Site-selective C(sp3)-H Alkylation of Saccharide Derivatives by Photocatalysts

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（光触媒による糖類の位置選択的なC(sp^3)–Hアルキル化反応）

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論 文 内 容 の 要 旨

Thesis Summary

In this thesis, three novel methods for the site-selective C(sp^3)–H alkylation of saccharide derivatives using photocatalysts were developed.

In Chapter 1, I introduced the site-selective alkylation of saccharide derivatives and its potential applications in various fields. This chapter briefly discussed the different approaches for modifying saccharides, emphasizing the importance and application of the site-selective C(sp^3)–H alkylation of saccharides.

In Chapter 2, I investigated C(sp^3)–H alkylation of 2,3:4,5-bis-*O*-(1-ethylethylidene)-*β*-D-fructopyranose methyl sulfamate using an iridium photocatalyst under blue LED. This reaction enables the introduction of various functional groups, such as ester, carbonyl, cyano, and sulfonyl groups, to the fructopyranose derivative by 1,6-HAT strategy. Furthermore, the *N*-methyl sulfamate group, acting as a hydrogen abstractor from the fructopyranose derivative, can be transformed into a hydroxy group.

In Chapter 3, I developed site-selective C(sp^3)–H alkylation of saccharides with electron-deficient alkenes using anthraquinone and tetrabutylammonium decatungstate (TBADT). Interestingly, the reaction sites can be switched by changing the photocatalysts. Anthraquinone-catalyzed C(sp^3)–H alkylation occurred at C(sp^3)–H bond with weak bond dissociation energy (BDE). On the other hand, the site-selectivity of TBADT-catalyzed C(sp^3)–H alkylation was dominated by steric effects. In the TBADT-catalyzed C(sp^3)–H alkylation, the mono-alkylated product was obtained in excellent yield, even on a gram scale. The reactions were compatible with several electron-deficient alkenes and saccharides, and provided a variety of *C*-saccharides.

In Chapter 4, I summarized the results of Chapters 2 and 3. Overall, the results offer promising methods for the site-selective C(sp^3)–H alkylation of saccharides and provide new platforms for the construction of complex saccharide derivatives. These methods can potentially be used in the synthesis of new bioactive molecules, which have important applications for drug discovery.