

FRAGRANCE PRECURSOR COMPOUNDS

TECHNICAL FIELD

The present invention relates generally to fragrance precursors, which release odorant compounds. The invention also relates to fragrance compositions and consumer products
5 containing said precursors. The invention further relates to methods of making said fragrance precursors, fragrance compositions and consumer products. Moreover, the present invention relates to a method of imparting a long-lasting odor, in particular green odor, to surfaces, such as skin or hair.

10 BACKGROUND

Consumer products comprising fragrances are well-known in the art. However, lack of substantivity of certain perfumery ingredients in consumer product applications pose an undesirable technical limit to perfume creation. There is an interest to overcome these limits using technologies such as fragrance precursors. Furthermore, some opportunities such as
15 the future plastic legislation in Europe (potentially threatening the use of synthetic microcapsules) might benefit the precursor technology. Any new development should however consider customer's and consumer's request for "green" alternatives (considering sustainability, renewability and biodegradability).

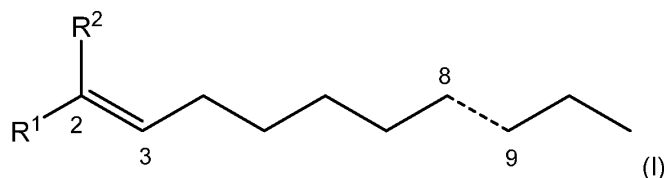
20 Fragrances are one of the most expensive shampoo ingredients, and end consumers typically select their shampoo based on smell. Unfortunately, most of the floral-, fresh green-, and/or fruity-smelling compounds evaporate rapidly or are easily washed out when used in consumer product bases comprising surfactants, such as shampoos. The main reason for this is due to the specific functional and physiochemical characteristics of shampoos.
25 Accordingly, the shampoo fragrance usually does not last long on hair. In addition, many fragrances, such as aldehydes, are prone to oxidation under ambient conditions, which can lead to a rapid loss of their desirable smell.

Accordingly, an efficient deposition of fragrances from consumer products, in particular rinse-
30 off products such as shampoos, body washes, and hair conditioners, onto hair is a challenging task.

Fragrance precursors imparting long-lasting green odor notes are described, for example, in WO2022063755, referring to nona-2,6-dienyl alkanoates, such as nona-2,6-dien-1-yl
35 hexadecanoate. Whereas the compounds tested seem to provide a more intense odor profile, no further details are provided regarding the odor profile of the precursors explicitly tested.

SUMMARY

In accordance with a first aspect of the present invention there is provided a compound of formula (I)



wherein

R¹ is selected from phenyl, naphthyl and phenyl substituted with 1 or 2 functional groups independently selected from hydroxy, methoxy and ethoxy,

R² is selected from hydrogen and methyl,

the dotted line represents a carbon-carbon double bond or a carbon-carbon triple bond.

In accordance with a second aspect of the present invention there are provided fragrance compositions and consumer products comprising the compound of the first aspect of the invention.

In accordance with a third aspect of the present invention there is provided a method of masking, reducing and/or preventing malodor, in particular scalp malodor.

In accordance with a fourth aspect the use of a compound of the first aspect as fragrance precursor.

In accordance with a fives aspect of the present invention there is provided the use as fragrance of 6-nonyl.

Certain embodiments of any aspect of the present invention may provide one or more of the following advantages:

- well balanced odor profile
- good deposition properties on substrates, such as hair and skin
- biodegradability
- scalp malodor counteraction

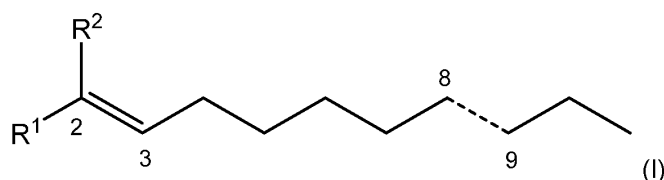
The details, examples and preferences provided in relation to any particular one or more of the stated aspects of the present invention will be further described herein and apply equally to all aspects of the present invention. Any combination of the embodiments, examples and

preferences described herein in all possible variations thereof is encompassed by the present invention unless otherwise indicated herein, or otherwise clearly contradicted by context.

DETAILED DESCRIPTION

- 5 The present invention is based on the surprising finding that compounds of formula (I) as herein defined can serve as fragrance precursors able to release over a long period an intense fresh green melon odor profiles when exposed to ambient air. Surprisingly, the compounds of formula (I) as herein defined have particularly good deposition properties on substrates, such as hair and skin. Furthermore, said compounds provide a particular long
10 lasting effect without a nominal loss in odor intensity over an extended time period.

There is therefor provided herein a compound of formula (I)



wherein

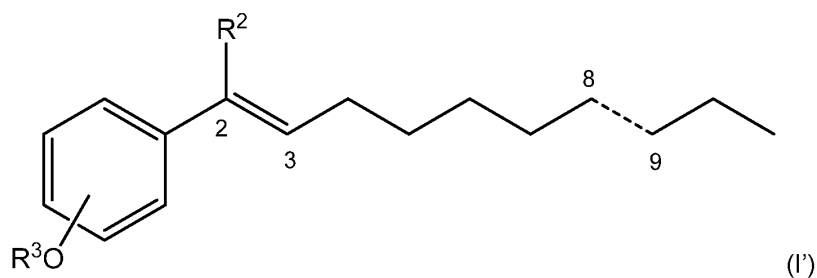
- 15 R¹ is selected from phenyl, naphthyl and phenyl substituted with 1 or 2 functional groups independently selected from hydroxy, methoxy and ethoxy,
R² is selected from hydrogen and methyl,
the dotted line represents a carbon-carbon double bond or a carbon-carbon triple bond.

- 20 In one particular embodiment the compound of formula (I) is a compound wherein R¹ is naphthyl (e.g. 2-naphthyl).

In another particular embodiment the compound of formula (I) is a compound wherein R¹ is 2-naphthyl and R² is methyl.

25

In another particular embodiment the compound of formula (I) is a compound of formula (I')

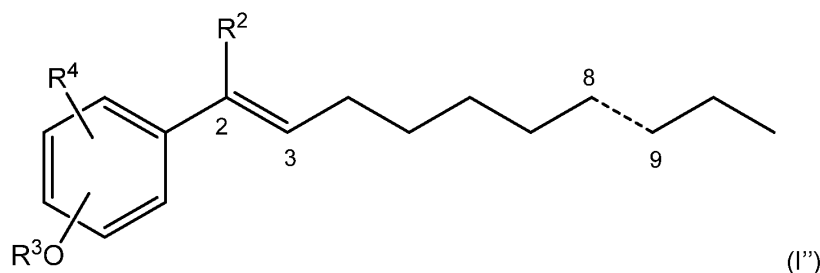


wherein R³ is selected from hydrogen and C₁ – C₂ alkyl.

In one particular embodiment the substituent -OR³ is in para-position or meta-position.

In another particular embodiment the compound of formula (I') is a compound wherein R² is
 5 hydrogen and R³ is selected from the group consisting of methyl and ethyl.

In another particular embodiment the compound of formula (I) is a compound of formula (I'')



wherein R³ is selected from hydrogen and C₁-C₂ alkyl and R⁴ is selected from hydroxyl,
 10 methoxy, and ethoxy.

In one particular embodiment the compound of formula (I'') is a compound wherein R³ is
 hydrogen and R⁴ is selected from methoxy, and ethoxy.

15 In another particular embodiment the compound of formula (I'') is a compound wherein R² is
 hydrogen, R³ is hydrogen and R⁴ is selected from methoxy, and ethoxy.

As specific examples of compounds of formula (I) one may cite
 2-(undeca-2,8-dien-2-yl)naphthalene, 2-(undec-2-en-8-yn-2-yl)naphthalene, 1-(deca-1,7-
 20 dien-1-yl)-4-methoxybenzene, 1-butoxy-3-(deca-1,7-dien-1-yl)benzene, 1-(dec-1-en-7-yn-1-
 yl)-4-methoxybenzene, 4-(deca-1,7-dien-1-yl)-2-ethoxyphenol, and 4-(deca-1,7-dien-1-yl)-2-
 methoxyphenol.

The compounds of formula (I), which encompasses the compounds of formula (I') and (I''),
 25 wherein the dotted line represents a carbon-carbon double bond exist in 4 different isomers.
 In one particular embodiment the compound of formula (I) is a compound wherein the double
 bond between C-2 and C-3 is in *Z*-configuration and the double bond between C-8 and C-9 is
 in *E*-configuration.

30 In another particular embodiment the compound of formula (I), which encompasses the
 compounds of formula (I') and (I''), is a compound wherein the both double bonds are in *E*-
 configuration.

In another particular embodiment the compound of formula (I), which encompasses the compounds of formula (I') and (I''), is a compound wherein the both double bonds are in *Z*-configuration.

5

In another particular embodiment the compound of formula (I), which encompasses the compounds of formula (I') and (I''), is a compound wherein the double bond between C-2 and C-3 is in *E*-configuration and the double bond between C-8 and C-9 is in *Z*-configuration.

- 10 The compounds of formula (I) as defined herein release on exposure to ambient air an aldehyde (non-6-enal and non-6-ynal respectively) and a carbonyl compound $R^1-C(O)-R^2$, wherein R^1 and R^2 have the same meaning as provided for the compound of formula (I).

