Anomeric *O*-Alkylation, 16[1]

Synthesis of Hetaryl Glycosides and Their Glycosyl Donor Properties[1]

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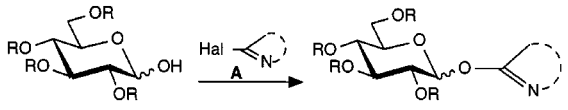
Anomeric *O*-hetarylation of tetra-*O*-benzyl- and tetra-*O*-acetylglucose (**1a**, **b**) can be directly performed with electron-deficient heteroaromatic/heterocyclic systems **2–14**, which contain imide halide moieties. The reactions were carried out in the presence of a base and led, through an exchange of the halide by the glucopyranosyloxy moiety, to the products **2a–14a**, **7b–14b**. Predominantly or exclusively β-products were obtained. Systems bearing more than one imide halide moiety, such as cyanuric fluoride (**15**) or 5-chloro-2,4,6-trifluoropyrimidine (**16**), can be employed for successive anomeric *O*-hetarylations. Investigation of the glycosyl donor properties of *O*-glucosyl heteroaromatic imidates with 6-*O*- and 4-*O*-unprotected glucose derivatives **18** and **19** as acceptors and comparison of the results obtained with data for the corresponding β-trichloroacetimidates **17aβ** and **17bβ**, reveals that 2,3,5,6-tetrafluoropyridin-4-yl glucopyranosides **14aβ** and **14bβ** exhibit similar properties. For specific tasks, for instance α-glucopyranoside formation, **14aβ** may even be advantageous.

Direct anomeric *O*-arylation and hetarylation of 2,3,4,6-tetra-*O*-benzyl-D-glucose (**1a**), 2,3,4,6-tetra-*O*-acetyl-D-glucose (**1b**), and even of glucose itself (**1c**) (Scheme 1) with electron-deficient aromatic and heteroaromatic compounds, leading directly to aryl and hetaryl glucopyranosides, has recently been shown to be quite efficient[2][3][4]. Clearly, the anomeric hydroxy group is the most acidic and the base-generated 1-oxide is sufficiently nucleophilic to preclude competing reactions at other hydroxy groups[5][6][7]. This method, which in a convenient manner ligates sugar residues through a glycosidic linkage onto heterocycles, has now been extended to heterocyclic imide chlorides and the corresponding fluorides (Scheme 1, **A**: Hal = Cl, F). The products **Aa−Ac** obtained in this reaction are not only of interest as *O*-glycosylated heterocycles, which possess interesting new physical and biological properties[8]; the generated *O*-glycosyl imidate moieties, being part of a strongly electron-withdrawing system, should, under acid catalysis, also exhibit potent glycosyl donor properties since they experience energy gain by the imidate to amide transformation[2][4][9][10]. Thus, their comparison with *O*-glycosyl trichloroacetimidates in glycosylation reactions[5] is of interest. Investigations along these lines are reported herein.

Scheme 1



1a: R = Bn
1b: R = Ac
1c: R = H

Aa
Ab
Ac

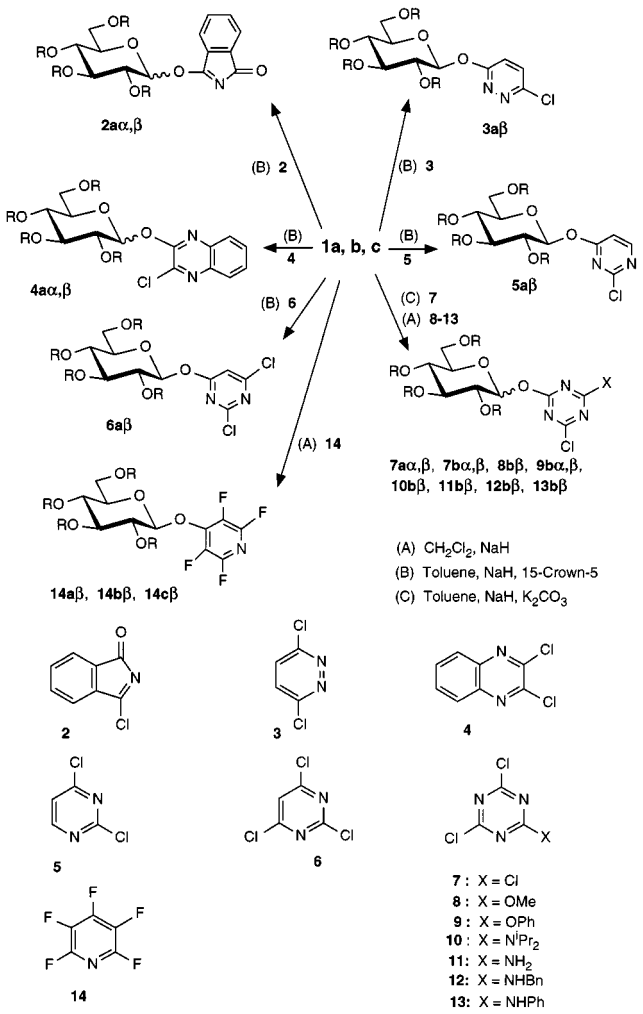
Anomeric O-Hetarylation

Nucleophilic substitution at heteroaromatic/heterocyclic compounds through an addition−elimination mechanism (S_N-Ar/AE) generally requires activation by electron-withdrawing groups and a good leaving group. Therefore, imide halide moieties that are incorporated into heteroaromatic systems bearing additional activating groups should be particularly suitable. Therefore, we investigated some typical electron-poor halogenated azines [3,6-dichloropyridazine (**3**), 2,3-dichloroquinoxaline (**4**), 2,4-dichloropyrimidine (**5**), 2,4,6-trichloropyrimidine (**6**), cyanuric chloride (**7**) and its monoalkyl- or aryloxy and amino substitution products (**8−13**), and pentafluoropyridine (**14**)], as well as one azole derivative [3-chloroisoindolenin-1-one (**2**)][11], with regard to their reactions with *O*-protected glucose derivatives **1a**[12], **1b**[13] and with glucose (**1c**) itself (Scheme 2). Reactions of **1a** with **2−7** and **14** were performed either in toluene in the presence of NaH as base and 15-crown-5 as activator (General Procedure 1 B), or in toluene in the presence of NaH and K_2CO_3 as base (General Procedure 1 C), or in CH_2Cl_2 solely in the presence of NaH as base (General Procedure 1 A). These reactions afforded hetaryl glucopyranosides **2a−7a** and **14a**. Due to the higher reactivity of the equatorial anomeric oxide oxygen compared to the axial oxygen[5][7], in most cases only the β-product (**3aβ**, **5aβ**, **6aβ**, **14aβ**) could be isolated. In the other cases, minor amounts of the α-products were also found (**2a**, **α/β** = 1:9; **4a**, **α,β** =

  1434−193X/98/0707−1353 $ 17.50+.50/0

1:9; **7a**, **α,β** = 1:2). Because of their high reactivity, cyanuric chloride (**7**) and pentafluoropyridine (**14**) also underwent reaction with the less reactive 2,3,4,6-tetra-*O*-acetylglucose (**1b**). However, a lower yield of **7bα**, **β** was obtained; only **14** afforded a high yield of the *O*-glucopyranosyl product **14bβ**. Donor **14** also reacted with *O*-unprotected glucose (**1c**) furnishing exclusively the *O*-(β-D-glucopyranosyl) derivative **14cβ**.

