Studies on the Transition Metal-Catalyzed Carbostannylation of Alkynes

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Contents

Abbreviations

Ac	acetyl	mp	melting point
acac	acetylacetonate(-o)	NMP	1-methyl-2-pyrrolidinone
atm	atmospheric pressure	NMR	nuclear magnetic resonance
brs	broad singlet (spectral)	Ph	phenyl
Bu	butyl	Pr	propyl
calcd	calculated	q	quartet (spectral)
cod	1,5-cyclooctadiene	R_f	relative mobility
Cy	cyclohexyl	s	singlet (spectral)
d	doublet (spectral)	t	triplet (spectral)
dba	dibenzylideneacetone	temp	temperature
DME	1,2-dimethoxyethane	THF	tetrahydrofuran
DMF	*N,N*-dimethylformamide	TLC	thin layer chromatography
δ	scale (NMR)	TMS	trimethylsilyl
ed.	edition		
ESI	electrospray ionization		
Et	ethyl		
GPC	gel permeation chromatography		
h	hour(s)		
Hex	hexyl		
HRMS	high-resolution mass spectra		
Hz	hertz		
J	coupling constant (NMR)		
m	multiplet (spectral)		
M	mol per liter		
Me	methyl		
min	minute(s)		
mL	mililiter		

Chapter 1

Introduction and General Summary

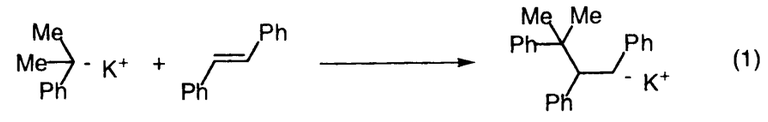
Carbometalation Reaction

The ultimate goal of organic synthesis is design and construction of such invaluable organic compounds as pharmaceuticals, agrochemicals, perfumes, dyes and functionality materials used for improvement of quality of life. In order to obtain target compounds in a straightforward manner and in high yields, development of powerful synthetic reactions and reagents endowed with high chemo-, regio- and stereoselectivities are indispensable. Therefore, it is no exaggeration to say that progress of organic synthesis depends totally on exploitation of novel synthetic methods.

Current problems in synthetic methods are classified into two categories as follows: (1) Construction of a molecular skeleton through a carbon–carbon bond forming reaction. (2) Introduction of a functional group at a suitable position of a target molecule. Needless to say, organometallic compounds have shown to be essential reagents or catalysts in modern organic synthesis; without use of metallic compounds, it is impossible to synthesize even structurally simple molecules.

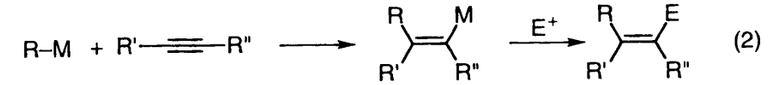
Traditionally, carbon–carbon bond formation has been achieved by reaction of organometallic reagents with polar carbon electrophiles. Among various carbon–carbon bond forming reactions, carbometalation of alkynes is unique and promising, because both organic and metallic moieties in organometallic reagents can be introduced into a nonpolar carbon–carbon multiple bond in regio- and stereoselective manners, leading to simultaneous formation of new carbon–carbon and carbon–metal bonds.[1] The resulting products also are organometallic compounds, which can be applied to subsequent carbon–carbon bond formation and/or introduction of a functional group. Because of great synthetic potential, search for truly useful carbometalation reaction has been an urgent research target in last decades.

Historically, pioneering work on carbometalation of carbon–carbon multiple bonds was performed in 1927 by Ziegler and Bähr, who observed that 1-methyl-1-phenylethylpotassium added to stilbene (eq 1).[2] Since then a number of organometallic reagents were found to add to alkenes, dienes and alkynes in the presence or absence of catalysts.



(1)

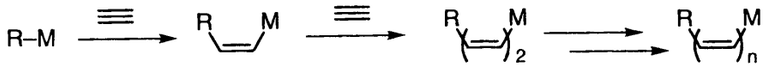
Carbometalation of alkenes and dienes has been limited to intramolecular reaction that affords carbocycles; no precedents are available for intermolecular carbometalation of particularly non-functionalized alkenes. In contrast, inter- and intramolecular carbometalation of alkynes is performed with a variety of organometallic reagents including Li,[3] Mg,[4] Zn,[5] Cu,[6] Al,[7] B,[8] Ga,[9] In,[10] Ti,[11] Zr,[12] Ta,[13] Mn[14] and Si.[15] In view of stereoselective olefin synthesis, carbometalation of alkynes is one of the most useful reactions, because the resulting alkenylmetals can react with a wide variety of electrophiles to afford variously substituted ethenes (eq 2).



(2)

M = Li, Mg, Zn, Cu, Al, B, Ga, In, Ti, Zr, Ta, Mn, Si, Sn

Of many organometallics, those having a polar carbon–metal bond, especially organolithium and organomagnesium reagents, readily add to alkynes. In addition, these reagents are basic enough to abstract a terminal alkynic or propargylic proton prior to the desired carbometalation. Moreover, the resulting alkenylmetals may compete with the initial reagents in the addition process, leading to oligomerization and/or polymerization of alkynes (eq 3). Furthermore, chemoselective carbometalation with these reagents is hard to achieve except for propargyl alcohols (eq 4).[16]



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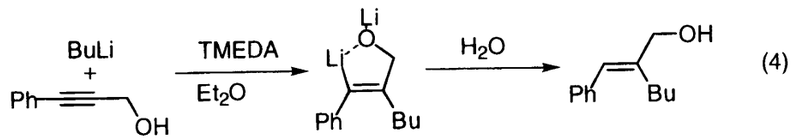
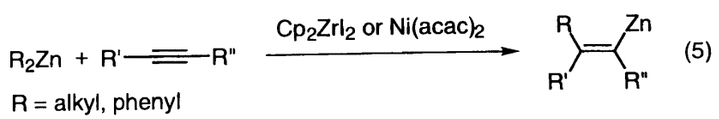


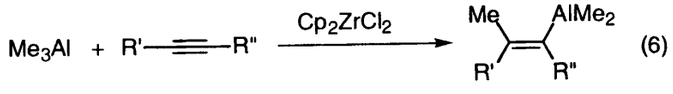
(4)

Less polarized organometallic reagents have been found to be superior in respect to controlled carbometalation. Organozinc[5] and organocopper[6] reagents undergo carbometalation with alkynes in the absence of a catalyst and thus have high synthetic potential. In particular, extended scope of substrates and improved stereoselectivity in carbozincation have been achieved by use of Cp_2ZrI_2[5f,5g] and $Ni(acac)_2$[5h] as catalysts, respectively (eq 5).



(5)

Of special interest in organic synthesis is Cp_2ZrCl_2-catalyzed carboalumination as disclosed by Negishi (eq 6).[7] Carbon–aluminum bonds of allyl-,[7d] benzyl-[7d] and methylalanes[7e] add to alkynes regio- and stereoselectively. The methylalumination, which has been applied to the synthesis of such a natural product as dendrolasin,[17] is significant since the introduction of methyl into alkynes can hardly be achieved with other organometallic reagents (Scheme 1). Alkyl- and alkenylalumination reactions of silylacetylenes are promoted by dihexylmagnesium as reported by Oshima.[7f]



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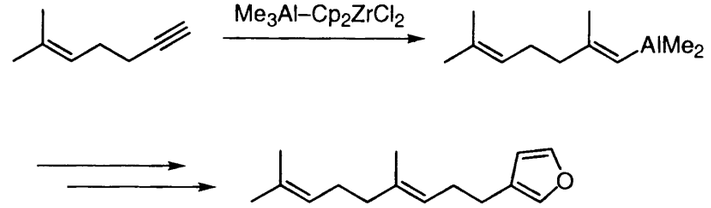
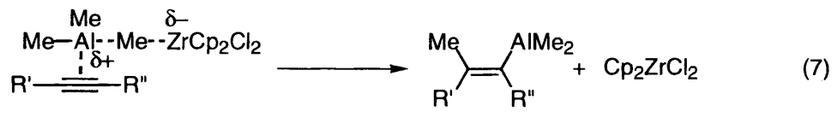


Scheme 1. Zirconium-catalyzed methylalumination of alkynes.

The zirconium-catalyzed carboalumination is considered to involve a Lewis acid–base interaction between aluminum–methyl–zirconium to assist addition of a carbon–aluminum bond to an alkyne (eq 7). Carbozincation catalyzed by Cp_2ZrI_2 seems to proceed through a similar pathway.



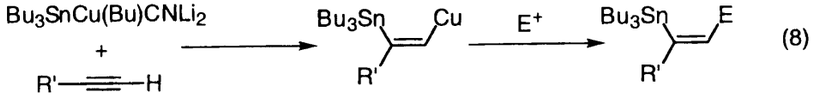
(7)

Regardless of the presence or absence of a catalyst, well polarized nucleophilic organometallics have been employed for carbometalation. In contrast, organostannanes, one of the least polarized organometallic compounds, have been considered to be unable to participate in the carbometalation of alkynes, except for particular combination of substrate and organometallic reagent (*vide infra*).

Alkenylstannanes in Organic Synthesis

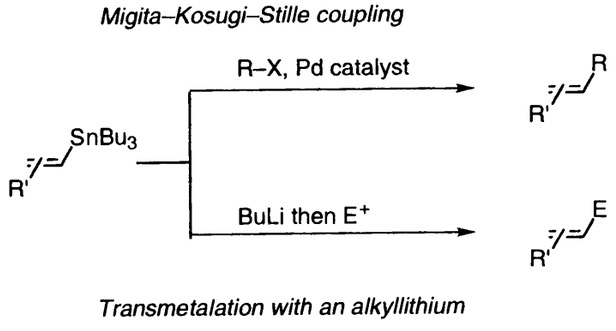
Organostannanes, one of the most stable organometallic reagents, have following characteristic features that distinguish them from other organometallic compounds. (1) They are insensitive to air and moisture and thus can be stored for a long period. (2) They are modestly basic and nucleophilic to be compatible with almost all functional groups both on organostannanes and electrophiles. (3) Organostannanes are readily prepared. Accordingly, they are frequently used especially in laboratory synthesis.[18]

General synthetic methods for alkenylstannanes involve either stannylation of an alkenylmetal with a tin halide[19] or hydrostannylation of an alkyne.[20] Alternatively, stannylmetalation, especially stannylcupration,[21] of alkynes and subsequent reaction with electrophiles also provide multi-substituted vinylstannanes (eq 8).



(8)

Alkenylstannanes thus obtained are readily converted into a wide variety of ethenes via various synthetic transformations. Among all, extensively employed are the Migita–Kosugi–Stille coupling reaction[22] and transmetalation with an alkyllithium followed by reaction with an electrophile (Scheme 2).[23] The Migita–Kosugi–Stille coupling is one of the most commonly used cross-coupling reactions. A carbon–tin bond of alkenylstannanes can be converted into a carbon–carbon bond with retention of configuration under mild conditions in the presence of a palladium catalyst. Coupling partner, R–X, is usually an aryl, alkenyl, alkynyl, allyl, heteroaryl or acyl halide (or triflate). The tin–lithium exchange also occurs readily and is far superior to other methods in preparation of alkenyllithium compounds. For example, the lithium reagents generated by halogen–lithium exchange is often contaminated by an inorganic or organic halide.



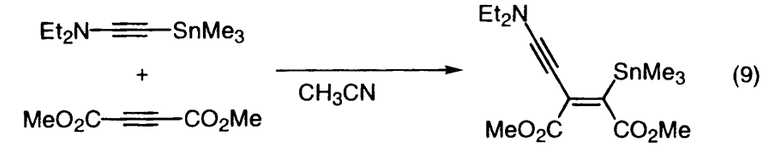
Scheme 2. Transformation of alkenylstannanes.

Carbostannylation of Alkynes

In sharp contrast to the above-mentioned synthesis of alkenylstannanes, the carbostannylation of alkynes has advantages in high synthetic utility, because both carbon–carbon and carbon–tin bonds are simultaneously introduced into the triple bond generally in a stereospecific manner, giving rise to more functionalized alkenylstannanes in a single step. Moreover, a variety of novel alkenylstannanes hardly accessible by conventional methods are easily prepared, starting with various alkynes and organostannanes.

In view of the stereo- and regio-defined synthesis of multi-substituted ethenes, carbostannylation of alkynes has advantages over the reaction with Zn, Cu or Al reagents, because the resulting alkenylstannanes are easily freed from catalysts and thus can be used for various subsequent transformations. In addition, high chemoselectivity of organostannanes allows many functional groups compatible to synthetic elaborations with a wide variety of substrates.

In 1979, Himbert disclosed the first carbostannylation of dimethyl acetylenedicarboxylate, using (stannylethynyl)amines. However, the reaction was restricted solely to this combination and thus not general (eq 9).[24] Alkenylation of ketones or phenols using terminal alkynes and $SnCl_4$–Bu_3N was demonstrated by Yamaguchi and was considered to proceed through the carbostannylation of stannylacetylenes (eq 10).[25] However, the resulting C–$SnCl_3$ bond was not demonstrated to be convertible to a C–C bond.



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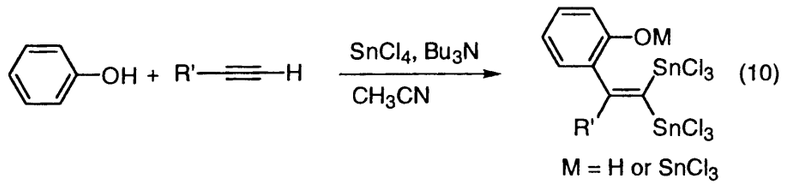
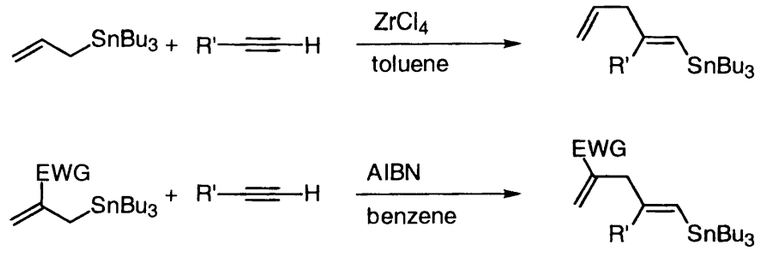


(10)

With the aid of suitable activators, allylstannanes participate in the carbostannylation of alkynes. For example, Yamamoto reported that allylstannanes could add to terminal alkynes with *anti*-selectivity using $ZrCl_4$ as a catalyst.[26] Hosomi showed that a radical initiator AIBN also promoted *anti*-selective allylstannylation of alkynes (Scheme 3).[27] Although these allylstannylation reactions may have synthetic utility higher than the foregoing ones, reagents other than allylic stannanes are not applicable to the reaction.



Scheme 3. Allylstannylation of alkynes.

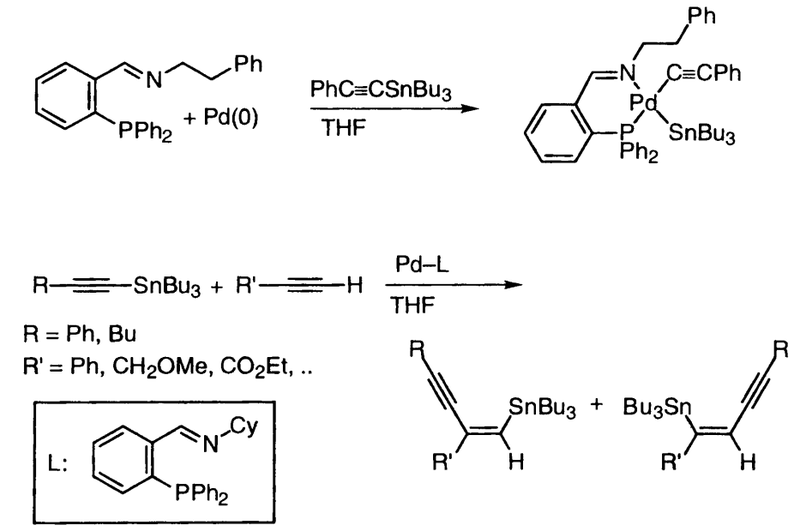
In spite of its high synthetic potential, the carbostannylation of alkynes has been lacking generality due mainly to the necessity of appropriate activation of a relatively stable carbon–tin bond.[28]

Accordingly, at the outset of his study, the author focused on exploration of methods for activation of a carbon–tin bond. After many experimental efforts, he observed that group 10 transition metal complexes activated diverse carbon–tin bonds to promote a variety of novel carbostannylation of alkynes.

Chapter 2 describes the synthesis of conjugate (stannyl)enynes from alkynylstannanes and alkynes catalyzed by palladium–iminophosphine complexes. In view that conjugate enynes are widely present in natural products, e.g., the sex pheromones of the family of Lepidoptera insects,[29] the disclosed reaction will definitely show wide applicability.

In 1997, a palladium complex coordinated by novel iminophosphine ligand *N*-(2-diphenylphosphinobenzylidene)-2-phenylethylamine[30a] was found to be a highly active catalyst for the cross-coupling reaction of organostannanes. In particular, reaction of

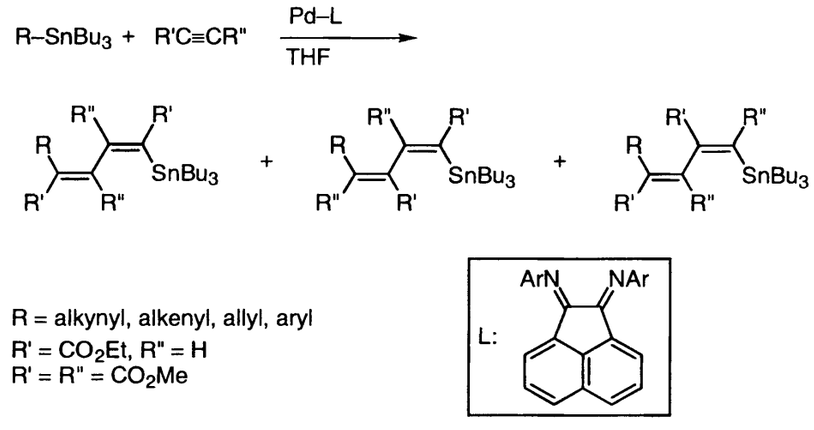
tributyl(phenylethynyl)tin with aryl iodides was shown to be initiated by oxidative addition of tributyl(phenylethynyl)tin to the palladium(0)–iminophosphine complex (Scheme 4).[30b] The author envisaged that if alkynes were present, an oxidative adduct would react to afford finally alkynylstannylation products. Indeed, alkynyl and tin moieties of alkynylstannanes were demonstrated to be introduced into alkynes with exclusive *syn*-selectivity to give conjugated (stannyl)enynes in the presence of the catalyst (Scheme 4). In contrast to the zirconium-catalyzed carboalumination of alkynes, the alkynylstannylation is the first demonstration of carbometalation that proceeds through oxidative addition of a carbon–metal bond to a transition metal. The alkynyl group is preferentially connected to the internal carbon of terminal alkynes, whereas opposite regioselectivities are observed with alkynoates and alkynyl ketones. The author discusses in detail ligand effect on the regioselectivity and the reaction rate as well as mechanism of the alkynylstannylation.



Scheme 4. Pd–iminophosphine-catalyzed alkynylstannylation of alkynes.

In Chapter 3, the author describes that a palladium complex coordinated by bis(arylimino)acenaphthene effectively promotes the dimerization–carbostannylation of

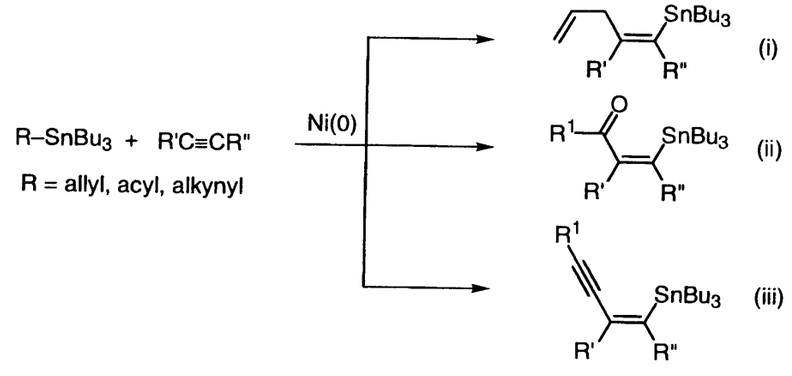
ethyl propiolate or dimethyl acetylenedicarboxylate. The ester functionality is essential, and the two alkyne molecules insert into a carbon–tin bond of alkynyl, alkenyl, allyl or arylstannanes in a *syn* manner, affording highly conjugated alkenylstannanes (Scheme 5). The reaction of ethyl propiolate proceeds with perfect regioselectivities particularly when a palladium–bis[(2,6-diisopropylphenyl)imino]acenaphthene complex is employed, giving rise straightforwardly to variously substituted *trans,trans*-muconic acid derivatives. The obtained alkenylstannanes are converted into more conjugated polyenes via cross- or homocoupling reaction. In addition to synthetic utility, mechanism of the dimerization–carbostannylation is worthy of note: the reaction is initiated by formation of a palladacyclopentadiene from the palladium(0)–diimine complex and 2 molecules of alkynes, taking a pathway distinct from the Pd–iminophosphine-catalyzed alkynylstannylation discussed in Chapter 2. The resulting palladacyclopentadiene then reacts with organostannanes to give products. The mechanism, involving reaction of a metallacycle with an organometallic reagent, has no precedents.



Scheme 5. Dimerization–carbostannylation of alkynes.

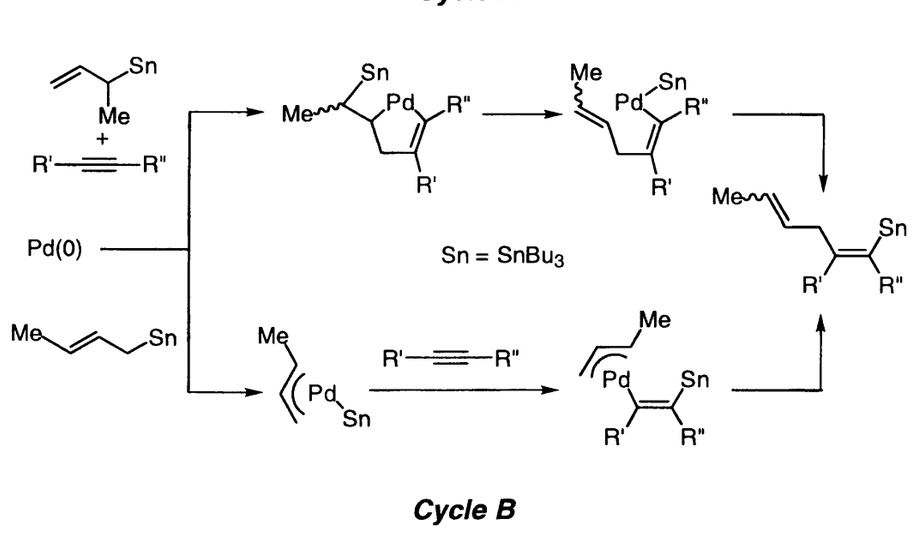
In addition to palladium, nickel(0) also catalyzes the carbostannylation of alkynes and is discussed in Chapter 4. Applicable to this reaction are allyl-, acyl- and alkynylstannanes. For example, allylstannanes react with a wide variety of alkynes with

syn-stereochemistry in the presence of a $Ni(cod)_2$ catalyst, providing 1,4-dienylstannanes (Scheme 6–(i)). The allylstannylation is extremely useful for the construction of a 1,4-pentadiene system, widely found in naturally occurring terpenoids. Worthy to note is that the stereochemistry of the allylstannylation contrasts sharply to that of the reaction with $ZrCl_4$ or AIBN. $Ni(cod)_2$ was found to promote also the acylstannylation to afford α,β-unsaturated carbonyl compounds, versatile synthetic intermediates frequently used for Michael addition (Scheme 6–(ii)). This is the first demonstration that an acylmetal can participate in the carbometalation reaction. Oxidative addition of a carbon–tin bond of an acylstannane to $Ni(cod)_2$ is considered to be an initiation step of the reaction. The nickel catalyst mediates alkynylstannylation of 1-alkynes effectively as well (Scheme 6–(iii)). This particular reaction complements the Pd–iminophosphine-catalyzed alkynylstannylation described in Chapter 2. Usefulness of the nickel-catalyzed carbostannylation is demonstrated by regio- and stereoselective syntheses of some tetrasubstituted ethenes, otherwise hardly accessible. For example, the carbostannylation of internal alkynes affords trisubstituted alkenylstannanes, which, upon the palladium-catalyzed cross-coupling with an electrophile, gives tetrasubstituted ethenes of desired stereochemistry.



Scheme 6. Ni(0)-catalyzed carbostannylation of alkynes.

Internal alkynes having such an electron-withdrawing substituent as an ester, trifluoromethyl, sulfonyl or cyano group easily undergo *syn*-selective allylstannylation in the presence of $Pd_2(dba)_3$ and is described in Chapter 5. The palladium catalyst is particularly specific to the reaction of the electron-deficient alkynes. The nickel catalyst discussed in Chapter 4, though similarly effective, induces self-trimerization and/or -oligomerization of the alkynes more than allylstannylation. Depending on structure of allylstannanes, two reaction mechanisms are suggested. The one involves a palladacyclopentene specially in the reaction of allylstannanes lacking a substituent at γ-carbon. Subsequent Sn–Pd elimination and reductive elimination give allylstannylation products (Cycle A in Scheme 7). The other mechanism is considered for the reaction of γ-substituted allylstannanes proceeding through oxidative addition of a carbon–tin bond of allylstannanes to palladium(0) (Cycle B in Scheme 7).



Scheme 7. Catalytic cycles of palladium-catalyzed allylstannylation.

In summary, the present Thesis describes chemistry of novel carbostannylation of alkynes based on the activation of a carbon–tin bond with various transition metal

complexes. A number of alkynes and organostannanes are made applicable to the carbostannylation by use of suitable catalysts. The novel reaction allows regio- and stereoselective synthesis of diverse alkenylstannanes of great synthetic versatilities.

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Chapter 2

Palladium–Iminophosphine-Catalyzed Alkynylstannylation of Alkynes

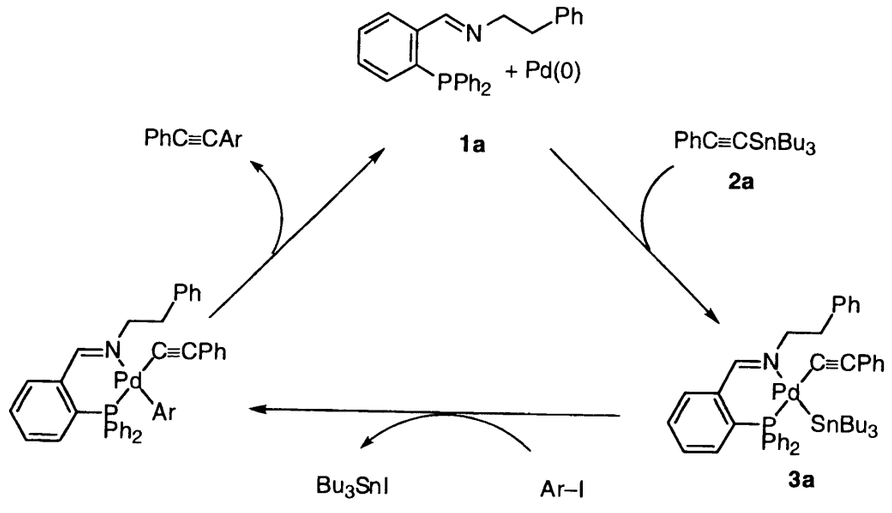
A palladium complex coordinated by an iminophosphine ligand was found to catalyze the addition of alkynylstannanes to a carbon–carbon triple bond of various alkynes in moderate to good yields with exclusive *syn* selectivity. An alkynyl group in the stannanes was attached mainly to an internal carbon of terminal alkynes, except for 1-alkyn-3-ones and alkynoates, where the alkynyl group was connected to a terminal carbon. Steric bulk of the ligand markedly influenced on regioselectivity and reaction rate: an iminophosphine with a bulkier imino moiety accelerated the alkynylstannylation and enhanced the regioselectivity. Based on these observations, a plausible mechanism of the reaction is discussed.

Introduction

Carbometalation of alkynes is one of the most useful reactions for stereoselective olefin synthesis, since the resulting alkenylmetals can be transformed further to variously substituted ethenes.[1] However, most of the organometallic compounds that can add to a C≡C bond have invariably a reactive polar C–M bond, and thus the resulting carbometalation products are still reactive. Very often trapping with suitable electrophiles in situ is necessary for synthetic purpose.

In contrast, carbostannylation of alkynes is much more beneficial in view of the stereo- and regio-defined synthesis of multi-substituted ethenes, because the resulting alkenylstannanes are easily purified prior to subsequent transformation such as the Migita–Kosugi–Stille coupling reaction.[2] However, limited number of reports have been available on the carbostannylation of alkynes probably due to low polarity of a C–Sn bond.[3,4,5,6,7]

Tributyl(phenylethynyl)tin (**2a**) has been shown to oxidatively add to a palladium(0) complex coordinated by *N*-(2-diphenylphosphinobenzylidene)-2-phenylethylamine (**1a**) and give nucleophilic palladium(II) complex **3a**, which is involved in the catalytic cycle of palladium-catalyzed cross-coupling of **2a** with aryl iodides (Scheme 1).[8] The author envisaged that palladium complex **3a** would react with alkynes to give alkynylstannylation products. This turned out to be the case.



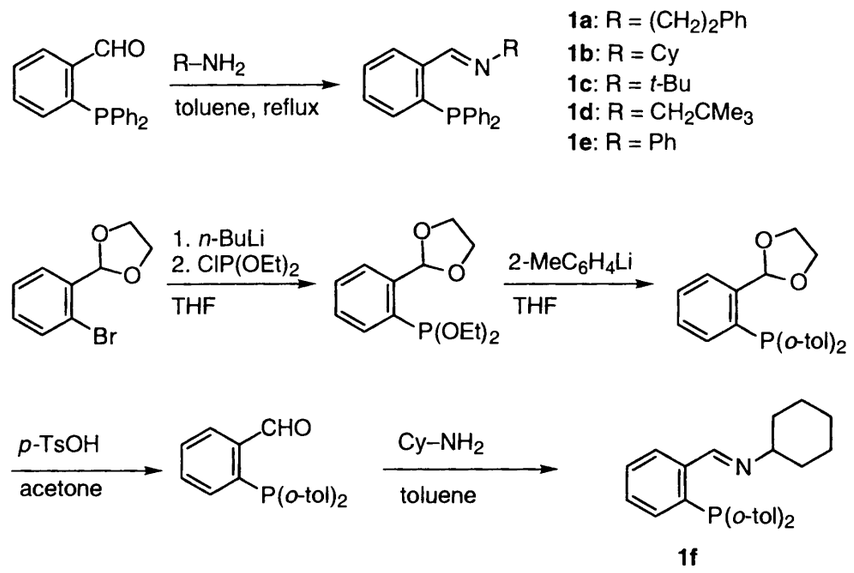
Scheme 1. A catalytic cycle of the cross-coupling of aryl iodides with **2a** catalyzed by Pd(0)–**1a**.

In this Chapter, the author shows that a palladium–iminophosphine complex catalyzes the addition of alkynylstannanes to alkynes, leading to the regio- and stereoselective formation of conjugated (stannyl)enynes.[9] In particular, a bulky ligand is found to improve both yields and regioselectivities. The characteristic features of the alkynylstannylation compared with other carbometalation reactions are as follows: (1) Alkynyl moieties are introduced into alkynes in a manner that can hardly be achieved with an organometallic reagent having a reactive polar C–M bond. (2) To the best of his knowledge, the present reaction is the first demonstration of carbometalation that proceeds through oxidative addition of a C–M bond to a transition metal complex.

Results and Discussion

Ligand preparation

Iminophosphines **1a–1e** were prepared by condensation of 2-diphenylphosphinobenzaldehyde[10] with an appropriate amine in refluxing toluene (Scheme 2). Similarly, **1f** was prepared from 2-[bis(*o*-tolyl)phosphino]benzaldehyde, which was synthesized from 2-(2-bromophenyl)-1,3-dioxolane and diethyl chlorophosphonite as shown in Scheme 2.[11]

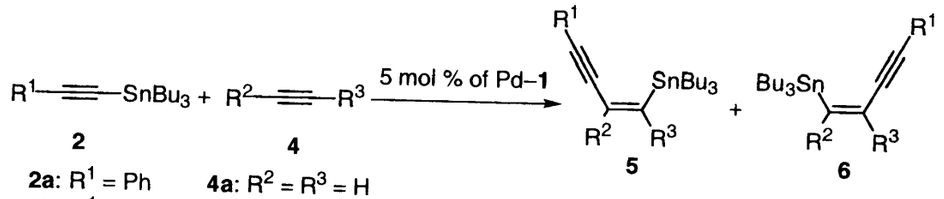


Scheme 2. Synthesis of iminophosphine **1**.

Alkynylstannylation of alkynes catalyzed by Pd–1a

The author first examined the reaction of alkynylstannanes **2** with alkynes **4** in the presence of complex Pd–**1a** and found that insertion of the carbon–carbon triple bond of **4** between the C–Sn bond of **2** took place to afford the corresponding conjugated (*Z*)-(stannyl)enynes in good to high yields (Scheme 3, Table 1). Whereas **2a** reacted with acetylene (1 atm) in THF at 50 °C and gave tributyl[(*Z*)-2-(phenylethynyl)ethenyl]tin (**5a**)[12] in 81% yield[13] as a single isomer through exclusive *syn*-addition (entry 1), the use of triphenylphosphine (two equivalents to Pd) or 1,3-bis(diphenylphosphino)propane in lieu of **1a** reduced the yield even after a prolonged reaction time (48% yield, 43 h; 28% yield, 22 h). The alkynylstannylation was applied to propargyl ether **4b**, which provided **5b** and **6b** in 67% yield with a ratio of 67 : 33 (entry 2). In addition to **4b**, propargylic amide **4c**, imide **4d**, and arylacetylenes **4e** and **4f** reacted with **2a** to give corresponding alkynylstannylation products (entries 3–6). The reaction of **2a** with ethoxyacetylene (**4g**) was completed in 5 h, giving exclusively **5g** (entry 7). Ethyl 2-butynoate (**4h**) afforded **6h** as the sole product, though higher temperature and longer reaction time were required (entry 8). The reaction of **2a** with ethyl propiolate (**4i**) gave

alkynylstannylation products consisting of regioisomers **5i** and **6i** in a 20 : 80 ratio (entry 9). A ketonic acetylene, 1-butyn-3-one (**4j**), reacted with **2a** smoothly with regioselectivity similar to **4i** (entry 10). Tributyl(1-hexyn-1-yl)tin (**2b**) also reacted with alkyne **4a**, **4e** or **4i**, giving the corresponding alkenylstannanes. The resulting regioselectivities were similar to those with **2a** (entries 11–13).[14]



Scheme 3. Pd–iminophosphine-catalyzed alkynylstannylation of alkynes.

