

Cycloaddition Reactions of 1,3-Diaza-2-azoniaallene Salts and Glycals

Min Weng, Armin Geyer, Anke Friemel, and Johannes C. Jochims*

Konstanz, Fakultät für Chemie der Universität

Martin Lutz

Utrecht/The Netherlands, Bijvoet Center for Biomolecular Research, Dep. Crystal & Structural Chemistry, University

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Abstract. The 1,3-diaza-2-azoniaallene salt **3a** reacts stereoselectively with glycals (**5a–e**) to afford pyrano[2,3-*d*]-1,2,3-triazolium salts **6a–e**. In contrast to other 1,3-dipolar cycloadditions of glycals reported so far, the stereoselectivity of compounds **6** is not determined by the substituent on C-3 of the glycal. Both *cis* (**6a,b**) and *trans* (**6d,e**) substitutions on C-7 and C-7a were found for bicyclic compounds **6** (crystal structure of **6a**). Under the influence of acid **6e** opens the

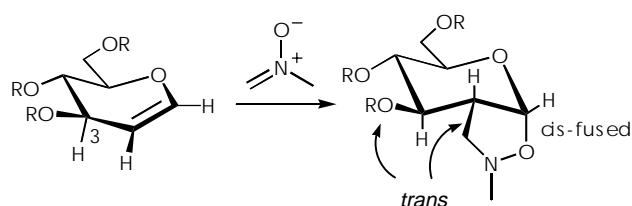
pyran ring to give the triazolium salt **9**. Addition of antimony pentachloride to a solution of the glycal **5e** and the chlorotriazene **2a** results in the formation of the pyranotriazene **12** containing two triazene units. In the presence of acid the pyranotriazene **6c** reacts with alcohols to afford 2-hydrazino glycosides **13a,b**, **15**, which with zinc dust in acetic acid are reduced to 2-amino glycosides **14a,b**.

Only a few reports deal with Diels–Alder or 1,3-dipolar cycloaddition reactions of glycals [1]. For instance, azodicarboxylates undergo Diels–Alder cycloaddition with glycals to afford oxadiazines [2–9]. The method allows the stereoselective introduction of a nitrogen atom on C-2 of a carbohydrate, and has been used to prepare complex 2-deoxy-2-amino saccharides under mild conditions in high yields. A synthesis of (–)-cryptosporin started with a two-step Diels–Alder cycloaddition of an isoquinolinium salt on L-fucal [10]. Effective Diels–Alder cycloadditions of α -oxothiones and glycals have been reported [11]. Cycloadditions of glycals with trichloroacetyl isocyanate afforded mixtures of β -lactams and Diels–Alder cycloadducts [12–14].

Little is known about 1,3-dipolar cycloaddition chemistry employing glycals. At $-78\text{ }^{\circ}\text{C}$ *N*-tosyl phenylaziridine in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ has been reported to react as 1,3-dipole with dihydropyran [15]. Under rather drastic conditions ($100\text{ }^{\circ}\text{C}$, long reaction times) certain cyclic nitrenes have been added to glycals in moderate yields [16, 17]. Better yields were obtained by intramolecular cycloaddition of nitrenes and also of nitrile oxides to the double bond of glycals [18]. Most noteworthy, a manganese nitrido complex upon activation with trifluoroacetic anhydride has been reported to serve as a reactive nitrogen transfer agent to glycals affording stereoselectively high yields of 2-deoxy-2-amino saccharides [19, 20]. Although the mechanism of this reaction does not seem to be clear, the isolation of an oxazoline intermediate is formally in line with a 1,3-dipolar cycloaddition reaction of an acyl nitrene ($\text{F}_3\text{CC}=\text{O})\text{N}$ to the electron-rich glycal double bond.

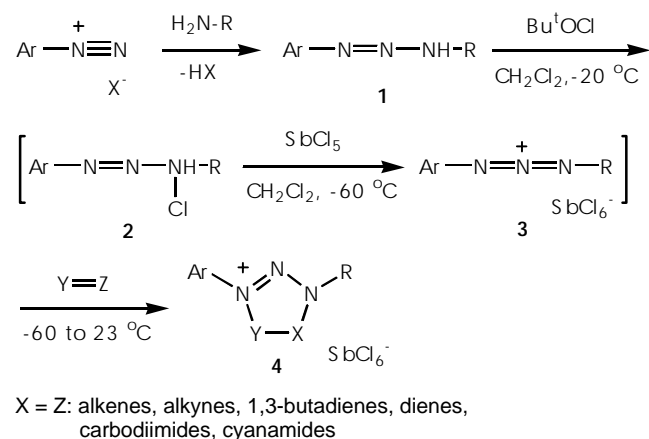
Acyl nitrenes produced photochemically from acyl azides have been reported to undergo 1,3-dipolar cycloaddition to the double bond of dihydropyran [21].

All cycloadditions reported so far proceeded with complete regio- and more than 90% stereoselectivity, the latter being determined by the pseudoequatorial substituent on C-3 of the glycal. Uniformly, 1,3-dienes or 1,3-dipoles added *trans* to this substituent to give *cis*-fused bicyclic ring systems (Scheme 1).



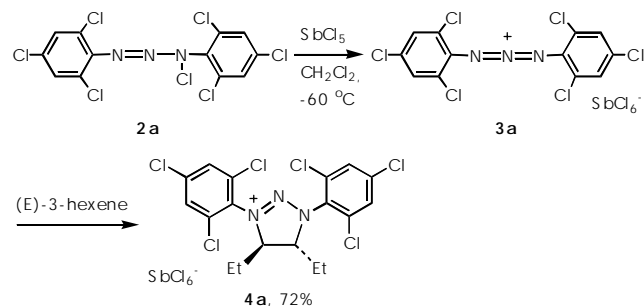
Scheme 1 1,3-Dipolar cycloaddition *trans* to the substituent on C-3 of glycals

Recently, we described the preparation of 1,3-diaza-2-azoniaallene salts **3** [22–26]. Chlorination of triazenes **1** with *tert*-butyl hypochlorite furnished *N*-chlorotriazenes **2**, which with Lewis acids such as antimony pentachloride were transformed to cationic heterocumulenes **3**. The electron-deficient reactive intermediates **3** underwent 1,3-dipolar cycloaddition to the electron-rich multiple bonds of alkenes, alkynes, of 1,3-butadienes, allenes, carbodiimides and cyanamides (Scheme 2).



