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(54) Title: PREPARATION AND USE OF BIFURAN AND BIPHENYL DICARBOXYLIC ACIDS, ALCOHOLS, AND ESTERS

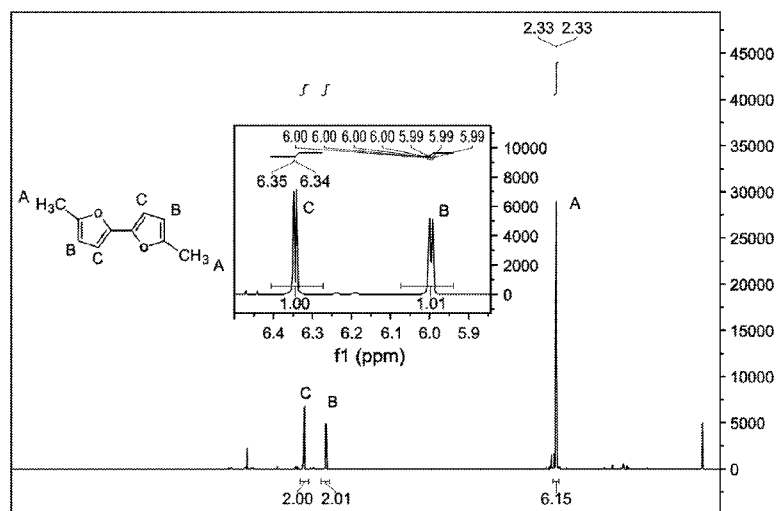
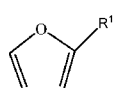
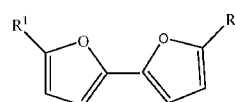


FIG. 1



(I)



(II)

(57) Abstract: A process for producing bifuran and/or biphenyl dicarboxylic acids, alcohols, and/or esters comprises reacting one or more furanyl compounds having the formula (I), where each R^1 is independently selected from the group consisting of -H, -CH₃, -CHO, -CH₂OH, -COOH or -COOR², where R^2 is an alkyl group having from 1 to 20 carbon atoms, in the presence of a first catalyst to produce a reaction product comprising a bifuran compound having the formula (II).



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**PREPARATION AND USE OF BIFURAN AND BIPHENYL DICARBOXYLIC
ACIDS, ALCOHOLS, AND ESTERS**

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5 **CROSS-REFERNCE OF RELATED APPLICATIONS**

[0001] This application claims the benefit of Provisional Application Serial No. 62/656,391, filed April 12, 2018, the disclosure of which are incorporated herein by reference.

FIELD

10 [0002] This disclosure relates to the preparation and use of bifuran and biphenyl dicarboxylic acids, alcohols, and esters, and particularly 2,2'-bifuran-5,5'-dicarboxylic acids, biphenyl-4,4'-dicarboxylic acids, and their corresponding alcohols and esters.

BACKGROUND

15 [0003] Bifuran and biphenyl dicarboxylic acids and alcohols are useful intermediates in the production of a variety of commercially valuable products, including polyesters and plasticizers for PVC and other polymer compositions. For example, bifuran and biphenyl dicarboxylic acids can be converted to plasticizers by esterification with long chain alcohols. In addition, bifuran and biphenyl dicarboxylic acids are potential precursors, either alone or as a modifier for polyethylene terephthalate (PET), in the production of polyester fibers, engineering plastics, liquid crystal polymers for electronic and mechanical devices, and films with high heat resistance and strength. With respect to biphenyls, the 4,4'-dicarboxylic acid isomers are the most desired due to the properties of the resulting products and hence have the broadest application.

20 [0004] As disclosed in US Patent Nos. 9,580,572 and 9,663,417, biphenyl carboxylic acids can be prepared by oxidation of dimethylbiphenyl (DMBP) compounds, which in turn may be produced by hydroalkylation of toluene followed by dehydrogenation of the resulting (methylcyclohexyl)toluene (MCHT). However, the DMBP product comprises a mixture of all six DMBP isomers, namely 2,2', 2,3' 2,4', 3,3', 3,4', and 4,4' DMBP, in which the 3,4' isomer is usually the most abundant and the 4,4' isomer normally comprises less than 20% of the overall isomer mixture. Thus, to maximize the production of the preferred 4,4' isomer, most of the product must be recycled to an isomerization reactor, which increases the cost and complexity of the process.

30 [0005] Alternative routes to DMBP compounds via benzene are described in US Patent No.

9,085,669, in which the benzene is initially converted to biphenyl, either by oxidative coupling or by hydroalkylation to cyclohexyl benzene (CHB) followed by dehydrogenation of the CHB, and then the biphenyl is alkylated with methanol. Again, the alkylated product comprises a mixture of DMBP isomers, in which the 4,4' isomer is a minor component.

5 [0006] There is, therefore, interest in developing alternative processes for producing biphenyl dicarboxylic acids, alcohols and esters in which the concentration of the 4,4' isomer is increased, especially where some or all of the feedstocks to these processes can be derived from renewable resources.

[0007] Recently, in 16 *Org. Lett.* 2732-2735 (2014), Yong-Qiang Wang et al. reported on
10 the development of a palladium-catalyzed process for the intermolecular direct C-H homocoupling of furans and thiophenes. The reaction uses molecular oxygen as the sole oxidant and is reported to result in complete C5-position regioselectivity. Both C2- and C3-substituted furans or thiophenes are indicated to be appropriate substrates. The approach is said to provide a straightforward, facile, and economical route to bifurans and bithiophenes under
15 mild reaction conditions.

[0008] Earlier, Burger et al. reported in 55 *S. Afr. J. Chem.* 56-66 (2002) that 5,5'-diformyl-2,2'-difuran can be synthesized in 60% yield by the palladium acetate-catalyzed aryl coupling of furfural in acetonitrile in the presence of dioxygen under pressure.

[0009] It is also known from, for example, US Patent No. 9,302,971 that substituted furan
20 compounds can be converted to terephthalic acid using a Diels Alder cycloaddition reaction with ethylene. In particular, the '971 patent discloses that 5-hydroxymethylfurfural (HMF) or 2,5-bis hydroxymethylfuran (BHMF) can be converted to a bicyclic ether which can then be dehydrated to a 2,5 substituted phenyl which in turn can be oxidized to terephthalic acid.

