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An easy access to anomeric glycosyl amides and imines (Schiff bases) via transformation of glycopyranosyl trimethylphosphinimides

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Dedicated to Professor Dr Joachim Thiem on the occasion of his 60th birthday

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Abstract—The preparation and application of anomeric glycosyl phosphinimides in preparative synthesis were studied. Starting from the appropriate glycosyl azides and trialkyl or triaryl phosphines, the corresponding phosphinimides were obtained by modified Staudinger reactions. The latter compounds were readily converted into 1-*N*-acyl-gluco- and galactopyranosyl amines with high yields by applying activated acid derivatives or simple carboxylic acids. 1-*N*-Alkylidene- or arylidenephosphinimines (Schiff bases) were obtained by means of aza-Wittig reactions using aliphatic or aromatic aldehydes, respectively.

1. Introduction

A conventional route[1] for the preparation of glycosyl amides is the reaction of glycosyl amines with activated carboxylic acid derivatives in the presence of bases (Method A). Recently, growing interest is devoted to the synthesis of glycosyl amides because of the recognition of the importance[2] of glycoproteins in diverse biochemical processes including intercellular communication, cell growth regulation, binding of pathogens to cells[2,3] and metastasis. Glycoproteins assist in protein folding and transport, by providing protection against proteolysis. One of the basic building blocks of the naturally occurring glycopeptides is the chitobiose-*N*-asparagine connection, and several chemical and chemoenzymatic approaches have been reported[4] for the development of such linkages. Most recently, solid-supported synthesis has also been conducted[4f] to produce a variety of glycopeptides in good overall yields.

A less frequently used method for the preparation of acylated glycosyl amines employs[5] isothiocyanates instead of the amine reactant (Method B), and the target amides are produced upon the simultaneous action of the appropriate acid and triethylamine.

In recent years, glycosyl azides have emerged as spectacular starting materials in the field of the synthesis of glycosyl amides. In related procedures the azide is first converted into an iminophosphorane (also called phosphinimine, λ^5-phosphazene, iminophosphine and phosphinimide), which is then transformed into the required amide[6] by treatment with an activated acid derivative or a carboxylic acid (Method C).

However, the scope and limitations of Method C have not been convincingly elaborated from the point of view of carbohydrate chemistry. Namely, acylation of the phosphinimines was first accomplished[7] with non-anomeric azides, and subsequent short papers reported the extension[8] of the methodology also to 1,2-*trans*-glycopyranosyl azides.

Three additional approaches have also been reported for the production of glycosyl amides. The first is based[9] on the glycosylation of silylated amides (Method D), and this procedure can be considered as an extension of the Vorbrüggen nucleoside synthesis.[10] The Fraser–Reid group prepared *N*-α- or *N*-β-linked amides from *n*-pentenyl glycosides via nitrilium ion intermediates, and this convergent strategy (Method E) was used for the synthesis[11] of the β-linked chitobiosyl-*N*-glycopeptide core. Finally, in the third procedure, Avalos et al.[12] assembled diacyl imides, including *N*,*N*-diacetyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl amine, from glycosyl thioamides and metal carboxylates under mild conditions (Method F).

Besides certain advantages, there are several drawbacks of the procedures A–F. Method A is frequently applied;[1] the

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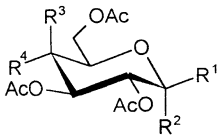


Nr.	R^1	R^2	R^3	R^4
1	N_3	H	H	OAc
2	H	N_3	H	OAc
3	H	N_3	OAc	H
4	N_3	H	OAc	H
5	$NHCOC_6H_5$	H	H	OAc
6	H	Cl	H	OAc

Scheme 1.

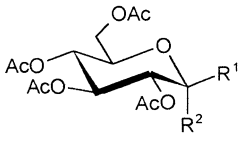
acylation can be performed even with unprotected glycosylamines[13] due to the greater nucleophilicity of the nitrogen atom. At the same time, the glycosylamines necessary for the acylation reactions are hardly available, in many cases, in the required anomeric- or ring-isomeric form[14] due to the weak anomeric effect of the C-1 amino group.[15] Additional drawbacks of this methodology include the low stability[1] of glycosyl amines due to hydrolysis and conversion into diglycosylamines[16] by loss of ammonia, as well as anomerization of the protected glycosyl azides upon hydrogenation into the amines and subsequent hydrolysis.[16]

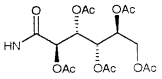
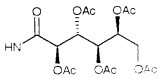
Method B is less frequently employed, and the published examples involve mainly acylated glycosylamines with β-configuration derived from β-isothiocyanates. The most recently described[17] glycosyl α-isothiocyanates have not been converted into amides.

Table 1. Reaction of 2 with benzoyl chloride and different phosphine

2 —(1. 1 equiv. R_3P/rt; 2. 2 equiv. PhCOCl/ 0°C)→ **5** or **6**

Run	R	Solvent	Formation of phosphinimine (min)	Reaction time (h)	Isolated yield (%)	
					5	**6**
1	Ph	CH_2Cl_2	30	12	82	–
2	Ph	PhMe	120	20	83	–
3	nBu	CH_2Cl_2	15	3	–	52
4	nBu	PhMe	30	6	28	29
5	Et	CH_2Cl_2	10	6	–	43
6	Et	PhMe	10	7	–	43
7	Me_2N	CH_2Cl_2	10	4	–	53
8	Me_2N	PhMe	10	3	–	53



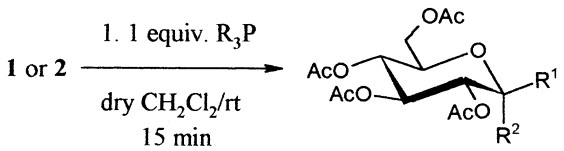
Nr.	R^1	R^2
13	$NHCOCF_3$	H
14	H	$NHCOCF_3$
15	H	$NHCOCCl_3$
16	$NHCOCH_3$	H
17	$NHCOC(CH_3)_3$	H
18	H	$NHCOC(CH_3)_3$
19		H
20		H

Scheme 2.

Based on the above results Method C, involving glycosyliminophosphoranes,[8] appears to be widely useful for the preparation of *N*-acyl glycosyl amines, since the starting glycosyl azides are readily available[16a] in form of α- or β-pyranosides or furanosides.

As shown by Horner,[6a] the thermal reaction of phenyliminotriphenylphosphorane with benzoic acid gave 30% of benzanilide, but attempted acylation[8] of glycopyranosyliminophosphoranes with acids failed. The conversion was also unsuccessful when *n*-Bu_3P or Et_3P was used instead of the aromatic phosphines. Following the recognition that both steric and electronic factors[6g,i] significantly influence the formation of the products, in the case of aromatic azides the reaction of iminophosphoranes[18] with mixed anhydrides[6d,h,k,p] was applied for the acylation. Formation of the amide from an azide, a phosphine, and an activated acid derivative is supposed to proceed in the Staudinger reaction, when first a triazaphosphadiene intermediate, and then a P-triaryl/(alkyl)-iminophosphorane is produced. The iminophosphorane reacts with an acyl chloride to yield an iminophosphonium salt which then forms the oxazaphosphetane. The latter undergoes an electrocyclic reversion to form the phosphine oxide and the chloroimines *E* and *Z*, the last being hydrolyzed into the acylamino compound, and according to Kosower[6i] this set of reactions constitutes the iminophosphorane pathway. Formation of

Table 2. Formation and structure elucidation of glucosyl phosphinimides and phosphazides



7-12

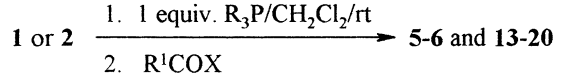
Run	Educt	Nr.	R	R^1	R^2	δ (H-1) ($^3J_{1,2}$, $^3J_{1,P}$) $CDCl_3$	δ (C-1) ($^2J_{C\text{-}1,P}$) $CDCl_3$	Crude product $[\alpha]_D$, (*c*) in $CHCl_3$	
								After evaporation	After 6 days
1	**2**	**7**		H	N=P(nBu)$_3$	5.35 (3.1, 23.0)	73.6 (21.2)	+94.8 (1.1)	+17.7 (1.1)
2	**1**	**8**	*n*Bu	N=P(nBu)$_3$	H	4.59 (8.9, 22.7)	75.8 (16.0)	+1.8 (1.1)	−3.7 (1.1)
3	**2**	**9**		H	N=PMe_3	5.36 (4.2, 22.1)	73.5 (22.0)	+96.6 (1.0)	+12.7 (1.0)
4	**1**	**10**	Me	N=PMe_3	H	4.61 (8.4, 27.0)	75.5 (12.2)	−4.9 (1.0)	+16.7 (1.0)
5	**2**	**11**		H	N=N–N=P(NMe_2)$_3$	5.18 (4.7, –)	91.0 –	+63.6 (1.3)	+55.4 (1.3)
6	**1**	**12**	Me_2N	N=N–N=P(NMe_2)$_3$	H	4.78 (8.6, –)	95.1 –	+53.4 (1.1)	+54.9 (1.1)

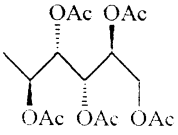
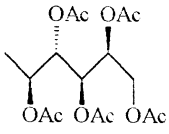
additional products (i.e. detection of chlorides, esters, and C-phosphonium ylides) in the complex reaction has also been discussed.[6i,j,8d] Recent reports describe the formation of imines (Schiff bases) in the reaction[18b] of phosphinimines with carbonyl compounds upon loss of the phosphine oxide, however, the so-called aza-Wittig reactions[19] require more vigorous conditions[20] on preparative scale. To our best knowledge, the aza-Wittig reaction of glycopyranosylphosphinimines has not been reported.