Scheme 2 Preparation and cycloadditions of 1,3-diaza-2-azoniaallene salts **3**

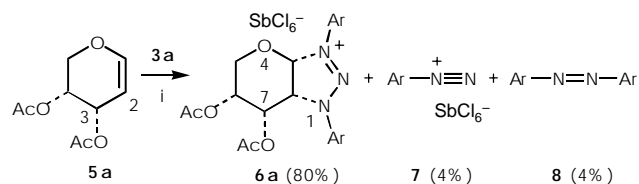
Cycloaddition of the 1,3-diaza-2-azoniaallene ion **3a** to (*E*)-3-hexene affording the 4,5-dihydro-1,2,3-triazolium salt **4a** proceeded with complete retention of the configuration of the alkene (Scheme 3). No products of a Wagner–Meerwein rearrangement were observed in cycloaddition reactions of cations **3** to the double bond of norbornene. These results and semiempirical AM1 calculations are in keeping with a concerted mechanism (1,3-dipolar cycloaddition with inverse electron demand) for cycloadditions of **3** to alkenes.



Scheme 3 Stereoselective cycloaddition of the 1,3-diaza-2-azoniaallene salt **3a** to (*E*)-3-hexene

Glycals **5** are electron-rich cyclic vinyl ethers appropriate for cycloaddition reactions with electron-deficient 1,3-dipoles. In this communication we report cycloaddition reactions of the 1,3-diaza-2-azoniaallene **3a** with glycals **5a–e**.

Between -60°C and -15°C the acetylated D-arabinal **5a** [26] reacted with heterocumulene **3a** to afford the cycloadduct **6a** in 80% yield. The reaction proceeded with complete regio- and stereoselectivity. The only side products observed were small amounts of the diazonium salt **7** and of the azo compound **8** [22] (Scheme 4).



Scheme 4 Reagents and conditions: Ar: 2,4,6-Cl₃C₆H₂; i, CH₂Cl₂, -60°C to -15°C , 26 h.

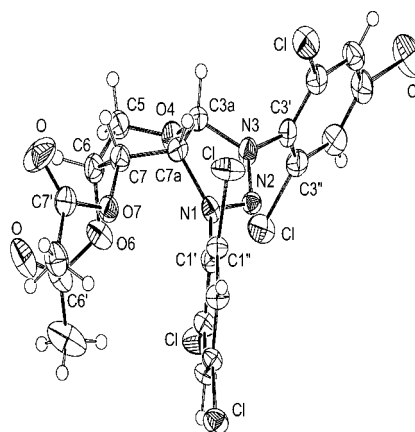


Fig. 1 Displacement ellipsoid plot (PLATON [28]) of the cation of **6a**, drawn at the 50% probability level

Compound **6a** was isolated in form of crystals suitable for X-ray structural analysis. A molecular plot of the cation **6a** is shown in Figure 1, and selected molecular data are collected in Table 1 [29]. Not unexpectedly, the rings of **6a** were found to be *cis*-fused.

However, it came as a surprise to find a *cis* relationship between the acetoxy group on C-7 and the triazolium ring. This is in sharp contrast to all reports on cycloadditions to glycals where always products with *trans* substituents at C-2 and C-3 of the glycal have been isolated [1–20]. The reason for the unusual stereochemistry of **6a** is probably a consequence of the allene-like geometry [22] of the cation **3a**.

In the crystal **6a** shows a pyranose ring with a distorted ¹C₄ conformation with axial *O*-acetyl group on C-6. The triazolium ring deviates slightly from planarity [N3–C3a–C7a–N1: $-20.9(4)^\circ$]. In Table 2 the ³J_{H,H} coupling constants observed for **6a** in solution (CDCl₃) are given. According to the Karplus equation [30] a ³J coupling constant of 9.1 Hz corresponds to a torsional angle of about 180° or 0° . A coupling of 9.1 Hz of the anomeric proton and the vicinal proton on C-2 of a pyranose is usually taken as evidence for an antiperiplanar arrangement of these protons. However, for **6a** only a torsional angle $\alpha_{\text{H-3a,H-7a}} \approx 0^\circ$ is in agreement with the

Tab. 1 Selected bond lengths (pm), bond angles (deg), and torsional angles (deg) of the cation **6a** [29]

N1–N2	129.4(4)	C3a–O4–C5	112.6(4)	C3a–O4–C5–C6	–67.0(5)
N2–N3	129.4(4)	O4–C5–C6	110.2(3)	O4–C5–C6–C7	56.9(6)
N3–C3a	148.5(5)	C5–C6–C7	109.5(4)	C5–C6–C7–C7a	–40.1(5)
C3a–C7a	153.4(6)	C6–C7–C7a	116.3(4)	C6–C7–C7a–C3a	29.6(5)
C3a–O4	137.1(6)	C7–C7a–C3a	113.6(4)	C6–C7–C7a–N1	–86.9(5)
O4–C5	143.2(5)	C7a–C3a–O4	115.3(4)	C7–C7a–C3a–O4	–36.3(5)
C5–C6	152.0(6)	C7–C7a–N1	118.1(3)	C7a–C3a–O4–C5	55.7(5)
C6–C7	152.7(7)	C3'–N3–C3a	124.1(3)	C7–C7a–N1–N2	145.3(4)
C7–C7a	151.8(6)	N2–N1–C1'	116.9(3)	C7–C7a–C3a–N3	–147.7(4)
C7a–N1	151.9(5)	N1–N2–N3–C3a	–4.7(5)	C7–C7a–N1–C1'	–55.1(6)
N1–N2–N3	108.9(3)	N2–N3–C3a–C7a	17.7(5)	C7a–N1–C1'–C1''	–56.5(6)
N2–N3–C3a	114.6(3)	N3–C3a–C7a–N1	–20.9(4)	N1–C7a–C3a–O4	90.4(4)
N3–C3a–C7a	99.3(3)	C3a–C7a–N1–N2	21.6(4)	N1–N2–N3–C3'	–179.8(4)
C3a–C7a–N1	99.9(3)	C7a–N1–N2–N3	–11.5(5)	N2–N3–C3'–C3''	75.5(6)
C7a–N1–N2	111.9(3)	N2–N3–C3a–O4	–101.7(4)	C6–C7–O7–C7'	–88.1(5)
N3–C3a–O4	104.8(4)	N3–C3a–O4–C5	163.8(3)	C5–C6–O6–C6'	–142.5(4)

results of the crystal structural analysis. The coupling constants of 7.6 and 3.2 Hz correspond to $\alpha_{\text{H-7a,H-7}} \approx -20^\circ$ and $\alpha_{\text{H-7,H-6}} \approx 70^\circ$.

