

Stereodivergent Synthesis of 2,3-Disubstituted 1,4-Dicarbonyls

Category

Organo- and Biocatalysis

Key words

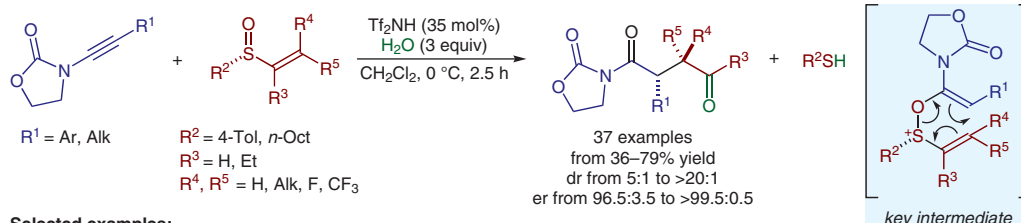
dicarbonyl compounds

stereodivergent synthesis

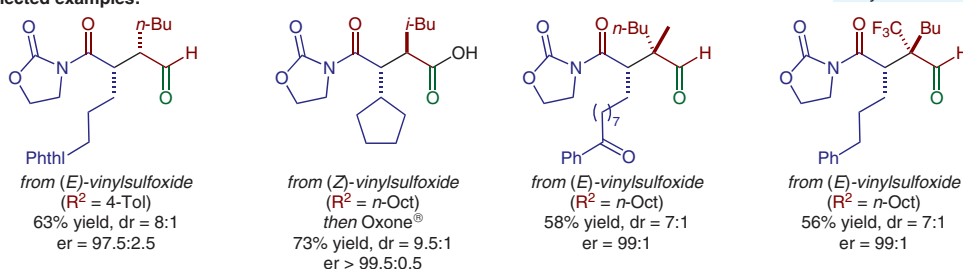
sulfonium rearrangement

vinyl sulfoxides

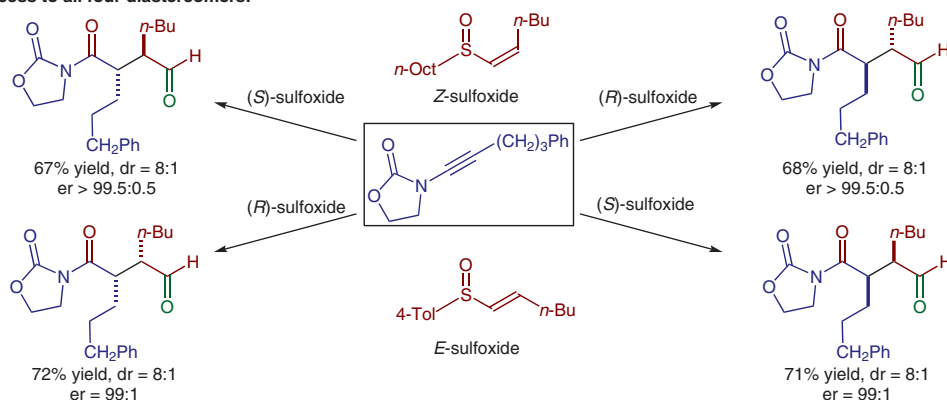
ynamides



Selected examples:



Access to all four diastereomers:



Significance: Maulide and co-workers report an acid-catalyzed [3,3]-sigmatropic sulfonium rearrangement toward acyclic polysubstituted 1,4-dicarbonyls in excellent yields and stereoselectivities. The method employs simple starting materials, i.e. ynamides and vinyl sulfoxides, the latter of which govern both the absolute configuration (via the stereochemistry at sulfur) and the relative configuration (via the double-bond geometry of the key intermediate). The authors exploit this substrate control to access all four possible diastereomers in high selectivities.

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Comment: The synthetic pursuit of 2,3-disubstituted 1,4-dicarbonyl compounds indeed represents a longstanding endeavor in organic synthesis (see, for example: M. P. DeMartino, K. Chen, P. S. Baran *J. Am. Chem. Soc.* **2008**, *130*, 11546). The highlighted method provides access to such compounds in a stereodivergent manner, even dictating the relative and absolute configuration for substrates containing all-carbon quaternary stereocenters along the chain. The method may not be described as ‘atom economical’, but it certainly holds promise as a robust approach to this highly sought-after motif.