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Novel bicyclisation of unsaturated polyols in PdCl$_2$–CuCl$_2$–AcOH catalytic system

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Abstract

Novel type of Pd(II)-catalysed transformation of sugar-derived alkenitols furnishing 7-benzyloxy-2,5-dioxabicyclo[2.2.1]heptanes was discovered. The investigated bicyclisation displays an exceptional substrate selectivity towards *xylo*-configured unsaturated polyols. Moreover, a newly build stereogenic centre is formed in a diastereospecific *cis*-manner. The observed stereochemical preference was corroborated by modelling of pertinent transition states at the semiempirical level of theory (PM5). In addition, the single crystal X-ray analysis of an acylated analogue D-*glycero*-L-*gulo*-21 was done in order to establish the relative configuration of related bicyclic products.
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Keywords: Palladium(II)-catalysis; Diastereoselectivity; Substrate selectivity; Bicyclisation; Semiempirical calculations

1. Introduction

The Wacker process for the palladium-catalysed oxidation of ethylene to acetaldehyde was developed forty-three years ago [1]. Since the development of this process a multitude of transformations mediated by palladium(II) compounds has been described. These comprise two major reaction types, a nucleophilic attack on Pd(II)-complexed olefin, and an insertion of olefins into σ-alkyl palladium(II) species [2]. Intramolecular versions of these processes are very useful in the synthesis of oxygen and nitrogen-containing heterocycles [3]. A catalytic system that is mostly efficient for oxidations, carbonylations, cycloacetalisations and the other type of such reactions contains both palladium(II) chloride and copper(II) chloride in acetic acid with sodium acetate as a buffer [3,4].

In this account, we will discuss the new type of bicyclisation of unsaturated polyols with this particular catalytic system.

2. Results and discussion

Our entry into this research area was initiated by isolation of an unexpected side product, namely L-*glycero*-D-*gulo*-2 formed in 9% yield in the Pd(II)-catalysed oxycarbonylation of L-*ido*-1 [5] along with the desired (+)-7-epi-goniofufurone as a major product, a naturally occurring cytotoxic styryl-lactone [6]. The bicyclic structure of L-*glycero*-D-*gulo*-2 lacking C=O moiety was determined using single crystal X-ray structure analysis [7]. Our suspicion, that compound L-*glycero*-D-*gulo*-2 was formed via competitive bicyclisation of **1,** was proved by an experiment with exclusion of carbon monoxide from the reaction mixture. Indeed, using palladium(II) chloride as catalyst (0.1 equiv.), copper(II) chloride as oxidant (3 equiv.) and sodium acetate (3 equiv.) in glacial acetic acid as buffer at room temperature [3,4,8] led to

the formation of bicycle **2** as a sole product in 73% yield (Scheme 1).

From the synthetic point of view, the aforementioned transformation represents a new type of functionalisation of terminal alkene moiety. Formally, two nucleophilic substituents are attached to both ends of C=C double bond. Thus, we decided to study this rather unusual reactivity pattern in a more detail.

2.1. Preparation of unsaturated polyols as substrates

Firstly, easily accessible C5–C8 alkenitols were chosen as suitable substrates for screening the optimal reaction conditions of key bicyclisation. Diastereomeric mixtures of various α-*O*-benzyl-alkenitols **6** were prepared from aldoses **3a** [9], **3b** [10], **3c** [11], **3d** [12] according to common synthetic sequence comprising the following steps: vinylmagnesium bromide addition to aldehydes **3** furnished corresponding allylalcohols **4**, followed by benzylation to fully protected alkenitols **5**. Final hydrolysis of acetonides **5** afforded the desired key substrates **6** as nearly equimolar diastereomeric mixtures (Scheme 2).

In addition, enantiomerically pure substrates L-*ido*-**1** and D-*gluco*-**1** were synthetised from the commercially available D-gluconolactone in 10 steps. Mesylation of the known triol **7** [15] followed by nucleophilic displacement of **8** furnished iodide **9** that subsequently underwent Zn–Cu promoted elimination to provide alkene **10**. Selective hydrolysis of the terminal acetonide followed by oxidative cleavage of triol **11** gave a crude aldehyde that was subjected, without any purification, to the phenylmagnesium bromide addition yielding the corresponding adducts L-*ido*-**12** and D-*gluco*-**12** as a diastereomeric mixture in the ratio 7:3. The highly regioselective reduction of benzylidene ring of pure L-*ido*-**12** and D-*gluco*-**12** diols (separated by flash column chromatography) was accomplished with the NaBH3CN/TiCl4 system, furnishing the required α-*O*-Bn-protected tetraols L-*ido*-**1** and D-*gluco*-**1** (Scheme 3).

## 2.2. Palladium(II)-catalysed bicyclisation of unsaturated polyols

With all prepared substrates on our hands, we subjected them to the key PdCl2/CuCl2-catalysed transformation under standard reaction conditions [16] (Scheme 4). There are two different modes of transformation, yielding three types of bicyclic products **I**, **II** and **III**, depending on a

starting polyol. This indicates that the chemoselectivity of reaction is directly correlated with the relative configuration of substrates **1** and **6**. It is noteworthy that from diastereomeric mixtures of starting polyols, those with all-*syn* (*xylo*) configuration on C3,C4,C5-atoms, i.e., D-*gluco*-**6b** (Entry 2) and D-*ido*-**6c** (Entry 3), led to corresponding bicycles of the type **I**. On the other hand, bicyclic acetals of types **II** and/or **III** were formed from all other diastereomers of substrates. As a proof of stereochemical dependence for necessary *xylo*-configuration, enantiomerically pure substrates L-*ido*-**1** (Entry 6) and D-*gluco*-**1** (Entry 7) furnished products L-*glycero*-D-*gulo*-**2** and/or D-*glycero*-D-*gulo*-**2** exclusively, while the non-*xylo* configured D-*manno*-**6b** [17,10b] (Entry 5) gave only acetals **16** and **17**. The only exception to this rule was the reaction of diastereomeric mixture D-*erythro*-**6a**/D-*threo*-**6a** (Entry 1), which afforded a single product D-*lyxo*-**13** due to its *C*-2 symmetry [18]. An important point to note is that *xylo*-configured diastereoisomers provide the desired bicyclic products of type **I** in synthetically useful yields (Entries 1–3, 6, 7). This certainly makes our novel transformation well suited for utilisation in total syntheses of tetrahydrofuran-containing natural products (Table 1).

The determination of chemical and relative configuration of bicycles of type **I** was done by single-crystal X-ray analysis of bis-acylated analogue D-*glycero*-L-*gulo*-**21** (Fig. 1). The structure exhibits considerable disorder at one of terminal phenyl groups, which obviously tends to rotate around the C–C bond connecting two phenyl rings. This fact has been approximated by two orientations of the corresponding aromatic substituent represented by atoms C26–C271–C281–C29–C301–C311 with occupancy of 59.5% and C26–C272–C282–C29–C302–C312 with occupancy of 40.5%, respectively, wherein the angle between the two ring planes is 65.9(5)°. Crystal data and selected bond lengths and angles are given in Tables 2 and 3, respectively.

The formation of 1,4:2,5-dianhydro-heptitols **I** represents a new type of PdCl2/CuCl2-catalysed bicyclisation of alkenitols and can be mechanistically rationalised as follows: intramolecular nucleophilic attack of (C-5)OH to Pd(II)-activated terminal C=C bond of D-*ido*-**6c** in π-complex **A** leads to σ-palladium intermediate **B**. The advantageous coplanar spatial arrangement of (C-1)C-2 and (C-4)OPd bonds of **B** is now ideally set for subsequent reductive elimination affording the bicyclic D-*glycero*-D-*gulo*-**20**. The required catalytic cycle is closed by reoxidation of Pd(0) with CuCl2. Moreover, we have found copper(II) chloride to be an indispensable reagent for this particular transformation as its replacement for other oxidant (benzoquinone) has a detrimental effect on the bicyclisation (Scheme 5).
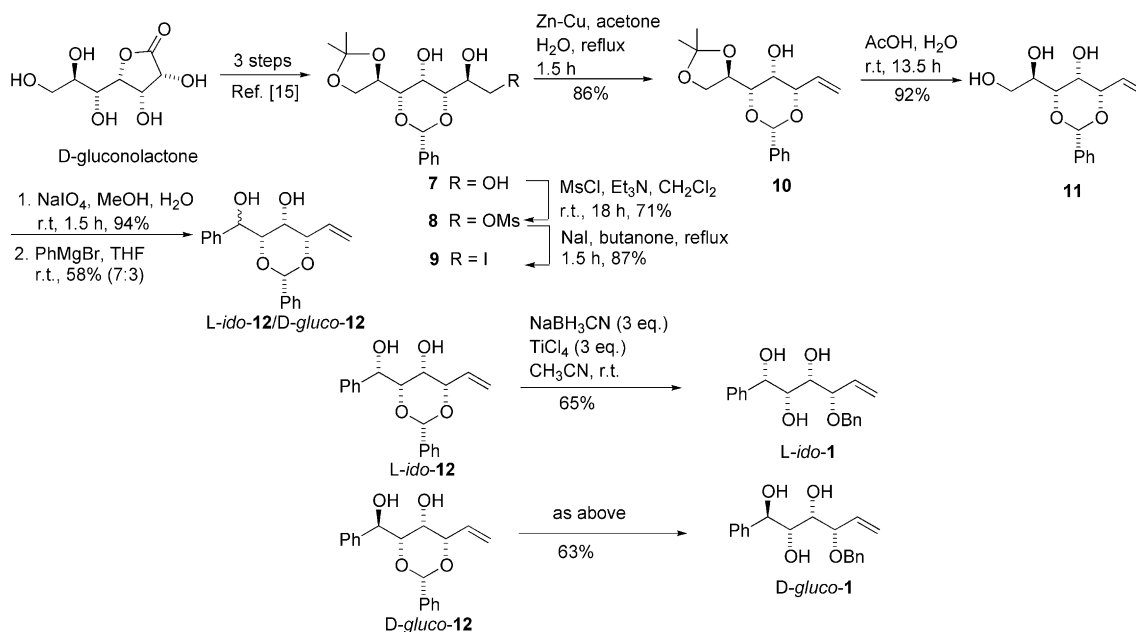
On the other hand, the formation of bicyclic acetals **II** and/or **III** can be easily explained by a known Pd(II)-catalysed cascade process [20] involving two steps: the first being the formation of a common intermediate **E** via complexes **C** and **D**, which subsequently undergoes an acid catalysed

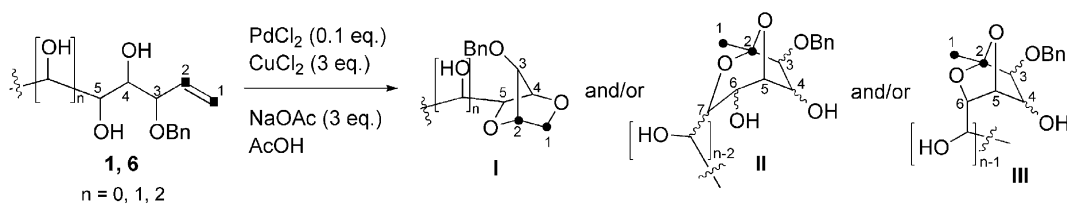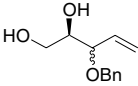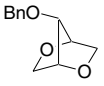L-*ido*-**1**   (+)-7-*epi*-goniofuforone   L-*glycero*-D-*gulo*-**2**

