

New Chiral Building Blocks and Branched 1,6-Anhydro Sugars from Regio- and Stereoisomeric Černý Epoxides^[‡]

Karsten Krohn,^{*,[a]} Dietmar Gehle,^[a] and Ulrich Flörke^[a]

Dedicated to Prof. Dieter Arlt on the occasion of his 70th birthday

Keywords: 1,6-Anhydro sugars / Chiral building blocks / Branched sugars / Černý epoxides / Gilman cuprates / Epoxide rearrangement / Vinyl tosylate cross coupling

The tandem epoxide→allyl alcohol rearrangement–cuprate cross-coupling previously described for the Černý epoxide **1**, to yield the allyl alcohol **2**, was extended to the regioisomeric epoxy-tosylate **3**, to yield allyl alcohol **4**, and to the stereoisomeric epoxide **5** to afford the allyl alcohols of type **6**. Further transformation of the products from this new two-step one-

pot reaction afforded regio- and stereodiverse branched 1,6-anhydrosugars of potential use as building blocks in natural product synthesis.

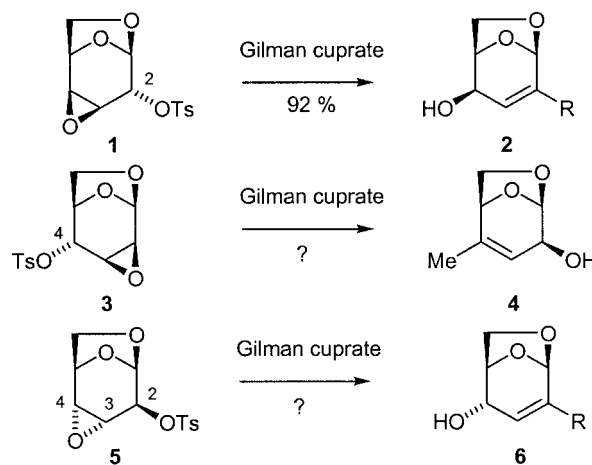
(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

In a previous communication,^[1] we reported on a new tandem epoxide→allyl alcohol rearrangement–cuprate cross-coupling reaction, induced by treatment of the “Černý” epoxide **1** (dioxirane at C-3,4)^[2] with Gilman cuprates, to afford the synthetically valuable allyl alcohol **2** (R = methyl, ethyl, *n*-butyl). This allyl alcohol could be converted to numerous new branched 1,6-anhydrosugars, sterically complementary to hitherto known branched sugar derivatives. The conversion of an intermediate allyl alcohol (**2**, R = OTs) to the methylated compound (R = methyl) supported the mechanism of initial deprotonation at C-2 by an excess of the basic Gilman cuprate, followed by epoxide→allyl alcohol rearrangement. The C–H acidity at C-2 of the tosylate **1** may be increased by the presence of the electron-withdrawing *O*-tosyl group, facilitating the subsequent epoxide→allyl alcohol rearrangement. In addition, complexation of the anomeric oxygen with the lithium cation of the Gilman cuprate might direct the attack of the base at 2-H.

To exploit the great potential of the new tandem reaction and to extend the stereochemical diversity of available chiral building blocks, we now report on investigations to probe the reaction on the regioisomeric 2,3-epoxide **3** and the stereoisomeric 3,4-epoxide **5** (Scheme 1). The outcome of the desired formation of the allyl alcohols **4** and **6** was

absolutely uncertain in view of the unknown stereoelectronic requirements of the two sequential reactions.^[1]



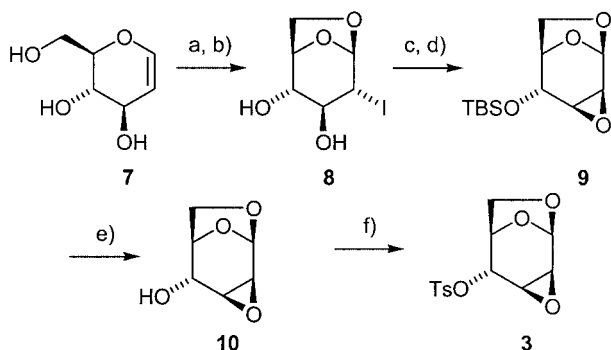
Scheme 1. Tandem epoxide→allyl alcohol rearrangement–cuprate cross-coupling of Černý epoxides **1**, **3**, and **5** with Gilman cuprates.

Results and Discussion

The synthesis of the required epoxide **3** started with glucal (**7**), which was converted into the iodo-1,6-anhydrosugar **8** as described by Czernecki et al.^[3] (Scheme 2). The further steps to **3** included silylation and base-catalyzed cyclization of the α -hydroxy iodide **8** to silylated epoxide **9** according to Samadi et al.^[4] Desilylation of the TBS ether **9** to the alcohol **10** using tetrabutylammonium fluoride (TBAF) was followed by tosylation to afford **3** in 86% combined yield.

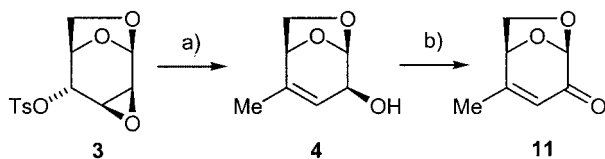
[‡] Highly Deoxygenated Sugars, 4. Part 3: Ref.^[1]

[a] Department Chemie, University of Paderborn, Warburger Straße 100, 33098 Paderborn, Germany
E-mail: Karsten.Krohn@uni-paderborn.de



Scheme 2. a) $(\text{Bu}_3\text{Sn})_2\text{O}$, 3-Å molecular sieves, acetonitrile, reflux, 6 h; b) I_2 , room temp., 12 h, 68–79%; c) TBSCl, imidazole, DMF, room temp., 4 h; d) NaH (3 equiv.), 2 h, 85%; e) TBAF, THF, room temp., 20 min, 95%; f) TsCl, Et_3N , DMAP, CH_2Cl_2 , room temp., 2 h, 91%.

