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Nickel-catalyzed acylstannylation and alkynylstannylation of 1,2-dienes

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Abstract

Carbostannylation of 1,2-dienes using acyl- and alkynylstannanes was achieved by means of nickel catalysis. In particular, acylstannylation of 1,2-dienes could be carried out with bis(1,5-cyclooctadiene)nickel [$Ni(cod)_2$] and acylstannanes to give selectively α-acylmethyl(vinyl)stannanes. The reaction was also applicable to acylstannanes prepared in situ by protonolysis of α-alkoxyalkenylstannanes or by reactions of α-silyloxyvinylstannanes with aldehyde acetals. For alkynylstannylation, a combination of $Ni(cod)_2$ and 1,3-bis(diphenylphosphino)propane (dppp) was found to be effective to afford α-alkynylmethyl(vinyl)stannanes, whereas the $Ni(cod)_2$–1,3-bis(dimethylphosphino)propane (dmpp) catalyst switched the regioselectivity to give (*Z*)-α-alkynylmethyl(alkenyl)stannanes. The acylstannylation products were successfully converted into various conjugated or unconjugated enones by a combination of cross-coupling and NaH-catalyzed isomerization. The alkynylstannylation products were transformed by cross- or homo-coupling reactions to various enynes or 2,3-bis(alkynylmethyl)-1,3-dienes, versatile precursors for variously substituted polycyclic compounds.

Keywords: Nickel; Carbometalation; 1,2-diene; Acylstanane; Alkynylstannane

1. Introduction

Carbometalation reaction denotes an addition reaction of nucleophilic organometallics across non-polar unsaturated bonds and has been a powerful and valuable synthetic tool, since the reaction allows simultaneous formation of both carbon–carbon and carbon–metal bonds in a single step [1]. Although alkynes and alkenes have been extensively studied for carbometalation, 1,2-dienes have remained yet to be explored. Indeed, alkoxyallenes or allenyl alcohols undergo carbometalation with organomagnesiums [2], -zincs [3], -coppers [4], and -indiums [5], whereas the reaction of allene with allylmagnesium or -borane compounds is reported to give cyclized products [6,7]. Very recently, allylmagnesiation is shown to be applicable to a wide range of 1,2-dienes [8]. Nevertheless, organometallics employed in carbometalation of 1,2-dienes are limited to those having a relatively polar carbon–metal bond. An alternative strategy for carbometalation is three-component coupling of inter-element compounds, 1,2-dienes and organic halides, as demonstrated independently by Fleming and Cheng [9], who prepared alkenyl- and/or allylsilanes, -stannanes, -boranes and -germanes that tolerate a wide variety of functional groups. During carbometalation, however, one metal atom in the inter-element reagent is lost.

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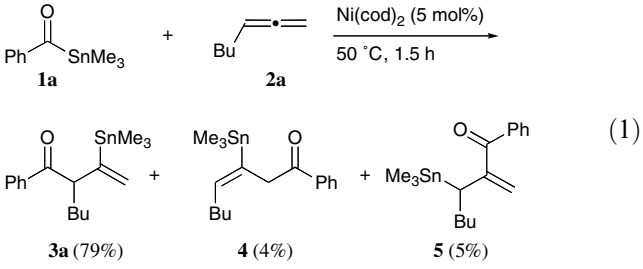
Direct carbostannylation of unsaturated bonds should be of significant synthetic value from the viewpoint of atom economy. In addition, the resulting organostannanes are compatible with a wide variety of functional groups and are easily purified prior to subsequent transformations such as the Migita–Kosugi–Stille coupling reaction [10]. We have disclosed that carbostannylation of alkynes and 1,3-dienes catalyzed by a palladium or nickel catalyst provides efficient access to variously functionalized alkenyl- and allylstannanes [11,12]. Accordingly, we envisaged that 1,2-dienes would also undergo the carbostannylation. This was found to be the case [13], as reported herein in detail.

2. Results and discussions

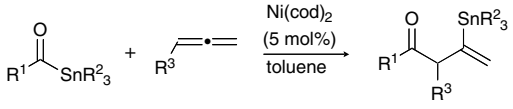
2.1. Acylstannylation of 1,2-dienes

We first examined the reaction of benzoyl(trimethyl)tin (**1a**) with 1,2-heptadiene (**2a**) in the presence of $Ni(cod)_2$ (5 mol%) in toluene at 50 °C, the standard conditions for the acylstannylation of alkynes and 1,3-dienes [11b,12] (Eq. (1)), and obtained 3-benzoyl-2-trimethylstannyl-1-heptene (**3a**) in 79% yield together with (*E*)-1-phenyl-3-trimethylstannyl-3-octen-1-one (**4**) (4% yield) and 2-methylene-1-phenyl-3-trimethylstannylheptan-1-one (**5**) (5% yield). Use of a ligand like PPh_3, 1,3-bis(diphenylphosphino)propane (dppp), pyridine, or 2,2'-bipyridyl or of a polar solvent like THF, 1,4-dioxane, or DMF resulted in predominant formation of trimethyl(phenyl)stannane, a decarbonylated product of **1a**, as was the case with 1,3-diene-acylstannylation [12].



(1)

The scope of the present reaction was examined next as summarized in Eq. (2) and Table 1. Benzoylstannylation of allene (**2b**) also proceeded under its atmosphere to give the benzoylstannylation product **3b** in 64% yield together with (*E*)-1-phenyl-3-trimethylstannyl-2-buten-1-one (2%), an isomerized product of **3b** (entry 1). Reaction of benzoyl(tributyl)tin (**1b**) proceeded in a similar way albeit in a lower yield and selectivity (entry 2). A bulky diene, 4,4-dimethyl-1,2-pentadiene (**2c**), underwent benzoylstannylation with similar regioselectivity (entry 3). The reaction is also applicable to arylallenes of different electronic nature. Thus, reactions of 4-methoxyphenylallene (**2d**) and phenylallene (**2e**) gave the benzoylstannylation products **3e** and **3f** in comparable yields and selectivities (entries 4 and 5), whereas that of 4-trifluoromethylphenylallene (**2f**) gave **3g** in a low yield (entry 6). Methoxyallene (**2g**) afforded the corresponding product **3h** exclusively albeit in a low yield (entry 7). Tributyl(propanoyl)tin (**1c**) also reacted with a series of 1,2-dienes successfully (entries 8–11), while the reaction of carbamoylstannane (**1d**) with allene afforded only a 25% yield of **3m** even under harsh conditions (entry 12). Although the minor isomer(s) could not be characterized thoroughly in these cases, ^{119}Sn NMR peak(s) observed at −42.2 to 14.2 ppm were attributed to an alkenyl- or allyl(trialkyl)stannane.



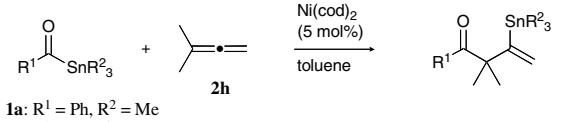
(2)

3

1a: R^1 = Ph, R^2 = Me
1b: R^1 = Ph, R^2 = Bu
1c: R^1 = Et, R^2 = Bu
1d: $R^1 = (CH_2)_5N$, R^2 = Me

2a: R^3 = Bu
2b: R^3 = H
2c: R^3 = *t*-Bu
2d: R^3 = 4-MeO-C_6H_4
2e: R^3 = Ph
2f: R^3 = 4-CF_3-C_6H_4
2g: R^3 = MeO

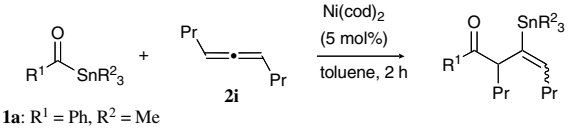
Disubstituted allenes also participated in the present reaction. Acylstannanes **1a** or **1c** reacted with 3-methyl-1,2-butadiene (**2h**) highly regioselectively to give **3n** or **3o**, respectively (Eq. (3)), while those with 4,5-nonadiene (**2i**) afforded a mixture of stereoisomers (Eq. (4)).



(3)

1a: R^1 = Ph, R^2 = Me
1c: R^1 = Et, R^2 = Bu

temp.	time		yield (**3**:isomers)
50 °C	6 h	**3n**: R^1 = Ph, R^2 = Me	63% (>99:1)
80 °C	5 h	**3o**: R^1 = Et, R^2 = Bu	49% (83:17)



(4)

1a: R^1 = Ph, R^2 = Me
1c: R^1 = Et, R^2 = Bu

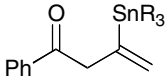
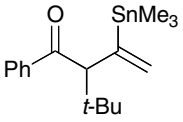
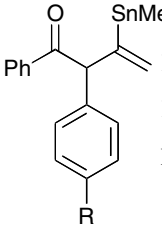
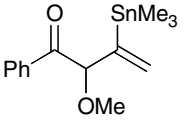
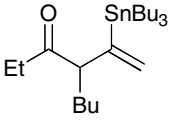
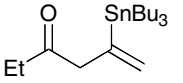
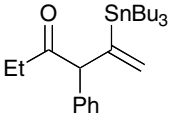
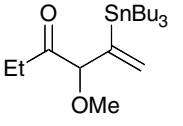
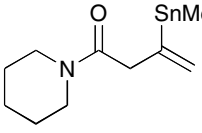
temp.		yield (**3**:isomers)	*E* :*Z*
50 °C	**3p**: R^1 = Ph, R^2 = Me	72% (>99:1)	63:37
80 °C	**3q**: R^1 = Et, R^2 = Bu	54% (81:19)	56:44

2.2. In situ preparation of acylstannanes

2.2.1. One-pot hydrolysis–acylstannylation

Although acylstannanes are readily available by the reported procedures [14], some of them are air-sensitive and thus are hard to deal with. To improve the utility of the acylstannylation reaction, we examined in situ preparation of acylstannanes from their stable precursors. It is reported that α-(alkoxy)alkenylstannanes, readily available by lithiation of the corresponding enol ethers followed by reaction with stannyl halides [15], are

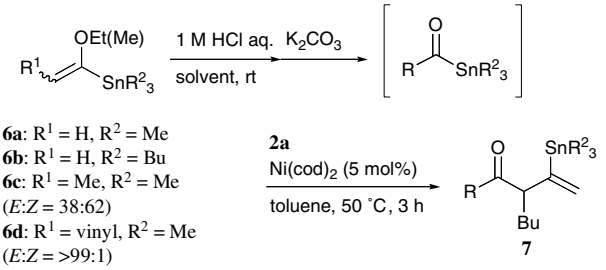
Table 1
Nickel-catalyzed acylstannylation of 1,2-dienes[a]

Entry	Acylstannane	1,2-Diene	Major product	Time (h)	Yield of **3** (%)[b]	**3**:isomers[c]
1[d]	**1a**	**2b**	 R = Me (**3b**)	1.5	64	97:3[e]
2[d]	**1b**	**2b**	R = Bu (**3c**)	4	48	79:21
3	**1a**	**2c**	 **3d**	1.5	59	86:14
4	**1a**	**2d**	 R = OMe (**3e**)	2	50	78:22
5	**1a**	**2e**	R = H (**3f**)	2	53	77:23
6	**1a**	**2f**	R = CF_3 (**3g**)	2	35	66:34
7	**1a**	**2g**	 **3h**	2	26	97:3
8[f]	**1c**	**2a**	 **3i**	2	53	89:11
9[d,f]	**1c**	**2b**	 **3j**	1.5	67	94:6
10[f]	**1c**	**2e**	 **3k**	3.5	43	79:21
11[f]	**1c**	**2g**	 **3l**	2.5	48	95:5
12[d,g]	**1d**	**2b**	 **3m**	2	25	—[h]

[a] The reaction was carried out unless otherwise stated in toluene (0.4 ml) at 50 °C using an acylstannane (0.30 mmol), a 1,2-diene (0.90 mmol), and $Ni(cod)_2$ (15 μmol).
[b] Isolated yields based on the acylstannane.
[c] Determined by ^{119}Sn NMR.
[d] The reaction was carried out under an allene atmosphere (1 atm).
[e] (*E*)-1-Phenyl-3-trimethylstannyl-2-buten-1-one (2%) was obtained.
[f] The reaction was carried out at 80 °C.
[g] The reaction was carried out at 100 °C in the presence of 60 μmol of $Ni(cod)_2$.
[h] Accompanied by a complex mixture of products other than **3m**.

convertible into acylstannanes upon hydrolysis [16]. Thus, we took this approach and then the resulting acylstannanes were used for reaction with 1,2-dienes.

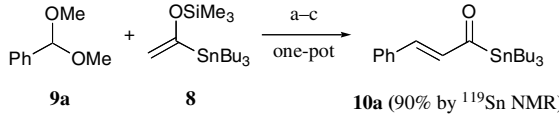
Hydrolysis of 1-ethoxyvinyl(trimethyl)tin (**6a**) with a 1 M aqueous hydrochloric acid solution in diethyl ether at room temperature for 1 h [16], followed by neutralization with K_2CO_3, gave acetyl(trimethyl)tin, which was, without isolation, treated with **2a** and a toluene solution of $Ni(cod)_2$ (5 mol%) at 50 °C for 3 h to give the acylstannylation product **7a** in 63% yield (Scheme 1 and entry 1 of Table 2). Similar operations were applied to reactions of tributyl(1-ethoxyvinyl)tin (**6b**), a tributylstannyl analog of **6a**, and 1-ethoxy-1-propenylstannane (**6c**), giving the corresponding acylstannylation products **7b** and **7c** (entries 2 and 3). The present one-pot hydrolysis–acylstannylation was also applicable to 1-methoxy-1,3-butadienylstannane (**6d**), which was reported to give (*E*)-2-butenoylstannane stereoselectively upon hydrolysis [15a], affording the corresponding enoylstannylation product **7d** albeit in a modest yield (entry 4).



Scheme 1.

2.2.2. One-pot aldol condensation–acylstannylation

Another precursor of acylstannanes is α-(silyloxy)vinylstannane (**8**) that is readily prepared [17] and derivatized [18]. We first examined the reaction of **8** with benzaldehyde dimethylacetal (**9a**) in the presence of trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) [19] and confirmed the formation of cinnamoylstannane **10a** in 90% yield by ^{119}Sn NMR (Eq. (5)). No trace of simple aldol adduct **11** was detected in a crude product mixture. Use of a less amount of Me_3SiOTf reduced the yield of **10a**. Although **11** could be formed also with $BF_3 \cdot Et_2O$ as a Lewis acid instead of Me_3SiOTf, the sample of **11** thus prepared failed to participate in the acylstannylation. In any case, these results encouraged us to study one-pot aldol condensation–acylstannylation reaction.



