

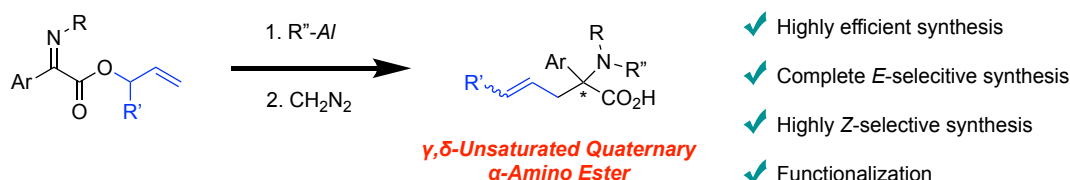
Highly Stereoselective Synthesis of γ,δ -Unsaturated Quaternary α -Amino Esters via the Tandem *N*-Alkylation/Claisen Rearrangement of α -Imino Allylesters

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γ,δ -Unsaturated α -amino acids are important molecular backbones present in many natural products and pharmaceuticals such as antithrombotic agents and antibacterial agents. γ,δ -Unsaturated α -amino esters are also important building blocks for the synthesis of α -methylene- γ -butyrolactone or pyrrolidine, which are the core units in many natural products. Therefore, much attention has been paid to the development of practical and efficient approaches to obtain γ,δ -unsaturated α -amino acid derivatives.

Previously, we have reported umpolung reactions for α -imino esters (*N*-alkylation) and integrated various reactions using *N*-alkylation.^{1,2} These methods allow the free introduction of various substituents on nitrogen and can yield α -amino acid derivatives in one-pot reactions. In addition, we have previously reported a tandem *N*-alkylation/Claisen rearrangement of α -iminoallyl esters to give γ,δ -unsaturated α -amino esters; however, there are some limitations to this reaction.³ Herein, we would like to report a more efficient synthetic method to achieve γ,δ -unsaturated quaternary α -amino esters using a broad range of substrates. In addition, a highly *E*- and *Z*-selective Claisen rearrangement was achieved by controlling the reaction conditions and substrates. Moreover, further transformations of the products was achieved.



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