# A general approach to difunctionalised 1,3-dienes containing silicon and halogen via hydrozirconation of (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes Xinglin Ye<sup>a,b</sup>, Pingping Wang<sup>b</sup> and Mingzhong Cai<sup>a</sup>\*

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Sonogashira coupling of (*E*)- $\alpha$ -iodovinylsilanes **1** with (trimethylsilyl)acetylene gave (*Z*)-1,3-bis(trimethylsilyl)alk-3en-1-ynes **2**, which underwent a desilylation reaction to afford (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes **3** in high yields. (1*E*,3*Z*)-1-Halo-3-(trimethylsilyl)-substituted 1,3-dienes **5** could be synthesised stereoselectively via hydrozirconation of (*Z*)-3-(trimethylsilyl)alk-3-en-1-ynes **3**, followed by trapping with iodine or *N*-bromosuccinimide.

Keywords: difunctionalised 1,3-diene, Sonogashira coupling, hydrozirconation, vinylsilane, vinylic iodide

The stereocontrolled synthesis of 1,3-dienes containing metal or heteroatom functional groups has been of considerable interest in organic synthesis because many useful functional group transformations can be achieved by the introduction and removal of metal or heteroatom functionalities. The stereoselective synthesis of 1,3-dienyl sulfides,<sup>1</sup> 1,3dienyl selenides,<sup>2</sup> 1,3-dienylsilanes<sup>3</sup> and 1,3-dienylstannanes<sup>4</sup> has already been described in the literature. Recently, the synthesis of difunctionalised 1,3-dienes has also attracted much attention since such dienes may find use as synthetic building blocks.<sup>5</sup> In addition, difunctionalised 1.3-dienes containing heteroatom can control both regio- and stereoselectivity and play a very important role in cycloadditions.<sup>6</sup> Jin and co-workers reported the stereoselective synthesis of 2-alkoxy-3-alkyl(aryl)thiobuta-1,3-dienes by Negishi coupling between  $\alpha$ -alkyl(aryl)thio vinyl zinc chloride and  $\alpha$ -bromo vinyl ether.<sup>7</sup> Coleman and Walczak 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.8 The stereoselective synthesis of 1,4-dihalo-1,3-dienes has also been described.<sup>9</sup> 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)- $\alpha$ iodovinylstannanes in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst.<sup>10</sup> However, to the best of our knowledge, there is no wellestablished method for the preparation of stereoselectively difunctionalised 1,3-dienes containing silicon and halogen. Herein, we report that (1E, 3Z)-1-halo-3-(trimethylsilyl)substituted 1,3-dienes can be conveniently synthesised via hydrozirconation of (Z)-3-(trimethylsilyl)alk-3-en-1-ynes, followed by trapping with iodine or N-bromosucanimide (NBS).

There has been a lively interest in terminal conjugated enynes, alk-3-en-1-ynes, due to 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 because the terminal conjugated enyne unit occurs in natural products such as laurenãn,<sup>11</sup> dactylyne,<sup>12</sup> quinolizidine,<sup>13</sup> and histrionicotoxin.<sup>14</sup> Very recently, Hoshi *et al.*<sup>15</sup> reported the synthesis of terminal conjugated enynes via Cu-mediated Suzuki-Miyaura cross-coupling reactions of alkenyldialkylboranes with (trimethylsilyl)ethynyl bromide. 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 prepared according to Scheme 1.

Sonogashira coupling of alkenyl iodides with terminal alkynes provides a simple and general route for the synthesis of conjugated enynes.<sup>16</sup> We observed that, when the coupling reactions of (E)- $\alpha$ -iodovinylsilanes 1 with (trimethylsilyl)acetylene were performed in piperidine at room temperature using  $Pd(PPh_3)_4$  and CuI as co-catalysts, fairly rapid reactions occurred affording stereoselectively the desired (Z)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes 2 in high yields, the typical results are summarised in Table 1. Kusumoto et al.<sup>17</sup> 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-(trimethylsilyl)but-1-en-3-yne, the desilylation reaction occurring selectively at the acetylenic carbon atom. We investigated the desilvlation reaction of (Z)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes 2 with KF in methanol in order to prepare (Z)-3-(trimethylsilyl)alk-3-en-1-ynes 3. We found that the desilvlation reaction of

Table 1 Coupling reaction of 1 with (trimethylsilyl)acetylenea and desilylation of  $\mathbf{2}^{\mathrm{b}}$ 

