Synthesis and Olfactory Characterization of Silicon-Containing Derivatives of the Acyclic Lily-of-the-Valley Odorant 5,7,7-Trimethyl-4-methylideneoctanal

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5-Methyl-4-methylidene-6-(trimethylsilyl)hexanal (**1b**), a sila analog of the acyclic lily-of-the-valley odorant 5,7,7-trimethyl-4-methylideneoctanal (**1a**), and the Si-containing derivatives **2**–**6** were prepared in multistep syntheses, starting from Cl_3SiH and Cl_2SiMe_2, respectively. Compounds **1b**, **2**–**6**, and their new precursors were characterized by elemental analyses (C, H, N) and NMR spectroscopic studies (^1H, ^{13}C, ^{15}N, and ^{29}Si). To gain more information about the structure–odor correlation in the family of lily-of-the-valley or 'muguet' odorants, C/Si analogs **1a**/**1b** and derivatives **2**–**6** were evaluated for their olfactory properties.

Introduction. – Lily-of-the-valley or 'muguet' odorants constitute the most important odor family both in terms of value and of volume, accounting for over 20% of the total perfumery raw-materials market. Accordingly, there has been a long history of structure–odor correlation in this odorant family [1][2]. Recently, 5,7,7-trimethyl-4-methylideneoctanal (**1a**; *Fig.*) was found to have interesting olfactory properties with a fresh-floral lily-of-the-valley odor close to *Lilial* (3-[4-(*tert*-butyl)phenyl]-2-methylpropanal) and with an odor threshold (th) of 15.8 ng/l air [3]. Compound **1a** is the first representative of a new class of muguet odorants, which *i*) neither possess aromatic rings as *Lilial* nor aliphatic ones as *Lyral* (4-(4-hydroxy-4-methylpentyl)cyclohex-3-ene-1-carbaldehyde), *ii*) have no bifunctional H-bond donor–acceptor units as 7-hydroxycitronellal (7-hydroxy-3,7-dimethyloctanal), and *iii*) possess C=C bonds that, contrary to *Pelzer*'s rule for the carbonyl fragment [4], are not situated in the main C-chain of the molecule. However, there are two drawbacks of the new muguet lead structure **1a** that have to be overcome: *i*) the molecular mass of **1a** (M_r 182.3) is significantly lower than that of *Lilial* (M_r 204.3), which affects substantivity and residuality in applications. The molecular mass of **1b** (*Fig.*, M_r 198.4), the sila analog of **1a**, is higher than that of **1a** and, therefore, should possess a notably lower vapor pressure. During our systematic studies on Si-based odorants[1]), we sometimes found even better substantivity and residuality than expected on the basis of the vapor pressure alone. Therefore, Si-replacement in **1a** ($\rightarrow$**1b**) was expected to improve its substantivity and residuality. *ii*) As the th of **1a** (15.8 ng/l air [3]) is much higher than that of *Lilial* (0.10 ng/l air [6e]), there seems to be some room to improve the receptor

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[1]) For a review on silicon-based odorants, see [5]; for further reports on silicon-based odorants, see [6].

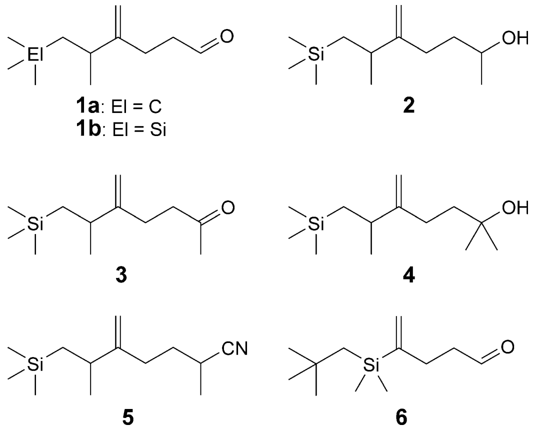


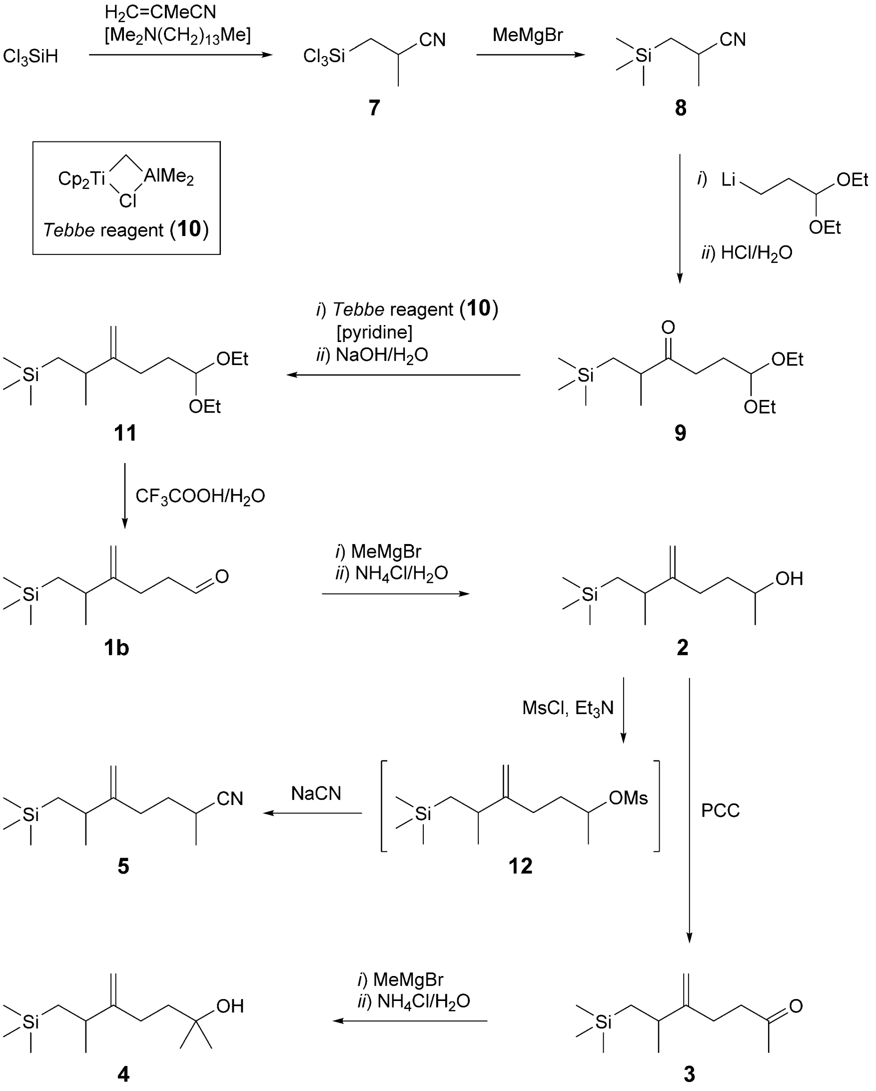
Figure. *Chemical structures of* **1a**, **1b**, *and* **2**–**6**

affinity of **1a** by increasing the hydrophobic volume by replacement of the C_q-atom of the lead compound **1a** with a Si-atom. While the th values of *Lilial* and *Bourgeonal* (3-[4-(*tert*-butyl)phenyl]propanal) are slightly increased upon Si replacement [6e], the situation in the case of **1a** could be opposite, as the fit of the molecule to the receptor binding pocket seems not yet perfect, so an increase in the molecular size might positively increase the hydrophobic interactions and thereby lower the th value.

Based on these considerations, we have synthesized the Si compound **1b** and some of its derivatives, and have studied their olfactory properties. We report here on the synthesis and olfactory characterization of 5-methyl-4-methylidene-6-(trimethylsilyl)-hexanal (**1b**) and its derivatives 6-methyl-5-methylidene-7-(trimethylsilyl)heptan-2-ol (**2**), 6-methyl-5-methylidene-7-(trimethylsilyl)heptan-2-one (**3**), 2,6-dimethyl-5-methylidene-7-(trimethylsilyl)heptan-2-ol (**4**), 2,6-dimethyl-5-methylidene-7-(trimethylsilyl)heptanenitrile (**5**), and 4-[dimethyl(2,2-dimethylpropyl)silyl]pent-4-enal (**6**; *Fig.*). The studies reported here were performed as part of our systematic investigations on Si-based odorants [5][6].

Results and Discussion. – *Syntheses.* Compounds **1b** and **2**–**5** were synthesized as outlined in *Scheme 1*, starting from Cl_3SiH. Thus, hydrosilylation of 2-methylprop-2-enenitrile with Cl_3SiH, in the presence of dimethyl(tetradecyl)amine, afforded 2-methyl-3-(trichlorosilyl)propanenitrile (**7**; 83% yield), which, upon reaction with MeMgBr, furnished 2-methyl-3-(trimethylsilyl)propanenitrile (**8**; 83% yield). Treatment of **8** with (3,3-diethoxypropyl)lithium and subsequent hydrolysis then afforded 6,6-diethoxy-2-methyl-1-(trimethylsilyl)hexan-3-one (**9**; 67% yield). Reaction of **9** with *Tebbe* reagent (**10**), in the presence of pyridine, and subsequent treatment with aqueous NaOH solution yielded (6,6-diethoxy-2-methyl-3-methylidenehexyl)trimethylsilane (**11**; 75% yield), which, upon hydrolysis with aqueous CF_3COOH, furnished **1b** (75% yield). Treatment of **1b** with MeMgBr, followed by aqueous workup, then afforded **2** (87% yield), which, upon oxidation with pyridinium chlorochromate (PCC), furnished **3** (76% yield). Reaction of **3** with MeMgBr and subsequent aqueous

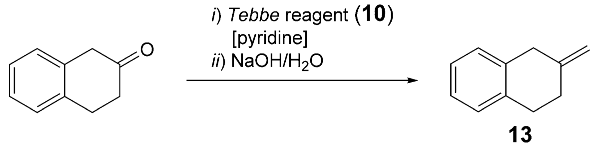
Scheme 1. *Synthesis of compounds* **1b** *and* **2**–**5**



workup finally gave **4** (82% yield). Treatment of **2** with MsCl, in the presence of Et_3N, yielded the intermediate 6-methyl-5-methylidene-7-(trimethylsilyl)heptan-2-yl methanesulfonate (**12**), which was then converted to **5** by treatment with NaCN (65% yield, based on **2**).

