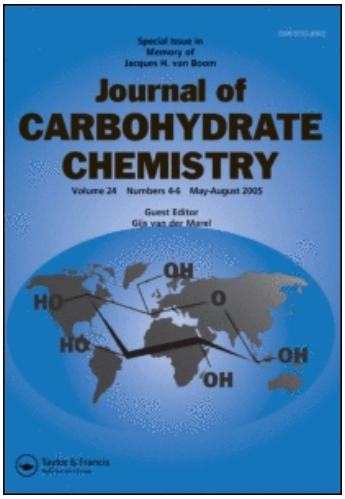

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Two Efficient Syntheses of Protected 4-Deoxy-D-lyxo-hexose (4-Desoxy-D-mannose)

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To cite this Article Krohn, Karsten and Shuklov, Ivan(2006) 'Two Efficient Syntheses of Protected 4-Deoxy-D-lyxo-hexose (4-Desoxy-D-mannose)', Journal of Carbohydrate Chemistry, 25: 4, 331 — 343
To link to this Article: DOI: 10.1080/07328300600770519
URL: http://dx.doi.org/10.1080/07328300600770519

Journal of Carbohydrate Chemistry, 25:331–343, 2006

ISSN: 0732-8303 print 1532-2327 online
DOI: 10.1080/07328300600770519

Two Efficient Syntheses of Protected 4-Deoxy-D-lyxo-hexose (4-Desoxy-D-mannose)

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The formation of four differently protected 4-deoxy-D-lyxo-hexose derivatives **7**, **8**, **12**, and **14** is described. In the first procedure, a nucleophilic displacement of the allylic mesylate **4** by hydride was combined with a highly stereoselective osmylation of olefin **6** to afford diol **7**. In the second radical procedure, tributyl tin hydride was substituted by the cheap and environmentally friendly hypophosphorous acid as a hydrogen donor in the reduction of xanthate **13** to 4-deoxy lyxo-hexose **14**.

Keywords 4-Deoxy-D-lyxo-hexose, $LiAlH_4$ reduction of allylic mesylate, Stereoselective *cis*-hydroxylation, Hypophosphorous acid, Deoxygenation

INTRODUCTION

3-Deoxy- and 4-deoxy-hexoses are rare sugar derivatives but are occasionally found as components in natural products such as neosidomycin and SF-2140, two indole nucleoside antibiotics.[1] Other 4-deoxy derivatives of oligosaccharides[2] and antibodies[3] are useful tools in the study of biological and biochemical properties. 4-Deoxy-D-lyxo-hexose (4-deoxy-D-mannose) was of particular value as a chiral starting material in natural product synthesis. For example, Nikolaou et al. used this sugar as starting material for the synthesis of brevetoxin B.[4] It was also used for the synthesis of hemibrevetoxin, myxovirecin B, neosidomycin, and SF-2140.[5] 4-Deoxy-D-lyxo-hexose is not commercially available; however, several methods for the synthesis of

Received February 13, 2006; accepted March 20, 2006.
Dedicated to Prof. Siegfried Blechert on the occasion of his 60th birthday.
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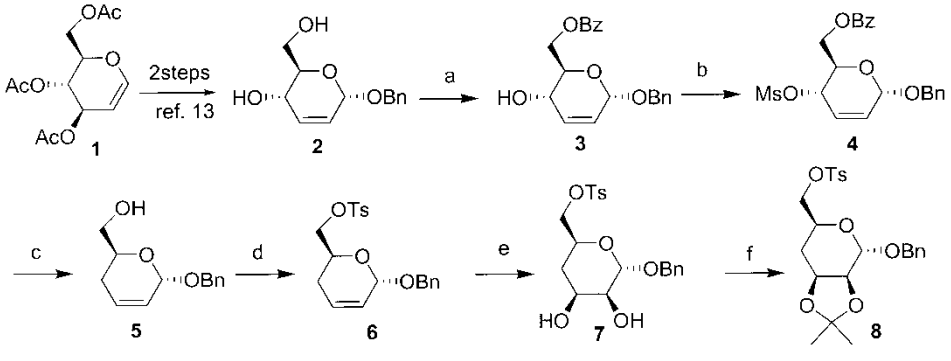
4-deoxylyxo-hexoses are known.[1b,4–7] The 4-deoxy sugar was first prepared by Černý et al. in a multi-step sequence employing 1,6-anhydro-β-D-glucopyranose as the starting material.[6] Mostly, the deoxygenation step was carried out by a Barton-McCombie reaction using tributylstannane as the hydrogen radical donor.[5,8] In connection with the synthesis of the macrolide LL-Z1640-2[9], we needed larger amounts of 4-deoxy-D-lyxo-hexose in different protected forms and therefore examined three new variations, two of them resulting in efficient, economical, and environmentally friendly routes to the target molecule in protected form.

RESULTS AND DISCUSSION

Our first synthetic approach used 3,4,6-triacetyl-D-glucal (**1**) as the staring material, easily available from D-glucose.[10] The idea behind this approach was placing the 4-hydroxyl group into an allylic position to make it easily reducible, for example, as a sulfonate by hydride donating agents. For this purpose, 3,4,6-triacetyl-D-glucal (**1**) was subjected to the Ferrier-type allylic rearrangement.[11,12] We recently employed that reaction in the α-selective synthesis of the benzyl glycoside **2**,[13] using iron trichloride as a very efficient catalyst.[14] Subsequent selective benzoylation of the primary hydroxyl group at C-6 afforded the monobenzoate **3.** Mesylation at C-4 then led to the allylic mesylate **4**, perfectly suited for nucleophilic hydride reduction (Sch. 1). In fact, upon treatment with lithium aluminum hydride, the mesylate reduction occurred concurrently with conversion of the benzoate into the alcohol to yield the deoxygenated unsaturated sugar **5** in good overall yield (60%). Next, the hydroxyl group at C-6 was protected as a tosylate **6**, facilitating the purification in the subsequent step. Gratifyingly, the anomeric α-benzyloxy group efficiently shielded the molecule from attack from the α-side in the



