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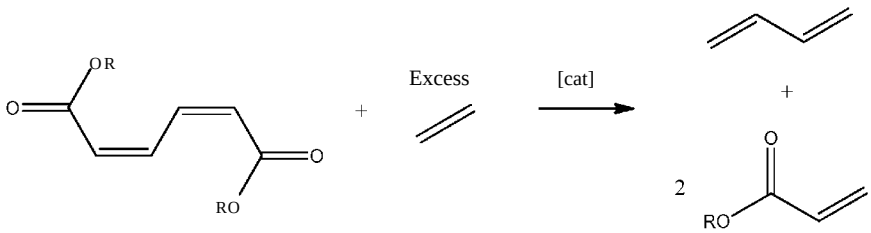

FIGURE 1A

(57) Abstract: Described herein are methods for producing 1,3-butadiene and one or more of acrylic acid and esters of acrylic acid from muconic acid or a derivative thereof.

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SYNTHESIS OF OLEFINS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of, and priority to, United States provisional patent application serial number 61/566,563 entitled "SYNTHESIS OF OLEFINS" filed 02 December 201 1, which is incorporated by reference herein in its entirety.

FIELD

[0002] Described herein are methods for the synthesis of olefins from muconic acid.

BACKGROUND

[0003] Butadiene, acrylic acid and acrylates are produced commercially in large volume from petroleum-derived chemicals.

[0004] A need exists for methods for making butadiene, acrylic acid and acrylates from renewable feedstocks that are not derived from petroleum sources.

SUMMARY

[0005] Described herein are methods of producing 1,3-butadiene, acrylic acid or one or more esters of acrylic acid, or both 1,3-butadiene and acrylic acid or one or more esters of acrylic acid from muconic acid or a derivative thereof. Muconic acid used in the methods described herein may be derived from any source. Any one of cis,cis-muconic acid, cis,trans-muconic acid, and trans,trans-muconic acid, or any combination thereof may be used. Advantageously, in some embodiments, muconic acid is derived microbially from genetically modified organisms using renewable, non-fossil fuel carbon sources.

[0006] In one aspect, provided herein are methods of producing 1,3-butadiene and acrylic acid and/or one or more acrylic acid esters by contacting a compound according to the formula $R^1OOC\text{-}CH=CH\text{-}CH=CH\text{-}COOR^2$ with ethylene or substituted ethylene under conditions suitable for the formation of 1,3-butadiene and one or more of $R^1OOC\text{-}CH=CH_2$ and $R^2OOC\text{-}CH=CH_2$. In the formulas, R^1 is hydrogen, hydrocarbyl or substituted hydrocarbyl, for instance Ci_{-30} hydrocarbyl, and R^2 is hydrogen, hydrocarbyl or substituted hydrocarbyl, for instance Ci_{-30} hydrocarbyl. In certain embodiments, R^1 and R^2 are the same. In other embodiments, R^1 and R^2 are different. In preferred embodiments, ethylene is unsubstituted. The compound can be contacted with ethylene or substituted ethylene under any conditions apparent to one of skill in the art for formation of 1,3-butadiene and one or more of$R^OC\text{-}CH=CH_2$ and $R^OOC\text{-}CH=CH_2$. Exemplary conditions are described herein. In certain

embodiments, the reaction is catalyzed by any catalyst apparent to those of skill in the art, or mixtures thereof. Exemplary catalysts are described herein including, for instance, metathesis catalysts. The compound R^1OOC-CH=CH-CH=CH-COOfC ^{2} can be obtained from any source or produced by any technique apparent to those of skill in the art such as those described herein. The compound $R^1OOC–CH=CH–CH=CH–COOR^2$ can have any stereochemistry including cis-cis, cis-trans, trans-trans, and mixtures thereof. The methods are also applicable to mixtures of compounds according to the formula R^1OOC-CH=CH-CH=CH-COOR ^{2}, for instance those having different R^1 groups, different R^2 groups or both different R^1 and R2 groups.. In some embodiments, provided herein are intermediates of such a reaction, comprising, for instance, catalyst bonded to the compound according to formula R^1OOC-CH=CH-CH=CH-COOR ^{2}, or a portion thereof, as illustrated in the methods and reaction schemes herein.

[0007] In some embodiments, described herein are methods for producing at least one of 1,3-butadiene and acrylic acid by reacting muconic acid with ethylene in the presence of a metathesis catalyst under conditions sufficient to produce at least one of 1,3-butadiene and acrylic acid. Also described herein are methods for producing at least one of 1,3-butadiene and an ester of acrylic acid by reacting an ester of muconic acid with ethylene in the presence of a metathesis catalyst under conditions sufficient to produce at least one of 1,3-butadiene and an ester of acrylic acid. For example, a dialkyl muconate having formula R^1OOC-CH=CH-CH=CH-COOR ^{1} may be reacted with ethylene in the presence of a metathesis catalyst to form at least one of 1,3-butadiene and an alkyl acrylate having formula R^1OOC-CH=CH2, where R^1 is any alkyl group, e.g., R^1 maybe a Ci-Cio alkyl group.

[0008] The muconic acid ester can be produced by any method apparent to those of skill in the art. In some embodiments, the methods comprise providing microbially-derived muconic acid, forming one or more of a cis,cis-muconic acid ester, a cis,trans-muconic acid ester, and a trans,trans-muconic acid ester or a mixture thereof from the microbially-derived muconic acid, and reacting the one or more muconic acid esters with ethylene in the presence of a metathesis catalyst to form one or more acrylic acid esters.

[0009] Certain variations of the methods comprise providing microbially-derived muconic acid, forming one or more of a cis,cis-muconic acid ester, a cis,trans-muconic acid ester, and a trans,trans-muconic acid ester or a mixture thereof from the microbially-derived muconic acid, and reacting the one or more muconic acid esters with ethylene in the presence of a metathesis catalyst to form one or more acrylic acid esters and 1,3-butadiene.

[0010] Some methods comprise reacting muconic acid or a muconic acid ester with ethylene in the presence of a metathesis catalyst in a reactor to produce gaseous reaction products in the reactor, and obtaining 1,3-butadiene from the gaseous reaction products. In some variations, the methods comprise withdrawing at least a portion of gaseous reaction products from the reactor during the reaction.

[0011] Certain variations of the methods comprise reacting muconic acid or a muconic acid ester with ethylene in the presence of a metathesis catalyst in a reactor to produce one or more reaction products in a liquid phase in the reactor, and obtaining acrylic acid or an acrylic acid ester from the liquid phase. In some variations, the method may comprise withdrawing at least a portion of gaseous content in a head space during the reaction.

[0012] Some variations of the methods comprise reacting muconic acid or a muconic acid ester with ethylene in the presence of a metathesis catalyst in a reactor to produce one or more reaction products in a gas phase in the reactor and one or more reaction products in a liquid phase in the reactor, obtaining 1,3-butadiene from the gaseous reaction products, and obtaining acrylic acid or an acrylate ester from the liquid phase. The methods may comprise withdrawing at least a portion of the gaseous reaction products from the reactor during the reaction.

[0013] For the methods described herein, any suitable metathesis catalyst or combination of catalysts may be used. In certain variations, the metathesis catalyst comprises ruthenium. In some variations, the catalyst is a second generation Grubbs catalyst or a second generation Hoveyda-Grubbs catalyst.

[0014] Also disclosed herein are reactors for carrying out the methods and reactors comprising one or more of the reactants, intermediates and products described herein. Further disclosed are industrial chemicals, polymers, and oils derived from 1,3-butadiene made from the methods described herein, and industrial chemicals, polymers and oils derived from acrylic acid or esters of acrylic acid made from the methods described herein. Advantageously, if the 1,3-butadiene, acrylic acid, or acrylates are synthesized using microbially-derived muconic acid and optionally plant-derived ethylene, such industrial chemicals, polymers and oils may be synthesized with little or no carbon content originating from fossil fuels.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIGURE 1A provides a schematic diagram showing the synthesis of one mole 1,3-butadiene and two moles acrylic acid or ester of acrylic acid from muconic acid or an ester of muconic acid.

[0016] FIGURE IB shows a reaction mechanism, with an inset providing a GC-FID spectrum of reaction products detected in the head space showing a retention time consistent with that of 1,3-butadiene, 1-butene and/or 2-butene. It should be noted that the GC-FID described for Examples 8-126 was used to prepare the inset, and the column cannot resolve 1,3-butadiene from butene.

[0017] FIGURE 2 depicts an experimental apparatus used to recover gaseous products from the reactor head space for Examples 2-7.

[0018] FIGURE 3A provides a non-limiting example of a reactor that can be used to carry out methods described herein.

[0019] FIGURE 3B provides a non-limiting example of a reactor that can be used to carry out methods described herein.

[0020] FIGURE 4A shows a GC-FID spectrum for the liquid phase reaction mixture for Example 2.

[0021] FIGURES 4B-4C shows GC-FID spectra of toluene comprising reaction products collected from the reactor head space for Example 2.

[0022] FIGURE 4D shows a GC-MS spectrum for the liquid phase reaction mixture of Example 2.

[0023] FIGURE 4E shows a mass spectrum for the peak at 5.3 19 minutes (reference FIG. 4D) for the reaction mixture for Example 2 (upper trace), as compared with a mass spectrum of butyl acrylate standard obtained from NIST (lower trace).

[0024] FIGURE 4F shows a mass spectrum for the peak at 7.376 min (reference FIG. 4D) for the liquid phase reaction mixture for Example 2, showing a species at m/z = 154.

[0025] FIGURE 4G shows a GC-MS spectrum of toluene comprising reaction products collected from the reactor head space for Example 2.

[0026] FIGURE 4H shows a mass spectrum for the peak at 2.432 minutes (reference FIG. 4G) for toluene comprising reaction products collected from the reactor head space for Example 2.

[0027] FIGURE 5A shows a GC-FID spectrum for the liquid phase reaction mixture for Example 3.

[0028] FIGURES 5B-5D shows a GC-FID spectrum for toluene comprising reaction products collected from the reactor head space for Example 3. FIGURE 5D includes overlays

showing GC-FID spectra for toluene comprising reaction products collected from the reactor head space for Example 2, for a 1,3-butadiene standard, and for a sample from Example 3 co-injected with 1,3-butadiene.

[0029] FIGURE 5E shows a GC-MS spectrum for the liquid phase reaction mixture of Example 3.

[0030] FIGURE 5F shows a mass spectrum for the peak at 5.316 minutes (reference FIG. 5E) for the liquid phase reaction mixture for Example 3 (upper trace), as compared with a mass spectrum of butyl acrylate standard obtained from NIST (lower trace).

[0031] FIGURE 5G shows GC-MS for spectra for toluene comprising reaction products collected from the reactor head space for Example 3.

[0032] FIGURE 5H shows a mass spectrum for the peak at 2.432 minutes (reference FIG. 5G) for toluene comprising reaction products collected from the reactor head space for Example 3.

[0033] FIGURE 6A shows a GC-FID spectrum for the liquid phase reaction mixture for Example 6.

[0034] FIGURE 6B shows a GC-FID spectrum for a butyl acrylate standard (upper trace), and overlays of the GC-FID spectrum for the butyl acrylate standard and the GC-FID spectrum for the liquid phase reaction mixture of Example 6 (lower trace).

[0035] FIGURE 6C shows a GC-FID spectrum of $CDCI_3$ comprising reaction products collected from the reactor head space for Example 6.

[0036] FIGURE 6D shows a GC-MS spectrum for the liquid phase reaction mixture of Example 6.

[0037] FIGURE 6E shows a mass spectrum for the peak at 5.316 minutes (reference FIG. 6D) for the liquid phase reaction mixture of Example 6 (upper trace), compared with that of a NIST butyl acetate standard (lower trace).

[0038] FIGURE 6F shows a GC-MS spectrum for $CDCI_3$ comprising reaction products collected from the reactor head space for Example 6.

[0039] FIGURE 6G shows a mass spectrum for the peak at 2.441 minutes (reference FIG. 6F) for $CDCI_3$ comprising reaction products collected from the reactor head space for Example 6.

[0040] FIGURE 6H shows a GC-MS spectrum for a 1,3-butadiene standard (upper trace), and a mass spectrum for the peak at 2.433 minutes (lower trace).

[0041] FIGURE 6I-6K show proton NMR spectra for $CDCI_3$ comprising reaction products collected from the reactor head space for Example 6. Note that the coupling constants inset into FIG. 6J are literature values.

[0042] FIGURE 6L-6O show C 13 NMR spectra for CDC13 comprising reaction products collected from the reactor head space for Example 6.

[0043] FIGURE 7A shows GC-FID spectra for toluene comprising reaction products collected from the reactor head space for Example 7, and overlays of a GC-FID spectrum for a 1,3-butadiene standard, and a GC-FID spectrum for the sample for Example 7 co-injected with a 1,3-butadiene standard.

[0044] FIGURE 7B shows a GC-FID spectrum for a butyl acrylate standard (upper trace), and overlays of the GC-FID spectra for the butyl acrylate standard and the liquid phase reaction mixture for Example 7 (lower trace).

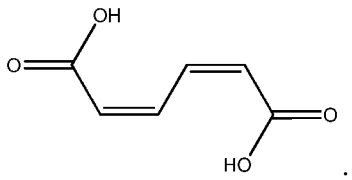
[0045] FIGURE 8 provides a graph of mol butyl acrylate formed as a function of mole di-n-butyl muconate converted for Examples 8-126. The solid line indicates a slope of 2, in which 2 moles butyl acrylate are formed per mole di-n-butyl muconate converted.

DETAILED DESCRIPTION

a) Definitions

[0046] "Muconic acid" or hexa-2,4-dienedioic acid has the formula HOOC-CH=CH-CH=CH-COOH. Muconic acid is known to have three stereoisomers: cis,cis-muconic acid, trans,trans-muconic acid, and cis,trans-muconic acid. Unless specifically indicated otherwise, "muconic acid" as used herein refers to any isomer, or any mixture thereof.

[0047] Cis,cis-muconic acid has the structure:



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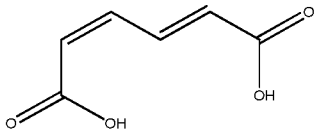
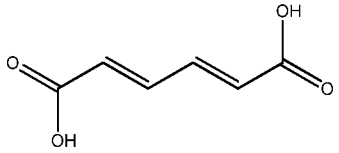
[0048] Cis,trans-muconic acid has the structure:



[0049] Trans,trans-muconic acid has the structure:

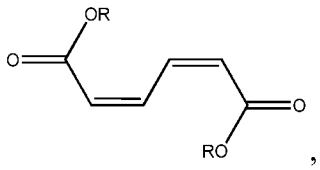


[0050] As used herein, the terms "muconic acid ester," "ester of muconic acid," "muconate ester" and "muconate" are used interchangeably, and each term encompasses diesters and monoesters of muconic acid, and mixtures thereof.

[0051] A muconic acid monoester has formula HOOC-CH=CH-CH=CH-COOR ^{1}, where R^{1} can be any aliphatic or aromatic hydrocarbyl group that is unsubstituted or substituted. A muconic acid diester has formula R^{1}OOC-CH=CH-CH=CH-COOR^{2}, where R^{1} and R^{2} can be the same or different, and R^{1} and R^{2} are each individually any aliphatic or aromatic hydrocarbyl group that is unsubstituted or substituted. A symmetric diester is a diester in which R^{1} and R^{2} are the same. An asymmetric diester is a diester in which R^{1} and R^{2} are different.

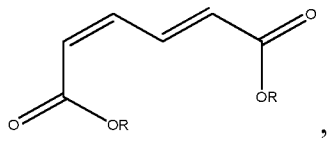
[0052] For muconic acid esters, any one of or any combination of three isomers may exist, cis,cis-muconic acid ester, cis,trans muconic acid ester, and trans,trans muconic acid ester. Muconic acid esters also encompass mixtures of the isomers.

[0053] Cis,cis-dialkyl muconate [(2Z,4Z-dialkyl hexa-2,4-dienedioate)] has the structure:



[0054] where R can be aliphatic or aromatic hydrocarbyl group that is unsubstituted or substituted, for example any alkyl group (e.g., a C1-C30 alkyl group, such as a C1-C20 alkyl group or a C1-C10 alkyl group). For R=n-butyl, cis,cis-dibutyl muconate [(2Z,4Z-dibutyl hexa-2,4-dienedioate)] has the structure:

[0055] Cis,trans-dialkyl muconate [(2Z,4E-dialkyl hexa-2,4-dienedioate)] has the structure:



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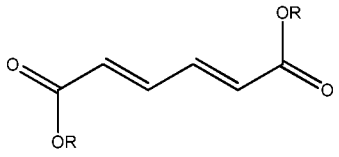
[0056] where R can be any aliphatic or aromatic hydrocarbyl group that is unsubstituted or substituted, for example any alkyl group (e.g., a C1-C30 alkyl group, such as a C1-C20 alkyl group or a C1-C10 alkyl group).

[0057] Trans,trans-dialkyl muconate [(2E,4E-dialkyl hexa-2,4-dienedioate)] has the structure:



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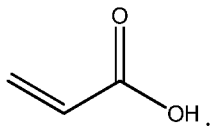
[0058] where R can be any aliphatic or aromatic hydrocarbyl group that is unsubstituted or substituted, for example any alkyl group (e.g., a C1-C30 alkyl group, such as a C1-C20 alkyl group or a C1-C10 alkyl group).

[0059] Acrylic acid, also known as 2-propenoic acid, has the structure:



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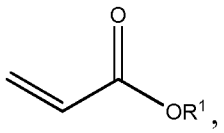
[0060] "Acrylic acid ester" or "acrylate ester" or "acrylate" refers to an ester of acrylic acid having the structure:



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where R^1 can be any aliphatic or aromatic hydrocarbyl group that is unsubstituted or substituted, for example any aliphatic or aromatic hydrocarbyl group that is unsubstituted or substituted.

[0061] As used herein, "ethenolysis" of muconic acid or a muconic acid ester refers to a reaction between muconic acid or muconic acid ester and ethylene in the presence of a metathesis catalyst such that one or more cross-metathesis products between ethylene and muconic acid or between ethylene and a muconic acid ester are formed. Ethylene can be

unsubstituted or substituted with any substituting group described herein. In particular embodiments, ethylene is unsubstituted.

[0062] "Hydrocarbyl" refers to a group containing one or more carbon atom backbones and hydrogen atoms, and the group may optionally contain one or more heteroatoms. Where the hydrocarbyl group contains heteroatoms, the heteroatoms may form one or more functional groups known to one of skill in the art. Hydrocarbyl groups may contain cycloaliphatic, aliphatic, or aromatic groups or any combination thereof. Aliphatic segments may be straight or branched. Aliphatic and cycloaliphatic groups may include one or more double and/or triple carbon-carbon bonds. Included in hydrocarbyl groups are alkyl, alkenyl, alkynyl, aryl, cycloalkyl, cycloalkenyl, alkaryl and aralkyl groups. Cycloaliphatic groups may contain both cyclic moieties and noncyclic portions. In some embodiments, the hydrocarbyl group is a saturated or unsaturated, cyclic or acyclic, unsubstituted or substituted C_1-C30 hydrocarbyl group *(e.g.,* C_1-C20 alkyl, C_1-C20 alkenyl, C_1-C20 alkynyl, cycloalkyl, aryl, aralkyl and alkaryl). A substituted hydrocarbyl group can be substituted with any described moiety, including, but not limited to, one or more moieties selected from the group consisting of halogen (fluoro, chloro, bromo or iodo), alkyl, haloalkyl, hydroxyl, amino, alkylamino, arylamino, alkoxy, aryloxy, nitro, cyano, sulfonic acid, sulfate, phosphonic acid, phosphate, or phosphonate, either unprotected, or protected as necessary, as known to those skilled in the art, for example, as taught in Greene, *et al., Protective Groups in Organic Synthesis,* John Wiley and Sons, Second Edition, 1991.

[0063] "Alkyl" refers to a group having the general formula C_nH_{2n+}i derived from a saturated, straight chain or branched aliphatic hydrocarbon, where n is an integer. In certain embodiments, n is from 1 to about 30, from 1 to about 20, or from 1 to about 10. Non-limiting examples of alkyl groups include Ci-Cs alkyl groups such as methyl, ethyl, propyl, isopropyl, 2-methylpropyl, 2-methylbutyl, 3-methylbutyl, 2,2,-dimethylpropyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 2-2-dimethylbutyl, 3,3-dimethylbutyl, 2-ethylbutyl, n-butyl, isobutyl, tert-butyl, isopentyl, n-pentyl, neopentyl, n-hexyl, isohexyl, n-heptyl, isoheptyl, n-octyl, isooctyl, n-nonyl, isononyl, n-decyl and isodecyl. An alkyl group may be unsubstituted, or may be substituted. In some embodiments, the alkyl group is straight chain having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12 carbons. In some embodiments, the alkyl group is branched having 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 or 12 carbons. Non-limiting examples of moieties with which the alkyl group can be substituted are selected from the group consisting of halogen (fluoro, chloro, bromo or iodo), hydroxyl, amino, alkylamino, arylamino, alkoxy, aryloxy, nitro, cyano, sulfonic acid, sulfate, phosphonic acid, phosphate, or phosphonate, either unprotected, or protected as

necessary, as known to those skilled in the art, for example, as taught in Greene, *et al.*, Protective Groups in Organic Synthesis, John Wiley and Sons, Second Edition, 1991, hereby incorporated by reference.

[0064] "Cycloaliphatic" encompasses "cycloalkyl" and "cycloalkenyl." Cycloaliphatic groups may be monocyclic or polycyclic. A cycloaliphatic group can be unsubstituted or substituted with one or more suitable substituents.

[0065] "Cycloalkyl" refers to a saturated carbocyclic mono- or bicyclic (fused or bridged) ring of 3-12 (e.g., 5-12) carbon atoms. Non-limiting examples of cycloalkyl include C_3-C_8 cycloalkyl groups, *e.g.*, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl groups and saturated cyclic and bicyclic terpenes. Cycloalkyl groups may be unsubstituted or substituted.

[0066] "Cycloalkenyl" refers to a non-aromatic carbocyclic mono- or bicyclic ring of 3 to 12 *{e.g.*, 4 to 8) carbon atoms having one or more double bonds. Non-limiting examples of cycloalkenyl include C_3-C_8 cycloalkenyl groups such as cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, cycloheptenyl, cyclooctenyl, and unsaturated cyclic and bicyclic terpenes. Cycloalkenyl groups may be unsubstituted or substituted.

[0067] "Aryl" refers to an organic radical derived from a monocyclic or polycyclic aromatic hydrocarbon by removing a hydrogen atom. Non-limiting examples of the aryl group include phenyl, naphthyl, benzyl, or tolanyl group, sexiphenylene, phenanthrenyl, anthracenyl, coronenyl, and tolanylphenyl. An aryl group can be unsubstituted or substituted with one or more suitable substituents. Furthermore, the aryl group can be monocyclic or polycyclic. In some embodiments, the aryl group contains at least 6, 7, 8, 9, or 10 carbon atoms. Non-limiting examples of moieties with which the aryl group can be substituted are selected from the group consisting of halogen (fluoro, chloro, bromo or iodo), hydroxyl, amino, alkylamino, arylamino, alkoxy, aryloxy, nitro, cyano, sulfonic acid, sulfate, phosphonic acid, phosphate, or phosphonate, either unprotected, or protected as necessary, as known to those skilled in the art, for example, as taught in Greene, *et al.,* Protective Groups in Organic Synthesis, John Wiley and Sons, Second Edition, 1991, hereby incorporated by reference.

[0068] In the following description, all numbers disclosed herein are approximate values, regardless whether the word "about" or "approximate" is used in connection therewith. Numbers may vary by 1 percent, 2 percent, 5 percent, or, sometimes, 10 to 20 percent. Whenever a numerical range with a lower limit, R^L, and an upper limit, R^u, is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers

within the range are specifically disclosed: $R=R^L+k*(R^u-R^L)$, wherein k is a variable ranging from 1 percent to 100 percent with a 1 percent increment, i.e., k is 1 percent, 2 percent, 3 percent, 4 percent, 5 percent,..., 50 percent, 51 percent, 52 percent,..., 95 percent, 96 percent, 97 percent, 98 percent, 99 percent or 100 percent. Moreover, any numerical range defined by two R numbers as defined in the above is also specifically disclosed.

Methods of Synthesis

[0069] Described herein are methods of producing 1,3-butadiene and acrylic acid and/or one or more acrylic acid esters by contacting a compound according to the formula R^OC-CH=CH-CH=CH-COOR ^{2} with ethylene or substituted ethylene under conditions suitable for the formation of 1,3-butadiene and one or more of R^1OOC-CH=CH_2 and R^2OOC-CH=CH_2. In certain embodiments, described herein are methods for synthesizing 1,3-butadiene, acrylic acid, acrylate esters and derivatives of 1,3-butadiene, acrylic acid, and acrylate esters. The methods may be capable of producing about 2 moles of acrylic acid and one mole 1,3-butadiene per mole muconic acid starting material, about 2 moles acrylate ester and one mole 1,3-butadiene per mole muconic acid diester, or one mole acrylic acid, one mole acrylate ester and one mole 1,3-butadiene per mole muconic acid monoester. Advantageously, in some variations, microbially-derived muconic acid is used in the methods described herein.

[0070] A schematic of an exemplary reaction scheme employed in the methods described herein is provided in FIG. 1A. In FIG. 1A, R may be H or any aliphatic or aromatic hydrocarbyl group, substituted or unsubstituted. In some embodiments, muconic acid is reacted with ethylene in the presence of a metathesis catalyst to produce at least one of 1,3-butadiene and acrylic acid. In some cases, both 1,3-butadiene and acrylic acid are produced. The reaction conditions may be tuned so that about 2 moles of acrylic acid are produced per mole muconic acid consumed, or about 1 mole 1,3-butadiene is produced per mole muconic acid consumed, or about 2 moles acrylic acid and about 1 mole 1,3-butadiene are produced per mole muconic acid consumed. In some embodiments, a muconic acid ester is reacted with ethylene in the presence of a metathesis catalyst to produce at least one of 1,3-butadiene and an acrylate ester. In some cases, both 1,3-butadiene and an acrylate ester are produced. The reaction conditions may be tuned so that about 2 moles of acrylate ester are produced per mole muconic acid ester consumed, or about 1 mole 1,3-butadiene is produced per mole muconic acid ester consumed, or about 2 moles acrylic acid ester and about 1 mole 1,3-butadiene are produced per mole muconic acid ester consumed.

[0071] It should be noted that although the reaction scheme is illustrated with the cis,cis-isomer of the muconic acid or muconic acid ester in FIG. 1A, the reaction may utilize any isomer or any combination of isomers (i.e., cis,cis- isomer, cis,trans- isomer, trans,trans- isomer, or any combination thereof). Also, it should be noted that although the reaction scheme is illustrated as using a symmetrical muconic acid diester in which both R groups are the same, variations exist in which a monoester of muconic acid is used, such that the reaction products are 1,3-butadiene, acrylic acid, and an acrylate ester, and other variations exist in which an asymmetric diester is used in which the two R groups are chemically different such that the reaction products are 1,3-butadiene, and 2 chemically different acrylate esters.

[0072] Some variations of the methods comprise synthesizing acrylic acid or an acrylate ester from muconic acid, muconic acid monoester, or muconic acid diester by reacting muconic acid or a muconic acid ester with ethylene in the presence of a metathesis catalyst. In certain variations, a method may further comprise providing microbially-derived muconic acid and optionally esterifying the microbially-derived muconic acid prior to reaction with ethylene.

[0073] Some variations of the methods comprise synthesizing 1,3-butadiene from muconic acid, muconic acid monoester, or muconic acid diester by reacting muconic acid or a muconic acid ester with ethylene in the presence of a metathesis catalyst. In certain variations, a method may further comprise providing microbially-derived muconic acid and optionally esterifying the microbially-derived muconic acid prior to reaction with ethylene.

[0074] In certain variations, the methods include contemporaneous synthesis of 1,3-butadiene and acrylic acid by reacting muconic acid with ethylene in the presence of a metathesis catalyst, or contemporaneous synthesis of 1,3-butadiene and one or more acrylate esters by reacting a muconic acid ester with ethylene in the presence of a metathesis catalyst. In certain variations, the method may further comprise providing microbially-derived muconic acid and optionally esterifying the microbially-derived muconic acid prior to reaction with ethylene.

Muconic Acid

[0075] Muconic acid used in the methods described herein can be obtained from any viable source or prepared by any technique apparent to one of skill in the art. In some cases, muconic acid is derived from a microbial organism that has been modified to produce muconic acid. Microbially-derived muconic acid may contain any one of or any combination of the cis,cis- , cis-trans- , and trans,trans- isomers of muconic acid. In some instances, the most prevalent isomer in microbially-derived muconic acid is cis,cis-muconic acid. In some instances, the most prevalent isomer in microbially-derived muconic acid is cis,trans-muconic

acid. In some instances, the most prevalent isomer in microbially-derived muconic acid is trans,trans-muconic acid. The muconic acid present in a cell culture medium or fermentation broth used in the microbial synthesis may be used as is, purified, or isolated before undergoing metathesis reaction. Non-limiting examples of purification or isolation methods include extraction, washing, filtration, centrifuge, and combinations thereof.

[0076] In certain variations, muconic acid is microbially synthesized from readily available carbon sources capable of biocatalytic conversion to erythrose 4-phosphate (E4) and phosphoenolpyruvate (PEP) in microorganisms having a common pathway of aromatic amino acid biosynthesis. Carbon sources used in the synthesis are advantageously renewable, being derived from starch, cellulose and sugars found, for example, in corn, sugar cane, sugar beets, wood pulp and other biomass. One carbon source that can be used to make muconic acid is **D**-glucose.

[0077] Any suitable method for microbial synthesis of muconic acid may be used. A host microbial organism is selected such that it produces the precursor of a muconate pathway, either as a naturally produced molecule or as an engineered product that produces the precursor or increases production of the precursor naturally produced by the host organism. In some cases, an engineered organism is generated from a host that contains the enzymatic capability to synthesize muconate. Increased synthesis or accumulation of muconate can be accomplished by overexpression of nucleic acids encoding one or more muconate pathway enzymes or proteins. Engineered organisms may be designed to produce muconate through overexpression of any number of the nucleic acids encoding muconate biosynthetic pathway enzymes or proteins. Non-limiting examples of pathways that can be used for microbial synthesis of muconic acid are provided in U.S. Pat. No. 5,616,496, International Patent application PCT/US20 10/02 1894, International patent application PCT/US201 1/020681, and International patent application PCT/US20 10/044606, each of which is incorporated herein by reference in its entirety.

[0078] Host microbial organisms suitable for synthesizing muconic acid may be selected from genera possessing an endogenous common pathway of aromatic amino acid biosynthesis. In certain embodiments, the host cells are recombinantly modified to produce the muconic acid, or a precursor thereof. Illustrative examples of suitable host cells include any Archae, prokaryotic, or eukaryotic cell. Examples of an Archae cell include, but are not limited to those belonging to the genera: *Aeropyrum, Archaeoglobus, Halobacterium, Methanococcus, Methanobacterium, Pyococcus, Sulfolobus, and Thermoplasma.* Illustrative examples of Archae strains include but are not limited to: *Aeropyrum pernix, Archaeoglobus fulgidus,*

Methanococcus jannaschii, Methanobacterium thermoautotrophicum, Pyococcus abyssi, Pyococcus horikoshii, Thermoplasma acidophilum, Thermoplasma volcanium.

[0079] Examples of a procaryotic cell include, but are not limited to those belonging to the genera: Agrobacterium, Alicyclobacillus, Anabaena, Anacystis, Arthrobacter, Azobacter, Bacillus, Brevibacterium, Chromatium, Clostridium, Corynebacterium, Enterobacter, Erwinia, Escherichia, Lactobacillus, Lactococcus, Mesorhizobium, Methylobacterium, Microbacterium, Phormidium, Pseudomonas, Rhodobacter, Rhodopseudomonas, Pvhodospirillum, Rhodococcus, Salmonella, Scenedesmun, Serratia, Shigella, Staphlococcus, Strepromyces, Synnecoccus, and Zymomonas.

[0080] Illustrative examples of prokaryotic bacterial strains include but are not limited to: Bacillus subtilis, Bacillus amyloliquefacines, Brevibacterium ammoniagenes, Brevibacterium immariophilum, Clostridium beigerinckii, Enterobacter sakazakii, Escherichia coli, Lactococcus lactis, Mesorhizobium loti, Pseudomonas aeruginosa, Pseudomonas mevalonii, Pseudomonas pudica, Rhodobacter capsulatus, Rhodobacter sphaeroides, Rhodospirillum rubrum, Salmonella enterica, Salmonella typhi, Salmonella typhimurium, Shigella dysenteriae, Shigella flexneri, Shigella sonnei, Staphylococcus aureus, and the like.

[0081] In general, if a bacterial host cell is used, a non-pathogenic strain is preferred. Illustrative examples of non-pathogenic strains include but are not limited to: *Bacillus subtilis, Escherichia coli, Lactibacillus acidophilus, Lactobacillus helveticus, Pseudomonas aeruginosa, Pseudomonas mevalonii, Pseudomonas pudita, Rhodobacter sphaeroides, Rodobacter capsulatus, Rhodospirillum rubrum,* and the like.

[0082] Examples of eukaryotic cells include but are not limited to fungal cells. Examples of fungal cell include, but are not limited to those belonging to the genera: *Aspergillus, Candida, Chrysosporium, Cryotococcus, Fusarium, Kluyveromyces, Neotyphodium, Neurospora, Penicillium, Pichia, Saccharomyces, Trichoderma and Xanthophyllomyces* (formerly *Phaffia).*

[0083] Illustrative examples of eukaryotic strains include but are not limited to: Aspergillus nidulans, Aspergillus niger, Aspergillus oryzae, Candida albicans, Chrysosporium lucknowense, Fusarium graminearum, Fusarium venenatum, Kluyveromyces lactis, Neurospora crassa, Pichia angusta, Pichia fmlandica, Pichia kodamae, Pichia membranaefaciens, Pichia methanolica, Pichia opuntiae, Pichia pastoris, Pichia pijperi, Pichia quercuum, Pichia salictaria, Pichia thermotolerans, Pichia trehalophila, Pichia stipitis, Streptomyces ambofaciens, Streptomyces aureofaciens, Streptomyces aureus, Saccaromyces bayanus, Saccaromyces

boulardi, Saccharomyces cerevisiae, Streptomyces fungicidicus, Streptomyces griseochromogenes, Streptomyces griseus, Streptomyces lividans, Streptomyces olivogriseus, Streptomyces rameus, Streptomyces tanashiensis, Streptomyces vinaceus, Trichoderma reesei and Xanthophyllomyces dendrorhous (formerly Phaffia rhodozyma).

[0084] In general, if a eukaryotic cell is used, a non-pathogenic strain is preferred. Illustrative examples of non-pathogenic strains include but are not limited to: *Fusarium graminearum, Fusarium venenatum, Pichia pastoris, Saccaromyces boulardi, and Saccaromyces cerevisiae.*

[0085] In addition, certain strains have been designated by the Food and Drug Administration as Generally Regarded As Safe (GRAS). These strains include: *Bacillus subtilis, Lactibacillus acidophilus, Lactobacillus helveticus,* and *Saccharomyces cerevisiae.* In certain embodiments, the strain has been designated by the Food and Drug Administration as Generally Regarded As Safe.

[0086] In some variations, host organisms include mutant strains of *Escherichia coli* genetically engineered to express selected genes endogenous to *Klebsiella pneumoniae* and *Acinetobacter calcoaceticus.* In one example, an *E. coli* mutant for use in making muconic acid is E. coli AB2834, an auxotrophic mutant that is unable to catalyze the conversion of dehydoshikimate (DHS), an intermediate along the common pathway of aromatic amino acid biosynthesis, into shikimic acid due to a mutation in the aroE locus which encodes the enzyme shikimate dehydrogenase. The common pathway of aromatic amino acid biosynthesis produces the aromatic amino acids phenylalanine, tyrosine, and tryptophan in bacteria and plants. The common pathway ends with the molecule chorismate, which is subsequently converted into phenylalanine, tyrosine, and tryptophan by three separate terminal pathways.

[0087] In some embodiments, carbon flow directed into aromatic amino acid biosynthesis can proceed along the common pathway to yield elevated intracellular levels of DHS, which accumulates due to a mutation along the common pathway of aromatic amino acid biosynthesis, which prevents the conversion of DHS to chorismate. The DHS serves as a substrate for the enzyme 3-dehydroshikimate dehydratase (aroZ), and action of this enzyme of DHS produces protocatechuate. Protocatechuate is thereafter converted to catechol via the enzyme known as protocatechuate decarboxylase (aroY). The catechol thus formed is converted to cis,cis-muconic acid by the action of the enzyme catechol 1,2-dixoygenase (catA).

[0088] The three enzymes (aroZ, aroY, and catA) catalyzing the biosynthesis of cis,cis-muconate from DHS can be expressed in a host cell using recombinant DNA comprising genes

encoding these three enzymes under control of a suitable promoter. Carbon flow can be forced away from the pathway of aromatic amino acid synthesis and into the divergent pathway to produce cis,cis muconate. The cis,cis muconate thus formed can accumulate in the extracellular medium which can be separated from the cells by centrifuge, filtration, or any other method known in the art.

