# Copper(I) *tert*-Butoxide-Promoted Allylation of β-Triphenylsilyl Allylic Alcohols via 1,3 $C^{sp2}$-to-O Silyl Migration

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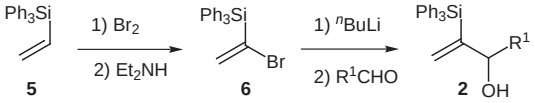
**Abstract:** The substitution of the silyl group in vinylsilanes by an allylic group proceeded when β-triphenylsilylallyl alcohols were treated with copper(I) *tert*-butoxide and allylic halides. This reaction is the first synthetic application of 1,3 $C^{sp2}$-to-O silyl migration which provides a useful method for generation of vinyl anion equivalents.

**Key words:** allylations, allylic alcohols, copper alkoxides, silyl rearrangement, silyl ethers

The Brook-type rearrangement of silicon from carbon to oxygen is a useful method for the preparation of reactive organometallic species from organosilicon compounds.[1] The generated active species have been employed for further transformations even in the case where the equilibrium is unfavorable to its formation by virtue of incorporation of a subsequent irreversible process. Although the $C^{sp3}$-to-O silyl migration has been frequently employed for organic synthesis, there has been limited synthetic application of the $C^{sp2}$-to-O silyl migration. Since this migration would be an attractive way for the generation of synthetically useful vinylmetal species,[2] we studied the copper(I) alkoxide-promoted 1,4 silyl migration from $C^{sp2}$-to-O leading to the formation of vinyl and arylcopper species.[3]

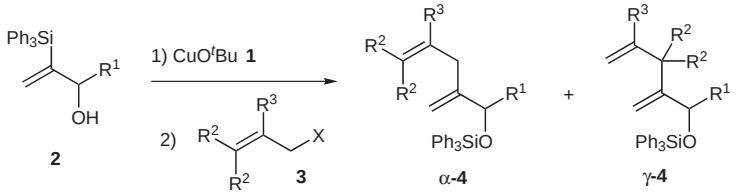
We expected that our methodology could be extended to 1,3 $C^{sp2}$-to-O silyl migration, which has not been thoroughly studied so far. Wilson et al. investigated such rearrangement of 1-[1-(trimethylsilyl)vinyl]adamantan-1-ol using potassium hydride as a base. They observed that only the protodesilylated product was formed and deuterium was not incorporated at the vinyl carbon when the reaction was quenched with $D_2O$.[2g] These results imply that a vinyl anion species generated by the silyl migration is rapidly protonated, as it forms, with the unreacted alcohol. Independently Sato and coworkers found a similar rearrangement of several 1-(hydroxyalkyl)-1-alkenylsilanes by treatment with a catalytic amount of NaH in HMPA or KH in THF.[2h,i] A formal 1,3 $C^{sp2}$-to-O silyl migration was also observed in the Red-Al® reduction of 4-siloxy propargylic alcohol, though its mechanism is ambiguous.[2j] All these preceding studies indicate that no prospect of practical use of the silyl migration in organic synthesis has yet emerged. Here we describe the copper(I) *tert*-butoxide (**1**) promoted coupling of β-triphenylsilylallyl alcohols **2** with allylic halides **3** via the 1,3 $C^{sp2}$-to-O silyl migration to form triphenylsilyl ethers of dienyl alcohols **4** (Scheme 1).

Starting materials **2** were readily prepared from commercially available triphenylvinylsilanes **5** using the literature procedures as shown in Scheme 2. The α-bromovinylsilanes **6** was obtained by treatment of **5** with bromine followed by the elimination of HBr with diethylamine.[4] The reaction of α-lithiovinylsilanes, generated by halogen–metal exchange of **6** with *n*-butyllithium, with aldehydes afforded **2**.[5]




**Scheme 2**

The coupling reactions of **2** with several allylic halides **3** were performed in the presence of copper(I) *tert*-butoxide (**1**) and the results are summarized in Table 1. Successive treatment of 5-phenyl-2-(trimethylsilyl)pent-1-en-3-ol (**2a**) with **1** (1.1 equiv), prepared in situ by reaction of cop-




