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The Enantioselective Tsuji Allylation

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The Enantioselective Tsuji Decarboxylative Allylic **Alkylation**

CO₂

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 phosphinooxazoline (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 α -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 β - and α -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.

Review: J. James, M. Jackson, P. J. Guiry *Adv. Synth.* Catal. 2019, 361, 3016-3049.

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