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Note

A facile stereoselective synthesis of difunctionalized 1,3-dienes containing tin and halogen via hydrozirconation of (*Z*)-3-(tributylstannyl)alk-3-en-1-ynes

Ming-Zhong Cai [a,*], Yue Wang [a], Ping-Ping Wang [b]

[a] School of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330027, PR China
[b] Department of Chemistry, Jiujiang University, Jiujiang 332000, PR China

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ABSTRACT

Sonogashira coupling of (*E*)-α-iodovinylstannanes **1** with (trimethylsilyl)acetylene gave (*Z*)-1-(trimethylsilyl)-3-(tributylstannyl)alk-3-en-1-ynes **2**, which underwent a desilylation reaction to afford (*Z*)-3-(tributylstannyl)alk-3-en-1-ynes **3** in high yields. (1*E*,3*Z*)-1-Halo-3-(tributylstannyl)-substituted 1,3-dienes **5** could be synthesized stereoselectively via hydrozirconation of (*Z*)-3-(tributylstannyl)alk-3-en-1-ynes **3**, followed by trapping with iodine or NBS.

1. Introduction

The stereocontrolled synthesis of 1,3-dienes containing metal or heteroatom functional groups is of considerable interest in organic synthesis because many useful functional group transformations can be achieved by introduction and removal of metal or heteroatom functions. In addition, heteroatom-substituted 1,3-dienes can control both regio- and stereoselectivity and play a very important role in cycloadditions [1]. The stereoselective synthesis of 1,3-dienyl sulfides [2], 1,3-dienyl selenides [3], 1,3-dienylsilanes [4], 1,3-dienylstannanes [5], and 1,3-dienyl sulfones [6] has already been described in the literature. Recently, the synthesis of difunctionalized 1,3-dienes has also attracted great interest in organic synthesis since such dienes may find use as synthetic building blocks [7]. The synthesis of 2,3-bisboryl-1,3-dienes [8], 1,4-dihalo-1,3-dienes [9], 1-sulfonyl-4-phenylseleno-1,3-dienes [10], 2-sulfonyl-3-phenylseleno-1,3-dienes [11], and 1-bromo-4-phenylthio-1,3-dienes [12] has been described in literature. Jin et al. reported the stereoselective synthesis of 2-alkoxy-3-alkyl(aryl)thiobuta-1,3-dienes by Negishi coupling between α-alkyl(aryl)thio vinyl zinc chloride and α-bromo vinyl ether [13]. Coleman et al. reported the stereoselective synthesis of (*E*,*E*)-1-tributylstannyl-4-borylbuta-1,3-diene and its use as an orthogonal Stille and Suzuki–Miyaura coupling partner [14]. Very recently, we have described the stereoselective synthesis of (*Z*,*Z*)-2-silyl-3-stannyl-substituted 1,3-dienes via the hydromagnesiation of alkynylsilanes, followed by the cross-coupling reaction with (*E*)-α-iodovinylstannanes in the presence of $Pd(PPh_3)_4$ catalyst [15]. However, to the best of our knowledge, no well-established method is used to prepare stereoselectively (1*E*,3*Z*)-1-halo-3-(tributylstannyl)-substituted 1,3-dienes. Herein, we wish to report that (1*E*,3*Z*)-1-halo-3-(tributylstannyl)-substituted 1,3-dienes could be conveniently synthesized via hydrozirconation of (*Z*)-3-(tributylstannyl)alk-3-en-1-ynes, followed by trapping with iodine or NBS.

2. Results and discussion

There has been a lively interest in terminal conjugated enynes, alk-3-en-1-ynes, due to its synthetic utility; the acetylenic hydrogen can be converted into various functionalities as well as undergo carbon–carbon bond formation. Furthermore, the terminal conjugated enyne is a useful building block for the synthesis of natural products in organic synthesis, because the terminal conjugated enyne unit occurs in natural products such as laurencin [16], dactylyne [17], quinolizidine [18], and histrionicotoxin [19]. Very recently, Hoshi et al. reported the synthesis of terminal conjugated enynes via Cu-mediated Suzuki–Miyaura cross-coupling reaction of alkenyldialkylboranes with (trimethylsilyl)ethynyl bromide [20]. Our methodology involves the preparation and the reactions of the building block (*Z*)-3-(tributylstannyl)-alk-3-en-1-ynes **3** which can be conveniently obtained according to Scheme 1:

* Corresponding author. Fax: +86 791 8120388.
E-mail address: caimzhong@163.com (M.-Z. Cai).

