



# New evidence on the regiochemistry of the *tert*-butyldiphenylsilylcupration of allene using the silylcuprate or silylcopper reagent

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**Abstract**—The regiochemistry in the *tert*-butyldiphenylsilylcupration of the allene depends on the temperature and also on the nature of the electrophile. Thus, the intermediate generated by addition of the silylcuprate at  $-78^{\circ}\text{C}$  reacted with electrophiles to give allylsilanes, except with oxo compounds which afforded vinylsilanes. On the other hand, the silylcopper reagent was added at  $-40^{\circ}\text{C}$  leading, in all cases, to the corresponding allylsilanes. When enones were used as electrophile the vinylsilanes were the 1,2-addition products and the allylsilanes those from 1,4-addition. These functionalized vinyl or allyl *tert*-butyldiphenylsilanes are interesting synthons for the preparation of conjugated *tert*-butyldiphenylsilyltrienes and functionalized exocyclic alkylidenecyclopentenes.  
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## 1. Introduction

Some years ago<sup>1</sup> we reported that lithium bis-(*tert*-butyldiphenylsilyl)cuprate reacts regioselectively with allenes affording allyl- or vinylsilanes. The regiochemistry depends not only on the substitution pattern of allene but also on the temperature. Thus, the lithium bis-(*tert*-butyldiphenylsilyl)cuprate reacts at  $-78^{\circ}\text{C}$  with allene itself **1** followed by hydrolysis at this temperature to give the allylsilane **2** resulting from addition of the bulky *tert*-butyldiphenylsilyl group at the less hindered extreme of allene. When the reaction was carried out at  $0^{\circ}\text{C}$ , the regiochemistry changed and we obtained the vinylsilane **3** (Scheme 1).

We also described<sup>1</sup> that the reaction of allylsilane–vinylcuprate intermediate **4**, generated at  $-78^{\circ}\text{C}$ , with other electrophiles different from proton such as methyl iodide, iodine, acetyl chloride, ethylene oxide and oxo compounds, yielded the corresponding allylsilanes **5a–i** (Scheme 2).

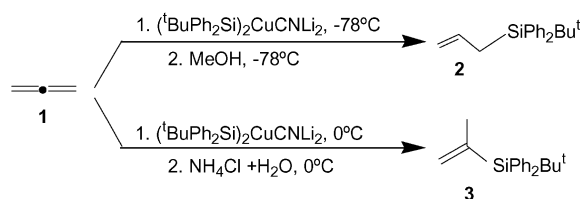
A recent revision of the reaction of the *tert*-butyldiphenylsilylcupration intermediates with carbonyl compounds has revealed that we committed a mistake in the assignment of the regiochemistry of the compounds **5e–i**, which was established in the base of the  $^1\text{H}$  NMR spectrum recorded at 80 MHz. When we repeated the reaction using acet-

aldehyde, acetone, cinnamaldehyde, methylvinylketone and 2-cyclohexenone as electrophiles and the products were identified by  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy at 300 MHz, we realized that they had a vinylsilane structure instead of allylsilane. Moreover, we have synthesized the allylsilane **5g** by silylcupration from allene with the *tert*-butyldiphenylsilylcopper reagent at  $-40^{\circ}\text{C}$  and subsequent treatment with cinnamaldehyde. In this case, **5g** (54%) was obtained together with the allylsilane **5k** (17%) resulting from 1,4-addition (Scheme 7). When enones were used as electrophiles, the reaction products were the allylsilanes from 1,4-addition rather than the vinylsilanes from 1,2-addition obtained by reaction with the silylcuprate.

## 2. Results and discussion

### 2.1. Silylcupration of allene using lithium bis-(*tert*-butyldiphenylsilyl)cuprate and reaction with electrophiles

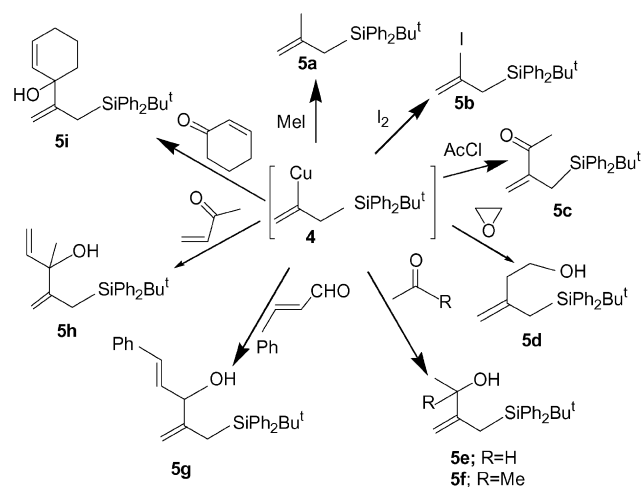
The lithium bis-(*tert*-butyldiphenylsilyl)cuprate reacts with



Scheme 1.

