Supporting Information

Synthesis of gasoline and jet fuel range cycloalkanes and aromatics with poly(ethyleneterephthalate) wastes

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1. **Characterization of activated carbon loaded noble metal catalysts**

The specific BET surface areas of activated carbon loaded noble metal (denoted as M/C, M = Pt, Ru or Pd) catalysts used in the solvent-free hydrogenation of DMT to DMCD were determined by N_2-physisorption at 77 K using a Micromeritics ASAP 2010 apparatus. The XRD patterns of M/C catalysts were obtained with a PW3040/60X' Pert PRO (PANalytical) diffractometer equipped with Cu K_α radiation source (λ = 0.15432 nm) at 40 kV and 40 mA. Based on the XRD results, the average particle sizes of catalysts were estimated by Debye-Scherrer equation. The metal dispersions in M/C catalysts were measured with a Micromeritics AutoChem II 2920 Automated Catalyst Characterization System by the molar ratios of CO chemisorption and noble metal in catalysts. These values correspond to the ratio of surface metal atoms to total metal atoms assuming that the stoichiometry of adsorbed CO to surface metal atom is one. Before the tests, the samples were dried in helium flow at 393 K for 0.5 h and cooled down to 323 K. After the stabilization of baseline, the CO adsorption was carried out at 323 K by the pulse adsorption of 5% CO in He.

2. **Preparation of 5,5'-(butane-1,1-diyl)bis(2-methylfuran)**

The 5,5'-(butane-1,1-diyl)bis(2-methylfuran) used in the solvent-free simultaneous HDO test was synthesized by the hydroxyalkylation/alkylation (HAA) of 2-methylfuran (2-MF) and butanal according to the method described in our previous work.[1] Typically, 1.5 g Amberlyst-15 resin, 32.8 g (0.4 mol) 2-MF, 14.4 g (0.2 mol) butanal were used for each reaction. The mixture was stirred at 338 K for 2 h, filtrated to remove the catalyst, and purified by vacuum distillation. The ^{13}C and ^{1}H NMR spectra of the 5,5'-(butane-1,1-diyl) bis(2-methylfuran) as obtained were shown in Figure S14.

3. Calculation method for the conversions of different feedstocks and the yields of different hydrocarbons from the solvent-free simultaneous HDO tests:

Conversion of DMCD (%) = (Mole of DMCD fed into the reactor – mole of unreacted DMCD in the HDO product)/(Mole of DMCD fed into the reactor)×100%

Conversion of biomass derived jet fuel precursor (%) = (Mole of biomass derived jet fuel precursor fed into the reactor – mole of unreacted biomass derived jet fuel precursor in the HDO product)/(Mole of biomass derived jet fuel precursor fed into the reactor)×100%

Yield of C_7-C_8 aromatics (%) = (Mole of C_7-C_8 aromatics in the HDO product/Mole of DMCD fed into the reactor)×100%

Yield of C_7-C_8 cycloalkanes (%) = (Mole of C_7-C_8 cycloalkanes in the HDO product/Mole of DMCD fed into the reactor)×100%

Yield of C_8-C_{16} chain alkanes (%) = (Mole of the C_8-C_{16} chain alkanes in the HDO product/Mole of the biomass derived jet fuel precursor fed into the reactor)×100%

Table S1. Specific BET surface areas (S_{BET}), average metal particle sizes and metal dispersions of activated carbon loaded noble metal catalysts.

Catalyst	S_{BET} (m^2 g^{-1})[a]	Average metal particle size (nm)[b]	Metal dispersion (%)[c]
Pt/C	882	0.9	5.7
Pd/C	1108	4.9	11.2
Ru/C	659	2.7	0.2

[a] Measured by N_2-physisorption. [b] Estimated from the XRD results by Debye-Scherrer equation. [c] Calculated based on the CO-chemisorption results.

Table S2. Selectivity of different products from the solvent-free HDO of DMCD over the Ru/SiO_2 and Ru-Cu/SiO_2 catalysts.[a]

	Ru/SiO_2	Ru-Cu/SiO_2
CH_4	90.3	17.0
CO	—	1.1
CO_2	—	—
C_7-C_8 aromatics	—	12.6
C_7-C_8 cycloalkanes	—	60.1

[a] Reaction conditions: 643 K, 6 MPa H_2; 1.8 g catalyst, DMCD feedspeed: 0.04 mL min^{-1}, H_2 flow rate: 120 mL min^{-1}. Selectivity of specific product (%) = (Carbon in the specific product)/(Carbon in the converted DMCD) × 100%

Table S3. Density, research octane numbers (RON) and motor octane numbers (MON) of the C_7-C_8 hydrocarbons generated during the solvent-free HDO of DMCD.

