

1 Producing Methylcyclopentadiene Dimer and Trimer based High- 2 Performance Jet Fuels using 5-Methyl Furfural

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10 1 Materials

11 Unless stated, all chemicals and catalysts in this work were used directly after purchasing without any
12 purification. 5-methyl furfural (MFF) (99%) was purchased from Shanghai Macklin Biochemical Co., Ltd. Urea(AR),
13 Methanol (99.5%), dichloromethane (AR), NiCl₂(AR), sodium hypophosphite (NaH₂PO₂, AR), ethanol (AR) and NaOH
14 (AR) were bought from Tianjin Yuanli Chemical Co. Ltd. CeCl₃·7H₂O (AR) was purchased from Tianjin Heowns Co.
15 LLC. NaBH₄ was purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. NaZSM-5 zeolite (SiO₂/Al₂O₃=80)
16 and HZSM-5 (SiO₂/Al₂O₃=25) purchased from Nankai Catalysts Co., Ltd. were calcined in air at 550 °C for 6 h before
17 use.

18 2 Experiment

19 2.1 Preparation of hierarchical HZSM-5

20 Hierarchical HZSM-5 was synthesized from NaZSM-5 according to our previous work¹. 20 g of calcined NaZSM-5
21 was heated in 200 mL of 0.5 M NaOH solution with stirring at 80 °C for 1 h. Then, the suspension was cooled to
22 room temperature, filtered, washed with deionized water until neutral, dried at 80 °C for 12 h and calcined at 550
23 °C for 5 h. Subsequently, the Na-form zeolites were transferred into H-form via a twice ion-exchange process with
24 NH₄NO₃ solution (1.5 M) at 100 °C for 4 h, and calcined at 550 °C in air for 5 h.

25 2.2 Synthesis of Ni₂P

26 Ni₂P was synthesized according to our previous work². Typically, 0.24 mmol of NiCl₂ and 4.8 mmol of urea were
27 dissolved in 100 mL of distilled water. After the mixture was stirred for 10 min, the mixed solution was kept at 90
28 °C for 48 h. Finally, the precipitates were washed three times with water and ethanol, respectively, and dried at 80

29 °C for 6 h to obtain Ni(OH)₂. To synthesize Ni₂P, 200 mg of sodium hypophosphite (NaH₂PO₂) was put in the uptake
30 and 30 mg of Ni(OH)₂ was put in the downtake, and then calcined at 325 °C for 1 h under Ar atmosphere to realize
31 phosphorization of nickel. After that, the powders were washed for 3 times using deionized water to remove
32 unconverted sodium hypophosphite, and then dried under 60 °C.

33 **2.3 Reductive ring-opening reaction of 5-methyl furfural (1) to 2,5-hexanedione (2)**

34 The reaction was performed in a 100 mL autoclave (EasyChem E100). 10 mL water and 30 mL dichloromethane
35 as solvents, 1 g MFF, 50 mg Ni₂P and 0.8 g commercial HZSM-5 were sealed in the reactor and hydrogenated under
36 hydrogen pressure of 30 bar and 140 °C for 20 h. After the reaction, the organic layer was separated and the
37 products was obtained by rotary evaporation for further use.

38 **2.4 Aldol condensation of 2 to 3-methyl-2-cyclopenten-1-one (3)**

39 The reaction was carried out in a round-bottom flask equipped with a reflux condenser and a mechanical stirrer.
40 1.4 g of **2** and 4.7 mL of water were heated to 150 °C in oil bath and then 8.3 mg NaOH was added. The products
41 were obtained by rotary evaporation.

42 **2.5 Selective hydrogenation of 3 to 3-methylcyclopent-2-en-1-ol (4)**

43 The reaction was carried out in a round-bottom flask equipped with a reflux condenser and a mechanical stirrer.
44 154 mg of **3**, 3.2 mL methanol and 149 mg CeCl₃·7H₂O were stirred in ice-water mixture bath for 10 min, and then
45 46 mg NaBH₄ was added. After 20 min, reaction was quenched with H₂O, dichloromethane was added to recover
46 the organic compounds. The products were obtained by rotary evaporation, and dichloromethane and methanol
47 were recycled.

48 **2.6 Dehydration and oligomerization of 4 to DMCPD (5) or mixture of DMCPD (5) and TMCPD (6)**

49 For the synthesis of **5**, the reaction was carried out in a round-bottom flask equipped with a reflux condenser
50 and a mechanical stirrer. 1.3 g hierarchical HZSM-5 (~ 5 wt%) was added into 25 g compound **4** and stirred at room
51 temperature for 72 h. For the synthesis of mixture of **5** and **6**, 50 mL autoclave (EasyChem E50) was used. 25 g of
52 compound **4** and 1.3 g hierarchical HZSM-5 (~ 5 wt%) were sealed in the reactor and heated to 150~220 °C for 15
53 h. The product was obtained by filtration.

54 **2.7 Hydrogenation of 5 and 5/6 mixture to Fuel 1 and Fuel 2**

55 The hydrogenation of **5** and/or 5/6 mixture was carried out with 50 mL autoclave (EasyChem E50). The reactor
56 was loaded with 25 g reactants and 1.5 g Ni₂P (6 wt%) catalyst, sealed and purged with N₂ for 4 times to exclude
57 air. Then it was heated to 150 °C and at 4 MPa of H₂ for 10 h. The product and catalyst were separated by filtration.

58 **3 Analytical method**

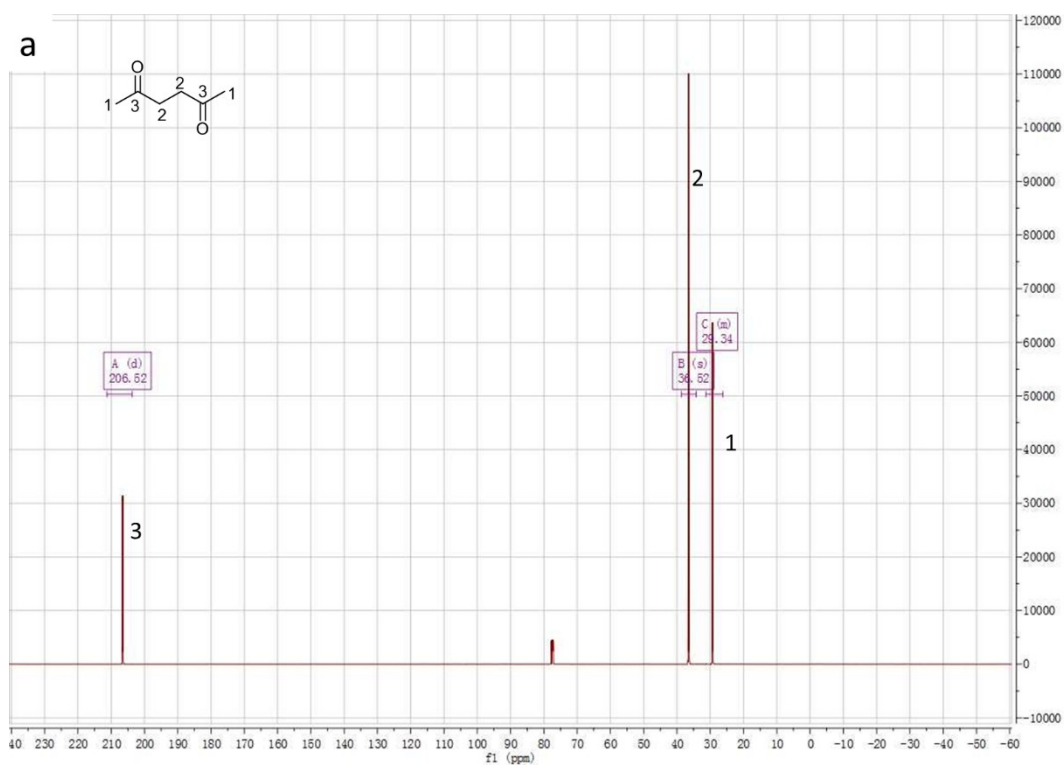
59 The products were determined qualitatively using an Agilent 6890/5975 gas chromatography-mass
60 spectrometry (GC-MS) equipped with HP-5 capillary column (30 m × 0.5 mm) and ¹³C and ¹H NMR spectra were
61 collected using Bruker Avance 400 M Spectrometers spectrometer. The liquid products were quantified by a gas
62 chromatography (Agilent-7820A) equipped with an FID detector and a capillary column HP-1 capillary column (30
63 m × 0.53 mm).

