ORGANIC CHEMISTRY SEMINAR

Thursday
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11:00 a.m.

Room 1315
Chemistry

New Approaches to Selective and Tunable Oxidations

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My group is inspired by important challenges in synthetic organic chemistry where traditional strategies have failed to lead to general solutions. For example, a long-standing goal in catalysis has been to mimic the exquisite selectivity of enzymes for the late-stage functionalization of molecules containing multiple reactive sites. The first part of this talk will describe how we have harnessed the ability of silver to adopt multiple coordination geometries to control both the mechanism and selectivity of nitrene transfer. Notable achievements include: 1) the ability to tune for either intramolecular aziridination or C-H amination by simple changes in the AgOTf:ligand ratio, 2) control over the chemoselectivity of intermolecular nitrene transfer through the ligand and nitrogen source and 3) tunable, site-selective amination of different C-H bonds in a molecule.

We have applied silver-catalyzed nitrene transfer to new methods for the flexible synthesis of complex amines. Stereodefined amino groups flanked by other heteroatom-bearing stereogenic centers are common motifs in many biologically important molecules. However, these motifs are difficult to access using conventional synthetic approaches. Our highly regio-, chemo- and stereoselective oxidative allene amination strategies solve this problem *via* three powerful design features: the ability to manipulate and tune the heteroatom diversity in amine triads, the ability to achieve stereochemical diversity from a single allene precursor and the ability to transform allenes into diverse and complex ring systems. This chemistry provides a powerful tool to address questions concerning the effect of systematic modifications to the positioning, stereochemistry and pK_a of amines on the efficacy and toxicity of several classes of bioactive molecules.