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(71) Applicants: **RHODIA OPERATIONS** [FR/FR]; 25, Rue De Clichy, 75009 Paris (FR). **LE CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE** [FR/FR]; 3 Rue Michel-ange, 75794 Paris Cedex 16 (FR). **UNIVERSITE DE POITIERS** [FR/FR]; 15, Rue De L'hotel Dieu, 86000 Poitiers (FR).

(72) Inventors: **JIANG, Shi**; No. 3 Xinguang, Xinjie Town, Taizhou, Jiangsu (CN). **PERA TITUS, Marc**; Appart 304, Block 19, 199 Mincheng Road, Shanghai 201100 (CN). **JEROME, François**; 1 Chemin de Savigny, 86800 Sèvres-Anxaumont (FR). **VIGIER, Karine**; 2 Rue des Chaumes, 86240 Fontaine le Comte (FR). **MA, Changru**; 2501/78/789 Fuzhuo Road, Shanghai (CN).

(74) Agent: **CHINA PATENT AGENT (H.K.) LTD.**; 22/F., Great Eagle Center, 23 Harbour Road, Wanchai, Hong Kong (CN).

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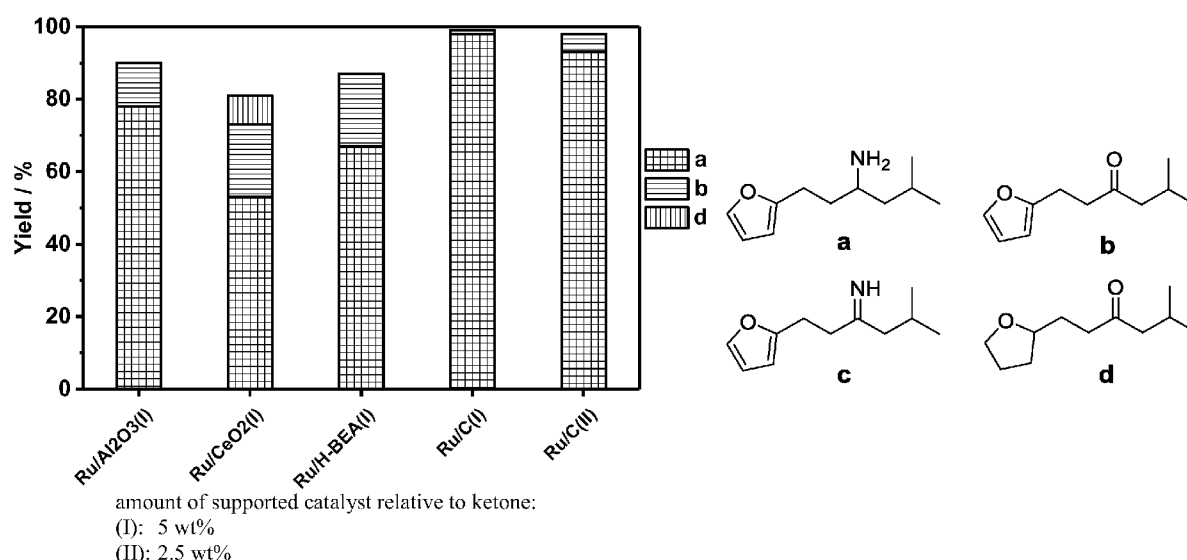
(54) Title: PROCESS FOR REDUCTIVE AMINATION OF α , β -UNSATURATED KETONE

Figure 1

(57) Abstract: A process for reductive amination of α , β -unsaturated ketone is disclosed. A process for preparation of furan-derived amine starting from furfural or derivative thereof is also disclosed. The process is conducted in the presence of supported Ru as catalyst, the support of the supported Ru is selected from ceramics and carbon and preferably from Al_2O_3 and C.

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PROCESS FOR REDUCTIVE AMINATION OF α , β -UNSATURATED KETONE**TECHNICAL FIELD OF THE INVENTION**

The invention relates to a process for the reductive amination of an α , β -unsaturated ketone. The invention furthermore relates to a process for the preparation of a furan-derived amine starting from furfural or a derivative thereof.

5 BACKGROUND

The depletion of fossil oil reserves has motivated intensive research on the development of chemical products from biomass. Biomass, mostly composed of carbohydrates, is a huge reservoir of renewable carbon with an annual production estimated at 180 billion metric tons. Hence, current research programs target the
10 conversion of carbohydrates into value added chemicals.

Among biomass-derived reagents, furanic compounds produced from carbohydrates (hexoses or pentoses) contained in lignocellulosic biomass are of prime interest, giving access to a rich variety of chemicals and fuels. In particular, furfural is a versatile platform chemical for the production of fuel additives,
15 solvents, polymers, surfactants, perfumes, and agrochemical ingredients. Despite the extensive literature dedicated to furanic compounds, the low selectivity of the chemical reactions due to partial cleavage and/or formation of larger oligomers, such as humines, still hamper the industrial-scale production of high-added valuable chemicals from furanic molecules.

20 Although the transformation of biomass into valuable nitrogen-containing compounds is highly desired, only few examples have been reported so far on furanic compounds. In particular, primary amines are widely used for the synthesis of polymers, dyes, surfactants, pharmaceuticals and agrochemicals. Reductive amination of carbonyl compounds with ammonia (NH_3) and hydrogen
25 (H_2) as a nitrogen source and reductant, respectively, has received much attention for the synthesis of primary amines as an alternative to synthetic processes with low atomic efficacy relying on toxic reagents and/or stoichiometric reductants.

Various heterogeneous catalysts have been developed for reductive amination reactions. Nonetheless, the synthesis of primary amines has been
30 limited to the reductive amination of simple aryl and alkyl aldehydes, such as benzaldehyde, due to the formation of secondary and tertiary amines and/or undesired hydrogenation of carbonyl groups. In particular, the selective reductive

amination of carbonyl compounds containing reduction-sensitive functional groups, such as heterocycles and halogens, is often difficult.

US 3,565,954 suggests a process for preparing primary amines by reaction of carbonyl compounds with ammonia followed by hydrogenation of the imine produced. As carbonyl compound, furfural is employed and the reaction is conducted in the presence of a catalyst, such as Raney nickel deposited on a kieselgur carrier. The highest yield obtained in one of the examples of this document is 92 %.

The direct reductive amination of aldehydes and ketones using potassium formate as reductant and catalytic palladium acetate is described by B. Basu, et al., Synlett 2003, No. 4, 555-557. This document contains only one example for the reductive amination of an α,β -unsaturated carbonyl compound, which is, however, an aldehyde, namely cinnamaldehyde. The yield in this example is only 69 % and the aromatic phenyl ring is not hydrogenated.