Table 1. Palladium–**1a**-catalyzed alkynylstannylation of alkynes[a]

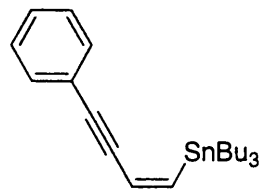
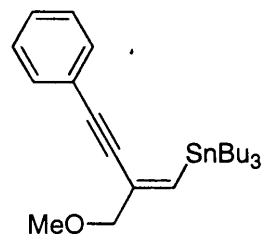
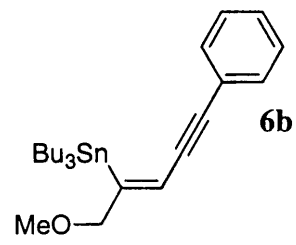
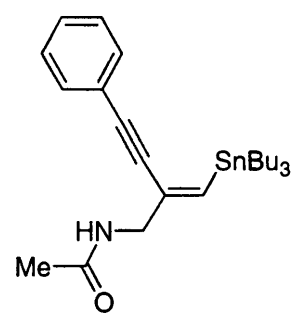
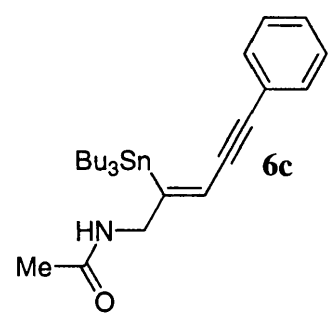
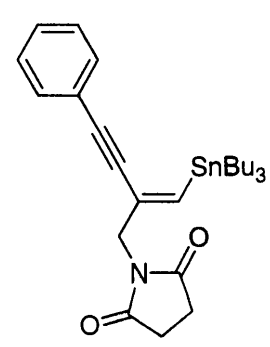
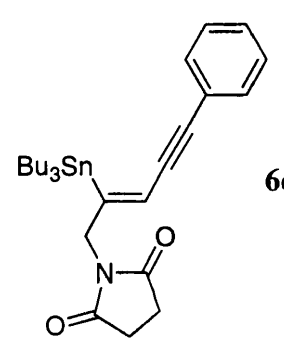
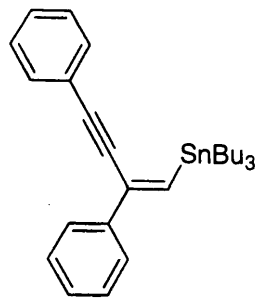
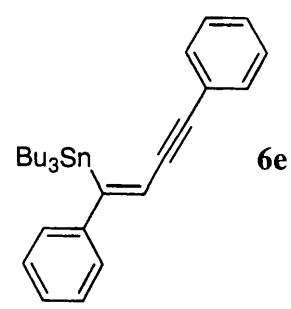
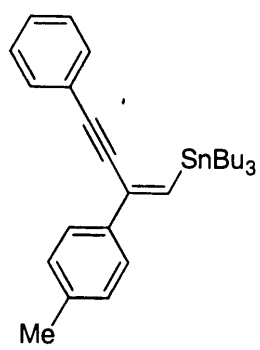
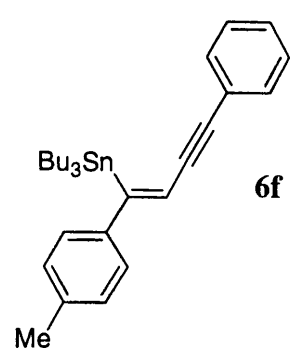
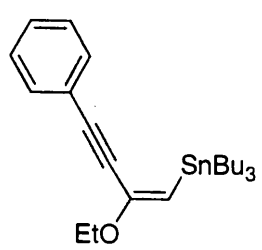
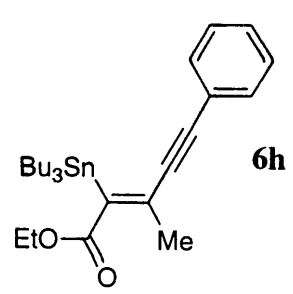
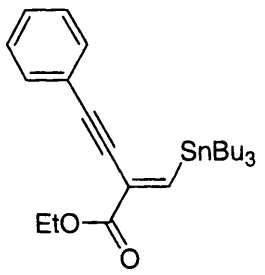
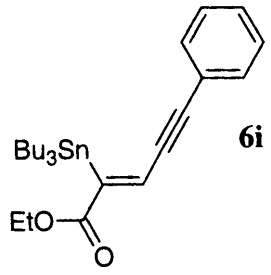
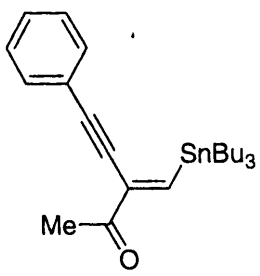
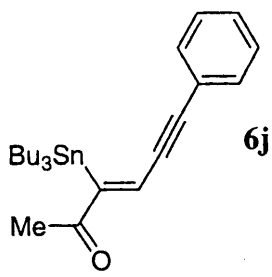
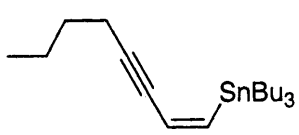
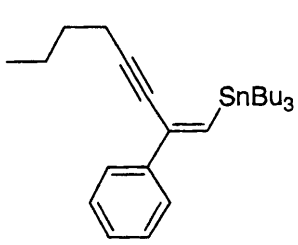
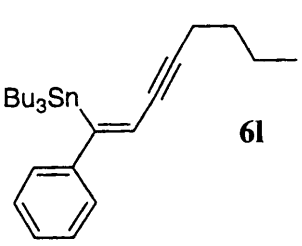
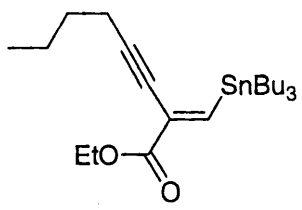
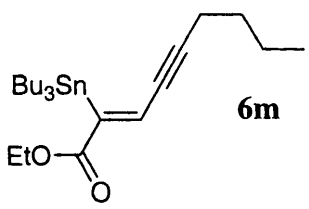
entry	alkynyl-stannane	alkyne	time (h)	yield (%)[b]	product(s)		ratio (**5** : **6**)[c]
1[d]	**2a**	**4a**	2	81	 **5a**		–
2	**2a**	**4b**	96	67	 **5b**	 **6b**	67 : 33
3	**2a**	**4c**	36	78	 **5c**	 **6c**	76 : 24
4	**2a**	**4d**	5	70	 **5d**	 **6d**	83 : 17
5	**2a**	**4e**	21	81	 **5e**	 **6e**	92 : 8
6	**2a**	**4f**	44	82	 **5f**	 **6f**	91 : 9
7[e]	**2a**	**4g**	5	52	 **5g**		>99 : 1
8[f]	**2a**	**4h**	90	57		 **6h**	1 : >99

Table 1 (continued).

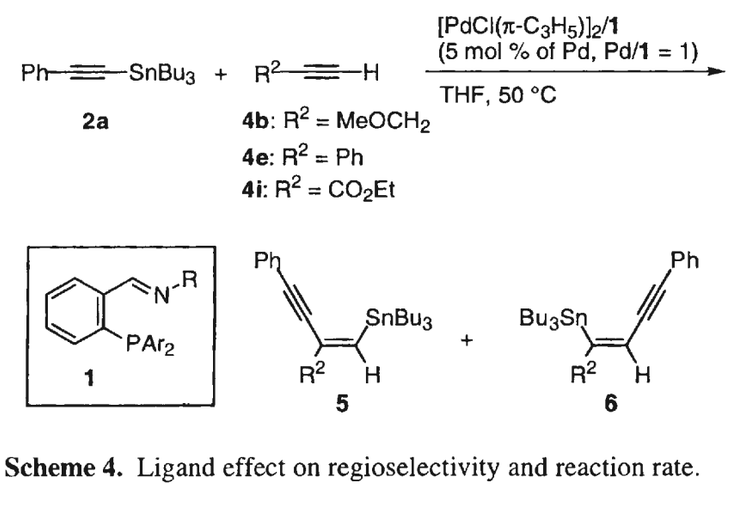
9	**2a**	**4i**	3	78		**5i**		**6i**	20 : 80
10	**2a**	**4j**	4	76		**5j**		**6j**	15 : 85
11[d]	**2b**	**4a**	4	66		**5k**			–
12	**2b**	**4e**	29	80		**5l**		**6l**	92 : 8
13	**2b**	**4i**	16	72		**5m**		**6m**	12 : 88

[a] The reaction was carried out in THF (3 mL) at 50 °C using an alkynylstannane (0.34 mmol) and an alkyne (1.0 mmol) in the presence of $[PdCl(\pi\text{-}C_3H_5)]_2$ (8.2 μmol) and **1a** (0.016 mmol). [b] Combined isolated yields of **5** and **6** based on **2** are given. [c] Determined by ^1H or ^{119}Sn NMR. [d] The reaction was carried out under an acetylene atmosphere (1 atm). [e] Ethoxyacetylene (0.34 mmol) was used. [f] Solvent = dioxane, Temperature = 90 °C.

Catalyst Improvements

1. Ligand effect on regioselectivity and reaction rate

Although the Pd–**1a** complex was applicable to the alkynylstannylation of various alkynes as described above, the regioselectivities and the reaction rates were not sufficient especially in the case of **4b**. Therefore, the author investigated how a substituent on ligands would affect the regioselectivity and the reaction rate of the alkynylstannylation using **2a** and **4b** as model substrates (Scheme 4, Table 2).

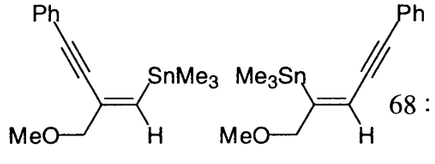


Scheme 4. Ligand effect on regioselectivity and reaction rate.

Conversion of **2a** and ratio of alkynylstannylation products **5** and **6** were monitored by ^{119}Sn NMR. When **2a** was allowed to react with **4b** in the presence of Pd–**1a** in THF at 50 °C for 3 h, **5b** and **6b** were produced in a ratio of 69 : 31 with 20% conversion (entry 1). Use of iminophosphine ligand **1b** derived from cyclohexylamine accelerated the reaction considerably and improved the regioselectivity (entry 2). The regioselectivity rose up to 97 : 3 with iminophosphine **1c** bearing such a bulky substituent as a *t*-Bu group on the imino moiety, although the reaction became slow (entry 3). Pd–**1d** gave the alkynylstannylation products with regioselectivity similar to Pd–**1a**, whereas use of **1e** as a ligand retarded the reaction (entries 4 and 5). In contrast, substituents on phosphorous did not explicitly affect the regioselectivity and the reaction rate. Thus, a Pd complex coordinated by iminophosphine **1f**, where the –PPh_2 moiety in

1b is replaced by –P(*o*-tolyl)$_2$, gave results similar to **1b** (entry 6). The reaction of trimethyl(phenylethynyl)tin gave alkynylstannylation products with regioselectivity almost same as **2a**, indicating that size of a stannyl group has little influence on regioselectivity (entry 7). Steric bulk of the imino moiety exerted similar influence on regioselectivity and reaction rate in the alkynylstannylation of phenylacetylene (**4e**). Acceleration and high regioselectivity of the reaction were observed with **1b** as a ligand, and Pd–**1c** complex gave **5e** as the sole product but in only 7% conversion (entries 8–10). The reaction of ethyl propiolate (**4i**) with **2a** gave **6i** predominantly. In this case, Pd–**1e** complex was found to exhibit regioselectivity higher than Pd–**1a** or Pd–**1b** complex (entries 11–13).

Table 2. Alkynylstannylation of alkynes catalyzed by palladium–iminophosphine **1**[a]

entry	alkyne	ligand	time (h)	conversion (%)[b]	product(s)		ratio (**5** : **6**)[b]
1	**4b**	**1a**	3	20	**5b**	**6b**	69 : 31
2	**4b**	**1b**	3	90	**5b**	**6b**	77 : 23
3	**4b**	**1c**	3	10[c]	**5b**	**6b**	97 : 3
4	**4b**	**1d**	3	58	**5b**	**6b**	68 : 32
5	**4b**	**1e**	3	12	**5b**	**6b**	83 : 17
6	**4b**	**1f**	3	96	**5b**	**6b**	76 : 24
7[d]	**4b**	**1a**	3	7			68 : 32
8	**4e**	**1a**	3	74	**5e**	**6e**	90 : 10
9	**4e**	**1b**	3	100	**5e**	**6e**	97 : 3
10	**4e**	**1c**	3	7[c]	**5e**	**6e**	>99 : 1
11	**4i**	**1a**	1	100	**5i**	**6i**	23 : 77
12	**4i**	**1b**	1	100	**5i**	**6i**	16 : 84
13	**4i**	**1e**	1	100	**5i**	**6i**	9 : 91

[a] The reaction was carried out in THF (3 mL) at 50 °C using **2a** (0.34 mmol) and an alkyne (1.0 mmol) in the presence of $[PdCl(\pi\text{-}C_3H_5)]_2$ (8.2 μmol) and iminophosphine **1** (0.016 mmol). [b] Determined by ^{119}Sn NMR. [c] Conversion after 24 h was 13% (entry 3) or 8% (entry 10). [d] Trimethyl(phenylethynyl)tin was used instead of **2a**.

2. Scope and limitations of alkynylstannylation

The author next examined the palladium-catalyzed alkynylstannylation of various alkynes using the optimized ligands (**1b** for alkynes **4a–h** and **4j**, **1e** for alkyne **4i**). The results are summarized in Table 3.

Noteworthy is high reaction rate: alkynylstannylation of **4b** with Pd–**1b** was completed in 5 h with a 79 : 21 ratio of **5b** : **6b**, and the products were isolated in 81% yield (entry 1, see also entry 2 of Table 1). Alkynes **4a** and **4c–g** were also reacted to give the corresponding alkynylstannylation products in high yields within 6 h with regioselectivities over 88% (entries 2–7). In contrast to the case of terminal alkynes, the Pd–**1b** catalyst system was less effective to internal alkyne **4h**; alkynylstannylation product **6h** was produced only in 29% yield (entry 8). The reaction of alkyne **4i** using Pd–**1e** was completed in 1 h to afford 7 : 93 mixture of **5i** and **6i** in 71% yield (entry 9). Iminophosphine **1b** was effective also for regioselective alkynylstannylation of **4j** (entry 10). Unfortunately, the Pd–**1b**-catalyzed alkynylstannylation of 1-hexyne, a typical aliphatic acetylene, did not give any products even under drastic conditions (90 °C, 26 h). Tributyl(1-hexyn-1-yl)tin (**2b**) also added to alkyne **4a**, **4e** or **4i** in the presence of the optimized catalyst with regioselectivity higher than Pd–**1a** (entries 11–13).

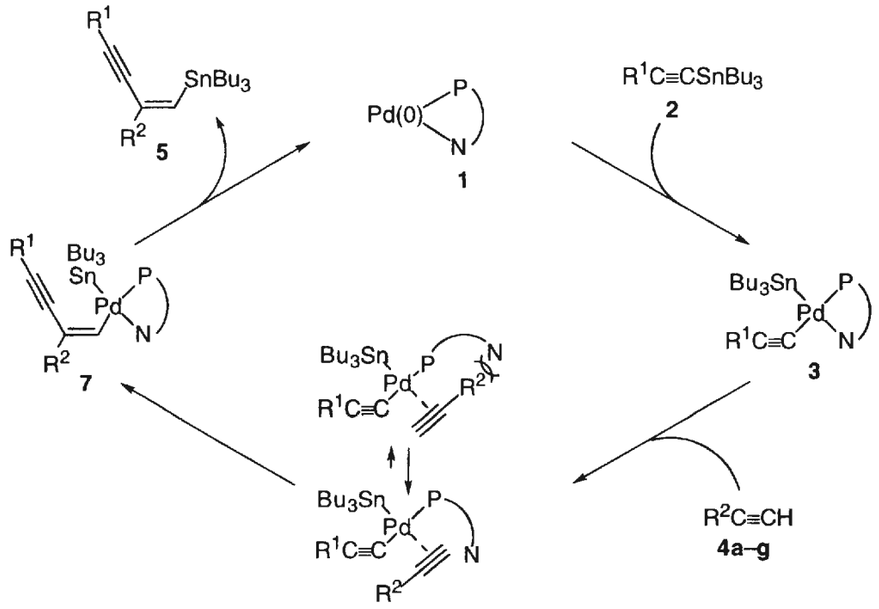
Table 3. Alkynylstannylation of alkynes catalyzed by Pd–**1b** or Pd–**1e**[a]

entry	alkynylstannane	alkyne	ligand	time (h)	yield (%)[b]	product(s)	ratio (**5** : **6**)[c]
1	**2a**	**4b**	**1b**	5	81	**5b, 6b**	79 : 21
2[d]	**2a**	**4a**	**1b**	1	70	**5a**	—
3	**2a**	**4c**	**1b**	3	71	**5c, 6c**	88 : 12
4	**2a**	**4d**	**1b**	3	77	**5d, 6d**	90 : 10
5	**2a**	**4e**	**1b**	5	73	**5e**	>99 : 1
6	**2a**	**4f**	**1b**	6	70	**5f, 6f**	97 : 3
7[e]	**2a**	**4g**	**1b**	5	58	**5g**	>99 : 1
8[f]	**2a**	**4h**	**1b**	93	29	**6h**	1 : >99
9	**2a**	**4i**	**1e**	1	71	**5i, 6i**	7 : 93
10	**2a**	**4j**	**1b**	1	83	**5j, 6j**	13 : 87
11[d]	**2b**	**4a**	**1b**	2	88	**5k**	—
12	**2b**	**4e**	**1b**	12	86	**5l**	>99 : 1
13	**2b**	**4i**	**1e**	24	62	**5m, 6m**	7 : 93

[a] The reaction was carried out in THF (3 mL) at 50 °C using an alkynylstannane (0.34 mmol) and an alkyne (1.0 mmol) in the presence of $[PdCl(\pi\text{-}C_3H_5)]_2$ (8.2 μmol) and iminophosphine (0.016 mmol). [b] Isolated yields based on alkynylstannane are given. [c] Determined by ^1H or ^{119}Sn NMR. [d] The reaction was carried out under an acetylene atmosphere (1 atm). [e] Ethoxyacetylene (0.34 mmol) was used. [f] Solvent = dioxane, Temperature = 90 °C.

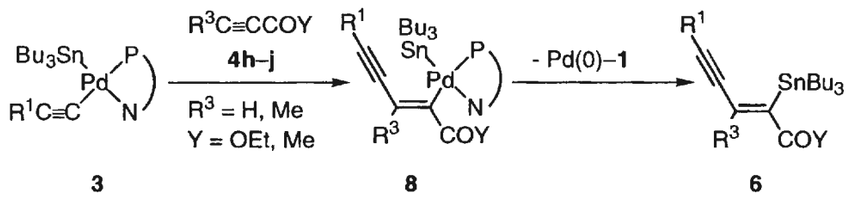
Catalytic cycle

Observation of similar ligand effect in the alkynylstannylation of alkynes **4a–g** should imply that the reaction proceeds through a similar catalytic cycle. A plausible catalytic cycle is depicted in Scheme 5. Oxidative addition of an alkynylstannane to a Pd(0) complex gives Pd(II) complex **3**, where the alkynyl group is located *cis* to the imino moiety as reported before.[8] Dissociation of the imino group from palladium makes a vacant coordination site for an alkyne, and the ligand dissociation would take place prior to insertion of the alkyne.[15] Successive insertion of an alkyne to the C–Pd bond (carbopalladation)[16] of **3** followed by reductive elimination is likely to afford the alkynylstannylation products and regenerate the Pd(0) complex. On the basis of the dissociative mechanism, the rate acceleration observed with **1b** as a ligand should be reasonable, since such a bulky substituent as a cyclohexyl group in **1b** would facilitate the dissociation from the palladium center. The dissociation would occur more easily with **1c**; excessive bulkiness of a *t*-Bu group in **1c** should retard the reaction, inhibiting the coordination of an alkyne. Compared with an alternative stannylpalladation pathway, the carbopalladation pathway seems to rationally explain the results that the regioselectivity and the reaction rates are definitely affected by the bulkiness of the imino moiety but in a lesser extent by the size of the phosphino and stannyl moieties. Predominant production of **5** over **6** should be ascribed to the direction of alkyne coordination leading to the formation of alkenylpalladium **7**, where steric repulsion between R^2 and a ligand is disfavored. Accordingly, the increase in the steric repulsion with bulkier ligands should result in higher regioselectivities.



Scheme 5. Plausible catalytic cycle of alkynylstannylation.

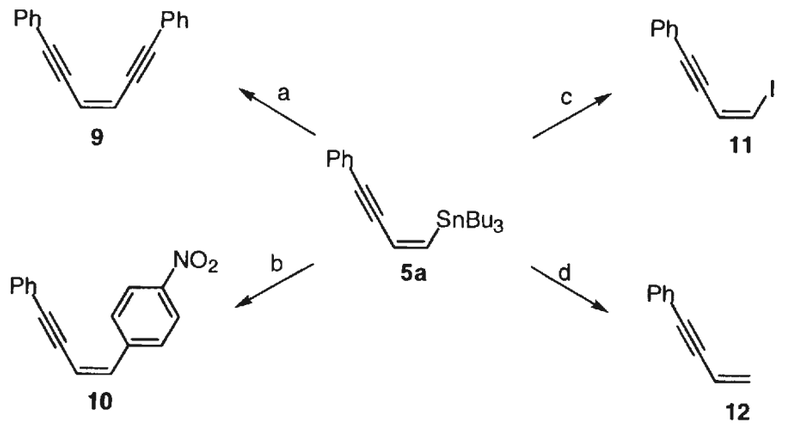
Electron-deficient alkynes **4h**, **4i** and **4j** are likely to suffer the Michael addition of an alkynyl group in **3**, giving predominantly **8** and finally **6** (Scheme 6). At present, the reason is not clear why the higher regioselectivity was observed with **1e** than any other iminophosphine ligand.



Scheme 6. Plausible catalytic cycle of alkynylstannylation of **4h–j**.

Transformation of alkynylstannylation product

Utility of alkynylstannylation products is demonstrated by transformation of **5a** to various compounds (Scheme 7). Cross-coupling[17] of **5a** with 1-bromo-2-phenylethyne or 4-nitroiodobenzene gave the corresponding coupled product **9** or **10**, respectively.[18] Iodolysis or hydrolysis of **5a** afforded alkenyl iodide **11** or enyne **12** , respectively.



(a) PhC≡CBr (0.92 equiv), $Pd_2(dba)_3$, $(2\text{-furyl})_3P$ (5 mol % of Pd, Pd/$(2\text{-furyl})_3P$ = 1/4), NMP, 50 °C, 18 h, 58% (based on PhC≡CBr). (b) $4\text{-}O_2NC_6H_4I$ (0.92 equiv), $Pd_2(dba)_3$, $(2\text{-furyl})_3P$ (5 mol % of Pd, Pd/$(2\text{-furyl})_3P$ = 1/4), toluene, 90 °C, 13 h, 85% (based on $4\text{-}O_2NC_6H_4I$). (c) I_2 (1.4 equiv), THF, 0 °C, 40 min, 92%. (d) conc. HCl, THF, rt, 1 h, 81%.

Scheme 7. Transformation of an alkynylstannylation product.

Conclusion

The author has disclosed that the alkynylstannylation of alkynes takes place with palladium–iminophosphine catalysts to give conjugated (stannyl)enynes in a *syn* selective manner, and that the resulting (*Z*)-alkenylstannanes can be transformed to variously substituted ethenes. Cyclohexylamine-derived iminophosphine **1b** was found to be a highly active and regioselective ligand for the palladium-catalyzed alkynylstannylation of various alkynes, whereas aniline-derived iminophosphine **1e** was suitable for regioselective alkynylstannylation of alkyne **4i**. The regioselectivities and the reaction rates depend on the steric bulk of an imino moiety of iminophosphines, suggesting the insertion of an alkyne via a dissociative carbopalladation pathway.

Experimental section

The description in General Remarks, Apparatus and Chemicals applies to all Chapters of the present Thesis.

General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with the standard Schlenk technique under a purified argon atmosphere (deoxygenated by passing through BASF-Catalyst R3-11 column at 80 °C). TLC analyses were carried out by means of Merck Kieselgel 60 F_{254} and silica-gel column chromatography was performed using Wakogel C-200.

Apparatus. NMR spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz; ^{31}P, 109 MHz; ^{119}Sn, 101 MHz) spectrometer or a Varian Mercury 200 (^{1}H, 200 MHz; ^{13}C, 50 MHz; ^{31}P, 81 MHz) spectrometer using tetramethylsilane (^{1}H and ^{13}C) as an internal standard or 85% phosphoric acid (^{31}P) and tetramethyltin (^{119}Sn) as an external standard. The preparative recycling GPC was performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and -2H columns (chloroform as an eluent). HRMS were obtained with a JEOL JMS-700 spectrometer or a Bruker Bio APEX 70e spectrometer. All melting points were measured with a Yanagimoto Micro Melting Point apparatus and uncorrected. Elemental analyses were performed at the Microanalytical Center, Kyoto University.

Chemicals. Unless otherwise noted, reagents were commercially available and were used without purification. Solvents were purified by distillation under argon after drying over a suitable drying reagent as follows: sodium/benzophenone ketyl for toluene, ether, THF, 1,4-dioxane, DME and octane; phosphorus pentoxide for chloroform and dichloromethane; calcium hydride for DMF and NMP.

The following compounds were prepared according to literature procedures: *N*-(2-Diphenylphosphinobenzylidene)-2-phenylethylamine (**1a**)[18], *N*-(2-diphenylphosphinobenzylidene)aniline (**1e**)[19], tributyl(phenylethynyl)tin (**2a**)[20], tributyl(1-hexyn-1-yl)tin (**2b**)[20], *N*-propargyl-acetamide (**4c**)[21], and *N*-propargylsuccinimide (**4d**).[22]

Preparation of iminophosphines 1b–1d. A mixture of 2-(diphenylphosphino)benzaldehyde[10] (0.20 g, 0.69 mmol) and an amine (0.76 mmol) in toluene (10 mL) was stirred under reflux. After the time specified below, evaporation of the solvent followed by GPC gave the corresponding iminophosphine.

***N*-(2-Diphenylphosphinobenzylidene)cyclohexylamine (1b)** A pale yellow powder, mp 117–119 °C, 52% yield (3 h). ^{1}H NMR ($CDCl_3$) δ 0.76–1.86 (m, 10 H), 2.86–3.16 (m, 1 H), 6.68–6.92 (m, 1 H), 7.05–7.46 (m, 12 H), 7.85–8.03 (m, 1 H), 8.88 (d, J = 5.4 Hz, 1 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ –13.1. HRMS Calcd for $C_{25}H_{26}NP$: M^+, 371.1802. Found: *m/z* 371.1806.

***N*-(2-Diphenylphosphinobenzylidene)-*tert*-butylamine (1c)** A pale yellow powder, mp 114–116 °C, 65% yield (13 h). ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 9 H), 6.72–6.89 (m, 1 H), 7.13–7.53 (m, 12 H), 7.83–8.03 (m, 1 H), 8.77 (d, J = 5.4 Hz, 1 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ –11.7. HRMS Calcd for $C_{23}H_{24}NP$: M^+, 345.1645. Found: *m/z* 345.1649.

***N*-(2-Diphenylphosphinobenzylidene)-2,2-dimethylpropylamine (1d)** A pale yellow powder, mp 57–62 °C, 59% yield (3 h). ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 9 H), 3.23 (s, 2 H), 6.75–6.95 (m, 1 H), 7.11–7.72 (m, 12 H), 7.90–8.13 (m, 1 H), 8.82 (d, J = 5.0 Hz, 1 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ –13.3. HRMS Calcd for $C_{24}H_{26}NP$: M^+, 359.1802. Found: *m/z* 359.1799.

***N*-[2-{Bis(*o*-tolyl)phosphino}benzylidene]cyclohexylamine (1f)** To a solution of 2-(2-bromophenyl)-1,3-dioxolane (0.34 g, 1.48 mmol) in THF (10 mL) was added dropwise butyllithium (1.5 M in hexanes, 1.10 mL, 1.65 mmol) at -78 °C. The reaction mixture was stirred for 1 h at -78 °C. To the mixture was added dropwise via a cannula a solution of diethyl chlorophosphonite (0.24 g, 1.53 mmol) in THF (5 mL) at -78 °C. The resulting mixture was allowed to warm slowly to room temperature and

stirred for 7 h. A solution of 2-methylphenyllithium (3.0 mmol) in THF (10 mL), prepared from 2-bromotoluene (0.51 g, 3.0 mmol) and butyllithium (1.5 M in hexanes, 2.2 mL, 3.3 mmol) in a similar manner as above, was added dropwise to the mixture via a cannula at -78 °C. The mixture was allowed to warm slowly to room temperature in 16 h before dilution with ethyl acetate (60 mL). The organic layer was separated, washed with a saturated $NaHCO_3$ aqueous solution, and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a crude product, which was then treated with *p*-toluenesulfonic acid monohydrate (22 mg, 0.116 mmol) in acetone at reflux temperature for 8 h with stirring. Evaporation of the solvent followed by silica-gel column chromatography using 20% ethyl acetate in hexane as an eluent gave 2-[bis(*o*-tolyl)phosphino]benzaldehyde (0.23 g, 47% yield based on 2-(2-bromophenyl)-1,3-dioxolane) as yellow plates, mp 106–112 °C. ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 6 H), 6.58–7.64 (m, 11 H), 7.89–8.10 (m, 1 H), 10.60 (d, *J* = 6.2 Hz, 1 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ –28.8. HRMS (ESI) Calcd for $C_{21}H_{19}OPNa$: M^++Na, 341.1066. Found: *m/z* 341.1066.

A mixture of 2-[bis(*o*-tolyl)phosphino]benzaldehyde (80 mg, 0.25 mmol) and cyclohexylamine (27 mg, 0.28 mmol) in toluene (5 mL) was stirred at reflux temperature for 2.5 h. Concentration in vacuo followed by GPC gave **1f** (80 mg, 79% yield) as a pale yellow powder, mp 119–121 °C. ^{1}H NMR ($CDCl_3$) δ 0.80–2.07 (m, 10 H), 2.39 (s, 6 H), 2.87–3.24 (m, 1 H), 6.54–7.53 (m, 11 H), 7.86–8.25 (m, 1 H), 8.92 (d, *J* = 5.5 Hz, 1 H); ^{31}P{^{1}H} NMR ($CDCl_3$) δ –29.9. HRMS Calcd for $C_{27}H_{30}NP$: M^+, 399.2114. Found: *m/z* 399.2115.

Alkynylstannylation of Alkynes. ***A General Procedure.*** A solution (3 mL) of **1** (16.4 μmol), $[PdCl(\pi\text{-}C_3H_5)]_2$ (3.0 mg, 8.2 μmol), and an alkyne (1.03 mmol) was degassed by four freeze-thaw cycles. To this solution was added an organostannane (0.34 mmol), and the mixture was stirred at the temperature for the period, both indicated in Tables 1 and 3. Concentration in vacuo followed by GPC purification gave the corresponding alkynylstannylation product. Yields are listed in Tables 1 and 3.

Alkynylstannylation of Alkynes using various iminophosphines (Table 2). A THF solution (3 mL) of **1** (16.4 μmol), $[PdCl(\pi\text{-}C_3H_5)]_2$ (3.0 mg, 8.2 μmol), and an alkyne (1.03 mmol) was degassed by four freeze-thaw cycles. To this solution was added **2a** (0.135 g, 0.34 mmol), and the resulting mixture was stirred at 50 °C for the time specified in Table 2. Small part of the reaction mixture was withdrawn, and the conversion of **2a** and the ratio of the alkynylstannylation products were assayed by ^{119}Sn NMR. The results are summarized in Table 2.

(*Z*)-4-Phenyl-1-(tributylstannyl)-1-buten-3-yne (5a). A brown oil, R_f 0.49 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.71–1.77 (m, 27 H), 6.69 (s, 2 H), 7.27–7.49 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.7, 27.3, 29.2, 89.8, 90.9, 123.5, 126.7, 128.1, 128.3, 131.4, 147.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –55.5. Anal. Calcd for $C_{22}H_{34}Sn$: C, 63.33; H, 8.21. Found: C, 63.53; H, 8.27.

(*Z*)-2-Methoxymethyl-4-phenyl-1-(tributylstannyl)-1-buten-3-yne (5b). A brown oil, R_f 0.28 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.73–1.78 (m, 27 H), 3.41 (s, 3 H), 4.07 (d, *J* = 1.5 Hz, 2 H), 6.62 (t, *J* = 1.5 Hz, 1 H), 7.24–7.53 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.1, 13.7, 27.3, 29.2, 58.0, 89.4, 90.1, 123.3, 128.1, 128.2, 131.5, 136.9, 140.1; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –55.7. Anal. Calcd for $C_{24}H_{38}OSn$: C, 62.49; H, 8.30. Found: C, 62.26; H, 8.07.

(*Z*)-1-Methoxy-5-phenyl-2-(tributylstannyl)-2-penten-4-yne (6b). A brown oil, R_f 0.39 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.75–1.77 (m, 27 H), 3.33 (s, 3 H), 4.11 (d, *J* = 1.6 Hz, 2 H), 6.51 (t, *J* = 1.6 Hz, 1 H), 7.20–7.51 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.7, 27.4, 29.2, 57.9, 79.1, 89.8, 119.56, 119.62, 128.0, 128.3, 131.3, 159.9; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –48.9. Anal. Calcd for $C_{24}H_{38}OSn$: C, 62.49; H, 8.30. Found as a mixture of **5b** and **6b**: C, 62.79; H, 8.15.

(*Z*)-2-Acetamidomethyl-4-phenyl-1-(tributylstannyl)-1-buten-3-yne (5c). A brown oil, R_f 0.33 (hexane–ethyl acetate = 1 : 1). ^{1}H NMR ($CDCl_3$) δ 0.72–1.70 (m, 27 H), 2.03 (s, 3 H), 4.00–4.10 (m, 2 H), 5.92 (bs, 1 H), 6.46 (s, 1 H), 7.22–7.46 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.1, 13.7, 23.4, 27.3, 29.2, 47.3, 89.9,

90.0, 123.0, 128.4, 131.5, 136.4, 140.0, 169.8; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –56.1. Anal. Calcd for $C_{25}H_{39}NOSn$: C, 61.49; H, 8.05. Found as a mixture of **5c** and **6c**: C, 61.62; H, 7.99.

(*Z*)-1-Acetamido-5-phenyl-2-(tributylstannyl)-2-penten-4-yne (6c). A brown oil, R_f 0.35 (hexane–ethyl acetate = 1 : 1). ^1H NMR ($CDCl_3$) δ 0.69–1.71 (m, 27 H), 2.00 (s, 3 H), 3.97–4.20 (m, 2 H), 5.42 (bs, 1 H), 6.42 (s, 1 H), 7.23–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.1, 13.7, 23.3, 27.4, 29.2, 47.7, 89.5, 90.5, 120.2, 123.4, 128.1, 128.3, 131.3, 158.4, 169.4; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –46.0. Anal. Calcd for $C_{25}H_{39}NOSn$: C, 61.49; H, 8.05. Found as a mixture of **5c** and **6c**: C, 61.62; H, 7.99.

