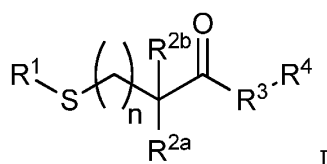


NEW COMPOUNDS

Field of the Invention

- 5 The present invention relates to compounds of formula I and their uses as precursors in the generation of fragrant thiols.



Background of the Invention

10

Thiol compounds are some of the strongest odourants used in perfume. The perception of their odour, of course, will depend upon their concentration, purity and in some cases, isomeric purity. However, generally speaking, when they are used in even in low amounts, they have the ability to greatly influence the overall olfactory impression of perfume compositions. They also tend to be rather labile compounds and degrade rapidly. For these reasons, although they can be very rewarding compounds to work with in the art of composing perfumes, they can also be difficult to dose correctly. The compounds described in US 2010/0310479 are an example of thiols that are useful in perfumery, but which are unstable and decompose over time in, for example, liquid detergents.

20

When a prolonged effect of fragrance is required, both in fine and functional perfumery, this instability can be a problem. By way of example, laundry applications require continuous effectiveness of a perfume over a certain period of time immediately after washing, during dry down, as well as on dry, laundered textiles. Also, in household care applications, a prolonged effectiveness of perfumes can often be required.

25

Due to their potency, as well as their instability, fragrant thiols cannot be overdosed (i.e. used in high concentration) to combat this issue. It is therefore a problem underlying the present invention to overcome these drawbacks in the prior art. In particular, it is a problem underlying the present invention to provide fragrant thiols that have an increased persistence and can be perceived over a prolonged period of time.

30

WO 2003/049666 describes β -thiocarbonyl precursor compounds which are capable of liberating fragrance molecules. However, in this document the released fragrance molecules are not a fragrant thiols.

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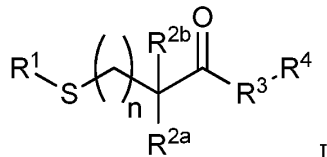
Other β -thiocarbonyl compounds and their use in perfumery applications are described in the prior art in WO 2021/123144, WO 2021/122997, WO 2015/032885, WO 2001/035768, Cerny *et al.* (Food Chemistry 141 (2013) 1078-1086), Starkenmann *et al.* (J. Agric. Food
 5 Che. 56 (2008) 9575-9580), Begnaud *et al.* (Flavour Fragr. J. 31 (2016) 235-240), Starkenmann *et al.* (Flavour Fragr. J. 23 (2008) 369-381).

Nevertheless, there is still a need in the perfumer's and flavourist's palette for compounds which are capable of degrading to in application to release only fragrant thiols. The
 10 inventors have now found β -thiocarbonyl compounds that are useful to generate fragrant thiols. Said compounds may provide a reservoir for a slow release of highly potent fragrant thiols over time.

The listing or discussion of an apparently prior-published document in this specification
 15 should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

Detailed Description of the Invention

20 According to the first aspect of the invention, there is provided a compound of formula I,



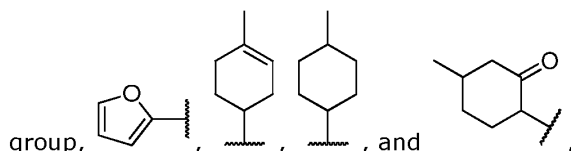
wherein:

n is 0 or 1;

25

R¹ is selected from the group consisting of a C₁₋₁₈ alkyl group, a C₁₋₁₈ alkenyl group, a C₃₋₈ cycloalkyl group, a C₃₋₆ cycloalkenyl group, a 4- to 6-membered heterocycloalkyl group, an aryl group, and a 5- or 6-membered heteroaryl group;

which C₁₋₁₈ alkyl and C₁₋₁₈ alkenyl groups are optionally substituted by one or more
 30 substituents each independently selected from the group consisting of =O, -OR⁵, a phenyl



which C₃₋₈ cycloalkyl, C₃₋₆ cycloalkenyl, and 4- to 6-membered heterocycloalkyl groups are optionally substituted by one or more substituents each independently selected from the group consisting of =O, a C₁₋₄ alkyl group, and a C₁₋₄ alkenyl group, which aryl and 5- or 6-membered heteroaryl groups are optionally substituted by one or more C₁₋₄ alkyl groups;

R^{2a} is selected from the group consisting of hydrogen, C₁₋₄ alkyl group, -N(R^{6a})R^{6b}, -N(R^{7a})C(O)R^{7b}, and -N(R^{8a})C(O)OR^{8b};

R^{2b} is selected from the group consisting of hydrogen and a C₁₋₄ alkyl group;

R³ is selected from the group consisting of -O- and -N(R⁹)-; and

R⁴ is selected from the group consisting of hydrogen, a C₁₋₁₈ alkyl group, a C₁₋₁₈ alkenyl group, and an aryl group, which C₁₋₁₈ alkyl, C₁₋₁₈ alkenyl and aryl groups is optionally substituted by one or more -OH or phenyl groups;

R⁵ is selected from the group consisting of hydrogen, a C₁₋₄ alkyl group and -C(O)R¹⁰;

R^{6a}, R^{6b}, R^{7a}, R^{7b}, R^{8a}, R^{8b} and R⁹ are each independently selected from the group consisting of hydrogen and a C₁₋₄ alkyl group, which C₁₋₄ alkyl group is optionally substituted by one or more phenyl group; and

R¹⁰ is a C₁₋₄ alkyl group;

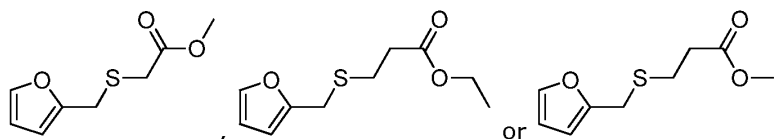
or a salt or solvate thereof;

provided that:

(a) when R¹ is an unsubstituted C₁₋₁₈ alkyl or a C₁₋₁₈ alkenyl group or a C₁₋₁₈ alkyl or a

C₁₋₁₈ alkenyl group substituted by one or more =O, -OR⁵ or  groups and R^{2a} is -NH₂ or -NHC(O)CH₃ and R^{2b} is hydrogen, then R⁴ is not hydrogen; and

(b) the compound of formula I is not:



These compounds, including salts and solvates thereof, may be referred to herein as the "compounds of the invention".

As provided herein,  indicates a point of attachment to the compound of formula I.

5

Salts of the compound of formula I may be prepared in accordance with techniques that are well known to those skilled in the art. For example, the compound of formula I may be reacted with the appropriate organic acid or mineral acid. Salt switching techniques may also be used to convert one salt into another salt.

10

Examples of salts include acid addition salts, for example, salts formed with inorganic acids such as hydrochloric, hydrobromic, sulfuric and phosphoric acid, with carboxylic acids or with organo-sulfonic acids; base addition salts; metal salts formed with bases, for example, the sodium and potassium salts.

15

The compounds disclosed herein may exist in unsolvated as well as solvated forms with solvents such as water, and it is intended that the invention embraces both solvated and unsolvated forms of the compounds of the invention.

20 The term "solvate" refers to a complex of variable stoichiometry formed by a solute and solvent. Such solvents for the purpose of the invention may not interfere with the activity of the solute. Examples of suitable solvents include, but are not limited to, water, methanol, ethanol, and acetic acid. Solvates in which water is the solvent molecule are typically referred to as hydrates. Hydrates include compositions containing stoichiometric
25 amounts of water, as well as compositions containing variable amounts of water.

Unless otherwise specified, alkyl groups defined herein may be straight-chain or, when there is a sufficient number (e.g. a minimum of three) of carbon atoms, be branched-chain. Alkyl groups that may be mentioned include methyl, ethyl, propyl, iso-propyl, butyl,
30 tert-butyl, methylbutyl, pentyl, methylpentyl, hexyl, methylhexyl, ethylhexyl, heptyl, methylheptyl, octyl, methyloctyl, decyl, octadecyl groups.

When there is a sufficient number (i.e. a minimum of three, as appropriate) of carbon atoms, an alkyl chain may be cyclic, (e.g. monocyclic or bicyclic) and so form a cycloalkyl
35 group. Such cycloalkyl groups may be bridged (so forming, for example, fused ring systems such as three fused cycloalkyl groups). The points of attachment of cycloalkyl groups may be *via* any atom in the ring system. Further, where there is a sufficient number (i.e. a minimum of four) such cycloalkyl groups may also be part cyclic, e.g.

forming an alkylene-cycloalkyl group (for example, $-\text{CH}_2-\text{C}_3\text{H}_5$). The points of attachment of cycloalkyl groups may be *via* any atom in the ring system. Cycloalkyl groups that may be mentioned include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, bicyclo[2.2.1]heptyl, and cyclooctyl groups.

5

Heterocycloalkyl groups that may be mentioned include non-aromatic monocyclic heterocycloalkyl groups in which at least one (e.g. one to four) of the atoms in the ring system is other than carbon (i.e. a heteroatom, e.g. sulphur, oxygen or, particularly, nitrogen), and in which the total number of atoms in the ring system is from four to six.

10 The point(s) of attachment of heterocycloalkyl groups may be *via* any atom in the ring system including (where appropriate) a heteroatom (such as a nitrogen atom), or an atom on any fused carbocyclic ring that may be present as part of the ring system. Heterocycloalkyl groups may also be in the *N*- or *S*- oxidised form (i.e. those heteroatoms may be substituted with one or two $=\text{O}$ substituents, as appropriate). For the avoidance
15 of doubt, optional substituents include those defined herein.

Alkenyl groups are unsaturated alkyl groups (i.e. having at least one carbon-carbon double bond). Unless otherwise specified, alkenyl groups defined herein may be straight-chain or, when there is a sufficient number (i.e. a minimum of two or three, as appropriate) of
20 carbon atoms, be branched-chain. Alkenyl groups that may be used include ethenyl, propenyl, butenyl, pentenyl, pentadienyl, hexenyl, and hexadienyl groups.

When there is a sufficient number (i.e. a minimum of three, as appropriate) of carbon atoms, an alkenyl chain may be cyclic, (e.g. monocyclic or bicyclic) and so form a
25 cycloalkenyl group. Such cycloalkenyl groups may be bridged (so forming, for example, fused ring systems such as three fused cycloalkenyl groups). The points of attachment of cycloalkenyl groups may be *via* any atom in the ring system. Cycloalkenyl groups that may be mentioned include cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclopentadienyl, cyclohexenyl and cyclohexadienyl groups.

30

Aryl groups that may be mentioned include C_{6-10} aryl groups. Such groups may be monocyclic or bicyclic and have between 6 and 10 ring carbon atoms, in which at least one ring is aromatic. C_{6-10} aryl groups include phenyl, naphthyl and the like. The points of attachment of aryl groups may be *via* any atom of the ring system. However, when
35 aryl groups are bicyclic, they are linked to the rest of the molecule *via* an aromatic ring.

The term "heteroaryl" when used herein refers to an aromatic group containing one or more heteroatom(s) (e.g. one to four heteroatoms) preferably selected from N, O and S.

Heteroaryl groups include those which have from 5 to 6 members. The points of attachment of heteroaryl groups may be *via* any atom in the ring system including (where appropriate) a heteroatom (such as a nitrogen atom). Substituents on heteroaryl groups may, where appropriate, be located on any atom in the ring system including a heteroatom. For the avoidance of doubt, optional substituents include those defined herein. Particular heteroaryl groups that may be mentioned include furanyl groups.

For the avoidance of doubt, in cases in which the identity of two or more substituents in a compound of formula I may be the same, the actual identities of the respective substituents are not in any way interdependent.

Where groups are referred to herein as being optionally substituted it is specifically contemplated that such optional substituents may be not present (i.e. references to such optional substituents may be removed), in which case the optionally substituted group may be referred to as being unsubstituted in certain embodiments.

Compounds of formula I may contain double bonds and may thus exist as *E* (*entgegen*) and *Z* (*zusammen*) geometric isomers about each individual double bond. All such isomers and mixtures thereof are included within the scope of the invention.

Compounds of formula I may exist as regioisomers and may also exhibit tautomerism. All tautomeric forms and mixtures thereof are included within the scope of the invention.

Compounds of the invention may also contain one or more asymmetric atoms (e.g. asymmetric carbon atoms) and may therefore exhibit optical isomerism and/or diastereoisomerism. Diastereoisomers may be separated using conventional techniques, e.g. chromatography or fractional crystallisation. The various stereoisomers may be isolated by separation of a racemic or other mixture of the compounds using conventional, e.g. fractional crystallisation or HPLC, techniques. Alternatively the desired optical isomers may be made by reaction of the appropriate optically active starting materials under conditions which will not cause racemisation or epimerisation (i.e. a 'chiral pool' method), by reaction of the appropriate starting material with a 'chiral auxiliary' which can subsequently be removed at a suitable stage, by derivatisation (i.e. a resolution, including a dynamic resolution), for example with a homochiral acid followed by separation of the diastereomeric derivatives by conventional means such as chromatography, or by reaction with an appropriate chiral reagent or chiral catalyst all under conditions known to the skilled person.

All stereoisomers (including but not limited to diastereoisomers, enantiomers and atropisomers) and mixtures thereof (e.g. racemic mixtures) are included within the scope of the invention.

- 5 In the structures shown herein, where the stereochemistry of any particular chiral atom is not specified, then all stereoisomers are contemplated and included as the compounds of the invention. Where stereochemistry is specified by a solid wedge or dashed line representing a particular configuration, then that stereoisomer is so specified and defined.
- 10 Throughout this specification, structures may or may not be presented with chemical names. Where any question arises as to nomenclature, the structure prevails. Where it is possible for the compound to exist as a tautomer (e.g. in an alternative resonance form) the depicted structure represents one of the possible tautomeric forms, wherein the actual tautomeric form(s) observed may vary depending on environmental factors such as
- 15 solvent, temperature or pH. All tautomeric (and resonance) forms and mixtures thereof are included within the scope of the invention.

Unless indicated otherwise, all technical and scientific terms used herein will have their common meaning as understood by one of ordinary skill in the art to which this invention

20 pertains.

For the avoidance of doubt, the skilled person will understand that references herein to particular aspects of the invention (such as the first aspect of the invention) will include references to all embodiments and particular features thereof, which embodiments and

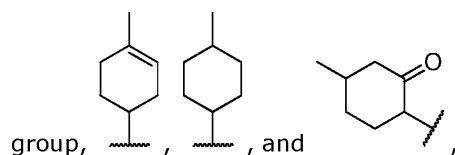
25 particular features may be taken in combination to form further embodiments and features of the invention.

Particular compounds of the invention that may be mentioned are those where n is 1 or 0. Preferably, n is 1.

30

In particular embodiments, R^1 is selected from the group consisting of a C_{1-18} alkyl group, a C_{1-18} alkenyl group, a C_{3-8} cycloalkyl group, a C_{3-6} cycloalkenyl group, a 4- to 6-membered heterocycloalkyl group, and an aryl group;

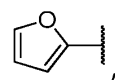
which C₁₋₁₈ alkyl and C₁₋₁₈ alkenyl groups are optionally substituted by one or more substituents each independently selected from the group consisting of =O, -OR⁵, a phenyl

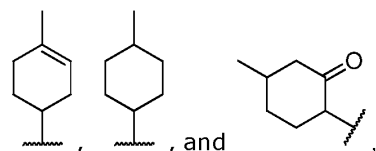


which C₃₋₈ cycloalkyl, C₃₋₆ cycloalkenyl, 4- to 6-membered heterocycloalkyl groups, aryl groups and R⁵ are as defined herein.

Particular compounds of the invention that may also be mentioned are those where R¹ is selected from the group consisting of a C₁₋₁₈ (e.g. C₁₋₆) alkyl group, a C₃₋₈ cycloalkyl group, a C₃₋₆ cycloalkenyl group, and a 5- to 6-membered heteroaryl group, wherein C₁₋₁₈ alkyl, C₃₋₈ cycloalkyl, C₃₋₆ cycloalkenyl group, and heteroaryl groups are as defined herein.

In particular embodiments, R¹ is selected from the group consisting of a C₁₋₆ (e.g. C₁₋₃) alkyl group, a C₆₋₇ (e.g. C₆) cycloalkyl group, a cyclohexenyl group, and a 5-membered heteroaryl group, which C₁₋₆ alkyl groups are optionally substituted by one or more substituents each

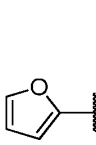
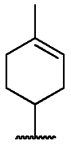
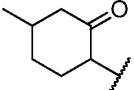
independently selected from the group consisting of =O, -OR⁵, a phenyl group, ,



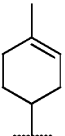
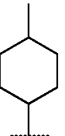
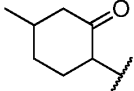
which C₆₋₇ cycloalkyl and cyclohexenyl groups are optionally substituted by one or more substituents each independently selected from the group consisting of =O, a C₁₋₄ alkyl group, and a C₁₋₄ alkenyl group, which 5-membered heteroaryl group is optionally substituted by one or more C₁₋₄ alkyl groups, wherein R⁵ is as defined herein.

25

In certain embodiments, R¹ is a C₁₋₁₈ (e.g. C₁₋₆, such as C₁₋₃) alkyl group, which C₁₋₁₈ alkyl group is optionally substituted by one or more substituents each independently selected

from the group consisting of =O, -OR⁵, a phenyl group, , , , and , and R⁵ is as defined herein.

In other embodiments, R¹ is a C₁₋₁₈ (e.g. C₁₋₆, such as C₁₋₃) alkyl group, which C₁₋₁₈ alkyl group is optionally substituted by one or more substituents each independently selected

from the group consisting of a phenyl group, , , and , and R⁵ is as defined herein.

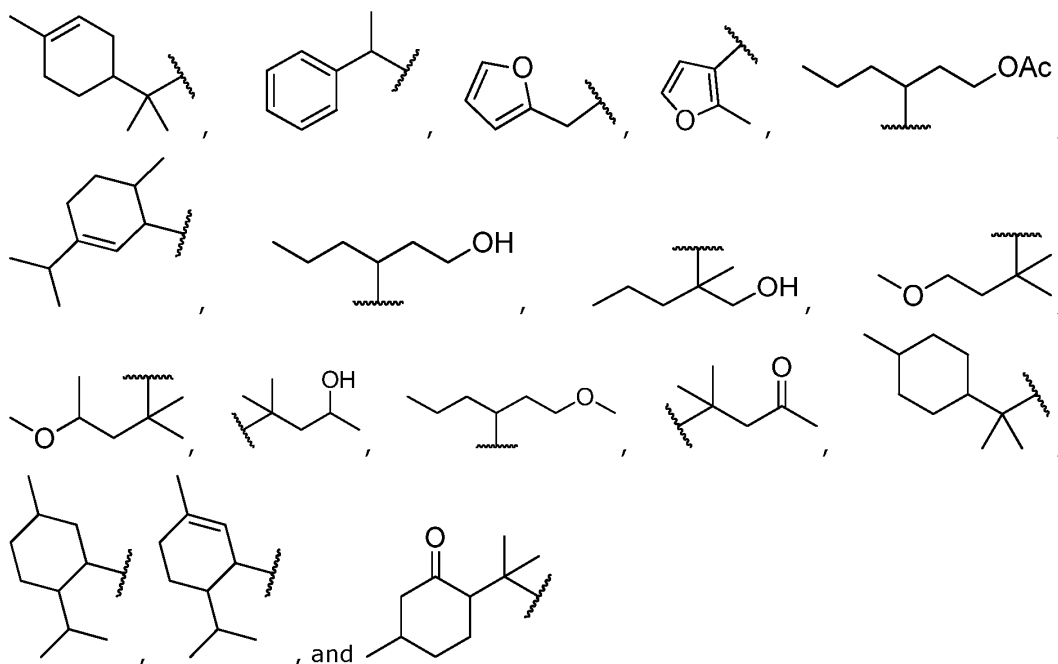
R⁵ is selected from the group consisting of hydrogen, a methyl group, and -C(O)CH₃.

In particular embodiments, R¹ is selected from the group consisting of 2-methylfuran-3-yl, furan-2-ylmethyl, 1-phenylethyl, 1-hydroxyhexan-3-yl, 1-acetoxyhexan-3-yl, benzyl, phenethyl, 6-isopropyl-3-methylcyclohex-2-en-1-yl, 5-methyl-2-(propan-2-ylidene)cyclohexyl, 1-isopropyl-4-methylcyclohex-3-en-1-yl, 2-(4-methylcyclohex-3-en-1-yl)propan-2-yl, 4-isopropyl-1-methylcyclohex-2-en-1-yl, 4-isopropyl-1-methylcyclohex-3-en-1-yl, 1-methyl-4-(propan-2-ylidene)cyclohexyl, 3-isopropyl-6-methylcyclohex-2-en-1-yl, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl, 2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl, 2-methyl-5-(propan-2-ylidene)cyclohexyl, 1-isopropyl-4-methylcyclohexyl, 2-(4-methylcyclohexyl)propan-2-yl, 2-isopropyl-5-methylcyclohexyl, 1-hydroxy-2-methylpentan-2-yl, 1-methoxy-3-methylbutan-3-yl, 2-methoxy-4-methylpentan-4-yl, 4-methylpentan-2-ol-4-yl, 1-methoxyhexan-3-yl, 2-methylpentan-4-on-2-yl and 2-(4-methyl-2-oxo-cyclohexyl)propan-2-yl.

In other embodiments, R¹ is selected from the group consisting of 2-methylfuran-3-yl, furan-2-ylmethyl, 1-phenylethyl, 1-hydroxyhexan-3-yl, 1-acetoxyhexan-3-yl, 2-(4-methylcyclohex-3-en-1-yl)propan-2-yl, 3-isopropyl-6-methylcyclohex-2-en-1-yl, 1-hydroxy-2-methylpentan-2-yl, 1-methoxy-3-methylbutan-3-yl, 2-methoxy-4-methylpentan-4-yl, 4-methylpentan-2-ol-4-yl, 1-methoxyhexan-3-yl and 2-methylpentan-4-on-2-yl.

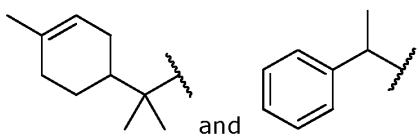
30

In certain embodiments of the invention, R¹ is selected from the group consisting of:



5

Particular compounds of the invention that may be mentioned are those where R¹ is selected from the group consisting of



10 In particular embodiments, R^{6a} and R^{6b} are both hydrogen.

In particular embodiments, R^{7a} is hydrogen and R^{7b} is a C₁₋₄ alkyl group, such as a methyl, ethyl, n-propyl or tert-butyl group.

15 In particular embodiments, R^{8a} is hydrogen and R^{8b} is a C₁₋₄ alkyl group optionally substituted by one or more phenyl groups, such as a benzyl group.

Thus, in particular embodiments of the invention, R^{2a} is selected from the group consisting of hydrogen, methyl, -NH₂, -NH(O)CH₃, -NHC(O)C(CH₃)₃, and -NHCOOCH₂Ph.

20

In particular embodiments, R^{2b} is hydrogen. In other embodiments, R^{2b} is a C₁₋₄ alkyl (e.g. methyl) group.

In a particular embodiment of the invention:

R^{2a} is a C₁₋₄ alkyl (e.g. methyl) group; and
R^{2b} is hydrogen or a C₁₋₄ alkyl (e.g. methyl) group.

In further embodiments, R^{2a} and R^{2b} are both hydrogen.

- 5 In certain embodiments, R^{2a} and R^{2b} are each independently a C₁₋₄ alkyl (e.g. methyl) group.

In particular embodiments that may be mentioned:

R^{2a} is selected from the group consisting of hydrogen, methyl and -NH₂; and

- 10 R^{2b} is hydrogen.

For example, R^{2a} is selected from the group consisting of hydrogen and methyl; and
R^{2b} is hydrogen.

- 15 In other embodiments, R^{2a} is -NH₂ and R^{2b} is hydrogen.

Particular compounds of the invention include those where R³ is -O-.

Alternatively, R³ is -N(R⁹)-, wherein R⁹ is as defined herein (e.g. hydrogen).

20

In certain embodiments of the invention, R⁴ is selected from the group consisting of a C₁₋₁₈ alkyl group, a C₁₋₁₈ alkenyl group, and an aryl group, which C₁₋₁₈ alkyl, C₁₋₁₈ alkenyl and aryl groups is optionally substituted by one or more optionally substituted by one or more -OH or phenyl groups.

25

In other embodiments of the invention, R⁴ is a C₁₋₁₈ alkyl group, which C₁₋₁₈ alkyl group may be optionally substituted with one or hydroxy groups or phenyl groups.

- 30 In further embodiments of the invention, R⁴ is selected from the group consisting of hydrogen, methyl, ethyl, butyl (e.g. n-butyl), hexyl (e.g. n-hexyl), benzyl, 1-phenylethyl, ethylhexyl, octyl (e.g. iso-octyl), octadecyl, 2-phenylethyl, hydroxyethyl, hydroxybutyl, and hydroxydecyl groups.

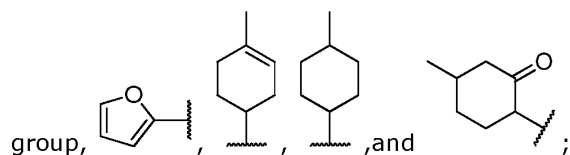
In particular embodiments, R⁴ is a C₁₋₈ alkyl group (e.g. methyl, ethyl, or butyl) group.

35

Particular embodiments of the invention include compounds of formula I (including all embodiments and particular features, and combinations thereof) wherein:

n is 1

R¹ is a C₁₋₆ (e.g. C₁₋₃) alkyl group optionally substituted by one or more substituents each independently selected from the group consisting of =O, -OH, -OCH₃, -C(O)CH₃, a phenyl



R^{2a} is selected from the group consisting of hydrogen, C₁₋₄ alkyl group, and -NH₂;

- 5 R^{2b} is selected from the group consisting of hydrogen and a C₁₋₄ alkyl group;

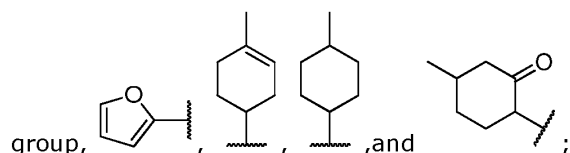
R³ is -O-; and

R⁴ is a C₁₋₁₈ (e.g. C₁₋₈) alkyl group optionally substituted with one or hydroxy groups or phenyl groups.

- 10 In particular embodiments:

n is 1

R¹ is a C₁₋₆ (e.g. C₁₋₃) alkyl group optionally substituted by one or more substituents each independently selected from the group consisting of =O, -OH, -OCH₃, -C(O)CH₃, a phenyl



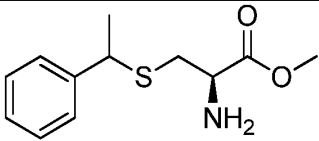
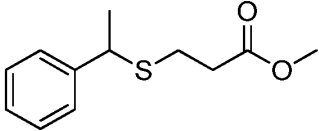
- 15 R^{2a} is selected from the group consisting of hydrogen, a methyl group, and -NH₂;

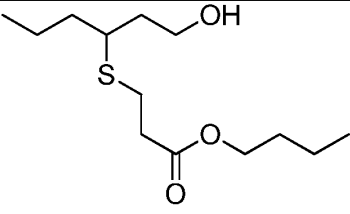
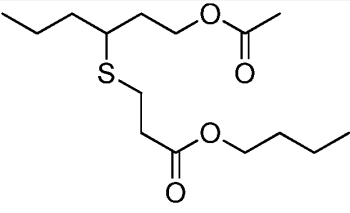
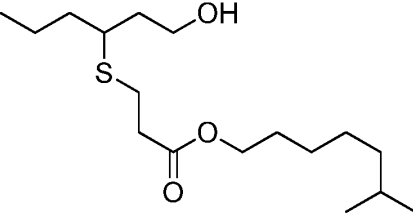
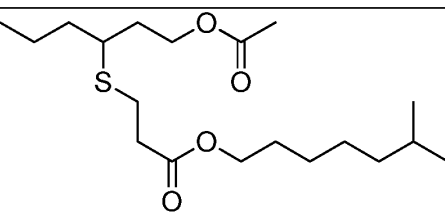
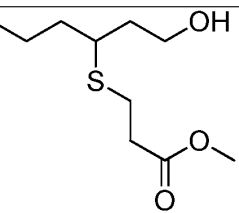
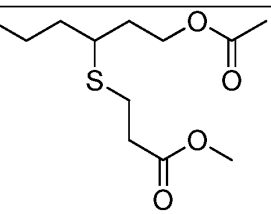
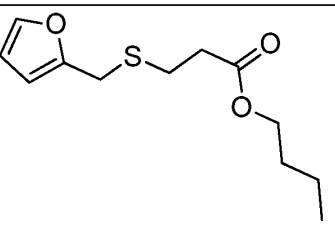
R^{2b} is hydrogen;

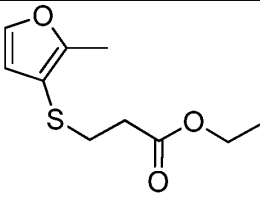
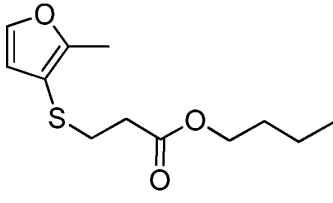
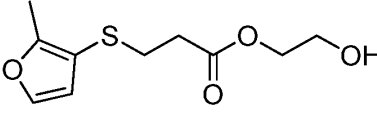
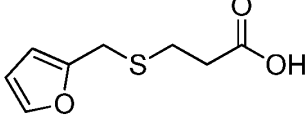
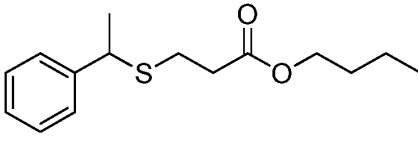
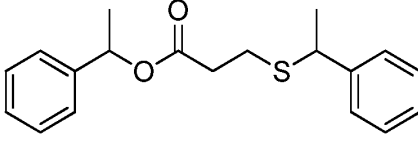
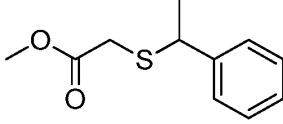
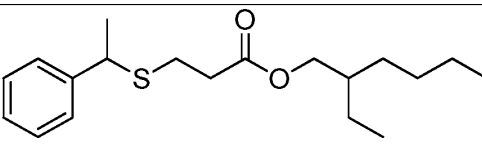
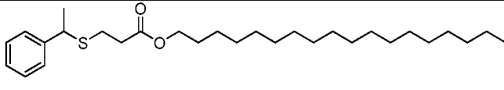
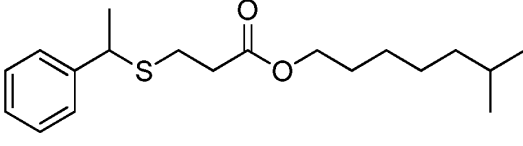
R³ is -O-; and

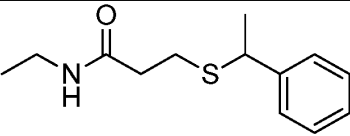
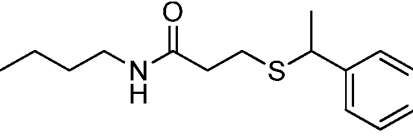
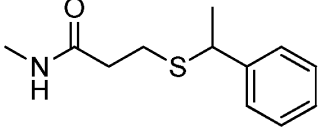
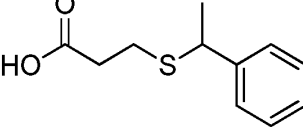
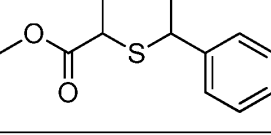
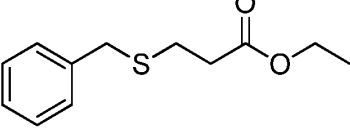
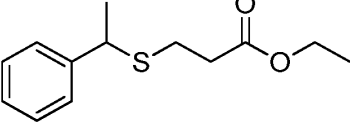
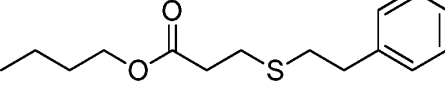
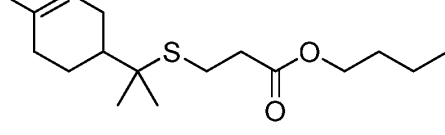
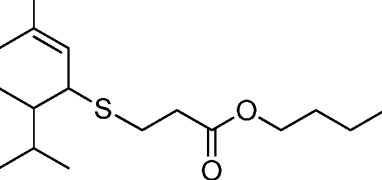
R⁴ is a C₁₋₁₈ alkyl group.

- 20 Particularly preferred compounds of the invention (or salts or solvates thereof) are depicted in Table 1, below.