A.) with CO   56%   9%
B.) without CO   0%   73%
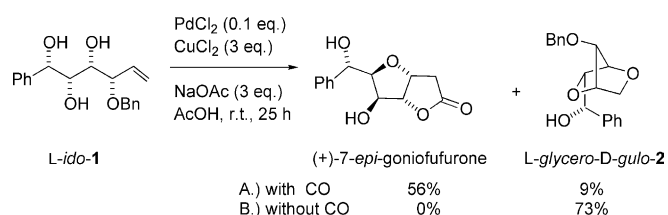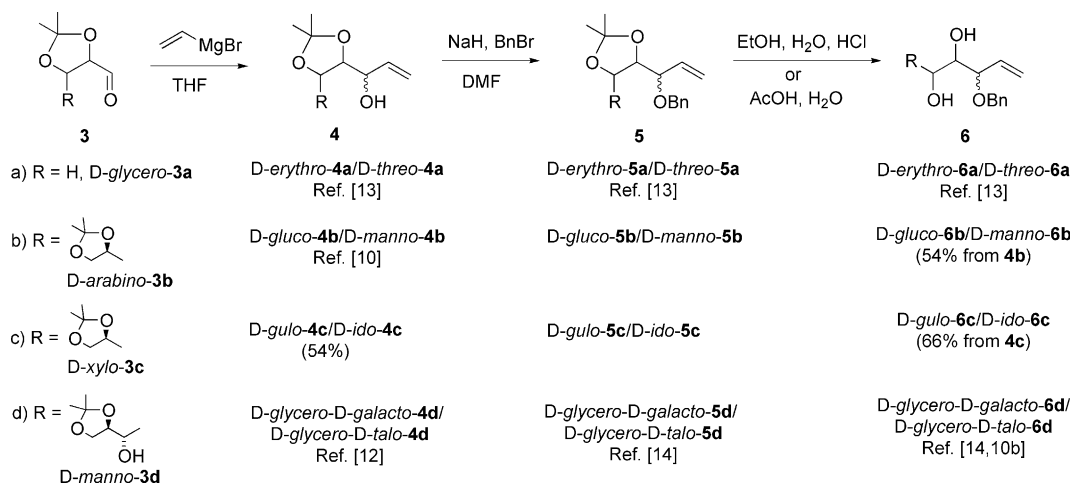
Scheme 1.

Scheme 2.

Scheme 3.
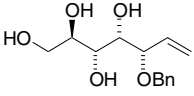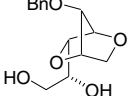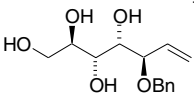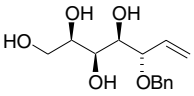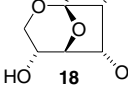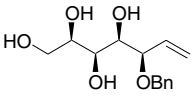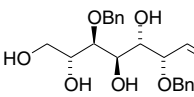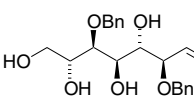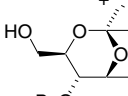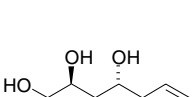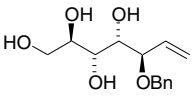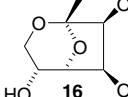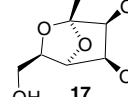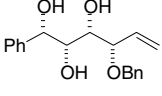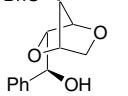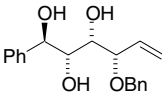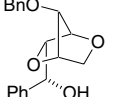
Scheme 4.

1,5- and/or 1,6-acetalisation to produce compounds **19** and/or **18** (Scheme 6).

As we already mentioned earlier, the stereochemical outcome of the transformation is highly dependent on the relative configuration of substrates. It is obvious that in polyols with the all-*syn* (*xylo*) stereochemistry there is a preferential nucleophilic attack from the *Re*-face of an alkene. This leads to the formation of 2,3-*trans*-σ-Pd-complex **F** thermodynamically more favoured due to the diminished sterical hindrance in comparison to its diastereomeric 2,3-*cis*-σ-Pd-complex **G**. As a consequence, the only product formed is the bicycle of type **I**. On the other hand, all other substrates with non-*xylo*-configuration prefer opposite *Si*-attack for the same reason as above, i.e., due to

Table 1
Pd(II)-Catalysed bicyclisations of polyols **1** and **6**

Entry	Substrate	Product (s)	Yield (%)
1	D-*erythro*-**6a**/D-*threo*-**6a**	D-*lyxo*-**13**	79
2	D-*gluco*-**6b**	D-*glycero*-D-*gulo*-**14**	60
	D-*manno*-**6b**	**16** + **17**	33
3	D-*gulo*-**6c**	**18** or **19**	30
	D-*ido*-**6c**	D-*glycero*-L-*gulo*-**20**	43
4	D-*glycero*-D-*galacto*-**6d**	**23**	14
	D-*glycero*-D-*talo*-**6d**	**22**	16
5	D-*manno*-**6b**	**16** and **17**	57
6	L-*ido*-**1**	L-*glycero*-D-*gulo*-**2**	73
7	D-*gluco*-**1**	D-*glycero*-D-*gulo*-**2**	71

the formation of sterically more favoured 2,3-*trans*-σ-Pd-complex **H**, which in turn, leads to acetals of the type **II** and/or **III** (Scheme 7).

This conclusion has been tentatively corroborated by modelling of pertinent transition states (TS) at the semiempirical level of theory (PM5).

Free energies of activation shown in Table 4 as well as the associated geometries of transition states (Fig. 2) indicate, in spite of being calculated for vacuum, that a

Re-attack, leading to σ-complex with a *trans*-arrangement of the methylenepalladium substituent and the neighbouring benzyloxy group, followed by reductive elimination giving rise to a bicycle of type **I** proceeded in *xylo*-substrates through energetically more favoured transition state. Although Scheme 7 boils the difference between *Si* and *Re* attack down to steric congestion created by two neighbouring bulky substituents, we felt that calculations were bound to be more reliable in assessing relative
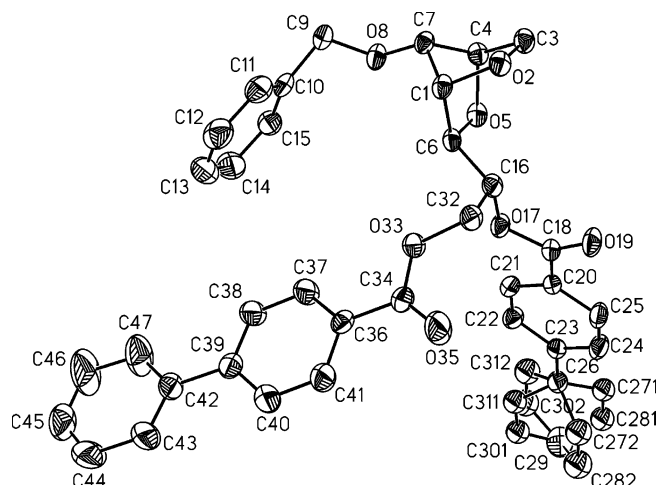
Fig. 1. An *ORTEP* [19] view of crystal and molecular structure of D-*glycero*-L-*gulo*-**21** (hydrogen atoms omitted).

Table 2
Crystal data for D-*glycero*-L-*gulo*-**21**

Empirical formula	$C_{40}H_{30}O_7$
Formula weight	622.64
Crystal system, space group	Monoclinic, P 2(1)
Unit cell dimensions	
a (Å)	5.800(4)
b (Å)	15.338(3)
c (Å)	18.263(4)
β (°)	94.28(3)
Z, volume (Å^3)	2, 1620.2(12)
D_{calc} (g cm^{-3})	1.276
μ (mm^{-1})	1.042
$F(000)$	652
Diffractometer	Siemens P4
Radiation type	Mo Kα $\lambda = 0.71073$ Å
Temperature (K)	293(2)
Diffractions collected/unique, R_{int}	7510/5697/0.0519
Refinement method	Full matrix, least-squares on F^2
Data/restraints/parameters	5697/1/425
Goodness-of-fit on F^2	1.000
Final R indices ($I > 2\sigma(I)$)	$R = 0.0660$, $Rw = 0.1705$
Largest diff. peak and hole (e Å$_{-3}$)	0.171 and −0.206

Table 3
Selected bond lengths (Å) and angles (°) of D-*glycero*-L-*gulo*-**21**

C1–O2	1.441(5)	O2–C1–C6	108.2(3)
C1–C6	1.525(6)	O2–C1–C7	101.6(3)
C1–C7	1.538(7)	C6–C1–C7	100.3(3)
O2–C3	1.446(6)	C1–O2–C3	105.4(3)
C3–C4	1.513(6)	O2–C3–C4	103.9(3)
C4–O5	1.449(5)	O5–C4–C3	105.9(3)
C4–C7	1.514(6)	O5–C4–C7	103.1(3)
O5–C6	1.449(5)	C3–C4–C7	99.8(3)
C6–C16	1.514(6)	C4–O5–C6	106.4(3)
C7–O8	1.406(5)	O5–C6–C16	110.4(3)
		O5–C6–C1	102.5(3)
		C16–C6–C1	113.6(4)
		O8–C7–C4	111.0(3)
		O8–C7–C1	116.8(3)
		C4–C7–C1	91.8(3)
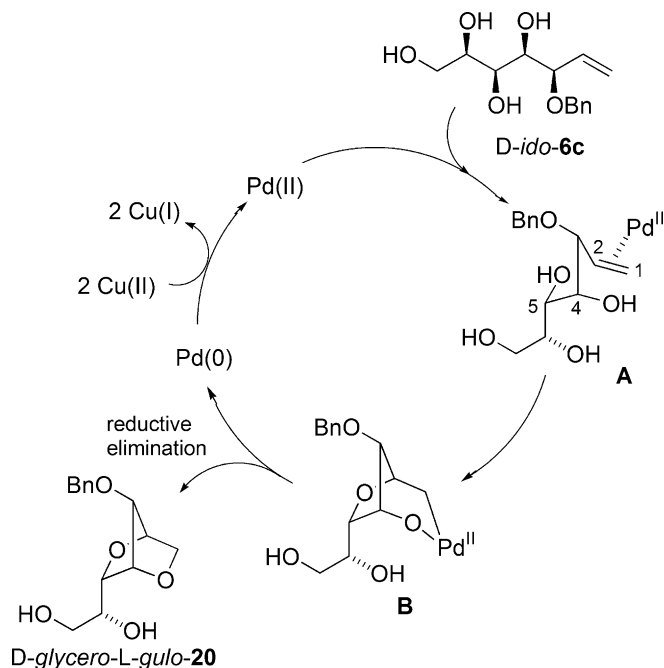
Scheme 5.

