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Sila-α-galbanone and Analogues: Synthesis and Olfactory Characterization of Silicon-Containing Derivatives of the Galbanum Odorant α-Galbanone

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Silicon compounds **1b**–**3b** are sila-analogues of the galbanum odorants α-galbanone (**1a**), α-spirogalbanone (**2a**), and *nor*-α-galbanone (**3a**), respectively. Sila-α-galbanone (**1b**), sila-α-spirogalbanone (**2b**), and sila-*nor*-α-galbanone (**3b**) were synthesized in multistep syntheses in isomerically pure form, starting from Me_2SiCl_2, $(CH_2{=}CH)_2SiCl_2$, and $Me_2(CH_2{=}CH)SiCl$, respectively. Hydroformylation of vinylsilanes, followed by either ring-closing aldol condensation or ring-closing alkene metathesis, were the key steps in these syntheses. The C/Si pairs **1a**/**1b**, **2a**/**2b**, and **3a**/**3b** were studied for their olfactory properties. All compounds possess green-fruity galbanum-type odors with pineapple aspects and thus are olfactorily related. However, sila-analogues **1b**–**3b** were found to be weaker than the corresponding parent carbon compounds **1a**–**3a**. This effect is most pronounced for the C/Si pair **2a**/**2b** as indicated by the odor thresholds of 0.023 $ng\,L^{-1}$ air (**2a**) and 3.8 $ng\,L^{-1}$ air (**2b**). However, due to their higher molecular mass, the silicon compounds are less volatile and thus more substantive in functional applications. In contrast to the stable 5-silacyclohex-1-enes **1b** and **2b**, the 4-silacyclopent-1-ene **3b** shows a limited chemical stability. For compound **3a** an extremely low odor threshold of 0.0087 $ng\,L^{-1}$ air was measured, and the silicon analogue **3b** with an odor threshold of 0.085 $ng\,L^{-1}$ air is the sila-odorant with the lowest odor threshold measured so far.

Introduction

α-Galbanone (α-dynascone, **1a**) was discovered in 1972 by its powerful galbanum odor as a trace impurity in an early α-damascone synthesis based on the cyclization of pseudo-damascone (Figure 1).[1] Resulting from allo-cyclization of the 10-methyl-6-methyleneundeca-1,9-dien-4-yne intermediate, the green, fruity-floral smelling homoallyl ketone **1a** that recalls galbanum resin, pineapples, and hyacinths, first led to the rejection of the early α-damascone batches, but after its structure elucidation, olfactory evaluation, and commercial synthesis in 1974 it became one of the most successful odorants in perfumery in its own right. α-Galbanone (α-dynascone, **1a**) and its use in the 'Galbex 183' base was essential for the modernization of the Fougère family, starting with Pierre Bourdon's 'Cool Water' (Davidoff, 1988).[2] A modern representative of such a Fougère fragrance with its light and fizzy green–galbanum freshness is, for instance 'Eros' (Versace, 2012) by Aurelien Guichard. A distinct pineapple character is even essential in such a woody-mossy composition as 'Legend' (Montblanc, 2011) that Olivier Pescheux and Céline Perdriel created around Evernyl and Pomarose. Replacement of the *gem*-dimethyl substituents of **1a** by a ring system (→ **2a**) was found to significantly enhance the substantivity of this modern note and thus transposes the fruity-green galbanum-pineapple freshness to the fond of a creation (Figure 1).[3] Consequently, α-spirogalbanone (**2a**) brings particular advantages to laundry-care applications, where substantivity is a key feature, and long-lasting freshness is in high demand. However, as 'Hugo Red' (Hugo Boss, 2013) or Olivier Gillotin's 'Polo Red' (Ralph Lauren, 2013) prove, a long-lasting fresh green-metallic galbanum character can also be of interest in fine fragrances. Most synthetic routes to **1a** and **2a** lead to isomeric mixtures composed, in large

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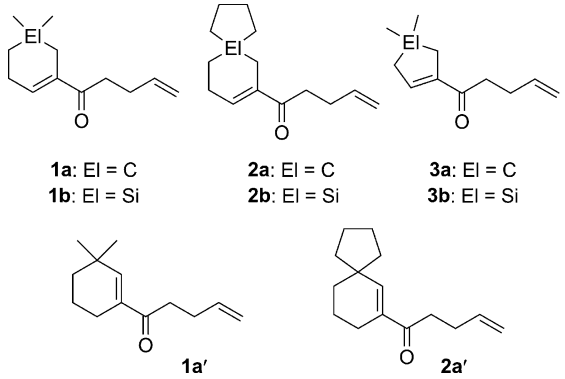
part, of the significantly weaker β-isomers **1a′** and **2a′**, which are also far less typical in their galbanum character (Figure 1).[3,4]



1a: El = C
1b: El = Si

2a: El = C
2b: El = Si

3a: El = C
3b: El = Si

1a′

2a′

Figure 1. Chemical structures of compounds **1a**, **1a′**, **1b**, **2a**, **2a′**, **2b**, **3a**, and **3b**.

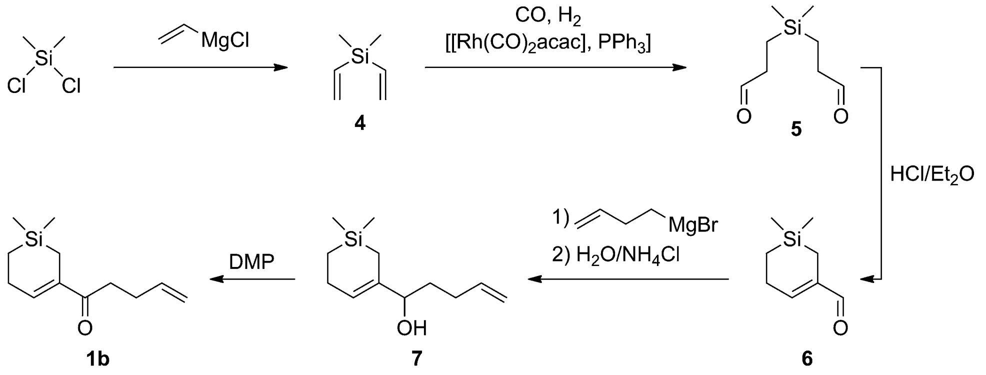
Here we report the synthesis of silicon compounds **1b** (sila-α-galbanone) and **2b** (sila-α-spirogalbanone), representing sila-analogues of the galbanum odorants **1a** and **2a** (replacement of the quaternary carbon atoms by silicon atoms; Figure 1). We have succeeded in developing an efficient synthetic strategy that exclusively leads to the desired α-isomers. The 5-silacyclohexene skeletons of **1b** and **2b** were built up by hydroformylation of divinylsilanes, followed by an intramolecular aldol condensation.[5,6] As we found in our systematic investigations on silicon-based odorants,[7,8] a sila-substitution generally much decreases the vapor pressure of odorants. Therefore, in addition to the synthesis and olfactory characterization of the C/Si pairs **1a/1b** and **2a/2b**, it was interesting to prepare the structurally related C/Si pair **3a/3b** as well and to compare its olfactory properties with those of the C/Si pairs **1a/1b** and **2a/2b** (Figure 1). *nor*-α-Galbanone (**3a**) was also patented for use in perfumery compositions,[9] but ascribed a strong, less distinct, aggressive fruity odor character reminiscent of plum and pear scents.[9] It was thus interesting to verify the odor description of **3a** and to study the influence of the sila-substitution (→ sila-*nor*-α-galbanone, **3b**) on the odor profile.

Results and Discussion

Syntheses

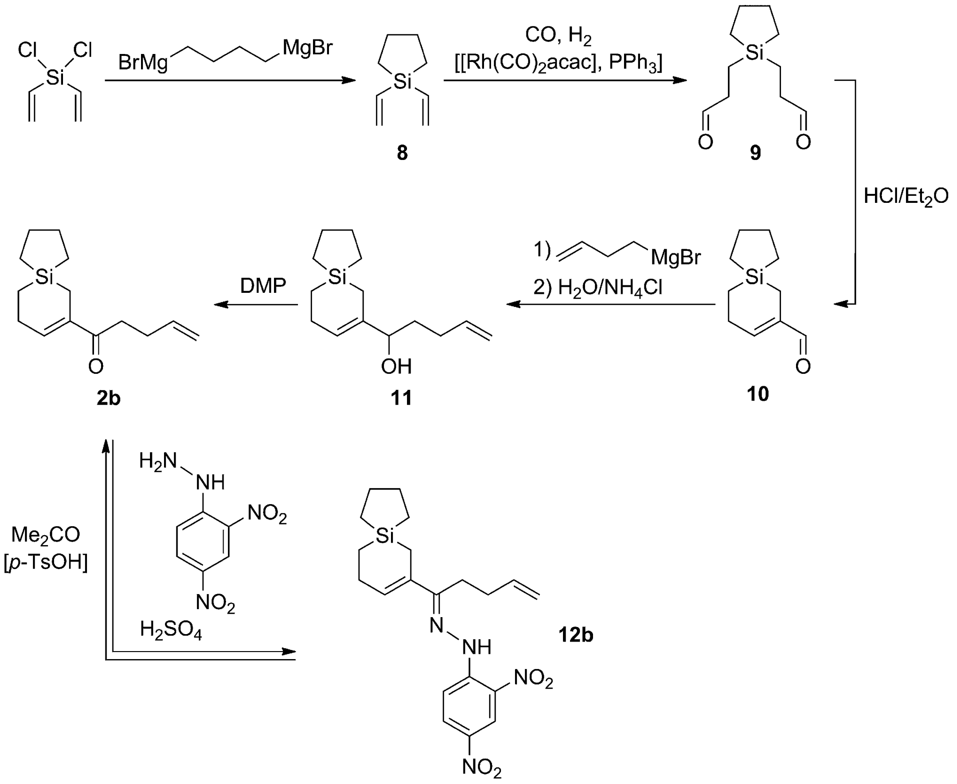
Sila-α-galbanone (**1b**) was synthesized according to Scheme 1, starting from dichlorodimethylsilane. Thus, reaction of Me_2SiCl_2 with vinylmagnesium chloride afforded dimethyldivinylsilane (**4**, 86% yield),[10] which upon rhodium-catalyzed {[Rh(CO)$_2$acac]} hydroformylation under an atmosphere of hydrogen and carbon monoxide, in the presence of triphenylphosphine, furnished 3,3′-(dimethylsilanediyl)dipropanal (**5**, 17% yield). Intramolecular aldol condensation of **5** under acidic conditions (HCl/Et_2O) then furnished 5,5-dimethyl-5-silacyclohex-1-ene-1-carbaldehyde (**6**). To optimize the yield of **6**, this compound was prepared from **4** in a one-pot synthesis, without isolation of intermediate **5**, to give **6** in 36% yield (relative to **4**). Reaction of **6** with but-3-en-1-ylmagnesium bromide and subsequent hydrolysis with water/ammonium chloride then afforded 1-(5,5-dimethyl-5-silacyclohex-1-en-1-yl)pent-4-en-1-ol (**7**, 92% yield). Oxidation of **7** with 1,1,1-tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (Dess–Martin periodinane, DMP) furnished sila-α-galbanone (**1b**) in 52% yield.

Sila-α-spirogalbanone (**2b**) was synthesized according to Scheme 2, starting from dichlorodivinylsilane. Thus, reaction of $(CH_2=CH)_2SiCl_2$ with 1,4-bis(bromomagnesio)butane afforded 1,1-divinylsilolane (**8**, 93% yield), which upon rhodium-catalyzed {[Rh(CO)$_2$acac]} hydroformylation under an atmosphere of hydrogen and carbon monoxide, in the presence of triphenylphosphine, furnished 3,3′-(silolane-1,1-diyl)dipropanal (**9**, 10% yield). Intramolecular aldol condensation of **9** under acidic conditions HCl/Et_2O) then furnished 5-silaspiro[4.5]dec-7-ene-7-carbaldehyde (**10**). To optimize the yield of **10**, this compound was also prepared from **8** in a one-pot synthesis, without isolation of intermediate **9**, to give **10** in 33% yield (relative to **8**). Reaction of **10** with but-3-en-1-ylmagnesium bromide and subsequent hydrolysis with water/ammonium chloride then afforded 1-(5-silaspiro[4.5]dec-7-en-7-yl)pent-4-en-1-ol (**11**, 86% yield). Oxidation of **11** with DMP furnished **2b** in 45% yield with a purity of 99.5%. Since further purification of **2b** could neither be achieved by chromatography nor by



4 **5** **6** **7** **1b**

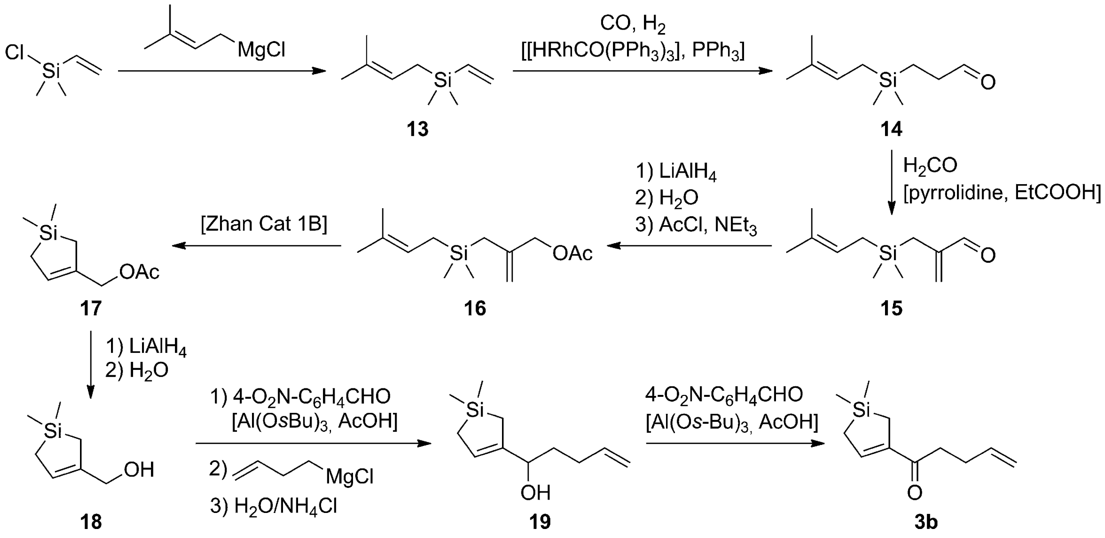
Scheme 1. Synthesis of compound **1b**.



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

distillation, ketone **2b** was converted by an acid-catalyzed (sulfuric acid) reaction with (2,4-dinitrophenyl)hydrazine to the corresponding (2,4-dinitrophenyl)hydrazone **12b** (55% yield), which could be purified by recrystallization and then transformed to **2b** by treatment with acetone in the presence of *p*-toluenesulfonic acid (*p*-TsOH). Thus, the olfactorily pure target compound **2b** was isolated in 72% yield (relative to **12b**).

