

ORGANIC COMPOUNDS**TECHNICAL FIELD**

The present invention is concerned with fragrance and flavor ingredients, and with compositions containing them that are useful in fragrance and flavor applications. It furthermore
5 relates to a method of making the compounds. In particular, the present invention is concerned with compounds of formula (I) and/or (II) possessing green-galbanum, and fruity-pineapple odor notes.

BACKGROUND

In the fragrance and flavor industry, perfumers and flavorists are continually looking for new
10 compounds possessing unique olfactory properties. For example, there is a need for ingredients that are suitable for the flavor and fragrance industry possessing green fruity-pineapple odor notes reminiscent of galbanum.

Galbanum oil is a natural perfuming ingredient highly appreciated by perfumers for its green character. However, its use is limited by a high cost. Synthetic replacers having an odor
15 reminiscent of galbanum oil are described, for example, in US 4147672 disclosing 3,3-dimethyl-cyclohexyl and 3,3-dimethyl-cyclohexenyl derivatives. Fragrance ingredients reminiscent of galbanum oil are also described in EP 913383 disclosing spirocyclic compounds, or WO2012110281 disclosing 1-(5-ethyl-5-methyl-1-cyclohexen-1-yl)-4-penten-1-one imparting odor notes of the galbanum type.

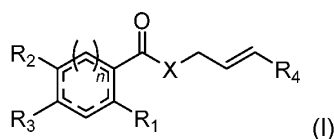
20 Galbanum is valued for its ability to impart a rich, spicy green scent. The green galbanum odor family is quite important for the creation of fragrance accords. Some famous fragrances get their character from this odor family.

There still remains a need for new fragrance ingredients reminiscent of galbanum. In addition to the primary objection to provide new fragrance ingredients of the galbanum odor family, the
25 ingredients should be preferably being derivable from renewable resources. The use of renewable starting material is becoming more and more significant because of the increasing market demand for new fragrances based on renewable raw materials and hence at least partial constituting a replacement of ingredients obtained from petrochemical raw materials.

Surprisingly inventors found a new class of ingredients of formula (I) as defined herein below possessing the highly sought-after green-galbanum, and fruity-pineapple odor and flavor notes, some of which are derivable from renewable starting materials.

SUMMARY

- 5 In accordance with a first aspect of the present invention there is provided a compound of formula (I) in the form of any one of its stereoisomers or mixture thereof



wherein

R₁ and R₄ are independently selected from H and Me;

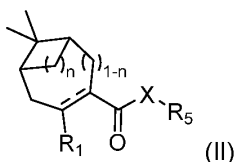
- 10 R₂ and R₃ are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and vinyl;
 n is 0 or 1;

X is selected from –O– and –CH₂–; and

the dotted line together with the carbon-carbon bond forms a single bond or a double bond in the ring system; and the ring system has no double bonds, one double bond or two double

- 15 bonds, or is an aromatic ring system.

In accordance with a second aspect of the present invention, there is provided a compound of formula (II) in the form of any one of its stereoisomers or mixture thereof



wherein

- 20 R₁ is H or Me;

R₅ is cyclopent-2-en-1-yl or but-2-en-1-yl;

n is 0 or 1;

X is selected from –O– and –CH₂–; and

the dotted line together with the carbon-carbon bond forms a single bond or a double bond.

In accordance with a third aspect of the present invention there is provided a fragrance composition comprising at least one compound of formula (I) or at least one compound of formula (II) as defined above.

5 In accordance with a fourth aspect of the present invention there is provided a fragranced article comprising

- a) at least one compound of formula (I) or at least one compound of formula (II) as defined above as odorant, or a fragrance composition as defined above, and
- b) a consumer product base.

10 In accordance with a fifth aspect of the present invention there is provided the use of the compound of formula (I) or the compound of formula (II) as defined above as odorant.

In accordance with a sixth aspect of the present invention there is provided a method of improving, enhancing or modifying a consumer product base by means of addition thereto of an olfactory acceptable amount of a compound of formula (I) or of a compound of formula (II) as defined above.

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

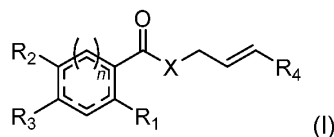
- green-galbanum, and fruity-pineapple odor profiles,
- powerful compounds,
- made from natural and/or renewable resources, and
- 20 • biodegradable.

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
25 invention unless otherwise indicated herein, or otherwise clearly contradicted by context.

DETAILED DESCRIPTION

The present invention is based on the surprising finding that compounds according to formula (I) possess green-galbanum, and fruity-pineapple odor notes.

There is therefore provided a compound of formula (I) in the form of any one of its stereoisomers or mixture thereof



wherein

- 5 R₁ and R₄ are independently selected from H and Me;
 R₂ and R₃ are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and vinyl;
n is 0 or 1;
 X is selected from –O– and –CH₂–; and
 the dotted line together with the carbon-carbon bond forms a single bond or a double bond in
 10 the ring system; and the ring system has no double bonds, one double bond or two double
 bonds, or is an aromatic ring system.

The two double bonds in the ring system are conjugated or isolated.

- If R₄ is methyl, the double bond between X and R₄ can have *E*- or a *Z*-configuration, or the
 compound can be a mixture of *E*- and *Z*-isomers. For example, said double bond has *E*- *Z*-
 15 configuration.

- For example, if the substituents R₂ and R₃ are independently selected from H and *i*Pr, the
 compounds of the present invention can be obtained from renewable resources. In case the
 substituents R₂ and R₃ are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and
 vinyl, the compounds of the present invention can be obtained from renewable resources or at
 20 least partially from renewable resources.

- The compounds of formula (I) can comprise one or more chiral centers and one or more CC
 double bonds, and as such may exist as a mixture of stereoisomers, or they may be resolved
 as isomerically pure forms. If it is desired to prepare individual stereoisomers, this may be
 achieved according to methodology known in the art, e.g. preparative HPLC and GC or by
 25 stereoselective syntheses, or simply by using as starting material the desired isomerically pure
 form, which are available from natural resources.

For example, there is provided a compound of formula (I) as described above, wherein one of
 R₂ and R₃ is H, while the other one is selected from *i*Pr, isopropenyl, cyclopropyl and vinyl. In

other words, if R_2 is H, then R_3 is selected from *i*Pr, isopropenyl, cyclopropyl and vinyl, or, if R_3 is H, then R_2 is selected from *i*Pr, isopropenyl, cyclopropyl and vinyl.

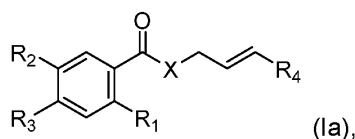
In one particular embodiment the compound of formula (I) is selected from the group consisting of 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-isopropylcyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-isopropylphenyl)pent-4-en-1-one, 1-(3-isopropylphenyl)pent-4-en-1-one, 1-(3-(prop-1-en-2-yl)phenyl)pent-4-en-1-one, 1-(4-(prop-1-en-2-yl)phenyl)pent-4-en-1-one, 1-(4-isopropylcyclohexyl)pent-4-en-1-one, 1-(4-vinylcyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)hex-4-en-1-one, 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one, allyl 4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate, allyl 4-isopropylbenzoate, but-2-en-1-yl 4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate, 1-(2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one, 1-(5-isopropyl-2-methyl-cyclohex-1-en-1-yl)pent-4-en-1-one, 1-(5-isopropyl-2-methylcyclohex-2-en-1-yl)pent-4-en-1-one, 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)hex-4-en-1-one, and 1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one.

In one example, there is provided a compound of formula (I) as described above, wherein one of R_2 and R_3 is H, while the other one is selected from *i*Pr and isopropenyl. For example, the compound is selected from the group consisting of 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-isopropylcyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-isopropylphenyl)pent-4-en-1-one, 1-(3-isopropylphenyl)pent-4-en-1-one, 1-(3-(prop-1-en-2-yl)phenyl)pent-4-en-1-one, 1-(4-(prop-1-en-2-yl)phenyl)pent-4-en-1-one, 1-(4-isopropylcyclohexyl)pent-4-en-1-one, 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)hex-4-en-1-one, 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one, allyl 4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate, allyl 4-isopropylbenzoate, but-2-en-1-yl 4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate, 1-(2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one, 1-(5-isopropyl-2-methyl-cyclohex-1-en-1-yl)pent-4-en-1-one, and 1-(5-isopropyl-2-methylcyclohex-2-en-1-yl)pent-4-en-1-one, and 1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one.

In one example, there is provided a compound of formula (I) as described above, wherein R_1 is H; R_4 is selected from H and Me; and one of R_2 and R_3 is H, while the other one is selected from *i*Pr and isopropenyl. For example, the compound is selected from the group consisting of 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-isopropylcyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-isopropylphenyl)pent-4-en-1-one, 1-(3-isopropylphenyl)pent-4-en-1-one, 1-(3-(prop-1-en-2-yl)phenyl)pent-4-en-1-one, 1-(4-(prop-1-en-2-yl)phenyl)pent-4-en-1-

one, 1-(4-isopropylcyclohexyl)pent-4-en-1-one, 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)hex-4-en-1-one, 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one, allyl 4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate, allyl 4-isopropylbenzoate, and but-2-en-1-yl 4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate, and 1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one.

- 5 In one particular embodiment there is provided a compound of formula (I) wherein n is 1 and the ring system is an aromatic system, i.e. a compound of formula (Ia)



wherein

R₁ and R₄ are independently selected from H and Me;

- 10 R₂ and R₃ are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and vinyl;
X is selected from –O– and –CH₂–.

For example, there is provided a compound of formula (Ia) as described above, wherein one of R₂ and R₃ is H, while the other one is selected from *i*Pr, isopropenyl, cyclopropyl and vinyl.

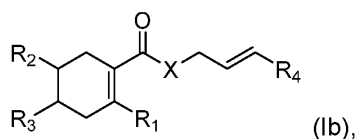
- 15 For example, the compound of formula (Ia) is selected from the group consisting of 1-(4-isopropylphenyl)pent-4-en-1-one, 1-(3-isopropylphenyl)pent-4-en-1-one, 1-(3-(prop-1-en-2-yl)phenyl)pent-4-en-1-one, 1-(4-(prop-1-en-2-yl)phenyl)pent-4-en-1-one, and allyl 4-isopropylbenzoate.

In one example, there is provided a compound of formula (Ia) as described above, wherein one of R₂ and R₃ is H, while the other one is selected from *i*Pr and isopropenyl.

- 20 In one example, there is provided a compound of formula (Ia) as described above, wherein R₁ is H; R₄ is selected from H and Me; and one of R₂ and R₃ is H, while the other one is selected from *i*Pr and isopropenyl.

In a further particular embodiment there is provided a compound of formula (I) wherein n is 1 and the ring system has one double bond between (C1) and (C2) of the six membered ring,

- 25 i.e. a compound of formula (Ib)



wherein

R_1 and R_4 are independently selected from H and Me;

R_2 and R_3 are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and vinyl;

5 X is selected from $-O-$ and $-CH_2-$.

For example, there is provided a compound of formula (Ib) as described above, wherein one of R_2 and R_3 is H, while the other one is selected from *i*Pr, isopropenyl, cyclopropyl and vinyl.

For example, the compound of formula (Ib) is selected from the group consisting of 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-isopropylcyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-vinylcyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)hex-4-en-1-one, allyl 4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate, but-2-en-1-yl 4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate, 1-(2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one, and 1-(5-isopropyl-2-methylcyclohex-1-en-1-yl)pent-4-en-1-one.

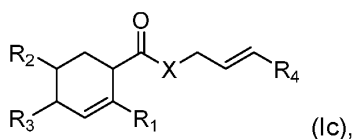
In one particular embodiment the compound of formula (Ib) is selected from the group consisting of (S)-1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one, (R)-1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one, (S)-1-(4-isopropylcyclohex-1-en-1-yl)pent-4-en-1-one, (S)-1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)hex-4-en-1-one, allyl (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate, but-2-en-1-yl (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate, and (S)-1-(5-isopropyl-2-methylcyclohex-1-en-1-yl)pent-4-en-1-one.

20 In one example, there is provided a compound of formula (Ib) as described above, wherein one of R_2 and R_3 is H, while the other one is selected from *i*Pr and isopropenyl.

In one example, there is provided a compound of formula (Ib) as described above, wherein R_1 is H; R_4 is selected from H and Me; and one of R_2 and R_3 is H, while the other one is selected from *i*Pr and isopropenyl.

25 In another particular embodiment there is provided a compound of formula (I) wherein n is 1 and the ring system has one double bond between (C2) and (C3) of the six membered ring, i.e. a compound of formula (Ic)

8



wherein

R_1 and R_4 are independently selected from H and Me;

R_2 and R_3 are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and vinyl;

5 X is selected from $-O-$ and $-CH_2-$.

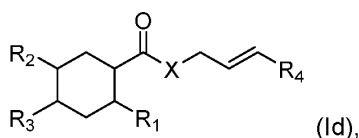
For example, there is provided a compound of formula (Ic) as described above, wherein one of R_2 and R_3 is H, while the other one is selected from *i*Pr, isopropenyl, cyclopropyl and vinyl.

For example, the compound of formula (Ic) is 1-(5-isopropyl-2-methylcyclohex-2-en-1-yl)pent-4-en-1-one, in particular (S)-1-(5-isopropyl-2-methylcyclohex-2-en-1-yl)pent-4-en-1-one.

10 In one example, there is provided a compound of formula (Ic) as described above, wherein one of R_2 and R_3 is H, while the other one is selected from *i*Pr and isopropenyl.

In one example, there is provided a compound of formula (Ic) as described above, wherein R_1 is H; R_4 is selected from H and Me; and one of R_2 and R_3 is H, while the other one is selected from *i*Pr and isopropenyl.

15 In another particular embodiment there is provided a compound of formula (I) wherein n is 1 and the ring system has no double bonds, i.e. a compound of formula (Id)



wherein

R_1 and R_4 are independently selected from H and Me;

20 R_2 and R_3 are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and vinyl;

X is selected from $-O-$ and $-CH_2-$.

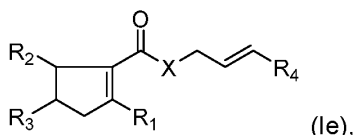
For example, there is provided a compound of formula (Id) as described above, wherein one of R_2 and R_3 is H, while the other one is selected from *i*Pr, isopropenyl, cyclopropyl and vinyl.

For example, the compound of formula (Id) is 1-(4-isopropylcyclohexyl)pent-4-en-1-one.

In one example, there is provided a compound of formula (Id) as described above, wherein one of R_2 and R_3 is H, while the other one is selected from *i*Pr and isopropenyl.

In one example, there is provided a compound of formula (Id) as described above, wherein R_1 is H; R_4 is selected from H and Me; and one of R_2 and R_3 is H, while the other one is selected from *i*Pr and isopropenyl.

In another particular embodiment there is provided a compound of formula (I) wherein n is 0 and the ring system has one double bond between (C1) and (C2) of the five membered ring, i.e. a compound of formula (Ie)



wherein

R_1 and R_4 are independently selected from H and Me;

R_2 and R_3 are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and vinyl;

X is selected from $-O-$ and $-CH_2-$.

For example, there is provided a compound of formula (Ie) as defined above, wherein one of R_2 and R_3 is H, while the other one is selected from *i*Pr, isopropenyl, cyclopropyl and vinyl.

In one example, there is provided a compound of formula (Ie) as described above, wherein one of R_2 and R_3 is H, while the other one is selected from *i*Pr and isopropenyl.

In one example, there is provided a compound of formula (Ie) as described above, wherein R_1 is H; R_4 is selected from H and Me; and one of R_2 and R_3 is H, while the other one is selected from *i*Pr and isopropenyl.

For example, the compound of formula (Ie) is 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one, 1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one and 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)hex-4-en-1-one.

In a particular embodiment, the compound of formula (Ie) is selected from the group consisting of (*R*)- 1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one, (*R*)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one and (*R*)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)hex-4-en-1-one.

Compound 1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one is described in GB2021574. It is obtained from Δ^1 -menthene (4-isopropyl-1-methylcyclohex-1-ene) as starting material. The document contains no information about the stereochemistry of the compound, therefore the skilled reader understands the disclosure to refer to a racemic compound. In consequence,
5 also the final compound is obtained in racemic form.

However, it is more likely that the starting material Δ^1 -menthene is obtained from d-limonene ((*R*)-limonene) by hydrogenation, and is therefore present in enantiopure or enantioenriched (*R*)-form. Until today, d-limonene is the prevailing limonene isomer resulting in a big stream from the orange/citrus industry. A modern overview can be found in Bioresource Technology
10 300 (2020) 122666. More importantly, before the filing date of GB2021574, d-limonene was (and still is) clearly the more common isomer, which can be obtained from citrus fruits, while the less common l-limonene was not commercially available at that time in bigger quantities, as summerized in Arctander (1969). When starting from d-limonene, the final compound of formula (Ie) is obtained in pure (*S*)-configuration or in (*S*)-configuration with low ee, if
15 racemization occurs at least during hydrogenation as explained by V. Anikeev et al in Ind. Eng. Chem. Res 2010,49, 2084 – 2090.

Overall, it is not credible, that in GB2021574 the starting material Δ^1 -menthene was obtained from l-limonene, which was a rare material at that time, and which is the only starting material that can lead to the compounds of formula (Ie) in (*R*)-configuration.

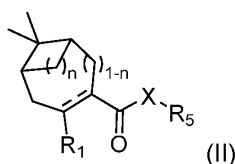
20 It was now surprisingly found that the *R*-enantiomer of 1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one, and also of its propenyl derivative, shows great natural green odour notes, has a significantly better odour threshold and performs better in HDLD than the corresponding *S*-enantiomer with the opposite optical rotation, especially the surprising long-lastingness.

The odour threshold values (in ng) for the *R*-enantiomers are superior to those of the *S*-
25 enantiomers, as shown in the table below.

Compound	R-enantiomer	S-enantiomer	racemic
1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one	0.002	0.044	0.0044

1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one.	0.0017	0.084	0.0056
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In a further aspect of the present invention, there is provided a compound of formula (II) in the form of any one of its stereoisomers or mixture thereof



5 wherein

R_1 is H or Me;

R_5 is cyclopent-2-en-1-yl or but-2-en-1-yl;

n is 0 or 1;

X is selected from $-O-$ and $-CH_2-$; and

10 the dotted line together with the carbon-carbon bond forms a single bond or a double bond.

For example, the double bond configuration of R_5 being but-2-en-1-yl is E or Z, or a mixture of them.

In one embodiment the compound of formula (II) is selected from the group consisting of but-2-en-1-yl 7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylate, cyclopent-2-en-1-yl 7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylate, 1-(7,7-dimethylbicyclo[4.1.0]hept-3-en-3-yl)hex-4-en-1-one, 1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)hex-4-en-1-one.

