Synthetic Communications®, 39: 2378–2391, 2009

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910802654864

Taylor & Francis
Taylor & Francis Group

Stereoselective Synthesis of Difunctionalized 1,3-Dienes Containing Silicon and Selenium via Hydrozirconation of (*Z*)-3-(Trimethylsilyl)alk-3-en-1-ynes

Xinglin Ye,[1,2] Pingping Wang,[2] Jiaqin Liu,[1] and Mingzhong Cai[1]
[1]Department of Chemistry, Jiangxi Normal University, Nanchang, China
[2]Department of Chemistry, Jiujiang University, Jiujiang, China

Abstract: Sonogashira coupling of (*E*)-α-iodovinylsilanes **1** with (trimethylsilyl)-acetylene gave (*Z*)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes **2**, which underwent a desilylation reaction to afford (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes **3** in good yields. (1*E*,3*Z*)-1-Arylseleno-3-(trimethylsilyl)-substituted 1,3-dienes **5** could be synthesized stereoselectively via hydrozirconation of (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes **3**, followed by trapping with arylselenenyl bromides.

Keywords: Difunctionalized 1,3-diene, hydrozirconation, (*E*)-α-iodovinylsilane, Sonogashira coupling, stereoselective synthesis

INTRODUCTION

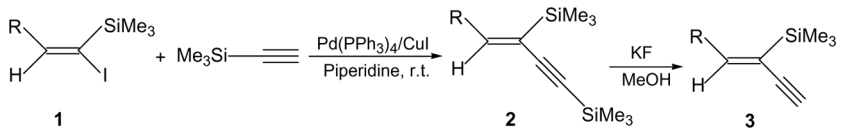
The stereocontrolled synthesis of 1,3-dienes containing metal or heteroatom functional groups is of considerable interest in organic synthesis because many useful functional group transformations can be achieved by introduction and removal of metal or heteroatom functions. The stereoselective synthesis of 1,3-dienyl sulfides,[1] 1,3-dienyl selenides,[2] 1,3-dienylsilanes,[3] and 1,3-dienylstannanes[4] has already been described in the literature. Recently, the synthesis of difunctionalized 1,3-dienes has

Received September 30, 2008.
Address correspondence to Mingzhong Cai, Department of Chemistry, Jiangxi Normal University, Nanchang 330022, China. E-mail: caimzhong@163.com

also attracted great interest in organic synthesis because such dienes may find use as synthetic building blocks.[5] In addition, difunctionalized 1,3-dienes containing heteroatoms can control both regio- and stereoselectivity and play a very important role in cycloadditions.[6] Su and coworkers 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.[7] Coleman and Walczak reported the stereoselective synthesis of (*E,E*)-1-tributylstannyl-4-boryl-buta-1,3-diene and its use as an orthogonal Stille and Suzuki–Miyaura coupling partner.[8] Very recently, we 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.[9] However, to the best of our knowledge, no well-established method was used to prepare stereoselectively the silicon/selenium 1,3-bis-metallo-1,3-dienes. Herein, we report that (1*E*,3*Z*)-1-arylseleno-3-(trimethylsilyl)-substituted 1,3-dienes could be conveniently synthesized via hydrozirconation of (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes, followed by trapping with arylselenenyl bromides.

RESULTS AND DISCUSSION

There has been a lively interest in terminal conjugated enynes, alk-3-en-1-ynes, because of their 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,[10] dactylyne,[11] quinolizidine,[12] and histrionicotoxin.[13] 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.[14] Our methodology involves the preparation and the reactions of the building block (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes **3**, which can be conveniently obtained according to Scheme 1.



Scheme 1. Synthesis of (*Z*)-3-(trimethylsilyl)alk-3-en-l-ynes.

Sonogashira coupling of alkenyl halides with terminal alkynes provides a simple and general route for the synthesis of conjugated enynes.[15] We observed that when the coupling reactions of (*E*)-α-iodovinylsilanes **1** with (trimethylsilyl)acetylene were performed in piperidine at room temperature using $Pd(PPh_3)_4$ and CuI as cocatalyst, fairly rapid reactions occurred, affording stereoselectively the desired (*Z*)-1,3-bis (trimethylsilyl)alk-3-en-1-ynes **2** in good yields. The typical results are summarized in Table 1. Kusumoto et al.[16] reported that the desilylation reaction of (*E*)-1,2,4-tri(trimethylsilyl)but-1-en-3-yne with KF in methanol afforded (*E*)-1,2-bis(trimethyl-silyl)but-1-en-3-yne; the desilylation reaction occurred selectively at acetylenic carbon atom. We investigated the desilylation reaction of (*Z*)-1,3-bis(trimethylsilyl)-alk-3-en-1-ynes **2** with KF in methanol to prepare (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes **3**. We found that the desilylation reaction of (*Z*)-1,3-bis(trimethylsilyl)-alk-3-en-1-ynes **2** with KF proceeded smoothly in methanol at 70°C to give the desired (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes **3** in good yields. The typical results are also summarized in Table 1.