Hydrocarbon	Density	Actual		Blending	
	(g mL^{-1})	RON	MON	RON	MON
Methylcyclohexane	0.769	75	71	104	84
p-Dimethylcyclohexane	0.786	68	65	66	63
Toluene	0.864	> 100	> 100	124	112
p-Xylene	0.861	> 100	> 100	146	127

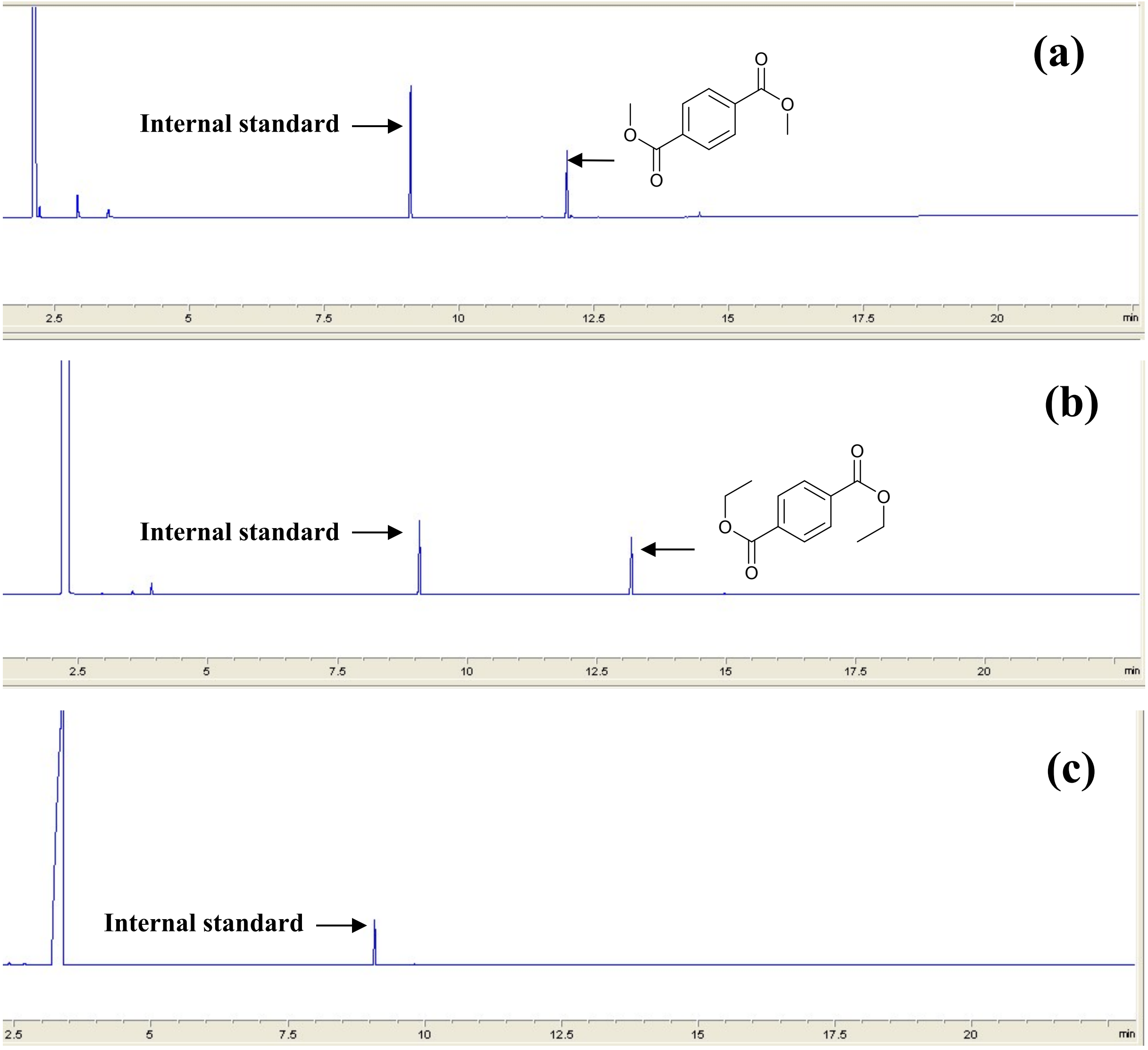


Figure S1. GC chromatograms of the alcoholysis products from the reaction of PET waste with methanol (a), ethanol (b) and butanol (c). Reaction conditions: 453 K, 3.5 h; 1 g PET waste and 40 mL alcohol were used in each test.

