 4.80 (d, 1 H, $J_{1,2}$ = 3.5, H-1), 3.96 (td, 1 H, $J_{2,3}$ = 10.2, H-2), 3.81 (dd, 1 H, $J_{5,6}$ = 2.2, $J_{6,6'}$ = 11.7, H-6), 3.76-3.67 (m, 4 H, H-3,4,6' and C*H*HCH$_3$), 3.44 (dq, 1 H, $^2J_{H,H}$ = 9.6, CH*H*CH$_3$), 3.04 (bs, 1 H, OH), 1.20 (t, 3 H, $^3J_{H,H}$ = 7.0, CH$_2$C*H*$_3$); ^{13}C NMR (50.3 MHz) δ 155.8 (C=O), 138.1-127.5 (18 C, 3 Ph), 97.5 (C-1), 80.9 (C-3), 77.9 (C-4), 75.2, 74.9, (2 CH$_2$Ph), 71.1 (C-5), 66.8 (CH$_2$ of Cbz), 63.2 (*C*H$_2$CH$_3$), 61.5 (C-6), 54.6 (C-2), 14.8 (CH$_2$*C*H$_3$); EIMS *m/z* 430 (4, M$^{+\cdot}$-tropylium$^{\cdot}$), 384 (4, M$^{+\cdot}$-BnOH-Et$^{\cdot}$), 370 (2, M$^{+\cdot}$-H$_2$NCO$_2$Bn), 368 (12, M$^{+\cdot}$-BnOH-EtO$^{\cdot}$), 322 (5, 430-BnOH), 296 (2, 322-C$_2$H$_2$), 278 (2, 296-H$_2$O), 108 (23, BnOH$^+$), 91 (100, tropylium$^+$), 77 (17, Ph$^+$). Anal. Calcd for $C_{30}H_{35}O_7N$: C, 69.07; H, 6.76; N, 2.68. Found: C, 68.78; H, 6.53; N, 2.31.

Ethyl 3-*O*-benzyl-2-benzyloxycarbonylamino-2-deoxy-α-D-glucopyranoside (**6**). The benzylation reaction was performed with **1** (1.0 g, 1.71 mmol) in dichloromethane (5 mL), aqueous 50% NaOH (6 mL), a catalytic amount of tetrabutylammonium hydrogensulphate and benzyl bromide (0.6 mL, 5.14 mmol) for 40 h as in the preparation of **4** until the drying with $MgSO_4$. The residue was solved in warm ethanol and cooled. The crystals formed were left in the mother liquor at rt for 24 h and the solution obtained was evaporated to dryness. Column chromatography (EtOAc-hexane 1:4, 2:3, and 1:1) of the residue gave **5** (0.28 g, 31%) and **6** (0.12g, 15%) as an amorphous solid. Compound **6** had $[\alpha]^{22}_D$ +87.6° (*c* 1.0); UV 226 (ε 200), 258 nm (ε 500); IR ν_{max} 3334, 3271, 3030, 2904, 2857, 1688, 1537, 1460, 1365, 1275, 1032, 737, 698 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.35-7.25 (m, 10 H, 2 Ph), 5.15, 5.06 (each d, each 1 H, $^2J_{H,H}$ = 12.2, CH$_2$ of Cbz), 5.00 (d, 1 H, $J_{2,NH}$ = 10.4, NH), 4.79 (d, 1 H, $J_{1,2}$ = 3.5, H-1), 4.74, 4.65 (each d, each 1 H, $^2J_{H,H}$ = 10.7, CH_2Ph), 3.97 (td, 1 H, $J_{2,3}$ = 10.4, H-2), 3.82-3.53 (m, 6 H, H-3,4,5,6,6' and C*H*HCH$_3$), 3.44 (dq, 1 H, $^2J_{H,H}$ = 10.3, CH*H*CH$_3$), 2.79 (bs, 1 H, OH), 2.29 (bt, 1 H, CH$_2$O*H*), 1.21 (t, 3 H, $^3J_{H,H}$ = 7.0, CH$_2$C*H*$_3$); ^{13}C NMR (50.3 MHz) δ 155.8 (C=O), 138.1-127.7 (12 C, 2 Ph), 97.7 (C-1), 80.9 (C-3), 74.4 (*C*H$_2$Ph), 71.4, 70.5 (C-4,5), 66.9 (CH$_2$ of Cbz), 63.3 (*C*H$_2$CH$_3$), 62.2 (C-6), 54.2 (C-2), 14.8 (CH$_2$*C*H$_3$); EIMS *m/z* 431 (1, M$^{+\cdot}$), 385 (1, M$^{+\cdot}$-EtOH), 340 (2, M$^{+\cdot}$-tropylium$^{\cdot}$), 233 (7, 385-H$_2$NCO$_2$Bn), 108 (51, BnOH$^+$), 91 (100, tropylium$^+$), 77 (25, Ph$^+$). Anal. Calcd for $C_{23}H_{29}O_7N$: C, 64.02; H, 6.77; N, 3.24. Found: C, 63.98; H, 6.82; N, 3.22.

Ethyl 4,6-di-*O*-acetyl-3-*O*-benzyl-2-benzyloxycarbonylamino-2-deoxy-α-D-glucopyranoside (**7**). To a solution of **6** (0.064 g, 0.15 mmol) in dry pyridine (1 mL) at 0 °C acetic anhydride (0.1 mL, 1.0 mmol) was added with stirring. The mixture was kept at rt for 16 h and then diluted with dichloromethane (10 mL). The resulting solution was extracted with M H_2SO_4 (2×5 mL), saturated aqueous $NaHCO_3$ (2×5 mL) and water (2×5 mL). The organic layer was dried (Na_2SO_4) and evaporated to dryness. The residue (0.063 g, 90%) had $[\alpha]^{22}_D$ +74.6° (*c* 0.8); UV 229 (ε 200), 266 nm (ε 600); IR ν_{max} 3334, 3063, 3031, 2936, 2904, 1746, 1682, 1580, 1555, 1460, 1381, 1238, 1270, 1047, 777, 710 cm^{-1}; ^{1}H NMR (200 MHz) δ 7.35-7.14 (m, 10 H, 2 Ph), 5.13 (d, 1 H, $^2J_{H,H}$ = 12.1, C*H*H of Cbz), 5.06-5.04 (m, 2 H, H-4 and CH*H* of Cbz), 4.90 (d, 1 H, $J_{2,NH}$ = 10.5, NH), 4.84 (d, 1 H, $J_{1,2}$ = 3.5, H-1), 4.58 (s, 2 H, CH_2Ph), 4.20 (dd, 1 H, $J_{5,6}$ = 5.2, $J_{6,6'}$ = 12.6, H-6), 4.15-4.00 (m, 2 H, H-2,6'), 3.87 (ddd, 1 H, $J_{4,5}$ = 10.5, $J_{5,6'}$ = 2.1, H-5), 3.80-3.63 (m, 2 H, H-3 and C*H*HCH$_3$), 3.48 (dq, 1 H, $^2J_{H,H}$ = 10.0, CH*H*CH$_3$), 2.08, 1.96 (each s, each 3 H, 2 Ac), 1.21 (t, 3 H, $^3J_{H,H}$ = 7.1, CH$_2$C*H*$_3$); ^{13}C NMR (50.3 MHz) δ 170.7, 169.3 (2 *C*OCH$_3$), 155.6 (C=O of Cbz), 137.8-127.5 (12 C, 2 Ph), 97.5 (C-1), 78.3 (C-3), 73.5 (*C*H$_2$Ph), 69.7 (C-4), 67.9 (C-5), 66.9 (CH$_2$ of Cbz), 63.7 (*C*H$_2$CH$_3$), 62.2 (C-6), 54.0 (C-2), 20.7 (2 C, 2 CO*C*H$_3$), 14.8 (CH$_2$*C*H$_3$); HREIMS *m/z* 472.1941 (1, M$^{+\cdot}$-Ac$^{\cdot}$), 470.1785 (1, M$^{+\cdot}$-EtO$^{\cdot}$), 424.1650 (2, M$^{+\cdot}$-Bn$^{\cdot}$), 407.1551 (1, M$^{+\cdot}$-tropylium$^{\cdot}$), 378.1174 (2, 424-EtOH), 364 (5, M$^{+\cdot}$-H$_2$NCO$_2$Bn), 318 (10, 364-EtOH), 275 (15, 318-Ac$^{\cdot}$), 210 (9, 318-BnOH), 167 (18, 318-H$_2$NCO$_2$Bn), 108 (18, BnOH$^+$), 91 (100, tropylium$^+$), 77 (9, Ph$^+$), 43 (20, Ac$^+$). HRFABMS obsd 516.2195, calcd for $C_{27}H_{33}O_9N$+H 516.2233.