Muconic Acid Esters

[0089] Muconic acid esters may be obtained from any source or prepared by any method apparent to those of skill in the art. In some embodiments, muconic acid esters are prepared by esterification of muconic acid. Any suitable esterification method known in the art may be used to obtain the desired monoester or diester. Muconic acid may be contacted with an esterifying agent under conditions suitable to form the desired ester. Non-limiting examples of esterifying agents include alkanols (e.g., Ci-Cio alkanols), polyols, polyalkylene glycols having one or more hydroxyl groups and one or more ether groups, aryl alcohols (e.g. phenol or isomers of dihydroxyl benzene), and aryl substituted alcohols (e.g., benzyl alcohol). In some cases, muconic acid is contacted with one or more esterifying agents in the presence of one or more acids. Non-limiting examples of suitable acids include sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid, p-toluene sulfonic acid, and Lewis acids. The esterification reaction may be carried out in the presence of acid at an elevated temperature, e.g., about 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C, 120°C, 130°C, 140°C, or 150°C. As another example, muconic acid may be esterified by reacting with an alcohol in the presence of a base (e.g., pyridine, a tertiary amine, or aqueous NaOH). Further non-limiting examples of esterification reactions for muconic acid are provided in International Patent Publication WO 2010/148063, which is incorporated herein in its entirety.

Isomers of Muconic Acid and Muconic Acid Esters

[0090] In some variations, the methods may comprise isomerizing the muconic acid or muconic acid ester prior to the metathesis reaction. In some instances, it may be desired to isomerize muconic acid to form predominantly the cis,cis- isomer, the cis,trans- isomer, or the trans,trans isomer. For example, in some cases muconic acid produced via microbial synthesis may be the cis,cis-muconic acid isomer or a mixture of cis,cis-muconic acid and cis,trans-muconic acid, and it may be desired to isomerize the cis,cis muconic acid (or ester) to form cis,trans muconic acid or trans,trans muconic acid (or ester), or to isomerize cis,trans muconic acid to form cis,cis-muconic acid or trans,trans-muconic acid before the metathesis reaction. Isomerization may occur using any suitable isomerization conditions and appropriate

isomerization conditions and catalysts (if needed). For example, the cis,cis- isomer can be isomerized to the cis,trans- isomer in boiling water without a need for a catalyst. In some variations, iodine is used as a catalyst for isomerization, and in some variations iodine-catalyzed photochemical isomerization of cis,cis- or cis,trans- isomers to trans,trans- isomers can be used. Non-limiting examples of methods for isomerizing muconic acid are provided in International Patent Publication WO 2010/148063 and in Elvidge J A et al., Journal of the Chemical Society, Chemical Society, Letchworth, GB, 1 January 1950 (1950-01-01), pages 2235-2241, each of which is incorporated by reference herein in its entirety. It should be understood that esterification of muconic acid may occur prior to isomerization to form desired isomers, or isomerization to form desired isomers may occur prior to esterification.

[0091] In certain variations, the methods comprise reacting an ester of muconic acid having a formula $R^1OOC-CH=CH-CH=CH-COOR^2$ with ethylene in the presence of a metathesis catalyst to form 1,3-butadiene and/or one or more acrylate esters having formula $R^1OOC-CH=CH_2$ and/or $R^2OOC-CH=CH_2$, where R^1 and R^2 may be the same or different, and R^1 and R^2 may independently be H or any hydrocarbyl group, with the proviso that R^1 and R^2 are not both H. In some cases, R^1 and R^2 are the same, and in other cases, R^1 and R^2 are different. In some cases, 1,3-butadiene is formed. In some cases, one or more acrylate esters are formed. In some cases, both 1,3-butadiene and one or more acrylate esters are formed. In certain variations, one or both of R^1 and R^2 are Ci-Cio alkyl groups. For example, one or both of R^1 and R^2 may be selected from the group consisting of methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, t-butyl, n-pentyl, isopentyl, 2-methylpentyl, 3-methylpentyl, 2-ethylbutyl, n-hexyl, isohexyl, 2-methylhexyl, 3-methylhexyl, 4-methylhexyl, n-heptyl, isoheptyl, 2-methylheptyl, 3-methylheptyl, 4-methylheptyl, 5-methylheptyl, 2-ethylhexyl, 3-ethylhexyl, 4-ethylhexyl, 5-ethylhexyl, 6-ethylhexyl, n-octyl, isooctyl, 2-methyloctyl, 3-methyloctyl, 4-methyloctyl, 5-methyloctyl, 6-methyloctyl, 2-ethylheptyl, 3-ethylheptyl, 4-ethylheptyl, 5-ethylheptyl, n-nonyl, isononyl, 2-methylnonyl, 3-methylnonyl, 4-methylnonyl, 5-methylnonyl, 6-methylnonyl, 7-methylnonyl, 2-ethyloctyl, 3-ethyloctyl, 4-ethyloctyl, 5-ethyloctyl, 6-ethyloctyl, n-decyl, and isodecyl. For example, a dialkyl muconate having formula $R^1OOC-CH=CH-CH=CH-COOR^1$ may be reacted with ethylene in the presence of ethylene to form 1,3-butadiene and/or an acrylate ester having formula $R^1OOC-CH=CH_2$. In some variations, dimethyl muconate is reacted with ethylene in the presence of a metathesis catalyst to form 1,3-butadiene and/or methyl acrylate. In some variations, diethyl muconate is reacted with ethylene in the presence of a metathesis catalyst to form 1,3-butadiene and/or ethyl acrylate. In some variations, di-n-propyl muconate is reacted with ethylene in the presence of a metathesis catalyst to form 1,3-

butadiene and/or propyl acrylate. In some variations, di-n-butyl muconate is reacted with ethylene in the presence of a metathesis catalyst to form 1,3-butadiene and/or n-butyl acrylate.

[0092] Without being bound by theory, a reaction mechanism is provided in FIG. IB, where for simplicity the muconate ester is illustrated as a symmetrical muconate ester or muconic acid having formula ROOC-CH=CH-CH=CH-COOR, where R can be H or any hydrocarbyl group. It should be understood that asymmetrical diesters or monoesters of muconic acid, or muconic acid may be used as the reactant. It should also be understood that although the cis,cis- isomer is illustrated in FIG. IB, any one of the cis,cis-, cis,trans-, or trans,trans- isomers of the muconic acid or muconic acid ester may be used in the metathesis reactions described herein. As shown in FIG. IB, the metathesis reaction of muconic acid or muconate ester with ethylene may include a first metathesis cycle in which an intermediate having formula CH_2=CH-CH=CH-COOR (hydrocarbyl penta-2,4-dienoate) may be formed. The intermediate product may then undergo a second metathesis cycle in which 1,3-butadiene and/or an acrylate ester (or acrylic acid) having formula CH_2=CH-COOR is formed.

Reaction Conditions and Catalysts

[0093] The methods provided herein can proceed under any reaction conditions deemed suitable for the production of 1,3-butadiene and acrylic acid and/or one or more acrylic acid esters apparent to those of skill in the art without limitation whatsoever. In certain embodiments, the reactions are catalyzed. The catalyst can be any catalyst deemed suitable by the practitioner of skill. In particular embodiments, the catalyst is a metathesis catalyst, or a mixture thereof. Exemplary catalysts are described in the sections below. Reaction conditions such as temperature, pressure, reaction time, solvent, amount of reactants, amount of catalyst, and so forth, are within the skill of the practitioner in the art. Exemplary conditions are provided herein.

[0094] In certain embodiments, any suitable metathesis catalyst, or any suitable combination of catalysts useful for metathesis may be used. Non-limiting examples of metathesis catalysts include metal carbene catalysts based on transition metals, such as ruthenium, osmium, nickel, tungsten, osmium, chromium, rhenium, or molybdenum wherein at least one ligand or complexing agent is coordinated with or bound to the metal atom. Non-limiting examples of ligands include phosphines, halides, and stabilized carbenes. It should be understood that some catalysts include more than one metal, and in some cases one or more metal-containing co-catalysts is used.

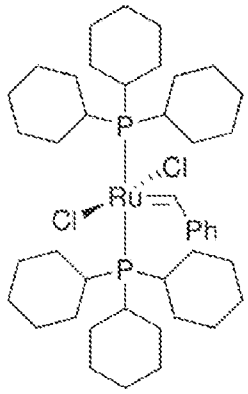
[0095] In some cases, a metathesis catalyst is selected that favors production of the desired ethenolysis reaction products over side reactions such as self-metathesis. Self-metathesis occurs when a substrate-bound catalyst reacts with another substrate molecule rather than ethylene, or ethylene reacts with another ethylene molecule instead of a substrate molecule. In some variations, a metathesis catalyst and reaction conditions are selected to favor kinetically controlled product ratios over thermodynamically controlled product ratios.

[0096] In some cases, a metathesis catalyst based on ruthenium is used. Non-limiting examples of ruthenium-based metathesis catalysts include: ruthenium carbene complexes such as phosphine-containing or phosphine-free ruthenium carbene species which may or may not contain carbene-containing ligands; phosphine-containing or phosphine-free ether-tethered ruthenium alkylidene derivatives; stable 16-electron ruthenium carbene complexes; ruthenium carbene species having ligands comprising Lewis bases such as pyridine; ruthenium benzylidene complexes; and ruthenium trichlorides prepared from late transition metal salts. One example of a phosphine-free carbene ruthenium catalyst is [l,3-bis(2,6-dimethylphenyl)4,5-dihydroimidazol-2-ylidene]$C_5H_5N)_2(Cl)_2Ru$=CHPh. Another example of a ruthenium based catalyst is $Cl_2(PCy_3)_2Ru$=CHPh, where PCy_3 is tricyclohexylphosphine. Additional non-limiting examples of ruthenium-based catalysts include dichloro-3,3-diphenylvinylcarbene-bis(trycyclohexylphosphine)ruthenium(II)bis(tricyclohexylphosphine)benzylidene ruthenium dichloride, bis(tricyclohexylphosphine benzylidene ruthenium dibromide, tricyclohexylphosphine[l,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] [benzylidne]ruthenium dichloride, tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5 -dihydroimidazol-2-ylidene] [benzylidene]ruthenium dibromide, tricyclohexylphosphine[l,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium diiodide, dichloro-3,3-diphenylvinylcarbene-bis(tricyclohexylphosphine)ruthenium(II), and bis(tricylcohexylphosphine)benzylidene ruthenium dichloride. Additional examples of useful metathesis catalysts are described in PCT patent publications WO 99/26949, WO 00/71554, WO 02/14376, and in U.S. patent publication 2002/0177710, each of which is incorporated by reference herein in its entirety.

[0097] In some variations, the methods employ a Grubbs metathesis catalyst based on a ruthenium atom and having general formula **(L)(L')X2RU=CHRG**, where L and L' refer to electron-donating moieties, **X** refers to mono-anionic moieties (e.g., halides such as chlorides, bromides, iodides), and one alkylidene group, and **RG** refers to H or an aliphatic or aromatic group or a group containing one or more heteroatoms. In some variations, both L and L' are phosphines (e.g., trialkyl phosphines, triaryl phosphines, diarylalkyl phosphines) (first

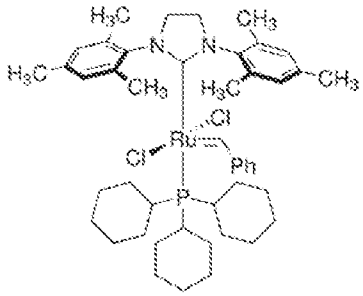
generation Grubbs catalysts). In some variations, one of L,L' is a phosphine group, and the other of L, L' is a saturated N-heterocyclic carbene (second generation Grubbs catalysts). In some variations, R_G is selected from the group consisting of H, phenyl, and -CH=C(CH3)$_2$.

[0098] In some variations, the methods employ a first generation Grubbs catalyst, or a variant or derivative thereof. One exemplary first generation Grubbs catalyst (bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride has structure (1):



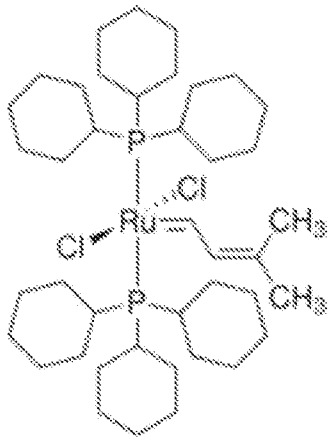
(1).

[0099] In some variations, the methods employ a second generation Grubbs catalyst, or a variant or derivative thereof. One exemplary second generation Grubbs catalyst (also known as [l,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro (phenylmethylene)(tricyclohexylphosphine)ruthenium or benzylidene[1,3-bis(2,4,6-trimethylpheny)-2-imidazolidinylidene] dichloro(tricyclohexylphosphine)ruthenium has structure (2):



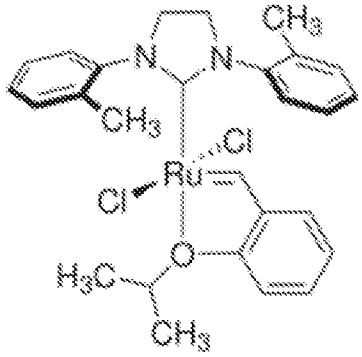
(2).

[00100] In some variations, a Grubbs catalyst dichloro(3-methyl-2-butenylidene)bis(tricyclohexylphosphine)ruthenium(II) having structure (3) is used:



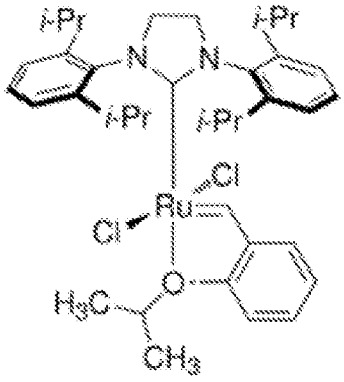
(3).

[00101] In some variations, a catalyst dichloro[l,3-bis(2-methylphenyl)-2-imidazolidinylidene](2-isopropoxyphenylmethylene)ruthenium(II) having structure (4) is used:



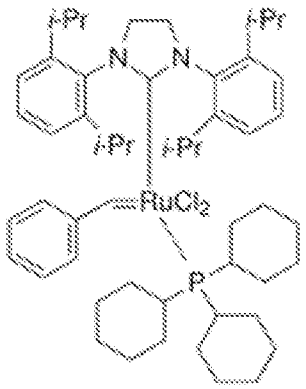
(4).

[00102] In some variations, a catalyst dichloro[l,3-bis(2,6-isopropylphenyl)-2-imidazolidinylidene](2-isopropoxyphenylmethylene)ruthenium(II) having structure (5) is used:



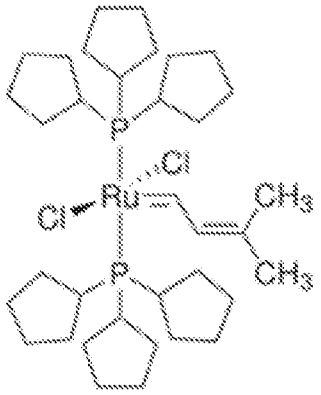
(5).

[00103] In some variations, a catalyst dichloro[l,3-bis(2,6-isopropylphenyl)-2-imidazolidinylidene](benzylidene)(tricyclohexylphosphine)ruthenium(II) and structure (6) is used:



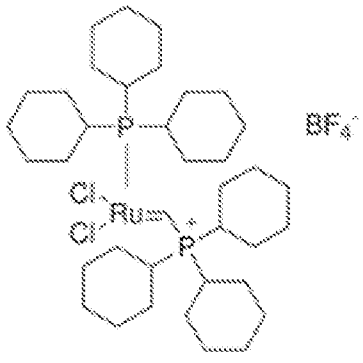
(6).

[00104] In some variations, a catalyst dichloro(3-methyl-2-butenylidene)bis(tricyclopentylphosphine)ruthenium(II) and having structure (7) is used:



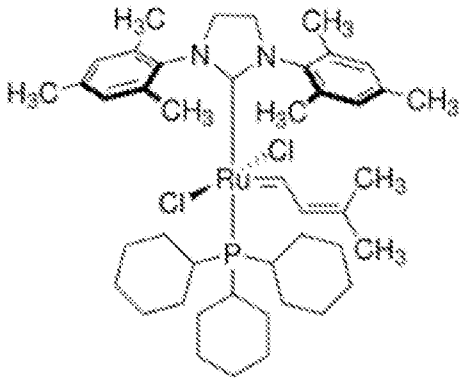
(7).

[00105] In some variations, a catalyst dichloro(tricyclohexylphosphine)[(tricyclohexylphosphoranyl)methylidene]ruthenium(II) tetrafluoroborate having structure (8) is used:



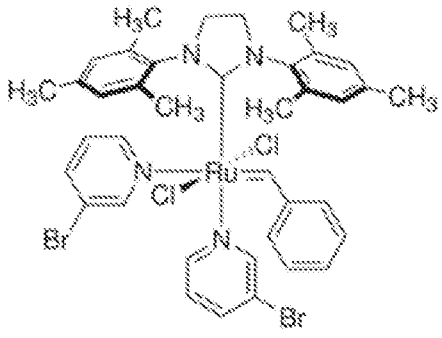
(8).

[00106] In some variations, a catalyst Dichloro[l,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](3-methyl-2-butenylidene) (tricyclohexylphosphine)ruthenium(II) and having structure (9) is used:



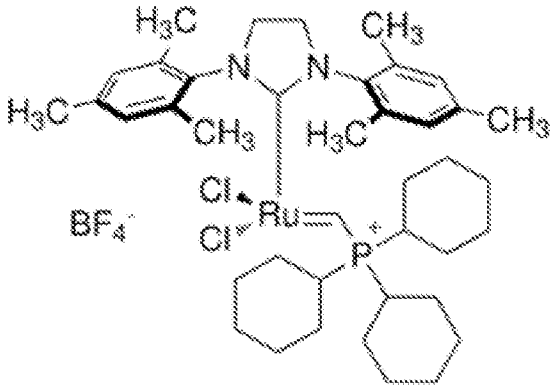
(9).

[00107] In some variations, a catalyst dichloro[l,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine)ruthenium(II) and having formula (10) is used:



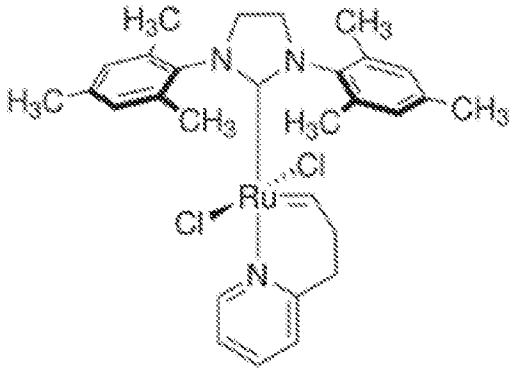
(10).

[00108] In some variations, a catalyst dichloro[l,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene][(tricyclohexylphosphoranyl)methylidene]ruthenium(II) tetrafluoroborate and having structure (11) is used:



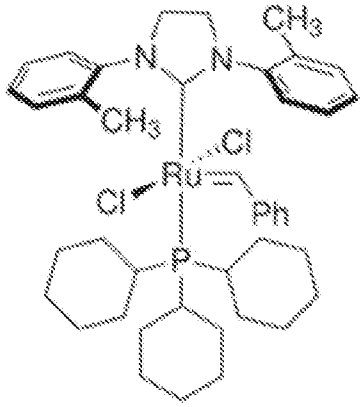
(11).

[00109] In some variations, a catalyst dichloro[l,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene][3-(2-pyridinyl)propylidene]ruthenium(II)and having structure (12) is used:



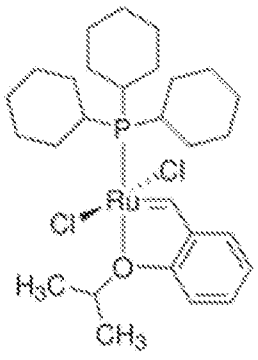
(12).

[00110] In some variations, a catalyst dichloro[l,3-Bis(2-methylphenyl)-2-imidazolidinylidene](benzylidene)(tricyclohexylphosphine)ruthenium(II) and having formula (13) is used:

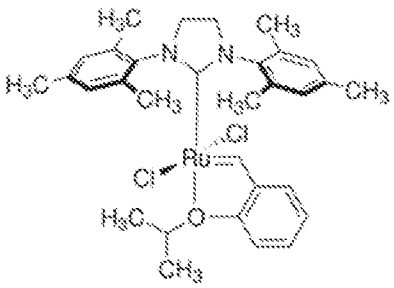


(13).

[00111] In some variations, a Hoveyda-Grubbs catalyst or a variant or derivative thereof is used. For example, one exemplary 1st generation Hoveyda-Grubbs catalyst is dichloro(o-isopropoxyphenylmethylene)(tricyclohexylphosphine)ruthenium(II) having structure (14); and one exemplary 2nd generation Hoveyda-Grubbs catalyst is (l,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isopropoxyphenylmethylene)ruthenium having structure (15):

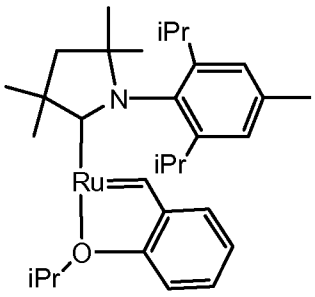


(14); and



(15).

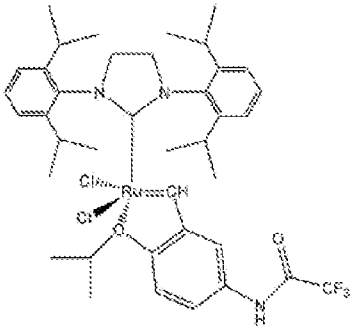
[00112] In some cases, cyclic (alkyl)(amino)carbene (CAAC) ruthenium catalysts are used. For example, a metathesis catalyst having structure (16) may be used:



(16).

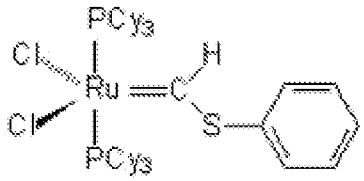
[00113] In another variation, a catalyst having structure (16), except with ethyl groups substituted for isopropyl on the aryl rings is used.

[00114] In some variations, a catalyst [l,3-bis(2,6-di-i-propylphenyl)-4,5-dihydroimidazol-2-ylidene]-[2-i-propoxy-5-(trifiuoroacetamido)phenyl]methylene ruthenium(II) dichloride, having structure (17) is used:



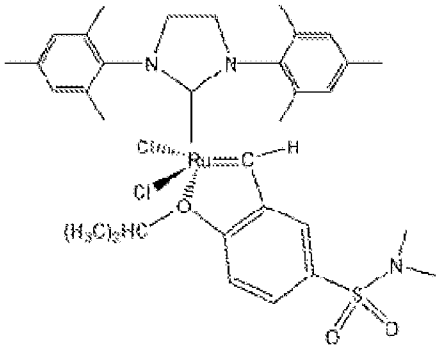
(17).

[00115] In some variations, a catalyst bis(tricyclohexylphosphine)[(phenylthio)methylene] ruthenium(II) dichloride, having structure (18) is used:



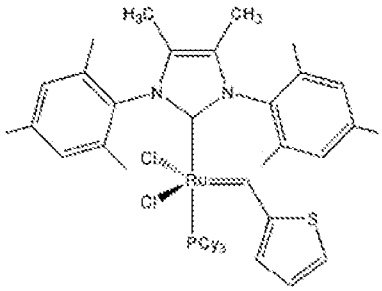
(18).

[00116] In some variations, a catalyst l,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene[2-(i-propoxy)-5-(N,N-dimethylaminosulfonyl)phenyl]methylene ruthenium(II) dichloride, having structure (19) is used:



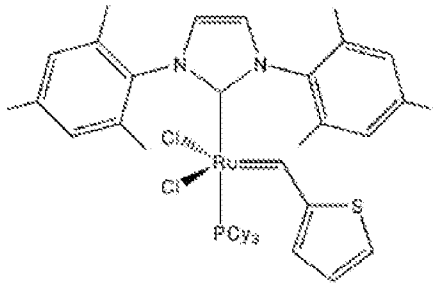
(19).

[00117] In some variations, a catalyst tricyclohexylphosphine[4,5-dimethyl-l,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] [2-thienylmethylene]ruthenium(II) dichloride, having structure (20) is used:



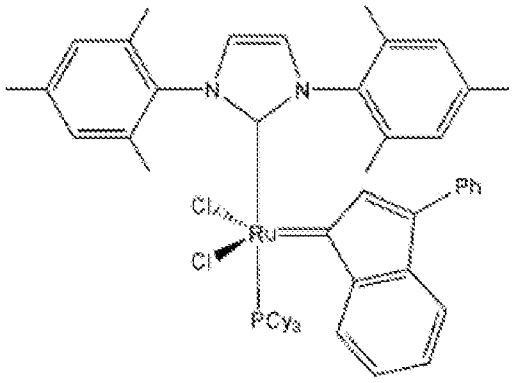
(20).

[001 18] In some variations, a catalyst tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] [2-thienylmethylene]ruthenium(II) dichloride, having structure (21) is used:



(21).

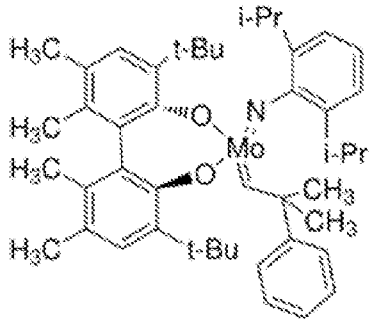
[001 19] In some variations, a catalyst tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] [3-phenyl- 1H-inden- 1-ylidene]ruthenium(II) dichloride, having structure (22) is used:



(22).

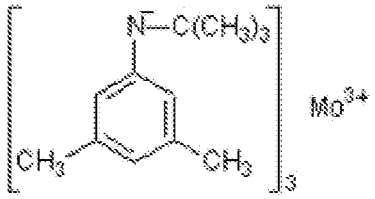
[00120] In some cases, N-aryl,N-aryl N-heterocyclic carbene (NHC) ruthenium metathesis catalysts are used. In some cases, N-aryl,N-alkyl N-heterocyclic carbene (NHC) ruthenium metathesis catalysts are used. Non-limiting examples of N-aryl, N-alkyl NHC ruthenium metathesis catalysts are provided in R.M. Thomas et al., J. Am. Chem. Soc. 201 1, 133, 7490-7496, which is incorporated by reference herein in its entirety.

[00121] In some variations, a Schrock metathesis catalyst or a variant or derivative thereof is used. In some cases, a Schrock-Hoveyda metathesis catalyst or a variant or derivative thereof is used. In some variations, a molybdenum-based catalyst is used. For example, a molybdenum alkoxyimidoalkylidene catalyst may be used. For example, a catalyst 2,6-Diisopropylphenylimido-neophylidene[(S)-(-)-BIPHEN]molybdenum(VI), having structure (23) is used:



(23).

[00122] In some variations, a catalyst tris(N-tert-butyl-3,5-dimethylanilino)molybdenum(III), having structure (24) is used:



(24).

[00123] In some cases, a ligand or other stabilizing compound may be added to the metathesis reaction mixture to stabilize the catalyst and/or to modify the distribution of products. Non-limiting examples of ligands or stabilizing compounds that can be added to the metathesis reaction include trialkylphosphines (e.g., tricyclohexylphosphine, tricyclopentylphosphine); triphenylphosphine; diarylalkylphines such as diphenylcylohexylphosphine; pryidines such as 2,6-dimethylpyridine or 2,4,6-trimethylpyridine; phosphine oxides; and phosphinites.

[00124] The quantity of metathesis catalyst that is used relative to the amount of muconic acid or muconic acid ester may be any quantity that provides for desired products at a desired yield in a desired reaction time. In certain embodiments the ratio moles muconic acid or muconate:moles catalyst is about 10:1 or greater, about 20:1 or greater, about 30:1 or greater, about 40:1 or greater, about 50:1 or greater, about 100:1 or greater, about 500:1 or greater, about 1000:1 or greater, about 5000:1 or greater, about 10,000:1 or greater, about 50,000:1 or greater, about 100,000:1 or greater, or even higher. In some cases, the catalyst is present at an amount such that the ratio moles muconic acid or muconate:moles catalyst is less than about 1,000,000:1, or less than about 500,000:1.

[00125] In some cases, the metathesis catalyst is homogeneous, meaning the catalyst is dissolved in a liquid reaction mixture. Homogeneous catalyst loadings (mol%, meaning (moles catalyst)/(moles muconic acid or muconate)xl00%) may be in a range from about 0.000001 mol% to about 10 mol%, from about 0.00001 mol% to about 10 mol%, from about 0.0001 mol% to about 10 mol%, from about 0.0001 mol% to about 10 mol%, from about 0.001 mol% to about

10 mol%, from about 0.01 mol% to about 10 mol%, from about 0.02 mol % to about 10 mol %, from about 0.05 mol% to about 10 mol%, from about 1 mol% to about 10 mol %, from about 2 mol% to about 10 mol%, from about 0.01mol% to about 5 mol%, from about 0.02mol% to about 5 mol%, from about 0.05mol% to about 5 mol%, from about 1 mol% to about 5 mol%, or from about 2 mol% to about 5 mol%, based on the moles of muconic acid or muconate ester starting material. In certain variations, a homogeneous catalyst loading is about 0.000001 mol%, 0.000005 mol%, 0.00001 mol%, 0.00005 mol%, 0.0001 mol%, 0.0005 mol%, 0.001 mol%, 0.005 mol%, 0.01 mol%, 0.02 mol%, 0.05 mol%, 0.1 mol%, 0.2 mol%, 0.5 mol%, 1 mol%, 1.5 mol%, 2 mol%, 2.5 mol%, 3 mol%, 3.5 mol%, 4 mol%, 4.5 mol%, 5 mol%, 5.5 mol%, 6 mol%, 6.5 mol%, 7 mol%, 7.5 mol%, 8 mol%, 8.5 mol%, 9 mol%, 9.5 mol%, or 10 mol%.

[00126] In other cases, the metathesis catalyst is heterogeneous, e.g., bound to, deposited on, or otherwise supported on any catalyst support known in the art. Use of a heterogeneous catalyst may simplify recovery of the catalyst (e.g., for recycling), increase catalyst strength, and reduce catalyst loss. Non-limiting examples of catalyst supports include silicas, aluminas, silica-aluminas, aluminosilicates, including zeolites and other crystalline porous aluminosilicates, titanias, titanosilicates, zirconia, magnesium oxide, carbon, and reticulated cross-linked polymeric resins, such as functionalized cross-linked polystyrenes (e.g., chloromethyl-functionalized cross-linked polystyrenes). Any suitable method may be used to deposit a catalyst onto a support. Non-limiting techniques include impregnation, ion-exchange, deposition-precipitation, and vapor deposition. In some cases, the catalyst is chemically bound to a support through one or more covalent bonds. Methods for chemically binding organometallic complexes to polymeric supports is known, and is described for example in S.B. Roscoe et al, J. Polymer Science: Part A: Polymer Chem., 2000, 38, 2979-2992 and in M. Ahmed et al., Tetrahedron Letters, 1999, 40, 8657-8662. Any suitable loading of the catalyst on a support may be used to provide the desired reactivity, reaction rate, and reaction products. For example, the catalyst may be loaded onto a support in an amount in a range between about 0.01 wt% and 50 wt%, in a range between about 0.05 wt% and 20 wt%, in a range between about 1 wt% and 10 wt%, where wt % is based on the total weight of the catalyst and support. In certain variations, a catalyst loading may be about 0.01 wt%, 0.05 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt %, 7 wt %, 8 wt %, 9 wt%, 10 wt%, 11 wt%, 12 wt%, 13 wt%, 14 wt %, 15 wt %, 20 wt %, 25 wt%, 30 wt%, 35 wt %, 40 wt%, 45 wt %, or 50 wt %.

[00127] The metathesis reactions described herein can be carried out under a variety of conditions. Reaction temperatures may be in a range from about 0°C to about 100°C, or from about 20°C to about 100°C, or from about 30°C to about 80°C. In some variations, the reaction

temperature is about 30°C, 35°C, 40°C, 45°C, 50°C, 55°C, 60°C, 65°C, 70°C, 75°C or 80°C. Reactions may be carried out at neutral pH, or at a pH that is acidic or basic. Any suitable solvent may be used, e.g., dichloromethane, toluene, dichloroethane, alcohols, water, other aqueous solutions, alcohol/water mixtures, and the like. In general, esterification of muconic acid prior to the metathesis reaction is carried out so that a desired acrylate results. In certain cases, esterification of muconic acid is carried out to make a muconic acid ester that is soluble in solvents in which the metathesis catalyst is soluble. In some cases, sonication is used to aid in solubilizing one or both of the muconic acid or ester and the metathesis catalyst.

[00128] The metathesis reaction can be carried out in a closed reactor with an excess of ethylene. The pressure of ethylene in the reactor can be kept at any level at which the reaction proceeds to provide a desired product mix. In some cases, the ethylene pressure can be kept at a pressure in a range from about 0.3 bar to about 100 bar, or from about 0.5 bar to about 50 bar, or from about 1 bar to about 50 bar, or from about 5 bar to about 50 bar, or from about 5 bar to about 40 bar, or from about 10 bar to about 40 bar. In certain variations, the ethylene pressure is about 1 bar, 5 bar, 10 bar, 15 bar, 20 bar, 25 bar, 30 bar, 35 bar, 40 bar, 45 bar, or 50 bar.

[00129] Any combination of temperature and pressure may be used in the metathesis reaction so that a desired product mix is formed. Referring to Table 10 below, temperatures are indicated in column headings, and pressures (bar) are indicated in row headings. Each "X" discloses a pressure/temperature combinations that may be used to carry out the metathesis reactions described herein.

Table 10. Non-limiting examples of temperature/pressure combinations that can be used to carry out the metathesis reactions described herein.

		Temperature (°C)																				
		0	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	100
Pressure (bar)	1	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	5	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	10	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	15	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	20	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	25	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	30	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	35	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	40	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	45	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	50	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	55	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	60	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

	65	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	70	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	75	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	80	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	85	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	90	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	95	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
	100	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

[00130] In some variations, the metathesis reaction is carried out at a temperature in a range from about 30°C to about 80°C and 10-20 bar ethylene pressure. In some variations, the metathesis reaction is carried out at a temperature in a range from about 30°C to about 80°C and 20-30 bar ethylene pressure. In some variations, the metathesis reaction is carried out at a temperature in a range from about 30°C to about 80°C and 30-40 bar ethylene pressure.

[00131] The reaction time can be any time that is long enough to convert a desired amount of starting material to produce a desired product mix, without being so long that undesired secondary reactions involving reaction products occur. Reaction times may depend on catalyst choice, temperature, solvent, type of reactor (e.g., batch or continuous) and/or pressure. In certain variations for batch reactions, reaction times are in a range from about 0.2 hours to about 24 hours, or from about 0.2 hours to about 10 hours, or from about 0.2 hours to about 6 hours (e.g., about 0.2, 0.5, 1, 1.5, 2, 2.5, 3, 4, 5, or 6 hours).

[00132] As described above, in some cases, the reaction conditions and metathesis catalyst can be selected so that about 2 moles acrylic acid are produced per mole muconic acid reactant, or 2 moles acrylate are produced per mole muconic acid ester reactant. In some variations, reaction conditions and catalyst can be selected so that about 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9 or 2 moles acrylic acid or acrylate are produced per mole reactant. In certain variations, reaction conditions and metathesis catalyst can be selected so that more than one mole acrylic acid or acrylate is produced per mole reactant. In some cases, acrylic acid or an acrylate is produced but no detectable amount of 1,3-butadiene is produced. In certain variations, reaction conditions and metathesis catalyst are selected so that about 1 mole 1,3-butadiene is produced per mole muconic acid or muconic acid ester reactant. In some variations, reaction conditions and catalyst are selected so that about 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, or 1 mol 1,3-butadiene is produced per mole muconic acid or muconic acid ester reactant. In some cases, 1,3-butadiene is produced but no detectable amount of acrylic acid or acrylate is produced. In those reactions that produce both 1,3-butadiene and acrylic acid or both 1,3-butadiene and an acrylate, any relative amounts of 1,3-butadiene and acrylic acid or 1,3 butadiene and acrylate may be present. In certain variations, reaction conditions and metathesis catalyst are selected so that about 2 moles acrylic acid and about 1 mole 1,3-butadiene are

produced per mole muconic acid. In some variations, reaction conditions and catalyst are selected so that about 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9 or 2 moles acrylic acid or acrylate and about 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, or 1 mole 1,3-butadiene are produced per mol muconic acid or muconic acid ester.

[00133] Examples 2-6 herein illustrate reactions in which both 1,3-butadiene and an acrylate was produced. Because the 1,3-butadiene trapped in a cooled solvent to aid in those Examples 2-6, no quantification of the amount of 1,3-butadiene produced was completed. FIG. 8 illustrates many Examples in which the ratio of moles butyl acrylate produced:moles dibutyl muconate consumed is greater than 1, many Examples in which the ratio of moles butyl acrylate produced:moles dibutyl muconate consumed is greater than 1.5, and several Examples in which the ratio of moles butyl acrylate produced:moles dibutyl muconate consumed is about 2. The data in FIG. 8 indicates that an ethylene pressure of about 20 - 40 bar (e.g., about 25 bar) promotes formation of butyl acrylate for several metathesis catalysts.

[00134] The presence of the penta-2,4-dienoate intermediate illustrated in FIG. IB (butyl penta-2,4-dieneoate in the liquid phase reaction mixture if the starting material is dibutyl muconate) is documented in several Examples, which supports the reaction mechanism schematically illustrated in FIG. IB. However, in some reactions, side reactions are possible, which may be due to ethylene-ethylene self-metathesis, or secondary side reactions of 1,3-butadiene or the acrylate after formation. Butene (1-butene or 2-butene) may be a side product that is formed in some instances. In Examples 2, 4, 5, and 6, a side product that is consistent with 1-butene or 2-butene is observed. In Example 7, 1,3-butadiene does not appear to be present, but a side product that is consistent with 1-butene or 2-butene is observed.

