

Zinc Iodide Catalyzed Allenylation of Terminal Alkynes towards Trisubstituted Allenes under Conventional or Microwave Irradiation Conditions

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The chemistry of allenes has significantly evolved, over the past decades. The synthesis of allenes is often approached by employing alkynes as the primary starting material. However, most of the known protocols require many steps, also using complex starting materials. In this work, we present a straightforward, user-friendly and efficient protocol for the one pot, ZnI₂-catalyzed allenylation of terminal alkynes with pyrrolidine and ketones, towards trisubstituted allenes (Figure 1). Trisubstituted allenes can be obtained under either conventional heating or microwave irradiation conditions, which significantly reduces reaction time, while employing a single, sustainable, widely-available, and low-cost metal salt catalyst. All reactions are carried out under solvent-free conditions. Among others, synthetically valuable allenes, bearing functionalities such as amide, hydroxyl, or phthalimide can be efficiently prepared. Mechanistic experiments, including kinetic isotope effect measurements, and DFT calculations, suggest a rate determining [1,5]-hydride transfer during the transformation of the intermediate propargylamine to the final allene.

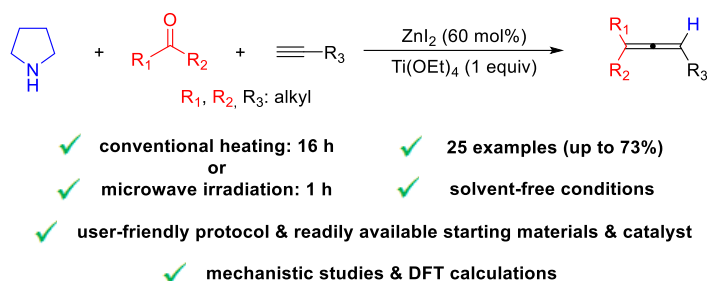


Figure 1: Allenylation of terminal alkynes with pyrrolidine and ketones, under ZnI₂ catalysis.

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