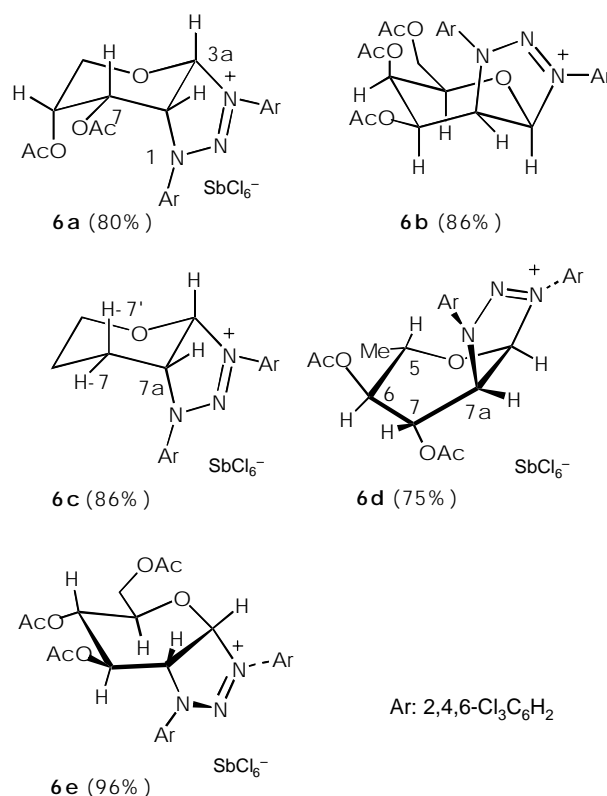
Under the conditions described for the preparation of **6a**, 3,4,6-tri-*O*-acetyl-*D*-galactal [27] **5b** reacted with **3a** to furnish the triazolium salt **6b** in 86% yield (Scheme 5). The rather similar sets of $^3J_{\text{HH}}$ coupling constants (Tab. 2) for **6b** and **6a** suggest similar spatial arrangements of the functional groups in these compounds, that is compound **6b** should have a pyranose ring with distorted 4C_1 conformation and *cis* substituents on C-7 and C-7a.

Tab. 2 $^3J_{\text{HH}}$ coupling constants used for configurational assignments for **6a–e** (600 MHz)

$^3J_{\text{HH}}$	6a	6b(d)	6c(e)	6d(c)	6e(b)
3a-7a	9.1	10.6	8.9	11.2	10.8
7a-7, 7a-7'	7.6	7.6	3.4, 6.1	2.1	2.6
7-6	3.2	3.5		5.0	5.0
6-5, 6-5'	4.1, 2.6	≈ 1		10.3	9.1

From 3,4-dihydro-2*H*-pyran **5c** the bicyclic salt **6c** was obtained (86%). Provided that the two rings in **6c** are *cis*-fused, the $^3J_{\text{HH}}$ couplings between H-7a and H-7, respectively H-7', can be regarded as characteristic for a *trans* and a *cis* synclinal arrangement of these protons, the *trans* coupling H-7a,H-7 (3.4 Hz) being smaller than the *cis* coupling (6.1 Hz).

Compound **6d** (75%) was prepared from 3,4-Di-*O*-acetyl-*L*-rhamnal [27]. The large $^3J_{\text{HH}}$ coupling of H-5 and H-6 indicates antiperiplanar alignment of these protons (Tab. 2). A 1C_4 conformation of the pyranose ring with *cis* substituents on C-7a and C-7 would require large couplings of H-7a with H-7 as well as of H-7 with H-6. Actually, the couplings were found to be rather small (2.1 and 5.0 Hz, Tab.2). The set of coupling constants observed for **6d** only fits to *trans* substitution on

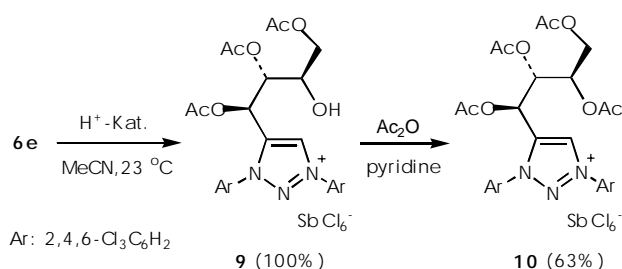
**Scheme 5** Cycloadducts prepared from the reaction of **3a** with glycals

C-7a and C-7 and a pyranose ring in a twist conformation. This was corroborated by a nuclear Overhauser effect (ROESY) between H-5 and H-7 but not between H-5 and either H-7a or H-3a.

Compound **6e** was obtained almost quantitatively from 3,4,6-tri-*O*-acetyl-*D*-glucal **5e**. The coupling constants and NOE's observed for **6d** and **6e** are very similar (Tab.2) proving *trans* configuration of H-7 and H-7a also for **6e**.

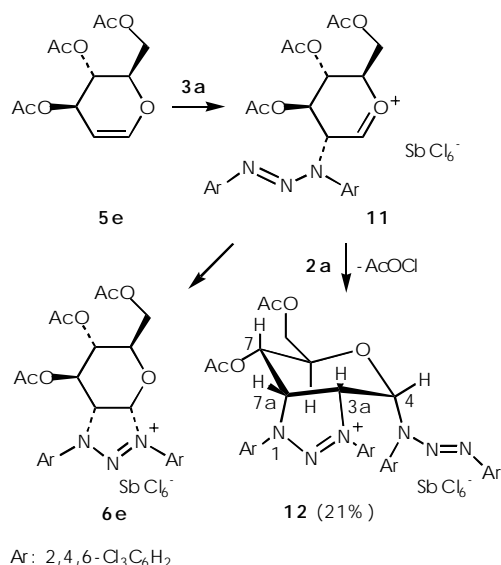
In conclusion, the substituent on C-3 of the glycal has little or no influence on the diastereofacial selectivity of the cycloaddition of **3a** to the double bond of the glycal.

At 23 °C in acetonitrile after addition of a drop of trifluoroacetic acid the pyranose ring of **6e** opened to give the triazolium salt **9** (100%), which was acetylated to **10**. The structural assignments are based on the NMR spectra and on comparison with the spectra of similar triazolium salts [22–26].