[00135] In some variations, the methods comprise obtaining gaseous reaction products (e.g., 1,3-butadiene) from the head space of a closed reactor in which the metathesis reaction is carried out. Acrylic acid or acrylate esters can be recovered from the reaction mixture. Some methods comprise extracting at least a portion of gaseous species in the reactor head space during the course of the reaction. By removing at least a portion of the gaseous reaction products from the head space, the reaction may be driven further to produce more 1,3-butadiene, and/or undesired side reactions (such as undesired secondary reactions or self-metathesis of 1,3-butadiene, undesired secondary reactions or self-metathesis of the penta-2,4-dieneoate intermediate, or reverse reactions) may be inhibited. Any suitable scheme and mechanism may be employed to remove at least a portion of the reactor head space during the reaction. In some cases, contents of the head space are periodically or intermittently removed by opening a valve

to a connected lower pressure vessel during the course of the reaction. In other cases, at least a portion of the contents of the head space is removed by periodically or intermittently evacuating or pumping out the head space during the course of the reaction. In some variations, a portion of the contents of the reactor head space is continuously or periodically or intermittently bled out of the reactor during the course of the reaction, and an appropriate amount of ethylene is pumped in continuously, periodically, or intermittently to maintain a desired ethylene pressure in the reactor.

Reactors

[00136] Also provided are reactors suitable for carrying out the methods described herein. Exemplary reactors include reactors that comprise a compound according to the formula $R^1OOC\text{-}CH=CH\text{-}CH=CH\text{-}COOR^2$, ethylene or substituted ethylene, one or more catalysts useful for the formation of 1,3-butadiene and/or one or more of $R^1OOC\text{-}CH=CH_2$ and $R^2OOC\text{-}CH=CH_2$.

[00137] One non-limiting example of a reactor that can be used to carry out the reactions described herein using a homogeneous catalyst is shown in FIG. 3A. As shown, the liquid phase reaction mixture in the closed reactor comprises solvent, reactant (muconic acid or muconic acid ester), and metathesis catalyst. Ethylene can be directed into the head space (or optionally bubbled into the solvent) using appropriate fixtures until the desired pressure is reached. At least a portion of the contents of the head space (including gaseous reaction products such as 1,3-butadiene) is allowed to exit from or is extracted from the head space using known techniques. The removal of head space contents can be done in any manner, e.g., on a continuous basis, periodically, or intermittently. The contents of the head space that are removed can then be directed into a separator that is capable of separating ethylene from reaction products such as 1,3-butadiene. Any suitable separator may be used, e.g., a distillation apparatus, a cold trap at a temperature cold enough to liquefy desired reaction products such as 1,3-butadiene but warm enough such that ethylene remains gaseous and can be removed from the separator. Ethylene recovered from the separator can be recycled back into the reactor for reuse. Although not illustrated in FIG. 3A, acrylic acid or acrylate reaction products can be isolated from the liquid phase reaction mixture using any known technique. Another example of a reactor is shown in FIG. 3B.

[00138] In some cases, one or more of the reaction products is used as it is made in a subsequent chemical reaction. For example, 1,3-butadiene may be reacted with a dienophile, or used in a polymerization reaction while it is still in the reactor or as it is extracted from the

reactor. Similarly, acrylic acid or an acrylate ester may be used in a polymerization reaction while it is still in the reactor or as it is extracted from the reaction mixture. Regular depletion of the desired reaction products may drive the reaction forward and inhibit undesired side reactions, reverse reactions, or secondary reactions. Scenarios in which butadiene, acrylic acid or acrylate are used as they are made or imminently thereafter (before being purified or stored) may be useful if the metathesis reactions described herein are used as a step in part of a larger industrial process (e.g., functionalization, oligomerization or polymerization). Thus, the metathesis reactions described herein may be a step or production module within a larger batchwise or continuous industrial process. In some variations, microbial synthesis of muconic acid may also be included as an upstream step or production module, which optionally feeds into an esterification step or module, which feeds into a metathesis reaction to produce 1,3-butadiene, acrylic acid, or an acrylate, and each of these products is directed into one or more downstream steps or production modules for making industrial chemicals, polymers, oils and the like.

[00139] Any suitable reactor configuration (batch mode, continuous, or flow through) may be used to carry out the methods described herein.

Uses

[00140] The 1,3-butadiene, acrylic acid and one or more acrylic acid esters can be used for any purpose apparent to those of skill in the art. Accordingly, also disclosed herein are industrial chemicals, polymers and oils made using 1,3-butadiene made by any of the methods described herein. For example, a wide variety of butadiene homopolymers or butadiene copolymers may be made using as a monomer or comonomer 1,3-butadiene synthesized from muconic acid or a muconic acid ester using the methods described herein. Advantageous, microbially-derived muconic acid can be used to make butadiene, which in turn, can be used to make industrial chemicals, homopolymers or copolymers of the butadiene, or oils. Similarly, industrial chemicals, polymers, and oils can be made using acrylic acid or acrylates made by any of the methods described herein. For example, a wide variety of polymers can be made that incorporate acrylic acid or acrylates made by the methods described herein. Advantageous, microbially-derived muconic acid can be used to make acrylic acid or an acrylate, which in turn, can be used to make industrial chemicals, homopolymers or copolymers of the acrylic acid or acrylate. In some cases, ethylene derived from plant sources may be used in the metathesis reactions. If the 1,3-butadiene, acrylic acid, or acrylates are synthesized using microbially-derived muconic acid and optionally plant-derived ethylene, such industrial chemicals, polymers and oils may be synthesized with little or no carbon content originating from fossil fuels. In

certain variations, chemicals or polymers comprising at least about 30%, at least 40%, at least 50%, at least 60%>, at least 70%>, at least 80%>, at least 90%>, or about 100% carbons originating from a non-fossil fuel carbon source. The number of carbons originating from non-fossil fuel carbon sources can be measured using radiocarbon analysis, e.g., according to any method described in ASTM D6866 - 11 "Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis," which is incorporated herein by reference in its entirety.

Exemplary Processes

[00141] Certain methods comprise optionally providing microbially-derived muconic acid, optionally esterifying the muconic acid to form an ester of muconic acid, reacting the muconic acid or ester of muconic acid with ethylene in the presence of a metathesis catalyst to form at least one of 1,3-butadiene and acrylic acid, or at least one of 1,3-butadiene and an acrylate ester at a pressure in a range from about 2 bar to about 50 bar ethylene, and a temperature in a range from about 0°C to about 100°C. In some cases, the metathesis catalyst comprises ruthenium. In some cases, the metathesis catalyst comprises a Grubbs catalyst. In one non-limiting example, the methods comprise reacting muconic acid or a muconic acid ester with ethylene in the presence of a metathesis catalyst at a catalyst loading of about 0.005mol% to about 10 mol% (e.g., 0.001 mol% to about 10 mol%, about 0.005 mol% to about 10 mol%, about 0.05 mol% to about 10 mol%, about 0.5mol% to about 5 mol%, about 1 mol% to about 5 mol%, or about 2 mol% to about 5 mol%) at a temperature in a range from about 0°C to about 100°C (e.g., about 20°C to about 100°C, about 20°C to about 80°C, or about 30°C to about 80°C) and an ethylene pressure in a range from about 1 bar to about 100 bar (e.g., about 1 bar to about 80 bar, about 1 bar to about 50 bar, about 5 bar to about 50 bar, or about 5 bar to about 40 bar) to form 1,3-butadiene and acrylic acid (if muconic acid is used as the starting material) or 1,3-butadiene and an acrylate ester (if a muconic acid ester is used as the starting material). In certain variations, the catalyst comprises ruthenium. In certain variations, the catalyst is selected from the group consisting of dichloro[l,3-bis(2-methylphenyl)-2-imidazolidinylidene](2-isopropoxyphenylmethylene)ruthenium(II), (l,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isopropoxyphenylmethylene)ruthenium, and [1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro (phenylmethylene)(tricyclohexylphosphine)ruthenium.

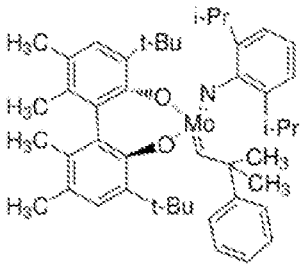
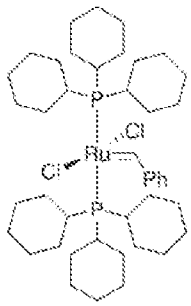
EXAMPLES

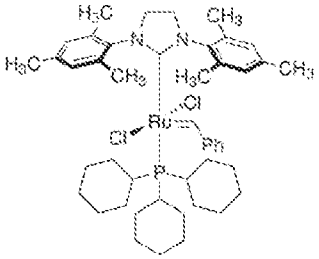
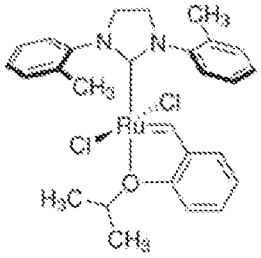
[00142] In the following Examples, a range of metathesis catalysts are screened for ethenolysis reaction of di-n-butyl muconate to prepare 1,3-butadiene and/or n-butyl acrylate.

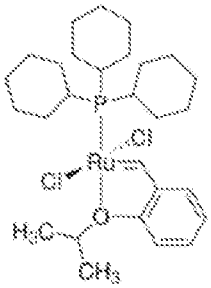
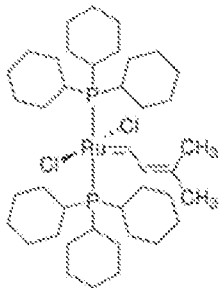
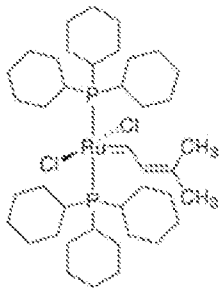
[00143] In some examples, 2,4-hexadiene is used as the substrate instead of muconic acid or a muconic acid ester. 2,4-hexadiene is observed to react with ethylene in the presence of a metathesis catalyst to form propylene and 1,3-butadiene. When certain metathesis catalysts are used (e.g., Gl), essentially all of the 2,4-hexadiene is converted.

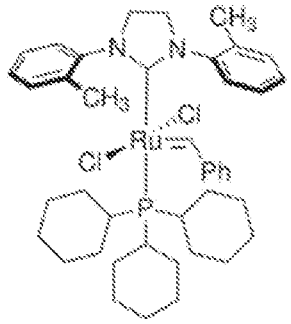
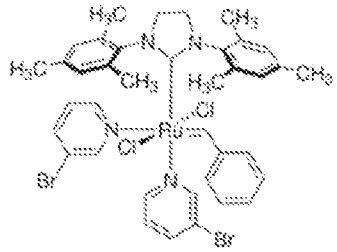
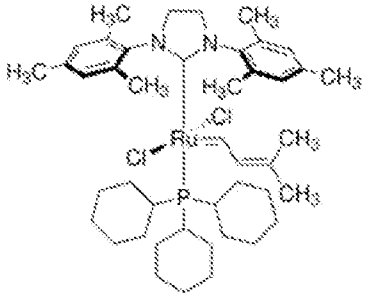
[00144] Table 1 provides metathesis catalysts used in the Examples. For Table 1, the following abbreviations are used: iPr=isopropyl, Ph=phenyl, t-Bu=tert-butyl, PCy_3=tricyclohexylphosphine, Me=methyl, BIPHEN=rac-3,3-di-tert-butyl-5,5',6,6'-tetramethyl-l,l'-biphenyl-2,2'-diolate, cy=cyclohexyl, hom.=homogeneous, and het.=heterogeneous.

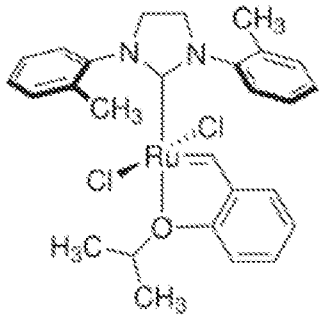
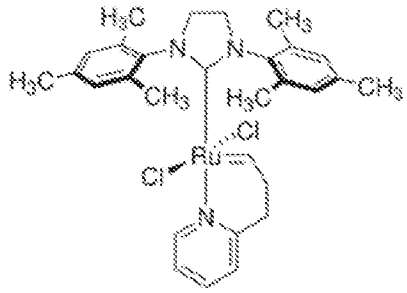
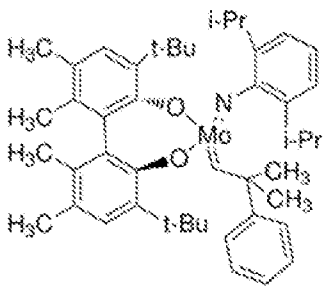
Table 1. Metathesis catalysts

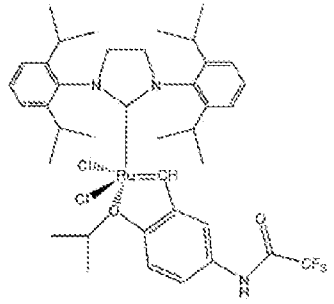
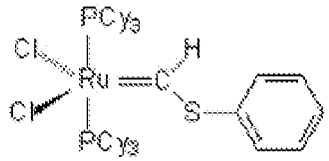
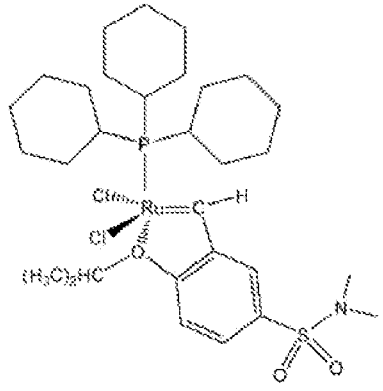
Supplier and product code	Structure	Metal	Type	Reference Code
Sigma-Aldrich 73022	2,6-Diisopropylphenylimido-neophylidene[(*S*)-(−)-BIPHEN]molybdenum(VI) **(Sigma Aldrich 73022)** **(*S*)-Schrock-Hoveyda Catalyst** 	Mo	Hom.	73022
Sigma-Aldrich 579726	Bis(tricyclohexylphosphine)benzylidine ruthenium(IV) dichloride or benzylidene-bis(tricyclohexylphosphine)dichlororuthenium **(Grubbs first generation catalyst)** 	Ru	Hom.	G1

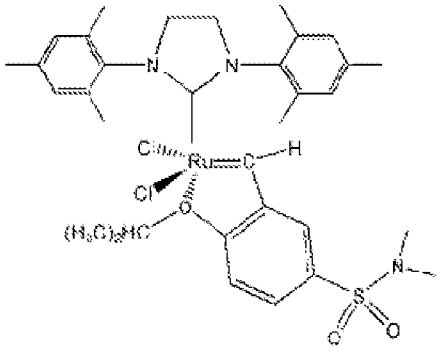
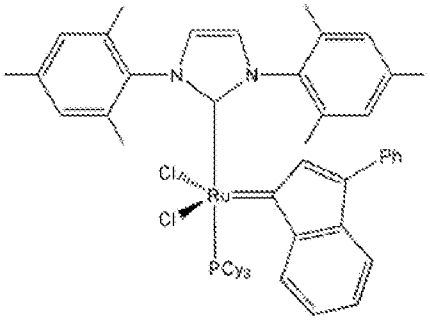
Supplier and product code	Structure	Metal	Type	Reference Code
Sigma-Aldrich 569747	[1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro (phenylmethylene)(tricyclohexylphosphine)ruthenium **(Grubbs second generation catalyst)** 	Ru	Horn.	G2
Sigma-Aldrich 569755	(l,3-Bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isopropoxyphenylmethylene)ruthenium **(Hoveyda-Grubbs second generation catalyst)** 	Ru	Horn.	HG2

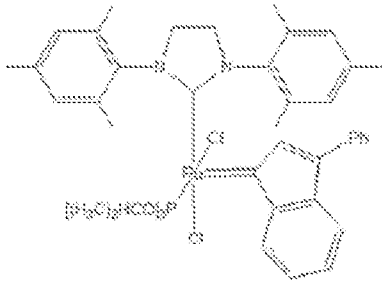
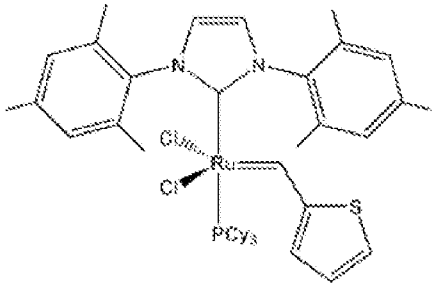
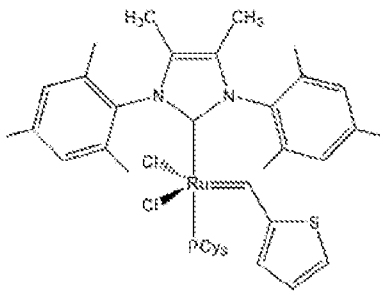
Supplier and product code	Structure	Metal	Type	Reference Code
Sigma-Aldrich 577944	Dichloro(o-isopropoxyphenylmethylene)(tricyclohexylphosphine) ruthenium(II) **(Hoveyda-Grubbs first generation catalyst)** 	Ru	Horn.	HG1
Sigma-Aldrich 57868 1	Dichloro(3 -methyl-2-butenylidene)bis(tricyclohexylphosphine)ruthenium(II) **Grubbs Catalyst 801** **(Sigma Aldrich 578681)** 	Ru	Horn.	57868 1
Sigma-Aldrich 578703	Dichloro(3 -methyl-2-butenylidene)bis(tricyclopentylphosphine) ruthenium(II) **(Sigma Aldrich 578703)** 	Ru	Horn.	578703

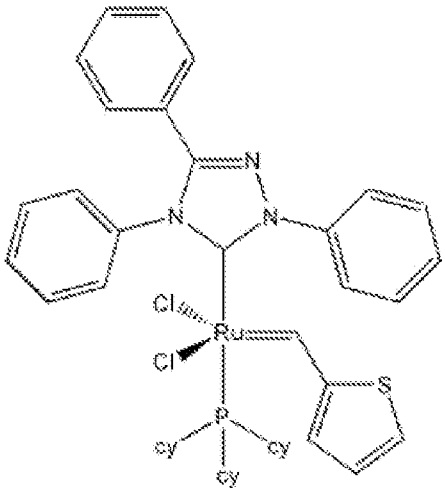
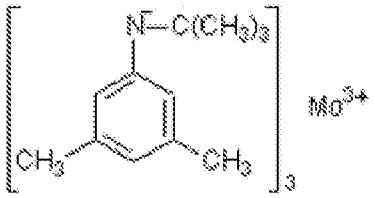
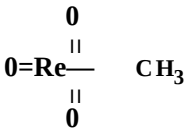
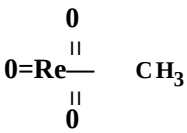
Supplier and product code	Structure	Metal	Type	Reference Code
Sigma-Aldrich 682284	Dichloro[1,3-Bis(2-methylphenyl)-2-imidazolidinylidene](benzylidene)(tricyclohexylphosphine)ruthenium(II) **(Sigma Aldrich 682284)** 	Ru	Horn.	682284
Sigma-Aldrich 682330	Dichloro[l,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] (benzylidene)bis(3 -bromopyridine)ruthenium(II) **(Sigma Aldrich 682330)** 	Ru	Horn.	682330
Sigma-Aldrich 682365	Dichloro[l,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] (3-methyl-2-butenylidene) (tricyclohexylphosphine)ruthenium(II) **(Sigma Aldrich 682365)** 	Ru	Horn.	682365

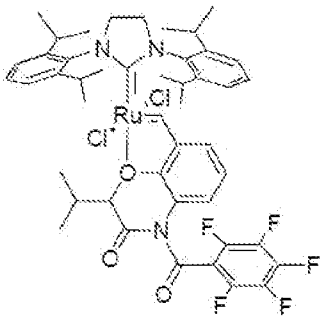
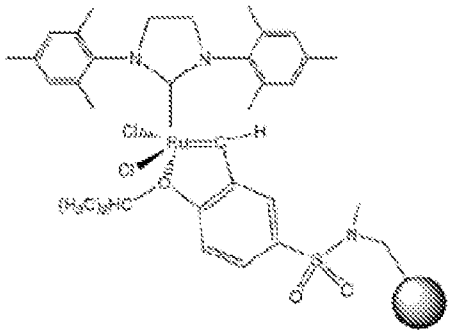
Supplier and product code	Structure	Metal	Type	Reference Code
Sigma-Aldrich 682373	Dichloro[1,3-bis(2-methylphenyl)-2-imidazolidinylidene] (2-isopropoxyphenylmethylene)ruthenium(II) **(Sigma Aldrich 682373)** 	Ru	Horn.	682373
Sigma-Aldrich 68238 1	Dichloro[l,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] [3-(2-pyridinyl)propylidene]ruthenium(II) **(Sigma Aldrich 682381)** 	Ru	Horn.	68238 1
Strem 42-1213	2,6-Diisopropylphenylimidoneophylidene [(R)-(+)-BIPHEN]molybdenum(VI), min. 97% (R) SCHROCK-HOVEYDA CATALYST **(Strem 42-1213)** 	Mo	Horn.	42-1213

Supplier and product code	Structure	Metal	Type	Reference Code
Strem 44-0055	[l,3-Bis(2,6-di-i-propylphenyl)-4,5-dihydroimidazol-2-ylidene] -[2-i-propoxy-5-(trifluoroacetamido)phenyl]methylene ruthenium(II) dichloride (omega CS1) **(Strem 44-0055)** 	Ru	Horn.	44-0055
Strem 44-0073	Bis(tricyclohexylphosphine)[(phenylthio)methylene] ruthenium(II) dichloride, min. 97% **(Strem 44-0073)** 	Ru	Horn.	44-0073
Strem 44-0078	{[2-(i-propoxy)-5-(N,N-dimethylaminosulfonyl)phenyl]methylene}(tricyclohexylphosphine) ruthenium(II) dichloride (Zhan Catalyst -1C) **(Strem 44-0078)** 	Ru	Horn.	44-0078

Supplier and product code	Structure	Metal	Type	Reference Code
Strem 44-0082	l,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene[2-(i-propoxy)-5-(N,N-dimethylaminosulfonyl)phenyl]methylene ruthenium(II) dichloride Zhan Catalyst-1B **(Strem 44-0082)** 	Ru	Horn.	44-0082
Strem 44-7775	Tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)imidazol-2 -ylidene][3-phenyl-1H-inden-l-ylidene]ruthenium(II) dichloride, min. 95% [catMETium® RF1] (Strem 44-7775) 	Ru	Horn.	44-7775

Supplier and product code	Structure	Metal	Type	Reference Code
Strem 44-7783	Tri(i-propoxy)phosphine(3 -phenyl- 1H-inden- 1-ylidene) [1,3-bis(2,4,6-trimethylphenyl) -4,5-dihydroirnidazol-2-ylidene]ruthenium (II) dichloride, min. 95% cis-Caz-1 (Strem 44-7783) 	Ru	Horn.	44-7783
Strem 44-7785	Tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)imidazol-2 -ylidene] [2-thienylmethylene]ruthenium(II) dichloride, min. 95% [catMETium® RF 2] (Strem 44-7785) 	Ru	Horn.	44-7785
Strem 44-7790	Tricyclohexylphosphine[4,5-dimethyl-l,3-bis(2,4,6-trimethylphenyl)imidazol-2 -ylidene] [2-thienylmethylene]ruthenium(II) dichloride, min. 95% [catMETium® RF 3] (Strem 44-7790) 	Ru	Horn.	44-7790

Supplier and product code	Structure	Metal	Type	Reference Code
Strem 44-7795	Tricyclohexylphosphine[2,4-dihydro-2,4,5-triphenyl-3H-1,2,4-triazol-3-ylidene][2-thienylmethylene]ruthenium(II) dichloride, min. 95% [catMETium® RF 4] 	Ru	Horn.	44-7795
TCI T2358	Tris(N-tert-butyl-3,5-dimethylanilino)molybdenum(III) (TCI Chemicals T2358) 	Mo	Horn.	T2358
Sigma-Aldrich 412910*	Methyltrioxorhenium(VII). *denotes addition of Me_4Sn 	Re	Horn.	412910*
Sigma-Aldrich 412910	Methyltrioxorhenium(VII) 	Re	Horn.	412910

Supplier and product code	Structure	Metal	Type	Reference Code
Omega $M8_{53}$-SiPr	 $M8_{53}$	Ru	Hom.	M853-SiPr
Strem 44-0083	1,3-Bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene[2-(i-propoxy)-5-(N,N-dimethyl aminosulfonyl)phenyl]methyleneruthenium(II) dichloride (resin supported) Zhan Catalyst II 	Ru	Het.	44-0083
10% Mo	Molybdenum oxide on alumina (10 wt% loading)	Mo	Het.	HC04a
10% W	Tungsten oxide on alumina (10 wt% loading)	W	Het.	HC05a
5% Re	Rhenium oxide on alumina (5 wt% loading)	Re	Het.	HC01b
10% Re	Rhenium oxide on alumina (10 wt% loading)	Re	Het.	HC02b
15% Re	Rhenium oxide on alumina (10 wt% loading)	Re	Het.	HC03b
10% Mo	Molybdenum oxide on alumina (10 wt% loading)	Mo	Het.	HC04b
10% W	Tungsten oxide on alumina (10 wt% loading)	W	Het.	HC05b

[00145] For Examples 1-7, GC-FID is carried out using an Agilent GC-FID equipped with an HP-1 column. The temperature is held at 60°C for 3 minutes, ramped at 20°C/min to 230°C, ramped at 25°C/min to 320°C, and held at 320°C for 3 minutes. The inlet temperature is 300°C. The carrier gas is hydrogen. GC-MS is carried out using an Agilent GC-MS equipped with an HP-1 column and an MSD detector. The temperature is held at 50°C for 3 minutes,

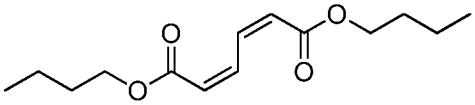
ramped at 25°C/min to 200°C, ramped at 20°C/min to 320°C, and held at 320°C for 5 minutes. The inlet temperature is 250°C, and the carrier gas is helium. For NMR, a JEOL ECX 400 (400 MHz) spectrometer is used.

[00146] **EXAMPLE 1.** Preparation of cis,cis-di-n-butyl muconate from microbially-derived cis,cis-muconic acid.

[00147] For this Example, a 5L 3-neck round bottom flask equipped with overhead stirrer, ¼" K-type thermocouple, Dean Stark trap, condenser and gas adapters was used. A heating mantle was used to heat the reaction and temperature was controlled by a J-KEM® temperature controller.

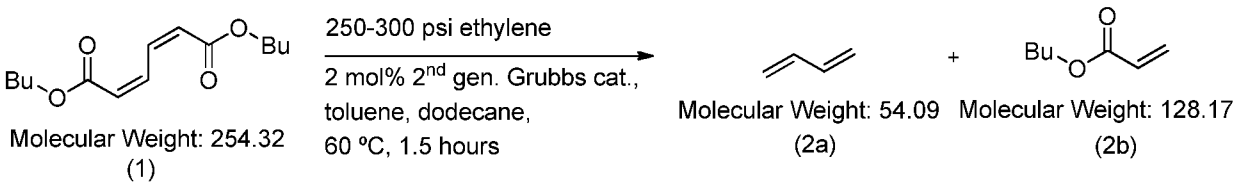
[00148] 2L heptane was added to the reactor followed by 190g of cis,cis-muconic acid (1.33mol, Lot # 1673-001-005, produced microbially by Draths Corp., e.g., using a procedure described in International Patent publication WO201 1/08531 1, which is incorporated herein by reference in its entirety), 10ml sulfuric acid (0.19mol), and 450ml of 1-butanol (4.92 mol). The reaction mixture was heated to 90°C. Approximately 200ml hexanes were added to the reaction mixture to remove water generated during the reaction azeotropically. After 4 hours at 90°C, the heat was removed and the reaction was allowed to cool to room temperature. Approximately 40ml water was collected (theoretical amount 48ml) in the Dean Stark trap. Solvent was removed by rotovap. The product was an oil that was adsorbed onto 900g of silica gel. 1L hexanes was added to the flask to ensure uniform adsorption onto silica gel, then solvent was removed by rotovap. The solid silica gel was loaded onto a fritted funnel with 1kg dry silica and the product was eluted with hexanes. The product fractions were combined and solvent removed via rotovap. The resulting oil was adsorbed onto silica gel again, and loaded into a 2kg silica gel column. The produce was eluted with hexane slowly. TLC was used as a test method for product detection. The product fractions were combined and solvent removed by rotovap. After the rotovap procedure, 180g di-n-butyl muconate was obtained (yield: 53%), which contained three isomers (80 area% cis,cis-di-n-butyl muconate, 15 area% cis,trans-di-n-butyl muconate, and 5 area% trans,trans-di-n-butyl muconate) by GC/MS and confirmed by proton NMR.

[00149] **EXAMPLES 2-5.** (2Z,4Z)-di-n-butyl hexa-2,4-dienedioate reacted with ethylene using homogeneous metathesis catalyst at 60°C, 250-300 psi.



(2Z,4Z)-dibutyl hexa-2,4-dienedioate

[00150] For each of Examples 2-5, the following reaction was carried out.



[00151] For Example 2 (RV-650-12), 8.6037g di-n-butyl muconate (prepared as in Example 1 and having about 80% of the cis,cis- isomer, 15%> of the cis,trans- isomer, and 5%> of the trans,trans- isomer by GC-MS and NMR) were dissolved in 8.00 mL toluene (1.08g/ml) and dried over molecular sieves. 0.4321 g 2nd generation Grubbs catalyst (Sigma-Aldrich catalog number 569747) was dissolved in 12.72 ml toluene dried over molecular sieves to prepare a 0.04 M solution. In an inert atmosphere glove box, a 75 mL Hastelloy reactor equipped with Teflon magnetic stir bar was charged with di-n-butyl muconate (l.OOg, 3.93 mmol, 0.926 mL solution), toluene (5.00 mL), dodecane (0.446 mL), and 2nd generation Grubbs catalyst (1.966 mL of 0.04 M solution). An aliquot was taken for initial GC-FID analysis.

[00152] The head space of the reactor was connected to a gas recovery system (GRS) as shown in FIG. 1 and described as follows. The head space of the reactor was connected via a valve to 2-150ml stainless steel reservoirs connected in series. The outlet of the second stainless steel reservoir was connected via a valve and directed via a needle directed through a rubber septum and the tip of the needle was submerged in 10 ml toluene contained in a 40-ml glass vial cooled to a temperature that is below the boiling point of 1,3-butadiene (-4°C) but is above the boiling point of ethylene (-104°C). The cooling of the vial is accomplished in this Example by immersion in a dry ice/acetone bath at -78°C. The assembled reactor was removed from the glove box and the screws on the reactor head were tightened. The Hastelloy reactor including its associated GRS was installed on a Parr 5000 multiple reactor system, to which was also connected a thermocouple, a pressure transducer, and ethylene line. The system was subjected to 3-cycles of house vacuum/nitrogen back-fill flush while stirring at 300 rpm. Following flushing, the whole system was left under vacuum. The GRS was isolated from the reactor using a valve and the reactor was filled with ethylene to achieve a pressure of 250-290 psi (17-20 bar). The reactor was heated to 60°C and stirring was increased to 1000 rpm. After 30 minutes the reactor head space was released into the GRS. The reactor was again isolated using a valve, re-pressurized with ethylene and the reaction continued. The contents of the GRS were

allowed to slowly bubble through toluene at -78 °C. The latter process was repeated after 50, 70, 90, and 110 minutes (for a total of 5 releases of the reactor head space). After 2 hours, heating was discontinued and the reactor head space was completely emptied into the GRS, then bubbled through toluene at -78 °C; and 8 microliters 4-tert-butyl catechol (TBC) solution (0.17 g/mL in methanol) was added to the toluene, which was subsequently analyzed by GC-FID using dodecane as an internal standard. The toluene was stored at -20 °C. The reactor was disassembled, the reaction mixture quenched with 1 mL of 2-propanol,10 microliters of TBC solution (0.17 g/mL in methanol) was added, and the reaction mixture was analyzed by GC-FID using dodecane as an internal standard. The % conversion of the cis,cis-di-n-butyl muconate was calculated to be 50.9% using the GC-FID results following calculation: % conversion = {1-[(final area di-n-butyl muconate)/(fmal area dodecane)]/[(initial area di-n-buty muconate)/(initial area dodecane)] }x 100%.

[00153] GC-FID for the liquid phase reaction mixture is shown in FIG. 4A. GC-FID of the cooled toluene that was used to trap gaseous reaction products from the head space are shown in FIG. 4B-4C. FIG. 4C shows overlaid spectra of GC-FID of the toluene used to trap gaseous reaction products from the head space on the day of the reaction and on the day following the reaction, and a spectrum of a 1,3-butadiene standard taken using the same equipment and conditions as used for analysis of the products of this reaction. As shown in FIG. 4C, peaks obtained from the toluene containing the reaction products were not observed to shift over a day. The peak at 1.835 min is believed to be due to ethylene, which decreases in area % > over a day. The toluene sample shows a peak at 1.876-1 .877 minutes, which is consistent with that of the 1,3-butadiene standard at 1.878 minutes. The toluene sample also shows a shoulder at 1.864 minutes. The shoulder at 1.864 minutes is attributed to a side product, and is thought to be 1-butene or 2-butene.

[00154] GC-MS spectra of the reaction mixture are shown in FIGS. 4D-4F. FIG. 4D shows the entire spectrum. FIG. 4E shows the m/z profile for the peak at 5.314 minutes, compared against that of a standard m/z profile for 2-propenoic acid, butyl ester (butyl acrylate) obtained from a standards database managed by NIST (National Institute of Standards and Technology). By this analysis, the peak at 5.314 minutes in the GC-MS is consistent with butyl acrylate (Quality 78). FIG. 4F shows the m/z scan for the peak at 7.376 min, which is attributed to n-butyl penta-2,4-dienoate. The ratio (mol muconate starting material) :(mol butyl acrylate) was determined to be 1.88 by GC-FID using an internal dodecane standard. The initial ratio of the amount of cis,cis- isomer to the amount of trans,trans- isomer in the di-n-butyl muconate was

6.31 by GC-FID, and the ratio was 7.32 for the muconate that was left unreacted, indicating that the rates of reaction for these isomers were similar.

[00155] The GC-MS spectra of the toluene used to trap the gaseous reaction products from the reactor head space is shown in FIG. 4G. FIG. 4H shows the m/z scan for the peak at 2.432 minutes. For comparison, the GC-MS for 1,3-butadiene and m/z scan for the peak eluting at 2.440 minutes is shown in FIG. 6H. The GC-MS for the toluene incorporating the head space reaction products for Example 2 may indicate the presence of 1,3-butadiene, 1-butene, and/or 2-butene.

[00156] Example 3 (RV-650-13) was conducted as in Example 2. FIG. 5A shows a GC-FID spectrum for the liquid phase reaction mixture of Example 3. FIG. 5B shows a GC-FID spectrum for toluene used to trap gaseous reaction products from the head space. FIGS. 5C-5D shows overlaid spectra of GC-FID of the toluene used to trap gaseous reaction products from the head space on the day of the reaction and on the day following the reaction, and a spectrum of a 1,3-butadiene standard taken using the same equipment and conditions as used for analysis of the products of this reaction. As shown in FIGS. 5C-5D, peaks obtained from the toluene containing the reaction products were not observed to shift over a day. The peak at 1.835 min is believed to be due to ethylene, which decreases in area % over a day. The toluene sample shows a peak at 1.876-1.877 minutes, which is consistent with that of the 1,3-butadiene standard at 1.878 minutes. In this particular example, the toluene sample does not clearly exhibit a shoulder at 1.864 minutes that may be attributable to 1-butene or 2-butene.

[00157] FIG. 5E shows a GC-MS spectrum for the reaction mixture of Example 3. FIG. 5F shows m/z scans for the peak at 5.316 minutes as compared with that of 2-propenoic acid, butyl ester (butyl acrylate) from a standards database managed by NIST. By this comparison, the peak at 5.316 minutes is consistent with butyl acrylate (Quality 83).

[00158] GC-MS spectra of the toluene used to trap the gaseous reaction products from the reactor head space is shown in FIGS. 5G-5H. FIG. 51 shows a m/z scan for the peak at 2.432 minutes. For comparison, the GC-MS for 1,3-butadiene and m/z scan for the peak eluting at 2.440 minutes is shown in FIG. 6H. The GC-MS for the toluene incorporating the head space reaction products for Example 3 may indicate the presence of 1,3-butadiene, 1-butene, and/or 2-butene.

[00159] GC-FID and GC-MS analysis of the reaction products for Examples 4-5 were similar to those for Example 2. In each of Examples 4 and 5, GC-FID and GC-MS indicated the presence of butyl acrylate in the liquid phase reaction mixture. GC-FID of the toluene used to

trap gaseous reaction products from the head space exhibited a peak at 1.876-1.877 minutes (consistent with the presence of 1,3-butadiene), and a shoulder at 1.864 minutes (side product that may be attributable to 1-butene or 2-butene).

[00160] Example 4 (RV-650-21) was carried out as Example 2, except that the amounts of muconate reactant was increased to 3.00g (11.8 mmol, 2.997 mL of a solution made by dissolving 12.0094g di-n-butyl muconate in 12.0 mL toluene and dried over molecular sieves), 6.0 mL toluene was used, 1.0 mL (4.4 mmol) dodecane was used, 5.90 mL catalyst solution (0.04 M solution) was used, the ethylene pressure in the reactor was 250 psi (17.2 bar), and the solvent in the receiving vial for the gaseous reaction products from the head space was 2.5 mL $CDCl_3$ cooled to -43°C using a dry ice/acetonitrile bath.

[00161] Example 5 (RV-650-22) was carried out as Example 4.