Scheme 2



In order to investigate systems with lower reactivity, 2,4-dichloro-1,3,5-triazines **8**−**13**[14][15][16][17][18][19] were treated with **1b**. In all cases, the expected 2-(2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyloxy) derivatives **8b**−**13b** were obtained in good yields. Only the monosubstituted β-products were isolated with **8bβ** and **10bβ**−**13bβ**, while some of the α-form was found with **9b** (**α/β** = 1:10). Thus, a broad application of this anomeric *O*-hetarylation is apparent.

This reaction should be also applicable for consecutive substitutions with systems bearing more than one imide halide moiety. To this end, reactions of cyanuric fluoride (**15**) and 5-chloro-2,4,6-trifluoropyrimidine (**16**) were investigated (Scheme 3), which are known to be amenable to consecutive halide exchange reaction[20]. Thus, reaction of **15** with **1a** was carried out under standard conditions but at low temperature. The monosubstitution product **15aβ** was only observed as an intermediate; exchange of the second fluorine atom followed immediately, leading to 2,4-bis(β-D-glucopyranosyloxy)triazine **15aaβ**. Both sugar residues were found to be in the β-configuration. Exchange of the remaining fluorine atom could be performed at room temperature with either **1a** or **1b**, affording **15aaa** and **15aab**, respectively. In the case of **1a**, only β-product formation was observed (leading to **15aaaβ**), whereas for **1b** a mixture of α.β-anomers (**15aabα/15aabβ** = 3:2) resulted. Similar results were obtained for **16**, although with **1a** and **1b** at low temperature, the monosubstituted products **16aβ** and **16bβ** could be isolated in high yields. Reaction of **16bβ** with **1b** at 4°C led to exchange of the fluorine atom in the 6-position, thereby furnishing **16bbβ**. The symmetrical structure of this material, as is evident from its NMR data, proves the expected higher reactivity of the fluorine atoms in the 4- and 6-positions and thus confirms the structural assignments. The remaining fluorine atom in the 2-position could be readily exchanged with **1b** at 30°C, thereby furnishing target molecule **16bbbβ**. Clearly, this chemistry is not only useful for the modification of biologically active compounds, but also for the construction of dendrimeric structures.

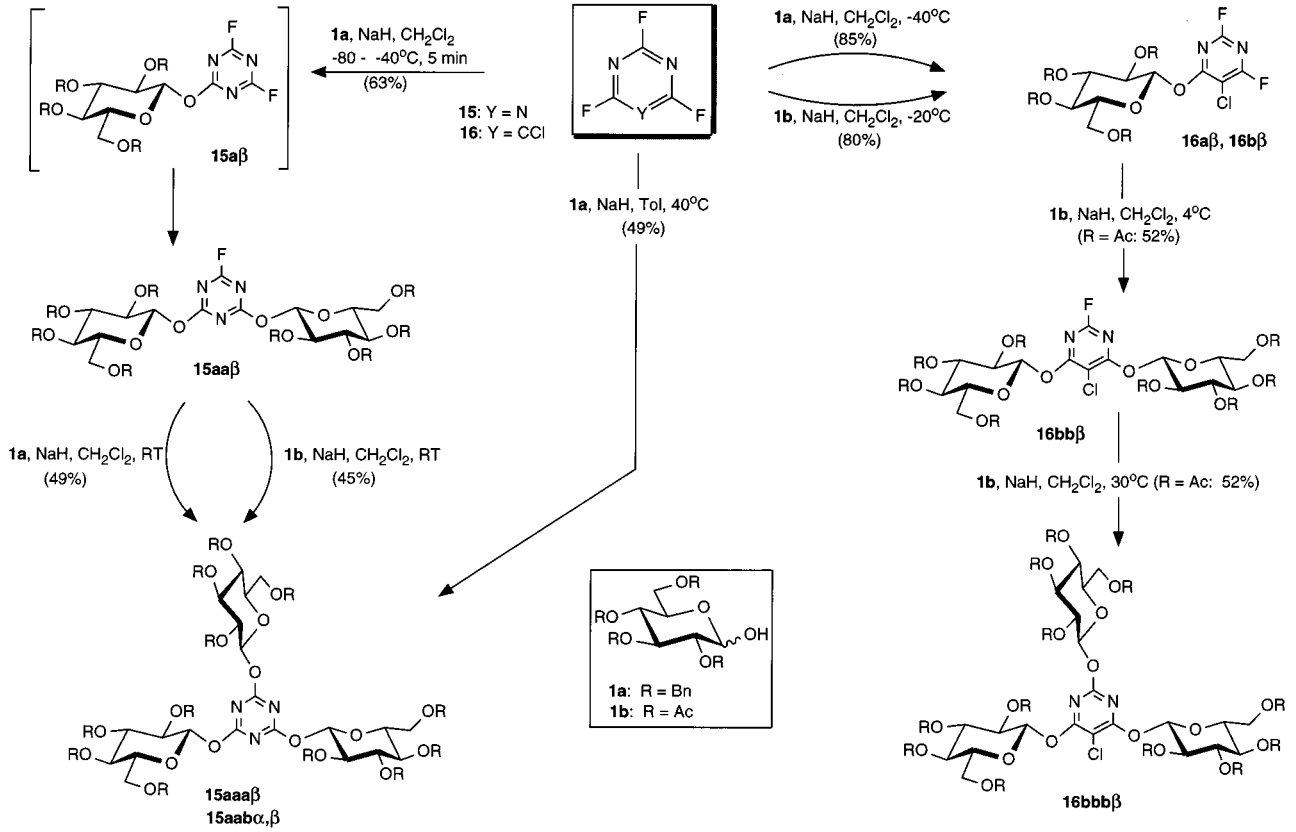
In order to further prove the usefulness of this chemistry, deprotection of the sugar residues is important. Because 1,3,5-triazines are quite sensitive to hydrolytic conditions, successful deacylation is particularly important. As shown in Scheme 4, under Zemplen conditions[21] at low temperatures, compounds **10bβ**−**13bβ** could be readily transformed into *O*-unprotected derivatives **10cβ**−**13cβ**. Because of their sensitivity to hydrolytic conditions, the products were re-*O*-acetylated with acetic anhydride in pyridine, furnishing the starting materials **10bβ**−**13bβ** in high yields.

Glycosylation Reactions

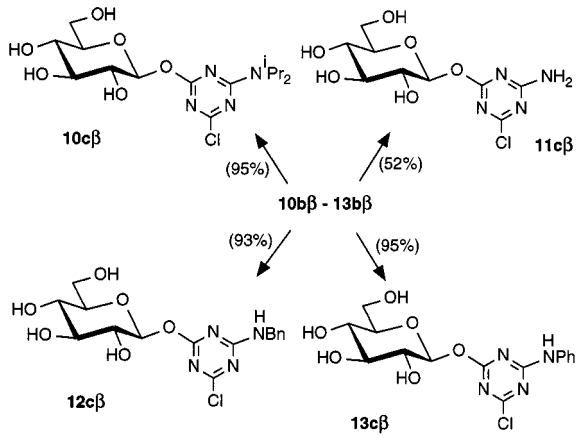
Heterocyclic imidates of types **B** and **C** (Scheme 5) have previously been investigated as potential glycosyl donors[2][4][9][10][22][23]. For instance, the leaving group qualities of the 2-pyridylthio and 2-pyridyloxy moieties have been tested[9][10][22][23], although only for reactive systems could good glycosylation yields be obtained. Recently, electron-donating substituents at the pyridyl moiety (**C**: Z = OMe)[10] and the related 2-pyridylthiocarbonyloxy system **D**[24] have also been probed with various sugar residues. However, despite these structural modifications through acid activation (which has also been termed "remote activation"[10]), no superior glycosyl donor properties were attained compared with those of the widely used *O*-glycosyl trichloroacetimidates.

