Alkanes from Bioderived Furans by using Metal Triflates and Palladium-Catalyzed Hydrodeoxygenation of Cyclic Ethers


Using a metal triflate and Pd/C as catalysts, alkanes were prepared from bioderived furans in a one-step hydrodeoxygenation (HDO) process. During the reaction, the metal triflate plays a crucial role in the ring-opening HDO of furan compounds. The entire reaction process has gone through two major phases: at low temperatures, saturation of the exocyclic double bond and furan ring are catalyzed by Pd/C; at high temperatures, the HDO of saturated furan compounds is catalyzed by the metal triflate. The reaction mechanism was verified by analyzing the changes of the intermediates during the reaction. In addition, different metal triflates, solvents, and catalyst recycling were also investigated.

Introduction

With the increasing global total energy consumption, the shortage of fossil energy resources has become a very serious constraint for global economic development.[1] Biomass is a clean and renewable source of energy. Energy conversion and chemical synthesis using biomass as feedstock for the sustainable development of energy and chemical industry is of great significance.[1–8] 5-Hydroxymethyl furfural (5-HMF) is an important biomass-based platform molecule, which can be prepared from the dehydration of fructose or isomeric glucose. It is a very promising precursor for the preparation of liquid fuels.[1] So far, a lot of research has focused on the conversion of 5-HMF into alkanes. Initially, in order to prepare alkanes from 5-HMF it is necessary to increase the number of carbon atoms. Dumesic et al. converted 5-HMF into alkanes through a three-step process: first, a base-catalyzed aldol condensation of 5-HMF and acetone grows of carbon chain; second, the condensation product is hydrogenated to give tetrahydrofuran compounds; and finally alkanes are obtained after the hydrodeoxygenation (HDO) of these tetrahydrofurans.[9] To achieve tandem aldol condensation and hydrogenation reactions, Dumesic, Guanzhong Lu, and Yong Wang have developed a series of base-supported catalysts, such as Pd/MgO-ZrO2, Pd/CoAlO4, Pt/CoAlO4, and Pd/CN@MgO,[10] in which basic supports and noble metals catalyze aldol condensation and hydrogenation reactions, respectively. However, alkanes are not obtained when using these systems because the tetrahydrofuran compounds are hydrodeoxygenated completely.

In order to achieve complete HDO and prepare alkanes from condensation products, Dumesic, Huber, and Tao Zhang et al.[4,6,7] studied the process under high temperature and pressure conditions. However, vigorous reaction conditions result in coking and complicated C–C bond cleavages, which are not beneficial for the selectivity of the reaction. To achieve the conversion of condensation products into alkanes under milder conditions, a method reported by Gordon et al. uses acetic acid as solvent for the reaction system.[11] The entire reaction process is divided into two steps: first, polyketones are obtained by the exocyclic double-bond hydrogenation and acid-catalyzed ring-opening of the aldol condensation products; then, polyketones are converted into alkanes after HDO. In the course of the reaction, in order to avoid conversion of the furan ring into a tetrahydrofuran ring by excessive hydrogenation, the reaction temperature and hydrogen pressure require strict control, which complicates the procedure. Thus, achieving the hydrodeoxygenation of tetrahydrofuran compounds under mild conditions will be very beneficial to optimize the process of preparing alkanes.

A catalytic system for aldol condensation hydrogenation (Pt/CoAlO4) and catalytic hydrogenolysis (Pt/NbOPo4) were integrated by Guanzhong Lu and Yanqin Wang et al.[9] In this reaction system, liquid alkanes were obtained through a condensa-
While NbOPO$_3$ can absorb tetrahydrofurans by bonding, and then catalyze the ring-opening process of these tetrahydrofurans. Meanwhile, NbOPO$_3$ can catalyze the dehydrogenation of intermediates. The aldol condensation of 5-HMF and ketones can be relatively easily achieved by homogeneous or heterogeneous catalysis. Therefore, finding a simple, gentle, and efficient catalytic system to achieve HDO of the condensation products would significantly promote the integration of the entire process of preparing liquid alkanes from biomass.

Previous studies have shown that metal triflate is an effective Lewis-acid catalyst for the cleavage of ether bonds. In this work, we use the Pd/C-Hf(OTf)$_3$ catalytic system to obtain alkanes from bioderived furans in one-pot. Under relatively mild conditions, we obtain none nonane yields of up to 92% by a simple temperature-programmed protocol. In addition, we study the influence of other reaction conditions including solvent, Lewis acid, hydrogen pressure, and reaction time. A reaction pathway is proposed and validated.

