Research Article

Applied Organometallic Chemistry

Received: 25 September 2007 Revised: 2 November 2007 Accepted: 2 November 2007

(www.interscience.com) DOI 10.1002/aoc.1360

Stereospecific synthesis of a family of novel (*E*)-2-aryl-1-silylalka-1,4-dienes or (*E*)-4-aryl-5-silylpenta-1,2,4-trienes via a cross-coupling of (*Z*)-silyl(stannyl)ethenes with allyl halides or propargyl bromide

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Stereospecific synthesis of a family of novel (*E*)-2-aryl-1-silylalka-1,4-dienes or (*E*)-4-aryl-5-silylpenta-1,2,4-trienes via a cross-coupling of (*Z*)-silyl(stannyl)ethenes with allyl halides or propargyl bromide is described. In the reaction with allyl bromide, either a $Pd(dba)_2$–CuI combination (dba, dibenzylideneacetone) in DMF or copper(I) iodide in DMSO–THF readily catalyzes or mediates the coupling reaction of (*Z*)-silyl(stannyl)ethenes at room temperature, producing novel vinylsilanes bearing an allyl group β to silicon with *cis*-disposition in good yields. Allyl chlorides as halides can be used in the CuI-mediated reaction. CuI alone much more effectively mediates the cross-coupling reaction with propargyl bromide in DMSO–THF at room temperature compared with a $Pd(dba)_2$–CuI combination catalysis in DMF, providing novel stereodefined vinylsilanes bearing an allenyl group β to silicon with *cis*-disposition in good yields.

Keywords: vinylstannanes; vinylsilanes; silylpenta-1,4-dienes; silylvinyl allenes; allenes; palladium catalysis; copper-mediated reaction; cross-coupling

Introduction

Alka-1,4-dienes are very interesting compounds, because the diene framework is an important part of the structure of a number of naturally occurring compounds possessing biological activity.[1,2] Penta-1,4-diene, considered as an allyl ethene, is itself a key component of the transition metal 1,4-diene complexes,[3] and can undergo a palladium-catalyzed reaction with 2-iodophenol or 2-iodoaniline to produce interesting annulation products.[4] In addition, the 1,4-diene undergoes deprotonation with the use of *n*-butyl lithium to produce penta-2,4-dienyl lithium reagents,[5–7] which can react with various electrophiles, e.g. carbonyl compounds,[6] benzyl bromide,[6] silyl chloride,[7] germyl chloride[7] or stannyl chloride,[7] producing carbon–carbon or carbon–group14 metal bond formation products. The copper reagent obtained from the penta-2,4-dienyl lithium and copper(I) iodide can add to a triple bond, producing new carbon–carbon double bond products.[8]

The reactions of 1-silylated penta-1,4-dienes will possibly open up a new area of 1,4-diene chemistry. For example, the deprotonation of the silylated diene is predicted to produce 1-silyl 2,4-butenyl lithium selectively according to the α-anion stabilizing effect of silicon, which can then take part in a Peterson-type olefination reaction.[9] Some stereospecific syntheses of the silylpenta-1,4-dienes have been reported – in the case of the synthesis of (*Z*)-1-silylpenta-1,4-dienes: (1) allylzincation of acetylenes;[10] (2) allyltitanation of 1-(trimethylsilyl)-2-phenylethyne mediated by Me_2AlCl;[11] (3) the reaction of zirconocene-alkyne complexes [e.g. alkyne, 1-(trimethylsilyl)-2-phenylethyne] with allyl phenyl ether;[12,13] (4) $EtAlCl_2$-catalyzed carbosilylation of acetylenes with an allylsilane in the presence of Me_3SiCl;[14,15] (5) carbosilylation of acetylenes with an allylsilane in the presence of $GaCl_3$;[16] and (6) silylcupration of acetylenes followed by reaction with allyl bromide.[17] In contrast, reported examples for the synthesis of the (*E*)-1-silylpenta-1,4-dienes are few. One example is the reaction of (*Z*)-1-phenyl-2-silylethenylcopper, prepared from the silacupration of acetylene, with allylic phosphates or allylic phosphinates.[18] Another is the Migita–Kosugi–Stille type cross-coupling reaction of (*Z*)-silyl(stannyl)ethenes **1**,[19–33] prepared by the addition of a silyltin to acetylenes, with allylic halides.[22,26] We have already reported the synthesis and characterization of a family of (*Z*)-silyl(stannyl)ethenes **1**[32,33] and then presented preliminary results for the stereospecific synthesis of (*E*)-2-aryl-1-silylalka-1,4-dienes using the (*Z*)-silyl(stannyl)ethenes **1** as a communication.[34]

Closely related to the synthesis of allylated vinylsilanes, the reaction with propargyl bromide is also of great interest because of the possibility of producing allenyl vinylsilanes or silylvinyl allenes, and (*E*)-4-aryl-5-silyl-1,2,4-trienes, which may

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be important in allene chemistry,[35] particularly in cycloaddition reaction.[36–39] Allenes also undergo: (1) hydrosilylation;[40] (2) hydrogermylation;[40] (3) hydrostannylation;[40] (4) bis-silylation;[40] (5) bis-stannylation;[40] (6) silastannylation;[40–42] (7) germastannylation;[40,43,44] (8) bisboration;[40,45–47] (9) silaboration;[40,48–54] and (10) carbosilylation.[55] Reported syntheses of silylvinyl allenes are quite few in number. One example is the palladium-catalyzed reaction of **1a** with 1-bromo-2-propyne[36] and another is the reaction of (*Z*)-2-amino-1-silyl-2-stannylethenes with propargyl bromide in the presence of a palladium catalyst.[26] Reported herein are the stereodefined syntheses of novel (*E*)-vinylsilanes bearing an allyl group or an allenyl group β to silicon with *cis*-disposition via the cross-coupling of (*Z*)-silyl(stannyl)ethenes **1**[32,33] with the respective allyl halides or propargyl bromide (Scheme 1).

Results and Discussion

Optimization of reaction conditions outlined in Scheme 2

The reaction of (*Z*)-2-(tri-*n*-butylstannyl)-1-(trimethylsilyl)-2-phenylethene **1a** with allyl bromide in the presence of $BnPdCl(PPh_3)_2$ (Bn = benzyl) has been reported to produce (*E*)-1-(trimethylsilyl)-2-phenylpenta-1,4-diene **2a-allyl** in 75% yield.[22] However, the reaction requires a rather high reaction temperature (80 °C) and a long reaction time (45 h). We recently found that a $Pd(dba)_2$ (dba = dibenzylideneacetone) and CuI combination is quite effective as a catalyst to accomplish the reaction under milder conditions. The combination allowed the reaction to take place at room temperature and to complete in a shorter time. Preliminary results have been reported as a communication.[34] Herein full results for the synthesis of a family of (*E*)-2-aryl-1-silylalka-1,4-dienes **2** are reported.

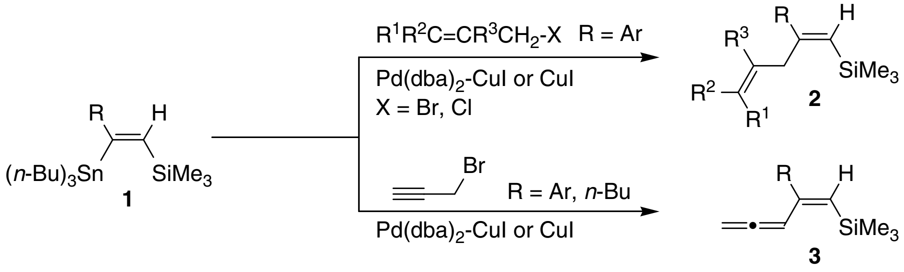
Table 1 shows the comparison of the product yields using various catalysts in the model reaction outlined in Scheme 2. A catalyst composed of $Pd(dba)_2$ and CuI was found to drive the reaction at room temperature and be complete within 2 h, producing (*E*)-1-(trimethylsilyl)-2-phenylpenta-1,4-diene **2a-allyl**[22,34] exclusively with 68% glc-yield (run 1 in Table 1). ^{1}H-NMR analysis of **2a-allyl** disclosed that the allyl group successfully replaced the tri-*n*-butylstannyl group. The vinyl proton α to the trimethylsilyl group was observed at 5.94 ppm as a singlet, which was a lower value than that reported for the *Z*-isomer (5.59 ppm).[13,14] The downfield shift of the vinyl proton in the *E*-isomer may be caused by a ring current effect of the neighboring phenyl group. Trimethylsilyl protons in the *E*-isomer were observed at 0.19 ppm, while those in the *Z*-isomer have been reported at −0.19 ppm.[13,14] The abnormal higher field shift of trimethylsilyl protons of the *Z*-isomer is probably due to the shielding effect caused by the neighboring phenyl group. A separate experiment to isolate **2a-allyl** under conditions similar to those shown for run 1 in Table 1 gave **2a-allyl** in 62% isolated-yield. Other combination catalysts such as a $PdCl_2$–CuI or a $Pd(OAc)_2$–CuI combination were also active at room temperature. A catalyst composed of $BnPdCl(PPh_3)_2$ and CuI was also effective at 50 °C. Catalysis with a $Pd(dba)_2$-PPh_3 combination needed heating to obtain the 1,4-diene in accessible yields. A combination of $Pd(dba)_2$ and $P(OEt)_3$ had a small effect, but $Pd(dba)_2$-$P(o\text{-tol})_3$ was ineffective.

