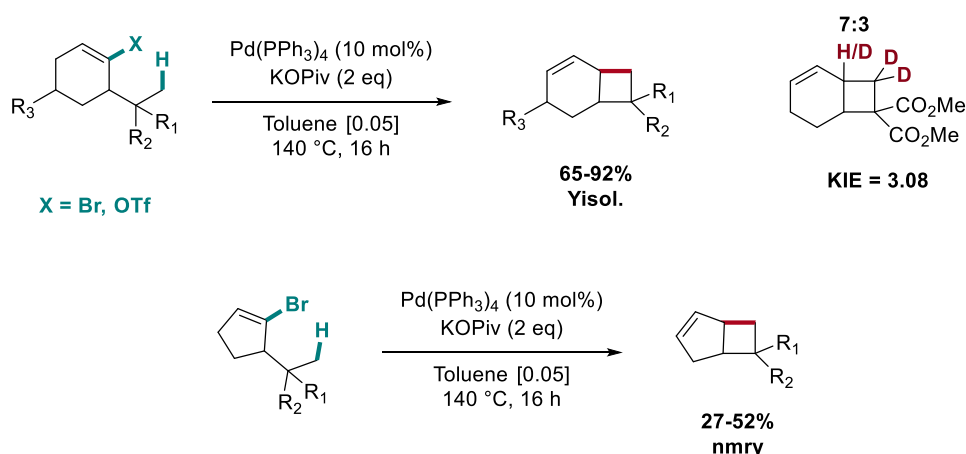


Construction of fused cyclobutanes through an intramolecular C(sp³)-H alkenylation realized via 1,4-Pd shift/Heck coupling

Maris Tsitopoulou, Olivier Baudoin

Department of Chemistry, University of Basel, St. Johannis-Ring 19, 4056, Basel, Switzerland

maria.tsitopoulou@unibas.ch



1,4-Palladium shift has been established as an elegant approach towards the functionalization of remote C-H bonds.¹ However, its application is restricted to using aryl halides as precursors.² In this work, we have successfully extended its appeal to C(sp³)-H alkenylations starting from alkenyl (pseudo)halides through a Pd⁰-catalyzed C(sp³)-H alkenylation process. This tandem procedure takes place via a 1,4-Pd shift followed by an intramolecular Heck coupling. The methodology performs adequately with cyclohexenyl precursors giving access to a variety of substituted bicyclo[4,2,0]octenes, and also shows a potential for accessing smaller ring systems starting from cyclopentenyl halides. Early kinetic studies indicate a Kinetic Isotope Effect of 3.08 establishing the C-H activation as the rate-determining step while deuterium incorporation suggests an irreversible 1,4-Pd shift process – probably arising from the fast trapping of the σ -alkylpalladium species through the Heck coupling.

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