***Synthesis of Nitrogen-Containing Molecules using* *Inexpensive Reagents and Catalysts:* *Hydroaminations, Aminocarbonylations and Tethering Catalysis***

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Despite the ubiquity of bioactive nitrogen-containing molecules, amination reactions of electron-rich alkenes and alkynes remain underdeveloped and offer excellent potential for broader applicability in the synthesis of nitrogen heterocycles, amines and imines. Even if significant efforts have been invested in the development of metal-catalyzed transformations, metal-free amination strategies utilizing bifunctional reagents are emerging as useful alternatives. For example, our group has significantly extended the concerted, Cope-type hydroamination reactivity of hydroxylamines and hydrazine derivatives, enabling efficient intermolecular reactions and difficult cyclizations. More recently, our lab has developed amino- and imino-isocyanates to achieve alkene aminocarbonylation reactivity and synthesize beta-aminocarbonyl motifs under mild conditions. In efforts to achieve elusive intermolecular hydroamination reactions of alkenes, aldehyde-based organocatalysts were developed to in-situ form a temporary tether between hydroxylamines and allylic amines, thus enabling room temperature *directed* intermolecular amination reactivity and the stereocontrolled synthesis vicinal diamines. This system highlights the potential of simple catalysts operating via temporary intramolecularity. Further developments of aldehyde-catalysis will also be presented.