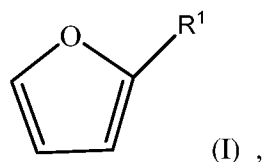
SUMMARY

25 [0010] According to the present disclosure, it has now been found that 2,2'-bifuran-5,5'-dicarboxylic acids, biphenyl-4,4'-dicarboxylic acids, and their corresponding alcohols and esters can be formed by a process including (1) dehydrogenative coupling of 2-methylfuran to produce 5,5'-dimethyl-2,2'-bifuran, optionally (2) followed by a tandem Diels-Alder/dehydration reaction of the 5,5'-dimethyl-2,2'-bifuran with a dienophile, particularly
30 ethylene. Similar results can be obtained when the 2-methylfuran is replaced by furan, furfural, furanol, furanoic acid or a furanoic ester, optionally with an intermediate reduction step in the case of furfural, furanol, furanoic acid or a furanoic ester so that the product of step (1) is 5,5'-dimethyl-2,2'-bifuran and the product of optional step (2) is 4,4' dimethyl-1,1'-biphenyl, either

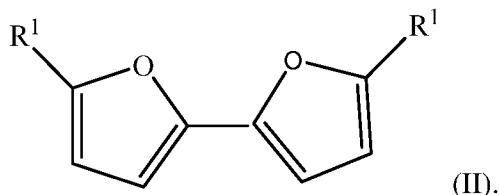
of which can then be oxidized to the desired dicarboxylic acid. Since both furfural and ethylene can be produced from renewable resources, this process sequence provides an attractive route to bifuran and/or biphenyl alcohols, dicarboxylic acids, and esters.

[0011] Thus, in one aspect, the present disclosure resides in a process for producing bifuran and/or biphenyl dicarboxylic acids, alcohols, and/or esters, the process comprising (or consisting of, or consisting essentially of):

(a) reacting one or more furanyl compounds having the formula (I):

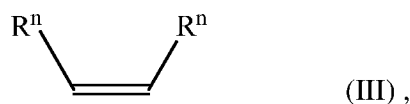


where each R^1 is independently selected from the group consisting of $-H$, $-CH_3$, $-CHO$, $-CH_2OH$, $-COOH$ or $-COOR^2$, where R^2 is an alkyl group having from 1 to 20 carbon atoms, and where each R^1 can be the same or different, in the presence of a first catalyst under conditions effective to produce a reaction product comprising a bifuran compound having the formula (II):



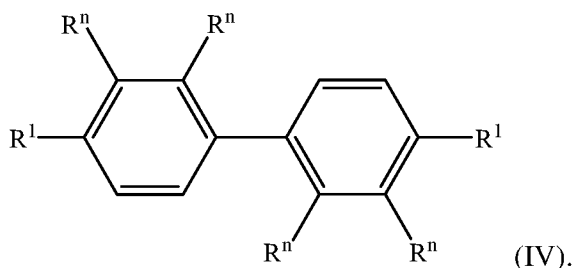
Optionally, the process further comprises:

(b) reacting a bifuran compound having the formula (II) with a dienophile of formula (III):



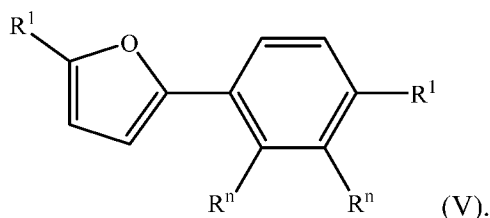
where each R^n is independently selected from the group consisting of $-R^3$, $-H$, $-CH_3$, $-CHO$, $-CH_2OH$, $-COOH$ or $-COOR^3$, where R^3 is an alkyl group having from 1 to 20 carbon atoms, and where each R^n can be the same or different, under cycloaddition reaction conditions and in the presence of a second catalyst to produce a bicyclic ether; and

(c) dehydrating the bicyclic ether from (b) to produce a biphenyl compound having the formula (IV):



[0012] In a further aspect, the present disclosure resides in a product composition comprising a mixture of the compound of formula (II) and the compound of formula (IV).

[0013] In a further aspect, the present disclosure resides in a product composition comprising (or consisting of, or consisting essentially of) a mixture of the compound of formula (IV) and a compound having the formula (V):



BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. 1 is the ¹H NMR spectrum of the 5,5'-dimethyl-2,2'-bifuran product of Example 1.

[0015] FIG. 2 depicts an enlarged aliphatic region of the ¹H NMR spectrum corresponding to the biphenyl-4,4'-dicarboxylic acid product mixture of Example 2.

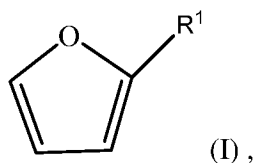
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] As used herein, “wt%” means percentage by weight, “vol%” means percentage by volume, “mol%” means percentage by mole, “ppm” means parts per million, and “ppm wt” and “wppm” are used interchangeably to mean parts per million on a weight basis. All “ppm” as used herein are ppm by weight unless specified otherwise. All concentrations herein are expressed on the basis of the total amount of the composition in question. Thus, the concentrations of the various components of the first mixture are expressed based on the total weight of the first mixture. All ranges expressed herein should include both end points as two specific embodiments unless specified or indicated to the contrary.

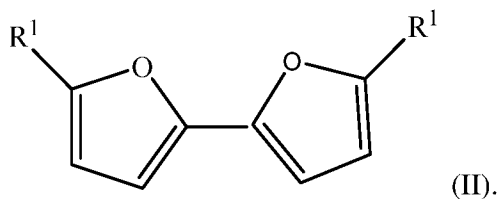
[0017] Described herein are novel processes for producing bifuran and/or biphenyl dicarboxylic acids and their corresponding alcohols and esters from furanyl compounds, especially 2-substituted furan compounds. In its simplest form the process includes dehydrogenative coupling of the furanyl compound to produce a bifuran compound, typically

a 5,5'-disubstituted 2,2' bifuran compound, which can then optionally be reacted with a dienophile, such as ethylene, in a tandem Diels-Alder/dehydration reaction to produce a 4,4'-disubstituted 1,1'-biphenyl compound.

