Synthesis of Glycosylamines from Glycosyl Isothiocyanates and Bis(tributyltin) Oxide

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The synthesis of glycopyranosylamines is described from the reaction of glycopyranosyl isothiocynates with bis(tributyltin) oxide. The method is simple and efficient allowing, under very mild conditions, the synthesis of *N*-acyl glycopyranosylamines in one pot. The reactions were performed using both 2-deoxy-2-iodo glycopyranosyl isothiocyanates and glycopyranosyl isothiocyanates derived from mono- and disaccharides. Anomerization was observed when the starting materials were α-glycopyranosyl derivatives. The methodology has also been applied for the preparation of several glycosyl amino acids.

Introduction

Cell surface glycolipid and glycoprotein oligosaccharides are known to play important roles in many biological events such as cellular recognition, adhesion and cell growth regulation. A major class of glycoprotein oligosaccharides consists of *N*-linked oligosaccharides which are linked to asparagine by an amide bond.[1,2] Glycosylamines are important compounds in the chemical synthesis of *N*-glycopeptides[3−5] and, therefore, valuable intermediates for the synthesis of glycoconjugates and neoglycoconjugates. The latter two are very useful tools for elucidating the biological roles of oligosaccharides.[6−8]

The most reliable methods for the synthesis of glycosylamines are based on the reaction of a nonprotected carbohydrate with aqueous ammonium hydrogen carbonate,[9,10] the hydrogenolysis of the corresponding azide[11−13] catalyzed by Pd/C,[14−16] Lindlar catalyst,[12,17] PtO_2, Raney-Ni[13,18] or with 1,3-propanedithiol in the presence of triethylamine and methanol.[19−22] The conversion of azides into amines or amino derivatives by the Staudinger reaction[23−25] provides an alternative mild route for the synthesis of *N*-acylglycopyranosylamines.[21,22,26−29] On the other hand, the use of glycosyl isothiocyanates[30−32] as the starting materials has also been described[33−35] as a method to avoid the azide step.

In the context of a project directed towards the study of the reactivity of 2-deoxy-2-iodoglycosyl isothiocyanates,[36] we now report a new method for the synthesis of glycosylamimes from glycosyl isothiocyanates by using bis(tributyltin) oxide.

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Results and Discussion

Several years ago, we described[36] a convenient one-step synthesis of 2-deoxy-2-iodoglycosyl isothiocyanates from glycal monosaccharides and disaccharides by treatment with silica-supported potassium thiocyanate and iodine. By this procedure, the *trans*-diaxial 2-deoxy-2-iodopyranosyl isothiocyanates are obtained as major products and the corresponding *trans*-diequatorial derivatives as the minor products. These 2-deoxy-2-iodo-pyranosyl isothiocyanates are bifunctional compounds with enhanced reactivity due to the presence of two active electrophilic groups — the isothiocyanate function and the halogen group. We thought that the conversion of these 2-deoxy-2-iodo-pyranosyl isothiocyanates into the corresponding glycosyl amino acids could be performed by treatment with an amino acid such as 1-benzyl-*N*-(benzyloxy)carbonyl-L-aspartate in dry toluene and triethylamine following the conditions described by Krepinsky et al.[34] However, when we tried this transformation with compound **1** we isolated the peracetylated D-glucal as the sole product of the reaction. For this reason, we investigated other reaction conditions. Thus, we found that the reaction of the *trans*-diequatorial 2-deoxy-2-iodo derivative **1** with bis(tributyltin) oxide with benzene as solvent in the presence of 3 Å molecular sieves at room temperature, followed by treatment with acetic anhydride/pyridine, led to the *N*-acetyl glucopyranosylamine **2** (77% yield) (see Scheme 1). This result showed that the isothiocyanate function is reduced under very mild conditions by the action of the tin reagent. To the best of our knowledge, the transformation of alkyl and arylisothiocyanates into the corresponding amines has only been reported by Cho et al.[37] with 4-methyl-1,2-benzenedithiol.

Then, we decided to perform the reaction of the 2-deoxy-2-iodo-glycosyl isothiocyanate monosaccharides **3** and **6** with bis(tributyltin) oxide under the same conditions as those described above. In these reactions we observed anomerization and isolated an almost equimolecular mixture of the corresponding amines **4** + **5** and **7** + **8**, respectively (see

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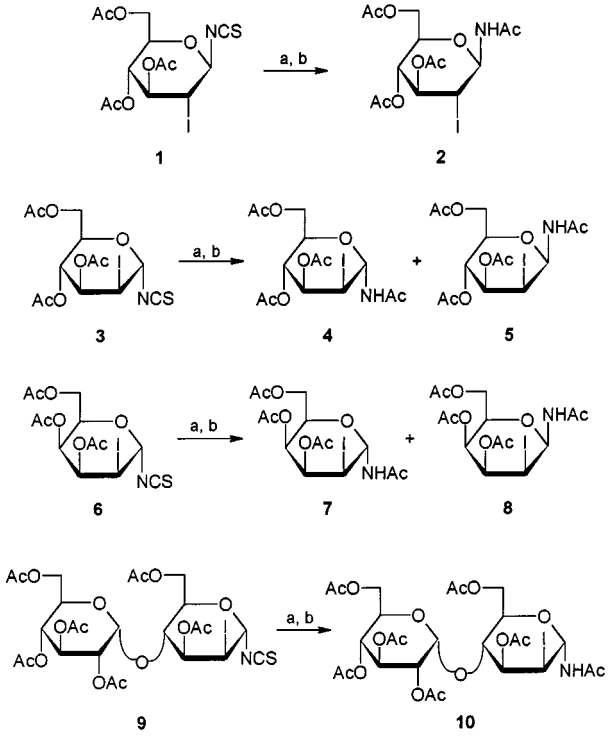


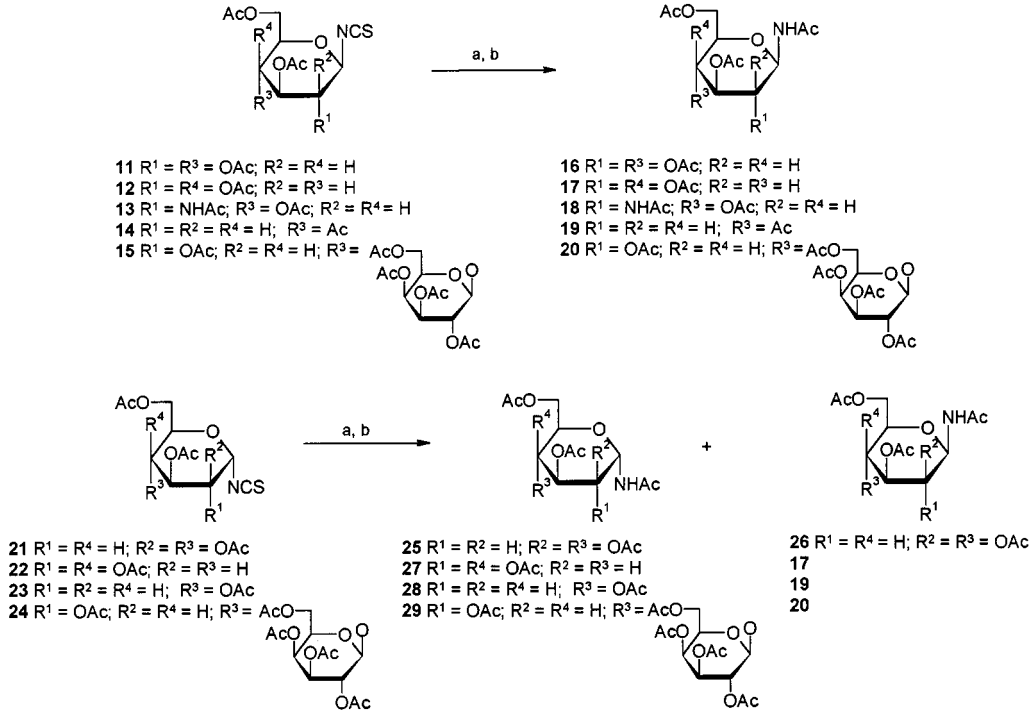
Scheme 1. Preparation of *N*-acetyl-2-deoxy-2-iodo-glycopyranosylamines; reagents and conditions: (a) $(Bu_3Sn)_2O$, benzene, room temp., 3 Å molecular sieves; (b) Ac_2O-py, room temp.