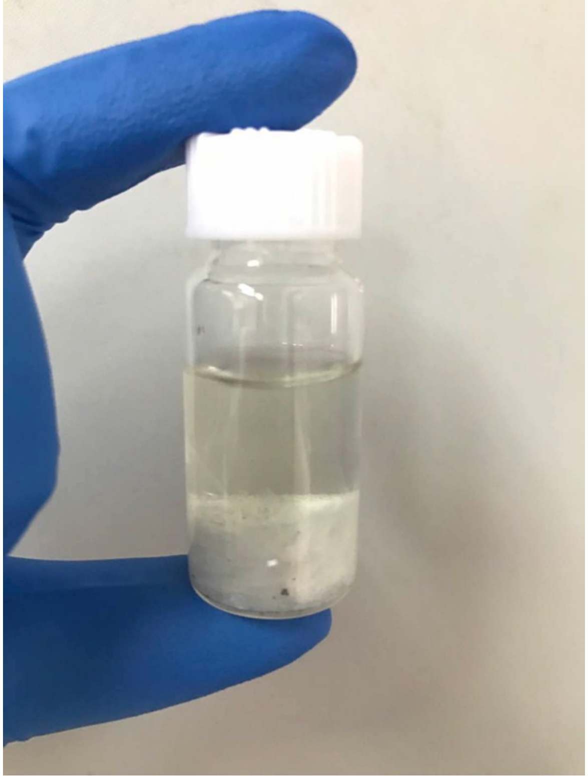


Figure S2. Photo of the DMT which was automatically separated from methanol phase when the reaction system was cooled down to room temperature.

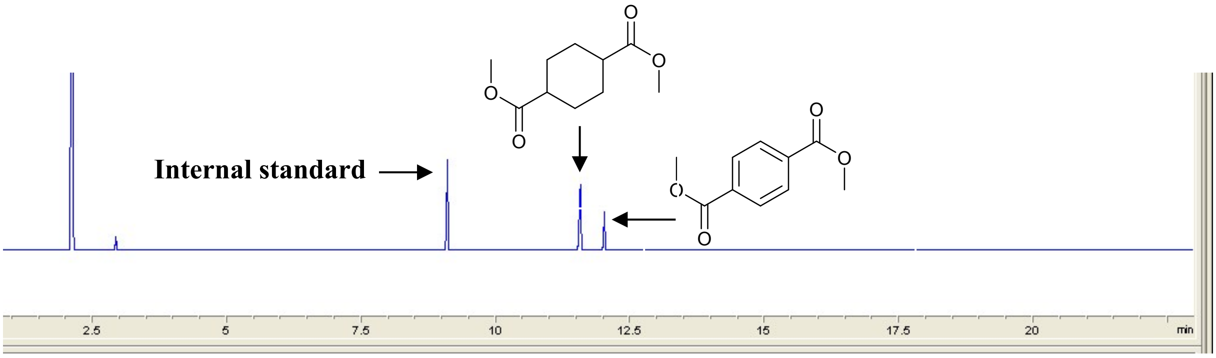


Figure S3. GC chromatogram of the solvent-free hydrogenation product of DMT over the Pt/C catalyst. Reaction conditions: 373 K, 5 MPa H_2, 7 h. 30 g DMT and 1 g Pt/C catalyst were used in the test.