(5)

Reagents and conditions: (a) Me_3SiOTf (2.5 equiv), CH_2Cl_2, –78 °C, 1h (b) sat. $NaHCO_3$ aq., –40 °C to rt (c) K_2CO_3

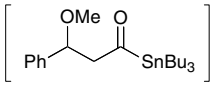
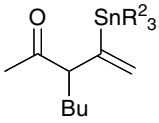
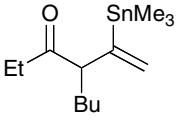
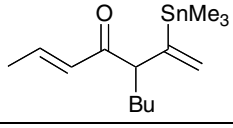
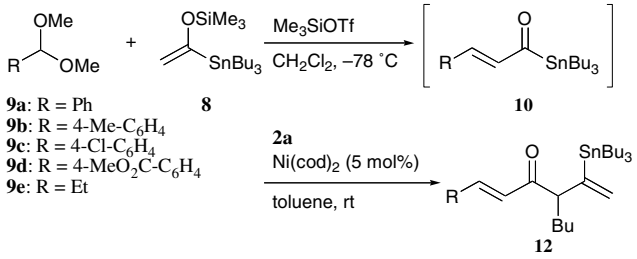


Table 2
One-pot hydrolysis–acylstannylation of 1,2-heptadiene

Entry	Alkenylstannane	Solvent	Time (h)[b]	Product	Yield (%)[c]	7:isomer(s)[d]
1	**6a**	Et_2O	1	 R^2 = Me (**7a**)	63	97:3
2[e]	**6b**	THF	1	R^2 = Bu (**7b**)	81	92:8
3	**6c**	Et_2O	3	 **7c**	61	98:2
4[f]	**6d**	THF	6.5	 **7d**	41	93:7

[a] Hydrolysis was carried out in THF or diethyl ether (0.1 ml) and a 1 M aqueous HCl solution (10 μl) using an α-(alkoxy)alkenylstannane (0.2 mmol). Acylstannylation was carried out in toluene (0.5 ml) using 1,2-heptadiene (0.6 mmol) and $Ni(cod)_2$ (10 μmol) at 50 °C.
[b] For hydrolysis.
[c] Isolated yields based on **6**.
[d] Determined by ^{119}Sn NMR.
[e] Acylstannylation was carried out at 80 °C for 1 h.
[f] Before addition of $Ni(cod)_2$ and 1,2-heptadiene, THF was evaporated.

At first, **10a** prepared as above was treated with **2a** and 5 mol% of a $Ni(cod)_2$ catalyst in toluene at room temperature for 1 h to give the acylstannylation product **12a** in 51% yield (Scheme 2 and entry 1 of Table 3). Neither electron-donating nor -withdrawing substituents on the aromatic aldehyde acetals interfered in the reaction, giving acylstannylation products **12b**–**12d** (entries 2–4) in moderate yields. However, the reaction of an aliphatic aldehyde acetal **9e** afforded the expected product **12e** in a low yield (entry 5).

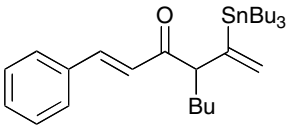
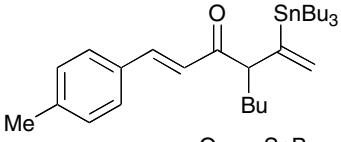
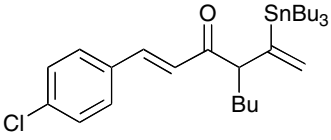
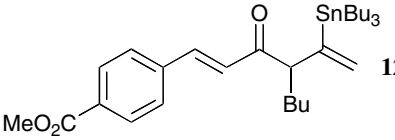
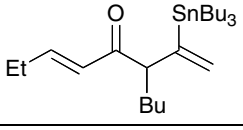


Scheme 2.

2.3. Alkynylstannylation of 1,2-dienes

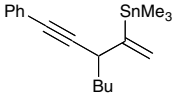
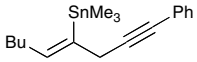
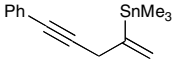
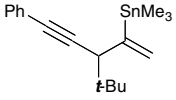
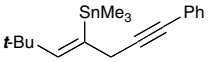
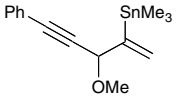
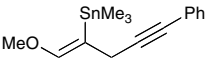
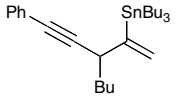
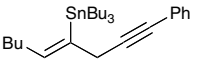
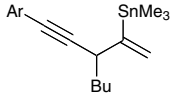
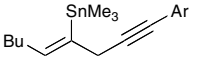
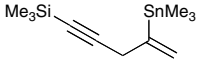
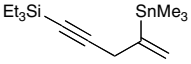
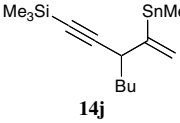
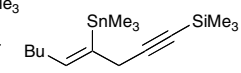
We next studied alkynylstannylation of 1,2-dienes using trimethyl(phenylethynyl)tin (**13a**) and **2a** under the conditions for acylstannylation. As all attempts failed to give the desired product selectively, we screened various ligands to find that bidentate bisphoshpine ligands to form a six-membered chelate to nickel played a crucial role. Use of dppp gave a mixture of alkynylstannylation products, 5-phenyl-2-trimethylstannyl-1-penten-4-yne (**14a**) and (*Z*)-1-phenyl-4-trimethylstannyl-4-nonen-1-yne (**15a**) (85:15) in a 72% combined yield (Eq. (6) and entry 1 of Table 4). Ligands for five- or seven-membered chelate retarded the reaction. Further study on the substituent effect led to the observation that a dialkylphosphorus analog of dppp reversed the regioselectivity. For example, 1,3-bis(dime-

Table 3
One-pot aldol condensation–acylstannylation of 1,2-heptadiene

Entry	Aldehyde acetal	Product		Time (h)[b]	Yield of **12** (%)[c]	**12**:isomer(s)[d]
1	**9a**		**12a**	1	51	>99:1
2	**9b**		**12b**	1	49	95:5
3	**9c**		**12c**	5	54	>99:1
4	**9d**		**12d**	5	42	95:5
5[e]	**9e**		**12e**	1	12[f]	89:11

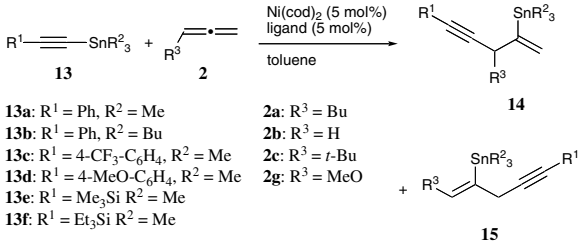
[a] Aldol condensation was carried out in CH_2Cl_2 (0.5 ml) using tributyl[1-(trimethylsilyloxy)vinyl]tin (0.20 mmol), an aldehyde acetal (0.22 mmol), and TMSOTf (0.5 mmol) at −78 °C. Acylstannylation was carried out in toluene (0.5 ml) using 1,2-heptadiene (0.6 mmol) and $Ni(cod)_2$ (10 μmol) at rt.
[b] Time for acylstannylation.
[c] Isolated yields based on **8**.
[d] Determined by ^{119}Sn NMR.
[e] Aldol condensation was carried out at −40 °C.
[f] Determined by ^{119}Sn NMR using tetrabutyltin as an internal standard.

Table 4
Nickel-catalyzed alkynylstannylation of 1,2-dienes[a]

Entry	Ligand	Alkynylstannane	1,2-diene	Temp. (°C)	Time (h)	Products	Yield (%)[b]	**14**:**15**[c]
1	dppp	**13a**	**2a**	50	10	 **14a**  **15a**	72	85:15
2	dmpp	**13a**	**2a**[d]	50	10		82	32:68
3[e]	dppp	**13a**	**2b**	30	10	 **14b**	63	–
4	dppp	**13a**	**2c**	50	70	 **14c**  **15c**	57	98:2
5	dmpp	**13a**	**2c**[d]	50	49		67	14:86
6	dppp	**13a**	**2g**	0	23	 **14d**  **15d**	53	28:72
7	dppp	**13b**	**2a**	60	40	 **14e**  **15e**	70	87:13
8	dmpp	**13b**	**2a**[d]	60	46		70[f]	37:63
9	dppp	**13c**	**2a**	30	5	 Ar = 4-CF_3-C_6H_4: **14f** Ar = 4-MeO-C_6H_4: **14g**  Ar = 4-CF_3-C_6H_4: **15f** Ar = 4-MeO-C_6H_4: **15g**	92	87:13
10	dppp	**13d**	**2a**	30	72		52	77:23
11[e]	dppp	**13e**	**2b**	50	7	 **14h**	91	–
12[e]	dppp	**13f**	**2b**	50	24	 **14i**	90	–
13	dmpp	**13e**	**2a**[d]	60	46	 **14j**  **15j**	81[f]	37:63

[a] The reaction was carried out in toluene (0.3 ml) at 50 °C using an alkynylstannane (0.20 mmol), a 1,2-diene (0.60 mmol), $Ni(cod)_2$ (10 μmol), and a ligand (10 μmol).
[b] Combined isolated yields of **14** and **15** based on the alkynylstannane.
[c] Determined by ^{119}Sn NMR.
[d] 1,2-Diene (0.30 mmol) was used.
[e] The reaction was carried out under an allene atmosphere.
[f] Determined by ^{119}Sn NMR using Bu_4Sn (entry 8) or Me_4Sn (entry 13) as an internal standard.

thylphosphino)propane (dmpp) gave a mixture of **14a** and **15a** in 32:68 (entry 2). We next examined the scope and limitation of the reaction. Allene (**2b**) also promoted the reaction (entry 3). A bulky 1,2-diene, 4,4-dimethyl-1,2-pentadiene (**2c**), reacted with **13a** with highly contrasting regiochemistry by the two catalysts (entries 4 and 5). It is worthy to note that the addition of **13a** across methoxyallene (**2g**) proceeded mainly at the terminal double bond at 0 °C even under the Ni–dppp catalysis (entry 6). We also studied the scope of alkynylstannanes. Tributylstannyl analog **13b** reacted with 1,2-heptadiene (**2a**) in a manner similar to **13a** (entries 7 and 8). An electron-withdrawing 4-CF_3 group on the phenyl in **13a** increased both reaction rate and yield, presumably due to enhanced reactivity at the oxidative addition step (vide infra, entry 9), while an electron-donating 4-MeO group behaved in an opposite manner (entry 10). (Trialkylsilyl)ethynylstannanes, **13e** and **13f**, also participated in the reaction with allene and 1,2-heptadiene, giving α-[(silylethynyl)methyl]vinylstannanes in good yields (entries 11–13).

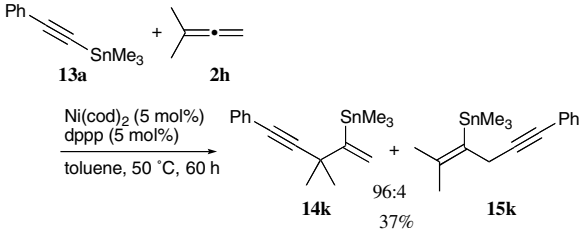


(6)

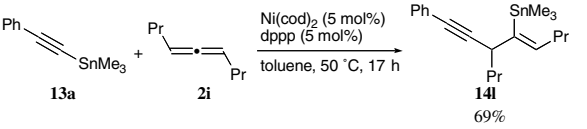
13a: R^1 = Ph, R^2 = Me
13b: R^1 = Ph, R^2 = Bu
13c: R^1 = 4-CF_3-C_6H_4, R^2 = Me
13d: R^1 = 4-MeO-C_6H_4, R^2 = Me
13e: R^1 = Me_3Si R^2 = Me
13f: R^1 = Et_3Si R^2 = Me

2a: R^3 = Bu
2b: R^3 = H
2c: R^3 = *t*-Bu
2g: R^3 = MeO

Disubstituted allenes also reacted with **13a** in the presence of Ni–dppp catalyst. For example, the reaction with **2h** gave less substituted vinylstannane **14k** selectively albeit in a low yield (Eq. (7)). The alkynylstannylation of **2i** afforded the (*Z*)-alkenylstannane **14l** exclusively (Eq. (8)).



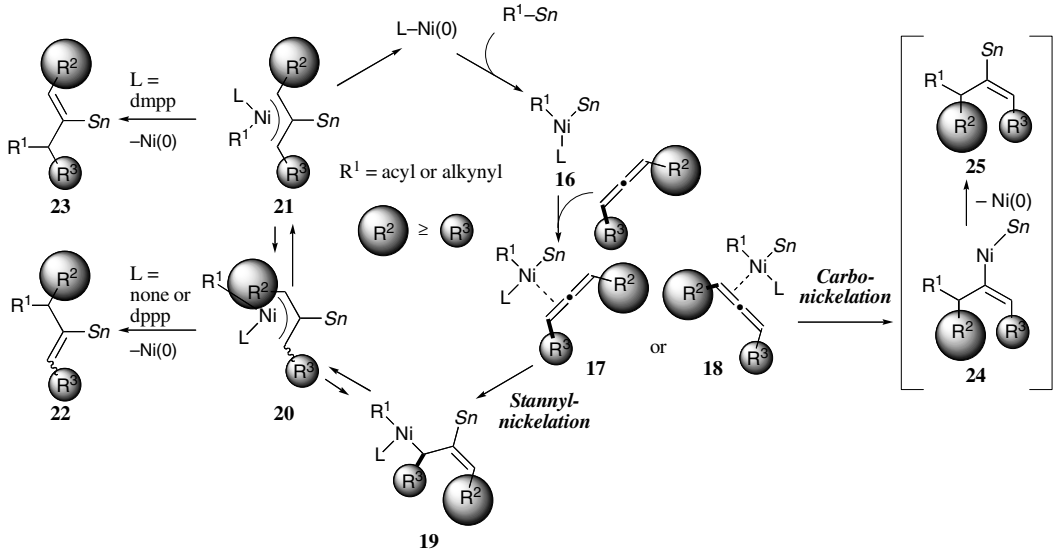
(7)



(8)

2.4. Reaction mechanism

A plausible mechanism of the carbostannylation of 1,2-dienes is summarized in Scheme 3. Based on the previous observations [11,20], we may reasonably assume that the reaction is initiated by the oxidative addition of a C–Sn bond of organostannanes to a Ni(0) complex. Oxidative adduct **16** is coordinated by a 1,2-diene at the less hindered double bond to avoid steric bulk around the nickel center as depicted in **17** rather than **18**. The Sn group on Ni then migrates to the cumulative carbon to give σ-allylnickel complex **19**, which should isomerize to *anti*-π-allylnickel intermediate **20**. Reductive elimination of the R^1 and R^2-substituted carbon that is *cis* to R^1 gives product **22** as was observed in the acylstannylation and alkynylstannylation with Ni–dppp catalyst [21]. The electron-withdrawing nature of an acyl moiety might facilitate reductive elimination from **20** to give **22** with rather higher regioselectivities than alkynylstannylation.



Scheme 3.

