



Method for hydrogenation of biomass using pincer complex catalysts and precatalysts

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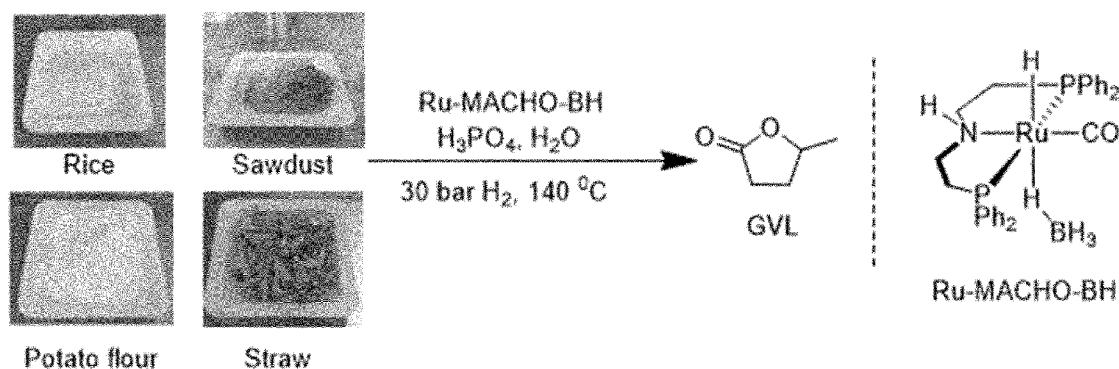


Fig. 1

(57) Abstract: The present invention relates to the field of biomass waste feedstock conversion into value-added chemicals. Specifically, the present invention relates to a method production of a chemical derived from biomass or derived from a biomass-derived material using homogenous catalysis.



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Method for hydrogenation of biomass using pincer complex catalysts and precatalysts

Technical field

5 The present invention relates to the field of biomass feedstock, including biomass waste, conversion into value chemicals. Specifically, the present invention relates to a method production of a chemical derived from biomass or derived from a biomass-derived material using homogenous catalysis.

10 Background

Biomass-based solutions to climate change are of unique interest to the formidable challenge of atmospheric carbon capture and utilization. One promising approach towards this end include the use of biomass to obtain a negative carbon footprint. In fact, biomass is the only perennial resource with the possibility of providing a negative carbon footprint, which can only be reached if it is used for producing value-added compounds instead of simply incinerating it back to CO₂.

Among various biomass, lignocellulose has gained much attention in terms of its wide abundance and the fact that the majority of value-added biomass-derived chemicals originate from polysaccharides (cellulose and hemicellulose). In fact, with suitable catalytic processes various platform molecules can be obtained from lignocellulose, among which γ -valerolactone (GVL) is emphasized as a versatile platform chemical with wide applications since GVL can be used as a feedstock for fuel additives/biofuel, liquid hydrocarbon diesel, bulk chemicals, green solvent, and for example syntheses of polymers or pharmaceuticals. It is therefore extremely attractive to directly convert biomass waste to GVL.

However, such a transformation is elusive, likely owing to the high complexity of biomass containing varying components that typically are of chemically relatively inert nature, and the process therefore normally requires several dedicated reaction steps and work-up manipulations to avoid undesirable cross-reactions in the reaction mixture and low product yields.

30 Conducting these processes in stepwise manners entails financially unviable, energy intensive, and waste-producing separation, intermediate isolation, and purification. The processes become even less viable when using sacrificial H-donor agents such as isopropanol or formic acid. On the contrary, obtaining GVL directly from real chemically

untreated biomass in a one-pot reaction manner would be extremely attractive, and even more so when employing H₂ as the H-donor.

As such, a catalytic system for a one-pot transformation of biomass to GVL must tolerate multiple distinct acid- and hydrogenation-mediated steps, all with very different substrates. In addition, all these highly differentiated steps must be carried out with high conversion and selectivity to reach reasonable yields of GVL. There thus remains a need in the field for improved systems and methods for converting real biomass into value-added chemicals, such as GVL in one-pot transformations and in high yields.

Summary

The inventors have surprisingly found that using specific pincer complexes, such as Ru-MACHO-BH or the compound defined herein as Ru-MACHO^{iPr} which is described by according to formula (V), as pre-catalysts for homogeneous catalysis under acidic conditions as described herein allows to integrate the myriad of cascade events necessary for producing value-added chemicals from raw woody- and starchy biomass into a one-pot process under mild conditions. Thus, the methods and system described herein are more efficient, less waste-producing and less energy intensive than existing stepwise methods.

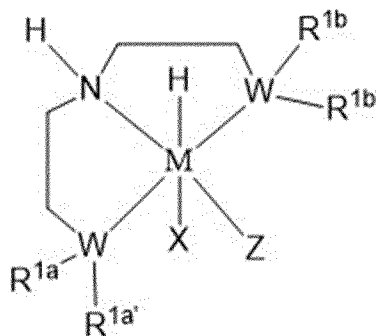
In one aspect, the present disclosure relates to a method for production of a chemical from biomass comprising:

- a) providing an amount of biomass or biomass-derived material,
- b) hydrogenating said biomass or biomass-derived material in the presence of a pincer complex, and
- c) isolating said produced chemical.

More particularly, the present disclosure relates in one aspect to a method for production of a chemical derived from biomass or derived from a biomass derived material, the chemical being selected from the group consisting of gamma-valerolactone (GVL), levulinic acid, 1,4-pentanediol, formic acid, methanol, sorbitol, humins, 1-hydroxyhexane-2,5-dione, alkyl levulinates, furfuryl alcohol, lactic acid and acetic acid, the method comprising:

- a) providing an amount of biomass or biomass-derived material,

b) hydrogenating said biomass or biomass-derived material in the presence of a Brønsted acid, a hydrogen source and a pincer complex according to formula (IIa):



(IIa)

5

wherein,

M is a metal selected from the group consisting of ruthenium, iron, iridium, manganese, rhodium, cobalt, platinum, palladium, nickel, osmium, rhenium, aluminium, gold, chromium and molybdenum;

10

W is an atom selected from the group consisting of P, C, O, and N;

R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are each independently selected from the group consisting of C1-C6 alkyl, isopropyl, tert-butyl, a C3-C7 cycloalkyl, a C3-C7 heterocycloalkyl, phenyl, and C5-C10 aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C1-C6 alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl;

15

Z is selected from CO, $P(R^{III})_3$, $As(R^{III})_3$, NO and N₂; and

X is selected from the group consisting of a hydridoborate, such as tetrahydridoborate (BH₄⁻), a halide, such as fluoride, chloride, bromide, or iodide, and H,

20

wherein R^{III} is each individually selected from C₁-C₆ alkyl, isopropyl, phenyl, and C₅-C₁₀ aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl, and

c) isolating the produced chemical.

25

In another aspect, the present disclosure provides a system comprising:

- a) a sealable reactor comprising an amount of biomass or biomass-derived material, a pincer complex, a Brønsted acid and an aqueous solvent;

- b) a hydrogen source, and
- c) a heat source.

5 More particularly, the system may be specifically configured for carrying out the method disclosed herein

Description of Drawings

10 **Figure 1:** typical reaction scheme of the method of the present invention. The method has in the present disclosure been demonstrated efficient for conversion of raw rice, potato flour, straw, sawdust and more (see detailed description) into gamma-valerolactone (GVL) in the presence of phosphoric acid and using Ru-MACHO-BH as a pre-catalyst.

15 Detailed description

One embodiment of the present disclosure provides for a method for production of a chemical derived from biomass or derived from a biomass-derived material, the method comprising:

- 20
- a) providing an amount of biomass or biomass-derived material,
 - b) hydrogenating said biomass or biomass-derived material in the presence of a pincer complex, and
 - c) isolating said produced chemical.

25 Pincer complex

A "pincer complex" as described herein refers to a transition metal coordination complex with a pincer ligand. Pincer ligands are compounds that coordinate with a metal through three coplanar sites. When the metal is surrounded by six ligation points in octahedral symmetry, this coordination form is also known as meridional coordination geometry.

In one embodiment, the pincer complex comprises a metal. In one embodiment, the pincer complex comprises a transition metal.

In one embodiment, the pincer complex comprises a metal selected from the group consisting of: ruthenium, iron, iridium, manganese, rhodium, cobalt, platinum, palladium, 35 nickel, osmium, rhenium, aluminum, gold, chromium, and molybdenum.

In another embodiment, the pincer complex comprises a metal selected from the group consisting of ruthenium, iron, manganese, and iridium. In one embodiment, the metal is ruthenium.

In one embodiment, the pincer complex comprises at least one tridentate organic ligand.

5 In one embodiment, the tridentate organic ligand comprises at least one heteroatom selected from the group P, N, As, O, Si, Se, Ge, S and B.

In one embodiment, the tridentate ligand comprises one heteroatom selected from P, N, As and O.

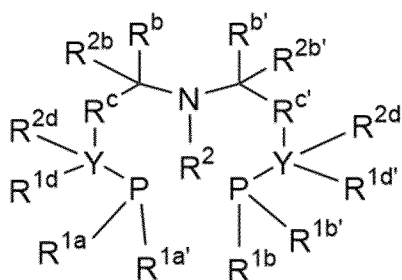
10 In one embodiment, the tridentate ligand is coordinated to the metal through three atoms, each individually selected from P, N, C, As, O, Si, Se, Ge, S and B. In one embodiment, the tridentate ligand is coordinated to the metal through three atoms, each individually selected from P, N, C and O. In one embodiment, the tridentate ligand is coordinated to the metal through three atoms, each individually selected from P, N, and C.

15 In another embodiment, the tridentate ligand coordinates to the metal through any one of the following combinations of three atoms: two P atoms and one N atom, two P atoms and one O atom, two S atoms and one N atom, two N atoms and one P atom, three N atoms, and two P atoms and one C atom.

In one embodiment, the tridentate ligand coordinates to the metal through two P atoms and one N atom.

20

In one embodiment, the tridentate ligand is according to formula (I):



(I)

wherein

25 R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are each independently selected from the group consisting of H, C_1 - C_6 alkyl, isopropyl, *tert*-butyl, a C_3 - C_7 cycloalkyl, a C_3 - C_7 heterocycloalkyl, phenyl and C_5 - C_{10} aryl, each of which may optionally be substituted by one or

more selected from halogen, cyano, amino, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl;

R² is absent or is selected from the group consisting of H, C₁-C₆ alkyl, isopropyl, phenyl and C₅-C₁₀ aryl, each of which may optionally be substituted by one or more
5 selected from halogen, cyano, amino, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl;

R^c and R^{c'} are each independently selected from a single bond or a double bond;

Y is an atom selected from C, O, and N;

R^b, R^{2b}, R^{b'} and R^{2b'} are each independently absent or selected from H, C₁-C₆ alkyl, C₃-
10 C₇ cycloalkyl, phenyl, and C₅-C₁₀ aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl or R^b and R^{b'} may come together to form a C₃-C₆ heterocycloalkyl, a C₅-C₁₀ heteroaryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, hydroxyl, C₁-C₆ alkyl, C₁-C₆
15 alkoxy, phenyl, and C₅-C₁₀ aryl; and

R^{1d}, R^{2d}, R^{1d'} and R^{2d'} are each independently absent or selected from a H, C₁-C₆ alkyl, C₃-C₇ cycloalkyl, phenyl and C₅-C₁₀ aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl or R^d and R^b may come together and/or
20 R^{d'} and R^{b'} may come together to form a C₅-C₇ cycloalkyl or a C₅-C₆ aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl.

The term "alkyl" as used herein refers to a linear or branched hydrocarbon moiety
25

The term "alkoxy" as used herein refers to a group of formula -O- alkyl, wherein alkyl is defined as above. In particular, C₁-C₃ -alkoxy is intended to indicate such hydrocarbon having 1, 2 or 3 carbon atoms. Examples of alkoxy groups include methoxy, ethoxy, n-propoxy, and isopropoxy.

30 As used herein the term "cycloalkyl" refers to a monocyclic or polycyclic system. The term "cycloalkyl" as used herein can optionally contain one or more unsaturations or substituents. The term "heterocycloalkyl" refers to monocyclic or polycyclic systems where at least one of the ring atoms are heteroatoms(s). Examples of heteroatoms
35 include N, O, S, As, B or P.