Comparison of the formation of imidates from either trichloroacetonitrile or imide halides (Scheme 6) highlights the advantages of the first system: with catalytic amounts of base in a kinetically or thermodynamically controlled reaction, the β- and α-adducts are often selectively accessible. Due to the electron-withdrawing trichloromethyl group and the basic imide moiety, these adducts exhibit good glycosyl

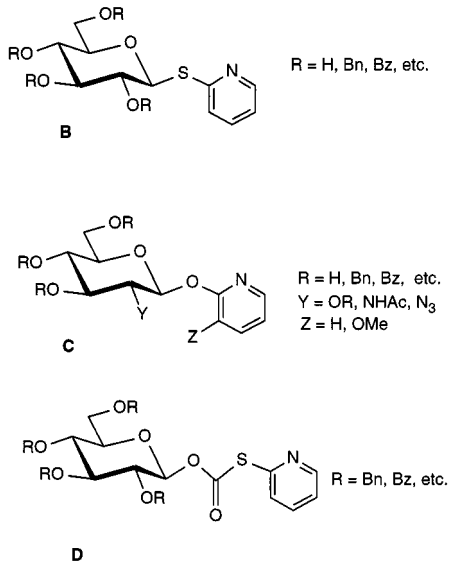
Scheme 3



Scheme 4. Reaction conditions: NaOMe, MeOH, −20°C, 3 h



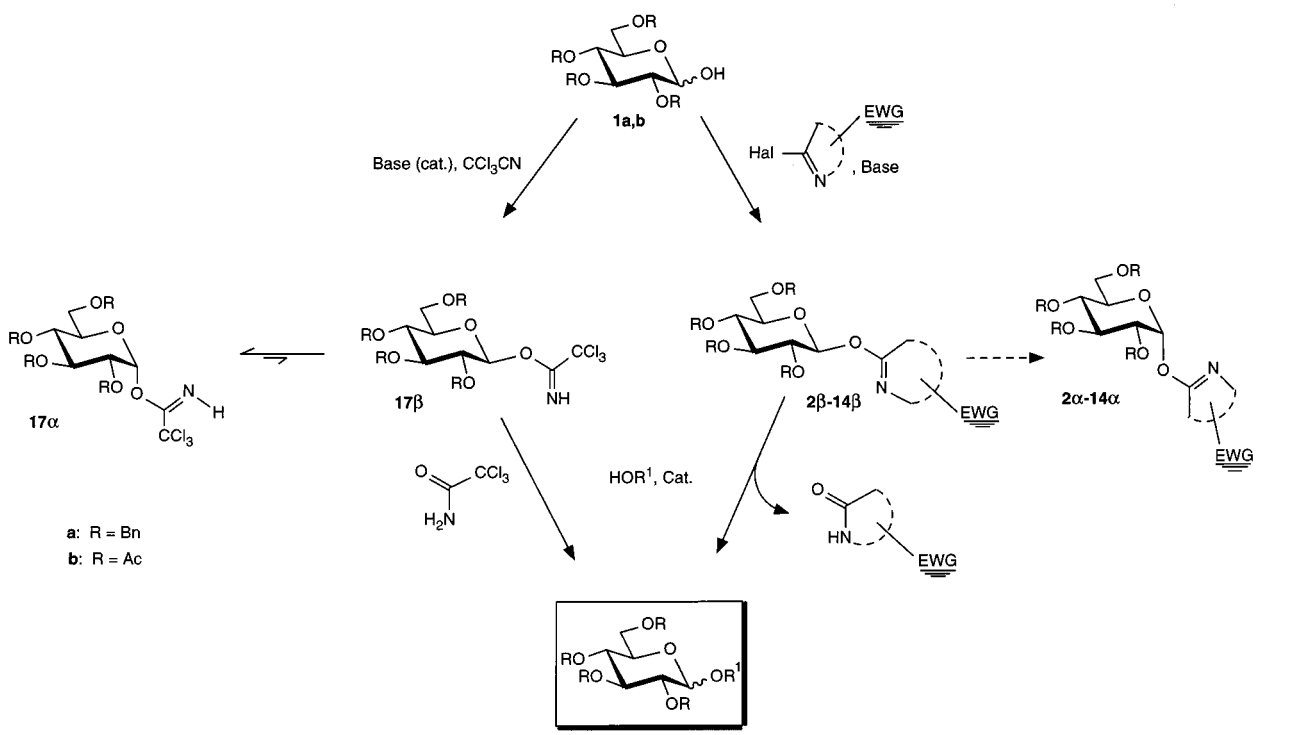
Scheme 5



donor properties under conditions of mild acid catalysis[5]. On the other hand, imide halides require equivalent amounts of base in order to form the imidates and, once formed, anomerisation is not possible. This is borne out by the experiments described above; mainly the β-products were obtained. However, by judicious selection of the heterocyclic system, i.e. those incorporating electron-withdrawing substituents or ring constituents, it should be possible to achieve high glycosyl donor properties under conditions of mild acid catalysis.

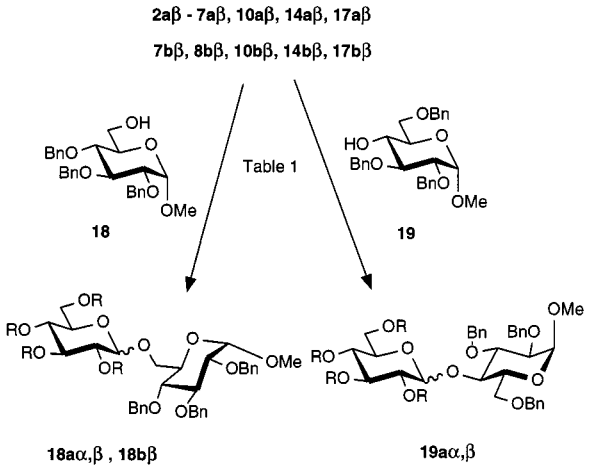
In order to demonstrate the glycosyl donor properties of such systems, compounds **2aβ−7aβ** and **14aβ** were reacted with the known 6-*O*- and 4-*O*-unprotected glucose derivatives **18**[25] and **19**[26], respectively, as acceptors (Scheme 7). Under trimethylsilyl trifluoromethanesulfonate (TMSOTf) catalysis in diethyl ether solution, these *O*-benzyl protected glycosyl donors afforded the known disaccharides **18aα**, **β**[27] and **19aα**, **β**[28] in good to high yields, mainly or even exclusively in the α-form (Table 1). Comparison of the results with data for the corresponding β-trichloroacetimidate

Scheme 6



17aβ shows that **14aβ** offers similar glycosyl donor properties. With **18**, only the α-isomer **18aα** was formed. Similar results were obtained for the *O*-acetyl protected compounds **7bβ**, **8bβ**, **10bβ**, and **14bβ**. Due to neighboring group participation, with **18** each of these gave the β-connected disaccharide **18bβ**[29], although only **14bβ** furnished a yield of **18bβ** comparable to that obtained from the reaction of **18** with the corresponding trichloroacetimidate **17bβ**.