Table 1. Optimization of the cross-coupling reaction outlined in Scheme 2[a]

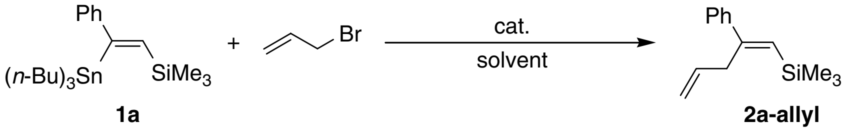
Run	[Pd] (mol%)[b]	Additive (mol%)[b]	Solvent (ml)	Conditions (°C, h)	Yield[c] (%)
1	$Pd(dba)_2$ (0.5)[d]	CuI (1.0)	A(1)[e]	r.t., 2	68
2	$PdCl_2$ (0.5)	CuI (1.0)	A(1)	r.t., 2	50
3	$Pd(OAc)_2$ (0.5)	CuI (1.0)	A(1)	r.t., 4	63
4	$BnPdCl(PPh_3)_2$ (1.0)[f]	CuI (2.0)	A(2)	50, 14	69
5	$Pd(dba)_2$ (2.0)	PPh_3 (4.0)	B(1)[g]	60, 5	49
6	$Pd(dba)_2$ (2.0)	$P(OEt)_3$ (4.0)	B(1)	60, 3	35
7	$Pd(dba)_2$ (2.0)	$P(o\text{-tol})_3$ (4.0)[h]	B(1)	60, 1	0

[a] Each reaction was carried out using **1a** (0.2 mmol) and allyl bromide (0.2 mmol).
[b] Mol% based on the **1a** employed.
[c] GLC-yields.
[d] dba, dibenzylideneacetone.
[e] A, DMF(*N*,*N*-dimethylformamide).
[f] Bn, benzyl.
[g] B, THF(tetrahydrofuran);
[h] *o*-tol, *o*-tolyl(2-methylphenyl).

Copper(I) iodide as a catalyst component and DMF as a solvent seem to be indispensable in producing the reaction at room



Scheme 1. Reaction of (*Z*)-silyl(stannyl)ethenes **1** with allyl halides or propargyl bromide.



Scheme 2. Reaction of **1a** with allyl bromide in the presence of a palladium catalyst.

temperature with allyl bromide. However, for the reaction of **1a** with allyl chloride, allylation did not occur under similar conditions.

Pd(dba)$_2$–CuI catalyzed cross-coupling of (*Z*)-silyl(stannyl)ethenes 1 with allyl bromides in DMF

A family of arylacetylenes was prepared by the Sonogashira–Hagihara method from the corresponding substituted bromo- or iodobenzenes in two steps in good yields.[56–58] Then, their acetylenes, including phenylacetylene, underwent an addition of tri-*n*-butyl (trimethylsilyl)tin at room temperature in the presence of a Pd(dba)$_2$–P(OEt)$_3$ combination catalyst affording (*Z*)-1-aryl-1-(tri-*n*-butylstannyl)-2-(trimethylsilyl)ethenes **1a–h**[32,33] in good isolated yields. The (*Z*)-silyl(stannyl)ethenes **1b–h** prepared in this way were treated with allyl bromide at a preparative scale and in the presence of a Pd(dba)$_2$–CuI combination in DMF. The reaction readily took place at room temperature and was completed in a short time to produce the corresponding (*E*)-2-aryl-1-(trimethylsilyl)penta-1,4-dienes in 65–99% isolated yields. NMR analysis of **2b-allyl–2h-allyl** showed the trimethylsilyl protons at 0.19 ppm, at essentially the same field as the protons of TMS, unlike those of the (*Z*)-isomer which resonated at a higher field. The results show that products **2b-allyl–2h-allyl** have the same disposition as **2a-allyl**. Selected spectral data for **2b-allyl–2h-allyl** as well as those for **2a-allyl** are compiled in Table 2.

Table 2. Stereospecific synthesis of (*E*)-2-aryl-1-silylpenta-1,4-dienes **2** via a cross-coupling of (*Z*)-(n-Bu)$_3$SnCAr=CHSiMe$_3$ with allyl bromide in DMF[a]

Run	X in Ar	Time (h)	Product no.	Yield[b] (%)
1	H **1a**	2	**2a-allyl**	62(68)
2	2-F **1b**	2	**2b-allyl**	70
3	3-F **1c**	2	**2c-allyl**	94
4	4-F **1d**	2	**2d-allyl**	94
5	4-Cl **1e**	3	**2e-allyl**	85
6	3-CF$_3$ **1f**	5	**2f-allyl**	89
7	4-CN **1g**	1	**2g-allyl**	99
8	4-COOEt **1h**	7	**2h-allyl**	93

[a] All the reactions were carried out in DMF at room temperature using Pd(dba)$_2$(1 mol%) and CuI(1.6 mol%).
[b] Isolated yields. In parentheses are shown glc yields.

Methallyl bromide also entered into the reaction with **1a** at room temperature, producing (*E*)-4-methyl-1-(trimethylsilyl)-2-phenylpenta-1,4-diene **2a-metha** in 76% yield (Scheme 3). The chemical shift of the trimethylsilyl protons of the **2a-metha** was observed at 0.18 ppm, but that of its *Z*-isomer was reported to appear at −0.17 ppm.[14]

CuI-mediated cross-coupling of (*Z*)-(n-Bu)$_3$SnCAr=CHSiMe$_3$ 1 with allyl halides in DMSO–THF

The transmetallation of Sn → Cu → Pd suggested by Liebeskind *et al.*[59] in the reaction of simple vinylstannane with organic halides and the copper(I) iodide-mediated reaction of simple vinylstannane with allyl halides reported by Takeda *et al.*[60] stimulated us to examine the copper(I) iodide-mediated cross-coupling of (*Z*)-silyl(stannyl)ethenes **1** with allyl halides in a polar aprotic solvent, particularly a DMSO–THF solvent. No precedent has been reported for the reaction of **1** with allyl halides in the sole presence of copper(I) halide. A model reaction of **1a** with allyl bromide was first examined in a DMSO–THF solvent in the presence of copper (I) iodide (1 equiv). The reaction readily took place even at room temperature and completed in 2 h producing (*E*)-1-(trimethylsilyl)-2-phenylpenta-1,4-diene **2a-allyl** in 92% isolated-yield. Interestingly, under similar conditions allyl chloride entered into the reaction, affording **2a-allyl** in 66% yield, though prolonged stirring was needed. Other examples are compiled in Table 3. As Table 3 shows, the reactions of **1a–h** with allyl bromide completed within 4 h and produced **2a-allyl–2h-allyl** in 68–99% isolated yields. Every product was identified by comparing its NMR spectra with that obtained from the Pd(dba)$_2$–CuI catalysis in DMF. In this mediated reaction, methallyl chloride also entered into the reaction more easily than did allyl chloride, producing (*E*)-4-methyl-1-(trimethylsilyl)-2-phenylpenta-1,4-diene **2a-metha** in 78% yield.

Table 3. CuI-mediated cross-coupling reaction of (*Z*)-(n-Bu)$_3$SnCAr=CHSiMe$_3$ **1** with several allyl halides in DMSO–THF[a]

Run	X in Ar	Allyl halide	Time (h)	Product no.	Yield[b] (%)
1	H **1a**	allyl-Br	2	**2a-allyl**	92
2	2-F **1b**	allyl-Br	0.7	**2b-allyl**	80
3	3-F **1c**	allyl-Br	0.3	**2c-allyl**	99
4	4-F **1d**	allyl Br	∼0[c]	**2d-allyl**	99
5	4-Cl **1e**	allyl-Br	0.3	**2e-allyl**	89
6	3-CF$_3$ **1f**	allyl-Br	1	**2f-allyl**	72
7	4-CN **1g**	allyl-Br	0.5	**2g-allyl**	99
8	4-COOEt **1h**	allyl-Br	1	**2h-allyl**	68
9	H **1a**	allyl-Cl	25	**2a-allyl**	66
10	H **1a**	methallyl-Cl	3	**2a-metha**	78
11	H **1a**	prenyl-Br	4	**2a-pre**	–[d]
12[e]	H **1a**	prenyl-Br	4	**2a-pre**	64

[a] Reaction was carried out in a DMSO–THF combined solvent in the presence of copper (I) iodide (1 equiv) at room temperature.
[b] Isolated yields.
[c] When a DMSO–THF solution of substrates including CuI was prepared at room temperature, the reaction completed, producing **2d-allyl**.
[d] (*E*)-Trimethyl(*trans*-styryl)silane[33] was exclusively produced.
[e] Five mol% of potassium carbonate with respect to the **1a** was added.

In contrast, the reaction of prenyl bromide did not produced the expected 1,4-diene, but (*E*)-styrylsilane.[33] However, upon addition of 5 mol% of potassium carbonate the reaction produced (*E*)-5-methyl-1-(trimethylsilyl)-2-phenylhexa-1,4-diene **2a-pre** in 64% yield. Trimethylsilyl protons of these products in NMR analysis were observed at 0.19 ppm. Table 4 compiles selected NMR data for allylated vinyltrimethylsilanes. The vinyl proton α to silicon was observed at 5.85–6.18 ppm, while the vinyl carbon bearing silicon appeared at 126.2–133.3 ppm, and silicon was observed at −9.4 to −10.3 ppm. Coupling constants for silicon–vinyl carbon and silicon–methyl carbon were in the ranges 60.1–67.8 Hz and 52.2–52.4 Hz, respectively.