The molarity of the *Tebbe* reagent (**10**) was determined on an analytical scale by reaction with 3,4-dihydro-1*H*-naphthalen-2-one, in the presence of pyridine, and subsequent treatment with aqueous NaOH solution to furnish 1,2,3,4-tetrahydro-2-methylidenenaphthalene (**13**), the concentration of which was then quantified by gas chromatography (*Scheme 2*; for further details, see the *Exper. Part*). To characterize

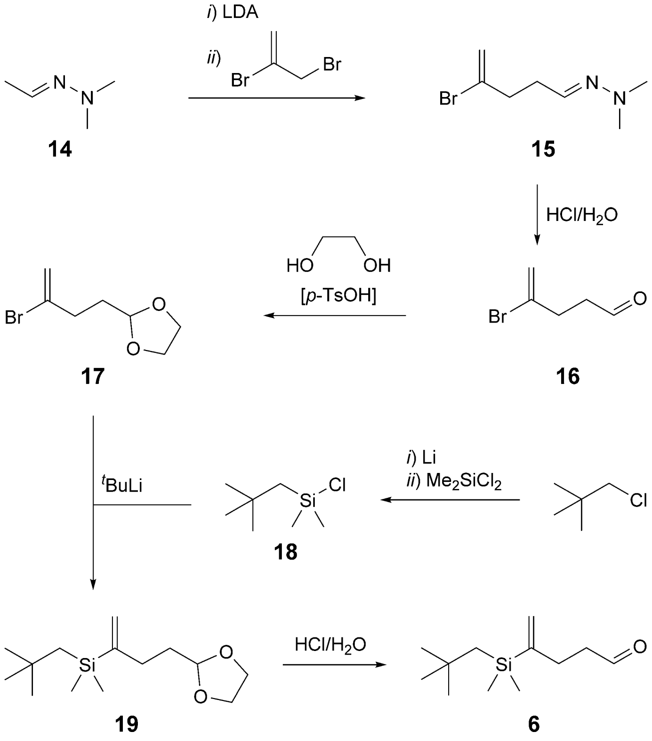
Scheme 2. *Synthesis of compound* **13** (determination of the molarity of the *Tebbe* reagent)



and to establish the identity of **13**, it was also synthesized on a preparative scale (78% yield).

Compound **6** was synthesized as delineated in *Scheme 3*, starting from ethanal dimethylhydrazone (**14**). Thus, lithiation of **14** with $\mathrm{LiN^iPr_2}$ (LDA) and subsequent treatment with 2,3-dibromoprop-1-ene gave 4-bromopent-4-enal dimethylhydrazone (**15**; 85% yield), which, upon hydrolysis with aqueous HCl, furnished 4-bromopent-4-enal (**16**; 82% yield). The aldehyde function of **16** was then protected as an acetal by an acid-catalyzed (*p*-toluenesulfonic acid (TsOH)) reaction with 1,2-ethanediol to afford 2-(3-bromobut-3-en-1-yl)-1,3-dioxolane (**17**; 93% yield), which, upon lithiation with ^{t}BuLi and subsequent treatment with chloro(2,2-dimethylpropyl)(dimethyl)silane (**18**) furnished [4-(1,3-dioxolan-2-yl)but-1-en-2-yl]dimethyl(2,2-dimethylpropyl)silane (**19**; 75% yield). Deprotection of **19** by treatment with aqueous HCl finally afforded the

Scheme 3. *Synthesis of compound* **6**



target compound **6** (73% yield). Compound **18** was prepared by lithiation of 1-chloro-2,2-dimethylpropane and subsequent treatment with Me_2SiCl_2 (79% yield).

Silicon compounds **1b**, **2**–**9**, **11**, and **13**–**19** were isolated as colorless liquids. Compounds **1b**, **3**, **4**, **7**–**9**, and **11** were obtained as racemates, and **2**, **5**, and **12** as mixtures of diastereoisomers (molar ratio (*R*,*R*)/(*S*,*S*):(*R*,*S*)/(*S*,*R*) 1:1). Their identities were established by elemental analyses (C, H, N) and NMR-spectroscopic studies (^{1}H, ^{13}C, ^{15}N, ^{29}Si).

Olfactory Properties. Compounds **1a**, **1b**, and **2**–**6** were evaluated for their olfactory properties (*Table*). While the aldehydic lily-of-the-valley odor of the lead compound **1a** clearly recalls *Lilial* and *Bourgeonal* with only some additional green-fatty and rubbery aspects, the green character of Si-analog **1b** is more pronounced, with additional resinous and metallic hot-iron aspects. However, the main odor character of **1b** is also floral, in the lily-of-the-valley direction. The substantivity indeed improves upon C/Si exchange, but the almost twice as high th value of 28.7 ng/l air negates and impairs this effect, as the overall odor impression becomes too weak. This indicates that there apparently is no space for additional hydrophobic binding interactions at the hydrophobic tail of lead compound **1a**, and that our initial assumptions were accordingly incorrect.

Silicon compound **2** (secondary alcohol) shows no typical muguet-type odor anymore. It is rather weak, with a slightly watery-floral odor character and some fruity facets. A th value of 119 ng/l air was measured, corresponding to the rather weak impression on the smelling blotter. The corresponding ketone **3** possesses an even higher th value of 443 ng/l air, and a fatty-green odor, with rubbery aspects as well as creamy-woody and floral facets recalling 4-(*tert*-butyl)cyclohexyl acetate with its typical sweet, creamy-woody, floral odor profile. Silicon compound **4** (tertiary alcohol) has a green-rooty odor, so also not in the lily-of-the-valley direction, and is again relatively weak, with a th value of 335 ng/l air. Nitrile **5** is the weakest Si compound of the series studied. With a th value of 750 ng/l air, it is almost odorless and possesses only an oily, clay-type, slightly floral odor, with distant green nuances. Vinylsilane **6** possesses an aldehydic metallic-floral odor, with oily aspects and slight clay nuances, and thus it is also not reminiscent of lily-of-the-valley flowers. With a th value of 29.7 ng/l air, however, **6** is comparable in strength to the lily-of-the-valley odorants **1a** and **1b**.

Table. *Olfactory Properties of* **1a**, **1b**, *and* **2**–**6**

Compound	Olfactory properties	Odor threshold [ng/l air]
1a	aldehydic lily-of-the-valley odor recalling *Lilial* and *Bourgeonal*, with green-fatty and rubbery aspects	15.8
1b	floral, lily-of-the-valley odor, with resinous-green, rubbery, metallic hot-iron-type aspects	28.7
2	weak, slightly watery-floral, with fruity facets	119
3	weak, fatty-green rubbery odor, with slightly creamy-woody, floral facets of 4-(*tert*-butyl)cyclohexyl acetate	443
4	relatively weak, green-rooty odor	355
5	very weak, oily, clay-type, slightly floral odor, with distant green nuances	750
6	aldehydic metallic-floral odor, with oily aspects and slight clay nuances	29.7

Conclusions. – In the series of Si compounds synthesized, only the sila analog **1b** of lead structure **1a** possesses a similar lily-of-the-valley odor profile as observed for **1a**; yet, in terms of th (28.7 ng/l air), it is almost twice as weak as **1a**, and it displays additional metallic hot-iron-type facets. Thus, contrary to our initial expectations, there is no further space for additional hydrophobic binding interactions at the hydrophobic tail of lead compound **1a**. A H-bond accepting aldehydic C=O function seems to be a prerequisite for the lily-of-the-valley odor character, since alcohols **2** and **4** are weak, and rather uncharacteristically floral-green. Even a ketone moiety as in **3** cannot replace the aldehyde function for its typical contribution to the lily-of-the-valley odor. Extending the H-bond acceptor function by one C-atom as in nitrile **5** leads to an almost total loss of odor, with a th value of 750 ng/l air. Increasing the steric bulk close to the essential $=CH_2$ group as in **6** also makes the muguet character of **1a** and **1b** disappear, albeit **6** is aldehydic in smell and with a th value of 29.7 ng/l air moderately strong.

In conclusion, Si replacement in **1a** (→**1b**) and further derivatization of **1b** (→**2**–**6**) did not improve the olfactory properties of the muguet lead structure **1a**. In this new class of muguet odorants, an aldehyde function seems to be essential for a lily-of-the-valley-type odor profile, and the distance of both the Me_3El-substituted (El = C, Si) hydrophobic tail and the C=C bond to the osmophoric H-bond acceptor are of crucial importance. Steric bulk in the vicinity of the C=C bond should be avoided, but only the olfactory characterization of further derivatives will allow more insight into the molecular parameters required to improve the performance of the muguet lead structure **1a**.