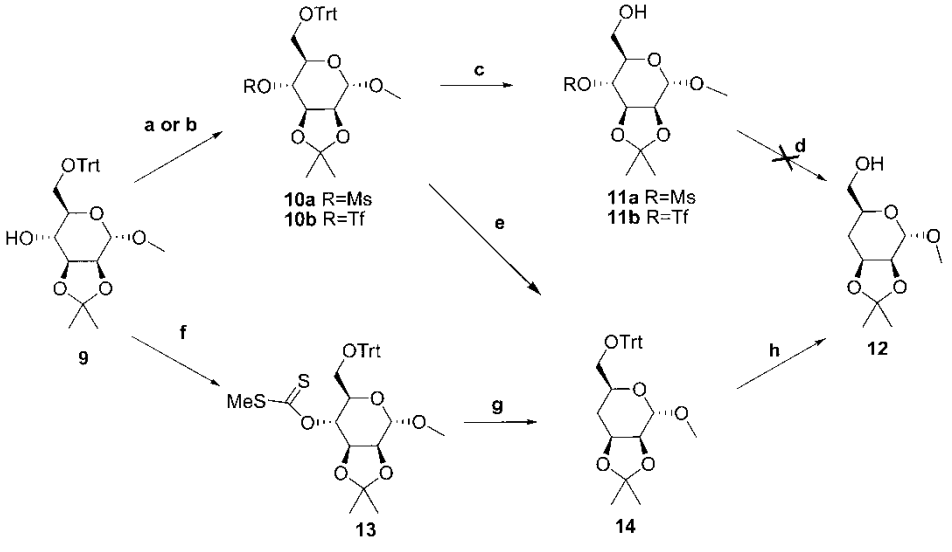
Scheme 1: Synthesis of 4-deoxy-lyxo-hexopyranosides **7** and **8**. Reagents and conditions: a) BzCl, 2,6-lutidine, 70%; b) MsCl, TEA, 4-DMAP, 95%; c) $LiAlH_4$, 60%; d) TsCl, TEA, DMAP, 98%; e) OsO_4, NMO, 90%; f) 1,3-dimethoxypropane, PPTS, 95%.

following *cis*-dihydroxylation step,[1b] using osmium tetroxide and *N*-morpholine-*N*-oxide (NMO) as the cooxidant.[15] Benzyl 4-deoxy-6-tosyl-α-D-lyxo-hexopyranoside (**7**) was isolated in 90% yield and 99% *de* (NMR). The two vicinal hydroxyl groups at C-2 and C-3 can be protected easily as an acetonide to yield the fully protected 4-deoxy-D-lyxo-hexose derivative (**8**) in 95% yield.

Encouraged by the facile $LiAlH_4$ reduction of mesylate **4** to the deoxy sugar **5**, we wanted to probe a related reduction of non allylic sulfonates. Thus, the second route required conversion of an appropriately protected known mannose derivative **9**[16] into the corresponding unknown mesylate **10a** or triflate **10b**, which could be achieved in 98% and 90% yield, respectively (Sch. 2).

However, not unexpectedly, the mesylate **10a** was completely inert to $LiAlH_4$ as well as $NaBH_4$ reduction, even at reflux in THF. This procedure was also applied to the corresponding alcohols **11a**/**11b** and an anchimeric assistance of the free hydroxyl group in the reduction process to **12** could not be observed. Although the triflate **10a** reacted with $NaBH_4$ to give deoxysugar **14** in moderate yield (35%), this procedure did not meet our requirements for a larger scale production of **14**.

In the third attempt, we therefore turned our attention to the radical procedure and converted the alcohol **9** into the xanthate **13**. In fact, this compound was shown to be a good substrate for the Barton-McCombie reaction[17] (review[18]). However, the tributyl tin hydride used in this procedure was



Scheme 2: Reagents and conditions: a) Tf_2O, Et_3N, -40°C, 65%; b) MsCl, NEt_3, rt, 95%; c) TMSCl, MeOH, **11a** = 90%, **11b** = 95%; d) $LiAlH_4$, or $NaBH_4$; e) $NaBH_4$, 35%; f) 1. NaH; 2. CS_2, 3. MeI, 98%; g) H_3PO_2/AIBN, Et_3N, dioxane, reflux, 90%; h) *p*-TsOH, acetone, 90%.

neither an ideal reagent for large-scale production nor environmentally friendly. We then tried the use of hypophosphorous acid, already suggested by Barton et al. as a hydrogen donor.[19] We were pleased to observe that the reaction of xanthate **13** with hypophosphorous acid produced the deoxysugar **14** nearly quantitatively. In the final step, the precursor **14** could be detritylated selectively using *p*-TsOH in 90% yield to give the desired partially protected 4-deoxy-D-lyxo-hexose derivative **12**.

In conclusion, two efficient routes, amenable to larger scale, for the synthesis of 4-deoxy-D-lyxo-hexose derivatives are proposed. In the first procedure, the facile nucleophilic displacement of an allylic mesylate group in **4** by hydride was combined with a highly stereoselective osmylation of **6**. In the second procedure, the cheap and environmentally friendly hypophosphorous acid was used as a hydrogen donor in the reduction of xanthate **13**. Another advantage of the two alternative approaches was the formation of differently protected 4-deoxy-D-lyxo-hexose derivatives such as **7**, **8**, **12**, and **14**.

EXPERIMENTAL

General

Thin-layer chromatography was performed on precoated TLC plates (silica gel). Melting points were measured with a Gallenkamp apparatus and are corrected. NMR spectra were recorded on Bruker Avance 500 at the following frequencies: 500.13 MHz (^{1}H) and 125.76 MHz. (^{13}C). Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in ppm downfield from TMS as an internal standard. Elemental analyses were performed with a Perkin-Elmer Elemental Analyzer 2400. Optical rotations were measured at 25°C on a Perkin-Elmer Polarimeter 241. Mass spectra were recorded using a Finnigan MAT 8430 spectrometer in the electron-impact mode at 70 eV and chemical ionization are given as m/z values and relative abundances. The infrared spectra were recorded using a FT-IR Spectrometer Nicolet 510 P.

