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Stereocontrolled synthesis of four diastereomeric *C*-aryl manno- and talofuranosides

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ABSTRACT

In a chiral-pool synthesis starting from D-mannono-1,4-lactone **1a**, the four diastereomeric *C*-aryl furanosides (1*S*,4*R*)-**4a**, (1*S*,4*S*)-**4b**, (1*R*,4*R*)-**4c,** and (1*R*,4*S*)-**4d** were obtained in a stereocontrolled manner. The key steps of the synthetic pathway comprise a stereoselective reduction of the diastereomeric hemiketals (4*R*)-**2a** and (4*S*)-**2b** as well as a stereospecific cycloetherification of the resulting diols (1*R*,4*R*)-**5a**, (1*S*,4*R*)-**5c,** and (1*S*,4*S*)-**5d**. This ring closure which led to the desired C-glycosides was achieved by a Mitsunobu reaction or by preparing the 1-*O*-benzoyl-4-*O*-methylsulfonyl derivative **7** which was then treated with sodium methoxide. Final hydrolysis of the 5,6-*O*-isopropylidene protecting group led to the diastereomeric diols (1*S*,4*R*)-**4a**, (1*S*,4*S*)-**4b**, (1*R*,4*R*)-**4c,** and (1*R*,4*S*)-**4d**, representing versatile building blocks for further synthetic transformations.

1. Introduction

C-glycosides, compounds in which the anomeric oxygen has been substituted with a carbon atom, are considered to be less prone to chemical and enzymatic hydrolysis and represent an important class of carbohydrate mimetics.[1,2] These structures are prevalent in many pharmacologically active compounds and natural products.[3–6] Therefore, the synthesis of C-glycosides has attracted considerable attention and was extensively reviewed in the literature.[7–10]

Searching for *C*-glycosidic LpxC inhibitors[11–14] we were interested in the synthesis of *C*-aryl furanosides. In the literature many synthetic strategies toward *C*-aryl glycosides are described. For example, sugars bearing an activating group at the anomeric center like glycosyl halides,[15,16] glycosyl acetates[17,18] and glycosyl trichloroacetimidates[19] can undergo electrophilic aromatic substitutions giving access to *C*-aryl glycosides. This class of compounds can also be obtained by reacting metallated aryl compounds with glycosyl halides,[20,21] 1,2-anhydro sugars[22] and sugar lactones. In case of the addition of organometallic reagents to lactones, the resulting lactols need to be reduced by the Lewis acid-trialkylsilane method or by the use of sodium cyanoborohydride in the presence of dichloroacetic acid in order to yield the desired C-glycosides.[23,24] Another strategy toward *C*-aryl glycosides is the transformation of glycal derivatives in Pd-mediated Heck-type couplings.[25,26] Alternatively, *C*-aryl glycosides can be obtained by establishing the sugar ring via intramolecular cyclization reactions, like electrophile-induced cyclizations of carbohydrate-derived alkenols[27] or intramolecular Mitsunobu cycloetherifications of diols.[28]

In this paper we wish to report the stereocontrolled preparation of the four diastereomeric *C*-phenyl furanosides (1*S*,4*R*)-**4a**, (1*S*,4*S*)-**4b**, (1*R*,4*R*)-**4c,** and (1*R*,4*S*)-**4d** serving as versatile building blocks, for example, for the synthesis of potential antibiotics and other pharmacologically active compounds.[14,29]

2. Results and discussion

First, the known *C*-phenyl β-D-mannofuranoside **3a** was synthesized according to a literature procedure:[29] After a nucleophilic attack of phenyllithium to D-mannono-1,4-lactone **1a**, the resulting hemiketal **2a** was reduced with Et_3SiH in the presence of $BF_3{\cdot}OEt_2$. Due to the presence of the Lewis acid $BF_3{\cdot}OEt_2$ a partial cleavage of the 5,6-isopropylidene acetal occurred. Therefore, in addition to the bisacetonide **3a** the diol **4a** was also isolated from the reaction mixture (Scheme 1).

The stereochemistry in position 1 of the *C*-phenyl β-D-mannofuranoside **3a** was confirmed by NOE experiments: Irradiation with the resonance frequency of 4-H (3.70 ppm) reinforces the signal of 1-H (4.61 ppm), while the signals of the aromatic protons are not influenced. This indicates the *cis*-orientation of 1-H relative to 4-H in the tetrahydrofuran ring.

In order to gain access to the (4*S*)-configured *C*-phenyl β-D-talofuranoside **3b**, the same strategy which led to the *C*-phenyl

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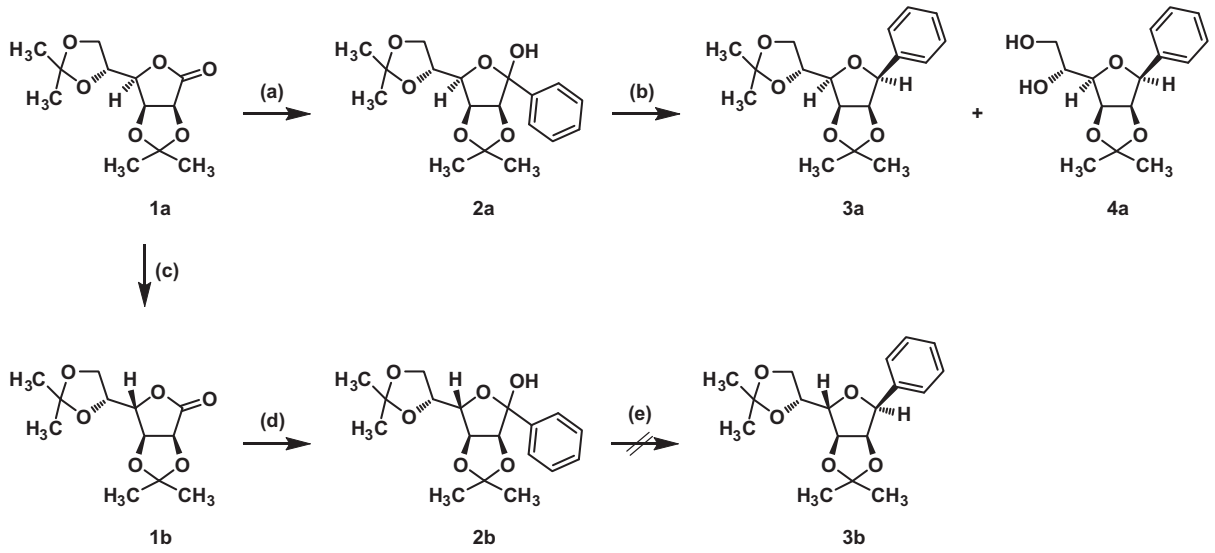


Scheme 1. Reagents and conditions: (a) PhLi, THF, −78 °C, 1 h, 95%; (b) Et_3SiH, $BF_3{\cdot}Et_2O$, ACN, −40 °C, 24% **3a** and 46% **4a**;[29] (c) (1) piperidine, EtOAc, (2) MsCl, NEt_3, DMAP, EtOAc, 66%;[30] (d) PhLi, THF, −78 °C, 1 h, 53%; (e) Et_3SiH, $BF_3{\cdot}Et_2O$, ACN, −40 °C.

β-D-mannofuranoside **3a** should be followed starting from the D-talono-1,4-lactone **1b**. Therefore, the D-mannono-1,4-lactone **1a** was transformed into the D-talono-1,4-lactone **1b** according to a reported one-pot sequence, which proceeded via opening of the lactone ring with piperidine, followed by mesylation and intramolecular S_N2-type O-alkylation.[30] Then, D-talono-1,4-lactone **1b** was treated with phenyllithium to give hemiketal **2b**.

The inversion of the stereocenter in position 4 led to changes in the ^1H NMR spectrum of **2b** compared to **2a**. As 4-H is *trans*-oriented relative to 3-H, a smaller coupling constant (J = 2.1 Hz) can be observed for the coupling between these protons in the ^1H NMR spectrum of **2b** compared to the same coupling in the spectrum of **2a** (J = 3.9 Hz).

However, the subsequent reduction of **2b** with Et_3SiH in the presence of $BF_3{\cdot}OEt_2$, which was performed under various conditions, did not yield the desired C-glycoside **3b** but gave a complex mixture of products.

