

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau



WIPO | PCT



(10) International Publication Number

WO 2014/145325 A1

(43) International Publication Date

18 September 2014 (18.09.2014)

(51) International Patent Classification:

A01N 25/00 (2006.01) A01P 19/00 (2006.01)

(21) International Application Number:

PCT/US2014/030065

(22) International Filing Date:

15 March 2014 (15.03.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/787,272 15 March 2013 (15.03.2013) US
61/817,006 29 April 2013 (29.04.2013) US

(71) Applicant: PROTIA, LLC [US/US]; 15025 Broili Dr, Reno, Nevada 89511 (US).

(72) Inventor: CZARNIK, Anthony; 15025 Broili Dr, Reno, Nevada 89511 (US).

(74) Agent: VANCE, David; 5467 Hill Top Street, Crozet, Virginia 22932 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: DEUTERIUM-ENRICHED ALDEHYDES

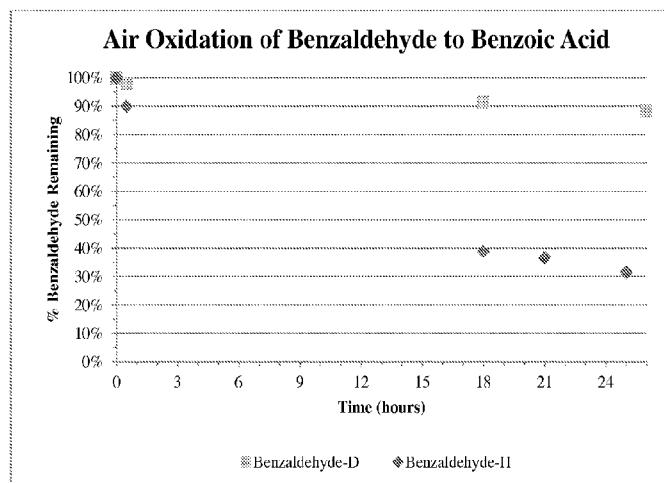
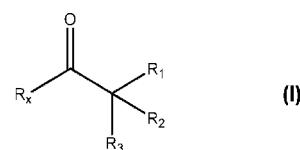


Figure 1



[Continued on next page]

WO 2014/145325 A1

**Published:**

— with international search report (Art. 21(3))

— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(57) Abstract: The present invention generally relates to deuterium-enriched aldehydes, compositions comprising deuterium-enriched aldehydes, and methods for slowing the rate of aldehyde autoxidation. In one aspect, the present invention provides a composition comprising a deuterium-enriched aldehyde wherein there are at least 6×10^{18} molecules of the aldehyde in the composition, and wherein the aldehydic deuterium isotope is present in the molecule, in an amount greater than 0.10 percent of the aldehydic hydrogen atoms present in the molecule..

DEUTERIUM-ENRICHED ALDEHYDES

FIELD OF THE INVENTION

[0001] The present invention generally relates to deuterium-enriched aldehydes, compositions comprising deuterium-enriched aldehydes, and methods for slowing the rate of aldehyde autoxidation.

BACKGROUND OF THE INVENTION

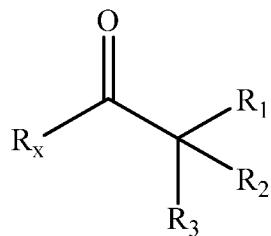
[0002] Aldehydes are organic compounds containing a H-C(O)- moiety. They are used extensively in industrial processes. Formaldehyde, for instance, is produced on a scale of about 6,000,000 tons/year. Aldehydes are mainly used in the production of resins, but they also find application as precursors to plasticizers and other compounds used in the manufacturing of polymers. On a smaller scale, some aldehydes are used as ingredients in perfumes, flavors and compositions that modulate the behavior of insects, e.g., pheromone containing compositions.

[0003] Aldehydes have a tendency to react with atmospheric oxygen to form carboxylic acids (H-C(O)- oxidizes to HO₂C-) in a process known as auto-oxidation or autoxidation. The acids produced by autoxidation can lower the quality and usefulness of aldehyde-containing compositions.

[0004] Despite all of the research and development that has been directed to preservation of aldehydes, there is still a need in the art for improved aldehyde-containing compositions and related methods.

SUMMARY OF THE INVENTION

[0005] In an aspect, the present invention provides a novel deuterium-enriched aldehyde of structure 1:



1.

[0006] In another aspect, the present invention provides a novel method of making a deuterium-enriched aldehyde of structure 1.

[0007] In another aspect, the present invention provides a novel composition, comprising: a deuterium-enriched aldehyde of structure 1.

[0008] In another aspect, the present invention provides a novel composition, comprising: a deuterium-enriched aldehyde of structure 1 and an organic solvent.

[0009] In another aspect, the present invention provides a novel composition for modulating the behavior of insects, comprising: a deuterium-enriched aldehyde of structure 1 and an optional additional component suitable for the composition.

[0010] In another aspect, the present invention provides a novel method of manufacturing a resin or polymer using a deuterium-enriched aldehyde of structure 1.

[0011] These and other aspects, which will become apparent during the following detailed description, have been achieved by the inventors' discovery that deuterium can slow the autoxidation of aldehydes.

BRIEF DESCRIPTION OF THE FIGURES

[0012] FIG. 1 shows a graph comparing the amount of air oxidation of benzaldehyde to benzoic acid where the hydrogen atom on the carbonyl group (*i.e.*, H-C(O)Ph) is enriched in its deuterium isotope (*i.e.*, >95% deuterium, “benzaldehyde-D”) and where it is not enriched (*i.e.*, naturally occurring isotopic abundance, “benzaldehyde-H”).

[0013] FIG. 2 shows a graph comparing the amount of air oxidation of hexanal to hexanoic acid where the hydrogen atom of the carbonyl group (*i.e.*, H-C(O)C₅H₁₁) is enriched in its deuterium isotope (*i.e.*, >95% deuterium, “hexanal-D”) and where it is not enriched (*i.e.*, naturally occurring isotopic abundance, “hexanal-H”).

DETAILED DESCRIPTION OF THE INVENTION

[0014] *Definitions*

[0015] All examples provided herein are not intended to be limiting.

[0016] “Alkyl” refers to an alkane chemical moiety. The alkanes may be linear, branched, or cyclic. Lower alkyl groups are those that include 1-6 carbon atoms. Higher alkyl groups are those that include 7-20 carbon atoms. Cyclic alkyl or cycloalkyl groups include 3-8 carbon atoms. Examples of such moieties include: CH₃, CH₂CH₃, CH₂CH₂CH₃, CH(CH₃)₂, CH₂CH₂CH₂CH₃, CH(CH₃)CH₂CH₃, CH₂CH(CH₃)₂, C(CH₃)₃, CH₂CH₂CH₂CH₂CH₃, CH(CH₃)CH₂CH₂CH₃, CH₂CH(CH₃)CH₂CH₃, CH₂CH₂CH(CH₃)₂, CH₂CH₂CH₂CH₂CH₂CH₃, cyclopropyl, cyclobutyl, and cyclopentyl.

[0017] “Substituted alkyl” refers to an alkyl group where one or more of the hydrogen atoms have been replaced with another chemical group. Examples of such other chemical groups include: halo, OH, OR₄ (where R₄ is a lower alkyl group), CF₃, OCF₃, NH₂, NHR₄ (where R₄ is

a lower alkyl group), NR₄R₅ (where R₄ and R₅ are independently lower alkyl groups), CO₂H, CO₂R₆ (where R₆ is a lower alkyl group), C(O)NH₂, C(O)NHR₇ (where R₇ is a lower alkyl group), C(O)NR₇R₈ (where R₇ and R₈ are independently lower alkyl groups), CN, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, aryl, substituted aryl, heteroaryl, and substituted heteroaryl.

[0018] “Halo” refers to Cl, F, Br, or I.

[0019] “Alkenyl” refers to a moiety containing only carbon and hydrogen that includes at least one double bond. The alkenes may be linear, branched, or cyclic. Lower alkenyl groups are those that include 2-6 carbon atoms. Higher alkenyl groups are those that include 7-20 carbon atoms. Cyclic alkenyl or cycloalkenyl groups include 5-8 carbon atoms. Examples of such moieties include: CH=CH₂; CH=CHCH₃; CH₂CH=CH; CH=CHCH₂CH₃; CH₂CH=CHCH₃; CH₂CH₂CH=CH₂; CH=CHCH₂CH₂CH₃; CH=CHCH(CH₃)₂; CH₂CH=CHCH₂CH₃; CH₂CH₂CH=CHCH₃; CH₂CH₂CH₂CH=CH₂; CH=CHCH₂CH₂CH₂CH₃; CH=CHCH₂CH(CH₃)₂; cyclopentenyl, and cyclohexenyl.

[0020] “Substituted alkenyl” refers to an alkenyl group where one or more of the hydrogen atoms have been replaced with another chemical group. Examples of such other chemical groups include: CO₂H, CO₂R₆ (where R₆ is a lower alkyl group), C(O)NH₂, C(O)NHR₇ (where R₇ is a lower alkyl group), C(O)NR₇R₈ (where R₇ and R₈ are independently lower alkyl groups), CN, alkyl, substituted alkyl, alkynyl, substituted alkynyl, aryl, substituted aryl, heteroaryl, and substituted heteroaryl. Where the replaced hydrogen atom is not on the carbon of the double bond, examples of such other chemical groups further include: halo, OH, OCH₃, CF₃, OCF₃, NH₂, NHR₄ (where R₄ is a lower alkyl group), and NR₄R₅ (where R₄ and R₅ are independently lower alkyl groups).

[0021] “Alkynyl” refers to refers to a moiety containing only carbon and hydrogen that includes a triple bond. The alkynes may be linear or branched. Lower alkynyl groups are those that include 2-6 carbon atoms. Higher alkynyl groups are those that include 7-20 carbon atoms. Examples of such moieties include: $\text{C}\equiv\text{CH}$; $\text{C}\equiv\text{CCH}_3$; $\text{CH}_2\text{C}\equiv\text{CH}$; $\text{C}\equiv\text{CCH}_2\text{CH}_3$; $\text{CH}_2\text{C}\equiv\text{CCH}_3$; $\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}_3$; $\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$; $\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_3$; $\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3$; $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$; $\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$; $\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$; $\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_3$; $\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_3$; $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$; and, $\text{C}\equiv\text{CCH}_2\text{CH}(\text{CH}_3)_2$.

[0022] “Substituted alkynyl” refers to an alkynyl group where one or more of the hydrogen atoms have been replaced with another chemical group. Examples of such other chemical groups include: CO_2H , CO_2R_6 (where R_6 is a lower alkyl group), $\text{C}(\text{O})\text{NH}_2$, $\text{C}(\text{O})\text{NHR}_7$ (where R_7 is a lower alkyl group), $\text{C}(\text{O})\text{NR}_7\text{R}_8$ (where R_7 and R_8 are independently lower alkyl groups), CN , alkyl, substituted alkyl, alkenyl, substituted alkenyl, aryl, substituted aryl, heteroaryl, and substituted heteroaryl. Where the replaced hydrogen atom is not on the carbon of the triple bond, Examples of such other chemical groups further include: halo, OH , OCH_3 , CF_3 , OCF_3 , NH_2 , NHR_4 (where R_4 is a lower alkyl group), NR_4R_5 (where R_4 and R_5 are independently lower alkyl groups).

[0023] “Heteroalkyl” refers to an alkyl group where at least one of the carbon atoms has been replaced with a heteroatom. Examples of heteroatoms include oxygen (“O”), nitrogen (“N”) and sulfur (“S”). The heteroalkanes may be linear, branched, or cyclic. Lower heteroalkyl groups are those that include 1-6 carbons and heteroatoms. Higher heteroalkyl groups are those that include 7-20 carbons and heteroatoms. Examples of heteroalkyl groups include: CH_2OCH_3 ; $\text{CH}_2\text{CH}_2\text{OCH}_3$; $\text{CH}_2\text{N}(\text{R}_9)\text{CH}_3$ (where R_9 is a lower alkyl group); $\text{CH}_2\text{CH}_2\text{N}(\text{R}_9)\text{CH}_3$ (where R_9

is a lower alkyl group); CH_2SCH_3 ; $\text{CH}_2\text{CH}_2\text{SCH}_3$; tetrahydrofuran, tetrahydropyran, and morpholine.

[0024] “Substituted heteroalkyl” refers to a heteroalkyl group where one or more of the hydrogen atoms has been replaced with another chemical group. The hydrogen atom that is replaced is typically not on a carbon atom directly attached to the heteroatom. Examples of such other chemical groups include: halo, OH, OCH_3 , CF_3 , OCF_3 , NH_2 , NHR_4 (where R_4 is a lower alkyl group), NR_4R_5 (where R_4 and R_5 are independently lower alkyl groups), CO_2H , CO_2R_6 (where R_6 is a lower alkyl group), $\text{C}(\text{O})\text{NH}_2$, $\text{C}(\text{O})\text{NHR}_7$ (where R_7 is a lower alkyl group), $\text{C}(\text{O})\text{NR}_7\text{R}_8$ (where R_7 and R_8 are independently lower alkyl groups), CN, alkyl, aryl, and heteroaryl.

[0025] “Aryl” refers to an aromatic group containing only carbon and hydrogen (*e.g.*, C_6H_5 and C_{10}H_8).

[0026] “Substituted aryl” refers to an aryl group where at least one of the hydrogen atoms has been replaced with another chemical group. Examples of such other chemical groups include: halo, OH, OCH_3 , CF_3 , OCF_3 , NH_2 , NHR_4 (where R_4 is a lower alkyl group), NR_4R_5 (where R_4 and R_5 are independently lower alkyl groups), CO_2H , CO_2R_6 (where R_6 is a lower alkyl group), $\text{C}(\text{O})\text{NH}_2$, $\text{C}(\text{O})\text{NHR}_7$ (where R_7 is a lower alkyl group), $\text{C}(\text{O})\text{NR}_7\text{R}_8$ (where R_7 and R_8 are independently lower alkyl groups), CN, alkyl, aryl, and heteroaryl.

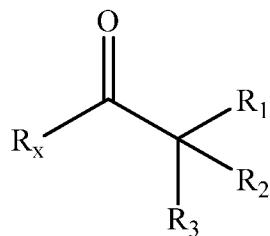
[0027] “Heteroaryl” refers to an aromatic group where at least one of the carbon atoms has been replaced by a heteroatom. Examples of such heteroatoms include oxygen (“O”), nitrogen (“N”) and sulfur (“S”). Examples of heteroaryl groups include: $\text{C}_4\text{H}_2\text{O}$; $\text{C}_4\text{H}_3\text{N}$; $\text{C}_4\text{H}_2\text{S}$; and, $\text{C}_5\text{H}_4\text{N}$.

[0028] “Substituted heteroaryl” refers to a heteroaryl group where at least one of the hydrogen atoms has been replaced with another chemical group. Examples of such other chemical groups

include: halo, OH, OCH₃, CF₃, OCF₃, NH₂, NHR₄ (where R₄ is a lower alkyl group), NR₄R₅ (where R₄ and R₅ are independently lower alkyl groups), CO₂H, CO₂R₆ (where R₆ is a lower alkyl group), C(O)NH₂, C(O)NHR₇ (where R₇ is a lower alkyl group), C(O)NR₇R₈ (where R₇ and R₈ are independently lower alkyl groups), CN, aryl, and heteroaryl.

[0029] Aspects

[0030] In an aspect, the present invention is directed to a deuterium-enriched aldehyde of structure 1:

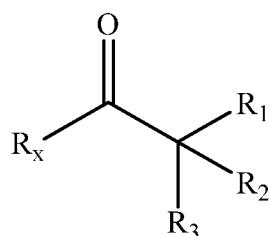


1

wherein, R_x is hydrogen, wherein the deuterium isotope is in an amount greater than 0.10 percent of the R_x hydrogen atoms. In certain cases, the deuterium isotope comprises greater than 1% of the R_x hydrogen atoms, or greater than 2%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 95% percent of the R_x hydrogen atoms. R₁, R₂ and R₃ are independently selected from hydrogen (where the hydrogen is un-enriched (*i.e.*, naturally occurring) or is enriched in its deuterium isotope, *e.g.*, more than 1%, 2%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 95%), alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, heteroalkyl, substituted heteroalkyl, aryl, substituted aryl, heteroaryl, and substituted heteroaryl. Alternatively, the CR₁R₂R₃ moiety forms a group selected from: an aryl, substituted aryl, heteroaryl, and substituted heteroaryl. Alternatively, the CR₁R₂ moiety forms a group selected from: an alkenyl and substituted alkenyl. Alternatively, the CR₁R₂R₃ moiety forms a group a

group selected from: an alkynyl and substituted alkynyl. Optionally, the aldehyde is substituted with C(O)R_y, wherein R_y is hydrogen, wherein the deuterium isotope is optionally present in an amount greater than 0.10% of the R_y hydrogen atoms, provided that R_x is optionally H when the deuterium isotope is present in an amount greater than 0.10% of the R_y hydrogen atoms. In certain cases, the deuterium isotope comprises greater than 1% of the R_y hydrogen atoms, or greater than 2%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 95% percent of the R_y hydrogen atoms.

[0031] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde of structure 1:



1

wherein, there are at least 6×10^{18} molecules of the aldehyde, of structure 1. Compositions of the invention will typically comprise at least 6×10^{19} molecules, and may, for example, comprise at least 6×10^{20} molecules, 6×10^{21} molecules, 6×10^{22} molecules, or 6×10^{23} molecules. R_x is hydrogen, wherein the deuterium isotope is in an amount greater than 0.10 percent of the R_x hydrogen atoms. In certain cases, the deuterium isotope comprises greater than 1% of the R_x hydrogen atoms, or greater than 2%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 95% percent of the R_x hydrogen atoms. R₁, R₂ and R₃ are independently selected from hydrogen (where the hydrogen is un-enriched (*i.e.*, naturally occurring) or is enriched in its deuterium isotope, *e.g.*, more than 1%, 2%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or

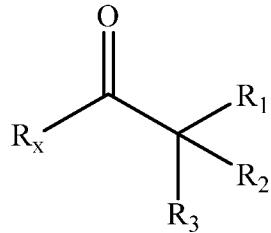
95%), alkyl, substituted alkyl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, heteroalkyl, substituted heteroalkyl, aryl, substituted aryl, heteroaryl, and substituted heteroaryl. Alternatively, the $\text{CR}_1\text{R}_2\text{R}_3$ moiety forms a group selected from: an aryl, substituted aryl, heteroaryl, and substituted heteroaryl. Alternatively, the CR_1R_2 moiety forms a group selected from: an alkenyl and substituted alkenyl. Alternatively, the $\text{CR}_1\text{R}_2\text{R}_3$ moiety forms a group a group selected from: an alkynyl and substituted alkynyl. Optionally, the aldehyde is substituted with $\text{C}(\text{O})\text{R}_y$, wherein R_y is hydrogen, wherein the deuterium isotope is optionally present in an amount greater than 0.10% of the R_y hydrogen atoms, provided that R_x is optionally H when the deuterium isotope is present in an amount greater than 0.10% of the R_y hydrogen atoms. In certain cases, the deuterium isotope comprises greater than 1% of the R_y hydrogen atoms, or greater than 2%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 95% percent of the R_y hydrogen atoms.

[0032] In another aspect, reference to compositions comprising the “aldehyde of structure 1”, means compositions comprising at least 0.1 mole of an aldehyde of structure 1. Compositions of the invention may, for example, comprise at least 0.2, 0.5, 1, 2, 3, 4, 5, 10, or 20 moles of an aldehyde of structure 1.

[0033] In another aspect, reference to compositions comprising the “aldehyde of structure 1”, means compositions comprising at least 1 gram of an aldehyde of structure 1. Compositions of the invention may, for example, comprise at least 5, 10, 20, 30, 40, 50, 100, 500, or 1,000 grams of an aldehyde of structure 1.

[0034] In another aspect, the present invention provides a composition, comprising: a

deuterium-enriched aldehyde of structure 1:



1

wherein:

there are at least 6×10^{18} molecules of the aldehyde;

R_x is hydrogen, wherein the deuterium isotope is present in an amount greater than 0.10% of the

R_x hydrogen atoms;

R_1 , R_2 and R_3 are independently selected from hydrogen, alkyl, substituted alkyl, alkenyl,

substituted alkenyl, alkynyl, substituted alkynyl, heteroalkyl, substituted heteroalkyl, aryl,

substituted aryl, heteroaryl, and substituted heteroaryl;

alternatively, the $CR_1R_2R_3$ moiety forms a group selected from: an aryl, substituted aryl,

heteroaryl, and substituted heteroaryl;

alternatively, the CR_1R_2 moiety forms a group selected from: an alkenyl and substituted

alkenyl;

alternatively, the $CR_1R_2R_3$ moiety forms a group selected from: an alkynyl and

substituted alkynyl; and,

optionally, the aldehyde is substituted with $C(O)R_y$, wherein R_y is hydrogen, wherein the

deuterium isotope is optionally present in an amount greater than 0.10% of the R_y

hydrogen atoms, provided that R_x is optionally H when the deuterium isotope is present in an amount greater than 0.10% of the R_y hydrogen atoms.

[0035] The following are examples of aldehydes according to the present invention:

1. A deuterium-enriched aldehyde of structure 1, where R_1 and R_2 are hydrogen, and R_3 is a lower alkyl.
2. A deuterium-enriched aldehyde of structure 1, where R_1 and R_2 are hydrogen, and R_3 is a higher alkyl.
3. A deuterium-enriched aldehyde of structure 1, where R_1 and R_2 are hydrogen, and R_3 is a substituted alkyl, where the substituted alkyl is a lower alkyl, and where the one or more other chemical groups are selected from: halo, OH, OR_4 (where R_4 is a lower alkyl group), CF_3 , OCF_3 , NH_2 , NHR_4 (where R_4 is a lower alkyl group), NR_4R_5 (where R_4 and R_5 are independently lower alkyl groups), CO_2H , CO_2R_6 (where R_6 is a lower alkyl group), $C(O)NH_2$, $C(O)NHR_7$ (where R_7 is a lower alkyl group), $C(O)NR_7R_8$ (where R_7 and R_8 are independently lower alkyl groups), CN, aryl, substituted aryl, heteroaryl, and substituted heteroaryl.
4. A deuterium-enriched aldehyde of structure 1, where R_1 and R_2 are hydrogen, and R_3 is a substituted alkyl, where the substituted alkyl is a higher alkyl, and where the one or more other chemical groups are selected from: halo, OH, OR_4 (where R_4 is a lower alkyl group), CF_3 , OCF_3 , NH_2 , NHR_4 (where R_4 is a lower alkyl group), NR_4R_5 (where R_4 and R_5 are independently lower alkyl groups), CO_2H , CO_2R_6 (where R_6 is a lower alkyl group), $C(O)NH_2$, $C(O)NHR_7$ (where R_7 is a lower alkyl group), $C(O)NR_7R_8$ (where R_7 and R_8 are independently lower alkyl groups), CN, aryl, substituted aryl, heteroaryl, and substituted heteroaryl.