Hydrozirconation has emerged as a unique hydrometallation with some attractive features such as the good regioselectivity and stereoselectivity observed with alkynes[17] and heteroatom-substituted alkynes.[18] However, the hydrozirconation of terminal conjugated enynes has received less attention.[19] With a convenient route to (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes **3**, we decided to establish the feasibility

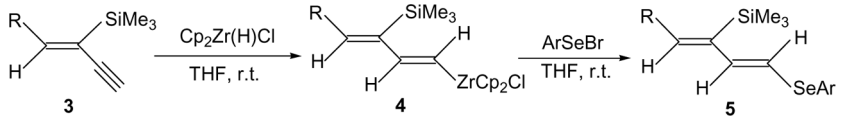
Table 1. Coupling reaction of **1** with (trimethylsilyl)acetylene[a] and desilylation of **2**[b]

Entry	R	Product	Yield (%)[c]
1	*n*-Bu	**2a**	92
2	Ph	**2b**	90
3	CH_3OCH_2	**2c**	88
4	*n*-C_6H_{13}	**2d**	91
5	*n*-Bu	**3a**	88
6	Ph	**3b**	87
7	CH_3OCH_2	**3c**	85
8	*n*-C_6H_{13}	**3d**	89

[a]The reaction of **1** (2 mmol) with (trimethylsilyl)acetylene (3 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.



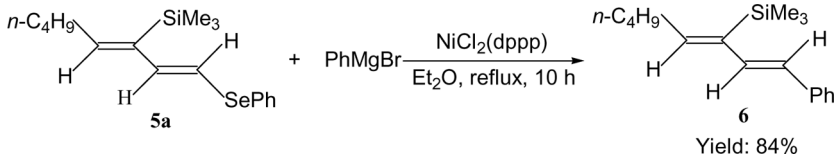
Scheme 2. Synthesis of (1*E*,3*Z*)-1-arylseleno-3-(trimethylsilyl)-substituted 1,3-dienes.

of using **3** in a hydrozirconation reaction with $Cp_2Zr(H)Cl$. We observed that when the hydrozirconation of **3** with $Cp_2Zr(H)Cl$ was performed in tetrahydrofuran (THF) at room temperature, fairly rapid reactions occurred, affording stereoselectively (1*E*,3*Z*)-3-(trimethylsilyl)-substituted 1,3-dienylzirconium(IV) complexes **4**. The intermediates **4** were then trapped with arylselenenyl bromides to give stereoselectively (1*E*,3*Z*)-1-arylseleno-3-(trimethylsilyl)-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-arylseleno-3-(trimethylsilyl)-substituted 1,3-dienes **5** could be synthesized stereoselectively via hydrozirconation of (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes **3**, followed by trapping with arylselenenyl bromides. The (1*E*)-configuration of compounds **5** has been proved by their ^1H NMR spectra, which show two doublets at $\delta = 6.53$–7.02 with a coupling constant of 15.6–16.0 Hz, and this also indicates that hydrozirconation of (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes **3** with $Cp_2Zr(H)Cl$ occurs highly regio- and stereoselectively, affording intermediates **4**. In addition, the (3*Z*)-configuration of compound **5a** was confirmed by nuclear Overhauser effect spectroscopy (NOESY) experiments. An enhancement of the allylic protons was

Table 2. Synthesis of (1*E*,3*Z*)-1-arylseleno-3-(trimethylsilyl)-substituted 1,3-dienes **5a–j**

Entry	R	Ar	Product	Yield[a] (%)
1	*n*-C_4H_9	Ph	**5a**	80
2	*n*-C_4H_9	4-ClC_6H_4	**5b**	76
3	*n*-C_4H_9	4-$CH_3C_6H_4$	**5c**	81
4	Ph	Ph	**5d**	80
5	Ph	4-ClC_6H_4	**5e**	83
6	Ph	4-$CH_3C_6H_4$	**5f**	75
7	*n*-C_6H_{13}	Ph	**5g**	74
8	*n*-C_6H_{13}	4-ClC_6H_4	**5h**	81
9	*n*-C_6H_{13}	4-$CH_3C_6H_4$	**5i**	84
10	CH_3OCH_2	Ph	**5j**	67

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



Scheme 3. Synthesis of (1*E*,3*Z*)-phenyl-3-(trimethylsilyl)-1,3-octadiene.

observed as the vinylic proton ($\delta = 5.82$ ppm) of **5a** was irradiated. There was a correlation between the allylic protons and the methyl protons of the trimethylsilyl. A correlation between the vinylic proton ($\delta = 5.82$ ppm) and one other vinylic proton ($\delta = 6.58$ ppm) was also observed. The NOE results indicate that **5a** has the expected (1*E*,3*Z*)-configuration.

We have also carried out the Ni-catalyzed cross-coupling reaction of compound **5a** with phenylmagnesium bromide in diethyl ether to afford the selenium-free (1*Z*,3*E*)-2-(trimethylsilyl)-substituted 1,3-diene **6** in 84% yield (Scheme 3).

EXPERIMENTAL

General

^{1}H NMR spectra were recorded on a Bruker AC-P400 (400-MHz) spectrometer with tetramethylsilane (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. Infrared (IR) spectra were determined on an FTS-185 instrument as neat films. Mass spectra (MS) were obtained on a Finnigan 8239 mass spectrometer. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer. All reactions were carried out in predried 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-Iodovinylsilanes **1** were prepared from alkynylsilanes according to the literature procedure.[20]

General Procedure for the Synthesis of (*Z*)-1,3-Bis(trimethylsilyl)alk-3-en-1-ynes 2a–d

(*E*)-α-Iodovinylsilane **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. (Trimethylsilyl)acetylene (3.0 mmol) was added to this solution, 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).