Heterogeneous Ru-based catalysts for one-pot synthesis of primary amines from aldehydes and ammonia are described by B. Dong, et al., in Catalysts 2015, 5, 2258-2270. The reductive amination of furfural to furfuryl amine using Ru/Al₂O₃ as catalyst is exemplified. However, in this reaction in a yield of only 75 % is obtained.

Furthermore, the aldol condensation of furanic compounds has been studied aiming at the production of liquid alkanes. For example, J. Yang, et al., ChemSusChem, 2013, 6, 1149-1152 describes the production of C₁₀ and C₁₁ branched alkanes by the aldol condensation of furfural with methyl isobutyl ketone followed by a one-step hydrodeoxygenation under solvent free conditions.

Also M. Li et al., Green Chem. 2014, 16, 4371-4377 report the tandem aldol condensation-hydrogenation reaction of furfural with acetone over a Pd/CN@MgO biofunctional catalyst in a single reactor.

However, in aldol condensation reactions, the desired nitrogen-containing compounds are not obtained. Further reactions are rather required.

It is therefore desirable to provide a process for the reductive amination of an α,β -unsaturated ketone, such as a furan derivative, which is highly selective towards the desired amine and which provides the desired amine in high yield without simultaneous reduction of the furan ring. It is furthermore desirable to provide a process for the preparation of furan-derived amines based on biomass-derived furfural which can be conducted in a single reactor (one-reactor tandem concept), i.e. a process wherein the aldol condensation and the

hydrogenation amination are conducted as one-pot process. Such process would afford the generation of furan-derived amines with molecular complexity and diversity without the need of separating the intermediates.

SUMMARY OF THE INVENTION

5 The present inventors have found that the reductive amination of an α,β -unsaturated ketone can be conducted in high yield and at high selectivity in the presence of a supported Ru catalyst.

10 The present invention therefore relates to a process for the reductive amination of an α,β -unsaturated ketone, wherein the process is conducted in the presence of supported Ru as catalyst.

15 The inventors furthermore found that furan-derived amines can be prepared in good yield starting from furfural or a derivative thereof, in particular from furfural or a derivative thereof being derived from biomass, by first conducting an aldol condensation between the furfural or derivative thereof and a ketone and then conducting a reductive amination of the product obtained in the first step in the presence of a supported Ru catalyst.

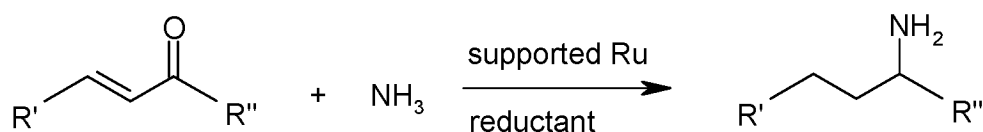
DETAILED DESCRIPTION

20 One embodiment of the present invention relates to a process for the reductive amination of an α,β -unsaturated ketone, wherein the process is conducted in the presence of supported Ru as catalyst.

25 It was found that supported Ru as catalyst in the reductive amination of an α,β -unsaturated ketone, in particular a furan derivative, results in high yield of the desired amine, in particular the furan-derived amine with only little undesired byproducts, compared to other known catalysts used in reductive amination. This effect will be further demonstrated by the examples and comparative examples below.

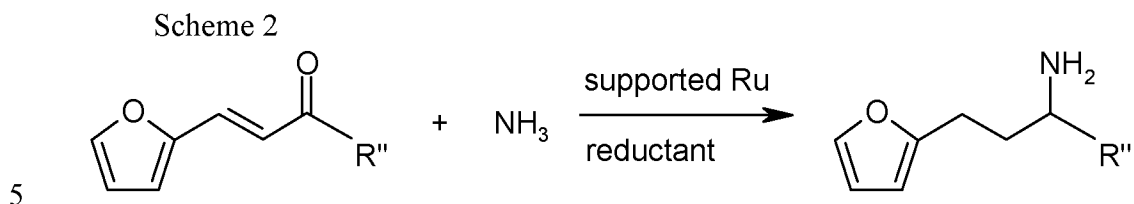
 The reductive amination of an α,β -unsaturated ketone in the presence of for example ammonia as amine is exemplified by the following general reaction scheme 1:

30 Scheme 1



wherein R' and R'' are any suitable residues.

In the preferred embodiment of the invention wherein the α,β -unsaturated ketone is a furan derivative, the general reaction scheme 2 is as follows:



wherein R'' is any suitable residue.

In the process of the invention any supported Ru may be used as catalyst.

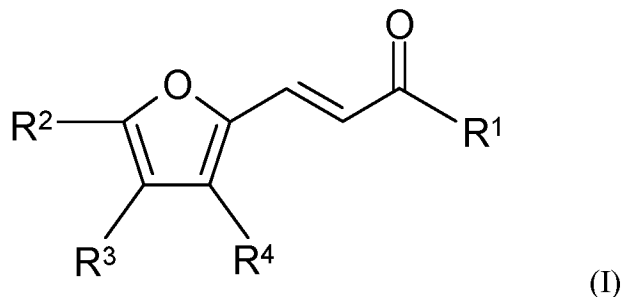
In the context of the present invention "supported Ru" is understood as
 10 metallic Ru which is supported on a solid support. Any solid material is suitable as solid support, such as those solid supports known to a person skilled in the art as being suitable for supporting a catalyst, such as ceramics and carbon (C). Suitable ceramics are, for example, Al_2O_3 , SiO_2 , CeO_2 , ZrO_2 , zeolites etc. Preferred supports are Al_2O_3 , zeolites (in particular H-BEA) and C, preferably Al_2O_3 and C,
 15 most preferably C.

In the reductive amination of the present invention any suitable reductant known to a person skilled in the art may be used. A preferred reductant is hydrogen (H_2).

In the reductive amination of the present invention any α,β -unsaturated
 20 ketone may be used. In the context of the invention, furan derivatives are, however, preferred because they can be obtained from biomass. Furthermore, it was found that if the α,β -unsaturated ketone is a furan derivative, only the double bond in the α,β -unsaturated ketone but not the double bonds in the furan ring are hydrogenated.

25 In one embodiment the α,β -unsaturated ketone is an α,β -ethylenically unsaturated ketone as exemplified in above Scheme 1, preferably an α,β -ethylenically unsaturated ketone furan derivative as exemplified in above Scheme 2.

The furan derivative used as α,β -unsaturated ketone in the preferred
 30 embodiment of the process of the present invention can have the chemical formula (I):



wherein R¹ is a hydrocarbon residue which may be interrupted by one or more heteroatoms and which may be substituted with one or more functional groups, and

R², R³ and R⁴ independently of each other are a hydrocarbon residue which may be interrupted by one or more heteroatoms and which may be substituted with one or more functional groups.

