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Synthetic Organic Chemistry

PROFESSOR

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SELECTED PUBLICATIONS

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Reversible Borylene Formation from Ring-Opening of Pinacolborane and Other Intermediates Generated From 5-Coordinate Trisboryl Complexes: Implications for Catalytic C-H Borylation, Ghaffari, B.; Vanchura, B. A., II; Chotana, G. A.; Staples, R. J.; Holmes, D.; Maleczka, R. E., Jr.; Smith, M. R., III, *Organometallics* **2015**, *34*, 4732-4740.

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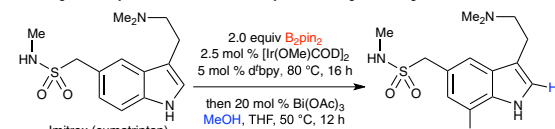
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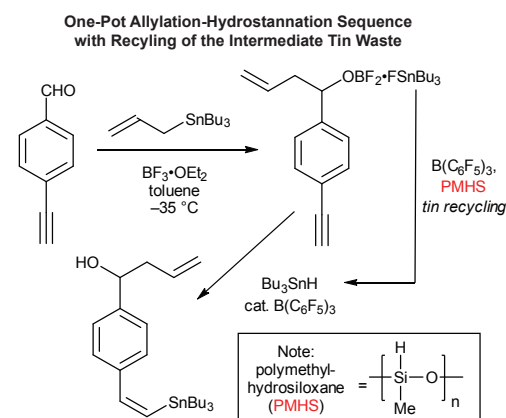
Our group is interested in a) the **total synthesis** of biologically important natural products, b) the **invention of new reactions** and strategies in organic synthesis, and c) **green chemistry**.

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

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

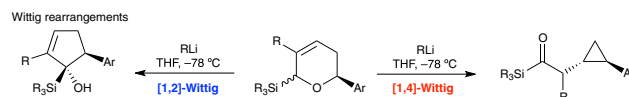


Another of our green chemistry ventures aims to minimizing the need for tin in various processes. For example, we have developed an allylation/hydrostannation sequence where the tin waste from the allylation is recycled *in situ* so as to allow its use in the hydrostannation. This chemistry employs polymethylhydrosiloxane (PMHS), which is an oligomeric non-toxic waste product of the silicon industry, as the stoichiometric reductant.

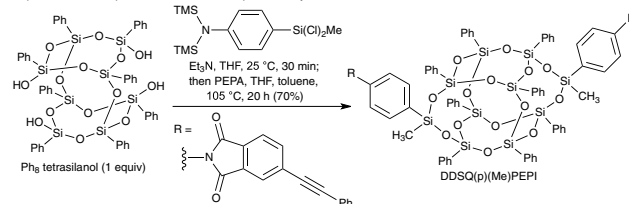


Invention of New Reactions: The principles of green chemistry also motivate us to create new synthetic methods. Here we have been focusing on the employment of organosilanes as both reagents and substrates in chemical transformations ranging from Wittig rearrangements to new approaches

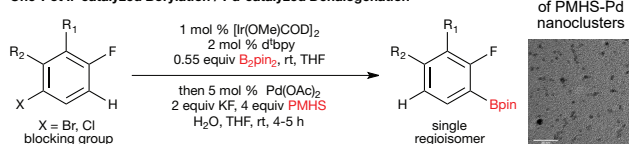
to double-decker silsesquioxanes (DDSQ's) for polymer applications. As part of a collaboration with Dow Chemical, we have also used PMHS in conjunction with our



Representative one-pot double-decker silsesquioxanes synthesis



One-Pot Ir-catalyzed Borylation / Pd-catalyzed Dehalogenation



borylation chemistry to regioselectively generate building blocks of interest to the agrochemical industry. Here the combination of Pd(OAc)₂ and PMHS generates siloxane encapsulated Pd(O) nanoclusters.

Total Synthesis: The 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. 🌱

