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Production of Low-Freezing-Point Highly Branched Alkanes via Michael Addition

Yaxuan Jing, Qineng Xia, Xiaohui Liu and Yanqin Wang*^[a]

Abstract: A new approach for the production of low freezing point, high-quality fuels from lignocellulose derived molecules was developed with Michael addition as the key step. Among the investigated catalysts, CoCl₂·6H₂O was found most active for the Michael addition of 2,4-pentanedione with FA (single aldol adduct of 4-(2-furanyl)-3-butene-2-one). furfural and acetone. Over CoCl₂·6H₂O, a high carbon yield of C₁₃ oxygenates (about 75%) can be achieved under mild conditions (353 K, 20 h). After hydrodeoxygenation, low freezing point (< 223 K) branched alkanes with 13 carbons within jet fuel ranges were obtained over Pd/NbOPO₄ catalyst. Furthermore, $C_{18,23}$ fuel precursors could be easily synthesized through Michael addition of 2,4-pentanedione with DFA (double-condensation product of furfural and acetone) under mild conditions and the molar ratio of C_{18}/C_{23} is dependent on reaction conditions of Michael addition After the hydrodeoxygenation, high density (0.8415 g/ml) and low freezing point (< 223 K) branched alkanes with 18, 23 carbons within lubricant range were also obtained over Pd/NbOPO₄ catalyst. These highly branched alkanes can be directly used as transportation fuels or additives. This work opens a novel strategy for the synthesis of highly branched alkanes with low-freezing-point from renewable biomass.

With the diminishing of fossil resources and the growing of environmental concerns, the conversion of biomass to chemicals and fuels has received increasing attention.[1] Liquid transportation fuels are mainly obtained from petroleum nowadays, while the increasing demand for transportation fuels requires ideal substitutes of oil-based ways. This demand has led to active research with the liquid fuels from lignocellulose, which accounts for more than 60% of the entire biomass.^[2] As we know, straight alkanes have lower octane numbers for gasoline, lower density and higher freezing points, and cannot directly used transportation fuels be as without hydroisomerization. To meet the specification of transportation fuels, high branched alkanes should be synthesized and added to the transportation fuels to increase the density, octane numbers and decrease the freezing point.

Generally, the process for producing gasoline, diesel, jet fuel and so on from lignocellulose-derived platform chemicals involves two steps, namely, the C-C bond coupling reaction and the following hydrodeoxygenation (HDO). Currently, there are three main routes for C-C bond coupling to convert lignocellulose-derived platform molecules into transportation fuel precursors (oxygenates). The first method is the aldol

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the document.

condensation, for example, the aldol condensation of furfural (or 5-hydroxymethylfurfural) with ketones containing α -H atoms to obtain long-chain oxygenates.[3] The second approach involves hydroxyalkylation/alkylation (HAA) of 2-methylfuran (2-MF) and lignocellulose-derived carbonyl compounds (furfural 5hydroxymethylfurfural, 5-methylfurfural, acetone, hydroxylacetone, etc.) to produce transportation fuel range oxycompounds.^[4] The third strategy adopts benzoin coupling of lignocellulose-derived platform molecules (furfural, 5hydroxymethylfurfural, aromatic aldehydes) synthesize to transportation fuel precursors.^[5]

Inspired by all of the above routes, we are interested in the exploration of potential C-C bond coupling reaction and a new approach for converting lignocellulose-derived platform chemicals into transportation fuel range branched alkanes. It is well-known that Michael addition of β -dicarbonyl compounds to α , β-unsaturated carbonyl compounds is one of the most important C-C bond forming reactions in organic chemistry. However, the Michael addition for converting lignocellulose-derived platform compounds into transportation fuels is not reported. 2,4pentanedione, as a β -dicarbonyl compound, can be produced by ring-opening and decarboxylation of biomass-derived chemicals (4-hydroxy-6-methyl-2-pyrone) in the absence of a catalyst when water is used as the solvent.^[6] Furfural-acetone [4-(2-furanyl)-3buten-2-one, FA], a C8 oxygenate, easily produced through the aldol condensation of acetone and furfural,^[3a] contains an enone group in the middle position of the C_8 oxygenate, which makes it an ideal acceptor of the Michael addition and an excellent precursor to generate high branched alkanes. Therefore, we developed a novel approach for the production of high branched C₁₃ alkanes from Michael addition of 2,4-pentanedione and the aldol adducts of furfural, followed by the one-step HDO process under mild conditions for the first time. This $C_{\rm 13}$ branched alkanes have low freezing points, high density and can be blended into transportation fuels without hydroisomerization. Furthermore, the highly branched C₁₈₋₂₃ alkanes that can be used as lubricant were also prepared.