Experimental Part

General. All syntheses involving chemicals sensitive to H_2O and/or O_2 were carried out under dry Ar. The org. solvents used were dried and purified according to standard procedures and stored under dry N_2. Starting materials and reagents were purchased from *ABCR*, *Acros*, or *Aldrich* and were used without further purification. Bulb-to-bulb distillations: *Büchi Glass Oven B-580* apparatus. Centrifugations: *Heraeus Megafuge 1.0* apparatus. Flash column chromatography (FC): silica gel *Aldrich 60752* (SiO_2; 40–63 μm); 1.5 bar. Medium-pressure liquid chromatography (MPLC): SiO_2 *YMC SL12S15* (15 μm; 50 × 2.5 cm); 16 mbar; *Knauer* variable-wavelength monitor detector. ^1H-, ^{13}C-, ^{15}N-, and ^{29}Si-NMR spectra: *Bruker Avance 500* NMR spectrometer (^1H: 500.1, ^{13}C: 125.8, ^{15}N: 50.7, and ^{29}Si: 99.4 MHz); in C_6D_6 at 23°; δ in ppm rel. to internal C_6HD_5 (δ(H) 7.28; C_6D_6), internal C_6D_6 (δ(C) 128.0; C_6D_6), external $HCONH_2$ (90% in (D_6)DMSO; δ(N) −268.0; C_6D_6), or external Me_4Si (δ(Si) 0; C_6D_6), J in Hz. ^1H-NMR Spectra of **1b** and **9**: *Bruker Avance DMX-600* NMR spectrometer (5-mm cryoprobe; 600.1 MHz); in C_6D_6 at 30°; δ in ppm rel. to internal C_6HD_5 (δ(H) 7.28; C_6D_6). Assignment of the ^1H-NMR data was supported by $^1H,^1H$ gradient-selected COSY and $^1H,^{13}C$ gradient-selected HMQC and HMBC experiments. Assignment of the ^{13}C-NMR data was supported by the aforementioned $^1H,^{13}C$-correlation experiments. ^{15}N-NMR Spectra were obtained by using inverse correlation $^1H,^{15}N$ HMBC experiments. The spin systems were analyzed by using the WIN-DAISY software package (version 4.05, *Bruker*) [7]. GC: *Varian 450-GC* (flow rate, 1 ml min^{-1}; injector split ratio, 1:80, 220°; carrier gas, He; detector, *Varian 320-MS*, electron ionization (EI-MS; 70 eV)) with *FactorFour VF-5ms* column (*Varian Inc.*; length, 30 m; 0.25 mm i.d.; film, 0.25 μm). Elemental analyses: *VarioMicro* apparatus (*Elementar Analysensysteme GmbH*) or *EURO EA* elemental analyzer (*EuroVector*); in %.

Synthesis of 5-Methyl-4-methylidene-6-(trimethylsilyl)hexanal (**1b**). A mixture of CF_3COOH (10 ml) and H_2O (15 ml) was added in a single portion at 0° to a stirred soln. of **11** (2.00 g, 7.34 mmol) in $CHCl_3$ (60 ml), and the resulting mixture was then stirred at this temp. for 1 h. H_2O (200 ml) was added to the mixture, the org. phase was separated, and the aq. phase was extracted with $CHCl_3$ (3 × 200 ml) and discarded. The combined org. solns. were washed with a sat. aq. soln. of $NaHCO_3$ (80 ml) and then dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by MPLC (SiO_2; pentane/Et_2O 96 :4; flow rate, 72 ml min^{-1}; detector wavelength, 280 nm), followed by bulb-to-bulb distillation (oven temp., 70°; 0.6 mbar) to furnish **1b** (1.10 g, 5.54 mmol, 75%). Colorless liquid. Odor description: floral, lily-of-the-valley odor, with resinous-green, rubbery, metallic hot-iron-type aspects; th: 28.7 ng/l air. ^{1}H-NMR (600.1 MHz, C_6D_6): 0.12 (*s*, Me_3Si); 0.61 (δ_A); 0.82 (δ_B); 1.09 (δ_E); 2.1553 (δ_K); 2.1554 (δ_L); 2.20 (δ_M); 2.21 (δ_N); 2.34 (δ_R); 4.60 (δ_U); 4.91 (δ_V); 9.45 (δ_Z) ($ABE_3KLMNRUVZ$ system, $^2J_{A,B}=14.7$, $^2J_{K,L}=18.0$, $^2J_{M,N}=18.0$, $^2J_{U,V}=1.1$, $^3J_{A,R}=8.1$, $^3J_{B,R}=6.5$, $^3J_{E,R}=6.8$, $^3J_{K,M}=8.2$, $^3J_{K,N}=3.9$, $^3J_{K,Z}=1.9$, $^3J_{L,M}=7.9$, $^3J_{L,N}=11.2$, $^3J_{L,Z}=1.2$, $^4J_{M,U}=1.7$, $^4J_{M,V}=1.0$, $^4J_{N,U}=1.5$, $^4J_{N,V}=1.0$, $^4J_{R,V}=0.8$, 13 H; $\mathrm{C}H_AH_B\mathrm{C}H_R(\mathrm{C}(H_E)_3)\mathrm{C}(=\mathrm{C}H_UH_V)\mathrm{C}H_MH_N\mathrm{C}H_KH_L\mathrm{C}H_Z$). ^{13}C-NMR (125.8 MHz, C_6D_6): −0.8 (Me_3Si); 23.4 (CH*Me*); 23.9 ($SiCH_2$); 24.8 (*C*H_2CH_2CH); 37.3 (*C*HMe); 42.0 (CH_2*C*H_2CH); 107.3 (C=*C*H_2); 155.0 (*C*=CH_2); 200.2 (CH_2CH_2*C*H). ^{29}Si-NMR (99.4 MHz, C_6D_6): 0.4. Anal. calc. for $C_{11}H_{22}OSi$ (198.38): C 66.60, H 11.18; found: C 66.23, H 11.19.

Synthesis of 6-Methyl-5-methylidene-7-(trimethylsilyl)heptan-2-ol (**2**). A 3M soln. of MeMgBr in Et_2O (8.23 ml, 24.7 mmol of MeMgBr) was added dropwise at 20° within 30 min to a stirred soln. of **1b** (4.90 g, 24.7 mmol) in Et_2O (100 ml), and the mixture was then stirred at this temp. for 3 h. A sat. aq. soln. of NH_4Cl (100 ml) was added to the mixture, the org. phase was separated, the aq. phase was extracted with Et_2O (3 × 100 ml) and discarded, and the combined org. solns. were dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by bulb-to-bulb distillation (oven temp., 100°; 0.2 mbar) to furnish **2** (4.60 g, 21.5 mmol, 87%). Colorless liquid. Odor description: weak, slightly watery-floral, with fruity facets; th: 119 ng/l air. ^{1}H-NMR (500.1 MHz, C_6D_6; data for two diastereoisomers (molar ratio 1:1)[2])): 0.15, 0.16 (*s*, Me_3Si); 0.68–0.74, 0.68–0.74 (*m*, 1 H, $SiCH_2$); 0.92–0.99, 0.92–0.99 (*m*, 1 H, $SiCH_2$); 1.146, 1.150 (*d*, $^3J=6.2$, OCH*Me*); 1.21, 1.21 (*d*, $^3J=6.8$, $SiCH_2CH$*Me*); 1.2, 1.2 (br. *s*, OH); 1.57–1.72, 1.57–1.72 (*m*, CH_2*C*H_2CH); 2.08–2.17, 2.08–2.17 (*m*, CH_2*CH*$_2$CH and 1 H of *CH*$_2CH_2CH$); 2.26–2.35, 2.26–2.35 (*m*, CH_2*CH*$_2$CH and 1 H of *CH*$_2CH_2CH$); 2.43–2.52, 2.43–2.52 (*m*, CH_2C*H*Me); 3.66–3.75, 3.66–3.75 (*m*, CH_2CH_2C*H*); 4.86–4.88, 4.86–4.88 (*m*, 1 H, C=CH_2); 5.00–5.02, 5.00–5.02 (*m*, 1 H, C=CH_2). ^{13}C-NMR (125.8 MHz, C_6D_6; data for two diastereoisomers (molar ratio 1:1)): −6.8, −6.8 (Me_3Si); 23.6, 23.7 ($SiCH_2CH$*Me*); 23.87, 23.89 (OCH*Me*); 24.20, 24.24 (Si*C*H_2); 29.36, 29.42 (*C*H_2CH_2CH); 37.18, 37.21 (CH_2*C*HMe); 37.99, 38.03 (CH_2*C*H_2CH); 67.6, 67.7 (CH_2CH_2*C*H); 106.88, 106.93 (C=*C*H_2); 156.72, 156.73 (*C*=CH_2). ^{29}Si-NMR (99.4 MHz, C_6D_6; data for two diastereoisomers): 0.4, 0.4. Anal. calc. for $C_{12}H_{26}OSi$ (214.42): C 67.22, H 12.22; found: C 66.97, H 12.45.

Synthesis of 6-Methyl-5-methylidene-7-(trimethylsilyl)heptan-2-one (**3**). PCC (1.50 g, 6.96 mmol) was added at 20° within 10 min to a stirred mixture of **2** (1.00 g, 4.66 mmol), *Celite* (9.50 g), and CH_2Cl_2 (100 ml), and the resulting mixture was then stirred at this temp. for 3 h. The mixture was filtered through a pad of *Celite* (20 g), followed by elution with CH_2Cl_2. The solvent of the filtrate (including the eluate) was removed under reduced pressure, and the residue was purified by FC (SiO_2; hexane/Et_2O 9:1), followed by bulb-to-bulb distillation (oven temp., 65°; 0.2 mbar) to furnish **3** (752 mg, 3.54 mmol, 76%). Colorless liquid. Odor description: weak, fatty-green rubbery odor, with slightly creamy-woody, floral facets of 4-(*tert*-butyl)cyclohexyl acetate; th: 443 ng/l air. ^{1}H-NMR (500.1 MHz, C_6D_6): 0.14 (*s*, Me_3Si); 0.67 (δ_A); 0.90 (δ_B); 1.16 (δ_E); 2.30 (δ_K); 2.31 (δ_L); 2.39 (δ_M); 2.40 (δ_N); 2.42 (δ_R); 4.68 (δ_X); 4.96 (δ_Y) ($ABE_3KLMNRXY$ system, $^2J_{A,B}=14.7$, $^2J_{K,L}=17.8$, $^2J_{M,N}=16.9$, $^2J_{X,Y}=1.3$, $^3J_{A,R}=8.0$, $^3J_{B,R}=6.5$, $^3J_{E,R}=6.8$, $^3J_{K,M}=9.0$, $^3J_{K,N}=7.0$, $^3J_{L,M}=4.9$, $^3J_{L,N}=9.9$, $^4J_{M,X}=2.5$, $^4J_{M,Y}=0.5$, $^4J_{N,X}=0.7$, $^4J_{N,Y}=1.6$, $^4J_{R,Y}=0.8$, 12 H; $\mathrm{C}H_AH_B\mathrm{C}H_R(\mathrm{C}(H_E)_3)\mathrm{C}(=\mathrm{C}H_XH_Y)\mathrm{C}H_MH_N\mathrm{C}H_KH_L$); 1.78 (*s*, C(O)Me). ^{13}C-NMR (125.8 MHz, C_6D_6): −0.8 (Me_3Si); 23.5 (CH*Me*); 24.0 ($SiCH_2$); 26.5 (*C*H_2CH_2C=O); 29.3 (*Me*C=O); 37.5 (*C*HMe); 41.7 (CH_2*C*H_2C=O); 106.8 (C=*C*H_2); 155.7 (*C*=CH_2); 205.6 (C=O). ^{29}Si-NMR (99.4 MHz, C_6D_6): 0.4. Anal. calc. for $C_{12}H_{24}OSi$ (212.41): C 67.86, H 11.39; found: C 67.94, H 11.41.

