

SURPRISINGLY SIMPLE CATALYTIC ACCESS TO STEREODEFINED FULLY-SUBSTITUTED ALDEHYDE ENOLATES

Itai Massad, Heiko Sommer, Ilan Marek

Schulich Faculty of Chemistry, Technion-Israel Institute of Technology,
32000 Haifa, Israel

Fully-substituted enolates (enolates bearing two substituents at the α -carbon) are valuable intermediates for the synthesis of complex chiral molecules, rendering their stereoselective synthesis an important goal. Herein, we demonstrate a conceptually simple yet powerful approach towards fully-substituted enolates, utilizing olefin isomerization as the key strategy. Using an Ir-based olefin isomerization catalyst, 2-substituted allyl silyl ethers are stereoselectively transformed to fully-substituted aldehyde-derived silyl enol ethers, a previously elusive class of enolates. The developed procedure employs low catalyst loadings, displays a broad substrate scope and affords the products with consistently high yields and stereoselectivities, without requiring column chromatography. Preliminary mechanistic studies support a 1,3-hydride shift mechanism and provide insight into the strong influence of the number of phosphine ligands on the nature of the active catalyst, revealing an interesting dichotomy between two competing catalytic cycles. Finally, by exploiting the mechanism and source of stereocontrol in the isomerization process, we have been able to form either of the two possible stereoisomers of a given enolate with high stereoselectivities, starting from regioisomeric substrates.