γ-Unsaturated Aldehydes as Potential *Lilial* Replacers

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A series of *Claisen* rearrangements was undertaken in order to find a replacement for *Lilial* (= 3-(4-(*tert*-butyl)phenyl)-2-methylpropanal), a high-tonnage perfumery ingredient with a lily-of-the-valley odour, which is a CMR2 material [1]. 5,7,7-Trimethyl-4-methyleneoctanal (**10**), the synthesis of which is described, became the main lead. It possesses an odour which is very close to that of *Lilial* but lacks its substantivity. Aldehydes with higher molecular weights than that of **10** were, therefore, synthesised in order to boost substantivity and to understand the structural requirements for a '*Lilial*' odour. The aldehydes were obtained *via Claisen* rearrangements of 'exo-methylidene' vinyl ethers, allenyl vinyl ethers, or allenyl allyl ethers. Alternatively, coupling of terminal alkynes with allyl alcohols led to the desired aldehydes. Derivatives of **10** and their sila analogues were also synthesised. The olfactory properties of all synthesised molecules were evaluated for possible structure–odour relationships (SOR).

Introduction. – *Lilial* (= 3-(4-(*tert*-butyl)phenyl)-2-methylpropanal) is a high-tonnage, low-cost perfumery ingredient with a lily-of-the-valley odour. It is mainly used in home and personal care, where it is appreciated for its relatively low odour threshold of 0.45 ng/l, and its bloom and tenacity. Recent studies have shown that *Lilial* may cause harm to the unborn child, which resulted in its classification as a CMR2 material [1]; restricting its usage. It became, therefore, necessary to search for replacement odorants. When choosing possible target molecules, one should bear in mind that not *Lilial* itself, but *tert*-butylbenzoic acid, an intermediate of the biodegradation process of *Lilial*, is responsible for the adverse effects observed in dogs and rats. Substituted aromatic aldehydes, which will generate similar degradation products as *Lilial*, should, therefore, not be considered as possible *Lilial* replacement. Modelling experiments undertaken by *Pelzer et al.* [2] showed that γ,δ-unsaturated carbonyl compounds, and certain secondary and tertiary alcohols are likely to have floral odours. The synthesis of γ,δ-unsaturated aldehydes was given priority in this context, since the odour thresholds of aldehydes tend to be lower than those of the corresponding alcohols or ketones. A convenient route to this type of aldehydes is the *Saucy–Marbet* variation of the *Claisen* rearrangement, in which allyl vinyl ethers undergo thermally induced [3,3] sigmatropic rearrangements, resulting in γ,δ-unsaturated aldehydes.

The synthesis of a number of γ,δ-unsaturated aldehydes *via Saucy–Marbet* rearrangement will be described herein, together with the discussion of their odour profiles in relation to their structural properties.

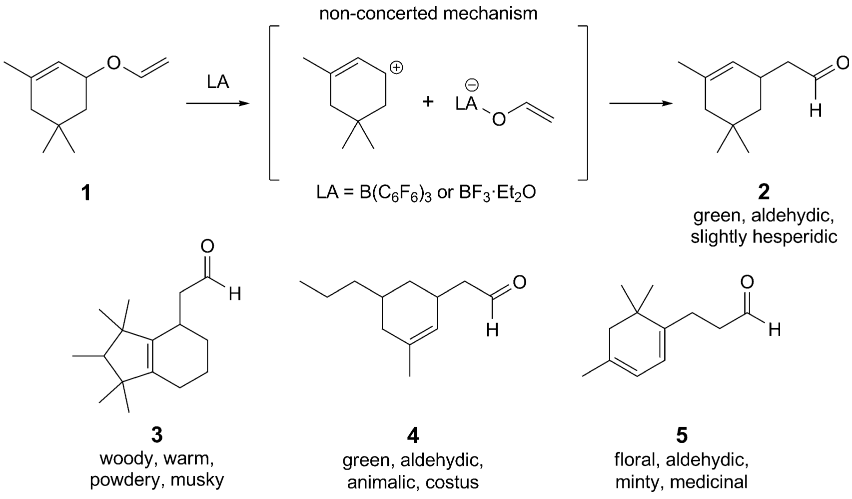
Results and Discussion. – *Gansäuer et al.* [3][4] reported an interesting rearrangement of allyl vinyl ethers, which proceeds *via* a non-concerted mechanism catalysed by a *Lewis* acid (*Scheme 1*). We synthesised a series of aldehydes, **2**–**5**, unfortunately, none of which possessed the desired lily-of-the-valley note. In our hands, the scope of this reaction proved to be limited, since the competing [3,3] *Claisen* rearrangement became the main pathway, if the allylic double bond was not at least trisubstituted.

A series of γ,δ-unsaturated aldehydes, **10**–**27**, was synthesised *via* [3,3] sigmatropic *Saucy–Marbet* rearrangement (*Scheme 2*). The intermediate allyl vinyl ethers were obtained from readily available unsaturated alcohols or ketones. This allowed us to obtain aldehydes of wide structural variety. The majority of these aldehydes had green, aldehydic odours with one notable exception, 5,7,7-trimethyl-4-methyleneoctanal (**10**), which is very difficult to distinguish from *Lilial* on a fresh smelling strip; it became, therefore, an important lead. Aldehyde **10** was obtained from isononyl aldehyde (**6**) *via Mannich* reaction, reduction of '*exo*-methylidene' aldehyde **7**, and heating the vinyl ether **8** obtained from **7**.

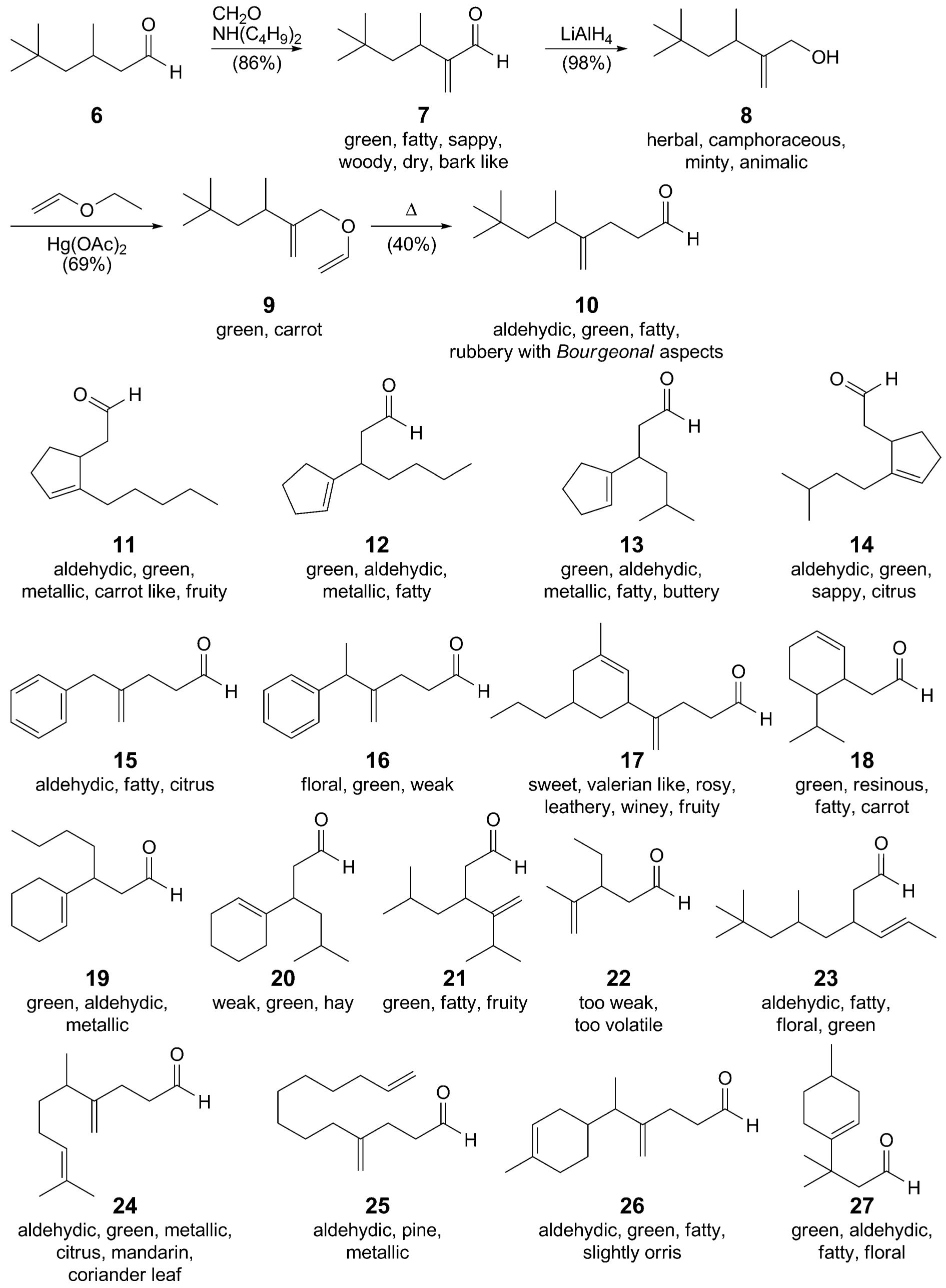
Five analogues, **28**–**32**, of **10** were synthesised to better understand the structural requirements for a lily-of-the-valley odour (*Fig. 1*). Variation was introduced at the pent-4-enal moiety of **10**, while its 4,4-dimethylpentan-2-yl moiety was left untouched. A change of the odour characteristics of **10** was expected when the C=C bond is hydrogenated, but it came as a surprise that an additional Me group in α-position to the C=C group or further substitution of the '*exo*-methylidene' group led to drastic changes of odour properties. It appeared that the pent-4-enal moiety is important for the lily-of-the-valley odour of **10** and should, therefore, be retained in future target molecules.

While the odour of **10** is an excellent match for *Lilial* when fresh, it lacks the substantivity. Since the substantivity is linked to the vapour pressure of a substance, lowering the former will result in an increased substantivity. This can be achieved by increasing the molecular weight of the target molecules. The introduction of further

Scheme 1. Lewis *Acid* (LA)-*Catalysed [1,3] Rearrangement of Allyl Vinyl Ethers*



Scheme 2. *Aldehydes* via Saucy–Marbet *Rearrangement*



6

7 green, fatty, sappy, woody, dry, bark like

8 herbal, camphoraceous, minty, animalic

9 green, carrot

10 aldehydic, green, fatty, rubbery with *Bourgeonal* aspects

11 aldehydic, green, metallic, carrot like, fruity

12 green, aldehydic, metallic, fatty

13 green, aldehydic, metallic, fatty, buttery

14 aldehydic, green, sappy, citrus

15 aldehydic, fatty, citrus

16 floral, green, weak

17 sweet, valerian like, rosy, leathery, winey, fruity

18 green, resinous, fatty, carrot

19 green, aldehydic, metallic

20 weak, green, hay

21 green, fatty, fruity

22 too weak, too volatile

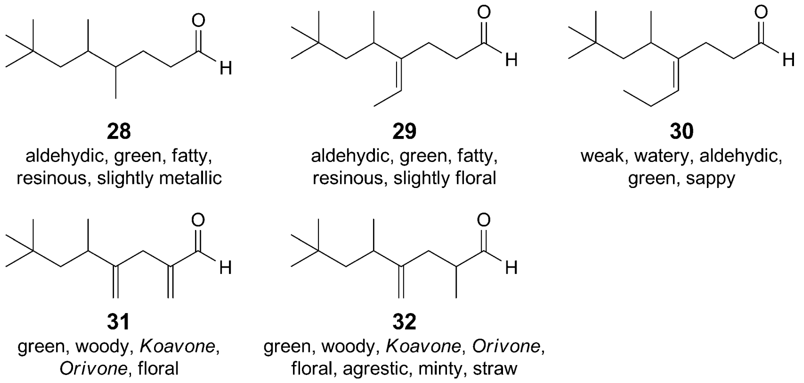
23 aldehydic, fatty, floral, green

24 aldehydic, green, metallic, citrus, mandarin, coriander leaf

25 aldehydic, pine, metallic

26 aldehydic, green, fatty, slightly orris

27 green, aldehydic, fatty, floral



28
aldehydic, green, fatty, resinous, slightly metallic

29
aldehydic, green, fatty, resinous, slightly floral

30
weak, watery, aldehydic, green, sappy

31
green, woody, *Koavone*, *Orivone*, floral

32
green, woody, *Koavone*, *Orivone*, floral, agrestic, minty, straw

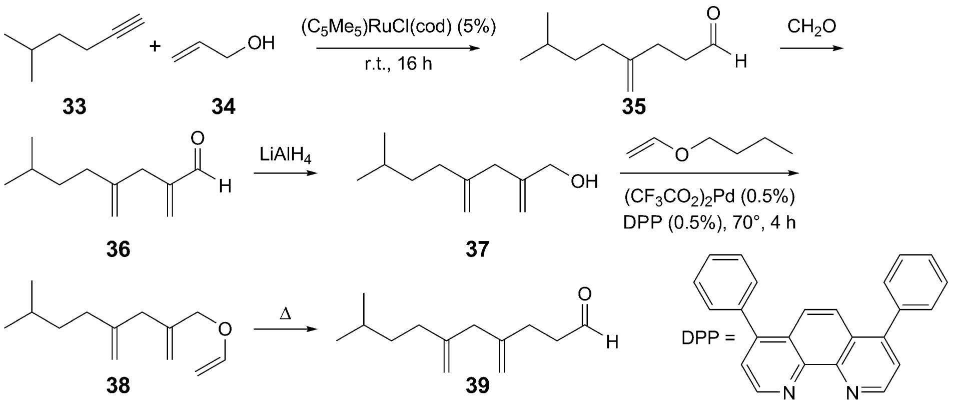
Fig. 1. *Analogues of 5,7,7-trimethyl-4-methylideneoctanal* (**10**)

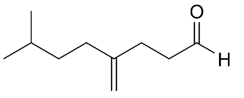
unsaturation should be beneficial for substantivity and odour threshold as well. *Dixneuf* and co-workers. reported the Ru-catalysed coupling of terminal alkynes with allylic alcohols, resulting in 'γ-*exo*-methylidene' aldehydes [5][6]. The 'γ-*exo*-methylidene' aldehydes **35**, **40**, **43**, and **47** were synthesised by applying *Dixneuf*'s procedure to commercially available alkynes (*Scheme 3*). The aldehydes **40**, **42** and **43** were employed in the synthetic route outlined in *Scheme 3* to giving the 'γ,ε-di-*exo*-methylidene' aldehydes **39**, **46**, and **47**. The vinyl ether used in this synthetic sequence was prepared from butyl vinyl ether, catalysed by 4,7-diphenyl-1,10-phenanthroline (DPP) and palladium trifluoroacetate [7], which reduces the reaction time and the quantity of vinyl ether engaged. None of the aldehydes synthesised in this context possessed predominately floral notes. They were mostly described as green, aldehydic with fruity, often agrestic notes.

A second series of conjugated '*exo*-methylidene' aldehydes was synthesised from cyclic ketones (*Scheme 4*), which were treated with EtMgBr to give the corresponding ethynyl alcohols **49**. These were dehydrated before being coupled with allyl alcohol. The direct coupling of **49** led to mixed acetals **53** as described by *Dixneuf* and co-workers. [8]. The γ-unsaturated aldehydes **51** and **54**–**59** synthesised by this route were described as green, aldehydic and fruity. Only aldehyde **51** possessed floral notes.

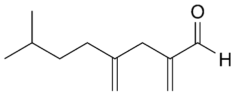
A series of 'β-*exo*-methylidene' aldehydes was synthesised in order to examine the influence of the distance between '*exo*-methylidene' and aldehyde group on the overall odour. These 'β-*exo*-methylidene' aldehydes could conveniently be obtained *via* Au-catalysed *Claisen* rearrangement of allenyl vinyl ether as described by *Krafft et al.* [9] (*Scheme 5*). The vinyl ethers of type **64** in this synthetic sequence were prepared from ethyl vinyl ethers at room temperature. The allenyl vinyl ethers were too unstable to support the higher temperatures used in the Pd-catalysed vinylation mentioned above. Some ethers already partially underwent *Claisen* rearrangement at room temperature in absence of the Au-catalyst. The odours of the 'β-*exo*-methylidene' aldehydes belonged to the same family as similar 'γ-*exo*-methylidene' aldehydes. They were also green and aldehydic, but had more pronounced agrestic notes like mandarin, orange or citrus. This is probably due the fact that they are long-chain aldehydes such as undecanal or dodec-2-enal, which have agrestic odours.

Scheme 3. *Di-*exo*-methylidene Aldehydes from Commercially Available Alkynes*

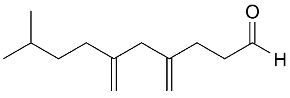




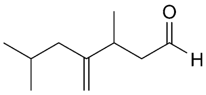
35
green, resinous, fir, citrus,
orange, parsley leaf, pineapple



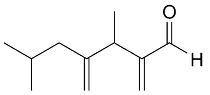
36
fruity, aldehydic, green



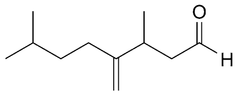
39
aldehydic, fatty,
straw like, metallic



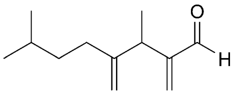
40
aldehydic, citrus, sweaty,
fruity, swimming pool



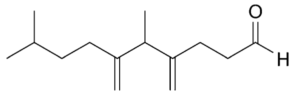
41
minty, agrestic, aldehydic,
green, metallic



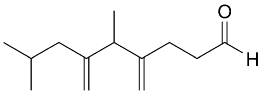
42
fruity, orange, metallic,
sweet, floral, rubbery



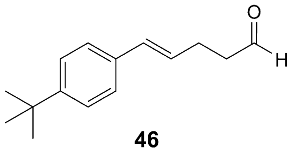
43
green, metallic, slightly
fruity, slightly floral



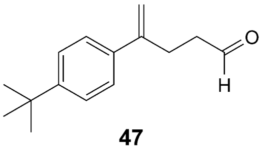
44
aldehydic, metallic,
mandarin, coriander



45
aldehydic, green,
slightly fatty, floral



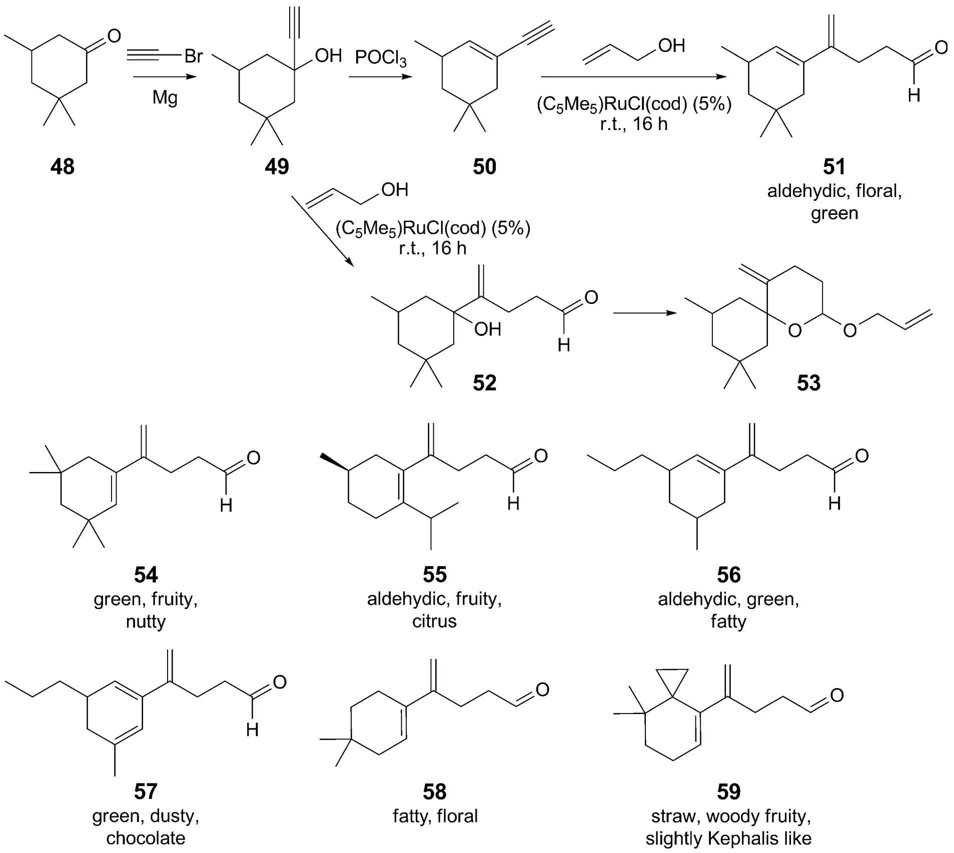
46
aldehydic, green, fatty,
citrus, orange, coriander



47
aldehydic, green,
floral, fatty, weak

The *Claisen* rearrangement of allenyl allyl ethers [10] would also lead to 'γ-methylidene' aldehydes as outlined in *Scheme 6*. While the alkynyl allyl ethers **73** were obtained in good yield, the allenyl allyl ethers **74** turned out to be unstable under the conditions employed for the rearrangement. The treatment of only two ethers led to a product. Allenyl allyl ether (**79**) reacted in an intramolecular *Diels–Alder* reaction to afford the tricyclic dihydroisobenzofuran **80** during the attempted synthesis of its

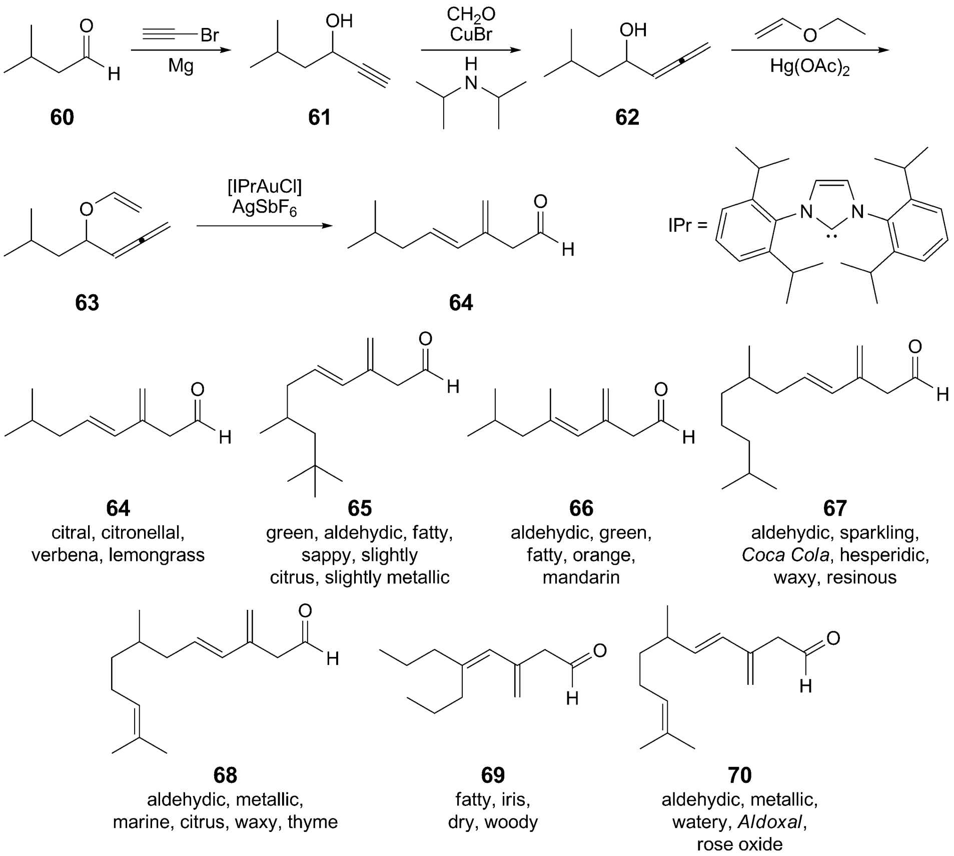
Scheme 4. *The Coupling of Allyl Alcohols with Alkynes* (conjugated '*exo*-methylidene' aldehydes from ketones)



allenyl allyl ether **74**.The only other allenyl allyl ether, which did not decompose under rearrangement conditions, was **81**, undergoing an ene-reaction to form hexahydrobenzofuran **82**.