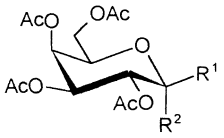
2. Results and discussion

Our primary goal was to investigate whether the α- and β-glycosyl amides can be derived in stereoselective reactions, and also to determine the properties (stability, reactivity) and behavior of the phosphinimides, prepared from glycosyl azides, towards acylating agents. Based on literature data, triphenyl-, tri-*n*-butyl-, triethyl-, trimethyl- and tris-dimethylaminophosphine, and the four acetylated

Table 3. Synthesis of 1-*N*-acyl-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl)amines



run	Educt	R	Reactants			Reaction time (min.)	Product (isolated yield, %)	
			equiv.	R^1	X		α-amide	β-amide
1	**1**	Ph	2	Ph	Cl	120	–	**5** (82)
2	**2**	Me	1	Ph	PhCOO	180	–	**5** (74)
3	**2**	Me	1	Ph	Cl	150	**6** (54–61)	
4	**1**	*n*Bu	2	CF_3	CF_3COO	15	–	**13** (76)
5	**2**	*n*Bu	2	CF_3	CF_3COO	30	**14** (52)	**13** (9)
6	**2**	Ph	2	CF_3	CF_3COO	60	**14** (68)	**13** (19)
7	**2**	Me	1	CCl_3	CCl_3COO	10	**15** (69)	–
8	**1**	*n*Bu	2	CH_3	CH_3COO	15	–	**16** (72)
9	**2**	*n*Bu	2	CH_3	CH_3COO	30	–	**16** (72)
10	**1**	*n*Bu	2	*t*Bu	*t*BuCOO	7 days	–	**17** (15)
11	**2**	*n*Bu	8	*t*Bu	*t*BuCOO	3 days	**18** (5)	**17** (21)
12	**2**	Me	1		Cl	15	–	**19** (84)
13	**2**	Me	1		Cl	15	–	**20** (55)



Cpd.	R^1	R^2
21	$NHCOCH_3$	H
22	H	$NHCOCF_3$
23	H	$NHCOCCl_3$
24	$NHCOC_6H_5$	H
25	$NHCOCF_3$	H
26	$NHCOCCl_3$	H

Scheme 3.

D-glucopyranosyl and D-galactopyranosyl azide educts (**1**–**4**)[16a] were involved in the present studies (Scheme 1).

Thin layer chromatography and ^1H NMR measurements showed (Table 1) that formation of the phosphinimide from the α-azide **2** is the slowest with triphenylphosphine in toluene, but upon the action of benzoyl chloride the benzamido compound **5** can be isolated in pure form, again in a slow reaction. A disadvantage in the work-up procedure is that triphenylphosphine oxide can be removed only by chromatography. The data in Table 1 also demonstrates that application of trialkylphosphines result in a fast reaction, however 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl chloride (**6**) is produced, presumably because of the much higher basicity[19] of the alkylphosphinimides (Scheme 2).

To produce the appropriate phosphinimine, selection of alkyl- or triarylphosphines should be considered. It is known[20] that in the case of aromatic phosphines the -I effect of the pyranose ring results in the stabilization of the negatively charged anomeric nitrogen atom. Formation of glycosyl chlorides from glycosyl azides (Table 3, entry 3) has not been observed till now. Parallel formation of the glycosyl chloride and the desired amide was recognized in some additional cases as well. With the expectation of the formation of the latter compounds, the structure of the primary products formed in the reaction of the above phosphines and the gluco-azides **1** and **2** was studied, and the results obtained at low temperature, and with an equimolar ratio of the reactants are shown in Table 2. From the data it is obvious that the reaction of **1** and **2** with trimethylphosphine gives exclusively the phosphinimide, similarly to the galacto-compounds **3** and **4** (these results are not included in the Table 2). By measuring the change of the optical rotation values, a very slow anomerization can be observed for the phosphinimines; constant values could only be obtained after 6 days. In the case of the β-tributylphosphinimines, Lafont et al.[8h] reported a fast equilibrium: after 5 min the trimethyl phosphinimide derived from **1** possesses β-configuration exclusively, the β/α ratio is ca. 22 after 40 min, and it is ca. 10 after 100 min, as deduced from the ^1H NMR data.

The last two entries of Table 2 demonstrate that with trisdimethylaminophosphine phosphazido compounds are produced, which is clearly substantiated by the lack of the $^3J_{1,P}$ couplings in the ^1H NMR spectra. The anomeric phosphazides could be very well characterized with the $^3J_{1,2}$ coupling constants. Since the transformation of phosphazides often led to the formation of glycosyl halides (such as **6**) these compounds were not used in further experiments to produce the required amides.

According to the data of Table 3, of the activated acid derivatives the transformation of acid chlorides into amides is a fast reaction. However, α-amides could be successfully synthesized only from the trihalogenoacetic anhydrides carrying strongly electron-withdrawing substituents (entries 5–7). When a bulky acylating agent (such as pivaloic anhydride) was used the conversion was not complete even after one week (entries 10 and 11). Acylation of the β-azide **1** with onic-acid chlorides (entries 12 and 13) was also successful. For a high-yielding preparation of the 2,3,4,6-tetra-*O*-acetyl-1-*N*-(2,3,4,5,6-penta-*O*-acetyl-D-gluconyl)-amides **19** and **20** a 15 min reaction time was sufficient, and the products were characterized according to the small optical rotation values, as well as to the ^1H NMR spectra (see Section 4).

The amides obtained with the corresponding educts **3** and **4**

Table 4. Synthesis of 1-*N*-acyl-(2,3,4,6-tetra-*O*-acetyl-D-galactopyranosyl)amines

3 or **4** $\xrightarrow[2.\ 1\ \text{equiv.}\ R^1COX]{1.\ 1\ \text{equiv.}\ R_3P/CH_2Cl_2/rt}$ **21-26**

Run	Educt	R	Reactant		Reaction time (min.)	Product (isolated yield, %)	
			R^1	X		α-amide	β-amide
1	**3**	Me, Et	CH_3	CH_3COO	60	–	**21** (80)
2	**3**	Me	CF_3	CF_3COO	30	**22** (51)	–
3	**3**	Me	CCl_3	CCl_3COO	40	**23** (66)	–
4	**3**	Me	C_6H_5	Cl	300	–	**24** (58)
5	**3**	Me	C_6H_5	C_6H_5COO	40	–	**24** (57)
6	**4**	Me, Et	CH_3	CH_3COO	60	–	**21** (80)
7	**4**	Me	CF_3	CF_3COO	45	**22** (60)	**25**[a]
8	**4**	Me	CCl_3	CCl_3COO	40	**23** (59)	**26**[a]
9	**4**	Me	C_6H_5	Cl	150	–	**24** (58)
10	**4**	Me	C_6H_5	C_6H_5COO	40	–	**24** (57)

[a] It could be not isolated in pure anomeric form.

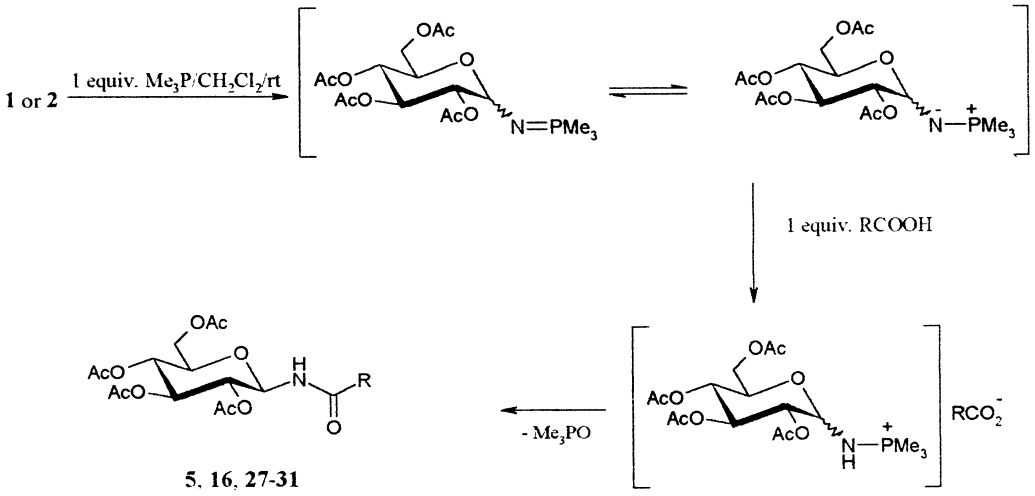
(Scheme 3) in the galacto-series are included in Table 4. The β-1-*N*-acetamido- (**21**) and -benzamido compound (**24**) could be prepared in homogeneous form either from the α-(**3**) or the β-azide (**4**). The α-1-*N*-trichloro- and -trifluoro-acetamides **23** and **22** were obtained by retention from the α-azide **3**, but traces of the β-products **25** and **26** were also detected by thin layer chromatography.

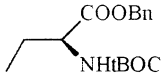
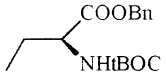
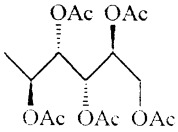
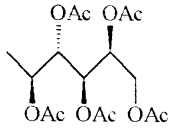
The application of trimethylphosphine (entries 2, 3, 7, and 8) clearly demonstrate that when anhydrides are used, the catalyst 3,4-dihydro-pyrido[2,1-*b*]pyrimidine-2*H*-one is not necessary for completion of the acylation reaction. However, the use of this catalyst is suggested[21] when triphenylphosphinimides and non-anomeric azides are applied.

Anomerization in the acylation reactions has been observed[8c,h,14b,22,23] earlier, as well, which is due to the anomeric effect of the amides. Namely, ring-opening of the product with the less-favored anomeric configuration, and subsequent ring-closure would lead to the more stable anomer, which is the β-compound in the present case.