**Scheme 1**

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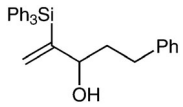
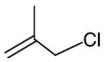
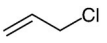
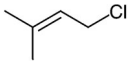
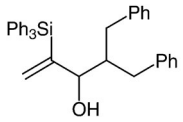
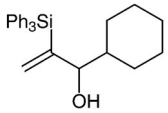
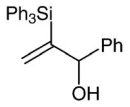
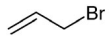
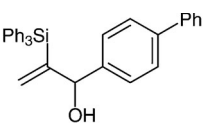
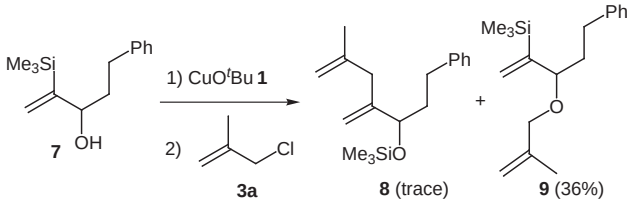
**Table 1** Copper(I) *tert*-Butoxide-Promoted Allylation of β-Triphenylsilyl Allylic Alcohols **2**[a]

| Run | Allylic Alcohol **2** | Allylic Halide **3** | Product **4** (Yield %) |
|---|---|---|---|
| 1[b] |  **2a** |  **3a** | **4a** (48) |
| 2[c] | **2a** | **3a** | **4a** (83) |
| 3 | **2a** | **3a** | **4a** (87) |
| 4 | **2a** |  **3b** | **4b** (82) |
| 5 | **2a** |  **3c** | α-**4c** (73); γ-**4c** (20) |
| 6 |  **2b** | **3a** | **4d** (90) |
| 7 | **2b** | **3b** | **4e** (81) |
| 8 | **2b** | **3c** | α-**4f** (55); γ-**4f** (22) |
| 9 |  **2c** | **3a** | **4g** (83) |
| 10 | **2c** | **3b** | **4h** (81) |
| 11 | **2c** | **3c** | α-**4i** (47); γ-**4i** (14) |
| 12 |  **2d** | **3a** | **4j** (91) |
| 13 | **2d** | **3b** | **4k** (77) |
| 14 | **2d** |  **3d** | **4k** (72) |
| 15 | **2d** | **3c** | α-**4l** (52); γ-**4l** (17) |
| 16 |  **2e** | **3a** | **4m** (75) |
| 17 | **2e** | **3b** | **4n** (66) |
| 18 | **2e** | **3c** | α-**4o** (58); γ-**4o** (16) |

[a] All reactions were performed in a procedure similar to that described in the text, unless otherwise noted.
[b] 1.5 equiv of **1** were used. The halide **3** was added 10 min after addition of **2** and the reaction was continued for 6 h.
[c] The halide **3** was added 10 min after addition of **2**.

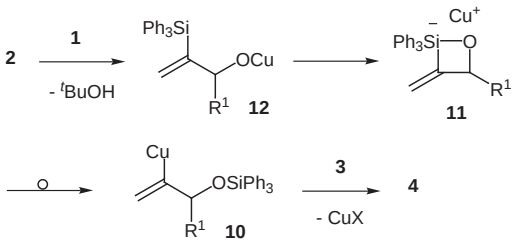
per(I) iodide with lithium *tert*-butoxide,[6] and methallyl chloride **3a** (2.0 equiv) at room temperature gave **4a** in 48% yield with a 33% recovery of the starting material **2a** (Run 1). When 2.0 equivalents of **1** were used, the yield of **2a** was significantly improved to 83% (Run 2), but the yield was not improved with further increase in the amount of **1**. Addition of a premixed solution of **2a** and **3a** to **1** gave **4a** in slightly better yield (Run 3). Under the optimized conditions, the coupling reactions of several β-triphenylsilylallyl alcohols **2** with allylic halides **3** were performed and the allylation products **4** were obtained in good to high yields. In the case of the reactions using prenyl chloride, the formal $S_N2$ and $S_N2'$ products α-**4** and γ-**4** were produced and the former was always the predominant product.

In contrast to the reactions of the triphenylsilylvinylsilane **2** described above, the similar allylation of the trimethylsilyl counterpart **7** with methallyl chloride **3a** resulted in the formation of only a trace amount of the C-allylation product **8** along with the major O-allylation product **9** (Scheme 3).




