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Six-Membered Silacycle Odorants: Synthesis and Olfactory Characterization of Si Analogues of Artemone, β-Dynascone, and Herbac

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Si-Artemone (**4a**), Si-β-Dynascone (**5a**), and Si-Herbac **6a**, which are Si analogues of the commercial fragrance ingredients Artemone (**1**), β-Dynascone (**2**), and Herbac (**3**), were synthesized expediently by the insertion of terminal alkynes into silacyclobutane **7a**. The sensory characterization results revealed that **4a** and **6a** had quite similar odor qualities compared with those of **1** and **3**, whereas **5a** had a totally different odor character relative to that of **2**. In terms of the odor threshold values, that of **4a** was slightly more substantive than that of its carbon analogue **1**, **6a** was less potent than its carbon analogue **3**, whereas that of **5a** was approximately one-sixth that of its carbon analogue **2**.

Introduction

The search to correlate the molecular structures and odors of chemical compounds has captivated chemists since the birth of synthetic organic chemistry in the middle of the nineteenth century.[1,2] Despite a great deal of research on structure–odor relationships, the hunt for new or improved odorants remains heavily dependent on structural similarities with known odorants rather than on knowledge of the mechanism of olfaction.[2,3] In this context, sila substitution,[1] in which a *gem*-dimethyl-substituted carbon center is replaced by a silicon atom, represents a promising avenue for the exploration of structure–odor relationships and the discovery of new odorants.[2b,4] The pioneering work of Wannagat,[5] Tacke,[6] and their co-workers demonstrated that sila substitution in known odorants would change and ideally optimize their olfactory properties.[7] Evidence has also accumulated that organosilicon molecules show no special features in their toxicology profiles compared with those of their parent carbon compounds.[8]

A *gem*-dimethyl-substituted six-membered ring motif is present in numerous carotenoid-derived odorants as well as many synthetic fragrance ingredients such as Artemone, Dynascone, Herbac, Aphermate, Romandolide, and Helvetolide;[1,9] however, the incorporation of Si into these compounds by sila substitution to give six-membered silacycle odorants has rarely been explored. Therefore, the objective of the present study was to synthesize and characterize the six-membered silacycle odorants **4a**, **5a**, and **6a**, for which the carbon relatives **1**,[10] **2**,[1] and **3**[11] are fragrance ingredients produced by Givaudan, Firmenich, and IFF, respectively (Figure 1).

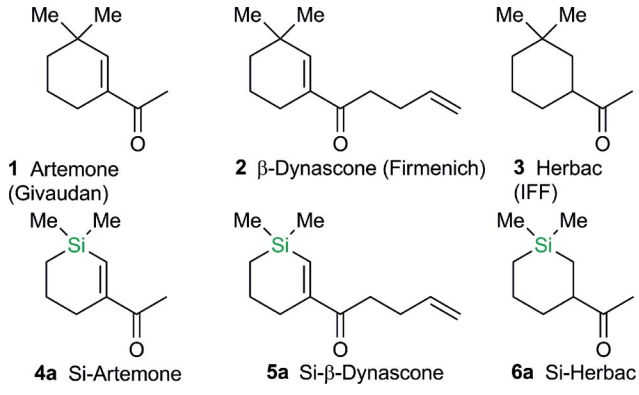

Figure 1. Six-membered carbocycles and corresponding silacycle odorants.

Results and Discussion

Four-membered silacycles are versatile building blocks in organosilicon chemistry and have many applications in organic, organometallic, and polymer chemistry.[12] The insertion reaction of alkynes into the Si–C bonds of four-membered silacycles,[13,14] that is, silacyclobutane and silacyclo-