64 **4 Measurements of fuel properties**

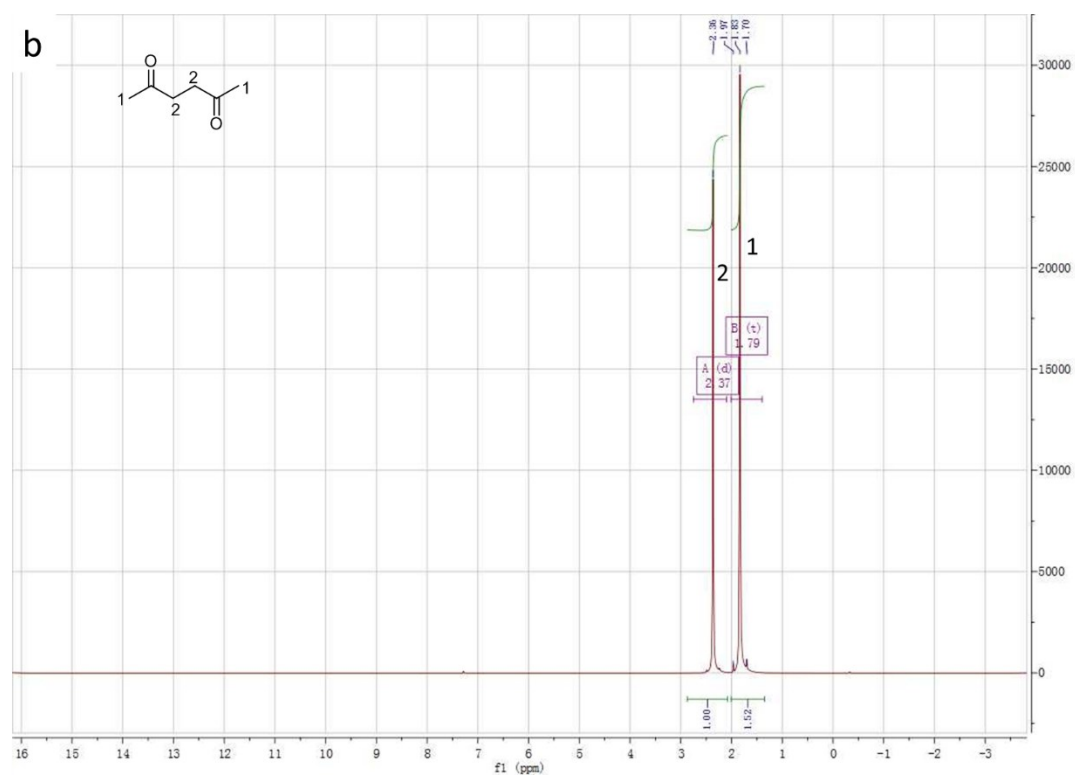
65 The fuel density was measured by a Mettler Toledo DE40 density meter according to ASTM D4052. Freezing
66 point was measured as outlined in ASTM D2386. Kinematic viscosity was determined using capillary viscometer
67 (ASTM D445). The net heat of combustion (NHOC) was measured by the IKA-C6000 isoperibol Package 2/10
68 Calorimeter (ASTM D240-02). Dynamic testing (JFTOT) was conducted continuously at 355 °C for 5 h in accordance
69 with ASTM D3241.

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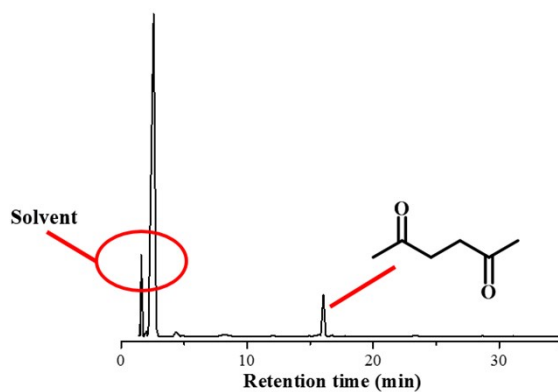


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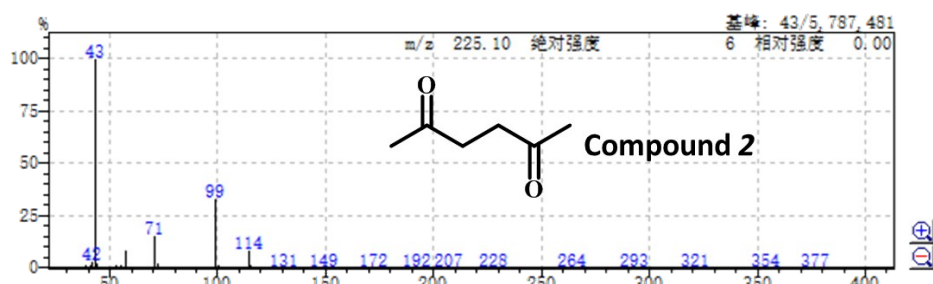
73 **Figure S1** ^{13}C (a) and ^1H (b) NMR spectra of 2,5-hexanedione (HD)(2). a: ^{13}C NMR (126 MHz, CDCl_3) δ 206.52 (d, $J =$ 74 6.1 Hz), 36.52 (s), 31.31 – 26.19 (m). b: ^1H NMR (500 MHz, CDCl_3) δ 2.37 (d, $J = 4.3$ Hz, 1H), 1.79 (t, $J = 34.3$ Hz, 2H).