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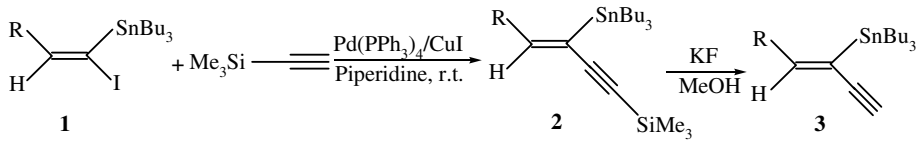


Scheme 1.

Table 1
Coupling reaction of **1** with (trimethylsilyl)acetylene[a] and desilylation of **2**[b]

Entry	R	Product	Yield[c] (%)
1	*n*-Bu	**2a**	86
2	Ph	**2b**	91
3	CH_3OCH_2	**2c**	84
4	n-C_6H_{13}	**2d**	87
5	*n*-Bu	**3a**	89
6	Ph	**3b**	89
7	CH_3OCH_2	**3c**	86
8	n-C_6H_{13}	**3d**	87

[a] The reaction of **1** (2 mmol) with (trimethylsilyl)acetylene (4 mmol) was carried out using $Pd(PPh_3)_4$ (0.1 mmol), CuI (0.2 mmol) and piperidine (6 ml) at room temperature for 2 h.
[b] The desilylation reaction of **2** (1 mmol) with KF (10 mmol) was performed in methanol (4 ml) at 70 °C for 5 h.
[c] Isolated yield of **2** based on the **1** used.

Sonogashira coupling of alkenyl iodides with terminal alkynes provides a simple and general route for the synthesis of conjugated enynes [21]. We observed that, when the coupling reactions of (*E*)-α-iodovinylstannanes **1** with (trimethylsilyl)acetylene were performed in piperidine at room temperature using $Pd(PPh_3)_4$ and CuI as co-catalyst, fairly rapid reactions occurred affording stereoselectively the desired (*Z*)-1-(trimethylsilyl)-3-(tributylstannyl)alk-3-en-1-ynes **2** in high yields, the typical results are summarized in Table 1. We next investigated the desilylation reaction of (*Z*)-1-(trimethylsilyl)-3-(tributylstannyl)alk-3-en-1-ynes **2** with KF in methanol in order to prepare (*Z*)-3-(tributylstannyl)alk-3-en-1-ynes **3**. We found that the desilylation reaction of (*Z*)-1-(trimethylsilyl)-3-(tributylstannyl)alk-3-en-1-ynes **2** with KF proceeded smoothly in methanol at 70 °C to give the desired (*Z*)-3-(tributylstannyl)alk-3-en-1-ynes **3** in high yields. The typical results are also summarized in Table 1. The stereochemistry of compounds **2** and **3** was readily apparent from the ^{1}H NMR spectra of compounds **2** and **3** which showed a ($^3J_{Sn-H}$) coupling constant of 102–108 Hz, fully in accord with an *Z* geometry.

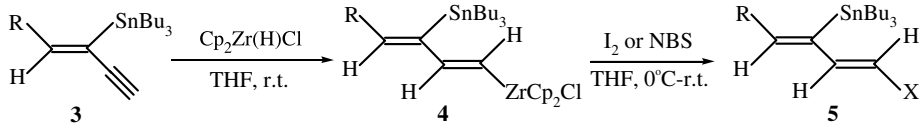
Hydrozirconation has emerged as a unique hydrometallation with some attractive features such as the high regioselectivity and stereoselectivity observed with alkynes [22] and heteroatom-substituted alkynes [23]. However, the hydrozirconation of terminal conjugated enynes has received less attention [24] and the hydrozirconation of 3-stannyl-substituted terminal conjugated enynes has not been reported. With a convenient route to (*Z*)-3-(tributylstannyl)alk-3-en-1-ynes **3** we decided to establish the feasibility of using **3** in hydrozirconation reaction with $Cp_2Zr(H)Cl$. We observed that, when the hydrozirconation of **3** with $Cp_2Zr(H)Cl$ was performed in THF at room temperature, fairly rapid reactions occurred affording stereoselectively (1*E*,3*Z*)-3-(tributylstannyl)-substituted 1,3-dienylzirconium(IV) complexes **4**, the intermediates **4** were then trapped with iodine or NBS at 0 °C to give stereoselectively (1*E*,3*Z*)-1-halo-3-(tributylstannyl)-substituted 1,3-dienes **5** in good yields (Scheme 2). The typical results are summarized in Table 2. As shown in Table 2, a variety of (1*E*,3*Z*)-1-halo-3-(tributylstannyl)-substituted 1,3-dienes **5** could be synthesized stereoselectively via hydrozirconation of (*Z*)-3-(tributylstannyl)alk-3-en-1-ynes **3**, followed by trapping with iodine or NBS. We found that the iododestannylation reaction did not occur due to higher reactivity of C–Zr bond than C–Sn bond. The (1*E*)-configuration of compounds **5** has been proved by their ^{1}H NMR spectra which show two doublets at δ = 6.02–7.18 with a coupling constant of 13.6 Hz, and this also indicates that hydrozirconation of (*Z*)-3-(tributylstannyl)alk-3-en-1-ynes **3** with $Cp_2Zr(H)Cl$ occurs highly regio- and stereoselectively, affording the intermediates **4**. The (3*Z*)-configuration of compounds **5** was readily apparent from the ^{1}H NMR spectra of compounds **5** which showed a ($^3J_{Sn-H}$) coupling constant of 108 Hz, fully in accord with an *Z* geometry [25]. The results indicate that compounds **5** has the expected (1*E*,3*Z*)-configuration.