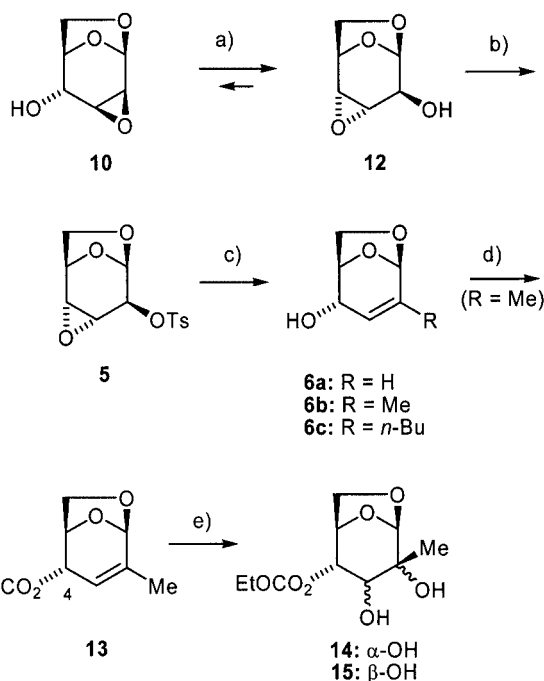
Having epoxide-tosylate **3** in hand, the stage was set to try the tandem epoxide→allyl alcohol rearrangement–cuprate cross-coupling reaction. To our delight, epoxide **3** was smoothly converted into the allyl alcohol **4** by treatment with the methyl Gilman cuprate (Scheme 3). The yield was lower (64%) than in the conversion of **1** to **2** (92%),^[1] but the product was a single stereoisomer. Similar to the previously described regioisomeric allyl alcohol **2**,^[1] the oxidation to the corresponding α,β -unsaturated ketone **11** was achieved in 94% yield using PDC as the oxidant. Both the alcohol **4** and the enone **11** have been synthesized previously by different routes, and both compounds are of great pharmaceutical interest. The allyl alcohol **4** was prepared in connection with α -glucosidase inhibition and cancer metastasis inhibitors.^[5] The enone **11** was used in a formal synthesis of (+)-grandisol from levoglucosenone^[6] and mentioned in a number of patents as part of an investigation of immuno-suppressing and anti-inflammatory agents.^[7–10] The further transformations of the densely packed functional groups in **4** and **11** are part of a future communication.



Scheme 3. a) CuCN (4 equiv.), MeLi (8 equiv.), $\text{Et}_2\text{O}/\text{THF}$, -78°C (1 h) to -20°C (2 h), 64%; b) PDC, CH_2Cl_2 , 18 h, 94%.

Next, we wanted to test the feasibility of the tandem epoxide→allyl alcohol rearrangement–cuprate cross-coupling reaction on the stereoisomeric 3,4-epoxide **5**. Epoxide **5** is not directly available from levoglucosan (**1**). However, already in 1965 Černý and coworkers discovered the base-catalyzed Payne rearrangement of epoxy alcohol **10**, easily available from levoglucosan or as shown in Scheme 2, to the regioisomeric epoxy alcohol **12**, as shown in Scheme 4.^[11] The equilibrium lies almost entirely on the side of epoxide **12**, possibly due to stabilizing chelation of 2-OH to the bridged oxygen. It is worth noting that base treatment of

iodolevoglucosan (**8**) also results in epoxide **12**, through intermediate **10**. Surprisingly, the chemistry of this easily available epoxide **12** was only occasionally exploited and its use as the starting material for the synthesis of 3-substituted D-mannose derivatives was the most noteworthy transformation.^[12] The tandem epoxide→allyl alcohol rearrangement–tosylate cross coupling reaction with **5** would not only permit alkylation at C-2 but also generate the inverse stereochemistry at C-4 with respect to alcohol **2**, available from epoxide **1** (see Scheme 1).



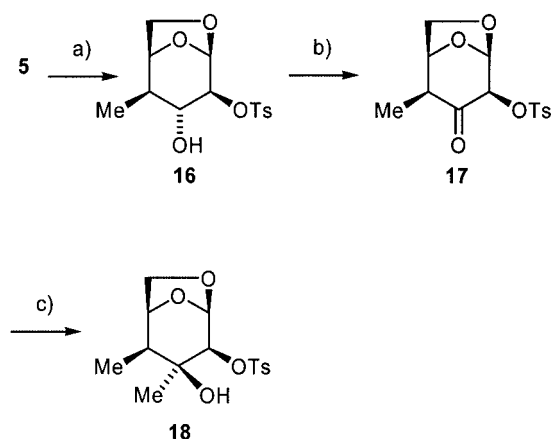
Scheme 4. a) NaOMe (4 equiv.), CH_2Cl_2 , (12 h), 95%; b) TsCl, Et_3N , DMAP, CH_2Cl_2 , 2 h, 92%; c) CuCN (4 equiv.), RLi (8 equiv.), $\text{Et}_2\text{O}/\text{THF}$, -78°C (1 h) to -20°C (2 h), 84%; d) TMEDA (0.6 equiv.), ethyl chlorocarbonate (1.2 equiv.), CH_2Cl_2 , (0.5 h), 90%; e) OsO_4 , NMO, acetone/ H_2O , 58%.

The reaction of epoxide **5** with the Gilman cuprate was performed as described previously for compound **1**^[1] to yield methylated allyl alcohol **6b** in 84% isolated yield as the only product. To further probe the generality of the reaction, **5** was also reacted with the corresponding *n*-butyl Gilman cuprate to afford the butyl compound **6c** in 68% yield in addition to 22% of the nonalkylated allyl alcohol **6a**. The product **6a** may be formed by hydrolysis of an intermediate metalated vinyl species.

Many more functional group transformations are awaiting the study of the chemistry of the allyl alcohols of type **6**, complementary in stereochemistry to the product **2**, described in the previous communication.^[1] In this paper, only one preliminary experiment was performed analysing the inverse stereochemical influence of the anhydro bridge and an axially orientated carbonate at C-4. Thus, the mixed carbonate **13** was subjected to the Upjohn osmylation conditions yielding a ca. 1.5:1 (NMR) mixture of the respective α and β *cis*-diols **14** and **15**. This result perfectly reflects the stereochemical situation with the opposing effect of the ax-

ial anhydro bridge and the axial substituents at C-4, shielding the 2,3-double bond to attack from both the top and bottom sides.^[13–15]

Finally, we wanted to extend the use of the tosylate **5**, readily available from the Payne rearrangement product **12**. In the reaction of **5** with Normant cuprates, we expected the formation of a C-3 methylated product, in agreement with the Fürst–Plattner rules, leading to the respective 3,4-diaxial products (Scheme 5).^[16] However, to our surprise, the reaction of **5** with methylmagnesium chloride, in the presence of catalytic amounts of copper iodide, led to methylation at C-4 to afford alcohol **16** in 89% yield with equatorial substituents at C-3 and C-4. This is one of the very rare examples^[17] in which the violation of the Fürst–Plattner rules is reported for a carbon nucleophile in the field of 1,6-anhydrosugars. Reports in the literature state that “hard” nucleophiles strictly open in a *trans*-diaxial manner, whereas “soft” ones occasionally open equatorially.^[14,15] Since the Normant cuprates are more on the “soft” side, our surprising result is in line with this explanation. The structure of **16** was confirmed by analysis of the ¹H NMR spectrum, showing a coupling of ³J_{3,4} = 7.5 Hz for *trans*-diaxial protons. Also the strong NOE correlation of 4-H with 2-H confirmed this assignment.



Scheme 5. Fürst–Plattner rule opposed opening of epoxide **5** followed by conversion to alcohol **18**. a) MeMgCl (4 equiv.), CuI (10 mol-%), THF, 40 °C, 12 h, 89%; b) RuCl₃·3 H₂O (1 mol-%), NaBrO₃ in H₂O (0.65 equiv.), acetonitrile/AcOH, 0 °C, 4 h, 99%; c) MeMgCl, Et₂O, 0 °C, 45 min, 93%.

