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The Synthesis of 1,4-anhydro-a-D-Mannopyranose

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Manuscript describing efforts, ultimately successful, to synthesize 1,4-anhydromannose. Full experimental details and spectroscopic characterization.

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SUPPLEMENTARY INFORMATION

The synthesis of 1,4-anhydro-α-D-mannopyranose

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Nuclear magnetic resonance (NMR) spectra:

1,2,3-Tri-O-acetyl-6-O-benzoyl-4-O-methanesulfonyl-α-D-talopyranoside (14)	S2
Methyl 2,3,6-tri- <i>O</i> -benzoyl-4- <i>O</i> -methanesulfonyl-α-D-talopyranoside (16)	S3
1-O-Acetyl-2,3,6-tri-O-benzoyl-4-O-methanesulfonyl-α-D-talopyranose (17)	S4
1,2,3,6-Tetra-O-benzoyl-4-O-methanesulfonyl-α-D-talopyranose (19)	S5
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Methyl 2,3,6-tri- <i>O</i> -benzyl-α-D-mannopyranoside (26)	S7
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4-O-Acetyl-2,3,6-tri-O-benzyl-α-D-mannopyranosyl chloride (28)	S9
2,3,6-Tri- <i>O</i> -benzyl-α-D-mannopyranose (30)	S10
1,4-Anhydro-2,3,6-tri- <i>O</i> -benzyl-α-D-mannopyranose (32)	S11
3,6-Di-O-benzyl-2-benzyloxy-D-glucal (25)	S12
1,4-Anhydro-2,3,6-tri- <i>O</i> -benzyl-α-D-glucopyranose (24)	S13
1,4-Anhydro-α-D-mannopyranose (9)	S14

1,2,3-Tri-O-acetyl-6-O-benzoyl-4-O-methanesulfonyl- α -D-talopyranoside 14 ¹H NMR



Methyl 2,3,6-tri-O-benzoyl-4-O-methanesulfonyl- α -D-talopyranoside 16 ¹H NMR





1,2,3,6-Tetra-O-benzoyl-4-O-methanesulfonyl- α -D-talopyranose **19**

¹H NMR



4-Methylphenyl 2,3,6-tri-O-benzoyl-1-thio- α -D-mannopyranoside 21 ¹H NMR



Methyl 2,3,6-tri-O-benzyl- α -D-mannopyranoside **26** ¹H NMR



1,4-Di-O-acetyl-2,3,6-tri-O-benzyl- α -D-mannopyranose 27



 $4\text{-}O\text{-}Acetyl\text{-}2,3,6\text{-}tri\text{-}O\text{-}benzyl\text{-}\alpha\text{-}D\text{-}mannopyranosyl\ chloride\ }28$





2,3,6-Tri-O-benzyl- α -D-mannopyranose **30**

¹H NMR



1,4-Anhydro-2,3,6-tri-O-benzyl- α -D-mannopyranose **32**

¹H NMR



3,6-Di-O-benzyl-2-benzyloxy-D-glucal **25** ¹H NMR



1,4-Anhydro-2,3,6-tri-O-benzyl- α -D-glucopyranose **24**

¹H NMR



1,4-Anhydro- α -D-mannopyranose **9**

¹H NMR (d₄-methanol)



¹³C NMR (d4-methanol)



The synthesis of 1,4-anhydro-α-D-mannopyranose

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Abstract

We report the first synthesis of 1,4-anhydro- α -D-mannopyranose. Several unsuccessful approaches were attempted, including azide-mediated cyclization of a 1-*O*-acetyl-4-*O*-mesyl derivatives of α -D-talopyranose, and *N*-iodosuccinimide/triflic acid cyclization of a 4-hydroxy thiomannoside. Ultimately, base-mediated intramolecular nucleophilic substitution of 2,3,6-tri-O-benzyl- α -D-mannopyranosyl chloride successfully provided the cyclized product in low yield, which could be deprotected by hydrogenolysis to afford the title 1,4-anhydrosugar.

Keywords 1,4-anhydrosugar; 1,4-anhydromannose; 2,7-dioxabicyclo[2.2.1]heptanes; 1,5anhydro-α-D-mannofuranose; chemical synthesis

INTRODUCTION

Anomeric anhydrosugars are intramolecular acetals formally derived by the loss of a water molecule from the parent sugar.^{1,2} 1,2-Anhydropyranoses have been widely exploited in glycosylation chemistry³ and have been implicated as intermediates in enzyme-catalyzed reactions.⁴ 1,6-Anhydropyranoses occur in nature both as products of enzymatic reactions and through pyrolysis of cellulose.² These compounds have been widely studied owing to their interesting and useful attributes in synthetic carbohydrate chemistry.^{2,5-7}

1,4-Anhydropyranoses (which may be considered 1,5-anhydrofuranoses) have received relatively less attention, although have been proposed as intermediates in enzymatic transformations,⁸ and have had only sporadic investigations into their synthesis and transformations.⁹⁻¹³ Studies on this class of sugars experienced an inauspicious start when in 1928, Freudenberg and Braun reported that treatment of 2,3,6-tri-O-methyl-α-D-glucosyl chloride 1 with sodium in ether afforded the protected 1,4-anhydro- α -D-glucopyranose 2 (Figure 1, *Method A*),¹⁴ a result that could not be replicated by Hess and Littmann in 1933.¹⁵ Instead, Hess and Littmann,¹⁵ and later Kops and Schuerch¹⁶ reported that treatment of 2,3,6tri-O-methyl-4-O-tosyl- α -D-glucose 3 with sodium isopropoxide afforded the protected 1,4anhydro- β -D-galactopyranose 4 (Figure 1, *Method B*). These two studies illustrate two of the main approaches used for the synthesis of this class of compounds, namely base-promoted intramolecular nucleophilic substitution by the 4-hydroxyl on an anomeric halide, or basepromoted intramolecular nucleophilic substitution by the anomeric hydroxyl on a sugar bearing a suitable leaving group at the 4-position.^{17,18} A third approach, related to the first, involves Lewis acid-catalyzed transacetalization of a 4-hydroxy glycoside9 or Lewis acidcatalyzed intramolecular glycosylation reactions, as exemplified by Thiem and Weisner through the BF₃.Et₂O-catalyzed reaction of 2,3,6-tri-O-benzoyl-α-D-galactopyranosyl fluoride 5 to afford the protected 1,4-anhydro- β -D-galactopyranose 6 (Figure 1, Method C).¹⁹ A fourth approach involves the intramolecular addition of the 4-hydroxy group to a glycal, promoted by a suitable electrophile, such as in the transformation of 7 to 8 (Figure 1, Method D).^{20,21} As the electrophile adds the alkene, this method yields a 2-substituted 1,4-anhydro-2deoxy sugar, and is not suitable for the synthesis of 1,4-anhydro sugars that are oxygenated at C2.



