

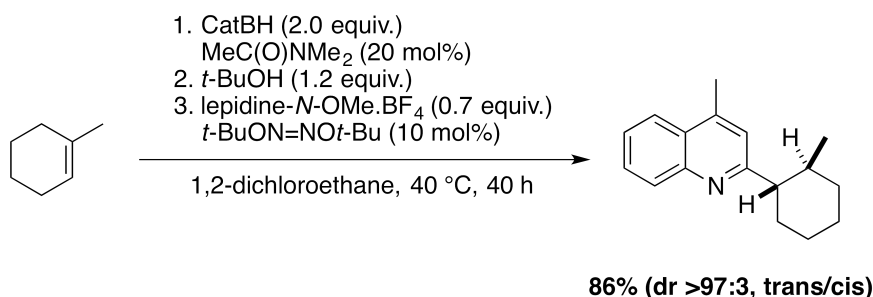
**Synthesis of Alkylated Pyridine Derivatives via  $S_HAr$  of N-Methoxypyridinium Salts**S. Rieder<sup>1</sup>, P. Renaud<sup>1\*</sup><sup>1</sup>Universität Bern

The homolytic aromatic substitution of nitrogen containing heterocycles is a versatile and well-studied class of transformations and is a viable reaction for late-stage functionalization of organic compounds.

The alkylation or acylation of a protonated, electron-poor heteroaromatic base using a nucleophilic carbon-centered radical was extensively studied by Minisci. Due to polar effects, the reaction shows selectivities that would be impossible to obtain under Friedel-Crafts reaction conditions.<sup>[1]</sup>

However, the reaction suffers from drawbacks such as use of a stoichiometric amount of oxidant, low regioselectivity and polyalkylation. Due to its viability in natural product synthesis and -functionalization, it is of great interest to overcome this reaction's limitations.

Herein, we describe a method that uses non-protic activation of the substrate. Alkylboranes (RBCat<sup>[2,3]</sup>, R<sub>3</sub>B) react with N-methoxypyridinium salts in the presence of a radical initiator to afford substituted pyridines. Interestingly, no external oxidizing agent is required to run this reaction. The scope and limitation of this reaction will be discussed.



[1] M. A. J. Dunston, *Med. Chem. Commun.* **2011**, 2, 1135–27.

[2] A.-P. Schaffner, P. Renaud, *Eur. J. Org. Chem.* **2004**, 2291–2298.

[3] C. E. Garrett, G. C. Fu, *J. Org. Chem.* **1996**, 61, 3224–3225.