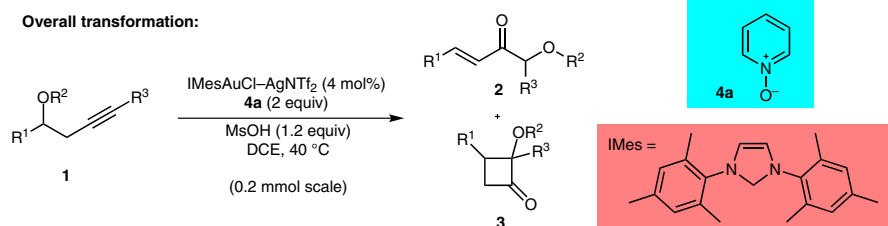


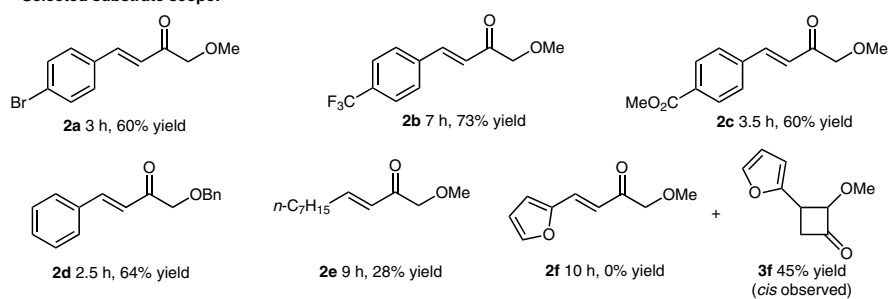
M. XU, T.-T. REN, C.-Y. LI* (ZHEJIANG SCI-TECH UNIVERSITY, HANGZHOU, P. R. OF CHINA)

Gold-Catalyzed Oxidative Rearrangement of Homopropargylic Ether via Oxonium Ylide
Org. Lett. **2012**, *14*, 4902–4905.

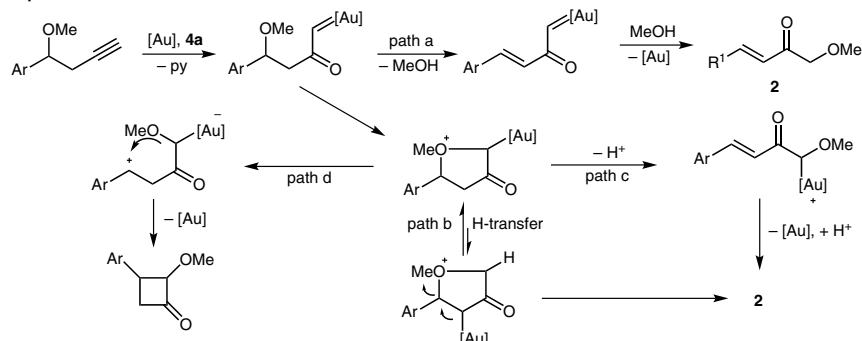
Homopropargylic Ether Rearrangement via Gold Catalysis



Selected substrate scope:



Proposed mechanism:



Significance: Gold catalysis has emerged as a powerful platform to conduct complex organic transformations. Specifically, the implementation of gold carbenoids has shown great promise in synthetic planning. These useful intermediates offer a convenient alternative to generate metal carbenes which are traditionally obtained from diazo compounds. The authors utilize these intermediates to synthesize α,β -unsaturated carbonyl compounds from homopropargylic ethers.

Comment: The authors report a silver-assisted gold(I)-catalyzed carbonyl synthesis. In an effort to obtain cyclobutanes **3** via a [1,2]-shift mechanism (path d), the authors unexpectedly obtained the corresponding α,β -unsaturated carbonyl compounds **2**. Control experiments show that neither IMesAuCl, nor AgNTf₂ or HNTf₂ alone could catalyze the reaction. The scope of the reported reaction is quite broad; however, yields are generally moderate to good. In some instances cyclobutanones are obtained as the major product.

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