[0018] Typically, the processes comprise initially reacting one or more furanyl compounds
5 having the formula (I):



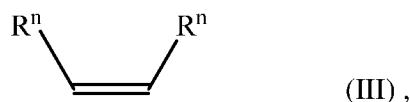
where each R¹ is independently selected from the group consisting of -H, -CH₃, -CHO, -CH₂OH, -COOH or -COOR², R² is an alkyl group having from 1 to 20 carbon atoms, and where each R¹ can be the same or different, in the presence of a first catalyst under conditions effective
10 to produce a bifuran compound, typically a substituted 2,2'-bifuran compound, having the formula (II):



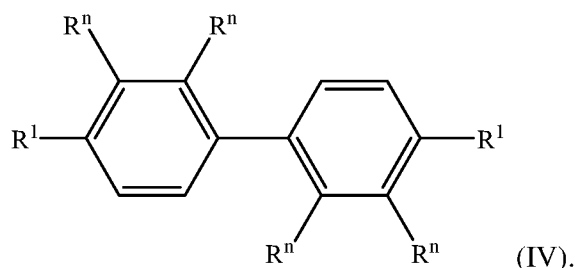
[0019] Often, each R¹ in the bifuran compound of formula (II) is the same, i.e., in aspects where the reacted furanyl compounds of formula (I) are identical, e.g., a reaction of two 2-methylfuran molecules. Alternatively, each R¹ in the bifuran compound of formula (II) may
15 be different, i.e., in aspects where the reacted furanyl compounds of formula (I) are not identical, e.g., a reaction of 2-methylfuran and furfural.

[0020] In some aspects, the initial reaction of the compound of formula (I) comprises oxidative coupling and the first catalyst comprises at least one metal or compound thereof from
20 Groups 8 to 13 of the Periodic Table, such as at least one of palladium or a palladium compound, zinc or a zinc compound, or a mixture thereof. Suitable reaction conditions for such an oxidative coupling step are described in 2(8) *ACS Catal.* 1787–1791 (2012), and include a temperature from 30°C to 250°C, preferably from 50°C to 150°C. The reaction may be conducted in the presence of an inorganic or organic oxidant. Preferred suitable oxidants
25 include oxygen or an oxygen containing gas, preferably at an oxygen partial pressure up to 5500 kPa-a, also as well as copper or silver based oxidants described in *ACS Catal.* (2012), e.g., AgOAc.

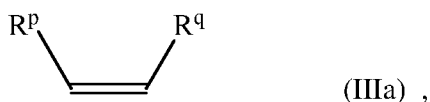
[0021] Optionally, at least part of the resultant bifuran compound of formula (II), or as discussed below, a reduction product thereof, is then reacted with a dienophile of formula (III):



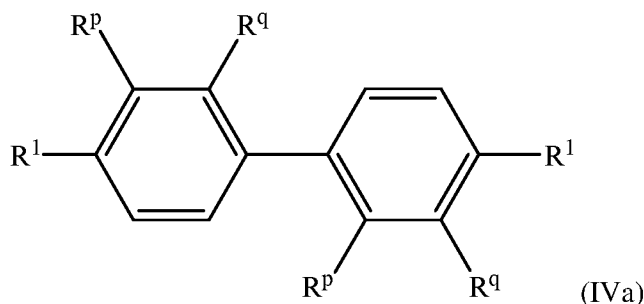
where each R^n is independently selected from the group consisting of $-R^3$, $-H$, $-CH_3$, $-CHO$, $-CH_2OH$, $-COOH$ or $-COOR^3$, where R^3 is an alkyl group having from 1 to 20 carbon atoms, and where each R^n can be the same or different, under cycloaddition reaction conditions and in the presence of a second catalyst to produce a bicyclic ether, which is a low-concentration intermediate with unfavorable equilibrium and readily dehydrates *in situ* under the reaction conditions to a biphenyl compound, typically a 4,4'-disubstituted biphenyl compound, having the formula (IV):

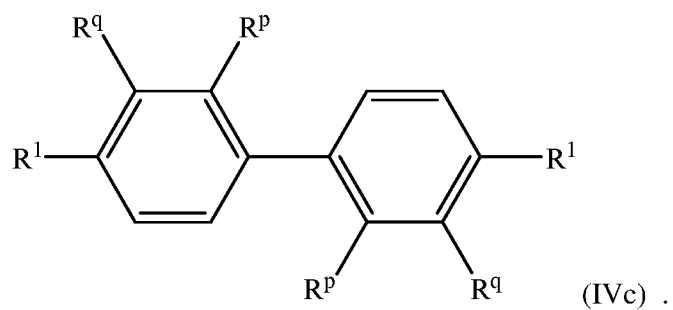
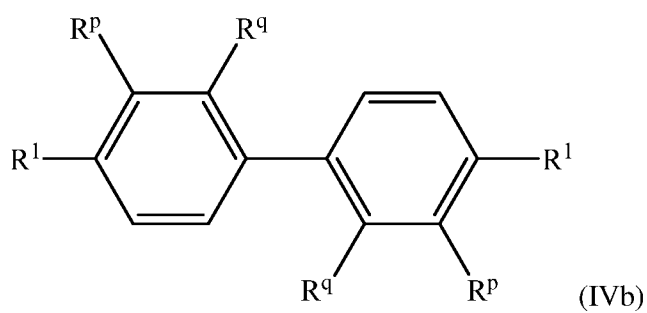


[0022] Often, the diphenophile of formula (III) is symmetric, e.g., ethylene. In such aspects, typically each R^n in the biphenyl compound of formula (IV) is the same. Alternatively, the dienophile of formula (III) may be asymmetric, as shown in formula (IIIa):



