

Regioselective C(sp³)–H Alkylation of Fructopyranose Derivative by 1,6-HAT

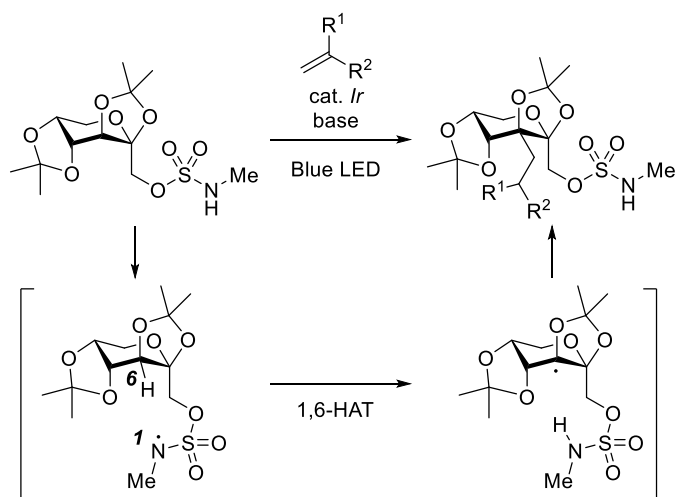
(¹*Institute for Materials Chemistry and Engineering, Kyushu University*, ²*Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*)

○Yanru Li,² Shoto Miyamoto,² Takeru Torigoe,^{1,2} and Yoichiro Kuninobu^{1,2}

Keywords: C–H transformation; Alkylation; Regioselectivity; Photoredox catalyst; Hydrogen atom transfer

Development of regioselective C(sp³)–H transformations is an important issue in recent synthetic organic chemistry. In many cases, C(sp³)–H transformations have been developed using simple substrates. From a practical perspective, it is also important to realize regioselective C(sp³)–H transformations of natural products, such as saccharides. One of the synthetic methods of saccharides is their modification, and high reactive primary and secondary hydroxy groups and anomer positions are generally modified. Although one of the most efficient transformations of saccharides is C–H transformations, the examples of regioselective C(sp³)–H transformations of saccharides are still rare. Recently, Knowles¹ and Rovis² reported amide-directed photoredox-catalyzed C(sp³)–H alkylation by 1,5-hydrogen atom transfer (HAT) using alkenes with an electron-withdrawing group as alkylation reagents. They reported only one example of C(sp³)–H alkylation of a saccharide derivative and the yield of the alkylated product was moderate.

We successfully achieved a regioselective C(sp³)–H alkylation of a fructopyranose derivative using alkenes with an electron-withdrawing group as alkylation reagents. The reaction proceeded by 1,6-HAT under photoredox iridium catalysis. Several functional groups can be introduced into the fructopyranose derivative in moderate yields. The *N*-methyl sulfamate group of the alkylated fructopyranose derivative can be converted to a hydroxy group.



1) Choi, G. J.; Zhu, Q.; Miller, D. C.; Gu, C. J.; Knowles, R. R. *Nature* **2016**, 539, 268. 2) Chu, J. C. K.; Rovis, T. *Nature* **2016**, 539, 272.