Data

(*Z*)-1,3-Bis(trimethylsilyl)oct-3-en-1-yne (**2a**)

Oil. IR (film): ν (cm^{-1}) 2959, 2928, 2120, 1719, 1581, 1406, 1249, 841, 759; ^1H NMR ($CDCl_3$): δ 6.71 (t, $J = 7.6$ Hz, 1H), 2.22–2.14 (m, 2H), 1.39–1.28 (m, 4H), 0.90 (t, $J = 7.2$ Hz, 3H), 0.22 (s, 9H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 156.0, 123.2, 109.0, 93.7, 32.3, 31.5, 22.5, 14.0, 0.2, −0.2; MS: m/z 252 (M^+, 18), 73 (100), 57 (43). Anal. calc. for $C_{14}H_{28}Si_2$: C, 66.58; H, 11.18. Found: C, 66.29; H, 11.02%.

(*Z*)-1,3-Bis(trimethylsilyl)-4-phenylbut-3-en-1-yne (**2b**)

Oil. IR (film): ν (cm^{-1}) 3058, 3026, 2959, 2898, 2118, 1717, 1557, 1490, 1407, 1250, 840, 759, 698; ^1H NMR ($CDCl_3$): δ 7.76 (s, 1H), 7.31–7.21 (m, 5H), 0.22 (s, 9H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 152.4, 138.6, 128.4, 127.9, 127.0, 125.2, 109.3, 96.9, 0.2, −0.1; MS: m/z 272 (M^+, 13), 91 (80), 78 (100), 77 (57), 73 (41). Anal. calc. for $C_{16}H_{24}Si_2$: C, 70.51; H, 8.88. Found: C, 70.23; H, 8.62%.

(*Z*)-1,3-Bis(trimethylsilyl)-5-methoxylpent-3-en-1-yne (**2c**)

Oil. IR (film): ν (cm^{-1}) 2960, 2154, 1716, 1683, 1251, 1124, 844; ^1H NMR ($CDCl_3$): δ 6.72 (t, $J = 6.4$ Hz, 1H), 4.03 (d, $J = 6.4$ Hz, 2H), 3.33 (s, 3H), 0.22 (s, 9H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 150.2, 127.4, 107.8, 96.6, 71.1, 58.1, 0.1, −0.2; MS: m/z 240 (M^+, 11), 73 (100), 45 (56). Anal. calc. for $C_{12}H_{24}OSi_2$: C, 59.93; H, 10.06. Found: C, 59.69; H, 9.92%.

(*Z*)-1,3-Bis(trimethylsilyl)dec-3-en-1-yne (**2d**)

Oil. IR (film): ν (cm^{-1}) 2959, 2930, 2121, 1712, 1580, 1456, 1406, 1249, 842, 759; ^1H NMR ($CDCl_3$): δ 6.71 (t, $J = 7.6$ Hz, 1H), 2.20–2.14

(m, 2H), 1.38–1.22 (m, 8H), 0.88 (t, $J = 6.8$ Hz, 3H), 0.22 (s, 9H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 156.0, 123.2, 109.1, 93.7, 32.6, 31.7, 29.3, 29.1, 22.6, 14.1, 0.2, −0.2; MS: m/z 280 (M^+, 21), 73 (100), 57 (54), 43 (39). Anal. calc. for $C_{16}H_{32}Si_2$: C, 68.49; H, 11.50. Found: C, 68.21; H, 11.32%.

General Procedure for the Synthesis of (*Z*)-3-(Trimethylsilyl)alk-3-en-1-ynes 3a–d

A mixture of (Z)-1,3-bis(trimethylsilyl)alk-3-en-1-yne (1 mmol) and 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).

Data

(*Z*)-3-(Trimethylsilyl)oct-3-en-1-yne (**3a**)

Oil. IR (film): ν (cm^{-1}) 3315, 2959, 2931, 2075, 1721, 1582, 1408, 1250, 843, 759; ^{1}H NMR ($CDCl_3$): δ 6.75 (t, $J = 7.6$ Hz, 1H), 2.93 (s, 1H), 2.22–2.16 (m, 2H), 1.38–1.29 (m, 4H), 0.90 (t, $J = 7.2$ Hz, 3H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 157.0, 122.0, 87.3, 76.7, 32.2, 31.5, 22.4, 14.0, −0.2; MS: m/z 180 (M^+, 24), 165 (100), 73 (86), 57 (65). Anal. calc. for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.39; H, 11.25%.

(*Z*)-3-(Trimethylsilyl)-4-phenylbut-3-en-1-yne (**3b**)

Oil. IR (film): ν (cm^{-1}) 3307, 3062, 2957, 2070, 1706, 1562, 1490, 1406, 1250, 841, 755, 698; ^{1}H NMR ($CDCl_3$): δ 7.79 (s, 1H), 7.31–7.21 (m, 5H), 3.13 (s, 1H), 0.07 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 153.5, 138.5, 128.4, 128.0, 127.9, 126.1, 87.6, 79.4, −0.1; MS: m/z 200 (M^+, 27), 185 (100), 73 (58). Anal. calc. for $C_{13}H_{16}Si$: C, 77.93; H, 8.05. Found: C, 77.70; H, 8.12%.