Sila-*nor*-α-galbanone (**3b**) was synthesized according to Scheme 3, starting from chlorodimethylvinylsilane. Thus, reaction of $Me_2(CH_2{=}CH)SiCl$ with 3-methylbut-2-en-1-ylmagnesium chloride afforded dimethyl(3-methylbut-2-en-1-yl)vinylsilane (**13**, 74% yield), which upon rhodium-catalyzed {$[HRhCO(PPh_3)_3]$} hydroformylation under an atmosphere of hydrogen and carbon monoxide, in the presence of triphenylphosphine, furnished 3-[dimethyl(3-methylbut-2-en-1-yl)silyl]propanal (**14**, 63% yield). In the next step, an α-methylenation with formaldehyde, catalyzed by pyrrolidine/propanoic acid,[11] provided 2-{[dimethyl(3-methylbut-2-en-1-yl)silyl]methyl}acrylaldehyde (**15**, 42% yield).

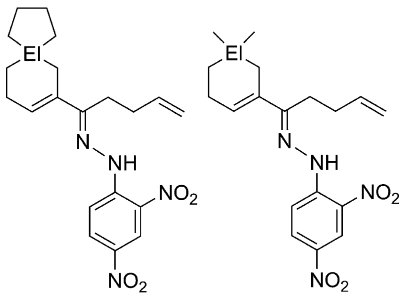


Scheme 3. Synthesis of compound **3b**.

Subsequent reduction with lithium aluminum hydride, followed by aqueous work-up, and treatment of the resulting crude alcohol with acetyl chloride, in the presence of triethylamine, furnished 2-{[dimethyl(3-methylbut-2-en-1-yl)-silyl]methyl}allyl acetate (**16**, 78% yield). Ruthenium-catalyzed (Zhan Cat 1B)[12] ring-closing metathesis[13] of **16** then afforded (4,4-dimethyl-4-silacyclopent-1-en-1-yl)methyl acetate (**17**, 62% yield). Reduction of **17** with lithium aluminum hydride, followed by aqueous work-up, furnished (4,4-dimethyl-4-silacylopent-1-en-1-yl)methanol (**18**, 90% yield). Subsequent Oppenauer oxidation using 4-nitrobenzaldehyde as the hydrogen acceptor, in the presence of aluminum tri-*sec*-butoxide and acetic acid, afforded the corresponding crude aldehyde. Treatment of the crude aldehyde with but-3-en-1-ylmagnesium chloride, followed by aqueous work-up, provided 1-(4,4-dimethyl-4-silacyclopent-1-en-1-yl)pent-4-en-1-ol (**19**, 21% yield). Oppenauer oxidation with 4-nitrobenzaldehyde, in the presence of aluminum tri-*sec*-butoxide and acetic acid, finally afforded **3b** (50% yield). Compound **3b** turned out to have only limited stability at ambient conditions, and attempts to purify **3b** by silica gel chromatography led to partial decomposition. However, compound **3b** proved to be thermally stable under mild distillation conditions, and an olfactorily pure sample of **3b** could be obtained by bulb-to-bulb distillation, thus allowing analytical characterization and olfactory evaluation (for the synthesis and characterization of the parent carbon compound **3a**, see the Supporting Information).

Compounds **1b**, **2b**, **3b**, and **4**–**19** were isolated as colorless or yellowish (**3b** and **19** only) liquids, whereas **12b** was obtained as a red crystalline solid. The chiral alcohols **7**, **11**, and **19** were obtained as racemates. 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 for sensory evaluation, if necessary, at the expense of the chemical yields. The identities of **1b**, **2b**, **3b**, **4**–**11**, **12b**, and **13**–**19** were established by elemental analyses or high-resolution mass spectrometry and by NMR spectroscopic studies. In addition, compound **12b** was structurally characterized by single-crystal X-ray diffraction.

To get some information about the structures of the cyclic and spirocyclic skeletons of the C/Si pairs **1a**/**1b** and **2a**/**2b**, the ketones **1a**, **1b**, and **2a** were also transformed into the corresponding crystalline (2,4-dinitrophenyl)hydrazones **12a**, **20a**, and **20b** (Figure 2), and the C/Si pairs **12a**/**12b** and **20a**/**20b** were structurally characterized by single-crystal X-ray diffraction (see section crystal structure analyses below). Compounds **12a**, **20a**, and **20b** were obtained by using the same synthetic method as described above for the generation of **12b** (see Scheme 2); for the characterizations of **12a**, **20a**, and **20b**, see the Supporting Information.



12a: El = C
12b: El = Si

20a: El = C
20b: El = Si

Figure 2. Chemical structures of compounds **12a**, **12b**, **20a**, and **20b**.

Crystal Structure Analyses

Compounds **12a**, **12b**, **20a**, and **20b** were structurally characterized by single-crystal X-ray diffraction.[14] The structures are depicted in Figures 3, 4, 5, and 6 (for further details, see the Supporting Information). As can be seen from superpositioning of the C/Si pairs **12/12b** and **20a/20b** (Figures 7 and 8), the structural features of the molecular skeletons of the respective C/Si analogues are similar; however, the different covalent radii of carbon and silicon also result in some striking structural differences.

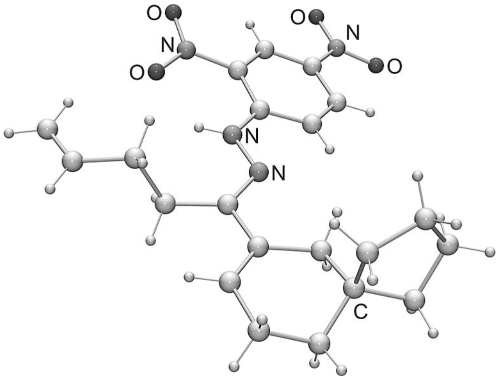


Figure 3. Molecular structure of **12a** in the crystal.

Figure 7 shows the superposition of the molecular skeletons of **12a** with **12b-I** and **12b-II**. Both the cyclohexene ring of **12a** and the silacyclohexene rings of **12b-I** and **12b-II** adopt half-chair conformations, with the silicon-based ring system being flatter. The cyclopentane ring of **12a** adopts an envelope conformation, whereas the silacyclopentane rings of **12b-I** and **12b-II** adopt half-chair conformations, leading to significant changes in the shape and size of the C/Si analogues.

Figure 8 shows the superpositions of the molecular skeletons of **20a-I** and **20a-II** with those of **20b-I** and **20b-II**,[15] clearly indicating the greater flexibility of the silacyclohexene ring. Whereas the cyclohexene rings of **20a-I** and **20a-II** are very similar and adopt a half-chair conformation, both a half-chair (**20b-I**) and a boat conformation (**20b-II**) were observed for the silacylohexene ring. Due to the longer Si–C distances compared to the analogous C–C bond lengths, the silacyclohexene ring is flatter than the cyclohexene ring.

In conclusion, the crystal structure analyses of the C/Si pairs **12a/12b** and **20a/20b** revealed some differences in the

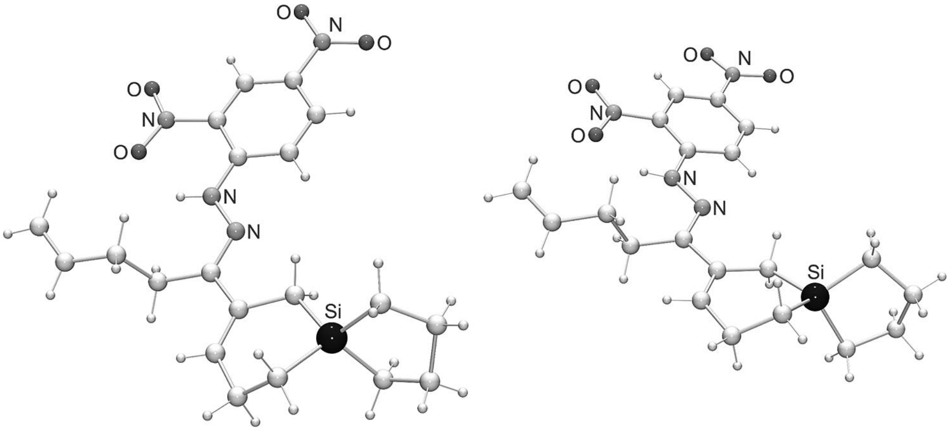


Figure 4. Molecular structures of the two crystallographically independent molecules in the crystal of **12b** (molecule I, left; molecule II, right).

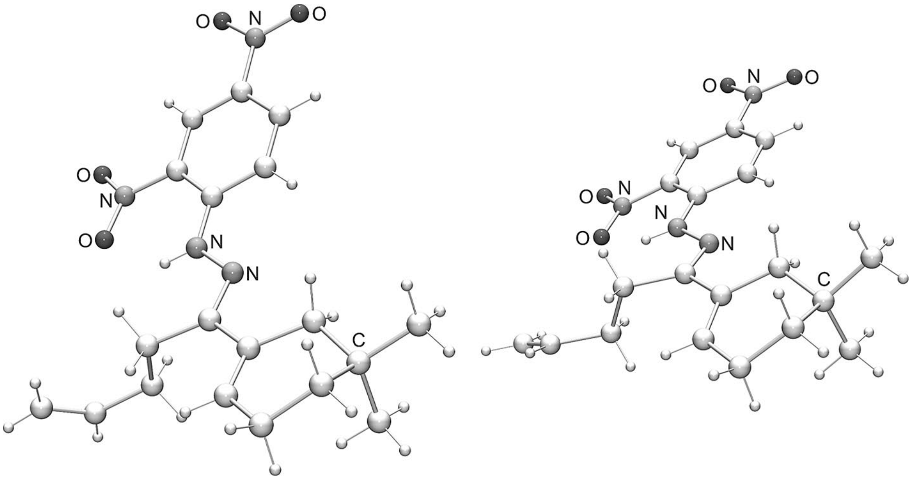


Figure 5. Molecular structures of two of the eight crystallographically independent molecules in the crystal of **20a** (molecule I, left; molecule II, right). The structures of the other six molecules are very similar. One of these molecules is disordered (two different conformations of the olefinic side chain).

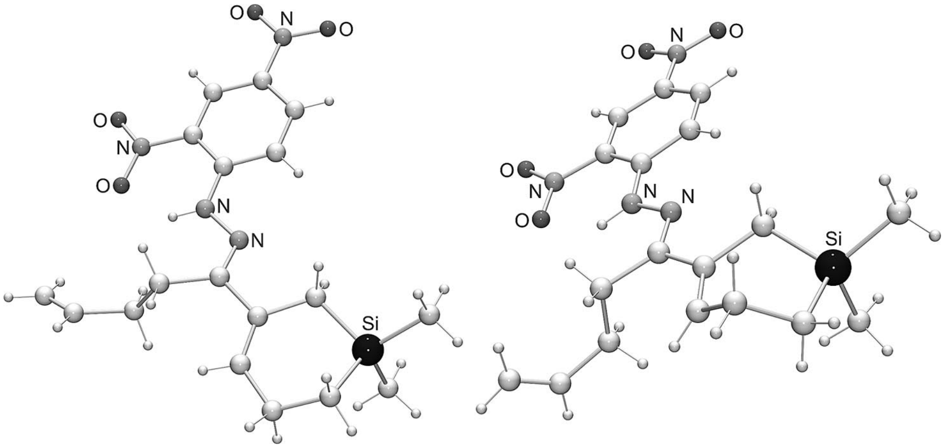


Figure 6. Molecular structures of two of the four crystallographically independent molecules in the crystal of **20b** (molecule I, left; molecule II, right). Molecules I and II are disordered (molecule I: two different conformations of the olefinic side chain, occupancy of the depicted structure 62%; molecule II: two different conformations of the silacyclohexene ring, occupancy of the depicted structure 57%; two different conformations of the olefinic side chain, occupancy of the depicted structure 70%). The other two molecules are also disordered, and the structures of the dominant conformers are very similar to those of the dominant conformers of molecules I and II, respectively.

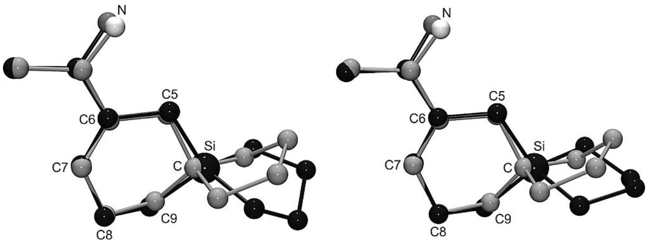


Figure 7. Superpositions (atoms C/Si and C5–C9) of the molecular skeletons of **12a** (grey) and **12b-I** (black, left) and **12a** (grey) and **12b-II** (black, right). Hydrogen atoms are omitted for clarity.

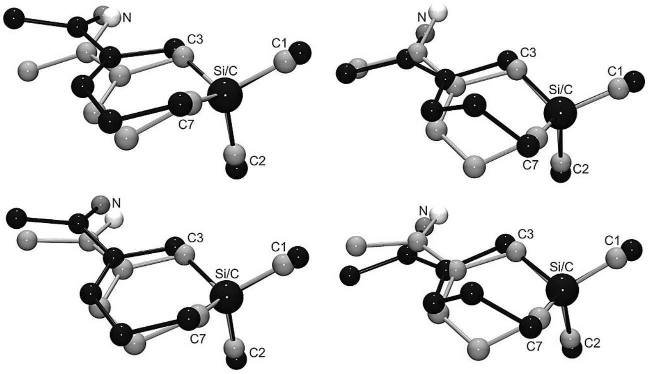


Figure 8. Superpositions (atoms C/Si, C1–C3, and C7) of the molecular skeletons of the dominant conformers of **20a-I** (grey) and **20b-I** (black, top left), **20a-I** (grey) and **20b-II** (black, top right), **20a-II** (grey) and **20b-I** (black, bottom left), and **20a-II** (grey) and **20b-II** (black, bottom right). Hydrogen atoms are omitted for clarity.

molecular structures of the respective C/Si analogues. Analogous structural differences may play a role in dictating odor perception characteristics of the odorants **1a**/**1b** and **2a**/**2b**.

Olfactory Characterization

Compounds **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** were studied for their olfactory properties (Table 1). All compounds possess green-fruity, galbanum-type odors with pineapple aspects and thus are olfactorily related.

With its hyacinth character, α-galbanone (**1a**) is the most floral, hyacinth-like compound within the series investigated. It exhibits an additional slightly oily impression and possesses an odor threshold of 0.027 $\mathrm{ng\,L^{-1}}$ air. Upon sila-substitution (→ **1b**), the floral facets vanish, and the slightly oily impression becomes somewhat more perceptible. As a result, the linear odor profile of sila-α-galbanone (**1b**) is more pronounced green. With an odor threshold of 0.094 $\mathrm{ng\,L^{-1}}$ air, sila-α-galbanone (**1b**) is almost 3 times less intense than α-galbanone (**1a**), but the increased molecular mass of **1b** leads to its enhanced substantivity in functional applications.

