Preparation of Glycosyltriazenes

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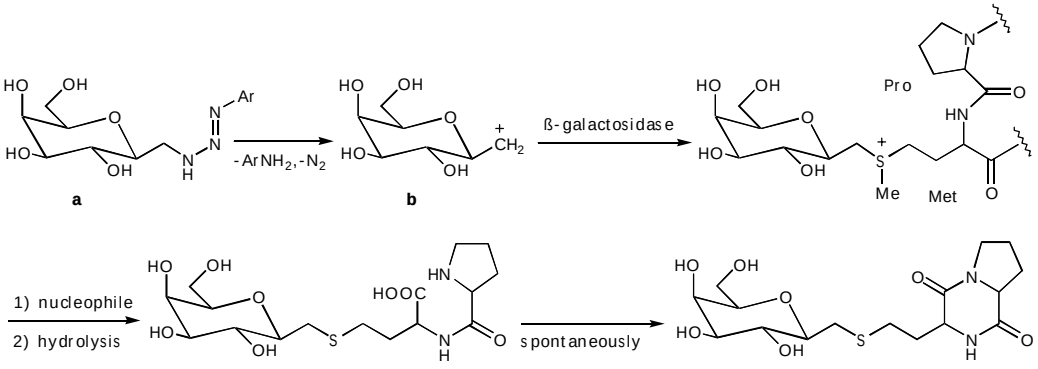
Abstract. *O*-Unprotected glycosyltriazenes are prepared for the first time by coupling of 1-anthraquinone-1-diazonium hydrogensulfate with *β*-glycopyranosylamines to afford 1-(anthraquinone-1-yl)-3-(*β*-glycopyranosyl)triazenes **3a**–**h**. Acetylation of compounds **3** furnished the *O*-acetates **4a**–**g**. The stability of triazenes **3** results from fixation of the NH proton in an intramolecular hydrogen bond to one of the anthraquinone carbonyl oxgen atoms. Treatment of triazenes **4** with *tert*-butyl hypochlorite afforded acetoglycosyl chlorides **6** and 1-azidoanthraquinone **7**. With acetic acid the triazene **4a** formed tetra-*O*-acetyl-*D*-xylopyranose **9** together with 1-aminoanthraquinone **10**.

Triazenes are well known for their broad range of biological and therapeutic activities. For example, 5-(3,3-dimethyl-1-triazeno)imidazole-4-carboxamide (DTIC) is an antitumor agent clinically used in the therapy of disseminated sarcoma of man, *etc*. [1]. The 1,3-bis(4-amidiniumphenyl)triazene berenil has veterinary application as an antitrypanosomal agent, and has cytotoxic and anti-viral properties [2]. 3-Glycopyranosylmethyl-1-aryltriazenes, *e.g*. **a**, are active-site-directed irreversible inhibitors of diverse glycosidases [3–12]. The enzyme inhibition results from an irreversible alkylation of a specific methionine of the protein chain by a cation **b** [3, 4].

[17]. However, attempts to prepare *O*-unprotected glycosyltriazenes so far met with failure [16, 18, 19]. Thus, no glucosyltriazenes were produced by reaction of *N*-(*p*-tolyl)-*D*-glucopyranosylamine with 4-methyl- or 2,5-dichlorobenzenediazonium chloride [16]. *O*-Unprotected glycosyltriazenes would be of interest, inter alia, because of possible pharmaceutic activities.

Our interest in glycosyltriazenes arose from the observation that certain 1,3-disubstituted triazenes **c** can be oxidized with *tert*-butyl hypochlorite to *N*-chlorotriazenes **d**, which with Lewis acids such as antimony pentachloride afford 1,3-diaza-2-azoniaallene salts **e** as reactive intermediates, which undergo 1,3-dipolar cy-



Scheme 1 1-Aryl-3-(glycopyranosylmethyl)triazenes as glycosidase inhibitors

Little has been reported about other triazene derivatives of carbohydrates. Stable triazenes have been prepared by coupling of 1-,3-,5- or 6-aminodeoxy sugars with aryldiazonium salts [13–16]. Treatment of 2,3,4,6-tetra-*O*-acetyl-*β*-*D*-glucopyranosylamine with *p*-chlorobenzenediazonium tetrafluoroborate afforded 3-(2,3,4,6-tetra-*O*-acetyl-*β*-*D*-glucopyranosyl)-1-(*p*-chlorophenyl)triazene, which with alcohols in the presence of an acidic catalyst furnished glycosides in moderate yields

cloaddition reactions with alkenes, alkynes, with 1,3-butadienes, allenes, carbodiimides and cyanamides to afford 1,2,3-triazolium salts **f** (Scheme 2) [20–24]. The question arose, whether R can also be a glycosyl substituent.

In conformity with literature reports [16], attempts to couple 2,4,6-trichlorobenzediazonium chloride with *β*-*D*-xylosylamine rendered mixtures of compounds containing only traces of triazene **g** (Scheme 3).

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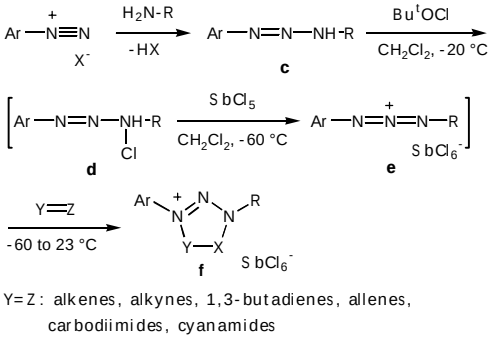
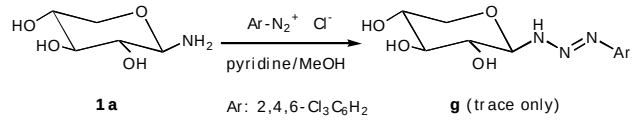