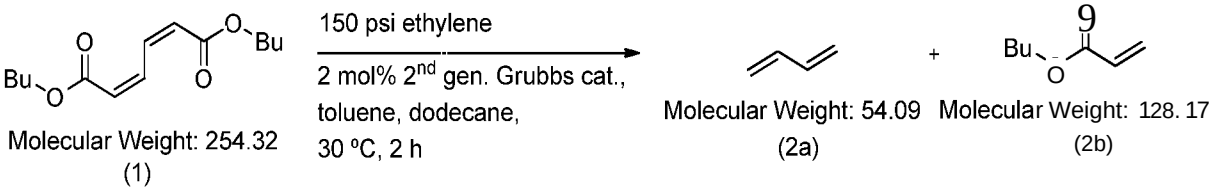
[00162] For each of Examples 4 and 5, GC-FID indicated the presence of butyl acrylate and GC-MS exhibited a peak at 2.432 minutes, which may indicate the presence of 1,3-butadiene, 1-butene, and/or 2-butene. Results for Examples 2-5 are summarized in Table 2.

Table 2. Results for Examples 2-5

Example	% conversion	Initial ratio cis,cis-isomer:cis,trans-isomer	Final ratio cis,cis-isomer:cis,trans-isomer
2 (RV-650-12)	50.9	6.31	7.32
3 (RV-650-13)	51.4	6.57	7.59
4 (RV-650-21)	46.7	6.62	6.64
5 (RV-650-22)	47.1	6.51	7.13
Average +/- std. dev.	49.0 +/- 2.5	6.50 +/- 0.13	7.13 +/- 0.42

[00163] **EXAMPLE 6 (RV-650-17) :** Di-n-butyl muconate reacted with ethylene using homogeneous metathesis catalyst at 30°C, 150 psi.

[00164] The following reaction was carried out for Example 6:



[00165] For Example 6, the procedure as in Example 2 was followed except the reaction was scaled up so that the amounts of muconate reactant was increased to 5.00g (19.7mmol, 4.63 mL of a solution made by dissolving 8.6037g di-n-butyl muconate in 8.0 mL toluene and dried over molecular sieves), 10.0 mL toluene was used, 2.23 mL dodecane used was used, 9.83 mL catalyst solution (0.04 M) was used, the ethylene pressure in the reactor was reduced to 150 psi (10.3 bar), and the temperature was reduced to 30°C, the solvent present in the receiving vial for the gaseous reaction products from the head space was 3.5 ml $CDCI_3$ and the bath used to cool the $CDCI_3$ through which the gaseous reaction products were bubbled was dry ice/acetonitrile at -43°C. The $CDCI_3$ in the receiving was stabilized with 10 microliters TBC solution (0.17 g/mL methanol). The reaction mixture was stabilized with 50 microliters TBC solution. The % conversion was 32.3%. The initial ratio of cis,cis-di-n-butyl muconate:cis,trans-di-n-butyl muconate was 6.83; the ratio of cis,cis di-n-butyl muconate:cis,trans-di-n-butyl muconate in the unreacted muconate following the reaction was 7.47.

[00166] FIG. 6A shows a GC-FID spectrum of the liquid phase reaction mixture. FIG. 6B shows a GC-FID spectrum of a butyl acrylate standard (upper trace) and an overlay of the GC-FID spectra for the butyl acrylate standard and the liquid phase reaction products (lower trace). FIG. 6C shows a GC-FID spectrum of the $CDCI_3$ used to trap gaseous reaction products from the head space. FIG. 6C shows a peak at 1.884 minutes that is consistent with 1,3-butadiene and a shoulder at about 1.872 minutes that may be a side product attributable to 1-butene or 2-butene. FIG. 6D provides a GC-MS spectrum for the liquid phase reaction mixture. The upper trace in FIG. 6E shows a m/z scan for the peak at 5.3 16 minutes, which is consistent with a m/z scan for a standard of butyl acrylate obtained from NIST shown in the lower trace of FIG. 6E (Quality 72). FIG. 6F shows a GC-MS spectrum for the $CDCI_3$ used to trap the gaseous reaction products from the head space. FIG. 6G shows a m/z scan for the peak at 2.441 minutes. FIG. 6H provides a GC-MS for a standard of 1,3-butadiene in the upper trace and a m/z scan for the peak at 2.443 minutes in the lower trace.

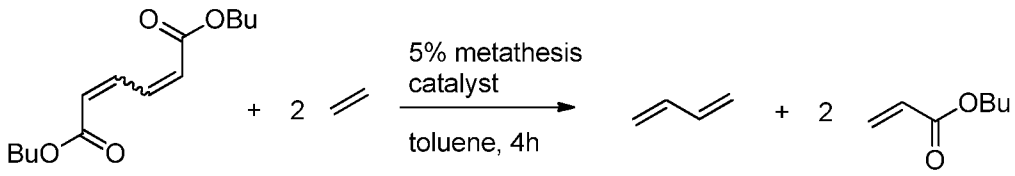
[00167] A sample of the cooled $CDCI_3$ used to trap gaseous reaction products from the head space was analyzed by proton NMR as shown in FIGS. 6I-6K and CI3 NMR as shown in FIGS. 6L-6N. The NMR was carried out in $CDC1_3$ at 5°C using a 400MHz JEOL ECX 400 spectrometer. As shown in FIGS. 6I-6J, the sample shows the presence of 1,3-butadiene that has been obtained from the head space of the reactor using the gas recovery system. The peak at 5.429ppm is believed to be ethylene. The multiplet centered at about 7.25ppm is toluene. Also observed in the proton NMR is 1-butene, as illustrated in FIG. 6K. Referring now to FIGS. 6L-6N, the following peak assignments are made: toluene 137.861ppm, 129.023ppm, 128.216ppm,

and 125.284 ppm. The peak at 122.957ppm is likely attributable to ethylene, based on estimated peak from ChemDraw® software. The peaks at 137.65ppm and 117.647ppm are attributed to 1,3-butadiene, based on reference spectra available at Sigma-Aldrich. The peaks at 137.5ppm, 117.479ppm, 26.653ppm, and 13.065ppm are attributed to 1-butene, based on estimates from ChemDraw® software.

[00168] **EXAMPLE 7** (RV-650-5A) was carried out as in Example 2, except that the GRS was emptied and repressurized twice (once after 20 minutes, and the second time after 49 minutes) instead of 5 times, the total reaction time was 1.5 hours, and cis,cis-muconic acid obtained from Acros Organics was esterified in a similar manner as Example 1, resulting in dibutyl muconate having an isomer ratio 99.7:0.25 cis,cis:trans,trans. FIG. 7A shows a GC-FID spectrum of toluene comprising reaction products in the receiving vial collected from the head space of the reactor. Also shown in FIG. 7A is a GC-FID spectrum for a 1,3-butadiene standard, and a GC-FID spectrum for toluene comprising the head space reaction products co-injected with 1,3-butadiene. As shown in FIG. 7A, the reaction products from the head space elute at 1.864 minutes, whereas 1,3-butadiene elutes at 1.878 minutes. FIG. 7B shows a GC-FID spectrum of a butyl acrylate standard (upper trace). FIG. 7B also provides a GC-FID spectrum of the liquid phase reaction products overlaid with that of the butyl acrylate standard, indicating the presence of butyl acrylate. Referring back to Examples 2-6, the head space reaction product of Example 7 is consistent with the side product observed in Examples 2-6, which may be 1-butene and/or 2-butene. GC-FID for the liquid phase reaction mixture of Example 7 shows the presence of butyl acrylate, which is consistent with Examples 2-6.

[00169] **EXAMPLES 8-126.** Ethenolysis reaction carried out using homogeneous metathesis catalysts at 10-40 bar ethylene and 30°C-80°C.

[00170] The following reaction was carried out for Examples 8-126.



[00171] Ethenolysis reaction carried out using homogeneous metathesis catalysts at 10 bar ethylene and 30°C (Examples 8-31), 40 bar ethylene and 30°C (Examples 31-54), 25 bar ethylene and 55°C (Examples 55-78), 10 bar ethylene and 80°C (Examples 79-102), and 40 bar ethylene and 80°C (Examples 103-126).

[00172] The following procedure was used for Example 11. In a glove box, a 7.7 ml TEFLON® tube containing a magnetic stir bar was loaded with 127 microliter (0.5 mmol) of cis,cis-di-n-butyl muconate having a purity of about 80% of the cis,cis isomer (as prepared in Example 1) and 200 microliters of an anhydrous toluene stock solution containing 0.025 mmol (5 mol%) of Hoveyda-Grubbs 2nd generation metathesis catalyst (available from Sigma-Aldrich), made by dissolving 94 mg catalyst in 1200 microliters of anhydrous toluene. To this mixture was added 673 microliters of anhydrous toluene to reach a total liquid reaction volume of 1000 microliters. The TEFLON® tube was capped with a TEFLON® septum and tightly sealed before transfer out of the glove box. The reactor was flushed three times with 35 bar of nitrogen and three times with 20 bar of ethylene before it was brought to the desired ethylene pressure of 10 bar (145 psi). Then the reactor was placed in a pre-heated aluminum mantle of 30°C and stirred for 4 hours. After cooling to room temperature the headspace of the reactor was sampled for GC-FID analysis. Then the reactor was opened and the mixture was diluted with 4 ml of isopropyl alcohol containing 2.5 wt% tetradecane as a standard. 500 microliters of the resulting mixture was used for GC-MS analysis of the liquid phase. The head space was sampled for GC-FID analysis. For GC-MS, a Thermo Trace GC with FID detection and DSQ II mass spectroscopy with electric ionization, using a VF-WaxMS 0.25mm x 0.25 micron x 30m column. The start temperature was 60°C, with a hold time of 1 minute, then a first ramp at 10°C/min to 150°C, with a hold time of 1 minute, and a second ramp at 60°C/min to 250°C, with a hold time of 2 minutes. The injection temperature was 250°C, and a split flow at 200 ml/min was used. The carrier flow rate was 2 ml/min. The FID temperature was 275°C. The injection volume was 0.5 microliter. For GC-FID analysis of the head space, an Interscience CompactGC using a sample loop valve oven at 50°C, and a 3-channel column/detector setup. The front channel was a 2m PBQ backflush column and a 23m PBQ analytical column with FID. The middle channel was a 2m PBQ backflush column and a 23m PBQ analytical column with a thermal conductivity detector (TCD). The back channel was a 2m PBQ backflush column and a 8m Molsieve analytical column with a TCD. The front channel was run at 80 kPa, 10 ml/min, 70°C, 20 seconds. The middle channel was run at 70kPa, 20 ml/min, 60°C, 14 seconds. The back channel was run at 200 kPa, 10 ml/min, 100°C, 18 seconds. Analysis of the reaction head space following the reaction by GC-FID revealed the presence of 1,3-butadiene, 1-butene and/or 2-butene. Analysis of the liquid phase following the reaction by GC-MS revealed the presence of butyl acrylate and butyl penta-2,4-dienoate.

[00173] Examples 8, 9, 10, and 12-123 are carried out as for Example 11, except that the metathesis catalyst, temperature, and pressure are varied as shown in Tables 3-7, with the source and description of the metathesis catalysts shown in Table 1.

[00174] For Table 3, the following abbreviations are used: BD= 1,3-butadiene and/or butene (1-butene and/or 2-butene), BA=butyl acrylate, MuBuE=di-n-butyl muconate, PD=n-butyl penta-2,4-dienoate, PR=propylene, HD=hexa-2,4-diene, tr=trace, sub.=substrate, n/a=not applicable and n.d.=none detected. The column labeled GC-FID refers to species detected in the reaction head space using GC-FID as described above, in addition to ethylene. The column labeled GC-MS refers to species detected in the reaction liquid phase (in addition to solvent, internal standard and substrate) using GC-MS as described above. "mmol MuBuE left" is measured using the tetradecane standard. The column labeled "% conv." refers to the % conversion of the MuBuE {(l-[fmal amount of MuBuE)/(initial amount of MuBuE)]xl00%}. The catalysts were screened in blocks of 12 experiments, with each block including a blank experiment that was run without a catalyst but with reactants. The total area of the reactant peaks in the blank, as measured by GC-MS, was used as a reference for the other experiments in the block to calculate % conversion. In addition, the amount of MuBuE reactant remaining after the reaction was calculated directly from a calibration line of the reactant relative to the external standard tetradecane.

Table 3. Experimental results for di-n-butyl muconate reacted with ethylene in the presence of a homogeneous metathesis catalyst at 30°C and 10 bar (145 psi)

Ex.	Sub.	T (°C)	P (bar)	Metathesis Catalyst	GC-FID[1]	GC-MS[2]	% conv.	mmol sub. left	mmol sub. converted	mmol BA
7	MuBuE	30	10	73022	n.d.	n.d.	15	0.39	0.08	-0.01
8	MuBuE	30	10	G1	n.d.	BA (tr)	29	0.32	0.15	-0.01
9	MuBuE	30	10	G2	BD	BA,PD	39	0.28	0.20	0.11
10	MuBuE	30	10	HG2	BD	BA,PD	57	0.20	0.29	0.23
11	MuBuE	30	10	HG1	BD (tr)	BA(tr) PD	10	0.42	0.05	0.00
12	MuBuE	30	10	578681	n.d.	n.d.	1	0.46	0.01	-0.01
13	MuBuE	30	10	578703	n.d.	n.d.	11	0.41	0.06	-0.01
14	MuBuE	30	10	682284	BD	BA,PD	30	0.32	0.15	0.04
15	MuBuE	30	10	682330	BD	BA,PD	25	0.25	0.13	0.10
16	MuBuE	30	10	682365	BD	BA,PD	17	0.38	0.09	0.04
17*	MuBuE	30	10	none	n.d.	n.d.	0	0.46	0.00	-0.01
18**	HD	30	10	G1	BD, PR	n.d.	87	0	0.44	n/a
19	MuBuE	30	10	682373	BD	BA,PD	52	0.09	0.26	0.12
20	MuBuE	30	10	682381	BD	BA,PD	54	0.09	0.27	0.11
21	MuBuE	30	10	42-1213	n.d.	n.d.	10	0.17	0.05	-0.01
22	MuBuE	30	10	44-0055	BD	BA,PD	35	0.12	0.18	0.06
23	MuBuE	30	10	44-0073	n.d.	n.d.	7	0.18	0.04	-0.01
24	MuBuE	30	10	44-0082	BD	BA,PD	24	0.15	0.12	0.05

Ex.	Sub.	T (°C)	P (bar)	Metathesis Catalyst	GC-FID[1]	GC-MS[2]	% conv.	mmol sub. left	mmol sub. converted	mmol BA
25	MuBuE	30	10	44-7775	ad.	ad.	8	0.18	0.04	-0.01
26	MuBuE	30	10	44-7785	ad.	ad.	6	0.18	0.03	-0.01
27	MuBuE	30	10	44-7790	BD	BA	9	0.17	0.05	0.00
28	MuBuE	30	10	T2358	ad.	ad.	27	0.14	0.14	-0.01
29*	MuBuE	30	10	None	ad.	ad.	0	0.19	0.00	-0.01
30**	HD	30	10	G1	BD, PR		88	0	0.44	n/a

[1] excluding ethylene

[2] excluding substrate

*blank

^reproducibility check using 2,4-hexadiene as substrate

[00175] Examples 31-54 were conducted as in Example 11, except that the pressure was increased to 40 bar. Results are shown in Table 4.

Table 4. Experimental results for di-n-butyl muconate reacted with ethylene in the presence of a homogeneous metathesis catalyst at 30°C and 40 bar

Ex.	Sub.	T (°C)	P (bar)	Metathesis Catalyst	GC-FID[1]	GC-MS[2]	% conv.	mmol sub. left	mmol sub. converted	mmol BA
31	MuBuE	30	40	73022	n.d.	n.d.	-10	0.40	-0.05	-0.01
32	MuBuE	30	40	G1	n.d.	n.d.	-4	0.37	-0.02	-0.01
33	MuBuE	30	40	G2	BD	BA, PD	23	0.28	0.12	0.11
34	MuBuE	30	40	HG2	BD	BA, PD	45	0.20	0.23	0.25
35	MuBuE	30	40	HG1	n.d.	BA (tr)	-5	0.38	-0.03	-0.01
36	MuBuE	30	40	578681	n.d.	BA (tr)	-6	0.38	-0.03	-0.01
37	MuBuE	30	40	578703	n.d.	PD	-2	0.37	-0.01	-0.01
38	MuBuE	30	40	682284	BD (tr)	BA (tr), PD	9	0.33	0.05	0.00
39	MuBuE	30	40	682330	BD	BA, PD	13	0.31	0.07	0.07
40	MuBuE	30	40	682365	BD	BA, PD	-1	0.36	-0.01	0.01
41*	MuBuE	30	40	none	n.d.	n.d.	0	0.36	0.00	-0.01
42**	HD	30	40	G1	BD, PR	n.d.	90	0	0.45	n/a
43	MuBuE	30	40	682373	BD	BA	46	0.21	0.23	0.23
44	MuBuE	30	40	682381	n.d.	n.d.	-1	0.39	-0.01	-0.01
45	MuBuE	30	40	42-1213	n.d.	n.d.	12	0.34	0.06	-0.01
46	MuBuE	30	40	44-0055	BD	BA	57	0.16	0.29	-0.05
47	MuBuE	30	40	44-0073	n.d.	n.d.	-3	0.40	-0.02	-0.01
48	MuBuE	30	40	44-0082	BD	BA, PD	19	0.31	0.10	0.08
49	MuBuE	30	40	44-7775	n.d.	n.d.	-1	0.39	-0.01	-0.01
50	MuBuE	30	40	44-7785	n.d.	n.d.	-7	0.41	-0.04	-0.01
51	MuBuE	30	40	44-7790	BD	BA (tr), PD	2	0.38	0.01	0.00
52	MuBuE	30	40	T2358	n.d.	n.d.	4	0.37	0.02	-0.01
53*	MuBuE	30	40	none	n.d.	n.d.	0	0.00	0.00	-0.01
54**	HD	30	40	G1	BD, PR	n.d.	92	0.46	0.46	n/a

[1] excluding ethylene

[2] excluding substrate

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^reproducibility check using 2,4-hexadiene as substrate

[00176] Examples 55-78 were conducted as in Example 11, except that the temperature was increased to 55°C and the pressure was increased to 25 bar. Results are shown in Table 5.

Table 5. Experimental results for di-n-butyl muconate reacted with ethylene in the presence of a homogeneous metathesis catalyst at 55°C and 25 bar

Ex.	Sub.	T (°C)	P (bar)	Metathesis Catalyst	GC-FID[1]	GC-MS[2]	% conv.	mmol sub. left	mmol sub. converted	mmol BA
55	MuBuE	55	25	73022	n.d.	n.d.	-1	0.36	-0.01	-0.01
56	MuBuE	55	25	G1	BD +others	BA (tr)	-3	0.37	-0.02	-0.01
57	MuBuE	55	25	G2	BD	BA, PD	37	0.23	0.19	0.16
58	MuBuE	55	25	HG2	BD	BA, PD	48	0.19	0.24	0.26
59	MuBuE	55	25	HG1	n.d.	BA (tr)	7	0.34	0.04	-0.01
60	MuBuE	55	25	578681	BD (tr)	BA (tr)	4	0.35	0.02	-0.01
61	MuBuE	55	25	578703	BD	n.d.	0	0.36	0.00	-0.01
62	MuBuE	55	25	682284	BD	BA, PD	17	0.30	0.09	0.04
63	MuBuE	55	25	682330	BD	BA, PD	18	0.30	0.09	0.12
64	MuBuE	55	25	682365	BD	BA, PD	9	0.33	0.05	0.06
65*	MuBuE	55	25	none	n.d.	n.d.	0	0.36	0.00	-0.01
66**	HD	55	25	G1	BD, PR	n.d.	92	0.00	0.46	n/a
67	MuBuE	55	25	682373	BD	BA, PD	27	0.25	0.14	0.17
68	MuBuE	55	25	682381	n.d.	n.d.	-12	0.38	-0.06	-0.01
69	MuBuE	55	25	42-1213	n.d.	n.d.	-7	0.36	-0.04	-0.01
70	MuBuE	55	25	44-0055	BD	BA, PD	6	0.32	0.03	0.10
71	MuBuE	55	25	44-0073	n.d.	n.d.	-25	0.42	-.13	-0.01
72	MuBuE	55	25	44-0082	BD	BA, PD	12	0.30	0.06	0.07
73	MuBuE	55	25	44-7775	BD	BA, PD	-5	0.36	-0.03	0.03
74	MuBuE	55	25	44-7785	BD	BA, PD	-1	0.34	-0.01	0.01
75	MuBuE	55	25	44-7790	BD	BA, PD	1	0.33	0.01	0.05
76	MuBuE	55	25	T2358	n.d.	n.d.	12	0.30	0.06	-0.01
77*	MuBuE	55	25	none	n.d.	n.d.	0	0.34	0.00	-0.01
78**	HD	55	25	G1	BD, PR	n.d.	92	0.00	0.46	n/a

[1] excluding ethylene

[2] excluding substrate

*blank

^reproducibility check using 2,4-hexadiene as substrate

[00177] Examples 79-102 were conducted as in Example 11, except that the temperature was increased to 80°C. Results are shown in Table 6.

Table 6. Experimental results for di-n-butyl muconate reacted with ethylene in the presence of a homogeneous metathesis catalyst at 80°C and 10 bar

Ex.	Sub.	T (°C)	P (bar)	Metathesis Catalyst	GC-FID[1]	GC-MS[2]	% conv.	mmol sub. left	mmol sub. converted	mmol BA
79	MuBuE	80	10	73022	n.d.	n.d.	1	0.42	0	-0.01
80	MuBuE	80	10	G1	BD	BA (tr)	8	0.39	0.04	-0.01
81	MuBuE	80	10	G2	BD	BA	44	0.24	0.22	0.19
82	MuBuE	80	10	HG2	BD+ others	BA, PD	57	0.18	0.29	0.26
83	MuBuE	80	10	HG1	BD	BA, PD	59	0	0.29	0.26
84	MuBuE	80	10	578681	BD	BA (tr)	10	0.38	0.05	-0.01
85	MuBuE	80	10	578703	BD	n.d.	3	0.41	0.01	-0.01
86	MuBuE	80	10	682284	BD	BA, PD	22	0.33	0.11	0.06
87	MuBuE	80	10	682330	BD	BA, PD	33	0.28	0.17	0.11
88	MuBuE	80	10	682365	BD	BA, PD	27	0.31	0.14	0.09
89*	MuBuE	80	10	none	n.d.	n.d.	0	0.43	0.00	-0.01
90**	HD	80	10	G1	BD, PR	n.d.	85	0.00	0.43	n/a
91	MuBuE	80	10	682373	BD	BA, PD	51	0.21	0.26	0.21
92	MuBuE	80	10	682381	BD	n.d.	8	0.40	0.04	-0.01
93	MuBuE	80	10	42-1213	n.d.	n.d.	5	0.41	0.03	-0.01
94	MuBuE	80	10	44-0055	BD	BA, PD	28	0.31	0.14	0.09
95	MuBuE	80	10	44-0073	n.d.	n.d.	5	0.41	0.03	-0.01
96	MuBuE	80	10	44-0082	BD	BA, PD	23	0.33	0.12	0.08
97	MuBuE	80	10	44-7775	BD	BA, PD	26	0.32	0.13	0.10
98	MuBuE	80	10	44-7785	BD	BA, PD	18	0.36	0.09	0.02
99	MuBuE	80	10	44-7790	BD	BA, PD	23	0.33	0.12	0.07
100	MuBuE	80	10	T2358	BD	n.d.	18	0.36	0.09	-0.01
101*	MuBuE	80	10	None	n.d.	n.d.	0	0.40	0.00	-0.01
102**	HD	80	10	G1	BD, PR	n.d.	87	0.00	0.44	n/a

[1] excluding ethylene

[2] excluding substrate

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^reproducibility check using 2,4-hexadiene as substrate

[00178] Examples 103-126 were conducted as in Example 11, except that the temperature was increased to 80°C and the pressure was increased to 40 bar. Results are shown in Table 7.

Table 7. Experimental results for di-n-butyl muconate reacted with ethylene in the presence of a homogeneous metathesis catalyst at 80°C and 40 bar

Ex.	Sub.	T (°C)	P (bar)	Metathesis Catalyst	GC-FID[1]	GC-MS[2]	% conv.	mmol MuBuE left	mmol MuBuE converted	mmol BA
103	MuBuE	80	40	73022	n.d.	n.d.	4	0.39	0.02	-0.01
104	MuBuE	80	40	G1	BD	BA	11	0.36	0.05	-0.01
105	MuBuE	80	40	G2	BD	BA, PD	49	0.19	0.24	0.21
106	MuBuE	80	40	HG2	BD +others	BA, PD	69	0.12	0.35	0.19
107	MuBuE	80	40	HG1	BD	BA	8	0.37	0.04	-0.01
108	MuBuE	80	40	578681	BD	BA	6	0.38	0.03	-0.01
109	MuBuE	80	40	578703	BD	n.d.	4	0.39	0.02	-0.01
110	MuBuE	80	40	682284	BD	BA, PD	27	0.29	0.14	0.04
111	MuBuE	80	40	682330	BD	BA, PD	43	0.23	0.21	0.06
112	MuBuE	80	40	682365	BD	BA, PD	18	0.33	0.09	0.08
113*	MuBuE	80	40	none	n.d.	n.d.	0	0.40	0	-0.01
114**	HD	80	40	G1	BD, PR	n.d.	90	0	0.45	n/a
115	MuBuE	80	40	682373	BD	BA, PD	63	0.15	0.31	0.21
116	MuBuE	80	40	682381	n.d.	n.d.	-2	0.41	-0.01	-0.01
117	MuBuE	80	40	42-1213	n.d.	n.d.	8	0.37	0.04	-0.01
118	MuBuE	80	40	44-0055	BD	BA, PD	42	0.23	0.21	0.08
119	MuBuE	80	40	44-0073	BD	n.d.	15	0.34	0.08	-0.01
120	MuBuE	80	40	44-0082	BD	BA, PD	23	0.31	0.11	0.06
121	MuBuE	80	40	44-7775	BD	BA, PD	25	0.30	0.13	0.07
122	MuBuE	80	40	44-7785	BD	BA, PD	15	0.34	0.08	0.01
123	MuBuE	80	40	44-7790	BD	BA, PD	52	0.27	0.26	0.06
124	MuBuE	80	40	T2358	n.d.	n.d.	16	0.34	0.08	-0.01
125	MuBuE	80	40	None	n.d.	n.d.	0	0.40	0.00	-0.01
126	HD	80	40	G1	BD, PR	n.d.	89	0.00	0.45	n/a

[1] excluding ethylene

[2] excluding substrate

*blank

^reproducibility check using 2,4-hexadiene as substrate

EXAMPLE 127. Ethenolysis reaction carried out using heterogeneous metathesis catalysts

[00179] Example 127 was carried out as in Example 11, except heterogeneous catalysts were used, and pressure and temperature were varied as described below. For heterogeneous catalysts prepared in-house, three metal containing stock solutions were made according to the following recipes. To make a rhenium stock solution, 2160.6 mg ammonium perrhenate(VII) (having a metal w/w of 0.694258) was added to 50000 microliters water to result in a stock solution having 30 mg metal/mL. To the Re-stock a few drops of 65% HNO_3 were added. To make a Mo stock solution, 2761.4 mg ammonium molybdate (para) tetrahydrate (having a metal w/w of 0.54321) was added to 10000 microliters water to result in a stock solution having 150

mg metal/mL. To make a W stock solution, 2010.5 mg ammonium metatungstate hydrate (having a metal w/w of 0.74607) were added to 10000 microliters water to result in a stock solution having 150 mg metal/mL.

[00180] The support (commercial gamma-alumina) was impregnated using the respective stock solutions by Incipient Wetness (IWI) or dilution (DIL) for at least 24 h. Table 9 provides compositions for the heterogeneous catalysts made in-house.

Table 9. Heterogeneous cata**ysts** made in-house

Catalyst ID	Method	Metal	Loading (wt%)	Support (g)	Metal needed (mg)	StockID	Stock volume (uL)	Water (uL)	Total volume (mL)	Impregnation time
HC04a	IWI	Mo	10	1	100	Mo-stock	667	833	1.5	24 h minimum
HC05a	IWI	W	10	1	100	W-stock	667	833	1.5	24 h minimum
HC01b	DIL	Re	5	1	50	Re-stock	1650	3350	5	24 h minimum
HC02b	DIL	Re	10	1	100	Re-stock	3350	1650	5	24 h minimum
HC03b	DIL	Re	15	1	150	Re-stock	5000	0	5	24 h minimum
HC04b	DIL	Mo	10	1	100	Mo-stock	667	4333	5	24 h minimum
HC05b	DIL	W	10	1	100	W-stock	667	4333	5	24 h minimum

[00181] The catalysts were dried in porcelain cups under air as follows. The temperature was ramped to 80°C at 2°C/min, with a 2 hour hold at 80°C, followed by a temperature ramp to 110°C at 2°C/min, with a 2 hour hold at 110°C, followed by a ramp to 525°C at 5°C/min, with a 24 hour hold at 525°C.

[00182] The following catalysts were screened under the following conditions 30°C, 10 bar; 30°C, 40 bar; 55°C, 25 bar; 80°C, 10 bar; and 80°C, 40 bar: HC04a at 30% loading, HC05a at 30% loading, HCOlb at 30% loading, HC02b at 30% loading, HC03b at 30% loading, HC04b at 30% loading, HC05b at 30% loading, 42190* at 16% loading, 42190 at 16% loading, and 44-0083 at 8%, loading. Of these reactions, only catalyst 44-0083 showed the presence of BA and PD by GC-MS in the liquid phase reaction mixture and BD in the reactor head space when reacted at 30°C, 10 bar (5% conversion of di-n-butyl muconate), 30°C, 40 bar (5% conversion of di-n-butyl muconate), 55°C, 25 bar (7% conversion), and 80°C, 10 bar (6%> conversion).

[00183] All publications, patents, and patent applications cited in this specification are herein incorporated by reference as if each individual publication, patent, or patent application were specifically and individually indicated to be incorporated by reference. While the claimed

subject matter has been described in terms of various embodiments, the skilled artisan will appreciate that various modifications, substitutions, omissions, and changes may be made without departing from the spirit thereof. Accordingly, it is intended that the scope of the claimed subject matter is limited solely by the scope of the following claims, including equivalents thereof.

CLAIMS

What is claimed is:

1. A method, comprising reacting muconic acid or an ester of muconic acid with ethylene in the presence of a metathesis catalyst to form 1,3-butadiene.

2. A method, comprising reacting muconic acid with ethylene in the presence of a metathesis catalyst to form acrylic acid.

3. A method, comprising reacting a muconic acid ester with ethylene in the presence of a metathesis catalyst to form an acrylic acid ester.

4. The method of claim 3, comprising reacting a dialkyl muconate having formula R^OOC-CH=CH-CH=CH-COOR^1 with ethylene in the presence of a metathesis catalyst to form an acrylic acid ester having formula R^{1}OOC-CH=CH$_2$, wherein R^1 is a Ci-Cio alkyl group.

5. A method, comprising reacting muconic acid with ethylene in the presence of a metathesis catalyst to form 1,3-butadiene and acrylic acid.

6. A method, comprising reacting a muconic acid ester with ethylene in the presence of a metathesis catalyst to form 1,3-butadiene and an acrylic acid ester.

7. The method of claim 6, comprising reacting a dialkyl muconate having formula R^OC-CH=CH-CH=CH-COOR^1 with ethylene in the presence of a metathesis catalyst to form 1,3-butadiene and an acrylic acid ester having formula R^{1}OOC-CH=CH$_2$, wherein R^1 is a Ci-Cio alkyl group.

8. The method of any one of claims 2-7, wherein at least about 1.2 moles acrylic acid or acrylate are formed per mole muconic acid or muconic acid ester.

9. The method of any one of claims 1-8, wherein the most prevalent isomer in the muconic acid or the muconic acid ester is the cis,cis isomer.

10. The method of any one of claims 1-8, wherein the most prevalent isomer in the muconic acid or the muconic acid ester is the cis,trans isomer.

11. The method of any one of claims 1-8, wherein the most prevalent isomer in the muconic acid or the muconic acid ester is the trans,trans isomer.

12. A method, comprising providing microbially-derived muconic acid, optionally esterifying the muconic acid to form a muconic acid ester, and reacting muconic acid or an ester of muconic acid with ethylene in the presence of a metathesis catalyst to form 1,3-butadiene.

13. A method, comprising providing microbially-derived muconic acid, and reacting muconic acid with ethylene in the presence of a metathesis catalyst to form acrylic acid.

14. A method, comprising providing microbially-derived muconic acid, and reacting the muconic acid with ethylene in the presence of a metathesis catalyst to form 1,3-butadiene and acrylic acid.

15. A method, comprising providing microbially-derived muconic acid, forming one or more of a cis,cis-muconic acid ester, a cis,trans-muconic acid ester, and a trans,trans-muconic acid ester or a mixture thereof from the muconic acid, and reacting the one or more muconic acid esters with ethylene in the presence of a metathesis catalyst to form one or more acrylic acid esters.

16. A method, comprising providing microbially-derived muconic acid, forming one or more of a cis,cis-muconic acid ester, a cis,trans-muconic acid ester, and a trans,trans-muconic acid ester or a mixture thereof from the muconic acid, and reacting the one or more muconic acid esters with ethylene in the presence of a metathesis catalyst to form one or more acrylic acid esters and 1,3-butadiene.

17. The method of any one of claims 1-16, wherein the reaction is carried out at a temperature in a range from about 30°C-80°C.

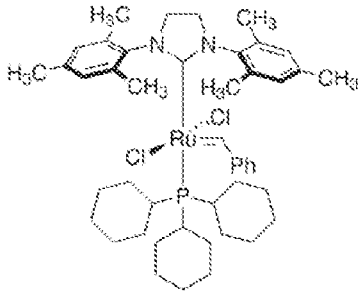
18. The method of any one of claims 1-16, wherein the reaction is carried out at an ethylene pressure in a range from about 2 bar to about 50 bar.

19. The method of any one of claims 1-16, wherein the reaction is carried out at a temperature in a range from about 30°C to about 80°C, and an ethylene pressure in a range from about 2 bar to about 50 bar.

20. The method of any one of claims 1-19, wherein the reaction is carried out at a temperature in a range from about 30°C to about 80°C, and an ethylene pressure in a range from about 5 bar to about 40 bar.

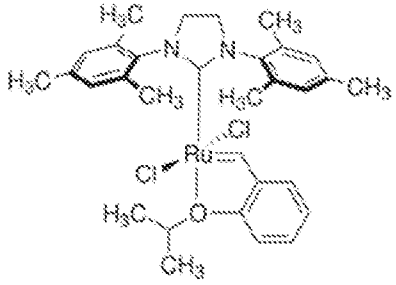
21. The method of any one of claims 1-20, wherein the metathesis catalyst comprises Ruthenium.

22. The method of any one of claims 1-21, wherein the metathesis catalyst comprises a Grubbs second generation catalyst having structure (2):



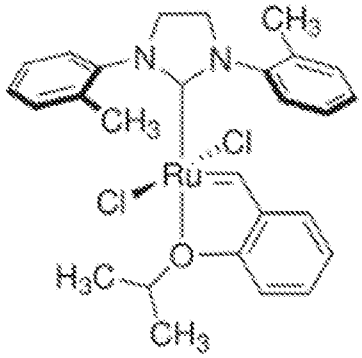
(2).

23. The method of any one of claims 1-21, wherein the metathesis catalyst comprises a second generation Hoveyda-Grubbs catalyst having structure (15):



(15).

24. The method of any one of claims 1-21, wherein the metathesis catalyst comprises a catalyst having structure (4):



(4)·

25. The method of any one of claims 1-24, wherein the catalyst is present at an amount of about 0.5-5mol% based on the amount of muconic acid or muconic acid ester.

26. The method of claim 25, wherein the catalyst is present at an amount of about 0.5 to 5 mol% based on the amount of muconic acid or muconic acid ester.

27. A method, comprising reacting muconic acid or a muconic acid ester with ethylene in the presence of a metathesis catalyst in a reactor to produce gaseous reaction products in the reactor, and obtaining 1,3-butadiene from the gaseous reaction products.

28. The method of claim 27, comprising withdrawing at least a portion of gaseous reaction products from the reactor during the reaction.

29. The method of claim 27 or 28, comprising providing microbially-derived muconic acid and reacting the microbially-derived muconic acid with ethylene in the presence of a metathesis catalyst.

30. The method of claim 27 or 28, comprising providing microbially-derived muconic acid, forming a muconate ester from the microbially-derived muconic acid, and reacting the muconate ester with ethylene in the presence of a metathesis catalyst.

31. A method, comprising reacting muconic acid or a muconic acid ester with ethylene in the presence of a metathesis catalyst in a reactor to produce one or more reaction products in a liquid phase in the reactor, and obtaining acrylic acid or an acrylic acid ester from the liquid phase.

32. The method of claim 31, comprising withdrawing at least a portion of gases in a head space of the reactor during the reaction.

33. The method of claim 31 or 32, comprising providing microbially-derived cis,cis-muconic acid and reacting the microbially-derived cis,cis-muconic acid with ethylene in the presence of a metathesis catalyst.

34. The method of claim 31 or 32, comprising providing microbially-derived cis,cis-muconic acid, forming a muconate ester from the microbially-derived cis,cis-muconic acid, and reacting the muconate ester with ethylene in the presence of a metathesis catalyst.

35. A method, comprising reacting muconic acid or a muconic acid ester with ethylene in the presence of a metathesis catalyst in a reactor to produce one or more reaction products in a gas phase in the reactor and one or more reaction products in a liquid phase in the reactor, obtaining 1,3-butadiene from the gaseous reaction products, and obtaining acrylic acid or an acrylate ester from the liquid phase.

