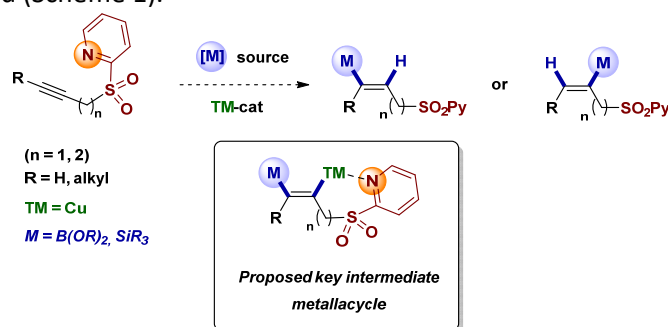


The original project proposed in this Marie Curie Career Integration Grant was based on two central ideas:

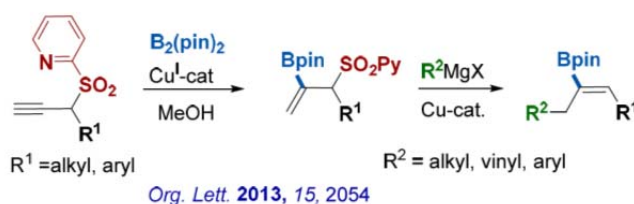
1. The design of tools that could plant the seeds for developing ecologically benign synthetic alternatives to the existing methods for the formation of C-C and C-X, in the context of the growing global interest to incorporate more environmentally benign organic compounds in chemical processes (Green or Sustainable Chemistry).[1]
2. Exploring the possibility of developing catalytic cycles that capitalize on hypervalent states.

This project is centered on the chemistry of boron and silicon. Both these elements have been proposed to operate in hypervalent cycles in processes in which they are transformed into other functionalities: therefore, it is expected that knowledge gained during this initial stoichiometric studies will eventually be transferred to catalytic versions of this work. It should also be mentioned that the transition metal used throughout the studies presented below is copper, arguably one of the more environmentally benign and non-toxic elements used in Organic Chemistry. In spite of the growing global interest to incorporate more environmentally benign organic compounds in chemical processes (Green or Sustainable Chemistry), there are only two types of organometallic reagents based on inexpensive, naturally occurring and environmentally benign elements: organoboranes and organosilanes. It would be desirable to increase the pool of benign stoichiometric organometallic reagents available to the synthetic organic chemist, both from academic and industrial standpoints.[1] This research project seeks to develop useful methods that will enable the preparation of a breadth of organometallic reagents based on boron and silicon. Specifically, we have sought to develop efficient strategies to synthesize a variety of vinylboranes and vinylsilanes via regioselective functionalization of unbiased alkynes (Scheme 1). The strategy is based on a two-step sequence that uses heteroarylsulfones as removable/traceless directing groups which can be easily functionalized (Scheme 1).



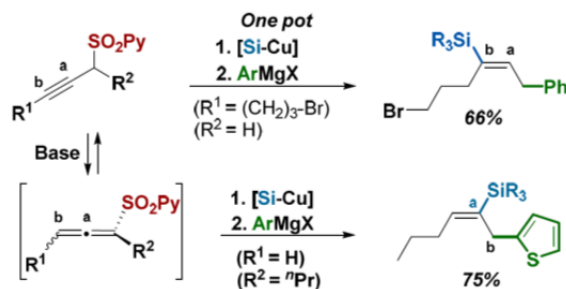
Scheme 1

This strategy has been successfully applied to the regio- and stereoselective synthesis of multisubstituted vinylboronates (Scheme 2)[3] and vinyl silanes (Scheme 3)[4] via regiocontrolled hydrometallation of internal and terminal alkynes.[5] Subsequently, and benefiting from hypervalent states displayed by boron and silicon under specific reaction conditions, these reagents have been used in the synthesis of a breadth of unsymmetrical multisubstituted olefins with substitution patterns not easily accessible by other synthetic strategies. Importantly, since alkenes are among the most important and versatile organic compounds with applications in global markets, the development of efficient methods for their preparation is of significant scientific and economic interest.



Org. Lett. **2013**, *15*, 2054

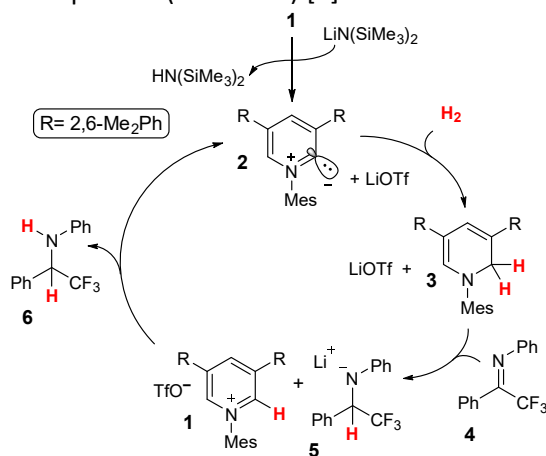
Scheme 2



J. Am. Chem. Soc. **2015**, *137*, 6857

Scheme 3

Additionally, the research developed over the course of this project has resulted in the development of a new research line based on the use of Pyridilidenes in the catalytic hydrogenation of organic compounds (Scheme 4).^[6]



Scheme 4

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- [1] <http://www.epa.gov/greenchemistry/>
- [2] Ackermann, L. "Modern Arylation Methods." Wiley VCH: Weinheim, 2009.
- [3] A. L. Moure, P. Mauleón, R. Gómez Arrayás, J. C. Carretero, *Org. Lett.* **2013**, *15*, 2054.
- [4] A. García-Rubia, J. A.; Romero-Revilla, P. Mauleón, R. Gómez Arrayás, J. C. Carretero, *J. Am. Chem. Soc.* **2015**, *137*, 6857.
- [5] For a review on hydrometallation of alkynes, see: Trost, B. M.; Ball, Z. T. *Synthesis* **2005**, 853.
- [6] J. Auth, J. Padevet, P. Mauleón, A. Pfaltz, *Angew. Chem. Int. Ed.* **2015**, *54*, 9542.