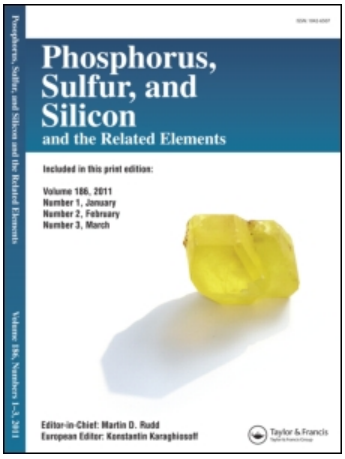

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Enantiomericaly Pure α-Substituted Cyanohydrins Derived from Benzaldehyde

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INTRODUCTION

Optically pure cyanohydrins are interesting chiral templates. Thus, their synthesis have been a goal for many authors,[1] who have obtained very good results in the case of just starting from aldehydes. The sulfinyl group showed a high efficiency to control the stereoselective hydrocyanation on β-ketosulfoxides.[2] More recently, it has also evidenced its ability to achieve remote control of stereoselectivity.[3] This was nicely explored by Toru in different nucleophilic additions to 2-*p*-tolylsulfinyl benzaldehyde,[4] although its hydrocyanation has never been considered.

RESULTS

We herein report on our results dealing with the hydrocyanation of (*S*)-2-*p*-tolylsulfinylbenzaldehyde (**1**) with Et_2AlCN and R_3SiCN under different conditions. The stereoselectivity was excellent (de > 98%) when the reactions were conducted in the presence of Lewis acids such as $Yb(OTf)_3$ or $Y(OTf)_3$. The observed diastereoselectivity is a consequence of the attack on the most stable conformer of a $Y(OTf)_3$ chelate involving aldehyde and sulfoxide coordination, as shown by calculation at DFT level. The two reactive faces of such a conformer are highly differentiated from a steric point of view (Scheme 1).

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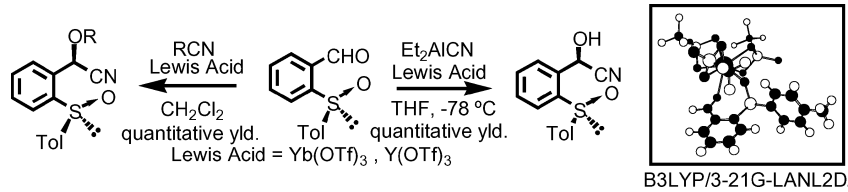
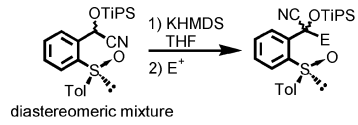


SCHEME 1

The remote stereocontrol of the sulfinyl group has also proved to be efficient in the reactions of the silylated cyanohydrins in the presence of bases and different electrophiles.[5] The use of KHMDS in THF afforded the best results on the OTIPS derivatives (Scheme 2).



E^+	d.r.	E^+	d.r.
$ClCO_2Me$	100:0	ROTf (R=Me, Et)	70:30
ClCOMe	100:0	$PhCH_2Br$	70:30
$CH_2{=}N^+Me_2\ I^-$	100:0	$CH_2{=}CHCH_2Br$	85:15

SCHEME 2

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