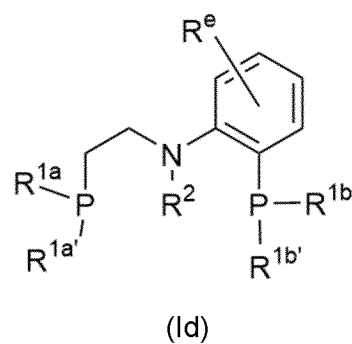
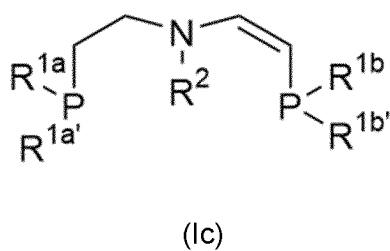
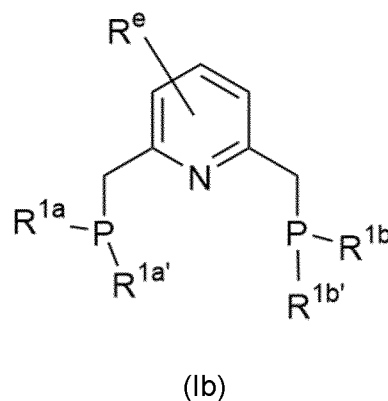
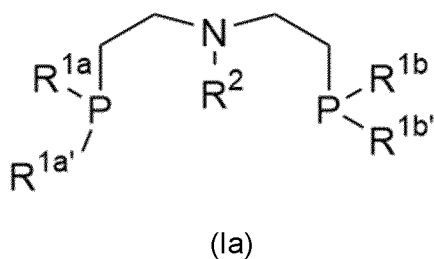
The term "aryl" refers to a cyclic or polycyclic moiety having a conjugated unsaturated $(4n+2)\pi$ electron system (where n is a positive integer), sometimes referred to as a delocalized π electron system. The term "heteroaryl" refers to aryl moieties wherein at least one of the ring atoms are heteroatom(s).

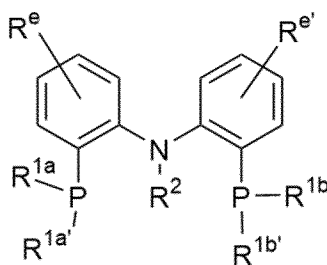
In one embodiment, R^b and $R^{b'}$ are H.

In one embodiment, R^d and $R^{d'}$ are H.

In one embodiment, R^c and $R^{c'}$ are a single bond.

In one embodiment, the tridentate ligand is selected from the group consisting of formula (1a), formula (1b), formula (1c), formula (1d) and formula (1e):





(Ie)

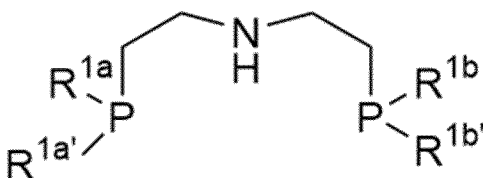
wherein

5 R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are each independently selected from the group consisting of C_1 - C_6 alkyl, isopropyl, *tert*-butyl, a C_3 - C_7 cycloalkyl, a C_3 - C_7 heterocycloalkyl, phenyl and C_5 - C_{10} aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl; R^2 is absent, or is selected from the group consisting of H, C_1 - C_6 alkyl, isopropyl, phenyl, and C_5 - C_{10} aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, hydroxyl, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl; and

10 R^e and $R^{e'}$ are each independently selected from the group consisting of H, halogen, cyano, amino, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl.

In one embodiment, R^2 is H.

15 In one embodiment, the tridentate ligand is according to formula (II):



(II)

wherein

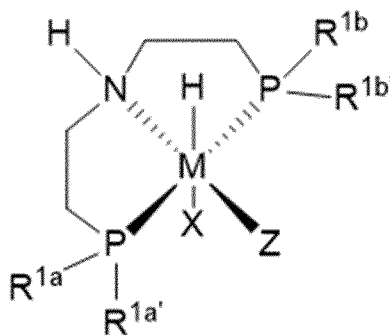
20 R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are each independently selected from the group consisting of C_1 - C_6 alkyl, isopropyl, *tert*-butyl, a C_3 - C_7 cycloalkyl, a C_3 - C_7 heterocycloalkyl, phenyl, and C_5 - C_{10} aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl.

Compounds and/or ligands having a structure according to formula (II) are often in the field of homogenous catalysis referred to as MACHO-type ligands, and also sometimes written as $\text{HN}(\text{CH}_2\text{CH}_2\text{PR}_2)_2$. In some embodiments of the present disclosure, R will be identical across all four positions, and in some embodiments R will be different across the four positions.

In one embodiment, wherein R^{1a} , $\text{R}^{1a'}$, R^{1b} and $\text{R}^{1b'}$ are phenyl.

In one embodiment, wherein R^{1a} , $\text{R}^{1a'}$, R^{1b} and $\text{R}^{1b'}$ are isopropyl.

In one embodiment, the pincer complex is according to formula (III):



(III)

wherein,

M is a metal selected from the group consisting of ruthenium, iron, iridium, manganese, rhodium, cobalt, platinum, palladium, nickel, osmium, rhenium, aluminium, gold, chromium and molybdenum;

R^{1a} , $\text{R}^{1a'}$, R^{1b} and $\text{R}^{1b'}$ are each independently selected from the group consisting of C_1 - C_6 alkyl, isopropyl, *tert*-butyl, a C_3 - C_7 cycloalkyl, a C_3 - C_7 heterocycloalkyl, phenyl, and C_5 - C_{10} aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl;

Z is selected from CO, $\text{P}(\text{R}^{\text{III}})_3$, As($\text{R}^{\text{III}})_3$, NO and N_2 ; and

X is selected from the group consisting of a hydridoborate, such as tetrahydridoborate (BH_4^-), a halide, such as fluoride, chloride, bromide, or iodide, and H, wherein R^{III} is each individually selected from C_1 - C_6 alkyl, isopropyl, phenyl, and C_5 - C_{10} aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl.

In one embodiment, M is selected from the group consisting of ruthenium, iron, iridium, and manganese.

In one embodiment, M is ruthenium.

In one embodiment R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are phenyl.

5 In one embodiment R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are isopropyl.

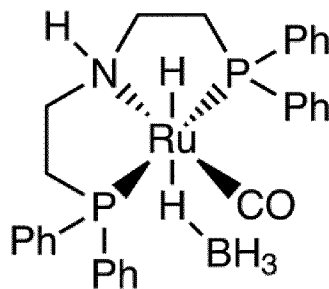
In one embodiment Z is CO.

In one embodiment X is tetrahydridoborate (BH_4^-).

In one embodiment X is chloride (Cl^-).

In one embodiment the pincer complex is according to formula (IV):

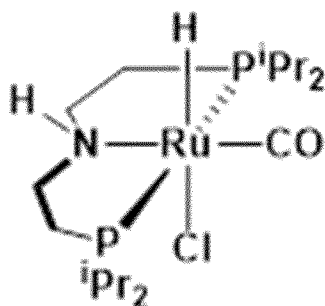
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(IV)

15 The pincer complex according to formula (IV) is herein referred to as also as Ru-MACHO-BH.

In one embodiment the pincer complex is according to formula (V):



(V)

The pincer complex according to formula (V) is herein referred to also as Ru-MACHO^{iPr} and may be further characterized by CAS identifier 1311164-69-8.

In one embodiment, the pincer complex is a catalyst.

5 In one embodiment, the pincer complex is a pre-catalyst

In one embodiment, the pincer complex is a homogeneous catalyst or pre-catalyst.

A “catalyst” as described herein is a substance that increases the rate of a chemical reaction or reactions without itself undergoing any permanent chemical change.

10 A “pre-catalyst” as described herein refers to a chemical compound or entity, which may be added to a reaction mixture in order to prepare a catalyst for the described reaction *in situ* under the described reaction conditions.

15 A “homogeneous catalyst” as described herein refers to a catalyst that is present in the same phase (e.g., liquid or gas) as the reactants during catalysis. By contrast, heterogeneous catalysts refers to catalysts that are in a different phase than the reactants during catalysis e.g., solid catalysts in gas-phase reactions. The same definition can be applied regarding “pre-catalysts”.

Biomass and chemicals produced

20 The present disclosure provides methods for production of chemicals from biomass. As described herein, the term “biomass” refers to organic matter from plant or animals, or their wastes, used as feedstock to obtain products. Examples of biomass include “cellulosic biomass”, “lignocellulosic biomass”, “starchy biomass”, “chitin-containing biomass” or mixtures of these.

25 The terms “cellulosic biomass” refers to biomass comprising cellulose. The term “lignocellulosic biomass” refers to biomass comprising cellulose (or hemicellulose) in combination with lignin. Examples of cellulosic and/or lignocellulosic matter include materials such as paper, paper products, paper waste, wood, particle board, sawdust, agricultural waste, sewage, silage, grasses, rice husk, bagasse, cotton, jute, hemp, flax,
30 bamboo, sisal, abaca, straw, corn cobs, corn stover, switchgrass, miscanthus, alfalfa, hay, coconut hair, cotton, cassava, coffee beans, coffee grounds, shells of nuts such as

walnut, almonds or pine nuts, fruit and vegetable peels or mixtures of these, such as peels of potato, banana, cucumber, carrot, and pineapple.

5 The term “starchy biomass” refers to biomass comprising starch. Examples of starchy biomass include materials comprising amylose and/or amylopectin, for example wheat, potatoes, maize, de-hulled rice grains or cassava as well as flours derived from these materials.

10 The term “chitin-containing biomass” refers to biomass containing chitin. Chitin is a polymer comprising N-acetylglucosamine units. Examples of chitin-containing biomass include the exoskeletons of arthropods such as crustaceans and insects, preferably from shrimp shells.

In one embodiment, the biomass is selected from cellulosic biomass, starchy biomass and chitin-containing biomass. In one embodiment, the biomass is agricultural biomass.

In one embodiment, the biomass is cellulosic biomass.

15 In one embodiment, the biomass is lignocellulosic biomass, such as wood, or sawdust, such as beech wood sawdust; or straw, preferably wheat straw; such as bamboo, such as poplar, such as rice husk or coffee grounds.

In one embodiment, the biomass is starchy biomass, such as flour or mixture of flours derived from materials including wheat, rye, rice, potato, maize or cassava.

20 In one embodiment, the biomass is starchy biomass, such as flour or de-hulled rice grains, for example potato flour.

In one embodiment, the biomass in step a) is not chemically treated before step b).

25 The present disclosure provides methods for production of chemicals from biomass-derived materials. Biomass-derived materials are chemicals obtained from raw biomass. Biomass-derived materials include for example, cellulose, hemicellulose, xylan, xylose, amylose, amylopectin, dextrans, disaccharides, starch oligosaccharides, C6 monosaccharides, C5 monosaccharides, hydroxymethylfurfural (HMF), furfural, levulinic acid, and mixtures thereof.

30 Thus, in one embodiment the biomass-derived material is selected from the group consisting of: cellulose, hemicellulose, xylan, xylose, amylose, amylopectin, dextrans, disaccharides, starch oligosaccharides, C6 monosaccharides, C5 monosaccharides, hydroxymethylfurfural (HMF), furfural, levulinic acid, and mixtures thereof.

In one embodiment, the biomass-derived material is cellulose.

In one embodiment, the biomass-derived material is hemicellulose.

In one embodiment, the biomass-derived material is xylan.

5 In one embodiment, the biomass-derived material is starch. In one embodiment, the biomass-derived material is amylose. In one embodiment, the biomass-derived material is amylopectin.

10 The present disclosure provides methods for production chemicals from biomass or a biomass-derived material as described herein. In one embodiment, the produced chemical is selected from the group consisting of: γ -valerolactone (GVL), levulinic acid, 1,4-pentanediol, formic acid, methanol, sorbitol, humins, 1-hydroxyhexane-2,5-dione, alkyl levulinates, furfuryl alcohol, lactic acid and acetic acid.

In one embodiment, the produced chemical is GVL.