Scheme 1). We have previously described anomerization in the reduction of 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl azide under the Staudinger conditions.[22] Isomerization at the anomeric position has also been observed by Takeda et al.[38] and Shiba et al.[15] in the catalytic hydrogenation of α-D-glycosyl azides. More recently García-Fernández et al. have also described an unexpected base-catalysed anomerization reaction for α- and β-D-mannopyranosyl thioureido derivatives.[39,40]

The ^{1}H NMR spectra of the *N*-acetyl glycopyranosylamines obtained from the reactions described above showed that the preferred conformation of compounds **2**, **5** and **8** is $^4C_1$ in a chloroform solution, as deduced from the *J* values. Thus, compound **2** shows values higher than 9.0 Hz for $J_{1,2}$, $J_{2,3}$, $J_{3,4}$ and $J_{4,5}$, in agreement with an axial disposition for 1-H, 2-H, 3-H, 4-H and 5-H. Compound **5** shows an axial-equatorial relationship for 1,2-H ($J_{1,2}$ = 1.4 Hz) and a *trans*-diaxial arrangement for 3,4-H ($J_{3,4}$ = 9.6 Hz). In compound **8**, the axial-equatorial arrangement between 1,2-H and 3,4-H is in accordance with the $J_{1,2}$ and $J_{3,4}$ values (2.0 and 4.2 Hz, respectively). However, a flip in the conformation is observed in the α-glycopyranosylamines **4** and **7** leading to an unusual $^1C_4$ preferred conformation as deduced from the $J_{1,2}$ value (7.8 and 9.4 Hz for **4** and **7**, respectively) indicative of a diaxial disposition for 1,2-H.

The reaction was also studied in the case of the disaccharide **9**. In this case, the *N*-acetyl glycosylamine **10** was obtained in high yield (94%) without anomerization (see Scheme 1). The analysis of the ^{1}H NMR spectra revealed that, again in this compound, the unit with the iodine group prefers the conformation $^1C_4$ as deduced from the $J_{1,2}$, $J_{2,3}$, $J_{3,4}$ and $J_{4,5}$ values (8.2, 3.4, 4.0 and 4.0 Hz, respectively), in accordance with an equatorial disposition for 3,4,5-H and a diaxial one for 1,2-H.

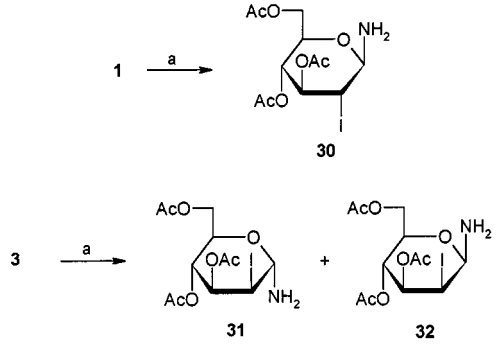
In order to extend this procedure to other substrates we studied the reaction with glycosyl isothiocyanates without



Scheme 2. Preparation of *N*-acetyl-glycopyranosylamines; reagents and conditions: (a) $(Bu_3Sn)_2O$, benzene, room temp., 3 Å molecular sieves; (b) Ac_2O-py, room temp.

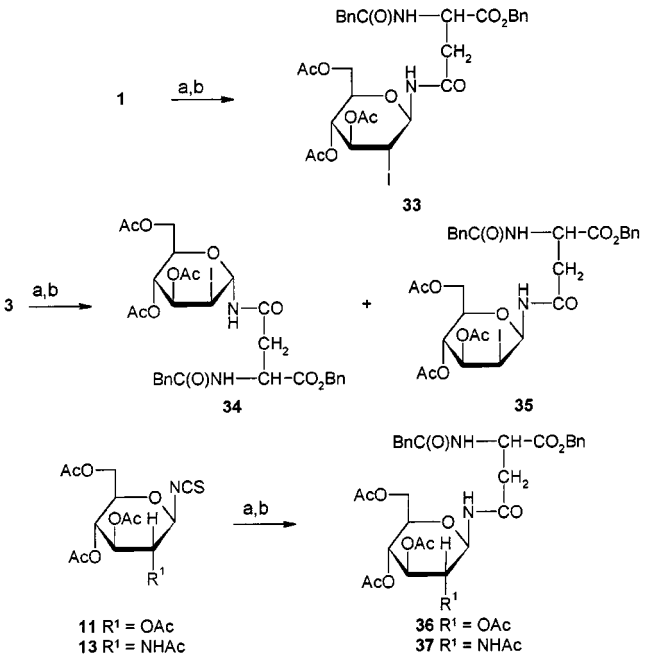
iodine at the C-2 position. For this purpose we selected the peracetylated β-anomer derivatives of D-glucose (**11**), D-galactose (**12**), *N*-acetyl-D-glucosamine (**13**), 2-deoxy-D-glucose (**14**) and lactose (**15**), as well as the α-anomer derivatives of D-mannose (**21**), D-galactose (**22**), 2-deoxy-D-glucose (**23**) and lactose (**24**) (see Scheme 2). All the β-glycopyranosyl derivatives showed a similar behaviour leading to the corresponding *N*-acetyl β-glycopyranosylamines **16**−**20** (36−93% yield) ($J_{1,2} \approx 9.0$ Hz). In all of these reactions anomerization was not detected. However, the α-glycopyranosyl isothiocyanate derivatives underwent anomerization giving rise to an α,β mixture of the *N*-acetyl glycopyranosylamines (**21** → **25** + **26**; **22** → **27** + **17**; **23** → **28** + **19**; **24** → **29** + **20**). For the α-anomer derivatives **25**, **27**, **28** and **29**, we observed that the preferred conformation is $^4C_1$ as deduced from the vicinal coupling constant values and NOE experiments for compounds **25** and **27**. In these compounds, the NOE experiments show correlations between NH, 3-H and 5-H and are consistent with the axial disposition of the NHAc group. Contrary to this observation, the *N*-acetyl-2-deoxy-2-iodo-α-glycopyranosyl derivatives **4**, **7** and **10** show a preferred $^1C_4$ conformation in chloroform solution.

