Category

Organo- and Biocatalysis

Key words vinylogous

reaction

catalyst enals

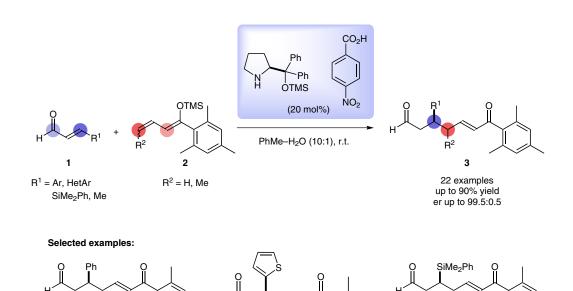
Mukaiyama-Michael

Jørgensen-Hayashi

dienol silyl ethers

V. GUPTA, S. SUDHIR V, T. MANDAL, C. SCHNEIDER* (UNIVERSITÄT LEIPZIG, GERMANY) Organocatalytic, Highly Enantioselective Vinylogous Mukaiyama-Michael Reaction of Acyclic Dienol Silyl Ethers *Angew. Chem. Int. Ed.* **2012**, *51*, 12609–12612.

Asymmetric Vinylogous Mukaiyama-Michael Reaction via Iminium Catalysis



74% yield, er = 99.5:0.5

50% yield, er = 85.5:14.5

72% yield, er = 99.5:0.5

77% yield, dr = 92:8 er = 99.5:05 from 3*7*-2

90% yield, er > 99.5:0.5

65% yield, dr = 77:23 er = 98:2 from 3*E*-**2** in ethanol

Significance: The authors report a highly enantioand diastereoselective vinylogous Mukaiyama— Michael reaction of acylic 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 regioand 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 $\bf 1$ to induce 1,4-addition of nucleophile $\bf 2$ with high γ -selectivity.

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