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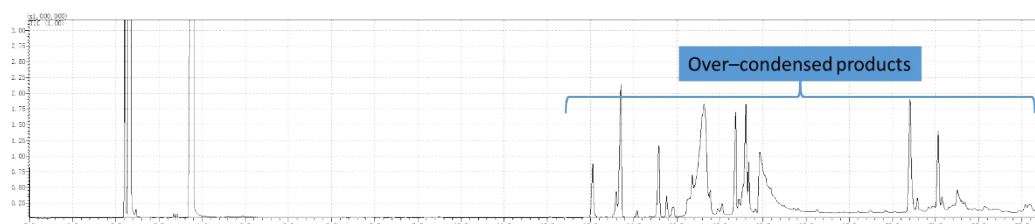


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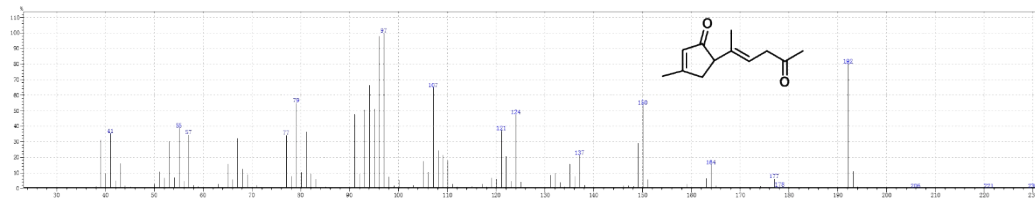
Figure S2 GC-MS spectra of 2,5-hexanedione (**2**) from the reductive ring-opening of 5-methyl furfural (**1**).

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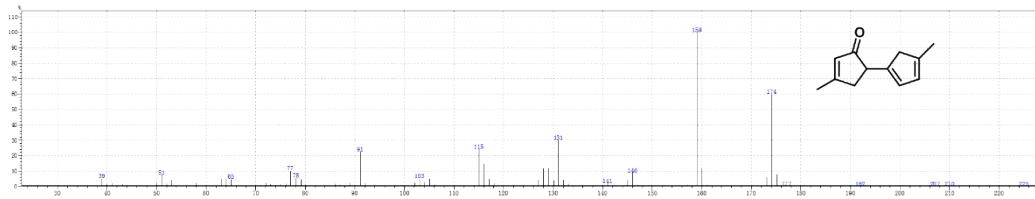
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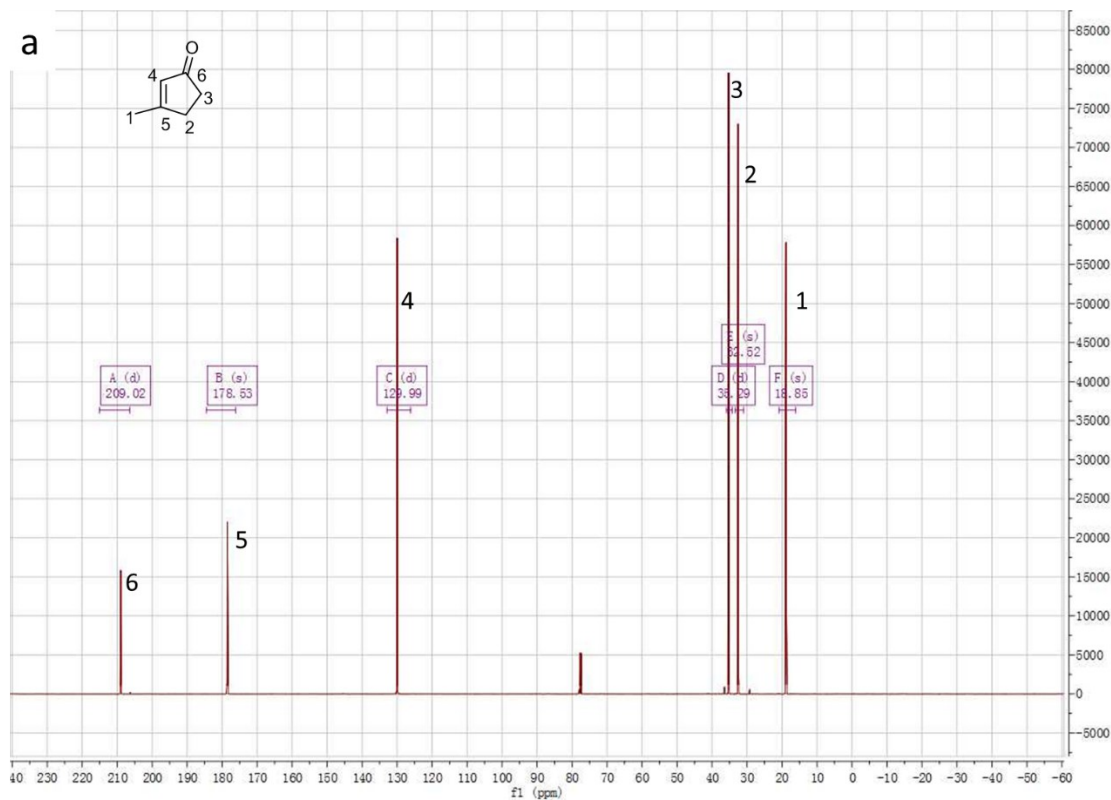


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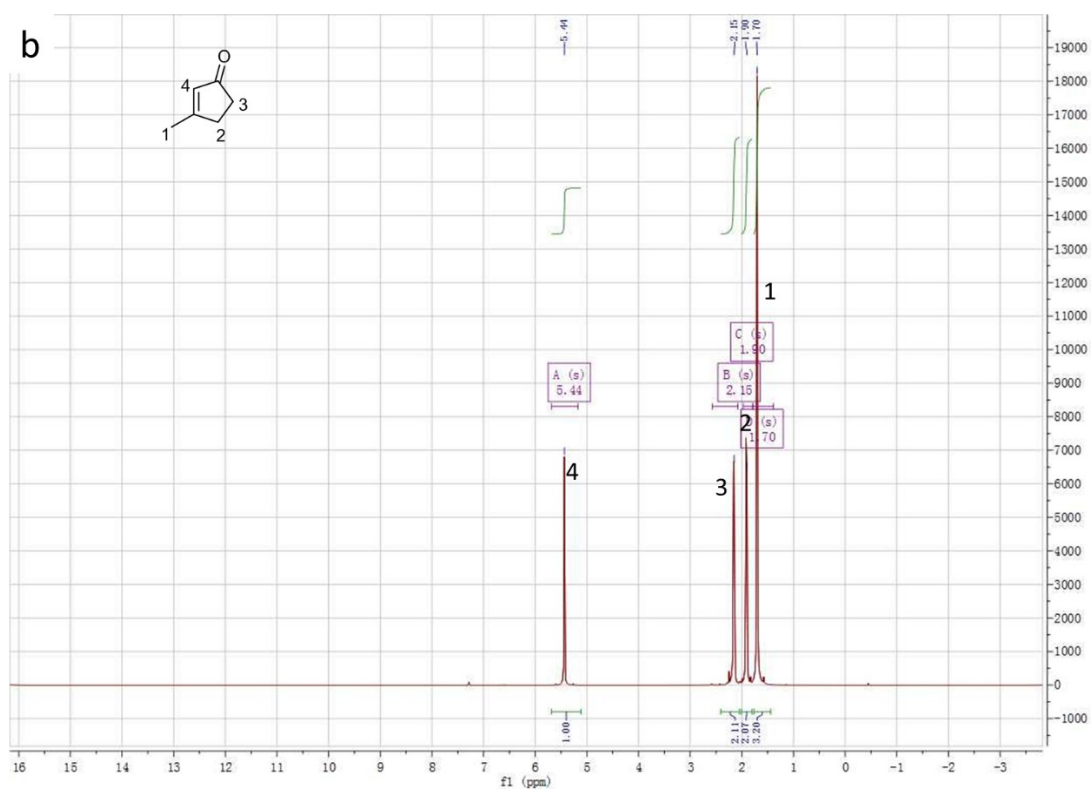
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Figure S3 GC-MS spectra of products from the aldol condensation of HD (**2**) by strong alkaline.

