

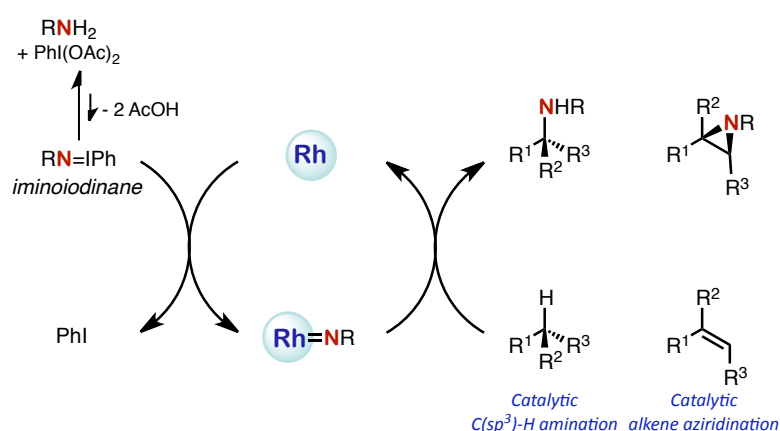


Catalyst-Controlled Selective Amination Reactions

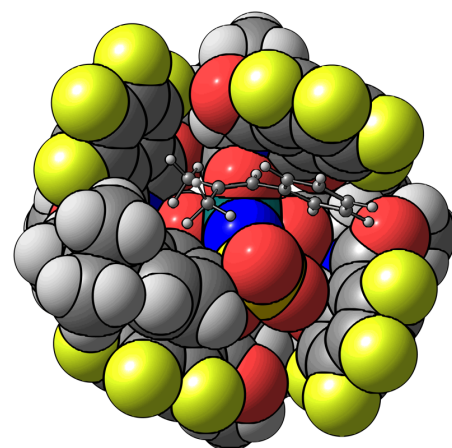
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The nitrogen atom is of prime importance in nature and life sciences. A recent study revealed that 84% of the FDA approved drugs contain at least one nitrogen atom.¹ The importance of nitrogen has translated into the search for several C-N bond forming reactions.² Among these methods, the development of catalytic nitrene additions culminated in the discovery of efficient transformations for the direct functionalization of C(sp³)-H bonds and the aziridination of alkenes. Particularly, synthetically useful methods were reported through the combination of hypervalent iodine chemistry and dirhodium(II) catalysis.³



Despite these achievements, the issues of enantioselectivity and site-selectivity remain to be addressed in catalytic INTERMOLECULAR nitrene additions, with the aim to design a streamlined access to a large variety of enantiopure amines. In this lecture, we will give an overview of our latest investigations dedicated to the design of new rhodium-bound nitrene species that led to design catalyst- and reagent-controlled selective C-N bond forming reactions.⁴



¹ E. Vitaku, D. T. Smith, J. T. Njardarson, *J. Med. Chem.* **2014**, *57*, 10257.

² a) *Amino Group Chemistry. From Synthesis to the Life Sciences* (Ed: A. Ricci), Wiley-VCH, Weinheim, **2008**. b) *Chiral Amine Synthesis* (Ed: T. C. Nugent), Wiley-VCH, Weinheim, **2010**.

³ a) J. Buendia, G. Grelier, P. Dauban, *Adv. Organomet. Chem.* **2015**, *64*, 77. b) B. Darses, R. Rodrigues, M. Mazurais, L. Neuvile, P. Dauban, *Chem. Commun.* **2017**, 53, 493.

⁴ a) A. Nasrallah, et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 8192. b) A. Nasrallah, et al. *Org. Process Res. Dev.* **2020**, *24*, 724. c) Y. Lazib, et al. *Angew. Chem. Int. Ed.* **2021**, *60*, 21708. d) E. Brunard, et al. *J. Am. Chem. Soc.* **2021**, *143*, 6407. e) V. Boquet, et al. *J. Am. Chem. Soc.* **2022**, *144*, 17156. f) E. Brunard et al. *J. Am. Chem. Soc.* **2024**, in press.