Category

Metal-Catalyzed Asymmetric Synthesis and Stereoselective Reactions

Key words

tautomerization

carbonylation

Tamao oxidation

T. J. HARRISON, P. M. A. RABBAT, J. L. LEIGHTON* (COLUMBIA UNIVERSITY, NEW YORK, USA)

An 'Aprotic' Tamao Oxidation/*Syn*-Selective Tautomerization Reaction for the Efficient Synthesis of the C(1)–C(9) Fragment of Fludelone

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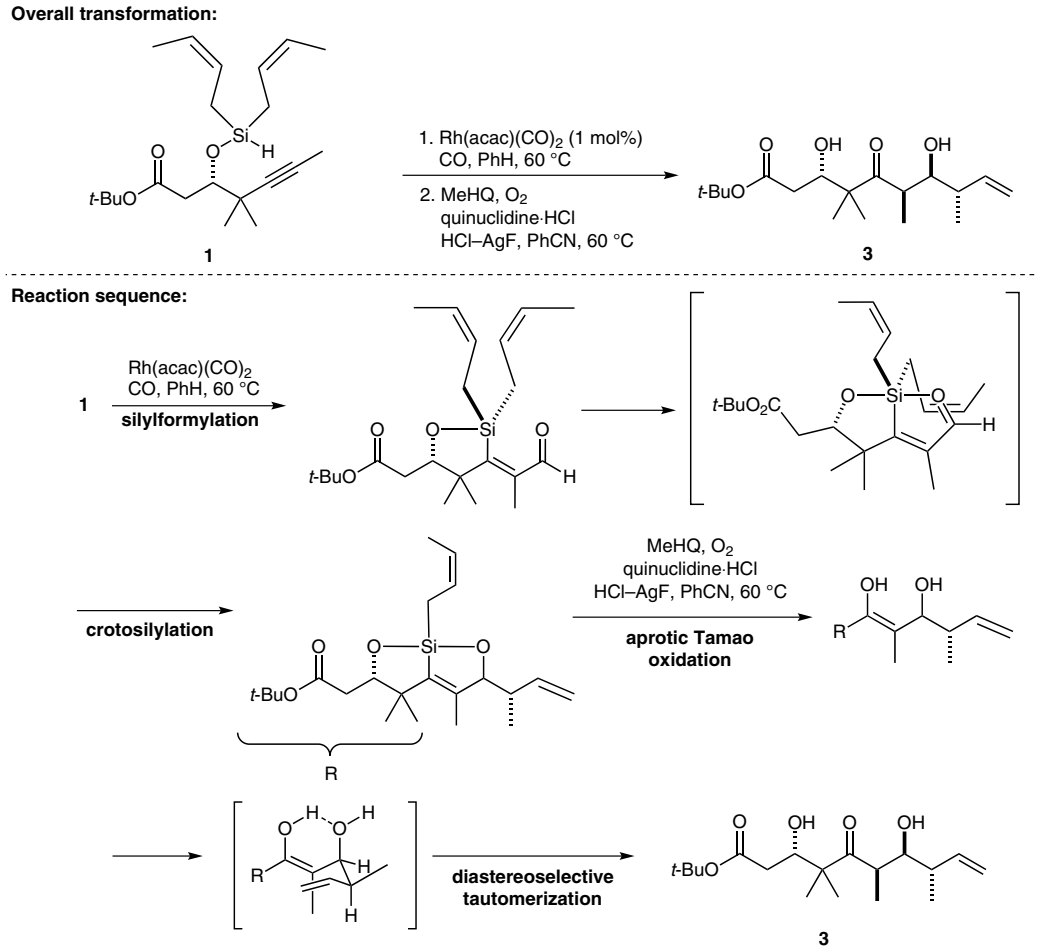
A Rhodium(I)-Catalyzed Silylformylation–Crotosilylation–Tamao Oxidation



Significance: Access to complex polyketide fragments typically consists of complex stepwise syntheses. Recent advances, including asymmetric crotylation and aldol cascades, have allowed chemists to synthesize extremely complex polyketide fragments with good step- and redox-economy, as well as minimal use of protecting groups. In this regard, silylformylation and silylcrotylation have emerged as complementary methods towards this end.

Comment: The authors report the synthesis of the C1–C9 fragment of fludelone, a polyketide natural product. The authors elegantly utilize their silylformylation–crotosilylation chemistry (*J. Am. Chem. Soc.* **2000**, *122*, 8587) in conjunction with this newly developed aprotic Tamao oxidation–diastereoselective tautomerization methodology to access this ketone containing four stereocenters, three of which are contiguous.

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