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(71) Applicant: FIRMENICH SA [CH/CH]; 1, route des
 Jeunes, P. O. Box 239, CH-121 1 Geneva 8 (CH).

(72) Inventors: INDRADAS, Brenda; Firmenich Incorporated,
 250 Plainsboro Road, Plainsboro, New Jersey 08536 (US).
 VIRTUCIO, Gilbert; Firmenich Incorporated, 250 Plains-
 boro Road, Plainsboro, New Jersey 08536 (US).
 WOMACK, Gary; Firmenich Incorporated, 250 Plains-
 boro Road, Plainsboro, New Jersey 08536 (US).

(74) Agent: CARINA, Riccardo; Firmenich SA, 1, route des
 Jeunes, P. O. Box 239, CH-121 1 Geneva 8 (CH).

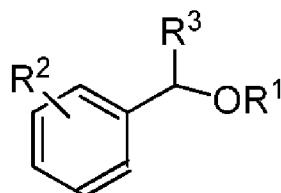
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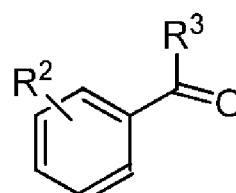
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(54) Title: PRO-FRAGRANCE COMPOUNDS



(I)



(II)

(57) Abstract: A compound of Formula (I) wherein R¹ represents a C₃ to C₂₀ hydrocarbon group derived from a fragrant alcohol of formula R'OH or from a fragrant aryl aldehyde or ketone of Formula (II), wherein: R² is, independently, hydrogen atom, hydroxyl group, acetoxy group, -O(C=O)CH(CH₃), optionally substituted C₁-C₆ alkyl group or C₁-C₆ alkoxy group, wherein any two of R² may form an optionally substituted 5 or 6 membered ring, and R¹ represents a radical derived from a fragrant alcohol of formula R'OH or from a fragrant aryl aldehyde or ketone of formula (II). The compounds are useful for example as a precursor for the prolonged delivery or release of fragrant compounds such as fragrant alcohols or aldehydes.

PRO-FRAGRANCE COMPOUNDS

FIELD

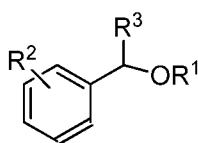
The present invention relates to the field of perfumery. More particularly, it concerns
5 the use of benzyl ether compounds as precursors for the release of fragrant alcohols and aldehydes over a prolonged period.

BACKGROUND

The perfumery industry has a particular interest in compounds which are capable of
10 being released over a prolonged time and that can deliver an odoriferous effect. Various means to control the release of fragrant compounds from pro-fragrances or precursor compounds have been reported. For example compounds have been reported that deliver a fragrance after they are hydrolyzed or exposed to light. In many applications it is desirable to begin and control the release of a fragrance at a time when an article or material containing
15 the precursor is exposed to for example ambient oxygen. Hence, oxidizable pro-fragrances are desirable that can deliver a fragrance over a prolonged period of time after exposure to air.

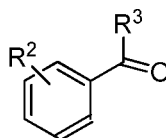
SUMMARY

20 Provided herein is a compound of Formula (I)



(I)

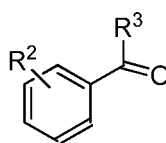
wherein R¹ represents a C₃ to C₂₀ hydrocarbon group derived from a fragrant alcohol of formula R¹OH or from a fragrant aryl aldehyde or ketone of Formula (II)



(II),

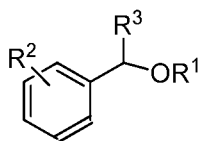
wherein R^2 , is, independently, hydrogen atom, hydroxyl group, acetoxy group, optionally substituted CrC_6 alkyl group, CrC_6 alkoxy group, or $-\text{O}(\text{C}=\text{O})\text{CH}(\text{CH}_3)_2$ wherein any two of R^2 may form an optionally substituted 5 or 6 membered ring; and R^3 is hydrogen atom or methyl group.

- 5 Also provided herein is a method of releasing a fragrant compound from a precursor compound, wherein the fragrant compound is selected from the group consisting of $R^4\text{H}$ and an aryl aldehyde or ketone of Formula (II):



(II),

- 10 by exposing precursor compound of Formula I:



(I)

to an environment wherein the compound is oxidized and wherein:

- R^2 is independently hydrogen atom, hydroxyl group, acetoxy group, $-\text{O}(\text{C}=\text{O})\text{CH}(\text{CH}_3)_2$,
 15 optionally substituted CrC_6 alkyl group, or CrC_6 alkoxy group, wherein any two of R^2 may form an optionally substituted 5 or 6 membered ring; R^1 represents a C_3 to C_{20} hydrocarbon group derived from a fragrant alcohol of formula $R^4\text{H}$ or from a fragrant aryl aldehyde or ketone of formula Formula (II); and wherein R^3 is hydrogen or methyl.

20 BRIEF DESCRIPTION OF THE DRAWINGS

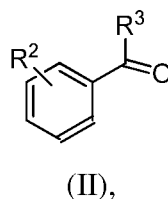
Figure 1 shows the disappearance rate of eight benzyl ethers measured using GC-FID.

DETAILED DESCRIPTION

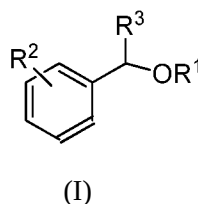
- For the Summary, Description and Claims, the use of "or" means "and/or" unless
 25 stated otherwise. It is to be further understood that where descriptions of various embodiments use the term "comprising," those skilled in the art would understand that in

some specific instances, an embodiment can be alternatively described using language "consisting essentially of" or "consisting of."

Further provided herein is a method wherein the method comprises the release of at least two compounds from the precursor compound, wherein at least one of the compounds is a fragrant compound wherein the two compounds are the same or different and each independently comprises the formula (II):



by exposing a precursor compound of Formula I:



to an environment wherein the compound is oxidized and wherein:

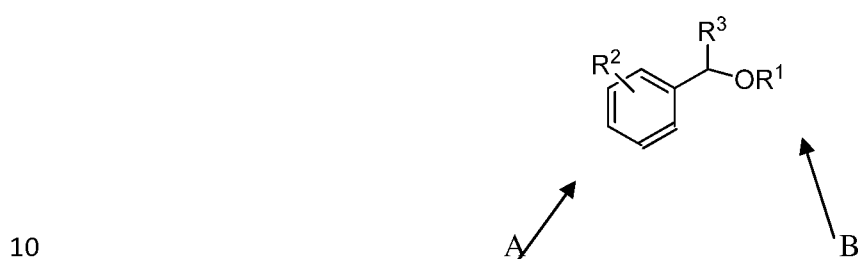
R¹ represents a C₃ to C₂₀ hydrocarbon group derived from a fragrant aryl aldehyde or ketone of Formula (II) wherein R² is, independently, hydrogen atom, hydroxyl group, acetoxy group, optionally substituted CrC₆ alkyl group, CrC₆ alkoxy group, or -O(C=O)CH(CH₃)₂ wherein any two of R² may form an optionally substituted 5 or 6 membered ring; and R³ is hydrogen atom or methyl group.

It is understood that by "... hydrocarbon group ..." it is meant that said group is consisting of hydrogen and carbon atoms and can be in the form of a linear, branched or cyclic, aromatic, alkyl, alkenyl, or alkynyl group, e.g., a linear alkyl group, or can also be in the form of a mixture of said type of groups, e.g. a specific group may comprise a linear alkyl, a branched alkenyl (e.g. having one or more carbon-carbon double bonds), a (poly)cyclic alkyl and an aryl moiety, unless a specific limitation to only one type is mentioned. Similarly, in all the embodiments of the invention, when a group is mentioned as being in the form of more than one type of topology (e.g. linear, cyclic or branched) and/or being saturated or unsaturated (e.g. alkyl, aromatic or alkenyl), it is meant also a group which

may comprise moieties having any one of said topologies or being saturated or unsaturated, as explained above. Similarly, in all the embodiments of the invention, when a group is mentioned as being in the form of one type of saturation or unsaturation, (e.g. alkyl), it is meant that said group can be in any type of topology (e.g. linear, cyclic or branched) or

5 having several moieties with various topologies.

It is understood that by "... alkyl group ..." it is meant that said group is in the form of a linear, branched or cyclic alkyl group.



It is understood that a fragrant compound may originate from either side of a compound of Formula I and that the benzyl moiety (A) or the radical defined by R¹ (B) may generate a fragrant compound and that B may also be a benzyl moiety that is the same or different from A. It is understood that both A and B may both represent a benzyl moiety that will deliver two compounds selected from the group consisting of an aryl aldehyde and an aryl ketones, where the compounds can be the same or different, with at least one of the

15 compounds being a fragrant compound. That is, the benzyl moiety (A) may or may not release a fragrant aryl aldehyde or ketone and the radical defined by R¹ also may represent a

20 benzyl moiety which may or may not deliver a fragrant aryl aldehyde or ketone. When both A and B represent a benzyl moiety, whether the same or different, the distinction between A and B is interchangeable of course as governed by the geometry or configuration of the molecule. It is also understood that when B is not a benzyl moiety, it will be released as a fragrant compound.

25 In a particular embodiment, a C₁-C₆ alkoxy group of a compound provided here is selected from the group consisting of methoxy, ethoxy, propoxy, isopropoxy and butoxy group; more particularly the C₁-C₆ alkoxy group is methoxy group.