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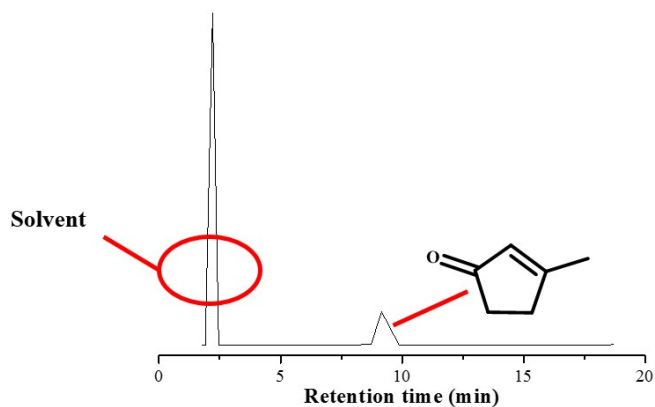
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88 **Figure S4** ¹³C (a) and ¹H (b) NMR spectra of 3-methyl-2-cyclopenten-1-one (**3**). a: ¹³C NMR (126 MHz, CDCl₃) δ

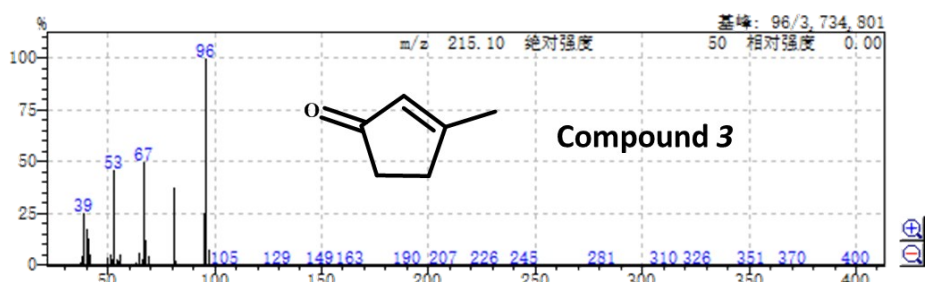
89 209.02 (d, *J* = 2.6 Hz), 178.53 (s), 129.99 (d, *J* = 8.2 Hz), 35.29 (d, *J* = 8.1 Hz), 32.52 (s), 18.85 (s). b: ¹H NMR (500

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MHz, CDCl₃) δ 5.44 (s, 1H), 2.15 (s, 2H), 1.90 (s, 2H), 1.70 (s, 3H).



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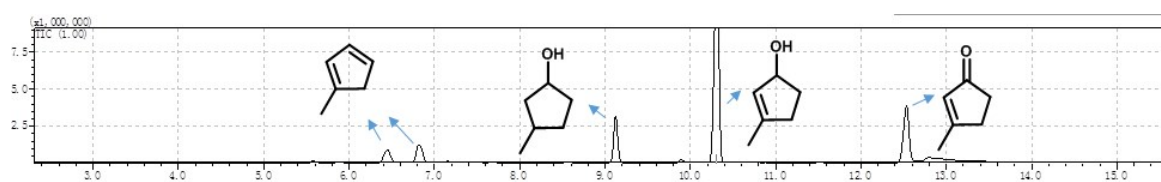
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Figure S5 GC-MS spectra of 3-methyl-2-cyclopenten-1-one (**3**) by aldol condensation of HD (**2**).

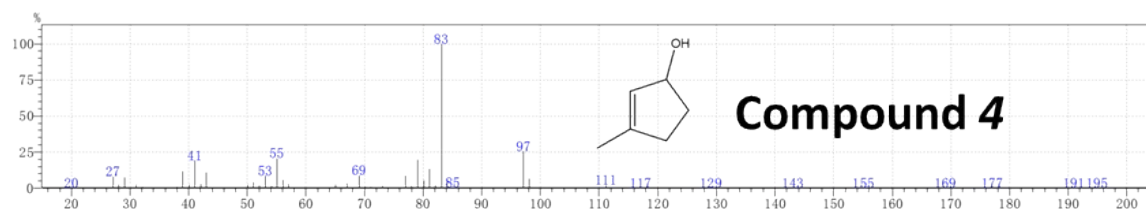
Table S1 Reaction conditions for conversion of 3 to 4 .					
Entry	Substrate (mg)	Sol./Vol.(mL)	Reducing agents/mass (mg)	Conv. of 3 (%)	Yield of 4 (%)
1 ^a	96	methanol/2.5	NaBH ₄ /38	95	36.1
2 ^a	96	methanol/2.5	NaBH ₄ /CeCl ₃ ·7H ₂ O 38/373	100	99
3 ^b	154	methanol/3.2	NaBH ₄ /CeCl ₃ ·7H ₂ O 46/149	100	98.5

