

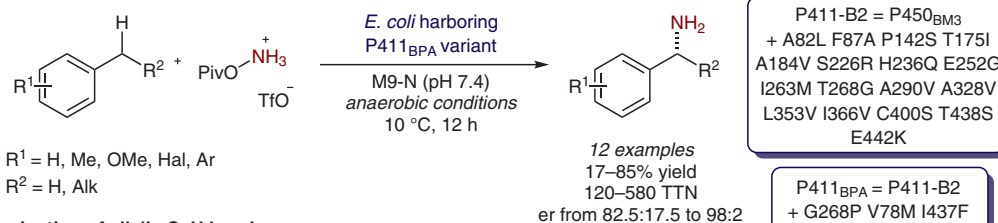
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Enzymatic Primary Amination of Benzylic and Allylic C(sp³)-H Bonds

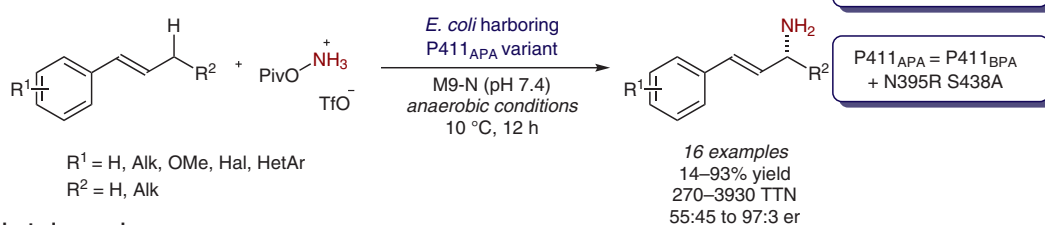
J. Am. Chem. Soc. **2020**, *142*, 10279–10283.

Enzyme-Catalyzed Asymmetric Primary Amination of Benzylic and Allylic C(sp³)-H Bonds

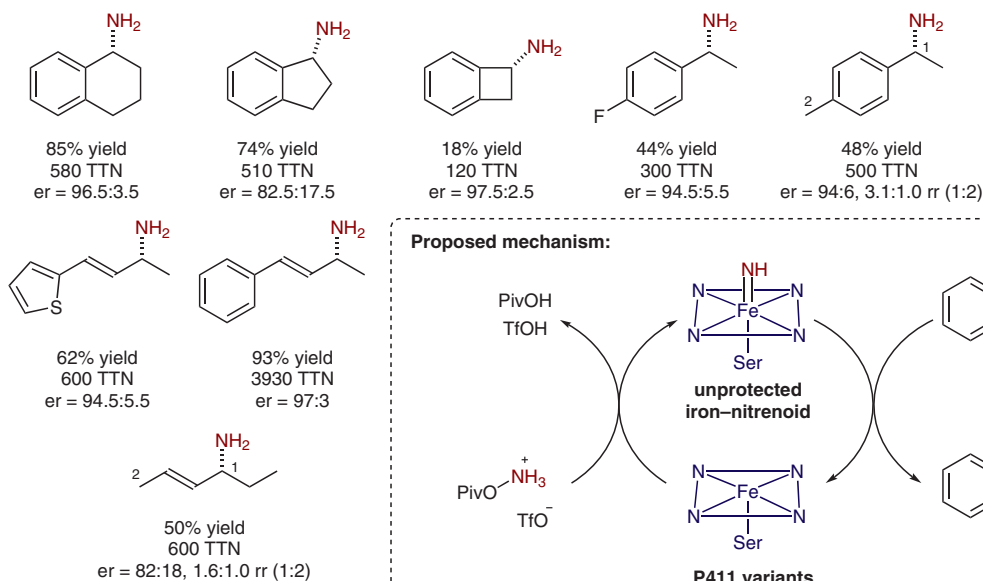
Primary amination of benzylic C-H bonds:



Primary amination of allylic C-H bonds:



Selected examples:



Significance: The Arnold group reports the directed evolution of P411-B2 to give efficient benzylic (P411_{BPA}) and allylic (P411_{APA}) C-H aminases. By using hydroxylamine derivatives as nitrogen sources under anaerobic conditions, the authors converted a variety of benzylic and allylic C(sp³)-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.

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Category

Organo- and Biocatalysis

Key words

amines

directed evolution

cytochrome P411 hydroxylamines

amination

C-H bond activation

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