**Scheme 3**

We tentatively assume that the present allylation involves the formation of vinylcopper species **10** as illustrated in Scheme 4. The intermediary hypercoordinated silicate **11** is formed from the copper alkoxide **12** as previously suggested for the 1,3 silyl migration[2g,7] and is transformed into the vinylcopper species **10** which reacts with allylic halide **3** to give the silyl ether of dienyl alcohol **4**. The difference in the reactivity between the triphenylsilyl- and trimethylsilyl-substituted derivatives **2** and **7** could be explained by the nature of the substituents on the silyl group; the electron-withdrawing phenyl group, in contrast to the electron-donating methyl group, would stabilize the intermediate silicate **11** to facilitate the silyl migration.[5,8] Although it is unclear at present why two equivalents of copper(I) *tert*-butoxide **1** are indispensable to complete the reaction, it might be possible to assume that an additional equivalent of **1** takes part in an activation of organocopper species through cuprate formation. Unlike in the case of vinylmetal species formed by the silyl migration from alkali metal alkoxides, the protonation of the vinylcopper species **10** thus generated with the unreacted alcohol **2** or *tert*-butyl alcohol produced during the reaction would be relatively slow.




**Scheme 4**

In conclusion, we have demonstrated the first synthetic application of 1,3 $C^{sp2}$-to-O silyl migration, which enable us to prepare vinylcopper species from various β-triphenylsilylallyl alcohols. The generated vinylmetal species react with allylic halides to give the coupling products. Further study on the preparation of organometallic species by silyl migration is currently underway.

$^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) spectra were recorded using TMS as internal standard. Chemical shifts (δ) are quoted in parts per million from TMS for $^1$H NMR and $CDCl_3$ for $^{13}$C NMR spectra. IR absorptions are reported in cm$^{-1}$. All reactions were performed under argon in dried glassware. DMF was distilled from $CaH_2$ under reduced pressure. Column chromatography was carried out using Merck aluminum oxide 90 deactivated by addition of $H_2O$ (5 wt%).

**Copper(I) *tert*-Butoxide-Promoted Allylation of the β-Triphenylsilylallyl Alcohol (2a) with Methallyl Chloride (3a); 2-Methyl-4-[3-phenyl-1-(triphenylsiloxy)propyl]penta-1,4-diene (4a); Typical Procedure**

CuI (76 mg, 0.40 mmol) and DMF (0.6 mL) were placed in a flask and cooled to 0 °C. *t*-BuOLi (0.94 M in THF, 0.47 mL, 0.44 mmol) was added under argon and the mixture was stirred for 30 min at 25 °C. A DMF (1.4 mL) solution of **2a** (84 mg, 0.20 mmol) and **3a** (36 mg, 0.40 mmol) was added to the mixture. After stirring for 3 h, the reaction mixture was diluted with hexane. The mixture was applied to a filter pad of Celite to remove copper salts and the pad was washed with hexane, $CH_2Cl_2$, and $Et_2O$. The solvent was removed under reduced pressure and the residue was purified by chromatography (hexane) to yield the triphenylsilyl ether **4a** (83 mg, 87%). In a similar manner, the triphenylsilyl ethers of dienyl alcohols **4b**–**o** were obtained.

IR (neat): 3068, 2929, 1648, 1590, 1454, 1428, 1116, 903, 741, 699 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 1.58 (s, 3 H), 1.86 (dt, *J* = 5.7, 8.3 Hz, 2 H), 2.43–2.59 (m, 2 H), 2.69 (d, *J* = 15.2 Hz, 1 H), 2.78 (d, *J* = 15.2 Hz, 1 H), 4.39 (t, *J* = 5.6 Hz, 1 H), 4.64 (d, *J* = 1.1 Hz, 1 H), 4.76 (s, 1 H), 4.88 (d, *J* = 1.3 Hz, 1 H), 5.12 (d, *J* = 0.9 Hz, 1 H), 6.95–7.01 (m, 2 H), 7.08–7.24 (m, 3 H), 7.32–7.46 (m, 9 H), 7.60–7.67 (m, 6 H).

$^{13}$C NMR ($CDCl_3$): δ = 21.8, 31.0, 37.3, 40.4, 76.0, 112.5, 113.1, 125.6, 127.7, 128.2, 128.3, 129.9, 134.6, 135.6, 142.3, 143.0, 147.2.

Anal. Calcd for $C_{33}H_{34}OSi$: C, 83.49; H, 7.22. Found: C, 83.51; H, 7.38.