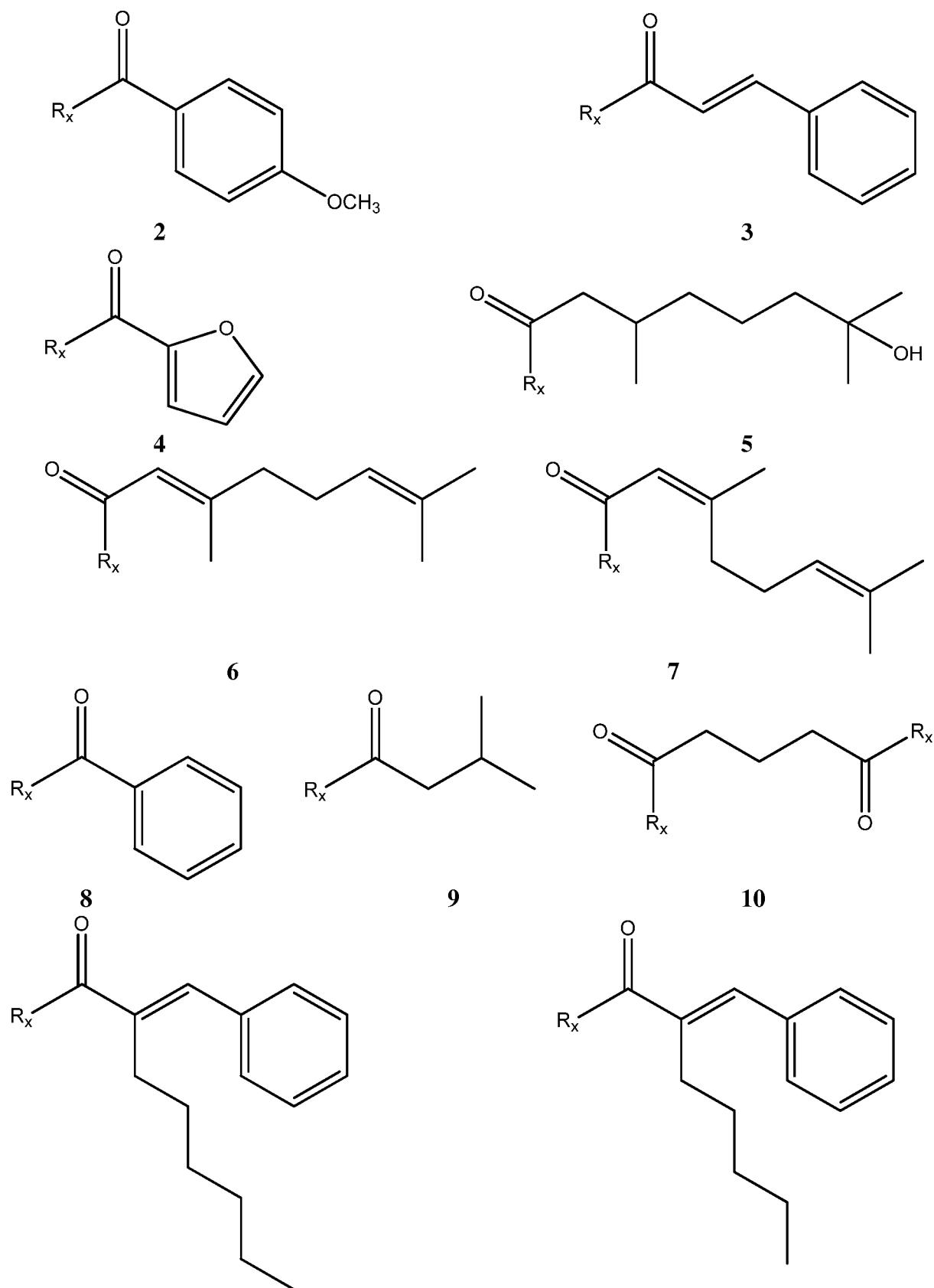
5. A deuterium-enriched aldehyde of structure 1, where R₁ and R₂ are hydrogen, and R₃ is a lower alkenyl.
6. A deuterium-enriched aldehyde of structure 1, where R₁ and R₂ are hydrogen, and R₃ is a higher alkenyl.
7. A deuterium-enriched aldehyde of structure 1, where R₁ and R₂ are hydrogen, and R₃ is a substituted alkenyl, where the substituted alkenyl is a lower alkenyl, and where the one or more other chemical groups are selected from: CO₂H, CO₂R₆ (where R₆ is a lower alkyl group), C(O)NH₂, C(O)NHR₇ (where R₇ is a lower alkyl group), C(O)NR₇R₈ (where R₇ and R₈ are independently lower alkyl groups), CN, aryl, substituted aryl, heteroaryl, and substituted heteroaryl.
8. A deuterium-enriched aldehyde of structure 1, where R₁ and R₂ are hydrogen, and R₃ is a substituted alkenyl, where the substituted alkenyl is a higher alkenyl, and where the one or more other chemical groups are selected from: CO₂H, CO₂R₆ (where R₆ is a lower alkyl group), C(O)NH₂, C(O)NHR₇ (where R₇ is a lower alkyl group), C(O)NR₇R₈ (where R₇ and R₈ are independently lower alkyl groups), CN, aryl, substituted aryl, heteroaryl, and substituted heteroaryl.
9. A deuterium-enriched aldehyde of structure 1, where R₁ and R₂ are hydrogen, and R₃ is a lower alkynyl.
10. A deuterium-enriched aldehyde of structure 1, where R₁ and R₂ are hydrogen, and R₃ is a higher alkynyl.
11. A deuterium-enriched aldehyde of structure 1, where R₁ and R₂ are hydrogen, and R₃ is a substituted alkynyl, where the substituted alkynyl is a lower alkynyl, and where the chemical groups are selected from: CO₂H, CO₂R₆ (where R₆ is a lower alkyl

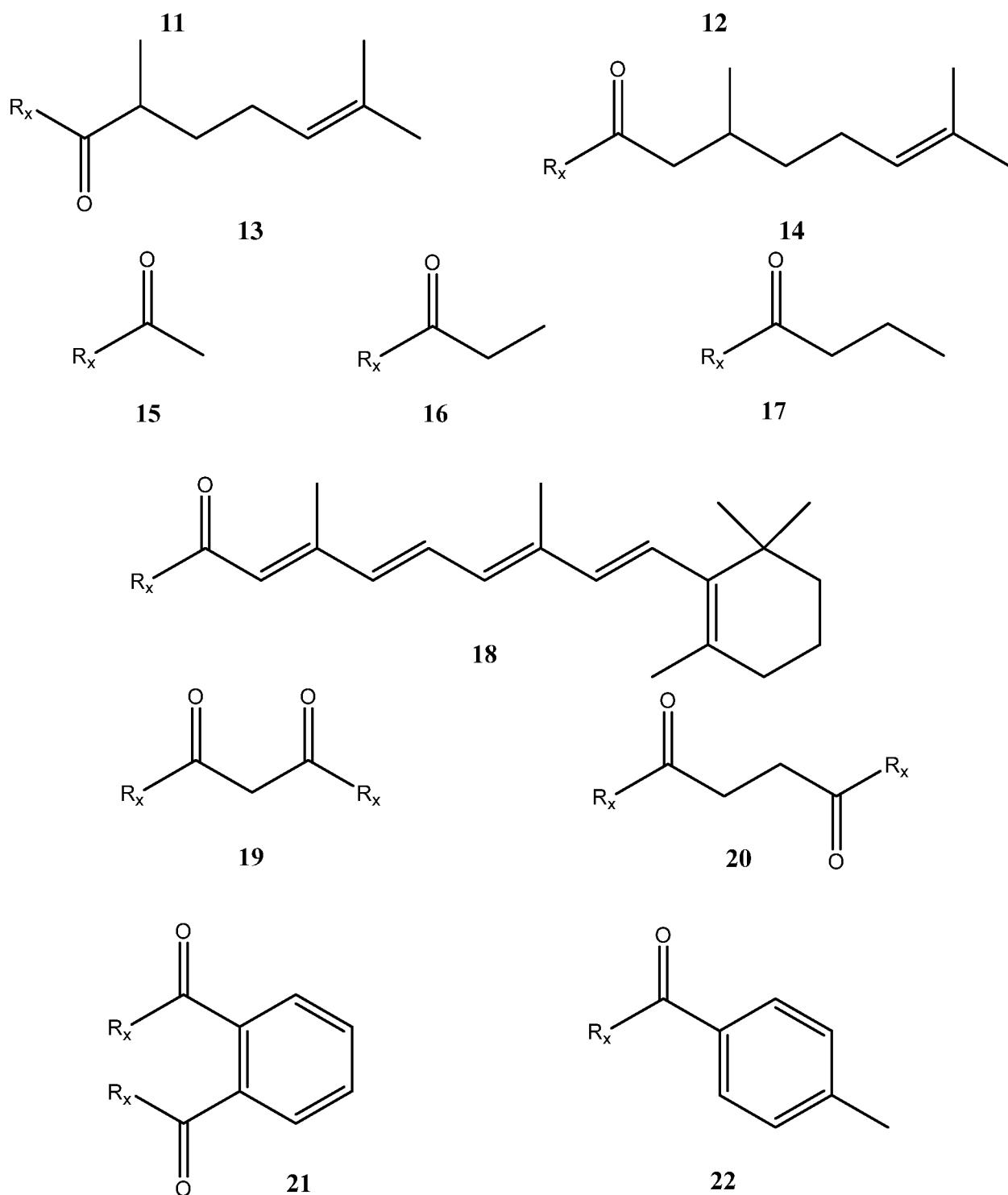
group), C(O)NH₂, C(O)NHR₇ (where R₇ is a lower alkyl group), C(O)NR₇R₈ (where R₇ and R₈ are independently lower alkyl groups), CN, aryl, substituted aryl, heteroaryl, and substituted heteroaryl.

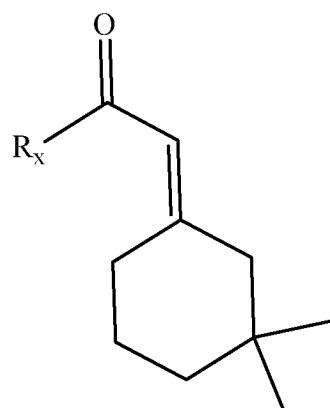
12. A deuterium-enriched aldehyde of structure **1**, where R₁ and R₂ are hydrogen, and R₃ is a substituted alkynyl, where the substituted alkynyl is a higher alkynyl, and where the chemical groups are selected from: CO₂H, CO₂R₆ (where R₆ is a lower alkyl group), C(O)NH₂, C(O)NHR₇ (where R₇ is a lower alkyl group), C(O)NR₇R₈ (where R₇ and R₈ are independently lower alkyl groups), CN, aryl, substituted aryl, heteroaryl, and substituted heteroaryl.
13. A deuterium-enriched aldehyde of structure **1**, where R₁ and R₂ are hydrogen, and R₃ is a lower heteroalkyl.
14. A deuterium-enriched aldehyde of structure **1**, where R₁ and R₂ are hydrogen, and R₃ is a higher heteroalkyl.
15. A deuterium-enriched aldehyde of structure **1**, where R₁ and R₂ are hydrogen, and R₃ is a substituted heteroalkyl, where the substituted heteroalkyl is a lower heteroalkyl.
16. A deuterium-enriched aldehyde of structure **1**, where R₁ and R₂ are hydrogen, and R₃ is a substituted heteroalkyl, where the substituted heteroalkyl is a higher heteroalkyl.
17. A deuterium-enriched aldehyde of structure **1**, where R₁ and R₂ are hydrogen, and R₃ is aryl.
18. A deuterium-enriched aldehyde of structure **1**, where R₁ and R₂ are hydrogen, and R₃ is substituted aryl.
19. A deuterium-enriched aldehyde of structure **1**, where R₁ and R₂ are hydrogen, and R₃ is heteroaryl.

20. A deuterium-enriched aldehyde of structure **1**, where $\text{CR}_1\text{R}_2\text{R}_3$ is aryl.
21. A deuterium-enriched aldehyde of structure **1**, where $\text{CR}_1\text{R}_2\text{R}_3$ is substituted aryl.
22. A deuterium-enriched aldehyde of structure **1**, where $\text{CR}_1\text{R}_2\text{R}_3$ is heteroaryl.
23. A deuterium-enriched aldehyde of structure **1**, where $\text{CR}_1\text{R}_2\text{R}_3$ is substituted heteroaryl.
24. A deuterium-enriched aldehyde of structure **1**, where CR_1R_2 is alkenyl and R_3 is hydrogen.
25. A deuterium-enriched aldehyde of structure **1**, where $\text{CR}_1\text{R}_2\text{R}_3$ is substituted alkenyl and R_3 is hydrogen.
26. A deuterium-enriched aldehyde of structure **1**, where CR_1R_2 is alkenyl and R_3 is alkyl.
27. A deuterium-enriched aldehyde of structure **1**, where $\text{CR}_1\text{R}_2\text{R}_3$ is substituted alkenyl and R_3 is alkyl.
28. A deuterium-enriched aldehyde of structure **1**, where R_1 is alkyl substituted with $\text{C}(\text{O})\text{R}_y$.
29. A deuterium-enriched aldehyde of structure **1**, where R_1 is alkyl substituted with $\text{C}(\text{O})\text{R}_y$ and R_2 and R_3 are hydrogens.
30. A deuterium-enriched aldehyde of structure **1**, where $\text{CR}_1\text{R}_2\text{R}_3$ aryl substituted with $\text{C}(\text{O})\text{R}_y$.
31. A deuterium-enriched aldehyde of structure **1**, where $\text{CR}_1\text{R}_2\text{R}_3$ substituted aryl substituted with $\text{C}(\text{O})\text{R}_y$.

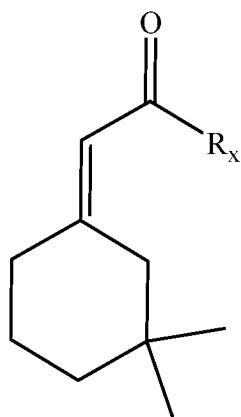
[0036] Additional deuterium-enriched aldehydes of the present invention include those numbered **2-64** shown below.



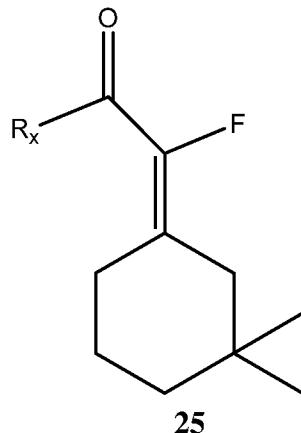




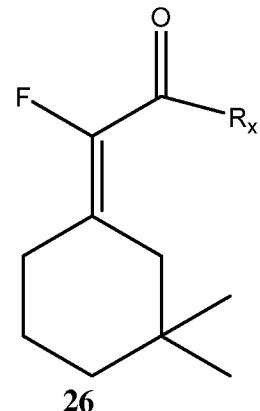
23 (grandlure IV, E-(3,3-dimethyl)-cyclohexylideneacetaldehyde)



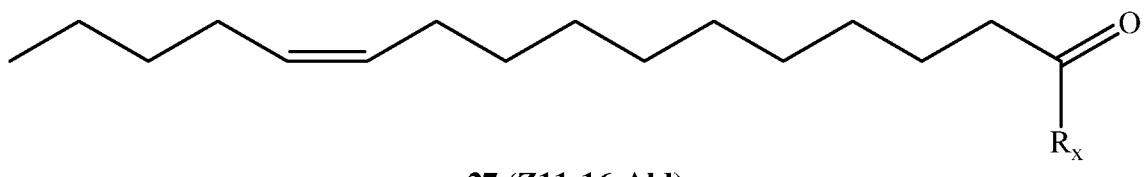
24 (grandlure III, Z-(3,3-dimethyl)-cyclohexylideneacetaldehyde)



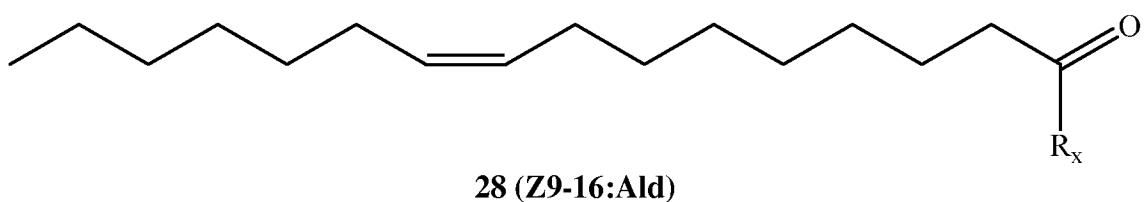
25



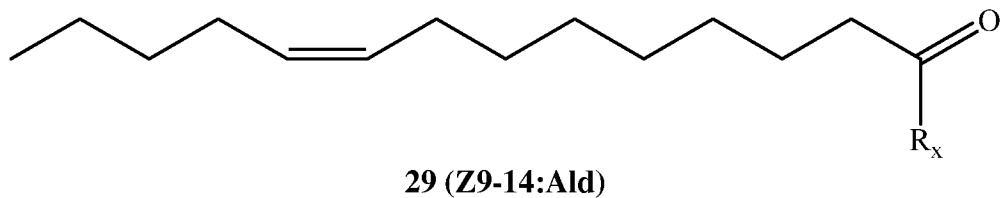
26



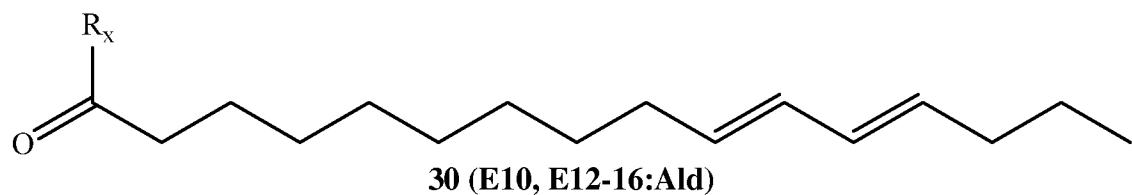
27 (Z11-16:Ald)



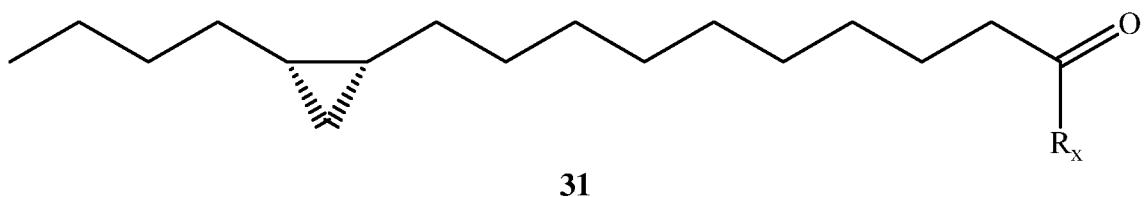
28 (Z9-16:Ald)



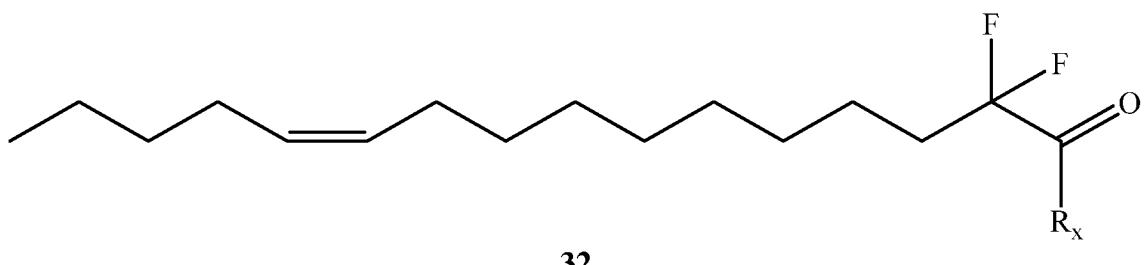
29 (Z9-14:Ald)



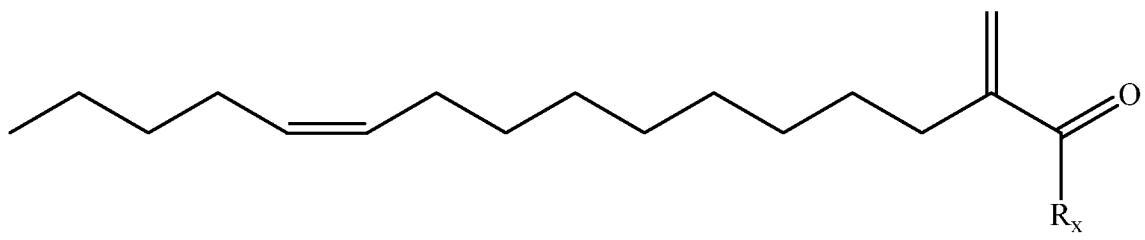
30 (E10, E12-16:Ald)



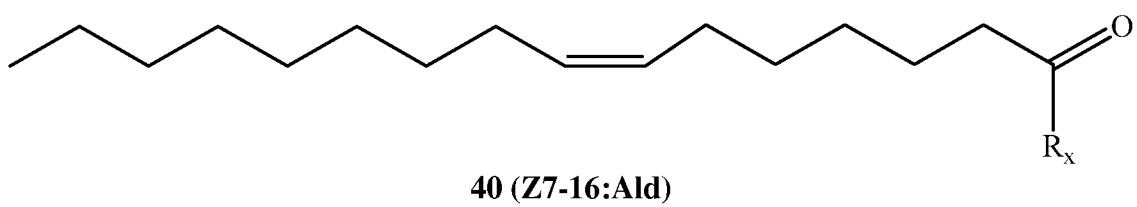
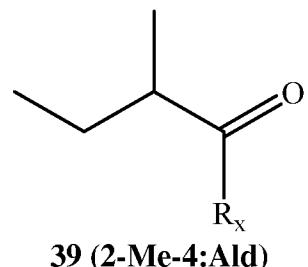
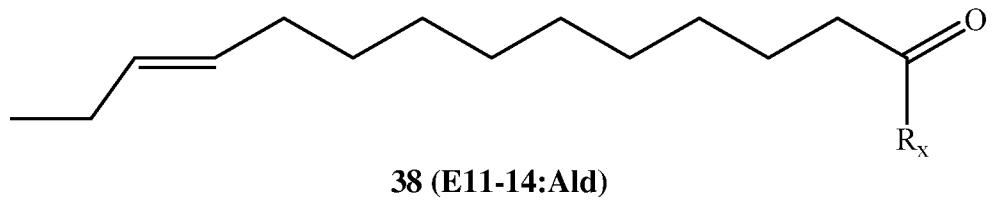
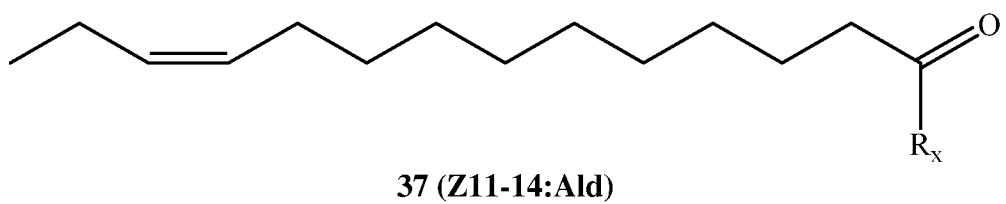
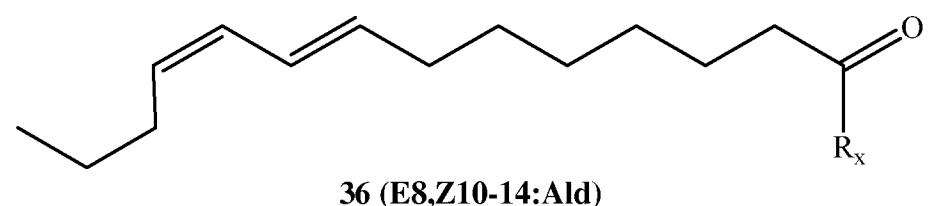
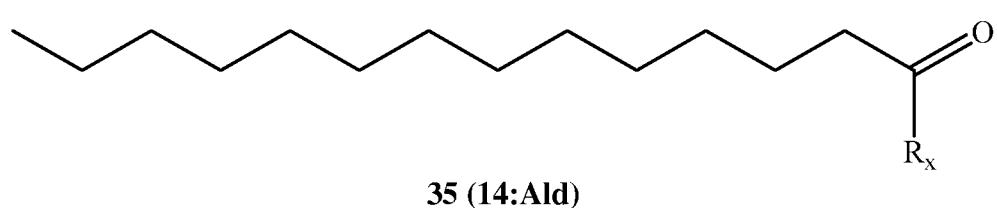
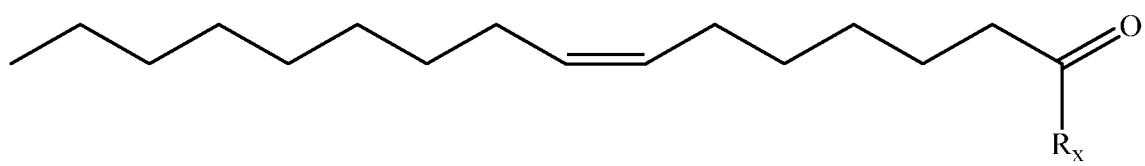
31

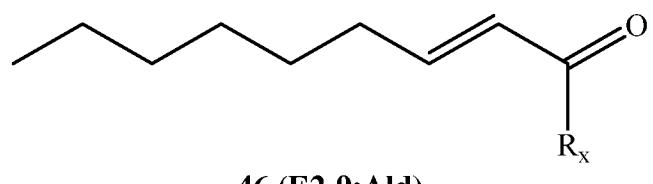
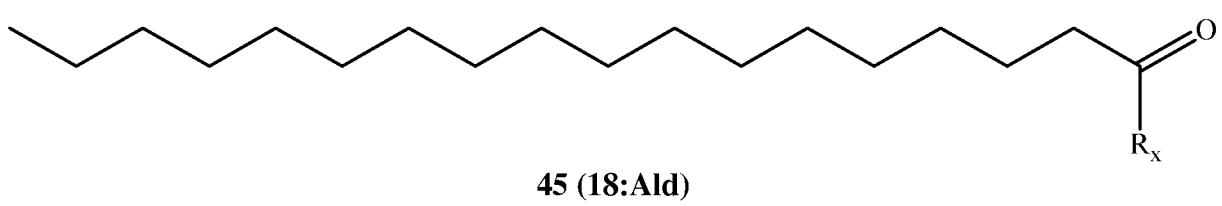
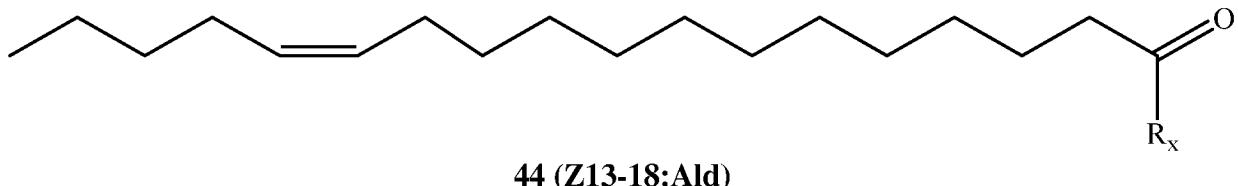
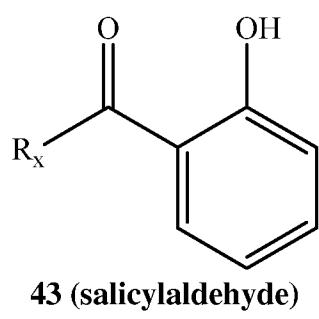
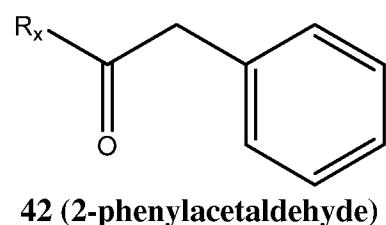
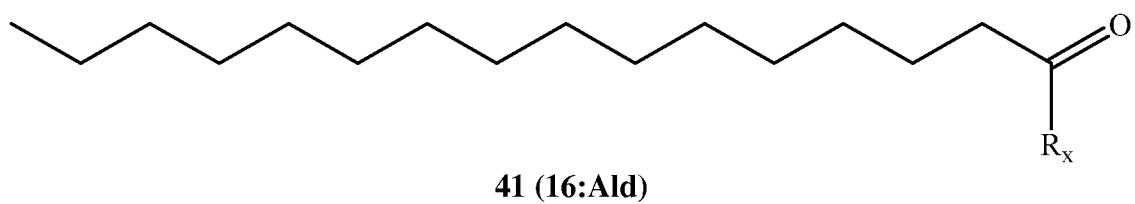