In one particular embodiment the compound of formula (II) is selected from the group consisting of but-2-en-1-yl (1S,6R)-7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylate, cyclopent-2-en-1-yl (1S,6R)-7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylate, 1-((1S,6R)-7,7-dimethylbicyclo[4.1.0]hept-3-en-3-yl)hex-4-en-1-one, 1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)hex-4-en-1-one.

The compounds of formula (I) or of formula (II) may be used alone, as isomeric mixture thereof, or in combination with known odorant molecules 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 a mixture with one or more ingredients or excipients conventionally used

in conjunction with odorants in fragrance compositions, for example, carrier materials, and other auxiliary agents commonly used in the art.

As used herein, "carrier material" means a material which is practically neutral from an odorant point of view, i.e. a material that does not significantly alter the organoleptic properties of odorants.

The term "auxiliary agent" refers to ingredients that might be employed in a fragrance composition for reasons not specifically related to the olfactory performance of said composition. For example, an auxiliary agent may be an ingredient that acts as an aid to processing a fragrance ingredient or ingredients, or a composition containing said ingredient(s), or it may improve handling or storage of a fragrance ingredient or composition containing same. It might also be an ingredient that provides additional benefits such as imparting color or texture. It might also be an ingredient that imparts light resistance or chemical stability to one or more ingredients contained in a fragrance composition. A detailed description of the nature and type of adjuvants commonly used in fragrance compositions containing same cannot be exhaustive, but it has to be mentioned that said ingredients are well known to a person skilled in the art.

As used herein, 'fragrance composition' means any composition comprising a compound of formula (I) or a compound of formula (II), or a mixture thereof and a base material, e.g. a diluent conventionally used in conjunction with odorants, such as diethyl phthalate (DEP), dipropylene glycol (DPG), isopropyl myristate (IPM), pentane-1,2-diol, triethyl citrate (TEC) and alcohol (e.g. ethanol). Optionally, the composition may comprise an anti-oxidant adjuvant. Said anti-oxidant may be selected from Tinogard® TT (BASF), Tinogard® Q (BASF), Tocopherol (including its isomers, CAS 59-02-9; 364-49-8; 18920-62-2; 121854-78-2), 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT, CAS 128-37-0) and related phenols, hydroquinones (CAS 121-31-9).

The following list comprises examples of known odorant molecules, which may be combined with a compound of formula (I), a compound of formula (II), or a mixture thereof:

— essential oils and extracts, e.g. castoreum, costus root oil, oak moss absolute, 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-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 ((2E,6Z)-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); 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-trimethylocta-2,6-dien-1-ol, and/or [1-methyl-2(5-methylhex-4-en-2-yl)cyclopropyl]-methanol;
- 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-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); 3-(4-isobutyl-2-methylphenyl)propanal; maltol; methyl cedryl ketone; 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-1H-benzo[e][1]benzofuran); geranyl methyl ether ((2E)-1-methoxy-3,7-dimethylocta-2,6-diene); 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 ((1S,6R,8aR)-1,4,4,6-tetramethyloctahydro-1H-5,8a-methanoazulen-6-yl acetate); delta-decalactone (6-pentyltetrahydro-2H-pyran-2-one); Helvetolide® (2-(1-(3,3-dimethylcyclohexyl)ethoxy)-2-methylpropyl propionate); delta-undecalactone (5-heptyloxolan-2-one); and / or vetiveryl acetate ((4,8-dimethyl-2-propan-2-ylidene-3,3a,4,5,6,8a-hexahydro-1H-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).

Thus there is provided in a further aspect of the invention a fragrance composition comprising a compound of formula (I) or a compound of formula (II).

The compounds of formula (I) or of formula (II) may be used in a broad range of fragranced articles, e.g. in any field of fine and functional perfumery, such as perfumes, air care products, household products, laundry products, body care products and cosmetics. The compound can be employed in widely varying amounts, depending upon the specific article and on the nature and quantity of other odorant ingredients. The proportion is typically from 0.01 to 3 weight per cent of the article. In one embodiment, the compound may be employed in a fabric softener in an amount from 0.1 to 3 weight per cent (e.g. 0.001 to 1 including 0.5, 0.3, and 0.05 weight %).

In another embodiment, the compound may be used in fine perfumery in amounts from 0.01 to 30 weight per cent (e.g. up to about 10 or up to 20 weight per cent), more preferably between 0.01 and 5 weight per cent (e.g. 0.01 to 0.1 weight per cent). 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.

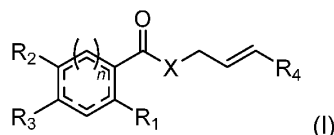
The compounds of formula (I) or of formula (II) may be employed in a consumer product base simply by directly mixing the compound, or a fragrance composition comprising a compound of formula (I) or of formula (II), or a mixture thereof, with the consumer product base, or it may, in an earlier step, be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

Thus, the invention additionally provides a method of manufacturing a fragranced article, comprising the incorporation a compound of formula (I), or a compound of formula (II), or a mixture thereof as a fragrance ingredient, either by directly admixing to the consumer product base or by admixing a fragrance composition comprising a compound of formula (I), or a compound of formula (II), or a mixture thereof, which may then be mixed with a consumer product base, using conventional techniques and methods. Through the addition of an olfactory acceptable amount of a compound of formula (I), or a compound of formula (II), or a mixture thereof the odor notes of a consumer product base will be improved, enhanced, or modified.

Thus, the invention furthermore provides a method for improving, enhancing or modifying a consumer product base by means of the addition thereto of an olfactory acceptable amount of a compound of formula (I), or a compound of formula (II), or a mixture thereof.

There is provided in a further aspect of the present invention a fragranced article comprising:

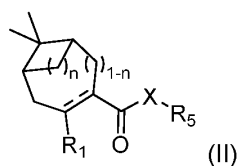
- a) a compound of formula (I), in the form of any one of its stereoisomers or mixture thereof



wherein

- 5 R₁ and R₄ are independently selected from H and Me;
 R₂ and R₃ are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and vinyl;
n is 0 or 1;
 X is selected from -O- and -CH₂-; and
 the dotted line together with the carbon-carbon bond forms a single bond or a double
 10 bond in the ring system; and the ring system has no double bonds, one double bond or
 two double bonds, or is an aromatic ring system;

or a compound of formula (II) in the form of any one of its stereoisomers or mixture thereof



- 15 wherein
 R₁ is H or Me;
 R₅ is cyclopent-2-en-1-yl or but-2-en-1-yl;
n is 0 or 1;
 X is selected from -O- and -CH₂-; and
 the dotted line together with the carbon-carbon bond forms a single bond or a double
 20 bond,
 and
 b) a consumer product base.

For example, the fragranced article comprises a compound of formula (I) wherein one of R₂
 25 and R₃ is H, while the other one is selected from *i*Pr, isopropenyl, cyclopropyl and vinyl.

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. Examples of such products include fine perfumery, e.g. perfume and eau de toilette; fabric care, household products and personal care products such as cosmetics, laundry care detergents, rinse
5 conditioner, personal cleansing composition, detergent for dishwasher, surface cleaner; laundry products, e.g. softener, bleach, detergent; body-care products, e.g. shampoo, shower gel; air care products (includes products that contain preferably volatile and usually pleasant-smelling compounds which advantageously can even in very small amounts mask unpleasant odors). Air fresheners for living areas contain, in particular, natural and synthetic essential oils
10 such as pine needle oils, citrus oil, eucalyptus oil, lavender oil, and the like, in amounts for example of up to 50% by weight. As aerosols they tend to contain smaller amounts of such essential oils, by way of example less than 5% or less than 2% by weight, but additionally include compounds such as acetaldehyde (in particular, <0.5% by weight), isopropyl alcohol (in particular, <5% by weight), mineral oil (in particular, <5% by weight), and propellants.

15 Cosmetic products include:

- (a) cosmetic skincare products, especially bath products, skin washing and cleansing products, skincare products, eye makeup, lip care products, nail care products, intimate care products, foot care products;
- (b) cosmetic products with specific effects, especially sunscreens, tanning products, de-
20 pigmenting products, deodorants, antiperspirants, hair removers, and shaving products;
- (c) cosmetic dental-care products, especially dental and oral care products, tooth care products, cleaners for dental prostheses, adhesives for dental prostheses; and
- (d) cosmetic hair care products, especially hair shampoos, hair care products, hair setting products, hair-shaping products, and hair coloring products.

25 This list of products is given by way of illustration, and is not to be regarded as being in any way limiting.

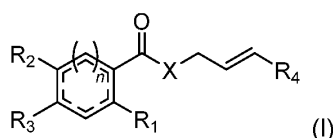
In one particular embodiment the consumer product base is selected from fine perfumery, and personal care products, including deodorants, hair care products, soaps, and the like. In one particular embodiment the consumer product base is a hair care product.

In a further particular embodiment the consumer product base is selected from fabric care products, including fabric softener, and home care products, including air fresheners, dish washers and the like.

The invention further provides a method for improving, enhancing or modifying a consumer product base by means of the addition thereto of a gustatory acceptable amount of a compound of formula (I), or a compound of formula (II), or a mixture thereof.

There is provided in a further aspect of the present invention a flavoured article comprising:

- a) a compound of formula (I), in the form of any one of its stereoisomers or mixture thereof



wherein

R_1 and R_4 are independently selected from H and Me;

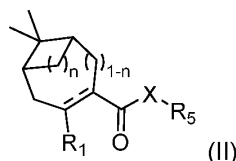
R_2 and R_3 are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and vinyl;

n is 0 or 1;

X is selected from $-O-$ and $-CH_2-$; and

the dotted line together with the carbon-carbon bond forms a single bond or a double bond in the ring system; and the ring system has no double bonds, one double bond or two double bonds, or is an aromatic ring system;

or a compound of formula (II) in the form of any one of its stereoisomers or mixture thereof



wherein

R_1 is H or Me;

R_5 is cyclopent-2-en-1-yl or but-2-en-1-yl;

n is 0 or 1;

X is selected from $-O-$ and $-CH_2-$; and

the dotted line together with the carbon-carbon bond forms a single bond or a double bond,

and

b) a consumer product base.

- 5 For example, the flavoured article comprises a compound of formula (I) wherein one of R_2 and R_3 is H, while the other one is selected from iPr, isopropenyl, cyclopropyl and vinyl.

The consumer product base is the combination of all the usual art-recognised ingredients required for the particular consumable composition. For example, the flavoured article is any composition that is taken into the mouth for ultimate spitting out or ingestion. The composition
10 may be in any physical form, solid, liquid or gaseous. Non-limiting examples include all food products, food additives, nutraceuticals, pharmaceuticals and any product placed in the mouth including (but not limited to) chewing gum, oral care products, and oral hygiene products including but not limited to, cereal products, rice products, tapioca products, sago products, baker's products, biscuit products, pastry products, bread products, confectionery products,
15 dessert products, gums, chewing gums, flavor or flavor-coated food/beverage containers, yeast products, baking-powder, salt and spice products, snack foods, savoury products, mustard products, vinegar products, sauces (condiments), soups, seasonings, ready-to-eat meals, gravies, nuts & nut products, processed foods, vegetable products, meat and meat products, egg products, milk and dairy products, yoghurts, cheese products, butter and butter substitute
20 products, milk substitute products, soy products, edible oils and fat products, beverages, carbonated beverages, alcoholic drinks such as beers, wines and spirits, non-alcoholic drinks such as soft drinks or other flavoured articles, including forms requiring reconstitution including, without limitation, beverage powder, milk based beverage powder, sugar-free beverage powder, beverage syrup, beverage concentrate, coffee and tea, food extracts, plant extracts,
25 meat extracts, condiments, gelatins, pharmaceutical and non-pharmaceutical gums, tablets, lozenges, drops, emulsions, elixirs, syrups and other preparations for making beverages, and combinations thereof.

For example, the compounds of formula (I) can be obtained from limonene, perillaldehyde, cuminaldehyde, cymene, limonene epoxide, α -phellandrene or carvone which are starting
30 materials obtainable from renewable resources. Some examples are biodegradable.

The compounds of formula (I) wherein n is 1 and X is $-\text{CH}_2-$ may, for example, be synthesized by Grignard reaction of aldehydes with Grignard reagents followed by oxidation to get the corresponding ketone. The aldehyde may be perillaldehyde or 4-vinylcyclohex-1-ene-1-carbaldehyde or cuminaldehyde or 3-iso-propylbenzaldehyde or hydrogenated perillaldehyde.

- 5 Alternatively, the aldehyde may, for example, be synthesized by rearrangement and oxidation of limonene epoxide or hydroformylation of α -phellandrene or coupling of boric acids with bromide or Wittig reaction of carvone followed by hydrolysis. Alternately, the compounds of formula (I) wherein n is 1 and X is $-\text{CH}_2-$ may, for example, be synthesized by directly Friedel-Crafts acylation of mono-hydrogenated limonene.

- 10 The compounds of formula (I) wherein n is 1 and X is $-\text{O}-$ may, for example, be synthesized by oxidation of aldehyde to acid and then esterification to form the corresponding ester.

The compounds of formula (I) wherein n is 0 and X is $-\text{CH}_2-$ may, for example, be synthesized by oxidative ring open of limonene epoxide followed by cyclization and then α alkylation of the corresponding ketone. Alternatively, it may, for example, be synthesized by hydrogenation

15 of limonene followed by epoxidation, or epoxidation of limonene followed by hydrogenation and then oxidative ring open, intramolecular aldol and finally Claisen rearrangement or α alkylation.

The compounds of formula (II) can be obtained from carene or pinene which are starting materials obtainable from renewable resources. Some examples are biodegradable.

- 20 The compounds of formula (II) wherein n is 1 and X is $-\text{CH}_2-$ may, for example, be synthesized by oxidation of α -pinene to its corresponding aldehyde myrtenal, followed by Grignard reaction and then oxidation to get the corresponding ketone.

- The compounds of formula (II) wherein n is 1 and X is $-\text{O}-$ may, for example, further be synthesized by stepwise oxidation of α -pinene to its corresponding acid, followed by
- 25 esterification to the corresponding ester.

The compounds of formula (II) wherein n is 0 and X is $-\text{CH}_2-$ may, for example, be synthesized by isomerization of 3-carene epoxide to 3(10)-carene-4-ol followed by oxidation, Grignard reaction and then oxidation to get the corresponding ketone.

The compounds of formula (II) wherein n is 0 and X is – O– may, for example, be synthesized by isomerization of 3-carene epoxide to 3(10)-caren-4-ol followed by oxidation to its corresponding acid, followed by esterification to form the corresponding ester.

The invention is now further described with reference to the following non-limiting examples.

- 5 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.

EXAMPLES

General Methods:

- 10 All reactions were performed under argon using solvents and reagents from commercial suppliers without further purification. Solvents for extraction and chromatography were technical grade and used without further purification. Flash chromatography was performed using Tsingdao Haiyang Chemical silica gel (200 – 300 mesh) and Santai Technologies silica flash columns. Unless otherwise noted, a mixture of heptane: MTBE was used as eluent. NMR spectra were recorded with AW 400 MHz Bruker spectrometer instrument. The chemical shifts for ¹H NMR spectra was reported in δ (ppm) referenced to the residual proton signal of the deuterated solvent; coupling constants were expressed in Hertz (Hz). ¹³C NMR spectra were referenced to the carbon signals of the deuterated solvent. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, bs = broad singlet. GC/MS spectral data were obtained from an Agilent 6890 N and MSD 5975 using
15
20 a column HP-5 MS, 30 m, 0.25 mm, 0.25 μm.

Example 1: (S)-1-(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one

1. To a solution of (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (S-perillaldehyde) (5.0 g, 33 mmol) in THF (100 mL) was added but-3-en-1-ylmagnesium bromide (73 mL, 37 mmol, 0.5 M) at 10°C and stirred at rt for 3 h. Saturated NH₄Cl aqueous solution (100 mL) was added.
25 The mixture was extracted with ethyl acetate (150 mL*3). The combined organic layer was washed with saturated NaHCO₃ aqueous solution (100 mL) and brine (100 mL), and then dried over MgSO₄ and filtered. Remove the solvent and the result crude oil was purified via silica gel chromatography (heptane:MTBE=9:1) to give 1-((S)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-ol (6.2 g, yield: 90%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 5.89 – 5.79 (m, 1H), 5.70 – 5.64 (m, 1H), 5.09 – 4.91 (m, 2H), 4.77 – 4.66 (m, 2H), 4.03 – 4.00 (m, 1H), 2.25 – 1.80 (m, 8H), 1.75 – 1.40 (m, 7H) ppm. ¹³C NMR (101 MHz, CDCl₃, mixture of isomers) δ 149.8, 149.7, 139.6, 139.4, 138.5, 138.4, 123.2, 122.2, 114.7, 108.7, 75.8, 75.7, 41.4, 41.1, 34.2, 33.9, 30.5, 30.4, 30.2, 30.0, 27.6, 27.4, 24.0, 23.6, 20.8, 20.7 ppm. GC/MS (EI): *m/z* (%): 206 (2) [*M*⁺], 191 (6), 163 (47), 151 (48), 133 (58), 105 (67), 93 (87), 81 (86), 67 (75), 55 (100).

2. A mixture of 1-((S)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-ol (5.0 g, 24.2 mmol), aluminiumtri-sec-butoxide (1.8 g, 7.3 mmol) and acetic acid (0.2 g, 2.4 mmol) in MTBE (100 mL) was stirred at rt for 20 min. 4-Nitrobenzaldehyde (14.6 g, 97 mmol) was added and stirred at rt for 3 h. Water was added (100 mL), and the mixture was extracted with MTBE (100 mL*3). The combined organic layer was dried over MgSO₄ and filtered. The solvent was removed and the result crude oil was purified via silica gel chromatography (heptane:MTBE=96:4) to give (S)-1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one (4.3 g, yield: 87%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 6.96 – 6.87 (m, 1H), 5.89 – 5.79 (m, 1H), 5.11 – 4.92 (m, 2H), 4.81 – 4.66 (m, 2H), 2.79 – 2.65 (m, 2H), 2.57 – 2.46 (m, 1H), 2.44 – 2.30 (m, 3H), 2.25 – 2.06 (m, 3H), 1.95 – 1.84 (m, 1H), 1.75 (s, 3H), 1.49 – 1.35 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 200.3, 148.8, 139.1, 138.9, 137.7, 115.0, 109.2, 40.2, 36.3, 31.4, 28.6, 27.0, 23.6, 20.7 ppm. GC/MS (EI): *m/z* (%): 204 (3) [*M*⁺], 189 (7), 176 (11), 161 (21), 149 (91), 135 (17), 121 (31), 105 (40), 93 (100), 79 (79), 67 (26), 55 (62).