- 15 The cleavage products of the compound of formula (I) could be olfactorily perceived over a long period (at least 2 days and longer, for example, up to 1, 2 or even 3 weeks). For example, the fresh green melon olfactory impression was still very well perceived even after 2 days after the contacting of a substrate, in particular hair, with a consumer product comprising a compound of formula (I) as herein defined.

- 20 Unsaturated C-9 aldehydes are known to possess a low odor threshold and thus preferably used in low concentrations, which leads to the fact that no long-lasting effects can be achieved when used in consumer products.

- 25 Thus there is provided in a further aspect of the present invention the use of a compound of formula (I) as fragrance precursor, in particular as a precursor which is capable of releasing long lasting fresh green melon olfactory impressions when exposed to ambient air.

- 30 Exposure to ambient air means exposure to molecular oxygen which might be responsible for the oxidative cleavage of the compound of formula (I). The concentration of oxygen in the air is sufficient for cleaving the compound of formula (I) so that the cleavage products can be detected in the ambient air, e.g. by olfaction or GC-MS analysis of collected organic volatiles from the precursor headspace.

- 35 Whereas some of the released aldehydes are known as fragrance some have never be described. Thus there is provided in a further aspect of the present invention the use as fragrance of 6-nonyl.

The fact that the compounds of formula (I) as herein defined have particularly good deposition properties on hair makes them particularly suitable for hair care products, in particular shampoo. The compound of formula (I) may however also find its use in any type of consumer products for example, rinse-off cleaning products in general.

5

Thus there is provided in a further aspect of the present invention a consumer product comprising a compound of formula (I) and a consumer product base.

The term "rinse-off products" as used herein are products that only come into contact with the substrate to be treated for a short time and are then washed off with water. As an examples one may cite cleaning products such as detergents (e.g. laundry detergent in liquid or powder form), and finishing agents including fabric softeners. Further examples are typically cosmetic products such as shower baths, shampoos and cleaning agents, which come into contact with the skin for a short time and are then washed off with water.

15

The consumer product for example is selected from fine fragrance, personal care products (body care products, hair care products, cosmetic products), fabric care products, home care products and air care products. As used herein, "consumer product base" means a composition for use as a consumer product to fulfill specific actions, such as cleaning, softening, and caring or the like.

20

Personal care products to which the compound of formula (I) can be added include, for example, all kinds of body care products (which include shower gel, body lotion, bar soaps for hand and body, and body mist products). Especially interesting products are hair care products, for example shampoos (including dry shampoo), conditioners and hair styling products, such as hair cream, combing cream, hair oil, hair spray, hair serums, hair coloring products, mousse or gel, and skin care products, like lotions or creams. Furthermore, the compound of formula (I) may be added to deodorants and sun care (including after sun products).

25

Home care products to which the compound of formula (I) can be added include all kinds of detergents, window cleaners, hard surface cleaners, all-purpose cleaners and furniture polishes. In one particular embodiment said products are liquids, e.g. fabric detergent or conditioner compositions.

30

Beside the particularly good deposition properties on hair of the compounds of formula (I) it was surprisingly observed that said compounds significantly reduce the perception of scalp

35

malodor. It was also observed that the compounds of formula (I) (including 2-(undeca-2,8-dien-2-yl)naphthalene, and 1-(deca-1,7-dien-1-yl)-4-methoxybenzene) are also particular suitable to mask and/or reduce other type of malodor, such as sweat, when used in consumer products, for example fabric care products (including fabric detergents, scent
5 booster products (e.g. scent booster beads) and fabric softener (e.g. fabric softener dryer sheets).

The compound of formula (I) can be employed in widely varying amounts to a consumer product base, depending upon the specific article and on the nature and quantity of other
10 odorant ingredients. The proportion of the formula (I) is typically from 0.0005 to 5 weight% of the article. In one embodiment, the compound of formula (I) may be employed in a fabric softener in an amount from 0.001 to 0.5 weight % (e.g. 0.01 to 0.1 including 0.2 weight%). In another embodiment, the compound of formula (I) may be employed in laundry detergent in an amount from 0.01 to 0.5 weight % (e.g. 0.1 to 0.3 including 0.2 weight%) based on the
15 final product. In another embodiment, the compound of formula (I) may be used in fine perfumery in amounts from 0.001 to 30 weight% (e.g. up to about 10 or up to 20 weight%), more preferably between 0.01 and 5 weight%. However, these values are given only by way of example, since the experienced perfumer may also achieve effects or may create novel accords with lower or higher concentrations.

20 The compound of formula (I) may be employed in a consumer product base simply by directly mixing the compound of the present invention, or a fragrance composition comprising the compound of formula (I), with the consumer product base, or it may, in an earlier step, be entrapped with an entrapment material, for example, polymers, capsules, microcapsules and
25 nanocapsules, liposomes, film formers, absorbents such as carbon or zeolites, cyclic oligosaccharides and mixtures thereof, and then mixed with the consumer product base. The consumer product base might further contain entrapment material able to release other fragrant compounds.

30 Thus, there is provided a method of manufacturing a consumer product, comprising the incorporation of a compound of formula (I) either by directly admixing it to the consumer product base or by admixing a fragrance composition comprising the compound of formula (I), which may then be mixed with a consumer product base, using conventional techniques and methods.

35 The compound of formula (I) may be used alone or in combination with further fragrance precursors and/or odorants well known in the art.

The odorant(s) may be selected from the extensive range of natural products and synthetic molecules currently available, such as essential oils, alcohols, aldehydes and ketones, ethers and acetals, esters and lactones, macrocycles and heterocycles, and/or in admixture
5 with one or more ingredients or excipients conventionally used in conjunction with odorants in perfume compositions, for example, carrier materials, and other auxiliary agents commonly used in the art.

The following non limiting list comprises examples of known odorants, which may be combined with the compound of formula (I) in a fragrance composition:

- 10 • Essential oils and extracts, e.g. castoreum, costus root oil, geranium oil, tree moss absolute, basil oil, fruit oils, such as bergamot oil and mandarine oil, myrtle oil, palmarose oil, patchouli oil, petitgrain oil, jasmine oil, rose oil, sandalwood oil, wormwood oil, lavender oil and/ or ylang-ylang oil;
- Alcohols, e.g. cinnamic alcohol ((*E*)-3-phenylprop-2-en-1-ol); cis-3-hexenol ((*Z*)-hex-3-en-1-ol); Citronellol (3,7-dimethyloct-6-en-1-ol); dihydro myrcenol (2,6-dimethyloct-15 7-en-2-ol); Ebanol™ ((*E*)-3-methyl-5-(2,2,3-trimethylcyclopent-3-en-1-yl)pent-4-en-2-ol); eugenol (4-allyl-2-methoxyphenol); ethyl linalool ((*E*)-3,7-dimethylnona-1,6-dien-3-ol); farnesol ((2*E*,6*Z*)-3,7,11-trimethyldodeca-2,6,10-trien-1-ol); geraniol ((*E*)-3,7-dimethylocta-2,6-dien-1-ol); Super Muguet™ ((*E*)-6-ethyl-3-methyloct-6-en-1-ol);
20 linalool (3,7-dimethylocta-1,6-dien-3-ol); menthol (2-isopropyl-5-methylcyclohexanol); Nerol (3,7-dimethyl-2,6-octadien-1-ol); phenyl ethyl alcohol (2-phenylethanol); Rhodinol™ (3,7-dimethyloct-6-en-1-ol); Sandalore™ (3-methyl-5-(2,2,3-trimethylcyclopent-3-en-1-yl)pentan-2-ol); terpineol (2-(4-methylcyclohex-3-en-1-yl)propan-2-ol); or Timberol™ (1-(2,2,6-trimethylcyclohexyl)hexan-3-ol); 2,4,7-
25 trimethylocta-2,6-dien-1-ol, [1-methyl-2(5-methylhex-4-en-2-yl)cyclopropyl]-methano, and/or Evernyl™ (methyl 2,4-dihydroxy-3,6-dimethylbenzoate);
- Aldehydes and ketones, e.g. anisaldehyde (4-methoxybenzaldehyde); alpha amyl cinnamic aldehyde (2-benzylideneheptanal); Georgywood™ (1-(1,2,8,8-tetramethyl-1,2,3,4,5,6,7,8-octahydronaphthalen-2-yl)ethanone); Hydroxycitronellal (7-hydroxy-30 3,7-dimethyloctanal); Iso E Super® (1-(2,3,8,8-tetramethyl-1,2,3,4,5,6,7,8-octahydronaphthalen-2-yl)ethanone); Isoraldeine® ((*E*)-3-methyl-4-(2,6,6-trimethylcyclohex-2-en-1-yl)but-3-en-2-one); Hedione® (methyl 3-oxo-2-pentylcyclopentaneacetate); Nympeal (3-(4-isobutyl-2-methylphenyl)propanal); Mahonial (5,9-dimethyl-9-hydroxy-decen-4-al); maltol; methyl cedryl ketone;
35 methylionone; verbenone; and/or vanillin;

- Ether and acetals, e.g. Ambrox® (3a,6,6,9a-tetramethyl-2,4,5,5a,7,8,9,9b-octahydro-1*H*-benzo[*e*][1]benzofuran); geranyl methyl ether ((2*E*)-1-methoxy-3,7-dimethylocta-2,6-diene); rose oxide (4-methyl-2-(2-methylprop-1-en-1-yl)tetrahydro-2*H*-pyran); and/or Spirambrene® (2',2',3,7,7-pentamethylspiro[bicyclo[4.1.0]heptane-2,5'-[1,3]dioxane]);
- Esters and lactones, e.g. benzyl acetate; cedryl acetate ((1*S*,6*R*,8a*R*)-1,4,4,6-tetramethyloctahydro-1*H*-5,8a-methanoazulen-6-yl acetate); γ -decalactone (6-pentyltetrahydro-2*H*-pyran-2-one); Helvetolide® (2-(1-(3,3-dimethylcyclohexyl)ethoxy)-2-methylpropyl propionate); γ -undecalactone (5-heptyloxolan-2-one); and / or vetiveryl acetate ((4,8-dimethyl-2-propan-2-ylidene-3,3a,4,5,6,8a-hexahydro-1*H*-azulen-6-yl) acetate
- Macrocycles, e.g. Ambrettolide ((*Z*)-oxacycloheptadec-10-en-2-one); ethylene brassylate (1,4-dioxacycloheptadecane-5,17-dione); and / or Exaltolide® (16-oxacyclohexadecan-1-one); and
- Heterocycles, e.g. isobutylquinoline (2-isobutylquinoline).

