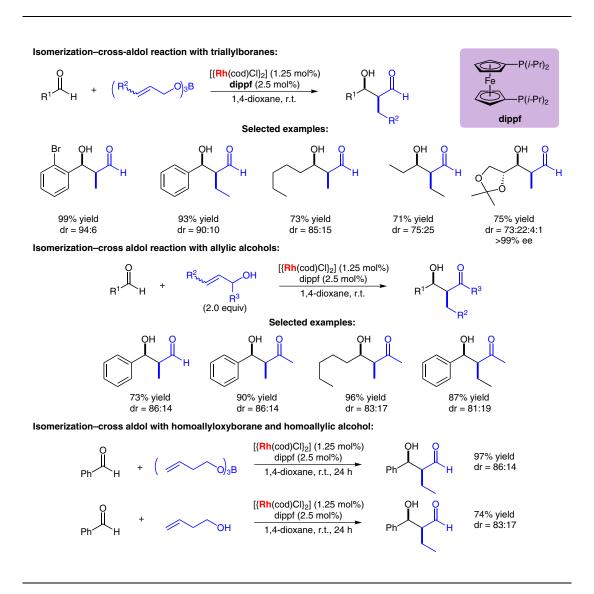
L. LIN, K. YAMAMOTO, S. MATSUNAGA,* M. KANAI* (THE UNIVERSITY OF TOKYO AND ERATO JAPAN SCIENCE AND TECHNOLOGY AGENCY, TOKYO, JAPAN) Rhodium-Catalyzed Cross-Aldol Reaction: In Situ Aldehyde-Enolate Formation from Allyloxyboranes and Primary Allylic Alcohols

Angew. Chem. Int. Ed. 2012, 51, 10275-10279.

In Situ Aldehyde Enolate Formation by Rhodium-Catalyzed Isomerization



Significance: Aldol reactions in which the aldol donor is derived from an aldehyde, are particularly challenging. This report describes a strategy in which aldehyde enolates are generated in situ by rhodium-catalyzed isomerization of triallylborox-anes. High *syn*-selectivity is obtained for a variety of aldehyde-donor and -acceptor partners.

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Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

rhodium

aldol reaction

aldehydes

allylic alcohols

allyloxyboranes

Comment: Remarkably, the use of triallyloxyboranes is not required; simple primary and secondary allylic alcohols also undergo the isomerization– cross-aldol sequence with similar levels of reactivity and selectivity, presumably through a rhodiumenolate or -enol mechanism.