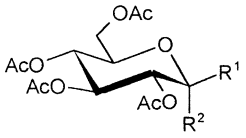
Acylation of the strongly basic trimethylphosphinimide educts[24] does not require[25] activated acid derivatives. The experimental data related to the conversion of the phosphinimides derived from the anomeric azides **1** and **2** with a few common aromatic acids (such as benzoic acid, *p*-chloro-, *p*-methyl-, and *p*-nitrobenzoic acid), Boc-L-aspartic acid benzyl ester, and peracetylated D-gluconic

Table 5. Synthesis of 1-*N*-acyl-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl)amines II



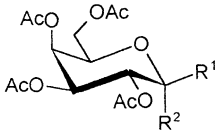
Educt	R	Reaction time (h)	Product (isolated yield, %)
	Ph	48	**5** (91)
	*p*Cl-C_6H_4	19	**27** (47)
	*p*Me-C_6H_4	18	**28** (41)
2	*p*NO_2-C_6H_4	48	**29** (23)
		18	**30** (70)
		16	**30** (83)
	Ph	15	**5** (82)
	*p*Cl-C_6H_4	16	**27** (83)
	*p*Me-C_6H_4	24	**28** (85)
	pNO_2-C_6H_4	16	**29** (57)
1	Et	3	**31** (52)
	Me	3	**16** (58)
		24	[a]
		24	[a]

[a] Complex reaction mixture.



Nr.	R^1	R^2
32	C_6H_5-CH=N	H
33	p$Cl-C_6H_4$-CH=N	H
34	CBr_3CH=N	H
35	H	CBr_3CH=N

Scheme 4.



Nr.	R^1	R^2
36	C_6H_5-CH=N	H
37	p$Cl-C_6H_4$-CH=N	H
38	1-$C_{10}H_7$-CH=N	H
39	p$CN-C_6H_4$-CH=N	H
40	CBr_3CH=N	H
41	H	CBr_3CH=N

Scheme 5.

acid and D-galactonic acid are shown in Table 5. The final products obtained from both of the anomeric azides **1** and **2** were the 1,2-*trans*-glycosylamides (**5**, **16**, **27**–**31**). During a reaction time between 3 h and 2 days only the above products appeared, which were isolated following removal of the solvent and the phosphine oxide by distillation (the yields relate to the recrystallised, pure products). When trifluoroacetic acid was applied, the reaction proceeded presumably only to salt-formation, and no amide was detected.

To prepare Schiff-bases, the reactivity of the in situ generated glycopyranosyl phosphinimines (characterized by means of ^{1}H NMR spectroscopy) towards simple carbonyl compounds was also studied. Until now, such *N*-1-arylidene compounds were generally prepared[26] by the reduction of *O*-protected glycopyranosyl azides, followed by treatment of the resulting amines with aldehydes in various solvents (methanol, heptane). Kovács reported[27] that the transformation of 1,2,3,4-tetra-*O*-acetyl-6-triphenylphosphinimido-β-D-glucopyranose with *p*-nitrobenzaldehyde could only be performed by boiling in diglyme for 15 h, and the Schiff-base could be isolated in 54% yield. Recently, the synthesis of the anomeric glycosyl imides is urged by their application, as the starting chiral imines,[28] in Diels–Alder cycloaddition reactions, and also for the preparation of tetrahydropyridines and β-lactam derivatives.

From the phosphinimides **8**–**12**, derived from the azides **1**–**4**, the Schiff-bases were prepared at room temperature in 10 min (Schemes 4 and 5). Following removal of the solvent and trimethylphosphine oxide by distillation, the solid products **32**–**41** were isolated and purified by recrystallization. Anomerization of the α-anomeric phosphinimides (e.g. **9**) could not be influenced during the reaction, even at low temperature (−80°C) the corresponding β-imines were isolated (Tables 6 and 7), and the yields were high in each case. The α-anomeric products (**35** and **41**) could only be synthesized with bromal, carrying a strong electron-withdrawing substituent, at low temperature.

Table 6. Synthesis of 1-*N*-arylidene-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl)imines

1 or **2** $\xrightarrow[2.\ 1\ \text{equiv. RCHO}]{1.\ 1\ \text{equiv. } Me_3P/CH_2Cl_2/rt}$ **32-35**

Educt	R	Reaction time (min)	Product (isolated yield, %)
2	Ph	180	**32** (87), β
1	Ph	10	**32** (81), β
2	p$Cl-C_6H_4$	10	**33** (75), β
1	p$Cl-C_6H_4$	10	**33** (73), β
2	CBr_3	60	**34** (53), α
1	CBr_3	10	**35** (95), β

Table 7. Synthesis of 1-*N*-arylidene-(2,3,4,6-tetra-*O*-acetyl-D-galactopyranosyl)imines

3 or **4** $\xrightarrow[2.\ 1\ \text{equiv. RCHO}]{1.\ 1\ \text{equiv. } Me_3P/CH_2Cl_2/rt}$ **36-41**

Educt	R	Reaction time (min)	Product (isolated yield, %)
3	Ph	10	**36** (97), β
4	Ph	10	**36** (96), β
3	p$Cl-C_6H_4$	10	**37** (90), β
3	$C_{10}H_7$	10	**38** (87), β
3	p$CN-C_6H_4$	5	**39** (90), β
3	CBr_3	5	**40** (69), β
4	CBr_3	60	**41** (80), α

3. Conclusions

The present studies were aimed at studying the preparation and application of anomeric glycosyl phosphinimides in preparative synthesis. It was established that the anomeric 1-*N*-acyl glycopyranosyl amines and 1-*N*-arylidene glycopyranosyl imines (Schiff-bases) with D-gluco and D-galacto configuration could be most conveniently prepared by the acylation or in the aza-Wittig reaction, respectively, of the strongly basic trimethylphosphiminides derived in situ from glycopyranosyl azides. The anomers of the prepared phosphinimides undergo slow anomerization (5–6 days), and during transformations the more stable β-anomers were produced even under mild conditions, as a result of ring-opening and subsequent recyclization. The corresponding α-anomers could be obtained from the appropriate glycosyl azides only with anhydrides or aldehydes carrying strong electron-withdrawing substituents. The trimethylphosphinimides can also be conveniently converted into 1-*N*-acyl derivatives with carboxylic acids.

4. Experimental

4.1. General

Distilled solvents (CH_2Cl_2, dioxane and toulene) were dried by storage over 4 Å molecular sieves. Melting points were measured on a Kofler hot-stage and are uncorrected. Optical rotations were recorded in chloroform solution on a Perkin–Elmer 241 polarimeter in a 1 dm cell at room temperature (22±2°C). IR spectra were taken with a Perkin–Elmer 16 PC FT-IR spectrometer. NMR spectra were recorded with Bruker WP 360 SY (360/90 MHz for $^1H/^{13}C$) and Varian UNITYINOVA 400 WB (400/100 MHz for $^1H/^{13}C$) spectrometers. Chemical shifts are referenced to Me_4Si (^1H) or the resiudal solvent signal (^{13}C: 77.00 ppm for $CDCl_3$). Measurements were run at 298 K probe temperature. The ^1H and ^{13}C assignments were based on $^1H–^1H$ COSY, gradient enhanced $^{13}C–^1H$ HSQC and $^{13}C–^1H$ HMBC experiments executed using standard Varian software. The designation of multiplicities of peaks are used as in general use (s: singlet, d: doublet, t: triplet, Ψt: pseudo triplet, q: quartet, m: multiplet). TLC-s were performed on DC-Alurolle, Kieselgel 60 F_{25} (Merck), (eluent A: ethylacetate–hexanes, 1:1; B: diethylether–hexanes, 1:1); the plates were visualized by gentle heating. For column chromatography Kieselgel 60 (Merck) was used. Organic solutions were concentrated in vacuo at 40–50°C (water bath). Glycosyl azides **1**–**4** were prepared as described in the literature.[15a,29] Me_3P solution is a commercial product of Fluka AG, Buchs, Swiket (1 M in toluene).

4.2. General procedure A

General procedure A for the reaction of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl azides (**1** and **2**) with trialkyl or triaryl phosphine: to a solution of **1** or **2** (0.15 mmol) in $CDCl_3$ (0.6 ml) 1 equiv. phosphine (Table 2) was added at once. The mixture was stirred at room temperature until the starting material had disappeared as judged by TLC. This solution was investigated by ^1H and ^{13}C NMR and optical rotation (See Table 2).

4.3. General procedure B

General procedure B for the reaction of 2,3,4,6-tetra-*O*-acetyl-D-glycopyranosyl azides (**1**–**4**) with trialkyl or triaryl phosphine and acylating agent (Tables 3 and 4): to a solution of glycosyl azide (**1**–**4**) (0.20 g, 0.54 mmol) in dry CH_2Cl_2 (2 ml) 1 equiv. phosphine was added at once. The mixture was stirred at room temperature until the N_2 evolution ceased. Then 1 equiv. acylating agent (acyl anhydride, acyl chloride) was added and the resulting mixture was stirred (**1** and **3** at room temperature, **2** and **4** at −78°C for the reaction time (Tables 3 and 4). Finally, the solution was evaporated. The crude product was purified by crystallisation (further referred as D) or column chromatography (further referred as E).

4.4. General procedure C

General procedure C for reaction of trimethyl phosphinimide with carboxylic acid or aldehyde: to a solution of glycosyl azide (**1**–**4**) (0.20 g, 0.54 mmol) in dry CH_2Cl_2 (2 ml) was added 0.55 ml Me_3P solution and stirred at room temperature. After 15 min 1 equiv. carboxylic acid or aldehyde (**1** and **3** at room temperature, **2** and **4** at −78°C was added (Tables 5–7). When the phosphimimide disappeared the solution was evaporated to dryness. The crude product was purified by D or E.