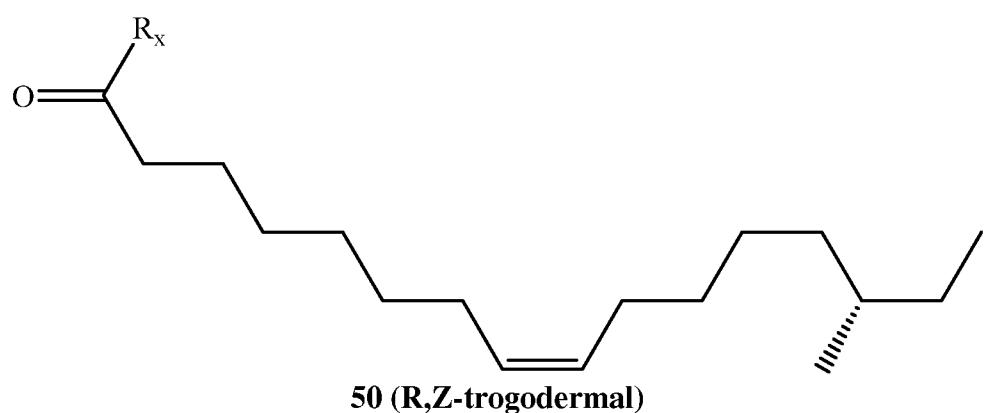
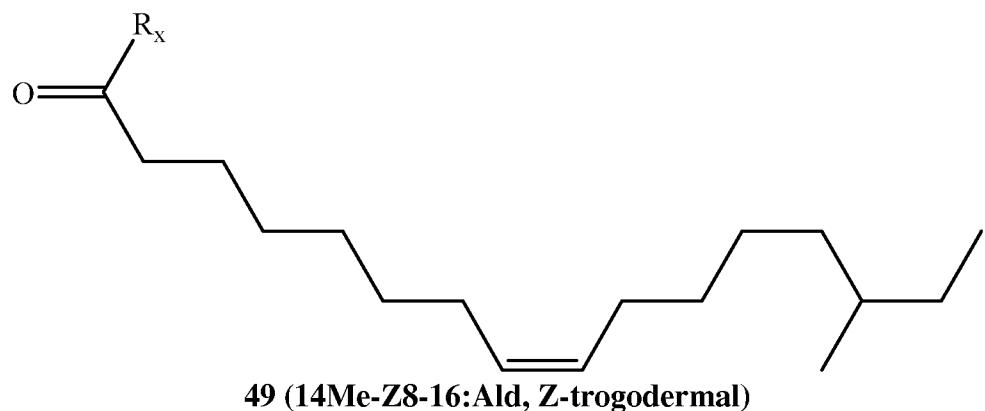
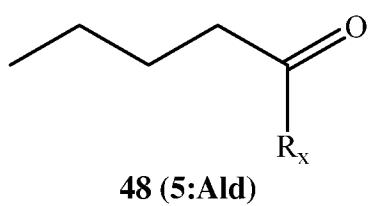
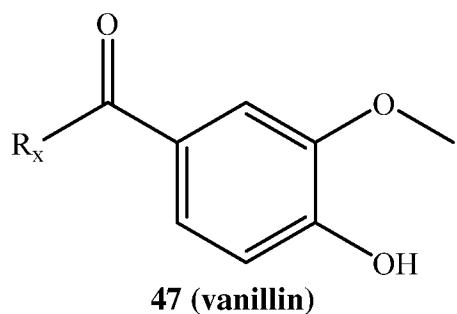
32

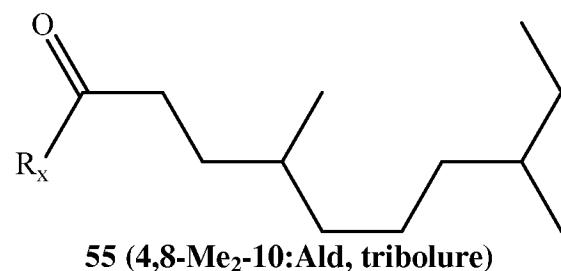
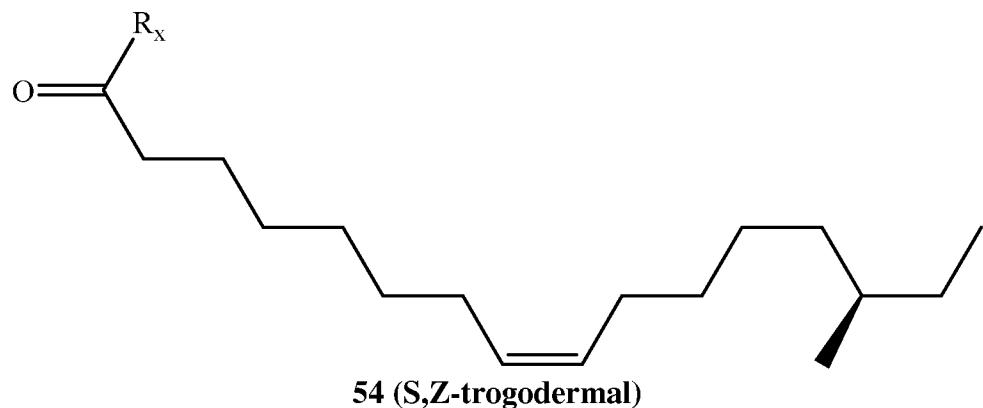
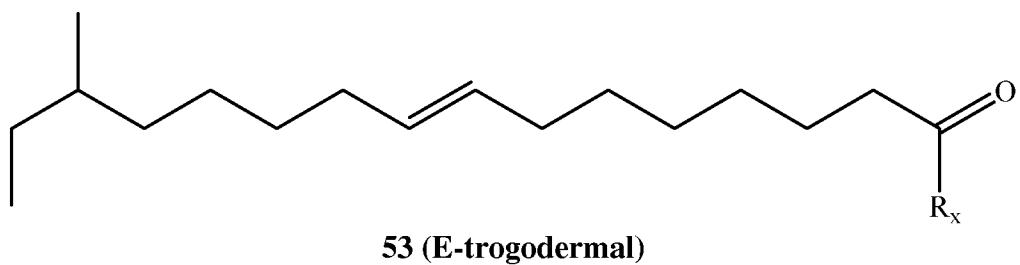
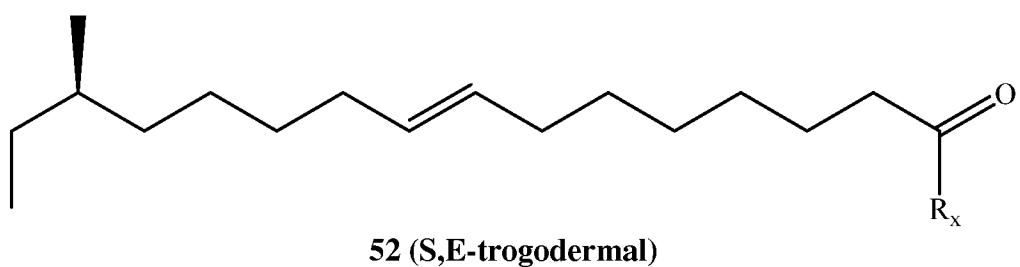
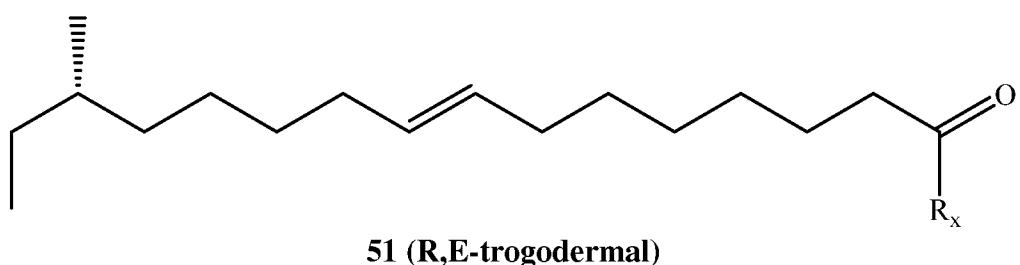


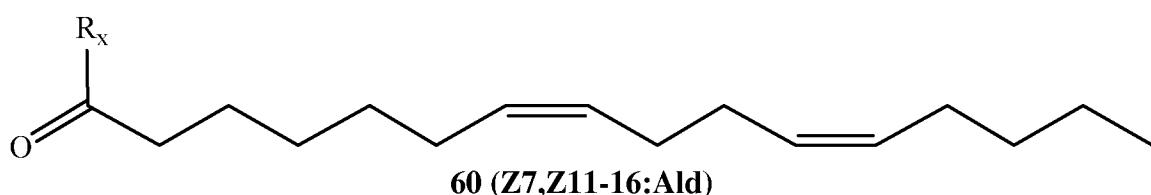
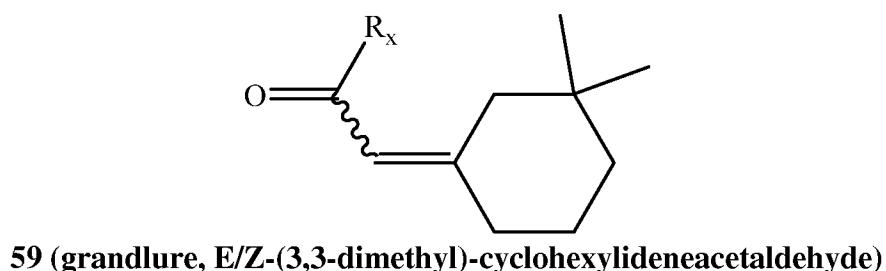
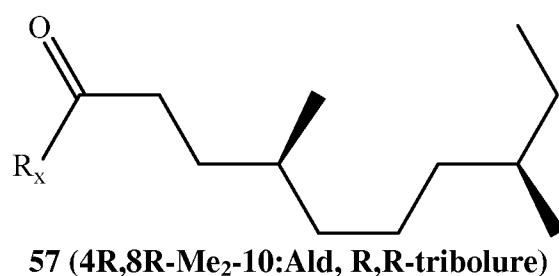
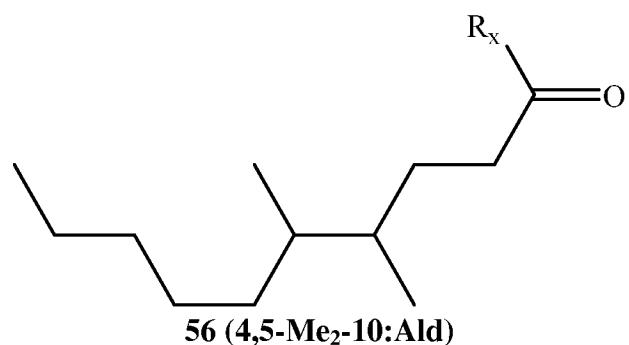
33

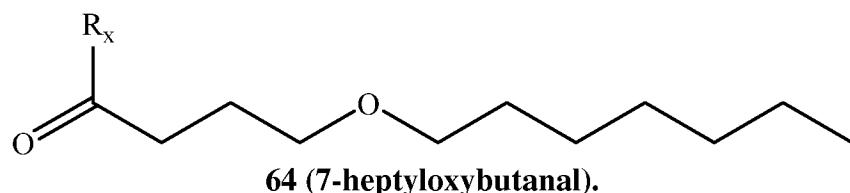
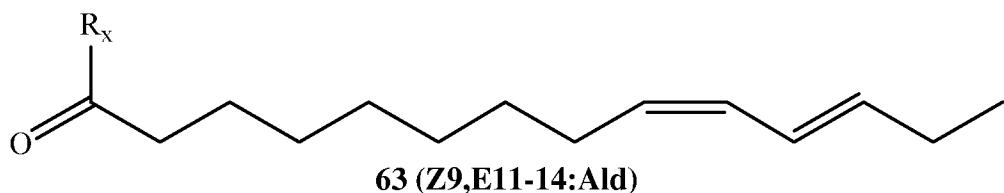
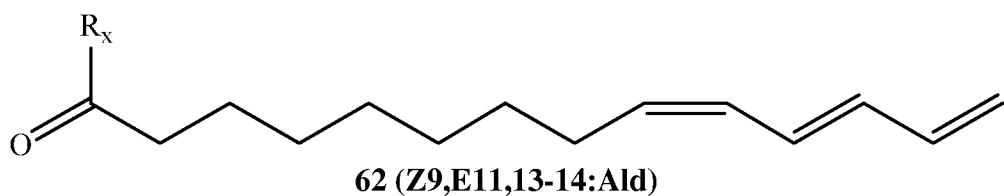
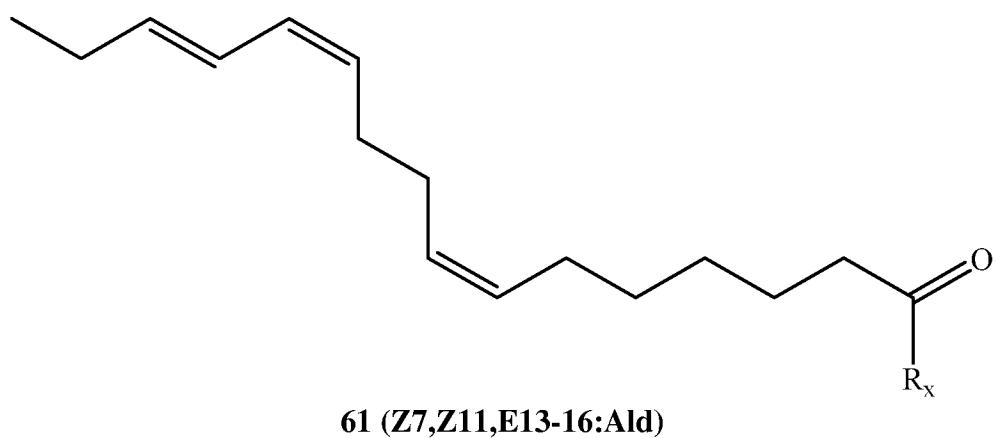












[0037] Additional deuterium-enriched aldehydes of the present invention include aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 2% of the hydrogen atoms present in R_x .

[0038] Additional deuterium-enriched aldehydes of the present invention include aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 10% of the hydrogen atoms present in R_x .

[0039] Additional deuterium-enriched aldehydes of the present invention include aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 20% of the hydrogen atoms present in R_x .

[0040] Additional deuterium-enriched aldehydes of the present invention include aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 30% of the hydrogen atoms present in R_x .

[0041] Additional deuterium-enriched aldehydes of the present invention include aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 40% of the hydrogen atoms present in R_x .

[0042] Additional deuterium-enriched aldehydes of the present invention include aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 50% of the hydrogen atoms present in R_x .

[0043] Additional deuterium-enriched aldehydes of the present invention include aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 60% of the hydrogen atoms present in R_x .

[0044] Additional deuterium-enriched aldehydes of the present invention include aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 70% of the hydrogen atoms present in R_x .

[0045] Additional deuterium-enriched aldehydes of the present invention include aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 80% of the hydrogen atoms present in R_x .

[0046] Additional deuterium-enriched aldehydes of the present invention include aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 90% of the hydrogen atoms present in R_x .

[0047] Additional deuterium-enriched aldehydes of the present invention include aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 95% of the hydrogen atoms present in R_x .

[0048] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **2-64**.

[0049] Reference to “compositions comprising compounds **2-64**” means compositions comprising at least 6×10^{18} molecules of at least one of aldehydes **2-64**, typically at least 6×10^{19} molecules, and may, for example, comprise at least 6×10^{20} molecules, 6×10^{21} molecules, 6×10^{22} molecules, or 6×10^{23} molecules. R_x is hydrogen, wherein the deuterium isotope is in an amount greater than 0.10 percent of the R_x hydrogen atoms. In certain cases, the deuterium isotope comprises greater than 1% of the hydrogen atoms, or even greater than 2%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 95% of the hydrogen atoms.

[0050] In another aspect, reference to “compositions comprising compounds **2-64**” means compositions comprising at least 0.1 mole of at least one of aldehydes **2-64**. Compositions of the invention may, for example, comprise at least 0.2, 0.5, 1, 2, 3, 4, 5, 10, to 20 moles of at least one of compounds **2-64**.

[0051] In another aspect, reference to “compositions comprising compounds **2-64**” means compositions comprising at least 1 gram of at least one of aldehydes **2-64**. Compositions of the invention may, for example, comprise at least 5, 10, 20, 30, 40, 50, 100, 500, to 1,000 grams of at least one of compounds **2-64**.

[0052] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 2% of the hydrogen atoms present in R_x .

[0053] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 10% of the hydrogen atoms present in R_x .

[0054] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 20% of the hydrogen atoms present in R_x .

[0055] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 30% of the hydrogen atoms present in R_x .

[0056] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 40% of the hydrogen atoms present in R_x .

[0057] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 50% of the hydrogen atoms present in R_x .

[0058] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 60% of the hydrogen atoms present in R_x .

[0059] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 70% of the hydrogen atoms present in R_x .

[0060] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 80% of the hydrogen atoms present in R_x .

[0061] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 90% of the hydrogen atoms present in R_x .

[0062] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **2-64** wherein the deuterium isotope in R_x is in an amount greater than 95% of the hydrogen atoms present in R_x .

[0063] Additional deuterium-enriched aldehydes of the present invention include aldehydes **65-358** listed in the Table A below. For each aldehyde listed in the table, the original aldehyde hydrogen ($C(O)-H$) has been replaced by R_x ($C(O)-R_x$). For example, formaldehyde- R_x ($CHO-R_x$) is $HC(O)-R_x$.

Table A

Ex.	Name	Formula
65.	Formaldehyde- R_x	$CHO-R_x$
66.	2-Methyl-2-propenal- R_x	$C_4H_5O-R_x$
67.	2-Methylpropanal- R_x	$C_4H_7O-R_x$
68.	2-Propenal- R_x	$C_3H_3O-R_x$
69.	2-Butenal- R_x	$C_4H_5O-R_x$
70.	2-Methyl-2-butenal- R_x	$C_5H_7O-R_x$
71.	2-Methylenebutanal- R_x	$C_5H_7O-R_x$
72.	3-Methyl-2-butenal- R_x	$C_5H_7O-R_x$
73.	3-Methyl-3-butenal- R_x	$C_5H_7O-R_x$
74.	3-Methylbutanal- R_x	$C_5H_9O-R_x$
75.	(E)-2-Pentenal- R_x	$C_5H_7O-R_x$

76.	2-Methylenepentanal-R _x	C ₆ H ₉ O-R _x
77.	2-Pentenal-R _x	C ₅ H ₇ O-R _x
78.	3-Methyl-1-(vinyloxy)-butane-R _x	C ₇ H ₁₃ O-R _x
79.	4-Methylpentanal-R _x	C ₆ H ₁₁ O-R _x
80.	Furan-2-carbaldehyde-R _x	C ₅ H ₃ O ₂ -R _x
81.	(E)-2-Hexenal-R _x	C ₆ H ₉ O-R _x
82.	(E)-4-oxo-2-Hexenal-R _x	C ₆ H ₇ O ₂ -R _x
83.	(E,E)-2,4-Dimethyl-2,4-hexadienal-R _x	C ₈ H ₁₁ O-R _x
84.	(E,E)-2,4-Hexadienal-R _x	C ₆ H ₇ O-R _x
85.	(Z)-2-Hexenal-R _x	C ₆ H ₉ O-R _x
86.	(Z)-3-Hexenal-R _x	C ₆ H ₉ O-R _x
87.	(Z)-4-oxo-2-Hexenal-R _x	C ₆ H ₇ O ₂ -R _x
88.	1-Hexenal-R _x	C ₆ H ₉ O-R _x
89.	2,3-Dihydroxybenzaldehyde-R _x	C ₇ H ₅ O ₃ -R _x
90.	2-Hexenal-R _x	C ₆ H ₉ O-R _x
91.	3-((E)-2-Hexenoxy)-hexanal-R _x	C ₁₂ H ₂₁ O ₂ -R _x
92.	3,5-Dimethylhexanal-R _x	C ₈ H ₁₅ O-R _x
93.	3-Ethoxyhexanal-R _x	C ₈ H ₁₅ O ₂ -R _x
94.	3-Hydroxybenzaldehyde-R _x	C ₇ H ₅ O ₂ -R _x
95.	3-Hydroxyhexanal-R _x	C ₆ H ₁₁ O ₂ -R _x
96.	4-Hydroxy-3,5-dimethoxybenzaldehyde-R _x	C ₉ H ₉ O ₄ -R _x
97.	4-Hydroxybenzaldehyde-R _x	C ₇ H ₅ O ₂ -R _x
98.	5-Methylhexanal-R _x	C ₇ H ₁₃ O-R _x
99.	Hexanal-R _x	C ₆ H ₁₁ O-R _x
100.	(1R,2S,5S)-Iridodial-R _x	C ₁₀ H ₁₅ O ₂ -R _x
101.	(1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-carbaldehyde-R _x	C ₁₀ H ₁₃ O-R _x
102.	(1S,2R,3S)-2-(1-Formylvinyl)-5-methylcyclopentanecarbaldehyde-R _x	C ₁₀ H ₁₃ O ₂ -R _x
103.	(3S,8R)-2-Methyl-5-(1-formylethyl)-1-cyclopentene-1-carbaldehyde-R _x	C ₁₀ H ₁₃ O ₂ -R _x
104.	(3S,8S)-2-Methyl-5-(1-formylethyl)-1-cyclopentene-1-carbaldehyde-R _x	C ₁₀ H ₁₃ O ₂ -R _x
105.	(5S,8S)-2-Methyl-5-(1-formylethyl)-1-cyclopentene-1-carbaldehyde-R _x	C ₁₀ H ₁₃ O ₂ -R _x
106.	(E)-2-(2-Hydroxyethyl)-6-methyl-2,5-heptadienal-R _x	C ₁₀ H ₁₅ O ₂ -R _x
107.	(E)-2-(2-Hydroxyethylidene)-6-methyl-5-heptenal-R _x	C ₁₀ H ₁₅ O ₂ -R _x
108.	(E)-2-Heptenal-R _x	C ₇ H ₁₁ O-R _x
109.	(E)-2-Isopropyl-5-methyl-2-hexenal-R _x	C ₁₀ H ₁₇ O-R _x
110.	(E,Z)-2,4-Heptadienal-R _x	C ₇ H ₉ O-R _x
111.	(R)-2-((1R,2R,3S)-3-Methyl-2-vinylcyclopentyl)-propanal-R _x	C ₁₁ H ₁₉ O ₂ -R _x
112.	(R)-2-((1S,2S,3S)-3-Methyl-2-vinylcyclopentyl)-propanal-R _x	C ₁₁ H ₁₉ O ₂ -R _x
113.	(R)-2,6-Dimethyl-5-heptenal-R _x	C ₉ H ₁₅ O-R _x
114.	(R)-7-Hydroxy-6,7-dihydro-5H-pyrrolizidine-1-carboxaldehyde-R _x	C ₈ H ₈ NO ₂ -R _x
115.	(S)-4-(Prop-1-en-2-yl)-cyclohex-1-enecarbaldehyde-R _x	C ₁₀ H ₁₃ O-R _x

116.	(S)-7-Hydroxy-6,7-dihydro-5H-pyrrolizidine-1-carboxaldehyde-R _x	C ₈ H ₈ NO ₂ -R _x
117.	(Z)-2-Isopropyl-5-methyl-2-hexenal-R _x	C ₁₀ H ₁₇ O-R _x
118.	1-Formyl-6,7-dihydro-5H-pyrrolizine-R _x	C ₈ H ₈ NO-R _x
119.	1-Formyl-7-hydroxy-6,7-dihydro-5H-pyrrolizine-R _x	C ₉ H ₁₂ NO ₂ -R _x
120.	2-(3-Methylcyclopentyl)-propanal-R _x	C ₉ H ₁₅ O-R _x
121.	2,6-Dimethyl-5-heptenal-R _x	C ₉ H ₁₅ O-R _x
122.	2-Acetyl-5-methylcyclopentanecarbaldehyde-R _x	C ₉ H ₁₃ O ₂ -R _x
123.	2-Methoxybenzaldehyde-R _x	C ₈ H ₇ O ₂ -R _x
124.	2-Methyl-1-cyclopentenecarbaldehyde-R _x	C ₇ H ₉ O-R _x
125.	3,3-Dimethyl-5-oxo-7-oxabicyclo[4.1.0]heptane-1-carbaldehyde-R _x	C ₉ H ₁₁ O ₃ -R _x
126.	3-Hydroxybenzene-1,2-dicarbaldehyde-R _x	C ₈ H ₅ O ₃ -R _x
127.	3-Methylbenzaldehyde-R _x	C ₈ H ₇ O-R _x
128.	4-(Heptyloxy)-butanal-R _x	C ₁₁ H ₂₁ O ₂ -R _x
129.	4-Methoxybenzaldehyde-R _x	C ₈ H ₇ O ₂ -R _x
130.	6,7-Dihydro-5H-pyrrolizine-1-carboxaldehyde-R _x	C ₈ H ₈ NO-R _x
131.	6,7-Dihydro-7-oxo-5H-pyrrolizine-1-carbaldehyde-R _x	C ₈ H ₆ NO ₂ -R _x
132.	6-Methylheptanal-R _x	C ₈ H ₁₅ O-R _x
133.	7-Hydroxy-6,7-dihydro-5H-pyrrolizine-1-carboxaldehyde-R _x	C ₈ H ₈ NO ₂ -R _x
134.	Benzaldehyde-R _x	C ₇ H ₅ O-R _x
135.	Cyclohexanodial-R _x	C ₈ H ₁₁ O ₂ -R _x
136.	Heptanal-R _x	C ₇ H ₁₃ O-R _x
137.	Plagiodial-R _x	C ₁₀ H ₁₃ O ₂ -R _x
138.	(1R,2S)-cis-2-Isopropenyl-1-methylcyclobutaneethanal-R _x	C ₁₀ H ₁₅ O-R _x
139.	(1R,2S,5R,8R)-Iridodial-R _x	C ₁₀ H ₁₅ O ₂ -R _x
140.	(4S)-(3-Oxoprop-1-en-2-yl)-cyclohex-1-enecarbaldehyde-R _x	C ₁₀ H ₁₁ O ₂ -R _x
141.	(E)-2-(3,3-Dimethylcyclohexylidene)-acetaldehyde-R _x	C ₁₀ H ₁₅ O-R _x
142.	(E)-2-(4-Methyl-3-pentenyl)-butenedial-R _x	C ₁₀ H ₁₃ O ₂ -R _x
143.	(E)-2-(4-Methyl-3-pentenylidene)-butanodial-R _x	C ₁₀ H ₁₃ O ₂ -R _x
144.	(E)-2,7-Octadienal-R _x	C ₈ H ₁₁ O-R _x
145.	(E)-2-Methyl-5-(3-furyl)-2-pentenal-R _x	C ₁₀ H ₁₁ O ₂ -R _x
146.	(E)-2-Octenal-R _x	C ₈ H ₁₃ O-R _x
147.	(E)-3,7-Dimethyl-2,6-octadienal-R _x	C ₁₀ H ₁₅ O-R _x
148.	(E)-3,7-Dimethyl-2,6-octadienal-R _x	C ₁₀ H ₁₅ O-R _x
149.	(E)-4-oxo-2-Octenal-R _x	C ₈ H ₁₁ O ₂ -R _x
150.	(E)-7-Methyl-2-octenal-R _x	C ₉ H ₁₅ O-R _x
151.	(E,E)-2,4-Octadienal-R _x	C ₈ H ₁₁ O-R _x
152.	(E,E)-2,6-Dimethyl-8-hydroxy-2,6-octadienal-R _x	C ₁₀ H ₁₅ O ₂ -R _x
153.	(E,E)-2,6-Octadienal-R _x	C ₈ H ₁₁ O-R _x
154.	(E,E)-2,6-Octadienedial-R _x	C ₈ H ₉ O ₂ -R _x
155.	(E,Z)-2,4-Octadienal-R _x	C ₈ H ₁₁ O-R _x
156.	(E,Z)-2,6-Octadienal-R _x	C ₈ H ₁₁ O-R _x
157.	(Z)-2-(3,3-Dimethylcyclohexylidene)-acetaldehyde-R _x	C ₁₀ H ₁₅ O-R _x
158.	(Z)-3,7-Dimethyl-2,6-octadienal-R _x	C ₁₀ H ₁₅ O-R _x
159.	(Z,E)-3,7-Dimethyl-2,6-octadienal-R _x	C ₁₀ H ₁₅ O-R _x