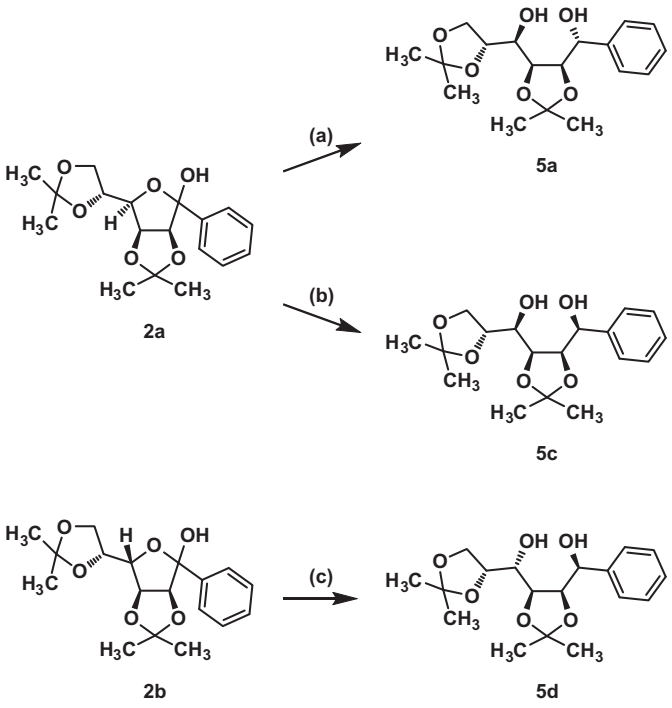
As the reduction of hemiketal **2b** did not afford the desired compound, another strategy for the synthesis of **3b** had to be followed. Therefore, for the synthesis of the (1*S*,4*S*)-, the (1*R*,4*R*)-, and the (1*R*,4*S*)-configured C-glycosides **3b**, **3c,** and **3d** a stereoselective reduction of a hemiketal and subsequent cycloetherification was envisaged.[28,31,32]

The reduction of the (4*R*)-configured hemiketal **2a** with L-Selectride in THF at −78 °C yielded diastereoselectively the (1*R*,4*R*)-configured diol **5a**. (Scheme 2) In contrast, when reducing **2a** with L-Selectride in CH_2Cl_2 at −78 °C in the presence of $ZnCl_2$, the (1*S*,4*R*)-configured diastereomer **5c** was obtained.[33]

The configuration of the stereocenter in position 1 of **5a** and **5c** was assigned from their subsequent cyclization products taking into account an inversion of configuration at that position.

In case of the L-Selectride reduction of the (4*S*)-configured hemiketal **2b** the (1*S*,4*S*)-configured diol **5d** was obtained both, in the presence and the absence of $ZnCl_2$. Recrystallization of **5d** gave colorless crystals that were suitable for X-ray crystal structure analysis. As the configuration of all the other chiral centers is given from the chiral-pool synthesis, the configuration in position 1 was confirmed by the X-ray structure to be (1*S*). (Fig. 1)

The different stereochemical outcomes of the reductions of hemiketals **2a** and **2b** can be rationalized taking into account models for the reduction of γ-lactols described in the literature:[33] The fact that the reduction of both lactols in the presence of $ZnCl_2$



Scheme 2. Reagents and conditions: (a) L-Selectride, THF, −78 °C, then rt, 16 h, 82%; (b) $ZnCl_2$, CH_2Cl_2, −78 °C, L-Selectride, then rt, 16 h, 66%; (c) L-Selectride, THF, −78 °C, then rt, 16 h, 75%.

yielded the *syn*(1,2-*threo*)-isomers **5c** and **5d** can be explained by the formation of the intermediate 7-membered cyclic chelate **A** involving the γ-hydroxy groups of the compounds (Fig. 2). Hydride delivery from the *exo*-face of this metallocycle would give the observed *syn*-isomers. By contrast, the outcome of the reductions in the absence of added $ZnCl_2$ was dependent on the substitution pattern of C-4 bearing the γ-hydroxy group: While the 3,4-*threo* derivative **2a** yielded the *anti*(1,2-*erythro*)-isomer **5a**, the 3,4-*erythro* derivative **2b** gave the *syn*-isomer **5d**. When **2a** is reduced with L-Selectride in the absence of $ZnCl_2$, the less strongly coordinating lithium ion might form the chelate **B** (R^1 = H, R^2 = 2,2-dimethyl-1,3-dioxolan-4-yl). As in this complex the *Re*-face of the carbonyl

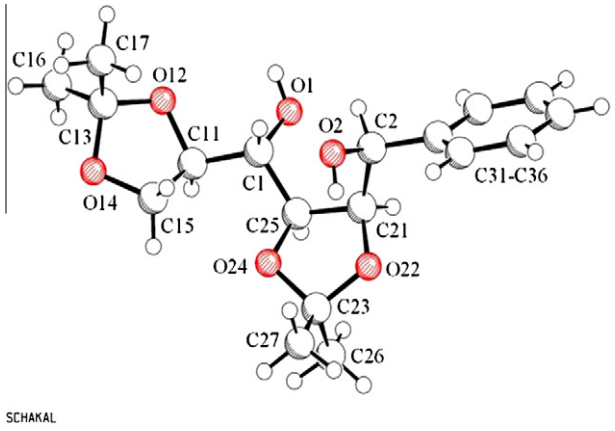


Figure 1. Molecular structure of compound **5d**.

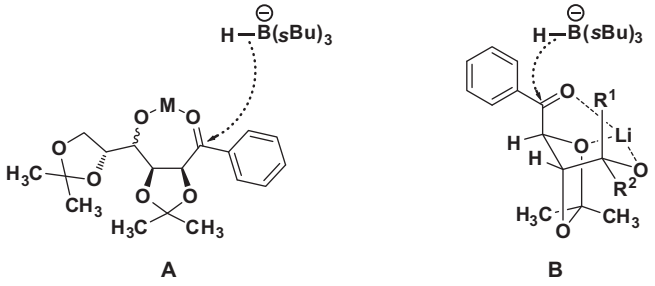


Figure 2. Models for the reductions of lactols **2a** and **2b**.

group is shielded by the axial substituent R^1, reduction occurs from the *Si*-face yielding the *anti*-diol **5a**. In contrast, the formation of complex **B** seems unlikely to occur in case of **2b** (R^1 = 2,2-dimethyl-1,3-dioxolan-4-yl, R^2 = H), as the dioxolanyl substituent would be placed in an axial position. However, the outcome of the reduction of **2b** with L-Selectride is in agreement with the prediction of the Felkin–Anh model.

In the next reaction step the *C*-glycosidic scaffolds should be established in a stereospecific manner. Therefore, an intramolecular cycloetherification under Mitsunobu conditions was performed.[28,31,32] The reaction of **5a** with diisopropyl azodicarboxylate and triphenylphosphine at ambient temperature gave the already known (1*S*,4*R*)-configured C-glycoside **3a** in 25% yield. (Scheme 3) The stereochemical outcome of the reaction showed that the nucleophilic substitution had taken place in the benzylic position and confirmed the (*R*)-configuration in position 1 of **3a**.

Compound **5c** was also transformed into a C-glycoside using Mitsunobu conditions. However, in order to improve the yield of the cyclization, a higher amount of the reagents was used and the reaction mixture was heated to reflux. These modifications gave the (1*R*,4*R*)-configured C-glycoside **3c** in 75% yield.

While in the ^{1}H NMR spectrum of **3a** the signal of 1-H appears as a doublet (J = 3.7 Hz), the corresponding proton of **3c** gives a singlet, indicating its *trans*-orientation relative to 2-H in the tetrahydrofuran ring. NOE experiments further confirmed this assignment: Irradiation with the resonance frequency of 4-H (3.89 ppm) did not increase the signal of 1-H (5.20 ppm). This proved the phenyl ring to be in the α-position of the D-mannofuranoside **3c**. The determined (1*R*,4*R*)-configuration of **3c** confirmed the (1*S*)-configuration of the precursor **5c**.

When **5d** was subjected to the Mitsunobu reaction, besides the (1*R*,4*S*)-configured C-glycoside **3d** bearing the phenyl ring in the α-position its (1*S*,4*S*)-configured diastereomer **3b** was also obtained, indicating that the transformation was not fully stereospecific. However, the main product of this cyclization which was isolated in 63% yield was the (1*R*,4*S*)-configured D-talofuranoside **3d**, which was generated via an inversion of configuration in position 1 of **5d**. The minor product **3d** which was obtained in 17% yield retained (*S*)-configuration in position 1.

In an alternative approach, **3d** should be formed via the 1-mesylate of **5d**.[34] Therefore, **5d** was treated with methanesulfonyl chloride in the presence of an excess of base. However, these reaction conditions gave lower yields and moreover, both diastereomers **3d** and **3b** were obtained in 30% and 10% yields, respectively.

The (1*R*,4*S*)-configuration of C-glycoside **3d** was confirmed by NOE experiments: Irradiation with the resonance frequency of 4-H (4.06 ppm) led to a reinforcement of the signal of 1-H (4.88 ppm) but not of the one of 2-H (4.52 ppm). This indicates that 1-H and 4-H lie on the same side of the tetrahydrofuran ring, but on the opposite side of 2-H.