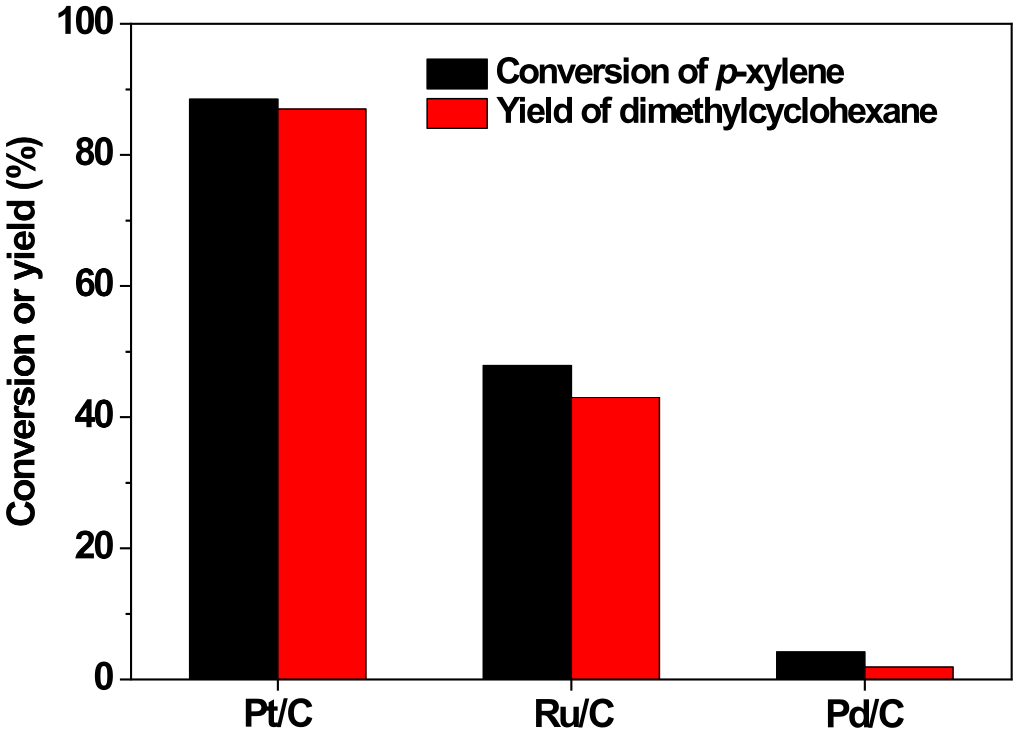


Figure S4. Conversions of *p*-xylene and the yields of dimethylcyclohexane over the activated carbon loaded noble metal catalysts. Reaction conditions: 373 K, 5 MPa H_2, 2 h; 30 g *p*-xylene and 1 g catalyst were used in each test.

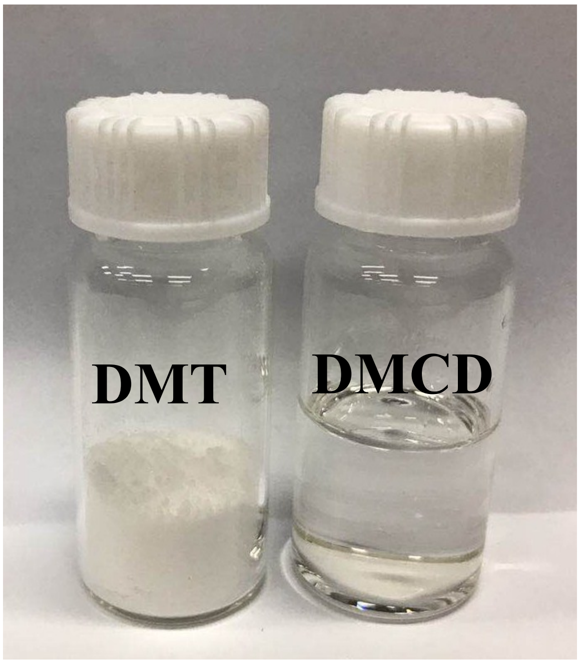


Figure S5. Photo of the DMT and DMCD at room temperature.

