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Synthesis and Olfactory Characterization of Novel Silicon-Containing Acyclic Dienone Musk Odorants

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Dedicated to Dr. Roman Kaiser[‡]

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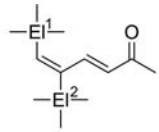
With an odor threshold value of 0.54 ng L^{-1} air, (3*E*,5*E*)-7,7-dimethyl-5-*tert*-butylocta-3,5-dien-2-one (**1a**) constitutes the most potent member of a new family of acyclic musk odorants with ionone aspects. Replacement of the quaternary carbon atoms of **1a** with silicon atoms leads to the (di)sila analogues **1b** (replacement of the carbon atom C-7), **1c** (replacement of the quaternary carbon atom of the 5-*tert*-butyl group), and **1d** (replacement of both quaternary carbon atoms). Compounds **1b**–**1d** were prepared in multistep syntheses, and their olfactory properties were characterized. The disila analogue **1d** turned out to be the weakest compound of the series (197 ng L^{-1} air), with only very faint musky aspects. The 7-sila analogue **1b** was very floral, of ionone and rose character, and also had a distinct musky note (1.63 ng L^{-1} air). The 5-trimethylsilyl analogue **1c** was the most musky sila odorant of the series (10.6 ng L^{-1} air), with rosy but not ionone-like facets. Thus, exchange of one or both *tert*-butyl groups of **1a** for a trimethylsilyl substituent had quite dramatic effects on the odor, and steric bulk at the carbon atom C-5 seems to be important for creating a musk odor impression.

Introduction

In 2002, Kula and co-workers[1] discovered an unusual bicyclic musk that unlike other polycyclic musks did not feature a pentamethylindane moiety, but instead a dienone backbone. This dienone backbone was utilized as a skeletal element in the design of *seco* structures[2] that led to a new family of musks,[3] which are referred to as dienone musks. Besides a dominant musk note, these dienone musks often possess pronounced sweet, fruity-floral side notes, often in the direction of ionones, with which they also share common structural features.[2,3] The most potent dienone musk reported so far is the (3*E*,5*E*)-octa-3,5-dien-2-one **1a**, which has an odor threshold value of 0.54 ng L^{-1} air, and a sweet violet note that joins with the main musk odor profile.[2] The musk character of this compound is mainly due to the bulky 5-*tert*-butyl substituent, whereas the 6-*tert*-butyl group enhances the floral-fruity ionone character, though the latter *tert*-butyl moiety can also be replaced by an isopropyl group without loss of the violet character.[2] In any case, the steric bulk of both the 5- and the 6-substituent is critical, and it is therefore very interesting to replace either one or both *tert*-butyl groups of **1a** with a more voluminous trimethylsilyl substituent, and to study the effect of these substitutions on the olfactory properties of this compound. In a series of recent studies, we have already demonstrated for other odorants that such a sila substitution (C/Si exchange) can significantly affect the olfactory properties of an odorant.[4] We report here the synthesis and olfactory characterization of the silicon compounds **1b** and **1c** (sila analogues of **1a**) and **1d** (disila analogue of **1a**) that are shown in Scheme 1.



1a: El^1 = C, El^2 = C
1b: El^1 = Si, El^2 = C
1c: El^1 = C, El^2 = Si
1d: El^1 = Si, El^2 = Si

Scheme 1. Compound **1a** and its three (di)sila analogues **1b**–**1d**.

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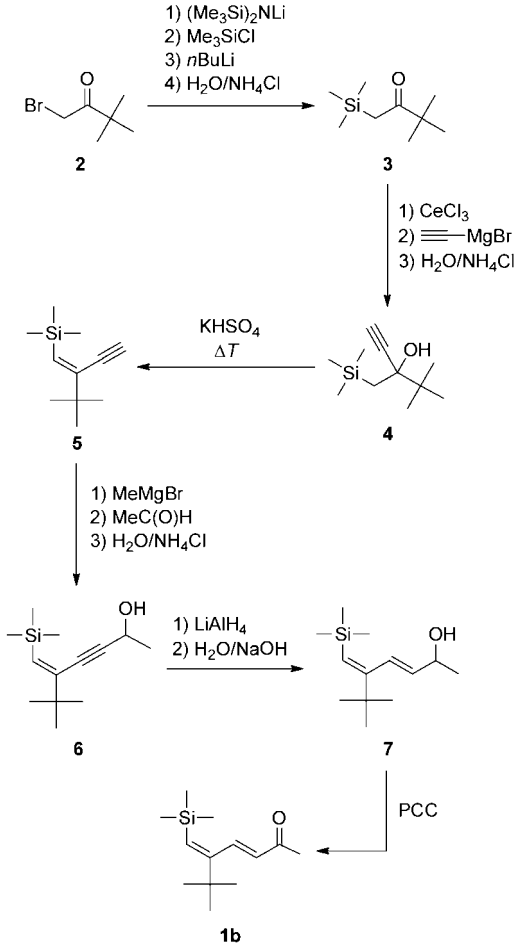
Results and Discussion

Syntheses

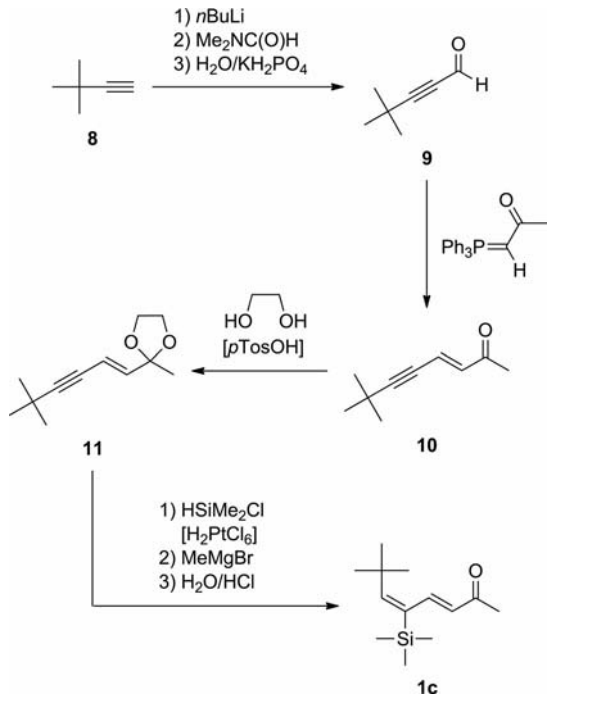
Compound **1b** was synthesized according to Scheme 2, starting from commercially available 1-bromo-3,3-dimethylbutan-2-one (**2**), and applying the general strategy for the synthesis of **1a** as reported in ref.[2] In the first step, 3,3-dimethyl-1-(trimethylsilyl)-butan-2-one (**3**) was synthesized according to ref.[5] Sequential treatment of **3** with cerium(III) chloride and ethynylmagnesium bromide, followed by hydrolysis with an aqueous solution of ammonium chloride, afforded 4,4-dimethyl-3-[(trimethylsilyl)-methyl]pent-1-yn-3-ol (**4**) in 81% yield. A mixture of **4** and potassium hydrogen sulfate was then heated in a bulb-to-bulb distillation apparatus (110 °C/240 mbar) to provide (*Z*)-(2-*tert*-butylbut-1-en-3-yn-1-yl)trimethylsilane (**5**) in 20% yield. This poor yield of **5** can be explained by the occurrence of a dominating side reaction that leads to 4,4-dimethyl-3-methylenpent-1-yne (identified by ^{1}H and ^{13}C NMR spectroscopy). Compound **5** was then treated with methylmagnesium bromide (transmetalation), followed by treatment with acetaldehyde and subsequent hydrolysis with water/ammonium chloride to furnish (*Z*)-6,6-dimethyl-5-[(trimethylsilyl)methylene]hept-3-yn-2-ol (**6**) in 78% yield.



