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Glucosamine derived DISAL donors for stereoselective glycosylations under neutral conditions

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Abstract—DISAL (methyl 3,5-*di*nitro*sal*icylate) D-glucosyl, D-galactosyl, D-mannosyl, and L-quinovosyl donors have previously provided the efficient glycosylation of a range of substrates under either strictly neutral, mildly basic, or very mildly Lewis acidic ($LiClO_4$) conditions. Herein we report the synthesis of new glucosamine DISAL donors, carrying *N*-TCP, -Troc, or -TFAc protecting groups, and their use in β-(1,2-*trans*) selective glycosylations, primarily in NMP in the absence of any added Lewis acids, or in CH_3NO_2 with $LiClO_4$. Finally, precise microwave heating proved effective in promoting the difficult glycosylation of the 3-OH of a glucosamine derivative.

1. Introduction

Glycoconjugates play crucial roles in the development, growth, and proper functioning of an organism.[1] Amino sugars are found in many biologically important poly- and oligosaccharides, for example, in glycans of *O*- and *N*-glycopeptides and -proteins, tumor associated antigens, lipochitin nodulation factors, and amino glycoside antibiotics, such as streptomycin. The synthesis of oligosaccharides of these glycoconjugates provides important tools for glycobiology. Often D-glucosamine (2-amino-2-deoxy-glucopyranose, GlcN) is linked by a β-(1,2-*trans*)-glycosidic bond. However, the syntheses of glycosides of amino sugars, such as GlcN and D-galactosamine, involve special problems.[2] Glycosyl donors with a 2-acylamino group give, upon electrophilic activation of an anomeric (C-1) leaving group, an oxocarbenium ion, which can form an oxazolinium ion. Abstraction of the amide proton then gives a relatively stable oxazoline. At elevated temperatures and in the presence of a competent Lewis acid, oxazolines can become glycosyl donors. Similarly, GlcNAc derived glycosyl donors can glycosylate under harsh conditions, without intermediate isolation of the oxazoline.[3] However, it is most often preferable to avoid formation of the rather unreactive oxazoline intermediate, by blocking the 2-amino group with either one or two monovalent protecting groups or a bivalent one. Protecting groups, which provide β-selectivity include phthaloyl (Phth),[2] tetrachlorophthaloyl (TCP),[4] dimethylmaleoyl (DMM),[5] 1,3-dimethyl-2,4,6 (1*H*,3*H*,5*H*)-trioxopyrimidine-5-ylidenemethyl (DTPM),[6] trifluoroacetyl (TFAc),[7] trichloroethoxycarbonyl (Troc),[8] dibenzyl,[9] allyloxycarbonyl (Alloc),[10] dithiasuccinoyl (Dts),[11] and dimethoxybenzyl (Dmob)/acetyl[12,13] Like Phth[14], TCP induces a very high β-selectivity, but TCP has been favored over Phth due to the more reliable removal of the TCP. Also, Troc has become a popular choice however, *N*-TFAc is interesting due to the reported very high degree of β-selectivity. Both Troc and TFAc groups appear to be less prone to oxazoline formation.

Novel methods for glycosylation in the absence of strong Lewis acids, that is, under mild conditions, hold great promise, for example, for combinatorial chemistry and solid-phase synthesis applications.[15] We have recently reported a new and efficient method for glycosylation under either strictly neutral, mildly basic, or

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very mildly acidic ($LiClO_4$) conditions.[16] In this glycosylation technique, the anomeric leaving group on the benzyl or benzoyl protected donors is methyl 3,5-*di*-nitro-*sal*-icylate (DISAL) or its *para* regioisomer. The potential of DISAL glycosyl donors was demonstrated in their successful application to solution[16a,d] and solid-phase[16b] oligosaccharide synthesis, as well as intramolecular glycosylation via a novel 1,9-glycosyl shift.[16c]

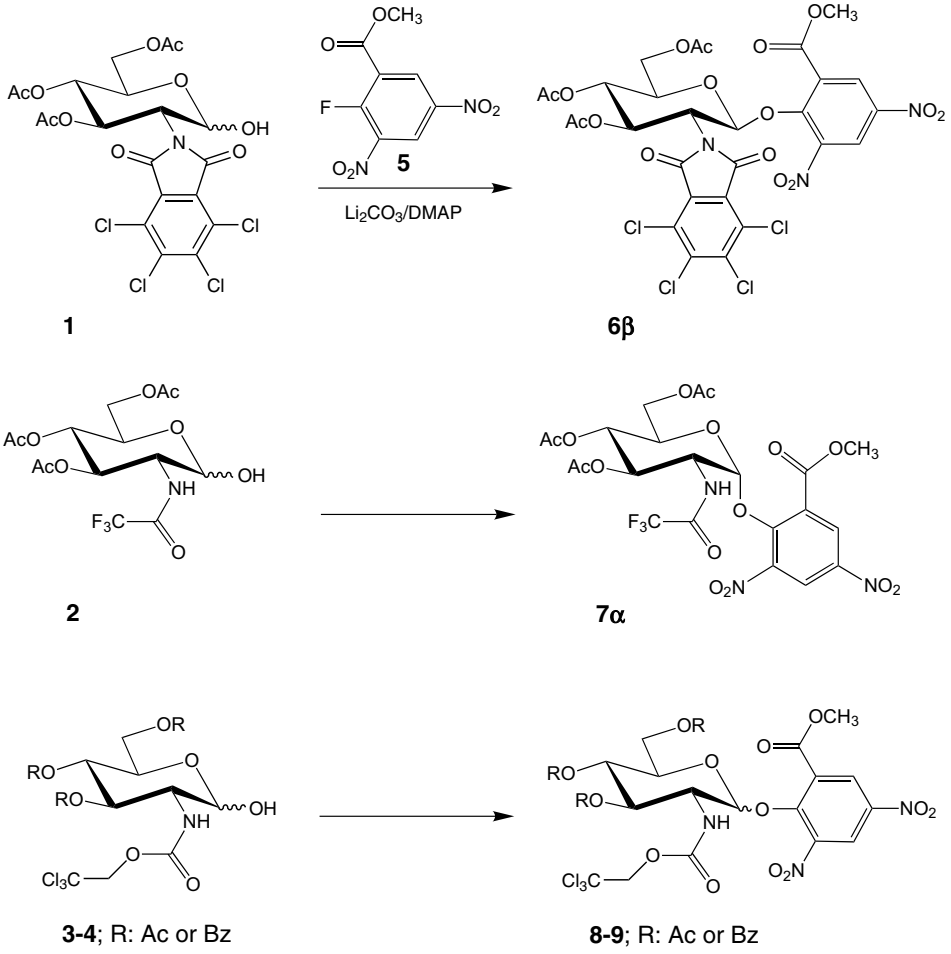
DISAL glycosyl donors are generally prepared by a convenient and robust nucleophilic aromatic substitution protocol. Here, DMAP catalyzed formation of DISAL glycosides predominantly gives α-anomers, while dimethylpiperazine (DMP) catalysis predominantly gives β-anomers. Whereas *O*-benzyl (Bn) protected DISAL donors can *O*-glycosylate simply by dissolution in *N*-methylpyrrolidinone (NMP) at 40–60 °C (with α-selectivity), the less reactive benzoyl (Bz) donors become efficient donors in CH_3NO_2 or $(CH_2Cl)_2$ in the presence of $LiClO_4$ (with β-selectivity). These glycosylations are operationally simple and can be carried out in standard plastic vials.[16]

Glucosamine derived glycosyl donors constitute a further and important challenge to the DISAL methodology. Herein we report the synthesis of novel glucosamine derived DISAL donors, carrying *N*-TCP, -Troc, or *N*-TFAc protecting groups, and their use in glycosylations, primarily in the absence of Lewis acids. This study thus has two aims, (i) the synthesis and evaluation of novel glucosamine derived DISAL glycosides and (ii) the comparison of amino protecting groups in stereo selective glycosylations.

2. Results and discussion

The *O*-acyl and *N*-TCP and -Troc protected lactols **1**, **3**, and **4** were prepared according to literature procedures (Scheme 1, Table 1); TFAc protected lactol **2** was obtained by 1-*O*-deacetylation, which proceeded through the formation of the bromide followed by hydrolysis. The two *N*-Troc protected lactols **3** and **4** were obtained in higher overall yields than **1** and **2** (data not shown). Then, treatment of the four lactols **1**–**4** with aryl fluoride **5** (DISAL-F) in CH_2Cl_2 in the presence of a previously established 'double base system'[16], DMAP and Li_2CO_3, converted them into the corresponding DISAL glycosides **6**–**9** in 61–95% yield.

The efficiency of this reaction provided proof for the robustness of our procedure for the synthesis of DISAL

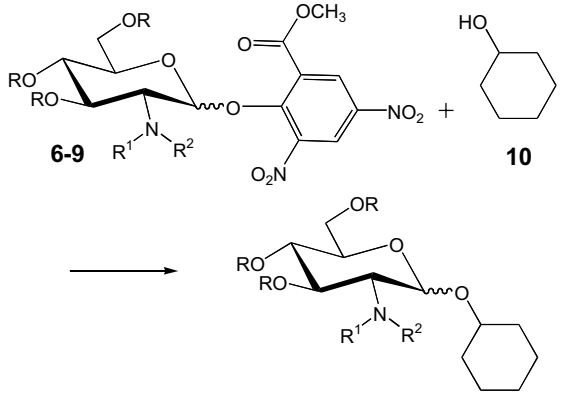


Scheme 1. Synthesis of glucosamine-derived DISAL donors by nucleophilic aromatic substitution; Table 1.

