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(54) Title: METHOD OF CARBON CHAIN EXTENSION USING NOVEL ALDOL REACTION

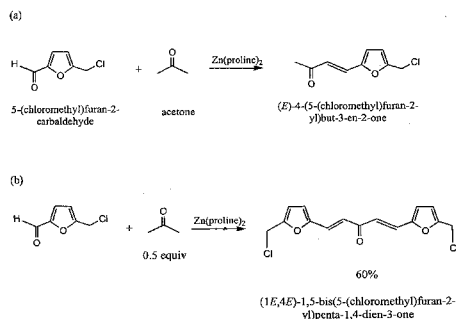
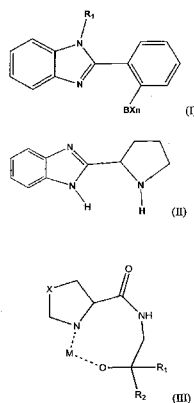


FIGURE 1



(57) Abstract: Method of producing C₈ - C₁₅ hydrocarbons, comprising providing a ketone starting material; providing an aldol starting material comprising chloromethylfurfural; mixing the ketone starting material and the aldol starting material in a reaction in the presence of a proline-containing catalyst selected from the group consisting of Zn(Pro)₂, Yb(Pro)₃, and combinations thereof, or a catalyst having one of the structures (I), (II) or (III), where (I), (II) and (III) respectively are: Formula (I) where R₁ is a C₁ - C₆ alkyl moiety, X = (OH) and n = 2. Formulas (II) and (III). In (III), X may be CH₂, sulfur or selenium, M may be Zn, Mg, or a lanthanide, and R₁ and R₂ each independently may be a methyl, ethyl, phenyl moiety.



ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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METHOD OF CARBON CHAIN EXTENSION USING NOVEL ALDOL REACTION

STATEMENT OF FEDERAL RIGHTS

5 The United States government has rights in this invention pursuant to Contract No. DE-AC52-06NA25396 between the United States Department of Energy and Los Alamos National Security, LLC for the operation of Los Alamos National Laboratory.

FIELD OF THE INVENTION

10 The present invention relates to methods of producing $C_8 - C_{15}$ hydrocarbons from renewable feedstocks such as cellulosics, sugars and glycerin, by means of an organo-catalyzed aldol reaction.

BACKGROUND OF THE INVENTION

Development of sustainable methods of making transportation fuels and chemical feedstocks such as surfactants from renewable resources is becoming increasingly important, due to the desirability of decreasing dependence on petroleum resources. Carbohydrates obtained from biomass are renewable and readily available, and there has been much focus on producing fuel and other useful materials from biomass-derived starting materials. Other readily available starting materials include simple sugars, glycerol and the oxidation product of glycerol, dihydroxyacetone (DHA). Compounds suitable for use as chemical feedstocks generally include $C_8 - C_{15}$ alcohols and olefins. Commercially useful surfactants may comprise from about 10 to about 22 carbon atoms. Therefore, in order to produce surfactants from biomass-derived starting materials, the carbon chain length of the starting material must be increased. One common method of achieving this is through the aldol reaction, which forms a carbon-carbon bond between an aldehyde and a ketone. Cellulosics, sugars and glycerin can readily be converted to suitable reagents for the aldol reaction. For example, cellulose and glucose can be converted to hydroxymethylfurfural (HMF). Dihydroxyacetone can be formed from glycerol.

Use of the aldol reaction with reagents derivable from cellulosics and sugars has been described previously (see, e.g., Huber et al., Science, vol. 208, June 3, 2005, pp. 1446 -1450). However, the reactions resulted in a range of carbon chain lengths, and thus exhibited poor selectivity. In addition, the reactions required high temperatures (approximately 100°C), and the

use of an organic solvent in addition to water. Most important, the reaction was shown to be unsuccessful with ketone reagents other than acetone. All of these factors contribute to making the process less suitable for large-scale industrial use.

The use of a zinc-proline (Zn(Pro)_2) catalyst has been shown to be successful in certain types of aldol reactions, and addresses some of the above drawbacks. Zinc-proline catalysts result in higher selectivity, and have been shown to work with DHA as a ketone reagent. To date, however, zinc-proline catalysts have shown only to successfully catalyze reactions between ketones and aromatic aldehydes (for example, benzaldehydes) and not between ketones and reagents derived from biomass sources, such as HMF. Although able to catalyze reactions in aqueous solvents and at lower temperatures, the reactions described to date using zinc-proline catalysts have required the addition of an organic co-solvent, such as tetrahydrofuran (THF).