Figure 1: Summary of approaches used for the targeted synthesis of 1,4-anhydro sugars.

In this work we report efforts, which were ultimately successful, to prepare 1,4anhydro- α -D-mannopyranose 9 (Figure 2). The synthesis of this anhydro sugar has not been reported previously, although it has been invoked as an intermediate in the solvolysis of α -Dmannopyranosyl fluoride.²²



Figure 2: 1,4-Anhydro-α-D-mannopyranose

RESULTS AND DISCUSSION

Brimacombe and co-workers²³ reported the synthesis of 1,4-anhydro-2,3-*O*-isopropylidene- α -L-rhamnopyranose **10**, which was prepared by utilizing an approach based on that outlined in *Method B* of Scheme 1, however they used sodium azide^{24,25} to displace the anomeric acetyl group of **11** to generate an anomeric alkoxide (Figure 3). As this represents the only literature example of a 1,4-anhydrosugar bearing exclusively *endo* substituents our initial efforts towards 1,4-anhydro- α -D-mannopyranose were dedicated to a similar approach. As it is unlikely that the 1,4-anhydro system would survive the conditions needed for isopropylidene deprotection,¹² and as it has been shown that non-anomeric ester groups are stable to the reaction conditions,²⁴ we chose to employ ester protecting groups.



Figure 3: Synthesis of 1,4-anhydro-2,3-*O*-isopropylidene-α-L-rhamnopyranose, by Brimacombe and co-workers.²³

Methyl talopyranoside 12 was prepared in 5 steps from methyl α -D-mannopyranoside (Figure 4).^{26,27} Acetylation with Ac₂O and pyridine afforded diacetate 13, which was subjected to acetolysis (2% H₂SO₄, Ac₂O) to afford the triacetate 14. Compound 14 was treated with sodium azide in DMF or DMSO; however, under a range of temperatures up to reflux the desired intramolecular substitution to afford 15 did not occur. Instead, only deacetylated talose mesylates were obtained after extended reaction times. In order to prevent cleavage of the acetates at the 2- and 3-positions, more robust benzoate protecting groups were installed by treatment of 12 with BzCl and pyridine, to afford the dibenzoate 16. Acetolysis of 16 (4% H₂SO₄, Ac₂O) afforded the anomeric acetate 17 in 85% yield. Treatment of 17 with sodium azide in DMF or DMSO at a range of temperatures for extended periods gave no evidence of the 1,4-anhydrosugar 18, and resulted in only decomposition of

the starting material. For example, trace amounts of tetrabenzoate **19** were isolated, formed by intermolecular transesterification.



Figure 4: Attempted preparation of 1,4-anhydromannose 15 and 18 by intramolecular substitution of a 4-mesylate by an anomeric alkoxide. *Reagents and conditions:* a) Ac₂O, pyr, 99%. b) 2% H₂SO₄, Ac₂O, 71%. c) NaN₃ in DMF or DMSO. d) BzCl, pyr, 100%. e) 2% H₂SO₄, Ac₂O, 85%. f) NaN₃, DMF or DMSO, traces only of 19.

Achieving no success in our attempts to generate the desired 1,4-anhydro bridge by *Method B*, which involves reaction of O1 with C4, we sought to reverse the approach and use O4 as nucleophile to react with C1 under Lewis acidic conditions as outlined in *Method C* in Figure 1. Accordingly, the thiotolyl α -D-mannoside **20**²⁸ was treated with 3.3 equivalents of BzCl at 0 °C in pyridine and allowed to warm to room temperature to afford the tribenzoate **21** in 85% yield (Figure 5). Disappointingly, activation of thiomannoside **21** with *N*-iodosuccinimide and triflic acid at a variety of temperature in a range of different solvents failed to form the 1,4-anhydrosugar **22**. We speculate that the deactivating benzoate protecting groups render the 4-hydroxyl insufficiently nucleophilic to effect the cyclization.



Figure 5: Attempted preparation of 1,4-anhydromannose 22 by intramolecular substitution of

C1 by the 4-hydroxyl. *Reagents and conditions:* a) BzCl, pyr, -50 °C, 65%. b) NIS, TfOH,

CH₂Cl₂.

With these disappointing results, we reconsidered our approach and decided to pursue Method A in Figure 1, in which the nucleophilicity of the O4 can be assured. When investigating the conversion of 2,3,6-tri-O-benzyl- α -D-glucopyranosyl chloride 23 to the 1,4anhydro sugar 24 using sodium hydride, Sato and co-workers identified a remarkable solvent dependence (Figure 6A).²⁹ Upon performing the reaction in DMSO mainly 2-benzyloxy-3,6di-O-benzyl-D-glucal 25 was obtained with the desired anhydro sugar 24 isolated in only 8% yield. However, using THF, an impressive 93% yield of 24 resulted. Accordingly, we set about the preparation of the equivalent D-manno configured precursor. Acetolysis of methyl 2,3,6-tri-O-benzyl- α -D-mannoside 26³⁰ afforded the anomeric acetate 27 in an unoptimized 26% yield (Figure 6B). Treatment of 26 with HCl in Et₂O gave the anomeric chloride 28 in good yield; however all attempts to obtain the 4-hydroxy chloride 29 through deacetylation were hampered by significant decomposition. Given that hemiacetals may also be converted to glycosyl chlorides by ethereal HCl, 27 was deacetylated by treatment with NaOMe in MeOH, affording an inseparable 7:1 mixture of the D-mannose and D-glucose epimers, 30 and **31**, respectively, the latter arising from Lobry de Bruyn-Alberda van Ekenstein reaction. Treatment of this mixture with HCl in Et₂O afforded a 7:1 epimeric mixture of D-mannosyl chloride 29 and D-glucosyl chloride 23. To effect the cyclization, treatment of the epimeric mixture of glycosyl chlorides 29/23 with NaH in THF at reflux for 2 days gave clean conversion to two compounds, in a 7:1 ratio as assessed by ¹H NMR analysis. The major product was isolated in 75% yield and was assigned as the elimination product 25. The less abundant material was isolated in a 15% yield and was assigned as a 1,4-anhydro sugar based on the distinctive signal in the ¹H NMR spectrum at δ 5.45 ppm. However, careful analysis of this material revealed it to be the 1,4-anhydro glucopyranose 24. This disappointing result suggested that the D-gluco-configured chloride cyclized essentially quantitatively to the 1,4anhydro glucopyranose 24, whereas the more abundant D-manno-configured chloride appears to be converted smoothly to the elimination product 25.



