



Robert E. Maleczka, Jr.

## Synthetic Organic Chemistry

### PROFESSOR

(b. 1962)  
B.S., 1984,  
Univ. of Illinois at Urbana-Champaign;  
Abbott Labs, 1984-87;  
Ph.D., 1992,  
The Ohio State Univ.;  
Postdoctoral Fellow, 1992-95,  
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### SELECTED PUBLICATIONS

*One-Pot Iridium Catalyzed C-H Borylation/Sonogashira Cross-Coupling: Access to Borylated Aryl Alkynes*, Chotana, G. A.; Montero Bastida, J. R.; Miller, S. L.; Smith, M. R., III; Maleczka, R. E., Jr., *Molecules* **2020**, *25*, 1754-1766.

*Para-Selective, Iridium-Catalyzed C-H Borylations of Sulfated Phenols, Benzyl Alcohols, and Anilines Directed by Ion-Pair Electrostatic Interactions*, M. Bastida, J. R.; Oleskey, T. J.; Miller, S. L.; Smith, M. R., III; Maleczka, R. E., Jr., *J. Am. Chem. Soc.* **2019**, *141*, 15483-15487.

*C-H Borylation Catalysts that Distinguish Between Similarly Sized Substituents Like Fluorine and Hydrogen*, Miller, S. L.; Chotana, G. A.; Fritz, J. A.; Chattopadhyay, B.; Maleczka, R. E., Jr.; Smith, M. R., III, *Org. Lett.* **2019**, *21*, 6388-6392.

*A General Diversity Oriented Synthesis of Asymmetric Double-Decker Shaped Silsesquioxanes*, Barry, B.-D.; Dannatt, J. E.; King, A. K.; Lee, A.; Maleczka, R. E., Jr., *Chem. Commun.* **2019**, published online July 2, 2019 (DOI: 10.1039/C9CC03972D).

*Phase Behavior of cis-trans Mixtures of Double-Decker Shaped Silsesquioxanes for Processability Enhancement*, Vogelsang, D. F.; Dannatt, J. E.; Shoen, B. W.; Maleczka, R. E., Jr.; Lee, A., *ACS Appl. Nano Mater.* **2019**, *2*, 1223-1231.

*Predictive Liquid Chromatography Separation for Mixtures of Functionalized Double-decker Shaped Silsesquioxanes Based on HPLC Chromatograms*, Vogelsang, D. F.; Maleczka, R. E., Jr.; Lee, A., *Ind. Eng. Chem. Res.* **2019**, *58*, 403-410.

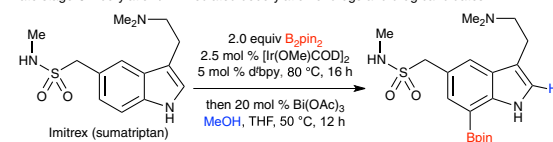
*HPLC Characterization of cis and trans Mixtures of Double-Decker Shaped Silsesquioxanes*, Vogelsang, D. F.; Maleczka, R. E., Jr.; Lee, A., *Silicon* **2019**, *11*, 5-13.

*Separation of Asymmetrically Capped Double-Decker Silsesquioxanes Mixtures*, Vogelsang, D. F.; Dannatt, J. E.; Maleczka, R. E., Jr.; Lee, A., *Polyhedron* **2018**, *155*, 189-193.

Our group is interested in a) green chemistry, b) the invention of new reactions and strategies in organic synthesis, and c) target synthesis of molecules with interesting properties ranging from biologically important natural products to nanomaterials.

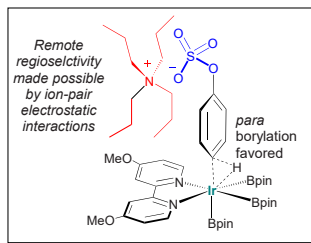
**Green Chemistry:** Central to our research is the development of efficient and environmentally benign reactions and strategies. The Pharmaceutical Roundtable of the American Chemical Society's Green Chemistry Institute deemed cross-couplings that avoid haloaromatics as their top aspirational reaction. In collaboration with Professor Mitch Smith, we are inventing such reactions. Specifically, we are using **catalytic C-H activation/borylation**, often combined with subsequent chemical events, to generate pharmaceutically relevant

Late stage CH borylation / Bi-mediated deborylation of drugs and drug candidates

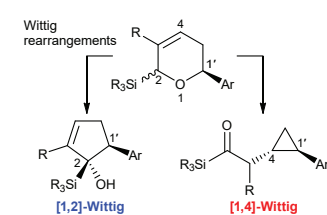


building blocks for organic synthesis and the late stage functionalization of drugs and drug candidates.

**Invention of New Reactions:** The principles of green chemistry also motivate us to create new synthetic methods. Within our catalytic borylation program, an example is our recently disclosed use of ion-pairing, where the alkyl groups of the cation create a steric shield that facilitates previously unheard of levels of para selectivity.



We are also focusing on the employment of organosilanes as both reagents and substrates in chemical transformations ranging from **Wittig rearrangements** to new approaches to double-decker silsesquioxanes (DDSQ's) for materials applications.

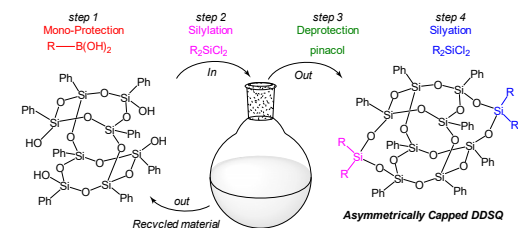


Since their discovery more than 70 years ago, Wittig rearrangements have evolved into powerful tools for the isomerization of  $\alpha$ -metalated ethers into alkoxides. Relative to the [2,3]- and [1,2]-shifts, [1,4]-Wittig rearrangements are unique in their ability to generate stereodefined enolates. In addition, [1,4]-Wittig rearrangements

have the potential to transfer chirality and stereoselectively form adjacent chiral centers. As such, we continue to study these mechanistically fascinating and synthetically intriguing rearrangements.

We have also teamed up with Chemical Engineering and Materials Science Professor Andre Lee, to apply our synthetic expertise to another remarkable class of compounds, namely **silsesquioxanes**. These caged structures have garnered significant attention over their ability to meet the demands of medical, aerospace and materials industries. This is due to the well-defined spatial dimensions, the presence of seven inert peripheral organic moieties to accommodate solubility and processability, and one polymerizable reactive organic group.

Like our other projects, we approach the synthesis of silsesquioxane through the lens of green chemistry. An example of this can be seen in our development of the first direct synthetic route leading to asymmetrically functionalized DDSQ compounds. By way of our route over 50% of the starting DDSQ tetraol that could have



otherwise contributed toward the synthesis of unwanted side products is recovered with a high purity and can be used in another cycle of synthesis. Efforts to use these compounds as nano-linkers to two different block copolymers are underway in our lab.

**Target Synthesis:** A unifying thesis behind all of our methodological and mechanistic studies is that the chemistry to emerge from such studies should be **applicable to real synthetic problems**. We view target synthesis as the best proof of this concept. For example, as part of our green chemistry program, we look to make TMC-95A and autolytimycin by the strategic application of our own synthetic methods. 🍀