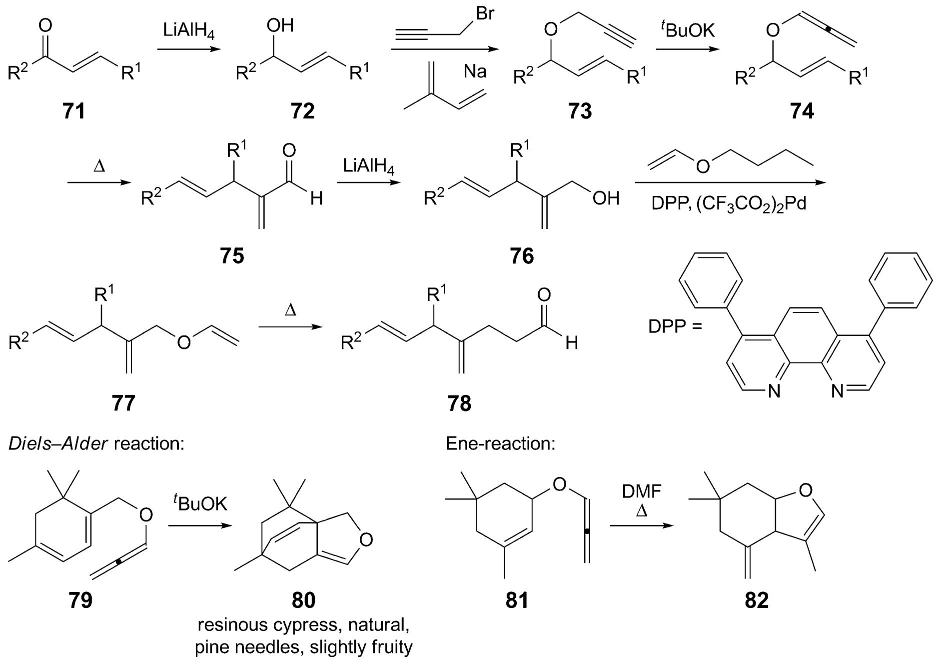
The molecular weight and, therefore, the substantivity of a compound can be increased by replacing one or more quaternary C-atoms with Si-atom(s). Aldehyde **10** is a perfect candidate for this approach, since it has a quaternary C-atom in its ^{t}Bu tail. *Tacke* and co-workers synthesised the sila analogues of **10** and its derivatives [11] (*Fig. 2*), and their odour thresholds and properties were compared with those of C-analogues. The introduction of the Si-atom improved the substantivity of the molecules without changing their odour properties significantly. The sila analogues had lower odour thresholds with the exception of pair **10**/**83**, where the odour threshold of the Si analogue is nearly twice as high. The aldehyde function, as expected, was essential for the lily-of-the-valley note of **10**. This note was missing in the corresponding alcohols and ketones, *i.e.*, **85**, **87**, and **89**.

Scheme 5. *The* Claisen *Rearrangement of Allenyl Vinyl Ethers* (conjugated '*β*-*exo*-methylidene' aldehydes from ketones)



Conclusions. – A series of *γ*-unsaturated aldehydes was synthesised and their odours were evaluated. Most aldehydes were described as green, aldehydic, often with fruity, agrestic notes, in contrast to *Pelzer*'s postulate [2] that *γ*-unsaturated aldehydes are likely to have floral odours. 5,7,7-Trimethyl-4-methyleneoctanal (**10**) was the only aldehyde with the typical lily-of-the-valley note of *Lilial*. Even small variations of its structure result in strong changes in odour. The presence of a short alkane chain in *α*- or *β*-position, or moving the '*exo*-methylidene' group into *β*-position shifts the odours of the resulting aldehydes towards fruity or agrestic notes. Aldehydes, the C(*γ*)=C(*δ*) bond is part of a six- or five-membered ring, are described as green and aldehydic, while aldehydes with open-chain C=C bonds retain their floral notes, but loose intensity quickly. Introducing Si into the skeleton of **10** and its derivatives does not change the odour characteristics dramatically, but lowers the odour intensity significantly. Keeping the pent-4-enal moiety and introducing variation only at C(4) does not lead to a distinct odour class. It can be concluded that the

Scheme 6. *Aldehyes* via Claisen *Rearrangement of Allenyl Allyl Ethers*



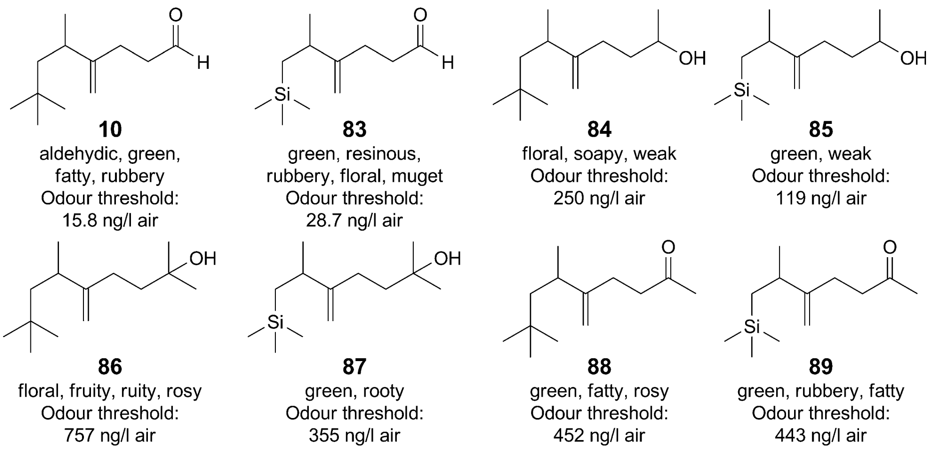


Fig. 2. *Sila analogues of 5,7,7-trimethyl-4-methylideneoctanal* (**10**) *and its derivatives*

pentenal skeleton is too flexible to interact very selectively with particular odour receptors. It is, therefore, not possible to predict the structural requirements for a floral, *Lilial*-like odour.

Experimental Part

General. Reagents and solvents were purchased from *Sigma–Aldrich* and were used without further purification. Moisture-sensitive reactions were conducted in oven-dried glassware under inert atmosphere. Flash chromatography (FC): *Isco Combi Flash RF* with silica cartridges; *Thermo Finnigan Trace GC*; *Supelco SPB-1*; (15 m × 0.53 mm × 1.5 μm) with He as carrier gas. ^{1}H- and ^{13}C-NMR spectra: *Bruker AVANCE DPX-400* spectrometer, δ in ppm rel. to $\mathrm{Me_4Si}$, J in Hz. GC/MS: *Hewlett-Packard MS 5973* instrument, rel. intensities in % of the base peak. HR-EI-MS: *Finnigan MAT 95* (EI: 70 eV). Olfactory evaluation: 10% soln. in dipropylene glycol (DPG) by two expert perfumers. GC–Threshold determination: different dilutions of the samples substances were injected into a gas chromatograph in descending order of concentration, until the panellist failed to detect the respective substance at the sniffing port. The panellists smelled in blind, and pressed a button upon perceiving an odour. 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 odour threshold. The reported threshold values are the geometrical means of the individual odour thresholds of six different panellists.

(3,5,5-Trimethylcyclohex-2-en-1-yl)acetaldehyde (**2**). *3-(Ethenyloxy)-1,5,5-trimethylcyclohexene* (**1**; 5.0 g, 30 mmol) was dissolved in $\mathrm{CH_2Cl_2}$ and cooled to 5°. One drop of $\mathrm{BF_3 \cdot Et_2O}$ was added. The mixture was stirred at 5° for 16 h. The mixture was taken up in $\mathrm{CH_2Cl_2}$ (100 ml), washed with $\mathrm{H_2O}$ (3 × 100 ml), and dried ($\mathrm{MgSO_4}$). The soln. was filtered, and the solvent was evaporated under reduced pressure. The crude product was subjected to bulb-to-bulb distillation (130°/0.1 mbar) and further purified *via* CC to yield 1.17 g (6 mmol) of a colorless liquid (purity: 90%; yield: 21%). ^{1}H-NMR (400 MHz, $\mathrm{CDCl_3}$): 0.90 (*s*, Me(5′)); 0.95–0.99 (*m*, $\mathrm{H_a}$–C(6′)); 0.97 (*s*, Me(5′)); 1.44–1.50 (*m*, $\mathrm{H_b}$–C(6′)); 1.59 (br. *d*, $J=17.4$, $\mathrm{H_a}$–C(4′)); 1.65 (*s*, Me(3′)); 1.82 (br. *d*, $J=17.4$, $\mathrm{H_b}$–C(4′)); 2.35 (*ddd*, $J=2.3$, 7.7, 16.4, $\mathrm{CH_2}$(2)); 2.42 (*ddd*, $J=2.3$, 6.8, 16.4, H–C(1′)); 5.20 (br. *s*, H–C(2′)); 9.80 (*dd*, $J=2.3$, 2.3, H–C(1)). ^{13}C-NMR (400 MHz, $\mathrm{CDCl_3}$): 24.2 (*q*, *Me*–C(3)); 25.7 (*q*, *Me*–C(5)); 29.3 (*d*, C(1′)); 30.4 (*s*, C(5′)); 32.1 (*q*, *Me*–C(5)); 42.8 (*t*, C(6′)); 50.7 (*t*, C(4′)); 50.7 (*t*, C(2)); 122.8 (*d*, C(2′)); 134.9 (*s*, C(3′)); 203.2 (*s*, C(1)). EI-MS (70 eV): 166 (31, M^{+}), 151 (33), 123 (52), 122 (54), 107 (100), 91 (35), 95 (43), 81 (70), 67 (36), 41 (28). Odor: green, aldehydic, slightly hesperidic.

*(2,3,4,5,6,7-Hexahydro-1,1,2,3,3-pentamethyl-1*H*-inden-4-yl)acetaldehyde* (**3**). From 4-(ethenyloxy)-2,3,4,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-1*H*-indene as described for **2**. Yield: 38% (two isomers, A and B). ^{1}H-NMR (400 MHz, $\mathrm{CDCl_3}$): 0.84 (*d*, $J=6.6$, Me–C(2) (A)); 0.87 (*d*, $J=5.8$, Me–C(2) (B)); 0.83, 0.92, 0.94, 1.01 (4*s*, $\mathrm{Me_2}$C(1), $\mathrm{Me_2}$C(3) (A)); 0.83, 0.86, 0.95, 1.00 (4*s*, $\mathrm{Me_2}$C(1), $\mathrm{Me_2}$C(3) (B)); 1.47–1.69 (*m*, H–C(2), $\mathrm{CH_2}$(4), $\mathrm{CH_2}$(5), $\mathrm{CH_2}$(6) (A and B)); 2.45 (*ddd*, $J=3.0$, 10.1, 16.7, $\mathrm{H_a}$–C(2′) (A)); 2.52 (*ddd*, $J=2.8$, 10.1, 17.2, $\mathrm{H_a}$–C(2′) (B)); 2.60–2.69 (*m*, $\mathrm{H_b}$–C(2′) (A and B)); 2.75–2.81 (*m*, H–C(7) (B)); 2.84–2.90 (*m*, H–C(7) (A)); 9.78–9.80 (*m*, H–C(1), (A + B)). ^{13}C-NMR (400 MHz, $\mathrm{CDCl_3}$): isomer A: 8.8 (*q*, *Me*–C(2)); 22.3, 24.4, 27.4, 28.1 (4*s*, *Me*$_2$C(1), *Me*$_2$C(3)); 19.0 (*t*, C(6)); 22.0 (*t*, C(7)); 28.1 (*d*, C(4)); 46.4 (*s*, C(3)); 46.8 (*s*, C(1)); 48.8 (*t*, C(2′)); 54.7 (*d*, C(2)); 140.9 (*s*, C(7a)); 143.0 (*s*, C(3a)); 203.4 (*d*, C(1′)). ^{13}C-NMR (400 MHz, $\mathrm{CDCl_3}$): isomer B: 8.5 (*q*, *Me*–C(2)); 21.9, 22.9, 28.4, 28.9 (4*s*, *Me*$_2$C(1), *Me*$_2$C(3)); 18.0 (*t*, C(6)); 21.5 (*t*, C(7)); 28.4 (*d*, C(4)); 46.4 (*s*, C(3)); 47.9 (*s*, C(1)); 48.9 (*t*, C(2′)); 53.2 (*d*, C(2)); 140.9 (*s*, C(7a)); 144.1 (*s*, C(3a)); 203.2 (*d*, C(1′)). EI-MS (70 eV): isomer A: 234 (11, M^{+}), 219 (51, $[M-15]^{+}$), 190 (66), 175 (100), 133 (17), 119 (25), 105 (32), 91 (26), 79 (15), 55 (19). EI-MS (70 eV): isomer B: 234 (9, M^{+}), 219 (36, $[M-15]^{+}$), 190 (54), 175 (100), 133 (14), 119 (18), 105 (22), 91 (21), 79 (10), 55 (15). Odor: woody, warm, powdery, musky.

(3-Methyl-5-propylcyclohex-2-en-1-yl)acetaldehyde (**4**). From ethenyl 3-methyl-5-propylcyclohex-2-en-1-yl ether as described for **2**. Yield: 50%. ^{1}H-NMR (400 MHz, $\mathrm{CDCl_3}$): 0.89 (*t*, $J=7.3$, Me(9′)); 1.20–1.45 (*m*, $\mathrm{CH_2}$(6′), $\mathrm{CH_2}$(7′), $\mathrm{CH_2}$(8′)); 1.53–1.67 (*m*, $\mathrm{H_a}$–C(4), H–C(5)); 1.64 (*s*, Me–C(3′)); 1.94–2.01 (*m*, $\mathrm{H_b}$–C(4)); 2.38 (*ddd*, $J=2.0$, 7.0, 16.8, $\mathrm{H_a}$–C(2)); 2.44 (*ddd*, $J=2.0$, 6.7, 16.8, $\mathrm{H_b}$–C(2)); 2.69–2.71 (*m*, H–C(1′)); 5.28–5.32 (*m*, H–C(2′)); 9.78 (*dd*, $J=2.0$, 2.0, H–C(1)). ^{13}C-NMR (400 MHz, $\mathrm{CDCl_3}$): 14.2 (*q*, C(9′)); 20.1 (*t*, C(8′)); 23.8 (*q*, *Me*–C(3)); 28.8 (*d*, C(5′)); 29.6 (*d*, C(1′)); 33.6 (*t*, C(6′)); 36.5 (*t*, C(4′)); 38.0 (*t*, C(7′)); 50.1 (*t*, C(2)); 123.2 (*d*, C(2′)); 135.0 (*s*, C(3′)); 202.7 (*d*, C(1)). EI-MS (70 eV): 180 (25, M^{+}), 137 (58), 135 (35), 95 (75), 93 (100), 91 (38), 81 (91), 67 (38), 55 (38), 41 (35). Odor: Green, aldehydic, animalic, costus.

3-(4,6,6-Trimethylcyclohexa-1,3-dien-1-yl)propanal (**5**). From 4-[(ethenyloxy)methyl]-1,5,5-trimethylcyclohexa-1,3-diene as described for **2**. Yield: 90%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.99 (*s*, Me$_2$C(6′)); 1.09 (br. *s*, Me–C(4′)); 1.96 (br. *s*, CH$_2$(5′)); 2.40 (br. *t*, $J=7.6$, CH$_2$(3)); 2.60 (*dt*, $J=1.8$, 7.6, CH$_2$(2)); 5.44–5.47 (*m*, H–C(2′)); 5.58–5.62 (*m*, H–C(3′)); 9.79 (*t*, $J=1.8$, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 23.6 (*q*, *Me*–C(4)); 23.6 (*t*, C(3)); 26.2 (*q*, *Me*$_2$C(6)); 34.9 (*s*, C(6′)); 42.2 (*t*, C(2)); 45.6 (*t*, C(5′)); 118.6 (*d*, C(3′)); 118.8 (*d*, C(2′)); 134.1 (*s*, C(4′)); 141.9 (*s*, C(1′)); 202.9 (*d*, C(1)). EI-MS (70 eV): 178 (22, M^+), 121 (23), 120 (16), 119 (100), 107 (8), 105 (15), 91 (15), 79 (7), 77 (9), 41 (7). Odor: floral, aldehydic, minty, medicinal.

3,5,5-Trimethyl-2-methylidenehexanal (**7**). *3,5,5-Trimethylhexanal* (**6**; 25.7 g, 181 mmol) was added to HCHO at 36% in H$_2$O (21.5 g, 258 mmol). The emulsion was heated to reflux (110°) under vigorous stirring. Bu$_2$NH (1.3 g, 10 mmol) was added, and stirring was continued for further 2 h. The mixture was cooled to r.t. and diluted with 200 ml of ^{t}BuOMe. The layers were separated, and the org. layer was dried (MgSO$_4$) and filtered. The solvent was removed under reduced pressure. The crude product was subjected to bulb-to-bulb distillation (90°/10 mbar) to yield 24.0 g (156 mmol) of a colorless liquid (yield: 86%). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.88 (*s*, *Me*$_3$C(5)); 1.08 (*d*, $J=6.8$, Me–C(3)); 1.31 (*dd*, $J=5.1$, 13.9, H$_a$–C(4)); 1.59 (*dd*, $J=6.8$, 13.9, H$_b$–C(4)); 2.85 (*ddq*, $J=5.1$, 6.8, 13.9, H–C(3)); 5.96 (*s*, 1 H of =CH$_2$)); 6.29 (*s*, 1 H of =CH$_2$)); 9.53 (*s*, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 23.7 (*q*, *Me*–C(3)); 28.3 (*d*, C(3)); 30.4 (*q*, *Me*$_3$C(5)); 31,7 (*s*, C(5)); 50.2 (*t*, C(4)); 133.6 (*t*, *C*H$_2$=*C*(2)); 158.0 (*s*, C(2)); 195.0 (*d*, C(1)). EI-MS (70 eV): 139 (30, $[M-15]^+$), 121 (37), 98 (34), 97 (54), 84 (22), 83 (30), 71 (20), 69 (22), 57 (100), 55 (36), 43 (38), 41 (48). Odour: green, fatty, sappy, woody, dry, bark like.