Figure 6: A) Summary of solvent dependence of substitution/elimination reactions of glucosyl chloride 31, reported by Sato *et al.*²⁹ B) Attempted preparation of 1,4-anhydromannose 22 by intramolecular substitution of C1 by the 4-hydroxyl. *Reagents and conditions:* a) 0.2% H₂SO₄, Ac₂O, 26%. b) HCl in Et₂O, 93%. c) NaOMe, MeOH. d)
NaOMe, MeOH, 91%, 7:1 30/31. e) HCl in Et₂O, 62%, 7:1 29/23. f) NaH, THF, reflux, 90%, 6:1 25/24.

To more carefully investigate this reaction, we developed an alternative synthesis of the chloride **29** (Figure 7). Thus acidic hydrolysis of **26** afforded the pure hemiacetal **30**. Treatment of **30** with ethereal HCl afforded a pure sample of the chloride **29**. Overnight reflux of a mixture of **29** and NaH in THF afforded a mixture of 2 compounds in a 13:1 ratio. After purification, the major compound was identified as **25**. Analysis of the minor component **32** led to its assignment as 1,4-anhydro-2,3,6-tri-*O*-benzyl- α -D-mannopyranose, albeit in a yield of 5%. Figure 8 shows a comparison of the ¹H NMR spectra of 1,4-anhydro-2,3,6-tri-*O*-benzyl- α -D-mannopyranose **(24)** and 1,4-anhydro-2,3,6-tri-*O*-benzyl- α -D-mannopyranose **32**. Characteristic features of the two 1,4-anhydro sugars are down-field signals for H1 (**24**: δ 5.45, s; **32**: δ 5.59, d, *J*_{1,2} 2.5 Hz), extensive long range "W" couplings,

particularly in the case of **24**, and upfield signals for H2 (**24**: 3.69, d, $J_{2,3}$ 2.5 Hz; **32**: 3.81, ddd, $J_{1,2}$ 2.5, $J_{2,3}$ 8.3, $J_{2,4}$ 0.9 Hz). Finally, compound **32** was deprotected using H₂ and Pd(OH)₂-C to yield 1,4-anhydro- α -D-mannopyranose **9** in 75% yield.



Figure 7: Preparation of 1,4-anhydromannose 9. *Reagents and conditions:* a) 1 M HCl, AcOH, 51%. b) HCl in Et₂O, 51%. c) NaH, THF, reflux, 71% of 25, 5% of 32. d) H₂, Pd(OH)₂/C, EtOAc/EtOH, 67%.



Figure 8: Excerpts of the ¹H NMR spectra (500 MHz, CDCl₃) of A) 1,4-anhydro-2,3,6-tri-*O*-benzyl-α-D-glucopyranose (24) and B) 1,4-anhydro-2,3,6-tri-*O*-benzyl-α-D-mannopyranose (32).

CONCLUSION

In summary, we report the first synthesis of the previously unreported 'all *endo*' 1,4anhydro sugar, 1,4-anhydro- α -D-mannopyranose. This work is significant as it highlights several unsuccessful approaches to this compound and reveals that conditions suitable for cyclization of 2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl chloride **23** to the corresponding 1,4anhydroglucose derivative **24** in high yield,²⁹ give predominantly the elimination product **25** when applied to the D-*manno*-configured epimer **29**. Nonetheless, this approach does provide small amounts of the desired 1,4-anhydro mannose derivative, which could be deprotected to yield the parent 1,4-anhydro- α -D-mannopyranose **9**.

EXPERIMENTAL

General methods

¹H and ¹³C NMR were recorded using Inova 400 or Inova 500 instruments (Melbourne). All signals were referenced to TMS (0.00 ppm), or solvent peaks (CDCl₃: δ 7.26 ppm for ¹H or 77.16 ppm for ¹³C; D₂O: δ 4.80 ppm for ¹H or TMS 0.00 ppm for ¹³C; d₄-MeOH: δ 3.49 ppm for ¹H or 49.0 ppm for ¹³C). Melting points were obtained using a Reichert-Jung hot-stage apparatus. TLC analysis used-aluminium backed Merck Silica Gel 60 F₂₅₄ sheets, detection was achieved using UV light, 5% H₂SO₄ in MeOH, or cerium molybdate ("Hanessian's stain") with charring as necessary. Flash chromatography was performed using Geduran silica gel according to the method of Still *et al.*³¹ Dry CH₂Cl₂, THF, and Et₂O were obtained from a dry solvent apparatus (Glass Contour of SG Water, Nashua, U.S.A.).³² DMF and DMSO were dried over 4 Å molecular sieves. Elemental analyses were performed by C.M.A.S. (Belmont, Victoria).

