

[Zr=O] Catalyzed Synthesis of α,β -Unsaturated Ketones from Alkynes and Aldehydes

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α,β -Unsaturated carbonyls are common functionalities or precursors in many natural products and pharmaceuticals. Unfortunately, commonly employed methods for the synthesis of these compounds involves prefunctionalization of starting materials and lead to a stoichiometric amount of byproducts, ultimately resulting in poor atom- and step-economy. We have proposed a catalytic cycle (Figure 1) where **1** undergoes a [2+2]-cycloaddition (*i*) with an alkyne to form oxazirconacyclobutene **2**, then an aldehyde inserts into the Zr–C bond (*ii*) to form dioxazirconacyclohexene **3**, and, finally, a retro-[4+2] cycloaddition (*iii*) generates the desired α,β -unsaturated ketone **4** and regenerates the zirconium-oxo catalyst. We have demonstrated, stoichiometrically, each step of the proposed catalytic cycle, and are exploring methods in which substoichiometric zirconium catalysis can occur.

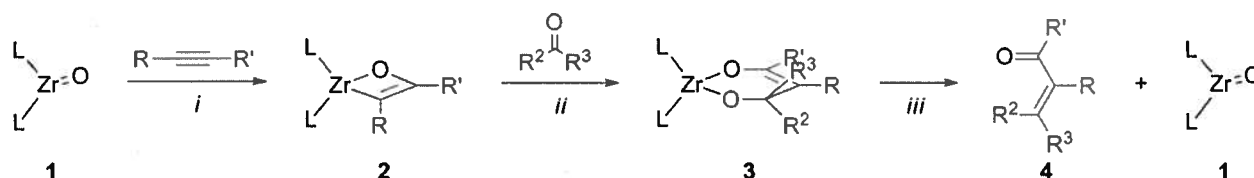


Figure 1: Proposed Zirconium-oxo Alkyne-Aldehyde Coupling Reaction

Compact and Stable Quantum Dots Provided by Multidentate Neutral Polymer Ligands

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Quantum dots (QDs) have attracted increasing interest in many fields particularly in bioimaging because of their high quantum yield and high extinction. Significant efforts have been made to achieve aqueous solubility and long-term stability for QDs synthesized in organic solvents. Traditional methods afford either QDs of large hydrodynamic size or QDs stable within a narrow pH window. Dihydroxylated polymers and/or polyglycerol-dendronized polymers can minimize QDs' hydrodynamic size, not at the cost of stability under a wide range of pH.