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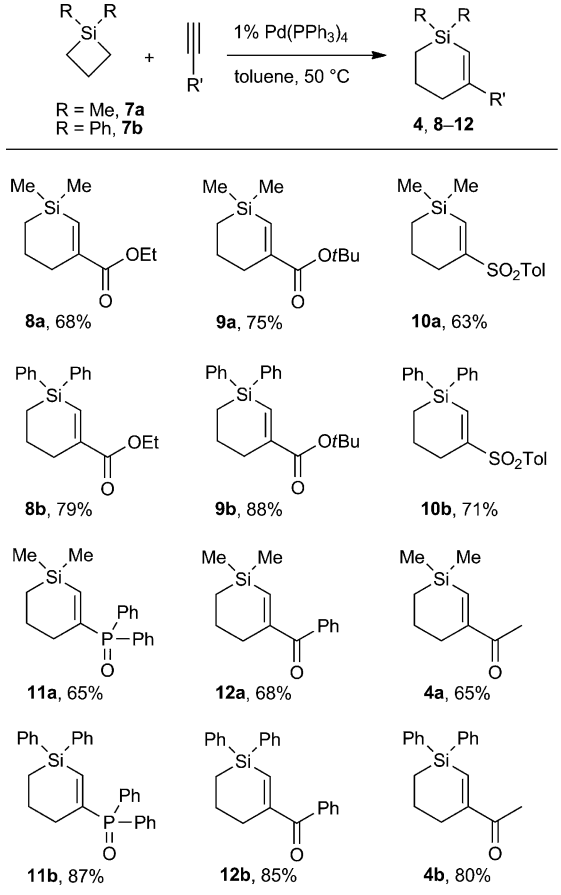
butene, is a short and elegant route to six-membered silacycles.[15]

Our interest in six-membered silacycle odorants motivated us to further investigate this insertion reaction. A variety of transition-metal catalysts, phosphine ligands, and reaction conditions have been tested. The screening results showed that among the nickel, palladium, and platinum complexes tested, $Pd(PPh_3)_4$ gave the highest yields, whereas other palladium catalysts only led to the formation of silacyclohexenes in less than 40% yields. No ring expansion occurred with nickel and platinum catalysts in the presence of phosphine ligands. Under the optimized conditions, a variety of terminal alkynes with electron-deficient groups were subjected to the ring expansions of silacyclobutanes **7a** and **7b**. These reactions occurred smoothly to afford the six-membered silacycles **4** and **8**–**12** in good to excellent yields (Scheme 1).



Scheme 1. Insertion reaction of terminal alkynes with **7a** and **7b**.

The generally superior performance of silacyclobutane **7b** to that of silacyclobutane **7a** implies that the bulky silyl group facilitates the reductive elimination rather than a β-H elimination process to afford silacyclohexene products. With a boiling point of 80 °C, silacyclobutane **7a** readily evaporated and escaped from the heating reaction systems. With regard to the terminal alkyne, $HC{\equiv}CSO_2Tol$ (SO_2Tol = tosyl) is much more reactive than diphenylphosphinoylethyne, the reactivity of which is comparable to that of propiolates and acetylenic ketones. For propiolates, the alkoxy group greatly influenced the insertion reaction yield. When $HC{\equiv}CCH(OEt)_2$ and HC≡COEt were employed, **7a** and **7b** disappeared, and six-membered silacycles were not detected.

As a representative case, the structure of **10b** was also confirmed by single-crystal analysis (Figure 2). The result clearly showed that the tosyl group was located at the β-position of the quaternary silicon center, which verifies that the alkyne adopts a position to put the electron-deficient group at the β-position to the Si atom during the insertion process.[13,14] To the best of our knowledge, the single-crystal structure of a six-membered silacycle as the insertion product of an unsymmetric alkyne into a four-membered silacycle has never been reported.