CuI-mediated reaction of (*Z*)-(n-Bu)$_3$SnCAr=CHSiMe$_3$ 1 with propargyl bromide

We first examined the optimum conditions for the reaction with **1a** outlined in Scheme 4. The reaction was carried out by wrapping the reaction flask with aluminum foil to prevent a possible oligomerization[61] of an allene product. As Table 5 shows, $Pd(dba)_2$, a $Pd(dba)_2-PPh_3$ combination, and $BnPdCl(PPh_3)_2$ were ineffective at 50 °C. On the other hand, $Pd(dba)_2-CuI$, $PdCl_2-CuI$ or $Pd(OAc)_2-CuI$ as a catalyst combination drove the reaction even at room temperature affording (*E*)-5-(trimethylsilyl)-4-phenylpenta-1,2,4-triene **3a**[36] in good yields. Spectral data (^{1}H-NMR, ^{13}C-NMR, ^{29}Si-NMR, IR, LRMS and HRMS) agreed well with those from the expected structure. Copper(I) iodide-mediated reaction in DMF or in DMSO–THF solvent[60] readily occurred at room temperature to give **3a** in 43–80% yields. Among them, CuI-mediated reaction in DMSO–THF recorded the highest yield (80% isolated-yield) of **3a**.

The reaction of several (*Z*)-silyl(stannyl)ethenes **1** with propargyl bromide was carried out in the presence of a $Pd(dba)_2-CuI$ combination under conditions similar to run 4 in Table 5 or CuI alone under conditions similar to run 8 in Table 5. Table 6 summarizes the results for both reactions, as well as selected NMR data of the products isolated. The product yields obtained in the CuI-mediated reaction were generally higher in every run than those in the $Pd(dba)_2-CuI$ catalysis. The vinylic proton α to silicon was observed near 5.65–5.76 ppm save for that of **3j**. Trimethylsilyl protons were observed at lower field than that of TMS (δ: 0.14–0.25 ppm). The configuration of all products was *E*, but *Z* for **3j**.

Other characteristic spectral data for silylvinyl allenes **3** are complied in Tables 7 and 8. Table 7 shows that a center-carbon of every allenyl group appeared in the range 210.6–211.7 ppm, and a vinyl carbon α to silicon was observed in the range 127.6–133.6 ppm with $J_{Si,C} = 62.3–66.2$ Hz. Furthermore, chemical shifts of silicon in **3a** ∼ **3j** were observed in the range −9.3 to −11.1 ppm.

Table 8 compiles coupling constants, *J*(H,H), between vinylic protons for the 4-substituted-5-silylpenta-1,2,4-trienes **3** described in Fig. 1. Proton–proton couplings, $J(H^1, H^2)$, for **3a**–**3j** were observed in the range 6.4–7.0 Hz. On the other hand, $J(H^1, H^3)$ for **3a**–**3h** were observed ($J = 1.2–1.6$ Hz), but splitting was not observed for **3i** ($R = 4\text{-}NO_2\text{-}C_6H_4$) and **3j** (R = *n*-butyl). A proton–proton coupling between H^2 and H^3 was observed for (*E*)-4-aryl-5-silylpenta-1,2,4-trienes **3** [$J(H^2, H^3) = 0.4–0.8$ Hz], except for the lone example of (*Z*)-4-(*n*-butyl)-5-silylpenta-1,2,4-triene, **3j**, where no coupling was observed.

We propose a putative mechanism for the $Pd(dba)_2-CuI$ catalyzed reaction that can accommodate all the observed results in Scheme 5. Thus, copper iodide may react with the silyl(stannyl)ethene **1a** to form a vinyl copper species **1a–Cu**,[59,62] which may spontaneously react with π-allyl palladium bromide[63] to form copper bromide and a putative silylvinyl(π-allyl)palladium intermediate **4a**, from which the expected 1,4-diene **2a** reductively eliminates to liberate the Pd(0) catalyst. The copper bromide produced probably enters into the catalysis as copper iodide.

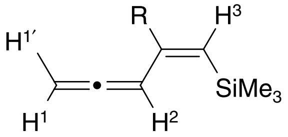


Figure 1. Structure of 4-substituted-5-silylpenta-1,2,4-trienes **3**.

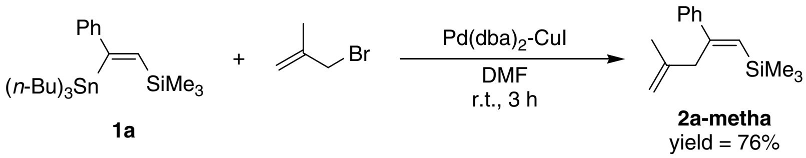
For the CuI-mediated reaction, putative vinylcopper intermediates[59,62] may be considered to attack an allyl halide or propargyl bromide in an S_N2 or S_N2' manner, producing 1-silylalka-1,4-dienes or 5-silylpenta-1,2,4-trienes.

In closing, a family of (*E*)-2-aryl-1-(trimethylsilyl)alka-1,4-dienes **2** that are promising compounds for a wide range of applications was successfully synthesized under room temperature conditions with good to high isolated yields by either a $Pd(dba)_2-CuI$ combination-catalyzed or copper(I) iodide-mediated reaction of (*Z*)-silyl(stannyl)ethenes with allyl halides. Another family of (*E*)-4-aryl- and (*Z*)-4-(*n*-butyl)-5-(trimethylsilyl)penta-1,2,4-trienes **3**, which are also promising compounds in many applications, were synthesized under room-temperature conditions with good isolated yields by either a $Pd(dba)_2-CuI$ catalyzed or copper(I) iodide-mediated cross-coupling of (*Z*)-2-aryl-2-(tri-*n*-butylstannyl)-1-(trimethylsilyl)ethenes or its (*Z*)-2-(*n*-butyl)-derivative **1** with propargyl bromide. The CuI-mediated reaction in DMSO–THF produced corresponding products **3** in better yields than did the palladium–catalysis. These reactions are operationally simple, and produce good yields of a family of novel stereochemically-defined (*E*)-2-aryl-1-silylalka-1,4-dienes **2**, (*E*)-4-aryl-5-silylpenta-1,2,4-trienes **3** and (*Z*)-4-(*n*-butyl)-5-silylpenta-1,2,4-triene **3j**. All new compounds were analyzed spectroscopically.

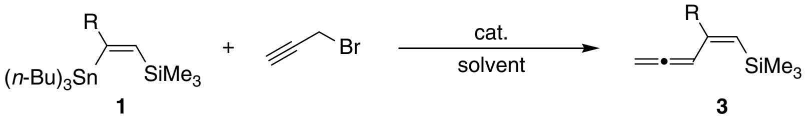
Experimental

Methods and measurements

The reaction was carried out using a small, round bottom flask under nitrogen and monitored by TLC (thin layer chromatography). GLC (gas–liquid chromatography) analysis of the reaction mixture or isolated products was performed using an Ohkura Model 730 gas chromatograph equipped with a thermal conductivity detector connected to a stainless steel column packed with 10%



Scheme 3. Palladium-catalyzed reaction of **1a** with prenyl bromide in DMF.



Scheme 4. Reaction of (*Z*)-silyl(stannyl)ethenes **1** with propargyl bromide.

Table 4. Selected NMR data[a] for allylated vinyltrimethylsilanes **2**

Run	X in Ar	=C**H**SiMe$_3$ (ppm)	=**C**HSiMe$_3$ (ppm)	$^1J_{Si,C}$[b] (Hz)	$^1J_{Si,C}$[c] (Hz)	δ_{Si} (ppm)
1	H **2a-allyl**	5.94	126.2	66.2	52.3	−10.1
2	2-F **2b-allyl**	5.71	133.0	66.1	52.3	−10.2
3	3-F **2c-allyl**	5.97	130.7	65.3	52.3	−9.8
4	4-F **2d-allyl**	5.88	129.4	67.8	52.3	−10.0
5	4-Cl **2e-allyl**	5.93	130.1	66.1	52.4	−9.9
6	3-CF$_3$ **2f-allyl**	6.03	131.6	65.4	52.3	−9.7
7	4-CN **2g-allyl**	6.06	133.3	64.4	52.3	−9.4
8	4-COOEt **2h-allyl**	6.04	131.7	65.4	52.3	−9.7
9	H **2a-metha**	6.01	130.5	66.2	52.3	−10.04
10	H **2a-pre**	5.85	128.1	66.9	52.3	−10.31

[a] Recorded in CDCl$_3$.
[b] Silicon–vinyl carbon coupling.
[c] Silicon–methyl carbon coupling.

silicone KF-96/celite 545 AW (60–80 mesh, 2 m × 3 mm). ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100.7 MHz) spectra were recorded on a Varian Unity-400 spectrometer in CDCl$_3$ using tetramethylsilane (TMS) as the internal standard. Chemical shifts are expressed as parts per million (ppm) with respect to TMS (for ^{1}H) and chloroform-d$_1$ (for ^{13}C, $\delta = 77.00$ ppm). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), quin. (quintet), sext (sextet), dd (doublet of doublets), dt (doublet of triplets), ddd (doublet of doublets of doublets) and m (multiplet). Coupling constants are given in Hz. The assignments of aromatic carbons in the ^{13}C-NMR of allylated vinylsilanes **2** and allenylated vinylsilanes **3** are based on the intensity information, coupling constants (e.g. $J_{F,C}$) and additivity for the ^{13}C chemical shifts of the aromatic ring.[64] ^{29}Si-NMR spectra were recorded at 79.6 MHz on a Varian Mercury *plus* 400 in CDCl$_3$ using TMS (for ^{29}Si) as the internal standard. Mass spectra were recorded on a Jeol JMS-AX-500 with a DA 7000 data system.