Odor description: green-galbanum, fruity-pineapple, aromatic, coniferous

Biodegradation: inherently biodegradable

Example 2: (R)-1-(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one

1. To a solution of (4R)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane (*R*-perillaldehyde) (30.0 g, 197mmol) in THF (300 mL) was added LDA solution (33 mL, 236 mmol) dropwise at 0°C and stirred at rt for 16 h. Saturated NH₄Cl aqueous solution(200 mL) was added, and the mixture was extracted with MTBE (150 mL*3). The combined organic layer was washed with saturated NaHCO₃ aqueous solution and brine, and dried over MgSO₄ and filtered. The solvent was removed and the result crude oil was purified via silica gel chromatography

(heptane : MTBE=97:3) to get (5*R*)-2-methylene-5-(prop-1-en-2-yl)cyclohexan-1-ol (20.1 g, yield: 67.0 %) as a colorless liquid.

¹³C NMR (101 MHz, CDCl₃, mixture of isomers, 1:1) δ 151.1, 151.1, 149.9, 149.4, 148.6, 109.7, 109.7, 109.1, 108.9, 104.0, 72.3, 72.3, 72.1, 72.1, 44.1, 42.0, 42.0, 39.0, 38.1, 33.8, 32.7, 32.6, 29.9, 21.0, 20.8 ppm. GC/MS (EI): *m/z* (%): peak 1: 152 (4) [*M*⁺], 134 (25), 119 (42), 109 (100), 91 (48), 67 (53), 55 (56). Peak 2: 152 (2) [*M*⁺], 134 (69), 119 (60), 109 (100), 91 (58), 69 (38), 55 (41).

2. To a solution of potassium dichromate (46.4 g, 158 mmol) in water (100 mL) was added sulfuric acid (27.7 g, 282mmol) at 0°C and stirred for 0.5 h. (5*R*)-2-methylene-5-(prop-1-en-2-yl)cyclohexan-1-ol (20.0 g, 131mmol) in DCM (120 mL) was added dropwise at 0°C and then stirred at rt for 2h. Water (100 mL) and MTBE (200 mL) were added, and the mixture was extracted with MTBE (200 mL*3). The combined organic layer was washed with saturated NaHCO₃ aqueous solution and brine, and dried over MgSO₄ and filtered. The solvent was removed and the result crude oil was purified via silica gel chromatography (heptane:MTBE=96:4) to give (*R*)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (3.2 g, yield: 16%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 9.44 (s, 1H), 6.86 – 6.78 (m, 1H), 4.79 – 4.73 (m, 2H), 2.75 – 1.37 (m, 10H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 193.9, 150.7, 148.4, 141.3, 109.5, 40.7, 31.7, 26.3, 21.6, 20.7 ppm. GC/MS (EI): *m/z* (%): 150 (16) [*M*⁺], 135 (30), 122 (32), 107 (57), 91 (45), 79 (87), 67 (100), 53 (53).

3. According the procedure of example 1 (step 1), 1-((*R*)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-ol was obtained from the reaction of (*R*)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (3.0 g, 20 mmol) and but-3-en-1-ylmagnesium bromide (44 mL, 22 mmol, 0.5 M) as a colorless liquid (1.3 g, yield: 32%)

¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 5.89 – 5.78 (m, 1H), 5.70 – 5.65 (m, 1H), 5.08 – 4.92 (m, 2H), 4.77 – 4.64 (m, 2H), 4.05 – 3.97 (m, 1H), 2.25 – 1.37 (m, 15H) ppm. ¹³C NMR (101 MHz, CDCl₃, mixture of isomers) δ 149.8, 149.7, 139.6, 139.4, 138.5, 138.4, 123.2, 122.2, 114.7, 108.7, 75.8, 75.7, 41.4, 41.1, 34.2, 33.8, 30.5, 30.4, 30.2, 30.0, 27.6, 27.4, 24.0, 23.6, 20.8, 20.8 ppm.

4. According the procedure of example 1 (step 2), (*R*)-1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one was obtained from the reaction of 1-((*R*)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-ol (1.2 g, 5.8 mmol), and 4-nitrobenzaldehyde (1.8 g, 12 mmol) as a colorless liquid (1.0 g, 81% yield).

5 ¹H NMR (400 MHz, CDCl₃) δ 6.99 – 6.87 (m, 1H), 5.89 – 5.79 (m, 1H), 5.09 – 4.92 (m, 2H), 4.81 – 4.69 (m, 2H), 2.78 – 2.68 (m, 2H), 2.56 – 2.30 (m, 4H), 2.24 – 2.08 (m, 3H), 1.95 – 1.84 (m, 1H), 1.76 (s, 3H), 1.53 – 1.33 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 200.3, 148.8, 139.1, 138.9, 137.7, 115.0, 109.2, 40.2, 36.3, 31.4, 28.6, 27.0, 23.6, 20.7 ppm. GC/MS (EI): *m/z* (%): 204 (2) [*M*⁺], 189 (6), 176 (10), 161 (18), 149 (83), 105 (40), 93 (100), 79 (81).

10 Odor description: fatty, green, fruity, rosy, winey, cork.

Example 3: 1-(4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one

1. According the procedure of example 1 (step 1), 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-ol was obtained from 4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (3.0 g, 20 mmol) and but-3-en-1-ylmagnesium bromide (52 mL, 26 mmol, 0.5M) as a colorless liquid (2.7 g, 65% yield).

15 ¹H NMR (400 MHz, CDCl₃) δ 5.83 (m, 1H), 5.68 (s, 1H), 5.07 – 4.91 (m, 2H), 4.77 – 4.67 (m, 2H), 4.01 (t, *J* = 6.6 Hz, 1H), 2.26 – 1.91 (m, 7H), 1.86 (m, 1H), 1.77 – 1.55 (m, 6H), 1.45 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 149.8, 149.7, 139.6, 139.4, 138.5, 138.4, 123.2, 122.2, 114.7, 108.7, 75.8, 75.7, 41.4, 41.1, 34.2, 33.8, 30.5, 30.4, 30.2, 30.0, 27.6, 27.4, 24.0, 23.6, 20.8, 20.7 ppm. GC/MS (EI): *m/z* (%): 206 (2) [*M*⁺], 191 (5), 177 (5), 163 (36), 151 (36), 105 (76), 93 (92), 81 (93), 55 (100).

2. According the procedure of example 1 (step 2), 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one was obtained from 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-ol (2.6 g, 13 mmol) and 4-nitrobenzaldehyde (3.8 g, 25 mmol) as a colorless liquid (2.1 g, 82% yield).

25 ¹H NMR (400 MHz, CDCl₃) δ 6.92 (d, *J* = 4.5 Hz, 1H), 5.84 (m, 1H), 5.01 (m, 2H), 4.74 (d, *J* = 16.1 Hz, 2H), 2.79 – 2.69 (m, 2H), 2.55 – 2.46 (m, 1H), 2.42 – 2.31 (m, 3H), 2.14 (m, 3H), 1.95 – 1.85 (m, 1H), 1.75 (s, 3H), 1.49 – 1.36 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 200.3, 148.8, 139.0, 138.9, 137.7, 115.0, 109.2, 40.2, 36.3, 31.4, 28.6, 27.0, 23.6, 20.7 ppm. GC/MS (EI): *m/z* (%): 204 (2) [*M*⁺], 189 (5), 176 (9), 149 (60), 121 (29), 105 (34), 93 (100), 79 (68).

Odor description: fatty, green-galbanum, fruity-pineapple, grapefruit peel

Example 4: (S)-1-(4-isopropylcyclohex-1-en-1-yl)pent-4-en-1-one

1. A mixture of (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (S-perillaldehyde) (20.0 g, 133 mmol) and platinum (0.5 g, 5%) in EA (100 mL) and hexane (100 mL) was hydrogenated
5 for 1.5 h at 1 atm. The solvent was removed and the residue was purified via silica gel chromatography (heptane:MTBE=87:13) to give (S)-4-isopropylcyclohex-1-ene-1-carbaldehyde (17.8 g, yield: 88%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 9.43 (s, 1H), 6.87 – 6.70 (m, 1H), 2.50 – 2.27 (m, 2H), 2.13 – 1.96 (m, 2H), 1.95 – 1.82 (m, 1H), 1.58 – 1.48 (m, 1H), 1.45 – 1.32 (m, 1H), 1.26 – 1.11 (m, 1H),
10 0.95 – 0.90 (m, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 194.1, 151.5, 141.6, 39.9, 32.0, 30.2, 24.9, 21.9, 19.8, 19.5 ppm. GC/MS (EI): *m/z* (%): 152 (15) [*M*⁺], 137 (12), 124 (12), 109 (100), 95 (34), 81 (49).

2. According the procedure of example 1 (step 1), 1-((S)-4-isopropylcyclohex-1-en-1-yl)pent-4-en-1-ol was obtained from (S)-4-isopropylcyclohex-1-ene-1-carbaldehyde (5.0 g, 32.8 mmol)
15 and but-3-en-1-ylmagnesium bromide (73 mL, 36 mmol, 0.5 M) as a colorless liquid (5.3 g, yield: 77%).

¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 5.89 – 5.73 (m, 1H), 5.68 – 5.62 (m, 1H), 5.08 – 4.87 (m, 2H), 3.96 – 4.00 (m, 1H), 2.22 – 1.40 (m, 11H), 1.34 – 1.09 (m, 2H), 0.92 – 0.83 (m, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃, mixture of isomers) δ 139.7, 139.5, 138.6, 138.5, 123.8,
20 122.5, 114.7, 76.0, 75.8, 40.4, 40.3, 34.2, 33.8, 32.3, 32.2, 30.2, 30.0, 28.7, 28.6, 26.2, 26.2, 24.5, 23.7, 20.0, 19.9, 19.7, 19.6 ppm.

3. According the procedure of example 1 (step 2), (S)-1-(4-isopropylcyclohex-1-en-1-yl)pent-4-en-1-one was obtained from 1-((S)-4-isopropylcyclohex-1-en-1-yl)pent-4-en-1-ol (5.0 g, 24 mmol), and 4-nitrobenzaldehyde (14.5 g, 96 mmol) as a colorless liquid (4.4 g, 88% yield).

25 ¹H NMR (400 MHz, CDCl₃) δ 6.93 – 6.85 (m, 1H), 5.89 – 5.79 (m, 1H), 5.08 – 4.88 (m, 2H), 2.77 – 2.66 (m, 2H), 2.55 – 2.42 (m, 1H), 2.41 – 2.22 (m, 3H), 2.12 – 1.92 (m, 2H), 1.90 – 1.81 (m, 1H), 1.57 – 1.45 (m, 1H), 1.38 – 1.24 (m, 1H), 1.21 – 1.08 (m, 1H), 0.94 – 0.82 (m, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 200.5, 139.8, 139.2, 137.7, 114.9, 39.4, 36.3, 32.0, 29.8, 28.6, 25.6, 23.9, 19.8, 19.6 ppm. GC/MS (EI): *m/z* (%): 206 (5) [*M*⁺], 191 (1), 178 (2), 163 (5),
30 151 (100), 81 (49), 55 (27).

Odor description: thin, fruity, green-pineapple, metallic, watery

Example 5: 1-(4-isopropylphenyl)pent-4-en-1-one

1. According the procedure of example 1 (step 1), 1-(4-isopropylphenyl)pent-4-en-1-ol was obtained from the reaction of 4-isopropylbenzaldehyde (cuminaldehyde) (5.0 g, 34 mmol) and but-3-en-1-ylmagnesium bromide (74 mL, 37mmol, 0.5M) as a colorless liquid (5.3 g, 75% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.15 (m, 4H), 5.89 – 5.79 (m, 1H), 5.09 – 4.94 (m, 2H), 4.72 – 4.61 (m, 1H), 2.93 – 2.88 (m, 1H), 2.22 – 2.03 (m, 2H), 1.94 – 1.72 (m, 3H), 1.25 (d, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 148.3, 142.1, 138.3, 126.5*2, 125.9*2, 114.9, 73.9, 38.0, 33.8, 30.2, 24.0*2 ppm. GC/MS (EI): m/z (%): 204 (2) [M^+], 186 (4), 174 (2), 162 (14), 149 (100), 105 (13), 79 (18).

2. According the procedure of example 1 (step 2), 1-(4-isopropylphenyl)pent-4-en-1-one was obtained from the reaction of 1-(4-isopropylphenyl)pent-4-en-1-ol (5.0 g, 25 mmol) and 4-nitrobenzaldehyde (14.8 g, 98 mmol) as a colorless liquid (4.2 g, 85% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 5.96 – 5.85 (m, 1H), 5.13 – 4.96 (m, 2H), 3.14 – 2.92 (m, 3H), 2.55 – 2.40 (m, 2H), 1.27 (d, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 199.1, 154.5, 137.5, 134.9, 128.3, 126.7, 115.2, 37.7, 34.3, 28.3, 23.7 ppm. GC/MS (EI): m/z (%): 202 (3) [M^+], 187 (1), 159 (3), 147 (100), 104 (6), 91 (13), 77 (6).

Odor description: green, fruity, fatty, galbanum, pineapple

Example 6: 1-(3-isopropylphenyl)pent-4-en-1-one

1. According the procedure of example 1 (step 1), 1-(3-isopropylphenyl)pent-4-en-1-ol was obtained from the reaction of 3-isopropylbenzaldehyde (5.0 g, 34 mmol) and but-3-en-1-ylmagnesium bromide (74 mL, 37 mmol, 0.5M) as a colorless liquid (5.3 g, 77% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.10 (m, 4H), 5.90 – 5.80 (m, 1H), 5.09 – 4.93 (m, 2H), 4.71 – 4.63 (m, 1H), 2.99 – 2.75 (m, 1H), 2.25 – 2.03 (m, 2H), 1.96 – 1.71 (m, 3H), 1.25 (d, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 149.2, 144.7, 138.3, 128.5, 125.7, 124.1, 123.3,

114.9, 74.3, 38.1, 34.2, 30.2, 24.1, 24.0 ppm. GC/MS (EI): m/z (%): 204 (2) [M^+], 186 (4), 162 (27), 149 (100), 107 (38), 79 (30).

2. According the procedure of example 1 (step 2), 1-(3-isopropylphenyl)pent-4-en-1-one was obtained from 1-(3-isopropylphenyl)pent-4-en-1-ol (5.0 g, 25 mmol) and 4-nitrobenzaldehyde
5 (14.8 g, 98 mmol) as a colorless liquid (4.3 g, 87% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.89 – 7.73 (m, 2H), 7.45 – 7.32 (m, 2H), 6.03 – 5.80 (m, 1H), 5.17 – 5.05 (m, 2H), 3.09 – 2.91 (m, 3H), 2.58 – 2.40 (m, 2H), 1.28 (d, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 199.7, 149.4, 137.4, 137.1, 131.3, 128.6, 126.0, 125.7, 115.3, 37.9, 34.1, 28.2, 23.9*2 ppm. GC/MS (EI): m/z (%): 202 (4) [M^+], 187 (1), 147 (100), 119 (10),
10 91 (14), 77 (6).

Odor description: fatty, green, metallic, rubbery, rooty, coniferous, galbanum

Example 7: 1-(3-(prop-1-en-2-yl)phenyl)pent-4-en-1-one

1. A mixture of 3-bromobenzaldehyde (20.0 g, 108 mmol), 4,4,5,5-tetramethyl-2-(prop-1-en-2-yl)-1,3,2-dioxaborolane (21.8 g, 130 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3.7 g, 3.2 mmol) and cesium carbonate
15 (70.4 g, 216 mmol) in THF (300 mL) was stirred at 60°C for 24 h. The mixture was filtered through a silica gel pad, and the filtrate was concentrated to give the crude product. It was then purified via silica gel chromatography (heptane:MTBE=96:4) to give 3-(prop-1-en-2-yl)benzaldehyde (10.3 g, yield: 65%) as a colorless liquid.

^1H NMR (400 MHz, CDCl_3) δ 10.03 (s, 1H), 7.96 (t, J = 1.7 Hz, 1H), 7.81 – 7.69 (m, 2H), 7.50
20 (t, J = 7.7 Hz, 1H), 5.47 – 5.44 (m, 1H), 5.25 – 5.08 (m, 1H), 2.25 – 2.14 (m, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 192.5, 142.2, 142.1, 136.5, 131.5, 129.0, 128.8, 126.6, 114.0, 21.7 ppm. GC/MS (EI): m/z (%): 146 (100) [M^+], 131 (4), 115 (52), 91 (24), 77 (14).

2. According the procedure of example 1 (step 1), 1-(3-(prop-1-en-2-yl)phenyl)pent-4-en-1-ol was obtained from the reaction of 3-(prop-1-en-2-yl)benzaldehyde (9.0 g, 62 mmol) and but-3-
25 en-1-ylmagnesium bromide (136 mL, 68 mmol, 0.5 M) as a colorless liquid (6.8 g, yield: 55%)

^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.01 (m, 4H), 5.90 – 5.75 (m, 1H), 5.43 – 5.30 (m, 1H), 5.17 – 4.85 (m, 3H), 4.71 – 4.64 (m, 1H), 2.26 – 1.66 (m, 8H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 144.6, 143.2, 141.5, 138.2, 128.4, 125.0, 124.8, 123.1, 115.0, 112.7, 74.1, 38.1, 30.1, 21.9

ppm. GC/MS (EI): *m/z* (%): 202 (1) [*M*⁺], 184 (26), 169 (9), 147 (100), 119 (24), 91 (72), 79 (23).

3. According the procedure of example 1 (step 2), 1-(3-isopropylphenyl)pent-4-en-1-one was obtained from 1-(3-(prop-1-en-2-yl)phenyl)pent-4-en-1-ol (5.0 g, 25 mmol), and 4-nitrobenzaldehyde (14.9 g, 99 mmol) as a colorless liquid (4.2 g, 85% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.05 (t, *J* = 1.7 Hz, 1H), 7.89 – 7.78 (m, 1H), 7.71 – 7.62 (m, 1H), 7.46 – 7.40 (m, 1H), 5.96 – 5.86 (m, 1H), 5.42 (s, 1H), 5.21 – 4.94 (m, 3H), 3.09 (t, *J* = 7.4 Hz, 2H), 2.56 – 2.42 (m, 2H), 2.18 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 199.5, 142.5, 141.8, 137.3, 137.0, 130.0, 128.5, 127.0, 125.0, 115.3, 113.6, 37.9, 28.2, 21.8 ppm. GC/MS (EI): *m/z* (%): 200 (4) [*M*⁺], 185 (1), 145 (100), 117 (14), 91 (15).

Odor description: green, galbanum, metallic, undecatriene, mushroom, hot iron, coniferous, terpenic, myrcene, pine needle

Example 8: 1-(4-(prop-1-en-2-yl)phenyl)pent-4-en-1-one

1. According the procedure of example 6 (step 1), 4-(prop-1-en-2-yl)benzaldehyde was obtained from 4-bromobenzaldehyde (20.0 g, 108 mmol) and 4,4,5,5-tetramethyl-2-(prop-1-en-2-yl)-1,3,2-dioxaborolane (21.8 g, 130 mmol) as a colorless liquid (10.5 g, 66% yield).

¹H NMR (400 MHz, CDCl₃) δ 10.00 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 5.51 (s, 1H), 5.33 – 5.10 (m, 1H), 2.18 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 191.8, 147.3, 142.4, 135.4, 129.8, 126.1, 115.5, 21.6 ppm. GC/MS (EI): *m/z* (%): 146 (100) [*M*⁺], 131 (1), 115 (53), 91 (23).