4.4.1. 1-*N*-Benzoyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-amine (5). Prepared from **2** (0.20 g, 0.54 mmol) with benzoic acid according to General procedure C; yield: 0.22 g, 91%, colourless crystalline product (D: diethylether–hexane), mp 197–199°C, $[\alpha]_D=-15.0$ (*c* 1.0, $CHCl_3$) [lit.[30] mp 196–198°C, $[\alpha]_D=-7.9$ (*c* 0.6, $CHCl_3$)]; $R_f=0.72$ (eluent A). ν_{max} (KBr): 3468, 2355, 1745, 1654, 1369 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 7.68 (2H, d, *J*=9.0 Hz, Ph), 7.60–7.40 (3H, m, Ph), 7.06 (1H, d, *J*=9.3 Hz, N*H*), 5.43 (1H, Ψt, *J*=9.3, 9.6 Hz, H-1), 5.38 (1H, Ψt, *J*=9.6, 9.7 Hz, H-3), 5.10 (1H, Ψt, *J*=9.7, 9.9 Hz, H-4), 5.05 (1H, t, *J*=9.6 Hz, H-2), 4.33 (1H, dd, *J*=4.3, 12.5 Hz, H-6), 4.09 (1H, dd, *J*=2.0, 12.5 Hz, 1H, H-6′), 3.89 (1H, ddd, *J*=2.0, 4.3, 9.9 Hz, 1H, H-5), 2.09, 2.06, 2.05, 1.99 (4×3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 171.5, 170.6, 169.8, 169.6 (acetyl *C*O), 167.1 (NH*C*O), 132.7, 132.4, 128.7, 127.2 (Ph), 78.9 (C-1), 73.6 (C-5), 72.6 (C-3), 70.8 (C-2), 68.2 (C-4), 61.6 (C-6), 20.7, 20.6 (acetyl *Me*). Anal. Calcd for $C_{21}H_{25}NO_{10}$ (451.43): C: 55.87, H: 5.58, N: 3.10. Found: C: 55.65, H: 5.53, N: 3.10.

4.4.2. 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl-chloride (6). Isolated from the reaction of **2** with benzoyl chloride and different phosphine; yield 54–61%, syrup, $[\alpha]_D=+88.8$ (*c* 0.6, $CHCl_3$); [lit.[31] mp 78–79°C (dec.), $[\alpha]_D=+177$ (*c* 1.0, $CHCl_3$)]. It was identified by NMR according to the literature.[31]

4.4.3. 1-*N*-Trifluoroacetyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-amine (13). Prepared from **1** (1.00 g, 2.68 mmol) with trifluoroacetic anhydride according to General procedure B; yield: 0.90 g, 76%, colourless crystalline product (D: diethylether–hexane), mp 125–126°C, $[\alpha]_D=+21.3$ (*c* 1.0, $CHCl_3$); $R_f=0.59$ (eluent B). ν_{max} (KBr): 3442, 2355, 1749, 1637, 1366 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 7.48 (1H, d, *J*=9.0 Hz, N*H*), 5.32 (1H, Ψt, *J*=9.6, 9.7 Hz, H-3), 5.22 (1H, Ψt, *J*=9.0, 9.2 Hz, H-1), 5.06 (1H, Ψt, *J*=9.7, 10.0 Hz, H-4), 5.00 (1H, Ψt, *J*=9.2, 9.6 Hz, H-2), 4.29 (1H, dd, *J*=4.7, 12.6 Hz, H-6), 4.08 (1H, dd, *J*=2.1, 12.6 Hz, H-6′), 3.85 (1H, ddd, *J*=2.1, 4.7, 10.0 Hz, H-5), 2.09, 2.06, 2.05, 2.04 (4×3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 171.0, 170.6, 169.8, 169.6 (acetyl *C*O), 157.4 (q, *J*=38.5 Hz, NH*C*O), 115.3 (q, *J*=288.0 Hz, *C*F$_3$), 78.4 (C-1), 74.1 (C-5), 72.3 (C-3), 70.5 (C-2), 67.9 (C-4), 61.5 (C-6), 20.6, 20.5, 20.4 (acetyl *Me*). Anal. Calcd for $C_{16}H_{20}F_3NO_{10}$ (443.27): C: 43.35, H: 4.55, N: 3.16. Found: C: 43.08, H: 4.45, N: 3.02.

4.4.4. 1-*N*-Trifluoroacetyl-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-amine (14). Prepared from **2** (0.38 g, 1.02 mmol) with trifluoroacetic anhydride according to General procedure B; yield: 0.31 g, 68%, colourless crystalline product (E: diethylether–hexane, 15:12), mp 157–159°C, $[\alpha]_D=+94.6$ (*c* 1.0, $CHCl_3$); $R_f=0.24$ (eluent B). ν_{max} (KBr): 3444, 2358, 1754, 1634, 1370 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 7.75 (1H, d, *J*=7.5 Hz, N*H*), 5.90 (1H,

dd, J=5.7, 7.5 Hz, H-1), 5.42 (1H, Ψt, J=9.4, 10.2 Hz, H-3), 5.20 (1H, dd, J=5.7, 10.2 Hz, H-2), 5.07 (1H, Ψt, J=9.4, 10.0 Hz, H-4), 4.26 (1H, dd, J=4.8, 12.4 Hz, H-6), 4.08 (1H, dd, J=2.4, 12.4 Hz, H-6′), 3.93 (1H, ddd, J=2.4, 4.8, 10.0 Hz, H-5), 2.18, 2.12, 2.09, 2.04 (4×3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.8, 170.5, 169.3, 169.2 (acetyl *C*O), 157.8 (q, J=38.5 Hz, NH*C*O), 115.4 (q, J=288.0 Hz, *C*F_3), 74.9 (C-1), 69.7 (C-3), 69.1 (C-5), 68.2 (C-2), 68.0 (C-4), 61.6 (C-6), 20.6, 20.5, 20.4, 20.3 (acetyl *Me*). Anal. Calcd for $C_{16}H_{20}F_3NO_{10}$ (443.27): C: 43.35, H: 4.55, N: 3.16. Found: C: 43.14, H: 4.42, N: 3.03.

4.4.5. 1-*N*-Trichloroacetyl-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-amine (15). Prepared from **2** (0.38 g, 1.00 mmol) with trichloroacetic anhydride according to General procedure B; yield: 0.34 g, 69%, colourless crystalline product (D: diethylether–hexane), mp 153–155°C, $[\alpha]_D$=+96.2 (*c* 1.1, $CHCl_3$); R_f=0.64 (eluent A). ν_{max} (KBr): 3420, 2345, 1761, 1619, 1359 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm): 7.24 (1H, d, J=6.9 Hz, N*H*), 5.82 (1H, dd, J=5.5, 6.9 Hz, H-1), 5.32 (1H, dd, J=9.1, 10.0 Hz, H-3), 5.22 (1H, dd, J=5.5, 10.0 Hz, H-2), 5.06 (1H, dd, J=9.1, 9.9 Hz, H-4), 4.29 (1H, dd, J=4.7, 12.3 Hz, H-6), 4.10 (1H, dd, J=2.3, 12.3 Hz, H-6′), 3.92 (1H, ddd, J=2.3, 4.7, 9.9 Hz, H-5), 2.08, 2.06, 2.04, 2.00 (4×3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.6, 170.1, 169.3, 168.9 (acetyl *C*O), 161.9 (NH*C*O), 92.0 (*C*Cl_3), 76.1 (C-1), 69.8 (C-3), 68.9 (C-5), 68.3 (C-2), 68.0 (C-4), 61.5 (C-6), 20.7, 20.6, 20.5, 20.4 (acetyl *Me*). Anal. Calcd for $C_{16}H_{20}Cl_3NO_{10}$ (492.69): C: 39.01, H: 4.09, N: 2.84. Found: C: 39.22, H: 4.23, N: 2.91.

4.4.6. 1-*N*-Acetyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-amine (16). Prepared from **1** (0.36 g, 0.96 mmol) with acetic anhydride according to General procedure B; yield: 0.28 g, 72%, crystalline product (D: ethylacetate–hexane), mp 155–157°C, $[\alpha]_D$=+16.5 (*c* 1.0, $CHCl_3$), [lit.[32] mp 161–162°C, $[\alpha]_D$=+17 (*c* 1.0, $CHCl_3$)]; R_f=0.22 (eluent A). This compound was identified by ^{1}H and ^{13}C NMR.[32]

4.4.7. 1-*N*-Pivaloyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-amine (17). Prepared from **1** (0.38 g, 1.02 mmol) with pivalic anhydride according to General procedure B; yield: 0.09 g, 21%, colourless crystalline product (E: ethylacetate–hexane, 5:12), mp 148–150°C, $[\alpha]_D$=+22.1 (*c* 1.0, $CHCl_3$); R_f=0.46 (eluent A). ν_{max} (KBr): 3404, 2358, 1750, 1662, 1372 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm): 6.42 (1H, d, J=9.3 Hz, N*H*), 5.29 (1H, Ψt, J=9.6, 9.7 Hz, H-3), 5.20 (1H, Ψt, J=9.3, 9.4 Hz, H-1), 5.03 (1H, Ψt, J=9.7, 10.0 Hz, H-4), 4.91 (1H, Ψt, J=9.4, 9.6 Hz, H-2), 4.29 (1H, dd, J=4.2, 12.5 Hz, H-6), 4.03 (1H, dd, J=2.1, 12.5 Hz, H-6′), 3.79 (1H, ddd, J=2.1, 4.2, 10.0 Hz, H-5), 2.04, 1.99, 1.98, 1.98 (4×3H, s, CH_3), 1.12 (9H, s, *t*Bu); ^{13}C NMR ($CDCl_3$) δ (ppm): 178.6 (NH*C*O), 171.0, 170.6, 169.8, 169.5 (acetyl *C*O), 78.5 (C-1), 73.5 (C-5), 72.5 (C-3), 70.6 (C-2), 68.2 (C-4), 61.6 (C-6), 38.7 (*C*Me_3), 27.0 (C(*C*H_3)$_3$) 20.7, 20.5, 20.5 (acetyl *Me*). Anal. Calcd for $C_{19}H_{29}NO_{10}$ (431.44): C: 52.89, H: 6.78, N: 3.25. Found: C: 53.00, H: 6.55, N: 3.12.