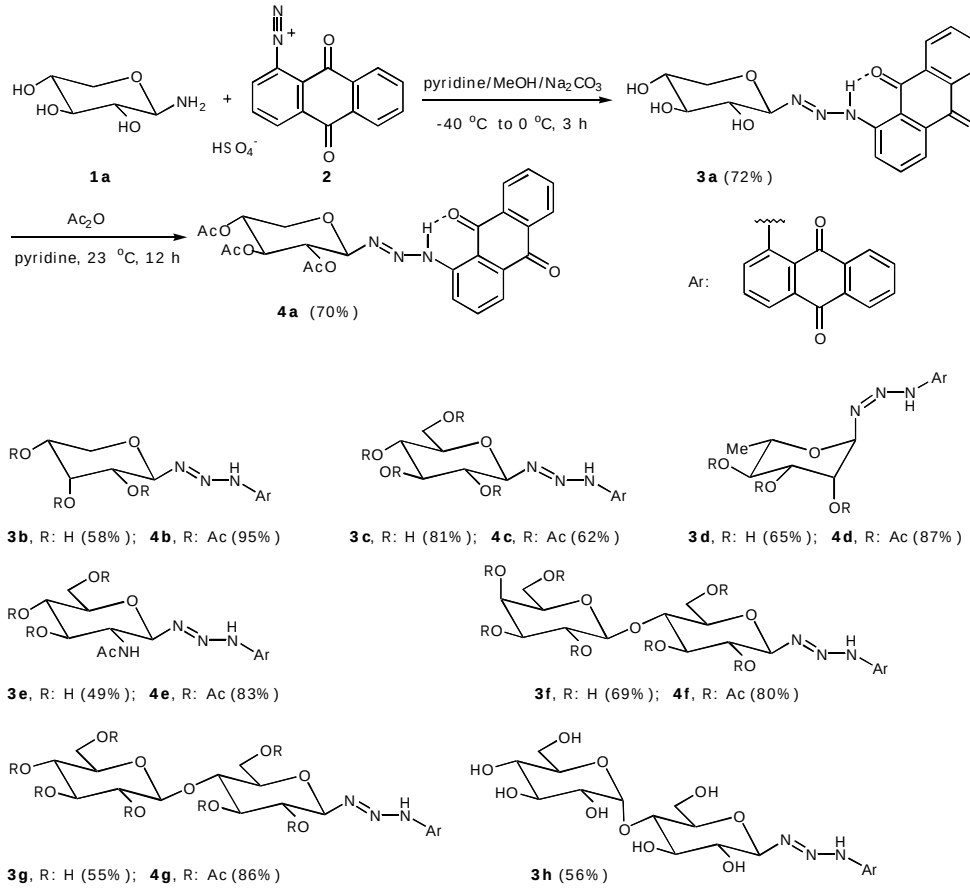
Scheme 2 Preparation and cycloaddition reactions of 1,3-diaza-2-azoniaallene salts



Scheme 3 Attempted coupling of a glycosylamine with an aryldiazonium salt

We pondered that either the mobility or the position of the NH proton has an impact on the instability of glycosyltriazenes of type **g**. 1-Aryl-3-alkyltriazenes are known to form tautomeric equilibria, in which the NH proton is preferently positioned distal from the aryl substituent [25–27]. We suspected that a glycosyltriazene **g** with the NH proton fixed proximal to aryl, for instance by an intramolecular hydrogen bond to one of the carbonyl oxygen atoms of a 1-anthraquinonyl substituent, might be stable. Indeed, coupling of the 1-anthraquinonyldiazonium salt (**2**) [28] with *β-D*-xylopyranosylamine (**1a**) [29] afforded a first *O*-unprotected stable glycosyltriazene **3a** in 72% yield. The yellow triazene **3a** proved to be quite stable melting with decomposition above 140 °C. Correspondingly, the stable glycosyltriazenes **3b**–**h** were prepared in good yields. Acetylation of compounds **3a**–**g** furnished the triazene **4a**–**g** (Scheme 4).

It is worth noting and can be taken as evidence for an intramolecular hydrogen bond (*cf*. Scheme 4, compounds **3a**, **4a**), that in no case the NH group of a compound **3** was acetylated, while *N*-acetylation of other 1-aryl-3-alkyltriazenes, *e.g*. of 3-methyl-1-*p*-tolyltriazene



Scheme 4 Preparation of 3-(anthraquinone-1-yl)-1-glycopyranosyltriazenes

[30, 31], has been reported to proceed at low temperatures without problems. In the ^{1}H NMR spectra ($CDCl_3$) of the acetates **4a**–**g** relatively sharp signals observed at low field between 13.30 and 14.43 ppm for the NH protons are strong evidence in favour of the postulated intramolecular hydrogen bond. For reason of comparison, the NH signal for the triazene 4-MeC_6H_4–N=N–NH–Me was found at 8.01 ppm ($CDCl_3$). In the ^{13}C NMR spectra of the glycosylazo compounds **3a**–**h**, respectively **4a**–**g**, the signals for the anomeric carbon atoms C-1' were observed between 92.4 and 95.0 ppm (**3a**–**h**, CD_3SO CD_3), respectively between 94.4 and 98.0 ppm (**4a**–**g**, $CDCl_3$), while the anomeric C-1 atom of the glycosylamine **1a** absorbs at higher field (86.9 ppm). Furthermore, very broad bands centered around 3225 cm^{-1} in the IR spectra of acetates **4a**–**g** are in line with intramolecularly hydrogen bonded NH protons.

In conclusion, in contrast to 1-aryl-3-glycosyltriazenes, unprotected 3-aryl-1-glycosyltriazenes **3** with the NH proton fixed in an intramolecular hydrogen bond are easily accessible and quite stable.

In order to test the transformation of triazenes **3** or **4** into *N*-chlorotriazenes **d** (Scheme 2), the acetate **4a** was treated at low temperatures (–60 °C to 0 °C) with tert-butyl hypochlorite (Scheme 5). However, instead of a chlorotriazene **d**, a mixture of 2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl chloride (**6a**), a trace of the α-anomer **6'a** [32–34], and of 1-azidoanthraquinone (**7**) [35] was obtained. These compounds were identified by comparison of their NMR spectra with those of the authentic compounds. Repetition of the experiment in the presence of methanol again afforded a mixture of **6a**, **6'a** and **7**, but no methylglycoside **8a**. Only at 23 °C in the presence of a large excess of methanol the glycoside **8a** (α:$\beta \approx$ 5:2) [36, 37] was formed, obviously by reaction of the primarily formed chlorides **6a** and **6'a** with the alcohol. Similarly, from the gluco compound **4b** and *tert*-butyl hypochlorite a mixture of the chloride **6b**, 1-azidoanthraquinone **7**, and an unidentified carbohydrate was obtained with no indication of the intermediate formation of a *N*-chlorotriazene **d**. Finally, a solution of the triazene **4a** in acetic acid was boiled under reflux to give a quantitative yield of a 1:1 mixture of the anomeric 1,2,3,4-tetra-*O*-acetyl-*D*-xylopyranoses **9** [38–40] and of 1-aminoanthraquinone **10**.