3,5,5-Trimethyl-2-methylidenehexan-1-ol (**8**). LiAlH$_4$ (0.8 g, 20 mmol) was placed under Ar in 100 ml of THF and cooled to 5°. Compound **7** (10.0 g, 65 mmol) was added at this temp. during 30 min. Stirring was continued for further 30 min. H$_2$O (0.8 ml), NaOH (0.8 ml; aq. soln. at 15%), and H$_2$O (2.4 ml) were added at 5°. Stirring was continued for 20 min until the grey suspension turned white. The suspension was filtered, and the solvent was evaporated under reduced pressure to yield 10.0 g (64 mmol) of a colorless liquid (yield: 98%). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.90 (br. *s*, Me$_3$C(5)); 1.08 (*d*, $J=7.1$, Me–C(3)); 1.20 (*dd*, $J=5.6$, 13.9, H$_a$–C(4)); 1.52 (*dd*, $J=5.8$, 13.9, H$_b$–C(4)); 2.3 (*m*, H–C(3)); 4.13 (br. *s*, H–C(1)); 4.91 (*m*, 1 H of =CH$_2$)); 5.00 (br. *s*, 1 H of =CH$_2$)). ^{13}C-NMR (400 MHz, CDCl$_3$): 23.7 (*q*, *Me*–C(3)); 30.3 (*q*, *Me*$_3$C(5)); 31.6 (*s*, C(5)); 34.1 (*d*, C(3)); 50.2 (*t*, C(4)); 64.7 (*t*, C(1)); 107.7 (*t*, H$_2$*C*=*C*(2)); 156.3 (*s*, C(2)). EI-MS (70 eV): 156 (1, M^+), 123 (7), 85 (9), 81 (14), 71 (16), 69 (25), 57 (100), 55 (16), 43 (35), 41 (34). Odour: herbal, camphoraceous, minty, animalic.

2-[(Ethenyloxy)methyl]-3,5,5-trimethylhex-1-ene (**9**). A mixture of ethenyl ethyl ether (69.2 g, 960 mmol), **8** (10.0 g, 64 mmol), and Hg(OAc)$_2$ (4.1 g, 12.8 mmol) was stirred at r.t. for 16 h. The mixture was washed with H$_2$O (3 × 200 ml). The aq. layers were united and extracted with ^{t}BuOMe (2 × 100 ml). The combined org. phases were dried (MgSO$_4$) and filtered. The solvent and the excess of ethenyl ethyl ether were evaporated under reduced pressure. The crude product was subjected to bulb-to-bulb distillation (130°/10 mbar) to yield 8.0 g (44 mmol) of a colorless liquid (yield: 69%). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.93 (*s*, Me$_3$C(5)); 1.12 (*d*, $J=6.8$, Me–C(3)); 1.22 (*dd*, $J=5.6$, 14.2, H$_a$–C(4)); 1.56 (*dd*, $J=5.6$, 14.2, H$_b$–C(4)); 2.23 (*m*, H–C(3)); 4.04 (*dd*, $J=2.0$, 6.8, H$_a$–C(2′)); 4.22 (br. *s*, CH$_2$(1)); 4.26 (*dd*, $J=2.0$, 14.2, H$_b$–C(2′)); 5.01 (*m*, 1 H of =CH$_2$)); 5.05 (*m*, 1 H of =CH$_2$)); 6.49 (*dd*, $J=6.8$, 14.2, H–C(1′)). ^{13}C-NMR (400 MHz, CDCl$_3$): 23.5 (*q*, C(3)); 30.3 (*q*, *Me*$_3$C(5)); 31.6 (*s*, C(5)); 34.0 (*d*, C(3)); 50.7 (*t*, C(4)); 70.4 (*t*, C(1)); 87.4 (*t*, C(2′)); 110.6 (*t*, *C*H$_2$=*C*(2)); 151.7 (*s*, C(2)); 152.1 (*d*, C(1′)). EI-MS (70 eV): 139 (2, $[M-43]^+$), 123 (7), 98 (7), 97 (6), 85 (11), 81 (11), 71 (21), 67 (21), 57 (100), 55 (20), 43 (31), 41 (36). Odour: green, carrot.

5,7,7-Trimethyl-4-methylideneoctanal (**10**). Compound **9** (1.0 g, 5.5mmol) was heated under Ar for 4 h at 160°. The crude product was cooled to r.t. and purified *via* CC to yield 0.4 g (2.2 mmol) of a colorless liquid (yield: 40%). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.91 (*s*, Me$_3$C(7)); 1.07 (*d*, $J=7.1$, Me–C(5)); 1.19 (*dd*, $J=5.3$, 14.2, H$_a$–C(6)); 1.51 (*dd*, 6.1, 14.2, H$_b$–C(6)); 2.31 (*m*, H–C(5)); 2.37 (*m*, CH$_2$(3)); 2.62 (*m*, CH$_2$(2)); 4.63 (br. *s*, 1 H of H$_2$C=C(4)); 4.87 (br. *s*, 1 H of H$_2$C=C(4)); 9.81 (*t*, $J=1.8$, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 23.4 (*q*, C(5)); 25.5 (*t*, C(3)); 30.3 (*q*, *Me*$_3$C(7)); 31.6 (*s*, C(7)); 42.4 (*t*, C(2)); 49.8 (*t*, C(6)); 108.3 (*t*, *H*$_2$*C*=*C*(4)); 154.8 (*s*, C(4)); 202.7 (*s*, C(1)). EI-MS (70 eV): 167 (1, $[M-15]^+$), 149 (2), 126 (13), 108 (31), 107 (13), 91 (24), 84 (27), 83 (19), 82 (16), 73 (18), 71 (19), 69 (14), 57 (100), 55 (38), 43 (32), 41 (39). Odour: aldehydic, green, fatty, rubbery with *Bourgeonal* aspects.

(2-Pentylcyclopent-2-en-1-yl)acetaldehyde (**11**). From 5-(ethenyloxy)-1-pentylcyclopentene as described for **10**. Yield: 70%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.91 (*t*, *J*=6.8, Me(10′)); 1.24–1.57 (*m*, H$_a$–C(5′), CH$_2$(7′), CH$_2$(8′), CH$_2$(9′)); 2.85–2.34 (*m*, H$_a$–C(2), CH$_2$(4′), H$_b$–C(5′), CH$_2$(6)); 2.63 (*ddd*, *J*=1.8, 4.0, 16.2, H$_b$–C(2)); 2.97–3.05 (*m*, H–C(1′)); 5.40–5.43 (*m*, H–C(3′)); 9.80 (*dd*, *J*=1.8, 2.5, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 14.4 (*q*, C(10′)); 22.9 (*t*, C(9′)); 27.7 (*t*, C(5′)); 29.4 (*t*, C(7′)); 30.8 (*t*, C(4′)); 31.1 (*t*, C(8′)); 32.1 (*t*, C(6′)); 41.8 (*d*, C(1′)); 48.3 (*t*, C(2)); 125.0 (*d*, C(3′)); 146.1 (*s*, C(2′)); 203.2 (*d*, C(1)). EI-MS (7 eV): 154 (7), 97 (14), 85 (6), 84 (100), 83 (23), 69 (6), 56 (10), 55 (20), 41 (17), 39 (7). Odor: aldehydic, green, metallic, carrot like, fruity.

2-(Cyclopent-1-en-1-yl)hexanal (**12**). From (2*Z*)-1-(ethenyloxy)-2-pentylidenecyclopentane as described for **10**. Yield: 48%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.89 (*t*, *J*=7.1, Me(7)); 1.18–1.46 (*m*, CH$_2$(4′), CH$_2$(4), CH$_2$(5), CH$_2$(6)); 1.82–1.89 (*m*, CH$_2$(3′)); 2.26–2.32 (*m*, CH$_2$(5′)); 2.41–2.45 (*m*, CH$_2$(2)); 2.82 (*tt*, *J*=7.1, 7.1, H–C(3)); 5.40–5.44 (*m*, H–C(2′)); 9.67 (*dd*, *J*=2.8, 2.8, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$):14.3 (*q*, C(7)); 23.1 (*t*, C(4)); 23.6 (*t*, C(6)); 29.6 (*t*, C(5)); 32.2 (*t*, C(3′)); 32.4 (*t*, C(5′)); 33.6 (*t*, C(4′)); 33.2 (*d*, C(3)); 47.9 (*t*, C(2)); 125.9 (*d*, C(1′)); 146.0 (*s*, C(2′)); 203.2 (*d*, C(1)). EI-MS (70 eV): 180 (14, M^+), 151 (33), 123 (30), 109 (39), 95 (100), 93 (32), 81 (45), 79 (46), 77 (24), 67 (60). Odor: green, aldehydic, metallic, fatty.

3-(Cyclopent-1-en-1-yl)-5-methylhexanal (**13**). From ethenyl (2*Z*)-2-(3-methylbutylidene)cyclopentyl ether as described for **10**. Yield: 62%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.88 (*d*, *J*=6.6, Me$_2$C(5)); 1.14 (*ddd*, *J*=5.8, 8.3, 13.4, H$_a$–C(4)); 1.38 (*ddd*, *J*=5.6, 9.4, 13.4, H$_b$–C(4)); 1.44–1.58 (*m*, H–C(5)); 1.79–1.87 (*m*, CH$_2$(4′)); 2.15–2.22 (*m*, CH$_2$(3′)); 2.24 –2.30 (*m*, CH$_2$(5′)); 2.36–2.40 (*m*, CH$_2$(2)); 2.88 (*m*, H–C(3)); 5.42–5.45 (*m*, H–C(2′)); 9.65 (*dd*, *J*=2.8, 2.8, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.4 (*q*, *Me*–C(5)); 23.5 (*q*, *Me*–C(5)); 23.6 (*t*, C(4′)); 25.8 (*d*, C(5)); 31.8 (*t*, C(5′)); 32.4 (*t*, C(3′)); 34.2 (*d*, C(3)); 43.3 (*t*, C(4)); 48.2 (*t*, C(2)); 126.1 (*d*, C(1′)); 145.9 (*s*, C(2′)); 203.1 (*d*, C(4)). MS (70 eV): 180 (8, M^+), 109 (17), 96 (18), 95 (100), 93 (27), 91 (20), 81(29), 79 (29), 77 (18), 67 (39), 41 (19). Odor: green, aldehydic, metallic, fatty, buttery.

2-[2-(3-Methylbutyl)cyclopent-2-en-1-yl]acetaldehyde (**14**). From ethenyl 2-(3-methylbutyl)cyclopent-2-en-1-yl ether as described for **10**. Yield: 64%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.90 (*d*, *J*=6.6, Me–C(8′)); 0.91 (*d*, *J*=6.6, Me–C(8′)); 1.27–1.41 (*m*, CH$_2$(7′)); 1.9–1.60 (*m*, H–C(8′), H$_a$–C(5′)); 1.87–2.23 (*m*, CH$_2$(6′), H$_b$–C(5′)); 2.24 –2.34 (*m*, CH$_2$(2), H$_a$–C(4′)); 2.63 (*ddd*, *J*=2.0, 4.0, 16.2, H$_b$–C(4′)); 2.97–3.06 (*m*, H–C(1′)); 5.39–5.40 (*m*, H–C(3′)); 9.80 (*dd*, *J*=1.8, 2.8, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$):22.7 (*q*, *Me*–C(8′)); 23.2 (*q*, *Me*–C(8′)); 27.2 (*t*, C(5′)); 28.3 (*d*, C(8′)); 30.8 (*t*, C(4′)); 31.2 (*t*, C(6′)); 37.2 (*t*, C(7′)); 41.8 (*d*, C(1′)); 48.2 (*t*, C(2)); 124.8 (*d*, C(3′)); 146.3 (*s*, C(2′)); 203.3 (*d*, C(1)). EI-MS (70 eV): 180 (2, M^+), 136 (28), 95 (43), 91 (21), 81 (40), 80 (100), 79 (37), 77 (23), 67 (28), 41 (24). Odor: aldehydic, green, sappy, citrus.

4-Benzylpent-4-enal (**15**). From 2-benzylprop-2-en-1-yl ethenyl ether as described for **10**. Yield: 55%. ^{1}H-NMR (400 MHz, CDCl$_3$): 2.34 (br. *t*, *J*=7.1, CH$_2$(3)); 2.57 (*dt*, *J*=1.8, 7.1, CH$_2$(2)); 3.40 (br. *s*, CH$_2$(5)); 4.87 (br. *s*, 1 H of CH$_2$=C(4)); 4.89 (br. *s*, 1 H of CH$_2$=C(4)); 7.20–7.25 (*m*, H–C(2′), H–C(6′)); 7.23 (*m*, H–C(4′)); 7.31–7.35 (*m*, H–C(3′), H–C(5′)); 9.74 (*t*, *J*=1.8, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 27.9 (*t*, C(3)); 42.1 (*t*, C(2)); 43.8 (*t*, C(5)); 112.4 (*t*, *C*H$_2$=*C*(4)); 126.7 (*d*, C(4′)); 128.8 (*d*, C(2′), C(6′)); 129.3 (*d*, C(3′), C(5′)); 139.6 (*s*, C(1′)); 147.3 (*s*, C(4)); 147.3 (*s*, C(4)); 202.4 (*s*, C(1)). EI-MS (70 eV): 174 (14, M^+), 156 (33), 181 (29), 129 (37), 128 (25), 118 (33), 117 (70), 115 (56), 91 (100), 65 (24). Odor: aldehydic, fatty, citrus.

4-Methylidene-5-phenylhexanal (**16**). From ethenyl 2-methylidene-3-phenylbutyl ether as described for **10**. Yield: 31%. ^{1}H-NMR (400 MHz, CDCl$_3$): 1.42 (*d*, *J*=7.1, Me(6)); 2.17–2.31 (*m*, CH$_2$(3)); 2.48–2.54 (*m*, CH$_2$(2)); 3.45 (*q*, *J*=7.1, H–C(5)); 4.92 (br. *s*, 1 H of CH$_2$=C(4)); 5.08 (br. *s*, 1 H of CH$_2$=C(4)); 7.21–7.26 (*m*, H–C(2′), H–C(4′), H–C(6′)); 7.30–7.34 (*m*, H–C(3′), H–C(5′)); 9.68 (*t*, *J*=1.8, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 21.0 (*q*, C(6)); 27.5 (*t*, C(3)); 42.4 (*t*, C(2)); 46.1 (*d*, C(5)); 115.9 (*t*, H$_2$*C*=*C*(4)); 126.8 (*d*, C(4′)); 127.9 (C(2′), C(6′)); 128.9 (C(3′), C(5′)); 145.2 (*s*, C(4)); 151.5 (*s*, C(1′)); 202.5 (*s*, C(1)). EI-MS (70 eV): 188 (12, M^+), 132 (56), 131 (71), 129 (100), 128 (38), 117 (49), 115 (45), 105 (81), 91 (64), 77 (40). Odor: floral, green, weak.

4-(3-Methyl-5-propylcyclohex-2-en-1-yl)pent-4-enal (**17**). From ethenyl 2-(3-methyl-5-propylcyclohex-2-en-1-yl)prop-2-en-1-yl ether as described for **10**. Yield: 72%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.89 (*t*, *J*=7.1, Me(9′)); 1.20–1.40 (*m*, CH$_2$(7′), CH$_2$(8′)); 1.54–1.65 (*m*, H$_a$–C(4′), CH$_2$(6′)); 1.70 (br. *s*, Me–C(3′)); 1.99 (br. *d*, *J* = 17.63, H_b–C(4′)); 2.30 – 2.51 (*m*, CH_2(3)); 2.58–2.65 (*m*, CH_2(2)); 2.72–2.78 (*m*, H–C(5′)); 4.79 (br. *s*, CH_2=C(4)); 5.26 (br. *s*, H–C(2′)); 9.80 (*t*, *J* = 1.5, H–C(1)). ^{13}C-NMR (400 MHz, $CDCl_3$): 14.7 (*q*, C(9′)); 20.5 (*t*, C(8′)); 24.2 (*q*, *Me*–C(3′)); 27.6 (*t*, C(3)); 29.6 (*d*, C(5′)); 33.0 (*t*, C(6′)); 37.3 (*t*, C(4′)); 38.6 (*t*, C(7′)); 41.0 (*d*, C(1′)); 42.7 (*t*, C(2)); 111.5 (*t*, *C*H_2=*C*(4)); 123.0 (*d*, C(2′)); 135.6 (*s*, C(3′)); 150.5 (*s*, C(4)); 202.7 (*d*, C(1)). EI-MS (70 eV): 220 (20, M^+), 164 (98), 121 (56), 107 (62), 105 (53), 93 (100), 91 (79), 79 (54), 55 (56), 41 (47). Odor: sweet, valerian like, rosy, leathery, winey, fruity.

2-[6-(Propan-2-yl)cyclohex-2-en-1-yl]acetaldehyde (**18**). From 3-(ethenyloxy)-6-(propan-2-yl)cyclohexene as described for **10**. Yield: 55%. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.84 (*d*, *J* = 6.8, Me–C(7′)); 0.91 (*d*, *J* = 6.8, Me–C(7′)); 1.13–1.20 (*m*, H_a–C(5′)); 1.37–1.44 (*m*, H–C(6′)); 1.62–1.81 (*m*, H_a–C(4′), H_b–C(5′)); 1.93–2.06 (*m*, H_b–C(4′), H–C(7′)); 2.38 (*ddd*, *J* = 2.8, 7.6, 16.2, H_a–C(2)); 2.55 (*ddd*, *J* = 2.0, 5.6, 16.2, H_b–C(2)); 2.59–2.67 (*m*, H–C(1′)); 5.51–5.56 (*m*, H–C(2′)); 5.71–5.77 (*m*, H–C(3′)); 9.79 (*dd*, *J* = 2.0, 2.8, H–C(1)). ^{13}C-NMR (400 MHz, $CDCl_3$): 17.8 (*q*, *Me*–C(7′)); 21.2 (*t*, C(4′)); 22.0 (*q*, *Me*–C(7′)); 24.7 (*t*, C(5′)); 27.7 (*d*, C(7′)); 33.3 (*d*, C(1′)); 44.5 (*d*, C(6′)); 49.1 (*t*, C(2)); 128.6 (*d*, C(3′)); 130.1 (*d*, C(2′)); 203.7 (*d*, C(1)). EI-MS (70 eV): 166 (17, M^+), 122 (36), 96 (31), 95 (30), 81 (39), 79 (100), 78 (33), 77 (29), 67 (74), 41 (37). Odor: green, resinous, fatty, carrot.

3-(Cyclohex-1-en-1-yl)heptanal (**19**). From (2*E*)-1-(ethenyloxy)-2-pentylidenecyclohexane as described for **10**. Yield: 67%. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.89 (*t*, *J* = 7.1, Me(7)); 1.15 – 1.45 (*m*, H_a–C(4), CH_2(5), CH_2(6), H_a–C(5′)); 1.51–1.64 (*m*, H_b–C(4), CH_2(4′), H_b–(5′)); 1.83–1.89 (*m*, H_a–C(3′), H_a–C(6′)); 1.96–2.03 (*m*, H_b–C(3′), H_b–C(6′)); 2.35 (*ddd*, *J* = 2.5, 6.6, 15.7, H_a–C(2)); 2.42 (*ddd*, *J* = 3.0, 8.3, 15.7, H_b–C(2)); 2.48–2.57 (*m*, H–C(3)); 5.46–5.50 (*m*, H–C(2′)); 9.66 (*dd*, *J* = 2.5, 3.0, H–C(1)). ^{13}C-NMR (400 MHz, $CDCl_3$): 14.4 (*q*, C(7)); 23.0 (2*t*, C(3′), C(4′)); 23.2 (*t*, C(6)); 25.1 (*t*, C(6′)); 25.5 (*t*, C(5′)); 29.8 (*t*, C(5)); 33.3 (*t*, C(4)); 42.5 (*d*, C(3)); 48.0 (*t*, C(2)); 123.7 (*d*, C(2′)); 138.5 (*s*, C(1′)); 203.5 (*d*, C(1)). EI-MS (70 eV): 194 (7, M^+), 137 (66), 109 (68), 95 (75), 93 (61), 91 (60), 81(84), 79 (86), 67 (100), 41 (60). Odor: green, aldehydic, metallic.

3-(Cyclohex-1-en-1-yl)-5-methylhexanal (**20**). From ethenyl (2*E*)-2-(3-methylbutylidene)cyclohexyl ether as described for **10**. Yield: 61%. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.89 (*d*, *J* = 6.8, Me_2C(5)); 1.08 (*ddd*, *J* = 5.6, 8.8, 13.6, H_a–C(4)); 1.38 (*ddd*, *J* = 5.1, 9.9, 13.6, H_b–C(4)); 1.46–1.63 (*m*, H–C(5), CH_2(4′), CH_2(5′)); 1.82–1.89 (*m*, H_a–C(3′), H_a–C(6′)); 1.95–202 (*m*, H_b–C(3′), H_b–C(6′)); 2.31 (*ddd*, *J* = 2.3, 6.3, 15.7, H_a–C(2)); 2.39 (*ddd*, *J* = 3.0, 8.6, 15.7, H_b–C(2)); 2.61–2.70 (*m*, H–C(3)); 5.49–5.53, H–C(2′)); 9.65 (*dd*, *J* = 2.3, 3.0, H–C(1)). ^{13}C-NMR (400 MHz, $CDCl_3$): 22.3 (*q*, *Me*$_2$C(5)); 23.0 (*t*, C(5′)); 23.2 (*t*, C(4′)); 24.7 (*t*, C(3′)); 25.5 (*t*, C(6′)); 25.7 (*d*, C(5)); 40.4 (*d*, C(3)); 42.9 (*t*, C(4)); 48.2 (*t*, C(2)); 123.9 (*d*, C(2′)); 138.4 (*s*, C(1′)); 203.4 (*d*, C(1)). EI-MS (70 eV): 194 (8, M^+), 138 (50), 109 (100), 107 (52), 95 (72), 94 (72), 91 (60), 81 (70), 79 (77), 67 (91). Odor: weak, green, hay.