(*Z*)-2-Succinimidomethyl-4-phenyl-1-(tributylstannyl)-1-buten-3-yne (5d). A brown oil, R_f 0.47 (hexane–ethyl acetate = 1 : 1). ^1H NMR ($CDCl_3$) δ 0.72–1.67 (m, 27 H), 2.75 (s, 4 H), 4.35 (d, *J* = 1.3 Hz, 2 H), 6.46 (t, *J* = 1.3 Hz, 1 H), 7.20–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.7, 27.3, 28.2, 29.1, 45.9, 89.3, 89.8, 122.9, 128.4, 131.4, 133.1, 141.5, 176.5; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –54.7. Anal. Calcd for $C_{27}H_{39}NO_2Sn$: C, 61.38; H, 7.44. Found: C, 61.26; H, 7.55.

(*Z*)-1-Succinimido-5-phenyl-2-(tributylstannyl)-2-penten-4-yne (6d). A brown oil, R_f 0.49 (hexane–ethyl acetate = 1 : 1). ^1H NMR ($CDCl_3$) δ 0.75–1.70 (m, 27 H), 2.77 (s, 4 H), 4.32 (d, *J* = 2.0 Hz, 2 H), 6.12 (t, *J* = 2.0 Hz, 1 H), 7.16–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.6, 27.3, 28.2, 29.0, 45.3, 89.2, 90.8, 118.9, 123.4, 128.1, 128.3, 131.2, 154.5, 176.5; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –43.5. Anal. Calcd for $C_{27}H_{39}NO_2Sn$: C, 61.38; H, 7.44. Found as a mixture of **5d** and **6d**: C, 61.54; H, 7.41.

(*Z*)-2,4-Diphenyl-1-(tributylstannyl)-1-buten-3-yne (5e). A brown oil, R_f 0.39 (hexane). ^1H NMR ($CDCl_3$) δ 0.70–1.91 (m, 27 H), 6.95–7.88 (m, 11 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.7, 27.4, 29.2, 89.9, 91.1, 123.4, 125.9, 127.8, 128.2, 128.3, 131.5, 138.9, 139.4, 140.9; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –54.3. Anal. Calcd for $C_{28}H_{38}Sn$: C, 68.17; H, 7.76. Found: C, 68.35; H, 7.63.

(*Z*)-1,4-Diphenyl-1-(tributylstannyl)-1-buten-3-yne (6e). A brown oil, R_f 0.39 (hexane). ^1H NMR ($CDCl_3$) δ 0.62–1.76 (m, 27 H), 6.50 (s, 1 H), 7.02–7.78 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 11.1, 13.6, 27.3, 29.1, 90.6, 91.3, 121.4, 123.6, 126.4, 126.5, 128.1, 128.2, 128.3, 131.3, 146.2, 163.0; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –43.0. Anal. Calcd for $C_{28}H_{38}Sn$: C, 68.17; H, 7.76. Found as a mixture of **5e** and **6e**: C, 68.16; H, 7.88.

(*Z*)-2-(4-Methylphenyl)-4-phenyl-1-(tributylstannyl)-1-buten-3-yne (5f). A brown oil, R_f 0.39 (hexane). ^1H NMR ($CDCl_3$) δ 0.77–1.84 (m, 27 H), 2.36 (s, 3 H), 7.06–7.74 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.7, 21.1, 27.4, 29.2, 89.7, 91.2, 123.5, 125.8, 128.2, 128.3, 128.9, 131.5, 136.8, 137.7, 138.8, 139.6; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –54.5. Anal. Calcd for $C_{29}H_{40}Sn$: C, 68.66; H, 7.95. Found: C, 68.57; H, 7.86.

(*Z*)-1-(4-Methylphenyl)-4-phenyl-1-(tributylstannyl)-1-buten-3-yne (6f). A brown oil, R_f 0.31 (hexane). ^1H NMR ($CDCl_3$) δ 0.71–1.90 (m, 27 H), 2.35 (s, 3 H), 6.49 (s, 1 H), 6.97–7.58 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 11.1, 13.7, 21.1, 27.3, 29.1, 90.8, 91.2, 120.8, 123.7, 126.3, 128.0, 128.3, 128.9, 131.3, 136.2, 143.2, 162.7; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –43.7. Anal. Calcd for $C_{29}H_{40}Sn$: C, 68.66; H, 7.95. Found as a mixture of **5f** and **6f**: C, 68.50; H, 7.96.

(*E*)-2-Ethoxy-4-phenyl-1-(tributylstannyl)-1-buten-3-yne (5g). A brown oil, R_f 0.65 (hexane–ethyl acetate = 10 : 1). ^1H NMR ($CDCl_3$) δ 0.68–1.73 (m, 30 H), 4.04 (q, *J* = 7.1 Hz, 2 H), 5.52 (s, 1 H), 7.17–7.56 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.3, 13.7, 15.2, 27.3, 29.2, 83.6, 89.7, 113.8, 122.6, 128.2, 128.3, 128.5, 131.6, 147.1; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –51.1. Anal. Calcd for $C_{24}H_{38}OSn$: C, 62.49; H, 8.30. Found: C, 62.46; H, 8.40.

Ethyl (*Z*)-3-methyl-5-phenyl-2-(tributylstannyl)-2-penten-4-ynoate (6h). A brown oil, R_f 0.45 (hexane–ethyl acetate = 9 : 1). ^1H NMR ($CDCl_3$) δ 0.74–1.67 (m, 30 H), 2.14 (s, 3 H), 4.21 (q, *J* = 7.1 Hz, 2 H), 7.19–7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.1, 13.6, 14.4, 22.7, 27.2, 28.9, 60.3, 91.1, 92.3, 122.9, 128.4,

128.5, 131.5, 134.8, 145.0, 171.9; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –36.0. Anal. Calcd for $C_{26}H_{40}O_2Sn$: C, 62.04; H, 8.01. Found: C, 62.33; H, 8.25.

Ethyl (*E*)-2-phenylethynyl-3-(tributylstannyl)-2-propenoate (5i). A brown oil, R_f 0.31 (hexane–ethyl acetate = 10 : 1). ^1H NMR ($CDCl_3$) δ 0.62–1.78 (m, 30 H), 4.28 (q, *J* = 7.1 Hz, 2 H), 7.25–7.54 (m, 5 H), 8.04 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.6, 14.2, 27.3, 29.1, 61.6, 87.9, 90.9, 123.1, 128.3, 128.4, 131.4, 131.6, 159.2, 163.5; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –52.0. Anal. Calcd for $C_{25}H_{38}O_2Sn$: C, 61.37; H, 7.83. Found as a mixture of **5i** and **6i**: C, 61.64; H, 7.58.

Ethyl (*Z*)-5-phenyl-2-(tributylstannyl)-2-penten-4-ynoate (6i). A brown oil, R_f 0.41 (hexane–ethyl acetate = 10 : 1). ^1H NMR ($CDCl_3$) δ 0.86 (t, *J* = 7.1 Hz, 9 H), 0.96–1.76 (m, 21 H), 4.21 (q, *J* = 7.1 Hz, 2 H), 7.27–7.54 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 11.4, 13.7, 14.3, 27.3, 29.0, 60.9, 89.0, 97.7, 122.7, 128.4, 128.9, 131.6, 133.4, 150.0, 170.9; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –38.3. Anal. Calcd for $C_{25}H_{38}O_2Sn$: C, 61.37; H, 7.83. Found: C, 61.53; H, 7.65.

(*E*)-3-Phenylethynyl-4-(tributylstannyl)-3-buten-2-one (5j). A brown oil, R_f 0.44 (hexane–ethyl acetate = 10 : 1). ^1H NMR ($CDCl_3$) δ 0.73–1.68 (m, 27 H), 2.33 (s, 3 H), 7.16–7.58 (m, 5 H), 7.91 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.6, 27.3, 27.5, 29.1, 88.9, 92.1, 122.8, 128.4, 128.6, 131.4, 139.0, 156.7, 194.2; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –50.7. Anal. Calcd for $C_{24}H_{36}OSn$: C, 62.77; H, 7.90. Found as a mixture of **5j** and **6j**: C, 63.03; H, 7.82.

(*Z*)-6-Phenyl-3-(tributylstannyl)-3-hexen-5-yne-2-one (6j). A brown oil, R_f 0.37 (hexane–ethyl acetate = 10 : 1). ^1H NMR ($CDCl_3$) δ 0.74–1.70 (m, 27 H), 2.50 (s, 3 H), 7.30–7.54 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 11.4, 13.7, 25.9, 27.3, 29.1, 88.6, 99.4, 122.6, 128.5, 129.0, 131.3, 131.6, 161.8, 204.1; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –39.5. Anal. Calcd for $C_{24}H_{36}OSn$: C, 62.77; H, 7.90. Found: C, 62.90; H, 8.09.

(*Z*)-1-(Tributylstannyl)-1-octen-3-yne (5k). A brown oil, R_f 0.68 (hexane). ^1H NMR ($CDCl_3$) δ 0.77–1.70 (m, 34 H), 2.31 (t, *J* = 6.3 Hz, 2 H), 6.44 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.0, 13.6, 13.7, 19.2, 22.1, 27.3, 29.2, 30.8, 82.0, 91.0,

127.2, 144.3; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –57.0. Anal. Calcd for $C_{20}H_{38}Sn$: C, 60.47; H, 9.64. Found: C, 60.21; H, 9.44.

(*Z*)-2-Phenyl-1-(tributylstannyl)-1-octen-3-yne (5l). A brown oil, R_f 0.45 (hexane). ^1H NMR ($CDCl_3$) δ 0.76–1.85 (m, 34 H), 2.42 (t, *J* = 7.0 Hz, 2 H), 6.93 (s, 1 H), 7.20–7.83 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.1, 13.6, 13.7, 19.3, 22.2, 27.4, 29.2, 30.8, 82.1, 91.1, 125.9, 127.6, 128.1, 138.2, 139.3, 139,9; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –55.3. Anal. Calcd for $C_{26}H_{42}Sn$: C, 65.98; H, 8.94. Found: C, 66.19; H, 9.02.

(*Z*)-1-Phenyl-1-(tributylstannyl)-1-octen-3-yne (6l). A brown oil, R_f 0.37 (hexane). ^1H NMR ($CDCl_3$) δ 0.63–1.79 (m, 34 H), 2.34 (td, *J* = 7.0, 2.2 Hz, 2 H), 6.25 (t, *J* = 2.2 Hz, 1 H), 6.92–7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.9, 13.6, 13.7, 19.5, 22.1, 27.3, 29.1, 30.8, 81.5, 92.6, 122.0, 126.1, 126.4, 127.2, 128.1, 129.5; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –45.0. Anal. Calcd for $C_{26}H_{42}Sn$: C, 65.98; H, 8.94. Found as a mixture of **5l** and **6l**: C, 66.15; H, 9.12.

Ethyl (*E*)-2-(1-hexyn-1-yl)-3-(tributylstannyl)-2-propenoate (5m). A brown oil, R_f 0.55 (hexane–ethyl acetate = 10 : 1). ^1H NMR ($CDCl_3$) δ 0.75–1.77 (m, 37 H), 2.38 (t, *J* = 7.0 Hz, 2 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 7.82 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.0, 13.6, 13.7, 14.2, 19.3, 22.1, 27.3, 29.1, 30.6, 61.4, 79.1, 92.3, 131.6, 156.5, 163.9; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –53.2. Anal. Calcd for $C_{23}H_{42}O_2Sn$: C, 58.87; H, 9.02. Found as a mixture of **5m** and **6m**: C, 58.91; H, 9.14.

Ethyl (*Z*)-2-(tributylstannyl)-2-nonen-4-ynoate (6m). A brown oil, R_f 0.59 (hexane–ethyl acetate = 10 : 1). ^1H NMR ($CDCl_3$) δ 0.72–1.65 (m, 37 H), 2.31 (td, *J* = 7.0, 2.4 Hz, 2 H), 4.10 (q, *J* = 7.1 Hz, 2 H), 7.18 (t, *J* = 2.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.2, 13.6, 13.7, 14.3, 19.6, 22.1, 27.3, 29.0, 30.4, 60.7, 80.4, 100.1, 134.5, 147.7, 171.1; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –40.2. Anal. Calcd for $C_{23}H_{42}O_2Sn$: C, 58.87; H, 9.02. Found: C, 58.93; H, 9.10.

Coupling of 5a with 1-bromo-2-phenylethyne. A solution of tri(2-furyl)phosphine (10.2 mg, 44 μmol) and $Pd_2(dba)_3$ (5.0 mg, 5.5 μmol) in 1-methyl-2-

pyrrolidinone (NMP, 2.5 mL) was degassed by three freeze-thaw cycles. To this solution was added 1-bromo-2-phenylethyne (40 mg, 0.22 mmol) and **5a** (0.100 g, 0.24 mmol), and the resulting mixture was stirred at 50 °C for 18 h before a 1 M KF aqueous solution (2 mL) was added. The mixture was stirred at room temperature for 30 min, filtered through a Celite plug, and extracted with ethyl acetate (50 mL). The organic layer was separated, washed successively with water and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave (*Z*)-1,6-diphenyl-3-hexen-1,5-diyne (**9**)[23] (29 mg, 58%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 6.10 (s, 2 H), 7.23–7.63 (m, 10 H).

Coupling of 5a with 4-nitroiodobenzene. ***With $Pd_2(dba)_3$–Tri(2-furyl)phosphine.*** A solution of tri(2-furyl)phosphine (20 mg, 88 μmol) and $Pd_2(dba)_3$ (10.1 mg, 11.0 μmol) in toluene (5 mL) was degassed by three freeze-thaw cycles. To this solution was added 4-nitroiodobenzene (0.110 g, 0.44 mmol) and **5a** (0.20 g, 0.48 mmol), and the mixture was stirred at 90 °C for 13 h before the addition of a 1 M KF aqueous solution (2 mL). The mixture was stirred at room temperature for 30 min, filtered through a Celite plug, and extracted with ethyl acetate (50 mL). The organic layer was separated, washed successively with water and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave (*Z*)-1-(4-nitrophenyl)-4-phenyl-1-buten-3-yne (**10**)[24] (93 mg, 85%) as a pale yellow powder: ^{1}H NMR ($CDCl_3$) δ 6.16 (d, *J* = 11.9 Hz, 1 H), 6.77 (d, *J* = 11.9 Hz, 1 H), 7.29–7.59 (m, 5 H), 7.96–8.14 (m, 2 H), 8.17–8.33 (m, 2 H).

With $[PdCl(\pi\text{-}C_3H_5)]_2$–1a. A solution of **1a** (8.6 mg, 22 μmol), 4-nitroiodobenzene (0.110 g, 0.44 mmol), and $[PdCl(\pi\text{-}C_3H_5)]_2$ (4.0 mg, 10.9 μmol) in toluene (5 mL) was degassed by three freeze-thaw cycles. To this solution was added **5a** (0.20 g, 0.48 mmol) and the mixture was stirred at 90 °C for 13 h. After a 1 M KF aqueous solution (2 mL) was added, the reaction mixture was stirred at room temperature for 30 min. Filtration through a Celite plug was followed by extraction with ethyl acetate (50 mL). The organic layer was washed successively with water and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave a

mixture of (*Z*)-1-(4-nitrophenyl)-4-phenyl-1-buten-3-yne (**10**) and (*E*)-1-(4-nitrophenyl)-4-phenyl-1-buten-3-yne (66 mg, 83:17 ratio, 60%) as a pale yellow powder.

Iododestannylation of 5a. To a solution of **5a** (0.100 g, 0.24 mmol) in THF (4 mL) was added iodine (87 mg, 0.34 mmol) at 0 °C, and the resulting reaction mixture was stirred for 40 min before ethyl acetate (10 mL) and a saturated $Na_2S_2O_3$ aqueous solution (5 mL) were added. After the organic layer was treated with a 1 M KF aqueous solution (2 mL) at room temperature for 30 min, insoluble materials were filtered through a Celite pad, and the organic layer was dried over magnesium sulfate. Evaporation of the solvent followed by GPC gave (*Z*)-1-iodo-4-phenyl-1-buten-3-yne (**11**) (56 mg, 92%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 6.82 (d, *J* = 8.3 Hz, 1 H), 6.86 (d, *J* = 8.3 Hz, 1 H), 7.30–7.39 (m, 3 H), 7.49–7.58 (m, 2 H). Anal. Calcd for $C_{10}H_7I$: C, 42.27; H, 2.78. Found: C, 42.27; H, 2.89.

Hydrolysis of 5a. A mixture of **5a** (58 mg, 0.139 mmol) and a concentrated hydrochloric acid (12 M, 80 μL, 0.96 mmol) in THF (8 mL) was stirred at room temperature for 1 h. After the addition of ethyl acetate (20 mL) to the reaction mixture, the organic layer was washed with saturated $NaHCO_3$ aqueous solution (5 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave 4-phenyl-1-buten-3-yne (**12**)[25] (15.0 mg, 81%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 5.55 (dd, *J* = 11.0, 2.4 Hz, 1 H), 5.73 (dd, *J* = 17.6, 2.4 Hz, 1 H), 6.03 (dd, *J* = 17.6, 11.0 Hz, 1 H), 7.01–7.60 (m, 5 H).

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Chapter 3

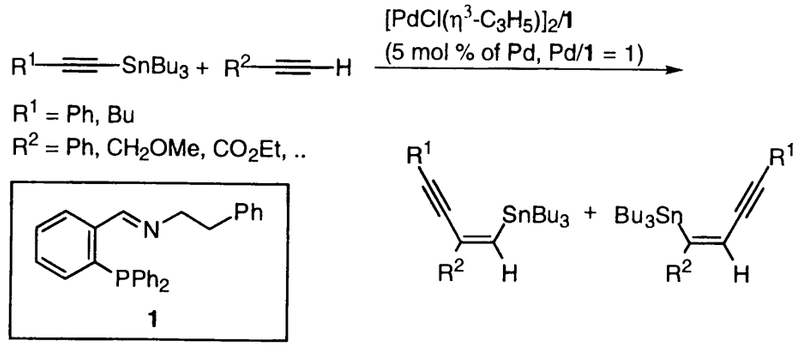
Dimerization–Carbostannylation of Alkynes Catalyzed by Palladium–Diimine Complexes

Double insertion of alkynes into a C–Sn bond of an alkynyl-, alkenyl-, allyl- or arylstannane proceeded in the presence of a palladium–diimine complex to afford highly conjugated alkenylstannanes with exclusive *syn*-selectivity. Perfect regioselectivities were observed in the dimerization–carbostannylation of ethyl propiolate with a Pd–bis[(2,6-diisopropylphenyl)imino]acenaphthene complex, which allowed regio- and stereoselective synthesis of stannyl-substituted muconic acid derivatives. The π-conjugation system of the dimerization–carbostannylation products was further extended through cross-coupling or homocoupling reaction. A palladacyclopentadiene is proposed as an intermediate species.

Introduction

As discussed in Chapter 2, carbostannylation of alkynes has become a powerful synthetic tool owing to the novel synthetic transformation: C–C and C–Sn bonds are simultaneously introduced across a triple bond of alkynes in a *syn*-manner to give alkenylstannanes, which can be converted into variously substituted ethenes with retention of configuration through the Migita–Kosugi–Stille coupling reaction.[1] Furthermore, high chemoselectivity and mild reactivity of organostannanes as compared with other organometallic reagents make the carbostannylation and subsequent reactions extremely useful and applicable to a wide variety of substrates. Although allylstannylation of alkynes, in particular, has been shown to be mediated by Lewis acids[2] or radical initiators,[3] alkynylstannanes also are demonstrated to participate in the newly uncovered carbostannylation of alkynes as disclosed in Chapter 2.[4,5,6,7]

In the palladium-catalyzed alkynylstannylation of alkynes, nature of a ligand influences significantly the catalyst activity. For example, a palladium complex coordinated by *N*-(2-diphenylphosphinobenzylidene)-2-phenylethylamine (**1**) efficiently catalyzes the reaction (Scheme 1), whereas such phosphorous ligands as triphenylphosphine and 1,3-bis(diphenylphosphino)propane were ineffective, suggesting that the imino moiety of **1** plays an important role in the catalysis. Since then, the author directed his research to improvement of efficiency of the palladium-catalyzed carbostannylation, and found that dimerization–carbostannylation reaction of alkynes took place when triggered by a palladium complex consisting of a rigid diimine ligand, i.e., bis(arylimino)acenaphthene (**2**).



Scheme 1. Pd–iminophosphine-catalyzed alkynylstannylation of alkynes.

In this Chapter, the author describes the palladium-catalyzed dimerization–carbostannylation of alkynes, demonstrating that the novel catalytic process provides a convenient method to produce a variety of highly π-conjugated alkenylstannanes with three to six covalent bonds being formed in one pot.

Results and Discussion

Reaction conditions for dimerization–carbostannylation

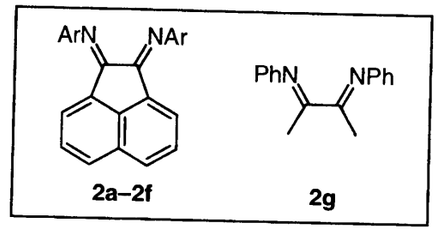
First the author investigated the reaction of ethyl propiolate (**3a**) with tributyl(phenylethynyl)tin (**4a**) in toluene at 25 °C for 1 h using a palladium–bis(phenylimino)acenaphthene (**2a**) complex and observed that diethyl (1*Z*,3*E*)-6-phenyl-1-tributylstannylhexa-1,3-dien-5-yne-1,4-dicarboxylate (**5a**) was produced as the sole product in 89% conversion (Scheme 2, entry 1 of Table 1). The product formation is ascribed to addition of a C–Sn bond in **4a** to **3a** accompanied by dimerization of the alkyne. Results of the reaction of **3a** with **4a** using other solvents and ligands are summarized in Table 1. In such a polar solvent as THF, dioxane, DME or DMF, the reaction using the Pd–**2a** catalyst was slow (entries 2–6); in octane, the reaction did not proceed at all probably due to low solubility of the catalyst (entry 7). Diimines having an electron-withdrawing or -donating substituent on Ar did not accelerate the reaction (entries 8–11). Bulky diimine **2f** was totally ineffective (entry 12).

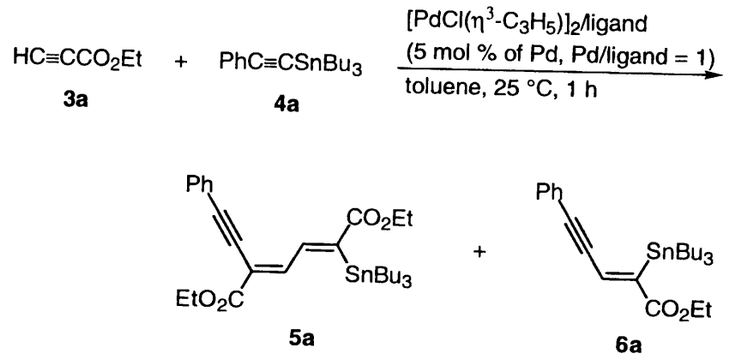
Table 1. Palladium-catalyzed dimerization–carbostannylation of ethyl propiolate (**3a**) with tributyl(phenylethynyl)tin (**4a**)[a]

entry	ligand (Ar in **2**)		solvent	conversion (%)[b]	product(s)
1	Ph	(**2a**)	toluene	89	**5a**
2	Ph	(**2a**)	THF	71	**5a**
3	Ph	(**2a**)	dioxane	70	**5a**
4	Ph	(**2a**)	$CHCl_3$	70	**5a**
5	Ph	(**2a**)	DME	64	**5a**
6	Ph	(**2a**)	DMF	53	**5a**
7	Ph	(**2a**)	octane	<5	**5a**
8	4-$CF_3C_6H_4$	(**2b**)	toluene	80	**5a**
9	3,5-$(CF_3)_2C_6H_3$	(**2c**)	toluene	49	**5a**
10	4-$MeOC_6H_4$	(**2d**)	toluene	68	**5a**
11	4-MeC_6H_4	(**2e**)	toluene	89	**5a**
12	2,6-(*i*-Pr)$_2C_6H_3$	(**2f**)	toluene	<5	**5a**
13	—	(**2g**)	toluene	31	**5a**, **6a**[c]
14	—	(**1**)	toluene	84	**6a**[d]
15	none		toluene	20	**6a**[e]

[a] The reaction was carried out in a solvent (3 mL) at 25 °C using **3a** (1.0 mmol) and **4a** (0.34 mmol) for 1 h in the presence of [PdCl(η^3-C_3H_5)]$_2$ (8.2 μmol) and a ligand (16 μmol). [b] Determined by ^{119}Sn NMR. [c] **5a**/**6a** = 54/46. [d] The regioisomer of **6a** was also detected (**6a**/isomer = 4/1). [e] Regioisomer was not detected.

Palladium complex with acyclic diimine ligand **2g** gave a mixture of 2 : 1 and 1 : 1 carbostannylation products (entry 13). Only 1 : 1 carbostannylation product **6a** was obtained with the palladium–**1** catalyst as shown in Chapter 2 (entry 14). In the absence of any of the ligands, the reaction was extremely sluggish (entry 15).





Scheme 2. Reaction of **3a** with **4a** in the presence of Pd–**2** complexes.

Dimerization–carbostannylation catalyzed by Pd–2a

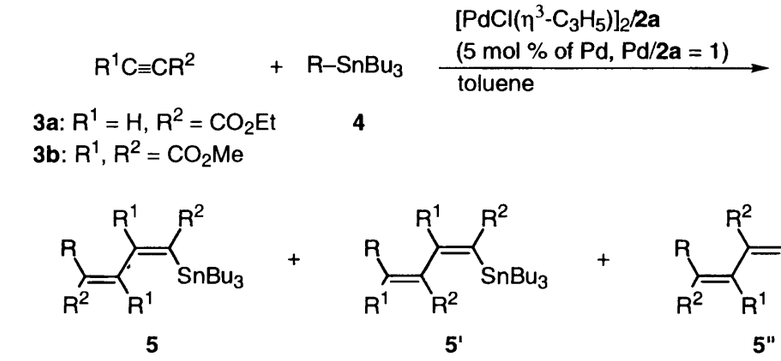
The author next examined the dimerization–carbostannylation of various organostannanes and alkynes using the Pd–**2a** catalyst (Scheme 3, Table 2). As mentioned above, the reaction of **3a** with **4a** proceeded smoothly to afford **5a** in 77% yield in a period of 40 min (entry 1). Tributyl(1-hexyn-1-yl)tin (**4b**) and tributyl(trimethylsilylethynyl)tin (**4c**) also reacted effectively with **3a** with perfect regioselectivities (entries 2 and 3). Alkenylstannanes **4d**, **4e** and **4f** were more reactive towards **3a** than alkynylstannanes and gave rise to the corresponding conjugated (stannyl)trienes consisting of two regioisomers **5** and **5'** (entries 4–6).

Table 2. Dimerization–carbostannylation of alkynes catalyzed by palladium–diimine **2a**[a]

entry	alkyne	R		temp (°C)	time (h)	yield (%)[b]	product(s)	ratio **5** : **5'** : **5''**[c]
1	**3a**	PhC≡C	(**4a**)	50	0.7	77	**5a**	100 : 0 : 0
2		BuC≡C	(**4b**)	30	3	93	**5b**	100 : 0 : 0
3		TMSC≡C	(**4c**)	20	0.5	75	**5c**	100 : 0 : 0
4		CH_2=CH	(**4d**)	50	0.7	72	**5d**, **5'd**	79 : 21 : 0
5		(*E*)-PhCH=CH	(**4e**)	50	1	78	**5e**, **5'e**	89 : 11 : 0
6		(*E*)-HexCH=CH	(**4f**)	50	1	76	**5f**, **5'f**	71 : 29 : 0
7		2-furyl	(**4g**)	50	14	81	**5g**, **5'g**, **5''g**	30 : 63 : 7
8		2-thienyl	(**4h**)	50	12	42	**5h**, **5'h**, **5''h**	13 : 69 : 18
9	**3b**	PhC≡C	(**4a**)	70	2	77	**5i**	—
10		BuC≡C	(**4b**)	90	19	32	**5j**	—
11		TMSC≡C	(**4c**)	90	2	52	**5k**	—
12		CH_2=CH	(**4d**)	50	2	76	**5l**	—
13		(*E*)-PhCH=CH	(**4e**)	50	1	75	**5m**	—
14		(*E*)-HexCH=CH	(**4f**)	50	8	75	**5n**	—
15		2-furyl	(**4g**)	50	19	63	**5o**	—
16		2-benzofuryl	(**4i**)	50	26	75	**5p**	—
17		(*E*)-PhCH=$CHCH_2$	(**4j**)	50	1	86	**5q**[d]	—

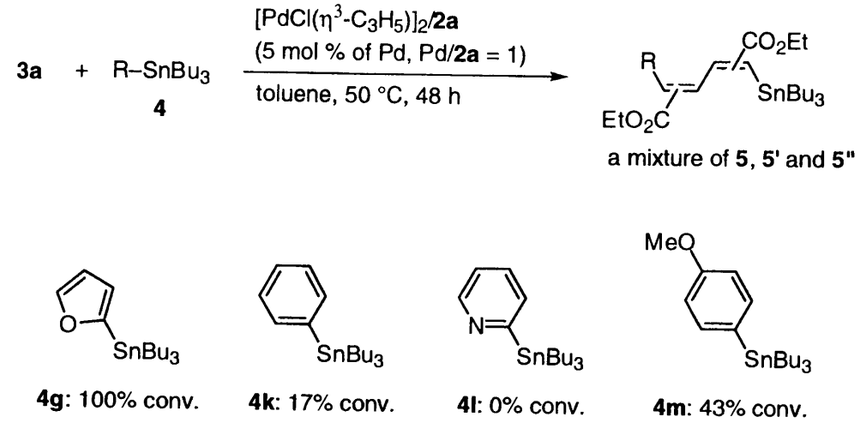
[a] The reaction was carried out in toluene (3 mL) using an alkyne (1.0 mmol) and an organostannane (0.34 mmol) in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (8.2 μmol) and **2a** (16 μmol). [b] Isolated yield based on the organostannane is given. [c] Determined by ^{119}Sn NMR. [d] A 1 : 1 carbostannylation product (**6b**) was also obtained in 4% yield.

The reaction of heteroarylstannanes such as tributyl(2-furyl)tin (**4g**) and tributyl(2-thienyl)tin (**4h**) with **3a** also proceeded, regioisomer **5'** being predominated over **5** and **5"** (entries 7 and 8). In all cases, the addition of organostannanes to **3a** occurred with exclusive *syn* selectivity (*vide infra*). The reaction was also applicable to dimethyl acetylenedicarboxylate (**3b**), giving **5i–5q**[8] in a stereoselective manner (entries 9–16). Tributyl(cinnamyl)tin (**4j**) and **3b** can participate in the dimerization–carbostannylation (entry 17). Ester functionality on acetylene seems to be essential for successful reaction: none of phenylacetylene, 1-octyne, and 1-butyn-3-one gave the corresponding carbostannylation product.



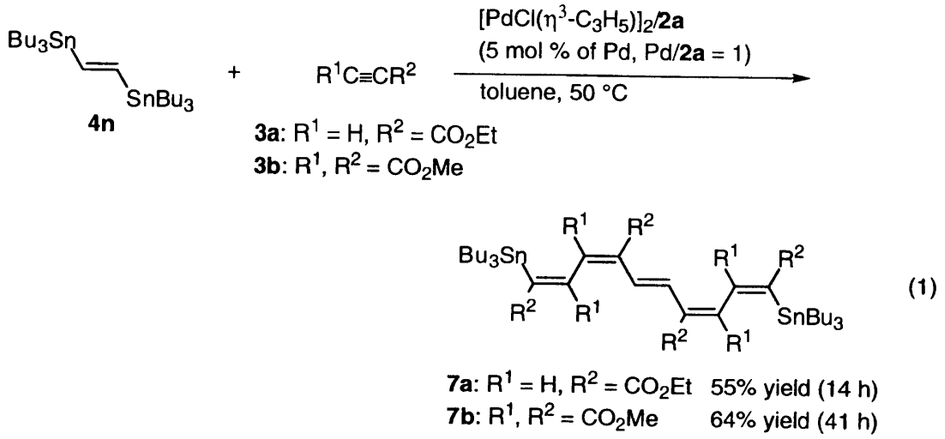
Scheme 3. Dimerization–carbostannylation of alkynes catalyzed by Pd–**2a**.

In contrast to five-membered heteroarylstannanes, tributyl(phenyl)tin (**4k**) gave a dimerization–carbostannylation product with **3a** only in 17% conversion after 48 h, and tributyl(2-pyridyl)tin (**4l**) was totally unreactive (Scheme 4). Such an electron-donating group as methoxy on the phenyl in **4k** assisted the reaction: with **4m** conversion increased to 43%. Thus reactivity order of arylstannanes is 2-furyl (**4g**) >> 4-$MeOC_6H_4$ (**4m**) > Ph (**4k**) > 2-pyridyl (**4l**), indicating that more electron-rich arylstannanes reacts faster.



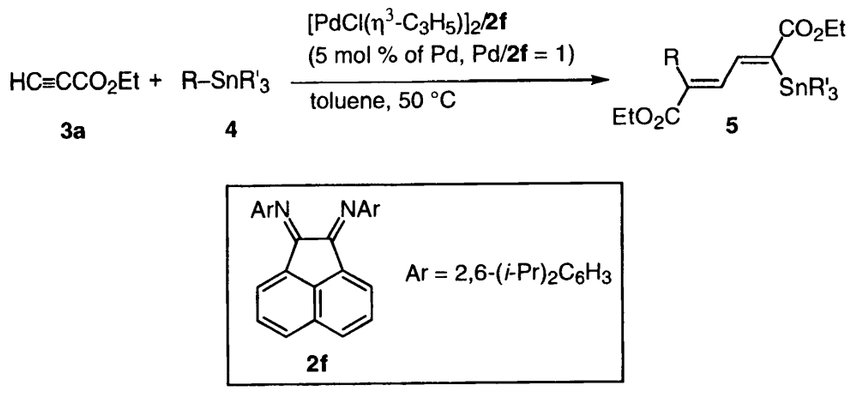
Scheme 4. Dimerization–carbostannylation of arylstannanes.

Application of the dimerization–carbostannylation to an organostannane containing two C–Sn bonds provided highly conjugated polyenylstannanes: the reaction of (*E*)-bis(tributylstannyl)ethene (**4n**) with alkynes **3a** and **3b** afforded α,ω-distannylpentaenes **7a** and **7b**, respectively, forming six new covalent bonds all in one pot.



Regioselective synthesis of stannyl-substituted muconic acid derivatives

Although palladium complex coordinated by bulky diimine ligand, bis[(2,6-diisopropylphenyl)imino]acenaphthene (**2f**), did not catalyze the reaction of **3a** with **4a** at 25 °C as stated above, this complex was found to promote the reaction at 50 °C, giving a single isomer regardless of the kind of organostannanes employed (Scheme 5).