15 Both cellulose and hemicellulose, which in total make up approximately 75-85 wt% of wood content, are potential substrates for producing GVL. Without wishing to be bound by theory, the present inventors believe GVL production from lignocellulosic feedstock can be divided into two specific multistep cascade processes. In the first path, hemicellulose is first hydrolyzed to xylose and dehydrated to form furfural, both steps mediated by acid. A subsequent hydrogenation leads to furfuryl alcohol, which is then
20 rehydrated by acid to levulinic acid (LA). Finally, a hydrogenation followed by cyclization leads to GVL. In the second path, acid mediates the hydrolysis of cellulose to glucose followed by the isomerization to fructose, dehydration to HMF, and then rehydration to LA. LA is then converted to GVL in the same way as in the 'hemicellulose pathway'. However, these reaction pathways come with several pitfalls. For example, in acidic
25 medium xylose or glucose can undergo retro-aldol condensation forming dihydroxyacetone and lactic acid. Alternatively, they can be hydrogenated to xylitol or sorbitol, respectively. Furthermore, the formation of insoluble humins from furan derivatives with the use of excess acid is favored significantly. In addition, formic acid formed in the reaction medium can undergo decomposition into CO₂ and H₂ or CO and
30 H₂O. Hydrogenation of formic acid can also produce MeOH in the reaction medium. The final product obtained may therefore be altered depending on the specific reaction conditions such as temperature and time.

In one embodiment, wherein the produced chemical is 1,4-pentanediol.

In one embodiment, wherein the produced chemical is levulinic acid.

In one embodiment, wherein the produced chemical is sorbitol.

5

In one embodiment, wherein the produced chemical is methanol.

Method to produce a chemical from biomass

10 In one embodiment of the method disclosed herein, step b) is performed in the presence of a solvent. In one embodiment, the solvent is an aqueous solution. In one embodiment, the solvent comprises an alcohol miscible with water. In one embodiment, the alcohol is selected from the group consisting of methanol, ethanol, isopropanol, glycol, glycerol, 2-butanol, 1,3-butanediol, 1,4-butanediol and 2,3-butanediol.

15 In one embodiment, the solvent is a mixture comprising one or more from the group consisting of: GVL, 1,4-dioxane, γ -butyrolactone, DMSO, butanone and dihydroxyacetone.

In one embodiment, the solvent is an aqueous solution. In one embodiment, the solvent is water.

20 In one embodiment of the method disclosed herein, step b) is performed in the presence of an acid. In one embodiment, the acid is an inorganic acid. In one embodiment, the acid is selected from the group consisting of: phosphoric acid, hydrochloric acid, sulphuric acid, trifluoromethanesulfonic acid and nitric acid.

In one embodiment, the acid is phosphoric acid or a derivatized phosphoric acid.

25 In one embodiment, the acid is an organic acid. In one embodiment, the acid is selected from the group consisting of: formic acid, trifluoroacetic acid, fumaric acid, oxalic acid, maleic acid and acetic acid.

30 In one embodiment, the acid is present in a concentration between 0.5 and 15 molar, for example between 0.5 and 1 molar, for example between 1 and 2 molar, for example between 2 and 3 molar, for example between 3 and 4 molar, for example between 4 and 5 molar, for example between 5 and 6 molar, for example between 6 and 7 molar, for example between 7 and 8 molar, for example between 8 and 9 molar, for example between 9 and 10 molar, for example between 10 and 11 molar, for example between 11 and 12 molar, for example between 12 and 13 molar, for example between 13 and 14 molar, for example between 14 and 15 molar.

In one embodiment, the acid is present in a concentration between 4 and 12 molar.

In one embodiment of the method disclosed herein, step b) is performed in the presence of a hydrogen source. In one embodiment, the hydrogen source is selected from hydrogen gas, an alcohol and formic acid.

5 In one embodiment, the hydrogen source is hydrogen gas.

In one embodiment, the pressure of the hydrogen gas is between 1 and 100 bars, such as between 1 and 10 bars, such as between 10 and 20 bars, such as between 20 and 30 bars, such as between 30 and 40 bars, such as between 40 and 50 bars, such as between 50 and 60 bars, such as between 60 and 70 bars, such as between 70 and 80
10 bars, such as between 80 and 90 bars, such as between 90 and 100 bars.

In one embodiment, the pressure of the hydrogen gas is between 1 and 50 bars, such as between 5 and 50 bars, such as between 10 and 50 bars, such as between 15 and 50 bars, such as between 20 and 50 bars.

15 In one embodiment, the hydrogen source is an alcohol. In one embodiment, the hydrogen source is an alcohol selected from the group consisting of: isopropanol, ethanol, methanol, 2-phenylethanol, 2,3-butanediol, 1,3-butanediol, 1,4-butanediol, glycol and glycerol.

In one embodiment of the method disclosed herein, step b) is performed at a temperature between 80 and 250 °C, such as between 80 and 100 °C, such as between 100 and 120
20 °C, such as between 120 and 140 °C, such as between 140 and 160 °C, such as between 160 and 180 °C, such as between 180 and 200 °C, such as between 200 and 220 °C, such as between 220 and 250 °C.

In one embodiment, the hydrogenation is performed between 100 and 150 °C, such as between 110 and 150 °C, such as between 125 and 150 °C.

25 In one embodiment of the method disclosed herein, step b) is performed between 1 hour and 7 days, such as between 1 and 6 hours, such as between 6 and 12 hours, such as between 12 and 24 hours, such as between 24 and 48 hours, such as between 48 and 72 hours, such as between 72 hours and 96 hours, such as between 3 days to 5 days, such as between 5 days and 7 days.

30 In one embodiment, step b) is performed between 6 and 96 hours, such as between 24 and 96 hours.

In one embodiment of the method disclosed herein, the pincer complex is present in an amount between 0.2 and 5 % (w/w), such as between 0.2 and 0.6% (w/w), such as between 0.6 and 1 % (w/w), such as between 1 and 1.5 % (w/w), such as between 1.5 and 2 % (w/w), such as between 2 and 2.5 % (w/w), such as between 2.5 and 3 % (w/w),
5 such as between 3 and 3.5 % (w/w), such as between 3.5 and 4 % (w/w), such as between 4 and 4.5 % (w/w), such as between 4.5 and 5 %.

In one embodiment of the method disclosed herein, step b) is a one-pot process step. The term "one-pot process" as used herein refers to a process wherein successive chemical reaction steps are performed in one reactor or reaction vessel without isolation
10 or purification of intermediates.

In one embodiment, the present disclosure provides a method for production of GVL from biomass, the method comprising:

- a) providing an amount of biomass,
- b) hydrogenating the biomass in the presence of a pincer complex, an aqueous
15 solution, an acid and a hydrogen source at a temperature between 100 and 150 °C, and
- c) isolating the produced GVL.

In one embodiment, the present disclosure provides a method for production of GVL from biomass, the method comprising:

- a) providing an amount of biomass,
- b) hydrogenating the biomass in the presence of a pincer complex according to
20 formula (IV) in an amount between 0.2 and 5 % (w/w), an aqueous solution, phosphoric acid in an amount between 0.5 and 15 molar and hydrogen gas at a pressure between 1 and 100 bars at a temperature between 100 and 150 °C, and
- 25 c) isolating the produce GVL.

In one embodiment, the present disclosure provides a method for production of GVL from biomass, the method consisting of:

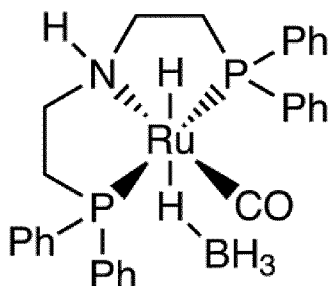
- a) providing an amount of biomass,
- b) hydrogenating the biomass in the presence of a pincer complex according to
30 formula (IV) in an amount between 0.2 and 5 % (w/w), an aqueous solution, phosphoric acid in an amount between 0.5 and 15 molar and hydrogen gas at a pressure between 1 and 100 bars at a temperature between 100 and 150 °C, and
- c) isolating the produce GVL.

A system

In one aspect, the present disclosure provides a system comprising:

- 5
- a) a sealable reactor comprising an amount of biomass or biomass-derived material, a pincer complex, an acid and an aqueous solvent;
 - b) a hydrogen source, and
 - c) a heat source.

In one embodiment, the system comprises a pincer complex according to formula (IV):



10

(IV)

In one embodiment, the biomass is cellulosic biomass.

In one embodiment, the heat source is capable of heating the reactor to 80 to 250 °C.

15

In one embodiment, the hydrogen source can provide a pressure of hydrogen between 1 and 100 bars. Consequently, in one embodiment, the seal of the sealable reactor can withstand a pressure of at least 1 bar of pressure without breaking the seal, such as at least 20 bars, such as at least 30 bars, such as at least 50 bars, such as at least 75 bars, such as at least 100 bars.

In one embodiment, the reactor is an acid-resistant reactor.

20

ExamplesExample 1: Catalytic hydrogenation of cellulose*Aim*

25

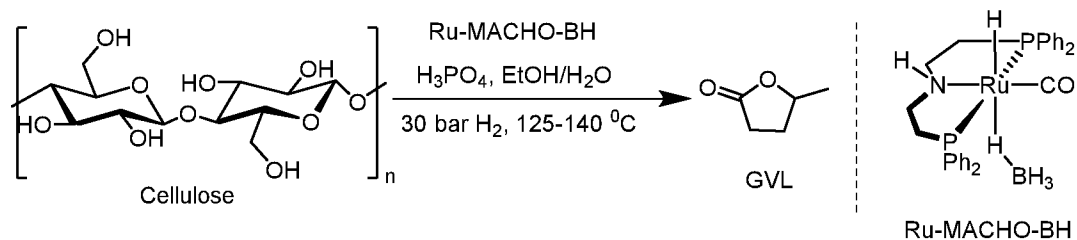
One-pot direct conversion of cellulose to GVL using the combination of Ru-MACHO-BH and H₃PO₄.

Materials and Methods

The following chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Ru-MACHO-BH (Strem Chemicals), 85% w/w H₃PO₄ (Merck), Microcrystalline cellulose (Sigma), Xylan from corn core (Sigma),
5 Xylan from beech wood (Carl Roth). H₂ gas (H₂O ≤ 3 ppm; O₂ ≤ 2 ppm) was purchased from Air Liquide. The reactor is a sealable steel high-pressure reactor capable of handling a pressure of at least 100 bar. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091J-413 HP-5, 5% Phenyl methyl
10 siloxane capillary column using 1,4-dioxane as the internal standard.

For a typical hydrogenation experiment the conditions are as follows unless specified otherwise. In a glove box, cellulose (118 mg) and Ru-MACHO-BH (1.9 mg) were weighed in a glass vial equipped with a magnetic stir bar and sealed with a Teflon-lined cap. Upon bringing the glass vial outside the glove box, the solid material was dissolved in 1.00 mL
15 of solvent (H₂O or 1:1 v/v EtOH/H₂O (0.50 mL each)) followed by 0.46 mL of 85% w/w H₃PO₄ which corresponds to 7.5 M of total H₃PO₄ concentration. Subsequently, the vial was placed in the reactor with a needle placed through the rubber stopper of the vial for the gas flow. The high-pressure reactor was sealed and flushed with argon and/or hydrogen (three times) and finally hydrogen pressure (30 bar) was loaded into the high-
20 pressure reactor. The reactor was then slowly heated to 140 °C under stirring (800 rpm) and kept at the 140 °C for 96 hours. The parameters such as acid concentration, amount of cellulose, solvent, temperature, and time of reaction were modified accordingly to the entries in Table 1 below. After the reaction was finished, the reactor was cooled to room temperature (approximately 20-25 °C) before the gas was released and the sample was
25 prepared for GC analysis. The liquid sample was prepared for GC analysis by adding 100 µl of 1,4-dioxane (internal standard) followed by dilution of the mixture with 3.75 mL of dichloromethane (DCM). The yield of GVL in the mixture is calculated by using calibration curve. To generate a calibration curve, standard GVL samples of various known concentrations along with 1,4-dioxane (100 µl) with total volume made up to 10
30 mL with DCM and are injected into the GC.

