Accepted Manuscript

Title: Chromium-catalyzed asymmetric synthesis of 1, 3-diols

Authors: Hong-Tao Ji, Qing-Shan Tian, Jian-Nan Xiang, Guo-Zhu Zhang

PII: S1001-8417(17)30095-5
DOI: http://dx.doi.org/doi:10.1016/j.cclet.2017.03.016
Reference: CCLET 4011

To appear in: *Chinese Chemical Letters*

Received date: 18-1-2017
Revised date: 8-3-2017
Accepted date: 9-3-2017

Please cite this article as: Hong-Tao Ji, Qing-Shan Tian, Jian-Nan Xiang, Guo-Zhu Zhang, Chromium-catalyzed asymmetric synthesis of 1, 3-diols, Chinese Chemical Lettershttp://dx.doi.org/10.1016/j.cclet.2017.03.016

Original article

Chromium-catalyzed asymmetric synthesis of 1, 3-diols

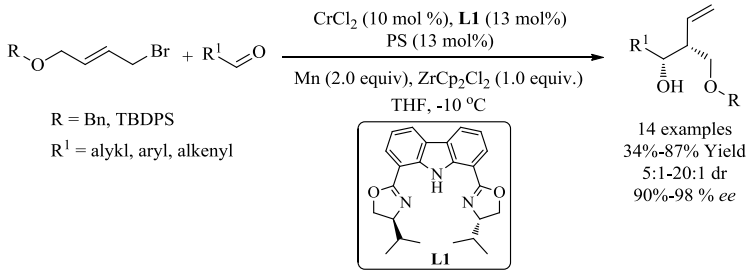
Hong-Tao Ji[a], Qing-Shan Tian[b], Jian-Nan Xiang[a*], Guo-Zhu Zhang*[b]

[a] *College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China*

[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

* Corresponding authors.
E-mail addresses: jnxiang@hnu.edu.cn (J.-N. Xiang); guozhuzhang@sioc.ac.cn (G.-Z. Zhang)

Graphical abstract



An efficient, chromium-catalyzed highly enantioselective preparation of protected 1, 3-diols has been achieved. In the presence of a chiral chromium catalyst using the carbazole-based bisoxazoline as the chiral ligand, a variety of optically pure 1,3-diols were synthesized in 34%-87% yields with up to 98% *ee*. The benzyl as well as silyl ethers were suitable substitutions for the hydroxyl group. Meanwhile, aromatic, aliphatic and *α, β*-unsaturated aldehydes are well tolerated under the mild reaction conditions.

ABSTRACT

An efficient, chromium-catalyzed highly enantioselective preparation of protected 1, 3-diols has been achieved. In the presence of a chiral chromium catalyst using the carbazole-based bisoxazoline as the chiral ligand, a variety of optically pure 1,3-diols were synthesized in 34%-87% yields with up to 98% *ee*. The benzyl as well as silyl ethers were suitable substitutions for the hydroxyl group. Meanwhile, aromatic, aliphatic and α, β-unsaturated aldehydes are well tolerated under the mild reaction conditions.

Keywords:
1,3-Diol
Asymmetric
Chromium-catalyzed
Allylation
Bisoxazoline

1. Introduction

The 1, 3-diol is a basic framework found in numerous natural products and organic materials (Fig. 1) [1-5]. It is also an important kind of synthetic intermediates that exist in a wide range of organic transformations. Therefore, 1, 3-diol subunits have been employed as the valuable building block for the synthesis of various natural products and biologically active compounds [6-11]. Quite a few synthetic methods have been developed to construct the 1, 3-diol core skeleton [12]. Recently, transition-metal-catalyzed reactions (Pd, In and $SnCl_2$) were applied to the preparation of 1, 3-diol derivatives from various starting substrates (such as 2-butene-1, 4-diol carboxylates or vinyl epoxides) [12a, 12b, 12c]. Among these transition-metals, the chromium-catalyzed protocols are attractive