**Keywords:** allene; silylcupration; allylsilanes; vinylsilanes.

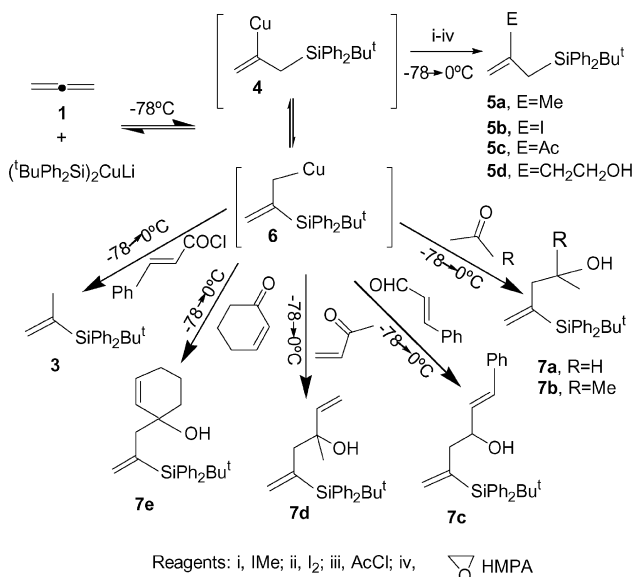
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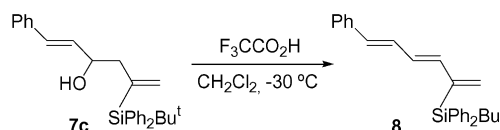
Scheme 2.

allene **1** at  $-78^\circ\text{C}$  and then with acetaldehyde, acetone, cinnamaldehyde, methylvinylketone and 2-cyclohexenone between  $-78^\circ\text{C}$  and  $0^\circ\text{C}$  to give the vinylsilanes **7a–e** by 1,2-addition from the intermediate **6** instead of the expected allylsilanes **5e–i**. The presumed intermediate **6** did not react with cinnamoyl chloride and only the vinylsilane **3** resulting from protodecupration was formed. Other electrophiles such as methyl iodide, iodine, acetyl chloride and ethylene oxide afforded the corresponding allylsilanes **5a–d** via the intermediate **4**, as was described in our earlier paper.<sup>1</sup> Presumably, the addition of the silylcuprate is reversible and the overall regiochemistry is controlled in either sense, not only by the temperature but also by the electrophile (Scheme 3).

Although the vinylsilanes bearing the bulky *tert*-butyldiphenylsilyl group can be substituted for electrophiles,<sup>2</sup> one advantage of this hindered group versus the dimethylphenylsilyl or trimethylsilyl group is the possibility of its heating with acids without protodesilylation.<sup>2</sup> This allowed us to synthesize the conjugated *tert*-butyldiphenylsilyltriene



Scheme 3.



Scheme 4.

**8** from the alcohol **7c** by dehydration with trifluoroacetic acid (Scheme 4).

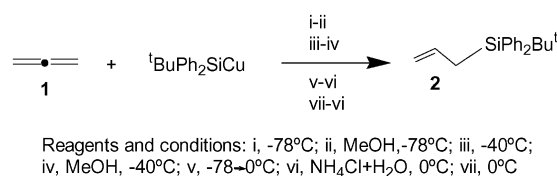
## 2.2. Silylcupration of allene with the *tert*-butyldiphenylsilylcopper reagent

We demonstrated earlier<sup>3</sup> that the dimethylphenylsilylcopper reagent is added to allene with the opposite regioselectivity to that shown by the corresponding silylcuprate. With the aim of obtaining allylsilanes, more interesting than their regioisomer vinylsilanes,<sup>4,5</sup> we have accomplished the silylcupration of allene using the *tert*-butyldiphenylsilylcopper reagent. In order to know the regioselectivity of the allene silylcupration with this new reagent, we have carried out the reaction at several temperatures. We have verified that, as opposed to the silylcuprate, the silylcopper reagent is always added to the end of the allenic system, independently of the temperature, to give an allylsilane intermediate **4**, whose hydrolysis afforded, in all cases, the allylsilane **2** (Scheme 5).