The compounds of formula (I) can be prepared according to standard methods known in the art as described herein-below.

- The invention is now further described with reference to the following non-limiting examples. These examples are for the purpose of illustration only and it is understood that variations and modifications can be made by one skilled in the art.

Example 1: 2-((8*Z*)-undeca-2,8-dien-2-yl)naphthalene

1a) 9-bromonon-3-yne

- Lithium (wire pieces, ca. 5 mm, 6.9 g, 0.99 mol, 1 equiv.) was suspended in dry THF (400 mL) and the suspension was heated to 40°C, then the solution of 1,2-butadiene (108 g, 2 mol, 2 equiv.) in THF (100 mL) was added dropwise during 3 h, keeping the temperature of the reaction between 35-50°C with occasional external cooling. After completed addition, stirring at 40°C was continued for 45 min (all lithium was consumed, the orange-brown suspension turned beige), then for additional 22 h at room temperature. To the beige suspension was added neat 1,5-dibromopentane (241 g, 1.05 mol, 1.05 equiv.) at room temperature during 15 min. The mixture was heated to reflux for 23 h, upon which GC-FID analysis revealed 60% of 9-bromonon-3-yne, 15% of 1,5-dibromopentane and 22% of trideca-3,10-diyne. The product solution in THF was directly used for the next step.

1b) 2-(naphthalen-2-yl)undec-8-yn-2-ol

Magnesium turnings (29.1 g, 1.2 mol, 1.2 equiv.) were suspended in THF (100 mL) and the reaction was started by addition of 1,2-dibromoethane (0.5 mL) and a portion of the above prepared product solution (40 mL). After the solution had become turbid, the remainder of the
5 above prepared product solution was added during 60 min at a rate to maintain a gentle reflux. Stirring was continued without heating for 60 min, then the solution of 1-(naphthalen-2-yl)ethan-1-one (136 g, 0.8 mol, 0.8 equiv.) in THF (200 mL) was added during 40 min, during which the temperature rose to 35°C. After complete addition, stirring was continued at room temperature for 2 h. The mixture was poured on ice-cold 1 N aq. HCl solution (600 mL) and
10 extracted with MTBE. The organic layer was washed with water and brine, then dried over MgSO₄ to yield a clear yellow liquid (242 g). The crude product was used in the subsequent step.

1c) 2-(undec-2-en-8-yn-2-yl)naphthalene

The above prepared crude product (121 g, 0.5 mol, 1 equiv.) was dissolved in toluene (300 mL) and p-toluene sulfonic acid (0.39 g, 0.5 mol%) was added. The solution was heated to reflux during 3 h in a Dean-Stark trap, collecting 4.5 mL of H₂O, followed by aqueous workup with water and brine as described above. The crude product was subjected to a thin film distillation (0.02 mbar/160 mbar) to remove volatile byproducts. The residue (51 g dark brown
20 liquid) comprises as main constituents a mixture of E-(2)-(undec-2-en-8-yn-2-yl)naphthalene (main product), 2-(undec-1-en-8-yn-2-yl)naphthalene and Z-(2)-(undec-2-en-8-yn-2-yl)naphthalene was used in the next step. A sample was purified by flash chromatography on SiO₂ (heptane/MTBE 60:1).

25 E/Z-(2)-(undec-2-en-8-yn-2-yl)naphthalene:

Odor description (1% EtOH solution on paper blotter, 24 h): green, floral, orange blossom, cucumber.

E-(2)-(undec-2-en-8-yn-2-yl)naphthalene

30 ¹H-NMR (400 MHz, CDCl₃): 7.80 - 7.88 (m, 3 H), 7.62 - 7.78 (m, 1 H), 7.44 - 7.54 (m, 2 H), 6.01 (t, *J*=6.9 Hz, 1 H), 2.07 - 2.36 (m, 7 H), 1.58 - 1.86 (m, 3 H), 1.27 - 1.55 (m, 2 H), 1.12 - 1.24 (t, *J*=7.4 Hz, 3 H).

¹³C-NMR (101 MHz, CDCl₃): 141.1 (s), 134.7 (s), 133.6 (s), 132.4 (s), 129.1 (d), 128.0 (d), 127.6 (d), 127.5 (d), 126.0 (d), 125.4 (d), 124.4 (d), 123.9 (d), 81.9 (s), 79.4 (s), 28.9 (t), 28.7
35 (t), 28.5 (t), 18.7 (t), 15.8 (q), 14.4 (q), 12.5 (t).

MS (EI, 70EV, GC-MS): 276 (M⁺, 3), 261 (18), 247 (99), 232 (26), 205 (37), 191 (19), 181 (23), 179 (43), 165 (100), 155 (31), 141 (30), 128 (20), 41 (21).

1d) 2-((8Z)-undeca-2,8-dien-2-yl)naphthalene

The above prepared crude product (43.6 g) was subjected to Lindlar hydrogenation in hexane (400 mL) in the presence of Lindlar's catalyst (5% of Pd on CaCO₃, poisoned with lead, 1.0 g) at ambient pressure and 25-32°C for 2 h. The mixture was filtered by suction and the filtrate was concentrated in vacuum to yield a clear, light brown liquid (43 g), which according to GC-MS analysis comprises 70% of 2-((2E,8Z)-undeca-2,8-dien-2-yl)naphthalene and 20% (Z)-2-(undeca-1,8-dien-2-yl)naphthalene.

- Odor description (1% solution in EtOH on paper blotter, 24 h): green, melon, orange blossom, cucumber.

2-((2E,8Z)-undeca-2,8-dien-2-yl)naphthalene EI-MS (70 eV, GC-MS): 278 (M⁺, 12), 249 (13), 193 (43), 181 (57), 165 (100), 155 (65), 141 (37), 115 (13), 41 (24).

- (Z)-2-(undeca-1,8-dien-2-yl)naphthalene EI-MS (70 eV, GC-MS): 278 (M⁺, 4), 249 (6), 193 (18), 181 (19), 168 (100), 152 (34), 141 (20), 128 (21), 41 (20).

In addition, the following products, present in minor amounts, were isolated and purified by flash column chromatography from the crude product.

20

(Z)-1-(naphthalen-2-yl)dec-7-en-1-one

¹H NMR (C₆D₆) δ: 8.30 (s, 1H), 8.11 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.52-7.58 (m, 2H), 7.20-7.27 (m, 2H), 5.38-5.48 (m, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.00-2.07 (m, 4H), 1.76 (quin, *J* = 7.3 Hz, 2H), 1.28-1.36 (m, 4H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm.

- ¹³C NMR (C₆D₆) δ: 198.8 (s), 135.8 (s), 135.1 (s), 133.0 (s), 131.9 (d), 129.69 (d), 129.68 (d), 129.4 (d), 128.6 (d), 128.1 (d), 128.0 (d), 126.7 (d), 124.4 (d), 38.5 (t), 30.0 (t), 29.3 (t), 27.3 (t), 24.5 (t), 20.9 (t), 14.6 (q) ppm.

GC-MS (EI, 70eV): 4280 (3, M⁺), 237 (2), 212 (4), 198 (84), 183 (16), 170 (44), 155 (100), 141 (6), 127 (98), 108 (3), 55 (18), 41 (21).

30

(Z)-2,2'-(3-(oct-5-en-1-yl)pent-1-ene-2,4-diyl)dinaphthalene

¹H NMR (C₆D₆) δ: 7.99 (s, 1H), 7.63-7.75 (m, 7H), 7.59 (s, 1H), 7.24-7.32 (m, 5H), 5.54 (s, 1H), 5.28-5.34 (m, 1H), 5.24 (s, 1H), 5.20-5.26 (m, 1H), 2.97-3.00 (m, 2H), 1.79-1.88 (m, 4H), 1.46-1.52 (m, 3H), 1.41 (d, *J* = 6.5 Hz, 3H), 1.23-1.28 (m, 1H), 1.10-1.17 (m, 2H), 0.80 (t, *J* = 7.6 Hz, 3H) ppm.