2. According the procedure of example 1 (step 1), 1-(4-(prop-1-en-2-yl)phenyl)pent-4-en-1-ol was obtained from 4-(prop-1-en-2-yl)benzaldehyde (8.0 g, 55 mmol) and but-3-en-1-ylmagnesium bromide (121 mL, 60 mmol) as a colorless liquid (8.9 g, 81% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.42 (m, 2H), 7.33 – 7.25 (m, 2H), 5.91 – 5.80 (m, 1H), 5.37 (s, 1H), 5.13 – 4.93 (m, 3H), 4.75 – 4.62 (m, 1H), 2.23 – 2.04 (m, 5H), 1.99 – 1.75 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 143.8, 142.9, 140.6, 138.2, 125.8, 125.6, 115.0, 112.4, 73.8, 38.0, 30.1, 21.8 ppm. GC/MS (EI): *m/z* (%): 202 (8) [*M*⁺], 184 (5), 160 (26), 147 (100), 91 (41).

3. According the procedure of example 1 (step 2), 1-(4-(prop-1-en-2-yl)phenyl)pent-4-en-1-one was obtained from 1-(4-(prop-1-en-2-yl)phenyl)pent-4-en-1-ol (5.0 g, 25 mmol) and 4-nitrobenzaldehyde (14.9 g, 99 mmol) as a colorless liquid (4.5 g, 91% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.98 – 7.87 (m, 2H), 7.58 – 7.48 (m, 2H), 5.96 – 5.86 (m, 1H),
5 5.49 – 5.45 (m, 1H), 5.24 – 5.17 (m, 1H), 5.14 – 4.92 (m, 2H), 3.13 – 2.98 (m, 2H), 2.56 – 2.42
(m, 2H), 2.21 – 2.11 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 199.0, 145.7, 142.4, 137.4,
135.8, 128.1, 125.7, 115.3, 114.7, 37.7, 28.2, 21.6 ppm. GC/MS (EI): m/z (%): 200 (5) [M⁺],
185 (1), 171 (1), 145 (100), 115 (26).

Odor description: fruit, sweet, ripe, berry, winey, green, metallic, cork, galbanum

10 Example 9: (S)-1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one and 1-(4-isopropylphenyl)pent-4-en-1-one (10:1)

1. According the procedure of example 1 (step 1), a mixture of 1-((S)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-ol and 1-(4-isopropylphenyl)pent-4-en-1-ol (10:1) was obtained from the reaction of (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde and (S)-4-
15 (prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (10.0 g, ratio=10:1) and but-3-en-1-ylmagnesium bromide (147 mL, 73 mmol) as a colorless liquid (12.2 g, 89% yield).

2. According the procedure of example 1 (step 2), a mixture of (S)-1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one and 1-(4-isopropylphenyl)pent-4-en-1-one (ratio=10:1) was obtained from the reaction of 1-((S)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-ol
20 and 1-(4-isopropylphenyl)pent-4-en-1-ol (12.0 g, 58 mmol, ratio=10:1) and 4-nitrobenzaldehyde (17.6 g, 116 mmol) as a colorless liquid (10.0 g, 84% yield, ratio=10:1).

Odor description: green-galbanum, fruity-pineapple, aromatic, coniferous

Analytics correspond to products as obtained in example 1 and 5.

Example 10: 1-(4-isopropylcyclohexyl)pent-4-en-1-one

25 1. A mixture of (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (S-perillaldehyde)(10.0 g, 67 mmol) and Pd/C (0.5 g, Pd/C 10%) in EA (100 mL) was hydrogenated at rt at 1atm for 12 h. The mixture was filtered through some silica gel, and the solvent was removed. The result crude oil was purified via silica gel chromatography (heptane:MTBE=94:6) to give 4-isopropylcyclohexane-1-carbaldehyde (7.5 g, yield: 73%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 9.73 – 9.56 (m, 1H), 2.45 – 2.13 (m, 2H), 2.07 – 1.78 (m, 2H), 1.61 – 1.23 (m, 4H), 1.03 (m, 3H), 0.85 (m, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃, mixture of isomers) δ 205.9, 205.0, 50.6, 47.1, 43.5, 43.2, 32.7, 32.0, 28.5, 26.4, 26.2, 24.7, 19.8, 19.7 ppm. GC/MS (EI): *m/z* (%): isomer one: 154 (10) [*M*⁺], 136 (27), 110 (55), 93 (100), 69 (77), 55 (83). Isomer two: 154 (11) [*M*⁺], 136 (22), 121 (45), 93 (90), 69 (100), 55 (79).

2. According the procedure of example 1 (step 1), 1-(4-isopropylcyclohexyl)pent-4-en-1-ol was obtained from the reaction of 4-isopropylcyclohexane-1-carbaldehyde (4.0 g, 26mmol) and but-3-en-1-ylmagnesium bromide (57 mL, 26mmol, 0.5 M) as a colorless liquid (2.6 g, yield: 48%).

¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 5.93 – 5.77 (m, 1H), 5.11 – 4.92 (m, 2H), 3.42 (m, 1H), 2.30 – 2.08 (m, 2H), 1.78 – 1.37 (m, 11H), 1.17 – 0.93 (m, 3H), 0.91 – 0.82 (m, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃, mixture of isomers) δ 138.9, 138.8, 114.7, 75.7, 73.1, 44.1, 43.8, 42.0, 41.8, 33.7, 33.4, 32.9, 30.4, 30.1, 29.5, 29.4, 29.2, 28.8, 27.9, 26.7, 26.4, 25.6, 24.3, 20.6, 19.8 ppm. GC/MS (EI): *m/z* (%): isomer one: 210 (1) [*M*⁺], 192 (5), 177 (3), 149 (35), 81 (100), 67 (98), 55 (70). isomer two: 210 (1) [*M*⁺], 192 (4), 177 (2), 149 (26), 81 (100), 67 (94), 55 (73).

3. According the procedure of example 1 (step 2), 1-(4-isopropylcyclohexyl)pent-4-en-1-one was obtained from the reaction of 1-(4-isopropylcyclohexyl)pent-4-en-1-ol (2.5 g, 12 mmol), and 1-(4-isopropylcyclohexyl)pent-4-en-1-ol (2.5 g, 12 mmol) as a colorless liquid (1.9 g, 78% yield).

¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 5.80 – 5.66 (m, 1H), 5.01 – 4.83 (m, 2H), 2.56 – 0.84 (m, 15H), 0.83 – 0.69 (m, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃, mixture of isomers) δ 213.4, 212.8, 137.5, 137.4, 115.0, 51.1, 47.9, 43.4, 42.8, 39.8, 39.4, 32.8, 30.6, 29.0, 28.7, 27.9, 27.7, 26.6, 25.9, 20.2, 19.7 ppm. GC/MS (EI): *m/z* (%): isomer one: 208 (6) [*M*⁺], 193 (1), 153 (36), 125 (82), 83 (72), 69 (100), 55 (86). isomer two: 208 (6) [*M*⁺], 193 (2), 153 (41), 125 (82), 83 (75), 69 (100), 55 (95).

Odor description: green, metallic, rhubarb

Example 11: 1-(4-vinylcyclohex-1-en-1-yl)pent-4-en-1-one

1. According the procedure of example 1 (step 1), 1-(4-vinylcyclohex-1-en-1-yl)pent-4-en-1-ol was obtained from the reaction of 1-vinylcyclohex-3-ene-1-carbaldehyde (10.0 g, 73 mmol) and

but-3-en-1-ylmagnesium bromide (162 mL, 81 mmol, 0.5M) as a colorless liquid (2.3 g, 16% yield).

¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 5.94 – 5.76 (m, 2H), 5.70 – 5.63 (m, 1H), 5.08 – 4.89 (m, 4H), 4.05 – 3.98 (m, 1H), 2.29 – 1.30 (m, 12H) ppm. ¹³C NMR (101 MHz, CDCl₃, mixture of isomers) δ 143.5, 143.3, 139.7, 139.5, 138.5, 138.4, 122.6, 121.8, 114.7, 112.7, 112.6, 75.8, 37.8, 37.5, 34.1, 33.9, 30.9, 30.6, 30.1, 30.0, 28.5, 28.3, 23.1, 22.9 ppm. GC/MS (EI): *m/z* (%): 192 (1) [*M*⁺], 174 (1), 159 (1), 108 (59), 93 (57), 79 (100).

2. According the procedure of example 1 (step 2), 1-(4-vinylcyclohex-1-en-1-yl)pent-4-en-1-one was obtained from the reaction of 1-(4-vinylcyclohex-1-en-1-yl)pent-4-en-1-ol (2.0 g, 10 mmol) and 4-nitrobenzaldehyde (6.3 g, 42 mmol) as a colorless liquid (1.5 g, 76% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.88 – 6.76 (m, 1H), 5.86 – 5.66 (m, 2H), 5.07 – 4.84 (m, 4H), 2.77 – 2.61 (m, 2H), 2.47 – 1.95 (m, 7H), 1.89 – 1.71 (m, 1H), 1.37 – 1.19 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 199.3, 141.5, 138.0, 137.5, 136.6, 114.0, 112.3, 35.7, 35.3, 30.7, 27.6, 26.9, 21.8 ppm. GC/MS (EI): *m/z* (%): 190 (5) [*M*⁺], 161 (21), 135 (100), 79 (77).

15 Odor description: fatty, green-galbanum, metallic, rooty, vegetable

Example 12: (S)-1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)hex-4-en-1-one

1. According the procedure of example 1 (step 1), 1-((S)-4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)hex-4-en-1-ol (E:Z=9:1) was obtained from the reaction of (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (S-perillaldehyde) (3.0 g, 20 mmol) and pent-3-en-1-ylmagnesium bromide (33 mL, 26 mmol, 0.8 M) as a colorless liquid (2.1 g, yield: 48%).

¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 5.71 – 5.64 (m, 1H), 5.53 – 5.32 (m, 2H), 4.77 – 4.67 (m, 2H), 4.01 – 3.99 (m, 1H), 2.26 – 1.91 (m, 7H), 1.90 – 1.80 (m, 1H), 1.74 (s, 3H), 1.67 – 1.39 (m, 7H) ppm. ¹³C NMR (101 MHz, CDCl₃, mixture of isomers) δ 149.8, 149.7, 139.6, 139.5, 130.9, 130.8, 125.3, 123.1, 122.0, 108.6, 108.5, 75.9, 75.8, 41.4, 41.2, 34.8, 34.5, 30.4, 30.4, 29.0, 28.8, 27.6, 27.4, 24.1, 23.6, 20.8, 20.7, 17.9 ppm. GC/MS (EI): *m/z* (%): 220 (4) [*M*⁺], 202 (7), 177 (30), 151 (36), 133 (43), 105 (77), 93 (83), 81 (88), 51 (100).

2. According the procedure of example 1 (step 2), (S)-1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)hex-4-en-1-one (E:Z=9:1) was obtained from the reaction of 1-((S)-4-(prop-1-en-2-

yl)cyclohex-1-en-1-yl)hex-4-en-1-ol (2.0 g, 9 mmol) and 4-nitrobenzaldehyde (1.5 g, 10 mmol) as a colorless liquid (1.6 g, 81% yield).

¹H NMR (400 MHz, CDCl₃, mixture of E/Z isomers) δ 6.91 – 6.90 (m, 1H), 5.56 – 5.32 (m, 2H), 4.77 – 4.72 (m, 2H), 2.78 – 2.63 (m, 2H), 2.52 – 2.48 (m, 1H), 2.43 – 2.09 (m, 6H), 1.94 – 1.85 (m, 1H), 1.75 (s, 3H), 1.68 – 1.59 (m, 3H), 1.49 – 1.33 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃, E isomer) δ 200.7, 148.8, 139.0, 138.9, 130.1, 125.6, 109.2, 40.2, 37.1, 31.4, 27.6, 27.0, 23.6, 20.7, 17.9 ppm. GC/MS (EI): *m/z* (%): 218 (8) [*M*⁺], 203 (5) 190 (42), 175 (44), 149 (82), 93 (100), 79 (78).

Odor description: green, metallic, slightly undecatriene, pineapple, galbanum, fatty, fruity-pineapple

Example 13: (S)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one

1. To a solution of (4*R*)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane ((4*R*)-limonene epoxide) (20.0 g, 131 mmol) in THF(200 mL) and water (80 mL) was added sodium periodate (36.5 g, 171 mmol) and the mixture was stirred at rt for 48 h. A solution of NH₄Cl aqueous solution (200 mL) was added, and the mixture was extracted with EA (150 mL*3). The combined organic layer was washed with saturated NaHCO₃ aqueous solution and brine and dried over MgSO₄ and filtered. The solvent was removed and the result crude oil was purified via silica gel chromatography (heptane:MTBE=80:20) to give (*R*)-6-oxo-3-(prop-1-en-2-yl)heptanal (17.3 g, yield: 78%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 9.67 (t, *J* = 2.3 Hz, 1H), 4.88 – 4.70 (m, 2H), 2.76 – 2.61 (m, 1H), 2.53 – 2.33 (m, 4H), 2.13 (s, 3H), 1.75 – 1.53 (m, 5H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 208.3, 201.8, 145.1, 113.3, 47.4, 40.9, 40.8, 30.1, 26.4, 18.4 ppm. GC/MS (EI): *m/z* (%): 168 (1) [*M*⁺], 150 (4), 135 (6), 122 (15), 107 (100), 95 (40), 82 (49), 67 (77), 55 (55).

2. To a solution of (*R*)-6-oxo-3-(prop-1-en-2-yl)heptanal (15.0 g, 89 mmol) in ethanol (60 ml) was added a solution of sodium hydroxide (8.9 g, 223 mmol) in water (160 mL) and stirred at rt for 12 h. Water (100 mL) was added, and the mixture was extracted with EA (150 mL*3). The combined organic layer was washed with saturated NaHCO₃ aqueous solution and brine, and dried over MgSO₄ and filtered. The solvent was removed and the crude oil was purified via silica gel chromatography (heptane:MTBE=90:10) to give a mixture of (S)-1-(4-(prop-1-en-2-

yl)cyclopent-1-en-1-yl)ethan-1-one and (S)-2-methyl-5-(prop-1-en-2-yl)cyclopent-1-ene-1-carbaldehyde (13.1 g, 87.2 mmol, yield: 98%) as a colorless liquid with a ratio of 4.88: 1.

(S)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)ethan-1-one: ^1H NMR (400 MHz, CDCl_3) δ 6.71 (s, 1H), 4.77 – 4.70 (m, 2H), 3.03 – 2.92 (m, 1H), 2.80 – 2.68 (m, 2H), 2.54 – 2.42 (m, 2H), 2.34 – 2.29 (m, 3H), 1.73 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 196.7, 147.4, 145.2, 143.3, 109.3, 44.8, 38.6, 35.3, 26.4, 20.6 ppm.

(S)-2-methyl-5-(prop-1-en-2-yl)cyclopent-1-ene-1-carbaldehyde: ^{13}C NMR (101 MHz, CDCl_3) δ 188.0, 163.7, 146.8, 139.1, 109.7, 50.7, 39.4, 28.6, 20.5, 14.5 ppm.

3. To a solution of (S)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)ethan-1-one and (S)-2-methyl-5-(prop-1-en-2-yl)cyclopent-1-ene-1-carbaldehyde (20.0 g, 133 mmol) in THF (100 ml) was added lithium bis(trimethylsilyl)amide solution (29.1 mL, 146mmol) dropwise at -20°C for 30 min. 3-Bromoprop-1-ene (15.3 g, 126mmol,) was added at 0°C and stirred at rt for 0.5 h. Saturated NH_4Cl aqueous solution(100mL) was added, and the mixture was extracted with MTBE (100 mL*3). The combined organic layer was dried over MgSO_4 and filtered. The solvent was removed and the result crude oil was purified via silica gel chromatography (heptane:MTBE=96:4) to give (S)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one (0.31 g, 1% yield) as a colorless liquid.

^1H NMR (400 MHz, CDCl_3) δ 6.75 – 6.64 (m, 1H), 5.89 – 5.79 (m, 1H), 5.10 – 4.92 (m, 2H), 4.75 – 4.66 (m, 2H), 3.04 – 2.92 (m, 1H), 2.81 – 2.67 (m, 4H), 2.54 – 2.31 (m, 4H), 1.73 (s, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 198.1, 147.4, 144.7, 142.1, 137.5, 115.1, 109.3, 44.7, 38.6, 37.9, 35.5, 28.4, 20.6 ppm. GC/MS (EI): m/z (%): 190 (4) [M^+], 175 (10), 161 (51), 135 (100), 107 (57), 91 (89), 79 (76), 55 (49). ee =99%. $[\alpha]_D^{25} = +9.7^\circ \cdot \text{mL} / (\text{g} \cdot \text{dm})$ (EtOH).

Odor description: fatty, galbanum, green, metallic.

Biodegradation: inherent biodegradable

Example 14: (R)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one

1. To a solution of sodium periodate (137 g, 641mmol) in water (300 mL) and THF (350 mL) was added (4S)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane (75 g, 493 mmol) in THF (300 mL) at rt and stirred for 16 h. The mixture was filtered to remove solid, and extracted with EA (100 mL*3). The result organic layer was combined, and dried over MgSO_4 and filtered. The solvent was removed and the crude oil was purified via silica gel chromatography

(heptane:MTBE=3:1) to give (S)-6-oxo-3-(prop-1-en-2-yl)heptanal (61 g, yield: 73%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 9.67 (t, *J* = 2.3 Hz, 1H), 4.84 – 4.78 (m, 2H), 2.71 – 2.64 (m, 1H), 2.54 – 2.35 (m, 4H), 2.13 (s, 3H), 1.77 – 1.58 (m, 5H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 208.3, 201.8, 145.1, 113.3, 47.4, 40.9, 40.8, 30.0, 26.4, 18.4 ppm. GC/MS (EI): *m/z* (%): 168 (1) [*M*⁺], 150 (3), 107 (100), 82 (46), 67 (71), 55 (46).

2. To a solution of (S)-6-oxo-3-(prop-1-en-2-yl)heptanal (20.0 g, 119 mmol) in ethanol (60 mL) was added a solution of sodium hydroxide (12.0 g, 297 mmol) in water (230 mL) at rt and stirred for 1 h. The mixture was added water (100 mL), and extracted with EA (100 mL*3). The result organic layer was combined, and dried over MgSO₄ and filtered. The solvent was removed and the crude oil was purified via silica gel chromatography (heptane:MTBE=94:6) to give (R)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)ethan-1-one (14 g, yield: 78%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 6.71 – 6.69 (m, 1H), 4.73 (d, *J* = 11.7 Hz, 2H), 3.00 – 2.94 (m, 1H), 2.81 – 2.67 (m, 2H), 2.57 – 2.41 (m, 2H), 2.32 (s, 3H), 1.73 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 196.7, 147.4, 145.2, 143.2, 109.3, 44.8, 38.6, 35.3, 26.4, 20.6 ppm. GC/MS (EI): *m/z* (%): 150 (46) [*M*⁺], 135 (100), 107 (75), 91 (84), 79 (73).