energies of transition states and hence relative reaction rates of the respective reaction courses. In addition, reaction hypersurfaces, once successfully generated from two variables plotted against energy, allowed one to glean possible alternative reaction pathways, even some contra
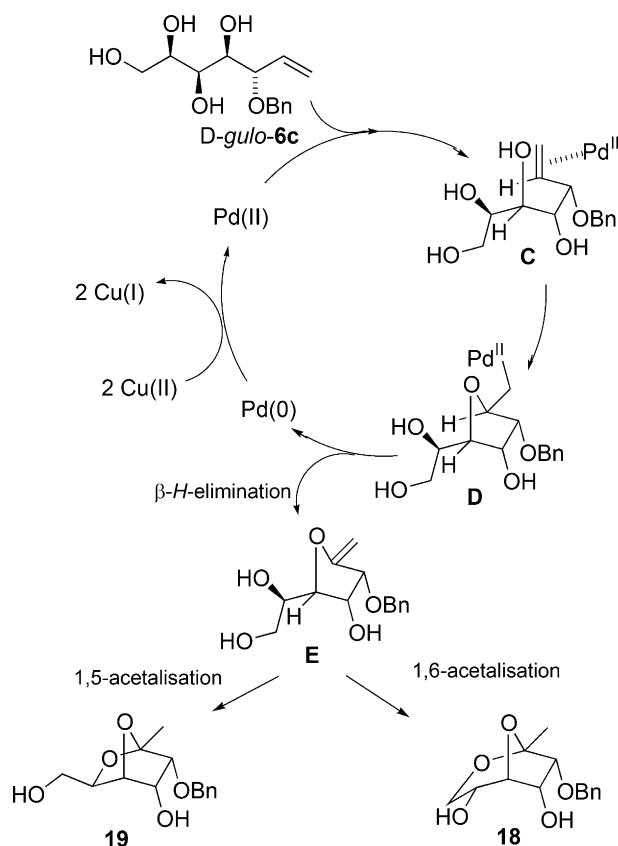
Scheme 6.
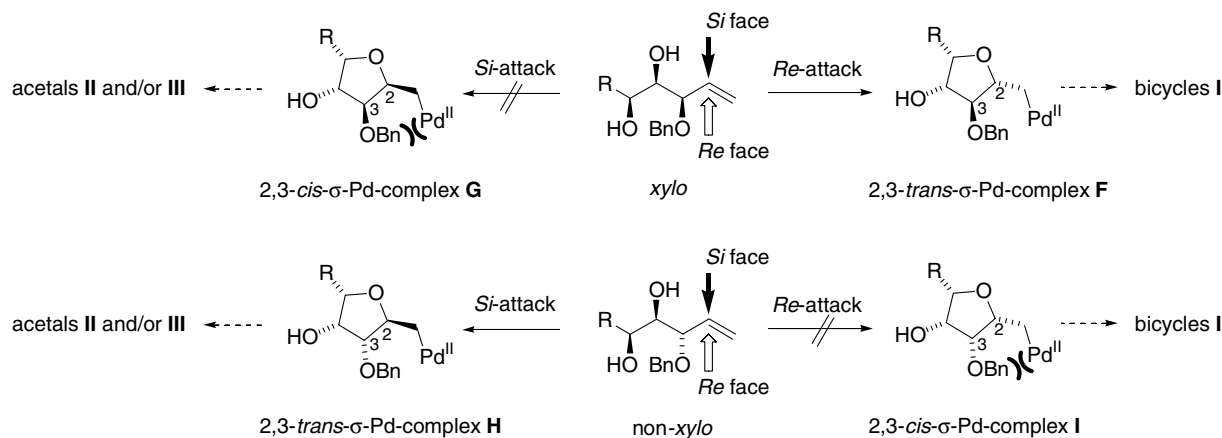
Scheme 7.

Table 4
Calculated free energie of TS$^{\#}$ for *Re*- and *Si*-attack on D-*ido*-**6c** (*xylo*) and D-*gulo*-**6c** (non-*xylo*) alkenitols (CAChe-DGauss energies at 298.13 K)

Type of attack	Enthalpy[a] (Kcal/mol)	$S^{\#}(T)$ (cal/mol/K)	Enthalpy correction (Kcal/mol)	$G^{\#}(T)$ (Kcal/mol)
Re attack at D-*ido*-**6c**	−261.6	204.7	19.5	−322.7
Si attack at D-*ido*-**6c**	−248.8	202.4	19.2	−309.1
Re attack at D-*gulo*-**6c**	−256.0	204.1	19.4	−316.8
Si attack at D-*gulo*-**6c**	−258.6	203.9	19.2	−319.3

[a] Heat of formation.
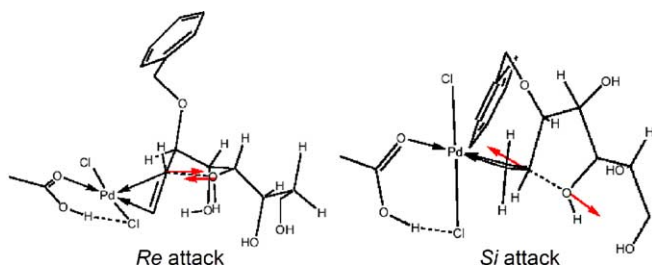
Fig. 2. Models of TS$^{\#}$ for *Re* and *Si* attack on D-*ido*-**6c**.

intuitive ones. In the absence of other accessible probes to monitor the exceedingly complex reaction mixtures, even such simplified theoretical models proved to be useful beyond expectation and we intend to develop it towards real predictive power [21].

3. Conclusion

In conclusion, we have found a novel type of PdCl$_2$/CuCl$_2$-catalysed bicyclisation of sugar-derived unsaturated polyols that leads to 1,4:2,5-dianhydroalditols in good yields [22]. This useful synthetic method is highly substrate-selective and displays a strong stereochemical preference for alkenitols with C3,C4,C5-all-*syn* (*xylo*) relative configuration. Moreover, the transformation is diastereospecific due to the formation of new C-2 stereogenic centre with *threo*-relationship exclusively (Scheme 8).

Finally, the tandem bicyclisation-ring opening represents a new synthetic access to 2,3-*trans*-tetrahydrofuran skeleton and thus is complementary to known oxycarbonylation methodology [5,8] producing diastereomeric 2,3-

cis-tetrahydrofurans. We believe that this efficient methodology is predisposed to become a powerful synthetic tool for the preparation of complex oxygenated natural products.

4. Experimental

4.1. General

Commercial reagents were used without further purification. All solvents were distilled before use. Hexanes and petrolether (PE) refer to the fraction boiling at 60–65 °C. Flash column liquid chromatography (FLC) was performed on silica gel Kieselgel 60 (40–63 μm, 230–400 mesh) and analytical thin-layer chromatography (TLC) was performed on aluminum plates pre-coated with either 0.2 mm (DC-Alufolien, Merck) or 0.25 mm silica gel 60 F_{254} (ALUGRAM® SIL G/UV$_{254}$, Macherey-Nagel). The compounds were visualised by UV fluorescence and by dipping the plates in an aqueous H$_2$SO$_4$ solution of cerium sulphate/ammonium molybdate followed by charring with a heat gun. HPLC analyses were performed on Varian Dynamax system with variable wavelength UV detector: column
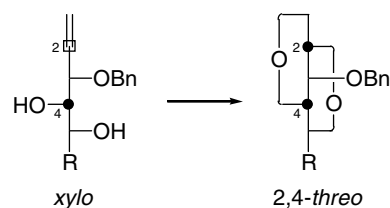
Scheme 8.

SEPARON SGX 10 μm, 25 × 4 mm, mobile phase: 4.7% MeOH in CHCl₃, flow rate: 1 ml/min, UV detection: 254 nm, 25 °C. Melting points were obtained using a Boecius apparatus and/or Kofler hot plate and are uncorrected. Optical rotations were measured with a POLAR L-μP polarimeter (IBZ Messtechnik) with a water-jacketed 10,000 cm cell at the wavelength of sodium line D ($\lambda = 589$ nm). Specific rotations are given in units of 10^{-1} deg cm² g⁻¹ and concentrations are given in g/100 mL. Elemental analyses were run on FISONS EA1108 instrument. Infrared spectra were recorded either on a Philips Analytical PU9800 FTIR spectrometer or a Perkin–Elmer 1750 FTIR spectrophotometer as KBr discs (KBr) or as thin films on KBr plates (film). NMR spectra were recorded on a Varian VXR-300 spectrometer. Chemical shifts (δ) are quoted in ppm and are referenced to the tetramethylsilane (TMS) as internal standard. The COSY, NOESY and DIFNOE techniques were used in assignment of ¹H–¹H relationships and the determination of relative configuration. The multiplicities of carbons were assigned from a broadband decoupled analysis used in conjunction with either APT or DEPT programs. The HETCOR and HMQC techniques were used throughout for the assignment of the ¹H–¹³C relationships. Compounds are numbered according to carbohydrate naming scheme.

4.2. Synthesis of polyols *1* and *6*

4.2.1. 3-O-Benzyl-D-gluco-1-heptenitol (D-gluco-*6b*) and 3-O-benzyl-D-manno-1-heptenitol (D-manno-*6b*)

The suspension of hexanes washed NaH (60% in paraffin, 140 mg, 3.44 mmol, 1.6 equiv.) in dry DMF (10 ml) was cooled to −30 °C and the solution of protected alkenitols D-gluco-*4b*/D-manno-*4b* [10] (556 mg, 2.15 mmol) in DMF (10 ml) was added in several portions. The resulting mixture was stirred for 1 h and benzyl bromide (0.28 ml, 404 mg, 2.37 mmol, 1.1 equiv.) was added at once. The reaction was left to stir overnight, quenched with water (25 ml) and aq. layer was extracted with Et₂O (3 × 25 ml). Combined org. extracts were dried (Na₂SO₄) and concentrated in vacuo. The obtained crude oil (750 mg) was dissolved in 70% EtOH (20 ml) and conc. HCl (2 ml) was added. The solution was stirred at r.t. under continuous TLC monitoring (ca. 4 h). When no isopropylidene intermediate was detected ($R_f = 0.66$, 17% AcOEt in toluene), solvents were removed in vacuo and the residue was dissolved in AcOEt (20 ml) and dried over anhydrous K₂CO₃. The crude product was concentrated and crystallised from AcOEt (ca. 10 ml) to afford D-gluco-*6b*/D-manno-*6b* (310 mg, 54%, 63:37) as colourless crystals; T_r: 10.8 min for D-gluco-*6b* and 12.0 min for D-manno-*6b*; R_f 0.2 (AcOEt); m.p. 132–136 °C; ¹H NMR (300 MHz, DMSO-d_6): 3.27–3.73 (5H, m, H-4, H-5, H-6, H-7), 3.87 (1H, m, H-3), 4.14–4.57 (12H, m, 4xOH, Ph*CH₂*), 5.27 (2H, m, $J_{1Z,2} = 11.0$, $J_{1E,2} = 15.7$ Hz, H-1E, H-1Z), 5.71-5.93 (1H, m, H-2), 7.23–7.46 (5H, m, Ph); ¹³C NMR (75 MHz, DMSO-d_6) D-gluco-*6b*: 63.4 (t, C-7), 69.7 (t,

Ph*CH₂*), 70.4, 71.0, 71.4 (all d, C-4, C-5, C-6), 82.5 (d, C-3), 118.2 (t, C-1), 127.1, 127.3, 128.0, (all d, Ph), 136.0 (d, C-2), 138.8 (s, Ph); D-manno-*6b* 63.7 (t, C-7), 69.9 (t, Ph*CH₂*), 69.6, 71.0, 71.1 (all d, C-4, C-5, C-6), 80.2, (d, C-3), 117.5, (t, C-1), 127.1, 127.3, 128.0, (all d, Ph), 137.7 (d, C-2), 138.7 (s, Ph).

