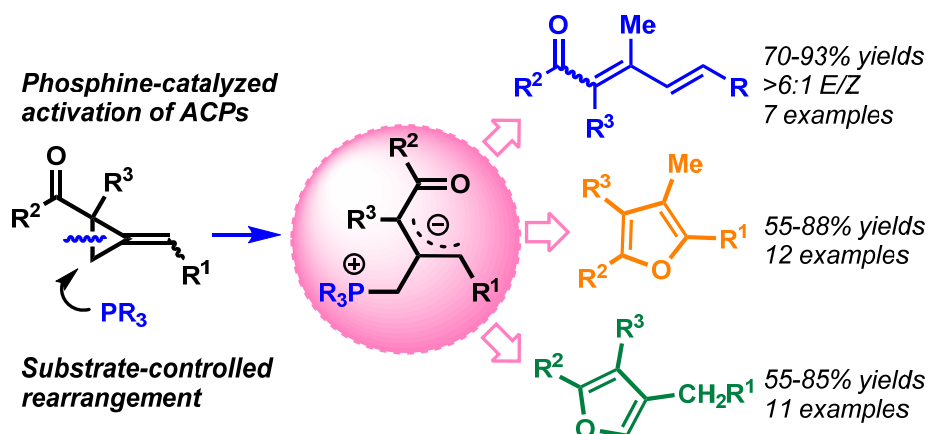


PHOSPHINE-CATALYZED ACTIVATION OF ALKYLIDENECYCLOPROPANES: REARRANGEMENT TO FORM POLYSUBSTITUTED FURANS AND DIENONES

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Alkylidenecyclopropanes (ACPs) are a type of extremely versatile yet readily available building blocks in organic synthesis [1]. By virtue of significant ring strain, a plethora of ring opening reactions of ACPs have been developed, typically by transition metal catalysis, Lewis acid catalysis, radical induced reactions, and thermally induced cyclizations. However, to the best of our knowledge, the organocatalytic activation of ACPs has not been reported. To this end, we envisioned that an organocatalytic strategy for the activation of ACPs might be possible by utilizing the homoconjugate addition process [2]. Herein, we report a phosphine-catalyzed ring-opening of electron-deficient ACPs in three types of substrate-controlled rearrangements of alkylidenecyclopropylketones, which chemoselectively afford tri- and tetrasubstituted furans, and trisubstituted dienones in good yields. Importantly, this organocatalytic activation of ACPs stands in contrast with previous transition metal-catalyzed counterparts [3] which significantly enriches the synthetic potential of ACPs. In addition, this chemistry broadens the scope of phosphine catalysis [4] by introducing a new subset of reactive substrates.

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