In another embodiment, a C₁-C₆ alkyl group of a compound provided is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, cyclopropyl, cyclopentyl and cyclohexyl group.

Optionally substituted means substituents, in relation to the C₁-C₆ alkyl group and 5 or 6 membered ring formed from the C₁-C₆ alkyl group, selected from the group consisting of methyl or dimethyl.

The expression "derived from" is meant to include for example to be chemically derived (e.g., to produce or obtain a compound from another substance by a chemical reaction). It is also meant to include "represented by." It is also meant to include radicals 10 for example that may be deduced or reasoned from the known literature that describes for example known compounds.

In a particular embodiment provided herein a compound is selected from the group consisting of: (((2,6-dimethyloctan-2-yl)oxy)methyl)benzene; (((3,7-dimethyloct-1-en-3-yl)oxy)methyl)benzene; 1-(((3,7-dimethyloct-1,6-dien-3-yl)oxy)methyl)-4-methoxybenzene; 1-(((2,6-dimethyloctan-2-yl)oxy)methyl)-4-methoxybenzene; 1-(((3,7-dimethyloctan-3-yl)oxy)methyl)-4-methoxybenzene; 2-(((4-methoxybenzyl)oxy)methyl)-2,5-dimethyl-2,3-dihydro-1H-indene; 4-(((3,7-dimethyloct-1,6-dien-3-yl)oxy)methyl)-2-methoxyphenol; 4-(((2,6-dimethyloctan-2-yl)oxy)methyl)-2-methoxyphenol; 4-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-2-methoxyphenol; 4-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-2-methoxyphenol; 4-(((3,7-dimethyloctan-3-yl)oxy)methyl)-2-methoxyphenol; 4-(((3,7-dimethyloct-1,6-dien-3-yl)oxy)methyl)-2-ethoxyphenol; 4-(((2,6-dimethyloctan-2-yl)oxy)methyl)-2-ethoxyphenol; 4-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-2-ethoxyphenol; 4-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-2-ethoxyphenol; 4-(((3,7-dimethyloctan-3-yl)oxy)methyl)-2-ethoxyphenol; 5-(((3,7-dimethyloct-1,6-dien-3-yl)oxy)methyl)benzo[d][1,3]dioxole; 5-(((2,6-dimethyloctan-2-yl)oxy)methyl)benzo[d][1,3]dioxole; 5-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)benzo[d][1,3]dioxole; 5-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)benzo[d][1,3]dioxole; 5-(((3,7-dimethyloctan-3-yl)oxy)methyl)benzo[d][1,3]dioxole; 4-(((3,7-dimethyloct-1,6-dien-3-yl)oxy)methyl)-1,2-dimethoxybenzene; 4-(((2,6-dimethyloctan-2-yl)oxy)methyl)-1,2-dimethoxybenzene; 4-

(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-1,2-dimethoxybenzene; 4-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-1,2-dimethoxybenzene; 4-(((3,7-dimethyloctan-3-yl)oxy)methyl)-1,2-dimethoxybenzene; 1-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)-4-methylbenzene; 1-(((2,6-dimethyloctan-2-yl)oxy)methyl)-4-methylbenzene; 1-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-4-methylbenzene; 1-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-4-methylbenzene; 1-(((3,7-dimethyloctan-3-yl)oxy)methyl)-4-methylbenzene; 1-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)-4-ethylbenzene; 1-(((2,6-dimethyloctan-2-yl)oxy)methyl)-4-ethylbenzene; 1-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-4-ethylbenzene; 1-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-4-ethylbenzene; 1-(((3,7-dimethyloctan-3-yl)oxy)methyl)-4-ethylbenzene; 1-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)-4-isopropylbenzene; 1-(((2,6-dimethyloctan-2-yl)oxy)methyl)-4-isopropylbenzene; 1-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-4-isopropylbenzene; 1-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-4-isopropylbenzene; 1-(((3,7-dimethyloctan-3-yl)oxy)methyl)-4-isopropylbenzene; 1-(tert-butyl)-4-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)benzene; 1-(tert-butyl)-4-(((2,6-dimethyloctan-2-yl)oxy)methyl)benzene; 1-(tert-butyl)-4-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)benzene; 1-(tert-butyl)-4-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)benzene; 1-(tert-butyl)-4-(((3,7-dimethyloctan-3-yl)oxy)methyl)benzene; 2-methoxy-4-(((4-methoxybenzyl)oxy)methyl)phenol; 4,4'-(oxybis(methylene))bis(2-methoxyphenol); 2-methoxy-4-((1-(4-methoxyphenyl)ethoxy)methyl)phenol; 4,4'-(oxybis(methylene))bis(2-ethoxyphenol); 2-methoxy-4-(((4-methylbenzyl)oxy)methyl)phenol; 4-(((4-ethylbenzyl)oxy)methyl)-2-methoxyphenol; 4-(((4-isopropylbenzyl)oxy)methyl)-2-methoxyphenol; 4-(((4-(tert-butyl)benzyl)oxy)methyl)-2-methoxyphenol; 1-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-4-methoxybenzene; 1-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-4-methoxybenzene; ((2,6-dimethyloct-7-en-2-yl)oxy)methyl)benzene; 1-(((5-ethylnonan-2-yl)oxy)methyl)-4-methoxybenzene; (E)-1-methoxy-4-(((4-(2,6,6-trimethylcyclohex-2-enyl)but-3-en-2-yl)oxy)methyl)benzene; (2,4-dimethyl-1-(phenethoxymethyl)benzene; ((E)-1-(1-(((3,7-dimethylocta-2,6-dien-1-yl)oxy)ethyl)-4-methoxybenzene); 2-(((4-methoxybenzyloxy)methyl)-2,5-dimethyl-2,3-dihydro-1H-indene; (4-((benzyloxy)methyl)-1,2-dimethoxybenzene); (5-((benzyloxy)methyl)benzo[d][1,3]dioxole; (1-((benzyloxy)methyl)-4-methoxybenzene; (1-

methoxy-4-(1-((4-methoxybenzyl)oxy)ethyl)benzene; (1-((benzyloxy)methyl)-4-(tert-butyl)benzene); 6-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-1,1,2,3,4,4,7-heptamethyl-1,2,3,4-tetrahydronaphthalene; 6-(tert-butoxymethyl)-1,1,2,3,4,4,7-heptamethyl-1,2,3,4-tetrahydronaphthalene; 1,1,2,3,4,4,6-heptamethyl-7-(((2-methyl-1-phenylpropan-2-yl)oxy)methyl)-1,2,3,4-tetrahydronaphthalene; and 6-(((4-methoxybenzyl)oxy)methyl)-1,1,2,3,4,4,7-heptamethyl-1,2,3,4-tetrahydronaphthalene;

More particularly in an embodiment provided herein is a compound selected from the group consisting of : 1-((2,6-dimethyloct-7-en-2-yloxy)methyl)-4-methoxybenzene; (1-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-4-methoxybenzene); ((2,6-dimethyloct-7-en-2-yloxy)methyl)benzene; 1-((5-ethylnonan-2-yloxy)methyl)-4-methoxybenzene; (*E*)-1-methoxy-4-((4-(2,6,6-trimethylcyclohex-2-enyl)but-3-en-2-yloxy)methyl)benzene; (2,4-dimethyl-1-(phenethoxymethyl)benzene); (*E*)-1-(1-((3,7-dimethylocta-2,6-dien-1-yl)oxy)ethyl)-4-methoxybenzene; 2-((4-methoxybenzyloxy)methyl)-2,5-dimethyl-2,3-dihydro-1H-indene; (4-((benzyloxy)methyl)-1,2-dimethoxybenzene); (5-((benzyloxy)methyl)benzo[d][1,3]dioxole; (1-((benzyloxy)methyl)-4-methoxybenzene; (1-methoxy-4-(1-((4-methoxybenzyl)oxy)ethyl)benzene; and (1-((benzyloxy)methyl)-4-(tert-butyl)benzene).

In another embodiment, a compounds provided herein for example according to Formula I is not selected from the group consisting of: ((2,6-dimethyloct-7-en-2-yloxy)methyl)benzene; 1-((benzyloxy)methyl)-4-methoxybenzene; and 1-((benzyloxy)methyl)-4-(tert-butyl)benzene.