Scheme 2. Synthesis of compound **1b**.

Reaction of **6** with 1 molar equivalent of lithium aluminum hydride and subsequent hydrolysis with an aqueous sodium hydroxide solution afforded (3*E*,5*E*)-6,6-dimethyl-5-[(trimethylsilyl)methylene]hept-3-en-2-ol (**7**) in 70% yield. Oxidation of **7** with pyridinium chlorochromate (PCC) finally furnished (3*E*,5*E*)-6,6-dimethyl-5-[(trimethylsilyl)methylene]hept-3-en-2-one (**1b**) in 75% yield.

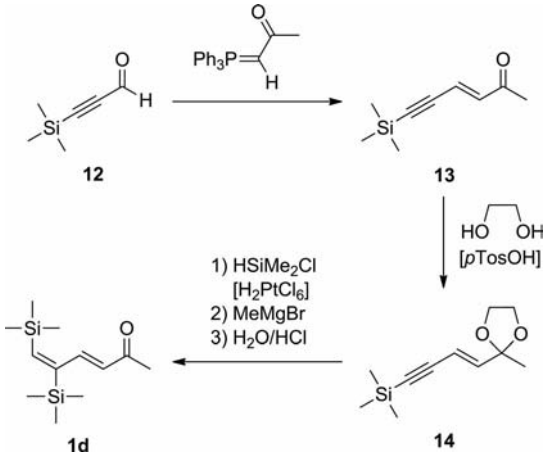
Compound **1c** was synthesized according to Scheme 3, starting from commercially available 3,3-dimethyl-1-butyne (**8**). In the first step, compound **8** was treated sequentially with *n*-butyllithium and *N*,*N*-dimethylformamide, followed by hydrolysis with an aqueous solution of potassium dihydrogen phosphate, to provide 4,4-dimethylpent-2-ynal (**9**) in 64% yield.[6] Subsequent reaction of **9** with (acetylmethylene)triphenylphosphorane afforded (*E*)-7,7-dimethyloct-3-en-5-yn-2-one (**10**) in 79% yield.[7] The acyl moiety of **10** was then protected as an acetal by an acid-catalyzed [*p*-toluenesulfonic acid (*p*TosOH)] reaction with 1,2-ethanediol to furnish (*E*)-2-(5,5-dimethylhex-1-en-3-yn-1-yl)-2-methyl-1,3-dioxolane (**11**) in 75% yield. The last three reaction steps in the synthesis of **1c** were performed in a one-pot procedure. In the first step the triple bond of **11** was hydrosilylated by reaction with chlorodimethylsilane, catalyzed by hexachloroplatinic acid. The resulting chlorodimethylsilane was then transformed into the corresponding trimethylsilane by treatment with methylmagnesium bromide. Finally, cleavage of the acetal protecting group with hydrochloric acid furnished (3*E*,5*E*)-7,7-dimethyl-5-(trimethylsilyl)octa-3,5-diene-2-one (**1c**) in 34% yield.



Scheme 3. Synthesis of compound **1c**.

Compound **1d** was synthesized according to Scheme 4, starting from commercially available 3-(trimethylsilyl)-2-propynal (**12**). In the first step, compound **12** was treated

with (acetylmethylene)triphenylphosphorane to provide (*E*)-6-(trimethylsilyl)hex-3-en-5-yn-2-one (**13**) in 76% yield.[7] The acyl moiety of **13** was then protected as an acetal by an acid-catalyzed (*p*TosOH) reaction with 1,2-ethanediol to furnish (*E*)-2-methyl-2-[4-(trimethylsilyl)but-1-en-3-yn-1-yl]-1,3-dioxolane (**14**) in 82% yield. The last three reaction steps in the synthesis of **1d** were also performed in a one-pot procedure. Accordingly, the triple bond of **14** was hydrosilylated in the first step by reaction with chlorodimethylsilane, catalyzed by hexachloroplatinic acid. The resulting chlorodimethylsilane was then transformed into the corresponding trimethylsilane by treatment with methylmagnesium bromide. Finally, cleavage of the acetal protecting group with hydrochloric acid furnished (3*E*,5*E*)-5,6-bis(trimethylsilyl)-3,5-hexadien-2-one (**1d**) in 33% yield.



Scheme 4. Synthesis of compound **1d**.

Compounds **1b**, **1c**, **4**–**7**, **9**–**11**, **13**, and **14** were isolated as colorless liquids, whereas **1d** was obtained as a colorless crystalline solid. At first glance, some of the product yields appear somewhat unsatisfactory; however, it is important to note that we were aiming to prepare olfactorily pure products, if necessary at the expense of the yield. The identities of all the compounds synthesized were established by elemental analyses (C, H) or high-resolution mass spectrometry (**5**, **9**) and NMR spectroscopic studies (^{1}H, ^{13}C, ^{29}Si). Compound **1d** was additionally characterized by a crystal structure analysis. The title compounds **1b**, **1c**, and **1d** were isolated as isomerically pure products (as confirmed by NMR analysis). The ^{1}H NMR spectroscopic data are in accordance with a (3*E*,5*E*) configuration for the hexa-3,5-dien-2-one backbone, and this configuration was also established by a crystal structure analysis of **1d**.