We have also carried out the Ni-catalyzed cross-coupling reaction of compound **5a** with Gringard reagents in THF to afford 1,3-dienylstannanes **6** in good yields. Compound **6a** underwent the cross-coupling reaction with diphenyliodonium chloride in the presence of $Pd(PPh_3)_4$ and CuI cocatalyst in DMF to give the tin-free 1,3-diene **7** in 74% yield (Scheme 3).

In summary, we have developed a highly stereoselective and general route to difunctionalized 1,3-dienes containing tin and halogen by hydrozirconation of (*Z*)-3-(tributylstannyl)alk-3-en-1-ynes, followed by trapping with iodine or NBS. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions, high stereoselectivity and good yields. Investigations into the synthetic applications of compounds **5** are currently in progress.

3. Experimental

^{1}H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer using $CDCl_3$ as the solvent. IR spectra were determined on an FTS-185 instrument as neat films. Mass spectra were obtained on a Finigan 8239 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer. All reactions were carried out in pre-dried glassware (150 °C, 4 h) and cooled under a stream of dry Ar. All solvents were dried, deoxygenated and freshly distilled before use. (*E*)-α-Iodovinylstannanes **1** were prepared from alkynylstannanes according to literature procedure [26].



Scheme 2.

Table 2
Synthesis of (1*E*,3*Z*)-1-halo-3-(tributylstannyl)-substituted 1,3-dienes **5**

Entry	R	X	Product	Yield[a] (%)
1	n-C_4H_9	Br	**5a**	76
2	Ph	Br	**5b**	80
3	CH_3OCH_2	Br	**5c**	72
4	n-C_6H_{13}	Br	**5d**	81
5	n-C_4H_9	I	**5e**	74
6	Ph	I	**5f**	78
7	CH_3OCH_2	I	**5g**	72
8	n-C_6H_{13}	I	**5h**	75

[a] Isolated yield based on the **3** used.

3.1. General procedure for the synthesis of (Z)-1-(trimethylsilyl)-3-(tributylstannyl)-alk-3-en-1-ynes **2a–d**

(*E*)-α-Iodovinylstannane **1** (2.0 mmol), $Pd(PPh_3)_4$ (0.1 mmol), piperidine (6 ml), and CuI (0.2 mmol) were added to a flask under Ar, and the resulting mixture was stirred at room temperature for 5 min. To this solution was added (trimethylsilyl)acetylene (4.0 mmol), and the reaction mixture was stirred at room temperature for 2 h, quenched with sat. NH_4Cl aq. solution (10 ml) at 0 °C and extracted with Et_2O (2 × 25 ml). The ethereal solution was washed with water (2 × 10 ml) and dried over $MgSO_4$. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 30–60 °C).

3.1.1. (Z)-1-(Trimethylsilyl)-3-(tributylstannyl)oct-3-en-1-yne (**2a**)

IR (film): ν (cm^{-1}) 2959, 2928, 2111, 1714, 1584, 1464, 1249, 842, 759; ^1H NMR ($CDCl_3$): δ 6.78 (t, J = 7.6 Hz, $^3J_{Sn-H}$ = 108 Hz, 1H), 2.11–2.02 (m, 2H), 1.57–1.48 (m, 6H), 1.39–1.28 (m, 10H), 1.02 (t, J = 8.0 Hz, 6H), 0.92–0.85 (m, 12H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 154.4, 123.8, 109.7, 94.6, 35.4, 31.7, 29.1, 27.4, 22.5, 14.0, 13.7, 11.0, 0.3; MS: m/z 470 (M^+, 4.2), 291 (25), 73 (100), 57 (93); Anal. Calc. for $C_{23}H_{46}SiSn$: C, 58.85; H, 9.88. Found: C, 58.59; H, 10.02%.