Synthesis of 2,6-Dimethyl-5-methylidene-7-(trimethylsilyl)heptan-2-ol (**4**). A 3M soln. of MeMgBr in Et_2O (1.00 ml, 3.00 mmol of MeMgBr) was added dropwise at 20° within 5 min to a stirred soln. of **3** (500 mg, 2.35 mmol) in Et_2O (30 ml), and the mixture was then stirred at this temp. for 2 h. A sat. aq.

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[2] Analysis of the spin systems by using the WIN-DAISY software package was not possible due to the superposition of the resonance signals of the two diastereoisomers.

soln. of NH_4Cl (20 ml) was added to the mixture, the org. phase was separated, the aq. phase was extracted with Et_2O (3 × 50 ml) and discarded, and the combined org. solns. were dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by FC (SiO_2; hexane/Et_2O 9 : 1), followed by bulb-to-bulb distillation (oven temp., 105°; 0.2 mbar) to furnish **4** (440 mg, 1.93 mmol, 82%). Colorless liquid. Odor description: relatively weak, green-rooty odor; th: 355 ng/l air. ^{1}H-NMR (500.1 MHz, C_6D_6): 0.16 (*s*, Me_3Si); 0.74 (δ_A); 0.98 (δ_B); 1.23 (δ_E); 1.69 (δ_K); 1.70 (δ_L); 2.261 (δ_M); 2.263 (δ_N); 2.51 (δ_R); 4.90 (δ_X); 5.03 (δ_Y) ($ABE_3KLMNRXY$ system, $^2J_{A,B} = 14.7$, $^2J_{K,L} = 16.3$, $^2J_{M,N} = 18.6$, $^2J_{X,Y} = 1.6$, $^3J_{A,R} = 7.9$, $^3J_{B,R} = 6.6$, $^3J_{E,R} = 6.8$, $^3J_{K,M} = 12.4$, $^3J_{K,N} = 4.6$, $^3J_{L,M} = 4.5$, $^3J_{L,N} = 12.5$, $^4J_{M,X} = 1.7$, $^4J_{M,Y} = 1.0$, $^4J_{N,X} = 1.3$, $^4J_{N,Y} = 0.8$, $^4J_{R,Y} = 0.8$, 12 H; $\mathrm{C}H_AH_B\mathrm{C}H_R(\mathrm{C}(H_E)_3)\mathrm{C}(=\mathrm{C}H_XH_Y)\mathrm{C}H_MH_N\mathrm{C}H_KH_L$); 1.18 (*s*, $(\mathit{Me})_2\mathrm{COH}$); OH not detected. ^{13}C-NMR (125.8 MHz, C_6D_6): −0.7 (Me_3Si); 23.7 (CH*Me*); 24.3 ($\mathrm{SiCH_2}$); 27.6 ($\mathit{C}\mathrm{H_2CH_2COH}$); 29.4 (*Me*COH); 29.5 (*Me*COH); 37.4 (*C*HMe); 42.5 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2COH}$); 70.0 (C–OH); 106.8 ($\mathrm{C{=}}\mathit{C}\mathrm{H_2}$); 157.1 ($\mathit{C}\mathrm{{=}CH_2}$). ^{29}Si-NMR (99.4 MHz, C_6D_6): 0.4. Anal. calc. for $C_{13}H_{28}OSi$ (228.45): C 68.35, H 12.35; found: C 68.42, H 12.53.

Synthesis of 2,6-Dimethyl-5-methylidene-7-(trimethylsilyl)heptanenitrile (**5**). MsCl (353 mg, 3.08 mmol) was added dropwise at −30° within 10 min to a stirred mixture of **2** (600 mg, 2.80 mmol), Et_3N (849 mg, 8.39 mmol), and CH_2Cl_2 (50 ml), and the mixture was stirred at this temp. for 15 min and then allowed to warm to 20° within 30 min. Pentane (50 ml) was added to the mixture, and the resulting precipitate was separated from the supernatant by centrifugation (2300 *g*, 5 min, 20°) and discarded. The volatile components of the supernatant were removed under reduced pressure (0.001 mbar, 20°, 2 h) to furnish the intermediate *6-methyl-5-methylidene-7-(trimethylsilyl)heptan-2-yl methanesulfonate* (**12**; crude product, not further purified; ^{1}H-NMR (500.1 MHz, C_6D_6; data for two diastereoisomers (molar ratio 1 : 1)[2])): 0.147, 0.153 (*s*, Me_3Si); 0.66–0.72, 0.66–0.72 (*m*, 1 H, $\mathrm{SiCH_2}$); 0.88–0.95, 0.88–0.95 (*m*, 1 H, $\mathrm{SiCH_2}$); 1.17, 1.17 (*d*, $^3J = 6.9$, $\mathrm{SiCH_2CH}\mathit{Me}$); 1.210, 1.212 (*d*, $^3J = 6.3$, *Me*CHOS); 1.58–1.69, 1.58–1.69 (*m*, 1 H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH}$); 1.77–1.88, 1.77–1.88 (*m*, 1 H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH}$); 2.03–2.13, 2.03–2.13 (*m*, $\mathrm{C}\mathit{H}\mathrm{HCH_2CH}$); 2.15–2.25, 2.15–2.25 (*m*, $\mathrm{CH}\mathit{H}\mathrm{CH_2CH}$); 2.349, 2.350 (*s*, $\mathrm{S(O)_2Me}$); 2.36–2.46, 2.36–2.46 (*m*, $\mathrm{SiCH_2C}\mathit{H}\mathrm{Me}$); 4.71–4.79, 4.71–4.79 (*m*, MeC*H*OS); 4.76–4.79, 4.76–4.79 (*m*, 1 H, $\mathrm{C{=}CH_2}$); 4.97–5.00, 4.97–5.00 (*m*, 1 H, $\mathrm{C{=}CH_2}$)).

Subsequently, NaCN (686 mg, 14.0 mmol) and 1,3-dimethyltetrahydropyrimidin-2(1*H*)-one (80 ml) were added sequentially in single portions to **12** (crude product) at 20°. The resulting mixture was stirred at 50° for 6 h and then allowed to cool to 20° within 20 min. The mixture was filtered through a pad of SiO_2 (20 g)[3]), followed by elution with hexane/Et_2O 9 : 1. The solvent of the filtrate (including the eluate) was removed under reduced pressure, and the residue was purified by FC (SiO_2; hexane/Et_2O 9 : 1)[3]), followed by bulb-to-bulb distillation (oven temp., 105°; 0.5 mbar), to furnish **5** (410 mg, 1.83 mmol, 65%). Colorless liquid. Odor description: very weak, oily, clay-type, slightly floral odor, with distant green nuances; th: 750 ng/l air. ^{1}H-NMR (500.1 MHz, C_6D_6; data for two diastereoisomers (molar ratio 1 : 1)[2])): 0.14, 0.15 (*s*, Me_3Si); 0.62–0.69, 0.62–0.69 (*m*, 1 H, $\mathrm{SiCH_2}$); 0.843, 0.845 (*d*, $^3J = 7.1$, *Me*CHCN); 0.85–0.90, 0.85–0.90 (*m*, 1 H, $\mathrm{SiCH_2}$); 1.12, 1.13 (*d*, $^3J = 6.8$, $\mathrm{CH_2CH}\mathit{Me}$); 1.29–1.37, 1.29–1.37 (*m*, 1 H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH}$); 1.44–1.54, 1.44–1.54 (*m*, 1 H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH}$); 1.96–2.09, 1.96–2.09 (*m*, $\mathrm{C}\mathit{H}\mathrm{HCH_2CH}$); 2.01–2.09, 2.01–2.09 (*m*, MeC*H*CN); 2.14–2.24, 2.14–2.24 (*m*, $\mathrm{CH}\mathit{H}\mathrm{CH_2CH}$); 2.31–2.40, 2.31–2.40 (*m*, $\mathrm{CH_2C}\mathit{H}\mathrm{Me}$); 4.66–4.68, 4.66–4.68 (*m*, 1 H, $\mathrm{C{=}CH_2}$); 4.93–4.95, 4.93–4.95 (*m*, $\mathrm{C{=}CH_2}$). ^{13}C-NMR (125.8 MHz, C_6D_6; data for two diastereoisomers (molar ratio 1 : 1): −0.7, −0.7 (Me_3Si); 17.7, 17.8 (*Me*CHCN); 23.4, 23.4 ($\mathrm{SiCH_2CH}\mathit{Me}$); 24.05, 24.10 ($\mathit{C}\mathrm{H_2CHMe}$); 25.25, 25.26 (Me*C*HCN); 30.25, 30.26 ($\mathit{C}\mathrm{H_2CH_2CH}$); 32.6, 32.7 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH}$); 37.04, 37.06 ($\mathrm{CH_2}\mathit{C}\mathrm{HMe}$); 107.6, 107.7 ($\mathrm{C{=}}\mathit{C}\mathrm{H_2}$); 122.37, 122.39 (*C*N); 155.02, 155.05 ($\mathit{C}\mathrm{{=}CH_2}$). ^{29}Si-NMR (99.4 MHz, C_6D_6; data for two diastereoisomers): 0.5, 0.5. Anal. calc. for $C_{13}H_{25}NSi$ (223.43): C 69.88, H 11.28, N 6.27; found: C 69.84, H 11.42, N 6.40.