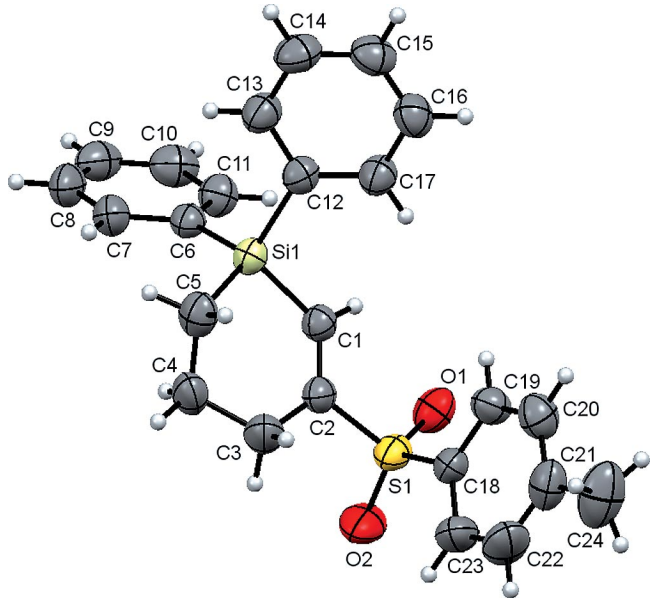
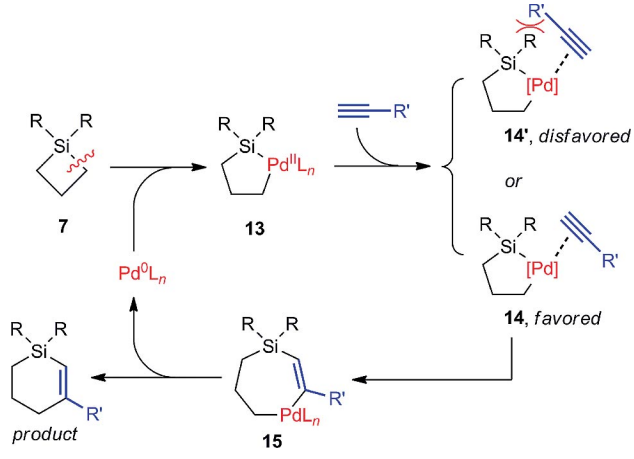


Figure 2. Crystal structure of **10b**.

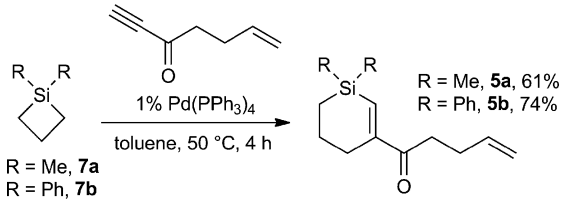
The regioselectivity for terminal alkyne insertion into the Si–C bond of silacyclobutane could be explained by the proposed mechanism shown in Scheme 2, which is similar to those reported previously.[13,14] Firstly, the oxidative in-



Scheme 2. Proposed reaction mechanism.

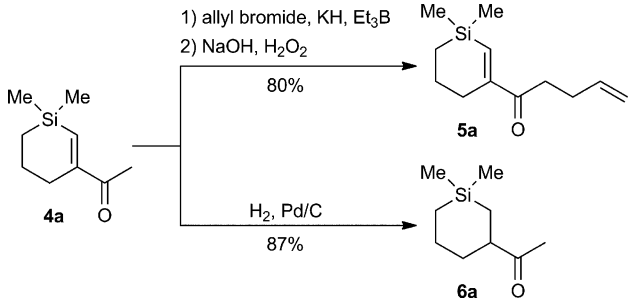
sertion of the Pd^0 species into the Si–C bond of **7** affords the five-membered palladasilacycle **13**. Then, the alkyne coordinates to the Pd center and favors the conformation with less steric repulsion (**14**/**14′**), from which the insertion of the C≡C bond occurs to provide the seven-membered palladasilacycle **15**. Finally, the reductive elimination of the Pd^{II} species gives the final six-membered silacycle and regenerates the Pd^0 species.

To further demonstrate the usefulness of this methodology for the preparation of Si-based odorants, hept-6-en-1-yn-3-one was obtained from its alcohol precursor[16] and subjected to the insertion process with **7a** and **7b** to provide the six-membered silacycles **5a** and **5b** (Scheme 3). Notably, **5a** is an Si analogue of β-Dynascone (**2**), which has a floral fruity, allyl ionone type note. Compound **2** combined with its stronger α isomer has been used as a captive material by Firmenich.[2b]



Scheme 3. Synthesis of Si analogues of β-Dynascone.

Furthermore, Artemone (**1**) is also known as dehydroherbac and has been employed as an ideal starting material for the synthesis of some common fragrance ingredients, for example, Dynascone, Herbac, Aphermate, Romandolide, and Helvetolide.[1,15] Thus, **4a** was considered likewise as an intermediate for the synthesis of related six-membered silacycle odorants. An initial attempt was made to synthesize Si-β-Dynascone (**5a**). As depicted in Scheme 4, **4a** readily reacted with allyl bromide in the presence of KH and Et_3B to furnish **5a** in 80% isolated yield. As the laborious preparation of a terminal acetylenic ketone is avoided, this reaction procedure seems more convenient than the above-mentioned insertion reaction. Moreover, **4a** was subjected to a Pd/C-catalyzed hydrogenation process,[17] and Si-Herbac (**6a**) was easily accessible in 87% yield (Scheme 4). Compound **6a** is an Si analogue of Herbac (**3**), which possesses a herbal, woody note and is commercially available from IFF.[10]



Scheme 4. Derivatization of Si-Artemone **4a**.