Table 1. Synthesis of DISAL donors; see Scheme 1

Lactol	R	R1, R2	Base	α/β ratio	DISAL donor	Yield (%)
1[4]	Ac	TCP	DMAP	β	**6β**	94
2[17]	Ac	TFAc, H	DMAP	α	**7α**	87
3[8c,18]	Ac	Troc, H	DMAP	α	**8α**	95
3	Ac	Troc, H	DMP	1:1.6	**8β**	61
4[18b,19]	Bz	Troc, H	DMAP	2:1	**9α**	95

donors. The *N*-TCP protected lactol **1** (β-anomer) gave the DISAL β-glycoside; this is in contrast to previous results, where DMAP promoted the formation of 2-*O*-Bn while -Bz DISAL glucosides gave α-anomers. Formation of a β-glycoside from *N*-TCP protected β-lactol **1** by retention could be due to the steric (β-directing) effects from the TCP moiety or due to kinetic control of the reaction (transient formation of the β-alkoxide and its fast reaction). In contrast, the *N*-Troc and *N*-TFAc protected lactols **2**–**4** (predominantly α-anomers), respectively, gave highly selective α-anomers (Scheme 2). Thus, the formation of DISAL glycosides under DMAP catalysis did predominantly occur with retention of anomeric configuration (except for *N*-TCP, i.e., conversion of **1** to **6**), as observed in previous[16a] syntheses. The synthesis of Troc protected DISAL glycoside **8** in the presence of DMP, instead of DMAP, gave an α/β ratio of 1:1.6 in 61% yield; this provided access to **8β**. These first results favored *N*-Troc for amino protection. DISAL glycosyl donors could be stored for prolonged periods at −18 °C.



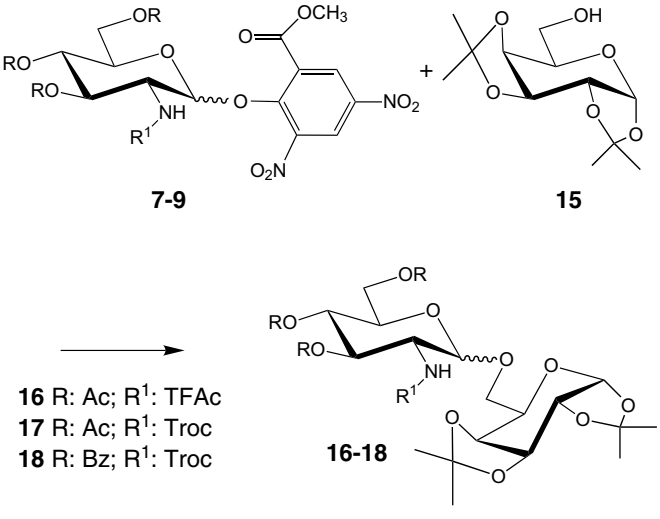
Scheme 2. Model glycosylation of cyclohexanol **10**; Table 2.

With the novel DISAL glycosides **6**–**9** in hand, their ability as glycosyl donors was first evaluated in the glycosylation of cyclohexanol **10**. Initial screening of solvents indicated that NMP was preferred over, for example, CH_3CN and CH_3NO_3. The glycosylations were performed with 5 equiv of alcohol **10** at 40 °C for 15–24 h in the absence of an added Lewis acid. Formation of the cyclohexyl glycosides proceeded with β-selectivity, however, with some differences. While *N*-TCP and -TFAc protected donors yielded the β-anomer, Troc protected donors **8** and **9** gave slightly reduced α/β ratios of 1:3 and 1:5, respectively (Scheme 2, Table 2).

Table 2. Glycosylation of cyclohexanol **10**

DISAL donor	Conditions	Glycoside	α/β ratio[a]	Yield (%)
6	A	**11**	β[b]	51
6	B	n.a.	n.a.	0
7	B	**12**	β	35
8α	B	**13**	1:3	54
8β	B	**13**	1:4	76
9	B	**14**	1:5[b]	63

A: CH_3NO_2, $LiClO_4$, 60 °C; B: NMP, 60 °C, 16–20 h.
[a] α/β ratio of product glycoside isolated after VLC.
[b] Isolated after prep. HPLC.



Scheme 3. Glycosylation of monosaccharide **15**; conditions: NMP, 40–60 °C; see Table 3.

The TCP protected DISAL donor **6** was the least reactive, as it required higher temperatures and activation by $LiClO_4$ for glycosylation. *N*-Troc protected DISAL donors **8** and **9** were the most reactive and gave higher yields. Furthermore, *N*-Troc protected donor **8β** proved more reactive than the corresponding α-anomer **8α**, as expected.

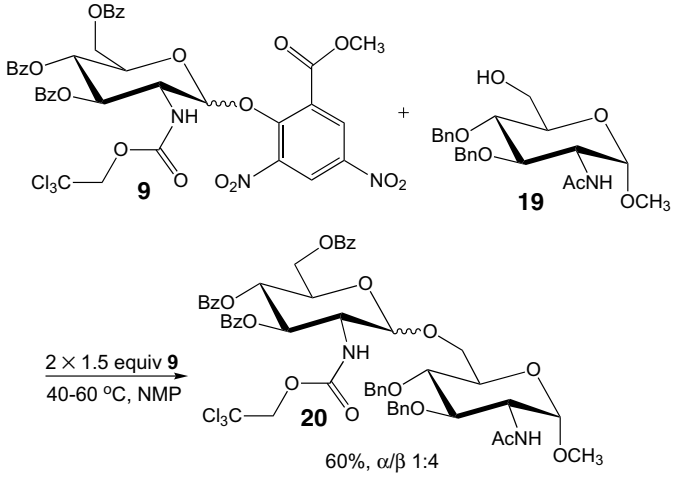
Next, we turned to the synthesis of disaccharides, abandoning the *N*-TCP protected donor **6** due to its low reactivity. In contrast to the above conditions, a slight excess of the DISAL donor was used here. Adapting previously[16a] developed conditions for the glycosylation of the 6-OH in 1,2:3,4-diisopropylidene-α-D-galactopyranose **15**, 1.5 equiv of the DISAL donors **7**–**9** were used in NMP at 40 °C; as expected from these previous results, higher yields were observed at 40 °C with a subsequent rise in temperature to 60 °C and/or by an additional 1.5 equiv of DISAL donor (Scheme 3, Table 3).

Table 3. Glycosylation of monosaccharide **15** in NMP

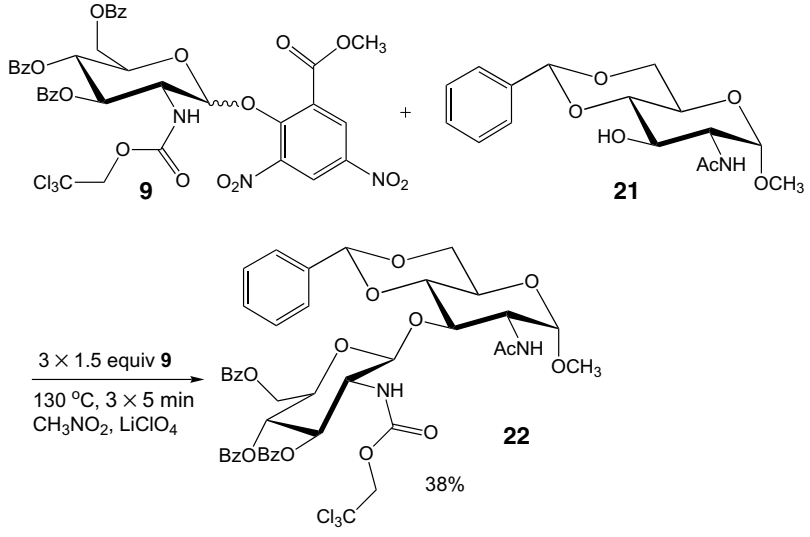
DISAL donor	Time/temp	Equiv. donor	Glycoside	α/β ratio[a]	Yield (%)
7	60 °C/40 h	2 × 1.5	**16**	β[b]	45
8	40 °C/18 h	1.5	**17**	1:1	71
9	40 °C/18 h	1.5	**18**	1:7	63
9	40 °C/24 h then 60 °C/2 h	1.5 1.5	**18**	1:6	85

[a] α/β ratio of product glycoside isolated after VLC.
[b] Isolated after prep. HPLC.

Thus, the *O*-benzoyl, *N*-Troc protected DISAL donor **9** gave disaccharide **18** in 85% yield with an α/β ratio of 1:6. Moving on to glucosamine acceptors, the 6-OH in methyl 2-acetamido-2-deoxy-3,4-di-*O*-benzyl-α-D-glucopyranoside[20] **19** was glycosylated with *O*-benzoyl protected *N*-Troc protected DISAL donor **9** (3 equiv) in 60% yield and with an α/β ratio of 1:4; this provided a simple analogue **20** of chitin oligosaccharides



Scheme 4. Glycosylation of GlcNAc derivative **19**.



Scheme 5. Glycosylation of GlcNAc derivative **21**.

(Scheme 4). Finally, the secondary hydroxyl in glucosamine derivative **21** was glycosylated with DISAL donor **9** (Scheme 5). After conventional heating (40–60 °C) of the reactants in NMP or CH_3NO_2 with $LiClO_4$ only gave sluggish reactions, microwave heating was applied to accelerate the reaction.[21] Since microwave heating can be slow in neat solvents in the absence of salts, we added $LiClO_4$ for this reaction. The glycosyl acceptor appears to be stable under these conditions. Thus, precise heating to 130 °C for 15 min in a closed vial caused this sterically demanding glycosylation to proceed in a yield of 38%.

3. Conclusion

In conclusion, novel *N*-Troc, -TCP, and -TFAc protected D-glucosamine derived DISAL donors were prepared and proved efficient for the glycosylation of cyclohexanol. Glycosylations were carried out in standard plastic vials in the absence of any added Lewis acids or in the presence of $LiClO_4$, thus under very mild conditions. While in general good β-selectivities were obtained, *N*-Troc protected DISAL donors gave the highest glycosylation yields, although, with lower β-selectivities. The *N*-TCP protected donor was the least reactive, thus only *N*-Troc and -TFAc protected donors were used for the glycosylation of monosaccharides. The *O*-Bz and *N*-Troc protected DISAL glycosyl donor gave the best overall performance. In NMP and CH_3NO_2, additional activation of less reactive donors could be achieved by the addition of $LiClO_4$. The sluggish glycosylation of a secondary hydroxyl in a glucosamine derivative was accelerated by precise microwave heating. With these and earlier results, the DISAL methodology has proven to be a competent glycosylation protocol. While further improvements would be required in all cases to reach the glycosylation yields of the very best literature methods, the exceptional mildness and operational simplicity of the DISAL methodology should make it applicable for many syntheses.