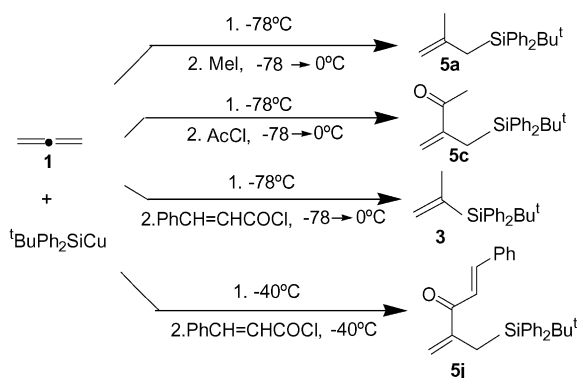
The reaction with other electrophiles different from proton is more complicated. Some electrophiles, like methyl iodide and acetyl chloride, react easily and in good yields at  $-78^\circ\text{C}$  via the allylsilane intermediate **4**, leading to the corresponding allylsilanes **5a** and **5c**, but the cinnamoyl chloride does not react at this temperature. We isolated only the vinylsilane **3** resulting from protodecupration of the vinylsilane intermediate **6**. Fortunately, the intermediate allylsilane **4**, generated at  $-40^\circ\text{C}$ , reacted successfully with cinnamoyl chloride to give the expected allylsilane **5j**, which was impossible to synthesize through the silylcuprate (Scheme 6).

At this temperature, the vinylcopper intermediate **4** reacted with  $\alpha,\beta$ -unsaturated oxo compounds such as cinnamaldehyde, benzalacetone and 2-cyclohexenone, affording the allylsilane **5g** resulting from 1,2-addition and the allylsilanes **5k–5m** from 1,4-addition. On the contrary, the 1-acetylcyclohexene and saturated oxo compounds, like acetaldehyde and acetone, did not react with the intermediate **4**. In the same conditions, the allylsilane **2** resulting from the final hydrolysis was exclusively obtained (Scheme 7).

The utility of vinyl and divinyl ketones containing an allylsilane moiety is well-documented. They can serve as substrates for the synthesis of methylenecyclopentanols by



Scheme 5.

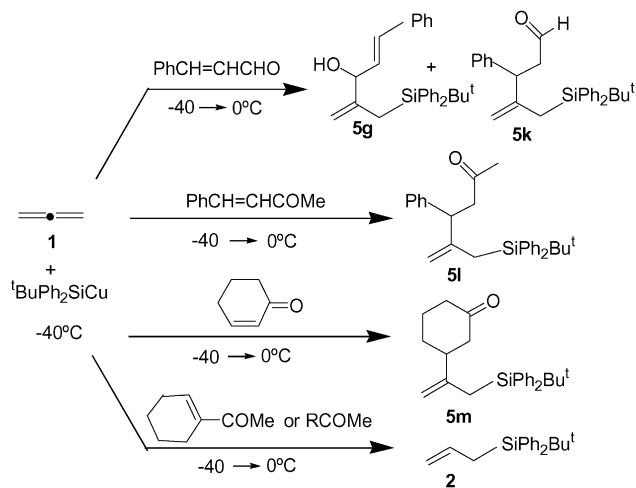


Scheme 6.

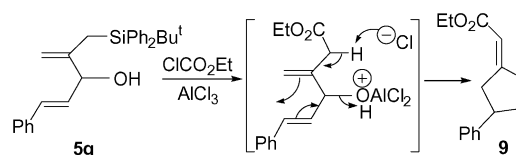
Lewis acid-catalyzed annulation<sup>6</sup> or cyclopentenones via silicon-directed Nazarov cyclizations.<sup>7</sup> Nevertheless, the synthetic possibilities of allylsilanes bearing a diallyl alcohol unit in annulation processes have not been exploited.

Attempts to induce the allyl-mediated cyclization of **5g** by protic or Lewis acids, such as TFA,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ ,  $\text{FeCl}_3$ , and  $\text{AlCl}_3$  were unsatisfactory. Nevertheless, when **5g** reacted with ethyl chloroformate in the presence of  $\text{AlCl}_3$ , the electrophilic substitution of the allylsilane moiety occurred with concomitant cyclization to give **9** as a 1:9 mixture of *Z/E* stereoisomers. The ester group, more electroattractive than the *tert*-butyldiphenylsilyl group, evidently enhances the acidity of the  $\alpha$ -hydrogen and promotes the annulation (Scheme 8). This result opens an interesting route to functionalized exocyclic alkylidenecyclopentenones.

In conclusion, as well as correcting an earlier error, we now report two complementary methods of regiocontrol in the *tert*-butyldiphenylsilylcupration of allene. Especially interesting is the reaction of the silylcupration intermediates with oxo compounds, which affords vinylsilanes with the silylcuprate and allylsilanes with the silylcopper reagent. Furthermore, with enones as electrophiles the vinylsilanes were the allylic alcohols resulting from 1,2-addition whereas the allylsilanes were the ketones from 1,4-addition. When cinnamaldehyde was used as an electrophile for quenching the silylcopper intermediate, a 3:1 mixture of



Scheme 7.



Scheme 8.