35

¹³C NMR (C₆D₆) δ: 152.4 (s), 144.2 (s), 141.8 (s), 134.3 (s), 134.1 (s), 133.3 (s), 133.0 (s), 131.7 (d), 129.3 (d), 128.54 (d), 128.45 (d), 128.3 (d), 128.0 (d), 127.92 (d), 127.89 (d), 126.7

(d), 126.4 (d), 126.2 (d), 126.1 (d), 126.0 (d), 125.88 (d), 125.85 (d), 125.5 (d), 114.6 (t), 52.0 (d), 46.5 (d), 34.0 (t), 29.9 (t), 27.4 (t), 27.3 (t), 21.7 (q), 20.7 (t), 14.5 (q) ppm.

GC-MS (EI, 70eV): 432 (<1, M⁺), 277 (2), 193 (1), 179 (4), 165 (4), 155 (100), 141 (5), 128 (5), 115 (3), 55 (2), 41 (4).

5

2,2'-((4E,10Z)-trideca-4,10-diene-2,4-diyl)dinaphthalene

GC-MS (EI, 70eV): 432 (<1, M⁺), 277 (3), 193 (1), 179 (4), 165 (4), 155 (100), 141 (5), 128 (5), 115 (3), 115 (4), 55 (3), 41 (5).

10 2,2'-((3E,10Z)-trideca-3,10-diene-2,4-diyl)dinaphthalene

GC-MS (EI, 70eV): 432 (<1, M⁺), 307 (51), 291 (5), 277 (6), 193 (9), 179 (86), 165 (31), 155 (100), 141 (64), 128 (19), 115 (3), 115 (10), 67 (6), 55 (23), 41 (33).

Example 2: 2-((2E,8Z)-undeca-2,8-dien-2-yl)naphthalene and 2-((2Z,8Z)-undeca-2,8-dien-2-yl)naphthalene

15

2a) 2-(1-bromoethyl)naphthalene

The solution of 1-(naphthalen-2-yl)ethan-1-one (50.0 g, 294 mmol, 1 equiv.) in MeOH (150 mL) was added dropwise to the suspension of NaBH₄ (11.11 g, 294 mmol, 1 equiv.) in MeOH (200 mL) at 25-35°C. Stirring was continued at room temperature for 2 h, after which additional NaBH₄ (11.11 g, 294 mmol, 1 equiv.) was added and stirring continued at room temperature for 30 min. The mixture was poured on ice-cold aq. 2 M aq. HCl-solution (200 mL) and extracted twice with MTBE. The organic layer was washed with water and brine and dried over MgSO₄ to yield 1-(naphthalen-2-yl)ethan-1-ol as a colourless liquid (48.7 g, 96%) which was used in the subsequent step without purification.

25

¹³C-NMR (101 MHz, CDCl₃): 143.2 (s), 133.3 (s), 132.9 (s), 128.3 (d), 128.0 (d), 127.7 (d), 126.2 (d), 125.8 (d), 123.9 (d), 123.9 (d), 70.5 (d), 25.2 (q).

30

1-(naphthalen-2-yl)ethan-1-ol (48 g, 279 mmol, 1 equiv.) was dissolved in toluene (150 mL) and the solution was heated to 60°C. PBr₃ (37.7 g, 139 mmol, 0.5 equiv.) was added dropwise, upon which the temperature rose to 85°C. After completed addition stirring was continued at 70°C for 2 h. The mixture was cooled to room temperature and poured on ice-cold aqueous 2 M NaOH solution (200 mL). The organic layer was washed with water and brine and dried over MgSO₄. After removal of the solvent in vacuum, 2-(1-bromoethyl)naphthalene was obtained as an orange solid (65.4 g, >99%), which was used without purification in the next step.

35

2b) bromo(1-(naphthalen-2-yl)ethyl)triphenyl-λ⁵-phosphane

2-(1-bromoethyl)naphthalene (65.6 g, 279 mmol, 1 equiv.) and triphenyl phosphane (73.2 g, 279 mmol, 1 equiv.) were dissolved in toluene (300 mL) and the solution was heated to reflux for 18 h, upon which a hard solid formed. The solvent was decanted, the solid was broken into small pieces and ground in a mortar after addition of 100 mL of diethyl ether. The resulting fine
5 suspension was filtered by suction to yield, after drying, bromo(1-(naphthalen-2-yl)ethyl)triphenyl- λ^5 -phosphane as a white, powdery solid (101 g, 73%).

2c) 2-((2E,8Z)-undeca-2,8-dien-2-yl)naphthalene and 2-((2Z,8Z)-undeca-2,8-dien-2-yl)naphthalene

10 To the suspension of K_{OT}Bu (8.80 g, 78.4 mmol, 1.1 equiv.) in THF (150 mL) was added bromo(1-(naphthalen-2-yl)ethyl)triphenyl- λ^5 -phosphane (39.0 g, 78.4 mmol, 1.1 equiv.) in 2 portions, upon which the temperature rose to 30°C and the mixture turned brown. Stirring was continued for 30 min at room temperature, before the dropwise addition of a solution of (Z)-6-nonenal (10.0 g, 71.3 mmol, 1.0 equiv.) in THF (50 mL) at 5-13°C (external cooling). The red
15 suspension was stirred for 1 h at room temperature, then standard acid workup was effected following the general procedure of Example 2a. The crude product was dissolved in pentane and the solution was left in the refrigerator overnight. The formed precipitate of triphenyl phosphine oxide was filtered by suction and the filtrate was concentrated in vacuo to yield 2-((8Z)-undeca-2,8-dien-2-yl)naphthalene in 2E/2Z ratio of 60:25 (yellow liquid, 15.5 g, 78%).
20 The two isomers were separated by flash column chromatography on SiO₂ (heptane).

2-((2Z,8Z)-undeca-2,8-dien-2-yl)naphthalene (clear, colourless liquid, 250 mg, purity according to GC-MS >99%).

25 Odor description (1% solution in EtOH on paper blotter, 24 h): orange blossom, green, aldehydic, melon, cucumber.

¹H-NMR (400 MHz, CDCl₃): 7.80 - 7.89 (m, 3 H), 7.65 (s, 1 H), 7.45 - 7.52 (m, 2 H), 7.37 (dd, *J*=8.3, 1.7 Hz, 1 H), 5.55 - 5.60 (m, 1 H), 5.27 - 5.45 (m, 2 H), 2.15 (q, *J*=1.4 Hz, 3 H), 1.91 -
30 2.12 (m, 6 H), 1.30 - 1.45 (m, 4 H), 0.94 (t, *J*=7.5 Hz, 3 H).

¹³C-NMR (101 MHz, CDCl₃): 139.8 (s), 136.0 (s), 133.3 (s), 132.2 (s), 131.6 (d), 129.1 (d), 128.3 (d), 127.8 (d), 127.6 (d), 127.5 (d), 126.8 (d), 126.4 (d), 125.9 (d), 125.5 (d), 29.7 (t), 29.3 (t), 29.0 (t), 26.9 (t), 25.6 (q), 20.5 (t), 14.4 (q).

35 EI-MS (70 eV, GC-MS): 278 (M⁺, 13), 263 (3), 249 (16), 235 (3), 193 (43), 181 (61), 165 (100), 155 (66), 141 (40), 128 (25), 115 (15), 55 (27), 41 (50).

2-((2*E*,8*Z*)-undeca-2,8-dien-2-yl)naphthalene (clear, colourless liquid, 350 mg, purity according to GC-MS >99%).

Odor description (1% solution in EtOH on paper blotter, 24 h): green, aldehydic, cucumber, melon, orange blossom.

¹H-NMR (400 MHz, CDCl₃): 7.77 - 7.87 (m, 4 H), 7.62 (dd, *J*=9.0, 2.0 Hz, 1 H), 7.42 - 7.52 (m, 2 H), 5.95 - 6.02 (m, 1 H), 5.35 - 5.48 (m, 2 H), 2.31 (q, *J*=7.4 Hz, 2 H), 2.18 (d, *J*=1.2 Hz, 3 H), 2.06 - 2.16 (m, 4 H), 1.44 - 1.61 (m, 4 H), 1.01 (t, *J*=7.6 Hz, 3 H).

¹³C-NMR (101 MHz, CDCl₃): 141.2 (s), 134.4 (s), 133.5 (s), 132.4 (s), 131.8 (d), 129.3 (d), 129.1 (d), 128.0 (d), 127.5 (d), 127.5 (d), 126.0 (d), 125.4 (d), 124.4 (d), 123.9 (d), 29.5 (t), 29.3 (t), 28.9 (t), 27.0 (t), 20.6 (t), 15.8 (q), 14.4 (q).

EI-MS (70 eV, GC-MS): 278 (M⁺, 17), 263 (3), 249 (15), 235 (3), 193 (45), 181 (63), 165 (100), 155 (69), 141 (40), 128 (23), 115 (15), 55 (28), 41 (51).

Example 3: 2-((2*E*,8*E*)-undeca-2,8-dien-2-yl)naphthalene and 2-((2*Z*,8*E*)-undeca-2,8-dien-2-yl)naphthalene

3a) non-6-yn-1-yl acetate

The mixture of 9-bromonon-3-yne (10.0 g, 49 mmol, 1 equiv.) and NaOAc (16.0g, 200 mmol, 4 equiv.) in dimethyl formamide (120 mL) was stirred at 80°C for 22 h. The mixture was poured on water and extracted with heptane. The organic layer was washed with water and brine, dried over MgSO₄ and concentrated in vacuo to yield a slightly yellow liquid (7.2 g, 80%). The crude product was purified by Kugelrohr distillation (80°C/0.09 mbar) to yield non-6-yn-1-yl acetate as a clear, colorless liquid (4.6 g).