4. Experimental

Analytical HPLC was performed on a Waters 600 system with a 996 diode array detector and a 717 Autosampler equipped with a 3.9 × 50 mm Nova-Pak C18 4 μm 60 Å column. The following solvents were used: 0.1% TFA/H_2O (A); 0.1% TFA/CH_3CN (B); H_2O (C); CH_3CN (D). Analytical HPLC was performed on microfiltered or centrifuged 0.1% solutions in MeCN (for more hydrophilic compounds, solubility was improved by addition of water).

The following programs were used:

Program IA: 0.00 min: 1.20 mL/min, 100.0% A; 0.10 min: 1.20 mL/min, 100.0% A; 6.00 min: 1.20 mL/min, 5.0% A, 95.0% B; 7.00 min: 1.20 mL/min, 5.0% A, 95.0% B; 7.10 min: 1.20 mL/min, 100.0% A; 12.00 min: 1.20 mL/min, 100.0% A.

Program IB: 0.00 min: 1.00 mL/min, 95.0% A, 5.0% B; 7.00 min: 1.00 mL/min, 5.0% A, 95.0% B; 8.50 min: 1.00 mL/min, 5.0% A, 95.0% B; 9.00 min: 1.00 mL/min, 95.0% A, 5.0% B; 15.00 min: 1.00 mL/min, 95.0% A, 5.0% B.

Program IIA: 0.00 min: 1.2 mL/min, 100% C; 0.10 min: 1.2 mL/min, 100% C; 6.00 min: 1.2 mL/min, 5.0% C, 95.0% D; 7.00 min: 1.2 mL/min, 5% C, 95% D; 7.10 min: 1.2 mL/min, 100% C; 12.00 min: 1.2 mL/min, 100% C.

Program IIB: 0.00 min: 1.00 mL/min, 95.0% C, 5.0% D; 7.00 min: 1.00 mL/min, 5.0% C, 95.0% D; 8.50 min: 1.00 mL/min, 5.0% C, 95.0% D; 9.00 min: 1.00 mL/min, 95.0% C, 5.0% D; 15.00 min: 1.00 mL/min, 95.0% C, 5.0% D.

Program C: 0.00 min: 1.00 mL/min, 95.0% A, 5.0% B; 12.00 min: 1.00 mL/min, 5.0% A, 95.0% B; 13.50 min: 1.00 mL/min, 5.0% A, 95.0% B; 14.00 min: 1.00 mL/min, 95.0% A, 5.0% B; 20.00 min: 1.00 mL/min, 95.0% A, 5.0% B.

Characteristic absorption maxima were: Bz: 228–229 and 273 nm, Bn: 256–257 nm, TCP: 235–239 and 337 nm, DISAL-OH: 220 and 286 nm.

Preparative HPLC was performed on a Waters 600 system with a Waters 996 diode array detector and three consecutive columns (40 × 100 mm prep. NOVA Pak HR C18 6 μm 60 Å units). Linear gradients of CH_3CN and water (MilliQ) were used (Program IA, IB, IIA, IIB, and C). ^1H, ^{13}C, gHSQC, and H,H-COSY NMR spectra were recorded on Varian Mercury 300, Bruker Avance 300, or Varian Unity Inova 500 spectrometers. The chemical shifts are referred to the residual solvent signal. In NMR data for disaccharide products, H^A designates protons from the acceptor moiety, while H^D designates protons from the donor moiety. Infrared spectroscopy was performed on a Perkin–Elmer System 2000 FT-IR. Mass determination (high resolution MS, HR-MS) was performed on a Micromass LCT instrument with an ESI probe.

All the solvents used for the synthesis were distilled, either freshly or kept over 4 Å molecular sieves (where appropriate, glass equipment was dried prior to usage). Uncorrected melting points were measured in open capillary tubes.

For TLC Merck TLC Aluminum Sheets Silica Gel 60 F_{254} were used. Compounds containing UV-absorbing groups were visualized under UV-light (254 nm); carbohydrates were developed with 2 M H_2SO_4 followed by charring with a heat gun. VLC was performed on columns of Merck 60H silica (*h* 15 cm, *d* 2–4 cm depending on amount of compound) packed under vacuum. The crude product was dissolved in CH_2Cl_2, an equivalent amount of silica added, concentrated, placed on the column and finally covered with acid rinsed sea sand. Chromatography was hereafter run with the appropriate eluents until the product was collected.

4.1. General procedure for the synthesis of DISAL glycosyl donors 6–9

In a dried flask, protected carbohydrate derivative lactols **1**–**4**, Li_2CO_3 (2 equiv), and methyl 2-fluoro-3,5-dinitrobenzoic ester **5** (1.2 equiv) were suspended in CH_2Cl_2 (1–2 mL/mmol). Reactions proceeded in the presence of 1,4-dimethylpiperazine (DMP) or DMAP. (1) DMP catalysis: DMP (0.5 equiv) was added to the suspension and the mixture stirred for 2–3 h. (2) DMAP catalysis: DMAP (0.3 equiv) was dissolved in CH_2Cl_2 (0.5 mL) and added to the suspension in five portions over 20 min. After addition of the first portion, the color changed from slightly discolored to a strong yellow/brown. After stirring for an additional 10 min, products were isolated by VLC chromatography eluting with CH_2Cl_2–Et_2O (1:0→9:1–19:1).

4.1.1. 2,4-Dinitro-6-(methoxycarbonyl)-phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(tetrachlorophthalimido)-β-D-glucopyranose 6β. Yield 94%, α/β < 1:49. Mp 114–117 °C. $[\alpha]_D = -4.7$ (c 4.84×10^{-3}, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.9 (d, 1H, Ar-**H**-3), 8.7 (d, 1H, Ar-**H**-5), 5.90 (dd, 1H, **H**-3, $J_{3,2}$ 10.66 Hz $J_{3,4}$ 9.38 Hz), 5.74 (d, 1H, **H**-1β, $J_{1,2}$ 8.11 Hz), 5.26 (t, 1H, **H**-4, $J_{4,3}$ 9.38 Hz, $J_{4,5}$ 9.81 Hz), 4.67 (ddd, 1H, **H**-2, $J_{2,1}$ 8.11 Hz $J_{2,3}$ 10.66 Hz), 4.17 (dd, 1H, **H**-6, $J_{6,5}$ 3.84 Hz $J_{6,6'}$ 12 Hz), 4.02 (dd, 1H, **H**-6′, $J_{6',5}$ 2.13Hz $J_{6',6}$ 12 Hz), 3.84 (s, 1H, C**H$_3$**O(DISAL)), 3.76 (ddd, 1H, **H**-5, $J_{5,4}$ 9.81 Hz $J_{5,6}$ 3.84 Hz $J_{5,6'}$ 2.13 Hz), 2.1–1.9 ($3 \times$ s, 3×3H, $3 \times$ C**H$_3$**(Ac)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 171.0, 169.9 ($3 \times$ **C**O(Ac)), 168.4 (**C**O(TCP)), 162.8 (**C**O(DISAL)), 151.9, 147.5, 144.5, 124.0 (Ar-**C**(DISAL)), 130.1 (Ar-**C**(TCP)), 100.3 (**C**-1β), 72.8, 70.7, 68.7, 61.7 (**C**-3/4/5/6), 55.7 (**C**-2), 53.9 (O**C**H$_3$(DISAL)), 21.3, 21.2, 21.2 ($3 \times$ **C**H$_3$(Ac)). IR (neat): 3580–3340 (w), 1735 (s), 1535 (s), 1346 (s), 1224 (s), 739 (m). ESMS: *m/z* calcd for $C_{28}H_{21}Cl_4N_3O_{16}$ 794.97/796.97, *m/z* calcd for $[M+Na]^+$, 817.96/819.96. Found 817.85/819.87. *m/z* calcd for $[M+NH_4]^+$, 813.00/815.00. Found 812.88/814.91. *m/z* calcd for $[M-DISAL\text{-}O-(AcOH)_2]^+$, 433.94/435.94. Found 434.17/436.18. HRMS (ES): calcd for $C_{28}H_{21}Cl_4N_3O_{16}NH_4$ $[M+NH_4]^+$, 813.0020; Found 812.9929; calcd for $C_{28}H_{21}Cl_4N_3O_{16}Na$ $[M+Na]^+$, 817.9574; Found, 817.9606.

4.1.2. 2,4-Dinitro-6-(methoxycarbonyl)-phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(trifluoroacetamido)-α-D-glucopyranose 7α. Yield 87%, α/β > 49:1. Mp 66–71 °C. $[\alpha]_D = +62.1$ (c 4.23×10^{-3}, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.92 (d, 1H, Ar-**H**-3), 8.76 (d, 1H, Ar-**H**-5), 7.59 (d, 1H, N**H**, $J_{NH,2}$ 7.3 Hz), 5.77 (d, 1H, **H**-1α, $J_{1,2}$ 3.4 Hz), 5.48 (dd, 1H, **H**-3, $J_{3,2}$ 10.7 Hz $J_{3,4}$ 9.8), 5.10 (dd, 1H, **H**-4, $J_{4,3}$ 9.8 Hz $J_{4,5}$ 10.2 Hz), 4.57 (ddd, 1H, **H**-2, $J_{2,1}$ 3.4 Hz $J_{2,3}$ 10.7 Hz $J_{2,NH}$ 7.3 Hz), 4.21 (dd, 1H, **H**-6, $J_{6,5}$ 4.3 Hz $J_{6,6'}$ 12.4 Hz), 4.04 (s, 1H, C**H$_3$**O(DISAL)), 4.00 (dd, 1H, **H**-6′, $J_{6',5}$ 2.1 Hz $J_{6',6}$ 12.4 Hz), 3.86 (ddd, 1H, **H**-5, $J_{5,4}$ 10.2 Hz $J_{5,6}$ 4.3 Hz $J_{5,6'}$ 2.1 Hz), 2.07–2.06 ($3 \times$ s, 3×3H, $3 \times$ C**H$_3$**(Ac)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.4, 171.0, 169.7 ($3 \times$ **C**O(Ac)), 163.5 (**C**O(DISAL)), 158.4 (**C**O(TFAc) $^2J_{C,F}$ 38.2), 152.6 (Ar-**C**-1), 145.0 (Ar-**C**-4), 143.0 (Ar-**C**-6), 130.8 (Ar-**C**-5), 127.1 (Ar-**C**-2), 124.7 (Ar-**C**-3), 117.4, 115.1 (**C**F$_3$), 102.4 (**C**-1α), 72.2–61.8 (**C**-3/4/5/6), 54.7, 52.9 (**C**-2 and O**C**H$_3$(DISAL)), 21.3, 21.1, 21.0 ($3 \times$ **C**H$_3$(Ac)). IR (neat) 3470–3250 (w), 1738 (s), 1542 (s), 1345 (s), 1219 (s). ESMS: *m/z* calcd for $C_{22}H_{22}F_3N_3O_{15}$, 625.10, *m/z* calcd for $[M+Na]^+$, 648.09. Found 648.19. *m/z* calcd for $[M+NH_4]^+$, 643.13. Found 643.22. *m/z* calcd for $[M-DISAL\text{-}O]^+$ calcd 384.09. Found 384.41. HRMS (ES): calcd for $C_{22}H_{22}F_3N_3O_{15}NH_4$ $[M+NH_4]^+$, 643.1347; Found, 643.1309.