We also investigated the reaction without subsequent treatment with an acylating agent (see Scheme 3). Thus, the reaction of **1** with bis(tributyltin) oxide gave **30**, in high yield (89%), after purification by column chromatography. This product is stable during handling and can be stored for several months at low temperature (−15 °C). A mixture of the α,β anomers **31** + **32** was obtained when the reaction was performed with compound **3**. The anomerization observed when the α-anomer derivatives were used as substrate can happen during the reaction with bis(tributyltin) oxide as well as during the acylation step. Thus, treatment of **27** under the same acetylation conditions previously used leads to a mixture of **27** and **17** in a 10:1 ratio as determined by ^{1}H NMR spectroscopy. It should also be mentioned that acetyl migration to the amino function[12] was not observed in any case. As is the case with the *N*-acetyl derivatives **2** and **5**, compounds **30** and **31** prefer the $^4C_1$ conformation in chloroform solution.



Scheme 3. Preparation of 2-deoxy-2-iodo-glycopyranosylamines; reagents and conditions: (a) $(Bu_3Sn)_2O$, benzene, room temp., 3 Å molecular sieves

Once that the procedure was well established, we again studied the synthesis of glycopyranosyl amino acids, although this time with amino acid chlorides as the acylating agent (see Scheme 4). Reaction of **1**, **3**, **11** and **13** with bis(tributyltin) oxide followed by *N*-acylation with the chloride derivative of α-benzyl *N*-(benzyloxy)carbonyl-L-asparaginate furnished the glycopyranosyl amino acids **33**, **34** + **35, 36** and **37**, respectively (33−53%).



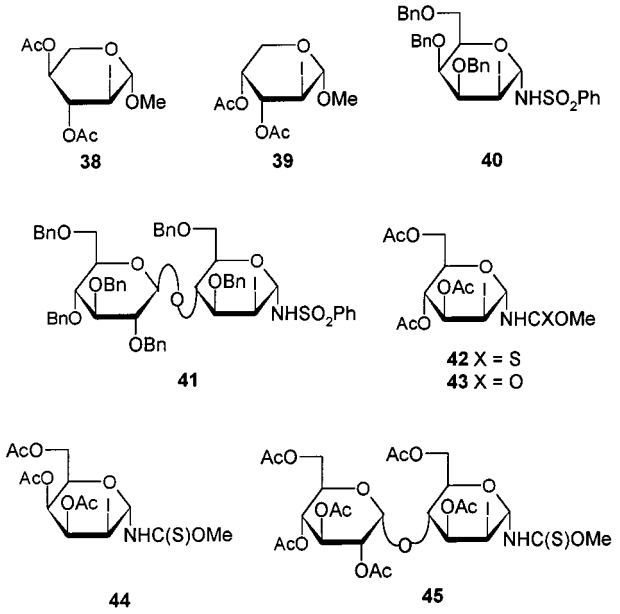
Scheme 4. Preparation of glycopeptides; reagents and conditions: (a) $(Bu_3Sn)_2O$, benzene, room temp., 3 Å molecular sieves; (b) N^{α}-Bn-Asp(Cl)-Obn/py, room temp.

The attempted mechanism that could explain the described reduction of the isothiocyanate to amine consists in the transformation of this function into the corresponding isocyanate by addition of bis(tributyltin) oxide and elimination of bis(tributyltin) sulfide,[41,42] followed by acylation.[43]

An additional comment is needed in relation to the observed conformational change in compounds **4**, **7**, **10** and **34.** As mentioned above, all these compounds prefer a $^1C_4$ conformation in chloroform solution. In this conformation the bulky iodine group and the acetamido group are in an equatorial position. Similar behaviour has been observed in other 2-deoxy-2-iodo-pyranosyl derivatives (compounds **38,**[44] **39,**[44] **40,**[45,46] **41,**[47] **42**−**45**[48]) (see Scheme 5) having an antiperiplanar substituent at the anomeric position in relation to the iodine group. Although a better understanding of the reasons that determine this conformational change is needed, steric factors can be identified as the main cause.

Conclusion

In conclusion, in this paper we have described a simple, efficient and mild one-pot procedure for the preparation of glycopyranosylamines and their *N*-acyl derivatives from glycopyranosyl isothiocyanates using bis(tributyltin) oxide



Scheme 5

as the reductive reagent. We have also applied this methodology to the synthesis of glycopyranosyl amino acids.

Experimental Section

General Remarks: TLC was performed on Merck silica gel $60F_{245}$ aluminium sheets with detection by charring with 5% H_2SO_4 in EtOH and by UV light when applicable. Flash column chromatography on silica gel (Merck or Scharlau, 230−400 mesh. ASTM) with the solvent systems indicated in Table 1. All the evaporations were carried out under reduced pressure at 40 °C. Solutions in non-hydroxylic solvents were dried with anhydrous Na_2SO_4. Melting points were determined with a Reichert hotplate microscope and are uncorrected. Optical rotations were measured at 24 °C with a Perkin−Elmer 141 Polarimeter. NMR spectra were recorded at room temperature on a Bruker AM-300 spectrometer. ^1H chemical shifts are given in ppm and referenced to internal $CHCl_3$ (δ = 7.26) for $CDCl_3$ solutions. ^{13}C chemical shifts are given in ppm and referenced to $CDCl_3$ (δ = 77.0). *J* values are given in Hz. Assignments were based on COSY, HMQC, NOESY, DEPT and APT. Mass spectra were recorded with a Fissons VG Autospec-Q spectrometer. Anhydrous solvents were prepared according to standard procedures and were freshly distilled prior to use. Compounds **1**, **3**, **6** and **9** were prepared from the corresponding glycals following the reported procedure by Santoyo-González et al.[36] The per-*O*-acetylated-glycopyranosyl isothiocyanates **11**−**15** and **21**−**24**[31] were prepared from the corresponding glycopyranosyl halides by treatment with KSCN in MeCN under phase-transfer conditions following the methodology of Camarasa et al.[49] or the method described by Lindhorst et al.[50]

General Procedure for the Synthesis of *N*-Acylglycosylamines: To a solution of the glycosyl isothiocyanate in dry benzene was added bis(tributyltin) oxide in the presence of 3 Å molecular sieves. The reaction was kept at room temp. until TLC showed complete disappearance of the starting material. Acetic anhydride or N^{α}-Bn-Asp(Cl)-OBn (see Table) and pyridine was then added and the reaction mixture was maintained at room temp. for an additional 12 h. Addition of EtOAc was followed by filtration of the molecular sieves and the resulting solution was successively treated with a 5% hydrochloric acid solution, a saturated aqueous $NaHCO_3$ solution and water. The organic layer was finally dried, filtered and evaporated under vacuum to give a crude product that was purified by column chromatography (see Table 1).