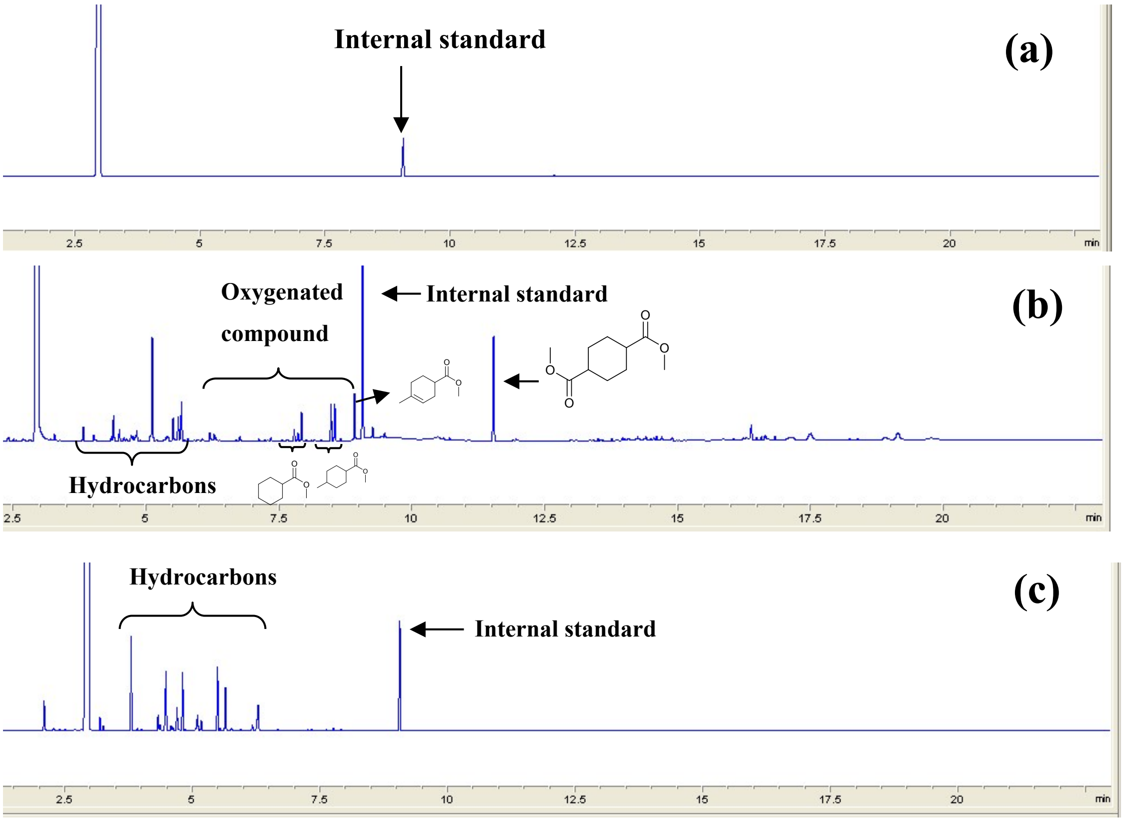


Figure S6. GC chromatogram of the liquid products from the solvent-free HDO of DMCD over the Ru/SiO_2 (a), Cu/SiO_2 (b) and Ru-Cu/SiO_2 (c) catalysts. Reaction conditions: 643 K, 6 MPa H_2; 1.8 g catalyst, DMCD feedspeed: 0.04 mL min^{-1}, H_2 flow rate: 120 mL min^{-1}.

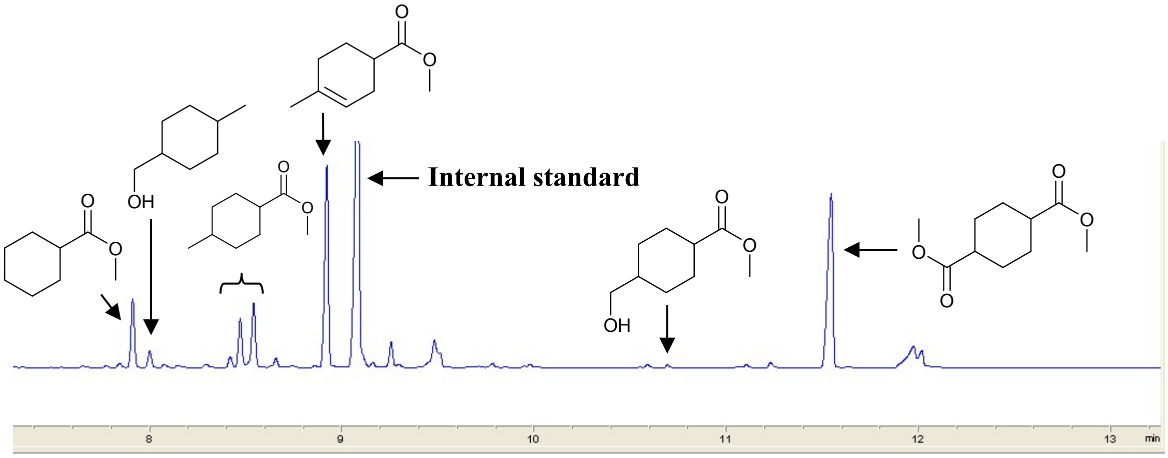


Figure S7. GC chromatogram of the liquid product from the solvent-free HDO of DMCD over the Ru-Cu/SiO_2 catalyst. Reaction conditions: 673 K, 4 MPa H_2; 1.8 g catalyst, DMCD feedspeed: 0.16 mL min^{-1}, H_2 flow rate: 120 mL min^{-1}.

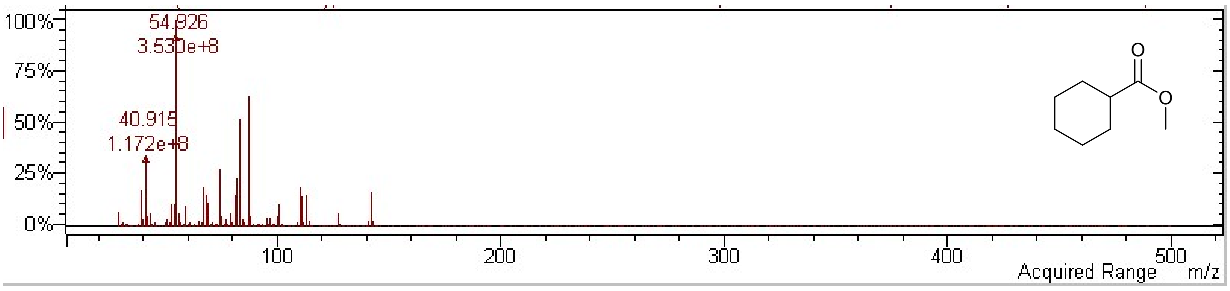


Figure S8. Mass spectrogram of methyl cyclohexanecarboxylate from the solvent-free HDO of DMCD over the Ru-Cu/SiO_2 catalyst.

