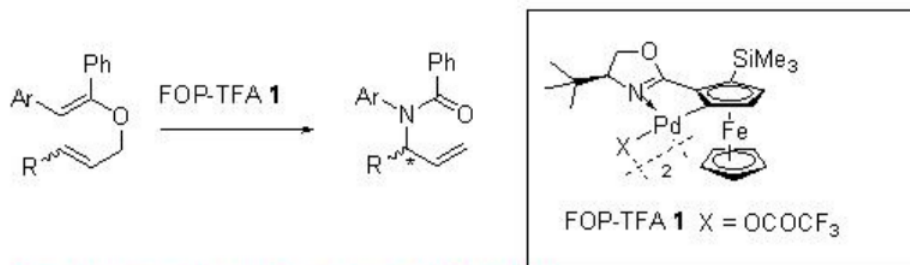


4.2: Aza-Claisen Rearrangement and Related Reactions

Aza-Claisen rearrangement, known as the Overman rearrangement, has been extensively studied that allows us to synthesize chiral allylic amines from achiral allylic imidates with excellent enantioselectivity. For example, prochiral *N*-arylbenzimidates can be converted into chiral *N*-arylbenzamides in the presence of ferrocenyloxazoline palladacycle, FOP-TFA, (Scheme 4.2.1).

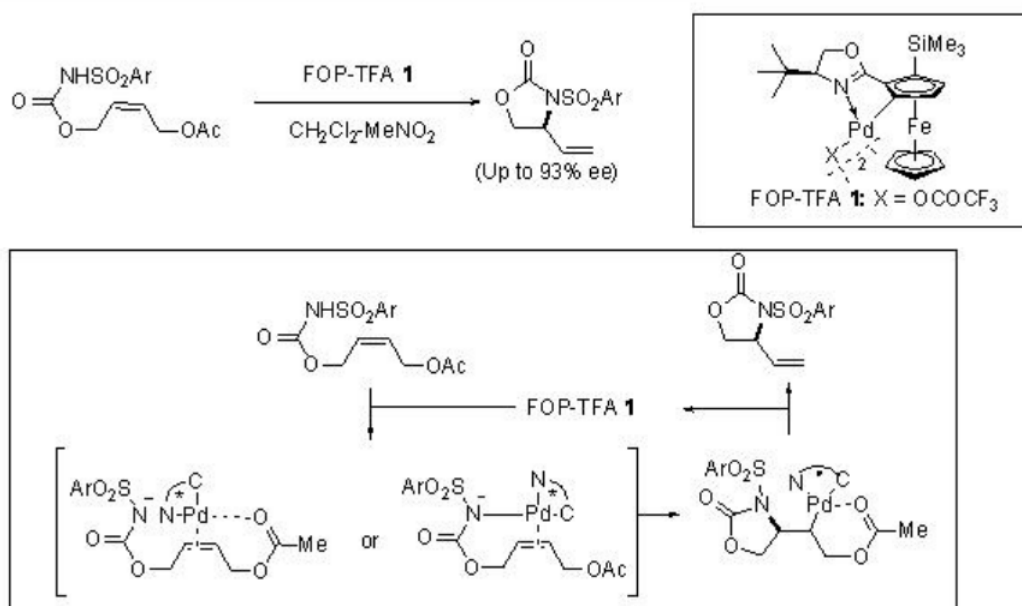


C. E. Anderson, et al., *J. Org. Chem.* **2005**, 70, 648.

Scheme 4.2.1

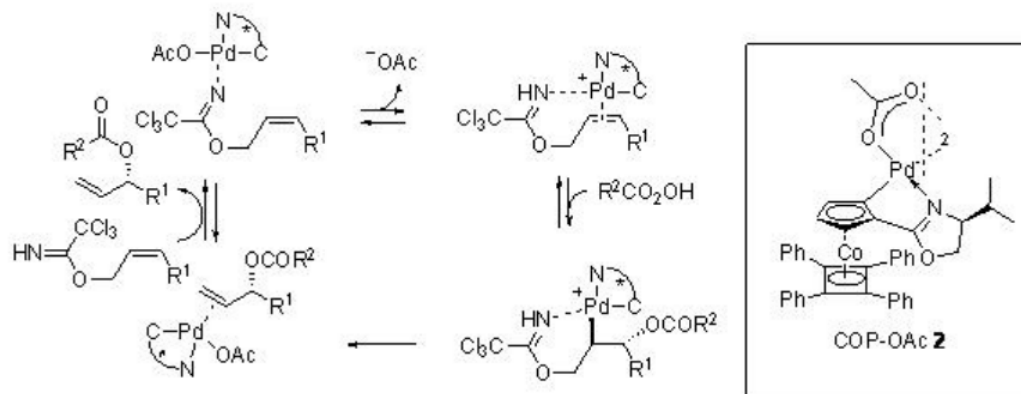
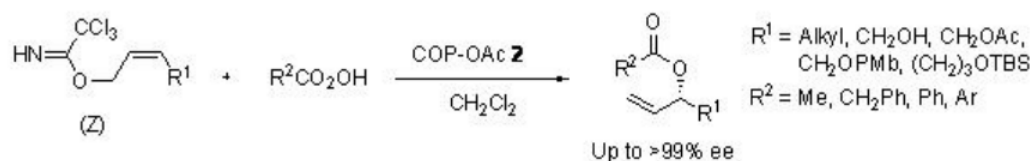
This catalytic system has also been shown to promote the cyclization of allylic *N*-arylsulfonyl carbamates to give five-membered nitrogen containing heterocycles (Scheme 2). An involvement of aminopalladation of the alkene followed by insertion of the alkene into the Pd-N has been proposed.

This procedure has also been extended for the allylic etherification reaction. For example, the reaction of (*Z*)-allylic trichloroacetimidates with carboxylic acids in the presence of COP-OAc **2** gives chiral allylic esters in high enantiopurity (Scheme 4.2.3). Under these reaction conditions, *E*-stereoisomer show inferior results. In these reactions, the COP-OAc activates the carbon-carbon double bond for attack by external oxygen nucleophile and the trichloroacetimidate group serves as a leaving group along with templating the catalyst to the double bond.



L. E. Overman, T. P. Remarchuk, *J. Am. Chem. Soc.* **2002**, 124, 12.

Scheme 4.2.2



S. F. Kirsch, L. E. Overman, *J. Am. Chem. Soc.* **2005**, 127, 2866.

Scheme 4.2.3

This page titled [4.2: Aza-Claisen Rearrangement and Related Reactions](#) is shared under a [CC BY-SA](#) license and was authored, remixed, and/or curated by [Tharmalingam Punniyamurthy](#) (National Programme on Technology Enhanced Learning (NPTEL)) .