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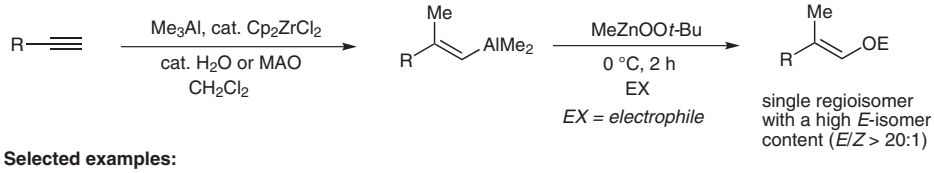
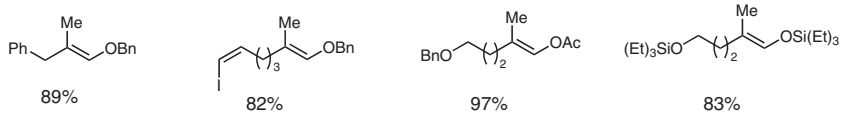
Preparation of Substituted Enol Derivates from Terminal Alkynes and Their Synthetic Utility
J. Am. Chem. Soc. **2008**, *130*, 7828-7829.

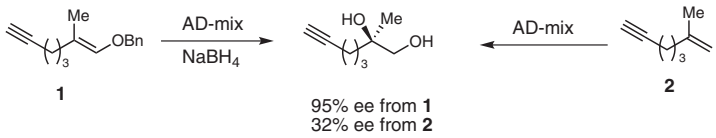
Synthesis of Substituted Enol Ethers and Their Synthetic Application



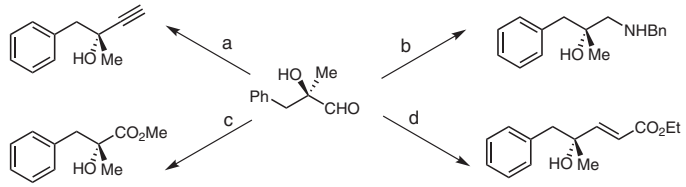
Selected examples:



Asymmetric dihydroxylation (AD) of enol benzoates:



Transformations of α-hydroxy aldehydes:



Reagents and conditions: (a) $(MeO)_2POCN_2COMe$, K_2CO_3, MeOH, 0 °C to r.t.; (b) $BnNH_2$, toluene, 4 Å MS, 105 °C; (c) I_2, KOH, MeOH, 0 °C; (d) $Bu_3PCH_2CO_2EtBr$, $NaHCO_3$, toluene, 90 °C.

Significance: The authors describe the preparation for trisubstituted enol derivatives via tandem carbometalation–oxygenation of terminal alkynes. The enol derivatives were isolated as a single regioisomer with a high *E*-selectivity (*E*/*Z* > 20:1). Stereodefined enol ethers can undergo asymmetric dihydroxylation to yield optically active α-hydroxy aldehydes. Finally, α-hydroxy aldehydes were shown to undergo homologation to a terminal alkyne, reductive amination, oxidation and olefination.

Comment: Recently, the Ready group reported carbocupration–oxygenation of terminal alkynes as an alternative method for trisubstituted enol derivatives (*Org. Lett.* **2005**, *7*, 5681). However, methyl-substituted products were not accessible by this method because of inefficient methyl-cupration of alkynes. In this paper, they described a general method for obtaining methyl-substituted enol ether and explored the asymmetric transformations of stereodefined enol derivatives. Although it is a simple idea, it works nicely. This method will have broad utility in the future.

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Synfacts 2008, 9, 0939-0939 Published online: 22.08.2008
DOI: 10.1055/s-2008-1078005; **Reg-No.:** H09108SF