Scheme 6 Acid catalyzed ring opening of the triazolium salt **6e**

While dropwise addition of a solution of 3,4,6-tri-*O*-acetyl-*D*-glucal **5e** to a solution of **3a** afforded the bicyclic compound **6e** almost quantitatively, slow addition at –60 °C of a solution of antimony pentachloride to a solution of **5e** and the chlorotriazene **2a** resulted in the formation of a mixture of compounds containing **6e**, the diazonium salt **7**, and a compound **12** (21%) embodying two triazene units. The $^3J_{\text{H,H}}$ coupling constants ($J_{4,3a} \approx 1$ Hz; $J_{3a,7a} \approx 12.7$ Hz; $J_{7a,7} \approx 6.3$ Hz; $J_{7,6} \approx 9.6$ Hz) are consistent with the structural proposal shown

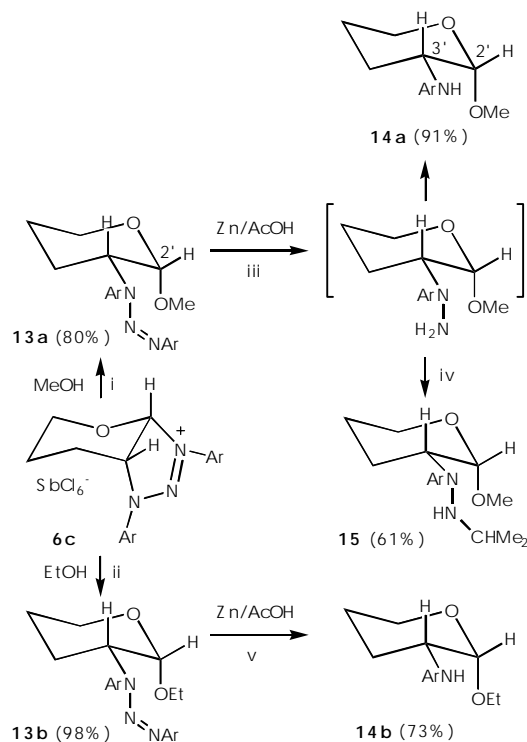


Scheme 7 Interception of an intermediate **11** of the cycloaddition of **3a** to **5e**

in Scheme 7. The formation of **12** points to a two-step mechanism of the cycloaddition of cation **3a** to the glycal double bond [10]. An intermediate **11** formed in the first step could either close the ring to afford **6e** or react in the presence of an excess of the chlorotriazene **2a** to give compound **12**.

Preliminary reactivity studies of the bicyclic triazoles **6** have been carried out with the pyran **6c**. With alcohols under the catalytic influence of *p*-toluenesulfonic acid the triazolium salt **6c** afforded 2-triazenoglycosides **13a,b** in good yields. With zinc dust in acetic acid the triazenes **13** were reduced to 2-aminoglycosides **14a,b**. In the presence of acetone reduction of **13a** afforded the hydrazine **15** (61%) together with some **14a** (18%). A rationale for the formation of these compounds is given in Scheme 8. The assignments of the anomeric configurations of compounds **13–15** must be regarded as provisional. For **13a** couplings $^3J_{2,3'}$ of 6.2 Hz and $^3J_{3,4'}$ of 4.3 and 10.1 Hz were observed, which are in accordance with a *trans* configuration [21]. The smaller couplings $^3J_{2,3'} = 2.4$, $^3J_{3,4'}$ of 2.4 and 4.0 Hz for **14a** may be interpreted as consistent with antiperiplanar substituents on C-2' and C-3' [31,32].

These results show that cycloadditions of 1,3-diaza-2-azoniaallene salts to glycals should find application for stereoselective syntheses of 2-deoxy-2-amino glycosides [33].



Scheme 8 Glycoside formation from the triazolium salt **6c**. Reagents and conditions: Ar: 2,4,6-Cl₃C₆H₂; i, TsOH·H₂O, MeOH, 20 min reflux; ii, TsOH·H₂O, EtOH/CH₂Cl₂, 20 min reflux; iii, 23 °C, 14 h; iv, acetone, 23 °C, 18 h.

The National Single Crystal Service Facility in Utrecht, The Netherlands, is acknowledged for providing the X-ray facilities. The work was supported by the Deutsche Forschungsgemeinschaft. We are grateful to Mr. S. Herzberger for technical assistance.

Experimental

The solvents were dried by standard methods. All experiments were carried out with exclusion of moisture. 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.

X-Ray structural analysis of compound **6a** [29]

$[\text{C}_{21}\text{H}_{16}\text{Cl}_6\text{N}_3\text{O}_5\text{Sb}]^+[\text{SbCl}_6]^-$, $M = 937.5$, crystal size $0.31 \times 0.25 \times 0.06$ mm, orthorhombic, space group $P2_12_12_1$ (No. 19), $Z = 4$, $a = 977.41(1)$, $b = 1855.38(2)$, $c = 1859.73(2)$ pm, $V = 3372.56(6) \times 10^6$ pm³, $d_{\text{calc}} = 1846.4$ kg m⁻³, $T = 150(2)$ K, $F(000) = 1832$. Lattice parameters and intensities were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator ($\lambda_{\text{Mo-K}\alpha} = 71.073$ pm); resolution up to $(\sin \theta/\lambda)_{\text{max}} = 65$ pm⁻¹. Absorption corrections are based on multiply measured symmetry related reflections (program PLATON [28], routine MULABS, $\mu = 18.06$ cm⁻¹, 0.65 – 0.90 transmission); 63444 reflections; 7758 independent reflections ($R_{\text{int}} = 0.0808$). The structure was solved by the Patterson method (program DIRDIF) [34] and refined using the program SHELXL97 [35] against F^2 of all reflections. Non-hydrogen atoms were refined anisotropically, hydrogen atoms according to the riding model. Core refinement of the Flack- x -Parameter [36] leading to $x = 0.018(18)$ permitted assignment of the absolute configuration. The refinement of 382 parameters (no restraints) led to agreement factors $R_1 = 0.0342$, $wR_2 = 0.0828$ ($I > 2\sigma(I)$) resp. $R_1 = 0.0352$, $wR_2 = 0.0833$ (all data); $S = 1.138$. In the final difference-Fourier map there were no residual peaks outside the range of $+1.080$ to $-0.594 \cdot 10^{-6}$ e \cdot pm⁻³.

(3*aS*,6*R*,7*S*,7*aR*)-6,7-Diacetoxy-3,3*a*,5,6,7,7*a*-hexahydro-1,3-bis(2,4,6-trichlorophenyl)pyrano[2,3-*d*]-1,2,3-triazolium Hexachloroantimonate (**6a**)

