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Dissertation Defense

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Sustainable Methodologies for Synthesis of Small Organic Molecules Using Micellar Catalysis

ABSTRACT:

Organic synthesis is a crucial process in creating small-molecule pharmaceuticals and agrochemicals. However, numerous methods for synthesizing these small molecules rely on toxic organic solvents. To avoid using these solvents, micellar chemistry in water has become more popular in the past ten years. Micellar catalysis involves using water as the primary or sole solvent with designer surfactants. Its usage as a solvent in organic synthesis significantly improved the reactions' efficiency.¹ Along these lines, our research group developed a proline-based nonionic amphiphile, PS-750-M, to mimic toxic organic solvents such as DMF, NMP, and DMAc, allowing for various synthetically relevant transformations in water.² A tertiary amide functional group within this amphiphile provides significant polarity to the micellar inner core, enhancing the accommodation of substrates and reaction intermediates to accomplish reactions efficiently. In addition, the inner core stabilizes metal nanoparticles (NPs) and can act as a ligand to facilitate various NP-mediated transformations.

The dissertation's first part describes the development of a ligand-free nickel-palladium (Ni-Pd) NP for the selective hydrogenation of unsaturated compounds such as enones, enamides, enenitriles, and α -ketoamides.³ These NPs were thoroughly characterized using state-of-the-art techniques such as XPS, HRTEM, and TGA. The methodology was amenable to substrates with diverse functional groups. Next, the regioselective hydroboration of unsymmetrical internal alkynes was explored under aqueous micellar conditions using a ligated copper (Cu) catalyst. Hydroboration of unsymmetrical internal alkyne has poor regioselectivity,^{4,5} so we developed a highly regioselective methodology. The developed methodology was highly selective for the β -alkenyl boronate esters, with broad substrate scope and scalability.⁶ Finally, we focused on applying an inexpensive Ni catalyst in the oxidative coupling of diverse arylboronic acids and primary amines under aqueous micellar conditions.⁷ The Ni catalyst was ligated with a substituted 1,10-phenanthroline ligand to enable the coupling under mild reaction conditions. The catalyst was further characterized using XPS to determine the active Ni species, and the reactivity was successfully applied to diverse substrates.

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