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Development of New Carbon–Carbon Bond Forming
Reactions Catalyzed by Palladium and Nickel

Naoki Ishida
2008
Preface

The studies described in this thesis have been carried out under the direction of Professor Masahiro Murakami from April 2002 to March 2008. These studies concern with novel carbon–carbon forming reactions catalyzed by palladium and nickel.

This thesis is completed with the aid of so many people such as a supervisor, collaborators and colleagues. The author would like to show his appreciation them.

First of all, the author would like to express his sincerest gratitude to Supervisor Professor Masahiro Murakami for providing an opportunity to study state-of-the-art organic chemistry. All the works in this thesis could be achieved with his constant supervisions.

The author also would like to acknowledge to:
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The author also thanks to Horomi Yoshida, Keiko Kuwata, and Haruo Fujita for the help on the measurement of mass and NMR spectra.
The author acknowledges to the Japan Society of the Promotion of Science for Young Scientist for the financial support.
Finally, the author would like to express his appreciation to his parents, Mr. Eiichi
Ishida and Mrs. Yoko Ishida for their constant assistance.

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March, 2008
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General Introduction

Transition metal-catalysis has attracted ever-increasing attention in organic synthesis because it provides unique transformations which are otherwise difficult to achieve. For example, construction of C$_{sp^2}$–C$_{sp^2}$ bonds, which are often seen in pharmaceuticals and optoelectronic materials, can be executed by palladium- or nickel-catalyzed cross-coupling reactions. Therefore, these catalysts play a crucial role in drug discovery and development of functional materials. Olefin metathesis reactions catalyzed by ruthenium and molybdenum complexes enable to form cyclic structures between two olefin moieties in the presence of many functional groups, causing a paradigm shift in the retrosynthesis of cyclic compounds including macrocyclic natural products. These transformations became feasible by means of transition metal catalysts, exemplifying the usefulness of transition metals for innovations.

In this thesis, the author would like to describe novel transition metal-catalyzed or -mediated reactions which are directed towards the following issues;

1) Stereoselective synthesis of trisubstituted alkenylboranes
2) Enantioselective construction of a chiral quaternary carbon center
3) Utilization of carbon dioxide as carbon resources

(1) Stereoselective synthesis of trisubstituted alkenylboranes

Organoboron compounds have received ever-increasing attention because of their interesting photophysical properties as well as facile reactivities. Representative optoelectronic materials based on organoboranes are light-emitting diodes, fluorescent sensors, non-linear optics, and two-photon emitters. So far, such organoboron-based materials have been synthesized by two conventional methods; a hydroboration reaction of terminal alkynes and a substitution reaction of halo- and alkoxyboranes with organometallic reagents. Alternative pathway is available starting from alkynyltriorganylborates, which react with a variety of electrophiles such as a proton, organic halides, carbon dioxide, oxiranes, chlorophosphanes, sulfenyl chlorides, and metal halides. An electrophile attacks the alkynyl carbon β to boron, inducing 1,2-migration of an organyl group from boron to the α-carbon to give alkenylboranes. For example, a reaction of hexyn-1-yltrihexylborate with allyl bromide afforded a 1,4-dienylborane. Allyl and hexyl groups were installed across the boron-substituted carbon–carbon double bond.
This class of reactions provides a valuable method to prepare di- and trisubstituted alkenylboranes which are difficult to synthesize through the other conventional methods mentioned above. However, it is difficult to control the stereoselectivity. It is hardly affected by solvent, temperature and other reaction parameters except for the structure of substrates including electrophiles. In this regards, the use of transition metal catalysis is intriguing because organometallic intermediates can work as electrophiles and interact with alkenylborates in a different way from usual electrophiles, affording an additional possibility to control the stereoselectivity as well as to expand the reaction scope. In this thesis, the author focused on the palladium-catalysis because it can catalyze a variety of reactions including Heck reaction, allylation reaction, and hydrogenation reaction.19

In chapter 1, the author deals with a palladium-catalyzed reaction of alkenyltriarylborates with aryl halides. In the presence of Pd(0) and P(o-tol)_3, alkenyltriarylborates reacted with aryl halides to give trisubstituted alkenylboranes stereoselectively. Two different aryl groups were installed across carbon–carbon double bond in a cis arrangement. The reaction would proceed through oxidative addition of aryl halides to palladium(0), carbopalladation across the carbon–carbon triple bond, migration of an aryl group on boron to palladium (intramolecular transmetalation), and reductive elimination.

In chapter 2, a palladium-catalyzed allylation reaction of alkenyltriarylborates is described. In the presence of palladium(0) ligated by xanthos, alkenyltriarylborates reacted with allyl bromide to give trisubstituted alkenylboranes. When
2,6-dimethoxyphenyl group was employed as substituents on boron, air-stable organoborane was obtained stereoselectively.

\[
[\text{Me}_4\text{N}]\[\text{Ph} \equiv \text{BAr}_3\] + \text{Br}
\]

\[
\text{toluene, rt}
\]

In chapter 3, a palladium-catalyzed rearrangement reaction of ammonioalkynyltriarylborates is described. In the presence of a palladium catalyst, alkynyltriarylborates having tethered tertiary ammonium moiety were rearranged to afford amine–borane intramolecular complexes in a stereoselective manner. Instead of the tertiary ammonium moiety, anilinium and pyridinium groups also participated in the reaction, affording the corresponding intramolecular B–N adducts. Some products exhibited strong fluorescence.

(2) Enantioselective construction of a chiral quaternary carbon center

The enantioselective construction of a chiral quaternary carbon center is an active research area in organic synthesis because chiral quaternary carbon centers are often seen in natural products. Catalytic asymmetric alkylation through a chiral \(\pi\)-allylpalladium complex has been intensively studied for the purpose. Most of the successful examples introduce a chiral center on an allylic substrate, whereas the enantioselective electrophilic attack to a prochiral nucleophile is difficult to be controlled by a chiral ligand on the palladium atom because the ligand is located at the opposite side of the \(\pi\)-allyl carbon structure from the approaching nucleophile.

In chapter 4, a palladium-catalyzed asymmetric alkylation reaction of prochiral
nucleophiles is depicted.\textsuperscript{23,24} In the presence of a palladium catalyst modified with a chiral phosphine ligand, allyl α-acetamido-β-ketoesters were decarboxylated to give α-aminoketones having a quaternary carbon center. The reaction proceeded through oxidative addition of allyl carboxylate to palladium, decarboxylation to generate an enolate, nucleophilic attack of the enolate to the chiral π-allylpalladium.\textsuperscript{25} The use of chiral ligand 1 and an addition of phenol derivatives is crucial for high enantioselectivity, affording the product with up to 90\% ee.

\[
\begin{array}{c}
\text{R}O
\end{array}
\begin{array}{c}
\text{NHAc}
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\begin{array}{c}
\text{2.5 mol\% Pd$_2$dba$_3$·CHCl$_3$
}\end{array}
\begin{array}{c}
\text{5 mol\% (R,R)-1
}\end{array}
\begin{array}{c}
\text{DCE, 1-naphthol (0.5 eq), rt}
\end{array}
\begin{array}{c}
\rightarrow
\end{array}
\begin{array}{c}
\text{up to 90\% ee}
\end{array}
\begin{array}{c}
\text{R}O
\end{array}
\begin{array}{c}
\text{NHAc}
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\begin{array}{c}
\text{(R,R)-1
}\end{array}
\]

(3) Utilization of carbon dioxide as carbon resources

There is an increased recognition by the world’s scientific, industrial, and political communities that the concentrations of greenhouse effect gases including carbon dioxide on the earth are increasing and causing a serious climate change.\textsuperscript{26} Many attempts to decrease the emission of carbon dioxide have been executed, however, it is still difficult to utilize carbon dioxide as carbon resources because of the high stability. A nickel(0) complex is potentially useful to convert carbon dioxide into carboxylic acids.\textsuperscript{27,28} Unsaturated hydrocarbons and carbon dioxide are reductively coupled on a nickel(0) complex to give five-membered nickelalactones. The nickelalactone has a reactive carbon–nickel bond, which can be utilized for subsequent transformations.\textsuperscript{29}

\[
\begin{array}{c}
\text{Ni}
\end{array}
\begin{array}{c}
\text{C}
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\begin{array}{c}
\rightarrow
\end{array}
\begin{array}{c}
\text{Ni}
\end{array}
\begin{array}{c}
\text{C}
\end{array}
\begin{array}{c}
\text{O}
\end{array}
\]

In chapter 5, nickel-mediated carboxylation reactions of methylenecyclopropanes is described. Methylenecyclopropanes were coupled with carbon dioxide on an amine-ligated nickel(0) complexes to give nickelalactones, which lead to various carboxylic acids depending on the reaction conditions. When DBU was employed as an
amine, oxidative cyclization occurred under atmospheric pressure of carbon dioxide to generate nickelalactones with a cyclopropane moiety. In a nonpolar solvent, cyclopropane carboxylic acids were obtained after acidic hydrolysis. Meanwhile in a polar solvent, acrylic acid derivatives were produced probably through $\beta$-carbon elimination of the generated nickelalactone. On the other hand, the use of MTBD as an amine altered the reaction course, affording $\gamma,\delta$-unsaturated carboxylic acids.

![Chemical equations and reactions](image)

In chapter 6, the author mentions about a nickel(0)-mediated sequential addition reaction of carbon dioxide and a diazene onto unsaturated hydrocarbons. A nickelalactone generated from carbon dioxide and an allene reacts with a diazene to furnish a hydrazine. Other unsaturated hydrocarbons such as alkynes and methylenecyclopropanes participated in the reaction, resulting in carboxylic acids having a $\beta$-hydrazino moiety. Treatment of SmI$_2$ with the hydrazines reductively cleaved the nitrogen–nitrogen bond, affording $\beta$-amino acid derivatives.
References


Chapter 1

Stereoselective Synthesis of Trisubstituted Alkenylboranes by Palladium-Catalyzed Reaction of Alkynyltriarylborates with Aryl Halides

Abstract: The palladium-catalyzed reaction of alkynyltriarylborates with aryl halides afforded trisubstituted alkenylboranes, in which two different aryl groups were installed across the carbon–carbon double bond in a cis arrangement.
Organoboron compounds are valuable reagents in organic synthesis, especially for carbon–carbon bond forming reactions such as Suzuki-Miyaura coupling reaction. In addition, recent studies on boron-containing compounds have demonstrated their potential as functional materials. Therefore, efficient methods to prepare organoboranes in a stereo-defined form are of significant interest. Di- and trisubstituted alkenylboranes can be synthesized by the reaction of alkynyltriorganylborates with electrophiles, such as a proton, alkyl halides, acyl halides, (π-allyl)palladium species, carbon dioxide, oxiranes, chlorophosphanes, sulfenyl chlorides and metal halides, which attack the β-position of the alkynyl group to induce 1,2-migration of the organyl group from boron to the α-position. However, an analogous reaction using aryl halides or pseudohalides has not been reported, although such an arylation reaction would significantly reinforce the potential of the 1,2-migration protocol for the synthesis of π-conjugated organic materials. Herein, the author report the palladium-catalyzed reaction of alkynyltriarylborates with aryl halides, which affords trisubstituted alkenylboranes in a highly stereoselective manner.

Alkynyltriarylborate $1a^{14}$ (1.0 equiv) was reacted with 4-bromotoluene (1.0 equiv) for 3 h at room temperature in the presence of a catalyst generated from $\text{Pd}_2\text{dba}_3\cdot\text{CHCl}_3$ and $\text{P}(\sigma\text{-tol})_3$. Subsequent treatment of the reaction mixture with acetic acid afforded trisubstituted alkene $3a$ in 89% yield ($E/Z = 7/93$, eq 1). The $^1\text{H}$ NMR spectrum of the reaction mixture showed that no 4-(hept-1-ynyl)toluene was formed and that only a trace amount (less than 5%) of 4-methylbiphenyl was produced.

When deuterated acetic acid was employed for hydrolysis, $3a-d_1$ was obtained in 91% yield (91% incorporation of D), indicating that the alkenylborane $2a$ was likely the precursor to $3a$. Although attempts to isolate $2a$ failed due to the lability of the carbon–boron linkage, the alkenylborane $2b$ ($E/Z = 1/>99$), generated from $1b$ at reflux in 1,2-dichloroethane, was stable enough to be isolated by column chromatography on silica.
gel (eq 2). The tertiary butyl group located cis to boron may have provided steric protection for the labile carbon–boron linkage.

\[ \text{[Me₄N][^tBu≡BPh₃]} \quad 1b \]

\[
\begin{align*}
2.5 \text{ mol\% Pd₂dba₃·CHCl₃} & \quad 6 \text{ mol\% P(o-tol)₃} \\
(CH₂Cl)₂, \text{ reflux} & \quad \rightarrow \\
\text{2b} & \quad 92\% \ (E/Z = 1/\sim 99)
\end{align*}
\]

A possible mechanism for the formation of 2b from 1b is shown in Scheme 1. Initially, oxidative addition of 4-bromotoluene to palladium(0) occurs, giving p-tolylpalladium species A. Regioselective carbopalladation across the carbon–carbon triple bond of 1b forms the intermediate B. Then, a phenyl group migrates from boron to palladium, replacing the bromide anion. Finally, the alkenylborane 2b is released by reductive elimination with regeneration of palladium(0). ¹⁷

**Scheme 1. Proposed mechanism**

A minor pathway leading to the formation of (E)-3a from 1a may arise from 1,2-phenyl migration from boron to the α-carbon, displacing palladium(0) and the bromide anion. Such a substitutive 1,2-phenyl migration can occur with inversion of the α-carbon stereochemistry. ¹⁸

Intramolecular transfer of the aryl group on boron was confirmed by a crossover experiment (eq 3). When a mixture of 1c and 1d was subjected to the reaction with
4-bromotoluene (2.0 equiv), 3c and 3d were obtained in 91 and 86% yield, respectively. No crossover products were detected by $^1$H NMR and GC-MS.

\[
\begin{align*}
\text{[Me}_4\text{N][PhCH}_{2}\text{CH}_{2}\text{BPh}_3]_1 \quad &+ \\
\text{[Me}_4\text{N][nC}_5\text{H}_1\text{B(4-MeOC}_6\text{H}_4\text{)}_3]_1 \quad &\xrightarrow{a} \\
\text{Br} \quad &\text{(2.0 equiv)}
\end{align*}
\]

\[
\begin{align*}
\text{3c} \quad &91\% \quad E/Z = 4/96 \\
\text{3d} \quad &86\% \quad E/Z = 1/99
\end{align*}
\]

\[a\] 5.0 mol% Pd$_2$dba$_3$·CHCl$_3$, 12 mol% P(o-tol)$_3$, CH$_2$Cl$_2$, rt, 3 h; then AcOH, rt, 3 h.

Trisubstituted alkenes 3 were synthesized by the reaction of 1a with various aryl halides (Table 1). The reaction of 4-iodotoluene was complete within 1 h, yielding the product 3a stereoselectively in 89% yield (entry 1). The corresponding chloride and triflate gave only a trace amount of the product. Aryl bromides having electron-donating and -withdrawing groups at the 4-positions both successfully participated in the reaction (entries 3 and 4). Ester, phthalimide and chloro groups remained intact under the reaction conditions (entries 5-7). Although 3-bromotoluene reacted smoothly (entry 8), the reaction with 2-bromotoluene was sluggish, probably due to steric reasons.

The use of other alkynyltriarylborates in the reaction with 4-bromotoluene was also examined (Table 2). Alkynylborates possessing a primary alkyl group as the R substituent gave 3l and 3m in good yield with high selectivities (entries 1 and 2). In the case where R = isopropyl, (Z)-3n was formed exclusively (entry 3). Both electron-donating and -withdrawing groups were tolerated as the substituents on the aryl group on boron (entries 4-6, eq 3). Furthermore, a 2-thienyl group was efficiently transferred onto the α-carbon (entry 7). In contrast, no or only a trace amount of the corresponding trisubstituted alkenes were obtained when triphenyl(2-phenylethynyl)borate 1l and triethyl(hept-1-ynyl)borate 1m were subjected to the reaction with 4-bromotoluene (Chart 1). Alkynylborates derived from phenyl boronic esters such as 1n failed to give the corresponding trisubstituted alkenyl boronic esters either.19
Table 1. Reaction of 1a with various aryl halides

<table>
<thead>
<tr>
<th>entry</th>
<th>aryl halide</th>
<th>product</th>
<th>yield / %b</th>
<th>E/Zc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d</td>
<td>4-MeC₆H₄I</td>
<td>3a</td>
<td>89</td>
<td>7/93</td>
</tr>
<tr>
<td>2</td>
<td>PhBr</td>
<td>3e</td>
<td>88</td>
<td>5/95</td>
</tr>
<tr>
<td>3</td>
<td>4-MeOC₆H₄Br</td>
<td>3f</td>
<td>93</td>
<td>7/93</td>
</tr>
<tr>
<td>4</td>
<td>4-CF₃C₆H₄Br</td>
<td>3g</td>
<td>90</td>
<td>4/96</td>
</tr>
<tr>
<td>5</td>
<td>4-EtO₂CC₆H₄Br</td>
<td>3h</td>
<td>93</td>
<td>7/93</td>
</tr>
<tr>
<td>6</td>
<td>4-PhthNC₆H₄Br</td>
<td>3i</td>
<td>84</td>
<td>6/94</td>
</tr>
<tr>
<td>7</td>
<td>4-ClC₆H₄Br</td>
<td>3j</td>
<td>88</td>
<td>5/95</td>
</tr>
<tr>
<td>8</td>
<td>3-MeC₆H₄Br</td>
<td>3k</td>
<td>93</td>
<td>5/95</td>
</tr>
</tbody>
</table>

α Reaction conditions: 1.0 equiv 1a, 1.0 equiv aryl halide, 2.5 mol% Pd₂dba₃·CHCl₃, 6 mol% P(o-tol)₃, CH₂Cl₂, rt, 3 h; then AcOH, rt, 3 h. b Isolated yield. c Determined by ¹H NMR. d Reaction time: 1 h.

Chart 1. Other alkynylborates

![Chemical structures](image)

The synthetic potential of the reaction was demonstrated by the one-pot procedures shown in Scheme 2. The Suzuki-Miyaura coupling reaction was consecutively executed by simply adding aryl iodide 4 and NaOH to a reaction mixture containing the alkenylborane 2s. (E)-Tamoxifen (5) was stereoselectively obtained in 79% yield (E/Z = 97/3). Stereo-specific iodination was accomplished by treatment of the ammonia complex of 2s with NIS, giving the alkenyl iodide 6 in 59% yield (E/Z = 96/4). An oxidation reaction with trimethylamine N-oxide produced the ketone 7 in 91% yield.
Table 2. Reaction of various alkynylborates 1 with 4-bromotoluene

\[
\text{[Me}_4\text{N][R} \equiv \equiv \text{BAR}_3] + \text{Br-4-toluene} \xrightarrow{2.5 \text{ mol}\% \text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3, 6 \text{ mol}\% \text{P(o-tol)}_3, \text{CH}_2\text{Cl}_2, \text{rt}} \text{AcOH} \rightarrow \text{Ar} \equiv \equiv \text{H}
\]

<table>
<thead>
<tr>
<th>entry</th>
<th>[Me_4N][R \equiv \equiv \text{BAR}_3]</th>
<th>product</th>
<th>yield / %\text{b}</th>
<th>E/Z\text{c}</th>
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<tr>
<td>1</td>
<td>1e (Et, Ph)</td>
<td>3l</td>
<td>85</td>
<td>6/94</td>
</tr>
<tr>
<td>2</td>
<td>1f ('Bu, Ph)</td>
<td>3m</td>
<td>86</td>
<td>6/94</td>
</tr>
<tr>
<td>3</td>
<td>1g ('Pr, Ph)</td>
<td>3n</td>
<td>74</td>
<td>1/&gt;99</td>
</tr>
<tr>
<td>4</td>
<td>1h ('C_3H_11, 4-MeC_6H_4)</td>
<td>3o</td>
<td>88</td>
<td>6/94</td>
</tr>
<tr>
<td>5</td>
<td>1i ('C_3H_11, 3-MeC_6H_4)</td>
<td>3p</td>
<td>89</td>
<td>4/96</td>
</tr>
<tr>
<td>6</td>
<td>1j ('C_3H_11, 4-FC_6H_4)</td>
<td>3q</td>
<td>86</td>
<td>6/94</td>
</tr>
<tr>
<td>7</td>
<td>1k ('C_3H_11, 2-thienyl)</td>
<td>3r</td>
<td>82</td>
<td>9/91</td>
</tr>
</tbody>
</table>

\text{a} Reaction conditions: 1.0 equiv 1, 1.0 equiv 4-bromotoluene, 2.5 mol\% Pd\_2dba\_3 \cdot \text{CHCl}_3, 6 mol\% P(o-tol)_3, CH\_2Cl\_2, rt, 3 h; then AcOH, rt, 3 h. \text{b} Isolated yield. \text{c} Determined by \textsuperscript{1}H NMR.

Installation of two aryl groups in juxtaposition across a boron-substituted alkene is attractive in terms of the synthesis of boron-containing \(\pi\)-conjugated materials. Thus, the reaction was successfully applied to the construction of diboranyl compound 8 (eq 4).

\[
\text{1b} + \xrightarrow{a} \text{8} \ 62\% \text{a}
\]

\text{a} 2.5 mol\% Pd\_2dba\_3 \cdot \text{CHCl}_3, 6 mol\% P(o-tol)_3, (CH\_2Cl\_2), reflux, 1 h.
In summary, a new method for the stereoselective synthesis of trisubstituted alkenylboranes was developed, in which two different aryl groups were installed across the carbon–carbon double bond in a cis arrangement. Application of this method to synthesis of boron-containing functional materials is underway.

**Scheme 2. Reactions of alkenylborane 2s**

\[ 1e + \text{PhBr} \xrightarrow{\text{cat. Pd}} 2s \]

\[ \text{NIS} \]

\[ \text{Me}_3\text{NO} \]

\[ ^a 2.5 \text{ mol}\% \text{Pd}_{2}\text{dba}_3\cdot\text{CHCl}_3, 6 \text{ mol}\% \text{P(o-tol)}_3, \text{CH}_2\text{Cl}_2, \text{rt}, 3 \text{ h} \]

\[ ^b 3.0 \text{ equiv 4, NaOH, H}_2\text{O, rt, 24 h} \]

\[ ^c \text{NH}_3 \text{aq.; then 5.0 equiv NIS, acetone, 0}^\circ\text{C, 1 h} \]

\[ ^d 5.0 \text{ equiv Me}_3\text{NO, rt, 3 h} \]
Experimental Section

General. NMR spectra were recorded on a Varian Gemini 2000 (1H at 300 MHz and 13C at 75 MHz) or Varian Mercury-400 (1H at 400 MHz and 11B at 128 MHz) spectrometers. Unless otherwise noted, CDCl3 was used as a solvent. Me4Si (1H, δ = 0.00), residual H of CD3CN (1H in CD3CN, δ = 1.94), CDCl3 (13C, δ = 77.0), CD3CN (13C, δ = 1.32), and BF3·OEt2 (11B, δ = 0.00) were used as standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. All reactions were carried out under an argon atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF254 (Merck). Gel permeation chromatography (GPC) was carried out with Japan Analytical Industry LC-908.

Materials. Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used as received. CH2Cl2 was purchased from Kanto chemicals. (CH2Cl)2 was dried over CaH2. Pd2dba3·CHCl3 was prepared according to the reported procedures.21 AcOH and AcOD were degassed by sonication. Ar3B·Py were prepared from thermolysis of Ar4B·HPy, which is prepared from ArLi and BF3·OEt223 or ArMgBr and B(OMe)3,23 followed by cation exchange with Py·HCl in water. Aryl iodide 4 was prepared according to reported procedures.24

Preparation of alkynyltriarylborate 1a. A typical procedure for the preparation of alkynyltriarylborates.

\[
\text{Ph}_3\text{B·Py} \rightarrow [\text{Me}_4\text{N}]\text{Cl} \rightarrow [\text{Me}_4\text{N}]\text{Ph}_3\text{B}
\]

To a stirred solution of hept-1-yne (580 mg, 6.0 mmol) in THF (20 ml) at -78 °C was added n-BuLi (1.6 M in hexane, 3.4 ml, 5.5 mmol). After 30 minutes at this temperature, Ph3B·Py (1.61 g, 5.0 mmol) was added and the cooling bath was removed. After being stirred for 1 h at room temperature, the reaction was quenched by adding a small amount of MeOH. Volatile materials were removed under reduced pressure and the residue was dissolved in MeOH. Me4NCl (1.1 g, 10 mmol) was added with stirring, resulting white solid. It was collected by filtration and was washed with cold MeOH to give alkynyltriarylborate 1a (1.95 g, 4.7 mmol, 95% yield).
Tetramethylammonium hept-1-ynyltriphenylborate (1a)

$\text{[Me}_4\text{N}]$

$^1$H NMR (CD$_3$CN): $\delta = 0.97$ (t, $J = 7.2$ Hz, 3H), 1.40-1.43 (m, 2H), 1.52-1.59 (m, 4H), 2.28 (t, $J = 6.6$ Hz, 2H), 2.89-2.95 (m, 12H), 6.89 (t, $J = 6.4$ Hz, 3H), 7.01-7.05 (m, 6H), 7.41 (br, 6H); $^{13}$C NMR (CD$_3$CN): $\delta = 14.5$, 21.1, 23.1, 31.3, 32.1, 56.0, 94.6, 107.1 (q, $J_{\text{B-C}} = 65.9$ Hz), 123.1, 126.6, 135.4, 162.9 (q, $J_{\text{B-C}} = 49.8$ Hz); $^{11}$B NMR (CD$_3$CN): $\delta = -7.1$; HRMS (FAB) Calcd for C$_{25}$H$_{26}$B [M-(NMe$_4$)]$^- 337.2128$. Found 337.2123.

