

acylation

dynamic kinetic resolution (DKR)

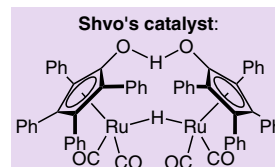
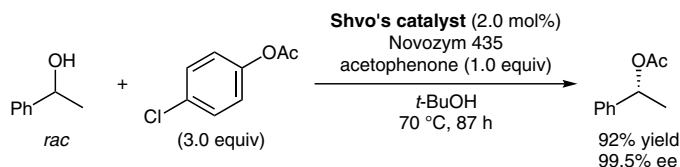
enzyme catalysis

racemization

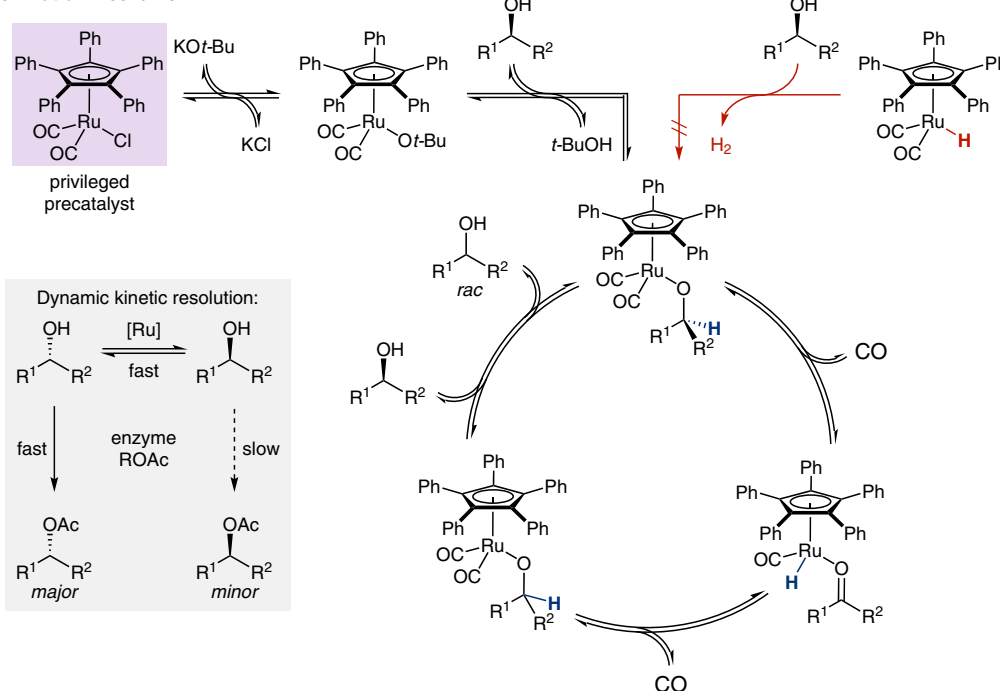
ruthenium catalysis

A. L. E. LARSSON, B. A. PERSSON, J.-E. BÄCKVALL* (UPPSALA UNIVERSITY, SWEDEN)
 Enzymatic Resolution of Alcohols Coupled with Ruthenium-Catalyzed Racemisation of the Substrate Alcohol
Angew. Chem., Int. Ed. Engl. **1997**, 36, 1211–1212, DOI: 10.1002/anie.199712111.

Bäckvall's Dynamic Kinetic Resolution



Racemization mechanism:



Significance: In 1997, Bäckvall and co-workers presented a ruthenium(II)-catalyzed racemization of secondary alcohols coupled with enzymatic kinetic resolution to form the corresponding acetates in high yields and enantiomeric excesses. This protocol's advantage over common kinetic resolution is a theoretical yield of the enantiomerically enriched acetates of 100%. A monomeric ruthenium complex later introduced is able to racemize alcohols in under 10 min at room temperature with a low catalyst loading of 0.5 mol% (*Angew. Chem. Int. Ed.* **2004**, 43, 6535). This catalyst is still the benchmark for the racemization of secondary alcohols.

Comment: Bäckvall's dynamic kinetic resolution (DKR) is the first example of a dual catalytic system combining transition-metal and enzyme catalysis. From a mechanistic point of view, a slippage of the Cp ring from η^5 - to η^3 -coordination to form a free coordination site was initially assumed in the racemization process, but computations as well as mechanistic experiments strongly suggest a CO dissociation mechanism (*Acc. Chem. Res.* **2013**, 46, 2545).