**2-[3-Phenyl-1-(triphenylsiloxy)propyl]penta-1,4-diene (4b)**

IR (neat): 3068, 2934, 1428, 1117, 1076, 913, 741, 699 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 1.77–1.96 (m, 2 H), 2.46–2.54 (m, 2 H), 2.70 (dd, *J* = 7.5, 8.2 Hz, 1 H), 2.87 (dd, *J* = 6.5, 8.2 Hz, 1 H), 4.36 (t, *J* = 6.0 Hz, 1 H), 4.82 (d, *J* = 1.7 Hz, 1 H), 4.94–5.03 (m, 3 H), 5.62–5.76 (m, 1 H), 6.97–7.02 (m, 2 H), 7.10–7.26 (m, 3 H), 7.32–7.47 (m, 9 H), 7.57–7.67 (m, 6 H).

$^{13}$C NMR ($CDCl_3$): δ = 31.2, 35.2, 37.4, 76.7, 112.2, 116.4, 125.6, 127.7, 128.2, 128.3, 129.9, 134.5, 135.5, 136.1, 142.1, 148.5.

Anal. Calcd for $C_{32}H_{32}OSi$: C, 83.43; H, 7.00. Found: C, 83.20; H, 7.34.

**Mixture of 5-Methyl-2-[3-phenyl-1-(triphenylsiloxy)propyl]hexa-1,4-diene (α-4c) and 3,3-Dimethyl-2-[3-phenyl-1-(triphenylsiloxy)propyl]penta-1,4-diene (γ-4c)**

IR (neat): 3068, 3026, 2927, 1453, 1428, 1116, 1076, 741, 698 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 0.92 (s, 0.66 H), 1.00 (s, 0.66 H), 1.53 (s, 2.34 H), 1.68 (s, 2.34 H), 1.78–1.92 (m, 2 H), 2.38–2.82 (m, 3.56 H), 4.36 (t, *J* = 6.0 Hz, 0.78 H), 4.41 (t, *J* = 5.0 Hz, 0.22 H), 4.73–4.82 (m, 1.22 H), 4.94 (s, 0.78 H), 5.06 (dd, *J* = 7.3, 7.3 Hz, 0.78 H), 5.17 (d, *J* = 0.9 Hz, 0.22 H), 5.51 (dd, *J* = 10.6, 17.4 Hz, 0.22 H), 5.54 (s, 0.22 H), 6.93–7.03 (m, 2 H), 7.08–7.24 (m, 3 H), 7.31–7.46 (m, 9 H), 7.56–7.69 (m, 6 H).

$^{13}$C NMR ($CDCl_3$): δ = 17.6, 25.7, 26.2, 26.6, 29.6, 31.3, 31.4, 37.5, 41.0, 41.2, 72.1, 76.7, 110.8, 111.0, 111.4, 121.6, 125.5, 125.6, 127.67, 127.71, 128.18, 128.22, 128.30, 128.33, 129.9, 133.0, 134.6, 134.8, 135.5, 135.7, 142.3, 142.6, 146.8, 149.0, 157.0.

Anal. Calcd for $C_{34}H_{36}OSi$: C, 83.56; H, 7.42. Found: C, 83.17; H, 7.52.

**2-Methyl-4-[3-phenyl-2-phenethyl-1-(triphenylsiloxy)propyl]penta-1,4-diene (4d)**

IR (neat): 3068, 3025, 2925, 1495, 1453, 1428, 1116, 898, 741, 699 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 1.34 (s, 3 H), 2.02–2.16 (m, 1 H), 2.28 (d, *J* = 14.5 Hz, 1 H), 2.44 (d, *J* = 15.0 Hz, 1 H), 2.49–2.68 (m, 3 H), 3.04 (dd, *J* = 3.7, 13.9 Hz, 1 H), 4.21 (s, 1 H), 4.29 (s, 1 H), 4.55 (s, 1 H), 4.88 (s, 1 H), 5.28 (s, 1 H), 6.55–6.59 (m, 2 H), 7.00–7.47 (m, 17 H), 7.58–7.69 (m, 6 H).

$^{13}$C NMR ($CDCl_3$): δ = 21.6, 34.5, 36.1, 42.1, 46.5, 75.7, 113.1, 113.3, 125.5, 125.6, 127.7, 128.0, 128.2, 129.0, 129.2, 129.9, 134.6, 135.8, 141.0, 141.7, 142.5, 146.5.