Next, the alcohol **16** was almost quantitatively oxidized to the ketone **17** using catalytic amounts of ruthenium trichloride and sodium bromate as the cooxidant.^[18,19] Suitable crystals for X-ray analysis were obtained from the ketone **17** and the molecule in the crystal is shown in Figure 1, confirming the “*anti*-Fürst–Plattner” addition of the methyl group at C-4 and its equatorial position.

The ketone **17** can serve to prepare further branched sugars and stereochemical “triads” for natural product synthesis. The reaction of **17** with methylmagnesium chloride afforded a single tertiary alcohol **18** isolated in 93% yield as a colorless solid. The equatorial position of the methyl group is in agreement with the missing NOE correlation

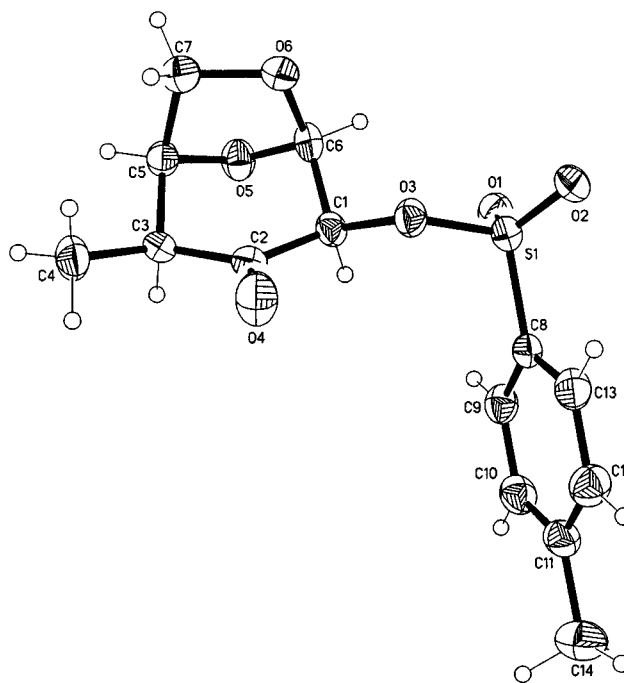


Figure 1. The molecular structure of **17**. Selected bond lengths [Å] and angles [°]: C1–O3 1.435(3), C2–O4 1.183(3), C6–O6 1.406(4), C7–O6 1.444(4), C1–C2 1.515(4), C1–C6 1.520(4), C2–C3 1.506(4), C3–C4 1.513(4), C3–C5 1.523(4), C5–C7 1.504(4); C5–O5–C6 102.3(2), C6–O6–C7 106.4(2).

with *endo* H-6. The stereochemical outcome is in agreement with the strong shielding of the top-side of the molecule, also clearly visible in the X-ray structure **17** (see Figure 1).

Experimental Section

General: For general methods and instrumentation see ref.^[20] and the preceding paper.^[1]

1,6-Anhydro-2-deoxy-2-iodo-β-D-glucopyranose (2-Iodolevoglucosan) (8): M.p. 101 °C (ref.^[3] m.p. 101–103 °C). [α]_D²⁰ = +10.1 (*c* = 0.92 in MeOH), (ref. ^[21] +10, *c* = 1.0, MeOH).

1,6,2,3-Dianhydro-4-O-tert-butyldimethylsilyl-β-D-mannopyranose (9): M.p. 55 °C (ref. m.p. 54–56 °C^[4]). [α]_D²⁰ = –22.8 (*c* = 0.99 in CH₂Cl₂), (ref. –23 (*c* = 1.0, CH₂Cl₂)^[4]).

1,6,2,3-Dianhydro-β-D-mannopyranose (10): A solution **9** (2.0 g, 7.74 mmol) in dry THF was treated with tetrabutylammonium fluoride (TBAF, 2.68 g, 8.5 mmol, 1.1 equiv.). After 1 h, the mixture was concentrated and the residue was filtered through a batch of silica gel (CH₂Cl₂/5% diethyl ether) to afford the epoxide **10** (1.05 g, 7.35 mmol, 95%) as colorless crystals. Aqueous workup leads to loss of products due to the remarkable water solubility of the unprotected epoxide. M.p. 70 °C (ref.^[22] 68–70 °C). [α]_D²⁰ = +32.9 (*c* = 1.0, MeOH), [ref.^[22] +33.8 (*c* = 1.02, MeOH)].

1,6,2,3-Dianhydro-4-O-p-tolylsulfonyl-β-D-mannopyranose (3): A solution of **10** (2.9 g, 20.1 mmol) in dry CH₂Cl₂ (50 mL) was treated with triethylamine (5.2 mL, 40.2 mmol, 2 equiv.) and DMAP (cat.). Tosyl chloride (7.6 g, 40.2 mmol, 2 equiv.) was then added to the cooled (0 °C) mixture in portions. After 2 h at 22 °C, the conversion was complete and the mixture was poured into ice water. Colorless needles of **3** formed, which were filtered off and

dried to yield **3**; (5.45 g, 18.2 mmol, 91%); m.p. 136 °C, (ref.^[11] 137–138 °C). $[\alpha]_D^{20} = -38.0$ ($c = 1.2$, CHCl₃), [ref.^[11] –37 ($c = 1.0$, CHCl₃)]. ¹H NMR (500 MHz, CDCl₃): $\delta = 2.49$ (s, 3 H, Ar–CH₃), 3.10 (ddd, $J_{3,2} = 3.6$, $J_{3,4} = 1.5$, $J_{3,5} = 0.8$ Hz, 1 H, 3-H), 3.47 (ddd, $J_{2,3} = 3.6$, $J_{2,1} = 3.3$, $J_{2,4} = 0.8$ Hz, 1 H, 2-H), 3.73–3.75 (m, 2 H, 6-H), 4.53 (m, 1 H, 5-H), 4.65 (d, $J_{4,3} = 1.5$ Hz, 1 H, 4-H), 5.72 (d, $J_{1,2} = 3.3$ Hz, 1 H, 1-H), 7.42 (d, $J_{Ar,Ar} = 8.3$ Hz, 2 H, Ar-H), 7.87 (d, $J_{Ar,Ar} = 8.3$ Hz, 2 H, Ar-H) ppm. ¹³C NMR (125 MHz, CDCl₃): $\delta = 21.7$ (q, Ar–CH₃), 47.1 (d, C-3), 54.4 (d, C-2), 65.6 (t, C-6), 71.8 (d, C-5), 74.1 (d, C-4), 97.4 (d, C-1), 127.9, 130.2 (d, 4 × C–Ar), 133.1 (s, S–C_{Ar}), 145.7 (s, C_{Ar}–CH₃) ppm.