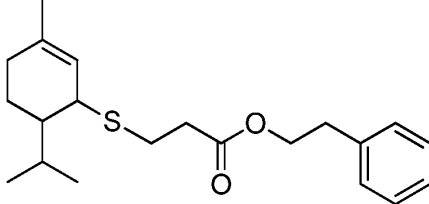
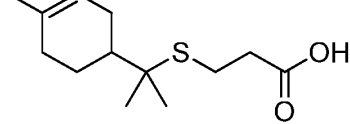
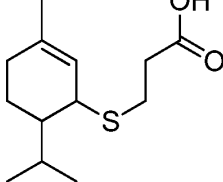
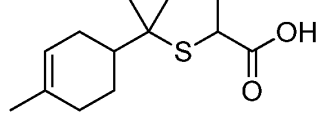
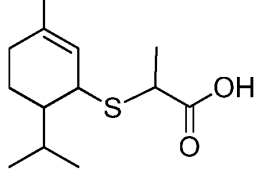
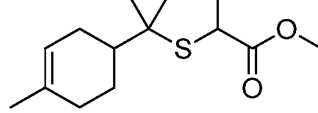
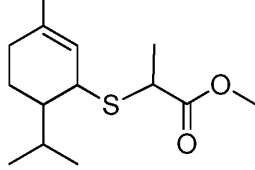
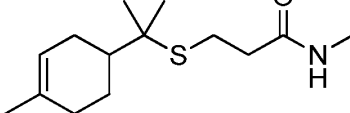
No.	Compound Name	Compound Structure
1	Ethyl S-(furan-2-ylmethyl)-L-cysteinate	
2	Methyl 3-((1-phenylethyl)thio)propanoate	

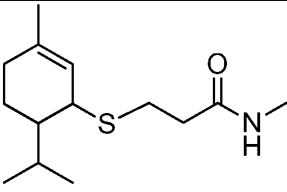
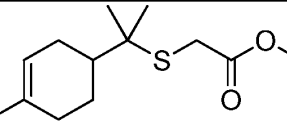
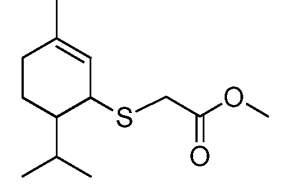
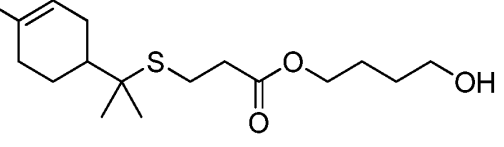
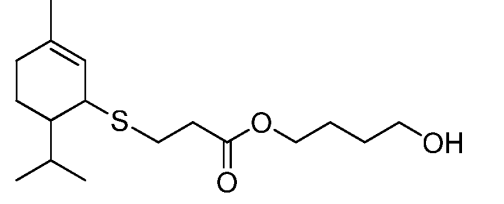
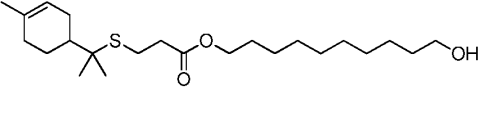
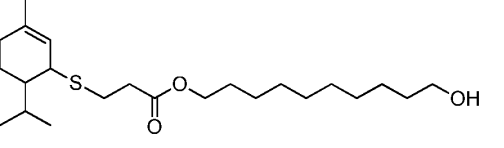
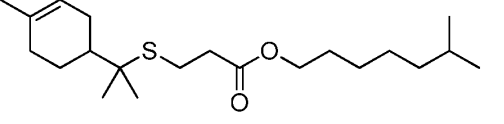
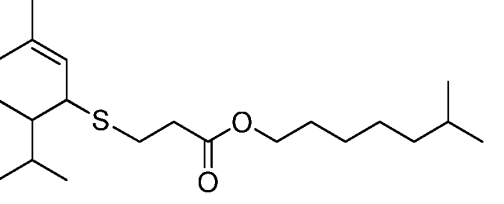
No.	Compound Name	Compound Structure
3	Butyl 3-((1-hydroxyhexan-3-yl)thio)propanoate	
4	Butyl 3-((1-acetoxyhexan-3-yl)thio)propanoate	
5	Isooctyl 3-((1-hydroxyhexan-3-yl)thio)propanoate	
6	6-Methylheptyl 3-((1-acetoxyhexan-3-yl)thio)propanoate	
7	Methyl 3-((1-hydroxyhexan-3-yl)thio)propanoate	
8	Methyl 3-((1-acetoxyhexan-3-yl)thio)propanoate	
11	Butyl 3-((furan-2-yl)methylthio)propanoate	

No.	Compound Name	Compound Structure
12	Ethyl 3-((2-methylfuran-3-yl)thio)propanoate	
13	Butyl 3-((2-methylfuran-3-yl)thio)propanoate	
14	2-Hydroxyethyl 3-((2-methylfuran-3-yl)thio)propanoate	
15	3-((Furan-2-ylmethyl)thio)propanoic acid	
17	Butyl 3-((1-phenylethyl)thio)propanoate	
18	1-Phenylethyl 3-((1-phenylethyl)thio)propanoate	
19	Methyl 2-((1-phenylethyl)thio)acetate	
20	2-Ethylhexyl 3-((1-phenylethyl)thio)propanoate	
21	Octadecyl 3-((1-phenylethyl)thio)propanoate	
22	Isooctyl 3-((1-phenylethyl)thio)propanoate	

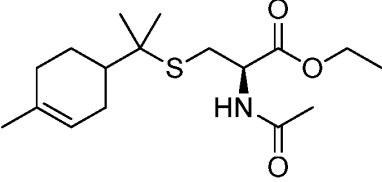
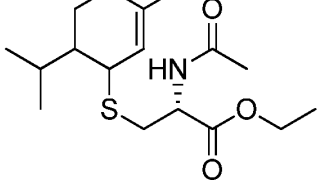
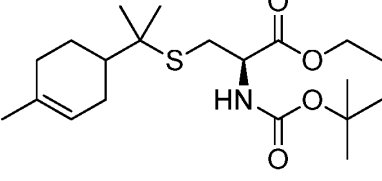
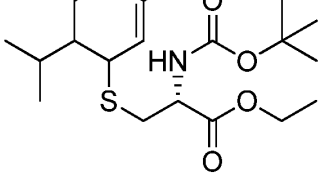
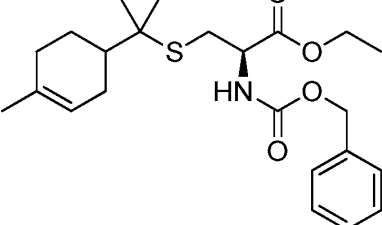
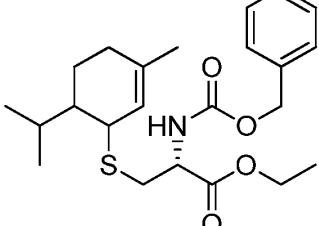
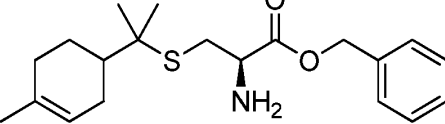
No.	Compound Name	Compound Structure
23	N-Ethyl-3-((1-phenylethyl)thio)propanamide	
24	N-Butyl-3-((1-phenylethyl)thio)propanamide	
25	N-Methyl-3-((1-phenylethyl)thio)propanamide	
26	3-((1-Phenylethyl)thio)propanoic acid	
27	Methyl 2-((1-phenylethyl)thio)propanoate	
28	Ethyl 3-(benzylthio)propanoate	
29	Ethyl 3-((1-phenylethyl)thio)propanoate	
30	Butyl 3-(phenethylthio)propanoate	
31a	Butyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
31b	Butyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	

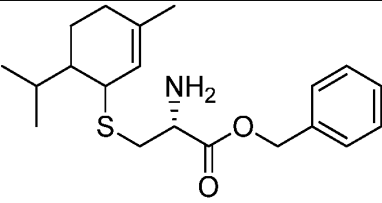
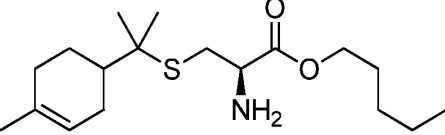
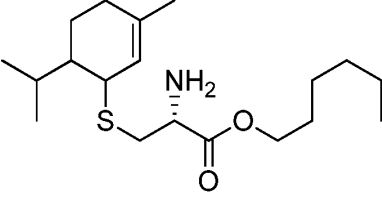
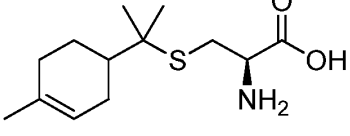
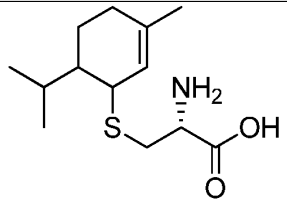
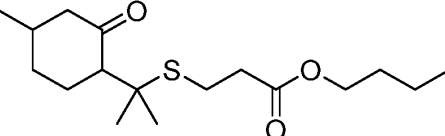
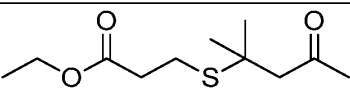
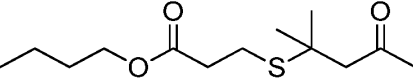
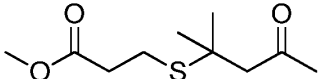
No.	Compound Name	Compound Structure
32a	Methyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
32b	Methyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
33a	Ethyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
33b	Ethyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
34a	Octadecyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
34b	Octadecyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
35a	2-Ethylhexyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
35b	2-Ethylhexyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
36a	Phenethyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	

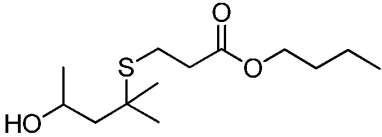
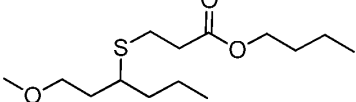
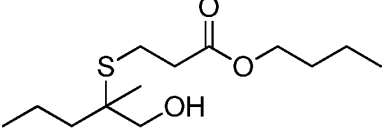
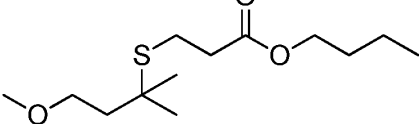
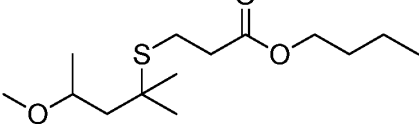
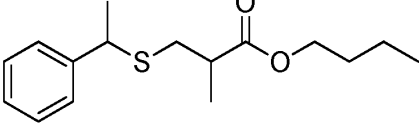
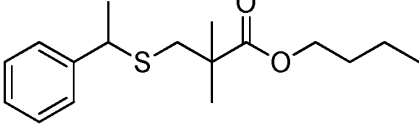
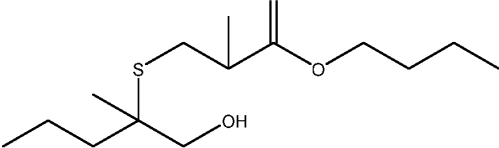
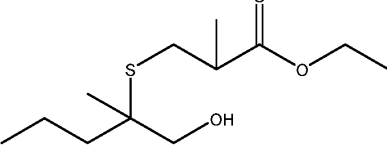
No.	Compound Name	Compound Structure
36b	Phenethyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
37a	3-((2-(4-Methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoic acid	
37b	3-((6-Isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoic acid	
38a	2-((2-(4-Methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoic acid	
38b	2-((6-Isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoic acid	
39a	Methyl 2-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
39b	Methyl 2-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
40a	N-Methyl-3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanamide	

No.	Compound Name	Compound Structure
40b	3-((6-Isopropyl-3-methylcyclohex-2-en-1-yl)thio)-N-methylpropanamide	
41a	Methyl 2-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)acetate	
41b	Methyl 2-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)acetate	
42a	4-Hydroxybutyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
42b	4-Hydroxybutyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
43a	10-Hydroxydecyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
43b	10-Hydroxydecyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
44a	6-Methylheptyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
44b	6-Methylheptyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	

No.	Compound Name	Compound Structure
45a	Methyl 3-((2-(4-methylcyclohexyl)propan-2-yl)thio)propanoate	
45b	Methyl 3-((2-isopropyl-5-methylcyclohexyl)thio)propanoate	
46a	(R)-Ethyl 2-amino-3-((2-(4-methylcyclohexyl)propan-2-yl)thio)propanoate	
46b	(2R)-Ethyl 2-amino-3-((2-isopropyl-5-methylcyclohexyl)thio)propanoate	
47a	(2R)-Ethyl 2-amino-3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
47a1	Ethyl 2-amino-3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate (racemic mixture)	
47b	(2R)-Ethyl 2-amino-3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
47b1	Ethyl 2-amino-3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate (racemic mixture)	

No.	Compound Name	Compound Structure
48a	(2R)-Ethyl 2-acetamido-3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
48b	(2R)-Ethyl 2-acetamido-3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
49a	(2R)-Ethyl 2-((tert-butoxycarbonyl)amino)-3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
49b	(2R)-Ethyl 2-((tert-butoxycarbonyl)amino)-3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
50a	(2R)-Ethyl 2-(((benzyloxy)carbonyl)amino)-3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
50b	(2R)-Ethyl 2-(((benzyloxy)carbonyl)amino)-3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
51a	(2R)-Benzyl 2-amino-3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	

No.	Compound Name	Compound Structure
51b	(2R)-Benzyl 2-amino-3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
52a	(2R)-Hexyl 2-amino-3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
52b	(2R)-Hexyl 2-amino-3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
53a	(2R)-2-Amino-3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoic acid	
53b	(2R)-2-Amino-3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoic acid	
54	Butyl 3-((2-(4-methyl-2-oxocyclohexyl)propan-2-yl)thio)propanoate	
55	Ethyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate	
56	Butyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate	
57	Methyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate	

No.	Compound Name	Compound Structure
58	Butyl 3-((4-hydroxy-2-methylpentan-2-yl)thio)propanoate	
59	Butyl 3-((1-methoxyhexan-3-yl)thio)propanoate	
60	Butyl 3-((1-hydroxy-2-methylpentan-2-yl)thio)propanoate	
61	Butyl 3-((4-methoxy-2-methylbutan-2-yl)thio)propanoate	
62	Butyl 3-((4-methoxy-2-methylpentan-2-yl)thio)propanoate	
63	Butyl 2-methyl-3-((1-phenylethyl)thio)propanoate	
64	Butyl 2,2-dimethyl-3-((1-phenylethyl)thio)propanoate	
65	Butyl 3-((1-hydroxy-2-methylpentan-2-yl)thio)-2-methylpropanoate	
66	Ethyl 3-((1-hydroxy-2-methylpentan-2-yl)thio)-2-methylpropanoate	

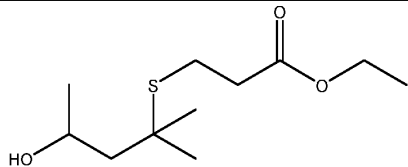
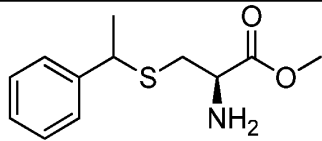
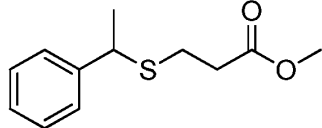
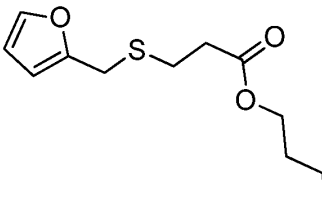
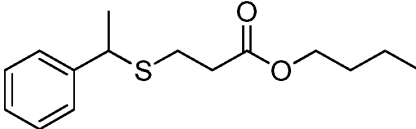
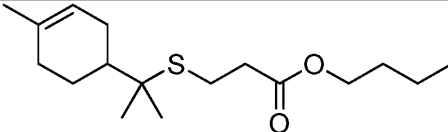
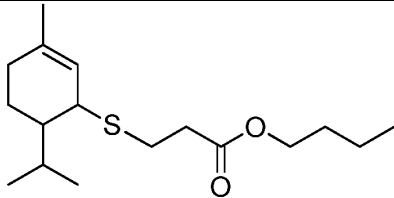
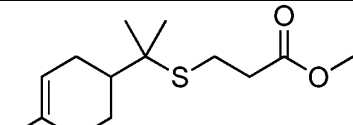
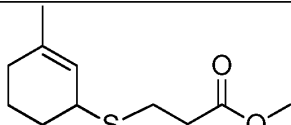
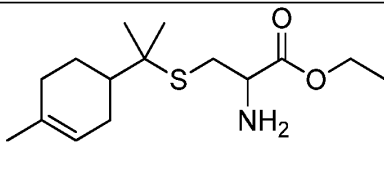
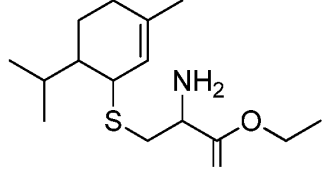
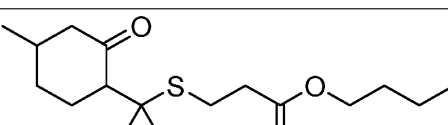
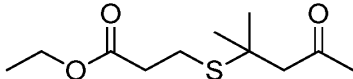
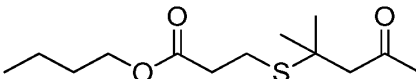
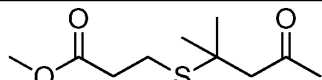
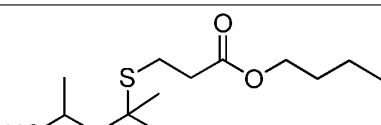
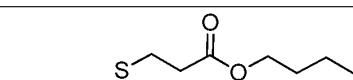
No.	Compound Name	Compound Structure
67	Ethyl 3-((4-hydroxy-2-methylpentan-2-yl)thio)propanoate	

Table 1.

Certain preferred compounds of the invention (or salts or solvates thereof) are depicted in Table 2, below.

No.	Compound Name	Compound Structure
1	Ethyl S-(furan-2-ylmethyl)-L-cysteinate	
2	Methyl 3-((1-phenylethyl)thio)propanoate	
11	Butyl 3-((furan-2-ylmethyl)thio)propanoate	
17	Butyl 3-((1-phenylethyl)thio)propanoate	
31a	Butyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
31b	Butyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	

No.	Compound Name	Compound Structure
32a	Methyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate	
32b	Methyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate	
47a1	Ethyl 2-amino-3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate (racemic mixture)	
47b1	Ethyl 2-amino-3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate (racemic mixture)	
54	Butyl 3-((2-(4-methyl-2-oxocyclohexyl)propan-2-yl)thio)propanoate	
55	Ethyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate	
56	Butyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate	
57	Methyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate	
58	Butyl 3-((4-hydroxy-2-methylpentan-2-yl)thio)propanoate	
59	Butyl 3-((1-methoxyhexan-3-yl)thio)propanoate	

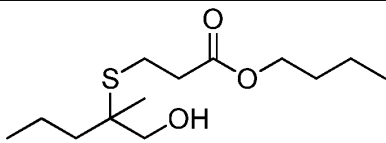
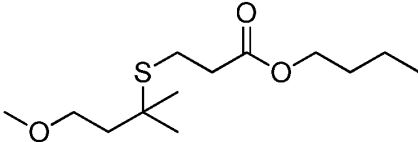
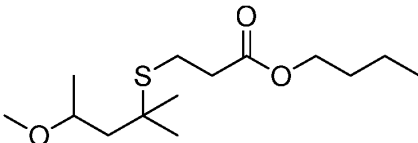
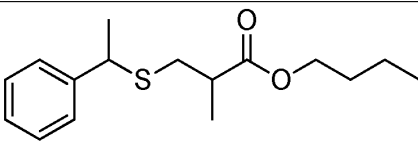
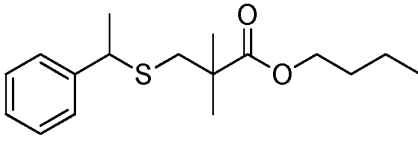
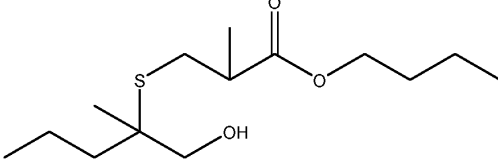
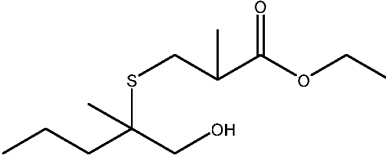
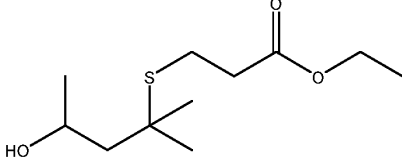
No.	Compound Name	Compound Structure
60	Butyl 3-((1-hydroxy-2-methylpentan-2-yl)thio)propanoate	
61	Butyl 3-((4-methoxy-2-methylbutan-2-yl)thio)propanoate	
62	Butyl 3-((4-methoxy-2-methylpentan-2-yl)thio)propanoate	
63	Butyl 2-methyl-3-((1-phenylethyl)thio)propanoate	
64	Butyl 2,2-dimethyl-3-((1-phenylethyl)thio)propanoate	
65	Butyl 3-((1-hydroxy-2-methylpentan-2-yl)thio)-2-methylpropanoate	
66	Ethyl 3-((1-hydroxy-2-methylpentan-2-yl)thio)-2-methylpropanoate	
67	Ethyl 3-((4-hydroxy-2-methylpentan-2-yl)thio)propanoate	

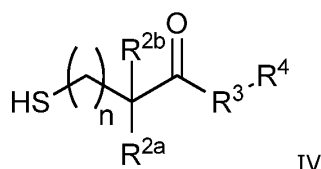
Table 2.

Preparation

Compounds of the invention as described herein may be prepared in accordance with techniques that are well known to those skilled in the art, such as those described in the examples provided hereinafter.

Compounds of formula I may be obtained by analogy with the processes known in the literature, or by conventional synthetic procedures, in accordance with standard techniques, from available starting materials using appropriate reagents and reaction conditions. In this respect, the skilled person may refer to inter alia "Comprehensive Organic Synthesis" by B. M. Trost and I. Fleming, Pergamon Press, 1991.

For example, according to a second aspect of the invention, there is provided a process for preparing a compound of formula I, which process comprises a reaction of a compound of formula IV,



with

(a) a compound of formula V,



wherein n, R¹, R^{2a}, R^{2b}, R³, and R⁴ are as defined above and X is a suitable leaving group (such as a chlorine atom, a bromide atom or a tosyl group), in the presence of, as appropriate, a suitable base (e.g. potassium carbonate and/or potassium iodide) and/or a suitable solvent (e.g. toluene or acetone) according to procedures known to the person skilled in the art.

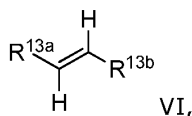
Compounds of formula IV and compounds of formula V may be commercially available, known in the literature, or may be obtained by conventional synthetic procedures, in accordance with standard techniques, from available starting materials using appropriate reagents and reaction conditions.

Alternatively, there is provided a process for preparing a compound of formula I, which process comprises a reaction of a compound of formula IV as defined hereinabove with a suitable alkene, in the presence of a suitable coupling agent (e.g. 1,8-

diazabicyclo[5.4.0]undec-7-ene) and a suitable solvent (e.g. tetrahydrofuran) according to procedures known to the person skilled in the art.

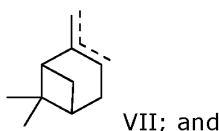
As defined herein, "suitable alkenes" include, for example:

- 5 (a) compounds of formula VI



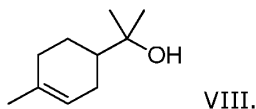
- wherein R^{13a} is hydrogen or a C_{1-3} alkyl group; and R^{13b} is a C_{1-3} alkyl group or a phenyl group, which C_{1-3} alkyl group is optionally substituted by one or more $=O$ or $-OR^4$ groups, and R^4 is as defined herein;
- 10

- (b) compounds of formula VII



15

- (c) a compound of formula VIII



- Compounds of formulae VI, VII and VIII may be commercially available, known in the literature, or may be obtained by conventional synthetic procedures, in accordance with standard techniques, from available starting materials using appropriate reagents and reaction conditions.
- 20

- The skilled person would recognise that fragrance molecules (particularly the fragrant thiol molecules described herein) are molecules used as ingredients in perfumery or flavour preparations or compositions which impart or modify in a positive or pleasant way the odour of a preparation or composition, and not just as having an odour.
- 25

- Conventionally, the skilled person would expect that in the synthesis of a precursor adapted to release a fragrant thiol, the fragrant thiol would be employed as a reagent to both introduce the sulphur atom and form the cleavable carbon-sulphur bond in the formed precursor. This is expected, not least, because it is the most labile bond. However, this approach would carry with it the disadvantage in the sense that a reagent in the formation
- 30

of the precursor would be the highly potent fragrant thiol. Using such reagents having such potent odours is not efficient in that the reaction vessel in its manufacture will need to be scrupulously cleaned before it can be used for other purposes, in a time-consuming and costly process.

5

The process of the present invention overcomes this disadvantage by using a low-odour sulphur-containing reagent to introduce the sulphur atom in the preparation of the precursor. In other words, the sulphur atom is introduced by a reagent that is not a fragrant thiol.

10

Formulations

In accordance with the third aspect of the invention, there is provided a perfume composition comprising the compound of formula I as defined in the first aspect of the invention. All embodiments and particular features thereof described herein in respect of the first aspect of the invention are disclosed herein in respect of the third aspect of the invention.

The perfume compositions in accordance with the third aspect of the invention may be prepared in accordance with standard and/or accepted manufacturing practice.

In particular embodiments of the invention, the perfume compositions contain a compound of formula (I) and at least one additional perfume ingredient or solvent used in perfumery such as diethyl phthalate (DEP), dipropylene glycol (DPG), isopropyl myristate (IPM), triethyl citrate (TEC) or an alcohol such as ethanol, or mixtures thereof.

Particular types of complementary perfume ingredients may be selected from citrus, orange flower, fruity esters, aldehydes, ketones, ingredients that possess a green odour note, musky and woody ingredients, as well as red berry and exotic fruit notes. It is preferred that a fragrance composition contains perfume ingredients independently selected from at least one, at least two, at least three, at least four, at least five, at least six, at least seven, at least eight, at least nine or at least ten ingredients from one or more of the aforementioned categories of ingredients.

Examples of fruity esters, aldehydes and ketones include but are not limited to allyl hexanoate, allyl cyclohexanepropionate, butyl acetate, ethyl butyrate, ethyl decanoate, ethyl 2-methylpropanoate, ethyl 3-methylbutanoate, ethyl 2-methylbutanoate, ethyl

octanoate, ethyl heptanoate, hex-3-en-1-yl acetate, hexyl acetate, hexyl 2-methylpropanoate, 3-methylbutyl acetate
isobutyl acetate, isobutyl 2-methylpropanoate, ethyl 2-methylpentanoate and octahydro-1H-4,7-methanoindene-1-carbaldehyde.

5

Examples of complementary perfume ingredients possessing a green note include but are not limited to allyl (3-methylbutoxy)acetate, 2,4-dimethylcyclohex-3-ene-1-carbaldehyde, allyl (cyclohexyloxy)acetate 1,1'-oxydibenzene, 1-(5,5-dimethylcyclohex-1-en-1-yl)pent-4-en-1-one, 1-phenylethyl acetate, hex-3-en-1-ol, hex-3-en-1-yl butyrate, 4-methyl-2-
10 (2-methylprop-1-en-1-yl)tetrahydro-2H-pyran, 2,4-dimethylcyclohex-3-ene-1-carbaldehyde, 4-methyl-3-decen-5-ol and (2,2-dimethoxyethyl)benzene.

Examples of musky or woody complementary perfume ingredients include but are not limited to 1,4-dioxacyclohexadecane-5,16-dione, 4-tert-butylcyclohexyl acetate, [3R-
15 (3 α ,3 β ,6 α ,7 β ,8 α)]-octahydro-6-methoxy-3,6,8,8-tetramethyl-1H-3a,7-methanoazulene, 1-(2,3,8,8-Tetramethyl-1,2,3,4,5,6,7,8-octahydronaphthalen-2-yl)ethanone and 3-Methyl-5-(2,2,3-trimethylcyclopent-3-en-1-yl)pentan-2-ol.

Other ingredients that can be used to complement the compounds of the present invention
20 in flavour or perfumery applications include but are not limited to (E)-3,7-dimethylocta-2,6-dienal (e.g. CITRAL); 1-methyl-4-prop-1-en-2-yl-cyclohexene (e.g. LIMONENE); 3,7-dimethyloct-6-enal (e.g. CITRONELLAL); (2E,6Z)-3,7-dimethylnona-2,6-dienitrile (e.g. LEMONILE); 1-methyl-4-propan-2-ylcyclohexa-1,4-diene (e.g. TERPINENE GAMMA); lemon oils; orange oils; mandarin oils; grapefruit oils; lime oils; tangerine oils; orange
25 terpenes; 1-(2-naphthalenyl)-ethanone (e.g. ORANGER CRYSTALS); 2-ethoxynaphthalene (e.g. NEROLINE); methyl 2-aminobenzoate (e.g. METHYL ANTHRANILATE); methyl 2-(methylamino)benzoate (e.g. DIMETHYL ANTHRANILATE); (2-(1-ethoxyethoxy)ethyl)benzene (e.g. ACETAL E); (2-(1-propoxyethoxy)ethyl)benzene (e.g. ACETAL R); prop-2-enyl 2-(3-methylbutoxy)acetate (e.g. ALLYL AMYL GLYCOLATE); (2-
30 (isopentyloxy)ethyl)benzene (e.g. ANTHER); 2,4-dimethylcyclohex-3-ene-1-carbaldehyde (e.g. CYCLAL C); allyl 2-(cyclohexyloxy)acetate (e.g. CYCLOGALBANATE); oct-2-ynoate (e.g. FOLIONE); 1-(5,5-dimethylcyclohex-1-en-1-yl)pent-4-en-1-one (e.g. GALBANONE PURE); 1-phenylethyl acetate (e.g. GARDENOL); (E)-hex-2-en-1-ol (e.g. HEXENOL TRANS-2); (Z)-hex-3-en-1-ol (e.g. HEXENOL-3-CIS); (Z)-hex-3-en-1-yl butanoate (e.g. HEXENYL-3-CIS BUTYRATE); (Z)-hex-3-en-1-yl formate; (Z)-hex-3-en-1-yl (Z)-hex-3-enoate (e.g. HEXENYL-3-CIS HEXENOATE); (Z)-hex-3-en-1-yl 2-methylpropanoate (e.g. HEXENYL-3-CIS ISOBUTYRATE); (Z)-hex-3-en-1-yl propanoate (e.g. HEXENYL-3-CIS PROPIONATE); (Z)-hex-3-enyl] (E)-2-methylbut-2-enoate (e.g. HEXENYL-3-CIS

TIGLATE); 2,4,6-trimethylcyclohex-3-enecarbaldehyde (e.g. ISOCYCLOCITRAL); (Z)-1-(1-ethoxyethoxy)hex-3-ene (e.g. LEAF ACETAL); methyl non-2-ynoate (e.g. METHYL OCTYNE CARBONATE); (E)-methyl non-2-enoate (e.g. NEOFOLIONE); (2E,6Z)-nona-2,6-dienal (e.g. NONADIENAL); (2Z,6E)-2,6-nonadien-1-ol (e.g. NONADIENOL-2,6); (Z)-non-6-enal (e.g. NONENAL-6-CIS); 1,1-dimethoxynon-2-yne (e.g. PARMAVERT); 4-methyl-2-(2-methylprop-1-en-1-yl)tetrahydro-2H-pyran (e.g. ROSE OXIDE); 4-methyl-2-phenyl-3,6-dihydro-2H-pyran (e.g. ROSYRANE SUPER); 1-(spiro[4.5]dec-6-en-7-yl)pent-4-en-1-one (e.g. SPIROGALBANONE); (E)-5-methylheptan-3-one oxime (e.g. STEMONE); 1-phenylethyl propanoate (e.g. STYRALLYL PROPIONATE); 2,4-dimethylcyclohex-3-enecarbaldehyde (e.g. TRICYCLAL); (3E,5Z)-undeca-1,3,5-triene (e.g. UNDECATRIENE); (E)-4-methyldec-3-en-5-ol (e.g. UNDECAVERTOL); (E)-undeca-1,3-dien-5-yne (e.g. VIOLETTYNE); undec-10-enenitrile (e.g. VIOLIFF); 2-(2,4-dimethylcyclohexyl)pyridine (e.g. ZINARINE); galbanum extracts; allyl 2-phenoxyacetate (e.g. ACETATE PA); prop-2-enyl hexanoate (e.g. ALLYL CAPROATE); prop-2-enyl heptanoate (e.g. ALLYL OENANTHATE); pentyl butanoate (e.g. AMYL BUTYRATE); (E)-methyl octa-4,7-dienoate (e.g. ANAPEAR); benzyl butanoate (e.g. BENZYL BUTYRATE); benzyl 3-phenylprop-2-enoate (e.g. BENZYL CINNAMATE); butyl acetate; 2-methylpropyl acetate; 2-cyclohexylethyl acetate; (E)-1-(2,6,6-trimethylcyclohexa-1,3-dien-1-yl)but-2-en-1-one (e.g. DAMASCENONE); (E)-1-(2,6,6-trimethylcyclohex-2-en-1-yl)but-2-en-1-one (e.g. DAMASCONE ALPHA); (E)-1-(2,6,6-trimethyl-1-cyclohexenyl)but-2-en-1-one (e.g. DAMASCONE BETA); 1-(2,6,6-trimethyl-1-cyclohex-3-enyl)but-2-en-1-one (e.g. DAMASCONE DELTA); 6-pentyltetrahydro-2H-pyran-2-one (e.g. DECALACTONE DELTA); 5-hexyloxolan-2-one (e.g. DECALACTONE GAMMA); 2-methyl-1-phenylpropan-2-yl butanoate (e.g. DIMETHYL BENZYL CARBINYL BUTYRATE); 6-heptyltetrahydro-2H-pyran-2-one (e.g. DODECALACTONE DELTA); 5-octyloxolan-2-one (e.g. DODECALACTONE GAMMA); ethyl acetate; ethyl 3-oxobutanoate (e.g. ETHYL ACETOACETATE); ethyl butanoate (e.g. ETHYL BUTYRATE); ethyl 3-phenylprop-2-enoate (e.g. ETHYL CINNAMATE); ethyl hexanoate (e.g. ETHYL HEXANOATE); ethyl 2-methylpropanoate (e.g. ETHYL ISOBUTYRATE); ethyl 3-methylbutanoate (e.g. ETHYL ISOVALERATE); ethyl 2-methylbutanoate (e.g. ETHYL METHYL-2-BUTYRATE); ethyl octanoate (e.g. ETHYL OCTANOATE); ethyl heptanoate (e.g. ETHYL OENANTHATE); ethyl propionate; ethyl 2-(2-methyl-1,3-dioxolan-2-yl)acetate (e.g. FRUCTONE); (Z)-hex-3-en-1-yl acetate (e.g. HEXENYL-3-CIS ACETATE); (Z)-hex-3-en-1-yl 2-methyl butanoate (e.g. HEXENYL-3-CIS METHYL-2-BUTYRATE); hexyl acetate; hexyl butanoate (e.g. HEXYL BUTYRATE); hexyl 2-methylpropanoate (e.g. HEXYL ISOBUTYRATE); hexyl propionate; 3-methylbutyl acetate (e.g. ISOAMYL ACETATE); 3-methylbutyl butanoate (e.g. ISOAMYL BUTYRATE); 3-methylbutyl propanoate (e.g. ISOAMYL PROPIONATE); 2-methylpropyl benzoate (e.g. ISOBUTYL BENZOATE); 3-methylbutyl 3-methylbutanoate (e.g. ISOPENTYL

ISOVALERATE); isopropyl 2-methylbutanoate (e.g. ISOPROPYL METHYL-2-BUTYRATE); (Z)-hex-3-en-1-yl methyl carbonate (e.g. LIFFAROME); 2-methyl-4-oxo-4H-pyran-3-yl 2-methylpropanoate (e.g. MALTYL ISOBUTYRATE); ethyl 2-methylpentanoate (e.g. MANZANATE); heptan-2-one (e.g. METHYL AMYL KETONE); butyl 2-methylpentanoate (e.g. METHYL CAMOMILLE); methyl 3-phenylprop-2-enoate (e.g. METHYL CINNAMATE); 5-hexyl-5-methyloxolan-2-one (e.g. METHYL DECALACTONE GAMMA); 6-methylhept-5-en-2-one (e.g. METHYL HEPTENONE PURE); methyl 2-methylbutanoate (e.g. METHYL METHYL-2 BUTYRATE); (E)-2-methylpent-2-enoic acid (e.g. METHYL-2-PENTENOIC ACID, 2-); 2-(2-(4-methylcyclohex-3-en-1-yl)propyl)cyclopentan-1-one (e.g. NECTARYL); 5-heptyldihydrofuran-2(3H)-one (e.g. PEACH PURE); 2-phenylethyl butanoate (e.g. PHENYL ETHYL BUTYRATE); 2-phenylethyl 2-methylpropanoate (e.g. PHENYL ETHYL ISOBUTYRATE); (2E,5E)-5,6,7-trimethylocta-2,5-dien-4-one (e.g. POMAROSE); 3-methylbut-2-en-1-yl acetate (e.g. PRENYL ACETATE); 4-(4-hydroxyphenyl)butan-2-one (e.g. RASPBERRY KETONE); (4aR,8aS,E)-6-ethylideneoctahydro-2H-5,8-methanochromene (e.g. RHUBOFLOL); 1,1-diethoxycyclohexane (e.g. RUM ACETAL); 6-hexyltetrahydro-2H-pyran-2-one (e.g. UNDECALACTONE DELTA); and mixtures thereof.

