

## Nitrogen-Containing Molecules: From Synthesis to Reaction

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Pr Lebel group is interested by the synthesis, but also the reactivity of nitrogen-containing molecules. The first part of the presentation will describe the use of *N*-sulfonyloxycarbamate reagents to perform metal-catalyzed C-H amination,<sup>[1]</sup> aziridination<sup>[2]</sup> as well as thioether and sulfoxide amination reactions.<sup>[3]</sup> Mechanistic studies including DFT calculations will also be discussed.<sup>[4]</sup> In the second part of the lecture the synthesis of diazo compounds and the reactivity of diazoniums will be presented.<sup>[5]</sup> Diazoniums can be in-situ generated from an amine and a nitrite reagent in the presence of an acid. The trapping of aliphatic diazoniums with carboxylates, electron rich aromatics and other nucleophiles afforded various synthetic compounds in high yields. The optimization details and the scope of this methods will be described in the presentation.

- [1] (a) H. Lebel, C. Trudel, C. Spitz (2012): **Stereoselective intermolecular C-H amination reactions**, *Chem. Commun.* 48, 7799-7801. (b) H. Lebel, L. Mamani Laparra, M. Khalifa, C. Trudel, C. Audubert, M. Szponarski, C. Dicaire Leduc, E. Azek and M. Ernzerhof (2017): **Synthesis of oxazolidinones: rhodium-catalyzed C-H amination of N-mesyloxycarbamates**, *Org. Biomol. Chem.* 15, 4144-4158.
- [2] H. Lebel, C. Spitz, O. Leogane, C. Trudel, M. Parmentier (2011): **Stereoselective Rhodium-Catalyzed Amination of Alkenes**, *Org. Lett.* 13, 5460-5463.
- [3] (a) H. Lebel, H. Piras, J. Bartholoméüs (2014): **Rhodium-Catalyzed Stereoselective Amination of Thioethers with N-Mesyloxycarbamates: DMAP and Bis(DMAP)CH<sub>2</sub>Cl<sub>2</sub> as Key Additives**, *Angew. Chem. Int. Ed.* 53, 7300-7304. (b) H. Lebel, H. Piras, M. Borduy (2016): **Iron-Catalyzed Amination of Sulfides and Sulfoxides with Azides in Photochemical Continuous Flow Synthesis**, *ACS Catal.* 6, 1109-1112.
- [4] E. Azek, M. Khalifa, J. Bartholomeus, M. Ernzerhof and H. Lebel (2019): **Rhodium(II)-catalyzed C-H aminations using N-mesyloxycarbamates: reaction pathway and by-product formation**, *Chem. Sci.* 10, 718-729.
- [5] (a) C. Audubert, O.J. Gamboa Marin, H. Lebel (2017): **Batch and Continuous-Flow One-Pot Processes using Amine Diazotization to Produce Silylated Diazo Reagents**, *Angew. Chem. Int. Ed.* 56, 6294-6297. (b) C. Audubert, H. Lebel (2017): **Mild Esterification of Carboxylic Acids via Continuous Flow Diazotization of Amines**, *Org. Lett.* 19, 4407-4410.