Triazenes can be looked at as aza analogues of amidines. Hence, an electrophile should preferently attack the monosubstituted nitrogen atom of a triazene, in conformity with recent ab initio calculations for the protonation of triazenes [41], although the energetic benefit for protonation of *N*-1 as compared to protonation of *N*-3 was calculated to be small. Accordingly, the electrophilic chlorination of the triazene **4a** with *tert*-butyl hypochlorite might be speculated to give an unstable *N*-1-chloro hemiaminal **5**, which decomposes to the pyranosyl chloride **6a** and azide **7**. Similarly, protonation of **4a** should give an intermediate **5'**, which decomposes to afford **9** and a monosubstituted triazene, which looses nitrogen to give the amine **10**.

In conclusion, the chance to prepare a 1,3-diaza-2-azoniaallene salt **e** (Scheme 2, R: glycosyl) from a glycosyltriazene is small.

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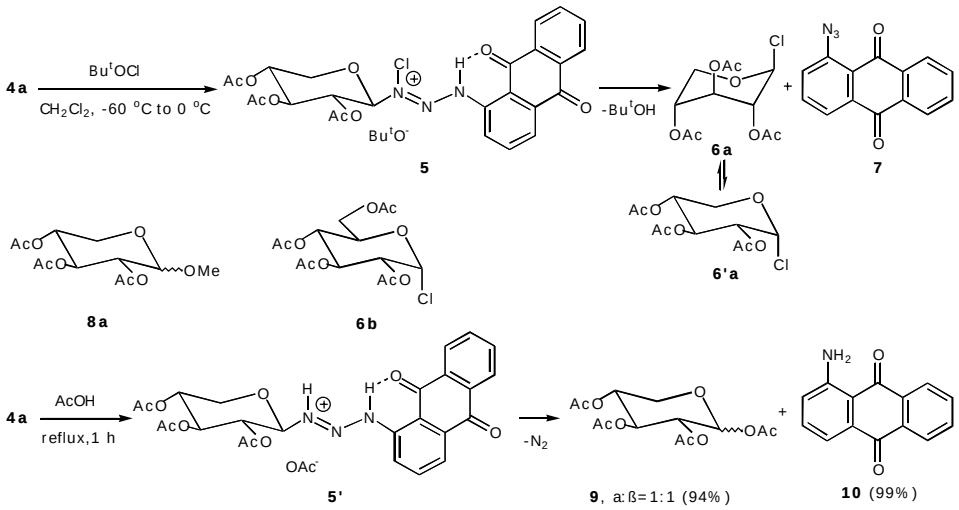

Scheme 5 Oxidation with *tert*-butyl hypochlorite and acetolysis of a 3-aryl-1-glycopyranosyltriazene

Experimental

The solvents were dried by standard methods. The melting points are uncorrected. – IR: Perkin-Elmer FTIR 1600; solvent CH_2Cl_2. – ^1H,^{13}C NMR: Bruker AC-250, WM-250, and DRX-600 spectrometers, JEOL JNM-LA 400 spectrometer; internal standard tetramethylsilane; coupling constants in Hz.

1-(Anthraquinone-1-yl-)3-(β-D-xylopyranosyl)triazene (**3a**)

1-Anthraquinonediazonium hydrogensulfate **2** [28] (3.32 g, 10 mmol) was added to a stirred cold (–40 °C) suspension of *β-D*-xylopyranosylamine **1a** [29] (1.49 g, 10 mmol) and Na_2CO_3 (1.17 g, 11 mmol) in pyridine (40 ml) and MeOH (20 ml). The brown suspension was warmed up to 0 °C in the course of the next 30 min. After stirring at 0 °C for 3 h the mixture was concentrated to a slurry, to which ice water (600 ml) was added. Stirring and centrifugation afforded a slurry, which was again treated with H_2O. Centrifugation and lyophilization afforded a yellow powder, which at –15 °C crystallized from pyridine (100 ml)/Et_2O (70 ml) to furnish a yellow powder (2.91 g, 72%); *m.p.* 140–142 °C (dec.). – $[\alpha]_D^{25}$= –148.0 (c = 0.1, pyridine). – IR (nujol): ν/cm^{-1} = 3300 (br, OH, NH), 1669, 1639, 1591. – ^1H NMR (250 MHz, CD_3SOCD_3): δ/ppm = 3.24–3.37 (m, H-4',5'), 3.45–3.54 (m, H-2',3'), 3.90 (dd, *J* = 5.0, 10.8, H-5''), 4.44 (d, *J* = 8.4, H-1'), 5.13 (d, *J* = 4.8), 5.17 (d, *J* = 4.7), 5.21 (d, *J* = 5.6) (3OH), 7.72–8.10 (m, 7H, aryl), 12.99 (NH). – ^{13}C NMR (62.9 MHz, CD_3SOCD_3): δ/ppm = 67.8, 69.5, 72.2, 77.1 (C-2',3',4',5'), 98.0 (C-1'), 113.6, 119.5, 120.6, 126.3, 126.7, 132.0, 133.3, 133.5, 134.3, 134.5, 135.7, 143.6 (=C), 181.7, 185.4 (C=O).

$C_{19}H_{17}N_3O_6 \cdot H_2O$	Calcd.: C 56.85	H 4.77	N 10.47
(401.4)	Found: C 56.50	H 4.72	N 10.36.