Ethyl 2-benzyloxycarbonylamino-3,4-di-*O*-benzoyl-2-deoxy-α-D-glucopyranoside (**9**) and ethyl 6-*O*-acetyl-2-benzyloxycarbonylamino-3,4-di-*O*-benzoyl-2-deoxy-α-D-glucopyranoside (**10**). A solution of **3** (0.3 g, 0.38 mmol) in acetic acid (5 mL) was cooled at 0 °C and treated with 33% HBr in acetic acid (0.28 mL) keeping the temperature at 0 °C. The mixture was stirred for 3 min, filtered and the solution poured into ice-water (50 mL). The resulting solution was

extracted with dichloromethane (3×20 mL) and the combined extracts were evaporated to dryness. The residual acetic acid was eliminated by co-evaporation with toluene (3×20 mL). Column chromatography (EtOAc 1:4, 1:2, 1:1) of the resulting syrup gave the compounds of the title.

Compound **9** (0.14 g, 66%) was an amorphous solid, which had R_f 0.42 (EtOAc:hexane 1:1); $[\alpha]^{22}_D$ +22.0° (*c* 0.7); UV 238 (ε 8800), 241 (ε 8300), 275 nm (ε 1300); IR ν_{max} 3428, 3331, 3063, 3030, 2952, 1730, 1720, 1650, 1600, 1507, 1460, 1258, 1095, 761, 714 cm^{-1}; ^1H NMR (200 MHz) δ 7.96-7.13 (m, 15 H, 3 Ph), 5.76 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.6, H-3), 5.40 (t, 1 H, $J_{4,5}$ = 9.6, H-4), 5.19 (d, 1 H, $J_{2,NH}$ = 9.6, NH), 5,00 (d, 1 H, $J_{1,2}$ = 3.5, H-1), 4.93 (s, 2 H, CH_2 of Cbz), 4.32 (td, 1 H, H-2), 3.84 (m, 1 H, H-5), 3.81-3.69 (m, 2 H, H-6, 6'), 3.81-3.42 (m, 2 H, CH_2CH_3), 2.72 (dd, 1 H, $J_{6,OH}$ = 6.4, $J_{6',OH}$ = 8.5, OH), 1.27 (t, 3 H, $^3J_{H,H}$ = 7.0, CH_2CH_3); ^{13}C NMR (50.3 MHz) δ 166.5, 166.3 (2 *C*OPh), 155.6 (C=O of Cbz), 133.5-127.7 (18 C, 3 Ph), 97.4 (C-1), 71.5 (C-3), 70.1 (C-5), 69.5 (C-4), 66.7 (CH_2 of Cbz), 63.8 (CH_2CH_3), 60.9 (C-6), 53.8 (C-2), 14.8 (CH_2CH_3); EIMS *m/z* 549 (1, $M^{+\cdot}$), 504 (1, $M^{+\cdot}$-EtO·), 503 (1, $M^{+\cdot}$-EtOH), 398 (1, $M^{+\cdot}$-H_2NCO_2Bn), 396 (1, 504-BnOH), 382 (1, 504-BzOH), 381 (1, 503-BzOH), 368 (1, 396-CO), 353 (1, 381-CO), 246 (5, 368-BzOH), 206 (12, 246-C_2H_2N), 122 (10, $BzOH^+$), 108 (8, $BnOH^+$), 105 (100, Bz^+), 91 (10, tropylium$^+$), 77 (13, Ph^+). Anal. Calcd for $C_{30}H_{31}O_9N$: C, 65.56; H, 5.68; N, 2.54. Found: C, 65.17; H, 6.08; N, 2.57.

Compound **10** (0.025 g, 11%) was a hygroscopic and amorphous solid, which had R_f 0.58 (EtOAc:hexane 1:1); $[\alpha]^{22}_D$ +28.1° (*c* 1,3); UV 244 (ε 5400), 275 nm (ε 1900); IR ν_{max} 3349, 3050, 3030, 2950, 1730, 1714, 1650, 1600, 1560, 1492, 1445, 1380, 1269, 1240, 1030, 714 cm^{-1}; ^1H NMR (200 MHz) δ 7.94-7.13 (m, 15 H, 3 Ph), 5.68 (t, 1 H, $J_{2,3} = J_{3,4}$ = 10.3, H-3), 5.53 (t, 1 H, $J_{4,5}$ = 10.3, H-4), 5.19 (d, 1 H, $J_{2,NH}$ = 10.3, NH), 4.98 (d, 1 H, $J_{1,2}$ = 3.7, H-1), 4.93 (s, 2 H, CH_2 of Cbz), 4.60-4.35 (m, 4 H, H-2,5,6,6'), 3.83, 3.57 (each dq, each 1 H, $^2J_{H,H}$ = 10.2, $^3J_{H,H}$ = 7.0, CH_2CH_3), 2.06 (s, 3 H, Ac), 1.28 (t, 3 H, CH_2CH_3); ^{13}C NMR (50.3 MHz) δ 170.5 ($COCH_3$), 166.4, 165.1 (2 *C*OPh), 155.7 (C=O of Cbz), 135.9-127.7 (18 C, 3 Ph), 97.4 (C-1), 71.6 (C-3), 69.1 (C-5), 67.8 (C-4), 66.7 (CH_2 of Cbz), 64.1 (C-6), 62.3 (CH_2CH_3), 53.9 (C-2), 20.6 ($COCH_3$), 14.8 (CH_2CH_3); EIMS *m/z* 591 (1, $M^{+\cdot}$), 546 (1, $M^{+\cdot}$-EtO·), 545 (1, $M^{+\cdot}$-EtOH), 469 (1, $M^{+\cdot}$-BzOH), 440, (1, $M^{+\cdot}$-H_2NCO_2Bn), 423 (1, 545-BzOH), 395 (1, 423-CO), 364 (1, 423-AcO·), 122 (5, $BzOH^+$), 105 (100, Bz^+), 77 (7, Ph^+). HREIMS obsd 591.2126, calcd for $C_{32}H_{33}O_{10}N$ 591.2104.

Methyl 2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-6-*O*-trityl-α-D-glucopyranoside (**11**). To a solution of 2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-α-D-glucopyranoside[11c] (9.25 g, 27.6 mmol) in dry pyridine (30 mL) was added trityl chloride (9.23 g, 33.1 mmol). The mixture was stirred at 80 °C for 8 h and then poured into ice-water. The solid product was removed and purified by column chromatography (gradient EtOAc:hexane 1:1, 2:1, 3:1) to give a white foam which crystallised from ethanol (3.62 g, 23%) had mp 134-135 °C; $[\alpha]^{22}_D$ +78.9° (*c* 1,0); UV 229 (ε 14300), 280 nm (ε 23800); IR ν_{max} 3416, 3290, 3063, 2944, 2904, 1701 (C=O free), 1674 (C=O chelated), 1622, 1492, 1447, 1380, 1262, 1223, 1090, 1049, 770, 702 cm^{-1}; ^1H NMR (500 MHz) δ 9.19 (dd, 1 H, $J_{NH,=CH}$ = 14.2, $J_{2,NH}$ = 9.4, NH), 8.04, (d, 1 H, =CH), 7.45-7.20 (m, 15 H, 3 Ph), 4.80 (d, 1 H, $J_{1,2}$ = 3.6, H-1), 3.95 (bs, 1 H, HO), 3.77, 3.66 (each s, each 3 H, 2 CO_2Me), 3.76 (td, 1 H, $J_{2,3} = J_{3,4}$ = 9.4, H-3), 3.70 (m, 1 H, H-5), 3.55 (bt, 1 H, $J_{4,5}$ = 9.4, H-4), 3.45 (dd, 1 H, $J_{5,6}$ = 4.1, $J_{6,6'}$ = 10.3, H-6), 3.44 (s, 3 H, OMe), 3.39 (dd, 1 H, $J_{5,6'}$ = 5.2, H-6'), 3.27 (td, 1 H, H-2), 2.88 (d, 1 H, $J_{3,OH}$ = 1.8, HO); ^{13}C NMR (50.3 MHz) δ 169.1 (C=O chelated), 166.2 (C=O free), 159.9 (=CH), 143.6 (3 C, C-1 of Ph), 128.5 (6 C, C-3,5 of Ph), 127.7 (6 C, C-2,6 of Ph), 127.0 (3 C, C-4 of Ph), 98.0 (C-1), 89.4 (=C), 86.7 (Ph_3C), 72.7 (C-3), 71.3 (C-4), 70.1 (C-5), 63.7 (C-2), 63.5 (C-6), 51.2, 51.1 (2 CO_2CH_3), 58.2 (OMe); EIMS *m/z* 546 (1, $M^{+\cdot}$-MeO·), 334 (1, $M^{+\cdot}$-Tr·), 333 (1, $M^{+\cdot}$-TrH), 317 (1, $M^{+\cdot}$-TrOH), 302 (1, 334-MeOH), 260 (1, $TrOH^+$), 244 (100, TrH^+), 243 (40, Tr^+), 165 (52, fluorenyl$^+$), 152 (30, biphenylene$^+$), 77 (2, Ph^+); FABMS *m/z* 578 (10, $[M+H]^+$), 546 (6, $M^{+\cdot}$-MeO·), 317 (14, $M^{+\cdot}$-TrOH), 243 (100, Tr^+). Anal. calcd for $C_{32}H_{35}O_9N$: C, 66.53; H, 6.10; N, 2.42. Found: C, 66.48; H, 6.44; N, 2.47.