There exists a need, therefore, for a method of increasing carbon chain length via the aldol reaction that utilizes reagents derived from biomass sources, is highly selective, can be performed at room temperature and does not require the use of an organic co-solvent, thus making the process more suitable for large-scale production with specificity. There exists a further need for additional catalysts that allow the aldol reaction to proceed under conditions suitable for large-scale use.

SUMMARY OF THE INVENTION

The present invention meets the aforementioned needs by providing a method of increasing carbon chain length by utilizing the aldol reaction that can be performed with either zinc-proline, ytterbium-proline, or metal chelated *N*-(2-hydroxy-2-methylpropyl)pyrrolidine-2-carboxamide based catalysts, and which can be performed at room temperature using only water as the solvent. The reaction utilizes DHA (and other ketones or aldehydes) as the ketone reagent and HMF as the aldehyde reagent, which can be obtained from biomass cellulosics. The reaction has high specificity, and results in formation of (*E*)-4-(5-(chloromethyl)furan-2-yl)but-3-en-2-one, (1*E*,4*E*)-1,5-bis(5-(chloromethyl)furan-2-yl)penta-1,4-dien-3-one, 3,4-dihydroxy-4-(5-(chloromethyl)furan-2-yl)butan-2-one, (E)-5-(5-(chloromethyl)furan-2-yl)-4,5-dihydroxy-1-(5-(hydroxymethyl)furan-2-yl)pent-1-en-3-one and/or 1,3,4-trihydroxy-4-(5-(chloromethyl)furan-2-yl)butan-2-one, with a yield of 60%.

The following describe some non-limiting embodiments of the present invention.

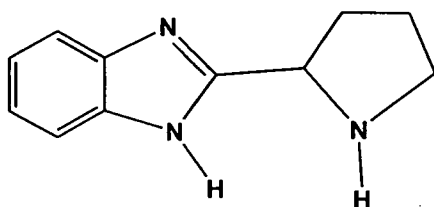
According to one embodiment of the present invention, a method of producing $\text{C}_8 - \text{C}_{15}$ hydrocarbons is provided, comprising providing a ketone starting material; providing an aldol

starting material comprising chloromethylfurfural; and mixing the ketone starting material and the aldol starting material in a reaction in the presence of a proline-containing catalyst selected from the group consisting of $\text{Zn}(\text{Pro})_2$, $\text{Yb}(\text{Pro})_3$, and combinations thereof, and a solvent, wherein the solvent comprises water and is substantially free of organic solvents, to produce the

5 $\text{C}_8 - \text{C}_{15}$ hydrocarbons.

According to another embodiment of the present invention, a method of producing $\text{C}_8 - \text{C}_{15}$ hydrocarbons is provided, comprising providing a ketone starting material; providing an aldol starting material; and mixing the ketone starting material and the aldol starting material in a reaction in the presence of a catalyst having the structure:

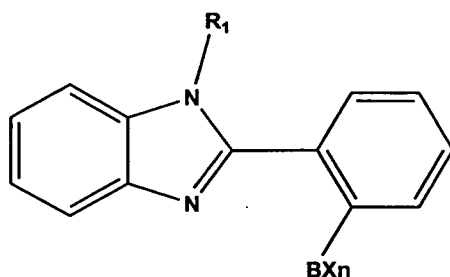
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and a solvent, wherein the solvent comprises water and is substantially free of organic solvents, to produce the $\text{C}_8 - \text{C}_{15}$ hydrocarbons.

According to yet another embodiment of the present invention, a method of producing $\text{C}_8 - \text{C}_{15}$ hydrocarbons is provided, comprising providing a ketone starting material; providing an aldol starting material; and mixing the ketone starting material and the aldol starting material in a reaction in the presence of a catalyst having the structure:

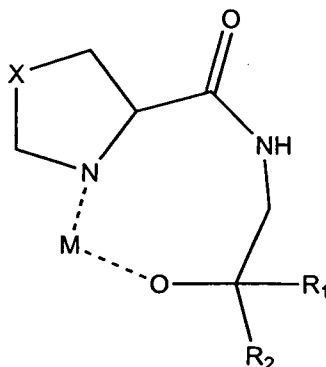
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20 wherein R is a $\text{C}_1 - \text{C}_6$ alkyl moiety, $\text{X} = (\text{OH})$ and $n = 2$, and in the presence of a solvent, wherein the solvent comprises water and is substantially free of organic solvents, to produce the $\text{C}_8 - \text{C}_{15}$ hydrocarbons.

