SYNFACTS

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Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

tin

enantioselective *N*-nitroso aldol reaction

δ-lactones

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Catalytic Enantioselective *N*-Nitroso Aldol Reaction of γ,δ-Unsaturated δ-Lactones
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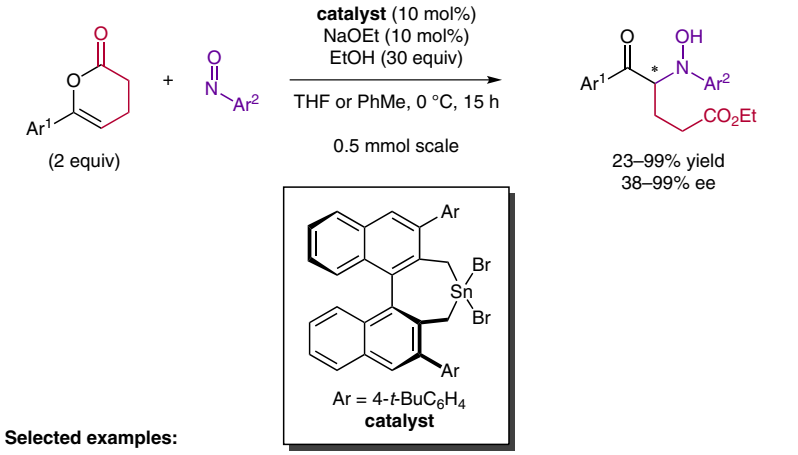
Chiral Tin Dibromide Catalyzed Enantioselective *N*-Nitroso Aldol Reaction



Significance: A tin dibromide catalyzed enantioselective *N*-nitroso aldol reaction is reported. While organocatalysis and Lewis acid catalysis have been employed in asymmetric variants of this reaction, the reported method confers stereoinduction via a chiral metal enolate intermediate. Good yields and high ee values were generally achieved.

Comment: The developed method is selective for the *N*-nitroso aldol, whereas the competing *O*-nitroso aldol reactivity has also been reported in literature. The active catalyst in the reaction is the tin alkoxide species, which catalyzes the opening of the γ,δ-unsaturated δ-lactones to generate chiral tin enolates. The reaction can also give tertiary hydroxylamine **2** with high yield and ee. However, steric bulk *ortho* to the nitroso group is required to afford efficient reactions and selectivity. Changing the ring size to the five-membered β,γ-unsaturated γ-butyrolactone also conferred reactivity, albeit with decreased yield and ee.

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