***N*-Acetyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-β-D-glucopyranosylamine (2):** Solid with m.p. 183−185 °C (dec.); $[\alpha]_D$ = +75° (*c* = 1, chloroform). − ^1H NMR (300 MHz, $CDCl_3$): δ = 2.03, 2.07, 2.07,

Table 1. Starting material, reaction and purification conditions, and compounds obtained

Starting material (g, mmol)	$(Bu_3Sn)_2O$ (mL, mmol)	Benzene (mL)	Time (h)	Acylating agent [a] Py (mL)	Chromatographic eluting solvent	Compound (g, % yield)
1 (0.31, 0.67)	0.5, 1.0	10	14	A (2)-(1)	Ether	**2** (0.24, 77)
3 (0.86, 1.87)	1.43, 2.8	60	6	A (5)-(4)	EtOAc	**4** (0.31, 36) and **5** (0.26, 30)
6 (0.52, 1.14)	0.87, 1.70	50	20	A (3)-(2)	EtOAc-hexane 3:1 then AcOEt	**7** (0.25, 49) and **8** (0.19, 37)
9 (0.33, 0.42)	0.32, 0.64	40	24	A (3)-(2)	EtOAc-hexane 3:1	**10** (0.32, 94)
11 (0.33, 0.85)	0.64, 1.27	30	30	A (2)-(1)	Ether then EtOAc	**16** (0.28, 86)
12 (0.39, 1.0)	0.76, 1.5	40	12	A (3)-(2)	EtOAc-Ether 1:3	**17** (0.28, 73)
13 (0.39, 1.0)	0.76, 1.5	40	16	A (3)-(2)	EtOAc	**18** (0.14, 36)
14[b]	0.35, 0.7	25	16	A (3)-(2)	EtOAc	**19** (0.06, 39[c])
15 (0.59, 0.9)	0.67, 1.3	50	40	A (4)-(2)	Ether then EtOAc	**20** (0.53, 90)
21 (0.59, 1.5)	1.16, 2.3	40	12	A (3)-(2)	EtOAc	**25** + **26** (0.35, 83)
22 (0.41, 1.1)	0.8, 1.6	30	24	A (4)-(2)	Ether then EtOAc	**17** (0.04, 10), **17** + **27** (0.16, 38) and **27** (0.15, 38)
23 [d]	1.1, 2.2	35	6	A (3)-(3)	EtOAc	**28** + **19** (2:1) (0.18, 36[e])
24 (0.32, 0.47)	0.36, 0.7	25	40	A (3)-(2)	EtOAc	**29** + **20** (0.22, 70)
1 (0.62, 1.35)	1.0, 2.0	25	14		Ether	**30** (0.5, 89)
3 (1.7, 3.72)	2.8, 5.5	30	6		Ether	**31** (1.0, 66), **31** + **32** (0.47, 30)
1 (0.46, 1.0)	0.76, 1.5	40	14	B (1.5)-(3)	EtOAc-Ether 1:3	**33** (0.27, 36)
3 (0.37, 0.84)	0.67, 1.26	25	18	B (1.3)-(3)	EtOAc-Ether 1:3	**34** (0.18, 29), **35**[f] (0.07, 11)
11 (0.24, 0.62)	0.47, 0.93	25	30	B (0.93)-(1)	Ether	**36** (0.18, 42)
13 (0.4, 1.0)	0.76, 1.5	25	16	B (0.4)-(3)	EtOAc-Ether 1:3	**37** (0.37, 53)

[a] A = Ac_2O (mL); B = N^{α}-Bn-Asp(Cl)-OBn.(mmol). − [b] Compound **14** was prepared as described from compound **1** (0.21 g, 0.46 mmol) and directly used without purification. − [c] Overall yield from **1**. − [d] Compound **24** was prepared as described from compound **3** (0.68 g, 1.5 mmol) and directly used without purification. − [e] Overall yield from **3**. − [f] This compound was isolated together with sligth amounts of **34** after repeated purification by column chromatography.

2.10 (3 s, 12 H, 4 MeCO), 3.87 (ddd, J = 10.1, 4.4 and 2.1 Hz, 1H, H-5), 3.92 (t, J = 10.6 Hz, 1 H, H-2), 4.07 (dd, J = 12.5 and 2.1 Hz, 1 H, H-6′), 4.34 (dd, J = 12.5 and 4.4 Hz, 1 H, H-6), 4.97 (dd, J = 10.0 and 9.2 Hz, 1 H, H-4), 5.35 (dd, J = 10.8 and 9.1 Hz, 1 H, H-3), 5.49 (t, J = 10.0 Hz, 1 H, H-1), 6.17 (d, J = 9.6 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 20.8, 23.3 (*Me*CO), 27.8 (C-2), 61.8 (C-6), 68.6, 74.0, 76.1 (C-3,4,5), 80.7 (C-1), 164.7, 169.4, 169.7, 170.6 (CO). − HRMS FAB+ ($C_{14}H_{20}INNaO_8$ [M + Na]$^+$): calcd. 480.01314; found. 480.01213.

***N*-Acetyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-D- (4) and -β-D-Mannopyranosylamine (5):** Compound **5** eluted first and was isolated as a solid: m.p. 63 °C; $[\alpha]_D$ = −19 (c = 1.7, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.04, 2.06, 2.07, 2.11 (4s, 12 H, 4 MeCO) 3.83 (ddd, J = 9.9, 4.7 and 2.3 Hz, 1 H, H-5), 4.12 (dd, J = 12.3 and 2.3 Hz, 1 H, H-6′), 4.22 (dd, J = 12.4 and 4.8 Hz, 1 H, H-6), 4.49 (dd, J = 9.6 and 4.1 Hz, 1 H, H-3), 4.70 (dd, J = 4.1 and 1.4 Hz, 1 H, H-2), 4.78 (d, J = 9.2 and 1.4 Hz, 1 H, H-1), 5.35 (t, J = 9.7 Hz, 1 H, H-4), 6.46 (d, 1 H, J = 9.2 Hz, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 20.7, 20.9 (3 *Me*COO), 23.3 (*Me*CONH), 38.5 (C-2), 62.0 (C-6), 66.8 (C-4), 71.7 (C-3), 74.6 (C-5), 75.4 (C-1), 169.2, 169.3, 169.6, 170.5 (4 CO). − HRMS FAB+ ($C_{14}H_{20}INNaO_8$ [M + Na]$^+$): calcd. 480.0131; found 480.0141.

Compound **4** eluted second and was isolated as a solid: m.p. 132−134 °C (dec.); $[\alpha]_D$ = +19.5 (c = 2, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.06, 2.10, 2.10, 2.18 (4s, 12 H, 4 MeCO), 4.14 (m, 1 H, H-5), 4.31 (dd, J = 11.9 and 4.8 Hz, 1 H, H-6′), 4.41 (dd, J = 11.9 and 6.7 Hz, 1 H, H-6), 4.51 (dd, J = 6.8 and 3.5 Hz, 1 H, H-2), 4.96 (dd, J = 5.4 and 3.5 Hz, 1 H, H-3), 5.02 (dd, J = 5.4 and 4.9 Hz, 1 H, H-4), 5.79 (t, J = 7.8 Hz, 1 H, H-1), 6.29 (d, J = 8.1 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 20.8, 21.0 (*Me*CO), 23.4 (*Me*CONH), 26.6 (C-2), 61.2 (C-6), 67.5 (C-4), 70.5 (C-3), 73.2 (C-5), 76.3 (C-1), 169.3, 169.4, 170.0, 170.6 (CO). − HRMS FAB+ ($C_{14}H_{20}INNaO_8$ [M + Na]$^+$): calcd. 480.0131; found 480.0134.

***N*-Acetyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-D- (7) and *N*-Acetyl-3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-β-D-talopyranosylamine (8):** Compound **8** eluted first and was isolated as a solid: m.p. 70−72 °C; $[\alpha]_D$ = −18 (c = 1.5, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.03, 2.07, 2.08, 2.16 (4s, 12 H, 4 *Me*CO), 4.23−4.08 (m, 3 H, H-5,6,6′), 4.48 (dd, J = 4.5 and 1.8 Hz, 1 H, H-2), 4.74 (dd, J = 9.3 and 2.0 Hz, 1 H, H-1), 4.84 (t, J = 4.2 Hz, 1 H, H-3), 5.34 (d, J = 3.6 Hz, 1 H, H-4), 6.49 (d, J = 9.2 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 20.7, 20.8 (3 *Me*CO), 23.4 (*Me*CONH), 30.9 (C-2), 61.6 (C-6), 64.4 (C-4), 68.1 (C-3), 73.9 (C-5), 76.4 (C-1), 169.4, 169.9, 170.4 (CO). − HRMS FAB+ ($C_{14}H_{20}INNaO_8$ [M + Na]$^+$): calcd. 480.0131; found 480.0132.