α-Spirogalbanone (**2a**), with an odor threshold of 0.023 $\mathrm{ng\,L^{-1}}$ air, is comparable with α-galbanone (**1a**), but due to its higher molecular mass it is even more substantive than sila-α-galbanone (**1b**) and is therefore useful in transferring a fresh-fruity green galbanum–pineapple effect to the dry-down of a fragrance or in fabric-care applications. Its powerful odor profile is green, galbanum, fruity, pineapple, and accompanied by slight allylic facets. The odor threshold of **2a** is drastically impaired by C/Si exchange (→ **2b**). With an odor threshold of 3.8 $\mathrm{ng\,L^{-1}}$ air, silicon analogue **2b** is almost 170 times less potent than its parent carbon compound **2a**, although it still constitutes a reasonable odorant. The structural differences in terms of shape and size of the C/Si analogues **2a** and **2b** (see Figure 7) likely impair the interactions of **2b** with the hydrophobic receptor binding pocket(s). Moreover, the relative position and orientation of the endocyclic double bond relative to the receptor binding site appears to be critically important. Although the odor threshold is strongly affected, the odor profile of **2a** changes rather subtly upon sila-substitution (→ **2b**). Sila-α-spirogalbanone (**2b**) also has a green-fruity odor recalling galbanum resin and pineapples, close to α-galbanone (**1a**), and also with metallic facets, yet without its hyacinth aspects. With its considerably enhanced substantivity and adhesive power on textile fibers – possibly as a consequence of the enhanced lipophilicity of the sila-analogue – silicon compound **2b** shows good performance in laundry applications (detergents, softeners), compensating to some extent for the poor odor threshold. The substantivity is thus enhanced both by replacement of the *gem*-dimethyl substituents with a spiro ring (**1a**→**2a** and **1b**→**2b**) and by C/Si exchange (**1a**→**1b** and **2a**→**2b**).

Table 1. Olfactory properties of the C/Si pairs **1a**/**1b**, **2a**/**2b**, and **3a**/**3b**.

	Olfactory properties	Odor threshold [$\mathrm{ng\,L^{-1}}$ air]
1a	Green-fruity, galbanum, pineapple, with a herbal-floral hyacinth character, slightly oily	0.027
1b	Green-fruity, galbanum, pineapple, with the typical character of α-galbanone (**1a**), yet without its hyacinth aspects, slightly fatty	0.094
2a	Powerful, green, galbanum, fruity, pineapple, slightly allylic	0.023
2b	Green-fruity, galbanum, pineapple, with metallic facets, close to α-galbanone (**1a**), yet without its hyacinth aspects	3.8
3a	Powerful, fruity, pineapple, green, α-galbanone-like, metallic, pungent, slightly sulfurous	0.0087
3b	Intense fruity-green, pineapple, α-galbanone-like, pungent, slightly sulfurous	0.085

Such an enhancement of substantivity should be especially useful for the α-galbanone homologue **3a**. Contrary to the strong, less distinct, aggressive fruity, plum- and pear-type odor ascribed in the patent literature,[9] **3a** was found to possess a typical α-galbanone-like, fruity-green, pineapple odor, accompanied by metallic, pungent facets, and slightly sulfurous aspects (Table 1). However, most interesting was its extremely low odor detection threshold of 0.0087 $\mathrm{ng\,L^{-1}}$ air, which is about three times lower than that of the commercial α-galbanum odorants **1a** and **2a**. Indeed, sila-analogue **3b** turned out to be very similar in odor profile, possessing an intense fruity-green, pineapple and galbanum odor with pungent facets, and slightly sulfurous aspects. However, silicon compound **3b** showed only a limited stability at ambient conditions, which was not observed for the less strained silacyclohexenes **1b** and **2b**. The reasons for this instability will be further investigated. Thus, an increased substantivity upon C/Si exchange could not be taken advantage of. Again sila-analogue **3b** turned out to possess a significantly higher odor threshold than the parent compound **3a**, with 0.085 ng L^{-1} air being almost about ten times higher than that of **3a** (0.0087 ng L^{-1} air). Concerning structure–odor correlations, silicon compound **3b** constitutes the most potent sila-odorant of the series, and is, in fact, the sila-odorant with the lowest threshold measured thus far in our laboratory.[7,8]

Conclusions

Sila-α-galbanone (**1b**), sila-α-spirogalbanone (**2b**), and sila-*nor*-α-galbanone (**3b**) are sila-analogues of the galbanum odorants α-galbanone (**1a**), α-spirogalbanone (**2a**), and *nor*-α-galbanone (**3a**), respectively. The silicon compounds **1b**–**3b** were prepared in multistep syntheses in isomerically pure form, starting from the silanes Me_2SiCl_2, $(CH_2{=}CH)_2SiCl_2$, and $Me_2(CH_2{=}CH)SiCl$, respectively. Hydroformylation of vinylsilanes, followed by either ring-closing aldol condensations or ring-closing alkene metatheses, were the key steps in these syntheses.

The olfactory evaluations of the three C/Si pairs **1a/1b**, **2a/2b**, and **3a/3b** once again demonstrated that the impact of sila-substitution on the olfactory properties of odorants is hardly predictable. Although the odor threshold of **1a** is affected very little upon sila-substitution, in the case of **2a** (→ **2b**) the receptor affinity, as indicated by the detection odor threshold, decreased almost 170-fold. Also, in the case of **3b**, the odor threshold increased significantly, but only by a factor of about 10. The odor profiles of the sila-analogues **1b**, **2b**, and **3b** and their parent carbon compounds **1a**, **2a**, and **3a** are, however, clearly related, albeit the floral hyacinth character of **1a** and **2a** was missing in the case of their sila-analogues **1b** and **2b**. Taken together, these results could indicate an interaction of **1a/1b**, **2a/2b**, and **3a/3b** with the same set of olfactory receptors, but with different steric constraints within the hydrophobic binding pockets, especially with respect to the position of the endocyclic double bonds. These effects are then multiplied by the steric expansion in the case of sila-α-spirogalbanone (**2b**), yet are somewhat less relevant for the monocyclic compounds sila-α-galbanone (**1b**) and sila-*nor*-α-galbanone (**3b**). A surprising finding was the extremely low odor threshold of 0.0087 ng L^{-1} air measured for *nor*-α-galbanone (**3a**). Importantly, sila-*nor*-α-galbanone (**3b**), with an odor threshold of 0.085 ng L^{-1} air, is the sila-odorant with the lowest odor threshold measured by us thus far. The strong impact of sila-substitution on odor thresholds reported in this study again emphasizes the high potential of the C/Si switch strategy in the exploration of structure–activity correlations.

Experimental Section

General Methods: All syntheses in organic solvents 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 and reagents were purchased from ABCR, Acros, Aldrich, or Wacker and were used without further purification. Filtrations were carried out by using silica gel (40–63 µm, Merck). Flash chromatography (pressure, 1.5 bar) was performed by using silica gel as the stationary phase (40–63 µm, Merck). Medium pressure liquid chromatography (MPLC) was carried out as follows: pressure, 16 bar; column, 50 × 2.5 cm; stationary phase, silica gel (YMC SL12S15, 15 µm); detector, Knauer Variable Wavelength Monitor. Compounds **1b** and **2b** were applied on the MPLC column as solutions in their respective eluent through the sample loop. Bulb-to-bulb distillations were performed by using a Büchi Glass Oven B-580 apparatus. Melting points were determined by differential scanning calorimetry using a Mettler Toledo DSC 823e apparatus. The ^{1}H, ^{13}C, ^{15}N (**12b** only) and ^{29}Si NMR spectra of compounds **1b**, **2b**, **4**–**11**, **12b**, **20a**, and **20b** were recorded at 23 °C with a Bruker Avance 500 NMR spectrometer (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{15}N, 50.7 MHz; ^{29}Si, 99.4 MHz) using C_6D_6 as the solvent. The ^{1}H and ^{13}C NMR spectra of compounds **3b** and **13**–**19** were recorded at ambient temperature with a Bruker AW 300 NMR spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz) using C_6D_6 (**3b**) or $CDCl_3$ (**13**–**19**) as the solvent. Chemical shifts (ppm) were determined relative to 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), internal $CHCl_3$ (^{1}H, δ = 7.24 ppm. $CDCl_3$), internal $CDCl_3$ (^{13}C, δ = 77.0 ppm. $CDCl_3$), external $H_2NC(O)H$ (90% in [D$_6$]DMSO) (^{15}N, δ = –268.0 ppm; C_6D_6), or external tetramethylsilane (^{29}Si, δ = 0 ppm; C_6D_6). Assignment of the ^{1}H NMR spectroscopic data was supported by ^{1}H,^{1}H gradient-selected COSY, ^{1}H,^{1}H EXSY/NOESY (mixing time, 500 ms; recycle delay, 2.0 s), ^{13}C,^{1}H gradient-selected HMQC and HMBC experiments, and DEPT-90 as well as DEPT-135 experiments. Assignment of the ^{13}C NMR spectroscopic data was supported by the aforementioned ^{13}C,^{1}H correlation experiments. The ^{15}N NMR spectra were obtained by using inverse correlation ^{15}N,^{1}H HSQC and HMBC experiments. The spin systems were analyzed with the WIN-DAISY (version 4.05, Bruker)[16] or MestReNova software packages (version 9.0.0, Mestrelab Research SL).[17] Coupling constants are given as their absolute values. High pressure liquid chromatography (HPLC) was performed as follows: LC pump, Merck Hitachi LaChrom L-7100; column, 25 cm, i.d. 400 nm; stationary phase, silica gel (YMC SL 12S052504QT, 5 µm); detector, Merck Hitachi L-4200 UV/Vis Detector. Elemental analyses were performed with a VarioMicro apparatus (Elementar Analysensysteme GmbH) or a EURO EA Elemental Analyzer (EuroVector). EI-MS spectra (70 eV) were recorded using an Agilent MSD 5975 mass spectrometer. The selected *m*/*z* values given refer to the isotopes ^{1}H, ^{12}C, ^{16}O, and ^{28}Si. HRMS spectra were recorded with a Bruker MicrOTOF II (**15**. ESI) or a Finnigan MAT 95 mass spectrometer (EI; **3b**, **13**, **14**, **16**–**19**).

1-(5,5-Dimethylcyclohex-1-en-1-yl)pent-4-en-1-one (α-Galbanone, 1a): This compound was synthesized according to ref.[4] Odor description: green-fruity, galbanum, pineapple, with a herbal-floral hyacinth character, slightly oily; odor threshold: 0.027 ng L^{-1} air.

1-(5,5-Dimethyl-5-silacyclohex-1-en-1-yl)pent-4-en-1-one (Sila-α-galbanone, 1b): 1,1,1-Tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (Dess–Martin periodinane) (1.61 g, 3.80 mmol) was added at 0 °C in a single portion to a stirred solution of **6** (800 mg, 3.80 mmol) in dichloromethane (60 mL), and the mixture was then warmed to 20 °C within 1 h. A saturated aqueous sodium hydrogen carbonate solution (50 mL) was added, the organic layer was separated, the aqueous layer was extracted with dichloromethane (3 × 50 mL) and discarded, the combined organic solutions were dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was filtered through a pad of silica gel (150 g), followed by elution with *n*-hexane/Et_2O (98:2 v/v). The solvent of the filtrate (including the eluate) was removed under reduced pressure, and the residue was purified by twofold MPLC on silica gel [eluent, *n*-hexane/Et_2O (99.5:0.5 v/v); flow rate, 65 mL min^{-1}; detector wavelength, 230 nm], followed by bulb-to-bulb distillation (oven temperature 115 °C, 0.01 mbar) to furnish **1b** as a colorless liquid (410 mg, 1.97 mmol; 52% yield). ^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.04 (s, 6 H, $\mathrm{SiC}H_3$), 0.56 ($\delta_{\mathrm{AA'}}$), 1.72 ($\delta_{\mathrm{DD'}}$), 2.21 ($\delta_{\mathrm{HH'}}$), 6.65 (δ_{X}) [AA′DD′HH′X system, $^{2}J(\mathrm{A,A'})$ = 12.4, $^{2}J(\mathrm{D,D'})$ = 12.4, $^{2}J(\mathrm{H,H'})$ = 15.2, $^{3}J(\mathrm{A,H})$ = $^{3}J(\mathrm{A',H'})$ = 6.1, $^{3}J(\mathrm{A,H'})$ = $^{3}J(\mathrm{A',H})$ = 7.8, $^{3}J(\mathrm{H,X})$ = $^{3}J(\mathrm{H',X})$ = 5.3, $^{4}J(\mathrm{D,X})$ = $^{4}J(\mathrm{D',X})$ = 1.4, $^{5}J(\mathrm{D,H})$ = $^{5}J(\mathrm{D',H'})$ = 1.2, $^{5}J(\mathrm{D,H'})$ = $^{5}J(\mathrm{D',H})$ = 1.8 Hz, 7 H; $\mathrm{SiC}H_{\mathrm{A}}H_{\mathrm{A'}}\mathrm{C}H_{\mathrm{H}}H_{\mathrm{H'}}\mathrm{C}H_{\mathrm{X}}\mathrm{=CC}H_{\mathrm{D}}H_{\mathrm{D'}}$], 2.52 ($\delta_{\mathrm{AA'}}$), 2.59 ($\delta_{\mathrm{DD'}}$), 5.06 ($\delta_{\mathrm{F}}$), 5.13 ($\delta_{\mathrm{M}}$), 5.93 ($\delta_{\mathrm{X}}$) [AA′DD′FMX system, $^{2}J(\mathrm{A,A'})$ = 15.0, $^{2}J(\mathrm{D,D'})$ = 16.8, $^{2}J(\mathrm{F,M})$ = 2.0, $^{3}J(\mathrm{A,D})$ = $^{3}J(\mathrm{A',D'})$ = 6.2, $^{3}J(\mathrm{A,D'})$ = $^{3}J(\mathrm{A',D})$ = 8.8, $^{3}J(\mathrm{A,X})$ = $^{3}J(\mathrm{A',X})$ = 6.6, $^{3}J(\mathrm{F,X})$ = 10.2, $^{3}J(\mathrm{M,X})$ = 17.1, $^{4}J(\mathrm{A,F})$ = $^{4}J(\mathrm{A',F})$ = 1.2, $^{4}J(\mathrm{A,M})$ = $^{4}J(\mathrm{A',M})$ = 1.6 Hz, 7 H; $\mathrm{C}H_{\mathrm{D}}H_{\mathrm{D'}}\mathrm{C}H_{\mathrm{A}}H_{\mathrm{A'}}\mathrm{C}H_{\mathrm{X}}\mathrm{=C}H_{\mathrm{F}}H_{\mathrm{M}}$] ppm. ^{13}C NMR (125.8 MHz, C_6D_6): δ = –2.7 ($\mathrm{Si}C\mathrm{H_3}$), 9.2 (*C*-4), 10.8 (*C*-6), 23.7 (*C*-3), 29.2 ($C\mathrm{H_2CH{=}CH_2}$), 36.4 [$\mathrm{C(O)}C\mathrm{H_2}$], 114.9 ($\mathrm{CH_2CH{=}}C\mathrm{H_2}$), 138.3 ($\mathrm{CH_2}C\mathrm{H{=}CH_2}$), 139.6 (*C*-1), 140.4 (*C*-2), 199.0 (*C*O) ppm. ^{29}Si NMR (99.4 MHz, C_6D_6): δ = –2.1 ppm. $C_{12}H_{20}OSi$ (208.38): calcd. C 69.17, H 9.67; found C 69.17, H 9.79; odor description: green-fruity, galbanum, pineapple, with the typical character of α-galbanone (**1a**), yet without its hyacinth aspects, slightly fatty; odor threshold: 0.094 ng L^{-1} air. For an alternative synthesis, see the Supporting Information.