3. To a solution of (R)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)ethan-1-one (15.0 g, 100 mmol) in THF (300 mL) was added a lithium bis(trimethylsilyl)amide solution (110 mL, 110 mmol) at -20°C and stirred for 1 h. Then 3-bromoprop-1-ene (12.1 g, 100 mmol) in THF (100 mL) was added at 10°C and stirred for 6h. The mixture was quenched by adding water (100 mL), and extracted with EA (100 mL*3). The organic layer was combined, and dried over MgSO₄ and filtered. The solvent was removed and the crude oil was purified via silica gel chromatography (heptane:MTBE=97:3) to give (R)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one (0.6 g, yield: 4%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 6.71 (s, 1H), 5.89 – 5.79 (m, 1H), 5.07 – 5.00 (m, 2H), 4.73 (d, *J* = 12.1 Hz, 2H), 3.00 – 2.93 (m, 1H), 2.83 – 2.66 (m, 4H), 2.56 – 2.33 (m, 4H), 1.73 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 198.1, 147.4, 144.7, 142.1, 137.5, 115.1, 109.3, 44.7, 38.6, 37.9, 35.5, 28.4, 20.6 ppm. GC/MS (EI): *m/z* (%): 190 (5) [*M*⁺], 175 (12), 161 (53), 135 (100), 107 (72), 91 (91), 79 (85). ee = 99%. [α]_D²⁵ = -13.1° · mL / (g · dm) (EtOH).

Odor description: green, metallic, undecatriene, fatty, galbanum

Example 15: allyl (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate and allyl 4-isopropylbenzoate

1. To a solution of (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (contain 10% of 4-isopropylbenzaldehyde) (10.0 g, 67 mmol), 2-methylbut-2-ene (23.3 g, 333 mmol) and 2-methylpropan-2-ol (24.7 g, 333 mmol) in water (100 mL) was added a solution of sodium chlorite (18.1 g, 200 mmol) and KH_2PO_4 (45.3 g, 333 mmol) in water (200 mL) at 10°C and stirred at rt for 16 h. The mixture was extracted with EA (100 mL*3). The combined organic layer was washed with saturated NaHCO_3 aqueous solution and brine, and dried over MgSO_4 and filtered. The solvent was removed and the crude oil was purified via silica gel chromatography (heptane:MTBE=94:6) to give (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylic acid (contain 10% of 4-isopropylbenzoic acid) (6.5 g, yield: 59%) as white solid.

(S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylic acid: ^1H NMR (400 MHz, CDCl_3) δ 7.16 – 7.14 (m, 1H), 4.79 – 4.69 (m, 2H), 2.53 – 2.33 (m, 2H), 2.30 – 2.06 (m, 3H), 2.00 – 1.84 (m, 1H), 1.75 (s, 3H), 1.57 – 1.41 (m, 1H), 1.27 (t, J = 5.8 Hz, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 172.8, 148.7, 141.9, 129.5, 109.3, 40.0, 31.3, 27.0, 24.2, 20.7 ppm.

4-isopropylbenzoic acid: ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 3.01 – 3.01 (m, 1H), 1.28 (d, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 172.1, 155.3, 130.4, 127.0, 126.6, 34.4, 23.7 ppm.

2. A mixture of (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylic acid and 4-isopropylbenzoic acid (5.0 g, 30 mmol), 3-bromoprop-1-ene (4.0 g, 33 mmol) and potassium carbonate (5.4 g, 39 mmol) in DMF (100 mL) was stirred at 80°C for 16h. EA (100 mL) was added and filtered. The solvent was removed and the residue was purified via silica gel chromatography (heptane:MTBE=96:4) to give allyl (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate (2.3 g, yield: 37%) as a colorless liquid and allyl 4-isopropylbenzoate (0.13 g, yield: 2%) as a colorless liquid.

(S)-4-(Prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate: ^1H NMR (400 MHz, CDCl_3) δ 7.08 – 6.97 (m, 1H), 6.04 – 5.92 (m, 1H), 5.38 – 5.21 (m, 2H), 4.78 – 4.68 (m, 2H), 4.66 – 4.62 (m, 2H), 2.56 – 2.40 (m, 1H), 2.38 – 2.04 (m, 4H), 1.93 – 1.84 (m, 1H), 1.75 (s, 3H), 1.55 – 1.39 (m, 1H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 166.9, 148.8, 139.4, 132.5, 130.0, 117.8, 109.2, 64.9, 40.1, 31.1, 27.1, 24.6, 20.7 ppm. GC/MS (EI): m/z (%): 206 (1) [M^+], 191 (1), 165 (41), 121 (62), 105 (65), 93 (87), 79 (75), 68 (100).

Odor description: fruity, pineapple, ripe berry, grape, green, metallic, galbanum

Allyl 4-isopropylbenzoate: ^1H NMR (400 MHz, CDCl_3) δ 8.04 – 7.93 (m, 2H), 7.29 (d, J = 8.3 Hz, 2H), 6.13 – 5.93 (m, 1H), 5.43 – 5.26 (m, 2H), 4.82 – 4.80 (m, 2H), 3.01 – 2.91 (m, 1H), 1.27 (d, J = 6.9 Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 166.3, 154.4, 132.4, 129.8, 127.8, 126.5, 118.0, 65.3, 34.3, 23.7 ppm. GC/MS (EI): m/z (%): 204 (7) [M^+], 189 (9), 147 (100), 117 (7), 91 (15).

Odor description: green leathery

Example 16: But-2-en-1-yl (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate

1. According the procedure of example 15(step 1), (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylic acid was obtained from the reaction of (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (40.0 g, 266 mmol) and sodium chlorite (72.3 g, 799 mmol) as a white solid (41.8 g, yield: 95%).

^1H NMR (400 MHz, CDCl_3) δ 7.16 – 7.11 (m, 1H), 4.80 – 4.66 (m, 2H), 2.53 – 2.30 (m, 2H), 2.27 – 2.08 (m, 3H), 1.94 – 1.84 (m, 1H), 1.75 (s, 3H), 1.32 – 1.23 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 172.7, 148.7, 141.9, 129.5, 109.3, 39.9, 31.3, 27.0, 24.2, 20.7 ppm. GC/MS (EI): m/z (%): 166 (14) [M^+], 151 (10), 121 (48), 79 (51), 68 (100).

2. To a solution of (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylic acid (2.00 g, 12 mmol), but-2-en-1-ol (0.95 g, 13 mmol) and triphenylphosphane (3.47 g, 13 mmol) in THF (50 mL) was added DIAD (2.68 g, 13.2 mmol) at 0 °C and stirred at rt for 16 h. The mixture was filtered and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel (heptane:MTBE=98:2) to get but-2-en-1-yl (S)-4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate (2.1 g, yield: 79%) as a colorless liquid.

^1H NMR (400 MHz, CDCl_3) δ 7.08 – 6.94 (m, 1H), 5.87 – 5.73 (m, 1H), 5.70 – 5.51 (m, 1H), 4.80 – 4.67 (m, 2H), 4.57 (d, J = 6.4 Hz, 2H), 2.54 – 2.43 (m, 1H), 2.38 – 2.03 (m, 4H), 1.93 – 1.84 (m, 1H), 1.80 – 1.69 (m, 6H), 1.50 – 1.39 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.2, 148.9, 139.1, 130.9, 130.1, 125.4, 109.2, 65.0, 40.1, 31.1, 27.1, 24.6, 20.8, 17.8 ppm. GC/MS (EI): m/z (%): 220 (1) [M^+], 205 (1), 191 (15), 165 (47), 149 (43), 93 (75), 79 (58), 55 (100).

Odor description: fruity, apricot, metallic, green

Example 17: 1-(2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one

1. To a solution of (methoxymethyl)triphenylphosphonium chloride (50.2 g, 146 mmol) in THF (300 mL) was added sodium hydride (5.8 g, 60% Wt, 146 mmol) slowly at 0°C and stirred at rt for 1 h. 2-Methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-one (20.0 g, 133 mmol) in THF (50 mL) was added at 0°C. The mixture was stirred at rt overnight. A solution of HCl (133 mL, 1.0 M, 133 mmol) was added slowly at 10°C and stirred at rt for 12 h. The mixture was extracted by EA (100 mL*3). The combined organic layer was washed with saturated NaHCO₃ (200 mL*3) aqueous solution and brine, and dried over MgSO₄ and filtered. The solvent was removed and the crude oil was purified via silica gel chromatography (heptane:MTBE=96:4) to give 2-methyl-5-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (13.0 mmol, 2.1 g, 10% yield) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 10.15 (s, 1H), 4.81 – 4.67 (m, 2H), 2.58 – 2.49 (m, 1H), 2.38 – 2.26 (m, 2H), 2.17 – 2.03 (m, 4H), 1.97 – 1.79 (m, 2H), 1.76 (s, 3H), 1.53 – 1.40 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 190.9, 155.7, 148.8, 133.2, 109.1, 40.2, 34.7, 27.5, 26.8, 20.8, 18.0 ppm. GC/MS (EI): *m/z* (%): 164 (24) [*M*⁺], 149 (31), 107 (39), 93 (55), 79 (42), 67 (100).

2. According the procedure of example 1 (step 1), 1-(2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-ol was obtained from 2-methyl-5-(prop-1-en-2-yl)cyclohex-1-ene-1-carbaldehyde (1.5 g, 9 mmol) and but-3-en-1-ylmagnesium bromide (24 mL, 12 mmol, 0.5 M) as colorless liquid (1.2 g, 60% yield).

¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 5.93 – 5.76 (m, 1H), 5.10 – 4.93 (m, 2H), 4.74 – 4.59 (m, 3H), 2.17 – 1.95 (m, 6H), 1.82 – 1.10 (m, 12H) ppm. ¹³C NMR (101 MHz, CDCl₃, mixture of isomers) δ 150.3, 150.1, 138.5, 138.5, 131.2, 130.9, 129.5, 128.4, 114.7, 108.7, 108.4, 70.7, 69.9, 41.5, 41.4, 34.3, 33.6, 33.0, 32.8, 30.3, 30.2, 28.1, 27.9, 27.8, 21.0, 20.8, 18.6, 18.5 ppm.

3. According the procedure of example 1 (step 2), 1-(2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one was obtained from 1-(2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-ol (1.2 g, 6 mmol) and 4-nitrobenzaldehyde (3.3 g, 22 mmol) as a colorless liquid (1.1 g, 93% yield).

¹H NMR (400 MHz, CDCl₃) δ 5.89 – 5.79 (m, 1H), 5.09 – 4.90 (m, 2H), 4.79 – 4.70 (m, 2H), 2.69 – 2.53 (m, 2H), 2.40 – 2.28 (m, 3H), 2.25 – 2.09 (m, 4H), 1.85 – 1.72 (m, 7H), 1.51 – 1.39 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 205.9, 149.0, 139.2, 137.5, 132.7, 115.0, 109.2, 40.9, 40.7, 33.4, 31.9, 28.0, 27.1, 21.1, 20.7 ppm. GC/MS (EI): *m/z* (%): 218 (8) [*M*⁺], 203 (22),

189 (20), 175 (28), 163 (85), 145 (27), 133 (42), 121 (40), 107 (100), 93 (99), 79 (37), 67 (28), 55 (52).

Odor description: green, metallic, fish scale, undecatriene, galbanum, fatty

Example 18: 1-(5-isopropyl-2-methylcyclohex-1-en-1-yl)pent-4-en-1-one

5 1. A mixture of 5-isopropyl-2-methylcyclohexa-1,3-diene (α -phellandrene) (30.0 g, 220 mmol), triphenylphosphane (5.8 g, 22mmol) and RhCOH(PPh₃)₃ (2.0 g, 2.2 mmol) was stirred under 45 atm of syngas in autoclave at 110°C for 16 h. The mixture was filtered, the solvent was removed and the crude oil was purified via silica gel chromatography (heptane:MTBE=97:3) to give 5-isopropyl-2-methylcyclohex-1-ene-1-carbaldehyde (2.0 g, yield: 6%) as a colorless oil.

10 ¹H NMR (400 MHz, CDCl₃) δ 10.14 (s, 1H), 2.44 (d, J = 16.9 Hz, 1H), 2.35 – 2.23 (m, 2H), 2.14 (s, 3H), 1.82 – 1.67 (m, 2H), 1.58 – 1.46 (m, 1H), 1.28 – 1.11 (m, 2H), 0.96 – 0.85 (m, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 191.2, 156.2, 133.6, 39.5, 35.1, 32.2, 25.8, 25.5, 19.8, 19.6, 18.0 ppm. GC/MS (EI): m/z (%): 166 (100) [M^+], 151 (29), 123 (78), 95 (94), 81 (58).

15 2. According the procedure of example 1 (step 1), 1-(5-isopropyl-2-methylcyclohex-1-en-1-yl)pent-4-en-1-ol was obtained from 5-isopropyl-2-methylcyclohex-1-ene-1-carbaldehyde (1.0 g, 6 mmol) and but-3-en-1-ylmagnesium bromide (18 mL, 9 mmol, 0.5 M) as a colorless liquid (1.1 g, yield: 82%).

20 ¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 5.92 – 5.77 (m, 1H), 5.10 – 4.92 (m, 2H), 4.68 – 4.57 (m, 1H), 2.25 – 1.93 (m, 5H), 1.81 – 1.45 (m, 8H), 1.38 (s, 1H), 1.29 – 1.12 (m, 2H), 0.96 – 0.83 (m, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃, mixture of isomers) δ 138.6, 138.5, 131.3, 131.1, 129.7, 128.6, 114.7, 70.8, 70.1, 40.5, 40.5, 34.3, 33.6, 33.2, 33.0, 32.4, 32.2, 30.3, 30.2, 26.4, 26.3, 26.2, 26.1, 19.9, 19.8, 18.6, 18.6 ppm. GC/MS (EI): m/z (%): 222 (4) [M^+], 207 (12), 167 (100), 149 (15), 123 (84), 107 (62), 93 (47).

25 3. According the procedure of example 1 (step 2), 1-(5-isopropyl-2-methylcyclohex-1-en-1-yl)pent-4-en-1-one was obtained from 1-(5-isopropyl-2-methylcyclohex-1-en-1-yl)pent-4-en-1-ol (1.0 g, 5 mmol), and 4-nitrobenzaldehyde (1.5 g, 10 mmol) as a colorless liquid (0.81 g, 82% yield).

¹H NMR (400 MHz, CDCl₃) δ 5.91 – 5.78 (m, 1H), 5.09 – 4.94 (m, 2H), 2.68 – 2.58 (m, 2H), 2.41 – 1.71 (m, 10H), 1.57 – 1.45 (m, 1H), 1.37 – 1.15 (m, 2H), 0.91 (d, J = 6.8 Hz, 6H) ppm.

^{13}C NMR (101 MHz, CDCl_3) δ 206.5, 139.2, 137.6, 133.0, 115.0, 40.7, 40.0, 33.6, 32.1, 30.2, 28.0, 25.6, 21.1, 19.8, 19.7 ppm. GC/MS (EI): m/z (%): 220 (5) [M^+], 205 (9), 191 (60), 165 (100), 95 (82).

Odor description: green, galbanum, metallic, undecatriene, pharaone, rubbery

5 Example 19: (S)-1-(5-isopropyl-2-methylcyclohex-1-en-1-yl)pent-4-en-1-one

1. To a solution of (S)-4-isopropyl-1-methylcyclohex-1-ene (10.0 g, 73 mmol) and zinc(II) chloride (3.0 g, 22.0 mmol) in DCM (10 mL) was added pent-4-enoic anhydride (14.7 g, 80 mmol) dropwise at 10°C and stirred for another 16 h. Saturated NaHCO_3 aqueous solution (100 mL) was added, and the result mixture was extracted with EA (150 mL*3). The combined
10 organic layer was washed with saturated NaHCO_3 aqueous solution (100 mL) and brine (100 mL), and dried over MgSO_4 and filtered. The solvent was removed and the crude oil was purified via silica gel chromatography (heptane:MTBE=97:3) to give 1-((5S)-5-isopropyl-2-methylcyclohex-2-en-1-yl)pent-4-en-1-one (7.1 g, 45% yield) as a colorless liquid.

^1H NMR (400 MHz, CDCl_3 , mixture of isomers) δ 5.86 – 5.76 (m, 1H), 5.68 – 5.59 (m, 1H), 5.10
15 – 4.94 (m, 2H), 3.26 – 3.03 (m, 1H), 2.70 – 2.48 (m, 2H), 2.37 – 2.32 (m, 2H), 2.14 – 1.98 (m, 1H), 1.93 – 1.89 (m, 1H), 1.75 – 1.37 (m, 6H), 1.34 – 1.23 (m, 1H), 0.93 – 0.81 (m, 6H) ppm.
 ^{13}C NMR (101 MHz, CDCl_3 , mixture of isomers) δ 213.2, 211.5, 137.3, 137.2, 130.5, 125.9, 125.3, 115.3, 115.2, 55.5, 53.3, 40.6, 40.0, 39.5, 35.5, 32.3, 31.9, 30.7, 29.1, 28.8, 28.0, 27.8, 22.9, 21.3, 19.8, 19.5, 19.4 ppm. GC/MS (EI): m/z (%): 220 (8) [M^+], 206 (3), 137 (40), 95 (38),
20 81 (100), 55 (90).

Odor description: green-galbanum, metallic, pelagonium, rose oxide.

2. A mixture of 1-((5S)-5-isopropyl-2-methylcyclohex-2-en-1-yl)pent-4-en-1-one (4.0 g, 18 mmol) and 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepine (8.5 g, 55 mmol) in THF (50 mL) was stirred at 50°C for 16h. Water (100 mL) was added, and the mixture was extracted with
25 MTBE (100 mL*3). The combined organic layer was dried over MgSO_4 and filtered. The solvent was removed and the crude oil was purified via silica gel chromatography (heptane:MTBE=98:2) to give (S)-1-(5-isopropyl-2-methylcyclohex-1-en-1-yl)pent-4-en-1-one (1.3 g, 33% yield) as a colorless liquid.

^1H NMR (400 MHz, CDCl_3) δ 5.89 – 5.79 (m, 1H), 5.09 – 4.87 (m, 2H), 2.67 – 2.56 (m, 2H),
30 2.38 – 2.33 (m, 2H), 2.28 – 2.23 (m, 1H), 2.13 – 2.08 (m, 2H), 2.00 – 1.87 (m, 1H), 1.83 – 1.71

(m, 4H), 1.56 – 1.48 (m, 1H), 1.36 – 1.13 (m, 2H), 0.91 (d, $J = 6.8$ Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 206.6, 139.3, 137.6, 133.0, 115.0, 40.7, 40.0, 33.6, 32.1, 30.2, 28.0, 25.6, 21.1, 19.8, 19.7 ppm. GC/MS (EI): m/z (%): 220 (7) [M^+], 205 (9), 191 (59), 165 (98), 95 (100), 81 (58).