Entry	R	Product	Yield/% <sup>c</sup>
1	<i>n</i> -Bu	2a	87
2	Ph	2b	90
3	CH <sub>3</sub> OCH <sub>2</sub>	2c	85
4	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	2d	88
5	<i>n</i> -Bu	3a	86
6	Ph	3b	87
7	CH <sub>3</sub> OCH <sub>2</sub>	3c	81
8	n-C <sub>6</sub> H <sub>13</sub>	3d	84

<sup>a</sup>The reaction of **1** (2 mmol) with (trimethylsilyl)acetylene (3 mmol) was carried out using  $Pd(PPh_3)_4$  (0.1 mmol), Cul (0.2 mmol) and piperidine (6 ml) at room temperature for 2 h. <sup>b</sup>The desilylation reaction of **2** (1 mmol) with KF (10 mmol) was performed in methanol (3 ml) at 70°C for 5 h. <sup>c</sup>lsolated yield of **2** based on the **1** used.



Scheme 1

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Scheme 2

(*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 high yields. Typical results are also summarised in Table 1.

Hydrozirconation has emerged as a unique hydrometallation with some attractive features such as the high regioselectivity and stereoselectivity observed with alkynes<sup>18</sup> and heteroatomsubstituted alkynes.<sup>19</sup> However, the hydrozirconation of terminal conjugated enynes has received less attention.<sup>20</sup> With a convenient route to (Z)-3-(trimethylsilyl)alk-3-en-1-ynes 3 established we deaded to investigate the feasibility of using 3 in a hydrozirconation reaction with Cp<sub>2</sub>Zr(H)Cl. We observed that, when the hydrozirconation of 3 with Cp<sub>2</sub>Zr(H)Cl was performed in THF at room temperature, fairly rapid reactions occurred affording stereoselectively (1E,3Z)-3-(trimethylsilyl)substituted 1,3-dienylzirconium(IV) complexes 4. The intermediates 4 were then trapped with iodine or NBS to give stereoselectively (1E,3Z)-1-halo-3-(trimethylsilyl)-substituted 1,3-dienes 5 in good yields (Scheme 2). Typical results are summarised in Table 2. As shown in Table 2, a variety of (1E,3Z)-1-halo-3-(trimethylsilyl)-substituted 1,3-dienes 5 could be synthesised stereoselectively via hydrozirconation of (Z)-3-(trimethylsilyl)alk-3-en-1-vnes 3. followed by trapping with iodine or NBS. The (1E)-configuration of compounds 5a-f has been proved by their <sup>1</sup>H NMR spectra which show two doublets at  $\delta = 6.03-7.47$  with coupling constants of 13.6-15.2 Hz, and this also indicates that hydrozirconation of (Z)-3-(trimethylsilyl)alk-3-en-1-ynes 3 with Cp<sub>2</sub>Zr(H)Cl occurs highly regio- and stereoselectively, affording intermediates 4. In addition, the (3Z)-configuration of compound 5a was confirmed by NOESY experiments. An enhancement of the allylic protons was observed as the vinylic proton  $(\delta = 6.17 \text{ ppm})$  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 ( $\delta = 6.17$  ppm) and one other vinylic proton ( $\delta = 6.03$  ppm) was also observed. The NOE results indicate that 5a has the expected (1E,3Z)-configuration.

We have also carried out the palladium-catalysed crosscoupling reaction of compound **5a** with phenylmagnesium bromide in THF to afford iodine-free ( $1Z_3E$ )-2-(trimethylsilyl)substituted 1,3-diene **6** in 87% yield (Scheme 3).

In summary, we have developed a highly stereoselective and general route to difunctionalised 1,3-dienes containing silicon and halogen by hydrozirconation of (Z)-3-(trimethylsilyl)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.

Table 2Synthesis of (1E,3Z)-1-halo-3-(trimethylsilyl)-sub-stituted 1,3-dienes 5

Entry	R	х	Product	Yieldª/%
1	<i>n</i> -C₄H <sub>9</sub>	I	5a	74
2	n-C₄H <sub>9</sub>	Br	5b	76
3	Ph	I	5c	78
4	Ph	Br	5d	80
5	n-C <sub>6</sub> H <sub>13</sub>	I	5e	73
6	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	Br	5f	81

<sup>a</sup>lsolated yield based on the **3** used.

Investigations into the synthetic applications of compounds **5** are currently in progress.