160.	1-Octenal-R _x	C ₈ H ₁₃ O-R _x
161.	2-(1-Formylvinyl)-5-methylcyclopentanecarbaldehyde-R _x	C ₁₀ H ₁₃ O ₂ -R _x
162.	2,6,6-Trimethyl-1-cyclohexene-1-carbaldehyde-R _x	C ₁₀ H ₁₅ O-R _x
163.	2-Ethyoctanal-R _x	C ₁₀ H ₁₉ O-R _x
164.	2-Hydroxy-6-methylbenzaldehyde-R _x	C ₈ H ₇ O ₂ -R _x
165.	2-Methyl benzaldehyde-R _x	C ₈ H ₇ O-R _x
166.	2-Octenal-R _x	C ₈ H ₁₃ O-R _x
167.	2-Phenylpropenal-R _x	C ₉ H ₇ O-R _x
168.	3,7-Dimethyl-6-octenal-R _x	C ₁₀ H ₁₇ O-R _x
169.	3-Ethoxy-4-hydroxybenzaldehyde-R _x	C ₉ H ₉ O ₃ -R _x
170.	3-Ethyl benzaldehyde-R _x	C ₉ H ₉ O-R _x
171.	3-Isopropyl-6-methyl benzaldehyde-R _x	C ₁₁ H ₁₃ O-R _x
172.	3-Octenal-R _x	C ₈ H ₁₃ O-R _x
173.	3-oxo-4-Isopropylidene-1-cyclohexene-1-carboxyaldehyde-R _x	C ₁₀ H ₁₁ O ₂ -R _x
174.	4-Hydroxy-2-methyl benzaldehyde-R _x	C ₈ H ₇ O ₂ -R _x
175.	4-Hydroxy-3-methoxybenzaldehyde-R _x	C ₈ H ₇ O ₃ -R _x
176.	4-Isopropenyl-1-cyclohexene-1-carbaldehyde-R _x	C ₁₀ H ₁₃ O-R _x
177.	4-Isopropenyl-3-oxo-1-cyclohexene-1-carboxyaldehyde-R _x	C ₁₀ H ₁₁ O ₂ -R _x
178.	4-oxo-Octenal-R _x	C ₈ H ₁₁ O ₂ -R _x
179.	4S-4-Isopropenyl-3-oxo-1-cyclohexene-1-carboxyaldehyde-R _x	C ₁₀ H ₁₁ O ₂ -R _x
180.	6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-carbaldehyde-R _x	C ₁₀ H ₁₃ O-R _x
181.	7-Methyoctanal-R _x	C ₉ H ₁₇ O-R _x
182.	Anisomorphal-R _x	C ₁₀ H ₁₃ O ₂ -R ₂
183.	cis-2-Isopropenyl-1-methylcyclobutaneethanal-R _x	C ₁₀ H ₁₅ O-R _x
184.	Octanal-R _x	C ₈ H ₁₅ O-R _x
185.	Peruphasmal-R _x	C ₁₀ H ₁₃ O ₂ -R _x
186.	(E)-4,8-Nonadienal-R _x	C ₉ H ₁₃ O-R _x
187.	(E)-8-Methyl-2-nonenal-R _x	C ₁₀ H ₁₇ O-R _x
188.	(E,E)-2,4-Nonadienal-R _x	C ₉ H ₁₃ O-R _x
189.	(E,E,E)-2,4,6-Nonatrienal-R _x	C ₉ H ₁₁ O-R _x
190.	(E,E,Z)-2,4,6-Nonatrienal-R _x	C ₉ H ₁₁ O-R _x
191.	(E,Z)-2,6-Nonadienal-R _x	C ₉ H ₁₃ O-R _x
192.	(E,Z,Z)-2,4,6-Nonatrienal-R _x	C ₉ H ₁₁ O-R _x
193.	(Z)-3-Nonenal-R _x	C ₉ H ₁₅ O-R _x
194.	(Z)-4,8-Nonadienal-R _x	C ₉ H ₁₃ O-R _x
195.	(Z)-4-Nonenal-R _x	C ₉ H ₁₅ O-R _x
196.	(Z)-8-Methyl-2-nonenal-R _x	C ₁₀ H ₁₇ O-R _x
197.	2-Phenyl-2-butenal-R _x	C ₁₀ H ₉ O-R _x
198.	3-(4-Methoxyphenyl)-2-propenal-R _x	C ₁₀ H ₉ O ₂ -R _x
199.	3-Phenyl-2-propenal-R _x	C ₉ H ₇ O-R _x
200.	3-Phenylpropanal-R _x	C ₉ H ₉ O-R _x
201.	6-Ethyl benzaldehyde-R _x	C ₉ H ₉ O-R _x
202.	8-Methylnonanal-R _x	C ₁₀ H ₁₉ O-R _x
203.	9-Acetyloxynonanal-R _x	C ₁₁ H ₁₉ O ₃ -R _x

204.	Nonanal-R _x	C ₉ H ₁₇ O-R _x
205.	(E)-2,9-Decadienal-R _x	C ₁₀ H ₁₅ O-R _x
206.	(E)-2-Decenal-R _x	C ₁₀ H ₁₇ O-R _x
207.	(E)-4-oxo-2-Decenal-R _x	C ₁₀ H ₁₅ O ₂ -R _x
208.	(E)-8-Hydroxy-4,8-dimethyl-4,9-decadienal-R _x	C ₁₂ H ₁₉ O ₂ -R _x
209.	(E)-9-Methyl-2-decenal-R _x	C ₁₁ H ₁₉ O-R _x
210.	(E,E)-2,4-Decadienal-R _x	C ₁₀ H ₁₅ O-R _x
211.	(E,Z)-2,4-Decadienal-R _x	C ₁₀ H ₁₅ O-R _x
212.	(Z)-4-Decenal-R _x	C ₁₀ H ₁₇ O-R _x
213.	(Z)-5-Decenal-R _x	C ₁₀ H ₁₇ O-R _x
214.	(Z)-9-Methyl-2-decenal-R _x	C ₁₁ H ₁₉ O-R _x
215.	1-Decenal-R _x	C ₁₀ H ₁₇ O-R _x
216.	2-Decenal-R _x	C ₁₀ H ₁₇ O-R _x
217.	2-Ethyldecanal-R _x	C ₁₂ H ₂₃ O-R _x
218.	Decanal-R _x	C ₁₀ H ₁₉ O-R _x
219.	(5E)-2,6,10-Trimethylundeca-5,9-dienal-R _x	C ₁₄ H ₂₃ O-R _x
220.	(E)-2-Undecenal-R _x	C ₁₁ H ₁₉ O-R _x
221.	(E)-6-Ethyl-2,10-dimethyl-5,9-undecadienal-R _x	C ₁₅ H ₂₅ O-R _x
222.	10-Undecenal-R _x	C ₁₁ H ₁₉ O-R _x
223.	2-Butyl-2-octenal-R _x	C ₁₂ H ₂₁ O-R _x
224.	5-Methyl-2-phenyl-2-hexenal-R _x	C ₁₃ H ₁₅ O-R _x
225.	8-Isopropyl-5-methyl-3,4,4a,5,6,7,8,8a-octahydronaphthalene-2-carbaldehyde-R _x	C ₁₅ H ₂₃ O-R _x
226.	syn-4,6-Dimethylundecanal-R _x	C ₁₃ H ₂₅ O-R _x
227.	Undecanal-R _x	C ₁₁ H ₂₁ O-R _x
228.	(3R,5R,9R)-3,5,9-Trimethyldodecanal-R _x	C ₁₅ H ₂₉ O-R _x
229.	(3S,6E)-7-Ethyl-3,11-dimethyldodeca-6,10-dienal-R _x	C ₁₆ H ₂₇ O-R _x
230.	(9R)-3,5,9-Trimethyldodecanal-R _x	C ₁₅ H ₂₉ O-R _x
231.	(E)-10-Dodecenal-R _x	C ₁₂ H ₂₁ O-R _x
232.	(E)-2-Dodecenal-R _x	C ₁₂ H ₂₁ O-R _x
233.	(E)-3,7,11-Trimethyl-6,10-dodecadienal-R _x	C ₁₅ H ₂₅ O-R _x
234.	(E)-6-Dodecenal-R _x	C ₁₂ H ₂₁ O-R _x
235.	(E)-7-Dodecenal-R _x	C ₁₂ H ₂₁ O-R _x
236.	(E)-8-Dodecenal-R _x	C ₁₂ H ₂₁ O-R _x
237.	(E)-9,11-Dodecadienal-R _x	C ₁₂ H ₁₉ O-R _x
238.	(E)-9-Dodecenal-R _x	C ₁₂ H ₂₁ O-R _x
239.	(E,E)-3,7,11-Trimethyl-2,6,10-dodecatrienal-R _x	C ₁₅ H ₂₃ O-R _x
240.	(E,E)-7-Ethyl-3,11-dimethyl-2,6,10-dodecatrienal-R _x	C ₁₆ H ₂₅ O-R _x
241.	(E,E)-8,10-Dodecadienal-R _x	C ₁₂ H ₁₉ O-R _x
242.	(E,E,E)-3,7-Dimethyl-8,11-dioxo-2,6,9-dodecatrienal-R _x	C ₁₄ H ₁₇ O ₃ -R _x
243.	(E,E,Z)-3,7-Dimethyl-8,11-dioxo-2,6,9-dodecatrienal-R _x	C ₁₄ H ₁₇ O ₃ -R _x
244.	(E,Z)-5,7-Dodecadienal-R _x	C ₁₂ H ₁₉ O-R _x
245.	(E,Z)-7,9-Dodecadienal-R _x	C ₁₂ H ₁₉ O-R _x
246.	(E,Z)-8,10-Dodecadienal-R _x	C ₁₂ H ₁₉ O-R _x

247.	(S,E)-3,7,11-Trimethyl-6,10-dodecadienal-R _x	C ₁₅ H ₂₅ O-R _x
248.	(Z)-2-Methyl-5-((1R,5R,6S)-2,6-dimethylbicyclo[3.1.1]hept-2-en-6-yl)-pent-2-enal-R _x	C ₁₅ H ₂₁ O-R _x
249.	(Z)-5-Dodecenal-R _x	C ₁₂ H ₂₁ O-R _x
250.	(Z)-7-Dodecenal-R _x	C ₁₂ H ₂₁ O-R _x
251.	(Z)-9,11-Dodecadienal-R _x	C ₁₂ H ₁₉ O-R _x
252.	(Z)-9-Dodecenal-R _x	C ₁₂ H ₂₁ O-R _x
253.	(Z,E)-3,7,11-Trimethyl-2,6,10-dodecatrienal-R _x	C ₁₅ H ₂₃ O-R _x
254.	(Z,E)-5,7-Dodecadienal-R _x	C ₁₂ H ₁₉ O-R _x
255.	(Z,E)-7-Ethyl-3,11-dimethyl-2,6,10-dodecatrienal-R _x	C ₁₆ H ₂₅ O-R _x
256.	(Z,E)-8,10-Dodecadienal-R _x	C ₁₂ H ₁₉ O-R _x
257.	(Z,Z)-5,7-Dodecadienal-R _x	C ₁₂ H ₁₉ O-R _x
258.	2-Ethyldecanal-R _x	C ₁₄ H ₂₇ O-R _x
259.	3,7,11-Trimethyl-(E)-6,10-dodecadienal-R _x	C ₁₅ H ₂₅ O-R _x
260.	Dodecanal-R _x	C ₁₂ H ₂₃ O-R _x
261.	syn-4,6-Dimethyldecanal-R _x	C ₁₄ H ₂₇ O-R _x
262.	(3S,4R,6E,10Z)-3,4,7,11-Tetramethyl-6,10-tridecadienal-R _x	C ₁₇ H ₂₉ O-R _x
263.	(Z)-4-Tridecenal-R _x	C ₁₃ H ₂₃ O-R _x
264.	13-Acetoxytridecanal-R _x	C ₁₅ H ₂₇ O ₃ -R _x
265.	Tridecanal-R _x	C ₁₃ H ₂₅ O-R _x
266.	(E)-11,13-Tetradecadienal-R _x	C ₁₄ H ₂₃ O-R _x
267.	(E,E)-8,10-Tetradecadienal-R _x	C ₁₄ H ₂₃ O-R _x
268.	(E,Z)-4,9-Tetradecadienal-R _x	C ₁₄ H ₂₃ O-R _x
269.	(Z)-11,13-Tetradecadienal-R _x	C ₁₄ H ₂₃ O-R _x
270.	(Z)-5-Tetradecenal-R _x	C ₁₄ H ₂₅ O-R _x
271.	(Z)-7-Tetradecenal-R _x	C ₁₄ H ₂₅ O-R _x
272.	(Z)-9,13-Tetradecadien-11-ynal-R _x	C ₁₄ H ₁₉ O-R _x
273.	(Z,E)-9,12-Tetradecadienal-R _x	C ₁₄ H ₂₃ O-R _x
274.	(Z,Z)-8,10-Tetradecadienal-R _x	C ₁₄ H ₂₃ O-R _x
275.	(Z,Z)-9,11-Tetradecadienal-R _x	C ₁₄ H ₂₃ O-R _x
276.	10,12-Tetradecadienal-R _x	C ₁₄ H ₂₃ O-R _x
277.	2-Ethyltetradecanal-R _x	C ₁₆ H ₃₁ O-R _x
278.	3-oxo-13-Tetradecenal-R _x	C ₁₄ H ₂₃ O ₂ -R _x
279.	3-oxo-Tetradecanal-R _x	C ₁₄ H ₂₅ O ₂ -R _x
280.	5,8-Tetradecadienal-R _x	C ₁₄ H ₂₃ O-R _x
281.	5-Tetradecenal-R _x	C ₁₄ H ₂₅ O-R _x
282.	(E)-5,9-Dimethyl-2-(6-methylhept-5-en-2-yl)-deca-4,8-dienal-R _x	C ₂₀ H ₃₃ O-R _x
283.	(E,Z)-9,11-Pentadecadienal-R _x	C ₁₅ H ₂₅ O-R _x
284.	(Z)-10-Pentadecenal-R _x	C ₁₅ H ₂₇ O-R _x
285.	(Z)-6,14-Pentadecadienal-R _x	C ₁₅ H ₂₅ O-R _x
286.	(Z,Z)-9,11-Pentadecadienal-R _x	C ₁₅ H ₂₅ O-R _x
287.	2-Hexyl-2-decenal-R _x	C ₁₆ H ₂₉ O-R _x
288.	Pentadecanal-R _x	C ₁₅ H ₂₉ O-R _x
289.	(1R)-Pimaral-R _x	C ₂₀ H ₂₉ O-R _x

290.	(E)-10-Hexadecenal-R _x	C ₁₆ H ₂₉ O-R _x
291.	(E)-11-Hexadecenal-R _x	C ₁₆ H ₂₉ O-R _x
292.	(E,E)-10,14-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
293.	(E,E)-11,13-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
294.	(E,E)-9,11-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
295.	(E,E,E)-10,12,14-Hexadecatrienal-R _x	C ₁₆ H ₂₅ O-R _x
296.	(E,E,E)-3,7,11,15-tetramethyl-2,6,10,14-hexadecatetraenal-R _x	C ₂₀ H ₃₁ O-R _x
297.	(E,E,Z)-10,12,14-Hexadecatrienal-R _x	C ₁₆ H ₂₅ O-R _x
298.	(E,E,Z)-4,6,11-Hexadecatrienal-R _x	C ₁₆ H ₂₅ O-R _x
299.	(E,E,Z,Z)-4,6,11,13-Hexadecatetraenal-R _x	C ₁₆ H ₂₃ O-R _x
300.	(E,Z)-10,12-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
301.	(E,Z)-11,13-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
302.	(E,Z)-4,6-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
303.	(E,Z)-6,11-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
304.	(E,Z)-8,11-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
305.	(E,Z)-9,11-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
306.	(Z)-10-Hexadecenal-R _x	C ₁₆ H ₂₉ O-R _x
307.	(Z)-12-Hexadecenal-R _x	C ₁₆ H ₂₉ O-R _x
308.	(Z)-13-Hexadecen-11-ynal-R _x	C ₁₆ H ₂₅ O-R _x
309.	(Z)-3-oxo-9-Hexadecenal-R _x	C ₁₆ H ₂₇ O ₂ -R _x
310.	(Z,E)-10,12-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
311.	(Z,E)-11,13-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
312.	(Z,E)-7,11-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
313.	(Z,E)-9,11-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
314.	(Z,Z)-10,12-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
315.	(Z,Z)-11,13-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
316.	(Z,Z)-9,11-Hexadecadienal-R _x	C ₁₆ H ₂₇ O-R _x
317.	11-Hexadecynal-R _x	C ₁₆ H ₂₇ O-R _x
318.	2-Methylhexadecanal-R _x	C ₁₇ H ₃₃ O-R _x
319.	7-Hexadecenal-R _x	C ₁₆ H ₂₉ O-R _x
320.	9-Hexadecenal-R _x	C ₁₆ H ₂₉ O-R _x
321.	(Z)-9-Heptadecenal-R _x	C ₁₇ H ₃₁ O-R _x
322.	1-Heptadecenal-R _x	C ₁₇ H ₃₁ O-R _x
323.	2-Heptadecenal-R _x	C ₁₇ H ₃₁ O-R _x
324.	Heptadecanal-R _x	C ₁₇ H ₃₃ O-R _x
325.	(E)-11-Octadecenal-R _x	C ₁₈ H ₃₃ O-R _x
326.	(E)-13-Octadecenal-R _x	C ₁₈ H ₃₃ O-R _x
327.	(E)-14-Octadecenal-R _x	C ₁₈ H ₃₃ O-R _x
328.	(E)-2-Octadecenal-R _x	C ₁₈ H ₃₃ O-R _x
329.	(E,E)-11,14-Octadecadienal-R _x	C ₁₈ H ₃₁ O-R _x
330.	(E,Z)-2,13-Octadecadienal-R _x	C ₁₈ H ₃₁ O-R _x
331.	(E,Z)-3,13-Octadecadienal-R _x	C ₁₈ H ₃₁ O-R _x
332.	(Z)-11-Octadecenal-R _x	C ₁₈ H ₃₃ O-R _x
333.	(Z)-13-Octadecenal-R _x	C ₁₈ H ₃₃ O-R _x

334.	(Z)-9-Octadecenal-R _x	C ₁₈ H ₃₃ O-R _x
335.	(Z,Z)-11,13-Octadecadienal-R _x	C ₁₈ H ₃₁ O-R _x
336.	(Z,Z)-13,15-Octadecadienal-R _x	C ₁₈ H ₃₁ O-R _x
337.	(Z,Z)-3,13-Octadecadienal-R _x	C ₁₈ H ₃₁ O-R _x
338.	(Z,Z)-9,12-Octadecadienal-R _x	C ₁₈ H ₃₁ O-R _x
339.	(Z,Z,Z)-9,12,15-Octadecatrienal-R _x	C ₁₈ H ₂₉ O-R _x
340.	1-Octadecenal-R _x	C ₁₈ H ₃₃ O-R _x
341.	9-Octadecenal-R _x	C ₁₈ H ₃₃ O-R _x
342.	Octadecanal-R _x	C ₁₈ H ₃₅ O-R _x
343.	(Z)-10-Nonadecenal-R _x	C ₁₉ H ₃₅ O-R _x
344.	(Z)-9-Nonadecenal-R _x	C ₁₉ H ₃₅ O-R _x
345.	(Z)-11-Eicosenal-R _x	C ₂₀ H ₃₇ O-R _x
346.	12-Deacetoxy-12-oxo-scalaradial-R _x	C ₂₅ H ₃₅ O ₃ -R _x
347.	1-Eicosenal-R _x	C ₂₀ H ₃₇ O-R _x
348.	Deacetylscalaradial-R _x	C ₂₅ H ₃₇ O ₃ -R _x
349.	Eicosanal-R _x	C ₂₀ H ₃₉ O-R _x
350.	Scalaradial-R _x	C ₂₇ H ₃₉ O ₄ -R _x
351.	Docosanal-R _x	C ₂₂ H ₄₃ O-R _x
352.	Tetracosanal-R _x	C ₂₄ H ₄₇ O-R _x
353.	Pentacosanal-R _x	C ₂₅ H ₄₉ O-R _x
354.	Hexacosanal-R _x	C ₂₆ H ₅₁ O-R _x
355.	Heptacosanal-R _x	C ₂₇ H ₅₃ O-R _x
356.	Octacosanal-R _x	C ₂₈ H ₅₅ O-R _x
357.	Triacosanal-R _x	C ₃₀ H ₅₉ O-R _x
358.	Dotriacosanal-R _x	C ₃₂ H ₆₃ O-R _x

[0064] Additional deuterium-enriched aldehydes of the present invention include aldehydes **65-358** listed in the Tables B-L below.

[0065] Table B: Examples **64-358** of Table A, except that the deuterium isotope in R_x is in an amount greater than 2% of the hydrogen atoms present in R_x.

[0066] Table C: Examples **64-358** of Table A, except that the deuterium isotope in R_x is in an amount greater than 10% of the hydrogen atoms present in R_x.

[0067] Table D: Examples **64-358** of Table A, except that the deuterium isotope in R_x is in an amount greater than 20% of the hydrogen atoms present in R_x.

[0068] Table E: Examples **64-358** of Table A, except that the deuterium isotope in R_x is in an amount greater than 30% of the hydrogen atoms present in R_x.

[0069] Table F: Examples **64-358** of Table A, except that the deuterium isotope in R_x is in an amount greater than 40% of the hydrogen atoms present in R_x.

[0070] Table G: Examples **64-358** of Table A, except that the deuterium isotope in R_x is in an amount greater than 50% of the hydrogen atoms present in R_x.

[0071] Table H: Examples **64-358** of Table A, except that the deuterium isotope in R_x is in an amount greater than 60% of the hydrogen atoms present in R_x.

[0072] Table I: Examples **64-358** of Table A, except that the deuterium isotope in R_x is in an amount greater than 70% of the hydrogen atoms present in R_x.

[0073] Table J: Examples **64-358** of Table A, except that the deuterium isotope in R_x is in an amount greater than 80% of the hydrogen atoms present in R_x.

[0074] Table K: Examples **64-358** of Table A, except that the deuterium isotope in R_x is in an amount greater than 90% of the hydrogen atoms present in R_x.

[0075] Table L: Examples **64-358** of Table A, except that the deuterium isotope in R_x is in an amount greater than 95% of the hydrogen atoms present in R_x.

[0076] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **65-358** of Table A.

[0077] Reference to “compositions comprising compounds **65-358**” means compositions comprising at least 6×10^{18} molecules of at least one of aldehydes **65-358**, typically at least 6×10^{19} molecules, and may, for example, comprise at least 6×10^{20} molecules, 6×10^{21} molecules, 6×10^{22} molecules, or 6×10^{23} molecules. R_x is hydrogen, wherein the deuterium isotope is in an amount greater than 0.10 percent of the R_x hydrogen atoms. In certain cases, the deuterium

isotope comprises greater than 1% of the hydrogen atoms, or even greater than 2%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, or 95% of the hydrogen atoms.

[0078] In another aspect, reference to “compositions comprising compounds **65-358**” means compositions comprising at least 0.1 mole of at least one of aldehydes **65-358**. Compositions of the invention may, for example, comprise at least 0.2, 0.5, 1, 2, 3, 4, 5, 10, to 20 moles of at least one of compounds **65-358**.

[0079] In another aspect, reference to “compositions comprising compounds **65-358**” means compositions comprising at least 1 gram of at least one of aldehydes **65-358**. Compositions of the invention may, for example, comprise at least 5, 10, 20, 30, 40, 50, 100, 500, to 1,000 grams of at least one of compounds **65-358**.

[0080] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **65-358** of Table B.

[0081] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **65-358** of Table C.

[0082] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **65-358** of Table D.

[0083] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **65-358** of Table E.

[0084] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **65-358** of Table F.

[0085] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **65-358** of Table G.

[0086] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **65-358** of Table H.

[0087] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **65-358** of Table I.

[0088] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **65-358** of Table J.

[0089] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **65-358** of Table K.

[0090] In another aspect, the present invention provides a composition, comprising: a deuterium-enriched aldehyde selected from aldehydes **65-358** of Table L.

[0091] Compounds of the present invention are more stable to autoxidation than the corresponding aldehydes where the hydrogen atom attached to the carbonyl moiety (*i.e.*, H-C(O)) is not enriched in the deuterium isotope. For instance, where the deuterium isotope comprises greater than 90 percent of the subject hydrogen atoms, the rate of autoxidation – *i.e.*, conversion of the aldehyde to its corresponding carboxylic acid through oxidation by atmospheric oxidation in the absence of an oxidation catalyst (*e.g.*, metal or transition metal-based catalyst) – is reduced by at least 10 percent (*e.g.*, if 10.0 percent of the aldehyde without deuterium enrichment experiences autoxidation, less than 9.0 percent of the aldehyde with deuterium enrichment experiences autoxidation under the same conditions). In certain cases, the rate is reduced by at least 20 percent, 30 percent, 40 percent, 50 percent, 60 percent, 70 percent, 80 percent or 90 percent.