1-(Spiro[4.5]dec-7-en-7-yl)pent-4-en-1-one (α-Spirogalbanone, 2a): This compound was synthesized according to ref.[3] Odor description: powerful, green, galbanum, fruity, pineapple, slightly allylic; odor threshold: 0.023 ng L^{-1} air.

1-(5-Silaspiro[4.5]dec-7-en-7-yl)pent-4-en-1-one (Sila-α-spirogalbanone, 2b). Method A: 1,1,1-Tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (Dess–Martin periodinane) (17.1 g, 40.3 mmol) was added at 0 °C in a single portion to a stirred solution of **10** (9.56 g, 40.4 mmol) in dichloromethane (400 mL), and the mixture was then warmed to 20 °C within 1 h. A saturated aqueous sodium hydrogen carbonate solution (150 mL) was added, the organic phase was separated, the aqueous phase was extracted with dichloromethane (3 × 100 mL) and discarded, the combined organic solutions were dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was filtered through a pad of silica gel (200 g), followed by elution with *n*-hexane/Et_2O (95:5 v/v). The solvent of the filtrate (including the eluate) was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel [eluent, *n*-hexane/Et_2O (98:2 v/v)], followed by MPLC on silica gel [eluent, *n*-hexane/acetone (99.8:0.2 v/v); flow rate, 50 mL min^{-1}; detector wavelength, 230 nm] and then by bulb-to-bulb distillation (oven temperature 135 °C, 0.01 mbar) to furnish **2b** as a colorless liquid (4.30 g, 18.3 mmol; purity 99.5%; 45% yield). For the NMR spectroscopic data, odor description, and odor threshold, see method B.

Method B: A mixture of **12b** (1.10 g, 2.65 mmol), *p*-toluenesulfonic acid monohydrate (46 mg, 242 µmol), and acetone (50 mL) was heated in a sealed tube at 60 °C for 65 h (for a similar method, see ref.[18]). The resulting mixture was then cooled to 20 °C within 1 h and filtered through a pad of silica gel (30 g), followed by elution with *n*-hexane/Et_2O (95:5 v/v). The solvent of the filtrate (including the eluate) was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel [eluent, *n*-hexane/Et_2O (98:2 v/v)], followed by bulb-to-bulb distillation (oven temperature 135 °C, 0.01 mbar) to furnish **2b** as a colorless liquid (450 mg, 1.92 mmol; 72% yield). ^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.60 ($\delta_{\mathrm{AA'}}$), 0.63 ($\delta_{\mathrm{BB'}}$), 1.62 ($\delta_{\mathrm{XX'}}$), 1.65 ($\delta_{\mathrm{YY'}}$) [AA′BB′XX′YY′ system, $^{2}J(\mathrm{A,B})$ = $^{2}J(\mathrm{A',B'})$ = 14.8, $^{2}J(\mathrm{X,Y})$ = $^{2}J(\mathrm{X',Y'})$ = 12.9, $^{3}J(\mathrm{A,X})$ = $^{3}J(\mathrm{A',X'})$ = 7.6, $^{3}J(\mathrm{A,Y})$ = $^{3}J(\mathrm{A',Y'})$ = 7.1, $^{3}J(\mathrm{B,X})$ = $^{3}J(\mathrm{B',X'})$ = 7.1, $^{3}J(\mathrm{B,Y})$ = $^{3}J(\mathrm{B',Y'})$ = 7.6, $^{3}J(\mathrm{X,X'})$ = 4.9, $^{3}J(\mathrm{X,Y'})$ = $^{3}J(\mathrm{X',Y})$ = 7.7, $^{3}J(\mathrm{Y,Y'})$ = 5.0, $^{4}J(\mathrm{A,X'})$ = $^{4}J(\mathrm{A',X})$ = 0.7, $^{4}J(\mathrm{A,Y'})$ = $^{4}J(\mathrm{A',Y})$ = 0.3, $^{4}J(\mathrm{B,X'})$ = $^{4}J(\mathrm{B',X})$ = 0.4, $^{4}J(\mathrm{B,Y'})$ = $^{4}J(\mathrm{B',Y})$ = 0.7 Hz, 8 H; $\mathrm{SiC}H_{\mathrm{A}}H_{\mathrm{B}}\mathrm{C}H_{\mathrm{X}}H_{\mathrm{Y}}\mathrm{C}H_{\mathrm{X'}}H_{\mathrm{Y'}}\mathrm{C}H_{\mathrm{A'}}H_{\mathrm{B'}}$], 0.67 ($\delta_{\mathrm{AA'}}$), 1.82 ($\delta_{\mathrm{DD'}}$), 2.23 ($\delta_{\mathrm{HH'}}$), 6.65 ($\delta_{\mathrm{X}}$) [AA′DD′HH′X system, $^{2}J(\mathrm{A,A'})$ = 11.0, $^{2}J(\mathrm{D,D'})$ = 9.4, $^{2}J(\mathrm{H,H'})$ = 13.6, $^{3}J(\mathrm{A,H})$ = $^{3}J(\mathrm{A',H'})$ = 6.0, $^{3}J(\mathrm{A,H'})$ = $^{3}J(\mathrm{A',H})$ = 7.8, $^{3}J(\mathrm{H,X})$ = $^{3}J(\mathrm{H',X})$ = 5.3, $^{4}J(\mathrm{D,X})$ = $^{4}J(\mathrm{D',X})$ = 1.4, $^{5}J(\mathrm{D,H})$ = $^{5}J(\mathrm{D',H'})$ = 2.1, $^{5}J(\mathrm{D,H'})$ = $^{5}J(\mathrm{D',H})$ = 0.8 Hz, 7 H; $\mathrm{SiC}H_{\mathrm{A}}H_{\mathrm{A'}}\mathrm{C}H_{\mathrm{H}}H_{\mathrm{H'}}\mathrm{C}H_{\mathrm{X}}\mathrm{=CC}H_{\mathrm{D}}H_{\mathrm{D'}}$], 2.51 ($\delta_{\mathrm{AA'}}$), 2.58 ($\delta_{\mathrm{DD'}}$), 5.06 ($\delta_{\mathrm{F}}$), 5.13 ($\delta_{\mathrm{M}}$), 5.93 ($\delta_{\mathrm{X}}$) [AA′DD′FMX system, $^{2}J(\mathrm{A,A'})$ = 15.0, $^{2}J(\mathrm{D,D'})$ = 16.8, $^{2}J(\mathrm{F,M})$ = 2.0, $^{3}J(\mathrm{A,D})$ = $^{3}J(\mathrm{A',D'})$ = 6.2, $^{3}J(\mathrm{A,D'})$ = $^{3}J(\mathrm{A',D})$ = 8.7, $^{3}J(\mathrm{A,X})$ = $^{3}J(\mathrm{A',X})$ = 6.6, $^{3}J(\mathrm{F,X})$ = 10.2, $^{3}J(\mathrm{M,X})$ = 17.1, $^{4}J(\mathrm{A,F})$ = $^{4}J(\mathrm{A',F})$ = 1.2, $^{4}J(\mathrm{A,M})$ = $^{4}J(\mathrm{A',M})$ = 1.6 Hz, 7 H; $\mathrm{C}H_{\mathrm{D}}H_{\mathrm{D'}}\mathrm{C}H_{\mathrm{A}}H_{\mathrm{A'}}\mathrm{C}H_{\mathrm{X}}\mathrm{=C}H_{\mathrm{F}}H_{\mathrm{M}}$] ppm.[19] ^{13}C NMR (125.8 MHz, C_6D_6): δ = 8.0 (*C*-10), 9.5 (*C*-6), 11.4 (*C*-1 and *C*-4), 23.9 (*C*-9), 27.3 (*C*-2 and *C*-3), 29.2 ($C\mathrm{H_2CH{=}CH_2}$), 36.4 [$\mathrm{C(O)}C\mathrm{H_2}$], 114.9 ($\mathrm{CH_2CH{=}}C\mathrm{H_2}$), 138.3 ($\mathrm{CH_2}C\mathrm{H{=}CH_2}$), 139.7 (*C*-7), 140.7 (*C*-8), 198.9 (*C*O) ppm. ^{29}Si NMR (99.4 MHz, C_6D_6): δ = 15.3 ppm. $C_{14}H_{22}OSi$ (234.41): calcd. C 71.73, H 9.46; found C 71.47, H 9.42; odor description: green-fruity, galbanum, pineapple, with metallic facets, close to α-galbanone (**1a**), yet without its hyacinth aspects; odor threshold: 3.8 ng L^{-1} air.

1-(4,4-Dimethyl-4-silacyclopent-1-en-1-yl)pent-4-en-1-one (Sila-*nor*-α-galbanone, 3b): Aluminum tri-*sec*-butoxide (113 mg, 459 µmol) was added at 20 °C to a stirred solution of **19** (300 mg, 1.53 mmol) in *tert*-butyl methyl ether (30 mL), followed by the addition of acetic acid (9.2 mg, 153 µmol). The resulting mixture was then stirred at this temperature for 20 min, prior to evacuation of the system and flushing twice with argon. Subsequently, 4-nitrobenzaldehyde (924 mg, 6.11 mmol) was added at 20 °C in three portions, and the reaction mixture was then stirred at this temperature for 30 min. *n*-Hexane (30 mL) and anhydrous magnesium sulfate were added, and the organic phase was separated by filtration. The solvent was removed under reduced pressure at 20 °C, and the residue was purified by bulb-to-bulb distillation (oven temperature 80 °C, 0.015 mbar) to furnish **3b** as a yellowish liquid (150 mg, 772 µmol; 50% yield). The product showed limited stability at ambient conditions and decomposed when chromatographic purification on silica gel was attempted. ^{1}H NMR (300.1 MHz, C_6D_6): δ = –0.03 (s, 6 H, $\mathrm{SiC}H_3$), 1.23 ($\delta_{\mathrm{AA'}}$), 1.62 ($\delta_{\mathrm{DD'}}$), 6.58 (δ_{X}) [AA′DD′X system, $^{2}J(\mathrm{AA'})$ = 17.5, $^{2}J(\mathrm{DD})'$ = 17.5, $^{3}J(\mathrm{DX})$ = $^{3}J(\mathrm{D'X})$ = 1.5, $^{4}J(\mathrm{AD})$ = $^{4}J(\mathrm{A'D'})$ = 1.8, $^{4}J(\mathrm{AD'})$ = $^{4}J(\mathrm{A'D})$ = 1.7, $^{4}J(\mathrm{AX})$ = $^{4}J(\mathrm{A'X})$ = 3.5 Hz, 5 H; $\mathrm{SiC}H_{\mathrm{D}}H_{\mathrm{D'}}\mathrm{C}H_{\mathrm{X}}\mathrm{=CC}H_{\mathrm{A}}H_{\mathrm{A'}}$], 2.43 ($\delta_{\mathrm{AA'}}$), 2.49 ($\delta_{\mathrm{BB'}}$), 4.96 ($\delta_{\mathrm{F}}$), 5.03 ($\delta_{\mathrm{M}}$), 5.84 ($\delta_{\mathrm{X}}$) [AA′BB′FMX system, $^{2}J(\mathrm{AA'})$ = 15.0, $^{2}J(\mathrm{BB'})$ = 16.8, $^{2}J(\mathrm{FM})$ = 2.0, $^{3}J(\mathrm{AB})$ = $^{3}J(\mathrm{A'B'})$ = 8.8, $^{3}J(\mathrm{AB'})$ = $^{3}J(\mathrm{A'B})$ = 6.2, $^{3}J(\mathrm{AX})$ = $^{3}J(\mathrm{A'X})$ = 6.6, $^{3}J(\mathrm{FX})$ = 10.2, $^{3}J(\mathrm{MX})$ = 17.1, $^{4}J(\mathrm{AF})$ = $^{4}J(\mathrm{A'F})$ = 1.2, $^{4}J(\mathrm{AM})$ = $^{4}J(\mathrm{A'M})$ = 1.6 Hz, 7 H; $\mathrm{C}H_{\mathrm{B}}H_{\mathrm{B'}}\mathrm{C}H_{\mathrm{A}}H_{\mathrm{A'}}\mathrm{C}H_{\mathrm{X}}\mathrm{=C}H_{\mathrm{F}}H_{\mathrm{M}}$] ppm. ^{13}C NMR (75.5 MHz, C_6D_6): δ = –2.2 ($\mathrm{Si}C\mathrm{H_3}$), 16.4 (*C*-5), 20.1 (*C*-3), 28.9 ($C\mathrm{H_2CH{=}CH_2}$), 37.6 [$\mathrm{C(O)}C\mathrm{H_2}$], 114.9 ($\mathrm{CH_2CH{=}}C\mathrm{H_2}$), 138.3 ($\mathrm{CH_2}C\mathrm{H{=}CH_2}$), 142.2 (*C*-2), 145.3 (*C*-1), 198.1 (*C*O) ppm. EI-MS: *m*/*z* (%) = 194 (10) $[M]^{+}$, 179 (24), 165 (67), 153 (14), 135 (11), 111

(17), 85 (14), 75 (100), 59 (15), 43 (8). HRMS (EI): *m*/*z* calcd. for $C_{11}H_{18}OSi$ 194.1127, found 194.1120; odor description: intense fruity-green, pineapple, α-galbanone-like, pungent, slightly sulfurous; odor threshold: 0.085 ng L^{-1} air.

