パラジウム/カルボン酸触媒を用いるフルフラール類のアルキンに よるアルケニル化反応

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Palladium/carboxylic acid-catalyzed alkenylation of furfural and its derivatives using alkynes (Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST)) Yasunori Minami, Hitomi Miyamoto, Yumiko Nakajima

Furfural is one of the important products derived from cellulosic biomass. The furan ring that is the main framework of furfural is a useful and versatile building block and a key component for functional molecules. Thus, development of a straightforward functionalization of furfural and its derivatives may contribute to advances in syntheses of high-value-added chemicals from biomass. At present, catalytic C–C bond-forming reaction via inert C–H bond cleavages is regarded as the most important and effective method for the facile construction of various highly functionalized molecules with atom- and step-economies. Herein we report that furfural and its derivatives underwent alkenylation with alkynes via α-C-H activation in the presence of a palladium/carboxylic acid catalyst. As a result, the corresponding alkenylated products were obtained. The reactive aldehyde group remained intact during this reaction. This catalytic system allowed selective alkenylation of furan substrates having electron-withdrawing substituents.

Keywords: Alkyne; Insertion Reaction; Heteroaromatic Compound; Palladium; Selective Synthesis

フルフラールはセルロースから製造できる有用なバイオマスの一つであり、現在、未来において重要な有機農資源として期待される.一方、フランは合成素子、および機能性分子の鍵骨格として多用されていることを踏まえると、フルフラールを構成するフラン環の触媒による直截官能基化反応が発展すれば、バイオマスからさまざまな高付加価値化合物の製造が可能となる.本研究では、パラジウム/カルボン酸触媒とアルキンにより、フルフラール類の α 位炭素-水素結合切断を経るアルケニル化反応を開発した 11 . 本触媒法は、フルフラールなど電子求引性の置換基を有するフラン類を優先して利用できる.

1) Yasunori Minami, Hitomi Miyamoto, Yumiko Nakajima, *ChemCatChem* **2021**, DOI: 10.1002/cctc.202001685.