Results

**Table 1:** Direct conversion of cellulose to GVL.

| Entry | Cellulose (M) | H ₃ PO ₄ [M] | Solvent | P/T [bar]/[°C] | Time [h] | GVL yield ^a [%] |
|-----------------|---------------|------------------------------------|------------------------------------|----------------|----------|----------------------------|
| 1 | 0.6 | 5.7 | EtOH/H ₂ O ^b | 30/125 | 48 | 7 |
| 2 | 0.6 | 7.5 | EtOH/H ₂ O ^b | 30/125 | 48 | 12 |
| 3 | 0.6 | 5.7 | H ₂ O | 30/125 | 48 | 20 |
| 4 | 0.6 | 5.7 | H ₂ O | 30/125 | 96 | 24 |
| 5 | 0.6 | 7.5 | H ₂ O | 30/125 | 96 | 30 |
| 6 | 0.6 | 5.7 | H ₂ O | 30/140 | 96 | 33 |
| 7 | 0.6 | 7.5 | H ₂ O | 30/140 | 48 | 30 |
| 8 | 0.6 | 7.5 | H ₂ O | 30/140 | 96 | 47 |
| 9 | 0.1 | 5.7 | H ₂ O | 30/140 | 48 | 37 |
| 10 | 0.1 | 7.5 | H ₂ O | 30/140 | 96 | 50 |
| 11 ^c | 0.5 | 7.5 | H ₂ O | 30/140 | 72 | 43 |

^a Determined by GC-FID using 1,4-dioxane as the internal standard. Catalyst loading and yield are relative to moles of glucose monomers contained in cellulose. ^b 1:1 v/v EtOH/H₂O (1 mL). ^c H₂O (15 mL)

Conclusion

- 5 The present example demonstrates an efficient route for the direct conversion of a biomass component (cellulose) to GVL under mild reaction conditions. Using low loadings of Ru-MACHO-BH in presence of H₃PO₄ allows the unprecedented transformation of cellulose to GVL in as much as 50% yield after 96 hours at 140 °C.

10 Example 2: Catalytic hydrogenation of hemicellulose

Aim

One-pot direct conversion of hemicellulose (xylan) to GVL using the combination of Ru-MACHO-BH and H₃PO₄.

Materials and Methods

The following chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Ru-MACHO-BH (Strem Chemicals), 85% w/w H₃PO₄ (Sigma), Xylan from corn core (Sigma), Xylan from beech wood (Carl Roth).
5 H₂ gas (H₂O ≤ 3 ppm; O₂ ≤ 2 ppm) was purchased from Air Liquide. The reactor is a sealable steel high-pressure reactor capable of handling a pressure of at least 100 bar. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091J-413 HP-5 5% Phenyl methyl siloxane capillary column using 1,4-dioxane as the internal standard.
10

For a typical hydrogenation experiment the conditions are as follows unless specified otherwise. In a glove box, for example, hemicellulose (xylan (99 mg)) and Ru-MACHO-BH (1.9 mg) were weighed in a glass vial equipped with a magnetic stir bar and sealed with a Teflon-lined cap. Upon bringing the glass vial outside the glove box, dissolved
15 1.00 mL of solvent (H₂O or EtOH or 1:1 v/v EtOH/H₂O (0.50 mL each)) followed by 0.46 mL of 85% w/w H₃PO₄ which corresponds to 7.5 M of total H₃PO₄ concentration. Subsequently, the vial was placed in the reactor with a needle placed through the rubber stopper of the vial for the gas flow. The high-pressure reactor was sealed and flushed with argon and/or hydrogen (three times) and finally hydrogen pressure (30 bar) was
20 loaded into the high-pressure reactor. The reactor was then slowly heated to the desired temperature under stirring (800 rpm) and held at the desired temperature (125 °C or 140 °C) for 48 hours. The parameters such as acid concentration, temperature, and solvent were modified according to the entries in Table 2 below. After the reaction was finished, the reactor was cooled to room temperature before the gas was released and the sample was prepared for GC analysis. The liquid sample was prepared by adding 100 µl of 1,4-dioxane (internal standard) then the mixture was diluted with 3.75 mL of DCM. The yield of GVL in the mixture is calculated by using calibration curve. To generate a calibration
25 curve, standard GVL samples of different known concentration along with 1,4-dioxane (100 µl) with total volume made up to 10 mL with DCM and are injected into the GC.

30

Results

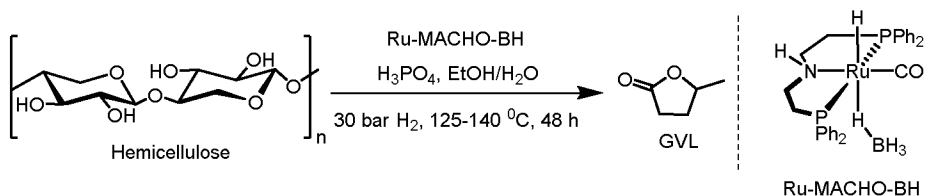


Table 2: Direct conversion of hemicellulose to GVL.

| Entry | Xylan (M) | H ₃ PO ₄ [M] | Solvent | P/T [bar]/[°C] | GVL yield ^a [%] |
|-------|------------------|------------------------------------|------------------------------------|----------------|----------------------------|
| 1 | 0.6 ^b | 3.8 | EtOH | 30/125 | 52 |
| 2 | 0.6 ^b | 5.7 | EtOH/H ₂ O ^c | 30/125 | 64 |
| 3 | 0.6 ^d | 5.7 | EtOH/H ₂ O ^c | 30/125 | 28 |
| 4 | 0.6 ^b | 7.5 | EtOH/H ₂ O ^c | 30/125 | 57 |
| 5 | 0.6 ^d | 7.5 | EtOH/H ₂ O ^c | 30/125 | 87 |
| 6 | 0.6 ^b | 5.7 | EtOH/H ₂ O ^c | 30/140 | 33 |
| 7 | 0.6 ^b | 8.4 | EtOH/H ₂ O ^c | 30/140 | 5 |
| 8 | 0.6 ^d | 5.7 | EtOH/H ₂ O ^c | 30/140 | 43 |
| 9 | 0.6 ^b | 7.5 | H ₂ O | 30/125 | 9 |
| 10 | 0.6 ^d | 5.7 | H ₂ O | 30/140 | 13 |
| 11 | 0.6 ^d | 8.4 | H ₂ O | 30/140 | 5 |

Catalyst loading and yield are relative to moles of xylose monomers contained in xylan. ^a Determined by GC-FID using 1,4-dioxane as the internal standard. ^b Corn core xylan. ^c 1:1 v/v EtOH/H₂O (1 mL). ^d Beech wood xylan

Conclusion

The present example demonstrates an efficient route for the direct conversion of a biomass component (hemicellulose) to GVL under mild reaction conditions. Using low loadings of Ru-MACHO-BH in presence of H₃PO₄ allows the unprecedented transformation of hemicellulose (xylan) to GVL in as much as 87% yield after only 48 hours at 125 °C.

10 Example 3: Direct conversion of biomass to GVL

Aim

One-pot direct catalytic conversion of biomass to GVL using the combination of Ru-MACHO-BH and H₃PO₄ under mild and sustainable conditions.

Materials and Methods

The following chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Ru-MACHO-BH (Strem Chemicals), biomass such as sawdust from beech wood (Mink) and wheat straw are dried in oven overnight before use. Potato flour, rice grains, tissue paper, coffee, potatoes and bananas (provision of peels) and shrimp (provision of chitin material), were purchased from conventional supermarkets and dried in vacuum overnight before use. H₂ gas (H₂O ≤ 3 ppm; O₂ ≤ 2 ppm) was purchased from Air Liquide. The reactor is a steel high-pressure reactor. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091J-413 HP-5, 5% Phenyl methyl siloxane capillary column using 1,4-dioxane as the internal standard. The batches for gas analysis, the gas phase was carefully collected in a gas sampling bag and analyzed by MicroGC.

For a typical hydrogenation experiment the standard conditions are as follows unless specified otherwise. In a glove box, biomass, such as sawdust, straw, potato flour, rice grains, or similar (91 mg) and Ru-MACHO-BH (1.6 mg) were weighed in a glass vial equipped with a magnetic stir bar and sealed with a Teflon-lined cap. Upon bringing the glass vial outside the glove box, dissolved 1.00 mL of H₂O followed by 0.70 mL of 85% w/w H₃PO₄ which corresponds to 10.9 M total concentration of H₃PO₄. Subsequently, the vial was placed in the reactor with a needle placed through the rubber stopper of the vial for the gas flow. The high-pressure reactor was sealed and flushed with argon/hydrogen (three times) and finally hydrogen pressure (30 bar) was loaded into the high-pressure reactor. The reactor was then slowly heated to 140 °C under stirring (800 rpm) and held at the 140 °C for 24 hours. The parameters such as acid concentration, reaction time, and solvent were modified according to the entries in Table 3 below. After the reaction was finished, the reactor was cooled to room temperature before the gas was released and the sample was prepared for GC analysis. The liquid sample was prepared by adding 100 µl of 1,4-dioxane (internal standard) then the mixture was diluted with 3.75 mL of DCM. The yield of GVL in the mixture is calculated by using calibration curve. To generate a calibration curve, standard GVL samples of different known concentration along with 1,4-dioxane (100 µl) with total volume made up to 10 mL with DCM and are injected into the GC.

Results

Table 3: Direct conversion of biomass to GVL.

| Biomass | | Entry | H ₃ PO ₄ [M] | Time [h] | GVL yield ^a [wt% (mol%)] |
|--------------------------|------|-----------------|---------------------------------------|-------------|--|
| Beechwood sawdust | | | | | |
| Lignocellulosic content | wt% | 1 | 7.5 | 96 | 15 (33) |
| Hemicellulose | 37 | 2 | 9.3 | 24 | 22 (48) |
| Cellulose | 42 | 3 | 9.3 | 96 | 23 (50) |
| Lignin | 19 | 4 | 9.3 | 168 | 20 (43) |
| | | 5 | 10.1 | 24 | 25 (54) |
| | | 6 | 10.1 | 38 | 21 (46) |
| | | 7 | 10.1 | 96 | 19 (41) |
| | | 8 | 10.9 | 18 | 21 (46) |
| | | 9 | 10.9 | 24 | 26 (57) |
| | | 10 | 10.9 | 96 | 18 (39) |
| | | 11 ^b | 10.9 | 24 | 14 (30) |
| Wheat straw | | | | | |
| Lignocellulosic content | wt% | 12 | 8.4 | 48 | 12 (38) |
| Hemicellulose | 25 | 13 | 9.3 | 24 | 12 (38) |
| Cellulose | 33 | 14 | 10.9 | 24 | 12 (38) |
| Lignin | 17 | 15 | 10.9 | 48 | 18 (56) |
| | | 16 | 10.9 | 72 | 16 (50) |
| | | 17 | 11.8 | 96 | 17 (53) |
| | | 18 ^b | 10.9 | 24 | 11 (34) |
| Rice grains | | | | | |
| Starch content | wt% | 19 | 11.8 | 72 | 16 (30) |
| Amylose | 35 | | | | |
| Amylopectin | 65 | | | | |
| Potato flour | | | | | |
| Starch content | wt% | 20 | 11.8 | 72 | 20 (36) |
| Amylose | 17.8 | | | | |
| Amylopectin | 82.2 | | | | |
| Tissue paper | | | | | |
| Lignocellulosic content | wt% | 21 | 10.9 | 24 | 18 (36-42) |

| | | | | | |
|---------------------------|-------|----|------|----|---------|
| Hemicellulose | 0 | | | | |
| Cellulose | 85-99 | | | | |
| Lignin | 0-15 | | | | |
| Coffee grounds | | | | | |
| Lignocellulosic content | wt% | 22 | 10.9 | 24 | 8 (26) |
| Hemicellulose | 42 | 23 | 10.9 | 48 | 11 (36) |
| Cellulose | 13 | | | | |
| Lignin | 25 | | | | |
| Potato peel | | | | | |
| Lignocellulosic content | wt% | 24 | 10.9 | 48 | 8 (42) |
| Hemicellulose | 7 | 25 | 10.9 | 72 | 10 (52) |
| Cellulose | 8 | | | | |
| Lignin | 33 | | | | |
| Starch | 23 | | | | |
| Banana peel | | | | | |
| Lignocellulosic content | wt% | 26 | 10.9 | 48 | 3 (14) |
| Hemicellulose | 26 | 27 | 10.9 | 96 | 10 (47) |
| Cellulose | 11 | | | | |
| Lignin | 10 | | | | |
| Grass (Miscanthus) | | | | | |
| Lignocellulosic content | wt% | 28 | 10.9 | 48 | 15 (40) |
| Hemicellulose | 44 | | | | |
| Cellulose | 24 | | | | |
| Lignin | 17 | | | | |
| Chitin | | | | | |
| Chitin content | wt% | 29 | 10.9 | 72 | 8 (17) |
| N-acetyl-D-glucomasine | 100 | 30 | 10.9 | 96 | 13 (26) |

Standard reaction condition: Ru-MACHO-BH (1.65 mg, 0.0028 mmol), 85 w/w% H₃PO₄(aq) in H₂O (1 mL) at 140 °C and 30 bar H₂. ^a Determined by GC-FID. Yields are calculated with respect to dry biomass. ^b1:1 v/v alcohol/water mixture (1 mL). For chitin, the yields are determined relative to moles of N-acetyl-D-glucomasine monomers contained in chitin.