1,2- and 1,4-addition products was isolated. Other electrophiles like cinnamoyl chloride, unreactive in the reaction with the silylcuprate, were shown to be very reactive when the silylcopper was used. In any case, the products of these reactions are functionalized allyl or vinylsilanes with many uses in organic synthesis,<sup>8</sup> whose two new applications are described here.

### 3. Experimental

#### 3.1. General

THF was distilled from sodium benzophenone ketyl in a recycling still. All chromatographic and work-up solvents were distilled prior to use. Copper (I) cyanide was dried in vacuo over  $\text{P}_2\text{O}_5$ . The allene **1** was bought. Lithium *tert*-butyldiphenylsilylcuprate was prepared as previously described<sup>1</sup> and the *tert*-butyldiphenylsilylcopper reagent was prepared in the same way mixing one equivalent of the *tert*-butyldiphenylsilyllithium and one equivalent of copper (I) cyanide. All reactions involving organometallic reagents were carried out under nitrogen atmosphere.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 300 and 75 MHz, respectively, in  $\text{CDCl}_3$  as an internal standard. Carbon multiplicities were assigned by DEPT experiments. Reactions were monitored by TLC on a pre-coated plate of silica gel 60 (nano-SIL-20, Macherey-Nagel). Flash chromatography was performed on silica gel 60 (230–400 mesh, M–N).

#### 3.2. *tert*-Butyldiphenylsilylcupration of allene with lithium *tert*-butyldiphenylsilylcuprate and reactions with electrophiles

The general procedure is the one previously described<sup>1</sup> and when we have used as electrophiles methyl iodide, iodine, acetyl chloride and ethylene oxide the products obtained were the same allylsilanes **5a–d** as described earlier.<sup>1</sup> Nevertheless, the products resulting from the reactions with carbonyl compounds have the structure of vinylsilanes **7a–e** rather than allylsilanes **5e–i**. To confirm it we describe below their spectroscopic properties.

**3.2.1. 4-(*tert*-Butyldiphenylsilyl)pent-4-en-2-ol (7a).** By reaction of allylcuprate **6** with acetaldehyde (70% yield);  $R_f=0.2$  (hexane/EtOAc, 20:1); IR ( $\text{CCl}_4$ ) 3600 sharp, 3200 broad, 1630, 1110, 1080 and  $870\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.65–7.53 (m, 4H), 7.47–7.29 (m, 6H), 6.09 (d,  $J=2.5$  Hz, 1H), 5.81 (d,  $J=2.5$  Hz, 1H), 3.58 (m, 1H), 2.40 (dd,  $J=15.1$ , 4.2 Hz, 1H), 2.25 (dd,  $J=15$ , 8.4 Hz, 1H), 1.58 (s br, 1H), 1.18 (s, 9H), and 1.04 (d,  $J=6.9$  Hz, 3H);  $^{13}\text{C}$  NMR  $\delta$  144.13, 136.36, 134.32, 132.41, 129.26, 127.78, 65.55, 47.64, 29.72, 22.76, 18.52; MS (EI)  $m/z$  267 ( $\text{M}^+ - \text{Bu}^t$ , 28%), 249 (8), 199 (100), 181 (10), 135 (5), 105 (12), 77

(10) and 57 (15). Anal. calcd for C<sub>21</sub>H<sub>28</sub>OSi: C, 77.72; H, 8.70. Found: C, 77.8; H, 8.75.

**3.2.2. 4-(*tert*-Butyldiphenylsilyl)-2-methylpent-4-en-2-ol (7b).** By reaction of **6** with acetone (45%);  $R_f=0.2$  (hexane/EtOAc, 20:1); IR (neat) 3300, 1630, 1190, 1100 and 850 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.70–7.55 (m, 4H), 7.49–7.37 (m, 6H), 6.10 (d,  $J=2.1$  Hz, 1H), 5.82 (d,  $J=2.1$  Hz, 1H), 2.35 (s, 2H), 1.56 (s br, 1H), 1.24 (s, 6H) and 1.17 (s, 9H); MS (EI)  $m/z$  281 (M<sup>+</sup>–Bu<sup>t</sup>, 8%), 199 (100), 181 (12), 135 (8), 105 (10), 77 (22) and 57 (28). Anal. calcd for C<sub>22</sub>H<sub>30</sub>OSi: C, 78.05; H, 8.93. Found: C, 77.90; H, 8.97.