1,6:3,4-Dianhydro-β-D-altropyranose (12): NaOMe (137 mL of a 0.8 M solution, 100 mmol, 4 equiv.) was added to a stirred solution of iodolevoglucosan (**8**) (7.5 g, 27.6 mmol) in CH₂Cl₂ (350 mL) at room temp. with a dropping funnel over a period of 1 h. After 12 h, the solution was neutralized to pH = 7 by addition of HCl (10%). The aqueous phase was extracted with EtOAc (10 × 25 mL) and the combined organic phases were dried (Na₂SO₄), filtered, and concentrated to obtain the epoxide **12** (3.45 g, 23.9 mmol, 87%) as a solid, which can be used without any further purification. M.p. 159 °C (ref.^[23] 161–162 °C). $[\alpha]_D^{20} = -120$ ($c = 1.3$, H₂O), [ref.^[23] –121 ($c = 0.6$, H₂O)]. ¹H NMR (500 MHz, MeOD): $\delta = 2.92$ (dd, $J_{3,2} = 3.0$, $J_{3,4} = 3.5$ Hz, 1 H, 3-H), 3.22 (d, $J_{4,3} = 3.5$ Hz, 1 H, 4-H), 3.70 (d, $J_{2,3} = 3.0$ Hz, 1 H, 2-H), 3.81 (dd, $J_{6a,6b} = 7.4$, $J_{6a,5} = 4.4$ Hz, 1 H, 6a-H), 4.08 (d, $J_{6b,6a} = 7.4$ Hz, 1 H, 6b-H), 4.69 (d, $J_{5,6a} = 4.4$ Hz, 1 H, 5-H), 5.22 (s, 1 H, 1-H) ppm. ¹³C NMR (50 MHz, CDCl₃): $\delta = 50.1$ (d, C-4), 51.0 (d, C-3), 65.4 (d, C-2), 66.8 (t, C-6), 69.7 (d, C-5), 99.4 (C-1) ppm.

1,6:3,4-Dianhydro-2-O-p-toluolsulfonyl-β-D-altropyranose (5): A solution of **12** (3.1 g, 21.5 mmol) in dried CH₂Cl₂ (50 mL) was treated with triethylamine (5.5 mL, 43.0 mmol, 2 equiv.) and DMAP (cat.). Tosyl chloride (8.2 g, 43.0 mmol, 2 equiv.) was added to the cooled (0 °C) mixture in portions. After 2 h at room temp. the conversion was complete and the mixture was poured into ice water while stirring. The colorless needles were filtered off to yield **5** (5.90 g, 19.8 mmol, 92%); m.p. 101 °C, (ref.^[24] 102–103 °C). $[\alpha]_D^{20} = -68$ ($c = 0.36$, CHCl₃), [ref.^[24] –70 ($c = 1.35$, CHCl₃)]. ¹H NMR (500 MHz, CDCl₃): $\delta = 2.49$ (s, 3 H, Ar–CH₃), 3.05 (dd, $J_{3,2} = 2.4$, $J_{3,4} = 3.5$ Hz, 1 H, 3-H), 3.15 (bd, $J_{4,3} = 3.5$ Hz, 1 H, 4-H), 3.88 (dd, $J_{6a,6b} = 7.6$, $J_{6a,5} = 4.4$ Hz, 1 H, 6a-H), 4.13 (d, $J_{6b,6a} = 7.6$ Hz, 1 H, 6b-H), 4.51 (dd, $J_{2,3} = 2.4$, $J_{2,1} = 2.6$ Hz, 1 H, 2-H), 4.73 (dd, $J_{5,6a} = 4.4$, $J_{5,4} = 0.8$ Hz, 1 H, 5-H), 5.26 (d, $J_{1,2} = 2.6$ Hz, 1 H, 1-H), 7.39 (d, $J_{Ar,Ar} = 8.3$ Hz, 2 H, Ar–H), 7.87 (d, $J_{Ar,Ar} = 8.3$ Hz, 2 H, Ar–H) ppm. ¹³C NMR (125 MHz, CDCl₃): $\delta = 21.7$ (q, Ar–CH₃), 49.0 (d, C-3), 49.7 (d, C-4), 67.5 (t, C-6), 69.9 (d, C-5), 71.8 (d, C-2), 97.1 (d, C-1), 128.0, 130.2 (d, 4 × C–Ar), 133.0 (s, S–C_{Ar}), 145.6 (s, C_{Ar}–CH₃) ppm.

General Procedure for the Reaction of Epoxides with the Gilman Cuprate: A suspension of CuCN (4 equiv.) in freshly distilled dry diethyl ether was treated under argon at –78 °C with a solution of the respective organolithium compound (8 equiv.) over a period of 5 min. The solution was then allowed to warm to 0 °C. During this time the suspension became transparent. After stirring for 10 min at 0 °C, the mixture was cooled to –78 °C and a solution of the respective epoxide was added in dry THF. The resulting yellow solution was stirred at –78 °C for 1 h and was then allowed to warm up to –20 °C. After complete conversion of the starting material (ca. 2 h, at –20 °C, TLC monitoring) the reaction was quenched by dropwise addition of water (15 mL) and then with a saturated aqueous NH₄Cl (15 mL) solution. The biphasic mixture was stirred until the aqueous phase turned blue. The aqueous phase was washed with diethyl ether (5 × 20 mL) and the combined ethereal

phases were dried (Na₂SO₄), evaporated at reduced pressure, and purified by column chromatography (CH₂Cl₂/acetone, 95:5).

1,6-Anhydro-3,4-dideoxy-4-methyl-β-D-threohex-3-enopyranose (4): Amounts of reagents: **3** (500 mg, 1.7 mmol) in dried THF (20 mL); CuCN (600 mg, 6.7 mmol, 4 equiv.) in dried diethyl ether (20 mL); methyllithium (1.6 M in diethyl ether, 8.4 mL, 13.4 mmol, 8 equiv.). Yield of **4**: colorless oil (155 mg, 1.1 mmol, 64%). $[\alpha]_D^{20} = -69.3$ ($c = 1.09$, MeOH). ¹H NMR (500 MHz, CDCl₃): $\delta = 1.75$ (s, 3 H, 7-H), 2.13 (br. s, 1 H, OH), 3.75 (dd, $J_{6a,6b} = 6.6$, $J_{6a,5} = 4.0$ Hz, 1 H, 6a-H), 3.79 (d, $J_{6b,6a} = 6.6$ Hz, 1 H, 6b-H), 4.29 (s, 1 H, 2-H), 4.44 (d, $J_{5,6a} = 4.0$ Hz, 1 H, 5-H), 5.32 (s, 1 H, 3-H), 5.49 (s, 1 H, 1-H) ppm. ¹³C NMR (125 MHz, CDCl₃): $\delta = 19.0$ (q, C-7), 69.0 (d, C-2), 69.9 (t, C-6), 74.8 (d, C-5), 100.6 (d, C-1), 122.2 (d, C-3), 139.1 (s, C-4) ppm. IR (Film): $\tilde{\nu} = 3411$ (s, O–H), 2980 (s, C–H), 2924 (m, C–H), 1677 (w, C=C), 1461 (m, C–H), 1365 (s, C–H), 1360 (s, C–H), 1251 (s, C–O), 1011 (s, C–O) cm^{–1}. MS (EI, 70 eV): m/z (%) = 142 (55) [M⁺], 111 (21), 99 (90), 95 (77), 82 (100), 71 (58), 57 (55), 43 (82) 29 (20). HRMS (EI): calcd. for C₇H₁₀O₃ 142.0629; found 142.0629. C₇H₁₀O₃ (142.15): calcd. C 59.14, H 7.09; found C 58.76, H 7.00.

