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Revisiting the Reactions of Sulfur Ylides with Acetylenic Esters: Facile and Stereoselective Synthesis of Electron-Deficient Trisubstituted 1,3-Dienes, α-Carbonyl Vinyl Sulfoxides and α-Carbonyl Vinyl Sulfoxonium Ylides

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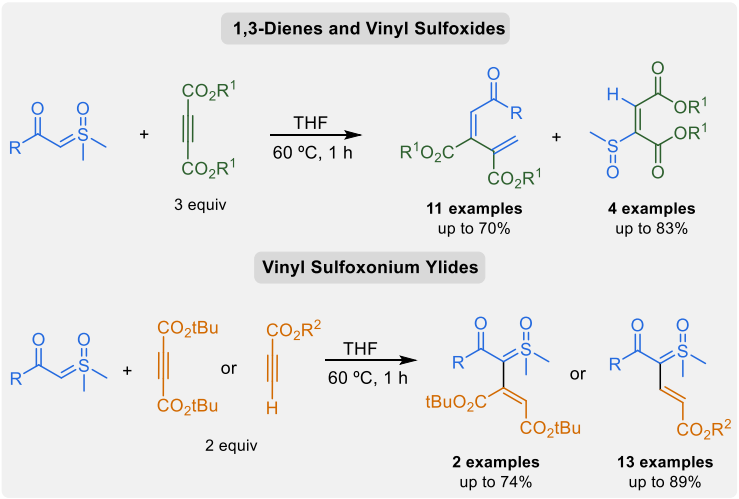
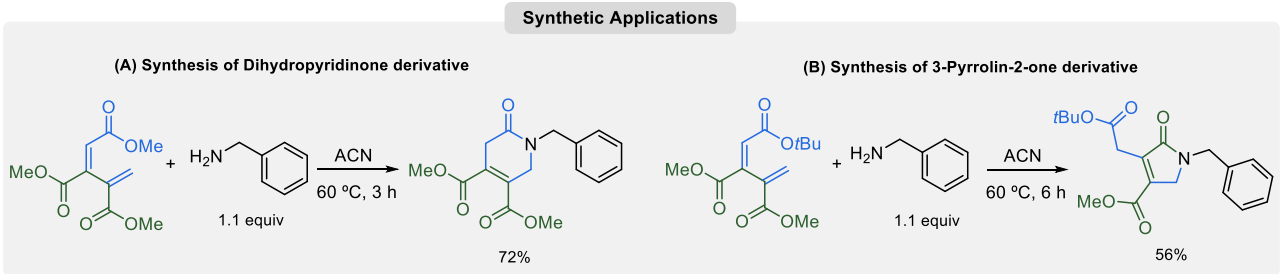
ABSTRACT

1,3-dienes and vinyl sulfoxides constitute the framework of numerous bioactive natural and synthetic compounds, often playing a crucial role as intermediates in total synthesis.[1-4] Continuing our previous study of conjugate additions using α-carbonyl sulfoxonium ylides,[5] we came across an interesting transformation when dimethyl acetylenedicarboxylate (DMAD) was employed as a Michael acceptor. Trisubstituted electron-deficient 1,3-dienes and α-carbonyl vinyl sulfoxides were obtained for the first time from these sulfur ylides, in a stereospecific manner, achieving yields of up to 70% and 83%, respectively. The proposed mechanism involves two sigmatropic rearrangements and the generation of sulfenic acid, leading to the formation of both products. Selected dienes were subsequently utilized in the synthesis of novel nitrogen heterocycles through conjugate addition reactions. On the other hand, when di-*tert*-butyl acetylenedicarboxylate (D*t*BAD) or alkyl propiolates were evaluated, the isolated product arose from the classical Michael addition, yielding α-carbonyl vinyl sulfoxonium ylides in yields of up to 89%.





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