A solution of SbCl_5 (2.99 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a cold (-60 °C) solution of **2a** [22] (4.38 g, 10 mmol) in CH_2Cl_2 (100 ml). Subsequently, a solution of 3,4-di-*O*-acetyl-*D*-arabinal **5a** [27] (2.00 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise. In the course of the next 2 h the mixture was warmed to -40 °C. After stirring at -40 °C for 4 h and then at -15 °C for 12 h the solvent was evaporated and the pale brown residue was suspended in CH_2Cl_2 (80 ml). Filtration from a small amount of **7** [22] and evaporation of the filtrate, suspension of the residue in MeCN (40 ml), filtration from a small amount of **8** [22] and evaporation of the solvent afforded a pale brown powder, which was suspended in Et_2O (100 ml). Stirring for 10 min and filtration furnished a pale brown powder (7.50 g, 80%). Colorless prisms suitable for X-ray structural analysis were obtained by slow crystallization at 23 °C from CHCl_3 (30 ml)/ Et_2O (10 ml);

m.p. dec. above 121 °C. – $[\alpha]_{\text{D}}^{25} = -54.5$ ($c = 1.0$, CHCl_3). – IR: $\nu/\text{cm}^{-1} = 1763, 1569, 1559$. – ^1H NMR (600 MHz, CD_3CN): $\delta/\text{ppm} = 1.94, 2.13$ (CH_3), 4.08 (dd, $J = 2.6, 13.2$), 4.46 (dd, $J = 4.1, 13.2$) (H-5,5'), 5.45 (m, H-6), 5.52 (dd, $J = 3.2, 7.9$, H-7), 5.83 (dd, $J = 7.6, 9.1$, H-7*a*), 6.92 (d, $J = 9.1$, H-3*a*), 7.84–7.87 (aryl). – ^{13}C NMR (150.9 MHz, CDCl_3): $\delta/\text{ppm} = 20.0, 21.0$ (CH_3), 64.1, 65.1 (C-6,7), 67.2 (C-7*a*), 67.4 (C-5), 92.2 (C-3*a*) 126.7, 127.9, 129.9, 130.0, 130.2, 133.7, 134.5, 134.6, 140.9, 141.1 (aryl), 168.8, 169.9 (C=O).

$\text{C}_{21}\text{H}_{16}\text{Cl}_{12}\text{N}_3\text{O}_5\text{Sb}$ Calcd.: C 26.90 H 1.72 N 4.48 (937.6) Found: C 26.82 H 1.82 N 4.24.

(3*aR*,5*R*,6*S*,7*R*,7*aS*)-6,7-Diacetoxy-5-acetoxymethyl-3,3*a*,5,6,7,7*a*-hexahydro-1,3-bis(2,4,6-trichlorophenyl)pyrano[2,3-*d*]-1,2,3-triazolium Hexachloroantimonate (**6b**)

From 3,4,6-*tri-O*-acetyl-*D*-galactal (**5b**) [27] (2.72 g, 10 mmol) in CH_2Cl_2 (5 ml) in the manner described for **6a**. After stirring at -40 °C for 4 h and at -15 °C for further 12 h the solvent was evaporated and the pale brown residue was suspended in CH_2Cl_2 (40 ml). Filtration and evaporation of the filtrate, suspension of the residue in MeCN (40 ml), filtration and evaporation of the filtrate afforded a pale brown powder, which was precipitated from CH_2Cl_2 (15 ml)/ Et_2O (120 ml) to give a pale brown powder (8.68 g, 86%); *dec.* above 115 °C. – $[\alpha]_{\text{D}}^{25} = +69.4$ ($c = 1.0$, CHCl_3). – IR: $\nu/\text{cm}^{-1} = 1765, 1569, 1559$. – ^1H NMR (600 MHz, CDCl_3): $\delta/\text{ppm} = 1.87, 2.02, 2.34$ (CH_3), 4.12 (dd, $J = 5.9, 12.0$), 4.24 (dd, $J = 6.8, 12.0$) (CH_2), 4.61 (br, t, $J = 6.5$, H-5), 5.46 (dd, $J = 3.5, 7.6$, H-7), 5.57 (br, dd, $J \approx 3, 1.5$, H-6), 5.92 (dd, $J = 7.6, 10.6$, H-7*a*), 7.34 (d, $J = 10.6$, H-3*a*), 7.69 (m, 2H), 7.70 (m, 2H) (aryl). – ^{13}C -NMR (62.9 MHz, CDCl_3): $\delta/\text{ppm} = 20.0, 20.6, 20.9$ (CH_3), 60.7, 62.9, 65.9, 66.6, 73.9 (CH_2 , C-5,6,7,7*a*), 93.2 (C-3*a*), 126.7, 128.2, 130.0, 130.1, 130.4, 133.6, 134.7, 134.9, 141.2, 141.3 (aryl), 168.7, 170.0, 170.3 (C=O).

$\text{C}_{24}\text{Cl}_{12}\text{H}_{20}\text{N}_3\text{O}_7\text{Sb}$ Calcd.: C 28.55 H 2.00 N 4.16 (1009.6) Found: C 28.91 H 2.35 N 4.43.

rac-(3*aS*,7*aR*)-3,3*a*,5,6,7,7*a*-Hexahydro-1,3-bis(2,4,6-trichlorophenyl)pyrano[2,3-*d*]-1,2,3-triazolium Hexachloroantimonate (**6c**)

From 3,4-dihydro-2*H*-pyran **5c** (0.84 g, 10 mmol) in CH_2Cl_2 (20 ml) in the manner described for **6a**. However, the reaction mixture was stirred at -40 °C for 4 h. After warming up to -10 °C in the course of the next 2 h and evaporation of the solvent the residue was precipitated from CH_2Cl_2 (40 ml)/ Et_2O (240 ml) to furnish **6c** as a colorless powder (7.06 g, 86%); *m.p.* 137 – 138 °C. – IR: $\nu/\text{cm}^{-1} = 1571, 1552$. – ^1H NMR (250 MHz, CD_3CN): $\delta/\text{ppm} = 1.91$ (m, H-6,6'), 2.24 (m, H-7,7'), 3.87 (ddd, $J = 4.9, 7.0, 11.9$), 4.03 (ddd, $J = 5.2, 6.4, 11.9$) (H-5,5'), 5.48 (ddd, $J = 3.4, 6.1, 8.9$, H-7*a*), 6.71 (d, $J = 8.9$, H-3*a*), 7.82 (2H), 7.86 (br, 2H) (aryl). – ^{13}C NMR (62.9 MHz, CD_3CN): $\delta/\text{ppm} = 18.2, 19.5$ (C-6,7), 64.4, 66.4 (C-5,7*a*), 92.7 (C-3*a*), 128.6, 129.1, 131.2, 131.5, 135.2, 135.3, 140.5, 141.0 (aryl).

$\text{C}_{17}\text{H}_{12}\text{Cl}_{12}\text{N}_3\text{OSb}$ Calcd.: C 24.86 H 1.47 N 5.12 (821.5) Found: C 25.17 H 1.54 N 4.91.

