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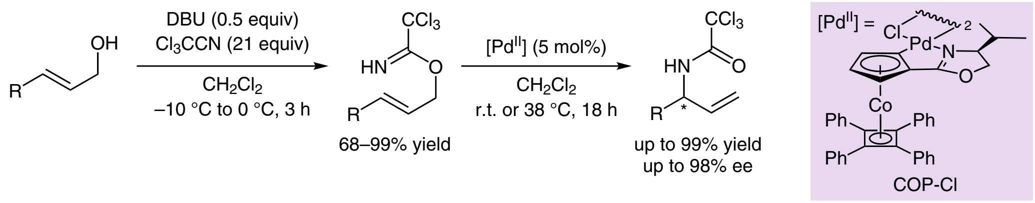
Catalytic Asymmetric Rearrangement of Allylic Trichloroacetamidates. A Practical Method for Preparing Allylic Amines and Congeners of High Enantiomeric Purity
J. Am. Chem. Soc. **2003**, *125*, 12412–12413, DOI: 10.1021/ja037086r.

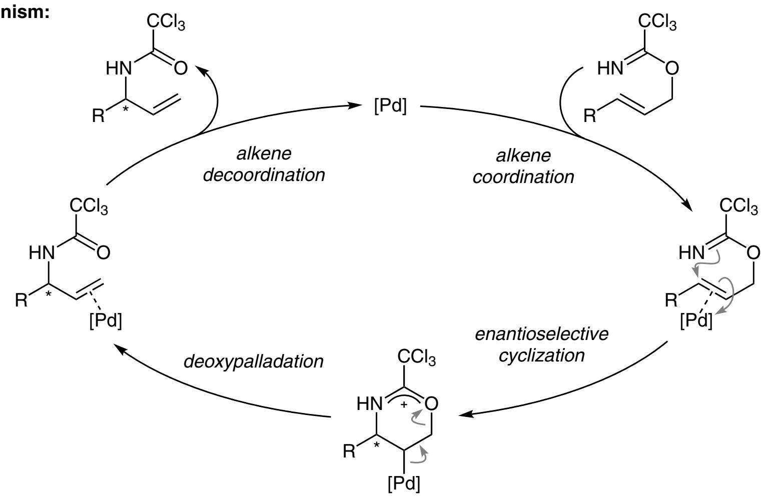
The Enantioselective Overman Rearrangement

Category
Metals in Synthesis

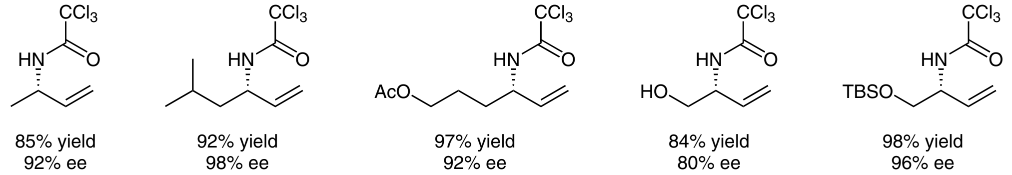
Key words
allylic alcohols
allylic amines
acetamidates
palladium catalysis
[3+3]-sigmatropic rearrangement



Proposed mechanism:



Selected examples:



Significance: Although first reported in 1974 (*J. Am. Chem. Soc.* **1974**, *96*, 597), an enantioselective variant of the Overman rearrangement remained challenging for the following decades. Competing elimination reactions, slow reaction rates, and low enantioselectivities were overcome by using the dimeric palladium catalyst COP-Cl. Starting from allylic alcohols, allylic amides are accessible in two steps with a formal [3+3]-sigmatropic rearrangement as the key step.

Comment: High enantioselectivities and yields were observed throughout. Only sterically demanding substituents and aryl groups revealed the limitation of this protocol. The potential of this method was further demonstrated by derivatization of the obtained allylic amides, e.g., providing unnatural amino acids in only a few steps. Aside from palladium, mercury-, platinum- and gold-based catalysts have also been disclosed (for a review, see: *Org. Biomol. Chem.* **2017**, *15*, 2672).

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