Iron-Catalyzed Asymmetric OH Bond Insertions

**Significance:** The authors developed a highly efficient iron-catalyzed protocol for the enantioselective carbene OH insertion. The reaction produces various α-alkoxy and α-hydroxy arylacetates, which are quite useful synthetic intermediates, in very high yield and enantioselectivities.

**Comment:** This work features not only the high efficiency of iron-catalyzed carbene insertion to alcohol OH bonds, but also the insertion to a water OH bond to generate corresponding chiral α-hydroxy arylacetates in high yields and enantioselectivities. The results are better than the authors’ previous work with copper catalysts (Angew. Chem. Int. Ed. 2008, 47, 932).

**Selected applications:**

86% yield, 89% ee intermediate to various synthetic targets

92% yield, 95% ee intermediate to clopidogrel

86–95% yield, 89–99% ee

66–93% yield 76–95% ee

NaBArF = sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

**Key words:**
- spirobox ligands
- OH insertion
- α-diazophenylacetates
- iron

**Equations:**

\[
\begin{align*}
\text{Ph} = \text{Alk, Bn, allyl, etc.} \\
\text{R}^1 = \text{substituted Ph, Naph, thiophenyl, Me} \\
\text{R}^2 = \text{Me or Bn}
\end{align*}
\]