Compound **7** eluted second and was isolated as a syrup: $[\alpha]_D$ = +25 (c = 1, pyridine). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05, 2.05, 2.09, 2.23 (3 s, 12 H, 4 MeCO), 4.32 (dd, J = 9.5 and 3.0 Hz, 1 H, H-2), 4.43−4.32 (m, 2 H, H-5,6′), 4.68 (m, 1 H, H-6), 5.27 (dd, J = 6.1 and 3.0 Hz, 1 H, H-4), 5.58 (t, J = 3.0 Hz, 1 H, H-3), 5.73 (t, J = 9.4 Hz, 1 H, H-1), 6.34 (d, J = 9.1 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 20.9, 21.0 (3 *Me*CO), 23.4 (*Me*CONH), 25.6 (C-2), 60.1 (C-6), 66.6 (C-4), 70.3 (C-3), 72.9 (C-5), 73.6 (C-1), 169.5, 169.6, 170.0, 170.6 (4 CO). − HRMS FAB+ ($C_{14}H_{20}INNaO_8$ [M + Na]$^+$): calcd. 480.0131; found 480.0128.

***N*-Acetyl-3,6-di-*O*-acetyl-2-deoxy-2-iodo-4-*O*-(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-mannopyranosylamine(10):** Isolated as a solid with m.p. 90 °C; $[\alpha]_D$ = +71 (c = 1, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02, 2.04, 2.06, 2.08, 2.09, 2.09, 2.17 (7 s, 21 H, 7 MeCO), 3.87 (t, J = 4.0 Hz, 1 H, H-4), 4.17−4.07 (m, 3 H, H-5′,6′,6′), 4.29 (m, 1 H, H-5), 4.36 (m, 2 H, H-6,6), 4.51 (dd, J = 8.2 and 3.4 Hz, 1 H, H-2), 4.90 (dd, J = 10.3 and 3.9 Hz, 1 H, H-2′), 4.92 (m, 1 H, H-3), 5.00 (t, J = 9.7 Hz, 1 H, H-4′), 5.29 (d, J = 3.8 Hz, 1 H, H-1′), 5.43 (t, J = 9.9 Hz, 1 H, H-3′), 5.75 (t, J = 8.7 Hz, 1 H, H-1), 6.54 (d, J = 9.0 Hz, 1 H, NH). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.6, 20.7, 20.8, 21.0 (*Me*CO), 23.3 (*Me*CO), 26.0 (C-2), 61.4 (C-6′), 61.9 (C-6), 68.4 (C-5′), 68.5 (C-4′), 69.8 (C-3′), 70.3 (C-2′), 72.6 (C-3), 73.7, 73.9 (C-4,5), 75.1 (C-1), 96.8 (C-1′), 169.5, 169.6, 170.0, 170.1, 170.3, 170.5, 170.8 (CO). − HRMS FAB+ ($C_{26}H_{36}INNaO_{16}$ [M + Na]$^+$): calcd. 768.0977; found. 768.0969.

***N*-Acetyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (16):** Isolated as a solid with m.p. 156−158 °C(ref.[51] 163 °C and ref.[52] 163−164 °C); $[\alpha]_D$ = +17 (c = 2, chloroform) [ref.[51] +17° (c = 1, chloroform) and ref.[52] +17.4° (chloroform)]. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.83, 1.86, 1.87, 1.89, 1.92 (5s, 15 H, 5 MeCO), 3.68 (ddd, J = 10.1, 4.4 and 2.1 Hz, 1 H, H-5), 3.92 (dd, J = 12.5 and 2.1 Hz, 1 H, H-6′), 4.15 (dd, J = 12.5 and 4.5 Hz, 1 H, H-6), 4.76 (t, J = 9.5 Hz, 1 H, H-2), 4.90 (dd, J = 9.9 and 9.5 Hz, 1 H, H-4), 5.10 (t, J = 9.6 Hz, 1 H, H-3), 5.15 (t, J = 9.4 Hz, 1 H, H-1), 6.38 (d, J = 9.4 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.5, 20.6, 20.7, 23.3 (5 *Me*CO), 61.7, 68.1, 70.6, 72.8, 73.5, 78.1 (C-2,3,4,5,6), 169.5,169.8, 170.5,170.6,170.8 (5 CO). − HRMS FAB+ ($C_{16}H_{23}NNaO_{10}$ [M + Na]$^+$): calcd. 412.1220; found 412.1218.

***N*-Acetyl-2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosylamine (17):** Isolated as a solid with m.p. 172−174 °C. (ref.[35] 172−173 °C); $[\alpha]_D$ = +33 (c = 1, chloroform) [ref.[35] +34° (c = 1, chlorofom)]. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00, 2.00, 2.04, 2.07, 2.15 (4 s, 15 H, 5 MeCO), 4.17−4.01 (m, 3 H, H-5,6,6′), 5.27−5.07 (m, 3 H, H-1,2,3), 5.45 (d, J = 2.1 Hz, 1 H, H-4), 6.35 (d, J = 9.3 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 20.8, 20.7, 23.4, 61.2, 67.5, 68.4, 70.8, 72.3, 78.5, 169.8, 170.0, 170.4; HRMS FAB+ ($C_{16}H_{23}NNaO_{10}$ [M + Na]$^+$): calcd. 412.1219; found 412.1222.

2-Acetamido-*N*-acetyl-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosylamine (18): Isolated as a solid with m.p. 235 °C (dec.) (ref.[35] 240−241 °C and ref.[53] 244−246 °C); $[\alpha]_D$ = +18 (c = 0.5, pyridine) [ref.[53] +41 (c = 1, chloroform) and ref.[35] +22 (c = 0.5, pyridine)]. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.96, 1.99, 2.05, 2.07, 2.09 (5 s, 15 H, 5 MeCO), 3.76 (ddd, J = 9.6, 4.3 and 2.1 Hz, 1 H, H-5), 4.09 (dd, J = 12.5 and 2.2 Hz, 1 H, H-6′), 4.14 (dd, J = 9.9 and 9.3 Hz, 1 H, H-2), 4.03 (dd, J = 12.5 and 4.3 Hz,1 H, H-6), 5.17−5.01 (m, 3 H, H-1,3,4), 6.02 (br s, 1 H, NH), 7.00 (d, J = 7.7 Hz, 1 H, NH); ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.73, 1.81, 1.90, 1.95, 1.98 (5 s, 15 H, 5 *Me*CO), 3.80 (m, 1 H, H-5), 3.86 (q, J = 9.5 Hz, 1 H, H-2), 3.94 (dd, J = 12.3 and 2.1 Hz, 1 H, H-6′), 4.15 (dd, J = 12.3 and 2.1 Hz, 1 H, H-6), 4.80 (t, J = 9.8 Hz, 1 H, H-4), 5.08 (t, J = 9.9 Hz, 1 H, H-3), 5.14 (t, J = 9.5 Hz, 1 H, H-1), 7.92 (d, J = 9.2 Hz, 1 H, NH), 8.49 (d, J = 9.4 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$) δ = 23.4, 23.1, 20.8, 20.7 (5 *Me*CO), 53.6 (C-2), 61.9 (C-6), 67.8, 73.1, 73.7 (C-3,4,5), 80.5 (C-1), 169.3, 170.7, 172.8, 176.8 (5 CO). − HRMS FAB+ ($C_{16}H_{24}N_2NaO_9$ [M + Na]$^+$): calcd. 411.1380; found 411.1380.