1,6-Anhydro-2,3-dideoxy-2-methyl-β-D-erythrohex-2-enopyranose (6b): Amounts of reagents: **5** (502 mg, 1.7 mmol) in dry THF (20 mL); CuCN (600 mg, 6.7 mmol, 4 equiv.) in dry diethyl ether (20 mL); methyllithium (1.6 M in diethyl ether, 8.4 mL, 13.4 mmol, 8 equiv.). Yield: **6b**, 202 mg, colorless oil (1.42 mmol, 85%). $[\alpha]_D^{20} = +131.7$ ($c = 1.35$, MeOH). ¹H NMR (500 MHz, CDCl₃): $\delta = 1.77$ (s, 3 H, H–CH₃), 2.35 (br. s, 1 H, OH), 3.45 (dd, $J_{6a,6b} = 7.7$, $J_{6a,5} = 1.9$ Hz, 1 H, 6a-H), 3.63 (ddd, $J_{4,5} = 3.0$, $J_{4,3} = 5.9$, $J_{4,6} = 1.3$ Hz, 1 H, 4-H), 3.91 (dd, $J_{6b,6a} = 7.7$, $J_{6b,5} = 7.0$ Hz, 1 H, 6b-H), 4.64 (dddd, $J_{5,4} = 3.0$, $J_{5,6a} = 1.9$, $J_{5,6b} = 7.0$, $J_{5,3} = 1.6$ Hz, 1 H, 5-H), 5.30 (s, 1 H, 1-H), 5.45 (ddd, $J_{3,4} = 5.9$, $J_{3,5} = 1.6$, $J_{3,1} = 3.0$ Hz, 1 H, 3-H) ppm. ¹³C NMR (125 MHz, CDCl₃): $\delta = 18.7$ (q, C-7), 63.0 (t, C-6), 67.1 (d, C-4), 76.5 (d, C-5), 99.4 (d, C-1), 119.6 (d, C-3), 138.9 (s, C-2). IR (Film): $\tilde{\nu} = 3400$ (s, O–H), 2969 (s, C–H), 2908 (m, C–H), 1679 (w, C=C), 1450 (m, C–H), 1369 (s, C–H), 1259 (s, C–O), 1086 (s, C–O) cm^{–1}. MS (EI, 70 eV): m/z (%) = 142 (52) [M⁺], 111 (24), 99 (100), 95 (55), 82 (95), 71 (55), 57 (58), 43 (72) 29 (30). HRMS (EI): calcd. for C₇H₁₀O₃ 142.0629; found 142.0630. C₇H₁₀O₃ (142.15): calcd. C 59.14, H 7.09; found C 59.76, H 7.56.

1,6-Anhydro-2-butyl-2,3-dideoxy-β-D-erythrohex-2-enopyranose (6c): Amounts of reagents: **5** (500 mg, 1.68 mmol) in THF (20 mL); CuCN [600 mg, 6.7 mmol, 4 equiv. in dry diethyl ether (10 mL)]; butyllithium (1.54 M in hexane, 8.78 mL, 13.4 mmol, 8 equiv.). Yield of **6c**: colorless oil (209 mg, 1.14 mmol, 68%). $[\alpha]_D^{20} = +94.3$ ($c = 0.86$, MeOH). ¹H NMR (500 MHz, CDCl₃): $\delta = 0.93$ (t, $J_{10,9} = 7.3$ Hz, 3 H, 10-H), 1.30–1.38 (m, 2 H, 9-H), 1.41–1.48 (m, 2 H, 8-H), 2.05–2.10 (m, 2 H, 7-H), 2.15 (br. s, 1 H, OH), 3.41 (dd, $J_{6a,6b} = 7.7$, $J_{6a,5} = 2.0$ Hz, 1 H, 6a-H), 3.66 (ddd, $J_{4,5} = 3.4$, $J_{4,3} = 2.9$, $J_{4,6a} = 1.2$ Hz, 1 H, 4-H), 3.92 (dd, $J_{6b,6a} = 7.7$, $J_{6b,5} = 6.5$ Hz, 1 H, 6b-H), 4.65 (ddd, $J_{5,6a} = 2.0$, $J_{5,6b} = 6.5$, $J_{5,4} = 3.4$ Hz, 1 H, 5-H), 5.34 (d, $J_{1,3} = 0.9$ Hz, 1 H, 1-H), 5.46 (dd, $J_{3,4} = 2.9$, $J_{3,1} = 0.9$ Hz, 1 H, 3-H) ppm. ¹³C NMR (125 MHz, CDCl₃): $\delta = 13.8$ (q, C-10), 22.2 (t, C-9), 29.0 (t, C-8), 32.6 (t, C-7), 63.0 (t, C-6), 67.2 (d, C-4), 76.8 (d, C-5), 99.0 (d, C-1), 118.6 (d, C-3), 142.9 (s, C-2) ppm. IR (Film): $\tilde{\nu} = 3402$ (m, O–H), 2966 (m, C–H), 2924 (m, C–H), 2865 (m, C–H), 1693 (m, C=C), 1591 (m, C–H), 1455 (s, C–H), 1366 (s, C–H), 1172 (s, C–O), 980 (s, C–O) cm^{–1}. MS (EI, 70 eV): m/z (%) = 184 (48) [M⁺], 155 (9), 141 (18), 111 (21), 95 (78), 85 (55), 82 (100), 81 (90), 71 (40) 68 (38), 57 (92), 55 (82), 43 (60), 41 (80) 27 (30). HRMS (EI): calcd. for C₁₀H₁₆O₃; 184.1099; found 184.1101. C₁₀H₁₆O₃ (184.23): calcd. C 65.19; H 8.75; found C 65.86; H 8.92.