## Experimental

<sup>1</sup>H NMR spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer with TMS as an internal standard using CDCl<sub>3</sub> as the solvent. <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Bruker AC-P400 (400 MHz) spectrometer using CDCl<sub>3</sub> 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 analyser. 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*)- $\alpha$ -Iodovinylsilanes 1 were prepared from alkynylsilanes according to a literature procedure.<sup>21</sup>

General procedure for the synthesis of (Z)-1,3-bis(trimethylsilyl)alk-3-en-1-ynes **2a-d** 

(*E*)- $\alpha$ -Iodovinylsilane 1 (2.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (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 (3.0 mmol), and the reaction mixture was stirred at room temperature for 2 h, quenched with sat. NH<sub>4</sub>Cl aq. solution (10 ml) at 0°C and extracted with Et<sub>2</sub>O (2 × 25 ml). The ethereal solution was removed under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp. 30–60°C).

(Z)-1,3-Bis(trimethylsilyl)oct-3-en-1-yne (**2a**): Oil. IR (film): v (cm<sup>-1</sup>) 2959, 2928, 2120, 1719, 1581, 1406, 1249, 841, 759; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup>, 18), 73 (100), 57 (43); Anal. Calc. for C<sub>14</sub>H<sub>28</sub>Si<sub>2</sub>: C, 66.58; H, 11.18. Found: C, 66.3; H, 11.0%.

(Z)-1,3-Bis(trimethylsilyl)-4-phenylbut-3-en-1-yne (2b): Oil. IR (film): v (cm<sup>-1</sup>) 3058, 3026, 2959, 2898, 2118, 1717, 1557, 1490, 1407, 1250, 840, 759, 698; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.76 (s, 1H), 7.31–7.21 (m, 5H), 0.22 (s, 9H), 0.09 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup>, 13), 91 (80), 78 (100), 77 (57), 73 (41); Anal. Calc. for C<sub>16</sub>H<sub>24</sub>Si<sub>2</sub>: C, 70.51; H, 8.88. Found: C, 70.2; H, 8.6%.



Scheme 3

(*Z*)-1,3-Bis(trimethylsilyl)-5-methoxypent-3-en-1-yne (**2c**): Oil. IR (film): v (cm<sup>-1</sup>) 2960, 2154, 1716, 1683, 1251, 1124, 844; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  150.2, 127.4, 107.8, 96.6, 71.1, 58.1, 0.1, -0.2; MS: *m/z* 240 (M<sup>+</sup>, 11), 73 (100), 45 (56); Anal. Calc. for C<sub>12</sub>H<sub>24</sub>OSi<sub>2</sub>: C, 59.93; H, 10.06. Found: C, 59.7; H, 9.9%.

(Z)-1,3-Bis(trimethylsilyl)dec-3-en-1-yne (2d): Oil. IR (film): v (cm<sup>-1</sup>) 2959, 2930, 2121, 1712, 1580, 1456, 1406, 1249, 842, 759; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  1560, 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<sup>+</sup>, 21), 73 (100), 57 (54), 43 (39); Anal. Calc. for C<sub>16</sub>H<sub>32</sub>Si<sub>2</sub>: C, 68.49; H, 11.50. Found: C, 68.2; H, 11.3%.

### General procedure for the synthesis of (Z)-3-(trimethylsilyl)alk-3-enl-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 ( $2 \times 20$  ml). The ethereal solution was washed with water ( $2 \times 10$  ml) and dried over MgSO<sub>4</sub>. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel eluting with light petroleum ether (h.p. 30–60°C).

(*Z*)-3-(*Trimethylsilyl*)*oct*-3-*en*-1-*yne* (**3***a*): Oil. IR (film): v (cm<sup>-1</sup>) 3315, 2959, 2931, 2075, 1721, 1582, 1408, 1250, 843, 759; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  157.0, 122.0, 87.3, 76.7, 32.2, 31.5, 22.4, 14.0, -0.2; MS: *m/z* 180 (M<sup>+</sup>, 24), 165 (100), 73 (86), 57 (65); Anal. Calc. for C<sub>11</sub>H<sub>20</sub>Si: C, 73.25; H, 11.18. Found: C, 73.4; H, 11.25%.