The process for converting furfural into jet fuel range branched alkanes (Scheme 1) consists of three steps: (1) the aldol condensation of furfural and acetone to C₈ oxygenate (4-(2-furanyl)-3-butene-2-one, FA), (2) the Michael addition of FA and 2,4-pentanedione to jet fuel range C₁₃ intermediates (furfural-acetone-diketone, FAD) (structural analysis see Figure S1-S4 in the Supporting Information), and (3) the one-step hydrodeoxygenation of FAD to aviation fuel range branched alkanes (structural analysis see Figure S5-S9 in the Supporting Information). The targeted alkane has low freezing point and can be added directly into jet fuel without hydroisomerization. The core of this route is to increase the carbon chain length by Michael addition. This new route not only supplies a fully undeveloped C-C bond coupling reaction for biomass-derived compounds, but also provides a new approach for converting lignocellulose derived platform chemicals into jet fuel ranged branched alkanes.

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Scheme 1. Reaction pathway for the production of jet fuel range branched alkanes.



Figure 1. Michael addition of FA with 2,4-pentanedione over various catalysts. 0.2 g of FA, 5 g of 2,4-pentanedione, 0.05 g of catalyst, 0.1 g of CaCl₂, 80 °C, 20h.

The aldol condensation of furfural with acetone can be carried out with a liquid or solid base. NaOH was used here to enable the complete conversion of furfural to synthesize FA (the details of the aldol adduct preparation see the Supporting Information).^[3a, 7] FA, which contains an enone group, is an ideal acceptor of Michael addition. Similarly, 2,4-pentanedione is considered to be one of the typical β-dicarbonyl compounds. 2,4-pentanedione plays two key roles in the Michael addition process: one is the suitable solvent to dissolve FA; another is the reactant involved in the conjugate addition.

Generally, Michael addition can be catalyzed by alkaline species. Figure 1 shows the conversions of FA and the yields of FAD over various catalysts. The mechanism for base catalysis involves the formation of an anion from the active methylene compound, and the 1,4-addition of the anion to the α , β -unsaturated carbonyl complex, followed by the acceptance of a proton.^[8] As typical alkaline species, potassium tert-butoxide (KTB) and KOH were used first, but demonstrated a relatively poor catalytic efficiency with 77.3% conversion of FA and 46.6% yield of FAD, 70.1% conversion of FA and 46.6% yield of FAD, respectively. This may be due to their strong basic properties, where a lot of side and subsequent reactions are

catalyzed, such as self condensations of FAD and the further aldol condensation of FAD with 2,4-pentanedione. Transition metal chlorides are also good catalysts for Michael addition, because they have ability to form chelate complexes with β -dicarbonyl compounds. CoCl₂·6H₂O, an eco-friendly substitution to classical basic catalyst, was used and exhibited the best catalytic activity for Michael addition with 82.9% FA conversion and 75.1% FAD yield. As chemically similar transition metal chlorides, both FeCl₃·6H₂O and NiCl₂·6H₂O which have ability to generate chelate compounds with β -dicarbonyl were also active for this reaction, but did not perform as well as CoCl₂·6H₂O. In contrast, AlCl₃·6H₂O was inert for this reaction. Therefore, highly active and inexpensive CoCl₂·6H₂O was employed as Michael addition catalyst for further investigations.