Odor description (10% DPG solution on paper blotter, 24 h): green, melon, floral, muguet, watery.

¹H-NMR (400 MHz, CDCl₃): 4.06 (t, *J*=6.7 Hz, 2 H), 2.10 - 2.33 (m, 4 H), 2.04 (s, 3 H), 1.59 - 1.68 (m, 2 H), 1.25 - 1.55 (m, 4 H), 1.11 (t, *J*=7.5 Hz, 3 H).

¹³C-NMR (101 MHz, CDCl₃): 171.2 (s), 81.9 (s), 79.0 (s), 64.4 (t), 28.7 (t), 28.2 (t), 25.1 (t), 21.0 (q), 18.6 (t), 14.3 (q), 12.4 (t).

3b) non-6-ynol

To the solution of non-6-yn-1-yl acetate (10.0 g, 55 mmol, 1 equiv.) in methanol (100 mL) was added K₂CO₃ (15 g, 110 mmol, 2 equiv.). The mixture was stirred at reflux for 1.5 h, then poured on water and extracted with methyl *t*-butyl ether. The organic layer was washed with

water and brine, dried over MgSO_4 and concentrated in vacuo to yield a slightly yellow liquid (6.9 g, 80%). The crude product was purified by Kugelrohr distillation ($80^\circ\text{C}/0.06$ mbar) to yield non-6-yn-1-ol as a clear, colorless liquid (4.2 g, 55%).

- 5 Odor description (10% DPG solution on paper blotter): watery, fatty, green, melon, floral.

^1H -NMR (400 MHz, CDCl_3): 3.66 (br t, $J=5.5$ Hz, 2 H), 2.13 - 2.21 (m, 4 H), 1.42 - 1.71 (m, 7 H), 1.12 (t, $J=7.3$ Hz, 3 H)

^{13}C -NMR (101 MHz, CDCl_3): 81.8 (s), 79.2 (s), 62.9 (t), 32.3 (t), 28.9 (t), 25.0 (t), 18.7 (t),

- 10 14.4 (q), 12.4 (t)

3c) non-6-ynal

- To liquid NH_3 (70 mL) were added dropwise at -78°C tert. butanol (10 g) and the solution of non-6-ynol (8.90 g, 63.5 mmol, 1 equiv.) in THF (50 mL). Then lithium (2.20 g, 317 mmol, 5 equiv.) was added in small pieces during 30 min at -60°C , upon which the mixture turned dark blue. After completed addition the mixture was stirred for 2 h at -78°C , then at room temperature for 18 h, letting ammonia to evaporate. Ice was carefully added to destroy residual lithium, then acidic workup was effected as described in Example 2a to yield (E)-non-6-en-1-ol as a colorless liquid (9.13 g, >99%). The crude product (9.13 g, 64.2 mmol, 1 equiv.) was dissolved in CH_2Cl_2 and pyridinium chlorochromate (PCC, 19.4 g, 89.9 mmol, 1.4 equiv) was added. After stirring for 1.5 h at room temperature, the mixture was filtered over a silica gel pad, rinsing with MTBE. Removal of the solvent in vacuo yielded crude (E)-non-6-enal as a clear, slightly green liquid (7.47 g, 83%). The product was used without purification in the subsequent step.

25

3d) 2-((2E,8E)-undeca-2,8-dien-2-yl)naphthalene and 2-((2Z,8E)-undeca-2,8-dien-2-yl)naphthalene

- The procedure described in Example 2c was repeated with KOtBu (2.64 g), bromo(1-(naphthalen-2-yl)ethyl)triphenyl- λ^5 -phosphane (11.7 g) and (E)-non-6-enal (2.75 g) to yield 2-((8E)-undeca-2,8-dien-2-yl)naphthalene in an 2E/2Z ratio of 60:25 (5.60 g, >99%, clear yellow liquid). The two isomers were isolated in pure form by flash column chromatography on SiO_2 (heptane) and subsequent Kugelrohr distillation (0.05 mbar, 145°C).

35

2-((2Z,8E)-undeca-2,8-dien-2-yl)naphthalene (250 mg, clear colourless liquid, 95% purity by GC-MS)

Odor description (1% solution in EtOH on paper blotter, 24 h): fatty, green, melon, powdery, cucumber, floral.

¹H-NMR (400 MHz, CDCl₃): 7.80 - 7.88 (m, 3 H), 7.66 (s, 1 H), 7.43 - 7.52 (m, 2 H), 7.38 (dd, *J*=8.4, 1.7 Hz, 1 H), 5.59 (td, *J*=7.3, 1.5 Hz, 1 H), 5.32 - 5.46 (m, 2 H), 2.15 (d, *J*=1.2 Hz, 3 H), 1.93 - 2.09 (m, 6 H), 1.28 - 1.47 (m, 4 H), 0.98 (t, *J*=7.5 Hz, 3 H).

5 ¹³C-NMR (101 MHz, CDCl₃): 139.8 (s), 135.9 (s), 133.3 (s), 132.2 (s), 132.0 (d), 129.2 (d), 128.4 (d), 127.8 (d), 127.6 (d), 127.5 (d), 126.8 (d), 126.4 (d), 125.9 (d), 125.5 (d), 32.4 (t), 29.7 (t), 29.2 (t), 29.1 (t), 25.7 (q), 25.6 (t), 14.0 (q).

EI-MS (70 eV, GC-MS): 278 (M⁺, 14), 263 (3), 249 (17), 235 (4), 193 (46), 181 (59), 165 (100), 155 (66), 141 (36), 128 (21), 115 (13), 55 (16), 41 (26).

10

2-((2*E*,8*E*)-undeca-2,8-dien-2-yl)naphthalene (400 mg, clear colourless liquid, >99% purity by GC-MS)

Odor description ((1% solution in EtOH on paper blotter, 24 h): fatty, green, melon, powdery, cucumber, floral.

15

¹H-NMR (400 MHz, CDCl₃): 7.80 - 7.87 (m, 4 H), 7.64 (dd, *J*=8.5, 1.8 Hz, 1 H), 7.45 - 7.51 (m, 2 H), 6.01 (t, *J*=7.1 Hz, 1 H), 5.43 - 5.56 (m, 2 H), 2.31 (q, *J*=7.1 Hz, 2 H), 2.19 (d, *J*=1.5 Hz, 3 H), 2.03 - 2.14 (m, 4 H), 1.47 - 1.59 (m, 4 H), 1.03 (t, *J*=7.5 Hz, 3 H)

20 ¹³C-NMR (101 MHz, CDCl₃): 141.2 (s), 134.4 (s), 133.6 (s), 132.4 (s), 132.2 (d), 129.4 (d), 129.2 (d), 128.0 (d), 127.6 (d), 127.5 (d), 126.0 (d), 125.4 (d), 124.4 (d), 123.9 (d), 32.6 (t), 29.5 (t), 29.2 (t), 28.9 (t), 25.7 (t), 15.8 (q), 14.1 (q).

EI-MS (70 eV, GC-MS): 278 (M⁺, 21), 263 (4), 249 (15), 235 (4), 193 (46), 181 (62), 165 (100), 155 (67), 141 (36), 128 (20), 115 (12), 55 (15), 41 (30).

25 Example 4: 1-((7*Z*)-deca-1,7-dien-1-yl)-4-methoxybenzene

4a) bromo(4-methoxybenzyl)triphenyl-λ⁵-phosphane

The solution of (4-methoxyphenyl)methanol (20.1 g, 145 mmol, 1 equiv.) and bromo triphenyl phosphorane (49.9 g, 145 mmol, 1 equiv.) was refluxed for 20 h. Upon cooling to room temperature, a white precipitate was formed which was collected by filtration, rinsed with THF
30 and dried under vacuum. This product (bromo(4-methoxybenzyl)triphenyl-λ⁵-phosphane, 42.1 g, 63%) was used without further purification in the next step.

4b) 1-((7*Z*)-deca-1,7-dien-1-yl)-4-methoxybenzene

Following the general procedure described in Example 2c, starting from bromo(4-methoxybenzyl)triphenyl-λ⁵-phosphane (prepared above, 18.2 g, 39.3 mmol, 1.1 equiv.),
35 KOtBu (4.41 g, 39.3 mmol, 1.1 equiv.) and (*Z*)-6-nonenal (5.01 g, 35.7 mmol, 1 equiv) 1-((7*Z*)-deca-1,7-dien-1-yl)-4-methoxybenzene was prepared. The crude product (6.55 g, 75%) was

purified by Kugelrohr distillation (0.08 mbar, 180°C) to yield 1-((7Z)-deca-1,7-dien-1-yl)-4-methoxybenzene as a colourless liquid (4.25 g, 48%, 2 isomers, 1E,7Z : 1Z,7Z = 64:37).

Odor description (1% solution in EtOH on paper blotter, 24 h): cucumber, fresh green, melon,
5 anisic, powdery.

