University of Louisville
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Research Seminar

When: March 23, 2023
Time: **12:00 p.m**.
Location: CBLL-16

Sustainable Catalytic Methodologies Utilizing Aqueous Micelles and Polymeric Cellulose

ABSTRACT:

For many decades, water, as a reaction solvent, has been neglected by organic chemists, mainly due to the low solubility of organic compounds and the instability of moisture-sensitive species or intermediates. As such, organic solvents, and when necessary, dry organic solvents have been the norm in traditional organic synthesis. However, issues related to toxicity and waste generation from these organic solvents have required developing safe, sustainable, and greener alternatives. Subsequently, employing water as the reaction solvent, especially the use of designer aqueous micelles, has gained popularity in recent decades.[1] The adoption of aqueous micelles by various research groups and pharmaceutical companies has showcased their reactivity, scalability, sustainability, and reduced waste generation.[2] Furthermore, our research group has developed PS-750-M, a benign proline-based amphiphile that instantaneously forms micelles under aqueous conditions. It has been explored to enable diverse synthetic transformations with improved selectivity and unique reactivity compared to traditional organic solvents.[3]

PS-750-M is an amphiphile consisting of a hydrophobic alkyl chain and a hydrophilic methyl polyethylene glycol chain linked by a proline unit. The presence of the ester and tertiary amide groups in the amphiphile provides improved polarity to the organic moieties inside the micellar core, thereby allowing to act as a green alternative to toxic dipolar-aprotic solvents, such as DMF, DMAc, and NMP. In addition, the structural characteristics of the amphiphile facilitate the stabilization of metal nanoparticles (NPs) through its tertiary amide core.[4] In this regard, the first part of my talk will be focused on the applications of PS-750-M for selective catalysis. It includes the synthesis and characterization of Ni(0) Pd(0) NPs stabilized by PS-750-M.[5] The NPs were synthesized from $Ni(OAc)_2$ and $Pd(OAc)_2$ and were thoroughly characterized using techniques such as HRTEM, XPS, EDAX, TGA, Optical Microscopy, and SERS imaging. The developed ligand-free bimetallic NPs were applied in selective 1,4-reduction of enones, enamides, enenitriles, and α-ketoamides, with broad functional group tolerance, high selectivity, and scalability. Next, I will discuss the copper-catalyzed regio-selective hydroboration of unsymmetrical internal alkynes.[6] The developed methodology was highly selective for the β-hydroboration product. The method was scalable, and the resulting products were further utilized to form C-C bonds using Suzuki-Miyaura cross-couplings. The Cu catalyst was characterized using HRTEM.

The last part of my talk will showcase the use of hydroxypropyl methylcellulose (HPMC) as an additive for “Nucleophilic Aromatic Substitution (S_NAr)”.[7] HPMC is a benign, sustainable, and inexpensive polymer with hydrophilic and hydrophobic groups which allows for its ability to interact with poorly water-soluble molecules while being water-soluble.[8] In an aqueous solution, the hydrophobic interactions between the hydrophobic groups of HPMC form unique pockets which enable organic transformations. The application of HPMC was explored in the S_NAr reaction between diverse nucleophiles and electrophiles. The reaction was mild, scalable, and displayed broad functional group tolerance, which can be further derivatized towards pharmaceutical intermediates.

References:

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