BRØNSTED ACID-CATALYZED ASYMMETRIC [3,3]-SIGMATROPIC REARRANGEMENTS OF SULFONIUMS AND APPLICATIONS

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Homogeneous catalysis has emerged as a powerful method in organic synthesis due to the unique ability of Lewis acids or Brønsted acids to activate unsaturated bonds. In addition, [3,3]-sigmatropic rearrangement is standing at the central position of organic synthesis for efficient and selective generation of carbon-carbon σ-bond.[1] Recently, in the laboratory, we have developed the synthesis of cyclopentenones with C4-quaternary stereocenters through a stereospecific gold-catalyzed [3,3]-sigmatropic rearrangement of sulfoniums, using substrates such as vinylsulfoxides and propargyl silanes.[2]

In the present work, we proposed a triflic acid-catalyzed reaction by using allenyl ketones or allenenoates for the synthesis of new highly functionalized C4-chiral cyclopentenones (Figure 1). The substituted cyclopentenones were directly isolated, without the need of a base-promoted aldolization step. Up to 18 examples were exemplified, with generally good yields (30% < yields < 85%) and excellent transfer of chirality from the sulfoxide substrate to the final product (92% < ee < 99%). Diels-Alder reaction and [3+2] cycloaddition reactions can be carried out in further transformations. Additionally, these cyclopentenones showed good biological activity against HL60 cells.[3]

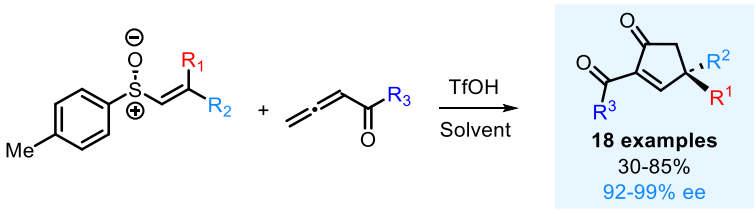

Figure 1: Brønsted acid-catalyzed [3,3]-sigmatropic rearrangements.

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