According to yet another embodiment of the present invention, a method of producing $\text{C}_8 - \text{C}_{15}$ hydrocarbons is provided, comprising providing a ketone starting material; providing an

aldol starting material; and mixing the ketone starting material and the aldol starting material in a reaction in the presence of a catalyst having the structure:



where X is CH₂, sulfur or selenium, M is Zn, Mg, or a lanthanide, and R₁ and R₂ each independently are a methyl, ethyl, or phenyl moiety; and in the presence of a solvent, wherein the solvent comprises water and is substantially free of organic solvents, to produce the C₈ – C₁₅ hydrocarbons.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURES 1(a) and (b) depict exemplary reaction schemes of the present invention, wherein chloromethylfurfural (5-(chloromethyl)furan-2-carbaldehyde) reacts with acetone (Figure 1(a), one molar equivalent and Figure 1(b), 0.5 molar equivalents) to form the hydrocarbon products (E)-4-(5-(chloromethyl)furan-2-yl)but-3-en-2-one and (1E,4E)-1,5-bis(5-(chloromethyl)furan-2-yl)penta-1,4-dien-3-one.

FIGURE 2 depicts the reaction between chloromethylfurfural with hydroxyacetone to form the hydrocarbon product 4-(5-(chloromethyl)furan-2-yl)-3,4-dihydroxybutan-2-one.

FIGURE 3 depicts the reaction of 4-(5-(chloromethyl)furan-2-yl)-3,4-dihydroxybutan-2-one with 5-(hydroxymethyl)furan-2-carbaldehyde to form the C₁₅ hydrocarbon (E)-5-(5-(chloromethyl)furan-2-yl)-4,5-dihydroxy-1-(5-(hydroxymethyl)furan-2-yl)pent-1-en-3-one.

FIGURE 4 depicts the reaction of dihydroxyacetone with chloromethylfurfural to form the hydrocarbon product 4-(5-(chloromethyl)furan-2-yl)-1,3,4-trihydroxybutan-2-one.

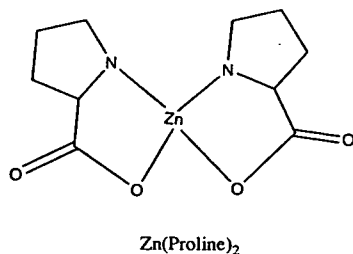
DETAILED DESCRIPTION OF THE INVENTION

All documents cited in the Detailed Description of the Invention are, in relevant part, incorporated herein by reference; the citation of any document is not to be construed as an admission that it is prior art with respect to the present invention. To the extent that any meaning or definition of a term in this document conflicts with any meaning or definition of the same term in a document incorporated by reference, the meaning or definition assigned to that term in this document shall govern.

The present invention relates to a method of producing $C_8 - C_{15}$ hydrocarbons by increasing the carbon chain length of carbohydrates, which may be derived from herbaceous and woody biomass. As used herein, "hydrocarbons" is understood to include alcohols, olefins, ketones and other compounds comprising carbon, hydrogen and oxygen (as depicted in Figures 1-4), and is not intended to mean only compounds consisting of carbon and hydrogen atoms. Suitable reagents may be obtained from abundant chemical feedstocks such as glycerin. The method results in production of $C_8 - C_{15}$ hydrocarbons, which may be subsequently hydrogenated and dehydrated to produce, among other compounds, transportation fuels and surfactants. The method utilizes the aldol reaction, also known as the aldol condensation reaction, which forms a carbon-carbon bond between an aldehyde and a ketone (herein referred to as an "aldehyde reagent" and a "ketone reagent," respectively).