1,2,3-Tri-O-acetyl-6-O-benzoyl-4-O-methanesulfonyl-α-D-talopyranoside (14)

(i) Methyl 2,3-di-O-acetyl-6-O-benzoyl-4-O-methanesulfonyl- α -D-talopyranoside (13)

A solution of methyl 6-*O*-benzoyl-4-*O*-methanesulfonyl- α -D-talopyranoside **12**^{26,27} (180 mg, 0.478 mmol) was dissolved in a mixture of acetic anhydride and pyridine (3 mL, 1:2) was stirred for 24 h. The solvent was evaporated under reduced pressure and the residue was dissolved in EtOAc. The organic phase was sequentially washed with 2 M aq. HCl (3×), sat. aq. NaHCO₃, water, and sat. aq. NaCl, before being dried (MgSO₄), filtered, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (acetone/PhMe 1:4) to give the diacetate **13** as a colourless oil (198 mg, 99%), ¹H NMR (500 MHz, CDCl₃) δ 2.11, 2.17 (6 H, 2 × s, 2 × COCH₃), 3.13 (3 H, s, Ms), 3.42 (3 H, s, OCH₃), 4.38 (1 H, dt, J_{4,5} 1.1, J_{5,6} 7.0, J_{5,6} 6.5 Hz, H5), 4.44 (1 H, dd, J_{5,6} 7.0, J_{6,6} 11.1 Hz, H6), 4.67 (1 H, dd, J_{1,2} 1.4, J_{2,3} 3.7, J_{2,4} 1.1 Hz, H2), 5.30 (1 H, t, J_{2,3} J_{3,4} 3.7 Hz, H3), 7.42-7.48 (2 H, m, Ar), 7.55-7.61 (1 H, m, Ar), 8.02-8.08 (2 H, m, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 20.9, 21.1 (2 C, COCH₃), 39.0 (1 C, Ms), 55.7 (1 C, OCH₃), 62.3, 65.4, 65.5, 67.5, 74.0 (5 C, C2,3,4,5,6), 99.5 (1 C, C1), 128.7, 129.4, 129.9, 133.6 (6 C, Ar), 166.1, 169.6, 170.3 (3 C, C=O).

(ii) 1,2,3-Tri-O-acetyl-6-O-benzoyl-4-O-methanesulfonyl- α -D-talopyranoside (14)

A solution of the diacetate **13** (170 mg, 0.408 mmol) in a 2% solution of H₂SO₄ in acetic anhydride (2 mL) was stirred overnight then poured onto ice and extracted with EtOAc. The organic phase was sequentially washed with sat. aq. NaHCO₃, H₂O and sat. aq. NaCl, dried (MgSO₄), filtered, and concentrated under reduced pressure to give a yellow oil. The oil was purified by flash chromatography (acetone/PhMe 1:4) to give the α-anomer **14** contaminated with 5% β-anomer, as a colourless oil (143 mg, 71%, 95% α-anomer by ¹H NMR), $[\alpha]_D^{19}$ 87 ° (c 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 2.11, 2.14, 2.18 (9 H, 3 × s, 3 × COCH₃), 3.12 (3 H, s, Ms), 4.40 (1 H, dd, *J*_{5,6} 8.0, *J*_{6,6}[,] 10.8 Hz, H6), 4.45-4.49 (1 H, m H5), 4.64 (1 H, dd, *J*_{5,6}[,] 5.8, *J*_{6,6}[,] 10.8 Hz, H6'), 5.15-5.16 (1 H, m, H4), 5.18 (1 H, ddd, *J*_{1,2} 1.6, *J*_{2,3} 3.7, *J*_{2,4} 1.1 Hz, H2), 5.34 (1 H, t, *J*_{2,3} = *J*_{3,4} 3.7 Hz, H3), 6.18 (1H, d, *J*_{1,2} 1.6 Hz, H1), 7.43-7.47 (2 H, m, Ar), 7.56-7.60 (1 H, m, Ar), 8.00-8.03 (2 H, m, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 20.85, 20.94, 20.97 (3 C, 3 × COCH₃), 39.0 (1 C, Ms), 61.5, 65.0, 66.3, 68.6, 73.2 (5 C, C2,3,4,5,6), 91.5 (1 C, C1), 128.7, 129.2, 129.9, 133.7 (6 C, Ar), 166.0, 168.0, 169.7, 170.0 (4 C, C=O); HRMS (ESI⁺): *m/z* 511.0879 [M+Na]⁺ (calcd. [C₂₀H₂₄O₁₂S+Na]⁺ 511.0880).

Methyl 2,3,6-tri-O-benzoyl-4-O-methanesulfonyl-α-D-talopyranoside (16)

Benzoyl chloride (94 μL, 0.810 mmol) was added dropwise to a stirred solution of methyl 6-*O*-benzoyl-4-*O*-methanesulfonyl-α-D-talopyranoside **12**^{26,27} (152 mg, 0.404 mmol) in dry pyridine (3.0 mL) under N₂ atmosphere. After 2 h at r.t. the mixture was poured into water (20 mL) and extracted with EtOAc. The organic phase was washed sequentially with 1 M aq. HCl, sat. aq. NaHCO₃, H₂O, and sat. aq. NaCl then dried over MgSO₄, filtered and evaporated to dryness under reduced pressure. Flash chromatography (30% EtOAc/pet. sp.) of the residue afforded the tribenzoate **16** as colourless oil (236 mg, 100%), $[\alpha]p^{19}$ -78 ° (c 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 2.88 (3 H, s, SCH₃), 3.49 (3 H, s, CH₃), 4.52-4.57 (2 H, m, H5,6), 4.75 (1 H, dd, *J*_{5,6} 9.5, *J*_{6,6} 14.0 Hz, H6'), 5.02 (1 H, d, *J*_{1,2} 1.5 Hz, H1), 5.36-5.38 (1 H, m, H4), 5.53 (1 H, ddd, *J*_{1,2} 1.5, *J*_{2,3} 3.7, *J*_{2,4} 1.0 Hz, H2), 5.69 (1 H, t, *J*_{2,3} = *J*_{3,4} 3.7 Hz, H3), 7.35-7.65 (9 H, m, Ar), 7.95-7.98 (2 H, m, Ar), 8.06-8.12 (2 H, m, Ar), 8.22-8.25 (2 H, m, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 39.0 (1 C, Ms), 55.8 (1 C, OCH₃), 62.5, 66.3, 66.7, 68.2, 74.4 (5 C, C2,3,4,5,6), 99.5 (1 C, C1), 128.61, 128.64, 128.69, 128.74, 129.1, 129.5, 129.6, 130.1, 130.3, 130.3 133.5, 133.7, 133.8 (18 C, Ar), 165.4, 165.9, 166.2 (3 C, C=O).