Results and Discussion

First, using Pd/C as hydrogenation catalyst and n-octane as solvent, under 5 MPa of hydrogen pressure with a temperature program (60 °C maintained for 8 h, then heating to 180 °C and held for 20 h), we studied the catalytic effect of metal triflates on the one-pot preparation of liquid alkanes by condensation.

The nonane yield was analyzed by gas chromatography (Table 1).

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(a) Reaction conditions: 5 MPa H$_2$, 60 °C 8 h, 180 °C 20 h, 332 mg (2 mmol) condensation substrate, 0.04 mmol metal triflate, 0.1 mmol 10% Pd/C, 10 mL n-octane. Detected by GC.

During the experiment, we first used previously reported La(OTf)$_3$ as Lewis acid catalyst. After the reaction, a nonane yield only 0.1% was detected. Subsequently, we studied the catalytic effects of a series of other metal triflates. La(OTf)$_3$, Ce(OTf)$_3$, Sm(OTf)$_3$, Yb(OTf)$_3$, Sc(OTf)$_3$, and Fe(OTf)$_3$ were found to have a relatively low catalytic activity. Al(OTf)$_3$ and Hf(OTf)$_3$ showed excellent catalytic effects, with nonane yields of 73% and 87%, respectively. When analyzing the reaction results, we found a certain relationship between catalytic activity and the effective charge density of the metal ion in the metal triflate.

In metal triflates, the effective charge density of each central metal ion gradually increases from La to Hf and brought about about an increase of the nonane yield. The increase of effective charge density leads to an increase of Lewis acidity, which may result in more effective activation of the ether bond and then achieve cleavage of the C–O bond through proton transfer.

We then explored the reaction process in detail. First, we studied conversion of the substrate at the low-temperature reaction stage (Figure 1). To our surprise we found that after stirring for 0.5 h under 5.0 MPa hydrogen pressure at room temperature (ca. 25 °C), 91% of raw material A had been converted into intermediates C (66%) and D (25%). Meanwhile, intermediate B was not detected. With an extension of the reaction time (RT, stirring for 2 h), raw material A has been completely converted into intermediates C (71%) and D (29%). The mild conditions and short reaction time indicate that hydrogenation of the furan ring into a tetrahydrofuran ring is easy. Accordingly, it is difficult to selectively obtain intermediate B. In the reaction system established by Gordon, strict control of the reaction temperature and hydrogen pressure was applied to avoid hydrogenation of the furan rings into tetrahydrofurans. Because it is difficult to precisely control the hydrogen pressure during the reaction process, we developed a method for the preparation of alkanes through a tetrahydrofuran ring-opening process by simple temperature control.

At 180 °C, the HDO of intermediates C and D was studied. Under 5.0 MPa H$_2$, and intermediates C and D reacting for 20 h, nonane yields of 23% and 89% were obtained, respectively (Supporting Information, Table S1, entries 4, 6). This shows that in the preparation of alkanes, the conversion of alcohols into intermediate D is easier than the keto intermediate C. The reason is that initially C is converted into intermediate D during the process of C to alkane, which lengthens the reaction process.
tion path. Therefore, in the low-temperature process, the raw material A needs to be converted into intermediate D, which is more conducive to high temperature HDO. Because the process of C to D is relatively slow at room temperature, we increased the temperature of this low-temperature process to 60 °C to accelerate the rate of the reaction in this low-temperature phase. Under 5.0 MPa of hydrogen pressure and at 60 °C, we found that the C=C double bond and the furan ring of raw material A were rapidly saturated. This saturation process generated intermediates C and D. With the extension of the reaction time in the low-temperature regime, the keto intermediate C gradually transforms into alcoholic intermediate D. When the low-temperature reaction phase is over, after 8 h, intermediate C has been mostly transformed into D (> 90%, Figure 1), which is very favorable for the HDO process to prepare alkanes. At the same time, control experiments show that Hf(OTf)_4 has no any adverse effect on the low-temperature phase of the reaction.