Scheme 5. Pd–**2f**-catalyzed dimerization–carbostannylation.

Table 3. Pd–**2f**-catalyzed dimerization–carbostannylation of ethyl propiolate (**3a**)[a]

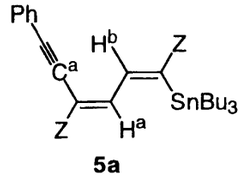
entry	R	R'		time (h)	yield (%)[b]	product
1	CH_2=CH	Bu	(**4d**)	1	72	**5d**
2	2-furyl	Bu	(**4g**)	13	78	**5g**
3	2-thienyl	Bu	(**4h**)	22	68	**5h**
4	2-benzofuryl	Bu	(**4i**)	23	79	**5r**
5	3-thienyl	Bu	(**4o**)	21	80	**5s**
6	Ph	Me	(**4'k**)	27	42	**5t**
7	4-$MeOC_6H_4$	Me	(**4'm**)	19	64	**5u**

[a] The reaction was carried out in toluene (3 mL) at 50 °C using an alkyne (1.0 mmol) and an organostannane (0.34 mmol) in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (8.2 μmol) and **2f** (16 μmol).
[b] Isolated yield based on the organostannane is given.

The dimerization–carbostannylation of **3a** in the presence of Pd–**2f** offers a straightforward method to synthesize variously substituted *trans,trans*-muconic acid derivatives. The results are summarized in Table 3. Tributyl(vinyl)tin (**4d**) smoothly reacted to afford **5d** as the sole product in 72% yield (entry 1). It is noteworthy that the Pd–**2f** catalyst allowed a variety of five-membered heteroarylstannanes to give **5** exclusively (entries 2–5) in contrast to the reaction of the heteroarylstannanes with the Pd–**2a** catalyst which gave **5'** as major products (entries 7 and 8 of Table 2). Phenyl- and *p*-anisylstannanes could participate in the reaction, when -$SnBu_3$ in **4k** and **4m** was replaced by -$SnMe_3$, affording desired products **5t** and **5u** in moderate yields (entries 6 and 7).

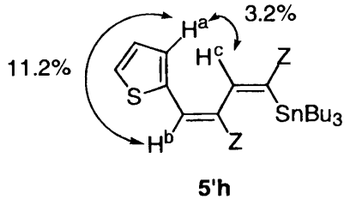
Structure determination of dimerization–carbostannylation products

Configuration of **5a–5h** and **5r–5u** was determined based on coupling constants in NMR.[9] Products **5'd–5'h**, **5"g** and **5"h** were confirmed to be regioisomers of **5d–5h**, respectively, on the basis of corresponding coupling constants between olefinic protons as well as between tin and olefinic proton and/or by NOE experiments. Typical coupling constants of **5a**, **5'h** and **5"h** are shown in Figure 1.



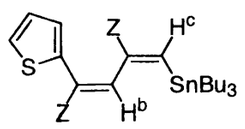
5a

$^3J_{H^a-H^b}$ = 12.2 Hz
$^3J_{C^a-H^a}$ = 12.2 Hz
$^3J_{H^b-Sn^{119}}$ = 92 Hz
$^3J_{H^b-Sn^{117}}$ = 88 Hz



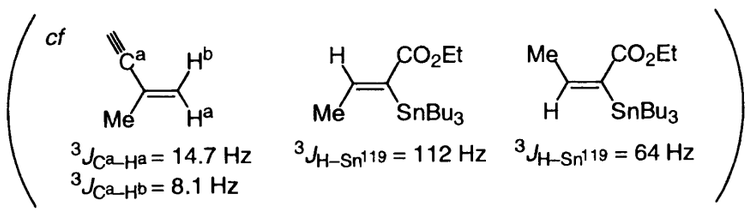
5'h

$^4J_{H^b-H^c}$ = 1.7 Hz
$^3J_{H^c-Sn}$ = 102 Hz
($^3J_{H^c-Sn^{119}}$ and $^3J_{H^c-Sn^{117}}$ were not resolved.)



5"h

$^4J_{H^b-H^c}$ = 0.6 Hz
$^2J_{H^c-Sn}$ = 48 Hz
$^4J_{H^b-Sn}$ = 20 Hz
($J_{H-Sn^{119}}$ and $J_{H-Sn^{117}}$ were not resolved.)



$^3J_{C^a-H^a}$ = 14.7 Hz
$^3J_{C^a-H^b}$ = 8.1 Hz

$^3J_{H-Sn^{119}}$ = 112 Hz

$^3J_{H-Sn^{119}}$ = 64 Hz

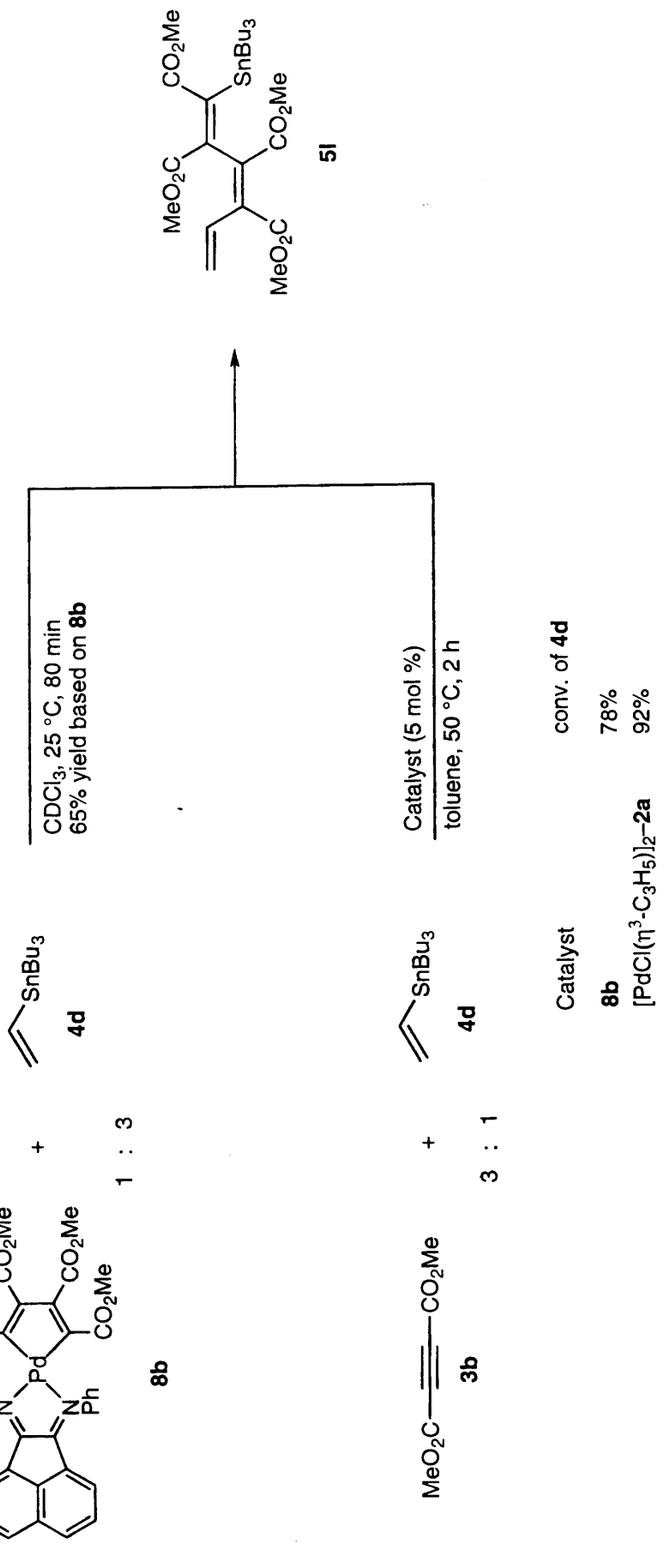
Figure 1

Catalytic cycle

Elsevier and his co-workers recently reported three component coupling of acetylenedicarboxylate, organic halide and tetramethyltin, using palladium–diimine **2e** complex as a catalyst.[10] The catalytic cycle is considered to involve reaction of

palladacyclopentadiene **8a** (cf. Figure 2), derived from Pd(0)–**2e** and dimethyl acetylenedicarboxylate (**3b**), with an organic halide followed by transmetalation with tetramethyltin.

In the course of the present study, no trace of a 1 : 1 carbostannylation product was observed except for the case of tributyl(cinnamyl)tin (**4j**). Furthermore, neither trimerization–carbostannylation products nor higher oligomers were produced. Consequently, the present reaction should also be initiated by formation of palladacyclopentadiene (**8** or **9**) from a Pd(0)–diimine complex and 2 mol of an alkyne. In order to confirm that the palladacyclopentadiene would be involved in the dimerization–carbostannylation, the author monitored the reaction by ^{1}H NMR, choosing **2e** as a ligand, because the methyl substituent gave distinct information. ^{1}H NMR spectra of the reaction of **3b** with **4d** showed no other peaks than those of palladacycle **8a** in addition to those of the substrate and the expected product (Figure 2). Furthermore, palladacycle **8b** was prepared from Pd(0)–**2a** and allowed to react with three equimolar amounts of **4d** to give carbostannylation product **5l** in a good yield, and **8b** was shown to be an equally active catalyst (Scheme 6). All these observations suggest that the catalytic cycle should be initiated by formation of the palladacyclopentadiene intermediate followed by reaction with an organostannane, although subsequent steps of the catalytic cycle remain yet to be studied.



Scheme 6. Reactions using palladacycle **8b**.

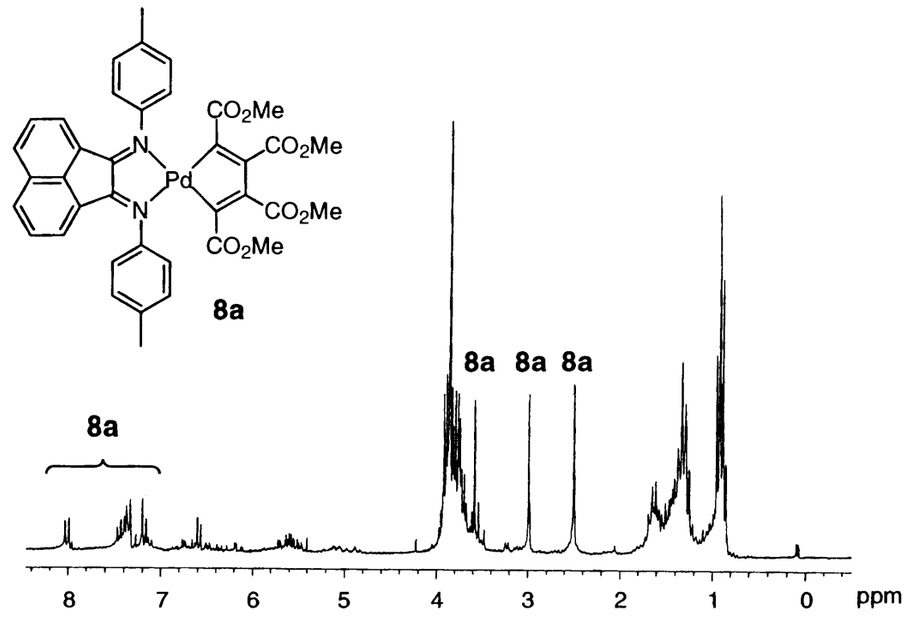
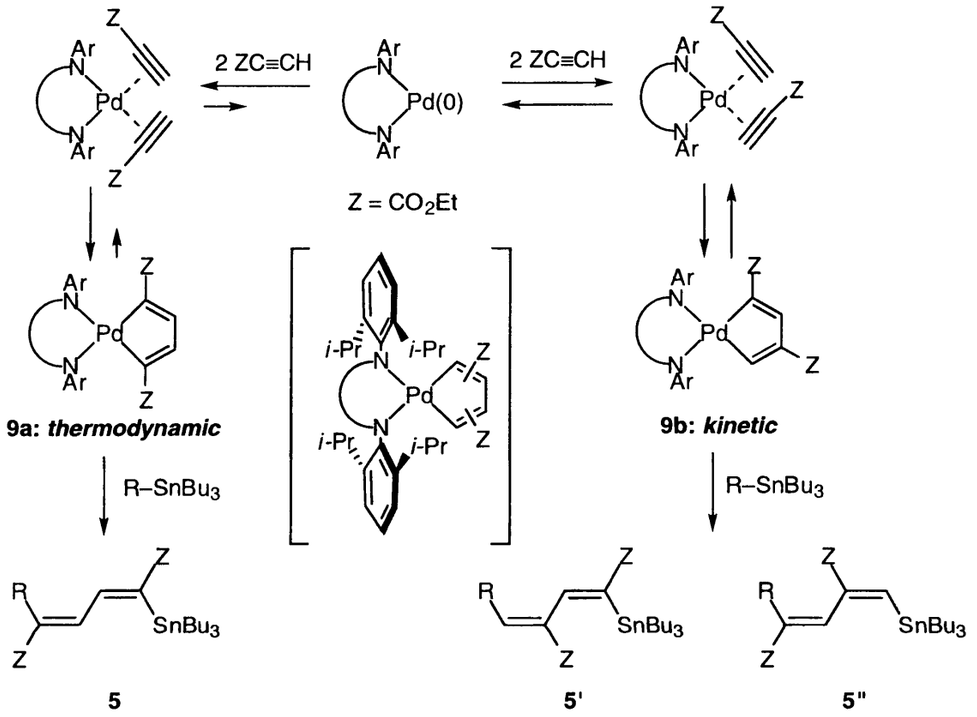


Figure 2. ^{1}H NMR (200 MHz) spectrum of the reaction mixture (at *ca*. 31% conversion) in the reaction of **3b** with **4d** in the presence of $[PdCl(\eta^3\text{-}C_3H_5)]_2$–**2e** complex (20 mol % of Pd, Pd/**2e** = 1) in $CDCl_3$ at 25 °C.

The different regioselectivities observed with Pd–**2a** and Pd–**2f** as catalysts in the reaction of ethyl propiolate (**3a**) can be explained as follows (Scheme 7). Formation of three regioisomeric products **5**, **5'** and **5"** upon use of Pd–**2a** is attributed to palladacycle intermediates, **9a** and **9b**, which might be equilibrated each other via a palladium(0)–diimine complex, since product ratios are considerably influenced by structure of the organostannane despite in an identical catalyst system (see Table 2). Among these palladacycles, **9a** should be thermodynamically stable, because two electron-withdrawing ester groups are attached to carbons next to the palladium atom.[11] In contrast, formation of **9b** would be kinetically favored due to less steric repulsion between the aryl groups of the diimine ligand and the ester groups of **3a**. In use of bulky diimine **2f**, two isopropyl groups in **2f** would prevent an organostannane from coordinating to an apical position of the palladacycle as in Scheme 7,[12] leading to slow reaction of the palladacycle with the organostannane (entry 1 vs 12 of Table 1). Hence, kinetically generated palladacycle **9b** should isomerize to thermodynamically stable **9a** prior to reaction with the

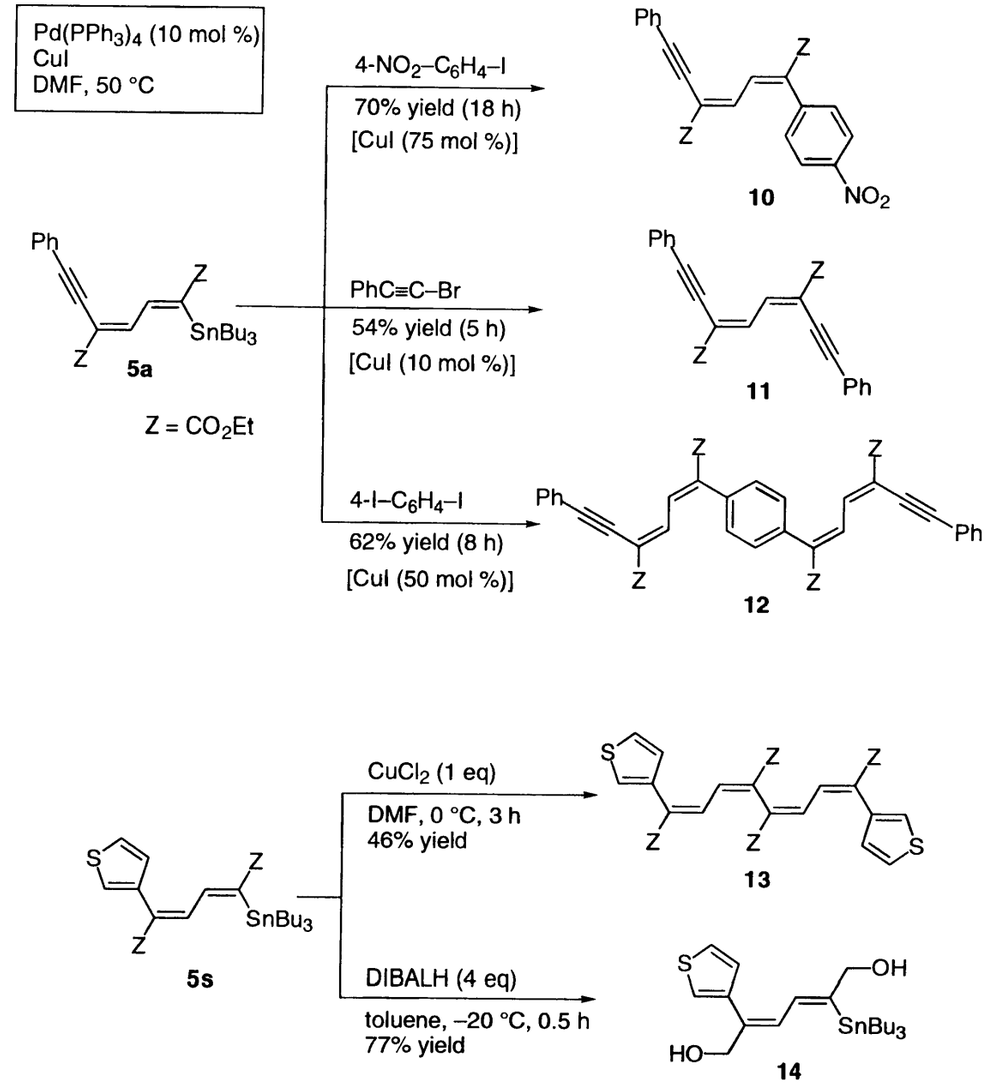
organostannane, resulting in the exclusive production of **5** irrespective of the organostannane used.



Scheme 7. Plausible catalytic cycle of the dimerization–carbostannylation.

Transformation of dimerization–carbostannylation products

Utility of the dimerization–carbostannylation reaction is demonstrated by transformation to more conjugated compounds through cross-coupling reaction (Scheme 8). Thus, cross-coupling reaction of **5a** with 4-iodonitrobenzene, bromo(phenyl)ethyne or 1,4-diiodobenzene in the presence of Pd(0)/CuI[13] gave **10**, **11** or **12**, respectively. Moreover, the π-conjugate system in **5s** could be extended by oxidative homocoupling reaction with $CuCl_2$ to afford **13** in 46% yield. Ester groups in **5s** could be reduced with diisobutylaluminum hydride to give stannyl-substituted allylic alcohol **14**.



Scheme 8. Transformation of dimerization–carbostannylation products.

Conclusion

The palladium–diimine complex has been disclosed to effectively catalyze the dimerization–carbostannylation of alkynes and give highly conjugated (*Z*)-alkenylstannanes stereoselectively. Furthermore, regio- and stereoselective dimerization–carbostannylation of ethyl propiolate has been achieved in the presence of a palladium complex coordinated by bulky diimine **2f**, providing a simple and convenient approach to stannyl-substituted muconic acid derivatives. The π-system of the dimerization–

carbostannylation products can be further extended to highly conjugated system through cross- or homocoupling reaction, proving that the dimerization–carbostannylation reaction offers a novel entry to the synthesis of various π-conjugated molecules.

Experimental section

Chemicals. The following compounds were prepared according to literature procedures: *N*-(2-Diphenylphosphinobenzylidene)-2-phenylethylamine (**1**),[14] bis(phenylimino)acenaphthene (**2a**),[15] bis[(4-trifluoromethylphenyl)imino]acenaphthene (**2b**),[15] bis[{3,5-bis(trifluoromethyl)phenyl}imino]acenaphthene (**2c**),[15] bis[(*p*-anisyl)imino]acenaphthene (**2d**),[15] bis[(*p*-tolyl)imino]acenaphthene (**2e**),[15] bis[(2,6-diisopropylphenyl)imino]acenaphthene (**2f**),[15] 2,3-bis(phenylimino)butane (**2g**),[16] tributyl(phenylethynyl)tin (**4a**),[17] tributyl(1-hexyn-1-yl)tin (**4b**),[17] tributyl(trimethylsilylethynyl)tin (**4c**),[17] tributyl(vinyl)tin (**4d**),[18] tributyl((*E*)-β-styryl)tin (**4e**),[19] tributyl((*E*)-1-octen-1-yl)tin (**4f**),[20] tributyl(2-furyl)tin (**4g**),[21] tributyl(2-thienyl)tin (**4h**),[22] 2-benzofuryl(tributyl)tin (**4i**),[23] tributyl(cinnamyl)tin (**4j**),[24] tributyl(phenyl)tin (**4k**),[25] tributyl(2-pyridyl)tin (**4l**),[26] *p*-anisyl(tributyl)tin (**4m**),[27] (*E*)-bis(tributylstannyl)ethene (**4n**),[28] tributyl(3-thienyl)tin (**4o**)[29] and *p*-anisyl(trimethyl)tin (**4'm**).[30]

Dimerization–Carbostannylation of Alkynes. ***A General Procedure.*** A solution of **2** (16.4 μmol), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (3.0 mg, 8.2 μmol) and an alkyne (1.03 mmol) in toluene (3 mL) was degassed by four freeze-thaw cycles. To this solution was added an organostannane (0.34 mmol), and the mixture was stirred at the specified temperature for the specified period indicated in Table 2 and Table 3. Concentration *in vacuo* followed by GPC purification gave the corresponding dimerization–carbostannylation products. Yields are listed in Table 2 and Table 3.

Diethyl (1*Z*,3*E*)-6-Phenyl-1-(tributylstannyl)hexa-1,3-dien-5-yne-1,4-dicarboxylate (5a). A brown oil, R_f 0.35 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.70–1.83 (m, 33 H), 4.24 (q, *J* = 7.2 Hz, 2 H), 4.32 (q, *J* = 7.2 Hz, 2 H), 7.15–7.74 (m, 6 H), 8.30 (d, *J* = 12.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.9, 13.6, 14.2, 14.3, 27.2, 28.9, 61.0, 61.8, 83.4, 100.8, 121.3, 122.6, 128.4, 129.0, 131.8, 144.3, 147.8, 153.0, 164.5, 171.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –42.8. Anal. Calcd for $C_{30}H_{44}O_4Sn$: C, 61.34; H, 7.55. Found: C, 61.60; H, 7.60.

Diethyl (1*Z*,3*E*)-1-(Tributylstannyl)deca-1,3-dien-5-yne-1,4-dicarboxylate (5b). A brown oil, R_f 0.38 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.72–1.72 (m, 40 H), 2.49 (t, *J* = 6.9 Hz, 2 H), 4.08–4.36 (m, 4 H), 7.53 (d, *J* = 11.9 Hz, 1 H), 8.17 (d, *J* = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.9, 13.59, 13.64, 14.2, 14.3, 19.6, 21.9, 27.2, 28.9, 30.5, 60.9, 61.6, 74.6, 102.8, 121.8, 143.6, 148.0, 151.8, 164.9, 171.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –43.3. Anal. Calcd for $C_{28}H_{48}O_4Sn$: C, 59.27; H, 8.53. Found: C, 59.12; H, 8.31.

Diethyl (1*Z*,3*E*)-1-(Tributylstannyl)-6-(trimethylsilyl)hexa-1,3-dien-5-yne-1,4-dicarboxylate (5c). A brown oil, R_f 0.43 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 0.71–1.73 (m, 33 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 7.59 (d, *J* = 12.1 Hz, 1 H), 8.18 (d, *J* = 12.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ –0.2, 11.9, 13.6, 14.1, 14.3, 27.2, 28.9, 61.0, 61.7, 98.1, 107.1, 121.1, 145.7, 147.7, 153.6, 164.3, 171.2; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –42.8. Anal. Calcd for $C_{27}H_{48}O_4SiSn$: C, 55.58; H, 8.29. Found: C, 55.66; H, 8.55.

Diethyl (1*Z*,3*E*)-1-(Tributylstannyl)hexa-1,3,5-triene-1,4-dicarboxylate (5d). A brown oil, R_f 0.38 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.82–1.74 (m, 33 H), 4.21 (q, *J* = 7.1 Hz, 2 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 5.54 (dd, *J* = 11.5, 1.6 Hz, 1 H), 5.74 (dd, *J* = 17.6, 1.6 Hz, 1 H), 6.71 (dd, *J* = 17.6, 11.5 Hz, 1 H), 7.24 (d, *J* = 12.7 Hz, 1 H), 8.15 (d, *J* = 12.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.6, 14.25, 14.29, 27.2, 29.0, 60.9, 61.0, 122.7, 128.9, 134.7, 136.9, 146.6, 149.7, 166.6, 171.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –44.4. Anal. Calcd for $C_{24}H_{42}O_4Sn$: C, 56.16; H, 8.25. Found: C, 56.01; H, 8.24.

Diethyl (1*Z*,3*E*)-1-(Tributylstannyl)hexa-1,3,5-triene-1,3-dicarboxylate (5'd). A brown oil, R_f 0.32 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.69–1.78 (m, 33 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 5.50 (d, *J* = 10.1 Hz, 1 H), 5.67 (d, *J* = 17.6, 1 H), 6.63 (ddd, *J* = 17.6, 11.2, 10.1 Hz, 1 H), 7.24 (d, *J* = 11.2 Hz, 1 H), 7.89 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 14.3, 27.3, 29.0, 60.9, 61.0, 126.5, 130.9, 132.9, 141.0, 144.2, 148.1, 166.3, 170.6;

^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –47.3. Anal. Calcd for $C_{24}H_{42}O_4Sn$: C, 56.16; H, 8.25. Found as a mixture of **5d** and **5'd**: C, 56.27; H, 8.22.

Diethyl (1*Z*,3*E*,5*E*)-6-Phenyl-1-(tributylstannyl)hexa-1,3,5-triene-1,4-dicarboxylate (5e). A brown oil, R_f 0.33 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.74–1.76 (m, 33 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 4.32 (q, *J* = 7.1 Hz, 2 H), 7.15–7.60 (m, 8 H), 8.29 (d, *J* = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.7, 14.3, 27.2, 29.0, 60.9, 61.1, 120.5, 127.0, 128.4, 128.6, 134.3, 136.1, 136.5, 137.0, 146.5, 149.3, 166.8, 171.5; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –44.1. Anal. Calcd for $C_{30}H_{46}O_4Sn$: C, 61.13; H, 7.87. Found: C, 60.87; H, 7.80.

Diethyl (1*Z*,3*E*,5*E*)-6-Phenyl-1-(tributylstannyl)hexa-1,3,5-triene-1,3-dicarboxylate (5'e). A brown oil, R_f 0.24 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.68–1.50 (m, 33 H), 4.26 (q, *J* = 7.1 Hz, 4 H), 6.95–7.02 (m, 2 H), 7.28–7.50 (m, 6 H), 8.00 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.4, 13.6, 14.3, 27.3, 29.0, 60.90, 60.95, 124.2, 127.4, 128.7, 129.2, 129.8, 136.0, 141.3, 141.5, 144.0, 148.6, 166.4, 170.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –47.3. Anal. Calcd for $C_{30}H_{46}O_4Sn$: C, 61.13; H, 7.87. Found as a mixture of **5e** and **5'e**: C, 61.35; H, 7.77.

Diethyl (1*Z*,3*E*,5*E*)-1-(Tributylstannyl)dodeca-1,3,5-triene-1,4-dicarboxylate (5f). A brown oil, R_f 0.47 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.74–1.77 (m, 44 H), 2.22 (q, *J* = 6.8 Hz, 2 H), 4.21 (q, *J* = 7.1 Hz, 2 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 6.21 (dt, *J* = 15.7, 6.8 Hz, 1 H), 6.40 (d, *J* = 15.7 Hz, 1 H), 7.11 (d, *J* = 11.9 Hz, 1 H), 8.17 (d, *J* = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.7, 13.6, 14.1, 14.2, 14.3, 22.6, 27.2, 28.89, 28.94, 29.0, 31.6, 33.9, 60.8, 60.9, 122.0, 134.8, 135.1, 140.7, 147.3, 147.7, 167.0, 171.5; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –45.0. Anal. Calcd for $C_{30}H_{54}O_4Sn$: C, 60.31; H, 9.11. Found as a mixture of **5f** and **5'f**: C, 60.30; H, 8.93.

Diethyl (1*Z*,3*E*,5*E*)-1-(Tributylstannyl)dodeca-1,3,5-triene-1,3-dicarboxylate (5'f). A brown oil, R_f 0.32 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.69–1.75 (m, 44 H), 2.17 (q, *J* = 6.8 Hz, 2 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 6.18 (dt, *J* = 15.2, 6.6 Hz, 1 H), 6.33 (dd, *J* = 15.2, 10.3

Hz, 1 H), 7.23 (d, J = 10.3 Hz, 1 H), 7.91 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 14.0, 14.3, 22.6, 27.3, 28.9, 29.0, 31.7, 33.5, 60.8, 126.6, 127.7, 141.7, 143.1, 146.4, 148.8, 166.6, 170.8; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –47.9. Anal. Calcd for $C_{30}H_{54}O_4Sn$: C, 60.31; H, 9.11. Found as a mixture of **5f** and **5'f**: C, 60.30; H, 8.93.

Diethyl (1*Z*,3*E*)-4-(2-Furyl)-1-(tributylstannyl)buta-1,3-diene-1,4-dicarboxylate (5g). A brown oil, R_f 0.30 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.73–1.75 (m, 33 H), 4.22 (q, J = 7.1 Hz, 2 H), 4.32 (q, J = 7.1 Hz, 2 H), 6.48 (dd, J = 3.5, 1.8 Hz, 1 H), 6.90 (d, J = 3.1 Hz, 1 H), 7.30 (d, J = 12.1 Hz, 1 H), 7.56 (dd, J = 1.8, 0.4 Hz, 1 H), 8.55 (d, J = 12.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.7, 14.3, 27.2, 29.0, 60.9, 61.4, 111.5, 114.4, 125.6, 135.6, 143.8, 148.5, 149.4, 151.3, 165.8; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –45.4. Anal. Calcd for $C_{26}H_{42}O_5Sn$: C, 56.44; H, 7.65. Found: C, 56.26; H, 7.75.

Diethyl (1*Z*,3*E*)-4-(2-Furyl)-1-(tributylstannyl)buta-1,3-diene-1,3-dicarboxylate (5'g). A brown oil, R_f 0.28 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.67–1.73 (m, 33 H), 4.247 (q, J = 7.1 Hz, 2 H), 4.254 (q, J = 7.1 Hz, 2 H), 6.44–6.54 (m, 1 H), 6.73 (d, J = 3.5 Hz, 1 H), 7.53 (d, J = 1.7 Hz, 1 H), 7.56 (d, J = 1.8 Hz, 1 H), 7.99 (d, J = 1.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 14.29, 14.32, 27.3, 29.0, 60.8, 61.2, 112.7, 117.0, 126.0, 128.1, 143.9, 145.1, 148.1, 151.0, 166.2, 171.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –46.1. Anal. Calcd for $C_{26}H_{42}O_5Sn$: C, 56.44; H, 7.65. Found: C, 56.22; H, 7.41.

Diethyl (1*E*,3*E*)-4-(2-Furyl)-1-(tributylstannyl)buta-1,3-diene-2,4-dicarboxylate (5"g). A brown oil, R_f 0.24 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.52–1.66 (m, 33 H), 4.16 (q, J = 7.0 Hz, 2 H), 4.18 (q, J = 7.1 Hz, 2 H), 6.41 (dd, J = 3.5, 1.8 Hz, 1 H), 6.62 (d, J = 3.5 Hz, 1 H), 7.44 (d, J = 1.7 Hz, 1 H), 7.57 (s, 1 H), 7.93 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.7, 13.6, 14.2, 14.3, 27.3, 28.9, 60.8, 61.0, 112.1, 115.8, 127.8, 128.0, 143.2, 144.6, 150.8, 151.8, 164.7, 166.9; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –57.7. Anal. Calcd for $C_{26}H_{42}O_5Sn$: C, 56.44; H, 7.65. Found as a mixture of **5g**, **5'g** and **5"g**: C, 56.59; H, 7.42.

Diethyl (1*Z*,3*Z*)-4-(2-Thienyl)-1-(tributylstannyl)buta-1,3-diene-1,4-dicarboxylate (5h). A brown oil, R_f 0.35 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.73–1.71 (m, 33 H), 4.19 (q, J = 7.1 Hz, 2 H), 4.32 (q, J = 7.1 Hz, 2 H), 7.07 (dd, J = 4.9, 3.5 Hz, 1 H), 7.15 (dd, J = 3.5, 1.3 Hz, 1 H), 7.46 (dd, J = 4.9, 1.3 Hz, 1 H), 7.52 (d, J = 11.6 Hz, 1 H), 8.07 (d, J = 11.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.7, 14.3, 27.2, 29.0, 60.9, 61.6, 126.6, 128.4, 130.7, 131.0, 134.7, 138.0, 148.0, 150.8, 166.4, 171.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –44.0. Anal. Calcd for $C_{26}H_{42}O_4SSn$: C, 54.85; H, 7.43. Found: C, 54.88; H, 7.57.

Diethyl (1*Z*,3*E*)-4-(2-Thienyl)-1-(tributylstannyl)buta-1,3-diene-1,3-dicarboxylate (5'h). A brown oil, R_f 0.28 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.65–1.76 (m, 33 H), 4.25 (q, J = 7.1 Hz, 2 H), 4.26 (q, J = 7.1 Hz, 2 H), 7.02–7.14 (m, 1 H), 7.33 (d, J = 3.3 Hz, 1 H), 7.48 (d, J = 5.1 Hz, 1 H), 7.87 (d, J = 1.7 Hz, 1 H), 8.00 (d, J = 1.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 14.3, 27.3, 29.0, 60.8, 61.2, 126.4, 127.5, 131.4, 133.3, 133.7, 138.5, 146.1, 147.9, 166.3, 170.8; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –45.7. Anal. Calcd for $C_{26}H_{42}O_4SSn$: C, 54.85; H, 7.43. Found: C, 54.95; H, 7.69.

