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Catalytic Enantioselective Decarboxylative Protonation
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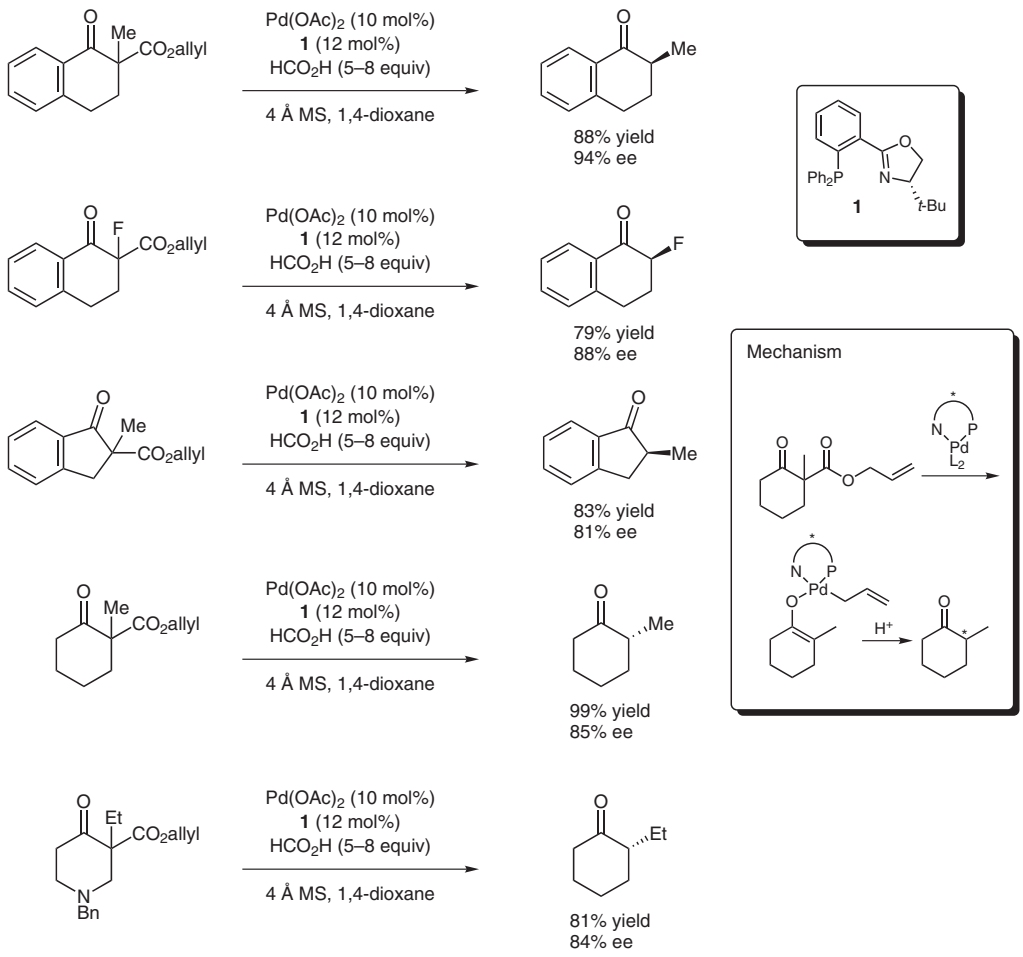
Catalytic Enantioselective Decarboxylation-Protonation



Significance: Asymmetric protonation remains an important challenge in organic chemistry. This report by Stoltz does an excellent job of extending their previous allylation work to protonation using formic acid as the achiral proton source. A variety of substrates are tolerated giving moderate to high enantioselectivity (60–95% ee). While only cyclic ketones are described, both fused aromatic and alkyl carbocycles work, as well as heterocyclic compounds.

Comment: This is a great step in the elusive area of asymmetric protonation. The authors have expertly used an achiral proton source and take advantage of their chiral palladium enolate species for the enantiodiscrimination. The mechanism is unknown and differs from the proposed allylation mechanism due to the 'opposite' absolute stereochemistry obtained with substrates containing aromatic moieties compared to all aliphatic substrates (not seen for allylation reaction).

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