¹H-NMR (400 MHz, CDCl₃, mixture of 1E,7Z- and 1Z,7Z-isomers): 7.22 - 7.51 (m, 2 H), 6.77 - 7.02 (m, 2 H), 6.34 - 6.40 (m, 1 H), 6.13 (t, *J*=7.0 Hz, 0.6 H, 1E,7Z-isomer), 6.09 (t, *J*=6.8 Hz, 0.4 H, 1Z,7Z-isomer), 5.60 (dt, *J*=11.6, 7.3 Hz, 0.4 H, 1Z,7Z-isomer), 5.31 - 5.53 (m, 2.6 H),
10 3.84 (s, 1.1 H, OCH₃, 1Z,7Z-isomer), 3.83 (s, 1.9 H, OCH₃, 1E,7Z-isomer), 2.31 - 2.53 (m, 1 H), 2.23 (qd, *J*=7.1, 1.5 Hz, 1 H), 2.02 - 2.13 (m, 3 H), 1.29 - 1.55 (m, 4 H), 0.95 - 1.08 (m, 3 H).

1-((1Z,7Z)-deca-1,7-dien-1-yl)-4-methoxybenzene:

15 ¹³C-NMR (101 MHz, CDCl₃): 158.2 (s), 131.5 (d), 130.5 (d), 129.2 (d), 129.1 (d), 129.0 (s), 128.9 (2d), 113.5 (2d), 55.2 (q), 31.9 (t), 29.1 (t), 27.0 (t), 20.5 (t), 14.4 (s), 14.1 (q).
EI-MS (70 eV, GC-MS): 244 (M⁺, 6), 215 (6), 173 (22), 162 (76), 147 (100), 134 (97), 121 (80), 91 (40), 41 (30).

20 1-((1E,7Z)-deca-1,7-dien-1-yl)-4-methoxybenzene:

¹³C-NMR (101 MHz, CDCl₃): 158.6 (s), 131.8 (d), 131.7 (d), 130.8 (s), 129.9 (d), 128.9 (d), 127.0 (2d), 113.9 (2d), 55.3 (q), 32.9 (t), 29.1 (t), 28.5 (t), 27.0 (t), 20.6 (t), 14.4 (q).
EI-MS (70 eV, GC-MS): 244 (M⁺, 10), 215 (7), 201 (5), 173 (24), 162 (76), 147 (100), 134 (93), 121 (85), 91 (41), 41 (33).

25

Example 5: 1-(dec-1-en-7-yn-1-yl)-4-methoxybenzene

5a) oct-1-en-5-yne

Following the general procedure described in Example 1a, starting from 1-bromo-3-butene (0.74 mol) oct-1-en-5-yne was prepared. The crude product was purified by distillation over a
30 Widmer column (1bar /128°C) to yield oct-1-en-5-yne (colourless liquid, 32.6 g, 41%).

¹H-NMR (400 MHz, CDCl₃): 5.76 - 5.98 (m, 1 H), 4.93 - 5.18 (m, 2 H), 2.13 - 2.36 (m, 6 H), 1.13 (t, *J*=7.5 Hz, 3 H).

¹³C-NMR (101 MHz, CDCl₃): 137.3 (d), 115.3 (t), 82.1 (s), 78.7 (s), 33.4 (t), 18.6 (t), 14.3 (q),
35 12.4 (t).

5b) non-6-ynal

The solution of oct-1-en-5-yne (8.3 g, 78 mmol, 1 equiv.), Rh-based hydroformylation catalyst (0.3 g) and Xantphos (0.6 g) was stirred under 25 bar syngas (H₂/CO) at 90°C for 2 h. The solution was concentrated in vacuo and the residue purified by flash column chromatography on SiO₂ (heptane/MTBE 30:1) to yield non-6-ynal as a colourless liquid (4.8 g, 42%).

5

Odor description (10% solution in dipropylene glycol on paper blotter, 0 and 24 h): powerful green, watery, cucumber, fresh.

¹H-NMR (400 MHz, CDCl₃): 9.76 (t, *J*=1.7 Hz, 1 H), 2.45 (td, *J*=7.3, 1.7 Hz, 2 H), 2.10 - 2.21 (m, 4 H), 1.66 - 1.80 (m, 2 H), 1.47 - 1.62 (m, 2 H), 1.10 (t, *J*=7.5 Hz, 3 H)
¹³C-NMR (101 MHz, CDCl₃): 202.5 (s), 179.0 (s), 82.2 (s), 82.1 (s), 78.6 (s), 78.6 (s), 43.4 (s), 33.4 (s), 28.4 (s), 28.3 (s), 23.8 (s), 21.2 (s), 18.5 (s), 18.4 (s), 14.3 (s), 12.3 (s)

10

5c) 1-(dec-1-en-7-yn-1-yl)-4-methoxybenzene

15 Following the general procedure described in Example 4b, starting from bromo(4-methoxybenzyl)triphenyl-λ⁵-phosphane (16.8 g, 36.2 mmol, 1 equiv.), KOtBu (4.06 g, 36.2 mmol, 1 equiv.) and non-6-ynal (5.0 g, 36.2 mmol, 1 equiv) 1-(dec-1-en-7-yn-1-yl)-4-methoxybenzene was prepared. The crude product was purified by flash column chromatography on SiO₂ (heptane/MTBE 60:1) to yield 1-(dec-1-en-7-yn-1-yl)-4-methoxybenzene as a clear, colourless oil (1.70 g, 18%), E/Z = 64:30, purity (sum of isomers, GC-MS) 94%.

20

Odor description (1% solution in EtOH on paper blotter, 24 h): green, melon, anisic.

25 ¹H-NMR (400 MHz, CDCl₃, mixture of E and Z isomers): 7.22 - 7.37 (m, 2 H), 6.82 - 6.94 (m, 2 H), 6.31 - 6.44 (m, 1 H), 6.05 - 6.16 (m, 1 H), 3.84 (s, 0.9 H), 3.83 (s, 2.1 H), 2.32 - 2.46 (m, 1 H), 2.12 - 2.29 (m, 5 H), 1.49 - 1.77 (m, 4 H), 1.07 - 1.22 (m, 3 H).

(E)-1-(dec-1-en-7-yn-1-yl)-4-methoxybenzene

30 ¹³C-NMR (101 MHz, CDCl₃): 158.7 (s), 130.7 (s), 129.9 (d), 129.3 (d), 127.0 (2d), 113.9 (2d), 81.8 (s), 79.3 (s), 55.3 (q), 32.6 (t), 28.7 (2t), 18.7 (t), 14.4 (q), 12.5 (t).

(Z)-1-(dec-1-en-7-yn-1-yl)-4-methoxybenzene

35 ¹³C-NMR (101 MHz, CDCl₃): 158.2 (s), 131.2 (d), 130.7 (s), 128.6 (2s), 128.4 (d), 113.6 (2d), 81.8 (s), 79.3 (s), 55.2 (q), 29.2 (t), 28.8 (t), 28.2 (t), 18.6 (t), 14.4 (q), 12.5 (t).

Example 6: 4-((7Z)-deca-1,7-dien-1-yl)-2-ethoxyphenol

Following the general procedure described in Example 1b, starting 1-bromo-6-nonene (56.3 g, 274 mmol) and 3-ethoxy-4-hydroxy benzaldehyde (38.0 g, 229 mmol) (Z)-2-ethoxy-4-(1-hydroxydec-7-en-1-yl)phenol was prepared after initial deprotonation of the phenolic hydroxy group with methyl magnesium bromide (3 N THF solution, 206 mmol). The crude (Z)-2-ethoxy-4-(1-hydroxydec-7-en-1-yl)phenol (70 g) was distilled in a Kugelrohr oven (0.05 mbar, 140-180°C) upon which spontaneous dehydration occurred to yield 4-((7Z)-deca-1,7-dien-1-yl)-2-ethoxyphenol as a clear, slightly yellow oil (37.5 g, 53%), purity (GC-MS) 95%.

Odor description (1% solution in EtOH on paper blotter, 24 h): green, powdery, vanilla, melon.

¹H-NMR (400 MHz, CDCl₃): 6.76 - 6.98 (m, 3 H), 6.24 - 6.52 (m, 1 H), 6.09 (dt, *J*=15.8, 6.9 Hz, 1 H), 5.72 - 5.81 (m, 1 H), 5.27 - 5.55 (m, 2 H), 4.12 - 4.19 (m, 2 H), 2.24 (qd, *J*=7.1, 1.3 Hz, 2 H), 1.93 - 2.17 (m, 4 H), 1.28 - 1.57 (m, 7 H), 1.02 (t, *J*=7.5 Hz, 3 H).

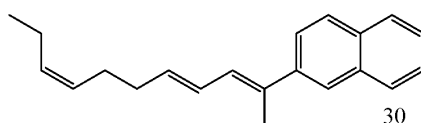
¹³C-NMR (101 MHz, CDCl₃): 145.9 (s), 145.0 (s), 131.7 (d), 130.5 (s), 129.7 (d), 129.1 (d), 128.6 (d), 119.4 (d), 114.4 (d), 109.0 (d), 64.4 (t), 32.9 (t), 29.4 (t), 29.2 (t), 27.0 (t), 20.6 (t), 14.9 (q), 14.4 (q).

EI-MS (70 eV, GC-MS): 274 (M⁺, 9), 245 (4), 192 (39), 164 (35), 151 (34), 131 (100), 123 (28), 103 (44), 91 (18), 77 (14), 55 (18), 41 (24).