4.1.3. 2,4-Dinitro-6-(methoxycarbonyl)-phenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranose 8α. Yield 95%, α/β > 49:1. Mp 72–82 °C. $[\alpha]_D = +95.8$ (c 4.92×10^{-3}, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.79 (d, 1H, Ar-**H**-3, $J_{H,H}$ 2.8 Hz), 8.67 (d, 1H, Ar-**H**-5, $J_{H,H}$ 2.8 Hz), 5.88 (d, 1H, N**H**, $J_{NH,2}$ 9.8 Hz), 5.73 (d, 1H, **H**-1α, $J_{1,2}$ 3.6 Hz), 5.41 (dd, 1H, **H**-3, $J_{3,2}$ 11.0 Hz $J_{3,4}$ 9.6 Hz), 5.10 (t, 1H, **H**-4, $J_{4,3}$ 9.6 Hz $J_{4,5}$ 10.1 Hz), 4.76 (d, 1H, C**H**H(Troc), $J_{H,H}$ 12.0 Hz), 4.58 (d, 1H, CH**H**(Troc), $J_{H,H}$ 12.0 Hz), 4.19 (ddd, 1H, **H**-2, $J_{2,1}$ 3.6 Hz $J_{2,3}$ 11.0 Hz $J_{2,NH}$ 9.8 Hz), 4.11 (dd, 1H, **H**-6, $J_{6,5}$ 4.6 Hz $J_{6,6'}$ 12.6 Hz), 3.98 (s, 1H, C**H$_3$**O(DISAL)), 3.90 (dd, 1H, **H**-6′, $J_{6',5}$ 2.1 Hz $J_{6',6}$ 12.6 Hz), 4.02 (ddd, 1H, **H**-5, $J_{5,6'}$ 2.1 Hz $J_{5,6}$ 4.6 Hz $J_{5,4}$ 10.1 Hz), 2.1–2.0 ($3 \times$ s, 3×3H, $3 \times$ C**H$_3$**(Ac)). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171–169 ($3 \times$ **C**O(Ac)), 169 (**C**O(DISAL)), 154 (**C**O-(Troc)), 152, 144, 142, 127 (Ar-**C**-1/2/4/6), 130.1 (Ar-**C**-5), 124.1 (Ar-**C**-3), 102.0 (**C**-1α), 75.0 (**C**H$_2$(Troc)), 71.5 (**C**-5), 69.8 (**C**-3), 67.5 (**C**-4), 61.5 (**C**-6), 54.3, 54.2 (**C**-2 and O**C**H$_3$(DISAL)), 20.8 ($3 \times$ **C**H$_3$(Ac)). IR (neat) 3520–3250 (w), 1743 (s), 1541 (s), 1259 (s), 815 (w). ESMS: *m/z* calcd for $C_{23}H_{24}Cl_3N_3O_{16}$, 703.02/705.02, *m/z* calcd for $[M+Na]^+$, 726.01/728.01. Found 726.02/728.03. *m/z* calcd for $[M-DISAL\text{-}O]^+$, 462.01. Found 462.01. *m/z* calcd for $[M-DISAL\text{-}O-(AcOH)_2]^+$, 341.99/343.99. Found 341.97/343.97. HRMS (ES): calcd for $C_{23}H_{24}Cl_3N_3O_{16}NH_4$ $[M+NH_4]^+$, 721.0566; Found, 721.0519; calcd for $C_{23}H_{24}Cl_3N_3O_{16}Na$ $[M+Na]^+$, 726.0120; Found, 726.0109.

4.1.4. 2,4-Dinitro-6-(methoxycarbonyl)-phenyl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranose 8β. Yield 61%, α/β 1.6:1. Anomers were separated by VLC: **11β**: 38%, mp 132–134 °C. **11α**: 23%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.85 (d, 1H, Ar-**H**-3), 8.75 (d, 1H, Ar-**H**-5) 5.62 (d, 1H, N**H**, $J_{NH,2}$ 8.53 Hz) 5.34–5.29 (m, 2H, **H**-1β/3), 5.15 (t, 1H, **H**-4), 4.76 (dd, 2H, C**H$_2$**(Troc), $J_{H,H}$ 11.95 Hz), 4.12 (dd, 1H, **H**-6, $J_{6,5}$ 4.69 Hz $J_{6,6'}$ 12.37 Hz), 4.07 (ddd, 1H, **H**-2), 4.01 (s, 1H, C**H$_3$**O(DISAL)), 3.98 (dd, 1H, **H**-6′, $J_{6',5}$ 2.56 Hz $J_{6,6'}$ 12.37 Hz), 4.02 (ddd, 1H, **H**-5), 2.1–2.0 ($3 \times$ s, 3×3H, $3 \times$ C**H$_3$**(Ac)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.2, 171.1, 169.9 ($3 \times$ **C**O(Ac)), 168.2 (**C**O-(DISAL)), 155.0 (**C**O(Troc)), 144.5, 143.4, 129.9, 123.9 (Ar-**C**(DISAL)), 102.8 (**C**-1β), 75.4–56.9 (**C**H$_2$(Troc), **C**-2/3/4/5/6 and O**C**H$_3$(DISAL)), 21.3–21.2 ($3 \times$ **C**H$_3$(Ac)). ESMS: *m/z* calcd for $C_{23}H_{24}Cl_3N_3O_{16}$, 703.02/705.02, *m/z* calcd for $[M+NH_4]^+$, 721.05/723.05. Found 720.97/723.01, *m/z* calcd for $[M-DISAL\text{-}O]^+$, 462.01/464.01. Found 461.95/463.95, *m/z* calcd for $[M-DISAL\text{-}O-(AcOH)_2]^+$, 341.99/343.99. Found

341.94/343.94. HRMS (ES): calcd for $C_{23}H_{24}Cl_3N_3O_{16}$-Na $[M+Na]^+$, 726.0120; Found, 726.0104.

4.1.5. 2,4-Dinitro-6-(methoxycarbonyl)-phenyl 3,4,6-tri-*O*-benzoyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl-amino)-α-D-glucopyranose 9α. Yield 95%, α/β > 49:1. Mp 91–98 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.65 (d, 1H, Ar-**H**-3, $J_{H,H}$ 2.7 Hz), 8.57 (d, 1H, Ar-**H**-5, $J_{H,H}$ 2.7 Hz), 7.90–7.80, 7.52–7.40, and 7.36–7.25 (3 × m, 15H, Ar-**H**(Bz)), 5.94 (d, 1H, **H**-1α, $J_{1,2}$ 3.4 Hz), 5.93 (dd, 1H, **H**-3, $J_{3,2}$ 10.9 Hz $J_{3,4}$ 9.7 Hz), 5.86 (d, 1H, N**H**, $J_{NH,2}$ 9.5 Hz), 5.59 (dd, 1H, **H**-4, $J_{4,3}$ 9.7 Hz $J_{4,5}$ 9.9 Hz); 4.64 (d, 1H, C**H**H(Troc), $J_{H,H}$ 12.0 Hz), 4.48 (m, 1H, **H**-2), 4.47 (d, 1H, CH**H**(Troc), $J_{H,H}$ 12.0 Hz) 4.40 (dd, 1H, **H**-6, $J_{6,5}$ 2.5 Hz $J_{6,6'}$ 12.4 Hz), 4.28 (dd, 1H, **H**-6′, $J_{6',5}$ 5.4 Hz $J_{6',6}$ 12.4 Hz), 4.16 (m, 1H, **H**-5, $J_{5,6}$ 2.5 Hz $J_{5,6}$ 5.4 Hz), 4.0 (s, 1H, C**H$_3$**O(DISAL)). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167–165 (3 × **C**O(Bz)), 154.6 (**C**O(Troc)), 152–124.1 (24 × Ar-**C**(Bz and DISAL)), 100.9 (**C**-1α), 74.9 (**CH$_2$**(Troc)), 72.0 (**C**-5), 70.2 (**C**-3), 68.6 (**C**-4), 62 (**C**-6), 54.6, 54.2 (**C**-2 and COO**CH$_3$**(DISAL)). IR (neat) 3460–3300 (w), 1728 (s), 1540 (s), 1269 (s), 814 (m), 708 (s). ESMS: *m/z* calcd for $C_{38}H_{30}Cl_3N_3O_{16}$, 889.07, *m/z* calcd for $[M+Na]^+$, 912.06. Found 911.06. *m/z* calcd for $[M+NH_4]^+$, 907.10. Found 906.50. *m/z* calcd for $[M-DISAL\text{-}O]^+$ calcd 648.06. Found 649.86. HRMS (ES): calcd for $C_{38}H_{30}Cl_3N_3O_{16}Na$ $[M+Na]^+$, 912.0589; Found, 912.0635.

4.2. General procedure for glycosylations with DISAL donors 6–9, synthesis of 11–14, 16–18, and 20

Glycosylations of cyclohexanol were performed under reaction conditions according to Table 2. Glycosylations of monosaccharide **15** were performed under the reaction conditions according to Table 3. Glycosylation of monosaccharide **20** was performed in NMP at 40 °C with donor **9** (1.5 equiv) for 19 h and then with an additional amount of **9** (1.5 equiv) for 5 h at 60 °C.