Dimethyldivinylsilane (4):[10] A 1.6 M solution of vinylmagnesium chloride (1.07 L, 1.71 mol of CH_2=CHMgCl) was added dropwise at 0 °C within 3 h to a stirred solution of dichlorodimethylsilane (200 g, 1.55 mol) in Et_2O (600 mL), and the resulting mixture was then heated under reflux for 2 h. The mixture was cooled to 20 °C within 30 min, water (500 mL) was added, the organic phase was separated, the aqueous phase was extracted with Et_2O (5 × 100 mL) and discarded, and the combined organic solutions were dried with anhydrous sodium sulfate. The solvent was removed by distillation at atmospheric pressure using a spinning band column, and the residue was then purified by a further distillation at atmospheric pressure with a spinning band column to furnish **4** as a colorless liquid (150 g, 1.34 mol; 86% yield). B.p. 78 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.24 (s, 6 H, SiCH_3), 5.83 (δ_A), 6.06 (δ_B), 6.28 (δ_C) [ABC system, ^2J(A,B) = 3.8, ^3J(A,C) = 20.3, ^3J(B,C) = 14.7 Hz, 6 H; CH_C=CH_AH_B] ppm. ^{13}C NMR (125.8 MHz, C_6D_6): δ = –3.2 (SiCH_3), 132.5 (CH_2), 138.1 (CH) ppm. ^{29}Si NMR (99.4 MHz, C_6D_6): δ = –13.8 ppm. $C_6H_{12}Si$ (112.25): calcd. C 64.20, H 10.78; found C 64.27, H 10.79.

3,3′-(Dimethylsilanediyl)dipropanal (5): A mixture of **4** (5.00 g, 44.5 mmol), triphenylphosphine (584 mg, 2.23 mmol), (acetylacetonato)dicarbonylrhodium(I) (80 mg, 310 µmol), and benzene (30 mL) was heated in an autoclave at 80 °C for 7 h under an atmosphere of hydrogen (45 bar) and carbon monoxide (45 bar) and was then cooled to 20 °C within 30 min. The mixture was filtered through a pad of silica gel (30 g), followed by elution with *n*-hexane/Et_2O (9:1 v/v). The solvent of the filtrate (including the eluate) was removed under reduced pressure (5 mbar), and the residue was suspended in a mixture of Et_2O (50 mL) and water (50 mL). The organic phase was separated, the aqueous phase was extracted with Et_2O (3 × 30 mL) and discarded, and the combined organic solutions were dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure (5 mbar), the residue was purified by a rapid bulb-to-bulb distillation (oven temperature 150 °C, 0.01 mbar), and the distillate was then further purified by a second bulb-to-bulb distillation (oven temperature 95 °C, 0.01 mbar) to furnish **5** as a colorless liquid (1.30 g, 7.55 mmol; 17% yield). ^{1}H NMR (500.1 MHz, C_6D_6): δ = –0.14 (s, 6 H, SiCH_3), 0.53 ($\delta_{AA'}$), 1.91 ($\delta_{DD'}$), 9.46 (δ_X) [AA′DD′X system, ^2J(A,A′) = 17.1, ^2J(D,D′) = 14.4, ^3J(A,D) = ^3J(A′,D′) = 5.5, ^3J(A,D′) = ^3J(A′,D) = 11.0, ^3J(D,X) = ^3J(D′,X) = 1.5 Hz, 10 H; C$H_AH_{A'}$C$H_DH_{D'}$CH_X] ppm. ^{13}C NMR (125.8 MHz, C_6D_6): δ = –3.9 (SiCH_3), 6.4 (SiCH_2), 38.0 (CH_2CH), 200.9 (CHO) ppm. ^{29}Si NMR (99.4 MHz, C_6D_6): δ = 4.3 ppm. $C_8H_{16}O_2Si$ (172.30): calcd. C 55.77, H 9.36; found C 55.60, H 9.55.

5,5-Dimethyl-5-silacyclohex-1-ene-1-carbaldehyde (6): A mixture of **4** (15.3 g, 136 mmol), triphenylphosphine (1.80 g, 6.86 mmol), (acetylacetonato)dicarbonylrhodium(I) (246 mg, 953 µmol), and benzene (50 mL) was heated in an autoclave at 80 °C for 7 h under an atmosphere of hydrogen (45 bar) and carbon monoxide (45 bar) and was then cooled to 20 °C within 30 min. The resulting mixture (containing **5** as an intermediate) was then added dropwise at 0 °C within 1 h to a stirred 0.5 M solution of HCl in Et_2O (400 mL, 200 mmol of HCl), and the resulting mixture was then kept undisturbed at 20 °C for 18 h. The mixture was filtered through a pad of silica gel (180 g), followed by elution with *n*-hexane/Et_2O (1:1 v/v). The solvent of the filtrate (including the eluate) was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel [eluent, *n*-hexane/Et_2O (8:2 v/v)], followed by bulb-to-bulb distillation (oven temperature 70 °C, 0.01 mbar) to furnish **6** as a colorless liquid (7.50 g, 48.6 mmol; 36% yield). ^{1}H NMR (500.1 MHz, C_6D_6): δ = –0.02 (s, 6 H, SiCH_3), 0.51 ($\delta_{AA'}$), 1.54 ($\delta_{DD'}$), 2.17 ($\delta_{HH'}$), 6.20 (δ_X) [AA′DD′HH′X system, ^2J(A,A′) = 12.4, ^2J(D,D′) = 12.4, ^2J(H,H′) = 15.2, ^3J(A,H) = ^3J(A′,H′) = 7.5, ^3J(A,H′) = ^3J(A′,H) = 6.3, ^3J(H,X) = ^3J(H′,X) = 4.8, ^4J(D,X) = ^4J(D′,X) = 1.5, ^5J(D,H) = ^5J(D′,H′) = 2.0, ^5J(D,H′) = ^5J(D′,H) = 1.4 Hz, 7 H; SiC$H_AH_{A'}$C$H_HH_{H'}$CH_X=CC$H_DH_{D'}$], 9.45 (CHO) ppm. ^{13}C NMR (125.8 MHz, C_6D_6): δ = –3.0 (SiCH_3), 8.4 (C-6), 9.4 (C-4), 21.1 (C-3), 141.2 (C-1), 152.4 (C-2), 194.0 (CHO) ppm. ^{29}Si NMR (99.4 MHz, C_6D_6): δ = –3.6 ppm. $C_8H_{14}OSi$ (154.28): calcd. C 62.28, H 9.15; found C 62.15, H 9.15.

1-(5,5-Dimethyl-5-silacyclohex-1-en-1-yl)pent-4-en-1-ol (7): 4-Bromo-1-butene (11.4 g, 84.4 mmol) was added dropwise within 30 min to a suspension of magnesium turnings (2.60 g, 107 mmol) in Et_2O (130 mL), causing the reaction mixture to boil under reflux. The mixture was heated under reflux for a further hour, cooled to 20 °C within 20 min, and then added dropwise at –10 °C within 30 min to a stirred solution of **6** (8.70 g, 56.4 mmol) in Et_2O (180 mL). The resulting mixture was warmed to 20 °C within 30 min and was then stirred at this temperature for a further hour, a saturated aqueous solution of ammonium chloride (150 mL) was added, the organic phase was separated, the aqueous phase was extracted with Et_2O (3 × 100 mL) and discarded, and the combined organic solutions were dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel [eluent, *n*-hexane/Et_2O (7:3 v/v)], followed by bulb-to-bulb distillation (oven temperature 130 °C, 0.01 mbar) to furnish **7** as a colorless liquid (10.9 g, 51.8 mmol; 92% yield). ^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.11 (s, 3 H, SiCH_3), 0.13 (s, 3 H, CH_3), 0.63–0.74 (m, 2 H, 4-H), 1.06–1.35 (m, 2 H, 6-H), 1.1 (br. s, 1 H, OH), 1.67–1.80 (m, 2 H, CH_2CHOH), 2.15–2.26 (m, 2 H, CH_2CH=CH_2), 2.24–2.31 (m, 2 H, 3-H), 3.93–3.98 (m, 1 H, CHOH), 5.09–5.14 (m, 1 H, CH_2CH=CHH), 5.17–5.23 (m, 1 H, CH_2CH=CHH), 5.68–5.73 (m, 1 H, 2-H), 5.91–6.01 (m, 1 H, CH_2CH=CH_2) ppm.[20] ^{13}C NMR (125.8 MHz, C_6D_6): δ = –2.5 (SiCH_3), –2.4 (CH_3), 10.4 (C-4), 11.1 (C-6), 22.7 (C-3), 30.6 (CH_2CH=CH_2), 34.5 (CH_2CHOH), 77.6 (CHOH), 114.6 (CH_2CH=CH_2), 125.2 (C-2), 139.0 ($CH_2$$C$H=$CH_2$), 140.1 ($C$-1) ppm. ^{29}Si NMR (99.4 MHz, C_6D_6): δ = –2.7 ppm. $C_{12}H_{22}OSi$ (210.39): calcd. C 68.51, H 10.54; found C 68.48, H 10.82.

1,1-Divinylsilolane (8): A solution of 1,4-dibromobutane (124 g, 574 mmol) in tetrahydrofuran (150 mL) was added dropwise within 1 h to a suspension of magnesium turnings (28.0 g, 1.15 mol) in tetrahydrofuran (100 mL), causing the reaction mixture to boil under reflux. The mixture was heated under reflux for a further 2 h, cooled to 20 °C within 30 min, and then added at 0 °C within 1 h to a stirred solution of dichlorodivinylsilane (80.0 g, 523 mmol) in tetrahydrofuran (250 mL). The resulting mixture was warmed to 20 °C within 20 min and stirred at this temperature for a further 2 h. Water (300 mL) was added, the organic phase was separated, the aqueous phase was extracted with Et_2O (4 × 200 mL) and discarded, and the combined organic solutions were dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the resulting residue purified by distillation in vacuo to furnish **8** as a colorless liquid (67.0 g, 485 mmol; 93% yield). B.p. 84 °C/100 mbar. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.85 ($\delta_{AA'A''A'''}$), 1.71 ($\delta_{XX'X''X'''}$) [AA′A″A‴XX′X″X‴ system, ^2J(A,A″) = ^2J(A′,A‴) = 14.6, ^2J(X,X″) = ^2J(X′,X‴) = 11.1, ^3J(A,X) = ^3J(A′,X′) = 7.9, ^3J(A,X″) = ^3J(A′,X‴) = 7.0, ^3J(A″,X) = ^3J(A‴,X′) = 6.4, ^3J(A″,X″) = ^3J(A‴,X‴) = 7.7, ^3J(X,X′) =

4.3, ^{3}J(X,X′′′) = ^{3}J(X′,X′′) = 7.6, ^{3}J(X′′,X′′′) = 5.6, ^{4}J(A,X′) = ^{4}J(A′,X) = 1.5, ^{4}J(A,X′′′) = ^{4}J(A′,X′′) = 0.6, ^{4}J(A′′,X′) = ^{4}J(A′′′,X) = 0.1, ^{4}J(A′′,X′′′) = ^{4}J(A′′′,X′′) = 0.1 Hz, 8 H; SiC$H_{\mathrm{A}}H_{\mathrm{A''}}CH_{\mathrm{X}}H_{\mathrm{X''}}CH_{\mathrm{X'}}H_{\mathrm{X'''}}CH_{\mathrm{A'}}H_{\mathrm{A'''}}$], 5.87 ($\delta_{\mathrm{A}}$), 6.08 ($\delta_{\mathrm{B}}$), 6.31 ($\delta_{\mathrm{C}}$) [ABC system, ^{2}J(A,B) = 3.8, ^{3}J(A,C) = 20.3, ^{3}J(B,C) = 14.6 Hz, 6 H; CH_{C}=C$H_{\mathrm{A}}H_{\mathrm{B}}$] ppm.[19] ^{13}C NMR (125.8 MHz, C_6D_6): δ = 11.1 (*C*-2 and *C*-5), 27.6 (*C*-3 and *C*-4), 133.4 (CH=*C*H_2), 136.2 (*C*H=CH_2) ppm. ^{29}Si NMR (99.4 MHz, C_6D_6): δ = 2.4 ppm. $C_8H_{14}Si$ (138.28): calcd. C 69.49, H 10.20; found C 69.49, H 10.30.

3,3′-(Silolane-1,1-diyl)dipropanal (9): A mixture of **8** (8.00 g, 57.9 mmol), triphenylphosphine (760 mg, 2.90 mmol), (acetyl acetonato)dicarbonylrhodium(I) (105 mg, 407 µmol), and benzene (30 mL) was heated in an autoclave at 80 °C for 7 h under an atmosphere of hydrogen (45 bar) and carbon monoxide (45 bar) and was then cooled to 20 °C within 30 min. The mixture was filtered through a pad of silica gel (15 g), followed by elution with *n*-hexane/Et_2O (1:1 v/v). The solvent of the filtrate (including the eluate) was removed under reduced pressure (5 mbar), and the residue was suspended in a mixture of Et_2O (100 mL) and water (50 mL). The organic phase was separated, the aqueous phase was extracted with Et_2O (3× 100 mL) and discarded, and the combined organic solutions were dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure (5 mbar), the residue was purified by a rapid bulb-to-bulb distillation (oven temperature 170 °C, 0.01 mbar), and the distillate was then further purified by a second bulb-to-bulb distillation (oven temperature 120 °C, 0.01 mbar) to furnish **9** as a colorless liquid (1.20 g, 6.05 mmol; 10% yield). ^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.44 ($\delta_{\mathrm{AA'A''A'''}}$), 1.55 ($\delta_{\mathrm{XX'X''X'''}}$) [AA′A′′A′′′XX′X′′X′′′ system, ^{2}J(A,A′′) = ^{2}J(A′,A′′′) = 14.4, ^{2}J(X,X′′) = ^{2}J(X′,X′′′) = 11.3, ^{3}J(A,X) = ^{3}J(A′,X′) = 7.9, ^{3}J(A,X′′) = ^{3}J(A′,X′′′) = 7.1, ^{3}J(A′′,X) = ^{3}J(A′′′,X′) = 6.3, ^{3}J(A′′,X′′) = ^{3}J(A′′′,X′′′) = 7.8, ^{3}J(X,X′) = 4.5, ^{3}J(X,X′′′) = ^{3}J(X′,X′′) = 7.4, ^{3}J(X′′,X′′′) = 5.6, ^{4}J(A,X′) = ^{4}J(A′,X) = 1.5, ^{4}J(A,X′′′) = ^{4}J(A′,X′′) = 0.6, ^{4}J(A′′,X′) = ^{4}J(A′′′,X) = 0.1, ^{4}J(A′′,X′′′) = ^{4}J(A′′′,X′′) = 0.1 Hz, 8 H; SiC$H_{\mathrm{A}}H_{\mathrm{A''}}CH_{\mathrm{X}}H_{\mathrm{X''}}CH_{\mathrm{X'}}H_{\mathrm{X'''}}CH_{\mathrm{A'}}H_{\mathrm{A'''}}$], 0.59 ($\delta_{\mathrm{AA'}}$), 1.89 ($\delta_{\mathrm{DD'}}$), 9.43 ($\delta_{\mathrm{X}}$) [AA′DD′X system, ^{2}J(A,A′) = 15.4, ^{2}J(D,D′) = 12.6, ^{3}J(A,D) = ^{3}J(A′,D′) = 5.5, ^{3}J(A,D′) = ^{3}J(A′,D) = 10.8, ^{3}J(D,X) = ^{3}J(D′,X) = 1.4 Hz, 10 H; C$H_{\mathrm{A}}H_{\mathrm{A'}}CH_{\mathrm{D}}H_{\mathrm{D'}}CH_{\mathrm{X}}$] ppm.[20] ^{13}C NMR (125.8 MHz, C_6D_6): δ = 5.0 (*C*H_2CH_2CH), 10.1 (*C*-2 and *C*-5), 27.5 (*C*-3 and *C*-4), 38.4 (*C*H_2CH), 200.6 (*C*HO) ppm. ^{29}Si NMR (99.4 MHz, C_6D_6): δ = 21.8 ppm. $C_{10}H_{18}O_2Si$ (198.34): calcd. C 60.56, H 9.15; found C 60.49, H 9.36.