(3*aR*,5*S*,6*S*,7*S*,7*aS*)-6,7-Diacetoxy-3,3*a*,5,6,7,7*a*-hexahydro-5-methyl-1,3-bis(2,4,6-trichlorophenyl)pyrano[2,3-*d*]-1,2,3-triazolium Hexachloroantimonate (**6d**)

From 3,4-di-*O*-acetyl-*L*-rhamnal **5d** [27] (2.72 g, 10 mmol)

in CH_2Cl_2 (10 ml) in the manner described for **6a**. After stirring at -15°C for 12 h and evaporation of the solvent the residue was suspended in CH_2Cl_2 (40 ml). Filtration from **7**, evaporation of the solvent and precipitation of the residue from CH_2Cl_2 (20 ml)/ Et_2O (60 ml) afforded **6d** as a pale brown powder (7.13 g, 75%); *m.p.* $114\text{--}120^\circ\text{C}$ (dec.). – $[\alpha]_{\text{D}}^{25} = +45.6$ ($c = 1.0$, CHCl_3). – IR: $\nu/\text{cm}^{-1} = 1761, 1570, 1559$. – ^1H NMR (600 MHz, CD_3CN): $\delta/\text{ppm} = 1.32$ (d, $J = 5.9$), 2.03, 2.05 (CH_3), 4.25 (m, $J = 5.9, 10.3$, H-5), 5.00 (dd, $J = 5.0, 10.3$, H-6), 5.14 (dd, $J = 2.1, 5.0$, H-7), 5.89 (dd, $J = 2.1, 11.2$, H-7a), 6.94 (d, $J = 11.2$, H-3a), 7.87 (2H), 7.89 (m, 2H) (aryl). – ^{13}C NMR (62.9 MHz, CD_3CN): $\delta/\text{ppm} = 17.7, 20.8, 21.0$ (CH_3), 67.4, 69.0, 71.5, 71.6 (C-5,6,7,7a), 92.8 (C-3a), 128.2, 128.5, 131.2, 131.3, 135.2, 135.3, 135.6, 141.0, 141.4 (aryl), 170.3, 170.8 (C=O).

$\text{C}_{22}\text{H}_{18}\text{Cl}_{12}\text{N}_3\text{O}_5\text{Sb}$ Calcd.: C 27.77 H 1.91 N 4.42 (951.6) Found: C 27.80 H 1.87 N 4.22.

(3a*S*,5*R*,6*R*,7*R*,7a*R*)-6,7-Diacetoxy-5-acetoxymethyl-3,3a,5,6,7,8-hexahydro-1,3-bis(2,4,6-trichlorophenyl)pyrano[2,3-*d*]-1,2,3-triazolium Hexachloroantimonate (**6e**)

From 3,4,6-*tri-O*-acetyl-*D*-glucal **5e** (2.72 g, 10 mmol) in CH_2Cl_2 (5 ml) in the manner described for **6c**. Evaporation of the solvent gave a pale brown residue, which was suspended in CH_2Cl_2 (40 ml). Filtration from **7** (0.11 g, 4%), evaporation of the solvent, suspension of the residue in MeCN (20 ml), filtration from **8** (0.16 g, 4%), and evaporation of the solvent afforded a pale brown powder, which was precipitated from CH_2Cl_2 (40 ml)/ Et_2O (40 ml) to give a pale brown powder (9.69 g, 96%); *m.p.* $120\text{--}130^\circ\text{C}$ (dec.). – $[\alpha]_{\text{D}}^{25} = -34.4$ ($c = 1.0$, CHCl_3). – IR: $\nu/\text{cm}^{-1} = 1770, 1751, 1570, 1556$. – ^1H NMR (600 MHz, CD_3CN): $\delta/\text{ppm} = 1.97, 2.01, 2.05$ (CH_3), 4.18 (dd, $J = 4.4, 14.4$, 1H, CH_2), 4.38 (m, 2H, H-5, CH_2), 5.24 (dd, $J = 5.0, 9.1$, H-6), 5.25 (dd, $J = 2.6, 5.0$, H-7), 5.94 (dd, $J = 10.8, 2.6$, H-7a), 7.02 (d, $J = 10.8$, H-3a), 7.88 (2H), 7.87–7.90 (m, 2H) (aryl). – ^{13}C -NMR (62.9 MHz, CD_3CN): $\delta/\text{ppm} = 20.7, 20.8, 20.9$ (CH_3), 61.9, 66.8, 67.6, 68.7, 73.0 (CH_2 , C-5,6,7,7a), 92.3 (C-3a), 128.1, 128.4, 131.3, 131.5, 135.2, 135.4, 141.1, 141.5 (aryl), 170.1, 170.5, 171.0 (C=O).

$\text{C}_{24}\text{H}_{20}\text{Cl}_{12}\text{N}_3\text{O}_7\text{Sb}$ Calcd.: C 28.55 H 2.00 N 4.16 (1009.6) Found: C 28.65 H 2.11 N 4.46.

4-[(1*R*,2*R*,3*R*)-1,2,4-Triacetoxy-3-hydroxybutyl]-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**9**)

CF_3COOH (5 drops) was added to a stirred solution of **6e** (10.09 g, 10 mmol) in MeCN (50 ml). After stirring for 15 min the solvent was removed under reduced pressure affording **9** as a pale brown powder (10.09 g, 100%); dec. above 82°C . – $[\alpha]_{\text{D}}^{25} = -30.5$ ($c = 1.0$, CHCl_3). – IR: $\nu/\text{cm}^{-1} = 3585$ (OH), 1759, 1570. – ^1H NMR (250 MHz, CD_3CN): $\delta/\text{ppm} = 2.01, 2.08, 2.09$ (CH_3), 3.74 (br, OH), 3.96 (m, H-3'), 4.06 (m, H-4',4''), 5.29 (dd, $J = 8.6, 3.3$, H-2'), 6.31 (d, $J = 3.3$, H-1'), 7.90 (2H), 7.96 (2H) (aryl), 9.14 (H-5). – ^{13}C NMR (62.9 MHz, CD_3CN): $\delta/\text{ppm} = 20.5, 21.2$ (2C) (CH_3), 64.1, 65.2, 68.4, 71.6 (C-1',2',3',4'), 128.0, 128.3, 129.8, 131.0, 131.4, 131.5, 134.4, 134.8, 135.2, 135.5, 141.6, 142.2, 145.7 (aryl, C-4,5), 169.8, 170.6, 171.5 (C=O).