3.1.2. (Z)-1-(Trimethylsilyl)-3-(tributylstannyl)-4-phenylbut-3-en-1-yne (**2b**)

IR (film): ν (cm^{-1}) 3058, 2957, 2925, 2104, 1638, 1558, 1489, 1249, 842, 752, 697; ^1H NMR ($CDCl_3$): δ 7.84 (s, $^3J_{Sn-H}$ = 104 Hz, 1H), 7.33–7.22 (m, 5H), 1.46–1.38 (m, 6H), 1.29–1.20 (m, 6H), 0.92–0.83 (m, 15H), 0.23 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 151.7, 139.9, 128.2, 127.9, 127.4, 127.2, 110.3, 98.2, 28.9, 27.2, 13.7, 11.8, 0.23; MS: m/z 490 (M^+, 3.3), 433 (100), 431 (69), 291 (58), 179 (57), 73 (73); Anal. Calc. for $C_{25}H_{42}SiSn$: C, 61.36; H, 8.65. Found: C, 61.13; H, 8.82%.

3.1.3. (Z)-1-(Trimethylsilyl)-3-(tributylstannyl)-5-methoxylpent-3-en-1-yne (**2c**)

IR (film): ν (cm^{-1}) 2958, 2928, 2114, 1711, 1457, 1249, 1124, 842; ^1H NMR ($CDCl_3$): δ 6.82 (t, J = 5.6 Hz, $^3J_{Sn-H}$ = 108 Hz, 1H), 3.94 (d, J;= 5.6 Hz, 2H), 3.32 (s, 3H), 1.54–1.48 (m, 6H), 1.37–1.28 (m, 6H), 1.02 (t, J = 8.0 Hz, 6H), 0.93–0.88 (m, 9H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 148.3, 127.9, 108.9, 97.7, 73.6, 58.1, 29.1, 27.4, 13.7, 11.5, 0.2; MS: m/z 458 (M^+, 2.1), 401 (94), 167 (100), 73 (62); Anal. Calc. for $C_{21}H_{42}OSiSn$: C, 55.15; H, 9.26. Found: C, 55.39; H, 9.42%.

3.1.4. (Z)-1-(Trimethylsilyl)-3-(tributylstannyl)dec-3-en-1-yne (**2d**)

IR (film): ν (cm^{-1}) 2958, 2927, 2112, 1713, 1583, 1464, 1249, 842, 759; ^1H NMR ($CDCl_3$): δ 6.77 (t, J = 7.6 Hz, $^3J_{Sn-H}$ = 108 Hz, 1H), 2.10–2.02 (m, 2H), 1.55–1.49 (m, 6H), 1.37–1.25 (m, 14H), 1.04–0.87 (m, 18H), 0.18 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 154.4, 123.7, 109.7, 94.6, 35.8, 31.8, 29.5, 29.2, 29.1, 27.4, 22.7, 14.1, 13.8, 11.0, 0.3; MS: m/z 498 (M^+, 2.6), 441 (100), 327 (45), 73 (42); Anal. Calc. for $C_{25}H_{50}SiSn$: C, 60.36; H, 10.13. Found: C, 60.10; H, 10.31%.

3.2. General procedure for the synthesis of (Z)-3-(tributylstannyl)alk-3-en-1-ynes **3a–d**

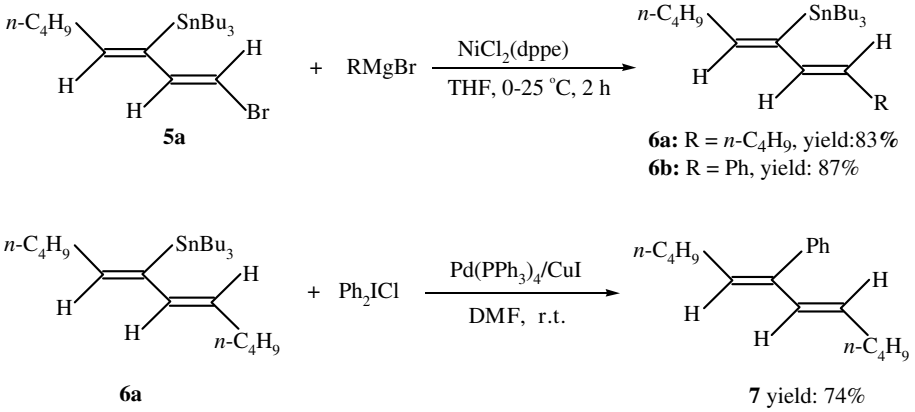
A mixture of (*Z*)-1-(trimethylsilyl)-3-(tributylstannyl)alk-3-en-1-yne (1 mmol), anhydrous KF (10 mmol) in methanol (4 ml) was heated at reflux for 5 h. After removal of the solvent under reduced pressure, the mixture was extracted with diethyl ether (2 × 20 ml). The ethereal solution was washed with water (2 × 10 ml) and dried over $MgSO_4$. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 30–60 °C).