4.4.8. 1-*N*-Pivaloyl-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-amine (18). Prepared from **2** (0.38 g, 1.02 mmol) with pivalic anhydride according to General procedure B; yield: 0.02 g, 5%, colourless crystalline product (E: ethylacetate–hexane, 5:12), mp 195–196°C, $[\alpha]_D$=+93.1 (*c* 1.0, $CHCl_3$); R_f=0.36 (eluent A). ν_{max} (KBr): 3439, 2362, 1749, 1631, 1365 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm): 6.65 (1H, d, J=7.4 Hz, N*H*), 5.87 (1H, dd, J=5.6, 7.4 Hz, H-1), 5.41 (1H, t, J=9.9 Hz, H-3), 5.10 (1 h, dd, J=5.6, 9.9 Hz, H-2), 5.07 (1H, Ψt, J=9.9, 10.0 Hz, H-4), 4.29 (1H, dd, J=4.4, 12.3 Hz, H-6), 4.04 (1H, dd, J=2.3, 12.3 Hz, H-6′), 3.89 (1H, m, H-5), 2.09, 2.04 (4×3H, s, CH_3), 1.15 (9H, s, *t*Bu); ^{13}C NMR ($CDCl_3$) δ (ppm): 176.3 (NH*C*O), 170.8, 170.6, 170.5, 169.3 (acetyl *C*O), 74.3 (C-1), 70.0 (C-3), 68.2 (C-2 and C-4), 68.1 (C-5), 61.8 (C-6), 38.7 (*C*Me_3), 26.7 (C(*C*H_3)$_3$), 23.2, 20.7, 20.5, 20.5 (acetyl *Me*). Anal. Calcd for $C_{19}H_{29}NO_{10}$ (431.44): C: 52.89, H: 6.78, N: 3.25. Found: C: 52.95, H: 6.89, N: 3.01.

4.4.9. 1-*N*-(2,3,4,5,6-Penta-*O*-acetyl-D-galactonoyl)-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-amine (19). Prepared from **1** (0.20 g, 0.54 mmol) with 2,3,4,5,6-penta-*O*-acetyl-D-galactonoyl chloride[33] according to General procedure B; yield: 0.33 g, 84%, crystalline colourless product (D: ethanol), mp 188–189°C, $[\alpha]_D$=+51.7 (*c* 1.0, $CHCl_3$); R_f=0.33 (eluent A). ν_{max} (KBr): 3428, 2342, 1754, 1652, 1372 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm): 6.76 (1H, d, J=9.6 Hz, N*H*), 5.67 (1H, dd, J=2.0, 10.1 Hz, H-3′), 5.34 (1H, dd, J=1.9, 10.1 Hz, H-4′), 5.27 (t, J=9.7 Hz, H-3), 5.20 (1H, m, H-5′), 5.12 (1H, d, J=2.0 Hz, H-2′), 5.09 (1H, t, J=9.6 Hz, H-1), 4.98 (1H, t, J=9.7 Hz, H-4), 4.85 (1H, Ψt, J=9.6, 9.7 Hz, H-2), 4.22 (2H, m, H-6a, H-6′a), 4.00 (1H, dd, J=2.0, 12.5 Hz, H-6b), 3.83 (1H, dd, J=7.3, 11.5 Hz, H-6′b), 3.77 (1H, ddd, J=2.0, 4.6, 9.7 Hz, H-5), 2.25, 2.09, 2.08, 2.06, 2.04, 2.03, 2.01, 2.01, 1.98 (9×3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 171.7, 170.4, 170.3, 170.3, 169.9, 169.6, 169.6, 169.5, 168.4 (acetyl *C*O), 167.3 (NH*C*O), 77.6 (C-1), 73.6 (C-5), 72.0 (C-3), 71.2 (C-2′), 70.0 (C-2), 68.1 (C-4), 67.5 (C-3′), 67.2 (C-4′), 67.1 (C-5′), 61.8 (C-6′), 61.5 (C-6), 20.6, 20.5, 20.4, 20.4, 19.9 (acetyl *Me*). Anal. Calcd for $C_{30}H_{41}NO_{20}$ (735.65): C: 48.98, H: 5.62, N: 1.90. Found: C: 49.12, H: 5.49, N: 1.94.

4.4.10. 1-*N*-(2,3,4,5,6-Penta-*O*-acetyl-D-gluconoyl)-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-amine (20). Prepared from **1** (0.20 g, 0.54 mmol) with 2,3,4,5,6-penta-*O*-acetyl-D-gluconoyl chloride[33] according to General procedure B; yield: 0.22 g, 55%, colourless crystalline product (E: ethanol), mp 153–155°C, $[\alpha]_D$=+36.5 (*c* 1.0, $CHCl_3$); R_f=0.21 (eluent A). ν_{max} (KBr): 3430, 2360, 1756, 1652, 1374 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm): 6.79 (1H, d, J=9.5 Hz, N*H*), 5.69 (1H, dd, J=3.0, 6.7 Hz, H-3′), 5.45 (1H, dd, J=4.9, 6.7 Hz, H-4′), 5.34 (1H, d, J=3.0 Hz, H-2′), 5.28 (1H, Ψt, J=9.5, 9.6 Hz, H-3), 5.11 (1H, Ψt, J=9.5, 9.6 Hz, H-1), 5.00 (1H, t, J=9.6, 10.1 Hz, H-4), 4.94 (1H, q, J=4.9, 5.2, 5.4 Hz, H-5′), 4.88 (1H, Ψt, J=9.5, 9.6 Hz, H-2), 4.31 (1H, dd, J=5.2, 12.0 Hz, H-6′a), 4.24 (1H, dd, J=4.7, 12.5 Hz, H-6a), 4.14 (1H, dd, J=5.4,12.0 Hz, H-6′b), 4.03 (1H, dd, J=2.1, 12.5 Hz, H-6b), 3.79 (1H, ddd, J=2.1, 4.7, 10.1 Hz, H-5), 2.31, 2.10, 2.08, 2.05, 2.04, 2.03, 2.01, 2.00, 1.98 (9×3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 171.7, 170.5, 170.4, 170.0, 169.7, 169.6, 168.9 (acetyl *C*O), 167.2 (NH*C*O), 77.8 (C-1), 73.6 (C-5), 72.5 (C-2′), 72.1 (C-3), 69.9 (C-2), 69.7 (C-4′), 68.9 (C-3′), 68.6 (C-5′), 68.1 (C-4), 61.6 (C-6), 61.0 (C-6′), 20.5, 20.5, 20.4, 20.3,

19.9 (acetyl *Me*). Anal. Calcd for $C_{30}H_{41}NO_{20}$ (735.65): C: 48.98, H: 5.62, N: 1.90. Found: C: 48.87, H: 5.71, N: 1.95.

4.4.11. 1-*N*-Acetyl-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-amine (21). Prepared from **3** (0.37 g, 1.00 mmol) with acetic anhydride according to General procedure B; yield: 0.31 g, 80%, colourless crystalline product, mp 170–171°C, (D: ethylacetate–hexane); $[\alpha]_D$=+37.0 (*c* 1.0, $CHCl_3$); [lit.[5b] mp 172–173°C, $[\alpha]_D$=+34.0 (*c* 1.0, $CHCl_3$)]; R_f=0.30 (eluent A). This compound was identified by ^1H and ^{13}C NMR in literature.[5b]

4.4.12. 1-*N*-Trifluoroacetyl-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-amine (22). Prepared from **4** (0.20 g, 0.54 mmol) with trifluoroacetic anhydride according to General procedure B; yield: 0.20 g, 60%, colourless crystalline product mp 140–141°C, (E: diethylether–hexane, 15:12), $[\alpha]_D$=+109.3 (*c* 1.0, $CHCl_3$); R_f=0.33 (eluent A). ν_{max} (KBr): 3418, 2358, 1758, 1652, 1378 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 7.82 (1H, d, *J*=8.3 Hz, N*H*), 6.01 (1H, dd, *J*=5.2, 8.3 Hz, H-1), 5.42 (1H, dd, *J*=5.2, 10.3 Hz, H-2), 5.37 (1H, dd, *J*=1.3, 3.3 Hz, H-4), 5.35 (1H, dd, *J*=3.3, 10.3 Hz, H-3), 4.23 (1H, m, H-5), 4.14 (1H, dd, *J*=5.6, 11.3 Hz, H-6), 4.07 (1H, dd, *J*=7.1, 11.3 Hz, H-6′), 2.15, 2.07, 2.05, 2.00 (4×3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 171.1, 171.0, 170.2, 169.5 (acetyl *C*O), 157.8 (q, *J*=38.5 Hz, NH*C*O), 115.4 (q, *J*=288.0 Hz, *C*F_3), 75.2 (C-1), 68.1 (C-5), 67.3 and 67.1 (C-3 and C-4), 65.6 (C-2), 61.8 (C-6), 20.6, 20.5, 20.4 (acetyl *Me*). Anal. Calcd for $C_{16}H_{20}F_3NO_{10}$ (443.27): C: 43.35, H: 4.55, N: 3.16. Found: C: 43.18, H: 4.45, N: 3.04.