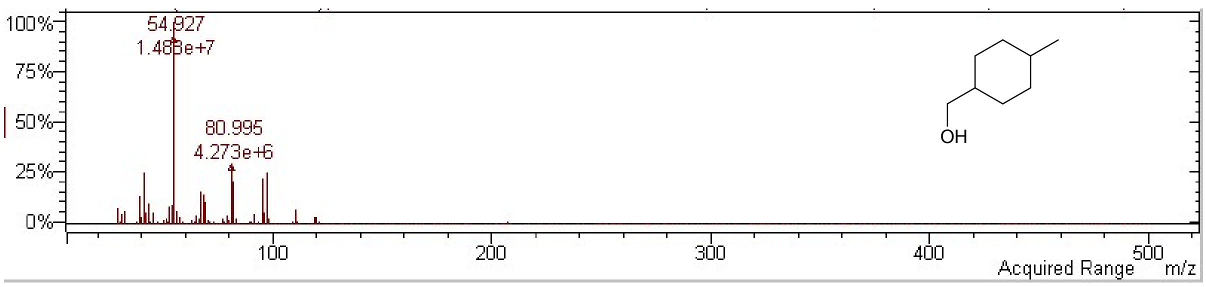


Figure S9. Mass spectrogram of (4-methylcyclohexyl)methanol from the solvent-free HDO of DMCD over the Ru-Cu/SiO_2 catalyst.

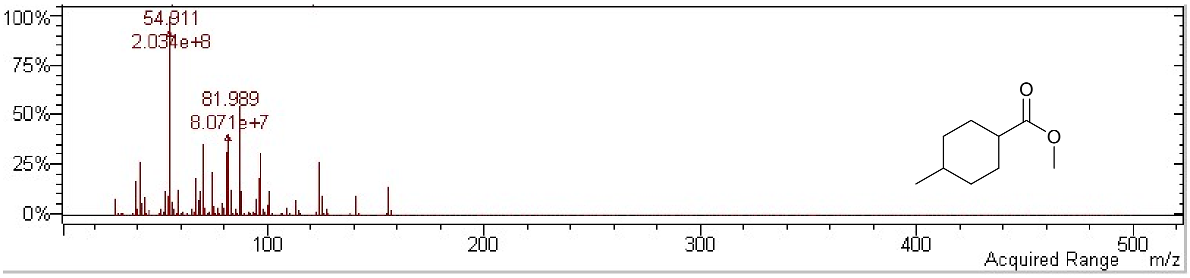


Figure S10. Mass spectrogram of methyl 4-methylcyclohexanecarboxylate from the solvent-free HDO of DMCD over the Ru-Cu/SiO_2 catalyst.

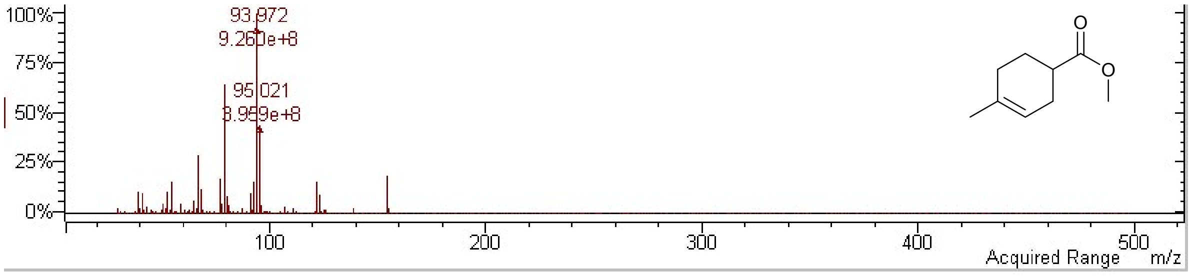


Figure S11. Mass spectrogram of methyl 4-methylcyclohex-3-enecarboxylate from the solvent-free HDO of DMCD over the Ru-Cu/SiO_2 catalyst.