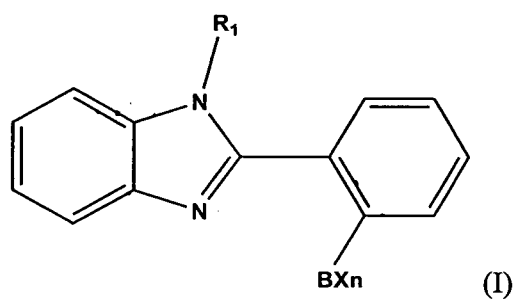
Aldehyde reagents suitable for use in the present invention include, but are not limited to, chloromethylfurfural (CMF, CAS# 1623-88-7) and furan-2-carbaldehyde. Other halide-substituted methylfurfurals also may be suitable, such as bromomethylfurfural and iodomethylfurfural. The carbon atom adjacent to the halide-substituted methyl group allows conversion to desirable alcohol and olefin end products. In addition, cellulose may also be converted directly to chloromethylfurfural, as described in Mascal et al., *Angew. Chem. Int. Ed.*, 47, pp 7924 – 7926 (2008). Suitable ketone reagents in the present invention include acetone, dihydroxyacetone (DHA), methylacetoacetate, ethylacetoacetate, and combinations thereof.

The reaction of the aldehyde and ketone reagents proceeds in the presence of a suitable catalyst. A suitable catalyst must allow the reaction to proceed at room temperature, with water as a solvent, and result in a selectively high yield of the desired product. One suitable catalyst of the present invention is $Zn(\text{Proline})_2$, which may have the following structure:

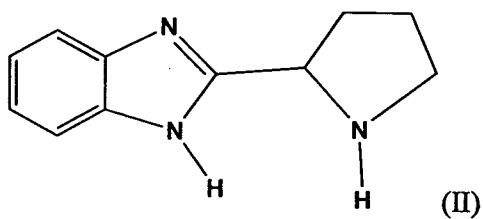


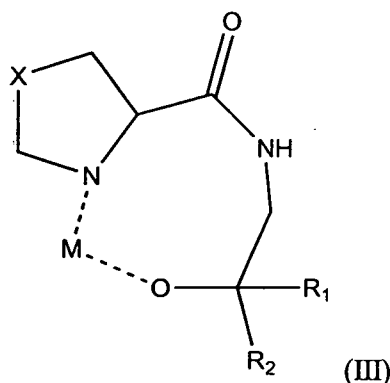
Another suitable catalyst is $\text{Yb}(\text{Proline})_3$, or $\text{Yb}(\text{Pro})_3$, which has a structure similar to $\text{Zn}(\text{Proline})_2$, wherein the Zn is replaced by Yb.

5 Other suitable catalysts include the following structures (I), (II) and (III):



where R_1 is a $\text{C}_1 - \text{C}_6$ alkyl moiety, where “alkyl” is understood to mean a substituted or unsubstituted alkane, alkene or alkyne, $\text{X} = (\text{OH})$ and $n = 2$.





In (III), X may be CH₂, sulfur or selenium, M may be Zn, Mg, or a lanthanide, and R₁ and R₂ each independently may be a methyl, ethyl, phenyl moiety. It is to be understood that the phenyl group may comprise heteroatoms such as nitrogen or oxygen, provided that the atoms in R₁ or R₂ which are closest to the *N*-(2-hydroxy-2-methylpropyl)pyrrolidine-2-carboxamide core structure are a CH₂ group. The reaction may be performed with or without the addition of a solvent to the reaction mixture. In one embodiment, the reaction is performed in a solvent which comprises water. In another embodiment, the solvent comprises water and is substantially free of organic solvents. By “substantially free of organic solvents” is meant that the amount of organic solvent is about 1% or less. By “organic solvent” is meant organic solvents other than water or salts that would be understood by one of skill in the art to be used in synthesis reactions, including but not limited to dimethylformamide (DMF), tetrahydrofuran (THF), alcohols, etc. The solvent further may comprise a salt, brine, saturated sodium chloride, or natural waters comprising salts. The reaction may be performed at room temperature (25°C), and alternatively at a temperature of from about 0°C to about 100 °C. The reaction may have a yield of at least 60%, alternatively of at least 75%, alternatively of at least 90%, and alternatively of at least 99%. The reaction sequence can be tuned to give desired fuel properties by reaction with, for example, the DHA-furan complex, by employing selective regiochemistry.

