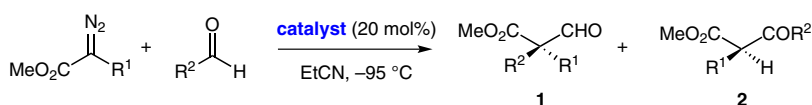
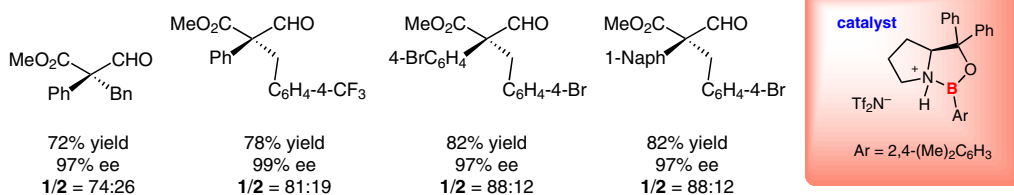


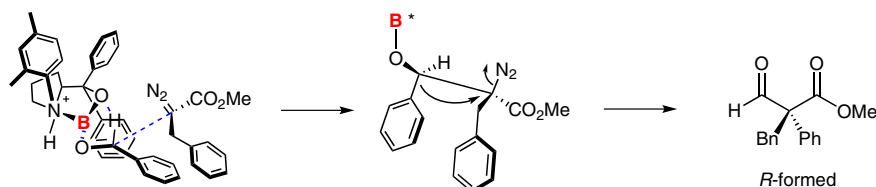
# Asymmetric Formal Insertion of Diazo Esters into Aryl-CHO Bonds



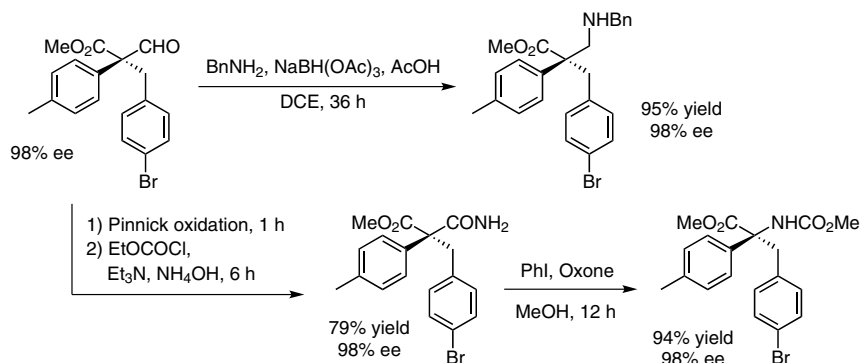
## Selected examples:



## 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  $\alpha$ -quaternary aldehydes in good yields (up to 83%) and excellent enantioselectivities (up to 99%). The products were transformed into synthetically useful  $\alpha$ - and  $\beta$ -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  $\alpha$ -keto esters (*Angew. Chem. Int. Ed.* **2013**, *52*, 10883).