P. ZHANG, L. A. BROZEK, J. P. MORKEN* (BOSTON COLLEGE, CHESTNUT HILL, USA)
Pd-Catalyzed Enantioselective Allyl–Allyl Cross-Coupling
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Pd-Catalyzed Asymmetric Cross-Coupling of Allyl Carbonates and Allyl Boronates

Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

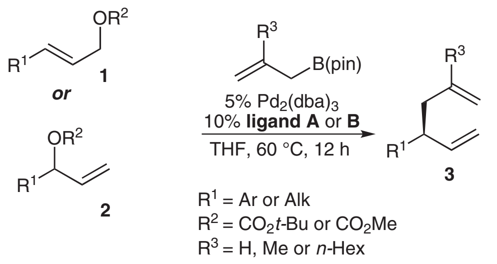
Key words

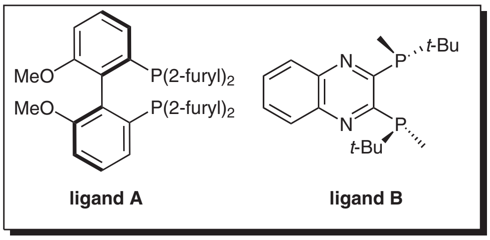
palladium-catalyzed cross-coupling

allyl carbonates

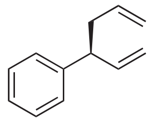
chiral phosphine ligands

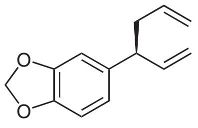
deuterium labeling

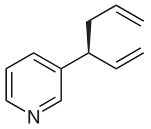


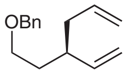


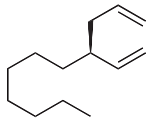
Selected examples:


72% yield
regioselectivity > 20:1
91% ee

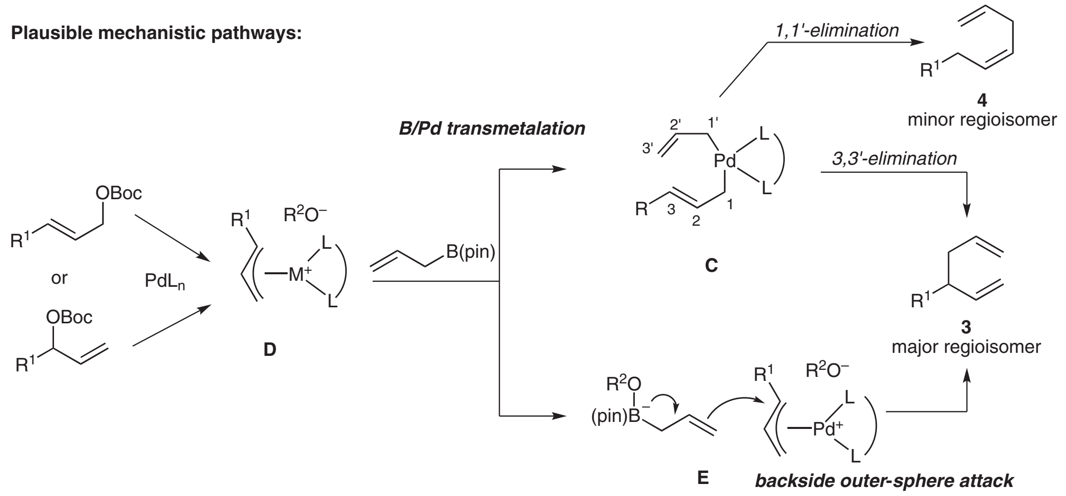

83% yield
regioselectivity > 20:1
91% ee


52% yield
regioselectivity > 20:1
90% ee


75% yield
regioselectivity > 20:1
85% yield


80% yield
regioselectivity = 11:1
84% ee

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.

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**).

SYNFACTS Contributors: Hisashi Yamamoto, Patrick Brady
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