R¹ and the substituents on the furan ring (R², R³ and R⁴) are not particularly limited because the reductive amination takes place at the carbonyl moiety and the double bonds. Therefore, the substituents on the furan ring and R¹ can be selected by the skilled person according to the desired end product. For example, R¹ can be a hydrocarbon residue comprising 1 to 30 carbon atoms, preferably 1 to 20 carbon atoms, more preferably 1 to 12 carbon atoms.

The hydrocarbon residue may be interrupted by one or more heteroatoms which can for example be selected from N, O, S and P. In this context, "interrupted" means that the heteroatom is situated between at least two carbon atoms.

The hydrocarbon residue may be substituted with one or more functional groups which may for example be selected from halogen, hydroxyl, carbonyl, carboxyl, ester, amine, amide, imide, cyanate, isocyanate, nitro, sulfonyl, thiocyanate, isothiocyanate, and phosphate. Any functional group may be situated at any position of the hydrocarbon residue, and, in case of for example carbonyl or ester, may interrupt the hydrocarbon residue.

Suitable hydrocarbon residues are for example alkyl which may be linear or branched, alkenyl which may be linear or branched, alkynyl which may be linear or branched, cycloalkyl and aryl, in particular phenyl. Combinations of these groups are possible as well, such as for example combinations of linear and cyclic groups, such as alkylaryl, alkyl-cycloalkyl, arylalkyl and cycloalkyl-aryl groups.

If the hydrocarbon residue comprises one or more carbon-carbon double or triple bond, it is possible that also such double or triple bond will be hydrogenated in the reductive amination reaction in the process of the invention.

Preferred groups for R^1 are methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl and decyl.

The substituents on the furan ring, R^2 , R^3 and R^4 , may be H or hydrocarbon residues which preferably are defined as the hydrocarbon residue for R^1 . In a certain embodiment, R^1 is a C_1 to C_{20} , preferably C_1 to C_{12} alkyl group which may be linear or branched, R^2 is H or $-CH=CH-CO-R^5$, wherein R^5 is a C_1 to C_{20} , preferably C_1 to C_{12} alkyl group which may be linear or branched, and R^3 and R^4 are both H. In this embodiment, R^5 and R^1 may be the same or different, preferably R^5 and R^1 are the same.

The reductive amination reaction in the process of the present invention may be conducted with ammonia, R^6-NH_2 or R^6-NH-R^7 , wherein R^6 and R^7 independently are a hydrocarbon residue which may be interrupted by one or more heteroatoms and which may be substituted with one or more functional groups. This hydrocarbon residue may have the same preferred embodiments as described for R^1 above. Additionally, in case of R^6-NH-R^7 , the substituents R^6 and R^7 together with the nitrogen atom to which they are attached may form a ring. Furthermore, among the functional groups with which the hydrocarbon residues for R^6 and R^7 may be substituted, amines are preferred.

In one embodiment, R^6 and, if present, R^7 , independently are a C_1 to C_{12} alkyl group which may be linear or branched and which may be substituted with one or more, preferably one amine(s).

Preferred amines used in the reductive amination of the α,β -unsaturated ketone in the process of the present invention are ammonia, methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, methyldiamine, ethyldiamine, propyldiamine, butyldiamine, pentyldiamine and hexyldiamine.

As catalyst any known supported Ru catalyst may be used. Suitable catalysts of this kind is, such as Ru/C are, for example, available from Johnson Matthey. Ru/ Al_2O_3 is for example available from Alfa Aesar.

The amount of supported Ru catalyst used in the process of the invention is not particularly limited but it was found that a certain minimum amount is desirable for obtaining good yield and selectivity. Therefore, in a preferred embodiment, the supported Ru is used in an amount of at least 1 wt%, preferably at least 2 wt%, more preferably at least 3 wt%, even more preferably at least 4 wt%

and most preferably at least 5 wt%, each based on the weight of the α,β -unsaturated ketone.

The reductive amination in the process of the invention can be conducted under usual process parameters well known to a person skilled in the art. In view of yield and selectivity of the process it is, however, preferred to conduct the reductive amination at a temperature of at least 80°C, preferably in the range of 80°C to 120°C, more preferably in the range of 90°C to 110°C, such as about 100°C.

The reductive amination in the process of the present invention can be conducted using H₂. The pressure of H₂ during the reaction is not particularly limited and can be selected according to the requirements. It was, however, found that in view of selectivity and yield it is desirable that the H₂ is used at a pressure of at least 5 bar, preferably in the range of 5 bar to 30 bar, more preferably in the range of 10 bar to 20 bar, such as in the range of 12 bar to 18 bar.

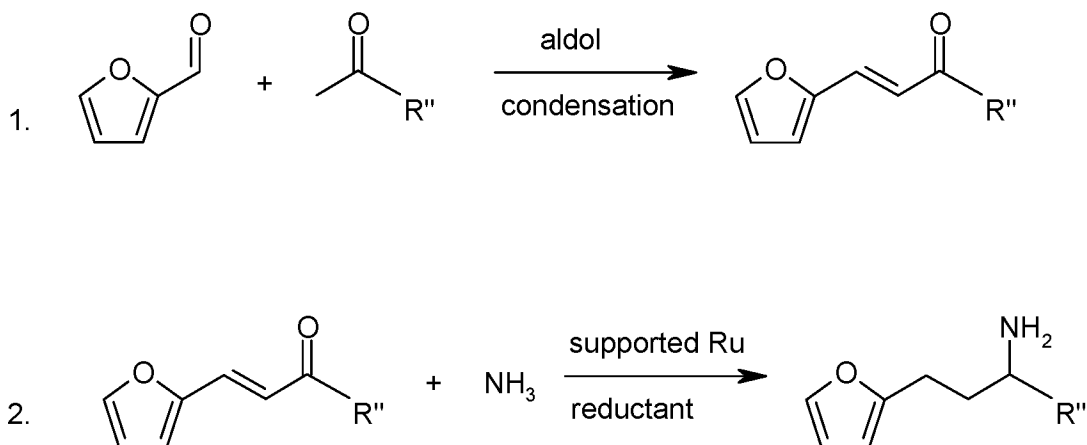
The reaction time is also not particularly limited and can be selected by the skilled person according to the desired yield and purity of the desired furan-derived amine product. For example, the reaction can be conducted for at least 8 hours, preferably at least 10 hours, more preferably at least 12 hours, such as about 14 hours.