Scheme 2. Proposed reaction mechanism of the Co(II)-catalyzed Michael addition of FA with 2,4-pentanedione.

Based on our results and previous reports,^[9] we proposed a reaction mechanism for Co(II)-catalyzed Michael addition and present in Scheme 2. Firstly, the chelate ligand 4 is formed by the coordination of donor 1 to the metal center. The chelate ligand 4 shows a planar configuration and it is commendably stabilized by II-delocalisation. Then the acceptor 2 of 1,4addition results in the formation of complex 5 by ligand exchange. The metal center is not only to hold the acceptor 2 in proximity to donor 1, but also activated acceptor 2 by its Lewis acidity. Subsequently, the complex 5 undergoes the nucleophilic conjugate addition to form new C-C bond, which affords the intermediate 6. Finally, the target product 3 is liberated from the intermediate 6 and the chelate ligand 4 is regenerated by coordination with donor 1. Christoffers et al. performed quantum chemical density functional calculations to prove the catalytic cycle,^[9b] but direct support from experiment for the catalytic cycle and the intermediates is still lacking so far. So, we tried to characterize the intermediates in the catalytic reaction by ESI-TOF MS and the result is present in Figure S10. An obvious molecular ion peak at 258.0 [M+1] was detected, may be attributed to intermediate 4 (the chelate ligand formed by the coordination of donor to the metal center). To conform this, the MS profile of the mixture of 2,4-pentanedione and CoCl₂ was also measured and a molecular ion peak at 258.0 [M+1] was also found (Figure S11 in the Supporting Information), so we believe that intermediate 4 does exist in the catalytic cycle. By analyzing the molecular weight, we found the molecular ion peak at 258.0 [M+1] was attributed to cobalt (II) acetylacetonate

 $(Co(C_5H_7O_2)_2)$. To further prove this, we employed cobalt (II) acetylacetonate instead of $CoCl_2 \cdot 6H_2O$ to catalyze the Michael addition of 2,4-pentanedione with FA and found it really showed good catalytic performance (74.4% yield), indicating cobalt (II) acetylacetonate is indeed a stable form of intermediate **4**. However, due to poor stability and low degree of ionization, other possible intermediates cannot be detected.

To optimize the reaction parameters, Michael addition was conducted under various conditions (such as reaction temperature and reaction time) over $CoCl_2 \cdot 6H_2O$ catalyst and the results are shown in Figure. 2. It is found that the increase of reaction temperature from 60 to 80 °C observably enhanced the conversion of FA from 47.2 to 82.9% and the yield of FAD from 44.3 to 75.1%. Further increase the reaction temperature to 100 °C, the conversion of FA also increased, reached 97.6%, however, the yield of FAD significantly decreased to 52.3%. We find that the subsequent reactions, such as the self-aldol condensation of FAD happened under higher temperature, resulted in the decrease of the yield of FAD. Therefore, 80 °C is a suitable temperature for Michael addition.







Figure 3. Michael addition of FA with 2,4-pentanedione with different reaction time over $CoCl_2 \cdot 6H_2O$. 0.2 g of FA, 5 g of 2,4-pentanedione, 0.05 g of $CoCl_2 \cdot 6H_2O$, 0.1 g of $CaCl_2$, 80 °C.

Figure 3 shows the conversion of FA and the yield of FAD as a function of time. The conversion of FA markedly increases

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from 44.2 to 89.4% and the yield of FAD significantly increases from 37.8 to 75.1% as the time prolongs from 4 to 20 h. However, further increase of time did not affect the yield of FAD, implying 20 h is an applicable time for Michael addition.

