Asymmetric Vinylogous Mukaiyama–Michael Reaction via Iminium Catalysis

**Significance:** The authors report a highly enantio- and diastereoselective vinylogous Mukaiyama–Michael reaction of acyclic dienol silyl ethers 2 to various enals 1 by employing a Jørgensen–Hayashi catalyst. 1,7-Dicarbonyl compounds 3 are obtained under mild reaction conditions with good to excellent yield and remarkable regioselectivity. Z/E-Configured γ-methyl-substituted dienol silyl ethers are selectively converted into the anti and syn products 3 with excellent enantioselectivity.

**Comment:** Vinylogous Michael reactions of dienol derivatives can form a C–C bond with high regio- and stereoselectivity in the presence of a chiral catalyst. However, a catalytic enantioselective process of this reaction with acyclic nucleophiles and enals was elusive since the reaction can produce a number of regio- and stereoisomers. Herein, the catalyst nicely operates presumably by forming an imminium species with enal 1 to induce 1,4-addition of nucleophile 2 with high γ-selectivity.

**Selected examples:**

- 74% yield, er = 99.5:0.5
- 72% yield, er = 99.5:0.5
- 90% yield, er > 99.5:0.5
- 50% yield, er = 85.5:14.5
- 77% yield, dr = 92:8 er = 99.5:0.5 from 3Z-2
- 65% yield, dr = 77:23 er = 98:2 from 3E-2 in ethanol