Glycosyl donor (1.5 equiv unless stated otherwise), glycosyl acceptor (1 equiv unless stated otherwise), $LiClO_4$ (3 equiv), crushed 3 Å molecular sieves, and a magnet were placed in a 5 mL plastic tube with a septum. The tube was dried under high vacuum for 1–2 h, filled with argon, CH_3NO_2 or NMP (0.7 mL) added and the reaction mixture stirred at room temperature. The temperature was raised as indicated in Table 2 or Table 3 and stirring was continued overnight. The reaction mixture was filtered and purified by preparative HPLC.

4.2.1. Cyclohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(tetrachlorophthalimido)-β-D-glucopyranoside 11. Yield 51%, α/β < 1:49. Mp 194–195 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.69 (dd, 1H, **H**-3, $J_{3,2}$ 10.67 Hz $J_{3,4}$ 8.96 Hz), 5.45 (d, 1H, **H**-1β, $J_{1,2}$ 8.53 Hz), 5.17 (dd, 1H, **H**-4, $J_{4,3}$ 8.96 Hz $J_{4,5}$ 10.23 Hz), 4.33 (dd, 1H, **H**-6, $J_{6,5}$ 4.69 Hz $J_{6,6'}$ 12.37 Hz), 4.30 (dd, 1H, **H**-2, $J_{2,3}$ 10.67 Hz), 4.15 (dd, 1H, **H**-6′, $J_{6',5}$ 2.56 Hz $J_{6',6}$ 12.37 Hz), 3.81 (ddd, 1H, **H**-5, $J_{5,4}$ 10.23 Hz $J_{5,6}$ 4.69 Hz $J_{5,6'}$ 2.56 Hz), 3.60 (m, 1H, C**H**-OGlc(cyclohexyl)), 2.1–1.9 (3 × s, 9H, 3 × C**H$_3$**(Ac)), 1.9–1.0 (m, 10H, C**H$_2$**(cyclohexyl)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.4, 171.3, 170.1 (3 × **C**O(Ac)), 168.4 (**C**O(TCP)), 141.3, 130.7, 127.6 (3 × Ar-**C**(TCP)), 97.0 (**C**-1β), 78.6, 72.4, 71.8, 69.6, 62.9 (**C**-3/4/5/6 and **C**H-OGlc(cyclohexyl)), 56.4 (**C**-2), 33.9, 32.3, 26.0, 24.5, 24.4 (5 × CH_2(cyclohexyl)), 21.4, 21.3, 21.2 (3 × **C**H_3(Ac)). ESMS: *m/z* calcd for $C_{26}H_{27}Cl_4NO_{10}$, 653.04/655.04, *m/z* calcd for $[M+Na]^+$, 676.03/678.03. Found 676.19/678.16. *m/z* calcd for $[M+NH_4]^+$, 671.07/673.07. Found 671.24/673.21, *m/z* calcd for $[M-cC_6H_{11}O-(AcOH)_2]^+$, 433.94/435.94. Found 434.24/436.25.

4.2.2. Cyclohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trifluoracetamido)-β-D-glucopyranoside 12. Yield 35%, α/β < 1:49. Mp 185–187 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.70 (d, 1H, N**H**, $J_{NH,2}$ 8.54 Hz), 5.35 (dd, 1H, **H**-3, $J_{3,2}$ 10.67 Hz $J_{3,4}$ 9.38 Hz), 5.08 (dd, 1H, **H**-4, $J_{4,3}$ 9.38 Hz $J_{4,5}$ 9.82 Hz), 4.80 (d, 1H, **H**-1β, $J_{1,2}$ 8.1 Hz), 4.28 (dd, 1H, **H**-6, $J_{6,5}$ 5.12 Hz $J_{6,6'}$ 12.37 Hz), 4.13 (dd, 1H, **H**-6′, $J_{6',5}$ 2.56 Hz $J_{6',6}$ 12.37 Hz), 3.91 (dd, 1H, **H**-2, $J_{2,3}$ 10.67 Hz $J_{2,NH}$ 8.54 Hz), 3.73 (ddd, 1H, **H**-5, $J_{5,4}$ 9.82 Hz $J_{5,6}$ 5.12 Hz $J_{5,6'}$ 2.56 Hz), 3.64 (m, 1H, C**H**-OGlc(cyclohexyl)), 2.2–2.0 (3 × s, 9H, 3 × C**H$_3$**(Ac)), 1.9–1.2 (m, 10H, C**H$_2$**(cyclohexyl)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 171.4, 170.1, 168.2 (3 × **C**O(Ac) and **C**O(TFAc)), 99.2 (**C**-1 β), 78.6, 72.5, 72.4, 69.4, 62.9 (**C**-3/4/5/6 and **C**H-OGlc(cyclohexyl)), 56.0 (**C**-2), 36.2–24.2 (5 × CH_2(cyclohexyl)), 21.4–21.1 (3 × **C**H_3(Ac)). ESMS: *m/z* calcd for $C_{20}H_{28}F_3NO_9$, 483.17, *m/z* calcd for $[M+Na]^+$, 506.16. Found 506.15. *m/z* calcd for $[M+NH_4]^+$, 501.20. Found 501.18. *m/z* calcd for $[M-cC_6H_{11}O]^+$, 384.09. Found 384.07; *m/z* calcd for $[M-cC_6H_{11}O-(AcOH)_2]^+$, 264.07. Found 264.02.

4.2.3. Cyclohexyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichlorethoxycarbonylamino)-α/β-D-glucopyranoside 13. From **8α**: Yield 54%, α/β 1:3. Mp 136–138 °C. From **8β**: Yield 76%, α/β 1:4. Mp 130–140 °C. ^{1}H NMR **13α** (500 MHz, $CDCl_3$): δ 5.25 (dd, 1H, **H**-3, $J_{3,2}$ 10.24 Hz $J_{3,4}$ 9.81 Hz), 5.19 (d, 1H, N**H**, $J_{NH,2}$ 9.81 Hz), 5.09 (dd, 1H, **H**-4, $J_{4,3}$ 9.81 Hz $J_{4,5}$ 9.81 Hz), 5.02 (d, 1H, **H**-1α, $J_{1,2}$ 3.41 Hz), 4.76 (d, 1H, C**H**H(Troc), $J_{H,H}$ 11.95 Hz), 4.68 (d, 1H, CH**H**(Troc), $J_{H,H}$ 11.95 Hz), 4.24 (dd, 1H, **H**-6, $J_{6,5}$ 4.70 Hz $J_{6,6'}$ 11.95 Hz), 4.11 (dd, 1H, **H**-6′, $J_{6',5}$ 2.56 Hz $J_{6',6}$ 12.37 Hz), 4.12–4.06 (m, 2H, **H**-5/6′), 4.03 (ddd, 1H, **H**-2, $J_{2,3}$ 10.24 Hz $J_{2,1}$ 3.41 Hz), 3.6 (m, 1H, C**H**-OGlc(cyclohexyl)), 2.09, 2.04, 2.01 (3 × s, 9H, 3 × C**H$_3$**(Ac)), 1.9, 1.7, 1.6, 1.4, 1.3 (5 × m, 10H, C**H$_2$**(cyclohexyl)). ^{13}C NMR **13α** (125 MHz, $CDCl_3$): δ 171.6, 171.3, 170.1 (3 × **C**O(Ac)), 154.9 (**C**O(Troc)), 96.3 (d, **C**-1α), 75.3, 75.3, 71.9, 69.2, 68.5, 62.8 (**C**-3/4/5/6, **C**H$_2$(Troc), and **C**H-OGlc(cyclohexyl)), 54.7 (**C**-2), 36.3–24.6 (5 × CH_2(cyclohexyl)), 21.4, 21.4, 21.3 (3 × **C**H_3(Ac)). ^{1}H NMR **13β** (500 MHz, $CDCl_3$): δ 5.37 (dd, 1H, **H**-3, $J_{3,2}$ 9.39 Hz $J_{3,4}$ 9.81 Hz), 5.14 (d, 1H, **H**-1β), 5.05 (dd, 1H, **H**-4, $J_{4,3}$ 9.81 Hz $J_{4,5}$ 9.38 Hz), 4.80–4.67 (m, 3H, C**H$_2$**(Troc), N**H**), 4.28 (dd, 1H, **H**-6, $J_{6,5}$ 5.12 Hz $J_{6,6'}$ 12.37 Hz), 4.11 (dd, 1H, **H**-6′, $J_{6',5}$ 2.56 Hz $J_{6',6}$ 12.37 Hz), 3.70 (m, 1H, **H**-5, $J_{5,6'}$ 2.56 Hz), 3.64 (m, 1H, C**H**-OGlc(cyclohexyl)), 3.53 (m, 1H, **H**-2, $J_{2,3}$ 9.39 Hz), 2.1–1.9 (3 × s, 9H, 3 × C**H$_3$**(Ac)), 1.9–1.2 (m, 10H, C**H$_2$**(cyclohexyl)). ^{13}C

NMR **13β** (125 MHz, $CDCl_3$): δ 171.4–168.4 (3 × **C**O(Ac)), 154.6 (**C**O(Troc)), 99.7 (**C**-1β), 78.7–72.3 (**C**-3/5, $\mathbf{C}H_2$(Troc), and **C**H-OGlc(cyclohexyl)), 69.7 (**C**-4), 63.0 (**C**-3), 57.4 (**C**-2), 34.0, 32.3, 26.2, 24.5, 24.4 (5 × CH_2(cyclohexyl)), 21.4, 21.3, 21.3 (3 × $\mathbf{C}H_3$(Ac)). ESMS: *m/z* calcd for $C_{21}H_{30}Cl_3NO_{10}$, 561.09/563.09, *m/z* calcd for $[M+Na]^+$, 584.08/586.08. Found 584.09/586.10. *m/z* calcd for $[M-cC_6H_{11}]^+$, 462.01/464.01. Found 462.01/464.01, *m/z* calcd for $[M-cC_6H_{11}O-(AcOH)_2]^+$, 341.99/343.99. Found 341.97/343.97.