4.4.13. 1-*N*-Trichloroacetyl-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-amine (23). Prepared from **4** (0.20 g, 1.00 mmol) with trichloroacetic anhydride according to General procedure B; yield: 0.28 g, 59%, colourless crystalline product (E: diethylether–hexane, 15:12), mp 128–130°C, $[\alpha]_D$=+109.0 (*c* 1.0, $CHCl_3$); R_f=0.45 (eluent A). ν_{max} (KBr): 3468, 2360, 1752, 1650, 1370 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 7.24 (1H, d, *J*=6.9 Hz, N*H*), 5.89 (1H, dd, *J*=5.4, 6.9 Hz, H-1), 5.45 (1H, dd, *J*=1.2, 3.1 Hz, H-4), 5.44 (1H, dd, *J*=5.4, 9.8 Hz, H-2), 5.20 (1H, dd, *J*=3.1, 9.8 Hz, H-3), 4.30–4.00 (3H, m, H-5, H-6, H-6′), 2.17, 2.08, 2.04, 2.03 (4×3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 171.2, 170.4, 169.9, 169.7 (acetyl *C*O), 161.9 (NH*C*O), 91.6 (*C*Cl_3), 80.2 (C-1), 72.7 (C-3), 70.4 (C-5), 67.9 (C-2), 66.8 (C-4), 60.9 (C-6), 20.5, 20.5, 20.4 (acetyl *Me*). Anal. Calcd for $C_{16}H_{20}Cl_3NO_{10}$ (492.69): C: 39.01, H: 4.09, N: 2.84. Found: C: 38.81, H: 4.15, N: 2.75.

4.4.14. 1-*N*-Benzoyl-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-amine (24). Prepared from **4** (0.37 g, 1.00 mmol) with benzoyl chloride or benzoic anhydride according to General procedure B; yield: 0.26 g, 57%, colourless crystalline product (E: ethylacetate–hexane, 5:12), mp 148–149°C, $[\alpha]_D$=+4.9 (*c* 1.0, $CHCl_3$); R_f=0.61 (eluent A). ν_{max} (KBr): 3444, 2360, 1748, 1652, 1374 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 7.78 (2H, d, *J*=8.9 Hz, Ph), 7.59–7.42 (3H, m, Ph), 7.04 (1H, d, *J*=9.5 Hz, N*H*), 5.49 (1H, dd, *J*=1.0, 2.6 Hz, H-4), 5.43 (1H, dd, *J*=9.0, 9.5 Hz, H-1), 5.27 (1H, dd, *J*=2.6, 10.0 Hz, H-3), 5.23 (1H, dd, *J*=9.0, 10.0 Hz, H-2), 4.20–4.05 (3H, m, H-5, H-6, H-6′), 2.17, 2.05, 2.02 (4×3H s, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 171.7, 170.3, 169.9, 169.7 (acetyl *C*O), 166.9 (NH*C*O), 132.8, 132.3, 128.7, 127.2 (Ph), 79.1 (C-1), 72.2 (C-5), 70.7 (C-3), 68.9 (C-2), 67.2 (C-4), 61.0 (C-6), 20.7, 20.6,20.5 (acetyl *Me*). Anal. Calcd for $C_{21}H_{25}NO_{10}$ (451.43): C: 55.87, H: 5.58, N: 3.10. Found: C: 55.60, H: 5.51, N: 3.15.

4.4.15. 1-*N*-(4-Chlorobenzoyl)-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-amine (27). Prepared from **2** (0.20 g, 0.54 mmol) with 4-chlorobenzoic acid according to General procedure C; yield: 0.21 g, 83%, colourless crystalline product (D: diethylether–hexane), mp 177–178°C, $[\alpha]_D$=−20.2 (*c* 1.1, $CHCl_3$); R_f=0.75 (eluent A). ν_{max} (KBr): 3430, 2360, 1754, 1632, 1232 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 7.72 (2H, d, *J*=8.4 Hz, Ph), 7.41 (2H, d, *J*=8.4 Hz, Ph), 7.31 (1H, d, *J*=9.0 Hz, N*H*), 5.45 (1H, Ψt, *J*=9.0, 9.5 Hz, H-1), 5.40 (1H, Ψt, *J*=9.1, 10.0 Hz, H-3), 5.10 (1H, Ψt, *J*=9.1, 9.8 Hz, H-4), 5.07 (1H, Ψt, *J*=9.5, 10.0 Hz, H-2), 4.34 (1H, dd, *J*=4.1, 12.3 Hz, H-6), 4.10 (1H, dd, *J*=1.1, 12.3 Hz, H-6′), 3.93 (1H, ddd, *J*=1.1, 4.1, 9.8 Hz, H-5), 2.07, 2.05, 2.04, 2.02 (4×3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 171.3, 170.5, 169.7, 169.5 (acetyl *C*O), 166.1 (NH*C*O), 138.6, 131.0, 128.9, 128.6 (Ph), 78.8 (C-1), 73.5 (C-5), 72.4 (C-3), 70.7 (C-2), 68.1 (C-4), 61.6 (C-6), 20.6, 20.4 (acetyl *Me*). Anal. Calcd for $C_{21}H_{24}ClNO_{10}$ (485.88): C: 51.91, H: 4.98, N: 2,88. Found: C: 51.76, H: 4.76, N: 3.05.

4.4.16. 1-*N*-(4-Methylbenzoyl)-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-amine (28). Prepared from **2** (0.20 g, 0.54 mmol) with 4-methylbenzoic acid according to General procedure C; yield: 0.21 g, 85%, colourless crystalline product (D: diethylether–hexane), mp 194–195°C, $[\alpha]_D$=−15.4 (*c* 1.0, $CHCl_3$); R_f=0.71 (eluent A). ν_{max} (KBr): 3428, 2365, 1764, 1634, 1238 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 7.67 (2H, d, *J*=8.2 Hz, Ph), 7.24 (2H, d, *J*=8.2 Hz, Ph), 7.15 (1H, d, *J*=9.0 Hz, N*H*), 5.45 (1H, Ψt, *J*=9.0, 9.5 Hz, H-1), 5.38 (1H, Ψt, *J*=9.4, 9.5 Hz, H-3), 5.10 (1H, Ψt, *J*=9.4, 9.5 Hz, H-4), 5.05 (1H, Ψt, *J*=9.4, 9.5 Hz, H-2), 4.33 (1H, dd, *J*=4.1, 12.1 Hz, H-6), 4.08 (1H, dd, *J*=2.0, 12.1 Hz, H-6′), 3.89 (1H, m, H-5), 2.40 (3H, s, PhC*H*$_3$), 2.07, 2.05, 2.03 (4×3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 171.3, 170.5, 169.8, 169.5 (acetyl *C*O), 167.0 (NH*C*O), 142.9, 129.8, 129.3, 127.2 (Ph), 78.8 (C-1), 73.5 (C-5), 72.6 (C-3), 70.7 (C-2), 68.2 (C-4), 61.6 (C-6), 21.4 (Ph*C*H_3), 20.6, 20.5 (acetyl *C*H_3). Anal. Calcd for $C_{22}H_{27}NO_{10}$ (465.46): C: 56.77, H: 5.85, N: 3.01. Found: C: 56.65, H: 5.54, N: 3.10.

4.4.17. 1-*N*-(4-Nitrobenzoyl)-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-amine (29). Prepared from **2** (0.20 g, 0.54 mmol) with 4-nitrobenzoic acid according to General procedure C; yield: 0.15 g, 57%, colourless crystalline product (D: diethylether–hexane), mp 168–170°C, $[\alpha]_D$=−16.5 (*c* 1.0, $CHCl_3$); R_f=0.73 (eluent A). ν_{max} (KBr): 3422, 2366, 1760, 1635, 1239 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 8.31 (2H, d, *J*=9.0 Hz, Ph), 7.96 (2H, d, *J*=9.0 Hz, Ph), 7.41 (1H, d, *J*=9.0 Hz, N*H*), 5.44 (1H, Ψt, *J*=9.0, 9.5 Hz, H-1), 5.38 (1H, t, *J*=9.5, 10.0 Hz, H-3), 5.10 (1H, Ψt, *J*=9.5, 9.8 Hz, H-4), 5.06 (1H, Ψt, *J*=9.5, 10.0 Hz, H-2), 4.34 (1H, dd, *J*=4.2, 12.6 Hz, H-6), 4.12 (1H, dd, *J*=2.1, 12.6 Hz, H-6′), 3.94 (1H, ddd, *J*=2.1, 4.2, 9.8 Hz, H-5), 2.08, 2.07, 2.06 (4×3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ

(ppm): 171.7, 170.6, 169.8, 166.6 (acetyl *C*O), 165.2 (NH*C*O), 150.0, 138.2, 128.5, 123.9 (Ph), 78.9 (C-1), 73.7 (C-5), 72.3 (C-3), 70.9 (C-2), 68.1 (C-4), 61.6 (C-6), 20.7, 20.5 (acetyl *Me*). Anal. Calcd for $C_{21}H_{24}N_2O_{12}$ (496.43): C: 50.81, H: 4.87, N: 5.64. Found: C: 50.65, H: 4.79, N: 5.51.