1,6-Anhydro-2,3-dideoxy- β -D-erythrohex-2-enopyranose (6a): Analysis of byproduct: $[a]_D^{20} = +154.2$ ($c = 0.59$, MeOH). ^1H NMR (500 MHz, CDCl_3): $\delta = 2.65$ (br. s, 1 H, OH), 3.46 (dd, $J_{6a,6b} = 7.9$, $J_{6a,5} = 2.2$ Hz, 1 H, 6a-H), 3.66 (m, 1 H, 4-H), 3.94 (dd, $J_{6b,6a} = 7.9$, $J_{6b,5} = 6.6$ Hz, 1 H, 6b-H), 4.67 (m, 1 H, 5-H), 5.57 (d, $J_{1,2} = 3.4$ Hz, 1 H, 1-H), 5.85 (m, 1 H, 3-H), 6.03 (ddd, $J_{2,1} = 3.4$, $J_{2,3} = 9.5$, $J_{2,4} = 0.6$ Hz, 1 H, 2-H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 62.6$ (t, C-6), 67.2 (d, C-4), 76.9 (d, C-5), 95.5 (d, C-1), 126.3 (d, C-3), 130.1 (d, C-2) ppm. IR (Film): $\tilde{\nu} = 3436$ (s, O-H), 2965 (s, C-H), 2918 (s, C-H), 2893 (s, C-H), 1734 (m, C=C), 1636 (m, C-H), 1387 (s, C-H), 1175 (s, C-O), 1093 (s, C-O), 1056 (s, C-O), 984 (s, C-O) cm^{-1} . MS (EI, 70 eV): m/z (%) = 128 (10) $[\text{M}^+]$, 97 (14), 85 (40), 81 (19), 70 (28), 68 (100), 57 (57), 54 (20), 41 (27), 39 (21), 29 (21), 27 (17). HRMS (EI): calcd. for $\text{C}_6\text{H}_8\text{O}_3$ 128.0473, found 128.0473. $\text{C}_6\text{H}_8\text{O}_3$ (128.13) calcd. C 56.24, H 6.29; found C 55.87, H 6.61.

1,6-Anhydro-3,4-dideoxy-4-methyl- β -D-glycerohex-3-enopyranose-2-ulose (11): Allyl alcohol **4** (130 mg, 0.9 mmol) in dry CH_2Cl_2 (30 mL) was treated with PDC (400 mg, 1.9 mmol, 2 equiv.). The mixture was stirred at room temp. for 24 h. After complete conversion of the starting material, the solution was diluted by addition of diethyl ether (50 mL), the inorganic product was filtered off (Celite, washing with diethyl ether, 10 mL), and the filtrate evaporated at reduced pressure. The residue was purified by flash chromatography (CH_2Cl_2 , 100:0 to 98:2) to yield enone **11** (119 mg, 0.85 mmol, 94%) as colorless crystals. $[a]_D^{20} = -482$ ($c = 0.95$, MeOH). ^1H NMR (500 MHz, CDCl_3): $\delta = 2.07$ (d, $J_{7,3} = 1.6$ Hz, 3 H, 7-H), 3.70 (dd, $J_{6a,6b} = 6.8$, $J_{6a,5} = 0.3$ Hz, 1 H, 6a-H), 3.89 (dd, $J_{6b,6a} = 6.8$, $J_{6b,5} = 4.8$ Hz, 1 H, 6b-H), 4.80 (d, $J_{5,6b} = 4.8$ Hz, 1 H, 5-H), 5.29 (d, $J_{1,3} = 1.4$ Hz, 1 H, 1-H), 5.85 (dd, $J_{3,7} = 1.4$, $J_{3,1} = 1.6$ Hz, 1 H, 3-H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 20.1$ (q, C-7), 66.5 (t, C-6), 75.9 (d, C-5), 100.9 (d, C-1), 122.5 (d, C-3), 161.0 (s, C-4), 189.2 (s, C-2) ppm. IR (Film): $\tilde{\nu} = 2979$ (s, C-H), 2893 (m, C-H), 2855 (m, C-H), 1748 (w, C=C), 1701 (s, C=C), 1677 (s, C=O), 1438 (m, C-H), 1381 (s, C-H), 1300 (s, C-H), 1261 (s, C-O), 1123 (s, C-O), 1066 (w, C-C), 961 (s, C-O) cm^{-1} . MS (EI, 70 eV): m/z (%) = 140 (80) $[\text{M}^+]$, 99 (19), 97 (100), 82 (24), 71 (7), 69 (22), 57 (5), 55 (5), 53 (7), 43 (8), 41 (42), 29 (8), 27 (14). HRMS (EI): calcd. for $\text{C}_7\text{H}_8\text{O}_3$ 140.04734; found 140.04734. $\text{C}_7\text{H}_8\text{O}_3$ (140.15): calcd. C 59.99, H 5.75; found C 59.99, H 5.70.

1,6-Anhydro-4-deoxy-4-methyl-2-O-p-tolylsulfonyl- β -D-idopyranose (16): A suspension of CuI (141 mg, 0.74 mmol, 10 mol-%) in abs. THF (20 mL) was treated at -20°C with MeMgCl (9.84 mL of a 3 M solution in THF, 29.5 mmol, 4 equiv.). A solution of epoxide **5** (2.20 g, 7.38 mmol) in abs. THF (100 mL) was added to this. The resulting mixture was kept at 40°C for 12 h and after complete conversion (TLC monitoring) it was diluted with EtOAc (200 mL). A sat. NH_4Cl solution (80 mL) was added and the biphasic mixture was stirred for 1 h. Extraction of the aqueous phase with EtOAc (3×30 mL) and concentration of the dried (Na_2SO_4) combined organic phases led to a crude product which was purified by flash column chromatography (CH_2Cl_2 /acetone, 98:2). Yield of pyranose **16** (colorless crystals): 2.06 g (6.57 mmol, 89%); m.p. 141°C . $[a]_D^{20} = -79$ ($c = 0.84$, MeOH). ^1H NMR (500 MHz, CDCl_3): $\delta = 1.06$ (d, $J_{7,4} = 6.9$ Hz, 1 H, 7-H), 2.06 (m, 1 H, 4-H), 2.48 (s, 3 H, Ar-CH₃), 2.50 (br. s, 1-H, OH), 3.64 (ddd, $J_{3,2} = 7.6$, $J_{3,4} = 7.5$, $J = 2.6$ Hz, 1 H, 3-H), 3.68 (dd, $J_{6a,6b} = 7.7$, $J_{6a,5} = 5.2$ Hz, 1 H, 6a-H), 3.89 (d, $J_{6b,6a} = 7.7$ Hz, 1 H, 6b-H), 4.27 (dd, $J_{2,3} = 7.6$, $J_{2,1} = 1.7$ Hz, 1 H, 2-H), 4.32 (dd, $J_{5,6a} = 5.2$, $J_{5,4} = 4.8$ Hz, 1 H, 5-H), 5.31 (d, $J_{1,2} = 1.7$ Hz, 1 H, 1-H), 7.38 (d, $J_{\text{Ar,Ar}} = 8.0$ Hz, 2 H, Ar-H), 7.87 (d, $J_{\text{Ar,Ar}} = 8.0$ Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 12.9$ (q, C-7), 21.7 (q, CH₃-Ar), 40.3 (d, C-4), 64.9 (t, C-6), 72.0 (d, C-3), 77.5 (d, C-5), 83.7 (d, C-2), 99.6 (d, C-1), 128.0,

130.0 ($2 \times \text{d}$, $2 \times \text{C-Ar}$), 133.0 (s, C-Ar), 145.4 (s, C-Ar) ppm. IR (Film): $\tilde{\nu} = 3508$ (br. O-H), 2960 (m, C-H), 2903 (m, C-H), 2898 (m, C-H), 1589 (w, C=C), 1455 (m, C-S), 1356 (s, C-H), 1175 (s, C-H), 1129 (s, C-H), 1020 (s, C-O), 953 (s, C-O), 917 (s, C-H) cm^{-1} . MS (CI, isobutane): m/z (%) = 315 (5) $[\text{M}^+ + 1]$, 159 (80), 155 (62), 113 (100), 91 (74), 85 (40), 83 (77), 71 (30), 57 (22), 55 (56), 43 (26). $\text{C}_{14}\text{H}_{18}\text{O}_6\text{S}$ (314.35): calcd. C 53.49, H 5.77; found C 53.56, H 5.71.