In the alkynylstannylation with Ni–dmpp, it is reasonable to assume that the electron-donative nature of dmpp might retard reductive elimination to allow **20** to isomerize to thermodynamically more stable *syn*-π-allylnickel complex **21**, whose R^1 is positioned *cis* to the less hindered allyl. Subsequent reductive elimination should give (*Z*)-alkenylstannane **23**. Migratory insertion of a 1,2-diene into the Ni–C bond via **18** seems unlikely, because this should lead to (*E*)-alkenylstannane **25** through (*E*)-alkenylnickel intermediate **24** followed by stereo-retained reductive elimination, a route inconsistent with the experimental observations: both acylstannylation and alkynylstannylation afford (*Z*)-alkeny- lstannanes or its mixture with (*E*)-isomers as shown in Eqs. (4) and (8).

2.5. Synthetic potential of carbostannylation products

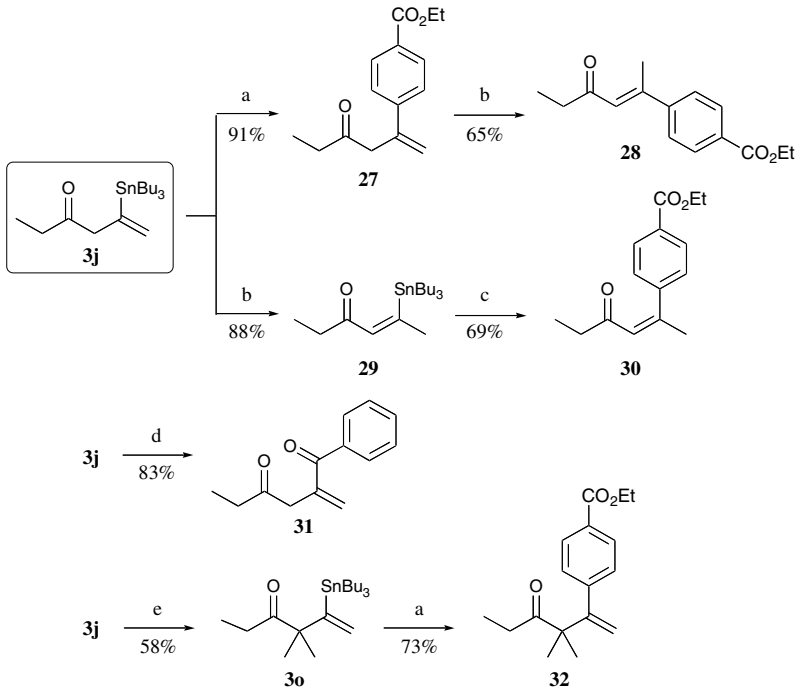
2.5.1. Transformation of acylstannylation products

The synthetic utility of acylstannylation products is obvious. With **3j** as a model, typical transformations are demonstrated in Scheme 4. Cross-coupling reaction of **3j** with ethyl 4-iodobenzoate (**26**) using a $Pd_2(dba)_3$ catalyst gave coupled product **27** in 91% yield without *cine*-substitution. Conjugation of **27** leading to (*E*)-β-arylenone **28** was performed with NaH. In contrast, the olefin isomerization can be carried out at first. Conjugation of **3j** with NaH gave (*Z*)-alkenylstannane **29** exclusively; subsequent cross-coupling of **29** with **26** afforded (*Z*)-β-arylenone **30**. Thus, both stereoisomers **28** and **30** were prepared selectively starting with **3j** simply by changing the order of operation. Stereoselective isomerization of **3j** to **29** might be attributed to an intramolecular interaction between the oxygen and tin atoms in **29** [12,22]. Cross-coupling reaction of **3j** with benzoyl chloride proceeded similarly to give enedione **31**. α-Dimethylation of **3j** gave **3o**, which also cross-coupled with **26** to afford **32**.

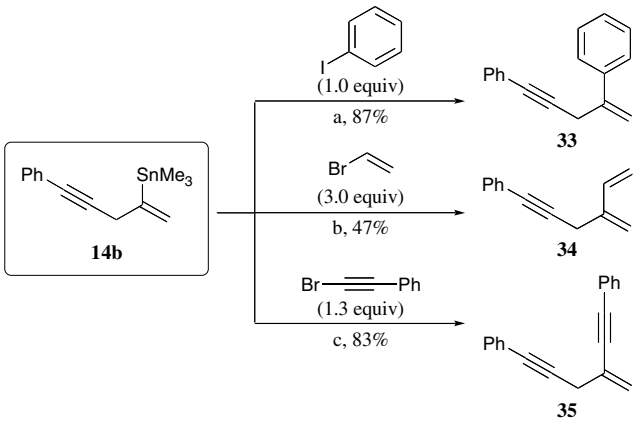
2.5.2. Transformation of alkynylstannylation products

The synthetic utility of the alkynylstannylation products is demonstrated with **14b** as a model (Scheme 5) [23]. Palladium-catalyzed cross-coupling reaction of **14b** with iodobenzene, vinyl bromide, or 1-bromo-2-phenylethyne successfully gave various kinds of the alkynylmethyl substituted conjugated π-system.

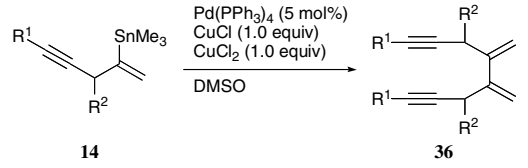
In addition to the cross-coupling reaction, oxidative homo-coupling reaction is another versatile transformation of the alkynylstannylation products (Eq. (9)). For example, oxidative homo-coupling [24] of **14a** with a palladium catalyst and a stoichiometric amount of $CuCl/CuCl_2$ afforded 2,3-disubstituted 1,3-butadiene **36a** as a mixture of *dl* and *meso* isomers in an almost 1:1 ratio but in a high yield. The diastereoisomerism is not present in the reaction of **14b** and **14i**, and the corresponding 2,3-bis(alkynylmethyl)-1,3-butadienes **36b** and **36c** were obtained in good yields.



Scheme 4. *Reagents and conditions*: (a) 4-EtO_2C-C_6H_4-I (**26**, 1.0 equiv), 2.5 mol% of $Pd_2(dba)_3$, NMP, 30 °C, 15 h (from **3j** to **27**) or 10 h (from **3o** to **32**); (b) NaH (0.2 equiv), THF, rt, 4 h (from **3j** to **29**) or 3 h (from **27** to **28**); (c) **26** (1.0 equiv), 5 mol% of $Pd_2(dba)_3$, NMP, 30 °C, 69 h; (d) PhCOCl (1.0 equiv), 2.5 mol% of $Pd_2(dba)_3$, NMP, 30 °C, 8 h; (e) Me–I (3.0 equiv), NaH (3.0 equiv), THF, rt, 17 h.



Scheme 5. *Reagents and conditions*: (a) $Pd(PPh_3)_4$ (5 mol%), LiCl (1.5 equiv), CuCl (1.0 equiv), DMSO, 50 °C, 4.5 h; (b) $Pd_2(dba)_3$ (2.6 mol%), LiCl (1.5 equiv), CuCl (1.0 equiv), DMSO–THF, 50 °C, 19 h; (c) $Pd(PPh_3)_4$ (5 mol%), LiCl (1.5 equiv), CuCl (1.0 equiv), DMSO, 50 °C, 4 h.



(9)

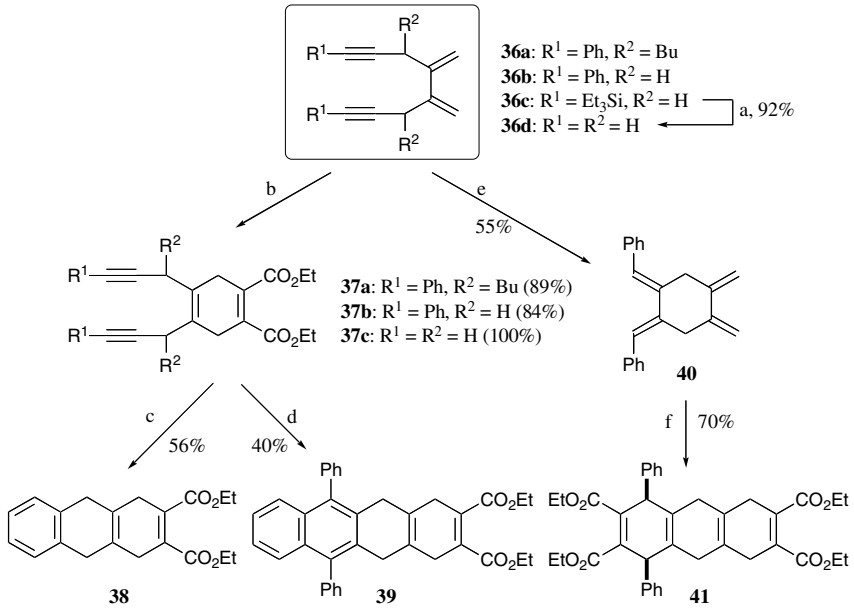
14 **36**

R^1	R^2	temp.	time	product	yield
Ph	Bu (**14a**)	50 °C	3 h	**36a**	82% (*dl*:*meso* = ca. 1:1)
Ph	H (**14b**)	50 °C	2 h	**36b**	86%
Et_3Si	H (**14h**)	40 °C	0.8 h	**36c**	73%

The versatility of dienediynes **36** as synthetic precursors of polycyclic compounds is demonstrated in Scheme 6. Desilylation of **36c** with TBAF gave **36d** [25], which underwent two different modes of cyclization either at a conjugated 1,3-diene or 1,6-diyne moiety. Thus, annulation through the Diels–Alder reaction with diethyl acetylenedicarboxylate followed by nickel-catalyzed acetylene trimerization gave **38**, a tetrahydroanthracene framework [26]. Similarly, the Diels–Alder reaction of dienediyne **36a** or **36b** gave **37a** or **37b**, respectively. The diyne moiety in **37b** was further transformed by zirconocene-mediated reaction with *o*-diiodobenzene to give **39** having a tetrahydrotetracene skeleton [27]. Alternatively, **36b** was first treated with a zirconium complex to afford tetraene **40**, which underwent double Diels–Alder reaction with diethyl acetylenedicarboxylate to give hexahydroanthracene **41**. Thus, variously functionalized polyacene structures that are gaining growing interest in material chemistry [28] are available by the synthetic scheme described herein.

3. Conclusion

In conclusion, we have demonstrated nickel-catalyzed acyl- and alkynylstannylation of 1,2-dienes and their synthetic potential for variously conjugated π-systems as well as linearly fused hydropolyacenes through cross-coupling and homo-coupling reactions followed



Scheme 6. *Reagents and conditions*: (a) Bu_4NF (4.0 equiv), AcOH (5.2 equiv), THF, rt, 44 h, 92%; (b) $EtO_2CC \equiv CCO_2Et$ (5.0 equiv), toluene, 100 °C, 37 h (from **36a** to **37a**); 28 h (from **36b** to **37b**); 23 h (from **36d** to **37c**); (c) $Ni(acac)_2$ (30 mol%), $(i\text{-}Bu)_2AlH$ (60 mol%), PPh_3 (1.2 equiv), $HC \equiv CH$ (1 atm), THF, rt, 21 h; (d) Cp_2ZrBu_2 (1.7 equiv), THF, −78 °C, 1 h then rt, 1 h, then $o\text{-}I_2C_6H_4$ (3.0 equiv), CuCl (3.9 equiv), *N,N′*-dimethylpropyleneurea (5.1 equiv), 50 °C, 15 h; (e) Cp_2ZrBu_2 (2.0 equiv), THF, −78 °C, 1 h then rt, 1 h, then CuCl (4.3 equiv), *N,N′*-dimethylpropyleneurea (6.0 equiv), rt, 2 h; (f) $EtO_2CC \equiv CCO_2Et$ (8.0 equiv), toluene, 100 °C, 28 h.

by annulation via cycloadditions. Acylstannylation selectively affords α-acylmethyl(vinyl)stannanes, whereas alkynylstannylation gives either of the regioisomers stereoselectively by proper choice of a ligand.

4. Experimental

4.1. General remarks

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under an argon or nitrogen atmosphere. Nuclear magnetic resonance spectra were taken on a Varian INOVA 500 (^{1}H, 500 MHz; ^{13}C, 126 MHz; ^{119}Sn, 186 MHz), Varian INOVA 400 (^{1}H, 400 MHz; ^{13}C, 101 MHz; ^{119}Sn, 149 MHz), Varian Gemini 2000 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz), JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz; ^{119}Sn, 101 MHz), or Varian Mercury 200 (^{1}H, 200 MHz; ^{13}C, 50 MHz) spectrometer using tetramethylsilane (^{1}H and ^{13}C) as an internal standard or tetramethyltin (^{119}Sn) as an external standard. Infrared spectra were recorded on a Shimadzu FTIR-8400 spectrometer. Preparative recycling gel permeation chromatography (GPC), preparative recycling reversed phase chromatography, or preparative recycling silica gel chromatography were performed with a JAI LC-908 chromatograph equipped with JAIGEL-1H and 2H (chloroform as an eluent), JAIGEL-ODS (acetonitrile–THF as an eluent), or JAIGEL-SIL (hexane–ethyl acetate as an eluent) column, respectively. High-resolution mass spectra (HRMS) were obtained with a JEOL JMS-700 (EI), JEOL JMS-HX110A (FAB+), or Bruker Bio APEX 70e (ESI) spectrometer. Unless otherwise noted, reagents were commercially available and used without further purification. Toluene and THF were distilled from sodium/benzophenone ketyl. Dichloromethane was distilled from phosphorus pentoxide. Anhydrous NMP and DMSO were purchased from Aldrich and used as received. Bis(1,5-cyclooctadiene)nickel, purchased from Kanto Chemicals, was recrystallized from toluene/1,5-cyclooctadiene (50:1). Acylstannanes [14], α-alkoxyalkenylstannanes [15], tributyl[1-(trimethylsilyloxy)vinyl]tin [17], alkynylstannanes [29], 1,2-dienes [30], and 1,3-bis(dimethylphosphino)propane [31] were prepared according to the corresponding literature procedure.

4.2. A general procedure for acylstannylation of 1,2-dienes

To a stirred solution of an acylstannane (0.30 mmol) and Ni(cod)$_2$ (4.1 mg, 15 μmol) in toluene (0.4 ml), 1,2-diene (0.90 mmol) was added, and the resulting mixture was stirred at the temperature shown in Table 1, Eqs. (3) and (4). After the time specified in Table 1, Eqs. (3) and (4), the reaction mixture was filtered through a Florisil pad. The filtrate was concentrated and purified by preparative GPC. Yields are listed in Table 1, Eqs. (3) and (4).