3.2.1. (Z)-3-(Tributylstannyl)oct-3-en-1-yne (**3a**)

IR (film): ν (cm^{-1}) 3314, 2958, 2928, 2076, 1716, 1586, 1464; ^1H NMR ($CDCl_3$): δ 6.82 (t, J = 7.2 Hz, $^3J_{Sn-H}$ = 108 Hz, 1H), 3.07 (s, 1H), 2.12–2.03 (m, 2H), 1.55–1.48 (m, 6H), 1.39–1.30 (m, 10H), 1.03 (t, J = 8.0 Hz, 6H), 0.93–0.88 (m, 12H); ^{13}C NMR ($CDCl_3$): δ 155.5, 122.6, 88.2, 77.7, 35.4, 31.6, 29.0, 27.3, 22.5, 14.0, 13.7, 10.8; MS: m/z 398 (M^+, 8.8), 342 (54), 178 (100), 57 (48); Anal. Calc. for $C_{20}H_{38}Sn$: C, 60.47; H, 9.64. Found: C, 60.21; H, 9.46%.

3.2.2. (Z)-3-(Tributylstannyl)-4-phenylbut-3-en-1-yne (**3b**)

IR (film): ν (cm^{-1}) 3312, 3060, 2957, 2078, 1644, 1490, 1456, 751, 698; ^1H NMR ($CDCl_3$): δ 7.88 (s, $^3J_{Sn-H}$ = 108 Hz, 1H), 7.32–7.23 (m, 5H), 3.34 (s, 1H), 1.44–1.37 (m, 6H), 1.27–1.21 (m, 6H), 0.93–0.82 (m, 15H); ^{13}C NMR ($CDCl_3$): δ 152.8, 139.8, 128.3, 128.0, 127.4, 127.2, 88.9, 81.1, 28.8, 27.2, 13.6, 11.6; MS: m/z 417



Scheme 3.

(M^+-1, 5.3), 361 (100), 177 (50); Anal. Calc. for $C_{22}H_{34}Sn$: C, 63.33; H, 8.21. Found: C, 63.11; H, 8.02%.

*3.2.3. (Z)-3-(Tributylstannyl)-5-methoxylpent-3-en-1-yne (**3c**)*

IR (film): ν (cm^{-1}) 3314, 2957, 2929, 2066, 1713, 1590, 1456, 1124; ^1H NMR ($CDCl_3$): δ 6.88 (t, J = 5.6 Hz, $^3J_{Sn-H}$ = 102 Hz, 1H), 3.95 (d, J = 5.6 Hz, 2H), 3.33 (s, 3H), 3.22 (s, 1H), 1.58–1.48 (m, 6H), 1.37–1.27 (m, 6H), 1.02 (t, J = 8.0 Hz, 6H), 0.92–0.88 (m, 9H); ^{13}C NMR ($CDCl_3$): δ 149.4, 126.8, 87.6, 80.6, 73.6, 58.2, 28.9, 27.3, 13.7, 11.4; MS: m/z 386 (M^+, 4.1), 329 (65), 291 (39), 235 (64), 177 (100); Anal. Calc. for $C_{18}H_{34}OSn$: C, 56.13; H, 8.90. Found: C, 56.37; H, 9.12%.

*3.2.4. (Z)-3-(Tributylstannyl)dec-3-en-1-yne (**3d**)*

IR (film): ν (cm^{-1}) 3314, 2958, 2928, 2071, 1713, 1586, 1464; ^1H NMR ($CDCl_3$): δ 6.82 (t, J = 7.6 Hz, $^3J_{Sn-H}$ = 108 Hz, 1H), 3.07 (s, 1H), 2.11–2.02 (m, 2H), 1.56–1.48 (m, 6H), 1.37–1.28 (m, 14H), 1.05–0.87 (m, 18H); ^{13}C NMR ($CDCl_3$): δ 155.5, 122.6, 88.2, 77.7, 35.7, 31.8, 29.5, 29.1, 29.0, 27.3, 22.6, 14.1, 13.7, 10.8; MS: m/z 426 (M^+, 1.4), 369 (40), 363 (100), 291 (32), 177 (34); Anal. Calc. for $C_{22}H_{42}Sn$: C, 62.13; H, 9.95. Found: C, 62.29; H, 10.22%.