Scheme 7



In conclusion, under conditions of acid catalysis, heterocyclic *O*-glycosyl imidates bearing electron-withdrawing groups (as substituents and/or ring members) are potent glycosyl donors, which may become as effective as the corresponding *O*-glycosyl trichloroacetimidates. In some cases, they may even exhibit advantages over this highly successful, established system.

Table 1. Glycosylation of acceptors **18** and **19** with *heterocyclic O*-glycosyl imidates and *O*-glycosyl trichloroacetimidates

Donor	Acceptor **18** Method[a]	Yield [%]	**18aα/18aβ**	Acceptor **19** Method[a]	Yield [%]	**19aα/19aβ**
2aβ	A	76	4:5	A	42	2:1
3aβ	A	80	1:1	A	63	5:2
	B	80	9:1	–	–	–
4aβ	A	98	5:2	A	76	3:1
5aβ	A	81	1:1	A	63	5:2
6αβ	A	69	2:1	A	72	7:2
7αβ	A	75	α	–	–	–
14aβ	A	98	α	3:1		
17aβ	A	98	3:2	A	85	1:1
	C	85	8:1	C	72	3:1
7bβ	A	66	**18bβ**	–	–	–
8bβ	A	45	**18bβ**	–	–	–
10bβ	A	42	**18bβ**	–	–	–
14bβ	A	74	**18bβ**	–	–	–
17bβ	A	81	**18bβ**	–	–	–

[a] A: TMSOTf, CH_2Cl_2, room temp. B: $BF_3{\cdot}OEt_2$, toluene, −25°C, C: TMSOTf, Et_2O, room temp.; for further details, see Experimental Section.

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Experimental Section

Solvents were purified by standard procedures. – ^{1}H-NMR spectra: Bruker AC-250 (250 MHz): internal standard tetramethylsilane

(TMS). − Flash chromatography: Silica gel 60 (Baker: 0.04−0.063 mm). − Thin-layer chromatography (TLC): Foil plates, silica gel 60 F_{254} (Merck: layer thickness 0.2 mm). − Optical rotations: Perkin-Elmer polarimeter 241 MC: 1-dm cell, 20°C. − Elemental analyses: Heraeus CHN-O-Rapid. − MALDI-MS: Kratos (Kompac Maldi 1).

General Procedure 1 (GP1 A,B,C) − Synthesis of Aryl Glycosides (**2a−7a**, **14a**, **7b−14b**, **14c**): Compound **1a**[12] (540 mg, 1 mmol) or **1b**[13] (340 mg, 1 mmol) was dissolved in (A): dry dichloromethane (5 ml) or (B/C): dry toluene (5 ml) at 70°C and stirred with 15-crown-5 (220 µl, 1.1 mmol) and NaH (26 mg, 1.1 mmol) and (C): K_2CO_3 (0.5 g) for 5 min. A solution of the heterocycle (1 mmol) (A): in dry dichloromethane (2 ml), (B): in dry toluene (3 ml), or (C): in dry toluene (10 ml) was then added dropwise while stirring at (A): room temp. or (B/C): 70°C. A/B: After 1−3 h, the solution was neutralized with ion-exchange resin (Amberlite IR 120, Na^+-form), filtered, and the filtrate was concentrated under reduced pressure. C: After 3 h at 70°C, the mixture was filtered and the filtrate was concentrated under reduced pressure to half of its original volume. Purification by flash chromatography gave the corresponding aryl glycoside.

General Procedure 2 (GP2) − Synthesis of Dendrimeric Structures (**15aa**, **15aaa**, **15aab**, **16a**, **16b**, **16bb**, **16bbb**): A solution of **1a**, **b**[12][13] (1 equiv.), 15-crown-5 (1.1 equiv.) and NaH (1.1 equiv.) in dry dichloromethane (5 ml, 1 mmol sugar) was added dropwise to a solution of the heterocyclic compound (1 equiv.) in dry dichloromethane (2 ml, 1 mmol heterocycle). After 15 min. at the temperature *T* given below, the reaction mixture was allowed to warm to room temp. Neutralization with ion-exchange resin (Amberlite IR 120, Na^+-form), filtration, and concentration of the filtrate under reduced pressure gave an oily residue, which was purified by flash chromatography.

General Procedure 3 (GP3) − Deprotection (**10c−13c**): To a solution of compound **10b−13b** (100 mg) in dry methanol (3 ml) at −20°C, a catalytic amount of NaOMe solution (0.1 M) was added and the mixture was stirred until deacetylation was complete. Finally, the solution was neutralized with ion-exchange resin (Amberlite IR 120, Na^+-form), concentrated under reduced pressure, and purified by flash chromatography (ethyl acetate/methanol, 16:1).

General Procedure 4 (GP4) − Acetylation (**10b−13b**): Crude **10c−13c** was dissolved in dry pyridine (3 ml) and the solution was cooled to 0°C. Acetic anhydride was added dropwise and the solution was stirred overnight at room temp. It was then concentrated in vacuo and the solvent was coevaporated with toluene (3 times). The residue was purified by flash chromatography (toluene/ethyl acetate, 6:1).

General Procedure 5 (GP5 A,B,C) − Glycosylation (**18a**, **b** *and* **19a**, **b**)[27][28]: Under argon, the glycosyl donor (0.26 mmol) and acceptor **18**[25] or **19**[26] (0.2 mmol) were dissolved in (0.4 ml) (A): dry dichloromethane, (B): dry toluene, or (C): dry diethyl ether. A catalytic amount of Lewis acid was then added (A/C): TMSOTf at room temp., (B): $BF_3 \cdot OEt_2$ at −25°C. After 1 h, the reaction mixture was neutralized with NEt_3 and concentrated in vacuo. Flash chromatography (toluene/ethyl acetate, 20:1) gave the corresponding disaccharide as a colorless oil.

1-(2,3,4,6-Tetra-O-benzyl-α/β-D-glucopyranosyloxy)isoindolenin-3-one (**2aα**, **β**): GP1 B, **2**[11] (165.5 mg), flash chromatography (toluene/ethyl acetate, 15:1), yield (348 mg, 52%), colorless syrup, α/β = 1:9. − TLC (toluene/ethyl acetate, 8:1): R_f = 0.47. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.59−3.87 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.42−4.90 (m, 8 H, 4 CH_2Ph), 6.34 (d, 0.9 H, $J_{1,2}$ = 7.8 Hz, 1-Hβ), 6.88 (d, 0.1 H, $J_{1,2}$ = 3.6 Hz, 1-Hα), 7.12−7.26 (m, 20 H, Ph), 7.61−7.72 (m, 2 H, 4′-H, 5′-H), 7.82 (m_c, 1 H, 6′-H), 8.03 (m_c, 1 H, 3′-H). − $C_{42}H_{39}NO_7$ (669.8): calcd. C 75.52, H 5.87, N 2.09; found C 75.05, H 6.01, N 1.93.