The olfactory properties of **1**, **2**, **3**, **4a**, **5a**, and **6a** were determined by using 10% solutions of the respective fragrances in EtOH applied to smelling blotters. As can be seen from Figure 3, a herbal, agrestic, thujone odor character was found for **1**, a floral, fruity, green character was found for **2**, and a herbal, woody character was found for **3**; the odor character was herbal and cedarwood for **4a**, pineapple for **5a**, and herbal, minty for **6a**. These results demonstrated that **4a** and **6a** had quite similar odor qualities compared with those of their carbon analogues **1** and **3**, whereas **5a** had a totally different odor character than that of **2**. By application of GC olfactometry,[9a] the odor detection threshold values were assigned to be 3.6 ng L^{-1} air for **1**, 37 ng L^{-1} air for **2**, and 0.74 ng L^{-1} air **3**, whereas those for **4a**, **5a**, and **6a** were 1.4, 5.9, and 1.9 ng L^{-1} air, respectively. Therefore, **4a** was slightly more substantive than its carbon analogue **1**, compound **6a** was less potent than its carbon analogue **3**, whereas the odor threshold of **6a** was approximately one-sixth that of its carbon analogue **2**.

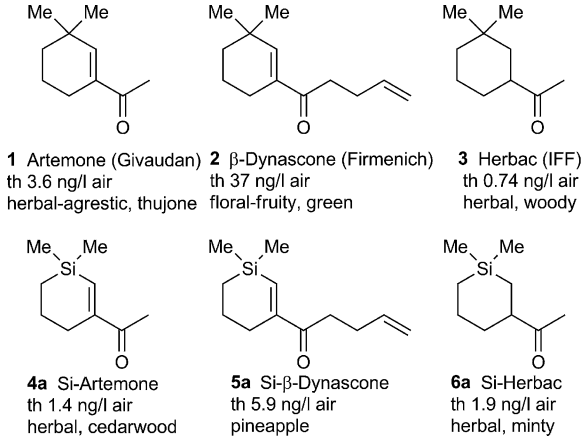


Figure 3. Olfactory properties of **1**, **2**, **3**, **4a**, **5a**, and **6a**.

Conclusions

We have synthesized the six-membered silacycle odorants **4a**, **5a**, and **6a** in high efficiency by insertion reactions of terminal alkynes with silacyclobutane **7a**; their carbon counterparts **1**, **2**, and **3** demand much more laborious synthetic procedures. With regard to their sensory character, **4a** and **6a** had quite similar odor qualities compared with those of their carbon analogues **1** and **3**, whereas **5a** had a totally different odor character relative to that of **2**. In terms of the odor detection threshold values, **4a** was slightly more substantive than its carbon analogue **1**, **6a** was less potent than its carbon analogue **3**, and that of **6a** was approximately one-sixth that of its carbon analogue **2**.

Experimental Section

General: Both silacyclobutanes **7a** and **7b** were conveniently synthesized by bench-scale[18] and large-scale[19] processes. Artemone (**1**) was also synthesized according to a published procedure.[20] Unless otherwise noted, all other chemicals were commercially available and used without further purification. Toluene was heated to reflux

and distilled from sodium benzophenone ketyl under nitrogen. Column chromatography was performed with silica gel (100–200 mesh, J & K Scientific). ^{1}H and ^{13}C NMR spectra were recorded with $CDCl_3$ as the solvent (^{1}H, 300 or 400 MHz; ^{13}C 75.5 or 100 MHz). Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ = 7.26 ppm), internal $CDCl_3$ (^{13}C, δ = 77.00 ppm), or external tetramethylsilane (TMS; ^{29}Si, δ = 0.00 ppm). HRMS was performed with a VG-ZAB-HS instrument. Elemental analysis of all new compounds was performed with an Elementar Vario EL instrument. The sensory properties of all odorants were determined by six expert perfumers with 10% solutions of the respective compounds in ethanol applied to smelling blotters. The odor thresholds were determined by GC olfactometry:[9a] different dilutions of the sample substances were injected into a GC instrument in descending order until the six panelists evaluating the thresholds in blind tests failed to detect the odor impression at the correct retention time. The reported threshold values are the geometrical means of the different values of all individual panelists, and the standard deviations for each panelist are below 2.0.