Methyl 3,4-di-*O*-acetyl- (**12**) and 3,4-di-*O*-benzoyl-2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-6-*O*-trityl-α-D-glucopyranoside (**13**). Conventional[21] treatment of **11** (1.01 g, 1.75 mmol) with dry pyridine (10 mL) and acetic anhydride (0.7 mL, 7.5 mmol) or pyridine (10 mL) and benzoyl chloride (0.8 mL, 7.0 mmol) gave **12** (amorphous solid) or **13** (syrup), respectively. Compounds **12** and **13** were purified in the following manners.

Compound **12** (1.05 g, 90%) crystallised from ethanol (10 min, 0 °C) had mp 172-173 °C; $[\alpha]^{22}_D$ +160° (*c* 1,0); UV 229 (ε 12100), 280 nm (ε 23900); IR ν_{max} 3301, 3015, 2968, 2936, 1762, 1698 (C=O free), 1666 (C=O chelated), 1603, 1500, 1460, 1397, 1238, 1047, 730 cm^{-1}; ^1H NMR (200 MHz) δ 9.05 (dd, 1 H, $J_{NH,=CH}$ = 13.5, $J_{2,NH}$ = 9.2, NH), 7.95 (d, 1 H, =CH), 7.45-7.22 (m, 15 H, 3 Ph), 5.26 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.9, H-3), 5.08 (t, 1 H, $J_{4,5}$ = 9.9, H-4), 4.94 (d, 1 H, $J_{1,2}$ = 3.6, H-1), 3.92 (ddd, 1 H, $J_{5,6}$ = 2.4, $J_{5,6'}$ = 4.8, H-5), 3.79, 3.71 (each s, each 3 H, 2 CO_2Me), 3.52 (m, 4 H, H-2, OMe), 3.25 (dd, 1 H, $J_{6,6'}$ = 10.6, H-6), 3.11 (dd, 1 H, H-6'), 1.97, 1.72 (each s, each 3 H, 2 Ac); ^{13}C NMR (50.3 MHz) δ 169.8, 168.8 (2 $COCH_3$), 169.2 (C=O chelated), 165.8 (C=O free), 158.8 (=CH), 143.4 (3 C, C-1 of Ph), 128.6 (6 C, C-3,5 of Ph), 127.7 (6 C, C-2,6 of Ph), 126.9 (3 C, C-4 of Ph), 97.7 (C-1), 90.9 (=C), 86.5 (Ph_3C), 71.7 (C-3), 69.1, 68.4 (C-4,5), 62.1 (C-2), 61.7 (C-6), 55.4 (OMe), 51.3, 51.1 (2 CO_2CH_3), 20.4. 20.3 (2 $COCH_3$); EIMS *m/z* 661.2482 (1, $M^{+\cdot}$), 630 (1, $M^{+\cdot}$-MeO·), 629 (2, $M^{+\cdot}$-MeOH), 598 (2, 629-MeO·), 418 (3, $M^{+\cdot}$-Tr·), 359 (2, $M^{+\cdot}$-TrOH-CH_2CO), 243 (100, Tr^+), 165 (28, fluorenyl$^+$), 152 (5, biphenylene$^+$), 105 (10, Bz^+), 77 (5, Ph^+), 60 (5, $AcOH^+$). Anal. calcd for $C_{36}H_{39}O_{11}N$: C, 65.34; H, 5.94; N, 2.11. Found: C, 65.26; H, 6.25; N, 2.12.

Compound **13** was chromatographed on silica gel column using a gradient EtOAc:hexane 1:3, 1:2, 1:1 as eluant. The resulting syrup crystallised from ethanol (15 min, 0 °C) gave a white product (1.32 g, 96%), which had mp 104-105 °C; $[\alpha]^{22}_D$ +129.7° (*c* 1,0); UV 230 (ε 37900), 289 nm (ε 23400); IR ν_{max} 3283, 3059, 2949, 1728 (C=O free), 1667 (C=O chelated), 1607, 1507, 1445, 1383, 1267, 1090, 758, 708 cm^{-1}; ^1H NMR (200 MHz) δ 9.18 (dd, 1 H, $J_{NH,=CH}$ = 13.8, $J_{2,NH}$ = 9.7, NH), 7.95 (d, 1 H, =CH), 7.86-7.05 (m, 25 H, 5 Ph), 5.70 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.7, H-3), 5.47 (t, 1 H, $J_{4,5}$ = 9.7, H-4), 5.03 (d, 1 H, $J_{1,2}$ = 3.7, H-1), 4.15 (ddd, 1 H, $J_{5,6}$ = 2.9, $J_{5,6'}$ = 5.4, H-5), 3.78, 3.59 (each s, each 3 H, 2 CO_2Me), 3.73 (m, 1 H, H-2), 3.46 (s, 3 H, OMe), 3.33 (dd, 1 H, $J_{6,6'}$ = 10.4, H-6), 3.25 (dd, 1 H, H-6'); ^{13}C NMR (50.3 MHz) δ 168.7 (C=O chelated), 165.5 (C=O free), 165.4, 164.9 (2 *C*OPh), 158.7 (=CH), 143.4 (3 C, C-1 of Ph of Tr), 133.0 (2 C, C-1 of Ph of Bz), 128.8 (4 C, C-2, 6 of Ph of Bz), 128.4 (6 C, C-3, 5 of Ph of Tr), 128.1 (4 C, C-3,5 of Ph of Bz), 127.6 (6 C, C-2, 6 of Ph of Tr), 126.8 (5 C, C-4 of Ph of Tr and Bz), 97.9 (C-1), 90.9 (=C), 86.6 (Ph_3C), 71.9 (C-3), 69.6, 68.9 (C-4,5), 62.6 (C-2), 62.2 (C-6), 55.4 (OMe), 51.3, 50.8 (2 CO_2CH_3); EIMS *m/z* 785.2846 (1, $M^{+\cdot}$), 754 (1, $M^{+\cdot}$-MeO·), 260 (6, $TrOH^+$), 259 (6, TrO^+), 244 (55, TrH^+), 243 (100, Tr^+), 165 (40, fluorenyl$^+$), 122 (33, $BzOH^+$), 105 (82, Bz^+), 77 (20, Ph^+). Anal. calcd for $C_{46}H_{43}O_{11}N$: C, 70.30; H, 5.51; N, 1.78. Found: C, 70.54; H, 5.68; N, 1.68.

Methyl 3,4-di-*O*-benzyl-2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-6-*O*-trityl-α-D-glucopyranoside (**14**). Compound **11** (1.04 g, 1.80 mmol) in dichloromethane (5 mL), aqueous 50% NaOH (5 mL), a catalytic amount of tetrabutylammonium hydrogensulphate and benzyl bromide (1.3 mL, 10.8 mmol) were processed as has been indicated in the preparation of **4** (stirring 18 h). Column chromatography (EtOAc:hexane 1:3, 1:2, 1:1) of the residue gave a white foam (0.88 g, 64%), which crystallised from ethanol (30 min, 0 °C) had mp 165-167 °C; $[\alpha]^{22}_D$ +112.6° (*c* 1,0); UV 228 (ε 10400), 281 nm (ε 14400); IR ν_{max} 3270, 3059, 2947, 2907, 1721 (C=O free), 1665 (C=O chelated), 1607, 1508, 1443, 1381, 1233, 1051, 745, 700 cm^{-1}; ^1H NMR (500 MHz) δ 9.27 (dd, 1 H, $J_{NH,=CH}$ = 13.9, $J_{2,NH}$ = 9.7, NH), 8.04 (d, 1 H, =CH), 7.49-7.16 (m, 25 H, 5 Ph), 4.91 (d, 1 H, $J_{1,2}$ = 3.5, H-1), 4.74, 4.46 (each d, each 1 H, $^2J_{H,H}$ = 10.5, CH_2Ph), 4.68, 4.33 (each d, each 1 H, $^2J_{H,H}$ = 10.5, CH_2Ph), 3.85-3.70 (m, 3 H, H-3,4,5), 3.83, 3.67 (each s, each 3 H, CO_2Me), 3.55 (d, 1 H, $J_{6,6'}$ = 10.5, H-6), 3.48 (s, 3 H, OMe), 3.44 (m, 1 H, H-2), 3.25 (dd, $J_{5,6'}$ = 4.0, H-6'); ^{13}C NMR (50.3 MHz) δ 169.4 (C=O chelated), 165.7 (C=O free), 159.9 (=CH), 143.6 (3 C, C-1 of Ph of Tr), 137.4, 137.0 (2 C-1 of Ph of Bn), 128.6-126.9 (25 C, C-2,3,4,5,6 of Ph), 97.9 (C-1), 89.9 (=C), 86.3 (Ph_3C), 81.0 (C-3), 78.1 (C-4), 76.1, 74.9 (2 CH_2Ph), 70.8 (C-5), 63.8 (C-2), 62.0 (C-6), 55.0 (OMe), 51.2, 50.0 (2 CO_2CH_3); EIMS *m/z* 757 (1, $M^{+\cdot}$), 726 (1, $M^{+\cdot}$-MeO·), 514 (1, $M^{+\cdot}$-Tr·), 4.82 (1, 514-MeOH), 244 (65, TrH^+), 243 (100, Tr^+), 165 (50, fluorenyl$^+$), 105 (20, Bz^+), 91 (38, tropylium$^+$), 77

