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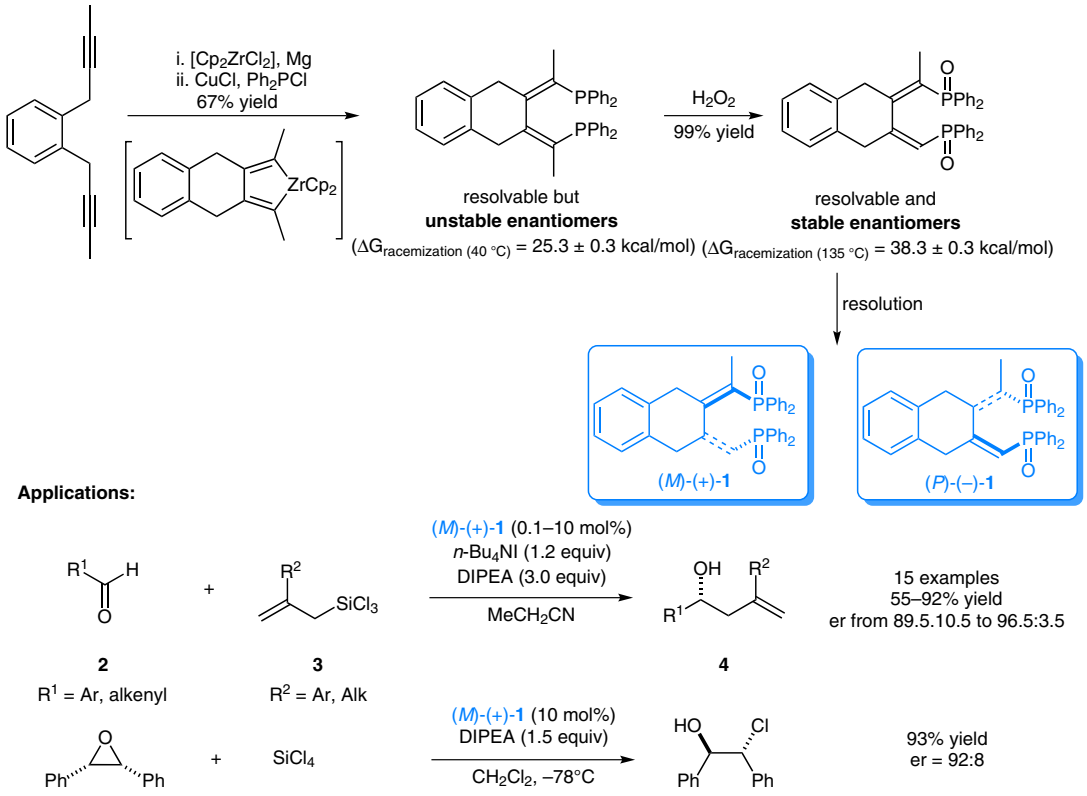
Atropisomeric Chiral Dienes in Asymmetric Catalysis: C_2-Symmetric (*Z*,*Z*)-2,3-Bis[1-(diphenylphosphynyl)-ethylidene]tetralin as a Highly Active Lewis Base Organocatalyst
Angew. Chem. Int. Ed. **2013**, DOI: 10.1002/anie.201308112.

Novel Atropisomeric Chiral Dienes in Lewis Base Organocatalysis



Significance: The authors report a novel tetraline-based, atropisomeric, and configurationally stable chiral diene catalyst **1**, which was successfully employed in the Lewis base catalyzed allylation of aldehydes **2** with trichlorosilanes **3** (see Review below). Products **4** were isolated in moderate to excellent yields and in good to excellent enantiomeric ratios. Catalyst **1** also proved to be effective in a single example of enantioselective ring opening of a *meso*-epoxide to afford a 1,2-chlorohydrin.

Review: S. E. Denmark, J. Fu *Chem. Rev.* **2003**, *103*, 2763–2794.

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Comment: Chiral atropisomeric biaryl scaffolds have been well studied and extensively applied in asymmetric catalysis. Yet, atropisomeric conjugated dienes have found limited application in asymmetric synthesis due to their low racemization-energy barrier. The authors avoid this major drawback by designing a catalyst bearing an extended conjugated system involving a diene and two phosphinoxide moieties, thus generating a stable conjugated helical system. Catalyst **1** proved to be configurationally stable even for prolonged periods (24 h) at high temperatures (135 °C). Its potential is well described by the reported allylation reaction as well as the promising results obtained in the ring opening of *meso*-epoxides with silicon tetrachloride.

Category
Organo- and Biocatalysis

Key words
atropisomerism
chiral dienes
Lewis base catalysis
aldehyde allylation