Conclusion

The present example demonstrates an efficient route for the direct production of GVL from wide variety of biomass feedstock, including biowaste, under mild and sustainable reaction conditions in good yield. The inventive one-pot direct conversion approach avoids the separation and isolation of intermediates which simplifies the whole process making it viable for industries. The exceptional activity of Ru-MACHO-BH along with a Brønsted acid (H_3PO_4) enabled direct conversion of real biomass, exemplified by at least wheat straw, rice grains, potato flour, sawdust, banana and potato peels, tissue paper, grass, shrimp shells and coffee grounds into value-chemicals such as GVL with up to 26 wt% yield at 140 °C under 30 bar H_2 .

Example 4: Direct conversion of biomass to other value-added chemicals

Aim

One-pot direct catalytic conversion of biomass to non-GVL value added chemicals, such as sorbitol and/or 1,4-pentanediol using the combination of Ru-MACHO^{iPr} and H_3PO_4 under mild and sustainable conditions.

Materials and Methods

The following chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Ru-MACHO-BH (Strem Chemicals), Ru-MACHO^{iPr} (Strem Chemicals), 85% w/w H_3PO_4 (Merck), Microcrystalline cellulose (Sigma). H_2 gas ($\text{H}_2\text{O} \leq 3$ ppm; $\text{O}_2 \leq 2$ ppm) was purchased from Air Liquide. The reactor is a sealable steel high-pressure reactor capable of handling a pressure of at least 100 bar. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091J-413 HP-5, 5% Phenyl methyl siloxane capillary column using 1,4-dioxane as the internal standard.

For a typical hydrogenation experiment the conditions are as follows unless specified otherwise. In a glove box, cellulose (0.1 M) and Ru-MACHO-BH (0.5 mol%) were weighed in a glass vial equipped with a magnetic stir bar and sealed with a Teflon-lined cap. Upon bringing the glass vial outside the glove box, the solid material was dissolved in 1.00 mL of 1:1 v/v EtOH/ H_2O (0.50 mL each) followed by 85% w/w H_3PO_4 to arrive at a total H_3PO_4 concentration corresponding to 5.7 M. Subsequently, the vial was placed in the reactor with a needle placed through the rubber stopper of the vial for the gas flow.

The high-pressure reactor was sealed and flushed with argon and/or hydrogen (three times) and finally hydrogen pressure (30 bar) was loaded into the high-pressure reactor. The reactor was then slowly heated to 125 °C under stirring (800 rpm) and kept at the 125 °C for 48 hours. The parameters such as catalyst, substrate, acid concentration, substrate amount, solvent, temperature, and time of reaction may be modified as done in the examples above. After the reaction was finished, the reactor was cooled to room temperature (approximately 20-25 °C) before the gas was released and the sample was prepared for GC analysis. The liquid sample was prepared for GC analysis by adding 100 µl of 1,4-dioxane (internal standard) followed by dilution of the mixture with 3.75 mL of dichloromethane (DCM). In addition to the amounts, GC analysis allows to determine the complete spectrum of chemicals produced by the catalytic conversion to identify suitable value-added chemicals for isolation and further development. In the present example, in particular sorbitol and 1,4-pentanediol were detected in significant yields as part of the product mixture.

15

| Entry | Substrate | Substrate amount [M] | Catalyst | P/T [bar]/[°C] | Time [h] | Product(s) detected in significant amounts ^a |
|-------|-----------|----------------------|-------------------------|----------------|----------|---|
| 1 | Cellulose | 0.1 | Ru-MACHO-BH | 30/125 | 48 | Sorbitol and 1,4-pentanediol |
| 2 | Cellulose | 0.1 | Ru-MACHO ^{iPr} | 30/125 | 48 | 1,4-pentanediol |
| 3 | Glucose | 0.1 | Ru-MACHO-BH | 30/125 | 48 | Sorbitol and 1,4-pentanediol |

^a Detected using GC-FID using 1,4-dioxane as the internal standard.

Conclusion

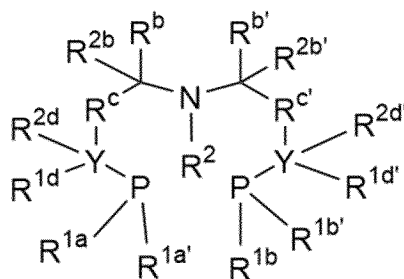
The present example demonstrates that using either of the catalysts Ru-MACHO-BH or Ru-MACHO^{iPr} it is possible to convert biomass such as cellulose or glucose into non-GVL value-added chemicals, specifically sorbitol and/or 1,4-pentanediol are produced in significant amounts which can be detected using GC methods known to those skilled in the art of chemical analysis, including GC-FID. The amounts have presently not been quantified due to limitations in the analysis using available equipment.

20

Items

- 5 1. A method for production of a chemical derived from biomass or derived from a biomass-derived material, the method comprising:
 - a) providing an amount of biomass or biomass-derived material,
 - b) hydrogenating said biomass or biomass-derived material in the presence of a pincer complex, and
 - c) isolating said produced chemical.
- 10 2. The method according to item 1, wherein the pincer complex comprises a metal.
3. The method according to item 2, wherein the metal is a transition metal.
- 15 4. The method according to item 2, wherein the metal is selected from the group consisting of: ruthenium, iron, iridium, manganese, rhodium, cobalt, platinum, palladium, nickel, osmium, rhenium, aluminum, gold, chromium and molybdenum.
- 20 5. The method according to any one of items 2 to 4, wherein the metal is selected from the group consisting of ruthenium, iron, manganese and iridium.
6. The method according to any one of items 2 to 5, wherein the metal is ruthenium.
- 25 7. The method according to any one of the preceding items, wherein the pincer complex comprises at least one tridentate organic ligand.
8. The method according to item 7, wherein the tridentate ligand comprises at least one heteroatom selected from the group P, N, As, O, Si, Se, Ge, S and B.
- 30 9. The method according to any one of items 7 or 8, wherein the tridentate ligand comprises one heteroatom selected from P, N, As and O.
- 35 10. The method according to any one of items 7 to 8, wherein the tridentate ligand is coordinated to the metal through three atoms, each individually selected from P, N, As, O, Si, Se, Ge, S and B.

11. The method according to any one of items 7 to 10, wherein the tridentate ligand is coordinated to the metal through three atoms, each individually selected from P, N, C and O.
12. The method according to any one of items 7 to 11, wherein the tridentate ligand is coordinated to the metal through three atoms, each individually selected from P, N, and C.
13. The method according to any one of items 7 to 12, wherein the tridentate ligand coordinates to the metal through any one of the following combinations of three atoms: two P atoms and one N atom, two P atoms and one O atom, two S atoms and one N atom, two N atoms and one P atom, three N atoms, and two P atoms and one C atom.
14. The method according to any one of items 7 to 13, wherein herein the tridentate ligand coordinates to the metal through two P atoms and one N atom.
15. The method according to any one of items 7 to 14, wherein the tridentate ligand is according to formula (I):



(I)

wherein

R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are each independently selected from the group consisting of H, C_1 - C_6 alkyl, isopropyl, *tert*-butyl, a C_3 - C_7 cycloalkyl, a C_3 - C_7 heterocycloalkyl, phenyl and C_5 - C_{10} aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, hydroxyl, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl;

R^2 is absent or is selected from the group consisting of H, C_1 - C_6 alkyl, isopropyl, phenyl and C_5 - C_{10} aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, hydroxyl, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl;

R^c and $R^{c'}$ are each independently selected from a single bond or a double bond;

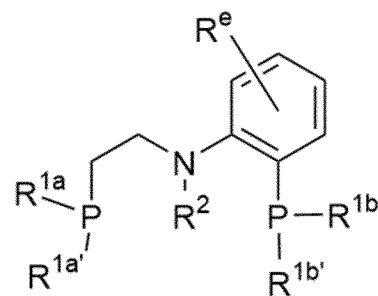
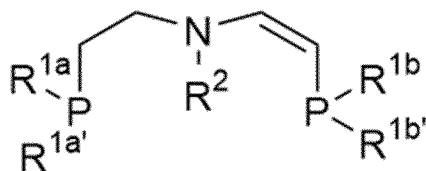
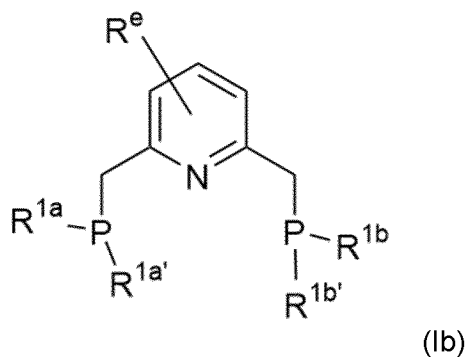
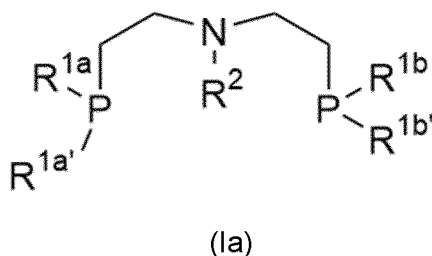
Y is an atom selected from C, O, and N;

R^b , R^{2b} , $R^{b'}$ and $R^{2b'}$ are each independently absent or selected from H, C₁-C₆ alkyl, C₃-C₇ cycloalkyl, phenyl, and C₅-C₁₀ aryl, each of which may optionally be

5 substituted by one or more selected from halogen, cyano, amino, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl or R^b and $R^{b'}$ may come together to form a C₃-C₆ heterocycloalkyl, a C₅-C₁₀ heteroaryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl; and

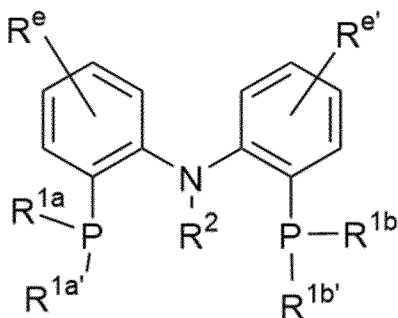
10 R^{1d} , R^{2d} , $R^{1d'}$ and $R^{2d'}$ are each independently absent or selected from a H, C₁-C₆ alkyl, C₃-C₇ cycloalkyl, phenyl and C₅-C₁₀ aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl or R^d and R^b may come together and/or $R^{d'}$ and $R^{b'}$ may come together to form a C₅-C₇ cycloalkyl or a C₅-C₆ aryl, each of
15 which may optionally be substituted by one or more selected from halogen, cyano, amino, hydroxyl, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl.

16. The method according to any one of items 14 to 15, wherein the tridentate ligand is selected from the group consisting of formula (Ia), formula (Ib), formula (Ic),
20 formula (Id) and formula (Ie):



(lc)

(ld)



(le)

wherein

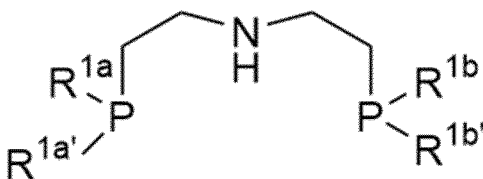
R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are each independently selected from the group consisting of C_1 - C_6 alkyl, isopropyl, *tert*-butyl, a C_3 - C_7 cycloalkyl, a C_3 - C_7 heterocycloalkyl, phenyl and C_5 - C_{10} aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl;

R^2 is selected from the group consisting of H, C_1 - C_6 alkyl, isopropyl, phenyl and C_5 - C_{10} aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, hydroxyl, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl; and

R^e and $R^{e'}$ are each independently selected from the group consisting of H, halogen, cyano, amino, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl.