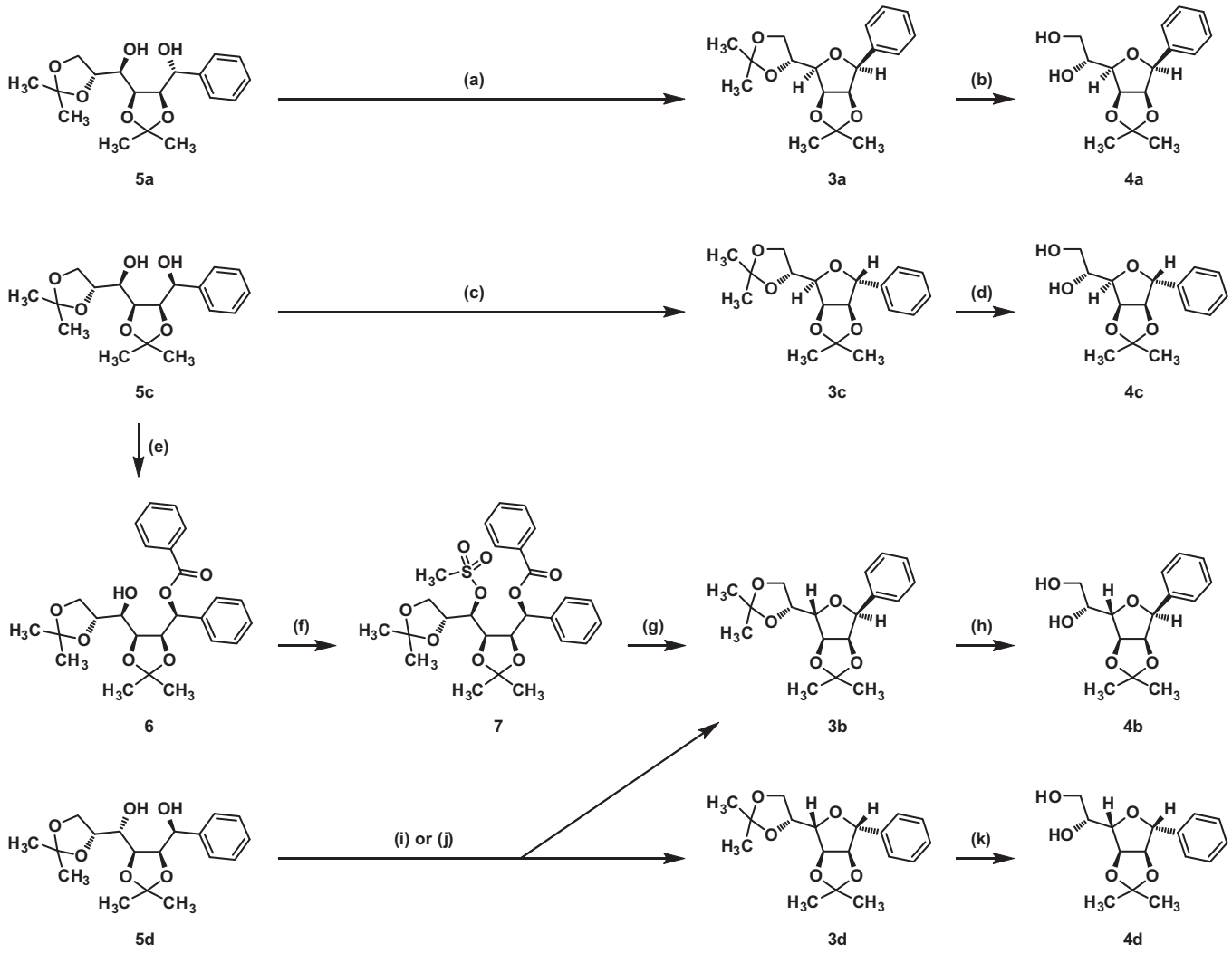
Finally, the (1*S*,4*S*)-configured C-glycoside **3b** should be synthesized. As the required (1*R*,4*S*)-configured diol was not available to perform a Mitsunobu reaction, another strategy was applied.[35] Therefore, the (1*S*,4*R*)-configured diol **5c** was reacted with benzoyl chloride to yield the 1-*O*-benzoyl derivative **6**. Its ^{1}H NMR spectrum clearly indicates that the benzoylation had taken place at the hydroxy group in position 1. Benzoylation of the sterically more hindered hydroxy group in position 4 was not observed.

In the next step, the remaining hydroxy group of **6** was mesylated giving access to the 1-*O*-benzoyl-4-*O*-methylsulfonyl derivative **7**. Treatment of **7** with methanolic sodium methoxide led to the cleavage of the benzoate and a subsequent S_N2 reaction in position 4 yielding the (1*S*,4*S*)-configured C-glycoside **3b**. NOE experiments with **3b** proved the relative *trans*-orientation of 1-H and 4-H, as irradiation with the resonance frequency of 1-H (5.28 ppm) did not enhance the signal of 4-H (4.21 ppm). Therefore the phenyl ring must be in the β-position of D-talofuranoside **3b**.

The treatment of the bisacetonides **3a**, **3b**, **3c,** and **3d** with methanol and catalytic amounts of *p*-toluenesulfonic acid selectively led to the cleavage of the 5,6-*O*-isopropylidene protecting group, while the bicyclic acetonide remained stable under these reaction conditions. The diols (1*S*,4*R*)-**4a**, (1*S*,4*S*)-**4b**, (1*R*,4*R*)-**4c,** and (1*R*,4*S*)-**4d** and were obtained in 36–73% yields. As the cleavage of the 2,3-*O*-isopropylidene protecting group requires harsher reaction conditions, the selective cleavage of the less stable acetonide allows further transformations of the resulting vicinal diols like, for example, a glycol cleavage, while the hydroxy groups of the tetrahydrofuran ring are still protected. Therefore, the four stereoisomeric *C*-phenyl furanosides (1*S*,4*R*)-**4a**, (1*S*,4*S*)-**4b**, (1*R*,4*R*)-**4c,** and (1*R*,4*S*)-**4d** with their two different substituents in positions 1 and 4 represent versatile building blocks for further transformations, allowing selective variations at the different positions of the tetrahydrofuran ring.[14,29]

3. Conclusion

Stereocontrolled syntheses starting from D-mannono-1,4-lactone **1a** yielded the four diastereomeric C-glycosides (1*S*,4*R*)-**4a**, (1*S*,4*S*)-**4b**, (1*R*,4*R*)-**4c,** and (1*R*,4*S*)-**4d**. These chiral pool syntheses comprised stereoselective reductions of the diastereomeric hemiketals (4*R*)-**2a** and (4*S*)-**2b**. The next key steps of the synthetic pathways were stereospecific cycloetherifications of the resulting diols (1*R*,4*R*)-**5a**, (1*S*,4*R*)-**5c,** and (1*S*,4*S*)-**5d**. These ring closures yielding the desired C-glycosides could be achieved by performing Mitsunobu reactions or by an intramolecular S_N2 reaction of the mesylate **7**. The final cleavage of the 5,6-*O*-isopropylidene protecting group gave access to the diastereomeric diols (1*S*,4*R*)-**4a**, (1*S*,4*S*)-**4b**, (1*R*,4*R*)-**4c,** and (1*R*,4*S*)-**4d**. With the phenyl ring in



Scheme 3. Reagents and conditions: (a) DIAD, PPh_3, THF, rt, 24 h, 25%; (b) *p*TsOH, MeOH, rt, 4 h, 73%; (c) DIAD, PPh_3, THF, Δ, 16 h, 75%; (d) *p*TsOH, MeOH, rt, 4 h, 62%; (e) BzCl, DIEA, DMAP, CH_2Cl_2, rt, 16 h, 52%; (f) MsCl, DIEA, CH_2Cl_2, rt, 16 h, 85%; (g) NaOMe, MeOH, rt, 16 h, 93%; (h) *p*TsOH, MeOH, rt, 4 h, 61%; (i) DIAD, PPh_3, THF, Δ, 16 h, 63% **3d,** and 17% **3b**; (j) MsCl, DIEA, CH_2Cl_2, rt, 16 h, 30% **3d,** and 10% **3b**; (k) *p*TsOH, MeOH, rt, 4 h, 36%.

position 1, the ethylene glycol structure in position 4 and the acetonide protected glycol structure of the tetrahydrofuran ring, these compounds represent versatile building blocks which allow selective transformations at the different ring positions.

4. Experimental

4.1. Chemistry: General

Unless otherwise mentioned, THF was dried with sodium/benzophenone and was freshly distilled before use. Thin layer chromatography (tlc): Silica Gel 60 F_{254} plates (Merck). Flash chromatography (fc): Silica Gel 60, 40–64 μm (Macherey-Nagel); parentheses include: diameter of the column, length of column, fraction size, eluent, and R_f value. Melting point (mp): Melting point apparatus SMP 3 (Stuart Scientific), uncorrected. Optical rotation α [deg] was determined with a Polarimeter 341 (Perkin Elmer); path length 1 dm, wavelength 589 nm (sodium D line); the unit of the specific rotation $[\alpha]_D^{20}$ [deg mL dm^{-1} g^{-1}] is omitted; the concentration of the sample c [mg mL^{-1}] and the solvent used are given in brackets. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz): Mercury plus 400 spectrometer (Varian); δ in ppm related to tetramethylsilane; coupling constants are given with 0.5 Hz resolution. Where necessary, the assignment of the signals in the ^1H NMR and ^{13}C NMR spectra was performed using ^1H–^1H and ^1H–^{13}C COSY NMR spectra as well as NOE (nuclear Overhauser effect) difference spectroscopy. IR: IR Prestige-21(Shimadzu). MS: HRMS: MicrOTOF-QII (Bruker); ESI: LCQ Finnigan MAT mass spectrometer (Thermo Finnigan), peaks are given in *m*/*z* (% of basis peak). HPLC method for the determination of product purity: Merck Hitachi Equipment; UV detector: L-7400; autosampler: L-7200; pump: L-7100; degasser: L-7614; column: LiChrospher® 60 RP-select B (5 μm); LiCroCART® 250-4 mm cartridge; flow rate: 1.00 mL/min; injection volume: 5.0 μL; detection at λ = 210 nm for 30 min; solvents: A: water with 0.05% (V/V) trifluoroacetic acid; B: acetonitrile with 0.05% (V/V) trifluoroacetic acid; gradient elution: (A%): 0–4 min: 90% , 4–29 min: gradient from 90% to 0%, 29–31 min: 0%, 31–31.5 min: gradient from 0% to 90%, 31.5–40 min: 90%. X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction Denzo-SMN;[36] absorption correction, Denzo;[37] structure solution SHELXS-97;[38] structure refinement SHELXL-97[39] and graphics, XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections. Exceptions and special features: Flack parameter was refined to −0.4(3).