Anal. Calcd for $C_{40}H_{40}OSi$: C, 85.06; H, 7.14. Found: C, 85.09; H, 7.20.

**2-[3-Phenyl-2-phenethyl-1-(triphenylsiloxy)propyl]penta-1,4-diene (4e)**

IR (neat): 3068, 3025, 2925, 1495, 1453, 1428, 1116, 911, 741, 700 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 2.05–2.17 (m, 1 H), 2.27 (dd, *J* = 7.7, 15.8 Hz, 1 H), 2.48–2.62 (m, 3 H), 2.69 (dd, *J* = 8.5, 11.2 Hz, 1 H), 3.01 (dd, *J* = 4.6, 13.9 Hz, 1 H), 4.27 (d, *J* = 1.5 Hz, 1 H), 4.64 (d, *J* = 17.1 Hz, 1 H), 4.78 (d, *J* = 10.1 Hz, 1 H), 4.84 (s, 1 H), 5.13 (s, 1 H), 5.20–5.36 (m, 1 H), 6.62–6.67 (m, 2 H), 7.02–7.47 (m, 17 H), 7.63 (dd, *J* = 1.5, 7.9 Hz, 6 H).

$^{13}$C NMR ($CDCl_3$): δ = 34.8, 36.1, 37.2, 46.7, 113.2, 116.3, 125.5, 125.6, 127.7, 128.0, 128.2, 129.0, 129.2, 129.9, 134.6, 135.6, 135.7, 141.0, 141.5, 147.7.

Anal. Calcd for $C_{39}H_{38}OSi$: C, 85.04; H, 6.95. Found: C, 84.73; H, 6.94.

**Mixture of 5-Methyl-2-[3-phenyl-2-phenethyl-1-(triphenylsiloxy)propyl]hexa-1,4-diene (α-4f) and 3,3-Dimethyl-2-[3-phenyl-2-phenethyl-1-(triphenylsiloxy)propyl]penta-1,4-diene (γ-4f)**

IR (neat): 3067, 3025, 2969, 2926, 1495, 1453, 1428, 1116, 1038, 983, 909, 741, 700 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 0.47 (s, 0.87 H), 0.71 (s, 0.87 H), 1.31 (s, 2.13 H), 1.56 (s, 2.13 H), 1.96–2.18 (m, 1 H), 2.30 (dd, *J* = 7.6, 16.2 Hz, 0.71 H), 2.40–2.77 (m, 3.71 H), 3.03 (dd, *J* = 4.2, 14.1 Hz, 0.71 H), 3.24 (dd, *J* = 2.5, 13.8 Hz, 0.29 H), 4.27 (s, 0.71 H), 4.47 (s, 0.29 H), 4.58 (dd, *J* = 1.2, 17.3 Hz, 0.29 H), 4.64 (dd, *J* = 1.2, 10.5 Hz, 0.29 H), 4.68 (dd, *J* = 7.7, 7.7 Hz, 0.71 H), 4.83 (s, 0.71 H), 5.13 (s, 0.71 H), 5.14 (s, 0.29 H), 5.32 (dd, *J* = 10.5, 17.3 Hz, 0.29 H), 5.55 (s, 0.29 H), 6.40–6.46 (m, 0.58 H), 6.54–6.64 (m, 1.42 H), 6.93–7.75 (m, 23 H).

$^{13}$C NMR ($CDCl_3$): δ = 17.4, 25.2, 25.6, 27.9, 31.7, 33.2, 34.7, 36.1, 36.3, 40.7, 46.6, 47.1, 72.9, 76.5, 110.4, 112.5, 113.3, 121.5, 125.4, 125.45, 125.53, 127.69, 127.71, 127.8, 128.0, 128.17, 128.21, 129.0, 129.2, 129.3, 129.4, 129.82, 129.84, 132.7, 134.7, 134.8, 135.5, 135.7, 135.9, 141.00, 141.04, 141.7, 142.2, 147.4, 148.4, 154.8.

Anal. Calcd for $C_{41}H_{42}OSi$: C, 85.07; H, 7.31. Found: C, 85.05; H, 7.52.