Diethyl (1*E*,3*Z*)-4-(2-Thienyl)-1-(tributylstannyl)buta-1,3-diene-2,4-dicarboxylate (5"h). A brown oil, R_f 0.22 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.53–1.65 (m, 33 H), 4.20 (q, J = 7.1 Hz, 2 H), 4.22 (q, J = 7.1 Hz, 2 H), 6.99–7.07 (m, 1 H), 7.22–7.41 (m, 2 H), 7.93 (d, J = 0.6 Hz, 1 H), 8.11 (d, J = 0.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.8, 13.6, 14.2, 14.3, 27.3, 29.0, 60.9, 127.0, 128.1, 130.3, 133.4, 134.0, 138.4, 142.7, 156.0, 164.5, 166.9; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –58.1. Anal. Calcd for $C_{26}H_{42}O_4SSn$: C, 54.85; H, 7.43. Found: C, 54.57; H, 7.18.

Tetramethyl (1*E*,3*Z*)-6-Phenyl-1-(tributylstannyl)hexa-1,3-dien-5-yne-1,2,3,4-tetracarboxylate (5i). A brown oil, R_f 0.39 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR ($CDCl_3$) δ 0.73–1.83 (m, 27 H), 3.71 (s, 3 H), 3.77 (s, 3 H), 3.86 (s, 3 H), 3.93 (s, 3 H), 7.16–7.65 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.1, 13.5, 27.2, 28.6, 51.6, 52.7, 53.2, 84.1, 104.9, 121.4, 128.4, 129.5, 129.9, 132.0, 132.5, 135.0,

137.1, 161.0, 163.0, 164.7, 172.5; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –26.1. Anal. Calcd for $C_{32}H_{44}O_8Sn$: C, 56.91; H, 6.57. Found: C, 56.92; H, 6.63.

Tetramethyl (1*E*,3*Z*)-1-(Tributylstannyl)deca-1,3-dien-5-yne-1,2,3,4-tetracarboxylate (5j). A brown oil, R_f 0.45 (hexane–ethyl acetate = 2 : 1). ^1H NMR ($CDCl_3$) δ 0.71–1.72 (m, 34 H), 2.32 (t, *J* = 7.1 Hz, 2 H), 3.68 (s, 3 H), 3.71 (s, 3 H), 3.77 (s, 3 H), 3.83 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 12.4, 13.5, 13.7, 19.7, 22.0, 27.2, 28.8, 30.1, 51.4, 52.5, 52.9, 75.3, 105.8, 127.9, 135.8, 136.0, 162.4, 164.9, 165.5, 166.7, 171.2; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –35.0. Anal. Calcd for $C_{30}H_{48}O_8Sn$: C, 54.98; H, 7.38. Found: C, 55.04; H, 7.46.

Tetramethyl (1*E*,3*Z*)-1-(Tributylstannyl)-6-(trimethylsilyl)hexa-1,3-dien-5-yne-1,2,3,4-tetracarboxylate (5k). A brown oil, R_f 0.62 (hexane–ethyl acetate = 2 : 1). ^1H NMR ($CDCl_3$) δ 0.19 (s, 9 H), 0.81–1.73 (m, 27 H), 3.70 (s, 3 H), 3.75 (s, 3 H), 3.80 (s, 3 H), 3.88 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ –0.7, 11.1, 13.6, 27.2, 28.6, 51.4, 52.5, 52.7, 53.1, 97.7, 112.3, 129.0, 134.7, 139.2, 160.6, 162.5, 164.4, 172.3; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –27.4. Anal. Calcd for $C_{29}H_{48}O_8SiSn$: C, 51.87; H, 7.21. Found: C, 51.86; H, 7.00.

Tetramethyl (1*E*,3*Z*)-1-(Tributylstannyl)hexa-1,3,5-triene-1,2,3,4-tetracarboxylate (5l). A brown oil, R_f 0.42 (hexane–ethyl acetate = 2 : 1). ^1H NMR ($CDCl_3$) δ 0.80–1.82 (m, 27 H), 3.70 (s, 3 H), 3.74 (s, 3H), 3.83 (s, 3 H), 3.92 (s, 3 H), 5.54 (d, *J* = 17.4 Hz, 1 H), 5.60 (d, *J* = 10.8 Hz, 1 H), 6.96 (dd, *J* = 17.4, 10.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.6, 27.2, 28.6, 51.7, 52.5, 52.7, 125.2, 127.6, 130.9, 134.6, 145.5, 161.1, 163.3, 165.2, 167.4, 172.4; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –26.5. Anal. Calcd for $C_{26}H_{42}O_8Sn$: C, 51.93; H, 7.04. Found: C, 51.82; H, 7.11.

Tetramethyl (1*E*,3*Z*,5*E*)-6-Phenyl-1-(tributylstannyl)hexa-1,3,5-triene-1,2,3,4-tetracarboxylate (5m). A brown oil, R_f 0.40 (hexane–ethyl acetate = 2 : 1). ^1H NMR ($CDCl_3$) δ 0.70–1.58 (m, 27 H), 3.69 (s, 3 H), 3.73 (s, 3 H), 3.85 (s, 3 H), 3.97 (s, 3 H), 6.75 (d, *J* = 16.2 Hz, 1 H), 6.96 (d, *J* = 16.2 Hz, 1 H), 7.20–7.54 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.5, 27.1, 28.6, 51.7, 52.4, 52.6, 52.7,

122.0, 126.4, 127.7, 128.8, 129.7, 134.9, 135.2, 139.5, 145.9, 161.3, 163.5, 165.4, 168.0, 172.6; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –30.3. Anal. Calcd for $C_{32}H_{46}O_8Sn$: C, 56.74; H, 6.84. Found: C, 56.62; H, 7.04.

Tetramethyl (1*E*,3*Z*,5*E*)-1-(Tributylstannyl)dodeca-1,3,5-triene-1,2,3,4-tetracarboxylate (5n). A brown oil, R_f 0.46 (hexane–ethyl acetate = 2 : 1). ^1H NMR ($CDCl_3$) δ 0.78–1.64 (m, 38 H), 2.16 (q, *J* = 7.0 Hz, 2 H), 3.67 (s, 3 H), 3.70 (s, 3 H), 3.81 (s, 3 H), 3.89 (s, 3 H), 6.00 (dt, *J* = 15.9, 6.8 Hz, 1 H), 6.23 (d, *J* = 15.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.6, 14.0, 22.5, 27.2, 28.5, 28.6, 28.9, 31.5, 33.7, 51.6, 52.3, 52.4, 52.6, 124.5, 134.9, 144.6, 146.1, 160.7, 163.5, 165.5, 168.0, 172.5; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –27.7. Anal. Calcd for $C_{32}H_{54}O_8Sn$: C, 56.07; H, 7.94. Found: C, 55.88; H, 7.98.

Tetramethyl (1*E*,3*Z*)-4-(2-Furyl)-1-(tributylstannyl)buta-1,3-diene-1,2,3,4-tetracarboxylate (5o). A white powder, mp 86–88 °C. ^1H NMR ($CDCl_3$) δ 0.67–1.49 (m, 27 H), 3.67 (s, 3 H), 3.76 (s, 3 H), 3.85 (s, 3 H), 3.97 (s, 3 H), 6.49 (dd, *J* = 3.7, 1.8 Hz, 1 H), 6.79 (dd, *J* = 3.7, 0.7 Hz, 1 H), 7.53 (dd, *J* = 1.8, 0.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.6, 13.6, 27.2, 28.5, 51.6, 52.6, 52.9, 112.8, 117.6, 122.9, 135.1, 136.0, 145.6, 148.0, 159.5, 163.4, 165.5, 166.6, 172.8; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –29.3. Anal. Calcd for $C_{28}H_{42}O_9Sn$: C, 52.44; H, 6.60. Found: C, 52.25; H, 6.73.

Tetramethyl (1*E*,3*Z*)-4-(2-Benzofuryl)-1-(tributylstannyl)buta-1,3-diene-1,2,3,4-tetracarboxylate (5p). A brown oil, R_f 0.38 (hexane–ethyl acetate = 2 : 1). ^1H NMR ($CDCl_3$) δ 0.64–1.40 (m, 27 H), 3.69 (s, 3 H), 3.79 (s, 3 H), 3.89 (s, 3 H), 4.02 (s, 3 H), 7.07 (d, *J* = 0.9 Hz, 1 H), 7.17–7.64 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 10.6, 13.4, 27.1, 28.5, 51.6, 52.7, 52.8, 53.1, 111.9, 113.5, 122.1, 123.7, 125.9, 127.1, 127.5, 135.2, 136.1, 147.3, 149.4, 155.5, 159.0, 163.4, 165.4, 172.8; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –28.7. Anal. Calcd for $C_{32}H_{44}O_9Sn$: C, 55.59; H, 6.41. Found: C, 55.30; H, 6.55.

Tetramethyl (1*E*,3*Z*,6*E*)-7-Phenyl-1-(tributylstannyl)hepta-1,3,6-triene-1,2,3,4-tetracarboxylate (5q). A brown oil, R_f 0.65 (hexane–ethyl acetate

= 2 : 1). ^{1}H NMR ($CDCl_3$) δ 0.82–1.67 (m, 27 H), 3.03–3.43 (m, 2 H), 3.60 (s, 3 H), 3.73 (s, 3 H), 3.82 (s, 3 H), 3.83 (s, 3 H), 6.04 (dt, *J* = 15.7, 7.0 Hz, 1 H), 6.43 (d, *J* = 15.7 Hz, 1 H), 7.14–7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.0, 13.5, 27.2, 28.6, 35.6, 51.6, 52.3, 52.45, 52.54, 122.7, 126.2, 127.5, 128.4, 130.3, 133.5, 135.0, 136.8, 145.4, 159.7, 163.3, 165.4, 168.6, 172.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –28.3. Anal. Calcd for $C_{33}H_{48}O_8Sn$: C, 57.32; H, 7.00. Found: C, 57.07; H, 7.27.

Diethyl (1*Z*,3*E*)-4-(2-Benzofuryl)-1-(tributylstannyl)buta-1,3-diene-1,4-dicarboxylate (5r). A brown oil, R_f 0.41 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.68–1.75 (m, 33 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 4.36 (q, *J* = 7.1 Hz, 2 H), 7.15–7.70 (m, 6 H), 8.69 (d, *J* = 12.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.9, 13.7, 14.3, 27.2, 29.0, 61.0, 61.6, 110.7, 111.3, 121.7, 123.1, 125.4, 125.7, 128.2, 138.4, 148.1, 153.2, 155.1, 165.6, 165.7, 174.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –45.0. Anal. Calcd for $C_{30}H_{44}O_5Sn$: C, 59.72; H, 7.35. Found: C, 59.98; H, 7.41.

Diethyl (1*Z*,3*E*)-4-(3-Thienyl)-1-(tributylstannyl)buta-1,3-diene-1,4-dicarboxylate (5s). A brown oil, R_f 0.37 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.74–1.67 (m, 33 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 4.29 (q, *J* = 7.1 Hz, 2 H), 7.13 (dd, *J* = 4.5, 1.8 Hz, 1 H), 7.29–7.36 (m, 2 H), 7.50 (d, *J* = 11.7 Hz, 1 H), 7.91 (d, *J* = 11.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.7, 14.3, 27.2, 29.0, 60.9, 61.3, 124.8, 126.9, 129.6, 133.0, 134.1, 138.1, 148.0, 150.1, 166.7, 171.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –44.2. Anal. Calcd for $C_{26}H_{42}O_4SSn$: C, 54.85; H, 7.43. Found: C, 54.84; H, 7.72.

Diethyl (1*Z*,3*E*)-4-Phenyl-1-(trimethylstannyl)buta-1,3-diene-1,4-dicarboxylate (5t). A brown oil, R_f 0.26 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 9 H), 1.25 (t, *J* = 7.1 Hz, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 4.27 (q, *J* = 7.1 Hz, 2 H), 7.17–7.45 (m, 5 H), 7.65 (d, *J* = 11.9 Hz, 1 H), 7.72 (d, *J* = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ –6.7, 14.2, 60.9, 61.3, 128.0, 128.3, 130.3, 134.0, 137.8, 138.9, 148.1, 149.5, 166.9, 170.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –38.1. Anal. Calcd for $C_{19}H_{26}O_4Sn$: C, 52.21; H, 6.00. Found: C, 52.41; H, 6.07.

Diethyl (1*Z*,3*E*)-4-(4-Methoxyphenyl)-1-(trimethylstannyl)buta-1,3-diene-1,4-dicarboxylate (5u). A brown oil, R_f 0.17 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 9 H), 1.25 (t, *J* = 7.1 Hz, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H), 3.83 (s, 3 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 6.91 (d, *J* = 8.6 Hz, 2 H), 7.19 (d, *J* = 8.6 Hz, 2 H), 7.60 (d, *J* = 11.9 Hz, 1 H), 7.77 (d, *J* = 11.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ –6.8, 14.1, 55.2, 60.8, 61.2, 113.4, 126.2, 131.6, 137.0, 138.4, 148.5, 148.6, 159.6, 167.1, 170.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –38.5. Anal. Calcd for $C_{20}H_{28}O_5Sn$: C, 51.42; H, 6.04. Found: C, 51.67; H, 6.12.

Dimerization–Carbostannylation of Alkynes with (*E*)-1,2-Bis(tributylstannyl)ethene. A solution of bis(phenylimino)acenaphthene (**2a**) (5.5 mg, 16.4 μmol), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (3.0 mg, 8.2 μmol) and an alkyne (1.03 mmol) in toluene (3 mL) was degassed by four freeze-thaw cycles. To this solution was added (*E*)-1,2-bis(tributylstannyl)ethene (**4n**) (0.104 g, 0.172 mmol), and the mixture was stirred at 50 °C. After the time specified in eq 1, the solvent was evaporated. GPC purification of the residue gave the corresponding dimerization–carbostannylation product.

Tetraethyl (1*Z*,3*E*,5*E*,7*E*,9*Z*)-1,10-Bis(tributylstannyl)deca-1,3,5,7,9-pentaene-1,4,7,10-tetracarboxylate (7a). A brown oil, R_f 0.69 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR ($CDCl_3$) δ 0.74–1.81 (m, 66 H), 4.20 (q, *J* = 7.1 Hz, 4 H), 4.31 (q, *J* = 7.1 Hz, 4 H), 7.26 (d, *J* = 12.1 Hz, 2 H), 7.32 (s, 2 H), 8.17 (d, *J* = 12.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 11.8, 13.7, 14.25, 14.29, 27.2, 29.0, 60.9, 61.2, 127.8, 134.0, 138.0, 145.9, 151.0, 166.5, 171.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –44.0. Anal. Calcd for $C_{46}H_{80}O_8Sn_2$: C, 55.33; H, 8.08. Found: C, 55.35; H, 7.88.

Octamethyl (1*E*,3*Z*,5*E*,7*Z*,9*E*)-1,10-Bis(tributylstannyl)deca-1,3,5,7,9-pentaene-1,2,3,4,7,8,9,10-octacarboxylate (7b). A white powder, mp 91–92 °C. ^{1}H NMR ($CDCl_3$) δ 0.69–1.93 (m, 54 H), 3.67 (s, 6 H), 3.73 (s, 6 H), 3.82 (s, 6 H), 3.94 (s, 6 H), 6.54 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 13.6, 27.1, 28.6, 51.6, 52.6, 52.7, 52.8, 130.7, 131.9, 134.3, 144.5, 162.1, 162.9, 164.8,

166.5, 172.1; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ –25.9. Anal. Calcd for $C_{50}H_{80}O_{16}Sn_2$: C, 51.13; H, 6.86. Found: C, 50.93; H, 6.89.

Cross-coupling of 5a with 4-iodonitrobenzene. A solution of **5a** (50 mg, 85 μmol) in DMF (1.5 mL) was degassed by three freeze-thaw cycles. To this solution was added 4-iodonitrobenzene (21 mg, 85 μmol), $Pd(PPh_3)_4$ (9.8 mg, 8.5 μmol) and CuI (12.2 mg, 64 μmol). The mixture was stirred at 50 °C for 18 h and then diluted with diethyl ether (25 mL). The organic layer was separated, washed with water, dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was diluted with diethyl ether (10 mL) and stirred for 30 min with a 1 M KF aqueous solution (2 mL). Filtration through a Celite plug was followed by extraction with diethyl ether (20 mL). The organic layer was washed successively with water and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave diethyl (1*E*,3*E*)-1-(4-nitrophenyl)-6-phenylhexa-1,3-dien-5-yne-1,4-dicarboxylate (**10**) (25 mg, 70% yield) as a yellow powder: mp 147–149 °C. ^1H NMR ($CDCl_3$) δ 1.26 (t, J = 7.1 Hz, 3 H), 1.27 (t, J = 7.1 Hz, 3 H), 4.21 (q, J = 7.1 Hz, 2 H), 4.24 (q, J = 7.1 Hz, 2 H), 7.09–7.75 (m, 8 H), 8.11 (d, J = 12.3 Hz, 1 H), 8.22 (d, J = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.09, 14.13, 61.9, 62.1, 83.4, 102.1, 122.2, 123.3, 123.5, 128.5, 129.4, 131.3, 131.9, 136.5, 137.5, 138.9, 140.9, 147.8, 164.0, 165.6. HRMS (ESI) Calcd for $C_{24}H_{21}NO_6Na$: M^++Na, 442.1261. Found: *m/z* 442.1261.

Cross-coupling of 5a with Bromo(phenyl)ethyne. A solution of **5a** (65 mg, 0.111 mmol) in DMF (1.5 mL) was degassed by three freeze-thaw cycles. To this solution was added 1-bromo-2-phenylethyne (20 mg, 0.110 mmol), $Pd(PPh_3)_4$ (12.7 mg, 11.0 μmol) and CuI (2.1 mg, 11.0 μmol). The mixture was stirred at 50 °C for 5 h and then diluted with diethyl ether (25 mL). The organic layer was washed with water and dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was diluted with diethyl ether (10 mL) and stirred for 30 min with a 1 M KF aqueous solution (2 mL). Filtration through a Celite plug was followed by extraction with diethyl ether (20 mL). The organic layer was washed successively with water and brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC

gave diethyl (3*E*,5*E*)-1,8-diphenylocta-3,5-diene-1,7-diyne-3,6-dicarboxylate (**11**) (24 mg, 54% yield) as a red powder: mp 112–114 °C. ^1H NMR ($CDCl_3$) δ 0.91 (t, J = 7.1 Hz, 6 H), 4.02 (q, J = 7.1 Hz, 4 H), 6.82 (s, 2 H), 7.13–7.45 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 13.8, 60.5, 117.3, 125.4, 127.8, 129.2, 131.2, 154.4, 154.8, 165.1. HRMS (ESI) Calcd for $C_{26}H_{22}O_4Na$: M^++Na, 421.1410. Found: *m/z* 421.1414.

Cross-coupling of 5a with 1,4-diiodobenzene. A solution of **5a** (48 mg, 81 μmol) in DMF (1.5 mL) was degassed by three freeze-thaw cycles. To this solution was added 1,4-diiodobenzene (13.5 mg, 41 μmol), $Pd(PPh_3)_4$ (9.4 mg, 8.1 μmol) and CuI (7.7 mg, 41 μmol). The mixture was stirred at 50 °C for 8 h and then diluted with diethyl ether (25 mL). The organic layer was washed with water, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. The residue was diluted with diethyl ether (10 mL) and stirred for 30 min with a 1 M KF aqueous solution (2 mL). Filtration through a Celite plug was followed by extraction with diethyl ether (20 mL). The organic layer was washed successively with water and brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave 1,4-bis[(1*E*,3*E*)-1,4-bis(ethoxycarbonyl)-6-phenylhexa-1,3-dien-5-yn-1-yl]benzene (**12**) (17.0 mg, 62% yield) as an orange powder: mp 164–167 °C. ^1H NMR ($CDCl_3$) δ 1.33 (t, J = 7.2 Hz, 6 H), 1.36 (t, J = 7.1 Hz, 6 H), 4.29 (q, J = 7.2 Hz, 4 H), 4.33 (q, J = 7.1 Hz, 4 H), 7.15–7.73 (m, 16 H), 8.12 (d, J = 12.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 14.2, 61.6, 61.9, 83.8, 101.3, 122.1, 122.5, 128.4, 129.1, 130.1, 131.8, 134.5, 135.2, 139.2, 140.6, 164.3, 166.6. HRMS (ESI) Calcd for $C_{42}H_{38}O_8Na$: M^++Na, 693.2459. Found: *m/z* 693.2464.

Homocoupling of 5s. To a solution of **5s** (29 mg, 52 μmol) in DMF (1.0 mL) was added $CuCl_2$ (6.9 mg, 52 μmol), and the mixture was stirred at 0 °C for 3 h. Saturated aqueous NH_4Cl–NH_3 (pH 8, 2 mL) was added, and the mixture was stirred under an aerial atmosphere until the color became deep blue. The mixture was extracted with diethyl ether (10 mL). The ethereal layer was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave tetraethyl (1*E*,3*E*,5*E*,7*E*)-1,8-bis(3-thienyl)-octa-1,3,5,7-tetraene-1,4,5,8-

tetracarboxylate (**13**) (6.6 mg, 46% yield) as a yellow oil: R_f 0.37 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR ($CDCl_3$) δ 1.24 (t, *J* = 7.1 Hz, 12 H), 4.22 (q, *J* = 7.1 Hz, 8 H), 7.12–7.48 (m, 8 H), 7.67 (d, *J* = 11.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 14.1, 14.2, 61.4, 61.5, 125.2, 127.6, 129.5, 132.5, 133.5, 134.1, 135.0, 138.2, 165.8, 166.2. Anal. Calcd for $C_{28}H_{30}O_8S_2$: C, 60.20; H, 5.41. Found: C, 60.04; H, 5.65.

Reduction of 5s. To a solution of **5s** (18.8 mg, 33 μmol) in toluene (1.0 mL) was added diisobutylaluminum hydride (0.9 M in hexanes, 0.150 mL, 0.135 mmol), and the mixture was stirred at –20 °C for 30 min. Saturated aqueous NH_4Cl (3 mL) was added, and the resulting mixture was extracted with ethyl acetate (10 mL). The organic layer was separated, dried over anhydrous magnesium sulfate, and concentrated *in vacuo*. GPC purification of the residue gave (2*Z*,4*E*)-5-(3-thienyl)-2-(tributylstannyl)hexa-2,4-diene-1,6-diol (**14**) (12.0 mg, 77%) as a yellow oil: R_f 0.51 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR ($CDCl_3$) δ 0.74–1.75 (m, 27 H), 4.28 (d, *J* = 4.8 Hz, 2 H), 4.41 (d, *J* = 5.5 Hz, 2 H), 6.32 (d, *J* = 11.0 Hz, 1 H), 7.00–7.44 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 10.5, 13.7, 27.3, 29.2, 67.7, 70.3, 123.8, 125.4, 128.2, 135.9, 136.7, 138.1, 152.6; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ –52.3. Anal. Calcd for $C_{22}H_{38}O_2SSn$: C, 54.45; H, 7.89. Found: C, 54.43; H, 7.61.

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Chapter 4

Nickel(0)-Catalyzed Carbostannylation of Alkynes with Allyl-, Acyl- and Alkynylstannanes

A Ni(0) complex catalyzes the carbostannylation of allyl-, acyl- and alkynylstannanes towards a wide variety of alkynes with an exclusive *syn*-stereochemistry and high regioselectivities. The resulting alkenylstannanes serve as versatile precursors of variously substituted ethenes. For example, tri-substituted vinylstannanes prepared by the carbostannylation of internal alkynes were transformed to tetra-substituted ethenes by palladium-catalyzed cross-coupling reaction.

Introduction

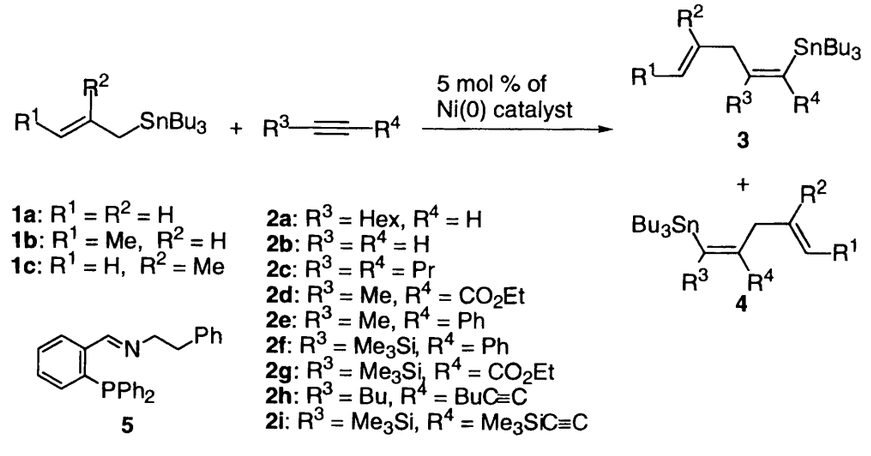
Carbostannylation of internal alkynes should be one of the most useful tools for stereoselective synthesis of olefins, since the resulting tri-substituted vinylstannanes are readily converted into various tetra-substituted ethenes via many kinds of synthetic transformations.[1] However, limited number of reports have been available on this synthetic subject.[1b,2] Although allylstannanes are demonstrated to add to terminal alkynes with *anti*-selectivity using a Lewis acid catalyst,[3] internal alkynes are not applicalble. *Anti*-selective allylstannylation of alkynes is mediated also by radical initiator AIBN to give a mixture of stereo- and regioisomers,[4] the internal alkynes being restricted to relatively electron-deficient ones. Whereas the palladium–iminophosphine-catalyzed alkynylstannylation of alkynes proceeds with exclusive *syn*-selectivity and acceptable regioselectivity, scope of the reaction is limited to alkynylstannanes and relatively electron-deficient alkynes. In this Chapter, the author describes nickel-catalyzed carbostannylation of alkynes that has following superb features: (1) A nickel(0) complex mediates the reaction of even relatively electron-rich internal alkynes, (2) the reaction is applicable not only to alkynylstannanes but also to acyl- and allylstannanes, (3) *syn*-selectivity results also in allylstannylation of alkynes and (4) regioselectivities are much higher than the palladium-catalyzed alkynylstannylation discussed in Chapter 2.

Results and Discussion

Nickel-catalyzed allylstannylation of alkynes

Catalytic activity of various nickel complexes was first compared in the reaction of allyl(tributyl)tin (**1a**, $R^1 = R^2 = H$) with 1-octyne (**2a**, R^3 = hexyl, $R^4 = H$) (Scheme 1). Conversion of **1a** and ratio of allylstannylation products **3a** and **4a** were readily monitored by ^{119}Sn NMR. Results obtained by the reaction carried out at 80 °C for 1 h are summarized in Table 1. As readily seen, reaction with 5 mol % of bis(1,5-cyclooctadiene)nickel(0), $Ni(cod)_2$, in toluene gave a 68 : 32 mixture of **3a** and **4a** in 85% conversion (entry 1). Polar solvents accelerated the reaction at the slight expense of regioselectivity (entries 2–4). Octane or pyridine as a solvent retarded the reaction

(entries 5 and 6). Use of triphenylphosphine (10 mol %) or *N*-(2-diphenylphosphinobenzylidene)-2-phenylethylamine (**5**) (5 mol %), an efficient ligand for the palladium-catalyzed alkynylstannylation of alkynes, inhibited the reaction .



Scheme 1. Nickel-catalyzed allylstannylation of alkynes.

Table 1. Nickel-catalyzed carbostannylation of 1-octyne (**2a**) with allyl(tributyl)tin (**1a**)[a]

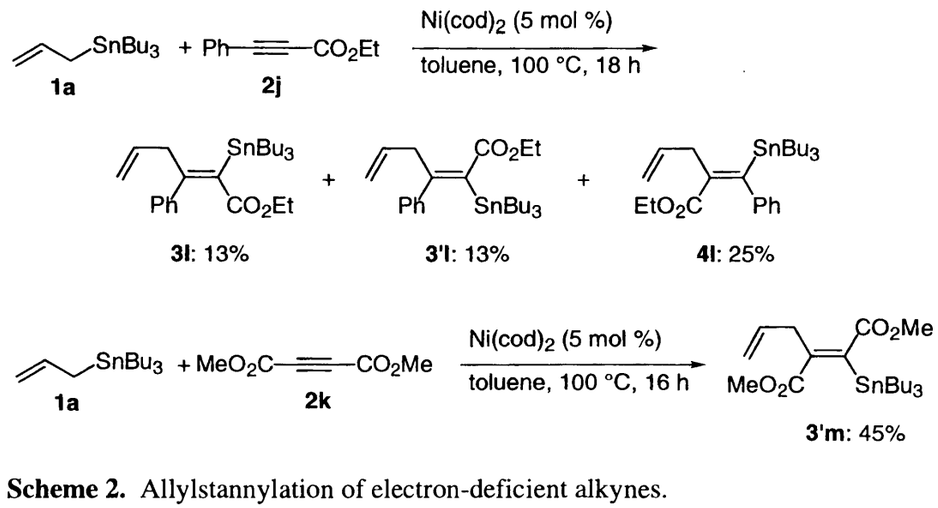
entry	solvent	conversion (%)[b]	**3a** : **4a**[b]
1	toluene	85	68 : 32
2	DMF	92	58 : 42
3	DME	91	60 : 40
4	1,4-dioxane	85	65 : 35
5	octane	70	58 : 42
6	pyridine	20	60 : 40

[a] The reaction was carried out in a solvent (0.3 mL) at 80 °C using allyl(tributyl)tin (0.46 mmol) and 1-octyne (1.38 mmol) for 1 h in the presence of $Ni(cod)_2$ (23 μmol). [b] Determined by ^{119}Sn NMR.

The allylstannylation with $Ni(cod)_2$ catalyst in toluene was next applied to various alkynes to afford a wide variety of 1,4-pentadienylstannanes with excellent regio- and stereoselectivity (Scheme 1 and Table 2). Whereas acetylene (**2b**) also reacted with **1a** in a good yield (entry 2), phenylacetylene and ethyl propiolate did not give significant amounts of carbostannylation products due to competitive self-polymerization of the alkynes. In contrast, internal alkynes gave good yields of corresponding carbostannylation products, irrespective of electron-withdrawing or -donating character of substituent R^3 and/or R^4 (entries 3–9). Furthermore, a single regioisomer formed in the reaction of unsymmetrical internal alkynes except for ethyl 2-butynoate (**2d**). The regioselectivity is proved to be extremely sensitive to the kind of R^3 and/or R^4: Bu_3Sn invariably adds to the carbon having a more electron-withdrawing group. Crotyltin (**1b**) added to 1-phenyl-1-propyne (**2e**) without any allylic rearrangement (entry 10). Methallyltin (**1c**) also gave the corresponding carbostannylation product (entry 11).

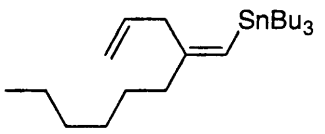
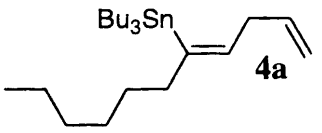
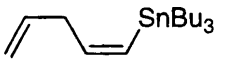
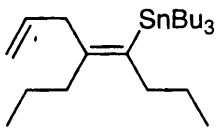
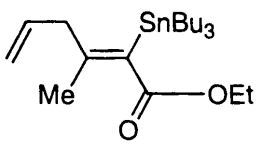
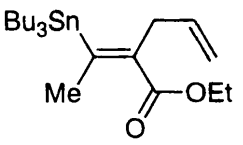
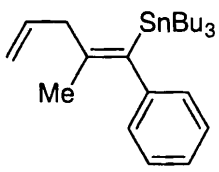
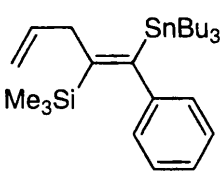
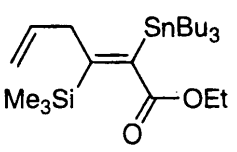
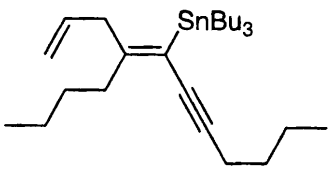
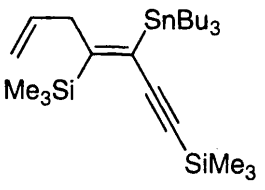
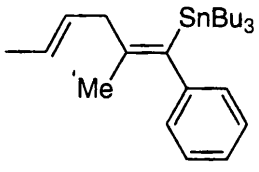
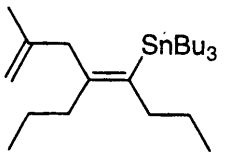
Thus, the allylstannylation has been demonstrated to be extremely useful for the construction of a 1,4-pentadiene system, widely found in naturally occurring terpenoids.

In contrast to the exclusive *syn*-selectivity for the above alkynes, reaction of ethyl phenylpropiolate (**2j**) with **1a** afforded a mixture of three isomeric products, including *anti*-adduct **3'l**. Furthermore, dimethyl acetylenedicarboxylate (**2k**) reacted with **1a** to afford solely *anti*-adduct **3'm** (Scheme 2).



Scheme 2. Allylstannylation of electron-deficient alkynes.

Table 2. Nickel-catalyzed allylstannylation of alkynes[a]

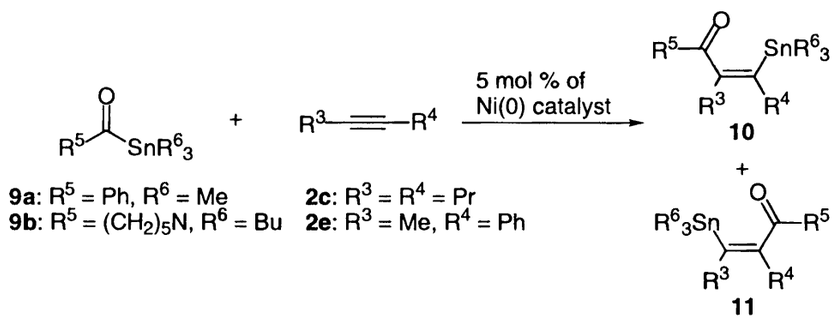
entry	allyl-stannane	alkyne	temp (°C)	time (h)	yield (%)[b]	product(s)				ratio (**3** : **4**)[c]
1	**1a**	**2a**	80	5	93		**3a**		**4a**	64 : 36
2[d]	**1a**	**2b**	80	14	80		**3b**			–
3	**1a**	**2c**	80	0.5	77		**3c**			–
4	**1a**	**2d**	100	12	78		**3d**		**4d**	65 : 35
5	**1a**	**2e**	100	12	77		**3e**			>99 : 1
6	**1a**	**2f**	100	14	76		**3f**			>99 : 1
7	**1a**	**2g**	100	40	78		**3g**			>99 : 1
8	**1a**	**2h**	100	14	64		**3h**			>99 : 1
9	**1a**	**2i**	100	8	70		**3i**			>99 : 1
10	**1b**	**2e**	100	14	64		**3j**			>99 : 1
11	**1c**	**2c**	80	3	87		**3k**			–

[a] The reaction was carried out in toluene (0.3 mL) using an organostannane (0.46 mmol), an alkyne (1.4 mmol) and $Ni(cod)_2$ (23 μmol). [b] Isolated yield based on the organostannane. [c] Determined by ^{119}Sn NMR. [d] The reaction was carried out under an acetylene atmosphere (1 atm).

