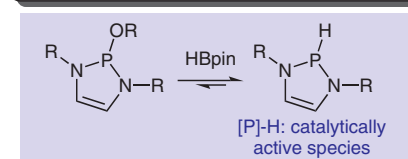
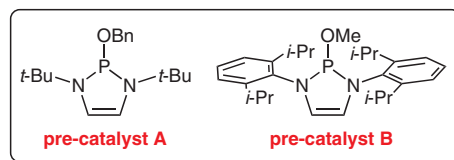
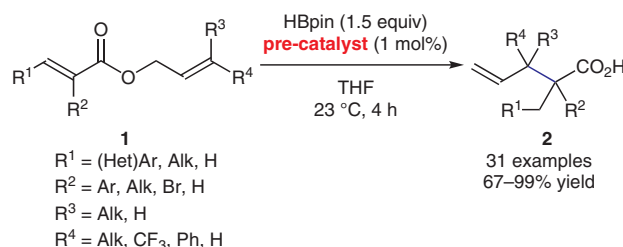


J. H. REED, P. A. DONETS, S. MIASKIEWICZ, N. CRAMER* (ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE, SWITZERLAND)

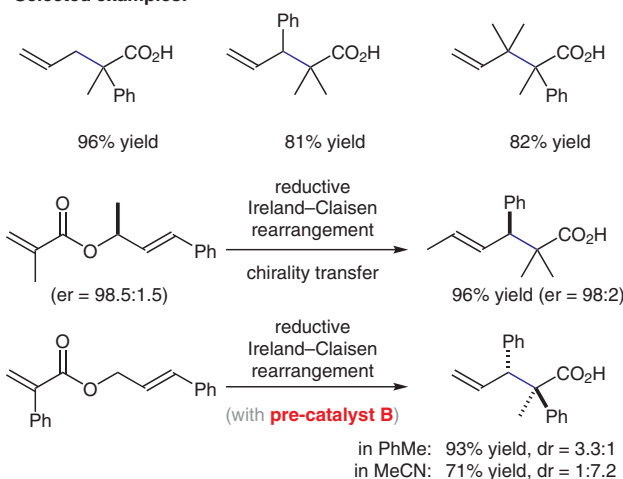
A 1,3,2-Diazaphospholene-Catalyzed Reductive Claisen Rearrangement

Angew. Chem. Int. Ed. 2019, 58, 8893–8897.

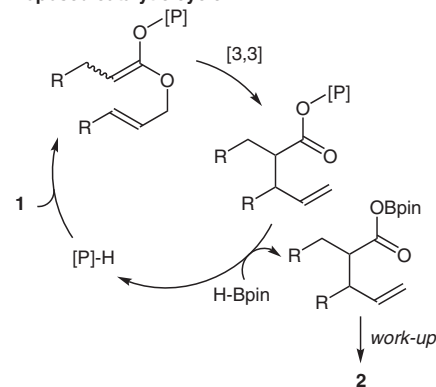
Diazaphospholene-Catalyzed Reductive Ireland–Claisen Rearrangement



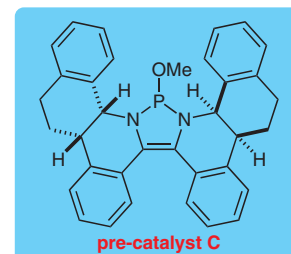
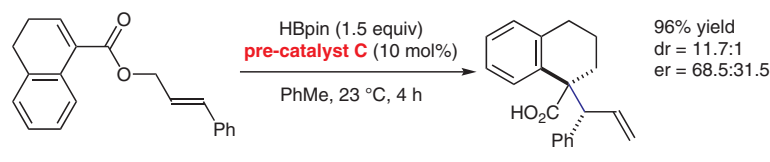
Selected examples:



Proposed catalytic cycle:



Catalytic asymmetric reductive Claisen rearrangement: proof-of-concept



Significance: Cramer and co-workers present the use of 1,3,2-diazaphospholenes (DAPs) as catalysts for the reductive Ireland–Claisen rearrangement. The reported method proceeds under very mild conditions, without requiring cryogenic temperatures and/or the addition of transition-metal hydrides, for a broad substrate scope. Furthermore, the use of a chiral DAP as catalyst is presented as a proof of concept and a promising result toward a catalytic asymmetric version of this reaction has been obtained.

Comment: The Ireland–Claisen rearrangement belongs to a group of fundamental reactions for stereoselective C–C bond formation. By using DAPs as catalysts, the reductive variant of this transformation can be performed in an operationally simple way, without requiring stepwise reduction and subsequent silylation. An enantioselective version of this reaction is highly desirable as an alternative for the asymmetric synthesis of chiral quaternary centers.