4-[(1*R*,2*R*,3*R*)-1,2,3,4-Tetraacetoxybutyl]-1,3-bis(2,4,6-trichlorophenyl)-1,2,3-triazolium Hexachloroantimonate (**10**)

At 23°C AcCl (20 ml) and pyridine (5 ml) were added dropwise to a solution of **9** (10.09 g, 10 mmol) in CH_2Cl_2 (150 ml). After stirring for 30 min the solvent was removed. The residue was suspended in CH_2Cl_2 (100 ml)/ Et_2O (50 ml). After filtration and evaporation of the filtrate the residue was dissolved in CH_2Cl_2 (150 ml). Addition of decolorizing charcoal (0.20 g) and silica gel (5.00 g), filtration and evaporation of the solvent afforded a pale brown powder (6.62 g, 63%); *m.p.* $96\text{--}98^\circ\text{C}$. – $[\alpha]_{\text{D}}^{25} = -19.7$ ($c = 1.0$, CHCl_3). – IR: $\nu/\text{cm}^{-1} = 1757, 1567$. – ^1H NMR (250 MHz, CD_3CN): $\delta/\text{ppm} = 1.94, 2.00, 2.04, 2.14$ (CH_3), 4.12 (dd, $J = 4.4, 12.7$), 4.28 (dd, $J = 3.1, 12.7$) (H-4',4''), 5.10 (m, H-3'), 5.59 (dd, $J = 2.2, 7.9$, H-2'), 6.31 (d, $J = 2.0, \text{H-1'}$), 7.90 (2H), 7.98 (2H) (aryl), 9.16 (d, $J = 0.4$, H-5). – ^{13}C NMR (62.9 MHz, CD_3CN): $\delta/\text{ppm} = 20.4, 20.8, 20.9$ (2 C) (CH_3), 61.8, 63.6, 69.2, 70.1 (C-1',2',3',4'), 127.9, 129.6, 130.9, 131.3, 131.5, 134.3, 134.5, 135.0, 135.1, 141.7, 142.4, 144.6 (aryl, C-4,5), 169.7, 170.3, 170.4, 171.1 (C=O).

$\text{C}_{26}\text{H}_{22}\text{Cl}_{12}\text{N}_3\text{O}_8\text{Sb}$ Calcd.: C 29.69 H 2.11 N 4.00 (1051.7) Found: C 30.11 H 2.18 N 4.15.

(3*aR*,4*S*,6*R*,7*S*,7a*S*)-7-Acetoxy-6-acetoxymethyl-3*a*,4,6,7,7a,1-hexahydro-1,3-bis(2,4,6-trichlorophenyl)-4-[1,3-bis(2,4,6-trichlorophenyl)triazeno]pyrano[3,4-*d*]-1,2,3-triazolium Hexachloroantimonate (**12**)

A solution of SbCl_5 (2.99 g, 10 mmol) in CH_2Cl_2 (20 ml) was added dropwise under stirring to a cold (-60°C) suspension of **2a** (4.38 g, 10 mmol) and **5e** (2.72 g, 10 mmol) in CH_2Cl_2 (40 ml). Stirring was continued between -60°C and -30°C for 2 h and then at 0°C for 30 min. Filtration from **10** (1.08 g, 18%) and evaporation of the filtrate afforded a brown residue, which was precipitated at -30°C from CH_2Cl_2 (10 ml)/ Et_2O (120 ml). Crystallisation at -15°C from CH_2Cl_2 (15 ml)/ Et_2O (15 ml) afforded **12** as colorless fine needles (1.40 g, 21%); *m.p.* $203\text{--}205^\circ\text{C}$ (dec.). The mother liquor of the crystallisation contained **6e**. The yield of **12** could not be increased by applying either 2 equiv. of **5e** or of SbCl_5 . No **12** was produced when the solution of **5e** was added to a solution of **2a** and SbCl_5 . – $[\alpha]_{\text{D}}^{25} = -145.5$ ($c = 1.0$, CHCl_3). – IR: $\nu/\text{cm}^{-1} = 1760, 1751, 1578, 1570$. – ^1H NMR (600 MHz, CD_3CN): $\delta/\text{ppm} = 1.74, 2.00$ (CH_3), 4.16 (dd, $J = 3.1, 13.0$), 4.23 (dd, $J = 3.4, 13.0$) (CH_2), 4.51 (dt, $J \approx 3.1, 9.8$, H-6), 5.45 (dd, $J = 6.2, 9.6$, H-7), 6.03 (br, $J < 1$, H-4), 6.20 (dd, $J = 6.2, 12.7$, H-7a), 6.23 (br, d, $J = 12.7$, H-3a), 7.58 (2H), 7.85 (2H), 7.64 (m, 2H), 7.89 (m, 2H) (aryl). – ^{13}C NMR (62.9 MHz, CD_3CN): $\delta/\text{ppm} = 20.3, 21.0$ (CH_3), 62.3, 65.2, 66.9, 70.3, 72.4, 82.8 (CH_2 , CH), 127.6–143.0 (20 lines, aryl), 169.7, 171.0 (C=O).

$\text{C}_{34}\text{H}_{21}\text{Cl}_{18}\text{N}_6\text{O}_5\text{Sb}$ Calcd.: C 30.17 H 1.56 N 6.21 (1353.5) Found: C 30.23 H 1.74 N 6.01.

rel-(2'*R*,3'*R*)-3-(Tetrahydro-2-methoxy-2*H*-pyran-3-yl)-1,3-bis(2,4,6-trichlorophenyl)triazene (**13a**)

A solution of **6c** (8.21 g, 10 mmol) and toluenesulfonic acid (0.95 g, 5 mmol) in MeOH (110 ml) was boiled under reflux for 20 min. After cooling NaHCO_3 (1.73 g, 25 mmol) was

added in portions. After cessation of the effervescence the solvent was evaporated and the residue was extracted with CHCl_3 (75 ml). Silica gel (5 g) was added to the extract. Filtration and evaporation of the solvent afforded a colorless powder (4.14 g, 80%), which was crystallized at 5 °C from petroleum ether (*b.p.* 50–70 °C) (5 ml) to give a crystalline powder; *m.p.* 123–125 °C. – MS (FAB): *m/z* 518 (MH^+ , 12%), 486 ($\text{MH}^+ - \text{CH}_3\text{OH}$, 5%). – IR: ν/cm^{-1} = 1571, 1551. – ^1H NMR (600 MHz, CDCl_3): δ/ppm = 1.70 (m, H-5'), 1.88 (m, 1H) (H-5''), 2.29 (m, H-4'), 2.43 (m, H-4''), 3.39 (OCH_3), 3.55 (m, H-6'), 3.82 (ddd, J = 4.3, 6.2, 10.1, H-3'), 3.98 (m, H-6''), 4.60 (d, J = 6.2, H-2'), 7.29 (2H), 7.42 (2H) (aryl). – ^{13}C NMR (62.9 MHz, CDCl_3): δ/ppm = 24.3, 26.3 (CH_2), 56.0 (CH_3), 63.7, 63.8, 103.1 (CH_2 , CH), 128.5, 128.6, 128.8, 129.1, 130.9, 134.0, 135.1, 136.5, 136.9, 144.2 (aryl). $\text{C}_{18}\text{H}_{15}\text{Cl}_6\text{N}_3\text{O}_2$ Calcd.: C 41.73 H 2.92 N 8.11 (518.1) Found: C 41.66 H 2.93 N 8.09.