1-O-Acetyl-2,3,6-tri-O-benzoyl-4-O-methanesulfonyl-α-D-talopyranose (17)

A solution of the methyl talopyranoside **16** (195 mg, 0.336 mmol) in 4% H₂SO₄/Ac₂O (5.0 mL) was stirred at r.t. for 5 h then ice-water was added and stirring continued for 30 min. The mixture was extracted with EtOAc (5 × 5 mL) and the organic phase sequentially washed with sat. aq. NaHCO₃ (5 ×), H₂O, and sat. aq. NaCl. The organic phase was dried over MgSO₄, filtered, and concentrated under reduced pressure to give a residue that was purified by flash chromatography (30 % EtOAc/pet. sp.) affording **17** as a clear oil (173 mg, 85%). $[\alpha]_{D^{19}}$ -71 ° (c 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 2.21 (3 H, s, COCH₃), 2.89 (3 H, s, Ms), 4.51 (1 H, dd, *J*_{5,6} 7.7, *J*_{6,6} 11.1 Hz, H6), 4.61-4.65 (1 H, m, H5), 4.73 (1 H, dd, *J*_{5,6} 6.1, *J*_{6,6} 11.1 Hz, H6'), 5.41-5.43 (1 H, m, H4), 5.56 (1 H, ddd, *J*_{1,2} 1.7, *J*_{2,3} 3.8, *J*_{2,4} 1.1 Hz, H2), 5.72 (1 H, t, *J*_{2,3} = *J*_{3,4} 3.8 Hz, H3), 6.39 (1 H, d, *J*_{1,2} 1.7 Hz), 7.36-7.65 (9 H, m, Ar), 7.94-7.99 (2 H, m, Ar), 8.04-8.08 (2 H, m, Ar), 8.21-8.24 (2 H, m, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 21.0 (1 C, COCH₃), 39.0 (1 C, Ms), 61.7, 66.0, 67.0, 68.8, 73.5 (5 C, C2,3,4,5,6), 91.6 (1 C, C1), 128.7, 128.8, 128.9, 129.3, 129.4, 130.1, 130.3, 133.6, 133.8, 133.9 (18 C, Ar), 165.5, 165.6, 166.1 (3 C, 3 × COPh), 168.10 (1 C, COCH₃); HRMS (ESI⁺): *m*/z 635.1192 [M+Na]⁺ (calcd. [C₃₈H₂₈O₁₂S+Na]⁺ 635.1194).

Attempted formation of 18; Preparation of 1,2,3,6-tetra-*O*-benzoyl-4-*O*methanesulfonyl-α-D-talopyranose (19)

Reaction of the tribenzoate **17** with NaN₃ in DMF or DMSO at temperatures above 80 °C afforded only decomposed materials and traces of the tetrabenzoate **19**. ¹H NMR (500 MHz, CDCl₃) δ 2.91 (3 H, s, Ms), 4.53 (1 H, dd, *J*_{5,6} 10.4, *J*_{6,6'} 13.9 Hz, H6), 4.70-4.75 (2 H, m, H5,6'), 5.49-5.51 (1 H, m, H4), 5.74 (1 H, ddd, *J*_{1,2} 1.7, *J*_{2,3} 3.7, *J*_{2,4} 1.1 Hz, H2), 5.86 (1 H, t, *J*_{2,3} = *J*_{3,4} 3.7 Hz, H3), 6.64 (1 H, d, *J*_{1,2} 1.7 Hz, H1), 7.37-7.56 (10 H, m, Ar), 7.63-7.67 (2 H, m, Ar), 7.99-8.03 (2 H, m, Ar), 8.08-8.11 (4 H, m, Ar), 8.24-8.27 (2 H, m, Ar); HRMS (ESI⁺): *m*/*z* 692.1798 [M+NH4]⁺ (calcd. [C₃₅H₃₀O₁₂+NH4]⁺ 692.1796). ¹³C data was not obtained.

4-Methylphenyl 2,3,6-tri-O-benzoyl-1-thio-α-D-mannopyranoside (21)

4-Methylphenyl 1-thio- α -D-mannopyranoside **20**²⁸ (503 mg, 1.76 mmol) was dissolved in dry pyridine (20 mL) and concentrated to dryness under reduced pressure, this process was repeated twice leaving a small volume of pyridine (10 mL) on the last cycle. The dried solution was cooled to -40 °C and benzoyl chloride (673 μ L, 5.80 mmol) was added dropwise over a period of 1 h with stirring. The solvent was evaporated under reduced pressure (50

°C), the residue dissolved in CH₂Cl₂, and the mixture extracted sequentially with 1 M aq. HCl $(2 \times)$, sat. aq. NaHCO₃ $(2 \times)$, H₂O and finally sat. aq. NaCl. The organic phase was dried (MgSO₄), filtered, and concentrated under reduced pressure to give a yellow oil which was purified flash chromatography to afford mostly pure tribenzoate 21 (95% by ¹H NMR) as a clear oil (280 mg, 65%), [α]_D¹⁹ 51 ° (c 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 2.30 (3 H, s, CH₃), 4.31 (1 H, t, J_{3,4} = J_{4,5} 9.8 Hz, H4), 4.65 (1 H, dd, J_{5,6} 2.0, J_{6,6'} 12.0 Hz, H6), 4.69 (1 H, ddd, J_{4,5} 9.8, J_{5,6} 2.0, J_{5,6} 4.6 Hz, H5), 4.91 (1 H, dd, J_{5,6} 4.6, J_{6,6} 12.0 Hz, H6'), 5.61 (1 H, dd, J_{2,3} 3.2, J_{3,4} 9.8 Hz, H3), 5.63 (1 H, d, J_{1,2} 1.6 Hz, H1), 5.89 (1 H, dd, J_{1,2} 1.6, J_{2,3} 3.2 Hz, H2), 7.06 (2 H, d, Ar), 7.32-7.63 (11 H, m, Ar), 7.92-7.99 (4 H, m, Ar), 8.10 (1 H, dd, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 21.3 (1 C, CH₃), 63.8, 68.9, 72.1, 72.4, 73.1 (5 C, C2,3,4,5,6), 86.6 (1 C, C1), 128.6, 128.6, 128.7, 129.2, 129.3, 129.6, 129.88, 129.97, 130.04, 130.05, 130.1, 132.8, 133.4, 133.58, 133.60, 138.5 (24 C, Ar), 165.4, 166.7, 167.1 (3 C, C=O); HRMS (ESI⁺): m/z 599.1742 [M+H]⁺ (calcd. [C₃₄H₃₀O₈S+H]⁺ 599.1734), 616.2009 $[M+NH_4]^+$ 616.2000), (calcd. $[C_{34}H_{30}O_8S+NH_4]^+$ 621.1564 $[M+Na]^+$ calcd. $[C_{34}H_{30}O_8S+Na]^+$ 621.1554).