(15, Ph^+); FABMS *m/z* 780 (7, $[M+Na]^+$), 758 (4, $[M+H]^+$). Anal. calcd for $C_{46}H_{47}O_9N$: C, 72.90; H, 6.25; N, 1.84. Found: C, 72.88; H, 6.00; N, 2.16.

General Procedure for the Preparation of *O*-protected Ethyl 2-benzyloxycarbonylamino-2-deoxy-α-D-gentiobiosides (**18-20**). To a solution of silver perchlorate (1.04 g, 5.02 mmol) in freshly distilled nitromethane (6.5 mL for **18**, 4.9 mL for **19**, 4.3 mL for **20**) was added drierite (0.5 g, 3.68 mmol) and the mixture was kept at 0 °C under nitrogen for 5 min. Then the corresponding 6-*O*-trityl ether **2-4** (5.02 mmol) and acetobromoglucose (2.06 g, 5.02 mmol) were added under nitrogen. The mixture was stirred for 5 min at 0 °C under nitrogen, then filtered through Celite. The insoluble material was washed with dichloromethane (10 mL), and the combined filtrate and washing were washed with water at 0 °C (10 mL), saturated aqueous sodium hidrogencarbonate (10 mL), and water (3×10 mL). The organic layer was diluted with dichloromethane (10 mL), dried ($MgSO_4$) and the solvent evaporated. The residue was purified as indicated. The following compounds were prepared in this manner.

Ethyl 3,4-di-*O*-acetyl-2-benzyloxycarbonylamino-2-deoxy-6-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**18**). Column chromatography (EtOAc:hexane 1:2, 1:1, 2:1) of the residue gave an amorphous solid (1.38 g, 37%) which had R_f 0.52 (EtOAc:hexane 1:1); $[\alpha]^{22}_D$ +55.5° (*c* 0.54); UV 222 (ε 700), 232 nm (ε 1500); IR ν_{max} 3347, 3031, 2924, 2855, 1753, 1640, 1524, 1456, 1377, 1235, 1040, 758, 700 cm^{-1}; ^1H NMR (500 MHz) δ 7.40-7.20 (m, 5 H, Ph), 5.19 (t, 1 H, $J_{2',3'} = J_{3',4'} = 9.6$, H-3'), 5.18 (t, 1 H, $J_{2,3} = J_{3,4} = 9.8$, H-3), 5.14, 5.10 (each d, each 1 H, $^2J_{H,H} = 12.5$, CH_2 of Cbz), 5.06 (t, 1 H, $J_{4',5'} = 9.6$, H-4'), 5.01 (d, 1 H, $J_{2,NH} = 9.8$, NH), 5.00 (dd, 1 H, $J_{1',2'} = 7.9$, H-2'), 4.90 (t, 1 H, $J_{4,5} = 9.8$, H-4), 4.81 (d, 1 H, $J_{1,2} = 2.5$, H-1), 4.53 (d, 1 H, H-1'), 4.26 (dd, 1 H, $J_{5',6'a} = 4.4$, $J_{6'a,6'b} = 12.6$, H-6'a), 4.12 (dd, 1 H, $J_{5',6'b} = 1.6$, H-6'b), 3.97 (td, 1 H, H-2), 3.93-3.86 (m, H-5, 6a), 3.73, 3.45 (each dq, each 1 H, $^2J_{H,H} = 10.2$, $^3J_{H,H} = 7.0$, CH_2CH_3), 3.68 (ddd, 1 H, H-5'), 3.52 (dd, 1 H, $J_{5,6b} = 6.5$, $J_{6a,6b} = 10.6$, H-6b), 2.09, 2.08, 2.05, 2.04, 2.02, 2.00 (each s, each 3 H, 6Ac), 1.25 (t, 3 H, CH_2CH_3); ^{13}C NMR (50.3 MHz) δ 170.9, 170.6, 170.2, 169.5, 169.3, 169.2 (6 $COCH_3$), 155.7 (C=O of Cbz), 136.1-128.0 (6 C, Ph), 100.8 (C-1'), 96.7 (C-1), 72.6 (C-3'), 71.7 (C-3), 71.4 (C-5'), 70.9 (C-2'), 68.7 (C-4), 68.4 (C-5), 68.2 (C-4'), 68.1 (C-6), 66.8 (CH_2 of Cbz), 63.5 (CH_2CH_3), 61.7 (C-6'), 53.5 (C-2), 20.6-20.5 (6 C, 6 $COCH_3$), 14.7 (CH_2CH_3); EIMS *m/z* 424 (1, $M^{+\cdot}$-$C_{14}H_{19}O_9^{\cdot}$), 331 (45, $C_{14}H_{19}O_9^+$), 271 (5, 331-AcOH), 169 (100, 271-Ac_2O), 108 (60, $BnOH^+$), 91 (42, tropylium$^+$), 43 (52, Ac^+); FABMS *m/z* 778 (100, $[M+Na]^{+\cdot}$). Anal. calcd for $C_{34}H_{45}O_{18}N$: C, 54.03; H, 6.00; N, 1.85. Found: C, 53.84; H, 5.65; N, 1.44.

Compound **18** (21%) was also prepared from **12** and acetobromoglucose using silver triflate as promotor[22].

Ethyl 2-benzyloxycarbonylamino-3,4-di-*O*-benzoyl-2-deoxy-6-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**19**). Colunm chromatography (EtOAc:hexane 1:3, 1:2, 1:1) of the residue gave an amorphous solid (2.83 g, 65%) which had R_f 0.44 (EtOAc:hexane 1:1); $[\alpha]^{22}_D$ +10.1° (*c* 0.7); UV 233 nm (ε 19900); IR ν_{max} 3334, 3015, 2952, 1761, 1714, 1667, 1580, 1500, 1445, 1365, 1240, 1223, 1030, 714 cm^{-1}; ^1H NMR (500 MHz) δ 8.00-7.02 (m, 15 H, 3 Ph), 5.66 (t, 1 H, $J_{2,3} = J_{3,4} = 9.7$, H-3), 5.34 (t, 1 H, $J_{4,5} = 9.7$, H-4), 5.18 (t, 1 H, $J_{2',3'} = J_{3',4'} = 9.4$, H-3'), 5.13 (d, 1 H, $J_{2,NH} = 9.7$, NH), 5.04 (t, 1 H, $J_{4',5'} = 9.4$, H-4'), 5.02 (dd, 1 H, $J_{1',2'} = 7.9$, H-2'), 4.94, (d, 1 H, $J_{1,2} = 3.7$, H-1), 4.93 (s, 2 H, CH_2 of Cbz), 4.54 (d, 1 H, H-1'), 4.24 (td, 1 H, H-2), 4.22 (dd, 1 H, $J_{5',6'a} = 4.9$, $J_{6'a,6'b} = 12.3$, H-6'a), 4.18 (m, 1 H, H-5), 4.04 (dd, 1 H, $J_{5',6'b} = 2.3$, H-6'b), 3.99 (dd, 1 H, $J_{5,6a} = 2.0$, $J_{6a,6b} = 10.9$, H-6a), 3.82, 3.51 (each dq, each 1 H, $^2J_{H,H} = 9.8$, $^3J_{H,H} = 7.0$, CH_2CH_3), 3.68-3.62 (m, 2 H, H-5', 6b), 2.08 (s, 3 H, Ac), 2.00 (s, 6 H, 2 Ac), 1.99 (s, 3 H, Ac), 1.27 (t, 3 H, CH_2CH_3); ^{13}C NMR (50.3 MHz) δ 170.5, 170.1, 169.3, 169.2 (4 $COCH_3$), 166.4, 165.2 ($COPh$), 155.6 (C=O of Cbz), 136.1-127.9 (6 C, Ph), 100.8 (C-1'), 96.9 (C-1), 72.5 (C-3'), 71.8 (C-3), 71.6 (C-5'), 70.9 (C-2'), 69.3 (C-4), 68.9 (C-5), 68.4 (C-4'), 68.1 (C-6), 66.7 (CH_2 of Cbz), 63.6 (CH_2CH_3), 61.6 (C-6'), 53.9 (C-2), 20.6 ($COCH_3$), 20.5 (2 $COCH_3$), 20.4 ($COCH_3$), 14.8 (CH_2CH_3); EIMS *m/z* 331 (7, $C_{14}H_{19}O_9^+$), 271 (1, 331-AcOH), 169 (14, 271-Ac_2O), 122 (8, $BzOH^+$), 108 (98, $BnOH^+$), 105 (100, Bz^+), 91 (18, tropylium$^+$), 77 (60, Ph^+), 43 (25, Ac^+); FABMS *m/z* 902 (10, $[M+Na]^+$). Anal. calcd for $C_{44}H_{49}O_{18}N$: C, 60.06; H, 5.61; N, 1.59. Found: C, 60.19; H, 5.90; N, 1.77.

