Vinylphosphonium salt-mediated reactions: a one-pot condensation approach for the highly *cis*-selective synthesis of *N*-benzoylaziridines and the green synthesis of 1,4,2-dioxazoles as two important classes of heterocyclic compounds.

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An efficient, one-pot, and convenient approach for the reaction of the same precursors, trialkyl(aryl) phosphines, acetylene diesters, and benzhydroxamic acids has been developed to produce two important classes of heterocyclic compounds: *N*-benzoylaziridines and 1,4,2-dioxazoles. The strategy utilizes the intermediate solvation as a key step in product selectivity. The usefulness of the developed approach has been confirmed in the unprecedented highly *cis*-selective formation of the *N*-benzoylaziridines. In addition, the procedure provides a green alternative method for the synthesis of 1,4,2-dioxazoles employing a β-cyclodextrin nanoreactor in aqueous media.

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