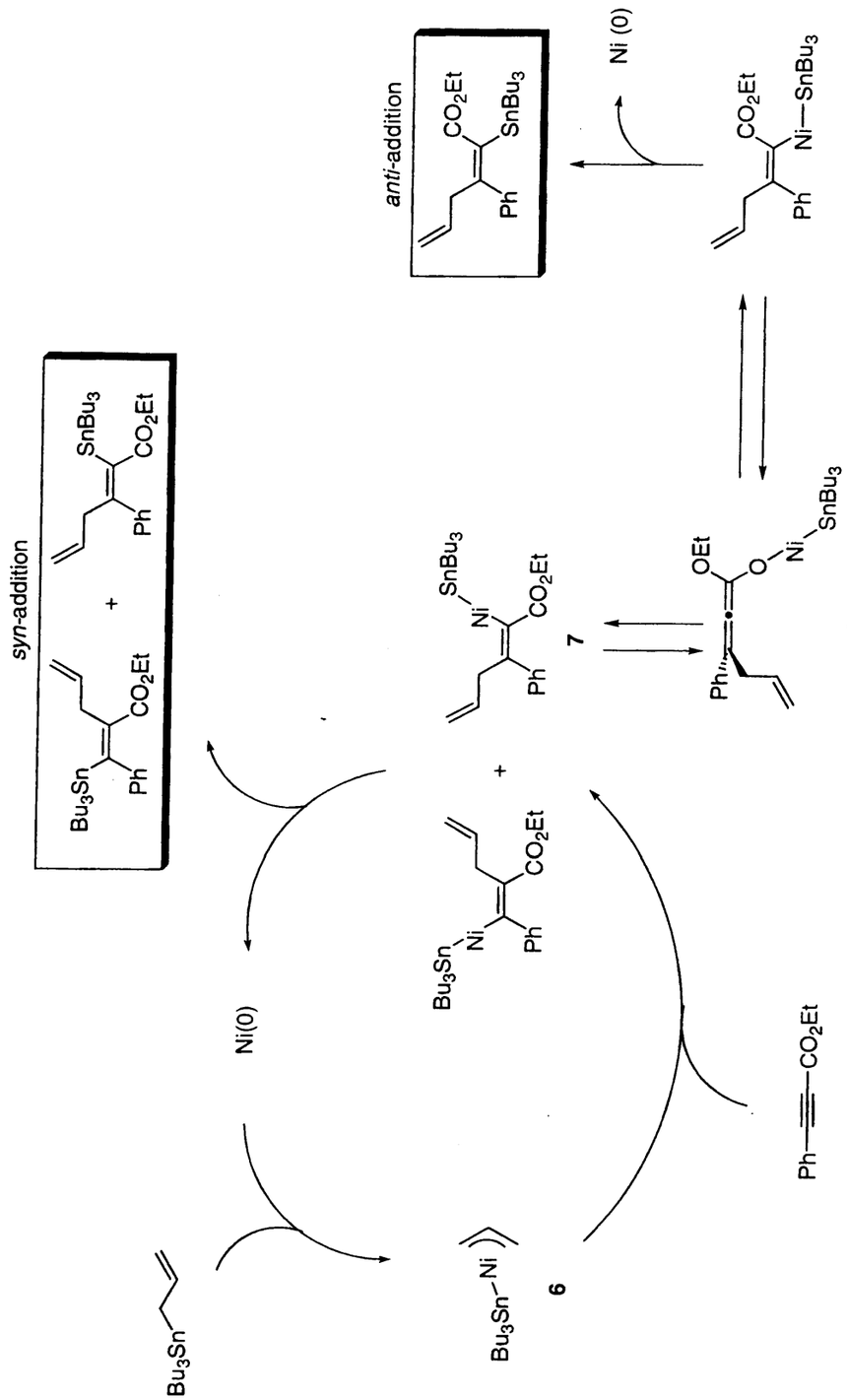
On the basis of these observation, a plausible catalytic cycle of the allylstannylation is depicted in Scheme 3. In a manner similar to the palladium–iminophosphine-catalyzed alkynylstannylation, oxidative addition of an allylstannane to a Ni(0) complex should be an initiation step of the reaction. Insertion of an alkyne into a C–Ni bond (carbonickelation) of **6** is followed by reductive elimination to provide *syn*-allylstannylation products. The *anti*-allylstannylation observed in the reaction of alkynes **2j** and **2k** can be rationalized by isomerization of alkenylnickel complex **7** to **7'** via ketene acetal intermediate **8** before reductive elimination, which should be retarded by electron-withdrawing substituents on the alkynes. Although evidences to support the mechanism remain yet to be detected, this catalytic cycle rationally explain the overall results.

Acylstannylation of alkynes catalyzed by Ni(cod)$_2$

The nickel catalyst was also effective for acylstannylation of alkynes. For example, benzoyl(trimethyl)tin (**9a**) and tributyl(piperidinocarbonyl)tin (**9b**) reacted with 4-octyne (**2c**) or 1-phenyl-1-propyne (**2e**) stereoselectively with Ni(cod)$_2$, giving (*Z*)-β-stannyl-α,β-unsaturated carbonyl compounds (Scheme 4 and Table 3). α,β-Unsaturated carbonyl compounds thus obtained are synthetic intermediates useful for Michael addition. To the best of the author's knowledge, the present reaction is the first demonstration that an acylmetal can participate in the carbometalation reaction.

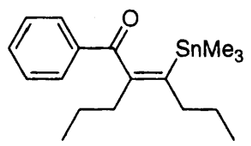
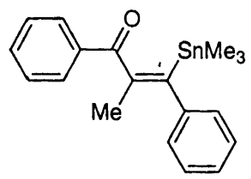
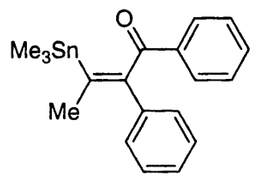
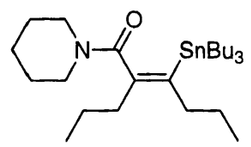
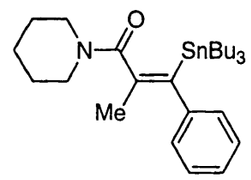
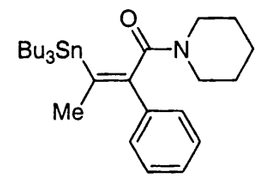


Scheme 4. Nickel-catalyzed acylstannylation of alkynes.



Scheme 3. Catalytic cycle of the allylstannylation.

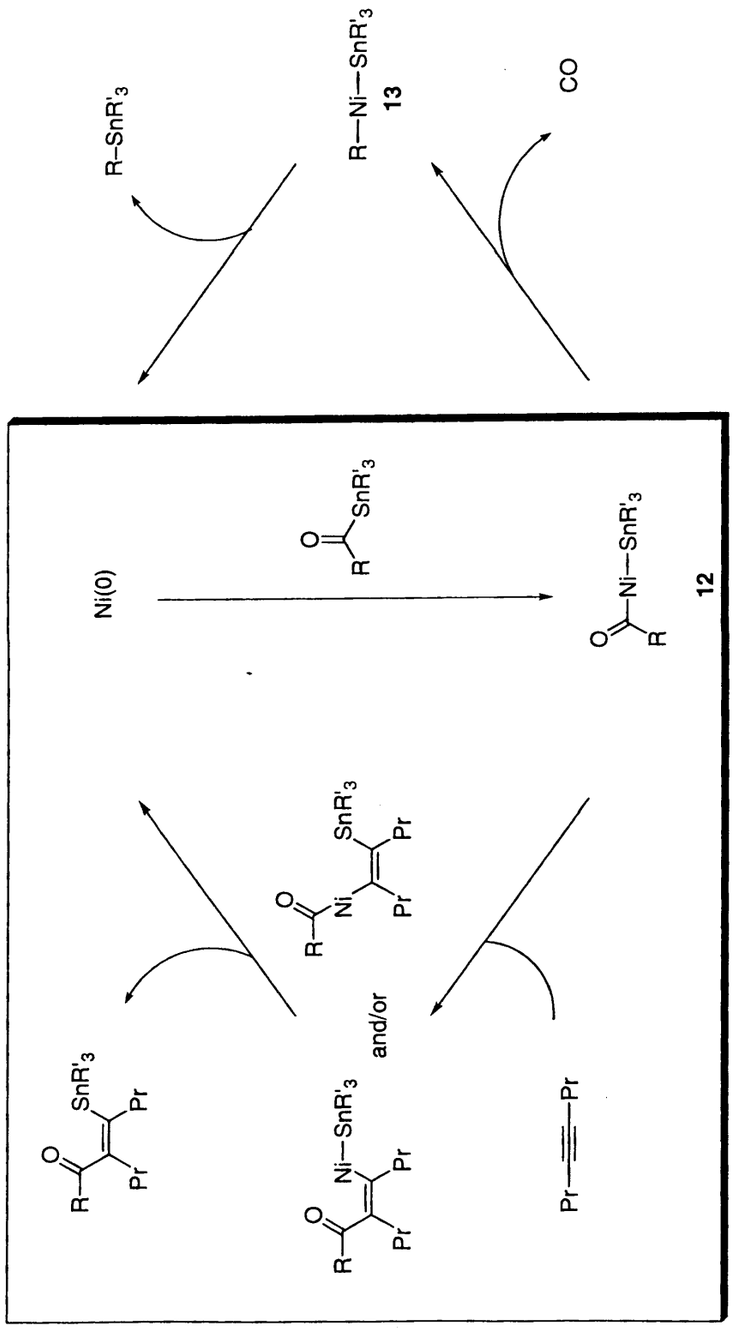
Table 3. Nickel-catalyzed acylstannylation of alkynes[a]

entry	acyl-stannane	alkyne	time (h)	yield (%)[b]	product(s)			ratio (**10** : **11**)[c]
1	**9a**	**2c**	2	65		**10a**		–
2	**9a**	**2e**	1.5	61		**10b**		**11b** 83 : 17
3	**9b**	**2c**	1.5	66		**10c**		–
4	**9b**	**2e**	2	81		**10d**		**11d** 64 : 36

[a] The reaction was carried out in toluene (0.3 mL) at 100 °C using an organostannane (0.46 mmol) and an alkyne (0.69 mmol) in the presence of $Ni(cod)_2$ (23 μmol). [b] Isolated yield based on the organostannane. [c] Determined by ^{119}Sn NMR.

Assuming that the acylstannylation might also be started by oxidative addition of a C–Sn bond of an acylstannane to a nickel(0) complex, the author treated **9a** with a catalytic amount of $Ni(cod)_2$ in the absence of an alkyne and observed formation of trimethyl(phenyl)tin in 56% yield (eq 1). The decarbonylation of **9a** is attributed to oxidative addition of **9a** to Ni(0) to give **12** followed by deinsertion of carbon monoxide from complex **12** and reductive elimination of trimethyl(phenyl)tin from **13** as illustrated in Scheme 5. Hence, the acylstannylation should be commenced by oxidative addition to give **12**, followed by insertion of an alkyne to give an alkenylnickel species, which then undergoes reductive elimination to give rise to acylstannylation products, although details of the insertion and reductive elimination steps remain yet to be studied.

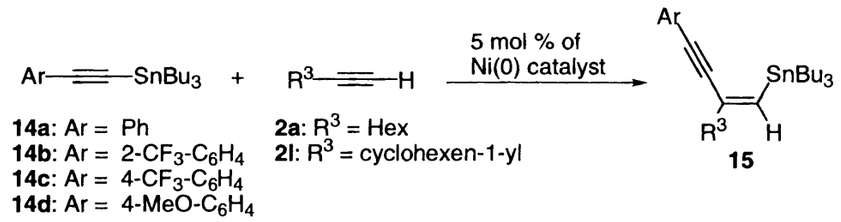
(1)



Scheme 5. Catalytic cycle of the acylstannylation.

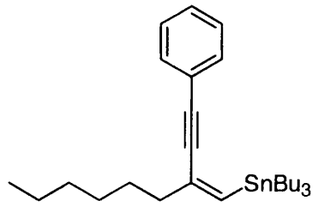
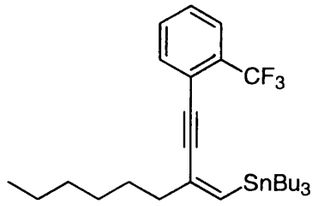
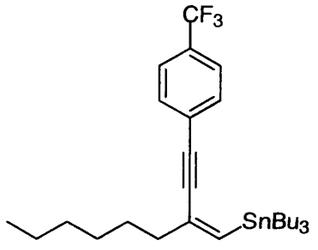
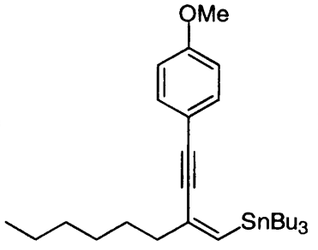
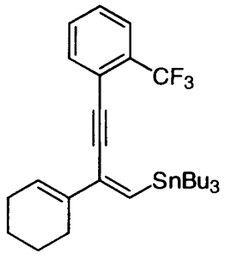
Alkynylstannylation of alkynes using $Ni(acac)_2$–DIBALH catalyst

Carbostannylation reaction with alkynylstannanes is also effected with a nickel(0) catalyst. Particularly, a catalyst prepared from $Ni(acac)_2$ and diisobutylaluminum hydride (1:2 ratio) (Scheme 6 and Table 4) was more effective than $Ni(cod)_2$ particularly for this reaction. For example, tributyl(phenylethynyl)tin (**14a**) reacted with 1-octyne (**2a**) in the presence of 5 mol % of the in situ-generated Ni(0) catalyst (toluene, 80 °C, 24 h) to give (*Z*)-2-hexyl-4-phenyl-1-tributylstannyl-1-buten-3-yne (**15a**) in 72% yield (entry 1). (Phenylethynyl)stannanes with a variety of substituents gave the corresponding carbostannylation products (entries 2–4). Alkynyl moiety of 1-ethynylcyclohexene (**2l**) solely participated in the reaction (entry 5). It is noteworthy that the regioselectivity is perfect in sharp contrast to palladium–iminophosphine-catalyzed alkynylstannylation that often gave mixtures of regioisomers. Internal alkynes failed to give products as was the case with a palladium catalyst. Although electron-deficient terminal alkynes were not suitable for the nickel catalysis as in the allystannylation, the palladium catalyst can complement the reaction of such substrates.



Scheme 6. Nickel-catalyzed alkynylstannylation of alkynes.

Table 4. Nickel-catalyzed alkynylstannylation of alkynes[a]

entry	alkynyl-stannane	alkyne	time (h)	yield (%)[b]	product
1	**14a**	**2a**	24	72	 **15a**
2	**14b**	**2a**	4	82	 **15b**
3	**14c**	**2a**	10	70	 **15c**
4	**14d**	**2a**	36	56	 **15d**
5	**14b**	**2l**	5	79	 **15e**

[a] The reaction was carried out in toluene (0.5 mL) at 80 °C using an organostannane (0.76 mmol) and an alkyne (2.3 mmol) in the presence of a Ni(0) catalyst prepared in situ from $Ni(acac)_2$ (38 μmol) and a 1.5 M toluene solution of diisobutylaluminum hydride (76 μmol). [b] Isolated yield based on the organostannane.

Structure determination of carbostannylation products

Configuration of the carbostannylation products was determined by NMR studies (coupling constants and NOE) of the alkenylstannanes and/or the alkenes obtained by protonolysis. For example, the configuration of **3a** and **4a** was determined on the basis of NOE (irradiation at the methine peak) and the H–Sn coupling constant as shown in Figure 1.[5]

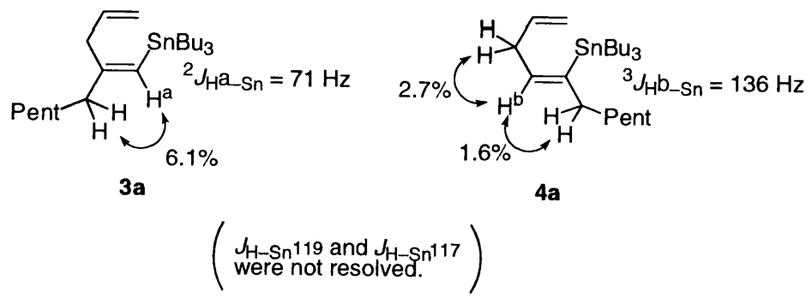
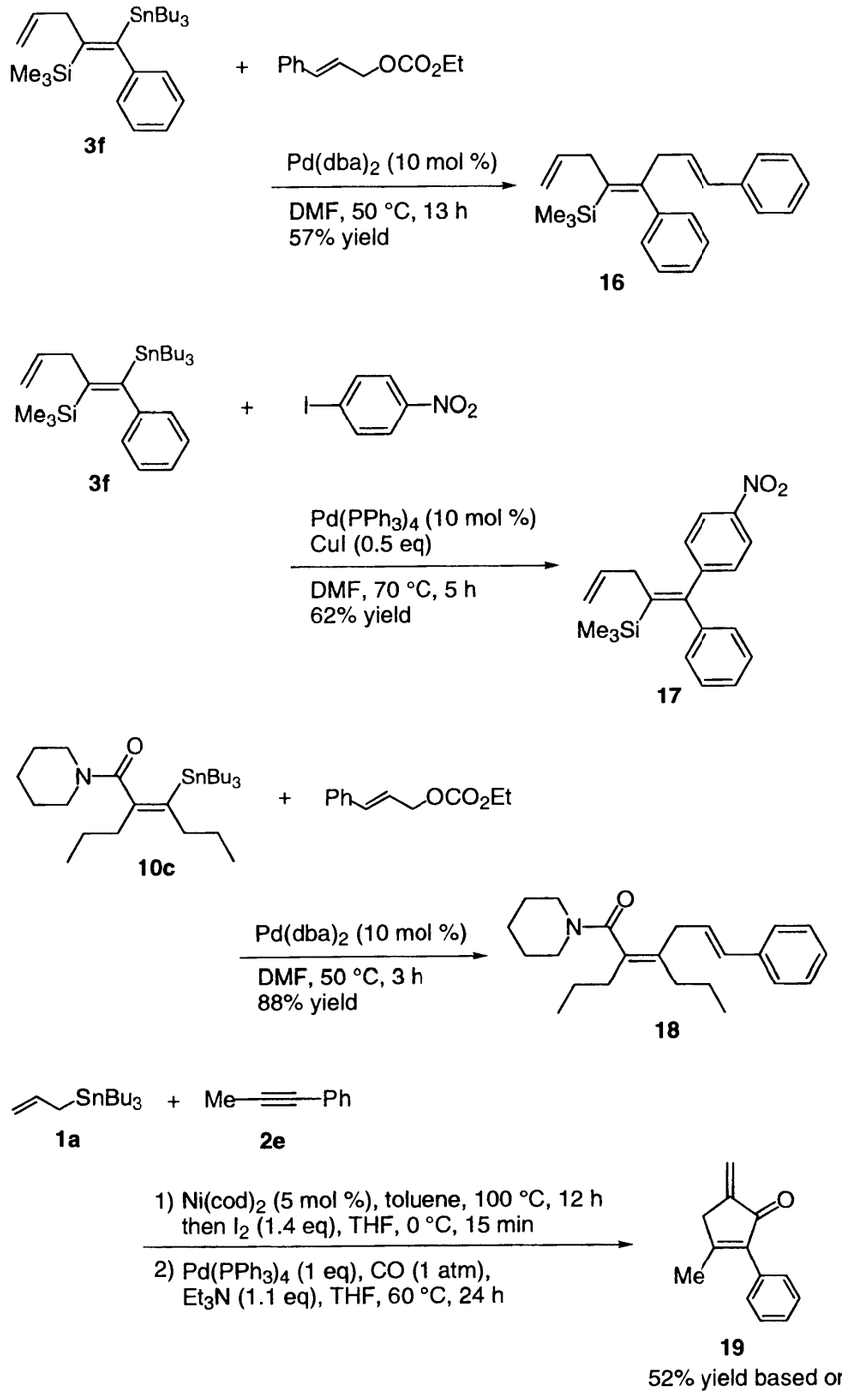


Figure 1

Synthesis of tetra-substituted ethenes utilizing carbostannylation products

Utility of the carbostannylation products derived from internal alkynes is demonstrated by transformation to tetra-substituted ethenes (Scheme 7). Dienylstannane **3f** could couple with cinnamyl carbonate or 4-iodonitrobenzene to give 1,4-diphenyl-1,4,7-octatriene **16** or 1,1-diaryl-1,4-pentadiene **17**; β-acylethenylstannane **10c** afforded α,β-unsaturated carboxamide **18** in good yields. Exclusive *syn*- and high regio-selectivities of the nickel-catalyzed carbostannylation reaction readily allows one to synthesize tetra-substituted ethenes without troublesome separation of isomers. For example, the reaction of 1-phenyl-1-propyne with **1a** followed by the Negishi cyclization[6] gave cyclopentenone **19** in 52% total yield.



Scheme 7. Synthesis of tetra-substituted ethenes.

Conclusion

The author has disclosed that in the presence of a nickel catalyst the carbostannylation of both electron-rich and -deficient alkynes takes place with allyl-, acyl- or alkynylstannanes to give stereo- and regioselectively 1,4-dienylstannanes, β-stannyl-α,β-unsaturated carbonyl compounds or (stannyl)enynes, respectively. This coupled with the palladium-catalyzed reaction has made multiply substituted ethenes readily accessible with high stereospecificity.

Experimental section

Chemicals. The following compounds were prepared according to literature procedures: Allyl(tributyl)tin (**1a**),[7] (*E*)-2-buten-1-yl(tributyl)tin (**1b**),[8] tributyl(2-methylallyl)tin (**1c**),[9] *N*-(2-diphenylphosphinobenzylidene)-2-phenylethylamine (**5**),[10] benzoyl(trimethyl)tin (**9a**),[11] tributyl(piperidinocarbonyl)tin (**9b**)[12] and tributyl(phenylethynyl)tin (**14a**).[13]

Preparation of Alkynylstannanes. Tributyl(2-trifluoromethylphenylethynyl)tin (**14b**), tributyl(4-trifluoromethylphenylethynyl)tin (**14c**) and tributyl(4-methoxylphenylethynyl)tin (**14d**) were synthesized by the reaction of tributyltin chloride with the corresponding alkynyllithium, which was prepared by the Corey's method[14] from the corresponding arenecarbaldehyde.

Tributyl(2-trifluoromethylphenylethynyl)tin (14b). A yellow oil, R_f 0.40 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.70–1.86 (m, 27 H), 7.22–7.72 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 11.2, 13.6, 27.0, 28.8, 102.1, 105.2, 125.57, 125.64, 127.4, 131.2, 134.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -63.0. Anal. Calcd for $C_{21}H_{31}F_3Sn$: C, 54.93; H, 6.80. Found: C, 55.19; H, 6.86.

Tributyl(4-trifluoromethylphenylethynyl)tin (14c). A yellow oil, R_f 0.48 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.85–1.82 (m, 27 H), 7.53 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 11.2, 13.7, 26.9, 28.9, 97.0, 108.4, 122.0, 124.96, 125.01, 125.07, 125.12, 126.0, 127.8, 132.1, 132.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -64.1. Anal. Calcd for $C_{21}H_{31}F_3Sn$: C, 54.93; H, 6.80. Found: C, 54.67; H, 6.87.

Tributyl(4-methoxylphenylethynyl)tin (14d). A yellow oil, R_f 0.19 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.83–1.84 (m, 27 H), 3.80 (s, 3 H), 6.80 (d, *J* = 8.4 Hz, 2 H), 7.39 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 11.1, 13.7, 27.0, 28.9, 55.2, 91.1, 110.0, 113.7, 116.3, 133.3, 159.2; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -66.6. Anal. Calcd for $C_{21}H_{34}OSn$: C, 59.88; H, 8.14. Found: C, 59.87; H, 8.24.

Allylstannylation of Alkynes. ***A General Procedure.*** A solution of $Ni(cod)_2$ (6.3 mg, 23 μmol) in toluene (0.3 mL) was added to a solution of an organostannane (0.46 mmol) and an alkyne (1.38 mmol), and the mixture was stirred at the temperature indicated in Table 2. After the time specified in Table 2, evaporation of the solvent followed by GPC gave the corresponding carbostannylation product. Yields are listed in Table 2.

(*Z*)-2-Hexyl-1-(tributylstannyl)-1,4-pentadiene (3a). A yellow oil, R_f 0.67 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.66–1.74 (m, 38 H), 2.11 (t, *J* = 7.0 Hz, 2 H), 2.77 (dt, *J* = 6.6, 1.5 Hz, 2 H), 4.91–5.14 (m, 2 H), 5.51 (t, *J* = 1.2 Hz, 1 H), 5.62–5.85 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.2, 13.7, 14.1, 22.7, 27.3, 28.1, 29.0, 29.2, 31.8, 38.5, 43.8, 115.7, 122.8, 137.2, 157.0; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -62.5. Anal. Calcd for $C_{23}H_{46}Sn$: C, 62.60; H, 10.51. Found as a mixuture of **3a** and **4a**: C, 62.40; H, 10.71.

(*Z*)-5-(Tributylstannyl)-1,4-undecadiene (4a). A yellow oil, R_f 0.58 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.71–1.69 (m, 38 H), 1.96–2.37 (m, 2 H), 2.74 (t, *J* = 6.6 Hz, 2 H), 4.91–5.12 (m, 2 H), 5.62–6.04 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.3, 13.7, 14.1, 22.7, 27.4, 28.9, 29.2, 30.6, 31.8, 39.0, 40.8, 114.8, 137.2, 137.5, 145.5; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -54.2. Anal. Calcd for $C_{23}H_{46}Sn$: C, 62.60; H, 10.51. Found as a mixuture of **3a** and **4a**: C, 62.40; H, 10.71.

(*Z*)-1-(Tributylstannyl)-1,4-pentadiene (3b). A yellow oil, R_f 0.62 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.70–1.70 (m, 27 H), 2.69–2.88 (m, 2 H), 4.93–5.13 (m, 2 H), 5.66–5.98 (m, 2 H), 6.41–6.58 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.3, 13.7, 27.3, 29.2, 41.1, 115.1, 129.6, 136.8, 146.0; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -61.6. Anal. Calcd for $C_{17}H_{34}Sn$: C, 57.17; H, 9.59. Found: C, 56.90; H, 9.32.

(*Z*)-4-Propyl-5-(tributylstannyl)-1,4-octadiene (3c). A colorless oil, R_f 0.66 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.77–1.60 (m, 37 H), 2.00–2.24 (m, 4 H), 2.74(dd, *J* = 5.1, 1.5, Hz, 2 H), 4.92–5.12 (m, 2 H), 5.58–5.81 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.7, 13.7, 14.1, 14.2, 22.2, 24.0, 27.4, 29.2, 32.1, 36.6, 44.6, 115.5, 137.9, 139.7, 146.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -50.0. Anal. Calcd for $C_{23}H_{46}Sn$: C, 62.60; H, 10.51. Found: C, 62.84; H, 10.75.

Ethyl (*Z*)-3-Methyl-2-(tributylstannyl)-2,5-hexadienoate (3d). A yellow oil, R_f 0.54 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.69–1.60 (m, 30 H), 1.78 (s, 3 H), 2.74 (dt, *J* = 6.6, 1.3 Hz, 2 H), 4.08 (q, *J* = 7.1 Hz, 2 H), 4.94–5.01 (m, 2 H), 5.55–5.80 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 14.4, 20.5, 27.3, 28.9, 45.7, 60.0, 117.1, 133.9, 135.5, 151.1, 173.0; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -43.9. Anal. Calcd for $C_{21}H_{40}O_2Sn$: C, 56.90; H, 9.10. Found: C, 57.07; H, 9.31.

Ethyl (*E*)-5-(Tributylstannyl)-1,4-hexadiene-2-carboxylate (4d). A yellow oil, R_f 0.54 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.78–1.67 (m, 30 H), 2.08 (s, 3 H), 3.03 (d, *J* = 6.1 Hz, 2 H), 4.19 (q, *J* = 7.1 Hz, 2 H), 4.94–5.15 (m, 2 H), 5.63–5.89 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.5, 13.6, 14.3, 23.2, 27.4, 29.1, 41.6, 60.0, 116.1, 135.7, 139.2, 150.4, 167.8; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -43.5. Anal. Calcd for $C_{21}H_{40}O_2Sn$: C, 56.90; H, 9.10. Found: C, 56.86; H, 9.05.

(*Z*)-2-Methyl-1-phenyl-1-(tributylstannyl)-1,4-pentadiene (3e). A yellow oil, R_f 0.54 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.59–1.76 (m, 30 H), 2.81–3.00 (m, 2 H), 5.01–5.27 (m, 2 H), 5.73–5.96 (m, 1 H), 6.78–6.95 (m, 2 H), 7.01–7.42 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 11.0, 13.6, 19.0, 27.3, 29.0, 46.1, 116.1, 124.3, 127.3, 128.0, 137.0, 142.2, 144.0, 146.9; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -53.5. Anal. Calcd for $C_{24}H_{40}Sn$: C, 64.45; H, 9.01. Found: C, 64.27; H, 9.06.

(*E*)-1-Phenyl-1-(tributylstannyl)-2-(trimethylsilyl)-1,4-pentadiene (3f). A yellow oil, R_f 0.59 (hexane). ^{1}H NMR ($CDCl_3$) δ 1.16 (s, 9 H), 0.93–1.36 (m, 15 H), 1.46–1.93 (m, 12 H), 3.30–3.47 (m, 2 H), 5.38–5.60 (m, 2 H), 6.08–6.32 (m, 1 H), 7.16–7.33 (m, 2 H), 7.40–7.70 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 1.3, 11.3, 13.6, 27.4, 29.1, 45.1, 115.7, 124.9, 127.1, 127.6, 138.5, 147.8, 151.4, 163.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -61.1. Anal. Calcd for $C_{26}H_{46}SiSn$: C, 61.78; H, 9.17. Found: C, 61.50; H, 9.32.

Ethyl (*E*)-2-(Tributylstannyl)-3-(trimethylsilyl)-2,5-hexadienoate (3g). A yellow oil, R_f 0.51 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9 H), 0.75–1.69 (m, 30 H), 2.95 (d, *J* = 4.0 Hz, 2 H), 4.11 (q, *J* = 7.1 Hz, 2 H), 4.95–5.13 (m, 2 H), 5.61–5.87 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 0.3, 11.7, 13.6, 14.3,

27.2, 28.9, 44.6, 60.2, 116.6, 136.9, 152.3, 158.9, 173.1; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -46.8. Anal. Calcd for $C_{23}H_{46}O_2SiSn$: C, 55.09; H, 9.25. Found: C, 55.05; H, 9.45.

(*Z*)-4-Butyl-5-(tributylstannyl)-1,4-undecadien-6-yne (3h). A yellow oil, R_f 0.54 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.75–1.69 (m, 41 H), 2.29–2.48 (m, 4 H), 2.79 (d, *J* = 6.4 Hz, 2 H), 4.96–5.13 (m, 2 H), 5.58–5.92 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.1, 13.6, 13.7, 14.0, 19.7, 22.0, 22.7, 27.4, 29.1, 30.5, 31.5, 34.3, 43.0, 83.2, 96.5, 116.2, 119.9, 136.6, 159.6; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -50.3. Anal. Calcd for $C_{27}H_{50}Sn$: C, 65.73; H, 10.21. Found: C, 65.57; H, 10.31.

(*E*)-4,7-Bis(trimethylsilyl)-5-(tributylstannyl)-1,4-heptadien-6-yne (3i). A yellow oil, R_f 0.60 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 9 H), 0.21 (s, 9 H), 0.72–1.69 (m, 27 H), 2.83–2.99 (m, 2 H), 4.87–5.07 (m, 2 H), 5.63–5.85 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ -0.4, -0.1, 11.5, 13.7, 27.3, 29.0, 44.3, 103.5, 109.5, 116.1, 137.3, 139.6, 167.1; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -56.6. Anal. Calcd for $C_{25}H_{50}Si_2Sn$: C, 57.14; H, 9.59. Found: C, 56.99; H, 9.65.

(1*Z*,4*E*)-2-Methyl-1-phenyl-1-(tributylstannyl)-1,4-hexadiene (3j). A yellow oil, R_f 0.54 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.60–1.00 (m, 15 H), 1.13–1.48 (m, 12 H), 1.55 (s, 3 H), 1.70 (d, *J* = 4.8 Hz, 3 H), 2.82 (d, *J* = 5.0 Hz, 2 H), 5.34–5.65 (m, 2 H), 6.76–6.90 (m, 2 H), 7.00–7.32 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 11.0, 13.6, 18.0, 19.0, 27.4, 29.0, 45.0, 124.3, 126.6, 127.4, 127.9, 129.4, 141.3, 144.9, 147.0; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -53.7. Anal. Calcd for $C_{25}H_{42}Sn$: C, 65.09; H, 9.18. Found: C, 65.14; H, 9.47.

(*Z*)-2-Methyl-4-propyl-5-(tributylstannyl)-1,4-octadiene (3k). A yellow oil, R_f 0.66 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.67–1.57 (m, 40 H), 1.95–2.26 (m, 4 H), 2.69 (s, 2 H), 4.70 (s, 1 H), 4.77 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.6, 13.7, 14.1, 14.3, 22.4, 22.5, 24.0, 27.5, 29.3, 32.2, 36.7, 48.1, 111.4, 140.8, 144.6, 146.2; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -51.1. Anal. Calcd for $C_{24}H_{48}Sn$: C, 63.31; H, 10.62. Found: C, 63.30; H, 10.39.

Ethyl (*E*)-3-Phenyl-2-(tributylstannyl)-2,5-hexadienoate (3l). A yellow oil, R_f 0.42 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.81–1.87 (m, 30 H), 3.20 (dt, *J* = 6.6, 1.5 Hz, 2 H), 3.85 (q, *J* = 7.0 Hz, 2 H), 4.96 (dtd, *J* = 10.2, 1.5, 1.3 Hz, 1 H), 5.00 (dtd, *J* = 17.2, 1.5, 1.3 Hz, 1 H), 5.65 (ddt, *J* = 17.2, 10.2, 6.6 Hz, 1 H), 7.13–7.46 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.5, 13.7, 13.9, 27.2, 28.9, 44.7, 59.8, 116.8, 127.1, 127.5, 127.8, 135.0, 137.7, 141.9, 153.5, 172.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -39.2. Anal. Calcd for $C_{26}H_{42}O_2Sn$: C, 61.80; H, 8.38. Found: C, 61.85; H, 8.10.

Ethyl (*E*)-1-Phenyl-1-(tributylstannyl)-1,4-pentadiene-2-carboxylate (4l). A yellow oil, R_f 0.43 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.63–1.74 (m, 30 H), 3.12 (dt, *J* = 6.2, 1.5 Hz, 2 H), 3.74 (q, *J* = 7.1 Hz, 2 H), 5.01 (ddt, *J* = 10.1, 1.6, 1.5 Hz, 1 H), 5.09 (ddt, *J* = 17.1, 1.6, 1.5 Hz, 1 H), 5.78 (ddt, *J* = 17.1, 10.1, 6.2 Hz, 1 H), 6.76–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.2, 13.6, 27.3, 28.9, 40.9, 59.9, 116.7, 125.1, 125.7, 125.8, 127.8, 135.0, 141.1, 145.7, 154.2, 168.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -44.8. Anal. Calcd for $C_{26}H_{42}O_2Sn$: C, 61.80; H, 8.38. Found: C, 61.63; H, 8.60.