Examples

Example 1

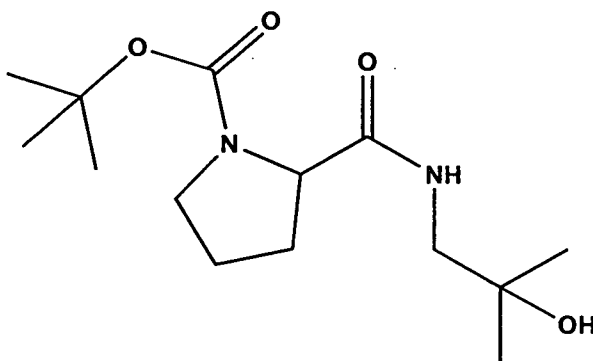
The reactions are performed in water without adjustment of pH. Piperidine was used in 5 mol%. Chloromethylfurfural (CMF) (0.631 g, 5.00 mmol) is charged in a small round bottom flask with a stirring bar, water (4.0 mL) is added. Acetone (0.290 g, 5.00 mmol (1 equivalent) or 0.25 mmol (0.5 equivalent) is then added (FIGURE 1). The mixture is then stirred while piperidine was added at room temperature. The reaction mixture is kept closed with a plastic cap and stirred for

20 hrs. The stirring bar is removed and silica gel added. The mixture is dried with rotary evaporation. The residue is loaded on silica gel and eluted with 50% ethyl acetate in hexanes. Di-HMF adduct also is produced.

As would be understood by one of skill in the art, substitution of reagents as shown in FIGURES 1-4 under similar reaction conditions results in the products depicted in FIGURES 1-4.

Example 2

In a 100 mL single-necked round bottom flask was placed HOBT (hydroxybenzotriazole) (1.95 g), L-Boc-proline (3.00 g), and 2-hydroxy-2-methyl-propyl-1-amine. To this was added 70 mL of anhydrous acetonitrile. This was stirred until homogenous and then chilled to 0°C. The EDC (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide), (3.20 g) was added in one portion to this mixture. The mixture was allowed to warm to room temperature and stirred overnight. The solvent was removed in vacuo. The remaining material was then taken up in 60 mL of methylene chloride and subsequently washed 4x with 10 mL of 5% citric acid. The suspension was filtered and dried over sodium sulfate. Filtration and removal of the solvent gave rise to the crude material. Purification by silica gel chromatography using 10% methanol/methylene chloride as eluent afforded 3.0336 g of an amide having the structure (IV), *tert*-butyl 2-(2-hydroxy-2-methylpropylcarbamoyl)pyrrolidine-1-carboxylate. ¹H NMR (CDCl₃) δ 4.29 (*J* = 4.2 Hz, 1H), 3.45 (m, 2H), 3.26 (m 2H), 1.92 (m, 2H), 1.62 (m, 2H), 1.47 (s, 9H), 1.22 (s, 6H).

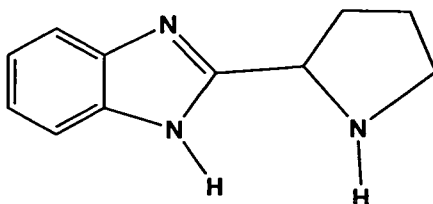


Whereas particular embodiments of the present invention have been illustrated and described, it would be clear to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.

CLAIMS

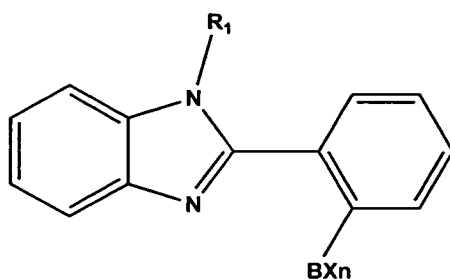
What is claimed is:

1. A method of producing $C_8 - C_{15}$ hydrocarbons comprising:
 - a) providing a ketone starting material;
 - b) providing an aldol starting material comprising chloromethylfurfural; and
 - c) mixing the ketone starting material and the aldol starting material in a reaction in the presence of a proline-containing catalyst selected from the group consisting of $Zn(Pro)_2$, $Yb(Pro)_2$, and combinations thereof, to produce the $C_8 - C_{15}$ hydrocarbons.
2. The method of claim 1, wherein the ketone starting material comprises acetone, dihydroxyacetone, or combinations thereof.
3. The method of claim 1, wherein the reaction occurs at about $25^\circ C$.
4. The method of claim 1, further comprising adding a solvent to the reaction, said solvent comprising water.
5. The method of claim 4, wherein the solvent further comprises a salt.
6. The method of claim 4, wherein the solvent is substantially free of organic solvents.
7. A method of producing $C_8 - C_{15}$ hydrocarbons comprising:
 - a) providing a ketone starting material;
 - b) providing an aldol starting material; and
 - c) mixing the ketone starting material and the aldol starting material in a reaction in the presence of a catalyst having the structure:



to produce the $C_8 - C_{15}$ hydrocarbons.

