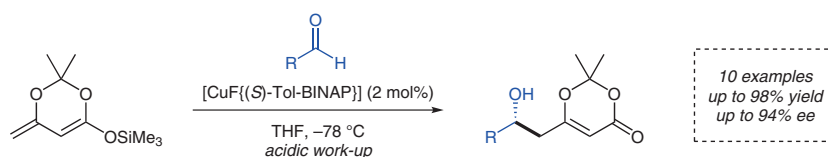
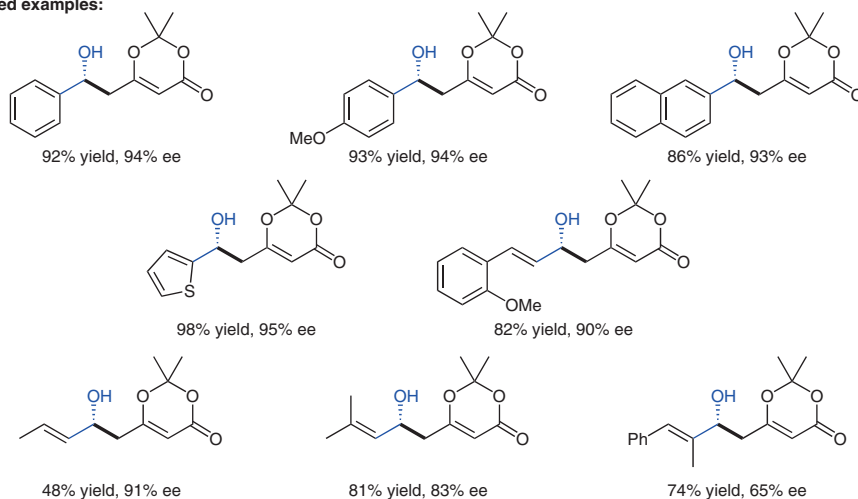


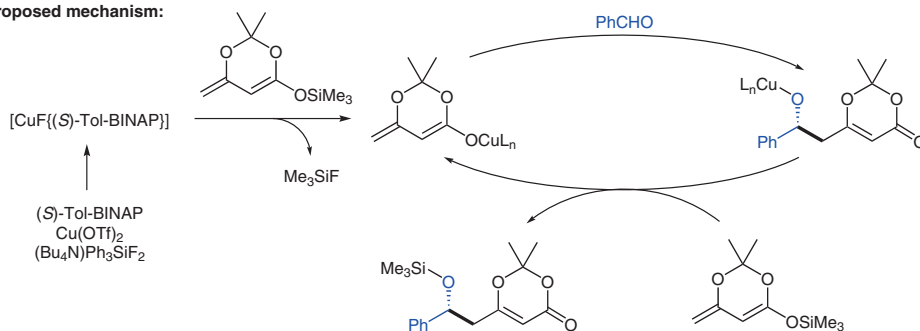
Copper-Catalyzed Enantioselective Dienolate Additions to Aldehydes



Selected examples:



Proposed mechanism:



Significance: In 1998, Carreira and Krüger reported the asymmetric addition of silyl dienolates to aldehydes using a bisphosphanyl-Cu(II)fluoride complex, generated in situ from (*S*)-Tol-BINAP, Cu(OTf)₂, and (Bu₄N)Ph₃SiF₂. While using a 2 mol% catalyst loading, various α,β-unsaturated, (hetero-)aromatic, and aliphatic aldehydes could react with high enantioselectivity (up to 95% ee). This method serves as an alternative to asymmetric Mukaiyama aldol reactions traditionally involving the Lewis acid mediated addition of *O*-silyl enolates to aldehydes.

Comment: Follow-up experimental and spectroscopic studies were used to elucidate the mechanism. The authors proposed that following the in situ reduction of the Cu(II) complex to Cu(I), the catalyst reacts to generate an *O*-bound metallodienolate. Addition to the aldehyde generates the corresponding Cu-bound enolate, and subsequent silylation delivers the product and regenerates the metalloenolate.

Review: B. L. Pagenkopf, J. Krüger, A. Stojanovic, E. M. Carreira *Angew. Chem. Int. Ed.* **1998**, *37*, 3124–3126.