

論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Regio- and Stereoselective Construction of Tertiary and Quaternary Stereogenic Carbon Centers via Allylic Substitution with Alkyl- and Arylcopper Reagents
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)
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論文要旨

THESIS SUMMARY

専攻：	生体分子機能工学	専攻	申請学位（専攻分野）：	博士	（工学）
Department of			Academic Degree Requested	Doctor of	
学籍番号：			指導教員（主）：	教授	小林 雄一
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要旨（英文 800 語程度）

Thesis Summary (approx.800 English Words)

Allylic substitution of chiral esters with complete CT (chirality transfer) is one of the most essential methods to generate stereogenic centers. In this thesis, construction of asymmetric tertiary and quaternary carbon centers via allylic substitution of picolinates are presented.

In the first part, regio- and stereo-specific allylic substitution of enantiomerically enriched β,β -disubstituted exocyclic picolinates with alkyl- and arylcopper reagents to form $C(sp^2/sp^3)-C(sp^3)$ bonds has been investigated to construct chiral tertiary carbon centers. In the second part, allylic substitution of chiral γ,γ -disubstituted picolinates with alkyl- and arylcopper reagents to form $C(sp^2/sp^3)-C(sp^3)$ bonds regio- and stereoselectively to construct enantioenriched all-carbon quaternary centers has been accomplished.

Chapter 1 General Introduction

General introduction of the background of the following research are presented.

Chapter 2 Installation of a Chiral Side Chain to a 2-Alkylidene-1-cycloalkan-1-ol Unit by Using Allylic Substitution

To obtain fundamental aspect such as reactivity, regio- and stereoselectivities to install chiral side chains to a 2-alkylidene-1-cycloalkan-1-ol unit, the author investigated allylic substitution of γ -alkyl substituted allylic cycloalkenyl picolinates with $RMgBr$ -based copper reagents ($R = Bu, Ph, etc.$), producing *anti* S_N2' products selectively.

Chapter 3 Synthesis of 2,6-*trans*-Disubstituted Cyclohexanone via Allylic Substitution of *exo*-Cyclic Picolinates Followed by Ozonolysis

Available methods oftentimes generate a mixture of 2,6-*trans*- and *cis*-disubstituted cyclohexanones. In this chapter, a strategy was developed by allylic substitution of exocyclic picolinates with nucleophiles and ozonolysis to generate 2,6-disubstituted cyclohexanones.

Chapter 4 Construction of Chiral Quaternary Carbon Centers with Arylcopper Reagents

Allylic substitution of secondary esters affording S_N2' products with excellent selectivity is limited to alkyl groups. In this chapter, aryl (Ar) groups were successfully transferred by $Cu(acac)_2$ to quaternary carbon centers with excellent regio- and stereoselectivity.

Chapter 5 Construction of Chiral Quaternary Carbon Centers with Alkylcopper Reagents

In this chapter, ZnI_2 was found to promote regio- and stereoselective substitution of acyclic γ,γ -disubstituted secondary allylic picolinates with alkylcopper reagents derived from alkyl- $MgBr$ and $CuBr \cdot Me_2S$ in a 2:1 ratio to furnish *anti* S_N2' products in good yields, which contain chiral quaternary carbon centers.

Chapter 6 Summary

Results of Chapters 2-5 are summarized in this chapter.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 2 部提出してください。

Note: Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 2 copies of 800 Words (English).