

STEREODIVERGENT SYNTHESIS OF 1,4-DICARBONYLS VIA A TRACELESS SULFONIUM REARRANGEMENT

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The synthesis of 1,4-dicarbonyl compounds remains an open challenge for organic chemists owing to the need to combine synthons of ‘unnatural’ polarity. In particular, diastereo- and enantioselectivity as well as the inclusion of quaternary centres are rarely addressed issues, despite the abundance of richly decorated 1,4-dicarbonyl motifs in natural products and drug scaffolds.

Following earlier investigations of sulfoxide rearrangements,[1,2] we have now developed a new protocol that allows stereodivergent access to all possible four stereoisomers of the 1,4-dicarbonyl motif, selectively and predictively (Figure 1).[3] This Brønsted acid-catalyzed reaction uses easily prepared vinyl sulfoxides to construct the new key carbon-carbon bond through chirality transfer from sulfur to carbon in a pivotal, traceless charge-accelerated sulfonium rearrangement.

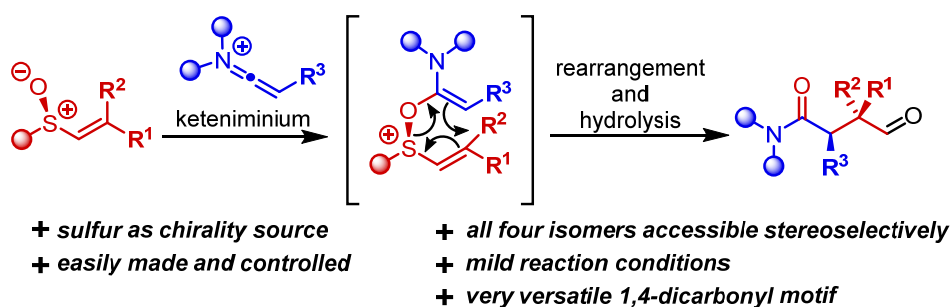


Figure 1. Vinyl sulfoxides as traceless reagents in the synthesis of 1,4-dicarbonyls.

The scope and limitations of this method, amenable to the stereoselective formation of all-carbon quaternary centres, shall be outlined.

[1] B. Peng, X. Huang, L.-G. Xie, N. Maulide, *Angew. Chem. Int. Ed.* **2014**, *53*, 8718.

[2] D. Kaldre, B. Maryasin, D. Kaiser, O. Gajsek, L. Gonzalez, N. Maulide, *Angew. Chem. Int. Ed.* **2017**, *56*, 2212.

[3] D. Kaldre, I. Klose, N. Maulide, *Science* **2018**, *361*, 664.