(*Z*)-3-(Trimethylsilyl)-5-methoxylpent-3-en-1-yne (**3c**)

Oil. IR (film): ν (cm^{-1}) 3305, 2960, 2064, 1250, 1128, 843; ^{1}H NMR ($CDCl_3$): δ 6.30 (t, $J = 6.4$ Hz, 1H), 4.24 (d, $J = 6.4$ Hz, 2H), 3.37

(s, 3H), 2.97 (s, 1H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 148.5, 144.0, 86.8, 76.6, 72.1, 58.0, −0.1; MS: m/z 168 (M^+, 21), 153 (83), 73 (100), 45 (48). Anal. calc. for $C_9H_{16}OSi$: C, 64.22; H, 9.58. Found: C, 64.39; H, 9.62%.

(*Z*)-3-(Trimethylsilyl)dec-3-en-1-yne (**3d**)

Oil. IR (film): ν (cm^{-1}) 3315, 2958, 2928, 2078, 1715, 1581, 1456, 1407, 1250, 843, 759; ^{1}H NMR ($CDCl_3$): δ 6.73 (t, $J = 7.6$ Hz, 1H), 2.90 (s, 1H), 2.22–2.15 (m, 2H), 1.38–1.21 (m, 8H), 0.87 (t, $J = 6.8$ Hz, 3H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 157.1, 121.9, 87.3, 76.7, 32.6, 31.7, 29.3, 29.0, 22.6, 14.1, −0.2; MS: m/z 208 (M^+, 31), 193 (100), 73 (69), 57 (46), 43 (52). Anal. calc. for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 74.68; H, 11.39%.

General Procedure for the Synthesis of (1*E*,3*Z*)-1-Arylseleno-3-(trimethylsilyl)-substituted 1,3-dienes 5a–j

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-(trimethylsilyl)alk-3-en-1-yne **3** (1 mmol). The mixture was stirred for 40 min at room temperature to yield a clear solution. A solution of ArSeBr (1.05 mmol) in THF (3 mL) was then added, 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 thin-layer chromatography (TLC) on silica gel, eluting with light petroleum ether (bp 30–60°C).

Data

(1*E*,3*Z*)-1-Phenylseleno-3-(trimethylsilyl)-1,3-octadiene (**5a**)

Oil. IR (film): ν (cm^{-1}) 3072, 2956, 2927, 1712, 1579, 1477, 1249, 951, 837, 734; ^{1}H NMR ($CDCl_3$): δ 7.47–7.25 (m, 5H), 6.96 (d, $J = 16$ Hz, 1H), 6.58 (d, $J = 16$ Hz, 1H), 5.82 (t, $J = 7.2$ Hz, 1H), 2.22–2.15 (m, 2H), 1.39–1.24 (m, 4H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.15 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 143.6, 138.0, 136.8, 131.5, 131.3, 129.3, 126.8, 118.9, 31.6, 28.9, 22.5, 14.1, −0.5; MS: m/z 338 (M^+, 94), 323 (77), 157 (51), 73 (100), 59 (62). Anal. calc. for $C_{17}H_{26}SiSe$: C, 60.50; H, 7.77. Found: C, 60.29; H, 7.55%.

(1*E*,3*Z*)-1-(4-Chlorophenylseleno)-3-(trimethylsilyl)-1,3-octadiene (**5b**)

Oil. IR (film): ν (cm^{-1}) 2956, 2926, 1711, 1558, 1474, 1249, 952, 837, 812; ^1H NMR ($CDCl_3$): δ 7.38 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 8.0$ Hz, 2H), 6.97 (d, $J = 16$ Hz, 1H), 6.53 (d, $J = 16$ Hz, 1H), 5.84 (t, $J = 7.2$ Hz, 1H), 2.20–2.16 (m, 2H), 1.39–1.25 (m, 4H), 0.90 (t, $J = 7.2$ Hz, 3H), 0.15 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 144.1, 137.9, 137.6, 133.0, 132.7, 129.6, 129.4, 118.3, 31.6, 29.0, 22.5, 14.1, −0.5; MS: m/z 374 (M^+, 23, ^{37}Cl), 372 (M^+, 61, ^{35}Cl), 357 (37), 191 (48), 73 (100), 59 (49). Anal. calc. for $C_{17}H_{25}SiSeCl$: C, 54.89; H, 6.77. Found: C, 54.62; H, 6.51%.

(1*E*,3*Z*)-1-(4-Methylphenylseleno)-3-(trimethylsilyl)-1,3-octadiene (**5c**)

Oil. IR (film): ν (cm^{-1}) 2956, 2925, 1586, 1489, 1248, 949, 837, 801; ^1H NMR ($CDCl_3$): δ 7.37 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 6.90 (d, $J = 16$ Hz, 1H), 6.57 (d, $J = 16$ Hz, 1H), 5.80 (t, $J = 7.2$ Hz, 1H), 2.33 (s, 3H), 2.21–2.15 (m, 2H), 1.38–1.24 (m, 4H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.14 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 143.2, 138.0, 137.0, 135.7, 132.0, 130.1, 127.1, 119.8, 31.6, 28.9, 22.5, 21.1, 14.0, −0.5; MS: m/z 352 (M^+, 81), 337 (34), 172 (47), 143 (74), 91 (88), 73 (100), 59 (69). Anal. calc. for $C_{18}H_{28}SiSe$: C, 61.51; H, 8.03. Found: C, 61.62; H, 8.23%.