To probe the influence of excessive reaction conditions, we tested the Michael addition over CoCl₂·6H₂O catalyst at 100 °C for 30h. The GC-MS trace reveals that the self-aldol condensation of FAD was really happened under excessive reaction conditions (Scheme S1, Figure S12-S14 in the Supporting Information). Interestingly, C13 cycloalkanes were seized by GC-MS after hydrodeoxygenation (Figure S15 and Figure S16 in the Supporting Information). This result is in good consistent with the above reduction of FAD yield with the increase of reaction temperature from 80 to 100 °C. As we know, cyclic hydrocarbons have relatively higher densities or volumetric heating values than chain alkanes due to strong ring strain and can be directly blended with conventional transportation fuels. The unexpected finding provides extensive insight in converting lignocellulose derived molecules to transportation fuel range cycloalkanes with Michael addition and aldol condensation for us.

To eliminate the influence of water in non-pretreated 2.4pentanedione, we added anhydrous calcium chloride as desiccant during reaction. Compared with the result without CaCl₂, the yield of FAD significantly increases from 48.6 to 75.2% (shown in Figure S17 in the Supporting Information). This result suggests that CaCl₂ can absorb water in the reaction system to prevent the hydrolysis of 2,4-pentanedione (2,4pentanedione easily hydrolyzes to acetone and acetic acid), so the side reaction was effectively prohibited. As comparison, when soly CaCl₂ was involved, not FAD was obtained, indicating that CaCl₂ does not have catalytic activity for Michael addition. To see whether the interactions of CaCl₂ with CoCl₂·6H₂O exist and affect reaction, 2,4-pentanedione was pre-treated with anhydrous calcium chloride to remove water, then the Michael addition of pre-treated 2,4-pentanedione, FA and CoCl₂·6H₂O was carried out and 72.0% FAD yield was achieved, a little bit lower than that (75.2%) with CaCl₂ co-added during reaction, this may be comes from the influence of crystalline water in CoCl₂·6H₂O. These results indicate that CaCl₂ just plays a desiccant role and it is better to add during reaction.

In order to get branched alkanes, the hydrodeoxygenation (HDO) of FAD was investigated. Our previous studies showed that Pd supported NbOPO4 catalyst had excellent activity and stability for the total HDO of biomass and biomass-derived oxygenated chemicals.^[10] Experimental and theoretical studies indicated that Pd supported NbOPO4 plays three key roles for HDO, namely, the noble metal for H₂ activation and dissociation, NbOx species for C-O bond activation and acid sites for dehydration. Therefore, the HDO of Michael addition products was carried out over Pd/NbOPO4 catalyst and very high yield of long carbon chain alkanes was achieved. As comparison, H-ZSM-5 and Al₂O₃ were also used as support and found that the activity for the HDO of Michael addition products decreases as follows: $Pd/NbOPO_4 > Pd/H-ZSM-5 > Pd/Al_2O_3$, indicating that NbOPO₄ is really the best support for HDO process. As comparison, Rh, Pt and Ru supported NbOPO₄ were also involved as HDO catalysts, but only 54.0, 46.8 and 29.0 % yield of C13 alkanes were obtained, respectively (Figure 4). Notably, a large amount of C-C cleavage products was formed over Rh, Pt and Ru supported NbOPO₄. Especially for Ru/NbOPO₄ catalyzed HDO, deep C-C cleavage products were obtained (mathane and ethane in gas phase). These results clearly



revealed that Pd/NbOPO4 was a more suitable catalyst for the HDO of Michael addition products.

produce C_{18,23} branched alkanes (Scheme 3), the molar ratio of C₁₈ to C₂₃ is dependent on reaction conditions of Michael addition (Figures S24-S26 in the Supporting Information). High carbon length alkanes with a molecular weight of 230-500 (from MSDS,(Material Safety Data Sheet)) are the main constituents of lubricants and highly branched alkanes can be added to lubricants to increase oxidation stability. Therefore, the highly branched C18,23 alkanes can be used as the components of lubricant. Generally, lubricant alkanes are mainly produced by hydrocracking and hydroisomerization of long-chain paraffinic and naphthenic compounds. However, similar to the process (C-C bond coupling reaction and the following hydrodeoxygenation) producing conventional transportation fuels of from lignocellulose-derived chemicals, the approach to convert lignocellulose-derived platform compounds into lubricant alkanes was rarely developed.^[3f,11] Here we open a new strategy for the synthesis of high-quality lubricant-based oil components from lignocellulose-derived chemicals.

