Visible-light-driven nucleophilic cobalt-catalyzed Giese reaction of alkyl tosylates

(Graduate School of Advanced Science and Engineering, Hiroshima University)

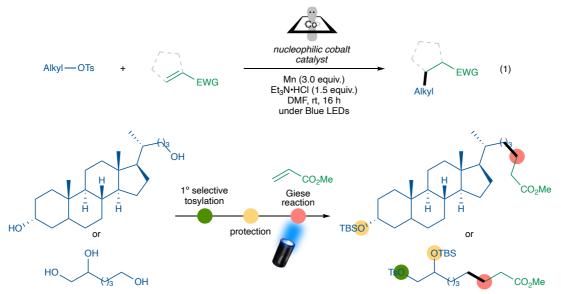
OKimihiro Komeyama, Takuya Michiyuki, Teshima Yoshikazu, Itaru Osaka

Keywords: Giese Reaction; Visible-light; Nucleophilic Cobalt Catalysts; Alkyl Tosylates;

Alkyl Radicals

The Giese reaction is recognized as a versatile tool for the selective construction of C(sp³)–C(sp³) bond linkages. Alkyl iodides and bromides have been traditionally used as alkyl radical sources in the reaction, but their preparation requires multi-step processes starting from commercially available chemicals. In this context, the Giese reaction using alkanol derivatives as the source of alkyl radicals has been intensively studied. However, these approaches involve the cleavage of the robust carbon–oxygen bond of alkanol derivatives and are limited to the generation of thermodynamically stable tertiary, secondary, and benzyl radicals. Hence, the Giese reaction using non-stabilized and simple primary alkyl radicals generated from alkanol derivatives is more challenging.

This paper reports a Giese reaction of readily available alkyl tosylates with activated olefins catalyzed by nucleophilic cobalt catalysts under visible-light irradiation (Eq. 1). The reaction well-tolerated a wide range of functional groups, providing the corresponding radical adducts. Additionally, it is demonstrated that the present reaction can be used in regioselective functionalizations of polyols, taking advantage of the fact that the tosylation of alkanols preferentially proceeds at the primary alcoholic position and that the nucleophilic cobalt catalyst preferentially reacts with less-bulky alkyl tosylates (Scheme 1).



Scheme 1. Regioselective functionalisations of polyols using the present protocol.