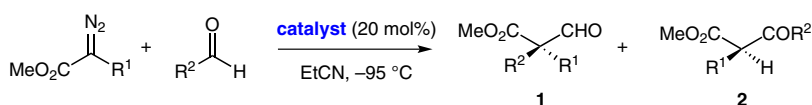
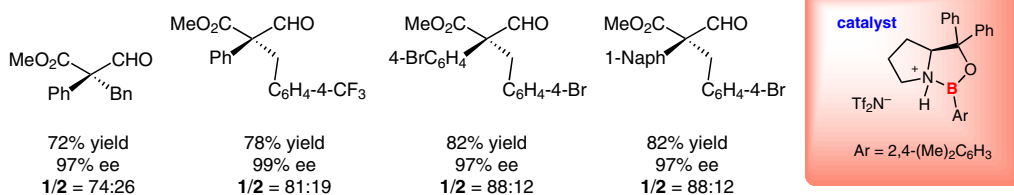


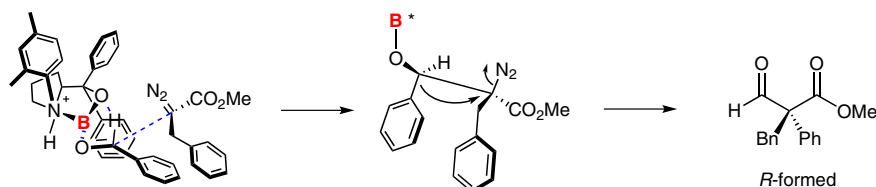
Asymmetric Formal Insertion of Diazo Esters into Aryl-CHO Bonds



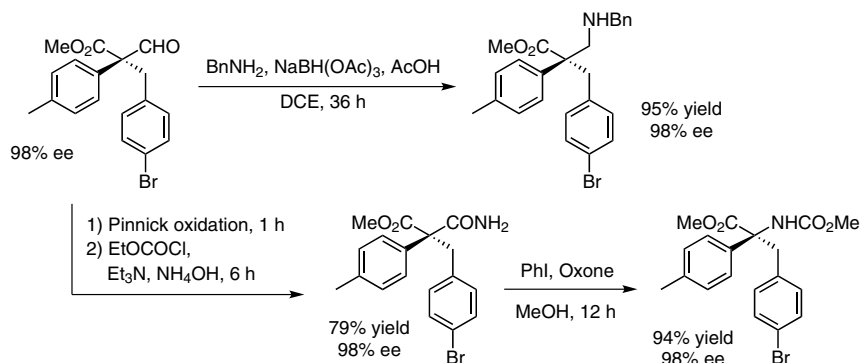
Selected examples:



Transition-state model:



Applications:



Significance: The authors developed an oxazaborolidinium ion catalyzed asymmetric formal C–C bond insertion of diazo esters into aryl-CHO bonds to give functionalized acyclic all-carbon α -quaternary aldehydes in good yields (up to 83%) and excellent enantioselectivities (up to 99%). The products were transformed into synthetically useful α - and β -amino esters with ease.

Comment: Contrary to the Roskamp reaction, the 1,2-aryl shift is preferred over the 1,2-hydride shift. It is the first catalytic asymmetric report of such a reaction. A variety of diazo esters and aldehydes were explored emphasizing synthetic flexibility. However, the regioselectivities are rather moderate (up to 88:12). Recently, Feng and co-workers reported a similar 1,2-aryl shift for the asymmetric homologation of α -keto esters (*Angew. Chem. Int. Ed.* **2013**, *52*, 10883).