100

90

80

70

60;

40

30

20

Yield (%) 50 C8 alkane

C₉ alkane

C₁₁ alkane

C₁₃ alkane

Figure 4. Results of HDO of FAD over various catalysts. Reaction conditions: FAD (0.2 g), cyclohexane (6.46 g), catalyst (0.1 g), 200 °C, 4 MPa H₂, 12 h.

The influence of reaction temperature on the yields of Michael addition products was investigated and shown in Figure 5. The increase of reaction temperature from 160 to 180 °C observably enhanced the yield of C₁₃ alkanes from 1.3 to 79.1%, indicating that a reasonably high temperature is required to overcome the energy barrier. We found that the yield of jet fuel range branched alkanes (C13 alkanes) reached up to 79.1% with a small amount of C-C cleavage products (C11, C9 and C8 alkanes). The C₁₁ and C₉ branched alkanes were generated by the hydrocracking of the branched C2 alkyl groups and the C8 alkanes were produced by the hydrocracking of the branched C5 alkyl groups (Scheme S2 in the Supporting Information), respectively, the other portion is owing to incomplete reaction of substrate, FA in Michael addition. Further increase of reaction temperature to 200 °C slightly decreased the yield of C13 alkanes to 69.3%, with the increase of C-C cleavage products (C11 and C9 alkanes). These results indicate that excessive temperature would promote C-C cleavage. Furthermore, none of oxygenates were seized by GC-MS as the temperature increased from 180 to 200 °C, however, a large amount of oxygenates were seized by GC-MS from 160 to 170 °C (Figure S18-S20 in the Supporting Information). Therefore, 180 °C is a suitable temperature for the HDO of Michael addition products. After five recycling experiments, Pd/NbOPO₄ catalyst shows a high reusability for the HDO of Michael addition products (Figure S21 and Figure S22 in the Supporting Information).

Based on the above results, we can conclude that Michael addition, just as the aldol condensation, alkylation reaction and benzoin coupling, is also an appropriate C-C bond coupling reaction for biomass-derived compounds. Similar to the FA, DFA (double-condensation products of furfural with acetone; see the Supporting Information for details of the aldol adduct preparation) also contains enone groups, which should be an ideal acceptor of the Michael addition(Figure S23 in the Supporting Information). Therefore, we utilized DFA and 2,4pentanedione as substitutes to synthesize C18 (molar ratio of 2,4-pentanedione to DFA = 1) and C_{23} (molar ratio of 2,4pentanedione to DFA = 2) intermediates (double-furfuralacetone-diketone, DFAD) through Michael addition. Then, the one-step hydrodeoxygenation of DFAD was performed to 160 170 180 190 200 Reaction temperature (°C)

10 0

Figure 5. Results of HDO of FAD under various reaction temperature over Pd/NbOPO₄. Reaction conditions: FAD (0.2 g), cyclohexane (6.46 g), Pd/NbOPO₄ (0.1 g), 4 MPa H₂, 12 h.



Scheme 3. Reaction pathway for the production of C18 and C23 branched alkanes

Similarly, CoCl₂·6H₂O and Pd/NbOPO₄ were employed as Michael addition and HDO catalysts for further investigations, respectively. One intractable problem in this approach is that DFAD has too higher molecular weight (molecular weight of C18



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intermediates = 314; molecular weight of C_{23} intermediates = 414) and boiling point to be analysized by GC; fortunately, the C_{18} and C_{23} branched alkanes can be seized by GC. Hence, the product distributions of the C_{13} , C_{18} and C_{23} branched alkanes achieved under different reaction time of Michael addition are analysized and shown in Figure 6.



Figure 6. The product distribution of the C₁₃, C₁₈ and C₂₃ branched alkanes under different reaction time of Michael addition. Reaction conditions of Michael addition: 0.5 g of DFA, 5 g of 2,4-pentanedione, 0.1 g of CoCl₂·6H₂O, 0.1 g of CaCl₂, 80 °C. Reaction conditions of HDO: DFAD (0.2 g), cyclohexane (6.46 g), Pd/NbOPO₄ (0.1 g), 4 MPa H₂, 12 h, 190 °C.