Methyl 2,3,6-tri-*O*-benzyl-α-D-mannopyranoside (26)

CF₃CO₂H (2.25 mL, 30.3 mmol) was added dropwise to a cold (0 °C) stirred mixture of methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside³⁰ (2.80 g, 6.06 mmol) and triethylsilane (4.84 mL, 30.3 mmol) in CH₂Cl₂ (25 mL). After 30 min the mixture was allowed to warm to r.t. and stirred for a further 4 h before being diluted with EtOAc (100 mL). The mixture was washed with sat. aq. NaHCO₃, then sat. aq. NaCl, dried (MgSO₄), filtered, and concentrated under reduced pressure. Flash chromatography (20% EtOAc/pet. sp.) of the resultant crude material gave the tribenzyl ether **26** as a clear oil (2.13 g, 76%), $[\alpha]_{\rm D}^{19}$ -3° (c 1.00, CHCl₃), lit.³³ $[\alpha]_{\rm D}^{25}$ 0° (c 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 2.52 (1 H, d, *J*_{4,OH} 2.0 Hz, OH), 3.36 (3 H, s, CH₃), 3.68-3.84 (5 H, m, H2,3,5,6,6'), 4.05 (1 H, dt, *J*_{3,4} = *J*_{4,5} 9.4, *J*_{4,OH} 2.0 Hz, H4), 4.49-4.69 (6 H, m, 3 × CH₂Ph), 4.79 (1 H, d, *J*_{1,2} 1.7 Hz, H1), 7.25-7.38 (15 H, m, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 55.0 (1 C, CH₃), 68.0, 70.6, 71.5, 71.9, 72.8, 73.7, 74.0, 79.8 (8 C, 3 × CH₂Ph, C2,3,4,5,6), 99.3 (1 C, C1), 127.64, 127.72, 127.78, 127.85, 127.90, 128.0, 128.4, 128.5, 128.6, 138.33, 138.35, 138.41 (18 C, Ar).

1,4-Di-O-acetyl-2,3,6-tri-O-benzyl-a-D-mannopyranose (27)

A solution of mannoside **26** (402 mg, 0.865 mmol) in 0.2% H₂SO₄ in Ac₂O (1 mL) was stirred at r.t. for 45 min then cold sat. aq. NaHCO₃ was added. The mixture was diluted with EtOAc and sequentially washed with sat. aq. NaHCO₃ (3 ×), water, and sat. aq. NaCl, dried (MgSO₄), filtered, and concentrated under reduced pressure. The crude residue was subjected to flash chromatography (30% EtOAc/pet. sp.) to give the diacetate **27** as white needles (120 mg, 26%), m.p. 102-103 °C. [α]p²⁰ 23 ° (c 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 1.93, 2.05 (6 H, 2 × s, 2 × CH₃), 3.55 (1 H, dd, *J*_{5,6} 3.6, *J*_{6,6} 10.8 Hz, H6), 3.59 (1 H, dd, *J*_{5,6} 5.5, *J*_{6,6} 10.8 Hz, H6'), 3.73 (1 H, dd, *J*_{1,2} 2.2, *J*_{2,3} 3.1 Hz, H2), 3.77 (1 H, dd, *J*_{3,4} 3.1, *J*_{4,5} 9.6 Hz, H3), 3.87-3.95 (1 H, m, *J*_{4,5} 9.5, *J*_{5,6} 3.6, *J*_{5,6} 5.5 Hz, H5), 4.44 (1 H, d, ²*J* 12.1 Hz, CH₂Ph), 4.50-4.54 (3 H, m, 3 × CH₂Ph), 4.72 (2 H, s, CH₂Ph), 5.43 (1 H, t, *J*_{3,4} = *J*_{4,5} 9.6 Hz, H4), 6.18 (1 H, d, *J*_{1,2} 2.2 Hz, H1), 7.23-7.37 (15 H, m, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 21.1, 21.2 (2 C, 2 × CH₃), 68.7, 70.0, 72.0, 72.8, 73.1, 73.2, 73.8, 76.3 (8 C, 3 × CH₂Ph, C2,3,4,5,6), 92.1 (1 C, C1), 127.67, 127.76, 127.89, 127.93, 128.1, 128.2, 128.46, 128.51, 137.8, 138.1 (18 C, Ar), 168.9, 169.9 (2 C, 2 × COCH₃); Anal. Calcd for C₃₁H₃₄O₈: C, 69.65; H, 6.41. Found: C, 69.71; H, 6.33.

4-O-Acetyl-2,3,6-tri-O-benzyl-α-D-mannopyranosyl chloride (28)

A solution of the diacetate **27** (10.0 mg, 18.7 mmol) in ether saturated with HCl (5 mL) was stirred for 30 min at 0 °C under N₂. The mixture was warmed to r.t. and stirred for a further 30 min. The solvent was evaporated under a stream of N₂ and Et₂O (10 mL) was added. This process was repeated five times, and the dried residue was subjected to flash chromatography (15% EtOAc/pet. sp.) giving the chloride **28** (8.9 mg, 93%). ¹H NMR (500 MHz, CDCl₃) δ 1.86, 1.98 (6 H, 2 × s, 2 × CH₃), 3.47 (1 H, dd, *J*_{5,6} 3.5, *J*_{6,6} 10.8 Hz, H6), 3.47 (1 H, dd, *J*_{5,6} 5.5, *J*_{6,6} 10.8 Hz, H6'); 3.66 (1 H, overlapping dd, *J*_{1,2} 2.6, *J*_{2,3} 2.8 Hz, H2), 3.70 (1 H, dd, *J*_{2,3} 2.8, *J*_{3,4} 9.7 Hz, H3), 3.82-3.86 (1 H, m, H5), 4.36-4.48 (4 H, m, CH₂Bn), 4.66 (2 H, s, CH₂Bn), 5.36 (1 H, t, *J*_{3,4} = *J*_{4,5} 9.7 Hz, H4), 6.11 (1 H, d, *J*_{1,2} Hz, H1), 7.16-7.31 (15 H, Ar). Owing to the instability of this compound it was not further characterized.