20

Example 7: 2-((2E,4E,8Z)-undeca-2,4,8-trien-2-yl)naphthalene – Comparative Compound B

Starting from (1-(2-naphthyl)ethyl)triphenylphosphonium bromide (2.40 g, 4.83 mmol, 1.0 equiv.), n-BuLi (1.6 M in hexanes, 3.0 mL, 4.83 mmol, 1.0 equiv.) and (2E,6Z)-Nona-2,6-dienal (1.00 g, 7.24 mmol, 1.5 equiv.), and after stirring the mixture at 25°C for 3 h, 0.90 g (67%) of the title compound as a colorless oil was obtained after purification by flash chromatography on SiO₂ (cyclohexane/EtOAc 997:3).



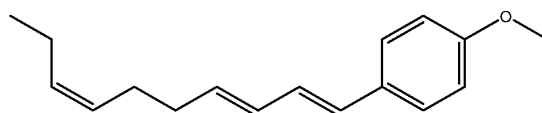
Compound B

Odor description (dry-down of a 10% DPG solution after 24 hours on a smelling strip): floral, green, watery, fatty, dark tea, mimosa.

Example 8 - 1-((7Z)-deca-1,3,7-trien-1-yl)-4-methoxybenzene – Comparative Compound C

Prepared from p-methoxyphenethyltriphenylphosphonium bromide and 2E,6Z-nona-2,6-dienal following the general procedure disclosed in WO2012085287A1 (Example 6.1).

35



Compound C

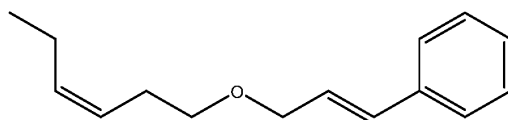
Odor description (1% solution in EtOH on paper blotter, 24 h): green, anisic, floral, oily.

- 5 ¹H-NMR (mixture of E/Z-isomers, 400 MHz, CDCl₃): 7.28 - 7.57 (m, 2 H), 6.84 - 7.02 (m, 2 H), 6.61 - 6.69 (m, 1 H), 6.40 - 6.59 (m, 1 H), 6.14 - 6.31 (m, 1 H), 5.77 - 5.92 (m, 1 H), 5.30 - 5.59 (m, 2 H), 3.78 - 3.90 (m, 3 H), 1.98 - 2.27 (m, 6 H), 0.80 - 1.08 (m, 3 H).
- ¹³C-NMR (mixture of E/Z-isomers 101 MHz, CDCl₃): 158.9 (s), 158.4 (s), 136.6 (d), 133.9 (d), 132.2 (d), 132.2 (d), 131.0 (d), 130.5 (d), 130.1 (d), 129.8 (d), 127.4 (d), 128.2 (d), 127.3 (d),
- 10 126.9 (d), 114.0 (d), 113.7 (d), 55.3 (q), 55.3 (q), 33.0 (t), 33.0 (t), 27.0 (t), 26.9 (t), 20.6 (t), 14.3 (q), 14.3 (q).

Example 9: ((E)-3-(((Z)-hex-3-en-1-yl)oxy)prop-1-en-1-yl)benzene - Comparative

Compound D

- 15 Prepared from (E)-(3-bromoprop-1-en-1-yl)benzene and Z-3-hexenol in the presence of sodium hydride following the general procedure disclosed in US2018001652.



Compound D

- 20 Colourless oil, odor description (1% solution in EtOH on paper blotter, 24 h): pleasant green note.

- ¹H-NMR (400 MHz, CDCl₃): 7.25 - 7.44 (m, 5 H), 6.64 (d, *J*=15.9 Hz, 1 H), 6.33 (dt, *J*=15.9, 6.0 Hz, 1 H), 5.37 - 5.56 (m, 2 H), 4.19 (dd, *J*=6.1, 1.5 Hz, 2 H), 3.53 (t, *J*=7.1 Hz, 2 H), 2.42 (qt, *J*=7.1, 0.7 Hz, 2 H), 2.07 - 2.16 (m, 2 H), 1.01 (t, *J*=7.6 Hz, 3 H).
- 25 ¹³C-NMR (MHz, CDCl₃): 136.8 (s), 133.8 (d), 132.2 (d), 128.5 (d), 127.6 (d), 126.5 (d), 126.3 (d), 124.8 (d), 71.5 (t), 70.1 (t), 27.9 (t), 20.7 (t), 14.3 (q).

Example 10: Application in shampoo base

- 30 Hair shampoo samples (20 g) were prepared by adding 0.2% by weight of the respective compound as indicated in Table 1 below to unperfumed clear hair shampoo base and mixing on a bottle roller for 24 h at room temperature. Odor-neutral human hair swatches were wetted with warm tap water and lathered delicately with 2 mL of the above hair shampoo samples for 30 sec. by hand wearing gloves. The lathered hair swatches were left in a plastic bowl for 2 min, then rinsed under running tap water for 20 sec. After removing excess water

by squeezing the hair swatches between two fingers, they were left to dry in open air. The wet and dried hair swatches (1 and 2 days) were assessed by a panel of 4-6 experts with regard to odor intensity and quality. The odor intensity was recorded on an intensity scale of 0 (odorless), 1 (very weak), 2 (weak), 3 (medium), 4 (strong) to 5 (very strong).

Table 1:

Entry		wet	1 day	2 days	odor on dry hair
1	2-((2E/Z,8Z)-undeca-2,8-dien-2-yl)naphthalene	2.9	3.5	3.2	melon, green, orange blossom
2	4-((1E,7Z)-deca-1,7-dien-1-yl)-2-ethoxyphenol	3.3	4.0	3.2	fresh vanilla with green melon contrast
A	(2E,6Z)-nona-2,6-dien-1-yl palmitate	1.4	1.9	2.3	green, fatty, fishy
B	2-((2E,4E,8Z)-undeca-2,4,8-trien-2-yl)naphthalene	3.4	2.6	2.5	fatty, oily, fishy
C	1-((1E,3E,7Z)-deca-1,3,7-trien-1-yl)-4-methoxybenzene	3.4	2.9	2.3	oily, fatty, fishy
D	((E)-3-(((Z)-hex-3-en-1-yl)oxy)prop-1-en-1-yl)benzene	1.5	1.3	1.5	weak powdery

The experiment demonstrates that precursors of the current invention (entry 1 & 2) are capable of releasing a fresh green-floral or green-vanilla fragrance on dry hair, whereas precursors with side chains of the same length and one additional double bond (entry 1 vs entry B; entry 2 vs entry C and D) impart unpleasant fatty, oily and fishy notes.

Surprisingly, the precursor D releases a pleasant green note when applied as 1% solution in ethanol on a paper blotter after 24 h (see Example 9), however in shampoo application only a very weak powdery odor can be perceived on dry hair.

The results furthermore show that even after 2 days the odor intensity of the compounds 1 & 2 observed was received as medium to strong (> 3) compared to the almost weak (< = 2.5) odor intensity observed for the compounds A – D.

Example 11: Application in liquid detergent

a) Sample preparation

0.2% by weight of precursors of the present invention were incorporated respectively into unperfumed liquid detergent base by magnetic stirring at room temperature for 24 h.

b) Washtest and sensory evaluation

A 40°C machine wash cycle was performed using 55 g of the above prepared liquid detergent samples and odor-neutral cotton/elastan mixed fabric T-shirts. The wet and line-dried fabric (1 and 4 days) was assessed by a panel of 4-6 experts with regard to odor intensity and quality. The odor intensity was recorded on an intensity scale of 0 (odorless), 1 (very weak), 2 (weak), 3 (medium), 4 (strong) to 5 (very strong).

Table 2:

Entry		wet	1 day	4 days	odor on dry fabric
1	2-((2E,8Z)-undeca-2,8-dien-2-yl)naphthalene	1.8	2.6	2.6	green, melon, orange blossom
2	4-((1E,7Z)-deca-1,7-dien-1-yl)-2-ethoxyphenol	3.4	3.3	4.1	cucumber, melon, vanilla
3	1-((1E,7Z)-deca-1,7-dien-1-yl)-4-methoxybenzene	1.8	3.6	3.7	melon, anisic
4	(E)-2-(undec-2-en-8-yn-2-yl)naphthalene	1.9	1.9	3.3	green, melon, orange flower

The results illustrate that strong fragrance intensities are achieved on dry fabric with compounds of the current invention and that green melon cucumber odors are modulated with anisic, vanilla or orange blossom notes resulting in fresh natural perfume accords.

Example 12: Headspace analysis of released volatiles

A solution of the precursor (100 µg, 1.0 mg/mL solution in MTBE) was evenly applied through a displacement pipette to a paper strip (1 cm x 8 cm). The paper strip was left to dry (1 h at room temperature), then folded in the middle and inserted in “V”-shape into a 20 mL headspace vial (details see, e.g. WO 2023/067040, Figure 2). The vial was closed with a septum screwcap and placed in a cabinet equipped with a fluorescent daylight imitation lamp and mirrored walls for 24 h (temperature 27-28°C).

Extraction and analysis of the released organic volatiles was effected in automated mode on a Trace 1310 gas chromatograph equipped with a TriPlus RSH autosampler (Thermo Fisher Scientific), coupled to a ISQ LT mass spectrometer (Thermo Fisher Scientific). The extraction of the organic volatiles from the headspace with SPME (solid phase microextraction) was carried out during 1 h at 40°C using a 50/30µm divinylbenzene/carboxen/ polydimethylsiloxane SPME fiber (DVB/CAR/PDMS, Supelco P/N 57298-U), and subsequently desorbed in splitless mode at 250°C for 1 min. GC-MS analysis (gas chromatography with mass spectrometric detection) was carried out with a VF-WAXms capillary column (Agilent, 30m length, 0.25mm I.D., 0.25µm film thickness). Helium was used as a carrier gas with a constant flow rate of 1ml/min. The GC oven temperature was programmed from 35°C with 2-min hold to 250°C at

5 °C/min with a 10-min final temperature hold. The mass spectrometer was operated at 70 eV in EI mode over a m/z range of 33-350, scanned at 0.2 s intervals and with a temperature of transfer line and ion source of 230 °C and 220°C, respectively. A list of identified volatiles released from each precursor is reported in the below table (indicated are relative peak area %).