Ethyl (*Z*)-3-Phenyl-2-(tributylstannyl)-2,5-hexadienoate (3'l). A yellow oil, R_f 0.50 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.51–1.47 (m, 30 H), 3.31 (dt, *J* = 6.8, 1.3 Hz, 2 H), 4.20 (q, *J* = 7.1 Hz, 2 H), 4.92 (dt, *J* = 11.5, 1.3 Hz, 1 H), 4.93 (dt, *J* = 15.6, 1.3 Hz, 1 H), 5.70 (ddt, *J* = 15.6, 11.5, 6.8 Hz, 1 H), 7.09–7.27 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.2, 13.6, 27.3, 28.9, 40.9, 59.9, 116.7, 125.1, 125.7, 125.8, 127.8, 135.0, 141.1, 145.7, 154.2, 168.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -44.8. Anal. Calcd for $C_{26}H_{42}O_2Sn$: C, 61.80; H, 8.38. Found: C, 61.52; H, 8.36.

Dimethyl (*Z*)-1-(Tributylstannyl)-1,4-pentadiene-1,2-dicarboxylate (3'm). A yellow oil, R_f 0.57 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.74–1.70 (m, 27 H), 3.10 (d, *J* = 6.2 Hz, 2 H), 3.74 (s, 3 H), 3.76 (s, 3 H), 5.00 (dd, *J* = 10.4, 1.1 Hz, 1 H), 5.02 (dd, *J* = 16.3, 1.1 Hz, 1 H), 5.80 (ddt, *J* = 16.3, 10.4, 6.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 12.1, 13.7, 27.2, 28.8, 35.6, 51.3, 52.4, 116.1,

135.1, 139.4, 156.4, 168.4, 173.2; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -42.1. Anal. Calcd for $C_{21}H_{38}O_4Sn$: C, 53.30; H, 8.09. Found: C, 53.56; H, 8.37.

Acylstannylation of Alkynes. ***A General Procedure.*** A solution of $Ni(cod)_2$ (6.3 mg, 23 μmol) in toluene (0.3 mL) was added to a solution of an organostannane (0.46 mmol) and an alkyne (0.69 mmol), and the mixture was stirred at the temperature indicated in Table 3. After the time specified in Table 3, evaporation of the solvent followed by GPC gave the corresponding carbostannylation product. Yields are listed in Table 3.

(*Z*)-1-Phenyl-2-propyl-3-(trimethylstannyl)-2-hexen-1-one (10a). A yellow oil, R_f 0.31 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 9 H), 0.80 (t, *J* = 7.2 Hz, 3 H), 1.01 (t, *J* = 7.3 Hz, 3 H), 1.14–1.70 (m, 4 H), 2.45 (t, *J* = 7.9 Hz, 4 H), 7.31–7.91 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ -7.3, 14.0, 14.3, 22.6, 23.2, 32.7, 36.4, 128.3, 128.4, 129.1, 132.2, 138.1, 149.3, 155.0, 201.6; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -37.8. Anal. Calcd for $C_{18}H_{28}OSn$: C, 57.02; H, 7.44. Found: C, 57.31; H, 7.29.

(*Z*)-2-Methyl-1,3-diphenyl-3-(trimethylstannyl)-2-propen-1-one (10b). A brown oil, R_f 0.45 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ -0.04 (s, 9 H), 1.89 (s, 3 H), 7.00 (dd, *J* = 8.2, 1.3 Hz, 2 H), 7.12–7.63 (m, 6 H), 7.78–7.94 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -7.4, 19.0, 125.5, 126.0, 128.4, 128.5, 129.2, 132.6, 137.4, 144.7, 157.2, 200.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -35.8. Anal. Calcd for $C_{19}H_{22}OSn$: C, 59.26; H, 5.76. Found as a mixuture of **10b** and **11b**: C, 59.18; H, 5.70.

(*Z*)-1,2-Diphenyl-3-(trimethylstannyl)-2-buten-1-one (11b). A brown oil, R_f 0.31 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 9 H), 2.20 (s, 3 H), 6.69–7.09 (m, 5 H), 7.16–7.43 (m, 3 H), 7.59–7.75 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -7.7, 22.7, 125.4, 127.2, 127.7, 128.1, 129.2, 132.6, 136.0, 143.5, 145.9, 147.0, 201.1; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -35.3. Anal. Calcd for $C_{19}H_{22}OSn$: C, 59.26; H, 5.76. Found as a mixuture of **10b** and **11b**: C, 59.18; H, 5.70.

(*Z*)-*N*-[2-Propyl-3-(tributylstannyl)-2-hexenoyl]piperidine (10c). An orange oil, R_f 0.35 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.65–1.74 (m, 43 H), 2.03–2.44 (m, 4 H), 3.31 (brs, 2 H), 3.49 (brs, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.5, 13.7, 14.3, 14.4, 22.3, 23.2, 24.6, 27.6, 29.2, 32.7, 36.1, 145.4, 146.4, 171.9; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -48.4. Anal. Calcd for $C_{26}H_{51}NOSn$: C, 60.94; H, 10.03. Found: C, 60.68; H, 10.24.

(*Z*)-*N*-[2-Methyl-3-phenyl-3-(tributylstannyl)-2-propenoyl]piperidine (10d). An orange oil, R_f 0.27 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.58–1.87 (m, 36 H), 3.45 (brs, 2 H), 3.56 (brs, 2 H), 6.84–7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.7, 13.6, 18.3, 24.6, 27.4, 29.0, 42.3, 47.8, 125.0, 126.5, 128.2, 142.5, 144.8, 147.6, 172.0; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -50.5. Anal. Calcd for $C_{27}H_{45}NOSn$: C, 62.56; H, 8.75. Found: C, 62.48; H, 8.91.

(*Z*)-*N*-[2-Phenyl-3-(tributylstannyl)-2-butenoyl]piperidine (11d). An orange oil, R_f 0.11 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.73–1.72 (m, 33 H), 2.02 (s, 3 H), 3.18 (brs, 2 H), 3.50 (brs, 2 H), 7.13–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.5, 13.7, 22.3, 24.4, 25.2, 27.5, 29.3, 42.8, 47.8, 126.8, 128.1, 129.1, 137.3, 146.5, 146.7, 170.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -43.9. Anal. Calcd for $C_{27}H_{45}NOSn$: C, 62.56; H, 8.75. Found as a mixuture of **10d** and **11d**: C, 62.82; H, 8.95.

Alkynylstannylation of Alkynes. ***A General Procedure.*** A 1.00 M toluene solution of DIBAL–H (76 μL, 76 μmol) was added to a solution of an organostannane (0.76 mmol) and $Ni(acac)_2$ (9.8 mg, 38 μmol) in toluene (0.5 mL). The mixture was stirred for 5 min, and then an alkyne (2.3 mmol) was added. The resulting mixture was stirred at 80°C for the time specified in Table 4. Evaporation of the solvent followed by GPC gave the corresponding carbostannylation product. Yields are listed in Table 4.

(*Z*)-2-Hexyl-4-phenyl-1-(tributylstannyl)-1-beten-3-yne (15a). A yellow oil, R_f 0.58 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.77–1.74 (m, 38 H), 2.33 (t, J = 7.1 Hz, 2 H), 6.24 (s, 1 H), 7.22–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.1, 13.7, 14.1, 22.6, 27.3, 28.5, 28.6, 29.2, 31.7, 41.5, 88.3, 92.3, 123.8, 127.9, 128.2, 131.4, 138.4, 141.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -59.6. Anal. Calcd for $C_{28}H_{46}Sn$: C, 67.08; H, 9.25. Found: C, 67.10; H, 9.49.

(*Z*)-2-Hexyl-1-(tributylstannyl)-4-(2-trifluoromethylphenyl)-1-beten-3-yne (15b). A yellow oil, R_f 0.54 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.76–1.74 (m, 38 H), 2.36 (t, J = 7.3 Hz, 2 H), 6.32 (s, 1 H), 7.31–7.71 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 10.0, 13.7, 14.1, 22.6, 27.3, 28.2, 28.5, 29.2, 31.6, 41.7, 84.2, 97.9, 121.5, 122.0, 125.5, 125.7, 125.8, 125.9, 127.5, 131.1, 131.3, 131.6, 133.6, 139.8, 141.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -59.3. Anal. Calcd for $C_{29}H_{45}F_3Sn$: C, 61.17; H, 7.97. Found: C, 61.01; H, 8.16.

(*Z*)-2-Hexyl-1-(tributylstannyl)-4-(4-trifluoromethylphenyl)-1-beten-3-yne (15c). A yellow oil, R_f 0.61 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.82–1.72 (m, 38 H), 2.34 (t, J = 6.8 Hz, 2 H), 6.34 (s, 1 H), 7.45–7.63 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 10.1, 13.7, 14.1, 22.6, 27.3, 28.46, 28.51, 29.2, 31.7, 41.4, 86.9, 94.7, 121.3, 125.1, 125.2, 125.25, 125.33, 126.7, 127.5, 129.2, 129.9, 131.6, 140.4, 140.8; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -59.2. Anal. Calcd for $C_{29}H_{45}F_3Sn$: C, 61.17; H, 7.97. Found: C, 61.45; H, 8.15.

(*Z*)-2-Hexyl-4-(4-methoxyphenyl)-1-(tributylstannyl)-1-beten-3-yne (15d). A yellow oil, R_f 0.21 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.79–1.75 (m, 38 H), 2.32 (t, J = 7.1 Hz, 2 H), 3.82 (s, 3 H), 6.19 (s, 1 H), 6.76–6.91 (m, 2 H), 7.30–7.42 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.1, 13.7, 14.1, 22.6, 27.3, 28.5, 28.6, 29.2, 31.7, 41.6, 55.3, 88.3, 91.0, 113.9, 115.9, 132.8, 137.3, 141.6, 159.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -59.8. Anal. Calcd for $C_{29}H_{48}OSn$: C, 65.55; H, 9.10. Found: C, 65.57; H, 9.29.

(*Z*)-2-(1-Cyclohexenyl)-1-(tributylstannyl)-4-(2-trifluoromethylphenyl)-1-beten-3-yne (15e). A colorless oil, R_f 0.47 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.74–1.81 (m, 31 H), 2.12–2.33 (m, 4 H), 6.43–6.54 (m, 1 H), 6.57 (s, 1 H), 7.31–7.74 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 10.0, 13.6, 22.1, 22.8, 25.0, 25.9, 27.3, 29.2, 85.2, 96.2, 121.5, 125.6, 125.8, 125.88, 125.95, 127.6, 128.7,

131.3, 133.8, 135.9, 136.3, 140.6; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -55.5. Anal. Calcd for $C_{29}H_{41}F_3Sn$: C, 61.61; H, 7.31. Found: C, 61.64; H, 7.51.

Coupling of 3f with (*E*)-cinnamyl ethyl carbonate. A solution of **3f** (42 mg, 84 μmol) in DMF (1.0 mL) was degassed by three freeze-thaw cycles. To this solution was added (*E*)-cinnamyl ethyl carbonate (15.7 mg, 76 μmol) and $Pd(dba)_2$ (4.8 mg, 8.4 μmol). The mixture was stirred at 50 °C for 13 h, then diluted with diethyl ether (25 mL), washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave (1*E*,4*Z*)-1,4-diphenyl-5-(trimethylsilyl)-1,4,7-octatriene (**16**) (15.0 mg, 57%) as a yellow oil: R_f 0.30 (hexane). ^1H NMR ($CDCl_3$) δ -0.24 (s, 9 H), 2.98–3.15 (m, 2 H), 3.28 (d, *J* = 6.4 Hz, 2 H), 4.97–5.20 (m, 2 H), 5.78–6.38 (m, 3 H), 7.03–7.39 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 0.5, 35.6, 39.6, 114.9, 126.0, 126.7, 126.8, 127.2, 127.7, 128.4, 129.1, 130.8, 137.4, 137.8, 144.9, 151.4. HRMS (ESI) Calcd for $C_{23}H_{28}SiNa$: M^++Na, 355.1852. Found: *m/z* 355.1850.

Coupling of 3f with 4-iodonitrobenzene. A solution of **3f** (49 mg, 96 μmol) in DMF (1.0 mL) was degassed by three freeze-thaw cycles. To this solution was added 4-iodonitrobenzene (22 mg, 87 μmol), $Pd(PPh_3)_4$ (10.1 mg, 8.7 μmol) and CuI (8.3 mg, 44 μmol). The mixture was stirred at 70 °C for 5 h and then diluted with diethyl ether (25 mL). The organic layer was washed with water, dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave (*E*)-1-(4-nitrophenyl)-1-phenyl-2-(trimethylsilyl)-1,4-pentadiene (**17**) (18.0 mg, 62%) as an orange oil: R_f 0.14 (hexane). ^1H NMR ($CDCl_3$) δ -0.11 (s, 9 H), 2.93 (dt, *J* = 6.0, 1.6 Hz, 2 H), 4.84–5.08 (m, 2 H), 5.61–5.86 (m, 1 H), 7.06–7.45 (m, 7 H), 8.10–8.20 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.8, 37.7, 115.8, 123.5, 127.5, 128.2, 129.3, 137.3, 140.3, 143.4, 146.4, 150.4, 152.2. HRMS (ESI) Calcd for $C_{20}H_{23}NO_2SiNa$: M^++Na, 360.1390. Found: *m/z* 360.1391.

Coupling of 10c with (*E*)-cinnamyl ethyl carbonate. A solution of **10c** (51 mg, 0.100 mmol) in DMF (1.0 mL) was degassed by three freeze-thaw cycles. To this solution was added (*E*)-cinnamyl ethyl carbonate (18.8 mg, 91 μmol) and $Pd(dba)_2$

(5.7 mg, 9.9 μmol). The mixture was stirred at 50 °C for 3 h, then diluted with diethyl ether (25 mL), washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave *N*-[(2*Z*,5*E*)-6-phenyl-2,3-dipropyl-2,5-hexadienoyl]piperidine (**18**) (27 mg, 88%) as a yellow oil: R_f 0.38 (hexane–ethyl acetate = 2 : 1). ^1H NMR ($CDCl_3$) δ 0.73–2.45 (m, 20 H), 2.72–3.01 (m, 2 H), 3.12–3.80 (m, 4 H), 5.98–6.22 (m, 1 H), 6.37 (d, *J* = 15.7 Hz, 1 H), 7.08–7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 14.36, 14.40, 21.4, 21.9, 24.6, 25.7, 26.5, 32.1, 32.7, 37.3, 41.8, 47.3, 126.1, 127.0, 128.1, 128.4, 131.4, 132.8, 135.1, 137.5, 171.0. HRMS (ESI) Calcd for $C_{23}H_{34}NO$: M^++H, 340.2635. Found: *m/z* 340.2635.

Iododestannylation of 3e. A solution of $Ni(cod)_2$ (44 mg, 0.160 mmol) in toluene (2.1 mL) was added to a solution of allyl(tributyl)tin (1.06 g, 3.2 mmol) and 1-phenyl-1-propyne (0.56 g, 4.8 mmol), and the mixture was stirred at 100 °C for 12 h. After the solvent was evaporated, THF (15 mL) and iodine (1.14 g, 4.5 mmol) were added. The mixture was stirred at 0 °C for 15 min before ethyl acetate (30 mL) and a saturated $Na_2S_2O_3$ aqueous solution (10 mL) were added. The organic layer was separated, and then treated with a 1 M KF aqueous solution (10 mL) at room temperature for 30 min. Insoluble materials were filtered through a Celite pad; the organic layer was dried over magnesium sulfate. Evaporation of the solvent followed by bulb-to-bulb distillation gave (*Z*)-1-iodo-2-methyl-1-phenyl-1,4-pentadiene (0.70 g, 77%) as a yellow oil: R_f 0.43 (hexane). ^1H NMR ($CDCl_3$) δ 1.70 (s, 3 H), 3.18 (dt, *J* = 6.6, 1.2 Hz, 2 H), 5.07–5.32 (m, 2 H), 5.73–6.01 (m, 1 H), 7.13–7.48 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.1, 48.5, 116.6, 127.4, 128.1, 128.2, 128.8, 134.0, 141.0, 144.7. Anal. Calcd for $C_{12}H_{13}I$: C, 50.73; H, 4.61. Found: C, 50.76; H, 4.90.

Reaction of (*Z*)-1-iodo-2-methyl-1-phenyl-1,4-pentadiene with carbon monoxide. To a solution of triethylamine (20 mg, 0.198 mmol) and $Pd(PPh_3)_4$ (0.20 g, 0.173 mmol) in THF (0.9 mL) under 1 atm of carbon monoxide was added (*Z*)-1-iodo-2-methyl-1-phenyl-1,4-pentadiene (50 mg, 0.176 mmol), and the mixture was stirred at 60 °C for 24 h. After the addition of ether (10 mL) to the reaction mixture, the organic layer was washed with a saturated NH_4Cl aqueous solution (5 mL)

and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by GPC gave 3-methyl-5-methylidene-2-phenyl-2-cyclopenten-1-one (**19**)[15] (22 mg, 68%) as a brown solid: ^{1}H NMR ($CDCl_3$) δ 2.23 (t, J = 1.0 Hz, 3 H), 3.28 (d, J = 1.0 Hz, 2 H), 5.46 (dd, J = 2.3, 1.3 Hz, 1 H), 6.17 (td, J = 1.8, 1.0 Hz, 1 H), 7.28–7.55 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 17.9, 37.3, 116.2, 127.7, 128.2, 129.1, 131.8, 132.2, 141.5, 141.7, 165.7.

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Chapter 5

Allylstannylation of Alkynes Catalyzed by Palladium Complexes

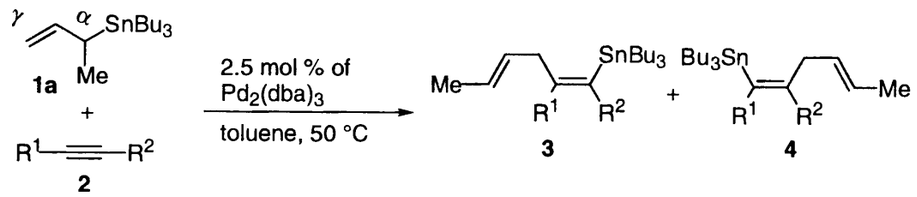
Electron-deficient alkynes bearing an ester, trifluoromethyl, sulfonyl or cyano moiety effectively undergo *syn*-selective allylstannylation in the presence a Pd(0) catalyst to afford various stannyl-substituted 1,4-pentadienes in high yields. Comparison of the reaction of isomeric butenylstannanes suggests two catalytic cycles are possible.

Introduction

Carbostannylation of alkynes has great synthetic significance, because the resulting alkenylstannanes are convertible to variously substituted ethenes.[1] In particular, the reaction with allylstannanes is an extremely convenient and straightforward approach for synthesis of 1,4-dienes, a structural moiety widely found in naturally occurring terpenoids. Although allylstannylation of alkynes has been achieved with a Lewis acid mediator,[2] radical initiator[3] or a nickel(0) complex as discussed in Chapter 4, electron-deficient alkynes are apt to undergo oligomerization by the Ni(0) catalyst rather than desired *syn*-selective allylstannylation. Herein, the author shows that allylstannylation of a variety of electron-deficient alkynes is efficiently promoted by a palladium(0) complex. Furthermore, based on high stereo- and regioselective reaction observed with α-methylallylstannane, he suggests a novel catalytic cycle.

Results and Discussion

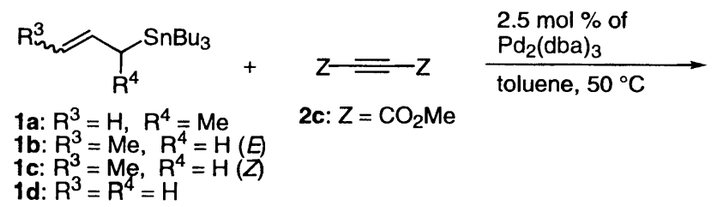
In a series of studies on carbostannylation of alkynes, the author observed that tris(dibenzylideneacetone)dipalladium, $Pd_2(dba)_3$, catalyzed allylstannylation of 1-buten-3-yl(tributyl)tin (**1a**) across ethyl phenylpropiolate (**2a**) (50 °C, 38 h) to give ethyl (2*E*,5*E*)-3-phenyl-2-(tributylstannyl)-2,5-heptadienoate (**3a**) and its regioisomer, ethyl (1*E*,4*E*)-1-phenyl-1-(tributylstannyl)-1,4-hexadiene-2-carboxylate (**4a**), in a ratio of 90 : 10 in 74% yield (Scheme 1). Noteworthy is that the γ-carbon in **1a** exclusively formed a bond with the alkyne. In a similar manner, **1a** reacted with phenylethynyl *p*-tolyl sulfone (**2b**) or dimethyl butynedioate (**2c**) to afford the corresponding γ-adduct as a sole product.

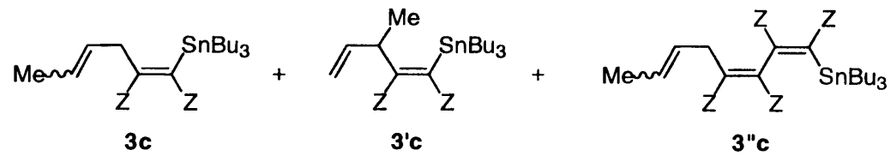


alkyne	yield (time)	3 : 4	
2a: R^1 = Ph, R^2 = CO_2Et	74% (38 h)	90 : 10	
2b: R^1 = Ph, R^2 = SO_2(*p*-tol)	74% (17 h)	>99[a] : 1	[a] *E* : *Z* = 76 : 24
2c: R^1 = R^2 = CO_2Me	72% (1 h)	—[b]	[b] *E* : *Z* = 48 : 52

Scheme 1. Palladium-catalyzed allylstannylation of alkynes with **1a**

Regioisomers of **1a**, (*E*)-2-buten-1-yl(tributyl)tin (**1b**) and (*Z*)-2-buten-1-yl(tributyl)tin (**1c**), also reacted with **2c** but in a different manner and gave roughly equal amounts of α- and γ-adducts in addition to dimerization–carbostannylation product **3"c** (Scheme 2).



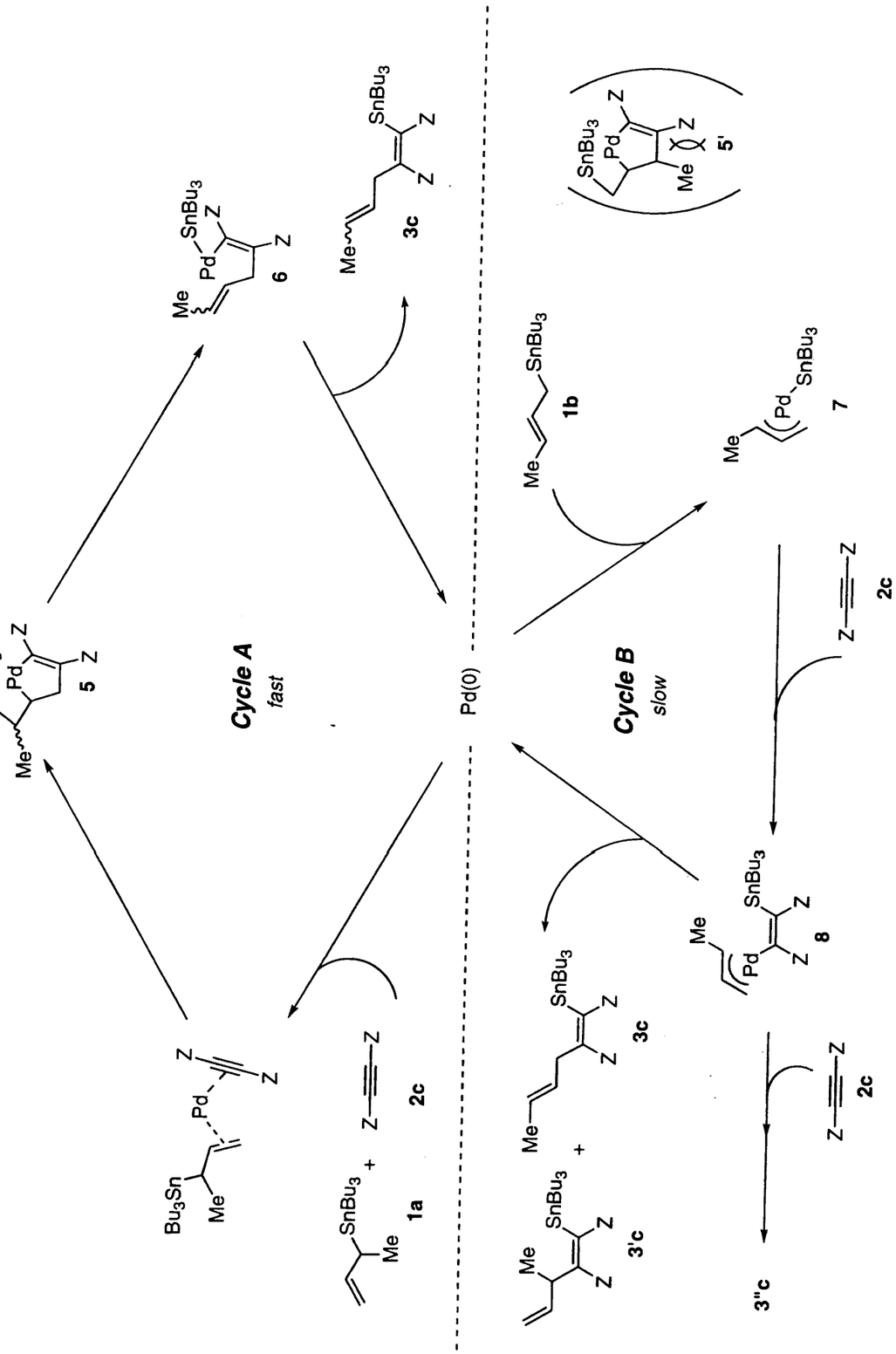


allylstannane	conv. (time)	**3c** : **3'c** : **3"c** (*E*/*Z*)
1a	>99% (1 h)	100 (48/52) : 0 : 0
1b	22% (3 h)	25 (100/0) : 0 : 0 (100/0)
1c	24% (10 h)	38 (0/100) : 0 : 0 (0/100)
[**1d**	>99% (1 h)]	

Scheme 2. Palladium-catalyzed allylstannylation of **2c** with butenylstannanes.

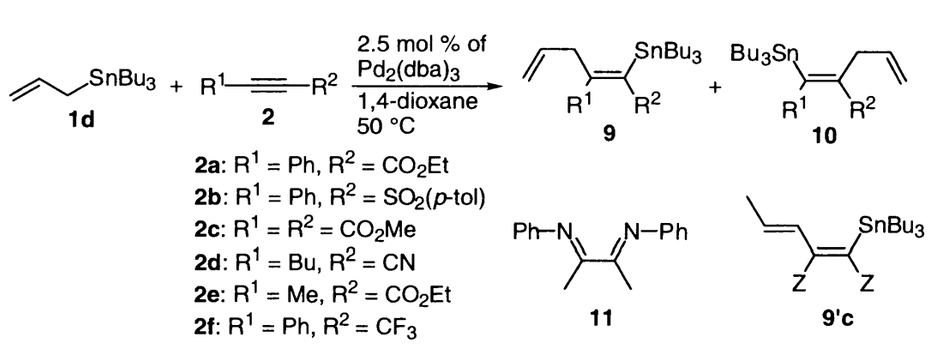
It is noteworthy that configuration of the crotyl group in **1b** or **1c** is retained in **3c**, in contrast to the fact that **3c** derived from **1a** consisted of a mixture of stereoisomers. Noteworthy is that allylstannanes **1a** and **1d**, both lacking the γ-methyl group, reacted much faster than **1b** or **1c**.

All these observations are explained rationally by two catalytic cycles depicted in Scheme 3, although evidences on the intermediates remain yet to be studied. Thus, **2c** and α-methylallylstannane **1a** might first undergo oxidative cyclization with a palladium(0) complex to afford palladacyclopentene **5** (Cycle A). Oxidative cyclization of a terminal alkene and **2c** with a palladium(0) complex has a precedent.[4] β-Tin elimination from **5** would give **6**, whose reductive elimination affords allylstannylation products **3c** as a mixture of stereoisomers. Cycle A explains well the C–C bond formation at γ-carbon of allylstannanes.[5] Substituent at γ-carbon reasonably retards the oxidative cyclization of crotylstannane **1b** (or **1c**), because steric repulsion between its γ-methyl and the ester moiety on **2c** should prevent the formation of palladacyclopentene **5'**. Thus, another pathway, Cycle B, becomes plausible. Oxidative addition of **1b** to a palladium(0) might give **7**,[6] which undergoes insertion of alkyne **2c** to produce π-allylpalladium(II) complex **8**. Retention of the double bond configuration in the reaction of **1b** or **1c** with **2c** to give *E* or *Z* **3c/3"c**, respectively, should imply that the isomerization between *syn*-**7/8** and *anti*-**7/8** does not take place under the reaction conditions. Reductive elimination from **8** would provide dienylstannanes (*E*)-**3c** and **3'c**, whereas trienylstannane **3"c** is obtained by insertion of another **2c** to **8** and the consequent reductive elimination. Trienylstannane **3"c** should not be formed through a palladacyclopentadiene because a stoichiometric reaction of 2,3,4,5-tetra(methoxycarbonyl)pallada-cyclopentadiene with **1b** (50 °C, 24 h, in toluene) did not afford the corresponding carbostannylation product (cf. Chapter 3).



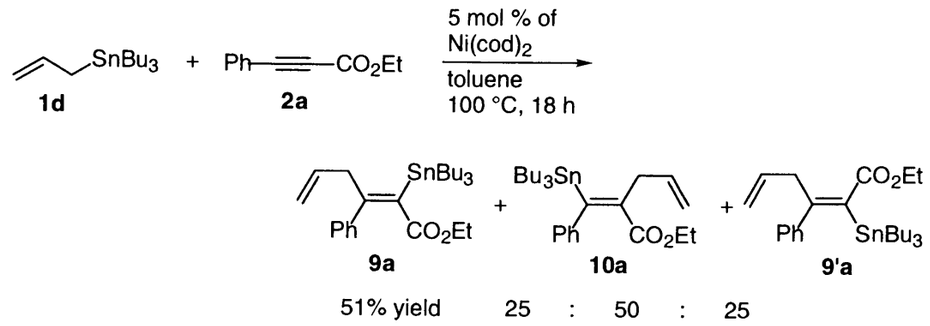
Scheme 3. Possible catalytic cycles of the palladium-catalyzed allylstannylation of alkynes.

The allylstannylation of various alkynes with allyltributyltin (**1d**) and a $Pd_2(dba)_3$ catalyst was next examined (Scheme 4 and Table 1). The author uses 1,4-dioxane as a solvent, since the solvent was found to accelerate the reaction to a great extent. Internal alkynes having such an electron-withdrawing group as ester, trifluoromethyl, sulfonyl or cyano reacted with **1d** in good to excellent yields. The regioselectivity was high with the alkynes where electronic difference between R^1 and R^2 was large, and a product predominated attaching $SnBu_3$ to the carbon substituted by a more electron-withdrawing group. Although the reaction of a highly electron-deficient alkyne, dimethyl butynedioate (**2c**), proceeded smoothly, isomerization of the product to **9'c** took place during purification (entry 3). Use of diimine **11** as a ligand increased the yield in the reaction of ethyl butynoate, indicating that a palladium–diimine complex does not always promote the dimerization–carbostannylation of alkynes discussed in Chapter 3 (entries 5–6).



Scheme 4. Palladium-catalyzed allylstannylation of alkynes.

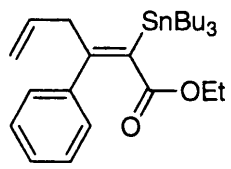
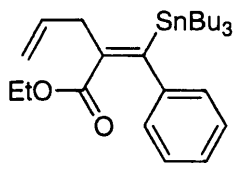
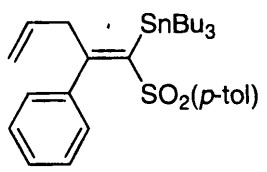
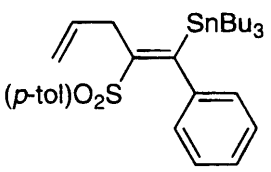
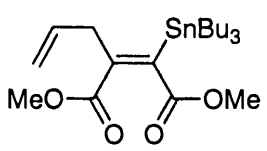
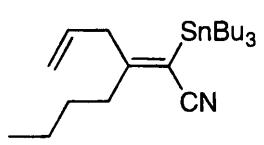
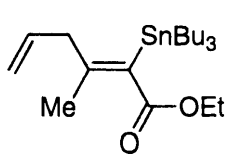
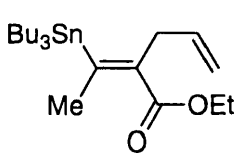
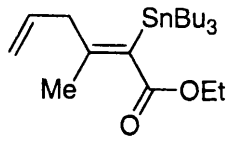
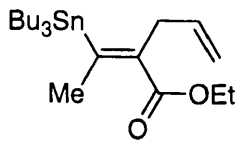
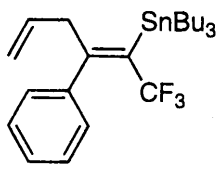
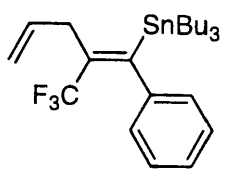
For the allylstannylation of these electron-deficient alkynes, $Pd_2(dba)_3$ is better suited than $Ni(cod)_2$, showing much higher catalytic activity with higher stereo- and regioselectivities. For example, reaction of **1d** with **2a** using $Ni(cod)_2$ proceeded at much higher temperature and gave the allylstannylation products as a mixture of three isomers including *anti*-adduct **9'a** (Scheme 5).