2,3,6-Tri-O-benzyl-α-D-mannopyranose (30)

(*i*) From mannoside (26)

A solution of the mannoside **26** (2.00 g, 4.31 mmol), AcOH (20 mL) and 1 M aq. HCl (5 mL) was heated in an oil bath at 105 °C for 2.5 h then poured into ice-water and extracted with EtOAc. The organic phase was washed with sat. aq. NaHCO₃ then sat. aq. NaCl, dried

(MgSO₄), filtered, and concentrated under reduced pressure. Flash chromatography (30% EtOAc/pet. sp.) of the residue gave the title compound **30** as a clear oil, which was used for subsequent reactions without further purification (710 mg, 37%), $[\alpha]_D^{19}$ -20° (c 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 2.49 (1 H, d, *J*_{1,OH} 2.0 Hz, OH), 3.45 (1 H, d, *J*_{4,OH} 2.0 Hz, OH), 3.69 (1 H, dd, *J*_{5,6} 7.0, *J*_{6,6} 10.3 Hz, H6), 3.76 (1 H, dd, *J*_{2,3} 3.1, *J*_{3,4} 9.5 Hz, H3), 3.79 (1 H, dd, *J*_{1,2} 1.8, *J*_{2,3} 3.1 Hz, H2), 3.81 (1 H, dd, *J*_{5,6} 2.8, *J*_{6,6} 10.3 Hz, H6[†]), 3.93 (1 H, dt, *J*_{3,4} = *J*_{4,5} 9.5, *J*_{4,OH} 2.0 Hz, CH₂Ph), 4.68 (1 H, d, ²*J* 12.4 Hz, CH₂Ph), 5.28 (1 H, br s, H1), 7.25-7.38 (15 H, m, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 67.8, 70.7, 71.5, 71.9, 72.8, 73.6, 74.2, 79.4 (8 C, 3 × CH₂Ph, C2,3,4,5,6), 92.9 (1 C, C1), 127.80, 127.88, 127.93, 128.0, 128.3, 128.47, 128.52, 128.6, 128.7, 138.00, 138.2, 138.3 (18 C, Ar); HRMS (ESI⁺): *m*/z 451.2127 [M+H]⁺ (calcd. [C₂₇H₃₀O₆+H]⁺ 451.2115), 468.2383 [M+NH4]⁺ (calcd. [C₂₇H₃₀O₆+NH₄]⁺ 468.2381), 473.1934 [M+Na]⁺ calcd. [C₂₇H₃₀O₆+Na]⁺ 473.1935). (*ii*) From diacetate (**27**)

A small piece of sodium metal was added to a stirring solution of diacetate **27** (63.5 mg, 0.12 mmol) in MeOH (5 mL). After stirring for 1 h at r.t. the mixture was neutralized by the addition of Amberlite IR-120 (H⁺), filtered and concentrated to an oil. Chromatography of the mixture as per above afforded the mannose derivative **30** as a mixture with the glucose epimer **31** (48.5 mg, 91%, 7:1 D-*manno*/D-gluco by ¹H NMR).

2,3,6-*Tri*-O-*benzyl*-α-*D*-*glucopyranose* **31**: Partial ¹H NMR (500 MHz, CDCl₃) δ 5.23 (1 H, t, $J_{1,2} \approx J_{1,OH}$ 2.8 Hz, H1).

1,4-Anhydro-2,3,6-tri-*O*-benzyl-α-D-mannopyranose (32) and 3,6-di-*O*-benzyl-2benzyloxy-D-glucal (25)

(i) 2,3,6-Tri-O-benzyl- α -D-mannopyranosyl chloride (29)

The crude hemiacetal **30** (250 mg, 0.555 mmol) was dissolved in dry Et₂O (10 mL) under an inert (N₂) atmosphere and the solution was saturated with HCl gas. After stirring for 72 h at r.t. the solvent was evaporated under a stream of N₂ and Et₂O (10 mL) was added. This process was repeated five times and the dried residue was subjected to flash chromatography (15% EtOAc/pet. sp.) giving the chloride **29** as a clear oil (133 mg, 51%), $[\alpha]_D^{19}$ 53 ° (c 1.00, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 3.76 (1 H, dd, *J*_{5,6} 3.5, *J*_{6,6'} 10.9 Hz, H6), 3.80 (1 H, dd, *J*_{5,6'} 4.8, *J*_{6,6'} 10.9 Hz, H6'), 3.89 (1 H, dd, *J*_{1,2} 1.7, *J*_{2,3} 3.1 Hz, H2), 3.99-4.04 (2 H, m, H3,5), 4.15 (1 H, t, *J*_{3,4} = *J*_{4,5} 9.5 Hz, H4), 4.54-4.71 (6 H, m, 3 × CH₂Ph), 6.12 (1 H, dd, *J*_{1,2})

1.7 Hz, H1), 7.25-7.38 (15 H, m, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 67.2, 69.4, 72.4, 73.1, 73.7, 74.4, 77.2, 77.8 (8 C, 3 × CH₂Ph, C2,3,4,5,6), 91.6 (1 C, C1), 127.78, 127.85, 128.05, 128.08, 128.13, 128.16, 128.51, 128.64, 128.71, 137.6, 137.9, 138.1 (18 C, Ar); HRMS (ESI⁺): *m/z* 433.20074 [M-Cl]⁺ (calcd. [C₂₇H₂₉O₅Cl-Cl]⁺ 433.20095).