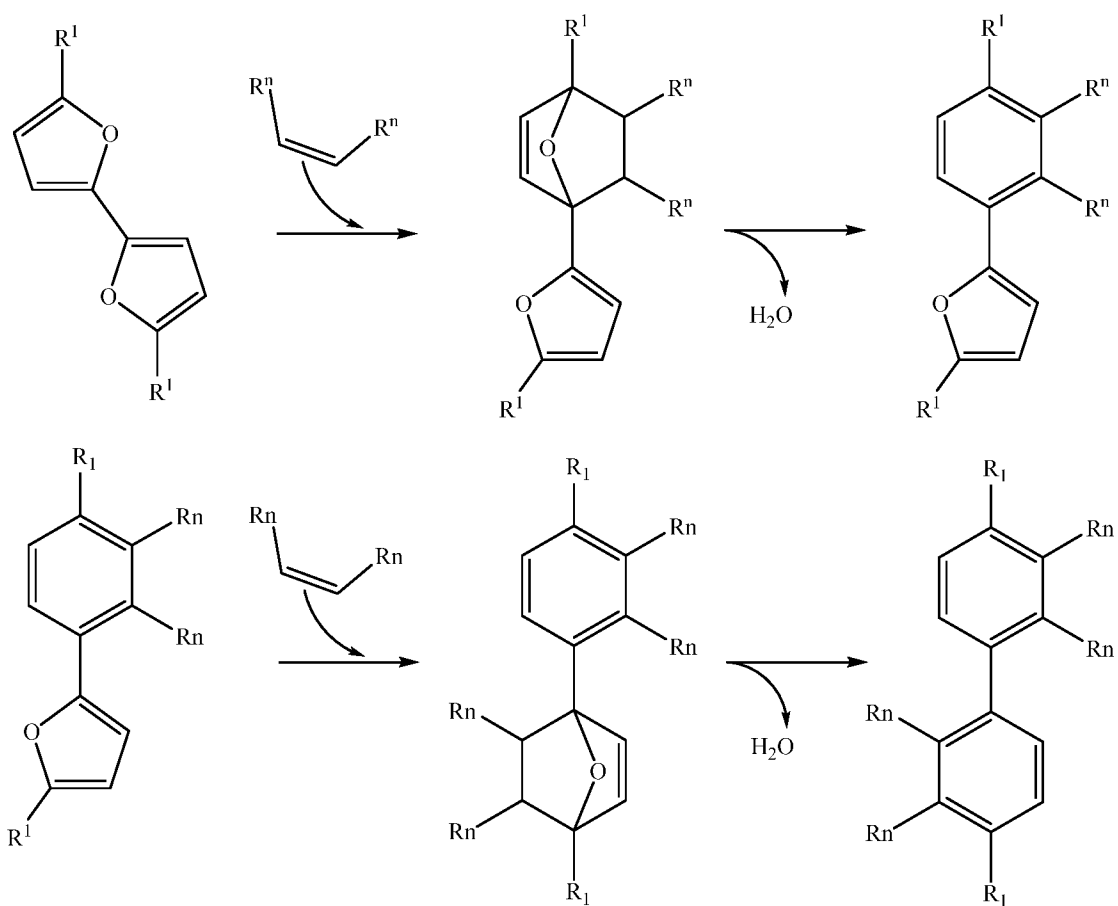
where R^p and R^q are independently selected from the group consisting of $-R^3$, $-H$, $-CH_3$, $-CHO$, $-CH_2OH$, $-COOH$ or $-COOR^3$, where R^3 is an alkyl group having from 1 to 20 carbon atoms, and where R^p and R^q are different. In such aspects, the compound of formula (IV) typically comprises one or more of the following compounds as shown in formulas (IVa)-(IVc):



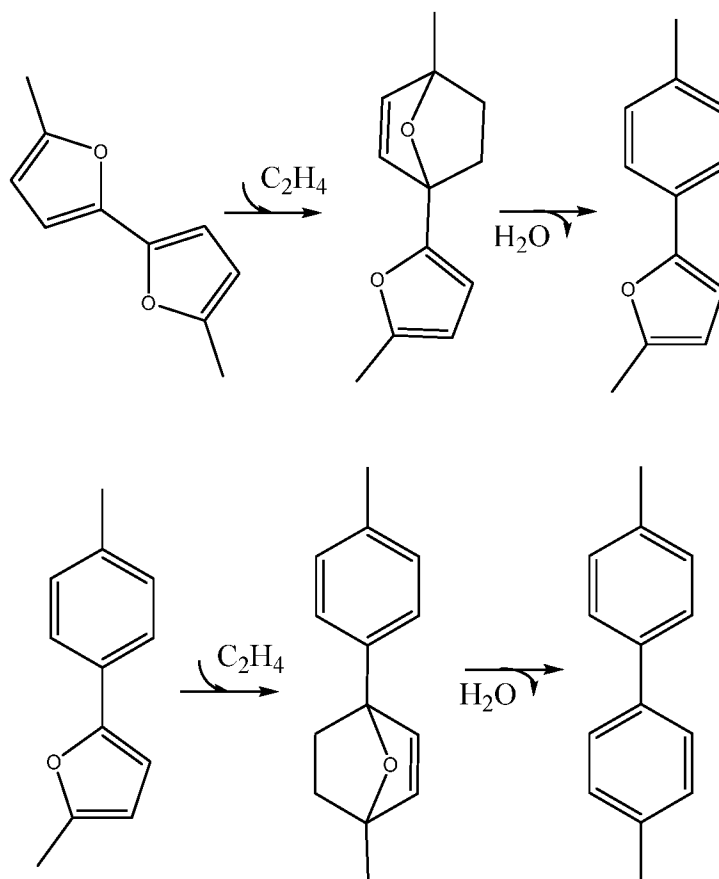


[0023] In any embodiment, the overall addition/dehydration sequence starting from a compound according to formula (II) can be summarized as follows:

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[0024] For example, the overall addition/dehydration starting from a compound of formula (II) and using ethylene as the dienophile can be summarized as follows:



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[0025] Apart from ethylene, other preferred dienophiles include propylene and methyl acrylate. Often, two or more dienophiles may be used.

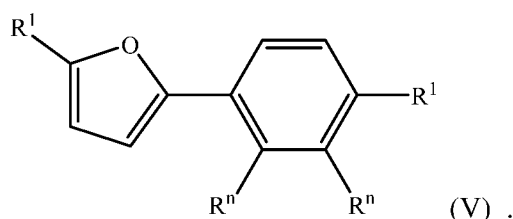
[0026] The Diels-Alder reaction is conducted in the presence of an acidic second catalyst, preferably with Lewis acidity. Often, the second catalyst comprises an acidic molecular sieve such as an aluminosilicate molecular sieve having a silica to alumina molar ratio less than 75, for example less than 50, or 30. Suitable molecular sieves comprise MFI, BEA, FAU, MOR, MTW, MFS, FER, CHA, and MWW structure type molecular sieves, and mixtures thereof. Additionally or alternatively, Brønsted and/or Lewis acids can be used as the second catalyst. Suitable Brønsted acid catalysts include acetic acid and its halogenated analogs, e.g., trifluoroacetic acid, trichloroacetic acid, hexachloroantimonate (HSbCl₆), trifluoromethanesulfonic acid (HSO₃CF₃), and *p*-toluenesulfonic acid (HSO₃Tos). Suitable Lewis acids include BX₃, AlX₃, RAlX₂, R₂AlX, TiX₄, SnX₂, SnX₄, ZnX₂, SbX₃, SbX₅, ScX₃, where X is selected from F, Cl, and Br, and where R is an alkyl group having from 1 to 22 carbon atoms. Additional suitable Lewis acids include, but are not limited to, Sc(OTf)₃,

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lanthanide (III) species, Lewis Acidic transition metal complexes, and $\text{Ti}(\text{OR}^4)_4$, where R^4 comprises an alkoxide or phenoxide group having from 1 to 22 carbon atoms.

