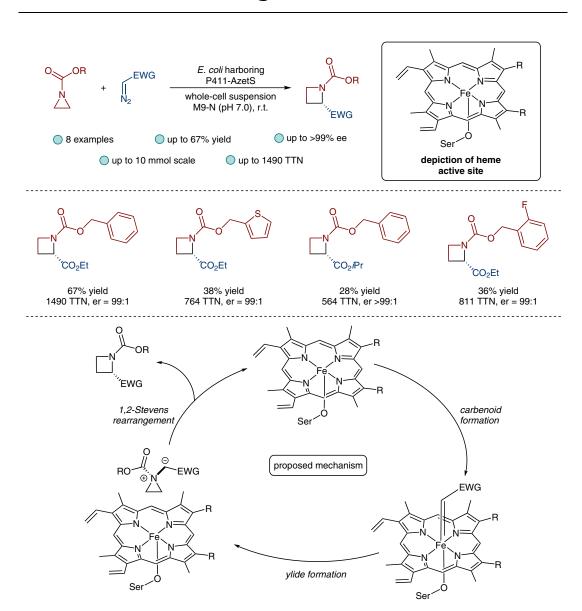
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Biocatalytic One-Carbon Ring Expansion of Aziridines to Azetidines via a Highly Enantioselective [1,2]-Stevens Rearrangement *J. Am. Chem. Soc.* **2022**, *144*, 4739–4745, DOI: 10.1021/jacs.2c00251.

Biocatalytic Enantioselective 1-Carbon Ring Expansion via 1,2-Stevens Rearrangement



Significance: The Arnold group reports an enantioselective biocatalytic one-carbon ring expansion of acylated aziridines to azetidines via a 1,2-Stevens rearrangement. The reaction was developed starting from hemoproteins, which have previously been demonstrated to enable the transfer of carbenoids in related reactions.

Comment: Directed evolution using iterative site-saturation mutagenesis (SSM) identified the azeti-dine synthase, P411-AzetS, as the optimal enzyme. The authors indicate that the solvent-caging effects of the active site influence enantioinduction and reactivity in this process, as free hemin is unsuccessful in catalyzing this reaction.

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