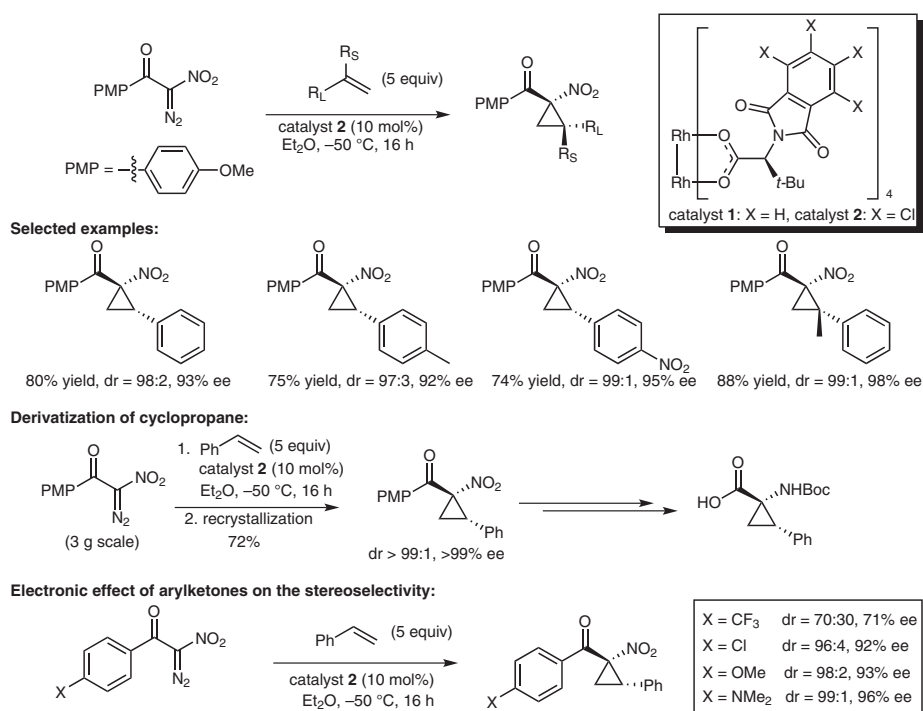


V. N. G. LINDSAY, W. LIN, A. B. CHARETTE* (UNIVERSITÉ DE MONTRÉAL, CANADA)
Experimental Evidence for the All-Up Reactive Conformation of Chiral Rhodium(II) Carboxylate Catalysts:
Enantioselective Synthesis of *cis*-Cyclopropane α -Amino Acids
J. Am. Chem. Soc. **2009**, *131*, 16383-16385.

Asymmetric Synthesis of *cis*-Cyclopropane α -Amino Acids by Rhodium(II) Carboxylate



Significance: The authors reported the first catalytic enantioselective cyclopropanation of alkenes with α -nitro diazoacetophenones leading to the corresponding cyclopropanes in good to high yields and excellent diastereo- and enantioselectivities. All experimental results suggested that the halogenated rhodium carboxylate catalysts used in this process react through an all-up conformation, which is responsible for the high stereoselectivity. Also, this suggestion is consistent with DFT calculations made on non-halogenated analogues (A. DeAngelis, O. Dmitrenko, G. P. Yap, J. M. Fox *J. Am. Chem. Soc.* **2009**, *131*, 7230).

Comment: Although chiral rhodium(I) carboxylate catalysts have found widespread use in asymmetric propanation (see Review below), little evidence is known on how the chirality is projected near the metal center by the chiral carboxylate ligands. The authors suggested that rigid all-up conformation from halogen bonding interaction would be responsible for higher enantioselectivity. From experiments for electronic effects of arylketones on stereoselectivity, they also suggested that the π -stacking between tetrachlorophthaloyl moieties from all-up conformation and the aryl ketone group on the substrate might be a key element in the enantiodiscriminating step of the reaction.

Review: H. Lebel, J.-F. Marcoux, C. Molinaro, A. B. Charette *Chem. Rev.* **2003**, *103*, 977-1050.

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