Synthesis of 4-[Dimethyl(2,2-dimethylpropyl)silyl]pent-4-enal (**6**). A mixture of **19** (890 mg, 3.47 mmol), MeOH (20 ml), and 0.5M HCl (7 ml) was stirred at 20° for 2 h. A sat. aq. soln. of $NaHCO_3$ (100 ml) was added to the mixture, the org. phase was separated, the aq. phase was extracted with Et_2O (3 × 100 ml) and discarded, and the combined org. solns. were dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by FC (SiO_2; hexane/AcOEt 9 : 1), followed by

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[3] SiO_2 was treated with conc. aq. NH_3 soln. (28% by weight related to SiO_2), and the resulting mixture was shaken until a homogenous powder was obtained.

bulb-to-bulb distillation (oven temp., 135°; 0.2 mbar), to furnish **6** (540 mg, 2.54 mmol, 73%). Colorless liquid. Odor description: aldehydic metallic-floral odor, with oily aspects and slight clay nuances; th: 29.7 ng/l air. ^{1}H-NMR (500.1 MHz, C_6D_6): 0.21 (*s*, Me_2Si); 0.81 (*s*, $SiCH_2$); 1.08 (*s*, ^{t}Bu); 2.18 ($\delta_{AA'}$); 2.37 ($\delta_{DD'}$); 5.45 (δ_U); 5.51 (δ_V); 9.46 (δ_Z) (*AA'DD'UVZ* system, $^2J_{A,A'}=15.0$, $^2J_{D,D'}=14.1$, $^2J_{U,V}=2.3$, $^3J_{A,D}=$ $^3J_{A',D'}=6.1$, $^3J_{A,D'}=^3J_{A',D}=8.9$, $^3J_{A,Z}=^3J_{A',Z}=1.6$, $^4J_{D,U}=^4J_{D',U}=1.4$, $^4J_{D,V}=^4J_{D',V}=1.8$, 7 H; $C(=CH_UH_V)CH_DH_{D'}CH_AH_{A'}CH_Z$). ^{13}C-NMR (125.8 MHz, C_6D_6): −0.96 (Me_2Si); 27.3 (*C*H_2CH_2CH); 31.1 (Me_3*C*); 31.9 ($SiCH_2$); 33.0 (*Me*$_3$C); 42.4 (CH_2*C*H_2CH); 124.2 (C=CH_2); 150.7 (*C*=*C*H_2); 200.2 (CH_2CH_2*C*H). ^{29}Si-NMR (99.4 MHz, C_6D_6): −5.9. Anal. calc. for $C_{12}H_{24}OSi$ (212.41): C 67.86, H 11.39; found: C 67.79, H 11.60.

Synthesis of 2-Methyl-3-(trichlorosilyl)propanenitrile (**7**). In [8], a similar reaction was described; however, prop-2-enenitrile instead of 2-methylprop-2-enenitrile was used as starting material. A mixture of Cl_3SiH (98.9 g, 730 mmol), 2-methylprop-2-enenitrile (49.0 g, 730 mmol), and dimethyl(tetradecyl)amine (8.82 g, 36.5 mmol) was heated in an autoclave at 140° for 2 h and was then allowed to cool to 20° within 1 h. The resulting mixture was purified by distillation *in vacuo* to furnish **7** (123 g, 607 mmol, 83%). Colorless liquid. B.p. 57°/2 mbar. ^{1}H-NMR (500.1 MHz, C_6D_6): 0.84 (δ_K); 0.87 (δ_A); 1.15 (δ_B); 2.27 (δ_M) ($ABMK_3$ system, $^2J_{A,B}=15.4$, $^3J_{A,M}=7.0$, $^3J_{B,M}=8.0$, $^3J_{K,M}=7.0$, 6 H; $CH_AH_BCH_MC(H_K)_3$). ^{13}C-NMR (125.8 MHz, C_6D_6): 20.0 (Me); 20.3 (CH); 28.0 (CH_2); 121.2 (CN). ^{15}N-NMR (50.7 MHz, C_6D_6): −129.3. ^{29}Si-NMR (99.4 MHz, C_6D_6): 9.0. Anal. calc. for $C_4H_6Cl_3NSi$ (202.54): C 23.72, H 2.99, N 6.92; found: C 23.70, H 3.01, N 6.96.

Synthesis of 2-Methyl-3-(trimethylsilyl)propanenitrile (**8**). A 3M soln. of MeMgBr in Et_2O (247 ml; 741 mmol of MeMgBr) was added at 0° within 90 min to a stirred soln. of **7** (50.0 g; 247 mmol) in Et_2O (350 ml). The resulting mixture was allowed to warm to 20° within 30 min, and stirring was continued for 17 h. H_2O (200 ml) was added to the mixture, the org. phase was separated, the aq. phase was extracted with Et_2O (3 × 150 ml) and discarded, and the combined org. solns. were dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by distillation *in vacuo* to furnish **8** (29.1 g, 206 mmol, 83%). Colorless liquid. B.p. 57°/12 mbar. ^{1}H-NMR (500.1 MHz, C_6D_6): 0.04 (*s*, Me_3Si); 0.37 (δ_A); 0.68 (δ_B); 0.94 (δ_K); 2.14 (δ_M) ($ABMK_3$ system, $^2J_{A,B}=14.7$, $^3J_{A,M}=6.3$, $^3J_{B,M}=9.2$, $^3J_{K,M}=7.0$, 6 H; $CH_AH_BCH_MC(H_K)_3$). ^{13}C-NMR (125.8 MHz, C_6D_6): −1.4 (Me_3Si); 21.3 (CH); 21.7 (CH*Me*); 22.3 (CH_2); 123.7 (CN). ^{15}N-NMR (50.7 MHz, C_6D_6): −133.1. ^{29}Si-NMR (99.4 MHz, C_6D_6): 0.5. Anal. calc. for $C_7H_{15}NSi$ (141.29): C 59.51, H 10.70, N 9.91; found: C 59.49, H 10.69, N 10.09.

Synthesis of 6,6-Diethoxy-2-methyl-1-(trimethylsilyl)hexan-3-one (**9**). A soln. of 3-chloro-1,1-diethoxypropane (29.5 g, 177 mmol) in Et_2O (50 ml) was added dropwise at 10° within 90 min to a vigorously stirred suspension of granular Li (2.95 g, 425 mmol) in Et_2O (150 ml; for a similar method, see [9])4)). The mixture was allowed to warm to 20° within 30 min, and stirring was continued for 17 h. The insoluble components were filtered off and discarded, the filtrate was cooled to −20°, and **8** (10.0 g, 70.8 mmol) was added dropwise at this temp. within 5 min. The mixture was allowed to warm to 20° within 30 min, and stirring was continued for 4 h, followed by the addition of H_2O (300 ml). The pH value of the mixture was adjusted to 6 by addition of 1M HCl, and stirring was continued for 30 min. The org. phase was separated, the aq. phase was extracted with Et_2O (4 × 150 ml) and discarded, and the combined org. solns. were washed with a sat. aq. soln. of $NaHCO_3$ (100 ml) and then dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by FC (SiO_2; pentane/Et_2O 4:1), followed by bulb-to-bulb distillation (oven temp., 110°; 0.1 mbar), to furnish **9** (13.0 g, 47.4 mmol, 67%). Colorless liquid. ^{1}H-NMR (600.1 MHz, C_6D_6): 0.09 (*s*, Me_3Si); 0.57 (δ_A); 1.10 (δ_B); 1.11 (δ_K); 2.52 (δ_M) ($ABMK_3$ system, $^2J_{A,B}=14.7$, $^3J_{A,M}=8.0$, $^3J_{B,M}=6.2$, $^3J_{K,M}=6.9$, 6 H; $CH_AH_BCH_MC(H_K)_3$); 1.2277 (δ_X); 3.455 (δ_A); 3.64 (δ_B) (ABX_3 system, $^2J_{A,B}=9.4$, $^3J_{A,X}=7.0$, $^3J_{B,X}=7.0$, 5 H; $CH_AH_BC(H_X)_3$); 1.2284 (δ_X); 3.458 (δ_A); 3.65 (δ_B) (ABX_3 system, $^2J_{A,B}=9.4$, $^3J_{A,X}=7.0$, $^3J_{B,X}=7.0$, 5 H; $CH_AH_BC(H_X)_3$); 2.1898 (δ_A); 2.1902 (δ_B); 2.55 (δ_M); 2.57 (δ_N); 4.63 (δ_X) (*ABMNX* system, $^2J_{A,B}=17.9$, $^2J_{M,N}=17.8$, $^3J_{A,M}=6.7$, $^3J_{A,N}=7.5$, $^3J_{B,M}=7.6$, $^3J_{B,N}=6.7$, $^3J_{A,X}=7.4$, $^3J_{B,X}=3.4$, 5 H; $CH_MH_NCH_AH_BCH_X$). ^{13}C-NMR (125.8 MHz, C_6D_6): −0.9 (Me_3Si); 15.6 (C(OCH_2*Me*)$_2$); 19.6 (CH*Me*); 20.6 (Si*C*H_2); 28.1 (CH_2*C*H_2CH); 34.9 (*C*H_2CH_2CH); 42.6 (*C*HMe); 61.23 (O*C*H_2Me); 61.26 (O*C*H_2Me); 102.2 (CH_2CH_2*C*H); 212.3 (C=O).