1-(Anthraquinone-1-yl-)3-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)triazene (**4a**)

At 0 °C Ac_2O (20 ml) was added dropwise to a stirred solution of **3a** (4.01 g, 10 mmol) in pyridine (50 ml). After stirring at 0 °C for 1 h and at 23 °C for 12 h the solvent was evaporated. The oily residue solidified when stirred in ice water (400 ml). Isolation, drying, and precipitation from EtOH (36 ml)/$CHCl_3$ (18 ml) afforded a yellow powder (3.56 g, 70%); *m.p.* 172–174 °C (dec.). – $[\alpha]_D^{25}$= –74.5 (c = 0.1, $CHCl_3$). – IR (CH_2Cl_2): ν/cm^{-1} = 3222 (br, NH), 1755, 1674, 1645, 1592, 1582. – ^1H NMR (250 MHz, $CDCl_3$): δ/ppm = 1.97, 2.07, 2.09 (CH_3), 3.56 (dd, *J* = 10.1, 11.3, H-5'), 4.33 (dd, *J* = 5.4, 11.4, H-5''), 4.85 (m, 1H), 5.16 (m, 1H), 5.34 (m, 2H) (H-4',1',2',3'), 7.67–8.31 (m, aryl), 13.37 (NH). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ/ppm = 20.6, 20.7 (2C) ($3CH_3$), 64.8, 68.8, 70.5, 72.6 (C-2',3',4',5'), 95.0 (C-1'), 114.9, 119.9, 121.8, 127.0, 127.4, 132.7, 133.9, 134.1, 134.2, 134.4, 135.3, 143.8 (=C), 169.2, 169.8, 170.3, 182.6, 185.8 (C=O).

$C_{25}H_{23}N_3O_9$	Calcd.: C 58.94	H 4.55	N 8.25
(509.5)	Found: C 58.83	H 4.37	N 8.00.

1-(Anthraquinone-1-yl-)-3-(β-D-ribopyranosyl)triazene (**3b**)

From *β-D*-ribopyranosylamine **1b** [42] (1.49 g, 10 mmol) in the manner described for **3a**. The reaction mixture was concentrated to half of its volume and then poured into ice water (200 ml). Workup as described afforded a brown powder, which was stirred for 5 min in CH_2Cl_2 (200 ml). Filtration furnished a yellow powder (2.28 g, 58%); *m.p.* 126–128 °C. – $[\alpha]_D^{25}$= –94.0 (c = 0.1, pyridine). – IR (nujol): ν/cm^{-1} = 3410, 3272 (br, OH, NH), 1667, 1637, 1590, 1574. – ^1H NMR (600 MHz, CD_3SOCD_3): δ/ppm = 3.60 (t, *J* = 10.2, H-5'), 3.67 (m, H-5'',2'), 3.71 (m, H-4'), 3.97 (s, br, H-3'), 4.72 (d, *J* = 8.1, H-1'), 4.83 (d, *J* = 6.2, OH-4'), 4.93 (m, OH-2',3'), 7.84–8.21 (aryl), 13.10 (NH). – ^{13}C NMR (150.9 MHz, CD_3SOCD_3): δ/ppm = 64.3, 67.1, 69.7, 70.4 (C-2',3',4',5'), 94.4 (C-1'), 115.6, 119.7, 120.7, 126.5, 126.9, 132.3, 133.6, 133.8, 134.5, 134.7, 135.9, 143.8 (=C), 182.1, 185.7 (C=O).

$C_{19}H_{17}N_3O_6 \cdot 1/2H_2O$	Calcd.: C 58.16	H 4.62	N 10.71
(392.4)	Found: C 58.56	H 4.99	N 10.26.

1-(Anthraquinone-1-yl-)-3-(2,3,4-tri-O-acetyl-β-D-ribopyranosyl)triazene (**4b**)

From **3b** (3.92 g, 10 mmol) in the manner described for **4a**. The product was isolated from its aqueous suspension by centrifugation. The yellow residue was washed with H_2O (5× 20 ml) and lyophilized to afford a yellow powder (4.84 g, 95%), which can be recrystallized at –15 °C from CH_2Cl_2 (75 ml)/Et_2O (12 ml); *m.p.* 170–173 °C (dec.). – $[\alpha]_D^{25}$ = –40.0 (c = 0.1, $CHCl_3$). – IR (CH_2Cl_2): ν/cm^{-1} = 3228 (br, NH), 1750, 1673, 1646, 1591, 1581. – ^1H NMR (250 MHz, $CDCl_3$): δ/ppm = 2.05, 2.11, 2.17 ($3CH_3$), 3.96 (dd, *J* = 7.8, 11.6), 4.23 (dd, *J* = 4.1, 11.6) (H-5',5''), 5.12 (d, *J* = 6.6, H-1'), 5.25 (m, H-2',4'), 5.70 (t, *J* = 2.9, H-3'), 7.69–8.29 (aryl), 13.37 (NH). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ/ppm = 20.7, 20.8 (2C) ($3CH_3$), 63.0, 66.6, 67.3, 68.7 (C-2',3',4',5'), 92.4 (C-1'), 114.8, 120.1, 121.8, 127.0, 127.3, 132.8, 133.9, 134.2, 134.3, 135.3, 143.9 (=C), 169.4, 169.7, 169.8, 182.5, 185.9 (C=O).

$C_{25}H_{23}N_3O_9$	Calcd.: C 58.94	H 4.55	N 8.25
(509.5)	Found: C 58.62	H 4.75	N 7.89.

1-(Anthraquinone-1-yl-)-3-(β-D-glucopyranosyl)triazene (**3c**)

From *β-D*-glucopyranosylamine [29, 43] (1.79 g, 10 mmol) in the manner described for **3a**. The crystalline red-orange product was stirred in ice water (200 ml) for 15 min. Filtration and recrystallization at –15 °C of the residue from pyridine (30 ml)/MeOH (15 ml) afforded brown prisms (3.48 g, 81%); *m.p.* 150–152 °C (dec.). – $[\alpha]_D^{25}$ = –54.2 (c = 0.1, pyridine). – IR (nujol): ν/cm^{-1} = 3100–3400 (br, OH, NH), 1673, 1643, 1589. – ^1H NMR (250 MHz, CD_3SOCD_3): δ/ppm = 3.39 (m, H-3',4',5'), 3.59 (m, H-2',6'), 3.83 (m, H-6''), 4.53 (d, *J* = 8.4, H-1'), 4.67 (t, *J* = 5.6, OH-6'), 5.10 (d, *J* = 4.7), 5.15 (d, *J* = 4.1) (OH-4',3'), 5.21 (d, *J* = 5.4, OH-2'), 7.65–8.05 (m, aryl), 12.95 (NH). – ^{13}C NMR (62.9 MHz, CD_3SOCD_3): δ/ppm = 61.2, 70.0, 72.3, 77.1, 79.2 (C-2',3',4',5',6'), 97.4 (C-1'), 113.5, 119.5, 120.6, 126.3, 126.7, 131.9, 133.1, 133.3, 134.3, 134.5, 135.7, 143.5 (=C), 181.6, 185.3 (C=O).