*3.3. General procedure for the synthesis of (1E,3Z)-1-halo-3-(tributylstannyl)-substituted 1,3-dienes **5a–h***

A dry 10 ml round-bottomed flask was charged with $Cp_2Zr(H)Cl$ (1.05 mmol) under Ar. THF (4 ml) was injected, followed by addition of (*Z*)-3-(tributylstannyl)alk-3-en-1-yne **3** (1 mmol). The mixture was stirred for 40 min at room temperature to yield a clear solution. It was then added dropwise a solution of iodine or NBS (1 mmol) in THF (2 ml) at 0 °C over 15 min and stirred at room temperature for 1 h. The mixture was diluted with diethyl ether (30 ml) and the mixture was filtered through a short plug of silica gel and concentrated to give a residue. The residue was purified by preparative TLC on silica gel eluting with light petroleum ether (bp 30–60 °C).

*3.3.1. (1E,3Z)-1-Bromo-3-(tributylstannyl)-1,3-octadiene **5a***

IR (film): ν (cm^{-1}) 2957, 2925, 1577, 1464, 960; ^1H NMR ($CDCl_3$): δ 6.84 (d, J = 13.6 Hz, 1H), 6.27 (t, J = 7.2 Hz, $^3J_{Sn-H}$ = 108 Hz, 1H), 6.02 (d, J = 13.6 Hz, 1H), 2.07–1.98 (m, 2H), 1.51–1.24 (m, 16H), 0.99–0.85 (m, 18H); ^{13}C NMR ($CDCl_3$): δ 147.0, 145.3, 139.3, 103.2, 34.3, 32.0, 29.1, 27.3, 22.6, 14.1, 13.7, 11.0; MS: m/z 479 (M^+, 1.6), 422 (65), 291 (43), 57 (100); Anal. Calc. for $C_{20}H_{39}BrSn$: C, 50.23; H, 8.22. Found: C, 50.39; H, 8.41%.

*3.3.2. (1E,3Z)-1-Bromo-3-(tributylstannyl)-4-phenyl-1,3-butadiene **5b***

IR (film): ν (cm^{-1}) 2957, 2918, 1708, 1560, 1489, 1455, 961, 770, 698; ^1H NMR ($CDCl_3$): δ 7.41 (s, $^3J_{Sn-H}$ = 108 Hz, 1H), 7.32–7.19 (m, 5H), 7.03 (d, J = 13.6 Hz, 1H), 6.21 (d, J = 13.6 Hz, 1H), 1.38–1.16 (m, 12H), 0.92–0.83 (m, 15H); ^{13}C NMR ($CDCl_3$): δ 145.2, 144.4, 143.9, 140.2, 128.2, 128.0, 127.6, 105.2, 28.9, 27.2, 13.7, 11.5; MS: m/z 499 (M^+, 1.3), 442 (75), 291 (54), 177 (100), 77 (52); Anal. Calc. for $C_{22}H_{35}BrSn$: C, 53.04; H, 7.08. Found: C, 53.23; H, 7.32%.

*3.3.3. (1E,3Z)-1-Bromo-3-(tributylstannyl)-5-methoxy-1,3-pentadiene **5c***

IR (film): ν (cm^{-1}) 2957, 2922, 1715, 1573, 1456, 1124, 960; ^1H NMR ($CDCl_3$): δ 6.87 (d, J = 13.6 Hz, 1H), 6.36 (t, J = 6.0 Hz, $^3J_{Sn-H}$ = 108 Hz, 1H), 6.11 (d, J = 13.6 Hz, 1H), 3.90 (d, J = 6.0 Hz, 2H), 3.33 (s, 3H), 1.52–1.41 (m, 6H), 1.38–1.25 (m, 6H), 1.04–0.85 (m, 15H); ^{13}C NMR ($CDCl_3$): δ 144.4, 143.6, 140.5, 104.7, 73.3, 58.2, 29.1, 27.3, 13.7, 11.4; MS: m/z 467 (M^+, 2.3), 410 (63), 291 (47), 45 (100); Anal. Calc. for $C_{18}H_{35}OBrSn$: C, 46.38; H, 7.57. Found: C, 46.11; H, 7.72%.