Tetramethylammonium (3,3-dimethylbut-1-ynyl)triphenylborate (1b)

$\text{[Me}_4\text{N}]$

$^1$H NMR (CD$_3$CN): $\delta = 1.31$ (s, 9H), 2.84-2.87 (m, 12H), 6.89 (t, $J = 7.2$ Hz, 3H), 7.03 (pseudo t, $J = 7.4$ Hz, 6H), 7.42 (br, 6H); $^{13}$C NMR (CD$_3$CN): $\delta = 28.8$, 33.1, 55.9, 104.2 (q, $J_{\text{B-C}} = 64.8$ Hz), 104.3, 123.0, 126.5, 135.3, 162.9 (q, $J_{\text{B-C}} = 49.5$ Hz); $^{11}$B NMR (CD$_3$CN): $\delta = -7.3$; HRMS (FAB) Calcd for C$_{24}$H$_{24}$B [M-(NMe$_4$)]$^- 323.1971$. Found 323.1965.

Tetramethylammonium triphenyl(4-phenylbut-1-ynyl)borate (1c)

$\text{[Me}_4\text{N}]$

$^1$H NMR (CD$_3$CN): $\delta = 2.60$ (t, $J = 7.4$ Hz, 2H), 2.74 (s, 12H), 2.91 (t, $J = 7.4$ Hz, 2H), 6.93 (tt, $J = 7.2$, 1.6 Hz, 3H), 7.05-7.09 (m, 6H), 7.24 (tt, $J = 7.2$, 1.6 Hz, 1H), 7.31-7.35 (m, 2H), 7.39-7.44 (m, 8H); $^{13}$C NMR (CD$_3$CN): $\delta = 23.6$, 37.8, 55.8, 94.1, 107.7 (q, $J_{\text{B-C}} = 64.1$ Hz), 123.1, 126.5, 128.9, 129.6, 135.4, 143.1, 162.6 (q, $J_{\text{B-C}} = 49.5$ Hz); $^{11}$B NMR (CD$_3$CN): $\delta = -7.0$; HRMS (FAB) Calcd for C$_{28}$H$_{24}$B [M-(NMe$_4$)]$^- 371.1971$. Found 371.1957.
Tetramethylammonium tris(4-methoxyphenyl)hept-1-ynylborate (1d)

\[
\begin{align*}
\text{Me}_4\text{N} & \quad \text{OMe} \\
\text{MeO} & \quad \text{OMe}
\end{align*}
\]

$^1$H NMR (CD$_3$CN): $\delta = 0.93$ (t, $J = 7.2$ Hz, 3H), 1.34-1.39 (m, 2H), 1.46-1.54 (m, 4H), 2.22 (t, $J = 6.6$ Hz, 2H), 2.98-3.00 (m, 12H), 3.68 (s, 9H), 6.60 (d, $J = 8.4$ Hz, 6H), 7.22 (br d, $J = 7.6$ Hz, 6H); $^{13}$C NMR (CD$_3$CN): $\delta = 14.6, 21.2, 23.1, 31.3, 32.1, 55.3, 55.8, 94.4, 107.7$ (q, $J_{B-C} = 63.6$ Hz), 112.2, 135.9, 154.3 (q, $J_{B-C} = 48.5$ Hz), 156.6; $^{11}$B NMR (CD$_3$CN): $\delta = -7.9$; HRMS (FAB) Calcd for C$_{28}$H$_{32}$BO$_3$ [M-(NMe$_4$)]$^-$ 427.2445. Found 427.2441.

Tetramethylammonium but-1-ynyltriphenylborate (1e)

\[
\begin{align*}
\text{Me}_4\text{N} & \quad \text{MeO} \\
\text{MeO} & \quad \text{MeO}
\end{align*}
\]

$^1$H NMR (CD$_3$CN): $\delta = 1.18$ (t, $J = 7.4$ Hz, 3H), 2.27 (q, $J = 7.4$ Hz, 2H), 2.92 (s, 12H), 6.87 (tt, $J = 7.2, 1.6$ Hz, 3H), 7.01 (pseudo t, $J = 7.2$ Hz, 6H), 7.37 (br, 6H); $^{13}$C NMR (CD$_3$CN): $\delta = 14.7, 16.5, 55.9, 96.2, 106.2$ (q, $J_{B-C} = 65.5$ Hz), 123.0, 126.5, 135.3, 162.8 (q, $J_{B-C} = 49.5$ Hz); $^{11}$B NMR (CD$_3$CN): $\delta = -7.1$; HRMS (FAB) Calcd for C$_{22}$H$_{20}$B [M-(NMe$_4$)]$^-$ 295.1658. Found 295.1652.

Tetramethylammonium 4-methylpent-1-ynyltriphenylborate (1f)

\[
\begin{align*}
\text{Me}_4\text{N} & \quad \text{MeO} \\
\text{MeO} & \quad \text{MeO}
\end{align*}
\]

$^1$H NMR (CD$_3$CN): $\delta = 1.05$ (d, $J = 6.8$ Hz, 6H), 1.78 (pseudo sept., $J = 6.6$ Hz, 1H), 2.14 (d, $J = 6.0$ Hz, 2H), 2.96-2.99 (br, 12H), 6.83-6.88 (m, 3H), 6.98-7.01 (m, 6H),
7.36 (br, 6H); $^{13}$C NMR (CD$_3$CN): $\delta$ = 22.6, 30.4, 30.7, 56.0, 93.4, 108.0 (q, $J_{B-C} = 65.3$ Hz), 123.2, 126.7, 135.5, 163.1 (q, $J_{B-C} = 50.0$ Hz); $^{11}$B NMR (CD$_3$CN): $\delta$ = -7.0; HRMS (FAB) Calcd for C$_{24}$H$_{24}$B [M-(NMe$_4$)]$^-$ 323.1971. Found 323.1964.

**Tetramethylammonium 3-methylbutyn-1-yltriphenylborate (1g)**

1H NMR (CD$_3$CN): $\delta$ = 1.23 (d, $J = 6.8$ Hz, 6H), 2.65 (sept., $J = 6.8$ Hz, 1H), 2.88 (s, 12H), 6.88 (tt, $J = 7.2$, 1.6 Hz, 3H), 7.00-7.04 (m, 6H), 7.39 (br, 6H); 13C NMR (CD$_3$CN): $\delta$ = 22.7, 25.4, 55.9, 123.0, 126.5, 135.3, 162.8 (q, $J_{B-C} = 49.8$ Hz); $^{11}$B NMR (CD$_3$CN): $\delta$ = -7.2; HRMS (FAB) Calcd for C$_{23}$H$_{22}$B [M-(NMe$_4$)]$^-$ 309.1815. Found 309.1806.

**Tetramethylammonium hept-1-ynyltris(4-methylphenyl)borate (1h)**

1H NMR (CD$_3$CN): $\delta$ = 0.97 (t, $J = 7.2$ Hz, 3H), 1.36-1.45 (m, 2H), 1.49-1.59 (m, 4H), 2.23-2.29 (m, 11H), 2.80 (s, 12H), 6.85 (d, $J = 7.6$ Hz, 6H), 7.27 (d, $J = 7.2$ Hz, 6H); 13C NMR (CD$_3$CN): $\delta$ = 14.6, 21.2, 23.1, 31.3, 32.1, 55.8, 94.2, 107.6 (q, $J_{B-C} = 63.8$ Hz), 127.3, 131.5, 135.4, 159.5 (q, $J_{B-C} = 49.0$ Hz); $^{11}$B NMR (CD$_3$CN): $\delta$ = -7.5; HRMS (FAB) Calcd for C$_{28}$H$_{32}$B [M-(NMe$_4$)]$^-$ 379.2597. Found 379.2582.

**Tetramethylammonium hept-1-ynyltris(3-methylphenyl)borate (1i)**
\(^1\)H NMR (CD\(_3\)CN): \(\delta = 0.98\) (t, \(J = 7.4\) Hz, 3H), 1.39-1.45 (m, 2H), 1.57-1.58 (m, 4H), 2.22 (s, 9H), 2.28 (m, 2H), 2.80-2.83 (m, 12H), 6.71-6.73 (m, 3H), 6.90-6.94 (m, 3H), 7.16 (br, 3H), 7.28 (br, 3H); \(^{13}\)C NMR (CD\(_3\)CN): \(\delta = 14.6, 21.2, 22.0, 23.2, 31.3, 32.1, 55.8, 94.5, 107.5\) (q, \(J_{B-C} = 63.4\) Hz), 123.7, 126.4, 132.6, 134.8, 136.3, 162.8 (q, \(J_{B-C} = 49.0\) Hz); \(^{11}\)B NMR (CD\(_3\)CN): \(\delta = -7.2\); HRMS (FAB) Calcd for C\(_{28}\)H\(_{32}\)B \([M-(\text{NMe}_4)]^{-}\) 379.2597. Found 379.2600.

**Tetramethylammonium tris(4-fluorophenyl)hept-1-ynyloborate (1j)**

\[
\text{[Me}_4\text{N]} \quad \begin{array}{c}
\text{F} \\
\text{F} \\
\text{B} \\
\text{F} \\
\text{F}
\end{array}
\]

\(^1\)H NMR (CD\(_3\)CN): \(\delta = 0.95\) (t, \(J = 7.2\) Hz, 3H), 1.36-1.41 (m, 2H), 1.48-1.58 (m, 4H), 2.26 (t, \(J = 6.8\) Hz, 2H), 2.97 (s, 12H), 6.75-6.81 (m, 6H), 7.32 (br, 6H); \(^{13}\)C NMR (CD\(_3\)CN): \(\delta = 14.5, 21.0, 23.1, 31.1, 32.1, 56.0, 95.0, 106.3\) (q, \(J_{B-C} = 64.8\) Hz), 112.8 (d, \(J_{C-F} = 18.2\) Hz), 136.2 (d, \(J_{C-F} = 5.8\) Hz), 157.7 (q, \(J_{B-C} = 50.7\) Hz), 160.9 (d, \(J_{C-F} = 235.1\) Hz); \(^{11}\)B NMR (CD\(_3\)CN): \(\delta = -7.8\); HRMS (FAB) Calcd for C\(_{25}\)H\(_{23}\)BF\(_3\) \([M-(\text{NMe}_4)]^{-}\) 391.1845. Found 391.1828.

**Tetramethylammonium hept-1-ynyltris(2-thienyl)borate (1k)**

\[
\text{[Me}_4\text{N]} \quad \begin{array}{c}
\text{S} \\
\text{S} \\
\text{B} \\
\text{S} \\
\text{S}
\end{array}
\]

\(^1\)H NMR (CD\(_3\)CN): \(\delta = 0.97\) (t, \(J = 7.2\) Hz, 3H), 1.38-1.44 (m, 2H), 1.52-1.62 (m, 4H), 2.25-2.28 (m, 2H), 2.77 (s, 12H), 6.89-6.93 (m, 6H), 7.12 (d, \(J = 4.4\) Hz, 3H); \(^{13}\)C NMR (CD\(_3\)CN): \(\delta = 14.5, 20.9, 23.1, 30.8, 32.0, 55.8, 94.5\) (q, \(J_{B-C} = 13.1\) Hz), 103.1 (q, \(J_{B-C} = 68.2\) Hz), 124.2, 127.0, 128.3, 164.7 (q, \(J_{B-C} = 54.6\) Hz); \(^{11}\)B NMR (CD\(_3\)CN): \(\delta = -12.6\); HRMS (FAB) Calcd for C\(_{19}\)H\(_{20}\)BS\(_3\) \([M-(\text{NMe}_4)]^{-}\) 355.0820. Found 355.0819.
Palladium-catalyzed reaction of alkynyltriarylborate 1a with 4-bromotoluene. A typical procedure for the palladium-catalyzed reaction of alkynyltriarylborates with aryl halides.

Under an argon atmosphere, a CH$_2$Cl$_2$ solution (0.5 ml) of alkynyltriarylborate 1a (82.2 mg, 0.20 mmol), Pd$_2$dba$_3$·CHCl$_3$ (5.2 mg, 2.5 µmol), and P(o-tol)$_3$ (3.6 mg, 6.0 µmol) was stirred for 30 minutes at room temperature. To the solution was added 4-bromotoluene (34.2 mg, 0.20 mmol) in CH$_2$Cl$_2$ (0.5 ml). After being stirred for 3 h, AcOH (1 ml) was added. After 3 h, the reaction mixture was neutralized with Na$_2$CO$_3$ solution. The aqueous layer was extracted with Et$_2$O (3 times), washed with water (once), brine (once), dried over MgSO$_4$ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane) to afford the trisubstituted alkene 3a with a small amount of impurities. Further purification was performed by GPC, affording the alkene 3a (46.9 mg, 0.18 mmol, 89% yield, $E/Z = 7/93$).

(Z)-2-(4-Methylphenyl)-1-phenylhept-1-ene (3a)

![Chemical Structure of 3a]

$^1$H NMR: δ = 0.86 (t, $J = 6.9$ Hz, 3H), 1.23-1.43 (m, 6H), 2.33 (s, 3H), 2.45 (t, $J = 6.9$ Hz, 2H), 6.40 (s, 1H), 6.92-6.95 (m, 2H), 7.00-7.21 (m, 7H); $^{13}$C NMR: δ = 14.2, 21.3, 22.6, 27.7, 31.5, 40.8, 125.7, 125.8, 127.7, 128.3, 128.8, 129.1, 136.2, 137.6, 138.2, 143.4; HRMS (CI) Calcd for C$_{20}$H$_{24}$ (M$^+$) 264.1878. Found 264.1884.

Preparation of trisubstituted alkenylborane 2b

Under an argon atmosphere, a (CH$_2$Cl)$_2$ solution (0.5 ml) of alkynyltriarylborate 1b (79.5 mg, 0.20 mmol), Pd$_2$dba$_3$·CHCl$_3$ (5.1 mg, 2.5 µmol), and P(o-tol)$_3$ (3.7 mg, 6.0 µmol) was stirred for 30 minutes at room temperature. To the solution was added 4-bromotoluene (35.0 mg, 0.20 mmol) in (CH$_2$Cl)$_2$ (0.5 ml). After being stirred at reflux for 3 h, water was added. The aqueous layer was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO$_4$ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane) to afford the trisubstituted alkenylborane 2b (76.0 mg, 0.18 mmol, 92% yield).
(Z)-3,3-Dimethyl-2-(4-methylphenyl)-1-phenyl-1-diphenylborylbut-1-ene (2b)

\[
\begin{align*}
\text{H NMR: } & \delta = 1.13 \text{ (s, 9H)}, 2.18 \text{ (s, 3H)}, 6.74-6.81 \text{ (m, 5H)}, 6.88 \text{ (d, } J = 8.1 \text{ Hz, 2H),} \\
& 6.99 \text{ (d, } J = 8.1 \text{ Hz, 2H), 7.43-7.49 \text{ (m, 6H)} 7.95 \text{ (d, } J = 7.8 \text{ Hz, 4H);} \\
\text{C NMR: } & \delta = 21.1, 31.8, 37.8, 124.7, 127.1, 127.2, 127.5, 130.9, 131.1, 131.4, 134.4, 138.1, 139.0, 140.2, \\
& 141.2, 152.7; \text{ B NMR: } \delta = 63.7; \text{ HRMS (Cl) Calcd for } C_{31}H_{31}B (M^+) 414.2519. \text{ Found 414.2526.}
\end{align*}
\]

(Z)-2-(4-Methylphenyl)-1,4-diphenylbut-1-ene (3c)

\[
\begin{align*}
\text{H NMR: } & \delta = 2.35 \text{ (s, 3H)}, 2.68-2.79 \text{ (m, 4H)}, 6.37 \text{ (s, 1H)}, 6.90-6.92 \text{ (m, 2H),} \\
& 7.01-7.30 \text{ (m, 12H);} \text{ C NMR: } \delta = 21.3, 34.6, 42.6, 125.7, 126.0, 126.4, 127.7, 128.2, \\
& 128.38, 128.45, 129.2, 136.5, 137.4, 137.7, 141.8, 142.1; \text{ HRMS (Cl) Calcd for } C_{23}H_{22} (M^+) 298.1721. \text{ Found 298.1720.}
\end{align*}
\]

(Z)-1-(4-Methoxyphenyl)-2-(4-methylphenyl)hept-1-ene (3d)

\[
\begin{align*}
\text{H NMR: } & \delta = 0.86 \text{ (t, } J = 6.9 \text{ Hz, 3H), 1.26-1.40 \text{ (m, 6H)}, 2.34 \text{ (s, 3H),} \\
& 2.43 \text{ (t, } J = 7.1 \text{ Hz, 2H), 3.71 \text{ (s, 3H), 6.33 \text{ (s, 1H),} 6.63 \text{ (d, } J = 9.0 \text{ Hz, 2H),} \\
& 6.86 \text{ (d, } J = 8.7 \text{ Hz, 2H), 7.04 \text{ (d, } J = 8.1 \text{ Hz, 2H),} 7.10 \text{ (d, } J = 8.1 \text{ Hz, 2H);} \\
\text{C NMR: } & \delta = 14.2, 21.3, 22.6, 27.7,
\end{align*}
\]

23

(Z)-1,2-Diphenylhept-1-ene (3e)

$^1$H NMR: $\delta = 0.87$ (t, $J = 7.1$ Hz, 3H), 1.26-1.45 (m, 6H), 2.48 (t, $J = 7.1$ Hz, 2H), 6.42 (s, 1H), 6.89-6.92 (m, 2H), 7.03-7.32 (m, 8H); $^{13}$C NMR: $\delta = 14.2$, 22.6, 27.6, 31.5, 40.7, 125.92, 125.95, 126.7, 127.7, 128.35, 128.43, 128.9, 137.4, 141.3, 143.4; HRMS (CI) Calcd for C$_{19}$H$_{22}$ (M$^+$) 250.1721. Found 250.1722.

(Z)-2-(4-Methoxyphenyl)-1-phenylhept-1-ene (3f)

$^1$H NMR: $\delta = 0.87$ (t, $J = 7.2$ Hz, 3H), 1.26-1.41 (m, 6H), 2.45 (t, $J = 6.9$ Hz, 2H), 3.80 (s, 3H), 6.39 (s, 1H), 6.81-6.84 (m, 2H), 6.92-6.96 (m, 2H), 7.03-7.09 (m, 5H); $^{13}$C NMR: $\delta = 14.2$, 22.6, 27.7, 31.5, 40.7, 55.1, 113.7, 125.7, 125.8, 127.7, 128.8, 129.5, 133.3, 137.7, 143.0, 158.3; HRMS (CI) Calcd for C$_{20}$H$_{24}$O (M$^+$) 280.1827. Found 280.1823.

(Z)-2-(4-Trifluoromethylphenyl)-1-phenylhept-1-ene (3g)
$^1$H NMR: $\delta = 0.87$ (t, $J = 7.1$ Hz, 3H), 1.26-1.43 (m, 6H), 2.49 (t, $J = 6.9$ Hz, 2H), 6.51 (s, 1H), 6.84-6.93 (m, 2H), 7.06-7.14 (m, 3H), 7.26 (d, $J = 7.8$ Hz, 2H), 7.52 (d, $J = 8.1$ Hz, 2H); $^{13}$C NMR: $\delta = 14.2$, 22.6, 27.6, 31.4, 40.3, 124.1 (q, $J_{C-F} = 270.2$ Hz), 125.3 (q, $J_{C-F} = 3.7$ Hz), 126.4, 127.2, 127.9, 128.4 (q, $J_{C-F} = 24.1$ Hz), 128.91, 128.93, 136.8, 141.9, 145.2; HRMS (CI) Calcd for C$_{20}$H$_{21}$F$_3$ (M$^+$) 318.1595. Found 318.1597.

(Z)-2-(4-Ethoxycarbonylphenyl)-1-phenylhept-1-ene (3h)

$^1$H NMR: $\delta = 0.86$ (t, $J = 7.1$ Hz, 3H), 1.27-1.43 (m, 9H), 2.49 (t, $J = 7.1$ Hz, 2H), 4.37 (q, $J = 7.1$ Hz, 2H), 6.49 (s, 1H), 6.88-6.91 (m, 2H), 7.05-7.12 (m, 3H), 7.22 (d, $J = 8.7$ Hz, 2H), 7.97 (d, $J = 8.1$ Hz, 2H); $^{13}$C NMR: $\delta = 14.1$, 14.4, 22.5, 27.6, 31.4, 40.3, 60.9, 126.2, 126.9, 127.8, 128.6, 128.7, 128.9, 129.6, 136.9, 142.4, 146.3, 166.4; HRMS (CI) Calcd for C$_{22}$H$_{26}$O$_2$ (M$^+$) 322.1933. Found 322.1925.

(Z)-1-Phenyl-2-(4-phthalimidophenyl)hept-1-ene (3i)
1H NMR: δ = 0.89 (t, J = 6.9 Hz, 3H), 1.26-1.47 (m, 6H), 2.50 (t, J = 7.4 Hz, 2H), 6.48 (s, 1H), 6.96-6.99 (m, 2H), 7.04-7.15 (m, 3H), 7.27-7.31 (m, 2H), 7.38-7.42 (m, 2H), 7.75-7.81 (m, 2H), 7.92-7.98 (m, 2H); 13C NMR: δ = 14.2, 22.5, 27.7, 31.5, 40.5, 123.6, 126.1, 126.7, 127.8, 128.9, 129.1, 130.2, 131.6, 134.3, 137.1, 141.0, 142.3, 167.1; HRMS (CI) Calcd for C27H25NO2 (M⁺) 395.1885. Found 395.1884.

(Z)-2-(4-Chlorophenyl)-1-phenylhept-1-ene (3j)

1H NMR: δ = 0.87 (t, J = 7.1 Hz, 3H), 1.25-1.39 (m, 6H), 2.45 (t, J = 7.4 Hz, 2H), 6.44 (s, 1H), 6.91 (m, 2H), 7.07-7.11 (m, 5H), 7.25 (m, 2H); 13C NMR: δ = 14.2, 22.6, 27.6, 31.4, 40.4, 126.2, 126.6, 127.8, 128.6, 128.9, 129.9, 132.4, 137.1, 139.6, 142.0; HRMS (CI) Calcd for C19H21Cl (M⁺) 284.1332. Found 284.1328.

(Z)-2-(3-Methylphenyl)-1-phenylhept-1-ene (3k)

1H NMR: δ = 0.87 (t, J = 7.1 Hz, 3H), 1.26-1.42 (m, 6H), 2.30 (s, 3H), 2.45 (t, J = 7.4 Hz, 2H), 6.39 (s, 1H), 6.90-7.08 (m, 8H), 7.17 (t, J = 7.5 Hz, 1H); 13C NMR: δ = 14.2, 21.6, 22.6, 27.7, 31.5, 40.9, 125.5, 125.7, 125.9, 127.4, 127.7, 128.2, 128.8, 137.4, 137.9, 141.3, 143.6; HRMS (CI) Calcd for C20H24 (M⁺) 264.1878. Found 264.1879.

(Z)-2-(4-Methylphenyl)-1-phenylbut-1-ene (3l)
\[\text{NOE}\]

$^1$H NMR: $\delta = 1.06$ (t, $J = 7.5$ Hz, 3H), 2.34 (s, 3H), 2.50 (q, $J = 7.4$ Hz, 2H), 6.40 (s, 1H), 6.91-6.96 (m, 2H), 7.01-7.11 (m, 7H); $^{13}$C NMR: $\delta = 13.0, 21.3, 33.6, 124.7, 125.8, 127.7, 128.3, 128.9, 129.1, 136.3, 137.6, 138.3, 144.8$; HRMS (CI) Calcd for C$^{17}$H$^{18}$ (M$^+$) 222.1409. Found 222.1406.

(Z)-4-Methyl-2-(4-methylphenyl)-1-phenylpent-1-ene (3m)

$^1$H NMR: $\delta = 0.90$ (d, $J = 6.3$ Hz, 6H), 1.56 (pseudo sept., $J = 6.8$ Hz, 1H), 2.33-2.36 (m, 5H), 6.38 (s, 1H), 6.93-6.95 (m, 2H), 7.02-7.11 (m, 7H); $^{13}$C NMR: $\delta = 21.3, 22.4, 25.9, 50.5, 125.9, 127.0, 127.7, 128.4, 128.9, 129.1, 136.3, 137.6, 138.0, 142.3$; HRMS (CI) Calcd for C$^{19}$H$^{22}$ (M$^+$) 250.1721. Found 250.1728.