4.2.1. 2-Butyl-1-phenyl-3-trimethylstannyl-3-buten-1-one (**3a**)

A colorless oil, R_f 0.52 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.15 (s, 9H), 0.88 (t, J = 7.0 Hz, 3H), 1.12–1.61 (m, 5H), 1.74–1.95 (m, 1H), 4.22 (t, J = 7.0 Hz, 1H), 5.35 (d, J = 2.2 Hz, 1H), 5.82 (dd, J = 2.2, 0.7 Hz, 1H), 7.34–7.58 (m, 3H), 7.66–8.05 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −8.1, 13.8, 22.5, 29.6, 32.6, 58.6, 128.1, 128.5, 128.6, 133.0, 137.1, 155.2, 202.2; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −31.7; IR (neat): 2957, 2930, 2858, 1676, 1597, 1580, 1448, 1344, 1221, 1200, 1180, 1003, 922, 841, 772, 733, 712, 694, 667, 529 cm^{-1}; HRMS (ESI) Calc. for $C_{17}H_{26}O^{120}SnNa$: M^+ + Na, 389.0903. Found: *m*/*z* 389.0896.

4.2.2. (*E*)-1-Phenyl-3-trimethylstannyl-3-nonen-1-one (**4**)

A colorless oil, R_f 0.53 (hexane–ethyl acetate = 9:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.09 (s, 9H), 0.87–0.97 (m, 3H), 1.18–1.48 (m, 4H), 2.17 (q, J = 6.9 Hz, 2H), 3.99 (d, J = 1.8 Hz, 2H), 5.79 (tt, J = 6.9, 1.8 Hz, J_{Sn-H} = 76.0 Hz, 1H), 7.43–7.61 (m, 3H), 7.93–8.02 (m, 2H); ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −29.4; HRMS (ESI) Calc. for $C_{17}H_{26}O^{120}SnNa$: M^+ + Na, 389.0903. Found: *m*/*z* 389.0914.

4.2.3. 2-Methylene-1-phenyl-3-trimethylstannyl-1-heptanone (**5**)

A colorless oil, R_f 0.56 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 9H), 0.90 (t, J = 7.0 Hz, 3H), 1.17–1.84 (m, 6H), 2.42 (t, J = 8.1 Hz, 1H), 5.39 (s, 1H), 5.61 (s, 1H), 7.38–7.57 (m, 3H), 7.70–7.76 (m, 2H); ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ 10.0; HRMS (ESI) Calc. for $C_{17}H_{26}O^{120}SnNa$: M^+ + Na, 389.0903. Found: *m*/*z* 389.0896.

4.2.4. 2-tert-Butyl-1-phenyl-3-trimethylstannyl-3-buten-1-one (**3d**)

A colorless oil, R_f 0.57 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 9H), 0.99 (s, 9H), 4.20 (s, 1H), 5.53 (d, J = 2.1 Hz, 1H), 5.87 (d, J = 2.1 Hz, 1H), 7.36–7.63 (m, 3H), 7.83–8.02 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −7.0, 28.5, 35.4, 65.5, 128.3, 128.6, 131.4, 132.8, 139.0, 153.2, 203.4; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −27.5; HRMS (ESI) Calc. for $C_{17}H_{26}O^{120}SnNa$: M^+ + Na, 389.0903. Found: *m*/*z* 389.0896.

*4.2.5. 2-(4-Methoxyphenyl)-1-phenyl-3-trimethylstannyl-3-buten-1-one (**3e**)*

A colorless oil, R_f 0.26 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 9H), 3.77 (s, 3H), 5.43 (t, J = 1.1 Hz, 1H), 5.47 (s, 1H), 5.65 (t, J = 1.5 Hz, 1H), 6.84 (dt, J = 8.8, 2.1 Hz, 2H), 7.12 (dt, J = 8.8, 2.1 Hz, 2H), 7.31–7.57 (m, 3H), 7.87–8.04 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −8.4, 55.1, 61.7, 114.1, 127.1, 128.6, 128.8, 130.2, 130.4, 133.0, 136.9, 155.4, 158.7, 200.2; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −28.3; HRMS (ESI) Calc. for $C_{20}H_{24}O_2{}^{120}$SnNa: M^+ + Na, 439.0695. Found: *m*/*z* 439.0696.

*4.2.6. 1,2-Diphenyl-3-trimethylstannyl-3-buten-1-one (**3f**)*

A colorless oil, R_f 0.39 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 9H), 5.45 (t, J = 1.5 Hz, 1H), 5.52 (s, 1H), 5.68 (t, J = 1.5 Hz, 1H), 7.15–7.58 (m, 8H), 7.87–8.02 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −8.4, 62.5, 127.2, 127.5, 128.6, 128.7, 128.9, 129.1, 133.1, 136.9, 138.5, 155.2, 200.0; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −27.6; HRMS (ESI) Calc. for $C_{19}H_{22}O^{120}$SnNa: M^+ + Na, 409.0589. Found: *m*/*z* 409.0603.

*4.2.7. 1-Phenyl-2-(4-trifluoromethylphenyl)-3-trimethylstannyl-3-buten-1-one (**3g**)*

A colorless oil, R_f 0.34 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 9H), 5.50 (t, J = 1.1 Hz, 1H), 5.59 (s, 1H), 5.69 (t, J = 1.4 Hz, 1H), 7.24–7.68 (m, 7H), 7.85–8.06 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −8.5, 62.0, 125.6 (q, J = 3.5 Hz), 128.4, 128.8, 128.9, 129.5 (q, J = 36.9 Hz), 129.6, 133.4, 136.6, 142.4, 154.2, 199.2; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −24.4; HRMS (ESI) Calc. for $C_{20}H_{21}F_3O^{120}$SnNa: M^+ + Na, 477.0463. Found: *m*/*z* 477.0467.

*4.2.8. 2-Methoxy-1-phenyl-3-trimethylstannyl-3-buten-1-one (**3h**)*

A colorless oil, R_f 0.32 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.18 (s, 9H), 3.35 (s, 3H), 4.94 (t, J = 1.9 Hz, 1H), 5.47 (t, J = 1.6 Hz, 1H), 5.84 (t, J = 1.6 Hz, 1H), 7.31–7.61 (m, 3H), 7.89–8.10 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −8.6, 57.1, 91.3, 127.4, 128.4, 129.5, 133.2, 135.0, 153.1, 199.1; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −27.8; HRMS (ESI) Calc. for $C_{14}H_{20}O^{120}$SnNa: M^+ + Na, 363.0383. Found: *m*/*z* 363.0373.

*4.2.9. 4-Butyl-5-tributylstannyl-5-hexen-3-one (**3i**)*

A colorless oil, R_f 0.61 (hexane–ethyl acetate = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77–1.80 (m, 39H), 2.21–2.61 (m, 2H), 3.25 (t, J = 7.1 Hz, 1H), 5.26 (d, J = 2.2 Hz, 1H), 5.75 (d, J = 2.2 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 7.5, 10.2, 13.6, 13.8, 22.5, 27.3, 28.9, 29.7, 31.3, 35.2, 64.0, 128.2, 154.5, 212.6; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −42.5; HRMS (ESI) Calc. for $C_{22}H_{44}O^{120}$SnNa: M^+ + Na, 467.2310. Found: *m*/*z* 467.2331.

*4.2.10. 4-Phenyl-5-tributylstannyl-5-hexen-3-one (**3k**)*

A colorless oil, R_f 0.57 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.64–1.48 (m, 30H), 2.50 (q, J = 7.4 Hz, 2H), 4.65 (s, 1H), 5.37 (t, J = 1.6 Hz, 1H), 5.60 (t, J = 1.6 Hz, 1H), 7.01–7.42 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 7.8, 10.2, 13.6, 27.3, 28.8, 36.1, 67.0, 127.16, 127.20, 128.5, 129.2, 137.9, 153.6, 210.6; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −38.1; HRMS (ESI) Calc. for $C_{24}H_{40}O^{120}$SnNa: M^+ + Na, 487.1997. Found: *m*/*z* 487.2011.

*4.2.11. 4-Methoxy-5-tributylstannyl-5-hexen-3-one (**3l**)*

A colorless oil, R_f 0.46 (hexane–ethyl acetate = 9:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.73–1.71 (m, 30H), 2.48 (qd, J = 7.3, 1.2 Hz, 2H), 3.31 (s, 3H), 4.18 (t, J = 1.8 Hz, 1H), 5.41 (t, J = 1.8 Hz, 1H), 5.87 (t, J = 1.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 7.3, 10.2, 13.7, 27.3, 29.0, 30.4, 57.2, 93.3, 127.0, 152.4, 210.5; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −40.6; HRMS (ESI) Calc. for $C_{19}H_{38}O_2{}^{120}$SnNa: M^+ + Na, 441.1789. Found: *m*/*z* 441.1792.

*4.2.12. 2,2-Dimethyl-1-phenyl-3-trimethylstannyl-3-buten-1-one (**3n**)*

A colorless oil, R_f 0.49 (hexane–ethyl acetate = 9:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.11 (s, 9H), 1.39 (s, 6H), 5.40 (d, J = 1.0 Hz, 1H), 5.85 (d, J = 1.0 Hz, 1H), 7.26–7.58 (m, 3H), 7.74–8.03 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −7.8, 27.4, 55.0, 124.0, 127.8, 129.9, 131.8, 136.6, 161.1, 204.5; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −27.6; Anal. Calc. for $C_{15}H_{22}OSn$: C, 53.45; H, 6.58. Found: C, 53.71; H, 6.53%.

*4.2.13. 4,4-Dimethyl-5-tributylstannyl-5-hexen-3-one (**3o**)*

A colorless oil, R_f 0.57 (hexane–ethyl acetate = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.76–1.56 (m, 30H), 1.22 (s, 6H), 2.40 (q, J = 7.1 Hz, 2H), 5.28 (t, J = 1.1 Hz, 1H), 5.72 (t, J = 1.1 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 8.1, 10.7, 13.5, 25.1, 27.3, 28.9, 30.5, 55.4, 124.7, 160.0, 214.6; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −38.3; HRMS (ESI) Calc. for $C_{20}H_{40}O^{120}$SnNa: M^+ + Na, 439.1997. Found: *m*/*z* 439.2006.

*4.2.14. (E)-1-Phenyl-2-propyl-3-trimethylstannyl-3-hepten-1-one [**(E)-3p**]*

A colorless oil, R_f 0.58 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 9H), 0.79–0.99 (m, 6H), 1.17–1.55 (m, 5H), 1.80–1.95 (m, 1H), 2.27 (q, J = 6.6 Hz, 2H), 4.67 (t, J = 7.0 Hz, 1H), 5.69 (td, J = 6.6, 0.8 Hz, J_{Sn-H} = 76.1 Hz, 1H), 7.38–7.58 (m,

3H), 7.90–7.97 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −7.7, 13.9, 14.1, 20.5, 22.6, 31.3, 35.2, 50.5, 128.4, 128.5, 132.9, 137.5, 142.6, 144.1, 203.2; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −29.1; HRMS (ESI) Calc. for $C_{19}H_{30}O^{120}SnNa$: M^+ + Na, 417.1216. Found: *m/z* 417.1207.

4.2.15. (*Z*)-1-Phenyl-2-propyl-3-trimethylstannyl-3-hepten-1-one [(*Z*)-3p]

A colorless oil, R_f 0.56 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.20 (s, 9H), 0.80 (t, J = 7.3 Hz, 3H), 0.92 (t, J = 7.1 Hz, 3H), 1.17–1.54 (m, 5H), 1.76–1.93 (m, 1H), 1.98 (q, J = 7.1 Hz, 2H), 4.00 (t, J = 6.9 Hz, 1H), 5.97 (t, J = 7.1 Hz, $J_{119Sn–H}$ = 139.8 Hz, 1H), 7.34–7.57 (m, 3H), 7.78–7.97 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −7.1, 13.4, 14.0, 20.9, 22.8, 34.7, 36.3, 56.7, 128.4, 128.5, 132.5, 137.3, 142.9, 143.7, 202.1; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −47.8; HRMS (ESI) Calc. for $C_{19}H_{30}O^{120}SnNa$: M^+ + Na, 417.1216. Found: *m/z* 417.1207.

4.2.16. (*E*)-4-Propyl-5-tributylstannyl-5-nonen-3-one [(*E*)-3q]

A colorless oil, R_f 0.63 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.71–1.80 (m, 42H), 2.20 (q, J = 6.9 Hz, 2H), 2.24–2.56 (m, 2H), 3.75 (t, J = 6.7 Hz, 1H), 5.67 (t, J = 6.9 Hz, $J_{Sn–H}$ = 66.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 7.5, 10.5, 13.6, 13.8, 14.0, 20.4, 22.8, 27.3, 29.0, 31.9, 33.7, 35.1, 55.4, 143.4, 143.7, 213.0; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −40.1; HRMS (ESI) Calc. for $C_{24}H_{48}O^{120}SnNa$: M^+ + Na, 495.2622. Found: *m/z* 495.2622.

4.2.17. (*Z*)-4-Propyl-5-tributylstannyl-5-nonen-3-one [(*Z*)-3q]

A colorless oil, R_f 0.66 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88–1.79 (m, 42H), 1.99 (q, J = 7.1 Hz, 2H), 2.15–2.54 (m, 2H), 3.13 (t, J = 6.6 Hz, 1H), 5.99 (t, J = 7.1 Hz, $J_{Sn–H}$ = 128.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 7.9, 10.9, 13.6, 13.7, 14.0, 20.9, 23.0, 27.3, 29.1, 33.6, 35.1, 36.8, 61.6, 142.0, 143.9, 213.0; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −40.1; HRMS (ESI) Calc. for $C_{24}H_{48}O^{120}SnNa$: M^+ + Na, 495.2622. Found: *m/z* 495.2622.

4.3. A general procedure for acylstannylation of allene

Allene was bubbled into a solution of an acylstannane (0.30 mmol) and $Ni(cod)_2$ (4.1 mg, 15 μmol) in toluene (0.4 ml) for 10 min at the temperature specified in Table 1. The reaction mixture was stirred for the time specified in Table 1 and filtered through a Florisil pad. The filtrate was concentrated and purified by preparative GPC. Yields are listed in Table 1.

4.3.1. 1-Phenyl-3-trimethylstannyl-3-buten-1-one (3b)

A colorless oil, R_f 0.39 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 9H), 3.98 (t, J = 1.4 Hz, 2H), 5.40 (dt, J = 1.6, 1.4 Hz, 1H), 5.82 (dt, J = 1.6, 1.4 Hz, 1H), 7.42–7.61 (m, 3H), 7.94–8.01 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −8.8, 49.6, 128.3, 128.4, 128.7, 133.2, 136.8, 149.6, 199.5; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −34.3; HRMS (ESI) Calc. for $C_{13}H_{18}O^{120}SnNa$: M^+ + Na, 333.0277. Found: *m/z* 333.0260.

