

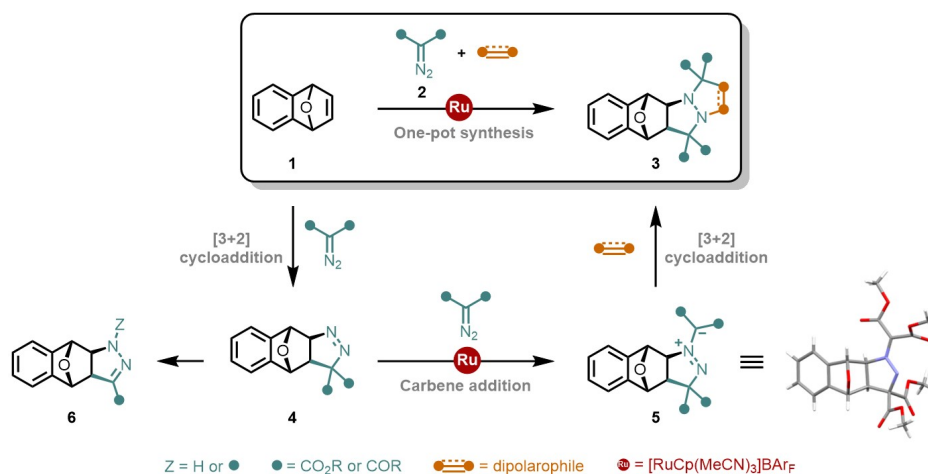
## CpRu-Catalyzed Multicomponent Synthesis of Polyheterocycles Pyrazolidines Through Cycloadditions and Metal-Carbene Addition

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Cyclopentadienyl-Ruthenium (II) complexes are known to efficiently promote the decomposition of diazo malonates and  $\alpha$ -diazo- $\beta$ -ketoesters to generate *Fischer*-type carbenes. These electrophilic intermediates form ylides in presence of various *Lewis* bases, such as cyclic ethers,<sup>[1]</sup> ketones,<sup>[2]</sup> and lactams,<sup>[3]</sup> among others. Subsequently, the reactive zwitterions can undergo different rearrangement or insertion reactions to obtain different classes of functionalized heterocycles.

Based on previous reactivities developed in our lab with oxonium<sup>[1]</sup> and ammonium<sup>[4]</sup> ylides, and in divergence with recently reported studies using 2,2,2-trifluorodiaoethane,<sup>[5]</sup> the reactivity of bicyclic ether **1** and diazomalonate **2** under ruthenium (II) catalysis was investigated. Herein, a fully-diastereoselective one-step synthesis of diaza polycyclic compounds **3** via a series of cascade reactions is obtained. More interestingly, this reaction can also be done stepwise, and each intermediate **4** and **5** can be isolated in high yields. Moreover, ylides **5** showed unusual stability, as they can be stored at room temperature under air conditions and can further react with various dipolarophiles to access symmetrical on non-symmetrical polycyclic pyrazolidines. In addition, the cycloadduct **4** can undergo rearrangements such as a 1,3-ester shift or a decarboxylation to afford corresponding pyrazolines scaffolds **6**. We thus report a direct methodology to access valuable N–N bond-containing heterocycles, which are presented in many natural products and bioactive molecules.<sup>[6]</sup>



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