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4) Shards of glass were added to activate the granular Li mechanically.

^{29}Si-NMR (99.4 MHz, C_6D_6): 1.0. Anal. calc. for $C_{14}H_{30}O_3Si$ (274.48): C 61.26, H 11.02; found: C 61.29, H 11.07.

Synthesis of the Tebbe *Reagent* (**10**). The *Tebbe* reagent was synthesized as described in [10]. A 2M soln. of $AlMe_3$ in toluene (200 ml, 400 mmol of $AlMe_3$) was added dropwise at 0° within 45 min to a stirred soln. of titanocene dichloride (50.0 g, 201 mmol) in toluene (150 ml). The resulting mixture was allowed to warm to 20° within 30 min and was then stirred at this temp. for 72 h. The volatile components of the mixture were removed under reduced pressure (0.001 mbar, 20°), and the residue was dissolved in deoxygenated toluene (650 ml). The concentration of the reagent was determined by reaction of the stock soln. (1 ml) with 3,4-dihydro-1*H*-naphthalen-2-one (135 mg, 923 μmol) in the presence of pyridine (100 μl). After stirring the mixture at 20° for 17 h, a 1M aq. soln. of NaOH (500 μl) was added dropwise at 0° within 2 min, followed by sequential addition of H_2O (2 ml) and Et_2O (5 ml). The resulting org. phase was then injected into the gas chromatograph. The chromatogram of the mixture indicated 20% conversion to **13**. Therefore, the concentration of the reagent was *ca.* 185 mM.

Synthesis of (6,6-Diethoxy-2-methyl-3-methylidenehexyl)(trimethyl)silane (**11**). A 185 mM soln. of *Tebbe* reagent in toluene (**10**; 400 ml, 74.0 mmol of *Tebbe* reagent ($C_{13}H_{18}AlClTi$)) was added dropwise at 0° within 30 min to a stirred mixture of **9** (20.0 g, 72.9 mmol), pyridine (1 ml), toluene (300 ml), and THF (60 ml). The resulting mixture was allowed to warm to 20° within 1 h and was then stirred at this temp. for 17 h, followed by dropwise addition of a 1M aq. soln. of NaOH (35 ml) at 0° within 15 min. The resulting mixture was filtered through a pad of SiO_2 (900 g), followed by elution with pentane/Et_2O (9 : 1). The solvent of the filtrate (including the eluate) was removed under reduced pressure, and the residue was purified by FC (SiO_2; pentane/Et_2O 9 : 1), followed by bulb-to-bulb distillation (oven temp., 70°, 0.03 mbar), to furnish **11** (15.0 g, 55.0 mmol, 75%). Colorless liquid. ^{1}H-NMR (500.1 MHz, C_6D_6): 0.13 (*s*, Me_3Si); 0.67 (δ_A); 0.94 (δ_B); 1.18 (δ_E); 2.01 (δ_K); 2.02 (δ_L); 2.295 (δ_M); 2.304 (δ_N); 2.46 (δ_R); 4.63 (δ_U); 4.88 (δ_X); 4.99 (δ_Y) ($ABE_3KLMNRUXY$ system, $^2J_{A,B}=14.7$, $^2J_{K,L}=13.5$, $^2J_{M,N}=15.7$, $^2J_{X,Y}=1.5$, $^3J_{A,R}=8.0$, $^3J_{B,R}=6.5$, $^3J_{E,R}=6.8$, $^3J_{M,K}=10.7$, $^3J_{M,L}=5.4$, $^3J_{N,K}=5.3$, $^3J_{N,L}=10.8$, $^3J_{K,U}=5.7$, $^3J_{L,U}=5.5$, $^4J_{M,X}=1.4$, $^4J_{M,Y}=0.8$, $^4J_{N,X}=1.4$, $^4J_{N,Y}=0.9$, $^4J_{R,Y}=0.8$, 13 H; $CH_AH_BCH_R(C(H_E)_3)C(=CH_XH_Y)CH_MH_NCH_KH_L$-$CH_U$); 1.2444 ($\delta_X$); 3.496 ($\delta_A$); 3.67 ($\delta_B$) ($ABX_3$ system, $^2J_{A,B}=9.3$, $^3J_{A,X}=7.1$, $^3J_{B,X}=7.0$, 5 H; $CH_AH_BC(H_X)_3$); 1.2440 (δ_X); 3.497 (δ_A); 3.68 (δ_B) (ABX_3 system, $^2J_{A,B}=9.4$, $^3J_{A,X}=7.1$, $^3J_{B,X}=7.0$, 5 H; $CH_AH_BC(H_X)_3$). ^{13}C-NMR (125.8 MHz, C_6D_6): −0.7 (Me_3Si); 15.6 ($C(OCH_2Me)_2$); 23.6 (CH*Me*); 24.2 ($SiCH_2$); 28.2 (CH_2CH_2CH); 32.5 (CH_2CH_2CH); 37.3 (*C*HMe); 60.72 (O*C*H_2Me); 60.73 (O*C*H_2Me); 102.8 (CH_2CH_2*C*H); 106.9 (C=*C*H_2); 156.4 (*C*=CH_2). ^{29}Si-NMR (99.4 MHz, C_6D_6): 0.4. Anal. calc. for $C_{15}H_{32}O_2Si$ (272.50): C 66.11, H 11.84; found: C 66.37, H 11.73.

Synthesis of 6-Methyl-5-methylidene-7-(trimethylsilyl)heptan-2-yl Methanesulfonate (**12**). See synthesis of **5**.

Synthesis of 1,2,3,4-Tetrahydro-2-methylidenenaphthalene (**13**)[5]. A 185 mM soln. of *Tebbe* reagent in toluene (**10**; 111 ml, 20.5 mmol of $C_{13}H_{18}AlClTi$) was added dropwise at 0° within 30 min to a stirred mixture of 3,4-dihydro-1*H*-naphthalen-2-one (3.00 g, 20.5 mmol), pyridine (200 μl), toluene (50 ml), and THF (15 ml). The resulting mixture was allowed to warm to 20° within 30 min and was then stirred at this temp. for 5 h, followed by dropwise addition of a 1M aq. soln. of NaOH (15 ml) at 0° during 15 min. The resulting mixture was filtered through a pad of SiO_2 (300 g), followed by elution with pentane. The solvent of the filtrate (including the eluate) was removed by distillation at atmospheric pressure, and the residue was purified by FC (SiO_2; pentane), followed by bulb-to-bulb distillation (oven temp., 80°; 6 mbar), to furnish **13** (2.10 g, 15.9 mmol, 78%). Colorless liquid. ^{1}H-NMR (500.1 MHz, C_6D_6): 2.45–2.50 (*m*, H–C(3)); 2.83–2.87 (*m*, H–C(4)); 3.53 (*m*, H–C(1)); 4.84–4.86 (*m*, C=C*H*H); 4.87–4.89 (*m*, C=CH*H*); 7.02–7.17 (*m*, H–C(5,6,7,8)). ^{13}C-NMR (125.8 MHz, C_6D_6): 31.5 (C(4)); 32.2 (C(3)); 37.5 (C(1)); 108.3 (C=*C*H_2); 125.9 (C(8)); 126.3 (C(5)); 128.6 (C(7)); 128.8 (C(6)); 136.9 (C(8a)); 137.5 (C(4a)); 146.2 (C(2)). Anal. calc. for $C_{11}H_{12}$ (144.22): C 91.61, H 8.39; found: C 91.42, H 8.48.

*Synthesis of (2*E*)-2-Ethylidene-1,1-dimethylhydrazine* (**14**). This compound was synthesized as described in [12].

*Synthesis of (2*E*)-2-(4-Bromopent-4-en-1-ylidene)-1,1-dimethylhydrazine* (**15**). A 2.5M soln. of BuLi in hexane (115 ml, 288 mmol of BuLi) was added dropwise at −78° within 30 min to a stirred soln. of

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[5] For alternative synthetic methods, see [11].

$^i\mathrm{Pr_2NH}$ (30.5 g, 301 mmol) in THF (100 ml), and the resulting mixture was then allowed to warm to 20° within 1 h, followed by dropwise addition of **14** (25.9 g, 301 mmol) at $-78°$ within 30 min. The resulting mixture was allowed to warm to 20° within 1 h (formation of a colorless precipitate), followed by dropwise addition of a soln. of 2,3-dibromoprop-1-ene (50.0 g, 250 mmol) in THF (400 ml) at $-78°$ during 40 min. The mixture was then allowed to warm to 20° within 1 h and was stirred at this temp. for 3 h. A sat. aq. soln. of NaOH (300 ml) and $\mathrm{Et_2O}$ (300 ml) were added sequentially, the org. phase was separated, and the aq. phase was extracted with $\mathrm{Et_2O}$ (3 × 200 ml) and discarded. The combined org. solns. were dried ($\mathrm{Na_2SO_4}$), the solvent was removed under reduced pressure, and the residue was purified by distillation *in vacuo* to furnish **15** (43.5 g, 212 mmol, 85%). Colorless liquid. B.p. 88°/10 mbar. ^{1}H-NMR (500.1 MHz, $\mathrm{C_6D_6}$): 2.50 ($\delta_{AA'}$); 2.57 ($\delta_{DD'}$); 2.368 (δ_U); 2.371 (δ_V); 6.32 (δ_Z) (*AA'DD'VZ* system, $^2J_{A,A'} = 15.1$, $^2J_{D,D'} = 14.9$, $^2J_{U,V} = 1.7$, $^3J_{A,D} = {}^3J_{A',D'} = 8.8$, $^3J_{A,D'} = {}^3J_{A',D} = 6.1$, $^3J_{A,Z} = {}^3J_{A',Z} = 4.9$, $^4J_{D,U} = {}^4J_{D',U} = 1.2$, $^4J_{D,V} = {}^4J_{D',V} = 0.6$, 7 H; $\mathrm{C}(=\mathrm{C}H_UH_V)\mathrm{C}H_DH_{D'}\mathrm{C}H_AH_{A'}\mathrm{C}H_Z$); 2.59 (*s*, $\mathrm{NMe_2}$). ^{13}C-NMR (125.8 MHz, $\mathrm{C_6D_6}$): 31.7 ($\mathrm{CH_2}C\mathrm{H_2CH}$); 39.6 ($C\mathrm{H_2CH_2CH}$); 42.8 ($\mathrm{NMe_2}$); 116.8 ($\mathrm{C}{=}C\mathrm{H_2}$); 135.5 ($\mathrm{CH_2CH_2}C\mathrm{H}$); 134.2 ($C{=}\mathrm{CH_2}$). ^{15}N-NMR (50.7 MHz, $\mathrm{C_6D_6}$): -278.8 ($\mathrm{N}N\mathrm{Me_2}$); -24.1 ($N\mathrm{NMe_2}$). Anal. calc. for $\mathrm{C_7H_{13}BrN_2}$ (205.10): C 40.99, H 6.39, N 13.66; found: C 40.88, H 6.50, N 13.50.