1,6-Anhydro-4-deoxy-4-methyl-2-O-p-tolylsulfonyl- β -D-lyxopyranose-3-ulose (17): A solution of **16** (1.00 g, 3.2 mmol) in acetonitrile (10 mL) was treated at 0°C with AcOH (0.93 mL) and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (8 mg, 0.03 mmol, 1 mol-%) under argon. An aqueous solution of NaBrO_3 (320 mg, 2.1 mmol, 0.65 equiv. in 1.5 mL H_2O) was added dropwise to this mixture over a period of 2 h, keeping the temperature below 10°C . After the addition, the reaction was stored for 2 h at 0°C . After complete conversion (TLC monitoring) the solution was diluted with EtOAc (50 mL) and extracted successively with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (2×15 mL, 10%), water (10 mL), NaHCO_3 (3×15 mL), and brine (10 mL). The dried (Na_2SO_4) organic phase was evaporated under reduced pressure to obtain 0.99 g of ketone **17** (99%, 3.17 mmol) as colorless crystals, which were used without any further purification. M.p. 158°C . $[a]_D^{20} = -38$ ($c = 0.94$, CH_2Cl_2). ^1H NMR (500 MHz, CDCl_3): $\delta = 1.08$ (d, $J_{7,4} = 6.9$ Hz, 1 H, 7-H), 2.48 (s, 3 H, Ar-CH₃), 2.06 (dt, $J_{4,7} = 6.9$, $J_{4,6a} = 1.0$ Hz, 1 H, 4-H), 3.78 (ddd, $J_{6a,6b} = 8.0$, $J_{6a,5} = 4.8$, $J_{6a,4} = 1.0$ Hz, 1 H, 6a-H), 3.83 (dd, $J_{6b,6a} = 8.0$, $J_{6b,5} = 0.8$ Hz, 1 H, 6b-H), 4.68 (dd, $J_{5,6a} = 4.8$, $J_{5,6b} = 0.8$ Hz, 1 H, 5-H), 4.96 (dd, $J_{2,1} = 2.2$, $J = 2.2$ Hz, 1 H, 2-H), 5.73 (d, $J_{1,2} = 2.2$ Hz, 1 H, 1-H), 7.38 (d, $J_{\text{Ar,Ar}} = 8.0$ Hz, 2 H, Ar-H), 7.89 (d, $J_{\text{Ar,Ar}} = 8.0$ Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, CDCl_3): $\delta = 8.8$ (q, C-7), 21.7 (q, CH₃-Ar), 49.3 (d, C-4), 66.2 (t, C-6), 78.2 (d, C-5), 80.3 (d, C-2), 101.8 (d, C-1), 128.1, 129.8 ($2 \times \text{d}$, $2 \times \text{C-Ar}$), 133.3 (s, C-Ar), 145.2 (s, C-Ar), 198.3 (s, C-3) ppm. IR (Film): $\tilde{\nu} = 2959$ (m, C-H), 2901 (m, C-H), 2860 (m, C-H), 1739 (w, C=O), 1579 (m, C-S), 1362 (s, C-H), 1170 (s, C-H), 1129 (s, C-H), 1041 (s, C-O), 968 (s, C-O), 917 (s, C-H) cm^{-1} . MS (EI, 70 eV): m/z (%) = 312 (30) $[\text{M}^+]$, 157 (88), 155 (68), 139 (14), 113 (40), 111 (100), 91 (94), 83 (90), 71 (39), 65 (50), 57 (22), 55 (93), 43 (28). HRMS (EI): calcd. for $\text{C}_{14}\text{H}_{16}\text{O}_6\text{S}$ 312.0667; found 312.0654. $\text{C}_{14}\text{H}_{16}\text{O}_6\text{S}$ (312.34): calcd. C 53.84, H 5.16; found C 53.91, H 4.68.

Crystal Structure Determination of 17:^[25] $\text{C}_{14}\text{H}_{16}\text{O}_6\text{S}$, $M_r = 312.3$, colorless crystal, size $0.05 \times 0.06 \times 0.45$ mm³, orthorhombic, space group $P2_12_12_1$, $a = 5.854(2)$, $b = 7.770(3)$, $c = 31.069(11)$ Å, $V = 1413.2(9)$ Å³, $Z = 4$, $\rho_{\text{calc}} = 1.468$ g/cm³, $F(000) = 656$, $T = 120(2)$ K. Bruker AXS SMART APEX,^[26] graphite-monochromated Mo- K_α radiation, $\mu = 0.254$ mm⁻¹, 14577 intensities collected $2.6 < \theta < 28.2^\circ$, $h \pm 7$, $k \pm 10$, $-40 < l < 41$, semi-empirical absorption correction^[26] from equivalents, 3472 unique reflections. Structure solution^[26] by direct methods, full-matrix least-squares refinement^[26] based on F^2 and 193 parameters, all but H atoms refined anisotropically, H atoms refined with riding model on idealized positions with $U_{\text{iso}} = 1.2 U_{\text{eq}}(\text{C})$ and $U_{\text{iso}} = 1.5 U_{\text{eq}}(\text{C-methyl})$, methyl groups were allowed to rotate but not to tip. Refinement with correct assignment of absolute configuration [Flack parameter^[27] = 0.0(1)] converged at $R_1[I > 2\sigma(I)] = 0.054$, $wR_2(\text{all data}) = 0.068$, max. $(\delta/\sigma) = 0.001$, min./max. height in final ΔF map $-0.29/0.33$ e/Å³.

1,6-Anhydro-4-deoxy-3,4-dimethyl-2-O-p-tolylsulfonyl- β -D-talopyranose (18): MeMgCl (0.35 mL, 3 M solution in THF, 1.06 mmol, 1.1 equiv.) was added dropwise to a cooled (0°C) solution of **17** (300 mg, 0.96 mmol) in dried diethyl ether (30 mL). After complete conversion (45 min, TLC monitoring), water was added (10 mL).