[0092] Compounds **1-358** can be synthesized using any appropriate method. Examples of such methods include: reduction of the corresponding acid halide with deuterium gas (see USP

5,149,820); reduction of the corresponding tertiary amide using $\text{Cp}_2\text{Zr}(\text{D})\text{Cl}$ (see Georg *et al.* *Tet. Lett.* 2004; **45**: 2787-2789); and, reduction of the corresponding ester using LiAlD_4 to produce an alcohol and subsequent oxidation (see Kim *et al.*, *J. Label Compd Radiopharm* 2004; **47**: 921-934)(or just oxidation of a corresponding alcohol);

[0093] Alternatively, an additional method includes reduction of the un-enriched aldehyde with NaBD_4 or NaCNBD_3 followed by re-oxidation with pyridinium chlorochromate or another suitable oxidant, in which the deuterium enrichment of the aldehyde is a result of the isotope effect.

[0094] In another aspect, the present invention provides compositions comprising one or more of aldehydes **1-64** and an organic solvent (*e.g.*, an alcohol (*e.g.*, ethyl alcohol and isopropyl alcohol), ether (*e.g.*, dimethyl ethyl), or alkane (*e.g.*, hexanes)). In another aspect, the organic solvent is ethyl alcohol. Examples of the concentration of the ethyl alcohol include 50-97.5 weight percent, 60-97 weight percent, and 70-96 weight percent.

[0095] In another aspect, the present invention provides compositions comprising one or more of aldehydes **65-358** and an organic solvent (*e.g.*, an alcohol (*e.g.*, ethyl alcohol and isopropyl alcohol), ether (*e.g.*, dimethyl ethyl), or alkane (*e.g.*, hexanes)). In another aspect, the organic solvent is ethyl alcohol. Examples of the concentration of the ethyl alcohol include 50-97.5 weight percent, 60-97 weight percent, and 70-96 weight percent.

[0096] In another aspect, the compositions of the present invention comprise an additional ingredient. Examples of additional ingredients include: dipropylene glycol; isopropyl myristate; oils (*e.g.*, coconut oil); and liquid waxes (*e.g.*, jojoba oil).

[0097] The compositions discussed herein also can be used, for example, in a perfume.

Reference to “perfume” means a mixture comprising fragrant compounds and solvents used to give the human body, animals, objects and living spaces a pleasant scent.

[0098] In another aspect, the present invention provides novel compositions for modulating the behavior of insects (*e.g.*, attracting or inhibiting insect species), comprising: a deuterium-enriched aldehyde selected from structures **1-64**, wherein the aldehyde is a pheromone and an optional additional component or components suitable for the composition (*e.g.*, a pesticide, dispensing material or device, solvent, adhesive capable of trapping the insect, etc.).

[0099] In another aspect, the present invention provides novel compositions for modulating the behavior of insects (*e.g.*, attracting or inhibiting insect species), comprising: a deuterium-enriched aldehyde selected from structures **65-358**, wherein the aldehyde is a pheromone and an optional additional component or components suitable for the composition (*e.g.*, a pesticide, dispensing material or device, solvent, adhesive capable of trapping the insect, etc.).

[00100] In another aspect, the composition comprises a pheromone blend.

[00101] A pheromone blend, comprises: at least one pheromone aldehyde selected from the deuterium-enriched aldehydes of the present invention and at least one additional pheromone that is either an un-enriched aldehyde or a different pheromone aldehyde selected from the deuterium-enriched aldehydes of the present invention.

[00102] In another aspect, the present invention provides novel methods for modulating the behavior of insects (*e.g.*, attracting insect species or inhibiting the mating or aggregation of insect species), comprising:

- a. applying a deuterium-enriched aldehyde pheromone of the present invention, or a composition comprising a deuterium-enriched aldehyde pheromone of the present

invention and a optionally a solvent or other additional component suitable for the composition, to a surface of an object (e.g., a lure within a trap wherein the insect enters but cannot leave, a lure or trap wherein the insect sticks to a surface of the trap, or a lure or trap containing a chemical capable of killing the insect); and,

- b. placing the object in a location where one desires either to attract insect species or inhibiting the mating or aggregation of insect species.

[00103] In another aspect, a pheromone blend is applied (either neat or as a part of a composition of the present invention).

[00104] In another aspect, two or more deuterium-enriched aldehyde pheromones of the present invention are applied (either neat or as a part of a composition of the present invention).

[00105] Alternatively, the method comprises: distributing a composition comprising a deuterium-enriched aldehyde pheromone of the present invention into an area (e.g., by aerial spraying over crops), into a stored product (e.g., traps or disruptant dispensers in grain crops), onto vegetation (e.g., by manual application of dollops of an emulsion (e.g., SPLAT® type formulation) onto plants, vines, leaves, or shoots), or by applying by aerial dissemination or manual placement a composition of pheromone-impregnated chips, pheromone containing polymer hollow fibers, or pheromone containing rubber septa, in order to modulate the behavior of insects by disruption of mating behavior. More than one composition or method may be combined to achieve the desired reduction of crop damage.

[00106] In another aspect, a pheromone blend is present in the distributed composition.

[00107] In another aspect, two or more deuterium-enriched aldehyde pheromones of the present invention are present in the distributed composition.

[00108] In another aspect, the deuterium-enriched aldehyde pheromone of the present invention is distributed impregnated on a chip, in a polymer hollow fiber, or adsorbed within a rubber septum.

[00109] In another aspect, a pheromone blend is distributed impregnated on a chip, in a polymer hollow fiber, or adsorbed within a rubber septum.

[00110] In another aspect, two or more deuterium-enriched aldehyde pheromones of the present invention are distributed impregnated on a chip, in a polymer hollow fiber, or adsorbed within a rubber septum.

[00111] The modulation of insect behavior can comprise attraction to an aldehyde pheromone trap, or alternatively, disruption of mate-finding and mating behavior. A benefit of such insect behavior modulation can be diminished crop damage, such as reducing damage to fruits, nuts, seeds, grains, grapes, leaves, shoots, bark, grain, or other valuable crops by reducing insect damage to said crop, whether in the field or in storage after harvesting said valuable crop.

[00112] In another aspect, the modulating composition of the present invention, comprises: a deuterium-enriched aldehyde pheromone of the present invention formulated to be used in an attractant trap (an attractant composition).

[00113] In another aspect, the modulating composition of the present invention, comprises: a pheromone blend formulated to be used in an attractant trap (an attractant composition).

[00114] In another aspect, two or more deuterium-enriched aldehyde pheromones of the present invention are present in the modulating composition.

[00115] In another aspect, the present invention provides a method of using an attractant composition in an attractant trap.

[00116] In another aspect, the present invention provides a method of using a deuterium-enriched aldehyde pheromone as a component of a composition to attract, trap, or monitor adult insects in a stored product with the goal of minimizing crop product infestation and loss. In another aspect, a pheromone blend is in the composition. In another aspect, two or more deuterium-enriched aldehyde pheromones of the present invention are present in the composition.

[00117] In another aspect, the modulating composition of the present invention, comprises a deuterium-enriched aldehyde pheromone of the present invention formulated to be used as a mating disruptant (a disruptant composition). A disruptant composition is typically dispersed throughout part or all of an area to be protected.

[00118] In another aspect, a pheromone blend is present in the disruptant composition.

[00119] In another aspect, two or more deuterium-enriched aldehyde pheromones of the present invention are present in the disruptant composition.

[00120] In another aspect, the present invention provides a method of using a disruptant composition in an area to be protected (e.g., a crop field). It will be understood by those skilled in the art that disruption of mating by adult insects will reduce the population of offspring. Frequently it is the offspring, or larvae, of the species that are responsible for damage to the field crop or harvested crop product. A skilled person will understand that disruption of mating may be an indirect method of reducing damage to field crops or harvested crop products by larval forms of the insects that feed on the crop or crop product.

[00121] In another aspect, the disruptant composition is made using an oil/water emulsion preparation to deposit the disruptant onto a carrier. Examples of carriers include a polymeric hollow loop, a rubber (e.g., septum) or polymeric carrier, and impregnable chips.

[00122] Examples of types of attractant and/or disruptant formulations include: microencapsulation, hollow tube dispensers, bait stations, oil-water emulsions, and other volatile deuterium-enriched aldehyde dispensers.

[00123] Microencapsulation refers to encapsulating at least one deuterium-enriched aldehyde pheromone of the present invention in a polymer. The polymer is selected to delay the release of the pheromone for at least a few days. The microencapsulated pheromone(s) can be applied by spraying.

[00124] Examples of hollow tube dispensers include plastic twist-tie type dispensers, plastic hollow fibers, and plastic hollow microfibers. These types of dispensers are filled with at least one disruptant or a disruptant composition of the present invention and then distributed throughout the area to be protected.

[00125] Bait stations are stationary devices that are typically used to attract and kill. Examples include platforms comprising at least pheromone aldehyde of the present invention and a glue board (or some other mechanism capable of trapping the attracted insect). Instead of or in addition to glue, the station can contain a pesticide that negatively affects the insect (e.g., reduces its ability to mate or reproduce).

[00126] Dispensers or high-emission dispensers are devices that either passively or actively release a pheromone aldehyde of the present invention. Examples of passive release include pheromone sachets or an emulsion (e.g., a SPLAT® (Specialized Lure And Pheromone Technology) formulation). Active dispensers may release bursts of at least one pheromone aldehyde of the present invention (or composition containing at least one pheromone aldehyde of the present invention) at timed intervals or by continuous release through volatilization from the dispenser.

[00127] As used herein, a pheromone is a deuterium-enriched aldehyde of structure **1** that has the traits of a natural pheromone, i.e., a chemical capable communicating with at least one insect species. Pheromones may act as alarm signals, provide trails to food sources, attract parasitoids or other predators, and/or attract insects of the same species for the purpose of mating.

[00128] Unless otherwise specified, when a pheromone is recited in the present invention it can be a single deuterium-enriched aldehyde of structure **1** or a blend of pheromones wherein at least one is a deuterium-enriched aldehyde of structure **1**. The second, third, fourth, fifth, or more pheromone can be a deuterium-enriched aldehyde of structure **1** or a non-deuterium-enriched aldehyde

[00129] In another aspect, a composition of the present invention, comprises: 2, 3, 4, 5, 6, 7, 8, 9, or 10 deuterium-enriched aldehyde pheromones of the present invention.

[00130] In another aspect, a composition of the present invention, comprises: 2 or more deuterium-enriched aldehyde pheromones of the present invention.

[00131] In another aspect, a composition of the present invention, comprises: 3 or more deuterium-enriched aldehyde pheromones of the present invention.

[00132] In another aspect, a composition of the present invention, comprises: 4 or more deuterium-enriched aldehyde pheromones of the present invention.

[00133] In another aspect, a composition of the present invention, comprises: 5 or more deuterium-enriched aldehyde pheromones of the present invention.

[00134] In another aspect, a composition of the present invention, comprises: at least 1, 2, 3, 4, or 5 deuterium-enriched aldehyde pheromones of the present invention and at least 1, 2, 3, 4, or 5 un-enriched/un-enriched pheromones.

[00135] In another aspect, a composition of the present invention, comprises: at least 1 deuterium-enriched aldehyde pheromone of the present invention and at least 1 un-enriched pheromone.

[00136] In another aspect, a composition of the present invention, comprises: at least 2 deuterium-enriched aldehyde pheromones of the present invention and at least 1 un-enriched pheromone.

[00137] In another aspect, a composition of the present invention, comprises: at least 1 deuterium-enriched aldehyde pheromones of the present invention and at least 2 un-enriched pheromones.

[00138] In another aspect, a composition of the present invention, comprises: at least 3 deuterium-enriched aldehyde pheromones of the present invention and at least 1 un-enriched pheromone.

[00139] In another aspect, a composition of the present invention, comprises: at least 3 deuterium-enriched aldehyde pheromones of the present invention and at least 2 un-enriched pheromones.

[00140] In another aspect, a composition of the present invention, comprises: at least 3 deuterium-enriched aldehyde pheromones of the present invention and at least 3 un-enriched pheromones.

[00141] Examples of insects for which a deuterium-enriched pheromone (or pheromones) can be prepared include: corn earworm (*Heliothis (Helicoverpa) zea*), tobacco budworm (*Heliothis virescens*), cotton bollworm (*Heliothis (Helicoverpa) armigera*), horse chestnut leaf miner (*Cameraria orchidella*), eastern spruce budworm (*Choristoneura fumiferana*), rice borer (*Chilo suppressalis*), grain weevils (*Trogoderma* spp.), grain/flower weevils (*Tribolium* spp.),

cotton boll weevil (*Anthonomus grandis*), citrus leaf miner (*Phyllocnistis citrella*), carob moth (*Ectomyelois ceratoniae*), and Asian longhorn beetle (*Anoplophora glabripennis*), among many others. A complete listing of aldehyde pheromones of insects and the target species using the pheromones is available on the Pherobase.com data base and is hereby incorporated in totality into this application (<http://www.pherobase.com/database/compound/compounds-aldes.php>).

One or more of the known aldehydic pheromones for these insects can be replaced by a deuterium-enriched aldehyde of the present invention.

[00142] For example, a pheromone composition for the corn earworm containing Z11-16:Ald can be replaced with compound **27** of the present invention. Representative examples of such deuterium-enriched aldehyde pheromones include compounds selected from: aldehydes **8, 15, 23, 24, 27, 28, 29, 30, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, and 64.**

[00143] In another aspect, the present invention provides novel compositions for modulating the behavior of insects, comprising: at least one deuterium-enriched aldehyde that is a pheromone, wherein the deuterium-enriched aldehyde is selected from: aldehydes **27, 28, and 35**.

[00144] In another aspect, the present invention provides novel compositions for modulating the behavior of insects, comprising: at least one deuterium-enriched aldehyde that is a pheromone, wherein the deuterium-enriched aldehyde is selected from: aldehydes **27 and 28**.

[00145] In another aspect, the present invention provides novel compositions for modulating the behavior of insects, comprising: at least one deuterium-enriched aldehyde that is a pheromone, wherein the deuterium-enriched aldehyde is: aldehyde **36**.

[00146] In another aspect, the present invention provides novel compositions for modulating the behavior of insects, comprising: at least one deuterium-enriched aldehyde that is a pheromone, wherein the deuterium-enriched aldehyde is selected from: aldehydes **37** and **38**.

[00147] In another aspect, the present invention provides novel compositions for modulating the behavior of insects, comprising: at least one deuterium-enriched aldehyde that is a pheromone, wherein the deuterium-enriched aldehyde is selected from: aldehydes **27**, **28**, and **44**.

[00148] In another aspect, the present invention provides novel compositions for modulating the behavior of insects, comprising: at least one deuterium-enriched aldehyde that is a pheromone, wherein the deuterium-enriched aldehyde is: aldehyde **49**.

[00149] In another aspect, the present invention provides novel compositions for modulating the behavior of insects, comprising: at least one deuterium-enriched aldehyde that is a pheromone, wherein the deuterium-enriched aldehyde is: aldehyde **55**.

[00150] In another aspect, the present invention provides novel compositions for modulating the behavior of insects, comprising: at least one deuterium-enriched aldehyde that is a pheromone, wherein the deuterium-enriched aldehyde is: aldehyde **59**.

[00151] In another aspect, the present invention provides novel compositions for modulating the behavior of insects, comprising: at least one deuterium-enriched aldehyde that is a pheromone, wherein the deuterium-enriched aldehyde is selected from: aldehyde **40**, **60**, and **61**.

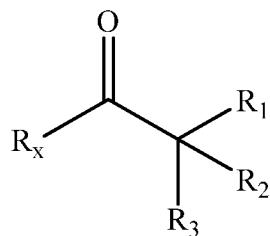
[00152] In another aspect, the present invention provides novel compositions for modulating the behavior of insects, comprising: at least one deuterium-enriched aldehyde that is a pheromone, wherein the deuterium-enriched aldehyde is: aldehyde **62**.

[00153] In another aspect, the present invention provides novel compositions for modulating the behavior of insects, comprising: at least one deuterium-enriched aldehyde that is a pheromone, wherein the deuterium-enriched aldehyde is: aldehyde **64**.

[00154] Compounds of the present invention are also more stable to autoxidation than their corresponding non-deuterium enriched counterparts when included in compositions of the present invention. The rate of auto oxidation is reduced by at least 10 percent. In certain cases, the rate is reduced by at least 20 percent, 30 percent, 40 percent, 50 percent, 60 percent, 70 percent, 80 percent or 90 percent.

[00155] The skilled person will recognize that pheromones or pheromone blends for a given species may include non-aldehyde components, such as an alkyl, alkenyl, alkynyl alcohol or an alkyl, alkenyl or alkynyl ester. When the blend for optimal attraction includes such an additional non-aldehyde component, the skilled person would augment the deuterium-labeled pheromone of the present invention with the additional attractant or disruptant compound that increases the efficacy of modulation of the insect behavior, e.g., mating disruption or attraction to a trap.

[00156] In Table 1 are described examples of compositions of the present invention:



1

wherein:

there are at least 6×10^{18} molecules of the aldehyde present in the composition;

R_x is hydrogen, wherein the deuterium isotope is present in an amount greater than 0.10% of the

R_x hydrogen atoms;

unless otherwise defined, R_1 , R_2 and R_3 are independently selected from hydrogen, alkyl,

substituted alkyl, alkenyl, substituted alkenyl, alkynyl, substituted alkynyl, heteroalkyl,

substituted heteroalkyl, aryl, substituted aryl, heteroaryl, and substituted heteroaryl;

alternatively, the $CR_1R_2R_3$ moiety forms a group selected from: an aryl, substituted aryl,

heteroaryl, and substituted heteroaryl;

alternatively, the CR_1R_2 moiety forms a group selected from: an alkenyl and substituted

alkenyl;

alternatively, the $CR_1R_2R_3$ moiety forms a group selected from: an alkynyl and

substituted alkynyl; and,

optionally, the aldehyde is substituted with $C(O)R_y$, wherein R_x is hydrogen, wherein the

deuterium isotope is present in an amount greater than 0.10% of the R_y hydrogen atoms.

[00157] Table 1:

Ex. #	Structure #	R_1, R_2, R_3	Solvent (weight%)
-------	-------------	-----------------	-------------------

A.	1	As defined	Ethyl alcohol 70-96% by weight
B.	1	one of R ₁ , R ₂ and R ₃ is alkyl	Ethyl alcohol 70-96% by weight
C.	1	one of R ₁ , R ₂ and R ₃ is substituted alkyl	Ethyl alcohol 70-96% by weight
D.	1	one of R ₁ , R ₂ and R ₃ is alkenyl	Ethyl alcohol 70-96% by weight
E.	1	one of R ₁ , R ₂ and R ₃ is substituted alkenyl	Ethyl alcohol 70-96% by weight
F.	1	one of R ₁ , R ₂ and R ₃ is alkynyl	Ethyl alcohol 70-96% by weight
G.	1	one of R ₁ , R ₂ and R ₃ is substituted alkynyl	Ethyl alcohol 70-96% by weight
H.	1	one of R ₁ , R ₂ and R ₃ is heteroalkyl	Ethyl alcohol 70-96% by weight
I.	1	one of R ₁ , R ₂ and R ₃ is substituted heteroalkyl	Ethyl alcohol 70-96% by weight
J.	1	one of R ₁ , R ₂ and R ₃ is aryl	Ethyl alcohol 70-96% by weight
K.	1	one of R ₁ , R ₂ and R ₃ is substituted aryl	Ethyl alcohol 70-96% by weight
L.	1	one of R ₁ , R ₂ and R ₃ is heteroaryl	Ethyl alcohol 70-96% by weight
M.	1	one of R ₁ , R ₂ and R ₃ is substituted heteroaryl	Ethyl alcohol 70-96% by weight
N.	1	one of R ₁ , R ₂ and R ₃ is alkyl and another is hydrogen	Ethyl alcohol 70-96% by weight
O.	1	one of R ₁ , R ₂ and R ₃ is substituted alkyl and another is hydrogen	Ethyl alcohol 70-96% by weight
P.	1	one of R ₁ , R ₂ and R ₃ is alkenyl and another is hydrogen	Ethyl alcohol 70-96% by weight
Q.	1	one of R ₁ , R ₂ and R ₃ is substituted alkenyl and another is hydrogen	Ethyl alcohol 70-96% by weight
R.	1	one of R ₁ , R ₂ and R ₃ is alkynyl and another is hydrogen	Ethyl alcohol 70-96% by weight
S.	1	one of R ₁ , R ₂ and R ₃ is substituted	Ethyl alcohol

		alkynyl and another is hydrogen	70-96% by weight
T.	1	one of R ₁ , R ₂ and R ₃ is heteroalkyl and another is hydrogen	Ethyl alcohol 70-96% by weight
U.	1	one of R ₁ , R ₂ and R ₃ is substituted heteroalkyl and another is hydrogen	Ethyl alcohol 70-96% by weight
V.	1	one of R ₁ , R ₂ and R ₃ is aryl and another is hydrogen	Ethyl alcohol 70-96% by weight
W.	1	one of R ₁ , R ₂ and R ₃ is substituted aryl and another is hydrogen	Ethyl alcohol 70-96% by weight
X.	1	one of R ₁ , R ₂ and R ₃ is heteroaryl and another is hydrogen	Ethyl alcohol 70-96% by weight
Y.	1	one of R ₁ , R ₂ and R ₃ is substituted heteroaryl and another is hydrogen	Ethyl alcohol 70-96% by weight
Z.	1	R ₁ , R ₂ and R ₃ is alkyl and the other two are hydrogen	Ethyl alcohol 70-96% by weight
AA.	1	one of R ₁ , R ₂ and R ₃ is substituted alkyl and the other two are hydrogen	Ethyl alcohol 70-96% by weight
BB.	1	one of R ₁ , R ₂ and R ₃ is alkenyl and the other two are hydrogen	Ethyl alcohol 70-96% by weight
CC.	1	one of R ₁ , R ₂ and R ₃ is substituted alkenyl and the other two are hydrogen	Ethyl alcohol 70-96% by weight
DD.	1	one of R ₁ , R ₂ and R ₃ is alkynyl and the other two are hydrogen	Ethyl alcohol 70-96% by weight
EE.	1	one of R ₁ , R ₂ and R ₃ is substituted alkynyl and the other two are hydrogen	Ethyl alcohol 70-96% by weight
FF.	1	one of R ₁ , R ₂ and R ₃ is heteroalkyl and the other two are hydrogen	Ethyl alcohol 70-96% by weight
GG.	1	one of R ₁ , R ₂ and R ₃ is substituted heteroalkyl and the other two are hydrogen	Ethyl alcohol 70-96% by weight
HH.	1	one of R ₁ , R ₂ and R ₃ is aryl and the other two hydrogen	Ethyl alcohol 70-96% by weight
II.	1	one of R ₁ , R ₂ and R ₃ is substituted aryl the other two are hydrogen	Ethyl alcohol 70-96% by weight
JJ.	1	one of R ₁ , R ₂ and R ₃ is heteroaryl and the other two are hydrogen	Ethyl alcohol 70-96% by weight
KK.	1	one of R ₁ , R ₂ and R ₃ is substituted heteroaryl and the other two are	Ethyl alcohol

		hydrogen	70-96% by weight
LL.	1	CR ₁ R ₂ R ₃ is aryl	Ethyl alcohol 70-96% by weight
MM.	1	CR ₁ R ₂ R ₃ is substituted aryl	Ethyl alcohol 70-96% by weight
NN.	1	CR ₁ R ₂ R ₃ is heteroaryl	Ethyl alcohol 70-96% by weight
OO.	1	CR ₁ R ₂ R ₃ is substituted heteroaryl	Ethyl alcohol 70-96% by weight
PP.	1	CR ₁ R ₂ alkenyl and R ₃ is hydrogen	Ethyl alcohol 70-96% by weight
QQ.	1	CR ₁ R ₂ substituted alkenyl and R ₃ is hydrogen	Ethyl alcohol 70-96% by weight
RR.	1	CR ₁ R ₂ alkenyl and R ₃ is alkyl	Ethyl alcohol 70-96% by weight
SS.	1	CR ₁ R ₂ substituted alkenyl and R ₃ is alkyl	Ethyl alcohol 70-96% by weight
TT.	1	R ₁ is alkyl substituted with C(O)R _y	Ethyl alcohol 70-96% by weight
UU.	1	R ₁ is alkyl substituted with C(O)R _y and R ₂ and R ₃ are hydrogens	Ethyl alcohol 70-96% by weight
VV.	1	CR ₁ R ₂ R ₃ is aryl substituted with C(O)R _y	Ethyl alcohol 70-96% by weight
WW.	1	CR ₁ R ₂ R ₃ is substituted aryl substituted with C(O)R _y	Ethyl alcohol 70-96% by weight
XX.	2	-	Ethyl alcohol 70-96% by weight
YY.	3	-	Ethyl alcohol 70-96% by weight
ZZ.	4	-	Ethyl alcohol 70-96% by weight
AAA.	5	-	Ethyl alcohol 70-96% by weight
BBB.	6	-	Ethyl alcohol 70-96% by weight

CCC.	7	-	Ethyl alcohol 70-96% by weight
DDD.	8	-	Ethyl alcohol 70-96% by weight
EEE.	9	-	Ethyl alcohol 70-96% by weight
FFF.	10	-	Ethyl alcohol 70-96% by weight
GGG.	11	-	Ethyl alcohol 70-96% by weight
HHH.	12	-	Ethyl alcohol 70-96% by weight
III.	13	-	Ethyl alcohol 70-96% by weight
JJJ.	14	-	Ethyl alcohol 70-96% by weight
KKK.	15	-	Ethyl alcohol 70-96% by weight
LLL.	16	-	Ethyl alcohol 70-96% by weight
MMM.	17	-	Ethyl alcohol 70-96% by weight
NNN.	18	-	Ethyl alcohol 70-96% by weight
OOO.	19	-	Ethyl alcohol 70-96% by weight
PPP.	20	-	Ethyl alcohol 70-96% by weight
QQQ.	21	-	Ethyl alcohol 70-96% by weight
RRR.	22	-	Ethyl alcohol

			70-96% by weight
SSS.	23	-	Ethyl alcohol 70-96% by weight
TTT.	24	-	Ethyl alcohol 70-96% by weight
UUU.	25	-	Ethyl alcohol 70-96% by weight
VVV.	26	-	Ethyl alcohol 70-96% by weight
WWW.	27	-	Ethyl alcohol 70-96% by weight
XXX.	28	-	Ethyl alcohol 70-96% by weight
YYY.	29	-	Ethyl alcohol 70-96% by weight
ZZZ.	30	-	Ethyl alcohol 70-96% by weight
AAAA.	31	-	Ethyl alcohol 70-96% by weight
BBBB.	32	-	Ethyl alcohol 70-96% by weight
CCCC.	33	-	Ethyl alcohol 70-96% by weight
DDDD.	34	-	Ethyl alcohol 70-96% by weight
EEEE.	35	-	Ethyl alcohol 70-96% by weight
FFFF.	36	-	Ethyl alcohol 70-96% by weight
GGGG.	37	-	Ethyl alcohol 70-96% by weight

HHHH.	38	-	Ethyl alcohol 70-96% by weight
III.	39	-	Ethyl alcohol 70-96% by weight
JJJJ.	40	-	Ethyl alcohol 70-96% by weight
KKKK.	41	-	Ethyl alcohol 70-96% by weight
LLLL.	42	-	Ethyl alcohol 70-96% by weight
MMMM.	43	-	Ethyl alcohol 70-96% by weight
NNNN.	44	-	Ethyl alcohol 70-96% by weight
OOOO.	45	-	Ethyl alcohol 70-96% by weight
PPPP.	46	-	Ethyl alcohol 70-96% by weight
QQQQ.	47	-	Ethyl alcohol 70-96% by weight
RRRR.	48	-	Ethyl alcohol 70-96% by weight
SSSS.	49	-	Ethyl alcohol 70-96% by weight
TTTT.	50	-	Ethyl alcohol 70-96% by weight
UUUU.	51	-	Ethyl alcohol 70-96% by weight
VVVV.	52	-	Ethyl alcohol 70-96% by weight
WWWW.	53	-	Ethyl alcohol

			70-96% by weight
XXXX.	54	-	Ethyl alcohol 70-96% by weight
YYYY.	55	-	Ethyl alcohol 70-96% by weight
ZZZZ.	56	-	Ethyl alcohol 70-96% by weight
AAAAA.	57	-	Ethyl alcohol 70-96% by weight
BBBBB.	58	-	Ethyl alcohol 70-96% by weight
CCCCC.	59	-	Ethyl alcohol 70-96% by weight
DDDDD.	60	-	Ethyl alcohol 70-96% by weight
EEEEEE.	61	-	Ethyl alcohol 70-96% by weight
FFFFF.	62	-	Ethyl alcohol 70-96% by weight
GGGGG.	63	-	Ethyl alcohol 70-96% by weight
HHHHH.	64	-	Ethyl alcohol 70-96% by weight

[00158] Table 2: Examples **A-HHHHH** of Table 2 correspond to examples **A-HHHHH** of Table 1, except that the deuterium isotope in R_x is in an amount greater than 2% of the hydrogen atoms present in R_x .

