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Two Chiral Building Blocks for the Stereocontrolled Synthesis of *Anti*- and *Syn*-1, 3-Diols

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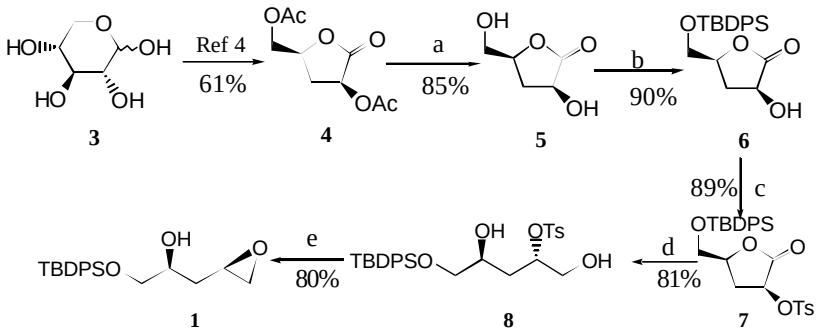
Abstract: Two chiral building blocks **1** and **2** for anti-and syn-1, 3-diols has been achieved in 8 steps and 7 steps respectively, starting from the readily available and inexpensive D (+)-xylose **3** .

Keywords: Chiral building block, anti-and syn-1, 3-diols, D (+)-xylose.

During the last decade, chiral building blocks for 1, 3-diols of various configurations have been synthesized and applied widely in the total synthesis of natural polyene macrolide antibiotics[1] and 1α, 25-dihydroxyvitamin D_3 analogues[2,3]. The synthesis of the building block has attracted much interest in recent years. Herein, we report the synthesis of two chiral building blocks **1** and **2** in 8 steps and 7 steps respectively, starting from the readily available and inexpensive D (+)-xylose **3** as outlined in **Scheme 1** and **Scheme 2**.

D-(+)-Xylose **3** was converted to a known diaceted-lactone **4** by our method[4]. Hydrolysis of **4** with KOH and subsequent TsOH treatment gave lactone **5**, in which the primary hydroxyl group was protected with TBDPSCl to afford silyl ether **6**.

Scheme 1



(a) i: KOH, EtOH-H_2O, r.t., 12 h. ii: TsOH, THF, r.t., 24 h.
(b) TBDPSCl, imid., DMF, r.t., 24 h.

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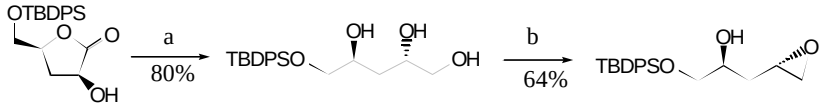
(c) TsCl, Et_3N,CH_2Cl_2, r.t., 60 h.
(d) BH_3, THF, r.t., 72 h.
(e) K_2CO_3, MeOH, r.t., 0.5 h.

The second hydroxy of **6** was tosylated to give tosylate **7**. Reduction of compound **7** with BH_3 in THF gave diol **8**, which was treated with K_2CO_3 to yield the target compound **1**[5].

Reduction of compound **6** with BH_3 gave triol **9**. The alcohol **9** was reacted with Me_2(OAc)CCOCl and treated with K_2CO_3 subsequently to yield the second target compound **2**[5].

Scheme 2



6 **9** **2**

(a) BH_3, THF, r.t., 72 h.
(b) i: Me_2(OAc)CCOCl, 1,4-dioxane, r.t., 72 h. ii: K_2CO_3, MeOH, r.t., 0.5 h.

In summary, we have provided a concise route starting from readily available and inexpensive D (+)-xylose to prepare two chiral building blocks **1** and **2** for anti-and syn-1,3-diols with good yield.

References and notes

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4. Y. Wu, *Chin. J Med. Chem.*, **1998**, *8*, 277.
5. All new compounds were characterized by elemental analysis, IR and ^{1}H-NMR spectral data. Selected analytical data (^{1}H-NMR in $CDCl_3$ at 400MHz) **1**: δ, 1.09 (s, 9H), 1.46 (ddd, 1H, J=14.2, 7.1, 3.4Hz), 1.82 (ddd, 1H, J=14.2,8.9,4.2Hz), 2.51 (dd, 1H, J=4.9, 2.8Hz), 2.61 (d, 1H,J=3.2Hz), 2.80 (1H, dd, 1H, J=4.9, 4.9Hz), 3.10 (m, 1H), 3.25 (dd, 1H, J=10.2, 7.2Hz), 3.70 (dd, 1H, J=10.2, 3.8Hz), 3.97 (m, 1H,), 7.42-7.68 (m, 10H) ppm. **2**: δ, 1.07 (s, 9H), 1.70 (m, 2H), 2.50 (dd, 1H, J=4.4, 2.7Hz), 2.62 (d, 1H, J=3.7Hz), 2.76 (dd, 1H, J=4.4, 4.4Hz), 3.05 (m, 1H), 3.58 (dd, 1H, J=10.2, 7.0Hz), 3.68 (dd, 1H, J=10.2, 3.9Hz), 3.94 (m, 1H), 7.40-7.72 (10H, m) ppm. $[\alpha]_D^{20}$: **1**,-9.70 (c 1.28, $CHCl_3$); **2**, +1.64 (c 1.20, $CHCl_3$).

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