(Z)-3-Methyl-2-(4-methylphenyl)-1-phenylbut-1-ene (3n)

$^1$H NMR: $\delta = 1.10$ (d, $J = 6.9$ Hz, 6H), 2.35 (s, 3H), 2.69 (sept., $J = 6.8$ Hz, 1H), 6.37 (s, 1H), 6.87 (dd, $J = 8.8, 1.4$ Hz, 2H), 7.01-7.12 (m, 7H); $^{13}$C NMR: $\delta = 21.3, 21.9, 37.5, 123.9, 125.8, 127.6, 128.7, 128.9, 129.0, 136.1, 137.6, 138.0, 149.3$; HRMS (CI) Calcd for C$^{18}$H$^{20}$ (M$^+$) 236.1565. Found 236.1562.

(Z)-1,2-Bis(4-methylphenyl)hept-1-ene (3o)
\[
\begin{align*}
\text{1H NMR: } & \delta = 0.86 \ (t, \ J = 7.2 \ Hz, \ 3H), \ 1.26-1.43 \ (m, \ 6H), \ 2.22 \ (s, \ 3H), \ 2.34 \ (s, \ 3H), \\
& 2.44 \ (t, \ J = 6.8 \ Hz, \ 2H), \ 6.36 \ (s, \ 1H), \ 6.82 \ (d, \ J = 8.4 \ Hz, \ 2H), \ 6.89 \ (d, \ J = 8.4 \ Hz, \ 2H), \\
& 7.03 \ (d, \ J = 8.1 \ Hz, \ 2H), \ 7.09 \ (d, \ J = 7.8 \ Hz, \ 2H); \ 13C \ NMR: \ \delta = 14.2, \ 21.1, \ 21.3, \ 22.6, \\
& 27.7, \ 31.5, \ 40.8, \ 125.6, \ 128.3, \ 128.4, \ 128.7, \ 129.1, \ 134.7, \ 135.4, \ 136.1, \ 138.4, \ 142.5; \\
& \text{HRMS (CI) Calcd for C}_{21}H_{26} \ (M^+) \ 278.2034. \ \text{Found} \ 278.2035.
\end{align*}
\]

(Z)-1-(3-Methylphenyl)-2-(4-methylphenyl)hept-1-ene (3p)

\[
\begin{align*}
\text{1H NMR: } & \delta = 0.87 \ (t, \ J = 6.9 \ Hz, \ 3H), \ 1.28-1.43 \ (m, \ 6H), \ 2.12 \ (s, \ 3H), \ 2.33 \ (s, \ 3H), \\
& 2.45 \ (t, \ J = 7.4 \ Hz, \ 2H), \ 6.36 \ (s, \ 1H), \ 6.68 \ (d, \ J = 7.5 \ Hz, \ 1H), \ 6.79 \ (s, \ 1H), \ 6.85 \ (d, \ J = \\
& 7.5 \ Hz, \ 1H), \ 6.94 \ (dd, \ J = 7.8, \ 7.2 \ Hz, \ 1H), \ 7.03 \ (d, \ J = 7.8 \ Hz, \ 2H), \ 7.09 \ (d, \ J = 7.8 \ Hz, \\
& 2H); \ 13C \ NMR: \ \delta = 14.2, \ 21.3, \ 21.4, \ 22.6, \ 27.7, \ 31.5, \ 40.8, \ 125.77, \ 125.82, \ 126.6, \ 127.5, \\
& 128.3, \ 129.0, \ 129.8, \ 136.1, \ 137.1, \ 137.5, \ 138.3, \ 143.2; \ \text{HRMS (CI) Calcd for C}_{21}H_{26} \\
& (M^+) \ 278.2034. \ \text{Found} \ 278.2042.
\end{align*}
\]

(Z)-1-(4-Fluorophenyl)-2-(4-methylphenyl)hept-1-ene (3q)

\[
\begin{align*}
\text{1H NMR: } & \delta = 0.86 \ (t, \ J = 7.1 \ Hz, \ 3H), \ 1.26-1.43 \ (m, \ 6H), \ 2.34 \ (s, \ 3H), \ 2.44 \ (t, \ J = 7.2 \\
& \text{Hz, } 2H), \ 6.35 \ (s, \ 1H), \ 6.72-6.80 \ (m, \ 2H), \ 6.85-6.91 \ (m, \ 2H), \ 7.01 \ (d, \ J = 7.8 \ Hz, \ 2H), \\
& 7.09 \ (d, \ J = 7.5 \ Hz, \ 2H); \ 13C \ NMR: \ \delta = 14.2, \ 21.3, \ 22.6, \ 27.7, \ 31.5, \ 40.7, \ 114.5 \ (d, \ J_{C-F} \\
& = 21.2 \ Hz), \ 124.5, \ 128.3, \ 129.2, \ 130.3 \ (d, \ J_{C-F} = 7.3 \ Hz), \ 133.6 \ (d, \ J_{C-F} = 2.9 \ Hz), \ 136.4, \\
& 137.9, \ 143.2, \ 160.9 \ (d, \ J_{C-F} = 243.2 \ Hz); \ \text{HRMS (CI) Calcd for C}_{20}H_{25}F \ (M^+) \ 282.1784. \\
& \text{Found} \ 282.1776.
\end{align*}
\]

(Z)-2-(4-Methylphenyl)-1-(2-thienyl)hept-1-ene (3r)
$^1$H NMR: $\delta = 0.87$ (t, $J = 6.9$ Hz, 3H), 1.28-1.45 (m, 6H), 2.36-2.42 (m, 5H), 6.58 (s, 1H), 6.73 (d, $J = 3.3$ Hz, 1H), 6.80 (dd, $J = 5.1$, 3.6 Hz, 1H), 6.92 (d, $J = 5.1$ Hz, 1H), 7.08 (d, $J = 7.8$ Hz, 2H), 7.21 (d, $J = 7.5$ Hz, 2H); $^{13}$C NMR: $\delta = 14.2$, 21.4, 22.6, 27.5, 31.5, 40.9, 119.5, 124.5, 125.8, 126.6, 128.4, 129.5, 137.0, 137.8, 141.1, 142.2; HRMS (Cl) Calcd for C$_{18}$H$_{22}$S (M$^+$) 270.1442. Found 270.1445.

Preparation of (E)-Tamoxifen (5)

Under an argon atmosphere, a CH$_2$Cl$_2$ solution (0.5 ml) of alkynyltriarylborate 1e (75.5 mg, 0.20 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (5.2 mg, 2.5 µmol), and P(o-tol)$_3$ (3.6 mg, 6.0 µmol) was stirred for 30 minutes at room temperature. To the solution was added bromobenzene (33.0 mg, 0.20 mmol) in CH$_2$Cl$_2$ (0.5 ml). After being stirred for 3 h, 4-(Me$_2$NCH$_2$CH$_2$O)C$_6$H$_4$I (4, 178 mg, 0.60 mmol) in CH$_2$Cl$_2$ (0.5 ml), powdered NaOH (78 mg, 1.8 mmol), and water (100 µl) were added. After 24 h, water was added to the reaction mixture. The aqueous layer was extracted with CH$_2$Cl$_2$ (3 times), washed with water (once), brine (once), dried over Na$_2$SO$_4$ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (benzene:AcOEt:NEt$_3$ = 100:40:1) to afford Tamoxifen (5, 58.4 mg, 0.16 mmol, 79% yield, $E/Z = 97/3$). The spectral data was identical to that reported.$^{20f}$

Preparation of alkenyl iodide 6

Under an argon atmosphere, a CH$_2$Cl$_2$ solution (0.5 ml) of alkynyltriarylborate 1e (75.9 mg, 0.20 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (5.2 mg, 2.5 µmol), and P(o-tol)$_3$ (3.6 mg, 6.0 µmol) was stirred for 30 minutes at room temperature. To the solution was added bromobenzene (33.2 mg, 0.20 mmol) in CH$_2$Cl$_2$ (0.5 ml). After being stirred for 3 h, aqueous ammonia (1 ml) was added. The aqueous layer was extracted with Et$_2$O (3 times), washed with water (once), brine (once), dried over Na$_2$SO$_4$ and concentrated. The residue was dissolved in acetone and treated with NIS (225 mg, 1.0 mmol) at 0 °C for 1 h. The reaction mixture was purified by preparative thin-layer chromatography on
silica gel (hexane), followed by GPC to afford alkenyl iodide 6 (39.2 mg, 0.12 mmol, 59% yield, E/Z = 96/4). The spectral data was identical to that reported.20d

**Preparation of ketone 7**

Under an argon atmosphere, a CH₂Cl₂ solution (0.5 ml) of alkynyltriarylborate 1e (75.9 mg, 0.20 mmol), Pd₂dba₃·CHCl₃ (5.2 mg, 2.5 µmol), and P(o-tol)₃ (3.6 mg, 6.0 µmol) was stirred for 30 minutes at room temperature. To the solution was added bromobenzene (33.2 mg, 0.20 mmol) in CH₂Cl₂ (0.5 ml). After being stirred for 3 h, trimethylamine-N-oxide (75.1 mg, 1.0 mmol) was added. After 3 h, water was added to the reaction mixture. The aqueous layer was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane:AcOEt = 50:1) to afford ketone 7 (40.8 mg, 0.18 mmol, 91% yield). The spectral data was identical to that reported.20i

**Preparation of diboranyl compound 8**

Under an argon atmosphere, a (CH₂Cl)₂ solution (0.5 ml) of alkynyltriarylborate 1b (79.5 mg, 0.20 mmol), Pd₂dba₃·CHCl₃ (2.5 mg, 1.2 µmol), and P(o-tol)₃ (2.9 mg, 3.0 µmol) was stirred for 30 minutes at room temperature. To the solution was added 1,4-dibromobenzene (23.7 mg, 0.10 mmol) in (CH₂Cl)₂ (0.5 ml). After being stirred at reflux for 1 h, water was added. The aqueous layer was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane:AcOEt = 10:1) to afford the diboranyl compound 8 (44.9 mg, 0.062 mmol, 62% yield).

**1,4-Bis[(Z)-1-tert-butyl-2-phenyl-2-(diphenylboryl)ethenyl]benzene (8)**

![Chemical Structure](image)

¹H NMR: δ = 0.98 (s, 18H), 6.71-6.76 (m, 14H), 7.40-7.48 (m, 12H), 7.91 (d, J = 6.8 Hz, 8H); ¹³C NMR: δ = 31.7, 37.6, 124.6, 127.0, 127.5, 129.5, 130.9, 131.3, 138.1,
139.1, 140.5, 141.3, 143.9, 153.3; $^{11}$B NMR: $\delta = 59.6$; HRMS (Cl) Caled for C$_{54}$H$_{52}$B$_2$ (M$^+$) 722.4255. Found 722.4252.
References


14. The borate 1a, isolated as solid, was prepared through cation exchange from the corresponding lithium borate. The direct use of the lithium borate generated in situ in THF also gave the product but in lower yield.

15. No reaction occurred in the absence of the palladium catalyst.


17. An alternative mechanism is also conceivable. The arylpalladium bromide A acts as an electrophile like alkyl halides, giving diorganylpalladium D. Subsequent reductive elimination affords the alkenylborane 2b and palladium(0).


19. Other boronic esters including catecholate and ethylene glycolate were also subjected to the reaction conditions. However, no desired alkenylboronic esters were formed, presumably due to the instabilities of the corresponding ate complexes under the reaction conditions.


Chapter 2

Palladium-Catalyzed Allylation of Alkynyltriarylborates

Abstract: In the presence of a palladium catalyst, alkynyltriarylborates reacted with allyl halides to give 1,4-dienylboranes in good yields.
Organoboron compounds have received ever-increasing attention because of their interesting chemical and photophysical properties\(^1\) as well as reactivities. In particular, organoboranes having \(\pi\)-conjugation extended through a vacant \(p\)-orbital on boron\(^2\) are attractive in terms of optoelectronic materials such as light-emitting diodes,\(^3\) fluorescent sensors,\(^4\) non-linear optics,\(^5\) and two-photon emitters.\(^6\) Therefore, skeletons containing alkenyl–boron linkages have become a synthetic target of current interest.

Palladium-catalyzed as well as non-catalyzed reactions of alkynyltriorganylborates with an alkylation agent such as allyl bromide produced trisubstituted alkenylboranes through alkylation on the alkynyl carbon \(\beta\) to boron accompanied with 1,2-migration of organyl group on boron.\(^7\) So far, the migrating organyl group was limited to alkyl and alkenyl groups. It would be more attractive in terms of potential as \(\pi\)-conjugated materials if an aryl group is installed by 1,2-migration. In this chapter, the author describes our synthetic study on the palladium-catalyzed reaction of alkynyltriarylborationes with allyl halides.

We initially examined a non-catalyzed reaction of alkynyltriphenylborate \(1a\) with allyl bromide. Alkynyltriphenylborate \(1a\) was treated with allyl bromide in toluene at 70 °C, and after 15 minutes, the reaction was quenched by addition of acetic acid. Only protonated alkene \(4\) was obtained in 87% yield, suggesting that allyl bromide was not electrophilic enough to form a carbon–carbon bond with the alkyne carbon. Instead, the proton of acetic acid acted as the electrophile to promote the 1,2-migration reaction of the phenyl group from boron to \(\alpha\)-carbon.\(^8\) Thus, it was indicated that alkynyltriarylborationes were less reactive than alkynyltrialkylborates. Next, we examined a palladium-catalyzed reaction. In the presence of a catalytic amount of \(\text{Pd(PPh}_3)_4\), the allylated alkene \(3a\) was obtained in 11% yield (entry 2). A palladium catalyst modified with \(\text{P(o-tol)}_3\), which was a suitable catalyst for the reaction with aryl halides,\(^9\) gave a complex mixture (entry 3). Although \(\text{DPPE}\) and \(\text{DPPF}\) afforded no desired product (entries 4 and 5), \(\text{BINAP}\) gave \(3a\) in 42% yield (entry 6). The bidentate phosphine ligand \(\text{XANTPHOS}\), possessing a rigid and planar skeleton with a large bite angle of 108 °,\(^10\) gave \(3a\) in 91% yield as a mixture of geometrical isomers (entry 7, \(E/Z=54/46\)). \(\text{DPEPHOS}\), which also has a large bite angle (104 °) but is more flexible than \(\text{XANTPHOS}\), gave the product in only 6% yield (entry 8).

Other alkylation reagents were examined (Table 2). Allyl chloride also reacted with \(1a\) to give the allylated product in 48% yield (entry 2). Allyl acetate and allyl methyl carbonate were ineffective, affording only a small amount of products (entries 3 and 4). Thus allyl bromide gave the best result.
### Table 1. Catalyst screening

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst (mol%)</th>
<th>yield of 3a / %</th>
<th>E/Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Pd(PPh&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt; (5)</td>
<td>11</td>
<td>72/28</td>
</tr>
<tr>
<td>3</td>
<td>Pd&lt;sub&gt;2&lt;/sub&gt;dba&lt;sub&gt;3&lt;/sub&gt;:CHCl&lt;sub&gt;3&lt;/sub&gt; (2.5)/P(o-tol)&lt;sub&gt;3&lt;/sub&gt; (6)</td>
<td>complex mixture</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Pd&lt;sub&gt;2&lt;/sub&gt;dba&lt;sub&gt;3&lt;/sub&gt;:CHCl&lt;sub&gt;3&lt;/sub&gt; (2.5)/DPPE (6)</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Pd&lt;sub&gt;2&lt;/sub&gt;dba&lt;sub&gt;3&lt;/sub&gt;:CHCl&lt;sub&gt;3&lt;/sub&gt; (2.5)/DPPF (6)</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Pd&lt;sub&gt;2&lt;/sub&gt;dba&lt;sub&gt;3&lt;/sub&gt;:CHCl&lt;sub&gt;3&lt;/sub&gt; (2.5)/BINAP (6)</td>
<td>42</td>
<td>29/71</td>
</tr>
<tr>
<td>7</td>
<td>Pd&lt;sub&gt;2&lt;/sub&gt;dba&lt;sub&gt;3&lt;/sub&gt;:CHCl&lt;sub&gt;3&lt;/sub&gt; (2.5)/XANTPHOS (6)</td>
<td>91 (90)&lt;sup&gt;d&lt;/sup&gt;</td>
<td>54/46</td>
</tr>
<tr>
<td>8</td>
<td>Pd&lt;sub&gt;2&lt;/sub&gt;dba&lt;sub&gt;3&lt;/sub&gt;:CHCl&lt;sub&gt;3&lt;/sub&gt; (2.5)/DPEPHOS (6)</td>
<td>6</td>
<td>27/73</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 1.0 equiv of 1a, 1.2 equiv of allyl bromide, 5 mol% Pd catalyst, toluene, 70 °C, 15 min.  
<sup>b</sup> Determined by GC analysis.  
<sup>c</sup> A protonated product 4 was isolated in 87% yield (E/Z = 7/93).  
<sup>d</sup> Isolated yield.

The following experiments were carried out in order to support the initial formation of alkenylborane 2a. When AcOD was employed instead of AcOH for protonolysis, deuterated alkene 3a-<sup>d</sup> was isolated in 91% yield (E/Z = 54/46, E: 72% incorporation of D, Z: 71% incorporation of D). Successive treatment of the reaction mixture with...
trimethylamine N-oxide caused oxidation of the carbon–boron bond to afford the ketone 5 in 79% yield. Thus, the alkenylborane 2a was initially formed with incorporation of an allyl group on the sp² carbon β to boron and a phenyl group on the α sp² carbon.

**Table 2. Examination on allylating reagents**

<table>
<thead>
<tr>
<th>entry</th>
<th>X</th>
<th>yield of 3a / %&lt;sup&gt;b&lt;/sup&gt;</th>
<th>E/Z&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br</td>
<td>91 (90)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>54/46</td>
</tr>
<tr>
<td>2</td>
<td>Cl</td>
<td>48</td>
<td>43/57</td>
</tr>
<tr>
<td>3</td>
<td>OAc</td>
<td>13</td>
<td>56/44</td>
</tr>
<tr>
<td>4</td>
<td>OC(O)OMe</td>
<td>3</td>
<td>52/48</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 1.0 equiv of 1a, 1.2 equiv of allylating reagent, 5 mol% Pd catalyst, toluene, 70 °C, 15 min. <sup>b</sup> Determined by GC analysis. <sup>c</sup> Isolated yield.

Next, a crossover experiment was carried out (eq 3). When a mixture of 1a (1.0 equiv.) and 1b (1.0 equiv.) was subjected to the reaction with 2.4 equiv. of allyl bromide, 3a and 3b were obtained in 93% and 88% yield, respectively. No crossover products were detected in the reaction mixture by ¹H NMR and GC-MS, suggesting that the 1,2-aryl migration occurred intramolecularly.
The plausible mechanism is depicted in Scheme 1. Initially, allyl bromide oxidatively adds to palladium(0) to yield π-allylpalladium species ligated by XANTPHOS. The π-allylpalladium species is electrophilic enough to induce a nucleophilic attack of the alkynyltriarylborate anion, which triggers 1,2-phenyl migration from boron to the α-carbon, giving the alkenylborane 2a and palladium(0).

**Scheme 1. Plausible mechanism**

Essentially no E/Z selectivities were observed in the products of the present reaction. This stereochemical outcome stands in contrast to the good stereoselectivities observed in the reaction with aryl halides. Thus, it is inferred that a mechanism different from the arylative variant is operating in the present reaction. We explain the difference in the stereoselectivities is attributed to the nature of π-allylpalladium complex ligated by a bidentate phosphine and σ-arylpalladium complex ligated by a monodentate phosphine. Tetracoordinated [(xantphos)Pd(π-allyl)]⁺, which would be generated by oxidative addition of allyl bromide, is sterically congested on palladium center, prohibiting the additional coordination of the alkynyl moiety to the palladium. Meanwhile, the side of the allyl ligand opposite to palladium is vulnerable enough to be directly attacked by the alkynyl group. Therefore, the alkynylborate is likely to attack the allyl ligand from the back side of palladium. The 1,2-phenyl migration can occur in both ways, in the syn- and anti-periplanar directions to the carbon–carbon bond developing at the sp carbon β to boron (Figure 1). On the other hand, tricoordinated
(o-tol)₃Pd(aryl)Br, which is generated by oxidative addition of aryl halide to the palladium(0) and is in equilibrium with the dimeric species bridged by bromide ligands, has a vacant site on palladium, allowing the alkynylborate to coordinate. Consequently, it tends to undergo carboxypalladation across the carbon–carbon triple bond.

**Figure 1.** Stereochemistry of 1,2-migration

![Stereochemistry of 1,2-migration](image)

**Table 3.** Allylation of various alkynyltriarylborates

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkynyltriarylborate</th>
<th>R</th>
<th>Ar</th>
<th>Yield (%)ᵇ</th>
<th>E/Zᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1c</td>
<td>&quot;C₅H₁₁</td>
<td>Ph</td>
<td>91</td>
<td>54/46</td>
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<tr>
<td>2</td>
<td>1d</td>
<td>'Bu</td>
<td>Ph</td>
<td>89</td>
<td>55/45</td>
</tr>
<tr>
<td>3</td>
<td>1e</td>
<td>'Pr</td>
<td>Ph</td>
<td>72</td>
<td>57/43</td>
</tr>
<tr>
<td>4</td>
<td>1f</td>
<td>Ph</td>
<td>Ph</td>
<td>24</td>
<td>50/50</td>
</tr>
<tr>
<td>5</td>
<td>1g</td>
<td>Me₃Si</td>
<td>Ph</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>6</td>
<td>1h</td>
<td>&quot;C₅H₁₁</td>
<td>4-MeC₆H₄</td>
<td>89</td>
<td>47/53</td>
</tr>
<tr>
<td>7</td>
<td>1i</td>
<td>&quot;C₅H₁₁</td>
<td>3-MeC₆H₄</td>
<td>91</td>
<td>48/52</td>
</tr>
<tr>
<td>8ᵈ</td>
<td>1j</td>
<td>&quot;C₅H₁₁</td>
<td>4-FC₆H₄</td>
<td>83</td>
<td>53/47</td>
</tr>
<tr>
<td>9</td>
<td>1k</td>
<td>&quot;C₅H₁₁</td>
<td>2-thienyl</td>
<td>79</td>
<td>71/29</td>
</tr>
</tbody>
</table>

ᵃ Reaction conditions: 1.0 equiv. of 1, 1.2 equiv. of allyl bromide, 2.5 mol% Pd₂dba₃·CHCl₃, 6 mol% XANTPHOS, toluene, 70 °C, 15 min.ᵇ Isolated yield.ᶜ Determined by ¹H NMR analysis.ᵈ Reaction time: 30 min.
Various alkynylborates were subjected to the palladium-catalyzed allylation reaction conditions (Table 3). Alkynylborates having a primary alkyl substituent yielded the corresponding 1,4-dienes in high yield (entries 1 and 2). In the case of a secondary alkyl substituent, the yield decreased to 72% (entry 3). Triphenyl(phenylethynyl)borate (1f) was less reactive, giving the product in 24% yield (entry 4). A complex mixture resulted from trimethylsilylethynylborate 1g (entry 5). As the aryl group on boron, both electron-donating and withdrawing groups could participated in the reaction (eq 3, entries 6-8). The reaction of alkynyltriarylborate 1j (Ar = 4-fluorophenyl) was slower than that of 1c, requiring 30 minutes to complete, indicating the electron poor borate is less reactive (entry 8). A 2-thienyl group was also migrated to give the corresponding product in 79% yield (entry 9).

The allylation reaction of alkynylborate 1l afforded 2l in 28% yield (eq 4, $E/Z = >99/1$) and 3l in 25% yield ($E/Z = 18/82$). The boron–carbon bond of the (E)-isomer of 2l was less labile to protonolysis with acetic acid and oxidation with air owing to the steric protection by the neighboring tertiary butyl group to allow partial isolation of 2l.

The reaction of alkynylborate 1m equipped with a methoxymethyl substituent gave a mixture of (E)-alkenyloborane 2m (eq 5, 48% yield) and (Z)-alkene 3m (38% yield). The (E)-alkenyloborane 2m was stabilized by the intramolecular coordination of the oxygen atom, whereas the corresponding (Z)-isomer was protonated to 3m.