17. The method according to any one of items 15 to 16, wherein R^2 is H.

18. The method according to any one of items 7 to 17, wherein the tridentate ligand is according to formula (II):



(II)

20

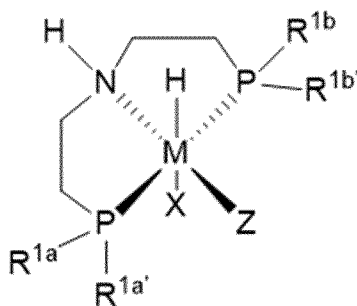
wherein

R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are each independently selected from the group consisting of C_1 - C_6 alkyl, isopropyl, *tert*-butyl, a C_3 - C_7 cycloalkyl, a C_3 - C_7 heterocycloalkyl, phenyl and C_5 - C_{10} aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl.

19. The method according to any one of items 7 to 0, wherein R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are phenyl.

20. The method according to any one of items 7 to 0, wherein R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are isopropyl.

21. The method according to any one of the preceding items, wherein the pincer complex is according to formula (III):



(III)

wherein,

M is a metal selected from the group consisting of ruthenium, iron, iridium, manganese, rhodium, cobalt, platinum, palladium, nickel, osmium, rhenium, aluminium, gold, chromium and molybdenum;

R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are each independently selected from the group consisting of C_1 - C_6 alkyl, isopropyl, *tert*-butyl, a C_3 - C_7 cycloalkyl, a C_3 - C_7 heterocycloalkyl, phenyl and C_5 - C_{10} aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl;

Z is selected from CO, $P(R^{III})_3$, $As(R^{III})_3$, NO and N_2 ; and

X is selected from the group consisting of a hydridoborate, such as tetrahydridoborate (BH_4^-), a halide, such as fluoride, chloride, bromide or iodide,

and H,

wherein R^{III} is each individually selected from C₁-C₆ alkyl, isopropyl, phenyl and C₅-C₁₀ aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl.

5

22. The method according to item 0, wherein M is selected from the group consisting of ruthenium, iron, iridium and manganese.

23. The method any one of items 0 or 0, wherein M is ruthenium.

10

24. The method according any one of items 0 to 0, wherein R^{1a}, R^{1a'}, R^{1b} and R^{1b'} are phenyl.

25. The method according any one of items 0 to 0, wherein R^{1a}, R^{1a'}, R^{1b} and R^{1b'} are isopropyl.

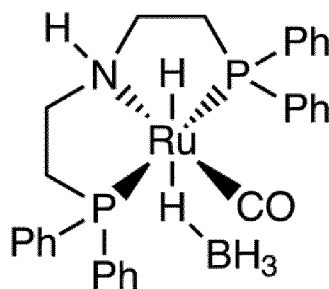
15

26. The method according any one of items 0 or 0, wherein Z is CO.

27. The method according any one of items 0 to 0, wherein X is tetrahydridoborate (BH₄⁻).

20

28. The method according to any one of the preceding items, wherein the pincer complex is according to formula (IV):



25

(IV)

29. The method according to any one of the preceding items wherein the pincer complex is a catalyst.

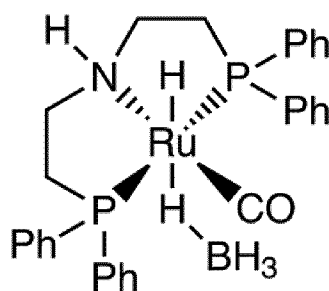
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30. The method according to item 29, wherein the catalyst is a homogeneous catalyst.
31. The method according to any one of the preceding items, wherein the biomass is selected from one or more from the group consisting of: cellulosic biomass, starchy biomass and chitin-containing biomass.
32. The method according to any one of the preceding items, wherein the biomass is agricultural biomass.
33. The method according to any one of items 31 to 32, wherein the biomass is cellulosic biomass.
34. The method according to any one of items 31 to 33, wherein the biomass is lignocellulosic biomass, such as wood, sawdust, such as beechwood sawdust; or straw, such as wheat straw; such as bamboo, such as poplar, such as rice husk, such as coffee grounds or any combination thereof.
35. The method according to any one of items 31 or **Fejl! Henvisningskilde ikke fundet.**, wherein the biomass is starchy biomass, such as flour or de-hulled rice grains, for example potato, wheat, corn or rice flour or a combination thereof.
36. The method according to any one of the preceding items, wherein the biomass in step a) is not chemically treated before step b).
37. The method according to any one of the preceding items, wherein the biomass-derived material is selected from the group consisting of: cellulose, hemicellulose, xylan, xylose, amylose, amylopectin, dextrans, disaccharides, starch oligosaccharides, C6 monosaccharides, C5 monosaccharides, hydroxymethylfurfural (HMF), furfural, levulinic acid, and mixtures thereof.
38. The method according to item 37, wherein the biomass-derived material is cellulose.
39. The method according to item 37, wherein the biomass-derived material is hemicellulose.
40. The method according to item 37, wherein the biomass-derived material is xylan.

41. The method according to item 37, wherein the biomass-derived material is starch.
42. The method according to any one of the preceding items, wherein the produced chemical is selected from the group consisting of: γ -valerolactone (GVL), levulinic acid, 1,4-pentanediol, formic acid, methanol, sorbitol, humins, 1-hydroxyhexane-2,5-dione, alkyl levulinates, furfuryl alcohol, lactic acid and acetic acid.
43. The method according to item 42, wherein the produced chemical is GVL.
44. The method according to item 42, wherein the produced chemical is 1,4-pentanediol.
45. The method according to item 42, wherein the produced chemical is levulinic acid.
46. The method according to item 42, wherein the produced chemical is sorbitol.
47. The method according to item 42, wherein the produced chemical is methanol.
48. The method according to any one of the preceding items, wherein step b) is performed in the presence of a solvent.
49. The method according to item 48, wherein the solvent is an aqueous solution.
50. The method according to any one of items 48 to 49, wherein the solvent comprises an alcohol miscible with water.
51. The method according to item 50, wherein the alcohol selected from the group consisting of methanol, ethanol, isopropanol, glycol, glycerol, 2-butanol, 1,3-butanediol, 1,4-butanediol and 2,3-butanediol.
52. The method according to any one of items 48, wherein the solvent is a mixture comprising one or more selected from the group consisting of: GVL, 1,4-dioxane, γ -butyrolactone, DMSO, butanone and dihydroxyacetone.
53. The method according to any one of items 48 to 49, wherein the solvent is water.
54. The method according to any one of the preceding items, wherein step b) is performed in the presence of an acid.

55. The method according to item 54, wherein step b) is performed in the presence of a Brønsted acid.
- 5 56. The method according to any one of items 54 to 55, wherein the acid is an inorganic acid.
57. The method according any one of items 54 or 56, wherein the acid is selected from the group consisting of phosphoric acid, hydrochloric acid, sulphuric acid, triflic acid, trifluoromethanesulfonic acid, and nitric acid.
- 10
58. The method according to any one of items 54 to 57, wherein the acid is phosphoric acid or a derivatized phosphoric acid.
- 15
59. The method according to item 54, wherein the acid is an organic acid.
60. The method according to any one of items 54 or 59, wherein the acid is selected from the group consisting of: formic acid, trifluoroacetic acid, fumaric acid, oxalic acid, maleic acid and acetic acid.
- 20
61. The method according to any one of items 54 to 60, wherein the acid is present in a concentration between 0.5 and 15 molar, preferably in a concentration between 4 and 12 molar.
- 25
62. The method according to any one of the preceding items, wherein the step b) is performed in the presence of a hydrogen source.
63. The method according to item 62, wherein the hydrogen source is selected from hydrogen gas, an alcohol and formic acid.
- 30
64. The method according to any one of items 62 to 63, wherein the hydrogen source is hydrogen gas.
65. The method according to item 64, wherein the hydrogen gas pressure is between 1 and 100 bars, such as between 1 and 50 bars, such as between 5 and 50 bars.
- 35
66. The method according to item 62, wherein the hydrogen source is an alcohol.

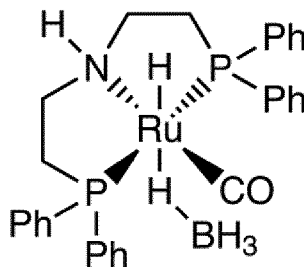
67. The method according to item 63, wherein the alcohol is selected from isopropanol, ethanol, methanol, 2-phenylethanol, 2,3-butanediol, 1,3-butanediol, 1,4-butanediol, glycol and glycerol.
- 5 68. The method according to any one of the preceding items, wherein step b) is performed at a temperature between 80 and 250 °C, such as between 100 and 150 °C.
69. The method according to any one of the preceding items, wherein step b) is
10 performed between 1 hour and 7 days, such as between 6 and 96 hours.
70. The method according to any one of the preceding items, wherein step b) is a one-pot process step.
- 15 71. The method according to any one of the preceding items, wherein the pincer complex is present in an amount between 0.2 and 5% (w/w).
72. The method according to any one of items 1 to 30, wherein the produced chemical is GVL and step b) is performed in the presence of an aqueous solution, an acid and
20 a hydrogen source.
73. The method according to item 72, wherein the pincer complex comprises ruthenium.
- 25 74. The method according to any one of items 72 to 73, wherein the pincer complex is according to formula (IV):



(IV)

- 30 75. The method according to any one of items 72 to 74, wherein the biomass is lignocellulosic biomass.

76. The method according to any one of items 72 to 74, wherein the biomass is starch-containing biomass.
- 5 77. The method according to any one of items 72 to 76, wherein step b) is a one-pot process step.
78. The method according to any one of items 72 to 77, wherein step b) is performed at a temperature between 100 and 150 °C.
- 10 79. A system comprising:
- a) a sealable reactor comprising an amount of biomass or biomass-derived material, a pincer complex, a Brønsted acid and an aqueous solvent;
 - 15 b) a hydrogen source, and
 - c) a heat source.
80. The system according to item 13, wherein the pincer complex is according to formula (IV):



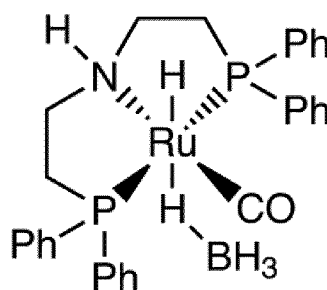
(IV)

- 20
81. The system according to any one of items 13 to 80, wherein the biomass is cellulosic biomass.
82. The system according to any one of items 13 to 81, wherein the heat source is capable of heating the reactor to 80 to 250 °C.
- 25 83. The system according to any one of items 13 to 82, wherein the hydrogen source can provide a pressure of hydrogen between 1 and 100 bars.
84. The system according to any one of items 13 to 83, wherein the reactor is an acid-resistant reactor.

Items 2

1. A method for production of a chemical derived from biomass or derived from a biomass-derived material, the method comprising:

- 5 a) providing an amount of biomass or biomass-derived material,
- b) hydrogenating said biomass or biomass-derived material in the presence of an aqueous solution, a Brønsted acid, a hydrogen source and a pincer complex according to formula (IV):

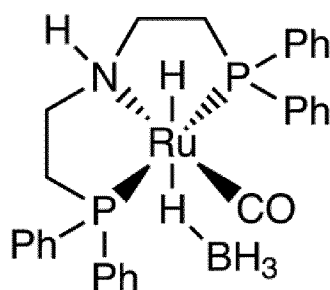


10 (IV)

and,

- c) isolating the produced chemical.
2. The method according to item 1, wherein the produced chemical is γ -valerolactone (GVL).
- 15 3. The method according to any one of items 1 to 2, wherein the biomass is selected from one or more from the group consisting of cellulosic biomass and starchy biomass.
4. The method according to item 3, wherein the biomass is selected from one or more of the group consisting of: wood, sawdust, straw, rice husks, de-hulled rice grains, fruit and vegetable waste, such as peels; coffee waste, such as beans and grounds;
- 20 flour, and chitin-containing biomass, such as shells of crustaceans.
5. The method according to any one of the preceding items, wherein the biomass-derived material is selected from the group consisting of: cellulose, hemicellulose, xylan, xylose, amylose, amylopectin, dextrans, disaccharides, starch oligosaccharides, C6 monosaccharides, C5 monosaccharides,
- 25 hydroxymethylfurfural (HMF), furfural, levulinic acid, and mixtures thereof.