4.2.2. 4,5:6,7-Di-O-isopropylidene-D-gulo-1-heptenitol (D-gulo-*4c*) and 4,5:6,7-di-O-isopropylidene-D-ido-1-heptenitol (D-ido-*4c*)

Vinylmagnesium bromide (1 M in THF, 4 ml, 4 mmol, 1.85 equiv.) was added at once to a CH₂Cl₂ solution (10 ml) of aldehyde D-xylo-*3c* [11] (500 mg, 2.17 mmol) at 15 °C under Ar and the resulting mixture was stirred overnight at r.t. The reaction was quenched with sat. aq. NH₄Cl solution (10 ml) and extracted with Et₂O (3 × 10 ml). Combined org. extracts were dried (Na₂SO₄) and concentrated in vacuo. Purification of the crude product by FLC (15 g, gradient elution: AcOEt/hexanes 25% → 33%) yielded D-gulo-*4c*/D-ido-*4c* as colourless oil (300 mg, 54%, syn/anti = 1:1); R_f 0.7 and 0.64 (AcOEt/toluene 1:1); ¹H NMR (300 MHz, CDCl₃) D-gulo-*4c*/D-ido-*4c* (1:1): 1.38, 1.43, 1.44 (12H, all s, all CH₃), 2.34 (1H, bs, OH), 3.86-4.22 (6H, m, H-3, H-4, H-5, H-6, H-7), 4.30 (1H, bs, OH), 5.28 (1H, dd, $J_{1E,1Z} = 1.7$, $J_{1Z,2} = 10.7$ Hz, H-1Z), 5.41 (1H, ddd, $J_{1E,3} = 1.3$, $J_{1E,1Z} = 1.7$, $J_{1E,2} = 17.5$ Hz, H-1E), 5.93 (1H, m, H-2); ¹³C NMR (75 MHz, CDCl₃): 25.5, 26.1, 27.0, 27.4, 27.2, 27.3 (all q, all CH₃), 65.7, 65.9 (2 × t, C-7), 71.9, 72.3, 74.9, 75.4, 76.7, 76.9, 79.2, 79.6 (all d, C-3, C-4, C-5, C-6), 109.6 (s, (CH₃)₂*C*), 109.7, 109.9 (2 × s, (CH₃)₂*C*), 116.9, 117.1 (2 × t, C-1), 135.9, 137.0 (2 × d, C-2).

4.2.3. 3-O-Benzyl-D-gulo-1-heptenitol (D-gulo-*6c*) and 3-O-benzyl-D-ido-1-heptenitol (D-ido-*6c*)

The suspension of hexanes washed NaH (60% in paraffin, 179 mg, 4.47 mmol, 1.5 equiv.) in dry DMF (10 ml) was cooled to 0 °C and the solution of acetonides D-gulo-*4c*/D-ido-*4c* (768 mg, 2.98 mmol) in DMF (5 ml) was added dropwise during 10 min. The resulting mixture was stirred for 1 h and benzyl bromide (0.4 ml, 560 mg, 3.3 mmol, 1.1 equiv.) was added at once. The reaction was left to stir at r.t. overnight, quenched with water (3 ml), volatiles were removed in vacuo and the residue was dissolved in Et₂O (30 ml). Insoluble solids (NaBr) were filtered off (Celite pad) and the filtrate was concentrated. Crude oil containing benzylated intermediate (R_f 0.72 (17% AcOEt in toluene)) was dissolved in 75% EtOH (20 ml), conc. HCl (1 ml) was added and the solution was stirred for 8 h at r.t. After concentration in vacuo, the crude material was purified by FLC (25 g, AcOEt) yielding an equimolar mixture of D-gulo-*6c*/D-ido-*6c* (530 mg, 66%, 1:1) as pale brown oil; R_f 0.26 (10% MeOH in CHCl₃); ¹H NMR (300 MHz, DMSO-d_6): 3.40–3.57, 3.67 (5H, m, H-4, H-5, H-6, H-7), 3.87 (1H, m, H-3), 4.32–4.56 (6H, m, 2 × OH, 2 × Ph*CH₂*), 5.27 (2H, m, $J_{1Z,2} = 9.2$, $J_{1E,2} = 16.3$ Hz, H-1E, H-1Z), 5.77-5.91 (1H, m, H-2), 7.29–7.41 (5H, m, Ph); ¹³C NMR

(75 MHz, DMSO-d_6): 62.4 (t, C-7), 69.7, 69.8 (2 × t, PhCH_2), 69.1, 70.0, 72.7, 72.9, 73.1, 73.5 (all d, C-4, C-5, C-6), 80.3, 81.7 (2 × d, C-3), 117.8, 118.1 (2 × t, C-1), 127.1, 127.1, 127.4, 128.0, 128.1 (all d, all Ph), 136.0, 136.9 (2 × d, C-2), 138.6, 138.7 (2 × s, Ph).

4.2.4. 3,5(R)-O-Benzylidene-6,7-O-isopropylidene-1-methanesulphonyl-D-glycero-D-gulitol (8)

To a mixture of triol 7 (5.0 g, 14.7 mmol) and Et$_3$N (1.78 g, 17.64 mmol, 1.2 equiv.) in dry CH_2Cl_2 (100 ml) a solution of MsCl (1.25 ml 16.16 mmol, 1.1 equiv.) in dichloromethane (50 ml) was added dropwise over 6 h under Ar at r.t. The reaction mixture was stirred for further 12 h, then water (50 ml) was added and the aq. layer was extracted with CH_2Cl_2 (3 × 30 ml). Combined org. extracts were dried (Na$_2$SO$_4$) and evaporated in vacuo. Purification of the crude product by FLC (60 g, 19 × 3 cm, PE:AcOEt 1:1) yielded 8 as a colourless solid (4.42 g, 72%); m.p. 163–164 °C; $[\alpha]_D^{18}$ − 6.3 (c 0.22, CHCl$_3$); IR (KBr): 3500–3200 (s, br, OH), 1453 (m), 1410 (m), 1345 (s), 1220 (m), 1181 (s), 1097 (s), 1071 (s), 1033 (s), 1020 (s), 956 (s), 811 (m), 755 (m), 700 (m); ^{1}H NMR (250 MHz, DMSO-d_6): 1.29, 1.35 (2 × 3H, 2 × s, 2 × CH$_3$), 3.14 (3H, s, CH$_3$SO$_2$), 3.76 (1H, ddd, $J_{4,OH}$ = 8.5, $J_{3,4}$ = 1.4, $J_{4,5}$ = 1.4 Hz, H-4), 3.80 (1H, dd, $J_{2,3}$ = 9.0, $J_{3,4}$ = 1.4 Hz, H-3), 3.85 (1H, dd, $J_{5,6}$ = 7.4, $J_{4,5}$ = 1.4 Hz, H-5), 3.96 (1H, dd, $J_{7A,7B}$ = 8.5, $J_{6,7A}$ = 5.4 Hz, H-7A), 3.97–4.04 (1H, m, H-2), 4.03 (1H, dd, $J_{7A,7B}$ = 8.5, $J_{6,7B}$ = 6.2 Hz, H-7B), 4.23 (1H, dd, $J_{1A,1B}$ = 10.6, $J_{1A,2}$ = 5.2 Hz, H-1A), 4.23–4.28 (1H, m, H-6), 4.33 (1H, dd, $J_{1A,1B}$ = 10.6, $J_{1B,2}$ = 2.4 Hz, H-1B), 4.75 (1H, d, $J_{4,OH}$ = 8.5 Hz, 4-OH), 5.43 (1H, d, $J_{2,OH}$ = 6.1 Hz, 2-OH), 5.65 (1H, s, PhCH), 7.35–7.50 (5H, m, Ph); ^{13}C NMR (63 MHz, DMSO-d_6): 25.3, 26.6 (2 × q, 2 × CH$_3$), 36.5 (q, CH$_3$SO$_2$), 60.7 (d, C-4), 65.7 (t, C-7), 66.0 (d, C-2), 71.9 (t, C-1), 73.4 (d, C-6), 78.6 (d, C-3), 80.0 (d, C-5), 99.6 (d, PhCH), 108.0 (s, (CH$_3$)$_2$C), 126.1, 127.8, 128.5, 138.1 (Ph); Found: C 51.84, H 6.22, S 7.46, C$_{18}$H$_{26}$O$_9$S (418.47) requires C, 51.66; H, 6.26; S, 7.66%.

4.2.5. 3,5(R)-O-Benzylidene-1-deoxy-6,7-O-isopropylidene-1-iodo-D-glycero-D-gulitol (9)

The mixture of mesylate 8 (3.0 g, 7.2 mmol) and NaI (8.6 g, 57.4 mmol, 8 equiv.) in butanone (250 ml) was refluxed for 1.5 h. After cooling and evaporation in vacuo, a mixture of dichloromethane (100 ml), H$_2$O (80 ml), K$_2$CO$_3$ (1.04 g) and Na$_2$S$_2$O$_5$ · 5H$_2$O (2.35 g) was added to the residue and the resulting mixture was stirred for 20 min at r.t.. Phases were separated and aq. layer was extracted with dichloromethane (3 × 40 ml). Combined org. extracts were dried (Na$_2$SO$_4$) and evaporated in vacuo. Purification of the crude product by FLC (55 g, 17 × 3 cm, AcOEt) yielded 9 as a colourless solid (2.82 g, 87%); m.p. 173–175 °C; $[\alpha]_D^{20}$ − 8.4 (c 0.213, CHCl$_3$); IR (KBr): 3500–3200 (m, br, OH), 2991 (m), 2935 (m), 2875 (m), 1387 (m), 1372 (m), 1210 (m), 1183 (m), 1168 (m), 1091 (s), 1063 (s), 1032 (s), 1016 (s), 838 (m), 752 (m), 702 (s); ^{1}H