Crystal Structure Analysis

Compound **1d** was structurally characterized by single-crystal X-ray diffraction. The molecular structure of **1d** is depicted in Figure 1; selected bond lengths, bond angles, and torsion angles are given in the caption. As can be seen from these data, the unsaturated molecular skeleton of **1d** with its three double bonds shows only small deviations from planarity. All bond lengths and angles lie within the typical range expected for the molecular bonds in question, and thus no further discussion is necessary.

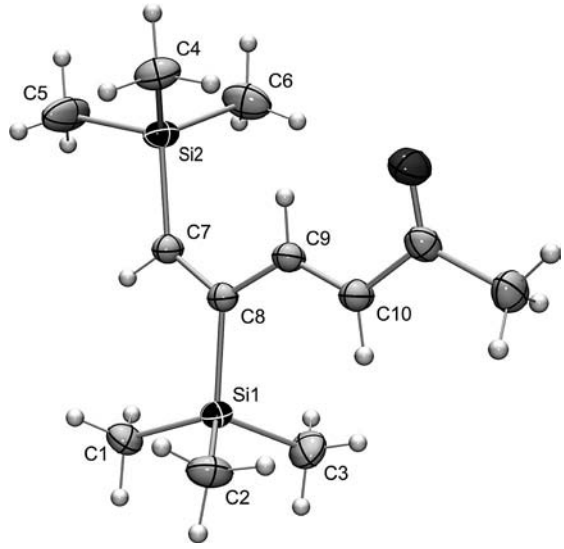


Figure 1. Molecular structure of **1d** in the crystal (the probability level of the displacement ellipsoids is 50%). Selected bond lengths [Å], bond angles [°], and torsion angles [°]: Si1–C1 1.8734(13), Si1–C2 1.8726(14), Si1–C3 1.8758(13), Si1–C8 1.9038(11), Si2–C4 1.8764(13), Si2–C5 1.8780(16), Si2–C6 1.8672(17), Si2–C7 1.8904(12), C7–C8 1.3615(16), C8–C9 1.4707(15), C9–C10 1.3400(16), C10–C11 1.4910(16), C11–C12 1.5024(18), C11–O 1.2205(16); Si1–C8–C7 120.39(8), Si1–C8–C9 120.48(8), Si2–C7–C8 130.22(9), C7–C8–C9 119.12(10), C8–C9–C10 127.62(10), C9–C10–C11 121.28(11), C10–C11–C12 115.96(11), O–C11–C10 121.90(11), O–C11–C12 122.13(11); Si1–C8–C7–Si2 –177.01(7), Si1–C8–C9–C10 6.80(17), Si2–C7–C8–C9 3.93(17), O–C11–C10–C9 12.25(19).

Olfactory Characterization

The silicon compounds **1b**, **1c**, and **1d** were studied for their olfactory properties and were compared with the parent carbon compound **1a**. The results of this study are summarized in Table 1. With an odor threshold of 0.54 ng L^{-1} air, the parent compound **1a** remains the most potent dienone musk,[2] with floral, sweet, and violet notes perfectly balancing the main musk theme, with some woody and slightly camphoraceous and agrestic facets in the background. Increasing the steric bulk of the C-6 substituent by replacing the 6-*tert*-butyl with a trimethylsilyl group lowers the musk intensity, and **1b** was found to be less musky than **1a**. With an overall odor threshold of 1.63 ng L^{-1} air, the odor of the 7-sila analogue **1b** was also slightly weaker than that of **1a**. Interestingly, however, the floral side of the scent was stressed, and **1b** is described as pronounced floral, violet, ionone-type in smell, accompanied by fatty-waxy aspects and a rose note in the direction of Rosalva (dec-9-en-1-ol). A musk character is still discernible, yet it is less in the foreground. This musk scent comes to the fore in the

sila analogue **1c**, in which the 5-*tert*-butyl group of **1a** is replaced with a trimethylsilyl moiety. Increasing the steric bulk of the C-5 substituent increases the musk intensity, and compound **1c** is the most musky of the (di)sila analogues **1b**–**1d**; it is, however, less musky than the parent carbon compound **1a**, which might also be due to its overall rather high odor threshold of 10.6 ng L^{-1} air. So overall, the odor of compound **1c** is weaker than those of **1b** and **1a**. Whereas the violet, ionone-type facets are completely lost, floral-fatty nuances in the rosy direction of Rosalva are still present, as are additional slightly green-acidic nuances. The odor of the disila analogue **1d** turned out to be the weakest of the series **1a**–**1d**, which is not only due to a diminished vapor pressure upon the twofold carbon/silicon exchange, since its odor threshold (which is independent of the vapor pressure) was measured to be 197 ng L^{-1} air. The disila analogue **1d** is also the least musky of the series **1a**–**1d**, with only slightly musky facets accompanied by weak clay-type aspects. The weak scent of **1d** is mainly powdery, green in tonality, with fatty-waxy nuances and a slightly fruity side, yet is devoid of floral character, and neither deflected in the violet nor rosy directions. Thus, concerning the muskiness of compounds **1a**–**1d**, the 5,6-*tert*-butyl substituents seem to be optimal, and further increase in the steric bulk is deleterious. Studying the importance of these substituents by their replacement with trimethylsilyl groups reveals that the bulky substituent at the carbon atom C-5 is of main importance for creating the muskiness of the odorants, whereas the C-6 substituent encodes floral, ionone, and rosy facets. When the bulkiness of both *tert*-butyl substituents is increased concurrently by sila substitution, the molecular dimensions of the floral and musky binding sites are both exceeded.

Table 1. Olfactory properties of compounds **1a**–**1d**.