**3.2.3. (*E*)-5-(*tert*-Butyldiphenylsilyl)-1-phenylhexa-1,5-dien-3-ol (7c).** By reaction of cinnamaldehyde with **6**; colorless oil (70%);  $R_f=0.18$  (hexane/EtOAc, 20:1); IR (CCl<sub>4</sub>) 3660 sharp, 3400 br, 1620, 1100, and 960 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.74–7.60 (m, 4H), 7.45–7.19 (m, 11H), 6.24 (d,  $J=15.9$  Hz, 1H), 6.15 (d,  $J=2.6$  Hz, 1H), 6.02 (dd,  $J=15.9$ , 6.4 Hz, 1H), 5.86 (d,  $J=2.6$  Hz, 1H); 4.02 (m, 1H), 2.53 (dd,  $J=15.4$ , 4.3 Hz, 1H), 2.43 (dd,  $J=15.4$ , 8.5 Hz, 1H), 1.75 (s br, 1H), and 1.18 (s, 9H); <sup>13</sup>C NMR  $\delta$  142.65, 136.11, 135.39, 134.65, 134.06, 132.74, 131.45, 129.23, 128.23, 127.55, 127.39, 126.17, 70.59, 54.52, 26.41, and 18.82; MS (EI)  $m/z$  355 (M<sup>+</sup>–Bu<sup>t</sup>, 51%), 337 (15), 277 (20), 259 (18), 199 (100), 183 (90), 135 (95), 105 (65), 77 (24), and 57 (26). Anal. calcd for C<sub>28</sub>H<sub>32</sub>OSi: C, 81.50; H, 7.82. Found: C, 81.73; H, 7.87.

**3.2.4. 5-(*tert*-Butyldiphenylsilyl)-3-methylhexa-1,5-dien-3-ol (7d).** By adding methylvinylketone to **6**; colorless oil (67%);  $R_f=0.19$  (hexane/EtOAc, 20:1); IR (neat) 3500, 1630, 1100, 990 and 830 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.76–7.61 (m, 4H), 7.42–7.34 (m, 6H), 6.17 (d,  $J=2.4$  Hz, 1H), 5.88 (d,  $J=2.4$  Hz, 1H), 5.63 (dd,  $J=17.1$ , 10.2 Hz, 1H), 5.26 (dd,  $J=17.1$ , 1.9 Hz, 1H), 4.92 (dd,  $J=10.2$ , 1.9 Hz, 1H), 2.53 (d,  $J=15.3$  Hz, 1H), 2.43 (d,  $J=15.3$  Hz, 1H), 2.07 (s br, 1H), 1.26 (s, 3H) and 1.18 (s, 9H); MS (EI)  $m/z$  293 (M<sup>+</sup>–Bu<sup>t</sup>, 6%), 199 (100), 163 (4), 105 (30), 77 (25), and 57 (16). Anal. calcd for C<sub>23</sub>H<sub>30</sub>OSi: C, 78.80; H, 8.63. Found: C, 78.66; H, 8.57.

**3.2.5. 1-[2-(*tert*-Butyldiphenylsilyl)prop-2-en-1-yl]cyclohex-2-enol (7e).** By reaction of 2-cyclohexenone with **6**; colorless oil (45%);  $R_f=0.20$  (hexane/EtOAc, 20:1); IR (neat) 3400, 1640, 1100, 1080, and 830 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.81–7.64 (m, 4H), 7.39–7.26 (m, 6H), 6.21 (d,  $J=1.8$  Hz, 1H), 5.85 (d,  $J=1.8$  Hz, 1H), 5.52 (dt,  $J=9.4$ , 4.6 Hz, 1H), 5.33 (d,  $J=9.4$  Hz, 1H), 2.42 (d,  $J=15.1$  Hz, 1H), 2.38 (d,  $J=15.1$  Hz, 1H), 1.94 (m, 2H), 1.78–1.42 (m, 4H), 1.21 (s, 1H) and 1.09 (s, 9H); MS (EI)  $m/z$  376 (M<sup>+</sup>, 1%), 319 (10), 279 (92), 199 (100), 135 (40), 77 (18), and 57 (29). Anal. calcd for C<sub>25</sub>H<sub>32</sub>OSi: C, 79.73; H, 8.56. Found: C, 79.85; H, 8.49.

### 3.3. *tert*-Butyldiphenylsilylcupration of allene with *tert*-butyldiphenylsilylcopper reagent and reactions with electrophiles

Allene **1** (1 mmol) was added to a solution of the *tert*-butyldiphenylsilylcopper reagent [prepared by mixing *tert*-butyldiphenylsilyllithium (1 mmol) and copper (I) cyanide (1 mmol)] in THF (5 mL). The mixture was cooled at

–40°C and stirred under nitrogen for 1 h. The electrophile (2 mmol) was added dropwise at –40°C and then the mixture was slowly allowed to warm to 0°C until TLC indicated complete reaction. Quenching at 0°C with aqueous ammonium chloride, aqueous workup with diethyl ether, drying (MgSO<sub>4</sub>), and chromatography gave the following products.