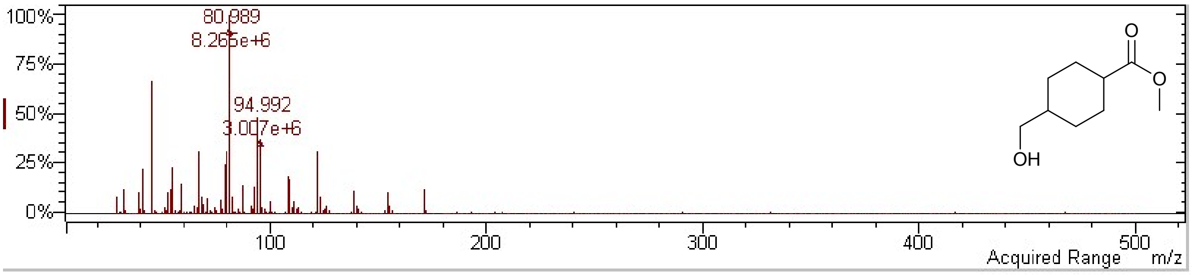


Figure S12. Mass spectrogram of methyl 4-(hydroxymethyl)cyclohexanecarboxylate from the solvent-free HDO of DMCD over the Ru-Cu/SiO_2 catalyst.

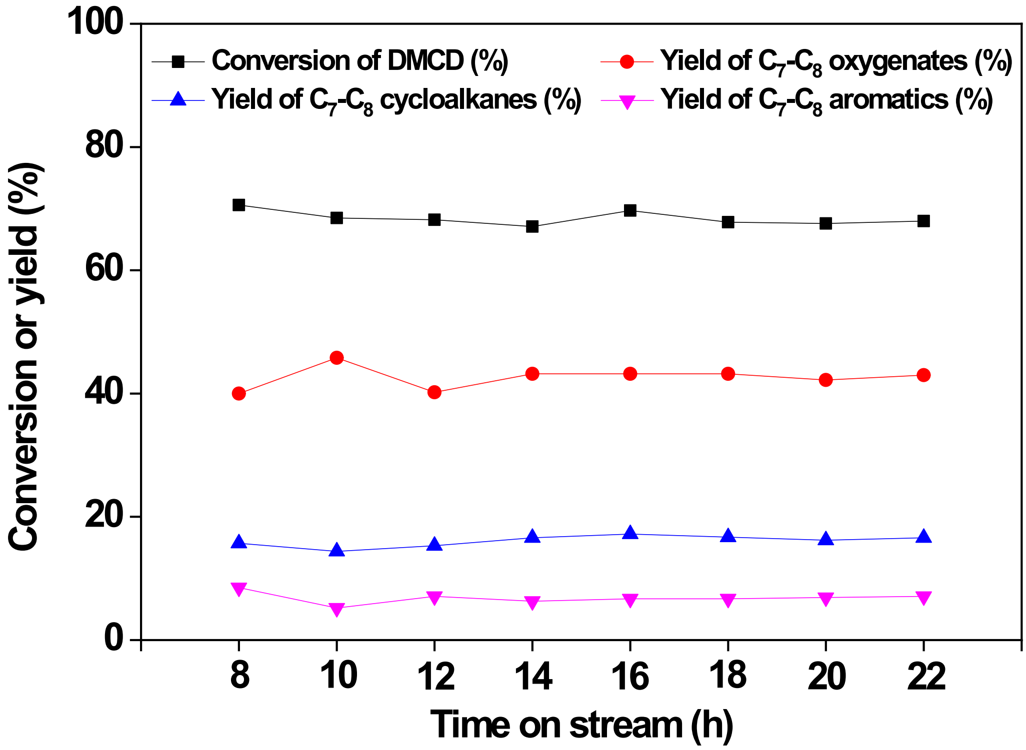
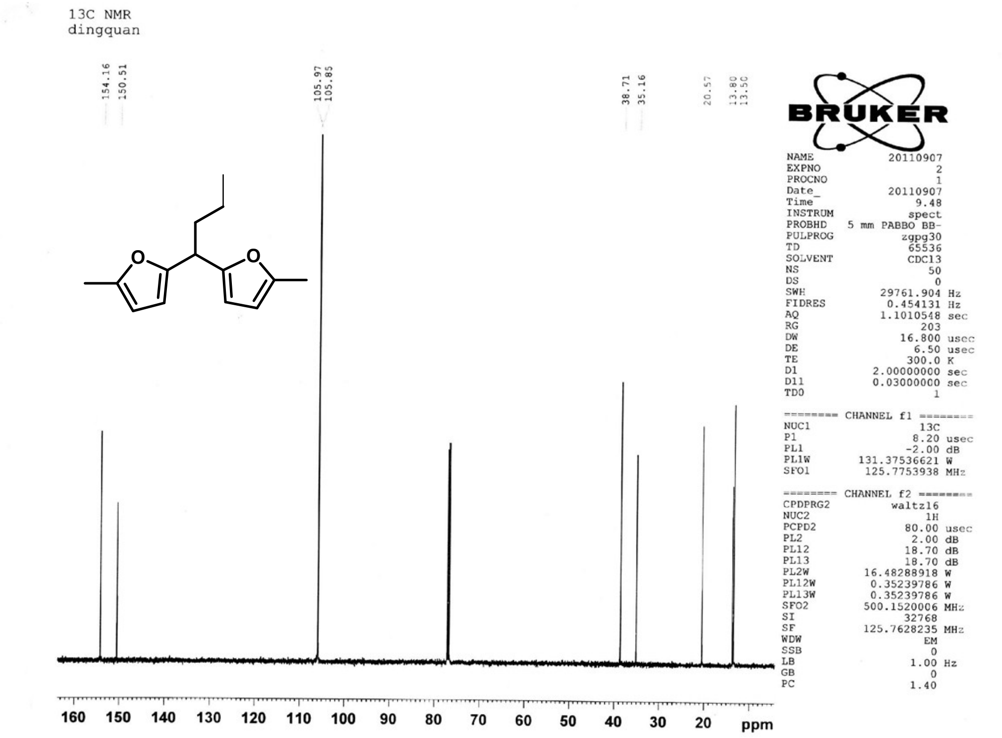