We next examined the effects of hydrogen pressure on the preparation of alkanes from alcoholic intermediate D (Figure 2) or feedstock A (Figure 3). As the hydrogen pressure increased, the nonane yield obtained from intermediate D was gradually increased. When the hydrogen pressure was 5 MPa, the nonane yield reached 89%. With the hydrogen pressure of the reaction further increased to 6 MPa, the nonane yield continued to increase to 93%. This suggests that increasing the hydrogen pressure is conducive to the conversion of intermediate D into alkanes. Then, the impact of the hydrogen pressure on the reaction in the whole process was studied. The results showed that the nonane yields increased with increasing hydrogen pressure. When the hydrogen pressure was 6 MPa, the nonane yield reached up to 90%. It is worth noting that in the case of lower hydrogen pressures (2, 3, 4 MPa), the yield of nonane from intermediate D was lower than from feedstock A. The solubilities of A and D in n-octane are low. The preparation of nonane from A through D is a continuous process. Hence, the in situ-generated D could disperse in the system better than when directly using D as substrate. This may be due to the poor solubility of intermediate D in the n-octane. When using D as substrate, D is mainly present at the bottom of the reactor, and not well-dispersed. When using A as a substrate, after the end of the low-temperature phase, the reaction system is directly heated to the high-temperature reaction stage. Such a continuous process is more conducive to the dispersion of intermediate D, and therefore the reaction performed better. The increasing of the hydrogen pressure (5 or 6 MPa) accelerated the conversion of intermediate D into nonane, so the influence of the dispersion of D to the reaction is not obvious.

The effects of different reaction times (at 180 °C) on nonane yield were also studied (Figure 4; Supporting Information, Table S2). The results showed that when the reaction did not go through the 180 °C stage, nonane is not generated (Table S2, entry 1). With a gradual extension of the reaction time at 180 °C, the nonane yield rapidly increases at first, and then levels off. When the reaction time was 24 h at 180 °C, we obtained a nonane yield of 92%. The high-temperature phase requires a long reaction time, which also reflects that the ring-opening of tetrahydrofuran compounds is a difficult process.

Based on the studies above, we propose a possible mechanism for the whole reaction process in Scheme 1.[8,14,15] The process can be divided into five steps: (1) At the 60 °C low-temperature stage, the feedstock A undergoes hydrogenation of its unsaturated bonds to give the alcohol intermediate D;
(2) removal of the hydroxyl groups of the alcohol intermediate D; (3) hydrogenation of unsaturated tetrahydrofurans over Pd/C; (4) in the course of the 180 °C-stage, ring-opening of tetrahydrofurans occurs, catalyzed by Hf(OTf)4, and generating unsaturated olefins; (5) the hydrogenation of olefins gives liquid alkanes. Step (2)–(5) occur under high-temperature conditions (180 °C), simultaneously. We monitored the reaction by using GC-MS, and detected the intermediate of step 3 (2-butyl-5-methyl tetrahydrofuran), which directly proves the above mechanism. As the reaction time was extended from 4 h to 8 h (at 180 °C), the ratio of 2-butyl-5-methyl tetrahydrofuran decreased and that of product nonane increased, which means that ring-opening is the key step. Eventually, after the above five steps, the raw material A is efficiently converted into nonane through tetrahydrofuran intermediates.

In addition, we explored the effect of solvents on the reaction (Figure 5). When using methanol, water, or DMF as solvent, the nonane yields were lower than 10%. When using THF as solvent, the nonane yield was 18%. Analysis of the reaction solution by GC-MS showed that ring-opening of THF generated n-butanol and a polyether compound (Supporting Information, Figure S5). Analysis of the reaction’s gas phase by GC showed that the deoxygenated ring-opening of THF occurred and generated butene and other gases (Supporting Information, Table S4). However, when using n-octane as the solvent, the nonane yield reached 87%. The results shows that when using a solvent that has a coordinating role, the nonane yield is low. n-Octane has many excellent features, such as better heat and mass transfer, greater ability to dissolve hydrogen, reduced molecules that are non-active for competitive adsorption in the case of heterogeneous catalysts, and azeotropic removal of water. Thus n-octane is the best choice as solvent.

A recycling test of the catalysts was performed in five consecutive runs under identical conditions (Figure 6). There was a slight efficiency loss when the catalysts were reused. When the catalyst was used for the first time, a nonane yield of 87% was obtained. With increased uses of the catalyst, the nonane yields were 86%, 80%, 77%, and 73%. In the cycle, the catalytic effect of the catalyst appeared partially decreased. Furthermore, we performed transmission electron microscopy (TEM) (Supporting Information, Figure S6) and X-ray diffraction (XRD) (Supporting Information, Figure S7) tests for both fresh and used catalysts to elucidate the decrease of yields during recycling process. TEM images revealed a cluster of partial catalysts, which could be an important reason for the loss of yield. However, there was no difference between fresh and used catalysts based on XRD characterization. In addition, the operating losses during the catalyst recovery process could also lead to a reduction of the yields.