5-Methyl-4-methylidene-3-(2-methylpropyl)hexanal (**21**). From ethenyl (2*E*)-5-methyl-2-(propan-2-yl)hex-2-en-1-yl ether as described for **10**. Yield: 94%. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.90 (*d*, *J* = 6.6, Me–C(2′)); 0.91 (*d*, *J* = 6.3, Me–C(2′)); 1.06 (*d*, *J* = 6.8, Me–C(5)); 1.06 (*d*, *J* = 6.8, Me–C(5)); 1.20 (*ddd*, *J* = 7.1, 7.1, 13.9, 1 H of CH_2(1′)); 1.40 (*ddd*, *J* = 6.6, 7.8, 13.9, 1 H of CH_2(1′)); 1.51–1.65 (*m*, H–C(2′)); 2.16–2.26 (*m*, H–C(5)); 2.42 (*ddd*, *J* = 2.3, 6.6, 16.2, H_a–C(2)); 2.49 (*ddd*, *J* = 2.5, 7.6, 16.2, H_b–C(2)); 2.65–2.74 (*m*, H–C(3)); 4.80 (*s*, 1 H of CH_2=C(4)); 4.91 (*s*, 1 H of CH_2=C(4)); 9.68 (*dd*, *J* = 2.3, 2.5, H–C(1)). ^{13}C-NMR (400 MHz, $CDCl_3$): 23.0 (*q*, *Me*–C(5)); 23.1 (*q*, *Me*–C(5)); 23.1 (*q*, Me–C(2′)); 23.2 (*q*, Me–C(2′)); 25.8 (*d*, C(2′)); 23.0 (*d*, C(5)); 37.8 (*d*, C(3)); 45.0 (*t*, C(1′)); 49.1 (*t*, C(2)); 108.1 (*d*, H_2*C*=*C*(4)); 158.7 (*s*, C(4)); 203.1(*d*, C(1)). EI-MS (70 eV): 167 (3, $[M-15]^+$), 108 (31), 97 (71), 84 (30), 83 (50), 70 (30), 69 (54), 55 (100), 43 (33), 41 (57). Odor: green, fatty, fruity.

3-Ethyl-4-methylpent-4-enal (**22**). From ethenyl (2*E*)-2-methylpent-2-en-1-yl ether as described for **10**. Yield: 60%. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.86 (*t*, *J* = 7.3, Me(2′)); 1.44 (*dq*, *J* = 7.3, 7.3, CH_2(1′)); 1.66 (*s*, Me(5)); 2.42–2.45 (*m*, CH_2(2)); 2.54–2.61 (*m*, H–C(3)); 4.77 (br. *s*, 1 H of CH_2=C(4)); 4.82 (br. *s*, 1 H of CH_2=C(4)); 9.68 (*t*, *J* = 2.5, H–C(1)). ^{13}C-NMR (400 MHz, $CDCl_3$): 11.8 (*q*, 2 C(2′)); 19.2 (*q*, 2 C(5)); 26.3 (*t*, C(1′)); 43.6 (*d*, C(3)); 47.6 (*t*, C(2)); 112.7 (*t*, H_2*C*=*C*(4)); 146.2 (*s*, C(4)); 202.9 (*d*, C(1)). EI-MS (70 eV): 111 (14, $[M-15]^+$), 97 (22), 84 (59), 69 (100), 67 (31), 56 (16), 55 (94), 53 (20), 41 (82), 39 (33). Odor: too weak, too volatile.

*5,7,7-Trimethyl-3-[(1*E*)-prop-1-en-1-yl]octanal* (**23**). From (3*E*)-2-(ethenyloxy)-6,8,8-trimethylnon-3-ene as described for **10**. Yield: 56% (two isomers; ratio 1:1). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.89, 0.90 (*s*, Me$_3$C(7)); 0.91, 0.96 (2*d*, *J* = 6.6, Me–C(5)); 0.99–1.36 (*m*, CH$_2$(4), CH$_2$(6)); 1.45 –1.58 (*m*, H–C(5)); 1.64–1.68 (*m*, Me(3′)); 2.28–2.43 (*m*, CH$_2$(2)); 2.60–2.69 (*m*, H–C(3)); 5.21, 5.26 (2*dq*, *J* = 15.4, 1.8, and *J* = 15.4, 1.5, resp., H–C(2′)); 5.47, 5.51 (2*ddq*, *J* = 6.3, 15.4, 0.8, H–C(1′)); 9.70, 9.71 (2*t*, *J* = 2.5 and *J* = 2.3, resp., H–C(1)).^{13}C-NMR (400 MHz, CDCl$_3$):18.2, 18.3 (2*q*, C(3′)); 22.3, 23.6 (2*q*, *Me*–C(5)); 26.8, 27.1 (2*d*, C(5)); 30.4, 30.7 (2*q*, *Me*$_3$C(7)); 31.6, 31.7 (2*s*, C(7)); 35.7, 36.0 (2*d*, C(3)); 45.7, 45.8 (2*t*, C(4)); 49.5 50.3 (2*t*, C(2)); 51.2, 52.3 (2*t*, C(6)); 126.3, 126.6 (2*d*, C(2′)); 133.9, 134.6 (2*d*, C(1′)); 203.3, 203.4 (2*d*, C(1)). EI-MS (70 eV): 159 (1, $[M-15]^+$), 139 (14), 98 (19), 97 (57), 95 (21), 83 (18), 69 (24), 57 (100), 55 (18), 41 (31). EI-MS (70 eV): 139 (14), 111 (11), 98 (18), 97 (57), 95 (21), 83 (18), 69 (25), 57 (100), 55 (18), 41 (30). Odor: aldehydic, fatty, floral, green.

5,9-Dimethyl-4-methylidenedec-8-enal (**24**). From 3,7-dimethyl-2-methylideneoct-6-en-1-yl ethenyl ether as described for **10**. Yield: 64%. ^{1}H-NMR (400 MHz, CDCl$_3$): 1.05 (*d*, *J* = 6.8, Me–C(5)); 1.29–1.38 (*m*, H$_a$–C(6)); 1.44–1.53 (*m*, H$_b$–C(6)); 1.60 (br. *s*, Me–C(9)); 1.69 (br. *s*, Me–C(9)); 1.93 (br. *dt*, *J* = 7.3, 7.3, CH$_2$(7)); 2.15 (*tq*, *J* = 7.1, 6.8, H–C(5)); 2.31–2.37 (*m*, CH$_2$(3)); 2.60 (*dt*, *J* = 1.5, 7.6, CH$_2$(2)); 4.69–4.70 (*m*, 1 H of CH$_2$=C(4)); 4.82–4.83 (*m*, 1 H of CH$_2$=C(4)); 5.07–5.12 (*m*, H–C(8)); 9.80 (*t*, *J* = 1.5, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 18.1 (*q*, *Me*–C(5)); 20.4 (*q*, *Me*$_2$C(9)); 25.9 (*t*, C(3)); 26.3 (*t*, C(7)); 36.0 (*t*, C(6)); 40.3 (*d*, C(5)); 42.4 (*t*, C(2)); 108.7 (*t*, H$_2$*C*=*C*(4)); 124.9 (*d*, C(8)); 131.8 (*s*, C(9)); 152.8 (*s*, C(4)); 202.6 (*d*, C(1)). EI-MS (70 eV): 150 (13, $[M-44]^+$), 107 (12), 83 (14), 82 (100), 81 (14), 69 (18), 67 (36), 55 (40), 53 (10), 41 (37). Odor: aldehydic, green, metallic, citrus, mandarin, coriander leaf.

4-Methylidenetridec-12-enal (**25**). From ethenyl 2-methylideneundec-10-en-1-yl ether as described for **10**. Yield: 69%. ^{1}H-NMR (400 MHz, CDCl$_3$): 1.26–1.47 (*m*, CH$_2$(6), CH$_2$(7), CH$_2$(8), CH$_2$(9), CH$_2$(10)); 2.00–2.08 (*m*, CH$_2$(5), CH$_2$(1)); 2.35 (br. *t*, *J* = 7.3, CH$_2$(3)); 2.57 (*dt*, *J* = 1.8, 7.3, CH$_2$(2)); 4.70 (br. *s*, 1 H, 1 H of H$_2$C=C(4)); 4.77 (br. *s*, 1 H of H$_2$C=C(4)); 4.93 (*ddt*, *J* = 2.3, 10.1, 1.5, H$_a$–C(13)); 4.98 (*ddt*, *J* = 2.3, 17.2, 1.5, H$_b$–C(13)); 5.81 (*ddt*, 10.1, 17.2, 6.8, 1 H, H–C(12)); 9.78 (*t*, *J* = 1.8, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 28.1 (*t*, C(6)); 28.5 (*t*, C(7)); 29.3 (*t*, C(3)); 29.5 (*t*, C(10)); 29.7 (*t*, C(8)); 29.7 (*t*, C(9)); 34.1 (*t*, C(11)); 36.7 (*t*, C(5)); 42.3 (*t*, C(2)); 109.9 (*t*, H$_2$*C*=*C*(4)); 114.5 (*t*, C(13)); 139.5 (*d*, C(12)); 148.2 (*s*, C(4)); 202.5 (*d*, C(1)). EI-MS (70 eV): 179 (2, $[M-29]^+$), 83 (41), 81 (55), 70 (46), 69 (66), 68 (31), 67 (61), 56 (56), 55 (100), 41 (89). Odor: aldehydic, pine, metallic.

5-(4-methylcyclohex-3-en-1-yl)-4-methylidenehexanal (**26**). From ethenyl 3-(4-methylcyclohex-3-en-1-yl)-2-methylidenebutyl ether as described for **10**. Yield: 93% (two isomers; 1:1). ^{1}H-NMR (400 MHz, CDCl$_3$): 1.02, 1.05 (2*d*, *J* = 7.1, Me–C(5)); 1.09–1.23 (*m*, H$_a$–C(6′)); 1.42–1.73 (*m*, H–C(1′), H$_b$–C(6′)); 1.63–1.73 (*m*, Me–C(4′)); 1.81–2.11 (*m*, H–C(5), CH$_2$(2′), CH$_2$(5′)); 2.23 –2.40 (*m*, CH$_2$(3)); 2.57–2.63 (*m*, CH$_2$(2)); 4.69–4.70, 4.71–4.72 (2*m*, 1 H of H$_2$C=C(4)); 4.79–4.81 (*m*, 1 H of H$_2$C=C(4)); 5.31–5.34, 5.35–5.38 (2*m*, H–C(3′)); 9.78–9.79 (*m*, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 17.5, 17.6 (2*q*, *Me*–C(5)); 23.7 (*q*, *Me*–C(4)); 25.8, 26.0 (2*t*, C(3)); 26.4 (*t*, C(2′)); 29.6, 30.8 (2*t*, C(6′)); 31.0, 31.2 (2*t*, C(5′)); 37.2 (*d*, C(5)); 42.3 (*t*, C(2)); 45.8, 46.5 (*d*, C(1′)); 109.4 (*t*, H$_2$*C*=*C*(4)); 120.9, 121.1 (2*d*, C(3′)); 134.1, 134.4 (2*s*, C(4′)); 152.0, 152.3 (2*s*, C(4)); 202.5 (*d*, C(1)). EI-MS (70 eV): isomers A and B: 206 (1, M^+), 95 (46), 94 (100), 93 (18), 79 (45), 77 (12), 67 (33), 55 (20), 53 (10), 41 (15). Odor: aldehydic, green, fatty, slightly orris.

3-Methyl-3-(4-methylcyclohex-1-en-1-yl)butanal (**27**). From 3-methyl-3-(4-methylcyclohex-1-en-1-yl)butanal as described for **10**. Yield: 83%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.93 (*d*, *J* = 6.3, Me–C(4′)); 1.15 (*s*, Me–C(3)); 1.13–1.23 (*m*, H$_a$–C(5′)); 1.16 (*s*, Me–C(3)); 1.54–1.77 (*m*, H$_a$–C(3′), H–C(4′), H$_b$–C(5)); 1.96–2.16 (*m*, H$_b$–C(3′), CH$_2$(6′)); 2.32 (*dd*, *J* = 3.3, 14.9, H$_a$–C(2)); 2.37 (*dd*, *J* = 3.0, 14.9, H$_b$–C(2)); 5.49–5.52 (*m*, H–C(2′)); 9.60 (*dd*, *J* = 3.0, 3.3, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.0 (*q*, C(4′)); 25.0 (*t*, C(6′)); 28.0 (*q*, *Me*–C(3)); 28.1 (*q*, *Me*–C(3)); 28.6 (*d*, C(4′)); 31.8 (*t*, C(5′)); 34.4 (*t*, C(3′)); 38.0 (*s*, C(3)); 53.6 (*t*, C(2)); 120.8 (*d*, C(2′)); 141.9 (*s*, C(1′)); 204.1 (*d*, C(1)). EI-MS (70 eV): 180 (14, M^+), 138 (40), 121 (40), 95 (100), 93 (36), 81 (70), 79 (30), 67 (31), 55 (31), 44 (33). Odor: green, aldehydic, fatty, floral.

4,5,7,7-Tetramethyloctanal (**28**). Compound **10** 12.0 g, 66 mmol) was dissolved in EtOH (60 ml), and Pd/C (100 mg, 5% loading) was added. The soln. was stirred for 24 h under H$_2$ at r.t. and ambient pressure. The soln. was filtered, and the solvent was evaporated under reduced pressure. The crude product was subjected to bulb-to-bulb distillation (120°/0.1 mbar) to yield 11.3 g of a colorless liquid (yield: 96%; two isomers; ratio 3:2). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.80 (*d*, *J* = 6.8, Me–C(4)); 0.83 (*d*,

J = 6.8, Me–C(5)); 0.88 (*s*, Me$_3$C(7)); 0.94–1.00 (*m*, H$_a$–C(6)); 1.24 (*dd*, J = 7.1, 13.9, H$_b$–C(6)); 1.31–1.55 (*m*, H$_a$–C(3), H–C(4), H–C(5)); 1.64–1.71 (*m*, H$_b$–C(3)); 2.37–2.47 (*m*, CH$_2$(2)); 9.77–9.78 (*m*, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 14.5, 16.0 (2*q*, *Me*–C(5)); 17.0, 19.1 (2*q*, C–4–Me), 25.1, 26.7 (2*t*, C(3)); 29.9, 30.0 (2*q*, *Me$_3$*C(7)); 30.9, 31.1 (2*s*, C(7)); 32.7 33.6 (2*d*, C(5)); 39.1 39.3 (2*d*, C(4)); 42.4, 42.5 (2*t*, C(2)); 47.5, 49.1 (2*t*, C(6)); 202.9, 203.0 (2*d*, C(1)). EI-MS (70 eV) isomers A and B: 128 (15), 109 (7), 95 (17), 85 (17), 84 (20), 69 (10), 57 (100), 55 (15), 43 (17), 41 (30). Odor: aldehydic, green, fatty, resinous, slightly metallic.

(4Z)-4-Ethylidene-5,7,7-trimethyloctanal (**29**). From 6-(ethenyloxy)-2,2,4-trimethyl-5-methylideneheptane as described for **10**. Yield: 50% (two isomers; ratio 3:2). Isomer A: ^{1}H-NMR (400 MHz, CDCl$_3$): 0.90 (*s*, Me$_3$C(7)); 1.00 (*d*, J = 7.1, Me–C(5)); 1.20 (*dd*, J = 5.1, 14.2, H$_a$–C(6)); 1.48 (*dd*, J = 7.3, 14.2, H$_b$–C(6)); 1.66 (*dt*, 6.5, 1.5, H–C(2′)); 2.85 (*ddq*, J = 5.1, 5.6, 7.1, H–C(5)); 5.09 (*tq*, J = 6.6, 1.5, H–C(1′)); 9.78 (*t*, J = 1.8, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 13.5 (*q*, C(2′)); 22.4 (*q*, C(5)); 23.7 (*t*, C(3)); 30.3 (*q*, *Me$_3$*C(7)); 30.4 (*d*, C(5)); 30.6 (*s*, C(7)); 43.1 (*t*, C(2)); 48.8 (*t*, C(6)); 117.0 (*d*, C(1′)); 144.2 (*s*, C(4)); 203.2 (*d*, C(1)). EI-MS (70 eV): 196 (2, M^+), 122 (30), 107 (29), 97 (32), 83 (31), 81 (30), 57 (100), 55 (87), 43 (42), 41 (59). Isomer B: ^{1}H-NMR (400 MHz, CDCl$_3$): 0.89 (*s*, Me$_3$C(7)); 1.01 (*d*, J = 6.8, Me–C(5)); 1.14 (*dd*, J = 5.6, 14.2, H$_a$–C(6)); 1.43 (*dd*, J = 6.1, 14.2, H$_b$–C(6)); 1.59 (*d*, J = 6.8, Me(2′)); 2.17–2.59 (*m*, H–C(5)); 5.32 (*q*, J = 6.8, H–C(1′)); 9.80 (*t*, J = 1.8, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$):13.7 (*q*, C(2′)); 21.5 (*t*, C(3)); 23.5 (*q*, *Me*–C(5)); 30.3 (*q*, *Me$_3$*C(7)); 30.9 (*d*, C(5)); 31.6 (*s*, C(7)); 44.1 (*t*, C(2)); 50.6 (*t*, C(6)); 119.2 (*d*, C(1′)); 145.0 (*s*, C(4)); 202.6 (*d*, C(1)). EI-MS (70 eV): 196 (3, M^+), 122 (33), 107 (31), 97 (34), 83 (31), 81 (31), 57 (100), 55 (86), 43 (41), 41 (57). Odor: aldehydic, green, fatty, resinous, slightly floral.

(4Z)-5,7,7-Trimethyl-4-propylideneoctanal (**30**). From 6-(ethenyloxy)-2,2,4-trimethyl-5-methylideneoctane as described for **10**. Yield: 60% (two isomers; ratio 1:1). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.88, 0.89 (2*s*, Me$_3$C(7)); 0.95, 0.96 (2*t*, J = 7.6, Me(3′)); 1.00, 1.01 (2*d*, J = 7.1, and J = 6.8, resp., Me–C(5)); 1.14, 1.18 (2*dd*, J = 5.6, 14.2, and J = 5.1, 14.2, resp., H$_a$–C(6)); 1.43, 1.45 (2*dd*, J = 6.1, 14.2, and J = 7.1, 14.2, resp., H$_b$–C(6)); 1.94–2.59 (*m*, CH$_2$(2), CH$_2$(3), CH$_2$(2′), H–C(5) (one isomer)); 2.81 (*dq*, J = 5.1, 7.1, H–C(5) (one isomer)); 4.91, 5.19 (*tq*, J = 7.6, 1.5, and *t*, J = 7.6, H–C(1′)); 9.77–9.79 (*m*, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 14.2, 14.4 (2*q*, C(3′)); 20.8, 21.0 (2*t*, C(2′)); 21.4, 22.9 (2*t*, C(3)); 22.4, 23.3 (2*q*, *Me*–C(5)); 29.9, 30.0 (2*q*, *Me$_3$*C(7)); 30.9 (*s*, C(7)); 31.2, 31.3 (2*d*, C(5)); 42.7, 44.2 (2*t*, C(2)); 48.5, 49.8 (2*t*, C(6)); 124.9, 126.9 (2*d*, C(2′)); 142.4, 143.0 (2*s*, C(4)); 202.1, 202.7 (2*d*, C(1)). EI-MS (70 eV): isomers A and B: 210 (1, M^+), 192 (4, $[M-18]^+$), 154 (4), 136 (15), 121 (17), 107 (15), 95 (35), 69 (33), 57 (100), 55 (55). Odor: weak, Watery, aldehydic, green, sappy.

5,7,7-Trimethyl-2,4-dimethylideneoctanal (**31**). From **28** as described for **7**. Yield: 69%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.91 (*s*, Me$_3$C(7)); 1.17 (*dd*, J = 5.8, 14.2, H$_a$–C(6)); 1.54 (*dd*, J = 5.3, 14.2, H$_b$–C(6)); 2.21–2.29 (*m*, H–C(5)); 2.96 (*d*, J = 17.2, H$_a$–C(3)); 3.01 (*d*, J = 17.2, H$_b$–C(3)); 4.58–4.60 (*m*, 1 H of CH$_2$=C(4)); 4.90 (br. *s*, 1 H of H$_2$C=C(4)); 6.14 (br. *s*, 1 H of CH$_2$=C(2)); 6.30–6.31 (*m*, 1 H of H$_2$C=C(2)); 9.61 (*s*, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 23.1 (*q*, *Me*–C(5)); 30.4 (*q*, *Me$_3$*C(7)); 31.7 (*s*, C(7)); 32.2 (*t*, C(3)); 37.1 (*d*, C(5)); 110.3 (*t*, *C*H$_2$=C(4)); 135.9 (*t*, CH$_2$=*C*(2)); 148.8 (*s*, C(2)); 153.3 (*s*, C(4)); 194.4 (*s*, C(1)). EI-MS (70 eV): 179 (2, M^+), 138 (29), 123 (100), 120 (23), 109 (32), 95 (46), 67 (25), 57 (68), 43 (26), 41 (36). Odor: green, woody, *Koavone*, *Orivone*, floral.