4.3.2. 1-Phenyl-3-tributylstannyl-3-buten-1-one (3c)

A colorless oil, R_f 0.57 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.74–1.04 (m, 15H), 1.18–1.67 (m, 12H), 3.93 (t, J = 1.4 Hz, 2H), 5.36 (dt, J = 1.6, 1.4 Hz, 1H), 5.82 (dt, J = 1.6, 1.4 Hz, 1H), 7.41–7.61 (m, 3H), 7.91–8.02 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 10.0, 13.6, 27.3, 29.0, 50.3, 128.4, 128.6, 128.8, 133.1, 136.9, 149.0, 199.4; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −42.9; HRMS (ESI) Calc. for $C_{22}H_{36}O^{120}SnNa$: M^+ + Na, 459.1684. Found: *m/z* 459.1686.

4.3.3. 5-Tributylstannyl-5-hexen-3-one (3j)

A colorless oil, R_f 0.60 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.76–1.13 (m, 18H), 1.17–1.61 (m, 12H), 2.43 (q, J = 7.4 Hz, 2H), 3.34 (s, 2H), 5.28 (dt, J = 1.6, 0.8 Hz, 1H), 5.73 (dt, J = 1.6, 0.8 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 7.7, 9.9, 13.6, 27.3, 28.8, 28.9, 35.4, 128.7, 148.7, 210.4; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −43.7; HRMS (ESI) Calc. for $C_{18}H_{36}O^{120}SnNa$: M^+ + Na, 411.1684. Found: *m/z* 411.1680.

4.3.4. N-(3-Trimethylstannyl-3-butenoyl)piperidine (3m)

A colorless oil, R_f 0.46 (hexane–ethyl acetate = 2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 9H), 1.40–1.75 (m, 6H), 3.30 (t, J = 1.6 Hz, 2H), 3.32–3.40 (m, 2H), 3.47–3.58 (m, 2H), 5.31 (dt, J = 2.4, 1.6 Hz, 1H), 5.71 (dt, J = 2.4, 1.6 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −8.8, 24.4, 25.5, 26.3, 42.6, 44.8, 46.7, 126.6, 150.3, 170.0; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −31.9; HRMS (ESI) Calc. for $C_{12}H_{23}NO^{120}SnNa$: M^+ + Na, 340.0699. Found: *m/z* 340.0681.

4.4. A general procedure for one-pot hydrolysis–acylstannylation of 1,2-dienes

To a solution of an α-alkoxyvinylstannane (0.20 mmol) in THF or Et_2O (0.10 ml), 1 M HCl aqueous solution (25 μl, 25 μmol) was added, and the resulting mixture was stirred at room temperature. After the time specified in Table 2, the mixture was treated with solid K_2CO_3 (14 mg, 0.10 mmol), and a solution of $Ni(cod)_2$ (2.8 mg, 10 μmol) in toluene (0.5 ml) and 1,2-heptadiene (58 mg, 0.60 mmol) were added successively. The result-

ing mixture was stirred at 50 °C for 3 h and filtered through a Florisil pad. The filtrate was concentrated and purified by preparative GPC to give an acylstannylation product. Yields are listed in Table 2.

*4.4.1. 3-Butyl-4-trimethylstannyl-4-penten-2-one (**7a**)*

A colorless oil, R_f 0.34 (hexane–ethyl acetate = 10:1). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.14 (s, 9H), 0.87 (t, J = 7.0 Hz, 3H), 1.08–1.45 (m, 5H), 1.63–1.82 (m, 1H), 2.10 (s, 3H), 3.27 (t, J = 7.1 Hz, 1H), 5.36 (d, J = 2.4 Hz, 1H), 5.78 (dd, J = 2.4, 0.1 Hz, 1H); ^{13}C NMR (50.0 MHz, $CDCl_3$) δ −8.2, 13.9, 22.5, 29.2, 29.5, 30.9, 64.8, 128.3, 154.3, 210.1; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ −31.3; HRMS (FAB+) Calc. for $C_{12}H_{24}O^{120}Sn$: M^+, 289.0614. Found: *m/z* 289.0616.

*4.4.2. 3-Butyl-4-tributylstannyl-4-penten-2-one (**7b**)*

A colorless oil, R_f 0.57 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.72–1.85 (m, 36H), 2.10 (s, 3H), 3.24 (t, J = 7.0 Hz, 1H), 5.32 (d, J = 2.2 Hz, 1H), 5.79 (dd, J = 2.2, 0.9 Hz, 1H); ^{13}C NMR (50.0 MHz, $CDCl_3$) δ 10.3, 13.6, 13.9, 22.6, 27.4, 29.0, 29.2, 29.8, 30.9, 64.7, 128.4, 153.9, 209.7; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ −41.8; HRMS (FAB+) Calc. for $C_{17}H_{33}O^{120}Sn$: M^+ – Bu, 373.1553. Found: *m/z* 373.1556.

*4.4.3. 4-Butyl-5-trimethylstannyl-5-hexen-3-one (**7c**)*

A colorless oil, R_f 0.60 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.13 (s, 9H), 0.78–1.48 (m, 11H), 1.60–1.82 (m, 1H), 2.26–2.61 (m, 2H), 3.28 (t, J = 7.2 Hz, 1H), 5.31 (d, J = 2.2 Hz, 1H), 5.75 (dd, J = 2.2, 0.7 Hz, 1H); ^{13}C NMR (50.0 MHz, $CDCl_3$) δ −8.2, 7.6, 14.0, 22.5, 29.6, 31.4, 35.3, 64.1, 127.9, 154.8, 212.8; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ −32.7; HRMS (EI) Calc. for $C_{12}H_{23}O^{120}Sn$: M^+ – Me, 303.0771. Found: *m/z* 303.0769.

*4.4.4. (E)-3-Butyl-2-trimethylstannyl-1,5-heptadien-4-one (**7d**)*

A colorless oil, R_f 0.50 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.12 (s, 9H), 1.01–1.95 (m, 9H), 1.87 (dd, J = 6.8, 1.6 Hz, 3H), 3.45 (t, J = 7.1 Hz, 1H), 5.33 (d, J = 2.6 Hz, 1H), 5.75 (dd, J = 2.4, 0.8 Hz, 1H), 6.15 (dq, J = 15.6, 1.6 Hz, 1H), 6.87 (dq, J = 15.6, 6.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ −8.0, 13.9, 18.2, 22.5, 29.6, 31.5, 61.9, 127.8, 131.1, 142.5, 154.7, 200.9; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ −32.9; HRMS (EI) Calc. for $C_{13}H_{23}O^{120}Sn$: M^+ – Me, 315.0771. Found: *m/z* 315.0774.

4.5. Reaction of tributyl[1-(trimethylsilyloxy)vinyl]tin with benzaldehyde dimethyl acetal

To a solution of tributyl[1-(trimethylsilyloxy)vinyl]tin (81 mg, 0.20 mmol) and benzaldehyde dimethyl acetal (34 mg, 0.22 mmol) in CH_2Cl_2 (0.5 ml) was added TMSOTf (111 mg, 0.5 mmol) at −78 °C, and the resulting mixture was stirred for 1 h at −78 °C before a saturated Na_2CO_3 aqueous solution (50 μl) was added at −40 °C. The mixture was allowed to warm to room temperature and treated with solid K_2CO_3 (69 mg, 0.50 mmol). Solvents were evaporated in vacuo, and the residue was dissolved in $CDCl_3$ (0.5 ml). To the solution was added Bu_4Sn (76 mg, 0.22 mmol) as an internal standard. ^{1}H and ^{119}Sn NMR showed the following peaks which was ascribed to (*E*)-tributyl(cinnamoyl)stannane (**10a**) [32] (90% yield by ^{119}Sn NMR). ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.71 (d, J = 15.0 Hz, 1H), 7.28 (d, J = 15.0 Hz, 1H), 7.38–7.64 (m, 5H) (multiplets in δ 0.65–1.90, including peaks of Bu_4Sn, were also obsereved); ^{119}Sn NMR (101 MHz, $CDCl_3$) δ −89.6.

4.6. A general procedure for one-pot aldol condensation–acylstannylation of 1,2-dienes

To a solution of tributyl[1-(trimethylsilyloxy)vinyl]tin (81 mg, 0.20 mmol) and an aldehyde acetal (0.22 mmol) in CH_2Cl_2 (0.5 ml) was added TMSOTf (111 mg, 0.5 mmol) at −78 °C, and the resulting mixture was stirred for 1 h at −78 °C before saturated Na_2CO_3 aqueous solution (50 μl) was added at −40 °C. The mixture was allowed to warm to room temperature and treated with solid K_2CO_3 (69 mg, 0.50 mmol). To the mixture were added a solution of $Ni(cod)_2$ (2.8 mg, 10 μmol) in toluene (0.5 ml) and 1,2-heptadiene (58 mg, 0.60 mmol), and the whole mixture was stirred at room temperature for the time specified in Table 3 before filtration through a Florisil pad. The filtrate was concentrated, the residue was purified by preparative GPC to give acylstannylation products in yields listed in Table 3.

*4.6.1. (E)-4-Butyl-1-phenyl-5-tributylstannyl-1,5-hexadien-3-one (**12a**)*

A colorless oil, R_f 0.56 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.74–1.08 (m, 18H), 1.14–1.59 (m, 17H), 1.77–1.96 (m, 1H), 3.51 (t, J = 7.0 Hz, 1H), 5.35 (d, J = 2.4 Hz, 1H), 5.86 (dd, J = 2.4, 0.8 Hz, 1H), 6.79 (d, J = 15.9 Hz, 1H), 7.32–7.43 (m, 3H), 7.48–7.64 (m, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 10.5, 13.8, 14.1, 22.8, 27.5, 29.1, 29.9, 31.3, 63.1, 125.5, 128.2, 128.6, 128.8, 130.2, 134.7, 141.9, 153.8, 200.2; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ −41.6; HRMS (FAB+) Calc. for $C_{24}H_{37}O^{120}Sn$: M^+ – Bu, 461.1866. Found: *m/z* 461.1861.

*4.6.2. (E)-4-Butyl-1-(4-methylphenyl)-5-tributylstannyl-1,5-hexadien-3-one (**12b**)*

A colorless oil, R_f 0.60 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.73–1.09 (m, 18H), 1.15–1.68 (m, 17H), 1.75–1.97 (m, 1H), 2.37 (s, 3H), 3.51 (t, J = 7.0 Hz, 1H), 5.34 (d, J = 2.2 Hz, 1H), 5.85

(dd, J = 2.2, 0.7 Hz, 1H), 6.74 (d, J = 15.9 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 15.9 Hz, 1H); ^{13}C NMR (50.0 MHz, $CDCl_3$) δ 10.4, 13.7, 14.0, 21.5, 22.7, 27.4, 29.0, 29.8, 31.3, 63.0, 124.7, 128.3, 128.5, 129.6, 132.0, 140.7, 142.1, 154.1, 200.5; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ −41.9; HRMS (FAB+) Calc. for $C_{25}H_{39}O^{120}Sn$: M^+ – Bu, 475.2023. Found: *m/z* 475.2013.

4.6.3. (*E*)-4-Butyl-1-(4-chlorophenyl)-5-tributylstannyl-1,5-hexadien-3-one (**12c**)

A colorless oil, R_f 0.60 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.72–1.09 (m, 18H), 1.13–1.64 (m, 17H), 1.76–1.96 (m, 1H), 3.49 (t, J = 6.9 Hz, 1H), 5.36 (d, J = 2.1 Hz, 1H), 5.87 (d, J = 2.1 Hz, 1H), 6.76 (d, J = 15.9 Hz, 1H), 7.34 (dt, J = 8.6, 2.1 Hz, 2H), 7.41–7.59 (m, 3H); ^{13}C NMR (50.0 MHz, $CDCl_3$) δ 10.4, 13.7, 14.0, 22.7, 27.4, 29.0, 29.8, 31.0, 63.3, 125.9, 128.9, 129.1, 129.4, 133.3, 136.1, 140.5, 153.8, 200.1; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ −41.2; HRMS (FAB+) Calc. for $C_{24}H_{36}ClO^{120}Sn$: M^+ – Bu, 495.1477. Found: *m/z* 495.1482.

4.6.4. (*E*)-4-Butyl-1-(4-methoxycarbonylphenyl)-5-tributylstannyl-1,5-hexadien-3-one (**12d**)

A colorless oil, R_f 0.29 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.73–1.09 (m, 18H), 1.13–1.63 (m, 17H), 1.76–1.97 (m, 1H), 3.51 (t, J = 6.9 Hz, 1H), 3.93 (s, 3H), 5.38 (d, J = 2.2 Hz, 1H), 5.88 (dd, J = 2.2, 0.7 Hz, 1H), 6.86 (d, J = 16.0 Hz, 1H), 7.58 (d, J = 16.0 Hz, 1H), 7.59 (d, J = 8.6 Hz, 2H), 8.04 (d, J = 8.6 Hz, 2H); ^{13}C NMR (50.0 MHz, $CDCl_3$) δ 10.4, 13.6, 14.0, 22.7, 27.4, 29.0, 29.8, 31.0, 52.2, 63.3, 127.5, 128.1, 129.0, 130.0, 131.3, 139.0, 140.5, 153.6, 166.4, 200.0; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ −40.9; HRMS (FAB+) Calc. for $C_{26}H_{39}O^{120}Sn$: M^+ – Bu, 519.1921. Found: *m/z* 519.1925.

4.6.5. (*E*)-3-Butyl-2-tributylstannyl-1,5-octadien-4-one (**12e**)

A colorless oil, R_f 0.59 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.69–1.92 (m, 39H), 2.12–2.33 (m, 2H), 3.42 (t, J = 6.9 Hz, 1H), 5.29 (d, J = 2.2 Hz, 1H), 5.77 (d, J = 2.2 Hz, 1H), 6.12 (dt, J = 15.7, 1.6 Hz, 1H), 6.89 (dt, J = 15.7, 1.6 Hz, 1H); ^{13}C NMR (50.0 MHz, $CDCl_3$) δ 10.4, 12.4, 13.7, 14.0, 22.6, 25.5, 27.4, 29.0, 29.8, 31.3, 62.1, 128.2, 128.6, 148.3, 154.2, 200.8; ^{119}Sn{^{1}H} NMR (101 MHz, $CDCl_3$) δ −42.3; HRMS (FAB+) Calc. for $C_{20}H_{37}O^{120}Sn$: M^+ – Bu, 413.1866. Found: *m/z* 413.1864.

4.7. A general procedure for alkynylstannylation of 1,2-dienes

To a solution of an alkynylstannane (0.20 mmol) were added successively a solution of $Ni(cod)_2$ (2.8 mg, 10 μmol) and 1,3-bis(diphenylphosphino)propane (4.1 mg, 10 μmol) in toluene (0.3 ml) and then a 1,2-diene (0.60 mmol). The resulting mixture was stirred at the temperature specified in Table 4, Eqs. (7) and (8). After the time shown in Table 4, Eqs. (7) and (8), the reaction mixture was filtered through a Florisil pad. The filtrate was concentrated and purified by preparative GPC to give alkynylstannylation products as a mixture of regioisomers. Combined yields are listed in Table 4, Eqs. (7) and (8). Regioisomeric mixtures were separated by preparative recycling reversed phase chromatography.