In some embodiments, stabilizing compounds, for example alpha tocopherol, EDTA, ascorbic acid, BHT, Tinogard TT, Tinogard DA, Tinogard TS can be added to the compounds of formula (I), for example in 0.001-1% by weight, to limit or prevent premature cleavage of the compound of formula (I). In particular, the stabilizing compounds can be used to enhance the stability of the neat compounds of formula (I). In a preferred embodiment, the stabilizing compound may be a biodegradable compound (for example alpha tocopherol, ascorbic acid or Tinogard DA).

The perfume compositions according to the invention are useful as such in fine perfumery, or can be used to fragrance all manner of consumer products, such as household care, personal care, laundry care and cosmetic products. Examples of such products include cosmetics, shampoos, shower gels, deodorants, antiperspirants, laundry detergents (in solid or liquid forms), rinse conditioners, fabric softeners, detergents for dishwashers, surface cleaners, in particular for hard and soft surfaces, soaps, especially bar soap, and air care products, especially air freshener or fine fragrances.

In a specific embodiment, the consumer product is selected from the group consisting of a powder detergent, liquid detergent, fabric softener, bar soap and air freshener.

Accordingly, in a fourth aspect of the invention there is provided a consumer product, such as a fine perfume or a household care, personal care, laundry care and cosmetic products, comprising a compound of formula (I) or a perfume composition containing same.

- 5 The compounds of the invention may be formulated at various concentrations, depending upon the particular hedonic effect the perfumer or flavourist would like to create. For example, the amount of the compound of the invention present in a perfume or flavour composition is from about 0.0001 to about 10 weight (wt.) %, preferably from about 0.001 to about 1 wt.%, and even more preferably from about 0.001 to about 0.5 wt.% of total
10 weight of the perfume or flavour composition. Perfume or flavour compositions may be incorporated into consumer products in typical dilutions, for example from about 0.5 to about 10 wt.% based on the weight of the consumer product.

- The term "about" as used herein when referring to a measurable value such as an amount
15 of a compound, dose, time, temperature, and the like, refers to variations of 20%, 10%, 5%, 1%, 0.5%, or even 0.1% of the specified amount. It is contemplated that, at each instance, such terms may be replaced with the notation " $\pm 10\%$ ", or the like (or by indicating a variance of a specific amount calculated based on the relevant value). It is also contemplated that, at each instance, such terms may be deleted.

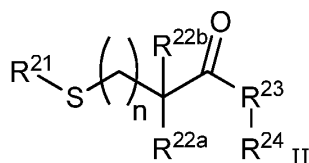
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Uses

- As indicated herein, the compounds of the invention are useful as precursors for the generation of fragrance molecules in consumer product, such as personal, laundry, or
25 household care products. Compounds of the invention are useful because they are capable of degrading under ambient conditions, e.g. of moisture and/or temperature and exposure to oxygen, to release highly potent fragrance molecules, particularly thiols, may give off a pleasant aroma (e.g. citrus fruits, cassis, coffee aromas). This is desirable in certain consumer (e.g. cosmetics, cleaning such as but not limited to house cleaning, leave on
30 and rinse-off applications, air-care such as but not limited to air freshener, and laundry) applications. Another possible application area is for fine fragrances.

- The fragrance molecules are unstable and decompose over time in, e.g. liquid detergents, and cannot be overdosed due to their potency, as this may be unpleasant for a consumer.
35 The compounds of the inventions, and compositions and consumer products comprising said compounds, provide a 'reservoir' for slow release of such highly fragrance molecules, particularly thiols, over time.

According to a fifth aspect of the invention, there is provided a use of a compound of formula II,



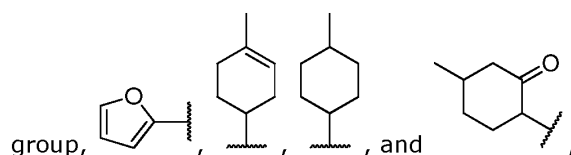
wherein:

5

n is 0 or 1;

R^{21} is selected from the group consisting of a C_{1-18} alkyl group, a C_{1-18} alkenyl group, a C_{3-8} cycloalkyl group, a C_{3-6} cycloalkenyl group, a 4- to 6-membered heterocycloalkyl group, an aryl group, and a 5- or 6-membered heteroaryl group, which C_{1-18} alkyl and C_{1-18} alkenyl groups are optionally substituted by one or more substituents each independently selected from the group consisting of $=\text{O}$, $-\text{OR}^{25}$, a phenyl

10



group, which C_{3-8} cycloalkyl, C_{3-6} cycloalkenyl, and 4- to 6-membered heterocycloalkyl groups are optionally substituted by one or more substituents each independently selected from the group consisting of $=\text{O}$, a C_{1-4} alkyl group, and a C_{1-4} alkenyl group, which aryl and 5- or 6-membered heteroaryl groups are optionally substituted by one or more C_{1-4} alkyl groups;

15

R^{22a} is selected from the group consisting of hydrogen, C_{1-4} alkyl group, $-\text{N}(\text{R}^{26a})\text{R}^{26b}$, $-\text{N}(\text{R}^{27a})\text{C}(\text{O})\text{R}^{27b}$, and $-\text{N}(\text{R}^{28a})\text{C}(\text{O})\text{OR}^{28b}$;

20

R^{22b} is selected from the group consisting of hydrogen and a C_{1-4} alkyl group;

R^{23} is selected from the group consisting of $-\text{O}-$ and $-\text{N}(\text{R}^{29})-$;

25

R^{24} is selected from the group consisting of hydrogen, a C_{1-18} alkyl group, a C_{1-18} alkenyl group, and an aryl group, which C_{1-18} alkyl, C_{1-18} alkenyl and aryl groups are optionally substituted by one or more $-\text{OH}$ or phenyl groups;

R^{25} is selected from the group consisting of hydrogen, a C_{1-4} alkyl group and $-\text{C}(\text{O})\text{R}^{30}$;

30

R^{26a} , R^{26b} , R^{27a} , R^{27b} , R^{28a} , R^{28b} and R^{29} are each independently selected from the group consisting of hydrogen and a C_{1-4} alkyl group, which C_{1-4} alkyl group is optionally substituted by one or more phenyl group; and

5 R^{30} is and a C_{1-4} alkyl group;

or a salt or a solvate thereof,

in a method of providing a fragrant thiol.

10

Compounds of formula II are also considered as compounds of the invention.

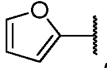
Compounds as defined according to the first aspect of the invention and any embodiments thereof may also be used in a method of providing a fragrant thiol.

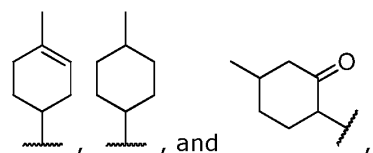
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In particular embodiments of the fifth aspect of the invention:

n is 0 or 1;

20 R^{21} is selected from the group consisting of a C_{1-6} (e.g. C_{1-3}) alkyl group, a C_{3-8} cycloalkyl group, a C_{3-6} cycloalkenyl group, and a 5- to 6-membered heteroaryl group, which C_{1-6} alkyl group is optionally substituted by one or more substituents each

independently selected from the group consisting of $=O$, $-OR^{25}$, a phenyl group, ,



25 which C_{3-8} cycloalkyl and C_{3-6} cycloalkenyl groups are optionally substituted by one or more substituents each independently selected from the group consisting of $=O$, a C_{1-4} alkyl group, and a C_{1-4} alkenyl group, which 5- or 6-membered heteroaryl groups are optionally substituted by one or more C_{1-4} alkyl groups;

30

R^{22a} is selected from the group consisting of hydrogen, methyl, $-NH_2$, $-NH(O)CH_3$, $-NHC(O)C(CH_3)_3$, and $-NHCOOCH_2Ph$;

R^{22b} is selected from the group consisting of hydrogen and a methyl;

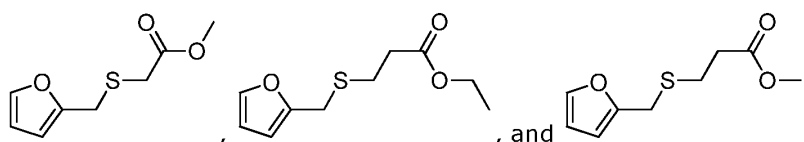
R²³ is selected from the group consisting of -O- and -NH-;

R²⁴ is a C₁₋₁₈ (e.g. C₁₋₈) alkyl group, which C₁₋₁₈ alkyl group may be optionally substituted
5 with one or hydroxy groups or phenyl groups.

R²⁵ is selected from the group consisting of hydrogen, a methyl group, and -C(O)CH₃.

In particular embodiments of the fifth aspect of the invention, the compound used in a
10 method of providing a fragrant thiol is a compound of formula I (as defined hereinbefore,
with reference to the first aspect of the invention and all embodiments thereof), or a salt
or solvate thereof.

In further embodiments of the fifth aspect of the invention, the compound used in a
15 method of providing a fragrant thiol is selected from the group consisting of:



It has been found that compounds of the invention (such as compound of formula II, and
particularly compounds of formula I) undergo efficient degradation to provide highly
20 potent fragrance thiols, which may be considered compounds of formula III,



Thus, in particular embodiments of the invention, the compounds of the invention (i.e. the
25 compound of formula II or the compounds of formula I) may be used in the preparation
of a compound of formula III,



30 wherein R²¹ is as defined herein.

As provided herein, compounds of the invention as such, or perfume compositions
containing said compounds, or a consumer product containing said compounds or
compositions may be used in a method for providing a fragrant thiol.

35

The above uses are particularly beneficial because the fragrant thiols are the only fragrant molecules released by the precursor compounds. If fragrant thiols are released alongside a counterpart fragrant molecule (e.g. a fragrant aldehyde), perfumers are presented with a problem with balancing the olfactive quality of the two molecules.

5

The compounds of the invention are therefore particularly useful as they may deliver the olfactive impression of fragrant thiols to any composition or consumer product in which they are employed, whilst avoiding any stability and overdosing issues which are associated with the direct inclusion of the thiols fragrant into said compositions and consumer products. Moreover, the compounds of the invention ensure that the olfactive signal of a fragrant thiol is unencumbered or attenuated by the release of a fragrant (or odorous) counterpart, which may create formulation complexities for the skilled perfumer/flavourist when designing and preparing desirable consumer products.

15 Accordingly, the compounds of the invention, and compositions and consumer products comprising said compounds as well as their use in providing a fragrant thiol, are advantageous over known compounds, and compositions, consumer products and uses thereof, which degrade to release either a non-sulfur-containing fragrance with a sulfur-containing non-fragrant counterpart or a fragrant thiol together with a fragrant counterpart.

The person skilled in the art is familiar with the conditions under which fragrance precursors (e.g. compounds of the invention) are generally used. More specifically, use of compounds of the present invention commonly takes place under ambient air at a temperature of from about -20 °C to about 100 °C, preferably from about -10 °C to about 60 °C, even more preferably from about 0 °C to about 40 °C, in particular at room temperature (about 25 °C).

Figures

30

The following drawings are provided to illustrate various aspects of the present inventive concept and are not intended to limit the scope of the present invention unless specified herein.

35 Figure 1 shows comparative results of a wash test and sensory evaluation using compound Examples 31a and 47a compared with comparative example 1 and a prior art compound.

Examples

The present invention is explained in greater detail in the following non-limiting examples.

- 5 The reaction schemes described below are intended to provide a general description of the methodology employed in the preparation of the compounds of the invention. The examples provided herein are offered to illustrate but not limit the compounds of the invention, as well as the preparation of such compounds and intermediates.

10 Abbreviations

	aq.:	Aqueous
	b.p.:	Boiling point
	br:	Broad
15	CDCl ₃ :	Deuteriochloroform
	C ₆ D ₆ :	Deuterated benzene
	DBU:	1,8-Diazabicyclo(5.4.0)undec-7-ene
	d:	Doublet
	dd:	Doublet of doublets
20	ddd:	Doublet of doublets of doublets
	dddd:	Doublet of doublets of doublets of doublets
	dq:	Doublet of quartets
	dt:	Doublet of triplets
	EI:	Electron ionisation
25	equiv:	Equivalents
	EtOH:	Ethanol
	GC:	Gas chromatography
	h:	Hour(s)
	HPLC:	High-performance liquid chromatography
30	J:	Coupling constant
	LC:	Liquid chromatography
	M:	Multiplet
	min:	Minute(s)
	MS:	Mass spectrometry
35	MTBE:	Methyl tert-butyl ether
	m/z:	Mass/charge ratio
	NMR:	Nuclear magnetic resonance
	q:	Quartet

sat:	Saturated
s:	Singlet
t:	Triplet
td:	Triplet of doublets
5 tdd:	Triplet of doublets of doublets
THF:	Tetrahydrofuran
t _R :	Retention time

Analytical Methods

10

GC-MS parameters: Column properties: Trajan (SGE) Capillary GC Column BPX5, 0.22 mm ID x 0.25 µm film thickness x 12 m length, 5% phenyl-95% methylpolysiloxane; Carrier gas: Helium at 1 ml/min constant flow; Temperature program: starting at 50 °C, hold for 2 min, then with 20 °C/min to 240 °C, 35 °C/min to 300 °C, hold for 3 min; 15 Injector temperature: 230 °C; Injector method: split (1:50) injection of 1 µL; Detector: Quadrupole Mass Spectrometer (MS), mass range used m/z 25-450.

¹H- and ¹³C-NMR spectra are referenced to 7.16 ppm and 128.0 ppm in C₆D₆ and to 7.26 ppm and 77.0 ppm in CDCl₃, respectively.

20

Example 1: ethyl S-(furan-2-ylmethyl)-L-cysteinate

A suspension of L-cysteine ethyl ester hydrochloride (5.68 g, 30.6 mmol, 1.0 equiv) and para-toluenesulfonic acid monohydrate (582 mg, 10 mol%) in toluene (30 mL) was heated 25 to 100°C followed by the dropwise addition of a solution of furan-2-ylmethanol (3.00 g, 30.6 mmol, 1.0 equiv) in toluene (10 mL) at 55-70°C over 10 minutes. After stirring for 2 hours, the reaction mixture was quenched with sat. NaHCO₃ (50 mL) and extracted with MTBE (3x 50 mL). The combined organic extracts were washed with water (3x), brine (1x), dried over MgSO₄ and the solvent was removed under reduced pressure. The crude 30 was purified twice by column chromatography (heptane/MTBE 9:1) to afford ethyl S-(furan-2-ylmethyl)-L-cysteinate (1.48 g, 19% yield, 90% purity) as an orange oil.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.37 - 7.31 (m, 1H), 6.32 - 6.27 (m, 1H), 6.19 (dd, J = 0.7, 3.4 Hz, 1H), 4.22 - 4.13 (m, 2H), 3.74 (s, 2H), 3.60 - 3.53 (m, 1H), 2.89 (dd, J = 4.6, 13.7 Hz, 1H), 2.77 - 2.69 (m, 1H), 1.71 (broad s, 2H), 1.29 - 1.23 (m, 3H).

35 ¹³C NMR (101 MHz, CDCl₃, δ/ppm): 173.9, 151.2, 142.2, 110.4, 107.7, 61.2, 54.2, 36.7, 28.7, 14.1.

GC/MS (EI): m/z (%): 229 (7, [M]⁺), 212 (3), 156 (15), 117 (11), 112 (20), 102 (30), 81 (100), 74 (26), 53 (22).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, coffee, roasted coffee, slightly metallic, salty impression.

Example 2: methyl 3-((1-phenylethyl)thio)propanoate

5

To a suspension of KI (1.03 g, 6.22 mmol, 10 mol%) and K₂CO₃ (17.2 g, 124 mmol, 2.0 equiv) in acetone (200 mL) was added methyl 3-mercaptopropanoate (6.90 mL, 62.2 mmol, 1.0 equiv). After stirring for 30 min at room temperature, (1-bromoethyl) benzene (8.50 mL, 62.2 mmol, 1.0 equiv) was added and the reaction mixture was stirred at 40°C for 16 hours. After quenching with water, the reaction mixture was extracted with MTBE (2x). The combined organic extracts were washed with brine, dried over MgSO₄ and the solvent was removed under reduced pressure. The crude was purified by column chromatography and fractional distillation (0.02 mbar) to afford methyl 3-((1-phenylethyl)thio)propanoate (8.70 g, 85% yield) as a colourless oil.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.35 - 7.28 (m, 4H), 7.25 - 7.20 (m, 1H), 3.98 (q, J = 7.1 Hz, 1H), 3.64 (s, 3H), 2.59 - 2.55 (m, 2H), 2.48 - 2.43 (m, 2H), 1.55 (d, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 172.2, 143.6, 128.4, 127.1, 127.1, 51.6, 44.1, 34.2, 26.1, 22.4.

GC/MS (EI): *m/z* (%): 224 (4, [M]⁺⁺), 137 (8), 105 (100), 77 (11), 59 (5).

b.p.: 98°C (0.2 mbar).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, salty, roasted.

Example 3: butyl 3-((1-hydroxyhexan-3-yl)thio)propanoate

25

To a solution of hex-2-enal (4 g, 40.8 mmol, 1.0 equiv) and butyl 3-mercaptopropanoate (6.61 g, 40.8 mmol, 1.0 equiv) in THF (50 mL) was added at 0°C DBU (4.51 g, 32.6 mmol, 0.8 equiv). After stirring for 2.5 hours at 0°C, the reaction mixture was quenched with ice-cold 2M aq. HCl and extracted with MTBE. The combined organic extracts were washed with water, brine and dried over MgSO₄. The solvent was removed under reduced pressure to give crude butyl 3-((1-oxohexan-3-yl)thio)propanoate (10 g), which was used without further purification for the next step.

To suspension of NaBH₄ (0.93 g, 24.6 mmol, 0.8 equiv) in methanol (40 mL) was added dropwise at 0°C crude butyl 3-((1-oxohexan-3-yl)thio)propanoate (8.0 g, 30.7 mmol, 1.0 equiv). After stirring for 1 hour at room temperature, the reaction mixture was poured on 2M aq. HCl and extracted with MTBE (2x). The combined organic extracts were washed with water, brine and dried over MgSO₄. The solvent was removed under reduced pressure.

The crude was purified by column chromatography to afford butyl 3-((1-hydroxyhexan-3-yl)thio)propanoate (4.84 g, 60% calcd. yield over 2 steps) as a colourless oil.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 4.09 (t, J = 6.7 Hz, 2H), 3.87 - 3.79 (m, 1H), 3.76 - 3.70 (m, 1H), 2.84 - 2.70 (m, 3H), 2.60 - 2.56 (m, 2H), 2.19 (br s, 1H), 1.86 (dddd, J = 4.6, 5.4, 7.8, 14.5 Hz, 1H), 1.71 - 1.30 (m, 9H), 0.95 - 0.87 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 172.2, 64.6, 60.6, 43.1, 37.9, 37.1, 35.0, 30.6, 25.3, 19.9, 19.1, 13.9, 13.6.

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulfurous, vegetable, onion, boiled vegetable.

Example 4: butyl 3-((1-acetoxyhexan-3-yl)thio)propanoate

To a solution of butyl 3-((1-hydroxyhexan-3-yl)thio)propanoate (4.0 g, 15.2 mmol, 1.0 equiv) and pyridine (2.2 mL, 27.4 mmol, 1.8 equiv) in cyclohexane (30 mL) was added dropwise at 0 °C a solution of acetyl chloride (1.6 mL, 22.9 mmol, 1.5 equiv) in cyclohexane (10 mL). After stirring for 1 hour at room temperature, the reaction mixture was quenched with ice-cold 2M aq. HCl (30 mL) and extracted with MTBE (50 mL). The organic layer was washed with water, 2M aq. NaOH, brine and dried over MgSO₄. The solvent was removed under reduced pressure and the crude was purified by column chromatography (heptane/MTBE 4:1) to afford butyl 3-((1-acetoxyhexan-3-yl)thio)propanoate (2.88 g, 62% yield) as a colourless oil.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 4.23 - 4.18 (m, 2H), 4.09 (t, J = 6.7 Hz, 2H), 2.77 - 2.64 (m, 3H), 2.58 - 2.53 (m, 2H), 2.04 (s, 3H), 1.96 - 1.86 (m, 1H), 1.82 - 1.72 (m, 1H), 1.65 - 1.49 (m, 4H), 1.49 - 1.31 (m, 4H), 0.95 - 0.87 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 172.0, 171.0, 64.6, 62.2, 42.6, 37.4, 35.0, 33.7, 30.6, 25.3, 21.0, 19.9, 19.1, 13.9, 13.7.

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulfurous, cassis, watermelon, eucalyptus bud, sweaty, neocaspirene, cassyrane.

Example 5: isooctyl 3-((1-hydroxyhexan-3-yl)thio)propanoate (mixture of isooctyl ester isomers)

The compound was obtained from isooctyl 3-mercaptopropanoate (8.90 g, 40.8 mmol, 1.0 equiv, CAS 30374-01-7), DBU (4.51 g, 32.6 mmol, 0.8 equiv) and hex-2-enal (4.0 g, 40.8 mmol, 1.0 equiv) followed by treatment of the intermediate with NaBH₄ (0.96 g, 25.3 mmol, 0.8 equiv) according to the procedure of example 3 as a colourless oil (6.97 g, 69% yield).

¹H NMR (400 MHz, CDCl₃, complex mixture of isomers, δ/ppm): 4.21 - 3.99 (m, 2H), 3.84 (ddd, J = 5.0, 7.8, 10.9 Hz, 1H), 3.74 (td, J = 5.6, 11.1 Hz, 1H), 2.82 - 2.75 (m, 3H), 2.61 - 2.56 (m, 2H), 2.11 (br s, 1H), 1.88 (tdd, J = 5.1, 7.6, 14.4 Hz, 1H), 1.74 - 1.01 (m, 12H), 0.96 - 0.73 (m, 11H).

- 5 ¹³C NMR (101 MHz, CDCl₃, complex mixture of isomers, δ/ppm): 172.2, 69.7, 65.3, 65.0, 63.9, 63.8, 63.4, 63.3, 60.6, 46.5, 43.1, 40.0, 39.4, 39.1, 38.8, 38.5, 38.2, 37.9, 37.1, 36.5, 36.1, 35.7, 35.4, 35.0, 35.0, 34.3, 33.4, 33.1, 33.0, 32.2, 31.9, 30.2, 29.8, 29.0, 27.9, 27.4, 27.2, 27.0, 26.6, 26.1, 25.6, 25.4, 25.1, 23.2, 22.9, 22.6, 22.2, 20.2, 20.0, 19.6, 19.5, 19.1, 17.9, 16.5, 15.6, 15.2, 14.3, 14.2, 13.9, 12.1, 11.3, 10.8, 10.6.
- 10 Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulfurous, vegetable, onion, gassy.

Example 6: 6-methylheptyl 3-((1-acetoxyhexan-3-yl)thio)propanoate

- 15 The compound was obtained from 6-methylheptyl 3-((1-hydroxyhexan-3-yl)thio)propanoate (6.0 g, 18.8 mmol, 1.0 equiv), pyridine (2.7 mL, 33.9 mmol, 1.8 equiv) and acetyl chloride (2.19 g, 28.3 mmol, 1.5 equiv) according to the procedure of example 4 to give a colourless oil (2.93 g, 43% yield).

¹H NMR (400 MHz, CDCl₃, complex mixture of isomers, δ/ppm): 4.22 - 4.18 (m, 2H), 4.14 - 4.04 (m, 2H), 2.76 - 2.65 (m, 3H), 2.58 - 2.53 (m, 2H), 2.04 (s, 3H), 1.95 - 1.86 (m, 1H), 1.82 - 1.74 (m, 1H), 1.66 - 1.00 (m, 12H), 0.92 - 0.75 (m, 12H).

¹³C NMR (101 MHz, CDCl₃, complex mixture of isomers, δ/ppm): 171.9, 171.0, 65.2, 64.9, 63.8, 63.7, 63.2, 62.2, 46.5, 42.6, 39.4, 39.1, 38.8, 38.5, 38.2, 37.3, 36.5, 36.1, 35.7, 35.4, 35.0, 35.0, 33.6, 33.7, 33.0, 32.2, 31.9, 29.8, 29.4, 29.1, 30.1, 28.6, 27.9, 27.4, 25.7, 25.6, 25.3, 25.1, 23.4, 23.2, 22.9, 22.6, 22.2, 21.0, 20.2, 20.0, 19.9, 19.6, 19.5, 19.5, 19.1, 17.9, 15.6, 15.2, 14.3, 14.2, 14.0, 13.9, 12.1, 12.1, 11.3, 10.8.

25 Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulfurous, cassis, watermelon, eucalyptus bud, sweaty, neocaspirene, cassyrane, straw, leaf.

30 Example 7: methyl 3-((1-hydroxyhexan-3-yl)thio)propanoate

The compound was obtained from methyl 3-mercaptopropanoate (2.54 g, 21.1 mmol, 1.0 equiv), DBU (2.34 g, 16.9 mmol, 0.8 equiv) and hex-2-enal (2.08 g, 21.1 mmol, 1.0 equiv) followed by treatment of the intermediate with NaBH₄ (0.59 g, 15.6 mmol, 0.8 equiv) according to the procedure of example 3 as a colourless oil (1.94 g, 45% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 3.85 - 3.78 (m, 1H), 3.75 - 3.69 (m, 1H), 3.68 - 3.66 (m, 3H), 2.80 - 2.73 (m, 3H), 2.61 - 2.57 (m, 2H), 2.32 - 2.14 (m, 1H), 1.85 (dddd, J =

4.6, 5.5, 7.7, 14.4 Hz, 1H), 1.66 (tdd, $J = 5.4, 9.1, 14.5$ Hz, 1H), 1.57 - 1.39 (m, 4H), 0.92 - 0.88 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3 , δ/ppm): 172.5, 60.5, 51.8, 43.1, 37.8, 37.1, 34.7, 25.2, 19.9, 13.9

- 5 Odour description (1% solution in EtOH on paper blotter, 24 h): cassis, sulfurous, onion, leek.

Example 8: methyl 3-((1-acetoxylhexan-3-yl)thio)propanoate

- 10 The compound was obtained from methyl 3-((1-hydroxyhexan-3-yl)thio)propanoate (1.08 g, 4.90 mmol, 1.0 equiv), pyridine (0.71 mL, 8.82 mmol, 1.8 equiv) and acetyl chloride (0.52 mL, 7.35 mmol, 1.5 equiv) according to the procedure of example 4 to give a colourless oil (0.53 g, 37% yield).

- ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 4.20 (t, $J = 6.7$ Hz, 2H), 3.68 (s, 3H), 2.74 - 2.63 (m, 3H), 2.59 - 2.55 (m, 2H), 2.03 (s, 3H), 1.95 - 1.85 (m, 1H), 1.81 - 1.71 (m, 1H), 1.56 - 1.39 (m, 4H), 0.90 (t, $J = 7.1$ Hz, 3H).

- ^{13}C NMR (101 MHz, CDCl_3 , δ/ppm): 172.3, 171.0, 62.2, 51.7, 42.6, 37.4, 34.7, 33.6, 25.3, 20.9, 19.9, 13.9.

- Odour description (1% solution in EtOH on paper blotter, 24 h): green sulphurous, cassis, 20 sweaty.

Example 9: methyl 3-((furan-2-ylmethyl)thio)propanoate

- The compound was obtained from furan-2-ylmethanethiol (2.0 g, 17.5 mmol, 1.0 equiv), methyl acrylate (1.51 g, 17.5 mmol, 1.0 equiv) and DBU (2.42 g, 17.5 mmol, 1.0 equiv) according to the procedure of example 3 to give an orange oil (2.79 g, 80% yield).

- ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.35 (dd, $J = 0.7, 2.0$ Hz, 1H), 6.30 (dd, $J = 2.0, 3.2$ Hz, 1H), 6.19 (dd, $J = 0.7, 3.4$ Hz, 1H), 3.73 (s, 2H), 3.68 (s, 3H), 2.77 (t, $J = 7.3$ Hz, 2H), 2.56 (t, $J = 7.3$ Hz, 2H).

- ^{13}C NMR (101 MHz, CDCl_3 , δ/ppm): 172.2, 151.3, 142.2, 110.4, 107.6, 51.8, 34.3, 28.3, 26.5.

Odour description (1% solution in EtOH on paper blotter, 24 h): green, coffee, roasted, sulphurous.

Example 10: ethyl 3-((furan-2-ylmethyl)thio)propanoate

The compound was obtained from furan-2-ylmethanethiol (1.0 g, 8.76 mmol, 1.0 equiv), ethyl acrylate (0.97 g, 9.64 mmol, 1.1 equiv) and DBU (1.21 g, 8.76 mmol, 1.0 equiv) according to the procedure of example 3 to give a pink oil (1.84 g, 98% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.35 (dd, J = 0.9, 1.8 Hz, 1H), 6.29 (dd, J = 2.0, 3.2 Hz, 1H), 6.20-6.17 (m, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.73 (s, 2H), 2.76 (t, J = 7.3 Hz, 2H), 2.54 (t, J = 7.2 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 171.8, 151.3, 142.1, 110.4, 107.5, 60.6, 34.5, 28.3, 26.5, 14.1.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, green, rubbery, burnt, coffee.

Example 11: butyl 3-((furan-2-ylmethyl)thio)propanoate

The compound was obtained from furan-2-ylmethanethiol (1.0 g, 8.76 mmol, 1.0 equiv), butyl acrylate (1.24 g, 9.64 mmol, 1.1 equiv) and DBU (1.21 g, 8.76 mmol, 1.0 equiv) according to the procedure of example 3 to give a pink oil (2.02 g, 95% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.35 (dd, J = 1.0, 2.0 Hz, 1H), 6.30 (dd, J = 2.0, 3.2 Hz, 1H), 6.20 - 6.18 (m, 1H), 4.09 (t, J = 6.6 Hz, 2H), 3.73 (s, 2H), 2.76 (t, J = 7.3 Hz, 2H), 2.55 (t, J = 7.3 Hz, 2H), 1.67 - 1.57 (m, 2H), 1.43 - 1.32 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 171.9, 151.3, 142.1, 110.4, 107.5, 64.5, 34.5, 30.6, 28.3, 26.6, 19.1, 13.6.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, green, rubbery, burnt, coffee, slightly fruity.