[00159] Table 3: Examples **A-HHHHH** of Table 2 correspond to examples **A-HHHHH** of Table 1, except that the deuterium isotope in R_x is in an amount greater than 10% of the hydrogen atoms present in R_x .

[00160] Table 4: Examples **A-HHHHH** of Table 2 correspond to examples **A-HHHHH** of Table 1, except that the deuterium isotope in R_x is in an amount greater than 50% of the hydrogen atoms present in R_x .

[00161] Table 5: Examples **A-HHHHH** of Table 2 correspond to examples **A-HHHHH** of Table 1, except that the deuterium isotope in R_x is in an amount greater than 90% of the hydrogen atoms present in R_x .

[00162] In another aspect, compounds according to the present invention can be used to make resins and/or polymers. The method comprises the steps of: mixing a deuterium-enriched aldehyde selected from structures **1-64** with an aromatic compound (*i.e.*, aryl-containing compound) or an olefinic compound (*i.e.*, alkenyl-containing compound) in a solvent and in the presence of a catalyst, in such a way as to initiate a reaction between the aromatic or olefinic compound and the aldehyde; and, isolating the reaction product (*e.g.*, resin or polymer) resulting from the reaction. The catalyst may be a Bronsted acid (*e.g.*, aqueous sulfuric or hydrochloric acid), a Lewis acid (*e.g.*, $AlCl_3$), a base (*e.g.*, KOH) or a metal (*e.g.*, transition metal). The reaction may be carried out at room temperature or at elevated temperature (*e.g.*, 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C, 110 °C or 120 °C). The reaction may also be carried out at atmospheric pressure or at elevated pressure (*e.g.*, 2 atm, 3 atm, 4 atm or 5 atm).

[00163] In another aspect, compounds according to the present invention can be used to make resins and/or polymers. The method comprises the steps of: mixing a deuterium-enriched aldehyde selected from structures **65-358** with an aromatic compound (*i.e.*, aryl-containing compound) or an olefinic compound (*i.e.*, alkenyl-containing compound) in a solvent and in the presence of a catalyst, in such a way as to initiate a reaction between the aromatic or olefinic compound and the aldehyde; and, isolating the reaction product (*e.g.*, resin or polymer) resulting

from the reaction. The catalyst may be a Bronsted acid (*e.g.*, aqueous sulfuric or hydrochloric acid), a Lewis acid (*e.g.*, AlCl₃), a base (*e.g.*, KOH) or a metal (*e.g.*, transition metal). The reaction may be carried out at room temperature or at elevated temperature (*e.g.*, 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C, 110 °C or 120 °C). The reaction may also be carried out at atmospheric pressure or at elevated pressure (*e.g.*, 2 atm, 3 atm, 4 atm or 5 atm).

[00164] The rate of autoxidation of aldehydes in the polymerization/resin producing reaction is reduced by at least 10 percent as compared to use of non-deuterium enriched aldehydes under the same conditions. In certain cases, the rate is reduced by at least 20 percent, 30 percent, 40 percent, 50 percent, 60 percent, 70 percent, 80 percent or 90 percent.

[00165] The following general methods of making a resin and/or polymer are meant to illustrate, not limit, the present invention.

[00166] *General Method 1*

[00167] An aromatic compound (*e.g.*, naphthalene, benzene, substituted benzene such as toluene) is heated in an acidic mixture (*e.g.*, sulfuric acid and water) for 6 hours at 160 °C. The mixture is cooled to 100 °C, and a deuterium-enriched aldehyde selected from structures **1-64** is added in an amount that is less than a molar equivalent of the aromatic compound. The resulting mixture is kept at 100 °C at a time period ranging from 30 minutes to 16 hours to afford a condensation polymer.

[00168] *General Method 1A*

[00169] An aromatic compound (*e.g.*, naphthalene, benzene, substituted benzene such as toluene) is heated in an acidic mixture (*e.g.*, sulfuric acid and water) for 6 hours at 160 °C. The mixture is cooled to 100 °C, and a deuterium-enriched aldehyde selected from structures **65-358** is added in an amount that is less than a molar equivalent of the aromatic compound. The

resulting mixture is kept at 100 °C at a time period ranging from 30 minutes to 16 hours to afford a condensation polymer.

[00170] *General Method 2*

[00171] To a mixture of a deuterium-enriched aldehydes selected from structures **1-64** and an aromatic alcohol (*e.g.*, resorcinol) at room temperature is added an acidic solution (*e.g.*, aqueous HCl). This affords a condensation polymer upon isolation.

[00172] *General Method 2B*

[00173] To a mixture of a deuterium-enriched aldehydes selected from structures **65-358** and an aromatic alcohol (*e.g.*, resorcinol) at room temperature is added an acidic solution (*e.g.*, aqueous HCl). This affords a condensation polymer upon isolation.

[00174] *General Method 3*

[00175] To an aromatic alcohol (*e.g.*, phenol, resorcinol) in an organic solvent (*e.g.*, ether such as dioxane) is slowly added acid (*e.g.*, sulfuric acid). A deuterium-enriched aldehyde selected from structures **1-64** is added dropwise with stirring. The reaction mixture is heated and the contents refluxed for 2 hours. The organic solvent and water are removed, and the reaction mixture is cooled. Precipitation of material provides the condensation polymer.

[00176] *General Method 3A*

[00177] To an aromatic alcohol (*e.g.*, phenol, resorcinol) in an organic solvent (*e.g.*, ether such as dioxane) is slowly added acid (*e.g.*, sulfuric acid). A deuterium-enriched aldehyde selected from structures **65-358** is added dropwise with stirring. The reaction mixture is heated and the contents refluxed for 2 hours. The organic solvent and water are removed, and the reaction mixture is cooled. Precipitation of material provides the condensation polymer.

[00178] **General procedure for measurement of aldehyde oxidations**

[00179] To a 12 mL clear, colorless, glass vial, fitted with a stir bar, was added the aldehyde (1mmol), triacetin (2.0 mL), and water (0.10 mL, purified by reverse osmosis). The top of the vial was covered with a tissue and the mixture was stirred vigorously at room temperature. In the benzaldehyde reactions, (both H and D), 4.0 μ L aliquots were withdrawn at 0, 0.5, 18, 25, 96, and 120 hour time points. These were diluted with ethanol (1.0 mL), and analyzed by HPLC. In the hexanal reactions (both H and D), 45 μ L aliquots were withdrawn at 2, 4, 6, and 24 hour time points. These were diluted with ethanol (1.0 mL) and analyzed by GC.

[00180] **Instruments and conditions used for analysis:**

[00181] High pressure liquid chromatography: Agilent XDB C18 50x4.6mm 1.8 micron column

[00182] Solvent A – Water (0.1% TFA)

[00183] Solvent B – Acetonitrile (0.07% TFA)

[00184] Gradient – 5 min 95%A to 95%B then 1minute hold. 1.5mL/min

[00185] UV Detection (integration) @ 210 and 254nm

[00186] **Gas chromatography:**

[00187] HP 6890GC Column = Agilent DB-5 15m x 0.25mm capillary column.

[00188] 35°C start (2min hold), ramping to 100°C at 5 °C per minute

[00189] 7.8mL/min gas flow

[00190] Flame Ion Detection (integration)

[00191] **Example 1:** The oxidation rate of deuterium enriched benzaldehyde (*i.e.*, >95% deuterium at the α -H, *i.e.*, H-C(O)Ph, “benzaldehyde-D”) to benzoic acid was compared against un-enriched benzaldehyde (*i.e.*, naturally occurring isotopic abundance, “benzaldehyde-H”).

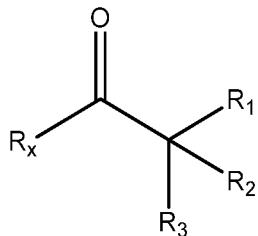
using the above-described procedure. The time and amount of aldehyde remaining were plotted as shown in **Figure 4**. After 24 hours, approximately 90% of benzaldehyde-D remained (a 10% loss). In contrast, after 24 hours, approximately 30% of benzaldehyde-H remained (a 70% loss). The autoxidation of deuterium enriched benzaldehyde was reduced by over 50 percent after a period of approximately 24 hours due to the presence of deuterium.

[00192] **Example 2:** The oxidation rate of deuterium enriched hexanal (*i.e.*, >95% deuterium at α -hydrogen *i.e.*, H-C(O)C₅H₁₁, “hexanal-D”) to hexanoic acid was compared against un-enriched hexanal (*i.e.*, naturally occurring isotopic abundance, “hexanal-H”) using the above-described procedure. The time and amount of aldehyde remaining were plotted as shown in **Figure 5**. After 24 hours, approximately 90% of hexanal-D remained (a 10% loss). In contrast, after 24 hours, approximately 30% of hexanal-H remained (a 70% loss). The autoxidation of deuterium-enriched hexanal was reduced by about 50 percent after a period of approximately 24 hours.

[00193] Numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

WHAT IS CLAIMED IS:

1. A composition, comprising: a deuterium-enriched aldehyde of structure 1:



1

wherein:

there are at least 6×10^{18} molecules of the aldehyde in the composition;

R_x is hydrogen, wherein the deuterium isotope is present in an amount greater than 0.10% of the

R_x hydrogen atoms;

R_1 , R_2 and R_3 are independently selected from hydrogen, alkyl, substituted alkyl, alkenyl,

substituted alkenyl, alkynyl, substituted alkynyl, heteroalkyl, substituted heteroalkyl, aryl, substituted aryl, heteroaryl, and substituted heteroaryl;

alternatively, the $CR_1R_2R_3$ moiety forms a group selected from: an aryl, substituted aryl,

heteroaryl, and substituted heteroaryl;

alternatively, the CR_1R_2 moiety forms a group selected from: an alkenyl and substituted

alkenyl;

alternatively, the $CR_1R_2R_3$ moiety forms a group selected from: an alkynyl and

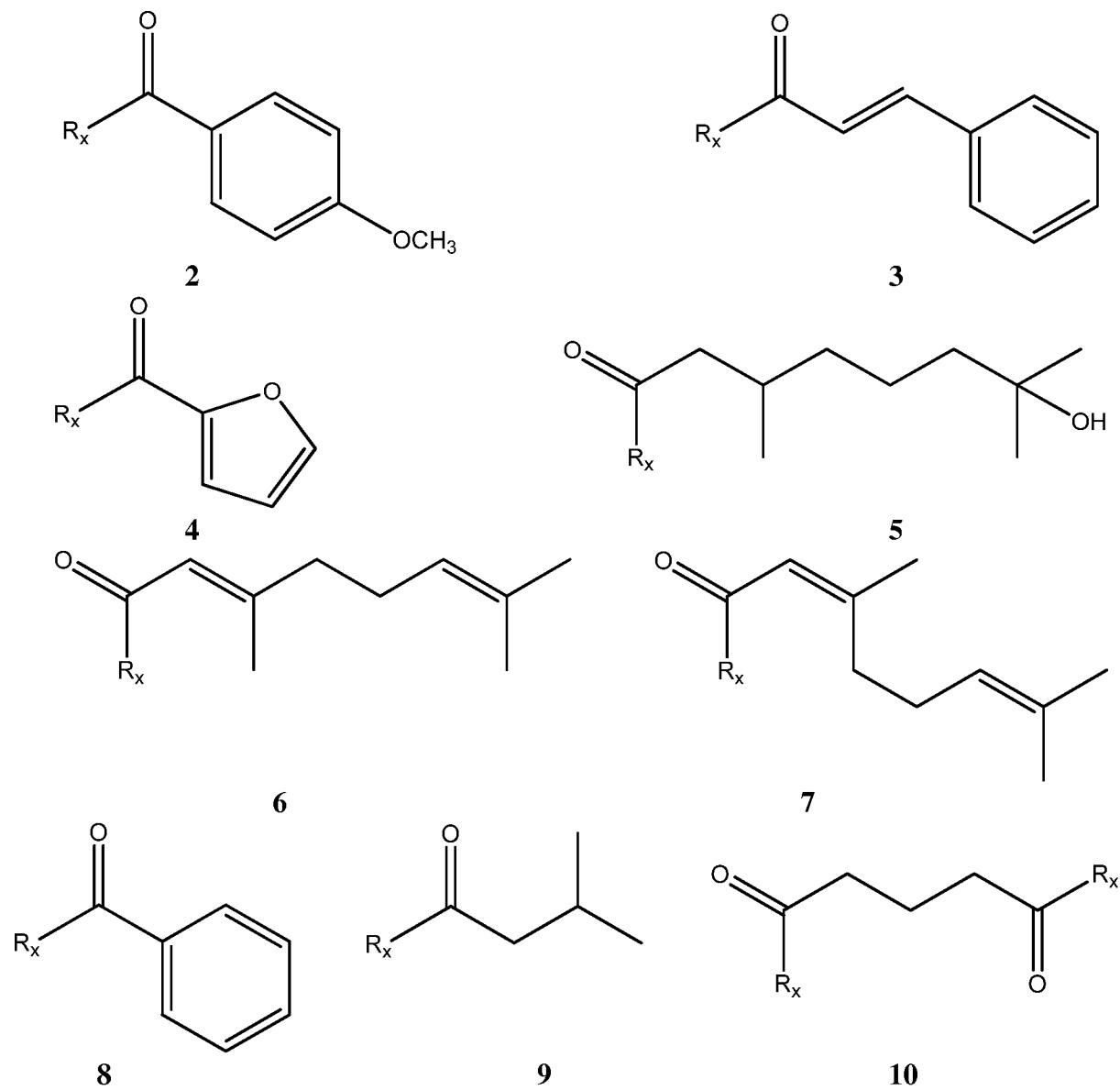
substituted alkynyl; and,

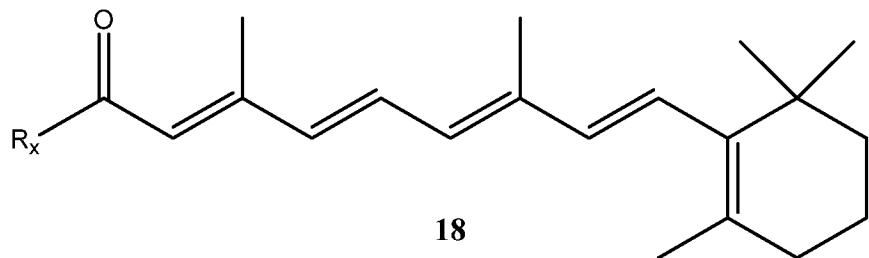
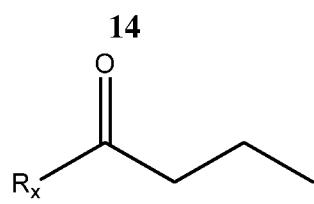
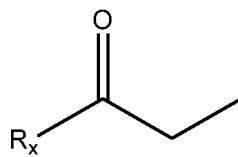
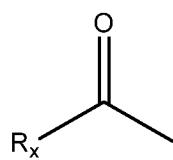
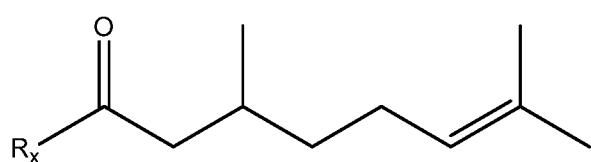
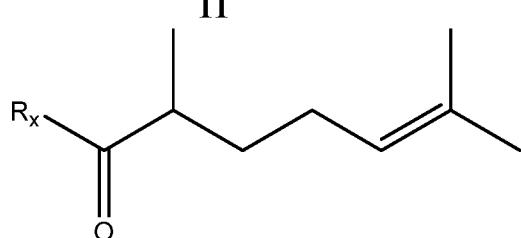
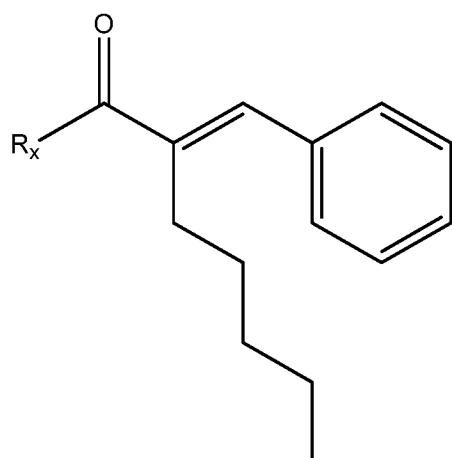
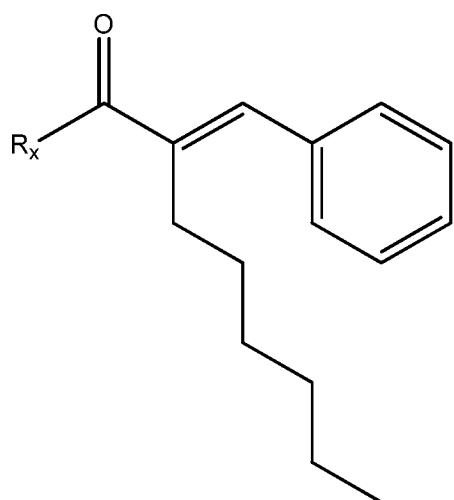
optionally, the aldehyde is substituted with $C(O)R_y$, wherein R_y is hydrogen, wherein the

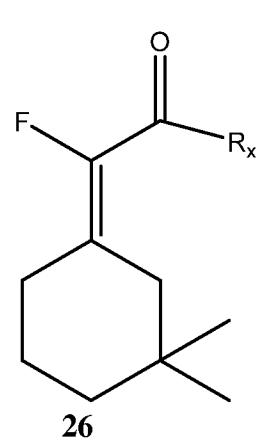
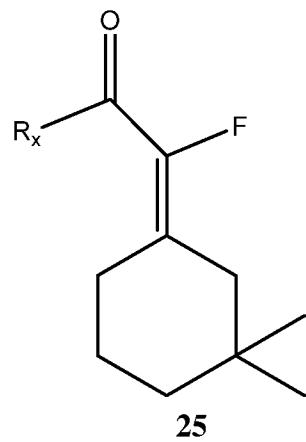
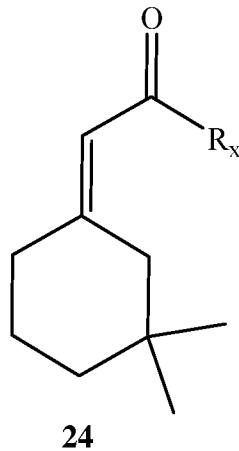
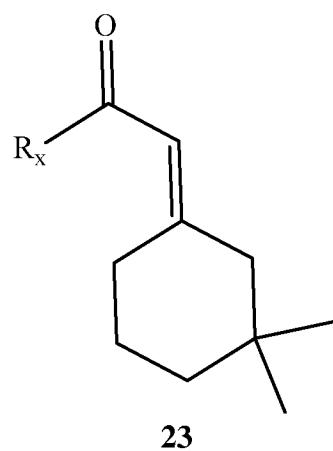
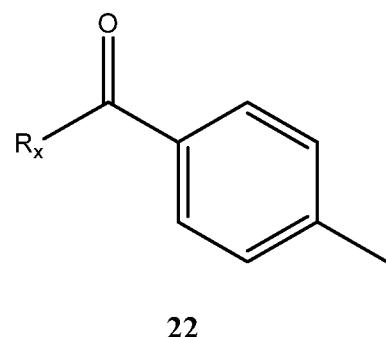
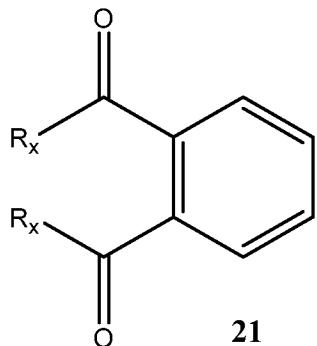
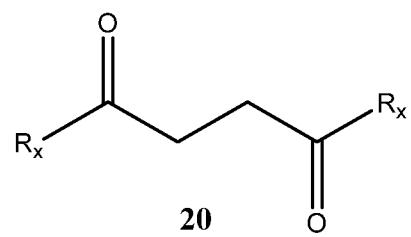
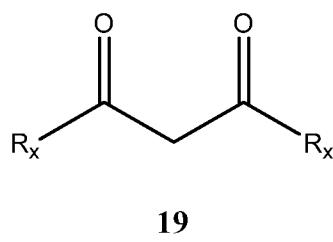
deuterium isotope is optionally present in an amount greater than 0.10% of the R_y

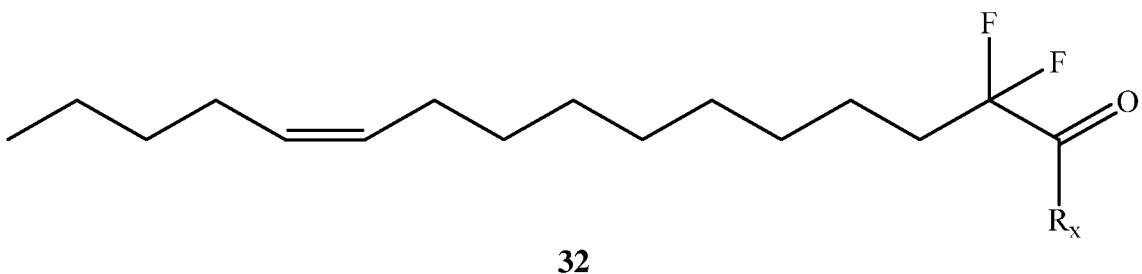
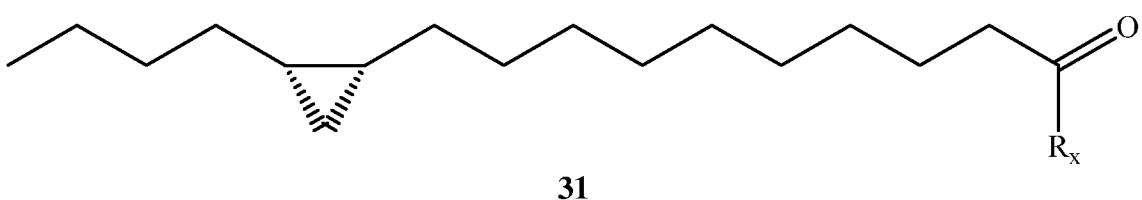
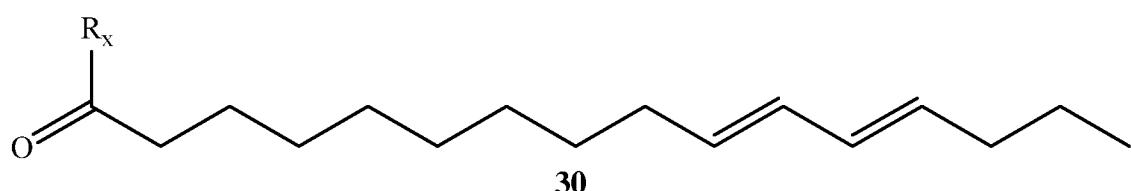
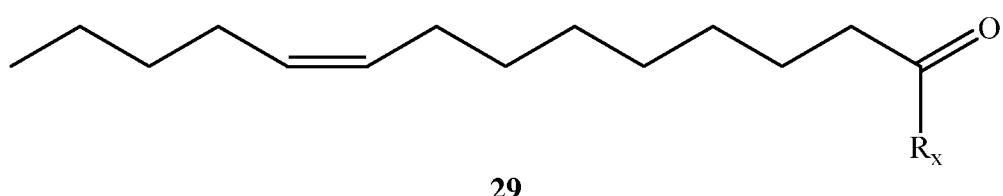
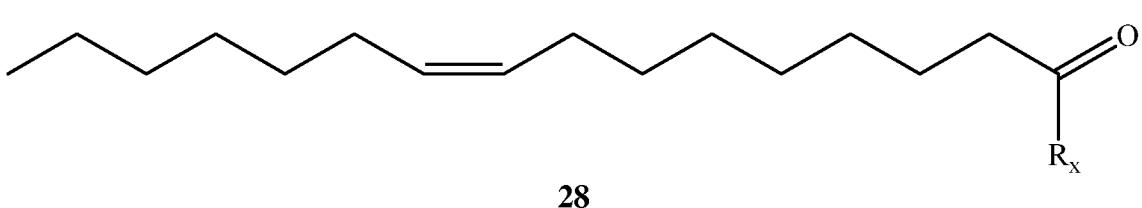
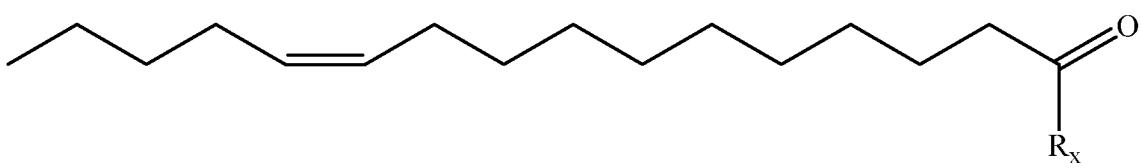
hydrogen atoms, provided that R_x is optionally H when the deuterium isotope is present in an amount greater than 0.10% of the R_y hydrogen atoms.