Compound	Olfactory properties	Odor threshold value [ng L^{-1} air]
1a[a]	Floral, sweet, violet, musky, with woody, slightly camphoraceous and agrestic facets	0.54
1b	Floral ionone odor with a distinct musk character, and a fatty-waxy, rosy tonality in the direction of Rosalva; less musky than **1a** and **1c**, but more musky than **1d**	1.63
1c	Floral-fatty musk odor in rosy direction with some reminiscence of Rosalva and slightly green-acidic nuances; the most musky compound in the series of the silicon compounds **1b**–**1d**	10.6
1d	Weak, powdery, green odor with fatty-waxy nuances and slightly fruity, slightly musky, and weak clay-type aspects; the least musky compound of the series **1a**–**1d**	197

[a] Data taken from ref.[2]

Conclusions

The odorant **1a** is the most potent representative of the novel family of dienone musks (odor threshold value, 0.54 ng L^{-1} air). Besides a pronounced musk character, it also features a sweet, ionone-type violet note. In an extension of earlier systematic studies of silicon-containing odorants, the (di)sila analogues **1b**, **1c**, and **1d** were synthesized in multistep syntheses and were evaluated for their olfactory properties and compared with **1a**. Replacement of one or both of the 5,6-di-*tert*-butyl substituents of the parent carbon compound **1a** with trimethylsilyl groups increases the volume of the 5,6-substituents and is thus an excellent way to study the influence of the steric bulkiness of each substituent on the olfactory properties of the compound. Whereas the 5,6-*tert*-butyl substituents of **1a** seem to be optimal for the muskiness of this compound, replacement of the 5-*tert*-butyl substituent with a trimethylsilyl group (to give **1c**) mainly modifies the muskiness (decrease of the musk intensity), while sila substitution of the carbon atom C-6 (to give **1b**) stressed the floral side of the scent, giving it pronounced floral, ionone, and rosy facets. When the bulkiness of both *tert*-butyl substituents is increased concurrently (to give **1d**), the molecular dimensions of the musky and floral receptor site(s) are close to being exceeded. The dramatic sila substitution effects on the odor observed in this study again emphasize the high potential of the carbon/silicon switch strategy for odorant design.

Experimental Section

General Methods: All reactions involving chemicals sensitive to water and/or oxygen were carried out under dry argon. The organic solvents used were dried and purified according to standard procedures and stored under dry nitrogen. Starting materials, reagents, and solvents were purchased from Aldrich, ABCR, or Acros and were used without further purification. Compounds **4**, **6**, and **7** were obtained as racemic mixtures. Bulb-to-bulb distillations were performed with a Büchi GKR-50 apparatus. Melting points were determined with a Büchi Melting Point B-540 apparatus and are uncorrected. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded at 23 °C with a Bruker DRX-300 (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz), a Bruker Avance 400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{29}Si, 79.5 MHz), or a Bruker Avance 500 NMR spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz) by using $CDCl_3$ or C_6D_6 as the solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ = 7.24 ppm; $CDCl_3$), internal $CDCl_3$ (^{13}C, δ = 77.0 ppm; $CDCl_3$), internal C_6HD_5 (^{1}H, δ = 7.28 ppm; C_6D_6), internal C_6D_6 (^{13}C, δ = 128.0 ppm; C_6D_6), or external tetramethylsilane (TMS, ^{29}Si, δ = 0.0 ppm; $CDCl_3$, C_6D_6). Analysis and assignment of the ^{1}H NMR spectroscopic data were supported by ^{1}H,^{1}H gradient-selected COSY, ^{13}C,^{1}H gradient-selected HMQC, and ^{13}C,^{1}H gradient-selected HMBC experiments. Assignment of the ^{13}C NMR spectroscopic data was supported by DEPT-135 and the aforementioned ^{13}C,^{1}H correlation experiments. Elemental analyses were performed with a VarioMicro apparatus (Elementar Analysensysteme GmbH). High-resolution mass spectra (HRMS) were recorded with a double-focusing Finnigan MAT 95 mass spectrometer (EI, 70 eV). Olfactory evaluations of the samples as 10% solutions in dipropylene glycol (DPG) and as 10%

solutions in ethanol (EtOH) on smelling blotters were performed by at least two expert perfumers. The odor threshold values were determined by GC–olfactometry. Different dilutions of the sample substances were injected into a gas chromatograph in descending order until the panelists evaluating in blind failed to detect the odor impression at the correct retention time. The reported threshold values are geometrical means of the different values reported by at least three individual panelists.

(3*E*,5*E*)-6,6-Dimethyl-5-[(trimethylsilyl)methylene]hept-3-en-2-one (1b): Pyridinium chlorochromate (285 mg, 1.32 mmol) was added in portions at 20 °C over 5 min to a stirred mixture of **7** (200 mg, 883 μmol), Celite® (1.80 g, standard super-cell, ABCR), and dichloromethane (10 mL), and the resulting mixture was then stirred at 20 °C for 4 h. Subsequently, diethyl ether (10 mL) was added to the reaction mixture, and the insoluble material was filtered off through a pad of Celite®, washed with diethyl ether (20 mL), and discarded. The filtrate and the wash solution were combined, then the solvent was removed under reduced pressure, and the residue was purified by twofold column chromatography on silica gel {silica gel, 35–70 μm; eluent, *n*-hexane/ethyl acetate [9:1 (v/v)]} to furnish **1b** (149 mg, 664 μmol, 75% yield) as a colorless oily liquid. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ = 0.05 (s, 9 H, SiCH_3), 1.07 (s, 9 H, CCH_3), 2.27 [s, 3 H, C(O)CH_3], 5.60 (d, $^4J_{HH}$ = 0.4 Hz, 1 H, C*H*=CCH=CH), 6.11 (d, $^3J_{HH}$ = 16.1 Hz, 1 H, CH=CCH=C*H*), 7.32 (dd, $^3J_{HH}$ = 16.1, $^4J_{HH}$ = 0.4 Hz, 1 H, CH=CC*H*=CH) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 0.7 (SiCH_3), 27.3 [C(O)CH_3], 29.6 (CCH_3), 37.6 (CCH_3), 126.8 (*C*H=CCH=CH), 132.0 (CH=CCH=*C*H), 145.8 (CH=C*C*H=CH), 162.7 (CH=*C*CH=CH), 198.2 [*C*(O)CH_3] ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ = –9.4 ppm. $C_{13}H_{24}OSi$ (224.42): calcd. C 69.58, H 10.78; found C 69.5, H 10.7. Odor description: floral ionone odor with distinct musk character and a fatty-waxy, rosy tonality in the direction of Rosalva; less musky than **1a** and **1c**, but more musky than **1d**; odor threshold: 1.63 ng L^{-1} air.

