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# TRANSFER HYDROAMINATION OF O-FORMYLATED HYDROXYLAMINES DERIVATIVES

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**Keywords:** Hydroamination; catalysis; synthetic methodology; hydroxylamines

**Summary:** C–N bond are present in many molecules from the pharmaceutical industry and the formation of this bond represents 35 % of all the reactions performed in this field.<sup>[1]</sup> Usually, they are formed by *N*-alkylation, cross-couplings, or reductive amination. Another type of reaction is presenting an important interest, the hydroamination<sup>[2]</sup> although overlooked. Indeed, despite being a powerful method to form C–N bonds, hydroamination is also limited by thermodynamic and kinetic effects such as a low difference of energy between reactants and products, or electrostatic repulsions. This reaction implies an amine<sup>[3]</sup>, and particularly an N–H bond which will be added across an unsaturated compound such as an alkene to form a C–N bond and a C–H bond with a perfect atom economy. Over the past years, *O*-acylated hydroxylamines<sup>[4]</sup> or azanyl esters<sup>[5]</sup> have also been used with alkenes and hydride donors to perform similar reactions.

We turned our interest toward developing a catalytic method to perform the hydroamination using *O*-formylated azanyl esters, without using hydride donor since the formate plays the role of a hydride donor. This reaction is, thus, a transfer hydroamination. Here, we use a linker, CO<sub>2</sub>, to make the nitrogen more electrophilic and the hydrogen more nucleophilic. The N–O bond is also weaker than a C–N bond, therefore, a catalyst can easily be inserted in that bond and the loss of CO<sub>2</sub> allows to drive the equilibrium. This methodology allows us to perform hydroamination with CO<sub>2</sub> as the only stoichiometric waste and to avoid the electrostatic repulsions between the lone pair of the nitrogen and π-orbitals of the alkene.

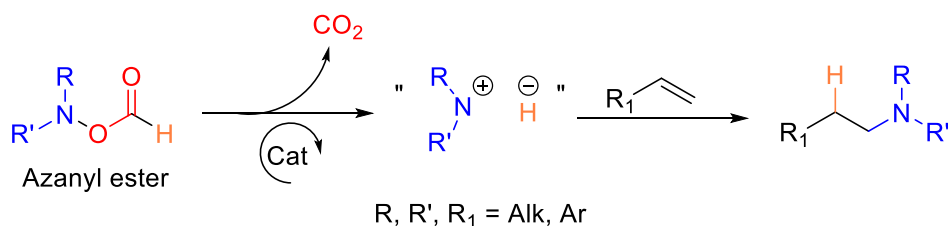


Fig. 1: Transfer hydroamination of azanyl esters

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