Typical Procedure for the Insertion Reaction of Terminal Alkynes with Silacyclobutanes in the Presence of Pd(PPh$_3$)$_4$: A catalytic amount of Pd(PPh$_3$)$_4$ (12 mg, 0.01 mmol) was added to a solution of silacyclobutane **7a** or **7b** (1.0 mmol) and a terminal alkyne (1.0 mmol) in toluene (5 mL) under nitrogen. The pale yellow mixture was then heated at 50 °C, stirred, and monitored by TLC or GC. Once **7a**, **7b**, or the terminal alkyne had disappeared, the reaction mixture was cooled and filtered through a thin pad of silica gel, and the dark brown mixture was concentrated. The resulting silacyclohexenes were obtained after flash chromatography (petroleum ether/diethyl ether, 10:1).

8a: Colorless oil, isolated yield 68% (135 mg). ^{1}H NMR ($CDCl_3$): δ = 6.97 (s, 1 H), 4.21–4.16 (q, 2 H), 2.40–2.37 (t, J = 6.0 Hz, 2 H), 1.85–1.79 (m, 2 H), 1.32–1.28 (t, J = 7.0 Hz, 3 H), 0.69–0.66 (t, J = 6.6 Hz, 2 H), 0.11 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 167.20, 148.22, 137.82, 60.63, 29.17, 21.14, 14.23, 11.04, –2.36 ppm. HRMS: calcd. for $C_{10}H_{18}O_2Si$ [M]$^+$ 198.1076; found 198.1075. $C_{10}H_{18}O_2Si$ (198.34): calcd. C 60.56, H 9.15; found C 60.51, H 9.16.

8b: Colorless oil, isolated yield 79% (254 mg). ^{1}H NMR ($CDCl_3$): δ = 7.55–7.53 (m, 4 H), 7.42–7.32 (m, 7 H), 4.24–4.19 (q, 2 H), 2.57–2.54 (t, J = 6.4 Hz, 2 H), 2.00–1.94 (m, 2 H), 1.32–1.29 (t, J = 6.0 Hz, 3 H), 1.24–1.21 (t, J = 6.6 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 166.86, 150.46, 135.02, 134.93, 133.22, 129.65, 127.99, 60.86, 29.30, 20.98, 14.23, 9.11 ppm. HRMS: calcd. for $C_{20}H_{22}O_2Si$ [M]$^+$ 322.1389; found 322.1384. $C_{20}H_{22}O_2Si$ (322.48): calcd. C 74.49, H 6.88; found C 74.45, H 6.86.

9a: Colorless oil, isolated yield 75% (170 mg). ^{1}H NMR ($CDCl_3$): δ = 6.86 (s, 1 H), 2.36–2.32 (q, 2 H), 1.84–1.76 (m, 2 H), 1.49 (s, 9 H), 0.67–0.63 (m, 2 H), 0.11 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 166.57, 149.72, 136.52, 80.22, 29.19, 28.03, 21.19, 11.06, –2.28 ppm. HRMS: calcd. for $C_{12}H_{22}O_2Si$ [M]$^+$ 226.1389; found 226.1387. $C_{12}H_{22}O_2Si$ (226.39): calcd. C 63.66, H 9.80; found C 63.69, H 9.81.

9b: White solid, isolated yield 88% (308 mg). ^{1}H NMR ($CDCl_3$): δ = 7.56–7.53 (m, 4 H), 7.42–7.23 (m, 6 H), 7.22 (s, 1 H), 2.53–2.50 (t, J = 6.0 Hz, 2 H), 1.99–1.93 (q, 2 H), 1.50 (s, 9 H), 1.23–1.19 (t, J = 6.0 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 166.17, 152.02, 135.22, 134.94, 131.82, 129.58, 127.95, 80.55, 29.32, 28.02, 21.02, 9.09 ppm. HRMS: calcd. for $C_{22}H_{26}O_2Si$ [M]$^+$ 350.1702; found 350.1703. $C_{22}H_{26}O_2Si$ (350.53): calcd. C 75.38, H 7.48; found C 75.34, H 7.52.