Benzyl 6-O-benzoyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (3)

Benzoyl chloride (2 mL, 17 mmol) was added to a solution of benzyl 2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2**) (2.20 g., 9.3 mmol) in a mixture of 2,6-lutidine (2 mL, 17 mmol) and dry CH_2Cl_2 (150 mL). The reaction mixture was stirred at rt for 18 h and the conversion was monitored by TLC (CH_2Cl_2/MeOH, 98:2). The mixture was then washed with saturated aqueous $NaHCO_3$ solution and brine. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated at reduced pressure. Purification by silica gel column chromatography (CH_2Cl_2) gave the benzoate **3** (2.20 g, 70%) as a colorless solid $R_f = 0.25$ (CH_2Cl_2/MeOH, 98:2). m.p. = 65°C. $[\alpha]_D^{20}$ −44.5

(c 1.0, $CHCl_3$). IR (KBr): 3462, 1720, 1277, 1051, 1039, 1026. ^{1}H NMR (500 MHz, $CDCl_3$): 4.00–4.03 (m, 1H, H-5), 4.15 (d, 1H, $J = 8.6$ Hz, H-4), 4.45 (dd, 1H, $J_{6a,5} = 1.7$ Hz $J_{gem} = 12.0$ Hz, H-6a), 4.60 (d, 1H, $J_{gem} = 11.7$ Hz, OCH_2Ph), 4.75 (dd, 1H, $J_{6b,5} = 5.0$ Hz, $J_{gem} = 12.0$ Hz, H-6b), 4.81 (d, 1H, $J_{gem} = 11.7$ Hz, OCH_2Ph), 5.12 (s, 1H, H-1) 5.79–5.82 (m, 1H, H-2), 6.00 (d, 1H, $J_{3,2} = 10.1$ Hz, H-3), 7.27–7.34 (m, 5H, Ph), 7.41–7.45 (m, 2H, Ph), 7.55–7.59 (m, 1H, Ph), 8.08 (m, 2H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): 64.0 (C-6), 64.2 (C-4), 70.2 (CH_2Ph), 70.8 (C-5), 77.2 (CPh_3), 93.8 (C-1), 126.6 (C-2), 127.8 (C_{Ar}), 127.9 (C_{Ar}), 128.4 (C_{Ar}), 129.7 (C_{Ar}), 129.8 (C_{Ar}), 133.1 (C-3), 133.3 (C_{Ar}), 137.8 (C_{Ar}), 167.3 (COO). Anal. Calc. for $C_{20}H_{20}O_5$; C, 70.57; H, 5.92. Found; C, 70.57; H, 5.72.

Benzyl 6-O-benzoyl-2,3-dideoxy-4-O-methanesulfonyl-α-D-erythro-hex-2-enopyranoside (4)

Methanesulfonyl chloride (1.4 mL, 18 mmol) was added to a solution of 2,3-dideoxy-α-D-erythro-hex-2-enopyranoside **3** (2.20 g, 6.4 mmol) in a mixture of dry pyridine (1.5 mL, 18 mmol) and dry CH_2Cl_2 (150 mL). The reaction mixture was stirred at rt for 12 h and the conversion was monitored by TLC (CH_2Cl_2/MeOH, 98:2). The reaction mixture was then washed with saturated aqueous $NaHCO_3$ solution and brine. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated at reduced pressure. Purification by silica gel column chromatography (CH_2Cl_2/MeOH, 98:2) gave methanesulfonate **4** (2.50 g, 95%) as a colorless solid $R_f = 0.7$ (CH_2Cl_2/MeOH, 98:2). m.p. = 82–84°C (decomp.). $[\alpha]_D^{20} + 45.8$ (c 1.0, $CHCl_3$). IR (KBr): 2920, 2360, 2339, 1724, 1346, 1277, 1217, 1176, 1117, 1095, 1041, 1016, 949. ^{1}H NMR (500 MHz, $CDCl_3$): 3.07 (s, 3H, SO_2CH_3), 4.31 (ddd, 1H, $J_{5,6a} = 2.2$ Hz, $J_{5,6b} = 5.2$ Hz, $J_{5,4} = 9.4$ Hz, H-5), 4.50 (dd, 1H, $J_{6b,5} = 5.2$ Hz, $J_{gem} = 12.2$ Hz, H-6b), 4.57–4.60 (m, 2H, OCH_2Ph, H-6a), 4.79 (d, 1H, $J_{gem} = 11.8$ Hz, OCH_2Ph), 5.12 (d, 1H, $J_{1,2} = 2.0$ Hz, H-1), 5.31 (m, 1H, H-4), 5.93–5.96 (m, 1H, H-2), 6.11 (d, 1H, $J_{2,3} = 10.3$ Hz, H-3), 7.27–7.34 (m, 5H, Ph), 7.41–7.45 (m, 2H, Ph), 7.55–7.59 (m, 1H, Ph), 8.06–8.08 (m, 2H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): 38.7 (CH_3SO_2), 62.9 (C-6), 67.1 (C-4), 70.5 (CH_2Ph), 70.8 (C-5), 93.5 (C-1), 127.9 (C-2), 128.0 (C_{Ar}), 128.5 (C_{Ar}), 128.6 (C_{Ar}), 129.3 (C_{Ar}), 129.7 (C_{Ar}), 129.8 (C_{Ar}), 133.2 (C-3), 137.3 (C_{Ar}), 166.2 (COO). MS (EI, 70 eV): m/z (%): 417 $[M]^+$ (0.3), 232 $[M\text{-}PhCH_2\text{-}CH_3SO_2]^+$, 91 $[PhCH_2]^+$ (27). Anal. Calc. for $C_{30}H_{34}O_8S$: C, 60.27; H, 5.30. Found: C, 60.26; H, 5.01.

Benzyl 2,3,4-trideoxy-α-D-glycero-hex-2-enopyranoside (5)

Lithium aluminium hydride (0.30 g, 8 mmol) was added to the solution of **4** (0.55 g, 1.4 mmol) in dry THF (50 mL) under nitrogen. The reaction mixture was stirred at rt for 5 h. The conversion was monitored by TLC (CH_2Cl_2/MeOH, 98:2). Excess $LiAlH_4$ was destroyed by addition of water (1 mL).