- 5 Odor description: green, metallic, sharp, geranium, pelargene, rosyane, rose oxide, floral, rosy

Example 20: But-2-en-1-yl (1*S*,6*R*)-7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylate

1. To a solution of (1*S*,6*R*)-3,7,7-trimethylbicyclo[4.1.0]hept-3-ene ((1*S*,6*R*)-carene) (50.0 g, 367 mmol) in CHCl_3 (400 mL) was added *m*-CPBA (80.5 g, 85% Wt, 396 mmol) slowly at 23–27°C and stirred at rt overnight. Heptane (200 mL) was added and the solid was filtered off.
10 500 mL of EA was added and the result mixture was washed with NaHSO_3 (200 mL*3), saturated NaHCO_3 aqueous solution (200 mL*3) and brine (200 mL). The result organic layer dried over MgSO_4 and then filtered. The solvent was removed by rotary evaporation. The crude product was purified by silica gel chromatography (heptane: MTBE=94:6) to give (1*S*,7*R*)-3,8,8-trimethyl-4-oxatricyclo[5.1.0.0^{3,5}]octane (51.6 g, 339 mmol, yield: 92%) as a colorless liquid.

- 15 ^1H NMR (400 MHz, CDCl_3) δ 2.84 – 2.79 (m, 1H), 2.33 – 2.11 (m, 2H), 1.66 – 1.47 (m, 2H), 1.26 (s, 3H), 1.01 (s, 3H), 0.73 (s, 3H), 0.57 – 0.41 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 58.1, 55.8, 27.7, 23.3, 23.1, 19.2, 16.0, 15.9, 14.6, 13.8 ppm.

2. To a solution of 2,2,6,6-tetramethylpiperidine (50.1 g, 355 mmol) in THF (500 mL) was added *n*-butyllithium (222 mL, 1.6 M, 355 mmol) slowly at 0°C and stirred at rt under argon for 30 min.
20 Diethylaluminumchloride (359 mL, 1.0 M, 358 mmol) was added slowly at 0°C and stirred at rt for 30 min. Then (1*S*,7*R*)-3,8,8-trimethyl-4-oxatricyclo[5.1.0.0^{3,5}]octane (30.0 g, 177 mmol) in THF (50 mL) was added slowly at 0°C and stirred at rt for 16 h. The mixture was quenched by adding 500 mL of 10% HCl aqueous solution, and the result mixture was extracted with MTBE (300 mL*3). The combined organic layer was washed with saturated NaHCO_3 aqueous solution
25 and brine, and then dried over MgSO_4 and filtered. The solvent was removed and the crude oil was distilled via kugelrohr distillation (0.11 mbar, 120°C) to give (1*R*,6*S*)-7,7-dimethyl-4-methylenebicyclo[4.1.0]heptan-3-ol with 85% purity as colorless liquid (29.2 g, 160 mmol, 92% yield).

- ^1H NMR (400 MHz, CDCl_3) δ 4.84 – 4.71 (m, 2H), 4.09 (t, $J = 3.2$ Hz, 1H), 2.75 – 2.13 (m, 3H),
30 1.76 (s, 1H), 1.60 – 1.49 (m, 1H), 1.01 (s, 3H), 0.88 (s, 3H), 0.86 – 0.63 (m, 2H) ppm.

3. To a solution of (1*R*,6*S*)-7,7-dimethyl-4-methylenebicyclo[4.1.0]heptan-3-ol (16.0 g, 85% Wt, 89 mmol) in toluene (300 mL) was added tris(triphenylsiloxy)vanadium oxide (5.3 g, 5.4 mmol) at 10°C and stirred at 110°C for 6 h. Water (50 mL) and MTBE (200 mL) were added, and the mixture was extracted with MTBE (200 mL*3). The combined organic layer was washed with
5 saturated NaHCO₃ aqueous solution (200 mL) and brine (200 mL), and dried over MgSO₄ and filtered. The solvent was removed and the result crude oil was purified via silica gel chromatography (heptane:MTBE=9:1) to give ((1*S*,6*R*)-7,7-dimethylbicyclo[4.1.0]hept-3-en-3-yl)methanol (12.1 g, 80 mmol, yield: 89%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 5.60 – 5.50 (m, 1H), 3.95 (s, 2H), 2.46 – 2.25 (m, 2H), 2.01 – 1.88
10 (m, 2H), 1.65 (s, 1H), 1.04 (s, 3H), 0.80 – 0.70 (m, 4H), 0.70 – 0.59 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 135.3, 121.7, 67.7, 28.3, 20.5, 20.4, 17.8, 17.1, 16.9, 13.3 ppm.

4. A mixture of ((1*S*,6*R*)-7,7-dimethylbicyclo[4.1.0]hept-3-en-3-yl)methanol (12.0 g, 79 mmol), sodium ethanolate (8.4 g, 102 mmol) and MgSO₄ (10 g) in DCM (200 mL) was stirred at 10°C for 10 min. Then a mixture of pyridinium chlorochromate (22.1 g, 102 mmol) and silica gel (30
15 g) was added slowly and stirred at rt for 6 h. MTBE (200 mL) was added, and the mixture was filtered through short silica gel column. The solvent was removed and the result crude oil was purified via silica gel chromatography (heptane:MTBE=97:3) to give (1*S*,6*R*)-7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carbaldehyde (8.6 g, 57mmol, yield: 83%) as a colorless liquid.

20 ¹H NMR (400 MHz, CDCl₃) δ 9.40 (s, 1H), 6.72 – 6.71 (m, 1H), 2.77 – 2.18 (m, 4H), 1.07 (s, 3H), 0.83 - 0.70 (m, 5H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 194.1, 150.6, 139.9, 28.2, 22.5, 17.7, 17.6, 17.1, 16.6, 13.5 ppm. GC/MS (EI): *m/z* (%): 150 (4) [*M*⁺], 135 (11), 121 (19), 107 (100), 91 (33), 79 (79).

5. To a mixture of (1*S*,6*R*)-7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carbaldehyde (25.0 g, 166
25 mmol), KH₂PO₄ (113 g, 832 mmol), 2-methylbut-2-ene (58.4 g, 832 mmol) and 2-methylpropan-2-ol (61.7 g, 832 mmol) in water (200 mL) was added a solution of sodium chlorite (45.2 g, 499 mmol) in water (100 mL) at 10°C and stirred at rt for 16 h. Saturated NH₄Cl (300 mL) solution was added. The mixture was extracted with EA (100 mL*3). The combined organic layer was washed with saturated NaHCO₃ aqueous solution and brine and then dried over
30 MgSO₄ and filtered. The solvent was removed and the crude oil was purified via silica gel

chromatography (heptane:MTBE=9:1) to give (1*S*,6*R*)-7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylic acid (25.2 g, 152 mmol, yield: 91%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ 7.13 – 6.96 (m, 1H), 2.65 – 2.47 (m, 2H), 2.28 – 2.10 (m, 2H), 1.06 (s, 3H), 0.87 – 0.78 (m, 1H), 0.76 – 0.65 (m, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 140.9, 127.7, 28.2, 22.1, 18.7, 17.7, 17.6, 16.5, 13.4 ppm.

GC/MS (EI): m/z (%): 166 (16) [*M*⁺], 123 (87), 105 (52), 91 (32), 79 (100).

6. To a solution of (1*S*,6*R*)-7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylic acid (1.5 g, 9 mmol), but-2-en-1-ol (0.7 g, 10 mmol) and triphenylphosphane (2.6 g, 10 mmol) in THF (50 mL) was added DIAD (2.0 g, 10 mmol) at rt and stirred for 16 h. MTBE (200 mL) was added and the solid was filtered. The solvent was removed and the crude oil was purified via silica gel chromatography (heptane:MTBE=98:2) to give but-2-en-1-yl (1*S*,6*R*)-7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylate (1.8 g, yield: 90%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 6.94 – 6.86 (m, 1H), 5.89 – 5.51 (m, 2H), 4.70 – 4.54 (m, 2H), 2.64 – 2.48 (m, 2H), 2.27 – 2.09 (m, 2H), 1.72 (m, 3H), 1.05 (s, 3H), 0.91 – 0.64 (m, 5H) ppm. ¹³C NMR (101 MHz, CDCl₃, E-isomer) δ 167.2, 138.2, 130.8, 128.4, 125.5, 65.0, 28.2, 21.8, 19.1, 17.8, 17.8, 17.5, 16.6, 13.5 ppm. GC/MS (EI): m/z (%): 220 (2) [*M*⁺], 165 (21), 123 (100), 105 (45), 79 (52), 55 (74).

Odor description: green, galbanum, resin, metallic, fir needle, aromatic, terpenic, coniferous, woody

Example 21: cyclopent-2-en-1-yl (1*S*,6*R*)-7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylate

According to the procedure of example 20 (step 6), cyclopent-2-en-1-yl (1*S*,6*R*)-7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylate was obtained from (1*S*,6*R*)-7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylic acid (1.0 g, 6 mmol) and cyclopent-2-en-1-ol (0.6 g, 7 mmol) as colorless liquid (1.2 g, 81% yield).

¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 7.01 – 6.74 (m, 1H), 6.12 – 6.03 (m, 1H), 5.96 – 5.59 (m, 2H), 2.63 – 2.04 (m, 7H), 1.90 – 1.65 (m, 3H), 1.05 (s, 3H), 0.85 – 0.64 (m, 5H) ppm. ¹³C NMR (101 MHz, CDCl₃, mixture of isomers) δ 167.4, 167.4, 167.2, 167.2, 137.9, 137.6, 137.6, 137.6, 137.6, 137.2, 129.6, 128.8, 128.6, 80.3, 77.2, 32.7, 31.1, 29.8, 28.2,

23.8, 21.7, 19.0, 19.0, 17.8, 17.5, 16.6, 13.5 ppm. GC/MS (EI): m/z (%): 246 (1) [M^+], 166 (22), 149 (10), 123 (53), 79 (34), 67 (100).

Odor description: fatty, green, metallic, galbanum, coniferous, bornyl

Example 22: 1-((1S,6R)-7,7-dimethylbicyclo[4.1.0]hept-3-en-3-yl)hex-4-en-1-one

- 5 1. According the procedure of example 1 (step 1), 1-((1S,6R)-7,7-dimethylbicyclo[4.1.0]hept-3-en-3-yl)hex-4-en-1-ol was obtained from the reaction of pent-3-en-1-ylmagnesium bromide (121 mL, 61mmol, 0.5 M) and (1S,6R)-7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carbaldehyde (7.0 g, 45 mmol) as a colorless liquid (7.1 g, yield: 74%).

^1H NMR (400 MHz, CDCl_3 , mixture of isomers) δ 5.59 – 5.33 (m, 3H), 4.00 – 3.93 (m, 1H), 2.46
10 – 1.82 (m, 6H), 1.70 – 1.44 (m, 6H), 1.04 (s, 3H), 0.79 – 0.54 (m, 5H) ppm.

^{13}C NMR (101 MHz, CDCl_3 , mixture of isomers) δ 137.7, 137.6, 130.9, 130.8, 130.1, 130.0, 125.2, 124.4, 124.3, 122.3, 122.2, 121.4, 121.3, 76.7, 76.6, 76.1, 76.0, 34.9, 34.8, 34.6, 34.5, 29.0, 28.9, 28.3, 28.2, 20.5, 20.4, 18.7, 17.9, 17.8, 17.7, 17.6, 17.6, 17.4, 17.2, 17.0, 13.4, 13.3, 12.8 ppm.

- 15 2. According the procedure of example 1 (step 2), 1-((1S,6R)-7,7-dimethylbicyclo[4.1.0]hept-3-en-3-yl)hex-4-en-1-one was obtained from the reaction of 1-((1S,6R)-7,7-dimethylbicyclo[4.1.0]hept-3-en-3-yl)hex-4-en-1-ol (7.0 g, 34 mmol), $\text{Al}(\text{Os-Bu})_3$ (2.5 g, 10 mmol), acetic acid (0.2 g) and 4-nitrobenzaldehyde (11.5 g, 76 mmol) as a colorless liquid (6.3 g, 91% yield).

20 ^1H NMR (400 MHz, CDCl_3 , mixture of isomers) δ 6.85 – 6.74 (m, 1H), 5.50 – 5.30 (m, 2H), 2.70 – 2.09 (m, 8H), 1.70 – 1.54 (m 3H), 1.15 – 0.97 (m, 3H), 0.90 – 0.62 (m, 5H) ppm. ^{13}C NMR (101 MHz, CDCl_3 , mixture of isomers) δ 200.5, 200.4, 138.4, 138.3, 137.2, 130.1, 129.2, 125.5, 124.7, 37.2, 37.0, 28.1, 27.7, 22.2, 22.1, 18.1, 17.9, 17.8, 17.5, 16.6, 13.5, 12.7 ppm. GC/MS (EI): m/z (%): 218 (11) [M^+], 203 (10), 189 (6), 175 (39), 121 (53), 105 (100), 55 (41).

- 25 Odor description: green, metallic, slightly undecatriene, pineapple, galbanum, fatty, galbanum, fruity, pineapple

Example 23: 1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)hex-4-en-1-one

1. According the procedure of example 1 (step 1), 1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)hex-4-en-1-ol was obtained from the reaction of pent-3-en-1-ylmagnesium bromide (63 mL, 50mmol, 0.8 M) and (1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-carbaldehyde (5.0 g, 33 mmol) as a colorless liquid (1.0 g, yield: 14%, E/Z=9:1)

5 ¹H NMR (400 MHz, CDCl₃, mixture of isomers) δ 5.56 – 5.34 (m, 3H), 4.05 – 3.94 (m, 1H), 2.53 – 1.90 (m, 7H), 1.75 – 1.44 (m, 6H), 1.29 (d, J = 1.6 Hz, 3H), 1.19 – 1.11 (m, 1H), 0.89 – 0.78 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃, mixture of E isomers) δ 150.6, 150.0, 131.0, 130.9, 125.3, 125.2, 117.9, 117.5, 74.5, 74.3, 42.0, 41.9, 41.0, 40.9, 37.8, 34.5, 34.3, 31.9, 31.8, 31.2, 31.1, 29.0, 28.8, 26.2, 26.1, 21.4, 21.3, 17.9 ppm. GC/MS (EI): m/z (%): 220 (1) [M^+], 202 (2),
10 152 (69), 107 (78), 91 (74), 81 (88), 55 (100).

2. According the procedure of example 1 (step 2), 1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)hex-4-en-1-one was obtained from the reaction of 1-((1R,5S)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)hex-4-en-1-ol (0.9 g, 2.0 mmol), Al(Os-Bu)₃ (0.2 g, 0.6 mmol), acetic acid (0.02 g) and 4-nitrobenzaldehyde (0.7 g, 4.6 mmol) as a colorless liquid (0.8 g, 90% yield, E/Z = 9:1).

¹H NMR (400 MHz, CDCl₃) δ 6.77 – 6.70 (m, 1H), 5.50 – 5.34 (m, 2H), 3.00 – 2.92 (m, 1H), 2.84 – 2.08 (m, 8H), 1.67 – 1.49 (m, 3H), 1.32 (s, 3H), 1.02 (d, J = 9.1 Hz, 1H), 0.74 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃, E isomer) δ 198.9, 149.2, 136.4, 130.0, 125.6, 40.3, 39.5, 37.3, 36.9, 32.5, 31.1, 28.0, 25.9, 20.8, 17.9 ppm. GC/MS (EI): m/z (%): 218 (1) [M^+], 203 (3),
20 175 (62), 105 (100), 91 (32), 69 (55).

Odor description: fatty, fruity, pineapple, over ripe, green, galbanum.

Example 24: 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one

1. To a mixture of sodium periodate (45.7 g, 213 mmol) in THF (100 mL) and water (100 mL) was added 1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane (25.0 g, 164 mmol) in THF
25 (100 mL) at r.t. and stirred at r.t. for 16 h. The mixture was filtered to remove solid, and extracted with EA (100 mL*3). The result organic layer was combined, and dried over MgSO₄ and filtered. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (heptane: MTBE= 3:1) to get 6-oxo-3-(prop-1-en-2-yl)heptanal (23.9 g, yield: 87%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ = 9.67 (t, *J* = 2.3 Hz, 1H), 4.93 – 4.72 (m, 2H), 2.82 – 2.58 (m, 1H), 2.55 – 2.36 (m, 4H), 2.13 (s, 3H), 1.78 – 1.56 (m, 5H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 208.2, 201.8, 145.1, 113.2, 77.4, 77.1, 76.8, 47.4, 40.9, 40.7, 30.0, 26.4, 18.4 ppm. GC/MS (EI): *m/z* (%): 168 (1) [*M*⁺], 150 (5), 107 (100), 82 (46), 67 (73), 55 (51).

- 5 2. To a solution of 6-oxo-3-(prop-1-en-2-yl)heptanal (22.8 g, 135 mmol) in ethanol (100 mL) was added sodium hydroxide solution (162 g, 5% in water) at 5°C. The mixture was stirred at 5°C for 1h. Water (150 mL) was added, the mixture was extracted with MTBE (100 mL *3), the combined organic phase was washed with brine (100mL) and dried over MgSO₄, the mixture was filtered, the solvent was removed by rotary evaporation, and the residue was purified by
10 flash chromatography (heptane: MTBE=97: 3) to get 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)ethan-1-one (9.7 g, yield: 48 %) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ = 6.78 – 6.64 (m, 1H), 4.75 – 4.69 (m, 2H), 3.06 – 2.91 (m, 1H), 2.84 – 2.63 (m, 2H), 2.61 – 2.41 (m, 2H), 2.32 (s, 3H), 1.73 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 196.7, 147.3, 145.2, 143.2, 109.3, 44.8, 38.5, 35.3, 26.4, 20.6 ppm. GC/MS (EI): *m/z*
15 (%): 150 (62) [*M*⁺], 135 (100), 117 (10), 107 (71), 91 (99), 79 (78), 65 (40).

3. To a solution of 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)ethan-1-one (3.0 g, 20.2 mmol) and triethylamine (2.8 g, 28.0 mmol) in DCM (50 mL) at 0°C under argon was added trimethylsilyl triflate (5.3 g, 24.0 mmol) dropwise. After addition, the mixture was stirred at 0°C for 1.5h, the resulting mixture was washed with aq. NaHCO₃ solution (100 mL) and brine (50 mL), the
20 organic phase was dried over MgSO₄, the mixture was filtered, and the organic phase was concentrated to give trimethyl((1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)vinyl)oxy)silane (4.4 g, yield: 99%) as a yellow liquid, which was used for next step directly.