2,5,7,7-Tetramethyl-4-methylideneoctanal (**32**). Compound **31** (5.5 g, 28 mmol) was dissolved in EtOH (60 ml), and *Lindlar* catalyst (200 mg, 5% Pd on CaCO$_3$) was added. The soln. was stirred for 2 h under H$_2$ at r.t. and ambient pressure. The soln. was filtered, and the solvent was evaporated under reduced pressure. The crude product was subjected to bulb-to-bulb distillation (120°/0.1 mbar) to yield 4.8 g of a colorless liquid (purity: 97% of two isomers; ratio 1:1; yield: 96%). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.91 (*s*, Me$_3$C(7)); 1.07 (*d*, J = 6.8, Me–C(5)); 1.11, 1.13 (2*d*, J = 7.1, Me–C(2)); 1.17, 1.18 (2*dd*, J = 5.8, 14.2, H$_a$–C(6)); 1.49, 1.50 (*dd*, J = 5.3, 14.2, and J = 5.6, 14.2, resp., H$_b$–C(6)); 2.00 (2 br. *d*, J = 15.7, H$_a$–C(3)); 2.18–2.28 (*m*, H–C(5)); 2.48, 2.50 (2br. *d*, J = 15.7, H$_b$–C(3)); 2.59–2.66 (*m*, H–C(2)); 4.68–4.70 (*m*, 1 H of CH$_2$=C(4)); 4.91 (br. *s*, 1 H of CH$_2$=C(4)); 9.64, 9.66 (2*d*, J = 2.3, and J = 2.0, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 14.1, 14.3 (2*q*, *Me*–C(2)); 23.2, 23.4 (2*q*, *Me*–C(5)); 30.4 (*q*, *Me$_3$*C(7)); 31.6 (*s*, C(7)); 35.2, 35.3 (2*t*, C(3)); 36.9, 37.1 (2*d*, C(5)); 44.7, 44.8 (2*d*, C(2)); 49.9, 50.3 (2*t*, C(6)); 109.7 (*t*, *C*H$_2$=*C*(4)); 153.2 (*s*, C(4)); 205.3, 205.4 (2*d*, C(1)). EI-MS (70 eV): isomers A and B: 181 (1, $[M-15]^+$), 107 (28), 97 (25), 84 (22), 83 (45), 69 (38), 57 (100), 55 (38), 43 (35), 41 (40). Odor: green, woody, *Koavone*, *Orivone*, floral, agrestic, minty, straw.

7-Methyl-4-methylideneoctanal (**35**). Chloro(pentamethylcyclopentadienyl)(cyclooctadiene)ruthenium(II) (0.4 g, 1 mmol) was added to *prop-2-en-1-ol* (**34**; 4.5 g, 78 mmol). The mixture was cooled to 10°, and *5-methylhex-1-yne* (**33**; 2.0 g, 21 mmol) was added during 1 h. Stirring was continued for further 16 h at r.t. Compound **34** was evaporated under reduced pressure. The crude product was subjected to bulb-to-bulb distillation (130°/0.1 mbar) to yield 2.4 g of a light yellow liquid (purity: 85%; yield: 84%; contains 15% 8-methylnon-4-enal). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.90 (*d*, $J=7.1$, Me$_2$C(7)); 1.29–1.35 (*m*, CH$_2$(6)); 1.49–1.59 (*m*, H–C(7)); 2.01–2.05 (*m*, CH$_2$(5)); 2.36 (br. *t*, $J=7.3$, CH$_2$(3)); 2.58 (*dt*, $J=1.8$, 7.3, CH$_2$(2)); 4.70 (br. *s*, 1 H of CH$_2$=C(4)); 4.78 (br. *s*, 1 H of CH$_2$=C(4)); 9.78 (*t*, $J=1.8$, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.5 (*q*, *Me*$_2$C(7)); 27.8 (*d*, C(7)); 28.1 (*t*, C(3)); 34.1 (*t*, C(5)); 37.0 (*t*, C(6)); 41.9 (*t*, C(2)); 109.3 (*t*, H$_2$*C*=*C*(4)); 148.1 (*s*, C(4)); 202.2 (*d*, C(1)). EI-MS (70 eV): 139 (2, $[M-15]^+$), 83 (25), 70 (41), 69 (52), 57 (43), 56 (100), 55 (67), 43 (31), 41 (72), 39 (26).

Data of 8-Methylnon-4-enal. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.87 (*d*, $J=6.8$, Me$_2$C(8)); 1.20 –1.24 (*m*, H$_a$–C(7)); 1.30–1.34 (*m*, H$_b$–C(7)); 1.49–1.59 (*m*, H–C(8)); 1.95–2.00 (*m*, H–C(6)); 2.30–2.35 (*m*, CH$_2$(3)); 2.48 (*dt*, $J=1.8$, 7.1, CH$_2$(2)); 5.37–5.51 (*m*, H–C(5)); 5.97–6.06 (*m*, H–C(4)); 9.76 (*t*, $J=1.8$, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.4 (*q*, *Me*$_2$C(8)); 25.2 (*t*, C(3)); 27.5 (*d*, C(8)); 30.3 (*t*, C(6)); 38.6 (*t*, C(7)); 43.5 (*t*, C(2)); 127.0 (*d*, C(4)); 132.2 (*d*, C(5)); 202.4 (*d*, C(1)). EI-MS (70 eV): 136 (7, $[M-18]^+$), 84 (58), 83 (36), 69 (43), 67 (44), 56 (66), 55 (75), 43 (43), 41 (100), 39 (22). Odor: green, resinous, fir, citrus, orange, parsley leaf, pineapple.

7-Methyl-2,4-dimethylideneoctanal (**36**). From 7-methyl-4-methylideneoctanal as described for **7**. Yield: 46% (contains 15% 8-methyl-2-methylidenenon-4-enal). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.90 (*d*, $J=6.51$, Me$_2$C(7)); 1.30–1.36 (*m*, CH$_2$(6)); 1.50–1.59 (*m*, H–C(7)); 2.00 (br. *dd*, $J=7.6$ 8.6, CH$_2$(5)); 3.00 (br. *s*, CH$_2$(3)); 4.73 (br. *s*, 1 H of CH$_2$=C(4)); 4.87 (br. *s*, 1 H of CH$_2$=C(4)); 6.12 (br. *s*, 1 H of CH$_2$=C(2)); 6.29 (br. *s*, 1 H of CH$_2$=C(2)); 8.59 (*s*, H–C(1)).^{13}C-NMR (400 MHz, CDCl$_3$): 22.9 (*q*, *Me*$_2$C(7)); 28.2 (*d*, C(7)); 34.1 (*t*, C(5)); 34.6 (*t*, C(6)); 37.3 (*t*, C(3)); 111.9 (*t*, *C*H$_2$=*C*(4)); 135.5 (*t*, *C*H$_2$=*C*(2)); 147.0 (*s*, C(2)); 148.5 (*s*, C(4)); 194.5 (*d*, C(1)). EI-MS (70 eV): 166 (2, M^+), 109 (64), 97 (31), 95 (100), 81 (47), 79 (33), 67 (49), 55 (44), 41 (64), 39 (34).

Data of 8-Methyl-2-methylenenon-4-enal. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.89 (*d*, $J=6.8$, Me$_2$C(7)); 1.24–1.28 (*m*, H$_a$–C(7)); 1.31–1.35 (*m*, H$_b$–C(7)); 1.50–1.59 (*m*, H–C(8)); 2.02–2.06 (*m*, CH$_2$(3)); 5.38–5.55 (*m*, 2 H, C(4), C(5)); 6.03 (br. *s*, 1 H of CH$_2$=C(2)); 6.26 (br. *s*, 1 H of CH$_2$=C(2)); 9.59 (*s*, C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.9 (*q*, *Me*$_2$C(8)); 27.9 (*d*, C(8)); 30.8 (*t*, C(6)); 31.2 (*t*, C(3)); 39.0 (*t*, C(7)); 125.5 (*d*, C(4)); 134.3 (*d*, C(5)); 136.6 (*t*, H$_2$*C*=*C*(2)); 148.5 (*s*, C(2)); 194.6 (*d*, C(1)). EI-MS (70 eV): 166 (2, M^+), 109 (17), 96 (26), 95 (100), 81 (26), 79 (31), 67 (47), 55 (38), 43 (22), 41 (47). Odor: fruity, aldehydic, green.

7-Methyl-2,4-dimethylideneoctan-1-ol (**37**). From **36** as described for **8**. Yield: 85% (contains 15% 8-methyl-2-methylidenenon-4-en-1-ol). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.90 (*d*, Me$_2$C(7)); 1.31–1.36 (*m*, CH$_2$(6)); 1.51–1.60 (*m*, CH$_2$(6)); 1.51–1.60 (*m*, H–C(7)); 2.01 (br. *dd*, $J=7.6$, 8.3, CH$_2$(5)); 2.83 (br. *s*, H–C(3)); 4.06–4.08 (*m*, 2 H, H–C(1)); 4.80–4.81 (*m*, 1 H of CH$_2$=C(4)); 4.83–4.85 (*m*, 1 H of CH$_2$=C(4)); 4.94–4.96 (*m*, 1 H of CH$_2$=C(2)); 5.13–5.14 (*m*, 1 H of CH$_2$=C(2)). ^{13}C-NMR (400 MHz, CDCl$_3$): 23.0 (*q*, *Me*$_2$C(7)); 28.2 (*d*, C(7)); 33.5 (*t*, C(5)); 37.2 (*t*, C(6)); 41.2 (*t*, C(3)); 65.8 (*t*, C(1)); 111.4 (*t*, *C*H$_2$=*C*(4)); 111.9 (*t*, H$_2$*C*=*C*(2)); 146.9 (*s*, C(2)); 147.9 (*s*, C(4)). EI-MS (70 eV): 168 (0.1, M^+), 107 (32), 97 (63), 93 (38), 79 (100), 55 (47), 43 (43), 41 (65), 29 (23).

Data of 8-Methyl-2-methylenenon-4-en-1-ol. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.90 (*d*, $J=6.6$, 6 H, Me$_2$C(8)); 1.24–1.29 (*m*, H$_a$–C(7)); 1.31–1.35 (*m*, H$_b$–C(7)); 1.51 1.60 (*m*, H–C(8)); 2.02–2.06 (*m*, CH$_2$(6)); 2.78 (br. *s*, CH$_2$(3)); 4.08–4.10 (*m*, CH$_2$(1)); 4.90–4.92 (*m*, 1 H of CH$_2$=C(2)); 5.04–5.06 (*m*, 1 H of CH$_2$=C(2)); 5.39–5.54 (*m*, H–C(4), H–C(5)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.9 (*q*, *Me*$_2$C(8)); 27.9 (*d*, C(8)); 30.8 (*t*, C(6)); 36.9 (*t*, C(3)); 39.1 (*t*, C(7)); 66.1 (*t*, C(1)); 110.3 (*t*, H$_2$*C*=*C*(2)); 127.1 (*d*, C(4)); 133.5 (*d*, C(5)); 148.6 (*s*, C(2)). EI-MS (70 eV): 150 (5, $[M-18]^+$), 135 (14), 107 (20), 95 (40), 79 (100), 69 (30), 67 (32), 55 (53), 43 (44), 41 (70).

Ethenyl 7-Methyl-2,4-dimethylideneoctyl Ether (**38**). Compound **37** (2.0 g, 12 mmol), 4,7-diphenyl-1,10-phenanthroline (0.02 g, 0.06 mmol), (CF$_3$CO$_2$)$_2$ Pd (0.02 g, 0.06 mmol), and Et$_3$N (0.05 g, 0.048 mmol) were dissolved in butyl ethenyl ether (23.8 g, 238 mmol).The mixture was stirred at 70°

for 6 h, cooled to r.t. and filtered. The vinyl ether was evaporated, and the crude product was purified *via* CC to yield 1.8 g (9 mmol) of a colorless liquid (yield: 75%; contains 15% ethenyl (4*E*)-8-methyl-2-methylidenenon-4-en-1-yl ether). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.91 (*d*, *J* = 6.8, Me$_2$C(7)); 1.30–1.36 (*m*, CH$_2$(6)); 1.51–1.61 (*m*, 1 H, H–7), 2.02 (br. *dd*, *J* = 7.3, 8.3, CH$_2$(5)); 2.83 (br. *s*, CH$_2$(3)); 4.04 (*dd*, *J* = 1.8, 6.8, H$_a$–C(2′)); 4.15 (br. *s*, CH$_2$(1)); 4.25 (*dd*, *J* = 1.8, 14.4, H$_b$–C(2′)); 4.80–4.82 (*m*, 1 H of CH$_2$=C(4)); 4.85–4.86 (*m*, 1 H of CH$_2$=C(4)); 5.02–5.03 (*m*, 1 H of CH$_2$=C(2)); 5.16–5.18 (*m*, 1 H of CH$_2$=C(2)); 6.47 (*dd*, *J* = 6.8, 14.4, H–C(1′)). ^{13}C-NMR (400 MHz, CDCl$_3$): 23.0 (*q*, *Me*$_2$C(7)); 28.2 (*d*, C(7)); 33.6 (*t*, C(6)); 37.4 (*t*, C(3)); 70.7 (*t*, C(1)); 87.5 (*t*, C(2′)); 111.7 (*t*, H$_2$*C*=*C*(4)); 114.3 (*t*, H$_2$*C*=*C*(2)); 142.9 (*s*, C(2)); 147.4 (*s*, C(4)); 152.0 (*d*, C(1′)). EI-MS (70 eV): 166 (31, $[M-28]^+$), 109 (36), 95 (100), 93 (39), 81 (62), 79 (62), 67 (51), 55 (45), 43 (45), 41 (58).

Data of Ethenyl 8-Methyl-2-methylidenenon-4-en-1-yl Ether. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.90 (*d*, *J* = 6.8, Me$_2$C(8)); 1.24–1.35 (*m*, CH$_2$(7)); 1.51–1.61 (*m*, H–C(8)); 2.03–2.07 (*m*, CH$_2$(3)); 2.79 (br. *s*, CH$_2$(3)); 4.04 (*dd*, *J* = 1.8, 6.5, H$_a$–C(2′)); 4.17 (br. *s*, CH$_2$(1)); 4.25 (*dd*, *J* = 1.8, 14.1, H$_a$–C(2′)); 4.98 4.99 (*m*, 1 H of CH$_2$=C(2)); 5.07–5.09 (*m*, 1 H of CH$_2$=C(2)); 5.39 – 5.54 (*m*, H–C(4), H–C(5)); 6.47 (*dd*, *J* = 6.5, 14.1, H–C(1′)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.9 (*q*, *Me*$_2$C(8)); 27.9 (*d*, C(8)); 30.6 (*t*, C(6)); 36.9 (*t*, C(3)); 39.0 (*t*, C(7)); 71.2 (*t*, C(1)); 87.5 (*t*, C(2′)); 112.8 (*t*, *C*H$_2$=*C*(2)); 126.7 (*d*, C(4)); 133.7 (*d*, C(5)); 144,5 C(2)); 152.0 (*d*, C(1′)). EI-MS (70 eV): 107 (23), 96 (72), 95 (94), 93 (49), 81 (74), 79 (100), 67 (65), 55 (59), 43 (57), 41 (84).

9-Methyl-4,6-dimethylidenedecanal (**39**). From compound **38** as described for **10**. Yield: 59% (contains 11% (6*E*)-10-methyl-4-methylideneundec-6-enal). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.90 (*d*, *J* = 6.6, Me$_2$C(9)); 1.29–1.35 (*m*, CH$_2$(8)); 1.50–1.60 (*m*, H–C(9)); 1.98 br. *t*, *J* = 7.3, CH$_2$(7)); 2.34 (br. *t*, *J* = 7.3, CH$_2$(3)); 2.59 (*dt*, *J* = 1.8, 7.3, CH$_2$(2)); 2.79 (br. *s*, CH$_2$(5)); 4.77–4.79 (*m*, 1 H of CH$_2$=C(6)); 4.82 4.84 (*m*, 1 H of CH$_2$=C(6), 1 H of CH$_2$=C(4)); 4.86–4.88 (*m*, 1 H of CH$_2$=C(4)); 9.78 (*t*, *J* = 1.8, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 23.0 (*q*, *Me*$_2$(9)); 27.8 (*t*, C(3)); 28.2 (*d*, C(9)); 33.4 (*t*, C(7)); 37.4 (*t*, C(8)); 42.2 (*t*, C(2)); 44.6 (*t*, C(5)); 111.7 (*t*, *C*H$_2$=*C*(6)); 112.5 (*t*, *C*H$_2$=*C*(4)); 145.7 (*s*, C(4)); 147.7 (*s*, C96)); 202.5 (*d*, C(1)). EI-MS (70 eV): 194 (0.1, M^+), 123 (36), 109 (91), 96 (100), 95 (71), 81 (72), 79 (56), 67 (40), 55 (43), 41 (53).

Data of 10-Methyl-4-methylideneundec-6-enal. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.89 (*d*, *J* = 6.6, Me$_2$C(10)); 1.23–1.34 (*m*, CH$_2$(9)); 1.50–1.60 (*m*, H–C(10)); 2.00–2.06 (*m*, CH$_2$(8)); 2.34–2.35 (*m*, CH$_2$(3)); 2.56–2.60 (*m*, CH$_2$(2)); 2.73 (br. *s*, CH$_2$(5)); 4.74–4.75 (*m*, 1 H of H$_2$C=C(4)); 4.83–4.85 (*m*, 1 H of CH$_2$=C(4)); 5.36–5.52 (*m*, H–C(6), H–C(7)); 9.79 (*t*, *J* = 1.8, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.9 (*q*, *Me*$_2$C(10)); 27.9 (*d*, C(10)); 28.3 (*t*, C(3)); 30.8 (*t*, C(8)); 39.1 (*t*, C(9)); 40.3 (*t*, C(5)); 42.2 (*t*, C(2)); 111.7 (*t*, *C*H$_2$=*C*(4)); 127.3 (*d*, C(6)); 133.5 (*d*, C(7)); 147.4 (*s*, C(4)); 201.3 (*d*, C(1)). EI-MS (70 eV): 194 (0.2, M^+), 150 (17), 133 (15), 119 (16), 109 (55), 95 (78), 81(95), 79 (82), 55 (78), 41 (100). Odor: aldehydic, fatty, straw like, metallic.

3,6-Dimethyl-4-methylideneheptanal (**40**). From 4-methylpent-1-yne and but-2-en-1-ol as described for **35**. Yield: 80% (contains 15% 3,7-dimethyloct-4-enal). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.90 (*d*, *J* = 6.6, Me–C(6)); 0.91 (*d*, *J* = 6.6, Me–C(6)); 1.11 (*d*, *J* = 6.8, Me–C(3)); 1.75–1.85 (*m*, H–C(6)); 1.85–1.99 (*m*, CH$_2$(5)); 2.39 (*ddd*, *J* = 2.3, 7.1, 16.2, H$_a$–C(2)); 2.59 (*ddd*, *J* = 2.3, 6.6, 16.2, H$_b$–C(2)); 2.62–2.78 (*m*, H–C(3)); 4.71 (*dt*, *J* = 1.3, 1.3, 1 H of CH$_2$=C(4)); 4.83 (br. *s*, 1 H of CH$_2$=C(4)); 9.73 (*t*, *J* = 2.3, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 20.5 (*q*, *Me*–C(3)); 22.9 (*q*, *Me*–C(6)); 23.0 (*q*, *Me*–C(6)); 26.6 (*d*, C(6)); 34.0 (*d*, C(3)); 45.0 (*t*, C(5)); 49.8 (*t*, C(2)); 110.2 (*t*, H$_2$*C*=*C*(3)); 152.0 (*s*, C(3)); 202.0 (*d*, C(1)). EI-MS (70 eV): 154 (0.8, M^+), 136 (2, $[M-18]^+$), 112 (33, $[M-42]^+$), 111 (28), 110 (29), 83 (74), 70 (73), 69 (78), 55 (76), 41 (100).

Data of 3,7-Dimethyloct-4-enal. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.87 (*d*, *J* = 6.6, Me–C(7)); 0.87 (*d*, *J* = 6.6, Me–C(7)); 1.08 (*d*, *J* = 6.8, Me–C(3)); 1.54–1.56 (*m*, H–C(7)); 5.35 (*dd*, *J* = 7.1, 15.4, H–C(4)); 5.45 (*dd*, *J* = 7.1, 15.4, H–C(5)); 9.74 (*t*, *J* = 3.0, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 20.3 (*q*, *Me*–C(3)); 22.6 (*q*, *Me*–C(7)); 22.6 (*q*, *Me*–C(7)); 26.6 (*d*, C(7)); 32.1 (*d*, C(3)); 40.8 (*t*, C(6)); 50.9 (*t*, C(2)); 129.0 (*d*, C(5)); 135.4 (*d*, C(4)); 203.0 (*d*, C(1)). EI-MS (70 eV): 154 (1, M^+), 139 (10), 111 (20), 98 (47), 97 (55), 83 (24), 69 (62), 55 (99), 43 (56), 41 (100). Odor: aldehydic, citrus, sweaty, fruity, swimming pool.