The reaction mixture was extracted with diethyl ether (3 × 50 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Purification by silica gel column chromatography (CH_2Cl_2) gave **5** (0.20 g, 70%) as a colorless oil. $R_f = 0.5$ (CH_2Cl_2/MeOH, 98:2). $[\alpha]_D^{20}$ −35.7 (c 0.33, $CHCl_3$). IR (KBr): 3448, 2924, 2881, 1454, 1400, 1219, 1184, 1113, 1086, 1043, 1022, 953; ^{1}H NMR (500 MHz, $CDCl_3$): 1.88 (dddd, 1H, $J_{4a,2} = 1.4$ Hz, $J_{4a,2} = 3.4$ Hz, $J_{4a,3} = 5.7$ Hz, $J_{gem} = 17.7$ Hz, H-4a), 2.11–2.19 (m, 1H, H-4b), 3.57 (dd, 1H, $J_{6a,5} = 3.1$ Hz, $J_{gem} = 11.6$ Hz, H-6a), 3.67 (dd, 1H, $J_{6b,5} = 6.2$ Hz, $J_{gem} = 11.6$ Hz, H-6b), 4.06 (ddd, 1H, $J_{5,6a} = 3.1$ Hz, $J_{5,6b} = 6.2$ Hz, $J_{5,4b} = 11.3$ Hz, H-5), 4.61 (d, 1H, $J_{gem} = 12.0$ Hz, CH_2Ph), 4.78 (d, 1H, $J_{gem} = 12.0$ Hz, CH_2Ph), 5.11 (t, 1H, $J = 1.3$ Hz, H-1), 5.77 (dddd, 1H, $J_{2,1} = 1.4$ Hz, $J_{2,4a} = 1.3$ Hz, $J_{2,4b} = 4.3$ Hz, $J_{2,3} = 10.1$ Hz, H-2), 6.03 (dddd, 1H, $J_{3,1} = 1.4$ Hz, $J_{3,4b} = 1.4$ Hz, $J_{3,4a} = 5.7$ Hz, $J_{3,2} = 10.1$ Hz, H-3), 7.28–7.39 (m, 5H, Ph). ^{13}C NMR (125 MHz, $CDCl_3$): 26.0 (C-4), 65.2 (C-6), 65.3 (C_{Ar}), 67.2 (C-5), 69.8 (*C*H_2Ph), 94.2 (C-1), 125.4 (C-2), 127.0 (C_{Ar}), 127.6 (C-3), 127.7, 128.6, 138.2, 140.1 (4 × C_{Ar}). MS (EI, 70 eV): m/z (%) = 220 (1) $[M]^+$, 203 (2) [M-OH], 129 (10) $[M\text{-}PhCH_2]^+$, 91 (100), $[PhCH_2]^+$, 77 (60) $[Ph]^+$.

Benzyl 6-O-tosyl-2,3,4-trideoxy-α-D-glycero-hex-2-enopyranoside (6)

Tosyl chloride (0.26 g, 1.2 mol) was added to the solution of **5** (0.25 g, 1.2 mmol), a catalytic amount of 4-DMAP, and pyridine (0.15 mL, 1.5 mmol) in dry CH_2Cl_2 (100 mL). The reaction mixture was stirred at rt for 12 h and the conversion was monitored by TLC (CH_2Cl_2/MeOH, 98:2). The reaction mixture was washed with saturated aqueous $NaHCO_3$ solution and brine. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Purification by silica gel column chromatography (CH_2Cl_2) gave tosylate **6** (0.40 g, 95%) as a colorless oil. $R_f = 0.9$ (CH_2Cl_2/MeOH, 98:2). $[\alpha]_D^{20}$ −28.7 (c 0.8, $CHCl_3$). IR (KBr): 3367, 2974, 2891, 1361, 1190, 1176, 1093, 1047, 1022, 1003, 991, 966, 949, 814. ^{1}H NMR (500 MHz, $CDCl_3$): 1.92 (dddd, 1H, $J_{4a,2} = 1.4$ Hz, $J_{4a,5} = 3.6$ Hz, $J_{4a,3} = 5.7$ Hz, $J_{gem} = 17.5$ Hz, H-4a), 2.02–2.10 (m, 1H, H-4b), 2.44 (s, 3H, CH_3Ph), 4.03–4.13 (m, 2H, H-6a, H-6b), 4.15–4.20 (m, 1H, H-5), 4.51 (d, 1H, $J_{gem} = 11.8$ Hz, CH_2Ph), 4.60 (d, 1H, $J_{gem} = 11.8$ Hz, CH_2Ph), 5.01 (t, 1H, $J = 1.3$ Hz, H-1), 5.72–5.76 (m, 1H, H-2), 5.95–6.00 (m, 1H, H-3), 7.26–7.36 (m, 7H, Ph, Ts), 7.80–7.83 (m, 2H, Ts). ^{13}C NMR (125 MHz, $CDCl_3$): 21.7 (C-4), 26.2 (*C*H_3), 64.4 (C-5), 69.5 (*C*H_2Ph), 71.4 (C-6), 93.7 (C-1), 125.6 (C-2), 127.6 (C-3), 127.7, 127.8, 128.0, 128.2 (4 × C_{Ar}), 128.4 ($C_{Ar,\ Ts}$), 133.1, 137.9, 144.8 (3 × C_{Ar}). MS (EI, 70 eV): m/z (%) = 375 $[M]^+$ (1), 172 $[CH_3C_6H_4SO_3H]^+$ (18), 91 $[C_6H_5CH_2]^+$ (100).

Benzyl 4-deoxy-6-O-tosyl-α-D-lyxo-hexopyranoside (7)

A 25-mL three-necked round-bottomed flask, with a magnetic stirrer and a nitrogen inlet, was charged with the monohydrate of *N*-methylmorpholin (0.16 g, 1.3 mmol), water (10 mL), and acetone (10 mL). To this solution was