The aqueous phase was extracted with diethyl ether (2 × 5 mL) and the dried (Na₂SO₄) combined organic phases were evaporated under reduced pressure to obtain 293 mg of **18** (93%, 0.89 mmol) as a colorless solid, which could be used without any further purification. M.p. 108 °C. $[α]_D^{20} = -61$ ($c = 0.81$, MeOH). ¹H NMR (500 MHz, CDCl₃): δ = 1.03 (d, $J_{7,4} = 7.2$ Hz, 1 H, 7-H), 1.09 (s, 3 H, 8-H), 2.04 (ddt, $J_{4,7} = 7.2$, $J_{4,5} = 3.8$, $J_{4,6a} = 0.9$ Hz, 1 H, 4-H), 2.48 (s, 3 H, Ar-CH₃), 3.62 (dd, $J_{6a,6b} = 6.9$, $J_{6a,5} = 5.9$ Hz, 1 H, 6a-H), 4.21 (dd, $J_{5,6a} = 5.9$, $J_{5,4} = 3.8$ Hz, 1 H, 5-H), 4.31 (d, $J_{2,1} = 1.7$ Hz, 1 H, 2-H), 4.36 (d, $J_{6a,6a} = 6.9$ Hz, 1 H, 6b-H), 5.31 (d, $J_{1,2} = 1.7$ Hz, 1 H, 1-H), 7.38 (d, $J_{Ar,Ar} = 8.0$ Hz, 2 H, Ar-H), 7.87 (d, $J_{Ar,Ar} = 8.0$ Hz, 2 H, Ar-H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ = 9.1 (q, C-7), 21.7 (q, CH₃-Ar), 25.7 (q, C-8), 42.3 (d, C-4), 64.9 (t, C-6), 72.1 (s, C-3), 77.5 (d, C-5), 81.1 (d, C-2), 99.7 (d, C-1), 128.0, 129.8 (2 × d, 2 × C-Ar), 133.3 (s, C-Ar), 145.4 (s, C-Ar) ppm. IR (Film): $\tilde{\nu} = 3539$ (br., O-H), 2981 (m, C-H), 2919 (m, C-H), 1605 (m, C=H), 1470 (m, O-S), 1382 (s, C-H), 1170 (s, C-H), 1155 (s, C-H), 1056 (s, C-O), 979 (s, C-O), 896 (s, C-H) cm⁻¹. MS (EI, 70 eV): m/z (%) = 328 (5) [M⁺], 257 (13), 173 (81), 157 (88), 155 (89), 139 (19), 127 (86), 113 (33), 111 (49), 109 (93), 99 (41), 91 (84), 85 (92), 83 (70), 71 (79), 57 (40), 55 (77), 43 (100). HRMS (EI): calcd. for C₁₅H₂₀O₆S 328.0980; found 328.0973. C₁₅H₂₀O₆S (328.38): calcd. C 54.86, H 6.14; found C 55.13, H 6.20.

- [1] K. Krohn, D. Gehle, U. Flörke, *Eur. J. Org. Chem.* **2005**, 2841–2848.
- [2] M. Černý, V. Gut, J. Pacak, *Collect. Czech. Chem. Commun.* **1961**, 26, 2542–2550.
- [3] S. Czernecki, C. Leteux, A. Veyrieres, *Tetrahedron Lett.* **1992**, 33, 221–224.
- [4] M. Samadi, C. Munoz-Letelier, S. Poigny, M. Guyot, *Tetrahedron Lett.* **2000**, 41, 3349–3353.
- [5] F. Kato, M. Kato, F. Tsukamoto, M. Tsukamoto (Ishihara Sangyo Kaisha, Japan), JP 07188205, December 27, **1993**; *Chem. Abstr.* **1995**, 124, 30251.
- [6] K. Okano, T. Ebata, K. Koseki, H. Kawakami, K. Matsumoto, H. Matsushita, *Chem. Pharm. Bull.* **1993**, 41, 861–865.
- [7] S. Mizukoshi, F. Kato, M. Tsukamoto, K. Mizukoshi, S. Kon (Ishihara Sangyo Kaisha Ltd., Japan), JP 2087805, January 21, **1993**; *Chem. Abstr.* **1994**, 121, 149078.
- [8] S. Mizukoshi, F. Kato, M. Tsukamoto, K. Kon (Ishihara Sangyo Kaisha, Ltd., Japan), EP 560055, February 5, **1993**; *Chem. Abstr.* **1994**, 121, 9922.
- [9] F. Kato, M. Kato, F. Tsukamoto, M. Tsukamoto (Ishihara Sangyo Kaisha, Japan) JP 08059646, August 12, 1994; *Chem. Abstr.* **1996**, 125, 11351.
- [10] S. Mizukoshi, F. Kato, M. Tsukamoto (Jpn. Kokai Tokkyo Koho) JP 06080565, March 22, **1994**; *Chem. Abstr.* **1994**, 121, 149078.
- [11] M. Černý, J. Pacak, J. Stanek, *Collect. Czech. Chem. Commun.* **1965**, 30, 1151–1157.
- [12] J. Dolezalova, T. Trnka, M. Cerny, *Collect. Czech. Chem. Commun.* **1982**, 47, 2415–2422.
- [13] Z. J. Witzak, *Levoglucosone and Levoglucosans. Chemistry and Applications*, in: *Frontiers in Biomedicine and Biotechnology*, vol. 2, ATL PRESS, Mount Prospect, USA, IL, **1994**.
- [14] M. Černý, J. J. Stanek, *Adv. Carbohydr. Chem. Biochem.* **1977**, 34, 23–177.
- [15] S. S. Kulkarni, J.-C. Lee, S.-C. Hung, *Curr. Org. Chem.* **2004**, 8, 475–509.
- [16] A. Fürst, P. A. Plattner, in *12th Internat. Congress of Pure and Applied Chemistry*, New York, **1951**, p. 409.
- [17] A. F. Sviridov, D. V. Yashunskii, M. S. Ermolenko, N. K. Kochetkov, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 723–725.
- [18] K. M. Belyk, W. R. Leonard, Jr., D. R. Bender, D. L. Hughes, *J. Org. Chem.* **2000**, 65, 2588–2590.
- [19] D. Cai, D. L. Hughes, T. R. Verhoeven, *Tetrahedron Lett.* **1996**, 37, 2537–2540.
- [20] K. Krohn, D. Gehle, O. Kamp, T. van Ree, *J. Carbohydr. Chem.* **2003**, 22, 377–383.
- [21] H. M. Bradley, R. G. Jones, D. W. Knight, *Synlett* **1992**, 479–480.
- [22] J. Thiem, A. Prahst, I. Lundt, *Liebigs Ann. Chem.* **1986**, 1044–1056.
- [23] M. Černý, L. Kalvoda, J. Pacak, *Collect. Czech. Chem. Commun.* **1968**, 33, 1143–1156.
- [24] M. Černý, I. Buben, J. Pacak, *Collect. Czech. Chem. Commun.* **1963**, 28, 1569–1575.
- [25] CCDC-267820 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.
- [26] Bruker (**2002**), SMART (Version 5.62), SAINT (Version 6.02), SHELXTL (Version 6.10) and SADABS (Version 2.03), Bruker AXS Inc., Madison, Wisconsin, USA.
- [27] H. D. Flack, *Acta Cryst.* **1983**, A39, 876–881.

Received: April 5, 2005

Published Online: September 8, 2005