5-Silaspiro[4.5]dec-7-ene-7-carbaldehyde (10): A mixture of **8** (13.6 g, 98.3 mmol), triphenylphosphine (1.29 g, 4.92 mmol), (acetylacetonato)dicarbonylrhodium(I) (178 mg, 690 µmol), and benzene (50 mL) was heated in an autoclave at 80 °C for 7 h under an atmosphere of hydrogen (45 bar) and carbon monoxide (45 bar) and was then cooled to 20 °C within 30 min. The resulting mixture (containing **9** as an intermediate) was then added dropwise at 0 °C within 1 h to a stirred 0.5 M solution of HCl in Et_2O (300 mL, 150 mmol of HCl), and the resulting mixture was then kept undisturbed at 20 °C for 18 h. The mixture was filtered through a pad of silica gel (180 g), followed by elution with *n*-hexane/Et_2O (1:1 v/v). The solvent of the filtrate (including the eluate) was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel [eluent, *n*-hexane/Et_2O (7:3 v/v)], followed by bulb-to-bulb distillation (oven temperature 110 °C, 0.02 mbar) to furnish **10** as a colorless liquid (5.88 g, 32.6 mmol; 33% yield). ^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.54 ($\delta_{\mathrm{AA'}}$), 0.55 ($\delta_{\mathrm{BB'}}$), 1.59 ($\delta_{\mathrm{XX'}}$), 1.60 ($\delta_{\mathrm{YY'}}$) [AA′BB′XX′YY′ system, ^{2}J(A,B) = ^{2}J(A′,B′) = 10.3, ^{2}J(X,Y) = ^{2}J(X′,Y′) = 13.2, ^{3}J(A,X) = ^{3}J(A′,X′) = 7.7, ^{3}J(A,Y) = ^{3}J(A′,Y′) = 6.7, ^{3}J(B,X) = ^{3}J(B′,X′) = 7.0, ^{3}J(B,Y) = ^{3}J(B′,Y′) = 7.8, ^{3}J(X,X′) = 5.1, ^{3}J(X,Y′) = ^{3}J(X′,Y) = 7.8, ^{3}J(Y,Y′) = 4.8, ^{4}J(A,X′) = ^{4}J(A′,X) = 0.2, ^{4}J(A,Y′) = ^{4}J(A′,Y) = 0.03, ^{4}J(B,X′) = ^{4}J(B′,X) = 0.01, ^{4}J(B,Y′) = ^{4}J(B′,Y) = 0.4 Hz, 8 H; SiC$H_{\mathrm{A}}H_{\mathrm{B}}CH_{\mathrm{X}}H_{\mathrm{Y}}CH_{\mathrm{X'}}H_{\mathrm{Y'}}CH_{\mathrm{A'}}H_{\mathrm{B'}}$], 0.60 ($\delta_{\mathrm{AA'}}$), 1.64 ($\delta_{\mathrm{DD'}}$), 2.19 ($\delta_{\mathrm{HH'}}$), 6.21 ($\delta_{\mathrm{X}}$) [AA′DD′HH′X system, ^{2}J(A,A′) = 12.4, ^{2}J(D,D′) = 12.4, ^{2}J(H,H′) = 15.2, ^{3}J(A,H) = ^{3}J(A′,H′) = 6.3, ^{3}J(A,H′) = ^{3}J(A′,H) = 7.5, ^{3}J(H,X) = ^{3}J(H′,X) = 4.9, ^{4}J(D,X) = ^{4}J(D′,X) = 1.5, ^{5}J(D,H) = ^{5}J(D′,H′) = 2.0, ^{5}J(D,H′) = ^{5}J(D′,H) = 1.3 Hz, 7 H; SiC$H_{\mathrm{A}}H_{\mathrm{A'}}CH_{\mathrm{H}}H_{\mathrm{H'}}CH_{\mathrm{X}}$=CC$H_{\mathrm{D}}H_{\mathrm{D'}}$], 9.42 (s, 1 H, C*H*O) ppm.[19] ^{13}C NMR (125.8 MHz, C_6D_6): δ = 7.2 (*C*-6), 8.0 (*C*-10), 11.1 (*C*-1 and *C*-4), 24.5 (*C*-9), 27.2 (*C*-2 and *C*-3), 141.4 (*C*-7), 152.5 (*C*-8), 193.8 (*C*HO) ppm. ^{29}Si NMR (99.4 MHz, C_6D_6): δ = 13.9 ppm. $C_{10}H_{16}OSi$ (180.32): calcd. C 66.61, H 8.94; found C 66.38, H 9.02.

1-(5-Silaspiro[4.5]dec-7-en-7-yl)pent-4-en-1-ol (11): 4-Bromo-1-butene (15.4 g, 114 mmol) was added dropwise within 30 min to a suspension of magnesium turnings (3.70 g, 152 mmol) in Et_2O (150 mL), causing the reaction mixture to boil under reflux. The mixture was heated under reflux for a further hour, cooled to 20 °C within 20 min, and then added at –10 °C within 30 min to a stirred solution of **10** (13.7 g, 76.0 mmol) in Et_2O (250 mL). The resulting mixture was warmed to 20 °C within 30 min and was then stirred at this temperature for a further hour, a saturated aqueous solution of ammonium chloride (200 mL) was added, the organic phase was separated, the aqueous phase was extracted with Et_2O (3× 100 mL) and discarded, and the combined organic solutions were dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel [eluent, *n*-hexane/Et_2O (7:3 v/v)], followed by bulb-to-bulb distillation (oven temperature 170 °C, 0.02 mbar) to furnish **11** as a colorless liquid (15.5 g, 65.6 mmol; 86% yield). ^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.63–0.74 (m, 4 H, 1-H and 4-H), 0.75–0.83 (m, 2 H, 10-H), 1.19–1.47 (m, 2 H, 6-H), 1.64–1.82 (m, 7 H, 2-H, 3-H, O*H*, and CH_2CHOH), 2.13–2.33 (m, 4 H, 9-H and CH_2CH=CH_2), 3.95–4.00 (m, 1 H, C*H*OH), 5.08–5.13 (m, 1 H, CH_2CH=C*H*H), 5.16–5.22 (m, 1 H, CH_2CH=CH*H*), 5.72–5.76 (m, 1 H, 8-H), 5.90–6.00 (m, 1 H, CH_2C*H*=CH_2) ppm.[20] ^{13}C NMR (125.8 MHz, C_6D_6): δ = 9.2 (*C*-10), 9.8 (*C*-6), 11.6 (*C*-1 or *C*-4), 11.7 (*C*-1 or *C*-4), 23.0 (*C*-9), 27.4 (*C*-2 or *C*-3), 27.5 (*C*-2 or *C*-3), 30.6 (*C*H_2CHOH), 34.5 (*C*H_2CH=CH_2), 77.5 (*C*HOH), 114.7 (CH_2CH=*C*H_2), 125.6 (*C*-8), 139.0 (CH_2*C*H=CH_2), 140.4 (*C*-7) ppm. ^{29}Si NMR (99.4 MHz, C_6D_6): δ = 14.9 ppm. $C_{14}H_{24}OSi$ (236.43): calcd. C 71.12, H 10.23; found C 71.29, H 10.40.

1-(5-Silaspiro[4.5]dec-7-en-7-yl)pent-4-en-1-one (2,4-Dinitrophenyl)hydrazone (12b): Sulfuric acid (11 mL), water (17 mL), and ethanol (45 mL) were added sequentially at 20 °C in single portions to (2,4-dinitrophenyl)hydrazine [5.58 g of a 50% suspension of (2,4-dinitrophenyl)hydrazine in water; 14.1 mmol of (2,4-dinitrophenyl)hydrazine], followed by dropwise addition of a solution of **2b** (3.00 g, 12.8 mmol; purity 99.5%) in ethanol (55 mL) at this temperature within 45 min. The resulting precipitate was separated by suction filtration and washed with water (5× 25 mL) to furnish a red solid, which was dried in vacuo (20 °C, 0.02 mbar, 2 h) and then recrystallized from methanol (750 mL; slow cooling of a boiling solution to 20 °C and crystallization over a period of 1 d). The precipitate was isolated by suction filtration, washed with methanol (–20 °C, 25 mL), and dried in vacuo (20 °C, 0.02 mbar, 4 h) to furnish a red crystalline solid, which was again recrystallized from methanol until HPLC analysis indicated no more impurity. Compound **12b** was then isolated as a pure red crystalline solid (2.90 g, 7.00 mmol; 55% yield). M.p. 135 °C. ^{1}H NMR (500.1 MHz, C_6D_6): δ = 0.74 ($\delta_{\mathrm{AA'}}$), 0.79 ($\delta_{\mathrm{BB'}}$), 1.73 ($\delta_{\mathrm{XX'}}$), 1.79 ($\delta_{\mathrm{YY'}}$) [AA′BB′XX′YY′ system, ^{2}J(A,B) = ^{2}J(A′,B′) = 14.9, ^{2}J(X,Y) = ^{2}J(X′,Y′) = 12.9, ^{3}J(A,X) = ^{3}J(A′,X′) = 7.4, ^{3}J(A,Y) = ^{3}J(A′,Y′) = 7.1, ^{3}J(B,X) = ^{3}J(B′,X′) = 7.2, ^{3}J(B,Y) = ^{3}J(B′,Y′) = 7.5, ^{3}J(X,X′) = 4.9, ^{3}J(X,Y′) = ^{3}J(X′,Y) = 7.6, ^{3}J(Y,Y′) = 4.8, ^{4}J(A,X′) = ^{4}J(A′,X) = 0.8, ^{4}J(A,Y′) = ^{4}J(A′,Y) = 0.4, ^{4}J(B,X′) = ^{4}J(B′,X) = 0.5, ^{4}J(B,Y′) = ^{4}J(B′,Y) = 0.8 Hz, 8 H; $\mathrm{SiC}H_{\mathrm{A}}H_{\mathrm{B}}\mathrm{C}H_{\mathrm{X}}H_{\mathrm{Y}}\mathrm{C}H_{\mathrm{X'}}H_{\mathrm{Y'}}\mathrm{C}H_{\mathrm{A'}}H_{\mathrm{B'}}$], 0.81 ($\delta_{\mathrm{AA'}}$), 2.06 ($\delta_{\mathrm{DD'}}$), 2.37 ($\delta_{\mathrm{HH'}}$), 6.26 ($\delta_{\mathrm{X}}$) [AA′DD′HH′X system, ^{2}J(A,A′) = 11.0, ^{2}J(D,D′) = 8.5, ^{2}J(H,H′) = 13.2, ^{3}J(A,H) = ^{3}J(A′,H′) = 5.9, ^{3}J(A,H′) = ^{3}J(A′,H) = 7.9, ^{3}J(H,X) = ^{3}J(H′,X) = 5.6, ^{4}J(D,X) = ^{4}J(D′,X) = 1.0, ^{5}J(D,H) = ^{5}J(D′,H′) = 0.6, ^{5}J(D,H′) = ^{5}J(D′,H) = 1.6 Hz, 7 H; $\mathrm{SiC}H_{\mathrm{A}}H_{\mathrm{A'}}\mathrm{C}H_{\mathrm{H}}H_{\mathrm{H'}}\mathrm{C}H_{\mathrm{X}}\mathrm{=CC}H_{\mathrm{D}}H_{\mathrm{D'}}$], 2.19 ($\delta_{\mathrm{AA'}}$), 2.44 ($\delta_{\mathrm{DD'}}$), 5.12 ($\delta_{\mathrm{F}}$), 5.21 ($\delta_{\mathrm{M}}$), 5.86 ($\delta_{\mathrm{X}}$) [AA′DD′FMX system, ^{2}J(A,A′) = 13.1, ^{2}J(D,D′) = 13.0, ^{2}J(F,M) = 1.5, ^{3}J(A,D) = ^{3}J(A′,D′) = 6.1, ^{3}J(A,D′) = ^{3}J(A′,D) = 10.3, ^{3}J(A,X) = ^{3}J(A′,X) = 6.8, ^{3}J(F,X) = 10.1, ^{3}J(M,X) = 17.0, ^{4}J(A,F) = ^{4}J(A′,F) = 1.1, ^{4}J(A,M) = ^{4}J(A′,M) = 1.5 Hz, 7 H; $\mathrm{C}H_{\mathrm{D}}H_{\mathrm{D'}}\mathrm{C}H_{\mathrm{A}}H_{\mathrm{A'}}\mathrm{C}H_{\mathrm{X}}\mathrm{=C}H_{\mathrm{F}}H_{\mathrm{M}}$], 7.70 ($\delta_{\mathrm{A}}$), 7.84 ($\delta_{\mathrm{D}}$), 8.95 ($\delta_{\mathrm{M}}$), 11.2 ($\delta_{\mathrm{X}}$) [ADMX system, ^{3}J(A,D) = 9.5, ^{4}J(D,M) = 2.6, ^{5}J(D,X) = 0.7 Hz, 4 H; $\mathrm{C_6}H_3\mathrm{(NO_2)_2N}H_{\mathrm{X}}$ (3-$\mathrm{H_M}$, 5-$\mathrm{H_D}$, 6-$\mathrm{H_A}$)] ppm.[19] ^{13}C NMR (125.8 MHz, C_6D_6): δ = 8.6 [*C*-10, 5-silaspiro[4.5]dec-7-en-7-yl (= 5-sila)], 11.3 (*C*-6, 5-sila), 11.6 (*C*-1 and *C*-4, 5-sila), 24.1 (*C*-9, 5-sila), 25.7 [$\mathrm{C(N)}C\mathrm{H_2}$], 27.4 (*C*-2 and *C*-3, 5-sila), 30.5 ($C\mathrm{H_2CH{=}CH_2}$), 116.0 [*C*-6, $\mathrm{C_6H_3(NO_2)_2}$], 116.7 ($\mathrm{CH_2CH{=}}C\mathrm{H_2}$), 123.4 [*C*-3, $\mathrm{C_6H_3(NO_2)_2}$], 129.57 [*C*-5, $\mathrm{C_6H_3(NO_2)_2}$], 129.62 [*C*-2, $\mathrm{C_6H_3(NO_2)_2}$], 134.5 (*C*-8, 5-sila), 136.1 ($\mathrm{CH_2}C\mathrm{H{=}CH_2}$), 136.8 (*C*-7, 5-sila), 138.1 [*C*-4, $\mathrm{C_6H_3(NO_2)_2}$], 144.8 [*C*-1, $\mathrm{C_6H_3(NO_2)_2}$], 157.2 [$C\mathrm{(N)CH_2}$] ppm. ^{15}N NMR (50.7 MHz, C_6D_6): δ = –234.3 [$\mathrm{C_6H_3(NO_2)_2}N\mathrm{HN}$], –77.2 [$\mathrm{C_6H_3(NO_2)_2NH}N$], –15.5 ($N\mathrm{O_2}$), –13.2 ($N\mathrm{O_2}$) ppm. ^{29}Si NMR (99.4 MHz, C_6D_6): δ = 15.8 ppm. $C_{20}H_{26}N_4O_4Si$ (414.54): calcd. C 57.95, H 6.32, N 13.52; found C 58.08, H 6.24, N 13.74.