¹H NMR (400 MHz, CDCl₃) δ = 5.93 – 5.87(m, 1H), 4.76 – 4.72(m, 1H), 4.70 – 4.64(m, 1H), 4.32 – 4.25(m, 2H), 3.08 – 2.96(m, 1H), 2.67 – 2.51(m, 2H), 2.45 – 2.28(m, 2H), 1.72(s, 3H),
25 0.22(s, 9H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 153.6, 148.7, 140.4, 127.8, 109.0, 93.2, 45.7, 37.9, 37.0, 20.4, 0.2 ppm. GC/MS (EI): *m/z* (%): 222 (40) [*M*⁺], 207 (52), 179 (56), 154 (31), 127 (26), 117 (30), 91 (24), 73 (100).

4. To a suspension of silver(I) 2,2,2-trifluoroacetate (5.3 g, 24.0 mmol) in DCM (50 mL) at -70°C under Ar was added trimethyl((1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)vinyl)oxy)silane
30 (4.4 g, 19.8 mmol) in DCM (20 mL) and 3-bromoprop-1-ene (2.9 g, 24.0 mmol). The reaction mixture was allowed to warm to r.t. over 1 h, and stirred for another 1 h. The mixture was filtered

through a pad of silica gel, the solvent was removed by rotary evaporation, and the residue was purified via flash chromatography (heptane: MTBE= 97:3) to get 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one (1.1 g, yield: 29 %) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ = 6.74 – 6.67(m, 1H), 5.90 – 5.77(m, 1H), 5.10 – 4.90(m, 2H),
 5 4.77 – 4.63 (m, 2H), 3.01 – 2.87 (m, 1H), 2.83 – 2.62(m, 4H), 2.56 – 2.26(m, 4H), 1.73(s, 3H)
 ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 198.0, 147.3, 144.7, 142.0, 137.4, 115.0, 109.3, 44.6,
 38.5, 37.9, 35.4, 28.4, 20.5 ppm. GC/MS (EI): *m/z* (%): 190 (5) [*M*⁺], 175 (12), 161 (52), 135
 (100), 107 (54), 91 (81), 79 (67), 55 (38).

Odor description: green, galbanum, sharp, metallic, mushroom, fruity, pineapple.

10 Example 25: 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)hex-4-en-1-one

According the procedure of example 24, step 4, trimethyl((1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)vinyl)oxy)silane (6.8 g, 30 mmol) reacted with 1-bromobut-2-ene (5.6 g, purity: 80%, 33 mmol) under silver(I) 2,2,2-trifluoroacetate (6.7 g, 30 mmol) gave 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)hex-4-en-1-one (2.6 g, E/Z=95:5, yield: 43%) as a colorless liquid.

15 ¹H NMR (400 MHz, CDCl₃) δ = 6.64 – 6.57 (m, 1H), 5.49 – 5.20 (m, 2H), 4.67 (s, 1H), 4.64 (s, 1H), 2.99 – 2.82 (m, 1H), 2.77 – 2.55 (m, 4H), 2.50 – 2.30 (m, 2H), 2.29 – 2.12 (m, 2H), 1.65 (s, 3H), 1.60 – 1.52 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃, E isomer) δ = 198.6, 147.6, 144.8, 142.1, 130.0, 125.8, 109.4, 44.8, 38.8, 38.7, 35.6, 27.6, 20.7, 18.0 ppm. GC/MS (EI): *m/z* (%): 204 (10) [*M*⁺], 189 (22), 175 (39), 135 (100), 107 (68), 91 (81), 79 (70).

20 Odor description: fatty, fruity, pineapple, green, galbanum.

Example 26: (R)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)hex-4-en-1-one

According the procedure of example 24, step 4, (R)-trimethyl((1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)vinyl)oxy)silane (11.9 g, 53 mmol) reacted with 1-bromobut-2-ene (9.8 g, purity: 80%, 58 mmol) under silver(I) 2,2,2-trifluoroacetate (11.7 g, 53 mmol) and gave (R)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)hex-4-en-1-one (5.7 g, E/Z=95:5, 99%ee, yield: 53%) as a colorless liquid.

25 ¹H NMR (400 MHz, CDCl₃) δ = 6.65 – 6.57 (m, 1H), 5.50 – 5.20 (m, 2H), 4.67 (s, 1H), 4.64 (s, 1H), 2.99 – 2.81 (m, 1H), 2.78 – 2.56 (m, 4H), 2.51 – 2.31 (m, 2H), 2.30 – 2.11 (m, 2H), 1.65 (s, 3H), 1.60 – 1.50 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃, E isomer) δ = 198.6, 147.6,

144.9, 142.1, 130.0, 125.8, 109.4, 44.8, 38.8, 38.7, 35.6, 27.6, 20.7, 18.0 ppm. GC/MS (EI): m/z (%): 204 (9) [M^+], 189 (19), 175 (35), 161 (29), 135 (95), 107 (76), 91 (100), 79 (87).

Odor description: green, galbanum, fruity, pineapple.

Example 27: (S)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)hex-4-en-1-one

- 5 According to the procedure of example 24, step 4, (S)-trimethyl((1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)vinyl)oxy)silane (14.8 g, 66 mmol) reacted with 1-bromobut-2-ene (11.8 g, purity: 80%, 72 mmol) under silver(I) 2,2,2-trifluoroacetate (14.5 g, 66 mmol) and gave (S)-1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)hex-4-en-1-one (6.3 g, E/Z=95:5, 99% ee, yield: 47%) as a colorless liquid.
- 10 ^1H NMR (400 MHz, CDCl_3) δ = 6.66 – 6.56 (m, 1H), 5.48 – 5.20 (m, 2H), 4.67 (s, 1H), 4.64 (s, 1H), 2.98 – 2.83 (m, 1H), 2.76 – 2.56 (m, 4H), 2.50 – 2.31 (m, 2H), 2.30 – 2.12 (m, 2H), 1.65 (s, 3H), 1.61 – 1.51 (m, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ = 198.6, 147.6, 144.9, 142.1, 130.0, 125.8, 109.4, 44.8, 38.8, 38.7, 35.6, 27.6, 20.7, 18.0 ppm. GC/MS (EI): m/z (%): 204 (10) [M^+], 189 (23), 175 (41), 135 (100), 107 (75), 91 (95), 79 (80).
- 15 Odor description: fatty, fruity, pineapple, green, galbanum.

Example 28: (R)-1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one

1. A mixture of (4S)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane (100.0 g, 657 mmol) and 10% platinum on carbon (1.9 g) in ethyl acetate (60 mL) and hexane (30 mL) was stirred for 1 h under hydrogen atmosphere. MgSO_4 (10 g) was added to the reaction mixture, the mixture was filtered, and the organic phase was concentrated to give (4S)-4-isopropyl-1-methyl-7-oxabicyclo[4.1.0]heptane (96.3 g, yield: 95%) as a colorless liquid, which was used for next step directly.
- 20

- ^1H NMR (400 MHz, CDCl_3 , mixture of cis/trans isomers) δ = 3.03 – 2.90 (m, 1H), 2.12 – 1.75 (m, 2H), 1.74 – 1.31 (m, 4H), 1.28 (s, 3H), 1.15 – 0.89 (m, 2H), 0.89 – 0.74 (m, 6H) ppm. ^{13}C NMR (101 MHz, CDCl_3 , mixture of cis/trans isomers) δ = 61.2, 59.8, 58.0, 57.8, 39.4, 35.2, 32.4, 31.8, 31.1, 29.4, 29.3, 28.0, 25.0, 24.6, 23.2, 22.6, 19.8, 19.8, 19.5 ppm. GC/MS (EI): m/z (%): 154 (2) [M^+], 139 (38), 125 (23), 111 (100), 69 (71), 55 (67).
- 25

2. According to the procedure of example 24 (step 1), (4S)-4-isopropyl-1-methyl-7-oxabicyclo[4.1.0]heptane (100.0 g, 648 mmol) reacted with sodium periodate (166.4 g, 778 mmol) to get (S)-3-isopropyl-6-oxoheptanal (87.6 g, yield: 79%) as a colorless liquid.
- 30

¹H NMR (400 MHz, CDCl₃) δ = 9.74 (t, J = 2.1 Hz, 1H), 2.46 – 2.33 (m, 3H), 2.25 – 2.16 (m, 1H), 2.10 (s, 3H), 1.92 – 1.78 (m, 1H), 1.75 – 1.55 (m, 2H), 1.53 – 1.36 (m, 1H), 0.85 (d, J = 6.8 Hz, 3H), 0.82 (d, J = 6.8 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 208.5, 202.8, 45.4, 41.6, 37.7, 30.1, 29.9, 25.5, 19.7, 18.3 ppm. GC/MS (EI): m/z (%): 170 (2) [M^+], 152 (2), 137 (3), 126 (26), 109 (53), 83 (36), 71 (70), 58 (100).

3. According to the procedure of example 24 (step 2), (S)-3-isopropyl-6-oxoheptanal (88.3 g, 519 mmol) treated with sodium hydroxide solution (310 g, 10% in water) to give (R)-1-(4-isopropylcyclopent-1-en-1-yl)ethan-1-one (34.5 g, yield: 44%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ = 6.70 – 6.60 (m, 1H), 2.71 – 2.53 (m, 2H), 2.26 (s, 3H), 2.25 – 2.12 (m, 2H), 2.08 – 1.96 (m, 1H), 1.60 – 1.46 (m, 1H), 0.87 (d, J = 6.7 Hz, 3H), 0.86 (d, J = 6.6 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 196.9, 145.6, 144.0, 45.5, 38.2, 34.7, 33.3, 26.3, 20.8, 20.8 ppm. GC/MS (EI): m/z (%): 152 (5) [M^+], 137 (36), 123 (3), 109 (100), 81 (24), 67 (37).

Odor description: green, metallic, aromatic, minty, carvone

4. According to the procedure of example 24 (step 3), (R)-1-(4-isopropylcyclopent-1-en-1-yl)ethan-1-one (34.4 g, 226 mmol) reacted with trimethylsilyl triflate (60.3 g, 271 mmol) under triethylamine (32.0 g, 316 mmol) to give (R)-((1-(4-isopropylcyclopent-1-en-1-yl)vinyl)oxy)trimethylsilane (49.0 g, yield: 97%) as a yellow liquid, which was used for next step directly.

¹H NMR (400 MHz, CDCl₃) δ = 5.92 – 5.86 (m, 1H), 4.28 (s, 1H), 4.26 (s, 1H), 2.57 – 2.41 (m, 2H), 2.21 – 2.00 (m, 3H), 1.60 – 1.50 (m, 1H), 0.90 (d, J = 6.9 Hz, 3H), 0.89 (d, J = 7.0 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 153.9, 140.7, 128.4, 92.9, 46.4, 37.4, 36.6, 33.6, 21.1, 21.0, 0.2 ppm. GC/MS (EI): m/z (%): 224 (26) [M^+], 209 (70), 181 (34), 154 (22), 91 (23), 75 (100).

5. According to the procedure of example 24 (step 4), (R)-((1-(4-isopropylcyclopent-1-en-1-yl)vinyl)oxy)trimethylsilane (50.6 g, 225 mmol) reacted with and 3-bromoprop-1-ene (35.4 g, 293 mmol) under silver(I) 2,2,2-trifluoroacetate (59.7 g, 27 mmol) to give (R)-1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one (15.1 g, yield: 35%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ = 6.69 – 6.61 (m, 1H), 5.87 – 5.72 (m, 1H), 5.05 – 4.87 (m, 2H), 2.69 (t, J = 7.2 Hz, 2H), 2.66 – 2.51 (m, 2H), 2.37 – 2.27 (m, 2H), 2.26 – 2.11 (m, 2H), 2.08 –

1.90(m, 1H), 1.59 – 1.44(m, 1H), 0.86(d, $J = 6.6$ Hz, 3H), 0.85(d, $J = 6.6$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 198.3, 145.1, 142.8, 137.5, 115.0, 45.4, 38.1, 37.8, 34.9, 33.2, 28.5, 20.8$ ppm. GC/MS (EI): m/z (%): 192 (7) [M^+], 177 (1), 149 (12), 137 (100), 109 (25), 67 (40). $ee = 99\%$. $[\alpha]_D^{25} = +12.4^\circ \cdot \text{mL} / (\text{g} \cdot \text{dm})$ (EtOH)

- 5 Odor description: green, metallic, iron, galbanum, allyl ionone, fruity, ripe pineapple, grapefruit.

Biodegradation: inherently biodegradable

GTH: 0.002 ng

10 Example 29: 1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one

1. A mixture of 1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene (100.0 g, 734 mmol) and 10% platinum on carbon (2.6 g) in ethyl acetate (50 mL) and hexane (50 mL) was stirred for 1 hour at r.t. under hydrogen atmosphere. MgSO_4 (10 g) was added to the reaction mixture, the mixture was filtered, and the organic phase was concentrated to give 4-isopropyl-1-methylcyclohex-1-ene (86.2 g, yield: 85%) as a colorless liquid, which was used for next step directly.

^1H NMR (400 MHz, CDCl_3) $\delta = 5.43 - 5.31(\text{m}, 1\text{H}), 2.11 - 1.85(\text{m}, 2\text{H}), 1.84 - 1.59(\text{m}, 5\text{H}), 1.56 - 1.32(\text{m}, 2\text{H}), 1.31 - 1.13(\text{m}, 2\text{H}), 0.93 - 0.84(\text{m}, 6\text{H})$ ppm. ^{13}C NMR (101 MHz, CDCl_3) $\delta = 134.1, 121.2, 40.2, 32.4, 31.0, 29.1, 26.6, 23.6, 20.1, 19.8$ ppm. GC/MS (EI): m/z (%): 138 (51) [M^+], 123 (25), 109 (5), 95 (100), 81 (42), 67 (75).

- 20 2. To a solution of 4-isopropyl-1-methylcyclohex-1-ene (81.7 g, 591 mmol) in DCM (500 mL) at 5°C was added portion-wise 3-chlorobenzoperoxoic acid (129.6 g, 85wt%, 638 mmol) in 30 min. After addition, the reaction mixture was allowed to stir at r.t. overnight. PE(500mL) was added to the reaction mixture, the mixture was filtered, the organic phase was washed with Na_2SO_3 solution (200mL *3), the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (heptane: MTBE=94:6) to get 4-isopropyl-1-methyl-7-oxabicyclo[4.1.0]heptane (64.1 g, yield: 70%) as a colorless oil.

^1H NMR (400 MHz, CDCl_3 , mixture of cis/trans isomers) $\delta = 3.04 - 2.91(\text{m}, 1\text{H}), 2.13 - 1.76(\text{m}, 2\text{H}), 1.74 - 1.32(\text{m}, 4\text{H}), 1.29(\text{s}, 3\text{H}), 1.16 - 0.90(\text{m}, 2\text{H}), 0.90 - 0.75(\text{m}, 6\text{H})$ ppm. ^{13}C NMR (101 MHz, CDCl_3 , mixture of cis/trans isomers) $\delta = 61.2, 59.8, 58.0, 57.8, 39.4, 35.2, 32.4, 31.8, 31.1, 29.4, 29.3, 28.0, 25.0, 24.6, 23.2, 22.6, 19.8, 19.8, 19.5$ ppm. GC/MS (EI): m/z (%): 154 (1) [M^+], 139 (34), 125 (21), 111 (100), 69 (81), 55 (76).

3. According to the procedure of example 24 (step 1), 4-isopropyl-1-methyl-7-oxabicyclo[4.1.0]heptane (63.1 g, 408mmol) treated with sodium periodate (104.9 g, 190 mmol) and gave 3-isopropyl-6-oxoheptanal (59.4 g, yield: 85%) as a colorless liquid.
- ¹H NMR (400 MHz, CDCl₃) δ = 9.73 (t, J = 2.1Hz, 1H), 2.46 – 2.33 (m, 3H), 2.25 – 2.14 (m, 1H), 2.09 (s, 3H), 1.91 – 1.78 (m, 1H), 1.75 – 1.55 (m, 2H), 1.52 – 1.37 (m, 1H), 0.84 (d, J = 6.8 Hz, 3H), 0.81 (d, J = 6.8Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 208.5, 202.9, 45.5, 41.6, 37.8, 30.2, 30.0, 25.5, 19.7, 18.3 ppm. GC/MS (EI): m/z (%): 170 (1) [M^+], 152 (1), 126 (30), 109 (56), 71 (66), 58 (100).
- 10 4. According to the procedure of example 24 (step 2), 3-isopropyl-6-oxoheptanal (58.2 g, 342 mmol) treated with sodium hydroxide solution (205.0 g, 10% in water, 512.5 mmol) and gave 1-(4-isopropylcyclopent-1-en-1-yl)ethan-1-one (21.4 g, yield: 41%) as a colorless liquid.
- ¹H NMR (400 MHz, CDCl₃) δ = 6.71 – 6.62 (m, 1H), 2.71 – 2.55 (m, 2H), 2.29 (s, 3H), 2.26 – 2.12 (m, 2H), 2.09 – 1.97 (m, 1H), 1.60 – 1.47 (m, 1H), 0.89 (d, J = 6.6Hz, 3H), 0.88 (d, J = 6.6 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 197.1, 145.7, 144.1, 45.7, 38.3, 34.9, 33.4, 26.5, 21.0, 20.9 ppm. GC/MS (EI): m/z (%): 152 (5) [M^+], 137 (36), 109 (100), 67 (41).
5. According to the procedure of example 24 (step 3), 1-(4-isopropylcyclopent-1-en-1-yl)ethan-1-one (21.3 g, 140 mmol) reacted with trimethylsilyl triflate (37.4 g, 168 mmol) under triethylamine (19.9 g, 196.2 mmol) and gave ((1-(4-isopropylcyclopent-1-en-1-yl)vinyl)oxy)trimethylsilane (31.1 g, yield: 99 %) as a yellow liquid.
- 20 ¹H NMR (400 MHz, CDCl₃) δ = 5.92 – 5.86(m, 1H), 4.28(s, 1H), 4.26(s, 1H), 2.57 – 2.41(m, 2H), 2.21 – 2.00(m, 3H), 1.60 – 1.50 (m, 1H), 0.90(d, J = 6.9 Hz, 3H), 0.89(d, J = 7.0 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 153.9, 140.7, 128.4, 92.9, 46.4, 37.4, 36.6, 33.6, 21.1, 21.0, 0.2 ppm. GC/MS (EI): m/z (%): 224 (37) [M^+], 209 (91), 181 (41), 154 (24), 91 (22), 75 (100).
- 25 6. According to the procedure of example 24 (step 4), ((1-(4-isopropylcyclopent-1-en-1-yl)vinyl)oxy)trimethylsilane (31.0 g, 138 mmol) reacted with 3-bromoprop-1-ene (20.1 g, 166 mmol) under silver(I) 2,2,2-trifluoroacetate (33.6 g, 152 mmol) and gave 1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one (14.1 g, yield: 53%) as a colorless liquid.
- 30 ¹H NMR (400 MHz, CDCl₃) δ = 6.68 – 6.60(m, 1H), 5.86 – 5.71(m, 1H), 5.04 – 4.86(m, 2H), 2.68(t, J = 7.2Hz, 2H), 2.65 – 2.51 (m, 2H), 2.37 – 2.26 (m, 2H), 2.25 – 2.10 (m, 2H), 2.07 – 1.89(m, 1H), 1.58 – 1.43(m, 1H), 0.85(d, J = 6.6Hz, 3H), 0.84(d, J = 6.6Hz, 3H) ppm. ¹³C NMR

(101 MHz, CDCl₃) δ = 198.3, 145.1, 142.8, 137.5, 115.0, 45.4, 38.2, 37.8, 34.9, 33.3, 28.5, 20.8 ppm. GC/MS (EI): m/z (%): 192 (6) [M⁺], 177 (1), 149 (9), 137 (100), 109 (20), 67 (32).