We subsequently conducted the reaction with substituted allylic bromides. The reaction of 1c with cinnamyl bromide afforded the 1,4-diene 6 in 93% yield (eq 6, $E/Z=42/58$), while the reaction with crotyl bromide resulted in the mixture of isomers.
Prenyl bromide was selectively incorporated at less hindered position to give 7 in 71% yield (eq 7, \(E/Z=53/47\)).

\[
\text{1c} + \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} \text{Br} \xrightarrow{2.5 \text{ mol\% Pd}_2\text{dba}_3 \cdot \text{CHCl}_3, 6 \text{ mol\% XANTPHOS, AcOH, toluene, 70 °C}} \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} \text{C}_6\text{H}_{11} \xrightarrow{\text{AcOH}} \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} \\
\begin{array}{c}
\text{nC}_6\text{H}_{11} \\
\text{nC}_6\text{H}_{11}
\end{array} \text{6, 93%} \begin{array}{c}
\text{E} \\
\text{Z}
\end{array} = 42/58
\]

\[
\begin{array}{c}
\text{1c} \\
\text{Ph}
\end{array} \text{Br} \xrightarrow{2.5 \text{ mol\% Pd}_2\text{dba}_3 \cdot \text{CHCl}_3, 6 \text{ mol\% XANTPHOS, AcOH, toluene, 70 °C}} \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} \text{C}_6\text{H}_{11} \xrightarrow{\text{AcOH}} \begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} \\
\begin{array}{c}
\text{nC}_6\text{H}_{11} \\
\text{nC}_6\text{H}_{11}
\end{array} \text{7, 71%} \begin{array}{c}
\text{E} \\
\text{Z}
\end{array} = 53/47
\]

We next tried to make the produced (\(\alpha\)-arylalkenyl)dialkylboranes less labile by increasing the steric bulkiness of the aryl groups. Our initial attempt to synthesize the borate by the reaction of trimesitylborane\(^{13}\) with alkynyllithium failed due to the severe steric hindrance around the boron atom. Next, a 2,6-dimethoxyphenyl group was examined as the aryl group on boron, since tris(2,6-dimethoxyphenyl)borane is known as air-stable to form stable complexes with a variety of Lewis bases and nucleophiles.\(^{14}\) Thus, alkynyllithiums were reacted with tris(2,6-dimethoxyphenyl)borane, and the following treatment with tetramethylammonium chloride afforded the corresponding alkynylborates 1n, 1o, and 1p as air-stable white powders.

To our delight, the palladium-catalyzed reaction of 1n and 1o with allyl bromide proceeded even at room temperature, giving the alkenylborane 2n and 2o with high stereoselectivity (eqs 8 and 9, \(E/Z=95/5\)) in 90 and 93% yield, respectively.\(^{15}\) The alkynylborates 1n and 1o were considerably more reactive than triphenyl(phenylethynyl)borate (1f). Although it was unclear which steric or electronic factor operated for the stereoselective formation of 2n and 2o, the higher reactivity could be attributed to the electron-rich nature of the 2,6-dimethoxyphenyl group. This trend is in agreement with the slower reaction rate observed with tris(4-fluorophenyl)borate 1j. The organoboranes 2n and 2o were so stable that they could be purified by column chromatography on silica gel. The stability can be ascribed either to steric hindrance of the 2,6-dimethoxyphenyl groups or to intramolecular coordination of the methoxy group to boron. In the \(^1\)H NMR spectra of 2n and 2o, the methoxy signals were observed as equivalent, making the intramolecular coordination unlikely.
The reaction of $^{1}p$ furnished a product totally different from that of $^{1}o$ (eq 10). 3-Borolene $^{8}$ was obtained in 77% yield together with a few percents of $(Z)-^{2}p$. The formation of $^{8}$ was explained by assuming that $(E)-^{2}p$, the major geometrical isomer of the initial product, underwent a cyclization reaction accompanied by 1,2-migration of the 2,6-dimethoxyphenyl group.\textsuperscript{16} On the other hand, $(Z)-^{2}p$, the minor geometrical isomer, remained as such.

Treatment of 1,4-dienylborane $^{2}n$ with a catalytic amount of DBU caused a shift of a carbon–carbon double bond to afford the conjugated $(E,E)$-1,3-dienylborane $^{9}$ as a single stereoisomer in 81% yield (eq 11). The steric hindrance around the boron atom would inhibit the complexation with DBU and the $\pi$-accepting ability of the boron facilitates isomerization via deprotonation.\textsuperscript{17}
Experimental Section

General. NMR spectra were recorded on a Varian Gemini 2000 (\(^1\)H at 300 MHz and \(^{13}\)C at 75 MHz) or Varian Mercury-400 (\(^1\)H at 400 MHz and \(^{11}\)B at 128 MHz) spectrometers. Me\(_4\)Si (\(^1\)H, \(\delta = 0.00\)), residual H of CD\(_3\)CN (\(^1\)H in CD\(_3\)CN, \(\delta = 1.94\)), CDCl\(_3\) (\(^{13}\)C, \(\delta = 77.0\)), CD\(_3\)CN (\(^{13}\)C, \(\delta = 1.32\)), and BF\(_3\)-OEt\(_2\) (\(^{11}\)B, \(\delta = 0.00\)) were used as standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. All reactions were carried out under an argon atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF\(_{254}\) (Merck). Gel permeation chromatography (GPC) was carried out with Japan Analytical Industry LC-908.

Materials. Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used as received. CH\(_2\)Cl\(_2\) was purchased from Kanto chemicals. Toluene was dried over Na-benzophenone ketyl. AcOH and AcOD were degassed by sonication.

Palladium-catalyzed alkylation of alkynyltriarylborate 1a. A typical procedure.

Under an argon atmosphere, a toluene solution (0.5 ml) of alkynyltriarylborate 1a (89.0 mg, 0.20 mmol), Pd\(_2\)dba\(_3\)-CHCl\(_3\) (5.2 mg, 2.5 \(\mu\)mol), and XANTPHOS (6.9 mg, 6.0 \(\mu\)mol) was stirred for 30 minutes at room temperature. To the solution was added allyl bromide (28.8 mg, 0.24 mmol) in toluene (0.5 ml). After being stirred at 70 °C for 15 minutes, AcOH (1 ml) was added at room temperature. After 3 h, the reaction mixture was neutralized with Na\(_2\)CO\(_3\) solution. The aqueous layer was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO\(_4\) and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane) to afford the trisubstituted alkene 3a (44.5 mg, 0.18 mmol, 91% yield, \(E/Z = 54/46\)).

\((E)\)- and \((Z)\)-1-Phenyl-2-(2-phenylethyl)penta-1,4-diene (3a)

\[ \begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph}
\end{align*} \]

\(A\) mixture of geometrical isomers \((E/Z = 54/46)\)

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.44-2.56 (('E)\)- and \((Z)\)-isomer, m, 2H), 2.75-2.85 (('E) and \((Z)\)-isomer, m, 2H), 2.96 (('E)-isomer, d, \(J = 6.8\) Hz, 2H), 3.02 (('Z)-isomer, d, \(J = 6.8\) Hz, 2H), 3.10-3.15 ('('E)-isomer, m, 2H), 3.85 ('('E)-isomer, q, \(J = 6.8\) Hz, 2H), 5.42 (('E)-isomer, s, 1H), 7.15 (('E)-isomer, s, 5H), 7.25-7.40 ('('E)-isomer, m, 7H), 7.50-7.70 ('('E)-isomer, m, 3H), 7.95-8.00 ('('E)-isomer, m, 2H).
$J = 6.0$ Hz, 2H), 5.09-5.19 ($E$- and (Z)-isomer, m, 2H), 5.82-5.97 ($E$- and (Z)-isomer, m, 1H), 6.34 ($E$-isomer, s, 1H), 6.37 ($Z$-isomer, s, 1H), 7.13-7.33 ($E$- and (Z)-isomer, m, 10H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 32.9, 34.4, 34.7, 35.6, 39.1, 42.0, 116.1, 116.5, 125.7, 125.8, 126.08, 126.13, 126.7, 126.8, 128.00, 128.02, 128.19, 128.22, 128.25, 128.37, 128.39, 128.41, 136.0, 136.4, 137.9, 138.0, 139.5, 140.5, 141.8, 141.9; HRMS (EI): Calcd for C$_{19}$H$_{20}$ (M$^+$) 248.1565. Found 248.1558.

One-pot oxidation procedure for alkenylborane 2a

Under an argon atmosphere, a toluene solution (0.5 ml) of alkynyltriarylborate 1a (89.2 mg, 0.20 mmol), Pd$_2$dba$_3$·CHCl$_3$ (5.0 mg, 2.5 $\mu$mol), and XANTPHOS (7.0 mg, 6.0 $\mu$mol) was stirred for 30 minutes at room temperature. To the solution was added allyl bromide (29.0 mg, 0.24 mmol) in toluene (0.5 ml). After being stirred at 70 °C for 15 minutes, Me$_3$NO (75 mg, 1.0 mmol) was added at room temperature. After 3 h, water was added to the reaction mixture. The aqueous layer was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO$_4$ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane:AcOEt = 20:1) to afford the ketone 5 (41.8 mg, 0.16 mmol, 79% yield).

$E$- and $Z$-1-(4-Methoxyphenyl)-2-pentylpenta-1,4-diene (3b)

A mixture of geometrical isomers ($E/Z$=51/49)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.86-0.93$ ($E$- and (Z)-isomer, m, 3H), 1.26-1.33 ($E$- and (Z)-isomer, m, 4H), 1.42-1.54 ($E$- and (Z)-isomer, m, 2H), 2.11-2.23 ($E$- and (Z)-isomer, m, 2H), 2.89 ($E$-isomer, d, $J = 6.9$ Hz, 2H), 2.97 ($Z$-isomer, d, $J = 6.0$ Hz, 2H), 3.81 ($E$- and (Z)-isomer, s, 3H), 5.06-5.13 ($E$- and (Z)-isomer, m, 2H), 5.81-5.95 ($E$- and (Z)-isomer, m, 1H), 6.21 ($E$-isomer, s, 1H), 6.31 ($Z$-isomer, s, 1H), 6.84-6.87 ($E$- and (Z)-isomer, m, 2H), 7.16 ($E$- and (Z)-isomer, pseudo t, $J = 8.6$ Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 14.1, 14.2, 22.6, 22.7, 27.8, 27.9, 30.8, 31.7, 32.0, 35.4, 37.3, 41.9, 55.2, 113.4, 115.7, 116.0, 125.2, 125.4, 129.5, 129.6, 130.7, 130.9, 136.3, 136.8, 139.2, 140.5, 157.6, 157.7; HRMS (EI): Calcd for C$_{17}$H$_{24}$O, (M$^+$) 244.1827. Found 244.1836.

$E$- and $Z$-2-Pentyl-1-phenylpenta-1,4-diene (3c)
A mixture of geometrical isomers (E/Z=54/46)

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 0.85-0.93\) ((E)- and (Z)-isomer, m, 3H), 1.26-1.34 ((E)- and (Z)-isomer, m, 4H), 1.43-1.56 ((E)- and (Z)-isomer, m, 2H), 2.13-2.24 ((E)- and (Z)-isomer, m, 2H), 2.91 ((E)-isomer, d, \(J = 6.6\) Hz, 2H), 2.98 ((Z)-isomer, d, \(J = 6.0\) Hz, 2H), 5.07-5.15 ((E)- and (Z)-isomer, m, 2H), 5.81-5.95 ((E)- and (Z)-isomer, m, 1H), 6.28 ((E)-isomer, s, 1H), 6.37 ((Z)-isomer, s, 1H), 7.16-7.33 ((E)- and (Z)-isomer, m, 5H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 14.1, 14.2, 22.5, 22.7, 27.8, 27.9, 30.9, 31.7, 32.0, 35.4, 37.2, 41.8, 115.8, 116.2, 125.8, 125.87, 125.92, 126.0, 127.9, 128.0, 128.4, 128.5, 136.2, 136.6, 138.1, 138.3, 140.6, 141.8; HRMS (EI): Calcd for C\(_{16}\)H\(_{22}\) (M\(^+\)) 214.1722. Found 214.1724.

\((E)-\) and \((Z)-\)2-(2-Methylpropyl)-1-phenylpenta-1,4-diene (3d)

A mixture of geometrical isomers (E/Z=55/45)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 0.83\) ((E)-isomer, d, \(J = 6.4\) Hz, 6H), 0.93 ((Z)-isomer, d, \(J = 6.6\) Hz, 6H), 1.87 ((E)- and (Z)-isomer, pseudo sept, \(J = 6.6\) Hz, 1H), 2.03 ((Z)-isomer, d, \(J = 7.2\) Hz, 2H), 2.15 ((E)-isomer, d, \(J = 7.2\) Hz, 2H), 2.89 ((E)-isomer, d, \(J = 6.8\) Hz, 2H), 2.95 ((Z)-isomer, d, \(J = 6.0\) Hz, 2H), 5.05-5.13 ((E)- and (Z)-isomer, m, 2H), 5.81-5.91 ((E)- and (Z)-isomer, m, 1H), 6.34 ((E)-isomer, s, 1H), 6.35 ((Z)-isomer, s, 1H), 7.14-7.30 ((E)- and (Z)-isomer, m, 5H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 22.56, 22.62, 26.3, 26.4, 35.2, 39.4, 41.7, 46.8, 115.8, 116.2, 125.8, 126.0, 127.0, 127.4, 127.9, 128.0, 128.4, 128.8, 136.2, 136.7, 138.1, 138.5, 139.4, 140.6; HRMS (EI): Calcd for C\(_{15}\)H\(_{20}\) (M\(^+\)) 200.1565. Found 200.1561.

\((E)-\) and \((Z)-\)2-Isopropyl-1-phenylpenta-1,4-diene (3e)

A mixture of geometrical isomers (E/Z=43/57)
$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 1.04$ ((Z)-isomer, d, $J = 6.9$ Hz, 6H), 1.12 ((E)-isomer, d, $J = 6.6$ Hz, 6H), 2.42 ((E)-isomer, sept, $J = 6.9$ Hz, 1H), 2.87 ((Z)-isomer, d, $J = 6.9$ Hz, 2H), 3.01 ((E)-isomer, d, $J = 6.0$ Hz, 2H), 3.11 ((Z)-isomer, sept, $J = 6.9$ Hz, 1H), 5.05-5.16 ((E) - and (Z)-isomer, m, 2H), 5.81-5.98 ((E) - and (Z)-isomer, m, 1H), 6.19 ((Z)-isomer, s, 1H), 6.39 ((E)-isomer, s, 1H), 7.17-7.33 ((E) - and (Z)-isomer, m, 5H);

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 21.3, 22.2, 29.2, 29.8, 30.4, 34.3, 34.9, 35.1, 115.7, 116.1, 123.9, 124.6, 125.8, 125.9, 127.9, 128.0, 128.4, 128.6, 136.7, 137.4, 138.3, 138.5, 146.4, 146.6; HRMS (EI): Calcd for C$_{14}$H$_{18}$ (M$^+$) 186.1409. Found 186.1406.

$(E)$- and $(Z)$-1-(4-Methylphenyl)-2-pentylpenta-1,4-diene (3h)

A mixture of geometrical isomers ($E$/Z=53/47)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.85-0.93$ ((E)- and (Z)-isomer, m, 3H), 1.25-1.39 ((E)- and (Z)-isomer, m, 4H), 1.43-1.55 ((E)- and (Z)-isomer, m, 2H), 2.11-2.24 ((E)- and (Z)-isomer, m, 2H), 2.33 ((E)- and (Z)-isomer, s, 3H), 2.89 ((E)-isomer, d, $J = 6.9$ Hz, 2H), 2.97 ((Z)-isomer, d, $J = 6.0$ Hz, 2H), 5.06-5.15 ((E) - and (Z)-isomer, m, 2H), 5.80-5.95 ((E) - and (Z)-isomer, m, 1H), 6.24 ((E)-isomer, s, 1H), 6.33 ((Z)-isomer, s, 1H), 7.08-7.15 ((E)- and (Z)-isomer, m, 4H);

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 14.1, 14.2, 21.2, 22.6, 22.7, 27.8, 27.9, 30.9, 31.7, 32.0, 35.5, 37.2, 41.9, 115.7, 116.1, 125.6, 125.8, 128.3, 128.4, 128.7, 135.2, 135.37, 135.42, 135.5, 136.3, 136.7, 139.9, 141.2; HRMS (EI): Calcd for C$_{17}$H$_{24}$ (M$^+$) 228.1878. Found 228.1889.

$(E)$- and $(Z)$-1-(3-Methylphenyl)-2-pentylpenta-1,4-diene (3i)

A mixture of geometrical isomers ($E$/Z=48/52)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.84-0.93$ ((E)- and (Z)-isomers, m, 3H), 1.26-1.39 ((E)- and (Z)-isomers, m, 4H), 1.43-1.55 ((E)- and (Z)-isomers, m, 2H), 2.12-2.24 ((E)- and (Z)-isomers, m, 2H), 2.33 ((E)- and (Z)-isomers, s, 3H), 2.90 ((E)-isomer, d, $J = 7.1$ Hz, 2H), 2.98 ((Z)-isomer, d, $J = 6.3$ Hz, 2H), 5.06-5.15 ((E) - and (Z)-isomers, m, 2H), 5.81-5.95 ((E) - and (Z)-isomers, m, 1H), 6.25 ((E)-isomer, s, 1H), 6.34 ((Z)-isomer, s, 1H), 7.00-7.05 ((E)- and (Z)-isomers, m, 3H), 7.17-7.24 ((E) - and (Z)-isomers, m, 1H);

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 14.1, 14.2, 21.5, 22.5, 22.7, 27.8, 27.9, 30.9, 31.7, 32.0,
35.5, 37.2, 41.8, 115.8, 116.1, 125.4, 125.5, 125.8, 126.0, 126.6, 126.7, 127.8, 127.9, 129.2, 129.3, 136.3, 136.7, 137.40, 137.45, 138.1, 138.2, 140.5, 141.7; HRMS (EI): Calcd for C₁₇H₂₄ (M⁺) 228.1878. Found 228.1889.

**(E)- and (Z)-1-(4-Fluorophenyl)-2-pentylpenta-1,4-diene (3j)**

![A mixture of geometrical isomers (E/Z=53/47)]

1H NMR (300 MHz, CDCl₃): δ = 0.85-0.93 ([(E)- and (Z)-isomers, m, 3H), 1.19-1.39 ([(E)- and (Z)-isomers, m, 4H), 1.41-1.52 ([(E)- and (Z)-isomers, m, 2H), 2.12-2.20 ([(E)- and (Z)-isomers, m, 2H), 2.89 ([(E)-isomer, d, J = 7.1 Hz, 2H), 2.93 ([(Z)-isomer, d, J = 6.0 Hz, 2H), 5.06-5.15 ([(E)- and (Z)-isomers, m, 2H), 5.79-5.94 ([(E)- and (Z)-isomers, m, 1H), 6.22 ([(E)-isomer, s, 1H), 6.32 ([(Z)-isomer, s, 1H), 6.95-7.03 ([(E)- and (Z)-isomers, m, 2H), 7.13-7.21 ([(E)- and (Z)-isomers, m, 2H); 13C NMR (75 MHz, CDCl₃): δ = 14.1, 14.2, 22.5, 22.7, 27.7, 27.8, 30.8, 31.7, 31.9, 35.3, 37.2, 41.7, 114.8 (d, J = 21.2 Hz), 116.1 (d, J = 30.6 Hz), 124.6, 124.8, 129.8-130.0 (m), 134.0-134.3 (m), 136.0, 136.5, 140.6, 159.4-152.8 (m); HRMS (EI): Calcd for C₁₆H₂₁F (M⁺) 232.1627. Found 232.1629.

**(E)- and (Z)-2-Pentyl-1-(2-thienyl)penta-1,4-diene (3k)**

![A mixture of geometrical isomers (E/Z=71/29)]

1H NMR (400 MHz, CDCl₃): δ = 0.88-1.19 ([(E)- and (Z)-isomers, m, 3H), 1.27-1.41 ([(E)- and (Z)-isomers, m, 4H), 1.43-1.54 ([(E)- and (Z)-isomers, m, 2H), 2.15 ([(Z)-isomer, t, J = 7.8 Hz, 2H), 2.37 ([(E)-isomer, m, 2H), 2.90 ([(E)-isomer, d, J = 7.2 Hz, 2H), 3.14 ([(Z)-isomer, d, J = 6.4 Hz, 2H), 5.04-5.14 ([(E)- and (Z)-isomers, m, 2H), 5.78-5.90 ([(E)- and (Z)-isomers, m, 1H), 6.36 ([(E)-isomer, s, 1H), 6.43 ([(Z)-isomer, s, 1H), 6.88-6.91 ([(E)- and (Z)-isomers, m, 1H), 6.94-6.97 ([(E)- and (Z)-isomers, m, 1H), 7.15-7.17 ([(E)- and (Z)-isomers, m, 1H); 13C NMR (75 MHz, CDCl₃): δ = 14.2, 22.63, 22.65, 27.5, 27.8, 31.7, 32.1, 32.2, 36.3, 37.9, 42.6, 115.9, 116.5, 118.7, 118.8, 123.9, 125.9, 126.2, 126.5, 126.7, 135.0, 136.2, 140.1, 140.7, 140.8, 141.0; HRMS (EI): Calcd for C₁₄H₂₀S (M⁺) 220.1286. Found 220.1284.
(E)-2-Methoxymethyl-1-phenyl-1-diphenylborypenta-1,4-diene (2m)

\[ \text{MeO----BPh}_2 \]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.00 (d, $J$ = 6.3 Hz, 2H), 3.40 (s, 3H), 4.73 (s, 2H), 5.09-5.21 (m, 2H), 5.83-5.96 (m, 1H), 6.83-6.87 (m, 2H), 7.02-7.13 (m, 3H), 7.22-7.33 (m, 6H), 7.40-7.44 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 32.0, 59.2, 83.3, 116.0, 125.3, 126.5, 127.0, 127.2, 127.4, 128.0, 133.9, 136.1, 140.0; $^{11}$B NMR (128 MHz, CDCl$_3$): $\delta$ = 18.5; HRMS (EI): Calcd for C$_{25}$H$_{25}$BO (M$^+$) 352.1998. Found 352.1997.

(Z)-2-Methoxymethyl-1-phenylpenta-1,4-diene (3m)

\[ \text{OMe----} \]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 3.03 (pseudo dt, $J$ = 6.9, 1.3 Hz, 2H), 3.31 (s, 3H), 4.02 (s, 2H), 5.10-5.19 (m, 2H), 5.86-6.00 (m, 1H), 7.20-7.36 (m, 5H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 39.8, 58.1, 70.2, 116.5, 126.6, 128.0, 128.7, 129.9, 136.0, 137.1, 137.6; HRMS (EI): Calcd for C$_{13}$H$_{16}$O (M$^+$) 188.1201. Found 188.1199.

(1E,4E)- and (1Z,4E)-2-Pentyl-1,5-diphenylpenta-1,4-diene (7)

A mixture of geometrical isomers (E/Z=42/58)

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 0.85-0.93 ((E)- and (Z)-isomers, m, 3H), 1.26-1.38 ((E)- and (Z)-isomers, m, 4H), 1.47-1.59 ((E)- and (Z)-isomers, m, 2H), 2.18-2.28 ((E)- and (Z)-isomers, m, 2H), 3.06 ((E)-isomer, d, $J$ = 7.2 Hz, 2H), 3.13 ((E)-isomer, d, $J$ = 6.3 Hz, 2H), 6.21-6.33 ((E)- and (Z)-isomers, m, 1H), 6.42-6.50 ((E)- and (Z)-isomers, m, 1H), 7.17-7.40 ((E)- and (Z)-isomers, m, 10H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ = 14.07, 14.13, 22.5, 22.6, 27.7, 27.9, 31.0, 31.6, 31.9, 34.5, 37.2, 40.9, 125.99, 126.03, 126.1, 126.2, 127.0, 128.0, 128.1, 128.3, 128.46, 128.49, 128.5, 131.0, 131.5, 137.6,
138.2, 138.3, 140.8, 142.1; HRMS (EI): Calcd for C_{22}H_{26} (M+) 290.2035. Found 290.2037.

(E)- and (Z)-5-Methyl-2-pentyl-1-phenylhexa-1,4-diene (8)

A mixture of geometrical isomers (E/Z=53/47)

^1^H NMR (300 MHz, CDCl_3): δ = 0.85-0.93 ((E)- and (Z)-isomers, m, 3H), 1.25-1.37 ((E)- and (Z)-isomers, m, 4H), 1.46-1.59 ((E)- and (Z)-isomers, m, 2H), 1.60 ((Z)-isomer, s, 3H), 1.67 ((E)-isomer, s, 3H), 1.72 ((Z)-isomer, d, J = 1.5 Hz, 3H), 1.76 ((E)-isomer, d, J = 1.5 Hz, 3H), 2.10-2.22 ((E)- and (Z)-isomers, m, 2H), 2.84 ((Z)-isomer, d, J = 7.2 Hz, 2H), 2.91 ((E)-isomer, d, J = 6.9 Hz, 2H), 5.12-5.18 ((E)-isomer, m, 1H), 5.20-5.27 ((Z)-isomer, m, 1H), 6.25 ((Z)-isomer, s, 1H), 6.28 ((E)-isomer, s, 1H), 7.15-7.32 ((E)- and (Z)-isomers, m, 5H); ^1^C NMR (75 MHz, CDCl_3): δ = 14.1, 14.2, 17.8, 18.0, 22.6, 22.7, 25.87, 25.90, 27.8, 28.1, 30.0, 31.1, 31.8, 32.1, 36.0, 37.3, 122.1, 122.4, 124.7, 125.7, 125.8, 127.91, 127.93, 128.5, 128.6, 132.5, 133.0, 138.5, 138.6, 142.8, 143.0; HRMS (EI): Calcd for C_{18}H_{26} (M+) 242.2035. Found 242.2037.