(1*E*,3*Z*)-1-Phenylseleno-3-(trimethylsilyl)-4-phenyl-1,3-butadiene (**5d**)

Oil. IR (film): ν (cm^{-1}) 2956, 1713, 1574, 1490, 1250, 961, 839, 734; ^1H NMR ($CDCl_3$): δ 7.47–7.23 (m, 10H), 7.02 (d, $J = 16$ Hz, 1H), 6.77 (s, 1H), 6.76 (d, $J = 16$ Hz, 1H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 140.5, 139.2, 137.7, 136.7, 132.3, 130.5, 129.4, 129.3, 128.1, 127.2, 127.1, 121.1, −0.4; MS: m/z 358 (M^+, 9.4), 314 (84), 312 (77), 157 (100), 77 (67), 73 (78). Anal. calc. for $C_{19}H_{22}SiSe$: C, 63.84; H, 6.20. Found: C, 63.54; H, 6.25%.

(1*E*,3*Z*)-1-(4-Chlorophenylseleno)-3-(trimethylsilyl)-4-phenyl-1,3-butadiene (**5e**)

Oil. IR (film): ν (cm^{-1}) 2956, 2854, 1716, 1573, 1490, 1250, 956, 838, 813, 696; ^1H NMR ($CDCl_3$): δ 7.39 (d, $J = 8.4$ Hz, 2H), 7.35–7.23 (m, 7H), 6.98 (d, $J = 16$ Hz, 1H), 6.79 (s, 1H), 6.70 (d, $J = 16$ Hz, 1H), 0.25 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 140.4, 139.6, 137.6, 137.3, 133.7, 133.5, 129.4, 129.3, 128.6, 128.1, 127.3, 120.4, −0.5; MS: m/z 394 (M^+, 25, ^{37}Cl), 392

(M^+, 64, ^{35}Cl), 377 (15), 204 (65), 185 (89), 128 (81), 73 (100). Anal. calc. for $C_{19}H_{21}SiSeCl$: C, 58.22; H, 5.40. Found: C, 58.34; H, 5.29%.

(1*E*,3*Z*)-1-(4-Methylphenylseleno)-3-(trimethylsilyl)-4-phenyl-1,3-butadiene (**5f**)

Oil. IR (film): ν (cm^{-1}) 2957, 2855, 1713, 1579, 1492, 1249, 957, 839, 816, 696; ^1H NMR ($CDCl_3$): δ 7.40 (d, $J = 8.0$ Hz, 2H), 7.30–7.23 (m, 7H), 6.96 (d, $J = 16$ Hz, 1H), 6.76 (d, $J = 16$ Hz, 1H), 6.75 (s, 1H), 2.35 (s, 1H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 140.5, 138.7, 137.7, 137.3, 135.6, 133.0, 132.9, 130.1, 129.4, 128.1, 127.1, 121.9, 21.1, −0.4; MS: m/z 372 (M^+, 21), 357 (15), 171 (56), 91 (79), 73 (100). Anal. calc. for $C_{20}H_{24}SiSe$: C, 64.66; H, 6.51. Found: C, 64.37; H, 6.39%.

(1*E*,3*Z*)-1-Phenylseleno-3-(trimethylsilyl)-1,3-decadiene (**5g**)

Oil. IR (film): ν (cm^{-1}) 3058, 2925, 2855, 1713, 1683, 1576, 1476, 1249, 953, 839, 735; ^1H NMR ($CDCl_3$): δ 7.49–7.25 (m, 5H), 6.96 (d, $J = 15.6$ Hz, Hz, 1H), 6.60 (d, $J = 15.6$ Hz, 1H), 5.83 (t, $J = 7.2$ Hz, 1H), 2.20–2.16 (m, 2H), 1.39–1.26 (m, 8H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.16 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 143.7, 138.1, 136.8, 131.5, 131.3, 129.2, 126.8, 118.9, 31.7, 29.4, 29.2, 29.1, 22.6, 14.1, −0.5; MS: m/z 366 (M^+, 14), 351 (17), 157 (31), 73 (100), 59 (42). Anal. calc. for $C_{19}H_{30}SiSe$: C, 62.43; H, 8.27. Found: C, 62.19; H, 8.35%.

(1*E*,3*Z*)-1-(4-Chlorophenylseleno)-3-(trimethylsilyl)-1,3-decadiene (**5h**)

Oil. IR (film): ν (cm^{-1}) 2956, 2926, 2856, 1683, 1562, 1474, 1249, 954, 838, 813; ^1H NMR ($CDCl_3$): δ 7.38 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 6.96 (d, $J = 16$ Hz, 1H), 6.53 (d, $J = 16$ Hz, 1H), 5.85 (t, $J = 7.2$ Hz, 1H), 2.20–2.16 (m, 2H), 1.38–1.26 (m, 8H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.15 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 144.1, 137.9, 137.6, 133.0, 132.7, 129.6, 129.4, 118.3, 31.7, 29.4, 29.3, 29.1, 22.6, 14.1, −0.6; MS: m/z 402 (M^+, 14, ^{37}Cl), 400 (M^+, 43, ^{35}Cl), 385 (26), 191 (37), 73 (100), 59 (51). Anal. calc. for $C_{19}H_{29}SiSeCl$: C, 57.05; H, 7.31. Found: C, 56.82; H, 7.23%.

