

## Synthesis of Novel Chiral Diol Ligands for the Enantioselective Reactions

Ming Xia LI<sup>1</sup>, Yan Ming WANG<sup>2</sup>, Ru Ru CHEN<sup>1\*</sup>

<sup>1</sup>Research Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071

<sup>2</sup>Pittsburgh University Medical Center, Pittsburgh, PA 15213, U. S. A

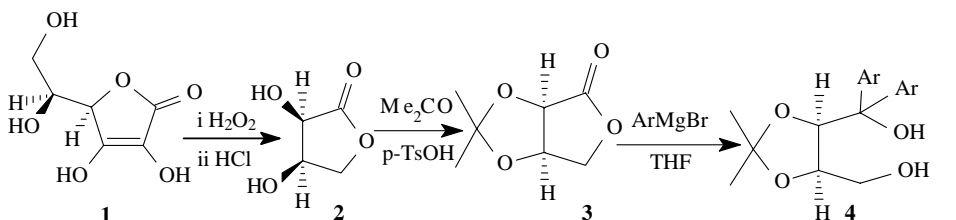
**Abstract:** A series of novel enantiomerically pure diols were synthesized from D-erythorbic acid in three steps, and the absolute configuration of one of them **4a** has been confirmed by X-ray analysis.

**Keywords:** Enantiomerically pure, chiral, diol ligands, X-ray analysis.

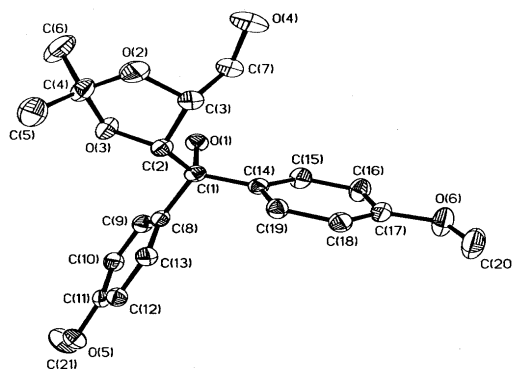
The chiral diols ( $\alpha, \alpha', \alpha', \alpha'$ -Tetraaryl-1,3-dioxolane-4,5-dimethanols) have been used for the formation of cyclic titanates and similar derivatives of Mg, Al and Zr. These complexes of oxophilic metal centers were employed in catalytic and stoichiometric enantioselective reactions such as enantioselective addition reactions of carbon-centered nucleophiles to aldehydes<sup>1</sup>, [2+2] cycloadditions<sup>2</sup>, and Diels-Alder reactions<sup>3</sup>. So far, the two hydrogen atoms of all this type of diols are in *trans* form. The *cis* configuration of the two hydrogen has never been reported. In this communication, we first synthesized a series of novel enantiomerically pure diols with hydrogen in *cis* form from new chiral resource (**Scheme 1**) by a new route. This route is simple and suitable for the preparation of chiral diols in large scale.

Compound **2** was synthesized from D-erythorbic acid by the treatment of H<sub>2</sub>O<sub>2</sub> (30%) and then HCl (yield: 66%; mp: 97.5-99.5°C,  $[\alpha]_D^{25} = -72.09$ (c, 0.498, H<sub>2</sub>O)). The

**Scheme 1**



**4a** Ar=4-OMePh, **4b** Ar=4-MePh, **4c** Ar=Ph, **4d** Ar=2-naphthyl

**Figure 1** X-ray structure of **4a**

OH groups of **2** were protected by acetone and TsOH to obtain **3** (yield: 65%; mp: 68-69°C,  $[\alpha]_D^{25} = -123.3$  (c, 0.96, H<sub>2</sub>O))<sup>4</sup>. The reaction of **3** with an excess of varies of aromatic Grignard reagents to give **4a-4c** in high yield (95%-96.5%), except **4d** in 60%. The low yield of **4d** is probably due to the bulky structure of 2-bromonaphthalene.

The *cis* configuration of **4a** (4R, 5R) was confirmed by X-ray analysis (**Figure 1**)<sup>5</sup>. The investigation of these ligands used in the addition of diethylzinc to aldehydes and the ring opening of cyclic meso-anhydrides is under way.

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### References and notes

1. D. Seebach, A. K. Beck, Y. M. Wang, *Tetrahedron*, **1994**, *50*, 4363.
2. T. A. Engler, M. A. Letavic, *et al.*, *J. Am. Chem. Soc.*, **1991**, *113*, 5068.
3. D. Seebach, R. Dahinden, *et al.*, *J. Org. Chem.*, **1995**, *60*, 1788.
4. N. Cohen, B. L. Banner, A. J. Laurenzano, L. Carozza, *Org. Syn. Collect. Vol. VII*, 297.
5. Crystallographic parameters and the spectral date of 4a-4d have been deposited in the

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