(Z)-3-(*Trimethylsilyl*)-4-phenylbur-3-en-1-yne (**3b**): Oil. IR (film): v (cm<sup>-1</sup>) 3307, 3062, 2957, 2070, 1706, 1562, 1490, 1406, 1250, 841, 755, 698; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.79 (s, 1H), 7.31–7.21 (m, 5H), 3.13 (s, 1H), 0.07 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  153.5, 138.5, 128.4, 128.0, 127.9, 126.1, 87.6, 79.4, –0.1; MS: *m/z* 200 (M<sup>+</sup>, 27), 185 (100), 73 (58); Anal. Calc. for C<sub>13</sub>H<sub>16</sub>Si: C, 77.93; H, 8.05. Found: C, 77.7; H, 8.1%.

(Z)-3-(Trimethylsilyl)-5-methoxypent-3-en-1-yne (**3c**): Oil. IR (film): v (cm<sup>-1</sup>) 3305, 2960, 2064, 1250, 1128, 843; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  148.5, 144.0, 86.8, 76.6, 72.1, 58.0, -0.1; MS: *m*/z 168 (M<sup>+</sup>, 21), 153 (83), 73 (100), 45 (48); Anal. Calc. for C<sub>9</sub>H<sub>16</sub>OSi: C, 64.22; H, 9.58. Found: C, 64.4; H, 9.6%.

(Z)-3-(Trimethylsilyl)dec-3-en-1-yne (**3d**): Oil. IR (film): v (cm<sup>-1</sup>) 3315, 2958, 2928, 2078, 1715, 1581, 1456, 1407, 1250, 843, 759; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup>, 31), 193 (100), 73 (69), 57 (46), 43 (52); Anal. Calc. for C<sub>13</sub>H<sub>24</sub>Si: C, 74.92; H, 11.61. Found: C, 74.7; H, 11.4%.

# General procedure for the synthesis of (1E,3Z)-1-halo-3-(trimethylsilyl)-substituted 1,3-dienes **5a–f**

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. Iodine or NBS (1.0 mmol) was then added and the mixture was stirred at room temperature for 30 min. After dilution with diethyl ether (30 ml) 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 (b.p. 30–60°C).

(*1E*,3*Z*)-*1*-*I*odo-3-(trimethylsilyl)-*1*,3-octadiene (**5a**): Oil. IR (film): v (cm<sup>-1</sup>) 2957, 2926, 1727, 1594, 1455, 1249, 946, 839, 763; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.04 (d, *J* = 14.2 Hz, 1H), 6.17 (t, *J* = 7.6 Hz, 1H), 6.03 (d, *J* = 14.2 Hz, 1H), 2.18–2.10 (m, 2H), 1.39–1.26 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.18 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  150.7, 148.8, 146.4, 140.3, 31.9, 31.7, 22.4, 14.1, 0.25; MS: *m/z* 308 (M<sup>+</sup>, 1.4), 73 (84), 57 (100); Anal. Calc. for C<sub>11</sub>H<sub>21</sub>Sil: C, 42.84; H, 6.86. Found: C, 42.6; H, 6.7%.

(*1E,3Z*)-*1-Bromo-3-(trimethylsilyl)-1,3-octadiene* (**5b**): Oil. IR (film): v (cm<sup>-1</sup>) 2956, 2926, 1718, 1596, 1455, 1405, 1250, 941, 839; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.73 (d, *J* = 13.6 Hz, 1H), 6.17 (t, *J* = 7.6 Hz, 1H), 6.05 (d, *J* = 13.6 Hz, 1H), 2.18–2.09 (m, 2H), 1.38–1.27 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H), 0.17 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  146.3, 142.7, 137.6, 102.6, 31.9, 31.8, 22.5, 14.1, 0.27; MS: m/z 261 (M<sup>+</sup>, 1.2), 85 (68), 73 (100), 57 (79); Anal. Calc. for C<sub>11</sub>H<sub>21</sub>SiBr: C, 50.55; H, 8.10. Found: C, 50.3; H, 8.2%.

(*1E*,*3Z*)-*1*-*Iodo*-*3*-(*trimethylsilyl*)-*4*-*phenyl*-*1*,*3*-*butadiene* (**5c**): Oil. IR (film): v (cm<sup>-1</sup>) 3025, 3064, 2955, 2897, 1714, 1590, 1492, 1249, 940, 840, 774, 697; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.47 (d, *J* = 15.2 Hz, 1H), 7.39–7.26 (m, 5H), 6.77 (s, 1H), 6.38 (d, *J* = 15.2 Hz, 1H), 0.25 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  145.8, 141.6, 140.0, 137.4, 129.6, 129.5, 128.3, 127.6, -0.65; MS: *m/z* 328 (M<sup>+</sup>, 2.1), 77 (34), 73 (100); Anal. Calc. for C<sub>13</sub>H<sub>17</sub>SiI: C, 47.55; H, 5.22. Found: C, 47.3; H, 5.0%.