Odor description: fatty green, galbanum, allyl ionone, fruity, ripe pineapple.

Biodegradation: inherently biodegradable

5 GTH: 0.0044 ng

Example 30: (S)-1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one

1. According to the procedure of example 28 (step 1), (4R)-1-methyl-4-(prop-1-en-2-yl)-7-oxabicyclo[4.1.0]heptane (150.0 g, 985 mmol) hydrogenated under 10% platinum on carbon
10 (2.9 g) and gave (4R)-4-isopropyl-1-methyl-7-oxabicyclo[4.1.0]heptane (140.9 g, yield: 93%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ = 2.94(d, *J* = 5.4Hz, 1H), 2.04 – 1.85 (m, 2H), 1.67 – 1.45 (m, 2H), 1.42 – 1.20 (m, 5H), 1.16 – 0.92 (m, 2H), 0.80 (d, *J* = 6.8 Hz, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 59.7, 57.9, 39.4, 32.4, 31.0, 28.0, 23.2, 22.6, 19.8, 19.4 ppm. GC/MS (EI):
15 m/z (%): 154 (2) [M⁺], 139 (41), 125 (25), 111 (100), 69 (63), 55 (55).

2. According to the procedure of example 24 (step 1), (4R)-4-isopropyl-1-methyl-7-oxabicyclo[4.1.0]heptane (140.0 g, 908mmol) oxidized by sodium periodate (233.0 g, 1.09 mol) and gave (R)-3-isopropyl-6-oxoheptanal (134.4 g, yield: 87%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ = 9.74 (t, *J* = 2.1Hz, 1H), 2.45 – 2.33 (m, 3H), 2.25 – 2.16 (m, 1H), 2.11 (s, 3H), 1.92 – 1.78 (m, 1H), 1.75 – 1.55 (m, 2H), 1.53 – 1.38 (m, 1H), 0.85 (d, *J* = 6.8Hz, 3H), 0.82 (d, *J* = 6.8Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 208.6, 202.9, 45.5, 41.6, 37.8, 30.2, 30.0, 25.6, 19.8, 18.4 ppm. GC/MS (EI): m/z (%): 170 (2) [M⁺], 152 (1), 126 (33), 109 (51), 71 (70), 58 (100).

3. According to the procedure of example 24 (step 2), (R)-3-isopropyl-6-oxoheptanal (131.1 g, 770 mmol) treated with sodium hydroxide solution (462 g, 10% in water) and gave (S)-1-(4-isopropylcyclopent-1-en-1-yl)ethan-1-one (57.7 g, yield: 49%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃) δ = 6.71 – 6.60 (m, 1H), 2.71 – 2.56 (m, 2H), 2.27 (s, 3H), 2.26 – 2.13 (m, 2H), 2.10 – 1.96 (m, 1H), 1.60 – 1.47 (m, 1H), 0.90 – 0.85 (m, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 197.0, 145.7, 144.0, 45.6, 38.3, 34.9, 33.4, 26.5, 20.9, 20.9 ppm. GC/MS (EI):
30 m/z (%): 152 (9) [M⁺], 137 (46), 109 (100), 81 (25), 67 (27).

4. According to the procedure of example 24 (step 3), (S)-1-(4-isopropylcyclopent-1-en-1-yl)ethan-1-one (44.0 g, 289 mmol) reacted with trimethylsilyl triflate (77.1 g, 347 mmol) dropwise under triethylamine (40.9 g, 404mmol) and gave (S)-((1-(4-isopropylcyclopent-1-en-1-yl)vinyl)oxy)trimethylsilane (57.1 g, yield: 88%) as a yellow liquid.

5 ¹H NMR (400 MHz, CDCl₃) δ = 5.92 – 5.86 (m, 1H), 4.28 (s, 1H), 4.26 (s, 1H), 2.57 – 2.41 (m, 2H), 2.21 – 2.00 (m, 3H), 1.60 – 1.50 (m, 1H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 153.7, 140.7, 128.3, 92.9, 46.4, 37.3, 36.6, 33.6, 21.1, 21.0, 0.2 ppm. GC/MS (EI): *m/z* (%): 224 (42) [*M*⁺], 209 (97), 181 (44), 154 (27), 91 (25), 75 (100).

10

5. According to the procedure of example 24 (step 4), (S)-((1-(4-isopropylcyclopent-1-en-1-yl)vinyl)oxy)trimethylsilane (57.0 g, 25mmol) reacted with 3-bromoprop-1-ene (40.0 g, 330 mmol) under silver(I) 2,2,2-trifluoroacetate (67.3 g, 304mmol) and gave (S)-1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one (23.6 g, yield: 48%) as a colorless liquid.

15

¹H NMR (400 MHz, CDCl₃) δ = 6.70 – 6.64 (m, 1H), 5.88 – 5.74 (m, 1H), 5.04 – 4.90 (m, 2H), 2.72 (t, *J* = 7.2Hz, 2H), 2.68 – 2.52 (m, 2H), 2.39 – 2.29 (m, 2H), 2.29 – 2.12 (m, 2H), 2.09 – 1.93 (m, 1H), 1.61 – 1.45 (m, 1H), 0.89 (d, *J* = 6.6Hz, 3H), 0.88 (d, *J* = 6.6Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 198.5, 145.2, 143.0, 137.6, 115.1, 45.5, 38.3, 38.0, 35.0, 33.4, 20.9 ppm. GC/MS (EI): *m/z* (%): 192 (5) [*M*⁺], 177 (1), 149 (6), 137 (100), 67 (22). ee = 99%. [α]_D²⁵ = –11.5° · mL / (g · dm) (EtOH).

20

Odor description: green, sharp, metallic, iron, galbanum, jasmine, fruit, pineapple, citrus peel, grapefruit

Biodegradation: inherently biodegradable

25

GTH: 0.044 ng

Example 31: (R)-1-(4-isopropylcyclopent-1-en-1-yl)hex-4-en-1-one

According the procedure of example 24, step 4, (R)-((1-(4-isopropylcyclopent-1-en-1-yl)vinyl)oxy)trimethylsilane (7.4 g, 33 mmol) reacted with 1-bromobut-2-ene (6.1 g, purity: 80%, 36 mmol) under silver(I) 2,2,2-trifluoroacetate (7.2 g, 33 mmol) to give (R)-1-(4-isopropylcyclopent-1-en-1-yl)hex-4-en-1-one (2.8 g, E/Z=95:5, 99%ee, yield: 42%) as a colorless liquid.

30

¹H NMR (400 MHz, CDCl₃) δ = 6.65 – 6.55 (m, 1H), 5.45 – 5.27 (m, 2H), 2.68 – 2.43 (m, 4H), 2.30 – 2.07 (m, 4H), 2.05 – 1.87 (m, 1H), 1.66 – 1.37 (m, 4H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃, E isomer) δ = 198.9, 145.3, 142.8, 130.1, 125.8, 45.5, 38.8, 38.3, 35.0, 33.4, 27.6, 21.0, 18.0 ppm. GC/MS (EI): *m/z* (%): 206 (6) [*M*⁺], 191 (5), 177 (5), 137 (100), 109 (24), 67 (28).

5 Odor description: green galbanum, sharp, fruity, pineapple.

Example 32: Fragrance accord 1

Ingredient	Parts by weight
Aldehyde C 12 MNA pure (2-methylundecanal)	25
Ambrofix™ (3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan)	5
Benzyl acetone (4-phenyl-2-butanone)	15
Coumarin pure crystals (2H-1-benzopyran-2-one)	5
Damascone delta (1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-2-buten-1-one)	3
Dihydro myrcenol (2,6-dimethyl-7-octen-2-ol)	150
Dipropylene glycol (Bis (1-hydroxyprop-2-yl) ether)	48
Galbanone 10™ (1-(5,5-dimethylcyclohex-1-en-1-yl)pent-4-en-1-one)	15
Geraniol (3,7-dimethyl-2,6-octadien-1-ol)	60
Hedione™ (Methyl 3-oxo-2-pentylcyclopentaneacetate)	85
Hexyl salicylate	200
Iso E super™ (2-acetyl-1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetra-methylnaphtalene)	86
Isoeugenol (2-methoxy-4-propenylphenol)	5
Javanol ((1-methyl-2-(1,2,2-trimethylbicyclo(3.1.0)-hex-3-ylmethyl)cyclopropyl)methanol)	0.5
Lavandin grosso oil france orpur	20
Lilial (2-methyl-3-(4-(1,1-dimethylethyl)phenyl)propanal)	125
Methyl salicylate	1.5
Peonile (2-cyclohexylidene-2-phenylacetonitrile)	60
Phenyl ethyl acetate	60
Rose oxide (4-methyl-2-(2-methyl-1-propenyl)tetrahydro-2H-pyran)	3
Tricyclal (2,4-dimethyl-3-cyclohexene-1-carbaldehyde)	8
Undecavertol (4-methyl-3-decen-5-ol)	20
total	1000

This fragrance accord is a classic fresh and clean accord, suitable for example for a fabric heavy duty liquid detergent (HDLD), and can be admixed in about 0.6% - 0.8% by weight to the HDLD base.

10

When 15 parts of DPG are replaced by the compound of example 1, the performance of the accord is clearly increased in use, in the wet phase assessment, and on dry fabric after 24 h as well. The compound of example 1 delivers a classical fresh and clean green, galbanum pineapple character that combines very well with the accord, and it is fitting very well to the fresh and clean expectation of the consumer.

Example 33: Fragrance accord 2

Ingredient	Parts by weight
2-methylundecanal	25
3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan	5
4-phenyl-2-butanone	15
2H-1-benzopyran-2-one	5
1-(2,6,6-trimethyl-3-cyclohexen-1-yl)-2-buten-1-one	3
2,6-dimethyl-7-octen-2-ol	150
3,7-dimethyl-2,6-octadien-1-ol(cis & trans)	60
Methyl 3-oxo-2-pentylcyclopentaneacetate	90
Hexyl 2-hydroxybenzoate	230
2-acetyl-1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetra-methylnaphtalene (	90
2-methoxy-4-propenylphenol	5
(1-methyl-2-(1,2,2-trimethylbicyclo(3.1.0)-hex-3-ylmethyl)cyclopropyl)methanol	5
Lavandin oils	20
Methyl 2-hydroxybenzoate	16
3-(4-isobutyl-2-methylphenyl)propanal	30
2-cyclohexylidene-2-phenylacetonitrile	60
2-phenylethyl acetate	60
4-methyl-2-(2-methyl-1-propenyl)tetrahydro-2H-pyran	3
2,4-dimethyl-3-cyclohexene-1-carbaldehyde	8
4-methyl-3-decen-5-ol	20
Dipropylene glycol (Bis (1-hydroxyprop-2-yl) ether)	100
total	1000

This fragrance accord is a fresh floral aldehydic clean accord, suitable for example for a fabric heavy duty liquid detergent (HDLD), and can be admixed in about 0.6% - 0.8% by weight to the HDLD base.

When 15 parts of DPG are replaced by the compound of example 28, the performance of the accord at the wet stage of the fabric is fresher greener than Reference comprising DPG only.

It is comparable with the racemate example 29, clearly stronger than example 30, and compares to Galbanone (1-(5,5-dimethyl-1-cyclohexen-1-yl) pent-4-en-1-one). After 1 day and 3 days of drying, the performance is better than with the racemate or with the other enantiomer. Compound of example 28 can act as a replacer for Galbanone, while the other enantiomer or
5 the racemate cannot.

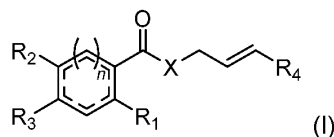
When 15 parts of DPG are replaced by the racemic compound the performance is good on neat and wet, and similar to the preferred isomer, but below said isomer after drying for 1 day and 3 days.

When 15 parts of DPG are replaced by the compound of example 30, the performance on fabric
10 is below the racemic and the preferred stereoisomer at all stages (wet, 1 day, and 3 days dry)

Compound of example 28 can act as a replacer for Galbanone, while the other enantiomer or the racemate cannot.

Claims

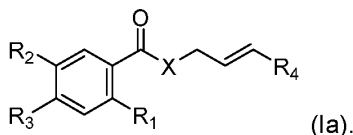
1. A compound of formula (I) in the form of any one of its stereoisomers or mixture thereof



wherein

- 5 R_1 and R_4 are independently selected from H and Me;
 R_2 and R_3 are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and vinyl;
 n is 0 or 1;
X is selected from -O- and -CH₂-; and
the dotted line together with the carbon-carbon bond forms a single bond or a double
10 bond in the ring system; and the ring system has no double bonds, one double bond or
two double bonds, or is an aromatic ring system,
and wherein the compound is not 1-(4-isopropylphenyl)pent-4-en-1-one, 1-(4-(prop-1-
en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one and 1-(4-isopropylcyclopent-1-en-1-yl)pent-
4-en-1-one.

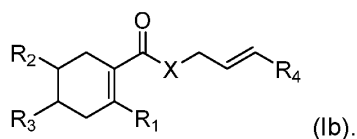
- 15 2. The compound according to claim 1 wherein one of R_2 and R_3 is H, while the other one
is selected from *i*Pr, isopropenyl, cyclopropyl and vinyl.
3. The compound according to claim 1 wherein the compound of formula (I) is a
20 compound of formula (Ia)



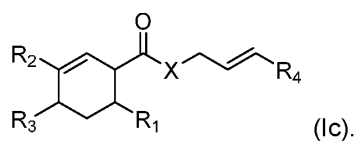
wherein

- R_1 and R_4 are independently selected from H and Me;
 R_2 and R_3 are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and vinyl;
25 X is selected from -O- and -CH₂-.
4. The compound according to claim 1 wherein the compound of formula (I) is a
compound of formula (Ib)

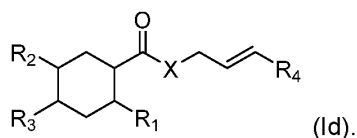
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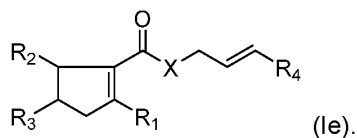
5. The compound according to claim 1 wherein the compound of formula (I) is a compound of formula (lc)



6. The compound according to claim 1 wherein the compound of formula (I) is a compound of formula (ld)



7. The compound according to claim 1 wherein the compound of formula (I) is a compound of formula (le)

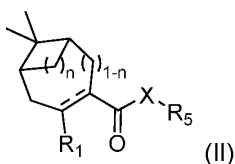


8. The compound according to claim 7, wherein the compound of formula (le) has (*R*)-configuration.
9. The compound according to claim 1 wherein the compound is selected from the group consisting of 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-isopropylcyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-isopropylphenyl)pent-4-en-1-one, 1-(3-isopropylphenyl)pent-4-en-1-one, 1-(3-(prop-1-en-2-yl)phenyl)pent-4-en-1-one, 1-(4-(prop-1-en-2-yl)phenyl)pent-4-en-1-one, 1-(4-isopropylcyclohexyl)pent-4-en-1-one, 1-(4-vinylcyclohex-1-en-1-yl)pent-4-en-1-one, 1-(4-(prop-1-en-2-yl)cyclohex-1-en-1-yl)hex-4-en-1-one, 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)pent-4-en-1-one, allyl 4-(prop-1-en-2-yl)cyclohex-1-ene-1-carboxylate, allyl 4-isopropylbenzoate, but-2-en-1-yl 4-(prop-1-

en-2-yl)cyclohex-1-ene-1-carboxylate, 1-(2-methyl-5-(prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-4-en-1-one, 1-(5-isopropyl-2-methyl-cyclohex-1-en-1-yl)pent-4-en-1-one, 1-(5-isopropyl-2-methylcyclohex-2-en-1-yl)pent-4-en-1-one, and 1-(4-(prop-1-en-2-yl)cyclopent-1-en-1-yl)hex-4-en-1-one.

5

10. A compound of formula (II) in the form of any one of its stereoisomers or mixture thereof



wherein

R_1 is H or Me;

10

R_5 is cyclopent-2-en-1-yl or but-2-en-1-yl;

n is 0 or 1;

X is selected from $-O-$ and $-CH_2-$; and

the dotted line together with the carbon-carbon bond forms a single bond or a double bond.

15

11. The compound according to claim 10 wherein the compound is selected from the group consisting of but-2-en-1-yl 7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylate, cyclopent-2-en-1-yl 7,7-dimethylbicyclo[4.1.0]hept-3-ene-3-carboxylate, 1-(7,7-dimethylbicyclo[4.1.0]hept-3-en-3-yl)hex-4-en-1-one, 1-(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)hex-4-en-1-one.

20

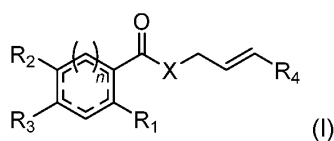
12. A fragrance or flavor composition comprising at least one compound of formula (I) as defined in claim 1 or at least one compound of formula (II) as defined in claim 10.

25

13. A fragranced article or flavoured article comprising
- a) at least one compound of formula (I) as defined in claim 1 or at least one compound of formula (II) as defined in claim 10 as odorant or flavor compound, or a fragrance or flavor composition as defined in claim 12, and
 - a) a consumer product base.

30

14. A fragranced article according to claim 13 wherein the consumer product bases is selected from fine fragrance, household products, laundry products, body care products, cosmetic products and air care products.
- 5 15. Use of a compound of formula (I) in the form of any one of its stereoisomers or mixture thereof



wherein

- R₁ and R₄ are independently selected from H and Me;
- 10 R₂ and R₃ are independently selected from H, *i*Pr, isopropenyl, cyclopropyl and vinyl;
 n is 0 or 1;
 X is selected from -O- and -CH₂-; and
 the dotted line together with the carbon-carbon bond forms a single bond or a double bond in the ring system; and the ring system has no double bonds, one double bond or
 15 two double bonds, or is an aromatic ring system,
 and wherein the compound is not 1-(4-isopropylcyclopent-1-en-1-yl)pent-4-en-1-one, or
 of a compound of formula (II) as defined in claim 10 as odorant or flavor compound.
- 20 16. A method of improving, enhancing or modifying a consumer product base by means of addition thereto of an olfactory or gustatory acceptable amount of a compound of formula (I) as defined in claim 1 or of a compound of formula (II) as defined in claim 10.