It can be seen from Figure 6 that the portion of C₂₃ and C₁₈ were 5.9 and 76.3% at the time of 4 h, suggesting that the Michael addition of C13 intermediates with 2,4-pentanedione is easily happened. The selectivity to C23 markedly increased from 5.9 to 49.9% as the time prolonged from 4 to 20 h, with the selectivity to C₁₈ significantly decreased from 76.3 to 39.5%, implying that Michael addition of C₁₈ intermediates and 2,4pentanedione is really involved. Further increase the reaction time to 28 h, the selectivity to C₂₃ slowly increased from 49.9 to 53.8% and the selectivity to C_{18} slightly decreased from 39.5 to 35.6%, which may be caused by the self-aldol condensation of C_{18} intermediates under excessive reaction time because C_{18} cycloalkanes were seized by GC-MS (Scheme S3, Figure S27 and Figure S28 in the Supporting Information). Therefore, we could control the product distribution of C18 and C23 branched alkanes by adjusting the reaction time of Michael addition.

The transportation fuel-related properties including density and freezing point were measured to evaluate the potential as aviation fuel and lubricant and shown Table 1. Freezing point was measured according to GB/T 510 standard test method by BF-13C Freezing Point Apparatus. Density was measured by DMA 4500M Density Meter of Anton Paar. The C₁₃ branched alkane has a density of 0.8005 g/ml at 298 K and a freezing point of lower than 223 K (equipment measurement limitation). In contrast, the density and the freezing point of n-tridecane are 0.7650 g/ml at 298 K and about 268 K, respectively. Therefore, the C13 targeted alkanes have three satisfactory advantages, namely, low freezing point, high density and excellent branched chain structure. These superiorities are ideal for the widely used aviation aircraft, suggesting the branched liquid alkane is suitable for jet fuel. The C18,23 branched alkane has a density of 0.8415 g/ml at 298 K and a freezing point of lower than 223 K, may be a good component of lubricant. Therefore, The C13 branched alkane and the C18,23 branched alkanes are desirable candidates for transportation fuels.

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Table [•]	1 . Pr	operties	of	C13	and	C18 23	branched	alkanes.
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Property	C ₁₃ ^a	C ₁₈₋₂₃ ^b
Density at 298 K(g/ml)	0.8005	0.8415
Freezing point(K)	< 223	< 223

[a] C_{13} are composed of C_{13} alkane (79.1%) and other carbon numbers alkanes.

[b] $C_{18,23}$ are composed of C_{18} alkane (39.5%), C_{23} alkane (49.9%) and other carbon numbers alkanes.

In summary, we have presented a novel process for converting furfural into liquid transportation fuels through three consecutive catalytic steps that involve aldol condensation, Michael addition and hydrodeoxygenation. It has been demonstrated that the Michael addition of 2.4-pentanedione with FA (single aldol adduct of furfural and acetone) can be carried out conveniently with cheap transition metal chloride to obtain jet fuel range (C₁₃) oxygenates with 75.1% yield with reaction at 353 K for 20 h. 79.1% yield of high branched C13 alkanes was achieved from C_{13} oxygenates by the total hydrodeoxygenation over Pd/NbOPO4 at 453 K, 4 MPa H2 for 12 h. With the successful expansion of the substrate, lubricant range (C18,23) oxygenates were achieved from Michael addition of 2,4pentanedione with DFA (double-condensation product of furfural and acetone) and the product distribution of C_{18} and C_{23} branched alkanes is dependent on the reaction time of Michael addition. Specifically, the C13 and C18,23 branched alkanes possess low freezing point, high density, excellent branched chain structure and can be directly blended with conventional transportation fuels or as the component of lubricant. This work opens a novel strategy for the synthesis of low-freezing-point and high branched alkanes from renewable biomass.