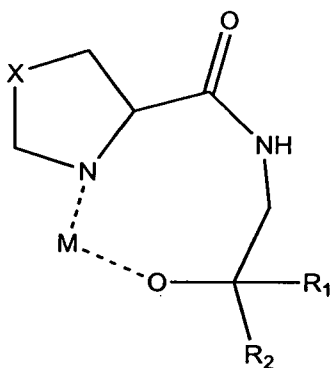
8. The method of claim 7, wherein the aldol starting material comprises chloromethylfurfural.
9. The method of claim 7, wherein the ketone starting material comprises acetone, dihydroxyacetone, or combinations thereof.
10. The method of claim 7, wherein the reaction occurs at about 25°C.
11. The method of claim 7, further comprising adding a solvent to the reaction, said solvent comprising water.
12. The method of claim 11, wherein the solvent is substantially free of organic solvents.
13. The method of claim 11, wherein the solvent further comprises a salt.
14. A method of producing C₈ – C₁₅ hydrocarbons comprising:
- a) providing a ketone starting material;
 - b) providing an aldol starting material; and
 - c) mixing the ketone starting material and the aldol starting material in a reaction in the presence of a catalyst having the structure:



wherein R₁ is a C₁ – C₆ alkyl moiety, X = (OH) and n = 2, to produce the C₈ – C₁₅ hydrocarbons.

15. The method of claim 14, wherein the aldol starting material comprises chloromethylfurfural.
16. The method of claim 14, wherein the ketone starting material comprises acetone, dihydroxyacetone, or combinations thereof.

17. The method of claim 14, wherein the reaction occurs at about 25°C.
18. The method of claim 14, further comprising adding a solvent to the reaction, said solvent comprising water.
19. The method of claim 18, wherein the solvent is substantially free of organic solvents.
20. The method of claim 18, wherein the solvent further comprises a salt.
21. A method of producing $C_8 - C_{15}$ hydrocarbons comprising:
- a) providing a ketone starting material;
 - b) providing an aldol starting material; and
 - c) mixing the ketone starting material and the aldol starting material in a reaction in the presence of a catalyst having the structure:

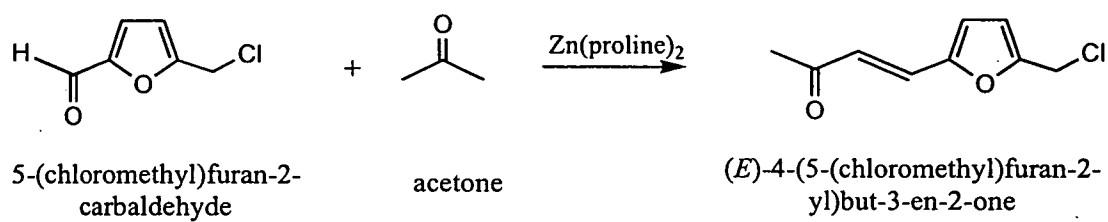


where X is CH₂, sulfur or selenium, M is Zn, Mg, or a lanthanide, and R₁ and R₂ each independently are a methyl, ethyl, or phenyl moiety, to produce the $C_8 - C_{15}$ hydrocarbons.

22. The method of claim 21, wherein the aldol starting material comprises chloromethylfurfural.
23. The method of claim 21, wherein the ketone starting material comprises acetone, dihydroxyacetone, or combinations thereof.

24. The method of claim 21, wherein the reaction occurs at about 25°C.
25. The method of claim 21, further comprising adding a solvent to the reaction, said solvent comprising water.
26. The method of claim 25, wherein the solvent is substantially free of organic solvents.
27. The method of claim 25, wherein the solvent further comprises a salt.