[0027] Suitable conditions for the cycloaddition/dehydration reaction include a temperature from 100°C to 400°C and a pressure of 25 to 5000 psig (270 to 34600 kPa-a). Since the cycloaddition product is unstable, the combination of the cycloaddition reaction and the dehydration reaction is generally conducted in the same reaction zone in the presence of the second catalyst. In any embodiment, the rate of the Diels-Alder reaction may be enhanced by employing strategies described in Pindur et al., "Acceleration Selectivity Enhancement of Diels-Alder Reactions by Special Catalytic Methods," 93 *Chem. Rev.* 741-61 (1993).

[0028] The product of the cycloaddition/dehydration reaction will generally contain a mixture of the compound of formula (IV) together with some unreacted compound of formula (II), optionally together with the monophenyl furanyl intermediate of formula (V):



[0029] The reaction product may also contain unreacted dienophile, e.g., ethylene, and water by-product. The desired compound of formula (IV) can then be recovered by known separation methods, including distillation and phase separation. Preferably, water may be removed as the cycloaddition/dehydration reaction proceeds.

[0030] In some embodiments, where at least one R^1 in the starting furanyl compound(s) (I) is $-\text{CHO}$, $-\text{CH}_2\text{OH}$, $-\text{COOH}$ or $-\text{COOR}^2$, it may be desirable to reduce the compound (II) to the corresponding 2-methyl derivative prior to Diels-Alder/hydration reaction to increase the rate of the reaction with the dienophile, e.g., ethylene. Such reduction can readily be effected using a supported Ni/Fe catalyst.

[0031] Where at least one R^1 in the starting furanyl compound(s) (I) is $-\text{CH}_3$, $-\text{CHO}$, or $-\text{CH}_2\text{OH}$, the compound (II) and/or the compound (IV) can be oxidized to the corresponding carboxylic acid by methods well known in the art, for example by reaction with an oxidant, such as oxygen, ozone or air, or any other oxygen source, such as hydrogen peroxide, in the presence of a catalyst and with or without a promoter, such as Br, at temperatures from 30°C to 300°C, more preferably from 60°C to 200°C. Suitable catalysts comprise Co or Mn or a combination of both metals. The oxidation is normally conducted in solution, generally in

acetic acid and/or water as solvent. In aspects where one or more R¹ groups in the starting furanyl compound(s) (I) is -H, the compound (II) and/or the compound (IV) can be alkylated by methods well known in the art, followed by oxidation to the corresponding carboxylic acid as described above. In any embodiment, the carboxylic acid product produced via oxidation or a combination of alkylation and oxidation may be converted to an ester by reaction with an alcohol.

[0032] It will be appreciated that where at least one R¹ in the starting furanyl compound(s) (I) is -COOH, the compound of formula (II) and/or the compound of formula (IV) can be converted to an ester by reaction with an alcohol. Similarly, where at least one R¹ in the starting furanyl compound(s) (I) is -CH₂OH, the compound of formula (II) and/or the compound of formula (IV) can be esterified by reaction with a carboxylic acid.

[0033] The invention will now be more particularly described with reference to the following non-limiting Examples and the accompanying drawings.

Example 1: Preparation of 5,5'-dimethyl-2,2'-bifuran

[0034] A 40-mL reaction vial was charged with palladium(II)acetate (157 mg, 0.7 mmol), dimethyl sulfoxide (DMSO, 10.5 mL), and trifluoroacetic acid (798 mg, 7 mmol). While stirring, 2-methyl furan (575 mg, 7 mmol) was added. The reaction vial was sealed with an air atmosphere and the reaction mixture stirred for 72 hours. The reaction product was then poured into 30 mL of water and extracted with diethyl ether (25 mL x 4). The organics were washed with brine, dried over MgSO₄ and concentrated. The concentrates were dissolved in 10% EtOAc/hexanes and were run through a silica plug. Concentration under reduced pressure gave crude product (171 mg, 30.1%) as a yellow oil. Additionally, when the reaction was carried out at 50°C, the product yield increased to approximately 50%.

[0035] Verification of the correct structure of the product was made by comparing the ¹H NMR [see FIG. 1] to literature values. In addition, GC-MS also produced a single major peak with the correct nominal mass 162.1 g/mol.

Example 2: Synthesis of 4,4'DMBP with AlCl₃ (5 wt%)

[0036] Under an inert atmosphere, a Parr reactor was charged with 5,5'-dimethyl-2,2'-bifuran (30 mg, 0.185 mmol), anhydrous dimethylformamide (20 mL) and AlCl₃ (1.5 mg, 5 wt%). The reactor was then sealed, charged with ethylene gas (500 psig (3450 kPa-g)) and heated to 150°C for 24 h. The reactor was then cooled to room temperature and vented. The reaction mixture was then combined with Et₂O (200 mL) and washed with brine (5x50 mL) to remove dimethylformamide. The organic phase was then dried with MgSO₄, filtered and

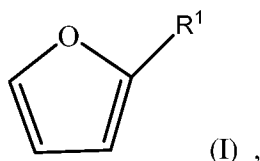
concentrated to a yellow oil by rotary evaporation. ^1H NMR (CDCl_3) spectroscopy was then utilized to analyze the sample and confirm the formation of 5-*p*-tolyl-2-methylfuran and 4,4'-dimethylbiphenyl. Verification of the correct structure of the product was made by comparing the ^1H NMR [see FIG. 2] to an authentic spectra of 4,4'-dimethylbiphenyl and a spectra of 5-*p*-tolyl-2-methylfuran reported in 62 *Tetrahedron*, 11740-11746 (2006).

[0037] While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention. All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text.

