ISGC 2022

N°737 / OC
TOPIC(s) : Homogenous, heterogenous and biocatalysis / Clean reactions

Direct amination of bio-based isohexides via borrowing hydrogen methodology

AUTHORS
Florence POPOWYCZ / INSA-ICBMS, BÂTIMENT LEDERER, 1 RUE VICTOR GRIGNARD, VILLEURBANNE

PURPOSE OF THE ABSTRACT

The synthetic valorization of biomass-derived chemicals produced from carbohydrates has received great attention from the chemistry community to extend the wide applications of these so-called bio-based platforms. In parallel with the comprehensive efforts made for increasing the efficiency and sustainability of their production, research for finding them original applications via the development of innovative and modern methodologies has been also intensified. In that approach, we have been involved in the development of synthetic methodologies to transform bio-based platforms such as isosorbide, a chiral isohexide produced by Roquette Frères (Lestrem, France), into more complex molecules with high-added value.

Over the last decades, functionalization of isohexides into amines has attracted considerable interest for polymer applications and for asymmetric induction in organic synthesis. Reported synthesis of isohexide-based amines involve the use of highly reactive leaving groups, such as tosylates. Although effective, this process has low atom efficiency and generates a high amount of waste. The advent of green chemistry has promoted innovative methodologies considering atom economy parameter. With respect to this point, borrowing hydrogen (BH) methodology has emerged as an important tool in organic chemistry for the construction of C-N bonds. We report herein the first direct and regio- and diastereoselective amination of bio-based isohexides (isosorbide and isomannide) through borrowing hydrogen methodology using a cooperative catalysis between an iridium catalyst and a Brønsted acid. The access to chiral amino-alcohol (NH2-OH) and diamine (NH2-NH2) as interesting optically pure bio-based monomers was also proposed using the BH strategy as a sustainable route for their preparation.

FIGURES

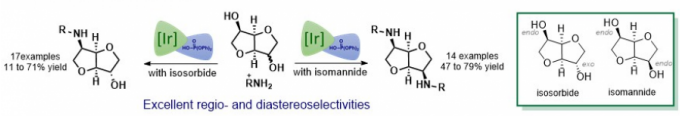

FIGURE 1

Scheme 1

Regio and stereoselective issues for borrowing hydrogen reaction on isohexide

FIGURE 2

KEYWORDS

biomass-platform | isohexide | catalysis | selectivities

BIBLIOGRAPHY

[1]. Froidevaux, V.; Negrell, C.; Caillol, S.; Pascault, J.P.; Boutevin, B. Chem. Rev. 2016, 116, 14181-14224

[2]. Janvier, M.; Moebs-Sanchez, S.; Popowycz, F. Chimia 2016, 70, 77-83

[3]. Jacolot, M.; Moebs-Sanchez, S.; Popowycz, F. J. Org. Chem. 2018, 83, 9456-9463; Bahé, F.; Grand, L.; Cartier, E.; Jacolot, M.; Moebs-Sanchez, S.; Portinha, D.; Fleury E.; Popowycz, F. Eur. J. Org. Chem. 2020, 5, 599-608