The pro-fragrance compounds provided herein are in particular used as a precursor to deliver a fragrant alcohol, a fragrant aryl aldehyde or a fragrant aryl ketone. Fragrant alcohol, fragrant aldehyde or fragrant ketone means an alcohol, aldehyde or ketone which is capable of imparting an odor, in particular one which imparts an odor to a material, more particularly to a fabric or textile. The fragrant alcohols generated from Formula I or which Formula I is derived from are meant to encompass any fragrant alcohol. While not providing an exhaustive list, provided here is a list of alcohols which are capable of imparting pleasant odors, particularly from surfaces, materials or even air. The fragrant alcohols may be selected from the group consisting such as, but not limited to: anisic alcohol, cinnamic alcohol,

fenchylic alcohol, 9-decen-1-ol, phenethylol, citronellol 3-methyl-5-phenyl-1-pentanol (origin: Firmenich SA. Geneva. Switzerland), Mayol® ((4-isopropylcyclohexyl)methanol; origin: Firmenich SA. Geneva. Switzerland), dihydromyrcenol (2,6-dimethyl-7-octen-2-ol), geraniol (3,7-dimethyl-2,6-octadien-1-ol), (Z)-3-hexen-1-ol, 1-hexanol, 2-hexanol, 5-ethyl-2-
 5 nonanol, 2,6-nonadien-1-ol, borneol, 1-octen-3-ol, 4-cyclohexyl-2-methyl-2-butanol (origin: Firmenich SA. Geneva. Switzerland), 2-methyl-4-phenyl-2-butanol, 2-methyl-1-phenyl-2-propanol, cyclomethylcitronellol, decanol, dihydroeugenol, 8-p-menthanol, 3,7-dimethyl-1-octanol, 2,6-dimethyl-2-heptanol, dodecanol, eugenol, Florol® (tetrahydro-2-isobutyl-4-methyl-4(2H)-pyranol; origin: Firmenich SA. Geneva. Switzerland), isoeugenol, linalool,
 10 Tarragol® (2-methoxy-4-propyl-1-cyclohexanol; origin: Firmenich SA. Geneva, Switzerland), α -terpineol, tetrahydromuguol, 3,7-dimethyl-3-octanol, Lylal® (4-(4-hydroxy-4-methylpentyl)-cyclohex-3-ene-1-carbaldehyde: origin International Flavors and Fragrances. USA), Furaneol® (origin: Firmenich SA. Geneva. Switzerland), 5,6-dimethyl-1-methylethenylbicyclo[2.2.1]hept-5-ene-2-methanol (Arbozol), α -terpineol, 2-phenylethanol,
 15 1-phenylpropanol, 2-phenylpropanol, Lilyflore® ((2,5-dimethyl-2,3-dihydro-1H-inden-2-yl)methanol; origin: Firmenich SA. Geneva. Switzerland), 2,2-dimethyl-3-(3-methylphenyl)propan-1-ol (Majantol), 2-pentylcyclopentanol, 7-hydroxy-3,7-dimethyloctanal (hydroxycitronellol), 1,1-dimethyl-2-phenylethanol, 4-cyclohexyl-2-methylbutan-2-ol, menthol, 2,6-dimethylheptan-2-ol, 2-tert-butylcyclohexanol, 4-tert-butylcyclohexanol, 2,6-
 20 dimethyl-3,5-octadien-2-ol (muguol), 2-methyl-6-methylene-7-octen-2-ol (myrcenol), 3,7,9-trimethyl-1,6-decadien-3-ol (isobutyl linalool), methyl salicylate, cis-3-hexenyl salicylate, 3,6-dimethyloctan-3-ol, 1,2-dimethyl-3-prop-1-en-2-ylcyclopentan-1-ol (plinol), 2-methyl-4-phenylpentanol (Pamplefleur), 3-methyl-5-phenylpentanol, 3-methyl-5-(2,2,3-trimethyl-1-cyclopent-3-enyl)pentan-2-ol (Sandalore®), (E)-3,3-dimethyl-5-(2,2,3-trimethyl-3-
 25 cyclopenten-1-yl)-4-penten-2-ol (Polysantol®), 1-(2,2,6-trimethylcyclohexyl)hexan-3-ol (Norlimbanol™), (E)-4-methyldec-3-en-5-ol, and 4-(4-hydroxyphenyl)butan-2-one.

In another embodiment a non-limiting example of a fragrant aryl aldehyde or ketone released from a compound of Formula I is selected from the group consisting of: benzaldehyde, anisaldehyde, 4-methylbenzaldehyde, 4-ethylbenzaldehyde, 4-
 30 isopropylbenzaldehyde, 4-(tert-butyl) benzaldehyde, 2-methoxybenzaldehyde, 3,4-

dimethoxybenzaldehyde, heliotropin, 4-hydroxybenzaldehyde, vanillin, 3-ethoxy-4-hydroxybenzaldehyde, 4-formyl-2-methylphenyl acetate, 4-formyl-2-methoxyphenyl isobutyrate, 3,5,5,6,7,8,8-heptanmethyl-5-6-7-8-tetrahydronaphthalene-2-carbaldehyde.

Many of these ingredients are in any case listed in reference texts such as the book by
5 S. Arctander, Perfume and Flavor Chemicals, 1969, Montclair, N.J., USA, or its more recent versions, or in other works of a similar nature.

In another embodiment provided herein is a method to improve, enhance or modify odoriferous properties of a perfuming composition or a perfumed article, which method comprises adding to said composition or article an effective amount of a compound of
10 Formula I.

In another embodiment, provided herein is a perfumed article comprising a compound provided herein wherein the perfumed article is provided in a perfumed product selected from the group consisting of perfume, cologne, bath gel, shower gel, hair-care product, cosmetic preparation, body deodorant, solid or liquid air-freshener, detergent, fabric softener,
15 and all purpose cleaner.

In another embodiment provided herein is a method as described wherein a compound provided herein is exposed to the environment through a perfumed article comprising the compound wherein the perfumed article is provided in a perfumed product selected from the group consisting of perfume, cologne, bath gel, shower gel, hair-care product, cosmetic
20 preparation, body deodorant, solid or liquid air-freshener, detergent, fabric softener, and all purpose cleaner.

In a particular embodiment the all purpose cleaner is an all purpose household cleaner, a window cleaner, a furniture polish, a fabric conditioner, softener or wash in form of a powder, a liquid or a tablet, a shampoo, a hair conditioner, a leave-in hair conditioner, or
25 a hairspray.

A precursor compound of Formula I provided herein may be used for the controlled release of perfuming ingredients. This use, for example concerns a method to confer, enhance, improve or modify the odor properties of a perfuming composition, of an article or of a surface. In a particular embodiment, the pro-fragrance is applied to a material such as a
30 fabric or textile upon the process of washing material or treating it with a fabric softener. In

one aspect, the perfuming effect of such compounds can be to prolong and intensify a perfuming effect upon the exposure of the material to ambient air.

In another aspect, the controlled release of a perfuming alcohol or aldehyde provided herein comprises adding to a composition or an article an effective amount of a compound (I) which is capable of imparting an odor to fabrics or textiles when oxidized after the process of washing with a detergent or with the treatment of a fabric softener. The release of the fragrance provided herein is sustained particularly for a period of greater than 1 day, most particularly greater than 1 week, and even more particularly greater than 2 weeks. In many applications it is desirable to begin and control the release of a fragrance at a time when an article or material, containing the precursor or which the precursor has been deposited on, is exposed to for example ambient oxygen.

In another embodiment, provided herein is a fragrance delivery system comprising a compound of Formula I which provides a long-lasting odor of volatile fragrance from a product or from a product deposited on a material. The release of the above-mentioned fragrant compounds from the compounds and delivery system described herein occurs upon the exposure for example of a precursor compound according to Formula I to oxygen or other oxidizing agents.

In another embodiment, a compound or method provided herein can be used in functional perfumery. Particularly, the precursor compounds and methods provided herein can be used in applications such as liquid or solid detergents for the treatment of textiles and fabric softeners, in which the fragrance of the ingredients must be effectively imparted to the textile during washing.

In one aspect, a precursor compound of Formula I provided, by release of the fragrant alcohol or aldehyde, a noticeable fragrance to the laundry, produced by an odoriferous alcohol or aldehyde, which would not be detected on the laundry over a sufficiently long period if the alcohol or aldehyde had been used as it is, i.e. without a precursor.

The invention will now be described in further detail by way of the following examples. These examples are not intended to be limiting and are for illustrative purposes only.

EXAMPLES

Example 1

Benzyl Ethers

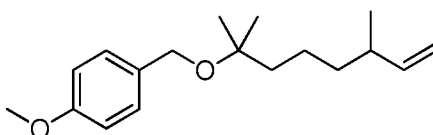
5 In a typical experiment, the required alcohol (50 mmol) was added dropwise to a mixture of 50-75 mmol of NaH (60% in mineral oil) in THF (25 ml) or DMF (25 ml) under a N₂ atmosphere. Either 1-(chloromethyl)-4-methoxybenzene or benzyl bromide (45 mmol) was added and the reaction mixture was stirred for 1-5 days at room temperature. When THF was the solvent, 45 mmol of NaI was added. Water was added carefully (under N₂) to consume
10 unreacted NaH and the mixture was transferred to a separatory funnel. It was diluted with diethyl ether and washed with water. The organic phase was dried (MgSO₄) and concentrated, and the crude product was subjected to silica gel flash chromatography. The collected product was then subjected to a final bulb-to-bulb distillation or placed under vacuum (40°C/30 mTor) to remove residual solvent.

15

Example 1.1

1-((2,6-dimethyloct-7-en-2-yloxy)methyl)-4-methoxybenzene

Using 2,6-dimethyloct-7-en-2-ol (dihydromyrcenol) and 1-(chloromethyl)-4-methoxybenzene, the product was obtained in 45% yield as a colorless oil.



20

¹H NMR (CDCl₃, 400 MHz): δ 0.97 (d, J=6.8 Hz, 3H), 1.22 (s, 6H), 1.25-1.60 (m, 6H), 2.13 (m, 1H), 3.77 (s, 3H), 4.32 (s, 2H), 4.90 (d, J=10.3 Hz, 1H), 4.96 (d, J=17.2, 1H), 5.69 (ddd, J=7.6, 10.3, 17.2 Hz, 1H), 6.85 (d, J=8.7 Hz, 2H), 7.25 (d, J=8.7 Hz, 2H).

