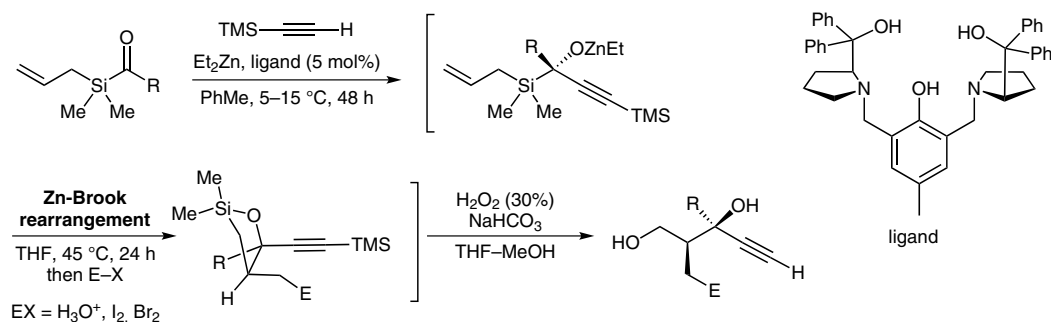


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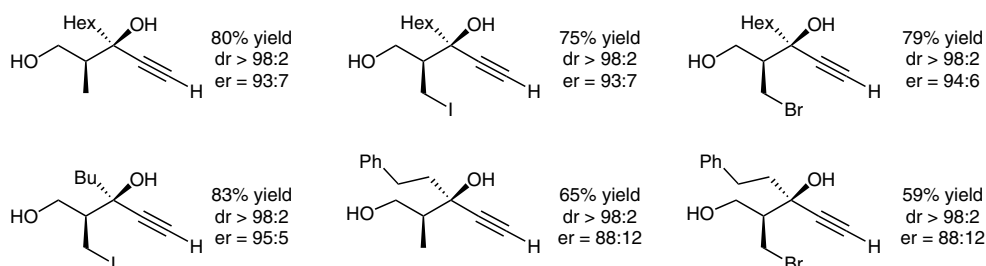
One-Pot Zinc-Promoted Asymmetric Alkynylation/Brook-Type Rearrangement/Ene-Allene Cyclization: Highly  
Selective Formation of Three New Bonds and Two Stereocenters in Acyclic Systems

*Angew. Chem. Int. Ed.* **2013**, *52*, 13717–13721.

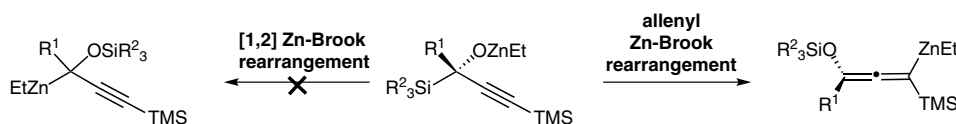
## Tandem Enantioselective Zinc-Promoted Reaction



### Selected examples:



### Allenyl Zn-Brook rearrangement



**Significance:** In a one-pot operation, two stereocenters 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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