FUSED AND SPIRO BICYCLES BY PHOTOCATALYZED RADICAL CYCLIZATIONS OF MALONATE ENOL ETHERS

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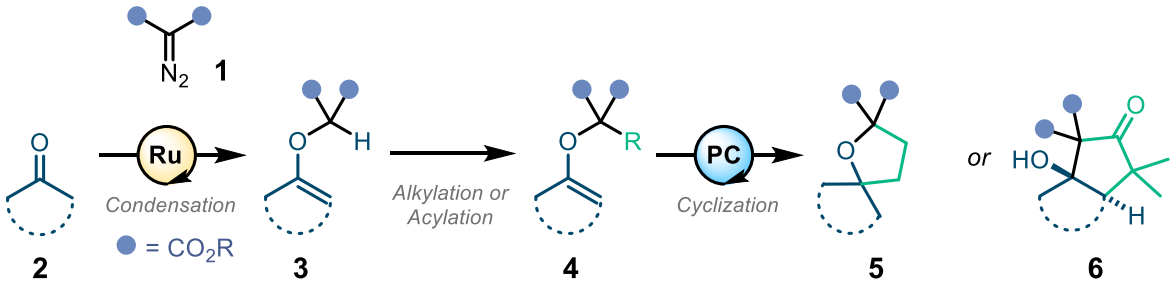
Diazo malonates **1** are among the most stable diazo reagents.[1] Yet, under metal catalysis, they decompose readily to form highly reactive electrophilic carbenes [2] that generate ylide intermediates upon trapping of *Lewis* bases.[3] In this context, with [CpRu(MeCN)$_3$][BAr$_F$] as catalyst,[4] ketones **2** and metal carbenes derived from diesters **1** condense to generate malonate enol ethers **3**.[5] These building blocks **3** present a bifunctional nucleophilic reactivity, that of enol and malonate moieties. Each functional group can be exploited separately but also in synergy to promote diverse annulation processes,[5] expanding the scope of cyclizations derived from carbonyl ylide intermediates.[2b, 2c] Playing on this dual reactivity of **3**, a novel post-functionalization strategy affords either spiro compound **5** or complex *trans* fused-bicycles **6** using visible-light photoredox catalysis or reductive photosynthesis.



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