(3*E*,5*E*)-7,7-Dimethyl-5-(trimethylsilyl)octa-3,5-dien-2-one (1c): A 0.1 M solution of hexachloroplatinic acid hexahydrate in 2-propanol (30.0 μL, 3.00 μmol of $H_2PtCl_6{\cdot}6H_2O$) was added in a single portion at 20 °C to a stirred solution of chlorodimethylsilane (438 mg, 4.63 mmol) in tetrahydrofuran (THF, 6 mL). Then compound **11** (300 mg, 1.54 mmol) was added dropwise at 20 °C over 10 min, and the resulting mixture was stirred at 20 °C for 2.5 h. Two identical reactions of this type were performed simultaneously. A 3 M solution of methylmagnesium bromide in diethyl ether (3.00 mL, 9.00 mmol of MeMgBr) was added dropwise at 0 °C over 5 min to each of the two reaction mixtures, followed by stirring at 0 °C for 30 min and then at 20 °C for a further 30 min. The two resulting mixtures were combined and then carefully poured into a vigorously stirred mixture of a saturated aqueous ammonium chloride solution (100 mL) and ice (100 g). The organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 70 mL), the combined organic extracts were dried (Na_2SO_4), and the solvent was removed under reduced pressure. The residue was taken up in methanol (20 mL), 0.5 M hydrochloric acid (6.20 mL, 3.10 mmol of HCl) was added in a single portion at 20 °C, and the resulting mixture was stirred at 20 °C for 1 h. Subsequently, a saturated aqueous sodium carbonate solution (50 mL) and diethyl ether (50 mL) were added, the organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 50 mL), the combined organic extracts were dried (Na_2SO_4), and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel {silica gel, 35–70 μm; eluent, *n*-hexane/ethyl acetate [96:4 (v/v)]} to afford a colorless oily liquid, which was further purified by column chromatography on silica gel {silica gel, 35–70 μm; eluent, *n*-hexane/ethyl acetate [9:1 (v/v)]} to furnish **1c** (234 mg, 1.04 mmol, 34% yield relative to **11**) as a colorless oily liquid. ^{1}H NMR (300.1 MHz, C_6D_6): δ = 0.22 (s, 9 H, SiCH_3), 1.18 (s, 9 H, CCH_3), 2.04 [s, 3 H, C(O)CH_3], 6.11 (d, $^4J_{HH}$ = 1.7 Hz, 1 H, C*H*=CCH=CH), 6.28 (d, $^3J_{HH}$ = 16.5 Hz, 1 H, CH=CCH=C*H*), 7.94 (dd, $^3J_{HH}$ = 16.5, $^4J_{HH}$ = 1.7 Hz, 1 H, CH=CC*H*=CH) ppm. ^{13}C NMR (75.5 MHz, C_6D_6): δ = 0.8 (SiCH_3), 27.1 [C(O)CH_3], 31.1 (CCH_3), 35.6 (CCH_3), 129.8 (CH=CCH=*C*H), 136.7 (CH=*C*CH=CH), 144.1 (CH=C*C*H=CH), 155.3 (*C*H=CCH=CH), 195.9 [*C*(O)CH_3] ppm. ^{29}Si NMR (59.6 MHz, C_6D_6): δ = –2.6 ppm. $C_{13}H_{24}OSi$ (224.42): calcd. C 69.58, H 10.78; found C 69.9, H 10.8. Odor description: floral-fatty musk odor in rosy direction with some reminiscence of Rosalva, and slightly green-acidic nuances; the most musky compound in the series of the silicon compounds **1b**–**1d**; odor threshold: 10.6 ng L^{-1} air.

(3*E*,5*E*)-5,6-Bis(trimethylsilyl)-3,5-hexadien-2-one (1d): A 0.1 M solution of hexachloroplatinic acid hexahydrate in 2-propanol (30.0 μL, 3.00 μmol of $H_2PtCl_6{\cdot}6H_2O$) was added in a single portion at 20 °C to a stirred solution of chlorodimethylsilane (405 mg, 4.28 mmol) in THF (6 mL). Then compound **14** (300 mg, 1.43 mmol) was added dropwise at 20 °C over 10 min, and the resulting mixture was stirred at 20 °C for 20 h. Two identical reactions of this type were performed simultaneously. A 3 M solution of methylmagnesium bromide in diethyl ether (3.00 mL, 9.00 mmol of MeMgBr) was added dropwise at 0 °C over 5 min to each of the two reaction mixtures, followed by stirring at 0 °C for 1 h and then at 20 °C for a further 2 h. The two resulting mixtures were combined and then carefully poured into a vigorously stirred mixture of a saturated aqueous ammonium chloride solution (100 mL) and ice (100 g). The organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 70 mL), the combined organic extracts were dried (Na_2SO_4), and the solvent was removed under reduced pressure. The resulting residue was taken up in methanol (10 mL), 0.5 M hydrochloric acid (6.00 mL, 3.00 mmol of HCl) was added in a single portion at 20 °C, and the resulting mixture was stirred at 20 °C for 90 min. Subsequently, a saturated aqueous sodium carbonate solution (50 mL) and diethyl ether (50 mL) were added, the organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 50 mL), the combined organic extracts were dried (Na_2SO_4), and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel {silica gel, 35–70 μm; eluent, *n*-hexane/ethyl acetate [96:4 (v/v)]} to afford a colorless oily liquid, which was then crystallized from *n*-hexane (2 mL; crystallization at –20 °C over a period of 8 d). The crystals were isolated by filtration and dried in vacuo (0.01 mbar, 20 °C, 1 h) to furnish **1d** (225 mg, 936 μmol, 33% yield relative to **14**) as a colorless crystalline solid; mp. 36–37 °C. ^{1}H NMR (300.1 MHz, C_6D_6): δ = 0.25 (s, 9 H, SiCH_3), 0.28 (s, 9 H, SiCH_3), 2.06 [s, 3 H, C(O)-CH_3], 6.44 (d, $^3J_{HH}$ = 16.4 Hz, 1 H, CH=CCH=C*H*), 6.81 (d, $^4J_{HH}$ = 1.1 Hz, 1 H, C*H*=CCH=CH), 7.81 (dd, $^3J_{HH}$ = 16.4, $^4J_{HH}$ = 1.1 Hz, 1 H, CH=CC*H*=CH) ppm. ^{13}C NMR (75.5 MHz, C_6D_6): δ = –0.8 (SiCH_3), 0.3 (SiCH_3), 27.1 [C(O)CH_3], 130.8 (CH=CCH=*C*H), 146.0 (CH=C*C*H=CH), 154.3 (*C*H=CCH=CH), 159.1 (CH=*C*CH=CH), 196.4 [*C*(O)CH_3] ppm. ^{29}Si NMR (59.6 MHz, C_6D_6): δ = –10.3, –4.2 ppm. $C_{12}H_{24}OSi_2$ (240.49): calcd. C 59.93, H 10.06; found C 59.8, H 10.1. Odor description: weak, powdery, green odor with fatty-waxy nuances and slightly fruity, slightly musky, and weak clay-type aspects; the least musky compound of the series **1a**–**1d**; odor threshold: 197 ng L^{-1} air.

1-Bromo-3,3-dimethylbutan-2-one (2): This compound was commercially available (ABCR).

