

# Asymmetric Protonation in Dienamine-Catalysis

Category

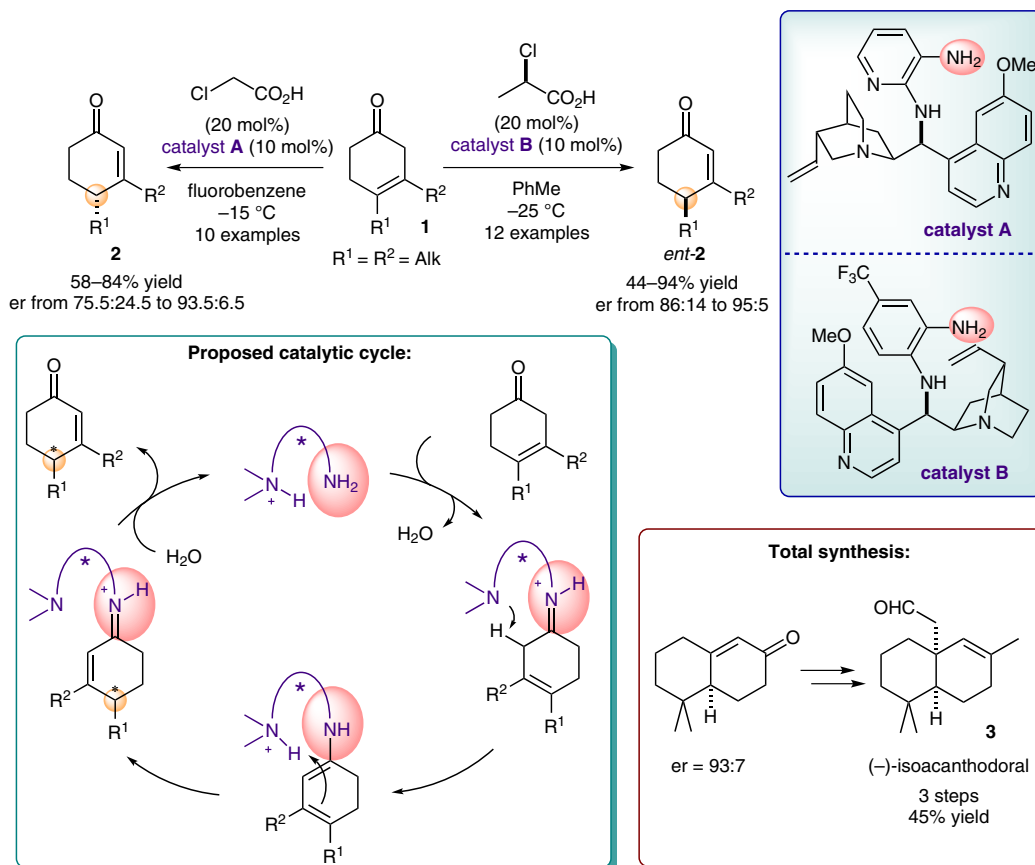
Organo- and Biocatalysis

Key words

double bond isomerization

bifunctional catalysts

total synthesis



**Significance:** The Deng group reports the catalytic enantioselective isomerization of  $\beta,\gamma$ -unsaturated cyclohex-3-en-1-ones **1** to the corresponding chiral  $\alpha,\beta$ -unsaturated cyclic enones **2**. The authors designed a new class of cinchona alkaloid-derived catalysts bearing substituted anilines as tunable handles. In particular, combining the newly synthesized catalysts **A** and **B** with carboxylic acid co-catalysts, they developed two different systems to achieve the synthesis of the two enantiomers of the desired products.

**Comment:** During the last few years interest has grown towards asymmetric primary amine catalyzed  $\gamma$ -functionalization of enones via dienamine intermediates. These methodologies mainly rely on the remote control of the stereochemistry achievable with the cinchona-alkaloid skeletons. Herein, the authors tackle the challenge of asymmetric  $\gamma$ -protonation and report the development of new bifunctional catalysts, which allow such transformations. Moreover, the usefulness of the process is highlighted by the first asymmetric total synthesis of the marine sesquiterpenoid isoacanthodoral (**3**).