4.2. Synthetic procedures

4.2.1. 2,3:5,6-Di-*O*-isopropylidene-1-*C*-phenyl-D-mannofuranose (2a)

Under N_2 atmosphere a 2.0 M solution of phenyllithium in dibutyl ether (5.5 mL, 11 mmol) was added to a solution of 2,3:5,6-di-*O*-isopropylidene-D-mannono-1,4-lactone (**1a**) (2.6 g, 10 mmol) in THF (50 mL) at −78 °C. After stirring at −78 °C for 1 h, the mixture was allowed to warm to room temperature. Then a saturated aqueous solution of $NaHCO_3$ (15 mL) was added and the mixture was extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The residue was purified by flash column chromatography (*Ø* = 8 cm, *h* = 15 cm, *V* = 60 mL, *n*-hexane/ethyl acetate = 8/2, R_f = 0.24) to give **2a** as colorless solid (3.2 g, 9.5 mmol, 95%). Mp: 116 °C; $[\alpha]_D^{20}$ +62.1 (5.1; CH_2Cl_2); ^{1}H NMR (DMSO-d_6): δ 1.15 (s, 3H, C*H*$_3$), 1.24 (s, 3H, C*H*$_3$), 1.30 (s, 3H, C*H*$_3$), 1.36 (s, 3H, C*H*$_3$), 3.99 (dd, *J* = 8.3/6.1 Hz, 1 H, 6-H), 4.06 (dd, *J* = 8.3/6.6 Hz, 1H, 6-H), 4.22 (dd, *J* = 5.9/3.9 Hz, 1H, 4-H), 4.39 (q, *J* = 6.1 Hz, 1H, 5-H), 4.47 (d, *J* = 5.8 Hz, 1H, 2-H), 4.85 (dd, *J* = 5.8/3.9 Hz, 1H, 3-H), 6.62 (s, 1H, O*H*), 7.25–7.35 (m, 3H, $H_{arom.}$), 7.43–7.47 (m, 2H, $H_{arom.}$); ^{13}C NMR (DMSO-d_6): δ 24.0 (1C, C(*C*H$_3$)$_2$), 25.3 (1C, C(*C*H$_3$)$_2$), 25.4 (1C, C(CH$_3$)$_2$), 26.6 (1C, C(*C*H$_3$)$_2$), 65.7 (1C, C-6), 73.2 (1C, C-5), 77.9 (1C, C-4), 79.9 (1C, C-3), 86.2 (1C, C-2), 105.1 (1C, C-1), 107.8 (1C, *C*(CH$_3$)$_2$), 111.3 (1C, *C*(CH$_3$)$_2$), 127.0 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 127.1 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 127.7 (1C, C-4′$_{phenyl}$), 140.3 (1C, C-1′$_{phenyl}$); IR (neat): ν [cm^{-1}] = 3358, 2975, 2937, 1450, 1371, 1209, 1062, 1033, 1011, 849, 699; HRMS (*m*/*z*): [M+Na]$^+$ calcd for $C_{18}H_{24}O_6Na$, 359.1465; found, 359.1465; HPLC: t_R = 17.9 min, purity 97.5%.

4.2.2. 2,3:5,6-Di-*O*-isopropylidene-D-talono-1,4-lactone (1b)

2,3:5,6-Di-*O*-isopropylidene-D-mannono-1,4-lactone (**1a**) (4.0 g 15.4 mmol) was dissolved in anhydrous EtOAc (40 mL) and piperidine (3.07 mL, 31 mmol) was added dropwise at 0 °C. The mixture was stirred at room temperature for 5 h. After TLC had revealed that the reaction was complete, the excess of piperidine and the solvent was removed in vacuo to give a white solid. The residue was dissolved in EtOAc (50 mL). Then triethylamine (3.45 mL, 24.5 mmol) and dimethylaminopyridine (25 mg, 0.2 mmol) were added. Subsequently, the reaction was cooled to 0 °C and methanesulfonyl chloride (1.8 mL) was added dropwise. The mixture was warmed to room temperature and stirred overnight. The reaction was then quenched with water and extracted with CH_2Cl_2 (4×). The organic layer was washed with 1% HCl solution, water, and brine. After treatment with sodium sulfate the organic phase was filtrated and concentrated under reduced pressure. The residue was purified by flash column chromatography (*Ø* = 5 cm, *h* = 15 cm, *V* = 60 mL, cyclohexane/ethyl acetate = 8/2, R_f = 0.19) to give **1b** as a colorless solid (2.66 g, 10.3 mmol, 66%). Mp: 129 °C; $[\alpha]_D^{20}$ +35.9 (4.1; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 1.33 (s, 3H, C*H*$_3$), 1.34 (s, 3H, C*H*$_3$), 1.38 (s, 3H, C*H*$_3$), 1.47 (s, 3H, C*H*$_3$), 3.99 (dd, *J* = 8.3/7.5 Hz, 1 H, 6-H), 4.12 (dd, *J* = 8.3/6.9 Hz, 1H, 6-H), 4.25–4.29 (m, 1H, 5-H), 4.54 (d, *J* = 1.1 Hz, 1H, 4-H), 4.76 (d, *J* = 5.5 Hz, 1H, 3-H), 4.78 (d, *J* = 5.5 Hz, 1H, 2-H); ^{13}C NMR ($CDCl_3$): δ 25.5 (1C, C(*C*H$_3$)$_2$), 25.6 (1C, C(*C*H$_3$)$_2$), 25.7 (1C, C(*C*H$_3$)$_2$), 26.9 (1C, C(*C*H$_3$)$_2$), 65.2 (1C, C-6), 75.1 (1C, C-2), 75.2 (1C, C-5), 78.6 (1C, C-3), 79.7 (1C, C-4), 110.7 (1C, *C*(CH$_3$)$_2$), 113.4 (1C, *C*(CH$_3$)$_2$), 174.3 (1C, C-1); IR (neat): ν [cm^{-1}] = 2990, 1787, 1372, 1218, 1151, 1085, 1067, 975, 859, 796; HRMS (*m*/*z*): [M+H]$^+$ calcd for $C_{12}H_{19}O_6$, 259.1176; found, 259.1188.

4.2.3. 2,3:5,6-Di-*O*-isopropylidene-1-*C*-phenyl-D-talofuranose (2b)

A 2.0 M solution of phenyllithium in dibutylether (4.64 mL, 9.27 mmol) was added to a solution of **1b** (2.19 g, 8.43 mmol) in dry THF (70 mL) at −78 °C. The reaction was stirred for 1 h and then warmed to room temperature. Afterward, a saturated aqueous solution of $NaHCO_3$ was added to quench the reaction. Extraction with CH_2Cl_2 (3×) was performed; the combined organic layers were dried over Na_2SO_4, filtered, and concentrated under diminished pressure. The residue was purified by flash chromatography (*Ø* = 5 cm, *h* = 15 cm, *V* = 80 mL, cyclohexane/ethyl acetate = 8/2, R_f = 0.27) to give **2b** as colorless solid (1.51 g, 4.49 mmol, 53%). Mp: 148 °C; $[\alpha]_D^{20}$ +44.8 (3.7; CH_2Cl_2); ^{1}H NMR (DMSO-d_6): δ 1.17 (s, 3H, C*H*$_3$), 1.28 (s, 3H, C*H*$_3$), 1.30 (s, 3H, C*H*$_3$), 1.37 (s, 3H, C*H*$_3$), 3.69 (dd, *J* = 8.4/7.0 Hz, 1 H, 6-H), 4.09 (dd, *J* = 8.2/2.1 Hz, 1H, 4-H), 4.14 (dd, *J* = 8.4/6.6 Hz, 1H, 6-H), 4.33–4.40 (m, 5-H), 4.49 (d, *J* = 5.7 Hz, 1H, 2-H), 4.73 (dd, *J* = 5.7/2.1 Hz, 1H, 3-H), 6.84 (s, 1H, O*H*), 7.25–7.36 (m, 3H, $H_{arom.}$), 7.46–7.50 (m, 2H, $H_{arom.}$); ^{13}C NMR (DMSO-d_6): δ 25.1 (1C, C(*C*H$_3$)$_2$), 25.4 (1C, C(*C*H$_3$)$_2$), 26.7 (1C, C(*C*H$_3$)$_2$), 26.8 (1C, C(*C*H$_3$)$_2$), 65.5 (1C, C-6), 77.4 (1C, C-5), 81.5 (1C, C-3), 86.6 (1C, C-2), 87.8 (1C, C-4), 106.9 (1C, C-1), 108.8 (1C, *C*(CH$_3$)$_2$), 112.0 (1C, *C*(CH$_3$)$_2$), 127.1 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 127.2 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 127.7 (1C, C-4′$_{phenyl}$), 140.6 (1C, C-1′$_{phenyl}$); IR (neat): ν [cm^{-1}] = 3528, 2982, 2936, 1376, 1208, 1056, 854, 696; HRMS (*m*/*z*): [M+H]$^+$ calcd for $C_{18}H_{25}O_6$, 337.1646; found, 337.1649; HPLC: t_R = 17.0 min, purity 99.0%.