***N*-Acetyl-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-hexopyranosylamine (19):** Isolated as a solid with m.p. 169−170 °C; $[\alpha]_D$ = −2 (c = 1, chloroform); $[\alpha]_{436}$ = −4 (c = 1, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70 (dt, J = 12.4 and 11.1 Hz, 1 H, H-2ax), 2.02, 2.03, 2.05, 2.08 (4 s, 12 H, 4 MeCO), 2.33 (ddd, J = 12.4, 5.1 and 2.1 Hz, 1 H, H-2ec), 3.74 (ddd, J = 9.7, 4.5 and 2.1 Hz, 1 H, H-5), 4.05 (dd, J = 12.4 and 2.1 Hz, 1 H, H-6′), 4.34 (dd, J = 12.4 and 4.5 Hz, 1 H, H-6), 4.98 (t, J = 9.6 Hz, 1 H, H-4), 5.07 (ddd, J =11.2, 9.5 and 5.2 Hz, 1 H, H-3), 5.38 (ddd, J =

11.1, 9.4 and 2.2 Hz,1 H, H-1), 6.29 (d, J = 9.4 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 20.8, 20.9 (3 *Me*CO), 23.4 (*Me*CONH), 36.0 (C-2), 62.2 (C-6), 68.6 (C-4), 71.1 (C-3), 73.8 (C-5), 75.7 (C-1), 169.7, 170.0, 170.1, 170.8 (CO). − HRMS FAB+ ($C_{14}H_{21}NNaO_8$ [M + Na]$^+$): calcd. 354.1165; found 354.1168.

_N_-Acetyl-2,3,6,2′,3′,4′,6′-hepta-_O_-acetyl-β-lactosylamine (20): Solid: m.p. 98−100 °C; $[\alpha]_D$ = +10 (c = 1.2, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.97, 1.98, 2.05, 2.06, 2.07, 2.12, 2.16 (7 s, 24 H, 8 MeCO), 3.77, 3.86, 4.18−4.03, 4.44 (4 m, 7 H, H-4,5,6,6,5′,6′,6′), 4.46 (d, J = 7.8 Hz, 1 H, H-1′), 4.82 (t, J = 9.6 Hz, 1 H, H-2), 4.94 (dd, J = 10.4 and 3.5 Hz, 1 H, H-3′), 5.11 (dd, J = 10.3 and 7.8 Hz, 1 H, H-2′), 5.20 (t, J = 9.3 Hz, 1 H, H-3), 5.30 (dd, J = 9.2 and 8.8 Hz, 1 H, H-1), 5.36 (d, J = 3.3 Hz, 1 H, H-4′), 6.16 (d, J = 9.2 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.5, 20.6, 20.7, 20.7, 20.8, 20.9 (7 MeCO), 23.4 (*Me*CON), 60.9, 62.1 (C-6,6′), 66.7, 69.1, 70.8, 71.1, 72.5, 74.6, 76.0 (C-2,3,4,5,2′,3′,4′,5′), 78.1 (C-1), 100.9 (C-1′), 169.0, 169.4, 170.1, 170.2, 170.4, 171.3 (8 CO). − HRMS FAB+ ($C_{28}H_{39}NNaO_{18}$ [M + Na]$^+$): calcd. 700.2064; found 700.2050.

_N_-Acetyl-2,3,4,6-tetra-_O_-acetyl-α-D- (25) and -β-D-mannopyranosylamine (26): Column chromatography (EtOAc) afforded an α,β mixture (see Table 1). Column chromatography (AcOEt/ether 1:3) of an aliquot allowed the separation of this mixture. Eluted first was **25** which was isolated as a solid: m.p. 98−100 °C; $[\alpha]_D$ = +58.5 (c = 1, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.06, 2.08, 2.09, 2.15 (4 s, 15 H, 5 MeCO), 4.04 (ddd, J = 8.5, 5.5 and 3.5 Hz, 1 H, H-5), 4.19 (dd, J = 12.2 and 3.4 Hz, 1 H, H-6), 4.37 (dd, J = 12.2 and 5.6 Hz, 1 H, H-6′), 5.23 (t, J = 8.1 Hz, 1 H, H-4), 5.28 (t, J = 3.4 Hz, 1 H, H-2), 5.33 (dd, J = 8.3 and 3.3 Hz, 1 H, H-3), 5.51 (dd, J = 7.6 and 3.0 Hz, 1 H, H-1), 6.60 (d, J = 7.8 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8−20.9 (5 *Me*CO), 62.1 (C-6), 66.8, 68.7, 69.0, 70.4 (C-2,3,4,5), 77.2 (C-1), 169.6, 170.3, 170.5, 170.9 (5 CO). − HRMS FAB+ ($C_{16}H_{23}NNaO_{10}$ [M + Na]$^+$): calcd. 412.1219; found 412.122.
Eluted second was **26** which was isolated as a solid: m.p. 61−63 °C; $[\alpha]_D$ = +34.6 (c = 1, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01, 2.07, 2.07, 2.10, 2.14 (5 s, 15 H, 5 MeCO), 3.99 (ddd, J = 7.6, 5.8 and 3.6 Hz, 1 H, H-5), 4.19 (dd, J = 12.2 and 3.6 Hz, 1 H, H-6), 4.38 (dd, J = 12.2 and 5.7 Hz, 1 H, H-6′), 5.21 (t, J = 7.8 Hz, 1 H, H-4), 5.23 (t, J = 3.6 Hz, 1 H, H-2), 5.31 (dd, J = 8.2 and 3.3 Hz, 1 H, H-3), 5.66 (dd, J = 8.5 and 3.9 Hz, 1 H, H-1), 7.01 (d, J = 8.5 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 20.9, 23.3 (5 *Me*CO), 61.9 (C-6), 66.8, 68.6, 69.1, 70.9, 75.1 (C-1,2,3,4,5), 170.4, 170.5, 170.7, 171.2 (5 CO). − HRMS FAB+ ($C_{16}H_{23}NNaO_{10}$ [M + Na]$^+$): calcd. 412.1219; found 412.1219.

_N_-Acetyl-2,3,4,6-tetra-_O_-acetyl-β-D- (17) and -α-D-galactopyranosylamine (27): Eluted first was **17**. Then a mixture of **17** + **27** was collected. Finally, pure **27** eluted (see Table 1) and was isolated as a solid with m.p. 168−170 °C; $[\alpha]_D$ = +96 (c = 1, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02, 2.04, 2.05, 2.09, 2.16 (5 s, 15 H, 5 MeCO), 4.21−4.05 (m, 3 H, H-5,6,6′), 5.45−5.30 (m, 3 H, H-2,3,4), 5.95 (dd, J = 8.0 and 5.0 Hz, 1 H, H-1), 7.28 (d, J = 8.0 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 23.2 (*Me*CO), 61.6 (C-6), 66.0 (C-4), 67.0, 67.5, 67.6 (C-2,3,5), 74.6 (C-1), 169.5, 170.1, 170.6, 171.3 (CO). − HRMS FAB+ ($C_{16}H_{23}NNaO_{10}$ [M + Na]$^+$): calcd. 412.1219; found 412.1215.