Synthesis of alkynylborates 1n: typical procedure for the preparation of alkynylborates 1n-1p

To an oven-dried, N_2-purged frask were added a solution of phenylacetylene (615 mg, 6.0 mmol) in THF (20 mL) and the mixture was cooled at -78 °C. n-BuLi in hexane (1.6 M, 3.4 ml, 5.5 mmol) was added to the solution and the mixture was stirred at this temperature for 30 minutes. Tris(2,6-dimethoxyphenyl)borane (2.1 g, 5.0 mmol) was added, and then the reaction mixture was stirred at room temperature for 1 h. After addition of a small amount of methanol for quenching, the solution was concentrated under high vacuum. The residue was dissolved in methanol and tetramethylammonium chloride (600 mg, 5.5 mmol) was added, resulting in a white precipitate. The precipitate
was collected by filtration, washed with cooled methanol, and dried under high vacuum to give the product 1n (2.6 g, 4.3 mmol, 86% yield).

Tetramethylammonium tris(2,6-dimethoxyphenyl)(phenylethynyl)borate (1n)

\[ \text{[Me}_4\text{N]} \]

\[ \text{MeO} \hspace{1cm} \text{OMe} \hspace{1cm} \text{OMe} \hspace{1cm} \text{OMe} \]

\[ \text{OMe} \hspace{1cm} \text{OMe} \hspace{1cm} \text{OMe} \hspace{1cm} \text{OMe} \]

\[ \text{MeO} \]

\[ \text{H NMR (400 MHz, CD}_3\text{CN): } \delta = 2.90 \text{ (s, 12H), 3.32 (s, 18H), 6.31 (d, } J = 8.0 \text{ Hz, 6H), 6.77 (t, } J = 8.0 \text{ Hz, 3H), 6.97 (tt, } J = 6.8, 1.6 \text{ Hz, 1H), 7.11 (t, } J = 7.6 \text{ Hz, 2H), 7.17 (m, 2H); } ^{13}\text{C NMR (75 MHz, CD}_3\text{CN): } \delta = 55.9, 56.7, 106.7, 123.1, 123.9, 128.5, 131.1, 132.5, 141.3 \text{ (q, } J = 52.9 \text{ Hz), 165.2; } ^{11}\text{B NMR (128 MHz, CD}_3\text{CN): } \delta = -13.9; \text{ HRMS (FAB): Calcd for C}_{32}\text{H}_{32}\text{BO (M-}[\text{Me}_4\text{N}])^+: 523.2292. \text{ Found 523.2307.} \]

Palladium-catalyzed allylation of alkynylborate 1n. A typical procedure for 1n-1p

\[ \text{[Me}_4\text{N]}\text{[Ph} \equiv \equiv \text{BAR}_3] + \text{Br} \]

\[ \text{Ar = 2,6-dimethoxyphenyl} \]

\[ \text{toluene, rt} \]

\[ \text{2n, 90%} \]

\[ \text{E/Z = 95/5} \]

To an oven-dried flask, alkynyltriarylborate 1n (89.0 mg, 0.20 mmol) and (xantphos)Pd(\(\pi\)-allyl)Cl (5.2 mg, 2.5 µmol) were placed. After purging with Ar, a toluene solution (0.5 ml) containing allyl bromide (14.8 mg, 0.12 mmol) was added and stirred at room temperature. After 15 minutes, water was added to the reaction mixture. The aqueous layer was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO\(_4\) and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane:AcOEt = 20:1) to afford the alkenylborane 2n (50.9 mg, 0.090 mmol, 90% yield, \(E/Z = 95/5\)).

\((E)-1-(2,6\text{-Dimethoxyphenyl})-1\text{-bis}(2,6\text{-dimethoxyphenyl})\text{boryl-2-phenylpenta-1,4-diene (2n)}\)
\[ \text{Tetramethylammonium (cyclohex-1-enyl)ethynyltris(2,6-dimethoxyphenyl)borate (1o)} \]

\[ \text{1H NMR (300 MHz, CDCl}_3\text{): } \delta = 1.42-1.59 (m, 4H), 1.92-2.45 (m, 4H), 2.97-2.98 (m, 12H), 3.28 (s, 18H), 5.43-5.49 (m, 1H), 6.26 (d, } J = 8.1 \text{ Hz, 6H), 6.73 (t, } J = 8.0 \text{ Hz, 3H); } \text{13C NMR (75 MHz, CDCl}_3\text{): } \delta = 23.2, 24.0, 26.3, 32.1, 56.0, 56.5, 106.6, 122.8, 124.4, 127.6, 165.2; \text{ 11B NMR (128 MHz, CD}_3\text{CN): } \delta = -14.1; \text{ HRMS (FAB): Calcd for C}_{32}\text{H}_{36}\text{BO (M-}[\text{Me}_4\text{N}])^{-} 527.2605. \text{ Found 527.2603.} \]

\[ \text{(E)-1-(2,6-Dimethoxyphenyl)-1-bis(2,6-dimethoxyphenyl)boryl-2-(cyclohex-1-enyl) penta-1,4-diene (2o)} \]

\[ \text{1H NMR (300 MHz, CDCl}_3\text{): } \delta = 1.00 (br, 4H), 1.64 (br, 2H), 1.83 (br, 2H), 2.88 (d, } J = 6.6 \text{ Hz, 2H), 3.43 (s, 6H), 3.57 (s, 3H), 4.85-4.95 (m, 2H), 5.73-5.87 (m, 1H), 5.95 (br,
1H), 6.24-6.28 (m, 6H), 6.89 (t, J = 8.3 Hz, 1H), 6.97 (t, J = 8.1 Hz, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 21.8, 22.1, 25.8, 27.2, 38.4, 54.7, 55.1, 55.8, 101.9, 102.9, 113.5, 123.1, 125.8, 127.9, 130.2, 138.4, 142.7, 157.4, 161.0, 161.5; $^{11}$B NMR (128 MHz, CDCl$_3$): δ = 67.1; HRMS (EI): Calcd for C$_{35}$H$_{41}$BO$_6$ (M$^+$) 568.2996. Found 568.2994.

Tetramethylammonium 3-methylbut-3-en-1-ynyltris(2,6-dimethoxyphenyl)borate (1p)

![Structure](image)

$^1$H NMR (300 MHz, CD$_3$CN): δ = 1.77 (s, 3H), 2.99 (s, 12H), 3.29 (s, 18H), 4.67 (br, 2H), 6.28 (d, J = 7.8 Hz, 6H), 6.75 (t, J = 8.0 Hz, 3H); $^{13}$C NMR (75 MHz, CD$_3$CN): δ = 25.9, 56.0, 56.5, 106.6, 112.0, 123.0, 134.2, 141.3 (q, J = 52.9 Hz), 165.2; $^{11}$B NMR (128 MHz, CD$_3$CN): δ = -14.0; HRMS (FAB): Calcd for C$_{29}$H$_{32}$ (M-$[\text{Me}_4\text{N}]^+$) 487.2292. Found 487.2286.

1,2,2-Tris(2,6-dimethoxyphenyl)-4-methyl-3-(prop-2-enyl)-3-borolene (9)

![Structure](image)

$^1$H NMR (300 MHz, CDCl$_3$): δ = 1.40 (d, J = 18.3 Hz, 1H), 1.70 (s, 3H), 2.48 (d, J = 18.3 Hz, 1H), 2.71 (s, 3H), 2.93 (dd, J = 16.1, 7.4 Hz, 1H), 3.08 (dd, J = 15.8, 1.4 Hz, 1H), 3.23 (br, 6H), 3.39 (s, 3H), 3.68 (s, 3H), 4.04 (s, 3H), 4.45 (d, J = 10.2 Hz, 1H), 4.55 (d, J = 17.1 Hz, 1H), 4.96-5.10 (m, 1H), 5.91 (d, J = 7.8 Hz, 1H), 6.18 (d, J = 7.5 Hz, 2H), 6.41-6.46 (m, 2H), 6.51 (d, J = 8.1 Hz, 1H), 6.75 (t, J = 8.1 Hz, 1H), 6.89 (t, J = 8.1 Hz, 1H), 6.99 (t, J = 8.3 Hz, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 18.0, 32.1, 35.1, 53.5, 54.5, 55.4, 56.1, 57.2, 100.1, 102.2, 102.7, 106.2, 106.9, 111.1, 123.1, 123.9, 124.0, 126.3, 128.1, 132.7, 139.2, 139.7, 155.3, 158.0, 158.5, 158.7, 162.2; $^{11}$B NMR (128 MHz, CDCl$_3$): δ = 25.2; HRMS (EI): Calcd for C$_{32}$H$_{37}$BO$_6$ (M$^+$) 528.2683. Found 528.2681.

DBU-catalyzed isomerization of 2n
Under Ar atmosphere, a toluene solution (0.5 ml) containing 2n (56.4 mg, 0.10 mmol) and DBU (3.0 µl, 0.02 mmol) was stirred at reflux. After 24 h, the reaction mixture was cooled to room temperature and water added to the solution. The aqueous layer was extracted with AcOEt (3 times), washed with water (once), brine (once), dried over MgSO₄ and concentrated. The residue was purified by preparative thin-layer chromatography on silica gel (hexane:AcOEt = 10:1) to afford the 1,3-dienylborane 10 (45.6 mg, 0.081 mmol, 81% yield).

(E,E)-1-(2,6-Dimethoxyphenyl)-1-bis(2,6-dimethoxyphenyl)boryl-2-phenylpenta-1,3-diene (10)

^1H NMR (300 MHz, CDCl₃): δ = 1.64 (dd, J = 7.4, 1.4 Hz, 3H), 3.42 (s, 12H), 3.60 (s, 6H), 5.27-5.39 (m, 1H), 6.07 (d, J = 8.1 Hz, 4H), 6.30 (dd, J = 15.5, 1.7 Hz, 1H), 6.32 (d, J = 8.1 Hz, 2H), 6.80-6.91 (m, 5H), 6.97 (t, J = 8.3 Hz, 1H), 7.20 (dd, J = 7.7, 1.7 Hz, 2H); ^13C NMR (75 MHz, CDCl₃) δ = 18.7, 55.06, 55.11, 102.5, 102.6, 122.6, 125.6, 126.2, 126.4, 128.3, 130.6, 131.1, 136.1, 142.1, 155.0, 157.9, 161.3; ^11B NMR (128 MHz, CD₃CN): δ = 68.5; HRMS (EI): Calcd for C₃₅H₃₇BO₆ (M⁺) 564.2683. Found 564.2683.
References


9. See chapter 1.


15. Instead of Pd$_2$dba$_3$·CHCl$_3$ and XANTPHOS, (xantphos)PdCl($\pi$-allyl) was used as a catalyst because dba disturbed the product isolation. Both catalysts gave similar results.


Chapter 3

Synthesis of Amine–Borane Intramolecular Complexes through Palladium-Catalyzed Rearrangement of Ammonioalkynyltriarylborates

Abstract: The palladium-catalyzed rearrangement reaction of alkynyltriarylborates having a tertiary ammonium moiety proceeded stereoselectively to give amine–borane intramolecular complexes, some of which exhibited significantly strong fluorescence.
Boron-modified \( \pi \)-conjugated compounds have attracted much attention because they exhibit unique photophysical and electrochemical properties.\textsuperscript{1} For example, when a nitrogen-containing \( \pi \)-conjugated skeleton forms an intramolecular complex with a triarylborane moiety suitably positioned within the molecule, it is constrained into a planar structure which leads to considerable lowering of the LUMO level.\textsuperscript{2} Thus, this class of compounds has become an intriguing synthetic target with the aim of developing novel electron-transporting materials. We recently reported a palladium-catalyzed reaction of alkynyltriarylborates with aryl halides, which resulted in the stereoselective synthesis of (trisubstituted alkenyl)diarylboranes via a 1,2-migration of an aryl group from boron to the \( \alpha \)-carbon.\textsuperscript{3} We attempted to employ this reaction for the synthesis of an intramolecular amine-borane complex by using an alkynylborate bearing a tethered amine. However, the reaction failed to proceed, likely due to the strong coordination of the nitrogen atom to palladium. This hypothesis led us to employ an alkynylborate in which the amino group is in the form of an ammonium salt instead of a free amine, in order to mask the coordinating character of the nitrogen atom. Herein, we report the successful application of this strategy to the stereoselective synthesis of amine–borane intramolecular complexes.

Alkynyltriarylborate Thus, zwitterionic alkynyltriarylborate 1a\textsuperscript{4} was treated with a catalytic amount of \textit{Pd}$_2$\textit{dba}$_3$·CHCl$_3$ and P(o-tol)$_3$ in refluxing THF. A rearrangement reaction took place, and after 1 h, the cyclic alkenylborane 2a, in which the unmasked tertiary amino group was coordinated to boron, was isolated by column chromatography on silica gel in 91% yield (eq 1). In this product, the ammonium proton on nitrogen had migrated onto the \( sp \) carbon \( \beta \) to boron, whereas the phenyl group on boron migrated to the \( \alpha \) \( sp \) carbon. Both the hydrogen atom and phenyl group were incorporated across the carbon–carbon double bond in a \textit{cis} fashion to give the (\textit{E})-isomer, which was the only stereoisomer detected in the \( ^1 \text{H} \) NMR spectrum of the reaction mixture. Of note is that the observed stereochemistry in which hydrogen and boron are vicinally attached across a carbon–carbon double bond in a \textit{trans} fashion is difficult to access by conventional hydroboration reactions. In the absence of a palladium catalyst, 1a remained unchanged in refluxing THF. On the other hand, a complex mixture resulted when 1a was treated with Brønsted acids such as acetic acid or methanesulfonic acid.\textsuperscript{5}
A possible mechanism is depicted in Scheme 1. Transfer of the proton from the tertiary ammonium moiety to palladium(0) takes place initially giving cationic palladium species A. Then, regioselective cis-hydropalladation across the carbon–carbon triple bond takes place, affording the zwitterionic intermediate B. Migration of one of the phenyl groups from boron to palladium takes place, furnishing the triorganylborane, which spontaneously forms a complex with the unmasked tertiary amino group to give diorganopalladium species C. Finally, the cyclic amine–borane adduct 2a is released through reductive elimination with the regeneration of palladium(0).

**Scheme 1. Possible Mechanism**

The sSubstrate 1b having a pyridinium group and 1c having an anilinium group underwent analogous reactions. Six-membered ring aniline–borane complex 2c as well as five-membered ring pyridine–borane complex 2b were produced in good to excellent yields, respectively (eqs 2 and 3). Interestingly, the pyridine-borane complex 2b exhibited strong fluorescence (vide infra).
A crossover experiment was carried out as shown in eq 4, and showed definitively that the aryl migration occurs intramolecularly, as with the previous case. A mixture of 1b and 1d was treated with the palladium catalyst, resulting in the formation of a mixture of 2b and 2d in 96, 84% respectively. No crossover products were observed by 1H NMR analysis of the reaction mixture.

The reactions of structurally modified substrates are summarized in Table 1. Both electron-donating and -withdrawing groups were tolerated as the aryl substituents (entry 1 and eq 4). Chloro substituents remained intact under the reaction conditions (entry 5). A reaction of 2-quinolinium derivative 1j, whose nitrogen atom was more sterically hindered than 1b, gave a 96% yield of quinoline-borane complex 2j (entry 6).

The photophysical properties of compounds 2b, 2h, and 2j are summarized in Table 2. The absorption wavelength of 2b (\(\lambda_{\text{abs}} = 356\) nm in MeOH) was apparently elongated in comparison with those of non-borylated counterparts such as (E)-2-styrylpyridine 3 (\(\lambda_{\text{abs}} = 309\) nm) and (E)-N-methyl-2-styrylpyridinium iodide 4 (\(\lambda_{\text{abs}} = 340\) nm, Chart 1), probably due to the planar structure enforced by the B–N coordination. In addition, 2b exhibited strong purple fluorescence in CH\(_2\)Cl\(_2\) solution (\(\lambda_{\text{em}} = 422\) nm, \(\Phi_F = 0.44\)). The extension of \(\pi\)-conjugation from 2b to the naphthyl analogue 2h caused a red shift of the emission maxima by 9 nm, whereas \(\pi\)-extension to
the quinoline derivative 2j shifted emission maxima by 51 nm. Thus, it seems possible to tune the emission color by simple structural modifications.

**Table 1. Reactions of Various Ammonioalkynyltriarylborates**

<table>
<thead>
<tr>
<th>entry</th>
<th>alkynylborate 1</th>
<th>product 2</th>
<th>yield / %$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^c$</td>
<td><img src="image" alt="Structure 1e" /></td>
<td>2e</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Structure 1f" /></td>
<td>2f</td>
<td>89</td>
</tr>
<tr>
<td>3$^d$</td>
<td><img src="image" alt="Structure 1g" /></td>
<td>2g</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="Structure 1h" /></td>
<td>2h</td>
<td>98</td>
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<td>96</td>
</tr>
<tr>
<td>6</td>
<td><img src="image" alt="Structure 1j" /></td>
<td>2j</td>
<td>96</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 2.5 mol% Pd$_2$dba$_3$·CHCl$_3$, 6 mol% P(o-tol)$_3$, THF, reflux, 1 h. $^b$ Isolated yield. $^c$ Reaction was conducted in refluxing cyclopentyl methyl ether. $^d$ Reaction was conducted in 1,2-dichloroethane at 70 °C.
Finally, we examined further functionalization of the produced amine–borane complex. When the pyridine–borane complex 2g was subjected to the Ir-catalyzed C–H borylation reaction,⁷ the 5-position of the pyridine ring, which is probably most sterically accessible, was selectively borylated to give boronic ester 5 in 82% yield. A subsequent cross-coupling reaction of 5 with 4-bromoanisole proceeded regioselectively on the pyridine ring to afford biaryl 6 in 95% yield with the other B–C bonds remaining unreacted by virtue of the nitrogen coordination. The resulting pyridine–borane 6 showed sky-blue fluorescence with a maximum wavelength of 465 nm (Φ_F = 0.40).

In summary, we have developed a palladium-catalyzed rearrangement reaction of ammonioalkynyltriaarylborates. Hydrogen and boron were stereoselectively installed across the resulting carbon–carbon double bond in a trans fashion to give intramolecular amine–borane complexes, some of which exhibited significantly strong fluorescence. Further investigations on the photophysical properties of these compounds are in progress.
Scheme 2. Functionalization of 2g

\[ \begin{align*}
\text{2g} \xrightarrow{(a)} & \quad \text{pinB} \quad \text{MeO} \\
\lambda_\text{em} & = 432 \text{ nm} \\
\Phi_F & = 0.43 \\
\text{5} \xrightarrow{(b)} & \quad \text{Ph} \\
\lambda_\text{em} & = 465 \text{ nm} \\
\Phi_F & = 0.40 \\
\end{align*} \]

a) 0.5 equiv (Bpin)$_2$, 2.5 mol% [Ir(OMe)(cod)]$_2$, 5 mol% dtbpy, \( p \)-xylene, 100 °C, 3 h. (b) 1.2 equiv 4-MeOC$_6$H$_4$Br, 5 mol% Pd(P$_3$Bu$_3$)$_2$, 3 equiv NaOH, THF, H$_2$O, 60 °C, 1 h.
Experimental Section

**General.** NMR spectra were recorded on a Varian Gemini 2000 (1H at 300 MHz and 13C at 75 MHz) or Varian Mercury-400 (1H at 400 MHz and 11B at 128 MHz) spectrometers. Me₄Si (1H, δ = 0.00), residual H of CD₃CN (1H in CD₃CN, δ = 1.94), residual H of DMSO-d₆ (1H in DMSO-d₆, δ = 2.50), CDCl₃ (13C, δ = 77.0), CD₃CN (13C, δ = 1.32), and BF₃·OEt₂ (11B, δ = 0.00) were used as standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. All reactions were carried out under an argon atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF254 (Merck). Gel permeation chromatography (GPC) was carried out with Japan Analytical Industry LC-908. UV–vis spectra were recorded on Agilent 8453 Spectrophotometer. Fluorescence spectra were recorded on JASCO FP-777.

**Materials.** Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used as received. (CH₂Cl)₂ was dried over CaH₂. Cyclopentyl methyl ether and p-xylene were dried over sodium benzophenone ketyl. [Ir(OMe)(cod)]₂,⁸ and Pd(PBU₃)₂⁹ were prepared according to the reported procedures.

**Preparation of alkynyltriarylborate 1a: A typical procedure for the preparation of alkynyltriarylborates**

![Chemical structure](image)

To a stirred solution of 3-(N,N-dimethylamino)prop-1-yn (500 mg, 6.0 mmol) in THF (20 ml) at -78 °C was added n-BuLi (1.6 M in hexane, 3.4 ml, 5.5 mmol). After 30 minutes at this temperature, Ph₃B-Py (1.61 g, 5.0 mmol) was added and the cooling bath was removed. After being stirred for 1 h at room temperature, the reaction was quenched by adding a small amount of MeOH. Volatile materials were removed under reduced pressure and the residue was dissolved in MeOH. Py·HCl (1.1g, 10 mmol) was added to the solution with stirring, resulting in white solid. It was collected by filtration and was washed with CH₂Cl₂ to give alkynyltriarylborate 1a (1.35 g, 4.2 mmol, 83% yield).

**3-(N,N-Dimethylammonio)prop-1-ynyltriphenylborate (1a)**
Triphenyl(2-pyridinoethynyl)borate (1b)

1H NMR (CD3CN): δ = 6.94-7.00 (m, 3H), 7.08-7.12 (m, 6H), 7.37 (d, J = 6.9 Hz, 6H), 7.62-7.67 (m, 1H), 7.82-7.85 (m, 2H); 13C NMR (CD3CN): δ = 122.6, 123.9, 127.1, 128.8, 135.2, 142.0, 142.7, 145.9; 11B NMR (CD3CN): δ = -6.5; HRMS (EI) Calcd for C25H20BN [M]+ 345.1689. Found 345.1692.

{2-(N,N-Dimethylammonio)phenyl}ethynyltriphenylborate (1c)

1H NMR (CD3CN): δ = 2.99 (s, 6H), 6.98 (tt, J = 7.2, 1.6 Hz, 3H), 7.09-7.14 (m, 6H), 7.36-7.59 (m, 10H); 13C NMR (CD3CN): δ = 47.0, 120.3, 122.4, 124.3, 127.6, 128.7, 131.4, 132.8, 135.5; 11B NMR (DMSO-d6): δ = -7.2; HRMS (EI) Calcd for C28H26BN (M+) 386.2158. Found 387.2152.

Tris(4-methoxyphenyl){3-(N,N-dimethylammonio)prop-1-ynyl}borate (1d)

1H NMR (CD3CN): δ = 2.86 (s, 6H), 3.69 (s, 9H), 3.92 (s, 2H), 6.62-6.67 (m, 6H), 7.18 (d, J = 8.4 Hz, 6H); 13C NMR (CD3CN): δ = 42.6, 50.9, 55.3, 112.5, 135.7, 156.9; 11B
NMR (CD$_3$CN): $\delta = -7.8$; HRMS (EI) Calcd for C$_{26}$H$_{30}$BNO$_3$ (M$^+$) 415.2319. Found 415.2319.

**Tris(4-fluorophenyl){3-($N,N$-dimethylammonio)prop-1-ynyl}borate (1e)**

![Structure](image)

$^1$H NMR (CD$_3$CN): $\delta = 2.77$ (s, 6H), 3.88 (s, 2H), 6.75-6.83 (m, 6H), 7.26 (pseudo t, $J = 7.5$ Hz, 6H); $^{13}$C NMR (CD$_3$CN): $\delta = 41.8, 49.5, 113.2$ (d, $J = 18.2$ Hz), 136.1 (d, $J = 6.6$ Hz), 161.1 (d, $J = 235.1$ Hz); $^{11}$B NMR (CD$_3$CN): $\delta = -7.7$; HRMS (EI) Calcd for C$_{23}$H$_{21}$BF$_3$ (M$^+$) 379.1719. Found 379.1715.

**3-($N,N$-Dibenzylammonio)prop-1-ynylitriphenylborate (1f)**

![Structure](image)

$^1$H NMR (DMSO-$d_6$): $\delta = 3.58$ (s, 2H), 4.25-4.45 (m, 4H), 6.88 (t, $J = 7.2$ Hz, 3H), 7.03 (pseudo t, $J = 7.2$ Hz, 6H), 7.36-7.51 (m, 16H); $^{13}$C NMR (DMSO-$d_6$): $\delta = 42.3, 55.2, 122.4, 125.7, 128.7, 129.5, 131.1, 134.1$; $^{11}$B NMR (DMSO-$d_6$): $\delta = -7.4$; HRMS (EI) Calcd for C$_{35}$H$_{32}$BN (M$^+$) 477.2628. Found 477.2626.