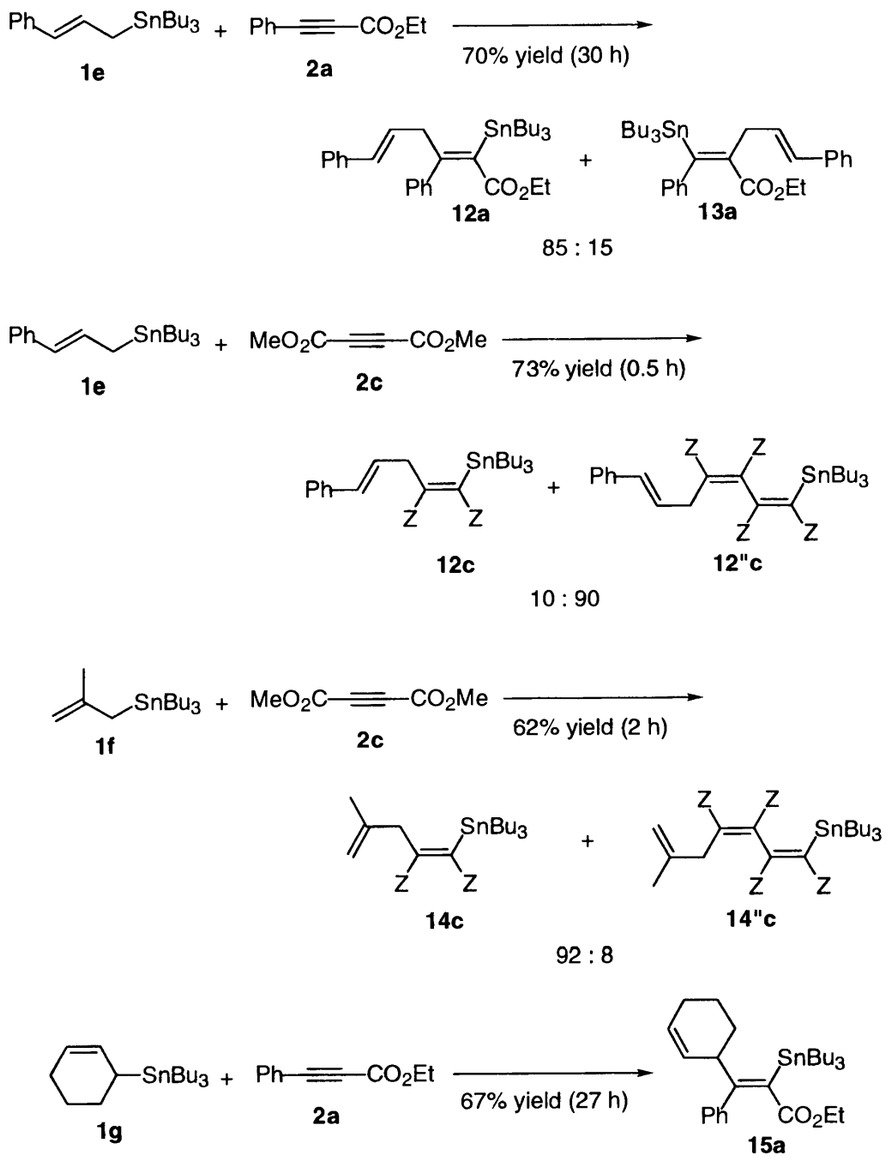
Scheme 5. Nickel-catalyzed allylstannylation of **2a** with **1d**.

The reaction of other allylstannanes was examined with alkynes **2a** and **2c** (Scheme 6). Unlike crotylstannanes, cinnamylstannane **1e** added to **2a** and **2c** without any allylic rearrangement, whereas **1e** reacted with **2c**, giving a dimerization–carbostannylation product as the major product. The addition of methallylstannane **1f** to **2c** was also accompanied by the dimerization of **2c**. The allylstannylation of **2a** using 2-cyclohexenylstannane **1g** proceeded in a highly regioselective manner to give a single isomer.

Table 1. Palladium-catalyzed allylstannylation of alkynes[a]

entry	allyl-stannane	alkyne	time (h)	yield (%)[b]	product(s)				ratio (**9** : **10**)[c]
1	**1d**	**2a**	43	100		**9a**		**10a**	79 : 21
2	**1d**	**2b**	1	73		**9b**		**10b**	92 : 8
3[d]	**1d**	**2c**	0.5	80		**9c**			–
4[e]	**1d**	**2d**	72	63		**9d**			>99 : 1
5	**1d**	**2e**	50	37		**9e**		**10e**	86 : 14
6[f]	**1d**	**2e**	62	55		**9e**		**10e**	91 : 9
7	**1d**	**2f**	14	98		**9f**		**10f**	72 : 28

[a] The reaction was carried out in 1,4-dioxane (3.0 mL) at 50 °C using allyl(tributyl)tin (0.33 mmol), an alkyne (0.99 mmol) and $Pd_2(dba)_3$ (8.2 μmol). [b] Isolated yield based on allyl(tributyl)tin. [c] Determined by ^{119}Sn NMR. [d] The reaction was carried out at 90 °C. [e] Diimine **11** (16 μmol) was used. [f] Conjugated dienylstannane **9'c** (8% yield) was also obtained.



[a] Reagents: $Pd_2(dba)_3$ (2.5 mol %), 1,4-dioxane, 50 °C.

Scheme 6. Carbostannylation of **2a** and **2c** with **1e–1g**[a]

Configuration of the carbostannylation products was determined by NOEs in ^1H NMR of the alkenylstannanes and/or the alkenes obtained by protodestannylation. For example, the configuration of **3a** and **4a** was determined on the basis of NOE (irradiation

at a methylene peak) as shown in Figure 1.

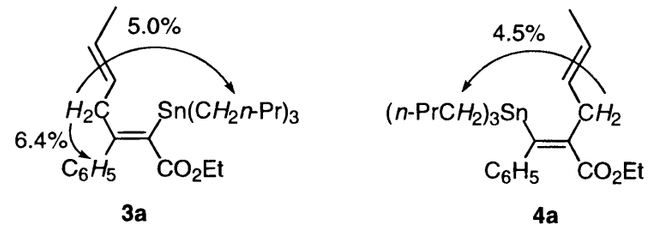


Figure 1

Conclusion

The author has demonstrated that the palladium-catalyzed allylstannylation of alkynes proceeds in different pathways depending on the presence or absence of a γ-substituent in allylstannanes. The reaction is applicable to various allylstannanes and electron-deficient alkynes. The results not only add new substrates to the family of the transition metal-catalyzed carbostannylation but also provide us with novel mechanistic possibility of "β-tin elimination".

Experimental section

Chemicals. The following compounds were prepared according to literature procedures: 1-Buten-3-yl(tributyl)tin (**1a**),[7] (*E*)-2-buten-1-yl(tributyl)tin (**1b**),[8] (*Z*)-2-buten-1-yl(tributyl)tin (**1c**),[9] allyl(tributyl)tin (**1d**),[10] (*E*)-cinnamyl(tributyl)tin (**1e**),[11] 2-methylallyl(tributyl)tin (**1f**),[12] 2-cyclohexen-1-yl(tributyl)tin (**1g**),[10] phenylethynyl *p*-tolyl sulfone (**2b**),[13] 2-heptynenitrile (**2d**)[14] and 3,3,3-trifluoro-1-phenyl-1-propyne (**2f**).[15]

Allylstannylation of Alkynes. ***A General Procedure.*** A solution (3 mL) of an organostannane (0.33 mmol), and an alkyne (0.99 mmol) was degassed by four freeze-thaw cycles. To this solution was added $Pd_2(dba)_3$ (7.5 mg, 8.2 μmol) and the mixture was stirred at 50 °C. After the time specified in Table 1 or Schemes, evaporation of the solvent followed by GPC gave the corresponding carbostannylation product.

Ethyl (2*E*,5*E*)-3-Phenyl-2-(tributylstannyl)-2,5-heptadienoate (3a). A yellow oil, R_f 0.36 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.75–1.70 (m, 33 H), 3.12 (d, *J* = 6.3 Hz, 2 H), 3.84 (q, *J* = 7.3 Hz, 2 H), 5.25 (dtq, *J* = 15.2, 6.3, 1.3 Hz, 1 H), 5.40 (dqt, *J* = 15.2, 6.3, 1.3 Hz, 1 H), 7.03–7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.4, 13.7, 13.9, 17.9, 27.3, 28.9, 43.6, 59.8, 127.0, 127.2, 127.4, 127.5, 127.7, 136.9, 142.2, 154.4, 172.8; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -39.6. Anal. Calcd for $C_{27}H_{44}O_2Sn$: C, 62.44; H, 8.54. Found as a mixture of **3a** and **4a**: C, 62.20; H, 8.30.

Ethyl (1*E*,4*E*)-1-Phenyl-1-(tributylstannyl)-1,4-hexadiene-2-carboxylate (4a). A yellow oil, R_f 0.34 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.63–1.75 (m, 33 H), 3.11 (d, *J* = 4.6 Hz, 2 H), 3.81 (q, *J* = 7.3 Hz, 2 H), 5.43 (dtq, *J* = 15.2, 4.6, 1.3 Hz, 1 H), 5.56 (dqt, *J* = 15.2, 5.9, 1.3 Hz, 1 H), 6.73–7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.2, 13.6, 18.0, 27.3, 28.9, 40.0, 59.9, 125.0, 125.8, 127.3, 127.4, 127.7, 142.0, 145.7, 152.9, 168.5; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -45.1. Anal. Calcd for $C_{27}H_{44}O_2Sn$: C, 62.44; H, 8.54. Found as a mixture of **3a** and **4a**: C, 62.20; H, 8.30.

(1*E*,4*E*)-2-Phenyl-1-(4-toluenesulfonyl)-1-(tributylstannyl)-1,4-hexadiene ((*E*)-3b). A yellow oil, R_f 0.22 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.70–1.79 (m, 30 H), 2.28 (s, 3 H), 3.02 (d, *J* = 6.3 Hz, 2 H), 5.09 (dtq, *J* = 15.2, 6.3, 1.3 Hz, 1 H), 5.27 (dq, *J* = 15.2, 6.3 Hz, 1 H), 6.55–7.11 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 13.7, 14.0, 17.9, 21.4, 27.3, 29.0, 45.4, 126.0, 127.0, 127.1, 127.2, 128.4, 128.5, 128.6, 139.6, 139.7, 141.7, 151.2, 162.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -37.9. Anal. Calcd for $C_{31}H_{46}O_2SSn$: C, 61.90; H, 7.71. Found as a mixture of **(*E*)-3b** and **(*Z*)-3b**: C, 62.16; H, 7.81.

(1*E*,4*Z*)-2-Phenyl-1-(4-toluenesulfonyl)-1-(tributylstannyl)-1,4-hexadiene ((*Z*)-3b). A yellow oil, R_f 0.23 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.54–1.93 (m, 30 H), 2.28 (s, 3 H), 3.09 (d, *J* = 6.8 Hz, 2 H), 5.13 (dt, *J* = 10.5, 6.8 Hz, 1 H), 5.40 (dq, *J* = 10.5, 6.5 Hz, 1 H), 6.54–7.11 (m, 9 H); ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -37.4. Anal. Calcd for $C_{31}H_{46}O_2SSn$: C, 61.90; H, 7.71. Found as a mixture of **(*E*)-3b** and **(*Z*)-3b**: C, 62.16; H, 7.81.

Dimethyl (1*E*,4*E*)-1-(Tributylstannyl)-1,4-hexadiene-1,2-dicarboxylate ((*E*)-3c). A yellow oil, R_f 0.18 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.80–1.80 (m, 30 H), 3.01 (d, *J* = 4.8 Hz, 2 H), 3.71 (s, 3 H), 3.73 (s, 3 H), 5.38 (dt, *J* = 15.4, 4.8 Hz, 1 H), 5.51 (dq, *J* = 15.4, 5.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 18.0, 27.2, 28.7, 38.2, 51.4, 52.0, 127.0, 127.6, 141.7, 149.9, 165.9, 172.9; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -32.5. Anal. Calcd for $C_{22}H_{40}O_4Sn$: C, 54.23; H, 8.27. Found: C, 54.02; H, 8.45.

Dimethyl (1*E*,4*Z*)-1-(Tributylstannyl)-1,4-hexadiene-1,2-dicarboxylate ((*Z*)-3c). A yellow oil, R_f 0.15 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.76–1.75 (m, 30 H), 3.08 (d, *J* = 6.6 Hz, 2 H), 3.70 (s, 3 H), 3.73

(s, 3 H), 5.24 (dt, J = 10.7, 6.6 Hz, 1 H), 5.54 (dq, J = 10.7, 6.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.1, 13.6, 27.2, 28.7, 33.5, 51.5, 52.0, 126.3, 126.4, 142.0, 149.9, 166.0, 172.9; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -32.2. Anal. Calcd for $C_{22}H_{40}O_4Sn$: C, 54.23; H, 8.27. Found: C, 53.94; H, 7.98.

Dimethyl (*E*)-3-Methyl-1-(tributylstannyl)-1,4-pentadiene-1,2-dicarboxylate (3'c). A yellow oil, R_f 0.20 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.81–1.76 (m, 30 H), 2.96 (qd, J = 7.1, 5.9 Hz, 1 H), 3.69 (s, 3 H), 3.71 (s, 3 H), 5.06 (dd, J = 10.2, 1.1 Hz, 1 H), 5.07 (dq, J = 17.4, 1.1 Hz, 1 H), 5.98 (ddd, J = 17.4, 10.2, 5.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.4, 13.6, 19.4, 27.2, 28.8, 45.9, 51.5, 51.7, 114.8, 139.9, 146.6, 148.6, 166.3, 172.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -34.7. Anal. Calcd for $C_{22}H_{40}O_4Sn$: C, 54.23; H, 8.27. Found: C, 54.31; H, 8.55.

Tetramethyl (1*E*,3*Z*,6*E*)-1-(Tributylstannyl)-1,3,6-octatriene-1,2,3,4-tetracarboxylate ((*E*)-3"c). A yellow oil, R_f 0.42 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR ($CDCl_3$) δ 0.81–1.71 (m, 30 H), 2.81–3.21 (m, 2 H), 3.70 (s, 3 H), 3.72 (s, 3 H), 3.81 (s, 3 H), 3.81 (s, 3 H), 5.28 (dtd, J = 15.2, 6.8, 1.5 Hz, 1 H), 5.52 (dq, J = 15.2, 6.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.9, 13.6, 17.9, 27.2, 28.6, 35.5, 51.6, 52.2, 52.4, 52.5, 123.7, 129.1, 129.5, 135.1, 146.7, 159.4, 163.4, 165.4, 168.7, 172.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -28.3. Anal. Calcd for $C_{28}H_{46}O_8Sn$: C, 53.43; H, 7.37. Found: C, 53.41; H, 7.64.

Tetramethyl (1*E*,3*Z*,6*Z*)-1-(Tributylstannyl)-1,3,6-octatriene-1,2,3,4-tetracarboxylate ((*Z*)-3"c). A yellow oil, R_f 0.41 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR ($CDCl_3$) δ 0.66–1.82 (m, 30 H), 2.89–3.27 (m, 2 H), 3.70 (s, 3 H), 3.71 (s, 3 H), 3.80 (s, 3 H), 3.81 (s, 3 H), 5.26 (dt, J = 10.3, 7.3 Hz, 1 H), 5.58 (dq, J = 10.3, 7.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.9, 12.7, 13.6, 27.2, 28.7, 30.1, 51.6, 52.3, 52.45, 52.54, 122.9, 127.5, 128.8, 130.9, 135.1, 146.9, 168.8, 172.4; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -28.0.

Ethyl (*E*)-3-Phenyl-2-(tributylstannyl)-2,5-hexadienoate (9a). A yellow oil, R_f 0.42 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.81–1.87 (m, 30 H), 3.20 (dt, J = 6.6, 1.5 Hz, 2 H), 3.85 (q, J = 7.0 Hz, 2 H), 4.96 (dtd, J = 10.2, 1.5, 1.3 Hz, 1 H), 5.00 (dtd, J = 17.2, 1.5, 1.3 Hz, 1 H), 5.65 (ddt, J = 17.2, 10.2, 6.6 Hz, 1 H), 7.13–7.46 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.5, 13.7, 13.9, 27.2, 28.9, 44.7, 59.8, 116.8, 127.1, 127.5, 127.8, 135.0, 137.7, 141.9, 153.5, 172.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -39.2. Anal. Calcd for $C_{26}H_{42}O_2Sn$: C, 61.80; H, 8.38. Found: C, 61.85; H, 8.10.

Ethyl (*E*)-1-Phenyl-1-(tributylstannyl)-1,4-pentadiene-2-carboxylate (10a). A yellow oil, R_f 0.43 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.63–1.74 (m, 30 H), 3.12 (dt, J = 6.2, 1.5 Hz, 2 H), 3.74 (q, J = 7.1 Hz, 2 H), 5.01 (ddt, J = 10.1, 1.6, 1.5 Hz, 1 H), 5.09 (ddt, J = 17.1, 1.6, 1.5 Hz, 1 H), 5.78 (ddt, J = 17.1, 10.1, 6.2 Hz, 1 H), 6.76–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.2, 13.6, 27.3, 28.9, 40.9, 59.9, 116.7, 125.1, 125.7, 125.8, 127.8, 135.0, 141.1, 145.7, 154.2, 168.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -44.8. Anal. Calcd for $C_{26}H_{42}O_2Sn$: C, 61.80; H, 8.38. Found: C, 61.63; H, 8.60.

Ethyl (*Z*)-3-Phenyl-2-(tributylstannyl)-2,5-hexadienoate (9'a). A yellow oil, R_f 0.50 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.51–1.47 (m, 30 H), 3.31 (dt, J = 6.8, 1.3 Hz, 2 H), 4.20 (q, J = 7.1 Hz, 2 H), 4.92 (dt, J = 11.5, 1.3 Hz, 1 H), 4.93 (dt, J = 15.6, 1.3 Hz, 1 H), 5.70 (ddt, J = 15.6, 11.5, 6.8 Hz, 1 H), 7.09–7.27 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.2, 13.6, 27.3, 28.9, 40.9, 59.9, 116.7, 125.1, 125.7, 125.8, 127.8, 135.0, 141.1, 145.7, 154.2, 168.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -44.8. Anal. Calcd for $C_{26}H_{42}O_2Sn$: C, 61.80; H, 8.38. Found: C, 61.52; H, 8.36.

(*E*)-2-Phenyl-1-(4-toluenesulfonyl)-1-(tributylstannyl)-1,4-pentadiene (9b). A yellow oil, R_f 0.43 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.84–1.88 (m, 27 H), 2.27 (s, 3 H), 3.10 (d, J = 6.4 Hz, 2 H), 4.88 (d, J =

16.9 Hz, 1 H), 4.94 (d, J = 10.3 Hz, 1 H), 5.50 (ddt, J = 16.9, 10.3, 6.4 Hz, 1 H), 6.64–7.16 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 13.7, 14.0, 21.3, 27.3, 29.0, 46.3, 117.8, 127.1, 127.2, 128.36, 128.44, 133.6, 139.4, 139.5, 141.7, 152.1, 161.7; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -37.6. Anal. Calcd for $C_{30}H_{44}O_2SSn$: C, 61.34; H, 7.55. Found as a mixture of **9b** and **10b**: C, 61.16; H, 7.58.

(*E*)-1-Phenyl-2-(4-toluenesulfonyl)-1-(tributylstannyl)-1,4-pentadiene (10b). A yellow oil, R_f 0.32 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.63–1.72 (m, 27 H), 2.34 (s, 3 H), 3.48 (dt, J = 5.6, 1.6 Hz, 2 H), 5.26 (dtd, J = 10.1, 1.6, 1.6 Hz, 1 H), 5.36 (d, J = 17.1, 1.6, 1.6 Hz, 1 H), 6.05 (ddt, J = 17.1, 10.1, 5.6 Hz, 1 H), 6.47–6.61 (m, 2 H), 6.91–7.40 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 11.7, 13.5, 21.5, 27.2, 28.7, 39.3, 117.4, 125.2, 125.8, 127.48, 127.51, 128.8, 135.3, 139.6, 141.8, 142.7, 146.5, 162.1; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -29.0. Anal. Calcd for $C_{30}H_{44}O_2SSn$: C, 61.34; H, 7.55. Found as a mixture of **9b** and **10b**: C, 61.16; H, 7.58.

Dimethyl (*E*)-1-(Tributylstannyl)-1,4-pentadiene-1,2-dicarboxylate (9c). A yellow oil, R_f 0.31 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.84–1.74 (m, 27 H), 3.08 (dt, J = 6.0, 1.6 Hz, 2 H), 3.71 (s, 3 H), 3.74 (s, 3 H), 5.07 (dtd, J = 10.3, 1.6, 1.5 Hz, 1 H), 5.09 (dtd, J = 17.0, 1.6, 1.5 Hz, 1 H), 5.81 (ddt, J = 17.0, 10.3, 6.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.4, 13.6, 27.2, 28.7, 39.2, 51.5, 52.0, 116.8, 134.6, 140.7, 151.2, 165.7, 172.8; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -31.9. Anal. Calcd for $C_{21}H_{38}O_4Sn$: C, 53.30; H, 8.09. Found: C, 53.01; H, 7.90.

Dimethyl (1*E*,3*E*)-1-(Tributylstannyl)-1,3-pentadiene-1,2-dicarboxylate (9'c). A yellow oil, R_f 0.29 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR ($CDCl_3$) δ 0.83–1.70 (m, 27 H), 1.85 (d, J = 5.4 Hz, 3 H), 3.70 (s, 3 H), 3.79 (s, 3 H), 5.99 (dq, J = 15.8, 5.4 Hz, 1 H), 6.11 (d, J = 15.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.9, 13.6, 19.0, 27.2, 28.8, 51.8, 52.1, 129.5, 135.1, 140.6, 149.0, 168.2, 171.6; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -34.9. Anal. Calcd for $C_{21}H_{38}O_4Sn$: C, 53.30; H, 8.09.

Found: C, 53.38; H, 8.30.

(Z)-3-Butyl-2-(tributylstannyl)-2,5-hexadienenitrile (9d). A yellow oil, R_f 0.52 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.73–1.83 (m, 34 H), 2.52 (t, J = 7.5 Hz, 2 H), 2.88 (dt, J = 6.4, 1.5 Hz, 2 H), 5.11 (dtd, J = 16.5, 1.5, 1.5 Hz, 1 H), 5.13 (dtd, J = 10.7, 1.5, 1.5 Hz, 1 H), 5.69 (ddt, J = 16.5, 10.7, 1.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 13.9, 22.5, 27.1, 28.8, 30.6, 36.7, 43.0, 109.2, 117.9, 121.0, 134.2, 174.3; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -37.8. Anal. Calcd for $C_{22}H_{41}NSn$: C, 60.29; H, 9.43. Found: C, 60.55; H, 9.35.

Ethyl (Z)-3-Methyl-2-(tributylstannyl)-2,5-hexadienoate (9e). A yellow oil, R_f 0.54 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.76–1.71 (m, 30 H), 1.85 (s, 3 H), 2.80 (dt, J = 6.6, 1.5 Hz, 2 H), 4.15 (q, J = 7.1 Hz, 2 H), 5.09 (ddt, J = 10.1, 1.7, 1.5 Hz, 1 H), 5.11 (ddt, J = 16.9, 1.7, 1.5 Hz, 1 H), 5.75 (ddt, J = 16.9, 10.1, 6.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 14.4, 20.5, 27.2, 28.9, 45.7, 60.0, 117.0, 133.8, 135.5, 151.0, 173.0; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -43.9. Anal. Calcd for $C_{21}H_{40}O_2Sn$: C, 56.90; H, 9.10. Found: C, 57.07; H, 9.31.

Ethyl (*E*)-5-(Tributylstannyl)-1,4-hexadiene-4-carboxylate (10e). A yellow oil, R_f 0.54 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.79–1.70 (m, 30 H), 2.08 (s, 3 H), 3.03 (d, J = 6.1 Hz, 2 H), 4.19 (q, J = 7.1 Hz, 2 H), 5.00 (dd, J = 10.1, 1.6 Hz, 1 H), 5.05 (dd, J = 17.2, 1.6 Hz, 1 H), 5.76 (ddt, J = 17.2, 10.1, 6.1 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.5, 13.6, 14.3, 23.2, 27.4, 29.1, 41.6, 60.0, 116.1, 135.7, 139.2, 150.4, 167.8; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -43.5. Anal. Calcd for $C_{21}H_{40}O_2Sn$: C, 56.90; H, 9.10. Found: C, 56.86; H, 9.05.

(*E*)-6,6,6-Trifluoro-4-phenyl-5-(tributylstannyl)-1,4-hexadiene (9f). A yellow oil, R_f 0.12 (hexane). ^{1}H NMR ($CDCl_3$) δ 0.81–1.80 (m, 27 H), 3.18 (dq, J = 6.6, 1.5 Hz, 2 H), 4.95 (dq, J = 16.8, 1.5 Hz, 1 H), 4.99 (dq, J = 10.3, 1.5 Hz, 1 H), 5.59 (ddt, J = 16.8, 10.3, 6.6 Hz, 1 H), 6.98–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.9, 13.7, 27.2, 28.8, 46.8, 117.6, 124.4, 127.0, 127.2, 127.4, 127.6, 128.5, 131.8,

132.3, 133.9, 141.7, 158.6, 158.7, 158.8; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -36.8 (q, *J* = 16.6 Hz). Anal. Calcd for $C_{24}H_{37}F_3Sn$: C, 57.51; H, 7.44. Found: C, 57.21; H, 7.27.

(*E*)-1-Phenyl-1-(tributylstannyl)-2-(trifluoromethyl)-1,4-pentadiene (10f). A yellow oil, R_f 0.13 (hexane). ^1H NMR ($CDCl_3$) δ 0.67–1.73 (m, 27 H), 3.11 (d, *J* = 5.8 Hz, 2 H), 5.16 (dtd, *J* = 10.2, 1.6, 1.5 Hz, 1 H), 5.21 (dtd, *J* = 17.2, 1.6, 1.5 Hz, 1 H), 5.89 (ddt, *J* = 17.2, 10.2, 5.8 Hz, 1 H), 6.76–7.44 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.5, 27.2, 28.8, 39.3, 116.7, 120.6, 124.7, 125.1, 125.2, 127.7, 134.7, 135.1, 135.2, 143.8, 158.29, 158.34; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -40.8. Anal. Calcd for $C_{24}H_{37}F_3Sn$: C, 57.51; H, 7.44. Found: C, 57.37; H, 7.67.

Ethyl (2*E*,5*E*)-3,6-Diphenyl-2-(tributylstannyl)-2,5-hexadienoate (12a). A yellow oil, R_f 0.46 (hexane–ethyl acetate = 10 : 1). ^1H NMR ($CDCl_3$) δ 0.83–1.78 (m, 30 H), 3.34 (dd, *J* = 6.6, 1.4 Hz, 2 H), 3.86 (q, *J* = 7.1 Hz, 2 H), 6.02 (dt, *J* = 15.8, 6.6 Hz, 1 H), 6.34 (dd, *J* = 15.8, 1.4 Hz, 1 H), 7.00–7.38 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 11.5, 13.7, 13.9, 27.3, 29.0, 43.9, 59.8, 126.0, 126.8, 127.1, 127.2, 127.5, 127.9, 128.4, 131.8, 137.3, 137.8, 142.0, 153.6, 172.7; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -39.3. Anal. Calcd for $C_{32}H_{46}O_2Sn$: C, 66.10; H, 7.97. Found: C, 66.06; H, 8.12.

Ethyl (1*E*,4*E*)-1,5-Diphenyl-1-(tributylstannyl)-1,4-pentadiene-2-carboxylate (13a). A yellow oil, R_f 0.43 (hexane–ethyl acetate = 10 : 1). ^1H NMR ($CDCl_3$) δ 0.71–1.67 (m, 30 H), 3.35 (dd, *J* = 6.4, 1.3 Hz, 2 H), 3.80 (q, *J* = 7.1 Hz, 2 H), 6.20 (dt, *J* = 15.9, 6.4 Hz, 1 H), 6.50 (d, *J* = 15.9 Hz, 1 H), 6.84–7.34 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 27.3, 28.9, 40.2, 60.0, 125.1, 125.7, 126.1, 126.7, 127.1, 127.8, 128.4, 131.9, 137.4, 141.2, 145.6, 154.4, 168.2; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -44.6. Anal. Calcd for $C_{32}H_{46}O_2Sn$: C, 66.10; H, 7.97. Found as a mixture of **12a** and **13a**: C, 65.86; H, 8.14.

Dimethyl (1*E*,4*E*)-5-Phenyl-1-(tributylstannyl)-1,4-pentadiene-1,2-dicarboxylate (12c). A yellow oil, R_f 0.15 (hexane–ethyl acetate = 10 : 1). ^1H

NMR ($CDCl_3$) δ 0.77–1.79 (m, 27 H), 3.27 (d, *J* = 6.0 Hz, 2 H), 3.73 (s, 3 H), 3.78 (s, 3 H), 6.17 (dt, *J* = 15.9, 6.0 Hz, 1 H), 6.45 (d, *J* = 15.9 Hz, 1 H), 7.12–7.48 (m, 5 H); ^{13}C NMR ($CDCl_3$) d 11.4, 13.6, 27.2, 28.7, 38.4, 51.5, 52.1, 126.1, 126.2, 127.3, 128.4, 132.0, 137.1, 140.6, 151.5, 165.6, 172.8; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) d -31.8. Anal. Calcd for $C_{27}H_{42}O_4Sn$: C, 59.03; H, 7.71. Found: C, 59.10; H, 7.84.

Tetramethyl (1*E*,3*Z*,6*E*)-7-Phenyl-1-(tributylstannyl)hepta-1,3,6-triene-1,2,3,4-tetracarboxylate (12"c). A brown oil, R_f 0.65 (hexane–ethyl acetate = 2 : 1). ^1H NMR ($CDCl_3$) δ 0.82–1.67 (m, 27 H), 3.03–3.43 (m, 2 H), 3.60 (s, 3 H), 3.73 (s, 3 H), 3.82 (s, 3 H), 3.83 (s, 3 H), 6.04 (dt, *J* = 15.7, 7.0 Hz, 1 H), 6.43 (d, *J* = 15.7 Hz, 1 H), 7.14–7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.0, 13.5, 27.2, 28.6, 35.6, 51.6, 52.3, 52.45, 52.54, 122.7, 126.2, 127.5, 128.4, 130.3, 133.5, 135.0, 136.8, 145.4, 159.7, 163.3, 165.4, 168.6, 172.3; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -28.3. Anal. Calcd for $C_{33}H_{48}O_8Sn$: C, 57.32; H, 7.00. Found: C, 57.07; H, 7.27.

Dimethyl (*E*)-4-Methyl-1-(tributylstannyl)-1,4-pentadiene-1,2-dicarboxylate (14c). A yellow oil, R_f 0.18 (hexane–ethyl acetate = 10 : 1). ^1H NMR ($CDCl_3$) δ 0.80–1.95 (m, 30 H), 2.99 (s, 2 H), 3.69 (s, 3 H), 3.74 (s, 3 H), 4.67 (s, 1 H), 4.81 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.3, 13.6, 23.4, 27.2, 28.7, 42.3, 51.5, 52.1, 111.7, 141.3, 142.6, 151.4, 166.1, 172.8; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -32.6. Anal. Calcd for $C_{22}H_{40}O_4Sn$: C, 54.23; H, 8.27. Found: C, 54.43; H, 8.52.

Tetramethyl (1*E*,3*Z*)-6-Methyl-1-(tributylstannyl)-1,3,6-heptatriene-1,2,3,4-tetracarboxylate (14"c). A yellow oil, R_f 0.46 (hexane–ethyl acetate = 2 : 1). ^1H NMR ($CDCl_3$) δ 0.75–1.84 (m, 30 H), 2.82–3.01 (m, 1 H), 3.09–3.27 (m, 1 H), 3.68 (s, 3 H), 3.73 (s, 3 H), 3.79 (s, 3 H), 3.81 (s, 3 H), 4.76 (s, 1 H), 4.81 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.9, 13.6, 22.3, 27.2, 28.6, 40.6, 51.6, 52.1, 52.3, 52.4, 114.5, 130.4, 135.0, 140.0, 146.5, 159.7, 163.4, 165.2, 168.7, 172.4; $^{119}Sn\{^1H\}$ NMR ($CDCl_3$) δ -27.6. Anal. Calcd for $C_{28}H_{46}O_8Sn$: C, 53.43; H, 7.37. Found: C, 53.64; H, 7.43.

Ethyl (*E*)-3-(2-Cyclohexen-1-yl)-3-phenyl-2-(tributylstannyl)-2-propenoate (15a). A yellow oil, R_f 0.47 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR ($CDCl_3$) δ 0.20–2.05 (m, 36 H), 2.89–3.12 (m, 1 H), 3.77 (q, *J* = 7.1 Hz, 2 H), 5.62–5.82 (m, 2 H), 7.00–7.52 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 11.4, 13.7, 13.9, 21.7, 24.5, 27.2, 28.2, 29.0, 48.2, 59.6, 126.6, 127.2, 128.5, 128.9, 129.2, 137.6, 140.3, 158.8, 172.5; ^{119}Sn{^{1}H} NMR ($CDCl_3$) δ -43.4. Anal. Calcd for $C_{29}H_{46}O_2Sn$: C, 63.87; H, 8.50. Found: C, 63.96; H, 8.22.

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List of Publications

I. Parts of the present Thesis have been, or are to be, published in the following journals.

Chapter 2

(1) Carbostannylation of Alkynes Catalyzed by an Iminophosphine–Palladium Complex.

Shirakawa, E.; Yoshida, H.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 2975–2976.

(2) Palladium–Iminophosphine-Catalyzed Alkynylstannylation of Alkynes.

Yoshida, H.; Shirakawa, E.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *Organometallics*, in press.

Chapter 3

(3) Palladium-Catalyzed Dimerization–Carbostannylation of Alkynes: Synthesis of Highly Conjugated Alkenylstannanes.

Shirakawa, E.; Yoshida, H.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 4290–4291.

(4) Dimerization–Carbostannylation of Alkynes Catalyzed by a Palladium–Diimine Complex: Regioselectivity, Stereoselectivity and Mechanism.

Yoshida, H.; Shirakawa, E.; Nakao, Y.; Honda, Y.; Hiyama, T. submitted for publication.

Chapter 4

(5) Nickel-Catalyzed Carbostannylation of Alkynes with Allyl-, Acyl-, and Alkynylstannanes: Stereoselective Synthesis of Trisubstituted Vinylstannanes.

Shirakawa, E.; Yamasaki, K.; Yoshida, H.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 10221–10222.

Chapter 5

(6) Mechanistic Aspects of Palladium-Catalyzed Allylstannylation of Alkynes. Shirakawa, E.; Yoshida, H.; Nakao, Y.; Hiyama, T. *Org. Lett.* **2000**, *2*, 2209–2211.

II. Following publications are not included in this Thesis.

(7) An Iminophosphine–Palladium Catalyst for Cross-Coupling of Aryl Halides with Organostannanes.
Shirakawa, E.; Yoshida, H.; Takaya, H. *Tetrahedron Lett.* **1997**, *38*, 3759–3762.

(8) On the Catalytic Cycle of the Palladium-Catalyzed Cross-Coupling Reaction of Alkynylstannane with Aryl Iodide.
Shirakawa, E.; Yoshida, H.; Hiyama, T. *Tetrahedron Lett.* **1997**, *38*, 5177–5180.

(9) Nickel-Catalyzed Acylstannylation of 1,3-Dienes: Synthesis and Reaction of ε-Oxoallylstannanes.
Shirakawa, E.; Nakao, Y.; Yoshida, H.; Hiyama, T. *J. Am. Chem. Soc.*, **2000**, *122*, 9030–9031.

(10) Diphenylphosphinophenolate: A Ligand for the Palladium-Catalysed Silylation of Aryl Halides Activating Simultaneously both Palladium and Silicon.
Shirakawa, E.; Kurahashi, T.; Yoshida, H.; Hiyama, T. *Chem. Commun.* **2000**, 1895–1896.

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