4.2.4. (1*R*)-2,3:5,6-Di-*O*-isopropylidene-1-*C*-phenyl-D-mannitol (5a)

L-Selectride (1 M in THF, 12.18 mL, 12.18 mmol) was added dropwise to a solution of **2a** (1.2 g, 3.58 mmol) in dry THF (70 mL) at −78 °C over a period of 30 min. The reaction is then slowly brought to room temperature and stirred overnight. The mixture was concentrated in vacuo, the residue was dissolved in CH_2Cl_2 (40 mL) and quenched with EtOH (1.1 mL), H_2O (0.24 mL), NaOH 6 M (0.9 mL), and H_2O_2 30% (0.9 mL). Stirring was continued for 1 h. Then the mixture was extracted with EtOAc, the organic phase dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (*Ø* = 5 cm, *h* = 15 cm, *V* = 60 mL, cyclohexane/EtOAc = 2:1, R_f = 0.35) to give **5a** as colorless oil (1.0 g, 2.95 mmol, 82%). $[\alpha]_D^{20}$ −16.5 (1.2; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 3H, C*H*$_3$), 1.33 (s, 3H, C*H*$_3$), 1.35 (s, 1H, C*H*$_3$), 1.50 (s, 1H, C*H*$_3$), 3.01–3.04 (m, 1H, O*H*), 3.13–3.16 (m, 1H, O*H*), 3.85–3.90 (m, 1H, 4-H), 4.02–4.09 (m, 3H, 5-H, 6-H), 4.39 (dd, *J* = 6.8/1.0 Hz, 1H, 3-H), 4.42–4.46 (m, 1H, 2-H), 5.11 (dd, *J* = 7.4/4.1 Hz, 1H, 1-H), 7.27–7.32 (m, 1H, $H_{arom.}$), 7.34–7.39 (m, 2H, $H_{arom.}$), 7.41–7.45 (m, 2H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): δ 25.0 (1C, C(*C*H$_3$)$_2$), 25.57 (1C, C(*C*H$_3$)$_2$),26.9 (1C, C(*C*H$_3$)$_2$), 27.1 (1C, C(*C*H$_3$)$_2$), 67.2 (1C, OCH*C*H$_2$O C-6), 69.7 (1C, C-4), 72.0 (1C, C-1), 75.9 (1C, C-3), 76.4 (1C, O*C*HCH$_2$O C-5), 79.9 (1C, C-2), 108.5 (1C, *C*(CH$_3$)$_2$), 109.5 (1C, *C*(CH$_3$)$_2$), 126.6 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 128.1 (1C, C-4′$_{phenyl}$), 128.7 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 141.1 (1C, C-1′$_{phenyl}$); IR (neat): ν [cm^{-1}] = 3321, 2986, 2936, 2361, 1369, 1215, 1065, 1038, 841, 702; HRMS (*m*/*z*): [M+H]$^+$ calcd for $C_{18}H_{27}O_6$, 399.1802; found, 399.1775; HPLC: t_R = 16.2 min, purity 98.4%.

4.2.5. (1*S*)-2,3:5,6-Di-*O*-isopropylidene-1-*C*-phenyl-D-mannitol (5c)

$ZnCl_2$ (1 M solution in diethyl ether, 3.55 mL, 3.55 mmol) was added to a solution of **2a** (884 mg, 2.63 mmol) in dry CH_2Cl_2 (80 mL) at −78 °C and the mixture was stirred for 40 min. Afterward, L-selectride (1 M in THF, 8.9 mL, 8.9 mmol) was added dropwise over a period of 30 min at −78 °C. The reaction was then slowly brought to room temperature and stirred overnight. To quench the reaction EtOH (1.1 mL), H_2O (0.24 mL), NaOH 6 M (0.9 mL), and H_2O_2 30% (0.9 mL) were added and stirring was continued for 1 h. Then the mixture was extracted with EtOAc, the organic layer dried over sodium sulfate, and concentrated. The residue was purified by flash column chromatography (*Ø* = 5 cm,

h = 15 cm, V = 60 mL, cyclohexane/EtOAc = 2/1, R_f = 0.30) to give **5c** as colorless oil (587 mg, 1.73 mmol, 66%). $[\alpha]_D^{20}$ +56.3 (1.5; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 1.27 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.40 (s, 1H, CH_3), 1.60 (s, 1H, CH_3), 3.24 (s br, 2H, OH), 3.60 (d, J = 7.0 Hz, 1H, 4-H), 4.00–4.11 (m, 3H, 5-H, 6-H), 4.38 (dd, J = 7.5/1.0 Hz, 1H, 3-H), 4.52 (dd, J = 7.5/4.0 Hz, 1H, 2-H), 4.97 (d, J = 4.0 Hz, 1H, 1-H), 7.29–7.34 (m, 1H, $H_{arom.}$), 7.35–7.40 (m, 2H, $H_{arom.}$), 7.42–7.46 (m, 2H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): δ 24.8 (1C, C(CH_3)$_2$), 25.5 (1C, C(CH_3)$_2$),26.6 (1C, C(CH_3)$_2$), 26.9 (1C, C(CH_3)$_2$), 67.3 (1C, C-6), 70.3 (1C, C-4), 72.1 (1C, C-1), 75.9 (1C, C-3), 76.2 (1C, C-5), 80.3 (1C, C-2), 108.7 (1C, C(CH$_3$)$_2$), 109.4 (1C, C(CH$_3$)$_2$), 127.2 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 128.4 (1C, C-4′$_{phenyl}$), 128.8 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 140.6 (1C, C-1′$_{phenyl}$); IR (neat): ν [cm^{-1}] = 3402, 3379, 2986, 2928, 2851, 1454, 1373, 1246, 1211, 1061, 845, 698; HRMS (m/z): [M+H]$^+$ calcd for $C_{18}H_{27}O_6$, 399.1802; found, 399.1776; HPLC: t_R = 15.5 min, purity 98.6%.

4.2.6. (1*S*)-2,3:5,6-Di-*O*-isopropylidene-1-*C*-phenyl-D-talitol (5d)

L-Selectride (1 M in THF, 12.18 mL, 12.18 mmol) was added dropwise to a solution of **2b** (1.2 g, 3.58 mmol) in dry THF (70 mL) at −78 °C over a period of 30 min. The reaction was then slowly brought to room temperature and stirred overnight. The mixture was concentrated in vacuo, the residue was dissolved in CH_2Cl_2 (40 mL) and quenched with EtOH (1.1 mL), H_2O (0.24 mL), NaOH 6 M (0.9 mL), and H_2O_2 30% (0.9 mL). After stirring for 1 h, the mixture was extracted with EtOAc, the organic phase dried over sodium sulfate, and concentrated in vacuo. The residue was purified by flash column chromatography ($Ø$ = 5 cm, h = 15 cm, V = 60 mL, cyclohexane/EtOAc = 2/1, R_f = 0.42) to give **5d** as colorless solid (909 mg, 2.69 mmol, 75%). Mp: 84 °C; $[\alpha]_D^{20}$ +47.4 (1.6; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.46 (s, 1H, CH_3), 1.54 (s, 1H, CH_3), 2.58 (s br, 1H, OH), 2.86 (s br, 1H, OH), 3.94 (dd, J = 8.5/6.8 Hz, 1H, 6-H), 4.07 (dd, J = 9.4/3.9 Hz, 1H, 4-H), 4.10 (dd, J = 8.5/6.8 Hz, 1H, 6-H), 4.17 (dd, J = 9.3/6.6 Hz, 1H, 3-H), 4.33 (td, J = 6.7/4.0 Hz, 1H, 5-H), 4.45 (dd, J = 6.6/1.8 Hz, 1H, 2-H), 5.18–5.22 (m, 1H, 1-H), 7.25–7.30 (m, 1H, $H_{arom.}$), 7.33–7.38 (m, 2H, $H_{arom.}$), 7.39–7.43 (m, 2H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): δ 24.7 (1C, C(CH_3)$_2$), 25.3 (1C, C(CH_3)$_2$), 26.6 (1C, C(CH_3)$_2$), 27.02 (1C, C(CH_3)$_2$), 66.4 (1C, 6-C), 69.7 (1C, C-4), 70.6 (1C, C-1), 76.5 (1C, C-5), 77.49 (1C, C-3), 80.4 (1C, C-2), 108.9 (1C, C(CH$_3$)$_2$), 109.4 C(CH$_3$)$_2$), 126.5 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 127.7 (1C, C-4′$_{phenyl}$), 128.5 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 142.5 (1C, C-1′$_{phenyl}$); IR (neat): ν [cm^{-1}] = 3468, 2986, 2928, 2301, 1740, 1454, 1373, 1250, 1211, 1061, 876, 849, 698; MS (ESI): m/z = 698 (2 M+Na$^+$, 19), 361 (M+Na$^+$); HPLC: t_R = 15.6 min, purity 95.3%.