Figure S13. Conversion of DMCD and the yields of different products over the Ru-Cu/SiO_2 catalyst as the function of time on stream. Reaction conditions: 673 K, 4 MPa H_2; 1.8 g Ru-Cu/SiO_2 catalyst, DMCD flow rate: 0.16 mL min^{-1}, H_2 flow rate: 120 mL min^{-1}.



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TE                 300.0 K
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D11           0.03000000 sec
TD0                    1

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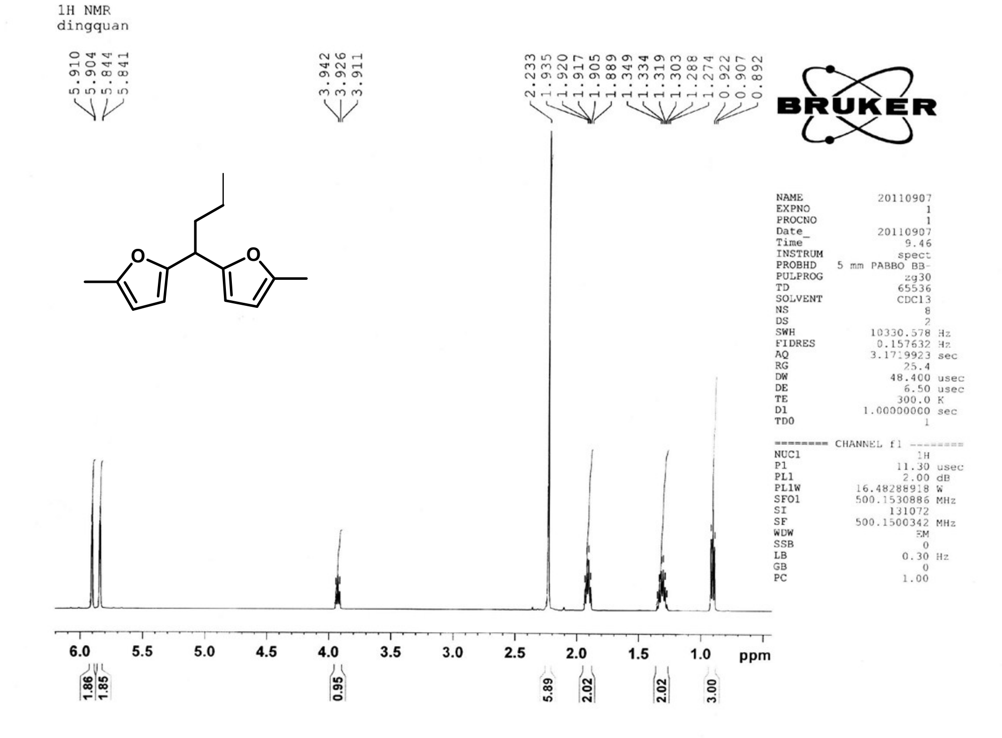

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Figure S14. ^{13}C and ^{1}H NMR spectra of 5,5'-(butane-1,1-diyl)bis(2-methylfuran) prepared by the HAA of 2-MF with butanal.

References

1 G. Li, N. Li, J. Yang, A. Wang, X. Wang, Y. Cong and T. Zhang, *Bioresour. Technol.*, 2013, **134**, 66-72.