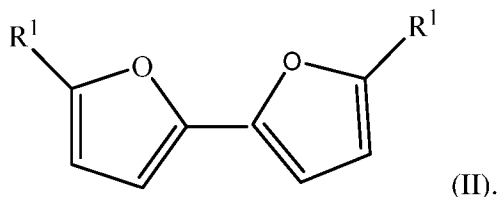
CLAIMS

1. A process for producing bifuran and/or biphenyl dicarboxylic acids, alcohols, and/or esters, the process comprising:

5 (a) reacting one or more furanyl compounds having the formula (I):

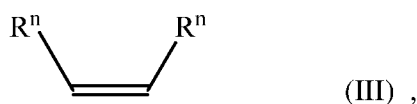


where each R¹ is independently selected from the group consisting of -H, -CH₃, -CHO, -CH₂OH, -COOH or -COOR², where R² is an alkyl group having from 1 to 20 carbon atoms, and where each R¹ can be the same or different, in the presence of a first catalyst under conditions effective to produce a reaction product comprising compound having the formula (II):



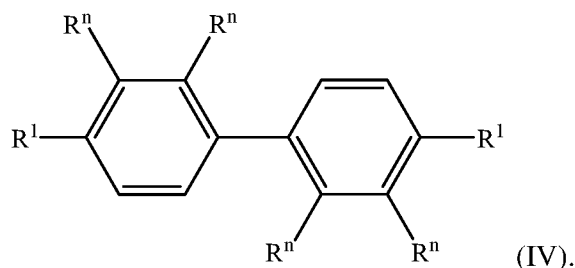
2. The process of claim 1, further comprising:

15 (b) reacting a compound having the formula (II) with a dienophile of formula (III):



where each Rⁿ is independently selected from the group consisting of -R³, -H, -CH₃, -CHO, -CH₂OH, -COOH or -COOR³, where R³ is an alkyl group having from 1 to 20 carbon atoms, and where each Rⁿ can be the same or different, under cycloaddition reaction conditions and in the presence of a second catalyst to produce a bicyclic ether; and

20 (c) dehydrating the bicyclic ether from (b) to produce a biphenyl compound having the formula (IV):



3. The process of claim 1 or 2, wherein the first catalyst comprises at least one metal or compound thereof from Groups 8 to 13 of the Periodic Table.

5

4. The process of any one of claims 1 to 3, wherein the first catalyst comprises at least one of palladium, zinc, or a compound thereof.

5. The process of any one of claims 1 to 4, wherein the reacting (a) is conducted in the presence of an oxidant.

10

6. The process of claim 5, wherein the conditions in (a) include a temperature from 30°C to 250°C and an oxygen partial pressure of up to 5500 kPa-a.

7. The process of any one of claims 2 to 6, wherein the second catalyst comprises an acidic molecular sieve.

15

8. The process of any one of claims 2 to 6, wherein the second catalyst comprises a member selected from the group consisting of an aluminosilicate molecular sieve having a silica to alumina molar ratio of less than 75, AlCl_3 , $\text{Ti}(\text{OR}^4)^4$, and mixtures or combinations thereof, wherein R^4 is an alkoxide or phenoxide group having from 1 to 22 carbon atoms.

20

9. The process of any one of claims 2 to 8, wherein the cycloaddition reaction conditions include a temperature from 100°C to 400°C and a pressure of 25 to 5000 psig (270 to 34600 kPa-a).

25

10. The process of any one of claims 2 to 9, wherein the dienophile is selected from the group consisting of ethylene, propylene, methyl acrylate, and mixtures or combinations

thereof.

11. The process of claim 10, wherein the dienophile comprises ethylene.

5 12. The process of claim 10 or 11, wherein the cycloaddition reaction conditions include an ethylene partial pressure of up to 7000 kPa-a.

13. The process of claim 11 or 12, wherein at least one of the compound(s) of formula (I) and/or the ethylene co-reactant are derived from renewable resources.

10

14. The process of any one of claims 2 to 13, wherein the reacting (b) and dehydrating (c) are conducted in the same reaction zone in the presence of the second catalyst.

15

15. The process of any one of claims 2 to 14, wherein at least one R^1 in the furanyl compound(s) (I) is -CHO, -CH₂OH, or -COOH and the process further comprises:

(d) reducing at least part of the reaction product of step (a) to 5,5'-dimethyl-2,2'-bifuran; and

(e) employing at least part of the 5,5'-dimethyl-2,2'-bifuran as the compound having the formula (II) in step (b).

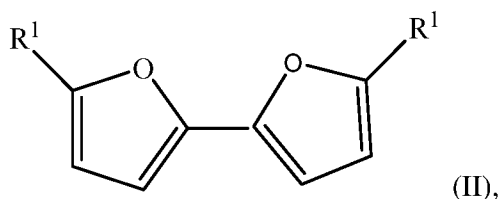
20

16. The process of claim 15, wherein the reducing (d) is conducted in the presence of a hydrogenation metal.

25

17. The process of claim 16, wherein the hydrogenation metal comprises at least one metal or compound thereof from Groups 8 to 13 of the Periodic Table.

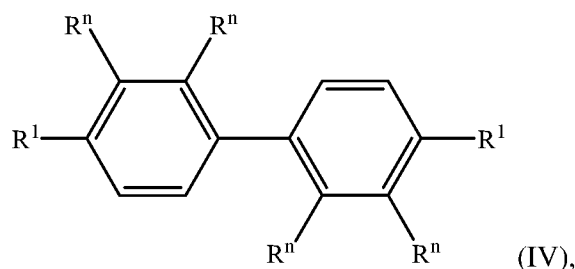
18. A product composition comprising a mixture of a compound having the formula (II):



where each R^1 is independently selected from the group consisting of -H, -CH₃, -CHO, -CH₂OH, -COOH or -COOR², where R^2 is an alkyl group having from 1 to 20 carbon

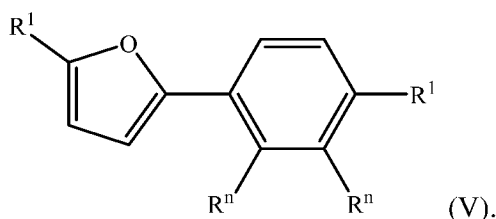
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atoms, and where each R^1 can be the same or different; and a biphenyl compound having the formula (IV):

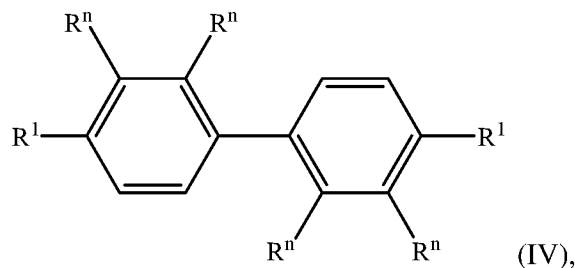


where each R^n is independently selected from the group consisting of $-R^3$, $-H$, $-CH_3$, $-CHO$, $-CH_2OH$, $-COOH$ or $-COOR^3$, where R^3 is an alkyl group having from 1 to 20 carbon atoms, and where each R^n can be the same or different.