6. The method according to any one of items of the preceding items, wherein the hydrogen source is hydrogen gas.
7. The method according to item 6, wherein the hydrogen pressure is between 1 and 100 bars.
- 5 8. The method according to any one of the preceding items, wherein the Brønsted acid is phosphoric acid.
9. The method according to item 8, wherein the phosphoric acid is present in a concentration between 4 and 12 molar.
- 10 10. The method according to any one of the preceding items, wherein the pincer complex is present in an amount between 0.2 and 5% (w/w).
11. The method according to any one of the preceding items, wherein the temperature is between 100 and 150 °C.
12. The method according to any one of the preceding items, wherein step b) is a one-pot process step.
- 15 13. A system comprising:
- a) a sealable reactor comprising an amount of biomass or biomass-derived material, a Brønsted acid, an aqueous solvent and a pincer complex according to formula (IV):



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(IV)

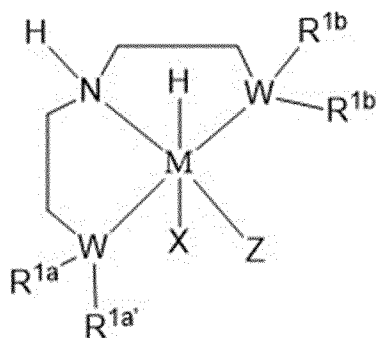
- b) a hydrogen source, and
- c) a heat source.
14. The system according to item 13, wherein the biomass is cellulosic biomass.

15. The system according to any one of items 13 to 14, wherein the reactor is an acid-resistant reactor.

Claims

1. A method for production of a chemical derived from biomass or derived from a biomass-derived material, the chemical being selected from the group consisting of γ -valerolactone (GVL), levulinic acid, 1,4-pentanediol, formic acid, methanol, sorbitol, humins, 1-hydroxyhexane-2,5-dione, alkyl levulinates, furfuryl alcohol, lactic acid and acetic acid, the method comprising:

- a) providing an amount of biomass or biomass-derived material,
- b) hydrogenating said biomass or biomass-derived material in the presence of a Brønsted acid, a hydrogen source and a pincer complex according to formula (IIa):



(IIa)

15 wherein,

M is a metal selected from the group consisting of ruthenium, iron, iridium, manganese, rhodium, cobalt, platinum, palladium, nickel, osmium, rhenium, aluminium, gold, chromium and molybdenum;

W is an atom selected from the group consisting of P, C, O, and N;

20 R^{1a} , $R^{1a'}$, R^{1b} and $R^{1b'}$ are each independently selected from the group consisting of C_1 - C_6 alkyl, isopropyl, *tert*-butyl, a C_3 - C_7 cycloalkyl, a C_3 - C_7 heterocycloalkyl, phenyl, and C_5 - C_{10} aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, and C_5 - C_{10} aryl;

Z is selected from CO, $P(R^{III})_3$, $As(R^{III})_3$, NO and N_2 ; and

25 X is selected from the group consisting of a hydridoborate, such as tetrahydridoborate (BH_4^-), a halide, such as fluoride, chloride, bromide, or iodide, and H,

wherein R^{III} is each individually selected from C_1 - C_6 alkyl, isopropyl, phenyl, and C_5 -

C₁₀ aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl, and

c) isolating the produced chemical.

5 2. The method according to claim 1, wherein the chemical is selected from the group consisting of γ -valerolactone (GVL), 1,4-pentanediol, and sorbitol.

3. The method according to any one of the preceding claims, wherein the chemical is γ -valerolactone (GVL).

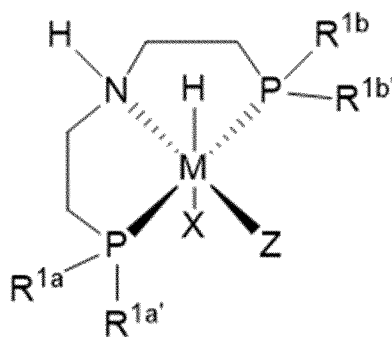
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4. The method according to any one of claims 1 to 2, wherein the chemical is 1,4-pentanediol.

5. The method according to any one of claims 1 to 2, wherein the chemical is sorbitol.

15

6. The method according to any one of the preceding claims, wherein the pincer complex is according to formula (III),



(III)

20 wherein,

M is ruthenium;

R^{1a}, R^{1a'}, R^{1b} and R^{1b'} are each independently selected from the group consisting of C₁-C₆ alkyl, isopropyl, *tert*-butyl, a C₃-C₇ cycloalkyl, a C₃-C₇ heterocycloalkyl, phenyl, and C₅-C₁₀ aryl, each of which may optionally be substituted by one or

more selected from halogen, cyano, amino, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl;

Z is selected from CO and NO; and

X is selected from the group consisting of tetrahydridoborate and chloride.

5

7. The method according to any one of the preceding claims, wherein

M is Ru; Z is CO; X is selected from chloride and tetrahydridoborate; and R^{1a}, R^{1a'}, R^{1b} and R^{1b'} are each independently selected from the group consisting of C₁-C₆ alkyl, isopropyl, *tert*-butyl, a C₃-C₇ cycloalkyl, a C₃-C₇ heterocycloalkyl, phenyl, and C₅-C₁₀ aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl.

10

8. The method according to any one of the preceding claims, wherein R^{1a}, R^{1a'}, R^{1b} and R^{1b'} are each independently selected as phenyl or isopropyl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl.

15

9. The method according to any one of the preceding claims, wherein R^{1a}, R^{1a'}, R^{1b} and R^{1b'} are each independently selected as phenyl or isopropyl.

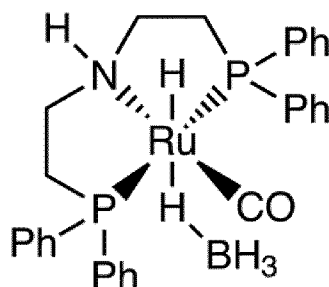
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10. The method according to any one of the preceding claims, wherein R^{1a}, R^{1a'}, R^{1b} and R^{1b'} are all selected as either phenyl or isopropyl.

11. The method according to any one of the preceding claims, wherein step b) is performed in the presence of an aqueous solution.

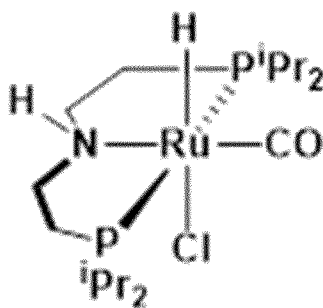
25

12. The method according to any one of the preceding claims, wherein the pincer complex is according to formula (IV):



(IV).

13. The method according to any one of claims 1 to 11, wherein the pincer complex is
5 according to formula (V):



(V).

14. The method according to any one of the preceding claims, wherein the pincer
10 complex is a catalyst.
15. The method according to any one of the preceding claims, wherein the pincer
complex is a homogeneous catalyst.
- 15 16. The method according to any one of the preceding claims, wherein the pincer
complex is present in an amount between 0.2 and 5% (w/w).
17. The method according to any one of claims 1 to 15, wherein the pincer complex is
present in an amount between 0.2 and 5% (mol%).
- 20 18. The method according to any one of the preceding claims, wherein the Brønsted
acid is an inorganic acid.

19. The method according any one of claims 18, wherein the inorganic acid is selected from the group consisting of phosphoric acid, hydrochloric acid, sulphuric acid, triflic acid, trifluoromethanesulfonic acid, and nitric acid.
- 5 20. The method according to any one of claims 18 to 19, wherein the inorganic acid is phosphoric acid or a derivatized phosphoric acid.
21. The method according to any one of claims 1 to 17, wherein the Brønsted acid is an organic acid.
- 10 22. The method according to claim 21, wherein the organic acid is selected from the group consisting of: formic acid, trifluoroacetic acid, fumaric acid, oxalic acid, maleic acid and acetic acid.
- 15 23. The method according to any one of the preceding claims, wherein the Brønsted acid is present in a concentration between 0.5 and 15 molar, preferably in a concentration between 4 and 12 molar.
24. The method according to any one of the preceding claims, wherein the step b) hydrogen source is selected from hydrogen gas, an alcohol and formic acid.
- 20 25. The method according to any one of the preceding claims, wherein the step b) hydrogen source is hydrogen gas.
- 25 26. The method according to claim 25, wherein the hydrogen gas is provided with a pressure between 1 and 100 bars, such as between 1 and 50 bars, such as between 5 and 50 bars.
27. The method according to any one of the preceding claims, wherein step b) is performed at a temperature between 80 and 250 °C, such as between 100 and 150 °C.
- 30 28. The method according to any one of the preceding claims, wherein step b) is performed at a temperature between 100 and 150 °C.
- 35 29. The method according to any one of the preceding claims, wherein step b) is performed between 1 hour and 7 days, such as between 6 and 96 hours.

30. The method according to any one of the preceding claims, wherein step b) is a one-pot process step.
- 5 31. The method according to any one of the preceding claims, wherein the biomass is selected from one or more from the group consisting of: cellulosic biomass, starchy biomass and chitin-containing biomass.
- 10 32. The method according to any one of the preceding claims, wherein the biomass is agricultural biomass.
33. The method according to any one of claims 31 to 32, wherein the biomass is cellulosic biomass.
- 15 34. The method according to any one of claims 31 to 33, wherein the biomass is lignocellulosic biomass, such as wood, sawdust, such as beechwood sawdust; or straw, such as wheat straw; such as bamboo, such as poplar, such as rice husk, such as coffee grounds or any combination thereof.
- 20 35. The method according to claim 31, wherein the biomass is starchy biomass, such as flour or de-hulled rice grains, for example potato, wheat, corn or rice flour or a combination thereof.
- 25 36. The method according to any one of the preceding claims, wherein the biomass-derived material is selected from the group consisting of: cellulose, hemicellulose, xylan, xylose, amylose, amylopectin, dextrans, disaccharides, starch oligosaccharides, C6 monosaccharides, such as glucose, C5 monosaccharides, hydroxymethylfurfural (HMF), furfural, levulinic acid, and mixtures thereof.
- 30 37. The method according to claim 36, wherein the biomass-derived material is cellulose.
38. The method according to claim 36, wherein the biomass-derived material is hemicellulose.
- 35 39. The method according to claim 36, wherein the biomass-derived material is xylan.

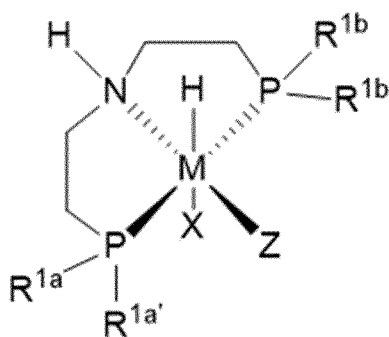
40. The method according to claim 36, wherein the biomass-derived material is starch.

41. The method according to claim 36, wherein the biomass-derived material is glucose.

5

42. A system specifically configured for carrying out the method according to any one of claims 1 to 41, said system comprising:

a) a sealable reactor comprising an amount of biomass or biomass-derived material, a Brønsted acid, and a pincer complex according to formula (III),



10

(III)

wherein,

M is ruthenium;

R^{1a}, R^{1a'}, R^{1b} and R^{1b'} are each independently selected from the group consisting of C₁-C₆ alkyl, isopropyl, *tert*-butyl, a C₃-C₇ cycloalkyl, a C₃-C₇ heterocycloalkyl, phenyl, and C₅-C₁₀ aryl, each of which may optionally be substituted by one or more selected from halogen, cyano, amino, C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, and C₅-C₁₀ aryl;

15

Z is selected from CO and NO; and

20

X is selected from the group consisting of tetrahydridoborate and chloride;

b) a hydrogen source, and

c) a heat source.