4.4.18. 1-*N*-(1-Benzyl *N*-(*tert*-butyloxycarbonyl)-4-aspart-4-oyl)-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-amine (30). Prepared from **1** (0.20 g, 0.54 mmol) with 1-benzyl *N*-(*tert*-butyloxycarbonyl)-L-aspartate according to General procedure C; yield: 0.29 g, 83%, colourless crystalline product, mp 164–166°C, (D: ethylacetate–hexane); $[\alpha]_D$=+23.3 (*c* 1.0, $CHCl_3$); [lit.[34] mp 169–171°C, $[\alpha]_D$=+22.0 (*c* 1.0, $CHCl_3$)]; R_f=0.40 (eluent A). This compound was identified by ^1H and ^{13}C NMR.[34]

4.4.19. 1-*N*-Propionyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-amine (31). Prepared from **1** (0.20 g, 0.54 mmol) with propionic acid according to General procedure C; yield: 0.11 g, 52%, colourless crystalline product (D: diethylether–hexane), mp 145–147°C, $[\alpha]_D$=+19.2 (*c* 1.0, $CHCl_3$), [lit.[30] mp 151–152°C, $[\alpha]_D$=+16.1 (*c* 0.7, $CHCl_3$)]; R_f=0.31 (eluent A). ν_{max} (KBr): 3440, 2358, 1750, 1654, 1376 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 6.21 (1H, d, *J*=9.4 Hz, N*H*), 5.25 (1H, Ψt, *J*=9.4, 9.5 Hz, H-1), 5.20 (1H, Ψt, *J*=9.5, 9.7 Hz, H-3), 5.00 (1H, Ψt, *J*=9.7, 10.0 Hz, H-4), 4.88 (1H, t, *J*=9.5 Hz, H-2), 4.25 (1H, dd, *J*=4.3, 12.7 Hz, H-6), 4.02 (1H, dd, *J*=1.7, 12.7 Hz, H-6′), 3.89 (1H, ddd, *J*=1.7, 4.3, 10.0 Hz, H-5), 2.15 (2H, dq, *J*=7.3 Hz, ethyl C*H*$_2$), 2.02, 1.98, 1.97, 1.96 (4×3H, s, acetyl C*H*$_3$), 1.07 (3H, t, *J*=7.3 Hz, ethyl C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 173.9 (NH*C*O), 170.7, 170.4, 169.7, 169.4 (acetyl *C*O), 78.0 (C-1), 73.4 (C-5), 72.6 (C-3), 70.5 (C-2), 68.1 (C-4), 61.6 (C-6), 29.4 (ethyl *C*H$_2$), 20.5, 20.4, 20.4 (acetyl *Me*), 9.0 (ethyl *C*H$_3$).

4.4.20. 1-*N*-Benzylidene-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-imine (32). Prepared from **1** (0.38 g, 1.02 mmol) with benzaldehyde according to General procedure C; yield: 0.34 g, 81%, colourless crystalline product (D: diethylether–hexane), mp 164–165°C, $[\alpha]_D$=−37.9 (*c* 1.1, $CHCl_3$) [lit.[26] mp 162–163°C, $[\alpha]_D$=−29.1 (*c* 1.0, $CHCl_3$)]; R_f=0.64 (eluent A). ν_{max} (KBr): 3442, 2370, 1758, 1632, 1370 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 8.42 (1H, s, =C*H*–), 7.75 (2H, d, *J*=8.5 Hz, Ph), 7.45–7.39 (3H, m, Ph), 5.38 (1H, Ψt, *J*=9.5, 9.6 Hz, H-3), 5.19 (1H, t, *J*=9.5 Hz, H-4), 5.04 (1H, Ψt, *J*=9.0, 9.6 Hz, H-2), 4.86 (1H, d, *J*=9.0 Hz, H-1), 4.32 (1H, dd, *J*=4.5, 12.3 Hz, H-6), 4.23 (1H, dd, *J*=2.2, 12.3 Hz, H-6′), 3.89 (1H, ddd, *J*=2.2, 4.5, 9.5 Hz, H-5), 2.11, 2.06, 2.03, 2.01 (4×3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.6, 170.1, 169.3, 169.0 (acetyl *C*O), 161.2 (=*C*H–), 135.0, 131.5, 128.7, 128.5 (Ph), 93.0 (C-1), 73.6, 73.3, 71.9, 68.4 (C-2, C-3, C-4, C-5), 62.0 (C-6), 20.6, 20.4 (acetyl *C*H$_3$).

4.4.21. 1-*N*-(4-Chlorobenzylidene)-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-imine (33). Prepared from **1** (0.38 g, 1.02 mmol) with 4-chlorobenzaldehyde according to General procedure C; yield: 0.34 g, 73%, colourless crystalline product (D: diethylether–hexane), mp 127–129°C, $[\alpha]_D$=−30.6 (*c* 1.1, $CHCl_3$); R_f=0.66 (eluent A). ν_{max} (KBr): 3438, 2370, 1759, 1633, 1366 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 8.39 (1H, s, =C*H*–), 7.68 (2H, d, *J*=8.2 Hz, Ph), 7.39 (2H, d, *J*=8.2 Hz, Ph), 5.38 (1H, Ψt, *J*=9.0, 9.6 Hz, H-2), 5.18 (1H, t, *J*=9.5 Hz, H-4), 5.00 (1H, Ψt, *J*=9.5, 9.6 Hz, H-3), 4.88 (1H, d, *J*=9.0 Hz, H-1), 4.33 (1H, dd, *J*=4.8, 12.7 Hz, H-6), 4.23 (1H, dd, *J*=2.1, 12.7 Hz, H-6′), 3.90 (1H, ddd, *J*=2.1, 4.8, 9.5 Hz, H-5), 2.11, 2.06, 2.03 (4×3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.6, 170.2, 169.3, 169.1 (acetyl *C*O), 160.0 (=*C*H–), 137.6, 133.6, 129.9, 128.9 (Ph), 92.5 (C-1), 73.7, 73.3, 71.9, 68.4 (C-2, C-3, C-4, C-5), 62.0 (C-6), 20.7, 20.6 (acetyl *Me*). Anal. Calcd for $C_{21}H_{24}ClNO_9$ (469.88): C: 53.68, H: 5.15, N: 2.98. Found: C: 53.95, H: 5.12, N: 2.79.

4.4.22. *N*-(2,2,2-Tribromoethylidene)-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-imine (34). Prepared from **1** (0.10 g, 0.27 mmol) with tribromoacetaldehyde according to General procedure C; yield: 0.16 g, 95%, colourless crystalline product (D: diethylether–hexane), mp 161–163°C, $[\alpha]_D$=−24.7 (*c* 1.0, $CHCl_3$); R_f=0.69 (eluent A). ν_{max} (KBr): 3444, 2924, 1748, 1374, 1224 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 7.68 (1H, d, *J*=2.1 Hz, =C*H*–), 5.35 (1H, Ψt, *J*=9.5, 9.6 Hz, H-3), 5.13 (1H, Ψt, *J*=9.6, 9.7 Hz, H-4), 5.06 (1H, dd, *J*=2.1, 9.3 Hz, H-1), 4.89 (1H, Ψt, *J*=9.3, 9.5 Hz, H-2), 4.31 (1H, dd, *J*=4.8, 12.5 Hz, H-6), 4.21 (1H, dd, *J*=2.3, 12.5 Hz, H-6′), 3.90 (1H, ddd, *J*=2.3, 4.8, 9.7 Hz, H-5), 2.08, 2.05, 2.04, 2.00 (4×3H, s, C*H*$_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.6, 170.2, 169.3, 169.1 (acetyl *C*O), 157.4 (=*C*H–), 88.2 (C-1), 74.0 (C-5), 73.0 (C-3), 71.3 (C-2), 68.3 (C-4), 61.6 (C-6), 37.8 (*C*Br$_3$), 20.7, 20.7, 20.6, 20.5 (acetyl *Me*). Anal. Calcd for $C_{16}H_{20}Br_3NO_9$ (610.05): C: 31.50, H: 3.30, N: 2.30. Found: C: 31.19, H: 3.49, N: 2.13.

4.4.23. *N*-(2,2,2-Tribromoethylidene)-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-imine (35). Prepared from **2** (0.20 g, 0.54 mmol) with tribromoacetaldehyde according to General procedure C; yield: 0.17 g, 53%, colourless crystalline product (E: ethylacetate–hexane, 5:12), mp 141–143°C, $[\alpha]_D$=+88.7 (*c* 1.1, $CHCl_3$); R_f=0.80 (eluent A). ν_{max} (KBr): 3438, 2920, 1744, 1370, 1221 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 7.51 (1H, s, =C*H*–), 5.41 (1H, Ψt, *J*=9.7, 10.0 Hz, H-3), 5.35 (1H, d, *J*=4.8 Hz, H-1), 5.18 (1H, Ψt, *J*=9.7, 10.2 Hz, H-4), 5.13 (1H, dd, *J*=4.8, 10.0 Hz, H-2), 4.56 (1H, ddd, *J*=2.2, 4.1, 10.2 Hz, H-5), 4.29 (1H, dd, *J*=4.1, 12.5 Hz, H-6), 4.15 (1H, dd, *J*=2.2, 12.5 Hz, H-6′),), 2.10, 2.08, 2.01, 1.98 (4×3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.7, 169.9, 169.7, 169.6 (acetyl *C*O), 160.1 (=*C*H–), 87.6 (C-1), 71.2 (C-2), 70.5 (C-3), 69.3 (C-5), 68.5 (C-4), 61.7 (C-6), 36.7 (*C*Br$_3$), 20.7, 20.7, 20.6 (acetyl *Me*). Anal. Calcd for $C_{16}H_{20}Br_3NO_9$ (610.05): C: 31.50, H: 3.30, N: 2.30. Found: C: 31.80, H: 3.24, N: 2.13.

4.4.24. 1-*N*-Benzylidene-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-imine (36). Prepared from **3** (0.37 g, 1.00 mmol) with benzaldehyde according to General procedure C; yield: 0.43 g, 97%, colourless crystalline product (D: diethylether–hexane), mp 108–111°C, $[\alpha]_D$=−3.3 (*c* 1.0, $CHCl_3$); R_f=0.64 (eluent A). ν_{max} (KBr): 3444, 2924, 1748, 1374, 1224 cm^{-1}; ^1H NMR ($CDCl_3$): δ (ppm): 8.38 (1H, d, *J*=1.4 Hz, =C*H*–), 7.70 (2H, m, Ph), 7.44–7.32 (3H, m, Ph), 5.44 (1H, dd, *J*=1.1, 3.1 Hz, H-4), 5.19 (1H, dd, *J*=8.1, 10.3 Hz, H-2), 5.14 (1H, dd, *J*=3.1, 10.3 Hz, H-3), 4.77 (1H, dd, *J*=1.4, 8.1 Hz, H-1), 4.20 (1H, dd, *J*=6.8, 11.3 Hz, H-6), 4.16 (1H, dd, *J*=6.2, 11.3 Hz,

H-6′), 4.06 (1H, m, H-5), 2.12, 2.06, 2.01, 1.99 (4×3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.4, 170.2, 170.1, 169.2 (acetyl *C*O), 161.6 (=*C*H–), 135.1, 131.5, 128.7, 128.5 (Ph), 93.6 (C-1), 72.3 (C-5), 71.3 (C-3), 69.4 (C-2), 67.3 (C-4), 61.5 (C-6), 20.6, 20.6, 20.5, 20.5 (acetyl *Me*). Anal. Calcd for $C_{21}H_{25}NO_9$ (435.43): C: 57.93, H: 5.79, N: 3.22. Found: C: 57.75, H: 5.63, N: 3.11.