**2-[Cyclohexyl(triphenylsiloxy)methyl]-4-methylpenta-1,4-diene (4g)**

IR (neat): 3067, 2920, 1648, 1429, 1119, 1038, 894, 852, 740, 700 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 0.77–0.95 (m, 2 H), 1.00–1.22 (m, 3 H), 1.32–1.75 (m, 5 H), 1.54 (s, 3 H), 1.93 (br d, *J* = 12.5 Hz, 1 H), 2.56 (d, *J* = 16.1 Hz, 1 H), 2.71 (d, *J* = 15.6 Hz, 1 H), 4.01 (d, *J* = 6.6 Hz, 1 H), 4.57 (s, 1 H), 4.75 (s, 1 H), 4.76 (s, 1 H), 4.88 (s, 1 H), 7.30–7.45 (m, 9 H), 7.58–7.66 (m, 6 H).

$^{13}$C NMR ($CDCl_3$): δ = 22.0, 26.3, 26.4, 26.5, 28.7, 29.7, 40.1, 41.8, 82.1, 112.7, 113.3, 127.6, 129.7, 134.8, 135.8, 143.2, 146.7.

Anal. Calcd for $C_{31}H_{36}OSi$: C, 82.25; H, 8.02. Found: C, 81.90; H, 8.06.

**2-[Cyclohexyl(triphenylsiloxy)methyl]penta-1,4-diene (4h)**

IR (neat): 3069, 2925, 2851, 1448, 1428, 1116, 998, 913, 846, 741, 699 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 0.70–0.91 (m, 2 H), 0.96–1.27 (m, 3 H), 1.34–1.73 (m, 5 H), 2.03 (br d, *J* = 12.8 Hz, 1 H), 2.58 (dd, *J* = 7.5, 16.9 Hz, 1 H), 2.84 (dd, *J* = 6.5, 16.8 Hz, 1 H), 3.94 (d, *J* = 7.7 Hz, 1 H), 4.71 (ddd, *J* = 1.7, 1.7, 1.7 Hz, 1 H), 4.74 (s, 1 H), 4.92 (d, *J* = 18.3 Hz, 1 H), 4.97 (d, *J* = 10.3 Hz, 1 H), 5.51–5.64 (m, 1 H), 7.30–7.45 (m, 9 H), 7.57–7.64 (m, 6 H).

$^{13}$C NMR ($CDCl_3$): δ = 26.16, 26.20, 26.5, 29.38, 29.43, 34.9, 41.7, 82.8, 113.0, 116.4, 127.6, 129.7, 134.7, 135.7, 136.0, 148.0.

Anal. Calcd for $C_{30}H_{34}OSi$: C, 82.14; H, 7.81. Found: C, 82.00; H, 7.96.

**Mixture of 5-Methyl-2-[cyclohexyl(triphenylsiloxy)methyl]hexa-1,4-diene (α-4i) and 3,3-Dimethyl-2-[cyclohexyl(triphenylsiloxy)methyl]penta-1,4-diene (γ-4i)**

IR (neat): 3068, 2925, 2851, 1428, 1116, 901, 700 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 0.71–1.83 (m, 9.46 H), 0.89 (s, 0.69 H), 0.96 (s, 0.69 H), 1.40 (d, *J* = 12.1 Hz, 0.77 H), 1.50 (s, 2.31 H), 1.67 (s, 2.31 H), 2.00 (br d, *J* = 11.9 Hz, 0.77 H), 2.57 (dd, *J* = 7.4, 17.0 Hz, 0.77 H), 2.71 (dd, *J* = 7.1, 17.0 Hz, 0.77 H), 3.95 (d, *J* = 7.3 Hz, 0.77 H), 4.23 (s, 0.23 H), 4.67–4.81 (m, 2 H), 4.96 (dd, *J* = 7.3, 7.3 Hz, 0.77 H), 5.15 (d, *J* = 1.3 Hz, 0.23 H), 5.36 (s, 0.23 H), 5.48 (dd, *J* = 10.5, 17.4 Hz, 0.23 H), 7.30–7.44 (m, 9 H), 7.58–7.66 (m, 6 H).

$^{13}$C NMR ($CDCl_3$): δ = 17.6, 25.7, 26.2, 26.3, 26.5, 26.9, 29.26, 29.31, 29.6, 31.5, 41.0, 41.9, 43.0, 76.8, 82.8, 110.4, 111.9, 112.3, 121.6, 127.48, 127.54, 129.66, 129.68, 132.7, 134.8, 135.1, 135.8, 135.9, 147.3, 148.4, 154.9.