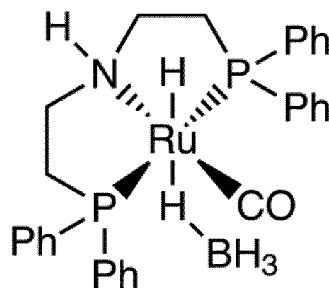
43. The system according to claim 42, wherein the biomass is cellulosic biomass.

25

44. The system according to any one of claims 42 to 43, wherein the reactor is an acid-resistant reactor.

45. The system according to any one of claims 42 to 44, wherein the pincer complex is according to formula (IV):

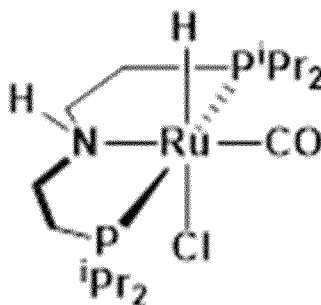
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(IV).

10

46. The system according to any one of claims 42 to 44, wherein the pincer complex is according to formula (V):



(V).

15

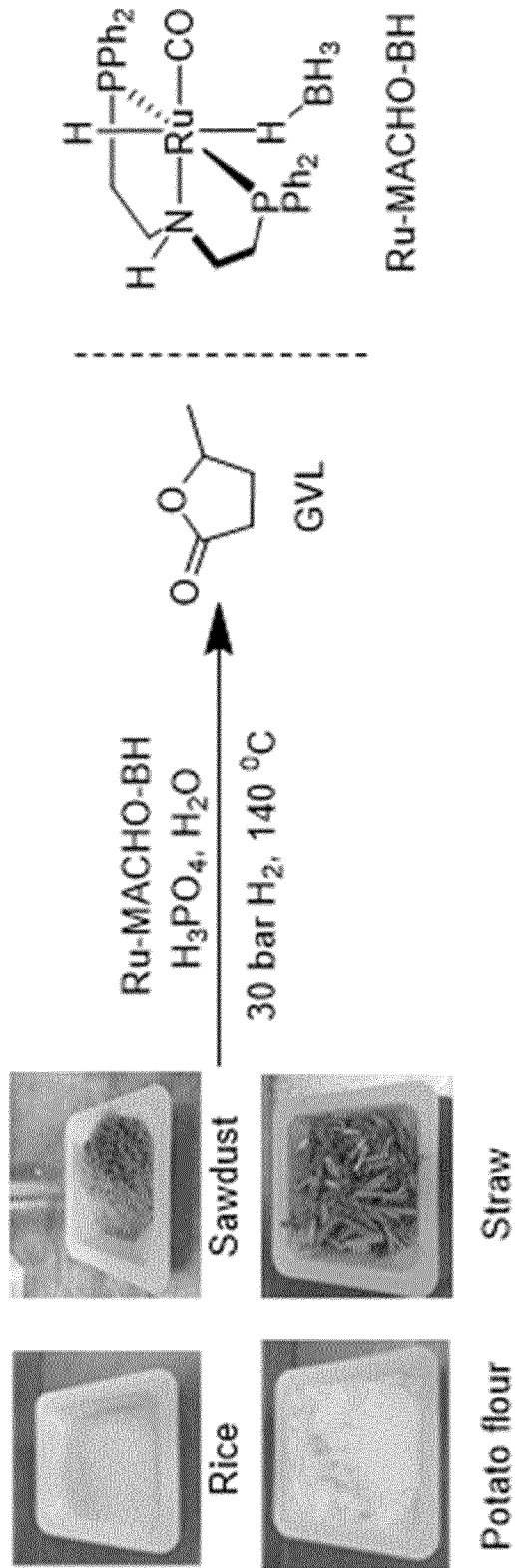


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/077991

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D307/32 C07F15/00 C07C29/149 C07C31/20 C07C31/26
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)
C07D C07F 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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| Y | <p>HUANG YAO-BING ET AL: "Simple and efficient conversion of cellulose to [gamma]-valerolactone through an integrated alcoholysis/transfer hydrogenation system using Ru and aluminium sulfate catalysts", CATALYSIS SCIENCE & TECHNOLOGY, vol. 8, no. 23, 26 November 2018 (2018-11-26), pages 6252-6262, XP093021108, UK</p> <p>ISSN: 2044-4753, DOI: 10.1039/C8CY01971A</p> <p>Whole document, particularly Tables 1 and 2, Figures and Schemes</p> <p style="text-align: center;">----- -/--</p> | 1-46 |

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

* Special categories of cited documents :

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|---|---|
| <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> | <p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p> |
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| Date of the actual completion of the international search | Date of mailing of the international search report |
| 19 December 2023 | 08/01/2024 |

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

International application No
PCT/EP2023/077991

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| Y | <p>AVELINO CORMA ET AL: "Chemical Routes for the Transformation of Biomass into Chemicals", CHEMICAL REVIEWS, AMERICAN CHEMICAL SOCIETY, US, vol. 107, no. 6, 1 January 2007 (2007-01-01), pages 2411-2502, XP002634035, ISSN: 0009-2665, DOI: 10.1021/CR050989D [retrieved on 2007-05-30] page 2431, 2nd column to page 2432, first column</p> <p style="text-align: center;">-----</p> | 1-46 |
| Y | <p>FIGLIOLIA ROSARIO ET AL: "CNN pincer ruthenium complexes for efficient transfer hydrogenation of biomass-derived carbonyl compounds", DALTON TRANSACTIONS, vol. 49, no. 2, 2 January 2020 (2020-01-02), pages 453-465, XP093021107, Cambridge ISSN: 1477-9226, DOI: 10.1039/C9DT04292J Whole document, particularly Scheme 8 in page 459</p> <p style="text-align: center;">-----</p> | 1-46 |
| Y | <p>WO 2012/162028 A1 (WISCONSIN ALUMNI RES FOUND [US]; DUMESIC JAMES [US] ET AL.) 29 November 2012 (2012-11-29) Whole document, particularly figure 1B</p> <p style="text-align: center;">-----</p> | 1-46 |
| Y | <p>WO 2010/151343 A1 (WISCONSIN ALUMNI RES FOUND [US]; DUMESIC JAMES A [US] ET AL.) 29 December 2010 (2010-12-29) examples 3 and 4 and Figure 1</p> <p style="text-align: center;">-----</p> | 1-46 |
| Y | <p>SVENJA WERKMEISTER ET AL: "Catalytic Hydrogenation of Carboxylic Acid Esters, Amides, and Nitriles with Homogeneous Catalysts", ORGANIC PROCESS RESEARCH & DEVELOPMENT, vol. 18, no. 2, 13 January 2014 (2014-01-13), pages 289-302, XP055311023, US ISSN: 1083-6160, DOI: 10.1021/op4003278 Whole document, particularly Scheme 11</p> <p style="text-align: center;">-----</p> | 1-46 |
| 4 | <p>Y US 2011/237814 A1 (KURIYAMA WATARU [JP] ET AL) 29 September 2011 (2011-09-29) examples 3-7, 14</p> <p style="text-align: center;">-----</p> <p style="text-align: center;">-/--</p> | 1-46 |
| 1 | | |

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2023/077991

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|---|--|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A,P | <p>PADILLA ROSA ET AL: "Catalytic Base-Free Transfer Hydrogenation of Biomass Derived Furanic Aldehydes with Bioalcohols and PNP Pincer Complexes", CHEMCATCHEM, vol. 15, no. 2, 20 January 2023 (2023-01-20), XP093112206, Hoboken, USA ISSN: 1867-3880, DOI: 10.1002/cctc.202200819 Retrieved from the Internet: URL:https://onlinelibrary.wiley.com/doi/full-xml/10.1002/cctc.202200819 Figure 2 in page 2, Scheme 1; page 1 second column, first paragraph; Table 2, entrances 7-9</p> | 1-46 |
| X | <p>-----</p> <p>PADILLA ROSA ET AL: "Efficient and selective catalytic hydrogenation of furanic aldehydes using well defined Ru and Ir pincer complexes", GREEN CHEMISTRY, vol. 22, no. 20, 19 October 2020 (2020-10-19), pages 6767-6772, XP093112215, GB ISSN: 1463-9262, DOI: 10.1039/D0GC01543A</p> | 1, 6-12, 14-17, 24-26, 29, 30, 42-45 |
| Y | <p>Scheme 1 in page 6768, Table 2 in page 6769</p> | 2-5, 13, 18-23, 27, 28, 31-41, 46 |
| X | <p>-----</p> <p>YI YUXUAN ET AL: "Highly Efficient Hydrogenation of Levulinic Acid into [gamma]-Valerolactone using an Iron Pincer Complex", CHEMSUSCHEM, vol. 11, no. 9, 9 May 2018 (2018-05-09), pages 1474-1478, XP093112217, DE ISSN: 1864-5631, DOI: 10.1002/cssc.201800435 Retrieved from the Internet: URL:https://api.wiley.com/onlinelibrary/tdm/v1/articles/10.1002%2Fcssc.201800435</p> | 1-3, 6-11, 14-17, 24-30, 42-44 |
| Y | <p>Figure 1 in page 1475, Table 1, entry 2</p> | 4, 5, 12, 13, 18-23, 31-41, 45, 46 |
| | <p>-----</p> <p style="text-align: center;">-/--</p> | |

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/077991

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|---|--|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| Y | TOWNSEND TANYA M ET AL: "Transfer hydrogenation of aromatic and linear aldehydes catalyzed using Cp*Ir(pyridinesulfonamide)Cl complexes under base-free conditions", JOURNAL OF ORGANOMETALLIC CHEMISTRY, ELSEVIER, AMSTERDAM, NL, vol. 843, 6 May 2017 (2017-05-06), pages 7-13, XP085051093, ISSN: 0022-328X, DOI: 10.1016/J.JORGANCHEM.2017.05.004 last paragraph in page 10 and Table 5 second entrance | 1-46 |
| X | WOZNIAK BARTOSZ ET AL: "Cyclopentanone Derivatives from 5-Hydroxymethylfurfural via 1-Hydroxyhexane-2,5-dione as Intermediate", CHEMSUSCHEM, vol. 11, no. 2, 23 January 2018 (2018-01-23), pages 356-359, XP093112208, DE ISSN: 1864-5631, DOI: 10.1002/cssc.201702100 Retrieved from the Internet: URL:https://api.wiley.com/onlinelibrary/tdm/v1/articles/10.1002%2Fcssc.201702100> | 1, 6-12, 14-17, 24-26, 29, 30, 42-45 |
| Y | HHD, 2, see Table 1, entry 4 | 2-5, 13, 18-23, 27, 28, 31-41 |
| Y | YUWEN JING ET AL: "Additive-Free Cobalt-Catalyzed Hydrogenation of Esters to Alcohols", ACS CATALYSIS, vol. 7, no. 5, 5 May 2017 (2017-05-05), pages 3735-3740, XP093112576, US ISSN: 2155-5435, DOI: 10.1021/acscatal.7b00623 Table 4 and Scheme 1, entry (b) in page 3738 | 1-46 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2023/077991

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|--|-------------------|---------------------------|-------------------|
| WO 2012162028 A1 | 29-11-2012 | US 2012302764 A1 | 29-11-2012 |
| | | WO 2012162028 A1 | 29-11-2012 |
| ----- | | | |
| WO 2010151343 A1 | 29-12-2010 | BR PI1011989 A2 | 20-02-2018 |
| | | EP 2445992 A1 | 02-05-2012 |
| | | US 2010324310 A1 | 23-12-2010 |
| | | US 2012149922 A1 | 14-06-2012 |
| | | US 2014094618 A1 | 03-04-2014 |
| | | WO 2010151343 A1 | 29-12-2010 |
| ----- | | | |
| US 2011237814 A1 | 29-09-2011 | CN 102177170 A | 07-09-2011 |
| | | EP 2492275 A1 | 29-08-2012 |
| | | JP 5671456 B2 | 18-02-2015 |
| | | JP WO2011048727 A1 | 07-03-2013 |
| | | US 2011237814 A1 | 29-09-2011 |
| | | WO 2011048727 A1 | 28-04-2011 |
| ----- | | | |