Materials

(*Z*)-Silyl(stannyl)ethenes were prepared according to our procedure.[32,33] Allyl halides, propargyl bromide and benzyl(chloro)bis(triphenylphosphine)palladium(II) were purchased from Tokyo Kasei Co. and used as received. Copper(I) iodide, triphenylphosphine, tri(*o*-tolyl)phosphine (*o*-tolyl: *o*-methylphenyl), triethylphosphite, palladium chloride and palladium acetate were purchased from Wako Chemical Co. and used as received. Bis(dibenzylideneacetone)palladium(0) was prepared according to the literature method.[65] *N*,*N*-dimethylformamide (DMF) was distilled from calcium hydride before use. 1,2-Dimethoxyethane and tetrahydrofuran (THF) were kept over 4 Å molecular sieves and distilled over lithium aluminum hydride just before using. Dimethyl sulfoxide (DMSO) was purchased from Wako Chemical Co. and distilled prior to use. Silica gel aluminum sheet (Silica gel 60 F$_{254}$) for TLC was purchased from Merk. Silica gel (60N, spherical, neutral) for column chromatography was purchased from Kanto Kagaku Co Ltd.

General procedure for the synthesis of (*E*)-2-aryl-1-silylalka-1,4-dienes via a cross-coupling of (*Z*)-1-aryl-1-(tri-*n*-butylstannyl)-2-(trimethylsilyl)ethenes with an allyl halide in DMF

A DMF (0.5 ml) mixture of Pd(dba)$_2$ (0.0028 g, 0.005 mmol) and CuI (0.0163 g, 0.085 mmol) was stirred under nitrogen. Then, a DMF (1 ml) solution of **1a** (0.456 g, 0.997 mmol) was added with a microsyringe and stirred for 5 min. Next, a DMF (0.5 ml) solution of allyl bromide (0.362 g, 2.99 mmol) was added. The mixture was stirred at room temperature. After 2 h, GLC analysis disclosed that **1a** was completely consumed. The resulting mixture was passed through a short silica gel (pre-treated with triethylamine) column (eluent:*n*-hexane) to

Table 5. Optimization of the reaction outlined in Scheme 4[a]

Run	A : B[b]	Catalyst (mol%)[c]	Additive (mol%)[c]	Solvent (ml)	Conditions (°C, h)	Yield[d] (%)
1	0.2 : 0.4	Pd(dba)$_2$ (0.5)[e]	–	THF (1.0)[f]	50, 20	0
2	0.2 : 0.4	Pd(dba)$_2$ (0.5)	PPh$_3$ (1.0)	THF (1.0)	50, 22	0
3	0.2 : 0.4	BnPdCl(PPh$_3$)$_2$ (0.5)[g]	–	DME (1.0)[h]	50, 5	0
4	0.5 : 3.0	Pd(dba)$_2$ (0.5)	CuI (1.0)	DMF(2.0)[i]	r.t., 2	(44)
5	0.2 : 0.4	PdCl$_2$ (0.5)	CuI (1.0)	DMF(1.0)	r.t., 2	52
6	0.2 : 0.4	Pd(OAc)$_2$ (0.5)	CuI (1.0)	DMF(1.0)	r.t., 2	71(48)
7	0.2 : 0.4	CuI (100)	–	DMF (1.0)	r.t., ∼0	43
8	0.5 : 1.0	CuI (100)	–	DMSO–THF (4.3–1.5)[j]	r.t., 24	(80)
9	0.2 : 0.4	CuI (50)	–	DMSO–THF (0.86–0.3)	r.t., ∼0	55
10	0.2 : 0.4	CuI (100)	–	DMSO–THF (0.86–0.3)	r.t., ∼0	43

[a] All reactions were carried out at room temperature.
[b] A, mmols of **1a**; B, mmols of propargyl bromide.
[c] Based on the **1a** employed.
[d] GLC yields (thermal conductivity was uncorrected). In parentheses are shown isolated yields by column chromatography (silica gel, hexane).
[e] dba, dibenzylideneacetone.
[f] THF, tetrahydrofuran.
[g] Bn, benzyl.
[h] DME, 1,2-dimethoxyethane.
[i] DMF, *N*,*N*-dimethylformamide.
[j] DMSO, dimethylsulfoxide.

Table 6. Synthesis of $CH_2{=}C{=}CHCR{=}CHSiMe_3$ **3** by the reaction depicted in Scheme 4; conditions, yields and selected NMR data[a]

Run[a]	R	Catalyst[b]	Time (h)	Product no.	Yield[c] (%)	Configuration
1	C_6H_5 **1a**	A	2	**3a**	47	*E*
2	**1a**	B	20	**3a**	81	*E*
3	4-Cl-C_6H_4 **1e**	A	4	**3e**	48	*E*
4	**1e**	B	~0[d]	**3e**	61	*E*
5	3-CF_3-C_6H_4 **1f**	A	2	**3f**	71	*E*
6	**1f**	B	1	**3f**	78	*E*
7	4-CO_2Et-C_6H_4 **1h**	A	2	**3h**	59	*E*
8	**1h**	B	~0[d]	**3h**	72	*E*
9	4-NO_2-C_6H_4 **1i**	A	2	**3i**	49	*E*
10	**1i**	B	2	**3i**	55	*E*
11	*n*-Bu **1j**	B	1	**3j**	28	*Z*

[a] All reactions were carried out at room temperature.
[b] A, $Pd(dba)_2$–CuI (solvent; DMF); B, CuI (100 mol%) (solvent; DMSO–THF).
[c] Isolated yields by column chromatography (silica gel, hexane).
[d] The reaction was complete when substrates and CuI were combined in DMSO–THF solvent.

Table 7. Selected NMR data for $CH_2{=}C{=}CHCR{=}CHSiMe_3$ **3** isolated by the reaction in Scheme 4

Run	Compound R	$CH_2{=}\mathbf{C}{=}$ (ppm)[a]	CH-=**C**H$SiMe_3$ (ppm)[a]	$^1J_{Si,C}$[b] (Hz)	$^1J_{Si,C}$[c] (Hz)	δ_{29Si}[d] (ppm)
1	C_6H_5 (*E*)-**3a**	211.7	132.1	63.8	53.1	−10.1
2	4-Cl-C_6H_4 (*E*)-**3e**	211.6	132.6	63.7	52.3	−9.9
3	3-CF_3-C_6H_4 (*E*)-**3f**	211.7	133.6	63.0	52.3	−9.7
4	4-CO_2Et-C_6H_4 (*E*)-**3h**	211.6	133.4	63.8	53.1	−9.7
5	4-NO_2-C_6H_4 (*E*)-**3i**	211.5	135.1	62.3	50.8	−9.3
6	*n*-Bu (*Z*)-**3j**	210.6	127.6	66.2	51.6	−11.1

[a] ^{13}C-chemical shifts referenced to $CDCl_3$ ($\delta = 77.00$ ppm).
[b] Coupling constant between vinyl carbon and silicon.
[c] Coupling constant between methyl carbon and silicon.
[d] Chemical shifts referenced to tetramethylsilane (TMS).

Table 8. Coupling constants, $J_{H,H}$, between vinylic protons in a penta-1,2,4-triene **3** described in Fig. 1

Run	R in **3**	$J(H^1, H^2)$[a]	$J(H^1, H^3)$[a]	$J(H^2, H^3)$[a]
1	C_6H_5 **3a**	6.8	1.2	0.8
2	4-Cl-C_6H_4 **3e**	6.6	1.6	0.4
3	3-CF_3-C_6H_4 **3f**	7.0	1.4	0.4
4	4-CO_2Et-C_6H_4 **3h**	6.4	1.2	0.8
5	4-NO_2-C_6H_4 **3i**	6.8	–[b]	0.8
6	*n*-Bu **3j**	6.6	–[b]	–[b]

[a] Hz.
[b] Coupling was not observed.

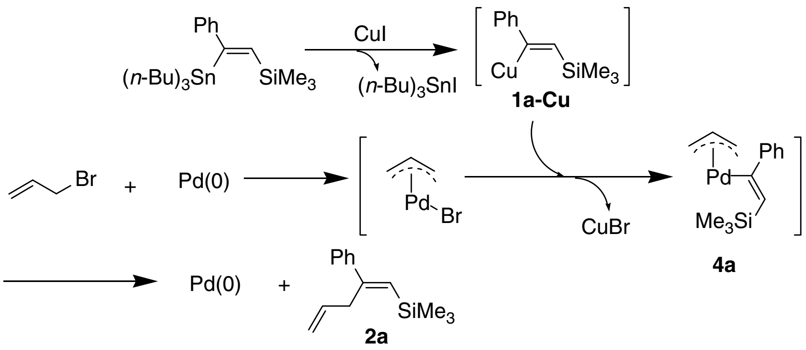
remove the catalyst. The eluents collected were concentrated with a rotary evaporator under aspirator vacuum to a volume of ca. 10 ml. Then, after addition of ether to the concentrate, the resulting solution was vigorously stirred with aqueous KF for 24–48 h. Filtration of the precipitated tri-*n*-butyltin fluoride, then column chromatography [silica gel (pre-treated with triethylamine or neutral), *n*-hexane] gave an analytically pure sample (0.133 g, 62%) of (*E*)-1-(trimethylsilyl)-2-phenylpenta-1,4-diene, **2a-allyl**.[22,34]

Spectral data for **2a-allyl** are fully shown below, and are accessible from the American Chemical Society as supplementary materials. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.43 (m, 2H), 7.27 (m, 3H), 5.94 (s, 1H), 5.80(ddt, 1H, $J = 17.2, 10.5, 6.2$ Hz), 5.05 (dt, 1H, $J = 17.2, 1.8$ Hz), 4.98 (dt, 1H, $J = 10.5, 1.8$ Hz), 3.38 (dt, 2H, $J = 6.2, 1.8$ Hz), 0.19 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 154.0 (vinyl carbon bearing aromatic ring), 143.3 (aromatic carbon bearing vinyl group), 136.5 (C4 of 1-silylpenta-1,4-diene), 129.4 (aromatic carbon *meta* to vinyl group), 128.1 (aromatic carbon *para* to vinyl group), 127.3 (aromatic carbon *ortho* to vinyl group), 126.2 ($^1J_{Si,C} = 66.2$ Hz, vinyl carbon bearing silicon), 116.1 (C5 of the penta-1,4-diene), 38.7 (C3 of the penta-1,4-diene), 0.2 ($^1J_{Si,C} = 52.3$ Hz, methyl carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, 79.6 MHz): δ −10.1 ppm. LRMS (EI, 70 eV): 216 (M^+), 201($M^+ - 15$).