**Triphenyl{2-(3-methylpyridinio)ethynyl}borate (1g)**

![Structure](image)

$^1$H NMR (CD$_3$CN): $\delta = 2.57$ (s, 3H), 6.94-7.00 (m, 3H), 7.07-7.13 (m, 6H), 7.38 (d, $J = 7.2$ Hz, 6H), 7.54 (pseudo t, $J = 6.8$ Hz, 1H), 8.14 (d, $J = 6.0$ Hz, 1H), 8.20-8.24 (m, 1H); $^{13}$C NMR (CD$_3$CN): $\delta = 19.7, 123.2, 124.0, 127.1, 135.1, 138.3, 140.9, 146.4$; $^{11}$B NMR (CD$_3$CN): $\delta = -6.3$; HRMS (EI) Calcd for C$_{26}$H$_{22}$BN (M$^+$) 359.1845. Found 359.1839.

**Tris(2-naphthyl)(2-pyridinioethynyl)borate (1h)**
$^1$H NMR (DMSO-$d_6$): $\delta = 7.27-7.33$ (m, 6H), 7.58-7.81 (m, 16H), 8.01 (d, $J = 8.4$ Hz, 1H), 8.39 (pseudo t, 7.8 Hz, 1H), 8.62 (d, $J = 5.1$ Hz, 1H); $^{13}$C NMR could not be recorded because of the low solubility; $^{11}$B NMR (DMSO-$d_6$): $\delta = -7.1$; HRMS (EI) Calcd for C$_{37}$H$_{26}$BN (M$^+$) 495.2158. Found 495.2157.

Tris(4-chlorophenyl)(2-pyridinioethynyl)borate (1i)

$^1$H NMR (CD$_3$CN): $\delta = 7.09-7.14$ (m, 6H), 7.30 (d, $J = 8.1$ Hz, 6H), 7.69 (ddd, $J = 7.7$, 6.2, 1.4 Hz, 1H), 7.85 (dd, $J = 8.6$, 1.1 Hz, 1H), 8.31-8.37 (m, 2H); $^{13}$C NMR (CD$_3$CN): $\delta = 124.1$, 127.1, 129.8, 130.6, 136.5, 141.3, 147.0; $^{11}$B NMR (CD$_3$CN): $\delta = -7.1$; HRMS (EI) Calcd for C$_{25}$H$_{17}$BNCl$_3$ (M$^+$) 447.0520. Found 447.0525.

Triphenyl(2-quinolinioethynyl)borate (1j)

$^1$H NMR (DMSO-$d_6$): $\delta = 6.90-6.95$ (m, 3H), 7.05 (pseudo t, $J = 7.2$ Hz, 6H), 7.33 (d, $J = 6.6$ Hz, 6H), 7.70-7.85 (m, 1H), 7.94 (d, $J = 9.0$ Hz, 1H), 8.03-8.12 (m, 2H), 8.26 (d, $J = 8.7$ Hz, 1H), 8.94 (d, $J = 8.7$ Hz, 1H); $^{13}$C NMR (DMSO-$d_6$): $\delta = 119.8$, 122.9, 125.8, 126.0, 128.5, 128.7, 134.1, 137.8, 140.3, 144.4; $^{11}$B NMR (DMSO-$d_6$): $\delta = -7.0$; HRMS (EI) Calcd for C$_{29}$H$_{22}$BN (M$^+$) 395.1845. Found 395.1847.
Palladium-catalyzed rearrangement of 1a: A typical procedure for the rearrangement reaction

Under Ar atmosphere, a mixture of alkynylborate 1a (32.4 mg, 0.10 mmol), Pd$_2$dba$_3$.CHCl$_3$ (2.6 mg, 0.0025 mmol) and P(o-tol)$_3$ (1.8 mg, 0.006 mmol) in THF (0.5 ml) was stirred at 70 °C. After 1 h, the reaction mixture was directly subjected to preparative TLC (hexane:DCM = 1:1) to afford 2a (29.5 mg, 0.091 mmol) in 91% yield.

**Dimethyl{(E)-3-phenyl-3-diphenylborylprop-2-enyl}amine (2a)**

$^1$H NMR (CDCl$_3$): $\delta = 2.39$ (s, 6H), 3.82 (d, $J = 2.1$ Hz, 2H), 6.18 (t, $J = 2.0$ Hz, 1H), 7.06-7.26 (m, 11H), 7.58 (dd, $J = 8.1$, 1.7 Hz, 4H); $^{13}$C NMR (CDCl$_3$): $\delta = 50.1$, 70.0, 120.4, 125.8, 125.9, 126.7, 127.2, 127.7, 135.2, 142.2; $^{11}$B NMR (CDCl$_3$): $\delta = 6.6$; HRMS (EI) Calcd for C$_{22}$H$_{22}$BN (M$^+$) 325.2002. Found 325.2003.

**2-{(E)-2-Phenyl-2-diphenylborylethenyl}pyridine (2b)**

$^1$H NMR (CDCl$_3$): $\delta = 7.04$ (ddd, $J = 7.2$, 6.1, 1.4 Hz, 1H), 7.11-7.31 (m, 14H), 7.48 (pseudo dt, $J = 8.4$, 1.5 Hz, 1H), 7.58-7.61 (m, 2H), 7.79 (ddd, $J = 8.3$, 7.3, 1.6 Hz, 1H), 8.23 (d, $J = 5.7$ Hz, 1H); $^{13}$C NMR (CDCl$_3$): $\delta =$119.32, 119.34, 120.9, 125.7, 127.4, 128.0, 128.2, 128.3, 133.6, 138.5, 139.9, 143.0, 160.1; $^{11}$B NMR (CDCl$_3$): $\delta = 3.5$; HRMS (EI) Calcd for C$_{23}$H$_{20}$BN (M$^+$) 345.1689. Found 345.1689.

**Dimethyl[2-{(E)-2-phenyl-2-diphenylboreylethenyl}phenyl]amine (2c)**

$^1$H NMR (CDCl$_3$): $\delta = 2.83$ (s, 6H), 6.95 (s, 1H), 7.02-7.13 (m, 9H), 7.20-7.24 (m, 3H), 7.31-7.34 (m, 3H), 7.55-7.58 (m, 4H); $^{13}$C NMR (CDCl$_3$): $\delta = 48.9$, 117.9, 125.6, 125.9, 126.6, 126.8, 127.2, 127.4, 128.0, 128.1, 129.7, 133.4, 136.7, 144.7, 147.1; $^{11}$B NMR
(CDCl₃): δ = 4.2; HRMS (EI) Calcd for C₂₈H₂₆BN (M⁺) 386.2158. Found 387.2161.

(E)-3-(4-Methoxyphenyl)-3-bis(4-methoxyphenyl)borylprop-2-enyldimethylamine (2d)

\[ \text{OMe} \]
\[ \text{Me₂N} \]
\[ \text{OMe} \]

\[ \text{OMe} \]
\[ \text{Me₂N} \]
\[ \text{OMe} \]

1H NMR (CDCl₃): δ = 2.33 (s, 6H), 3.71 (s, 3H), 3.75 (d, J = 2.1 Hz, 2H), 3.77 (s, 6H), 6.07 (t, J = 2.1 Hz, 1H), 6.67 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.7 Hz, 4H), 7.11 (d, J = 9.0 Hz, 2H), 7.50 (d, J = 8.7 Hz, 4H); 13C NMR (CDCl₃): δ = 49.9, 54.9, 55.1, 69.7, 112.7, 113.2, 118.2, 127.9, 134.7, 136.3, 157.8; 11B NMR (CDCl₃): δ = 6.4; HRMS (EI) Calcd for C₂₆H₃₀BNO₃ (M⁺) 415.2319. Found 415.2314.

(E)-3-(4-Fluorophenyl)-3-bis(4-fluorophenyl)borylprop-2-enyldimethylamine (2e)

\[ \text{F} \]
\[ \text{Me₂N} \]
\[ \text{B} \]
\[ \text{F} \]

\[ \text{F} \]
\[ \text{Me₂N} \]
\[ \text{B} \]
\[ \text{F} \]

1H NMR (CDCl₃): δ = 2.35 (s, 6H), 3.79 (d, J = 1.8 Hz, 2H), 6.12 (br, 1H), 6.80 (pseudo t, J = 8.9 Hz, 2H), 6.93 (pseudo t, J = 9.0 Hz, 4H), 7.07 (dd, J = 8.7, 5.7 Hz, 2H), 7.48 (dd, J = 8.6, 6.3 Hz, 4H); 13C NMR (CDCl₃): δ = 50.1, 69.9, 114.2 (d, J = 18.2 Hz), 114.7 (d, J = 21.2 Hz), 120.2 (d, J = 1.4 Hz), 128.1 (d, J = 8.0 Hz), 136.5 (d, J = 6.6 Hz), 137.7 (d, J = 2.9 Hz), 161.5 (d, J = 242.5 Hz), 161.8 (d, J = 243.2 Hz); 11B NMR (CDCl₃): δ = 5.9; HRMS (EI) Calcd for C₂₃H₂₁BNF₃ (M⁺) 379.1719. Found 379.1722.

Dibenzyl{(E)-3-phenyl-3-diphenylborylprop-2-enyl}amine (2f)
$^1$H NMR (CDCl$_3$): $\delta = 3.62$ (d, $J = 2.1$ Hz, 2H), 3.8-4.4 (br, 4H), 6.01 (t, $J = 2.0$ Hz, 1H), 6.70-6.73 (m, 4H), 7.06-7.31 (m, 17H), 7.71 (dd, $J = 8.0$, 1.7 Hz, 4H); $^{13}$C NMR (CDCl$_3$): $\delta =$ 59.2, 61.2, 123.0, 125.7, 126.2, 126.6, 127.5, 127.8, 128.1, 128.4, 131.8, 133.4, 135.6, 143.5; $^{11}$B NMR (CDCl$_3$): $\delta =$ 10.3; HRMS (EI) Calcd for C$_{35}$H$_{32}$BN (M$^+$) 477.2628. Found 477.2626.

3-Methyl-2-{$(E)$-2-phenyl-2-diphenylborylethenyl}pyridine (2g)

$^1$H NMR (CDCl$_3$): $\delta =$2.55 (s, 3H), 7.00 (pseudo t, $J = 6.5$ Hz, 1H), 7.10-7.30 (m, 14H), 7.58-7.63 (m, 3H), 8.08 (d, $J = 5.4$ Hz, 1H); $^{13}$C NMR (CDCl$_3$): $\delta =$18.1, 119.1, 119.2, 125.6, 127.3, 128.0, 128.19, 128.22, 128.8, 133.6, 138.9, 140.3, 140.5, 159.1; $^{11}$B NMR (CDCl$_3$): $\delta =$ 3.9; HRMS (EI) Calcd for C$_{26}$H$_{22}$BN (M$^+$) 359.1845. Found 359.1845.

2-{$(E)$-2-(2-Naphthyl)-2-bis(2-naphthyl)borylethenyl}pyridine (2h)

$^1$H NMR (CDCl$_3$): $\delta =$ 7.06 (ddd, $J = 7.5$, 6.0, 1.1 Hz, 1H), 7.28-7.38 (m, 7H), 7.49-7.87 (m, 16H), 8.13 (s, 1H), 8.33 (d, $J = 5.7$ Hz, 1H); $^{13}$C NMR (CDCl$_3$): $\delta =$119.4, 119.6, 121.7, 124.7, 125.0, 125.7, 126.0, 126.4, 127.30, 127.34, 127.5, 127.7, 128.6, 128.7, 132.0, 132.4, 132.7, 133.2, 133.3, 133.5, 136.0, 140.1, 143.2, 160.3; $^{11}$B NMR (CDCl$_3$): $\delta =$ 3.9; HRMS (EI) Calcd for C$_{37}$H$_{26}$BN (M$^+$) 495.2158. Found 495.2158.

2-{$(E)$-2-(4-Chlorophenyl)-2-bis(4-chlorophenyl)borylethenyl}pyridine (2i)
$^1$H NMR (CDCl$_3$): $\delta = 7.11-7.22$ (m, 12H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.1$ Hz, 1H), 7.88 (pseudo dt, $J = 7.8$, 1.2 Hz, 1H), 8.14 (d, $J = 5.7$ Hz, 1H); $^{13}$C NMR (CDCl$_3$): $\delta =$119.8, 119.9, 121.5, 127.7, 128.4, 129.3, 132.0, 134.4, 134.8, 136.5, 140.5, 142.7, 159.9; $^{11}$B NMR (CDCl$_3$): $\delta = 3.1$; HRMS (EI) Calcd for C$_{25}$H$_{17}$BNCl$_3$ (M$^+$) 447.0520. Found 447.0517.

2-\{(E)-2-Phenyl-2-diphenylborylethenyl\}quinoline (2j)

$^1$H NMR (CDCl$_3$): $\delta = 7.07-7.16$ (m, 7H), 7.18-7.23 (m, 3H), 7.28-7.32 (m, 4H), 7.36-7.45 (m, 4H), 7.70 (d, $J = 8.7$ Hz, 1H), 7.81-7.90 (m, 2H), 8.35 (d, $J = 8.7$ Hz, 1H); $^{13}$C NMR (CDCl$_3$): $\delta =$118.2, 122.1, 123.1, 125.3, 125.7, 126.2, 127.3, 128.0, 128.1, 128.3, 128.5, 131.3, 133.2, 139.3, 141.1, 141.5, 161.9; $^{11}$B NMR (CDCl$_3$): $\delta = 3.9$; HRMS (EI) Calcd for C$_{29}$H$_{22}$BN (M$^+$) 395.1845. Found 395.1849.

Ir-catalyzed borylation of 2g

Under Ar atmosphere, a $p$-xylene (1.0 ml) solution containing 2g (71.8 mg, 0.20 mmol), (Bpin)$_2$ (25.3 mg, 0.10 mmol), [Ir(OMe)(cod)]$_2$ (3.3 mg, 0.005 mmol) and dtbpy (2.7 mg, 0.01 mmol) was stirred at 100 °C for 3 h. After cooling to room temperature, the reaction mixture was passed through a short pad of silica gel. Subsequent purification with GPC afforded pure boronic ester 5 (79.3 mg, 0.16 mmol) in 82% yield.
3-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-{(E)-2-phenyl-2-diphenylborylethenyl}pyridine (5)

$$\text{Ph}$$

$$\text{BPh}_2$$

$$\text{N}$$

$$\text{B}$$

$$\text{O}$$

$$\text{O}$$

$${}^{1}H\text{ NMR (CDCl}_3{}): \delta = 1.27 (s, 12H), 2.53 (s, 3H), 7.11-7.33 (m, 14H), 7.58-7.63 (m, 2H), 7.98 (s, 1H), 8.43 (s, 1H); {}^{13}\text{C NMR (CDCl}_3{}): \delta =17.8, 24.9, 84.4, 119.2, 125.5, 127.3, 127.9, 128.0, 128.3, 128.4, 133.8, 138.7, 146.1, 146.2, 160.8; {}^{11}\text{B NMR (CDCl}_3{}): \delta = 3.5, 30.1; \text{HRMS (EI) Calcd for C}_{32}\text{H}_{33}\text{B}_{2}\text{NO}_{2} (M^+) 485.2697. Found 485.2691.}

**Pd-catalyzed cross-coupling reaction of 5 with 4-bromoanisole**

Under Ar atmosphere, a THF solution containing 5 (48.5 mg, 0.10 mmol), p-bromoanisole (22.0 mg, 0.12 mmol), Pd(P\text{Bu}_3)\text{2} (2.6 mg, 0.005 mmol), NaOH (12.0 mg, 0.30 mmol), and H\text{2O (5 µl)} was stirred at 60 °C for 1 h. After cooling the reaction mixture to room temperature, water was added. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic phase was washed with water, brine, and dried over MgSO\text{4}. Removal of the solvent under reduced pressure and subsequent purification with GPC afforded biaryl 6 (44.0 mg, 0.095 mmol) in 95 % yield.

5-(4-Methoxyphenyl)-3-methyl-2-{(E)-2-phenyl-2-diphenylborylethenyl}pyridine (6)

$$\text{MeO}$$

$$\text{O}$$

$$\text{MeO}$$

$${}^{1}H\text{ NMR (CDCl}_3{}): \delta = 2.60 (s, 3H), 3.80 (s, 3H), 6.89-6.94 (m, 2H), 7.11-7.26 (m, 10H), \text{71}$$
7.31-7.37 (m, 6H), 7.60-7.64 (m, 2H), 7.775-7.784 (m, 1H), 8.26 (d, \( J = 1.8 \) Hz, 1H);

\(^{13}\)C NMR (CDCl\(_3\)): \( \delta = 18.2, 55.4, 114.5, 118.9, 125.6, 127.4, 127.8, 128.0, 128.1, 128.2, 128.3, 128.6, 132.8, 133.7, 138.2, 138.4, 138.9, 157.2, 159.8; \(^{11}\)B NMR (CDCl\(_3\)): \( \delta = 3.9 \); HRMS (EI) Calcd for C\(_{33}\)H\(_{28}\)BN (M\(^+\)) 465.2264. Found 465.2259.
References


3. See Chapter 1.

4. The alkynylborate 1a was prepared in 83% yield by the reaction of the corresponding lithium acetylide with triphenylborane-pyridine adduct followed by treatment with pyridinium chloride.


6. These values were determined in MeOH solutions. Williams, J. L. R.; Webster, S. K.; Van Allan, J. A. J. Org. Chem. 1961, 26, 4893.


Chapter 4

Asymmetric Carroll Rearrangement of Allyl α-Aacetamido-β-ketocarboxylates Catalyzed by a Chiral Palladium Complex

Abstract: Asymmetric decarboxylative rearrangement (Carroll rearrangement) of allyl α-acetamido-β-ketocarboxylates was catalyzed by a palladium complex modified with a chiral phosphine ligand, giving optically active γ,δ-unsaturated α-aminoketones with up to 90% ee.
Carroll rearrangement, a variant of ester Claisen rearrangement, is an efficient carbon–carbon bond forming method to produce \( \gamma, \delta \)-unsaturated carbonyl compounds from allylic esters of \( \beta \)-ketocarboxylic acids.\(^1\) Two mechanisms can operate for the decarboxylative rearrangement (Scheme 1). The reaction, occurring at a high temperature or under strongly basic conditions, proceeds by an electrocyclic pathway (path \( a \)), and has often been used in natural products syntheses.\(^2\) Alternatively, the rearrangement is catalyzed by palladium(0)/phosphine complexes under milder conditions (path \( b \)).\(^3\) Oxidative addition, decarboxylation, and recombination constitute the catalytic cycle. This catalytic pathway inspired us to explore asymmetric Carroll rearrangement by means of chiral phosphine–palladium complexes. In this chapter, the author describes catalytic asymmetric Carroll rearrangement,\(^4,5\) which affords optically active \( \gamma, \delta \)-unsaturated ketones bearing an \( N \)-substituted quaternary chiral \( \alpha \)-carbon with up to 90% ee.

**Scheme 1. Carroll rearrangement**

![Chemical Diagram](image)

It was reported that a palladium complex modified with BINAP catalyzed a highly enantioselective allylation of \( \alpha \)-acetamido-\( \beta \)-ketoesters, whose acetamido group was crucial for the control of stereochemistry.\(^6\) Thus, an allylic esters of \( \alpha \)-acetamido-\( \beta \)-ketocarboxylic acids was employed as the substrate for asymmetric Carroll rearrangement. A variety of chiral phosphine ligands were examined in the palladium-catalyzed decarboxylative rearrangement of 2-propenyl 2-(\( N \)-acetylamino)-2-methyl-3-oxobutanoate (1), with the selected results listed in Table 1. Only 25% ee was observed with BINAP, which was the chiral ligand of choice in the
asymmetric allylation reaction previously reported (entry 1). So-called Trost ligand (naphthyl) showed a better enantioselectivity (entry 2). Dichloroethane (DCE) was superior to THF as the solvent (entry 3). Finally, it was found that addition of phenol derivatives brought about a dramatic enhancement of the enantioselectivity (entries 4-6). A satisfactory result in terms of both chemical yield and selectivity was obtained when the reaction was carried out in the presence of 0.5 equiv 1-naphthol.

Table 1. Asymmetric Carroll rearrangement of \(1^a\)

<table>
<thead>
<tr>
<th>entry</th>
<th>chiral ligand</th>
<th>solvent</th>
<th>additive</th>
<th>yield / %</th>
<th>ee / % (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(R)-BINAP</td>
<td>THF</td>
<td>-</td>
<td>81</td>
<td>25 (-)</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>THF</td>
<td>-</td>
<td>99</td>
<td>36 (+)</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>DCE</td>
<td>-</td>
<td>89</td>
<td>51 (+)</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>DCE</td>
<td>phenol (1 eq)</td>
<td>72</td>
<td>81 (+)</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>DCE</td>
<td>1-naphthol (1 eq)</td>
<td>70</td>
<td>88 (+)</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>DCE</td>
<td>1-naphthol (0.5 eq)</td>
<td>79</td>
<td>87 (+)</td>
</tr>
</tbody>
</table>

* Reactions were conducted on 0.2 mmol scale at room temperature. * Isolated yield. * By GC analysis with Chiraldex G-BP. Signs of optical rotation are given in parentheses. * \([\alpha]^{20}_D=+7.0\) (c 0.50, CHCl₃).

The results of the asymmetric Carroll rearrangement of allyl \(\alpha\)-acetamido-\(\beta\)-ketocarboxylates catalyzed by palladium/3 are summarized in Table 2. A higher enantioselectivity (90% ee) was observed with the substrate having a propanoyl group (entry 1, \(R^1 = \text{Et}\)). Substrates bearing ethyl and benzyl groups at the \(\alpha\)-position gave the corresponding products with 80% ee and 71% ee, respectively (entries 2, 3). Lower reactivities were observed with allylic ester groups other than a 2-propenyl group, like methallyl (low yield), cinnamyl (low yield), crotol \((E)-\alpha\, , (Z)-\alpha\, and diastereomeric
mixture of γ-coupling products), and prenyl (no prenylated product) groups.

For comparison, Carroll rearrangement of allyl β-ketocarboxylates lacking an α-acetamido group was examined (Scheme 2). The reaction of cyclohexanone 4 gave γ,δ-unsaturated ketone 5 with only 14% ee. No asymmetric induction was observed in the reaction of acyclic β-ketoester 6. These results indicated that the α-acetamido group played a crucial role in enantioface-selection of the enolate generated from β-ketocarboxylate via decarboxylation.

In conclusion, the chiral palladium catalyst generated in situ from Pd₂(dba)₃·CHCl₃ and the optically active bisphosphine ligand 3 accomplished a high degree of asymmetric induction on a N-substituted quaternary chiral carbon center (up to 90% ee) in the Carroll rearrangement of allyl α-acetamido-β-ketocarboxylates.

Table 2. Palladium-catalyzed asymmetric Carroll rearrangement of allyl α-acetamido-β-ketocarboxylates

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate 1</th>
<th>product 2</th>
<th>yield / %</th>
<th>ee / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="#" alt="Image" /></td>
<td><img src="#" alt="" /></td>
<td>81</td>
<td>90c</td>
</tr>
<tr>
<td>2</td>
<td><img src="#" alt="Image" /></td>
<td><img src="#" alt="" /></td>
<td>55</td>
<td>80d</td>
</tr>
<tr>
<td>3</td>
<td><img src="#" alt="Image" /></td>
<td><img src="#" alt="" /></td>
<td>82</td>
<td>71e</td>
</tr>
</tbody>
</table>

---

a Reactions were conducted on 0.2 mmol scale at room temperature. b Isolated yield. c By GC analysis with Chiraldex G-BP. d By HPLC analysis with Chiralcel OJ-H. e By HPLC analysis with Chiralcel OD-H.
Scheme 2. Carroll rearrangement of allyl β-ketocarboxylates

4. 2.5 mol% Pd\(_2\text{dba}_3\cdot\text{CHCl}_3\)
   5.0 mol% Ligand 3
   DCE, 1-naphthol (0.5 eq.), rt
   57% yield, 14% ee

6. 2.5 mol% Pd\(_2\text{dba}_3\cdot\text{CHCl}_3\)
   5.0 mol% Ligand 3
   DCE, 1-naphthol (0.5 eq.), rt
   57% yield, 0% ee
Experimental Section

**General.** NMR spectra were recorded on a Varian Gemini 2000 ($^1$H at 300 MHz and $^{13}$C at 75 MHz) or Varian Mercury-400 ($^1$H at 400 MHz) spectrometers. CDCl$_3$ was used as a solvent. Me$_4$Si ($^1$H, $\delta$ = 0.00), CDCl$_3$ ($^{13}$C, $\delta$ = 77.0) were used as standards. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. All reactions were carried out under an argon atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF$_{254}$ (Merck).

**Materials.** Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used as received. (CH$_2$Cl)$_2$ was dried over CaH$_2$.

Prop-2-enyl 2-acetamido-2-methyl-3-oxobutanoate (1a)

\[
\begin{align*}
\text{\text{O}} & \text{\text{O}} \\
\text{NHAc} & \\
\end{align*}
\]

$^1$H NMR (300 MHz): $\delta$ = 1.74 (s, 3H), 2.03 (s, 3H), 2.21 (s, 3H), 4.65-4.69 (m, 2H), 5.25-5.36 (m, 2H), 5.81-5.92 (ddd, $J$ = 17.1, 10.2, 5.7 Hz, 1H), 7.01 (br, 1H); $^{13}$C NMR: $\delta$ = 20.2, 23.0, 24.1, 66.9, 68.4, 119.4, 131.0, 168.8, 169.1, 200.2; HRMS (EI): Calcd for C$_{10}$H$_{15}$NO$_4$ (M)$^+$ 213.1001. Found 213.1006.