Experimental Section

The Michael addition of FA and 2,4-pentanedione was performed in 50ml round-bottom flask. Typically, 2,4-pentanedione (5g), FA (0.2g), $CoCl_2 \cdot 6H_2O$ (0.05g) and $CaCl_2$ (0.1g) were transferred into the flask, which was then heated to a certain temperature (60 to 100 °C) and allowed to react for a certain time (4–28 h). The reactor was quenched in an ice-water bath to stop the reaction immediately. The liquid solution was separated from the solid catalyst by centrifugation and analyzed qualitatively by GC-MS (Agilent 7890A-5975C) and quantitatively by GC-FID (Agilent 7890) using tridecane as the internal standard. Conversion of FA and yield of FAD were calculated by using the equation: FA conversion [%] = (moles of FA reacted) / (moles of starting FA) × 100%, FAD yield [%] = (moles of FAD produced) / (moles of starting FA) × 100%.

For the separation of product (FAD) and recovery of un-reacted substitutes, 10ml of deionized water were put into the flask after Michael reaction. Then, FAD, FA and 2,4-pentanedione were extracted from the flask by 3 * 20 ml of dichloromethane. Finally the mixture of FAD and FA were directly obtained by removing dichloromethane with rotary evaporation at 40 °C and 2,4-pentanedione with rotary evaporation at 75 °C. Dichloromethane and 2,4-pentanedione can be reused without further purification. The relatively pure FAD was purified by silica gel column chromatography and used as standard, the structure and purity were confirmed by ¹H NMR, ¹³C NMR spectroscopy and mass spectrometry.

The HDO of as-prepared products and FA mixture was conducted in a 50 mL Teflon-lined stainless-steel autoclave. Typically, mixture (0.2 g), Pd/NbOPO₄ (0.1 g), and cyclohexane (6.46 g) were transferred into the autoclave. The reactor was then sealed, purged with H₂ for three times and charged to 4MPa H₂ pressure. The reaction was then carried out at 160 to 200 °C and 4 MPa under magnetic stirring for 12 h. After the reaction, the autoclave was quenched in an ice–water bath to room temperature. The liquid solution was separated from the solid catalyst by centrifugation and analyzed qualitatively by GC-MS (Agilent 7890A-

5975C) and quantitatively by GC-FID (Agilent 7890) using pentadecane as the internal standard. Here, we employed pure straight alkanes (C_9 , C_{11} , C_{13}) to replace branched targeted alkanes as standards, because pure branched targeted alkanes cannot be purchased or synthesized at present. The product yields were calculated by using the equation: yield [%] = (moles of carbon in product)/ (moles of carbon in 1a) ×100%.

Similarly, the Michael addition of DFA and 2,4-pentanedione was performed in 50ml round-bottom flask. Typically, 2,4-pentanedione (5g), DFA (0.5g), $CoCl_2 \cdot 6H_2O$ (0.1g) and $CaCl_2$ (0.1g) were transferred into the flask, which was then heated to a certain temperature (60 to 100 °C) and allowed to react for a certain time (4-28 h). After the reaction, the reactor was quenched in an ice-water bath to room temperature and the products were separated as FAD did above. The HDO of as-prepared DFAD was also conducted in a 50 mL Teflon-lined stainless-steel autoclave. Typically, DFAD (0.2 g), Pd/NbOPO4 (0.1 g), and cyclohexane (6.46 g) were transferred into the autoclave. The reactor was then sealed. purged with H₂ for three times and charged to 4MPa H₂ pressure. The reaction was then carried out at 190 °C and 4 MPa for 12 h. After the reaction, the autoclave was quenched in an ice-water bath to room temperature. The liquid solution was separated from the solid catalyst by centrifugation and analyzed qualitatively by GC-MS (Agilent 7890A-5975C) and quantitatively by GC (Agilent 7890) equipped with an HP-5 and column а flame ionization detector (FID) usina area normalization method. The product distribution was calculated by using the equation: The product seclectivity [%] = (product peak area)/ (total peak area) ×100%.

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