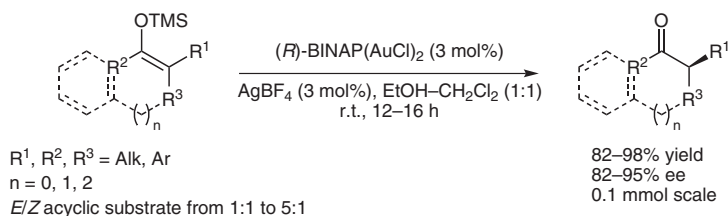
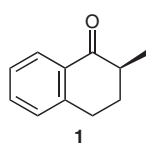


C. H. CHEON, O. KANNO, F. D. TOSTE* (UNIVERSITY OF CALIFORNIA, BERKELEY, USA)
Chiral Brønsted Acid from a Cationic Gold(I) Complex: Catalytic Enantioselective Protonation of Silyl Enol Ethers of Ketones
J. Am. Chem. Soc. **2011**, *133*, 13248-13251.

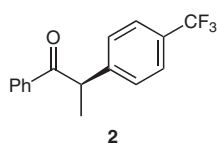
Gold-Catalyzed Enantioselective Protonation



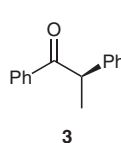
Selected examples:



96% yield
93% ee



E/Z^a = 1:1
92% yield
92% ee



E/Z = 2:1, 97% yield, 92% ee
E/Z = 3:1, 96% yield, 90% ee

^a refers to *E/Z* ratio of substrate

Significance: The catalytic enantioselective protonation of silyl enol ethers was realized via a cationic gold-activated Brønsted acid. While enantioselective protonations of cyclic silyl enol ethers of ketones are known (see Review below), no prior precedents on Brønsted acid catalyzed protonation existed for the acyclic variants.

Review: J. T. Mohr, A. Y. Hong, B. M. Stoltz
Nat. Chem. **2009**, *1*, 359-369.

Comment: The cationic gold(I) is proposed to complex with the alcohol and acidify the hydroxyl proton forming a Brønsted acid. The possibility of AgBF₄·BINAP-mediated protonation was ruled out as the silver complex was unreactive. However, excellent yields and ee values were achieved regardless of the *E/Z* ratio of the silyl enol ethers **2** and **3**. Mechanistic investigations suggest that the catalyst approaches the substrate from the same prochiral face with respect to each geometric isomer.

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Category

Metal-Catalyzed
Asymmetric
Synthesis and
Stereoselective
Reactions

Key words

cationic gold

enantioselective
protonation

silyl enol ethers

SYNFACTS
of the month

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1195