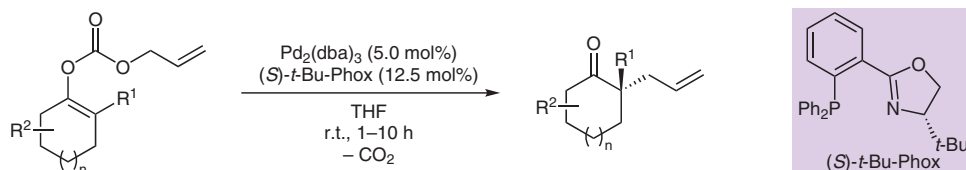
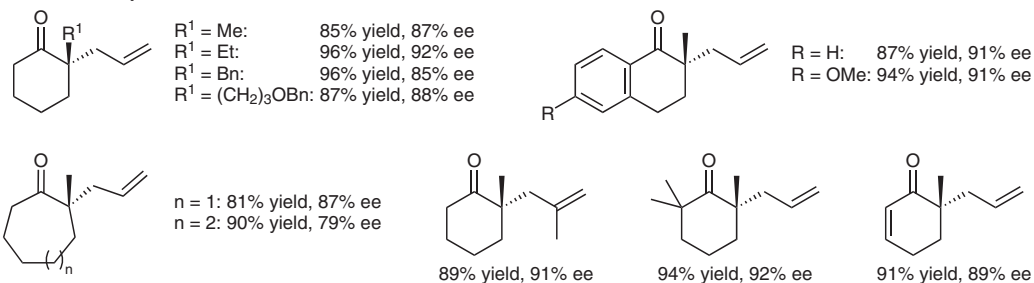


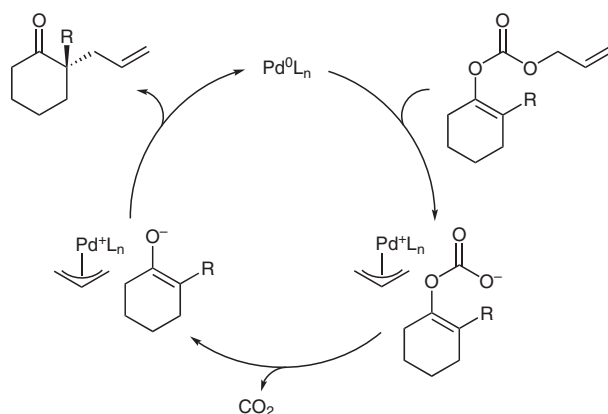
# The Enantioselective Tsuji Decarboxylative Allylic Alkylation



## Selected examples:



## Proposed mechanism:



**Significance:** Although introduced as early as 1980 by Tsuji (*Tetrahedron Lett.* **1980**, *21*, 3199) and Saegusa (*J. Am. Chem. Soc.* **1980**, *102*, 6381), the enantioselective version of a decarboxylative allylation had not been disclosed until more than two decades later by Behenna and Stoltz. Using a chiral phosphino-oxazoline (Phox) ligand, the palladium(0)-catalyzed decarboxylative asymmetric allylic alkylation (Pd-DAAA) of simple allyl enol carbonates provided access to chiral cycloalkanones with quaternary stereocenters at the  $\alpha$ -position.

**Comment:** Using Trost-type ligands, Tunge (*Org. Lett.* **2004**, *6*, 4113) and Trost (*J. Am. Chem. Soc.* **2005**, *127*, 2846) independently reported related decarboxylative allylations controlling the stereochemistry at the  $\beta$ - and  $\alpha$ -position of the ketone, respectively. Since its discovery, the Tsuji decarboxylative allylic alkylation has been studied in-depth, and the scope of this transformation has been considerably extended.

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