SYNFACTS

Highlights in Current
Synthetic Organic
Chemistry

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Thieme

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

aldol reaction

enolates

tin

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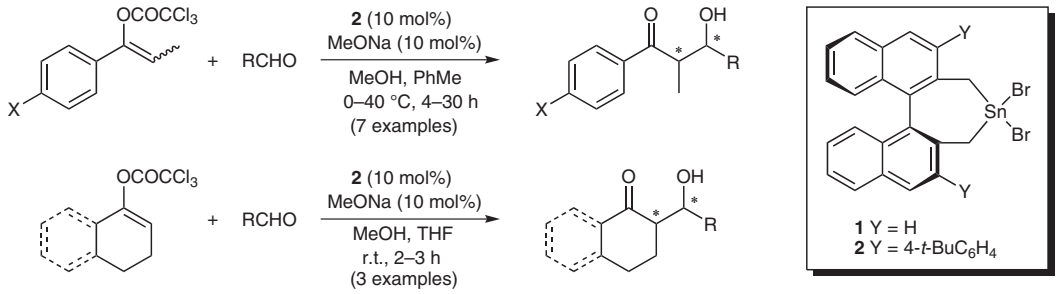
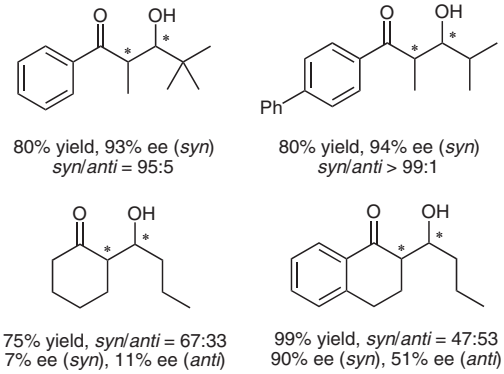
Methanol-Assisted Catalysis by Chiral Tin Methoxides: An Alternative Asymmetric Aldol Process
Chem. Eur. J. **2009**, *15*, 11450-11453.

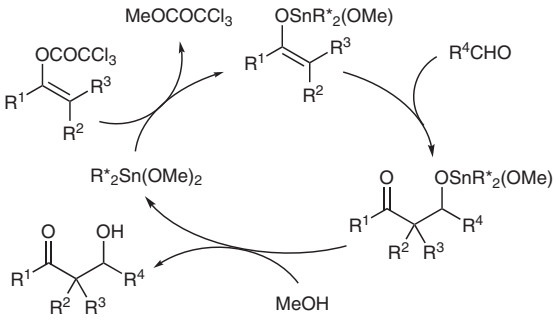
Aldol Process Catalyzed by Chiral Tin Methoxides



Selected examples:



Plausible catalytic cycle:



Significance: The importance of the catalytic asymmetric aldol reaction can hardly be overestimated. Among numerous existing methods there are, however, few examples of enantioselective aldol reaction proceeding via a chiral metal enolate. The authors previously found that $Bu_2Sn(OMe)_2$ catalyzes the reaction between alkenyl trichloroacetates and aldehydes in the presence of methanol. In this paper they expand this methodology to a chiral version using chiral tin methoxide formed in situ from dibromide **2**. The use of 10 mol% of catalyst furnished a number of acyclic products with yields of 41–80% and high enantioselectivities (88–99%). The diastereoselectivity ranged from 85:15 to >99:1. A number of cyclic substrates were also employed with moderate success.

Comment: The authors first attempted to test BINOL derivative **1** in an aldol reaction. The isolation of the corresponding dimethoxide failed due to its low stability. The in situ formed mono-methoxy derivative demonstrated some catalytic activity; however, both yield and enantioselectivity were low. As 3,3′-substituents were shown to be important for a high enantiocontrol in the aldol reaction, compound **2** was synthesized which showed superior results. Generally, despite the high stereocontrol levels, the toxic nature of organotin compounds decreases the competitiveness of the developed method.

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