**3.3.1. 3-(*tert*-Butyldiphenylsilyl)propene (2).** By hydrolysis of the intermediate from silylcupration (95% yield);  $R_f=0.55$  (hexane); IR (neat) 1660, 1100, and 810 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.81–7.62 (m, 4H), 7.49–7.36 (m, 6H), 5.84 (ddt,  $J=18.0$ , 10.1, 7.8 Hz, 1H), 4.98 (dd,  $J=18.0$ , 2.0 Hz, 1H), 4.89 (dd,  $J=10.1$ , 2.0, 1H), 2.27 (d,  $J=7.8$  Hz, 2H), and 1.16 (s, 9H); <sup>13</sup>C NMR  $\delta$  134.71, 136.05, 134.45, 129.16, 127.61, 114.61, 27.94, 18.84, and 18.56; MS (EI)  $m/z$  280 (M<sup>+</sup>, 3%), 239 (20), 223 (35), 197 (19), 181 (22), 145 (21), 135 (100), and 105 (77).

**3.3.2. 3-(*tert*-Butyldiphenylsilyl)-2-methylpropene (5a).** Using methyl iodide as an electrophile at –78°C (85%);  $R_f=0.59$  (hexane); IR (neat) 1640, 1100, and 880 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.90–7.81 (m, 4H), 7.52–7.46 (m, 6H), 4.76 (d,  $J=1.3$  Hz, 1H), 4.73 (d,  $J=1.3$  Hz, 1H), 2.39 (s, 2H), 1.56 (s, 3H), and 1.21 (s, 9H); <sup>13</sup>C NMR  $\delta$  143.15, 136.12, 134.79, 129.03, 127.39, 110.85, 27.76, 25.46, 22.17, and 18.55; MS (EI)  $m/z$  294 (M<sup>+</sup>, 4%), 237 (80), 135 (100), 105 (58), and 57 (39).

**3.3.3. 3-[(*tert*-Butyldiphenylsilyl)methyl]but-3-en-2-one (5c).** By reaction of intermediate generated at –78°C with acetyl chloride (88%);  $R_f=0.36$  (hexane/EtOAc, 20:1); IR (neat) 1700, 1670, 1610, 1100, and 810 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.62–7.59 (m, 4H), 7.40–7.33 (m, 6H), 5.68 (s, 1H), 5.38 (s, 1H), 2.49 (s, 2H), 1.97 (s, 3H), and 1.09 (s, 9H); <sup>13</sup>C NMR  $\delta$  199.27, 146.30, 136.21, 133.76, 128.96, 127.26, 123.36, 27.57, 24.91, 18.31, and 12.69; MS (EI)  $m/z$  322 (M<sup>+</sup>, 1%), 265 (100), 181 (24), 135 (81), 105 (83), 77 (32), and 43 (83).

**3.3.4. 2-(*tert*-Butyldiphenylsilyl)propene (3).** By reaction of intermediate formed at –78°C with cinnamoyl chloride (86%);  $R_f=0.75$  (hexane); IR (neat) 1620, 1100, and 810 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.75–7.54 (m, 4H), 7.42–7.30 (m, 6H), 5.95 (d,  $J=3.2$  Hz, 1H), 5.48 (d,  $J=3.2$  Hz, 1H), 1.98 (s, 3H), and 1.16 (s, 9H); <sup>13</sup>C NMR  $\delta$  142.22, 136.17, 135.34, 129.10, 127.44, 131.54, 27.46, 25.22, and 18.29; MS (EI)  $m/z$  280 (M<sup>+</sup>, 1%), 223 (100), 197 (38), 183 (30), and 105 (58).

**3.3.5. (*E*)-4-[(*tert*-Butyldiphenylsilyl)methyl]-1-phenylpenta-1,4-dien-3-one (5j).** By reaction with cinnamoyl chloride at –40°C (74%);  $R_f=0.27$  (hexane/EtOAc, 20:1); IR (CCl<sub>4</sub>) 1705, 1680, 1600, 1100, 990, and 815 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.65–7.62 (m, 4H), 7.46–7.26 (m, 11H), 7.43 (d,  $J=15.7$  Hz, 1H), 6.88 (d,  $J=15.7$  Hz, 1H), 5.70 (s, 1H), 5.40 (s, 1H), 2.63 (s, 2H), and 1.10 (s, 9H); <sup>13</sup>C NMR  $\delta$  192.13, 147.19, 142.89, 136.35, 134.93, 133.75, 129.94, 129.10, 128.69, 128.05, 127.41, 122.41, 121.74, 27.68, 18.47, and 13.97; MS (EI)  $m/z$  353 (M<sup>+</sup>–Bu<sup>t</sup>, 100%), 275 (4), 199 (23), 135 (31), 105 (34), and 57 (68). Anal. calcd for C<sub>28</sub>H<sub>30</sub>OSi: C, 81.90; H, 7.36. Found: C, 81.73; H, 7.41.