*3.3.4. (1E,3Z)-1-Bromo-3-(tributylstannyl)-1,3-decadiene **5d***

IR (film): ν (cm^{-1}) 2919, 1683, 1576, 1464, 960, 737; ^1H NMR ($CDCl_3$): δ 6.85 (d, J = 13.6 Hz, 1H), 6.27 (t, J = 7.2 Hz, $^3J_{Sn-H}$ = 108 Hz, 1H), 6.02 (d, J = 13.6 Hz, 1H), 2.07–1.98 (m, 2H), 1.60–1.24 (m, 20H), 0.97–0.82 (m, 18H); ^{13}C NMR ($CDCl_3$): δ 147.0, 145.3, 139.3, 103.2, 34.6, 31.8, 29.8, 29.1, 29.0, 27.3, 22.6, 14.1, 13.7, 11.0; MS: m/z 507 (M^+, 1.2), 450 (78), 291 (39), 177 (100), 57 (56); Anal. Calc. for $C_{22}H_{43}BrSn$: C, 52.19; H, 8.56. Found: C, 52.41; H, 8.72%.

*3.3.5. (1E,3Z)-1-Iodo-3-(tributylstannyl)-1,3-octadiene **5e***

IR (film): ν (cm^{-1}) 2959, 2927, 1682, 1567, 1463, 962; ^1H NMR ($CDCl_3$): δ 6.70 (d, J = 13.6 Hz, 1H), 6.61 (d, J = 13.6 Hz, 1H), 5.92 (t, J = 7.2 Hz, $^3J_{Sn-H}$ = 108 Hz, 1H), 2.30–2.21 (m, 2H), 1.62–1.25 (m, 22H), 0.95–0.87 (m, 12H); ^{13}C NMR ($CDCl_3$): δ 146.2, 142.4, 105.4, 83.8, 35.9, 30.2, 29.2, 26.6, 22.3, 13.9, 13.6, 11.4; MS: m/z 469 (M^+-Bu, 38), 291 (47), 57 (100); Anal. Calc. for $C_{20}H_{39}SnI$: C, 45.74; H, 7.49. Found: C, 45.58; H, 7.26%.

*3.3.6. (1E,3Z)-1-Iodo-3-(tributylstannyl)-4-phenyl-1,3-butadiene **5f***

IR (film): ν (cm^{-1}) 2957, 2921, 1566, 1492, 1463, 967, 759, 690; ^1H NMR ($CDCl_3$): δ 7.61–7.56 (m, 2H), 7.40–7.32 (m, 3H), 7.05 (s, $^3J_{Sn-H}$ = 108 Hz, 1H), 6.92 (d, J = 13.6 Hz, 1H), 6.85 (d, J = 13.6 Hz, 1H), 1.68–1.59 (m, 6H), 1.45–1.26 (m, 12H), 0.95–0.92 (m, 9H); ^{13}C NMR ($CDCl_3$): δ 149.1, 143.7, 129.1, 128.5, 128.3, 128.2, 102.6, 86.7, 29.1, 26.7, 13.6, 11.3; MS: m/z 489 (M^+-Bu, 63), 291 (43), 177 (100), 77 (61); Anal. Calc. for $C_{22}H_{35}SnI$: C, 48.47; H, 6.47. Found: C, 48.20; H, 6.60%.

*3.3.7. (1E,3Z)-1-Iodo-3-(tributylstannyl)-5-methoxy-1,3-pentadiene **5g***

IR (film): ν (cm^{-1}) 2919, 2850, 1589, 1456, 1123, 961; ^1H NMR ($CDCl_3$): δ 7.18 (d, J = 13.6 Hz, 1H), 6.36 (t, J = 5.4 Hz, $^3J_{Sn-H}$ = 108 Hz, 1H), 6.10 (d, J = 13.6 Hz, 1H), 3.89 (d, J = 5.4 Hz, 2H), 3.33 (s, 3H), 1.54–1.41 (m, 6H), 1.39–1.26 (m, 6H), 1.05–0.85 (m, 15H); ^{13}C NMR ($CDCl_3$): δ 152.2, 146.3, 140.5, 75.2, 73.2, 58.2, 29.1, 27.4, 13.7, 11.2; MS: m/z 514 (M^+, 1.4), 457 (67), 291 (36), 45 (100); Anal. Calc. for $C_{18}H_{35}OSnI$: C, 42.14; H, 6.88. Found: C, 42.39; H, 6.97%.