A further advantage of the use of supported Ru as catalyst in the reductive amination in the process of the present invention is that the catalyst can be reused in several consecutive reactions and/or recycled after the first use or after the first or one of the further reuses. Recycling can be conducted for example by washing with ethanol, drying under vacuum at 80°C and reducing at 180°C. Such recycled catalyst shows almost the same activity as fresh catalyst. Therefore, in the process of the invention, fresh catalyst, recycled catalyst or a mixture thereof can be employed.

In a second embodiment, the present invention relates to a process for the production of a furan-derived amine comprising the steps of

1. conducting an aldol condensation between furfural or a derivative thereof and a ketone, and
2. conducting a reductive amination of the product received in step 1, wherein the reductive amination is conducted as described with respect to the first embodiment of the invention including the preferred embodiments thereof.

This embodiment of the invention is exemplified by the following general reaction scheme:



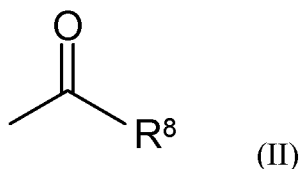
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wherein R^{''} is any suitable residue.

The aldol condensation is conducted with furfural or a derivative thereof. Suitable derivatives are, for example, 5-hydroxymethyl furfural, 5-aminomethyl furfural and diformylfuran. Among the furfural derivatives diformylfuran is preferred.

The ketone used in the aldol condensation is not particularly limited and can be selected by a person skilled in the art according to the desired furan-derived amine. For example, the ketone can have the chemical formula (II):

15



wherein R⁸ is a hydrocarbon residue which maybe interrupted by one or more heteroatoms and which may be substituted with one or more functional groups. Preferably, R⁸ is selected such that in the aldol condensation a furan derivative of the above chemical formula (I) is obtained (i.e. R⁸ is defined as R¹ above). Thus, also the above preferred embodiments for R¹ are applicable for R⁸.

The aldol condensation can be conducted using usual process parameters well known to a person skilled in the art. For example, the aldol condensation can be conducted in the presence of a base catalyst, such as Amberlyst[®] A26 in hydroxide form, available from Sigma-Aldrich. The reaction can, for example be

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conducted at an elevated temperature of about 120°C for about 2 hours without the presence of any additional solvent.

It was furthermore found that in the process of the second embodiment of the present invention steps 1 and 2 can be conducted as one-pot process. Thus, the
5 aldol condensation and the reductive amination can be conducted in one reactor without separating the α,β -unsaturated ketone obtained in the aldol condensation step. It is rather possible to charge the reactor with the furfural or a derivative thereof, the ketone, the amine, the catalysts and H₂ and then conduct both reaction steps, i.e. the aldol condensation and the reductive amination without separating
10 any intermediate products. It was found that nevertheless the desired furan-derived amine can be obtained at high overall yield of about 70 %.

In a further embodiment of the present invention the furfural or derivative thereof used in the aldol condensation in step 1 of the above process is derived from biomass. In this case, the process comprises the further step of deriving the
15 furfural or the derivative thereof from biomass. This additional step is conducted prior to step 1 above.

The conversion of biomass to furfural can be conducted as described for example in WO 2014/008364, the content of which is incorporated herein by reference.

20 In the attached figures,

Figure 1 shows the influence of a catalyst on the yields of the desired product (a) and the undesired byproduct (b and d),

Figure 2 shows the influence of H₂ pressure on the yields of the desired product (a) and the undesired byproduct (b),

25 Figure 3 shows the influence of NH₃ pressure on the yields of the desired product (a) and the undesired byproduct (b),

Figure 4 shows the yields of the desired product (a) and the undesired byproduct (b) depending on the use of fresh, reused and refreshed catalyst.

The following examples are given by way of non-limiting illustration of the
30 present invention.

EXAMPLES

Materials

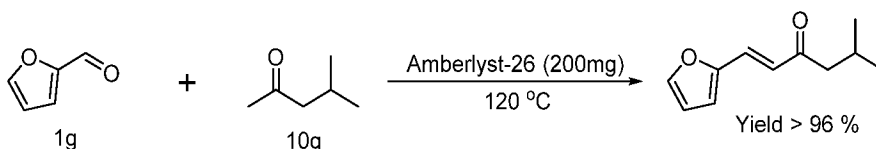
5%Ru/C (49.90% moisture, Johnson Matthey), 5%Ru/Al₂O₃ (Alfa Aesar),
5%Ru/CeO₂, H-BEA (beta zeolite, Clariant), Amberlyst-26 in hydroxide form
35 (moisture 66-75%, Sigma-Aldrich), furfural (99%, Sigma-Aldrich), methyl isobutyl ketone (MIBK) ($\geq$ 99%, Sigma-Aldrich), ethanol (99.5%, J&K),

acetophenone ($\geq 99\%$, Sigma-Aldrich), 2-pentanone ($\geq 99\%$, Sigma-Aldrich), 2-heptanone ($\geq 98\%$, Sigma-Aldrich).

Example 1

1.1 Aldol Condensation

5



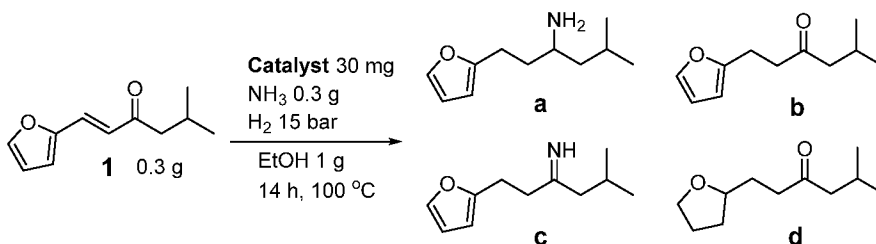
The experiment was performed in a 30-mL tubular glass reactor with a sealable arrangement on top. The reaction was performed using 1 g of furfural, 10 g of MIBK and 0.2 g of Amberlyst-26 catalyst in the glass tube preheated in an oil bath at 120°C for 2 h with stirring speed of 600 rpm. The product was analyzed and quantified using an Agilent 7890 GC equipped with a HP-5 capillary column with 5 wt% phenyl groups and using *n*-dodecane as an internal standard. ^1H and ^{13}C NMR and GCMS analysis were also carried out.

1.2 Reductive Amination

The experiments were carried out in a 20-mL stainless steel reactor equipped with a pressure gauge and a safety rupture disk. In a given experiment, the reactor was charged with 0.3 g of the aldol condensation product from experiment 1.1 above, 1 g of ethanol and 30 mg of the pre-reduced catalyst. The reactor was sealed and flushed with N_2 three times. Then, NH_3 (5 bar) and H_2 (15 bar) were introduced to the reactor. The reactor was placed on hot plate provided with magnetic stirring at 100°C for 14 h. After the reaction, the reactor was cooled down to room temperature and the mixture was analyzed using an Agilent 7890 GC equipped with a HP-5 capillary column with 5wt% phenyl groups and using *n*-dodecane as an internal standard. ^1H and ^{13}C NMR, as well as GC-MS analyses, were further conducted.