Dimethyl(3-methylbut-2-en-1-yl)vinylsilane (13): A solution of 1-chloro-3-methylbut-2-ene (66.7 g, 638 mmol) in tetrahydrofuran (500 mL) was added dropwise within 45 min to a suspension of magnesium turnings (16.9 g, 695 mmol) in tetrahydrofuran (10 mL), causing the reaction mixture to boil under reflux. Subsequently, chlorodimethylvinylsilane (70.0 g, 580 mmol) was added at 20 °C within 15 min to the stirred reaction mixture. Upon cooling to 0 °C, a saturated aqueous solution of ammonium chloride (200 mL) was added, the organic phase was separated, and the aqueous phase was extracted with ethyl acetate (3× 100 mL) and discarded. The combined organic solutions were washed with a saturated aqueous solution of sodium chloride and dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by distillation under reduced pressure to furnish **13** as a colorless liquid (66.5 g, 431 mmol; 74% yield). B.p. 45–49 °C/5 mbar. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.07 (s, 6 H, $\mathrm{SiC}H_3$), 1.48 (d, ^{3}J = 8.3 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH{=}C}$), 1.58 (br. s, 3 H, $\mathrm{C}H_3\mathrm{C{=}CH}$), 1.72 (br. s, 3 H, $\mathrm{C}H_3\mathrm{C{=}CH}$), 5.16 (tspt, ^{3}J = 8.3, ^{4}J = 1.4 Hz, 1 H, $\mathrm{C}H\mathrm{{=}C}$), 5.69 (dd, ^{3}J = 20.0, ^{2}J = 4.2 Hz, 1 H, $\mathrm{CH{=}CH}_{cis}H_{trans}$), 5.96 (dd, ^{3}J = 14.7, ^{2}J = 4.2 Hz, 1 H, $\mathrm{CH{=}C}H_{cis}\mathrm{H}_{trans}$), 6.17 (dd, ^{3}J = 20.0, ^{3}J = 14.7 Hz, 1 H, $\mathrm{C}H\mathrm{{=}CH}_{cis}\mathrm{H}_{trans}$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –3.6 ($\mathrm{Si}C\mathrm{H_3}$), 17.3 [$\mathrm{CH{=}C(}C\mathrm{H_3)}_{cis}\mathrm{(CH_3)}_{trans}$], 17.6 ($C\mathrm{H_2}$), 25.7 [$\mathrm{CH{=}C(CH_3)}_{cis}\mathrm{(}C\mathrm{H_3)}_{trans}$], 119.4 [$C\mathrm{H{=}C(CH_3)}_{cis}\mathrm{(CH_3)}_{trans}$], 129.1 [$\mathrm{CH{=}}C\mathrm{(CH_3)}_{cis}\mathrm{(CH_3)}_{trans}$], 131.5 ($\mathrm{SiCH{=}}C\mathrm{H_2}$), 139.0 ($\mathrm{Si}C\mathrm{H{=}CH_2}$) ppm. EI-MS: *m*/*z* (%) = 154 (13) $[\mathrm{M}]^+$, 139 (3), 126 (2), 111 (1), 98 (1), 85 (100), 73 (4), 59 (38), 43 (6). HRMS (EI): *m*/*z* calcd. for $C_9H_{18}Si$ 154.1178, found 154.1184.

3-[Dimethyl(3-methylbut-2-en-1-yl)silyl]propanal (14): A mixture of carbonylhydridotris(triphenylphosphine)rhodium(I) (510 mg, 555 µmol), triphenylphosphine (2.04 g, 7.78 mmol), **13** (60.0 g, 389 mmol), and toluene (20 mL) was heated in an autoclave to 80 °C for 3 h under an atmosphere of hydrogen (40 bar) and carbon monoxide (40 bar), and the reaction mixture was then cooled to 20 °C within 60 min. The solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (oven temperature 105 °C, 0.1 mbar) to furnish **14** as a colorless liquid (45.0 g, 244 mmol; 63% yield). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = –0.02 (s, 6 H, $\mathrm{SiC}H_3$), 0.75 ($\delta_{\mathrm{AA'}}$), 2.36 ($\delta_{\mathrm{DD'}}$), 9.72 (δ_{X}) [AA′DD′X system, ^{2}J(AA′) = 17.3, ^{2}J(DD)′ = 15.1, ^{3}J(AD) = ^{3}J(A′D′) = 9.9, ^{3}J(AD′) = ^{3}J(A′D) = 5.1, ^{3}J(DX) = ^{3}J(D′X) = 1.8 Hz, 5 H; $\mathrm{C}H_{\mathrm{A}}H_{\mathrm{A'}}\mathrm{C}H_{\mathrm{D}}H_{\mathrm{D'}}\mathrm{C}H_{\mathrm{X}}\mathrm{O}$], 1.39 (d, ^{3}J = 8.5 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH{=}C}$), 1.54 (s, 3 H, $\mathrm{C}H_3\mathrm{C{=}CH}$), 1.67 (s, 3 H, $\mathrm{C}H_3\mathrm{C{=}CH}$), 5.10 (tspt, ^{3}J = 8.5, ^{4}J = 1.3 Hz, 1 H, $\mathrm{C}H\mathrm{{=}C}$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –3.7 ($\mathrm{Si}C\mathrm{H_3}$), 6.7 (*C*-3), 16.9 [$\mathrm{Si}C\mathrm{H_2CH{=}C(CH_3)_2}$], 17.6 [$\mathrm{CH{=}C(}C\mathrm{H_3)}_{cis}\mathrm{(CH_3)}_{trans}$], 25.7 [$\mathrm{CH{=}C(CH_3)}_{cis}\mathrm{(}C\mathrm{H_3)}_{trans}$], 38.3 (*C*-2), 119.1 [$C\mathrm{H{=}C(CH_3)}_{cis}\mathrm{(CH_3)}_{trans}$], 129.3 [$\mathrm{CH{=}}C\mathrm{(CH_3)}_{cis}\mathrm{(CH_3)}_{trans}$], 202.8 ($C\mathrm{HO}$) ppm. EI-MS: *m*/*z* (%) = 184 (1) $[\mathrm{M}]^+$, 141 (2), 127 (3), 115 (100), 99 (14), 85 (35), 75 (7), 59 (31). HRMS (EI): *m*/*z* calcd. for $C_{10}H_{20}OSi$ 184.1283, found 184.1254.

2-{[Dimethyl(3-methylbut-2-en-1-yl)silyl]methyl}acrylaldehyde (15): A mixture of **14** (45.0 g, 244 mmol) and a 36% (w/w) aqueous solution of formaldehyde (73.3 g, 880 mmol of CH_2O) was heated with vigorous stirring to 70 °C. Subsequently, a mixture of pyrrolidine (3.47 g, 48.8 mmol) and propanoic acid (4.34 g, 58.6 mmol) was added dropwise within 10 min to the reaction mixture, and stirring was continued at this temperature for a further 3 h. Water (50 mL) was added, the organic phase was separated, the aqueous phase was extracted with *tert*-butyl methyl ether (3× 200 mL) and discarded, and the combined organic solutions were dried with anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel [eluent, isohexane/*tert*-butyl methyl ether (50:1 v/v)], followed by bulb-to-bulb distillation (oven temperature 110 °C, 0.1 mbar) to furnish **15** as a colorless liquid (20.0 g, 102 mmol; 42% yield). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = –0.05 (s, 6 H, $\mathrm{SiC}H_3$), 1.40 (d, ^{3}J = 8.3 Hz, 2 H, $\mathrm{C}H_2\mathrm{CH{=}C}$), 1.55 (s, 3 H, $\mathrm{C}H_3\mathrm{C{=}CH}$), 1.69 (br. s, 3 H, $\mathrm{C}H_3\mathrm{C{=}CH}$), 1.77 (br. s, 2 H, $\mathrm{C}H_2\mathrm{C{=}CH_2}$), 5.11 (tspt, ^{3}J = 8.3, ^{4}J = 1.3 Hz, 1 H, $\mathrm{C}H\mathrm{{=}C}$), 5.85 (m, 1 H, $\mathrm{C{=}CH_A}H_{\mathrm{B}}$), 6.09 (m, 1 H, $\mathrm{C{=}C}H_{\mathrm{A}}\mathrm{H_B}$), 9.47 (s, 1 H, $\mathrm{C}H\mathrm{O}$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = –3.6 ($\mathrm{Si}C\mathrm{H_3}$), 16.5 (*C*-3), 16.9 [$\mathrm{Si}C\mathrm{H_2CH{=}C(CH_3)_2}$], 17.6 [$\mathrm{CH{=}C(}C\mathrm{H_3)}_{cis}\mathrm{(CH_3)}_{trans}$], 25.8 [$\mathrm{CH{=}C(CH_3)}_{cis}\mathrm{(}C\mathrm{H_3)}_{trans}$], 119.1 [$C\mathrm{H{=}C(CH_3)}_{cis}\mathrm{(CH_3)}_{trans}$], 129.5 [$\mathrm{CH{=}}C\mathrm{(CH_3)}_{cis}\mathrm{(CH_3)}_{trans}$], 131.5 ($\mathrm{C{=}}C\mathrm{H_2}$), 148.3 (*C*-2), 194.4 ($C\mathrm{HO}$) ppm. EI-MS: *m*/*z* (%) = 196 (1) $[\mathrm{M}]^+$, 127 (100), 113 (5), 97 (10), 85 (7), 75 (12), 59 (16). HRMS (ESI): *m*/*z* calcd. for $C_{11}H_{22}NaOSi$ $[\mathrm{M + Na}]^+$ 219.1181, found 219.1357.

2-{[Dimethyl(3-methylbut-2-en-1-yl)silyl]methyl}allyl Acetate (16): Compound **15** (20.0 g, 102 mmol) was added at 0 °C within 15 min to a stirred suspension of lithium aluminum hydride (4.64 g, 122 mmol) in tetrahydrofuran (100 mL). The resulting mixture was then stirred at this temperature for 3 h, water (20 mL) was added dropwise, the organic phase was separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (50 mL) and discarded. The combined organic solutions were dried with anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. Dichloromethane (50 mL) and triethylamine (19.4 g, 192 mmol) were added to the residue, followed by dropwise addition of acetyl chloride (9.02 g, 115 mmol) at 0 °C within 5 min. The resulting mixture was stirred at 20 °C for 3 h, water (50 mL) was added, the organic phase was separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 100 mL) and discarded. The combined organic solutions were dried with anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel [eluent, isohexane/*tert*-butyl methyl ether (100:1 v/v)], followed by bulb-to-bulb distillation (oven temperature 122 °C, 0.1 mbar) to furnish **16** as a colorless liquid (19.0 g, 79.0 mmol; 78 % overall yield). ^{1}H NMR (300.1 MHz, CDCl$_3$): δ = 0.01 (s, 6 H, SiC*H*$_3$), 1.42 (d, ^3J = 8.3 Hz, 2 H, C*H*$_2$CH=C), 1.55 (br. s, 5 H, C*H*$_3$C=CH, C*H*$_2$C=CH$_2$), 1.69 (s, 3 H, C*H*$_3$C=CH), 2.09 [s, 3 H, C*H*$_3$C(O)O], 4.42 (s, 2 H, C*H*$_2$O), 4.72 (br. s, 1 H, C=CH_AH$_\text{B}$), 4.88 (m, 1 H, C=CH$_\text{A}$$H_\text{B}$), 5.11 (tspt, ^3J = 8.3, ^4J = 1.3 Hz, 1 H, C*H*=C) ppm. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = –3.3 (Si*C*H$_3$), 17.1 [Si*C*H$_2$CH=C(CH$_3$)$_2$], 17.6 [CH=C(*C*H$_3$)$_{cis}$(CH$_3$)$_{trans}$], 20.9 [*C*H$_3$C(O)O], 22.0 (*C*-3), 25.7 [CH=C(CH$_3$)$_{cis}$(*C*H$_3$)$_{trans}$], 67.8 (*C*H$_2$O), 109.7 (C=*C*H$_2$), 119.2 [*C*H=C(CH$_3$)$_{cis}$(CH$_3$)$_{trans}$], 129.4 [CH=*C*(CH$_3$)$_{cis}$(CH$_3$)$_{trans}$], 141.5 (*C*-2), 170.5 [CH$_3$*C*(O)O] ppm. EI-MS: *m*/*z* (%) = 240 (1) [M]$^+$, 129 (12), 117 (100), 99 (6), 87 (7), 75 (58), 59 (9). HRMS (EI): *m*/*z* calcd. for C$_8$H$_{15}$O$_2$Si {[M – C$_5$H$_9$ (prenyl)]$^+$} 171.0841, found 171.0815.