Synthesis of 4-Bromopent-4-enal (**16**)[6]. A mixture of **15** (10.0 g, 48.8 mmol), 1M HCl (240 ml), and pentane (60 ml) was stirred at 20° for 17 h. The org. layer was separated, the aq. layer was extracted with pentane (3 × 100 ml) and discarded, and the combined org. solns. were washed with a sat. aq. soln. of $\mathrm{NaHCO_3}$ (30 ml) and then dried ($\mathrm{Na_2SO_4}$). The solvent was removed under reduced pressure, and the residue was purified by FC ($\mathrm{SiO_2}$; pentane/$\mathrm{Et_2O}$ 9:1), followed by bulb-to-bulb distillation (oven temp., 60°; 10 mbar), to furnish **16** (6.50 g, 39.9 mmol, 82%). Colorless liquid. ^{1}H-NMR (500.1 MHz, $\mathrm{C_6D_6}$): 2.02 ($\delta_{AA'}$); 2.39 ($\delta_{DD'}$); 5.21 (δ_U); 5.26 (δ_V); 9.18 (δ_Z) (*AA'DD'UVZ* system, $^2J_{A,A'} = 8.7$, $^2J_{D,D'} = 11.4$, $^2J_{U,V} = 1.9$, $^3J_{A,D} = {}^3J_{A',D'} = 6.1$, $^3J_{A,D'} = {}^3J_{A',D} = 8.5$, $^3J_{A,Z} = {}^3J_{A',Z} = 1.1$, $^4J_{D,U} = {}^4J_{D',U} = 1.2$, $^4J_{D,V} = {}^4J_{D',V} = 0.5$, 7 H; $\mathrm{C}(=\mathrm{C}H_UH_V)\mathrm{C}H_DH_{D'}\mathrm{C}H_AH_{A'}\mathrm{C}H_Z$). ^{13}C-NMR (125.8 MHz, $\mathrm{C_6D_6}$): 33.9 ($C\mathrm{H_2CH_2CH}$); 41.9 ($\mathrm{CH_2}C\mathrm{H_2CH}$); 117.5 ($\mathrm{C}{=}C\mathrm{H_2}$); 132.8 ($C{=}\mathrm{CH_2}$); 198.3 ($\mathrm{CH_2CH_2}C\mathrm{H}$). Anal. calc. for $\mathrm{C_5H_7BrO}$ (163.01): C 36.84, H 4.33; found: C 36.92, H 4.42.

Synthesis of 2-(3-Bromobut-3-en-1-yl)-1,3-dioxolane (**17**) [13b][13c]. A mixture of **16** (8.00 g, 49.1 mmol), $\mathrm{HOCH_2CH_2OH}$ (9.20 g, 148 mmol), $\mathrm{TsOH \cdot H_2O}$ (420 mg, 2.44 mmol), and hexane (200 ml) was heated under reflux for 17 h, and the resulting $\mathrm{H_2O}$ was removed with a water separator. The mixture was then allowed to cool to 20° within 1 h, and a cold (10°) sat. aq. $\mathrm{NaHCO_3}$ soln. (100 ml) was added. The org. layer was separated, the aq. layer was extracted with hexane (3 × 50 ml) and discarded, and the combined org. solns. were dried ($\mathrm{Na_2SO_4}$). The solvent was removed under reduced pressure, and the residue was purified by FC ($\mathrm{SiO_2}$; hexane/$\mathrm{Et_2O}$ 9:1) to furnish **17** (9.50 g, 45.9 mmol, 93%)[3]). Colorless liquid. ^{1}H-NMR (500.1 MHz, $\mathrm{C_6D_6}$): 2.03 ($\delta_{AA'}$); 2.62 ($\delta_{DD'}$); 4.84 (δ_M); 5.34 (δ_X); 5.36 (δ_Y) (*AA'DD'MXY* system, $^2J_{A,A'} = 15.2$, $^2J_{D,D'} = 13.8$, $^2J_{X,Y} = 1.7$, $^3J_{A,D} = {}^3J_{A',D'} = 5.5$, $^3J_{A,D'} = {}^3J_{A',D} = 10.1$, $^3J_{A,M} = {}^3J_{A',M} = 4.6$, $^4J_{D,X} = {}^4J_{D',X} = 0.5$, $^4J_{D,Y} = {}^4J_{D',Y} = 1.2$, 7 H; $\mathrm{C}(=\mathrm{C}H_XH_Y)\mathrm{C}H_DH_{D'}\mathrm{C}H_AH_{A'}\mathrm{C}H_M$); 3.41 ($\delta_{A,A'}$); 3.62 ($\delta_{B,B'}$) (*AA'BB'* system, $^2J_{A,B} = {}^2J_{A',B'} = 7.7$, $^3J_{A,A'} = 6.9$, $^3J_{A,B'} = {}^3J_{A',B} = 6.1$, $^3J_{B,B'} = 7.3$, 4 H; $\mathrm{OC}H_AH_B\text{-}\mathrm{C}H_{A'}H_{B'}\mathrm{O}$). ^{13}C-NMR (125.8 MHz, $\mathrm{C_6D_6}$): 32.9 ($\mathrm{CH_2}C\mathrm{H_2CH}$); 36.3 ($C\mathrm{H_2CH_2CH}$); 64.8 ($\mathrm{O}C\mathrm{H_2}C\mathrm{H_2O}$); 103.2 ($\mathrm{CH_2CH_2}C\mathrm{H}$); 116.7 ($\mathrm{C}{=}C\mathrm{H_2}$); 134.2 ($C{=}\mathrm{CH_2}$). Anal. calc. for $\mathrm{C_7H_{11}BrO_2}$ (207.07): C 40.60, H 5.35; found: C 40.46, H 5.44.

Synthesis of Chloro(2,2-dimethylpropyl)(dimethyl)silane (**18**). 1-Chloro-2,2-dimethylpropane (3.00 g, 28.1 mmol) was added dropwise within 5 min to a boiling suspension of Li powder (3.65 g, 526 mmol) in benzene (180 ml). The heating source was removed, whereupon boiling of the mixture was assured by further dropwise addition of 1-chloro-2,2-dimethylpropane (11.0 g, 103 mmol) within 30 min. The mixture was heated for 1 h under reflux and was then allowed to cool to 20° within 1 h. The insoluble components were filtered off, washed with $\mathrm{Et_2O}$ (2 × 20 ml), and discarded. The filtrate (including the wash solns.) was added dropwise at 0° within 2 h to a stirred soln. of $\mathrm{Me_2SiCl_2}$ (100 g, 775 mmol) in $\mathrm{Et_2O}$ (400 ml). The mixture was allowed to warm to 20° within 1 h, and stirring was continued at this temp. for 17 h. The insoluble components were filtered off, washed with $\mathrm{Et_2O}$ (3 × 50 ml), and discarded. The solvent of the filtrate (including the wash solns.) was removed by distillation at atmospheric pressure, and the residue was purified by distillation at atmospheric pressure to furnish **18** (16.9 g, 103 mmol, 79%).

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[6]) For alternative synthetic methods, see [13].

Colorless liquid. B.p. 146°. ^{1}H-NMR (500.1 MHz, C_6D_6): 0.41 (*s*, Me_2Si); 0.97 (*s*, $SiCH_2$); 1.05 (*s*, Me_3C). ^{13}C-NMR (125.8 MHz, C_6D_6): 4.2 (Me_2Si); 30.7 ($Me_3\mathit{C}$); 32.7 (Me_3C); 36.0 ($SiCH_2$). ^{29}Si-NMR (99.4 MHz, C_6D_6): 28.9. Anal. calc. for $C_7H_{17}ClSi$ (164.75): C 51.03, H 10.40; found: C 51.12, H 10.22.

