Divergent Regio- and Enantioselective Synthesis of Spirocycles *via* Phenol-Directed Cobalt(III)-Catalyzed Dearomative Annulations with Alkynyl Triazenes

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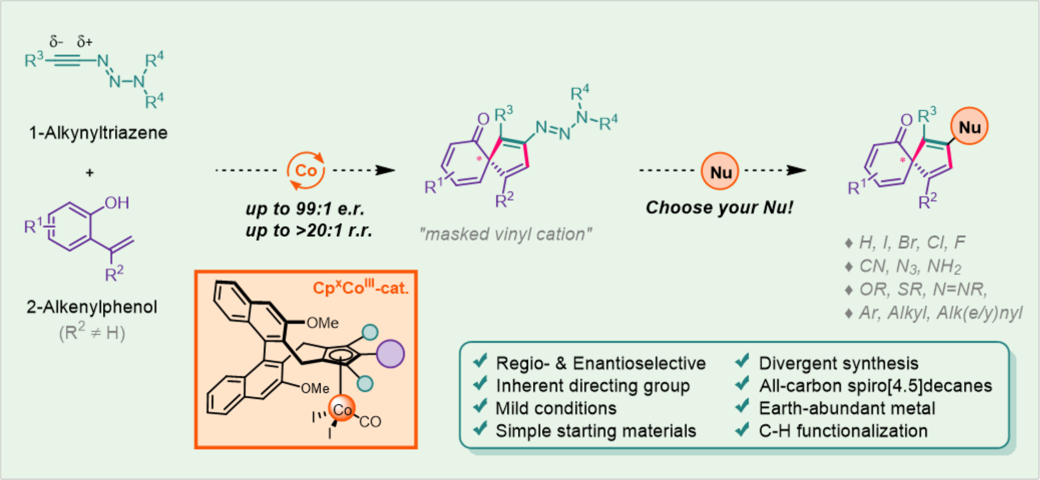
Answering the global call for sustainability, we aim to trade the use of precious noble metals in catalysis for Earth-abundant 3d-metals, such as cobalt, considering their vastly reduced environmental footprint, substantially lower cost, and significantly reduced toxicity.[1] Notably, it also holds tremendous potential, since they can display both similar as orthogonal reactivity patterns compared to their 4d- and 5d-congeners.

Herein, we disclose the ongoing development of a highly regio- and enantioselective dearomative [3+2] C-H annulation reaction of 2-alkenylphenols with 1-alkynyltriazenes, catalyzed by an Earth-abundant cobalt(III) complex bearing a tailored chiral cyclopentadienyl (Cp^x) ligand. The asymmetric transformation occurs under mild aerobic conditions, and provides rapid access to attractive all-carbon spiro[4.5]decane derivatives, using straightforward raw materials that are readily prepared *via* one-step or one-pot procedures. The obtained enantioenriched spirocycles possess substantial and divergent derivatization potential due to the presence of a valuable triazene moiety, which allows installing a plethora of other functionalities by tapping into its very broad reactivity portfolio.[2,3] Additionally, the use of a simple, inherent phenol directing group, which gets incorporated in the product, contributes further to the good step-economy and sustainability of this methodology.



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