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Pd-Catalyzed Heck-Type Cascade Reactions with *N*-Tosyl Hydrazones: An Efficient Way to Alkenes via in Situ Generated Alkylpalladium

Org. Lett. **2013**, *15*, 4814–4617.

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

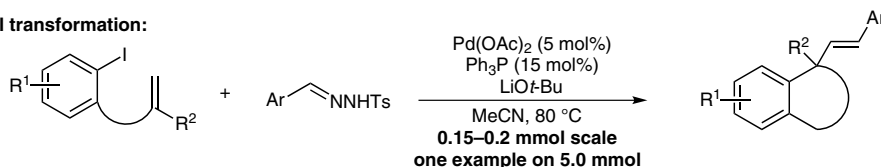
palladium

Heck reaction

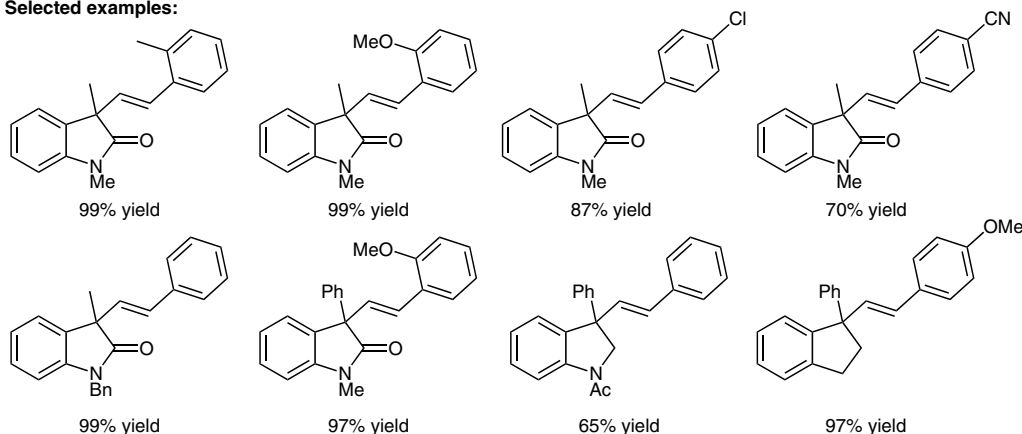
N-tosyl hydrazones

Catalytic Alkenylation of Neopentyl Palladium Species Using *N*-Tosyl Hydrazones

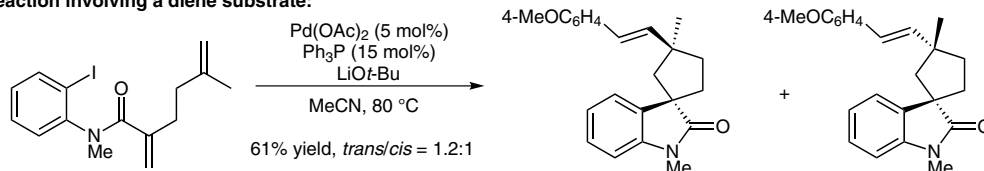
Overall transformation:



Selected examples:



Reaction involving a diene substrate:



Significance: Palladium-catalyzed Heck-type cascades have long been used to install molecular complexity in a single transformation. In early pioneering work, Negishi and Grigg have reported cascade processes involving carbonylation sequences, Stille and Suzuki couplings, as well as C–H functionalization as terminating steps. However, despite these advances, terminations involving palladium carbenes have been far less explored. Gu and co-workers report the combination of *N*-tosyl hydrazone derived carbenes and in situ generated alkyl palladiums in a new alkenylation reaction.

Comment: The authors present a palladium-catalyzed Heck-type cascade reaction en route to alkene products. By terminating the cyclization sequence with a reaction with *N*-tosyl hydrazones, products can be obtained with high *E/Z* ratios. The method benefits from the ability to generate diverse hetero- and carbocycles in good to excellent yields under relatively mild conditions, using a simple palladium(II) pre-catalyst. Cyclization onto electron-deficient alkenes was shown to be preferred in a competition experiment involving a diene substrate.

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Synfacts 2014, 10(1), 0061 Published online: 13.12.2013
DOI: 10.1055/s-0033-1340447; Reg-No.: L15713SF