3,3-Dimethyl-1-(trimethylsilyl)butan-2-one (3): This compound was synthesized according to the procedure reported in ref.[5]

4,4-Dimethyl-3-[(trimethylsilyl)methyl]pent-1-yn-3-ol (4): Compound **3** (12.0 g, 69.6 mmol) was added in a single portion at 0 °C to a stirred suspension of anhydrous cerium(III) chloride (17.1 g, 69.4 mmol) in THF (170 mL), and the mixture was stirred at 20 °C for 5 h. The resulting suspension was added dropwise at 0 °C over 15 min to a stirred 0.5 M solution of ethynylmagnesium bromide in THF (208 mL, 104 mmol of HC≡CMgBr), and the mixture was then stirred at 20 °C for 20 h, followed by the addition of a cold (10 °C) saturated aqueous ammonium chloride solution (200 mL). The organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 200 mL), the combined organic extracts were dried (Na_2SO_4), the solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel {silica gel, 35–70 μm; eluent, *n*-hexane/ethyl acetate [96:4 (v/v)]} to furnish **4** (11.2 g, 56.5 mmol, 81% yield) as a colorless liquid. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.11 (s, 9 H, SiCH_3), 1.01 (s, 9 H, CCH_3), 1.05 (δ_A), 1.12 (δ_B), and 1.78 (δ_X, ABX system, $^2J_{AB}$ = –14.6, $^4J_{AX}$ = 1.2, $^4J_{BX}$ = 0 Hz, 3 H, SiC$H_A H_B$COH_X), 2.41 (s, 1 H, C≡CH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 0.3 (SiCH$_3$), 24.78 (SiCH$_2$COH), 24.83 (CCH$_3$), 39.6 (CCH$_3$), 73.0 (C≡CH), 75.8 (SiCH$_2$$C$OH), 87.7 ($C$≡CH) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = –0.3 ppm. $C_{11}H_{22}OSi$ (198.38): calcd. C 66.60, H 11.18; found C 66.3, H 11.2.

(*Z*)-(2-*tert*-Butylbut-1-en-3-yn-1-yl)trimethylsilane (5): A mixture of **4** (5.00 g, 25.2 mmol) and potassium hydrogen sulfate (700 mg, 5.14 mmol) was heated in a bulb-to-bulb distillation apparatus at 110 °C/240 mbar for 2 h. The resulting volatile constituents were trapped in a bulb cooled to –78 °C, and the product was separated and purified by distillation in vacuo to furnish **5** (917 mg, 5.08 mmol, 20% yield) as a colorless liquid; bp. 95–96 °C/100 mbar. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.14 (s, 9 H, SiCH_3), 1.11 (s, 9 H, CCH_3), 3.06 (s, 1 H, CH=CC≡CH), 5.88 (s, 1 H, CH=CC≡CH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –1.0 (SiCH$_3$), 29.0 (CCH$_3$), 37.6 (CCH$_3$), 81.4 (CH=CC≡CH), 83.9 (CH=CC≡CH), 133.6 (CH=CC≡CH), 147.9 (CH=CC≡CH) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ = –8.9 ppm. HRMS (EI): calcd. for $C_{11}H_{20}Si$ [M^+] 180.13343; found 180.13424.

(*Z*)-6,6-Dimethyl-5-[(trimethylsilyl)methylene]hept-3-yn-2-ol (6): A solution of **5** (794 mg, 4.40 mmol) in THF (15 mL) was added dropwise at 20 °C over 5 min to a stirred 3.0 M solution of methylmagnesium bromide in diethyl ether (1.76 mL, 5.28 mmol of MeMgBr), and the resulting mixture was heated under reflux for 3 h. Then the mixture was allowed to cool to 20 °C, a solution of acetaldehyde (233 mg, 5.29 mmol) in THF (7 mL) was added dropwise at 20 °C over 5 min, and the resulting mixture was again heated under reflux for 20 h. The mixture was allowed to cool to 20 °C, and a cold (10 °C) saturated aqueous ammonium chloride solution (80 mL) was added. The organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 150 mL), the combined organic extracts were dried (Na_2SO_4), the solvent was removed under reduced pressure, and the resulting residue was purified by column chromatography on silica gel {silica gel, 35–70 μm; eluent, *n*-hexane/ethyl acetate [9:1 (v/v)]} to furnish **6** (769 mg, 3.43 mmol, 78% yield) as a colorless liquid. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.14 (s, 9 H, SiCH_3), 0.95 (s, 9 H, CCH_3), 1.48 [d, $^3J_{HH}$ = 6.6 Hz, 3 H, CH(OH)CH_3], 1.72 [br. s, 1 H, CH(OH)CH$_3$], 4.67 [q, $^3J_{HH}$ = 6.6 Hz, 1 H, CH(OH)CH$_3$], 5.81 (s, 1 H, CH=C) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –0.8 (SiCH$_3$), 24.2 [CH(OH)CH$_3$], 29.1 (CCH$_3$), 37.7 (CCH$_3$), 58.9 [CH(OH)CH$_3$], 84.5 (CH=CC≡C), 94.8 (CH=CC≡C), 132.1 (CH=CC≡C), 148.3 (CH=CC≡C) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ = –9.0 ppm. $C_{13}H_{24}OSi$ (224.42): calcd. C 69.58, H 10.78; found C 69.3, H 10.8.