*3.3.8. (1E,3Z)-1-Iodo-3-(tributylstannyl)-1,3-decadiene **5h***

IR (film): ν (cm^{-1}) 2955, 2926, 1683, 1464, 961; ^1H NMR ($CDCl_3$): δ 6.70 (d, J = 13.6 Hz, 1H), 6.60 (d, J = 13.6 Hz, 1H), 5.93 (t, J = 7.2 Hz, $^3J_{Sn-H}$ = 108 Hz, 1H), 2.26–2.20 (m, 2H), 1.59–1.21 (m, 26H), 0.95–0.82 (m, 12H); ^{13}C NMR ($CDCl_3$): δ 146.1, 142.5, 105.5, 83.9, 36.2, 31.7, 29.8, 29.4, 28.9, 27.5, 22.6, 14.1, 13.8, 11.2; MS: m/z 497 (M^+-Bu, 43), 291 (33), 177 (100), 57 (62); Anal. Calc. for $C_{22}H_{43}SnI$: C, 47.77; H, 7.84. Found: C, 47.51; H, 7.62%.

*3.4. Synthesis of 1,3-dienylstannanes **6a–b***

To a mixture of (1*E*,3*Z*)-1-bromo-3-(tributylstannyl)-1,3-octadiene **5a** (1 mmol) and $NiCl_2$(dppe) (0.03 mmol) in THF (2 ml) was added a solution of RMgBr (1.5 mmol) in THF (3 ml) under Ar at 0 °C with stirring. The resulting mixture was slowly brought to room temperature and stirred for 2 h. The mixture was treated with sat. NH_4Cl aq. solution (15 ml) at 0 °C and extracted with diethyl ether (2 × 30 ml). The ethereal solution was washed with water (2 × 20 ml) and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave an oil, which was purified by preparative TLC on silica gel eluting with light petroleum ether (bp 30–60 °C). Compound **6a**: oil. IR (film): ν (cm^{-1}) 3024, 2925, 2872, 1589, 1464, 1378, 961; ^1H NMR ($CDCl_3$): δ 6.25–6.19 (m, 2H),

5.46 (dt, J = 15.4, 7.2 Hz, 1H), 2.09–1.95 (m, 4H), 1.51–0.82 (m, 41H); MS: m/z 456 (M^+, 1.2), 399 (46), 291 (43), 287 (33), 177 (100), 57 (72). Anal. Calc. for $C_{24}H_{48}Sn$: C, 63.31; H, 10.63. Found: C, 63.53; H, 10.88%. Compound **6b**: oil. IR (film): ν (cm^{-1}) 3060, 3025, 2927, 2872, 1620, 1598, 1578, 1490, 1376, 957, 747, 690; ^1H NMR ($CDCl_3$): δ 7.47–7.22 (m, 5H), 6.95 (d, J = 16.0 Hz, 1H), 6.46 (t, J = 7.2 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 2.21–2.14 (m, 2H), 1.54–0.85 (m, 34H); MS: m/z 476 (M^+, 1.5), 419 (27), 362 (41), 291 (38), 177 (56), 77 (81), 57 (100). Anal. Calc. for $C_{26}H_{44}Sn$: C, 65.70; H, 9.33. Found: C, 65.48; H, 9.40%.

3.5. Synthesis of 1,3-diene **7**

1,3-Dienylstannnane **6a** (1.0 mmol) and diphenyliodonium chloride (1.0 mmol) were dissolved in DMF (10 ml) under Ar at room temperature. $Pd(PPh_3)_4$ (0.05 mmol) and CuI (0.75 mmol) were then added. The mixture was stirred for 24 h at room temperature and monitored by TLC (SiO_2) for the disappearance of the starting 1,3-dienylstannane **6a**. The reaction mixture was diluted with diethyl ether (30 ml), filtered and then treated with 20% aqueous KF (10 ml) for 30 min before being dried and concentrated. The residue was purified by column chromatography on silica gel (eluent: light petroleum ether). Oil. IR (film): ν (cm^{-1}) 3058, 3023, 2958, 2872, 1600, 1575, 1494, 1466, 1379, 983, 703; ^1H NMR ($CDCl_3$): δ 7.37–7.27 (m, 3H), 7.11–7.09 (m, 2H), 6.23 (d, J = 15.6 Hz, 1H), 5.58 (t, J = 7.6 Hz, 1H), 5.11 (dt, J = 15.6, 7.6 Hz, 1H), 2.05–2.00 (m, 2H), 1.92–1.86 (m, 2H), 1.36–1.20 (m, 8H), 0.86 (t, J = 6.8 Hz, 3H), 0.80 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 141.1, 139.0, 134.2, 131.6, 131.3, 129.5, 127.9, 126.5, 32.5, 32.1, 31.6, 28.7, 22.3, 22.2, 14.0, 13.9; MS: m/z 242 (M^+, 1.8), 159 (18), 105 (100), 77 (52). Anal. Calc. for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 88.97; H, 10.65%.

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