Conclusions

Using metal triflates and Pd/C as catalysts, alkanes can be prepared from bioderived furans under mild conditions through a hydrodeoxygenation process in one pot. A high pressure of hydrogen can accelerate the saturation of furan rings, and metal triflates can catalyze the deoxygenated ring-opening of cyclic ethers. Hence, we achieve a complete hydrodeoxygenation process in one pot, converting biomass-derived furan...
compounds into alkanes. The reaction can be divided into two processes: saturation of the exocyclic double bond and furan ring at low temperature; and the removal of hydroxyl groups and the ring-opening of tetrahydrofurans at high temperature. The reaction process is simple and the utilized catalysts are commercially available. The catalytic effect of different metal triflates, the effects of different solvents, and catalyst recycling were studied separately. When using n-octane as solvent and Hf(OTf)₄ as metal triflate, the highest nonane yield was 92%.

Experimental Section

Materials

All the chemicals used in the experiments are commercially available. 5-HMF was generously gifted by Hefei Leaf Energy Biotechnology Co., Ltd. Hf(OTf)₄ (98%), Pd/C (10%) from Alfa Aesar (China) Chemicals Co., Ltd. La(OTf)₃ (99%), Ce(OTf)₃ (98%), Sm(OTf)₃ (98%), Yb(OTf)₃ (98%), Sc(OTf)₃ (98%), Fe(OTf)₃ (99%), Al(OTf)₃ (99%) by Adamas Reagent Co., Ltd. n-Octane (98.0%), ethyl acetate (99.5%), petroleum ether (60–90 °C), methanol (99.5%), acetone (99.5%), tetrahydrofuran (99.0%), dichloromethane (99.5%), N,N-dimethylformamide (99.5%), sodium hydroxide (96.0%), sodium borohydride (96%), MgSO₄ (98.0%) from Sinopharm Chemical Reagent Co., Ltd. Dodecane (98%) by Energy Chemical. Silica gel (HG/T2354–2010) from Branch Qingdao Haiyang Chemical Co., Ltd. Regent water was purchased from Wahaha. The autoclave was provided by Anhui Kemi Machinery Technology Co., Ltd.

Preparation of material A (aldol condensation) [4–7, 16]

10 g 5-HMF was added to a 500 mL round bottom flask, followed by addition of 150 mL of acetone, and the 5-HMF was dissolved with stirring at room temperature. After 5-HMF was completely dissolved, 50 mg NaOH powder was added to the flask, and the mixture was stirred at room temperature for 10 h. After the reaction, the material was filtered and dried over MgSO₄ overnight. After filtering again, the liquid was evaporated in vacuo, and separation by column chromatography (petroleum ether/ethyl acetate = 1:1) afforded 8.3 g raw material A (Supporting Information, Figure S8–1).

Preparation of intermediates B, C, and D [8, 17]

2 g A and 200 mg Pd/C were weighed in a 100 mL Schlenk flask. 50 mL of methanol was added to the flask and the contents were mixed well. At 1 atm hydrogen pressure and 60 °C, the reaction was carried out for 10 h. After the reaction was cooled to room temperature, filtered, and the liquid evaporated in vacuo, separation by column chromatography (petroleum ether/ethyl acetate = 2:1) afforded 1.2 g of intermediate B (Figure S8–2).

2 g A and 200 mg Pd/C were weighed in a 100 mL autoclave reactor. 50 mL of methanol was added to the reactor and the contents were mixed well. At 5 MPa hydrogen pressure and room temperature, the reaction was carried out for 0.5 h. After completion of the reaction, the mixture was filtered and the liquid evaporated in vacuo. Separation by column chromatography (petroleum ether/ethyl acetate = 1:1) gave 1.4 g of intermediate D (Figure S8–4).

Preparation of alkanes

332 mg of raw materials A, 39 mg Hf(OTf)₄, and 106 mg Pd/C were charged in a 30 mL autoclave reactor. 10 mL of n-octane was added to the reactor, and it was then filled with hydrogen to 5 MPa. Then, the reaction started at an elevated temperature programme (60 °C for 16 h, 180 °C for 20 h). After completion of the reaction and cooling to room temperature, 10 mL of ethyl acetate and the internal standard dodecane were added. The nonane yield was detected by gas chromatography.

Reusability

After completion of the reaction, Pd/C was filtered off and washed with ethyl acetate and then dried in vacuo. The filtrate was extracted with 5 × 3 mL water, the aqueous phase was evaporated to dryness in vacuo, and dried in vacuo. Then, the obtained Pd/C and metal triflate were used to catalyze the next reaction round.