rel-(2'*R*,3'*R*)-*N*-(Tetrahydro-2-methoxy-2*H*-pyran-3-yl)-2,4,6-trichloroaniline (**14a**)

Zinc dust (26 g) was added in portions to a suspension of **13a** (5.18 g, 10 mmol) in AcOH (70 ml). After stirring for 2 h acetone (10 ml) was added. Stirring was continued for 12 h. The solvent was evaporated and the residue was extracted with CH_2Cl_2 (2 × 50 ml). The extracts were washed with H_2O (2 × 50 ml) and dried over Na_2SO_4 . Evaporation of the solvent afforded an oil, which was purified by column chromatography [6 × 50 cm; silica gel (150 g); eluent CHCl_3]. Workup gave a colorless oil (2.82 g, 91%), which crystallized at –15 °C from CHCl_3 (5 ml)/pentane (20 ml) to afford **14a** as colorless needles; *m.p.* 68–70 °C. – MS (EI, 50 °C): *m/z* 309 (M^+ , 30%), 279 ($\text{M}^+ - \text{MeOH}$, 15%), 221 ($\text{M}^+ - \text{CH}_2\text{CH}_2\text{OCHOMe}$, 100%). – IR: ν/cm^{-1} = 3358 (NH), 1562. – ^1H NMR (600 MHz, CDCl_3): δ/ppm = 1.46 (m, H-5'), 1.61 (m, H-4'), 1.86 (m, H-5''), 2.02 (m, H-4''), 3.39 (OCH_3), 3.56 (m, H-6'), 3.68 (dt, J ≈ 2.4, 4.0, H-3'), 3.82 (m, H-6''), 4.39 (br, NH), 4.43 (d, J = 2.4, H-2'), 7.23 (aryl). – ^{13}C NMR (62.9 MHz, CDCl_3): δ/ppm = 21.1, 24.5 (C-3,4), 53.5, 55.1, 60.4 (CH_3 , C-2,5), 101.5 (C-1), 125.5, 126.5, 128.6, 140.8 (aryl). $\text{C}_{12}\text{H}_{14}\text{Cl}_3\text{N}_2\text{O}_2$ Calcd.: C 46.40 H 4.54 N 4.51 (310.6) Found: C 46.54 H 4.81 N 4.49.

rel-(2'*R*,3'*R*)-*N*-(2-Ethoxytetrahydro-2*H*-pyran-3-yl)-2,4,6-trichloroaniline (**14b**)

Compound **13b** was prepared from **6c** (8.21 g, 10 mmol) in EtOH (80 ml) and CH_2Cl_2 (40 ml) in the manner described for **13a**. The crude colorless resin (5.21 g, 98%) was used without further purification. – ^1H NMR (600 MHz, CDCl_3): δ/ppm = 3.87 (m, J = 4.6, 6.2, 9.9, H-3'), 4.70 (d, J = 6.2, H-2'). – A suspension of **13b** (5.32 g, 10 mmol) and zinc dust (26 g) in AcOH (70 ml) was stirred for 12 h. Filtration, evaporation of the filtrate, extraction of the residue with AcOEt (2 × 50 ml), washing of the combined extracts with H_2O (2 × 50 ml), drying over Na_2SO_4 , and evaporation of the solvent afforded a residue, which was purified by column chromatography in the manner described for **14a**. At –15 °C the resulting oil (2.37 g, 73%) solidified to a colorless powder; *m.p.* 56–58 °C. – IR: ν/cm^{-1} = 3359 (NH), 1559. – ^1H NMR (250 MHz, CDCl_3): δ/ppm = 1.15 (t, J = 7.0, CH_3), 1.26–2.08 (m's, 4H), 3.40–3.92 (m's, 5H), 4.50 (d, J = 3.2, H-2'), 7.24 (aryl).

– ^{13}C NMR (62.9 MHz, CDCl_3): δ/ppm = 15.0, 21.4, 25.0 (CH_3 , C-3,4), 53.9, 60.9, 63.3 (OCH_2 , C-2), 100.6 (C-1), 126.5 (2 C), 128.5, 140.9 (aryl).

$\text{C}_{13}\text{H}_{16}\text{Cl}_3\text{N}_2\text{O}_2$ Calcd.: C 48.10 H 4.97 N 4.31 (324.6) Found: C 48.41 H 4.90 N 4.34.

rel-(2'*R*,3'*R*)-*N*-(Tetrahydro-2-methoxy-2*H*-pyran-3-yl)-*N'*-isopropyl-2,4,6-trichlorophenylhydrazine (**15**)

A suspension of **13a** (5.18 g, 10 mmol) and zinc dust (26 g) in AcOH (70 ml) was stirred for 2 h. Acetone (2.5 ml) was added and stirring was continued for 16 h. Further portions of acetone (2.5 ml) were added after 1, 3 and 5 h. Evaporation of the solvent and chromatography of the residue in the manner described for **14b** afforded **14b** (0.56 g, 18%) and **15** (2.24 g, 61%) as colorless oils. At 5 °C compound **15** solidified in the course of the next 7 d to a colorless crystalline powder; *m.p.* 41–42 °C. – IR: ν/cm^{-1} = 3300 (br, NH), 1570, 1546, 1539. – ^1H NMR (250 MHz, CDCl_3): δ/ppm = 0.96 (d, J = 6.3), 0.98 (d, J = 6.1) (CH_3), 1.55 (m, 1H), 1.74 (m, 1H), 1.94 (m, 1H), 2.10 (m, 1H), 2.50 (sept, J = 6.1, NCH), 3.08 (m, H-3'), 3.36 (OCH_3), 3.44 (m, 1H), 3.87 (m, 1H), 4.46 (d, J = 4.9, H-2'), 4.47 (NH), 7.27 (m, aryl). – ^{13}C NMR (62.9 MHz, CDCl_3): δ/ppm = 21.1 (2 CH_3), 24.5, 25.4 (C-3,4), 47.9, 55.9, 62.9, 63.9 (CH_3 , CHN, C-2,5), 102.7 (C-1), 129.2, 129.4, 129.9, 133.6, 134.9, 141.9 (aryl).

$\text{C}_{15}\text{H}_{21}\text{Cl}_3\text{N}_2\text{O}_2$ Calcd.: C 49.00 H 5.76 N 7.62 (367.7) Found: C 49.00 H 5.89 N 7.55.

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- Address for correspondence:
Prof. Dr. J. C. Jochims
Universität Konstanz
Fachbereich Chemie
Fach M 733
D-78434 Konstanz
Fax: Internat. code (0) 7531-883898
e-Mail: johannes.jochims@uni-konstanz.de