Anal. Calcd for $C_{32}H_{38}OSi$: C, 82.35; H, 8.21. Found: C, 82.32; H, 8.25.

**2-Methyl-4-[phenyl(triphenylsiloxy)methyl]penta-1,4-diene (4j)**

IR (neat): 3069, 2913, 1453, 1428, 1189, 1116, 1028, 894, 861, 741, 698 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 1.41 (s, 3 H), 2.38 (d, *J* = 15.2 Hz, 1 H), 2.61 (d, *J* = 15.2 Hz, 1 H), 4.49 (s, 1 H), 4.66 (s, 1 H), 4.87 (s, 1 H), 5.27 (s, 1 H), 5.41 (s, 1 H), 7.17–7.42 (m, 14 H), 7.51–7.60 (m, 6 H).

$^{13}$C NMR ($CDCl_3$): δ = 21.6, 40.4, 78.0, 111.3, 112.8, 126.9, 127.2, 127.7, 127.9, 129.9, 134.3, 135.5, 142.2, 143.0, 148.1.

Anal. Calcd for $C_{31}H_{30}OSi$: C, 83.36; H, 6.77. Found: C, 83.35; H, 7.10.

**2-[Phenyl(triphenylsiloxy)methyl]penta-1,4-diene (4k)**

IR (neat): 3069, 1429, 1117, 1065, 914, 741, 698 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 2.42 (dd, *J* = 7.3, 16.3 Hz, 1 H), 2.70 (dd, *J* = 6.4, 16.5 Hz, 1 H), 4.82 (dd, *J* = 0.6, 1.6 Hz, 1 H), 4.83 (ddd, *J* = 1.7, 3.6, 17 Hz, 1 H), 4.90 (dddd, *J* = 1.1, 1.1, 2.2, 10.1 Hz, 1 H), 5.25 (dd, *J* = 1.1, 1.5 Hz, 1 H), 5.31 (s, 1 H), 5.53 (dddd, *J* = 6.7, 7.2, 10.2, 17.1 Hz, 1 H), 7.17–7.43 (m, 14 H), 7.53–7.60 (m, 6 H).

$^{13}$C NMR ($CDCl_3$): δ = 35.3, 78.7, 111.2, 116.3, 126.6, 127.1, 127.7, 128.0, 129.9, 134.2, 135.5, 135.8, 142.2, 149.2.

Anal. Calcd for $C_{30}H_{28}OSi$: C, 83.29; H, 6.52. Found: C, 83.32; H, 6.58.

**Mixture of 5-Methyl-2-[phenyl(triphenylsiloxy)methyl]hexa-1,4-diene (α-4l) and 3,3-Dimethyl-2-[phenyl(triphenylsiloxy)methyl]penta-1,4-diene (γ-4l)**

IR (neat): 3068, 3050, 3027, 3000, 2968, 2925, 2855, 1428, 1117, 1085, 1063, 1028, 741, 698 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 0.76 (s, 0.72 H), 0.89 (s, 0.72 H), 1.36 (s, 2.28 H), 1.60 (s, 2.28 H), 2.38 (dd, *J* = 7.9, 16.9 Hz, 0.76 H), 2.59 (dd, *J* = 6.7, 16.8 Hz, 0.76 H), 4.68 (dd, *J* = 1.3, 10.5 Hz, 0.24 H), 4.71 (dd, *J* = 1.3, 17.6 Hz, 0.24 H), 4.80 (d, *J* = 1.5 Hz, 0.76 H), 4.91 (dd, *J* = 7.2, 7.2 Hz, 0.76 H), 5.22 (s, 0.76 H), 5.26 (d, *J* = 1.3 Hz, 0.24 H), 5.30 (s, 1 H), 5.38 (dd, *J* = 10.5, 17.4 Hz, 0.24 H), 5.88 (s, 0.24 H), 7.16–7.59 (m, 20 H).

$^{13}$C NMR ($CDCl_3$): δ = 17.4, 25.6, 26.5, 27.3, 29.8, 41.2, 75.5, 78.9, 110.3, 110.6, 110.8, 121.4, 126.6, 127.1, 127.6, 127.7, 127.87, 127.90, 128.2, 129.8, 129.9, 133.0, 134.3, 134.4, 135.5, 135.56, 135.61, 142.4, 143.1, 147.1, 149.9, 156.2.