NMR (250 MHz, DMSO-d_6): 1.29, 1.35 (2 × 3H, 2 × s, 2 × CH$_3$), 3.34 (1H, dd, $J_{1A,1B}$ = 10.0, $J_{1A,2}$ = 4.9 Hz, H-1A), 3.46 (1H, dd, $J_{1A,1B}$ = 10.0, $J_{1B,2}$ = 2.1 Hz, H-1B), 3.54 (1H, dddd, $J_{2,3}$ = 8.4, $J_{2,0H}$ = 5.3, $J_{1A,2}$ = 4.9, $J_{1B,2}$ = 2.1 Hz, H-2), 3.59 (1H, dd, $J_{2,3}$ = 8.4, $J_{3,4}$ = 1.3 Hz, H-3), 3.75 (1H, ddd, $J_{4,OH}$ = 8.6, $J_{4,5}$ = 1.4, $J_{3,4}$ = 1.3 Hz, H-4), 3.83 (1H, dd, $J_{5,6}$ = 7.4 Hz, $J_{4,5}$ = 1.4 Hz, H-5), 3.95 (1H, dd, $J_{7A,7B}$ = 8.5, $J_{6,7A}$ = 5.5 Hz, H-7A), 4.02 (1H, dd, $J_{7A,7B}$ = 8.5, $J_{6,7B}$ = 6.3 Hz, H-7B), 4.26 (1H, ddd, $J_{5,6}$ = 7.4, $J_{6,7B}$ = 6.3, $J_{6,7A}$ = 5.5 Hz, H-6), 4.72 (1H, d, $J_{4,OH}$ = 8.6 Hz, 4-OH), 5.36 (1H, d, $J_{2,0H}$ = 5.3 Hz, 2-OH), 5.61 (1H, s, PhCH), 7.35–7.49 (5H, m, Ph); ^{13}C NMR (63 MHz, DMSO-d_6): 15.5 (t, C-1), 25.3, 26.6 (2 × q, 2 × CH$_3$), 60.8 (d, C-4), 65.7 (t, C-7), 66.3 (d, C-2), 73.4 (d, C-6), 80.0 (d, C-5), 82.1 (d, C-3), 99.7 (d, PhCH), 108.0 (s, (CH$_3$)$_2$C), 126.0, 127.8, 128.5, 138.1 (Ph); Found: C, 45.33; H, 5.15; I, 27.93. C$_{17}$H$_{23}$O$_6$I (450.27) requires C, 45.35; H, 5.15; I, 28.18%.

4.2.6. 3,5(S)-O-Benzylidene-1,2-dideoxy-6,7-O-isopropylidene-D-gluco-1-heptenitol (10)

The suspension of iodide 9 (7.13 g, 15.83 mmol) and Zn–Cu (19 g) in a mixture of acetone/water (300 ml, 4:1) was refluxed for 1.5 h. After cooling, filtration of solids and evaporation in vacuo, the residual aqueous layer was extracted with dichloromethane (3 × 60 ml). Combined org. phases were dried (Na$_2$SO$_4$) and evaporated in vacuo. Purification of the crude product by FLC (45 g, 15 × 3 cm, PE:AcOEt 3:1) yielded 10 as a colourless oil (4.17 g, 86%); $[\alpha]_D^{22}$ + 10.6 (c 0.368, CHCl$_3$); IR (film): 3600–3300 (m, br, OH), 2986 (s), 2934 (m), 2872 (m), 1453 (m), 1381 (s), 1339 (m), 1257 (s), 1219 (s), 1148 (s), 1094 (s), 1064 (s), 1029 (s), 928 (m), 889 (m), 844 (s), 812 (w), 759 (s), 700 (s); ^{1}H NMR (250 MHz, CDCl$_3$): 1.38, 1.45 (2 × 3H, 2 × s, 2 × CH$_3$), 2.29 (1H, d, $J_{4,OH}$ = 10.2 Hz, OH), 3.75 (1H, "dt", ddd, $J_{4,OH}$ = 10.2, $J_{3,4}$ = 1.3, $J_{4,5}$ = 1.3 Hz, H-4), 3.80 (1H, dd, $J_{5,6}$ = 8.0, $J_{4,5}$ = 1.3 Hz, H-5), 4.05 (1H, dd, $J_{7A,7B}$ = 8.7, $J_{6,7A}$ = 6.0 Hz, H-7A), 4.12 (1H, dd, $J_{7A,7B}$ = 8.7, $J_{6,7B}$ = 4.8 Hz, H-7B), 4.38 (1H, ddd, $J_{5,6}$ = 8.0, $J_{6,7A}$ = 6.0, $J_{6,7B}$ = 4.8 Hz, H-6), 4.45 (1H, dddd, $J_{2,3}$ = 4.9, $J_{1E,3}$ = 1.6, $J_{1Z,3}$ = 1.6, $J_{3,4}$ = 1.3 Hz, H-3), 5.34 (1H, "dt", ddd, $J_{1E,2}$ = 10.7, $J_{1E,1Z}$ = 1.6, $J_{1E,3}$ = 1.6 Hz, H-1E), 5.48 (1H, "dt", ddd, $J_{1Z,2}$ = 17.4, $J_{1E,1Z}$ = 1.6, $J_{1Z,3}$ = 1.6 Hz, H-1Z), 5.67 (1H, s, PhCH), 5.99 (1H, ddd, $J_{1Z,2}$ = 17.4, $J_{1E,2}$ = 10.7, $J_{2,3}$ = 4.9 Hz, H-2), 7.34–7.52 (5H, m, Ph); ^{13}C NMR (63 MHz, DMSO-d_6): 25.2, 27.0 (2 × q, 2 × CH$_3$), 65.2 (d, C-4), 66.7 (t, C-7), 73.4 (d, C-6), 80.6 (d, C-3), 100.8 (d, PhCH), 109.3 (s, (CH$_3$)$_2$C), 117.8 (t, C-1), 126.0, 128.3, 129.1, 134.1 (Ph), 137.5 (d, C-2); Found: C, 66.56; H, 7.32; C$_{17}$H$_{22}$O$_5$ (306.36) requires C, 66.65; H, 7.24%.

4.2.7. 3,5(S)-O-Benzylidene-1,2-dideoxy-D-gluco-1-heptenitol (11)

The solution of acetonide 10 (1.519 g, 4.96 mmol) in 85% AcOH (90 ml) was stirred at r.t. for 13.5 h. After evaporation in vacuo, the crude solid was purified by FLC

(80 g, 26 × 3.5 cm, CH_2Cl_2:MeOH 3:1) to furnish **11** as colourless solid (1.212 g, 92%); m.p. 170–171 °C; $[\alpha]_D^{21}$ + 4.5 (*c* 0.11, MeOH); IR (KBr): 3400–3200 (s, br, OH), 2947 (m), 2923 (m), 2868 (w), 1453 (m), 1420 (m), 1383 (m), 1352 (m), 1324 (m), 1166 (m), 1105 (s), 1071 (s), 1024 (s), 991(w), 918 (m), 887 (m), 848 (m), 731 (m), 696 (s), 669 (m); ^1H NMR (500 MHz, CD_3OD): 3.67 (1H, dd, $J_{7A,7B} = 11.6$, $J_{6,7A} = 5.0$ Hz, H-7A), 3.77 (1H, "t", dd, $J_{3,4} = J_{4,5} = 1.5$ Hz, H-4), 3.78 (1H, dd, $J_{7A,7B} = 11.6$, $J_{6,7B} = 2.7$ Hz, H-7B), 3.87 (1H, dd, $J_{5,6} = 8.8$, $J_{4,5} = 1.5$ Hz, H-5), 3.91 (1H, ddd, $J_{5,6} = 8.8$, $J_{6,7A} = 5.0$, $J_{6,7B} = 2.7$ Hz, H-6), 4.45 (1H,"dq", dddd, $J_{2,3} = 5.5$, $J_{3,4} = J_{1Z,3} = 1.5$ Hz, $J_{1E,3} = 1.5$ Hz, H-3), 5.25 (1H, ddd, $J_{1E,2} = 10.7$, $J_{1Z,1E} = 1.6$, $J_{1E,3} = 1.5$ Hz, H-1E), 5.41 (1H, "dt", ddd, $J_{1Z,2} = 17.4$, $J_{1Z,1E} = 1.6$, $J_{1Z,3} = 1.5$ Hz, H-1Z), 5.67 (1H, s, PhC*H*), 3.03 (1H, ddd, $J_{1Z,2} = 17.4$, $J_{1E,2} = 10.7$, $J_{2,3} = 5.5$ Hz, H-2), 7.30–7.57 (5H, m, Ph); ^{13}C NMR (125 MHz, CD_3OD): 64.2 (t, C-7), 66.2 (d, C-4), 70.8 (d, C-6), 80.6 (d, C-5), 82.7 (d, C-3), 102.2 (d, PhCH), 117.2 (t, C-1), 127.5, 129.0, 129.7, 136.7 (Ph), 139.9 (d, C-2) ; Found: C, 63.27; H, 6.88; $C_{14}H_{18}O_5$ (266.30) requires C, 63.14; H, 6.81%.

4.2.8. 3,5(S)-O-Benzylidene-1,2-dideoxy-6-phenyl-L-ido-1-hexenitol (L-ido-**12**) and 3,5(S)-O-benzylidene-1,2-dideoxy-6-phenyl-D-gluco-1-hexenitol (D-gluco-**12**)

The suspension of triol **11** (5.104 g, 19.17 mmol) and $NaIO_4$ (4.51 g, 21.08 mmol, 1.1 equiv.) in a mixture of $MeOH/H_2O$ (900 ml, 2:1) was stirred at r.t. for 1.5 h. After filtration and evaporation in vacuo, the residual aq. layer was extracted with dichloromethane (4 × 100 ml). Combined org. phases were dried (Na_2SO_4) and evaporated in vacuo obtaining a crude aldehyde as colourless oil (4.2 g), which was immediately used in a Grignard addition without any purification. Thus, a solution of crude aldehyde (4.20 g, 17.93 mmol) in dry THF (40 ml) was slowly added dropwise to the stirred solution of PhMgBr (freshly prepared from PhBr (15.42 g, 98.19 mmol, 5.5 equiv.) and magnesium turnings (2.40 g, 98.19 mmol, 5.5 equiv.)) in dry THF (100 ml) under Ar. The reaction mixture was stirred at r.t. for 24 h and then hydrolysed with sat. aq. NH_4Cl solution (20 ml). The mixture was extracted with Et_2O (3 × 40 ml). Combined org. phases were dried (Na_2SO_4) and evaporated in vacuo. Purification of the crude residue by FLC (60 g, 20 × 5 cm, PE:AcOEt 8:2) yielded L-ido-**12** (2.246 g, 41%) and D-gluco-**12** (0.613 g, 21%) as colourless solids. Data for L-ido-**12**: m.p. 89–90 °C; $[\alpha]_D^{24}$ + 27.0 (*c* 0.13, CHCl$_3$); IR (KBr): 3550–3300 (s, br, OH), 3034 (m), 2938 (m), 2901 (m), 2866 (m), 1557 (s), 1495 (m), 1422 (s), 1323 (m), 1198 (m), 1155 (s), 1117 (m), 1067 (s, br). 927 (s), 891 (m), 845 (m), 760 (s), 700 (s); ^1H NMR (400 MHz, CDCl$_3$): 2.46 (1H, d, $J_{4,OH} = 10.7$ Hz, OH-4), 2.95 (1H, s, OH-6), 3.20 (1H, "dt", ddd, $J_{4,OH} = 10.7$, $J_{3,4} = 1.5$, $J_{4,5} = 1.2$ Hz, H-4), 3.83 (1H, dd, $J_{5,6} = 8.5$, $J_{4,5} = 1.5$ Hz, H-5), 4.27 (1H, dddd, $J_{2,3} = 5.0$, $J_{3,4} = J_{1Z,3} = J_{1E,3} = 1.5$ Hz, H-3), 5.03 (1H, d, $J_{5,6} = 8.5$ Hz, H-6), 5.28 (1H, "dt", ddd, $J_{1E,2} = 10.8$, $J_{1E,3} = J_{1Z,1E} = 1.5$ Hz, H-1E), 5.39