(ii) 1,4-Anhydro-2,3,6-tri-O-benzyl-α-D-mannopyranose (**32**) and 3,6-di-O-benzyl-2benzyloxy-D-glucal (**25**)

Chloride 29 (30.0 mg, 0.064 mmol) was dissolved in dry THF (15 mL) under an N₂ atmosphere and an excess of NaH (20 mg) was added with stirring. The mixture was heated to reflux and stirred overnight. The reaction was quenched by the addition of MeOH (1 mL) and the mixture was poured into water and extracted three times with CHCl₃. The CHCl₃ extract was washed with 0.5 M HCl and sat. aq. NaHCO₃, dried (MgSO₄), filtered, and concentrated under reduced pressure. The resultant oil was subjected to flash chromatography on silica gel (15% EtOAc/pet. sp.) to afford the anhydro sugar 32 as a white solid (1.3 mg, 5%), m.p. 71-73 °C (CHCl₃; $[\alpha]_D^{18}$ -45 ° (c 0.415, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 3.81 (1 H, ddd, J_{1,2} 2.5, J_{2,3} 8.3, J_{2,4} 0.9 Hz, H2), 3.94 (1 H, ddd, J_{2,3} 8.3, J_{3,4} 4.6, J_{3,5} 1.0 Hz, H3), 3.97 (1 H, dd, J_{5,6} 3.7, J_{6,6'} 10.1 Hz, H6), 4.21 (1 H, dd, J_{5,6'} 7.7, J_{6,6'} 10.1 Hz, H6'), 4.25 (1 H, dp, *J*_{3,5} 1.0, *J*_{4,5} 3.7, *J*_{5,6} 3.7, *J*_{5,6'} 7.7 Hz, H5), 4.46 (2 H, 2 × d, 2 × CH₂Ph), 4.56-4.71 (5 H, m, 2 × CH₂Ph, H4), 5.59 (1 H, d, $J_{1,2}$ 2.5 Hz, H1), 7.23-7.39 (15 H, m, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 69.1, 72.2, 73.0, 73.4, 74.6, 74.7, 78.3, 79.5 (8 C, 3 × CH₂Ph, C2,3,4,5,6), 101.9 (1 C, C1), 127.6, 127.78, 127.86, 127.89, 127.92, 127.97, 128.4, 128.5, 138.0, 138.2, 138.6 (18 C, Ar); HRMS (ESI⁺): *m/z* 455.1828 [M+Na]⁺ (calcd. [C₂₇H₂₈O₅+Na]⁺ 455.1829). Also obtained was compound 25, colourless oil (19.3 mg, 71%), $[\alpha]_D^{18}$ -25° (CHCl₃; lit.²⁹ -22°); ¹H NMR (500 MHz, CDCl₃) δ 2.28 (1 H, d, J_{4,OH} 5.5 Hz, OH), 3.71 (1 H, dd, J_{5,6} 3.7, J_{6,6'} 10.7 Hz, H6), 3.79 (1 H, dd, J_{5,6'} 5.9, J_{6,6'} 10.7 Hz, H6'), 3.95 (1 H, m, H5), 4.06 (1 H, overlapping dt, J_{3,4} 5.6, J_{4,5} 7.5, J_{4,OH} 5.5 Hz, H4), 4.15 (1 H, d, J_{3,4} 5.6 Hz, H3), 4.57 (2 H, d, CH₂Ph), 4.67-4.74 (3 H, m, $3 \times$ CH₂Ph), 4.84 (1 H, d, ²J 11.7 Hz, CH₂Ph), 6.27 (1 H, d, H1), 7.25-7.38 (15 H, m, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 68.83, 68.87, 71.3, 72.7, 73.7, 77.0, 77.3 (7 C, 3 × CH₂Ph, C3,4,5,6), 127.66, 127.85, 127.90, 127.93, 127.96, 128.04, 128.08, 128.55, 128.57, 128.59 (16 C, 15 × Ar, C1), 137.2, 138.0, 138.6, 139.0 (4 C, 3 × Ar, C2). The NMR data was consistent with literature.²⁹

1,4-Anhydro-2,3,6-tri-O-benzyl-α-D-glucopyranose (24)³⁴

Reaction of the mixed chlorides **29** and **23** according to the protocol described for the synthesis of the anhydro mannose derivative **32** afforded a mixture of the anhydro glucopyranose **24** and the alkene **25** by (10.0 mg, 90%, 6:1 alkene **25**/1,4-anhydroglucose **24**), ¹H NMR (500 MHz, CDCl₃) δ 3.69 (1 H, d, *J*_{2,3} 2.5 Hz, H2), 3.82 (1 H, dd, *J*_{5,6} 4.2, *J*_{5,6} 10.6 Hz, H6), 3.88 (1 H, dd, *J*_{5,6} 7.7, *J*_{5,6} 10.6 Hz, H6'), 3.99 (1 H, m, H3), 4.13 (1 H, m, H5), 4.42-4.58 (6 H, m, 3 × CH₂Ph), 4.64 (1 H, dd, *J*_{3,4} 4.7, *J*_{4,5} 3.1 Hz, H4), 5.45 (1 H, s, H1), 7.21-7.37 (15 H, m, Ar).

1,4-Anhydro-α-D-mannopyranose (9)

The protected anhydro sugar **32** (6.0 mg, 0.014 mmol) was dissolved in a mixture of EtOAc/EtOH (3 mL, 9:1) and Pd(OH)₂/C (3 mg) was added. The mixture was stirred under H₂ for 70 h then filtered through Celite and concentrated under reduced pressure. The crude residue was purified by flash chromatography (97:2:1 EtOAc:MeOH:H₂O) and reverse phase chromatography (H₂O, C₁₈) to give 1,4-anhydro- α -D-mannopyranose **9** as a colourless gum (1.5 mg, 67%), [α]D¹⁹ -54 ° (c 0.10, MeOH); ¹H NMR (500 MHz, d4-methanol) δ 3.85 (1 H, dd, *J*_{1,2} 2.6, *J*_{2,3} 8.7, *J*_{2,4} 0.8 Hz, H2), 3.95 (1 H, dd *J*_{5,6} 2.9, *J*_{6,6} 11.4 Hz, H6), 3.99-4.07 (3 H, m, H3,5,6'), 4.54 (1 H, ddd, *J*_{2,4} 0.8, *J*_{3,4} 3.2, *J*_{4,5} 4.8 Hz, H4), 5.45 (1 H, d, *J*_{1,2} 2.6 Hz, H1); ¹³C NMR (125 MHz, d4-methanol) δ 60.7, 67.8, 70.2, 81.3, 82.4 (5 C, C2,3,4,5,6), 103.7 (1 C, C1); HRMS (ESI⁺): *m*/z 185.0420 [M+Na]⁺ (calcd. [C₂₇H₂₈O₅+Na]⁺ 185.0420).

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Table of Contents Graphic



1,4-Anhydro- α -D-mannopyranoside