Analysis methods

Substrates and products were detected by flame ionization detector gas chromatography (GC-FID, Shimadzu GC-2014), which used Rtx-5 (30 m (ø)w0.32 mm (ø)w0.25 m) as capillary column. Intermediates were detected by gas chromatography–ion trap mass spectrometry (GC–MS, Thermo Scientific ITQ1100), which used TR-5 MS (30 m (ø)w0.25 mm (ø)w0.25 m) as capillary column. The NMR spectra of compounds were detected by using a Bruker nuclear magnetic resonance spectrometer (400 MHz).

Acknowledgements

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Keywords: alkanes • fuels • hydrodeoxygenation • renewable resources • ring-opening reactions


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Supporting Information

Alkanes from Bioderived Furans by using Metal Triflates and Palladium-Catalyzed Hydrodeoxygenation of Cyclic Ethers


cssc_201500907_sm_messellaneous_information.pdf
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S 2: Effects of different reaction time (at 180 °C) on nonane yield
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S 8: NMR spectrum of different substances
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S 10: The comparison of previous major work (and this work)
S 11: Preparation process of intermediates
The batch reactor
Table S 1: The nonane yield of different substrates.

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[^a] Reaction conditions: 180 °C 20 h, 2 mmol C or D as substrate, 0.04 mmol Hf(OTf)₃, 0.1 mmol 10% Pd/C, 10 mL n-octane. 
[^b] Reaction conditions: 60 °C 8 h, 180 °C 20 h, 2 mmol A as substrate, 0.04 mmol Hf(OTf)₃, 0.1 mmol 10% Pd/C, 10 mL n-octane. 
[^c] Detected by GC.
Table S 2: Effects of different reaction time (at 180 °C) on nonane yield.\textsuperscript{[a]}

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\textsuperscript{[a]} Reaction conditions: 5 MPa H\textsubscript{2}, 60 °C 8 h, 332 mg (2 mmol) feedstock A, 0.04 mmol Hf(OTf)\textsubscript{3}, 0.1 mmol 10% Pd/C, 10 mL n-octane. \textsuperscript{[b]} Detected by GC.
**Figure S 3:** GC-MS of different intermediates

Figure S 3-1, 2, 3, 4, 5, 6 were detected by gas chromatograph ion trap mass spectrometer (GC-MS, Thermo Scientific ITQ1100), which used TR-5MS (30 m × 0.25 mm × 0.25 μm) as capillary column.

**Figure S 3-1:** Gas chromatogram of the reaction (D at 180 °C for 8h)

**Figure S 3-2:** Gas chromatogram of the reaction (D at 180 °C for 4h)
Figure S 3-3: Mass spectrum of n-nonane

Figure S 3-4: Mass spectrum of 2-butyl-5-methyl tetrahydrofuran
Figure S 3-5: Mass spectrum of 2-butyl-5-hydroxymethyl tetrahydrofuran

Figure S 3-6: Mass spectrum of dinonyl ether
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[a] Reaction conditions: 5 MPa H<sub>2</sub>, 180 °C 16 h, 0.04 mmol Hf(OTf)<sub>3</sub>, 0.1 mmol 10% Pd/C, 10 mL THF. [b] Detected by GC.
**Figure S5:** GC-MS of the reaction (THF)

Figure S 5-1, 2, 3, 4, 5 were detected by gas chromatograph ion trap mass spectrometer (GC-MS, Thermo Scientific ITQ1100), which used TR-5MS (30 m × 0.25 mm × 0.25 μm) as capillary column.

**Figure S 5-1:** Gas chromatogram of the reaction (THF at 180 °C for 16h)

**Figure S 5-2:** Mass spectrum of dibutyl ether
Figure S 5-3: Mass spectrum of butyl alcohol

Figure S 5-4: Mass spectrum of Trimer
Figure S 5-5: Mass spectrum of Tetramer
Figure S6: TEM images of Pd/C (fresh and used)

Figure S 6-1: The TEM image of fresh Pd/C

Figure S 6-2: The TEM image of used Pd/C
**Figure S7:** XRD of Pd/C (fresh and used)
Figure S 8: NMR spectrum of different substances