Prop-2-enyl 2-acetamido-2-methyl-3-oxopentanoate (1b)

\[
\begin{align*}
\text{\text{O}} & \text{\text{O}} \\
\text{NHAc} & \\
\end{align*}
\]

$^1$H NMR (400 MHz): $\delta$ = 1.08 (t, $J$ = 7.2 Hz, 3H), 1.74 (s, 3H), 2.04 (s, 3H), 2.43-2.63 (m, 2H), 4.63-4.67 (m, 2H), 5.25 (d, $J$ = 10.4 Hz, 1H), 5.32 (d, $J$ = 17.2 Hz, 1H), 8.86 (ddd, $J$ = 17.2, 10.4, 5.6 Hz, 1H), 7.05 (br, 1H); $^{13}$C NMR: $\delta$ = 7.9, 20.3, 23.0, 29.7, 66.8, 68.1, 119.4, 131.1, 169.0, 169.1, 203.4; HRMS (FAB): Calcd for C$_{11}$H$_{18}$NO$_4$ (M+H)$^+$ 228.1236. Found 228.1229.

Prop-2-enyl 2-acetamido-2-ethyl-3-oxobutanoate (1c)
Prop-2-enyl 2-acetamido-2-benzyl-3-oxobutanoate (1d)

$^1$H NMR (400 MHz): $\delta = 2.05$ (s, 3H), 2.25 (s, 3H), 3.58 (d, $J = 14.0$ Hz, 2H), 5.33 (d, $J = 10.4$ Hz, 1H), 5.38 (d, $J = 14.0$ Hz, 1H), 4.69 (d, $J = 6.0$ Hz, 2H), 5.33 (d, $J = 10.4$ Hz, 1H), 5.88-5.92 (m, 1H), 6.66 (br, 1H), 6.95-6.98 (m, 2H), 7.24-7.27 (m, 3H); $^{13}$C NMR: $\delta = 23.0$, 24.7, 37.1, 67.2, 72.7, 120.1, 127.3, 128.4, 129.7, 130.7, 135.2, 167.9, 169.3, 198.7; HRMS (EI): Calcd for C$_{16}$H$_{19}$NO$_4$ (M$^+$) 289.1314. Found 289.1311.

Palladium-catalyzed Carroll rearrangement of 1a: A typical procedure

Under nitrogen atmosphere, a CH$_2$Cl$_2$ solution (1.0 ml) containing Pd$_2$dba$_3$·CHCl$_3$ (5.2 mg, 0.005 mmol), (R,R)-3 (8.0 mg, 0.01 mmol), 1-naphthol (14.4 mg, 0.10 mmol) was stirred at room temperature. After 30 minutes, 1a was added and stirred until the substrate was consumed. The reaction mixture was concentrated and purified with preparative column chromatography (Hexane:AcOEt = 1:1) to afford 2a (26.7 mg, 0.16 mmol, 79% yield).

4-Acetamido-4-methylhex-1-en-5-one (2a)

$^1$H NMR (400 MHz): $\delta = 1.53$ (s, 3H), 1.99 (s, 3H), 2.19 (s, 3H), 2.49 (q, $J = 8.0$ Hz, 1H), 3.05 (q, $J = 8.0$ Hz, 1H), 5.08 (m, 1H), 5.12 (m, 1H), 5.51-5.62 (m, 1H), 6.41 (br, 1H); $^{13}$C NMR: $\delta = 21.6$, 23.6, 23.7, 39.3, 64.3, 119.2, 132.2, 169.4, 208.0; HRMS (Cl): Calcd for C$_9$H$_{16}$NO$_2$ (M$^+$H$^+$) 170.1181, Found 170.1179.
4-Acetamido-4-methylhept-1-en-5-one (2b)

\[
\begin{align*}
 &\text{O} \\
 &\text{\text{NHAc}}
\end{align*}
\]

\(^1\)H NMR (400 MHz): \(\delta = 1.08\) (t, \(J = 7.2\) Hz, 3H), 1.54 (s, 3H), 2.00 (s, 3H), 2.46-2.61 (m, 3H), 3.06 (q, \(J = 7.2\) Hz, 1H), 5.06 (d, \(J = 4.0\) Hz, 1H), 5.11 (d, \(J = 3.2\) Hz, 1H), 5.50-5.60 (m, 1H), 6.47 (br, 1H); \(^{13}\)C NMR: \(\delta = 7.9, 21.8, 23.8, 28.8, 39.6, 64.2, 119.2, 132.3, 169.4, 210.8\); HRMS (EI): Calcd for C\(_{10}\)H\(_{17}\)NO\(_2\) (M)\(^+\) 183.1259. Found 183.1259.

4-Acetamido-4-ethylhex-1-en-5-one (2c)

\[
\begin{align*}
 &\text{O} \\
 &\text{\text{NHAc}}
\end{align*}
\]

\(^1\)H NMR (300 MHz): \(\delta = 0.70\) (t, \(J = 7.5\) Hz, 3H), 1.74 (q, \(J = 7.5\) Hz, 1H), 2.02 (s, 3H), 2.17 (s, 3H), 2.42 (dd, \(J = 14.4, 7.5\) Hz, 1H), 2.63 (q, \(J = 7.5\) Hz, 1H), 3.40 (dd, \(J = 14.4, 7.5\) Hz, 1H), 5.02-5.11 (m, 2H), 5.42-5.54 (m, 1H), 6.60 (br, 1H); \(^{13}\)C NMR: \(\delta = 8.0, 23.3, 24.0, 26.9, 38.2, 69.5, 118.6, 132.1, 169.2, 207.8\); HRMS (FAB): Calcd for C\(_{10}\)H\(_{18}\)NO\(_2\) (M+H)\(^+\) 184.1338. Found 184.1333.

4-Acetamido-4-benzylhex-1-en-5-one (2d)

\[
\begin{align*}
 &\text{O} \\
 &\text{\text{NHAc}} \\
 &\text{Ph}
\end{align*}
\]

\(^1\)H NMR (300 MHz): \(\delta = 1.97\) (s, 3H), 2.30 (s, 3H), 2.54 (dd, \(J = 14.4, 7.8\) Hz, 1H), 3.11 (d, \(J = 14.4\) Hz, 1H), 3.45 (dd, \(J = 14.4, 7.8\) Hz, 1H), 3.80 (d, \(J = 14.4\) Hz, 1H), 5.09 (d, \(J = 8.7\) Hz, 1H), 5.13 (d, \(J = 14.4\) Hz, 1H), 5.45-5.60 (m, 1H), 6.38 (br, 1H), 7.00-7.03 (m, 2H), 7.21-7.27 (m, 3H); \(^{13}\)C NMR: \(\delta = 24.1, 24.4, 38.3, 39.2, 69.5, 119.1, 127.0, 128.3, 129.6, 131.6, 135.9, 169.6\); HRMS (EI): Calcd for C\(_{15}\)H\(_{19}\)NO\(_2\) (M)\(^+\) 245.1416. Found 245.1417.
References


8. The chiral ligand 3 is commercially available from Strem Chemicals, Inc.

9. It might be that hydrogen bonding between the protic hydrogens with the amido groups of 3 favors a desired conformation or disfavors undesired amido coordination to palladium. For a similar effect of alcohol addition to improve an enantioselectivity, see: Trost, B. M.; Soldermann, C. P.; Chen, I.; Schroeder, G. *M. J. Am. Chem. Soc.* 2004, 126, 4480.
Chapter 5

Solvent and Ligand Partition Reaction Pathways in
Nickel-Mediated Carboxylation of Methylene cyclopropanes

Abstract: Methylene cyclopropanes are carboxylated with carbon dioxide in the presence of a stoichiometric amount of a nickel complex. The reaction pathways are significantly influenced by the reaction solvent and the amine ligand.
The incorporation of carbon dioxide into organic compounds presents an important challenge in chemistry, as reduction of greenhouse gases has emerged as a pressing global issue. In addition, due to its abundance as a raw material and innocuous nature, the development of methods to activate intrinsically inert carbon dioxide and to fix it into organic compounds becomes of practical value to synthetic chemists. On the other hand, a number of transition metal-mediated processes involving carbon–carbon bond cleavage of methylenecyclopropanes have been reported. Methylenecyclopropanes are unique in that coordination of their carbon–carbon double bonds to low-valent transition metals triggers cleavage at either the proximal Csp2–Csp3 bond or the distal Csp3–Csp3 bond of the cyclopropane core. There has been, however, only one example of carboxylation of methylenecyclopropanes with carbon dioxide; a palladium-catalyzed reaction at relatively high temperature forms unsaturated five-membered ring lactones through a sequence involving oxidative addition of the distal carbon–carbon bond to palladium, insertion of carbon dioxide and finally, reductive elimination (eq 1).

\[
\text{R} + \text{CO}_2 \xrightarrow{40 \text{ atm}} \text{cat. Pd} \quad \xrightarrow{125–165 \ ^\circ\text{C}} \text{O} \quad \xrightarrow{\text{O}} \text{R and/or O} \quad (1)
\]

It has been reported recently that low-valent nickel species mediate the coupling of carbon dioxide with various unsaturated hydrocarbons under mild conditions, which encouraged us to explore a new nickel-mediated carboxylation reaction of methylenecyclopropanes. Notably, it was found that diverse reaction pathways are partitioned in response to reaction conditions, such as a reaction solvent and the amine ligand employed, affording products essentially different from those obtained in the palladium case mentioned above.

A solution of benzylidenecyclopropane (1a, 1.1 equiv), Ni(cod)2 (1.0 equiv, cod = cycloocta-1,5-diene), and an amine ligand (2.2 equiv) was stirred at 0 °C for 4 h under an atmosphere of carbon dioxide (1 atm). An acidic workup followed by methylation with Me3SiCHN2 afforded a mixture of methyl esters of the carboxylated products. The distribution of these products varied significantly as a function of reaction solvent and amine ligand (Table 1). When 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 2.2 equiv) was used as the amine ligand in toluene solvent, cyclopropane derivative 2a was obtained along with a small amount of the branched α,β-unsaturated ester 3a (73%, 2a:3a:4a = 93:7:0, entry 1). In contrast, the use of more polar solvents favored the formation of 3a (entries 2–5). In particular, the reaction with DBU in N-methyl-2-pyrrolidinone (NMP)
gave 3a in 78% yield as the major product (2a:3a:4a = 6:94:0). Here, the formation of the linear γ,δ-unsaturated ester 4a was not observed. However, to our surprise, use of 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) instead of DBU altered the reaction course to favor production of the linear γ,δ-unsaturated ester 4a; the reaction with MTBD in NMP gave 4a in 52% yield exclusively (entry 8). At a higher CO₂ pressure of 5 atm, the yield was improved (67%, 2a:3a:4a = 0:1:99, entry 9). Suppression of the formation of 4a with DBU, and of 2a and 3a with MTBD suggests different mechanisms operate with DBU and MTBD (vide infra).

**Table 1. Nickel-mediated carboxylation of 1a with CO₂ under various conditions**

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>amine</th>
<th>yield / %</th>
<th>ratio</th>
<th>2a</th>
<th>3a</th>
<th>4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>toluene</td>
<td>DBU</td>
<td>73</td>
<td>93</td>
<td>7</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>DBU</td>
<td>77</td>
<td>40</td>
<td>60</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
<td>DBU</td>
<td>68</td>
<td>23</td>
<td>77</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>CH₃CN</td>
<td>DBU</td>
<td>66</td>
<td>4</td>
<td>96</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>NMP</td>
<td>DBU</td>
<td>78</td>
<td>6</td>
<td>94</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>toluene</td>
<td>MTBD</td>
<td>27</td>
<td>0</td>
<td>0</td>
<td>&gt;99</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>THF</td>
<td>MTBD</td>
<td>40</td>
<td>0</td>
<td>0</td>
<td>&gt;99</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>NMP</td>
<td>MTBD</td>
<td>52</td>
<td>0</td>
<td>0</td>
<td>&gt;99</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>NMP</td>
<td>MTBD</td>
<td>67</td>
<td>0</td>
<td>1</td>
<td>99</td>
<td></td>
</tr>
</tbody>
</table>

*a Conditions: 1a (1.1 equiv), CO₂ (1 atm), Ni(cod)₂ (1.0 equiv), amine (2.2 equiv), solvent, 0 °C, 4 h; hydrolysis with diluted HCl; then methylation with TMSCHN₂, MeOH. **Combined yields. * Ratio determined by ¹H NMR. * E:Z = 94:6. " CO₂ (5 atm)."*

The partitioning of the various reaction pathways can be explained by assuming the mechanism shown in Scheme 1. Initially, nickel(0) forms the π-complex I with the carbon–carbon double bond of methylenecyclopropane and carbon–oxygen double bond of carbon dioxide. For the formation of the products 2a and 3a, oxidative cyclization occurs to give the nickelacycle II. Direct hydrolysis of II followed by methylation with
Me$_3$SiCHN$_2$ affords 2a. Alternatively, the intermediate II may undergo β-carbon elimination to give the six-membered nickelacycle IV, probably through the dissociated zwitterionic complex III, which would allow a syn (or synclinal) conformation of the nickel–carbon linkage with the cleaving carbon–carbon bond. Hydrolysis and methylation then leads to the production of 3a. We assume that β-carbon elimination occurs more easily with the ionic intermediate III than with the nickelacycle II and that a polar solvent such as NMP facilitates the formation of the ionic intermediate to favor the formation of 3a. On the other hand, when MTBD is used as the amine ligand, the proximal carbon–carbon bond cis to the phenyl group of 1a undergoes oxidative addition to give the nickelacycle V. Insertion of carbon dioxide into the nickel–sp$^3$ carbon linkage affords VI. The corresponding E product 4a is selectively produced by subsequent protonolysis and methylation.

**Scheme 1. Proposed mechanism for the carboxylation reaction of 1a**

We quenched the reactions with DCI/D$_2$O (2 M) in order to support the intermediacy of II, IV and VI. With the products 2a and 3a obtained, deuterium atoms were incorporated at the expected positions (eq 2), whereas no deuterium incorporation was observed with 4a (eq 3). On the contrary, when MTBD-d$_3$ having a CD$_3$ group on nitrogen, was used as the base, the vinylic position of product 4a was deuterated (eq 4). These contrasting results shown in eqs 3 and 4 can be explained by assuming that the intermediate nickelacycle VI abstracts a proton from the methyl group of MTBD prior to an aqueous workup.
Under the optimized conditions, a structurally diverse set of methylenecyclopropanes 1 was examined (Table 2). The reactions of (arylmethylidene)cyclopropanes 1a–1f in toluene produced the corresponding cyclopropane derivatives 2a–2f with moderate to good selectivities, except in the case of 1d (entries 1–5). The chlorophenyl moiety of 1f remained intact in the presence of nickel(0). The alkylidenecyclopropane derivative 1g gave the ring-opening product 3g as the major product, even when toluene was used as solvent (entry 6). All the reactions in NMP gave the branched α,β-unsaturated esters 3 selectively (entries 7–12). The use of MTBD as the amine ligand resulted in highly selective formation of the E linear γ,δ-unsaturated esters 4, although the yields were moderate (entries 13–18).

In conclusion, we have described the nickel-mediated carboxylation of methylenecyclopropanes with carbon dioxide. Three types of carboxylated products, which are all different from that obtained by the palladium-catalyzed reaction, are prepared exclusively or preferentially depending on the reaction solvent and the amine ligand employed.
**Table 2. Nickel-mediated carboxylation of 1 with CO₂**

![Chemical structure](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>1 (R)</th>
<th>conditions&lt;sup&gt;a&lt;/sup&gt;</th>
<th>yield / %&lt;sup&gt;b&lt;/sup&gt;</th>
<th>2</th>
<th>3 (E/Z)&lt;sup&gt;d&lt;/sup&gt;</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1b (4-MeC₆H₄)</td>
<td>A</td>
<td>75</td>
<td>78</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1c (2-MeC₆H₄)</td>
<td>A</td>
<td>77</td>
<td>92</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1d (4-MeOC₆H₄)</td>
<td>A</td>
<td>78</td>
<td>51</td>
<td>49 (91/9)</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>1e (4-FC₆H₄)</td>
<td>A</td>
<td>79</td>
<td>89</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1f (4-ClC₆H₄)</td>
<td>A</td>
<td>79</td>
<td>93</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>1g (PhCH₂CH₂)</td>
<td>A</td>
<td>70</td>
<td>20</td>
<td>80 (65/35)</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>1b</td>
<td>B</td>
<td>70</td>
<td>1</td>
<td>99 (93/7)</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>1c</td>
<td>B</td>
<td>72</td>
<td>3</td>
<td>97 (97/3)</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>1d</td>
<td>B</td>
<td>79</td>
<td>1</td>
<td>99 (91/9)</td>
<td>0</td>
</tr>
<tr>
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<td>1e</td>
<td>B&lt;sup&gt;e&lt;/sup&gt;</td>
<td>81</td>
<td>1</td>
<td>99 (93/7)</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>1f</td>
<td>B&lt;sup&gt;e&lt;/sup&gt;</td>
<td>87</td>
<td>8</td>
<td>92 (93/7)</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>1g</td>
<td>B</td>
<td>68</td>
<td>0</td>
<td>&gt;99 (56/44)</td>
<td>0</td>
</tr>
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<td>1b</td>
<td>C</td>
<td>58</td>
<td>0</td>
<td>3</td>
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<td>14</td>
<td>1c</td>
<td>C</td>
<td>55</td>
<td>0</td>
<td>4</td>
<td>96</td>
</tr>
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<td>0</td>
<td>1</td>
<td>99</td>
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<td>17</td>
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<td>18</td>
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<td>C</td>
<td>37</td>
<td>0</td>
<td>6</td>
<td>94</td>
</tr>
</tbody>
</table>

<sup>a</sup> Common conditions: 1 (1.1 equiv), CO₂, Ni(cod)₂ (1.0 equiv), amine (2.2 equiv), 0 °C, 4 h; then workup. Conditions A: 1 atm of CO₂, DBU, in toluene; conditions B: 1 atm of CO₂, DBU, in NMP; conditions C: 5 atm of CO₂, MTBD, in NMP. <sup>b</sup> Combined yields. <sup>c</sup> Ratio determined by <sup>1</sup>H NMR. <sup>d</sup> Obtained as a mixture of E and Z isomers. The ratio given in parenthesis if determined. <sup>e</sup> 6 h.
Experimental Section

**General.** NMR spectra were recorded on a Varian Gemini 2000 (1H at 300 MHz and 13C at 75 MHz) spectrometers. CDCl₃ was used as a solvent. Me₄Si (1H, δ = 0.00), CDCl₃ (13C, δ = 77.0) were used as standards. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. All reactions were carried out under an argon atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF₅₂₅₄ (Merck).

**Materials.** Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used as received. Toluene was dried over Na-benzophenone ketyl.

**Carboxylation of methylenecyclopropane 1a: Procedure A.**

To a stirred suspension of Ni(cod)₂ (82.5 mg, 0.30 mmol) in toluene (3 ml) in a Schlenk-type flask under a nitrogen atmosphere at 0 °C was added DBU (0.66 mmol). The mixture was degassed by a freeze-pump-thaw method, and then carbon dioxide was introduced. Substrate 1a (0.33 mmol) was added to the resulting pale yellow suspension at 0 °C. After the reaction mixture was stirred at 0 °C for 4 h, diluted HCl aq. (2 M) was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated. The residue was treated with TMSCHN₂ in Et₂O/MeOH. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate) to give the product.

**Carboxylation of methylenecyclopropane 1a: Procedure B.**

To a stirred suspension of Ni(cod)₂ (82.5 mg, 0.30 mmol) in NMP (3 mL) in a Schlenk-type flask under a nitrogen atmosphere at 0 °C was added DBU (0.66 mmol). The mixture was degassed by a freeze-pump-thaw method, and then carbon dioxide was introduced. Substrate 1a (0.33 mmol) was added to the resulting pale yellow suspension at 0 °C. After the reaction mixture was stirred at 0 °C for 4 h, diluted HCl aq. (2 M) was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated. The residue was treated with TMSCHN₂ in Et₂O/MeOH. The solvent was removed
under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate) to give the product.

**Carboxylation of methylencyclopropane 1a: Procedure C.**

To a stirred suspension of Ni(cod)$_2$ (82.5 mg, 0.30 mmol) in NMP (3 mL) in a Schlenk-type flask under a nitrogen atmosphere at 0 °C was added DBU (0.66 mmol) and the substrate 1a (0.33 mmol). The mixture was frozen and then pressurized with carbon dioxide (5 atm). After the reaction mixture was stirred at 0 °C for 4 h, the pressure of carbon dioxide was released and diluted HCl aq. (2 M) was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$ and concentrated. The residue was treated with TMSCHN$_2$ in Et$_2$O/MeOH. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate) to give the product.

**Methyl 1-phenylmethylcyclopropane-1-carboxylate (2a)**

\[
\text{Ph} \quad \text{CO}_2\text{Me}
\]

$^1$H NMR: $\delta = 0.80$ (dd, $J = 7.2$, 4.2 Hz, 2H), 1.28 (dd, $J = 7.2$, 4.2 Hz, 2H), 2.99 (s, 2H), 3.62 (s, 3H), 7.16-7.30 (m, 5H); $^{13}$C NMR: $\delta = 15.2$, 23.8, 38.3, 51.8, 126.0, 128.0, 128.4, 129.1, 139.3, 175.3;

**Methyl (E)-2-ethyl-3-phenylprop-1-enoate (3a)**

\[
\text{Ph} \quad \text{CO}_2\text{Me}
\]

$^1$H NMR: $\delta = 1.16$ (t, $J = 7.5$ Hz, 3H), 2.55 (q, $J = 7.5$ Hz, 2H), 3.82 (s, 3H), 7.20-7.40 (m, 5H), 7.65 (s, 1H); $^{13}$C NMR: $\delta = 14.0$, 20.9, 52.0, 128.2, 128.4, 129.1, 134.6, 135.7, 138.5, 168.7;

**Methyl 1-(4-methylphenyl)methylcyclopropane-1-carboxylate (2b)**

\[
\begin{array}{c}
\text{Ph} \\
\text{CO}_2\text{Me}
\end{array}
\]
$^1$H NMR: $\delta = 0.79$ (dd, $J = 6.9, 3.9$ Hz, 2H), 1.25 (dd, $J = 6.9, 3.9$ Hz, 2H), 2.31 (s, 3H), 2.95 (s, 2H), 3.62 (s, 3H), 7.06-7.14 (m, 4H); $^{13}$C NMR: $\delta = 15.1, 21.1, 23.8, 37.8, 51.8, 128.7, 129.0 135.5, 136.2, 175.4;

**Methyl (E)-2-ethyl-3-(4-methylphenyl)prop-1-enoate (3b)**

$^1$H NMR: $\delta = 1.17$ (t, $J =7.5$ Hz, 3H), 2.37 (s, 3H), 2.56 (q, $J = 7.5$ Hz, 2H), 3.81 (s, 3H), 7.08-7.30 (m, 4H), 7.62 (s, 1H); $^{13}$C NMR: $\delta = 13.9, 20.9, 21.4, 51.9, 129.1, 129.2, 132.7, 133.7, 138.4, 138.5, 168.8;

**Methyl 1-(2-methylphenyl)methylcyclopropane-1-carboxylate (2c)**

$^1$H NMR: $\delta = 0.66$ (dd, $J = 6.6, 4.2$ Hz, 2H), 1.28 (dd, $J = 6.6, 4.2$ Hz, 2H), 2.26 (s, 3H), 3.05 (s, 2H), 3.64 (s, 3H), 7.09-7.22 (m, 4H); $^{13}$C NMR: $\delta = 14.5, 19.7, 21.9, 34.2, 52.0, 125.6, 126.1, 128.5, 129.8, 136.6, 136.7, 175.7;

**Methyl (E)-2-ethyl-3-(2-methylphenyl)prop-1-enoate (3c)**

$^1$H NMR: $\delta = 1.07$ (t, $J = 7.5$ Hz, 3H), 2.27 (s, 3H), 2.38 (q, $J = 7.5$ Hz, 2H), 3.83 (s, 3H), 7.17-7.25 (m, 4H), 7.69 (s, 1H); $^{13}$C NMR: $\delta = 14.1, 20.0, 20.9, 51.9, 125.5, 128.0, 128.1, 129.9, 135.1, 135.2, 136.5, 138.1, 168.4;

**Methyl 1-(4-methoxyphenyl)methylcyclopropane-1-carboxylate (2d)**

$^1$H NMR: $\delta = 0.78$ (dd, $J = 6.6, 3.9$ Hz, 2H), 1.24 (dd, $J = 6.6, 3.9$ Hz, 2H), 2.92 (s, 2H), 3.62 (s, 3H), 3.77 (s, 3H), 6.78-6.84 (m, 2H), 7.12-7.17 (m, 2H); $^{13}$C NMR: $\delta = 14.9, 24.0, 37.4, 51.8, 55.2, 113.4, 130.0, 131.3, 157.8, 175.4;
Methyl (E)-2-ethyl-3-(4-methoxyphenyl)prop-1-enoate (3d)

\[\text{MeO} \quad \text{CO}_2\text{Me}\]

