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One-Pot Zinc-Promoted Asymmetric Alkynylation/Brook-Type Rearrangement/Ene–Allene Cyclization: Highly
Selective Formation of Three New Bonds and Two Stereocenters in Acyclic Systems

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Tandem Enantioselective Zinc-Promoted Reaction

Category

Metal-Catalyzed
Asymmetric
Synthesis and
Stereoselective
Reactions

Key words

zinc

Brook
rearrangement

alkynylation

SYNFACT
of the month

Selected examples:

Allenyl Zn-Brook rearrangement

Significance: In a one-pot operation, two stereo-centers and three new bonds were created with high selectivity. The reaction proceeds through a sequence of asymmetric alkynylation of an acyl silane, tandem Brook-type rearrangement, ene–allene cyclization, addition of an electrophile, and finally oxidation. It will be extremely useful in organic synthesis, and it is a new approach to synthetic transformations.

Comment: Quantum mechanical calculations show that this method passes through an allenyl Zn-Brook rearrangement and that this transformation bypasses the intermediate derived from the classic [1,2]-Brook rearrangement. This important finding nicely rationalizes the observation that the rearrangement proceeds without racemization.

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