By a procedure similar to that for **2a-allyl**, other penta-1,4-dienes were obtained from the corresponding (*Z*)-silyl(stannyl)ethenes **1**. Amounts of selected substrates and spectral data of products are shown below. NMR chemical shifts and coupling constants were determined after multi-time sweeps.

(E)-2-(2-fluorophenyl)-1-(trimethylsilyl)penta-1,4-diene, **2b-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMF was carried out with **1b** (0.243 g, 0.50 mmol) and allyl bromide (0.2446 g, 2.0 mmol). Purification of the resulting mixture by



Scheme 5. A plausible mechanism for Pd(dba)$_2$–CuI catalyzed cross-coupling of **1** with allyl bromide.

column chromatography eluted with *n*-hexane gave **2b-allyl**[34] as a colorless oil (0.082 g, 70%). ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.21 (m, 2H), 7.05 (m, 1H), 6.98 (ddd, 1H, $J = 10.7, 8.2, 1.0$ Hz), 5.71 (s, 1H), 5.73–5.62 (broad m, 1H), 5.0 (ddt, 1H, $J = 17.0, 2.0, 1.6$ Hz), 4.91 (ddt, 1H, $J = 10.0, 2.0, 1.6$ Hz), 3.35 (a set of two multiplets, 2H, $J = 6.8$ Hz), 0.20 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 159.3 (d, $^1J_{F,C} = 246.8$ Hz, aromatic carbon bearing fluorine), 151.3 (C2 of the 1-silylpenta-1,4-diene), 135.8 (C4 of the penta-1,4-diene), 133.0 ($^1J_{Si,C} = 66.1$ Hz, $^4J_{F,C} = 1.5$ Hz, C1 of the penta-1,4-diene), 132.4 (d, $^2J_{F,C} = 14.6$ Hz, quart. aromatic carbon bearing C2 of the penta-1,4-diene), 130.3 (d, $^3J_{F,C} = 4.6$ Hz, aromatic carbon *meta* to fluorine and *para* to C2 of the penta-1,4-diene), 128.5 (d, $^3J_{F,C} = 8.5$ Hz, aromatic carbon *ortho* to C2 of the penta-1,4-diene and *meta* to fluorine), 123.8 (d, $^4J_{F,C} = 3.8$ Hz, aromatic carbon *para* to fluorine), 116.1 (C5 of the penta-1,4-diene), 115.5 (d, $^2J_{F,C} = 23.1$ Hz, aromatic carbon *ortho* to fluorine and *meta* to C2 of the penta-1,4-diene), 40.1 (d, $^4J_{F,C} = 3.1$ Hz, C3 of the penta-1,4-diene), 0.2 ($^1J_{Si,C} = 52.3$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, 79.6 MHz): δ −10.2 ppm. LRMS (EI, 70 eV): 234(M$^+$), 219 (M$^+$ − 15).

(E)-2-(3-fluorophenyl)-1-(trimethylsilyl)penta-1,4-diene, **2c-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMF was carried out with **1c** (0.0816 g, 0.168 mmol) and allyl bromide (0.362 g, 3.0 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **2c-allyl**[34] as a colorless oil (0.037 g, 94%).^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.23 (m, 2H), 7.12 (m, 1H), 6.93 (m, 1H), 5.97 (s, 1H), 5.78 (ddt, 1H, $J = 17.2, 10.0, 6.0$ Hz), 5.05 (dt, 1H, $J = 17.2, 1.6$ Hz), 5.01 (dt, 1H, $J = 10.2, 1.6$ Hz), 3.35 (dd, 2H, $J = 6.0, 1.6$ Hz), 0.19 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 162.8 (d, $^1J_{F,C} = 245.3$ Hz, aromatic carbon bearing F), 152.7 (d, $^4J_{F,C} = 2.3$ Hz, C2 of 1-silylpenta-1,4-diene), 145.7 (d, $^3J_{F,C} = 6.9$ Hz, quart. aromatic carbon bearing C2 of the penta-1,4-diene), 136.1 (C4 of the penta-1,4-diene), 130.7 ($^1J_{Si,C} = 65.3$ Hz, C1 of the penta-1,4-diene), 129.4 (d, $^3J_{F,C} = 8.5$ Hz, aromatic carbon *meta* to F and C2 of the penta-1,4-diene), 121.9 (d, $^4J_{F,C} = 3.1$ Hz, aromatic carbon *para* to F and *ortho* to C2 of the penta-1,4-diene), 116.4(C5 of the penta-1,4-diene), 114.0 (d, $^2J_{F,C} = 21.5$ Hz, aromatic carbon *ortho* to F and *para* to C2 of the penta-1,4-diene), 113.2 (d, $^2J_{F,C} = 22.3$ Hz, aromatic carbon *ortho* to F and C2 of the peta-1,4-diene), 38.6 (C3 of the penta-1,4-diene), 0.1 ($^1J_{Si,C} = 52.3$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, 79.6 MHz): δ −9.8 ppm. LRMS (EI, 70 eV): 234(M$^+$), 219 (M$^+$ − 15).

(E)-2-(4-fluorophenyl)-1-(trimethylsilyl)penta-1, 4-diene, **2d-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMF was carried out with **1d** (0.082 g, 0.17 mmol) and allyl bromide (0.182 g, 1.50 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **2d-allyl**[34] as a colorless oil (0.037 g, 94%). ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.39 (dd, 2H, $J = 9.0, 5.4$ Hz), 6.97 (m, 2H), 5.88 (s, 1H), 5.77 (ddt, 1H, $J = 17.2, 10.4, 6.0$ Hz), 5.04(ddt, 1H, $J = 17.2, 1.8, 1.8$ Hz), 5.00 (ddt, 1H, $J = 10.4, 1.8, 1.8$ Hz), 3.35 (ddd, 2H, $J = 6.0, 1.8, 1.8$ Hz), 0.19 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 162.2 (d, $^1J_{F,C} = 246.7$ Hz, aromatic carbon bearing F), 152.9 (C2 of 1-silylpenta-1,4-diene), 139.3 (d, $^4J_{F,C} = 3.0$ Hz, quart. aromatic carbon bearing C2 of the penta-1,4-diene), 136.3 (C4 of the penta-1,4-diene), 129.4 ($^1J_{Si,C} = 67.8$ Hz, C1 of the penta-1,4-diene), 127.8 (d, $^3J_{F,C} = 7.7$ Hz, aromatic carbon *meta* to F), 116.3 (C5 of the penta-1,4-diene), 114.8 (d, $^2J_{F,C} = 21.3$ Hz, aromatic carbon *ortho* to F), 38.8 (C3 of the penta-1,4-diene), 0.2 ($^1J_{Si,C} = 52.3$ Hz, carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, 79.6 MHz): δ- 10.0 ppm. LRMS (EI, 70 eV): 234(M$^+$), 219 (M$^+$ − 15).

(E)-2-(4-chlorophenyl)-1-(trimethylsilyl)penta-1, 4-diene, **2e-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMF was carried out with **1e** (0.2351 g, 0.47 mmol) and allyl bromide (0.370 g, 3.06 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **2e-allyl**[34] as a colorless oil (0.1004 g, 85%).^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.34 (ddd, 2H, $J = 8.8, 2.4, 2.4$ Hz), 7.24 (ddd, 2H, $J = 8.8, 2.4, 2.4$ Hz), 5.93 (s, 1H), 5.77 (ddt, 1H, $J = 17.2, 10.2, 6.0$ Hz), 5.03 (ddt, 1H, $J = 17.2, 1.6, 1.6$ Hz), 5.0 (ddt, 1H, $J = 10.2, 1.6, 1.6$ Hz), 3.35 (ddd, 2H, $J = 6.0, 1.6, 1.6$ Hz), 0.19 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 152.7 (C2 of 1-silylpenta-1,4-diene), 141.7 (aromatic carbon bearing C2 of the penta-1,4-diene), 136.2 (C4 of the penta-1,4-diene), 133.1 (aromatic carbon bearing chlorine), 130.1 ($^1J_{Si,C} = 66.1$ Hz, C1 of the penta-1,4-diene), 128.2 (aromatic carbon *ortho* to chlorine), 127.6 (aromatic carbon *meta* to chlorine), 116.4 (C5 of the penta-1,4-diene), 38.6 (C3 of the penta-1,4-diene), 0.2 ($^1J_{Si,C} = 52.4$ Hz) ppm. ^{29}Si-NMR (CDCl$_3$, 79.6 MHz): δ −9.9 ppm. LRMS (EI, 70 eV): 250 (M$^+$), 235 (M$^+$ − 15).