(a)



(b)

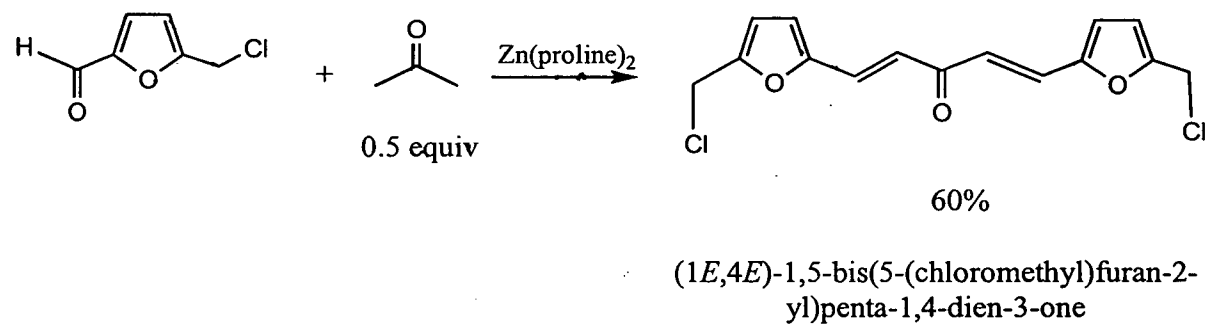


FIGURE 1

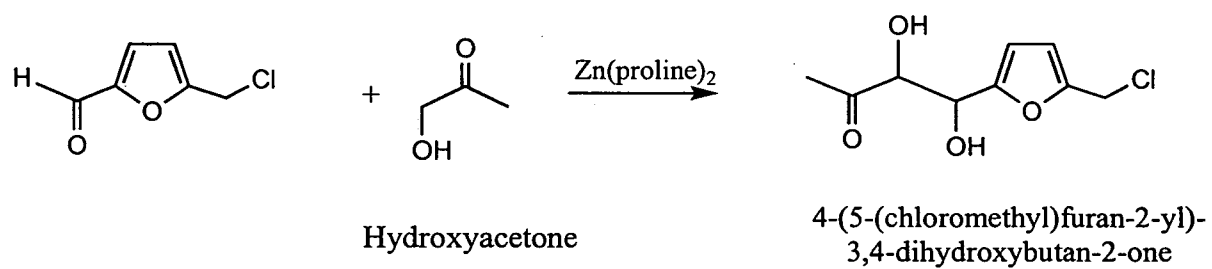


FIGURE 2

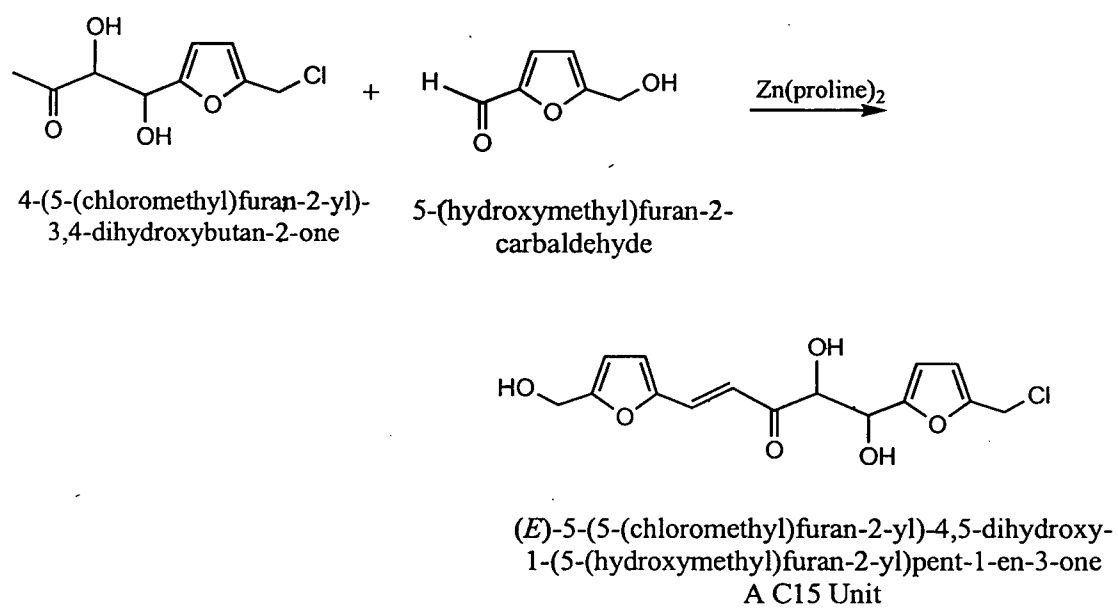


FIGURE 3

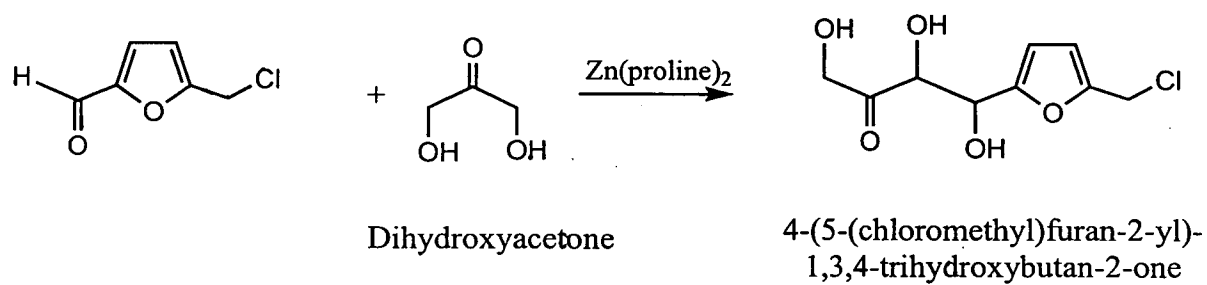


FIGURE 4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/02216

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 1/00; C07C 27/00; C07C 205/00; C07C 49/00 (2010.01)

USPC - 526/907; 585/251; 585/240; 568/303; 568/36; 568/34

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8) - C07C 1/00; C07C 27/00; C07C 205/00; C07C 49/00 (2010.01)

USPC - 526/907; 585/251; 585/240; 568/303; 568/36; 568/34

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

IPC(8) - C07C 1/00; C07C 27/00; C07C 205/00; C07C 49/00 (2010.01)

USPC - 526/907; 585/251; 585/240; 568/303; 568/36; 568/34 (keyword delimited)

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

PubWEST (USPT,PGPB,EPAB,JPAB); Google, Google Patent

Search terms used: ketone aldol chloromethyl furfural furan acetone proline zinc zn yb catalyst condensation halo

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Darbre et al. "Zn-Proline catalyzed direct aldol reaction in aqueous media." CHEM. COMMUN., 2003, 1090-1091 31 March 2003 (31.03.2003), pg 1090, 1091; abstract; Table 1	1-6
Y	US 2009/0124839 A1 (Dumesic et al.) 14 May 2009 (14.05.2009), para [0002], [0058], [0008], [0056]	1-6

☐ Further documents are listed in the continuation of Box C.


* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

09 December 2010 (09.12.2010)

Date of mailing of the international search report

16 DEC 2010

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

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PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/02216

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

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack unity of invention because they are not so linked as to form a single general inventive concept under PCT Rule 13.1.

In order for more than one species to be examined, the appropriate additional examination fees must be paid. The species are as follows:

In general, the embodiments are directed to a method of producing C8 - C15 hydrocarbons comprising:

- a) providing a ketone starting material;
- b) providing an aldol starting material; and
- c) mixing the ketone starting material and the aldol starting material in a reaction in the presence of a catalyst

-- see extra sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-6

Remark on Protest

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

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/02216

Continuation of Box No. III -- Observations where Unity of Invention is Lacking

The species of the generic invention are:

Group I: a proline-containing catalyst selected from the group consisting of Zn(Pro)₂, Yb(Pro)₂, and combinations thereof

Group II: a catalyst having the structure as shown in claim 7

Group III: a catalyst having the structure as shown in claim 14

Group IV: a catalyst having the structure as shown in claim 21

The claims are deemed to correspond to the species listed above in the following manner:

Group I: Claims 1-6

Group II: Claims 7-13

Group III: Claims 14-20

Group IV: Claims 21-27

Claims considered as generic: none

The inventions listed as Groups I-IV do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Groups I-IV lack unity of invention, because even though the inventions of these groups require the technical feature of producing C8 - C15 hydrocarbons comprising: a) providing a ketone starting material; b) providing an aldol starting material; and c) mixing the ketone starting material and the aldol starting material in a reaction in the presence of a catalyst, this technical feature is not a special technical feature as it does not make a contribution over the prior art in view of US 2008/0058563 A1 to Dumesic et al., which discloses producing C8 - C15 hydrocarbons comprising: a) providing a ketone starting material; b) providing an aldol starting material; and c) mixing the ketone starting material and the aldol starting material in a reaction in the presence of a catalyst (para [0028], [0026], [0053], [0054], [0011] - furfural-acetone in catalyzed reaction to form C6+ alkanes).

Further, the catalysts disclosed in each species of the generic invention do not share a common unifying structure.

The species listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features.