$C_{20}H_{19}N_3O_7 \cdot H_2O$	Calcd.: C 55.68	H 4.91	N 9.74
(431.4)	Found: C 55.50	H 4.63	N 9.54.

1-(Anthraquinone-1-yl-)-3-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)triazene (**4c**)

From **3c** (4.31 g, 10 mmol) in the manner described for **4a**. Crystallization at –15 °C from $CHCl_3$ (65 ml)/Et_2O (7 ml)

afforded a brown powder (4.32 g, 62%); *m.p.* 190–191 °C (dec.). – $[\alpha]_D^{25} = -65.0$ (c = 0.1, $CHCl_3$). – IR(CH_2Cl_2): ν/cm^{-1} = 3216 (br, NH), 1756, 1673, 1647, 1591, 1576. – ^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm = 1.95, 2.05, 2.07, 2.11 ($4CH_3$), 3.94 (ddd, *J* = 2.2, 4.6, 10.0, H-5'), 4.23 (dd, *J* = 2.1, 12.5), 4.34 (dd, *J* = 4.7, 12.5) (H-6',6''), 4.93 (d, *J* = 8.5, H-1'), 5.28 (t, *J* = 9.5, H-4'), 5.39 (t, *J* = 9.5, H-3'), 5.43 (t, *J* = 9.4, H-2'), 7.72–8.27 (m, aryl), 13.43 (NH). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ/ppm = 20.6 (2C), 20.7, 20.8 ($4CH_3$), 62.0 (C-6'), 68.1 (C-4'), 70.4 (C-2'), 73.4 (C-3'), 74.1 (C-5'), 94.7 (C-1'), 115.1, 119.8, 122.0, 127.0, 127.4, 132.8, 134.0, 134.2, 134.3, 134.4, 135.3, 143.7 (=C), 169.1, 169.4, 170.4, 170.8, 182.6, 185.8 (C=O).

$C_{28}H_{27}N_3O_{11}\cdot CHCl_3$	Calcd.: C 49.70	H 4.03	N 6.00
(700.9)	Found: C 49.52	H 4.07	N 6.05.

1-(Anthraquinone-1-yl-)-3-(α-L-rhamnopyranosyl)triazene (**3d**)

From *α-D*-rhamnopyranosylamine **1d** [29] (1.63 g, 10 mmol) in the manner described for **3a**. Crystallization at 23 °C from DMSO (50 ml) afforded a yellow powder (2.71 g, 65%); *m.p.* 155–158 °C (dec.). – $[\alpha]_D^{25} = -90$ (c = 0.1, pyridine). – IR (nujol): ν/cm^{-1} = 3100–3500 (br, NH, OH), 1670, 1634, 1589, 1573. – ^{1}H NMR (600 MHz, CD_3SOCD_3): δ/ppm = 1.25 (d, *J* = 5.1, CH_3), 3.30 (m, H-4',5'), 3.39 (br, m, H-3'), 3.90 (br, H-2'), 4.65 (d, *J* ≈ 5.0, OH-2'), 4.68 (d, *J* = 6.0, OH-3'), 4.81 (s, H-1'), 4.82 (d, *J* = 4.5, OH-4'), 7.72–7.91 (m, aryl), 13.00 (NH). – ^{13}C NMR (62.9 MHz, CD_3SOCD_3, 323 K): δ/ppm = 18.0 (CH_3), 71.4, 71.9, 73.8, 74.4 (C-2',3',4',5'), 94.8 (C-1').

$C_{20}H_{19}N_3O_6\cdot H_2O$	Calcd.: C 57.83	H 5.10	N 10.12
(415.4)	Found: C 57.36	H 4.97	N 9.95.

1-(Anthraquinone-1-yl-)-3-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)triazene (**4d**)

From **3d** (4.15 g, 10 mmol) in pyridine (200 ml)/Ac_2O (60 ml) in the manner described for **4a**. The product was dissolved in CH_2Cl_2 (100 ml). Filtration and evaporation of the filtrate afforded a yellow powder, which was crystallized at 5 °C from $CHCl_3$ (20 ml)/Et_2O (40 ml) to furnish a yellow powder (4.56 g, 87%); *m.p.* 195–197 °C (dec.). – $[\alpha]_D^{25} = +25.0$ (c = 0.1, $CHCl_3$). – IR (CH_2Cl_2): ν/cm^{-1} = 3228 (br, NH), 1749, 1673, 1645, 1591, 1576. – ^{1}H NMR (250 MHz, $CDCl_3$): δ/ppm = 1.41 (d, *J* = 6.1), 2.03, 2.11, 2.19 ($4CH_3$), 3.79 (m, H-5'), 5.08 (d, *J* = 1.2, H-1'), 5.17 (dd, *J* ≈ 2, 10, H-3'), 5.26 (t, *J* ≈10, H-4'), 5.73 (dd, *J* ≈ 1.2, 2.0, H-2'), 7.68–8.30 (m, aryl), 13.39 (NH). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ/ppm = 17.7, 20.7, 20.8, 20.9 ($4CH_3$), 69.5, 70.6, 71.7, 73.2 (C-2',3',4',5'), 93.1 (C-1'), 114.9, 120.2, 121.9, 127.0, 127.4, 132.9, 134.0, 134.1, 134.2, 134.3, 135.4, 143.9 (=C), 169.8, 170.2, 170.4, 182.7, 185.9 (C=O).

$C_{26}H_{25}N_3O_9$	Calcd.: C 59.65	H 4.81	N 8.03
(523.5)	Found: C 59.58	H 4.71	N 7.88.