Example 12: ethyl 3-((2-methylfuran-3-yl)thio)propanoate

The compound was obtained from 2-methylfuran-3-thiol (1.0 g, 8.76 mmol, 1.0 equiv), ethyl acrylate (0.97 g, 9.64 mmol, 1.1 equiv) and DBU (1.21 g, 8.76 mmol, 1.0 equiv) according to the procedure of example 3 to give a yellow oil (1.26 g, 66% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.28 (d, J = 2.0 Hz, 1H), 6.34 (d, J = 2.0 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 2.86 (t, J = 7.3 Hz, 2H), 2.52 (t, J = 7.2 Hz, 2H), 2.33 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 171.8, 155.5, 140.6, 115.0, 109.2, 60.6, 34.8, 30.8, 14.2, 11.7.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulfurous, green, broth, gaïac wood, roasted chicken, milky, warm milk, sulfurol.

Example 13: butyl 3-((2-methylfuran-3-yl)thio)propanoate

5

The compound was obtained from 2-methylfuran-3-thiol (1.0 g, 8.76 mmol, 1.0 equiv), butyl acrylate (1.24 g, 9.64 mmol, 1.1 equiv) and DBU (1.21 g, 8.76 mmol, 1.0 equiv) according to the procedure of example 3 to give a yellow oil (1.42 g, 62% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.27 (d, J = 2.2 Hz, 1H), 6.33 (d, J = 2.0 Hz, 1H), 4.07 (t, J = 6.7 Hz, 2H), 2.85 (t, J = 7.3 Hz, 2H), 2.54 - 2.49 (m, 2H), 2.32 (s, 3H), 1.68 - 1.54 (m, 2H), 1.45 - 1.31 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 171.8, 155.4, 140.6, 115.0, 109.3, 64.5, 34.8, 30.8, 30.6, 19.1, 13.7, 11.7.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulfurous, green, broth, gaïac wood, roasted chicken, milky, warm milk, sulfurol.

15

Example 14: 2-hydroxyethyl 3-((2-methylfuran-3-yl)thio)propanoate

The compound was obtained from 2-methylfuran-3-thiol (1.97 g, 17.2 mmol, 1.0 equiv), 2-hydroxyethyl acrylate (2.00 g, 17.2 mmol, 1.0 equiv) and DBU (2.62 g, 17.2 mmol, 1.0 equiv) according to the procedure of example 3 to give a yellow oil (1.20 g, 30% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.29 (d, J = 2.0 Hz, 1H), 6.35 (d, J = 1.7 Hz, 1H), 4.23 - 4.20 (m, 2H), 3.83 - 3.80 (m, 2H), 2.87 (t, J = 7.2 Hz, 2H), 2.59 (t, J = 7.2 Hz, 2H), 2.46 - 2.26 (m, 4H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 172.0, 155.5, 140.7, 115.0, 109.0, 66.1, 60.9, 34.5, 30.7, 11.7.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, burnt, foodlike, sausage, warm milk, sulfurol.

30

Example 15: 3-((furan-2-ylmethyl)thio)propanoic acid

The compound was obtained from furan-2-ylmethanol (5.0 g, 51 mmol, 1.05 equiv), 3-mercaptopropanoic acid (5.2 g, 49 mmol, 1.0 equiv) and p-toluenesulfonic acid monohydrate (0.46 g, 5 mol%) according to the procedure of example 1 to give a yellow oil (3.3 g, 27% yield).

GC/MS (EI): *m/z* (%): 186 (19, [M]⁺), 113 (9), 81 (100), 59 (3), 53 (16), 45 (12), 27 (9).

^{13}C NMR (101 MHz, CDCl_3 , δ/ppm): 178.2, 151.1, 142.1, 110.3, 107.5, 34.2, 28.1, 26.0.
Odour description (1% solution in EtOH on paper blotter, 24 h): acidic, animalic, castoreum, green, sulphurous, roasted coffee.

5 Example 16: methyl S-(1-phenylethyl)-L-cysteinate

To a solution of methyl L-cysteinate hydrochloride (1.20 g, 7.00 mmol, 1.05 equiv), in 7M NH_3 in methanol (5.0 mL, 35 mmol, 5 equiv) was added dropwise at 0°C (1-chloroethyl)benzene (1.08 g, 7.70 mmol, 1.1 equiv). After stirring at room temperature
10 for 3 hours, the reaction mixture was concentrated and the crude was purified by column chromatography to afford methyl S-(1-phenylethyl)-L-cysteinate (0.23 g, 14% yield, mixture of two diastereoisomers) as an orange oil.

^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.36 - 7.28 (m, 4H), 7.28 - 7.21 (m, 1H), 3.99 (q, J = 7.0 Hz, 1H), 3.71 (s, 1.5H), 3.68 (s, 1.5H), 3.55 (dd, J = 4.5, 7.7 Hz, 0.5H), 3.45 (dd, J = 4.9, 7.3 Hz, 0.5H), 2.76 - 2.67 (m, 1H), 2.61 (dd, J = 7.3, 13.4 Hz, 0.5H), 2.52 (dd, J = 7.8, 13.4 Hz, 0.5H), 1.72 (br s, 2H), 1.63 - 1.50 (m, 3H).
15

^{13}C NMR (101 MHz, CDCl_3 , δ/ppm): 174.4, 174.3, 143.6, 143.4, 128.5, 128.5, 127.2, 127.2, 127.2, 127.2, 54.1, 53.9, 52.1, 44.8, 44.3, 36.3, 36.3, 22.7, 22.4.

Odour description (1% solution in EtOH on paper blotter, 24 h): strong, anjeruk, salty,
20 burnt, green, rubbery, mandarin peel.

Example 17: butyl 3-((1-phenylethyl)thio)propanoate

The compound was obtained from (1-bromoethyl)benzene (11.5 g, 62.2 mmol, 1.0 equiv), butyl 3-mercaptopropanoate (10.1 g, 62.2 mmol, 1.0 equiv), K_2CO_3 (17.2 g, 124 mmol, 2.0 equiv) and KI (1.03 g, 10 mol%) according to the procedure of example 2 to afford a yellow oil (12.7 g, 76% yield).
25

^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.36 - 7.29 (m, 4H), 7.26 - 7.21 (m, 1H), 4.06 (t, J = 6.7 Hz, 2H), 3.98 (q, J = 7.1 Hz, 1H), 2.60 - 2.56 (m, 2H), 2.47 - 2.43 (m, 2H), 1.62 - 1.55 (m, 5H), 1.41 - 1.33 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H).
30

^{13}C NMR (101 MHz, CDCl_3 , δ/ppm): 171.8, 143.6, 128.4, 127.1, 127.0, 64.3, 44.1, 34.5, 30.5, 26.2, 22.4, 19.0, 13.6.

b.p.: 126°C (0.2 mbar).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, citrus, sulphurous,
35 mandarin peel, burnt, roasted salty.

Example 18: 1-phenylethyl 3-((1-phenylethyl)thio)propanoate

The compound was obtained from (1-bromoethyl)benzene (1.30 g, 7.00 mmol, 1.0 equiv), 3-mercaptopropanoic acid (0.74 g, 7.00 mmol, 1.0 equiv), K₂CO₃ (1.93 g, 14.0 mmol, 2.0 equiv) and KI (0.12 g, 10 mol%) according to the procedure of example 2 to afford a yellow oil (0.45 g, 20% yield, mixture of diastereoisomers).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.35 - 7.20 (m, 10H), 5.87 (dq, J = 0.7, 6.6 Hz, 1H), 3.95 (dq, J = 1.6, 7.1 Hz, 1H), 2.60 - 2.53 (m, 2H), 2.50 - 2.44 (m, 2H), 1.56 - 1.50 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 171.1, 171.1, 143.6, 143.6, 141.5, 128.5, 128.4, 127.8, 127.2, 127.1, 126.0, 126.0, 72.5, 44.2, 44.1, 34.8, 34.8, 26.2, 26.2, 22.4, 22.2.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, burnt, rubbery, mandarin peel.

Example 19: methyl 2-((1-phenylethyl)thio)acetate

The compound was obtained from (1-bromoethyl)benzene (1.30 g, 7.00 mmol, 1.0 equiv), methyl 2-mercaptoacetate (0.74 g, 7.00 mmol, 1.0 equiv), K₂CO₃ (1.93 g, 14.0 mmol, 2.0 equiv) and KI (0.12 g, 10 mol%) according to the procedure of example 2 to afford a yellow oil (1.04 g, 71% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.37 - 7.29 (m, 4H), 7.26 - 7.22 (m, 1H), 4.14 (q, J = 7.1 Hz, 1H), 3.67 (s, 3H), 3.05 (d, J = 14.9 Hz, 1H), 2.92 (d, J = 15.2 Hz, 1H), 1.58 (d, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 170.9, 142.7, 128.4, 127.4, 127.3, 52.2, 44.2, 32.7, 21.8.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, burnt, rubbery, mandarin peel.

Example 20: 2-ethylhexyl 3-((1-phenylethyl)thio)propanoate

The compound was obtained from (1-bromoethyl)benzene (2.00 g, 10.8 mmol, 1.0 equiv), 2-ethylhexyl 3-mercaptopropanoate (2.36 g, 10.8 mmol, 1.0 equiv), K₂CO₃ (2.99 g, 21.6 mmol, 2.0 equiv) and KI (0.18 g, 10 mol%) according to the procedure of example 2 to afford a yellow oil (3.0 g, 86% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.35 - 7.29 (m, 4H), 7.26 - 7.21 (m, 1H), 4.05 - 3.94 (m, 3H), 2.59 - 2.55 (m, 2H), 2.47 - 2.43 (m, 2H), 1.59 - 1.50 (m, 1H), 1.56 (d, J = 7.1 Hz, 3H), 1.37 - 1.25 (m, 8H), 0.91 - 0.85 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 172.0, 143.6, 128.5, 127.2, 127.1, 67.0, 44.2, 38.7, 34.6, 30.3, 28.9, 26.3, 23.7, 22.9, 22.4, 14.0, 11.0.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, burnt, rubbery, mandarin peel.

5

Example 21: octadecyl 3-((1-phenylethyl)thio)propanoate

The compound was obtained from (1-bromoethyl)benzene (2.00 g, 10.8 mmol, 1.0 equiv), octadecyl 3-mercaptopropanoate (3.88 g, 10.8 mmol, 1.0 equiv), K₂CO₃ (2.99 g, 21.6 mmol, 2.0 equiv) and KI (0.18 g, 10 mol%) according to the procedure of example 2 to afford a yellow oil (2.8 g, 56% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.36 - 7.28 (m, 4H), 7.26 - 7.19 (m, 1H), 4.05 (t, J = 6.7 Hz, 2H), 3.98 (q, J = 6.9 Hz, 1H), 2.61 - 2.54 (m, 2H), 2.49 - 2.37 (m, 2H), 1.69 - 1.58 (m, 2H), 1.56 (d, J = 7.1 Hz, 3H), 1.42 - 1.17 (m, 30H), 0.90 - 0.86 (m, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 171.9, 143.6, 128.5, 127.2, 127.1, 64.7, 44.2, 34.5, 31.9, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 28.5, 26.2, 25.8, 22.6, 22.5, 14.1.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, burnt, rubbery, mandarin peel.

Example 22: isooctyl 3-((1-phenylethyl)thio)propanoate (mixture of isooctyl ester isomers)

The compound was obtained from (1-bromoethyl)benzene (2.00 g, 10.8 mmol, 1.0 equiv), isooctyl 3-mercaptopropanoate (3.88 g, 10.8 mmol, 1.0 equiv, CAS 30374-01-7), K₂CO₃ (2.99 g, 21.6 mmol, 2.0 equiv) and KI (0.18 g, 10 mol%) according to the procedure of example 2 to afford a yellow oil (2.7 g, 77% yield).

¹H NMR (400 MHz, CDCl₃, complex mixture of isomers, δ/ppm): 7.36 - 7.28 (m, 4H), 7.27 - 7.19 (m, 1H), 4.16 - 4.01 (m, 2H), 3.98 (q, J = 7.1 Hz, 1H), 2.60 - 2.55 (m, 2H), 2.48 - 2.42 (m, 2H), 1.69 - 1.49 (m, 2H), 1.56 (d, J = 6.9 Hz, 3H), 1.43 - 1.00 (m, 5H), 0.92 - 0.75 (m, 8H).

¹³C NMR (101 MHz, CDCl₃, complex mixture of isomers (peak list), δ/ppm): 171.9, 143.6, 128.5, 128.2, 127.2, 127.1, 65.1, 64.7, 63.9, 63.7, 63.6, 63.2, 63.1, 46.5, 44.2, 42.2, 39.4, 39.1, 38.8, 38.5, 38.2, 36.5, 36.1, 35.7, 35.6, 35.4, 34.6, 34.6, 34.2, 34.1, 33.9, 33.4, 33.2, 33.1, 33.0, 32.1, 31.8, 31.4, 31.4, 30.1, 29.7, 29.3, 29.3, 29.0, 28.8, 28.6, 28.1, 27.8, 27.3, 27.2, 26.9, 26.5, 26.2, 26.1, 25.8, 25.6, 25.1, 23.3, 23.2, 23.2, 22.9, 22.7, 22.6, 22.5, 22.2, 20.2, 20.0, 19.6, 19.6, 19.1, 18.7, 17.9, 16.5, 15.6, 15.2, 14.4, 14.3, 14.2, 14.1, 14.0, 12.1, 11.9, 11.3, 10.6.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, burnt, rubbery, mandarin peel.

Example 23: N-ethyl-3-((1-phenylethyl)thio)propanamide

5

Methyl 3-mercaptopropanoate (5.0 g, 42 mmol, 1.0 equiv) and 69% aq. ethylamine (4.9 g, 75 mmol, 1.8 equiv) were stirred at room temperature overnight. The reaction mixture was poured on water, diluted with MTBE and the layers were separated. The organic layer was washed with water, 2M aq. HCl, brine, dried over MgSO₄ and filtered.

10 The solvent was removed under reduced pressure to give crude N-ethyl-3-mercaptopropanamide (2.6 g, 45%), which was used without further purification.

The compound was obtained from (1-bromoethyl)benzene (1.4 g, 7.6 mmol, 1.0 equiv), N-ethyl-3-mercaptopropanamide (1.0 g, 7.6 mmol, 1.0 equiv), K₂CO₃ (2.1 g, 15 mmol, 2.0 equiv) and KI (0.13 g, 10 mol%) according to the procedure of example 2 to afford a

15 yellow oil (1.0 g, 56% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.34 - 7.27 (m, 4H), 7.25 - 7.19 (m, 1H), 5.71 (br s, 1H), 3.95 (q, J = 6.9 Hz, 1H), 3.26 - 3.19 (m, 2H), 2.69 - 2.54 (m, 2H), 2.28 - 2.20 (m, 2H), 1.55 (d, J = 7.1 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 170.9, 143.8, 128.4, 127.1, 127.1, 44.5, 36.3, 34.3, 20 27.1, 22.4, 14.7.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, burnt, rubbery, mandarin peel.

Example 24: N-butyl-3-((1-phenylethyl)thio)propanamide

25

Methyl 3-mercaptopropanoate (5.0 g, 42 mmol, 1.0 equiv) and butan-1-amine (5.8 g, 75 mmol, 1.8 equiv) were stirred at room temperature over night. The reaction mixture was poured on water, diluted with MTBE and the layers were separated. The organic layer was washed with water, 2M aq. HCl, brine, dried over MgSO₄ and filtered. The solvent was

30 removed under reduced pressure to give crude N-butyl-3-mercaptopropanamide (4.8 g, 71%), which was used without further purification.

The compound was obtained from (1-bromoethyl)benzene (1.4 g, 7.6 mmol, 1.0 equiv), N-butyl-3-mercaptopropanamide (1.2 g, 7.6 mmol, 1.0 equiv), K₂CO₃ (2.1 g, 15 mmol, 2.0 equiv) and KI (0.13 g, 10 mol%) according to the procedure of example 2 to afford a

35 colorless oil (1.3 g, 65% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.34 - 7.28 (m, 4H), 7.24 - 7.20 (m, 1H), 5.66 (br s, 1H), 3.96 (q, J = 7.1 Hz, 1H), 3.22 - 3.16 (m, 2H), 2.67 - 2.56 (m, 2H), 2.24 (dt, J = 2.7,

7.2 Hz, 2H), 1.56 (d, $J = 7.1$ Hz, 3H), 1.48 - 1.40 (m, 2H), 1.36 - 1.27 (m, 2H), 0.90 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3 , δ/ppm): 171.0, 143.8, 128.4, 127.1, 127.1, 44.6, 39.2, 36.4, 31.5, 27.2, 22.4, 20.0, 13.7.

- 5 Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, burnt, anjeruk, mandarine.

Example 25: N-methyl-3-((1-phenylethyl)thio)propanamide

- 10 Methyl 3-mercaptopropanoate (5.0 g, 42 mmol, 1.0 equiv) and 40% aq. methylamine (6.0 g, 77 mmol, 1.9 equiv) were stirred at room temperature overnight. The reaction mixture was poured on water, diluted with MTBE and the layers were separated. The organic layer was washed with water, 2M aq. HCl, brine, dried over MgSO_4 and filtered. The solvent was removed under reduced pressure to give crude 3-mercapto-N-methylpropanamide (4.0 g, 80%), which was used without further purification.

- 15 The compound was obtained from (1-bromoethyl)benzene (1.4 g, 7.6 mmol, 1.0 equiv), 3-mercapto-N-methylpropanamide (0.9 g, 7.6 mmol, 1.0 equiv), K_2CO_3 (2.1 g, 15 mmol, 2.0 equiv) and KI (0.13 g, 10 mol%) according to the procedure of example 2 to afford a colorless oil (0.47 g, 28% yield).

- 20 ^1H NMR (400 MHz, CDCl_3 , δ/ppm): 7.35 - 7.28 (m, 4H), 7.26 - 7.18 (m, 1H), 6.02 (br s, 1H), 3.96 (q, $J = 7.0$ Hz, 1H), 2.73 (d, $J = 4.9$ Hz, 3H), 2.67 - 2.56 (m, 2H), 2.30 - 2.24 (m, 2H), 1.56 (d, $J = 7.1$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3 , δ/ppm): 171.8, 143.7, 128.4, 127.0, 127.0, 44.4, 36.1, 27.0, 26.1, 22.3.

- 25 Odour description (1% solution in EtOH on paper blotter, 24 h): green, burnt, burnt mandarin peel, anjeruk.

Example 26: 3-((1-phenylethyl)thio)propanoic acid

- 30 To a solution of butyl 3-((1-phenylethyl)thio)propanoate (3.3 g, 12 mmol, 1.0 equiv) in ethanol (30 mL) and water (30 mL) was added KOH (2.1 g, 37 mmol, 3 equiv) and the reaction mixture was refluxed for 3 hours. Some of the ethanol was removed under reduced pressure and the reaction mixture was then extracted with MTBE (which was discarded). The aqueous layer was then acidified with aq. HCl and extracted with MTBE, washed with water, brine, dried over MgSO_4 and filtered. The solvent was removed under reduced pressure. The crude was purified by column chromatography to afford butyl 3-((1-phenylethyl)thio)propanoate (1.85 g, 71% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 11.50 (br s, 1H), 7.41 - 7.28 (m, 4H), 7.25 - 7.20 (m, 1H), 3.97 (q, J = 6.9 Hz, 1H), 2.59 - 2.53 (m, 2H), 2.53 - 2.45 (m, 2H), 1.56 (d, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 178.4, 143.5, 128.5, 127.2, 127.2, 44.2, 34.3, 25.7, 22.4.

Odour description (1% solution in EtOH on paper blotter, 24 h): green, burnt, burnt mandarin peel, anjeruk.

Example 27: methyl 2-((1-phenylethyl)thio)propanoate

The compound was obtained from (1-bromoethyl)benzene (1.4 g, 7.6 mmol, 1.0 equiv), methyl 2-mercaptopropanoate (0.91 g, 7.6 mmol, 1.0 equiv), K₂CO₃ (2.1 g, 15 mmol, 2.0 equiv) and KI (0.13 g, 10 mol%) according to the procedure of example 2 to afford a colorless oil (0.95 g, 76% yield, 1:1 mixture of diastereoisomers).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.38 - 7.28 (m, 4H), 7.26 - 7.20 (m, 1H), 4.12 (qd, J = 7.1, 10.1 Hz, 1H), 3.71 (s, 1.5H), 3.54 (s, 1.5H), 3.37 (q, J = 7.1 Hz, 0.5H), 3.00 (q, J = 7.3 Hz, 0.5H), 1.60 (d, J = 7.1 Hz, 1.5H), 1.52 (d, J = 7.1 Hz, 1.5H), 1.39 (d, J = 7.1 Hz, 1.5H), 1.26 (d, J = 7.1 Hz, 1.5H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 173.8, 173.4, 143.5, 143.1, 128.4, 128.4, 127.3, 127.2, 127.2, 52.1, 52.1, 44.5, 44.4, 41.5, 40.3, 22.7, 22.3, 17.6, 16.9.

Odour description (1% solution in EtOH on paper blotter, 24 h): green, burnt, burnt mandarin peel, anjeruk, soft floral, rosy, creamy, heavy, fatty, acetophenone.

Example 28: ethyl 3-(benzylthio)propanoate

The compound was obtained from ethyl 3-mercaptopropanoate (1.00 g, 7.45 mmol, 1.0 equiv), (chloromethyl)benzene (1.04 g, 8.20 mmol, 1.1 equiv) and 7M NH₃ in methanol (5.3 mL, 37.3 mmol, 5 equiv) according to the procedure of example 16 to give a colorless oil (1.22 g, 73% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.37 - 7.20 (m, 5H), 4.14 (q, J = 7.1 Hz, 2H), 3.73 (s, 2H), 2.74 - 2.62 (m, 2H), 2.56 - 2.50 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 171.8, 138.0, 128.8, 128.5, 127.0, 60.6, 36.3, 34.5, 26.2, 14.2.

Odour description (1% solution in EtOH on paper blotter, 24 h): fruity, ethereal, winey, rosy, rubbery metallic burnt.

Example 29: ethyl 3-((1-phenylethyl)thio)propanoate

The compound was obtained from ethyl 3-mercaptopropanoate (1.00 g, 7.45 mmol, 1.0 equiv), (1-chloroethyl)benzene (1.15 g, 8.20 mmol, 1.1 equiv) and 7M NH₃ in methanol (5.3 mL, 37.3 mmol, 5 equiv) according to the procedure of example 16 to give a colorless oil (0.47 g, 84% yield).

GC/MS (EI): *m/z* (%): 238 (3, [M]⁺), 137 (8), 105 (100), 77 (10).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 171.9, 143.7, 128.5, 127.2, 127.1, 60.5, 44.2, 34.5, 26.2, 22.5, 14.2.

Odour description (1% solution in EtOH on paper blotter, 24 h): green, salty, roasted.

Example 30: butyl 3-(phenethylthio)propanoate

To a solution of butyl 3-mercaptopropanoate (1.0 gf, 6.16 mmol, 1.0 equiv) and DBU (0.75 g, 4.93 mmol, 0.8 equiv) in THF (40 mL) was added dropwise at 0°C (2-chloroethyl)benzene (0.87 g, 6.16 mmol, 1.0 equiv). After stirring for 15 min at 0°C, the reaction mixture was quenched with 2M aq. HCl and extracted with MtBE. The organic layer was washed with water, brine, dried over MgSO₄ and the solvent was removed under reduced pressure. The crude was purified by column chromatography to afford butyl 3-(phenethylthio)propanoate (0.32 g, 19% yield) as a light yellow oil.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.32 - 7.28 (m, 2H), 7.24 - 7.19 (m, 3H), 4.11 (t, J = 6.7 Hz, 2H), 2.92 - 2.86 (m, 2H), 2.83 - 2.78 (m, 4H), 2.62 - 2.58 (m, 2H), 1.66 - 1.58 (m, 2H), 1.44 - 1.34 (m, 2H), 0.94 (t, J = 7.5 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 13C NMR (101 MHz, CDCl₃, 298 K) Shift (ppm) = 171.9, 140.3, 128.4, 126.3, 64.5, 36.2, 34.8, 33.6, 30.6, 27.1, 19.1, 13.6.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, gassy, unpleasant.

Example 31: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with butyl 3-mercaptopropanoate:

Synthesis of a mixture of structural isomers:

butyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate,
 butyl 3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 butyl 3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoate,
 butyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate,
 butyl 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoate,
 butyl 3-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanoate,

butyl 3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 butyl 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoate,
 butyl 3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 butyl 3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate and
 5 butyl 3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanoate

To a solution of (–)-β-pinene (49.0 g, 0.36 mol, 1.0 equiv) and butyl 3-
 mercaptopropanoate (58.4 g, 0.36 mol, 1.0 equiv) in CH₂Cl₂ (450 mL) was added
 dropwise at 0°C boron trifluoride diethyl etherate (19.0 mL, 150 mmol, 0.4 equiv). After
 10 stirring for 1.5 hours at room temperature, the reaction mixture was poured on ice-cold
 2M aq. HCl (400 mL) and extracted with CH₂Cl₂ (150 mL). The combined organic extracts
 were washed with water, brine and dried over MgSO₄ and the solvent was removed under
 reduced pressure. The crude was purified by fractional distillation over a Vigreux-column
 under high vacuum (0.1 mbar) to afford a complex mixture of structural isomers (71.9 g,
 15 67% yield) as a colourless oil.

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm):
 172.1, 172.1, 172.1, 172.1, 137.1, 135.9, 134.2, 133.9, 132.8, 131.9, 122.6, 122.0,
 120.7, 64.5, 64.5, 54.8, 52.7, 49.4, 49.1, 48.8, 48.6, 47.2, 45.9, 45.8, 44.9, 44.3, 44.0,
 43.7, 43.1, 40.9, 39.0, 38.5, 37.9, 35.5, 35.2, 35.1, 34.8, 34.8, 31.8, 31.8, 31.3, 31.2,
 20 30.6, 29.8, 29.6, 29.3, 28.4, 27.9, 27.3, 27.1, 26.9, 26.4, 25.9, 25.6, 25.4, 25.3, 25.0,
 24.5, 24.4, 23.5, 23.3, 23.2, 22.8, 22.7, 22.2, 21.6, 21.1, 21.0, 20.8, 20.3, 19.7, 19.1,
 18.2, 17.7, 14.4, 13.9, 13.6.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
 t_R/min (peak area/%) = 10.65 (1), 10.70 (52), 10.76 (5), 10.80 (7), 10.82 (9), 10.91 (3),
 25 11.10 (20), 11.15 (2).

b.p.: 123-132°C (0.1 mbar).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulfurous,
 grapefruit juice, tropical fruit, passion fruit juice, mango, multivitamin juice.

30 *Alternative procedure:* reaction product of 2,6,6-trimethylbicyclo[3.1.1]hept-2-ene with
 butyl 3-mercaptopropanoate.

The compound was obtained from 2,6,6-trimethylbicyclo[3.1.1]hept-2-ene (2.0 g,
 14.7 mmol, 1.0 equiv), butyl 3-mercaptopropanoate (2.38 g, 14.7 mmol, 1.0 equiv) and
 boron trifluoride diethyl etherate (0.78 mL, 6.12 mmol, 0.4 equiv) according to the
 35 procedure of example 31 to give a colorless oil (4.02 g, 91% crude yield). The analytical
 data were identical to those reported above.

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, fruity,
 grapefruit juice, gazy.

Individual isomers of example 31 were separated by preparative HPLC and their structure was determined by 2D-NMR spectroscopy:

Butyl 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoate:

5 ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 171.6, 134.9, 131.8, 64.2, 46.4, 41.3, 36.1, 35.3, 32.0, 30.9, 28.0, 24.1, 22.9, 19.6, 19.3, 19.2, 13.7.

Butyl 3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate:

10 ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 171.6, 64.2, 51.1, 49.4, 48.9, 40.5, 38.2, 36.7, 36.2, 34.9, 31.8, 30.9, 25.5, 25.1, 24.8, 19.3, 13.7.

Butyl 3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoate:

15 ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 171.6, 130.6, 120.9, 64.3, 46.5, 39.3, 35.1, 30.9, 28.9, 26.1, 22.6, 19.9, 19.4, 13.7.

Butyl 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoate:

¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 171.5, 145.9, 120.6, 64.2, 49.4, 35.7, 35.3, 34.1, 30.9, 29.4, 25.3, 24.8, 21.5, 21.5, 19.8, 19.3, 13.8.

20 Butyl 3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoate:

¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 171.6, 133.3, 119.0, 64.3, 51.7, 35.4, 34.9, 32.5, 30.9, 30.7, 28.4, 23.5, 23.1, 19.3, 18.1, 17.5, 13.8.

Butyl 3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate

25 ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 171.5, 64.1, 55.0, 49.5, 47.4, 46.1, 41.2, 38.6, 35.3, 30.9, 30.0, 27.5, 20.6, 20.2, 19.3, 14.2, 13.7.

Butyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate (*syn* isomer):

30 ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 171.6, 135.3, 123.5, 64.2, 46.3, 44.1, 35.8, 31.4, 30.9, 29.6, 26.4, 23.4, 22.4, 21.3, 21.0, 19.3, 13.8.

Butyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate (*anti* isomer):

35 ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 171.5, 136.6, 123.0, 64.3, 45.3, 44.6, 35.5, 31.0, 28.5, 27.2, 25.8, 23.5, 21.8, 21.4, 19.3, 18.5, 13.7.

Butyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate:

¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 171.5, 133.5, 121.2, 64.2, 48.5, 43.3, 34.9, 31.4, 30.9, 27.4, 26.6, 25.5, 24.9, 23.4, 23.0, 19.3, 13.7.

Example 32: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with methyl 3-mercaptopropanoate:

- 5 Synthesis of a mixture of structural isomers:
- methyl 3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 methyl 3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoate,
 methyl 3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 methyl 3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 10 methyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate,
 methyl 3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 methyl 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoate,
 methyl 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoate,
 methyl 3-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanoate,
 15 methyl 3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanoate and
 methyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate

The compound was obtained from (–)-β-pinene (20.0 g, 147 mmol, 1.0 equiv), methyl 3-mercaptopropanoate (17.6 g, 147 mmol, 1.0 equiv) and boron trifluoride diethyl etherate (7.75 mL, 61.2 mmol, 0.4 equiv) according to the procedure of example 31 to give a colourless oil (21.8 g, 58% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm): 172.5, 172.5, 172.4, 137.2, 136.0, 133.9, 122.6, 122.0, 120.7, 54.9, 51.7, 49.4, 48.9, 25 47.2, 45.9, 45.8, 45.0, 44.3, 44.1, 43.1, 40.9, 38.5, 35.2, 35.1, 35.0, 34.9, 34.5, 31.8, 31.8, 31.3, 31.3, 29.8, 29.6, 29.3, 28.4, 27.9, 27.7, 27.3, 27.1, 27.0, 26.4, 25.9, 25.6, 25.4, 25.2, 24.6, 23.5, 23.3, 23.2, 22.8, 22.6, 22.2, 21.6, 21.1, 21.0, 20.8, 20.3, 20.2, 19.8, 19.7, 19.6, 18.2, 13.9.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
 30 t_R/min (peak area/%) = 9.14 (<1), 9.35 (2), 9.43 (53), 9.48 (2), 9.51 (7), 9.55 (9), 9.60 (3), 9.66 (<1), 9.88 (19), 9.93 (1).

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, grapefruit, juicy, pink grapefruit.

35 Example 33: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with ethyl 3-mercaptopropanoate:

Synthesis of a mixture of structural isomers:

- ethyl 3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 ethyl 3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoate,
 ethyl 3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 ethyl 3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 5 ethyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate,
 ethyl 3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 ethyl 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoate,
 ethyl 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoate,
 ethyl 3-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanoate,
 10 ethyl 3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanoate and
 ethyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate

The compound was obtained from (–)-β-pinene (2.89 g, 21.2 mmol, 1.0 equiv), ethyl 3-mercaptopropanoate (2.85 g, 21.2 mmol, 1.0 equiv) and boron trifluoride diethyl etherate (1.12 mL, 8.85 mmol, 0.4 equiv) according to the procedure of example 31 to give a colorless oil (4.3 g, 75% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm): 172.1, 172.0, 172.0, 137.2, 135.9, 133.9, 132.8, 131.9, 131.9, 122.7, 122.0, 120.7, 83.5, 60.6, 60.6, 54.8, 49.1, 48.9, 45.9, 45.8, 44.9, 44.3, 44.0, 43.1, 40.9, 38.5, 36.0, 35.8, 35.5, 35.2, 35.2, 34.8, 33.8, 31.8, 31.3, 31.3, 29.8, 29.3, 28.4, 27.3, 27.1, 27.0, 26.4, 20
 25.9, 25.6, 25.2, 24.6, 23.5, 23.3, 23.2, 22.7, 22.2, 21.6, 21.1, 21.0, 20.8, 20.3, 20.2, 19.8, 19.6, 18.5, 18.2, 14.4, 14.2, 13.9.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C): t_R/min (peak area/%) = 9.56 (1), 9.75 (2), 9.82 (56), 9.87 (3), 9.93 (15), 10.00 (2), 10.05 (<1), 10.25 (20), 10.30 (1).

25 Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, grapefruit, juicy, pink grapefruit, passion fruit, tropical fruit.

Example 34: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with octadecyl 3-mercaptopropanoate:

30

Synthesis of a mixture of structural isomers:

- octadecyl 3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 octadecyl 3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoate,
 octadecyl 3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 35 octadecyl 3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 octadecyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate,
 octadecyl 3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 octadecyl 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoate,

octadecyl 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoate,
 octadecyl 3-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanoate,
 octadecyl 3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 octadecyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate

5

The compound was obtained from (–)-β-pinene (1.00 g, 7.34 mmol, 1.0 equiv), octadecyl 3-mercaptopropanoate (2.63 g, 7.34 mmol, 1.0 equiv) and boron trifluoride diethyl etherate (0.39 mL, 3.06 mmol, 0.4 equiv) according to the procedure of example 31 to give a colorless oil (1.67 g, 46% yield).