(1*E*,3*Z*)-1-(4-Methylphenylseleno)-3-(trimethylsilyl)-1,3-decadiene (**5i**)

Oil. IR (film): ν (cm^{-1}) 2956, 2926, 1682, 1562, 1489, 1456, 1249, 950, 839, 802; ^1H NMR ($CDCl_3$): δ 7.37 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H),

6.90 (d, $J = 15.6$ Hz, 1H), 6.56 (d, $J = 15.6$ Hz, 1H), 5.80 (t, $J = 7.2$ Hz, 1H), 2.33 (s, 3H), 2.20–2.14 (m, 2H), 1.38–1.26 (m, 8H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.14 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 143.2, 138.1, 136.9, 135.8, 132.0, 130.0, 127.1, 119.7, 31.7, 29.4, 29.2, 29.1, 22.6, 21.1, 14.1, −0.6; MS: m/z 380 (M^+, 31), 365 (28), 91 (76), 73 (100), 59 (57). Anal. calc. for $C_{20}H_{32}SiSe$: C, 63.29; H, 8.50. Found: C, 63.52; H, 8.43%.

(1*E*,3*Z*)-1-Phenylseleno-3-(trimethylsilyl)-5-methoxy-1,3-pentadiene (**5j**)

Oil. IR (film): ν (cm^{-1}) 3057, 2961, 1682, 1594, 1249, 1123, 954, 843, 734; ^{1}H NMR ($CDCl_3$): δ 7.48–7.24 (m, 5H), 6.94 (d, $J = 15.6$ Hz, 1H), 6.56 (d, $J = 15.6$ Hz, 1H), 6.45 (t, $J = 6.4$ Hz, 1H), 4.07 (d, $J = 6.4$ Hz, 2H), 3.38 (s, 3H), 0.24 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 149.8, 138.3, 136.9, 131.4, 131.1, 129.2, 127.6, 118.5, 71.2, 58.4, −0.1; MS: m/z 326 (M^+, 23), 311 (29), 157 (33), 73 (100), 45 (62). Anal. calc. for $C_{15}H_{22}OSiSe$: C, 55.36; H, 6.81. Found: C, 55.13; H, 6.65%.

Synthesis of (1*E*,3*Z*)-1-Phenyl-3-(trimethylsilyl)-1,3-octadiene 6

PhMgBr (2.5 mmol) in diethyl ether (4 mL) was added to a mixture of (1*E*,3*Z*)-1-phenylseleno-3-(trimethylsilyl)-1,3-octadiene **5a** (1 mmol) and $NiCl_2$(dppp) (0.03 mmol) in diethyl ether (8 mL) under Ar at room temperature with stirring. The resulting mixture was heated to reflux for 10 h. The mixture was treated with sat. NH_4Cl aq. solution (15 mL) at 0°C and extracted with diethyl ether (2×20 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). Oil. IR (film): ν (cm^{-1}) 3059, 3024, 2958, 1620, 1590, 1491, 1249, 962, 841, 745; ^{1}H NMR ($CDCl_3$): δ 7.46–7.18 (m, 5H), 6.84 (d, $J = 16.2$ Hz, 1H), 6.51 (d, $J = 16.2$ Hz, 1H), 6.41 (t, $J = 7.0$ Hz, 1H), 2.29–2.20 (m, 2H), 1.42–1.20 (m, 4H), 0.89 (t, $J = 7.2$ Hz, 3H), 0.16 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 145.4, 138.2, 134.9, 128.7, 128.5, 127.2, 126.6, 126.1, 32.2, 31.9, 22.5, 14.0, 0.6; MS: m/z 258 (M^+, 12), 243 (26), 77 (38), 73 (100), 57 (42). Anal. calc. for $C_{17}H_{26}Si$: C, 78.99; H, 10.14. Found: C, 78.73; H, 9.95%.

CONCLUSION

In conclusion, we have developed a highly stereoselective and general route to difunctionalized 1,3-dienes containing silicon and selenium by hydrozirconation of (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes, followed by

trapping with arylselenenyl bromides. The present method has the advantages of readily available starting materials, straightforward and simple procedures, mild reaction conditions, good stereoselectivity, and good yields. Investigations into the synthetic applications of compounds **5** are currently in progress.

ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China (Project No. 20462002) and the Natural Science Foundation of Jiangxi Province (Project No. 2007GZW0172) for financial support.