added a solution of osmium tetroxide (0.005 g, 0.02 mmol) in *tert*-butanol (0.05 mL) and then olefin **6** (0.40 g, 1.3 mmol). This two-phase solution was stirred vigorously under N_2 at rt. After 18 h of stirring, TLC monitoring showed the reaction to be complete. Sodium hydrogensulfite (0.1 g.) and 0.5 g of Fluorosil in water (20 mL) were added, the slurry was stirred for 10 minutes, and the mixture was filtered through a pad of Celite (5 g) on a 150-mL sintered-glass funnel. The Celite cake was washed with acetone (3 × 15 mL). The filtrate, combined with the acetone wash, was neutralized to pH 7 by addition of 2 N sulfuric acid. The acetone was removed in vacuum and the aqueous phase was washed with butanol (50 mL). The butanol extracts were evaporated under vacuum, giving the crude product as a white solid, which was recrystallized from chloroform to yield diol **7** as a white solid (0.40 g, 90%). m.p. 136–138 °C. $R_f = 0.3$ (CH_2Cl_2/MeOH, 98:2). $[\alpha]_D^{20}$ +62.2 (c 0.5, $CHCl_3$). IR (KBr): 3346, 2916, 2360, 2341, 1363, 1186, 1173, 1080, 1061, 1047, 1020, 987, 960, 847, 810. ^{1}H NMR (500 MHz, $CDCl_3$): 1.53–1.60 (m, 1H, H-4a). 1.70 (ddd, 1H, $J = 2.5$ Hz, $J = 5.2$ Hz, $J_{gem} = 12.6$ Hz, H-4b), 2.12 (s br, 2H, OH), 2.43 (s, 3H, Ph-CH_3), 3.74–3.76 (m, 1H, H-2), 3.97–4.04 (m, 3H, H-3, H-5, H-6a), 4.12 (m, 1H, H-6b), 4.46 (d, 1H, $J_{gem} = 11.7$ Hz, OCH_2Ph), 4.66 (d, 1H, $J_{gem} = 11.7$ Hz, OCH_2Ph), 4.90 (d, 1H, $J_{1,2} = 1.6$ Hz, H-1), 4.26–4.35 (m, 7H, H_{Ts}, H_{Bn}), 7.81 (d, 2H, $J = 7.8$ Hz, $H_{o,Ts}$). ^{13}C NMR (125 MHz, $CDCl_3$): 21.6 (Ph*C*H_3), 30.3 (C-4), 65.2 (C-3), 66.1 (C-2), 68.9 (C-5), 69.3 (*C*H_2Ph), 71.5 (C-6), 99.2 (C-1), 128.0, 128.1, 128.5, 129.9, 133.0, 136.9, 145.0 (7 × C_{Ar}). MS (70 eV) m/z (%) = 448 $[M]^+$. Anal. Calc. for $C_{23}H_{28}O_7S$: C, 58.81; H, 5.93. Found: C, 58.23; H, 5.78.

Benzyl 2,3-O-isopropylidene 4-deoxy-6-O-tosyl-α-D-lyxo-hexopyranoside (8)

p-Toluenesulfonic acid (0.1 g, 0.52 mmol.) was added to the solution of **7** (0.90 g., 2.6 mmol) in 1,1-dimethoxypropane (5 mL). The reaction mixture was stirred at rt for 3 h and the conversion was monitored by TLC (CH_2Cl_2/MeOH, 98:2). The reaction mixture was subsequently washed with saturated aqueous $NaHCO_3$ solution and brine. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Purification by silica gel column chromatography (CH_2Cl_2) gave acetonide **8** (0.94 g, 95%) as a colorless oil, $R_f = 0.6$ (CH_2Cl_2/MeOH, 98:2). $[\alpha]_D^{20}$ +43 (c 1.0, $CHCl_3$). IR (KBr): 2931, 1363, 1190, 1176, 1138, 1090, 1065, 987. ^{1}H NMR (500 MHz, $CDCl_3$): 1.29 (s, 3H, CCH_3), 1.42 (s, 3H, CC'H_3), 1.47–1.53 (m, 1H, H-4a), 1.91 (ddd, 1H, $J_{4b,5} = 3.3$ Hz, $J_{4b,3} = 6.0$ Hz, $J_{gem} = 13.4$ Hz, H-4b), 2.43 (s, 3H, Ph-CH_3), 3.97–4.04 (m, 3H, H-2, H-5, H-6b), 3.97–4.04 (m, 3H, H-2, H-5, H-6b), 4.32–4.36 (ddd, 1H, $J_{3,4b} = 6.0$ Hz, $J_{3,4a} = 6.0$ Hz, $J_{3,2} = 8.2$ Hz, H-3), 4.46 (d, 1H, $J_{gem} = 11.7$ Hz, OCH_2Ph), 4.66 (d, 1H, $J_{gem} = 11.7$ Hz, OCH_2Ph), 4.99 (d, 1H, $J_{1,2} = 1.6$ Hz, H-1), 4.26–4.35 (m, 7H, H_{Ts}, H_{Bn}), 7.81 (d, 2H, $J = 7.82$ Hz, H_o-Ts). ^{13}C NMR (125 MHz, $CDCl_3$): 21.6 (Ph*C*H_3), 25.9 (C*C*H_3), 27.7 (C*C*'H_3), 28.9 (C-4), 64.6 (C-2), 69.3 (*C*H_2Ph), 70.0 (C-3), 72.0 (C-6), 73.0 (C-5), 96.63 (CMe_2), 109.13 (C-1), 127.99,

128.27, 128.49, 129.84, 133.08, 136.98, 144.85 (7 × C_{Ar}). MS (CI) m/z (%) = 446 $[M\text{-}H_2]^+$ (1). Anal. Calc. for $C_{20}H_{24}O_7S$: C, 61.59; H, 6.29. Found: C, 61.43; H, 6.18.

Methyl 2,3-O-isopropylidene-4-O-methanesulfonyl-6-O-triphenylmethyl-α-D-mannopyranoside (10a)

A 50-mL flask equipped with a magnetic stirring bar and septum was charged with 1.3 g (2.7 mmol) of mannopyranoside **9**, triethylamine (0.5 mL, 3.1 mmol), and anhydrous CH_2Cl_2 (30 mL). Mesylchloride (0.25 mL, 3.1 mmol) was added slowly to the reaction mixture at 0°C. The reaction was allowed to warm to rt, stirred for 1 h, and then quenched by addition of saturated $NaHCO_3$ (2 mL) solution. The organic phase was dried with Na_2SO_4 and the solvent removed at reduced pressure. The crude product was purified by silica gel column chromatography (CH_2Cl_2) to afford mesylate **10a** (1.5 g, 93%) as white crystals. Yield: 95%. m.p. 183°C (decomposition). $R_f = 0.8$ (CH_2Cl_2). $[\alpha]_D^{20}$ +7.2 (c 1.0, $CHCl_3$). IR (KBr): 1635, 1612, 1464, 1454, 1261, 1203, 1167. ^{1}H NMR (500 MHz, $CDCl_3$): 1.40 (s, 3H, CCH_3), 1.61 (s, 3H, CC'H_3), 2.97 (s, 3H, OCH_3), 3.33–3.37 (m, 1H, H-6b), 3.42–3.45 (m, 1H, H-6a), 3.55 (s, 3H, CH_3SO$_2$), 3.85–3.88 (m, 1H, H-5), 4.21–4.22 (m, 1H, H-2), 4.26–4.29 (m, 1H, H-3), 4.57–4.61 (m, 1H, H-4), 5.05 (s, 1H, H-1), 7.24–7.29 (m, 3H, H_o, Trt), 7.30–7.35 (m, 6H, H_p, Trt), 7.50–7.53 (m, 6H, H_m, Trt). ^{13}C NMR (125 MHz, $CDCl_3$): 26.3 (CCH$_3$), 27.7 (CC'H$_3$), 38.8 (CH$_3$SO$_2$), 55.0 (OCH_3), 62.7 (C-6), 67.2 (C-5), 76.2 (C-3), 76.23 (C-2), 78.8 (C-4), 86.9 (CPh$_3$), 97.8 (C-1), 110.3 (CMe$_2$), 127.0 (Trt, Cp), 127.8 (Trt, C_o), 127.9 (Trt, C_m), 128.8 (Trt, C_m), 143.8 (Trt, C_{ipso}). MS (CI) m/z (%): 554 (66) $[M]^+$, 522 (11) $[M\text{-}CH_4O]^+$, 477 (68) $[M\text{-}C_6H_5]^+$, 311 (60) $[M\text{-}Ph_3C]^+$, 243 $[Ph_3C]^+$, 77 (42) $[C_6H_5]^+$. Anal. Calc. for $C_{30}H_{34}O_8S$: C, 64.96; H, 6.18. Found: C, 64.83; H, 6.12.