4.2.4. Cyclohexyl 3,4,6-tri-*O*-benzoyl-2-deoxy-2-(2,2,2-trichlorethoxycarbonylamino)-α/β-D-glucopyranoside 14. Yield **14α**: 11%. Mp 165–167 °C. Yield **14β**: 52%. Mp. 82–86 °C. Total yield 63%, α/β 1:5. ^{1}H NMR **14α** (500 MHz, $CDCl_3$): δ 8.1–7.0 (m, 15H, Ar-**H**(Bz)), 5.75 (dd, 1H, **H**-3, $J_{3,2}$ 10.67 Hz $J_{3,4}$ 9.81 Hz), 5.61 (dd, 1H, **H**-4, $J_{4,3}$ 9.81 Hz $J_{4,5}$ 9.38 Hz), 5.34 (d, 1H, N**H**, $J_{NH,2}$ 9.81 Hz), 5.15 (d, 1H, **H**-1α, $J_{1,2}$ 3.83 Hz), 4.66 (d, 1H, C**H**H(Troc), $J_{H,H}$ 11.94 Hz), 4.57 (m, 1H, **H**-6), 4.54 (d, 1H, CH**H**(Troc), $J_{H,H}$ 11.94 Hz), 4.5–4.4 (m, 2H, **H**-5/6′), 4.32 (ddd, 1H, **H**-2, $J_{2,1}$ 3.83 Hz $J_{2,3}$ 10.67 Hz), 3.65 (m, 1H, C**H**-OGlc(cyclohexyl)), 2.04–1.19 (m, 10H, $\mathbf{C}H_2$(cyclohexyl)). ^{13}C NMR **14α** (75 MHz, $CDCl_3$): δ 166.5, 166.1, 165.2 (3 × **C**O(Bz)), 154.2 (**C**O(Troc)), 133.3–128.3 (18 × Ar-**C**(Bz)), 95.8 (**C**-1α); 77.3, 74.3, 71.5, 69.5, 68.2, 63.1, (**C**-3/4/5/6, $\mathbf{C}H_2$(Troc), and **C**H-OGlc(cyclohexyl)), 54.4 (**C**-2) 33.4, 31.6, 25.3, 24.1, 23.9 (5 × CH_2(cyclohexyl)). ^{1}H NMR **14β** (500 MHz, $CDCl_3$): δ 8.1–7.2 (m, 15H, Ar-**H**(Bz)), 5.86 (dd, 1H, **H**-3, $J_{3,2}$ 9.81 Hz $J_{3,4}$ 9.81 Hz), 5.58 (dd, 1H, **H**-4, $J_{4,3}$ 9.81 Hz $J_{4,5}$ 9.38 Hz), 5.35 (broad d, 1H, N**H**), 4.96 (d, 1H, **H**-1β, $J_{1,2}$ 8.11 Hz), 4.71 (d, 1H, C**H**H(Troc), $J_{H,H}$ 11.51 Hz), 4.54 (d, 1H, CH**H**(Troc), $J_{H,H}$ 11.51Hz), 4.60 (dd, 1H, **H**-6, $J_{6,5}$ 2.56 Hz), 4.51 (dd, 1H, **H**-6′, $J_{6',5}$ 5.97 Hz), 4.12 (m, 1H, **H**-5), 3.86 (m, 1H, **H**-2), 3.66 (m, 1H, C**H**-OGlc(cyclohexyl)), 1.95–1.14 (m, 10H, $\mathbf{C}H_2$(cyclohexyl)). ^{13}C NMR **14β** (75 MHz, $CDCl_3$): δ 166.3, 166.1, 165.3 (3 × **CO(Bz)**), 154.1 (**C**O(Troc)), 133.4–128.4 (18 × Ar-**C**(Bz)), 99.4 (**C**-1β), 78.3, 74.4, 72.4, 71.9, 70.2, 63.5 (**C**-3/4/5/6, $\mathbf{C}H_2$(Troc), and **C**H-OGlc(cyclohexyl)), 57.0 (**C**-2); 33.3, 31.7, 25.4, 23.7 (5 × CH_2(cyclohexyl)). ESMS: *m/z* calcd for $C_{36}H_{36}Cl_3NO_{10}$, 747.14/749.14, *m/z* calcd for $[M+Na]^+$ calcd 770.13/772.13. Found 770/772.17. *m/z* calcd for $[M+NH_4]^+$ calcd 765.17/767.17. Found 765.20/767.21. *m/z* calcd for $[M-cC_6H_{11}O]^+$, 648.06/650.06. Found 648/650.08. *m/z* calcd for $[M-cC_6H_{11}O-(BzOH)_2]^+$, 404.01/406.01. Found 404.01/405.98.

4.2.5. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(trifluoroacetamido)-β-D-glucopyranosyl-(1→6)-(1,2;3,4)-diisopropylidene-α-D-galactopyranose 16. Yield 45%, α/β < 1:49, oil. $[\alpha]_D$ = −21.7 (*c* 2.80 × 10^{-3}, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.75 (broad s, 1H, N**H**), 5.48 (d, 1H, $\mathbf{H}^{\mathbf{A}}$-1α, $J_{1,2}$ 5.12 Hz), 5.24 (dd, 1H, $\mathbf{H}^{\mathbf{D}}$-3, $J_{3,2}$ 10.66 Hz $J_{3,4}$ 9.39 Hz), 5.10 (dd, 1H, $\mathbf{H}^{\mathbf{D}}$-4, $J_{4,3}$ 9.39 Hz $J_{4,5}$ 9.81 Hz), 4.79 (d, 1H, $\mathbf{H}^{\mathbf{D}}$-1β, $J_{1,2}$ 8.10 Hz), 4.56 (dd, 1H, $\mathbf{H}^{\mathbf{A}}$-3, $J_{3,2}$ 8.11 Hz $J_{3,4}$ 2.56 Hz), 4.31–4.27 (m, 2H, $\mathbf{H}^{\mathbf{A}}$-2, $\mathbf{H}^{\mathbf{D}}$-6), 4.17–4.14 (m, 2H, $\mathbf{H}^{\mathbf{A}}$-4, $\mathbf{H}^{\mathbf{D}}$-6′), 4.07 (dd, 1H, $\mathbf{H}^{\mathbf{D}}$-2), 3.97–3.92 (m, 2H, $\mathbf{H}^{\mathbf{A}}$-5/6), 3.79–3.71 (m, 2H, $\mathbf{H}^{\mathbf{A}}$-6′, $\mathbf{H}^{\mathbf{D}}$-5), 2.1–2.0 (3 × s, 9H, 3 × $\mathbf{C}H_3$(Ac)), 1.4–1.3 (4 × s, 12H, 4 × $\mathbf{C}H_3$C(isopropylidene)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.7, 171.4, 170.0 (3 × **C**O(Ac)), 158.3, 158.0 (**C**O(TFAc)), 116.3 (q, **C**F_3(TFAc)), 110.1, 109.5 (2 × **C**$(CH_3)_2(OR)_2$), 101.4 ($\mathbf{C}^{\mathbf{D}}$-1β), 96.9 (d, $\mathbf{C}^{\mathbf{A}}$-1α), 73.0–68.9 ($\mathbf{C}^{\mathbf{D}}$-3/4/5 and $\mathbf{C}^{\mathbf{A}}$-2/3/4/5/6), 62.7 ($\mathbf{C}^{\mathbf{D}}$-6), 55.2 ($\mathbf{C}^{\mathbf{D}}$-2), 26.6, 26.4, 25.5, 25.0 (4 × $\mathbf{C}H_3$C(isopropylidene)), 21.4, 21.2, 21.0 (3 × $\mathbf{C}H_3$(Ac)). IR (neat) 3600–3240 (w), 1749 (s), 1370 (m), 1221 (s), 1037 (s). HRMS (ES): calcd for $C_{26}H_{36}F_3NO_{14}NH_4$ $[M+NH_4]^{+\cdot}$, 661.2432; Found, 661.2418; calcd for $C_{26}H_{36}F_3NO_{14}Na$ $[M+Na]^{+\cdot}$, 666.1986; Found, 666.2025; calcd for $C_{26}H_{36}F_3NO_{14}K$ $[M+K]^{+\cdot}$, 682.1725; Found, 682.1661.