**3.3.6. (*E*)-4-[(*tert*-Butyldiphenylsilyl)methyl]-1-phenylpenta-1,4-dien-3-ol (**5g**).** Using cinnamaldehyde as an electrophile (54%);  $R_f=0.15$  (hexane/EtOAc, 20:1); IR (CCl<sub>4</sub>) 3660 sharp, 3400 br, 1645, 1100, and 960 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.74–7.66 (m, 4H), 7.47–7.14 (m, 11H), 6.33 (d,  $J=15.9$  Hz, 1H), 5.96 (dd,  $J=15.9, 6.7$  Hz, 1H), 5.00 (s, 1H), 4.80 (s, 1H), 4.18 (d,  $J=6.7$  Hz, 1H), 92.34 (d,  $J=14.9$ , 1H), 2.09 (d,  $J=14.9$  Hz, 1H), 1.69 (s br, 1H), and 1.06 (s, 9H); <sup>13</sup>C NMR  $\delta$  147.37, 136.33, 136.27, 134.44, 134.25, 130.98, 130.12, 129.26, 128.44, 127.53, 126.46, 110.79, 76.22, 27.73, 18.51, and 15.66; MS (EI)  $m/z$  355 (M<sup>+</sup>–Bu<sup>t</sup>, 27%), 311 (10), 277 (12), 225 (15), 199 (50), 183 (52), 135 (74), 105 (80), and 57 (100). Anal. calcd for C<sub>28</sub>H<sub>32</sub>OSi: C, 81.50; H, 7.82. Found: C, 81.34; H, 7.76.

**3.3.7. 4-[(*tert*-Butyldiphenylsilyl)methyl]-3-phenylpent-4-enal (**5k**).** Using cinnamaldehyde as an electrophile (17%);  $R_f=0.21$  (hexane/EtOAc, 20:1); IR (neat) 1720, 1620, 1100, and 865 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  9.01 (t,  $J=2.3$  Hz, 1H), 7.65 (m, 4H), 7.41 (m, 6H), 7.28 (m, 3H), 7.03 (m, 2H), 4.91 (s, 1H), 4.76 (s, 1H), 3.23 (t,  $J=7.6$  Hz, 1H), 2.46 (dd,  $J=2.3, 7.6$  Hz, 2H), 2.27 (d,  $J=14.5$  Hz, 1H), 1.88 (d,  $J=14.5$  Hz, 1H), and 1.04 (s, 9H); <sup>13</sup>C NMR  $\delta$  201.34, 147.20, 141.58, 136.19, 134.29, 129.13, 128.37, 127.44, 127.39, 126.66, 110.75, 48.26, 46.35, 27.57, 19.15, and 18.33. MS (EI)  $m/z$  355 (M<sup>+</sup>–Bu<sup>t</sup>, 25%), 277 (4), 199 (100), 135 (45), 105 (28), and 57 (72). Anal. calcd for C<sub>28</sub>H<sub>32</sub>OSi: C, 81.50; H, 7.82. Found: C, 81.63; H, 7.78.

**3.3.8. 5-[(*tert*-Butyldiphenylsilyl)methyl]-4-phenylhex-5-en-2-one (**5l**).** By adding benzalacetone to the intermediate of silylcupration (65%);  $R_f=0.20$  (hexane/EtOAc, 20:1); IR (neat) 1710, 1620, 1100, and 860 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.70–7.66 (m, 4H), 7.47–7.37 (m, 6H), 7.30–7.21 (m, 3H), 7.07–7.04 (m, 2H), 4.83 (s, 1H), 4.78 (s, 1H), 3.37 (dd,  $J=9.6, 5.3$  Hz, 1H), 2.68 (dd,  $J=15.6, 9.6$ , 1H), 2.51 (dd,  $J=5.6, 5.3$  Hz, 1H), 2.25 (d,  $J=14.8$  Hz, 1H), 1.92 (d,  $J=14.8$  Hz, 1H), 1.78 (s, 3H), and 1.06 (s, 9H); <sup>13</sup>C NMR  $\delta$  207.24, 142.30, 136.23, 135.76, 135.13, 134.74, 129.00, 128.39, 128.16, 127.66, 116.10, 50.32, 48.26, 30.61, 26.50, 22.70, and 18.16; MS (EI)  $m/z$  369 (M<sup>+</sup>–Bu<sup>t</sup>, 23%), 291 (5), 239 (8), 199 (100), 135 (51), 105 (37), and 43 (79). Anal. calcd for C<sub>29</sub>H<sub>34</sub>OSi: C, 81.64; H, 8.03. Found: C, 81.79; H, 8.08.