_N_-Acetyl-3,4,6-tri-_O_-acetyl-2-deoxy-β-D- (19) and -α-D-_Arabino_-hexopyranosylamine (28): An inseparable mixture of **19** + **28** was obtained as a syrup (see Table 1). Selected signals for **28**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05, 2.06, 2.08 (3 s, MeCO), 2.13 (m, H-2_{ax}), 2.27 (m, H-2_{ec}), 3.92 (ddd, J = 9.2, 4.4 and 2.8 Hz, H-5), 4.05 (dd, J = 12.3 and 2.0 Hz, H-6), 4.38 (dd, J = 12.2 and 4.5 Hz, H-6′), 5.01 (t, J = 9.1 Hz, H-4), 5.24 (ddd, J = 9.8, 9.3 and 6.0 Hz, H-3), 5.77 (ddd, J = 7.5, 4.6 and 2.7 Hz, H-1), 7.22 (br s, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 20.8, 20.9 (3 MeCO), 23.2 (*Me*CON), 33.3 (C-2), 62.3 (C-6), 68.9, 68.9, 69.2 (C-3,4,5), 73.6 (C-1), 169.6, 170.3, 170.5, 170.9 (4 CO).

_N_-Acetyl-2,3,6,2′,3′,4′,6′-hepta-_O_-acetyl-β- (20) and -α-Lactosylamine (29): An inseparable mixture of **20** + **29** was obtained as a syrup (see Table 1). Selected signals for **29**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.47 (d, J = 7.8 Hz, H-1′), 5.78 (dd, J = 7.2 and 6.0 Hz, H-1), 6.39 (d, J = 7.4 Hz, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 66.8, 68.5, 69.5, 69.9, 70.9, 75.9, 77.3, 101.3.

3,4,6-Tri-_O_-acetyl-2-deoxy-2-iodo-β-D-glucopyranosylamine (30): Solid with m.p. 98−100 °C; $[\alpha]_D$ = +93 (c = 1, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02, 2.08, 2.09 (3 s, 9 H, 3 MeCO), 3.76 (ddd, J = 10.0, 4.8 and 2.2 Hz, 1 H, H-5), 3.80 (t, J = 10.3 Hz, 1 H, H-2), 4.11 (dd, J = 12.4 and 2.2 Hz, 1 H, H-6′), 4.26 (dd, J = 12.3 and 4.9 Hz, 1 H, H-6), 4.45 (d, J = 9.9 Hz, 1 H, H-1), 4.94 (t, J = 10.0 Hz, 1 H, H-4), 5.33 (dd, J = 10.7 and 9.4 Hz, 1 H, H-3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6, 20.7, 20.8 (*Me*CO), 31.3 (C-2), 62.2 (C-6), 69.1, 73.1, 76.4 (C-3,4,5), 87.3 (C-1), 169.6, 170.6 (CO). − HRMS FAB+ ($C_{12}H_{18}INO_7Na$ [M + Na]$^+$): calcd. 438.0025; found 438.0019.

3,4,6-Tri-_O_-acetyl-2-deoxy-2-iodo-β-D- (31) and α-D-Mannopyranosylamine (32): Eluted first was **31** as a foamy solid: $[\alpha]_D$ = −72 (c = 1, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.04, 2.09, 2.09 (2s, 9 H, 3 MeCO), 2.35 (br s, 2 H, NH_2), 3.47 (br s, 1 H, H-1), 3.67 (ddd, J = 9.9, 4.5 and 3.1 Hz, 1 H, H-5), 4.20−4.10 (m, 2 H, H-6,6′), 4.47 (dd, J = 9.5 and 4.2 Hz, 1 H, H-3), 4.74 (d, J = 4.2 Hz, 1 H, H-2), 5.33 (t, J = 9.8 Hz, 1 H, H-4). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 20.8, 20.9 (*Me*CO), 41.0 (C-2), 62.6 (C-6), 67.6 (C-4), 72.2 (C-3), 73.8 (C-5), 81.7 (C-1), 169.5, 169.9, 170.7 (CO). − MS EI+: m/z = 399 [M$^+$ − NH_2]. − HRMS FAB+ ($C_{12}H_{18}INNaO_7$ [M + Na]$^+$): calcd. 438.0026; found 438.0022. Eluted second was a mixture of **31** + **32.** Selected signals for **32**: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 61.9, 68.2, 69.6, 70.7, 74.5, 78.6.

3,4,6-Tri-_O_-acetyl-_N_-[1-benzyl-_N_-(benzyloxy)carbonyl-L-aspart-4-oyl]-2-deoxy-2-iodo-β-D-glucopyranosylamine (33): Isolated as a solid with m.p. 117−118 °C; $[\alpha]_D$ = +49 (c = 1, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02, 2.05, 2.09 (3 s, 9 H, 3 MeCO), 2.82 (dd, J = 16.2 and 4.5 Hz, 1 H, NHCOCH_2), 3.04 (dd, J = 16.2 and 3.5 Hz, 1 H, NHCOCH_2), 3.84 (m, 2 H, H-2,5), 4.04 (br d, J = 12.4 Hz, 1 H, H-6′), 4.32 (dd, J = 12.5 and 4.2 Hz, 1 H, H-6), 4.66 (m, 1 H, C*H*COOBn), 4.96 (t, J = 9.6 Hz,1 H, H-4), 5.12, 5.20 (2 s, 4 H, 2 PhCH_2), 5.31 (dd, J = 10.4 and 9.4 Hz, 1 H, H-3), 5.42 (dd, J = 9.7 and 9.1 Hz, 1 H, H-1), 5.94 (d, J = 8.0 Hz, 1 H, NH), 6.27 (d, J = 9.0 Hz, 1 H, NH−C1), 7.34 (s, 10 H, 2 C_6H_5). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 20.8, 20.9, 27.6, 37.9, 50.7, 61.7, 67.2, 67.8, 68.5, 74.0, 76.0, 80.5, 80.5, 128.1, 128.4, 128.5, 128.6, 128.7, 135.2, 136.1 (2 C_6H_5), 156.2 (CONH), 169.5, 169.7, 169.8, 170.7 (4 CO). − HRMS FAB+ ($C_{31}H_{35}IN_2O_{12}Na$ [M + Na]$^+$): calcd. 777.1132; found 777.1132.

3,4,6-Tri-_O_-acetyl-_N_-[1-benzyl-_N_-(benzyloxy)carbonyl-L-aspart-4-oyl]-2-deoxy-2-iodo-α-D-mannopyranosylamine (34): Isolated as a solid with m.p. 66−68 °C; $[\alpha]_D$ = +16 (c = 1, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05, 2.05, 2.14 (3 s, 9 H, 3 MeCO), 3.10−2.85 (m, 2 H, NHCOCH_2), 4.10 (m, 1 H, H-5), 4.25 (dd, J = 12.0 and 4.7 Hz, 1 H, H-6′), 4.35 (dd, J = 12.0 and 6.4 Hz, 1 H, H-6), 4.47 (dd, J = 6.5 and 3.5 Hz, 1 H, H-2), 4.60 (m, 1 H, C*H*COOBn), 4.92 (dd, J = 5.9 and 3.6 Hz, 1 H, H-3), 5.05 (t, J = 5.6 Hz, 1 H, H-4), 7.33 (s, 10 H, 2 C_6H_5), 5.18, 5.11 (2 s, 4 H, 2

PhCH_2), 5.75 (dd, J = 8.2 and 6.8 Hz, 1 H, H-1), 6.05 (d, J = 8.0 Hz, 1 H, NH−C-1), 7.05 (br s, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 20.9 (*Me*CO), 26.7 (C-2), 38.2 (NHCO*C*H_2), 50.9 (*C*HCOOBn), 61.2 (C-6), 67.3 (C-4), 67.4, 67.8 (2 × Ph*C*H_2), 70.4 (C-3), 73.0 (C-5), 76.1 (C-1), 128.0, 128.3, 128.5, 128.6, 128.7, 135.0, 136.0 (2 C_6H_5), 156.0 (CONH), 169.3, 169.5, 170.8 (4 CO). − HRMS FAB+ ($C_{31}H_{35}IN_2NaO_{12}$ [M + Na]$^+$): calcd. 777.1132; found 777.1131.