1-(Anthraquinone-1-yl-)-3-(2-acetamido-2-deoxy-β-D-glucopyranosyl)triazene (**3e**)

From *β-D*-2-acetamido-2-deoxy-glucopyranosylamine **1e** [43, 44] (2.20 g, 10 mmol) in the manner described for **3b**. The product was suspended in CH_2Cl_2 (150 ml). Filtration and crystallization of the residue at –15 °C from pyridine (60 ml)/Et_2O (25 ml) afforded a brown powder (2.27 g, 49%); *m.p.* 207–209 °C (dec.). – $[\alpha]_D^{25} = +51.0$ (c = 0.05, pyridine). – IR (nujol) ν/cm^{-1} = 3530, 3367, 3275 (br, OH, NH), 1667, 1651, 1592, 1574, 1547. – ^{1}H NMR (600 MHz, CD_3SOCD_3): δ/ppm = 1.67 (CH_3), 3.25 (m, H-4',5'), 3.48 (td, *J* = 9.2, 5.8, H-3'), 3.54 (m, H-6'), 3.77 (m, *J* = 0.8, 5.8, 11.9, H-6''), 3.79 (q, *J* = 9.2, H-2'), 4.61 (d, *J* = 9.3, H-1'), 4.63 (t, *J* = 5.8, OH-6'), 5.05 (d, *J* = 5.6, OH-3'), 5.12 (d, *J* = 5.3, OH-4'), 7.78 (d, *J* = 9.3, NH-2), 7.88–8.23 (aryl), 13.01 (NH). – ^{13}C NMR (150.9 MHz, CD_3SOCD_3): δ/ppm = 22.8 (CH_3), 54.2 (C-2'), 61.0 (C-6'), 70.4 (C-4'), 74.1 (C-3'), 79.2 (C-5'), 95.9 (C-1'), 113.9, 119.2, 120.6, 126.4, 126.9, 132.3, 133.5, 133.8, 134.5, 134.6, 135.8, 143.7 (=C), 168.8, 182.0, 185.7 (C=O).

$C_{22}H_{22}N_4O_7\cdot 1/2H_2O$	Calcd.: C 57.02	H 5.00	N 12.09
(463.4)	Found: C 56.93	H 5.18	N 11.76.

1-(Anthraquinone-1-yl-)-3-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)triazene (**4e**)

From **3e** (4.63 g, 10 mmol) in 140 ml pyridine (140 ml) and Ac_2O (40 ml) in the manner described for **4b**. Crystallization at –15 °C from CH_2Cl_2 (80 ml)/30 ml Et_2O afforded an orange powder (4.83 g, 83%); *m.p.* 201–203 °C (dec.). – $[\alpha]_D^{25} = -86.0$ (c = 0.1, $CHCl_3$). – IR (CH_2Cl_2): ν/cm^{-1} = 3424, 3221 (br, NH), 1751, 1690, 1674, 1646, 1592, 1581. – ^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm = 1.86, 2.08 (6H), 2.10 (CH_3), 3.94 (ddd, *J* = 2.3, 4.7, 10.0, H-5'), 4.23 (dd, *J* = 2.3, 12.3, H-6'), 4.34 (dd, *J* = 4.7, 12.3, H-6''), 4.39 (dd, *J* = 9.2, 10.0, H-2'), 5.00 (d, *J* = 9.1, H-1'), 5.29 (t, *J* = 9.7, H-4'), 5.45 (t, *J* = 10.0, H-3'), 5.71 (d, *J* = 9.1, NH), 7.63–8.22 (aryl), 13.30 (NH). – ^{13}C NMR (150.9 MHz, $CDCl_3$): δ/ppm = 20.6, 20.7, 20.8, 23.3 ($4CH_3$), 53.5 (C-2'), 62.3 (C-6'), 68.4 (C-4'), 73.0 (C-3'), 74.1 (C-5'), 95.2 (C-1'), 114.9, 119.7, 121.7, 126.9, 127.4, 132.7, 133.9, 134.1, 134.2, 134.3, 135.1, 143.8 (=C), 169.4, 170.0, 170.8, 171.1, 182.5, 185.6 (C=O).

$C_{28}H_{28}N_4O_{10}$	Calcd.: C 57.93	H 4.86	N 9.65
(580.5)	Found: C 57.74	H 5.06	N 9.44.

1-(Anthraquinone-1-yl-)-3-(β-D-lactopyranosyl)triazene (**3f**)

From *β-D*-lactopyranosylamine **1f** [45, 46] (3.41 g, 10 mmol) in pyridine (80 ml)/MeOH (40 ml) in the manner described for **3b**. The product was suspended in CH_2Cl_2 (250 ml). Stirring for 15 min and filtration afforded an orange-red powder (4.09 g, 69%); *m.p.* 175–177 °C (dec.). – $[\alpha]_D^{25} = -31.0$ (c = 0.1, pyridine). – IR (nujol): ν/cm^{-1} = 3200–3500 (br, NH, OH), 1676, 1651, 1595, 1582. – ^{1}H NMR (600 MHz, CD_3SOCD_3): δ/ppm = 3.36 (m, 2H), 3.54 (m, 7H), 3.66 (m, 2H), 3.83 (dd, *J* = 5.5, 11.4, 1H), 4.28, d, *J* = 7.3, H-1''), 4.53 (d, *J* = 4.6, OH), 4.55 (d, *J* = 8.4, H-1'), 4.66 (t, *J* ≈ 6.1), 4.67 (t, *J* ≈ 4.6) (OH-6',6''), 4.79 (d, *J* = 5.2, OH), 4.83 (OH), 5.11 (d, *J* = 4.6, OH-2''), 5.32 (d, *J* = 5.5, OH-2'), 7.87–8.21 (aryl), 13.15 (NH). – ^{13}C NMR (150.9 MHz, CD_3SOCD_3): δ/ppm = 60.4 (2C), 68.2, 70.6, 72.0, 73.3, 75.2, 75.5, 77.1, 80.4 (C-2',3',4',5',6', 2'',3'',4'',5'',6''), 96.9, 103.8 (C-1',1''), 114.1, 119.6, 120.8, 126.5, 126.9, 132.3, 133.6, 133.8, 134.5, 134.7, 136.0, 143.7 (=C), 182.1, 185.8 (C=O).

$C_{26}H_{29}N_3O_{12}\cdot H_2O$	Calcd.: C 52.61	H 5.26	N 7.08
(593.5)	Found: C 52.62	H 5.47	N 6.79.