Ethyl 3,4-di-*O*-benzyl-2-bezyloxycarbonylamino-2-deoxy-6-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-gluco-pyranoside (**20**). The residue crystallised from ethanol gave a white solid (0.42 g, 42%) which had mp 72-73 °C; R_f 0.42 (EtOAc:hexane 1:1); $[\alpha]^{22}_D$ +28.0° (*c* 1.0); UV 225 (ε 1200), 265 nm (ε 900); IR ν_{max} 3349, 3031, 2952, 2873, 1746, 1714, 1698, 1523, 1445, 1360, 1235, 1223, 1031, 746, 698 cm^{-1}; ^1H NMR (500 MHz) δ 7.33-7.26 (m, 15 H, 3 Ph), 5.18 (t, 1 H, $J_{2',3'} = J_{3',4'} = 9.4$, H-3'), 5.12, 5.06 (each d, each 1 H, $^2J_{H,H} = 12.7$, CH_2 of Cbz), 5.09 (t, 1 H, $J_{4',5'} = 9.4$, H-4'), 5.04 (dd, 1 H, $J_{1',2'} = 7.9$, H-2'), 4.75 (d, 1 H, $J_{1,2} = 3.7$, H-1), 4.86 (d, 1 H, $J_{2,NH} = 9.5$, NH), 4.83, 4.52 (each d, each 1 H, $^2J_{H,H} = 10.9$, C*H*$_2$Ph), 4.76, 4.66 (each d, each 1 H, $^2J_{H,H} = 11.1$, C*H*$_2$Ph), 4.54 (d, 1 H, H-1'), 4.24 (dd, 1 H, $J_{5',6'a} = 4.6$, $J_{6'a,6'b} = 12.4$, H-6'a), 4.12 (dd, 1 H, $J_{5',6'b} = 2.0$, H-6'b), 4.07 (dd, $J_{5,6a} = 1.3$, $J_{6a,6b} = 10.1$, H-6a), 3.97 (td, 1 H, $J_{2,3} = 9.5$, H-2), 3.79 (ddd, 1 H, $J_{4,5} = 9.5$, $J_{5,6b} = 4.8$, H-5), 3.70-3.61 (m, 4 H, C*H*HCH$_3$, H-3, 5', 6b), 3.48 (t, 1 H, $J_{3,4} = 9.5$, H-4), 3.39 (dq, 1 H, $^2J_{H,H} = 9.5$, $^3J_{H,H} = 7.0$, CH*H*CH$_3$), 2.05 (s, 6 H, 2 Ac), 2.02, 2.00 (each s, each 3 H, 2 Ac), 1.16 (t, 3 H, CH$_2$C*H*$_3$); ^{13}C NMR (75.5 MHz) δ 170.6, 170.3, 169.3, 169.0 (4 *C*OCH$_3$), 155.8 (C=O of Cbz), 138.2-127.2 (18 C, 3 Ph), 100.7 (C-1'), 97.5 (C-1), 81.3 (C-3), 78.3 (C-4), 75.3, 74.9 (2 *C*H$_2$Ph), 72.9 (C-3'), 71.8 (C-5'), 71.2 (C-2'), 70.4 (C-5), 68.4 (C-4'), 68.2 (C-6), 66.9 (CH_2 of Cbz), 63.2 (*C*H$_2$CH$_3$), 61.9 (C-6'), 54.7 (C-2), 20.7, 20.6 (2 CO*C*H$_3$), 20.5 (2 C, 2 CO*C*H$_3$), 14.9 (CH$_2$*C*H$_3$); ^{15}N NMR (30.39 MHz) δ 303 (J_{NH} = 91.3, *N*H); EIMS *m/z* 331 (7, $C_{14}H_{19}O_9^+$), 271 (2, 331-AcOH), 108 (92, BnOH$^+$), 91 (100, tropylium$^+$), 77 (58, Ph$^+$), 43 (48, Ac$^+$); FABMS *m/z* 874 (27, [M+Na]$^+$). Anal. calcd for $C_{44}H_{53}O_{16}N$: C, 62.03; H, 6.27; N, 1.64. Found: C, 62.29; H, 6.31; N, 1.30.

General Procedure for the Preparation of *O*-protected Methyl 2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-α-D-gentiobiosides (**21-23**). To a solution of dry silver perchlorate (0.16 g, 0.75 mmol) in freshly distilled nitromethane (0.65 mL) was added drierite (0.09 g, 0.66 mmol) and the mixture was cooled at 0 °C under nitrogen. After 5 min the corresponding 6-*O*-trityl ether **12-14** (0.75 mmol) and acetobromoglucose (0.31 g, 0.75 mmol) were added under nitrogen. The mixture was stirred at 0 °C for 5 min and then filtered through Celite. The insoluble material was washed with nitromethane (5 mL), and the combined filtrate and washing were washed with cold (0 °C) water (5 mL), saturated aqueous sodium hydrogencarbonate (5 mL) and water (3×5 mL). The organic layer was diluted with dichloromethane (10 mL), dried ($MgSO_4$) and evaporated to dryness. Column chromatography (EtOAc:hexane 1:1, 2:1, 3:1) of the residue gave the compound **21-23** and the respective methyl 3,4-di-*O*-acyl(benzyl)-2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-α-D-glucopyranoside (**15-17**) as by-product.

Methyl 3,4-di-*O*-acetyl-2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-6-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**21**). Was an hygroscopic and amorphous solid (0.18 g, 33%) which had R_f 0.36 (EtOAc:hexane 2:1); $[\alpha]^{22}_D$ +88.5° (*c* 0.6); UV 226 (ε 5000), 278 nm (ε 17500); IR ν_{max} 3279, 2951, 2845, 1753, 1720 (C=O free), 1665 (C=O chelated), 1611, 1445, 1379, 1231, 1042 cm^{-1}; ^1H NMR (500 MHz) δ 8.98 (dd, 1 H, $J_{2,NH} = 9.8$, $J_{NH,=CH} = 13.8$, NH), 7.86 (d, 1 H, =CH), 5.23 (t, 1 H, $J_{2,3} = J_{3,4} = 9.8$, H-3), 5.15 (t, 1 H, $J_{2',3'} = J_{3',4'} = 9.6$, H-3'), 5.03 (t, 1 H, $J_{4',5'} = 9.6$, H-4'), 4.96 (dd, 1 H, $J_{1',2'} = 7.9$, H-2'), 4.88 (t, 1 H, $J_{4,5} = 9.8$, H-4), 4.80 (d, 1 H, $J_{1,2} = 3.5$, H-1), 4.48 (d, 1 H, H-1'), 4.21 (dd, 1 H, $J_{5',6'a} = 4.8$, $J_{6'a,6'b} = 12.4$, H-6'a), 4.08 (dd, 1 H, $J_{5',6'b} = 2.4$, H-6'b), 3.93-3.89 (m, 2 H, H-5, 6a), 3.73, 3.65 (each s, each 3 H, 2 CO_2Me), 3.66-3.63 (m, 1 H, H-5'), 3.48 (dd, 1 H, $J_{5,6b} = 5.2$, $J_{6a,6b} = 10.8$, H-6b), 3.41 (s, 3 H, OMe), 3.39 (td, 1 H, H-2), 2.02, 2.01, 1.97, 1.96, 1.95, 1.91 (each s, each 3 H, 6 Ac); ^{13}C NMR (50.3 MHz) δ 170.5, 170.1, 169.7, 169.4, 169.2, 169.1 (6 *C*OCH$_3$), 168.7 (C=O chelated), 165.8 (C=O free), 158.7 (=CH), 100.6 (C-1'), 97.7 (C-1), 91.0 (=C), 72.5 (C-3'), 71.7 (C-5'), 71.3 (C-3), 70.8 (C-2'), 68.3 (C-5), 68.1 (C-4'), 68.0 (C-4), 67.4 (C-6), 61.7 (2C, C-2, 6'), 55.5 (OMe), 51.2, 51.1 (2 CO_2*C*H$_3$), 20.6, 20.5, 20.4 (each 2 C, CO*C*H$_3$); HREIMS *m/z* 749.2361 (23, M$^{+\cdot}$, calcd for $C_{31}H_{43}O_{20}N$ 749.2378), 718.2119 (22, M$^{+\cdot}$-MeO$^\cdot$), 689.2144(5, M$^{+\cdot}$-AcOH), 657 (1, 689 -MeOH), 629.1964 (5, M$^{+\cdot}$-2AcOH), 597 (1, 689-MeOH-AcOH), 587.1855 (5, M$^{+\cdot}$-2AcOH-CH_2CO), 569.1541 (5, 689-2ACOH), 545.1550 (10, M$^{+\cdot}$-2Ac_2O), 530.1109 [2, M$^{+\cdot}$-AcOH-$H_2NCH{=}C(CO_2Me)_2$] , 402.1470 (5, M$^{+\cdot}$- glucosyloxy moiety), 331.1023 (40)[9b], 243.0775 (39, Tr$^+$). These fragmentations were proved by B^2/E linked scans.

