

Asymmetric Allylic Substitution in Water with a Polymeric Pd Catalyst

Category

Polymer-Supported Synthesis

Key words

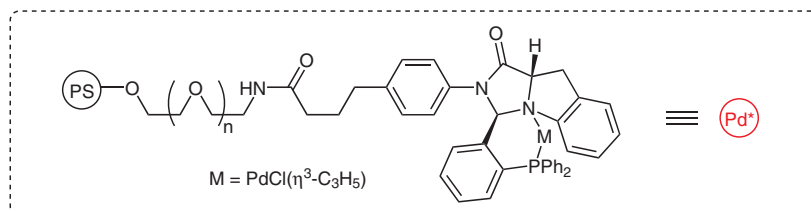
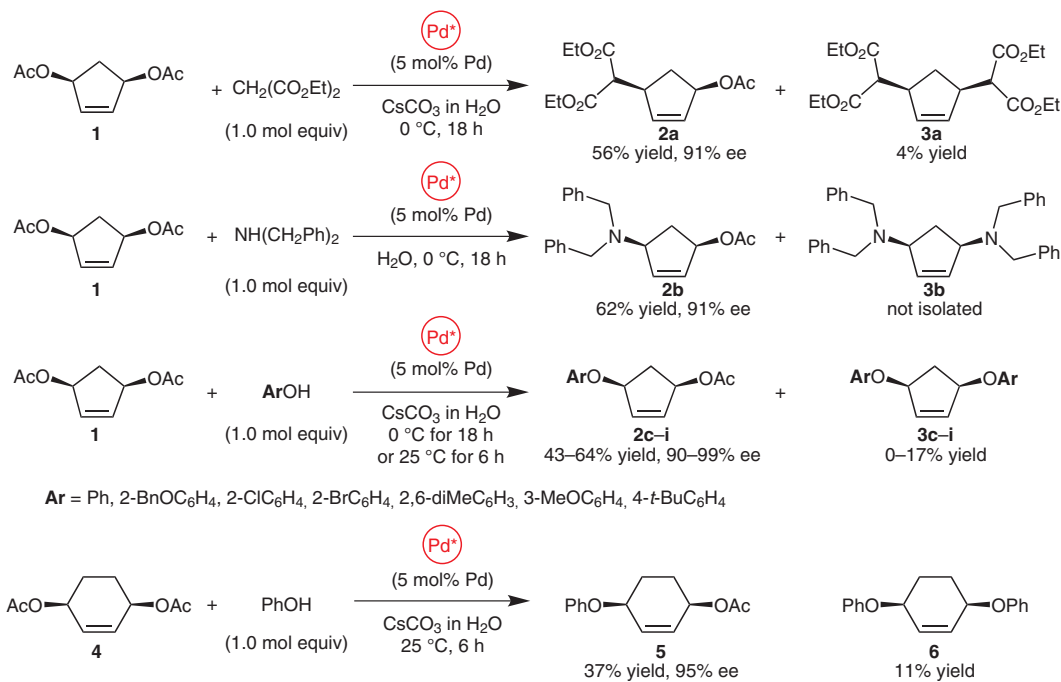
π -allylpalladium

asymmetric catalysis

aqueous media

PS-PEG polymer supports

SYNFACTS
of the month



Significance: Asymmetric π -allylic substitution of *meso*-1,4-diacetoxycycloalkenes was performed with an amphiphilic PS-PEG resin-supported chiral phosphine-palladium complex. Thus, the reaction of *cis*-1,4-diacetoxycyclopentene (*meso*-**1**) with diethyl malonate, dibenzylamine and phenols in water gave the corresponding 1-acetoxy-4-substituted cyclopentenes **2a-i** with 90–99% ee in 43–64% yield. Cyclohexenyl ester (*meso*-**4**) also underwent etherification with phenol to give **5** in 37% yield (95% ee) and 11% of **6**.

Comment: The authors have reported earlier the preparation and utility of the polymeric chiral phosphine-palladium complex used here (*J. Am. Chem. Soc.* **2001**, *123*, 2919; *Org. Lett.* **2004**, *6*, 281; *Org. Lett.* **2005**, *7*, 291; *Tetrahedron: Asymmetry* **2006**, *17*, 161; *J. Org. Chem.* **2006**, *71*, 8644). The reaction pathway giving high enantiomeric excess of the monosubstituted products includes kinetic resolution steps forming disubstituted **3**.

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