4.2.6. 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α/β-D-glucopyranosyl-(1→6)-(1,2; 3,4)-diisopropylidene-α-D-galactopyranose 17. Yield 71%, α/β 1:1, oil. ^{1}H NMR **17α** (500 MHz, $CDCl_3$): δ 5.56 (d, 1H, $\mathbf{H}^{\mathbf{A}}$-1α, $J_{1,2}$ 5.12 Hz), 5.44 (d, 1H, N**H**, $J_{NH,2}$ 9.81 Hz), 5.25 (dd, 2H, $\mathbf{H}^{\mathbf{D}}$-1α, and $\mathbf{H}^{\mathbf{D}}$-3, $J_{3,2}$ 10.23 Hz $J_{3,4}$ 9.38 Hz), 5.12 (dd, 1H, $\mathbf{H}^{\mathbf{D}}$-4, $J_{4,3}$ 9.38 Hz $J_{4,5}$ 9.81 Hz), 4.79 (d, 1H, C**H**H(Troc), $J_{H,H}$ 12.37 Hz), 4.64 (d, 1H, CH**H**(Troc), $J_{H,H}$ 12.37 Hz), 4.61 (dd, 1H, $\mathbf{H}^{\mathbf{A}}$-3, $J_{3,2}$ 2.56 Hz), 4.33 (dd, 1H, $\mathbf{H}^{\mathbf{A}}$-2, $J_{2,1}$ 5.12 Hz $J_{2,3}$ 2.56 Hz), 4.27 (dd, 1H, $\mathbf{H}^{\mathbf{A}}$-4, $J_{4,5}$ 1.71 Hz $J_{4,3}$ 8.11 Hz), 4.23 (m, 2H, $\mathbf{H}^{\mathbf{D}}$-5/6), 4.13 (dd, 1H, $\mathbf{H}^{\mathbf{D}}$-6), 4.05 (m, 1H, $\mathbf{H}^{\mathbf{D}}$-2), 3.89–3.83 (m, 2H, $\mathbf{H}^{\mathbf{A}}$-5/6), 3.74 (dd, 1H, $\mathbf{H}^{\mathbf{A}}$-6′), 2.10, 2.03, 2.01 (3 × s, 9H, 3 × $\mathbf{C}H_3$(Ac)), 1.53, 1.45, 1.34 (3 × s, 12H, 4 × $\mathbf{C}H_3$C(isopropylidene)). ^{13}C NMR **17α** (75 MHz, $CDCl_3$): δ 171.0–169.4 (3 × **C**O(Ac)), 154.2 (**C**O(Troc)), 109.5, 108.7 (2 × **C**$(CH_3)_2(OR)_2$), 96.2 ($\mathbf{C}^{\mathbf{A}}$-1α), 91.7 ($\mathbf{C}^{\mathbf{D}}$-1α), 75.4–62.0 ($\mathbf{C}^{\mathbf{D}}$-3/4/5/6 and $\mathbf{C}^{\mathbf{A}}$-2/3/4/5/6), 54.2 ($\mathbf{C}^{\mathbf{D}}$-2), 26.0, 25.9, 24.9, 24.2 (4 × $\mathbf{C}H_3$C(isopropylidene)), 20.7–20.6 (3 × $\mathbf{C}H_3$(Ac)). ^{1}H NMR **17β** (500 MHz, $CDCl_3$): δ 5.52 (d, 1H, $\mathbf{H}^{\mathbf{A}}$-1α, $J_{1,2}$ 5.52 Hz), 5.25 (dd, 2H, $\mathbf{H}^{\mathbf{D}}$-3, and N**H**, $J_{3,2}$ 9.81 Hz $J_{3,4}$ 9.38 Hz), 5.07 (dd, 1H, $\mathbf{H}^{\mathbf{D}}$-4, $J_{4,3}$ 9.38 Hz $J_{4,5}$ 9.81 Hz), 4.92 (d, 1H, C**H**H(Troc)), 4.80 (d, 1H, $\mathbf{H}^{\mathbf{D}}$-1β, $J_{1,2}$ 8.53 Hz), 4.58 (dd, 1H, $\mathbf{H}^{\mathbf{A}}$-3, $J_{3,2}$ 7.68 Hz $J_{3,4}$ 2.13 Hz), 4.52–4.51 (m, 1H, CH**H**(Troc)), 4.31 (dd, 1H, $\mathbf{H}^{\mathbf{A}}$-2), 4.28 (m, 1H, $\mathbf{H}^{\mathbf{D}}$-6), 4.18 (dd, 1H, $\mathbf{H}^{\mathbf{A}}$-4, $J_{4,5}$ 1.71 Hz $J_{4,3}$ 8.11 Hz), 4.13 (dd, 1H, $\mathbf{H}^{\mathbf{D}}$-6′, $J_{6,5}$ 2.55 Hz $J_{6',6}$ 12.37Hz), 3.99–3.95 (m, 2H, $\mathbf{H}^{\mathbf{A}}$-5/6), 3.78(dd, $\mathbf{H}^{\mathbf{A}}$-6′), 3.72–3.69 (m, 1H, $\mathbf{H}^{\mathbf{D}}$-2/5), 2.09, 2.02, 2.01 (3 × s, 9H, 3 × $\mathbf{C}H_3$(Ac)), 1.54. 1.44, 1.32 (4 × s, 12H, 4 × $\mathbf{C}H_3$C(isopropylidene)). ^{13}C NMR **17β** (75 MHz, $CDCl_3$): δ 170.6, 170.5, 169.4 (3 × **C**O(Ac)), 154.2 (**C**O(Troc)), 109.4, 108.7 (2 × **C**$(CH_3)_2(OR)_2$), 101.0 ($\mathbf{C}^{\mathbf{D}}$-1β), 96.1 ($\mathbf{C}^{\mathbf{A}}$-1α), 74.4–68.2 ($\mathbf{C}^{\mathbf{D}}$-3/4/5 and $\mathbf{C}^{\mathbf{A}}$-2/3/4/5/6), 62.0 ($\mathbf{C}^{\mathbf{D}}$-6), 56.1 ($\mathbf{C}^{\mathbf{D}}$-2), 26.0, 25.9, 24.9, 24.2 (4 × $\mathbf{C}H_3$C(isopropylidene)), 21.4, 20.7, 20.5 (3 × $\mathbf{C}H_3$(Ac)). ESMS: *m/z* calcd for $C_{28}H_{40}Cl_3NO_{15}$, 735.15/737.15, *m/z* calcd for $[M+Na-CH_3]^+$ calcd 743.12. Found 743.13. *m/z* calcd for $[M+NH_4-CH_3]^+$, 738.16/740.16. Found 739.13/741.15, *m/z* calcd for $[M-GalpO]^+$calcd 462.02/464.02. Found 461.98/464.

4.2.7. 3,4,6-Tri-*O*-benzoyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α/β-D-glucopyranosyl-(1→6)-(1,2;3,4)-diisopropylidene-α-D-galactopyranose 18. 18: Yield 63%, α/β 1:7, mp 91–96 °C. **18**: Yield 85%, α/β 1:6. ^{1}H NMR **18α** (500 MHz, $CDCl_3$): δ 8.0–7.3 (m, 15H,

Ar-**H**(Bz)), 5.78 (dd, 1H, $\mathbf{H^D}$-3, $J_{3,2}$ 10.36 Hz $J_{3,4}$ 9.76 Hz), 5.70 (d, 1H, N**H**), 5.68 (dd, 1H, $\mathbf{H^D}$-4, $J_{4,3}$ 9.76 Hz $J_{4,5}$ 10.07 Hz), 5.55 (d, 1H, $\mathbf{H^A}$-1α, $J_{1,2}$ 4.88 Hz), 5.06 (d, 1H, $\mathbf{H^D}$-1α, $J_{1,2}$ 3.36 Hz), 4.75 (d, 1H, C**H**H(Troc), $J_{H,H}$ 11.89 Hz), 4.68 (dd, 1H, $\mathbf{H^A}$-3, $J_{3,2}$ 7.93 Hz $J_{3,4}$ 2.44 Hz), 4.59 (dd, 1H, $\mathbf{H^D}$-6, $J_{6,5}$ 2.75 Hz), 4.49 (dd, 1H, $\mathbf{H^D}$-5, $J_{5,4}$ 10.1 Hz $J_{5,6}$ 2.75 Hz $J_{5,6'}$ 4.27 Hz), 4.45 (dd, 1H, $\mathbf{H^D}$-6′, $J_{6',5}$ 4.27 Hz), 4.43 (d, 1H, CH**H**(Troc), $J_{H,H}$ 11.89 Hz), 4.37–4.33 (m, 3H, $\mathbf{H^D}$-2, $\mathbf{H^A}$-2/4, $J_{2(D),3(D)}$ 10.36 Hz $J_{2(A),3(A)}$ 7.93 Hz $J_{2(A),1(A)}$ 4.88 Hz $J_{4,3}$ 2.44 Hz $J_{4,5}$ 1.83 Hz), 4.10 (ddd, 1H, $\mathbf{H^A}$-5, $J_{5,4}$ 1.83 Hz $J_{5,6'}$ 6.40 Hz), 4.02 (dd, 1H, $\mathbf{H^A}$-6, $J_{6,6'}$ 10.06 Hz), 3.79 (dd, 1H, $\mathbf{H^A}$-6′, $J_{6',5}$ 6.40 Hz $J_{6',6}$ 10.06 Hz), 1.6–1.3 (4 × s, 12H, 4 × C**H**$_3$C(isopropylidene)). ^{13}C NMR **18α** (125 MHz, $CDCl_3$): δ 166.9 (3 × **C**O(Bz)), 155.1 (**C**O(Troc)), 134.0–129.0 (18 × Ar-**C**(Bz)), 110.3, 109.4 (2 × **C**(CH$_3$)$_2$(OR)$_2$), 98.8 (d, $\mathbf{C^D}$-1α), 97.0 ($\mathbf{C^A}$-1α), 75.2–66.5 ($\mathbf{C^D}$-3/4/5, **C**H$_2$(Troc), and $\mathbf{C^A}$-2/3/4/5/6), 63.6 ($\mathbf{C^D}$-6), 55.3 ($\mathbf{C^D}$-2), 26.9, 26.7, 25.6, 25.1 (4 × **C**H$_3$C(isopropylidene)). ^{1}H NMR **18β** (500 MHz, $CDCl_3$): δ 8.0–7.3 (m, 15H, Ar-**H**(Bz)), 5.72 (dd, 1H, $\mathbf{H^D}$-3, $J_{3,2}$ 10.23 Hz $J_{3,4}$ 9.81 Hz), 5.61 (dd, 1H, $\mathbf{H^D}$-4, $J_{4,3}$ 9.81 Hz $J_{4,5}$ 9.39 Hz), 5.55 (d, 1H, $\mathbf{H^A}$-1α, $J_{1,2}$ 5.12 Hz), 5.35 (d, 1H, N**H**, $J_{NH,2}$ 8.95 Hz), 5.04 (d, 1H, $\mathbf{H^D}$-1β, $J_{1,2}$ 8.0 Hz), 4.85 (d, 1H, C**H**H(Troc)), 4.62 (dd, 1H, $\mathbf{H^D}$-6, $J_{6,5}$, 11.95Hz $J_{6,6'}$ 2.99 Hz), 4.57 (dd, 1H, $\mathbf{H^A}$-3, $J_{3,2}$ 2.56 Hz $J_{3,4}$ 8.10 Hz), 4.47 (dd, 1H, $\mathbf{H^D}$-6′, $J_{6',5}$ 5.12 Hz $J_{6',6}$ 12.37 Hz), 4.39 (d, 1H, CH**H**(Troc)), 4.32 (ddd, 1H, $\mathbf{H^A}$-2, $J_{2,1}$ 5.12 Hz $J_{2,3}$ 2.56 Hz), 4.17 (dd, 1H, $\mathbf{H^A}$-4, $J_{4,3}$ 8.10 Hz), 4.10 (ddd, 1H, $\mathbf{H^D}$-5, $J_{5,6'}$ 5.12 Hz), 4.05–3.98 (m, 3H, $\mathbf{H^D}$-2 & $\mathbf{H^A}$-5/6, $J_{6,6'}$ 11.95 Hz), 3.89 (ddd, 1H, $\mathbf{H^A}$-6′, $J_{6',6}$ 11.95 Hz), 1.54, 1.42, 1.33, 1.31 (4 × s, 12H, 4 × C**H**$_3$C(isopropylidene)). ^{13}C NMR **18β** (125 MHz, $CDCl_3$): δ 166.9, 166.8, 165.9 (3 × **C**O(Bz)), 155 (**C**O(Troc)), 134.0–129 (18 × Ar-**C**(Bz)), 110.1, 109.5 (2 × **C**(CH$_3$)$_2$(OR)$_2$), 102.0 (d,$\mathbf{C^D}$-1β), 96.5 (d, $\mathbf{C^A}$-1α), 75.0–69.3 ($\mathbf{C^D}$-3/4/5/6, **C**H$_2$(Troc), and $\mathbf{C^A}$-2/3/4/5/6), 64.0 ($\mathbf{C^D}$-6), 57.2 ($\mathbf{C^D}$-2), 26.7, 26.6, 25.6, 25.0 (4 × **C**H$_3$C(isopropylidene)). ESMS: *m/z* calcd for $C_{43}H_{46}Cl_3NO_{15}$, 921.19/923.19, *m/z* calcd for $[M+Na-CH_3]^+$, 929.16/931.16. Found 929.74/931.17. *m/z* calcd for $[M+NH_4-CH_3]^+$ calcd 924.20/926.20. Found 924.76/926.76. *m/z* calcd for $[M-GalpO]^+$ calcd 648.06/650.06. Found 648/649.99.