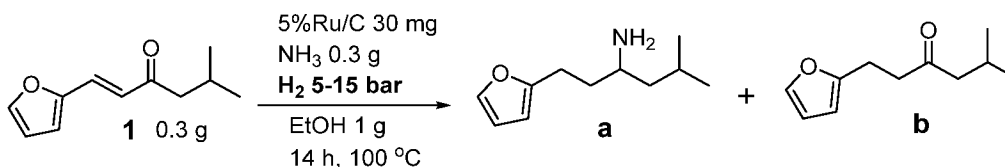
A series of catalysts based on supported Ru (5 wt% Ru/ Al_2O_3 , 5 wt% Ru/ CeCO_2 , 5 wt% Ru/H-BEA, 5 wt% Ru/C; here wt% relates to Ru loading on the support) were tested to perform the reductive amination of the aldolization. The results are shown in Figure 1. Among the different catalysts, 5wt%Ru/C exhibits the best performance towards the primary amine (**a**). Two additional byproducts are also observed: **b** with the α,β insaturation reduced, and the reduced byproduct **d**. Noteworthy, the imine intermediate **c** was not detected.

- 11 -



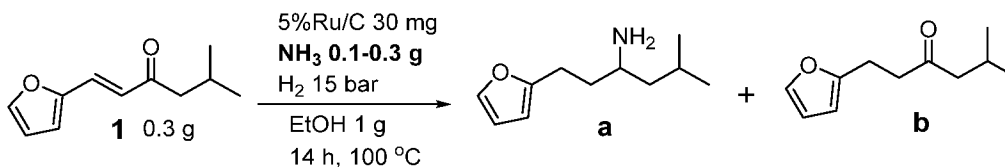
Example 2

By repeating Example 1.2 the effect of the H_2 pressure on the reductive amination reaction was further explored on one of the best performing catalysts (5%Ru/C). The results are shown in Figure 2. The H_2 pressure exerts a positive effect on the yield to the target product **a** in detriment to byproduct **b**. A H_2 pressure of 15 bar affords full conversion of the aldolization reactant and a yield of 96% to **a** after 14 h reaction at 100 °C using a molar ratio between the reactant **1** and NH_3 of 1/10.



Example 3

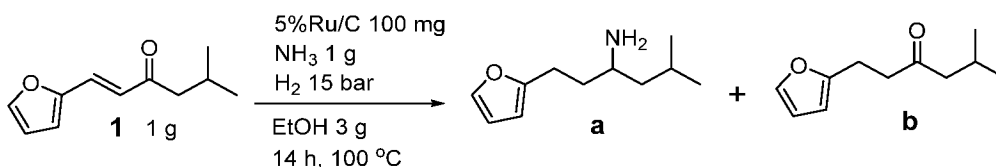
By repeating Example 1.2 the effect of the NH_3 pressure on the reductive amination reaction over 5%Ru/C was further explored. The results are shown in Figure 3. The NH_3 pressure only exerts a moderate effect on the formation rate of the amine product **a**.



Example 4

Analog to example 1.2 recyclability and reuse of 5%Ru/C was further studied. The results are shown in Figure 4. The catalyst show an excellent catalytic performance for 5 consecutive runs with neither loss of activity nor effect on the carbon balance. The yield to the product decreases slightly from 96% to 82% after the 4th run. A further catalytic test on the refreshed catalyst after the 4th run

followed by washing with ethanol, drying under vacuum at 80°C overnight and reducing at 180°C for 1 h shows an activity almost unchanged.

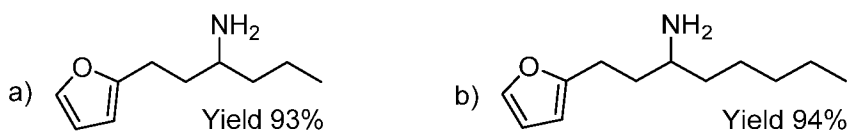


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Example 5

The reduction amination over 5%Ru/C was further extended to other α,β -unsaturated ketones issued from the aldol condensation reaction of furfural with biobased ketones with variable chain length. In all cases a yield higher than 90% to the desired product is obtained.

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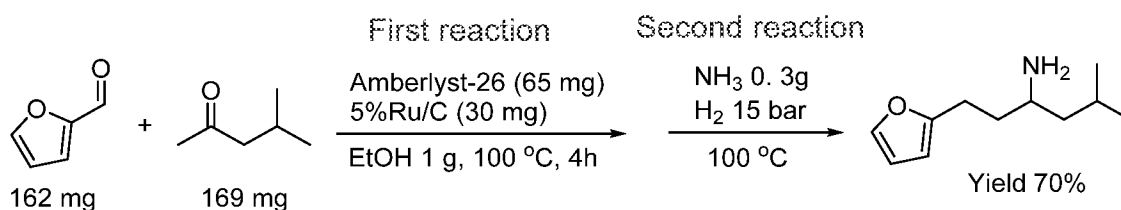
Reaction conditions: 5%Ru/C (30 mg), α,β -unsaturated ketone (0.3 g), EtOH (1 g), NH₃ (0.3 g), H₂ (15 bar), 100°C, 6 h.

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Example 6

In this example the aldolization and reductive amination reactions were conducted simultaneously in the same reactor (one-reactor tandem concept). To this aim, two catalysts were introduced to the reactor: (1) Amberlyst-26 (65 mg) for catalyzing the aldol condensation reaction between furfural (162 mg) and MIBK (169 mg) in ethanol (1 g), and (2) 5%Ru/C (30 mg) for catalyzing the reductive amination. The reaction was kept constant at 100°C for the two reactions. NH₃ (0.3 g) and H₂ (15 bar) were introduced after 4 h to ensure that enough aldolization product was formed. The amine product **a** was generated with a yield of 70%.

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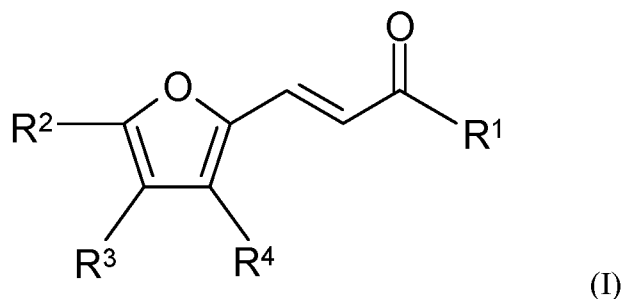
1. Process for the reductive amination of an α,β -unsaturated ketone, wherein the process is conducted in the presence of supported Ru as catalyst.