6-Chloro-3-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyloxy)-pyridazine (**3aβ**): GP1 B, **3**[30] (150 mg), flash chromatography (toluene/ethyl acetate, 20:1), yield (415 mg, 65%), colorless solid, m.p. 118°C. − TLC (toluene/ethyl acetate, 6:1): R_f = 0.47. − $[\alpha]_D^{20}$ = +10 (*c* = 1, CH_2Cl_2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.58−3.83 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.35−5.01 (m, 8 H, 4 CH_2Ph), 6.24 (d, 1 H, $J_{1,2}$ = 7.8 Hz, 1-Hβ), 6.81 (d, 1 H, $J_{4',5'}$ = 9.9 Hz, 4′-H), 7.08−7.31 (m, 20 H, Ph), 7.34 (d, 1 H, $J_{5',4'}$ = 9.9 Hz, 5′-H). − $C_{42}H_{39}ClN_2O_6$ (702.8): calcd. C 69.88, H 5.71, N 4.28; found C 69.49, H 5.65, N 4.60.

3-Chloro-2-(2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyloxy)-quinoxaline (**4aα**, **β**): GP1 B, **4**[30] (199.5 mg), flash chromatography (toluene/ethyl acetate, 20:1), yield (588 mg, 83%), colorless solid, m.p. 110°C, α/β = 1:9. − TLC (toluene/ethyl acetate, 8:1): R_f = 0.62. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.59−3.92 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.44−5.03 (m, 8 H, 4 CH_2Ph), 6.17 (d, $J_{1,2}$ = 7.7 Hz, 0.90 H, 1-Hβ), 6.56 (d, $J_{1,2}$ = 3.7 Hz, 0.1 H, 1-Hα), 7.60−7.71 (m, 2 H, 6′-H, 7′-H), 7.84 (m_c, 1 H, 5′-H), 7.90 (m_c, 1 H, 8′-H). − $C_{42}H_{39}ClN_2O_6$ (702.8): calcd. C 71.72, H 5.59, N 3.99; found C 71.06, H 5.31, N 3.92.

2-Chloro-4-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyloxy)-pyrimidine (**5aβ**): GP1 B, **5**[30] (153 mg), flash chromatography (toluene/ethyl acetate, 20:1), yield (398 mg, 60%), colorless syrup. − TLC (toluene/ethyl acetate, 8:1): R_f = 0.38. − $[\alpha]_D^{20}$ = +13 (*c* = 1, CH_2Cl_2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.63−3.82 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.42−4.98 (m, 8 H, CH_2Ph), 6.01 (d, 1 H, $J_{1,2}$ = 7.7 Hz, 1-Hβ), 6.63 (d, 1 H, $J_{5',4'}$ = 5.5 Hz, 5′-H), 7.14−7.39 (m, 20 H, Ph), 8.33 (d, 1 H, $J_{4',5'}$ = 5.5 Hz, 4′-H). − $C_{38}H_{37}ClN_2O_6$ (653.2): calcd. C 69.88, H 5.71, N 4.28; found C 69.58, H 5.65, N 4.60.

2,4-Dichloro-6-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyloxy)-pyrimidine (**6aβ**): GP1 B, **6**[30] (184.5 mg), flash chromatography (toluene/ethyl acetate, 20:1), yield (478 mg, 68%), colorless syrup. − TLC (toluene/ethyl acetate, 8:1): R_f = 0.39. − $[\alpha]_D^{20}$ = +194 (*c* = 1, CH_2Cl_2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.54−4.21 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.48−4.98 (m, 8 H, 4 CH_2Ph), 5.97 (d, 1 H, $J_{1,2}$ = 7.9 Hz, 1-Hβ), 6.55 (s, 1 H, 6′-H), 7.12−7.42 (m, 20 H, Ph). − $C_{38}H_{36}Cl_2N_2O_6$ (687.6): calcd. C 66.38, H 5.28, N 4.02; found C 66.48, H 5.29, N 3.97.

4,6-Dichloro-2-(2,3,4,6-tetra-O-benzyl-α/β-D-glucopyranosyloxy)triazine (**7aα**, **β**): GP1 C, **7**[30] (180 mg), flash chromatography (toluene/ethyl acetate, 20:1), yield (220 mg, 32%), colorless syrup, α/β = 1:2. − TLC (toluene/ethyl acetate, 6:1): R_f = 0.67. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.68−3.78 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.43−4.92 (m, 8 H, 4 CH_2Ph), 5.93 (d, 0.66 H, $J_{1,2}$ = 6.9 Hz, 1-Hβ), 6.60 (d, 0.34 H, $J_{1,2}$ = 3.5 Hz, 1-Hα). − MALDI-MS (positive mode, matrix: DHB): *m/z* = [M^+] = 688. − $C_{37}H_{35}Cl_3N_3O_6$ (688.5).

4,6-Dichloro-2-(2,3,4,6-tetra-O-acetyl-α/β-D-glucopyranosyloxy)-triazine (**7bα**, **β**): GP1 C, **7**[30] (180 mg), flash chromatography (toluene/ethyl acetate, 8:1), yield (48 mg, 10%), colorless foam, α/β = 1:2. − TLC (toluene/ethyl acetate, 4:1): R_f = 0.52. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.01−2.11 (m, 12 H, 4 OAc), 3.83 (ddd, 0.67 H, $J_{5,4}$ = 9.8 Hz, $J_{5,6A}$ = 5.2 Hz, $J_{5,6B}$ = 2.3 Hz, 5-Hβ), 4.02−4.32 (m, 3.33 H, 5-Hα, 6-H_A, 6-H_B), 5.03−5.19 (m, 2 H, 2-H, 4-H), 5.22 (dd, 0.67 H, $J_{3,2}$ = 9.6 Hz, $J_{3,4}$ = 9.9 Hz, 3-Hβ), 5.30

(dd, 0.33 H, $J_{3,2}$ = 9.6 Hz, $J_{3,4}$ = 9.9 Hz, 3-Hα), 5.71 (d, 0.67 H, $J_{1,2}$ = 8.4 Hz, 1-Hβ), 6.33 (d, 0.37 H, $J_{1,2}$ = 3.7 Hz, 1-Hα). − $C_{17}H_{19}Cl_2N_3O_{10}$ (496.1): calcd. C 41.12, H 3.90, N 8.45; found C 41.11, H 4.26, N 8.34.

4-Chloro-6-methoxy-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)triazine (**8bβ**): GP1 A, **8**[14] (180 mg), flash chromatography (toluene/ethyl acetate, 6:1), yield (287 mg, 59%), colorless foam. − TLC (toluene/ethyl acetate, 6:1): R_f = 0.21. − $[\alpha]_D^{20}$ = −1 (*c* = 1, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.96−2.09 (m, 12 H, 4 OAc), 3.93 (ddd, 1 H, $J_{5,4}$ = 9.9 Hz, $J_{5,6A}$ = 4.4 Hz, $J_{5,6B}$ = 2.3 Hz, 5-H), 4.06 (s, 3 H, OMe), 4.18 (dd, dd, 2 H, J_{gem} = 12.4 Hz, $J_{6A,5}$ = 4.4 Hz, $J_{6B,5}$ = 2.3 Hz, 6-H_A, 6-H_B), 5.12−5.23 (m, 3 H, 2-H, 3-H, 4-H), 6.04 (d, 1 H, $J_{1,2}$ = 7.8 Hz, 1-Hβ). − $C_{18}H_{22}ClN_3O_{11}$ (491.8): calcd. C 43.96, H 4.51, N 8.54; found C 43.82, H 4.88, N 7.89.

