C(sp^3)-H Alkylation Assisted by Non-Covalent Interaction Between Substrates and Decatungstate Catalyst

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論文名　Ｔｉｔｌｅ：C(sp^3)–H Alkylation Assisted by Non-Covalent Interaction Between Substrates and Decatungstate Catalyst
(基質とデカタングステン酸塩光触媒間の非共有結合性相互作用による 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, decatungstate-catalyzed alkylation of benzylic carbon–hydrogen (C–H) bond assisted by non-covalent interaction is described.

In **Chapter 1**, a general introduction to C–H transformations is provided. In C–H transformations, controlling the site-selectivity is highly important. The known strategies for controlling the site-selectivity in C–H transformations are based on the steric or electronic properties of the catalysts or substrates, directing groups of substrates, and non-covalent interactions between substrates and reagents or substrates and ligands (catalysts). Although significant progress has been made in achieving site-selective C–H transformations, challenges remain particularly for site-selective C(sp^3)–H transformations compared to C(sp^2)–H transformations. Our group is dedicated to developing "*non-covalent method*" for site-selective C(sp^3)–H transformations. During the research program in our group, the following chapters present my researches on non-covalent interaction-assisted C(sp^3)–H alkylation reactions.

Chapter 2: Boronic acid derivatives are indispensable molecules in synthetic organic chemistry because, despite the high stability of their carbon–boron bonds, they can be readily transformed into carbon–carbon and carbon–heteroatom bonds. Herein, I achieved the benzylic C(sp^3)–H alkylation of phenylboronic acids assisted by hydrogen bond between the boronyl group and decatungstate. This work offers a novel approach for the synthesis of aryl boronic acids.

Chapter 3: In the study of Chapter 2, while the C(sp^3)–H alkylation of 2-methylphenylboronic acids was successfully achieved, the site-selective reaction was not feasible. It was probably because the relatively weak hydrogen bond between the boronyl group of substrates and decatungstate. If anilide derivatives were used as a substrate, the stronger hydrogen bond between substrates and decatungstate was expected. Based on this strategy, I have developed the proximal-selective C(sp^3)–H alkylation of *N*-(*o*-tolyl)benzenesulfonanilide derivatives. Moreover, the reaction was applicable to

N-(3,4-dicyano-2-phenylbutyl)benzenesulfonamide.

Chapter 4: (unpublished content)

I explored the role of non-covalent interactions between substrates and catalysts. First, I achieved boronyl group-assisted decatungstate-catalyzed benzylic C(sp^3)–H alkylation. Second, I developed a site-selective C(sp^3)–H alkylation of sulfonanilides. Third, (unpublished content for Chapter 4). These studies provide new insights and methodologies for advancing C(sp^3)–H transformations