MS (EI): 276 (M⁺, <1), 137 (17), 121 (100), 109 (5), 78 (5), 77 (5), 55 (7), 41 (6).

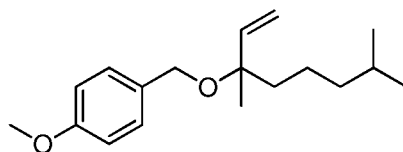
25

Example 1.2

1-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-4-methoxybenzene

Using 3,7-dimethyloct-1-en-3-ol (dihydrolinalol) and para-methoxybenzyl chloride, the product was obtained in 40% yield as a colorless oil.

12



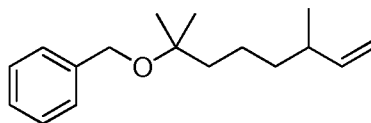
¹H NMR (CDCl₃, 400 MHz): δ 0.87 ppm (d, 6.4 Hz, 6H), 1.11-1.21 (m, 2H), 1.30 (s, 3H), 1.30-1.38 (m, 2H), 1.48-1.66 (m, 3H), 3.77 (s, 3H), 4.28 (s, 2H), 5.17 (dd, J=11.2, 1.3 Hz, 1H), 5.19 (dd, J=17.7, 1.3 Hz, 1H), 5.85 (dd, J=17.7, 11.2 Hz, 1H), 6.83-6.89 (m, 2H), 7.22-7.30 (m, 2H).

MS (EI): 276 (M⁺, <1), 137 (10), 122 (9), 121 (100), 77 (4), 55 (3).

Example 1.3

1-((2,6-dimethyloct-7-en-2-yloxy)methyl)benzene

Using 2,6-dimethyloct-7-en-2-ol (dihydromyrcenol) and benzyl bromide, the product was obtained in 39% yield as a colorless oil.



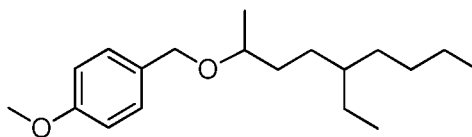
¹H NMR (CDCl₃, 400 MHz): δ 0.98 (d, 6.7 Hz, 3H), 1.2 (s, 6H), 1.27-1.45 (m, 4H), 1.46-1.60 (m, 2H), 2.13 (m, 1H), 4.40 (s, 2H), 4.90 (ddd, J=0.9, 2.0, 10.2 Hz, 1H), 4.95 (ddd, J=1.0, 2.0, 17.3 Hz, 1H), 5.69 (ddd, J=7.2, 10.2, 17.3 Hz, 1H), 7.2 (m, 1H), 7.3 (m, 4H).

MS (EI): 246 (M⁺, 0), 149 (14), 140 (3), 92 (9), 91 (100), 77 (3), 65 (5), 55 (8), 41 (6).

Example 1.4

1-((5-ethylnonan-2-yloxy)methyl)-4-methoxybenzene

Using 5-ethylnonan-2-ol and 1-(chloromethyl)-4-methoxybenzene, the product was obtained in 76% yield as a colorless oil (dr=1:1).



¹H NMR (CDCl₃, 400 MHz): δ 0.81 (t, J=7.2 Hz, 3H), 0.83 (t, J=6.8 Hz, 3H), 1.1 (d, J=6.0 Hz, 3H), 1.18-1.62 (m, 13H), 3.45 (sextet, J=6.0 Hz, 1H), 3.7 (s, 3H), 4.39 (d,

J=11.3 Hz, 1H), 4.49 (d, J=11.3 Hz, 1H), 6.86 (d, J=8.7 Hz, 2H), 7.26 (d, J=8.7 Hz, 2H).

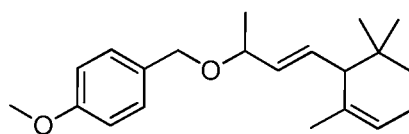
MS (EI): 292 (M^+ , 1), 171 (1), 153 (1), 137 (2), 122 (22), 121 (100), 109 (3), 97 (3), 78 (4), 77 (5), 57 (5), 55 (4), 43 (6), 41 (6).

5

Example 1.5

(E)-1-methoxy-4-((4-(2,6,6-trimethylcyclohex-2-enyl)but-3-en-2-yloxy)methyl)benzene

Using (E)-4-(2,6,6-trimethylcyclohex-2-enyl)but-3-en-2-ol (a-ionol) and 1-(chloromethyl)-4-methoxybenzene, the product was obtained in 69% yield as a colorless oil (dr=1:1).



10

^1H NMR (CDCl_3 , 400 MHz): δ 0.81, 0.88, 0.89, 0.91 (all s, 6H), 1.11-1.22 (m, 1H), 1.26 and 1.36 (both d, $1=6.19$ Hz, 6.37 Hz, 3H), 1.36-1.50 (m, 1H), 1.58 and 1.65 (both s, 3H), 1.91-2.05 (m, 2H), 2.10-2.18 (m, 1H), 3.78 (s, 3H), 3.84-3.93 (m, 1H), 4.27, 4.28, 4.50, 4.51 (all d, $1=11.7$ Hz, $-\text{CH}_2\text{O}-$, 2H), 5.39 (m, 3H), 6.85 and 6.86 (both d, $1=8.7$ Hz, 2H), 7.23 and 7.24 (both d, $1=8.7$ Hz, 2H).

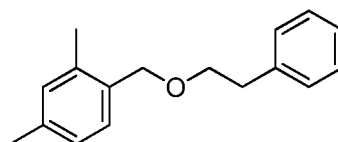
15

MS (EI): 314 (M^+ , <1), 191 (2), 190 (18), 178 (1), 137 (4), 123 (6), 122 (16), 121 (100), 93 (9), 91 (6), 77 (6), 43 (3).

20 Example 1.6

(2,4-dimethyl-1-(phenethoxymethyl)benzene)

Using 2-phenylethanol (phenylethanol) and 2,4-dimethylbenzyl bromide, the product was obtained in 53% yield as a colorless oil.



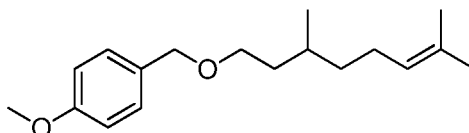
25

^1H NMR (CDCl_3 , 400 MHz): δ 2.23 (s, 3H), 2.29 (2s, 3H), 2.91 (t, J=7.2 Hz, 2H), 3.67 (t, J=7.2 Hz, 2H), 4.46 (s, 2H), 6.92-7.30 (m, 8H).

MS (EI): 240 (M^+ , 10), 210 (5), 119 (100), 118 (13), 105 (6), 91 (12), 77 (5).

Example 1.7((E)-1-(1-((3,7-dimethylocta-2,6-dien-1-yl)oxy)ethyl)-4-methoxybenzene)

Using 3,7-dimethylocta-6-en-1-ol (citronellol) and para-methoxybenzyl chloride, the product
 5 was obtained in 79% yield as a colorless oil.

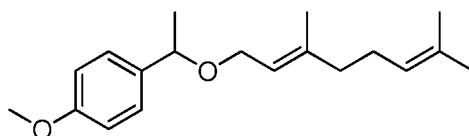


¹H NMR (CDCl₃, 400 MHz): δ 0.88 (d, J=6.7 Hz, 3H), 1.09-1.20 (m, 1H), 1.28-1.47 (m,
 2H), 1.59 (s, 3H), 1.68 (s, 3H), 1.51-1.70 (m, 2H), 1.87-2.06 (m, 2H), 3.40-3.52 (m,
 2H), 3.78 (s, 3H), 4.42 (s, 2H), 5.09 (t, J=7.1 Hz, 1H), 6.84-6.89 (m, 2H), 7.22-7.28
 10 (m, 2H).

MS (EI): 276 (M⁺, <1), 137 (4), 122 (23), 121 (100), 95 (5), 81 (12), 69 (16), 55 (6), 41 (14).

Example 1.8((E)-1-(1-((3,7-dimethylocta-2,6-dien-1-yl)oxy)ethyl)-4-methoxybenzene)

Using 1-(4-methoxyphenyl)ethanol and geranyl bromide, the product was obtained in 60%
 15 yield as a colorless oil.

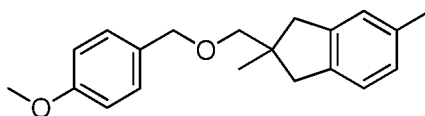


¹H NMR (CDCl₃, 400 MHz): δ 1.42 (d, J=6.4 Hz, 3H), 1.54 (s, 3H), 1.59 (s, 3H), 1.68 (s,
 20 3H), 1.94-2.05 (m, 2H), 2.05-2.14 (m, 2H), 3.74-3.88 (m, 2H), 3.79 (s, 3H), 4.40 (q,
 J=6.54 Hz, 1H), 5.09 (t, J=6.9 Hz, 1H), 5.35 (t, J=6.9 Hz, 1H), 6.84-6.90 (m, 2H),
 7.21-7.28 (m, 2H).

MS (EI): 288 (M⁺, 0), 151 (7), 135 (77), 134 (100), 119 (52), 91 (70), 69 (46), 41 (38).

Example 1.92-((4-methoxybenzyloxy)methyl)-2,5-dimethyl-2,3-dihydro-1H-indene

Using (2,5-dimethyl-2,3-dihydro-1H-inden-2-yl)methanol (Lilyflore®, Firmenich) and 1-(chloromethyl)-4-methoxybenzene, the product was obtained in 90% yield as a colorless oil.