3,4,6-Tri-*O*-acetyl-*N*-[1-benzyl-*N*-(benzyloxy)carbonyl-L-aspart-4-oyl]-2-deoxy-2-iodo-β-D-mannopyranosylamine (35): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.06, 2.08, 2.11 (3 s, 9 H, 3 MeCO), 2.80 (dd, J = 16.6 and 4.3 Hz, 1 H, NHCOCH_2), 3.00 (dd, J = 16.6 and 4.2 Hz, 1 H, NHCOCH_2), 3.74 (ddd, J = 9.9, 4.6 and 2.2 Hz, 1 H, H-5), 4.09 (dd, J = 12.5 and 2.2 Hz, 1 H, H-6′), 4.20 (dd, J = 12.5 and 4.5 Hz, 1 H, H-6), 4.42 (dd, J = 9.7 and 4.2 Hz, 1 H, H-3), 4.56 (dd, J = 4.2 and 1.5 Hz, 1 H, H-2), 4.63 (dd, J = 9.2 and 1.6 Hz, 1 H, H-1), 4.65 (m, 1 H, C*H*COOBn), 5.11 (s, 2 H, PhCH_2), 5.16 (d, J = 12.4 Hz, 1 H, PhCH_2), 5.22 (d, J = 12.4 Hz, 1 H, PhCH_2), 5.34 (t, J = 9.7 Hz, 1 H, H-4), 5.93 (d, J = 8.5 Hz, 1 H, NH), 6.29 (d, J = 9.2. Hz, 1 H, NH−C1), 7.33, 7.34 (2 s, 10 H, 2 C_6H_5). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 20.8, 20.9 (*Me*CO), 37.8 (NHCO*C*H_2), 38.0 (C-2), 50.6 (*C*HCOOBn), 62.0 (C-6), 66.9 (C-4), 67.2, 67.6 (2 × Ph*C*H_2), 71.8 (C-3), 74.9 (C-5), 75.4 (C-1), 128.1, 128.4, 128.6, 128.6, 128.7, 139.0 (2 C_6H_5), 158.4 (CONH), 169.5, 170.5 (4 CO). − HRMS FAB+ ($C_{31}H_{35}IN_2NaO_{12}$ [M + Na]$^+$): calcd. 777.1132; found 777.1132.

2,3,4,6-Tetra-*O*-acetyl-*N*-[1-benzyl-*N*-(benzyloxy)carbonyl-L-aspart-4-oyl]-β-D-glucopyranosylamine (36): Isolated as a solid with m.p. 142° C (ref.[35] 143.5−144 °C); $[\alpha]_D$ = +19 (c = 1, chloroform) [ref.[35] +20 (c = 1, chloroform)]. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.95, 2.02, 2.03, 2.05 (4 s, 12 H, 4 MeCO), 2.72 (dd, J = 16.4 and 4.2 Hz, 1 H, HNCOCH_2), 2.90 (dd, J = 16.6 and 4.4 Hz, 1 H, HNCOCH_2), 3.78 (ddd, J = 10.0, 4.2 and 2.1 Hz, 1 H, H-5), 4.05 (dd, J = 12.5, 5.2 and 2.1 Hz, 1 H, H-6), 4.29 (dd, J = 12.5 and 4.3 Hz, 1 H, H-6′), 4.66 (m, 1 H, CHCOO), 4.89 (t, J = 9.5 Hz, 1 H, H-2), 5.05 (t, J = 9.7 Hz, 1 H, H-4), 5.10, 5.16 (2 s, 4 H, 2 PhCH_2), 5.20 (t, J = 9.3 Hz, 1 H, H-1), 5.29 (t, J = 9.5 Hz, 1 H, H-3), 6.00 (d, J = 8.8 Hz, 1 H, NH), 6.49 (d, J = 9.2 Hz, 1 H, NH), 7.32 (br s, 10 H, 2 C_6H_5). − ^{13}C NMR (75 Hz, $CDCl_3$): δ = 20.5, 20.6, 20.7, 37.8, 50.7, 61.7, 67.2, 67.5, 68.1, 70.6, 72.6, 73.8, 78.2, 128.1, 128.3, 128.4, 128.6, 136.0, 137.9, 156.2, 169.6, 169.9, 170.6. − HRMS FAB+ ($C_{33}H_{38}N_2NaO_{14}$ [M + Na]$^+$): calcd. 709.2220; found 709.2219.

2-Acetamido-3,4,6-tri-*O*-acetyl-*N*-[1-benzyl-*N*-(benzyloxy)carbonyl-L-aspart-4-oyl]-2-deoxy-β-D-glucopyranosylamine (37): Solid with m.p. 213−215° C; $[\alpha]_D$ = +9 (c = 1, chloroform). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98, 2.05, 2.06, 2.07 (4 s, 12 H, 4 MeCO), 2.71 (dd, J = 16.3 and 4.5 Hz, 1 H, CH_2CH), 2.87 (dd, J = 16.0 and 4.8 Hz, 1 H, CH_2CH), 3.71 (ddd, J = 9.9, 4.1 and 2.1 Hz, 1 H, H-5), 4.05 (m, 1 H, H-2), 4.07 (dd, J = 12.6 and 2.3 Hz, 1 H, H-6), 4.29 (dd, J = 12.4 and 4.3 Hz, 1 H, H-6), 4.66 (m, 2 H, H-5, CH_2CH), 4.92 (dd, J = 9.7 and 8.1 Hz, 1 H, H-4), 4.97 (dd, J = 10.6 and 9.4 Hz, 1 H, H-3), 5.24−5.03 (m, 5 H, H-1, H-2, CH_2OBn), 5.76 (d, J = 8.0 Hz, 1 H, NH), 6.01 (d, J = 8.7 Hz, 1 H, NH), 7.18 (d, J = 8.0 Hz, 1 H, NH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 20.8, 20.8 (3 *Me*CO), 23.0 (*Me*CONH), 37.8 (CH_2CON), 50.7 (CHN), 53.4 (C-2), 61.7 (C-6), 67.2, 67.3 (2*C*H_2OBn), 67.6, 72.8, 73.7 (C-3,4,5), 80.5 (C-1), 128.1, 128.2, 128.2, 128.5, 128.6, 135.6, 136.3 (2 C_6H_5), 156.2 (CONH), 169.3, 170.8, 171.0, 172.0, 172.6 (CO). − HRMS FAB+ ($C_{33}H_{39}N_3NaO_{13}$ [M + Na]$^+$): calcd. 708.2380; found. 708.2374.

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