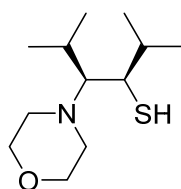


ZIRCONIUM IN THE CROWN. ENANTIOSELECTIVE ALKENYLATION OF ALDEHYDES WITH PROTECTED PROPARGYLIC ALCOHOLS IN THE PRESENCE OF CROWN ETHER: A NOVEL APPROACH TO THE INHIBITION OF ACHIRAL BACKGROUND REACTIONS

Tomasz Bauer, Benon Maliszewski

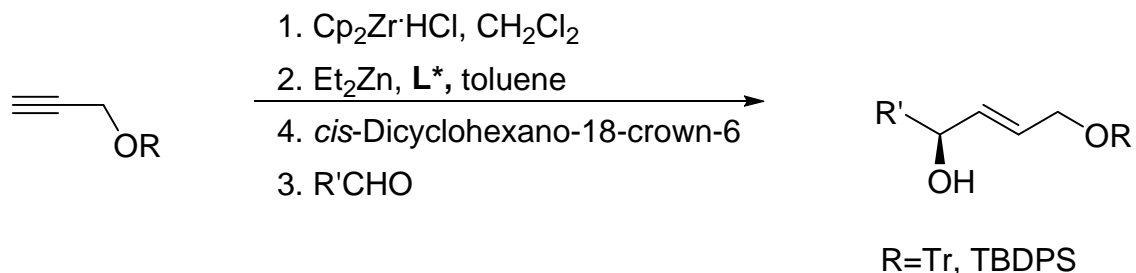
Faculty of Chemistry, University of Warsaw
ul. Ludwika Pasteura 1, 02-093 Warszawa
tbauer@chem.uw.edu.pl

The first enantioselective alkenylation of aldehydes with protected propargylic alcohols catalyzed by chiral amino thiol has been developed. The best results were obtained for the hydrozirconation-transmetalation to zinc protocol in the presence of an amino thiol L^* as a chiral ligand.



L^*

The key element of the method is the first use of crown ether *cis*-dicyclohexano-18-crown-6 as achiral background reaction inhibitor. The enantioselectivity of the reaction performed in the presence of the crown ether was substantially higher than in the absence of this additive and the enantiomer ratio exceeded 98:2.



The reaction in the presence of the cheaper 18-crown-6 ether is only slightly less selective. So the use of this less expensive additive can be considered, especially for the larger scale reactions. The highest enantiomeric ratio was observed for aromatic aldehydes, particularly benzaldehydes substituted with electron-withdrawing substituents; the position of the substituent in the phenyl ring did not influence the enantioselectivity. The reactions with aliphatic, cycloaliphatic and α, β – unsaturated aldehydes were less selective.