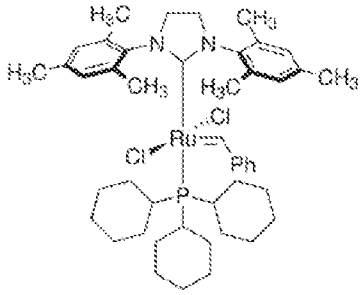
36. The method of claim 35, comprising withdrawing at least a portion of the gaseous reaction products from the reactor during the reaction.

37. The method of claim 35 or 36, comprising providing microbially-derived muconic acid and reacting the microbially-derived muconic acid with ethylene in the presence of a metathesis catalyst.

38. The method of claim 35 or 36, comprising providing microbially-derived muconic acid, forming a muconate ester from the microbially-derived muconic acid, and reacting the muconate ester with ethylene in the presence of a metathesis catalyst.

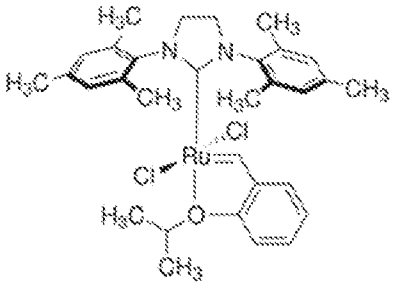
39. The method of any one of claims 27-38, wherein the metathesis catalyst comprises ruthenium.

40. The method of any one of claims 27-39, wherein the metathesis catalyst comprises a 2nd generation Grubbs catalyst having structure (2):



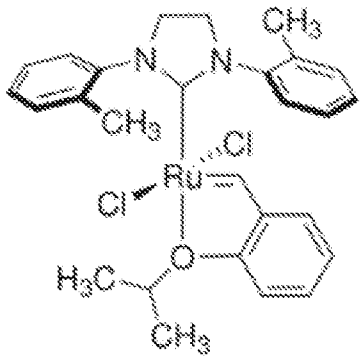
(2).

41. The method of any one of claims 27-39, wherein the metathesis catalyst comprises a second generation Hoveyda-Grubbs catalyst having structure (15):



(15).

42. The method of any one of claims 27-39, wherein the metathesis catalyst comprises a catalyst having structure (4):



(4).

43. The method of any one of claims 27-42, conducted at a temperature in a range from about 30°C to about 80°C.

44. The method of any one of claims 27-42, conducted at an ethylene pressure in a range from about 2 bar to about 50 bar.

45. The method of any one of claims 27-42, conducted at a temperature in a range from about 30°C to about 80°C and an ethylene pressure in a range from about 2 bar to about 50 bar.

46. The method of claim 45, conducted at a temperature in a range from about 30°C to about 80°C and an ethylene pressure in a range from about 10 bar to about 40 bar.

47. A method, comprising making a polymer using 1,3-butadiene made by a method of any one of claims 1-46.

48. A method, comprising making a polymer using acrylic acid or an acrylic acid ester made by a method of any one of claims 1-46.

49. A composition, comprising or derived from 1,3-butadiene made by a method of any one of claims 1-46.

50. A composition, comprising or derived from acrylic acid or an acrylic acid ester made by a method of any one of claims 1-46.

51. A composition, comprising or derived from 1,3-butadiene and acrylic acid made by a method of any one of claims 1-46.

52. A composition, comprising or derived from 1,3-butadiene and an acrylate ester made by a method of any one of claims 1-46.

53. An oil derived from 1,3-butadiene made by a method of any one of claims 1-46.

54. A polymer derived from 1,3-butadiene made by a method of any one of claims 1-46.

55. An oil derived from acrylic acid or an acrylate ester made by the method of any one of claims 1-46.

56. A polymer derived from acrylic acid or an acrylate ester made by the method of any one of claims 1-46.

57. The method of any one of claims 1-46, wherein the ethylene is plant-derived.

58. The composition of any one of claims 50-52, comprising at least 30% carbons originating from a non-fossil fuel carbon source.

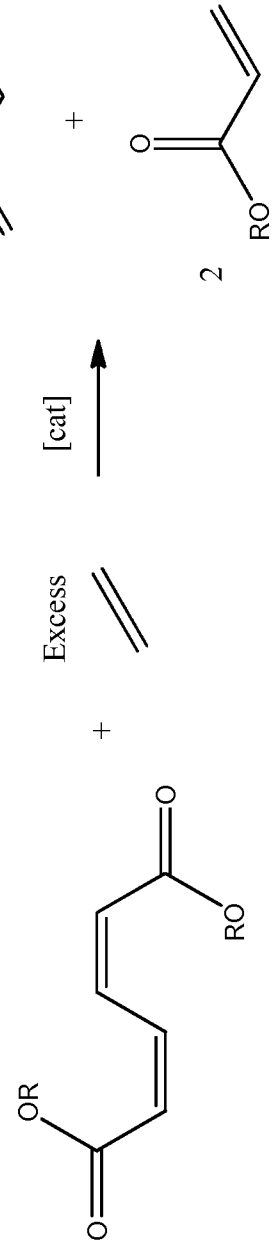


FIGURE 1A

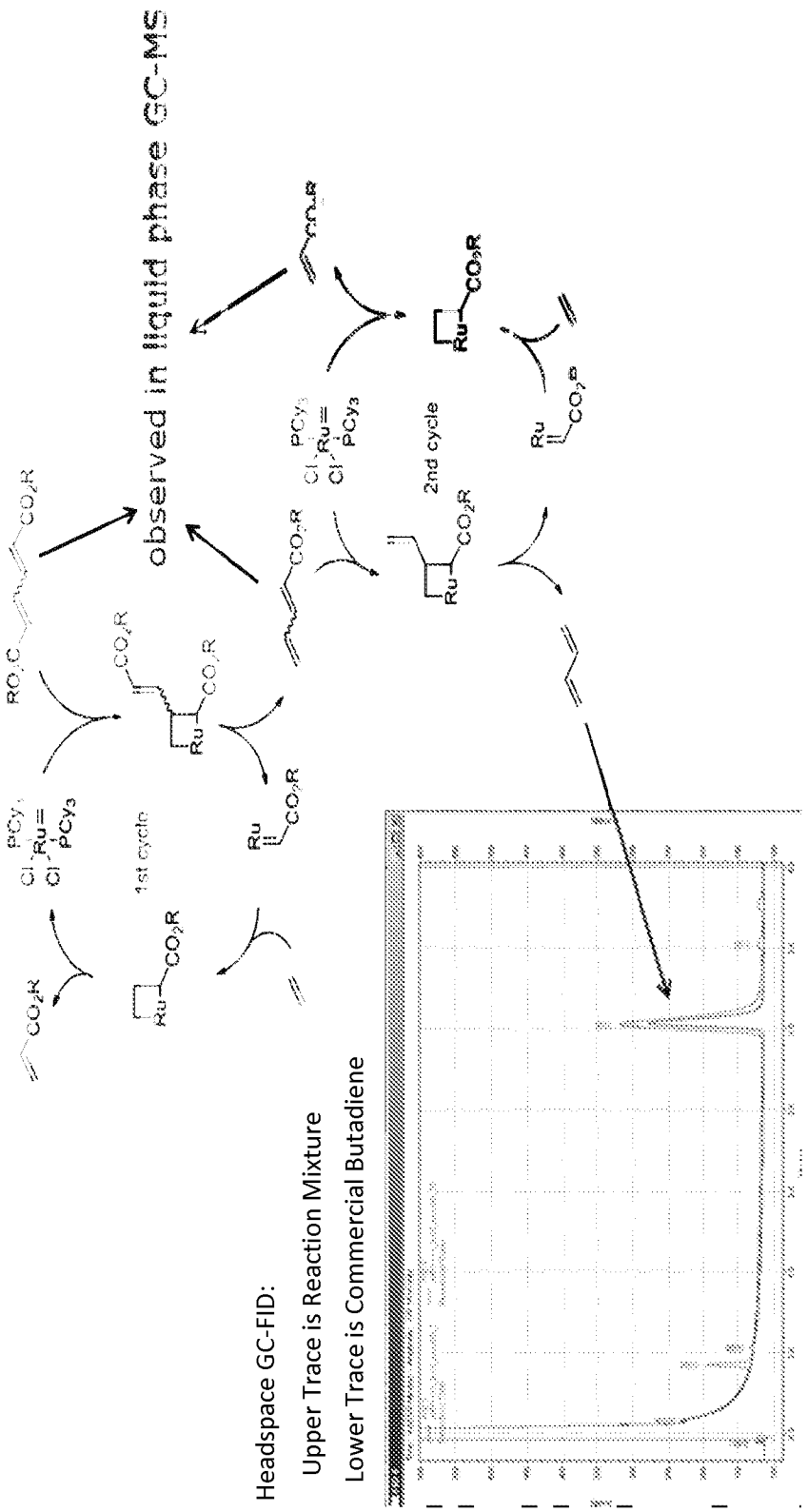

observed in liquid phase GC-MS
1st cycle
2nd cycle
Headspace GC-FID:
Upper Trace is Reaction Mixture
Lower Trace is Commercial Butadiene

FIGURE 1B

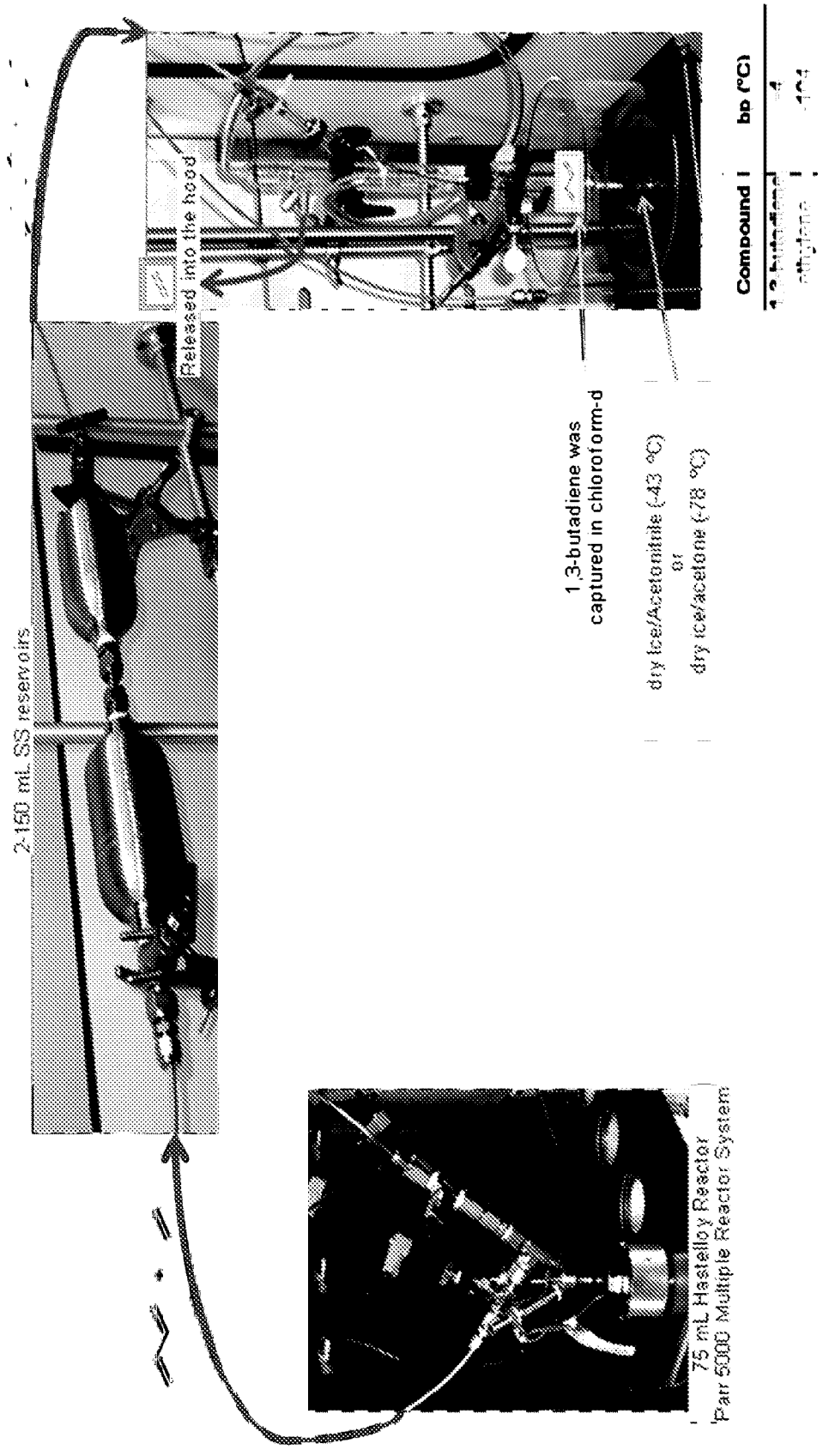

2-150 mL SS reservoirs
Released into the hood
1,3-butadiene was
captured in chloroform-d
dry ice/Acetonitrile (-43 °C)
or
dry ice/acetone (-78 °C)
75 mL Hastelloy Reactor
Parr 5000 Multiple Reactor System
Compound
bp (°C)
1,3-butadiene
-4
ethylene
-104

FIGURE 2

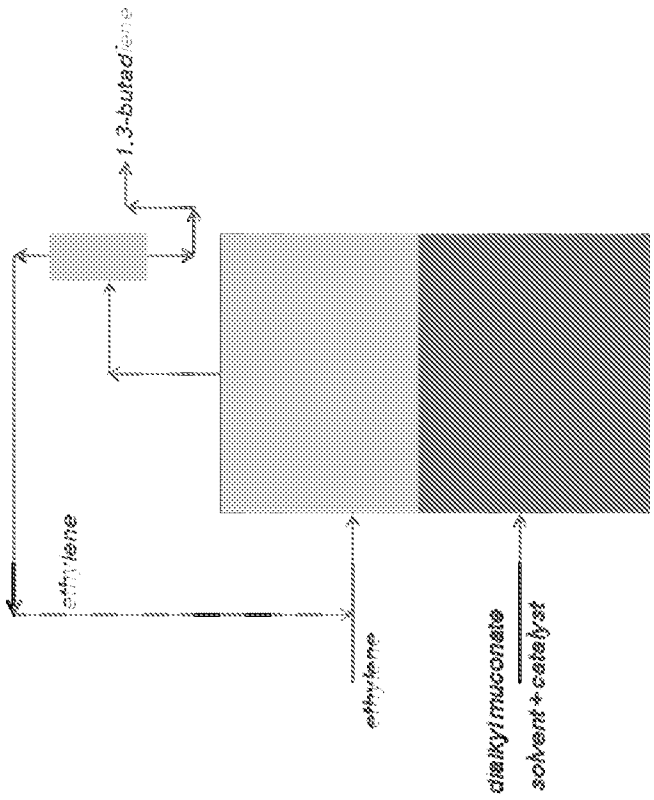

1,3-butadiene
ethylene
ethylene
dialkyl muconate
solvent + catalyst

FIGURE 3A

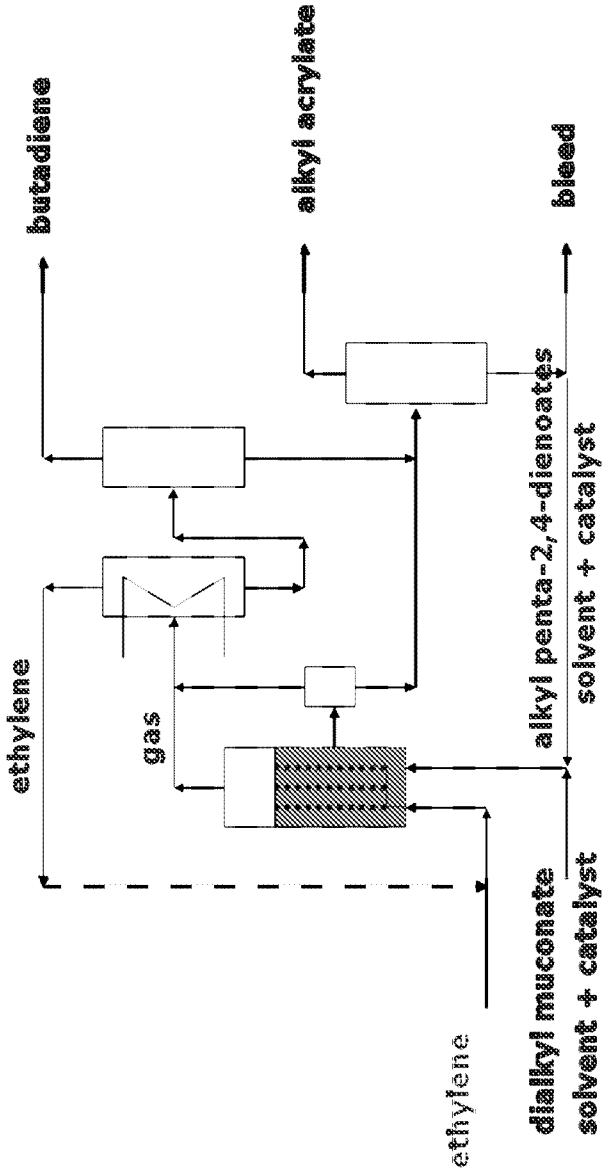

butadiene
alkyl acrylate
bleed
ethylene
gas
alkyl penta-2,4-dienoates
solvent + catalyst
ethylene
dialkyl muconate
solvent + catalyst

FIGURE 3B

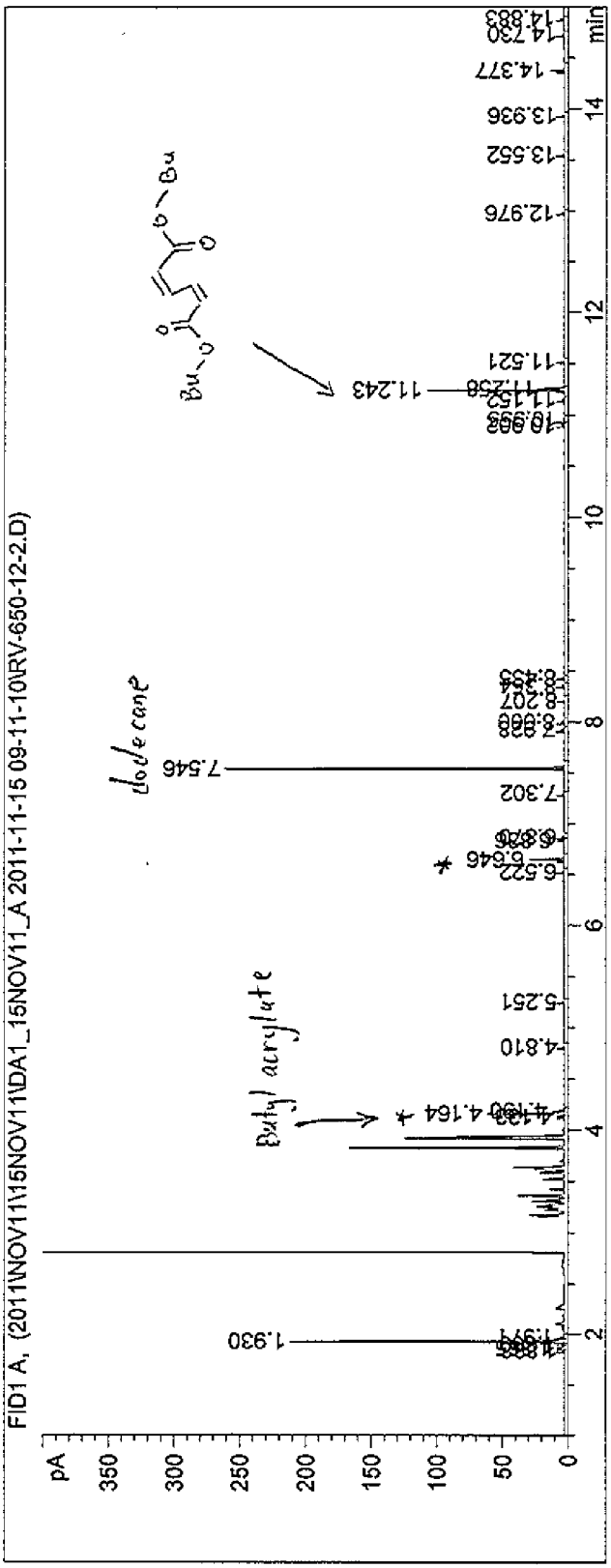

FID1 A, (2011NOV11\15NOV11\DA1_15NOV11_A 2011-11-15 09-11-10\RV-650-12-2.D)
pA
350
300
250
200
150
100
50
0
2
4
6
8
10
12
14
min
1.930
4.164
7.546
11.243
Butyl acrylate
Dodecane
Bu
O

FIGURE 4A

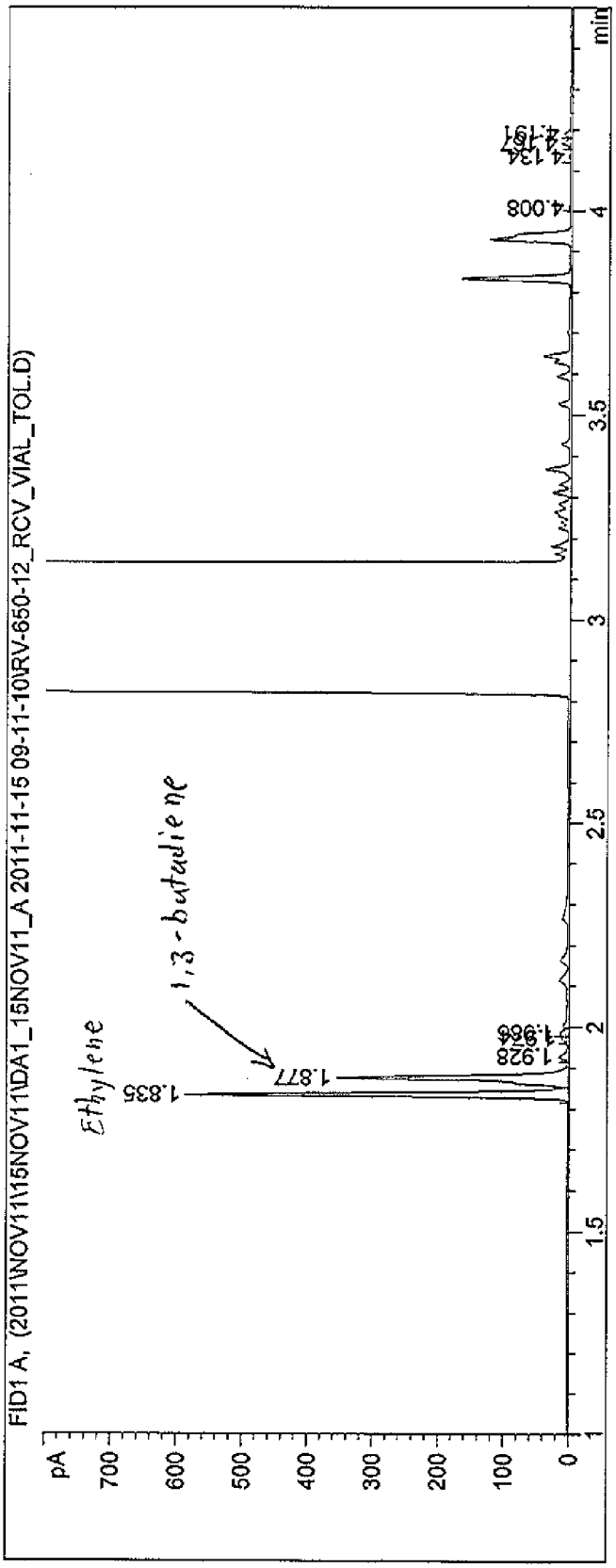

FID1 A, (2011\NOV11\15NOV11\DA1_15NOV11_A 2011-11-15 09-11-10\RV-650-12_RCV_VIAL_TOL.D)
pA
700
600
500
400
300
200
100
0
1
1.5
2
2.5
3
3.5
4
min
Ethylene
1,3-butadiene
1.835
1.877
1.928
1.965
4.008
4.134
4.191

FIGURE 4B

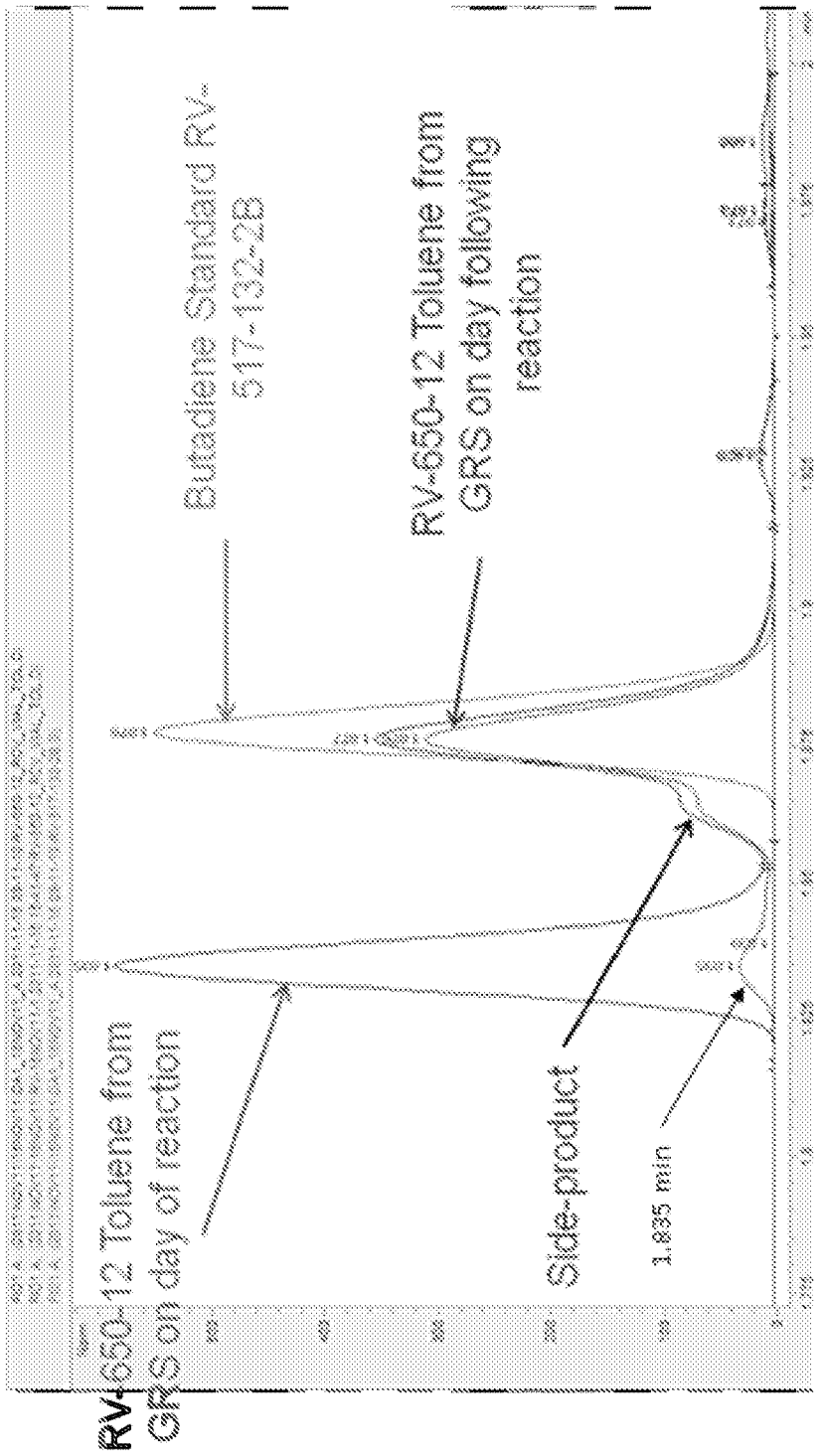

RV-650-12 Toluene from GRS on day of reaction
Butadiene Standard RV-517-132-28
RV-650-12 Toluene from GRS on day following reaction
Side-product
1.835 min
1. The peak profile does not change over time
2. The peak at 1.835 min is likely ethylene

FIGURE 4C

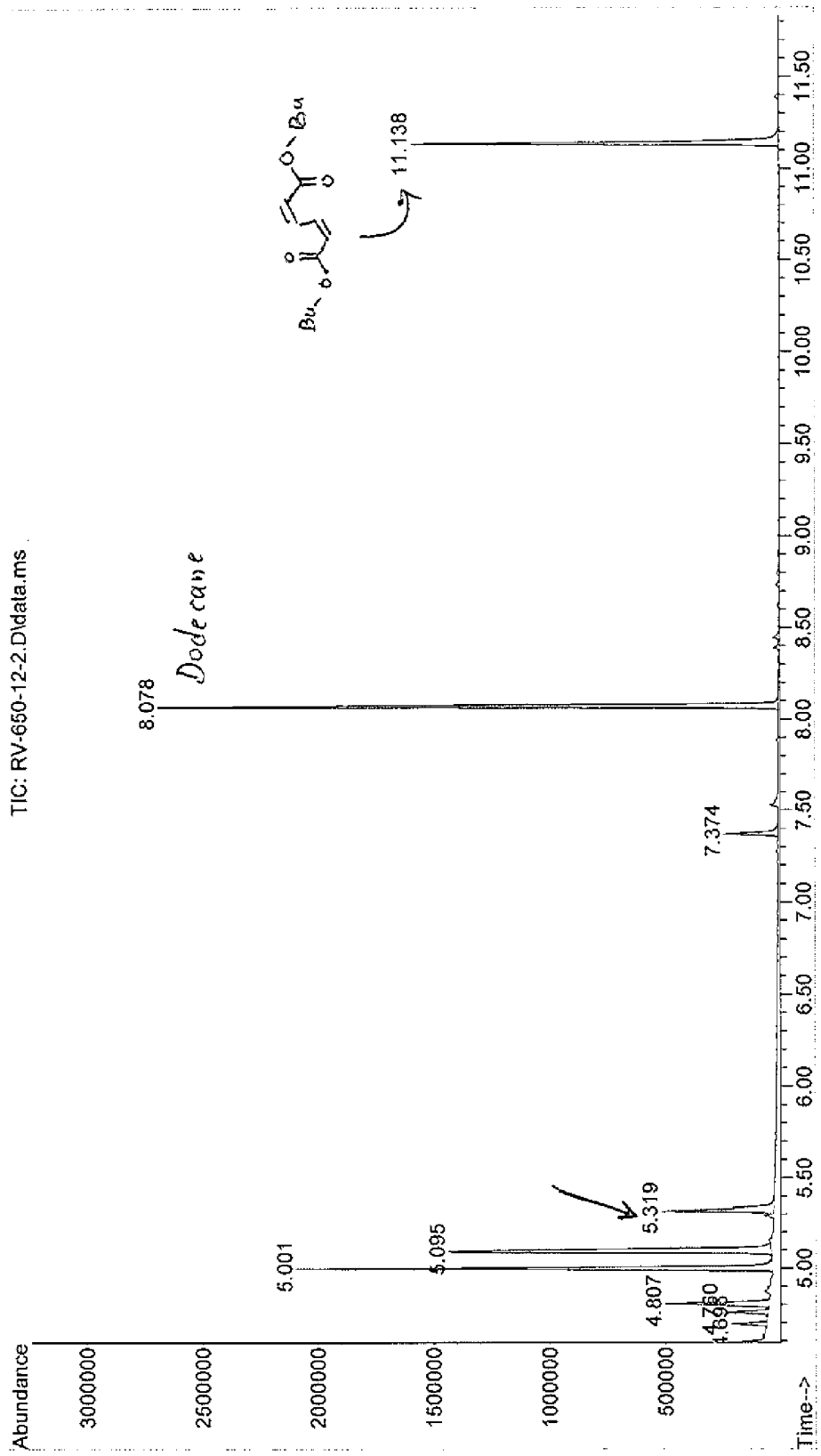

TIC: RV-650-12-2.D\data.ms
Abundance
3000000
2500000
2000000
1500000
1000000
500000
Time-->
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
9.00
9.50
10.00
10.50
11.00
11.50
8.078
Dodecane
11.138
Bu
Bu
7.374
5.319
5.095
5.001
4.807
4.760
4.698

FIGURE 4D

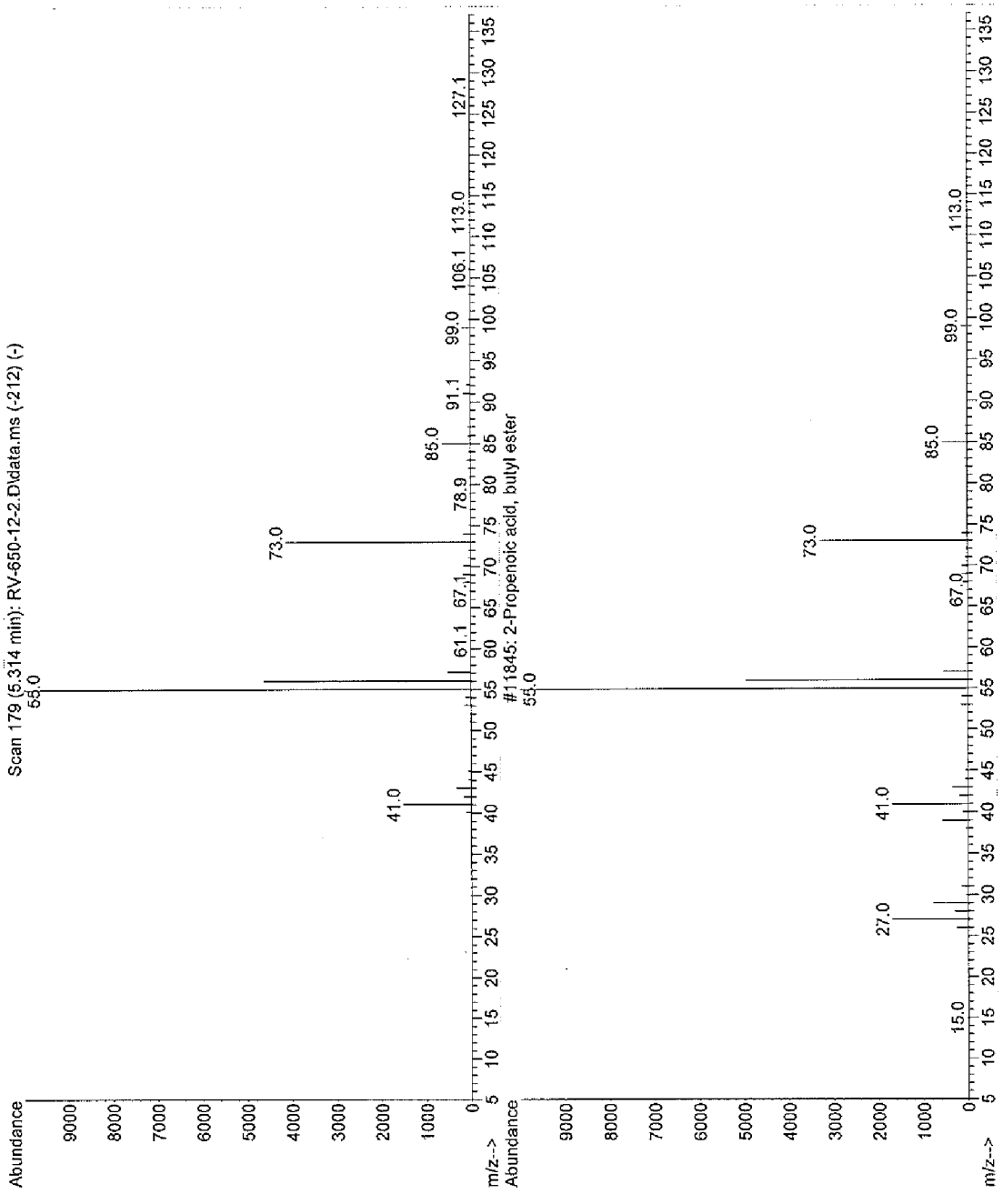

Scan 179 (5.314 min): RV-650-12-2.D\data.ms (-212) (-)
#11845: 2-Propenoic acid, butyl ester
Abundance
m/z-->