4.2.8. 3,4,6-Tri-*O*-benzoyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α/β-D-glucopyranosyl-(1→6)-methyl-2-acetamido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside 20. Yield 60%, α/β 1:4, oil. ^{1}H NMR **20α** (300 MHz, $CDCl_3$): δ 8.1–7.2 (m, 25H, Ar-**H**(Bz/Bn)), 5.70 (dd, 1H, $\mathbf{H^D}$-3, $J_{3,2}$ 10.3 Hz $J_{3,4}$ 9.6 Hz), 5.60 (dd, 1H, $\mathbf{H^D}$-4, $J_{4,3}$ 9.6 Hz $J_{4,5}$ 9.5 Hz), 5.21 (d, 1H, N$\mathbf{H^D}$, $J_{NH,2}$ 9.9 Hz), 5.29 (d, 1H, N$\mathbf{H^A}$, $J_{NH,2}$ 9.3 Hz), 5.06 (d, 1H, $\mathbf{H^D}$-1α, $J_{1,2}$ 3.4 Hz), 4.94–4.61 (m, 9H, $\mathbf{H^A}$-1α, $\mathbf{H^D}$-6/6′, C$\mathbf{H_2}$(Troc), and 2 × C$\mathbf{H_2}$(Bn)), 4.39–4.34 (m, 1H, $\mathbf{H^D}$-5), 4.30 (dd, 1H, $\mathbf{H^D}$-2), 4.19 (ddd, 1H, $\mathbf{H^A}$-2), 3.88–3.75 (m, 3H, $\mathbf{H^A}$-5/6/6′), 3.70 (dd, 1H, $\mathbf{H^A}$-3), 3.46 (dd, 1H, $\mathbf{H^A}$-4), 3.42 (s, 3H, C$\mathbf{H_3}$O), 1.8 (s, 3H, C$\mathbf{H_3}$(Ac)). ^{13}C NMR **20α** (125 MHz, $CDCl_3$): δ 170.3 (**C**O(Ac)), 167.2, 166.8, 165.9 (3 × **C**O(Bz)), 154 (**C**O(Troc)), 138.9–128.6 (30 × Ar-**C**(Bz/Bn)), 99.2 (d, $\mathbf{C^A}$-1α), 98.1 (d, $\mathbf{C^D}$-1 α), 81.3–63.5 ($\mathbf{C^D}$-3/4/5/6, **C**H$_2$(Troc), $\mathbf{C^A}$-3/4/5/6 and 2 × **C**H$_2$(Bn)), 55.8 ($\mathbf{C^A}$-2), 55.2 ($\mathbf{C^D}$-2), 53.2 (**C**H$_3$O), 24.1 (**C**H$_3$(Ac)). ^{1}H NMR **20β** (300 MHz, $CDCl_3$): δ 8.0–7.3 (m, 25H, Ar-**H**(Bz/Bn)), 5.75 (dd, 1H, $\mathbf{H^D}$-3, $J_{3,2}$ 10.3 Hz $J_{3,4}$ 9.5 Hz), 5.60 (dd, 1H, $\mathbf{H^D}$-4, $J_{4,3}$ 9.5 Hz $J_{4,5}$ 9.8 Hz), 5.29 (d, 1H, N$\mathbf{H^A}$, $J_{NH,2}$ 9.3 Hz), 5.21 (d, 1H, N$\mathbf{H^D}$, $J_{NH,2}$ 8.4 Hz), 4.85–4.78 (m, 2H, $\mathbf{H^D}$-1β, and C**H**H(Troc)), 4.63–4.46 (m, 8H, $\mathbf{H^A}$-1α, $\mathbf{H^D}$-6/6′, CH**H**(Troc), and 2 × C$\mathbf{H_2}$(Bn)), 4.23 (dd, 1H, $\mathbf{H^A}$-2), 4.15 (m, 2H, $\mathbf{H^A}$-6/6′), 4.07 (m, 1H, $\mathbf{H^D}$-5), 3.94 (ddd, 1H, $\mathbf{H^D}$-2), 3.78 (m, 1H, $\mathbf{H^A}$-5), 3.66 (dd, 1H, $\mathbf{H^A}$-3), 3.54 (dd, 1H, $\mathbf{H^A}$-4), 3.3 (s, 3H, C$\mathbf{H_3}$O), 1.8 (s, 3H, C$\mathbf{H_3}$(Ac)). ^{13}C NMR **20β** (125 MHz, $CDCl_3$): δ 170.4 (**C**O(Ac)), 166.9, 166.8, 165.9 (3 × **C**O(Bz)), 154.7 (**C**O(Troc)), 139.0–128.5 (30 × Ar-**C**(Bz/Bn)), 101.8 ($\mathbf{C^D}$-1β), 99.2 ($\mathbf{C^A}$-1α), 81.1–64.0 ($\mathbf{C^D}$-3/4/5/6, **C**H$_2$(Troc), $\mathbf{C^A}$-3/4/5/6 & 2 × **C**H$_2$(Bn)), 57.2 ($\mathbf{C^A}$-2), 55.7 ($\mathbf{C^D}$-2), 53.1 (**C**H$_3$O), 24.1 (**C**H$_3$(Ac)). ESMS: *m/z* calcd for $C_{54}H_{55}Cl_3N_2O_{15}$, 1076.27/1078.27, *m/z* calcd for $[M+NH_4-MeO]^+$, 1063.28/1065.28. Found 1063.31/1065.29.

4.3. Microwave assisted synthesis of 3,4,6-tri-*O*-benzoyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→3)-methyl-2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside 22

Glycosyl donor **9** (0.05 mmol, 1.5 equiv), glycosyl acceptor **21** (0.033 mmol, 1 equiv), $LiClO_4$ (10 mg) and crushed 3 Å molecular sieves (15 mg) and a magnet were placed in a 5 mL microwave reaction vial and fitted with a septum. The tube was dried under high vacuum for 2 h and filled with argon. Dry CH_3NO_2 (300 μL) was added under argon and the reaction mixture subjected to microwave radiation for 5 min at 130 °C. The coupling was repeated twice with 1.5 equiv of donor **9** in dry CH_3NO_2 (300 μL). The reaction mixture was centrifuged (3 min, 4000 rpm) and the supernatant concentrated under a stream of air. The residue was loaded onto a preparative HPLC column with 2 mL of CH_3CN and purified.

Yield 38%, pure β, oil. $[\alpha]_D = +57.3$ (c 2.08×10^{-3}, $CHCl_3$). ^{1}H NMR **22β** (300 MHz, $CDCl_3$): δ 8.12, 7.93, 7.73 (3 × (d, 2H, Ar-**H** (Bz))), 7.65–6.87 (m, 14H, Ar-**H**(Bz/benzylidene)), 6.47 (d, 1H), 6.17 (dd, 1H), 5.54 (dd, 1H), 5.51 (s, 1H, PhC**H**(benzylidene)), 5.44 (d, 1H, $\mathbf{H^D}$-1β, $J_{1,2}$ 8.73 Hz), 5.12 (d, 1H), 4.97 (dd, 1H), 4.82 (d, 1H, $\mathbf{H^A}$-1α, $J_{1,2}$ 3.28 Hz), 4.63 (dd, 1H), 4.27–4.14 (m, 5H), 4.08–4.00 (m, 4H), 3.21 (s, 3H, C$\mathbf{H_3}$O), 3.18 (m, 1H), 2.02 (s, 3H, C$\mathbf{H_3}$(Ac)). ^{13}C NMR **20β** (125 MHz, $CDCl_3$): δ 170.8 (**C**O(Ac)), 166.4, 165.3, 165.1 (3 × **C**O(Bz)), 153.6 (**C**O(Troc)), 136.3–125.9 (24 × Ar-**C**(Bz/Bn)), 102.5 (Ph**C**H(benzylidene)), 99.3 ($\mathbf{C^A}$-1α), 96.7 ($\mathbf{C^D}$-1β), 80.8–52.9 ($\mathbf{C^D}$-2/3/4/5/6, **C**H$_2$(Troc), and $\mathbf{C^A}$-2/3/4/5/6), 55.1 (**C**H$_3$O), 23.1 (**C**H$_3$(Ac)). IR (neat) 3500–3300 (w), 1729 (s), 1652 (m), 1532 (m), 1267 (s), 1096 (s), 709 (s). ESMS: *m/z* calcd for $C_{46}H_{45}Cl_3N_2O_{15}$, 970.22/972.22, *m/z* calcd for $[M+H]^+$, 971.22/973.22. Found 971.19/973.19. *m/z* calcd for $[M+Na]^+$, 993.21/995.21. Found 993.17/995.17. HRMS (ES): calcd for $C_{46}H_{45}Cl_3N_2O_{15}H$ $[M+H]^+$, 971.1964; Found, 971.1868.

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