**3.3.9. 3-[3-(*tert*-Butyldiphenylsilyl)prop-1-en-2-yl]cyclohexenone (**5m**).** By reaction with 2-cyclohexenone (52%);  $R_f=0.30$  (hexane/EtOAc, 20:1); IR (CCl<sub>4</sub>) 1680, 1630, 1100, and 860 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.75–7.72 (m, 4H), 7.44–7.34 (m, 6H), 4.72 (s, 1H), 4.58 (s, 1H), 2.19 (m, 3H), 2.11 (dd,  $J=14.0, 4.4$  Hz, 1H), 2.05 (d,  $J=14.0$  Hz, 1H), 1.86–1.71 (m, 2H), 1.65 (s, 2H), 1.40–1.23 (m, 2H), and 1.08 (s, 9H); <sup>13</sup>C NMR  $\delta$  211.74, 148.96, 135.97, 132.87, 129.55, 127.64, 109.17, 46.78, 44.97, 41.08, 29.66, 26.52, 24.71, 19.26, and 18.50; MS (EI)  $m/z$  319 (M<sup>+</sup>–Bu<sup>t</sup>, 17%), 241 (3), 199 (32), 183 (9), 135 (56), 105 (40), 57 (64), 55 (24), and 41 (100). Anal. calcd for C<sub>25</sub>H<sub>32</sub>OSi: C, 79.73; H, 8.56. Found: C, 79.87; H, 8.68.

**3.3.10. (*E,E*)-2-(*tert*-Butyldiphenylsilyl)-6-phenylhexa-1,3,5-triene (**8**).** **7c** (0.51 g, 1.2 mmol) and a 1% solution of F<sub>3</sub>CCO<sub>2</sub>H in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) were stirred at –30°C for 1 h. The mixture was washed with a 1 M aqueous solution of NaHCO<sub>3</sub>, and the organic layer washed with water, dried (MgSO<sub>4</sub>) concentrated in vacuo and the residue chromatographed to give **8** (89%); colorless oil;  $R_f=0.63$  (hexane); IR (neat) 1610, 1595, 1580, 1100, 960 and 830 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.66–7.62 (m, 4H), 7.47–7.19 (m, 11H), 6.75 (dd,  $J=15.6, 10.4$  Hz, 1H), 6.64 (d,  $J=15.6$  Hz, 1H), 6.54 (d,  $J=15.4$  Hz, 1H), 6.37 (dd,  $J=15.4, 10.4$  Hz, 1H), 6.23 (d,  $J=3.1$  Hz, 1H), 5.60 (d,  $J=3.1$  Hz, 1H), and 1.17 (s, 9H); MS (EI)  $m/z$  337 (M<sup>+</sup>–Bu<sup>t</sup>, 100), 259 (12), 183 (58), 155 (7), 105 (38), and 57 (19). Anal. Calcd. for C<sub>28</sub>H<sub>30</sub>Si: C, 85.22; H, 7.66. Found: C, 85.09; H, 7.61.

**3.3.11. *E*-3-(Ethoxycarbonylmethylene)-5-phenylcyclopentene (**9**).** To a solution of AlCl<sub>3</sub> (4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) at –30°C was slowly added ClCO<sub>2</sub>Et (2 mmol) and stirred for 30 min. Then the alcohol **5g** (1 mmol) was added and the mixture was stirred at this temperature for 90 min, hydrolyzed with an aqueous solution of ammonium chloride, extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried (MgSO<sub>4</sub>) and chromatographed using hexane/CH<sub>2</sub>Cl<sub>2</sub> as eluent to give **9** as major product. Oil (63%);  $R_f=0.69$  (CH<sub>2</sub>Cl<sub>2</sub>); IR (neat) 1715, 1625, and 830 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.73 (d,  $J=5.7$  Hz, 1H), 7.66–7.07 (m, 6H), 6.67 (d,  $J=5.7$  Hz, 1H), 4.38 (q,  $J=7.1$  Hz, 2H), 3.52 (dd,  $J=10.3, 8.5$  Hz, 1H), 3.02 (dd,  $J=10.3, 17.6$  Hz, 1H), 2.89 (dd,  $J=8.5, 17.6$  Hz, 1H), and 1.38 (t,  $J=7.1$  Hz, 3H); <sup>13</sup>C NMR  $\delta$  168.03, 156.02, 145.31, 135.89, 134.74, 134.16, 130.90, 129.57, 128.03, 61.59, 51.18, 34.50, and 23.20; MS (EI)  $m/z$  228 (M<sup>+</sup>, 2%), 213 (100), 183 (28), 155 (6), 105 (10), and 77 (5). Anal. calcd for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>: C, 78.92; H, 7.06. Found: C, 78.79; H, 7.11.

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