FIGURE 4E

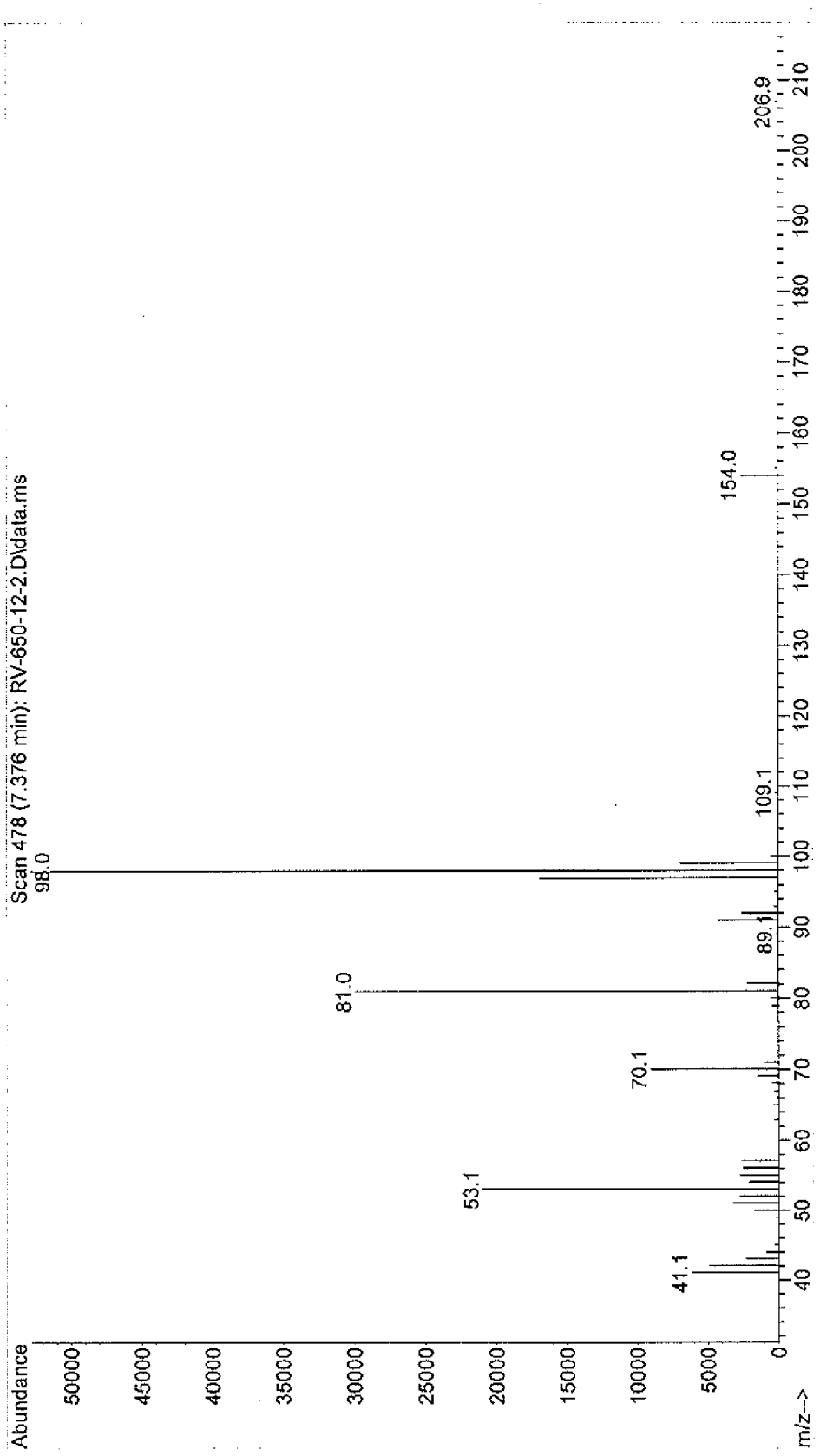

Scan 478 (7.376 min): RV-650-12-2.D\data.ms
Abundance
m/z-->
98.0
81.0
53.1
41.1
70.1
89.1
109.1
154.0
206.9

FIGURE 4F

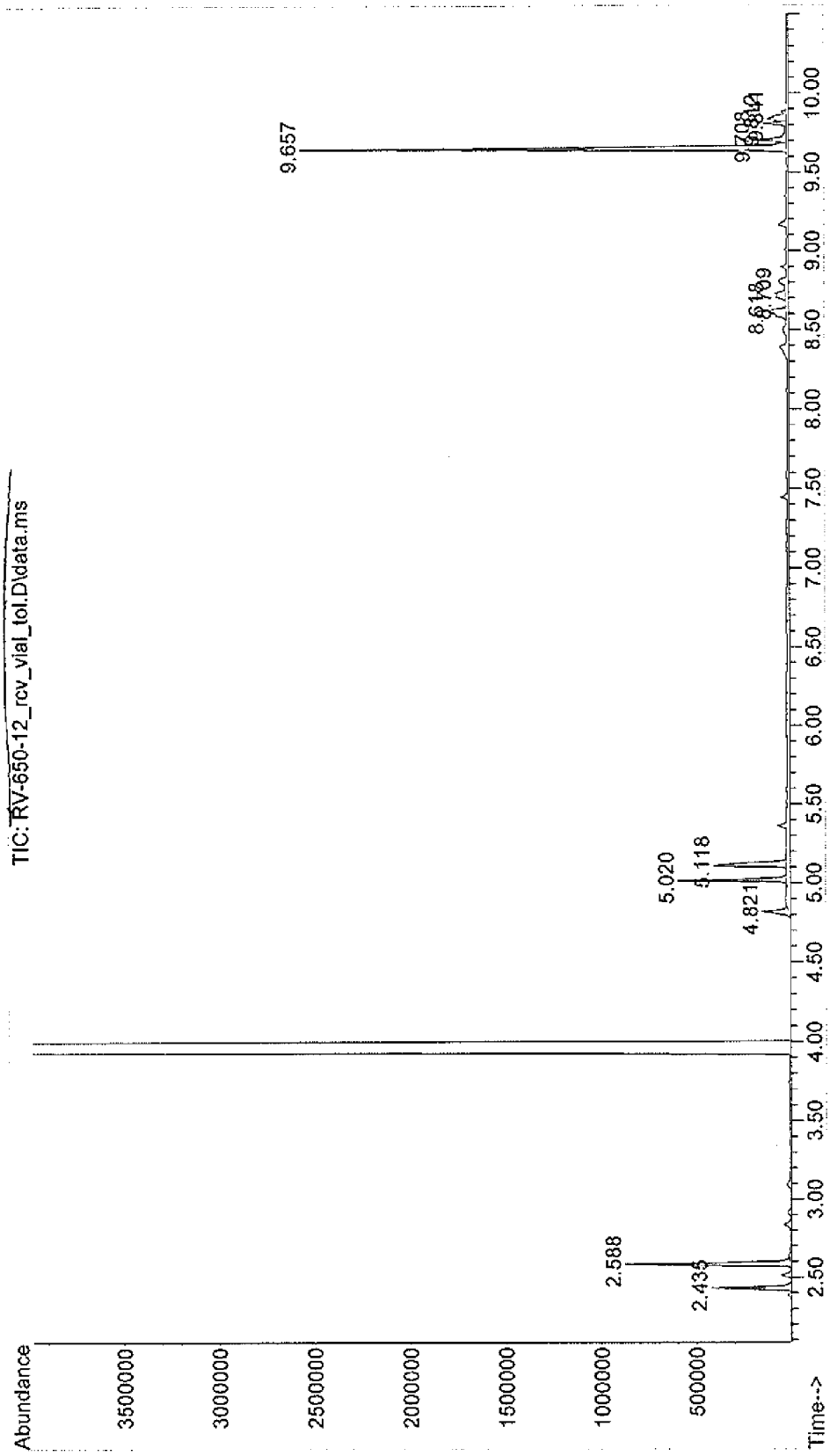

TIC: RV-650-12_rcv_vial_tol.D\data.ms
Abundance
3500000
3000000
2500000
2000000
1500000
1000000
500000
Time-->
2.50
3.00
3.50
4.00
4.50
5.00
5.50
6.00
6.50
7.00
7.50
8.00
8.50
9.00
9.50
10.00
2.588
2.435
4.821
5.020
5.118
8.618
8.789
9.657

FIGURE 4G

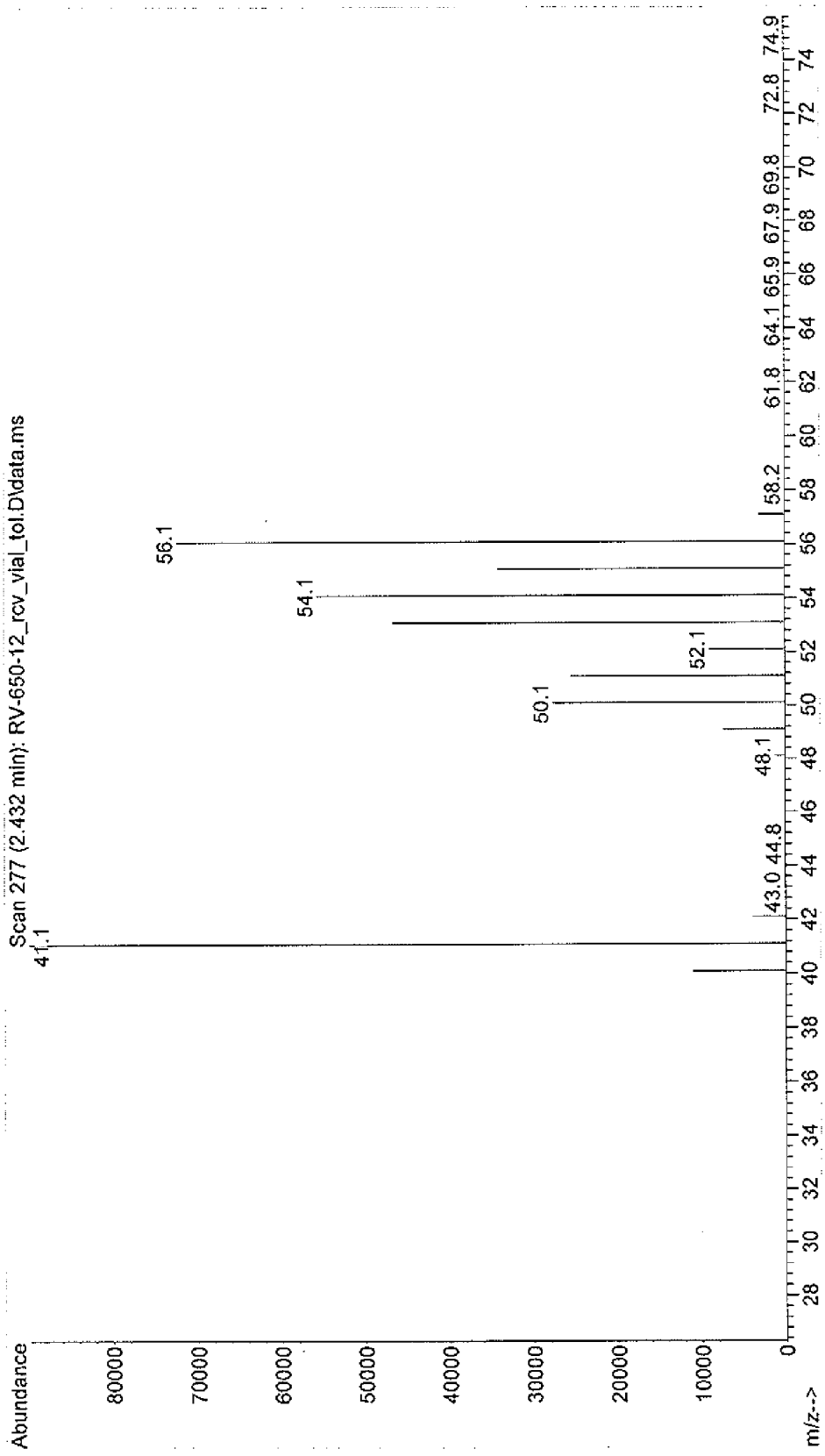

Scan 277 (2.432 min): RV-650-12_rcv_vial_tol.D\data.ms
Abundance
m/z-->
41.1
43.0
44.8
48.1
50.1
52.1
54.1
56.1
58.2
61.8
64.1
65.9
67.9
69.8
72.8
74.9

FIGURE 4H

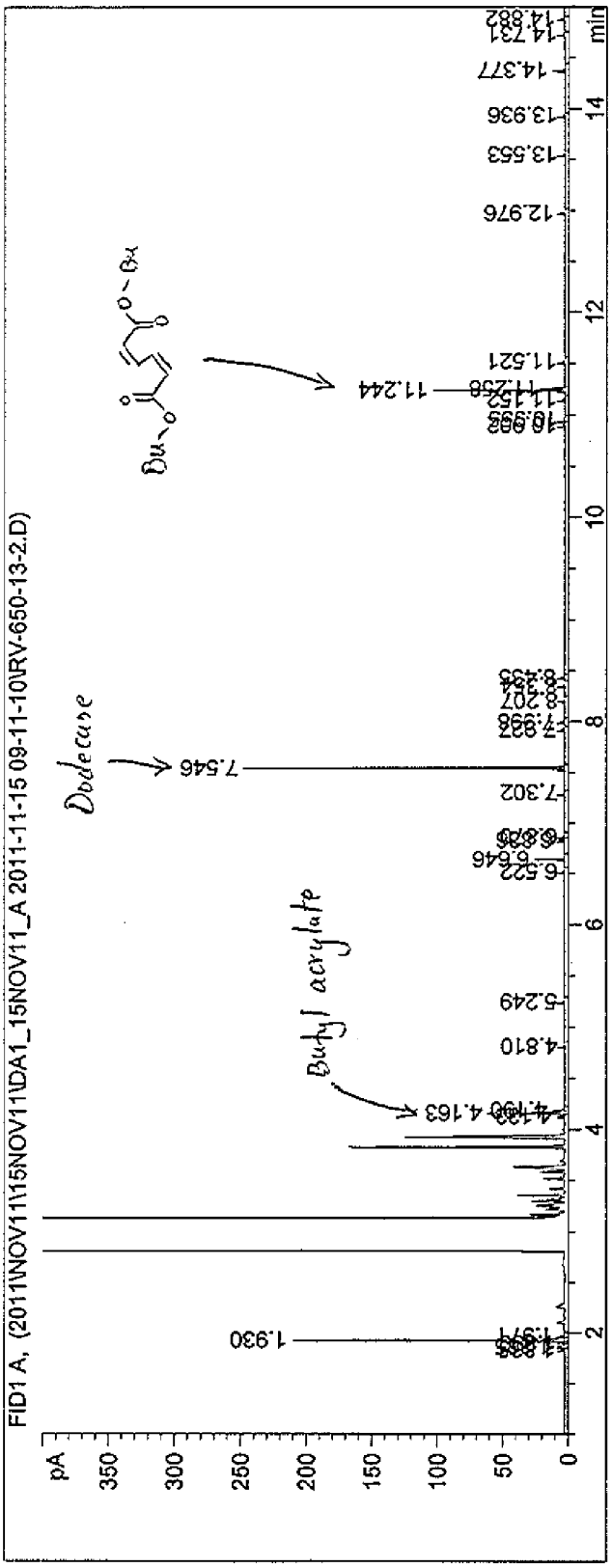

FID1 A, (2011\NOV11\15NOV11\DA1_15NOV11_A 2011-11-15 09-11-10\RV-650-13-2.D)
pA
min
Dodecane
Butyl acrylate
1.930
4.163
7.546
11.244

FIGURE 5A

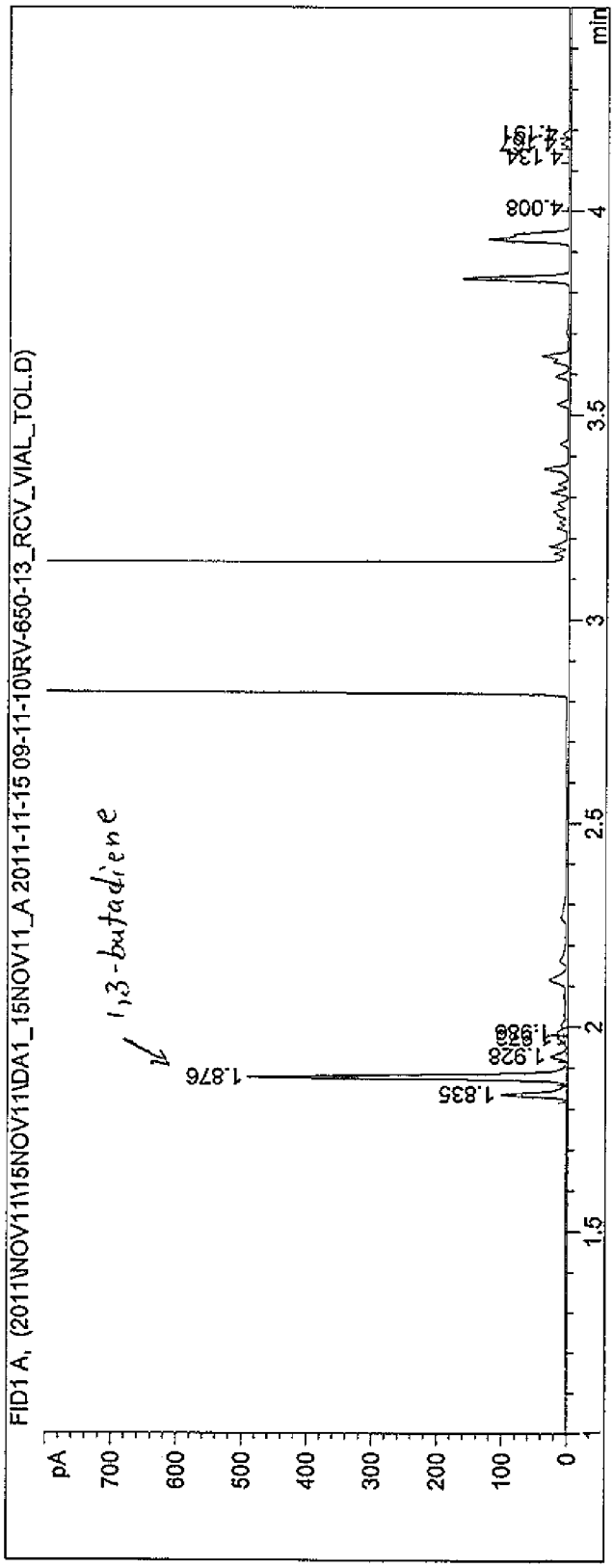
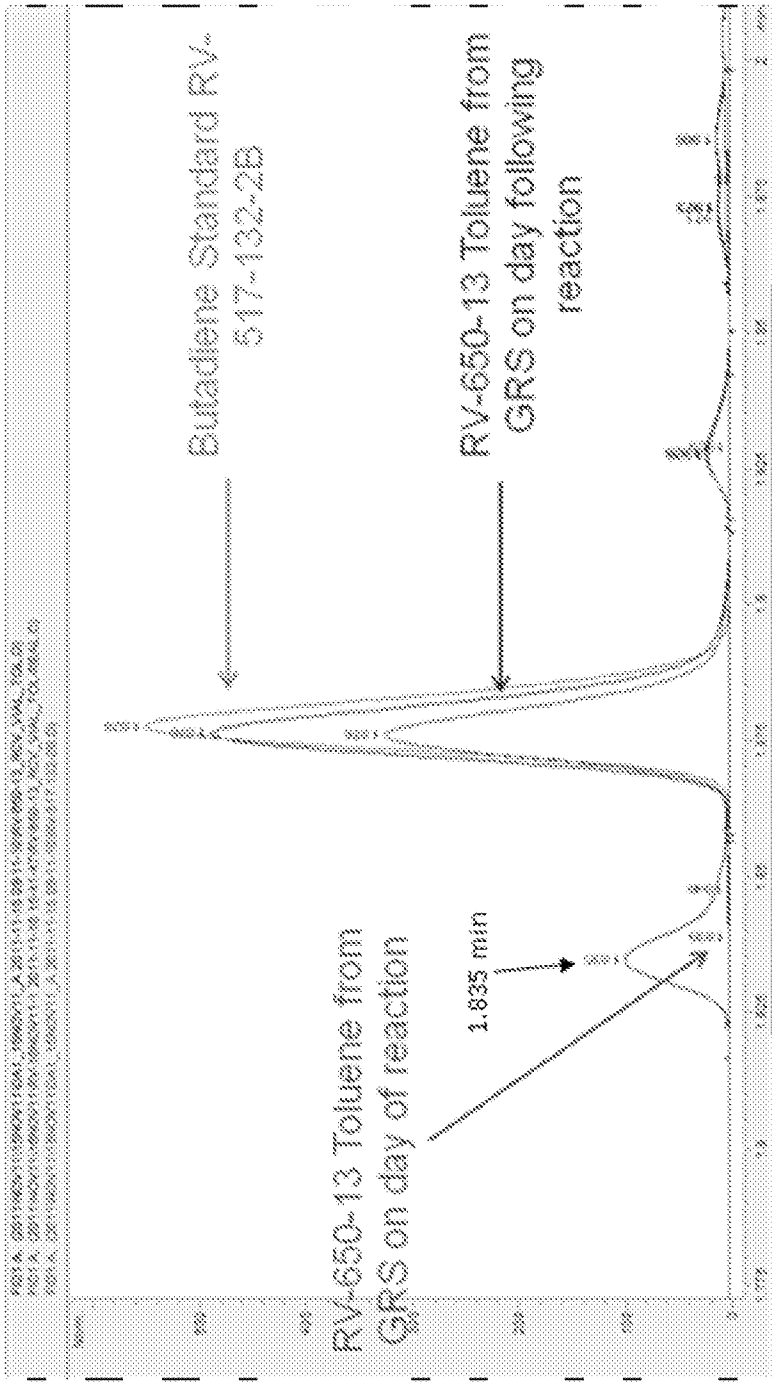

FID1 A, (2011\NOV11\15NOV11\DA1_15NOV11_A 2011-11-15 09-11-10\RV-650-13_RCV_VIAL_TOL.D)
pA
700
600
500
400
300
200
100
0
1
1.5
2
2.5
3
3.5
4
min
1,3-butadiene
1.835
1.876
1.928
1.988
4.008
4.134
4.181

FIGURE 5B



1. **The peak profile** does not change over time
2. **The peak at 1.835 min is likely ethylene**
3. Side-product not present

FIGURE 5C

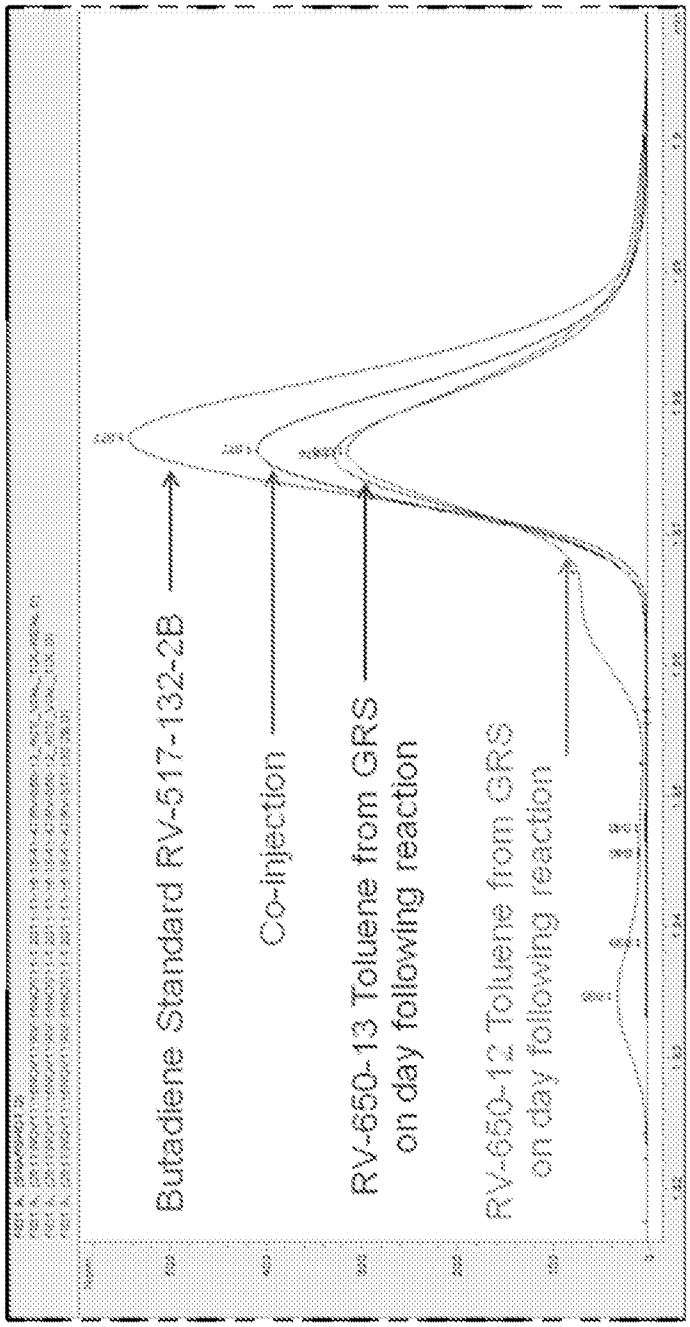

Butadiene Standard RV-617-132-2B
Co-injection
RV-650-13 Toluene from GRS
on day following reaction
RV-650-12 Toluene from GRS
on day following reaction

FIGURE 5D

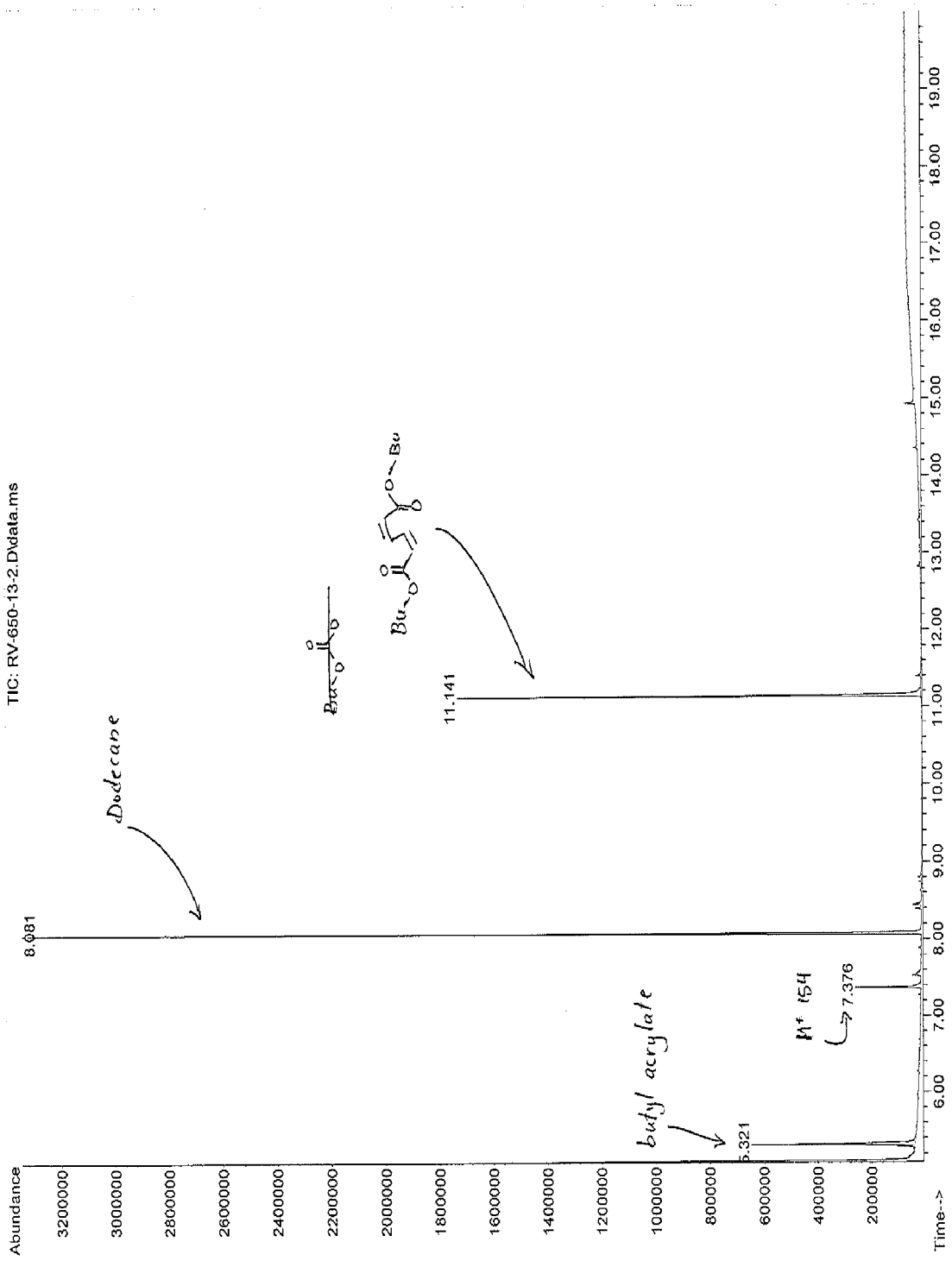

TIC: RV-650-13-2.Dvdata.ms
Abundance
Time-->
Dodecane
8.081
butyl acrylate
5.321
M+ 154
7.376
11.141

FIGURE 5E

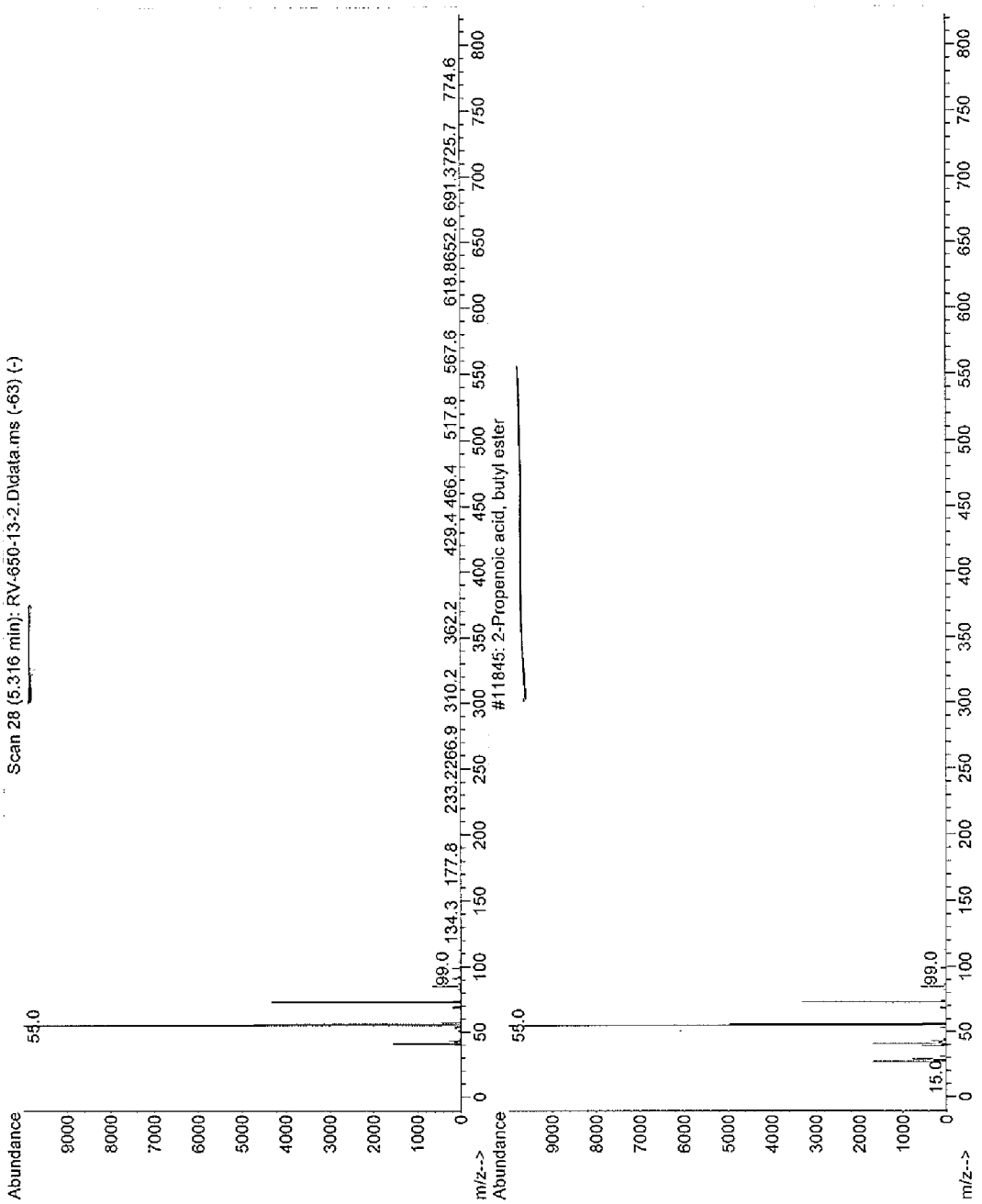

Scan 28 (5.316 min): RV-650-13-2.Dldata.ms (-63) (-)
Abundance
m/z-->
#11845: 2-Propenoic acid, butyl ester
Abundance
m/z-->

FIGURE 5F

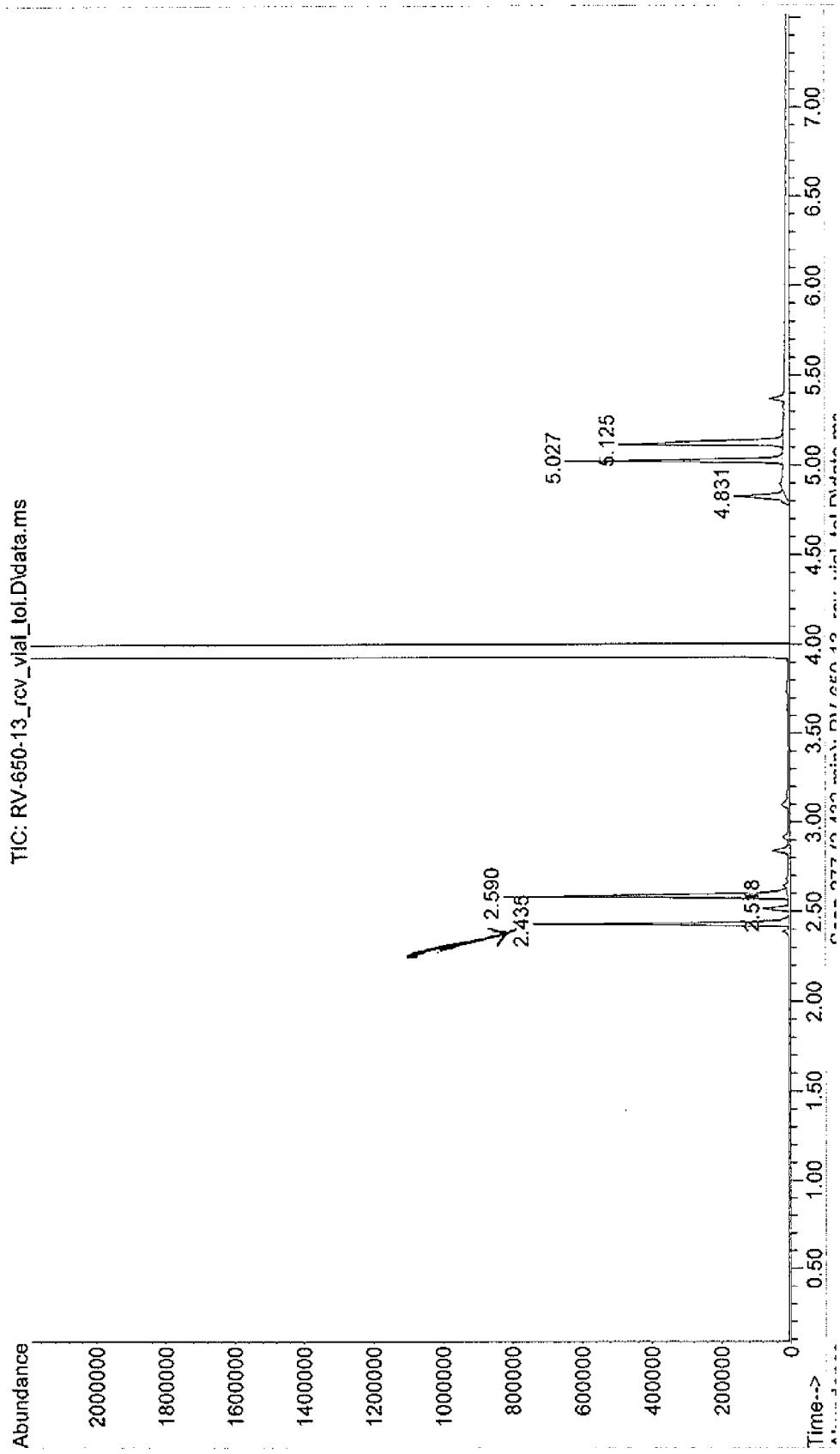

TIC: RV-650-13_rcv_vial_tol.D\data.ms
Abundance
Time-->
2.590
2.435
4.831
5.027
5.125

FIGURE 5G

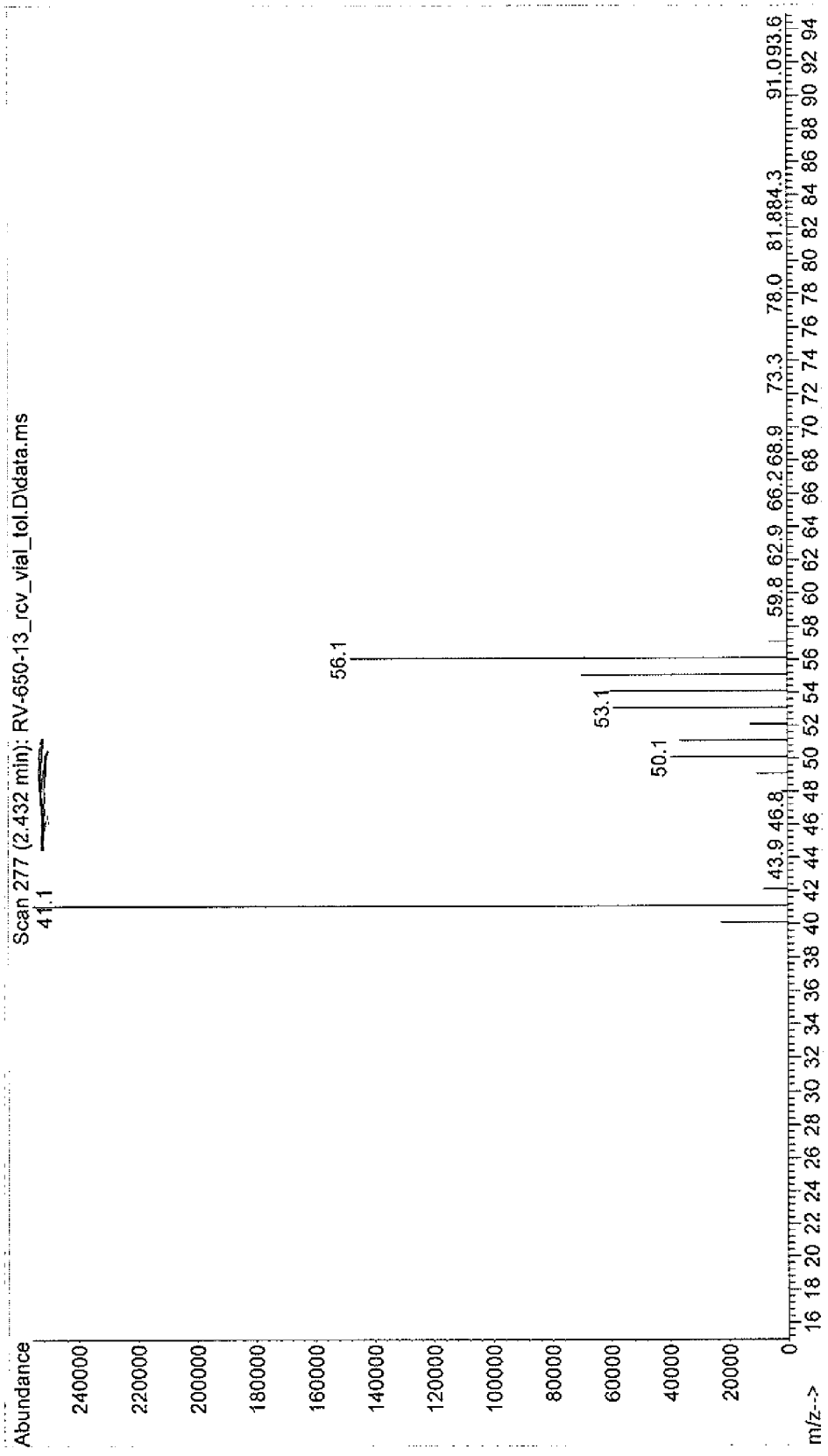

Abundance
Scan 277 (2.432 min): RV-650-13_rcv_vial_tol.D\data.ms
41.1
56.1
53.1
50.1
43.9
46.8
59.8
62.9
66.2
68.9
73.3
78.0
81.8
84.3
91.0
93.6
m/z-->