3,6-Dimethyl-2,4-dimethylideneheptanal (**41**). From **40** as described for **7**. Yield: 56% (contains 14% 3,7-dimethyl-2-methylideneoct-4-enal). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.87 (*d*, *J* = 6.3, Me–C(6)); 0.88 (*d*, *J* = 6.3, Me–C(6)); 1.18 (*d*, *J* = 7.1, Me–C(3)); 1.75–1.91 (*m*, CH$_2$(5), H–C(6)); 3.35 (br. *q*, *J* = 7.1, H–C(3)); 4.87 (br. *s*, CH$_2$=C(4)); 6.06 (*s*, 1 H of CH$_2$=C(2)); 6.27 (*s*, 1 H of CH$_2$=C(2)); 9.58 (*s*, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 19.2 (*q*, *Me*–C(3)); 22.6 (*q*, *Me*$_2$C(6)); 26.5 (*d*, C(6)); 36.4 (*d*, C(3)); 45.8 (*t*, C(5)); 111.2 (*t*, *C*H$_2$=*C*(4)); 134.0 (*t*, *C*H$_2$=*C*(2)); 150.6 (*s*, C(2)); 154.0 (*s*, C(4)); 194.4 (*d*, C(1)). EI-MS (70 eV): 166 (0.8, M^+), 151 (9, [$M-15$]$^+$), 123 (100, [$M-43$]$^+$), 109 (39), 95 (49), 83 (48), 67 (34), 55 (37), 43 (33), 41 (48).

Data of 3,7-Dimethyl-2-methylideneoct-4-enal. ^{1}H-NMR (400 MHz, CDCl$_3$): 1.17 (*d*, $J=7.1$, Me–C(3)); 1.55–1.66 (*m*, H–C(7)); 3.38 (*dq*, $J=6.3$, 7.1, H–C(3)); 5.38–5.51 (*m*, H–C(4), H–C(5)); 5.99 (*s*, 1 H of CH$_2$=C(2)); 6.24 (*s*, 1 H of CH$_2$=C(2)); 9.55 (*s*, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 19.6 (*q*, *Me*–C(3)); 22.6 (*q*, *Me*$_2$C(7)); 28.8 (*d*, C(7)); 34.7 (*d*, C(3)); 42.3 (*t*, C(6)); 129.6 (*d*, C(5)); 133.4 (*t*, *C*H$_2$=*C*(2)); 133.6 (*d*, C(4)); 150.6 (*s*, C(2)); 194.4 (*d*, C(1)). EI-MS (70 eV): 151 (2, [$M-15$]$^+$), 123 (9, [$M-43$]$^+$), 109 (100), 95 (26), 81 (41), 79 (20), 67 (28), 55 (29), 43 (20), 41 (34). Odor: minty, agrestic, aldehydic, green, metallic.

3,7-Dimethyl-4-methylideneoctanal (**42**). From **33** and but-2-en-1-ol as described for **35**. Yield: 86% (contains 13% 3,8-dimethylnon-4-enal). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.92 (*d*, $J=6.6$, Me$_2$C(7)); 1.11 (*d*, $J=7.1$, Me–C(3)); 1.31–1.37 (*m*, CH$_2$(6)); 1.51–1.62 (*m*, H–C(7)); 2.02–2.06 (*m*, CH$_2$(5)); 2.39 (*ddd*, $J=$ 2.3, 7.8, 16.4, H$_a$–C(2)); 2.58 (*ddd*, $J=2.3$, 6.6, 16.4, H$_b$–C(2)); 2.69–2.77 (*m*, H–C(3)); 4.78 (br. *s*, 1 H of CH$_2$=C(4)); 4.80 (br. *s*, 1 H of CH$_2$=C(4)); 9.72 (*dd*, $J=2.3$, 2.3, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 20.6 (*q*, *Me*–C(3)); 22.9 (*q*, *Me*$_2$C(7)); 28.3 (*d*, C(7)); 32.6 (*t*, C(5)); 34.6 (*d*, C(3)); 37.7 (*t*, C(6)); 49.8 (*t*, C(2)); 108.0 (*t*, H$_2$*C*=*C*(4)); 153.6 (*s*, C(4)); 202.9 (*d*, C(9)). EI-MS (70 eV): 168 (0.8, M^+), 126 (11, [$M-42$]$^+$), 111 (17), 109 (15), 107 (17), 83 (48), 70 (100), 69 (56), 55 (92), 41 (86).

Data of 3,8-Dimethylnon-4-enal. ^{1}H-NMR (400 MHz, CDCl$_3$; selected signals): 0.88 (*d*, $J=6.6$, Me$_2$C(8)); 1.07 (*d*, $J=6.6$, Me–C(3)); 1.20–1.26 (*m*, CH$_2$(7)); 1.50–1.57 (*m*, H–C(8)); 5.33–5.49 (*m*, H–C(4), H–C(5)); 9.73 (*dd*, $J=2.3$, 2.3, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 21.1 (*q*, *Me*–C(3)); 23.0 (*q*, *Me*$_2$C(8)); 27.9 (*d*, C(8)); 30.7 (*t*, C(6)); 32.0 (*d*, C(3)); 37.7 (*t*, C(7)); 50.9 (*t*, C(2)); 130.5 (*d*, C(5)); 134.0 (*d*, C(4)); 203.2 (*d*, C(1)). EI-MS (70 eV): 168 (0.6, M^+), 124 (11), 111 (22), 109 (8), 107 (9), 97 (75), 69 (69), 55 (100), 43 (53), 41 (92). Odor: fruity, orange, metallic, sweet, floral, rubbery.

3,7-Dimethyl-2,4-dimethylideneoctanal (**43**). From **42** as described for **7**. Yield: 57% (contains 13% 3,8-dimethyl-2-methylidenenon-4-enal). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.88 (*d*, $J=6.6$, Me–C(7)); 0.89 (*d*, $J=6.6$, Me–C(7)); 1.19 (*d*, $J=7.1$, Me–C(3)); 1.29–1.35 (*m*, CH$_2$(6)); 1.46–1.49 (*m*, H–C(7)); 1.88–2.05 (*m*, CH$_2$(5)); 3.39 (br. *q*, $J=7.1$, H–C(3)); 4.82 (br. *s*, 1 H of CH$_2$=C(4)); 4.88 (br. *s*, 1 H of CH$_2$=C(4)); 6.06 (*s*, 1 H of CH$_2$=C(2)); 6.26 (*s*, 1 H of CH$_2$=C(2)); 9.58 (*s*, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$):19.1 (*q*, *Me*–C(3)); 23.0 (*q*, *Me*$_2$C(7)); 28.2 (*d*, C(7)); 33.7 (*t*, C(5)); 37.6 (*t*, C(6)); 109.1 (*t*, *C*H$_2$=*C*(4)); 134.0 (*t*, *C*H$_2$=*C*(2)); 152.2 (*s*, C(4)); 154.0 (*s*, C(2)); 194.5 (*d*, C(1)). EI-MS (70 eV): 165 (5, [$M-15$]$^+$), 123 (100), 109 (99), 95 (68), 91 (34), 81 (55), 67 (48), 55 (62), 41 (71), 39 (39).

Data of 3,8-Dimethyl-2-methylidenenon-4-enal: ^{1}H-NMR (400 MHz, CDCl$_3$, selected signals): 0.88 (*d*, $J=6.6$, Me–C(8)); 0.89 (*d*, $J=6.6$, Me–C(8)); 1.16 (*d*, $J=7.1$, Me–C(3)); 5.40–5.51 (*m*, H–C(4), H–C(5)); 5.99 (*s*, 1 H of H$_2$C=C(2)); 6.24 (br. *s*, 1 H of H$_2$C=C(2)); 9.55 (*s*, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 19.6 (*q*, *Me*–C(3)); 22.8 (*q*, *Me*$_2$C(8)); 27.9 (*d*, C(8)); 30.7 (*t*, C(6)); 34.6 (*d*, C(3)); 39.0 (*t*, C(7)); 131.0 (*d*, C(5)); 132.2 (*d*, C(4)); 133.5 (*t*, H$_2$*C*=*C*(2)); 154.8 (*s*, C(2)); 194.5 (*d*, C(1)). EI-MS (70 eV): 165 (2, [$M-15$]$^+$), 109 (100), 95 (23), 91 (14), 81 (52), 77 (17), 67 (25), 55 (35), 41 (42), 39 (20). Odor: green, metallic, slightly fruity, slightly floral.

5,9-Dimethyl-4,6-dimethylidenedecanal (**44**). From 3,7-dimethyl-4-methylidene-2-(vinyloxymethyl)-oct-1-ene as described for **10**. Yield: 48% (contains 13% 5,10-dimethyl-4-methylideneundec-6-enal). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.89 (*d*, $J=6.6$, Me–C(9)); 0.90 (*d*, $J=6.6$, Me–C(9)); 1.18 (*d*, $J=7.1$, Me–C(5)); 1.29–1.35 (*m*, CH$_2$(8)); 1.49–1.59 (*m*, H–C(9)); 1.87–2.00 (*m*, CH$_2$(7)); 2.23–2.37 (*m*, CH$_2$(3)); 2.56–2.60 (*m*, CH$_2$(2)); 2.85 (br. *q*, $J=7.1$, H–C(5)); 4.81 (br. *s*, 1 H of CH$_2$=C(6)); 4.84 (br. *s*, 1 H of CH$_2$=C(6), 1 H of CH$_2$=C(4)); 4.93 (br. *s*, 1 H of CH$_2$=C(4)); 9.77 (*t*, $J=1.8$, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$):18.7 (*q*, *Me*–C(5)); 22.9 (*q*, *Me*–C(9)); 23.1 (*q*, *Me*–C(9)); 26.4 (*t*, C(3)); 28.3 (*d*, C(9)); 32.2 (*t*, C(7)); 37.8 (*t*, C(8)); 42.5 (*t*, C(2)); 46.8 (*d*, C(5)); 109.5 (*t*, *C*H$_2$=*C*(6)); 110.2 (*t*, *C*H$_2$=*C*(4)); 150.6 (*s*, C(4)); 152.5 (*s*, C(6)); 202.7 (*d*, C(1)). MS (70 eV): 165 (11), 164 (11, [$M-44$]$^+$), 137 (52), 123 (66), 109 (70), 95 (100), 93 (80), 81 (52), 55 (51), 41 (62).

Data of 5,10-Dimethyl-4-methylideneundec-6-enal. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.89 (*d*, $J=6.6$, Me–C(10)); 0.90 (*d*, $J=6.6$, Me–C(10)); 1.14 (*d*, $J=6.8$, Me–C(5)); 1.22–1.28 (*m*, CH$_2$(8), CH$_2$(9)); 2.77

(br. *dq*, J=7.1, 6.8, H–C(5)); 4.72–4.73 (*m*, 1 H of CH$_2$=C(4)); 4.86–4.87 (*m*, 1 H of CH$_2$=C(4)); 5.32 (*dddd*, J=1.3, 1.3, 7.3, 15.2, H–C(6)); 5.45 (*dddd*, J=0.8, 6.6, 6.6, 15.2, H–C(7)); 9.78 (*t*, J=1.8, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 19.7 (*q*, *Me*–C(5)); 22.9 (*q*, *Me*$_2$C(10)); 26.7 (279 (*t*, C(3)); 27.9 (*d*, C–10); 30.7 (*t*, C(8)); 39.1(*t*, C(9)); 43.4 (*d*, C(5)); 46.7 (*t*, C(2)); 108.9 (*t*, H$_2$*C*=*C*(4)); 130.7 (*d*, C(7)); 133.9 (*d*, C(6)); 202.7 (*d*, C(1)). EI-MS (70 eV): 165 (7), 123 (22), 109 (50), 95 (76), 93 (71), 82 (100), 81 (52), 67 (49), 55 (59), 41 (64). Odor: aldehydic, metallic, mandarin, coriander.

5,8-Dimethyl-4,6-dimethylidenenonanal (**45**). From 3,6-dimethyl-2,4-dimethylideneheptyl ethenyl ether as described for **10**. Yield: 71% (contains 13% 5,9-dimethyl-4-methylidenedec-6-enal). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.88 (*d*, J=6.3, Me–C(8)); 0.90 (*d*, J=6.3, Me–C(8)); 1.18 (*d*, J=7.1, Me–C(5)); 1.73–1.93 (*m*, CH$_2$(7), H–C(8)); 2.33–2.39 (*m*, CH$_2$(3)); 2.59 (*dd*, J=1.8, 7.6, CH$_2$(2)); 2.81 (br. *q*, J=7.1, H–C(5)); 4.80 (*s*, 1 H of CH$_2$=C(6)); 4.84 (*s*, 1 H of CH$_2$=C(4)); 4.89 (*s*, 1 H of CH$_2$=C(6)); 4.93 (*s*, 1 H of CH$_2$=C(4)); 9.77 (*t*, J=1.8, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$):18.7 (*q*, *Me*–C(5)); 22.8 (*q*, *Me*–C(8)); 23.2 (*q*, *Me*–C(8)); 26.2 (*t*, C(3)); 26.6 (*d*, C(8)); 42.5 (*t*, C(2)); 44.7 (*t*, C(7)); 46.4 (*d*, C(5)); 110.3 (*t*, *C*H$_2$=*C*(4)); 110.9 (*t*, H$_2$*C*=*C*(6)); 150.6 (*s*, C(4)); 152.0 (*s*, C(6)); 202.7 (*d*, C(1)). EI-MS (70 eV): 179 (9, [$M-15$]$^+$), 137 (95), 107 (95), 95 (100), 93 (82), 91 (56), 81 (82), 67 (54), 55 (63), 41 (87).

Data of 5,9-Dimethyl-4-methylidenedec-6-enal. ^{1}H-NMR (400 MHz, CDCl$_3$, selected signals): 0.88 (*d*, J=6.3, Me–C(9)); 0.90 (*d*, J=6.3, Me–C(9)); 1.15 (*d*, J=6.8 Me–C(5)); 4.73–4.74 (*m*, 1 H of CH$_2$=C(4)); 4.87–4.88 (*m*, 1 H of CH$_2$=C(4)); 5.31 (*dddd*, J=1.0, 1.0, 7.6, 15.2, H–C(7)); 5.44 (*ddd*, J=0.75, 7.1, 7.1, H–C(6)); 978 (*t*, J=1.8, H–C(1)). EI-MS (70 eV): 179 (5, [$M-15$]$^+$), 109 (73), 107 (82), 95 (100), 93 (82), 81 (78), 79 (74), 67 (72), 55 (91), 41 (99). Odor: aldehydic, green, slightly fatty, floral.

*(4*E*)-5-[4-(*tert*-Butyl)phenyl]pent-4-enal* (**46**). By-product of the condensation of 1-(*tert*-butyl)-4-ethynylbenzene with **34** as described for **35**. Yield: 3%. ^{1}H-NMR (400 MHz, CDCl$_3$): 1.35 (*s*, Me$_3$C(7′)); 2.58 (*ddt*, J=1.5, 6.3, 6.8, CH$_2$(3)); 2.65 (*dt*, J=1.5, 7.6, CH$_2$(2)); 6.21 (*dt*, J=15.7, 6.3, H–C(4)); 6.46 (br. *d*, J=15.7, H–C(5)); 7.32 (*d*, J=8.8, H–C(2′), H–C(6′)); 7.37 (*d*, J=8.8, H–C(3′), H–C(5′)); 9.85 (*d*, J=1.5, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 26.0 (*t*, C(3)); 31.7 (*q*, *Me*$_2$C(7′)); 34.9 (*s*, C(7)); 43.8 (*t*, C(2)); 125.9 (*d*, C(3′), C(5′)); 126.2 (*d*, C(2′), C(6′)); 127.8 (*d*, C(4)); 131.3 (*d*, C(5)); 134.9 (*s*, C(1′)); 150.7 (*s*, C(4′)); 202. (*d*, C(1)). EI-MS (70 eV): 216 (14, M^+), 201 (100), 1445 (53), 131 (33), 129 (38), 128 (3), 117 (15), 115 (30), 91 (17), 57 (31). Odor: aldehydic, green, fatty, citrus, orange, coriander.

*4-[4-(*tert*-Butyl)phenyl]pent-4-enal* (**47**). From 1-(*tert*-butyl)-4-ethynylbenzene and **34** as described for **35**. Yield: 16%. ^{1}H-NMR (400 MHz, CDCl$_3$): 1.36 (*s*, Me$_3$C(7′)); 2.65 (*dt*, J=1.5, 7.6, CH$_2$(2)); 2.88 br. *t*, J=7.6, CH$_2$(3)); 5.08–5.10 (*m*, 1 H of CH$_2$=C(4)); 5.36 (br. *s*, 1 H of CH$_2$=C(4)); 7.37 (*d*, J=8.8, H–C(2′), H–C(6′)); 7.40 (*d*, J=7.8, H–C(3′), H–C(5′)); 9.82 (*d*, J=1.5, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 28.0 (*t*, C(3)); 31.7 (*q*, *Me*$_3$C(7′)); 34.9 (*s*, C(7′)); 42.9 (*t*, C(2)); 112.7 (*t*, *C*H$_2$=*C*(4)); 125.8 (*d*, C(3′), C(5′)); 126.1 (*d*, C(2′), C(6′)); 137.7 (*d*, C(1′)); 146.7 (*s*, C(4)); 151.2 (*s*, C(4′)); 202.4 (*d*, C(1)). EI-MS (70 eV): 201 (6, [$M-15$]$^+$), 174 (40), 173 (13), 160 (28), 159 (100), 131 (32), 129 (15), 128 (18), 115 (17), 91 (13).Odor: aldehydic, green, floral, fatty, weak.

1-Ethynyl-3,3,5-trimethylcyclohexanol (**49**). *3,3,5-Trimethylcyclohexanone* (**48**; 4.0 g, 29 mmol) was added dropwise to a 0.5M EtMgBr soln. (63 ml, 32 mmol) at 5°. The mixture was stirred for 3 h, and the temp. was allowed to rise to r.t. The mixture was poured onto ice-cold, sat. NH$_4$Cl soln. (100 ml). ^{t}BuOMe was added (150 ml). The org. phase was washed with H$_2$O (2 × 80 ml) and brine (80 ml), dried (MgSO$_4$), and filtered. The solvent was evaporated under reduced pressure. The crude product was subjected to bulb-to-bulb distillation (100°/10 mbar) to yield 3.0 g (18 mmol) of a colorless liquid (purity: 78%; yield: 49%). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.83 (*dd*, J=12.6, 12.6, H$_a$–C(4)), 0.91 (*d*, J=5.3, Me–C(5)); 0.92 (*s*, Me–C(3)); 1.10 (*s*, Me–C(3)); 1.26 (*dd*, J=12.9, 13.1, H$_a$–C(6)); 1.43 (*dddd*, J=2.0, 2.0, 3.0, 13.1, H$_b$–C(6)); 1.52 (*d*, J=14.4, H$_a$–C(2)); 1.79 (*ddd*, J=2.3, 2.3, 14.4, H$_b$–C(2)); 1.91–2.04 (*m*, H$_b$–C(4), H–C(5)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.5 (*q*, *Me*–C(5)); 23.9 (*q*, *Me*$_2$C(3)); 27.7 (*s*, C(5)); 31.6 (*s*, C(3)); 47.6 (*t*, C(6)); 48.2 (*t*, C(4)); 50.3 (*t*, C(2)); 68.6 (*s*, C(1)); 70.0 (*s*, C(2′)); 90.1 (*s*, C(1′)). EI-MS (70 eV): 166 (2, M^+), 151 (21), 133 (25), 123 (18), 109 (100), 95 (85), 83 (35), 55 (31), 53 (28), 41 (29).

1-Ethynyl-3,5,5-trimethylcyclohexene (**50**). Compound **49** (3.0 g, 78%;13.9 mmol) was dissolved in pyridine (30 ml) and cooled to 0°. POCl$_3$ (3.2 g, 21 mmol) was added dropwise. The mixture was stirred for 16 h, while allowing the temp. to rise to r.t. The mixture was poured onto ice-cold 2N HCl. Hexane (100 ml) was added. The org. layer was washed with 2N HCl (2 × 50 ml), sat. NaHCO$_3$ soln. (50 ml), H$_2$O

(2 × 60 ml), and brine (60 ml). The soln. was dried ($MgSO_4$) and filtered: The solvent was evaporated under reduced pressure. The crude product was subjected to bulb-to-bulb distillation (80°/10 mbar) and further purified *via* CC to afford 0.8 g (5 mmol) of a colorless liquid (yield: 39%; contains 28% 1-ethynyl-3,3,5-trimethylcyclohex-1-ene). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.97 (*d*, *J* = 6.6, Me–C(3)); 1.01 (*s*, Me–C(5)); 1.02 (*s*, Me–C(5)); 1.07 (*m*, H_a–C(4)); 1.45–1.50 (*m*, H_b–C(4)); 1.72 (*dd*, *J* = 2.5, 16.2, H_a–C(6)); 1.75–1.85 (*m*, H–C(3)); 2.14–2.19 (*m*, H_b–C(6)); 2.80 (*s*, H–C(2′)); 5.94 (*m*, H–C(2)). ^{13}C-NMR (400 MHz, $CDCl_3$): 22.3 (*q*, *Me*–C(3)); 26.1 (*q*, *Me*–C(5)); 28.9 (*d*, C(3)); 31.0 (*q*, *Me*–C(5)); 34.1 (*s*, C(5)); 38.1 (*t*, C(6)); 45.6 (*t*, C(4)); 74.8 (*s*, C(2′)); 85.9 (*s*, C(1′)); 117.7 (*s*, C(1)); 146.3 (*d*, C(2)). EI-MS (70 eV): 148 (41, M^+), 133 (100, $[M-15]^+$), 119 (10), 117 (11), 115 (13), 106 (13), 105 (54), 91 (55), 77 (14), 41 (14).