10a: Colorless oil, isolated yield 63% (176 mg). ^{1}H NMR ($CDCl_3$): δ = 7.72 (d, J = 8.0 Hz, 2 H), 7.32 (d, J = 8.0 Hz, 2 H), 7.07 (s, 1 H), 2.43 (s, 3 H), 2.29–2.26 (t, J = 5.3 Hz, 2 H), 1.78–1.76 (q, 2 H), 0.67–0.64 (m, 2 H), 0.14 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 155.67, 144.12, 135.88, 135.14, 129.74, 128.29, 27.34, 21.58, 21.18, 10.64, –2.54 ppm. HRMS: calcd. for $C_{14}H_{20}O_2SSi$ [M]$^+$ 280.0953; found 280.0953. $C_{14}H_{20}O_2SSi$ (280.46): calcd. C 59.96, H 7.19; found C 59.99, H 7.14.

10b: Colorless crystals, isolated yield 71% (287 mg), m.p. 151–153 °C. ^{1}H NMR ($CDCl_3$): δ = 7.76 (d, J = 8.5 Hz, 2 H), 7.50–7.44 (m, 4 H), 7.42–7.36 (m, 8 H), 7.33 (d, J = 8.0 Hz, 2 H), 2.45–2.44 (m, 5 H), 1.94–1.91 (q, 2 H), 1.22–1.19 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 157.98, 144.38, 135.59, 134.83, 133.68, 131.05, 130.04, 129.86, 128.38, 128.16, 27.49, 21.63, 21.03, 8.74 ppm. HRMS: calcd. for $C_{24}H_{24}O_2SSi$ [M]$^+$ 404.1266; found 404.1269. $C_{24}H_{24}O_2SSi$ (404.60): calcd. C 71.25, H 5.98; found C 71.21, H 5.96.

11a: Colorless oil, isolated yield 65% (212 mg). ^{1}H NMR ($CDCl_3$): δ = 7.70–7.65 (m, 4 H), 7.54–7.49 (m, 2 H), 7.49–7.45 (m, 4 H), 6.68 (d, J = 30.4 Hz, 1 H), 2.30–2.29 (d, J = 5.6 Hz, 2 H), 1.84–1.82 (t, J = 5.8 Hz, 2 H), 0.76–0.72 (t, J = 6.4 Hz, 2 H), 0.11 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.8 ($J_{C,P}$ = 81.7 Hz), 144.6, 132.0 (d, J = 10.4 Hz), 131.8 (d, J = 8.4 Hz), 130.7, 128.5 (d, J = 11.9 Hz), 29.9 (d, J = 13.9 Hz), 21.6 (d, J = 8.4 Hz), 11.5, –2.2 ppm. ^{31}P NMR (200 MHz, $CDCl_3$): δ = 30.77 ppm. HRMS: calcd. for $C_{19}H_{23}OPSi$ [M]$^+$ 326.1256; found 326.1257. $C_{19}H_{23}OPSi$ (326.45): calcd. C 69.91, H 7.10; found C 69.95, H 7.06.

11b: Yellow solid, isolated yield 87% (392 mg). ^{1}H NMR ($CDCl_3$): δ = 7.73–7.68 (m, 4 H), 7.56–7.52 (m, 2 H), 7.50–7.45 (m, 8 H), 7.43–7.34 (m, 6 H), 7.00 (d, J = 30 Hz, 1 H), 2.50–2.46 (q, 2 H), 2.01–1.96 (q, 2 H), 1.30–1.27 (t, J = 6.4 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 155.22 ($J_{C,P}$ = 81.3 Hz), 139.60, 134.84, 132.03, 131.92 (d, J = 4.6 Hz), 131.70 (d, J = 99.4 Hz), 130.52, 129.74, 128.57 (d, J = 11.6 Hz), 128.06, 29.97 (d, J = 13.8 Hz), 21.41 (d, J = 8.5 Hz), 9.67 ppm. ^{31}P NMR (200 MHz, $CDCl_3$): δ = 31.54 ppm. HRMS: calcd. for $C_{29}H_{27}OPSi$ [M]$^+$ 450.1569; found 450.1566. $C_{29}H_{27}OPSi$ (450.59): calcd. C 77.30, H 6.04; found C 77.32, H 6.04.