FIGURE 5H

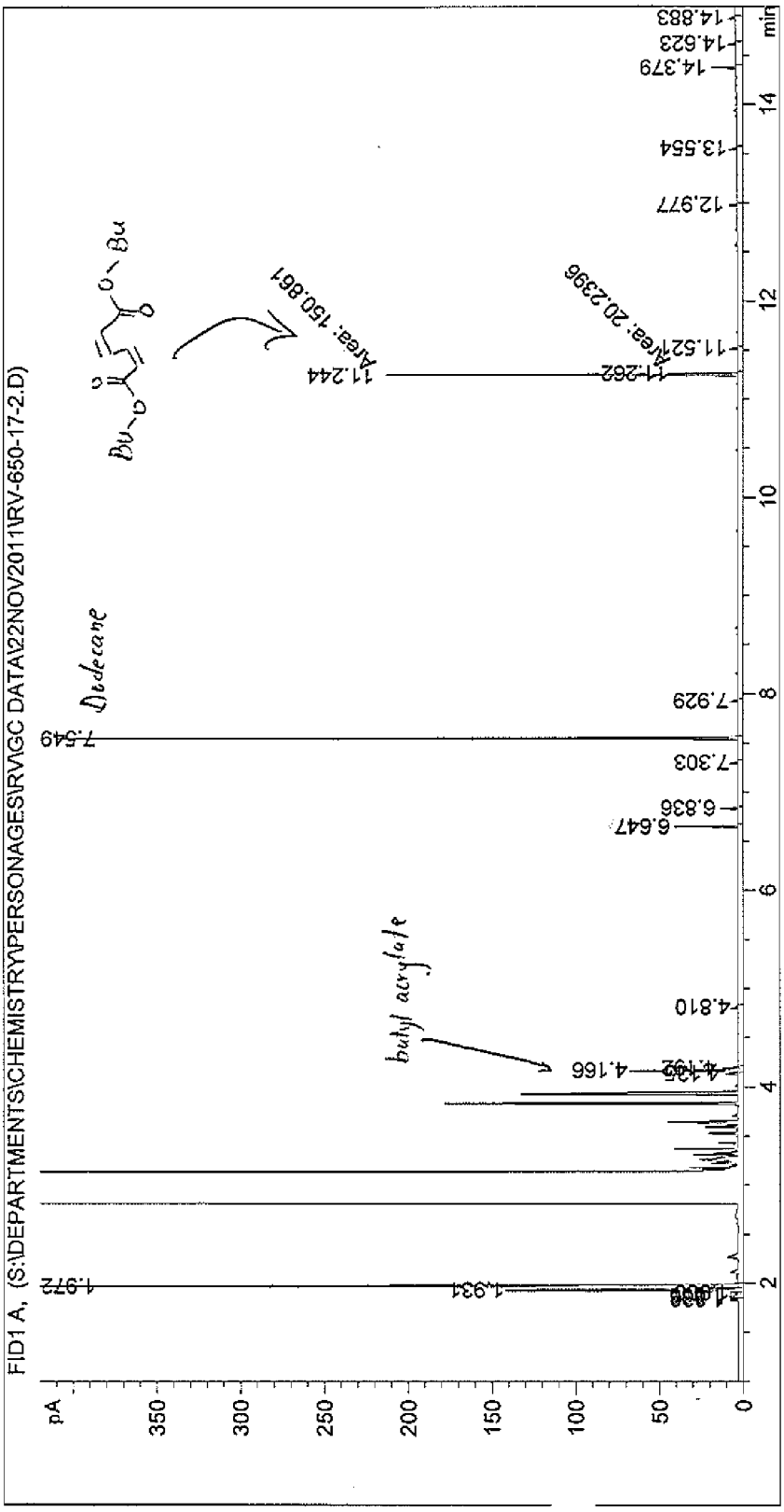

FID1 A, (S:\DEPARTMENTS\CHEMISTRY\PERSONAGES\RV\GC DATA\22NOV2011\RV-650-17-2.D)
pA
min
1.972
1.931
4.166
4.810
6.647
7.303
7.549
7.929
11.244
Area: 150.861
11.262
Area: 20.2396
11.521
12.977
13.554
14.379
14.623
14.883
Dodecane
butyl acrylate
Bu
Bu

FIGURE 6A

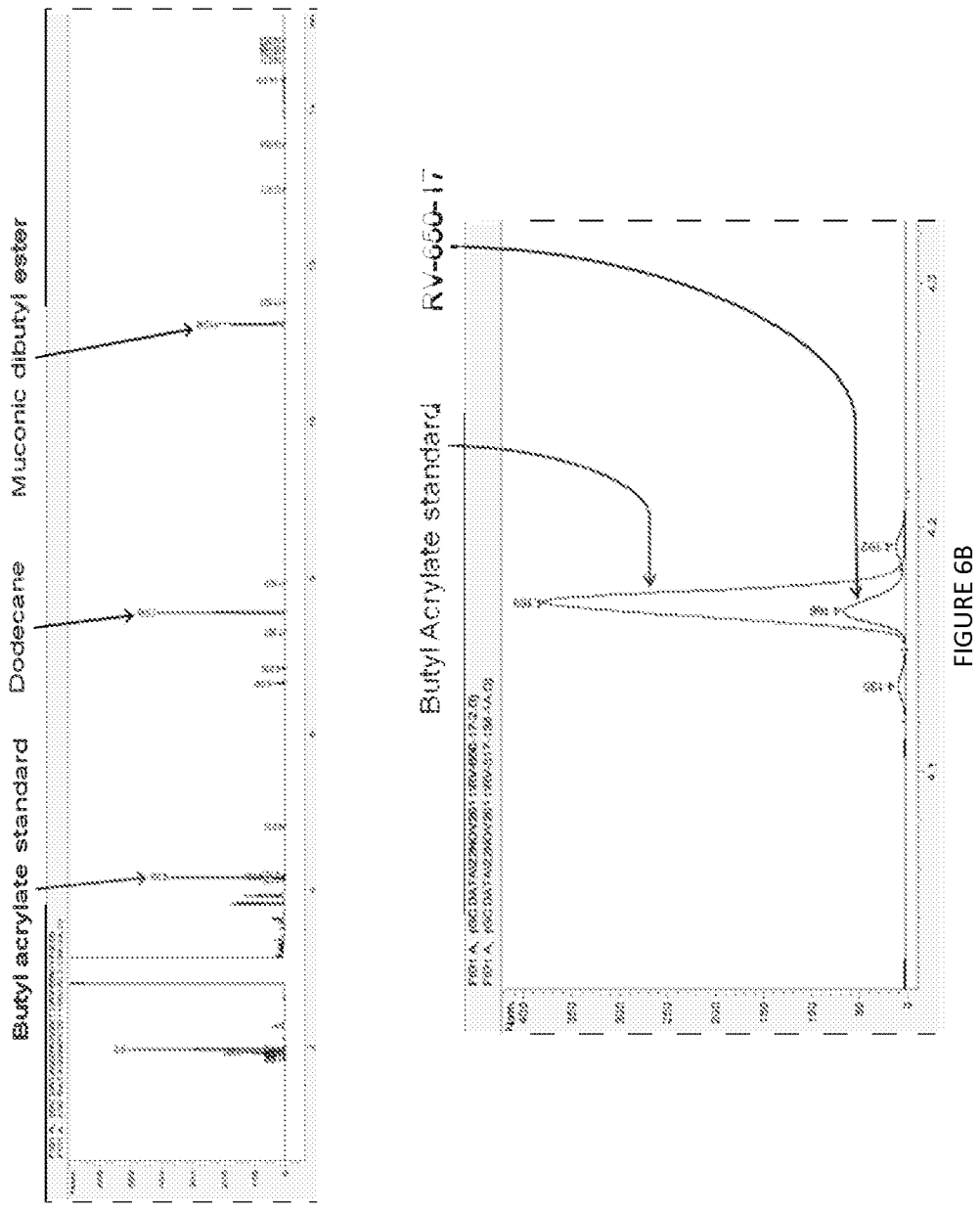

Butyl acrylate standard
Dodecane
Muconic dibutyl ester
Butyl Acrylate standard
RV-650-17

FIGURE 6B

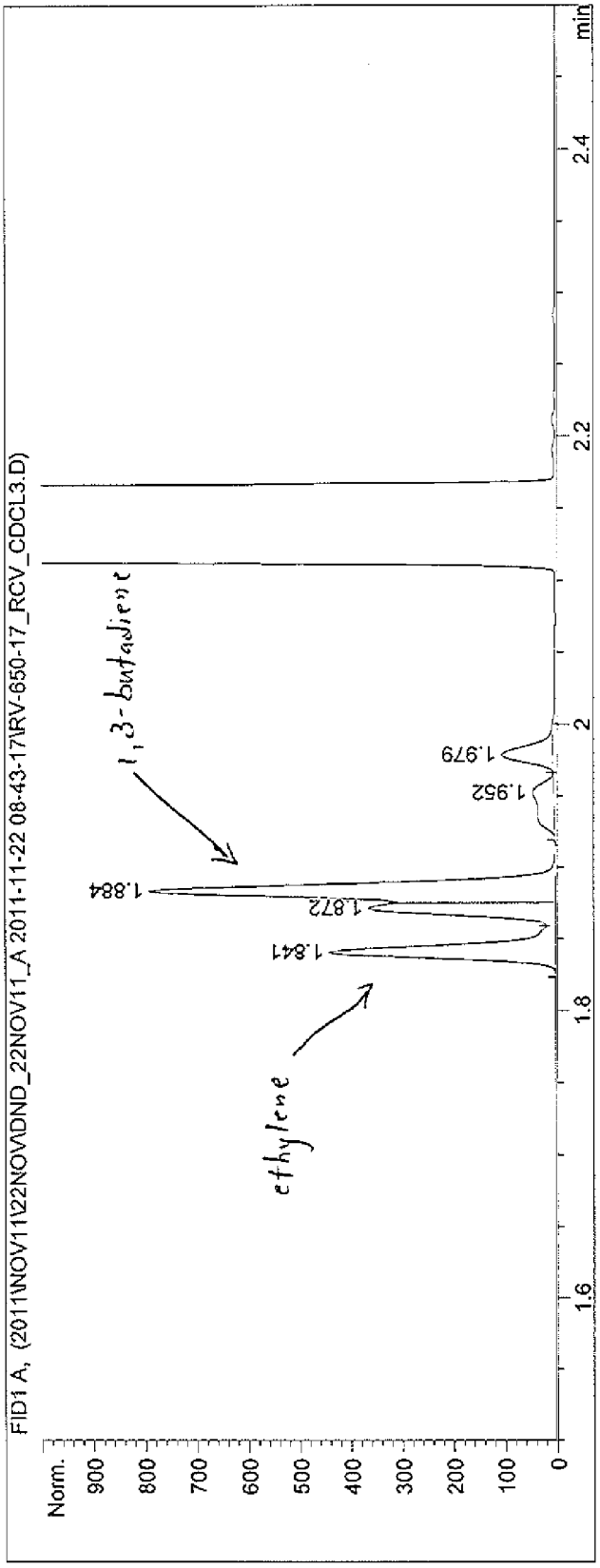

FID1 A, (2011\NOV11\22NOV\DND_22NOV11_A 2011-11-22 08-43-17\RV-650-17_RCV_CDCL3.D)
Norm.
900
800
700
600
500
400
300
200
100
0
1.6
1.8
2
2.2
2.4
min
1.884
1.872
1.841
1.979
1.952
1,3-butadiene
ethylene

FIGURE 6C

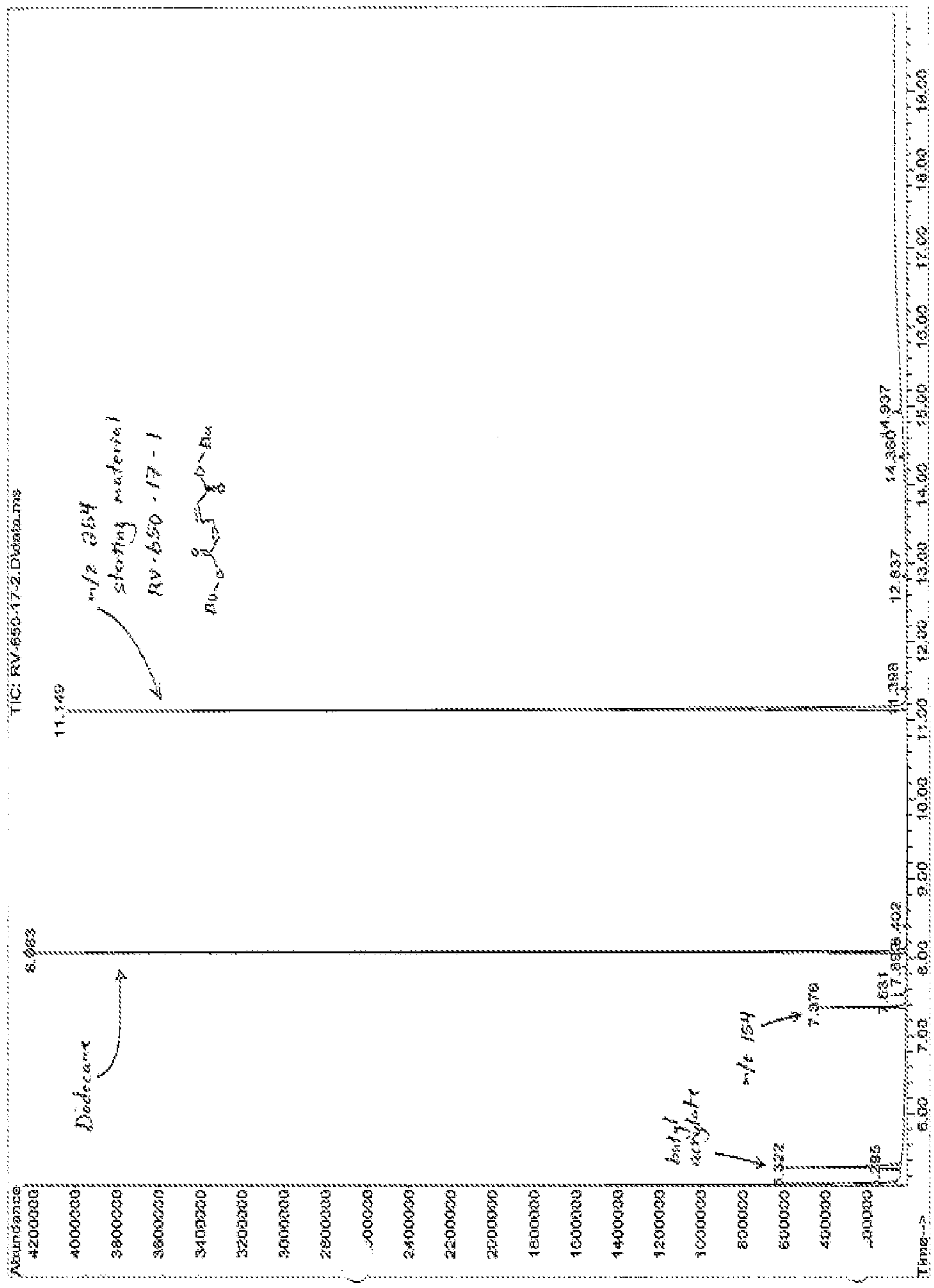

TIC: RV-650-17-2.D\data.ms
Abundance
Time-->
8.083
11.149
7.376
Dodecane
butyl acrylate
m/z 154
m/z 284
starting material
RV-650-17-1

FIGURE 6D

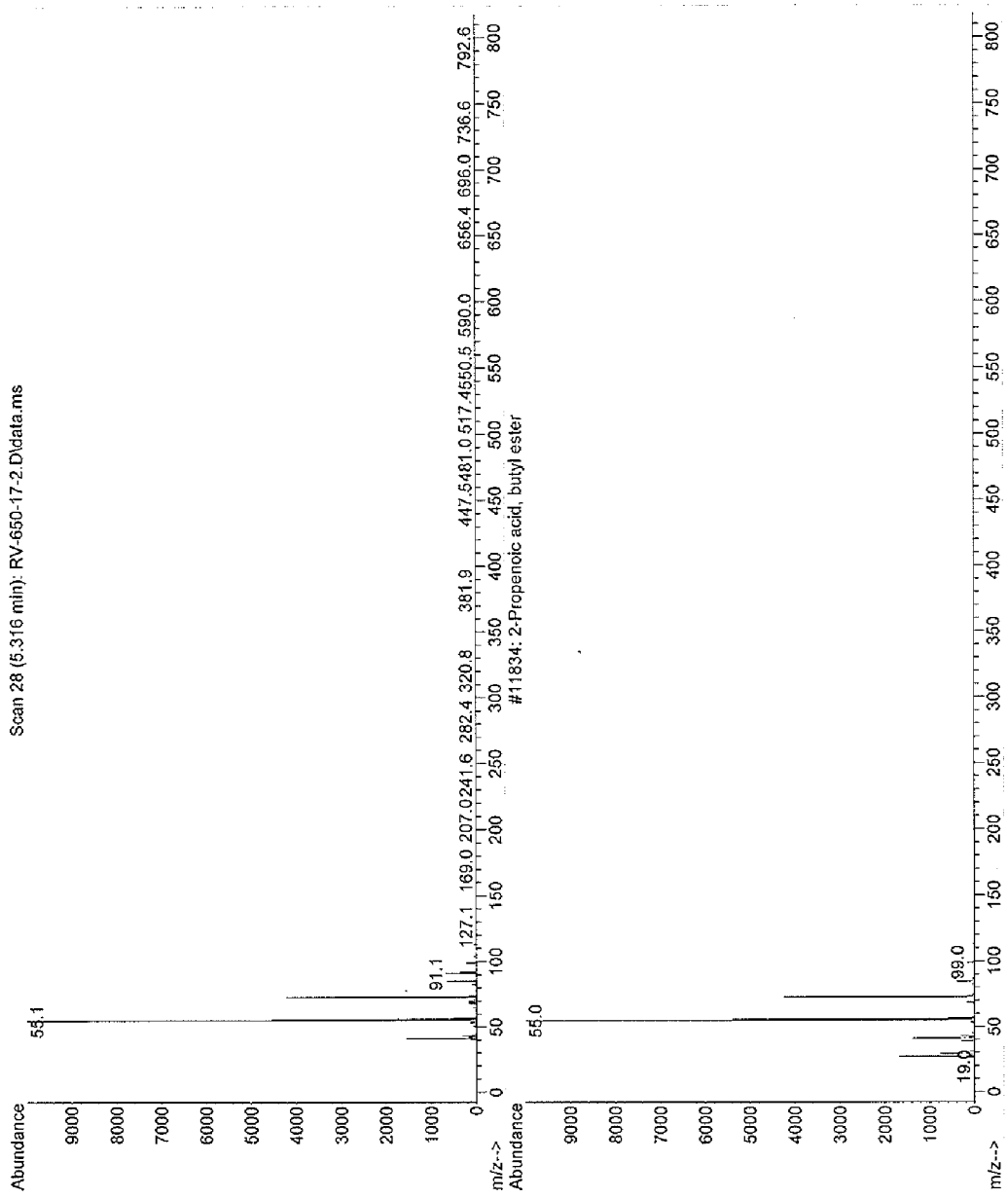

Scan 28 (5.316 min): RV-650-17-2.D\data.ms
Abundance
m/z-->
#11834: 2-Propenoic acid, butyl ester
Abundance
m/z-->

FIGURE 6E

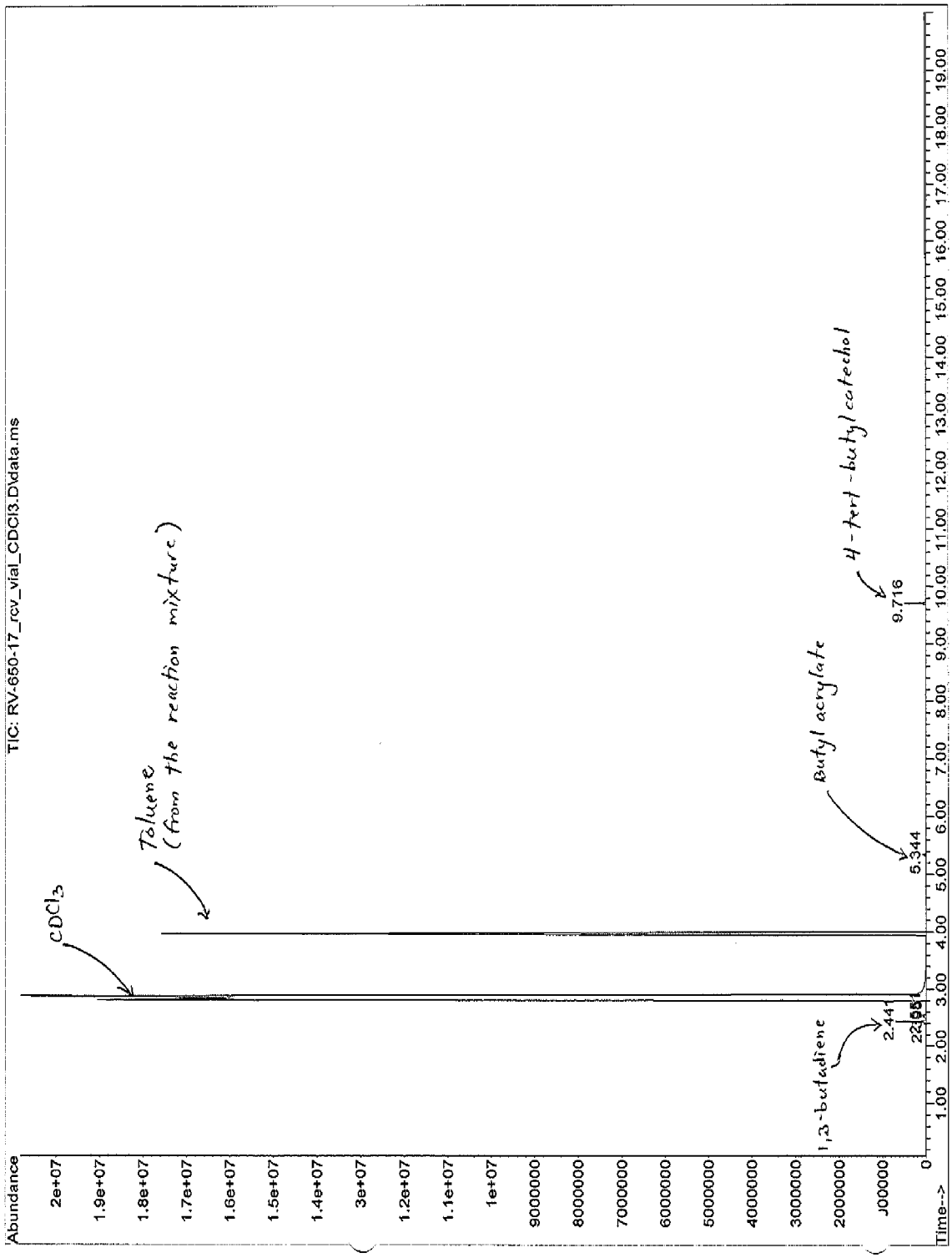

TIC: RV-650-17_rcv_vial_CDCl3.Dvdata.ms
Abundance
Time-->
$CDCl_3$
Toluene
(from the reaction mixture)
Butyl acrylate
4-tert-butylcatechol
1,3-butadiene
2.441
5.344
9.716

FIGURE 6F

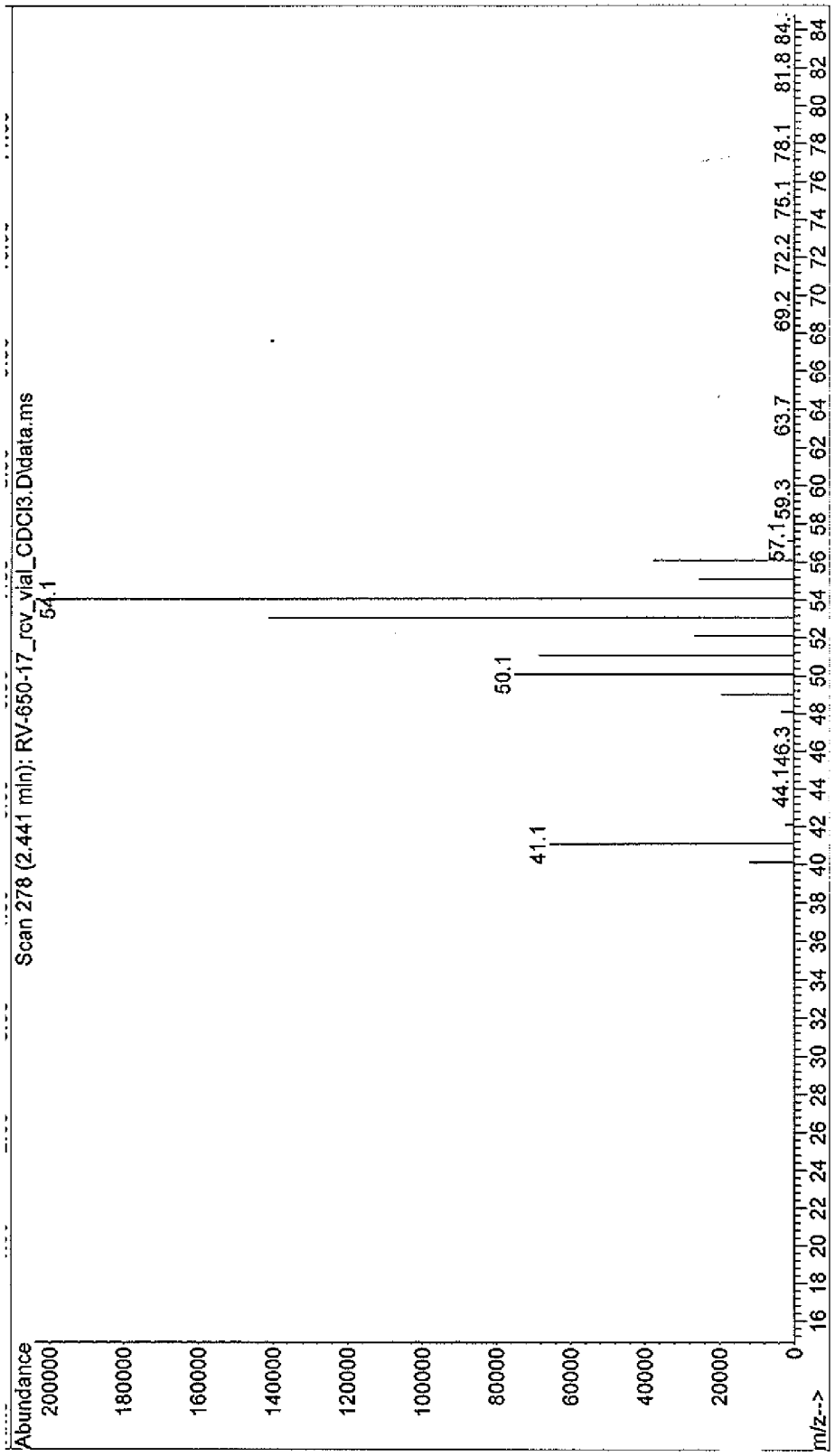

Abundance
Scan 278 (2.441 min): RV-650-17_rcv_vial_CDCl3.D\data.ms
54.1
50.1
41.1
44.1
46.3
57.1
59.3
63.7
69.2
72.2
75.1
78.1
81.8
84.
m/z-->

FIGURE 6G

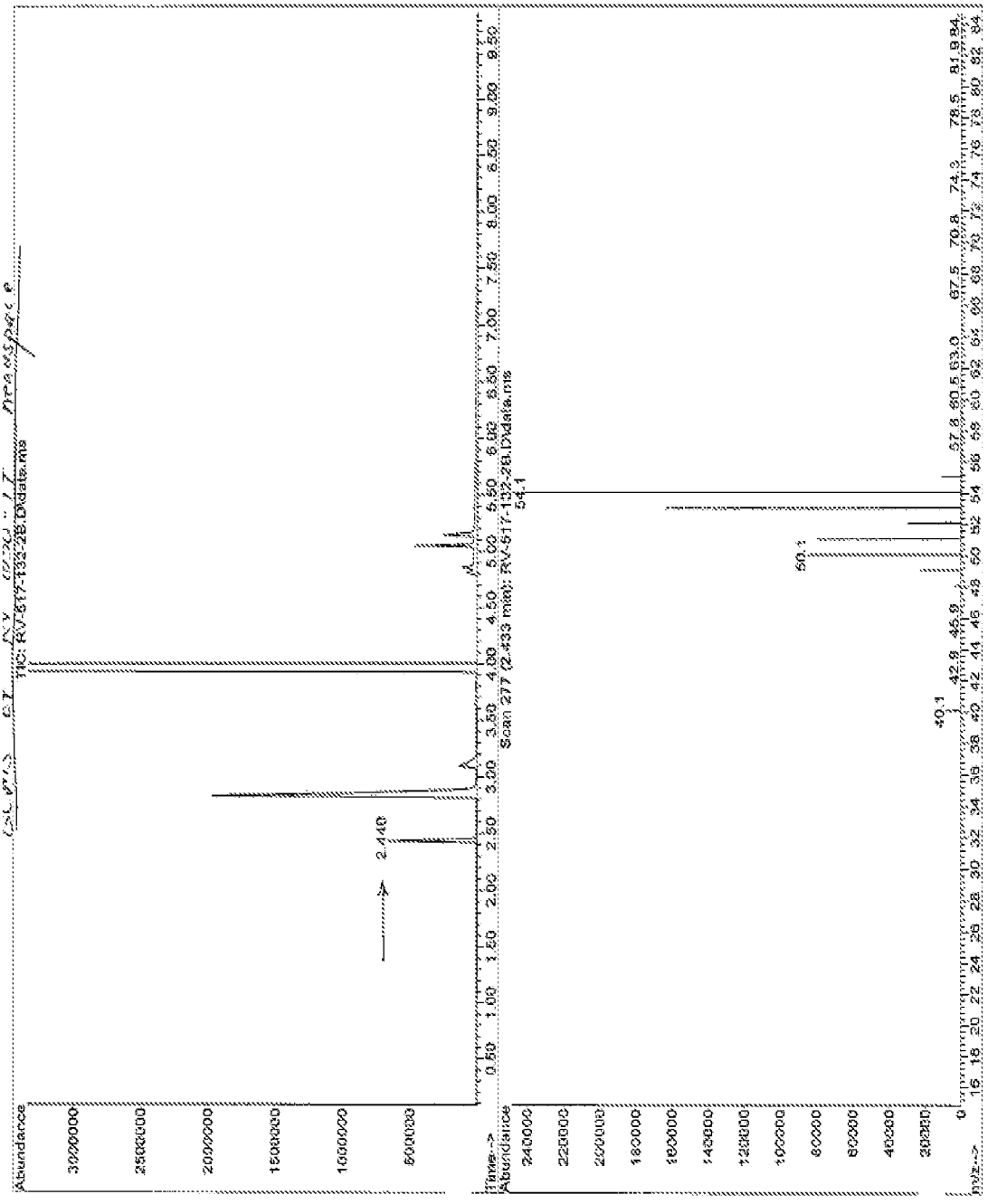

Abundance
TIC: RV-517-133-28.D\data.ms
2.448
Scan 277 (2.433 min): RV-517-133-28.D\data.ms
54.1
50.1
40.1
Time
Abundance

FIGURE 6H

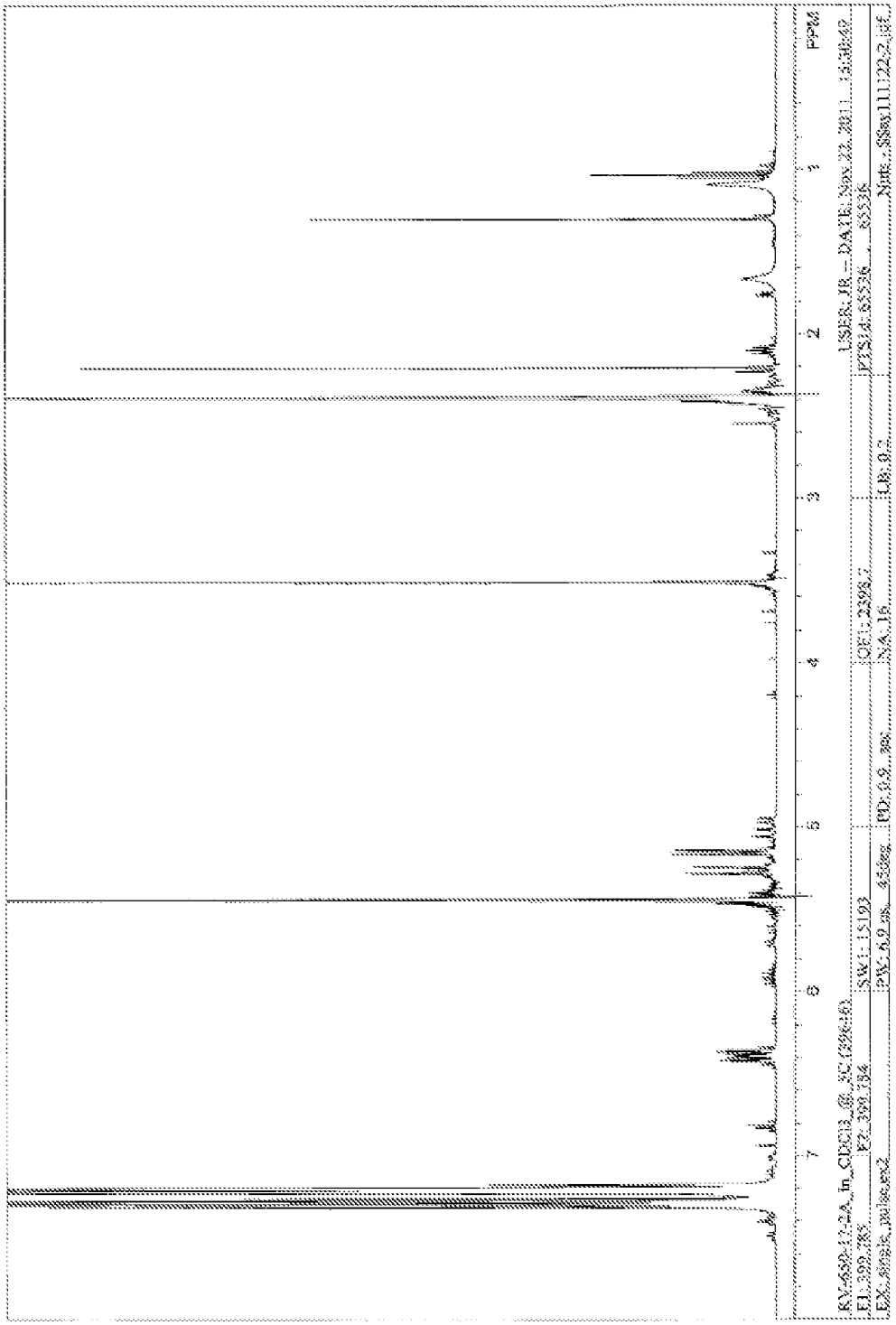
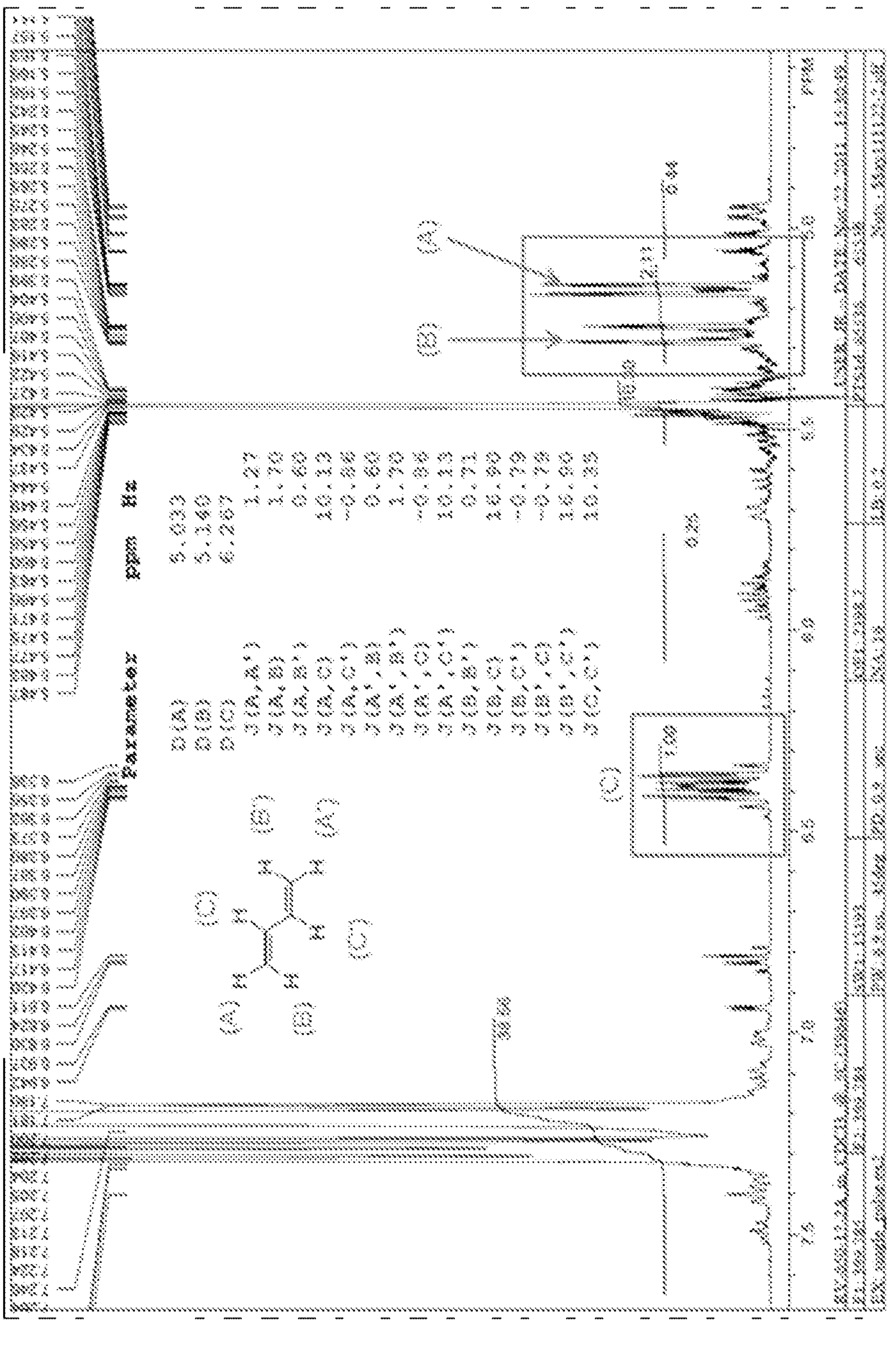

