

Pd-Catalyzed Asymmetric Cross-Coupling of Allyl Carbonates and Allyl Boronates

Category

Metal-Catalyzed
Asymmetric
Synthesis and
Stereoselective
Reactions

Key words

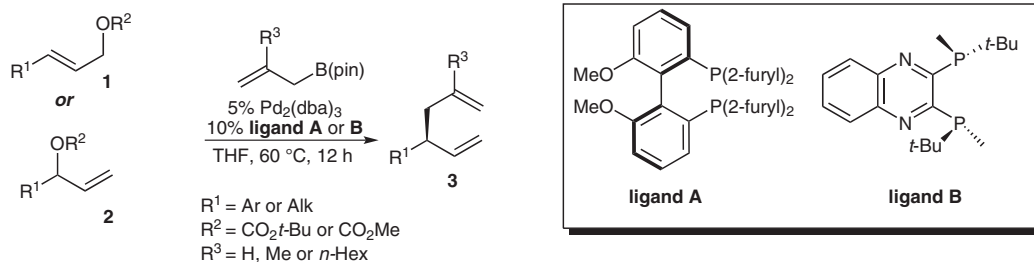
palladium-catalyzed
cross-coupling

allyl carbonates

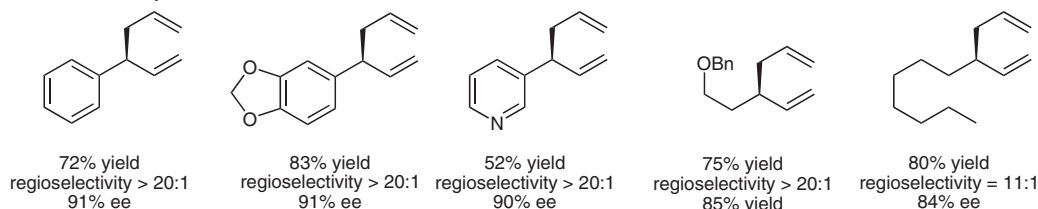
chiral phosphine
ligands

deuterium labeling

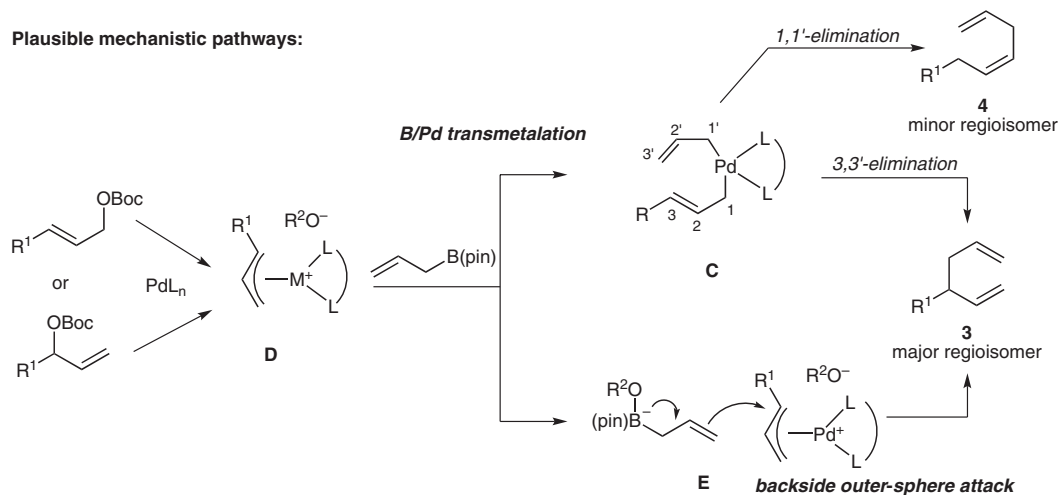
SYNFACT
of the month



Selected examples:



Plausible mechanistic pathways:



Significance: The authors describe here a high-yielding, highly regio- and enantioselective cross-coupling of allyl carbonates and allyl boronates. Remarkably, nearly identical results are obtained for regioisomers **1** and **2**. Importantly, aromatic and aliphatic allyl carbonates are tolerated under the reaction conditions. Allyl–allyl coupling in high regio- and stereoselectivity is a long-standing challenge in organic synthesis and this method provides an excellent solution.

SYNFACTS Contributors: Hisashi Yamamoto, Patrick Brady
Synfacts 2010, 11, 1255–1255 Published online: 21.10.2010
DOI: 10.1055/s-0030-1258743; Reg-No.: H12010SF

Comment: High regioselectivity for the branched product **3** rather than the linear product **4** is obtained by choosing bidentate ligands with small bite angles. Mechanistic studies including deuterium labeling and stereochemical analysis support a B–Pd transmetalation pathway to generate intermediate **C**, followed by $3,3'$ -elimination, rather than a backside outer-sphere attack (**E**).