(3*E*,5*E*)-6,6-Dimethyl-5-[(trimethylsilyl)methylene]hept-3-en-2-ol (7): A solution of **6** (600 mg, 2.67 mmol) in THF (15 mL) was added dropwise at 20 °C over 5 min to a stirred suspension of lithium aluminum hydride (102 mg, 2.69 mmol) in THF (2 mL). The resulting mixture was heated under reflux for 3 h and was then allowed to cool to 20 °C. Water (150 μL), a 15% (w/w) aqueous sodium hydroxide solution (150 μL), and again water (450 μL) were then added dropwise in turn over 5 min. After the resulting mixture had been stirred at 20 °C for 30 min, the precipitate was removed by suction filtration and washed with diethyl ether (20 mL). The filtrate and the wash solution were combined and dried (Na_2SO_4), the solvent was removed under reduced pressure, and the resulting residue was purified by threefold column chromatography on silica gel {silica gel, 35–70 μm; eluent, *n*-hexane/ethyl acetate [9:1 (v/v)]} to furnish **7** (424 mg, 1.87 mmol, 70% yield) as a colorless oily liquid. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.04 (s, 9 H, SiCH_3), 1.02 (s, 9 H, CCH_3), 1.30 [d, $^3J_{HH}$ = 6.4 Hz, 3 H, CH(OH)CH_3], 1.43 [br. s, 1 H, CH(OH)CH$_3$], 4.28–4.40 [m, 1 H, CH(OH)CH$_3$], 5.34 (d, $^4J_{HH}$ = 0.6 Hz, 1 H, CH=CCH=CH), 5.57 (dd, $^3J_{HH}$ = 15.7, $^3J_{HH}$ = 6.2 Hz, 1 H, CH=CCH=CH), 6.25 (ddd, $^3J_{HH}$ = 15.7, $^4J_{HH}$ = 0.6, $^4J_{HH}$ = 0.7 Hz, 1 H, CH=CCH=CH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 1.0 (SiCH$_3$), 23.2 [CH(OH)CH$_3$], 29.5 (CCH$_3$), 37.5 (CCH$_3$), 68.9 [CH(OH)CH$_3$], 121.7 (CH=CCH=CH), 130.5 (CH=CCH=CH), 136.7 (CH=CCH=CH), 165.0 (CH=CCH=CH) ppm. ^{29}Si NMR (59.6 MHz, $CDCl_3$): δ = –10.0 ppm. $C_{13}H_{26}OSi$ (226.43): calcd. C 68.96, H 11.57; found C 68.7, H 11.3.

3,3-Dimethyl-1-butyne (8): This compound was commercially available (ABCR).

4,4-Dimethylpent-2-ynal (9): A 2.5 M solution of *n*-butyllithium in hexanes (48.8 mL, 122 mmol of *n*BuLi) was added dropwise at 0 °C over 10 min to a stirred solution of **8** (10.0 g, 122 mmol) in THF (150 mL), and the resulting mixture was stirred at 20 °C for 1 h. Then *N*,*N*-dimethylformamide (8.92 g, 122 mmol) was added in a single portion at 0 °C, and stirring was continued at 20 °C for 30 min. The reaction mixture was then carefully poured at 20 °C into a stirred biphasic system of a 10% (w/w) aqueous potassium dihydrogen phosphate solution (664 mL) and *tert*-butyl methyl ether (500 mL). The aqueous layer was separated, the organic layer was washed with water (2 × 400 mL), and the combined aqueous layers were extracted with *tert*-butyl methyl ether (400 mL). The combined organic extracts were dried ($MgSO_4$), the solvent was removed under reduced pressure, and the resulting residue was purified by distillation to furnish **9** (8.61 g, 78.2 mmol, 64% yield) as a colorless liquid; bp. 132 °C. ^{1}H NMR (300.1 MHz, C_6D_6): δ = 1.05 (s, 9 H, CCH_3), 8.94 [s, 1 H, C(O)H] ppm. ^{13}C NMR (75.5 MHz, C_6D_6): δ = 27.6 (CCH$_3$), 29.6 (CCH$_3$), 80.8 [C≡CC(O)H], 104.3 [C≡CC(O)H], 176.2 [C≡CC(O)H] ppm. HRMS (EI): calcd. for C_7H_9O [M^+ – H] 109.06534; found 109.06496; calcd. for $C_7H_{10}O$ [M^+] 110.07316; found 110.07188.

(*E*)-7,7-Dimethyloct-3-en-5-yn-2-one (10): (Acetylmethylene)triphenylphosphorane (24.7 g, 77.6 mmol) was added in a single portion at 0 °C to a stirred solution of **9** (8.00 g, 72.6 mmol) in THF (300 mL), and the resulting mixture was stirred at 0 °C for 90 min and then at 20 °C for a further 3 h. The reaction mixture was concentrated under reduced pressure to a volume of approximately 30 mL, *n*-hexane/ethyl acetate [9:1 (v/v), 150 mL] was added, the resulting mixture was filtered through a pad of silica gel (63–200 μm, 150 g), and the solid residue was washed with *n*-hexane/

ethyl acetate [9:1 (v/v), 500 mL]. The filtrate and the wash solution were combined, the solvent was removed under reduced pressure, and the resulting residue was purified by bulb-to-bulb distillation (oven temperature 70–74 °C, 2 mbar) to furnish **10** (8.56 g, 57.0 mmol, 79% yield) as a colorless liquid. ^{1}H NMR (300.1 MHz, C_6D_6): δ = 1.25 (s, 9 H, CCH_3), 1.79 [s, 3 H, C(O)CH_3], 6.41 (d, $^3J_{HH}$ = 16.1 Hz, C≡CC*H*=CH), 6.59 (d, $^3J_{HH}$ = 16.1 Hz, C≡CCH=C*H*) ppm. ^{13}C NMR (75.5 MHz, C_6D_6): δ = 27.0 [C(O)*C*H$_3$], 28.4 (*C*CH$_3$), 30.5 (C*C*H$_3$), 77.6 (*C*≡CCH=CH), 108.9 (C≡*C*CH=CH), 123.8 (C≡C*C*H=CH), 137.8 (C≡CCH=*C*H), 195.3 [*C*(O)CH$_3$] ppm. $C_{10}H_{14}O$ (150.22): calcd. C 79.96, H 9.39; found C 79.6, H 9.5.

(*E*)-2-(5,5-Dimethylhex-1-en-3-yn-1-yl)-2-methyl-1,3-dioxolane (11): A mixture of **10** (7.51 g, 50.0 mmol), 1,2-ethanediol (9.31 g, 150 mmol), *p*-toluenesulfonic acid monohydrate (290 mg, 1.52 mmol), and toluene (500 mL) was heated under reflux for 17 h, and the water that formed was removed with a water separator. The reaction mixture was then allowed to cool to 20 °C, and a cold (10 °C) saturated aqueous sodium hydrogen carbonate solution (500 mL) was added. The organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 200 mL), the combined organic extracts were dried (Na_2SO_4), the solvent was removed under reduced pressure, and the resulting residue was purified by threefold column chromatography on aluminum oxide {neutral aluminum oxide, activated with 6% (w/w) water, 150 mesh, Brockmann I; eluent, *n*-hexane/dichloromethane [10:1 (v/v)]} to furnish **11** (7.33 g, 37.7 mmol, 75% yield) as a colorless liquid. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 1.20 [s, 9 H, C(CH_3)$_3$], 1.41 (s, 3 H, CCH_3), 3.34–3.48 (m, 4 H, OCH_2C), 6.06 (d, $^3J_{HH}$ = 15.8 Hz, C≡CC*H*=CH), 6.11 (d, $^3J_{HH}$ = 15.8 Hz, C≡CCH=C*H*) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.2 (C*C*H$_3$), 28.2 [*C*(CH$_3$)$_3$], 31.1 [C(*C*H$_3$)$_3$], 64.6 (OCH_2C), 77.5 (C≡*C*CH=CH), 100.4 (*C*≡CCH=CH), 107.2 (*C*CH$_3$), 111.2 (C≡C*C*H=CH), 142.2 (C≡CCH=*C*H) ppm. $C_{12}H_{18}O_2$ (194.27): calcd. C 74.19, H 9.34; found C 74.0, H 9.3.