^a Reference ³; ^b Room temperature

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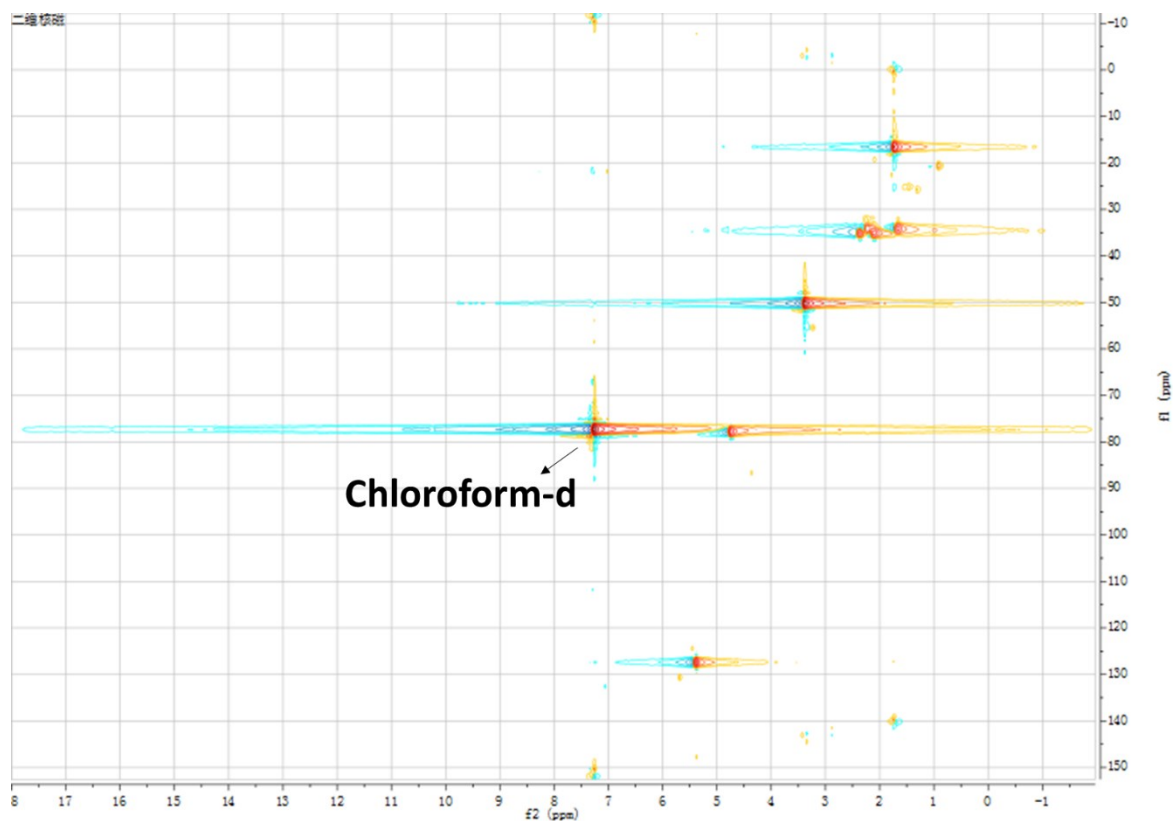
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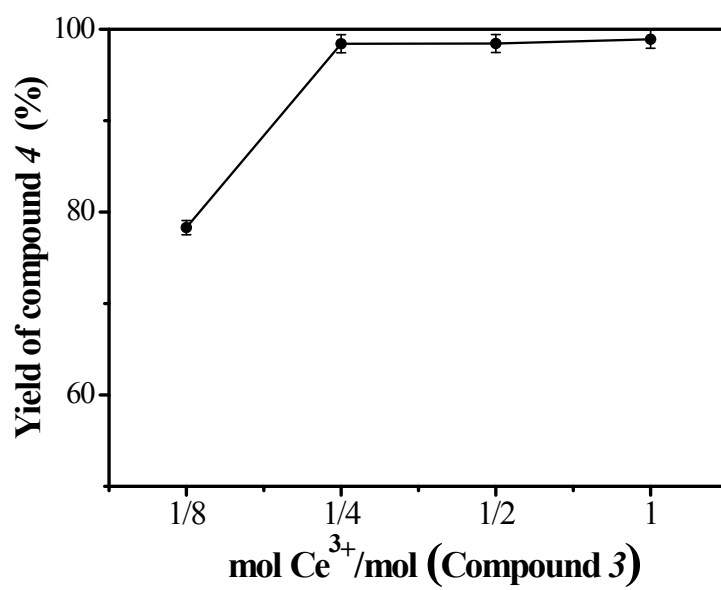
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Figure S6 GC-MS spectra of 3-methylcyclopent-2-en-1-ol (**4**) from the selective hydrogenation of **3**.



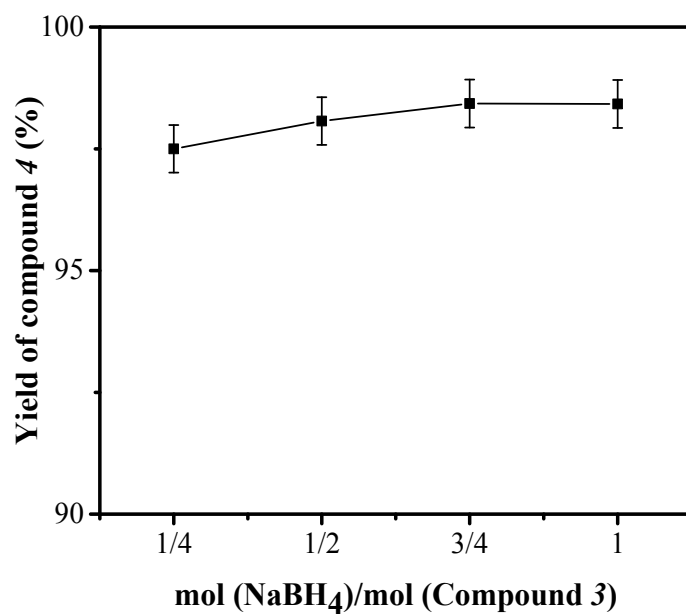
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Figure S7 The 2D-HSQC NMR spectra of 3-methylcyclopent-2-en-1-ol (**4**).



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Figure S8 Effect of molar ratio of [Ce³⁺]/[Compound **3**] on reaction.

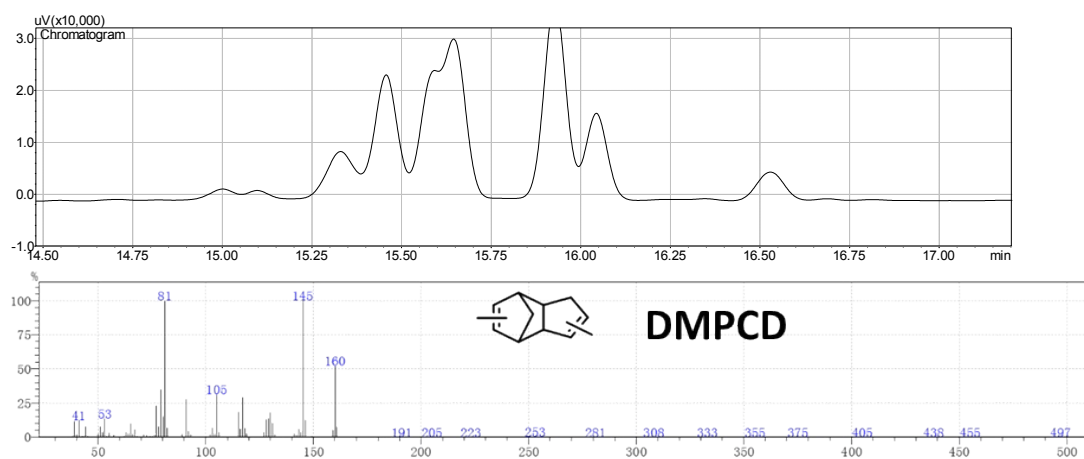


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Figure S9 Effect of molar ratio of [NaBH₄]/[Compound 3] on reaction.

