E. J. ALEX, H. ZHANG*, B. M. STOLTZ* (CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA AND GENENTECH INC., SOUTH SAN FRANCISCO, USA)
Catalytic Enantioselective Synthesis of Acyclic Quaternary Centers: Palladium-Catalyzed Decarboxylative Allylic Alkylation of Fully Substituted Acyclic Enol Carbonates
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Asymmetric Decarboxylative Allylic Alkylation of Acyclic Enol Carbonates

Selected examples:

Significance: The authors present the first enantioselective palladium-catalyzed decarboxylative allylic alkylation of fully substituted non-cyclic enol carbonates. The reaction delivers the linear α -quaternary ketones in excellent yields. The phosphino-oxazolidine ligand controls the stereoselectivity of the reaction regardless of the *Z/E* geometry of the enolate starting material.

Comment: This work outlines a general method to access linear α -quaternary ketones with high enantioselectivity. A dynamic kinetic resolution of the two *Z/E* geometries of the enolate starting material is postulated under optimal reaction conditions, which comprise the use of an electron-deficient phosphino-oxazolidine ligand.

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