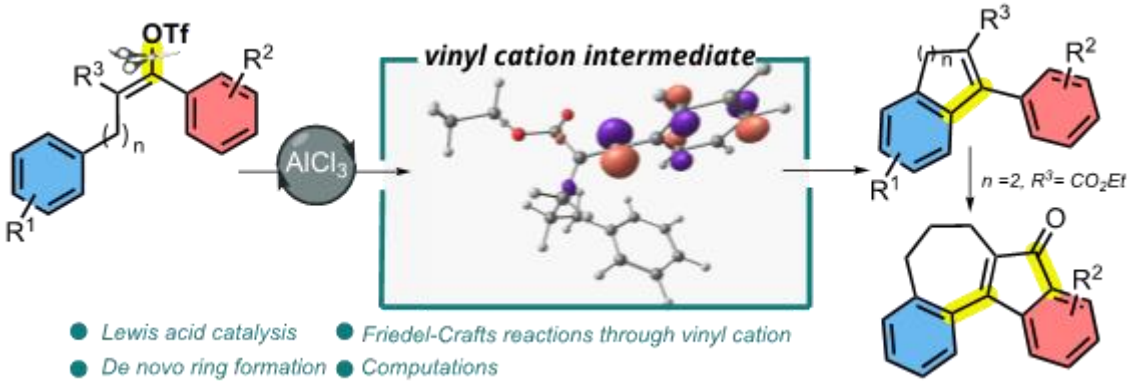
Aluminum-Catalyzed Intramolecular Vinylation of Arenes by Vinyl Cations

W. LIN. A. ALIX, V. GANDON, and C. BOUR.

ECM, ICMMO, Universite Paris-Saclay, UMR CNRS 8182, Batiment Henri Moissan, 91400, Orsay, France

From the preparation of pharmaceuticals to enzymatic construction of nature products, carbocations are central to molecular synthesis because of their fundamental properties and potent modes of reactivity. Trisubstituted cations are commonly used as electrophiles in many organic reactions while vinyl cations are neglected because they are uncontrollable.[1] Only very recently, the subject of new investigations into vinyl cations' physical and chemical properties led to new applications in homogeneous catalysis via vinyl cations intermediate.[2] In our previous work, we succeed in the bimolecular vinylation of arenes and direct S_N1 reaction by vinyl cations,[3] here we describe our group's updated progress concerning vinyl cations intermediate. This is a novel intramolecular vinylation of arenes catalyzed by aluminum(III) chloride, utilizing practical conditions and readily available vinyl triflates derived from 2-aceto-3-arylpropionates. DFT computations reveal a Lewis acid-driven mechanism involving triflate moiety abstraction to generate a reactive vinyl cation. An interesting de novo ring formation is observed and valuable application to synthesize bioactive molecule in this methodology.



References

[1] (a) T. Jin *Org. Lett.* **2020**, 22, 8920–8924; (b) L.-X. Wang *Org. Biomol. Chem*., **2021**, 19, 7690-7694; (c) Y. Xie. *Org. Chem. Front*. **2022**, 9, 4277-4286 P. Name *Journal,* **Year**, Vol, page1-page2

[2] (a) H. M. Nelson. *Science*, **2018**, 361, 381-387; (b) H. M. Nelson. *J. Am. Chem. Soc*, **2019**, 141, 9140-9144; (c) H. M. Nelson. *Science*, **2022**, 378, 1085-1091.

[3] (a) V. Gandon, B. Christophe. *Chem. Commun*, **2020**, 56, 6507; (b) V. Gandon, B. Christophe. *Org. Lett.*, **2022**, 24, 6978-6982