5

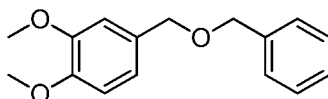
¹H NMR (CDCl₃, 400 MHz): δ 1.16 (s, 3H), 2.29 (s, 3H), 2.58 (overlapping doublets, J=15.9 Hz, 2H), 2.90 and 2.91 (overlapping doublets, J=15.9 Hz, 2H), 3.29 (s, 2H), 3.7 (s, 3H), 4.4 (s, 2H), 6.85 (d, J=8.7 Hz, 2H), 6.91 (d, J=7.6 Hz, 1H), 6.96 (s, 1H), 7.02 (d, J=7.7 Hz, 1H), 7.2 (d, J=8.9 Hz, 2H).

10 MS (EI): 296 (M⁺, <1), 175 (38), 157 (48), 145 (42), 129 (16), 121 (100), 115 (8), 105 (9), 91 (9), 77 (12).

Example 1.10

(4-((benzyloxy)methyl)-1,2-dimethoxybenzene)

15 Using (3,4-dimethoxyphenyl)methanol and benzyl bromide, the product was obtained in 70% yield as a colorless oil.



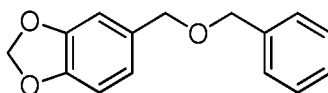
¹H NMR (CDCl₃, 400 MHz): δ 3.85 (s, 3H), 3.86 (s, 3H), 4.48 (s, 2H), 4.52 (s, 2H), 6.78-6.98 (m, 3H), 7.23-7.39 (m, 5H).

20 MS (EI): 258 (M⁺, 19), 167 (9), 152 (67), 151 (76), 137 (26), 121 (32), 91 (100), 77 (38), 65 (35).

Example 1.11

(5-((benzyloxy)methyl)benzodioxole)

25 Using benzo[d][1,3]dioxol-5-ylmethanol and benzyl bromide, the product was obtained in 93% yield as a colorless oil.



¹H NMR (CDCl₃, 400 MHz): δ 4.43 (s, 2H), 4.51 (s, 2H), 5.91 (s, 2H), 6.72-6.90 (m, 3H), 7.23-7.39 (m, 5H).

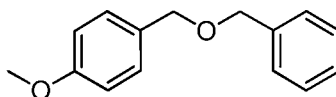
MS (EI): 242 (M⁺, 23), 151 (19), 136 (88), 135 (100), 123 (7), 106 (22), 92 (37), 91 (64), 77 (38), 65 (30).

5

Example 1.12

(1-((benzyloxy)methyl) -4-methoxybenzene)

Using 1-(4-methoxyphenyl)methanol and benzyl bromide, the product was obtained in 89% yield as a colorless oil.



10

¹H NMR (CDCl₃, 400 MHz): δ 3.76 ppm (s, 3H), 4.47 (s, 2H), 4.51 (s, 2H), 6.84-6.90 (m, 2H), 7.23-7.37 (m, 7H).

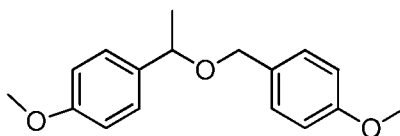
MS (EI): 228 (M⁺, 6), 137 (63), 121 (100), 109 (18), 91 (65), 77 (33), 65 (17), 51 (11).

15

Example 1.13

(1-methoxy-4-(1-((4-methoxybenzyl)oxy)ethyl)benzene)

Using 1-(4-methoxyphenyl)ethanol and para-methoxybenzyl chloride, the product was obtained in 79% yield as a colorless oil.



20

¹H NMR (CDCl₃, 400 MHz): δ 1.44 ppm (d, J=6.5 Hz, 3H), 3.77 (s, 3H), 3.79 (s, 3H), 4.19 (d, J=11.5 Hz, 1H), 4.34 (d, J=11.5 Hz, 1H), 4.42 (q, J=6.4 Hz, 1H), 6.82-6.92 (m, 4H), 7.18-7.30 (m, 4H).

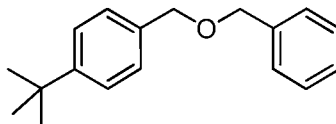
MS (EI): 272 (M⁺, 6), 164 (16), 136 (18), 135 (47), 121 (100), 91 (8), 77 (10).

25

Example 1.14

(1-((benzyloxy)methyl) -4-(tert-butyl)benzene)

Using benzyl alcohol and 4-tertbutylbenzyl bromide, the product was obtained in 89% yield as a colorless oil.



5 ¹H NMR (CDCl₃, 400 MHz): δ 1.31 ppm (s, 9H), 4.52 (s, 2H), 4.54 (s, 2H), 7.23-7.39 (m, 9H).

MS (EI): 254 (M⁺, <1), 239 (7), 163 (45), 148 (18), 117 (18), 91 (100), 77 (11), 57 (37), 41 (7).

Example 2

10 Olfactive Evaluation with Fabric Softener

Example 2.1

Application in fabric softener using machine wash and machine drying

15 White, cotton terry towels (2.5 kg) were washed with 46 g of unfragranced detergent (Tide® 2X Ultra Free) using a top-loading washing machine (Maytag, Model LS7806). Upon completion of the wash cycle, 25 g of Downy® Ultra Free & Sensitive fabric softener mixed with 0.5 g of profragrance Ex. 1.1 was added to the load at the rinse stage. Upon completion of the rinse and spin stages, the towels were transferred to a dryer and dried under the "normal" temperature setting for 50 minutes. Towels were separated into bundles of 6 in
20 3 bins (Sterilite 5.7 L) and stored at RT. A set of control towels were prepared in the same manner using 25 g of fabric softener mixed with molar equivalent amounts of dihydromyrcenol (0.28 g) and anisaldehyde (0.25 g).

The coded towels were assessed blind by panelists for intensity from 0 (odorless) to 7 (strong) after initial dry, 3 days, 7 days and 14 days of storage. The results, average of the
25 intensity ratings for each time point, are presented in Table 1 below. The average intensity values for the precursor-treated towels were always higher than the control towels for all days tested showing that the precursor provided a controlled release effect.

Table 1: Fragrance intensity of the control towels vs. the precursor-treated towels

	initial dry	day 3	day 7	day 14
# of panelists	14	17	20	17
Ex. 1.1 precursor	3.07	4.03	4.70	4.32
Control	2.64	3.59	3.30	3.68

Example 2.2

Application in fabric softener using machine wash and dry

An ester-quat type fabric softener base was prepared with the following composition:

5 12.2 wt% Stepanex® VL 90 (Stepan), 0.4 wt% (10% aqueous CaCl_2) and 87.4 wt% deionized water. Using the washing/drying procedure described in Ex. 2.1, terry towels (2.5 kg) were treated with profragrance Ex. 1.5 (0.15 g) mixed with 30 g of fabric softener. Control towels for comparison were prepared using 30 g of fabric softener mixed with a-

10 ionol, α -ionone and anisaldehyde at a molar equivalent level to the profragrance. After machine drying, the towels were stored in large bins (Sterilite 63 L) until panel evaluations. For each evaluation (initial, 3 d, 7 d and 14 d), panelists were asked to compare the control and profragrance towels in a two-alternative forced choice (2AFC) design. Twenty-four panelists were asked to choose the sample with the strongest odor then, in a different location with another set of towels, they were given the same task. The binomial model was used to

15 calculate statistical significance (at cc-value of 0.05) between the samples. At days 3, 7 and 14 the precursor-treated towels were judged to have a stronger odor at a 95% confidence level (Table 2), this shows that a release of fragrant materials was occurring

Table 2 : 2AFC comparison between control towels and precursor-treated towels (Ex. 1.5)

	initial dry	day 3	day 7	day 14
# of evaluations	48	48	48	48
times profragrance-treated towels were selected as stronger	24	33	38	39

Example 2.3

Application in fabric softener using machine wash and dry

Following the procedure of Ex. 2.2, the towels were treated with profragrance Ex 1.6 (0.15 g) and controls were prepared using a molar equivalent of phenylethanol. On day 14 the precursor-treated towels were judged to have a stronger odor at a 95% confidence level (Table 3), this shows that a release of fragrant materials was occurring.

Table 3 : 2AFC comparison between control towels and precursor-treated towels (Ex. 1.6)

	initial dry	day 3	day 7	day 14
# of evaluations	48	48	48	48
times profragrance-treated towels were selected as stronger	21	19	25	34

Example 310 Dynamic headspace analysis from fabric softener application

a) *Deposition*: The ether profragrance Ex 1.1 (0.2 mmol) was added to 9 g of fabric softener base described in Ex. 2.2, and the mixture was rinsed into a 4 L beaker with water and if necessary with 1 ml of acetone. The beaker was then filled to 3 L total volume with water. Six, 5.0 g cloth squares (cotton fabric, weight 270 g/m², item 403 from Testfabrics, West Pittston, PA) were placed in the 4 L beaker and manually agitated for 3 min. After an additional 2 min of standing, the cloths were removed and the excess water squeezed out. The cloths were hung to dry for 24 h at RT and then individually encased in aluminum foil until analyzed. This procedure was repeated for a duplicate set of samples. Control clothes were prepared by the same process using 0.2 mmol each of the expected volatiles (alcohol and aryl aldehyde or ketone).

b) *Analysis*: Dynamic headspace analyses of dried swatches were performed in duplicate at 1, 3 and 7 days after deposition. The swatch to be analyzed was placed inside a thermostatted (25°C), headspace sampling cell to which a clean Tenax® cartridge was attached. A constant flow of air (200 ml/min) was drawn through the sampling cell and

Tenax® cartridge using an air sampling pump. Prior to entering the sample cell, the air was drawn through a plug of active charcoal and then through a saturated NaCl solution to maintain a constant relative humidity of 75%. The swatches were sampled for 15 min at 0-15 and 15-30 min using a clean Tenax® cartridge for each time period.