Data of 1-Ethynyl-3,3,5-trimethylcyclohex-1-ene. ^{1}H-NMR (400 MHz, $CDCl_3$, selected signals): 1.70 (*dd*, *J* = 2.5, 16.4, H_a–C(6)); 1.97–2.03 (*m*, H_b–C(6)); 2.79 (*s*, H–C(2′)); 6.03–6.05 (*m*, H–C(2)). ^{13}C-NMR (400 MHz, $CDCl_3$): 21.4 (*q*, *Me*$_2$C(5)); 25.5 (*q*, *Me*–C(3)); 29.3 (*d*, C(5)); 30.2 (*s*, C(3)); 32.0 (*q*, *Me*–C(3)); 42.9 (*t*, C(6)); 44.3 (*t*, C(4)); 74.6 (*s*, C(2′)); 86.1 (*s*, C(1′)); 118.4 (*s*, C(1)); 141.3 (*d*, C(2)). EI-MS (70 eV): 148 (42, M^+), 133 (75, $[M-15]^+$), 119 (21), 117 (11), 115 (13), 105 (47), 91 (100), 83 (21), 77 (19), 41 (16).

4-(3,5,5-Trimethylcyclohex-1-en-1-yl)pent-4-enal (**51**). From **50** as described for **35**: Yield: 44% (contains 23% 4-(3,3,5-trimethylcyclohex-1-en-1-yl)pent-4-enal, and 8% 5-(3,5,5-trimethylcyclohex-1-en-1-yl)pent-4-enal, and 5-(3,3,5-trimethylcyclohex-1-en-1-yl)pent-4-enal). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.00–1.04 (*m*, Me–C(3′), $Me_2C(5′)$, H_a–C(4′)); 1.46–1.51 (*m*, H_b–C(4′)); 2.02 (*dd*, *J* = 2.0, 16.2, H_a–C(6′)); 1.73–1.84 (*m*, H–C(3′)); 2.25 (br. *dd*, *J* = 4.0, 16.2, H_b–C(6′)); 2.60–2.64 (*m*, $CH_2(2)$, $CH_2(3)$); 4.86 (*s*, 1 H of CH_2=C(4)); 5.05 (*s*, 1 H of CH_2=C(4)); 5.55 (br. *s*, H–C(2′)); 9.80 (*m*, H–C(1)). ^{13}C-NMR (400 MHz, $CDCl_3$): 22.8 (*q*, *Me*–C(3′)); 26.5 (*t*, C(3)); 29.3 (*q*, *Me*$_2$C(5′)); 32.6 (*d*, C(3′)); 33.8 (*s*, C(5′)); 35.7 (*t*, C(6′)); 40.4 (*t*, C(2)); 43.5 (*t*, C(4′)); 110.6 (*t*, H_2*C*=*C*(4)); 124.8 (*s*, C(1′)); 130.0 (*d*, C(2′)); 133.0 (*s*, C(4)); 202.7 (*d*, C(1)). EI-MS (70 eV): 206 (20, M^+), 191 (17, $[M-15]^+$), 173 (55, $[M-33]^+$), 164 (23), 150 (53), 149 (74), 121 (85), 107 (100), 105 (72), 91 (79). Odor: aldehydic, floral, green.

4-(3,3,5,5-Tetramethylcyclohex-1-en-1-yl)pent-4-enal (**54**). From 1-ethynyl-3,3,5,5-tetramethylcyclohex-1-ene and **34** as described for **35**. Yield: 56%. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.98 (*s*, $Me_2C(5′)$); 1.05 (*s*, $Me_2C(3′)$); 1.36 (*s*, $CH_2(4′)$); 1.91 (br. *d*, *J* = 1.5, $CH_2(6′)$); 2.60–2.68 (*m*, 4 H, $CH_2(2)$, $CH_2(3)$); 4.87 (br. *s*, 1 H of CH_2=C(4)); 5.03 (br. *s*, 1 H of CH_2=C(4)); 5.55–5.56 (*m*, H–C(2′)); 9.80–9.81 (*m*, H–C(1)). ^{13}C-NMR (400 MHz, $CDCl_3$): 26.7 (*t*, C(3)); 30.5 (*q*, *Me*–C(3′), *Me*–C(5′)); 32.0 (*q*, *Me*–C(3′), *Me*–C(5′)); 33.3 (*s*, C(5′)); 38.5 (*s*, C(3′)); 40.3 (*t*, C(6′)); 43.5 (*t*, C(2)); 49.8 (*t*, C(4′)); 110.7 (*t*, *H*$_2$C=C(4)); 132.1 (*s*, C(1′)); 134.0 (*d*, C(2′)); 147.1 (*s*, C(4′)); 202.7 (*d*, C(1)). EI-MS (70 eV): 220 (17), 177 (31), 161 (22), 137 (21), 135 (18), 121 (100), 107 (30), 105 (22), 91 (31), 41 (22). Odor: green, fruity, nutty.

*4-[(5*R*)-5-Methyl-2-(propan-2-yl)cyclohex-1-en-1-yl]pent-4-enal* (**55**). From (4*R*)-2-ethynyl-4-methyl-1-(propan-2-yl)cyclohexene and **34** as described for **35**: Yield: 7%. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.93 (*d*, *J* = 6.6, 6 H, Me–C(7′)); 0.85 (*d*, *J* = 7.1, Me–C(5′)); 1.11–1.20 (*m*, H_a–C(4′)); 1.59–1.76 (*m*, H_a–C(3′), H_b–C(4′), H–C(5′)); 1.90–2.11 (*m*, H_b–C(3′), $CH_2(6′)$); 2.43–2.55 (*m*, H–C(2), H–C(3)); 2.78 (*qq*, *J* = 6.6, 6.6, H–C(7′)); 4.71 (*m*, 1 H of CH_2=C(4)); 4.78 (*m*, 1 H of CH_2=C(4)). ^{13}C-NMR (400 MHz, $CDCl_3$): 21.3 (*q*, *Me*–C(7′)); 21.8 (*q*, *Me*–C(7′)); 22.1 (*q*, *Me*–C(5′)); 22.6 (*t*, C(3)); 28.6 (*t*, C(3′)); 29.4 (*d*, C(5′)); 30.8 (*d*, C(7′)); 31.6 (*t*, C(4′)); 39.0 (*t*, C(6′)); 42.2 (*t*, C(2)); 11.8 (*t*, *C*H$_2$=*C*(4)); 131.1 (*s*, C(1′)); 137.4 (*s*, C(2′)); 150.0 (*s*, C(4)); 202.6(*d*, C(1)). EI-MS (70 eV): 220 (13, M^+), 176 (43), 161 (100), 135 (57), 121 (77), 119 (72), 107 (91), 105 (87), 93 (71), 91(83). Odor: aldehydic, fruity, citrus.

4-(5-methyl-3-propylcyclohex-1-en-1-yl)pent-4-enal (**56**). From 1-ethynyl-5-methyl-3-propylcyclohexene and **34** as described for **35**. Yield: 3%. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.93 (*t*, *J* = 7.1, Me(9′)); 1.03 (*d*, *J* = 6.8, Me–C(5′)); 1.25–1.44 (*m*, H–C(3′), H_a–C(4′), $CH_2(7′)$, $CH_2(8′)$); 1.55–1.84 (*m*, H_b–C(4′), H–C(5′), $CH_2(6′)$); 2.62–2.63 (*m*, $CH_2(2)$, $CH_2(3)$); 4.86 (br. *s*, 1 H of CH_2=C(4)); 5.06 (*s*, 1 H of CH_2=C(4)); 5.68 (br. *s*, H–C(2′)); 9.80 (br. *s*, H–C(1)). ^{13}C-NMR (400 MHz, $CDCl_3$): 14.7 (*q*, C(9′)); 20.3 (*t*, C(8′)); 22.4 (*q*, *Me*–C(5′)); 26.5 (*t*, C(3)); 29.7 (*d*, C(5′)); 33.6 (*t*, C(6′)); 34.5 (*d*, C(3′)); 35.7 (*t*, C(4′)); 43.4 (*t*, C(2)); 110.4 (*t*, H_2*C*=*C*(4)); 130.1 (*d*, C(2′)); 135.9 (*s*, C(1′)); 146.8 (*s*, C(4)); 202.7 (*d*, C(1)). EI-MS (70 eV): 220 (15, M^+), 164 (100), 135 (49), 121 (38), 105 (61), 93 (84), 91 (88), 79 (54), 55 (73), 41 (59). Odor: aldehydic, green, fatty.

4-(5-Methyl-3-propylcyclohexa-1,5-dien-1-yl)pent-4-enal (**57**). From 3-ethynyl-1-methyl-5-propylcyclohexa-1,3-diene and **34** as described for **35**. Yield: 5%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.93 (*t*, $J = 7.1$, Me(9′)); 130–1.44 (*m*, CH$_2$(7′), CH$_2$(8′)); 1.65–1.8 (*m*, H$_a$–C(4′)); 1.80 (*t*, $J = 1.8$, Me–C(5′)); 1.87–20.9 (*m*, H–C(3′), H$_b$–C(4′)); 2.38–2.47 (*m*, CH$_2$(3)); 2.65–2.66 (*m*, CH$_2$(2)); 4.89 (br. *s*, 1 H of CH$_2$=C(4)); 4.92 (br. *s*, 1 H of CH$_2$=C(4)); 4.99 (br. *s*, H–C(2′)); 5.21 (*s*, H–C(6′)); 9.82 (*m*, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 14.7 (*q*, C(9′)); 20.4 (*t*, C(8′)); 21.9 (*q*, *Me*–C(5′)); 26.2 (*t*, C(3)); 30.9 (*t*, C(4′)); 34.4 (*d*, C(3′)); 37.0 (*t*, C(7′)); 43.7 (*t*, C(2)); 112.5 (*t*, H$_2$*C*=*C*(4)); 126.5 (*d*, C(6′)); 127.6 (*d*, C(2′)); 131.6 (*s*, C(1′)); 137.9 (*s*, C(5′)); 144.3 (*s*, C(4)); 202.4 (*d*, C(1)). EI-MS (70 eV): 218 (11, M^+), 200 (1, $[M-18]^+$), 176 (55, $[M-42]^+$), 133 (86), 119 (39), 105 (77), 91 (100), 77 (36), 55 (34), 41 (37). Odor: green, dusty, chocolate.

4-(4,4-Dimethylcyclohex-1-e **34** as described for **35**: Yield: 35% (contains 18% (4*E*)-5-(4,4-dimethylcyclohex-1-en-1-yl)pent-4-enal). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.92 (*s*, Me$_2$C(4′)); 1.42 (*t*, $J = 6.6$, CH$_2$(5′)); 1.92–1.95 (*m*, CH$_2$(3′)); 2.16–2.20 (*m*, CH$_2$(6′)); 260 (*s*, CH$_2$(2), CH$_2$(3)); 4.84 (*s*, 1 H of CH$_2$=C(4)); 5.03 (br. *s*, 1 H of CH$_2$=C(4)); 5.78–5.82 (*m*, H–C(2′)); 9.78 (br. *s*, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 23.8 (*t*, C(6′)); 26.0 (*t*, C(3)); 28.1 (*q*, *Me$_2$*C(4)); 28.4 (*s*, C(4′)); 35.6 (*t*, C(5′)); 39.7 (*t*, C(3′)); 43.1 (*t*, C(2′)); 109.7 (*t*, H$_2$*C*=*C*(4)); 123.8 (*d*, C(2′)); 134.0 (*s*, (C(1′)); 146.3 (*s*, C(4)); 202.3 (*d*, C(1)). EI-MS (70 eV): 192 (6, M^+), 150 (70, $[M-42]^+$), 107 (55), 93 (75), 92 (33), 91 (87), 79 (100), 77 (52), 41 (51), 29 (51). Odor: fatty floral.

4-(8,8-Dimethylspiro[2.5]oct-4-en-4-yl)pent-4-enal (**59**). From 4-ethynyl-8,8-dimethylspiro[2.5]oct-4-ene and **34** as described for **35**. Yield: 44%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.40 (*m*, H$_a$–C(7′), H$_a$–C(8′)); 0.64 (*m*, H$_b$–C(7′), H$_b$–C(8′)); 0.80 (*s*, Me$_2$C(5′)); 1.51 (*t*, $J = 6.6$, CH$_2$(4′)); 2.14 (*dt*, $J = 3.54$, 6.6, CH$_2$(3′)); 2.34 (br. *t*, $J = 7.3$, CH$_2$(3)); 2.54 (*dd*, $J = 1.8$, 6.8, CH$_2$(2)); 4.63–4.64 (*m*, 1 H of CH$_2$=C(4)); 4.77–4.78 (*m*, 1 H of CH$_2$=C(4)); 5.34 (*t*, $J = 3.54$, H–C(2′)); 9.78 (*t*, $J = 1.8$, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 7.9 (*t*, C(7′), C(8′)); 23.0 (*t*, C(3′)); 24.5 (*q*, *Me$_2$*C(5′)); 26.2 (*s*, C(6′)); 31.1 (*s*, C(1′)); 35.8 (*t*, C(4′)); 42.3 (*t*, C(2)); 113.1 (*t*, H$_2$*C*=*C*(4)); 123.5 (*d*, C(2′)); 142.7 (*s*, C(1′)); 147.5 (*s*, C(4)); 202.3 (*d*, C(1)). EI-MS (70 eV): 218 (1, M^+), 203 (19), 159 (41), 131 (62), 119 (59), 117 (56), 105 (80), 91 (100), 41 (48), 29 (50). Odor: straw, woody fruity, slightly *Kephalis* like.

5-Methylhex-1-yn-3-ol (**61**). From *3-methylbutanal* (**60**) as described for **49**. Yield: 84%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.94 (*d*, $J = 6.6$, Me–C(3)); 0.96 (*d*, $J = 6.6$, Me–C(3)); 1.59 (*ddd*, $J = 6.8$, 6.8, 13.4, H$_a$–C(2)); 1.66 (*ddd*, $J = 7.3$, 7.3 13.4, H$_b$–C(2)); 1.82–1.92 (*m*, H–C(3)); 2.47 (*d*, $J = 2.3$, H–C(2′)); 4.39–4.45 (*m*, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.8 (*q*, *Me*–C(3)); 22.9 (*q*, *Me*–C(3)); 25.1 (*d*, C(3)); 47.1 (*t*, C(2)); 61.1 (*d*, C(1)); 73.0 (*d*, C(2′)); 85.7 (*s*, C(1′)). EI-MS (70 eV): 97 (39), 79 (37), 77 (18), 70 (15), 57 (100), 56 (41), 55 (90), 41 (65), 39 (27), 29 (26).

6-Methylhepta-1,2-dien-4-ol (**62**). Compound **61** (10.8 g, 96 mmol) was dissolved in dioxane (120 ml). Paraformaldeyde (7.2 g, 241 mmol), CuBr (6.9 g, 48 mmol), and ^{i}Pr$_2$NH (20.5 g, 202 mmol) were added. The mixture was stirred under reflux for 1 h. The suspension was cooled to r.t. and filtered *via* a *Celite* pad. The filtrate was taken up in ^{t}BuOMe (200 ml) and washed with 2N HCl (80 ml), H$_2$O (3 × 80 ml), and brine (80 ml). The soln. was dried (MgSO$_4$) and filtered. The solvents were evaporated under reduced pressure. The crude product was subjected to bulb-to-bulb distillation (100°/10 mbar) to give 5.4 g (41 mmol) of a light yellow liquid (purity: 96%; yield: 43%). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.93 (*d*, $J = 6.8$, Me–C(3)); 0.93 (*d*, $J = 6.6$, Me–C(3)); 1.38 (*ddd*, $J = 5.8$, 7.8, 13.6, H$_a$–C(2)); 1.52 (*ddd*, $J = 6.6$, 8.1, 13.6, H$_b$–C(2)); 1.75–1.85 (*m*, H–C(3)); 4.22–4.28 (*m*, H–C(1)); 4.84–4.86 (*m*, CH$_2$(3′)); 5.24 (*ddd*, $J = 6.6$, 6.6, 6.6, H–C(1′)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.7 (*q*, *Me*–C(3)); 23.9 (*q*, *Me*–C(3)); 25.0 (*d*, C(3)); 47.0 (*t*, C(2)); 68.5 (*d*, C(1)); 77.7 (*t*, C(3′)); 95.5 (*d*, C(1′)); 207.4 (*s*, C(2′)). EI-MS (70 eV): 111 (6), 87 (26), 70 (23), 69 (100), 57 (7), 45 (11), 43 (27), 41 (35), 39 (20), 27 (5).

Ethenyl 6-Methylhepta-1,2-dien-4-yl ether (**63**). From **62** as described for **9**. Yield: 54% (purity: 94%). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.94 (*d*, $J = 6.8$, Me$_2$C(3)); 1.45 (*ddd*, $J = 5.8$, 7.3, 13.6, H$_a$–C(2)); 1.68 (*ddd*, $J = 6.6$, 7.8, 13.6, H$_b$–C(2)); 1.75–1.85 (*m*, H–C(3)); 4.05 (*dd*, $J = 1.5$, 6.6, H–C(2′)); 4.34 (*dd*, $J = 1.5$, 14.2, H–C(2′)); 4.30–4.34 (*m*, H–C(1)); 4.82 (*ddd*, $J = 1.5$, 6.3, 10.8, H$_a$–C(3′)); 4.86 (*ddd*, $J = 1.5$, 6.6, 10.9, H$_b$–C(3′)); 5.12 (*ddd*, $J = 6.6$, 6.6, 7.6, H–C(1′)); 6.38 (*dd*, $J = 6.6$, 14.2, H–C(1′)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.8 (*q*, *Me*–C(3)); 23.1 (*q*, *Me*–C(3)); 24.8 (*d*, C(3)); 44.6 (*t*, C(2)); 76.7 (*d*, C(1)); 76.8 (*t*, C(3)); 89.2 (*t*, C(2′)); 92.1 (*d*, C(1′)); 150.8 (*d*, C(1′)); 208.9 (*s*, C(2′)). EI-MS (70 eV): 137 (3, $[M-15]^+$), 109 (47), 96 (20), 81 (39), 67 (100), 55 (23), 53 (37), 43 (44), 41 (37), 39 (23).

(4E)-7-Methyl-3-methylideneoct-4-enal (**64**). **63** as described for **10**. Yield: 67%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.89 (*d*, *J* = 6.6, Me$_2$C(7)); 1.62 (*tqq*, *J* = 6.8, 6.6, 6.6, H–C(7)); 2.01 (*dd*, *J* = 6.8, 7.3, CH$_2$(6)); 3.25 (*dd*, *J* = 1.0, 2.5, CH$_2$(2)); 5.05 (br. *s*, 1 H of CH$_2$=C(3)); 5.20 (br. *s*, 1 H of CH$_2$=C(3)); 5.62 (*dt*, *J* = 15.9, 7.3, H–C(5)); 6.12 (br. *d*, *J* = 15.9, H–C(5)); 9.59 (*t*, *J* = 2.5, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$):22.6 (*q*, *Me*$_2$C(7)); 28.9 (*d*, C(7)); 42.5 (*t*, C(6)); 48.1 (*t*, C(2)); 118.4 (*t*, H$_2$*C*=*C*(3)); 132.0 (*d*, C(5)); 137.7 (*d*, C(4)); 137.9 (*s*, C(3)); 200.8 (*d*, C(1)). EI-MS (70 eV): 152 (16, M^+), 137 (10, $[M-15]^+$), 109 (48), 95 (83), 81 (100), 79 (68), 68 (42), 67 (73), 43 (35), 41 (52). Odor: Citral, citronellal, verbena, lemongrass.

(4E)-7,9,9-Trimethyl-3-methylidenedec-4-enal (**65**). From 4-(ethenyloxy)-6,8,8-trimethylnona-1,2-diene as described for **10**. Yield: 47%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.90 (*s*, Me$_3$C(9)); 0.92 (*d*, *J* = 6.8, Me–C(7)); 1.05 (*dd*, *J* = 6.6, 13.9, H$_a$–C(8)); 1.25 (*dd*, *J* = 3.54, 13.9, H$_b$–C(8)); 1.55 – 1.65 (*m*, (H–C(7)); 1.96 (*dddd*, *J* = 1.3, 7.3, 7.3, 18.9, H$_a$–C(6)); 2.11 (*dddd*, *J* = 1.3, 7.1 7.1, 18.9, H$_b$–C(6)); 3.25 (*d*, *J* = 2.5, CH$_2$(2)); 5.06 (br. *s*, 1 H of CH$_2$=C(3)); 5.21 (br. *s*, 1 H of CH$_2$=C(3)); 5.61 (*ddd*, *J* = 7.1, 7.5, 15.7, H–C(5)); 6.17 (br. *d*, 15.7, H–C(4)); 9.60 (*t*, *J* = 2.5, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.9 (*q*, *Me*–C(7)); 30.0 (*s*, C(7)); 30.4 (*q*, *Me*$_3$C(7)); 31.5 (*s*, C(9)); 43.1 (*t*, C(6)); 48.1 (*t*, C(8)); 50.9 (*t*, C(8)); 118.4 (*t*, *C*H$_2$=*C*(3)); 131.9 (*d*, C(4)); 132.1 (*d*, C(5)); 137.9 (*s*, C(3)); 200.8 (*d*, C(1)). EI-MS (70 eV): 208 (3, M^+), 175 (3), 137 (5), 110 (7), 109 (13), 95 (58), 81 (13), 79 (13), 57 (100), 41 (23). Odor: green, aldehydic, fatty, sappy, slightly citrus, slightly metallic.

