Asymmetric β-Hydroxylation of Enals Catalyzed by an N-Heterocyclic Carbene

**Significance:** White and Rovis report an asymmetric β-hydroxylation of alkyl and aryl enals via oxygen transfer from electron-deficient nitroarenes. The reaction is catalyzed by an N-heterocyclic carbene to furnish the corresponding β-hydroxy esters in moderate to good yields (up to 73%) and with good to excellent enantioselectivities (er up to 96:4).

**Comment:** N-Heterocyclic carbenes are powerful catalysts in organic synthesis, with applications in various transformations. In this report, the authors present a novel NHC-catalyzed reaction that proceeds by a radical pathway. A significantly reduced yield of product was observed when the reaction was conducted in the presence of a radical inhibitor. Investigations of the stereoselectivities of the reaction when using cis and trans enals further support the proposed radical mechanism.

**Proposed catalytic cycle:**

\[ \text{Proposed catalytic cycle} \]

\[ \text{A (10 mol%) NaOAc (1 equiv) CCl}_4-\text{MeOH (20:1) 23}^\circ \text{C, 12 h} \]

\[ \text{R}_1 = \text{Ar, Alk} \]

\[ \text{15 examples 20–73% yield er from 81.5:18.5 to 96:4} \]

\[ \text{R}_1 = \text{Ar, Alk} \]

\[ \text{R}_2 = \text{Ar} \]

\[ \text{N} \]

\[ \text{Bu} \]

\[ \text{OTBS} \]

\[ \text{BF}_4^- \]