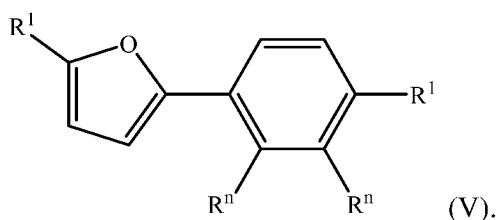
19. The product composition of claim 18 and also comprising a compound of formula (V):



20. A product composition comprising a mixture of a biphenyl compound having the formula (IV):



where each R^1 is independently selected from the group consisting of $-H$, $-CH_3$, $-CHO$, $-CH_2OH$, $-COOH$ or $-COOR^2$, where R^2 is an alkyl group having from 1 to 20 carbon atoms, where each R^1 can be the same or different, where each R^n is independently selected from the group consisting of $-R^3$, $-H$, $-CH_3$, $-CHO$, $-CH_2OH$, $-COOH$ or $-COOR^3$, where R^3 is an alkyl group having from 1 to 20 carbon atoms, and where each R^n can be the same or different; and a compound of formula (V):



21. The process of any one of claims 1 to 20, where at least one R^1 in the furanyl compound(s) (I) is $-CH_3$, $-CHO$, or $-CH_2OH$ and the process further comprises:

- 5 (f) oxidizing the compound of formula (II) to produce 2,2'-bifuran-5,5'-dicarboxylic acid; and optionally
 (g) reacting the 2,2'-bifuran-5,5'-dicarboxylic acid with an alcohol under conditions effective to produce a bifuran ester.

10 22. The process of any one of claims 2 to 21, where at least one R^1 in the furanyl compound(s) (I) is $-CH_3$, $-CHO$, or $-CH_2OH$ and the process further comprises:

- (h) oxidizing the compound of formula (IV) to produce biphenyl-4,4'-dicarboxylic acid; and optionally
 (i) reacting the biphenyl-4,4'-dicarboxylic acid with an alcohol under conditions
 15 effective to produce a biphenyl ester.

23. The process of any one of claims 1 to 20, where at least one R^1 in the furanyl compound(s) (I) is $-H$ and the process further comprises:

- 20 (j) alkylating the compound of formula (II) and/or the compound of formula (IV) to produce one or more alkylated compounds;
 (k) oxidizing the one or more alkylated compounds to produce 2,2'-bifuran-5,5'-dicarboxylic acid and/or biphenyl-4,4'-dicarboxylic acid; and optionally
 (l) reacting the 2,2'-bifuran-5,5'-dicarboxylic acid and/or biphenyl-4,4'-dicarboxylic acid with an alcohol under conditions effective to produce a bifuran ester and/or
 25 biphenyl ester.

24. The process of any one of claims 1 to 20, where at least one R^1 in the furanyl compound(s) (I) is $-COOH$ and the process further comprises:

- (m) reacting the compound of formula (II) and/or the compound of formula (IV) with

an alcohol under conditions effective to produce a bifuran ester and/or biphenyl ester.