Methyl 3,4-di-*O*-acetyl-2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-α-D-glucopyranoside (**15**). Was an hygroscopic and amorphous solid (0.08 g, 26%) wich had R_f 0.25 (EtOAc:hexane 2:1); $[\alpha]^{22}_D$ +155.5° (*c*,1.0); UV 227 (ε 7300), 278 nm (ε 8900); IR ν_{max} 3413, 3270, 2957, 1759, 1719 (C=O free), 1661 (C=O chelated), 1611, 1451, 1385, 1236, 1038 cm^{-1}; ^1H NMR (200 MHz) δ 9.08 (dd, 1 H, $J_{2,NH}$ = 10.2, $J_{NH,=CH}$ = 12.7, NH), 7.93, (d, 1 H, =CH), 5.38 (t, 1 H, $J_{2,3} = J_{3,4}$ = 10.2, H-3), 5.00 (t, 1 H, $J_{4,5}$ = 10.2, H-4), 4.89 (d, 1 H, $J_{1,2}$ = 3.4, H-1), 3.88-3.55 (m, 3 H, H-5,6,6'), 3.79, 3.71 (each s, each 3 H, 2 CO_2Me), 3.48 (s, 3 H, OMe), 3.45 (td, 1 H, H-2), 2.36 (dd, 1 H, $J_{6,OH}$ = 7.9, $J_{6',OH}$ = 5.7, OH), 2.07, 2.00 (each s, each 3 H, 2 Ac); ^{13}C NMR (50.3 MHz) δ 170.5, 169.6 (2 $COCH_3$), 168.6 (C=O chelated), 165.3 (C=O free), 158.6 (=CH), 97.9 (C-1), 91.0 (=C), 70.7 (C-3), 69.6 (C-5), 68.2 (C-4), 62.0 (C-2), 60.6 (C-6), 55.5 (OMe), 51.2, 51.1 (2 CO_2CH_3), 20.5, 20.3 (2 $COCH_3$); HREIMS *m/z* 419.1423 (15, $M^{+\cdot}$), 401.1247 (5, $M^{+\cdot}$-H_2O), 359.0806 (5, 401-CH_2CO), 329.0970 (7, 359-MeOH), 296.0766 (5, 327-MeOH), 201 [100, $M^{+\cdot}$-HNCH=C(CO_2Me)$_2$'-AcOH]. HREIMS obsd 419.1427, calcd for $C_{17}H_{25}O_{11}N$ 419.1423.

Methyl 3,4-di-*O*-benzoyl-2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-6-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**22**). Was an amorphous solid (0.19 g, 24%) which had R_f 0.61 (EtOAc:hexane 3:1); $[\alpha]^{22}_D$ +84.9° (*c* 1,0); UV 230 (ε 22700), 279 nm (ε 19000); IR ν_{max} 3281, 3019, 2951, 1759, 1720 (C=O free), 1667 (C=O chelated), 1607, 1451, 1379, 1252, 1240, 1040, 756, 712 cm^{-1}; ^1H NMR (200 MHz) δ 9.17 (dd, 1 H, $J_{2,NH}$ = 9.7, $J_{NH,=CH}$ = 13.7, NH), 8.00-7.02 (m, 10 H, 2 Ph), 7.80 (d, 1 H, =CH), 5.75 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.7, H-3), 5.37 (t, 1 H, $J_{4,5}$ = 9.7, H-4), 5.21 (t, 1 H, $J_{2',3'} = J_{3',4'}$ = 9.3, H-3'), 5.06 (t, 1 H, $J_{4',5'}$ = 9.3, H-4'), 5.05 (dd, 1 H, $J_{1',2'}$ = 7.6, H-2'), 4.97 (d, 1 H, $J_{1,2}$ = 3.4, H-1), 4.52 (d, 1 H, H-1'), 4.22 (dd, 1 H, $J_{5',6'a}$ = 4.6, $J_{6'a,6'b}$ = 11.8, H-6'a), 4.18 (m, 1 H, H-5), 4.11-4.02 (m, 2 H, H-6a, 6'b), 3.76, 3.58 (each s, each 3 H, CO_2Me), 3.73-3.58 (m, 3 H, H-2, 5', 6b), 3.50 (s, 3 H, OMe), 2.04 (s, 9 H, 3 Ac), 2.14 (s, 3 H, Ac); ^{13}C NMR (50.3 MHz) δ 170.5, 170.1, 169.4, 169.3, (4 $COCH_3$), 168.6 (C=O chelated), 165.3 (2 C, 2 *C*OPh), 165.0 (C=O free), 158.7 (=CH), 133.4-128.1 (12 C, 2 Ph), 100.7 (C-1'), 97.9 (C-1), 91.1 (=C), 72.5 (C-3'), 71.6 (2C, C-3, 5'), 70.9 (C-2'), 68.8, 68,5 (C-5, 4), 68.1 (C-4'), 67.6 (C-6), 62.2 (C-2), 61.7 (C-6'), 55.6 (OMe), 51.3, 50.8 (2 CO_2CH_3), 20.6 ($COCH_3$), 20.5 (2 C, 2 $COCH_3$), 20.4 ($COCH_3$); EIMS *m/z* 873 (1, $M^{+\cdot}$), 331 (5, $C_{14}H_{19}O_9^+$), 169 (12, 331-Ac_2O), 122 (60, $BzOH^+$), 105 (100, Bz^+), 77 (35, Ph^+); FABMS *m/z* 896 (30, $[M+Na]^+$), 874 (12, $[M+H]^+$). HREIMS obsd 873.2553, calcd for $C_{41}H_{47}O_{20}N$ 873.2714. HRFABMS obsd 874.2801, calcd for $C_{41}H_{48}O_{20}N$+H 874.2769. Anal. Calcd for $C_{41}H_{47}O_{20}N$: C, 56.35; H, 5.42; N, 1.60. Found: C, 56.20; H, 5.14; N, 1.56.

Methyl 3,4-di-*O*-benzoyl-2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-α-D-glucopyranoside (**16**). Was an amorphous and hygroscopic solid (0.04 g, 8%) which had R_f 0.37 (EtOAc:hexane 3:1); $[\alpha]^{22}_D$ +118.7° (*c* 0.6); UV 231 (ε 18700), 279 nm (ε 27900); IR ν_{max} 3509, 3285, 3011, 2951, 2843, 1730, 1715 (C=O free), 1667 (C=O chelated), 1609, 1451, 1385, 1269, 1090, 756, 710 cm^{-1}; ^1H NMR (200 MHz) δ 9.21 (dd, 1 H, $J_{2,NH}$ = 8.5, $J_{NH,=CH}$ = 14.6, NH), 7.93, (d, 1 H, =CH), 7.93-7.28 (m, 10 H, 2 Ph), 5.88 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.9, H-3), 5.41 (t, 1 H, $J_{4,5}$ = 9.9, H-4), 5.02 (d, 1 H, $J_{1,2}$ = 3.5, H-1), 4.01 (m, 1 H, H-5), 3.79-3.49 (m, 3 H, H-2,6,6'), 3.77, 3.56 (each s, each 3 H, 2 CO_2Me), 3.47 (s, 3 H, OMe), 2.82 (bs, 1 H, OH); ^{13}C NMR (50.3 MHz) δ 168.6 (C=O chelated), 165.4 (C=O free), 166.3, 165.3 (2 *C*OPh), 158.7 (=CH), 133.7-128.2 (12 C, 2 Ph), 98.1 (C-1), 91.1 (=C), 71.2 (C-3), 70.1, 69.0 (C-4,5), 62.2 (C-2), 60.6 (C-6), 55.6 (OMe), 51.2, 50.8 (2 CO_2CH_3); EIMS *m/z* 543 (5, $M^{+\cdot}$), 512 (2, $M^{+\cdot}$-MeO·), 480 (1, 512-MeOH), 421 (4, $M^{+\cdot}$-BzOH), 389 (3, 421-MeOH), 122 (18, $BzOH^+$), 105 (100, Bz^+), 77 (20, Ph^+), 60 (5, $AcOH^+$), 43 (5, Ac^+). HREIMS obsd 543.1768, calcd for $C_{27}H_{29}O_{11}N$ 543.1740.