- 5 The cartridges were thermally desorbed (Perkin Elmer Turbo Matrix 650) and analyzed by GC-MS (Agilent 6890/5975C). The MSD (EI, 70 eV) was operated in the selected ion monitoring mode for quantitative measurements. The GC was equipped with a Varian VF-lms capillary column (30 m, 0.25 mm i.d. 0.25 μ m film). The desorber parameters were: valve temperature 240°C, desorption temperature 240°C, transfer line 250°C, trap -30°C to
 10 250°C at 40°C/sec, purge time 1.0 min, desorption time 5 min, trap hold time 5 min, trap desorption flow time 0 min, cycle time 13 min, outlet split (5.2% injected), column flow 1.1 ml/min, desorption flow 50 ml/min.

- c) *Calculation*: The amount of each fragrance volatile collected (reported as ng/L of air) was
 15 determined using linear external-standard calibration curves. At least four acetone solutions were prepared with concentrations ranging from 0.5 mM to 20 mM of the volatile compounds. The solutions were injected (0.2 μ L) onto Tenax® cartridges and desorbed as described above. Each solution was analyzed in duplicate. Calibration curves were forced through the origin.

20

Table 4 : Headspace concentrations (ng/L) of volatiles released from the precursor-treated towels or the corresponding control towels (controls in parentheses) at 1, 3 and 7 days after deposition

precursor	perfume alcohol			aryl aldehyde		
	1 d	3d	7d	1d	3d	7d
Ex. 1.1	15 (0.2)	244 (0.6)	158 (0.3)	4 (0.3)	13 (4)	13 (2)

25

Oxidative Decomposition of Benzyl Ethers

A series of paper blotters (6 x 0.7 cm) were each loaded with 40 μ l of a benzyl ether using a positive displacement pipette. The following benzyl ethers were tested: Ex. 1.1, 1.3, 1.4, 1.7, 1.10, 1.11, 1.12, 1.14. Each blotter was placed inside a transparent 15 ml clear vial (Supelco, 27159) and sealed with a septum-equipped screw cap. The vials were purged with oxygen (20-26 ml/min) for one minute and then placed 10 inches away from a 365 nm UV-A lamp (UVP, 95-0042-07). Periodically a vial was retrieved and 1 ml of the internal standard solution (40 mg/ml of dodecane in acetone) was injected through the septum into the vial. After shaking the vial by hand, the cap was removed and another 15 ml of acetone (graduated cylinder) was added. The vial was recapped, agitated by hand for 1 minute, and then allowed to sit for another 9 minutes. The acetone solution was analyzed by GC-FID utilizing a 30 m x 0.25 mm (25 μ m film) HP-1 column and an Agilent 6850 gas chromatograph. The oven temperature was set to 100°C and raised 30°C/minute to 140°C, then by 2°C/minute to 150°C, then by 40°C/minute to 280°C and finally held for 3 minutes at this temperature. The amount of remaining benzyl ether was determined by a comparison of the GC peak areas to that of the internal standard and is reported as the percent remaining relative to the initial analysis at time zero. Figure 1 presents the loss of each benzyl ether. This graph shows that the volatiles are released progressively over a period of 2 to 14 days. GC-MS analyses of these extracts also revealed the formation of volatile compounds. The most abundant volatile compounds formed by the decomposition of each benzyl ether is indicated in Table 5.

Table 5 : Most abundant volatiles released by the tested benzyl ethers

Benzyl ether	Most abundant volatile(s) released
Ex. 1.1	dihydromyrcenol, anisaldehyde
Ex. 1.3	dihydromyrcenol, anisaldehyde
Ex. 1.4	5-ethylnonan-2-ol, anisaldehyde, 5-ethylnonan-2-one
Ex. 1.7	citronellol, anisaldehyde
Ex. 1.10	3,4-dimethoxybenzaldehyde, benzaldehyde, benzyl alcohol
Ex. 1.11	benzo[d][1,3]dioxole-5-carbaldehyde, benzaldehyde, benzyl alcohol
Ex. 1.12	anisaldehyde, benzaldehyde, benzyl alcohol

Ex. 1.14	4-(tert-butyl)benzaldehyde, benzaldehyde, benzyl alcohol
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Example 5

Analysis of Volatiles Released by Benzyl Ethers

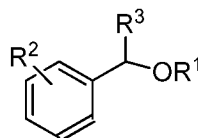
The formation of volatile products under ambient conditions was shown by performing headspace analysis of paper blotters (6 x 0.7 cm) loaded with a benzyl ether and aged for 6, 7 or 14 days. The tested benzyl ethers were Ex. 1.1, 1.4, 1.5, 1.7, 1.9 and 1.12. Just the tips of the blotters were dipped into the ether samples and the dipped end of individual blotters were placed inside transparent 15 ml borosilicate vials. The vials were not capped. In this manner the blotters were left exposed to the ambient laboratory conditions. After aging for the specified time, the blotters were sealed in a 20 ml vial with a septum-equipped cap. The headspace was equilibrated at 40° C. and the headspace sampled for 30 minutes with a 2 cm 50/30µm DVB/CAR/PDMS, StableFlex™ fiber (Supelco) inserted into the vial through the septum. The fiber then was desorbed (250°C, 5 minutes) into a GC-MS system (Agilent 6890N coupled with a 5973 mass selective detector) equipped with a 30 m x 0.25 mm (0.25 µm film) DB-1 capillary column. The oven temperature was kept at 50° C for 3 minutes, then raised to 6°C/minute to 240° C and finally kept at this temperature for 10 minutes. The chromatograms show the appearance of volatile compounds as a result of exposure to the ambient atmosphere. . The fragrant compounds formed by the decomposition of the benzyl ethers under ambient conditions are indicated in Table 6.

Table 6 : Volatiles released by the benzyl ethers after exposure to the ambient atmosphere

Benzyl ether	Fragrant compounds observed
1.1	dihydromyrcenol, anisaldehyde
1.4	5-ethylnonan-2-ol, anisaldehyde, 5-ethylnonan-2-one
1.5	anisaldehyde, α -ionol, a -ionone
1.7	citronellol, anisaldehyde, citronellal
1.9	2,5-dimethyl-2-indanmethanol, anisaldehyde
1.12	benzyl alcohol, benzaldehyde, anisaldehyde

CLAIMS

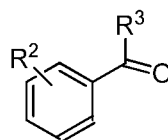
1. A compound of Formula (I)



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(I)

wherein R¹ represents a C₃ to C₂₀ hydrocarbon group derived from a fragrant alcohol of formula R¹H or from a fragrant aryl aldehyde or ketone of Formula (II)



(II),

- 10 wherein R², is, independently, hydrogen atom, hydroxyl group, acetoxy group, optionally substituted CrC₆ alkyl group, CrC₆ alkoxy group, or -C(=O)CH(CH₃)₂ wherein any two of R² may form an optionally substituted 5 or 6 membered ring; and R³ is hydrogen atom or methyl group.

- 15 2. The compound as recited in Claim 1 wherein the CrC₆ alkoxy group is selected from the group consisting of methoxy, ethoxy, propoxy, isopropoxy and butoxy group.

3. The compound as recited in Claim 2 wherein the C₁-C₆ alkoxy group is methoxy group.

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4. The compound as recited in any one of claims 1-3 wherein the C₁-C₆ alkyl group is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, cyclopropyl, cyclopentyl and cyclohexyl group.

- 25 5. The compound as recited in Claim 1 wherein the fragrant aldehyde is selected from the group consisting of: benzaldehyde, 4-methoxybenzaldehyde (anisaldehyde), 4-

methylbenzaldehyde, 4-ethylbenzaldehyde, 4-isopropylbenzaldehyde, 4-(tert-butyl)benzaldehyde, 2-methoxybenzaldehyde, 3,4-dimethoxybenzaldehyde, benzo[d][1,3]dioxole-5-carbaldehyde (heliotropin), 4-hydroxybenzaldehyde, 4-hydroxy-3-methoxybenzaldehyde (vanillin), 3-ethoxy-4-hydroxybenzaldehyde, 4-formyl-2-methoxyphenyl acetate, 4-formyl-2-methoxyphenyl isobutyrate; and 3,5,5,6,7,8,8-heptamethyl-5,6,7,8-tetrahydronaphthalene-2-carbaldehyde