(E)-2-[3-(trifluoromethyl)phenyl]-1-(trimethylsilyl)penta-1, 4-diene, **2f-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMF was carried out with **1f** (0.265 g, 0.497 mmol) and allyl bromide (0.183 g, 1.5 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **2f-allyl**[34] as a colorless oil (0.126 g, 89%). ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.71 (m, 1H), 7.62 (a set of two multiplets, 1H, $J = 7.6$ Hz), 7.51 (a set of two multiplets, 1H, $J = 7.6$ Hz), 7.42 (a set of three multiplets, 1H, $J = 7.6$ Hz), 6.03 (s, 1H), 5.81 (ddt, 1H, $J = 17.2$, 10.0, 6.0 Hz), 5.08 (ddt, 1H, $J = 17.2$, 1.6, 1.6 Hz), 5.04 (ddt, 1H, $J = 10.0$, 1.6, 1.6 Hz), 3.43 (ddd, 2H, $J = 6.0$, 1.6, 1.6 Hz), 0.25 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 152.5 (C2 of 1-silylpenta-1,4-diene), 144.1 (aromatic carbon bearing C2 of the penta-1,4-diene), 135.9 (C4 of the penta-1,4-diene), 131.6 ($^1J_{\text{Si,C}} = 65.4$ Hz, C1 of the penta-1,4-diene), 130.5 (q, $^2J_{\text{F,C}} = 32.0$ Hz), 129.5 (aromatic carbon *para* to CF$_3$), 128.5 (aromatic carbon *meta* to CF$_3$), 124.3 (q, $^1J_{\text{F,C}} = 272.1$ Hz, carbon of CF$_3$), 123.9 (q, $^3J_{\text{F,C}} = 3.8$ Hz, aromatic carbon *ortho* to CF$_3$ and *para* to C2 of the penta-1,4-diene), 123.1 (q, $^3J_{\text{F,C}} = 3.8$ Hz, aromatic carbon *ortho* to CF$_3$ and to C2 of the penta-1,4-diene) 116.6 (C5 of the penta-1,4-diene), 38.6 (C3 of the penta-1,4-diene), 0.1 ($^1J_{\text{Si,C}} = 52.3$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, 79.6 MHz): δ - 9.7 ppm. LRMS (EI, 70 eV): 284 (M$^+$), 269 (M$^+$ − 15).

(E)-2-(4-cyanophenyl)-1-(trimethylsilyl)penta-1,4-diene, **2g-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMF was carried out with **1g** (0.245 g, 0.499 mmol) and allyl bromide (0.1234 g, 1.03 mmol). Purification of the resulting mixture by column chromatography eluted with 10% ethyl acetate in *n*-hexane gave **2g-allyl**[34] as a colorless oil (0.119 g, 99%). ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.58 (ddd, 2H, $J = 8.4$, 2.0, 2.0 Hz), 7.50 (ddd, 2H, $J = 8.4$, 2.0, 2.0 Hz), 6.06 (s, 1H), 5.76 (ddt, 1H, $J = 17.8$, 10.2, 6.0 Hz), 5.03 (ddt, 1H, $J = 17.8$, 2.0, 1.8 Hz), 4.99 (ddt, 1H, $J = 10.2$, 2.0, 1.8 Hz), 3.39 (ddd, 2H, $J = 6.0$, 1.8, 1.8 Hz), 0.21 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 151.9 (C2 of the 1-silylpenta-1,4-diene), 147.6 (aromatic carbon bearing C2 of the penta-1,4-diene), 135.6 (C4 of the penta-1,4-diene), 133.3 ($^1J_{\text{Si,C}} = 64.4$ Hz, C1 of the penta-1,4-diene), 131.8 (aromatic carbon *ortho* to CN), 126.8 (aromatic carbon *meta* to CN), 118.8 (carbon of CN), 116.6 (C5 of the penta-1,4-diene), 110.5 (aromatic carbon bearing CN), 38.2 (C3 of the penta-1,4-diene), −0.1 ($^1J_{\text{Si,C}} = 52.3$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, 79.6 MHz): δ −9.4 ppm. LRMS (EI, 70 eV): 241 (M$^+$), 226 (M$^+$ − 15).

(E)-2-[4-(ethoxycarbonyl)phenyl]-1-(trimethylsilyl)penta-1,4-diene, **2h-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMF was carried out with **1h** (0.268 g, 0.498 mmol) allyl bromide (0.181 g, 1.5 mmol). Purification of the resulting mixture by column chromatography eluted with 10% ethyl acetate in *n*-hexane gave **2h-allyl**[34] as a colorless oil (0.133 g, 93%). ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.97 (dd, 2H, $J = 8.7$, 2.0 Hz), 7.48 (dd, 2H, $J = 8.7$, 2.0 Hz), 6.04 (s, 1H), 5.77 (ddt, 1H, $J = 17.2$, 10.2, 6.0 Hz), 5.03 (ddt, 1H, $J = 17.2$, 2.0, 2.0 Hz), 4.99 (ddt, 1H, $J = 10.2$, 2.0, 2.0 Hz), 4.37 (q, 2H, $J = 7.0$ Hz), 3.39 (ddd, 2H, $J = 6.0$, 2.0, 2.0 Hz), 1.39 (t, 3H, $J = 7.0$ Hz), 0.21 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 166.3 (carbonyl carbon), 153.0 (C2 of the 1-silylpenta-1,4-diene), 147.6 (aromatic carbon bearing C2 of the penta-1,4-diene), 135.9 (C4 of the penta-1,4-diene), 131.7 ($^1J_{\text{Si,C}} = 65.4$ Hz, C1 of the penta-1,4-diene), 129.3 (aromatic carbon *ortho* to COOEt), 129.1 (aromatic carbon bearing COOEt), 126.1 (aromatic carbon *meta* to COOEt) 116.4 (C5 of the penta-1,4-diene), 60.7 (C1 of ethyl group), 38.5 (C3 of the penta-1,4-diene), 14.3 (C2 of ethyl group), 0.02 ($^1J_{\text{Si,C}} = 52.3$ Hz, carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, 79.6 MHz): δ −9.7 ppm. LRMS (EI, 70 eV): 288 (M$^+$), 273 (M$^+$ − 15).

(E)-4-methyl-1-(trimethylsilyl)-2-phenylpenta-1,4-diene, **2a-metha**

A procedure similar to that for the synthesis of **2a-allyl** in DMF was carried out with **1a** (0.2334 g, 0.50 mmol) and methallyl bromide (0.2900 g, 2.15 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **2a-metha** as a colorless oil (0.0887 g, 76%). ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.41 (m, 2H), 7.25 (m, 3H), 6.01 (s, 1H), 4.76 (m, 1H), 4.63 (m, 1H), 3.30 (s, 2H), 1.70 (d, 3H, $J = 0.6$ Hz), 0.18 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 153.7 (C2 of 1-silylpenta-1,4-diene), 143.6 (C4 of the penta-1,4-diene), 143.4 (aromatic carbon bearing C4 of penta-1,4-diene), 130.5 ($^1J_{\text{Si,C}} = 66.2$ Hz, C1 of the penta-1,4-diene), 128.0 (aromatic carbon *meta* to C2 of the penta-1,4-diene), 127.2 (aromatic carbon *para* to C2 of the penta-1,4-diene), 126.1 (aromatic carbon *ortho* to C2 of the penta-1,4-diene), 112.3 (C5 of the penta-1,4-diene), 42.4 (C3 of the penta-1,4-diene), 23.0 (methyl carbon connecting to C4 of the penta-1,4-diene), 0.1 ($^1J_{\text{Si,C}} = 52.3$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, 79.6 MHz): δ −10.04 ppm. IR (neat): 3080 (w), 3020 (w), 2950 (s), 1650 (w), 1600 (m), 1570 (m), 1500 (m), 1440 (s), 1380 (w), 1250 (s), 1080 (w), 1020 (w), 890 (s), 860 (s), 840 (s), 780 (w), 760 (s), 720 (w), 700 (s), 630 (w) cm^{-1}. LRMS (EI, 70 eV): 230 (M$^+$), 215 (M$^+$ − 15), 156 (M$^+$ − 74). HRMS (EI, 70 eV): calcd for C$_{15}$H$_{22}$Si, 230.1491; found, 230.1504.

General procedure for the CuI-mediated cross-coupling of (*Z*)-1-aryl-1-(tri-*n*-butylstannyl)-2-(trimethylsilyl)ethenes with an allyl halide in DMSO–THF

To a mixture of copper iodide (0.0976 g, 0.5 mmol) and THF (0.5 ml), a solution of **1a** (0.2347 g, 0.5 mmol) in THF (1.0 ml) and DMSO (1.3 ml) were successively added under nitrogen and resulting mixture was stirred for 5 min. To the mixture, allyl bromide (0.1242 g, 1.0 mmol) and DMSO (3 ml) was added. The resulting mixture was stirred and the reaction monitored by TLC. The TLC spot of **1a** was quickly consumed (reaction time ∼0 h). The mixture was concentrated under vacuum, then diluted with ether and washed with aqueous NH$_3$ (3.5%) solution. The organic layer was separated and washed with saturated brine. Drying with anhydrous sodium sulfate and column chromatography eluted with *n*-hexane gave **2a-allyl**[22,34] as a colorless oil (0.1015 g, 92%). Identification of the product was made by comparing its ^{1}H-NMR and MS spectra with those of **2a-allyl** obtained with a Pd(dba)$_2$–CuI combination-catalyzed reaction in DMF.

By a procedure similar to that for **2a-allyl** in DMSO–THF, other penta-1,4-dienes were obtained from the corresponding (*Z*)-silyl(stannyl)ethenes **1**. Amounts of selected substrates and spectral data of products are shown below.