4.4.25. 1-*N*-(4-Chlorobenzylidene)-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-imine (37). Prepared from **3** (0.37 g, 1.00 mmol) with 4-chlorobenzaldehyde according to General procedure C; yield: 0.42 g, 90%, colourless crystalline product (D: diethylether–hexane), mp 146–147°C, $[\alpha]_D$=−16.5 (*c* 1.0, $CHCl_3$); R_f=0.64 (eluent A). ^{1}H NMR ($CDCl_3$): δ (ppm): 8.39 (1H, d, *J*=1.1 Hz, =C*H*–), 7.69 (2H, d, *J*=8.2 Hz, Ph), 7.40 (2H, d, *J*=8.2 Hz, Ph), 5.50 (1H, dd, *J*=1.1, 3.2 Hz, H-4), 5.21 (1H, dd, *J*=9.0, 10.2 Hz, H-2), 5.19 (1H, dd, *J*=3.2, 10.2 Hz, H-3), 4.84 (1H, dd, *J*=1.1, 9.0 Hz, H-1), 4.25 (1H, dd, *J*=6.8, 11.0 Hz, H-6), 4.21 (1H, dd, *J*=6.3, 11.0 Hz, H-6′), 4.11 (1H, m, H-5), 2.17, 2.07, 2.04, 2.01 (4×3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.3, 170.1, 170.1, 169.2 (acetyl *C*O), 159.9 (=*C*H–), 137.5, 133.6, 129.8, 128.8 (Ph), 93.1 (C-1), 72.4 (C-5), 71.3 (C-3), 69.7 (C-2), 68.0 (C-4), 61.8 (C-6), 20.9, 20.7 (acetyl *Me*). Anal. Calcd for $C_{21}H_{24}ClNO_9$ (469.88): C: 53.68, H: 5.15, N: 2.98. Found: C: 53.49, H: 5.01, N: 2.68.

4.4.26. 1-*N*-(1-Naphthylidene)-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-imine (38). Prepared from **3** (0.20 g, 0.54 mmol) with 1-naphthaldehyde according to General procedure C; yield: 0.23 g, 87%, colourless crystalline product (D: diethylether–hexane), mp 115–117°C, $[\alpha]_D$=−17.5 (*c* 1.0, $CHCl_3$); R_f=0.57 (eluent A). ^{1}H NMR ($CDCl_3$): δ (ppm): 9.11 (1H, s, =C*H*–), 8.80 (1H, m, Npht), 7.99–7.87 (3H, m, Npht), 7.63–7.50 (2H, m, Npht), 5.54 (1H, dd, *J*=1.0, 3.2 Hz, H-4), 5.38 (1H, dd, *J*=8.4, 10.5 Hz, H-2), 5.25 (1H, dd, *J*=3.2, 10.5 Hz, H-3), 4.95 (1H, d, *J*=8.4 Hz, H-1), 4.32 (1H, dd, *J*=6.6, 10.9 Hz, H-6), 4.21 (1H, dd, *J*=6.3, 10.9 Hz, H-6′), 4.16 (1H, m, H-5), 2.19, 2.09, 2.04, 2.02 (4×3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.4, 170.3, 170.1, 169.3 (acetyl *C*O), 161.1 (=*C*H–), 133.7, 132.0, 131.4, 130.5, 129.7, 128.6, 127.2, 126.0, 125.2, 123.8 (Npht), 93.9 (C-1), 72.5 (C-5), 71.4 (C-3), 69.6 (C-2), 67.4 (C-4), 61.5 (C-6), 20.7, 20.6, 20.6, 20.5 (acetyl *Me*). Anal. Calcd for $C_{25}H_{27}NO_9$ (485.49): C: 61.85, H: 5.61, N: 2.89. Found: C: 61.66, H: 5.64, N: 2.69.

4.4.27. 1-*N*-(4-Cyanobenzylidene)-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-imine (39). Prepared from **3** (0.37 g, 1.00 mmol) with 4-cyanobenzaldehyde according to General procedure C; yield: 0.41 g, 89%, colourless crystalline product (D: diethylether–hexane), mp 81–83°C, $[\alpha]_D$=+12.4 (*c* 1.0, $CHCl_3$); R_f=0.50 (eluent A). ν_{max} (KBr): 3440, 2927, 1752, 1380, 1230 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm): 8.49 (1H, d, *J*=1.0 Hz, =C*H*–), 7.85 (2H, d, *J*=8.3 Hz, Ph), 7.72 (2H, d, *J*=8.3 Hz, Ph), 5.51 (1H, dd, *J*=1.0, 3.1 Hz, H-4), 5.23 (1H, dd, *J*=9.1, 10.9 Hz, H-2), 5.16 (1H, dd, *J*=3.1, 10.9 Hz, H-3), 4.95 (1H, dd, *J*=1.0, 9.1 Hz, H-1), 4.31–4.08 (3H, m, H-5, H-6, H-6′), 2.17, 2.09, 2.08, 2.01 (4×3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.3, 170.1, 170.0, 169.3 (acetyl *C*O), 158.5 (=*C*H–), 139.1, 132.3, 128.9, 118.9 (Ph), 114.5 (*C*N), 91.8 (C-1), 72.5 (C-5), 71.2 (C-3), 69.4 (C-2), 67.2 (C-4), 61.4 (C-6), 20.7, 20.6, 20.5, 20.4 (acetyl *Me*). Anal. Calcd for $C_{22}H_{24}N_2O_9$ (460.44): C: 57.39, H: 5.25, N: 6.08. Found: C: 57.65, H: 5.43, N: 6.10.

4.4.28. *N*-(2,2,2-Tribromoethylidene)-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-imine (40). Prepared from **3** (0.10 g, 0.27 mmol) with tribromoacetaldehyde according to General procedure C; yield: 0.11 g, 69%, crystalline product (E: ethylacetate–hexane, 5:12), mp 140–142°C, $[\alpha]_D$=−11.4 (*c* 1.0, $CHCl_3$); R_f=0.76 (eluent A). ν_{max} (KBr): 3440, 2927, 1752, 1369, 1229 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm): 7.71 (1H, d, *J*=2.1 Hz, =C*H*–), 5.49 (1H, dd, *J*=1.1, 3.4 Hz, H-4), 5.19 (1H, dd, *J*=3.4, 10.2 Hz, H-3), 5.09 (1H, dd, *J*=9.0, 10.2 Hz, H-2), 5.01 (1H, dd, *J*=2.1, 9.0 Hz, H-1), 4.25 (1H, dd, *J*=6.6, 11.2 Hz, H-6), 4.19 (1H, dd, *J*=6.5, 11.2 Hz, H-6′), 4.09 (1H, ddd, *J*=1.1, 6.5, 6.6, H-5), 2.15, 2.08, 2.06, 1.99 (4×3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.5, 170.3, 170.2, 169.4 (acetyl *C*O), 157.5 (=*C*H–), 88.7 (C-1), 72.9 (C-5), 71.2 (C-3), 68.8 (C-2), 67.1 (C-4), 61.3 (C-6), 37.9 (*C*Br_3), 20.8, 20.7, 20.6, 20.5 (acetyl *Me*). Anal. Calcd for $C_{16}H_{20}Br_3NO_9$ (610.05): C: 31.50, H: 3.30, N: 2.30. Found: C: 31.35, H: 3.13, N: 2.42.

4.4.29. *N*-(2,2,2-Tribromoethylidene)-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-imine (41). Prepared from **4** (0.40 g, 1.07 mmol) with tribromoacetaldehyde according to General procedure C; yield: 0.52 g, 80%, colourless crystalline product (E: ethylacetate–hexane, 5:12), mp 135–137°C, $[\alpha]_D$=+81.7 (*c* 1.1, $CHCl_3$); R_f=0.63 (eluent A). ν_{max} (KBr): 3440, 2920, 1754, 1370, 1228 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ (ppm): 7.51 (1H, s, =C*H*–), 5.56 (1H, dd, *J*=1.4, 3.2 Hz, H-4), 5.41 (1H, d, *J*=4.6 Hz, H-1), 5.37 (1H, dd, *J*=4.6, 10.5 Hz, H-2), 5.29 (1H, dd, *J*=3.2, 10.5 Hz, H-3), 4.74 (1H, m, H-5), 4.19 (1H, dd, *J*=6.7, 11.3 Hz, H-6), 4.09 (1H, dd, *J*=6.5, 11.3 Hz, H-6′), 2.19, 2.07, 2.05, 2.00 (4×3H, s, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.4, 170.2, 170.0, 169.9 (acetyl *C*O), 160.2 (=*C*H–), 88.2 (C-1), 68.6 (C-2), 68.4 (C-5), 68.1 (C-4), 68.0 (C-4), 61.5 (C-6), 36.7 (*C*Br_3), 20.7, 20.7, 20.6, 20.5 (acetyl *Me*). Anal. Calcd for $C_{16}H_{20}Br_3NO_9$ (610.05): C: 31.50, H: 3.30, N: 2.30. Found: C: 31.65, H: 3.43, N: 2.01.

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