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# Enantioselective Copper-Catalyzed Conjugate Additions of *in situ* Generated Organozirconium Reagents to *N*-Heterocyclic Michael Acceptors

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## Abstract

Stereoselective conjugate additions of organometallic reagents provide access to many useful chiral compounds. In this work, we have studied the enantioselective Cu-catalyzed conjugate addition of organozirconium reagents, which were generated *in situ* by hydrozirconation of alkenes. We show that *N*-heterocyclic Michael acceptors, represented by unsaturated lactams and 2,3-dihydropyridin-4(1*H*)-ones can be useful substrates for Cu-catalyzed conjugate additions of organozirconium reagents. Phosphorus ligands screening identified Feringa's phosphoramidite as the most active and enantioselective ligand for this transformation, which afforded corresponding conjugate addition products with an enantiomeric purity of up to 92:8 e.r. The absolute configuration of one of the conjugate addition products was established by comparison of DFT calculated and experimental electronic CD spectra. The study also showed that mildly reactive organozirconium reagents combined with relatively unreactive Michael acceptors afford typically conjugate addition products in medium yields. DFT calculations of LUMO maps also supported non-reactivity of heterocyclic Michael acceptors. LUMO maps showed decreasing electrophilicity at the  $\beta$ -carbon due to donor substituents present near unsaturated carbonyl scaffold.

## Keywords

Conjugate addition, organozirconium reagents, copper, *N*-heterocycles

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