4.7.1. 3-Butyl-5-phenyl-2-trimethylstannyl-1-penten-4-yne (**14a**)

A colorless oil, R_f 0.65 (hexane–ethyl acetate = 9:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.22 (s, 9H), 0.92 (t, J = 7.3 Hz, 3H), 1.25–1.70 (m, 6H), 3.41 (t, J = 7.1 Hz, 1H), 5.27 (dd, J = 1.8, 0.9 Hz, 1H), 5.86 (dd, J = 1.8, 1.2 Hz, 1H), 7.24–7.47 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ −8.4, 14.0, 22.4, 29.5, 35.9, 43.0, 83.7, 92.0, 123.9, 125.3, 127.5, 128.2, 131.5, 155.5; ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$) δ −32.1; HRMS (ESI) Calc. for $C_{18}H_{26}SnNa$: M^+ + Na, 385.0953. Found: *m/z* 385.0952. Anal. Calc. for $C_{18}H_{26}Sn$: C, 59.87; H, 7.26. Found: C, 59.87; H, 7.23%.

4.7.2. (*Z*)-1-Phenyl-4-trimethylstannyl-4-nonen-1-yne (**15a**)

A colorless oil, R_f 0.64 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 9H), 0.92 (t, J = 7.0 Hz, 3H), 1.24–1.49 (m, 4H), 2.07 (dd, J = 7.4, 7.1 Hz, 2H), 3.29 (d, J = 1.3 Hz, 2H), 6.27 (tt, J = 7.4, 1.3 Hz, 1H), 7.18–7.46 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ −8.2, 14.1, 22.5, 30.4, 32.2, 34.1, 82.9, 88.8, 124.0, 127.5, 128.2, 131.5, 137.5, 142.1; ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$) δ −45.0; HRMS (ESI) Calc. for $C_{18}H_{26}SnNa$: M^+ + Na, 385.0953. Found: *m/z* 385.0957. Anal. Calc. for $C_{18}H_{26}Sn$: C, 59.87; H, 7.26. Found: C, 59.58; H, 7.12%.

4.7.3. 3-tert-Butyl-5-phenyl-2-trimethylstannyl-1-penten-4-yne (**14c**)

A colorless oil, R_f 0.39 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.22 (s, 9H), 1.04 (s, 9H), 3.25 (s, 1H), 5.41 (d, J = 1.7 Hz, 1H), 5.82 (dd, J = 1.7, 0.9 Hz, 1H), 7.25–7.32 (m, 3H), 7.39–7.43 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −7.1, 28.2, 34.9, 54.8, 84.5, 92.0, 124.1, 127.5, 128.2, 129.5, 131.5, 153.7; ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$) δ −31.2; HRMS (EI) Calc. for $C_{17}H_{23}Sn$: M^+ – Me, 347.0821. Found: *m/z* 347.0826. Anal. Calc. for $C_{18}H_{26}Sn$: C, 59.87; H, 7.26. Found: C, 60.04; H, 7.10%.

*4.7.4. (Z)-6,6-Dimethyl-1-phenyl-4-trimethylstannyl-4-hepten-1-yne (**15c**)*

A colorless oil, R_f 0.34 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.30 (s, 9H), 1.09 (s, 9H), 3.29 (d, J = 1.4 Hz, 2H), 6.42 (t, J = 1.4 Hz, 1H), 7.25–7.31 (m, 3H), 7.37–7.42 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −5.7, 30.9, 33.4, 34.1, 83.4, 89.3, 124.0, 127.5, 128.2, 131.4, 132.2, 154.1; ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$) δ −43.4; HRMS (EI) Calc. for $C_{17}H_{23}Sn$: M^+ – Me, 347.0821. Found: *m/z* 347.0818. Anal. Calc. for $C_{18}H_{26}Sn$: C, 59.87; H, 7.26. Found: C, 59.60; H, 7.30%.

*4.7.5. 3-Methoxy-5-phenyl-2-trimethylstannyl-1-penten-4-yne (**14d**)*

A colorless oil, R_f 0.56 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.22 (s, 9H), 3.43 (s, 3H), 4.78 (t, J = 1.4 Hz, 1H), 5.44 (t, J = 1.7 Hz, 1H), 6.07 (t, J = 1.8 Hz, 1H), 7.28–7.34 (m, 3H), 7.42–7.49 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −8.7, 55.9, 77.9, 86.9, 87.8, 122.7, 126.2, 128.2, 128.3, 131.7, 153.6; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −30.7; HRMS (EI) Calc. for $C_{14}H_{17}OSn$: M^+ – Me, 321.0301. Found: *m/z* 321.0304.

*4.7.6. (Z)-1-Methoxy-5-phenyl-2-trimethylstannyl-1-penten-4-yne (**15d**)*

A colorless oil, R_f 0.50 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 9H), 3.19 (d, J = 1.4 Hz, 2H), 3.55 (s, 3H), 6.62 (t, J = 1.4 Hz, 1H), 7.23–7.42 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −9.0, 23.0, 59.0, 81.7, 89.2, 111.9, 123.9, 127.6, 128.2, 131.5, 154.0; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −35.1; HRMS (EI) Calc. for $C_{14}H_{17}OSn$: M^+ – Me, 321.0301. Found: *m/z* 321.0303.

*4.7.7. 3-Butyl-5-phenyl-2-tributylstannyl-1-penten-4-yne (**14e**)*

A colorless oil, R_f 0.43 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.76–1.04 (m, 18H), 1.22–1.64 (m, 18H), 3.38 (t, J = 7.4 Hz, 1H), 5.23 (dd, J = 2.3, 1.0 Hz, 1H), 5.91 (dd, J = 2.3, 0.9 Hz, 1H), 7.24–7.30 (m, 3H), 7.37–7.42 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.3, 11.6, 13.7, 14.1, 27.4, 29.1, 29.6, 35.8, 43.1, 83.7, 92.2, 124.0, 125.5, 127.5, 128.1, 131.5, 155.0; ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$) δ −43.2; HRMS (EI) Calc. for $C_{23}H_{35}Sn$: M^+ – Bu, 431.1759. Found: *m/z* 431.1770.

*4.7.8. (Z)-1-Phenyl-4-tributylstannyl-4-nonen-1-yne (**15e**)*

A colorless oil, R_f 0.39 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85–1.06 (m, 18H), 1.25–1.59 (m, 16H), 2.03 (q, J = 7.3 Hz, 2H), 3.27 (d, J = 1.4 Hz, 2H), 6.23 (tt, J = 7.3, 1.4 Hz, 1H), 7.25–7.30 (m, 3H), 7.37–7.41 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.4, 13.7, 14.1, 22.6, 27.5, 29.2, 30.7, 32.3, 34.5, 82.9, 89.1, 124.1, 127.5, 128.1, 131.5, 137.0, 142.2; ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$) δ −50.4; HRMS (EI) Calc. for $C_{23}H_{35}Sn$: M^+ – Bu, 431.1759. Found: *m/z* 431.1776. Anal. Calc. for $C_{27}H_{44}Sn$: C, 66.54; H, 9.10. Found: C, 66.70; H, 9.01%.

*4.7.9. 3-Butyl-5-(4-trifluoromethylphenyl)-2-trimethylstannyl-1-penten-4-yne (**14f**)*

A colorless oil, R_f 0.43 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.23 (s, 9H), 0.93 (t, J = 7.1 Hz, 3H), 1.30–1.71 (m, 6H), 3.44 (t, J = 7.3 Hz, 1H), 5.30 (dd, J = 2.3, 1.2 Hz, 1H), 5.87 (dd, J = 2.3, 1.2 Hz, 1H), 7.50 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −8.4, 14.0, 22.4, 29.5, 35.7, 43.0, 82.6, 94.9, 124.3 (q, J = 272.1 Hz), 125.1 (q, J = 3.7 Hz), 125.7, 127.7, 129.4 (q, J = 32.5 Hz), 131.7, 154.9; ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$) δ −31.5; HRMS (EI) Calc. for $C_{18}H_{22}F_3Sn$: M^+ – Me, 415.0694. Found: *m/z* 415.0689. Anal. Calc. for $C_{19}H_{25}F_3Sn$: C, 53.18; H, 5.87. Found: C, 52.88; H, 5.84%.

*4.7.10. (Z)-1-(4-Trifluoromethylphenyl)-4-trimethylstannyl-4-nonen-1-yne (**15f**)*

A colorless oil, R_f 0.39 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.24 (s, 9H), 0.91 (t, J = 7.1 Hz, 3H), 1.28–1.41 (m, 4H), 2.06 (q, J = 7.3 Hz, 2H), 3.29 (s, 2H), 6.25 (t, J = 7.3 Hz, 1H), 7.48 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 8.7 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −8.2, 14.0, 22.4, 30.4, 32.2, 34.1, 81.7, 91.8, 122.9, 125.1 (q, J = 3.8 Hz), 127.8, 129.3 (q, J = 32.6 Hz), 131.7, 136.9, 142.6; ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$) δ −44.6; HRMS (EI) Calc. for $C_{18}H_{22}F_3Sn$: M^+ – Me, 415.0694. Found: *m/z* 415.0693.

*4.7.11. 3-Butyl-5-(4-methoxyphenyl)-2-trimethylstannyl-1-penten-4-yne (**14g**)*

A colorless oil, R_f 0.49 (hexane–ethyl acetate = 9:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.21 (s, 9H), 0.92 (t, J = 7.3 Hz, 3H), 1.30–1.67 (m, 6H), 3.39 (t, J = 7.4 Hz, 1H), 3.80 (s, 3H), 5.26 (dd, J = 1.8, 0.9 Hz, 1H), 5.85 (dd, J = 1.8, 1.2 Hz, 1H), 6.82 (d, J = 9.3 Hz, 2H), 7.34 (d, J = 9.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −8.4, 14.1, 22.4, 29.5, 36.0, 43.0, 55.2, 83.5, 90.5, 113.8, 116.1, 125.1, 132.8, 155.8, 159.0; ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$) δ −32.7; HRMS (EI) Calc. for $C_{18}H_{25}OSn$: M^+ – Me, 377.0926. Found: *m/z* 377.0910. Anal. Calc. for $C_{19}H_{28}OSn$: C, 58.34; H, 7.22. Found: C, 58.38; H, 7.31%.

*4.7.12. (Z)-1-(4-Methoxyphenyl)-4-trimethylstannyl-4-nonen-1-yne (**15g**)*

A colorless oil, R_f 0.49 (hexane–ethyl acetate = 9:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.23 (s, 9H), 0.90 (t, J = 7.1 Hz, 3H), 1.18–1.44 (m, 4H), 2.05 (td, J = 7.3, 6.9 Hz, 2H), 3.26 (s, 2H), 3.80 (s, 3H), 6.24 (t, J = 7.3 Hz, 1H), 6.81 (d, J = 8.9 Hz, 2H), 7.32 (d, J = 8.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −8.2, 14.0, 22.4,

30.4, 32.3, 34.1, 55.2, 82.7, 87.2, 113.8, 116.2, 132.8, 137.7, 141.9, 159.0; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −45.3; HRMS (EI) Calc. for $C_{18}H_{25}OSn$: M^+ – Me, 377.0926. Found: *m/z* 377.0928.

4.7.13. 3-Butyl-5-trimethylsilyl-2-trimethylstannyl-1-penten-4-yne (**14j**)

A colorless oil, R_f 0.41 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.15 (s, 9H), 0.19 (s, 9H), 0.90 (t, J = 7.1 Hz, 3H), 1.25–1.59 (m, 6H), 3.20 (td, J = 7.4, 0.9 Hz, 1H), 5.22 (dd, J = 2.1, 0.9 Hz, 1H), 5.77 (dd, J = 2.1, 0.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −8.2, 0.2, 14.0, 22.3, 29.3, 35.7, 43.3, 87.4, 109.0, 125.3, 155.3; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −31.8; HRMS (EI) Calc. for $C_{14}H_{27}SiSn$: M^+ – Me, 343.0903. Found: *m/z* 343.0907. Anal. Calc. for $C_{15}H_{30}SiSn$: C, 50.44; H, 8.47. Found: C, 50.67; H, 8.70%.

4.7.14. (Z)-1-Trimethylsilyl-4-trimethylstannyl-4-nonen-1-yne (**15j**)

A colorless oil, R_f 0.40 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.15 (s, 9H), 0.21 (s, 9H), 0.90 (t, J = 7.1 Hz, 3H), 1.28–1.39 (m, 4H), 2.03 (dt, J = 7.3, 6.9 Hz, 2H), 3.09 (d, J = 1.3 Hz, 2H), 6.16 (tt, J = 7.3, 1.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −8.1, 0.1, 14.0, 22.4, 30.9, 32.2, 34.0, 86.9, 105.9, 137.3, 142.1; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −44.9; HRMS (EI) Calc. for $C_{14}H_{27}SiSn$: M^+ – Me, 343.0903. Found: *m/z* 343.0892. Anal. Calc. for $C_{15}H_{30}SiSn$: C, 50.44; H, 8.47. Found: C, 50.05; H, 8.39%.

4.7.15. 3,3-Dimethyl-5-phenyl-2-trimethylstannyl-1-penten-4-yne (**14k**)

A colorless oil, R_f 0.63 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 9H), 1.43 (s, 6H), 5.25 (d, J = 1.4 Hz, 1H), 5.99 (d, J = 1.4 Hz, 1H), 7.18–7.43 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ −7.4, 30.3, 39.6, 82.2, 96.6, 122.0, 123.9, 127.5, 128.1, 131.5, 161.3; ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$) δ −31.7; HRMS (ESI) Calc. for $C_{16}H_{22}SnNa$: M^+ + Na, 357.0640. Found: *m/z* 357.0641.

4.7.16. 5-Methyl-1-phenyl-4-trimethylstannyl-4-hexen-1-yne (**15k**)

A colorless oil, R_f 0.25 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.24 (s, 9H), 1.83 (s, 6H), 3.30 (s, 2H), 7.24–7.29 (m, 3H), 7.35–7.38 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −7.8, 19.6, 24.7, 27.8, 81.0, 89.3, 106.7, 124.1, 127.4, 128.1, 131.5, 142.3; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −42.1; HRMS (EI) Calc. for $C_{15}H_{19}Sn$: M^+ – Me, 319.0508. Found: *m/z* 319.0505.