Synthesis of [4-(1,3-Dioxolan-2-yl)but-1-en-2-yl](dimethyl)(2,2-dimethylpropyl)silane (**19**). A 1.6M soln. of ^{t}BuLi in pentane (24.2 ml, 38.7 mmol of ^{t}BuLi) was added dropwise at −78° within 20 min to a stirred soln. of **17** (4.00 g, 19.3 mmol) in THF (100 ml). The resulting mixture was stirred at this temp. for 1 h and was then allowed to warm to 20° within 30 min. Subsequently, a soln. of **18** (3.18 g, 19.3 mmol) in THF (15 ml) was added dropwise to the mixture at −78° during 15 min, and the resulting mixture was stirred at this temp. for 1 h. The mixture was then allowed to warm to 20° within 1 h and was stirred at this temp. for 17 h. H_2O (100 ml) was added to the mixture, the org. phase was separated, the aq. phase was extracted with Et_2O (3 × 100 ml) and discarded, and the combined org. solns. were dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by FC (SiO_2; hexane/AcOEt 85:15) to furnish **19** (3.70 g, 14.4 mmol, 75%). Colorless liquid. ^{1}H-NMR (500.1 MHz, C_6D_6): 0.29 (*s*, Me_2Si); 0.89 (*s*, $SiCH_2$); 1.10 (*s*, Me_3C); 2.11 ($\delta_{AA'}$); 2.58 ($\delta_{DD'}$); 4.99 (δ_M); 5.53 (δ_X); 5.78 (δ_Y) (*AA'DD'MXY* system, $^2J_{A,A'} = 14.1$, $^2J_{D,D'} = 15.7$, $^2J_{X,Y} = 2.7$, $^3J_{A,D} = {}^3J_{A',D'} = 5.1$, $^3J_{A,D'} = {}^3J_{A',D} = 11.3$, $^3J_{A,M} = {}^3J_{A',M} = 4.8$, $^4J_{D,X} = {}^4J_{D',X} = 1.2$, $^4J_{D,Y} = {}^4J_{D',Y} = 1.7$, 7 H; $C(=CH_XH_Y)CH_DH_{D'}CH_AH_{A'}CH_M$); 3.50 ($\delta_{AA'}$); 3.67 ($\delta_{BB'}$) (*AA'BB'* system, $^2J_{A,B} = {}^2J_{A',B'} = 7.7$, $^3J_{A,A'} = 6.9$, $^3J_{A,B'} = {}^3J_{A',B} = 6.1$, $^3J_{B,B'} = 7.4$, 4 H; $OCH_AH_BCH_{A'}H_{B'}O$). ^{13}C-NMR (125.8 MHz, C_6D_6): −0.76 (Me_2Si); 30.0 ($\mathit{C}H_2CH_2CH$); 31.2 ($Me_3\mathit{C}$); 32.1 ($Si\mathit{C}H_2$); 33.0 (Me_3C); 33.8 ($CH_2\mathit{C}H_2CH$); 64.8 ($O\mathit{C}H_2\mathit{C}H_2O$); 104.5 ($CH_2CH_2\mathit{C}H$); 124.3 ($C{=}\mathit{C}H_2$); 151.9 ($\mathit{C}{=}CH_2$). ^{29}Si-NMR (99.4 MHz, C_6D_6): −6.1. Anal. calc. for $C_{14}H_{28}O_2Si$ (256.46): C 65.57, H 11.00; found: C 65.23, H 10.86.

Olfactory Evaluation. Compounds **1a**, **1b**, and **2**–**6** were olfactorily evaluated on smelling blotters by a panel of at least two expert perfumers as 10% solns. in dipropylene glycol (DPG) and in EtOH, resp. The blotters were dipped 4 and 8 h in advance and compared with the freshly dipped samples for top, middle, and dry-down odor character. The compounds investigated proved to be olfactorily pure and linear in their evaporation profile.

The detection odor th values were determined by 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 panelists smelled in blind and pressed a button upon perceiving an odor. If the recorded time matched the retention time (t_R), the sample was further diluted. The last concentration detected at the correct t_R is the individual odor th. The reported th values are the geometrical means of the individual odor th values of at least three different panelists.

REFERENCES

[1] K. J. Rossiter, *Chem. Rev.* **1996**, *96*, 3201.

[2] G. Ohloff, W. Pickenhagen, P. Kraft, 'Scent and Chemistry – The Molecular World of Odors', Verlag Helvetica Chimica Acta, Zürich, and Wiley–VCH, Weinheim, 2012, pp. 105, and references cited therein.

[3] M. Schröder, M. Mathys, N. Ehrensperger, M. Büchel, *Chem. Biodiversity* **2014**, *11*, 1651.

[4] R. Pelzer, U. Harder, A. Krempel, H. Sommer, H. Surburg, P. Hoever, in 'Recent Developments in Flavor and Fragrance Chemistry – Proceedings of the 3rd International Haarmann & Reimer Symposium', Eds. R. Hopp, K. Mori, VCH Verlagsgesellschaft mbH, Weinheim, **1993**, p. 29.

[5] R. Tacke, S. Metz, *Chem. Biodiversity* **2008**, *5*, 920.

[6] a) R. Tacke, T. Schmid, C. Burschka, M. Penka, H. Surburg, *Organometallics* **2002**, *21*, 113; b) R. Tacke, T. Schmid, M. Hofmann, T. Tolasch, W. Francke, *Organometallics* **2003**, *22*, 370; c) T. Schmid, J. O. Daiss, R. Ilg, H. Surburg, R. Tacke, *Organometallics* **2003**, *22*, 4343; d) M. W. Büttner, M. Penka, L. Doszczak, P. Kraft, R. Tacke, *Organometallics* **2007**, *26*, 1295; e) L. Doszczak, P. Kraft, H.-P. Weber, R. Bertermann, A. Triller, H. Hatt, R. Tacke, *Angew. Chem.* **2007**, *119*, 3431; f) L. Doszczak, P. Kraft, H.-P. Weber, R. Bertermann, A. Triller, H. Hatt, R. Tacke, *Angew. Chem., Int. Ed.* **2007**, *46*, 3367; g) M. W. Büttner, S. Metz, P. Kraft, R. Tacke, *Organometallics* **2007**, *26*, 3925; h) M. W. Büttner, C. Burschka, K. Junold, P. Kraft, R. Tacke, *ChemBioChem* **2007**, *8*, 1447; i) S.

Metz, J. B. Nätscher, C. Burschka, K. Götz, M. Kaupp, P. Kraft, R. Tacke, *Organometallics* **2009**, *28*, 4700; j) J. B. Nätscher, N. Laskowski, P. Kraft, R. Tacke, *ChemBioChem* **2010**, *11*, 315; k) A. Sunderkötter, S. Lorenzen, R. Tacke, P. Kraft, *Chem. – Eur. J.* **2010**, *16*, 7404; l) J. B. G. Gluyas, C. Burschka, P. Kraft, R. Tacke, *Organometallics* **2010**, *29*, 5897; m) M. Geyer, J. Bauer, C. Burschka, P. Kraft, R. Tacke, *Eur. J. Inorg. Chem.* **2011**, 2769; n) S. Dörrich, J. B. Bauer, S. Lorenzen, C. Mahler, S. Schweeberg, C. Burschka, J. A. Baus, R. Tacke, P. Kraft, *Chem. – Eur. J.* **2013**, *19*, 11396; o) B. Förster, R. Bertermann, P. Kraft, R. Tacke, *Organometallics* **2014**, *33*, 338; p) J. Friedrich, S. Dörrich, A. Berkefeld, P. Kraft, R. Tacke, *Organometallics* **2014**, *33*, 796; q) S. Dörrich, A. Ulmer, C. Mahler, C. Burschka, J. A. Baus, R. Tacke, A. Chai, C. Ding, Y. Zou, G. Brunner, A. Goeke, P. Kraft, *J. Inorg. Chem.* **2014**, 4394.

[7] WIN-DAISY 4.05, *Bruker-Franzen GmbH*, Bremen, Germany, 1998; U. Weber, A. Germanus, H. Thiele, *Fresenius' J. Anal. Chem.* **1997**, *359*, 46.

[8] B. C. Abele, *Wacker-Chemie GmbH*, DE 10041597 C1, September 6, 2001.

[9] E. W. Thomas, *J. Org. Chem.* **1986**, *51*, 2184.

[10] W. A. Kinney, M. J. Coghlan, L. A. Paquette, *J. Am. Chem. Soc.* **1985**, *107*, 7352.

[11] H. Morrison, D. Giacherio, *J. Chem. Soc.*, *Chem. Commun.* **1980**, 1080; L. Clawson, S. L. Buchwald, R. H. Grubbs, *Tetrahedron Lett.* **1984**, *25*, 5733; J. Hibino, T. Okazoe, K. Takai, H. Nozaki, *Tetrahedron Lett.* **1985**, *26*, 5579; C. R. Johnson, B. D. Tait, *J. Org. Chem.* **1987**, *52*, 281; G. Z. Wu, F. Lamaty, E. Negishi, *J. Org. Chem.* **1989**, *54*, 2507; S. Matsubara, M. Sugihara, K. Utimoto, *Synlett* **1998**, 313; S. Matsubara, T. Mizuno, T. Otake, M. Kobata, K. Utimoto, K. Takai, *Synlett* **1998**, 1369; T.-H. Yan, C.-C. Tsai, C.-T. Chien, C.-C. Cho, P.-C. Huang, *Org. Lett.* **2004**, *6*, 4961; M. Sada, S. Komagawa, M. Uchiyama, M. Kobata, T. Mizuno, K. Utimoto, K. Oshima, S. Matsubara, *J. Am. Chem. Soc.* **2010**, *132*, 17452.

[12] S. Dörrich, L. Gelis, S. Wolf, A. Sunderkötter, C. Mahler, E. Guschina, R. Tacke, H. Hatt, P. Kraft, *ChemPlusChem* **2014**, DOI: 10.1002/cplu.201402160.

[13] a) A. I. Meyers, J. L. Durandetta, *J. Org. Chem.* **1975**, *40*, 2021; b) S. A. Kozmin, *Org. Lett.* **2001**, *3*, 755; c) A. J. Barlow, B. J. Compton, R. T. Weavers, *J. Org. Chem.* **2005**, *70*, 2470; d) M.-Y. Lei, Y.-J. Xiao, W.-M. Liu, K. Fukamizu, S. Chiba, K. Ando, K. Narasaka, *Tetrahedron* **2009**, *65*, 6888.

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