10 ¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm):
 172.2, 172.1, 172.1, 137.2, 136.0, 135.0, 133.9, 122.7, 122.0, 120.7, 64.9, 64.8, 64.8,
 48.9, 46.0, 45.0, 44.3, 44.0, 43.1, 41.0, 40.1, 38.5, 38.5, 35.5, 35.3, 35.2, 34.8, 31.9,
 31.3, 31.3, 29.7, 29.6, 29.6, 29.5, 29.3, 29.2, 29.2, 28.6, 28.5, 27.1, 27.0, 26.4, 26.0,
 25.9, 25.6, 25.3, 24.6, 23.5, 23.3, 23.2, 22.8, 22.7, 22.7, 22.2, 21.6, 21.1, 21.1, 20.8,
 15 20.4, 20.2, 19.8, 18.3, 14.1.

DIP-MS: *m/z*: 494.5 ([M]⁺).

Odour description (1% solution in EtOH on paper blotter, 24 h): weak, sulphurous, citrus, grapefruit.

20 Example 35: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with 2-ethylhexyl 3-mercaptopropanoate:

Synthesis of a mixture of structural isomers:

2-ethylhexyl 3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 25 2-ethylhexyl 3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoate,
 2-ethylhexyl 3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 2-ethylhexyl 3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 2-ethylhexyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate,
 2-ethylhexyl 3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 30 2-ethylhexyl 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoate,
 2-ethylhexyl 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoate,
 2-ethylhexyl 3-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanoate,
 2-ethylhexyl 3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 2-ethylhexyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate

35

The compound was obtained from (–)-β-pinene (2.00 g, 14.7 mmol, 1.0 equiv), 2-ethylhexyl 3-mercaptopropanoate (3.21 g, 14.7 mmol, 1.0 equiv) and boron trifluoride

diethyl etherate (0.78 mL, 6.12 mmol, 0.4 equiv) according to the procedure of example 31 to give a colorless oil (2.8 g, 54% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm): 172.3, 172.2, 137.2, 133.9, 130.3, 122.6, 122.0, 120.7, 77.2, 67.1, 67.0, 48.9, 46.0, 45.0, 44.3, 44.0, 43.1, 41.0, 38.8, 38.7, 35.6, 35.3, 35.2, 34.9, 31.9, 31.3, 30.4, 29.3, 29.0, 28.9, 28.4, 27.1, 27.0, 26.5, 26.0, 25.6, 25.4, 24.6, 23.8, 23.5, 23.3, 23.2, 23.0, 22.8, 22.7, 21.6, 21.1, 20.8, 20.4, 20.2, 18.3, 14.1, 14.0, 11.0.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C): t_R/min (peak area/%) = 12.03 (<1), 12.08 (42), 12.16 (20), 12.22 (9), 12.27 (4), 12.39 (19).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, citrus, sulphurous, grapefruit juice, corps pamplemousse.

Example 36: Transesterification product of example 31 with 2-phenylethan-1-ol:

Synthesis of a mixture of structural isomers:

phenethyl 3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
phenethyl 3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoate,
phenethyl 3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoate,
phenethyl 3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
phenethyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate,
phenethyl 3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanoate,
phenethyl 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoate,
phenethyl 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoate,
phenethyl 3-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanoate,
phenethyl 3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanoate,
phenethyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate

A solution of butyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate (1.00 g, 3.35 mmol, 1.0 equiv, mixture of structural isomers, example 31), 2-phenylethan-1-ol (819 mg, 6.70 mmol, 2.0 equiv) and titanium(IV) propan-2-olate (48 mg, 5 mol%) was heated to 150°C for 3 hours, while n-butanol was distilled off via a short Vigreux column. The crude was purified by column chromatography to afford a colorless liquid (0.51 g, 44% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm): 172.0, 171.9, 137.7, 137.2, 136.0, 133.9, 128.9, 128.5, 126.5, 122.6, 122.0, 120.7, 65.1, 48.9, 47.3, 46.0, 45.8, 45.0, 44.3, 44.1, 43.1, 40.9, 35.4, 35.2, 35.1, 35.1, 34.8, 31.3,

31.3, 29.6, 28.4, 27.1, 27.0, 26.4, 25.9, 25.6, 25.2, 24.6, 23.5, 23.3, 23.2, 22.6, 21.6, 21.1, 21.1, 20.8, 20.4, 20.2, 18.3.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
 t_R/min (peak area/%) = 12.69 (42), 12.76 (11), 12.82 (7), 12.87 (2), 12.93 (1), 12.97
 5 (36), 13.06 (1).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, grapefruit, juicy, slightly floral, rosy.

Example 37: Ester saponification product of example 31 using KOH:

10

Synthesis of a mixture of structural isomers:

- 3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoic acid,
 3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoic acid,
 3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoic acid,
 15 3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoic acid,
 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoic acid,
 3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanoic acid,
 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoic acid,
 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoic acid,
 20 3-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanoic acid,
 3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanoic acid,
 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoic acid

The compound was obtained from butyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate (2.00 g, 6.70 mmol, 1.0 equiv, mixture of structural isomers, example
 25 31, AlCl₃ procedure was used) and KOH (1.77 g, 26.8 mmol, 4.0 equiv, 85%) according to the procedure of example 26 to give a brown oil (0.72 g, 44% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm):
 178.3, 178.3, 178.0, 137.4, 133.9, 121.9, 120.7, 77.2, 58.8, 53.3, 52.9, 51.2, 49.9, 49.5,
 30 49.2, 49.1, 48.5, 47.3, 45.9, 45.8, 45.2, 45.1, 44.3, 43.7, 43.1, 40.9, 40.1, 39.0, 38.5,
 38.2, 35.7, 35.3, 35.1, 34.9, 34.6, 34.5, 32.1, 31.3, 29.8, 29.3, 29.2, 28.4, 28.3, 28.1,
 27.3, 27.3, 27.1, 27.0, 26.6, 26.4, 26.2, 25.5, 24.7, 24.7, 24.6, 24.3, 24.0, 23.7, 23.6,
 23.5, 23.4, 23.2, 22.3, 21.9, 21.6, 21.1, 20.9, 20.8, 20.4, 20.2, 19.8, 18.5, 18.2, 14.4

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
 35 t_R/min (peak area/%) = 9.44 (1), 9.63 (1), 9.72 (19), 9.81 (3), 9.84 (3), 9.87 (5), 9.94
 (3), 10.17 (62), 10.70 (1), 10.76 (<1), 11.12 (2), 11.18 (<1).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, grapefruit, juicy.

Alternative procedure: reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with 3-mercaptopropanoic acid.

- 5 The compound was obtained from (–)-β-pinene (2.0 g, 14.7 mmol, 1.0 equiv), 3-mercaptopropanoic acid (1.56 g, 14.7 mmol, 1.0 equiv) and boron trifluoride diethyl etherate (0.78 mL, 6.12 mmol, 0.4 equiv) according to the procedure of example 31 to give a colorless oil (2.11 g, 59% yield).
 Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, green, garlic,
 10 sweaty, grapefruit peel.

Example 38: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with 2-mercaptopropanoic acid:

- 15 Synthesis of a mixture of structural isomers:
 2-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoic acid,
 2-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoic acid,
 2-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoic acid,
 2-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoic acid,
 20 2-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoic acid,
 2-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanoic acid,
 2-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoic acid,
 2-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoic acid,
 2-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanoic acid,
 25 2-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanoic acid,
 2-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoic acid

- The compound was obtained from (–)-β-pinene (2.00 g, 14.7 mmol, 1.0 equiv), 2-mercaptopropanoic acid (1.56 g, 14.7 mmol, 1.0 equiv) and boron trifluoride diethyl
 30 etherate (0.87 g, 6.13 mmol, 0.4 equiv) according to the procedure of example 31 to give a colorless oil (2.04 g, 57% yield).

- ¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm):
 180.4, 180.3, 180.2, 179.6, 138.3, 137.2, 136.8, 136.3, 122.7, 122.2, 121.5, 120.8,
 120.3, 119.9, 118.7, 118.1, 53.6, 53.2, 49.4, 49.2, 46.2, 46.0, 45.9, 45.7, 45.6, 45.5,
 35 45.2, 44.5, 44.4, 43.8, 43.7, 43.5, 43.4, 42.5, 41.3, 41.2, 41.0, 40.8, 40.7, 40.6, 40.2,
 40.2, 40.0, 38.9, 38.7, 38.6, 38.4, 38.3, 36.2, 35.0, 35.0, 33.8, 33.4, 33.3, 33.3, 31.9,
 31.4, 31.1, 30.0, 30.0, 29.3, 29.2, 29.0, 28.6, 28.3, 27.9, 27.7, 27.6, 27.5, 27.2, 27.1,
 26.8, 26.6, 26.1, 24.1, 24.0, 23.8, 23.6, 23.5, 23.2, 23.1, 22.7, 22.3, 22.1, 21.9, 21.5,

21.5, 21.3, 21.3, 21.2, 21.1, 21.0, 20.8, 20.7, 20.6, 20.3, 20.0, 19.2, 18.8, 18.3, 18.0, 17.8, 17.8, 17.6, 17.3, 17.2, 17.2, 16.9, 16.8, 16.5, 14.1, 13.9, 13.8.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):

t_R /min (peak area/%) = 9.29 (4), 9.37 (22), 9.39 (30), 9.43 (15), 9.48 (12), 9.52 (3), 9.57 (3), 9.64 (1), 9.84 (1), 9.89 (7).

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, green, animalic, leathery, burnt, grapefruit peel.

Example 39: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with methyl 2-mercaptopropanoate:

Synthesis of a mixture of structural isomers:

methyl 2-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
methyl 2-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoate,
methyl 2-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoate,
methyl 2-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
methyl 2-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate,
methyl 2-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanoate,
methyl 2-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoate,
methyl 2-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoate,
methyl 2-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanoate,
methyl 2-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanoate,
methyl 2-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate

The compound was obtained from (–)-β-pinene (2.20 g, 16.1 mmol, 1.0 equiv), methyl 2-mercaptopropanoate (1.94 g, 16.1 mmol, 1.0 equiv) and boron trifluoride diethyl etherate (0.94 g, 6.62 mmol, 0.4 equiv) according to the procedure of example 31 to give a colorless oil (2.13 g, 53% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm):

174.4, 174.2, 137.9, 136.7, 121.7, 121.2, 120.6, 120.5, 120.0, 52.2, 52.2, 52.1, 50.9, 45.9, 45.6, 45.3, 45.2, 44.9, 44.4, 44.4, 43.2, 43.0, 41.6, 41.6, 41.4, 40.3, 38.8, 38.3, 38.3, 35.0, 31.3, 31.2, 29.3, 28.3, 27.9, 27.1, 26.8, 26.7, 26.6, 25.5, 25.0, 24.6, 24.5, 23.5, 23.4, 23.3, 23.2, 23.2, 21.5, 21.5, 21.3, 21.3, 21.2, 21.0, 20.9, 20.7, 20.5, 20.5, 20.0, 19.5, 19.0, 18.3, 18.0, 17.9, 14.0.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
 t_R /min (peak area/%) = 8.72 (2), 8.81 (35), 8.85 (5), 8.87 (27), 8.92 (7), 8.95 (5), 9.01 (1), 9.25 (12), 9.33 (1).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, garlic, leek.

Example 40: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with 3-mercapto-N-methylpropanamide:

Synthesis of a mixture of structural isomers:

3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)-N-methylpropanamide,
 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)-N-methylpropanamide,
 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)-N-methylpropanamide,
 3-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)-N-methylpropanamide,
 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)-N-methylpropanamide,
 N-methyl-3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanamide,
 N-methyl-3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanamide,
 N-methyl-3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanamide,
 N-methyl-3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanamide,
 N-methyl-3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanamide,
 N-methyl-3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanamide

The compound was obtained from (–)-β-pinene (1.14 g, 8.39 mmol, 1.0 equiv), 3-mercapto-N-methylpropanamide (1.00 g, 8.39 mmol, 1.0 equiv) and boron trifluoride diethyl etherate (0.50 g, 3.52 mmol, 0.4 equiv) according to the procedure of example 31 to give a colorless oil (1.09 g, 51% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm):
 171.9, 137.3, 133.9, 133.9, 122.6, 121.9, 120.8, 120.6, 120.6, 120.5, 108.3, 72.7, 49.1,
 48.7, 45.9, 45.2, 44.9, 44.5, 44.2, 43.1, 41.4, 37.2, 36.9, 36.4, 31.3, 31.1, 31.0, 30.8,
 30.5, 29.3, 28.4, 27.9, 27.4, 27.1, 27.0, 26.8, 26.8, 26.6, 26.4, 26.3, 26.2, 26.0, 25.9,
 25.6, 24.6, 23.9, 23.5, 23.4, 23.3, 23.2, 22.3, 22.2, 21.8, 21.6, 21.1, 20.8, 19.0, 18.3.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
 t_R/min (peak area/%) = 10.79 (1), 10.85 (31), 10.90 (2), 11.00 (1), 11.30 (16).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, gazy, garlic, grapefruit.

Example 41: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with methyl 2-mercaptoacetate:

Synthesis of a mixture of structural isomers:

methyl 2-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)acetate,

- methyl 2-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)acetate,
 methyl 2-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)acetate,
 methyl 2-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)acetate,
 methyl 2-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)acetate,
 5 methyl 2-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)acetate,
 methyl 2-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)acetate,
 methyl 2-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)acetate,
 methyl 2-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)acetate,
 methyl 2-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)acetate,
 10 methyl 2-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)acetate

The compound was obtained from (–)-β-pinene (2.00 g, 14.7 mmol, 1.0 equiv), methyl
 2-mercaptoacetate (1.56 g, 14.7 mmol, 1.0 equiv) and boron trifluoride diethyl etherate
 (0.87 g, 6.13 mmol, 0.4 equiv) according to the procedure of example 31 to give a
 15 colorless oil (2.32 g, 65% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm):
 171.5, 138.3, 137.0, 133.9, 121.8, 121.1, 121.0, 120.5, 54.8, 52.4, 52.3, 49.7, 49.4,
 47.3, 45.8, 45.3, 43.9, 43.8, 42.9, 40.4, 38.3, 35.8, 33.4, 32.1, 31.9, 31.8, 31.8, 31.8,
 31.3, 31.2, 30.4, 29.3, 29.0, 28.6, 28.3, 27.2, 27.0, 26.9, 26.2, 25.2, 24.5, 24.3, 23.5,
 20 23.3, 23.2, 22.6, 22.1, 22.0, 21.5, 21.0, 20.9, 20.4, 20.1, 19.7, 19.5, 19.4, 18.4, 14.1,
 13.7.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
 t_R/min (peak area/%) = 8.77 (2), 8.83 (1), 8.86 (73), 8.91 (2), 8.95 (2), 9.01 (12), 9.35
 (8).

25 Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, green, burnt,
 garlic.

Example 42: Transesterification product of example 31 with butane-1,4-diol:

- 30 Synthesis of a mixture of structural isomers:
 4-hydroxybutyl 3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 4-hydroxybutyl 3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoate,
 4-hydroxybutyl 3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 4-hydroxybutyl 3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 35 4-hydroxybutyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate,
 4-hydroxybutyl 3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 4-hydroxybutyl 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoate
 4-hydroxybutyl 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoate,

4-hydroxybutyl 3-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanoate,
 4-hydroxybutyl 3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 4-hydroxybutyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate

- 5 The compound was obtained from butyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate (1.00 g, 3.35 mmol, 1.0 equiv, mixture of structural isomers, example 36), butane-1,4-diol (0.60 g, 6.70 mmol, 2.0 equiv) and titanium(IV) propan-2-olate (48 mg, 5 mol%) according to the procedure of example 36 to give a colorless oil (0.38 g, 36% yield).
- 10 ¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm): 172.1, 172.1, 162.2, 137.2, 136.0, 133.9, 122.6, 121.9, 120.7, 64.4, 62.2, 54.8, 48.9, 45.9, 45.8, 45.0, 44.3, 44.0, 43.1, 40.9, 35.4, 35.2, 35.1, 34.7, 31.3, 31.3, 29.6, 29.3, 29.0, 28.4, 27.3, 27.1, 26.9, 26.4, 25.9, 25.6, 25.3, 25.0, 24.5, 23.5, 23.3, 23.2, 22.7, 22.2, 21.6, 21.1, 20.8, 20.3, 20.1, 18.3, 13.9.
- 15 GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C): t_R/min (peak area/%) = 12.01 (41), 12.09 (15), 12.15 (9), 12.33 (35).
 Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, grapefruit, juicy.

20 Example 43: Transesterification product of example 31 with decane-1,10-diol:

Synthesis of a mixture of structural isomers:

- 10-hydroxydecyl 3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 10-hydroxydecyl 3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoate,
 25 10-hydroxydecyl 3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 10-hydroxydecyl 3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
 10-hydroxydecyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate,
 10-hydroxydecyl 3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 30 10-hydroxydecyl 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoate,
 10-hydroxydecyl 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoate,
 10-hydroxydecyl 3-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanoate,
 10-hydroxydecyl 3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanoate,
 10-hydroxydecyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate

- 35 The compound was obtained from butyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate (1.00 g, 3.35 mmol, 1.0 equiv, mixture of structural isomers, example 31), decane-1,10-diol (1.17 g, 6.70 mmol, 2.0 equiv) and titanium(IV) propan-2-olate

(48 mg, 5 mol%) according to the procedure of example 36 to give a colorless oil (0.38 g, 28% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm): 172.2, 172.1, 137.2, 133.9, 122.0, 120.7, 64.8, 64.8, 63.0, 48.9, 45.9, 45.8, 44.9, 44.3, 43.1, 35.5, 35.2, 35.2, 34.8, 32.7, 31.8, 31.3, 29.6, 29.4, 29.4, 29.4, 29.3, 29.2, 29.0, 28.5, 28.4, 27.1, 27.0, 26.4, 25.9, 25.8, 25.7, 25.6, 25.3, 24.6, 23.5, 23.3, 23.2, 22.7, 22.6, 22.2, 21.6, 21.1, 20.8, 20.2, 18.3, 14.1, 13.9.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C): t_R/min (peak area/%) = 13.68 (<1), 13.73 (38), 13.79 (9), 13.83 (2), 13.84 (1), 13.86 (4), 13.91 (6), 13.95 (2), 13.97 (2), 14.00 (<1), 14.05 (35).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, grapefruit, juicy.

Example 44: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with isooctyl 3-mercaptopropanoate (mixture of isooctyl ester isomers):

Synthesis of a mixture of *iso*-octyl and structural isomers:

iso-octyl 3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
iso-octyl 3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanoate,
iso-octyl 3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanoate,
iso-octyl 3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanoate,
iso-octyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate,
iso-octyl 3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanoate,
iso-octyl 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanoate,
iso-octyl 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanoate,
iso-octyl 3-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanoate,
iso-octyl 3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanoate,
iso-octyl 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanoate

The compound was obtained from (–)-β-pinene (2.00 g, 14.7 mmol, 1.0 equiv), isooctyl 3-mercaptopropanoate (3.21 g, 14.7 mmol, 1.0 equiv, CAS 30374-01-7) and boron trifluoride diethyl etherate (0.87 g, 6.13 mmol, 0.4 equiv) according to the procedure of example 31 to give a colorless oil (2.79 g, 54% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of isooctyl and structural isomers (peak list), δ/ppm): 172.1, 137.2, 133.9, 122.7, 122.0, 120.7, 65.1, 64.8, 63.1, 48.9, 47.3, 46.5, 46.0, 45.8, 45.0, 44.3, 43.1, 39.4, 39.2, 38.8, 38.5, 38.5, 38.4, 38.2, 36.6, 35.8, 35.5, 35.5, 35.3, 35.2, 34.8, 34.3, 33.5, 33.2, 33.0, 32.2, 31.9, 31.4, 31.3, 31.3, 30.2, 29.8, 29.8, 29.4, 29.3, 29.1, 29.0, 28.9, 28.5, 27.9, 27.4, 27.3, 27.2, 27.1, 26.6, 26.4, 26.2,

25.8, 25.7, 25.6, 25.3, 25.1, 24.6, 23.5, 23.4, 23.3, 23.2, 23.2, 22.9, 22.7, 22.7, 22.6, 22.2, 22.2, 21.6, 21.1, 21.1, 20.8, 20.2, 20.1, 19.6, 19.5, 19.1, 18.3, 17.9, 16.5, 15.6, 15.2, 14.3, 14.1, 14.0, 13.9, 12.1, 11.3.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):

5 t_R /min (peak area/%) = 12.03 (6), 12.08 (2), 12.11 (3), 12.17 (8), 12.23 (25), 12.27 (8), 12.31 (10), 12.34 (14), 12.48 (4), 12.53 (16).

Odour description (1% solution in EtOH on paper blotter, 24 h): weak, cassis.

10 Example 45: Reaction product of 2-(4-methylcyclohexyl)propan-2-ol with methyl 3-mercaptopropanoate:

Synthesis of a mixture of structural isomers:

methyl 3-((1-isopropyl-4-methylcyclohexyl)thio)propanoate,
methyl 3-((2-(4-methylcyclohexyl)propan-2-yl)thio)propanoate,
15 methyl 3-((2-isopropyl-5-methylcyclohexyl)thio)propanoate

To a solution of 2-(4-methylcyclohexyl)propan-2-ol (2.0 g, 12.8 mmol, 1.0 equiv), ZnCl₂ (1.74 g, 12.8 mmol, 1.0 equiv) in CH₂Cl₂ (30 mL) was added methyl 3-mercaptopropanoate (1.54 g, 12.8 mmol, 1.0 equiv). After stirring for 6 hours at room
20 temperature, triethylamine (1.3 g, 12.8 mmol, 1.0 equiv) was added to the reaction mixture and stirring was continued for 18 hours. After quenching with water (30 mL), the reaction mixture was extracted with MTBE (40 mL). The organic layer was washed with brine (40 mL) and dried over MgSO₄. The solvent was removed under reduced pressure to give a colorless oil (1.62 g, 49% yield).

25 ¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm): 172.5, 51.7, 49.5, 49.3, 47.6, 47.0, 46.9, 45.7, 43.8, 43.4, 38.3, 38.2, 35.5, 34.9, 34.6, 34.5, 34.5, 32.7, 32.6, 32.3, 32.2, 31.5, 27.7, 26.7, 26.3, 26.2, 25.8, 25.3, 23.7, 22.7, 22.5, 22.2, 22.0, 21.7, 19.9, 19.9, 17.4, 17.2.

30 GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C): t_R /min (peak area/%) = 9.49 (22), 9.66 (62), 9.74 (9), 9.83 (7).

Odour description (1% solution in EtOH on paper blotter, 24 h): weak, burnt, sulfury, anjeruk.

35 Example 46: Reaction product of 2-(4-methylcyclohexyl)propan-2-ol with ethyl 2-amino-3-mercaptopropanoate hydrochloride:

Synthesis of a mixture of structural isomers:

ethyl S-(1-isopropyl-4-methylcyclohexyl)cysteinate,
 ethyl S-(2-(4-methylcyclohexyl)propan-2-yl)cysteinate,
 ethyl S-(2-isopropyl-5-methylcyclohexyl)cysteinate

- 5 The compound was obtained from 2-(4-methylcyclohexyl)propan-2-ol (2.0 g, 12.8 mmol, 1.0 equiv), (*R*)-ethyl 2-amino-3-mercaptopropanoate hydrochloride (2.38 g, 12.8 mmol, 1.0 equiv), ZnCl₂ (1.74 g, 12.8 mmol, 1.0 equiv) and triethylamine (1.30 g, 12.8 mmol, 1.0 equiv) according to the procedure of example 45 to give a colorless oil (1.77 g, 48% crude yield, 16% GC purity as a complex mixture with monoterpenes and monoterpene
- 10 alcohols).
¹³C NMR (101 MHz, CDCl₃, complex reaction mixture (peak list), δ/ppm): 172.9, 143.2, 133.9, 131.7, 121.0, 117.8, 107.8, 71.1, 69.2, 61.8, 54.1, 49.9, 47.1, 45.2, 43.4, 43.4, 43.2, 41.5, 40.3, 40.0, 38.9, 37.2, 36.2, 35.5, 35.4, 35.3, 35.1, 35.0, 34.2, 33.9, 32.8, 32.7, 32.6, 32.6, 32.6, 32.5, 32.3, 32.2, 32.0, 31.9, 31.9, 31.8, 31.4, 31.3, 30.8, 30.7,
- 15 30.4, 29.6, 28.9, 28.7, 28.0, 27.7, 27.7, 27.4, 27.2, 27.0, 26.7, 26.5, 26.5, 26.4, 26.4, 26.0, 25.6, 25.5, 25.1, 23.5, 22.7, 22.5, 22.2, 22.1, 21.8, 21.6, 21.3, 21.0, 20.0, 20.0, 20.0, 19.9, 19.8, 19.7, 17.6, 14.2.
 GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
 t_R/min (peak area/%) = 10.54 (1), 10.71 (11), 10.79 (4).
- 20 Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, green, slightly grapefruit.

Example 47: Reaction product of 2-(4-methylcyclohex-3-en-1-yl)propan-2-ol with ethyl 2-amino-3-mercaptopropanoate hydrochloride:

25

Synthesis of a mixture of structural isomers:

- ethyl S-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)cysteinate,
 ethyl S-(1-isopropyl-4-methylcyclohex-3-en-1-yl)cysteinate,
 ethyl S-(1-methyl-4-(propan-2-ylidene)cyclohexyl)cysteinate,
- 30 ethyl S-(2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)cysteinate,
 ethyl S-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)cysteinate,
 ethyl S-(2-methyl-5-(propan-2-ylidene)cyclohexyl)cysteinate,
 ethyl S-(3-isopropyl-6-methylcyclohex-2-en-1-yl)cysteinate,
 ethyl S-(4-isopropyl-1-methylcyclohex-2-en-1-yl)cysteinate,
- 35 ethyl S-(4-isopropyl-1-methylcyclohex-3-en-1-yl)cysteinate,
 ethyl S-(5-methyl-2-(propan-2-ylidene)cyclohexyl)cysteinate,
 ethyl S-(6-isopropyl-3-methylcyclohex-2-en-1-yl)cysteinate

The compound was obtained from (S)-2-(4-methylcyclohex-3-en-1-yl)propan-2-ol (2.0 g, 13.0 mmol, 1.0 equiv), (R)-ethyl 2-amino-3-mercaptopropanoate hydrochloride (2.41 g, 12.8 mmol, 1.0 equiv), ZnCl₂ (1.77 g, 13.0 mmol, 1.0 equiv) and triethylamine (1.31 g, 13.0 mmol, 1.0 equiv) according to the procedure of example 45 to give a yellow oil
 5 (1.77 g, 50% crude yield, 73% purity along with a mixture of monoterpenes and monoterpene alcohols, 98% purity after removal of a head fraction by Kugelrohr distillation).

¹³C NMR (101 MHz, CDCl₃, complex reaction mixture (peak list), δ/ppm): 173.8, 137.7, 137.5, 133.9, 122.3, 121.8, 121.5, 120.7, 120.6, 120.5, 119.9, 61.3, 54.6, 54.5, 54.4,
 10 46.0, 46.0, 45.5, 45.0, 45.0, 44.6, 44.4, 44.2, 43.2, 35.8, 35.4, 32.9, 31.8, 31.5, 31.4, 31.2, 31.0, 30.9, 29.5, 29.3, 28.9, 28.4, 28.2, 27.5, 27.4, 27.1, 27.0, 26.9, 26.8, 26.6, 26.4, 26.2, 25.7, 24.6, 23.9, 23.5, 23.5, 23.4, 23.3, 23.3, 23.2, 22.8, 21.6, 21.6, 21.3, 21.1, 21.1, 21.0, 20.9, 20.8, 18.5, 18.2, 14.2, 14.1.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
 15 t_R/min (peak area/%) = 10.37 (1), 10.39 (3), 10.45 (59), 10.52 (4), 10.54 (17), 10.87 (12), 10.92 (1), 11.4 (1).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, juicy, citrus, grapefruit, natural, bitter pith, juicy.

Individual isomers of example 47 were separated by preparative HPLC and their structure
 20 *was determined by 2D-NMR spectroscopy:*

Ethyl S-(3-isopropyl-6-methylcyclohex-2-en-1-yl)cysteinate:

GC/MS (EI), t_R = 10.54 min: m/z (%): 285 (2, [M]⁺•), 169 (14), 168 (15), 137 (43), 95 (20), 93 (19), 81 (100), 79 (10), 69 (13), 43 (16), 41 (14).

25 Diastereoisomer 1: ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 174.0, 144.9, 120.8, 60.8, 55.4, 49.3, 38.7, 35.2, 33.8, 27.1, 26.1, 21.5, 19.0, 14.2.

Diastereoisomer 2: ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 174.0, 146.1, 120.2, 60.6, 55.1, 49.5, 35.6, 35.2, 34.1, 29.1, 24.6, 21.4, 19.7, 14.1.

30 Ethyl S-(6-isopropyl-3-methylcyclohex-2-en-1-yl)cysteinate:

GC/MS (EI), t_R = 10.45 min: m/z (%): 285 (1, [M]⁺•), 169 (11), 168 (13), 137 (40), 136 (10), 95 (19), 93 (17), 81 (100), 69 (13), 43 (15), 41 (14).

Diastereoisomer 1: ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 174.0, 135.6, 123.5, 60.8, 55.4, 46.4, 44.4, 36.5, 31.5, 29.5, 23.3, 22.4, 21.4, 21.0, 14.2.

35 Diastereoisomer 2: ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 173.9, 136.8, 122.9, 60.7, 55.3, 45.5, 44.9, 36.2, 28.5, 27.2, 23.6, 21.8, 21.3, 18.6, 14.2.

Ethyl S-(4-isopropyl-1-methylcyclohex-2-en-1-yl)cysteinate:

¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 174.0, 133.3, 132.0, 60.8, 55.1, 45.8, 42.0, 36.5, 34.9, 32.1, 30.1, 22.5, 19.9, 19.6, 14.2.

Ethyl S-(5-methyl-2-(propan-2-ylidene)cyclohexyl)cysteinate:

5 ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 174.1, 131.4, 124.7, 60.8, 55.2, 44.8, 41.0, 36.9, 36.3, 27.5, 25.1, 22.6, 20.5, 20.4, 14.2.

Ethyl S-(4-isopropyl-1-methylcyclohex-3-en-1-yl)cysteinate:

10 ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 174.0, 142.2, 116.5, 60.7, 55.1, 44.0, 38.8, 35.1, 34.9, 33.0, 27.1, 24.1, 21.5, 14.2.

Ethyl S-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)cysteinate:

GC/MS (EI), t_R = 10.87 min: m/z (%): 285 (2, [M]⁺), 137 (20), 136 (100), 121 (64), 95 (18), 93 (48), 81 (64), 69 (21), 55 (15), 43 (26), 41 (32).

15 ¹³C NMR (151 MHz, benzene-d₆, δ/ppm): 174.0, 133.6, 121.3, 60.8, 55.1, 48.6, 43.6, 33.3, 31.6, 27.6, 26.8, 25.7, 25.0, 23.5, 14.3.

Alternative procedure using racemic 2-(4-methylcyclohex-3-en-1-yl)propan-2-ol:

20 The compound was obtained from (*rac.*)-2-(4-methylcyclohex-3-en-1-yl)propan-2-ol (2.0 g, 13.0 mmol, 1.0 equiv), (*R*)-ethyl 2-amino-3-mercaptopropanoate hydrochloride (2.41 g, 13.0 mmol, 1.0 equiv), ZnCl₂ (1.77 g, 13.0 mmol, 1.0 equiv) and triethylamine (1.31 g, 13.0 mmol, 1.0 equiv) according to the procedure of example 45 to give a yellow oil (2.07 g, 56% crude yield, 46% purity along with a mixture of monoterpenes and
25 monoterpene alcohols).

¹³C NMR (126 MHz, CDCl₃, complex reaction mixture (peak list), δ/ppm): 173.2, 138.0, 137.8, 134.2, 134.0, 127.5, 122.3, 121.6, 121.6, 121.2, 120.7, 120.5, 118.8, 108.3, 73.6, 72.7, 69.8, 61.7, 54.3, 54.1, 46.4, 45.9, 45.6, 44.9, 44.6, 44.4, 44.2, 42.4, 41.3, 41.0, 40.2, 37.2, 35.0, 34.9, 34.5, 33.0, 32.9, 32.9, 31.4, 31.4, 31.2, 31.2, 31.0, 30.8, 30.7,
30 30.7, 30.5, 29.7, 29.5, 29.3, 28.8, 28.4, 28.1, 28.1, 27.5, 27.5, 27.4, 27.0, 26.9, 26.8, 26.6, 26.4, 26.2, 26.0, 25.7, 24.7, 23.9, 23.5, 23.5, 23.4, 23.4, 23.3, 23.3, 23.2, 23.0, 22.8, 21.9, 21.6, 21.6, 21.3, 21.2, 21.2, 21.1, 21.0, 20.9, 20.8, 20.2, 20.0, 19.7, 18.6, 18.3, 18.1, 14.1, 14.1, 14.1.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
35 t_R/min (peak area/%) = 10.36 (<1), 10.39 (1), 10.44 (25), 10.52 (2), 10.54 (11), 10.87 (5), 10.92 (2).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, citrus, sulphurous, grapefruit juice.