Further recrystallization from diisopropyl ether gave colorless crystals that were suitable for X-ray crystal structure analysis. X-ray crystal structure analysis of **5d**: formula $C_{18}H_{26}O_6$, M = 338.39, colorless crystal, 0.15 × 0.05 × 0.03 mm, a = 9.8969(7), b = 10.7879(7), c = 17.3024(9) Å, V = 1847.3(2) Å^3, ρ_{calc} = 1.217 g cm^{-3}, μ = 0.749 mm^{-1}, empirical absorption correction ($0.895 \leqslant T \leqslant 0.977$), Z = 4, orthorhombic, space group $P2_12_12_1$ (No. 19), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 12,125 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.59 Å^{-1}, 2836 independent (R_{int} = 0.073) and 2257 observed reflections [$I > 2\sigma(I)$], 223 refined parameters, R = 0.048, wR^2 = 0.111, max. (min.) residual electron density 0.18 (−0.21) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms. CCDC-872980 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.2.7. *C*-Phenyl 2,3:5,6-di-*O*-isopropylidene-β-D-mannofuranoside (3a)

(a) Under N_2 atmosphere Et_3SiH (0.58 mL, 419 mg, 3.6 mmol) was added to a solution of **2a** (1.01 g, 3.0 mmol) and $BF_3{\cdot}Et_2O$ (0.38 mL, 425.8 mg, 3.0 mmol) in acetonitrile (30 mL) at −40 °C. The mixture was stirred at −40 °C for 1 h, then a saturated aqueous solution of K_2CO_3 (3 mL) was added and the mixture was stirred for 1 h at ambient temperature. Then water was added and the mixture was extracted with ethyl acetate (3×). The combined organic layers were dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The residue was purified by flash column chromatography ($Ø$ = 4 cm, h = 15 cm, V = 30 mL, n-hexane/ethyl acetate = 8/2 → 1/2) to give **3a** (n-hexane/ethyl acetate = 8/2, R_f = 0.29) as colorless oil (233 mg, 0.73 mmol, 24%) and **4a** (n-hexane/ethyl acetate = 1/2, R_f = 0.14) as colorless solid (389 mg, 1.39 mmol, 46%). (b) Under N_2 atmosphere, triphenylphosphine (262.3 mg, 1 mmol) was added to a solution of **5a** (170 mg, 0.5 mmol) in dry THF (45 mL). Then diisopropyl azodicarboxylate (0.19 mL, 1 mmol) was added at 0 °C and the reaction was stirred for 24 h at room temperature. Afterward, the mixture was concentrated in vacuo and the residue was purified by flash column chromatography ($Ø$ = 2.5 cm, h = 15 cm, V = 15 mL, cyclohexane/EtOAc = 9:1, R_f = 0.29) to give **3a** as a colorless oil (40 mg, 0.13 mmol, 25% yield). Analytical data of **3a**: $[\alpha]_D^{20}$ +75.3 (5.4; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 3.70 (dd, J = 7.3/3.7 Hz, 1H, 4-H), 4.17 (d, J = 5.6 Hz, 2H, 6-H), 4.53 (dt, J = 7.3/5.6 Hz, 1H, 5-H), 4.61 (d, J = 3.7 Hz, 1H, 1-H), 4.81 (dd, J = 6.0/3.7 Hz, 1H, 2-H), 4.87 (dd, J = 6.0/3.7 Hz, 1H, 3-H), 7.26–7.39 (m, 5H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): δ 24.4 (1C, C(CH_3)$_2$), 25.5 (1C, C(CH_3)$_2$), 25.7 (1C, C(CH_3)$_2$), 27.1 (1C, C(CH_3)$_2$), 67.2 (1C, C-6), 73.4 (1C, C-5), 80.9 (1C, C-3), 81.7 (1C, C-4), 82.4 (1C, C-2), 83.8 (1C, C-1), 109.2 (1C, C(CH$_3$)$_2$), 112.7 (1C, C(CH$_3$)$_2$), 127.6 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 128.0 (1C, C-4′$_{phenyl}$), 128.1 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 135.6 (1C, C-1′$_{phenyl}$); IR (neat): ν [cm^{-1}] = 2986, 2935, 1455, 1206, 1065, 843, 698; HRMS (m/z): [M+Na]$^+$ calcd for $C_{18}H_{24}O_5Na$, 343.1516; found, 343.1528; HPLC: t_R = 19.6 min, purity 97.3%.

4.2.8. *C*-Phenyl 2,3-*O*-isopropylidene-β-D-mannofuranoside (4a)

p-Toluenesulfonic acid monohydrate (36 mg, 0.19 mmol) was added to a solution of **3a** (676 mg, 2.1 mmol) in methanol (20 mL). The mixture was stirred at ambient temperature for 4 h. Then a saturated aqueous solution of $NaHCO_3$ was added and the mixture was extracted with ethyl acetate (3×). The combined organic layers were dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The residue was purified by flash column chromatography ($Ø$ = 3 cm, h = 15 cm, V = 20 mL, n-hexane/ethyl acetate = 1/2, R_f = 0.14) to give **4a** as colorless solid (430 mg, 1.5 mmol, 73%). Mp: 114 °C; $[\alpha]_D^{20}$ +72.2 (5.3; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 1.29 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 3.71 (dd, J = 7.9/4.1 Hz, 1H, 4-H), 3.81 (dd, J = 11.5/5.8 Hz, 1H, 6-H), 3.93 (dd, J = 11.5/3.6 Hz, 1H, 6-H), 4.18 (ddd, J = 7.9/5.8/3.6 Hz, 1H, 5-H), 4.62 (d, J = 3.7 Hz, 1H, 1-H), 4.82 (dd, J = 6.1/3.7 Hz, 1H, 2-H), 4.94 (dd, J = 6.1/4.1 Hz, 1H, 3-H), 7.27–7.40 (m, 5H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): δ 24.6 (1C, C(CH_3)$_2$), 25.8 (1C, C(CH_3)$_2$), 64.9 (1C, C-6), 70.5 (1C, C-5), 81.1 (1C, C-4), 81.5 (1C, C-3), 82.3 (1C, C-2), 83.7 (1C, C-1), 112.8 (1C, C(CH$_3$)$_2$), 127.6 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 128.1 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 128.2 (1C, C-4′$_{phenyl}$), 135.4 (1C, C-1′$_{phenyl}$); IR (neat): ν [cm^{-1}] = 3473, 2984, 2925, 2872, 1384, 1208, 1096, 1011, 858, 734; HRMS (m/z): [M+Na]$^+$ calcd for $C_{15}H_{20}O_5Na$, 303.1203; found, 303.1206; HPLC: t_R = 13.9 min, purity 98.4%.

4.2.9. *C*-Phenyl 2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranoside (3c)

Triphenylphosphine (525 mg, 2.0 mmol) was added to a solution of **5c** (340 mg, 1.0 mmol) in dry THF (40 mL), under N_2 atmosphere. Then diisopropyl azodicarboxylate (0.4 mL, 2.0 mmol) was added at 0 °C and the reaction was heated to reflux. After 2 h a solution of triphenylphosphine (787 mg, 3.0 mmol) and diisopropyl

azodicarboxylate (0.6 mL, 3.0 mmol) in THF (30 mL) was added dropwise. The mixture was heated to reflux for 16 h, then it was concentrated in vacuo and the residue was purified by flash column chromatography (Ø = 5 cm, h = 15 cm, V = 60 mL, cyclohexane/EtOAc = 9:1, R_f = 0.28) to give **3c** as colorless oil (240 mg, 0.75 mmol, 75%). $[\alpha]_D^{20}$ +3.9 (1.4; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 3.89 (dd, 7.6/3.7 Hz, 1H, 4-H), 4.17–4.24 (m, 2H, 6-H), 4.50 (ddd, J = 10.8/6.1/4.7 Hz, 1H, 5-H), 4.76 (dd, J = 6.0/3.7 Hz, 1H, 3-H), 4.97 (dd, J = 6.0/1.0 Hz, 1H, 2-H), 5.20 (s, 1H, 1-H), 7.28-7.40 (m, 5H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): δ 24.9 (1C, C(*C*H$_3$)$_2$), 25.3 (1C, C(*C*H$_3$)$_2$), 26.3 (1C, C(*C*H$_3$)$_2$), 26.9 (1C, C(*C*H$_3$)$_2$), 67.0 (1C, C-6), 73.5 (1C, C-5), 81.1 (1C, C-3), 81.4 (1C, C-4), 85.0 (1C, C-1), 87.5 (1C, C-2), 109.2 (1C, *C*(CH$_3$)$_2$), 112.8 (1C, *C*(CH$_3$)$_2$), 125.4 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 127.5 (1C, C-4′$_{phenyl}$), 128.7 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 138.4 (1C, C-1′$_{phenyl}$); IR (neat): ν [cm^{-1}] = 2986, 2936, 2874, 1450, 1369, 1207, 1161, 1065, 845, 733, 698; HRMS (*m*/*z*): [M+H]$^+$ calcd for $C_{18}H_{25}O_5$, 321.1697; found, 321.1706; HPLC: t_R = 20.5 min, purity 98.1%.