REFERENCES

1. (a) Naso, F. Stereospecific synthesis of olefins through sequential cross-coupling reactions. *Pure Appl. Chem.* **1988**, *60*, 79–88; (b) Pearson, W. H.; Lin, K.-C.; Poon, Y.-F. A stereoselective route to 2-(phenylthio)-1,3-butadienes. *J. Org. Chem.* **1989**, *54*, 5814–5819; (c) Grieco, P. A.; May, S. A.; Kaufman, M. D. A new strategy for the preparation of 11-oxygenated steroids synthesis of (±)adrenosterone. *Tetrahedron Lett.* **1998**, *39*, 7047–7050; (d) Cai, M.; Wang, D.; Wang, P. Novel stereoselective synthesis of 1-substituted 1,3-dien-2-yl sulfides via Stille coupling reactions of (*E*)-α-stannylvinyl sulfides with alkenyl iodides. *J. Organomet. Chem.* **2006**, *691*, 737–741.
2. (a) Camasseto, J. V.; Brandt, C. A. Selenium in organic synthesis: A novel route to 1-phenylselenobutadienes and 1,4-dicarbonyl compounds. *Synthesis* **1987**, 146–148; (b) Hevesi, L.; Hermans, B.; Allard, C. Nickel and palladium catalyzed coupling of vinyl selenides with trimethylsilylmethylmagnesium chloride: A new synthesis of allyl silanes. *Tetrahedron Lett.* **1994**, *35*, 6729–6730; (c) Zhu, L. S.; Huang, Z. Z.; Huang, X. Stereoselective synthesis of (*E,E*)-1-arylselenobutadienes by cross-coupling reactions in the presence of palladium catalyst. *Tetrahedron* **1996**, *52*, 9819–9822; (d) Ma, Y.; Huang, X. Novel stereoselective synthesis of 1,3-dienyl selenides by palladium–copper cocatalyzed cross coupling reaction of (*E*)-α-selanylvinylstannanes. *J. Chem. Soc., Perkin Trans.* **1997**, *1*, 2953–2955.
3. (a) Negishi, E.; Luo, F. T. A stereoselective route to 2-(phenylthio)-1,3- butadienes. *J. Org. Chem.* **1983**, *48*, 1560–1562; (b) Luh, T.-Y.; Wong, K.-T. Silyl-substituted conjugated dienes: Versatile building blocks in organic synthesis. *Synthesis* **1993**, 349–370; (c) Ni, Z.-J.; Yang, P.-F.; Ng, D. K. P.; Tzeng, Y.-L.; Luh, T.-Y. Transition metal promoted reaction, 34: Unified synthesis of vinylsilanes and silylated butadienes: Nickel-catalyzed olefination and silylolefination of dithioacetals. *J. Am. Chem. Soc.* **1990**, *112*, 9356–9364.
4. (a) Suzenet, F.; Blart, E.; Quintard, J. P. Regio- and stereoselective synthesis of polyenic vinyltinacetals: The unexpected effect of the nature of a remote acetal function on the regioselectivity of the stannylmetalation. *Synlett*

1998, 879–881; (b) Lipshutz, B. H.; Lindsley, C. A streamlined route to highly conjugated, *all-E* polyenes characteristic of oxo polyene macrolide antibiotics. *J. Am. Chem. Soc.* **1997**, *119*, 4555–4556; (c) Betzer, J. F.; Delaloge, F.; Muller, B.; Pancrazi, A. Radical hydrostannylation, Pd(0)-catalyzed hydrostannylation, stannylcupration of propargyl alcohols and enynols: Regio- and stereoselectivities. *J. Org. Chem.* **1997**, *62*, 7768–7780.

5. (a) Banert, K.; Fendel, W.; Schlott, J. Double functionalized dienes of 6 and 9 may find use as synthetic building blocks. *Angew. Chem. Int. Ed.* **1998**, *37*, 3289–3293; (b) Wang, C.; Song, Q.; Xi, Z. Reactions of 1,4-dilithiobutadienes with isothiocyanates: Preparation of iminocyclopentadiene derivatives via cleavage of the C=S double bond of a RN=C=S molecule. *Tetrahedron* **2004**, *60*, 5207–5214; (c) Banert, K.; Schlott, J. Stereospecific synthesis of 1,2-difunctionalized buta-1,3-dienes via tandem [3,3]-[3,3] sigmatropic rearrangements. *Tetrahedron* **2000**, *56*, 5413–5419; (d) Li, J.-H.; Liang, Y.; Xie, Y.-X. Mild and selective palladium-catalyzed dimerization of terminal alkynes to form symmetrical (Z,Z)-1,4-dihalo-1,3-dienes. *J. Org. Chem.* **2004**, *69*, 8125–8127; (e) Shimizu, M.; Kurahashi, T.; Hiyama, T. Novel synthesis of 2,3-bisboryl-1,3-dienes from 1-bromo-1-lithioethene and 1,1-bisborylalkenes. *Synlett* **2001**, 1006–1008; (f) Herndon, J. W.; Patel, P. P. Reaction of propargylsilanes with chromium carbene complexes: Synthesis of conjugated diene enol ethers through a tandem alkyne insertion-1,2-silicon shift process. *J. Org. Chem.* **1996**, *61*, 4500–4501; (g) Desurmont, G.; Dalton, S.; Giolando, D. M.; Srebnik, M. Sequential transformations of 1,3-dibora butadienes to enones or tetrasubstituted 1,3-butadienes. *J. Org. Chem.* **1996**, *61*, 7943–7946; (h) Lipshutz, B. H.; Lee, J. I. A one-pot, lynchpin approach to 1,4-disubstituted E,E-butadienes via multiple cyanocuprate-mediated transmetalations. *Tetrahedron Lett.* **1991**, *32*, 7211–7214; (i) Babudri, F.; Fiandanese, V.; Mazzone, L.; Naso, F. A general approach to conjugated (E,E)-dienes through sequential coupling reactions. *Tetrahedron Lett.* **1994**, *35*, 8847–8850.
6. (a) Trost, B. M.; Vladuchick, W. C.; Bridges, A. J. Sulfur as a regiochemical control element: Cycloadditions of 2-alkoxy(acyloxy)-3-alkyl(aryl)thiobuta-1,3-dienes. *J. Am. Chem. Soc.* **1980**, *102*, 3554–3572; (b) Padwa, A.; Norman, B. H. Intramolecular cycloaddition reaction of oximes with vinyl sulfones. *Tetrahedron Lett.* **1988**, *29*, 2417–2419; (c) Pegram, J. J.; Anderson, C. B. The synthesis of 1-benzyldimethylsilyl-4-phenylthio-1,3-butadiene: A new diene-regenerable Diels–Alder synthon. *Tetrahedron Lett.* **1988**, *29*, 6719–6720; (d) Padwa, A.; Harrison, B.; Norman, B. H. The uncatalyzed Diels–Alder reaction of imines with bis(phenylsulfonyl) substituted dienes. *Tetrahedron Lett.* **1989**, *30*, 3259–3262; (e) Aversa, M. C.; Barattucci, A.; Bonaccorsi, P.; Giannetto, P.; Jones, D. N. Synthesis and asymmetric Diels-Alder reactions of enantiopure 3-(alkylsulfinyl)-1-methoxy-1,3-butadienes. *J. Org. Chem.* **1997**, *62*, 4376–4384.
7. Su, M.; Kang, Y.; Yu, W.; Hua, Z.; Jin, Z. Negishi coupling between α-alkyl (aryl)thio vinyl zinc chloride and α-bromovinyl ether: A convergent synthesis of 2-alkoxy-3-alkyl(aryl)thiobuta-1,3-dienes. *Org. Lett.* **2002**, *4*, 691–694.
8. Coleman, R. S.; Walczak, M. C. Tandem Still/Suzuki coupling of a hetero-bis-metalated diene. *Org. Lett.* **2005**, *7*, 2289–2291.