Example 48: Reaction product of 2-(4-methylcyclohex-3-en-1-yl)propan-2-ol with ethyl 2-acetamido-3-mercaptopropanoate:

- 5 Synthesis of a mixture of structural isomers:
- ethyl N-acetyl-S-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)cysteinate,
 ethyl N-acetyl-S-(1-isopropyl-4-methylcyclohex-3-en-1-yl)cysteinate,
 ethyl N-acetyl-S-(1-methyl-4-(propan-2-ylidene)cyclohexyl)cysteinate,
 ethyl N-acetyl-S-(2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)cysteinate,
 10 ethyl N-acetyl-S-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)cysteinate,
 ethyl N-acetyl-S-(2-methyl-5-(propan-2-ylidene)cyclohexyl)cysteinate,
 ethyl N-acetyl-S-(3-isopropyl-6-methylcyclohex-2-en-1-yl)cysteinate,
 ethyl N-acetyl-S-(4-isopropyl-1-methylcyclohex-2-en-1-yl)cysteinate,
 ethyl N-acetyl-S-(4-isopropyl-1-methylcyclohex-3-en-1-yl)cysteinate,
 15 ethyl N-acetyl-S-(5-methyl-2-(propan-2-ylidene)cyclohexyl)cysteinate,
 ethyl N-acetyl-S-(6-isopropyl-3-methylcyclohex-2-en-1-yl)cysteinate

The compound was obtained from (*S*)-2-(4-methylcyclohex-3-en-1-yl)propan-2-ol (2.0 g, 13.0 mmol, 1.0 equiv), (*R*)-ethyl 2-acetamido-3-mercaptopropanoate (2.48 g, 13.0 mmol, 1.0 equiv), ZnCl₂ (1.77 g, 13.0 mmol, 1.0 equiv) and triethylamine (1.31 g, 13.0 mmol, 1.0 equiv) according to the procedure of example 45 to give a yellow oil (2.41 g, 57% crude yield, 60% purity along with a mixture of monoterpenes and monoterpene alcohols).

¹³C NMR (101 MHz, CDCl₃, complex reaction mixture (peak list), δ/ppm): 170.8, 170.8, 25 169.7, 169.6, 137.8, 134.1, 133.9, 127.5, 122.1, 122.0, 121.4, 121.2, 120.7, 120.6, 120.5, 115.9, 108.3, 73.6, 72.6, 69.7, 62.0, 61.7, 52.2, 52.0, 49.4, 45.9, 45.9, 45.6, 45.0, 44.9, 44.6, 44.5, 44.4, 43.1, 41.0, 36.2, 34.5, 32.9, 32.5, 32.4, 31.5, 31.4, 31.4, 31.2, 31.2, 30.9, 30.7, 30.5, 29.7, 29.7, 29.4, 29.2, 28.8, 28.3, 28.2, 27.8, 27.5, 27.5, 27.4, 27.1, 26.9, 26.8, 26.5, 26.2, 24.5, 23.9, 23.5, 23.5, 23.4, 23.4, 23.3, 23.1, 23.1, 30 22.9, 22.8, 21.9, 21.5, 21.5, 21.2, 21.1, 21.0, 21.0, 20.9, 20.8, 20.7, 20.7, 19.7, 18.5, 18.3, 14.1.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
 t_R/min (peak area/%) = 11.58 (42), 11.65 (9), 11.67 (6), 11.97 (3).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous,
 35 grapefruit, creamy, mango.

Example 49: Reaction product of 2-(4-methylcyclohex-3-en-1-yl)propan-2-ol with ethyl (tert-butoxycarbonyl)cysteinate:

Synthesis of a mixture of structural isomers:

ethyl N-(tert-butoxycarbonyl)-S-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)cysteinate, ethyl N-(tert-butoxycarbonyl)-S-(1-isopropyl-4-methylcyclohex-3-en-1-yl)cysteinate, ethyl N-(tert-butoxycarbonyl)-S-(1-methyl-4-(propan-2-ylidene)cyclohexyl)cysteinate, ethyl N-(tert-butoxycarbonyl)-S-(2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)cysteinate, ethyl N-(tert-butoxycarbonyl)-S-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)cysteinate, ethyl N-(tert-butoxycarbonyl)-S-(2-methyl-5-(propan-2-ylidene)cyclohexyl)cysteinate, ethyl N-(tert-butoxycarbonyl)-S-(3-isopropyl-6-methylcyclohex-2-en-1-yl)cysteinate, ethyl N-(tert-butoxycarbonyl)-S-(4-isopropyl-1-methylcyclohex-2-en-1-yl)cysteinate, ethyl N-(tert-butoxycarbonyl)-S-(4-isopropyl-1-methylcyclohex-3-en-1-yl)cysteinate, ethyl N-(tert-butoxycarbonyl)-S-(5-methyl-2-(propan-2-ylidene)cyclohexyl)cysteinate, ethyl N-(tert-butoxycarbonyl)-S-(6-isopropyl-3-methylcyclohex-2-en-1-yl)cysteinate

The compound was obtained from (S)-2-(4-methylcyclohex-3-en-1-yl)propan-2-ol (2.0 g, 13.0 mmol, 1.0 equiv), ethyl (tert-butoxycarbonyl)-L-cysteinate (3.23 g, 13.0 mmol, 1.0 equiv), ZnCl₂ (1.77 g, 13.0 mmol, 1.0 equiv) and triethylamine (1.31 g, 13.0 mmol, 1.0 equiv) according to the procedure of example 45 to give a yellow oil (3.65 g, 73% crude yield, 16% purity along with a mixture of monoterpenes and monoterpene alcohols). ¹³C NMR (101 MHz, CDCl₃, complex reaction mixture (peak list), δ/ppm): 171.0, 133.9, 121.4, 120.7, 120.5, 79.9, 72.7, 72.7, 61.8, 61.7, 61.6, 49.4, 44.9, 34.5, 32.9, 31.4, 31.4, 31.2, 31.0, 30.8, 29.5, 29.2, 28.8, 28.3, 28.1, 27.5, 27.4, 26.9, 26.8, 26.2, 23.9, 23.5, 23.3, 22.8, 20.9, 20.8, 14.1, 14.1.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C): t_R/min (peak area/%) = 11.97 (9), 12.04 (6), 12.16 (1).

Odour description (1% solution in EtOH on paper blotter, 24 h): sulfurous, metallic, grapefruit, gaseous, then weak, grapefruit.

Example 50: Reaction product of 2-(4-methylcyclohex-3-en-1-yl)propan-2-ol with ethyl ((benzyloxy)carbonyl)cysteinate:

Synthesis of a mixture of structural isomers:

ethyl N-((benzyloxy)carbonyl)-S-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)cysteinate,
ethyl N-((benzyloxy)carbonyl)-S-(1-isopropyl-4-methylcyclohex-3-en-1-yl)cysteinate,

- ethyl N-((benzyloxy)carbonyl)-S-(1-methyl-4-(propan-2-ylidene)cyclohexyl)cysteinate,
 ethyl N-((benzyloxy)carbonyl)-S-(2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)cysteinate,
 5 ethyl N-((benzyloxy)carbonyl)-S-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)cysteinate,
 ethyl N-((benzyloxy)carbonyl)-S-(2-methyl-5-(propan-2-ylidene)cyclohexyl)cysteinate,
 ethyl N-((benzyloxy)carbonyl)-S-(3-isopropyl-6-methylcyclohex-2-en-1-yl)cysteinate,
 10 ethyl N-((benzyloxy)carbonyl)-S-(4-isopropyl-1-methylcyclohex-2-en-1-yl)cysteinate,
 ethyl N-((benzyloxy)carbonyl)-S-(4-isopropyl-1-methylcyclohex-3-en-1-yl)cysteinate,
 15 ethyl N-((benzyloxy)carbonyl)-S-(5-methyl-2-(propan-2-ylidene)cyclohexyl)cysteinate,
 ethyl N-((benzyloxy)carbonyl)-S-(6-isopropyl-3-methylcyclohex-2-en-1-yl)cysteinate
- 20 The compound was obtained from (S)-2-(4-methylcyclohex-3-en-1-yl)propan-2-ol (1.0 g, 6.48 mmol, 1.0 equiv), ethyl ((benzyloxy)carbonyl)-L-cysteinate (1.84 g, 6.48 mmol, 1.0 equiv), ZnCl₂ (0.88 g, 6.48 mmol, 1.0 equiv) and triethylamine (0.66 g, 6.48 mmol, 1.0 equiv) according to the procedure of example 45 to give a colourless oil (1.39 g, 73% crude yield, >99% purity).
- 25 ¹³C NMR (126 MHz, CDCl₃, complex reaction mixture (peak list), δ/ppm): 170.7, 155.7, 155.6, 137.9, 137.8, 136.2, 136.2, 128.5, 128.1, 128.1, 128.1, 121.6, 121.2, 67.0, 67.0, 61.8, 53.8, 46.0, 45.6, 45.1, 44.6, 44.4, 44.4, 35.0, 32.7, 32.7, 31.2, 31.2, 29.2, 28.4, 28.2, 26.9, 26.9, 24.4, 24.3, 23.5, 23.5, 23.3, 23.3, 22.7, 21.9, 21.6, 21.5, 21.2, 21.1, 21.0, 20.8, 18.5, 18.2, 14.1.
- 30 GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C): t_R/min (peak area/%) = 13.54 (1), 13.55 (2), 13.59 (75), 13.64 (5), 13.65 (8), 13.67 (3), 13.89 (1), 13.93 (4).
 Odour description (1% solution in EtOH on paper blotter, 24 h): green, metallic, burnt, coffee.
- 35

Example 51: Reaction product of 2-(4-methylcyclohex-3-en-1-yl)propan-2-ol with benzyl cysteinate hydrochloride:

Synthesis of a mixture of structural isomers:

- 5 benzyl S-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)cysteinate,
benzyl S-(1-isopropyl-4-methylcyclohex-3-en-1-yl)cysteinate,
benzyl S-(1-methyl-4-(propan-2-ylidene)cyclohexyl)cysteinate,
benzyl S-(2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)cysteinate,
benzyl S-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)cysteinate,
10 benzyl S-(2-methyl-5-(propan-2-ylidene)cyclohexyl)cysteinate,
benzyl S-(3-isopropyl-6-methylcyclohex-2-en-1-yl)cysteinate,
benzyl S-(4-isopropyl-1-methylcyclohex-2-en-1-yl)cysteinate,
benzyl S-(4-isopropyl-1-methylcyclohex-3-en-1-yl)cysteinate,
benzyl S-(5-methyl-2-(propan-2-ylidene)cyclohexyl)cysteinate,
15 benzyl S-(6-isopropyl-3-methylcyclohex-2-en-1-yl)cysteinate

The compound was obtained from (*S*)-2-(4-methylcyclohex-3-en-1-yl)propan-2-ol (5.23 g, 33.9 mmol, 1.2 equiv), benzyl L-cysteinate hydrochloride (7.0 g, 28.3 mmol, 1.0 equiv, prepared according to WO2010006682A1) and ZnCl₂ (3.85 g, 28.3 mmol, 1.0 equiv) in toluene followed by removal of a head fraction by Kugelrohr distillation (40 °C / 0.02 mbar) according to the procedure of example 45 to give a yellow oil (4.4 g, 23% yield, 86% purity along with a mixture of monoterpenes and monoterpene alcohols).

¹³C NMR (101 MHz, CDCl₃, complex reaction mixture (peak list), δ/ppm): 173.8, 173.8, 141.1, 137.5, 137.3, 136.3, 136.2, 135.4, 133.8, 133.8, 132.6, 132.5, 132.2, 132.2, 128.5, 128.3, 128.3, 128.2, 128.2, 128.2, 128.1, 127.3, 126.8, 122.4, 122.2, 121.8, 25 121.5, 120.6, 120.5, 72.5, 66.8, 64.8, 54.8, 54.6, 54.6, 54.6, 54.5, 54.4, 54.4, 48.9, 45.9, 45.9, 45.4, 44.9, 44.9, 44.5, 44.3, 44.3, 44.1, 43.2, 43.1, 41.5, 41.1, 38.7, 35.8, 35.8, 35.4, 35.3, 34.1, 34.1, 32.5, 32.5, 31.7, 31.4, 31.2, 31.1, 30.9, 29.8, 29.2, 28.8, 28.3, 28.2, 27.3, 27.0, 26.9, 26.8, 26.8, 26.4, 26.1, 25.5, 24.5, 23.9, 23.4, 23.4, 23.3, 23.2, 23.1, 22.5, 22.1, 21.9, 21.9, 21.5, 21.0, 20.9, 20.9, 20.7, 20.7, 19.5, 19.4, 19.4, 30 19.1, 18.3, 18.2.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C): t_R/min (peak area/%) = 12.78 (46), 12.84 (25), 12.85 (2), 13.05 (9), 13.08 (1), 13.32 (1), 13.38 (1), 13.44 (1).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, 35 grapefruit.

Example 52: Reaction product of 2-(4-methylcyclohex-3-en-1-yl)propan-2-ol with hexyl cysteinate hydrochloride:

Synthesis of a mixture of structural isomers:

- 5 hexyl S-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)cysteinate,
hexyl S-(1-isopropyl-4-methylcyclohex-3-en-1-yl)cysteinate,
hexyl S-(1-methyl-4-(propan-2-ylidene)cyclohexyl)cysteinate,
hexyl S-(2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)cysteinate,
hexyl S-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)cysteinate,
10 hexyl S-(2-methyl-5-(propan-2-ylidene)cyclohexyl)cysteinate,
hexyl S-(3-isopropyl-6-methylcyclohex-2-en-1-yl)cysteinate,
hexyl S-(4-isopropyl-1-methylcyclohex-2-en-1-yl)cysteinate,
hexyl S-(4-isopropyl-1-methylcyclohex-3-en-1-yl)cysteinate,
hexyl S-(5-methyl-2-(propan-2-ylidene)cyclohexyl)cysteinate,
15 hexyl S-(6-isopropyl-3-methylcyclohex-2-en-1-yl)cysteinate

The compound was obtained from (S)-2-(4-methylcyclohex-3-en-1-yl)propan-2-ol (5.23 g, 33.9 mmol, 1.1 equiv), hexyl L-cysteinate hydrochloride (7.4 g, 30.6 mmol, 1.0 equiv, prepared in analogy according to WO2010006682A1) and ZnCl₂ (4.17 g, 28.3 mmol, 1.0 equiv) in toluene followed by removal of a head fraction by Kugelrohr distillation (40 °C / 0.02 mbar) according to the procedure of example 45 to give a yellow oil (6.6 g, 32% yield, 95% purity along with a mixture of monoterpenes and monoterpene alcohols).

25 ¹³C NMR (101 MHz, CDCl₃, complex reaction mixture (peak list), δ/ppm): 174.1, 137.5, 137.3, 136.2, 136.2, 133.8, 122.6, 122.3, 121.8, 121.6, 120.7, 120.6, 65.2, 62.7, 54.9, 54.6, 54.5, 54.5, 48.9, 46.0, 45.9, 45.4, 44.9, 44.5, 44.4, 44.4, 44.0, 43.2, 43.1, 36.2, 36.0, 35.6, 32.8, 32.8, 32.7, 31.8, 31.6, 31.4, 31.3, 31.2, 31.2, 29.4, 29.2, 28.8, 28.5, 28.4, 28.2, 27.8, 27.5, 27.1, 26.9, 26.9, 26.5, 26.4, 26.2, 25.6, 25.6, 25.5, 24.5, 23.4,
30 23.4, 23.3, 23.2, 23.1, 22.7, 22.5, 22.4, 22.0, 21.5, 21.2, 21.1, 21.0, 20.9, 20.7, 19.5, 19.5, 18.4, 18.2, 13.9.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
t_R/min (peak area/%) = 12.04 (1), 12.10 (56), 12.16 (24), 12.40 (11), 12.43 (2), 12.76 (1).

35 Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, grapefruit, floral.

Example 53: Ester saponification product of example 47 with KOH:

Synthesis of a mixture of structural isomers:

- 5 S-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)cysteine,
 S-(1-isopropyl-4-methylcyclohex-3-en-1-yl)cysteine,
 S-(1-methyl-4-(propan-2-ylidene)cyclohexyl)cysteine,
 S-(2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)cysteine,
 S-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)cysteine,
 S-(2-methyl-5-(propan-2-ylidene)cyclohexyl)cysteine,
 10 S-(3-isopropyl-6-methylcyclohex-2-en-1-yl)cysteine,
 S-(4-isopropyl-1-methylcyclohex-2-en-1-yl)cysteine,
 S-(4-isopropyl-1-methylcyclohex-3-en-1-yl)cysteine,
 S-(5-methyl-2-(propan-2-ylidene)cyclohexyl)cysteine,
 S-(6-isopropyl-3-methylcyclohex-2-en-1-yl)cysteine

15

To a solution of ethyl S-(6-isopropyl-3-methylcyclohex-2-en-1-yl)-L-cysteinate (4.00 g, 14.0 mmol, 1.0 equiv, mixture of structural isomers, example 47) in ethanol (40 mL) and water (40 mL) was added KOH (2.40 g, 3.05 mmol, 3 equiv) and the reaction mixture was refluxed for 3 hours. The reaction mixture was acidified with aq. HCl and concentrated under reduced pressure. The crude was purified by ion exchange chromatography (Dowex 50WX8-200, hydrogen form, nanopure water then aq. NH₃ solution for elution) to afford the free amino acid (1.2 g, 17% yield) as a beige solid.

¹³C NMR (101 MHz, DMSO-d₆, complex mixture of structural isomers (peak list), δ/ppm):
 13C NMR (101 MHz, CD₃SOCD₃, 298 K) Shift (ppm) = 169.1, 168.3, 136.3, 135.8, 122.2,
 25 121.7, 54.2, 54.1, 44.6, 44.0, 43.6, 43.6, 32.3, 32.2, 27.7, 27.4, 26.6, 26.4, 23.3, 23.2,
 23.0, 21.5, 21.5, 20.6, 20.4, 18.9, 18.6.

LC/MS (ESI+): *m/z* (%): 258.2 ([M+H]⁺), 515.3 ([2M+H]⁺).

LC/MS (ESI-): *m/z* (%): 256.6 ([M-H]⁻), 513.5 ([2M-H]⁻).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous,
 30 grapefruit, onion, sweaty.

Example 54: butyl 3-((2-(4-methyl-2-oxocyclohexyl)propan-2-yl)thio)propanoate

The compound was obtained from butyl 3-mercaptopropanoate (2.13 g, 13.1 mmol, 1.0 equiv), DBU (1.82 g, 13.1 mmol, 1.0 equiv) and (R)-5-methyl-2-(propan-2-ylidene)cyclohexan-1-one (2.0 g, 13.1 mmol, 1.0 equiv) according to the procedure of example 3 as a colorless oil (3.47 g, 84% yield, mixture of diastereoisomers).

GC/MS (EI): *m/z* (%): 314 (2, [M]⁺), 296 (11), 203 (11), 153 (62), 152 (60), 109 (96), 81 (95), 69 (72), 67 (55), 41 (100).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 211.2, 210.6, 172.1, 172.1, 64.6, 64.5, 58.1, 57.8, 52.3, 50.8, 50.3, 47.5, 47.4, 36.7, 34.8, 34.6, 34.5, 34.1, 33.2, 32.8, 32.6, 31.6, 31.4, 30.6, 29.6, 28.6, 28.1, 27.8, 27.0, 25.4, 24.5, 23.9, 23.0, 22.9, 22.8, 22.2, 22.1, 21.7, 19.1, 13.7.

Odour description (1% solution in EtOH on paper blotter, 24 h): fruity, cassis, tropical fruit, eucalyptus bud.

10 Example 55: ethyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate

The compound was obtained from ethyl 3-mercaptopropanoate (0.82 g, 6.1 mmol, 1.0 equiv), DBU (0.93 g, 6.1 mmol, 1.0 equiv) and 4-methylpent-3-en-2-one (0.60 g, 6.1 mmol, 1.0 equiv) according to the procedure of example 3 as a colorless oil (0.85 g, 59% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 4.13 (q, *J* = 7.3 Hz, 2H), 2.80 - 2.76 (m, 2H), 2.68 (s, 2H), 2.55 - 2.51 (m, 2H), 2.15 (s, 3H), 1.40 (s, 6H), 1.24 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 206.6, 171.8, 60.6, 54.4, 43.8, 34.4, 32.2, 28.3, 23.1, 14.1.

20 Odour description (1% solution in EtOH on paper blotter, 24 h): green, fruity, sulphurous, rubbery, tropical fruit, sweaty, garlic.

Example 56: butyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate

25 The compound was obtained from butyl 3-mercaptopropanoate (0.99 g, 6.1 mmol, 1.0 equiv), DBU (0.93 g, 6.1 mmol, 1.0 equiv) and 4-methylpent-3-en-2-one (0.60 g, 6.1 mmol, 1.0 equiv) according to the procedure of example 3 as a colorless oil (0.70 g, 44% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 4.06 (t, *J* = 6.7 Hz, 2H), 2.81 - 2.73 (m, 2H), 2.67 (s, 2H), 2.55 - 2.50 (m, 2H), 2.14 (s, 3H), 1.61 - 1.54 (m, 2H), 1.41 - 1.29 (m, 2H), 1.39 (s, 6H), 0.89 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 206.5, 171.9, 64.5, 54.4, 43.7, 34.4, 32.2, 30.5, 28.3, 23.1, 19.0, 13.6.

35 Odour description (1% solution in EtOH on paper blotter, 24 h): green fruity, sulphurous, rubbery, tropical fruit, sweaty, leek.

Example 57: methyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate

The compound was obtained from methyl 3-mercaptopropanoate (2.4 g, 20 mmol, 1.0 equiv), DBU (3.1 g, 20 mmol, 1.0 equiv) and 4-methylpent-3-en-2-one (2.0 g, 20 mmol, 1.0 equiv) according to the procedure of example 3 as a colorless oil (1.8 g, 38% yield).

¹H NMR (400 MHz, CDCl₃, δ/ppm): 3.67 (s, 3H), 2.81 - 2.76 (m, 2H), 2.67 (s, 2H), 2.57 - 2.52 (m, 2H), 2.15 (s, 3H), 1.40 (s, 6H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 206.5, 172.2, 54.3, 51.7, 43.8, 34.2, 32.2, 28.3, 23.1.

Odour description (1% solution in EtOH on paper blotter, 24 h): green, rubbery sulphurous, fruity, garlic, sweaty.

Example 58: Butyl 3-((4-hydroxy-2-methylpentan-2-yl)thio)propanoate

a) To a solution of 4-methylpent-3-en-2-one (5.1 g, 52 mmol, 1.2 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (6.6 g, 43 mmol, 1.0 equiv) in THF (40 mL) was added dropwise at 0°C butyl 3-mercaptopropanoate (7.0 g, 43 mmol, 1.0 equiv). After stirring for 16 hours at room temperature, the reaction mixture was quenched with 2M aq. HCl and extracted with MTBE. The combined organic extracts were washed with 2M aq. HCl and brine, dried over MgSO₄ and concentrated under reduced pressure. The crude was purified by Kugelrohr distillation (120°C at 0.05 mbar) to give butyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate (10.5 g, 93%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 4.04 (t, J = 6.7 Hz, 2H), 2.78 - 2.73 (m, 2H), 2.65 (s, 2H), 2.50 (t, J = 7.6 Hz, 2H), 2.13 (s, 3H), 1.60 - 1.52 (m, 2H), 1.37 (s, 6H), 1.36 - 1.28 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H)

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 206.4, 171.8, 64.5, 54.3, 43.7, 34.4, 32.1, 30.5, 28.2, 23.0, 19.0, 13.6.

Odour description (1% solution in EtOH on paper blotter, 24 h): green fruity(sulphurous, rubbery, tropical fruit, sweaty, leak).

b) To a suspension of NaBH₄ (0.15 g, 3.8 mmol, 0.5 equiv) in EtOH (10 mL) was added dropwise at 0°C butyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate (2.0 g, 7.7 mmol, 1.0 equiv). After stirring for 16 hours, the reaction mixture was poured on 2M aq. HCl and extracted with MTBE. The combined organic extracts were washed with water and brine, dried over MgSO₄ and concentrated under reduced pressure. The crude was purified by column chromatography to furnish butyl 3-((4-hydroxy-2-methylpentan-2-yl)thio)propanoate (0.9 g, 40% yield) as a colorless liquid. In addition, ethyl 3-((4-hydroxy-2-methylpentan-2-yl)thio)propanoate (0.35 g, 19% yield) was isolated as a side product.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 4.10 - 4.00 (m, 3H), 3.51 - 3.44 (m, 1H), 2.77 (tq, J = 7.6, 11.8 Hz, 2H), 2.53 (t, J = 7.5 Hz, 2H), 1.79 - 1.73 (m, 1H), 1.63 - 1.51 (m, 2H), 1.46 (dd, J = 1.8, 15.0 Hz, 1H), 1.39 - 1.27 (m, 8H), 1.13 (d, J = 6.1 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 171.8, 65.1, 64.6, 49.1, 44.7, 34.1, 30.9, 30.5, 28.1, 24.3, 23.0, 19.0, 13.6.

Odour description (1% solution in EtOH on paper blotter, 48 h): slightly green (sulphurous, grapefruit, grapefruit peel) fruity (grapefruit juice).

Example 60: Butyl 3-((1-hydroxy-2-methylpentan-2-yl)thio)propanoate

To a solution of butyl acrylate (1.99 g, 15 mmol, 2 equiv) and 2-mercapto-2-methylpentan-1-ol (1.0 g, 7.4 mmol, 1.0 equiv) was added dropwise 1,8-diazabicyclo[5.4.0]undec-7-ene (1.1 mL, 7.4 mmol, 2 equiv) at 0°C. After stirring for 3 hours at room temperature, the crude reaction mixture was directly purified by column chromatography to afford butyl 3-((1-hydroxy-2-methylpentan-2-yl)thio)propanoate (0.90 g, 50% yield) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 4.07 (t, J = 6.7 Hz, 2H), 3.38 (dq, J = 6.5, 11.7 Hz, 2H), 2.68 - 2.64 (m, 2H), 2.57 (t, J = 6.5 Hz, 1H), 2.54 - 2.49 (m, 2H), 1.62 - 1.54 (m, 2H), 1.51 - 1.25 (m, 6H), 1.17 (s, 3H), 0.95 - 0.83 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 172.1, 67.5, 64.6, 52.1, 39.4, 34.2, 30.5, 22.1, 21.8, 19.0, 17.0, 14.4, 13.6.

Odour description (1% solution in EtOH on paper blotter, 48 h): green(sulphurous, rubbery, grapefruit, grapefruit peel).

Example 63: Butyl 2-methyl-3-((1-phenylethyl)thio)propanoate

To a solution of butyl methacrylate (1.3 g, 8.9 mmol, 2 equiv) and 1-phenylethane-1-thiol (0.61 g, 4.4 mmol, 1.0 equiv) was added dropwise 1,8-diazabicyclo[5.4.0]undec-7-ene (0.66 mL, 4.4 mmol, 2 equiv) at 0°C. After stirring for 3 hours at room temperature, the crude reaction mixture was directly purified by column chromatography to afford butyl 2-methyl-3-((1-phenylethyl)thio)propanoate (1.0 g, 80% yield, 1:1 mixture of diastereoisomers) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.37 - 7.20 (m, 5H), 4.12 - 4.00 (m, 2H), 4.00 - 3.85 (m, 1H), 2.68 - 2.59 (m, 1H), 2.59 - 2.41 (m, 1H), 2.38 - 2.30 (m, 1H), 1.65 - 1.50 (m, 5H), 1.47 - 1.23 (m, 2H), 1.15 (2d, J = 7.0, 3H), 0.93 (2d, J = 7.4 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 175.2, 175.1, 143.8, 143.7, 128.4, 128.4, 127.3, 127.2, 127.1, 64.3, 44.5, 44.3, 40.0, 39.9, 34.5, 34.4, 30.6, 22.5, 22.5, 19.1, 19.1, 16.9, 16.7, 13.7.

Odour description (1% solution in EtOH on paper blotter, 24 h): green sulphurous(thiol, burnt, salted snack, tangerine peel, grapefruit peel).

Examples 59, 61, 62 and 64

5

Example compounds 59, 61, 62 and 64, described in Tables 1 and 2 above, are prepared using techniques analogous to those for preparing Examples 1 to 57, as appropriate.

Example 65: Butyl 3-((1-hydroxy-2-methylpentan-2-yl)thio)-2-methylpropanoate

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To a solution of butyl methacrylate (1.2 g, 8.7 mmol, 2 equiv) and 2-mercapto-2-methylpentan-1-ol (0.58 g, 4.3 mmol, 1.0 equiv) was added dropwise 1,8-diazabicyclo[5.4.0]undec-7-ene (0.65 mL, 4.3 mmol, 2 equiv) at 0°C. After stirring for 3 hours at room temperature, the crude reaction mixture was directly purified by column chromatography to afford butyl 3-((1-hydroxy-2-methylpentan-2-yl)thio)-2-methylpropanoate (0.73 g, 61% yield, mixture of diastereoisomers) as a colorless liquid.

15

¹H NMR (400 MHz, CDCl₃, δ/ppm): 4.10 (t, J = 6.7 Hz, 2H), 3.45 - 3.30 (m, 2H), 2.75 - 2.64 (m, 1H), 2.64 - 2.53 (m, 1H), 2.53 - 2.45 (m, 2H), 1.65 - 1.57 (m, 2H), 1.50 - 1.30 (m, 6H), 1.25 - 1.15 (m, 6H), 0.99 - 0.84 (m, 6H).

20

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 175.3, 175.2, 67.5, 67.4, 64.6, 52.1, 52.1, 40.1, 39.5, 39.5, 30.6, 30.0, 22.2, 22.1, 19.1, 17.3, 17.2, 17.0, 17.0, 14.5, 13.6.

Odour description (1% solution in EtOH on paper blotter, 24 h): weak, slightly green sulphurous (cassis).

25 Example 66: Ethyl 3-((1-hydroxy-2-methylpentan-2-yl)thio)-2-methylpropanoate

To a solution of ethyl methacrylate (0.99 g, 8.7 mmol, 2 equiv) and 2-mercapto-2-methylpentan-1-ol (0.58 g, 4.3 mmol, 1.0 equiv) was added dropwise 1,8-diazabicyclo[5.4.0]undec-7-ene (0.65 mL, 4.3 mmol, 2 equiv) at 0°C. After stirring for 3 hours at room temperature, the crude reaction mixture was directly purified by column chromatography to afford ethyl 3-((1-hydroxy-2-methylpentan-2-yl)thio)-2-methylpropanoate (0.65 g, 60% yield, mixture of diastereoisomers) as a colorless liquid.

30

¹H NMR (400 MHz, CDCl₃, δ/ppm): 4.14 (q, J = 7.2 Hz, 2H), 3.45 - 3.29 (m, 2H), 2.75 - 2.65 (m, 1H), 2.62 - 2.43 (m, 3H), 1.50 - 1.30 (m, 4H), 1.28 - 1.19 (m, 6H), 1.17 (d, J = 5.5 Hz, 3H), 0.92 - 0.86 (m, 3H).

35

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 175.2, 175.1, 67.5, 67.4, 60.7, 52.1, 52.1, 40.0, 39.5, 39.5, 29.9, 29.9, 22.2, 22.1, 17.2, 17.2, 17.0, 17.0, 14.5, 14.1.

Odour description (1% solution in EtOH on paper blotter, 24 h): green (cassis leaf) sulphurous (cassis, tropical fruit, grapefruit peel).

Example 67: Ethyl 3-((4-hydroxy-2-methylpentan-2-yl)thio)propanoate

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a) To a solution of 4-methylpent-3-en-2-one (0.60 g, 6.1 mmol, 1.0 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.93 g, 6.1 mmol, 1.0 equiv) in THF (10 mL) was added dropwise at 0°C ethyl 3-mercaptopropanoate (0.82 g, 6.1 mmol, 1.0 equiv). After stirring for 16 hours at room temperature, the reaction mixture was quenched with water and
10 extracted with MTBE. The combined organic extracts were washed with 2M aq. HCl, water and brine, dried over MgSO₄ and concentrated under reduced pressure. The crude was purified by column chromatography to give ethyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate (0.85 g, 59%) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 4.13 (q, J = 7.3 Hz, 2H), 2.80 - 2.76 (m, 2H), 2.68 (s, 2H), 2.55 - 2.51 (m, 2H), 2.15 (s, 3H), 1.40 (s, 6H), 1.24 (t, J = 7.2 Hz, 3H).
15

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 206.6, 171.8, 60.6, 54.4, 43.8, 34.4, 32.2, 28.3, 23.1, 14.1.

Odour description (1% solution in EtOH on paper blotter, 24 h): green fruity (sulphurous, rubbery, tropical fruit, sweaty, garlic).

b) To a suspension of NaBH₄ (0.07 g, 1.8 mmol, 0.5 equiv) in EtOH (10 mL) was added dropwise at 0°C ethyl 3-((2-methyl-4-oxopentan-2-yl)thio)propanoate (0.85 g, 3.7 mmol, 1.0 equiv). After stirring for 16 hours, the reaction mixture was poured on 2M aq. HCl and extracted with MTBE. The combined organic extracts were washed with water and brine, dried over MgSO₄ and concentrated under reduced pressure. The crude was purified by
25 column chromatography to furnish ethyl 3-((4-hydroxy-2-methylpentan-2-yl)thio)propanoate as a colorless liquid.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 4.10 (q, J = 7.1 Hz, 2H), 4.06 - 3.99 (m, 1H), 3.47 (d, J = 2.0 Hz, 1H), 2.76 (tq, J = 7.4, 12.0 Hz, 2H), 2.55 - 2.48 (m, 2H), 1.74 (dd, J = 9.4, 15.0 Hz, 1H), 1.45 (dd, J = 1.8, 15.0 Hz, 1H), 1.29 (d, J = 13.2 Hz, 6H), 1.21 (t, J = 7.2
30 Hz, 3H), 1.12 (d, J = 6.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 171.7, 65.0, 60.6, 49.1, 44.7, 34.1, 30.8, 28.0, 24.3, 22.9, 14.1.

