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Chiral Brønsted Acid from a Cationic Gold(I) Complex: Catalytic Enantioselective Protonation of Silyl Enol Ethers of Ketones

**Gold-Catalyzed Enantioselective Protonation**

![Chemical structure]

**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.


**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.

**Selected examples:**

- **1**
  - 96% yield
  - 93% ee

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

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

* refers to E/Z ratio of substrate