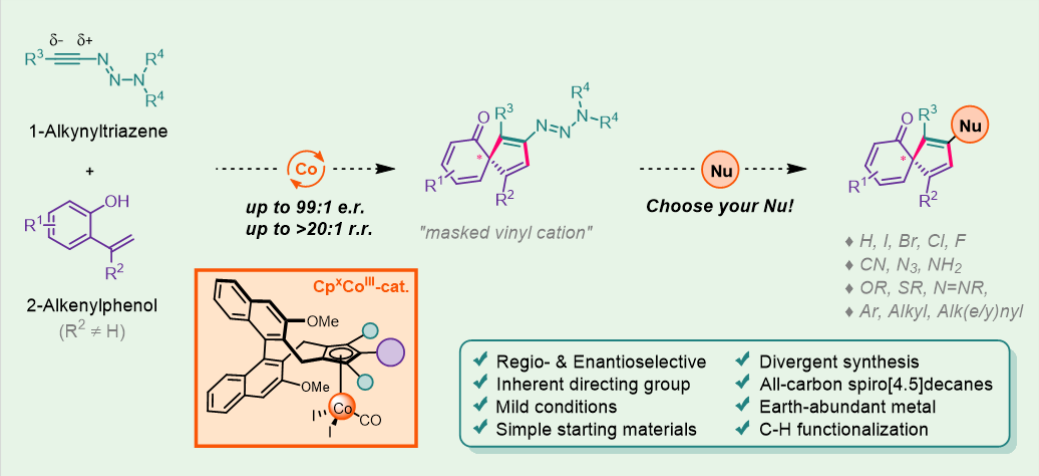
Divergent Regio- and Enantioselective Synthesis of Spirocycles *via* Phenol-Directed Cobalt(III)-Catalyzed Dearomative Annulations with Alkynyl Triazenes

B. Van Den Bossche[1], N. Cramer[1]*

[1]Ecole Polytechnique Fédérale de Lausanne (EPFL), Laboratory of Asymmetric Catalysis and Synthesis (LCSA), 1015 Lausanne, Switzerland

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.



[1] R. M. Bullock, J. G. Chen, L. Gagliardi, P. J. Chirik, O. K. Farha, C. H. Hendon, C. W. Jones, J. A. Keith, J. Klosin, S. D. Minteer, R. H. Morris, A. T. Radosevich, T. B. Rauchfuss, N. A. Strotman, A. Vojvodic, T. R. Ward, J. Y. Yang, Y. Surendranath, *Science* **2020**, *369*, eabc3183.
[2] D. Kossler, F. G. Perrin, A. A. Suleymanov, G. Kiefer, R. Scopelliti, K. Severin, N. Cramer, *Angew. Chem. Int. Ed.* **2017**, *56*, 11490–11493.
[3] J.-F. Tan, C. T. Bormann, F. G. Perrin, F. M. Chadwick, K. Severin, N. Cramer*J. Am. Chem. Soc.* **2019**, *141*, 10372–10383.