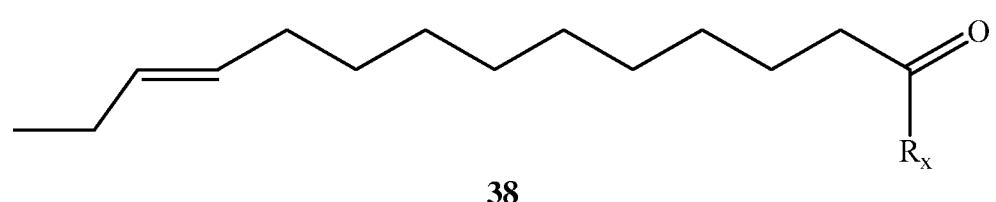
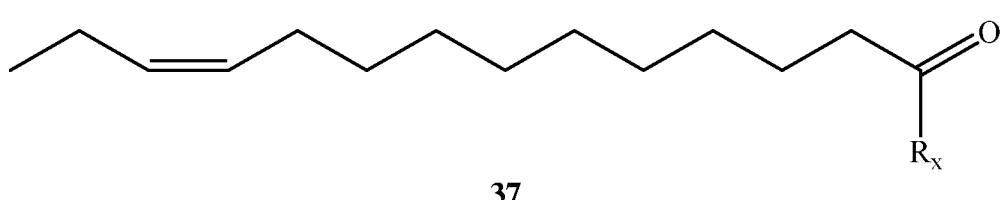
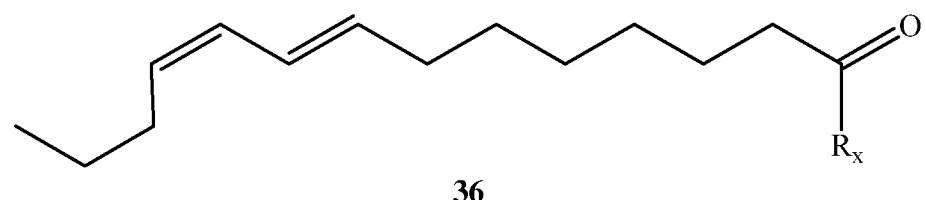
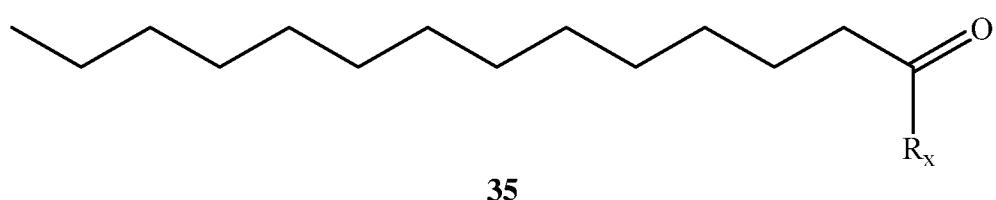
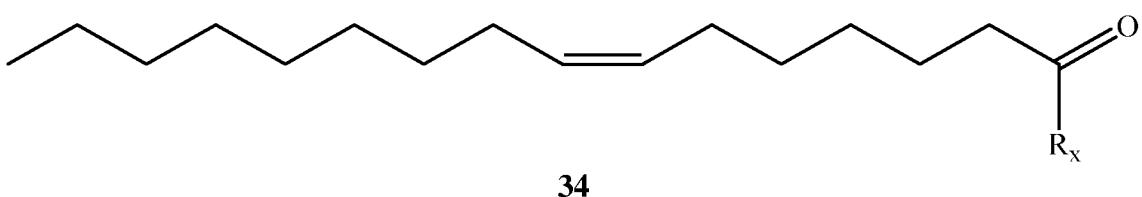
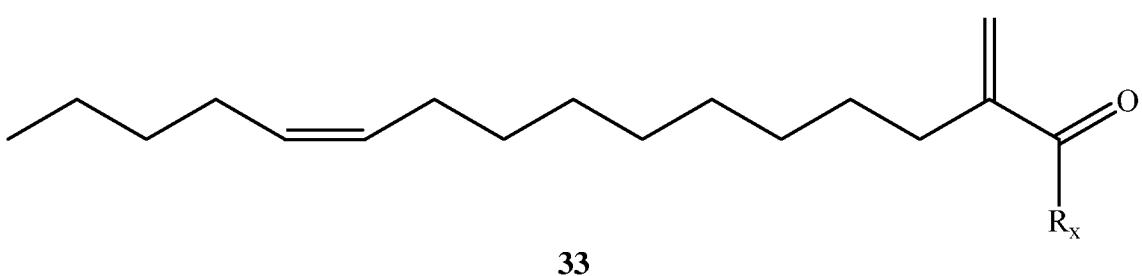
2. The composition according to claim 1, wherein the deuterium-enriched aldehyde is selected from aldehydes 2-64:

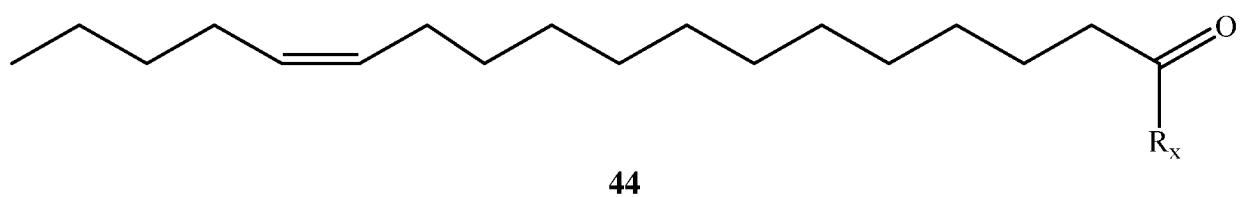
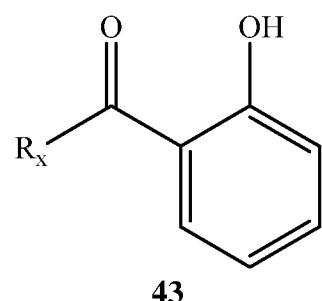
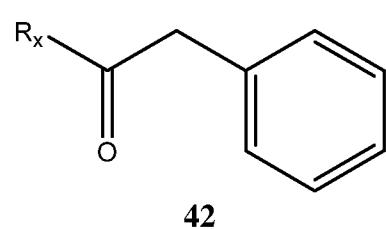
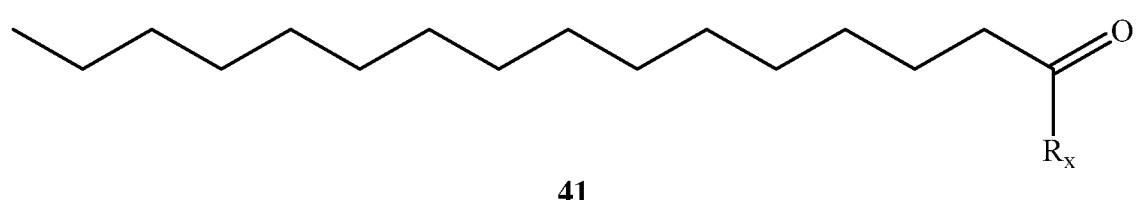
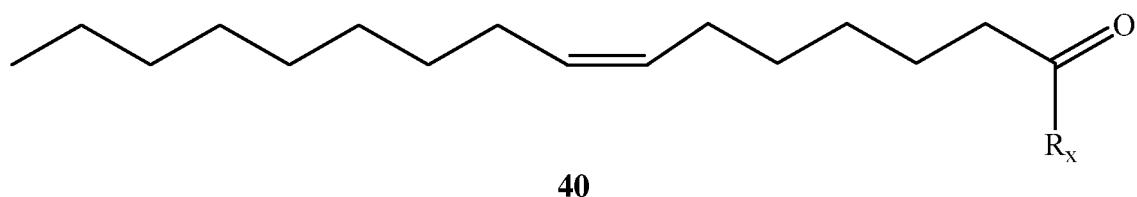
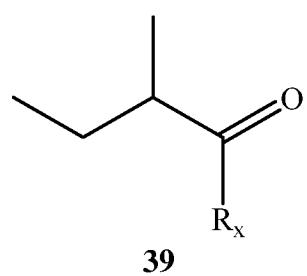


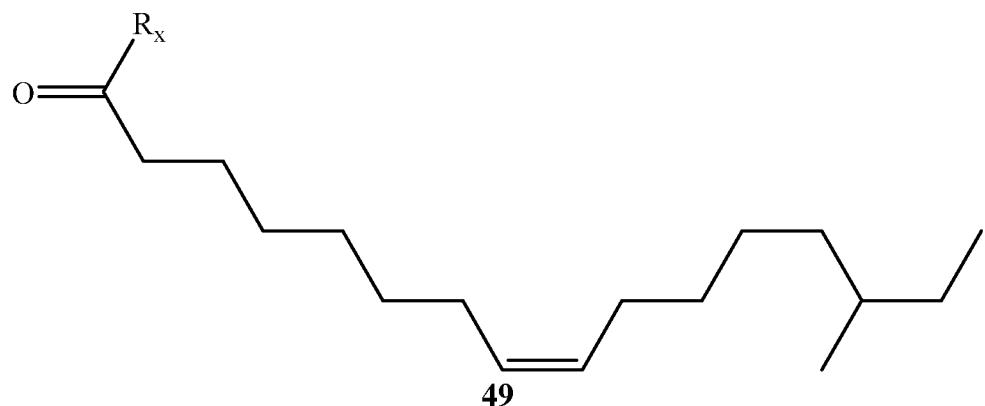
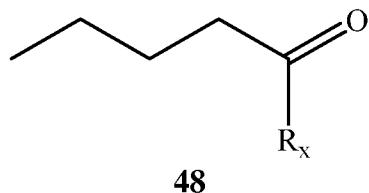
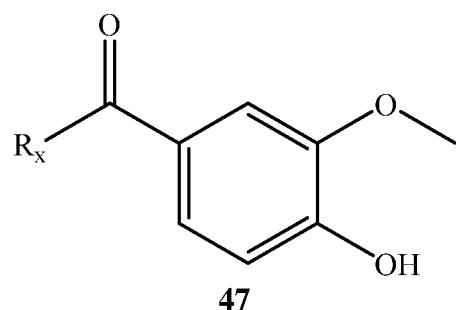
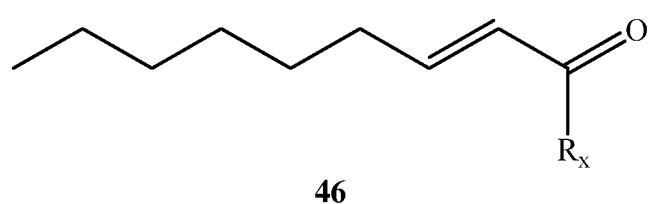
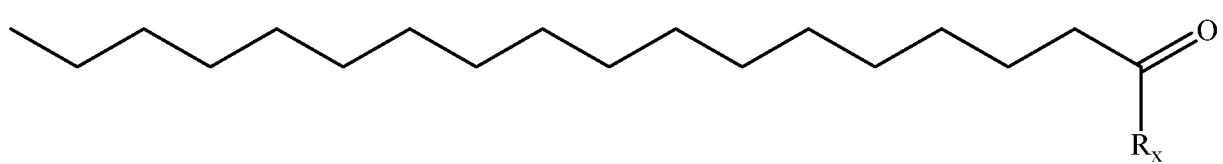


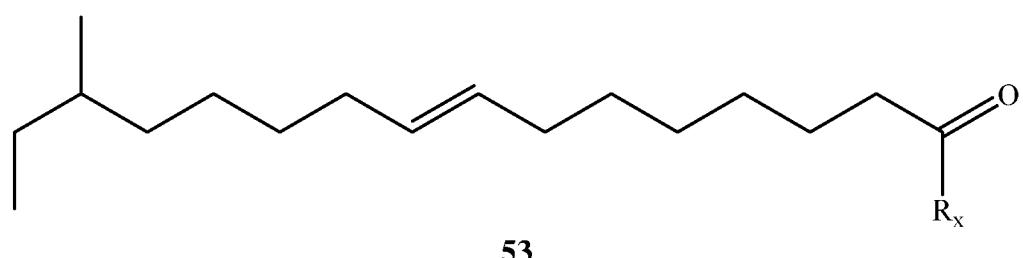
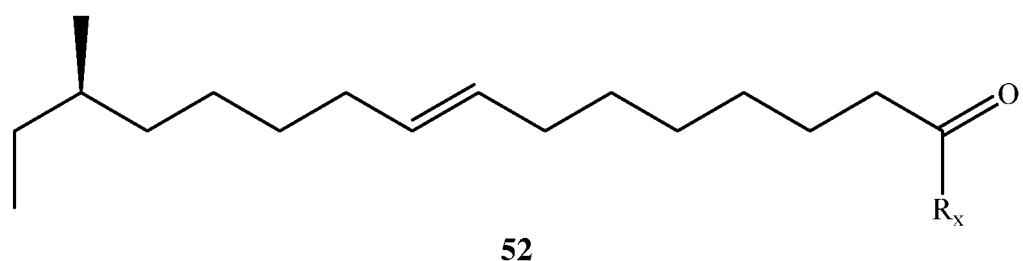
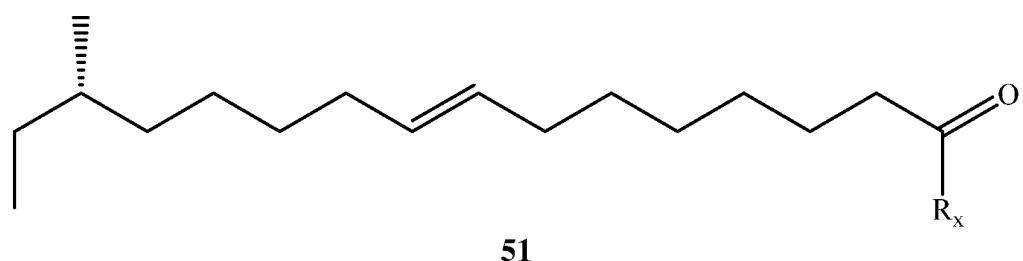


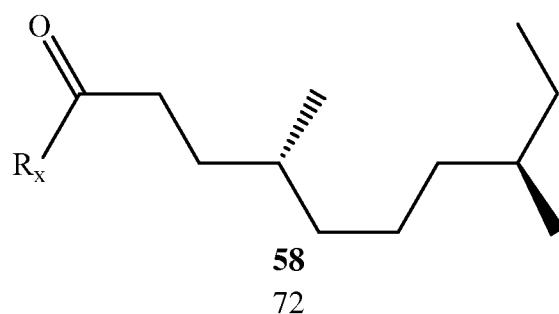
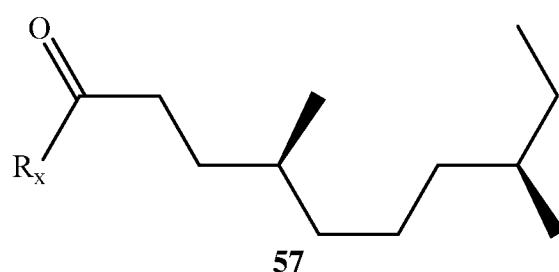
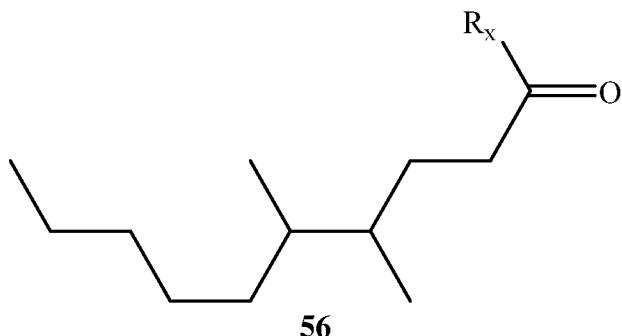
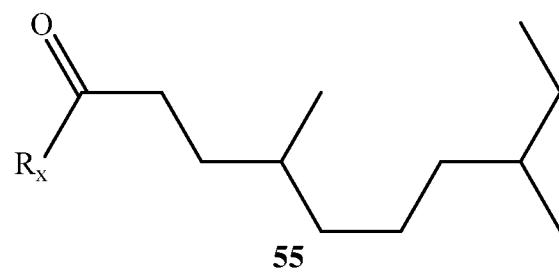
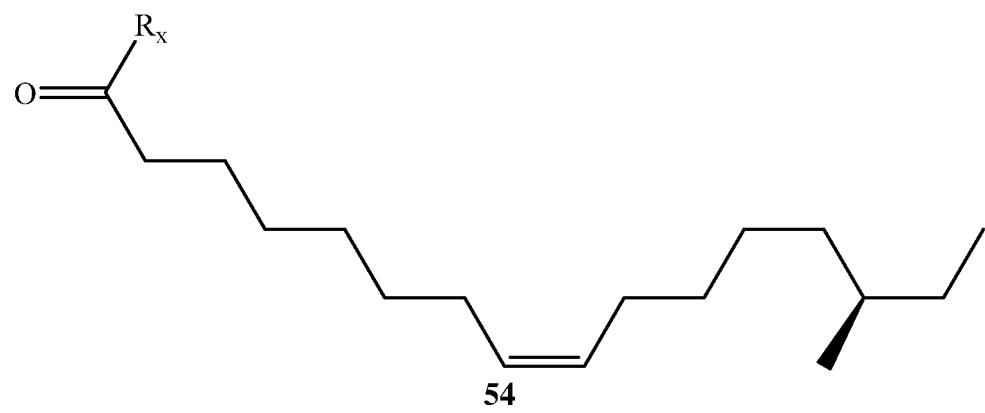






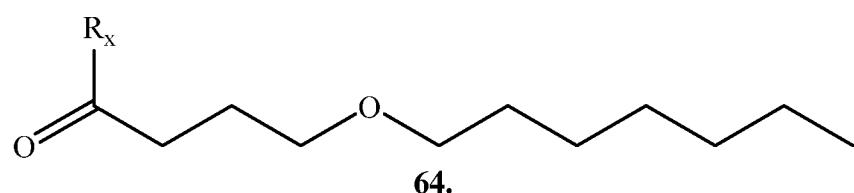
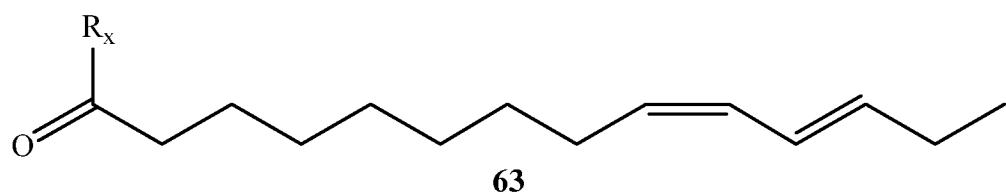
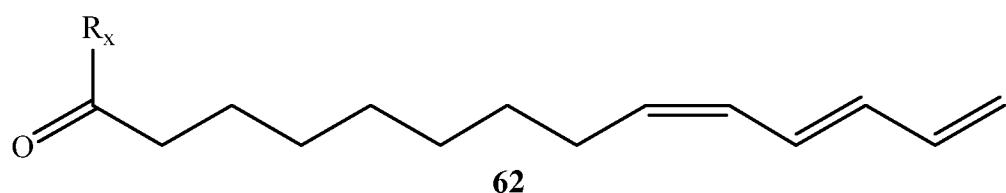
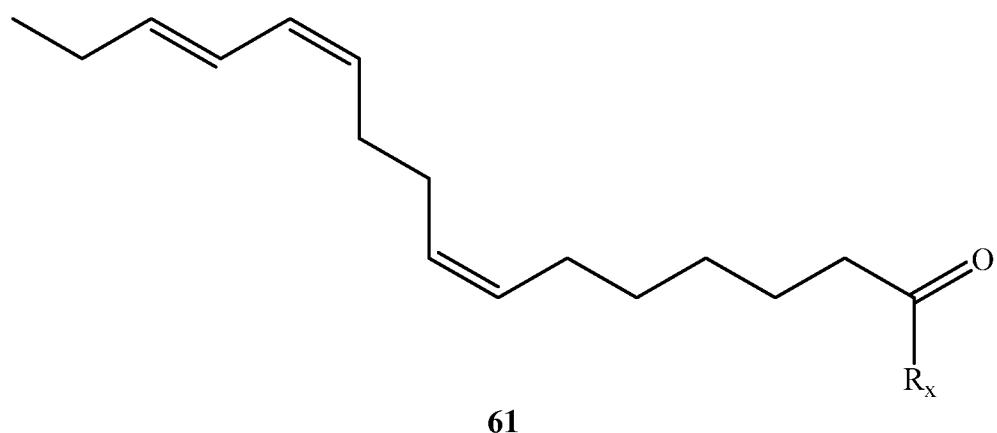
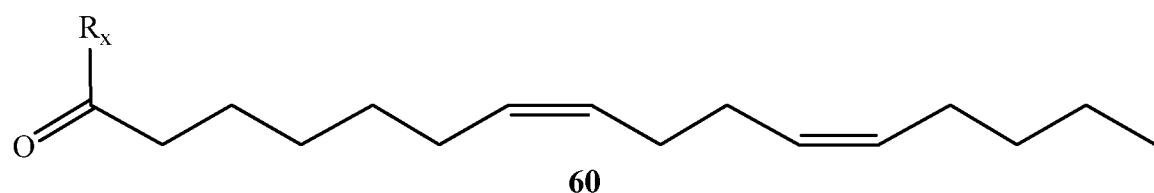
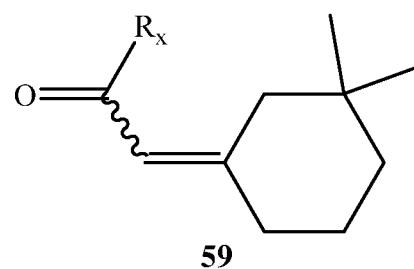






58

72



3. The composition according to claim 1, wherein the deuterium-enriched aldehyde is selected from aldehydes **65-358**:

Ex.	Name
65.	Formaldehyde- R_x
66.	2-Methyl-2-propenal- R_x
67.	2-Methylpropanal- R_x
68.	2-Propenal- R_x
69.	2-Butenal- R_x
70.	2-Methyl-2-butenal- R_x
71.	2-Methylenebutanal- R_x
72.	3-Methyl-2-butenal- R_x
73.	3-Methyl-3-butenal- R_x
74.	3-Methylbutanal- R_x
75.	(E)-2-Pentenal- R_x
76.	2-Methylenepentanal- R_x
77.	2-Pentenal- R_x
78.	3-Methyl-1-(vinyloxy)-butane- R_x
79.	4-Methylpentanal- R_x
80.	Furan-2-carbaldehyde- R_x
81.	(E)-2-Hexenal- R_x
82.	(E)-4-oxo-2-Hexenal- R_x
83.	(E,E)-2,4-Dimethyl-2,4-hexadienal- R_x
84.	(E,E)-2,4-Hexadienal- R_x
85.	(Z)-2-Hexenal- R_x
86.	(Z)-3-Hexenal- R_x
87.	(Z)-4-oxo-2-Hexenal- R_x
88.	1-Hexenal- R_x
89.	2,3-Dihydroxybenzaldehyde- R_x
90.	2-Hexenal- R_x
91.	3-((E)-2-Hexenoxy)-hexanal- R_x
92.	3,5-Dimethylhexanal- R_x
93.	3-Ethoxyhexanal- R_x
94.	3-Hydroxybenzaldehyde- R_x
95.	3-Hydroxyhexanal- R_x
96.	4-Hydroxy-3,5-dimethoxybenzaldehyde- R_x
97.	4-Hydroxybenzaldehyde- R_x
98.	5-Methylhexanal- R_x
99.	Hexanal- R_x
100.	(1R,2S,5S)-Iridodial- R_x
101.	(1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-carbaldehyde- R_x
102.	(1S,2R,3S)-2-(1-Formylvinyl)-5-methylcyclopentanecarbaldehyde- R_x
103.	(3S,8R)-2-Methyl-5-(1-formylethyl)-1-cyclopentene-1-carbaldehyde- R_x