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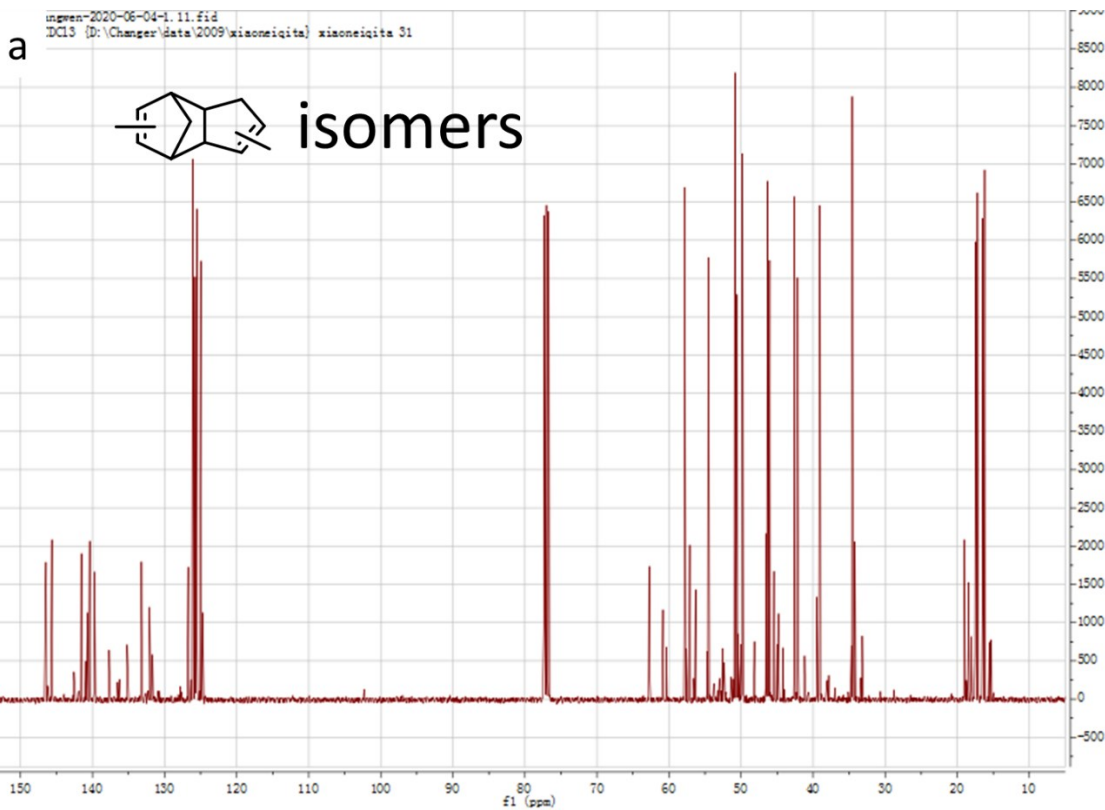


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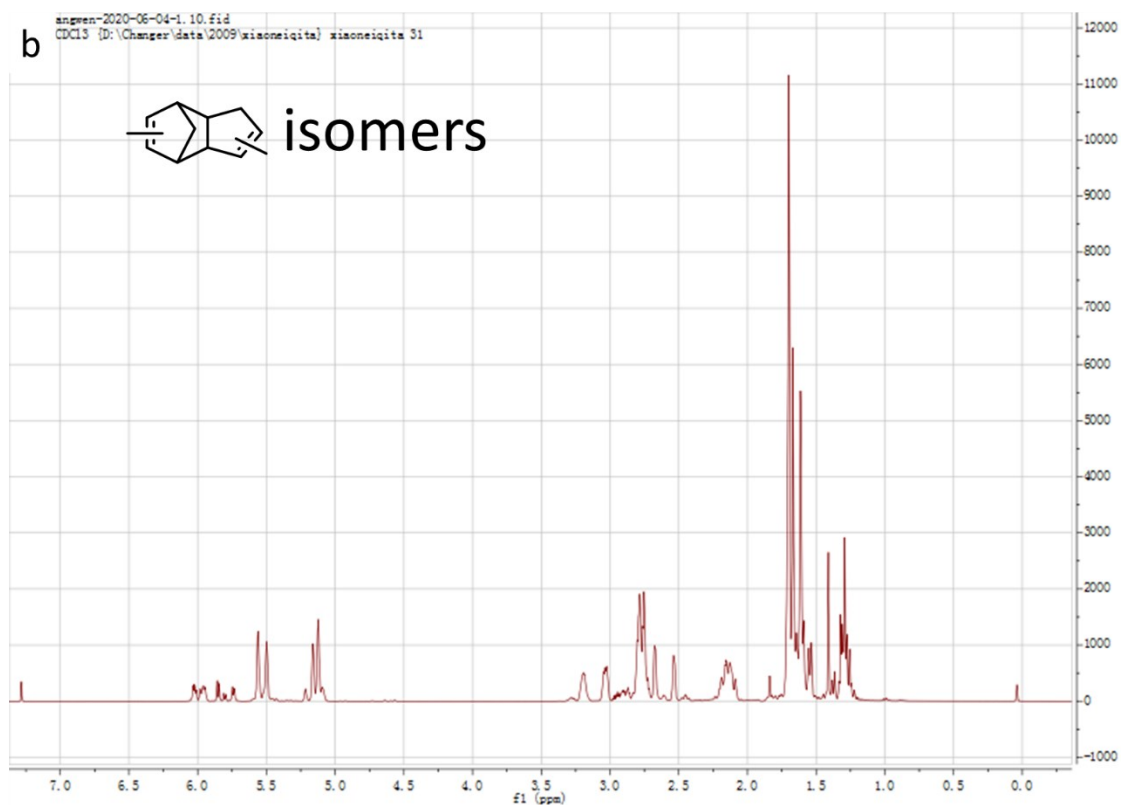
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Figure S10 GC-MS chromatogram of DMCPD from compound 4



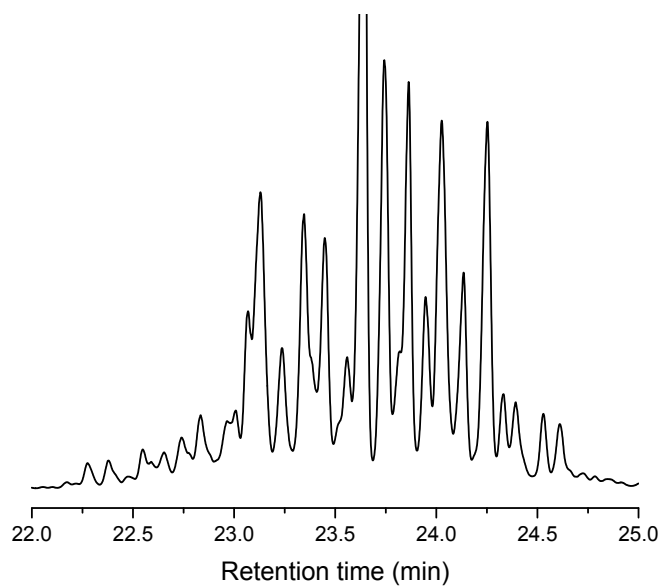
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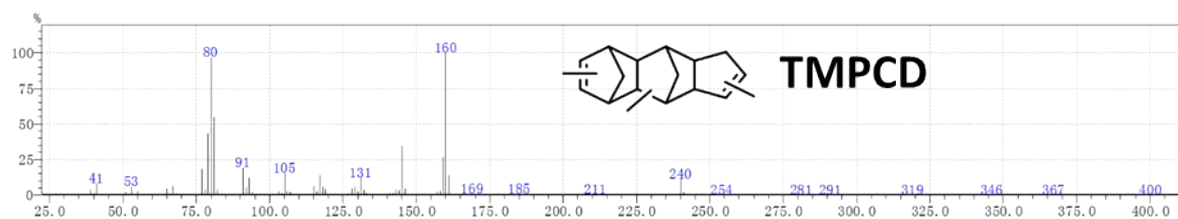
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Figure S11 ^{13}C (a) and ^1H (b) NMR spectra of DMCPD from compound **4**.



