

## Rhodium-Catalyzed, Chemo- and Regioselective Markovnikov Hydroamination of Allylimines

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The incorporation of amines into organic frameworks in a step- and atom-economical fashion remains a challenge to synthetic chemists. Transition metal-mediated hydroamination, the addition of an N-H bond across a C=C bond, is one of the most attractive routes for the generation of C-N bonds, as it couples two easily accessible functionalities and does not generate any stoichiometric byproducts. Challenges with current catalytic methods include: regioselectivity, chemoselectivity, and the need for an excess of olefin due to the better coordinating ability of the amine nucleophile, which can shut down the catalyst.

Our approach to the regioselectivity problem is to employ substrates that have heteroatom groups that can bind to the catalyst, bringing the olefin near to the metal center. Upon the aminometallation, a metallacycle is generated, directing both the regioselectivity of the nucleophilic attack and helping to prevent  $\beta$ -hydride elimination yielding only the hydroaminated product (Scheme 1). Due to ease of synthesis and ability to generate a metallocyclopentane following the proposed mechanism, allylamine was condensed with a variety of aldehyde and ketone substrates to form the desired allylimines. The desired Markovnikov-substituted product was first discovered using the benzophenone-derived substrate. Upon further optimization of phosphine ligand, counteranion, solvent, time, temperature, concentration, and equivalents of morpholine (excess), calibrated GC yields were observed up to 98% yield (Scheme 2).