(1H, "dt", ddd, $J_{1Z,2} = 17.3$, $J_{1Z,3} = J_{1Z,1E} = 1.5$ Hz, H-1Z), 5.70 (1H, s, PhC*H*), 5.86 (1H, ddd, $J_{1Z,2} = 17.3$, $J_{1E,2} = 10.8$, $J_{2,3} = 5.0$ Hz, H-2), 7.27–7.60 (10H, m, 2 × Ph); ^{13}C NMR (100 MHz, CDCl$_3$): 65.0 (d, C-4), 73.3 (d, C-6), 80.6 (d, C-3), 84.8 (d, C-5), 101.2 (d, PhCH), 117.9 (t, C-1), 126.2, 127.3, 128.3, 128.3, 128.5, 129.3, (all d, all Ph) 133.6 (d, C-2), 137.3, 138.3, (2 × s, 2 × Ph); Found: C, 73.02; H, 6.45; $C_{19}H_{20}O_4$ (312.36) requires C, 73.06; H, 6.45%. Data for D-gluco-**12**: m.p. 144–147 °C; $[\alpha]_D^{22}$ + 30.8 (*c* 0.08, CHCl$_3$); IR (KBr): 3500–3250 (s, br, OH), 3057 (m), 3034 (m), 2910 (m), 2926 (m), 2861 (m), 2845 (m), 1497 (w), 1458 (m), 1450 (m), 1418 (m), 1340 (m), 1333 (m), 1213 (m), 1163 (s), 1097 (s), 1086 (s), 1074 (s), 1061 (s), 1038 (s), 1013 (s), 935 (s), 839 (s), 756 (s), 700 (s); ^1H NMR (400 MHz, CDCl$_3$): 2.94 (1H, s, OH), 3.29 (1H, s, OH), 3.83 (1H, s, H-4), 3.89 (1H, dd, $J_{5,6} = 6.6$, $J_{3,5} = 1.2$ Hz, H-5), 4.36 (1H, dddd, $J_{2,3} = 5.0$, $J_{1E,3} = J_{1Z,3} = 1.6$, $J_{3,5} = 1.2$ Hz, H-3), 5.05 (1H, d, $J_{5,6} = 6.6$ Hz, H-6), 5.33 (1H, "dt", ddd, $J_{1E,2} = 10.7$, $J_{1E,3} = 1.6$, $J_{1Z,1E} = 1.5$ Hz, H-1E), 5.34 (1H, "dt", ddd, $J_{1Z,2} = 17.3$, $J_{1Z,3} = 1.6$, $J_{1Z,1E} = 1.5$ Hz, H-1Z), 5.61 (1H, s, PhC*H*), 5.96 (1H, ddd, $J_{1Z,2} = 17.3$, $J_{1E,2} = 10.7$, $J_{2,3} = 5.0$ Hz, H-2), 7.25-7.48 (10H, m, 2 × Ph); ^{13}C NMR (100 MHz, CDCl$_3$): 65.5 (d, C-4), 73.3 (d, C-6), 80.5 (d, C-3), 82.3 (d, C-5), 100.6 (d, PhCH), 117.7 (t, C-1), 125.0, 126.5, 127.8, 128.1, 128.3, 128.9, (all d, all Ph), 133.9 (d, C-2), 137.5, 140.7 (2 × s, 2 × Ph); Found: C 73.06, H 6.40, $C_{19}H_{20}O_4$ (312.36) requires C, 73.06; H, 6.45%.

4.2.9. 3-O-Benzyl-1,2-dideoxy-6-phenyl-L-ido-1-hexenitol (L-ido-**1**)

To a solution of acetal L-ido-**12** (372 mg, 1.19 mmol) and NaBH$_3$CN (236 mg, 3.57 mmol, 3 equiv.) in dry MeCN (40 ml) was added through septum TiCl$_4$ (678 mg, 3.57 mmol, 3 equiv.) dropwise at 0 °C over 1 min under Ar. The reaction mixture was stirred for 24 h, while the temperature reached r.t. After hydrolysis with sat. aq. NH$_4$Cl solution (20 ml), the mixture was evaporated in vacuo. The residue was extracted with CH$_2$Cl$_2$ (3 × 20 ml), combined org. extracts were dried (Na$_2$SO$_4$) and evaporated in vacuo. Purification of the crude product by FLC (14 g, 9 × 2.5 cm, PE:AcOEt 7:3) yielded L-ido-**1** as colourless oil (242 mg, 65%); $[\alpha]_D^{24}$ + 54.0 (*c* 0.12, CHCl$_3$); IR (film): 3600–3150 (s, br, OH), 3063 (m), 3031 (m), 2902 (m, br), 1604 (w), 1495 (m), 1454 (m), 1393 (m), 1200 (m), 1070 (s, br), 933 (w), 761 (m), 754 (m), 700 (s); ^1H NMR (500 MHz, CDCl$_3$): 2.88 (1H, d, $J_{5,OH} = 7.6$ Hz, OH-5), 3.01 (1H, dd, $J_{4,OH} = 2.9$, $J_{5,4OH} = 1.1$ Hz, OH-4), 3.24 (1H, d, $J_{6,OH} = 1.8$ Hz, OH-6), 3.43 (1H, ddd, $J_{3,4} = 7.7$, $J_{4,OH} = 2.9$, $J_{4,5} = 1.3$ Hz, H-4), 3.62 (1H, dddd, $J_{5,OH} = 7.6$, $J_{5,6} = 6.5$, $J_{4,5} = 1.3$, $J_{5,4OH} = 1.1$ Hz, H-5), 3.96 (1H, "t", dd, $J_{2,3} = 7.9$, $J_{3,4} = 7.7$ Hz, H-3), 4.32, 4.61 (2 × 1H, 2 × d, $J_{OCH2Ph} = 11.4$ Hz, OC*H*$_2$Ph), 4.81 (1H, dd, $J_{5,6} = 6.5$, $J_{6,OH} = 1.8$ Hz, H-6), 5.38 (1H, dd, $J_{1E,2} = 10.0$, $J_{1Z,1E} = 1.6$ Hz, H-1E), 5.39 (1H, dd, $J_{1Z,2} = 17.6$, $J_{1Z,1E} = 1.6$ Hz, H-1Z), 5.59 (1H, ddd, $J_{1Z,2} = 17.6$, $J_{1E,2} = 10.0$, $J_{2,3} = 7.9$ Hz, H-2), 7.28–7.40

(10H, m, 2 × Ph); ^{13}C NMR (125 MHz, CDCl$_3$): 70.6 (t, OCH$_2$Ph), 73.1 (d, C-4), 74.4 (d, C-5), 75.6 (d, C-6), 82.0 (d, C-3), 121.5 (t, C-1), 126.9, 128.0, 128.0, 128.4, 128.6 (all d, all Ph), 134.0 (d, C-2), 137.5, 140.1 (2 × d, 2 × Ph); Found: C, 72.18; H, 7.07. C$_{19}$H$_{22}$O$_4$ (314.38) requires C, 72.59; H, 7.05%.

4.2.10. 3-O-Benzyl-1,2-dideoxy-6-phenyl-D-gluco-1-hexenitol (D-gluco-1)

To a solution of acetal D-gluco-12 (400 mg, 1.28 mmol) and NaBH$_3$CN (254 mg, 3.84 mmol, 3 equiv.) in dry MeCN (40 ml) was added through septum TiCl$_4$ (729 mg, 3.84 mmol, 3 equiv.) dropwise at 0 °C over 1 min under Ar. The reaction mixture was stirred for 24 h, while the temperature reached r.t. After hydrolysis with sat. aq. NH$_4$Cl solution (20 ml), the mixture was evaporated. The residue was extracted with CH$_2$Cl$_2$ (3 × 20 ml), combined org. extracts were dried (Na$_2$SO$_4$) and evaporated in vacuo. Purification of the crude product by FLC (13 g, 9 × 2.5 cm, PE:AcOEt 3:1) yielded D-gluco-1 as colourless solid (254 mg, 63%); m.p. 86–88 °C; [α]$_D^{21}$ + 13.6 (c 0.12, CHCl$_3$); IR (KBr): 3533 (s, OH), 3463 (s, br, OH), 3398 (s, br, OH), 3029 (w), 2946 (w), 2910 (w), 2887 (m), 2871 (m), 1496 (w), 1454 (m), 1391 (m), 1329 (m), 1285 (m), 1206 (m), 1129 (s), 1059 (s), 1038 (s), 1020 (s), 988 (m), 939 (m), 769 (s), 730 (s), 700 (s); ^{1}H NMR (500 MHz, CDCl$_3$): 3.04 (1H, d, $J_{5,OH}$ = 8.0 Hz, OH-5), 3.10 (1H, dd, $J_{4,OH}$ = 2.8, $J_{5,OH-4}$ = 1.0 Hz, OH-4), 3.40 (1H, d, $J_{6,OH}$ = 7.3 Hz, OH-6), 3.64 (1H, ddd, $J_{3,4}$ = 7.3, $J_{4,OH}$ = 2.8, $J_{4,5}$ = 1.2 Hz, H-4), 3.76 (1H, dddd, $J_{5,OH}$ = 8.0, $J_{5,6}$ = 5.3, $J_{4,5}$ = 1.2, $J_{5,4OH}$ = 1.0 Hz, H-5), 3.97 (1H, dd, $J_{2,3}$ = 8.2, $J_{3,4}$ = 7.3 Hz, H-3), 4.30, 4.60 (2×1H, 2×d, J_{OCH2Ph} = 11.4 Hz, OCH$_2$Ph), 4.93 (1H, dd, $J_{5,6}$ = 5.3, $J_{6,OH}$ = 7.3 Hz, H-6), 5.38 (1H, dd, $J_{1Z,2}$ = 17.9, $J_{1Z,1E}$ = 1.8 Hz, H-1Z), 5.39 (1H, dd, $J_{1E,2}$ = 9.8, $J_{1Z,1E}$ = 1.6 Hz, H-1E), 5.64 (1H, ddd, $J_{1Z,2}$ = 17.9, $J_{1E,2}$ = 9.8, $J_{2,3}$ = 8.2 Hz, H-2), 7.28–7.40 (10H, m, 2 × Ph); ^{13}C NMR (125 MHz, CDCl$_3$): 70.6 (t, OCH$_2$Ph), 72.2 (d, C-4), 73.1 (d, C-5), 76.3 (d, C-6), 82.2 (d, C-3), 121.2 (t, C-1), 125.8, 127.6, 128.0, 128.0, 128.5, 128.6, (all d, all Ph), 134.1 (d, C-2), 137.5, 140.9 (2 × d, 2 × Ph); Found: C 72.21, H 7.12, C$_{19}$H$_{22}$O$_4$ (314.38) requires C, 72.59; H, 7.05%.