4-Chloro-6-phenoxy-2-(2,3,4,6-tetra-O-acetyl-α/β-D-glucopyranosyloxy)triazine (**9bα**, **β**): GP1 A, **9**[15] (241.5 mg), flash chromatography (toluene/ethyl acetate, 6:1), yield (228 mg, 42%), colorless foam, α/β = 1:10. − TLC (toluene/ethyl acetate, 5:1): R_f = 0.30. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90−2.01 (m, 12 H, 4 OAc), 3.43 (ddd, 1 H, $J_{5,4}$ = 9.9 Hz, $J_{5,6A}$ = 4.3 Hz, $J_{5,6B}$ = 2.1 Hz, 5-H), 3.93 (dd, dd, 2 H, J_{gem} = 12.5 Hz, $J_{6A,5}$ = 4.3 Hz, $J_{6B,5}$ = 2.1 Hz, 6-H_A, 6-H_B), 5.02−5.16 (m, 2.9 H, 2-H, 3-Hβ, 4-H), 5.54 (dd, 0.1 H, $J_{3,2}$ = 10.2 Hz, $J_{3,4}$ = 10.4 Hz, 3-Hα), 5.67 (d, 0.9 H, $J_{1,2}$ = 7.8 Hz, 1-Hβ), 6.5 (d, 0.1 H, $J_{1,2}$ = 3.6 Hz, 1-Hα). − $C_{23}H_{24}ClN_3O_{11}$ (553.9): calcd. C 49.87, H 4.37, N 7.59; found C 50.27, H 4.48, N 7.38.

4-Chloro-6-diisopropylamino-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)triazine (**10bβ**): GP1 A, **10**[16] (248.5 mg), flash chromatography (toluene/ethyl acetate, 6:1), yield (262 mg, 42%), colorless foam. − TLC (toluene/ethyl acetate, 3:1): R_f = 0.38. − $[\alpha]_D^{20}$ = −15 (*c* = 1, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20−1.38 (m, 14 H, N*i*Pr_2), 2.01−2.03 (m, 12 H, 4 OAc), 3.82 (ddd, 1 H, $J_{5,4}$ = 9.6 Hz, $J_{5,6A}$ = 5.2 Hz, $J_{5,6B}$ = 2.3 Hz, 5-H), 4.15 (dd, dd, J_{gem} = 12.4 Hz, $J_{6A,5}$ = 5.3 Hz, $J_{6B,5}$ = 2.3 Hz, 6-H_A, 6-H_B), 5.23 (m, 3 H, 2-H, 3-H, 4-H), 5.95 (d, 1 H, $J_{1,2}$ = 7.7 Hz, 1-Hβ). − $C_{23}H_{33}ClN_4O_{10}$ (560.9): calcd. C 49.25, H 5.93, N 9.98; found C 49.61, H 5.93, N 9.82.

6-Amino-4-chloro-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)triazine (**11bβ**): GP1 A, **11**[17] (164 mg), flash chromatography (toluene/ethyl acetate, 4:1), yield (145 mg, 31%), colorless or light-yellow foam. − TLC (toluene/ethyl acetate, 2:1): R_f = 0.25 (color reaction with ninhydrin). − $[\alpha]_D^{20}$ = +33 (*c* = 1, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.62 (d, 2 H, NH_2), 1.94−2.08 (m, 12 H, 4 OAc), 3.91 (ddd, 1 H, $J_{5,4}$ = 9.7 Hz, $J_{5,6A}$ = 4.6 Hz, $J_{5,6B}$ = 2.4 Hz, 5-H), 4.18 (dd, dd, 2 H, J_{gem} = 12.3 Hz, $J_{6A,5}$ = 4.6 Hz, $J_{6B,5}$ = 2.4 Hz, 6-H_A, 6-H_B), 5.96 (d, 1 H, $J_{1,2}$ = 7.8 Hz, 1-Hβ). − MALDI-MS (positive mode, matrix: DHB): *m/z* = $[M^+ + Na]$ = 499. − $C_{17}H_{21}ClN_4O_{10}$ (476.5).

6-Benzylamino-4-chloro-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)triazine (**12bβ**): GP1 A, **12**[18] (254.5 mg), flash chromatography (toluene/ethyl acetate, 5:1), yield (202 mg, 36%), colorless foam. − TLC (toluene/ethyl acetate, 3:1): R_f = 0.31. − $[\alpha]_D^{20}$ = +20 (*c* = 1, $CHCl_3$). − ^{1}H NMR (250 MHz, DMSO, 100°C): δ = 1.88−2.03 (m, 12 H, 4 OAc), 4.01−4.22 (m, 3 H, 5-H, 6-H_A, 6-H_B), 4.55 (d, 2 H, J_{CH2} = 6.4 Hz, CH_2Ph), 4.95−5.05 (m, 2 H, 2-H, 4-H), 5.54 (dd, 1 H, $J_{3,2}$ = 9.6 Hz, $J_{3,4}$ = 9.9 Hz, 3-H), 6.32 (d, 1 H, $J_{1,2}$ = 8.1 Hz, 1-Hβ), 7.17−7.34 (m, 6 H, Ph, NH). − $C_{24}H_{26}ClN_4O_{10}$ (565.9): calcd. C 50.94, H 4.63, N 9.89; found C 50.79, H 4.86, N 9.51.

4-Chloro-6-phenylamino-2-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)triazine (**13bβ**): GP1 A, **13**[19] (240.5 mg), flash chromatography (toluene/ethyl acetate, 5:1), yield (315 mg, 57%), colorless oil. − TLC (toluene/ethyl acetate, 6:1): R_f = 0.17. − $[\alpha]_D^{20}$ = −21 (*c* = 1, $CHCl_3$). − ^{1}H NMR (250 MHz, DMSO, 90°C): δ = 1.89−2.01 (m, 12 H, 4 OAc), 4.05−4.22 (m, 3 H, 5-H, 6-H_A, 6-H_B), 5.00−5.14 (m, 2 H, 2-H, 4-H), 5.36 (dd, 1 H, $J_{3,2}$ = 9.3 Hz, $J_{3,4}$ = 9.6 Hz, 3-H), 6.19 (d, 1 H, $J_{1,2}$ = 7.9 Hz, 1-Hβ), 7.12−7.62 (m, 5 H, N-Ph), 10.76 (s, 1 H, NH). − $C_{23}H_{25}ClN_4O_{10}$ (552.9): calcd. C 49.96, H 4.56, N 10.12; found C 49.83, H 4.65, N 9.32.

2,3,5,6-Tetrafluoro-4-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyloxy)pyridine (**14aβ**): GP1 A, **14**[30] (169 mg), flash chromatography (toluene/ethyl acetate, 20:1), yield (635 mg, 92%), colorless oil. − TLC (petroleum ether/ethyl acetate, 7:3): R_f = 0.62. − $[\alpha]_D^{20}$ = +8 (*c* = 1, $CHCl_3$). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.45−3.70 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.35−4.87 (m, 8 H, 4 CH_2Ph), 5.19 (d, 1 H, $J_{1,2}$ = 7.3 Hz, 1-Hβ), 7.05−7.30 (m, 20 H, 4 phenyl). − FAB-MS (positive mode, matrix: glycerine): *m/z* = $[M^+ + H]$ = 688. − $C_{39}H_{35}F_4NO_6$ (689).