Odour description (1% solution in EtOH on paper blotter, 48 h): green (sulphurous, rubbery, grapefruit, grapefruit peel).

35

Comparative Examples

Comparative Example 1: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with dodecane-1-thiol:

5

Synthesis of a mixture of structural isomers:

- dodecyl(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)sulfane,
 dodecyl(1-isopropyl-4-methylcyclohex-3-en-1-yl)sulfane,
 dodecyl(1-methyl-4-(propan-2-ylidene)cyclohexyl)sulfane,
 10 dodecyl(2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)sulfane,
 dodecyl(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)sulfane,
 dodecyl(2-methyl-5-(propan-2-ylidene)cyclohexyl)sulfane,
 dodecyl(3-isopropyl-6-methylcyclohex-2-en-1-yl)sulfane,
 dodecyl(4-isopropyl-1-methylcyclohex-2-en-1-yl)sulfane,
 15 dodecyl(4-isopropyl-1-methylcyclohex-3-en-1-yl)sulfane,
 dodecyl(5-methyl-2-(propan-2-ylidene)cyclohexyl)sulfane,
 dodecyl(6-isopropyl-3-methylcyclohex-2-en-1-yl)sulfane

The compound was obtained from (–)-β-pinene (5.00 g, 36.7 mmol, 1.0 equiv),
 20 dodecane-1-thiol (7.43 g, 36.7 mmol, 1.0 equiv) and AlCl₃ (0.98 g, 7.34 mmol, 0.2 equiv)
 according to the procedure of example 31 to give a colorless oil (4.83 g, 39% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm):
 142.2, 136.5, 133.9, 123.3, 122.4, 120.9, 116.1, 48.2, 46.1, 45.3, 44.7, 44.4, 43.9, 43.4,
 43.1, 39.1, 38.6, 34.8, 33.0, 31.9, 31.9, 31.4, 31.4, 31.3, 30.5, 30.3, 30.1, 29.8, 29.7,
 25 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.3, 29.3, 29.1, 29.1, 28.4, 27.6, 27.2, 27.0, 26.5,
 25.7, 24.6, 23.8, 23.5, 23.3, 23.3, 22.7, 22.3, 21.7, 21.4, 21.3, 21.1, 20.9, 19.9, 19.9,
 18.4, 14.5, 14.1.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
 t_R/min (peak area/%) = 12.09 (2), 12.14 (38), 12.18 (7), 12.21 (14), 12.25 (3), 12.31
 30 (1), 12.42 (30), 12.46 (6).

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, green,
 grapefruit juice, grapefruit peel, rubbery, plastic.

*Individual isomers of example 53 were separated by column chromatography and/or
 35 preparative HPLC: Their structure was determined by 2D-NMR spectroscopy:*

Dodecyl(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)sulfane:

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 133.9, 120.9, 48.2, 43.1, 31.9, 31.4, 29.7, 29.7, 29.6, 29.6, 29.5, 29.3, 29.3, 29.3, 27.6, 27.2, 26.5, 25.7, 24.6, 23.3, 22.7, 14.1.

Dodecyl(6-isopropyl-3-methylcyclohex-2-en-1-yl)sulfane (*anti* isomer):

5 ¹³C NMR (101 MHz, CDCl₃, δ/ppm): 136.5, 122.4, 44.7, 44.4, 31.9, 30.5, 30.1, 29.6, 29.6, 29.6, 29.5, 29.3, 29.3, 29.1, 28.4, 27.0, 23.5, 22.7, 21.7, 21.1, 18.4, 14.1.

Comparative Example 2: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with octane-1-thiol:

10

Synthesis of a mixture of structural isomers:

(1-isopropyl-4-methylcyclohex-3-en-1-yl)(octyl)sulfane,
 (1-methyl-4-(propan-2-ylidene)cyclohexyl)(octyl)sulfane,
 (2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)(octyl)sulfane,
 15 (2-methyl-5-(propan-2-ylidene)cyclohexyl)(octyl)sulfane,
 (3-isopropyl-6-methylcyclohex-2-en-1-yl)(octyl)sulfane,
 (4-isopropyl-1-methylcyclohex-2-en-1-yl)(octyl)sulfane,
 (4-isopropyl-1-methylcyclohex-3-en-1-yl)(octyl)sulfane,
 (5-methyl-2-(propan-2-ylidene)cyclohexyl)(octyl)sulfane,
 20 (6-isopropyl-3-methylcyclohex-2-en-1-yl)(octyl)sulfane,
 octyl(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)sulfane,
 octyl(2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)sulfane

The compound was obtained from (–)-β-pinene (5.00 g, 36.7 mmol, 1.0 equiv), octane-1-thiol (5.37 g, 36.7 mmol, 1.0 equiv) and AlCl₃ (0.98 g, 7.34 mmol, 0.2 equiv) according to the procedure of example 31 to give a colorless oil (5.01 g, 48% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm): 136.5, 135.2, 133.9, 123.3, 122.4, 120.9, 116.1, 48.2, 46.1, 44.7, 44.4, 43.9, 43.1, 39.1, 38.6, 34.8, 34.7, 31.9, 31.8, 31.4, 31.4, 31.3, 30.5, 30.3, 30.1, 29.7, 29.3, 29.3, 29.2, 30 29.2, 29.1, 29.1, 29.0, 28.4, 27.6, 27.2, 27.0, 26.6, 26.5, 25.9, 25.7, 24.6, 23.8, 23.5, 23.3, 22.7, 22.7, 22.3, 21.7, 21.4, 21.3, 21.1, 20.9, 18.4, 14.1, 14.1.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C): t_R/min (peak area/%) = 10.29 (2), 10.37 (33), 10.41 (11), 10.46 (10), 10.54 (1), 10.76 (38), 10.81 (5).

35 Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, slightly metallic, fatty, floral, garlic, onion direction.

Comparative Example 3: 3-(dodecylthio)hexan-1-ol

To a solution of hex-2-enal (10 g, 102 mmol, 1.0 equiv) and dodecane-1-thiol (26.8 mL, 112 mmol, 1.1 equiv) in THF (100 mL) was added at room temperature DBU (3.80 mL, 25.5 mmol, 25 mol%). After stirring for 5 hours, the reaction mixture was quenched with water and extracted with MTBE. The combined organic extracts were washed with brine, dried over MgSO₄ and the solvent was removed under reduced pressure. Crude 3-(dodecylthio)hexanal (32 g) was used for the next step without further purification.

To suspension of NaBH₄ (1.01 g, 26.6 mmol, 0.8 equiv) in methanol (100 mL) was added dropwise at 0°C crude 3-(dodecylthio)hexanal (10 g, 33.3 mmol, 1.0 equiv). After stirring for 16 hours at room temperature, the reaction mixture was poured on 2M aq. HCl and extracted with MTBE (2x). The combined organic extracts were washed with water, brine, dried over MgSO₄ and the solvent was removed under reduced pressure. The crude was purified by column chromatography to afford 3-(dodecylthio)hexan-1-ol (5.6 g, 56% calcd. yield over 2 steps) as a colorless oil.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 3.87 - 3.79 (m, 1H), 3.78 - 3.70 (m, 1H), 2.75 - 2.66 (m, 1H), 2.55 - 2.43 (m, 2H), 2.30 (s, 1H), 1.89 - 1.81 (m, 1H), 1.74 - 1.65 (m, 1H), 1.59 - 1.49 (m, 4H), 1.49 - 1.40 (m, 2H), 1.39 - 1.18 (m, 18H), 0.93 - 0.82 (m, 6H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 61.1, 43.1, 37.7, 37.0, 31.9, 30.1, 29.8, 29.6, 29.6, 29.6, 29.3, 22.6, 20.0, 14.1, 13.9.

Odour description (1% solution in EtOH on paper blotter, 24 h): green. grapefruit, decatone, nootkatone.

Comparative Example 4: 3-(dodecylthio)hexyl acetate

To a solution of 3-(dodecylthio)hexan-1-ol (4.0 g, 13.2 mmol, 1.0 equiv), pyridine (2.13 mL, 26.4 mmol, 2.0 equiv) and DMAP (0.2 g, 12 mol%) in cyclohexane (40 mL) was added dropwise at 0 °C a solution of acetyl chloride (1.77 mL, 25.1 mmol, 1.9 equiv) in cyclohexane (10 mL). After stirring for 1 hour at room temperature, more acetyl chloride (0.35 g) was added and stirring was continued for 23 hours. The reaction mixture was quenched with ice-cold 2M aq. HCl (30 mL) and extracted with MTBE (40 mL). The organic layer was washed with 2M aq. NaOH, water, brine and dried over MgSO₄. The solvent was removed under reduced pressure and the crude was purified by column chromatography (heptane/MTBE 30:1) to afford 3-(dodecylthio)hexyl acetate (2.90 g, 64% yield) as a brown oil.

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 171.0, 62.5, 42.3, 37.5, 33.8, 31.9, 31.9, 30.3, 29.9, 29.6, 29.6, 29.6, 29.5, 29.5, 29.3, 29.2, 29.0, 22.7, 20.0, 14.1, 13.9.

GC/MS (EI): *m/z* (%): 344 (6, [M]⁺), 257 (8), 241 (12), 201 (17), 115 (100), 83 (45), 55 (55), 43 (86).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, rubbery, cassis, gassy, fruity, aromatic, eucalyptus bud.

5

Comparative Example 5: dodecyl(1-methoxyhexan-3-yl)sulfane

To a solution of 3-(dodecylthio)hexan-1-ol (4.0 g, 13.2 mmol, 1.0 equiv) in THF (30 mL) was added at 0 °C sodium hydride (0.79 g, 19.8 mmol, 1.5 equiv, 60% wt). After stirring
10 for 45 min at room temperature, MeI (3.73 g, 26.4 mmol, 2.0 equiv) was added. After stirring for 22 hours, the reaction mixture was quenched with ice-cold 2M aq. HCl (30 mL) and extracted with MTBE (40 mL). The organic layer was washed with sat. aq. Na₂S₂O₃, water, brine and dried over MgSO₄. The solvent was removed under reduced pressure and the crude was purified by column chromatography (heptane/MTBE 30:1) to afford
15 dodecyl(1-methoxyhexan-3-yl)sulfane (2.38 g, 57% yield) as a brown oil.

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 70.3, 58.6, 42.5, 37.7, 35.1, 31.9, 30.5, 29.6, 29.5, 29.5, 29.3, 29.3, 29.5, 22.7, 20.0, 14.1, 14.0.

GC/MS (EI): *m/z* (%): 316 (9, [M]⁺), 273 (2), 257 (4), 201 (5), 147 (16), 115 (33), 114 (47), 82 (63), 71 (100), 55 (44), 45 (63), 29 (15).

20 Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, rubbery, cassis, gazy, garlic, oxane, aromatic, eucalyptus bud.

Comparative Example 6: 3-(dodecylthio)-2-methylfuran

25 To a solution of 2-methylfuran-3-thiol (2.0 g, 17.5 mmol, 1.0 equiv), NaOEt (1.19 g, 17.5 mmol, 1.0 equiv) in ethanol (30 mL) was added dropwise at 0°C 1-bromododecane (8.73 g, 35.0 mmol, 2.0 equiv). After stirring for 2 days at room temperature, the reaction mixture was quenched with water (30 mL) and extracted with MTBE (50 mL). The organic layer was washed with water and brine, dried over MgSO₄ and the solvent was removed
30 under reduced pressure. The crude was purified twice by column chromatography and Kugelrohr distillation to give 3-(dodecylthio)-2-methylfuran (1.87 g, 38% yield) as a colourless oil.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.27 (d, *J* = 2.0 Hz, 1H), 6.33 (d, *J* = 2.0 Hz, 1H), 2.60 (t, *J* = 7.3 Hz, 2H), 2.33 (s, 3H), 1.55 - 1.48 (m, 2H), 1.40 - 1.23 (m, 18H), 0.90 - 0.86
35 (m, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 154.5, 140.4, 115.0, 110.5, 36.0, 31.9, 29.6, 29.6, 29.6, 29.5, 29.3, 29.2, 28.5, 22.7, 14.1, 11.8.

Odour description (1% solution in EtOH on paper blotter, 24 h): creamy, warm milk, sulfurol, lactic, chestnut cream.

Comparative Example 7: dodecyl(1-phenylethyl)sulfane

5

To a solution of dodecane-1-thiol (6.00 g, 29.6 mmol, 1.0 equiv) in 7M NH₃ in methanol (6.35 mL, 44.5 mmol, 1.5 equiv) was added dropwise at room temperature (1-bromoethyl)benzene (6.03 g, 32.6 mmol, 1.1 equiv). After stirring at 40°C for 1 day, the reaction mixture was quenched with 2M aq. HCl (30 mL) and extracted with MTBE (40 mL).

10 The organic layer was washed with water, brine, dried over MgSO₄ and the solvent was removed under reduced pressure. The crude was purified by column chromatography and the lights were removed by Kugelrohr distillation (100°C/6 mbar) to afford dodecyl(1-phenylethyl)sulfane (1.25 g, 14% yield) as a yellow oil.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.42 - 7.30 (m, 4H), 7.27 - 7.20 (m, 1H), 3.97 (q, J = 7.1 Hz, 1H), 2.40 - 2.22 (m, 2H), 1.59 (d, J = 7.1 Hz, 3H), 1.35 - 1.19 (m, 20H), 0.94 - 0.89 (m, 3H).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 144.2, 128.4, 127.2, 126.9, 44.0, 31.9, 31.3, 29.6, 29.6, 29.5, 29.3, 29.2, 28.9, 22.7, 22.6, 14.1.

Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, anjeruk, salty, burnt rubber.

20

Comparative Example 8: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with 3-(trimethoxysilyl)propane-1-thiol:

25 Synthesis of a mixture of structural isomers:

(3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propyl)trimethoxysilane,
 (3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propyl)trimethoxysilane,
 (3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propyl)trimethoxysilane,
 (3-((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propyl)trimethoxysilane,
 30 (3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propyl)trimethoxysilane,
 trimethoxy(3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propyl)silane,
 trimethoxy(3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propyl)silane,
 trimethoxy(3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propyl)silane,
 trimethoxy(3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propyl)silane,
 35 trimethoxy(3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propyl)silane,
 trimethoxy(3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propyl)silane

The compound was obtained from (–)-β-pinene (2.0 g, 14.7 mmol, 1.0 equiv), 3-(trimethoxysilyl)propane-1-thiol (2.88 g, 14.7 mmol, 1.0 equiv) and boron trifluoride diethyl etherate (0.78 mL, 6.12 mmol, 0.4 equiv) according to the procedure of example 31 to give a colourless oil (2.30 g, 47% yield).

5 ¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm): 136.6, 133.9, 123.3, 122.4, 120.8, 119.9, 50.5, 50.3, 48.3, 46.0, 44.6, 44.4, 43.7, 43.3, 43.3, 43.2, 33.5, 31.9, 31.3, 30.6, 29.3, 28.4, 27.1, 26.9, 26.6, 25.7, 24.6, 23.5, 23.4, 23.3, 23.2, 23.2, 22.2, 21.6, 21.6, 21.1, 20.8, 18.4, 9.0, 8.7.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
10 t_R/min (peak area/%) = 10.32 (1), 10.49 (1), 10.57 (43), 10.66 (14), 10.73 (1), 10.76 (1), 10.93 (27), 10.98 (3), 11.19 (1), 11.24 (1).

Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, grapefruit, juicy, pink grapefruit.

15 Comparative Example 9: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with octadecane-1-thiol:

Synthesis of a mixture of structural isomers:

(1-isopropyl-4-methylcyclohex-3-en-1-yl)(octadecyl)sulfane,
20 (1-methyl-4-(propan-2-ylidene)cyclohexyl)(octadecyl)sulfane,
(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)(octadecyl)sulfane,
(2-methyl-5-(propan-2-ylidene)cyclohexyl)(octadecyl)sulfane,
(3-isopropyl-6-methylcyclohex-2-en-1-yl)(octadecyl)sulfane,
(4-isopropyl-1-methylcyclohex-2-en-1-yl)(octadecyl)sulfane,
25 (4-isopropyl-1-methylcyclohex-3-en-1-yl)(octadecyl)sulfane,
(5-methyl-2-(propan-2-ylidene)cyclohexyl)(octadecyl)sulfane,
(6-isopropyl-3-methylcyclohex-2-en-1-yl)(octadecyl)sulfane,
octadecyl(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)sulfane,
octadecyl(2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)sulfane

30

The compound was obtained from (–)-β-pinene (5.00 g, 36.7 mmol, 1.0 equiv), octadecane-1-thiol (10.5 g, 36.7 mmol, 1.0 equiv) and AlCl₃ (0.98 g, 7.34 mmol, 0.2 equiv) according to the procedure of example 31 to give a colourless oil (3.18 g, 21% yield).

35 ¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm): 142.2, 136.5, 135.2, 133.9, 123.3, 122.4, 120.9, 116.1, 48.2, 46.1, 44.7, 44.4, 43.9, 43.4, 43.2, 39.1, 34.8, 34.7, 31.9, 31.9, 31.4, 30.5, 30.3, 30.1, 30.0, 29.9, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.3, 29.3, 29.1, 29.1, 28.4, 27.6, 27.2, 27.0, 26.6, 26.5,

25.9, 25.7, 24.6, 23.8, 23.5, 23.3, 23.3, 22.7, 22.3, 21.7, 21.4, 21.3, 21.1, 20.9, 19.9, 18.4, 14.1.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
t_R/min (peak area/%) = 13.84 (15), 13.90 (13), 13.97 (2), 14.15 (70).

- 5 Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, green, grapefruit juice, grapefruit peel.

Comparative Example 10: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with decane-1-thiol:

10

Synthesis of a mixture of structural isomers:

- decyl(1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)sulfane,
decyl(1-isopropyl-4-methylcyclohex-3-en-1-yl)sulfane,
decyl(1-methyl-4-(propan-2-ylidene)cyclohexyl)sulfane,
15 decyl(2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)sulfane,
decyl(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)sulfane,
decyl(2-methyl-5-(propan-2-ylidene)cyclohexyl)sulfane,
decyl(3-isopropyl-6-methylcyclohex-2-en-1-yl)sulfane,
decyl(4-isopropyl-1-methylcyclohex-2-en-1-yl)sulfane,
20 decyl(4-isopropyl-1-methylcyclohex-3-en-1-yl)sulfane,
decyl(5-methyl-2-(propan-2-ylidene)cyclohexyl)sulfane,
decyl(6-isopropyl-3-methylcyclohex-2-en-1-yl)sulfane

- The compound was obtained from (–)-β-pinene (5.00 g, 36.7 mmol, 1.0 equiv), decane-1-thiol (6.40 g, 36.7 mmol, 1.0 equiv) and AlCl₃ (0.98 g, 7.34 mmol, 0.2 equiv) according
25 to the procedure of example 31 to give a colorless oil (3.22 g, 28% yield).

- ¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm):
142.3, 136.5, 133.9, 123.3, 122.4, 120.9, 77.2, 48.2, 46.1, 44.7, 44.4, 43.9, 43.4, 43.1,
39.1, 38.6, 34.8, 34.7, 31.9, 31.4, 30.5, 30.3, 30.1, 29.7, 29.6, 29.5, 29.3, 29.3, 29.3,
29.1, 29.1, 29.0, 28.4, 27.6, 27.2, 27.0, 26.6, 26.5, 25.9, 25.7, 24.6, 23.8, 23.5, 23.3,
30 23.3, 22.7, 21.7, 21.3, 21.1, 20.9, 19.9, 18.4, 14.1.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C):
t_R/min (peak area/%) = 11.25 (1), 11.33 (22), 11.37 (9), 11.41 (9), 11.52 (1), 11.69
(52), 11.74 (6).

- Odour description (1% solution in EtOH on paper blotter, 24 h): sulphurous, green,
35 grapefruit juice, grapefruit peel.

Comparative Example 11: 2-(2-(dodecylthio)propan-2-yl)-5-methylcyclohexan-1-one

The compound was obtained from dodecane-1-thiol (5.00 g, 24.7 mmol, 1.0 equiv), DBU (3.76 g, 24.7 mmol, 1.0 equiv) and (R)-5-methyl-2-(propan-2-ylidene)cyclohexan-1-one
 5 (4.14 g, 27.2 mmol, 1.1 equiv) according to the procedure of example 3 as a colorless oil (3.52 g, 40% yield, mixture of two diastereoisomers).

¹³C NMR (101 MHz, CDCl₃, δ/ppm): 211.5, 210.7, 58.2, 58.0, 52.4, 50.4, 46.9, 46.8, 36.7, 34.7, 32.7, 31.9, 31.8, 31.4, 29.6, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 28.3, 27.9, 27.8, 27.7, 25.5, 24.6, 23.9, 22.7, 22.2, 19.2, 14.1.

10 Odour description (1% solution in EtOH on paper blotter, 24 h): green, sulphurous, grapefruit, cassis.

Comparative Example 12: 4-((1-phenylethyl)thio)butan-2-one

15 To a solution of 3-((1-phenylethyl)thio)propanoic acid (1.0 g, 4.8 mmol, 1.0 equiv) in Et₂O (20 mL) was added dropwise at 0°C methyllithium (3.4 mL, 10 mmol, 2.2 equiv, 3.1M in DME) over 10 minutes. After stirring for 2 hours at room temperature, the reaction mixture was quenched with 2M aq. HCl and extracted with MTBE (2x). The combined organic
 20 extracts were washed with water and brine, dried over MgSO₄ and concentrated under reduced pressure. The crude was purified by column chromatography to afford 4-((1-phenylethyl)thio)butan-2-one (0.70 g, 71% yield) as a colorless liquid.

¹H NMR (400 MHz, CDCl₃, δ/ppm): 7.35 - 7.28 (m, 4H), 7.27 - 7.20 (m, 1H), 3.96 (q, J = 7.0 Hz, 1H), 2.66 - 2.45 (m, 4H), 2.07 (s, 3H), 1.56 (d, J = 7.1 Hz, 3H).

25 ¹³C NMR (101 MHz, CDCl₃, δ/ppm): 206.9, 143.8, 128.5, 127.2, 127.1, 44.6, 43.3, 29.9, 25.1, 22.5.

Odour description (1% solution in EtOH on paper blotter, 24 h): green (burnt citrus peel, anjeruk) fruity.

30 Comparative Example 13: Reaction product of 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane with 3-mercaptopropanenitrile:

Synthesis of a mixture of structural isomers: 3-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanenitrile, 3-((1-isopropyl-4-methylcyclohex-3-en-1-yl)thio)propanenitrile, 3-((1-methyl-4-(propan-2-ylidene)cyclohexyl)thio)propanenitrile, 3-((2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl)thio)propanenitrile, 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanenitrile, 3-((2-methyl-5-(propan-2-ylidene)cyclohexyl)thio)propanenitrile, 3-((3-isopropyl-6-methylcyclohex-2-en-1-yl)thio)propanenitrile, 3-((4-isopropyl-1-methylcyclohex-2-en-1-yl)thio)propanenitrile, 3-

((4-isopropyl-1-methylcyclohex-3-en-1-yl)thio)propanenitrile, 3-((5-methyl-2-(propan-2-ylidene)cyclohexyl)thio)propanenitrile, 3-((6-isopropyl-3-methylcyclohex-2-en-1-yl)thio)propanenitrile

The compound was obtained from (–)-β-pinene (0.86 g, 6.3 mmol, 1.1 equiv), 3-mercaptopropanenitrile (0.50 g, 5.7 mmol, 1.0 equiv) and boron trifluoride diethyl etherate (81 mg, 0.57 mmol, 0.1 equiv) in CH₂Cl₂ (10 mL) according to the procedure of example 31 to give a colorless oil (0.07 g, 3% yield).

¹³C NMR (101 MHz, CDCl₃, complex mixture of structural isomers (peak list), δ/ppm): 138.1, 137.2, 133.8, 133.7, 132.8, 132.8, 132.0, 121.6, 121.4, 120.4, 118.9, 118.3, 118.3, 118.3, 49.7, 49.4, 49.3, 47.3, 46.6, 45.8, 45.3, 44.4, 44.1, 43.2, 43.0, 41.5, 41.1, 38.9, 36.3, 36.0, 34.9, 33.9, 31.7, 31.7, 31.1, 31.1, 30.7, 29.8, 29.2, 29.0, 28.4, 28.3, 27.7, 27.0, 26.9, 26.7, 26.4, 26.0, 25.7, 25.5, 25.5, 25.0, 24.9, 24.5, 24.5, 24.4, 24.0, 23.4, 23.2, 23.1, 22.9, 22.7, 22.0, 21.9, 21.5, 21.3, 21.1, 21.0, 20.9, 20.7, 19.8, 19.6, 19.5, 19.4, 19.3, 19.3, 19.2, 19.1, 19.1, 19.0, 18.9, 18.9, 18.7, 18.1.

GC-MS (Trajan (SGE), BPX5, 50°C, 2 min -> 20°C/min -> 240°C -> 35°C/min -> 300°C): t_R/min (peak area/%) = 9.08 (1), 9.10 (3), 9.17 (60), 9.20 (4), 9.25 (2), 9.31 (14), 9.44 (1), 9.68 (7), 9.71 (3).

Odour description (1% solution in EtOH on paper blotter, 48 h): weak, slightly green (sulphurous, vegetable, tropical, juicy, grapefruit).

Wash Test Examples

Test Example 1: Application in liquid detergent

A) Sample preparation

0.002% by weight multiplied by the content of precursor odour vector in the benchmark 4-(dodecylthio)-4-methylpentan-2-one (in %, i.e. 100%, WO2019166315) divided by the content of the precursor odour vector in the test substance (in %) were incorporated into unperfumed liquid detergent base (Dalli, commercially sourced) by magnetic stirring at room temperature for 24 h. Table 3 describes how much precursor of the major contributing thiol odour vector (i.e. 4-mercapto-4-methylpentan-2-one (**E**): GCTH 0.0004 ng; 2-(4-methylcyclohex-3-en-1-yl)propane-2-thiol (**F**): OTH 0.0009 ng/L) is contained in each sample and which normalized dosage was then applied in the respective liquid detergent base sample:

Sample	Example No.	major odor vector	retention time precursor (GC-MS)	area percent (GC-MS)	calculated dosage
4-(dodecylthio)-4-methylpentan-2-one (A)	Reference	E	11.05 min	100%	0.002%
ethyl S-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)-L-cysteinate (B)	47a	F	10.87 min	12%	0.017%
butyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate (C)	31a	F	11.10 min	20%	0.010%
dodecyl(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)sulfane (D)	Comparative Example 1	F	12.42 min	30%	0.007%

Table 3.

In Sample **A**, 100 % of the GC-MS peak ("area percent") is the isomer responsible for the odour (i.e. the "odour vector"). In Samples **B** to **D**, "area percent" refers to the % contribution of the isomer (as measured by GC-MS) that is responsible for the odour. For Example, for Sample **B**, the odour vector represents 12 % of the sample. Accordingly, the concentration of the samples are normalized to Sample **A** in order to fairly compare the relevant odour vectors.

10 B) Wash test and sensory evaluation

A 40 °C machine wash cycle was performed using 55 g of the above prepared liquid detergent samples **A** to **D** and odour-neutral cotton/elastane mixed fabric T-shirts. The wet and line-dried fabric (1, 4 and 7 days) was assessed by a panel of 4-6 experts with regard to odour intensity and quality. The odour intensity was recorded on an intensity scale of 0 (odourless) to 5 (extremely strong).

The results are tabulated in Table 4 below and are shown graphically in Figure 1.

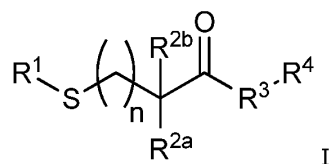
As can be seen from Table 4, the results show that only compounds of the present invention having an ester group as in samples **B** and **C** release a strong odour on dry fabrics even up to 7 days (entries 2 and 3). In contrast, thioethers having an n-alkyl group (**D**) or a beta-methyl ketone group (**A**) without an ester were very weak on dry fabrics throughout the study period (entries 1 and 4).

Entry	Sample	wet	1 day	4 days	7 days
1	4-(dodecylthio)-4-methylpentan-2-one (A)	1.9	1.4	1.8	1.3
2	ethyl S-(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)-L-cysteinate (B)	3.9	3.6	3.3	2.9
3	butyl 3-((2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)thio)propanoate (C)	1.4	2.0	2.7	2.9
4	dodecyl(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)sulfane (D)	1.6	1.0	0.8	0.5

Table 4.

Claims

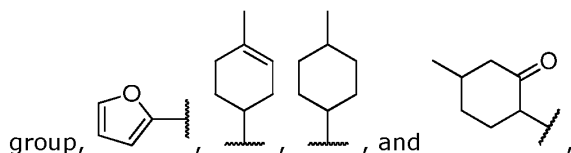
1. A compound of formula I,



5 wherein:

n is 0 or 1;

R¹ is selected from the group consisting of a C₁₋₁₈ alkyl group, a C₁₋₁₈ alkenyl group, a
 10 C₃₋₈ cycloalkyl group, a C₃₋₆ cycloalkenyl group, a 4- to 6-membered heterocycloalkyl
 group, an aryl group, and a 5- or 6-membered heteroaryl group,
 which C₁₋₁₈ alkyl and C₁₋₁₈ alkenyl groups are optionally substituted by one or more
 substituents each independently selected from the group consisting of =O, -OR⁵, a phenyl



group,
 15 which C₃₋₈ cycloalkyl, C₃₋₆ cycloalkenyl, and 4- to 6-membered heterocycloalkyl groups are
 optionally substituted by one or more substituents each independently selected from the
 group consisting of =O, a C₁₋₄ alkyl group, and a C₁₋₄ alkenyl group,
 which aryl and 5- or 6-membered heteroaryl groups are optionally substituted by one or
 more C₁₋₄ alkyl groups;

20

R^{2a} is selected from the group consisting of hydrogen, C₁₋₄ alkyl group, -N(R^{6a})R^{6b}, -
 N(R^{7a})C(O)R^{7b}, and -N(R^{8a})C(O)OR^{8b};

R^{2b} is selected from the group consisting of hydrogen and a C₁₋₄ alkyl group;

25

R³ is selected from the group consisting of -O- and -N(R⁹)-;

R⁴ is selected from the group consisting of hydrogen, a C₁₋₁₈ alkyl group, a C₁₋₁₈ alkenyl
 group, and an aryl group, which C₁₋₁₈ alkyl, C₁₋₁₈ alkenyl and aryl groups are optionally
 30 substituted by one or more -OH or phenyl groups;

R⁵ is selected from the group consisting of hydrogen, a C₁₋₄ alkyl group and -C(O)R¹⁰;

R^{6a}, R^{6b}, R^{7a}, R^{7b}, R^{8a}, R^{8b} and R⁹ are each independently selected from the group consisting of hydrogen and a C₁₋₄ alkyl group, which C₁₋₄ alkyl group is optionally substituted by one or more phenyl group; and

5

R¹⁰ is a C₁₋₄ alkyl group;

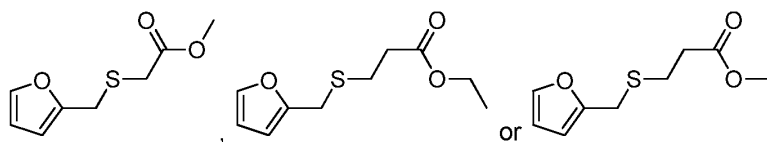
or a salt or a solvate thereof;

10 provided that:

(a) when R¹ is an unsubstituted C₁₋₁₈ alkyl or a C₁₋₁₈ alkenyl group or a C₁₋₁₈ alkyl or a

C₁₋₁₈ alkenyl group substituted by one or more =O, -OR⁵ or  groups and R^{2a} is -NH₂ or -NHC(O)CH₃ and R^{2b} is hydrogen, then R⁴ is not hydrogen; and

15 (b) the compound of formula I is not:



2. The compound according to Claim 1, wherein R¹ is selected from the group consisting of a C₁₋₁₈ alkyl group, a C₃₋₈ cycloalkyl group, a C₃₋₆ cycloalkenyl group, and a

20 5- to 6-membered heteroaryl group,

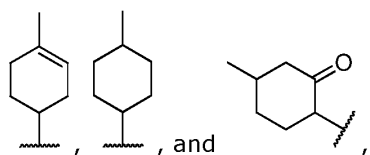
which C₁₋₁₈ alkyl, C₃₋₈ cycloalkyl, C₃₋₆ cycloalkenyl group, and 5- to 6-membered heteroaryl groups are as defined in Claim 1.