4.3. Palladium(II)-catalysed bicyclisation of polyols 1 and 6

4.3.1. General procedure: 1,4:2,5-Dianhydro-3-O-benzyl-D-glycero-D-gulo-heptitol (D-glycero-D-gulo-14)

The mixture of benzylated alkenitols D-gluco-6b/D-manno-6b (150 mg, 0.56 mmol, 63:37), PdCl$_2$ (10 mg, 0.06 mmol, 0.1 equiv.), anhydrous CuCl$_2$ (225 mg, 1.68 mmol, 3 equiv.) and anhydrous AcONa (138 mg, 1.68 mmol, 3 equiv.) in glacial AcOH (15 ml) were stirred at 25–30 °C under Ar for 23 h. Reaction mixture was filtered through Celite® pad (1 × 2 cm) and washed with AcOH (2 × 5 ml). Solvent was evaporated in vacuo and the residue distributed between water (30 ml) and AcOEt (20 ml). Water

phase was extracted with AcOEt (2 × 20 ml) and combined org. layers were washed with 10% aq. NaHCO$_3$ solution (30 ml), dried (Na$_2$SO$_4$) and concentrated in vacuo. Purification of the crude product by FLC (12 g, 33% AcOEt in hexanes) yielded two fractions: first one with R_f 0.5 contained a mixture of acetals 16/17 (50 mg, 33%) as colourless oil; ^{1}H NMR (300 MHz, CDCl$_3$): 1.46 (3H, s, CH$_3$), 1.48 (3H, s, CH$_3$), 3.50 (bd, J = 4.8 Hz), 3.63 (1H, bs), 3.81 (2H, dd, J = 7.6, J = 5.8 Hz), 3.93 (1H, bs), 4.04 (2H, dd, J = 2.2, J = 12.4 Hz), 4.05 (1H, s), 4.25 (1H, d, J = 7.7 Hz), 4.46 (2H, m), 4.51 (2H, d, $J_{A,B}$ = 11.7 Hz, PhCH$_2$), 4.67 (1H, s), 4.71 (2H, d, $J_{A,B}$ = 11.7 Hz, PhCH$_2$), 7.27–7.38 (5H, m, Ph); ^{13}C NMR (75 MHz, CDCl$_3$) *major isomer*: 20.8 (q, C-1), 65.6 (t, PhCH$_2$), 68.9 (d, C-6), 71.2 (t, C-7), 71.8 (d, C-5), 75.5 (d, C-4), 77.4 (d, C-3), 107.2 (s, C-2), 127.7, 128.1, 128.5 (all d, all Ph), 136.9 (s, Ph), *minor isomer*: 20.3 (q, C-1), 63.6 (d, C-6), 66.9 (t, PhCH$_2$), 72.0 (t, C-7), 78.2 (d, C-5), 79.3 (d, C-4), 81.0 (d, C-3), 107.0 (s, C-2), 127.7, 128.1, 128.5 (all d, all Ph), 136.9 (s, Ph). The second fraction with R_f 0.36 contained pure bicycle D-glycero-D-gulo-14 (90 mg, 60%) as colourless oil; ^{1}H NMR (300 MHz, CDCl$_3$): 3.78 (1H, d, $J_{1A,1B}$ = 8.7 Hz, H-1A), 3.85 (1H, d, $J_{1A,1B}$ = 8.7 Hz, H-1B), 3.91 (1H, m, H-6), 4.01 (1H, bs, OH), 4.11 (3H, m, H-3, H-7), 4.17 (1H, m, H-5), 4.24 (1H, m, H-3), 4.39 (1H, m, H-4), 4.60 (2H, s, PhCH$_2$), 7.27–7.38 (5H, m, Ph); ^{13}C NMR (75 MHz, CDCl$_3$): 64.5 (t, PhCH$_2$), 70.0 (d, C-6), 72.2 (t, C-7), 73.6 (t, C-1), 75.8 (d, C-4), 76.8 (d, C-2), 80.8 (d, C-5), 81.4 (d, C-3), 127.8, 128.0, 128.5 (all d, all Ph), 137.1 (s, Ph).

An analogous bicyclisation of diastereomerically pure D-manno-6b [17,10b] in the same reaction conditions gave identical mixture of acetals 16/17 (57%).

4.3.2. 1,4:2,5-Dianhydro-3-O-benzyl-7-O-(1,1′-biphenyl-4-yl)carbonyl-D-glycero-D-gulo-heptitol (D-glycero-D-gulo-15)

To a solution of crude D-glycero-D-gulo-14 (50 mg, 0.19 mmol) and Et$_3$N (96 mg, 0.95 mmol, 5 equiv.) in CH$_2$Cl$_2$ (7 ml) was added 1,1′-biphenyl-4-carbonyl chloride (103 mg, 0.47 mmol, 2.5 equiv.) in CH$_2$Cl$_2$ (3 ml) and the reaction mixture was stirred at r.t. for 36 h. Solvents were removed in vacuo and the residue was purified by FLC (30 g, 5% AcOEt in toluene). Combined fractions with R_f 0.45 (17% AcOEt in toluene) were concentrated in vacuo and the obtained solid was crystallised from AcOEt/Et$_2$O providing D-glycero-D-gulo-15 (46 mg, 54%) as colourless needles; m.p. 166–167 °C; [α]$_D^{25}$ − 30.4 (c 0.17, CHCl$_3$); ^{1}H NMR (300 MHz, CDCl$_3$): 3.89 (1H, d, $J_{1A,1B}$ = 8.3 Hz, H-1A), 3.95 (1H, bd, $J_{1A,1B}$ = 8.3 Hz, H-1B), 4.25 (2H, bs, H-5, H-6), 4.26 (1H, bs, H-4), 4.33 (1H, bs, H-3), 4.42 (1H, d, $J_{1B,2}$ = 2.7 Hz, H-2), 4.50 (1H, dd, $J_{6,7A}$ = 4.3, $J_{7A,7B}$ = 11.3 Hz, H-7A), 4.62, 4.69 (2H, 2 × d, $J_{A,B}$ = 12.2 Hz, PhCH$_2$), 4.78 (1H, d, $J_{7A,7B}$ = 11.3 Hz, H-7B), 7.29–7.51, 7.60–7.70 (14H 2 × m, Ph); ^{13}C NMR (75 MHz, CDCl$_3$): 67.6 (t, PhCH$_2$), 72.3 (d, C-6), 69.1 (t, C-7), 73.7 (t, C-1), 75.9 (C-2), 77.0 (d, C-4), 81.0 (t, C-5, C-3), 127.0, 127.2, 127.8, 128.1, 128.2, 128.5, 128.9, 130.2 (all d, all Ph), 137.2, 139.9, 143.9 (all

s, all Ph), 167.0 (s, CO); Found: C, 72.84; H, 5.82. $C_{27}H_{26}O_6$ (446.49) requires C, 72.63; H, 5.87%.

4.3.3. 1,4:2,5-Dianhydro-3-O-benzyl-D-glycero-L-gulo-heptitol (D-glycero-L-gulo-20)

According to general procedure 4.3.1.: mixture of D-*gulo*-**6c**/D-*ido*-**6c** (150 mg, 0.56 mmol, 52:48), $PdCl_2$ (10 mg, 0.06 mmol, 0.1 equiv.), $CuCl_2$ (225 mg, 1.68 mmol, 3 equiv.), AcONa (138 mg, 1.68 mmol, 3 equiv.) in glacial AcOH (10 ml), r.t., 44 h: D-*glycero*-L-*gulo*-**20** (64 mg, 43%) as colourless oil; R_f 0.21 (AcOEt); ^{13}C NMR (75 MHz, $CDCl_3$): 64.3 (t, PhCH_2), 70.9 (d, C-6), 72.3 (t, C-7), 73.6 (t, C-1), 76.1 (d, C-4), 77.2 (d, C-2), 78.4 (d, C-5) 81.4 (d, C-3), 127.8, 127.9, 128.2, 128.5, 128.7 (all d, all Ph), 137.3 (s, Ph) and **18** or **19** (44 mg, 30%) as colourless oil; R_f 0.56 (AcOEt); ^{13}C NMR (75 MHz, $CDCl_3$): 20.9 (q, C-1), 64.3 (t, PhCH_2), 71.3 (d, C-6), 72.0 (t, C-7), 75.3 (d, C-5), 76.0 (t, C-7), 77.4 (d, C-4), 81.4 (d, C-3), 107.3 (s, C-2), 127.8–128.7 (2 × d, Ph), 137.1 (s, Ph).

4.3.4. 1,4:2,5-Dianhydro-3-O-benzyl-6,7-bis-O-(1,1′-biphenyl-4-yl)carbonyl-D-glycero-L-gulo-heptitol (D-glycero-L-gulo-21)

To a solution of crude D-*glycero*-L-*gulo*-**20** (50 mg, 0.19 mmol) and Et_3N (96 mg, 0.95 mmol, 5 equiv.) in CH_2Cl_2 (10 ml) was added 1,1′-biphenyl-4-carbonyl chloride (103 mg, 0.47 mmol, 2.5 equiv.) and the reaction mixture was stirred at r.t. for 36 h. Solvents were removed in vacuo and the residue was purified by FLC (30 g, 5% AcOEt in toluene). Combined fractions with R_f 0.45 (17% AcOEt in toluene) were concentrated in vacuo and the obtained solid was crystallised from AcOEt/Et_2O providing D-*glycero*-L-*gulo*-**21** (60 mg, 50%) as colourless needles; m.p. 188–189 °C; $[\alpha]_D^{25}$ + 30.6 (c 0.06, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): 3.94 (1H, bd, $J_{1A,1B}$ = 8.8 Hz, H-1A), 4.12 (1H, d, $J_{1A,1B}$ = 8.8 Hz, H-1B), 4.66 (1H, d, $J_{5,6}$ = 8.3 Hz, H-5), 4.63 (1H, bs, H-4), 4.61 (1H, s, H-3), 4.35 (1H, s, H-2), 4.28 (1H, ddd, $J_{6,7A}$ = $J_{6,7B}$ = 3.0, $J_{7A,7B}$ = 9.4 Hz, H-7), 4.58, 4.72 (4H, 2 × d, $J_{A,B}$ = 11.7 Hz, PhCH_2), 5.90 (1H, ddd, $J_{6,7A}$ = 3.8, $J_{6,7B}$ = 4.7, $J_{5,6}$ = 8.3 Hz, H-6), 7.29–7.51, 7.59–7.70 (23H, 2 × m, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): 63.7 (t, PhCH_2), 72.3 (d, C-6), 72.4 (t, C-7), 73.5 (t, C-1), 75.6 (d, C-2), 76.1 (d, C-4), 80.7 (d, C-5), 81.5 (d, C-3), 127.0, 127.1, 127.3, 127.9, 128.1, 128.2, 128.3, 128.6, 128.7, 128.9, 130.2, 130.4 (all d, all Ph), 137.2, 139.9, 140.0, 145.7, 145.9 (all s, all Ph), 166.0 (s, CO). Found: C, 72.84; H, 5.82. $C_{40}H_{43}O_7$ (626.67) requires C, 76.63; H, 5.52%.