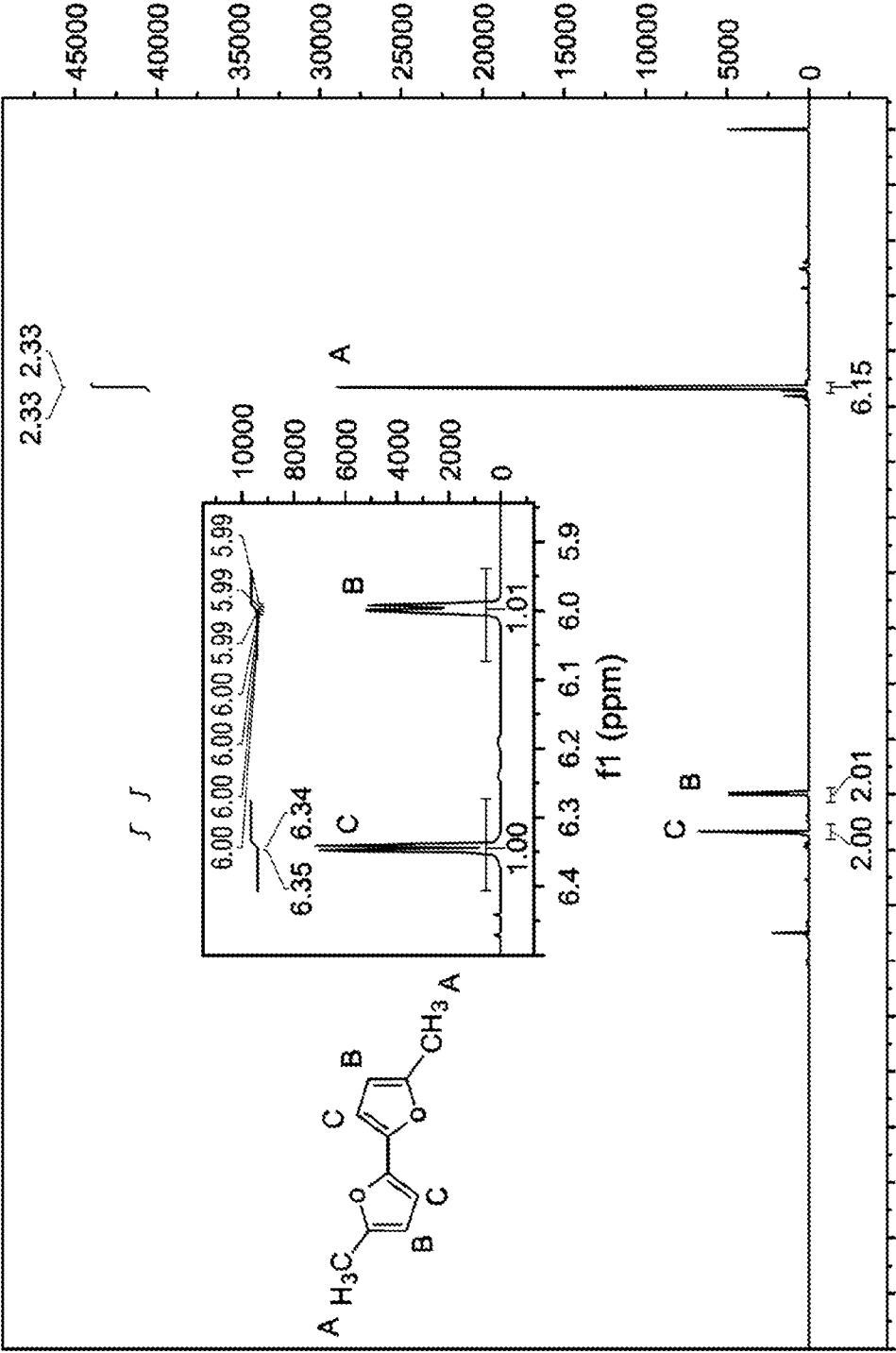


FIG. 1

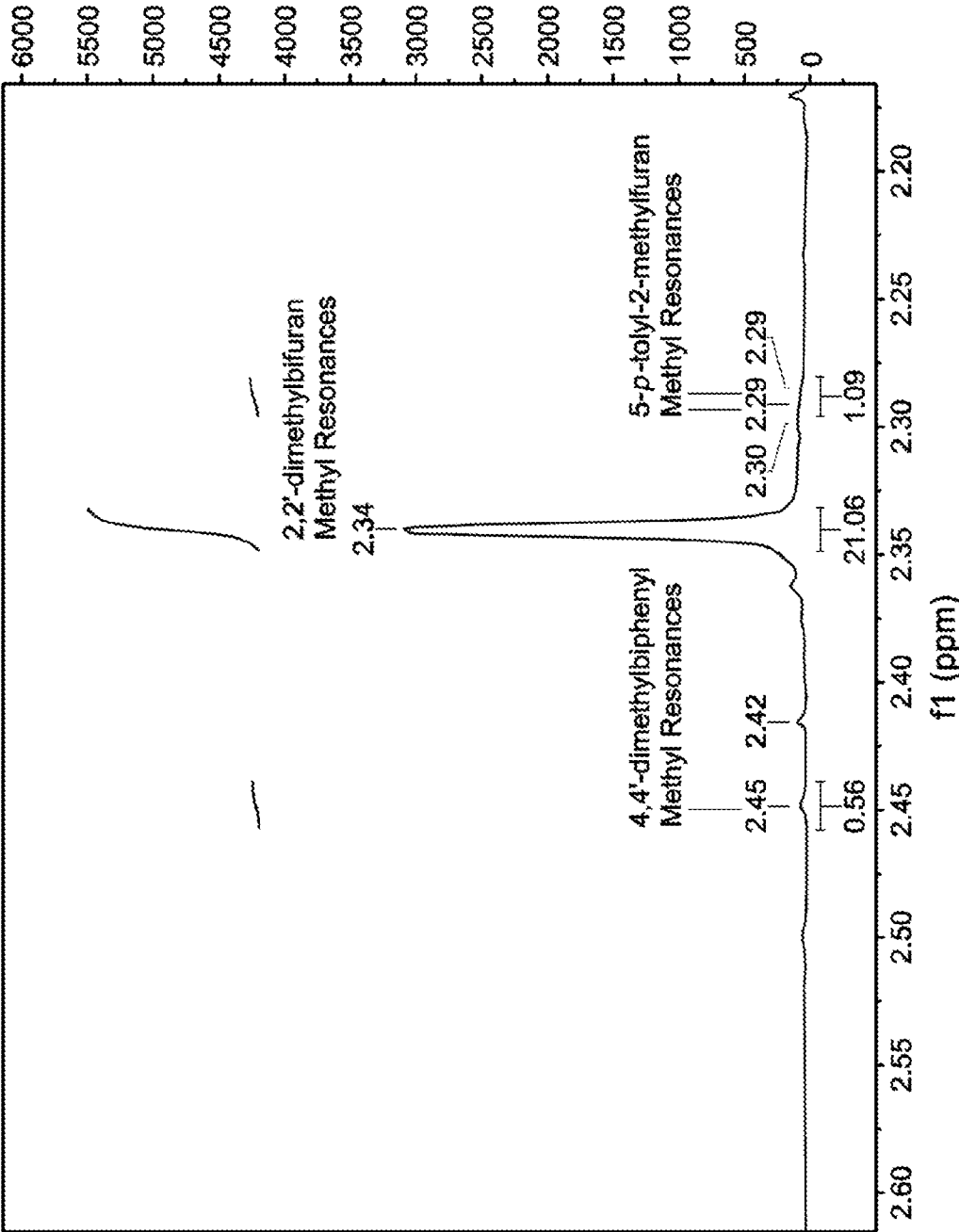


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2019/024309

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C1/247 C07C15/14 C07D307/42
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 C07D

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

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

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LI ET AL.: "Palladium-Catalyzed C-H Homocoupling of Furans and Thiophenes Using Oxygen as the Oxidant", ORGANIC LETTERS, vol. 16, no. 10, 7 May 2014 (2014-05-07), pages 2732-2735, XP002791263, Table 2, entry 2	1,3-6, 18-20
Y A		2,9-14 7,8, 15-17, 21-24
X	----- WO 2017/111598 A1 (NEDERLANDSE ORGANISATIE VOOR TOEGEPAST-NATUURWETENSCHAPPELIJK ONDERZOE) 29 June 2017 (2017-06-29) Cpds. (IId); claims 1,3	18-20
Y A		2,9-14 7,8, 15-17, 21-24
	----- -/-	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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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

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"&" document member of the same patent family

Date of the actual completion of the international search

13 June 2019

Date of mailing of the international search report

24/06/2019

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INTERNATIONAL SEARCH REPORT

International application No

PCT/US2019/024309

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016/069229 A1 (EXXONMOBIL CHEM PATENTS INC [US]) 6 May 2016 (2016-05-06) the whole document -----	1-24

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2019/024309

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2017111598 A1	29-06-2017	EP 3184507 A1	28-06-2017
		EP 3394025 A1	31-10-2018
		US 2019010111 A1	10-01-2019
		WO 2017111598 A1	29-06-2017

WO 2016069229 A1	06-05-2016	NONE	