9. Cai, M.-Z.; Zhou, Z.; Wang, P.-P. A facile stereoselective synthesis of difunctionalized 1,3-dienes containing silicon and tin via palladium-catalyzed cross-coupling reaction. *Synthesis* **2006**, 789–793.
10. Tsushima, K.; Murai, A. Total synthesis of (+)-laurencin. *Tetrahedron Lett.* **1992**, *33*, 4345–4348, and references therein.
11. Gao, L.-X.; Murai, A. Total synthesis of (−)-dactylyne and (−)-isodactylyne. *Tetrahedron Lett.* **1992**, *33*, 4349–4352, and references therein.
12. Maloney, K. M.; Danheiser, R. L. Total synthesis of quinolizidine alkaloid (−)-217A. Application of iminoacetonitrile cycloadditions in organic synthesis. *Org. Lett.* **2005**, *7*, 3115–3118, and references therein.
13. (a) Karle, I. L. Structure of dihydroisohistrionicotoxin, a unique unsaturated alkaloid and anticholinergic agent. *J. Am. Chem. Soc.* **1973**, *95*, 4036–4040; (b) Stork, G.; Zhao, K. Total syntheses of (−)-histrionicotoxin and (−)-histrioni- cotoxin 235A. *J. Am. Chem. Soc.* **1990**, *112*, 5875–5876.
14. Hoshi, M.; Kawamura, N.; Shirakawa, K. Construction of terminal conjugated enynes: Cu-mediated cross-coupling reaction of alkenyldialkylborane with (trimethylsilyl)ethynyl bromide. *Synthesis* **2006**, 1961–1970.
15. (a) Sonogashira, K.; Tohda, Y.; Hagihara, N. A convenient synthesis of acetylenes: Catalytic substitutions of acetylenic hydrogen with bromoalkenes, iodoarenes, and bromopyridines. *Tetrahedron Lett.* **1975**, 4467–4470; (b) Sonogashira, K. *Comprehensive Organic Synthesis*; B. M. Trost, I. Fleming (Eds.); Pergamon Press: Oxford, 1991; vol. 3, chap. 2.4, pp. 521–549, and references therein.
16. Kusumoto, T.; Ando, K.; Hiyama, T. Hydrosilylation of 1,4-bis-(trimethylsilyl)butadiynes and silyl-substituted butenynes. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1280–1290.
17. (a) Schwartz, J.; Labinger, J. A. Hydrozirconation: A new transition metal reagent for organic synthesis. *Angew. Chem. Int. Ed.* **1976**, *15*, 333–340; (b) Hart, D. W.; Blackburn, T. F.; Schwartz, J. Hydrozirconation, III: Stereospecific and regioselective functionalization of alkylacetylenes via vinylzirconium (IV) intermediates. *J. Am. Chem. Soc.* **1975**, *97*, 679–680.
18. (a) Deloux, L.; Srebnik, M. Preparation of (Z)-1-alkenyl dioxaborolanes by hydrolysis of boryl zirconocene 1,1-dimetalloalkenes. *J. Org. Chem.* **1994**, *59*, 6871–6873; (b) Dabdoub, M. J.; Baroni, A. C. M. Hydrozirconation of stannyl-acetylenes: Synthesis and reactions of ketene stannyl(telluro) acetals. *J. Org. Chem.* **2000**, *65*, 54–60; (c) Arefolov, A.; Langille, N. F.; Panek, J. S. Stereoselective synthesis of functionalized trisubstituted olefins via palladium(0)-catalyzed cross-coupling reaction. *Org. Lett.* **2001**, *3*, 3281–3284; (d) Huang, X.; Duan, D.; Zheng, W. Studies on hydrozirconation of 1-alkynyl sulfoxides or sulfones and the application for the synthesis of stereodefined vinyl sulfoxides or sulfones. *J. Org. Chem.* **2003**, *68*, 1958–1963.
19. Fryzuk, M. D.; Bates, G. S.; Stone, C. Preparation and isomerization of 1-phenylseleno 1,3-dienes. *J. Org. Chem.* **1991**, *56*, 7201–7211.
20. Cai, M.; Huang, J.; Ye, X.; Song, C. Stereoselective synthesis of (*E*)-α-halovinylsilanes via hydrozirconation of alkynylsilanes. *J. Chem. Res.* **2003**, 770–772.