Table 3:

Compound of formula (I)	Released Volatiles (MS-TIC peak area %)
2-((2E,8Z)-undeca-2,8-dien-2-yl)naphthalene	(Z)-6-nonenal (70.6%), 1-(naphthalen-2-yl)ethan-1-one (10.1%)
1-((1E,7Z)-deca-1,7-dien-1-yl)-4-methoxybenzene	(Z)-6-nonenal (76.1%), anisic aldehyde (3.2%)

10 It should be noted that the indicated relative peak area % values are not related to molar release rates. The relative amount of each volatile in the gas phase depends mainly on volatility.

15 The results show that compounds of general formula (I) release high amounts of the strong green melon aldehyde (Z)-6-nonenal and an aromatic carbonyl fragrance compound such as 1-(naphthalen-2-yl)ethan-1-one (Oranger Crystals) or anisic aldehyde under ambient conditions.

Example 13: Assessment of biodegradability

The results of the biodegradability assessment by the manometric respirometry test (OECD 10 guidelines for the testing of materials No. 301F, Paris 1992) are summarized in Table 4.

Table 4:

Compound of formula (I)	Biodegradation in %	result
2-((2E,8Z)-undeca-2,8-dien-2-yl)naphthalene	81	inherently biodegradable
1-((1E,7Z)-deca-1,7-dien-1-yl)-4-methoxybenzene	82	readily biodegradable

The results show that compounds of the present invention with varying aromatic moieties are biodegradable.

A compound can be classified biodegradable, if it reaches the pass level of 60% oxygen

consumption of theory required for complete mineralization. It is readily biodegradable, if the pass level is reached within 10 days within the 28-day period of the test. The 10-day window begins when the degree of biodegradation has reached 10%. If the pass level is obtained after 28-day period of the test, the compound can be classified as inherently biodegradable.

5

Example 14: Assessment of the scalp malodor counteractancy

Hair switches were wetted under hand hot running water and then 2.5g of shampoo was massaged into the hair switch for 30 seconds. The lathered hair switches were left for 1 minute, then rinsed under hand hot running water for 30 seconds, and then left to air dry on a clothes drying rack for either 24 hours or 48 hours prior to testing.

10

On the day of the assessment, 5µL of Scalp malodor @ 1% (DPG) was pipetted onto a cotton pad, wrapped in the hair switch and held in place with a hairnet which was then placed inside a 500ml glass powder jar containing another cotton pad soaked with 2ml of water and lidded. Samples were put in a 37°C oven and left to equilibrate for 4 hours (with humidity) prior to assessment.

15

A control jar was also prepared with malodor only. Where malodor and a clean hair switch was placed in the 500ml powder jar (with humidity). Another jar was prepared as a 'hidden control' and contained malodor only but the panelists were unaware that it did not contain a fragranced product. Each sample was coded with a random code number. The 24 hour and 48 hour air dry hair was tested in the same session.

20

For the assessment trained sensory panelists were asked to unscrew the lid of the 500ml jar and assess both, the perceived malodor intensity (PMI) and the perceived fragrance intensity (PFI) directly from the jar, using a 0-100 linear scale. Each sample was assessed twice by 18 panelists, thus giving 36 assessments per sample.

25

All malodor and fragrance perceived intensities were scaled against the malodor control sample (clean hair switch). The malodor perceived intensity was set at 35 for Scalp malodor and the fragrance perceived intensity was set at 0.

30

The order of samples assessed by the panelists was pre-determined using a balanced randomization. The samples were assessed in a sequential monadic way and 2 minutes was left between assessing each sample to minimize fragrance carry-over effects. The results are summarized in Table 5 and 6 below.

35

Table 5: Perceived Malodor Intensity (PMI)

Product	PMI	SoD ²⁾
Shampoo comprising 2-((8Z)-undeca-2,8-dien-2-yl) naphthalene @ 0.01wt% - 48hours	22.2	A
Shampoo comprising 2-((8Z)-undeca-2,8-dien-2-yl) naphthalene @ 0.01wt% - 24 hours	26.3	B
Unfragranced Shampoo – 48 hours	30.8	C
Control (Scalp Malodor only)	31.6	C
Unfragranced Shampoo – 24 hours	32.6	C

2) Significance of Differences: Where the same letter is shown there are no statistically significant differences between the relevant figures.

5

The jars containing hair switches washed with ‘Shampoo comprising 2-((8Z)-undeca-2,8-dien-2-yl) naphthalene @ 0.01% - 48 hours’ were perceived to be significantly weaker in perceived malodor intensity (PMI) than the jars containing hair switches washed with ‘Shampoo comprising 2-((8Z)-undeca-2,8-dien-2-yl) naphthalene @ 0.01% - 24 hours’ and these jars were perceived to be significantly weaker in PMI than the jars containing hair switches washed with ‘Unfragranced Shampoo - 24 hours’, ‘Unfragranced Shampoo - 48 hours’ and ‘Scalp Malodor only’ which were not perceived to be significantly different in PMI.

10

Table 6: Perceived Fragrance Intensity (PFI)

Product	PFI	SoD ²⁾
Shampoo comprising 2-((8Z)-undeca-2,8-dien-2-yl) naphthalene @ 0.01wt% - 48hours	21.3	C
Shampoo comprising 2-((8Z)-undeca-2,8-dien-2-yl) naphthalene @ 0.01wt% - 24 hours	13.3	B
Unfragranced Shampoo – 48 hours	2.9	A
Control (Scalp Malodor only)	2.4	A
Unfragranced Shampoo – 24 hours	2.1	A

15

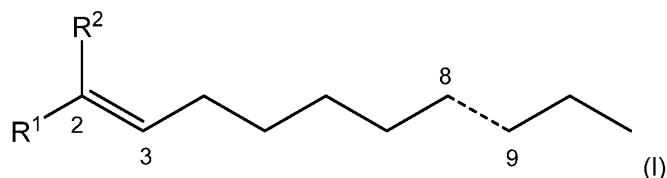
2) Significance of Differences: Where the same letter is shown there are no statistically significant differences between the relevant figures.

When the products were assessed in the presence of the scalp malodor, jars containing hair washed with 'Shampoo comprising 2-((8Z)-undeca-2,8-dien-2-yl) naphthalene @ 0.01% - 48 hours' were perceived to be significantly stronger in perceived fragrance intensity (PFI) than the jars containing hair washed with 'Shampoo comprising 2-((8Z)-undeca-2,8-dien-2-yl) naphthalene @ 0.01% - 24 hours' and these jars were perceived to be significantly stronger in PFI than the jars containing hair washed with 'Unfragranced Shampoo - 24 hours', 'Unfragranced Shampoo - 48 hours' and 'Scalp Malodor only' which were not perceived to be significantly different in PFI.

As can be seen from the result above, the precursor of the present invention, when tested in shampoo base, significantly reduced the perception of the scalp malodor when assessed on hair switches which had been dried for 24 and 48 hours respectively.

Claims

1. A compound of formula (I)



wherein

- 5 R^1 is selected from phenyl, naphthyl and phenyl substituted with 1 or 2 functional groups independently selected from hydroxy, methoxy and ethoxy,
 R^2 is selected from hydrogen and methyl,
the dotted line represents a carbon-carbon double bond or a carbon-carbon triple bond.
- 10 2. A compound according to claim 1 or claim 2, wherein the double bond between C-2 and C-3 is in E-configuration and the double bond between C-8 and C-9 is in Z-configuration.
- 15 3. A compound according to claim 1 or claim 2, wherein the dotted line represents a carbon-carbon double bond and the double bond between C-8 and C-9 is in Z-configuration.
- 20 4. A compound according to claim 1 selected from the group consisting of 2-(undeca-2,8-dien-2-yl)naphthalene, 2-(undec-2-en-8-yn-2-yl)naphthalene, 1-(deca-1,7-dien-1-yl)-4-methoxybenzene, 1-butoxy-3-(deca-1,7-dien-1-yl)benzene, 1-(dec-1-en-7-yn-1-yl)-4-methoxybenzene, 4-(deca-1,7-dien-1-yl)-2-ethoxyphenol, and 4-(deca-1,7-dien-1-yl)-2-methoxyphenol.
- 25 5. A fragrance composition comprising a compound of formula (I) as defined in any one of the preceding claims, or a mixture thereof.
6. A consumer product comprising a compound of formula (I) as defined in claim 1 to 4, or a fragrance composition according to claim 5, and a consumer product base.
- 30 7. The use of a compound of formula (I) as defined in claim 1 to 4 as fragrance precursor.
8. The use according to claim 7 comprising the step of generating (Z)-6-nonenal.

9. (Z)-6-nonenal.
10. A method of masking, reducing and/or preventing scalp malodor, said method
comprising the step of applying a compound according to formula (I) as define in
5 claim 1 to 4 to the human scalp or hair.