2,3,5,6-Tetrafluoro-4-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)pyridine (**14bβ**): GP1 A, **14**[30] (169 mg), flash chromatography (toluene/ethyl acetate, 6:1), yield (398 mg, 80%), colorless solid, m.p. 135°C. − TLC (petroleum ether/ethyl acetate, 6:4): R_f = 0.81. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.01, 2.03, 2.05, 2.08 (4 s, 12 H, 4 OAc), 3.85 (ddd, 1 H, $J_{4,5}$ = 9.8 Hz, $J_{5,6A}$ = 5.2 Hz, $J_{5,6B}$ = 2.3 Hz, 5-H), 4.11 (dd, 1 H, $J_{6B,5}$ = 5.2 Hz, $J_{6B,6A}$ = 12.4 Hz, 6-H_B), 4.21 (dd, 1 H, $J_{6A,5}$ = 5.2 Hz, $J_{6A,6B}$ = 12.4 Hz, 6-H_A), 5.11−5.30 (m, 3 H, 2-H, 3-H, 4-H), 5.44 (d, 1 H, $J_{1,2}$ = 7.8 Hz, $J_{H,F}$ = 3.6 Hz, 1-Hβ). − $C_{19}H_{19}F_4NO_6$ (498.1) calcd. C 45.81, H 3.85, N 2.81; found C 45.65, H 3.79, N 2.69.

2,3,5,6-Tetrafluoro-4-(1-O-β-D-glucopyranosyloxy)pyridine (**14cβ**): GP1, **1c** (180 mg), **14**[30] (169 mg), 10 ml dry *N*,*N*-dimethylformamide, flash chromatography (ethyl acetate/methanol, 16:1), yield (157 mg, 48%), colorless syrup. − TLC (dichloromethane/ethyl acetate, 4:1): R_f = 0.23. − ^{1}H NMR (250 MHz, CD_3OD): δ = 3.34−3.85 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.82 (H_2O), 5.34 (d, 1 H, $J_{1,2}$ = 7.5 Hz, 1-Hβ). − For further characterization, **14c** was peracetylated (GP4) and identified as compound **14b**.

6-Fluoro-2,4-bis-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyloxy)triazine (**15aaβ**): GP2, **15**[30] (135 mg, 1 mmol), **1a**[12] (540 mg, 1 mmol), NaH (26 mg, 1.1 mmol), 15-crown-5 (220 µl, 1.1 mmol), *T* = −80°C, flash chromatography (alumina N32-63 active, dry toluene/ethyl acetate, 20:1), yield (370 mg, 63%), colorless syrup. − TLC (toluene/ethyl acetate, 6:1): R_f = 0.23. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.50−3.98 (m, 12 H, 2-H, 2′-H, 3-H, 3′-H, 4-H, 4′-H, 5-H, 5′-H, 6-H_A, 6-H_B, 6′-H_A, 6′-H_B), 4.41−4.97 (m, 16 H, 8 CH_2Ph), 5.89 (d, 2 H, $J_{1,2}$ = 7.4 Hz, 1-Hβ, 1′-Hβ), 7.06−7.31 (m, 40 H, Ph). − MALDI-MS (positive mode, matrix: DHB): *m/z* = $[M^+]$ = 1174, $[M^+ + Na]$ = 1197. − $C_{71}H_{70}FN_3O_{12}$ (1175). − No further purification was performed because of the sensitivity of **15aa** to moisture.

2,4,6-Tris-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyloxy)-triazine (**15aaaβ**): GP2, **15aaβ** (117 mg, 0.1 mmol), **1a**[12] (54 mg, 0.1 mmol), NaH (3 mg, 0.11 mmol), 15-crown-5 (22 µl, 0.11 mmol), room temp., flash chromatography (alumina N32-63 active, dry toluene/ethyl acetate, 20:1), yield (83 mg, 45%), colorless syrup. − TLC (toluene/ethyl acetate, 6:1): R_f = 0.18. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.48−3.99 (m, 18 H, 2-H, 2′-H, 2′′-H, 3-H, 3′-H, 3′′-H, 4-H, 4′-H, 4′′-H, 5-H, 5′-H, 5′′-H, 6-H_A, 6′-H_A, 6′′-H_A, 6-H_B, 6′-H_B, 6′′-H_B), 4.38−4.91 (m, 24 H, 12 CH_2Ph), 5.86 (d, 3 H, $J_{1,2}$ = $J_{1'',2''}$ = $J_{1'',2''}$ = 7.4 Hz, 1-Hβ, 1′-Hβ, 1′′-Hβ), 7.07−7.35 (m, 60 H, Ph). − MALDI-MS (positive mode, matrix: DHB): *m/z* = $[M^+ + Na]$ = 1718. − $C_{105}H_{105}N_3O_{18}$ (1695). − No further

purification was performed because of the sensitivity of **15aaa** to moisture.

6-(2,3,4,6-Tetra-O-acetyl-α/β-D-glucopyranosyloxy)-2,4-di-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyloxy)triazine (**15aabα**, **β**): GP2, **15aaβ** (117 mg, 0.1 mmol), **1b**[13] (34 mg, 0.1 mmol), NaH (3 mg, 0.11 mol), 15-crown-5 (22 µl, 0.11 mmol), room temp., flash chromatography (alumina N32-63 active, dry toluene/ethyl acetate, 6:1), yield (68 mg, 45%), colorless syrup. − TLC (toluene/ethyl acetate, 4:1): R_f = 0.43. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.94−2.02 (m, 12 H, 4 OAc), 3.51−4.36 (m, 18 H, 2-H, 2′-H, 2′′-H, 3-H, 3′-H, 3′′-H, 4-H, 4′-H, 4′′-H, 5-H, 5′-H, 5′′-H, 6-H_A, 6′-H_A, 6′′-H_A, 6-H_B, 6′-H_B, 6′′-H_B), 4.39−4.92 (m, 16 H, 8 CH_2Ph), 5.32 (d, 2 H, $J_{1,2} = J_{1',2'}$ = 7.6 Hz, 1-Hβ, 1′-Hβ), 5.78 (d, 0.4 H, $J_{1'',2''}$ = 7.5 Hz, 1′′-Hβ), 6.02 (d, 0.6 H, $J_{1'',2''}$ = 3.7 Hz, 1-Hα), 7.06−7.28 (m, 40 H, Ph). − MALDI-MS (positive mode, matrix: DHB): *m/z* = [M^+ + Na] = 1525. − $C_{85}H_{89}N_3O_{22}$ (1503). − No further purification was performed because of the sensitivity of **15aabα**, **β** to moisture.

5-Chloro-2,6-difluoro-4-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyloxy)pyrimidine (**16aβ**): GP2, **16**[30] (168.5 mg, 1 mmol), **1a**[12] (540 mg, 1 mmol), NaH (26 mg, 1.1 mmol), 15-crown-5 (220 µl, 1.1 mmol), T = −40°C, flash chromatography (toluene/ethyl acetate, 20:1), yield (555 mg, 85%), colorless oil. − TLC (toluene/ethyl acetate, 6:1): R_f = 0.64. − $[\alpha]_D^{20}$ = +3 (c = 1, CH_2Cl_2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.62−3.91 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.43−5.02 (m, 8 H, 4 CH_2Ph), 5.93 (d, 1 H, $J_{1,2}$ = 7.5 Hz, 1-Hβ), 7.15−7.39 (m, 20 H, Ph). − $C_{38}H_{35}ClF_2N_2O_6$ (653.1): calcd. C 66.22, H 5.12, N 4.06; found C 66.15, H 5.21, N 4.28.