4.7.17. (Z)-1-Phenyl-3-propyl-4-trimethylstannyl-4-octen-1-yne (**14l**)

A colorless oil, R_f 0.67 (hexane–ethyl acetate = 9:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 9H), 0.78–1.05 (m, 6H), 1.18–1.68 (m, 6H), 2.06 (dd, J = 7.4, 7.1 Hz, 2H), 3.36 (t, J = 6.6 Hz, 1H), 6.20 (t, J = 7.1 Hz, 1H), 7.23–7.44 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ −7.1, 13.8, 13.9, 20.6, 23.2, 36.1, 38.4, 42.5, 83.5, 92.8, 124.1, 127.4, 128.1, 131.5, 141.2, 144.1; ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$) δ −49.6; HRMS (ESI) Calc. for $C_{20}H_{30}SnNa$: M^+ + Na, 413.1266. Found: *m/z* 413.1260.

4.8. A general procedure for alkynylstannylation of allene

A solution of an alkynylstannane (0.20 mmol), $Ni(cod)_2$ (2.8 mg, 10 μmol), and 1,3-bis(diphenylphosphino)propane (4.1 mg, 10 μmol) in toluene (0.3 ml) was stirred under an atmospheric pressure of allene at the temperature specified in Table 4. After the time shown in Table 4, the reaction mixture was filtered through a Florisil pad. The filtrate was concentrated and purified by preparative GPC to give an alkynylstannylation product. Yields are listed in Table 4.

4.8.1. 5-Phenyl-2-trimethylstannyl-1-penten-4-yne (**14b**)

A colorless oil, R_f 0.63 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.22 (s, 9H), 3.38 (t, J = 1.6 Hz, 2H), 5.30 (dd, J = 3.6, 1.9 Hz, 1H), 5.94 (dd, J = 3.6, 1.8 Hz, 1H), 7.20–7.47 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ −9.4, 30.3, 83.2, 87.8, 123.8, 125.8, 127.7, 128.2, 131.5, 149.5; ^{119}Sn{^{1}H} NMR (186 MHz, $CDCl_3$) δ −29.1; HRMS (ESI) Calc. for $C_{14}H_{18}SnNa$: M^+ + Na, 329.0327. Found: *m/z* 329.0192. Anal. Calc. for $C_{14}H_{18}Sn$: C, 55.13; H, 5.95. Found: C, 55.31; H, 5.90%.

4.8.2. 5-Trimethylsilyl-2-trimethylstannyl-1-penten-4-yne (**14h**)

A colorless oil, R_f 0.48 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 9H), 0.19 (s, 9H), 3.19 (t, J = 1.6 Hz, 2H), 5.25 (q, J = 1.9 Hz, 1H), 5.85 (q, J = 1.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ −9.2, 0.1, 30.8, 87.2, 104.7, 125.8, 149.2; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −28.3; HRMS (ESI) Calc. for $C_{11}H_{22}SiSnNa$: M^+ + Na, 325.0409. Found: *m/z* 325.0582. Anal. Calc. for $C_{11}H_{22}SiSn$: C, 43.88; H, 7.36. Found: C, 43.90; H, 7.47%.

4.8.3. 5-Triethylsilyl-2-trimethylstannyl-1-penten-4-yne (**14i**)

A colorless oil, R_f 0.72 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.18 (s, 9H), 0.59 (q, J = 8.0 Hz, 6H), 0.99 (t, J = 8.0 Hz, 9H), 3.21 (t, J = 1.7 Hz, 2H), 5.26 (q, J = 1.7 Hz, 1H), 5.91 (q, J = 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ −9.5, 4.4, 7.3, 30.6, 84.6, 105.4, 125.8, 149.2; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −28.5; HRMS (EI) Calc. for $C_{14}H_{28}SiSnNa$: M^+–Me, 329.0746. Found: *m/z* 329.0745.

4.9. Synthetic applications

4.9.1. Cross-coupling reaction of **3j** with ethyl 4-iodobenzoate

A solution of **3j** (39 mg, 0.10 mmol) and ethyl 4-iodobenzoate (28 mg, 0.10 mmol) in NMP (0.5 ml) was degassed by 4 freeze–thaw cycles. To the degassed solution was added $Pd_2(dba)_3$ (2.3 mg, 2.5 μmol). The resulting mixture was stirred at 30 °C for 15 h before quenching with a 1 M KF aqueous solution (1.0 ml) and subsequent stirring for 1 h. The whole was filtered through a Celite pad; the filtrate was extracted with ethyl acetate; the combined organic extracts were dried over anhydrous magnesium sulfate. The crude product was purified by chromatography on silica gel (hexane–ethyl acetate = 4:1) to give 5-(4-ethoxycarbonylphenyl)-5-hexen-3-one (**27**) (22 mg, 91% yield) as a colorless oil, R_f 0.24 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (t, J = 7.4 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H), 2.45 (q, J = 7.4 Hz, 2H), 3.61 (s, 2H), 4.36 (q, J = 7.1 Hz, 2H), 5.23 (s, 1H), 5.66 (s, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 7.6, 14.1, 35.0, 49.4, 60.9, 118.5, 125.8, 129.8, 141.0, 144.3, 166.4, 208.9; HRMS (ESI) Calc. for $C_{15}H_{18}O_3Na$: M^+ + Na, 269.1153. Found: *m/z* 269.1144.

4.9.2. Cross-coupling reaction of **3o** with ethyl 4-iodobenzoate

The procedure for 4.9.1 was applied to the reaction of **3o** (42 mg, 0.10 mmol), the time being 10 h. Purification by chromatography on silica gel (hexane–ethyl acetate = 4:1) afforded 4,4-dimethyl-5-(4-ethoxycarbonylphenyl)-5-hexen-3-one (**32**) (20 mg, 73% yield) as a colorless oil, R_f 0.24 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01 (t, J = 7.4 Hz, 3H), 1.30 (s, 6H), 1.38 (t, J = 7.1 Hz, 3H), 2.54 (q, J = 7.4 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 5.35 (s, 1H), 5.41 (s, 1H), 7.16 (d, J = 8.5 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 8.4, 14.2, 24.9, 30.2, 53.3, 60.9, 116.8, 127.6, 129.4, 146.0, 152.8, 166.5, 214.2; HRMS (ESI) Calc. for $C_{17}H_{22}O_3Na$: M^+ + Na, 297.1465. Found: *m/z* 297.1466.

4.9.3. Isomerization of **3j**

To a solution of **3j** (194 mg, 0.50 mmol) in THF (5.0 ml) was added NaH (60% dispersion in mineral oil, 4.0 mg, 0.10 mmol), and the resulting mixture was stirred at room temperature for 4 h before quenching with water (5.0 ml) and extraction with ethyl acetate (5.0 ml). The organic layer was separated and dried over anhydrous magnesium sulfate and concentrated in vacuo. The residue was purified by preparative GPC to give (*Z*)-5-tributylstannyl-4-hexen-3-one (**29**) (171 mg, 88% yield) as a colorless oil, R_f 0.67 (hexane–ethyl acetate = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77–1.57 (m, 30H), 2,15 (t, J = 1.2 Hz, 3H), 2.48 (q, J = 7.4 Hz, 2H), 6.85 (t, J = 1.2 Hz, J_{Sn-H} = 109.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 8.2, 10.7, 13.6, 27.3, 29.1, 36.0, 136.2, 171.8, 200.9; ^{119}Sn{^{1}H} NMR (149 MHz, $CDCl_3$) δ −43.7; HRMS (ESI) Calc. for $C_{18}H_{36}O^{120}SnNa$: M^+ + Na, 411.1684. Found: *m/z* 411.1680.

4.9.4. Isomerization of **27**

The procedure for 4.9.3 was applied to the reaction of **27** (25 mg, 0.10 mmol) carried out for 3 h. Purification by preparative GPC gave (*E*)-5-(4-ethoxycarbonylphenyl)-4-hexen-3-one (**28**) (16.3 mg, 65% yield) as a pale yellow oil, R_f 0.31 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (t, J = 7.1 Hz, 3H), 1.40 (t, J = 7.1 Hz, 3H), 2.54 (d, J = 1.1 Hz, 3H), 2.59 (q, J = 7.1 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 6.52 (d, J = 1.1 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 8.0, 14.2, 18.2, 38.0, 61.1, 125.3, 126.5, 129.8, 130.8, 147.1, 152.3, 166.3, 202.0; HRMS (ESI) Calc. for $C_{15}H_{18}O_3Na$: M^+ + Na, 269.1153. Found: *m/z* 269.1147.

4.9.5. Cross-coupling reaction of **29** with ethyl 4-iodobenzoate

A procedure similar to 4.9.1 using **29** (38 mg, 0.10 mmol) and 5 mol% of $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol) for 69 h was followed by chromatography on silica gel (hexane–ethyl acetate = 4:1) to give (*E*)-5-(4-ethoxycarbonylphenyl)-4-hexen-3-one (**30**) (17 mg, 69% yield) as a pale yellow oil, R_f 0.31 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (t, J = 7.1 Hz, 3H), 1.40 (t, J = 7.1 Hz, 3H), 2.54 (d, J = 1.1 Hz, 3H), 2.59 (q, J = 7.1 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 6.52 (d, J = 1.1 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 8.04 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 8.0, 14.2, 18.2, 38.0, 61.1, 125.3, 126.5, 129.8, 130.8, 147.1, 152.3, 166.3, 202.0; HRMS (ESI) Calc. for $C_{15}H_{18}O_3Na$: M^+ + Na, 269.1153. Found: *m/z* 269.1147.

4.9.6. Cross-coupling reaction of **3j** with benzoyl chloride

In a manner similar to 4.9.1, the reaction of **3j** (37 mg, 96 μmol) with benzoyl chloride (15 mg, 0.10 mmol) for 8 h followed by chromatography on silica gel (hexane–ethyl acetate = 4:1) afforded 2-methylene-1-phenyl-1,4-hexandione (**31**) (16 mg, 83% yield) as a colorless oil, R_f 0.34 (hexane–ethyl acetate = 2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.07 (t, J = 7.4 Hz, 3H), 2.56 (t, J = 7.4 Hz, 2H), 3.62 (s, 1H), 5.78 (s, 1H), 5.92 (s, 1H), 7.34–7.61 (m, 3H), 7.73–7.89 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 7.5, 35.8, 46.0, 128.2, 129.1, 129.8, 132.3, 137.4, 142.1, 208.5; HRMS (ESI) Calc. for $C_{13}H_{14}O_2Na$: M^+ + Na, 225.0891. Found: *m/z* 225.0881.

*4.9.7. Cross-coupling reaction of **14b** with iodobenzene*

A mixture of **14b** (62 mg, 0.20 mmol), iodobenzene (40 mg, 0.20 mmol), and LiCl (13 mg, 0.30 mmol) in DMSO (1.0 ml) was degassed by four freeze–thaw cycles. To this were added $Pd(PPh_3)_4$ (12 mg, 10 μmol) and CuCl (20 mg, 0.20 mmol), successively. The mixture was stirred for 4.5 h at 50 °C and then diluted with diethyl ether. The resulting mixture was treated with a 1 M KF aqueous solution (2.0 ml) for 1 h, and all the insoluble materials were filtered through a Celite pad. The organic layer was washed with water (2.0 ml) and then with brine (2.0 ml), dried over anhydrous magnesium sulfate, and concentrated in vacuo. Preparative GPC of the residue gave 2,5-diphenyl-1-penten-4-yne (**33**) (38 mg, 87% yield) as an orange solid, mp 41.5–42.4 °C, R_f 0.53 (hexane–ethyl acetate = 9:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.63 (s, 2H), 5.57 (d, J = 1.4 Hz, 1H), 5.59 (d, J = 0.9 Hz, 1H), 7.28–7.53 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 25.8, 83.7, 86.9, 113.8, 123.6, 125.8, 127.77, 127.79, 128.2, 128.3, 131.6, 139.9, 142.5; HRMS (EI) Calc. for $C_{17}H_{14}$: M^+, 218.1095. Found: *m*/*z* 218.1094.

*4.9.8. Cross-coupling reaction of **14b** with vinyl bromide*

The procedure for 4.9.7 was applied to **14b** (154 mg, 0.50 mmol) and a 1 M solution of vinyl bromide in THF (1.5 ml, 1.5 mmol) using $Pd_2(dba)_3$ (11.9 mg, 13 μmol) as a catalyst. Purification by preparative GPC gave 3-methylene-6-phenyl-1-hexen-5-yne (**34**) (39 mg, 47% yield) as a colorless oil, R_f 0.61 (hexane–ethyl acetate = 9:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.35 (t, J = 1.4 Hz, 2H), 5.14 (dd, J = 11.0, 0.9 Hz, 1H), 5.21 (s, 1H), 5.30 (d, J = 17.4 Hz, 1H), 5.50 (t, J = 1.4 Hz, 1H), 6.49 (dd, J = 17.4, 11.0 Hz, 1H), 7.27–7.32 (m, 3H), 7.40–7.46 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.4, 83.4, 86.6, 113.8, 117.5, 123.7, 127.8, 128.2, 131.5, 137.7, 140.8; HRMS (EI) Calc. for $C_{13}H_{12}$: M^+, 168.0938. Found: *m*/*z* 168.0947.

*4.9.9. Cross-coupling reaction of **14b** with 1-bromo-2-phenylethyne*

A procedure similar to 4.9.7 using **14b** (48 mg, 0.16 mmol) and 1-bromo-2-phenylethyne (37 mg, 0.20 mmol) followed by preparative GPC gave 3-methylene-1,6-diphenyl-1,5-hexadiyne (**35**) (32 mg, 83% yield) as a yellow oil, R_f 0.54 (hexane–ethyl acetate = 9:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.43 (t, J = 1.4 Hz, 2H), 5.64 (d, J = 0.9 Hz, 1H), 5.79 (d, J = 1.4 Hz, 1H), 7.29–7.36 (m, 6H), 7.44–7.50 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 27.5, 84.3, 85.3, 88.8, 90.0, 122.1, 122.9, 123.4, 126.3, 127.9, 128.2, 128.3, 128.4, 131.6; HRMS (EI) Calc. for $C_{19}H_{14}$: M^+, 242.1095. Found: *m*/*z* 242.1078.

