Chemodivergent Synthesis of Isocoumarins and Isoquinolones by Rhodium-catalyzed Consecutive Reaction of *N*-Methoxybenzamide with *in situ* Generated Iodonium Ylides

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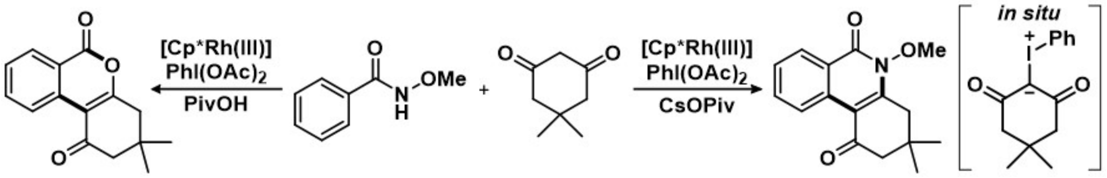
Over the past decade, transition metal-catalyzed direct C-H bond activation, insertion, and annulation reactions using diverse carbene precursors such as diazo compounds, sulfoxonium ylides, iodonium ylides, and others have been developed for the synthesis of various heterocyclic compounds.[1] However, almost all reactions required the preparation of carbene precursors from 1,3-dicarbonyl compounds in advance. In addition, attempts to use only 1,3-dicarbonyl compounds for catalytic construction of diverse heterocyclic scaffolds have been failed. In 2020, Li and co-workers first reported that Rh-catalyzed coupling reaction of benzoic acids with 1,3-dicarbonyl compounds gave isocoumarins, selectively, in which the generated iodonium ylides would give a carbene species.[2] Thus, the development of environmentally benign and atom-efficient catalytic synthesis of heterocyclic compounds using *in situ* generated carbene species from simple 1,3-dicarbonyl compounds is highly demanded.[3]

In a continuation of our study on catalytic synthesis of several *N*-heterocyclic compounds via C(sp^2)-H bond activation, we succeeded in developing novel Rh-catalyzed consecutive reaction, which consists of catalytic cleavage of C(sp^2)-H bond of *N*-methoxybenzamide to give a five-membered rhodacyclic intermediate, and insertion of *in situ* generated carbene species by only mixing 1,3-diketones with (diacetoxyiodo)benzene, followed by two-kinds of distinct intramolecular cyclization, enabled chemodivergent synthesis of isocoumarins and isoquinolones in one-pot. The two-kinds of distinct intramolecular cyclization pathways could be controlled, completely, by appropriate use of either Lewis acids (for isoquinolones) or carboxylic acids (for isocoumarins) in the presence of the same [Cp*$RhCl_2$]$_2$ catalyst.



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