(E)-2-(2-fluorophenyl)-1-(trimethylsilyl)penta-1,4-diene, **2b-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMSO–THF, just above, was carried out with **1b** (0.4848 g, 1.00 mmol) and allyl bromide (0.2446 g, 2.0 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **2b-allyl**[34] as a colorless oil (0.187 g, 80%). Identification of the product was made by comparing its ^{1}H-NMR and MS spectra with those of **2b-allyl** obtained with a Pd(dba)$_2$–CuI combination-catalyzed reaction in DMF.

(E)-2-(3-fluorophenyl)-1-(trimethylsilyl)penta-1,4-diene, **2c-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMSO–THF was carried out with **1c** (0.2417 g, 0.51 mmol) and allyl bromide (0.2446 g, 1.0 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **2c-allyl**[34] as a colorless oil (0.1193 g, 99.6%). Identification of the product was made by comparing its ^{1}H-NMR and MS spectra with those of **2c-allyl** obtained with a Pd(dba)$_2$–CuI combination-catalyzed reaction in DMF.

(E)-2-(4-fluorophenyl)-1-(trimethylsilyl)penta-1, 4-diene, **2d-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMSO–THF was carried out with **1d** (0.2446 g, 0.50 mmol) and allyl bromide (0.1229 g, 1.0 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **2d-allyl**[34] as a colorless oil (0.1159 g, 99%). Identification of the product was made by comparing its ^{1}H-NMR and MS spectra with those of **2d-allyl** obtained with a Pd(dba)$_2$–CuI combination-catalyzed reaction in DMF.

(E)-2-(4-chlorophenyl)-1-(trimethylsilyl)penta-1, 4-diene, **2e-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMSO–THF was carried out with **1e** (0.2127 g, 0.426 mmol) and allyl bromide (0.1273 g, 1.05 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **2e-allyl**[34] as a colorless oil (0.0951 g, 89%). Identification of the product was made by comparing its ^{1}H-NMR and MS spectra with those of **2e-allyl** obtained with a Pd(dba)$_2$–CuI combination-catalyzed reaction in DMF.

(E)-2-[3-(trifluoromethyl)phenyl]-1-(trimethylsilyl)penta-1, 4-diene, **2f-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMSO–THF was carried out with **1f** (0.2708 g, 0.507 mmol) and allyl bromide (0.1257 g, 1.04 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **2f-allyl**[34] as a colorless oil (0.1038 g, 72%). Identification of the product was made by comparing its ^{1}H-NMR and MS spectra with those of **2f-allyl** obtained with a Pd(dba)$_2$–CuI combination-catalyzed reaction in DMF.

(E)-2-(4-cyanophenyl)-1-(trimethylsilyl)penta-1,4-diene, **2g-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMSO–THF was carried out with **1g** (0.2498 g, 0.501 mmol) and allyl bromide (0.1234 g, 1.03 mmol). Purification of the resulting mixture by column chromatography eluted with 10% ethyl acetate in *n*-hexane gave **2g-allyl**[34] as a colorless oil (0.1205 g, 99.8%). Identification of the product was made by comparing its ^{1}H-NMR and MS spectra with those of **2g-allyl** obtained with a Pd(dba)$_2$–CuI combination-catalyzed reaction in DMF.

(E)-2-[4-(ethoxycarbonyl)phenyl]-1-(trimethylsilyl)penta-1,4-diene, **2h-allyl**

A procedure similar to that for the synthesis of **2a-allyl** in DMSO–THF was carried out with **1h** (0.2686 g, 0.499 mmol) and allyl bromide (0.1230 g, 1.0 mmol). Purification of the resulting mixture by column chromatography eluted with 10% ethyl acetate in *n*-hexane gave **2h-allyl**[34] as a colorless oil (0.0974 g, 68%). Identification of the product was made by comparing its ^{1}H-NMR and MS spectra with those of **2h-allyl** obtained with a Pd(dba)$_2$–CuI combination-catalyzed reaction in DMF.

(E)-5-methyl-1-(trimethylsilyl)-2-phenylhexa-1,4-diene, **2a-pre**

A procedure similar to that for the synthesis of **2a-allyl** in DMSO–THF was carried out with **1a** (0.2398 g, 0.51 mmol), prenyl bromide (0.1545 g, 1.0 mmol) and potassium carbonate (0.0037 g, 0.027 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **2a-pre** as a colorless oil (0.0755 g, 64%).

^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.40 (m, 2H), 7.25 (m, 3H), 5.85 (s, 1H), 4.99 (m, 1H), 3.31 (dt, 2H, $J = 6.4, 1.2$ Hz), 1.66 (d, 3H, $J = 1.2$ Hz), 1.63 (d, 3H, $J = 1.2$ Hz), 0.19 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 156.0 (C2 of 1-silylhexa-1,4-diene), 143.6 (aromatic carbon bearing C2 of the hexa-1,4-diene), 131.9 (C5 of the hexa-1,4-diene), 128.1 ($^1J_{\mathrm{Si,C}} = 66.9$ Hz, C1 of the hexa-1,4-diene), 128.0 (aromatic carbon *meta* to C2 of the hexa-1,4-diene), 127.2 (aromatic carbon *para* to C2 of the hexa-1,4-diene), 126.2 (aromatic carbon *ortho* to C2 of the hexa-1,4-diene), 123.1 (C4 of the hexa-1,4-diene), 33.9 (C3 of the hexa-1,4-diene), 25.6 (C5 of the hexa-1,4-diene), 18.1 (methyl carbon connecting to C4 of the hexa-1,4-diene), 0.2 ($^1J_{\mathrm{Si,C}} = 52.3$ Hz, methyl carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, 79.6 MHz): δ −10.31 ppm. IR (neat): 3050 (w), 2950 (s), 2925 (m), 2825 (w), 1600 (m), 1570 (w), 1500 (w), 1450 (m), 1380 (w), 1250 (s), 1100(w), 860 (s), 840 (s), 760 (m), 700 (m), 620 (w) cm^{-1}. LRMS (EI, 70 eV): 244(M$^+$). HRMS (EI, 70 eV): calcd for $C_{16}H_{24}Si$, 244.1647; found, 244.1622.

General procedure for the CuI-mediated cross-coupling of (*Z*)-1-aryl-1-(tri-*n*-butylstannyl)-2-(trimethylsilyl)ethenes with propargyl bromide in DMSO–THF

To a mixture of copper iodide (0.0955g, 0.5 mmol) and THF (0.5 ml), a solution of **1a** (0.2343 g, 0.50 mmol) in THF (1 ml) and DMSO (1.3 ml) were successively added under nitrogen. The resulting mixture was stirred for 5 min. Then, propargyl bromide (0.1220 g, 1.0 mmol) in DMSO (3 ml) was added and the resulting mixture was stirred. TLC was used to monitor the reaction. After 20 h, the (*Z*)-**1a** was completely consumed. The mixture was concentrated under vacuum, diluted with ether, then washed with aqueous NH$_3$ (3.5%) solution. The organic layer was separated, washed with saturated brine and dried with anhydrous magnesium sulfate. Concentration of the ether solution and column chromatography eluted with *n*-hexane gave (*E*)-5-(trimethylsilyl)-4-phenylpenta-1,2,4-triene **3a**[36] as a colorless oil (0.0863g, 81%). ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.35 (m, 2H), 7.27(m, 3H), 6.30 (dt, 1H, $J = 6.8, 0.8$ Hz), 5.68 (dt, 1H, $J = 1.2, 0.8$ Hz), 4.83 (dd, 2H, $J = 6.8, 1.2$ Hz), 0.22 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 211.7 (C2 of 5-silylpenta1,2,4-triene), 150.5 (C4 of the1,2,4-triene), 142.9 (aromatic carbon bearing C4 of the 1,2,4-triene), 132.1 ($^1J_{\mathrm{Si,C}} = 63.8$ Hz, C5 of the 1,2,4-triene), 127.8 (aromatic carbon *meta* to C4 of the 1,2,4-triene), 127.6 (aromatic carbon *para* to C4 of the 1,2,4-triene), 127.4 (aromatic carbon *ortho* to C4 of the 1,2,4-triene), 94.5 (C3 of the 1,2,4-triene), 77.7 (C1 of the 1,2,4-triene), 0.09 ($^1J_{\mathrm{Si,C}} = 53.1$ Hz, carbon of SiMe$_3$) ppm. ^{29}Si-NMR (CDCl$_3$, 79.6 MHz) δ −10.1 ppm. IR (neat): 3400 (w), 2950 (s), 1940 (s), 1560 (s), 1250 (s), 850 (s) cm^{-1}. LRMS (EI, 70 eV): 214 (M$^+$), 199 (M$^+$ − 15). HRMS (EI, 70 eV): calcd for $C_{14}H_{18}Si$, 214.1178; found, 214.1186.

By a procedure similar to that for **3a**, other alka-1,2,4-trienes, **3e, 3f, 3h,3i** and **3j** were obtained from the corresponding (*Z*)-silyl(stannyl)ethenes **1**. Analytical data of the new compounds are shown below.