12a: Colorless oil, isolated yield 68% (156 mg). ^{1}H NMR ($CDCl_3$): δ = 7.72–7.71 (t, J = 4.0 Hz, 2 H), 7.54–7.50 (m, 1 H), 7.44–7.41 (t, J = 7.5 Hz, 2 H), 6.36 (s, 1 H), 2.51–2.49 (m, 2 H), 1.94–1.89 (m, 2 H), 0.78–0.75 (m, 2 H), 0.14 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 198.84, 155.92, 138.95, 137.35, 131.91, 129.60, 128.07, 29.50, 21.09, 11.36, –2.19 ppm. HRMS: calcd. for $C_{14}H_{18}OSi$ [M]$^+$ 230.1127; found 230.1127. $C_{14}H_{18}OSi$ (230.38): calcd. C 72.99, H 7.88; found C 72.95, H 7.92.

12b: White solid, isolated yield 85% (301 mg). ^{1}H NMR ($CDCl_3$): δ = 7.79–7.77 (m, 2 H), 7.54–7.51 (m, 5 H), 7.44–7.35 (m, 8 H), 6.70 (s, 1 H), 2.68–2.66 (t, J = 6.0 Hz, 2 H), 2.09–2.04 (m, 2 H), 1.33–1.30 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 198.52, 158.17, 137.04, 135.05, 134.86, 133.90, 132.21, 129.72, 129.71, 128.21, 128.06, 29.75, 20.95, 9.51 ppm. HRMS: calcd. for $C_{24}H_{22}OSi$ [M]$^+$ 354.1440; found 354.1437. $C_{24}H_{22}OSi$ (354.52): calcd. C 81.31, H 6.25; found C 81.35, H 6.26.

4a: Colorless oil, isolated yield 65% (109 mg). ^{1}H NMR ($CDCl_3$): δ = 6.80 (s, 1 H), 2.33–2.31 (t, J = 6.5 Hz, 5 H), 1.80–1.75 (m, 2 H), 0.68–0.66 (m, 2 H), 0.13 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 200.08, 156.35, 137.97, 27.64, 25.18, 20.85, 11.04, –2.42 ppm. HRMS: calcd. for $C_9H_{16}OSi$ [M]$^+$ 168.0970; found 168.0973. $C_9H_{16}OSi$ (168.31): calcd. C 64.23, H 9.58; found C 64.22, H 9.54.

4b: Colorless oil, isolated yield 80% (234 mg). ^{1}H NMR ($CDCl_3$): δ = 7.48–7.46 (m, 4 H), 7.37–7.29 (m, 6 H), 7.05 (s, 1 H), 2.44–2.42

(q, 2 H), 2.32 (s, 3 H), 1.90–1.85 (m, 2 H), 1.18–1.15 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 199.97, 158.34, 134.85, 134.76, 133.41, 129.72, 128.03, 27.82, 25.44, 20.75, 9.18 ppm. HRMS: calcd. for $C_{19}H_{20}OSi$ $[M]^+$ 292.1283; found 292.1287. $C_{19}H_{20}OSi$ (292.45): calcd. C 78.03, H 6.89; found C 78.02, H 6.94.

5a: Colorless oil, isolated yield 61% (127 mg). ^{1}H NMR ($CDCl_3$): δ = 6.78 (s, 1 H), 5.89–5.79 (m, 1 H), 5.06–4.96 (m, 2 H), 2.82–2.78 (t, J = 5.5 Hz, 2 H), 2.37–2.32 (m, 4 H), 1.82–1.76 (m, 2 H), 0.70–0.67 (m, 2 H), 0.14 (s, 6 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 201.47, 156.24, 137.58, 136.69, 114.92, 36.22, 28.53, 27.99, 20.96, 11.17, –2.31 ppm. HRMS: calcd. for $C_{12}H_{20}OSi$ $[M]^+$ 208.1283; found 208.1282. $C_{12}H_{20}OSi$ (208.38): calcd. C 69.17, H 9.67; found C 69.14, H 9.71.