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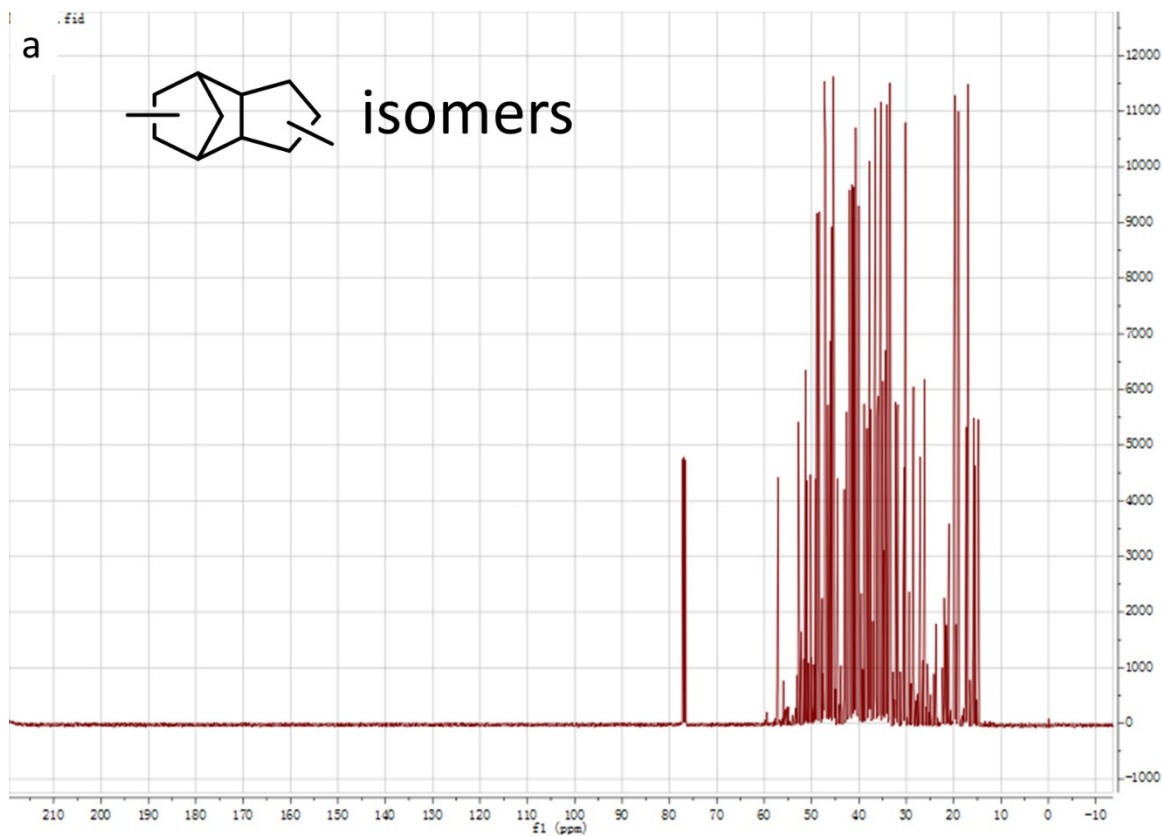


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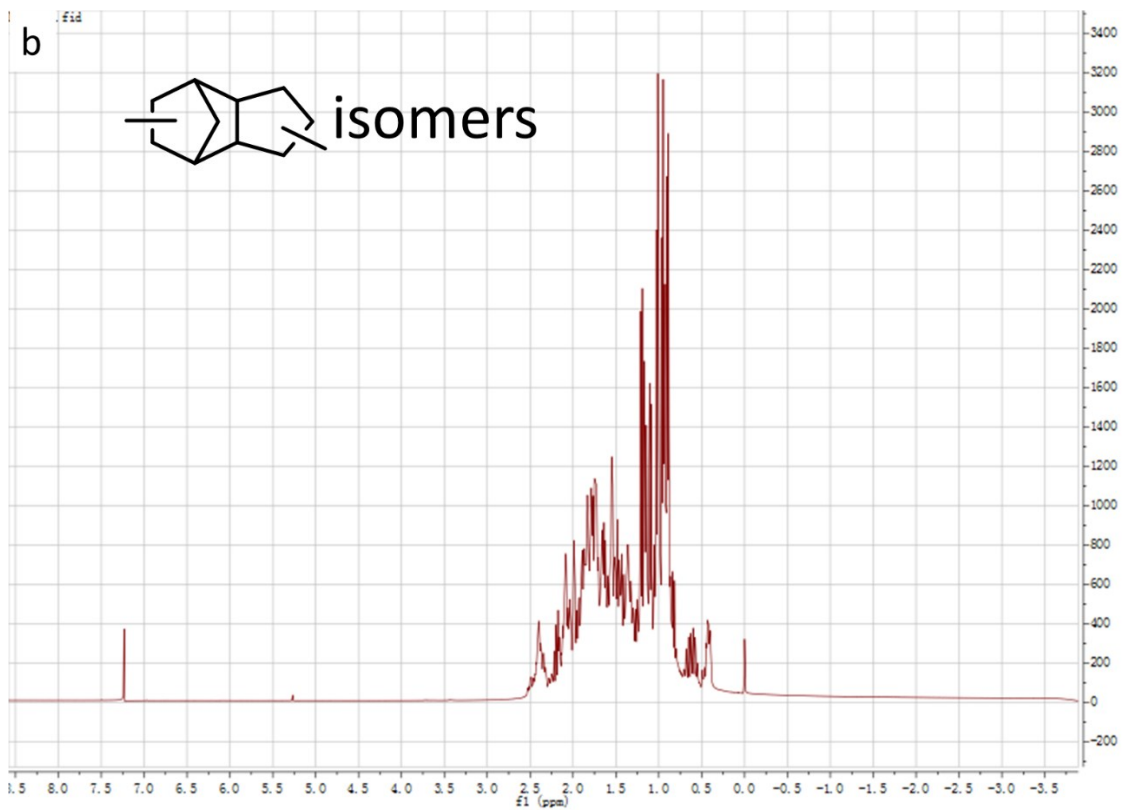
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Figure S12 GC-MS chromatogram of TMPCD from compound 4.