PPM
1
2
3
4
5
6
7
USER: JR -- DATE: Nov 22 2011 13:50:49
PTS14: 65536
Note: SSsx111122-2.jrf

FIGURE 6I



Reference chemical shift for 1,3-butadiene in CCl_4 (300 MHz) was taken from SEGRE A.L. ET AL. J.MOL.SPECTROSC. 22, 290 (1967)

FIGURE 6J

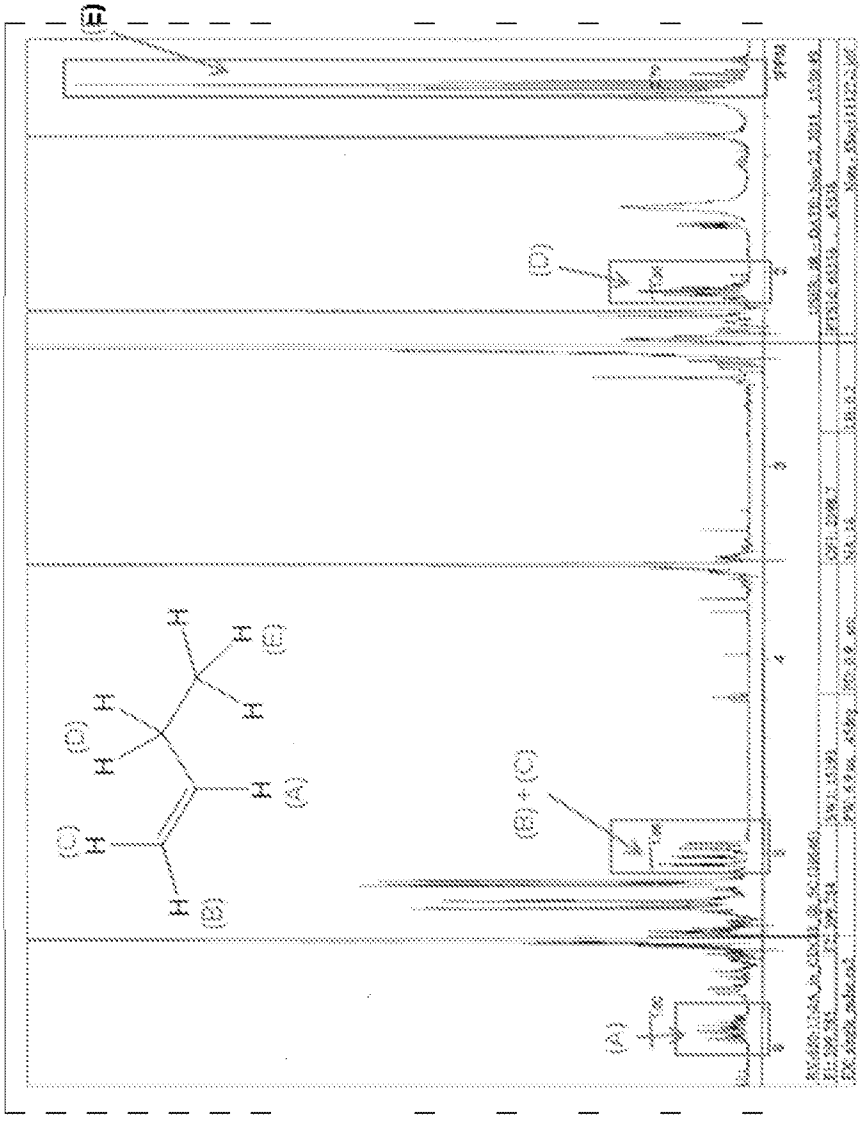


FIGURE 6K

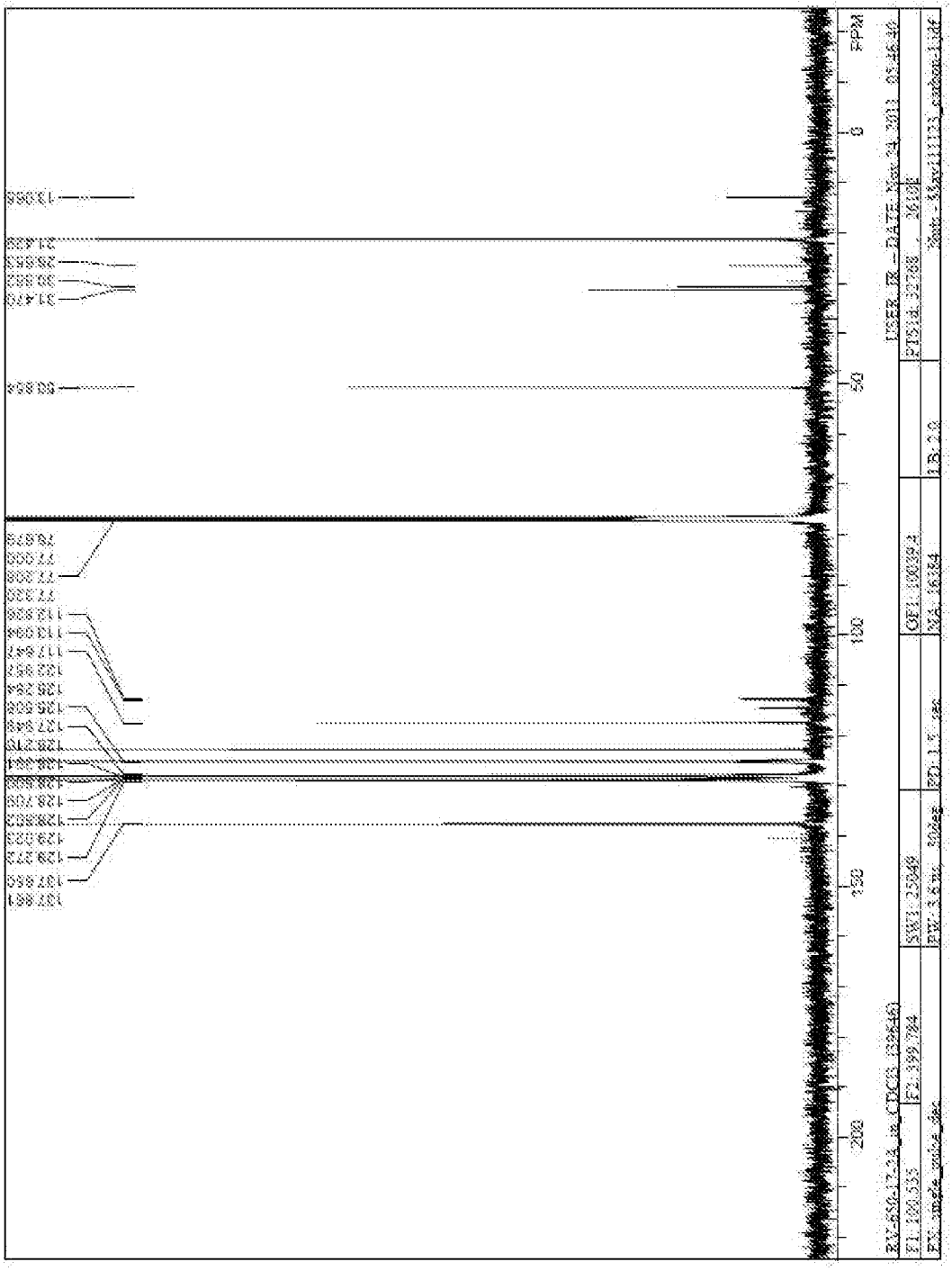


FIGURE 6L

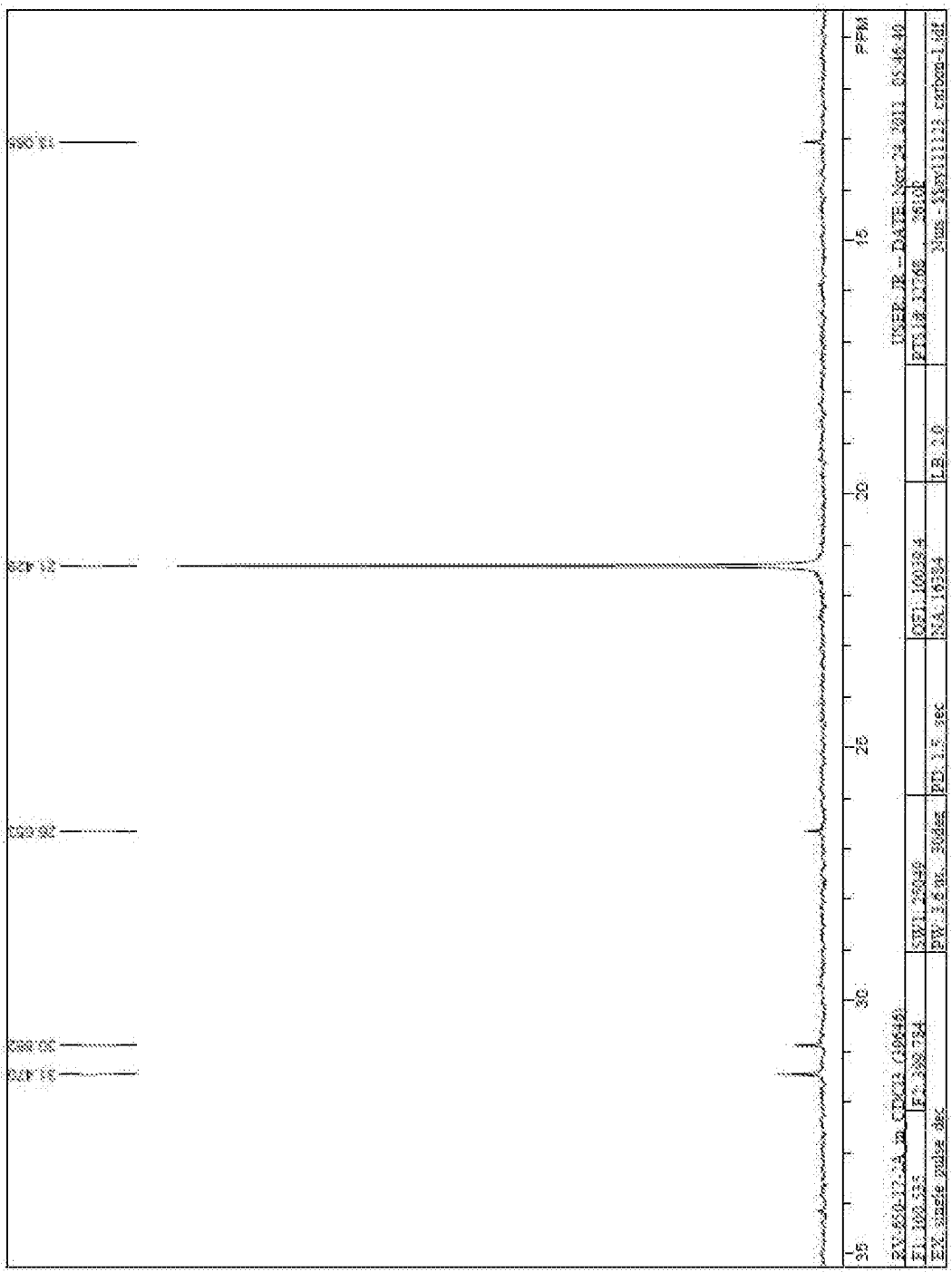


FIGURE 6M

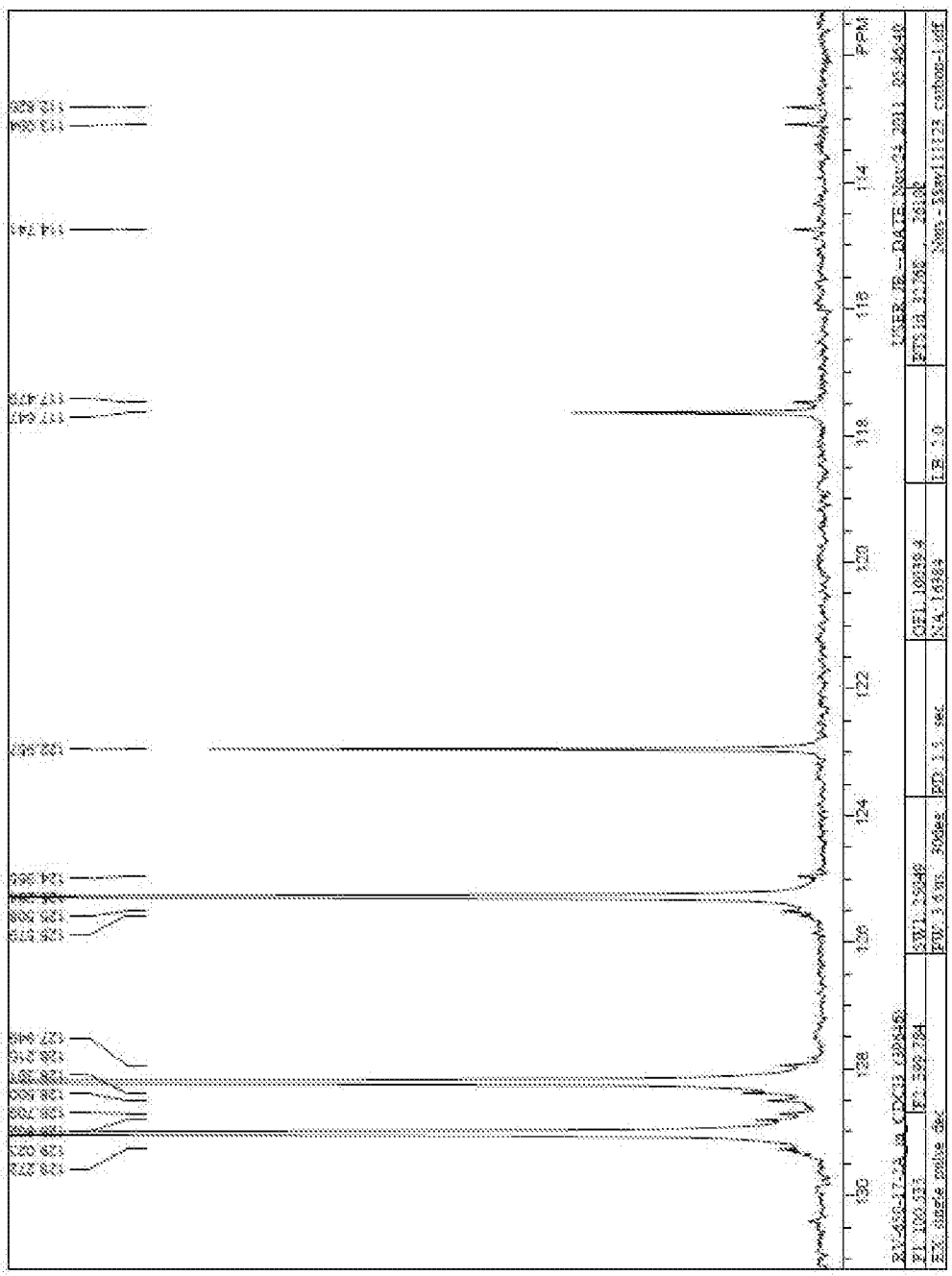


FIGURE 6N

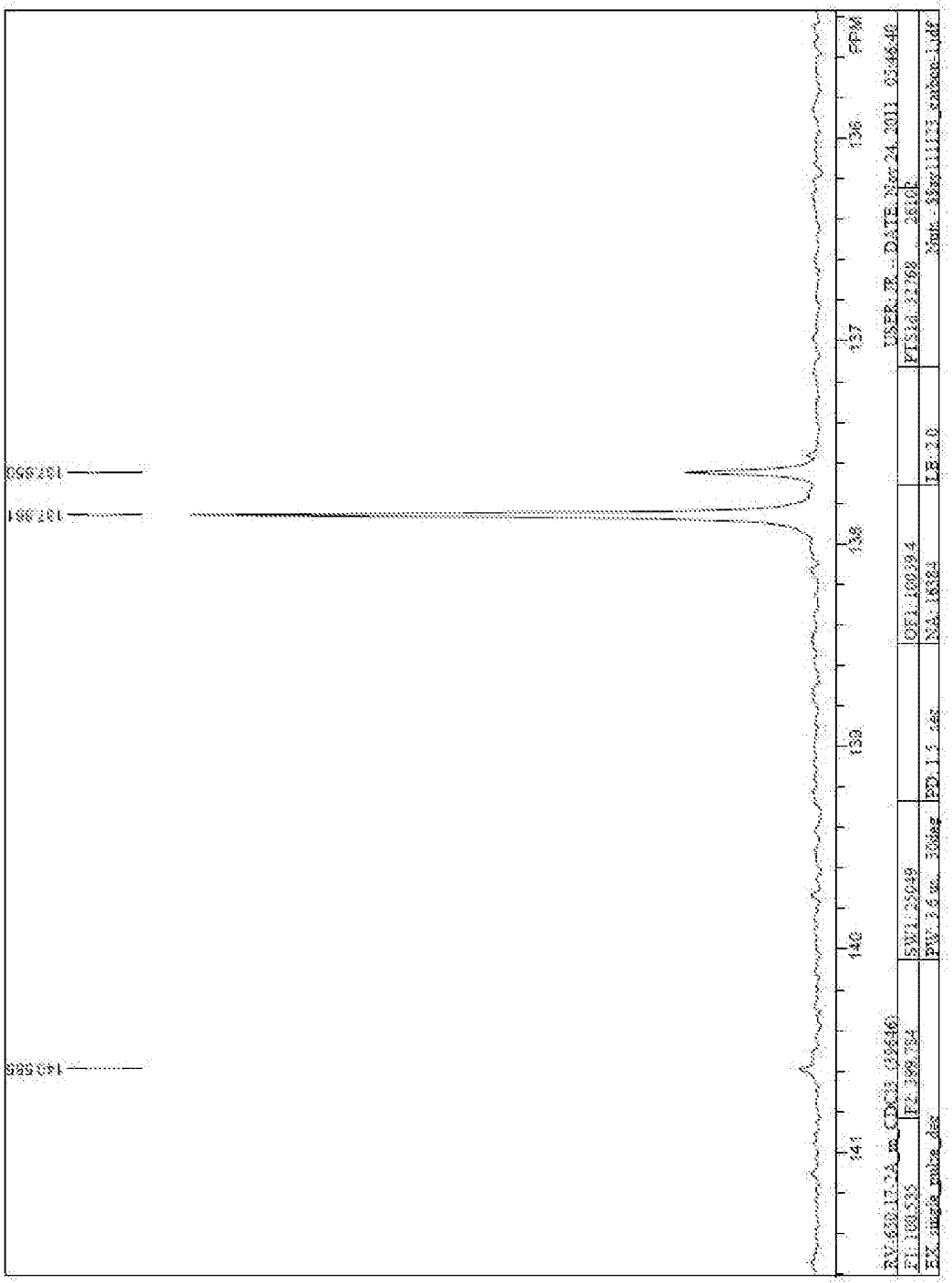


FIGURE 6O

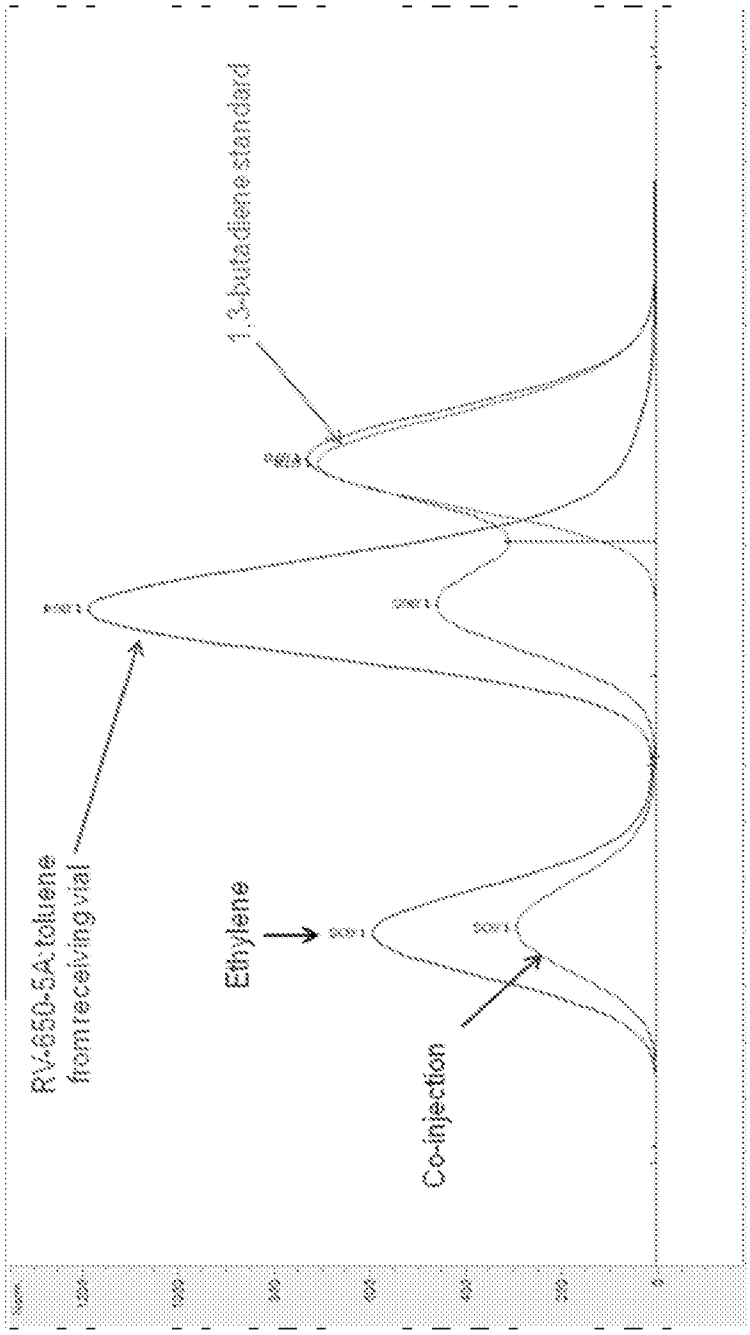

RV-650-5A toluene
from receiving vial
Ethylene
Co-injection
1,3-butadiene standard

FIGURE 7A

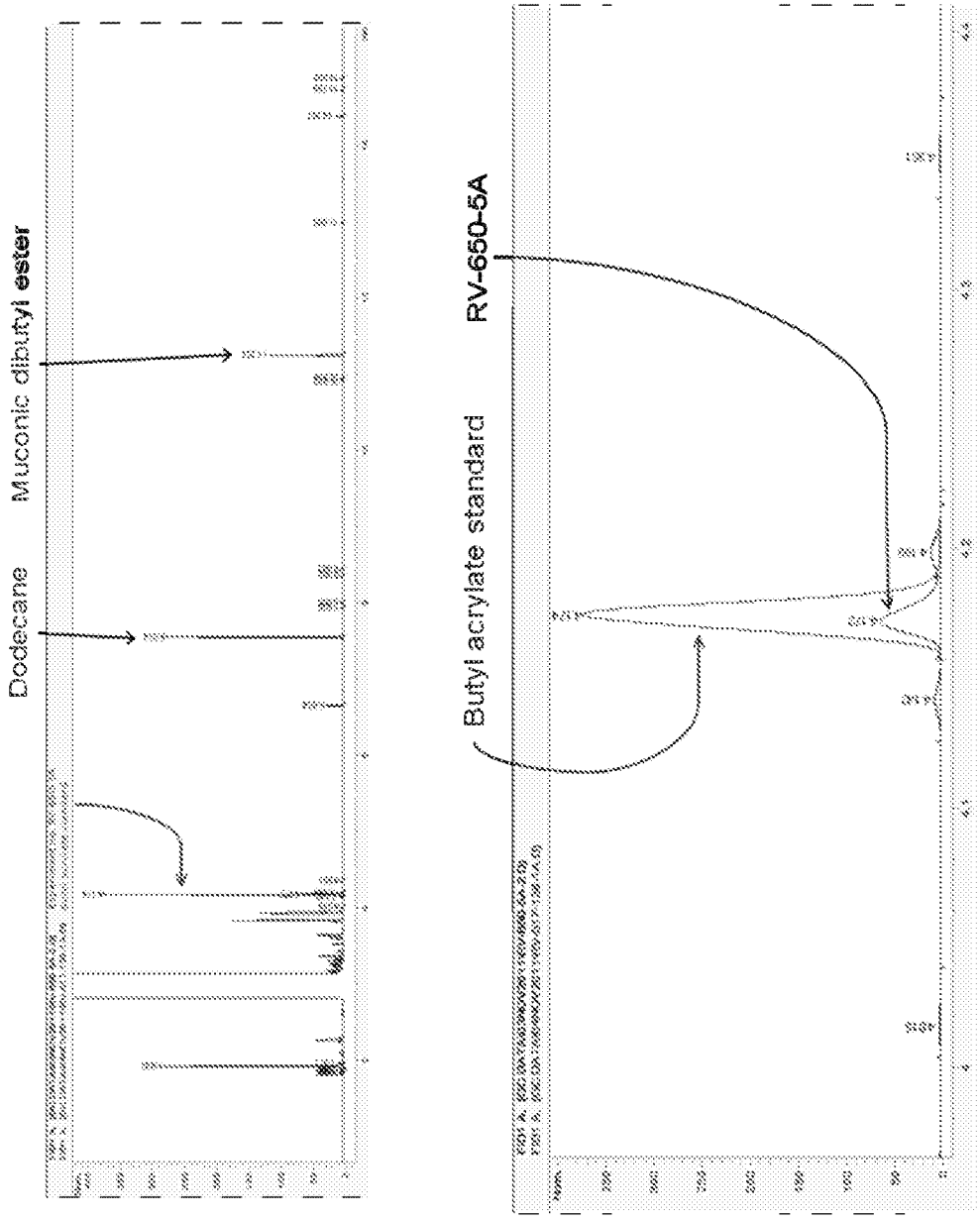

Dodecane
Muconic dibutyl ester
Butyl acrylate standard
RV-650-5A

FIGURE 7B

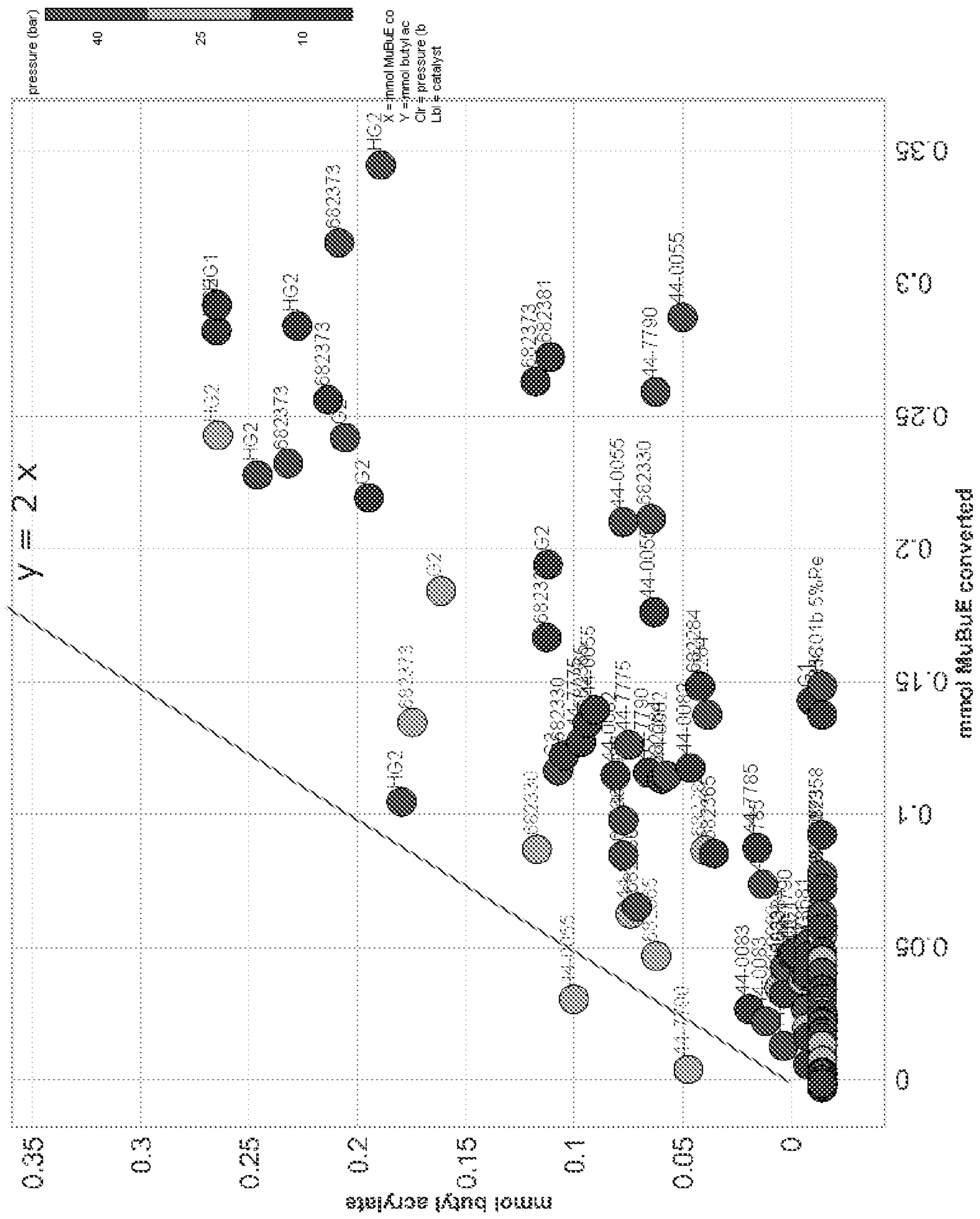

y = 2 x
mmol butyl acrylate
mmol MuBuE converted
pressure (bar)
40
25
10
X = mmol MuBuE co
Y = mmol butyl ac
Clr = pressure (b
Lbl = catalyst
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35

FIGURE 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/067027

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C1/213 C07C11/167 C07C51/353 C07C57/04 C07C67/333 C07C69/54
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal , CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/045637 A2 (GENOMATICA INC [US] ; BURK MARK J [US] ; PHARKYA PRITI [US] ; VAN DIEN ST) 9 April 2009 (2009-04-09) claims 1, 12, 25 -----	2-4, 8-11 , 13 , 15 , 17-26, 31-34, 39-46, 50,55-58

-/- .

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents :

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

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"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	Date of mailing of the international search report
15 January 2013	25/01/2013

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Guazzelli, Giuditta

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 269 974 Al (STICHTING DI ENST LANDBOUWKUNDI [NL]) 5 January 2011 (2011-01-05)	2-4, 8-11 , 13 , 15 , 17-26, 31-34, 39-46, 50,55-58
	claims 1, 11, 14, column 1, paragraph 0006 page 3, paragraph 0016 column 6, paragraph 0031	

X	W0 2004/062763 A2 (CARGI LL INC [US] ; MILU S JAMES R [US] ; TUPY MICHAEL J [US] ; ABRAHAM TI) 29 July 2004 (2004-07-29)	47 ,49 ,53
A	claims 12, 14 Scheme 6; page 15	1 ,5-7 , 12 , 14, 16, 27-30, 35-38

X	M. HI RAN0 ET AL. : "Stoi chometri c and catalyti c cross dimeri sati on between butadi ene and methyl acryl ate promoted by a Rutheni um(O) compl ex" , 0RGAN0METALLICS, vol . 29, 2010, pages 5741-5747 , XP002690208, abstract Scheme (2) ; page 5742 , column 2	49-53 ,55

X	US 3 215 647 A (DUNN EDWIN R) 2 November 1965 (1965-11-02) column 6; example 1	47-56

X	US 4 956 258 A (WATANABE YOICHI RO [JP] ET AL) 11 September 1990 (1990-09-11) claim 1 column 4; example 1	48,50, 55 ,56

X	US 4 555 546 A (PATEL RAMAN [US]) 26 November 1985 (1985-11-26) claims 1, 3 column 11, lines 26-31	48,50, 55 ,56

X	US 2011/172475 Al (PETERS MATTHEW W [US] ET AL) 14 July 2011 (2011-07-14)	47 ,49 , 53 ,54
A	abstract claims 1, 2 page 24; example 9 page 18, paragraph 145-148	1 ,5-7 , 12 , 14, 16, 27-30, 35-38

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/067027

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2012/075053 A2 (STRATEGIC ENZYME APPLIC INC [US] ; ALBIZATI KIM [US] ; TRACEWELL CARA [U) 7 June 2012 (2012-06-07) pages 63-64, paragraph 267-229 page 83 ; exampl e 17 -----	1-58

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2012/067027

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009045637 A2	09-04-2009	AU 2008307381 Al	09-04-2009
		CA 2696018 Al	09-04-2009
		EP 2188243 A2	26-05-2010
		EP 2348008 Al	27-07-2011
		EP 2543657 A2	09-01-2013
		TW 200914619 A	01-04-2009
		US 2009155866 Al	18-06-2009
		US 2012094341 Al	19-04-2012
		WO 2009045637 A2	09-04-2009
EP 2269974 Al	05-01-2011	EP 2269974 Al	05-01-2011
		EP 2448903 Al	09-05-2012
		US 2012178961 Al	12-07-2012
		WO 2011002284 Al	06-01-2011
WO 2004062763 A2	29-07-2004	BR PI0406756 A	20-12-2005
		CA 2512815 Al	29-07-2004
		CN 1802341 A	12-07-2006
		EP 1603857 A2	14-12-2005
		US 2007270621 Al	22-11-2007
		WO 2004062763 A2	29-07-2004
US 3215647 A	02-11-1965	BE 633652 A	15-01-2013
		DE 1544742 Al	07-08-1969
		GB 1023202 A	23-03-1966
		MY 7300090 A	31-12-1973
		NL 127334 C	15-01-2013
		NL 294225 A	15-01-2013
		US 3215647 A	02-11-1965
US 4956258 A	11-09-1990	JP 63280262 A	17-11-1988
		US 4956258 A	11-09-1990
US 4555546 A	26-11-1985	AU 566143 B2	08-10-1987
		AU 3705584 A	04-07-1985
		BR 8406665 A	22-10-1985
		CA 1258144 Al	01-08-1989
		DE 3478031 Dl	08-06-1989
		EP 0158764 Al	23-10-1985
		JP 7055993 B	14-06-1995
		JP 60156738 A	16-08-1985
		US 4555546 A	26-11-1985
US 2011172475 Al	14-07-2011	CA 2786607 Al	14-07-2011
		CN 102770397 A	07-11-2012
		EP 2521705 Al	14-11-2012
		SG 182407 Al	30-08-2012
		US 2011172475 Al	14-07-2011
		WO 2011085223 Al	14-07-2011
WO 2012075053 A2	07-06-2012	NONE	