5b: Colorless oil, isolated yield 74% (246 mg). ^{1}H NMR ($CDCl_3$): δ = 7.54–7.37 (m, 10 H), 7.12 (s, 1 H), 5.90–5.80 (m, 1 H), 5.08–4.97 (m, 2 H), 2.90–2.87 (t, J = 5.5 Hz, 2 H), 2.54–2.51 (m, 2 H), 2.41–2.36 (m, 2 H), 1.99–1.93 (m, 2 H), 1.27–1.23 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 201.30, 158.26, 137.46, 134.91, 132.09, 129.76, 128.08, 115.13, 36.47, 28.52, 28.14, 20.85, 9.32 ppm. HRMS: calcd. for $C_{22}H_{24}OSi$ $[M]^+$ 332.1596; found 332.1598. $C_{22}H_{24}OSi$ (332.52): calcd. C 79.47, H 7.28; found C 79.45, H 7.28.

Synthesis of Si-β-Dynascone 5a from 4a: To a solution of **4a** (1.0 mmol, 169 mg) and allyl bromide (1.0 mmol, 120 mg) in tetrahydrofuran (THF; 5 mL) was added KH (1.0 mmol, 40 mg) at 0 °C. The cold bath was removed, and the mixture was kept at room temperature for 0.5 h. The mixture was again cooled to 0 °C, and Et_3B (1.0 mmol, 0.14 μL, 100 mg) was added. The mixture was then warmed and kept at room temperature for 4 h. The resulting solution was quenched with NaOH (1 mL, 1 M solution in water) and H_2O_2 (0.8 mL, 30% v/v) and stirred at 0 °C for 0.5 h. The crude product was purified by flash chromatography (silica gel; petroleum ether) to afford **5a** in 80% isolated yield.

Si-Herbac (6a): A solution of **4a** (1.0 mmol, 169 mg) in dry MeOH (20 mL) and 10% Pd/C (54 mg, 5 mol-%) were placed in a stainless-steel autoclave, which was filled with dry nitrogen. The autoclave was sealed, flushed three times with hydrogen, and pressurized with H_2 to 10 bar. The reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated, and the crude product was purified by column chromatography (silica gel; petroleum ether) to afford **6a** as a colorless oil in 87% isolated yield (148 mg). ^{1}H NMR ($CDCl_3$): δ = 2.46–2.40 (m, 1 H), 2.12 (s, 3 H), 2.07–2.01 (m, 1 H), 1.85–1.83 (d, J = 13.5 Hz, 1 H), 1.47–1.40 (m, 1 H), 1.20–1.12 (m, 1 H), 0.89–0.86 (d, J = 13.5 Hz, 1 H), 0.74–0.71 (d, J = 17.5 Hz, 1 H), 0.60–0.54 (t, J = 13.5 Hz, 1 H), 0.48–0.41 (m, 1 H), 0.07 (s, 3 H), 0.04 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 212.47, 49.50, 31.01, 26.68, 22.91, 16.65, 13.17, –1.97, –4.41 ppm. HRMS: calcd. for $C_9H_{18}OSi$ $[M]^+$ 170.1127; found 170.1129. $C_9H_{18}OSi$ (170.33): calcd. C 63.47, H 10.65; found C 63.45, H 10.69.

X-ray Crystallographic Studies of 10b: The data collection for **10b** was performed with a Rigaku RAXIS RAPID IP diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The determination of the crystal class and unit-cell parameters was performed by the Rapid-AUTO (Rigaku 2000) program package. CCDC-95262410 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Screening results for the reaction conditions, scanned ^{1}H and ^{13}C NMR spectra of all new compounds.

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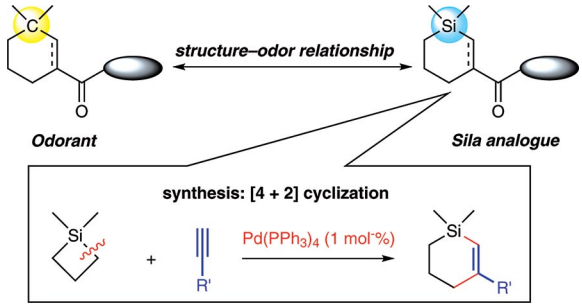

The combination of the sila-substitution concept with the insertion reactions of terminal alkynes into silacyclobutane efficiently led to the sila-odorants Si-Artemone, Si-β-Dynascone, and Si-Herbac. Si-Artemone and Si-Herbac have sensory characters similar to those of their unsubstituted analogues, whereas Si-β-Dynascone has an odor quite different to that of its unsubstituted analogue.