Methyl 3,4-di-*O*-benzyl-2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-6-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranoside (**23**). Was an amorphous and hygroscopic solid (0.15 g, 25%) which had R_f 0.56 (EtOAc:hexane 2:1); $[\alpha]^{22}_D$ +81.9° (*c* 0.8); UV 281 nm (ε 16200); IR ν_{max} 3275, 3028, 2949, 2855, 1757, 1718 (C=O free), 1663 (C=O chelated), 1607, 1445, 1379, 1229, 1240, 1053, 750, 710 cm^{-1}; ^1H NMR (200 MHz) δ 9.21 (dd, 1 H, $J_{2,NH}$ = 9.1, $J_{NH,=CH}$ = 12.5, NH), 8.04 (d, 1 H, =CH), 7.37-7.12 (m, 10 H, 2 Ph), 5.20 (t, 1 H, $J_{2',3'} = J_{3',4'}$ = 9.1, H-3'), 5.10 (t, 1 H, $J_{4',5'}$ = 9.1, H-4'), 5.07 (dd, 1 H, $J_{1',2'}$ = 7.6, H-2'), 4.83, 4.55 (each d, each 1 H, $^2J_{H,H}$ = 11.5,

C*H*$_2$Ph), 4.79 (d, 1 H, $J_{1,2}$ = 3.7, H-1), 4.72, 4.47 (each d, each 1 H, $^2J_{H,H}$ = 10.7, C*H*$_2$Ph), 4.55 (d, 1 H, H-1'), 4.28 (dd, 1 H, $J_{5',6'a}$ = 4.7, $J_{6'a,6'b}$ = 12.3, H-6'a), 4.12 (dd, 1 H, $J_{5',6'b}$ = 2.7, H-6'b), 4.10 (m, 1 H, H-6a), 3.85-3.66 (m, 4 H, H-3, 5, 5', 6b), 3.81, 3.67 (each s, each 3 H, 2 CO_2Me), 3.48 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.1, H-4), 3.43 (s, 3 H, OMe), 3.31 (td, 1 H, $J_{2,3}$ = 9.1, H-2), 2.06, 2.02, 2.01, 1.97 (each s, each 3 H, 4 Ac); ^{13}C NMR (50.3 MHz) δ 170.5, 170.2, 169.4, 169.2, (4 *C*OCH$_3$), 168.9 (C=O chelated), 165.6 (C=O free), 159.8 (=CH), 137.5-127.5 (12 C, 2 Ph), 100.5 (C-1'), 98.0 (C-1), 90.1 (=C), 80.9 (C-3), 77.8 (C-4), 76.1, 74.9 (2 *C*H$_2$Ph), 72.8 (C-3'), 71.8 (C-5'), 71.1 (C-2'), 70.1 (C-5), 68.2 (C-4'), 67.7 (C-6), 63.5 (C-2), 61.8 (C-6'), 55.3 (OMe), 51.2, 50.9 (2 CO_2*C*H$_3$), 20.6 (2 C, 2 COCH$_3$), 20.5 (2 C, 2 COCH$_3$); EIMS *m/z* 845 (1, M$^{+\cdot}$), 814 (1, M$^{+\cdot}$-MeO$^{\cdot}$), 754 (1, M$^{+\cdot}$-tropylium$^+$), 331 (10, $C_{14}H_{19}O_9^+$), 169 (35), 91 (100, tropylium$^+$), 77 (15, Ph$^+$), 60 (10, AcOH$^+$), 43 (20, Ac$^+$). HREIMS obsd 845.3101, calcd for $C_{41}H_{51}O_{18}N$ 845.3106.

Methyl 3,4-di-*O*-benzyl-2-deoxy-2-[(2',2'-dimethoxycarbonylvinyl)amino]-α-D-glucopyranoside (**17**). Was an amorphous and hygroscopic solid (0.001 g, 3%) which had *Rf* 0.32 (EtOAc:hexane 2:1); [α]$^{22}_D$ +168.3° (*c* 0.6); UV 281 nm (ε 9600); IR ν$_{max}$ 3503, 3277, 3047, 2949, 1715 (C=O free), 1663 (C=O chelated), 1607, 1445, 1381, 1233, 1088, 745, 698 cm^{-1}; ^{1}H NMR (200 MHz) δ 9.22 (dd, 1 H, $J_{2,NH}$ = 9.7, $J_{NH,=CH}$ = 12.5, NH), 8.04 (d, 1 H, =CH), 7.35-7.20 (m, 10 H, 2 Ph), 4.88, 4.49 (each d, each 1 H, $^2J_{H,H}$ = 11.4, C*H*$_2$Ph), 4.76, 4.68 (each d, each 1 H, $^2J_{H,H}$ = 11.4, C*H*$_2$Ph), 4.79 (d, 1 H, $J_{1,2}$ = 3.3, H-1), 3.81-3.70 (m, 5 H, H-3,4,5,6,6'), 3.81, 3.66 (each s, each 3 H, 2 CO_2Me), 3.43 (s, 3 H, OMe), 3.37 (td, 1 H, $J_{2,3}$ = 9.7, H-2), 2.30 (bs, 1 H, OH); ^{13}C NMR (50.3 MHz) δ 169.4 (C=O chelated) 165.7 (C=O free), 159.9 (=CH), 137.6-127.9 (12 C, 2 Ph), 98.1 (C-1), 90.1 (=C), 80.9 (C-3), 77.4 (C-4), 76.0, 75.0 (2 *C*H$_2$Ph), 71.3 (C-5), 63.7 (C-2), 61.4 (C-6), 55.3 (OMe), 51.3, 50.9 (2 CO_2*C*H$_3$); EIMS *m/z* 515 (8, M$^{+\cdot}$), 484 (5, M$^{+\cdot}$-MeO$^{\cdot}$), 452 (5, 484-MeOH), 344 (5, 452-BnOH), 304 (40, 484-BnOCH$_2$COCH$_2$OH), 272 (6, 304-MeOH), 91 (100, tropylium$^+$), 77 (6, Ph$^+$). HREIMS obsd 515.2118, calcd for $C_{27}H_{33}O_9N$ 515.2155.

Ethyl 3,4-di-*O*-acetyl-2-amino-2-deoxy-6-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranoside hydrobromide (**24**). To a solution of **18** (1.05 g, 1.39 mmol) in dry ether (6 mL) was added 33% HBr in acetic acid (6 mL) at 0 °C. The mixture was kept at 0 °C for 2.5 h and then poured into dry ether (50 mL). The hygroscopic solid product (0.86 g, 88%) was washed with ether (30 mL); [α]$^{22}_D$ +63.2° (*c* 0.9); UV 304 nm (ε 100); IR ν$_{max}$ 3000, 2938, 1746, 1653, 1385, 1240, 1044 cm^{-1}; ^{1}H NMR (200 MHz) δ 8.34 (bs, 3 H, NH_3^+) 5.42 (d, 1 H, $J_{1,2}$ = 2.9, H-1), 5.37 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.5, H-3), 5.19 (t, 1 H, $J_{2',3'}$ = $J_{3',4'}$ = 9.3, H-3'), 5.06 (t, 1 H, $J_{4',5'}$ = 9.3, H-4'), 4.92 (t, 1 H, $J_{4,5}$ = 9.5, H-4), 4.98 (dd, 1 H, $J_{1',2'}$ = 7.8, H-2'), 4.51 (d, 1 H, H-1'), 4.24 (dd, 1 H, $J_{5',6'a}$ = 4.4, $J_{6'a,6'b}$ = 12.3, H-6'a), 4.11 (dd, 1 H, $J_{5',6'b}$ = 2.4, H-6'b), 4.06 (m, 1 H, H-5), 3.92 (m, 1 H, H-6a), 3.79-3.61 (m, 3 H, C*H*$_2$CH$_3$, H-5'), 3.79-3.50 (m, 1 H, H-2), 3.61-3.50 (m, 1 H, H-6b), 2.16, 2.08, 2.04, 2.03, 2.00, 1.99 (each s, each 3 H, 6 Ac), 1.32 (t, 3 H, $^3J_{H,H}$ = 7.0, CH$_2$C*H*$_3$); ^{13}C NMR (50.3 MHz) δ 171.5, 170.6, 170.1, 169.4 (4 *C*OCH$_3$), 169.3 (2 C, 2 *C*OCH$_3$), 100.6 (C-1'), 94.3 (C-1), 72.5 (C-3'), 71.7 (C-5'), 70.8 (C-2'), 69.6 (C-3), 68.3, 67.6 (C-4, 5), 68.1 (C-4'), 67.5 (C-6), 64.7 (*C*H$_2$CH$_3$), 61.6 (C-6'), 52.9 (C-2), 21.7, 20.6 (2 COCH$_3$), 20.5, 20.4 (each 2 C, COCH$_3$), 15.0 (CH$_2$*C*H$_3$); FABMS *m/z* 702 (10, M$^{+\cdot}$), 622 (60, M$^{+\cdot}$-Br$^{\cdot}$), 576 (5, M$^{+\cdot}$-Br$^{\cdot}$-EtOH), 516 (22, M$^{+\cdot}$-Br$^{\cdot}$-EtOH-AcOH), 331 (33, $C_{14}H_{19}O_9^+$). HREIMS obsd 622.2329, calcd for $C_{26}H_{41}O_{16}$NBr-Br 622.2347.