Methyl 2,3-O-isopropylidene-4-O-trifluoromethanesulfonyl-6-O-triphenylmethyl-α-D-mannopyranoside (10b)

A 50-mL flask equipped with a magnetic stirring bar and septum was charged with methyl mannopyranoside **9** (1.80 g, 3.2 mmol), pyridine (0.3 mL, 3.5 mmol), and anhydrous CH_2Cl_2 (50 mL). Trifluoromethanesulfonic anhydride (0.6 mL, 0.035 mmol) was added slowly to the reaction mixture at −40°C. The reaction mixture was allowed to warm to 0°C and stirring was continued for 1 h at this temperature. The reaction was quenched by addition of a saturated aqueous $NaHCO_3$ solution (2 mL). The organic phase was dried with Na_2SO_4 and the solvent removed in vacuum. The crude product was recrystallized from CH_2Cl_2-hexane to afford the triflate **10b** (1.50 g, 65%) as white crystals, m.p. 50°C (decomposition). $R_f = 0.9$ (CH_2Cl_2). $[\alpha]_D^{20}$ −1.9 (c 1.1, $CHCl_3$). IR (KBr): 3535, 2987, 2937, 1354, 1174, 1090, 960, 858. ^{1}H NMR (500 MHz, $CDCl_3$): 1.38 (s, 1H, 3H, CCH_3), 1.55 (s, 1H, 3H, CC'H_3), 3.30 (dd, 1H, $J_{6a,5} = 6.5$ Hz, $J_{gem} = 10.5$ Hz, H-6a), 3.37 (dd, 1H, $J_{6b,5} = 2.4$ Hz,

$J_{gem} = 10.5$ Hz, H-6b), 3.53 (s, 1H, 3H, OCH_3), 3.95 (ddd, 1H, $J_{5,6b} = 2.4$ Hz, $J_{5,6a} = 6.5$ Hz, $J_{5,4} = 10.4$ Hz, H-5), 4.21 (d, 1H, $J_{2,3} = 5.5$ Hz, H-2), 4.29 (dd, 1H, $J_{3,2} = 5.5$ Hz, $J_{3,4} = 7.2$ Hz, H-3), 4.80 (dd, 1H, $J_{4,3} = 7.2$ Hz, $J_{5,4} = 10.4$ Hz, H-4), 5.03 (s, 1H, H-1), 7.23–7.26 (m, 6H, Trt), 7.28–7.33 (m, 6H, Trt), 7.47–7.49 (m, 3H, Trt). ^{13}C NMR (125 MHz, $CDCl_3$): 26.2 (CCH_3), 27.5 ($CC'H_3$), 55.2 (OCH_3), 62.4 (C-6), 66.6 (C-5), 75.4 (C-3), 76.6 (C-2), 83.9 (C-4), 97.8 (C-1), 127.1, 127.3, 127.8, 127.9, 128.8 ($5 \times C_{Ar,\ Tr}$), ($5 \times C_{Ar,Tr}$), 118.5 (q, $J_{C,F} = 319$ Hz, CF_3). MS (EI, 70 eV): m/z (%) = 608 (0.1) $[M]^+$, 244 (100) $[Ph_3CH]^+$.

Methyl 2,3-O-isopropylidene-4-O-methanesulfonyl-α-D-mannopyranoside (11a)

Trimethylsilyl chloride (0.1 mL, 8 mmol) was added to the solution of **10a** (0.40 g, 0.7 mmol) in anhydrous CH_2Cl_2 (50 mL) and MeOH (1 mL, 25 mmol). After 1 h, the reaction was completed and quenched by addition of saturated aqueous $NaHCO_3$ solution (2 mL). The organic solution was washed with brine and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Product **11a** was isolated as a white solid after column chromatography on SiO_2 (CH_2Cl_2/MeOH 98:2), 1.30 mg (60%). $R_f = 0.35$ (CH_2Cl_2/MeOH 98:2). m.p. = 90°C. $[\alpha]_D^{20}$ −48 (c 0.6, $CHCl_3$). IR (KBr): 1373, 1354, 1223, 1174, 1140, 1090, 1020, 1005, 960, 858, 802. ^{1}H NMR (500 MHz, $CDCl_3$): 1.37 (s, 3H, CCH_3), 1.59 (s, 3H, $CC'H_3$), 3.21 (s, 3H, SO_2CH_3), 3.42 (s, 3H, OCH_3), 3.68–3.73 (m, 1H, H-5), 3.88 (m, 2H, H-6), 4.20 (d, 1H, $J_{2,3} = 5.6$ Hz, H-2), 4.33 (m, 1H, H-3), 4.61 (dd, $J_{4,3} = 7.6$ Hz, $J_{4,5} = 10.4$ Hz, H-4), 5.0 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$): 26.2 (CCH_3), 27.8 ($CC'H_3$), 38.9 (SO_2CH_3), 55.2 (OCH_3), 60.8 (CH_2OH), 67.5 (C-5), 75.8 (C-3), 76.2 (C-2), 78.9 (C-4), 97.9 (C-1), 110.3 (CMe_2). MS (CI) m/z (%) = 313 (35) $[M + H]^+$, 281 (3) $[M\text{-}CH_4O]^+$. Anal. Calc. for $C_{11}H_{20}O_8S$: C; 42.30; H, 6.45. Found: C, 42.35; H, 6.51.

