α-Selective Hydroboration of Alkynoate Esters Catalyzed by Ionic Liquids

P. Huninik, 1,2 J. Szyling, 1 A. Czapik, 2 J. Walkowiak 1

¹Center for Advanced Technologies, Adam Mickiewicz University, Uniwersytetu Poznańskiego 10, 61-614 Poznań, Poland.

²Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland.

pawhun@amu.edu.pl

Organoboron compounds play a pivotal role in organic chemistry, owing to the remarkable versatility of the C–B bond, which facilitates a wide range of transformative reactions, most notably the Suzuki–Miyaura cross-coupling.[1] Among these, alkenylboronates stand out as particularly effective substrates for cross-coupling processes. Beyond their utility as synthetic intermediates, organoboron compounds are increasingly recognized for their potential in medicinal applications, underscoring their value as both intermediates and final products. This dual significance drives the need for innovative methodologies in their synthesis and application. Transition metal-catalyzed hydroboration of alkynoate esters with pinacolborane offers an atom-economic route to these compounds. However, challenges such as high catalyst concentration, metal contamination, complex catalyst preparation, and poor stability hinder their practical use. Additionally, hydroboration of unsaturated C–C bonds faces selectivity issues due to possibility of forming different regioisomers. These limitations underscore the need for efficient, transition metal-free methods to advance sustainable hydroboration strategies.[2-5]

In this study, we examined a synthetic approach to alkenylboronates through the hydroboration of alkynoate esters catalyzed by simple ionic liquids (ILs). The protocol is effective for internal alkynoate esters with various functional groups and allows the highly selective synthesis of (E) and (Z) isomers. The presentation will cover the results of optimizing reaction conditions, including catalyst screening, substrate scope and mechanistic experiments.

The authors acknowledge the financial support from the National Science Centre in Poland, Grant No. UMO-2019/34/E/ST4/00068 and UMO-2024/53/N/ST4/00526.

- [1] J. Walkowiak, M. Jankowska-Wajda, B. Marciniec, *Chem. Eur. J.*, **2008**, *14*, 2695-2697.
- [2] S. J. Geier, C. M. Vogels, J. A. Melandson, S. A. Westcott, *Chem. Soc. Rev.*, **2022**, *51*, 8877-8922.
- [3] Y. Wu, C. Shan, J. Ying, J. Su, J. Zhu, L. L. Liu, Y. Zhao, Green Chem., 2017, 19, 4169-4175.
- [4] P. Huninik; J. Szyling, A. Czapik, J. Walkowiak, *Green Chem.*, **2023**, *5*, 3715-3722.
- [5] P. Huninik, H. Im, J. Szyling, M.-H. Baik, J. Walkowiak, *ChemRxiv*, **2024**, doi: 10.26434/chemrxiv-2024-zf116.