Figure S 8-1: NMR spectrum of feedstock A

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.25 (d, 2H), 6.63 (m, 2H), 6.40 (d, 2H), 4.66 (s, 2H), 2.32 (s, 3H), 2.12 (s, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 197.93, 156.85, 150.77, 129.29, 124.13, 116.68, 110.48, 57.61, 28.03.
**Figure S 8-2: NMR spectrum of Intermediate B**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.16 (d, 1H), 5.94 (d, 1H), 4.53 (s, 2H), 2.89 (t, 2H), 2.79 (t, 3H), 2.17 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 207.51, 154.66, 152.68, 108.56, 106.01, 57.38, 41.61, 29.92, 22.22.
**Figure S 8-3: NMR spectrum of Keto intermediate C**

$^1$H NMR (400 MHz, CDCl$_3$): δ 3.99 (m, 1H), 3.89 (m, 1H), 3.67 (m, 1H), 3.47 (m, 1H), 2.57 (m, 2H), 2.41 (s, 1H), 2.17 (s, 3H), 1.99 (m, 1H), 1.89 (m, 1H), 1.80 (m, 2H), 1.72 (m, 1H), 1.53 (m, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 209.20, 79.69, 79.17, 65.06, 40.38, 31.32, 30.04, 29.69, 26.90.
**Figure S 8-4: NMR spectrum of Alcoholic intermediate D**

$^{1}H$ NMR (400 MHz, CDCl$_3$): $\delta$ 4.03 (m, 1H), 3.90 (m, 2H), 3.70 (m, 1H), 3.49 (m, 1H), 2.92 (s, 2H), 1.99 (m, 1H), 1.91 (m, 1H), 1.76 (m, 1H), 1.64 (m, 2H), 1.55 (m, 3H), 1.19 (d, 3H).

$^{13}C$ NMR (100 MHz, CDCl$_3$): $\delta$ 80.33, 80.17, 79.88, 79.76, 68.07, 67.52, 64.97, 64.90, 36.18, 35.67, 32.62, 31.56, 31.53, 31.36, 26.91, 26.89, 23.59, 23.37.
Figure S 9: Gas chromatogram of different substances

Figure S 9-1, 2, 3, 4, 5 were detected by flame ionization detector gas chromatography (GC-FID, Shimadzu GC-2014), which used DM WAX (30 m × 0.32 mm × 0.25 μm) as capillary column.

Figure S 9-1: Gas chromatogram of feedstock A

Figure S 9-2: Gas chromatogram of intermediate D
Figure S 9-3: Gas chromatogram of intermediate C

Figure S 9-4: Gas chromatogram of intermediate B
Figure S 9-5: Gas chromatogram of low temperature reaction stage

Figure S 9-6 were detected by flame ionization detector gas chromatography (GC-FID, Shimadzu GC-2014), which used Rtx-5 (30 m × 0.32 mm × 0.25 μm) as capillary column.

Figure S 9-6: Gas chromatogram of the whole reaction process
Figure S10-1: The comparison of previous major work

Table S10-2: The comparison of previous major work and this work

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Catalyst</th>
<th>Hydrogen Pressure/MPa</th>
<th>Temp.</th>
<th>Yield/%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>Pd/C, La(OTf)₃</td>
<td>0.37, 2.07</td>
<td>100, 200</td>
<td>74</td>
<td>[a]</td>
</tr>
<tr>
<td>scCO₂</td>
<td>Pd/Al-MCM-41</td>
<td>4, (18)</td>
<td>80</td>
<td>99</td>
<td>[b]</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>Pd/NbOPO₄</td>
<td>2.0</td>
<td>170</td>
<td>94</td>
<td>[c]</td>
</tr>
<tr>
<td>Free</td>
<td>Pd/C</td>
<td>6</td>
<td>370</td>
<td>90</td>
<td>[d]</td>
</tr>
<tr>
<td>n-Octane</td>
<td>Pd/C, Hf(OTf)₄</td>
<td>5</td>
<td>60, 180</td>
<td>92</td>
<td>[e]</td>
</tr>
</tbody>
</table>

[e] This work.
Figure S11: Preparation process of intermediates

[a] Method 4: 1 atm H₂, 60 °C, 1 h (Nat. Chem. 2013, 5, 428-432)
[b] Method 2: 1 atm H₂, 60 °C, 24 h (Nat. Chem. 2013, 5, 428-432)
[c] Our method: 5 MPa H₂, r.t., 0.5 h (Ref.: Rajeev S. Assary, Paul C. Redfern, Jeff R. Hammond, Jeffrey Greeley, Larry A. Curtiss, Chem Phys Lett 2010, 497, 123-128)
[d] NaBH₄, room temperature.