Methyl 2,3-O-isopropylidene-4-O-trifluoromethanesulfonyl-α-D-mannopyranoside (11b)

Trimethylsilyl chloride (0.1 mL, 8 mmol) was added to the solution of **10b** (0.40 g, 0.66 mmol) in anhydrous CH_2Cl_2 (50 mL) and MeOH (1 mL, 25 mmol). After 1 h the reaction was completed and quenched by addition of saturated aqueous $NaHCO_3$ solution. The reaction mixture was washed with brine and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated. Product **11b** was isolated as an oil after column chromatography on SiO_2 (CH_2Cl_2/MeOH 98:2), 0.16 g (67%). $R_f = 0.3$ (CH_2Cl_2/MeOH 98:2). $[\alpha]_D^{20}$ +23 (c 1.1, $CHCl_3$). IR (KBr): 3471, 1714, 1414, 1363, 1221, 1140, 1092. ^{1}H NMR (500 MHz, $CDCl_3$): 1.38 (s, 1H, 3H, CCH_3), 1.55 (s, 1H, 3H, $CC'H_3$), 3.30 (dd, 1H, $J_{6a,5} = 6.5$ Hz, $J_{gem} = 10.5$ Hz, H-6a), 3.37 (dd, 1H, $J_{6b,5} = 2.4$ Hz, $J_{gem} = 10.5$ Hz, H-6b), 3.53 (s, 1H, 3H, H-10), 3,95 (ddd, 1H, $J_{5,6b} = 2.4$ Hz, $J_{5,6a} = 6.5$ Hz, $J_{5,4} = 10.4$ Hz, H-5), 4.21 (d, 1H, $J_{2,3} = 5.5$ Hz, H-2), 4.29 (dd, 1H, $J_{3,2} = 5.5$ Hz, $J_{3,4} = 7.2$ Hz, H-3), 4.78 (dd, 1H,

$J_{4,3} = 7.2$ Hz, $J_{5,4} = 10.4$ Hz, H-4), 5.01 (s, 1H, H-1). ^{13}C NMR (125.76 MHz, $CDCl_3$): 26.3 (C*C*H$_3$), 27.4 (C*C'*H$_3$), 55.2 (OCH_3), 62.4 (C-6), 66.6 (C-5), 75.4 (C-3), 76.7 (C-2), 83.9 (C-4), 97.8 (C-1), 118.4 (q, $J_{C,F} = 319$ Hz, CF_3). MS (CI) m/z (%) = 367 $[M+1]^+$ (13), 233 $[M\text{-}CF_3SO_2]^+$ (12), 217 $[M\text{-}CF_3SO_3]^+$ (46). Fluor, kein E.a.

Methyl 2,3-O-isopropylidene-4-deoxy-6-O-triphenylmethyl-α-D-lyxo-hexopyranoside (14)

Method A: $NaBH_4$ (0.20 g, 5.3 mmol) was added to the solution of triflate **10b** (1.80 g, 2.9 mmol) in dry acetonitrile (100 mL). The reaction mixture was stirred for 2 h at rt and the excess of sodium borohydride was destroyed by addition of water. The mixture was extracted with dichloromethane (3 × 100 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography (CH_2Cl_2) to give the deoxy compound **14** (0.48 g, 35%) as a white foam.

Method B: A solution of xanthate **11** (0.70 g, 1.25 mmol), hypophosphorous acid (50% solution in water, 0.64 mL, 6.2 mmol), and triethylamine (0.69 mL, 6.82 mmol) in dioxane (15 mL) was degassed and refluxed under an argon atmosphere for 0.25 h. The reaction mixture was cooled to rt. A 0.2 M solution of AIBN in dioxane (1 mL) was then added slowly by refluxing with a help of syringe pump. The reaction mixture was cooled and poured into water. Extraction with ether and subsequent flash chromatography afforded the reduced compound **14** (0.55 g, 95%). $R_f = 0.55$ (CH_2Cl_2). m.p. 186°C. $[\alpha]_D^{20}$ +15 (c 0.6, $CHCl_3$). IR (KBr): 1730, 1599, 1433, 1267, 1153, 1043, 1020, 922. ^{1}H NMR (500 MHz, $CDCl_3$): 1.36 (s, 3H, CC*H*$_3$), 1.50 (s, 3H, CC'*H*$_3$), 1.52–1.57 (m, 1H, H-4a), 1.85–1.89 (m, 1H, H-4b), 3.04 (dd, 1H, $J_{6a,5} = 4.2$ Hz, $J_{gem} = 9.6$, H-6a), 3.35 (dd, 1H, $J_{6b,5} = 6.8$ Hz, $J_{gem} = 9.6$, H-6b), 3.50 (s, 3H, OC*H*$_3$), 3.87-3.91 (m, 1H, H-5), 3.9 (d, 1H, $J_{2,3} = 5.7$ Hz, H-2), 4.25 (m, 1H, H-3), 5.00 (s, 1H, H-1), 7.25–7.28 (m, 3H, Hp, Trt), 7.30–7.36 (m, 6H, Ho, Trt), 7.50–7.52 (m, 6H, Hm, Trt). ^{13}C NMR (125.76 MHz, $CDCl_3$): 26.3 (C*C*H$_3$), 28.1 (C*C'*H$_3$), 31.1 (C-4), 54.9 (C-5), 66.6 (C-6), 70.9 (C-3), 73.2 (C-2), 86.6 (*C*Ph$_3$), 98.7 (C-1), 108.9 (*C*Me$_2$), 127.0, 127.3, 127.8, 127.9, 128.8, 144.1 (6 × $C_{Ar,\ Trt}$). MS (EI, 70 eV): m/z (%) = 458 (10) $[M\text{-}H_2]^+$, 243 (100) $[CPh_3^+]$, 215 (10) $[M\text{-}H_2\text{-}CPh_3]^+$, 185 (80) $[M\text{-}CH_3OH\text{-}CPh_3]^+$. Anal. Calc. for $C_{29}H_{32}O_5$: C, 75.60; H, 7.00. Found: C, 75.40; H, 6.87.

