Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

copper dialkylzinc conjugate addition M. MAGREZ-CHIQUET, M. S. T. MORIN, J. WENCEL-DELORD, S. D. AMRAOUI, O. BASLÉ, A. ALEXAKIS, C. CRÉVISY,* M. MAUDUIT* (ECOLE NATIONALE SUPÉRIEURE DE CHIMIE DE RENNES, FRANCE AND UNIVERSITÉ DE GENÈVE, SWITZERLAND)

Enantioselective 1,6-Conjugate Addition of Dialkylzinc Reagents to Acyclic Dienones Catalyzed by Cu-DiPPAM Complex–Extension to Asymmetric Sequential 1,6/1,4-Conjugate Addition *Chem. Eur. J.* **2013**, *19*, 13663–13667.

Cu-Catalyzed Asymmetric 1,6-Conjugate Addition of Dialkylzinc

$$\begin{array}{c} \text{Cu(OTf)}_2 \text{ (5 mol\%)} \\ \text{MeTHF-cyclohexane} \\ \text{R}_1 \\ \text{MeTHF-cyclohexane} \\ \text{R}_2 \\ \text{MeTHF-cyclohexane} \\ \text{R}_3 \\ \text{MeTHF-cyclohexane} \\ \text{R}_4 \\ \text{MeTHF-cyclohexane} \\ \text{R}_4 \\ \text{R}_4$$

Significance: The authors reported the asymmetric 1,6-conjugate addition of dialkylzinc to acyclic dienones catalyzed by copper/phosphinoazomethinylate salt (DiPPAM). After the isomerization of the conjugate adducts, stereoselective sequential 1,4-conjugate addition of diethylzinc was also demonstrated.

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Comment: The control of regioselectivity of the 1,6-conjugate addition is difficult due to many parameters. Using copper and the DiPPAM ligand, a highly enantio- and regioselective 1,6-conjugate addition was achieved. With the BINAP ligand, unprecedented highly stereoselective induction is noteworthy.