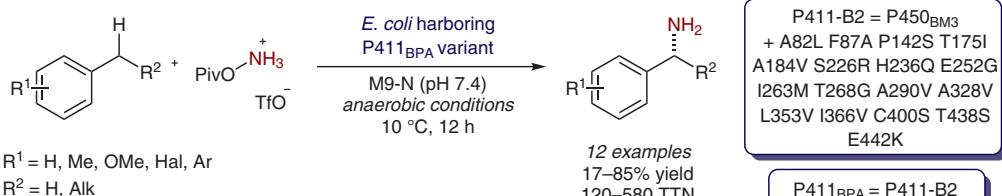
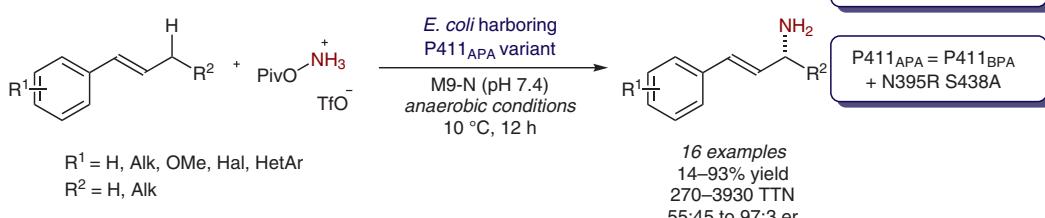


# Enzyme-Catalyzed Asymmetric Primary Amination of Benzylic and Allylic C(sp<sup>3</sup>)-H Bonds

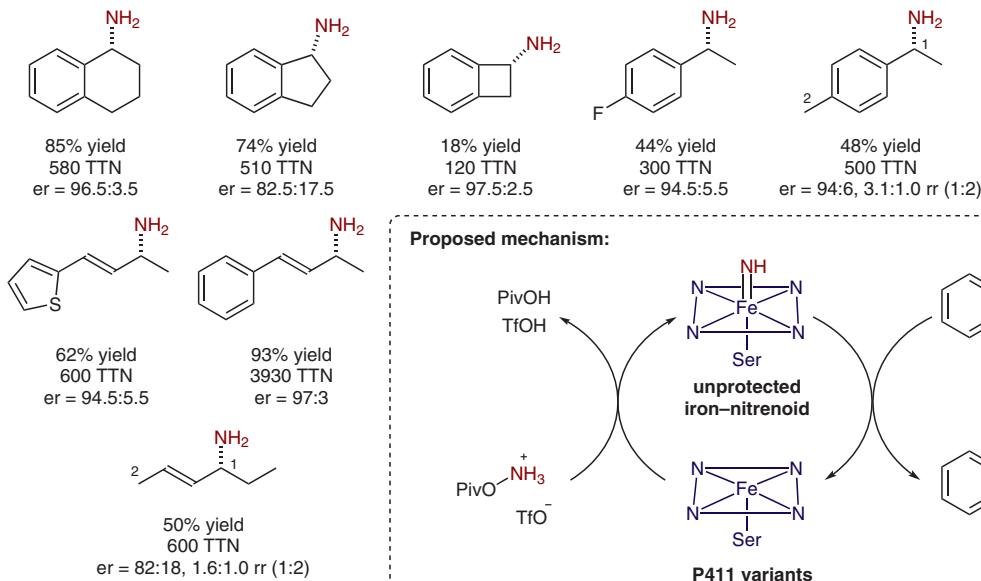
## Primary amination of benzylic C–H bonds:



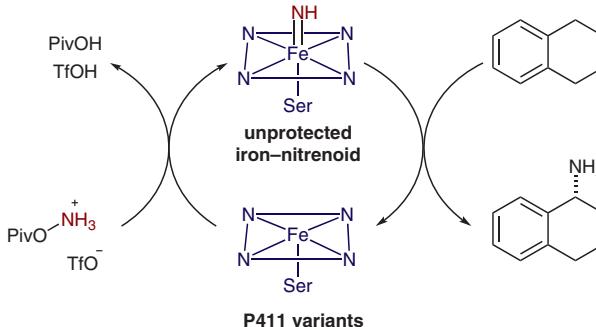
## Primary amination of allylic C–H bonds:



## Selected examples:



## Proposed mechanism:



**Significance:** The Arnold group reports the directed evolution of P411-B2 to give efficient benzylic (P411<sub>BPA</sub>) and allylic (P411<sub>APA</sub>) C–H aminases. By using hydroxylamine derivatives as nitrogen sources under anaerobic conditions, the authors converted a variety of benzylic and allylic C(sp<sup>3</sup>)-H bonds into primary amines in good yields with high chemo- and enantioselectivities and promising regioselectivities.

**Comment:** This work represents a milestone in the development of a general C–H amination reaction. Mechanistic investigations are highly desirable in further developing this method to overcome the limitation toward alkyl-substituted allyl systems. In addition, this work encourages and challenges other groups to develop small-molecule catalysts to enable this reaction.