(4E)/(4Z)-5,7-Dimethyl-3-methylideneoct-4-enal (**66**). From 4,6-dimethylhepta-1,2-dien-4-yl ethenyl ether as described for **10**. Yield: 90% (two isomers; (*E*)/(*Z*) 1:1). Odor: aldehydic, green, fatty, orange, mandarin. (*E*)-Isomer: ^{1}H-NMR (400 MHz, CDCl$_3$): 0.88 (*d*, *J* = 6.6, Me$_2$C(7)); 1.79 (*d*, *J* = 1.5, Me–C(5)); 1.80 – 1.90 (*m*, H–C(7)); 2.14 (*dd*, *J* = 1.0, 7.8, CH$_2$(6)); 3.16 (*dd*, *J* = 1.3, 2.5, CH$_2$(2)); 5.09 (br. *s*, 1 H of CH$_2$=C(3)); 5.15 (br. *s*, 1 H of CH$_2$=C(3)); 5.58 (br. *s*, H–C(4)); 9.63 (*t*, *J* = 2.5, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$):18.4 (*q*, *Me*–C(5)); 22.8 q, *Me*$_2$C(7)); 26.6 (*d*, C(7)); 50.6 (*t*, C(2)); 52.6 (*t*, C(6)); 118.1 (*t*, *C*H$_2$=*C*(3)); 126.2 (*d*, C(4)); 137.5 (*s*, C(3)); 140.2 (*s*, C(5)); 200.6 (*d*, C(1)). EI-MS (70 eV): 166 (2, M^+), 151 (14), 123 (43), 109 (100), 95 (39), 81 (31), 67 (26), 55 (15), 41 (20). (*Z*)-Isomer: ^{1}H-NMR (400 MHz, CDCl$_3$): 0.88 (*d*, *J* = 6.6, Me$_2$C(7)); 1.76 (*d*, *J* = 1.5, Me–C(5)); 1.80 – 1.90 (*m*, H–C(7)); 1.93 (*dd*, *J* = 1.0, 7.6, CH$_2$(6)); 3.13 (*dd*, *J* = 1.3, 2.5, CH$_2$(2)); 5.09 (br. *s*, 1 H of CH$_2$=C(3)); 5.11 (br. *s*, 1 H of CH$_2$=C(3)); 5.58 (br. *s*, H–C(4)); 9.63 (*t*, *J* = 2.5, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 22.9 (*q*, *Me*$_2$C(7)); 24.2 (*q*, *Me*–C(5)); 26.7 (*d*, C(7)); 41.8 (*t*, C(6)); 52.8 (*t*, C(2)); 118.0 (*t*, *C*H$_2$=*C*(3)); 126.2 (*d*, C(4)); 137.6 (*s*, C(3)); 140.2 (*s*, C(5)); 200.6 (*d*, C(1)). EI-MS (70 eV): 166 (2, M^+), 151 (15), 123 (39), 109 (100), 95 (29), 81 (29), 67 (26), 55 (15), 41 (18).

(4E)-7,11-Dimethyl-3-methylidenedodec-4-enal (**67**). From 6,10-dimethylundeca-1,2-dien-4-yl ethenyl ether as described for **10**. Yield: 78%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.87 (*d*, *J* = 6.8, Me–C(11)); 0.89 (*d*, *J* = 6.8, Me–C(11)); 0.89 (*d*, *J* = 7.3, Me–C(7)); 1.08 (*m*, CH$_2$(8), CH$_2$(9), CH$_2$(10)); 1.48 (*m*, H–C(7), H–C(11)); 1.91 – 1.98 (*m*, H$_a$–C(6)); 2.10 – 2.18 (*m*, H$_b$–C(6)); 3.26 (*dd*, *J* = 1.0, 2.5, CH$_2$(2)); 5.06 (br. *s*, 1 H of H$_2$C=C(3)); 5.20 (br. *s*, 1 H of H$_2$C=C(3)); 5.63 (*ddd*, *J* = 7.3, 8.3, 15.7, H–C(5)); 6.18 (br. *d*, *J* = 15.7, H–C(4)); 9.63 (*t*, *J* = 2.5, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 1.92 (*q*, *Me*–C(7)); 23.0 (*q*, *Me*–C(11)); 23.1 (*q*, *Me*–C(11)); 25.2 (*t*, C(9)); 28.4 (*d*, C(11)); 33.6 (*d*, C(7)); 33.6 (*t*, C(8)); 37.3 (*t*, C(6)); 39.6 (*t*, C(10)); 48.2 (*t*, C(2)); 118.4 (*t*, H$_2$*C*=*C*(3)); 132.0 (*d*, C(4)); 137.6 (*s*, C(3)); 140.2 (*s*, C(5)); 200.6 (*d*, C(1)). EI-MS (70 eV): 222 (2, M^+), 137 (12), 109 (29), 96 (29), 95 (100), 81 (27), 71 (35), 57 (43), 43 (34) 41 (29). Odor: aldehydic, sparkling, Coca Cola, hesperidic, waxy, resinous.

(4E)-7,11-Dimethyl-3-methylidenedodeca-4,10-dienal (**68**). From 6,10-dimethylundeca-1,2,9-trien-4-yl ethenyl ether as described for **10**. Yield: 32% (purity: 95%). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.88 (*d*, *J* = 6.8, Me–C(7)); 1.13 – 1.20 (*m*, H$_a$–C(8)); 1.30 – 1.39 (*m*, H$_b$–C(8)); 1.49 – 1.60 (*m*, H–C(7)); 1.62 (br. *s*, Me–C(11)); 1.70 (br. *s*, Me–C(11)); 1.92 – 2.05 (*m*, CH$_2$(9), H$_a$–C(6)); 2.11 – 2.18 (*m*, H$_b$–C(6)); 3.25 (*dd*, *J* = 0.8, 2.5, CH$_2$(2)); 4.78 (br. *s*, 1 H of CH$_2$=C(3)); 5.08 – 5.13 (*m*, H–C(10)); 5.20 (br. *s*, 1 H of CH$_2$=C(3)); 5.62 (*ddd*, *J* = 7.3, 8.8, 15.7, H–C(5)); 6.18 (br. *d*, *J* = 15.7, H–C(4)); 9.60 (*t*, *J* = 2.5, H–C(1)). ^{13}C-NMR (400 MHz, CDCl$_3$): 18.0 (*q*, *Me*$_2$C(11)); 19.8 (*q*, *Me*–C(7)); 26.0 (*t*, C(9)); 33.2 (*d*, C(7)); 37.1 (*t*, C(8)); 40.6 (*t*, C(6)); 48.1 (*t*, C(2)); 118.4 (*t*, H$_2$*C*=*C*(3)); 125.1 (*d*, C(10)); 131.7 (*s*, C(11)); 131.8 (*d*, C(5)); 132.8 (*d*, C(4)); 137.9 (*s*, C(3)); 200.7 (*d*, C(1)). EI-MS (70 eV): 220 (3, M^+), 176 (18), 135 (49), 109 (74), 95 (100), 81 (38), 69 (86), 55 (32), 41 (78). Odor: aldehydic, metallic, marine, citrus, waxy, thyme.

3-Methylidene-5-propyloct-4-enal (**69**). From 4-(ethenyloxy)-4-propylhepta-1,2-diene as described for **10**. Yield: 59%. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.90 (*d*, *J* = 7.3, Me(8)); 0.92 (*d*, *J* = 7.3, Me–C(3′)); 1.39–1.46 (*m*, CH_2(7), CH_2(2′)); 2.04 (*m*, H_a–C(6), H_a–C(1′)); 2.18 (*m*, H_b–C(6), H_b–C(1′)); 3.14 (*dd*, *J* = 1.0, 1.5, CH_2(2)); 4.47 (br. *s*, 1 H of CH_2=C(3)); 5.10 (br. *s*, 1 H of CH_2=C(3)); 5.60 (br. *s*, H–C(4)); 9.63 (*t*, *J* = 1.5, H–C(1)). ^{13}C-NMR (400 MHz, $CDCl_3$): 14.2 (*q*, C(8)); 14.6 (*q*, C(3′)); 21.5 (*t*, C(7)); 22.2 (*t*, C(2′)); 33.4 (*t*, C(6)); 39.4 (*t*, C(1′)); 52.8 (*t*, C(2)); 117.4 (*t*, CH_2=*C*(3)); 125.2 (*d*, C(4)); 137.6 (*s*, C(3)); 145.2 (*s*, C(5)); 200.6 (*d*, C(1)). EI-MS (70 eV): 180 (2, M^+), 162 (5), 137 (100), 109 (40), 95 (29), 91 (15), 81 (24), 67 (20), 55 (14), 41 (13). Odor: fatty, iris, dry, woody.

*(4*E*)-6,10-Dimethyl-3-methylideneundeca-4,9-dienal* (**70**). From 5,9-dimethyldeca-1,2,8-trien-4-yl ethenyl ether as described for **10**. Yield: 59%. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.02 (*d*, *J* = 6.8, Me–C(6)); 1.32–1.38 (*m*, CH_2(7)); 1.60 (br. *s*, Me–C(10)); 1.70 (br. *s*, Me–C(10)); 1.92–1.97 (*m*, CH_2(8)); 2.16–2.17 (*m*, H–C(6)); 3.25 (*dd*, *J* = 0.5, 2.5, CH_2(2)); 5.06 (*m*, 1 H of CH_2=C(3)); 5.07–5.11 (*m*, H–C(9)); 5.21 (*m*, 1 H of CH_2=C(3)); 5.51 (*dd*, *J* = 7.8, 15.9, H–C(5)); 6.15 (br. *d*, *J* = 15.9, H–C(4)); 9.60 (*t*, *J* = 2.5, H–C(1)). ^{13}C-NMR (400 MHz, $CDCl_3$): 18.1 (*q*, *Me*–C(11)); 20.8 q, *Me*–C(6)); 26.1 (*q*, *Me*–C(11)); 26.2 (*t*, C(8)); 37.0 (*d*, C(6)); 37.4 (*t*, C(7)); 48.1 (*t*, C(2)); 118.5 (*t*, H_2*C*=*C*(3)); 124.0 (*d*, C(9)); 130.1 (*d*, C(4)); 131.9 (*s*, C(10)); 138.0 (*s*, C(3)); 138.9 (*d*, C(5)); 200.8 (*d*, C(1)). EI-MS (70 eV): 206 (9, M^+), 191 (9), 163 (25), 135 (36), 107 (41), 95 (100), 69 (47), 67 (33), 55 (39), 41 (45). Odor: aldehydic, metallic, watery, *Aldoxal*, rose oxide.

6,7-Dihydro-6,9,9-trimethyl-3a,6-ethano-2-benzofuran (**80**). Prop-2-yn-1-yl (4,6,6-trimethylcyclohexa-1,3-dien-1-yl)methyl ether (1.0 g, 5 mmol) was dissolved in THF (60 ml). Potassium 2-methylpropan-2-olate (0.6 g, 5 mmol) was added at r.t. The mixture was stirred for 7 h at r.t. and filtered. The solvent was evaporated under reduced pressure. The crude product was further purified by CC to give 0.4 g (2 mmol) of a light-yellow liquid (purity: 87%; yield: 37%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.81 (*s*, Me–C(9)); 1.01 (*s*, Me–C(6)); 1.17 (*d*, *J* = 12.6, H_a–C(8)); 1.17 (*s*, Me–C(9)); 1.23 (*d*, *J* = 12.6, H_b–C(8)); 1.92 (*ddd*, *J* = 2.1, 3.0, 15.7, H_a–C(7)); 2.05 (*dd*, *J* = 2.0, 15.7, H_b–C(7)); 4.14 (*d*, *J* = 9.6, H_a–C(3)); 4.41 (*d*, *J* = 9.6, H_b–C(3)); 5.91 (*d*, *J* = 8.1, H–C(1)); 5.95 (*dd*, *J* = 2.0, 2.0, H–C(6)); 6.09 (*d*, *J* = 8.1, H–C(5)). ^{13}C-NMR (400 MHz, $CDCl_3$): 25.1 (*q*, *Me*–C(9)); 27.1 (*q*, *Me*–C(9)); 27.6 (*q*, *Me*–C(6)); 33.7 (*t*, C(7)); 38.2 (*s*, C(6)); 38.6 (*s*, C(9)); 52.0 (*t*, C(8)); 58.2 (*t*, C(3a)); 73.6 (*t*, C(3)); 117.8 (*s*, C(7a)); 133.8 (*d*, C(5)); 137.1 (*d*, C(6)); 137.5 (*d*, C(1)). EI-MS (70 eV): 190 (1, M^+), 134 (100), 133 (41), 119 (50), 106 (23), 105 (49), 91 (35), 77 (12), 53 (4), 39 (5). Odor: resinous, cypress, natural, pine needles, slightly fruity.

3a,4,5,6,7,7a-Hexahydro-3,6,6-trimethyl-4-methylidene-1-benzofuran (**82**). propadienyl 3,5,5-trimethylcyclohex-2-en-1-yl ether (**81**; 1.0 g, 5.6 mmol) was dissolved in DMF (70 ml) and stirred at 120° for 1 h. The mixture was cooled to r.t. and poured onto H_2O (150 ml). The aq. layer was extracted with Et_2O (3 × 80 ml). The combined org. layers were washed with brine (2 × 50 ml), dried ($MgSO_4$), and filtered. The solvent was evaporated under reduced pressure. The crude product was subjected to bulb-to-bulb distillation to yield 0.4 g (2 mmol) of a light-yellow liquid (yield: 36%). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.81 (*s*, Me–C(6)); 0.97 (*s*, Me–C(6)); 1.47 (br. *dd*, *J* = 9.1, 13.1, H–C(7)); 1.53 (br. *s*, Me–C(3)); 1.61 (*ddd*, *J* = 2.3, 6.6, 13.1, H–C(7)); 1.87 (br. *d*, *J* = 13.1, H_a–C(5)); 1.96 (br. *d*, *J* = 13.1, H_b–C(5)); 3.49 (br. *d*, *J* = 7.3, H_a–C(3)); 4.70 (*ddd*, *J* = 6.6, 7.3, 9.1, H_a–C(7)); 4.82–4.83 (*m*, 1 H of CH_2=C(4)); 4.84–4.85 (*m*, 1 H of CH_2=C(4)); 6.05–6.06 (*m*, H–C(2)). ^{13}C-NMR (400 MHz, $CDCl_3$): 9.7 (*q*, *Me*–C(3)); 25.6 (*q*, *Me*–C(6)); 31.3 (*s*, C(6)); 32.1 (*q*, *Me*–C(6)); 41.4 (*t*, C(7)); 45.5 (*t*, C(5)); 52.5 (*d*, C(3a)); 80.9 (*d*, C(7a)); 112.3 (*s*, C(3)); 113.0 (*t*, CH_2=*C*(4)); 139.6 (*d*, C(2)); 145.0 (*s*, C(4)). EI-MS (70 eV): 178 (73), 163 (32, $[M-15]^+$), 145 (29), 122 (100), 121 (58), 107 (87), 93 (55), 91 (70), 79 (75), 41 (70).

6,8,8-Trimethyl-5-methylidenenonan-2-ol (**84**). Compound **10** (20.6 g, 113 mmol) was added dropwise to a 3M MeMgBr soln. (45.2 ml, 136 mmol) at 0° during 30 min. The mixture was stirred for 2 h, allowing the temp. to rise to r.t. The mixture was poured onto ice-cold, sat. NH_4Cl soln. (200 ml) and diluted with 2N HCl (100 ml). ^{t}BuOMe was added (200 ml). The org. phase was washed with H_2O (3 × 100 ml) and brine (80 ml), dried ($MgSO_4$), and filtered. The solvent was evaporated under reduced pressure. The crude product was subjected to bulb-to-bulb distillation (120°/0.02 mbar) and further purified by CC to yield 18.8 g (18 mmol) of a colorless liquid (yield 95%, two isomers, ratio 1:1). Odor threshold: 250 ng/l air. Isomers A and B: ^{1}H-NMR (400 MHz, $CDCl_3$): 0.90 (*s*, Me_3C(7)); 1.05 (*d*, *J* = 7.1, Me–C(5)); 1.16 (*dd*, *J* = 5.6, 14.2, H_a–C(6)); 1.23 (*d*, *J* = 6.3, Me–C(1)); 1.49 (*ddd*, *J* = 1.0, 6.1, 14.2, H_b–C(6)); 1.59–1.66 (*m*, CH_2(2)); 1.99–2.31 (*m*, CH_2(3), H–C(5)); 3.80–3.88 (*m*, H–C(1)); 4.68–4.69

(*m*, 1 H of CH$_2$=C(4)); 4.80–4.81 (*m*, 1 H of CH$_2$=C(4)). Isomer A: ^{13}C-NMR (400 MHz, CDCl$_3$): 23.5 (*q*, *Me*–C(5)); 24.0 (*q*, *Me*–C(1)); 29.8 (*t*, C(3)); 30.4 (*q*, *Me*$_3$C(7)); 31.6 (*s*, C(7)); 37.4 (*d*, C(5)); 38.0 (*t*, C(2)); 50.0 (*t*, C(6)); 68.5 (*d*, C(1)); 107.6 (*t*, *C*H$_2$=*C*(4)); 156.6 (*s*, C(4)). Isomer B: ^{13}C-NMR (400 MHz, CDCl$_3$): 23.5 (*q*, *Me*–C(5)); 24.0 (*q*, *Me*–C(1)); 29.9 (*t*, C(3)); 30.4 (*q*, *Me*$_3$C(7)); 31.6 (*s*, C(7)); 37.5 (*d*, C(5)); 38.0 (*t*, C(2)); 50.1 (*t*, C(6)); 68.6 (*d*, C(1)); 107.6 (*t*, *C*H$_2$=*C*(4)); 156.8 (*s*, C(4)). EI-MS (70 eV): Isomers A and B: 198 (1, *M*$^+$), 142 (5), 123 (22), 109 (31), 95 (18), 84 (32), 67 (24), 57 (100), 43 (44), 41 (34). Odor: floral, soapy, weak.

2,6,8,8-Tetramethyl-5-methylidenenonan-2-ol (**86**). From **88** as described for **84**. Yield: 87%. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.91 (*q*, Me$_3$C(7)); 1.06 (*d*, *J* = 6.8, Me–C(5)); 1.17 (*dd*, *J* = 5.6, 14.2, H$_a$–C(6)); 1.27 (*s*, Me$_2$C(1)); 1.51 (*dd*, *J* = 6.1, 14.2, H$_b$–C(6)); 1.63 – 1.67 (*m*, CH$_2$(2)); 2.07–2.12 (*m*, CH$_2$(3)); 2.24–2.33 (*m*, H–C(5)); 4.68–4.69 (*m*, 1 H of CH$_2$C=C(4)); 4.80 (br. *s*, 1 H of CH$_2$=C(4)). ^{13}C-NMR (400 MHz, CDCl$_3$): 23.5 (*q*, *Me*–C(6)); 28.1 (*t*, C(3)); 29.8 (*q*, *Me*$_2$C(1)); 30.4 (*q*, *Me*$_3$C(7)); 31.6 (*s*, (C(7)); 37.6 (*d*, C(5)); 42.6 (*t*, C(2)); 50.1 (*t*, C(6)); 71.4 (*s*, C(1)); 107.4, *C*H$_2$=*C*(4)); 157.0 (*s*, C(4)). EI-MS (70 eV): 194 (7, M$^+$ – 18), 179 (38), 138 (30), 123 (100), 95 (41), 81 (31), 59 (59), 57 (84), 43 (44), 41 (34). Odor: floral, fruity, fruity, rosy. Odour threshold: 757 ng/l air.

6,8,8-Trimethyl-5-methylidenenonan-2-one (**88**). Compound **84** (15.0 g, 76 mmol) was added dropwise to a suspension of PCC (22.8 g, 106 mmol) and *Celite* (24.1 g) in CH$_2$Cl$_2$ at r.t. The temp. of the mixture rose to35°. The suspension was stirred for 2 h at r.t. and filtered. The solvent was evaporated under reduced pressure. The crude product was subjected to bulb-to-bulb distillation (110°/0.02 mbar) and further purified by CC to yield 13.0 g (66 mmol) of a colorless liquid (yield: 87%). ^{1}H-NMR (400 MHz, CDCl$_3$): 0.89 (*s*, Me$_3$C(7)); 1.04 (*d*, *J* = 6.8, Me–C(5)); 1.15 (*dd*, *J* = 5.6, 14.2, H$_a$–C(6)); 1.49 (*dd*, *J* = 6.1, 14.2, H$_b$–C(6)); 2.17 (*s*, Me–C(1)); 2.23–2.30 (*m*, CH$_2$(3), H–C(5)); 2.58–2.62 (*m*, CH$_2$(2)); 4.58–4.59 (*m*, 1 H of CH$_2$=C(4)); 4.80 (br. *s*, 1 H of CH$_2$=C(4)). ^{13}C-NMR (400 MHz, CDCl$_3$): 23.4 (*q*, *Me*–C(5)); 27.0 (*t*, C(3)); 30.3 (*q*, *Me*$_3$C(7), *Me*–C(1)); 31.6 (*s*, C(7)); 37.8 (*d*, C(5)); 42.4 (*t*, C(2)); 49.8 (*t*, C(6)); 107.6 (*t*, H$_2$*C*=*C*(4)); 155.4 (*s*, C(4)); 208.8 (*s*, C(1)). EI-MS (70 eV): 139 (15), 123 (21), 122 (52), 107 (30), 97 (24), 83 (20), 82 (15), 57 (74), 43 (100), 41 (24). Odor: green, fatty, rosy. Odour threshold: 452 ng/l air.

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