*4.9.10. Homo-coupling reaction of **14a***

A solution of **14a** (73 mg, 0.20 mmol) in DMSO (1.0 ml) was degassed by four freeze–thaw cycles. To this were added $Pd(PPh_3)_4$ (12 mg, 10 μmol), CuCl (20 mg, 0.20 mmol), and $CuCl_2$ (27 mg, 0.20 mmol) successively. The mixture was stirred for 3 h at 50 °C and then diluted with diethyl ether (5.0 ml). The resulting mixture was treated with a 1 M KF aqueous solution (1.0 ml) for 3 h and filtered through a Celite pad. The organic layer was washed with water (1.0 ml) and brine (1.0 ml) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by preparative GPC gave a mixture of *dl* and *meso* isomers of 4,7-dibutyl-4,5-dimethylene-1,8-diphenyl-1,7-octadiyne (**36a**) (32 mg, 82% yield). These diastereomers (**36a′** and **36a″**) were separated by preparative recycling reversed phase chromatography, although their stereochemistry have not been determined. **36a′**: a colorless oil, R_f 0.14 (hexane). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, J = 7.1 Hz, 6H), 1.16–1.89 (m, 12H), 3.65 (dd, J = 8.4, 5.0 Hz, 2H), 5.28 (s, 2H), 5.44 (s, 2H), 7.21–7.51 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.2, 22.6, 29.8, 34.6, 36.9, 83.3, 91.6, 113.9, 123.8, 127.5, 128.1, 131.5, 147.1; HRMS (FAB) Calc. for $C_{30}H_{35}$: $M^+ + H$, 395.2737. Found: *m*/*z* 395.2722. **36a″**: a colorless oil, R_f 0.13 (hexane). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, J = 7.1 Hz, 6H), 1.10–1.86 (m, 12H), 3.52–3.63 (m, 2H), 5.28 (s, 2H), 5.55 (s, 2H), 7.14–7.54 (m, 10H); ^{13}C NMR (50.0 MHz, $CDCl_3$) δ 14.1, 22.5, 29.4, 34.4, 36.1, 84.1, 91.1, 113.7, 123.8, 127.7, 128.2, 131.6, 147.2; HRMS (FAB) Calc. for $C_{30}H_{35}$: $M^+ + H$, 395.2737. Found: *m*/*z* 395.2737.

*4.9.11. Homo-coupling reaction of **14b***

The procedure for 4.9.10 was applied to **14b** (154 mg, 0.50 mmol). Purification of the crude product by flash column chromatography on silica gel (hexane) gave 4,5-dimethylene-1,8-diphenyl-1,7-octadiyne (**36b**) (61 mg, 73% yield) as a pale yellow solid, mp 101.2–102.3 °C, R_f 0.43 (hexane–ethyl acetate = 9:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.47 (s, 4H), 5.40 (s, 2H), 5.59 (s, 2H), 7.27–7.37 (m, 6H), 7.43–7.51 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 24.8, 83.6, 86.9, 114.0, 123.6, 127.8, 128.2, 131.6, 140.7; HRMS (EI) Calc. for $C_{22}H_{18}$: M^+, 282.1408. Found: *m*/*z* 282.1371.

*4.9.12. Homo-coupling reaction of **14i***

In a manner similar to 4.9.10, **14h** (4.0 g, 11.7 mmol) was homo-coupled at 40 °C for 0.8 h. Purification by flash column chromatography on silica gel (hexane) gave 4,5-dimethylene-1,8-bis(triethysilyl)-1,7-octadiyne (**36c**) (1.53 g, 73% yield) as a pale yellow oil, R_f 0.31 (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.60 (q, J = 8.0 Hz, 12H), 0.99 (t, J = 8.0 Hz, 18H), 3.25 (s, 4H), 5.24 (s, 2H), 5.50 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 4.4, 7.3, 25.2, 85.3, 104.7, 113.6, 140.7; HRMS (ESI) Calc. for $C_{22}H_{38}Si_2Na$: $M^+ + Na$, 381.2408. Found: *m*/*z* 381.2400.

*4.9.13. Desilylation of **36c***

To a THF (43 ml) solution of **36c** (500 mg, 1.39 mmol) was added AcOH (0.44 g, 7.3 mmol) and TBAF (5.5 ml, 5.5 mmol, 1 M THF solution) successively at 0 °C. The solution was warmed up to room temperature and stirred for 45 h. The resulting solution was treated with water (5.0 ml); the aqueous phase was extracted for three times with pentane (40 ml). The combined organic layers were washed for five times with water (5.0 ml) and successively with a saturated $NaHCO_3$ aqueous solution (5.0 ml) and brine (5.0 ml), and then was dried over anhydrous sodium sulfate. Careful evaporation of the solvent followed by purification by flash column chromatography on silica gel (pentane) gave 4,5-dimethylene-1,7-octadiyne (**36d**) [25] (166 mg, 92% yield) as a colorless oil: R_f 0.44 (hexane–ethyl acetate = 100:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.18 (t, J = 2.7 Hz, 2H), 3.18–3.23 (m, 4H), 5.29 (s, 2H), 5.49 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.8, 71.3, 81.3, 114.2, 140.1.

*4.9.14. Diels–Alder reaction of **36a** with diethyl acetylenedicarboxylate*

A mixture of **36a** (32 mg, 82 μmol) and diethyl acetylenedicarboxylate (70 mg, 0.41 mmol) in toluene (0.8 ml) was stirred for 37 h at 100 °C. Evaporation of the solvent followed by preparative GPC gave diethyl 4,5-bis(1-butyl-3-phenyl-2-propynyl)-1,4-cyclohexadiene-1,2-dicarboxylate (**37a**) (41 mg, 89% yield). These diastereomers (**37a′** and **37a″**) were separated by preparative recycling silica gel chromatography, although their stereochemistry could not be determined. **37a′**: a colorless oil, R_f 0.20 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.93 (t, J = 6.9 Hz, 6H), 1.22–1.88 (m, 18H), 2.96–3.56 (m, 4H), 3.85 (dd, J = 7.7, 7.1 Hz, 2H), 4.26 (q, J = 7.1 Hz, 4H), 7.22–7.45 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.1, 22.6, 29.1, 29.8, 33.7, 33.8, 61.2, 82.2, 90.5, 123.5, 127.0, 127.6, 128.1, 131.5, 132.1, 167.7; HRMS (ESI) Calc. for $C_{38}H_{44}O_4Na$: M^+ + Na, 587.3135. Found: *m/z* 587.3115. **37a″**: a colorless oil, R_f 0.18 (hexane–ethyl acetate = 10:1). ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.84–1.04 (m, 6H), 1.23–1.94 (m, 18H), 2.94–3.55 (m, 4H), 3.85 (dd, J = 9.3, 5.1 Hz, 2H), 4.25 (q, J = 7.1 Hz, 4H), 7.22–7.46 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.11, 14.14, 22.6, 29.6, 30.1, 33.9, 34.2, 61.2, 82.4, 90.4, 123.5, 127.3, 127.6, 128.0, 131.5, 132.1, 167.6; HRMS (ESI) Calc. for $C_{38}H_{44}O_4Na$: M^+ + Na, 587.3135. Found: *m/z* 587.3120.

*4.9.15. Diels–Alder reaction of **36b** with diethyl acetylenedicarboxylate*

The procedure of 4.9.14 was applied to **36b** (14 mg, 50 μmol). Preparative GPC of the crude product gave diethyl 4,5-bis(3-phenyl-2-propynyl)-1,4-cyclohexadiene-1,2-dicarboxylate (**37b**) (19 mg, 84% yield) as a pale yellow oil, R_f 0.42 (hexane–ethyl acetate = 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.31 (t, J = 7.1 Hz, 6H), 3.25 (s, 4H), 3.31 (s, 4H), 4.25 (q, J = 7.1 Hz, 4H), 7.24–7.31 (m, 6H), 7.36–7.42 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.0, 22.6, 32.5, 61.2, 81.5, 86.1, 123.4, 123.9, 127.8, 128.2, 131.6, 132.1, 167.6; HRMS (ESI) Calc. for $C_{30}H_{28}O_4Na$: M^+ + Na, 475.1884. Found: *m/z* 475.1885.

*4.9.16. Diels–Alder reaction of **36d** with diethyl acetylenedicarboxylate*

In a way similar to 4.9.14, **36d** (100 mg, 0.77 mmol) was allowed to undergo the Diels–Alder reaction. Purification of the product by flash column chromatography on silica gel (hexane–ethyl acetate = 7:1) gave diethyl 4,5-bis(2-propynyl)-1,4-cyclohexadiene-1,2-dicarboxylate (**37c**) (0.23 g, 100% yield) as a colorless oil: R_f 0.22 (hexane–ethyl acetate = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (t, J = 7.2 Hz, 6H), 2.01 (t, J = 2.7 Hz, 2H), 3.03 (d, J = 2.7 Hz, 4H), 3.15 (s, 4H), 4.24 (q, J = 7.2 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9, 21.4, 32.1, 61.2, 69.5, 80.3, 123.6, 132.0, 167.6; HRMS (EI) Calc. for $C_{18}H_{20}O_4$: M^+, 301.1360. Found: *m/z* 301.1364.

*4.9.17. Annulation of **37c** with acetylene catalyzed by $Ni(acac)_2$–DIBAL–PPh_3 [26]*

A solution of $Ni(acac)_2$ (7.7 mg, 30 μmol) and PPh_3 (325 mg, 0.12 mmol) in THF (7.5 ml) was degassed by four freeze–thaw cycles. To this was added a 1 M solution of DIBAL in toluene (60 μl, 60 μmol) dropwise at room temperature. The mixture was stirred at room temperature for 15 min, and then a solution of **37c** (30 mg, 0.1 mmol) in THF (1.0 ml) was added to the mixture at 0 °C. The resulting mixture was warmed up to room temperature, stirred for 21 h under an acetylene gas atmosphere (1 atm), then diluted with ethyl acetate, and finally filtered through a Florisil pad. Evaporation of the solvent followed by purification by flash column chromatography on silica gel (hexane–ethyl acetate = 7:1) gave diethyl 1,4,5,10-tetrahydroanthracene-2,3-dicarboxylate (**38**) (18.1 mg, 56% yield) as an orange solid, mp 82.0–83.3 °C: R_f 0.35 (hexane–ethyl acetate = 7:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, J = 7.2 Hz, 6H), 3.04 (s, 4H), 3.31 (s, 4H), 4.26 (q, J = 7.2 Hz, 4H), 7.11–7.19 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9, 32.3, 33.8, 61.1, 122.3, 126.1, 128.0, 132.6, 133.9, 168.0; HRMS (EI) Calc. for $C_{20}H_{22}O_4$: M^+, 326.1517. Found: *m/z* 326.1511.

4.9.18. Tetrahydrotetracene synthesis [27]

To a solution of Cp_2ZrCl_2 (44 mg, 0.15 mmol) in THF (4.0 ml) was added *n*-BuLi (0.19 ml, 0.30 mmol, 1.59 M hexane solution) dropwise at −78 °C, and the reaction mixture was stirred at −78 °C for 1 h. To the resulting solution was added a THF (1.0 ml) solution

of **37b** (40 mg, 88 μmol). The mixture was warmed up to room temperature and stirred for 1 h at room temperature. To this were added successively CuCl (34 mg, 0.34 mmol), *N,N′*-dimethylpropyleneurea (58 mg, 0.45 mmol) and *o*-diiodobenzene (88 mg, 0.26 mmol) at room temperature, and the whole was stirred at 50 °C for 15 h before quenching with a 1 M HCl aqueous solution (1.0 ml) and subsequent filtration through a Celite pad. The organic layer was separated; the aqueous phase was extracted twice with ethyl acetate (10 ml). The combined organic extracts were washed with a saturated $NaHCO_3$ aqueous solution (2.0 ml), water (2.0 ml) and brine (2.0 ml) and then dried over anhydrous sodium sulfate. Evaporation of the solvent followed by purification by flash column chromatography on silica gel (hexane–ethyl acetate = 5:1) gave **39** (19 mg, 40% yield) as a pale yellow solid, mp 138.0–139.2 °C: R_f 0.50 (hexane–ethyl acetate = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (t, J = 7.2 Hz 6H), 2.90 (s, 4H), 3.14 (s, 4H), 4.20 (q, J = 7.2 Hz, 4H), 7.22–7.60 (m, 14H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.7, 32.0, 33.6, 60.8, 121.9, 124.8, 125.9, 127.0, 128.5, 129.8, 129.9, 131.2, 132.4, 137.1, 139.6, 167.7; HRMS (ESI) Calc. for $C_{36}H_{32}O_4Na$: M^+ + Na, 551.2196. Found: *m/z* 551.2200.

4.9.19. Synthesis of tetrakis(exomethylene)cyclohexane 40 [27]

To a solution of Cp_2ZrCl_2 (41 mg, 0.14 mmol) in THF (3.0 ml) was added *n*-BuLi (0.18 ml, 0.28 mmol, 1.55 M hexane solution) dropwise at −78 °C, and the reaction mixture was stirred at −78 °C for 1 h. To the resulting solution was added a THF (0.5 ml) solution of **36b** (19.8 mg, 70 μmol). The mixture was warmed up to room temperature and stirred for 1 h at room temperature. To this were added CuCl (30 mg, 0.30 mmol) and *N,N′*-dimethylpropyleneurea (54 mg, 0.42 mmol) at room temperature and stirred for 2 h before quenching with a 1 M HCl aqueous solution (1.0 ml) and filtration through a Celite pad. The organic layer was separated; the aqueous phase was extracted twice with ethyl acetate (10 ml); the combined organic layer was washed with a saturated $NaHCO_3$ aqueous solution (2.0 ml), water (2.0 ml) and brine (2.0 ml) and then dried over anhydrous sodium sulfate. Evaporation of the solvent followed by purification by flash column chromatography on silica gel (hexane–ethyl acetate = 60:1) gave (*1E,2E*)-1,2-bis(phenylmethylene)-4,5-dimethylenecyclohexane (**40**) (10.9 mg, 55% yield) as a pale yellow solid, mp 119.9–121.3 °C: R_f 0.70 (hexane–ethyl acetate = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.46–3.51 (m, 4H), 4.75–4.79 (m, 2H), 5.18 (dt, J = 1.5, 1.2 Hz, 2H), 6.86 (s, 2H), 7.22–7.43 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 36.3, 109.0, 123.7, 126.7, 128.3, 129.4, 137.7, 140.2, 144.6; HRMS (EI) Calc. for $C_{22}H_{20}$: M^+, 284.1560. Found: *m/z* 284.1564.

4.9.20. Synthesis of hexahydroanthracene 41

A mixture of **40** (10 mg, 35 μmol) and diethyl acetylenedicarboxylate (48 mg, 0.28 mmol) in toluene (0.5 ml) was stirred for 28 h at 100 °C. Evaporation of the solvent followed by flash column chromatography on silica gel (hexane–ethyl acetate = 2:1) gave tetraethyl 1,4-diphenyl-1,4,5,6,9,10-hexahydroanthracene-2,3,7,8-tetracarboxylate (**41**) (15.3 mg, 70% yield) as a pale yellow solid, m.p. 138.0–139.2 °C: R_f 0.11 (hexane–ethyl acetate = 4:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (t, J = 7.0 Hz, 6H), 1.25 (t, J = 7.2 Hz, 6H), 2.30–2.47 (m, 4H), 2.64–2.90 (m, 4H), 3.94–4.07 (m, 4H), 4.18 (q, J = 7.2 Hz, 4H), 4.25 (s, 2H), 7.25–7.36 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.6, 13.9, 31.7, 33.3, 48.3, 60.8, 61.0, 121.3, 125.6, 127.3, 128.6, 129.1, 132.4, 135.1, 140.4, 167.4, 167.9; HRMS (ESI) Calc. for $C_{38}H_{40}O_8Na$: M^+ + Na, 647.2618. Found: *m/z* 647.2605.

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