Methyl 2,3-O-isopropylidene-4-O-(methylthio)thiocarbonyl-6-O-triphenylmethyl-α-D-mannopyranoside (13)

A 250-mL three-necked round-bottomed flask equipped with a magnetic stirring bar, a nitrogen-inlet adapter, pressure-equalizing addition funnel, and stopper was charged with methyl mannopyranoside **9** (5.05 g, 10.6 mmol), imidazole (0.025 g, 4 mmol), and anhydrous THF (100 mL). The

reaction vessel was flushed with nitrogen and a nitrogen atmosphere was maintained during the ensuing steps. Over a 5-min period, a 50% sodium hydride dispersion (0.76 g, 15 mmol) was added. Vigorous gas evolution was observed. After the reaction mixture was stirred for 20 min, CS_2 (2.3 mL, 15.0 mmol) was added all at once. Stirring was continued for 30 min, after which time iodomethane (1.2 mL, 17.7 mmol) was added in a single portion. The reaction mixture was stirred for another 15 min, and acetic acid (5.0 mL) was added dropwise to destroy the excess of sodium hydride. The solution was filtered and the filtrate was concentrated on a rotary evaporator. The semi-solid residue was extracted with three portions of ether (each 100 mL), and the combined organic extracts were washed with two 100-mL portions of saturated $NaHCO_3$ solution and two 100-mL portions of water. The etheral solution was dried over anhydrous magnesium sulfate, the drying agent was removed by filtration, and the solvent was removed by rotary evaporation. Product **13** was isolated by column chromatography to give xanthate **13** (5.96 g, 98%). $R_f = 0.85$ (CH_2Cl_2). m.p. 204°C. $[\alpha]_D$ +22.0 (c 1.2, $CHCl_3$). IR (KBr): 1630, 1265. ^{1}H NMR (500 MHz, $CDCl_3$): 1.26 (s, 3H, CCH_3), 1.47 (s, 3H, CC'H_3), 2.31 (s, 3H, SCH_3), 2.97 (dd, 1H, $J_{6a,5} = 2.2$ Hz, $J_{gem} = 10.4$, H-6a), 3.16 (dd, 1H, $J_{6b,5} = 7.1$ Hz, $J_{gem} = 10.4$, H-6b), 3.47 (s, 3H, OCH_3), 3.85 (ddd, $J_{5,6a} = 2.2$ Hz, $J_{5,6b} = 7.1$ Hz, $J_{5,4} = 10.4$ Hz, 1H, H-5), 4.11 (d, 1H, $J_{2,3} = 5.6$ Hz, H-2), 4.25 (m, 1H, H-3), 4.95 (s, 1H, H-1), 5.78 (dd, 1H, $J_{4,3}$ =7.4, $J_{4,5} = 10.4$, H-4), 7.11–7.16 (m, 3H, H_p, Trt), 7.17–7.21 (m, 6H, H_o, Trt), 7.37–7.39 (m, 6H, H_m, Trt). ^{13}C NMR (125 MHz, $CDCl_3$): 19.2 (CCH_3), 26.4 (C$C'H_3$), 27.6 (SCH_3), 55.0 (OCH_3), 63.2 (C-6), 68.1 (C-5), 75.8 (C-3), 76.0 (C-2), 78.4 (C-4), 86.8 (CPh_3), 98.0 (C-1), 110.1, 126.9, 127.8, 128.0, 128.8, 143.8, 215.6 ($7 \times C_{Ar,\ Tr}$). MS (70 eV) m/z (%): 566 (0.1) $[M]^+$, 551 (10) $[M\text{-}CH_3]^+$, 458 (71) $[M\text{-}C_2H_4OS_2]^+$, 398 (32) $[M\text{-}C_8H_5S_2]^+$, 323 (19) $[M\text{-}CPh_3]^+$, 243 (100) $[Ph_3C]^+$, 228 (59) $[M\text{-}CH_3\text{-}CPh_3]^+$, 185 (94) $[M\text{-}CH_4O\text{-}CPh_3\text{-}C_2H_4OS_2]^+$, 165 (98). Anal. Calc. for $C_{31}H_{34}O_6S_2$: C, 65.70; H, 6.05. Found: C, 65.40; H, 5.83.

Methyl 2,3-O-isopropylidene-4-deoxy-α-D-lyxo-hexopyranoside (12)

p-TsOH (1.0 g, 5.2 mmol) was added to the solution of methyl lyxo-hexopyranoside **14** (5.00 g, 10.9 mmol) in a mixture of acetone (100 mL) and 2,2-dimethoxypropane (10 mL). After 12 h the reaction was completed and diluted with dichloromethane (300 mL), and the organic solution was washed with $NaHCO_3$ (50 mL) and brine (50 mL) solution. The solution was dried and evaporated, and the alcohol **14** (1.91 g, 80%) was isolated as a colorless oil after flash chromatography on SiO_2 (CH_2Cl_2/MeOH 98:2). $[\alpha]_D^{20}$ +70.0 (c 0.8, $CHCl_3$), lit. $[\alpha]_D^{20}$ +66.0[7], ^{1}H NMR (500 MHz, $CDCl_3$): 1.35 (s, 3H, CCH_3), 1.53 (s, 3H, CC'H_3), 1.66 (ddd, 1H, $J_{4a,3} = 8.6$ Hz, $J_{4a,5} = 9.8$ Hz, $J_{gem} = 13.6$ Hz, H-4a), 1.88 (ddd, 1H, $J = 3.5$ Hz, $J = 4.5$ Hz, $J_{gem} = 13.6$ Hz, H-4b), 2,17 (s, br, 1H, OH), 3.42 (s, 3H, OCH_3), 3.63 (dd, 1H, $J_{gem} = 11.6$ Hz,

H-6a), 3.66 (dd, 1H, $J_{gem} = 11.6$ Hz, H-6a), 3.80–3.84 (m, 1H, H-5), 3.93 (d, 1H, $J_{2,3} = 5.9$ Hz, H-2), 4.36 (dt, 1H, $J_{3,4a} = 8.6$ Hz, $J_{3,2} = 5.9$ Hz, H-3), 4.92 (s, 1H, H-1). ^{13}C NMR (125 MHz, $CDCl_3$): 26.1 (C*C*H$_3$), 27.9 (C*C'*H$_3$), 29.1 (C-4), 55.2 (O*C*H$_3$), 65.6 (C-6), 66.8 (C-5), 70.4 (C-3), 73.1 (C-2), 98.9 (*C*Me$_2$), 109.1 (C-1).

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