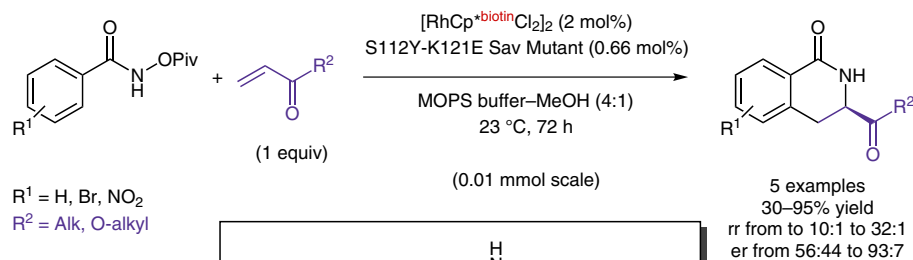
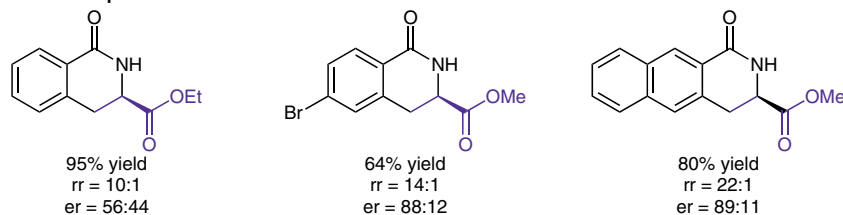


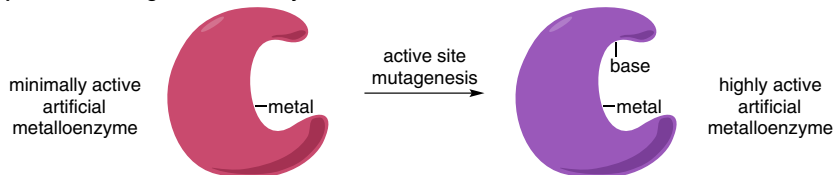
Artificial Rh(III)–Metalloenzyme-Catalyzed Asymmetric C–H Activation



Selected examples:



Streptavidin with engineered carboxylate mutation:



Significance: A highly active, artificial rhodium(III) metalloenzyme that catalyzes an asymmetric synthesis of dihydroisoquinolones through C–H activation is reported. A biotinylated rhodium(III) complex is successfully incorporated into streptavidin. With active-site mutagenesis, the engineered enzyme displayed up to 100-fold reaction rate increase compared to the activity of the unbound rhodium complex.

Comment: As Cp is the only permanently bound ligand on rhodium in the catalytic cycle, it has been difficult to render this reaction enantioselective until recently. This report provides an alternative solution for this problem. Based on the concerted metalation–deprotonation mechanism, the authors used docking modeling and introduced a basic carboxylate moiety in the active site. With kinetic isotope effect experiments, the importance of this mutation in accelerating the catalysis is demonstrated.