$^1$H NMR: $\delta = 1.18$ (t, $J = 7.5$ Hz, 3H), 2.57 (q, $J = 7.5$ Hz, 2H), 3.81 (s, 3H), 3.83 (s, 3H), 6.91-6.95 (m, 2H), 7.33-7.38 (m, 2H), 7.60 (s, 1H); $^{13}$C NMR: $\delta = 13.8, 20.8, 51.9, 55.3, 113.9, 128.1, 130.9, 132.4, 138.1, 159.6, 168.9;

Methyl 1-(4-fluorophenyl)methylcyclopropane-1-carboxylate (2e)

\[\text{F} \quad \text{CO}_2\text{Me}\]

$^1$H NMR: $\delta = 0.80$ (dd, $J = 7.2, 4.2$ Hz, 2H), 1.28 (dd, $J = 7.2, 4.2$ Hz, 2H), 2.94 (s, 2H), 3.62 (s, 2H), 6.91-6.99 (m, 2H), 7.17-7.23 (m, 2H); $^{13}$C NMR: $\delta = 15.1, 37.7, 51.8, 52.0, 114.8$ (d, $J = 21$ Hz), 130.3 (d, $J = 8.0$ Hz), 135.0 (d, $J = 3.7$ Hz), 161.3 (d, $J = 242$ Hz), 175.1;

Methyl (E)-2-ethyl-3-(4-fluorophenyl)prop-1-enoate (3e)

\[\text{F} \quad \text{CO}_2\text{Me}\]

$^1$H NMR: $\delta = 1.17$ (t, $J = 7.5$ Hz, 3H), 2.51 (q, $J = 7.5$ Hz, 2H), 3.82 (s, 3H), 7.04-7.12 (m, 2H), 7.32-7.38 (m, 2H), 7.60 (s, 1H); $^{13}$C NMR: $\delta = 13.8, 20.8, 52.0, 115.2$ (d, $^2J_{C-F} = 21$ Hz), 130.9 (d, $^1J_{C-F} = 8.0$ Hz), 131.7 (d, $^4J_{C-F} = 3.6$ Hz), 134.4, 137.3, 162.4 (d, $^1J_{C-F} = 247$ Hz), 168.5;

(E)-Methyl 2-ethyl-5-phenylpent-1-enoate (3g)

\[\text{CO}_2\text{Me}\]

$^1$H NMR: $\delta = 0.94$ (t, $J = 7.5$ Hz, 3H), 2.30 (q, $J = 7.5$ Hz, 2H), 2.50 (pseudo q, $J = 7.5$ Hz, 2H), 2.74 (t, $J = 7.5$ Hz, 2H), 3.73 (s, 3H), 6.77 (t, $J = 7.5$ Hz, 1H), 7.18-7.32 (m, 5H); $^{13}$C NMR: $\delta = 13.9, 20.1, 30.4, 35.1, 51.6, 126.0, 128.2, 128.3, 134.4, 140.8, 141.1, 168.1;

(Z)-Methyl 2-ethyl-5-phenylpent-1-enoate (3g)
$^1$H NMR: $\delta = 1.01$ (t, $J = 7.2$ Hz, 3H), 2.26 (q, $J = 7.2$ Hz, 2H), 2.72 (s, 2H), 2.74 (s, 2H), 3.73 (s, 3H), 5.90 (m, 1H), 7.16-7.31 (m, 5H); $^{13}$C NMR: $\delta = 13.7, 27.5, 31.3, 35.7, 51.2, 125.8, 128.2, 128.4, 133.9, 139.4, 141.4, 168.4$;
References


6. A mixture of stereoisomers.

7. Production of 4a was not observed with other amines like DBN, TMEDA, 2,2'-bipyridyl, 1,2-dimethylimidazole and 2-methyl-2-oxazoline.


10. The branched ester 3a was obtained as the major product (72%, 2a:3a:4a = 20:80:0) when the reaction was carried out initially in toluene for 4 h and then CH₃CN was added to the reaction mixture which was further stirred for additional 4 h prior to an aqueous workup.


14. Product 4a can result from carboxylation of 1-phenylbuta-1,3-diene, to which 1a may possibly isomerise in the presence of nickel(0). The present reaction conditions, however, caused no carboxylation reaction of 1-phenylbuta-1,3-diene prepared independently.

15. The contrasting results obtained with 1g and (aryl methylidene)cyclopropanes 1a–1f are accounted for by assuming the more stable nature of the nickel–benzylic carbon linkage of II.
Chapter 6

Synthesis of β-Amino Acid Derivatives by Nickel(0)-Mediated Sequential Addition of Carbon Dioxide and Dibenzoyldiazene onto Unsaturated Hydrocarbons

Abstract: A stoichiometric amount of nickel(0) complex mediated the aminative carboxylation of unsaturated hydrocarbons through oxidative cyclization with carbon dioxide followed by insertion of dibenzoyldiazene into the carbon–nickel bond, giving β-amino acid derivatives.
The development of reactions which incorporate carbon dioxide into organic molecules has been an important challenge in chemistry. In recent years, oxidative cyclization on nickel(0) has emerged as an efficient elementary step to activate carbon dioxide which is thermodynamically very stable. Oxanickelacycle intermediates formed by oxidative cyclization of carbon dioxide and unsaturated hydrocarbons can undergo further transformations including oxidation, carbon–carbon bond formation, rearrangement, etc. The nickel(0)-mediated carboxylation reactions possess good functional group compatibility, and thus, provide unique preparative methods of carboxylic acid derivatives. On the other hand, β-amino acid is an intriguing structural motif because it is a valuable constituent of designed peptides and biologically active compounds. It would become a novel synthetic method of amino acids if the carbon–nickel bond of an oxanickelacycle intermediate is transformed into a carbon–nitrogen bond. In this chapter, the author reports the synthesis of β-amino acids via nickel(0)-mediated oxidative cyclization and subsequent amination of the carbon–nickel bond.

Terminal allene 1a was reacted with bis(1,5-cyclooctadiene)nickel (Ni(cod)₂, 1.0 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 2.2 equiv) at 0 °C in THF under atmospheric pressure of carbon dioxide for 2 h according to the literature procedure. The resulting reaction mixture containing an oxanickelacycle intermediate was then treated with various nitrogen nucleophiles such as potassium phthalimide and trimethylsilyl azide with the expectation that transmetalation with the nickel carboxylate moiety followed by reductive elimination would form a carbon–nitrogen bond. However, the reactions with nitrogen nucleophiles have all failed so far, which encouraged us to examine electrophilic aminating reagents. To our delight, dibenzoyldiazene (2, 1.1 equiv) was successfully incorporated into the oxanickelacycle intermediate. Acidic hydrolysis of the nickel carboxylate moiety followed by esterification with (CH₃)₃SiCHN₂ afforded β-amino carboxylate 3a together with a small amount of the regioisomeric aminated product 4a (72% total yield, 3a:4a = 94:6). The product 3a in which the terminal allene carbon was aminated predominated over the regioisomeric aminated product 4a. This regiochemical outcome is in marked contrast to that of the reaction of oxanickelacycles with aldehydes. The plausible mechanism is shown in Scheme 1. Initially, oxanickelacycle A having an allylnickel moiety is formed by oxidative cyclization of carbon dioxide and the allene on nickel(0). Diazene 2 was subsequently inserted into the carbon–nickel bond of A, forming the seven-membered nickelacycle B. The intermediate B is protonated and the resulting acid is esterified with TMSCHN₂.
Scheme 1. Sequential addition of carbon dioxide and dibenzoyldiazene (2) onto (2-phenylethyl)allene (1a)

\[
\begin{align*}
1a & \quad + \quad \text{CO}_2 \quad \text{(1 atm)} \\
& \quad \xrightarrow{1.0 \text{ equiv Ni(cod)}_2, 2.2 \text{ equiv DBU}} \quad \text{THF, 0 °C} \\
& \quad \xrightarrow{1.1 \text{ equiv Bz-}N\equiv N\text{-Bz}} \quad \text{(Bz = PhCO)} \\
& \quad \xrightarrow{1) 2N \text{ HCl}, 2) (CH}_3\text{)}_3\text{SiCHN}_2\text{)} \\
\end{align*}
\]

The results of the nickel(0)-mediated aminative carboxylation of allenes are shown in Table 1. Ether and ester functionalities were tolerated under the reaction conditions (entries 1 and 2). A phtalimide remained intact (entry 3). 1-Methyl-1-phenylallene (1e) selectively gave 3e in 82% yield (entry 4). The lower yield observed with phenylallene (1f) can be ascribed to its competitive oligomerization (entry 5).

Next, we examined the use of other unsaturated hydrocarbons (Scheme 2). Terminal alkynes 5a and 5b, afforded the corresponding alkenylhydrazine 6a and 6b in 47 and 41% yield, respectively. These results indicate that an oxanickelacycle containing a sp² carbon–nickel bond can also react with 2. Methylenecyclopropane 7 yielded the aminative carboxylation product 8 without concomitant cleavage of the cyclopropane ring. In contrast to allenes (1,2-dienes), 1,3-dienes such as 1,3-cyclohexadiene and 1-phenyl-1,3-butadiene underwent only carboxylation but no insertion of 2 occurred, suggesting that the resulting allylic oxanickelacycle intermediate is less reactive than that derived from an allene.
Scheme 2. Reactions with other unsaturated hydrocarbons

Table 1. Sequential addition of carbon dioxide and 2 onto allenes

<table>
<thead>
<tr>
<th>entry</th>
<th>substrate (R, R')</th>
<th>yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>3</th>
<th>4</th>
<th>E/Z of 3&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1b (BnO(CH₂)₂, H)</td>
<td>68</td>
<td>92</td>
<td>8</td>
<td>87/13</td>
</tr>
<tr>
<td>2</td>
<td>1c (BzO(CH₂)₂, H)</td>
<td>64</td>
<td>94</td>
<td>6</td>
<td>94/6</td>
</tr>
<tr>
<td>3</td>
<td>1d (PhthN(CH₂)₂, H)</td>
<td>74</td>
<td>94</td>
<td>6</td>
<td>94/6</td>
</tr>
<tr>
<td>4</td>
<td>1e (Ph, Me)</td>
<td>82</td>
<td>&gt;99</td>
<td>1</td>
<td>&gt;99/1</td>
</tr>
<tr>
<td>5</td>
<td>1f (Ph, H)</td>
<td>47</td>
<td>94</td>
<td>6</td>
<td>&gt;99/1</td>
</tr>
</tbody>
</table>

<sup>a</sup>For the experimental procedure, see experimental section. <sup>b</sup>Combined yield. <sup>c</sup>Ratio was determined by ¹H NMR. <sup>d</sup>The geometry of the olefin was determined by ¹H NMR. Phth: phthaloyl.

Finally, reductive cleavage of the nitrogen–nitrogen bond was performed using Sml₂ (Scheme 3).<sup>9</sup> Treatment of the dibenzoylhydrazine 3a with Sml₂ in THF/MeOH at
−10 °C gave the benzamide 9a in 86% yield. The α,β-unsaturated ester group remained at this temperature. The reaction of 8 with SmI₂ was also successful under the same reaction conditions, giving the product 10 in 80% yield.

**Scheme 3.** Reductive cleavage of the hydrazine moiety

In summary, the author have described the synthesis of β-amino acid derivatives through a nickel(0)-mediated oxidative cyclization reaction of carbon dioxide with unsaturated hydrocarbons followed by an amination reaction with dibenzoyldiazene. Simple unsaturated hydrocarbons such as allenes, alkynes, and methylenecyclopropanes could be employed, giving β-hydrazinocarboxylic acids in one-pot. The present study provides a new example of utilization of carbon dioxide as C1 source.
Experimental Section

General. NMR spectra were recorded on a Varian Gemini 2000 (1H at 300 MHz and 13C at 75 MHz) spectrometers. CDCl3 was used as a solvent. Me₄Si (1H, δ = 0.00), CDCl₃ (13C, δ = 77.0) were used as standards. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. All reactions were carried out under an argon atmosphere. Column chromatography was performed with silica gel 60 N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF₂₅₄ (Merck).

Materials. Unless otherwise noted, all chemicals and anhydrous solvents were obtained from commercial suppliers and used as received. Dibenzoyldiazene was prepared according to the reported procedure.¹

Sequential addition of carbon dioxide and dibenzoyldiazene onto allene 1a: a typical procedure

To a stirred suspension of Ni(cod)₂ (82.5 mg, 0.30 mmol) in a freshly distilled THF (2.5 mL) in a Schlenk-type flask under a nitrogen atmosphere at 0 °C was added DBU (100 µL, 0.66 mmol). The mixture was degassed by a freeze-pump-thaw method, and then carbon dioxide was introduced. To the resulting pale yellow solution at 0 °C was added a THF solution (0.5 mL) of substrate 1a (47.6 mg, 0.33 mmol) dropwise (20 µL/min). After the reaction mixture was stirred at 0 °C for 2 h, a THF solution (1 mL) of dibenzoyldiazene (2, 79.2 mg, 0.33 mmol) was added. After 2 h, dilute hydrochloric acid (2 N) was added to the reaction mixture. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with water and brine, dried over MgSO₄, and concentrated. The residue was treated with (CH₃)₃SiCHN₂ in Et₂O/MeOH. The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (dichloromethane:ethyl acetate = 10:1) to give the product (E)-3a:

(E)-Methyl 2-((N,N’-dibenzoylhydrazinomethyl)-5-phenylpent-2-enoate (3a)
1H NMR: δ = 2.74 (br, 4H), 3.70 (s, 3H), 3.8–5.6 (br, 2H), 7.04 (t, J = 6.9 Hz, 1H), 7.1–7.6 (m, 15H), 8.83 (s, 1H); 13C NMR: δ = 30.4, 34.6, 45.8, 52.0, 125.95, 126.01, 126.6, 127.0, 127.8, 128.23, 128.28, 128.31, 128.5, 130.0, 131.8, 132.1, 134.7, 140.5, 148.3, 166.4, 171.9; HRMS (EI): Caled for C_{27}H_{26}N_{2}O_{4} (M^+) 442.1893. Found 442.1895.

*(E*)-Methyl 2-(N,N'-dibenzoylhydrazinomethyl)-5-benzyloxypent-2-enoate (3b)

![Chemical Structure](image)

1H NMR: δ = 2.6–3.0 (br, 2H), 3.6 (br, 2H), 3.71 (s, 3H), 3.8–5.5 (br, 2H), 4.45 (s, 2H), 2.74 (br, 4H), 7.14 (t, J = 7.4 Hz, 1H), 7.20–7.55 (m, 15H), 8.84 (s, 1H); 13C NMR: δ = 29.4, 45.3, 52.1, 68.6, 73.1, 126.9, 127.0, 127.1, 127.56, 127.61, 127.8, 128.3, 128.5, 129.5, 130.0, 131.9, 132.0, 134.7, 137.6, 146.2, 166.4, 172.0; HRMS (EI): Caled for C_{28}H_{28}N_{2}O_{5} (M^+) 472.1998. Found 472.1987.

*(E*)-Methyl 5-benzoyl-2-(N,N'-dibenzoylhydrazinomethyl)pent-2-enoate (3c)

![Chemical Structure](image)

1H NMR: δ = 2.98 (br, 2H), 3.72 (s, 3H), 3.8–5.6 (br, 2H), 4.4 (br, 2H), 7.09 (t, J = 7.4 Hz, 1H), 7.27–7.57 (m, 13H), 8.00 (d, J = 7.5 Hz, 2H), 9.09 (s, 1H); 13C NMR: δ = 28.3, 46.0, 52.2, 63.1, 127.0, 127.1, 127.8, 128.2, 128.5, 129.4, 129.7, 130.0, 131.7, 132.1, 132.9, 134.5, 144.1, 166.3, 166.4, 172.0; HRMS (EI): Caled for C_{28}H_{28}N_{2}O_{6} (M^+) 486.1791. Found 486.1789.

*(E*)-Methyl 2-(N,N'-dibenzoylhydrazinomethyl)-5-phtalimidopent-2-enoate (3d)

![Chemical Structure](image)
1H NMR: δ = 2.88 (br, 2H), 3.70 (s, 3H), 3.8-5.6 (br, 2H), 3.87 (br, 2H), 7.04 (t, J = 7.7 Hz, 1H), 7.2-7.8 (m, 14H), 9.07 (s, 1H); 13C NMR: δ = 28.5, 36.7, 45.7, 52.2, 123.2, 127.0, 127.1, 127.7, 128.5, 130.0, 131.77, 131.79, 132.1, 133.9, 134.4, 144.3, 166.3, 168.1, 171.8; HRMS (EI): Calcd for C29H25N3O6 (M+) 511.1743. Found 511.1739.

(E)-Methyl 2-((N,N'-dibenzoylhydrazinomethyl)-3-phenylbut-2-enoate (3e)

1H NMR: δ = 2.18 (s, 4H), 3.8-5.4 (br, 2H), 3.83 (s, 3H), 6.99 (d, J = 2.7 Hz, 2H), 7.25-7.52 (m, 13H), 8.37 (s, 1H); 13C NMR: δ = 23.8, 47.3, 52.1, 124.6, 126.7, 126.9, 127.6, 127.7, 127.8, 128.4, 128.5, 128.6, 130.0, 131.8, 132.1, 134.5, 140.5, 165.7, 169.9, 172.4; HRMS (EI): Calcd for C26H24N2O4 (M+) 428.1736. Found 428.1735.

(E)-Methyl 2-((N,N'-dibenzoylhydrazinomethyl)-3-phenylprop-2-enoate (3f)

1H NMR: δ = 3.79 (s, 3H), 4.0-5.8 (br, 2H), 7.28-7.53 (m, 15H), 7.91 (s, 1H), 8.80 (s, 1H); 13C NMR: δ = 46.8, 52.4, 126.5, 127.0, 127.1, 127.8, 128.49, 128.53, 129.1, 129.4, 130.0, 131.8, 132.1, 134.0, 134.6, 144.6, 166.4, 168.5, 172.3; HRMS (EI): Calcd for C25H22N2O4 (M+) 414.1580. Found 4414.1581.

(Z)-Methyl 2-((N,N'-dibenzoylhydrazino)-2-phenylprop-2-enoate (6a)
\[ \text{CO}_2\text{Me} \quad \text{N} \quad \text{NH} \quad \text{O} \]

$^1$H NMR: $\delta = 3.79$ (s, 3H), 6.04 (s, 1H), 7.19-7.65 (m, 11H), 7.75 (d, $J = 6.9$ Hz, 2H), 8.09 (br, 2H), 10.1 (br, 1H); $^{13}$C NMR: $\delta = 52.2$, 109.8, 127.3, 127.5, 127.7, 127.9, 128.5, 128.6, 130.8, 131.0, 131.8, 132.3, 134.0, 136.4, 157.5, 165.9, 166.3; HRMS (EI): Calcd for C$_{24}$H$_{20}$N$_2$O$_4$ (M$^+$) 400.1423. Found 400.1423.

(Z)-Methyl 2-(N,N'-dibenzoylhydrazino)hept-2-enoate (6b)

\[ \text{CO}_2\text{Me} \quad \text{N} \quad \text{NH} \quad \text{O} \]

$^1$H NMR: $\delta = 0.87-0.92$ (m, 3H), 1.33-1.35 (m, 4H), 1.63-1.68 (m, 2H), 2.79 (t, $J = 7.7$ Hz, 2H), 3.72 (s, 3H), 5.80 (s, 1H), 7.32-7.50 (m, 6H), 7.60-7.66 (m, 4H), 9.74 (s, 1H); $^{13}$C NMR: $\delta = 14.0$, 22.5, 26.8, 31.2, 36.0, 51.9, 112.7, 127.1, 127.2, 128.0, 128.6, 130.7, 131.7, 132.3, 134.1, 161.5, 166.0, 171.0; HRMS (EI): Calcd for C$_{23}$H$_{26}$N$_2$O$_4$ (M$^+$) 394.1893. Found 394.1892.

Methyl 1-{N,N'-dibenzoylhydrazino(phenyl)methyl}cyclopropanecarboxylate (8)

\[ \text{CO}_2\text{Me} \quad \text{N} \quad \text{NH} \quad \text{O} \]

$^1$H NMR: $\delta = 0.89$ (br, 1H), 1.50 (br, 1H), 1.56-1.63 (m, 1H), 1.72 (br, 1H), 3.77 (s, 3H), 5.69 (s, 1H), 7.07-7.64 (m, 15H), 9.59 (s, 1H); $^{13}$C NMR: $\delta = 14.6$, 19.6, 26.7, 52.4, 64.1, 126.2, 127.2, 127.4, 127.8, 128.1, 129.5, 129.7, 131.2, 132.5, 134.8, 135.5, 164.9, 171.8, 176.5; HRMS (EI): Calcd for C$_{26}$H$_{24}$N$_2$O$_4$ (M$^+$) 428.1736. Found 428.1735.

(E)-Methyl 2-(benzamidomethyl)-5-phenylpent-2-enoate (9)
Methyl 1-\{benzamido(phenyl)methyl\}cyclopropanecarboxylate (10)

\[\text{Methyl 1-\{benzamido(phenyl)methyl\}cyclopropanecarboxylate (10)}\]

\[^1H\text{NMR: } \delta = 1.13-1.35 (m, 3H), 1.69-1.76 (m, 1H), 3.64 (s, 3H), 4.93 (d, } J = 9.3 \text{ Hz, 1H), 7.22-7.35 (m, 3H), 7.42-7.56 (m, 5H), 7.86-7.90 (m, 2H), 7.94 (d, } J = 9.6 \text{ Hz, 1H);}\]

\[\text{\[^{13}C\text{NMR: } \delta = 15.3, 16.2, 27.8, 52.0, 56.6, 126.5, 127.0, 127.1, 128.3, 128.5, 131.5, 134.2, 140.2, 166.4, 174.5; HRMS (EI): Caled for C}_{19}\text{H}_{19}\text{NO}_{3} \text{ (M}^+\text{) 309.1365. Found 309.1363.}\]

\[^1H\text{NMR: } \delta = 2.80-2.82 (m, 4H), 3.76 (s, 3H), 4.21 (d, } J = 6.0 \text{ Hz, 2H), 6.67 (br t, 1H), 6.92-6.98 (m, 1H), 7.13-7.30 (m, 5H), 7.38-7.52 (m, 3H), 7.69-7.74 (m, 2H);}\]

\[\text{\[^{13}C\text{NMR: } \delta = 30.5, 34.8, 35.8, 52.0, 126.0, 126.8, 128.2, 128.3, 128.37, 128.42, 128.7, 131.3, 134.3, 140.6, 145.4, 166.7, 167.7; HRMS (EI): Caled for C}_{20}\text{H}_{21}\text{NO}_{3} \text{ (M}^+\text{) 323.1521. Found 323.1520.}\]

Methyl 1-\{benzamido(phenyl)methyl\}cyclopropanecarboxylate (10)
References


6. Diethyl diazodicarboxylate (DEAD) can be also used for amination. However, 2 was preferred over DEAD for the ease of isolation of the products.

7. Both σ- and π-allyl structures are conceivable.

8. Methylene cyclopropane 7 was consumed and, besides 8, a complex mixture of various products was obtained. However, it was hardly possible to identify other aminated products such as a cyclopropane opened one.


10. Because 3a was contaminated with (Z)-isomer and the regioisomer 4a, the product was obtained with the saturated ester 11a, which probably resulted from (Z)-3a, and the regioisomeric ester 12a.
Ph\text{CO}_2\text{Me} \quad 11a \quad \text{NHBz} \quad \text{Ph}\text{CO}_2\text{Me} \quad 12a \quad \text{NHBz}
List of Publications

Chapter 1  
Stereoselective Synthesis of Trisubstituted Alkenylboranes by Palladium-Catalyzed Reaction of Alkynyltriarylborates with Aryl Halides  
Naoki Ishida, Tomoya Miura, and Masahiro Murakami  

Chapter 2  
Palladium-Catalyzed Allylation of Alkynyltriarylborates  
Naoki Ishida, Tatsuo Shinmoto, Tomoya Miura, and Masahiro Murakami.  
*In preparation*.

Chapter 3  
Synthesis of Amine–Borane Intramolecular Complexes through Palladium-Catalyzed Rearrangement of Ammonioalkynyltriarylborates  
Naoki Ishida, Mizuna Narumi, and Masahiro Murakami  
*Org. Lett.* **2008**, *10*, 1279-1281.

Chapter 4  
Asymmetric Carroll Rearrangement of Allyl α-Aacetamido-β-ketocarboxylates Catalyzed by a Chiral Palladium Complex  
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Chapter 5  
Solvent and Ligand Partition Reaction Pathways in Nickel-Mediated Carboxylation of Methylene cyclopropanes  
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Chapter 6  
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