Ethyl 2-amino-3,4-di-*O*-benzoyl-2-deoxy-6-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranoside hydrobromide (**25**). To a solution of **19** (2.0 g, 2.27 mmol) in dry ether (10 mL) was added 33% HBr in acetic acid (2.5 mL) at rt. The mixture was kept at rt for 1 h and then evaporated to dryness. The residue was triturated with dry ether, collected and washed with ether (15 mL). The solid product (1.49 g, 80%) had [α]$^{22}_D$ -15.5° (*c* 0.7); UV 233 nm (ε 16200); IR ν$_{max}$ 3015, 3000, 2961, 2899, 1750, 1730, 1445, 1373, 1240, 1229, 1090, 1042 cm^{-1}; ^{1}H NMR (200 MHz) δ 8.46 (bs, 3 H, NH_3^+), 7.89-7.23 (m, 10 H, 2 Ph), 5.72 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.6, H-3), 5.51 (d, 1 H, $J_{1',2'}$ = 7.7, H-1'), 5.49 (d, 1 H, $J_{1,2}$ = 3.2, H-1), 5.25 (t, 1 H, $J_{4,5}$ = 9.6, H-4), 5.17 (t, 1 H, $J_{2',3'}$ = $J_{3',4'}$ = 9.6, H-3'), 5.02 (t, 1 H, $J_{4',5'}$ = 9.6, H-4'), 4.97 (dd, 1 H, H-2'), 4.22-4.17 (m, 2 H, H-5, 6'a), 4.05-3.93 (m, 2 H, H-6a, 6'b), 3.72-3.56 (m, 5 H, C*H*$_2$CH$_3$, H-2, 5', 6b), 2.04, 2.00, 1.99, 1.97 (each s, each 3 H, 4 Ac), 1.26 (t, 3 H, $^3J_{H,H}$ = 7.0, CH$_2$C*H*$_3$); ^{13}C NMR (50.3 MHz) δ 170.5, 170.1, 169.3, 169.2 (4 *C*OCH$_3$), 166.6, 165.0 (2 *C*OPh), 128.1-133.5 (12 C, 2 Ph), 100.6 (C-1'), 94.5 (C-1), 72.6 (C-3'),

71.6 (C-5'), 70.9 (C-2'), 70.5 (C-3), 68.7, 68.6 (C-4, 5), 68.1 (C-4'), 67.8 (C-6), 64.8 (CH_2CH_3), 61.7 (C-6'), 52.9 (C-2), 20.6, 20.5 (2 $COCH_3$), 20.4 (2 C, 2 $COCH_3$), 15.0 (CH_2CH_3); FABMS *m/z* 826 (15, $M^{+\cdot}$), 746 (100, $M^{+\cdot}$-Br$^{\cdot}$), 700 (8, $M^{+\cdot}$-Br$^{\cdot}$-EtOH), 578 (50, $M^{+\cdot}$-Br$^{\cdot}$-EtOH-BzOH), 331 (90, $C_{14}H_{19}O_9^+$). Anal. Calcd for $C_{36}H_{44}O_{16}NBr$: C, 52.30; H, 5.36; N, 1.69. Found: C, 52.06; H, 5.06; N, 1.61.

Methyl 3,4-di-*O*-acetyl-2-amino-2-deoxy-6-*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-D-glucopyranoside hydrochloride (**26**). Chlorine was bubbled through a solution of **21** (0.154 g, 0.21 mmol) in dichloromethane (10 mL) until total consumption of the starting material was observed by TLC (dichloromethane:methanol 20:1). The solvent was evaporated and the residue was treated with dry ether (10 mL) until a solid product was obtained. This product filtered and washed with dry ether (3×10 mL) was a white and amorphous solid (0.009 g, 67%) which had $[\alpha]^{22}_D$ +60.0° (*c* 1.0); UV 301 nm (ε 200); IR ν_{max} 3000, 2963, 2909, 1753, 1597, 1437, 1377, 1240, 1233, 1088, 1038 cm^{-1}; ^1H NMR (200 MHz) δ 8.68 (bs, 3 H, NH_3^+), 5.36 (t, 1 H, $J_{2,3} = J_{3,4} = 9.0$, H-3), 5.22 (m, 1 H, H-1), 5.20 (t, 1 H, $J_{2',3'} = J_{3',4'} = 9.4$, H-3'), 5.07 (t, 1 H, $J_{4',5'} = 9.4$, H-4'), 4.98 (dd, 1 H, $J_{1',2'} = 7.8$, H-2'), 4.91 (t, 1 H, $J_{4,5} = 9.0$, H-4), 4.53 (d, 1 H, H-1'), 4.27 (dd, 1 H, $J_{5',6'a} = 4.4$, $J_{6'a,6'b} = 12.4$, H-6'a), 4.13 (dd, 1 H, $J_{5',6'b} = 1.7$, H-6'b), 4.03-3.86 (m, 3 H, H-5, 6a, 6b), 3.69 (m, 1 H, H-5'), 3.61-3.55 (m, 1 H, H-2), 3.49 (s, 3 H, OMe), 2.14, 2.10, 2.06, 2.02 (each s, each 3 H, 4 Ac), 2.04 (s, 6 H, 2 Ac); ^{13}C NMR (50.3 MHz) δ 171.2, 170.5, 170.0, 169.3 ($COCH_3$), 169.2 (2 C, 2 $COCH_3$), 100.6 (C-1'), 95.8 (C-1), 72.5 (C-3'), 71.7 (C-5'), 70.8 (C-2'), 69.5 (C-3), 68.3 (2C), 67.6 (C-4,5,4'), 67.5 (C-6), 61.6 (C-6'), 55.8 (OMe), 52.8 (C-2), 20.6, 20.5, 20.4 (each 2 C, 6 $COCH_3$); FABMS *m/z* 644 (30, $M^{+\cdot}$), 608 (60, $M^{+\cdot}$-Cl$^{\cdot}$), 576 (3, $M^{+\cdot}$-Cl$^{\cdot}$-MeOH), 516 (20, $M^{+\cdot}$-Cl$^{\cdot}$-MeOH-AcOH), 331 (40, $C_{14}H_{19}O_9^+$). Anal. Calcd for $C_{25}H_{38}O_{16}NCl$: C, 46.62; H, 5.94; N, 2.17. Found: C, 46.34; H, 5.72; N, 2.21.

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20. HREIMS of **27** obsd 672.2463, calcd for $C_{30}H_{42}O_{16}N+H$ 672.2503. EIMS *m/z* 552 (3, $M^{+\cdot}$-AcOH-AcO$^{\cdot}$), 492 (8, $M^{+\cdot}$-2 AcOH-AcO$^{\cdot}$), 458 (20, $M^{+\cdot}$-AcOH-EtO$^{\cdot}$), 398 (3, $M^{+\cdot}$-2 AcOH-BnOH-EtO$^{\cdot}$), 331 (20, $C_{14}H_{19}O_9^+$), 91 (100, tropylium$^+$).
21. For complete procedure see for example 15b.
22. To a stirred solution of acetobromoglucose (0.60 g, 1.5 mmol) in dry dichloromethane (10 mL) containing molecular sieves 4 Å (0.25 g) were successively added at rt under nitrogen, **12** (0.88 g, 1.33 mmol) and silver triflate (0.38 g, 1.5 mmol). The mixture was stirred at rt for 15 min under nitrogen, then filtered through Celite. The solution was washed with water (10 mL), saturated aqueous hydrogencarbonate (10 mL), and water (2×10 mL), dried ($MgSO_4$) and concentrated. Column chromatography (EtOAc:hexane 2:1, 3:1, 4:1) of the residue gave **18** (0.22 g, 21%).