(E)-4-(4-chlorophenyl)-5-(trimethylsilyl)penta-1,2,4-triene, **3e***:*

A procedure similar to that for the synthesis of **3a** was carried out with **1e** (0.2500 g, 0.499 mmol) and propargyl bromide (0.1199 g, 1.0 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **3e** as a colorless oil (0.0761 g, 61%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.26 (m, 4H), 6.28 (dt, 1H, $J = 6.6, 0.4$ Hz), 5.65 (dt, 1H, $J = 1.6, 0.4$ Hz), 4.85 (dd, 2H, $J = 6.6, 1.6$ Hz), 0.22 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 211.6 (C2 of the 5-silylpenta-1,2,4-triene), 149.3 (C4 of the penta-1,2,4-triene), 141.3 (aromatic carbon bearing C4 of the penta-1,2,4-triene), 133.1 (aromatic carbon bearing chlorine), 132.6 ($^1J_{Si,C} = 63.7$ Hz, C5 of the penta-1,2,4-triene), 129.2 (aromatic carbon *ortho* to chlorine), 127.8 (aromatic carbon *meta* to chlorine), 94.3 (C3 of the penta-1,2,4-triene), 78.0 (C1 of the penta-1,2,4-triene), 0.02 ($^1J_{Si,C} = 52.3$ Hz, carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, 79.6 MHz): δ −9.9 ppm. IR (neat): 3400 (m), 3020 (w), 2950 (s), 1940 (s), 1740 (s), 1580 (s), 1480 (s), 1250 (s), 850 (s), 790 (s) cm^{-1}. LRMS (EI, 70 eV): 248(M^+), 233($M^+ - 15$). HRMS (EI, 70 eV): calcd for $C_{14}H_{17}ClSi$, 248.0788; found, 248.0809.

(E)-4-[3-(trifluoromethyl)phenyl]-5-(trimethylsilyl)penta-1,2,4-triene, **3f**

A procedure similar to that for the synthesis of **3a** was carried out with **1f** (0.2671 g, 0.50 mmol) and propargyl bromide (0.1193 g, 1.0 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **3f** as a colorless oil (0.1102 g, 78%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, 1H, $J = 0.4$ Hz), 7.51 (dd, 2H, $J = 7.6, 0.8$ Hz), 7.39 (dt, 1H, $J = 7.6, 0.4$ Hz), 6.32 (dt, 1H, $J = 7.0, 0.4$ Hz), 5.72 (dt, 1H, $J = 1.4, 0.4$ Hz), 4.85 (dd, 2H, $J = 7.0, 1.4$ Hz), 0.24 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 211.7 (C2 of 5-silylpenta-1,2,4-triene), 149.3 (C4 of the penta-1,2,4-triene), 143.6 (aromatic carbon bearing C4 of the penta-1,2,4-triene), 133.6 ($^1J_{Si,C} = 63.0$ Hz, C5 of the penta-1,2,4-triene), 131.2 (aromatic carbon *para* to CF_3), 130.0 (q, $^2J_{F,C} = 32.0$ Hz, aromatic carbon bearing CF_3), 128.1 (aromatic carbon *meta* to CF_3), 124.8 (q, $^3J_{F,C} = 3.8$ Hz, aromatic carbon *ortho* to CF_3 and *para* to C4 of the penta-1,2,4-triene), 124.3 (q, $^1J_{F,C} = 272.4$ Hz, carbon of CF_3), 124.0 (q, $^3J_{F,C} = 3.8$ Hz, aromatic carbon *ortho* to CF_3 and to C4 of the penta-1,2,4-triene), 94.3 (C3 of the penta-1,2,4-triene), 78.2 (C1 of the penta-1,2,4-triene), −0.02 ($^1J_{Si,C} = 52.3$ Hz, carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, 79.6 MHz) δ −9.7 ppm. IR (neat): 3400 (w), 3020 (w), 2950 (s), 1940 (s), 1740 (w), 1580 (m), 1480 (m), 1420 (m), 1320 (s), 1250 (s), 1100 (s), 850 (s), 790 (s) cm^{-1}. LRMS (EI, 70 eV): 282 (M^+), 267 ($M^+ - 15$). HRMS (EI, 70 eV): calcd for $C_{15}H_{17}F_3Si$, 282.1052; found, 282.1031.

(E)-4-[4-(ethoxycarbonyl)phenyl]-5-(trimethylsilyl)penta-1,2,4-triene, **3h**

A procedure similar to that for the synthesis of **3a** was carried out with **1h** (0.2682 g, 0.50 mmol) and propargyl bromide (0.1203 g, 1.0 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **3h** as a colorless oil (0.1032 g, 72%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, 2H, $J = 8.0$ Hz), 7.39 (d, 2H, $J = 8.0$ Hz), 6.30 (dt, 1H, $J = 6.4, 0.8$ Hz), 5.75 (dt, 1H, $J = 1.2, 0.8$ Hz), 4.84 (dd, 2H, $J = 6.4, 1.2$ Hz), 4.38 (q, 2H, $J = 7.0$ Hz), 1.38 (t, 2H, $J = 7.0$ Hz), 0.24 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 211.6 (C2 of 5-silylpenta-1,2,4-triene), 166.4 (carbon of ester carbonyl group), 149.7 (C4 of the penta-1,2,4-triene), 147.3 (aromatic carbon bearing C4 of the penta-1,2,4-triene), 133.4 ($^1J_{Si,C} = 63.8$ Hz, C5 of the penta-1,2,4-triene), 129.8 (aromatic carbon bearing COOEt), 128.9 (aromatic carbon *ortho* to COOEt), 127.8 (aromatic carbon *meta* to COOEt), 94.1 (C3 of the penta-1,2,4-triene), 78.0 (C1 of the penta-1,2,4-triene), 60.8 (C1 of ethyl group), 14.3 (C2 of ethyl group), −0.04 ($^1J_{Si,C} = 53.1$ Hz, carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, 79.6 MHz) δ −9.7 ppm. IR (neat): 3400 (m), 3020 (w), 2950 (s), 1940 (s), 1720 (s), 1280 (s), 1250 (s), 1100 (s), 850 (s) cm^{-1}. LRMS (EI, 70 eV): 286(M^+), 271($M^+ - 15$). HRMS (EI, 70 eV): calcd for $C_{17}H_{22}O_2Si$, 286.1389; found, 286.1397.

(E)-5-(trimethylsilyl)-4-(4-nitrophenyl)penta-1,2,4-triene, **3i**

A procedure similar to that for the synthesis of **3a** was carried out with **1i** (0.2499 g, 0.489 mmol) and propargyl bromide (0.1205 g, 1.0 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **3i** as a colorless oil (0.0661 g, 55%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.16 (dd, 2H, $J = 8.4, 1.6$ Hz), 7.48 (dd, 2H, $J = 8.4, 1.6$ Hz), 6.31 (t, 1H, $J = 6.8$ Hz), 5.76 (t, 1H, $J = 0.8$ Hz), 4.87 (dt, 2H, $J = 6.8, 0.8$ Hz), 0.25 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 211.5 (C2 of 5-silylpenta-1,2,4-triene), 149.4 (C4 of the penta-1,2,4-triene), 148.6 (aromatic carbon bearing nitro group), 147.0 (aromatic carbon bearing C4 of the penta-1,2,4-triene), 135.1 ($^1J_{Si,C} = 62.3$ Hz, C5 of the penta-1,2,4-triene), 128.7 (aromatic carbon *meta* to nitro group), 123.0 (aromatic carbon *ortho* to nitro group), 93.9 (C3 of the penta-1,2,4-triene), 78.4 (C1 of the penta-1,2,4-triene), −0.1 ($^1J_{Si,C} = 50.8$ Hz, carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, 79.6 MHz): δ −9.3 ppm. IR (neat): 3400 (w), 3020 (w), 2590 (s), 1940 (s), 1600 (m), 1520 (s), 1350 (s) 1250 (s), 850 (s) cm^{-1}. LRMS (EI, 70 eV): 259 (M^+), 244 ($M^+ - 15$). HRMS (EI, 70 eV): calcd for $C_{14}H_{17}NO_2Si$, 259.1029; found, 259.1013.

(Z)-4-(n-butyl)-5-(trimethylsilyl)penta-1,2,4-triene, **3j**

A procedure similar to that for the synthesis of **3a** was carried out with **1j** (0.2220 g, 0.498 mmol) and propargyl bromide (0.1214 g, 1.0 mmol). Purification of the resulting mixture by column chromatography eluted with *n*-hexane gave **3j** as a colorless oil (0.0267 g, 28%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 6.08 (t, 1H, $J = 6.6$ Hz), 5.35 (s, 1H), 4.95 (d, 2H, $J = 6.6$ Hz), 2.19 (t, 2H, $J = 7.8$ Hz), 1.44 (quin., 2H, $J = 7.4$ Hz), 1.31 (sext., 2H, $J = 7.6$ Hz), 0.9 (t, 3H, $J = 7.4$ Hz), 0.14 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 210.6 (C2 of 5-silylpenta-1,2,4-triene), 150.6 (C4 of penta-1,2,4-triene), 127.6 ($^1J_{Si,C} = 66.2$ Hz, C5 of the penta-1,2,4-triene), 95.3 (C3 of the penta-1,2,4-trienen), 77.5 (C1 of the penta-1,2,4-triene), 37.0 (C1 of butyl group), 31.2 (C2 of butyl group), 22.5 (C3 of butyl group), 14.0 (C4 of butyl group), 0.3 ($^1J_{Si,C} = 51.6$ Hz, carbon of $SiMe_3$) ppm. ^{29}Si-NMR ($CDCl_3$, 79.6 MHz) δ: −11.1 ppm. IR (neat): 2950 (s), 2930 (s), 2870 (m), 1930 (m), 1730 (w), 1700 (w), 1580 (s), 1465 (m), 1455 (w), 1420 (w), 1380 (w), 1250 (s), 910 (m), 840 (s), 770 (w), 740 (s), 700 (w), 620 (w) cm^{-1}. LRMS (70 eV): 194 (M^+), 179 ($M^+ - 15$), 73($M^+ - 121$). HRMS (EI): calcd for $C_{12}H_{22}Si$; 194.1491; found, 194.1503.

Acknowledgment

The authors thank Ms Ayumi Shirai of Tokai University for recording the mass spectra (LRMS and HRMS) of compounds obtained in this work.

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