4.3.5. 2,7-Anhydro-3,6-di-O-benzyl-D-glycero-β-D-talo-oct-2-ulofuranose (22) and 2,7-anhydro-3,6-di-O-benzyl-D-glycero-β-D-galacto-oct-2-ulofuranose (23)

According to general procedure 4.3.1.: mixture of D-*glycero*-D-*talo*-**6d**/D-*glycero*-D-*galacto*-**6d** [14] (220 mg, 0.57 mmol), $PdCl_2$ (10 mg, 0.06 mmol, 0.1 equiv.), $CuCl_2$ (264 mg, 1.71 mmol, 3 equiv.) and AcONa (140 mg,

1.71 mmol, 3 equiv.) in glacial AcOH (5 ml), r.t., 8 h, colour of the reaction mixture remained blue-green, FLC (10 g, 33% AcOEt in hexanes): D-*glycero*-β-D-*talo*-ulofuranose **22** (35 mg, 16%) as a pale yellow oil; R_f 0.45; ^{1}H NMR (300 MHz, $CDCl_3$): 1.51 (3H, s, H-1), 3.36 (1H, ddd, $J_{7,8B}$ = 2.5, $J_{7,8A}$ = 3.0, $J_{5,7}$ = 9.2 Hz, H-7), 3.58 (1H, dd, $J_{7,8A}$ = 3.5, $J_{8A,8B}$ = 11.5 Hz, H-8A), 3.61 (1H, dd, $J_{5,6}$ = 4.3, $J_{6,7}$ = 9.2 Hz, H-6), 3.69 (1H, dd, $J_{7,8B}$ = 2.6, $J_{8A,8B}$ = 11.5 Hz, H-8B), 4.01 (1H, d, $J_{3,4}$ = 6.2 Hz, H-4), 4.38 (1H, d, $J_{5,6}$ = 4.3 Hz, H-5), 4.50 (1H, d, $J_{3,4}$ = 6.2 Hz, H-3), 4.53 (1H, d, $J_{A,B}$ = 11.3 Hz, PhCH_2), 4.66 (1H, d, $J_{A,B}$ = 11.5 Hz, PhCH_2), 4.68 (1H, d, $J_{A,B}$ = 11.3 Hz, PhCH_2), 4.73 (1H, d, $J_{A,B}$ = 11.5 Hz, PhCH_2), 7.28–7.44 (10H, m, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): 19.5 (q, C-1), 62.3 (t, PhCH_2), 69.2, 69.8 (2 × d, C-4, C-7), 72.1 (t, C-8), 73.9 (d, C-6), 74.7 (t, PhCH_2), 81.6, 82.2 (2 × d, C-3, C-5), 106.8 (s, C-2), 128.0, 128.1, 128.3, 128.5, 128.6 (all d, all Ph), 136.6, 137.4 (all s, Ph) and D-*glycero*-β-D-*galacto*-ulofuranose **23** (30 mg, 14%) as a colourless oil; R_f 0.61; ^{1}H NMR (300 MHz, $CDCl_3$): 1.46 (3H, s, H-1), 3.60-3.85 (5H, m, J = 2.4, J = 2.7, J = 11.4, J = 12.0 Hz, H-4, H-5, H-7, H-8), 4.07 (1H, d, J = 3.9 Hz, H-3), 4.37 (1H, d, J = 1.8 Hz, H-6), 4.60 (2H, "dd", overlapped 2 × d, $J_{A,B}$ = 11.5 Hz, PhCH_2), 4.71 (2H, s, PhCH_2); ^{13}C NMR (75 MHz, $CDCl_3$): 22.5 (q, C-1), 61.8 (t, PhCH_2), 69.8 (d, C-7), 72.4, 72.9 (2 × t, C-8, PhCH_2), 74.0, 75.5 (2 × d, C-4, C-6), 81.8 (d, C-5), 91.0 (d, C-3), 104.3 (s, C-2), 127.9, 128.0, 128.1, 128.2, 128.5, 128.6 (all d, all Ph), 137.4, 137.9 (2 × s, 2 × Ph).

4.3.6. 1,4:2,5-Dianhydro-3-O-benzyl-6-phenyl-L-glycero-D-gulitol (L-glycero-D-gulo-2)

According to general procedure 4.3.1.: mixture of hexenitol L-*ido*-**1** (200 mg, 0.636 mmol), $PdCl_2$ (11 mg, 0.064 mmol, 0.1 equiv.), $CuCl_2$ (257 mg, 1.91 mmol, 3 equiv.) and AcONa (157 mg, 1.91 mmol, 3 equiv.) in glacial AcOH (8 ml), r.t., 26 h, colour of the reaction mixture changed from grass-green to ochre, FLC (3 g, 8 × 1 cm, PE:AcOEt 1:2): L-*glycero*-D-*gulo*-**2** (145 mg, 73%) as colourless solid; m.p. 129–130 °C; $[\alpha]_D^{20}$ − 5.1 (c 0.415, $CHCl_3$). IR (KBr): 3454 (s, br, OH), 3030 (m), 3006 (m), 2958 (m), 2935 (m), 2894 (m), 1493 (m), 1450 (m), 1403 (m), 1359 (m), 1114 (s), 1152 (s), 1143 (s), 1006 (s), 958 (m), 895 (s), 872 (s), 832 (m), 764 (s), 753 (s), 703 (s); ^{1}H NMR (500 MHz, $CDCl_3$): 2.83 (1H, d, $J_{6,OH}$ = 1.7 Hz, OH), 3.73 (1H, dd, $J_{2,3}$ = 2.6, $J_{1A,2}$ = 1.2 Hz, H-2), 3.95 (1H, "dt", ddd, $J_{1A,1B}$ = 8.6, $J_{1A,2}$ = 1.2, $J_{1A,4}$ = 1.0 Hz, H-1A), 4.04 (1H, d, $J_{1A,1B}$ = 8.6 Hz, H-1B), 4.15 (1H, d, $J_{2,3}$ = 2.6 Hz, H-3), 4.20 (1H, d, $J_{5,6}$ = 8.9 Hz, H-5), 4.37 (1H, bs, H-4), 4.50, 4.61 (2H, 2 × d, $J_{A,B}$ = 11.9 Hz, PhCH_2), 4.99 (1H, dd, $J_{5,6}$ = 8.9, $J_{6,OH}$ = 1.7 Hz, H-6), 7.24–7.42 (10H, m, 2 × Ph); ^{13}C NMR (125 MHz, $CDCl_3$): 72.3 (t, PhCH_2), 73.7 (t, C-1), 74.3 (d, C-6), 75.8 (d, C-2), 77.3 (d, C-4), 81.6 (d, C-5), 86.8 (d, C-3), 126.7, 127.8, 128.0, 128.1, 128.4, 128.5 (all d, all Ph), 137.2, 139.7 (2 × s, Ph). Found: C 73.15, H 6.46, $C_{19}H_{20}O_4$ (312.36) requires C, 73.06; H, 6.45%.

4.3.7. 1,4:2,5-Dianhydro-3-O-benzyl-6-phenyl-D-glycero-D-gulitol (D-glycero-D-gulo-2)

According to general procedure 4.3.1.: mixture of hexenitol D-gluco-**1** (164 mg, 0.522 mmol) PdCl$_2$ (9 mg, 0.052 mmol, 0.1 equiv.), CuCl$_2$ (210 mg, 1.56 mmol, 3 equiv.) and AcONa (128 mg, 1.56 mmol, 3 equiv.) in glacial AcOH (6 ml), 50 °C, 26 h, colour of the reaction mixture changed from grass-green to ochre, FLC (8 g, 7 × 2 cm, PE:AcOEt 2:1): D-glycero-D-gulo-**2** (115 mg, 71%); m.p. 86–88 °C; $[\alpha]_D^{20}$ − 54.4 (c 0.125, CHCl$_3$). IR (KBr): 3385 (s, br, OH), 3062 (w), 3024 (w), 2956 (w), 2910 (m), 2890 (m), 1492 (m), 1450 (m), 1364 (m), 1197 (m), 1143 (s), 1049 (s), 1009 (s), 901 (s), 870 (s), 845 (m), 751 (s), 741 (s), 701 (s); ^{1}H NMR (500 MHz, CDCl$_3$): 2.53 (1H, d, $J_{6,OH}$ = 4.8 Hz, OH), 3.97 (1H, "dt", ddd, $J_{1A,1B}$ = 8.5, $J_{1A,2}$ = 1.2, $J_{1A,4}$ = 1.0 Hz, H-1A), 4.02 (1H, d, $J_{1A,1B}$ = 8.5 Hz, H-1B), 4.23 (1H, d, $J_{2,3}$ = 2.6 Hz, H-3), 4.31 (1H, d, $J_{1A,4}$ = 1.0 Hz, H-4), 4.36 (1H, d, $J_{5,6}$ = 8.2 Hz, H-5), 4.40 (1H, dd, $J_{2,3}$ = 2.6, $J_{1A,2}$ = 1.2 Hz, H-2), 4.56, 4.65 (2H, 2 × d, $J_{A,B}$ = 11.9 Hz, PhCH$_2$), 4.92 (1H, dd, $J_{5,6}$ = 8.2, $J_{6,OH}$ = 4.8 Hz, H-6), 7.27–7.50 (10H, m, 2 × Ph); ^{13}C NMR (125 MHz, CDCl$_3$): 72.2 (t, PhCH$_2$), 72.8 (d, C-6), 74.0 (t, C-1), 76.2 (d, C-2), 76.8 (d, C-4), 81.1 (d, C-3), 84.7 (d, C-5), 126.8, 127.8, 128.0, 128.1, 128.5(all d, all Ph), 137.3, 141.9 (2 × s, Ph). Found: C, 72.85; H, 6.52. C$_{19}$H$_{20}$O$_4$ (312.36) requires C, 73.06; H, 6.45%.

4.4. Crystal structure determination of D-glycero-L-gulo21

Crystals of D-glycero-L-gulo-**21** suitable for X-ray structure analysis were obtained by crystallisation from AcOEt/Et$_2$O. Diffraction data have been collected on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and Siemens XSCANS software [23]. The structure was solved by direct methods with SHELXS-97 [24] and refined by LSQ procedure against $F^2(hkl)$ with SHELXL-97 [25]. Geometrical calculations were performed using SHELXL-97 [25].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 285097.

Acknowledgements

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