2. Process according to claim 1, wherein the support of the supported Ru is selected from ceramics and carbon and preferably from Al_2O_3 and C, and wherein the support most preferably is C.

3. Process according to claim 1 or 2, wherein the reductive amination is conducted in the presence of H_2 as reductant.

4. Process according to any one of the preceding claims, wherein the α,β -unsaturated ketone is a furan derivative.

5. Process according to claim 4, wherein the furan derivative has the chemical formula (I):



wherein

R¹ is a hydrocarbon residue which may be interrupted by one or more heteroatoms and which may be substituted with one or more functional groups, and

R², R³ and R⁴ independently of each other are H or a hydrocarbon residue which may be interrupted by one or more heteroatoms and which may be substituted with one or more functional groups.

6. Process according to claim 5, wherein in the chemical formula (I) R^1 is C_1 to C_{20} alkyl group which may be linear or branched, R^2 is H or $-CH=CH-CO-R^5$, wherein R^5 is a C_1 to C_{20} alkyl group which may be linear or branched, and R^3 and R^4 are H.

5 7. Process according to any one of the preceding claims wherein the α,β -unsaturated ketone is reacted with ammonia, R^6-NH_2 or R^6-NH-R^7 , wherein R^6 and R^7 independently are a hydrocarbon residue which may be interrupted by one or more heteroatoms and which may be substituted with one or more functional groups and wherein R^6 and R^7 together with the nitrogen atom to which
10 they are attached may form a ring.

8. Process according to claim 7, wherein R^6 and R^7 are a C_1 to C_{12} alkyl group which may be linear or branched and which may be substituted with one or more, preferably one amine(s).

9. Process according to any one of the preceding claims, wherein the
15 supported Ru catalyst is used in an amount of at least 1 wt%, preferably at least 2 wt%, more preferably at least 3 wt%, even more preferably at least 4 wt% and most preferably at least 5 wt%, each based on the weight of the α,β -unsaturated ketone.

10. Process according to any one of the preceding claims, wherein the
20 reductive amination is conducted at a temperature of at least $80^\circ C$, preferably in the range of $80^\circ C$ to $120^\circ C$, more preferably in the range of $90^\circ C$ to $110^\circ C$.

11. Process according to any one of the preceding claims, wherein the reductive amination is conducted at a H_2 pressure of at least 5 bar, preferably in the range of 5 bar to 30 bar, more preferably in the range of 10 bar to 20 bar.

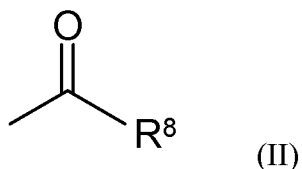
25 12. Process for the preparation of a furan-derived amine comprising the steps of

1. conducting an aldol condensation between furfural or a derivative thereof and a ketone, and

2. conducting a reductive amination of the product obtained in step 1.

30 according to the process of any one of claims 1 to 11.