1-(Anthraquinone-1-yl-)-3-(2',3',6',2'',3'',4'',6''-hepta-O-acetyl-β-D-lactopyranosyl)triazene (**4f**)

From **3f** (5.94 g, 10 mmol) in 70 ml pyridine (70 ml) and Ac_2O (35 ml) in the manner described for **4b**. Crystallization at –15 °C from CH_2Cl_2 (240 ml)/Et_2O (24 ml) afforded a brown powder (6.96 g, 80%); *m.p.* 177–179 °C (dec.). –

$[\alpha]_D^{25} = -26.0$ (c = 0.1, $CHCl_3$). – IR (CH_2Cl_2): ν/cm^{-1} = 3228 (br, NH), 1753, 1674, 1646, 1592, 1581. – ^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm = 1.94, 1.98, 2.07, 2.08 (6H), 2.14, 2.17 (CH_3), 3.85 (ddd, *J* = 2.0, 4.9, 9.9, H-5'), 3.92 (t, *J* = 6.9, H-5''), 3.98 (t, *J* = 9.3, H-4'), 4.12 (dd, *J* = 7.4, 11.2, H-6''), 4.16 (dd, *J* = 6.2, 11.4, H-6''), 4.18 (dd, *J* = 5.1, 12.3, H-6'), 4.54 (dd, *J* = 1.8, 12.2, H-6'), 4.56 (d, *J* = 7.9, H-1''), 4.88 (d, *J* = 8.6, H-1'), 4.99 (dd, *J* = 3.5, 10.4, H-3''), 5.16 (dd, *J* = 7.8, 10.4, H-2''), 5.32 (t, *J* = 9.1, H-2'), 5.37 (m, H-3',4''), 7.73–8.28 (m, aryl), 13.41 (NH). – ^{13}C NMR (150.9 MHz, $CDCl_3$): δ/ppm = 20.5, 20.7 (4C), 20.8, 20.9 (CH_3), 60.7 (C-6''), 62.2 (C-6'), 66.6 (C-4''), 69.1 (C-2''), 70.6 (C-2'), 70.7 (C-5''), 71.0 (C-3''), 73.3 (C-3'), 74.8 (C-5'), 76.1 (C-4'), 94.5 (C-1'), 101.2 (C-1''), 115.0, 119.8, 121.9, 126.9, 127.3, 132.7, 133.9, 134.1, 134.2, 134.3, 135.3, 143.7 (=C), 169.1, 169.3, 169.9, 170.0, 170.1, 170.3, 170.4, 182.6, 185.8 (C=O).

$C_{40}H_{43}N_3O_{19}$	Calcd.: C 55.24	H 4.98	N 4.83
(869.8)	Found: C 55.07	H 4.97	N 4.46.

1-(Anthraquinone-1-yl-)-3-(β-D-cellobiosyl)triazene (**3g**)

From *β-D*-cellobiosylamine **1g** [46] (3.41 g, 10 mmol) in pyridine (100 ml)/MeOH (50 ml) in the manner described for **3b**. The product was suspended in CH_2Cl_2 (300 ml). After stirring for 5 min an orange-red powder was isolated by filtration. Crystallization at 5 °C from pyridine (30 ml) afforded a brown powder (3.26 g, 55%); *m.p.* 174–177 °C (dec.). – $[\alpha]_D^{25} = -52.0$ (c = 0.05, pyridine). – IR (nujol): ν/cm^{-1} = 3200–3600 (br, OH, NH), 1676, 1650, 1592, 1580. – ^{1}H NMR (600 MHz, CD_3SOCD_3): δ/ppm = 3.15 (m, 1H), 3.33 (m, 1H), 3.47 (m, 1H), 3.56 (m, 5H), 3.67 (m, 3H), 3.84 (m, 1H), 4.56 (d, *J* = 8.4, H-1''), 4.59 (t, *J* = 5.5), 4.67 (t, *J* = 5.6) (OH-6',6''), 4.98 (m, H-1', OH), 5.15 (d, *J* = 3.0, OH), 5.35 (d, *J* = 5.6, OH), 5.59 (d, *J* = 6.0, OH), 5.74 (br, OH), 7.74–8.10 (aryl), 13.04 (NH). – ^{13}C NMR (100.6 MHz, CD_3SOCD_3): δ/ppm = 60.3, 61.0, 70.0, 71.9, 73.2, 75.2, 76.4, 76.7, 77.0, 80.2 (C-2',3',4',5',6',2'',3'',4'',5'',6''), 96.9, 103.1 (C-1'',1'), 113.9, 119.5, 120.7, 126.4, 126.8, 132.2, 133.4, 133.6, 134.5, 134.6, 135.9, 143.6 (=C), 181.9, 185.6 (C=O).

$C_{26}H_{29}N_3O_{12}\cdot H_2O$	Calcd.: C 52.61	H 5.26	N 7.08
(593.5)	Found: C 52.86	H 5.32	N 6.76.

1-(Anthraquinone-1-yl-)-3-(2',3',6',2'',3'',4'',6''-hepta-O-acetyl-β-D-cellobiosyl)triazene (**4g**)

From **3g** (5.94 g, 10 mmol) in the manner described for **4b**. Cristallization at –15 °C from $CHCl_3$ (50 ml)/Et_2O (10 ml) afforded a yellow powder (7.48 g, 86%); *m.p.* 190–230 °C (dec.). – $[\alpha]_D^{25} = -36.0$ (c = 0.1, $CHCl_3$). – IR (CH_2Cl_2): ν/cm^{-1} = 3234 (br, NH), 1753, 1674, 1646, 1592, 1581. – ^{1}H NMR (600 MHz, $CDCl_3$): δ/ppm = 1.94, 2.00, 2.03, 2.06, 2.09, 2.11, 2.15 (7 CH_3), 3.71 (ddd, *J* = 2.6, 4.3, 10.0, H-5''), 3.84 (ddd, *J* = 2.0, 5.1, 10.0, H-5'), 3.97 (t, *J* = 9.3, H-4'), 4.09 (dd, *J* = 2.4, 12.4, H-6''), 4.20 (dd, *J* = 5.1, 12.2, H-6''), 4.41 (dd, *J* = 4.3, 12.4, H-6''), 4.57 (dd, *J* = 2.0, 12.2, H-6'), 4.59 (d, *J* = 7.9, H-1''), 4.88 (d, *J* = 8.1, H-1'), 4.98 (dd, *J* = 7.9, 9.3, H-2''), 5.11 (t, *J* = 9.7, H-4''), 5.18 (t, *J* = 9.5, H-3''), 5.33 (t, *J* ≈ 9, H-2'), 5.35 (t, *J* ≈ 9, H-3'), 7.72–8.25 (m, aryl), 13.36 (NH). – ^{13}C NMR (150.9 MHz, $CDCl_3$): δ/ppm = 20.48 (3C), 20.53 (2C), 20.6, 20.8 (7CH_3), 61.4 (C-6''), 62.0 (C-6'), 67.7 (C-4''), 70.4 (C-2'), 71.5 (C-2''), 71.9 (C-5''), 73.0 (C-3'), 74.8 (C-5'), 76.2 (C-4'), 94.5 (C-1'), 100.8 (C-1''), 114.9, 119.8, 121.9, 126.9, 127.3, 132.7, 133.8, 134.1, 134.2, 134.3, 135.3, 143.7 (=C), 169.1, 169.3 (2 C), 169.8, 170.1, 170.3, 170.4, 182.5, 185.8 (C=O).