4.2.10. *C*-Phenyl 2,3-*O*-isopropylidene-α-D-mannofuranoside (4c)

p-Toluenesulfonic acid monohydrate (15 mg, 0.08 mmol) was added to a solution of **3c** (240 mg, 0.75 mmol) in methanol (40 mL). The mixture was stirred at ambient temperature for 4 h. Then a saturated aqueous solution of sodium bicarbonate was added and the mixture was extracted with ethyl acetate (3×). The combined organic layers were dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The residue was purified by flash column chromatography (Ø = 2 cm, h = 15 cm, V = 10 mL, cyclohexane/ethyl acetate = 1/1, R_f = 0.20) to give **4c** as colorless oil (130 mg, 0.46 mmol, 62%). $[\alpha]_D^{20}$ +20.1 (1.7; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 1.39 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 2.18–2.60 (s br, 2H, O*H*), 3.86 (dd, J = 11.3/5.6 Hz, 1H, 6-H), 3.95 (dd, J = 11.3/3.5 Hz, 1H, 6-H), 3.98 (dd, J = 8.1/4.2 Hz, 1H, 4-H), 4.13 (ddd, J = 8.2/5.6/3.5 Hz, 1H, 5-H), 4.84 (dd, J = 6.1/4.2 Hz, 1H, 3-H), 4.95 (dd, J = 6.1/1.2 Hz, 1H, 2-H), 5.21 (s, 1H, 1-H), 7.27-7.39 (m, 5H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): δ 25.0 (1C, C(*C*H$_3$)$_2$), 26.4 (1C, C(*C*H$_3$)$_2$), 64.7 (1C, C-6), 70.7 (1C, C-5), 80.5 (1C, C-4), 81.7 (1C, C-3), 84.9(1C, C-1), 87.4 (1C, C-2), 113.2 (1C, *C*(CH$_3$)$_2$), 125.6 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 127.7 (1C, C-4′$_{phenyl}$), 128.8 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 138.3 (1C, C-1′$_{phenyl}$); IR (neat): ν [cm^{-1}] = 3410, 2937, 1373, 1207, 1084, 1065, 887, 856, 733, 702; HRMS (*m*/*z*): [M+H]$^+$ calcd for $C_{15}H_{21}O_5$, 281.1384; found, 281.1428; HPLC: t_R = 13.9 min, purity 96.2%.

4.2.11. *C*-Phenyl 2,3:5,6-di-*O*-isopropylidene-α-D-talofuranoside (3d)

(a) Triphenylphosphine (160 mg, 0.6 mmol) was added to a solution of **5d** (100 mg, 0.3 mmol) in dry THF (40 mL), under N_2 atmosphere. Then diisopropyl azodicarboxylate (0.12 mL, 0.6 mmol) was added at 0 °C and the reaction was heated to reflux. After 2 h a solution of triphenylphosphine (240 mg, 0.9 mmol) and diisopropyl azodicarboxylate (0.18 mL, 0.9 mmol) in THF (20 mL) was added dropwise. The mixture was heated to reflux for 16 h, then it was concentrated in vacuo and the residue was purified by flash column chromatography (Ø = 3 cm, h = 15 cm, V = 20 mL, cyclohexane/EtOAc = 9:1) to give **3d** (R_f = 0.31) as colorless oil (60 mg, 0.19 mmol, 63%) and **3b** (R_f = 0.18) as a colorless oil (17 mg, 0.05 mmol, 17%). (b) **5d** (190 mg, 0.56 mmol) was dissolved in CH_2Cl_2 (30 mL) and the solution was cooled to 0 °C. Then DIEA (0.46 mL, 2.8 mmol) and methanesulfonyl chloride (0.05 mL, 0.67 mmol) were added. The mixture was stirred at ambient temperature for 16 h. Then a saturated aqueous solution of $NaHCO_3$ was added and the mixture was extracted with CH_2Cl_2 (3×). The combined organic phases were dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The residue was purified by flash column chromatography (Ø = 2 cm, h = 15 cm, V = 10 mL, cyclohexane/EtOAc = 9:1) to give **3d** (R_f = 0.31) as a colorless oil (54 mg, 0.17 mmol, 30%) and **3b** (R_f = 0.18) as a colorless oil (18 mg, 0.06 mmol, 10%). Analytical data of **3d**: $[\alpha]_D^{20}$ +16.5 (2.0; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.62 (s, 3H, CH_3), 3.95 (dd, 8.3/7.1 Hz, 1H, 6-H), 4.06 (t, J = 5.1 Hz, 1H, 4-H), 4.12 (dd, J = 8.3/6.8 Hz, 1H, 6-H), 4.34 (td, J = 6.8/5.3 Hz, 1H, 5-H), 4.52 (dd, J = 7.0/5.1 Hz, 1H, 2-H), 4.63 (dd, J = 7.0/5.0 Hz, 1H, 3-H), 4.88 (d, J = 5.0 Hz, 1H, 1-H), 7.28–7.41 (m, 5H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): δ 25.5 (1C, C(*C*H$_3$)$_2$), 25.6 (1C, C(*C*H$_3$)$_2$), 26.6 (1C, C(*C*H$_3$)$_2$), 27.7 (1C, C(*C*H$_3$)$_2$), 65.5 (1C, C-6), 67.1 (1C, C-5), 81.7 (1C, C-3), 84.1 (1C, C-4), 85.8 (1C, C-1), 87.1 (1C, C-2), 110.0 (1C, *C*(CH$_3$)$_2$), 115.4 (1C, *C*(CH$_3$)$_2$), 126.0 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 128.0 (1C, C-4′$_{phenyl}$), 128.5 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 139.5 (1C, C-1′$_{phenyl}$); IR (neat): ν [cm^{-1}] = 2986, 2928, 1454, 1373, 1254, 1211, 1157, 1072, 853, 698; HRMS (*m*/*z*): [M+H]$^+$ calcd for $C_{18}H_{25}O_5$, 321.1697; found, 321.1741; HPLC: t_R = 20.2 min, purity 95.2%.

4.2.12. *C*-Phenyl 2,3-*O*-isopropylidene-α-D-talofuranoside (4d)

p-Toluenesulfonic acid monohydrate (4 mg, 0.02 mmol) was added to a solution of **3d** (54 mg, 0.17 mmol) in methanol (10 mL). The mixture was stirred at ambient temperature for 4 h. Then a saturated aqueous solution of sodium bicarbonate was added and the mixture was extracted with ethyl acetate (3×). The combined organic layers were dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The residue was purified by flash column chromatography (Ø = 1 cm, h = 15 cm, V = 5 mL, cyclohexane/ethyl acetate = 1/1, R_f = 0.22) to give **4d** as colorless oil (17 mg, 0.06 mmol, 36%). $[\alpha]_D^{20}$ +9.8 (1.0; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 1.35 (s, 3H, CH_3), 1.61 (s, 3H, CH_3), 3.77–3.92 (m, 3H, 6-H, 5-H), 4.12 (dd, J = 4.6/3.5 Hz, 1H, 4-H), 4.55 (dd, J = 7.0/5.3 Hz, 1H, 2-H), 4.83 (dd, J = 7.0/4.6 Hz, 1H, 3-H), 4.88 (d, J = 5.3 Hz, 1H, 1-H), 7.28–7.41 (m, 5H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): δ 25.6 (1C, C(*C*H$_3$)$_2$), 27.7 (1C, C(*C*H$_3$)$_2$), 64.7 (1C, C-6), 71.4 (1C, C-5), 81.9 (1C, C-3), 85.9 (1C, C-4), 86.2 (1C, C-1), 86.7 (1C, C-2), 115.4 (1C, *C*(CH$_3$)$_2$), 126.0 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 128.3 (1C, C-4′$_{phenyl}$), 128.8 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 139.7 (1C, C-1′$_{phenyl}$); IR (neat): ν [cm^{-1}] = 3325, 2928, 1450, 1369, 1204, 1069, 1034, 856, 752, 698; HRMS (*m*/*z*): [M+H]$^+$ calcd for $C_{15}H_{21}O_5$, 281.1384; found, 281.1395; HPLC: t_R = 14.4 min, purity 95.1%.

4.2.13. (1*S*)-1-*O*-benzoyl-2,3:5,6-di-*O*-isopropylidene-1-*C*-phenyl-D-mannitol (6)

Compound **5c** (677 mg, 2.0 mmol) was dissolved in CH_2Cl_2 (50 mL) and the solution was cooled to 0 °C. Then *N*,*N*-diisopropylethylamine (0.4 mL, 310 mg, 2.4 mmol), 4-dimethylaminopyridine (24 mg, 0.2 mmol), and benzoyl chloride (0.26 mL, 310 mg, 2.2 mmol) were added and the mixture was stirred at ambient temperature for 16 h. Then a saturated aqueous solution of $NaHCO_3$ was added and the mixture was extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated in vacuo. The residue was purified by flash column chromatography (Ø = 4 cm, h = 15 cm, V = 30 mL, cyclohexane/EtOAc = 8/2, R_f = 0.30) to give **6** as a colorless solid (460 mg, 1.04 mmol, 52%). Mp: 156 °C; $[\alpha]_D^{20}$ +5.4 (1.8; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ 1.10 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.45 (s, 1H, CH_3), 1.59 (s, 1H, CH_3), 2.26 (d br, J = 7.6 Hz, 1H, O*H*), 3.24–3.30 (m, 1H, 4-H), 3.88–3.95 (m, 2H, 5-H, 6-H (1H)), 3.99–4.04 (m, 1H, 6-H), 4.28 (dd, J = 7.1/2.0 Hz, 1H, 3-H), 4.90 (t, J = 7.4 Hz, 1H, 2-H), 6.46 (d, J = 7.8 Hz, 1H, 1-H), 7.30–7.44 (m, 5H, $H_{arom.}$), 7.51–7.58 (m, 3H, $H_{arom.}$), 8.04–8.07 (m, 2H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): δ 25.0 (1C, C(*C*H$_3$)$_2$), 25.6 (1C, C(*C*H$_3$)$_2$),26.7 (1C, C(*C*H$_3$)$_2$), 26.8 (1C, C(*C*H$_3$)$_2$), 67.2 (1C, C-6), 70.1 (1C, C-4), 74.9 (1C, C-1), 75.9 (1C, C-3), 76.3 (1C, C-5), 78.5 (1C, C-2), 108.9 (1C, *C*(CH$_3$)$_2$), 109.4 (1C, *C*(CH$_3$)$_2$), 128.4 (4C, $C_{arom.}$), 128.9 (2C, $C_{arom.}$), 129.1 (1C, $C_{arom.}$), 129.9 (2C, $C_{arom.}$), 130.6 (1C, $C_{arom.}$), 133.0 (1C,

$C_{arom.}$), 137.1 (1C, $C_{arom.}$), 165.6 (1C, *C*=O); IR (neat): *ν* [cm^{-1}] = 3568, 2986, 2936, 1705, 1450, 1373, 1273, 1211, 1111, 1069, 1053, 1026, 841, 706; MS (ESI): *m*/*z* = 465 (M+Na^+, 100); HPLC: t_R = 21.3 min, purity 95.2%.