13. Process according to claim 12, wherein the ketone has the chemical formula (II):

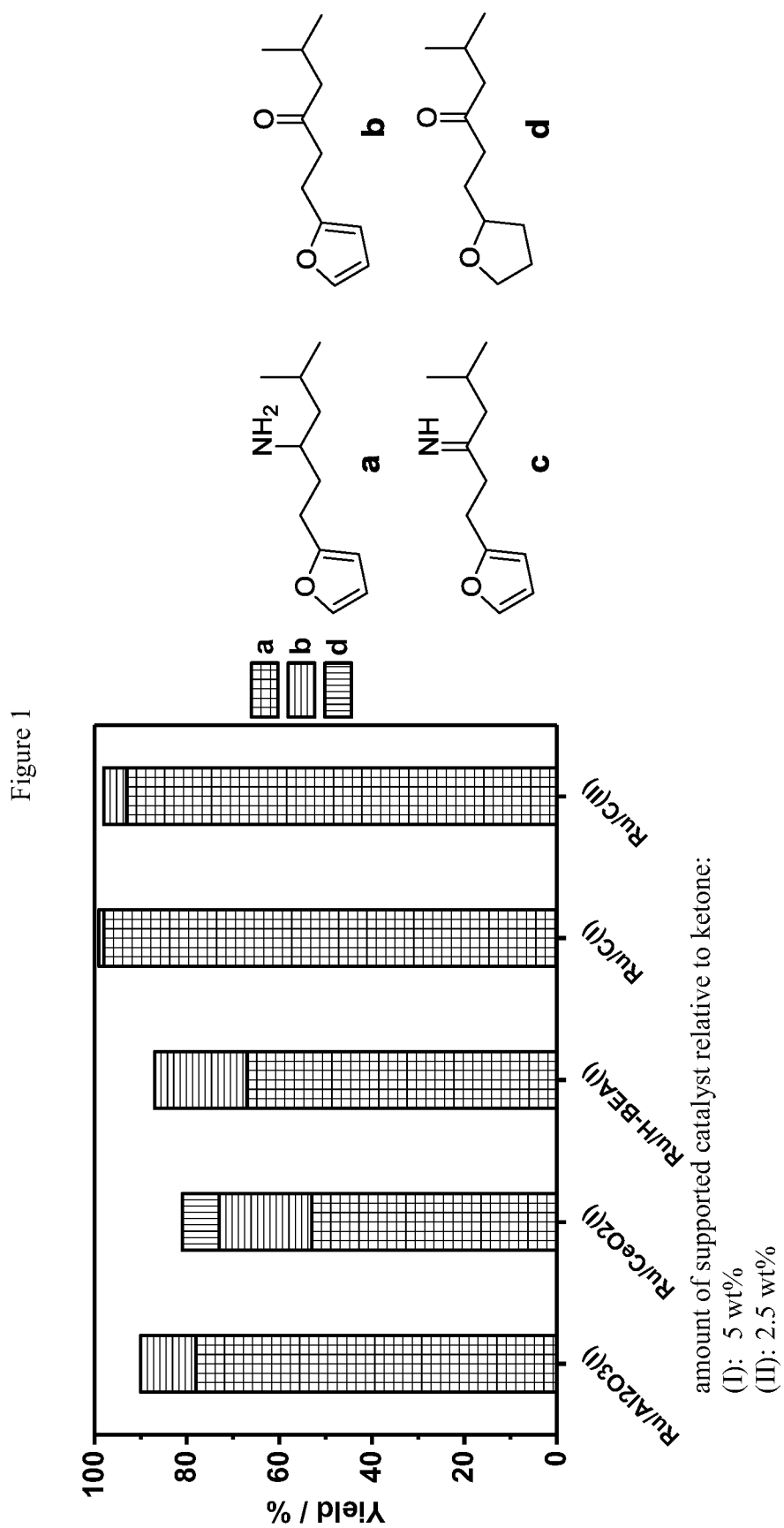


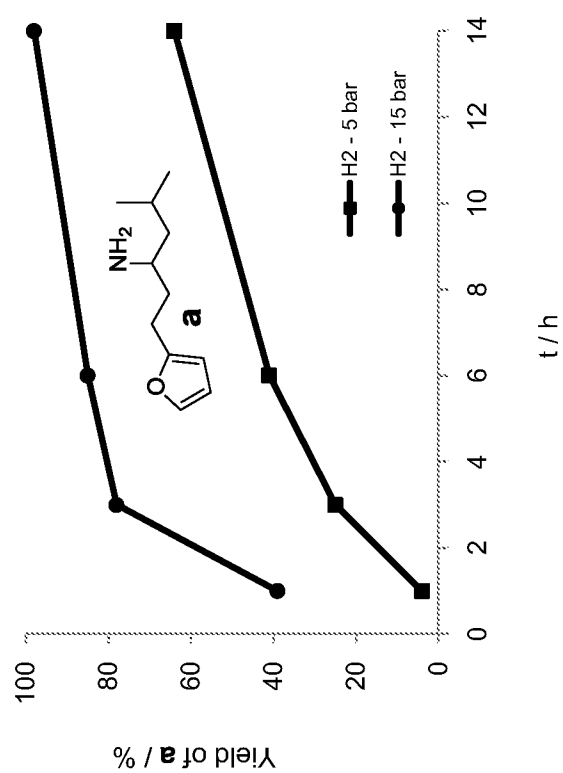
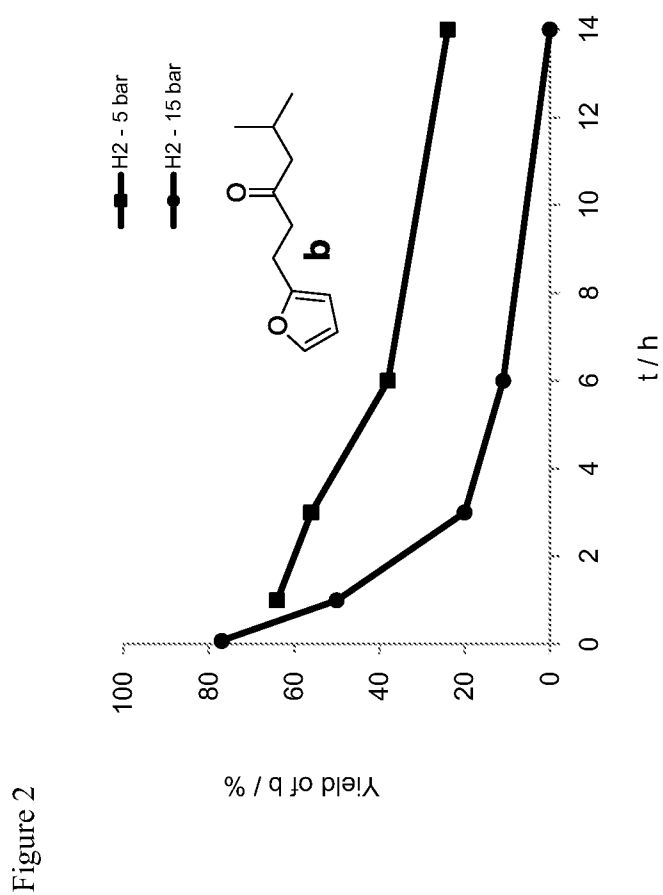
5

wherein R⁸ is a hydrocarbon residue which may be interrupted by one or more heteroatoms and which may be substituted with one or more functional groups.

14. Process according to claim 12 or 13, wherein steps 1 and 2 are
10 conducted as one-pot process.

15. Process according to any one of claims 12 to 14, further comprising the step of deriving the furfural or the derivative thereof from biomass.