6. A compound as recited in Claim 1 wherein the compound of Formula (I) are selected from the group consisting of (((2,6-dimethyloctan-2-yl)oxy)methyl)benzene; (((3,7-dimethyloct-1-en-3-yl)oxy)methyl)benzene; 1-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)-4-methoxybenzene; 1-(((2,6-dimethyloctan-2-yl)oxy)methyl)-4-methoxybenzene; 1-(((3,7-dimethyloctan-3-yl)oxy)methyl)-4-methoxybenzene; 2-(((4-methoxybenzyl)oxy)methyl)-2,5-dimethyl-2,3-dihydro-1H-indene; (E)-1-methoxy-4-(((4-(2,6,6-trimethylcyclohex-2-en-1-yl)but-3-en-2-yl)oxy)methyl)benzene; 4-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)-2-methoxyphenol; 4-(((2,6-dimethyloctan-2-yl)oxy)methyl)-2-methoxyphenol; 4-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-2-methoxyphenol; 4-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-2-methoxyphenol; 4-(((3,7-dimethyloctan-3-yl)oxy)methyl)-2-methoxyphenol; 4-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)-2-ethoxyphenol; 4-(((2,6-dimethyloctan-2-yl)oxy)methyl)-2-ethoxyphenol; 4-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-2-ethoxyphenol; 4-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-2-ethoxyphenol; 4-(((3,7-dimethyloctan-3-yl)oxy)methyl)-2-ethoxyphenol; 5-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)benzo[d][1,3]dioxole; 5-(((2,6-dimethyloctan-2-yl)oxy)methyl)benzo[d][1,3]dioxole; 5-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)benzo[d][1,3]dioxole; 5-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)benzo[d][1,3]dioxole; 5-(((3,7-dimethyloctan-3-yl)oxy)methyl)benzo[d][1,3]dioxole; 4-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)-1,2-dimethoxybenzene; 4-(((2,6-dimethyloctan-2-yl)oxy)methyl)-1,2-dimethoxybenzene; 4-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-1,2-dimethoxybenzene; 4-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-1,2-dimethoxybenzene; 4-(((3,7-dimethyloctan-3-yl)oxy)methyl)-1,2-dimethoxybenzene; 1-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)-4-methylbenzene; 1-

(((2,6-dimethyloctan-2-yl)oxy)methyl)-4-methylbenzene; 1-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-4-methylbenzene; 1-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-4-methylbenzene; 1-(((3,7-dimethyloctan-3-yl)oxy)methyl)-4-methylbenzene; 1-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)-4-ethylbenzene; 1-(((2,6-dimethyloctan-2-yl)oxy)methyl)-4-ethylbenzene; 1-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-4-ethylbenzene; 1-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-4-ethylbenzene; 1-(((3,7-dimethyloctan-3-yl)oxy)methyl)-4-ethylbenzene; (E)-1-ethyl-4-(((4-(2,6,6-trimethylcyclohex-2-en-1-yl)but-3-en-2-yl)oxy)methyl)benzene; 1-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)-4-isopropylbenzene; 1-(((2,6-dimethyloctan-2-yl)oxy)methyl)-4-isopropylbenzene; 1-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)-4-isopropylbenzene; 1-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-4-isopropylbenzene; 1-(((3,7-dimethyloctan-3-yl)oxy)methyl)-4-isopropylbenzene; 1-(tert-butyl)-4-(((3,7-dimethylocta-1,6-dien-3-yl)oxy)methyl)benzene; 1-(tert-butyl)-4-(((2,6-dimethyloctan-2-yl)oxy)methyl)benzene; 1-(tert-butyl)-4-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)benzene; 1-(tert-butyl)-4-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)benzene; 1-(tert-butyl)-4-(((3,7-dimethyloctan-3-yl)oxy)methyl)benzene; 2-methoxy-4-(((4-methoxybenzyl)oxy)methyl)phenol; 4,4'-(oxybis(methylene))bis(2-methoxyphenol); 2-methoxy-4-((1-(4-methoxyphenyl)ethoxy)methyl)phenol; 4,4'-(oxybis(methylene))bis(2-ethoxyphenol); 2-methoxy-4-(((4-methylbenzyl)oxy)methyl)phenol; 4-(((4-ethylbenzyl)oxy)methyl)-2-methoxyphenol; 4-(((4-isopropylbenzyl)oxy)methyl)-2-methoxyphenol; 4-(((4-(tert-butyl)benzyl)oxy)methyl)-2-methoxyphenol; 1-((2,6-dimethyloct-7-en-2-yloxy)methyl)-4-methoxybenzene; 1-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-4-methoxybenzene; ((2,6-dimethyloct-7-en-2-yloxy)methyl)benzene; 1-((5-ethylnonan-2-yloxy)methyl)-4-methoxybenzene; (E)-1-methoxy-4-((4-(2,6,6-trimethylcyclohex-2-enyl)but-3-en-2-yloxy)methyl)benzene; 2,4-dimethyl-1-(phenethoxymethyl)benzene; ((E)-1-(1-((3,7-dimethylocta-2,6-dien-1-yl)oxy)ethyl)-4-methoxybenzene); 2-(((4-methoxybenzyloxy)methyl)-2,5-dimethyl-2,3-dihydro-1H-indene); 4-((benzyloxy)methyl)-1,2-dimethoxybenzene; 5-((benzyloxy)methyl)benzo[d][1,3]dioxole; 1-((benzyloxy)methyl)-4-methoxybenzene; 1-methoxy-4-(1-(((4-methoxybenzyl)oxy)ethyl)benzene; and 1-((benzyloxy)methyl)-4-(tert-butyl)benzene); 6-(tert-butoxymethyl)-1,1,2,3,4,4,7-heptamethyl-1,2,3,4-

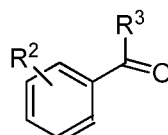
tetrahydronaphthalene; 6-(((2,6-dimethyloct-7-en-2-yl)oxy)methyl)- 1,1,2,3,4,4,7-heptamethyl- 1,2,3,4-tetrahydronaphthalene; 1,1,2,3,4,4,6-heptamethyl-7-(((2-methyl- 1-phenylpropan-2-yl)oxy)methyl)- 1,2,3,4-tetrahydronaphthalene; and 6-(((4-methoxybenzyl)oxy)methyl)- 1,1,2,3,4,4,7-heptamethyl- 1,2,3,4-tetrahydronaphthalene.

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7. A compound as recited in Claim 6 wherein the compound of Formula (I) is selected from the group consisting of: 1-(((2,6-dimethyloct-7-en-2-yloxy)methyl)-4-methoxybenzene; 1-(((3,7-dimethyloct-1-en-3-yl)oxy)methyl)-4-methoxybenzene; ((2,6-dimethyloct-7-en-2-yloxy)methyl)benzene; 1-((5-ethylnonan-2-yloxy)methyl)-4-methoxybenzene; (E)-1-methoxy-4-((4-(2,6,6-trimethylcyclohex-2-enyl)but-3-en-2-yloxy)methyl)benzene; (2,4-dimethyl-1-(phenethoxymethyl)benzene; ((E)-1-(1-((3,7-dimethylocta-2,6-dien-1-yl)oxy)ethyl)-4-methoxybenzene; 2-((4-methoxybenzyloxy)methyl)-2,5-dimethyl-2,3-dihydro-1H-indene; 4-((benzyloxy)methyl)-1,2-dimethoxybenzene; 5-((benzyloxy)methyl)benzo[d][1,3]dioxole; 1-((benzyloxy)methyl)-4-methoxybenzene; 1-methoxy-4-(1-((4-methoxybenzyl)oxy)ethyl)benzene; and 1-((benzyloxy)methyl)-4-(tert-butyl)benzene.

8. A compound as recited in any one of claims 1, 5-7 provided that that the compound does not comprise a compound selected from the group consisting of ((2,6-dimethyloct-7-en-2-yloxy)methyl)benzene; 1-((benzyloxy)methyl)-4-methoxybenzene; and 1-((benzyloxy)methyl)-4-(tert-butyl)benzene.

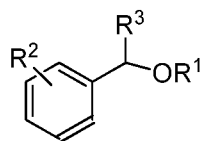
9. A method of releasing a fragrant compound from a precursor compound, wherein the fragrant compound is selected from the group consisting of R^1OH and an aryl aldehyde or ketone of Formula (II):



(II),

by exposing a precursor compound of Formula I:

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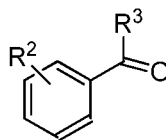


(I)

to an environment wherein the compound is oxidized and wherein:

- 5 R^2 is, independently, hydrogen atom, hydroxyl group, acetoxy group, $-O(C=O)CH(CH_3)_2$, optionally substituted C_1-C_6 alkyl or C_1-C_6 alkoxy group, wherein any two of R^2 may form an optionally substituted 5 or 6 membered ring; R^1 represents a C_3 to C_{20} hydrocarbon group derived from a fragrant alcohol of formula R^1H or from a fragrant aryl aldehyde or ketone of formula Formula (II); and wherein R^3 is hydrogen atom or methyl group.

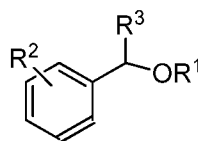
- 10 10. The method as recited in claim 9 wherein the method comprises the release of at least two compounds from the precursor compound, wherein at least one of the compounds is a fragrant compound wherein the two compounds are the same or different and each independently comprises the formula (II):



(II),

15

by exposing a precursor compound of Formula I:



(I)

- 20 to an environment wherein the compound is oxidized and wherein:
 R^1 represents a C_3 to C_{20} hydrocarbon group derived from a fragrant aryl aldehyde or ketone of Formula (II) wherein R^2 is, independently, hydrogen atom, hydroxyl group, acetoxy group, optionally substituted C_1-C_6 alkyl group or C_1-C_6 alkoxy group, $-O(C=O)CH(CH_3)_2$ wherein

any two of R^2 may form an optionally substituted 5 or 6 membered ring; and R^5 is hydrogen atom or methyl group.