(*1E*,3*Z*)-*1*-*Bromo-3-(trimethylsilyl)-4-phenyl-1,3-butadiene* (**5d**): Oil. IR (film): v (cm<sup>-1</sup>) 3024, 3064, 2955, 1713, 1586, 1490, 1249, 937, 839, 774; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.35–7.20 (m, 6H), 6.95 (d, J = 13.6 Hz, 1H), 6.28 (d, J = 13.6 Hz, 1H), 0.01 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 143.5, 142.6, 141.6, 139.2, 128.7, 127.9, 127.6, 104.5, 0.29; MS: *m/z* 281 (M<sup>+</sup>, 1.1), 77 (57), 73 (100); Anal. Calc. for C<sub>13</sub>H<sub>17</sub>SiBr: C, 55.50; H, 6.09. Found: C, 55.2; H, 6.15%.

(*1E*,3*Z*)-*1*-*Iodo*-3-(*trimethylsilyl*)-*1*,3-*decadiene* (**5e**): Oil. IR (film): v (cm<sup>-1</sup>) 2955, 2925, 2856, 1716, 1594, 1456, 1249, 944, 839; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.04 (d, *J* = 14.2 Hz, 1H), 6.16 (t, *J* = 7.6 Hz, 1H), 6.03 (d, *J* = 14.2 Hz, 1H), 2.16–2.09 (m, 2H), 1.40–1.26 (m, 8H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.17 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 150.7, 148.6, 146.4, 140.3, 32.0, 31.8, 29.7, 29.1, 22.6, 14.1, 0.26; MS: *m/z* 336 (M<sup>+</sup>, 1.5), 127 (45), 73 (100); Anal. Calc. for C<sub>13</sub>H<sub>25</sub>SiI: C, 46.41; H, 7.49. Found: C, 46.1; H, 7.3%.

(*1E*,*3Z*)-*1*-*Bromo-3-(trimethylsilyl*)-*1*,*3*-decadiene (**5f**): Oil. IR (film): v (cm<sup>-1</sup>) 2957, 2927, 2856, 1729, 1595, 1458, 1250, 937, 839; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.73 (d, J = 13.6 Hz, 1H), 6.17 (t, J = 7.6 Hz, 1H), 6.05 (d, J = 13.6 Hz, 1H), 2.16–2.10 (m, 2H), 1.39–1.26 (m, 8H), 0.89 (t, J = 7.2 Hz, 3H), 0.18 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  146.1, 142.4, 137.2, 102.3, 31.8, 31.5, 29.5, 28.8, 22.4, 13.8, 0.01; MS: *m/z* 289 (M<sup>+</sup>, 1.1), 149 (54), 73 (100); Anal. Calc. for C<sub>13</sub>H<sub>25</sub>SiBr: C, 53.95; H, 8.71. Found: C, 53.7; H, 8.6%.

## Synthesis of (1E,3Z)-1-phenyl-3-(trimethylsilyl)-1,3-octadiene 6

To a mixture of (1E,3Z)-1-iodo-3-(trimethylsilyl)-1,3-octadiene 5a (1.0 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 mmol) in THF (2 ml) was added a solution of Ph MgBr (1.5 mmol) in THF (3 ml) under Ar at room temperature. The resulting mixture was stirred for 14 h at room temperature. The mixture was treated with sat. NH<sub>4</sub>Cl aq. solution (20 ml) at 0°C and extracted with diethyl ether ( $2 \times 20$  ml). The ethereal solution was washed with water (2  $\times$  20 ml) and dried (MgSO<sub>4</sub>). Removal of the solvent under reduced pressure gave an oil, which was purified by preparative TLC on silica gel eluting with light petroleum ether (b.p. 30-60°C). IR (film): v (cm<sup>-1</sup>) 3059, 3024, 2958, 1620, 1590, 1491, 1249, 962, 841, 745; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 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); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup>, 12), 243 (26), 77 (38), 73 (100), 57 (42); Anal. Calc. for C<sub>17</sub>H<sub>26</sub>Si: C, 78.99; H, 10.14. Found: C, 78.7; H, 9.95%.

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