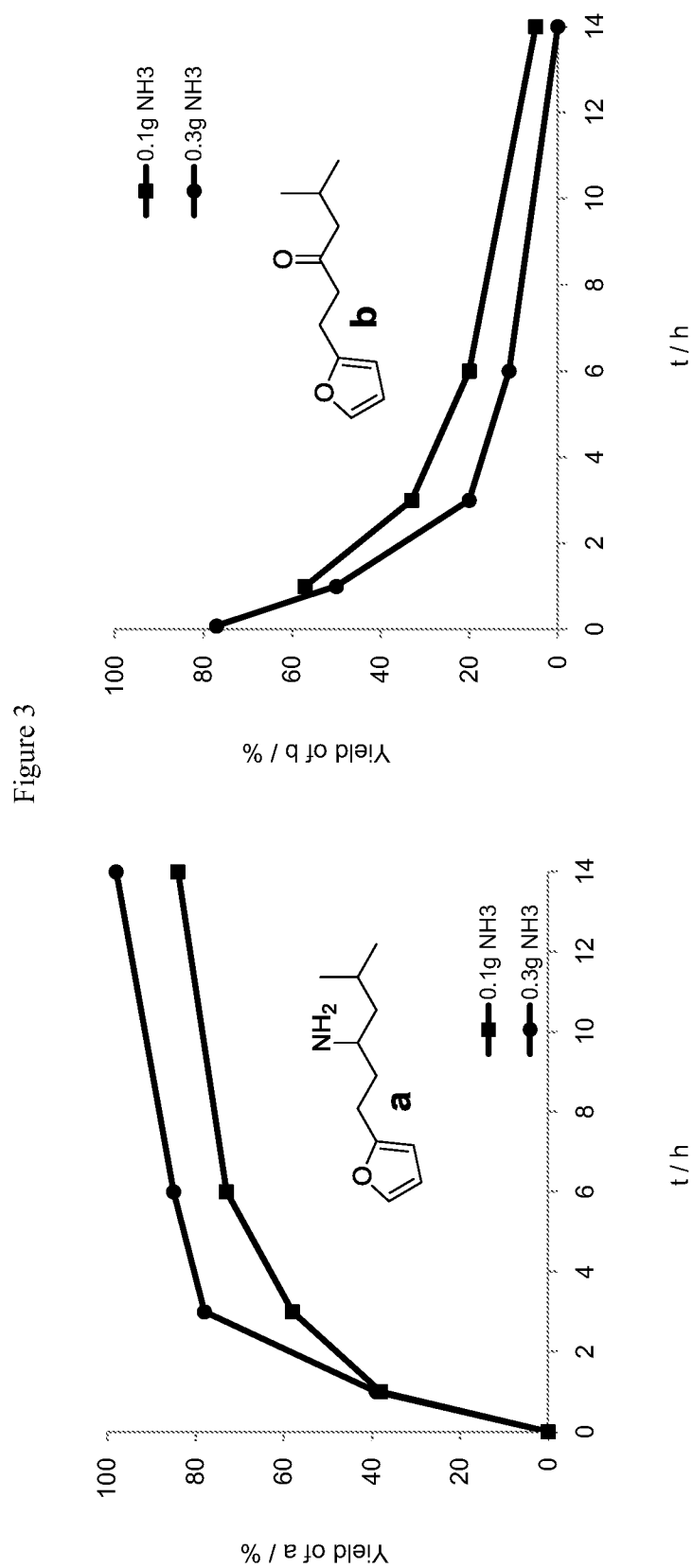
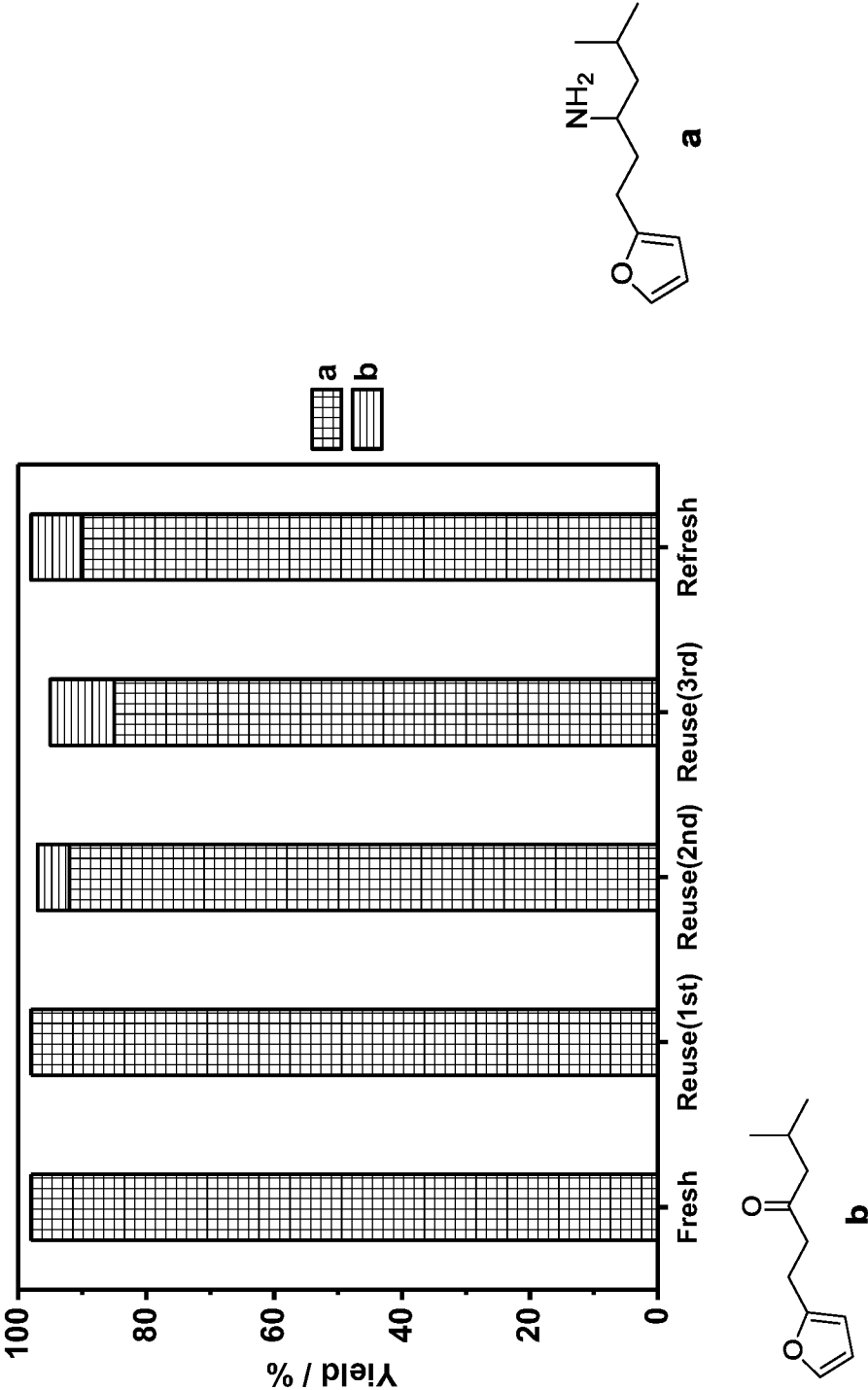


Figure 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2018/100180

A. CLASSIFICATION OF SUBJECT MATTER

C07C 211/03(2006.01)i; C07C 209/60(2006.01)i; B01J 23/46(2006.01)i

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)

C07C211/-; C07C209/-; B01J23/-

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)

CNABS, CNTXT, WPI, EPODOC, CASREACT (STN), CAPLUS(STN), CNKI: unsaturated, ketone, aldehyde, furan, reductive amination, ruthenium, hydrogen, ammonia

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 20160034084 A (KOREA RESEARCH INSTITUTE OF CHEMICAL TECHNOLOGY ET AL.) 29 March 2016 (2016-03-29) abstract, description, paragraphs [0018]-[0020]	1-4, 11
X	SU 1204617 A1 (SARAT AGRIC. INST. ET AL.) 15 January 1986 (1986-01-15) abstract, description, columns 1-6	1, 3-15
A	US 2004267051 A1 (BOERNER AMIN ET AL.) 30 December 2004 (2004-12-30) examples 16-66	1-15

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

* Special categories of cited documents:

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

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

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

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

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

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

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

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

“&” document member of the same patent family

Date of the actual completion of the international search

28 April 2019

Date of mailing of the international search report

08 May 2019

Name and mailing address of the ISA/CN

National Intellectual Property Administration, PRC
6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
100088
China

Authorized officer

GAN, Yu

Facsimile No. (86-10)62019451

Telephone No. (86-10)-53962246

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2018/100180

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				JP	2004537588	A	16 December 2004
				US	7230134	B2	12 June 2007
				EP	1414783	B1	15 July 2009
				DE	50213687	D1	27 August 2009
				CN	1538950	A	20 October 2004
				DE	10138140	A1	20 February 2003
				EP	1414783	A1	06 May 2004