104.	(3S,8S)-2-Methyl-5-(1-formylethyl)-1-cyclopentene-1-carbaldehyde-R _x
105.	(5S,8S)-2-Methyl-5-(1-formylethyl)-1-cyclopentene-1-carbaldehyde-R _x
106.	(E)-2-(2-Hydroxyethyl)-6-methyl-2,5-heptadienal-R _x
107.	(E)-2-(2-Hydroxyethylidene)-6-methyl-5-heptenal-R _x
108.	(E)-2-Heptenal-R _x
109.	(E)-2-Isopropyl-5-methyl-2-hexenal-R _x
110.	(E,Z)-2,4-Heptadienal-R _x
111.	(R)-2-((1R,2R,3S)-3-Methyl-2-vinylcyclopentyl)-propanal-R _x
112.	(R)-2-((1S,2S,3S)-3-Methyl-2-vinylcyclopentyl)-propanal-R _x
113.	(R)-2,6-Dimethyl-5-heptenal-R _x
114.	(R)-7-Hydroxy-6,7-dihydro-5H-pyrrolizidine-1-carboxaldehyde-R _x
115.	(S)-4-(Prop-1-en-2-yl)-cyclohex-1-enecarbaldehyde-R _x
116.	(S)-7-Hydroxy-6,7-dihydro-5H-pyrrolizidine-1-carboxaldehyde-R _x
117.	(Z)-2-Isopropyl-5-methyl-2-hexenal-R _x
118.	1-Formyl-6,7-dihydro-5H-pyrrolizine-R _x
119.	1-Formyl-7-hydroxy-6,7-dihydro-5H-pyrrolizine-R _x
120.	2-(3-Methylcyclopentyl)-propanal-R _x
121.	2,6-Dimethyl-5-heptenal-R _x
122.	2-Acetyl-5-methylcyclopentanecarbaldehyde-R _x
123.	2-Methoxybenzaldehyde-R _x
124.	2-Methyl-1-cyclopentenecarboxaldehyde-R _x
125.	3,3-Dimethyl-5-oxo-7-oxabicyclo[4.1.0]heptane-1-carbaldehyde-R _x
126.	3-Hydroxybenzene-1,2-dicarbaldehyde-R _x
127.	3-Methylbenzaldehyde-R _x
128.	4-(Heptyloxy)-butanal-R _x
129.	4-Methoxybenzaldehyde-R _x
130.	6,7-Dihydro-5H-pyrrolizine-1-carboxaldehyde-R _x
131.	6,7-Dihydro-7-oxo-5H-pyrrolizine-1-carbaldehyde-R _x
132.	6-Methylheptanal-R _x
133.	7-Hydroxy-6,7-dihydro-5H-pyrrolizin-1-carboxaldehyde-R _x
134.	Benzaldehyde-R _x
135.	Cyclohexanodial-R _x
136.	Heptanal-R _x
137.	Plagiodial-R _x
138.	(1R,2S)-cis-2-Isopropenyl-1-methylcyclobutaneethanal-R _x
139.	(1R,2S,5R,8R)-Iridodial-R _x
140.	(4S)-(3-Oxoprop-1-en-2-yl)-cyclohex-1-enecarbaldehyde-R _x
141.	(E)-2-(3,3-Dimethylcyclohexylidene)-acetalddehyde-R _x
142.	(E)-2-(4-Methyl-3-pentenyl)-butenedial-R _x
143.	(E)-2-(4-Methyl-3-pentenylidene)-butanodial-R _x
144.	(E)-2,7-Octadienal-R _x
145.	(E)-2-Methyl-5-(3-furyl)-2-pentenal-R _x
146.	(E)-2-Octenal-R _x
147.	(E)-3,7-Dimethyl-2,6-octadienal-R _x

148.	(E)-3,7-Dimethyl-2,6-octadienal-R _x
149.	(E)-4-oxo-2-Octenal-R _x
150.	(E)-7-Methyl-2-octenal-R _x
151.	(E,E)-2,4-Octadienal-R _x
152.	(E,E)-2,6-Dimethyl-8-hydroxy-2,6-octadienal-R _x
153.	(E,E)-2,6-Octadienal-R _x
154.	(E,E)-2,6-Octadienodial-R _x
155.	(E,Z)-2,4-Octadienal-R _x
156.	(E,Z)-2,6-Octadienal-R _x
157.	(Z)-2-(3,3-Dimethylcyclohexylidene)-acetaldehyde-R _x
158.	(Z)-3,7-Dimethyl-2,6-octadienal-R _x
159.	(Z,E)-3,7-Dimethyl-2,6-octadienal-R _x
160.	1-Octenal-R _x
161.	2-(1-Formylvinyl)-5-methylcyclopentanecarbaldehyde-R _x
162.	2,6,6-Trimethyl-1-cyclohexene-1-carbaldehyde-R _x
163.	2-Ethyoctanal-R _x
164.	2-Hydroxy-6-methylbenzaldehyde-R _x
165.	2-Methyl benzaldehyde-R _x
166.	2-Octenal-R _x
167.	2-Phenylpropenal-R _x
168.	3,7-Dimethyl-6-octenal-R _x
169.	3-Ethoxy-4-hydroxybenzaldehyde-R _x
170.	3-Ethyl benzaldehyde-R _x
171.	3-Isopropyl-6-methyl benzaldehyde-R _x
172.	3-Octenal-R _x
173.	3-oxo-4-Isopropylidene-1-cyclohexene-1-carboxyaldehyde-R _x
174.	4-Hydroxy-2-methyl benzaldehyde-R _x
175.	4-Hydroxy-3-methoxybenzaldehyde-R _x
176.	4-Isopropenyl-1-cyclohexene-1-carbaldehyde-R _x
177.	4-Isopropenyl-3-oxo-1-cyclohexene-1-carboxyaldehyde-R _x
178.	4-oxo-Octenal-R _x
179.	4S-4-Isopropenyl-3-oxo-1-cyclohexene-1-carboxyaldehyde-R _x
180.	6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-carbaldehyde-R _x
181.	7-Methyloctanal-R _x
182.	Anisomorphal-R _x
183.	cis-2-Isopropenyl-1-methylcyclobutaneethanal-R _x
184.	Octanal-R _x
185.	Peruphasmal-R _x
186.	(E)-4,8-Nonadienal-R _x
187.	(E)-8-Methyl-2-nonenal-R _x
188.	(E,E)-2,4-Nonadienal-R _x
189.	(E,E,E)-2,4,6-Nonatrienal-R _x
190.	(E,E,Z)-2,4,6-Nonatrienal-R _x
191.	(E,Z)-2,6-Nonadienal-R _x

192.	(E,Z,Z)-2,4,6-Nonatrienal-R _x
193.	(Z)-3-Nonenal-R _x
194.	(Z)-4,8-Nonadienal-R _x
195.	(Z)-4-Nonenal-R _x
196.	(Z)-8-Methyl-2-nonenal-R _x
197.	2-Phenyl-2-butenal-R _x
198.	3-(4-Methoxyphenyl)-2-propenal-R _x
199.	3-Phenyl-2-propenal-R _x
200.	3-Phenylpropanal-R _x
201.	6-Ethyl benzaldehyde-R _x
202.	8-Methylnonanal-R _x
203.	9-Acetyloxynonanal-R _x
204.	Nonanal-R _x
205.	(E)-2,9-Decadienal-R _x
206.	(E)-2-Decenal-R _x
207.	(E)-4-oxo-2-Decenal-R _x
208.	(E)-8-Hydroxy-4,8-dimethyl-4,9-decadienal-R _x
209.	(E)-9-Methyl-2-decenal-R _x
210.	(E,E)-2,4-Decadienal-R _x
211.	(E,Z)-2,4-Decadienal-R _x
212.	(Z)-4-Decenal-R _x
213.	(Z)-5-Decenal-R _x
214.	(Z)-9-Methyl-2-decenal-R _x
215.	1-Decenal-R _x
216.	2-Decenal-R _x
217.	2-Ethyldecanal-R _x
218.	Decanal-R _x
219.	(5E)-2,6,10-Trimethylundeca-5,9-dienal-R _x
220.	(E)-2-Undecenal-R _x
221.	(E)-6-Ethyl-2,10-dimethyl-5,9-undecadienal-R _x
222.	10-Undecenal-R _x
223.	2-Butyl-2-octenal-R _x
224.	5-Methyl-2-phenyl-2-hexenal-R _x
225.	8-Isopropyl-5-methyl-3,4,4a,5,6,7,8,8a-octahydronaphthalene-2-carbaldehyde-R _x
226.	syn-4,6-Dimethylundecanal-R _x
227.	Undecanal-R _x
228.	(3R,5R,9R)-3,5,9-Trimethyldodecanal-R _x
229.	(3S,6E)-7-Ethyl-3,11-dimethyldodeca-6,10-dienal-R _x
230.	(9R)-3,5,9-Trimethyldodecanal-R _x
231.	(E)-10-Dodecenal-R _x
232.	(E)-2-Dodecenal-R _x
233.	(E)-3,7,11-Trimethyl-6,10-dodecadienal-R _x
234.	(E)-6-Dodecenal-R _x
235.	(E)-7-Dodecenal-R _x

236.	(E)-8-Dodecenal- R_x
237.	(E)-9,11-Dodecadienal- R_x
238.	(E)-9-Dodecenal- R_x
239.	(E,E)-3,7,11-Trimethyl-2,6,10-dodecatrienal- R_x
240.	(E,E)-7-Ethyl-3,11-dimethyl-2,6,10-dodecatrienal- R_x
241.	(E,E)-8,10-Dodecadienal- R_x
242.	(E,E,E)-3,7-Dimethyl-8,11-dioxo-2,6,9-dodecatrienal- R_x
243.	(E,E,Z)-3,7-Dimethyl-8,11-dioxo-2,6,9-dodecatrienal- R_x
244.	(E,Z)-5,7-Dodecadienal- R_x
245.	(E,Z)-7,9-Dodecadienal- R_x
246.	(E,Z)-8,10-Dodecadienal- R_x
247.	(S,E)-3,7,11-Trimethyl-6,10-dodecadienal- R_x
248.	(Z)-2-Methyl-5-((1R,5R,6S)-2,6-dimethylbicyclo[3.1.1]hept-2-en-6-yl)-pent-2-enal- R_x
249.	(Z)-5-Dodecenal- R_x
250.	(Z)-7-Dodecenal- R_x
251.	(Z)-9,11-Dodecadienal- R_x
252.	(Z)-9-Dodecenal- R_x
253.	(Z,E)-3,7,11-Trimethyl-2,6,10-dodecatrienal- R_x
254.	(Z,E)-5,7-Dodecadienal- R_x
255.	(Z,E)-7-Ethyl-3,11-dimethyl-2,6,10-dodecatrienal- R_x
256.	(Z,E)-8,10-Dodecadienal- R_x
257.	(Z,Z)-5,7-Dodecadienal- R_x
258.	2-Ethylundecanal- R_x
259.	3,7,11-Trimethyl-(E)-6,10-dodecadienal- R_x
260.	Dodecanal- R_x
261.	syn-4,6-Dimethyldodecanal- R_x
262.	(3S,4R,6E,10Z)-3,4,7,11-Tetramethyl-6,10-tridecadienal- R_x
263.	(Z)-4-Tridecenal- R_x
264.	13-Acetoxytridecanal- R_x
265.	Tridecanal- R_x
266.	(E)-11,13-Tetradecadienal- R_x
267.	(E,E)-8,10-Tetradecadienal- R_x
268.	(E,Z)-4,9-Tetradecadienal- R_x
269.	(Z)-11,13-Tetradecadienal- R_x
270.	(Z)-5-Tetradecenal- R_x
271.	(Z)-7-Tetradecenal- R_x
272.	(Z)-9,13-Tetradecadien-11-ynal- R_x
273.	(Z,E)-9,12-Tetradecadienal- R_x
274.	(Z,Z)-8,10-Tetradecadienal- R_x
275.	(Z,Z)-9,11-Tetradecadienal- R_x
276.	10,12-Tetradecadienal- R_x
277.	2-Ethyltetradecanal- R_x
278.	3-oxo-13-Tetradecenal- R_x
279.	3-oxo-Tetradecanal- R_x

280.	5,8-Tetradecadienal-R _x
281.	5-Tetradecenal-R _x
282.	(E)-5,9-Dimethyl-2-(6-methylhept-5-en-2-yl)-deca-4,8-dienal-R _x
283.	(E,Z)-9,11-Pentadecadienal-R _x
284.	(Z)-10-Pentadecenal-R _x
285.	(Z)-6,14-Pentadecadienal-R _x
286.	(Z,Z)-9,11-Pentadecadienal-R _x
287.	2-Hexyl-2-decenal-R _x
288.	Pentadecanal-R _x
289.	(1R)-Pimaral-R _x
290.	(E)-10-Hexadecenal-R _x
291.	(E)-11-Hexadecenal-R _x
292.	(E,E)-10,14-Hexadecadienal-R _x
293.	(E,E)-11,13-Hexadecadienal-R _x
294.	(E,E)-9,11-Hexadecadienal-R _x
295.	(E,E,E)-10,12,14-Hexadecatrienal-R _x
296.	(E,E,E)-3,7,11,15-tetramethyl-2,6,10,14-hexadecatetraenal-R _x
297.	(E,E,Z)-10,12,14-Hexadecatrienal-R _x
298.	(E,E,Z)-4,6,11-Hexadecatrienal-R _x
299.	(E,E,Z,Z)-4,6,11,13-Hexadecatetraenal-R _x
300.	(E,Z)-10,12-Hexadecadienal-R _x
301.	(E,Z)-11,13-Hexadecadienal-R _x
302.	(E,Z)-4,6-Hexadecadienal-R _x
303.	(E,Z)-6,11-Hexadecadienal-R _x
304.	(E,Z)-8,11-Hexadecadienal-R _x
305.	(E,Z)-9,11-Hexadecadienal-R _x
306.	(Z)-10-Hexadecenal-R _x
307.	(Z)-12-Hexadecenal-R _x
308.	(Z)-13-Hexadecen-11-ynal-R _x
309.	(Z)-3-oxo-9-Hexadecenal-R _x
310.	(Z,E)-10,12-Hexadecadienal-R _x
311.	(Z,E)-11,13-Hexadecadienal-R _x
312.	(Z,E)-7,11-Hexadecadienal-R _x
313.	(Z,E)-9,11-Hexadecadienal-R _x
314.	(Z,Z)-10,12-Hexadecadienal-R _x
315.	(Z,Z)-11,13-Hexadecadienal-R _x
316.	(Z,Z)-9,11-Hexadecadienal-R _x
317.	11-Hexadecynal-R _x
318.	2-Methylhexadecanal-R _x
319.	7-Hexadecenal-R _x
320.	9-Hexadecenal-R _x
321.	(Z)-9-Heptadecenal-R _x
322.	1-Heptadecenal-R _x
323.	2-Heptadecenal-R _x

324.	Heptadecanal- R_x
325.	(E)-11-Octadecenal- R_x
326.	(E)-13-Octadecenal- R_x
327.	(E)-14-Octadecenal- R_x
328.	(E)-2-Octadecenal- R_x
329.	(E,E)-11,14-Octadecadienal- R_x
330.	(E,Z)-2,13-Octadecadienal- R_x
331.	(E,Z)-3,13-Octadecadienal- R_x
332.	(Z)-11-Octadecenal- R_x
333.	(Z)-13-Octadecenal- R_x
334.	(Z)-9-Octadecenal- R_x
335.	(Z,Z)-11,13-Octadecadienal- R_x
336.	(Z,Z)-13,15-Octadecadienal- R_x
337.	(Z,Z)-3,13-Octadecadienal- R_x
338.	(Z,Z)-9,12-Octadecadienal- R_x
339.	(Z,Z,Z)-9,12,15-Octadecatrienal- R_x
340.	1-Octadecenal- R_x
341.	9-Octadecenal- R_x
342.	Octadecanal- R_x
343.	(Z)-10-Nonadecenal- R_x
344.	(Z)-9-Nonadecenal- R_x
345.	(Z)-11-Eicosenal- R_x
346.	12-Deacetoxy-12-oxo-scalaradial- R_x
347.	1-Eicosenal- R_x
348.	Deacetylscalaradial- R_x
349.	Eicosanal- R_x
350.	Scalaradial- R_x
351.	Docosanal- R_x
352.	Tetracosanal- R_x
353.	Pentacosanal- R_x
354.	Hexacosanal- R_x
355.	Heptacosanal- R_x
356.	Octacosanal- R_x
357.	Triacontanal- R_x
358.	Dotriacontanal- R_x

4. The composition according to one of Claims 1-3, wherein the deuterium-enriched aldehyde is a pheromone and the composition is useful for modulating the behavior of insects.

5. The composition according to Claim 4, further comprising: an optional additional component suitable for the composition, the component being selected from: a pesticide, solvent, dispensing material or device, and an adhesive capable of trapping an insect.
6. The composition according to one of Claims 1-5, wherein the deuterium isotope in R_x is in an amount greater than 50 percent of the hydrogen atoms present in R_x .
7. The composition according to one of Claims 1-5, wherein the deuterium isotope in R_x is in an amount greater than 90 percent of the hydrogen atoms present in R_x .
8. A method of modulating the behavior of insects, comprising: introducing a modulating composition to an area to be protected from the insects, the modulating composition, comprising: a deuterium-enriched aldehyde of Claim 1.
9. The method of claim 8, wherein the deuterium-enriched aldehyde pheromone is selected from an aldehyde of Claim 2.
10. The method of claim 8, wherein the deuterium-enriched aldehyde pheromone is selected from an aldehyde of Claim 3.
11. The method according to one of Claims 8-10, wherein modulation, comprises: attracting an insect to a trap.

12. The method according to one of Claims 8-10, wherein modulation, comprises: disrupting insect mating.
13. The method according to one of Claims 8-12, wherein the deuterium isotope in R_x is in an amount greater than 50 percent of the hydrogen atoms present in R_x .
14. The method according to one of Claims 8-12, wherein the deuterium isotope in R_x is in an amount greater than 90 percent of the hydrogen atoms present in R_x .
15. The method according to one of Claims 8-14, wherein the method further comprises: applying the pheromone to a surface of a trap wherein the insect enters but cannot leave,
16. The method according to one of Claims 8-14, wherein introducing, comprises: distributing the pheromone into the area to be protected, wherein the pheromone disrupts insect mating and is distributed impregnated on a chip, in a polymer hollow fiber, or adsorbed in a rubber septum.

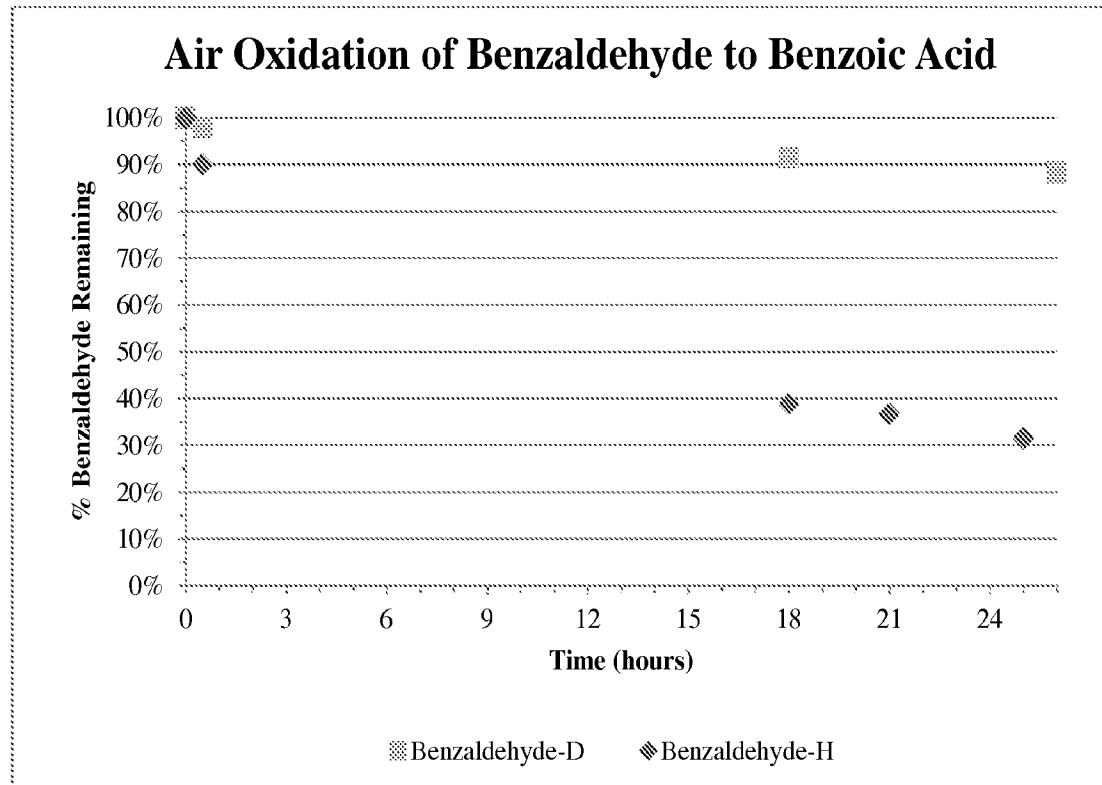


Figure 1

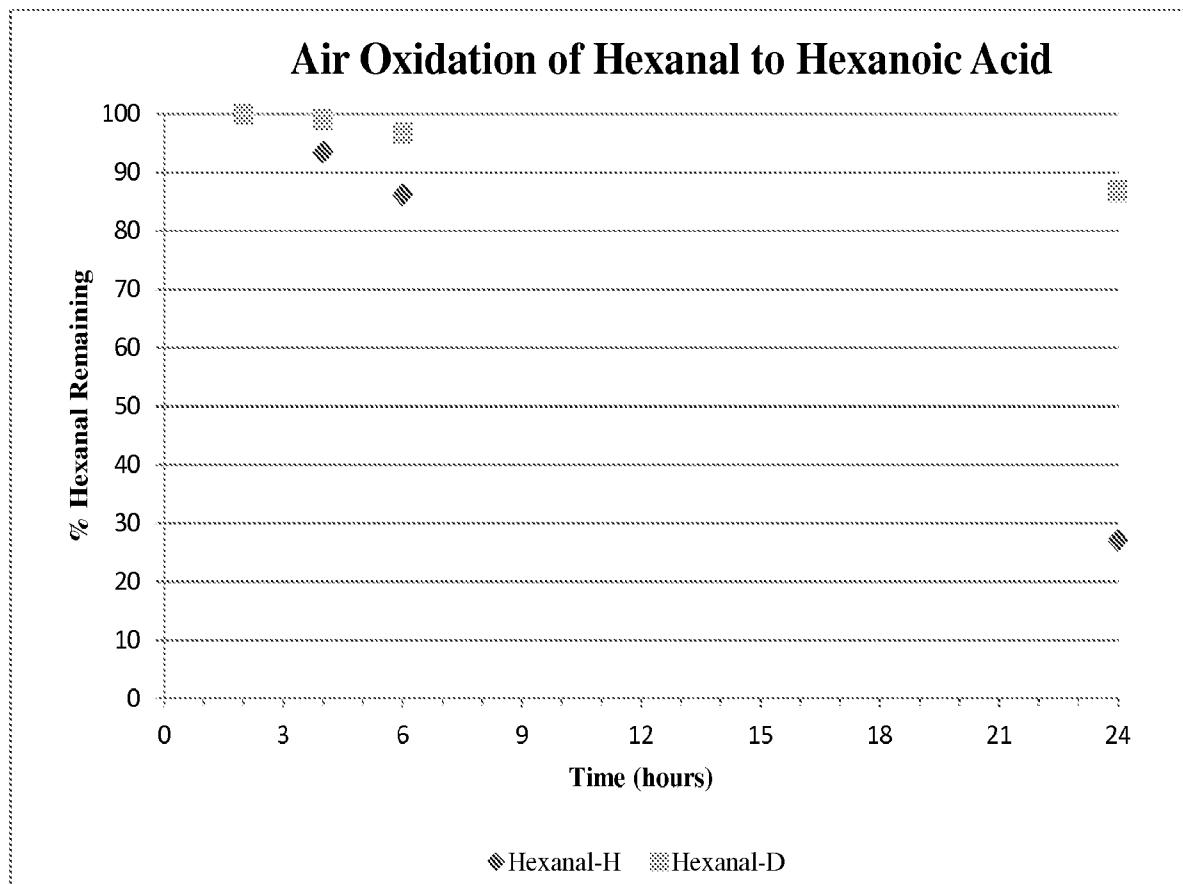


Figure 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US14/30065

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - A01N 25/00, 35/02; A01P 19/00 (2014.01)

USPC - 514/693, 703

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - A01N 25/00, 35/02; A01P 19/00 (2014.01)

USPC - 514/693, 703

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

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

MicroPatent (US Granted, US Applications, EP-A, EP-B, WO, JP, DE-G, DE-A, DE-T, DE-U, GB-A, FR-A); ProQuest; Google Advanced Search; IP.com; deuter*, *decanal, *decenal, pheromon*, insect* pheromon*, deuter* isotop*, aldehyd*, *hexadecadienal*, sex* pheromon*, composition*, formulation*, attract*, insect*, mat*, dispens*, dispers*

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,149,820 A (BORRETZEN, B et al.) 22 September 1992; column 4, lines 11-20, 34-35, 45-68; column 5, lines 1-31	1-3, 4/1-3, 5/4/1-3, 8
A	KIM, J et al., Deuterated analogues of 4,8-dimethyldecanal, the aggregation pheromone of <i>Tribolium castaneum</i> : synthesis and pheromonal activity, <i>Journal of Labelled Compounds and Radiopharmaceuticals</i> , 2004, Vol. 47, pages 921-934 [retrieved on 2014-06-29]. Retrieved from the Internet: <URL: http://www.reocities.com/junheon/Publications/2004deuterated.pdf > <DOI: 10.1002/jlcr.881>; page 921, summary; page 922, figure 1; page 928, paragraph 4; page 929, paragraph 1	1-3, 4/1-3, 5/4/1-3, 8
A	WANG, HL et al., Biosynthesis of Unusual Moth Pheromone Components Involves Two Different Pathways in the Navel Orangeworm, <i>Amyelois transitella</i> , <i>Journal of Chemical Ecology</i> , 15 April 2010, Vol. 36, pages 535-547 [retrieved on 2014-06-29]. Retrieved from the Internet: <URL: http://www.escholarship.org/uc/item/0xd477sr#page-1 > <DOI: 10.1007/s10886-010-9777-3>; page 543, see figure 4, the structure for D3-11Z,13Z-11, 13-Hexadecadienal	1-3, 4/1-3, 5/4/1-3, 8
A	US 4,632,829 A (HEDIN, PA et al.) 30 December 1986; abstract; claim 3	1-3, 4/1-3, 5/4/1-3, 8
A	US 2012/0034288 A1 (MCKIBBEN, GH) 09 February 2012; paragraphs [0005], [0015], [0031]-[0032]	1-3, 4/1-3, 5/4/1-3, 8

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

03 July 2014 (03.07.2014)

Date of mailing of the international search report

28 JUL 2014

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-3201

Authorized officer:

Shane Thomas

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US14/30065

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.: 6-7, 9-16
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.