3-(Trimethylsilyl)-2-propynal (12): This compound was commercially available (Aldrich).

(*E*)-6-(Trimethylsilyl)hex-3-en-5-yn-2-one (13): (Acetylmethylene)-triphenylphosphorane (13.0 g, 40.8 mmol) was added in a single portion at 0 °C to a stirred solution of **12** (4.67 g, 37.0 mmol) in THF (160 mL), and the resulting mixture was stirred at 0 °C for 90 min. The reaction mixture was concentrated under reduced pressure to a volume of approximately 15 mL, *n*-hexane/ethyl acetate [9:1 (v/v), 50 mL] was added, the resulting mixture was filtered through a pad of silica gel (63–200 μm, 100 g), and the solid residue was washed with *n*-hexane/ethyl acetate [9:1 (v/v), 470 mL]. The filtrate and the wash solution were combined, the solvent was removed under reduced pressure, and the resulting residue was purified by bulb-to-bulb distillation (oven temperature 40–60 °C, 1 mbar) to furnish **13** (4.67 g, 28.1 mmol, 76% yield) as a colorless liquid. ^{1}H NMR (300.1 MHz, C_6D_6): δ = 0.27 (s, 9 H, SiCH_3), 1.73 [s, 3 H, C(O)CH_3], 6.40 (d, $^3J_{HH}$ = 16.1 Hz, C≡CC*H*=CH), 6.52 (d, $^3J_{HH}$ = 16.1 Hz, C≡CCH=C*H*) ppm. ^{13}C NMR (75.5 MHz, C_6D_6): δ = –0.4 (Si*C*H$_3$), 27.1 [C(O)*C*H$_3$], 102.6 (*C*≡CCH=CH), 105.3 (C≡*C*CH=CH), 122.4 (C≡C*C*H=CH), 139.2 (C≡CCH=*C*H), 195.1 [*C*(O)CH$_3$] ppm. ^{29}Si NMR (59.6 MHz, C_6D_6): δ = –17.2 ppm. $C_9H_{14}OSi$ (166.30): calcd. C 65.00, H 8.49; found C 64.6, H 8.6.

(*E*)-2-Methyl-2-[4-(trimethylsilyl)but-1-en-3-yn-1-yl]-1,3-dioxolane (14): A mixture of **13** (2.00 g, 12.0 mmol), 1,2-ethanediol (2.24 g, 36.1 mmol), *p*-toluenesulfonic acid monohydrate (70.0 mg, 386 μmol), and toluene (150 mL) was heated under reflux for 17 h, and the water that formed was removed with a water separator. The reaction mixture was then allowed to cool to 20 °C, and a cold (10 °C) saturated aqueous sodium hydrogen carbonate solution (100 mL) was added. The organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 70 mL), the combined organic extracts were dried (Na_2SO_4), the solvent was removed under reduced pressure, and the resulting residue was purified by threefold column chromatography on aluminum oxide {neutral aluminum oxide, activated with 6% (w/w) water, 150 mesh, Brockmann I; eluent, *n*-hexane/dichloromethane [10:1 (v/v)]} to furnish **14** (2.08 g, 9.89 mmol, 82% yield) as a colorless liquid. ^{1}H NMR (300.1 MHz, C_6D_6): δ = 0.31 (s, 9 H, SiCH_3), 1.47 (s, 3 H, CCH_3), 3.39–3.57 (m, 4 H, OCH_2C), 6.13 (d, $^3J_{HH}$ = 15.9 Hz, C≡CC*H*=CH), 6.31 (d, $^3J_{HH}$ = 15.9 Hz, C≡CCH=C*H*) ppm. ^{13}C NMR (75.5 MHz, C_6D_6): δ = –0.1 (Si*C*H$_3$), 24.9 (C*C*H$_3$), 64.5 (O*C*H$_2$C), 96.4 (*C*≡CCH=CH), 103.6 (C≡*C*CH=CH), 106.9 (*C*CH$_3$), 110.6 (C≡C*C*H=CH), 144.8 (C≡CCH=*C*H) ppm. ^{29}Si NMR (59.6 MHz, C_6D_6): δ = –18.3 ppm. $C_{11}H_{18}O_2Si$ (210.35): calcd. C 62.81, H 8.63; found C 62.7, H 8.6.

Crystal Structure Analysis: A suitable single crystal of **1d** was isolated directly from the reaction mixture. The crystal was mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS, graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å). The structure was solved by direct methods.[8] The non-hydrogen atoms were refined anisotropically.[8] A riding model was employed in the refinement of the CH hydrogen atoms. The crystal data and the experimental parameters used for this study are given in Table 2. CCDC-816167 contains the supplementary crystallographic data for this paper. These data can be obtained free of

Table 2. Crystallographic data for compound **1d**.

Empirical formula	$C_{12}H_{24}OSi_2$
M_r [g mol^{-1}]	240.49
T [K]	173(2)
λ(Mo-K_α) [Å]	0.71073
Crystal system	orthorhombic
Space group (no.)	*Pbca* (61)
a [Å]	10.2495(10)
b [Å]	11.9183(11)
c [Å]	25.228(3)
V [Å^3]	3081.8(5)
Z	8
$\rho_{calcd.}$ [g cm^{-3}]	1.037
μ [mm^{-1}]	0.209
F(000)	1056
Crystal dimensions [mm]	0.5 × 0.5 × 0.4
2θ range [°]	5.12–58.12
Index ranges	$-13 \le h \le 12$, $-16 \le k \le 16$, $-34 \le l \le 34$
Reflections collected	22985
Independent reflections	4080
R_{int}	0.0362
Parameters	143
S[a]	1.073
Weight parameters a/b[b]	0.0595/0.5766
R_1[c] [$I > 2\sigma(I)$]	0.0352
wR_2[d] (all data)	0.1022
Max./min. residual electron density [e Å^{-3}]	+0.317/–0.175

[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; n = number of reflections; p = number of parameters. [b] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [\max(F_o^2,0) + 2F_c^2]/3$. [c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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