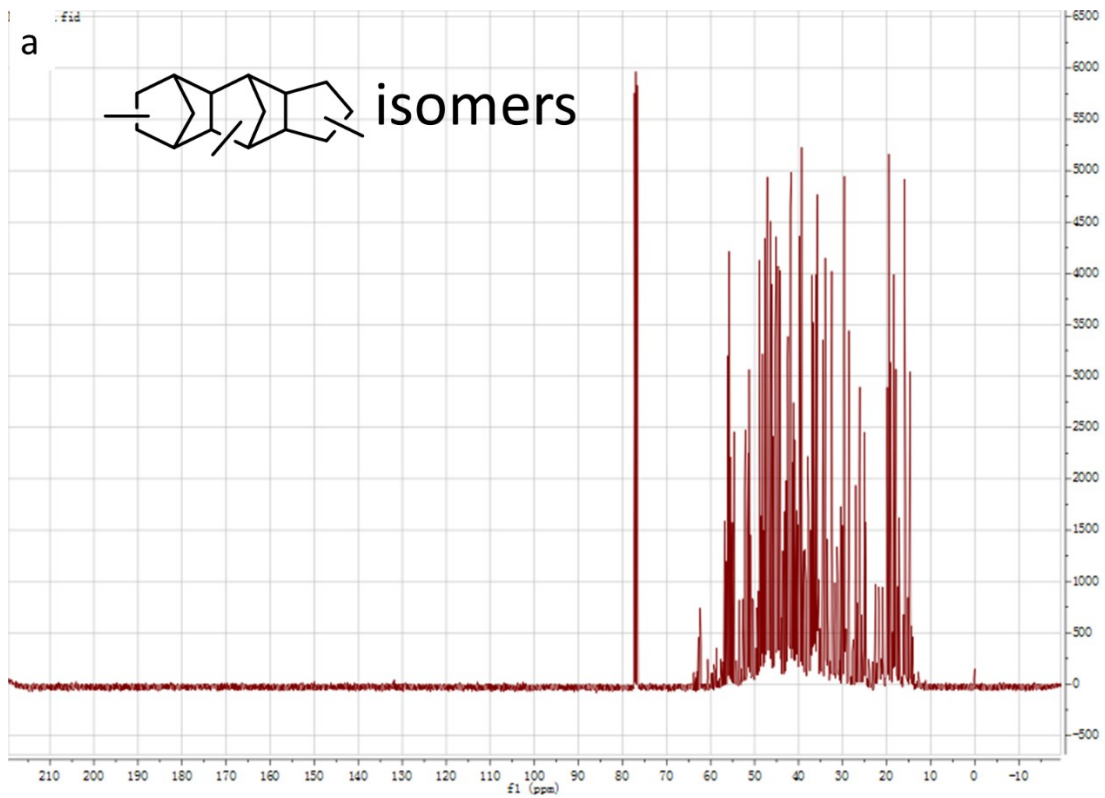


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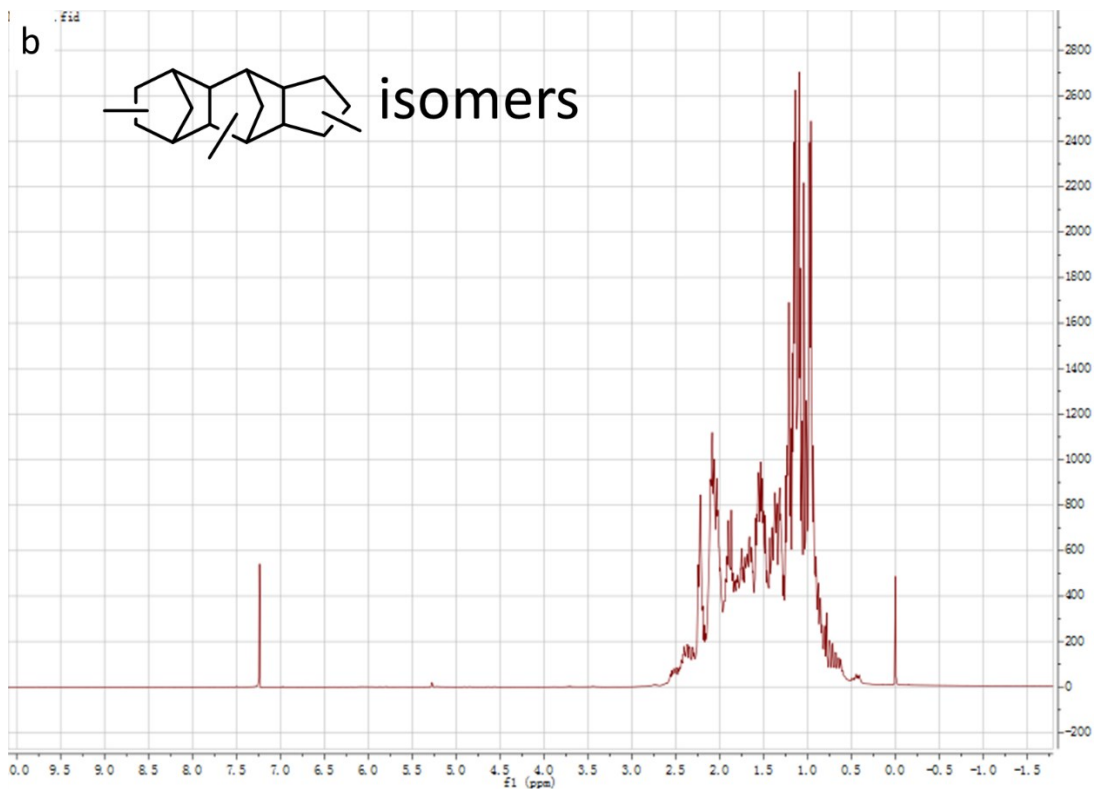


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Figure S13 ^{13}C (a) and ^1H (b) NMR spectra of DMCPD derived fuels.

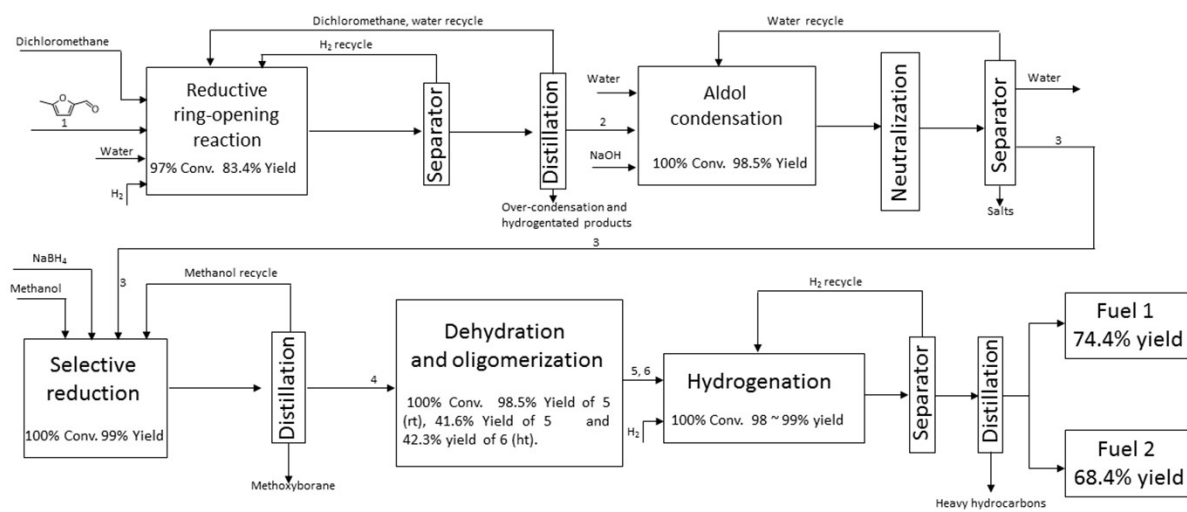


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Figure S14 ¹³C(a) and ¹H (b) NMR spectra of TMPCD derived fuels.



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126 **Figure S15** Conceptual diagram of integrated biorefinery for synthesis of DMPCD /TMPCD derived fuels from
127 biomass (rt: room temperature; ht: high temperature).

128 **References**

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