Anal. Calcd for $C_{32}H_{32}OSi$: C, 83.43; H, 7.00. Found: C, 83.22; H, 7.09.

**2-[4-Biphenylyl(triphenylsiloxy)methyl]-4-methylpenta-1,4-diene (4m)**

IR (neat): 3069, 2916, 1486, 1428, 1117, 1074, 864, 765, 741, 699 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 1.26 (s, 3 H), 2.43 (d, *J* = 15.2 Hz, 1 H), 2.66 (d, *J* = 15.4 Hz, 1 H), 4.53 (s, 1 H), 4.69 (s, 1 H), 4.91 (s, 1 H), 5.32 (s, 1 H), 5.46 (s, 1 H), 7.26–7.47 (m, 16 H), 7.58 (dd, *J* = 1.6, 8.0 Hz, 8 H).

$^{13}$C NMR ($CDCl_3$): δ = 21.6, 32.9, 40.6, 77.8, 111.4, 112.9, 126.6, 127.0, 127.1, 127.4, 127.7, 128.7, 129.9, 134.2, 135.5, 140.0, 141.0, 141.3, 143.0, 148.0.

Anal. Calcd for $C_{37}H_{34}OSi$: C, 85.01; H, 6.56. Found: C, 85.31; H, 6.71.

**2-[Biphenylyl(triphenylsiloxy)methyl]penta-1,4-diene (4n)**

IR (neat): 3068, 3050, 3027,1486, 1428, 1117, 1074, 912, 858, 765, 742, 712, 698 cm$^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 2.48 (dd, *J* = 7.5, 16.5 Hz, 1 H), 2.75 (dd, *J* = 6.4, 16.5 Hz, 1 H), 4.80–4.95 (m, 3 H), 5.29 (s, 1 H), 5.37 (s, 1 H), 5.50–5.64 (m, 1 H), 7.26–7.49 (m, 16 H), 7.53–7.63 (m, 8 H).

$^{13}$C NMR ($CDCl_3$): δ = 35.4, 78.5, 111.3, 116.4, 126.7, 127.0, 127.08, 127.13, 127.7, 128.7, 129.9, 134.2, 135.5, 135.8, 140.0, 141.0, 141.3, 149.2.

Anal. Calcd for $C_{36}H_{32}OSi$: C, 84.99; H, 6.34. Found: C, 85.20; H, 6.39.

**Mixture of 5-Methyl-2-[biphenylyl(triphenylsiloxy)methyl]hexa-1,4-diene (α-4o) and 3,3-Dimethyl-2-[biphenylyl(triphenylsiloxy)methyl]penta-1,4-diene (γ-4o)**

IR (neat): 3068, 2968, 2913, 1486, 1428, 1117, 1072, 862, 764, 741, 711 $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ = 0.80 (s, 0.66 H), 0.93 (s, 0.66 H), 1.38 (s, 2.34 H), 1.61 (s, 2.34 H), 2.43 (dd, *J* = 8.1, 16.5 Hz, 0.78 H), 2.63 (dd, *J* = 6.4, 16.9 Hz, 0.78 H), 4.71 (dd, *J* = 1.3, 10.5 Hz, 0.22 H), 4.74 (dd, *J* = 1.3, 17.4 Hz, 0.22 H), 4.83 (d, *J* = 1.7 Hz, 0.78 H), 4.93 (dd, *J* = 7.3, 7.3 Hz, 0.78 H), 5.25 (s, 0.78 H), 5.29 (dd, *J* = 1.0, 1.0 Hz, 0.22 H), 5.34 (s, 1 H), 5.42 (dd, *J* = 10.5, 17.4 Hz, 0.22 H), 5.91 (s, 0.22 H), 7.17–7.62 (m, 24 H).

$^{13}$C NMR ($CDCl_3$): δ = 17.5, 25.6, 26.6, 27.3, 29.9, 41.3, 75.2, 78.7, 110.4, 110.7, 110.9, 121.4, 126.6, 126.7, 126.99, 127.01, 127.1, 127.6, 127.65, 127.69, 128.6, 128.68, 128.70, 129.8, 129.9, 133.0, 134.3, 134.4, 135.5, 135.6, 139.9, 140.0, 140.97, 141.02, 141.5, 142.2, 147.1, 149.9, 156.2.

Anal. Calcd for $C_{38}H_{36}OSi$: C, 85.03; H, 6.76. Found: C, 84.71; H, 7.00.

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