5-Chloro-2,6-difluoro-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)pyrimidine (**16bβ**): GP2, **16**[30] (168.5 mg, 1 mmol), **1b**[13] (340 mg, 1 mmol), NaH (26 mg, 1.1 mmol), 15-crown-5 (220 µl, 1.1 mmol), T = −20°C, flash chromatography (toluene/ethyl acetate, 6:1), yield (397 mg, 80%), colorless foam. − TLC (toluene/ethyl acetate, 6:1): R_f = 0.24. − $[\alpha]_D^{20}$ = +10 (c = 1, CH_2Cl_2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.97−2.06 (m, 12 H, 4 OAc), 3.95 (ddd, 1 H, $J_{5,4}$ = 9.8 Hz, $J_{5,6A}$ = 4.8 Hz, $J_{5,6B}$ = 2.4 Hz, 5-H), 4.27 (dd, dd, 2 H, J_{gem} = 12.4 Hz, $J_{6A,5}$ = 4.8 Hz, $J_{6B,5}$ = 2.4 Hz, 6-H_A, 6-H_B), 5.14−5.40 (m, 3 H, 2-H, 3-H, 4-H), 5.99 (d, 1 H, $J_{1,2}$ = 7.7 Hz, 1-Hβ). − $C_{18}H_{19}ClF_2N_2O_{10}$ (496.8): calcd. C 43.52, H 3.85, N 5.64; found C 43.52, H 3.82, N 5.59.

5-Chloro-4,6-bis-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)-2-fluoropyrimidine (**16bbβ**): GP2, **16bβ** (130 mg, 0.27 mmol), **1b**[13] (92 mg, 0.27 mmol), NaH (8 mg, 0.3 mmol), 15-crown-5 (66 µl, 0.3 mmol), T = 4°C, flash chromatography (toluene/ethyl acetate, 6:1), yield (107 mg, 52%), colorless foam. − TLC (toluene/ethyl acetate, 2:1): R_f = 0.57. − $[\alpha]_D^{20}$ = +11 (c = 1, CH_2Cl_2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.93−2.04 (m, 24 H, 8 OAc), 3.92 (ddd, 2 H, $J_{5,4} = J_{5',4'}$ = 9.8 Hz, $J_{5,6A} = J_{5',6'A}$ = 4.8 Hz, $J_{5,6B} = J_{5',6'B}$ = 2.4 Hz, 5-H, 5′-H), 4.14 (dd, dd, 4 H, $J_{gem} = J_{gem'}$ = 12.4 Hz, $J_{6A,5} = J_{6'A,5'}$ = 4.8 Hz, $J_{6B,5} = J_{6'B,5'}$ = 2.4 Hz, 6-H_A, 6-H_B, 6′-H_A, 6′-H_B), 5.11−5.38 (m, 6 H, 2-H, 2′-H, 3-H, 3′-H, 4-H, 4′-H), 5.92 (d, 2 H, $J_{1,2} = J_{1',2'}$ = 7.7 Hz, 1-Hβ, 1′-Hβ). − $C_{32}H_{38}ClFN_2O_{20}$ (825.1): calcd. C 46.58, H 4.64, N 3.34; found C 46.70, H 4.64, N 3.54.

5-Chloro-2,4,6-tris-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyloxy)pyrimidine (**16bbbβ**): GP2, **16bbβ** (82 mg, 0.1 mmol), **1b**[13] (34 mg, 0.1 mmol), NaH (3 mg, 0.11 mmol), 15-crown-5 (22 µl, 0.11 mmol), T = 30°C, flash chromatography (toluene/ethyl acetate, 3:1), yield (56 mg, 49%), colorless syrup. − TLC (toluene/ethyl acetate, 1:1): R_f = 0.29. − $[\alpha]_D^{20}$ = +19 (c = 0.5, CH_2Cl_2). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.95−2.03 (m, 36 H, 12 OAc), 3.86−4.31 (m, 9 H, 5-H, 5′-H, 5′′-H, 6-H_A, 6′-H_A, 6′′-H_A, 6-H_B, 6′-H_B, 6′′-H_B), 4.96−5.94 (m, 9 H, 2-H, 2′-H, 2′′-H, 3-H, 3′-H, 3′′-H, 4-H, 4′-H, 4′′-H), 5.82 (d, 1 H, $J_{1'',2''}$ = 7.7 Hz, 1′′-Hβ), 5.92 (d, 2 H, $J_{1,2} = J_{1',2'}$ = 7.7 Hz, 1-Hβ, 1′-Hβ). − $C_{49}H_{57}ClN_2O_{30}$ (1126): calcd. C 47.90, H 4.98, N 2.43; found C 47.94, H 5.13, N 2.50.

4-Chloro-6-diisopropylamino-2-(1-O-β-D-glucopyranosyloxy)-triazine (**10cβ**): GP3, yield (59 mg, 95%), colorless syrup. − TLC (dichloromethane/methanol, 4:1): R_f = 0.18. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.18−1.42 (m, 14 H, N*i*Pr_2), 3.38−4.14 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 5.63 (d, 1 H, $J_{1,2}$ = 7.6 Hz, 1-Hβ). − MALDI-MS (positive mode, matrix: DHB): *m/z* = [M^+] = 383, [M^+ + Na] = 405. − $C_{15}H_{24}ClN_4O_6$ (382.5). − Because of its sensitivity to moisture, **10cβ** was peracetylated (GP4) and identified as compound **10bβ**.

6-Amino-4-chloro-2-(1-O-β-D-glucopyranosyloxy)triazine (**11cβ**): GP3, yield (34 mg, 52%), colorless syrup. − TLC (dichloromethane/methanol, 2:1): R_f = 0.18 (color reaction with ninhydrin). − Because of its sensitivity to moisture, **11cβ** was peracetylated (GP4) and identified as compound **11bβ**.

*6-Benzylamino-4-chloro-2-(1-O-β-*D-glucopyranosyloxy)triazine (**12cβ**): GP3, yield (66 mg, 93%), colorless syrup. − TLC (dichloromethane/methanol, 3:1): R_f = 0.35. − ^{1}H NMR (250 MHz, CD_3OD): δ = 3.38−4.72 (m, 8 H, CH_2Ph, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.94 (H_2O, 1-Hβ), 7.21−7.53 (m, 5 H, Ph). − MALDI-MS (positive mode, matrix: DHB): *m/z* = [M^+ + Na] = 422. − $C_{16}H_{19}ClN_4O_6$ (398.8). − Because of its sensitivity to moisture, **12cβ** was peracetylated (GP4) and identified as compound **12bβ**.

6-Phenylamino-4-chloro-2-(1-O-β-D-glucopyranosyloxy)triazine (**13cβ**): GP3, yield (65 mg, 96%), colorless syrup. − TLC (dichloromethane/methanol, 4:1): R_f = 0.25. − ^{1}H NMR (250 MHz, CD_3OD): δ = 3.34−4.03 (m, 6 H, 2-H, 3-H, 4-H, 5-H, 6-H_A, 6-H_B), 4.88 (H_2O), 5.23 (d, 1 H, $J_{1,2}$ = 7.7 Hz, 1-Hβ), 7.12 (m_c, 1 H, 4′-H), 7.33 (m_c, 2 H, 3′-H, 5′-H), 7.62 (m_c, 2 H, 2′-H, 6′-H). − MALDI-MS (positive mode, matrix: DHB): *m/z* = [M^+ + Na] = 408. − $C_{15}H_{17}ClN_4O_6$ (384.5). − Because of its sensitivity to moisture, **13cβ** was peracetylated (GP4) and identified as compound **13bβ**.

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[30] These compounds are commercially available.

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