4.2.14. (1*S*)-1-*O*-benzoyl-2,3:5,6-di-*O*-isopropylidene-4-*O*-methylsulfonyl-1-*C*-phenyl-D-mannitol (7)

Compound **6** (330 mg, 0.75 mmol) and *N*,*N*-diisopropylethylamine (0.25 mL, 194 mg, 1.5 mmol) were dissolved in CH_2Cl_2 (30 mL) and the solution was cooled to 0 °C. Then, methanesulfonyl chloride (0.09 mL, 127 mg, 1.1 mmol) was added and the mixture was stirred at ambient temperature for 16 h. Then a saturated aqueous solution of $NaHCO_3$ was added and the mixture was extracted with CH_2Cl_2 (3×). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated in vacuo. The residue was purified by flash column chromatography (*Ø* = 3 cm, *h* = 15 cm, *V* = 20 mL, cyclohexane/EtOAc = 8/2, R_f = 0.32) to give **7** as colorless solid (330 mg, 0.63 mmol, 85%). Mp: 69 °C; $[\alpha]_D^{20}$ −22.1 (0.7; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): *δ* 1.15 (s, 3H, C*H*$_3$), 1.30 (s, 3H, C*H*$_3$), 1.55 (s, 1H, C*H*$_3$), 1.61 (s, 1H, C*H*$_3$), 3.24 (s, 3H, OSO_2CH_3), 4.04–4.17 (m, 3H, 5-H, 6-H), 4.28 (dd, *J* = 6.1/3.8 Hz, 1H, 3-H), 4.71 (dd, *J* = 6.5/3.8 Hz, 1H, 4-H), 4.85 (dd, *J* = 7.5/6.1 Hz, 1H, 2-H), 6.57 (d, *J* = 7.5 Hz, 1H, 1-H), 7.33–7.46 (m, 5H, $H_{arom.}$), 7.53–7.58 (m, 1H, $H_{arom.}$), 7.60–7.64 (m, 2H, $H_{arom.}$), 8.05–8.09 (m, 2H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): *δ* 25.6 (1C, C(CH_3)$_2$), 25.7 (1C, C(CH_3)$_2$), 26.2 (1C, C(CH_3)$_2$), 26.4 (1C, C(CH_3)$_2$), 39.8 (1C, OSO_2CH_3), 67.3 (1C, C-6), 73.1 (1C, C-1), 74.9 (1C, C-5), 75.8 (1C, C-3), 78.4 (1C, C-4), 79.0 (1C, C-2), 110.1 (1C, *C*(CH_3)$_2$), 110.3 (1C, *C*(CH_3)$_2$), 128.1 (2C, $C_{arom.}$), 128.5 (2C, $C_{arom.}$), 129.1 (2C, $C_{arom.}$), 129.3 (1C, $C_{arom.}$), 130.0 (2C, $C_{arom.}$), 130.0 (1C, $C_{arom.}$), 133.3 (1C, $C_{arom.}$), 136.4 (1C, $C_{arom.}$), 165.7 (1C, *C*=O); IR (neat): *ν* [cm^{-1}] =2986, 2936, 1717, 1454, 1335, 1265, 1215, 1172, 1064, 949, 891, 710; MS (ESI): *m*/*z* = 543 (M+Na^+, 100); HPLC: t_R = 22.4 min, purity 96.1%.

4.2.15. *C*-Phenyl 2,3:5,6-di-*O*-isopropylidene-β-D-talofuranoside (3b)

Sodium methoxide (2 M solution in methanol, 0.8 mL, 1.6 mmol) was added to a solution of **7** (210 mg, 0.4 mmol) in methanol (30 mL) and the mixture was stirred at ambient temperature for 16 h. Then a saturated aqueous solution of sodium bicarbonate was added and the mixture was extracted with dichloromethane (3×). The combined organic layers were dried (Na_2SO_4), filtered, and the solvent was evaporated in vacuo. The residue was purified by flash column chromatography (*Ø* = 2 cm, *h* = 15 cm, *V* = 10 mL, cyclohexane/ethyl acetate = 9/1, R_f = 0.18) to give **3b** as colorless solid (120 mg, 0.37 mmol, 93%). Mp: 91 °C; $[\alpha]_D^{20}$ +45.3 (1.6; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): *δ* 1.29 (s, 3H, C*H*$_3$), 1.38 (s, 3H, C*H*$_3$), 1.44 (s, 3H, C*H*$_3$), 1.45 (s, 3H, C*H*$_3$), 3.98 (t, *J* = 8.2 Hz, 1H, 6-H), 4.06 (dd, *J* = 8.0/6.5 Hz, 1H, 6-H), 4.21 (dd, *J* = 3.0/1.2 Hz, 1H, H-4), 4.27 (ddd, *J* = 9.4/6.4/3.1 Hz, 1H, 5-H), 4.88 (dd, *J* = 6.0/4.1 Hz, 1H, 2-H), 4.94 (dd, *J* = 5.9/1.2 Hz, 1H, 3-H), 5.28 (d, *J* = 4.0 Hz, 1H, 1-H), 7.28-7.40 (m, 5H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): *δ* 24.8 (1C, C(CH_3)$_2$), 25.7 (1C, C(CH_3)$_2$), 26.3 (1C, C(CH_3)$_2$), 26.3 (1C, C(CH_3)$_2$), 65.9 (1C, C-6), 77.6 (1C, C-5), 82.7 (1C, C-4), 83.0 (1C, C-2), 84.0 (1C, C-3a C-3), 85.0 (1C, C-6 C-1), 109.8 (1C, *C*(CH_3)$_2$), 112.9 (1C, *C*(CH_3)$_2$), 127.7 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 127.9 (1C, C-4′$_{phenyl}$), 128.0 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 136.8 (1C, C-1′$_{phenyl}$); IR (neat): *ν* [cm^{-1}] = 2986, 2916, 1748, 1454, 1377, 1204, 1157, 1076, 1053, 968, 895, 856,702; HRMS (*m*/*z*): [M+H]+ calcd for $C_{18}H_{25}O_5$, 321.1697; found, 321.1675; HPLC: t_R = 19.3 min, purity 98.2%.

4.2.16. *C*-Phenyl 2,3-*O*-isopropylidene-β-D-talofuranoside (4b)

p-Toluenesulfonic acid monohydrate (4 mg, 0.02 mmol) was added to a solution of **3b** (66 mg, 0.21 mmol) in methanol (15 mL). The mixture was stirred at ambient temperature for 4 h. Then water was added and the mixture was extracted with ethyl acetate (3×). The combined organic layers were dried (Na_2SO_4), filtered, and the solvent was removed in vacuo. The residue was purified by flash column chromatography (*Ø* = 1 cm, *h* = 15 cm, *V* = 5 mL, cyclohexane/ethyl acetate = 1/1, R_f = 0.19) to give **4b** as colorless solid (35 mg, 0.12 mmol, 61%). Mp: 97 °C; $[\alpha]_D^{20}$ +68.8 (1.1; CH_2Cl_2); ^{1}H NMR ($CDCl_3$): *δ* 1.29 (s, 3H, C*H*$_3$), 1.45 (s, 3H, C*H*$_3$), 2.45 (s br, 1H, O*H*), 2.81 (s br, 1H, O*H*), 3.80–3.84 (m, 3H, 6-H, 5-H), 4.25–4.27 (m, 1H, 4-H), 4.87 (dd, *J* = 6.0/4.0 Hz, 1H, 2-H), 4.94 (dd, *J* = 6.0/1.3 Hz, 1H, 3-H), 5.17 (d, *J* = 4.0 Hz, 1H, 1-H), 7.28–7.40 (m, 5H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): *δ* 24.8 (1C, C(CH_3)$_2$), 26.3 (1C, C(CH_3)$_2$), 64.2 (1C, C-6), 71.8 (1C, C-5), 82.9 (1C, C-2), 83.5 (1C, C-3), 84.4 (1C, C-1), 85.3 (1C, C-4), 112.9 (1C, *C*(CH_3)$_2$), 127.6 (2C, C-2′$_{phenyl}$, C-6′$_{phenyl}$), 128.0 (2C, C-3′$_{phenyl}$, C-5′$_{phenyl}$), 128.1 (1C, C-4′$_{phenyl}$), 136.3 (1C, C-1′$_{phenyl}$); IR (neat): *ν* [cm^{-1}] = 3283, 2936, 1454, 1373, 1207, 1069, 868, 698; HRMS (*m*/*z*): [M+H]$^+$ calcd for $C_{15}H_{21}O_5$, 281.1384; found, 281.1387; HPLC: t_R = 12.7 min, purity 97.0%.

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