$C_{40}H_{43}N_3O_{19}$	Calcd.: C 55.24	H 4.98	N 4.83
(869.8)	Found: C 55.54	H 5.19	N 4.46.

1-(Anthraquinone-1-yl-)-3-(β-D-maltosyl)triazene (**3h**)

From *β-D*-maltosylamine **1h** [45, 46] (3.41 g, 10 mmol) in pyridine (100 ml)/MeOH (50 ml)in the manner described for **3b**. Crystallization at –15 °C from pyridine (45 ml)/Et_2O (15 ml) afforded a brown powder (3.22 g, 56%); *m.p.* 145–200 °C. – $[\alpha]_D^{25} = +15.0$ (c = 0.1, pyridine). – IR (nujol): ν/cm^{-1} = 3200–3600 (br, OH, NH), 1670, 1639, 1589, 1585 (shoulder). – ^{1}H NMR (600 MHz, CD_3SOCD_3): δ/ppm = 3.12 (br, 1H), 3.30 (br, H-2''), 3.44 (br, 1H), 3.45–3.58 (m, 5H), 3.65 (m, 3H), 3.80 (m, 1H), 4.52 (d, *J* = 8.4, H-1'), 4.55 (t, *J* = 5.6), 4.63 (t, *J* = 5.7) (OH-6',6''), 4.94 (m, 2OH), 5.11 (d, *J* = 3.1, H-1''), 5.31 (d, *J* = 5.6, OH), 5.55 (d, *J* = 6.0, OH), 5.70 (d, *J* ≈ 2, OH), 7.71–8.06 (m, aryl), 13.00 (NH). – ^{13}C NMR (150.9 MHz, CD_3SOCD_3): δ/ppm = 60.7, 60.9 (C-6',6''), 69.9, 71.9, 72.6, 73.4, 73.6, 76.8, 77.4, 79.6 (C-2',3',4',5',2'',3'',4'', 5''), 97.2, 101.0 (C-1',1''), 113.8, 119.6, 120.8, 126.4, 126.9, 132.1, 133.4, 133.6, 134.3, 134.7, 135.9, 143.6 (=C), 181.9, 185.6 (C=O).

$C_{26}H_{29}N_3O_{12}$	Calcd.: C 54.26	H 5.08	N 7.30
(575.5)	Found: C 53.97	H 5.17	N 7.08.

Reaction of **4a** *with tert-butyl hypochlorite*

a) At –10 °C in the dark Bu^{t}OCl [47] (1.19 g, 11 mmol) was added dropwise to a suspension of **4a** (5.10 g, 10 mmol) in CH_2Cl_2 (100 ml). After stirring at 0 °C for 1 h the solvent was evaporated. Comparison with the ^{1}H NMR spectra of authentic compounds showed the residue (5.55 g) to be a mixture of **7** [35], and mainly the *β*-form **6a** [32] together with a small amount of the *α*-compound **6'a** [34]. – Unreported spectra of authentic compounds: **7**: IR (CH_2Cl_2): ν/cm^{-1} = 2141, 2107 (N_3), 1678 (C=O), 1588. – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ/ppm = 124.4, 126.3, 126.8, 127.5, 132.4, 133.8, 133.9, 134.3, 134.5, 135.8, 141.1 (aryl), 181.9, 182.6 (C=O). – **6a**: ^{13}C NMR (62.9 MHz, $CDCl_3$): δ/ppm = 20.7, 20.8, 20.9 (3 CH_3), 61.6, 66.9, 67.3, 70.1, 88.5 (C-1,2,3,4,5), 169.1, 169.3, 169.8 (3 C=O). – **6'a**: ^{13}C NMR (62.9 MHz, $CDCl_3$): δ/ppm = 20.58, 20.62, 20.66 (3 CH_3), 60.9, 68.3, 68.9, 71.0, 90.8 (C-1,2,3,4,5), 169.78, 169.82, 169.90 (3 C=O).

b) At –60 °C in the dark Bu^{t}OCl (2.16 g, 20 mmol) was added dropwise to a suspension of **4a** (5.10 g, 10 mmol) in MeOH (50 ml)/CH_2Cl_2 (50 ml). After stirring at 23 °C for 12 h the solvent was evaporated. The residue (5.18 g) proved to be a mixture of **7** and **8a** (α:β ≈ 5:2) [37, 38, 48]).

1,2,3,4-Tetra-O-acetyl-D-xylopyranose (**9**)

A solution of **4a** (5.01 g, 10 mmol) in AcOH (250 ml) was boiled under reflux for 1 h. The solvent was evaporated and the residue was separated by column chromatography (5 cm × 60 cm, silica gel, eluent $CHCl_3$) to afford **9** (3.00 g, 94%; α:β ≈ 1:1) [38–40, 50] and 1-aminoanthraquinone (**10**) (2.22 g, 99%).

Reaction of **4c** *with tert-butyl hypochlorite*

At –10 °C in the dark Bu^{t}OCl (1.19 g, 11 mmol) was added dropwise to a suspension of **4c** (7.01 g, 10 mmol) in CH_2Cl_2

(100 ml). After stirring at 0 °C for 1 h the solvent was evaporated. The residue (5.21 g) consisted of a mixture of **6b** [33, 34, 49], of **7**, and a carbohydrate of unknown structure. Two crystallizations at −15 °C from CH_2Cl_2 (40 ml)/pentane (80 ml) afforded yellow needles of pure **7** (2.01 g, 81%).

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