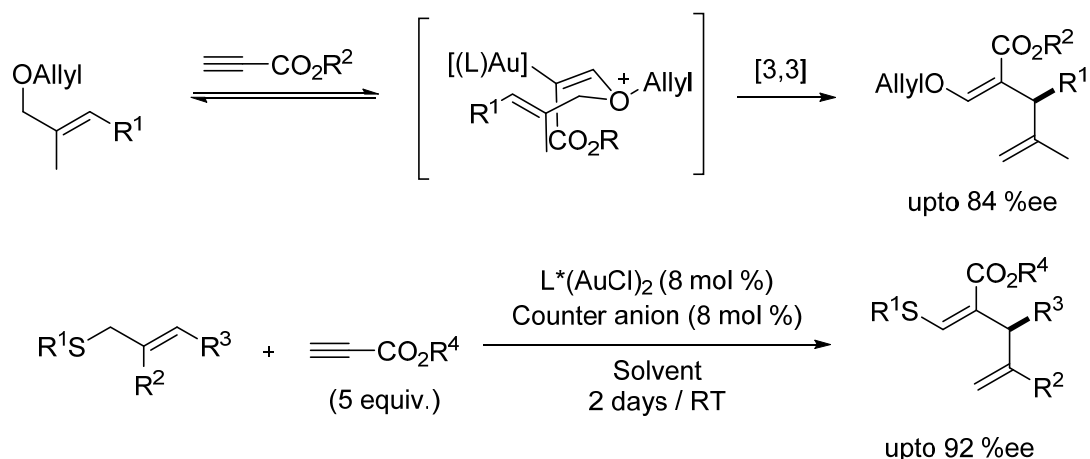


ASYMMETRIC [3,3]-SIGMATROPIC REARRANGEMENT IN GOLD(I)-CATALYZED INTERMOLECULAR CARBOALKOXYLATION

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Enantioselective gold-catalyzed catalysis is challenging, especially in an intermolecular mode, because of the linear coordination geometry of the alkyne-gold(I) complex where the chiral ligand lies away from the reaction site. Promoted by our recent success in promoting intermolecular enantioselective coupling of propiolates and alkenes [1], we embarked on the enantioselective reaction between allyl ethers and propiolates [2], where the reaction proceeded through *O*-attack of allyl ether, followed by a [3,3]-sigmatropic rearrangement. In this reaction, allyl ethers provided the corresponding products with upto 84 % ee. Interestingly, allyl sulfides displayed a complementary scope of the migrating allyl moiety and gave upto 92 % ee of the rearranged products.



[1] Kim, H.; Choi, S. Y.; Shin, S. *Angew. Chem. Int. Ed.* **2018**, *57*, 13130.

[2] Racemic version: (a) Jun, J.; Yeom, H. -S.; An, J. -H.; Shin, S. *Beilstein J. Org. Chem.* **2013**, *9*, 1724; (b) Park, S. R.; Kim, C.; Kim, D. -G.; Thrimurtulu, N.; Yeom, H. -S.; Jun, J.; Shin, S.; Rhee, Y. H., *Org. Lett.* **2013**, *15*, 1166.