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Enantioselective Iron-Catalysed O-H Bond Insertions

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Iron-Catalyzed Asymmetric OH Bond Insertions

$$\begin{array}{c} N_2 \\ \text{Ph} \end{array} + \text{ROH} \begin{array}{c} \text{FeCl}_2\text{·}4H_2\text{O} \text{ (5 mol\%)} \\ \text{ligand A (6 mol\%)} \\ \text{NaBAr}_F^* \text{ (6 mol\%)} \\ \text{CHCl}_3, 40 \text{ °C} \end{array} \begin{array}{c} \text{OR} \\ \text{Ph} \end{array} \begin{array}{c} \text{OR} \\ \text{OMe} \end{array}$$

R = Alk, Bn, allyl, etc.

86-95% yield, 89-99% ee

R¹ = substituted Ph, Naph, thiophenyl, Me

 R^2 = Me or Bn

ligand A

ligand B

66-93% yield 76–95% ee

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

Selected applications:

Significance: The authors developed a highly efficient iron-catalyzed protocol for the enantioselective carbene OH insertion. The reaction produces various α -alkoxy and α -hydroxyl 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-hydroxyl 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).

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