## **Rhodium-Catalyzed Chemo- and Stereoselective Amide Bond Formation**

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Transition metal-catalyzed dehydrogenative coupling of alcohols and aldehydes with amines is a promising alternative to traditional amidation methods, which require expensive coupling reagents and generate significant quantities of waste. Herein, we report a general and mild one-pot isomerization/amidation of allylic alcohols (X=OH) using acetone or styrene as the hydrogen acceptor. The conditions are general, affording good to excellent yields with a wide array of amine and aniline nucleophiles. Further, the reactions are chemoselective as other alcohols, including aliphatic, homoallylic, and benzylic, do not undergo amidation. Utilization of biphasic conditions is critical, as they promote the equilibrium between the imine/enamine byproducts and the hemiaminal, which can undergo oxidation to the amide.

Current work is focusing on developing the asymmetric variant of this methodology - a general synthetic route to  $\beta$ -chiral amides. This is be achieved by using prochiral allylic diethyl amine as the substrate (X=NR<sub>2</sub>), which undergoes an asymmetric hydride shift followed by amine exchange and oxidation using water as the oxygen source.

$$\begin{array}{c} R^{2} X & \underbrace{\text{cat. [Rh]}}_{R^{1}} & \underbrace{R^{2} X}_{R-\text{BINAP}} & \begin{bmatrix} R^{2} X \\ R^{1} & \end{bmatrix} + \underbrace{HN}_{R^{3}}^{R^{4}} & \underbrace{\text{cat. [Rh]}}_{R-\text{BINAP}} & R^{1} & \underbrace{N}_{R^{3}}^{R^{2}} & \underbrace{R^{2} O}_{R^{3}} \\ X=OH, NR_{2} & H_{2}O & H_{$$