(4,4-Dimethyl-4-silacyclopent-1-en-1-yl)methyl Acetate (17): A solution of **16** (19.0 g, 79.0 mmol) and dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]{5-[(dimethylamino)sulfonyl]-2-(1-methylethoxy-O)phenyl}(methylene-C)ruthenium(II) (Zhan Catalyst 1B; 1.16 g, 1.58 mmol) in 1,2-dichloroethane (100 mL) was heated under reflux for 17 h. The reaction mixture was then cooled to 20 °C, triethylamine (300 µL) was added in a single portion, and the volatile components were removed under reduced pressure. The residue was purified by flash chromatography on silica gel [eluent, isohexane/*tert*-butyl methyl ether (99:1 v/v)], followed by bulb-to-bulb distillation (oven temperature 85 °C, 0.1 mbar) to furnish **17** as a colorless liquid (9.00 g, 48.8 mmol; 62 % yield). ^{1}H NMR (300.1 MHz, CDCl$_3$): δ = 0.18 (s, 6 H, SiC*H*$_3$), 1.24 ($\delta_{\text{AA}'}$), 1.31 ($\delta_{\text{DD}'}$), 4.53 ($\delta_{\text{MM}'}$), 5.79 (δ_X) [AA′DD′MM′X system, ^2J(AA′) = 17.5, ^2J(DD)′ = 17.5, ^2J(MM′) = 14.0, ^3J(DX) = ^3J(D′X) = 2.9, ^4J(AD) = ^4J(A′D′) = 1.8, ^4J(AD′) = ^4J(A′D) = 0.8, ^4J(AM) = ^4J(A′M′) = ^4J(AM′) = ^4J(A′M) = 0.1, ^4J(AX) = ^4J(A′X) = 2.0, ^4J(MX) = ^4J(M′X) = 0.6, ^5J(DM) = ^5J(D′M′) = ^5J(DM′) = ^5J(D′M) = 1.3 Hz, 7 H; SiC$H_\text{D}H_{\text{D}'}$CH_X=CC$H_\text{A}H_{\text{A}'}$C$H_\text{M}H_{\text{M}'}$O], 2.08 [s, 3 H, C*H*$_3$C(O)O] ppm. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = –1.9 (Si*C*H$_3$), 18.1 (*C*-3), 18.2 (*C*-5), 20.8 [*C*H$_3$C(O)O], 67.0 (*C*H$_2$O), 128.6 (*C*-2), 138.2 (*C*-1), 170.7 [CH$_3$*C*(O)O] ppm. EI-MS: *m*/*z* (%) = 184 (1) [M]$^+$, 117 (74), 75 (100), 59 (8). HRMS (EI): *m*/*z* calcd. for C$_9$H$_{16}$O$_2$Si 184.0920, found 184.0894.

(4,4-Dimethyl-4-silacyclopent-1-en-1-yl)methanol (18): Compound **17** (2.00 g, 10.9 mmol) was added dropwise at 0 °C within 15 min to a stirred suspension of lithium aluminum hydride (494 mg, 13.0 mmol) in tetrahydrofuran (100 mL). The resulting mixture was then stirred at this temperature for 1 h, water (10 mL) was added dropwise, the organic phase was separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 100 mL) and discarded. The combined organic solutions were dried with anhydrous magnesium sulfate, the solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (oven temperature 95 °C, 0.1 mbar) to furnish **18** as a colorless liquid (1.40 g, 9.84 mmol; 90 % yield). ^{1}H NMR (300.1 MHz, CDCl$_3$): δ = 0.18 (s, 6 H, SiC*H*$_3$), 1.27 ($\delta_{\text{AA}'}$), 1.33 ($\delta_{\text{DD}'}$), 4.10 ($\delta_{\text{MM}'}$), 5.79 (δ_X) [AA′DD′MM′X system, ^2J(AA′) = 17.5, ^2J(DD)′ = 17.5, ^2J(MM′) = 14.0, ^4J(AD) = ^4J(A′D′) = 1.5, ^3J(DX) = ^3J(D′X) = 2.9, ^4J(AD′) = ^4J(A′D) = 1.0, ^4J(AM) = ^4J(A′M′) = ^4J(AM′) = ^4J(A′M) = 0.5, ^4J(AX) = ^4J(A′X) = 2.0, ^4J(MX) = ^4J(M′X) = 1.5, ^5J(DM) = ^5J(D′M′) = ^5J(DM′) = ^5J(D′M) = 1.3 Hz, 7 H; SiC$H_\text{D}H_{\text{D}'}$CH_X=CC$H_\text{A}H_{\text{A}'}$C$H_\text{M}H_{\text{M}'}$O] ppm. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = –1.8 (Si*C*H$_3$), 17.8 (*C*-3), 18.0 (*C*-5), 66.2 (*C*H$_2$O), 125.6 (*C*-2), 143.2 (*C*-1) ppm. EI-MS: *m*/*z* (%) = 142 (1) [M]$^+$, 125 (2), 109 (7), 99 (3), 87 (2), 75 (100), 61 (4), 43 (5). HRMS (EI): *m*/*z* calcd. for C$_7$H$_{14}$OSi 142.0814, found 142.0817.

1-(4,4-Dimethyl-4-silacyclopent-1-en-1-yl)pent-4-en-1-ol (19): Aluminum tri-*sec*-butoxide (727 mg, 2.95 mmol) was added at 20 °C to a stirred solution of **18** (1.40 g, 9.84 mmol) in *tert*-butyl methyl ether (100 mL), followed by the addition of acetic acid (53 mg, 883 µmol). The resulting mixture was then stirred at 0 °C for 10 min, 4-nitrobenzaldehyde (1.78 g, 11.8 mmol) was added, and the reaction mixture was stirred at 20 °C for 2 h. Subsequently, *n*-hexane (100 mL) and anhydrous magnesium sulfate were added, and the organic phase was separated by filtration. The solvent was removed under reduced pressure, *n*-hexane (10 mL) was added, and the resulting supernatant was separated by filtration. The solvent was removed under reduced pressure, and the residue was dissolved in tetrahydrofuran (20 mL), followed by dropwise addition of a 0.90 M solution of but-3-en-1-ylmagnesium chloride [21.9 mL, 19.7 mmol of CH$_2$=CHCH$_2$CH$_2$MgCl; prepared from magnesium turnings (7.40 g, 304 mmol) and 4-chloro-1-butene (25.2 g, 278 mmol) and then stored at 0 °C for different batches] at 0 °C within 1 h. Subsequently, water (20 mL) was added dropwise, the organic phase was separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 25 mL) and discarded. The combined organic solutions were dried with anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel [eluent, isohexane/*tert*-butyl methyl ether (100:1 v/v)], followed by bulb-to-bulb distillation (oven temperature 110 °C, 0.1 mbar) to furnish **19** as a colorless liquid (405 mg, 2.06 mmol; 21 % overall yield). ^{1}H NMR (300.1 MHz, CDCl$_3$): δ = 0.16 (s, 3 H, SiC*H*$_3$), 0.17 (s, 3 H, SiC*H*$_3$), 1.06–1.35 [m, 4 H, CH(OH)C*H*$_2$, SiC*H*$_2$C=CH], 1.59–1.68 (m, 2 H, SiC*H*$_2$CH=C), 1.80 (br. s, 1 H, O*H*), 1.93–2.14 (m, 2 H, C*H*$_2$CH=CH$_2$), 4.14 [br. t, ^3J = 4.2 Hz, 1 H, C*H*(OH)CH$_2$], 4.94 (ddt, ^3J = 10.2, ^2J = 2.1, ^4J = 1.2 Hz, 1 H, CH=CH_{cis}H$_{trans}$), 5.01 (ddt, ^3J = 17.0, ^2J = 2.1, ^4J = 1.5 Hz, 1 H, CH=CH$_{cis}$$H_{trans}$), 5.76 (m, 1 H, C*H*=C), 5.82 (ddt, ^3J = 17.0, ^3J = 10.2, ^3J = 6.6 Hz, 1 H, C*H*=CH$_2$) ppm. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = –1.9 (Si*C*H$_3$), –1.8 (Si*C*H$_3$), 15.2 (*C*-5), 17.8 (*C*-3), 29.3 (CH$_2$*C*H$_2$CH=CH$_2$), 34.1 (*C*H$_2$CH$_2$CH=CH$_2$), 74.2 [*C*H(OH)], 114.6 (CH$_2$CH$_2$CH=*C*H$_2$), 126.3 (*C*-2), 138.5 (CH$_2$CH$_2$*C*H=CH$_2$), 145.6 (*C*-1) ppm. EI-MS: *m*/*z* (%) = 196 (1) [M]$^+$, 178 (4), 155 (3), 137 (20), 109 (7), 95 (3), 85 (3), 75 (100), 59 (13), 43 (4). HRMS (EI): *m*/*z* calcd. for C$_{11}$H$_{20}$OSi 196.1283, found 196.1275.

Olfactory Evaluation: The test compounds were evaluated on smelling blotters by a panel of at least two expert perfumers as 10 % solutions in dipropylene glycol (DPG) and in ethanol. The blotters were dipped 4 h and 8 h in advance and compared with the freshly dipped samples for top, middle, and dry down odor character, linearity of the smell as well as olfactory purity.

The detection odor thresholds were determined using GC-olfactometry: different dilutions of the sample substance were injected into a gas chromatograph in descending order of concentration until the panelist failed to detect the respective substance at the sniffing port. The panelist smelled in blind and pressed a button upon perceiving an odor. If the recorded time matched the retention time, the sample was further diluted. The last concentration detected at the correct retention time is the individual odor threshold. The reported threshold values are the geometrical means of the individual odor thresholds of at least three different panelists.

Supporting Information (see footnote on the first page of this article): Alternative synthesis of **1b** and syntheses of **3a**, **12a**, **20a**, **20b**, and **21**–**28**;

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[14] Crystal structure analyses of **12a**, **12b**, **20a**, and **20b**: Suitable single crystals were mounted in inert oil (perfluoropolyalkyl ether, ABCR) on a glass fiber and then transferred to a cold nitrogen gas stream of the diffractometer [Bruker Nonius KAPPA APEX II (**12a**, **20a**, and **20b**; Montel mirror, Mo-K_α radiation; λ = 0.71073 Å); Stoe IPDS (**12b**; graphite-monochromated Mo-K_α radiation; λ = 0.71073 Å)]. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 for all unique reflections (SHELXL-97 and SHELXL-2013).[21] A riding model was employed for the CH hydrogen atoms. CCDC-1000185 (for **12a**), -1000186 (for **12b**), -1000187 (for **20a**), and -1000188 (for **20b**) contain 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. Selected data for **12a**: single crystal of dimensions 0.48 × 0.26 × 0.22 mm obtained by crystallization from methanol at 20 °C. $C_{21}H_{26}N_4O_4$; M_r = 398.46; analysis at 100(2) K; triclinic; space group $P\bar{1}$(no. 2); a = 9.2591(4), b = 10.2143(5), c = 11.6545(6) Å; α = 78.913(2), β = 68.012(2), γ = 84.167(2)°; V = 1002.45(8) Å^3; Z = 2; $\rho_{\text{calcd.}}$ = 1.320 g cm^{-3}; μ = 0.093 mm^{-1}; $F(000)$ = 424; $2\theta_{\max}$ = 56.818°; 24317 collected reflections; 5026 unique reflections (R_{int} = 0.0293); 265 parameters; S = 1.033; 0 restraints; R_1 = 0.0382 [$I>2\sigma(I)$]; wR_2 (all data) = 0.1050; max./min. residual electron density: +0.375/–0.222 e Å^{-3}. Selected data for **12b**: single crystal of dimensions 0.3 × 0.15 × 0.1 mm obtained by crystallization from methanol at 20 °C. $C_{20}H_{26}N_4O_4Si$; M_r = 414.54; analysis at 173(2) K; triclinic; space group $P\bar{1}$ (no. 2); a = 10.743(3), b = 14.579(3), c = 14.860(4) Å; α = 82.65(3), β = 73.58(3), γ = 70.58(3)°; V = 2104.0(9) Å^3; Z = 4; $\rho_{\text{calcd.}}$ = 1.309 g cm^{-3}; μ = 0.145 mm^{-1}; $F(000)$ = 880; $2\theta_{\max}$ = 52.04°; 23019 collected reflections; 7754 unique reflections (R_{int} = 0.0624); 531 parameters; S = 0.819; 0 restraints; R_1 = 0.0410 [$I>2\sigma(I)$]; wR_2 (all data) = 0.0904; max./min. residual electron density: +0.443/–0.312 e Å^{-3}. Selected data for **20a**: single crystal of dimensions 0.46 × 0.43 × 0.41 mm obtained by crystallization from methanol at 20 °C. $C_{19}H_{24}N_4O_4$; M_r = 372.42; analysis at 100(2) K; triclinic; space group $P\bar{1}$ (no. 2); a = 17.6528(7), b = 21.4017(9), c = 22.7819(10) Å; α = 63.3330(10), β = 86.908(2), γ = 84.006(2)°; V = 7649.2(6) Å^3; Z = 16; $\rho_{\text{calcd.}}$ = 1.294 g cm^{-3}; μ = 0.092 mm^{-1}; $F(000)$ = 3168; $2\theta_{\max}$ = 49.478°; 144055 collected reflections; 26087 unique reflections (R_{int} = 0.0398); 2013 parameters; S = 1.012; 5 restraints; R_1 = 0.0396 [$I>2\sigma(I)$]; wR_2 (all data) = 0.1065; max./min. residual electron density: +0.602/–0.230 e Å^{-3}. Selected data for **20b**: single crystal of dimensions 0.5 × 0.5 × 0.5 mm obtained by crystallization from methanol at 20 °C. $C_{18}H_{24}N_4O_4Si$; M_r = 388.50; analysis at 296(2) K; triclinic; space group $P\bar{1}$ (no. 2); a = 10.9364(9), b = 17.4897(14), c = 22.236(2) Å; α = 86.583(5), β = 84.257(5), γ = 72.568(4)°; V = 4035.5(6) Å^3; Z = 8; $\rho_{\text{calcd.}}$ = 1.279 g cm^{-3}; μ = 0.147 mm^{-1}; $F(000)$ = 1648; $2\theta_{\max}$ = 55.202°; 128375 collected reflections; 18586 unique reflections (R_{int} = 0.0384); 1184 parameters; S = 1.027; 296 restraints; R_1 = 0.0475 [$I>2\sigma(I)$]; wR_2 (all data) = 0.1462; max./min. residual electron density: +0.394/–0.287 e Å^{-3}.

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Sila-Galbanones

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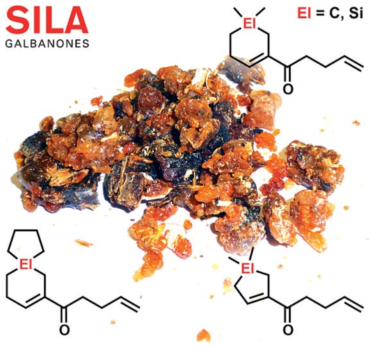
Sila-α-galbanone and Analogues: Synthesis and Olfactory Characterization of Silicon-Containing Derivatives of the Galbanum Odorant α-Galbanone

Keywords: Silicon / Spiro compounds / Metathesis / Hydroformylation / Fragrances / Galbanum



Sila-α-galbanone, sila-α-spirogalbanone, and sila-*nor*-α-galbanone (sila-analogues of α-galbanone, α-spirogalbanone, and *nor*-α-galbanone) were synthesized starting from Me_2SiCl_2, $(CH_2{=}CH)_2SiCl_2$, and $Me_2(CH_2{=}CH)SiCl$, respectively. These sila-analogues proved to be less volatile and thus more tenacious than the parent carbon compounds while also providing insight into structure–odor correlations.