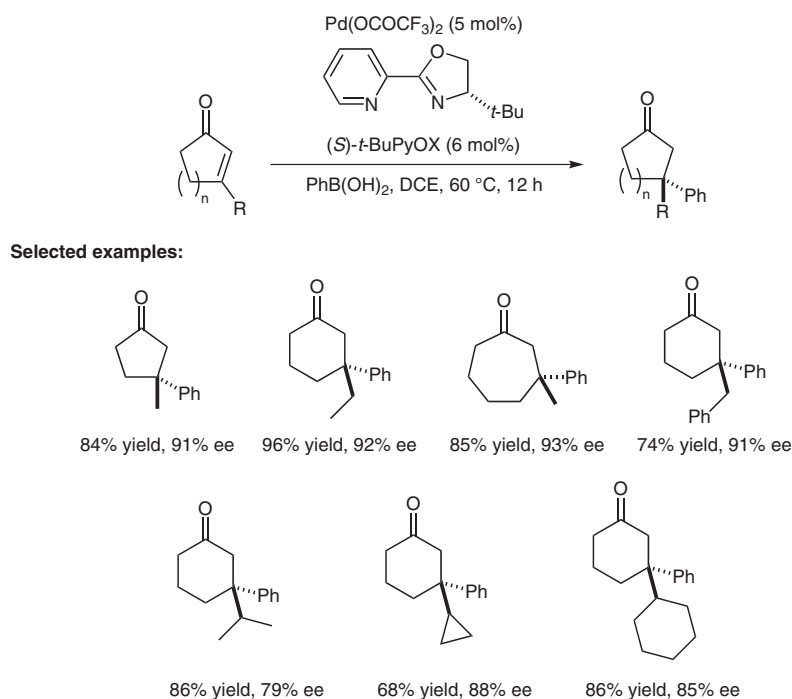


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Palladium-Catalyzed Asymmetric Conjugate Addition of Arylboronic Acids to Five-, Six-, and Seven-Membered β -Substituted Cyclic Enones: Enantioselective Construction of All-Carbon Quaternary Stereocenters
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Pd-Catalyzed Asymmetric Conjugate Addition of Arylboronic Acids to Cyclic Enones



Significance: The authors report the first asymmetric palladium-catalyzed 1,4-addition of phenylboronic acids to β -substituted cyclic enones to construct quaternary centers in high yields and generally good enantioselectivities. The method is general for five-, six-, and seven-membered enones. Furthermore, a variety of electronically rich and poor arylboronic acids can be employed with moderate to excellent yields and fair to excellent asymmetric induction. Various substitution patterns at the β -position of the cyclic enones are tolerated without substantial loss of yield or enantioselectivity.

Comment: Although there are many related transformations, this is the first palladium-catalyzed variant for the construction of quaternary stereocenters in high yields and enantioselectivities. The ease with which the ligand can be synthesized is also noteworthy [the (S) - t -BuPyOX ligand can be prepared in two synthetic steps from commercially available materials]. The methodology exhibits broad functional group tolerance and can be performed in the presence of both air and water. This could prove to be a very useful contribution to the field.

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