3. The compound according to Claim 1 or Claim 2, wherein:

25 R¹ is selected from the group consisting of a C₁₋₆ alkyl group, a C₆₋₇ cycloalkyl group, a cyclohexenyl group, and a 5-membered heteroaryl group,

which C₁₋₆ alkyl group is optionally substituted by one or more substituents each

independently selected from the group consisting of =O, -OR⁵, a phenyl group, ,



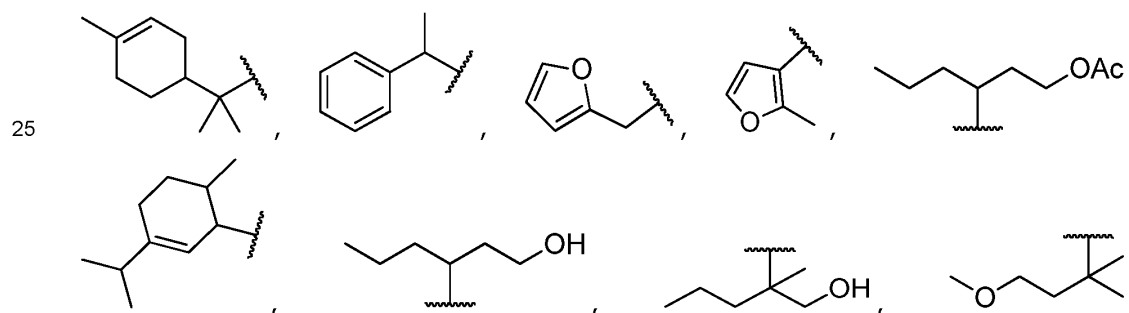
which C₆₋₇ cycloalkyl and cyclohexenyl groups are optionally substituted by one or more substituents each independently selected from the group consisting of =O, a C₁₋₄ alkyl group, and a C₁₋₄ alkenyl group,

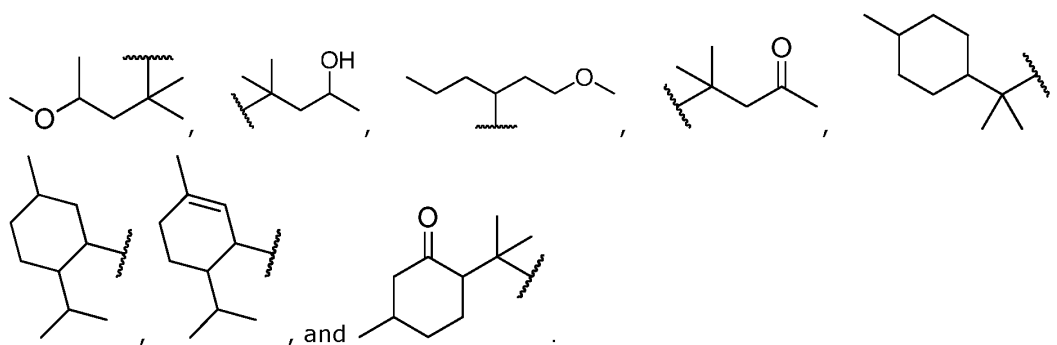
which 5-membered heteroaryl group is optionally substituted by one or more C₁₋₄ alkyl groups; and

R⁵ is as defined in Claim 1.

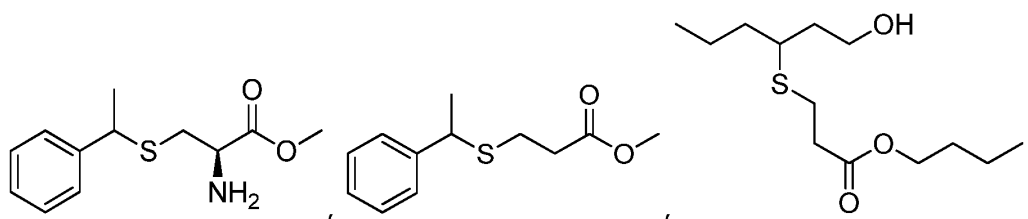
4. A compound according to any of Claims 1 to 3, wherein R¹ is selected from the group consisting of 2-methylfuran-3-yl, furan-2-ylmethyl, 1-phenylethyl, 1-hydroxyhexan-3-yl, 1-acetoxylhexan-3-yl, benzyl, phenethyl, 6-isopropyl-3-methylcyclohex-2-en-1-yl, 5-methyl-2-(propan-2-ylidene)cyclohexyl, 1-isopropyl-4-methylcyclohex-3-en-1-yl, 2-(4-methylcyclohex-3-en-1-yl)propan-2-yl, 4-isopropyl-1-methylcyclohex-2-en-1-yl, 4-isopropyl-1-methylcyclohex-3-en-1-yl, 1-methyl-4-(propan-2-ylidene)cyclohexyl, 3-isopropyl-6-methylcyclohex-2-en-1-yl, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl, 2,5,5-trimethylbicyclo[2.2.1]heptan-2-yl, 2-methyl-5-(propan-2-ylidene)cyclohexyl, 1-isopropyl-4-methylcyclohexyl, 2-(4-methylcyclohexyl)propan-2-yl, 2-isopropyl-5-methylcyclohexyl, 1-hydroxy-2-methylpentan-2-yl, 1-methoxy-3-methylbutan-3-yl, 2-methoxy-4-methylpentan-4-yl, 4-methylpentan-2-ol-4-yl, 1-methoxyhexan-3-yl, 2-methylpentan-4-on-2-yl and 2-(4-methyl-2-oxo-cyclohexyl)propan-2-yl.

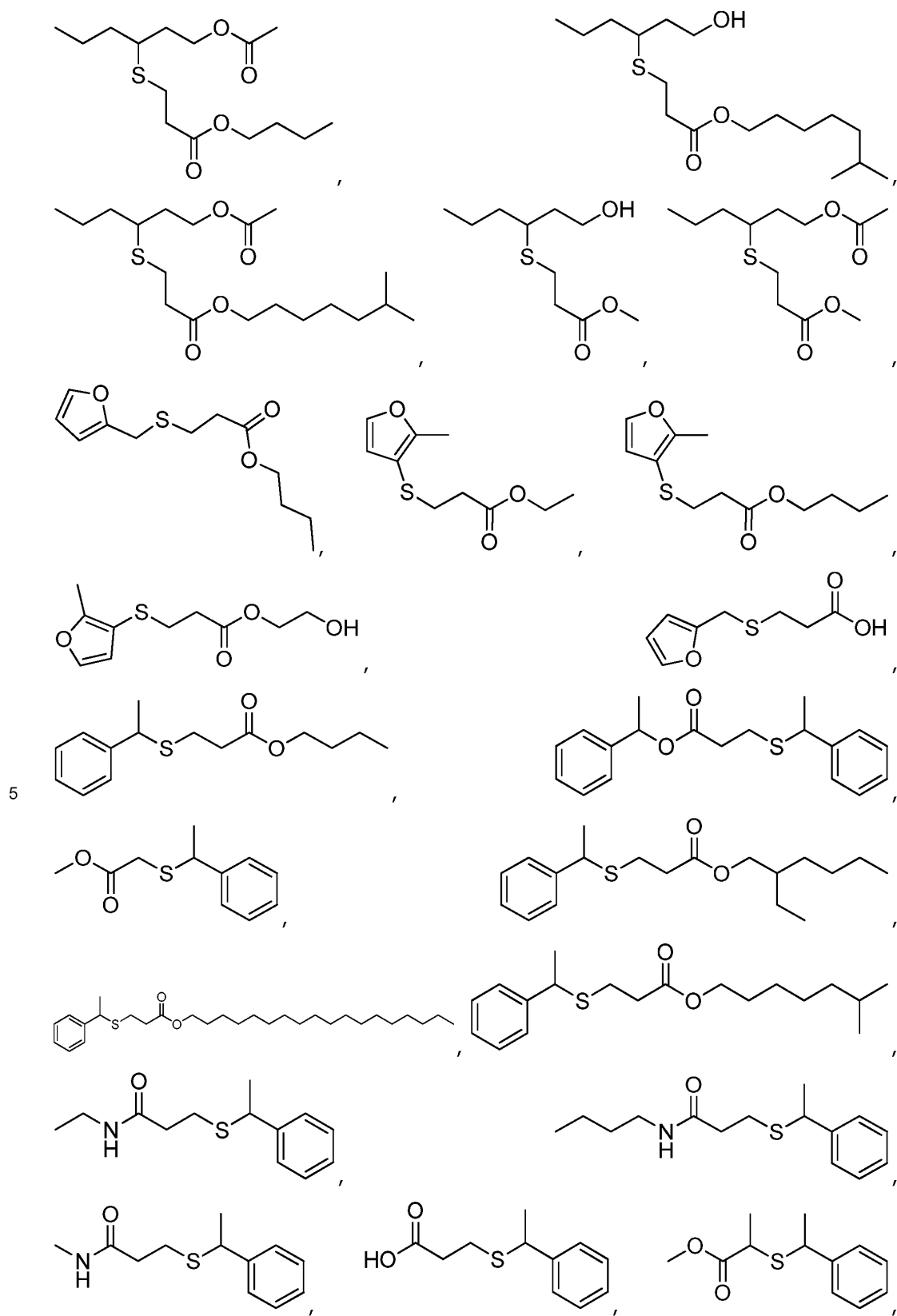
5. A compound according to any one of Claims 1 to 4, wherein R¹ is selected from the group consisting of:

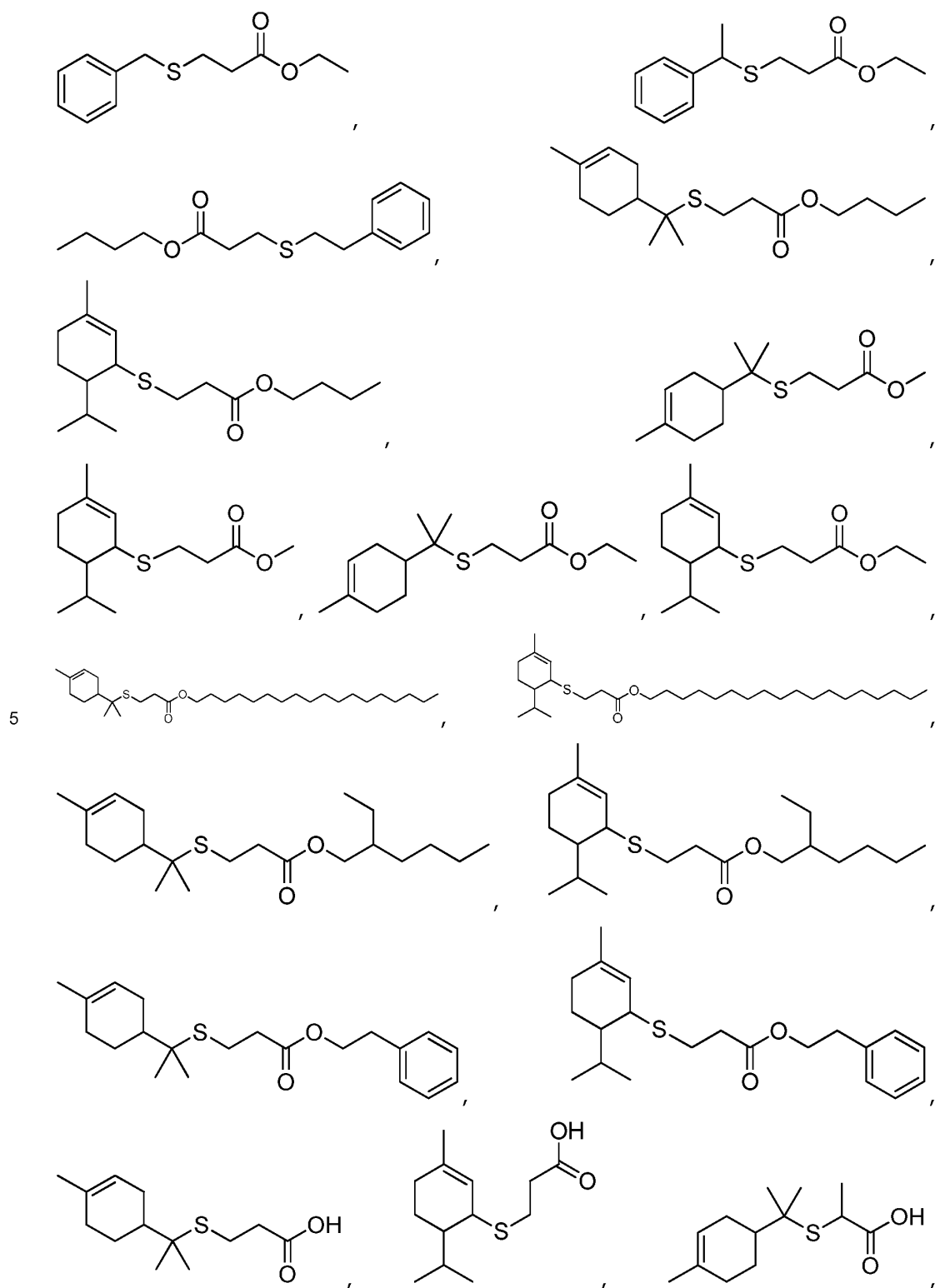


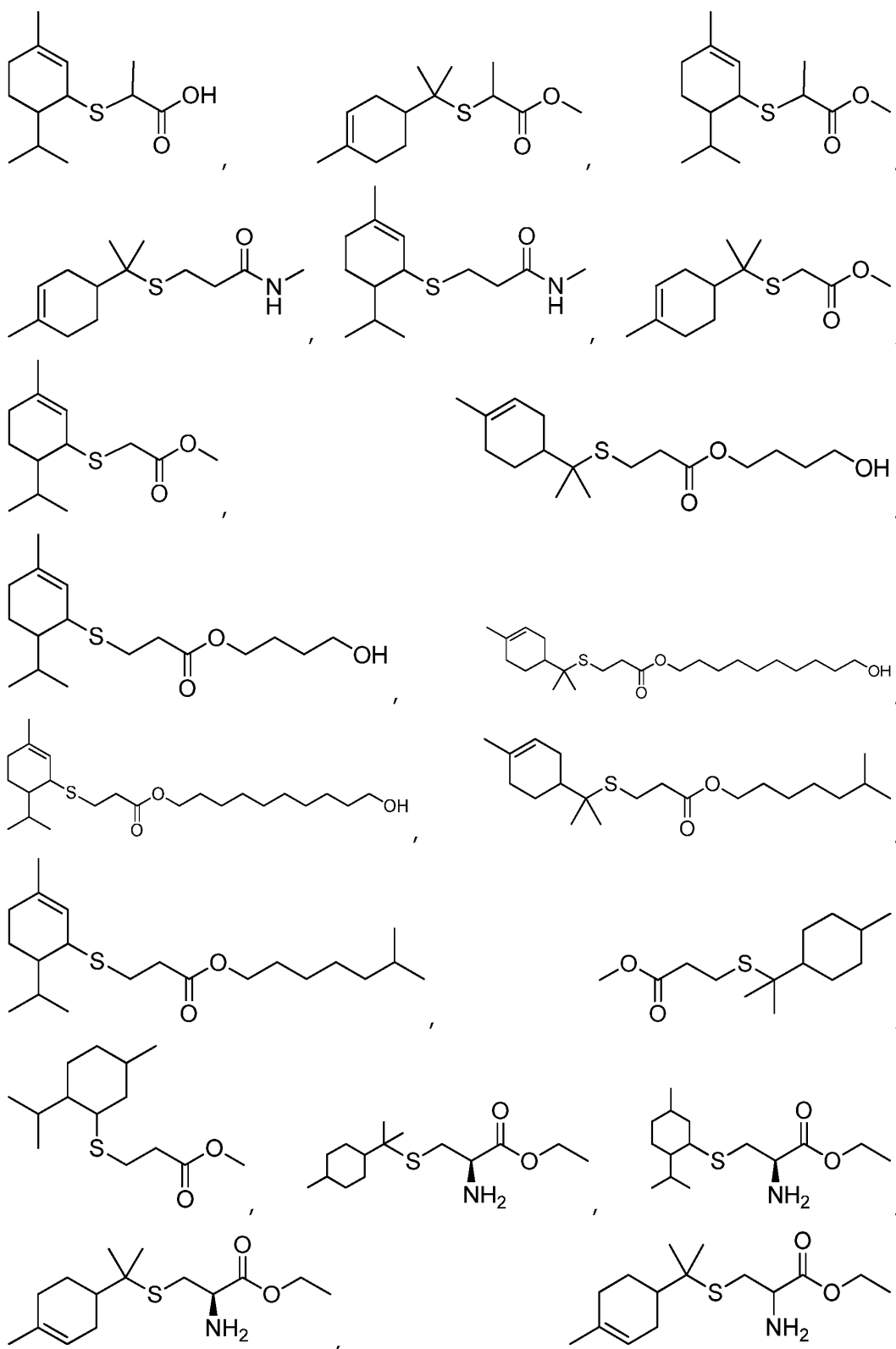


6. A compound according to any one of Claims 1 to 5, wherein R^{2a} is selected from the group consisting of hydrogen, methyl, -NH₂, -NH(O)CH₃, -NHC(O)C(CH₃)₃, and -NHCOOCH₂Ph.
7. A compound according to Claim 6, wherein:
R^{2a} is selected from the group consisting of hydrogen, methyl and -NH₂; and
R^{2b} is hydrogen.
8. A compound according to any of one of Claims 1 to 7, wherein R³ is -O-.
9. A compound according to any one of Claims 1 to 8, wherein R⁴ is a C₁₋₁₈ alkyl group, which C₁₋₁₈ alkyl group may be optionally substituted with one or more hydroxy groups or phenyl groups.
10. A compound according to Claim 9, wherein R⁴ is selected from the group consisting of methyl, ethyl, butyl, hexyl, benzyl, 1-phenylethyl, ethylhexyl, octyl, octadecyl, 2-phenylethyl, hydroxyethyl, hydroxybutyl, and hydroxydecyl groups.
11. A compound according to Claim 9 or Claim 10, wherein R⁴ is selected from methyl, ethyl, and butyl.
12. A compound according to Claim 1, wherein the compound is selected from the group consisting of:

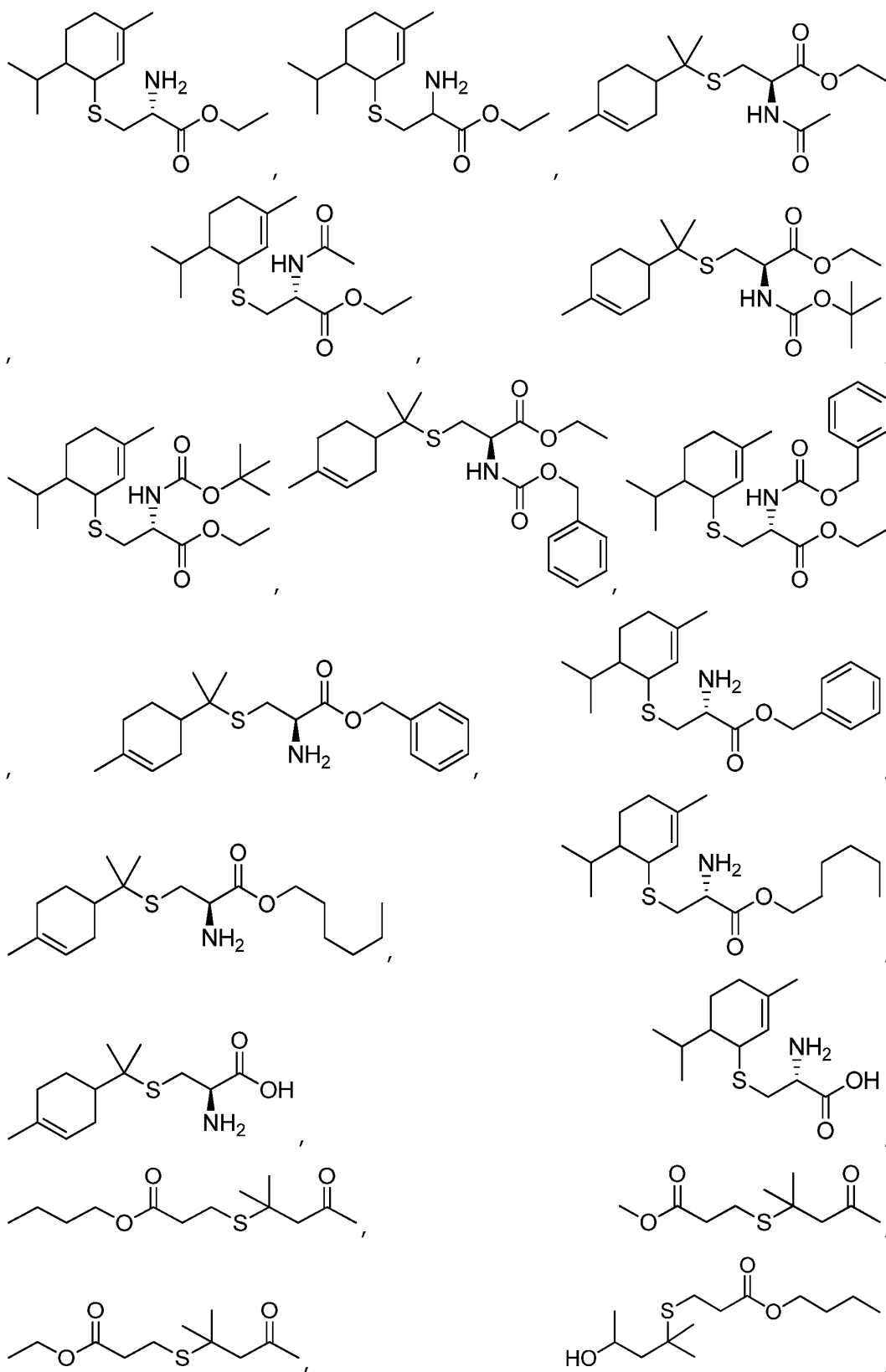


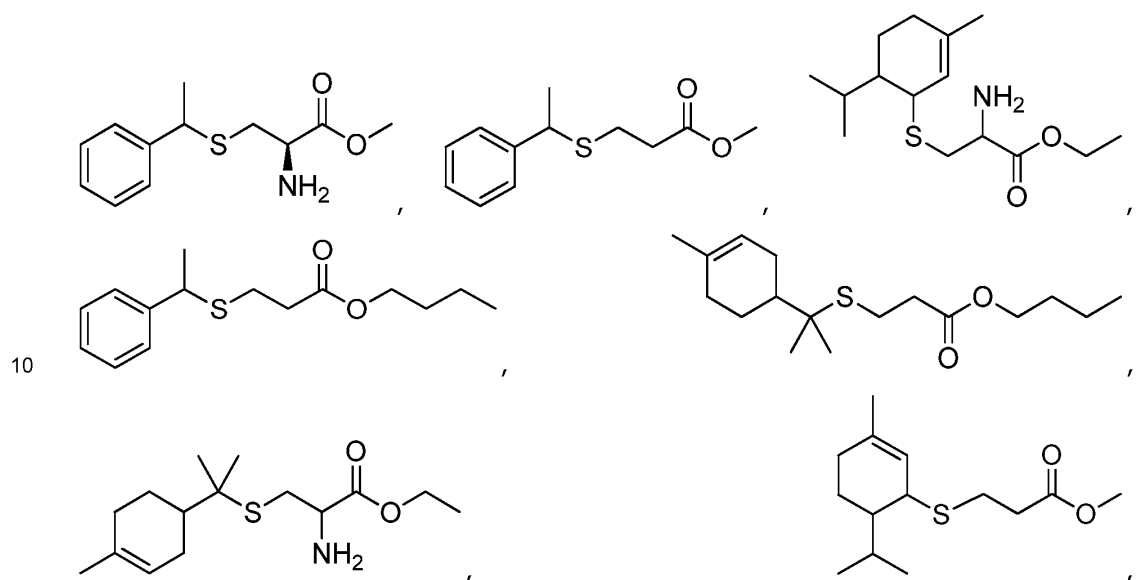
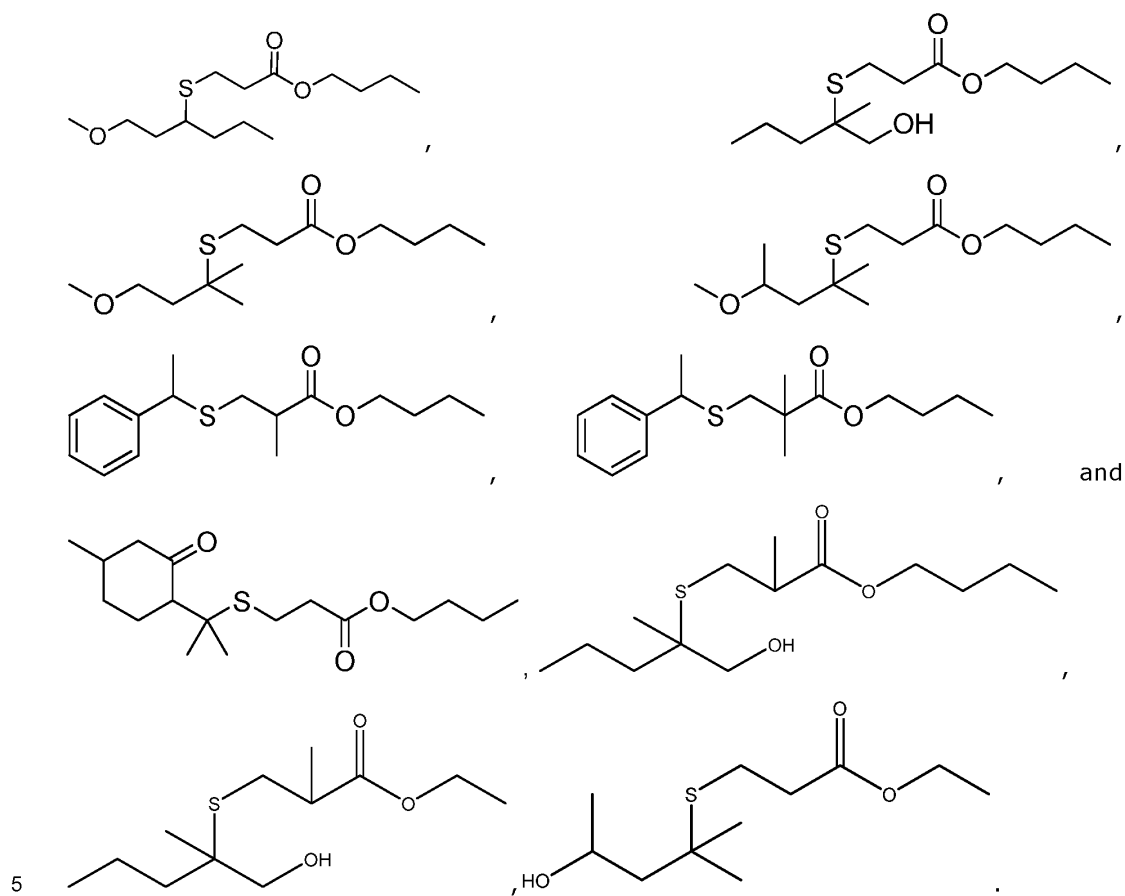


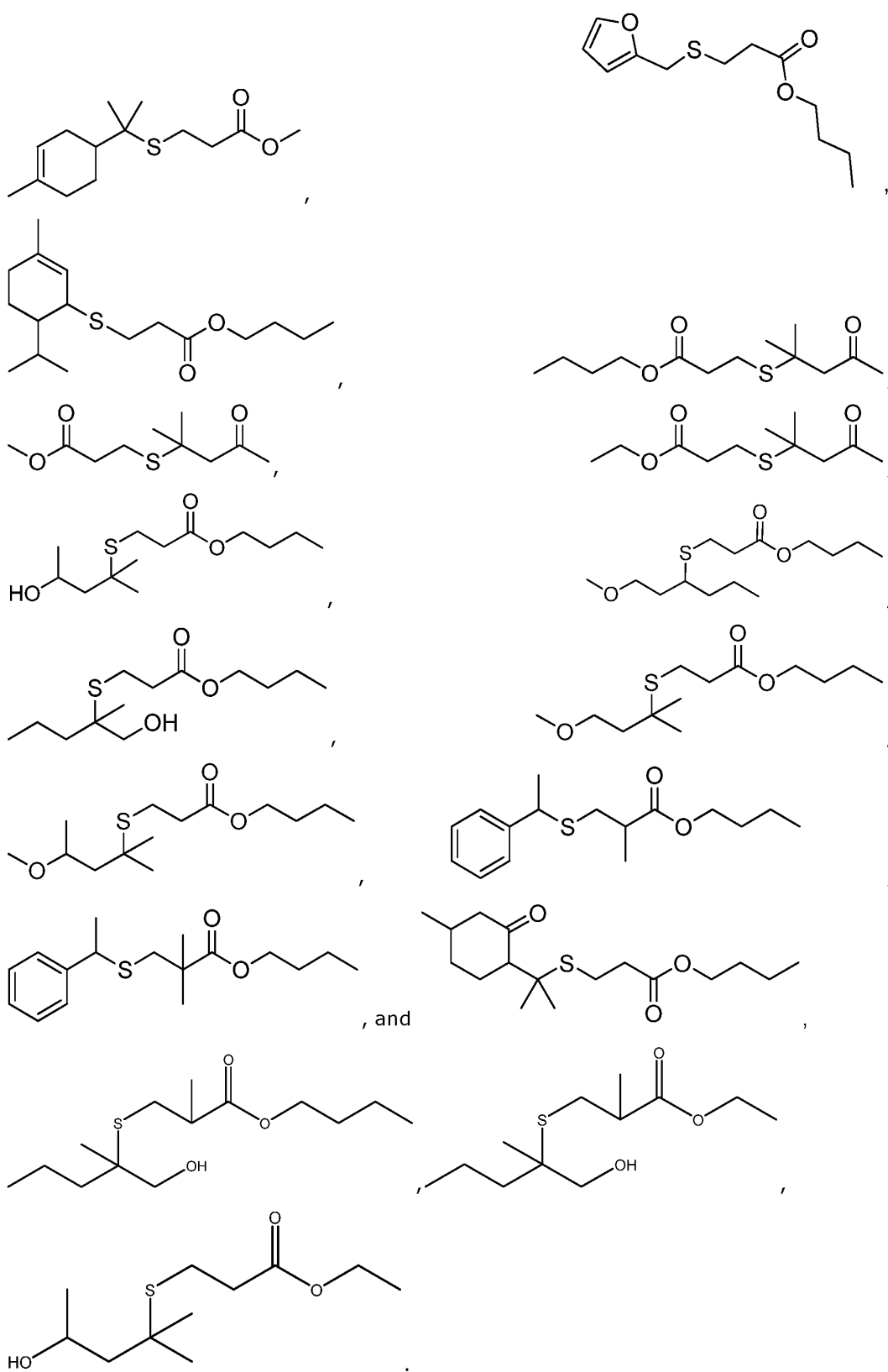




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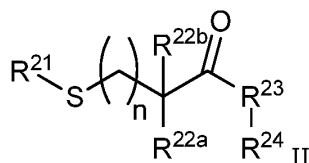




14. A composition comprising the compound of formula I as defined in any one of Claims 1 to 13.

15. A consumer product comprising the compound of formula I as defined in any one of Claims 1 to 13, or the composition as defined in Claim 14.

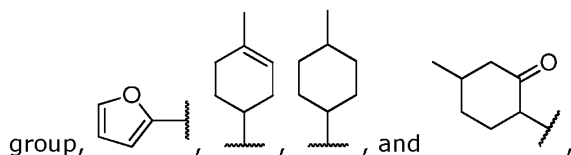
16. Use of a compound of formula II,



wherein:

n is 0 or 1;

R²¹ is selected from the group consisting of a C₁₋₁₈ alkyl group, a C₁₋₁₈ alkenyl group, a C₃₋₈ cycloalkyl group, a C₃₋₆ cycloalkenyl group, a 4- to 6-membered heterocycloalkyl group, an aryl group, and a 5- or 6-membered heteroaryl group, which C₁₋₁₈ alkyl and C₁₋₁₈ alkenyl groups are optionally substituted by one or more substituents each independently selected from the group consisting of =O, -OR²⁵, a phenyl



group, which C₃₋₈ cycloalkyl, C₃₋₆ cycloalkenyl, and 4- to 6-membered heterocycloalkyl groups are optionally substituted by one or more substituents each independently selected from the group consisting of =O, a C₁₋₄ alkyl group, and a C₁₋₄ alkenyl group, which aryl and 5- or 6-membered heteroaryl groups are optionally substituted by one or more C₁₋₄ alkyl groups;

R^{22a} is selected from the group consisting of hydrogen, C₁₋₄ alkyl group, -N(R^{26a})R^{26b}, -N(R^{27a})C(O)R^{27b}, and -N(R^{28a})C(O)OR^{28b};

R^{22b} is selected from the group consisting of hydrogen and a C₁₋₄ alkyl group;

R²³ is selected from the group consisting of -O- and -N(R²⁹)-;

R²⁴ is selected from the group consisting of hydrogen, a C₁₋₁₈ alkyl group, a C₁₋₁₈ alkenyl group, and an aryl group, which C₁₋₁₈ alkyl, C₁₋₁₈ alkenyl and aryl groups are optionally substituted by one or more -OH or phenyl groups;

5 R²⁵ is selected from the group consisting of hydrogen, a C₁₋₄ alkyl group and -C(O)R³⁰;

R^{26a}, R^{26b}, R^{27a}, R^{27b}, R^{28a}, R^{28b} and R²⁹ are each independently selected from the group consisting of hydrogen and a C₁₋₄ alkyl group, which C₁₋₄ alkyl group is optionally substituted by one or more phenyl group; and

10

R³⁰ is and a C₁₋₄ alkyl group;

or a salt or a solvate thereof,

15 in a method of providing a fragrant thiol.

17. Use of the compound of formula II as defined in Claim 16 in the preparation of a compound of formula III,

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R¹-SH III.

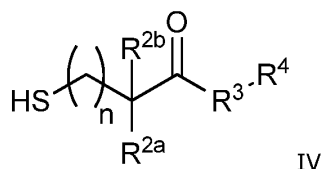
18. Use of a composition comprising the compound of formula II as defined in Claim 17 in a method of providing a fragrant thiol.

25 19. Use of a consumer product comprising the compound of formula II as defined in Claim 16 or the composition as defined in Claim 18, in a method of providing a fragrant thiol.

20. The use of Claims 16 to 19, wherein the use is in a laundry application.

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21. A process for preparing a compound as defined in any one of Claims 1 to 13, which process comprises a reaction of a compound of formula IV,



with

35

(a) a compound of formula V,



wherein X is a suitable leaving group; or

5

(b) a suitable alkene;

wherein n, R¹, R², R³, and R⁴ are as defined in any one of Claims 1 to 13.