11. The method as recited in Claim 9 wherein the C_1 - C_6 alkoxy group is selected from the group consisting of methoxy, ethoxy, propoxy, isopropoxy and butoxy group.

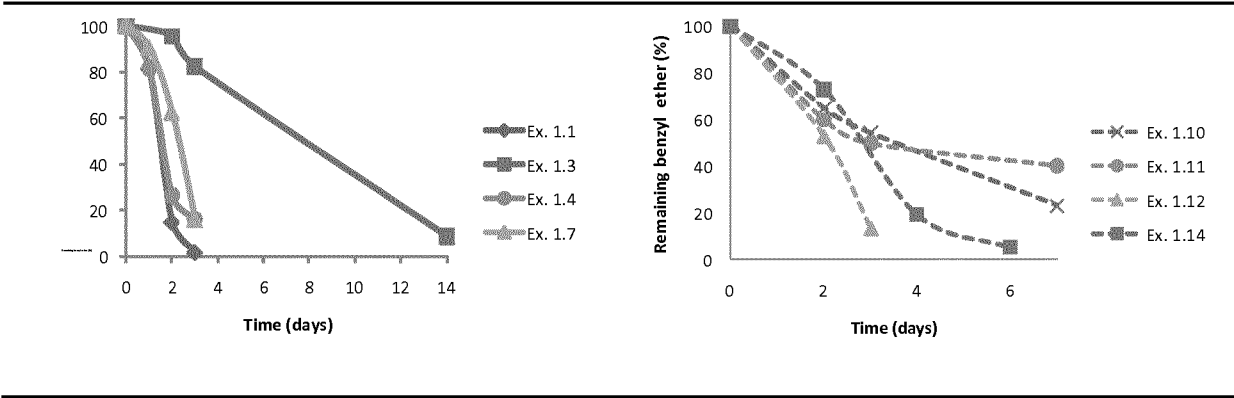
12. A perfumed article comprising a compound according to any one of claims 1-7 wherein the perfumed article is provided in a perfumed product selected from the group consisting of perfume, cologne, bath gel, shower gel, hair-care product, cosmetic preparation, body deodorant, solid or liquid airfreshener, detergent, fabric softener, and all purpose cleaner.

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FIGURE

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Figure 1. Disappearance of benzyl ethers



INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/059102

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	C07C29/50	C07D317/54	C07C41/26	C07C43/164	C07C43/166
	C07C43/168	C07C43/205	C07C43/215	C07C43/23	C07C45/51
	C07C33/025	C07C47/575	C07C33/03	C07C47/54	C07C31/125
According to International Patent Classification (IPC) or to both national classification and IPC					

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C C07D C07B C11B A61K A61Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal , WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHENLU SHEN ET AL: "Aerobi c oxi dati ve deprotecti on of benzyl -type ethers under atmospheri c pressure catalyzed by 2,3-di chl oro-5 ,6-di cyano-l ,4-benzoqui none (DDQ)/tert-butyl ni tri te" , TETRAHEDRON LETTERS, vol . 54, no. 12, 1 March 2013 (2013-03-01) , pages 1579-1583 , XP055133004, ISSN: 0040-4039 , DOI : 10.1016/j.tetl et.2013.01.045 entri es 1-6; page 1581; tabl e 2; compounds la-f ----- -/- .	1-3 , 5 , 8



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

6 August 2014

Date of mailing of the international search report

25/08/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040,
 Fax: (+31-70) 340-3016

Authorized officer

van Bergen , Marc

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/059102

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FUK&EMSP14; LOI LAM ET AL: "Palladium-(S,pR)-FerroNPS-Catalyzed Asymmetric Allylic Etherification: Electronic Effect of Nonconjugated Substituents on Benzyl Alcohol on Enantioselectivity", ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 47, no. 7, 1 February 2008 (2008-02-01), pages 1280-1283, XP055133011, ISSN: 1433-7851, DOI: 10.1002/anie.200703955 entries 1-3; page 1281; table 2 -----	1-5, 8
X	LAURA E. BOURQUE ET AL: "Metal-Catalyzed Silylene Insertions of Allylic Ethers: Stereoselective Formation of Chiral Allylic Silanes", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 129, no. 42, 1 October 2007 (2007-10-01), pages 12602-12603, XP055133028, ISSN: 0002-7863, DOI: 10.1021/ja073758s page 12603, paragraph 1 -----	1-3, 5, 8
X	BAI-PING YING ET AL: "Oxidative C-C Bond-Forming Reaction of Electron-Rich Alkyl benzyl Ether with Trimethyl vinyl oxysilane", ORGANIC LETTERS, vol. 6, no. 10, 1 May 2004 (2004-05-01), pages 1523-1526, XP055133037, ISSN: 1523-7060, DOI: 10.1021/ol036314j entries 2-4; page 1525; table 2; compounds 9a-c -----	1, 5, 8
X	MORALES ET AL: "Aqueous-sensitive reaction sites in sulfonic acid-functionalized mesoporous silicas", JOURNAL OF CATALYSIS, ACADEMIC PRESS, DULUTH, MN, US, vol. 254, no. 2, 20 February 2008 (2008-02-20), pages 205-217, XP022494001, ISSN: 0021-9517, DOI: 10.1016/J.JCAT.2007.12.011 scheme 1; page 209 ----- -/--	1-3, 5, 8

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/059102

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YANG W-C ET AL: "Cu(OTf)₂-catalyzed Et₃SiH-reductive etherification of various carbonyl compounds with trimethyl silyl ethers", TETRAHEDRON LETTERS, PERGAMON, GB, vol. 44, no. 42, 13 October 2003 (2003-10-13), pages 7837-7840, XP004457102, ISSN: 0040-4039, DOI: 10.1016/J.TETLET.2003.08.085 entries 1, 2, 5, 6; page 7839; table 2; compounds 4,6, 12, 14 -----	1-3, 5, 8
X	KAZUAKI ISHIHARE ET AL: "Homogeneous Debenzylating Using Extremely Active Catalysts: Tri(silyl)methane, Scandium(III) Tri(silyl)methide, and Copper(II) Tri(silyl)methide", SYNLETT, no. 1, 1999, pages 80-82, XP002728136, ISSN: 0936-5214 page 81; table 2 -----	1-3, 5, 8
X	US 2009/299102 A1 (BOWDEN NED [US] ET AL) 3 December 2009 (2009-12-03) paragraph [0120] -----	1, 5, 8
X	R. L. HUANG ET AL: "648. The relative stabilizing influences of substituents on free alkyl radicals. Part VII. The cleavage of monosubstituted dibenzyl ethers by free t-butoxy-radicals", JOURNAL OF THE CHEMICAL SOCIETY (RESUMED), 1 January 1959 (1959-01-01), page 3190, XP055133177, ISSN: 0368-1769, DOI: 10.1039/jr9590003190 page 3191, paragraph 2 -----	1-8
X	US 2 841 620 A (JOSEPH COLAIANNI LOUIS ET AL) 1 July 1958 (1958-07-01) example 17 -----	1, 5, 8, 12
X	MAN B Y W ET AL: "Substitution reactions in ionic liquids. A kinetic study", TETRAHEDRON LETTERS, PERGAMON, GB, vol. 46, no. 44, 31 October 2005 (2005-10-31), pages 7641-7645, XP027863675, ISSN: 0040-4039 [retrieved on 2005-10-31] page 7641; figure 1 ----- -/--	1, 5, 8

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/059102

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BRINDABAN C. RANU ET AL: "Unusual Cleavage of Ethers by Thiophenol on the Surface of Silica Gel Impregnated with Indium(III) Chloride under Microwave Irradiation: Efficient Procedure for the Synthesis of Thiethers through Transthietherification", SYNLETT, 2002, pages 987-989, XP002728204, ISSN: 0936-5214, entries 13 and 14; page 988; table 1 -----	1-3, 5-8
X	JACQUELINE A. HEMMINGSON; GORDON LEARY: "The Self-Condensation Reactions of the Lignin Model Compounds, Vanillyl and Veratryl Alcohol", AUSTRALIAN JOURNAL OF CHEMISTRY, vol. 33, 1980, pages 917-925, XP008171021, ISSN: 0004-9425, page 918; compounds 3a-b -----	1-3, 5, 6, 8
A	Wo 2012/085287 Al (GIVAUDAN SA [CH]; BAUMGARTNER CORINNE [CH]; FLACHSMANN FELIX [CH]; KRA) 28 June 2012 (2012-06-28) abstract claim 1 -----	1-12
A	US 2007/053860 Al (EH MARCUS [DE] ET AL) 8 March 2007 (2007-03-08) claims 1, 4 examples 1-28 -----	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/059102

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009299102	AI	03-12-2009	NONE

US 2841620	A	01-07-1958	NONE

Wo 2012085287	AI	28--06 -2012	CN 103261139 A 21-08-2013
			EP 2655307 AI 30-10-2013
			JP 2014508121 A 03-04-2014
			SG 190848 AI 31-07-2013
			US 2013316938 AI 28-11-2013
			Wo 2012085287 AI 28-06-2012

US 2007053860	AI	08--03 -2007	AT 466564 T 15-05-2010
			DE 10348062 AI 19-05-2005
			EP 1677749 AI 12-07-2006
			JP 2007509199 A 12-04-2007
			US 2007053860 AI 08-03-2007
			wo 2005037243 AI 28-04-2005
